Impact of Glacial/Interglacial Sea Level Change on the Ocean Nitrogen Cycle

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Impact of glacial/interglacial sea level change on the ocean nitrogen cycle


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The continental shelves are the most biologically dynamic regions of the ocean, and they are extensive worldwide, especially in the western North Pacific. Their area has varied dramatically over the glacial/interglacial cycles of the last million years, but the effects of this variation on ocean biological and chemical processes remain poorly understood. Conversion of nitrate to N₂ by denitrification in sediments accounts for half or more of the removal of biologically available nitrogen (“fixed N”) from the ocean. The emergence of continental shelves during ice ages and their flooding during interglacials have been hypothesized to drive changes in sedimentary denitrification. Denitrification leads to the occurrence of phosphorus-bearing, N-depleted surface waters, which encourages N₂ fixation, the dominant N input to the ocean. An 860,000-y record of foraminifera shell-bound N isotopes from the South China Sea indicates that N₂ fixation covaried with sea level. The N₂ fixation changes are best explained as a response to changes in regional excess phosphorus supply due to sea level-driven variations in shallow sediment denitrification associated with the cyclic drowning and emergence of the continental shelves. This hypothesis is consistent with a glacial ocean that hosted globally lower rates of fixed N input and loss and a longer residence time for oceanic fixed N—a “sluggish” ocean N budget during ice ages. In addition, this work provides a clear sign of sea level-driven glacial/interglacial oscillations in biogeochemical fluxes at and near the ocean margins, with implications for coastal organisms and ecosystems.

Biologically productivity in much of the ocean is limited by the supply of biologically available nitrogen (“fixed N”) (1). Biologically processes are central to the input and output of fixed N to and from the ocean: N₂ fixation by cyanobacteria in surface waters appears to dominate the input of N to the ocean, whereas the main sink is biological reduction to N₂ (generalized here as “denitrification”) in sediments and in suboxic zones of the water column (2). Given this biologically determined input/output budget, the variation or constancy of the oceanic fixed N reservoir has broader implications for the potential of ocean life to regulate environmental conditions on a global scale. Because the “major nutrients” N and phosphorus (P) fuel the biological sequestration of CO₂ in the deep ocean, changes in the oceanic fixed N reservoir have also been proposed as a driver of glacial/interglacial CO₂ change (3, 4).

Sediment records show N isotopic evidence of reduced water column denitrification during the Last Glacial Maximum (LGM) and other cold phases of the glacial cycles relative to the current interglacial (the “Holocene”) and past warm time intervals (5, 6). “Benthic” denitrification (that which occurs in seafloor sediments) is equally as or more important than water column denitrification in the removal of N from the global ocean, and it has been hypothesized to decrease during glacial periods (times of high land ice volume) as well (7). This hypothesis is based on the generally rapid rate of denitrification in continental shelf sediments and on calculations that indicate the importance of shelf denitrification in the global ocean rate of denitrification (8). The continental shelves are characterized by high fluxes of organic matter to the sediments both because their shallow depth allows sinking matter to reach the bottom quickly and because the breakdown of organic matter in the shallow sediments returns nutrients immediately to the sunlit upper ocean. As a result, the nutrients supplied to the waters overlying the continental shelf drive multiple rapid cycles of productivity, sedimentation, and remineralization over its broad extent of shallow seafloor. During glacial maxima, the ~120-m decline in sea level converted the continental shelves into coastal land, removing much of this environment as a site of oceanic N loss. The greater mean depth and steepness of the seaward continental slope should render the slope far less efficient at returning the nutrients released from the sediments to the upper ocean. Thus, upon sea level lowering, the coastal environment would be less favorable as an environment for both coastal productivity and benthic N loss. However, because the direct impact of benthic N loss on the N isotopes is typically nil or very weak (9, 10), there have been, as yet, no direct tests of this hypothesis.

