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Insights from Fossil-Bound Nitrogen Isotopes in Diatoms, Foraminifera, and Corals

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Abstract

Nitrogen is a major limiting element for biological productivity, and thus understanding past variations in nitrogen cycling is central to understanding past and future ocean biogeochemical cycling, global climate cycles, and biodiversity. Organic nitrogen encapsulated in fossil biominerals is generally protected from alteration, making it an important archive of the marine nitrogen cycle on seasonal to million-year timescales. The isotopic composition of fossil-bound nitrogen reflects variations in the large-scale nitrogen inventory, local sources and processing, and ecological and physiological traits of organisms. The ability to measure trace amounts of fossil-bound nitrogen has expanded with recent method developments. In this article, we review the foundations and ground truthing for three important fossil-bound proxy types: diatoms, foraminifera, and corals. We highlight their utility with examples of high-resolution evidence for anthropogenic inputs of nitrogen to the oceans, glacial–interglacial-scale assessments of nitrogen inventory change, and evidence for enhanced CO_2 drawdown in the high-latitude ocean. Future directions include expanded method development, characterization of ecological and physiological variation, and exploration of extended timescales to push reconstructions further back in Earth's history.

1. MOTIVATION FOR INVESTIGATING THE MARINE NITROGEN CYCLE

Reactive N: N that is readily available for biological assimilation, excluding the large quantities of N_2 available only through N_2 fixation

N_2 fixation: assimilation of atmospheric nitrogen (N_2) by a range of autotrophic and heterotrophic microorganisms, typically under N-limited conditions

Denitrification: a microbial process that reduces nitrate and nitrite to gaseous forms of N (N_2 or N_2O)

Nitrification: biological oxidation of ammonia to nitrate, either in two steps (with a nitrite intermediary) or in one step (directly to nitrate)

Assimilation: uptake and incorporation of inorganic nutrients into organic biomass during growth

Remineralization: the breakdown or transformation of organic matter into its simplest inorganic components

Isotopic fractionation: partitioning of heavier and lighter isotopes during physical, chemical, and biological processes

Nitrogen (N) is a biologically important element that plays a fundamental role in regulating global production, biodiversity, and climate. The total availability of reactive N in the ocean and its distribution in the surface ocean are first-order constraints on primary production and thus ocean fertility. Variations in the ocean inventory and surface availability of N over geologic time have impacted global biogeochemical cycling of N, carbon (C), and oxygen (O) throughout Earth's history (Falkowski 1997). More recently, significant modification of the global N cycle by humans has had major consequences, both positive (in terms of food production) and negative (related to ecosystem health, biodiversity loss, and global climate) (Erisman et al. 2013).

In the ocean, reactive N is present primarily as nitrate, with lesser but still significant amounts of nitrite, ammonium, and dissolved organic forms. The processes that are responsible for the transfers of N between these pools and into organisms include N addition by diazotrophic bacteria through N_2 fixation (Karl et al. 1997), removal by denitrification (Cline & Kaplan 1975) and the anaerobic ammonium oxidation (anammox) reaction (Kuypers et al. 2003), and internal N cycling processes such as nitrification, N assimilation, and remineralization. The processes tend to impart predictable N isotopic fractionations stemming from differences in reaction rates between ^{14}N and ^{15}N (Wellman et al. 1968, Codispoti 1989, Altabet & Francois 1994, Montoya 1994). Therefore, the N isotopic composition (as $\delta^{15}N$) of the different N pools in the ocean can be used to evaluate the relative roles of these various processes within the N cycle (Altabet & Francois 1994, Brandes & Devol 2002, Deutsch et al. 2004, Sigman et al. 2009).