Since the first studies of the ocean N budget, it has been recognized that a balance is required between inputs (dominantly N₂ fixation and the biological fixation of CO₂) and removals (primarily by denitrification) of fixed N. Estimates of the ocean N budget during ice ages are based on paleoecological and paleochemical proxy records (11). Whereas the paleoecological proxy record provides a clear sign of sea level-driven glacial/interglacial oscillations in biogeochemical fluxes at and near the ocean margins (12), there have been, as yet, no direct tests of this hypothesis.
However, it has been pointed out that N2 fixers have other sensitivities suggesting that the SCS may be prone to coupling between denitrification and N2 fixation (11). These features include the N/P of the shallow water column in the region. These features may be important constraints on N2 fixation (3, 15).

The South China Sea (SCS) repeats end of paragraph is a marginal sea characterized by a high ratio of shelf area to basin area (~1.2). Deep SCS water has oceanographic characteristics similar to the western Pacific open ocean (16), with continuous exchange with the open western Pacific mainly through the Luzon Strait, which is ~2,200 m deep, too deep for the exchange of thermocline and deeper water masses to have been affected by glacial/interglacial sea level change. The warm tropical surface waters of the SCS and the adjacent Asian dust sources and ocean margins appear to leave N2 fixation unconstrained by temperature or iron (17). The extensive East Asian and Sunda shelves host rapid sedimentary denitrification (8), which effectively removes fixed N and lowers the fixed nitrogen-to-phosphorus ratio (N/P) of the shallow water column in the region. These features suggest that the SCS may be prone to coupling between benthic denitrification and N2 fixation.

The nitrogen isotopes can be used to reconstruct past changes in N2 fixation in environments where the nitrogen isotopic signature of N2 fixation can be clearly observed in the thermocline. N2 fixation introduces N with a δ15N of ∼−1‰ versus atmospheric N2 (18), which is distinctly lower than the δ15N of oceanic nitrate (Fig. 1B). Mean ocean nitrate δ15N is elevated above that of the newly fixed N (9) because water column denitrification removes nitrate (NO3−) that is depleted in 15N (19). As a result, the remineralization of newly fixed N to nitrate causes regional lowering of nitrate δ15N underneath the surface waters in which N2 fixation occurs. This lowering is most intense in the shallow thermocline for two reasons. First, organic N is remineralized rapidly as it sinks, causing most of the sinking N and its isotopic signal of N2 fixation to be emplaced at shallow depths. Second, nitrate concentration decreases upward across the thermocline, helping the nitrate that derives from local or regional N2 fixation to represent a greater proportion of the total nitrate in the water. The lowering of nitrate δ15N by N2 fixation is perhaps most obvious today in the tropical and subtropical North Atlantic (20). However, a nitrate δ15N minimum in the shallow thermocline is also observed in the North Pacific (21), including the SCS (22) (Fig. 1C).

The upward decline in nitrate δ15N in the SCS thermocline is not observed everywhere in the tropical and subtropical North Pacific; for example, it is not observed in the equatorial or subarctic North Pacific (23, 24). Thus, it must be a reflection of N2 fixation occurring in the western tropical/subtropical North Pacific. The shallow thermocline (i.e., the depth range of 100 m to 200 m) of the modern SCS has a much higher nitrate concentration (10 μM to 15 μM) than the same water depth or density level in the open subtropical North Pacific (<5 μM; Fig. 1B and Fig. S1). As a result, lateral exchange of the upper 200 m of the water column with the open western North Pacific has minimal capacity to change the δ15N of nitrate in this depth.

Fig. 1. Core location and modern context for this study. (A) Topographic map showing the change in basin configuration around the SCS between interglacial sea level high stand and full glacial sea level low stand, assuming a 120-m lowering of the shore line on modern topography (63) (black contour; modern land area shown in gray). The locations of the coring site for core MD97-2142, the SEATS, and the hydrographic transect in the open western Pacific are shown with a star, triangle, and line, respectively. Colors depict model-simulated benthic denitrification rate (millimoles of N per square meter per day) (8). The 120-m ice age sea level lowering exposes almost all of the shallow shelf where benthic denitrification is rapid in the present day. (B and C) The depth profiles of the concentration and δ15N of nitrate plus nitrite in the upper 500 m at SEATS. The samples are collected from four cruises from 2012 summer to 2013 winter (indicated with different colors and symbols). The error bar at each depth indicates 1 SD associated with water collections from multiple casts during each cruise. The depth profile of the nitrate plus nitrite concentration in the open western Pacific is also shown for comparison (black square). The remineralization of newly fixed N is taken as the dominant contributor to the subsurface nitrate δ15N minimum and also lowers the nitrate δ15N throughout the water column (22). The FB-δ15N of both G. ruber and O. universa measured at the surface sediment are 4.9‰ (black arrow), similar to the δ15N of the shallow thermocline nitrate being supplied to the photic zone.
observed for *G. ruber* than for *O. universa* during the last ice age, with an average offset of 0.39‰ for 20 ka to 60 ka compared with 0.25‰ for the entire overlapping period (Fig. 2). The same sense of divergence (with the δ¹⁵N of *O. universa* greater than that of *G. ruber*) is also observed in LGM samples from the Caribbean Sea (13), where it was tentatively interpreted to provide secondary support of the idea of reduced N₂ fixation during the LGM (13); a similar explanation may apply in the SCS. In any case, the changes in interspecies FB-δ¹⁵N difference are minor relative to the FB-δ¹⁵N changes shared by the two species.

The FB-δ¹⁵N records have no clear correspondence with the bulk sediment records from the SCS, which do not show systematic glacial/interglacial changes (Fig. 2). Several of the existing bulk sediment records from the SCS are substantially dissimilar from one another (Fig. 24) (27). Moreover, although foraminifera-bound N content is low and stable over glacial cycles, bulk sediment N content varies substantially over time and across records (Fig. 2B). Similar observations regarding SCS bulk sedimentary N records have previously been attributed to diagenesis and to multiple sources of N to the bulk sediment (28). Variation in terrigenous input at our study site has been documented to be associated with sea level change over the glacial cycles, for example, with higher concentrations of n-alkanes coinciding with lower sea level (29). A general disconnect between FB-δ¹⁵N and bulk sediment δ¹⁵N has been observed in the Caribbean Sea as well, where sedimentological data also point to terrestrial/shelf N inputs to the bulk sediments, especially in glacial intervals (13, 14). These findings argue against the utility

range of the SCS. Therefore, the upward decline in nitrate δ¹⁴N observed in the SCS thermocline (Fig. 1C) is probably mostly generated within the SCS.

Nitrate from the shallow thermocline supplied by vertical mixing is the dominant N source to the tropical and subtropical surface ocean on an annual basis (25). Thus, the δ¹⁵N of the shallow thermocline nitrate is the dominant control on the δ¹⁵N of net biomass production in the surface ocean each year, which, in turn, sets the δ¹⁵N of the various species of planktonic foraminifera, the shells of which can be analyzed for the δ¹⁵N of their fossil-bound organic N (26). As a consequence, foraminifera-bound N has a lower δ¹⁵N in the modern SCS than in, for example, most of the equatorial Pacific (Fig. 2). Moreover, a higher rate of N₂ fixation in the SCS would cause a further decline in foraminifera-bound δ¹⁵N (FB-δ¹⁵N), whereas slower N₂ fixation would cause a δ¹⁵N rise.

**Results and Discussion**

Here we report a record of FB-δ¹⁵N in the SCS over the last 860 ky, covering eight major glacial cycles (Methods). The sediment core is from site MD97-2142 on the slope off Palawan Island (Fig. L4, 12°41′N, 119°27′E, water depth of 1,557 m, sedimentation rate of 10 cm/ky, age model shown in Fig. S2). The full record uses a single planktonic species, *Orbulina universa*. To test the generality of the *O. universa* FB-δ¹⁵N record, the FB-δ¹⁵N of *Globigerinoides ruber* was also analyzed over the last glacial cycle (back to ~125 ka). FB-δ¹⁵N is expected to be similar for these two euphotic zone-dwelling species (26), and the data fit this expectation (Figs. 2 and 3). Slightly lower δ¹⁴N is