Paleoceanographic N isotope measurements have been used to examine the marine N cycle in the past, including controls on the whole-ocean inventory, water-mass movements, and the role of the biological pump in the global C cycle (Galbraith et al. 2004, 2013; Sigman et al. 2021). They also provide a baseline for understanding human impacts on the marine N cycle (e.g., Oczkowski et al. 2016). Transfer of diagnostic N isotope signatures into the paleo-archives typically starts with assimilation of N through photosynthesis (**Figure 1**). The $\delta^{15}N$ value of the dissolved-N source is imprinted on the organic matter of phytoplankton and then passed on to heterotrophs, with potential offsets in values due to fractionation at each step. After death, marine organisms sink, and the small fraction of organic N (N_{org}) that survives remineralization in the water column delivers the $\delta^{15}N$ signal of those marine organisms to the seafloor, where this signal can be preserved by burial or lost due to N consumption by benthic micro- and macroorganisms (e.g., corals). However, processes that occur after death, during sinking and burial, have the potential to offset the original isotopic value (Altabet & Francois 1994, Robinson et al. 2012). Sinking particles demonstrate alterations in $\delta^{15}N$ values with depth, particularly in regions with low overall sediment flux or primary production, perhaps due to the loss of specific N_{org} fractions during remineralization or the addition of N from other sources (Macko & Estep 1984, Altabet et al. 1991, Altabet & Francois 2001, Lehmann et al. 2002, Lourey et al. 2003, Straub et al. 2013b).

The encapsulation of N within a biomineral (i.e., fossil-bound N) is thought to protect N from addition and removal processes that can alter the isotopic composition of exposed or external N_{org} (Altabet 1988, Shemesh et al. 1993). This review focuses on three fossil-bound N isotope archives and some insights they provide: diatom-bound N_{org}, planktic foraminifera–bound N_{org}, and coral-bound N_{org} (**Figure 1**). These three groups reflect distinct but geographically overlapping environments that together possess the potential to reconstruct a robust picture of the open-ocean marine N cycle in the past (**Figure 2**). These archives complement a number of other important biomineral N archives not covered here, such as those for bivalve shells, otoliths, radiolarians, tooth enamel, and bone.