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**Fig. 2.** Compilation of the (A) δ¹⁵N and (B) N content of foraminifera-bound N and bulk sedimentary N records in the SCS and open Pacific. In SCS core MD97-2142, FB-δ¹⁵N (filled circles) and N content (open circles) are shown for the planktonic foraminifera species *O. universa* (red circles) and *G. ruber* (blue circles) and for bulk sedimentary N (black line). Previously published bulk sedimentary δ¹⁵N and N content from SCS cores 17940 and 17954 are also shown (green and brown lines) (27, 28). One open Pacific data set is a last ice age/Holocene FB-δ¹⁵N comparison in cores from along the Line Islands in the central equatorial Pacific (purple diamonds) (36). The latitudes of the five cores are 0.22°S, 1.27°N, 2.46°N, 2.97°N, 5.22°N, and 6.83°N. Each core corresponds to paired LGM and Holocene data, with the FB-δ¹⁵N from both the LGM and the Holocene increasing northward from the equator; from the assemblage of cores, no LGM-to-Holocene difference is observed. A second open Pacific data set is a record of FB-δ¹⁵N from the western tropical north Pacific [ODP Site 871 (5.56°N, 172.35°E); blue triangles]. This record shows no clear FB-δ¹⁵N decrease from the last ice age to the Holocene, in contrast to SCS FB-δ¹⁵N. The locations of the sediment cores are shown in Fig. 59.

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**Fig. 3.** Records of planktonic FB-δ¹⁵N and planktonic and benthic foraminiferal calcite δ¹⁸O over the last eight glacial cycles. FB-δ¹⁵N is plotted decreasing upward, such that N₂ fixation increases upward. FB-δ¹⁵N of *O. universa* (A–C, red) at MD97-2142 is similar to the FB-δ¹⁵N of *G. ruber* (A, blue) during the last 130 ky. Error bars indicate 1 SD of the oxidation replicates (Methods). FB-δ¹⁵N is highly correlated with the δ¹⁸O of *G. ruber* (B, gray) (64) and of *C. wuellerstorfi* (C, black). The glacial/interglacial change in the δ¹⁸O of the benthic foraminifera *C. wuellerstorfi* is typically considered to be mostly due to change in global ice volume (and hence sea level), with deep-water temperature change having a smaller effect. The light gray bars indicate the glacial terminations.
of bulk sediment δ¹⁵N records for reconstructing the δ¹⁵N of export production in marine environments such as the SCS and Caribbean Sea, where terrestrial and shelf inputs are significant, export production is modest, and sedimentary organic matter preservation is not exceptionally high. The FB-δ¹⁵N record from MD97-2142 indicates an increase in the δ¹⁵N of subsurface nitrate of the SCS during the glacials (Fig. 3). Throughout the ocean, the δ¹⁵N of subsurface nitrate is affected by lateral communication with other regions. Accordingly, one might propose that Pacific-wide processes raised the δ¹⁵N of the nitrate in the SCS by ~3‰ during glacials. This might be driven by a whole ocean nitrate δ¹⁵N rise. Alternatively, it might be driven by a change in the rate of circulation in and out of the SCS and/or a change in N-cycle processes outside the SCS.

With regard to changes in lateral circulation, as described above, there is no clear mechanism by which communication with open western North Pacific waters shallower than ~200 m could have a strong influence on SCS nitrate δ¹⁵N. Accordingly, this scenario must involve waters deeper than ~200 m. However, modern oceanic nitrate isotope data do not indicate that a change in lateral circulation by itself would significantly change intermediate-depth nitrate δ¹⁵N in the SCS. For the western expanses of subtropical, subpolar, and tropical Pacific, even when including the western equatorial Pacific and existing measurements from the central South Pacific, the δ¹⁵N of nitrate in intermediate-depth waters falls between 5.5‰ and 7.0‰, with most measurements in a still narrower range (23, 24, 30–35). Intermediate-depth nitrate in the modern SCS falls squarely in this range (Fig. 1 and Fig. S1), in part because of the rapid lateral exchange of the SCS with the neighboring open western North Pacific through the Luzon Strait. If this weak variation in intermediate-depth nitrate δ¹⁵N also applied in the past, even major changes in the circulation of intermediate or mode waters would have had only modest effects on the δ¹⁵N of the nitrate imported into the SCS.