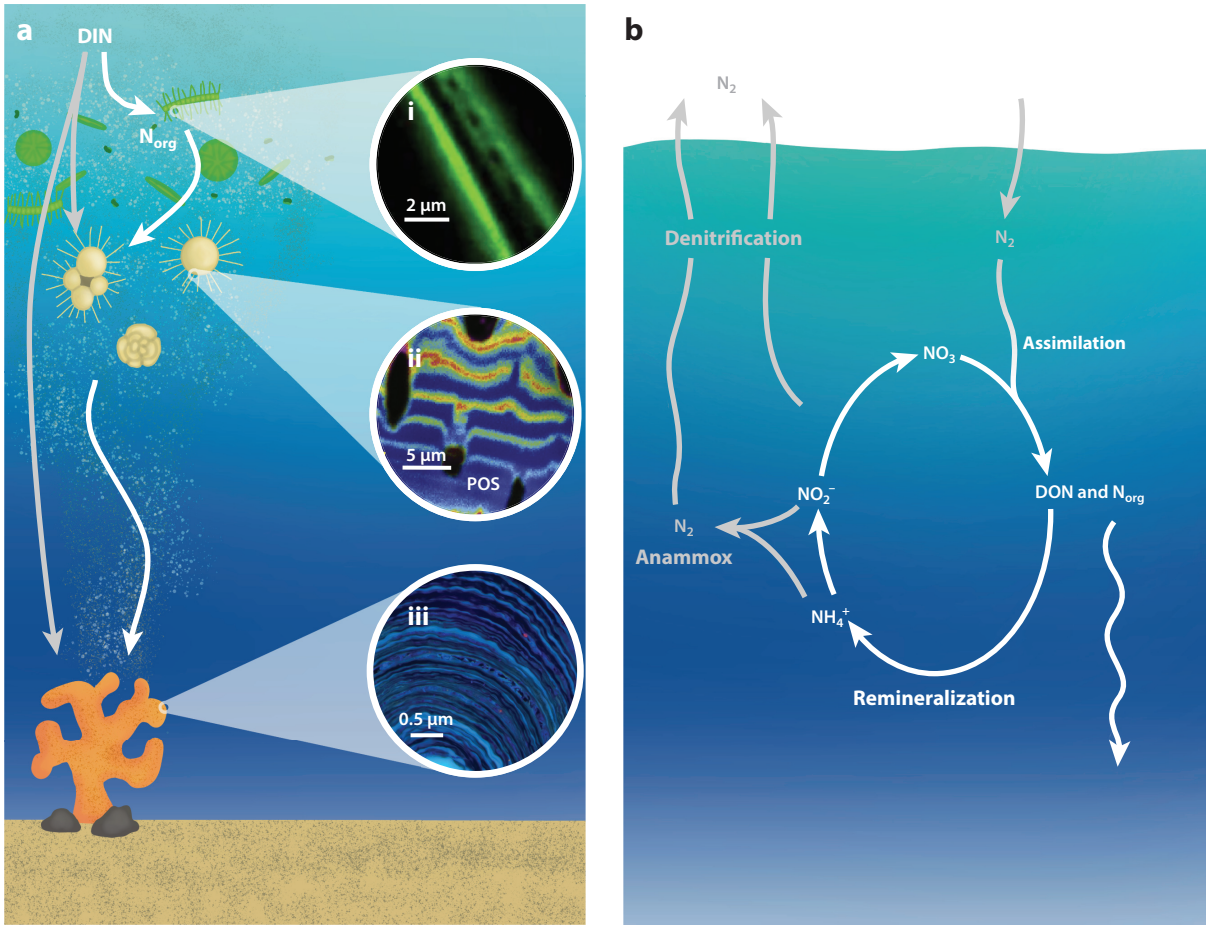

Figure 1

(*a*) Movement of N from the dissolved inorganic phase into phytoplankton, including diatoms, where a fraction is incorporated into the silica biomineral (subpanel *i*) and organic matter (as N_{org}). N_{org} in the water column, both particulate and dissolved, becomes part of the larger N_{org} pool, which is a source of N for foraminifera and corals. Incorporation of N (from DIN or N_{org} pools) into foraminiferal shells (subpanel *ii*) and coral skeletons (subpanel *iii*) occurs in layers between the calcium carbonate biominerals. Subpanels *i–iii* show, respectively, a diatom frustule stained with calcofluor, illuminating regions with high organic matter content; a NanoSIMS image of a foraminifera shell, with a N-rich primary organic sheet indicated beneath calcite layers; and coral proteinaceous skeleton gorgonin (*dark blue*) and calcite (*light blue*) layers imaged under UV light. (*b*) Marine N cycle schematic showing sources, sinks, and transformations of N in the ocean as described in the text. Abbreviations: DIN, dissolved inorganic N; DON, dissolved organic N; NanoSIMS, nanoscale secondary ion mass spectrometry; N_{org}, organic N; POS, primary organic sheet. Panel *a* adapted from Tesson & Hildebrand (2013) (CC BY 4.0); panel *b* adapted with permission from Spero et al. (2015); subpanel *iii* image by Catherine Nowakowski.

2. FOSSIL-BOUND NITROGEN

2.1. Why Target Fossil-Bound Nitrogen?

Fossil-bound N associated with biogenic silica and carbonate can generally be considered the template molecules for biomineralization (King & Hare 1972, Allemand et al. 1998, Sumper & Kröger 2004) (**Figure 1**). As discussed in Sections 2.3.1 (for diatoms), 2.4.1 (for foraminifera), and 2.5.1 (for corals), N is considered to be protected from external processes that may cause isotopic alteration once it is incorporated within these biominerals. Interpreting these fossil-bound

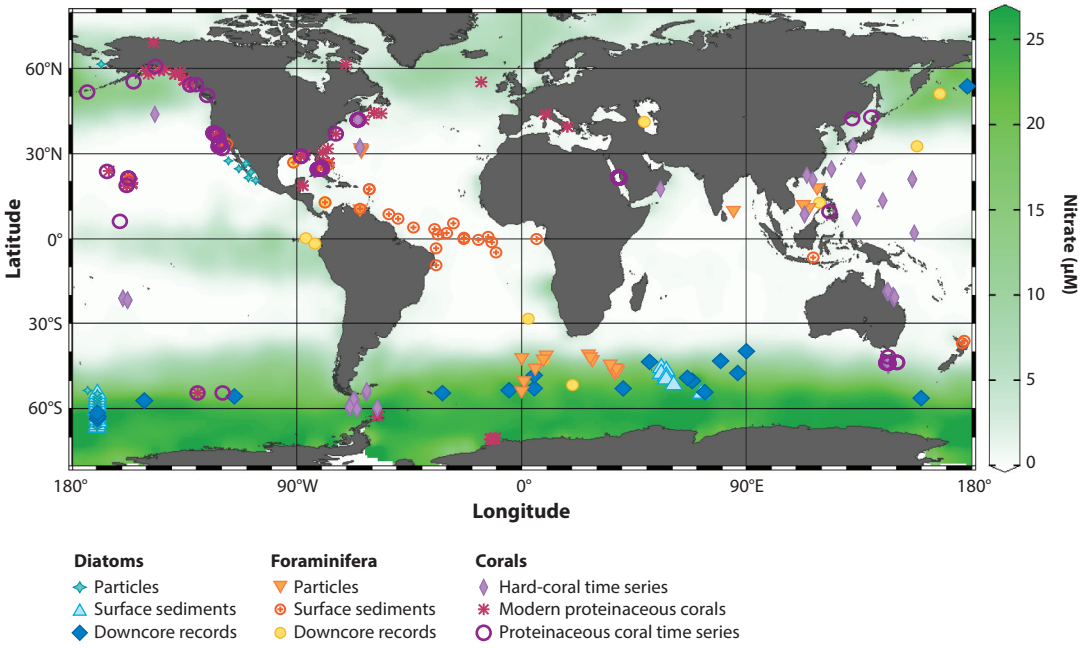

Figure 2

Location map of diatom-, foraminifera-, and coral-bound N isotope measurements overlaid on surface-ocean nitrate concentrations (Boyer et al. 2018). Diatom-bound data are shown as particles (*stars*, from large volume pumps and net tows), surface sediments (*triangles*), and downcore records (*blue diamonds*). Foraminifera-bound data are also shown as particles (*inverted triangles*, from net tows and sediment traps), surface sediments (*circles with crosses*), and downcore records (*circles*). Coral-bound data are shown as hard-coral time series (*purple diamonds*), modern proteinaceous corals (*asterisks*), and proteinaceous coral time series (*open circles*). For locations and citations, see the **Supplemental Material**.

Supplemental Material >

$\delta^{15}N$: $\{[(^{15}N/^{14}N)_{sample} / (^{15}N/^{14}N)_{standard}] - 1\} \times 1{,}000$ (‰), where the standard is atmospheric N_2

Biological pump: the production, export, and remineralization of organic matter leading to CO_2 sequestration below the surface mixed layer of the ocean

N_{org}: organic N (including both particulate and dissolved forms in the ocean)

$\delta^{15}N$ records, in turn, requires an understanding of the organism's N source(s); fractionation(s) associated with incorporation, photosymbionts, and alternative metabolisms; and potential preservation issues associated with biomineral diagenesis. If the isotopic fractionation associated with biosynthesis and incorporation of N within the mineral is systematic, the fossil-bound $\delta^{15}N$ value should relate to the $\delta^{15}N$ value of its N source, as discussed in the sections on ground truthing (Sections 2.3.2, 2.4.2, and 2.5.2). However, the N bound within biominerals is a very small fraction of the total sedimentary N_{org} content. In Section 2.2, we first address the challenges of making fossil-bound isotopic measurements that target this trace amount of N, which is less practical to do using methods designed for bulk sediments or organismal tissues.

2.2. Measuring Trace Amounts of Fossil-Bound Nitrogen

The relatively high N content in bulk sediment (2,800–14,000 μmol/g) and proteinaceous corals (6,000–9,000 μmol/g) means the $\delta^{15}N$ values in these archives are typically measured using elemental analyzer–isotope ratio mass spectrometry (EA-IRMS). However, given a typical opal-bound N content on the order of 10–15 μmol/g for diatoms and a carbonate-bound N of <10 μmol/g for foraminifera and corals, the mineral-bound N fraction is <1% of the total N in sediment or proteinaceous corals. Thus, the relatively large sample sizes needed for fossil-bound N combustion (typically >1 μmol N) often make it impractical to analyze on a standard EA-IRMS instrument. However, recent work has brought the sensitivity of EA-IRMS into the nanomolar