We next consider the possibility of global and/or Pacific-wide changes in nitrate δ¹⁵N that are communicated into the SCS. To compare with our record, we generated a 120-ky FB-δ¹⁵N record using Globigerinoides sacculifer from western tropical North Pacific ([Ocean Drilling Program (ODP) 807]. This new record as well as paired LGM and Holocene FB-δ¹⁵N data from the central equatorial Pacific (36) show only small δ¹⁵N differences between the LGM and the Holocene (Fig. 2). Bulk sediment records from the eastern Pacific show the opposite sense of δ¹⁵N change compared with that in the SCS (Fig. 4) (5, 37, 38). These and other records from across the global ocean argue against the possibility that the elevated FB-δ¹⁵N observed in the SCS during the LGM reflects a change in the δ¹⁵N of subsurface nitrate imported laterally from the open Pacific.

One might hypothesize greater vertical mixing in the SCS during ice ages, which might weaken the δ¹⁵N decline upward through the SCS thermocline, thus increasing the δ¹⁵N of the nitrate supply to the euphotic zone. However, this mechanism would predict simultaneous changes in productivity and FB-δ¹⁵N in the oligotrophic SCS, and yet the productivity proxies are not particularly well correlated with FB-δ¹⁵N (Fig. S3). Moreover, because deep thermocline waters have a substantially lower N/P ratio than the shallow thermocline waters (16), an increase in the supply of deeper-held nutrients to the surface would have encouraged an increase in N₂ fixation, which would have worked to lower the δ¹⁵N of the sinking flux and of the shallow subsurface nitrate. This increase in N₂ fixation would have countered the tendency for increased vertical mixing to raise the δ¹⁵N of the nitrate supply and, in turn, FB-δ¹⁵N. Finally, if changes in vertical mixing were the dominant driver of the δ¹⁵N changes, we would expect synchronous changes in the sea surface temperature (SST) and δ¹⁵N, which is not supported by our data (Figs. 3, 4, and 5A). Similarly, it is observed that a planktonic foraminiferal index of vertical mixing (39) changes early in the deglaciation and then stabilizes, whereas FB-δ¹⁵N evolves through the deglaciation and Holocene (Fig. 2) (40). As the effect of vertical exchange on nitrate δ¹⁵N would be essentially instantaneous (decadal at most), this lag argues against SCS hydrographic conditions as the dominant signal in FB-δ¹⁵N.

Nitrogen inputs from river and atmospheric sources are also unlikely to explain the FB-δ¹⁵N variations. Clear signs of riverine N input are confined to the inner shelf above 30 m, and our preliminary data from two summer cruises show high δ¹⁵N values for the shallow shelf nitrate (up to 12‰). Atmospheric N deposition is low in δ¹⁵N relative to oceanic nitrate (41), so an increase in deposition would have been required during interglacials to explain the low FB-δ¹⁵N. However, the interglacial δ¹⁵N impact, when neglecting the recent rise in anthropogenic N, is far too low for its removal to have caused a 3‰ rise in FB-δ¹⁵N during ice ages (42, 43).

Fig. 4. Records of N₂ fixation, sea level, sea surface temperature, water column denitrification, and atmospheric iron supply. (A) Within the SCS, N₂ fixation is generally higher (FB-δ¹⁵N is lower) in the interglacials (red; FB-δ¹⁵N increases downward). N₂ fixation increases upon each termination and is tightly correlated with the mean relative sea level stack (black) generated using seven independent sea level reconstructions (49). (B) The structure of N₂ fixation variability is also similar to changes in sea surface temperature at MD97-2142 (29) but lags behind temperature changes, especially during the latter half of the record. Among the three records sensitive to water column denitrification from (C) the California margin (37), (D) eastern Equatorial Pacific (65), and (E) Arabian Sea (66), the bulk δ¹⁵N record from the California margin is (negatively) correlated with FB-δ¹⁵N in the SCS (note reversal of δ¹⁵N scales between A and C–E). (F) A Chinese loess record shows generally higher iron flux in the glacials (67), which would increase N₂ fixation during glacials if iron availability were the primary control for N₂ fixation, inconsistent with the FB-δ¹⁵N data. The light gray bars indicate the glacial terminations.
A changing rate of \( N_2 \) fixation is the sole remaining mechanism with the potential to explain the cycles in \( FB-\delta^{15}N \) at this site in the SCS. We conclude that the \( \delta^{15}N \) of the shallow thermocline nitrate was lowered less by \( N_2 \) fixation during glacial, due to an ice age reduction in the rate of this process. The amplitude of the SCS \( \delta^{15}N \) rise in the glacial is similar to that observed in the tropical western North Atlantic (13, 14), where \( N_2 \) fixation also has a strong imprint on thermocline nitrate \( \delta^{15}N \) (20). The \( \delta^{15}N \) of the global/interglacial \( FB-\delta^{15}N \) change in the SCS is comparable to the largest regional declines in ocean nitrate \( \delta^{15}N \) attributed to \( N_2 \) fixation in the modern ocean (44, 45); this suggests that the ice age decline in \( N_2 \) fixation rate was dramatic, most likely to less than half of the modern rate based on a two end-member mixing calculation (Estimate for Glacial–Interglacial Changes in \( N_2 \) Fixation Rate).