THE PERSULFATE-DENITRIFIER METHOD

The denitrifier method was developed to measure the high-precision (<0.2‰) $\delta^{15}N$ values from natural abundances (~1 μM) of nitrate in seawater (Sigman et al. 2001). This process involves feeding the inorganic N to denitrifying bacteria (*Pseudomonas* spp.), which then denitrify and respire it as N_2O gas, which is collected for isotopic analysis (Sigman et al. 2001, Weigand et al. 2016). This method was expanded for paleoecology contexts to include extensive external cleaning and a persulfate-oxidation step, allowing for the extraction of N_{org} bound within the opal silicate of diatoms and subsequent conversion to N_2O gas for isotopic analysis (Robinson et al. 2004). Since the original diatom-bound method was created, additional subfossil methods using mostly biogenic carbonates have been created for foraminifera (Ren et al. 2009), fish otoliths (Lueders-Dumont et al. 2018), and coral skeletons (Wang et al. 2014).

range, as low as 40 nmol of N_2 (nano-EA-IRMS; Polissar et al. 2009), opening this method for fossil-bound N applications.

In an effort to find a more sensitive method for measuring fossil-bound $\delta^{15}N$ values, Robinson et al. (2004) developed a wet chemical technique that dissolves diatom frustules, releasing N_{org} that is oxidized to nitrate for subsequent bacterial conversion to N_2O using the denitrifier method (Sigman et al. 2001). The persulfate-denitrifier method (see also the sidebar titled The Persulfate-Denitrifier Method) avoids the potential influence of atmospheric N_2 contamination associated with traditional flash combustion and increases its sensitivity by a factor of 50 or more (Robinson et al. 2004). The improved sensitivity from this method combined with further refinement of the isotope analysis of sample N_2O (e.g., McIlvin & Casciotti 2011) allowed the development of analogous carbonate-bound methods for corals (Wang et al. 2015) and foraminifera (Ren et al. 2009) and the implementation of ground-truthing studies using laboratory cultures and field-collected samples (Horn et al. 2011; Morales et al. 2013; Smart et al. 2018, 2020; Robinson et al. 2020).

2.3. Diatoms

Diatoms are a diverse group of photosynthetic protists from the class Bacillariophyceae that first appeared in the fossil record during the Cretaceous (~120 Ma) and expanded significantly in the Cenozoic. They produce ornate amorphous silica frustules that are well represented in the fossil record.

2.3.1. Diatom foundations. Diatom distribution is regulated by the availability of dissolved silica, a nutrient that is depleted in much of the surface ocean. As a consequence of their dissolved-silica requirement, they are found in abundance in regions where dissolved-silica-rich deeper waters are delivered to the surface, such as high latitudes and productive, low-latitude upwelling regions. Diatoms serve as particularly important archives for polar oceans and water depths where carbonate microfossils are less abundant or poorly preserved.

Diatom frustule template molecules include silaffins, long-chain polyamines, silicalemma-associated proteins, silicanins, and chitins, which play major roles in silica morphogenesis (Kröger et al. 2000, Sumper & Kröger 2004, Brunner et al. 2009, Scheffel et al. 2011, Tesson & Hildebrand 2013). The diatom-bound $\delta^{15}N$ ($\delta^{15}N_{DB}$) values are likely influenced by the particular blend of these biomineral-associated molecules, which vary among species (Kröger et al. 2000, Sumper & Kröger 2004). The exact isotope effects associated with frustule production and how they may vary with species or environment remain unknown.

Biomineral: a mineral created by an organism, typically as part of a structurally important component (e.g., teeth, bones, or shells)

Photosymbiont: an organism in a mutually beneficial relationship with another organism that lives in close physical proximity, where one of the organisms is capable of photosynthesis

Diagenesis: alteration of the original physical/chemical characteristics of a material (e.g., sediments or fossils) through microbial activity, water–material interactions, and depositional compaction

Elemental analyzer–isotope ratio mass spectrometry (EA-IRMS): a method for measuring total N as N_2 after flash combustion and passage through oxidation–reduction and chromatography columns

Last Glacial Maximum: the most recent time during the last glacial period when ice sheets were at their maximum extent

Shemesh et al. (1993, 1995) first recognized that targeting the organic C and N bound with biogenic silica would avoid measuring an altered isotopic signal. These first results were flawed, due to the use of nitric acid in the cleaning procedures (Sigman et al. 1999), yet they were groundbreaking in their identification of a robust, protected archive of organic matter. Since 1993, significant advances have been made in isolating the frustule-bound N_{org} through a series of chemical cleaning steps (Shemesh et al. 1993, Sigman et al. 1999, Robinson et al. 2004, Kalansky et al. 2011, Morales et al. 2013).