A question that arises is how \( FB-\delta^{15}N \) glacial–interglacial variations of \( \sim \delta^{150} \) could result when the modern nitrate \( \delta^{15}N \) decline from \( \sim 500 \) m depth into the shallow SCS thermocline is only 1 to \( \sim 2 \delta^{150} \) (Fig. 1B). First, the Holocene does not represent the minimum observed \( FB-\delta^{15}N \), so shallow thermocline nitrate \( \delta^{15}N \) is reconstructed to have been still lower during previous interglacials. Second, the role of \( N_2 \) fixation in lowering the \( \delta^{15}N \) of subsurface nitrate is greater than indicated by the local vertical gradient in nitrate \( \delta^{15}N \) alone, as low \( \delta^{15}N \) from \( N_2 \) fixation spreads horizontally and vertically, as nitrate and sinking particulate nitrogen (45). This latter point also reinforces the arguments above against a hydrographic (e.g., vertical mixing) explanation for the observed \( FB-\delta^{15}N \) changes.

At all nine glacial terminations covered by our \( FB-\delta^{15}N \) record, a reconstructed increase in \( N_2 \) fixation in the SCS coincides with decreases in planktonic and benthic \( \delta^{18}O \), a rise in sea level and thus an increase in shelf area (Fig. 4 and Figs. S4 and S5), a rise in SST, and an apparent deglacial increase in water column denitrification in the eastern tropical Pacific (Figs. 3 and 4). The length of the SCS \( FB-\delta^{15}N \) record allows for the use of time series analysis to identify the correlations that are most consistent with a causal connection.

Variability in SST is highly coherent with that in \( FB-\delta^{15}N \) (Fig. S4). However, \( FB-\delta^{15}N \) lags SST by more than 4 ky in the dominant 41- and 100-ky bands for the latter half of the record (Fig. S4). Because the physiological and biochemical response of \( N_2 \) fixers to SST would be effectively instantaneous, the lag argues against \( N_2 \) fixation as the driver of the greatest \( FB-\delta^{15}N \) variations. Moreover, based on observed sensitivities (15), the reconstructed SCS SSTSs fall into the optimal range for \( N_2 \) fixation, and a 3°C cooling would be far too small to explain the dramatic reduction in \( N_2 \) fixation during glacials. Dust fluxes are lowest when reconstructed \( N_2 \) fixation is highest, arguing against iron supply as the explanation for the reconstructed \( N_2 \) fixation changes (Fig. 4F). This lack of positive correlation between \( N_2 \) fixation and dust supply is consistent with high iron availability in the SCS even during interglacials, both from the margins and from atmospheric deposition.

There are three bulk sediment \( \delta^{15}N \) records from near water column zones of suboxia and that are adequately long to compare with our SCS \( FB-\delta^{15}N \) record (Figs. 4 C–E and 5B). These environments are characterized by high export production and relatively good preservation of sedimentary organic matter, such that the potential of bulk sediment \( \delta^{15}N \) to robustly record the \( \delta^{15}N \) of N export is greater than in most other ocean regions (46). Of these records, only ODP Site 1012 (37) from the California margin shows significant coherency (Figs. 4C and 5B). The anticorrelation of the records might be taken to suggest that enhanced water column denitrification in the eastern tropical North Pacific during interglacials was responsible for coincident \( N_2 \) fixation in the SCS. However, the coherency is limited to periods near 100 ky, suggesting that observed similarities in the records reflect independent but similarly timed responses to glacial cycles.