2.3.2. Diatom ground truthing. Early work sought to investigate whether $\delta^{15}N_{DB}$ values reflect the surface-ocean $\delta^{15}N$ value of nitrate and to what extent this relationship varies by species or location. In Southern Ocean surface sediments, $\delta^{15}N_{DB}$ values increase equatorward with increasing surface-nitrate $\delta^{15}N$ values, associated with progressive drawdown of nitrate by phytoplankton (Sigman et al. 1999; Robinson et al. 2004, 2020; Robinson & Sigman 2008) (**Figure 2**). The existing data present deviations from the first-order expectation of a northward increase in $\delta^{15}N_{DB}$ that parallels the increase in $\delta^{15}N$ of nitrate, including significant differences in the degree of isotopic enrichment between expected and observed values. The observed northward increase in $\delta^{15}N_{DB}$ in the Pacific sector is steeper than expected based on the northward increase of nitrate $\delta^{15}N$ in the Pacific sector (Robinson et al. 2004, 2020; Robinson & Sigman 2008; Smart et al. 2020), and $\delta^{15}N_{DB}$ also increases toward Antarctica, south of the Antarctic Polar Front in the Pacific sector. This was not observed in the Indian sector (Robinson et al. 2004, 2020; Robinson & Sigman 2008). These differences, which are possibly due to regional differences in nutrient uptake dynamics and/or sea ice extent, are not yet explained.

Relationships between species abundance and $\delta^{15}N_{DB}$ values have been probed in downcore records where diatom assemblage data were available (Jacot Des Combes et al. 2008, Robinson & Sigman 2008, Studer et al. 2015). Jacot Des Combes et al. (2008) specifically highlighted *Eucampia antarctica* resting spores, a sea ice indicator and marker species of the Last Glacial Maximum. Resting spores tend to form when nutrients are near depletion, which is also when the $\delta^{15}N$ of nitrate is elevated. Because *E. antarctica* is abundant in Last Glacial Maximum sediment, which tends to have the highest $\delta^{15}N_{DB}$ values of the last 50 ka, it was posited that *E. antarctica*, or resting spores more generally, may bias the record toward higher values, reflecting times of nutrient stress.

One way to avoid bias due to assemblage variations is to examine a given species through time, akin to making stable isotope measurements on foraminiferal calcite (see Section 2.4). However, separation of diatoms at the species or even genus level remains exceedingly difficult given the amount of opal needed for analysis. Exciting progress on this front now allows for the isolation of morphologically distinct pennate and centric groups based on hydrodynamic differences during centrifugation (Studer et al. 2015). Sample comparisons of pennates and centrics reveals differences in the groups' $\delta^{15}N_{DB}$ values. Whether these are species-intrinsic differences strictly due to fractionation associated with N incorporation or are related to seasonal/growth conditions of the different species is an open question (Studer et al. 2015).

Given the difficulties in separating species from sediments, culture is likely the best way to examine potential isotopic differences among species. We specify "potential" because culture experiments tend to optimize growth conditions and may not reflect growing conditions in the ocean. The first culture work seeking to isolate species-related differences in $\delta^{15}N_{DB}$ suggested that diatoms grown in a closed system fractionate N during its incorporation into their frustules, recording a $\delta^{15}N$ value that is lower than that of the diatoms' biomass (Horn et al. 2011). However, these initial culture observations are inconsistent with subsequent field and culture estimates. In diatom-dominated samples from a Bering Sea net tow and in surface-ocean particles >10 μm in diameter from the Southern Ocean, the $\delta^{15}N_{DB}$ values were consistently greater than the $\delta^{15}N$