The SCS \( FB-\delta^{15}N \) and \( \delta^{18}O \) records are similar in large-scale structure (Figs. 3 B and C), suggesting a connection between \( N_2 \) fixation and sea level. A stack of sea level records (47–49) shows high coherency with the SCS \( FB-\delta^{15}N \) over a wide range of frequencies (Fig. 5C; significant against red noise with 95% confidence), as strong as the coherency between independent sea level reconstructions (Figs. S6–S8). Thus, the reconstructed glacial/interglacial changes in \( N_2 \) fixation appear to require a mechanism that involves ice volume and/or sea level change. The correlation of markers of terrigenous input with \( FB-\delta^{15}N \) in MD972142, with greater terrigenous material when \( FB-\delta^{15}N \) is high (29), provides additional support for this interpretation (Fig. S3D). As no relatively direct, low-lag connection between ice volume and \( N_2 \) fixation appears plausible for the SCS, the data argue for sea level as the dominant driver of \( N_2 \) fixation change.
The extensive continental shelf area of the tropical western North Pacific adjacent to the SCS, the Sunda shelf in particular, appears to be an important locus of benthic denitrification (8). This shelf area was nearly completely lost during peak glacials (Fig. 1A). The reduction in shelf area has been proposed to reduce shelf sedimentary denitrification in the glacialis (7), which, in turn, would lead to higher N/P (less excess P) in the upper water column. This change would have discouraged N2 fixation in the SCS and neighboring regions, explaining the remarkable coherency of the sea level records and our SCS FB-$\delta^{15}$N record (Fig. 6).

The SCS FB-$\delta^{15}$N record thus provides the most direct evidence to date for the long-hypothesized scenario in which sea level drives glacial cycles in benthic N loss along the continental margins. Such a mechanism implies that SCS N2 fixation responded to changes in nearby shelf area, as changes in N loss on distant shelves should have been compensated by N2 fixation in those regions. N2 fixation compensation for N loss might be confounded by changes in iron availability in other tropical/subtropical ocean regions. However, for regions such as the SCS that are characterized by high iron supply, local compensation for N loss changes is arguably to be expected.

Continental slopes are known to deposit substantial quantities of margin-derived organic matter at their base (50), and the resulting accumulation drives denitrification on the slope (31, 51, 52). It is possible that this process was accelerated during ice ages and, in part, replaced the sedimentary denitrification on the continental shelves. N loss on the slope may not lead to synchronous changes in N2 fixation because the N deficit would accumulate in deep water, not directly affecting the N/P of the nutrient supply to the locally overlying surface ocean. However, the funneling of organic matter into the deep ocean prevents the upper ocean nutrient recycling and other processes that render N loss so rapid on the shelves. Therefore, any increased N loss by denitrification on the slope is unlikely to have substantially compensated for the reduced N loss on the shallow margins.

N2 fixation slowed substantially during ice ages, as reconstructed here for the western tropical Pacific and previously for the North Atlantic, in both cases consistent with the response of N2 fixation to excess P supply as the dominant driver of the changes (13, 14). The correlation between SCS N2 fixation and sea level provides data-based support for the hypothesis of reduced sedimentary denitrification during ice ages (7, 53, 54), and bulk sediment $\delta^{15}$N records argue for reductions in water column denitrification as well (5, 6). With these lower rates of both input and loss, the residence time of fixed N in the ocean [currently $\sim$3 ky (55, 56)] would have become longer and thus less distinct from the residence time of phosphorus [15 ky to 40 ky (57)], although the latter may also have changed over glacial cycles.

Benthic N loss on the continental margins reflects the high flux of organic matter to the coastal seabed (50–52), a consequence of both the shallow continental shelf and the high productivity of the coastal water column (Fig. 6). The high productivity is, in turn, supported by the shelf, which traps sinking organic matter and quickly returns nutrients to the sunlit surface ocean. Thus, the reduction in benthic N loss during ice ages implies a net decline in the organic matter supply to coastal ecosystems, especially those organisms that rely on the benthos. In part because of their extraordinarily high productivity and benthic activity, the modern continental shelves have tremendous importance for seafloor fauna, fish, and marine mammals. The reconstructed biogeochemical changes imply that these higher trophic levels would have suffered a notable decline in food supply during the low sea level stands of ice ages (Fig. 6), potentially impacting the evolution and current characteristics of coastal species and ecosystems (e.g., ref. 58).