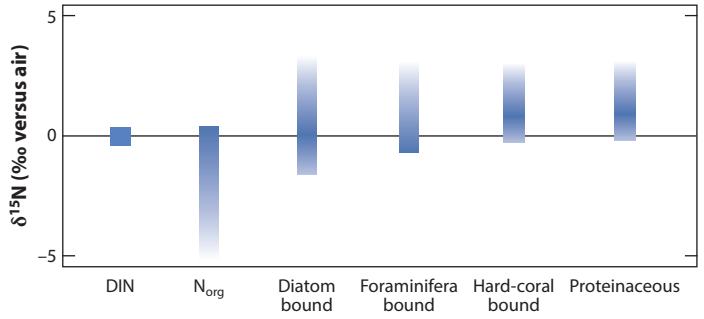

Figure 3

Approximate ranges of fossil-bound $\delta^{15}N$ values relative to source N pools. The $\delta^{15}N$ value of DIN is set to 0‰. Phytoplankton N_{org} tends to have a $\delta^{15}N$ less than or equal to the DIN used for growth. Diatom-bound $\delta^{15}N$ values tend to be elevated relative to phytoplankton N_{org} values by ~3.5‰ on average (Morales et al. 2014, Robinson et al. 2020). Foraminifera-bound $\delta^{15}N$ values tend to be equal to or greater than the $\delta^{15}N$ values of sub-euphotic-zone nitrate, on the order of 0–2‰ (Ren et al. 2009; Smart et al. 2018, 2020). Coral-bound $\delta^{15}N$ values tend to be offset slightly higher than those of the ambient DIN pool, on the order of 0–2‰ (Sherwood et al. 2014, Wang et al. 2016). Note that the uncertainty in these values remains quite large, necessitating future ground truthing. Abbreviations: DIN, dissolved inorganic N; N_{org}, organic N.

values of the biomass or total particulate N (Morales et al. 2014, Robinson et al. 2020). More recent work with batch cultures, investigating community-level $\delta^{15}N_{DB}$ variability in bottles seeded with populations collected in the dissolved-silica-rich region south of the Sub-Antarctic Front (Jones 2020), was consistent with the field-based data—all show $\delta^{15}N_{DB}$ to be approximately 3–5‰ higher than the $\delta^{15}N$ of biomass or particulate N (**Figure 3**). Importantly, the relationship between $\delta^{15}N_{DB}$ and the $\delta^{15}N$ of the total N in the community cultures was indistinguishable between two stations at 66°S and 61°S, despite their distinct diatom community compositions. The prevailing field and experimental data suggest that the incorporation of N into diatom frustules favors ^{15}N and that species composition does not set community $\delta^{15}N_{DB}$ values, at least in the more nutrient-rich regions of the Southern Ocean (Morales et al. 2014, Jones 2020, Robinson et al. 2020).

2.4. Foraminifera

Foraminifera are unicellular zooplankton with calcite shells that emerged in the mid-Jurassic (~170 Ma). Their advantage as a fossil-bound N reservoir lies in their widespread occurrence from the tropics to the poles across all major ocean basins. The relatively large size and often distinctive morphologies of foraminifera shells allow different species to be identified (e.g., as stratigraphic markers) and separated under a microscope to produce species-specific geochemical records, which is not possible for most microfossils (e.g., diatoms and radiolarians). For the same reasons, there is a wealth of O and C isotope data to provide the chronology and climate context for foraminifera-bound $\delta^{15}N$ (as $\delta^{15}N_{FB}$) records (Altabet & Curry 1989).

2.4.1. Foraminifera foundations. The utility of planktic (upper-ocean-dwelling) foraminifera as a recorder of oceanic N was recognized by Altabet & Curry (1989) and supported by the stability of downcore N content and amino acid composition of foraminifera shells (King & Hare 1972, Robbins & Brew 1990) over tens to hundreds of thousands of years. Yet it is only in the last decade that method developments have made it practical to perform paleoceanographic reconstructions using $\delta^{15}N_{FB}$.