### Methods

**FB-$\delta^{15}$N Analyses.** The protocol follows and is modified from that of refs. 13 and 14. The individual foraminifera species (250- to 425-μm-size fraction, ~5 mg per sample) are picked manually and gently crushed under a dissecting microscope.

Samples are first sonicated for 5 min in an ultrasonic bath using 2% polyphosphate solution to remove clay particles. To remove metal coatings, bicarbonate-buffered dithionite–citric acid solution is then added to each sample, and the samples are placed in a water bath at 80 °C for 1 h. The final cleaning step is oxidative: Basic potassium persulfate solution is added to each sample, and the samples are autoclaved (at 121 °C) for 1 h. The cleaned samples are rinsed in deionized water and dried overnight at 55 °C. The cleaned foraminifera (~3 mg to 4 mg per sample) are weighed into a 15N reagent blank. Three different organic standards were used: USGS 40 ($\delta^{15}$N = −4.5% vs. air), USGS 41 ($\delta^{15}$N = 47.6% vs. air), and a laboratory standard made of a mixture of 6-aminocaproic acid
and glycine (δ15N = 5.4% vs. air). A minimum of 18 organic standards and three to five blanks were analyzed per batch of samples. To determine the N content of the samples, nitrate concentration is measured in the oxidation solution after autoclaving. The nitrate analysis is estimated from the means of separate oxidations of cleaned foraminiferal material, which averaged 0.22 ppm. The denitrifier method typically has a SD (1 SD of the nitrate concentration of the blanks ranged between 0.3 μM and 0.7 μM (less than 5%, typically less than 2%, of the total N per sample). The δ15N of the samples is determined using the denitrifier method in conjunction with gas chromatography and isotope ratio mass spectrometry (60, 61). The denitrifier method involves the transformation of dissolved nitrate and nitrite into nitrous oxide gas (N2O) via a naturally occurring denitrifying bacterial strain that lacks an active form of the enzyme N2O reductase. Before adding the foraminifera samples to the bacteria, the sample solution is acidified to pH 3 to 7. The denitrifier Pseudomonas chlororaphis was used for this work. Normally, 5-nmol samples are added to 1.5 mL of bacterial concentrate after degassing of the bacteria. Along with the samples, the organic standards as well as replicate analyses of nitrate reference material International Atomic Energy Agency NO3 reference (IAEA-N3 δ15N = −4.7‰ vs. air) and a bacterial blank are also measured. The IAEA-N3 standards are used to monitor the bacterial conversion and the stability of the mass spectrometry, and the oxidation standards are used to correct for the oxidation blanks. If possible, samples were oxidized in duplicate, and oxidized samples were also sometimes analyzed by the denitrifier method in duplicate. The denitrifier method typically has a SD (1 SD of the nitrate concentration of the blanks ranged between 0.3 μM and 0.7 μM (less than 5%, typically less than 2%, of the total N per sample). The error bars in Fig. 1 represent 1 SD of the nitrate δ15N analyzed at the same depth from the different casts, which averaged 0.20‰. ACKNOWLEDGMENTS. We thank M. A. Weigand and S. Olenyi for assistance with the nitrate and foraminifera-bound δ15N analyses; Tung-Yuan Ho, Kuo-Yuan Lee, and Yao-Chu Wu for their assistance on cruises and water sampling; and M. P. Hain for discussions. Funding was provided by Taiwan Ministry of Science and Technology (MOST) Grant 105-2628-M-002-007-MY3, by National Taiwan University Grant NTU-CESRP-106-76251 (to H.R.), by MOST Grant NSC 101-2611-M-001-03-MY3 and a grant from the Sustainability Science Research Partnership of the Academia Sinica (to G.T.F.W.), by the US National Science Foundation (through Grants OCE-1060947 and PLR-1401489 to D.M.S.), and by the Grand Challenges Program of Princeton University.