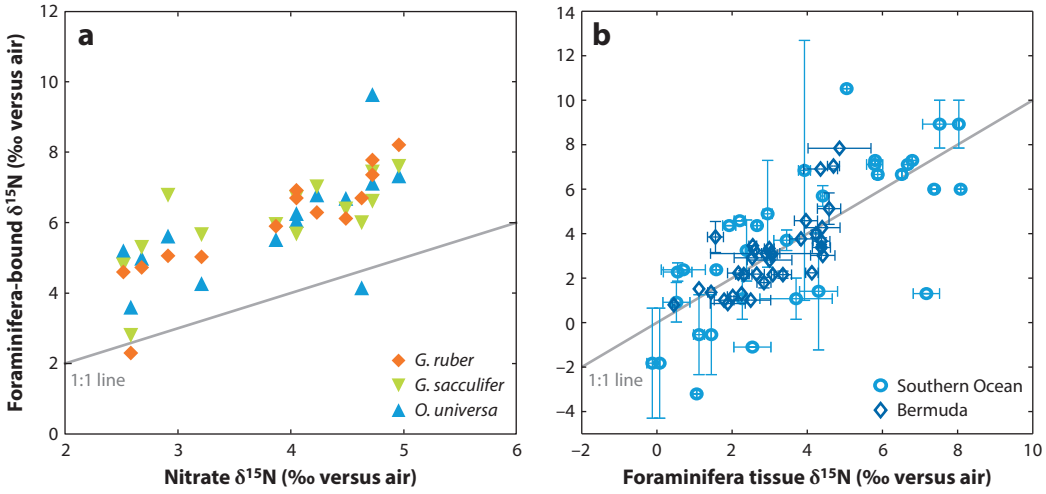

Figure 4

(*a*) Relationship between surface-sediment foraminifera-bound $\delta^{15}N$ (Ren et al. 2009, 2012b, 2015; Schiebel et al. 2018) and overlying thermocline nitrate $\delta^{15}N$ (averaged over 200–400-m depth) (Marconi et al. 2017) from a zonal transect across the equatorial Atlantic. The three species shown—*Globigerinoides ruber* (*diamonds*), *Globigerinoides sacculifer* (*inverted triangles*), and *Orbulina universa* (*triangles*)—are all dinoflagellate-bearing, shallow-dwelling organisms. (*b*) Compilation of upper-ocean (0–200-m depth) net-tow collections from high-latitude (African sector of the Southern Ocean; *circles*) (Smart et al. 2020) and low-latitude (subtropical North Atlantic near Bermuda; *diamonds*) (Smart et al. 2018) waters, showing the strong coupling between shell-bound and tissue $\delta^{15}N$ from the same species and net tow (measurements are not necessarily from the same individuals). Error bars show the standard error of replicate persulfate oxidations. The light gray lines in both panels are 1:1 lines.

The organic content of foraminifera shells derives from the calcification process, during which foraminifera use a protein-rich organic template to initiate chamber building (the primary organic sheet shown in **Figure 1*a*, subpanel *ii***) (Bé et al. 1977, Spero 1988). Further thickening of the shell walls during subsequent growth, reproduction, and any postmortem encrustation traps these organic layers and other minor organic components inside the calcite matrix (Bé & Hemleben 1970, Hemleben et al. 1985). In the low-latitude open ocean, where surface nitrate is fully consumed, a pattern has emerged in which core-top $\delta^{15}N_{FB}$ closely tracks, and in some cases nearly matches in absolute value, the present-day $\delta^{15}N$ value of the subsurface nitrate supplied annually to overlying surface waters (Ren et al. 2009, 2012b) (**Figure 4*a***). However, as zooplankton that straddle the trophic space between mixotrophy and heterotrophy (Stoecker et al. 2017, LeKieffre et al. 2018), foraminifera are further removed from nitrate than phytoplankton such as diatoms. Quantifying such additional effects calls for thorough ground truthing in the modern ocean and a better process-based understanding of N pathways in living foraminifera.

2.4.2. Foraminifera ground truthing. Calibration of the $\delta^{15}N_{FB}$ proxy has focused on three main questions: (*a*) What processes control the $\delta^{15}N$ of living foraminifera, (*b*) does $\delta^{15}N_{FB}$ accurately reflect the living organism's $\delta^{15}N$ (i.e., metabolically active tissue), and (*c*) is the original $\delta^{15}N_{FB}$ signal preserved in fossil shells? For the first question, photosymbiont activity, diet, and depth habitat all appear to play a role in setting the $\delta^{15}N$ of living (metabolically active) foraminifera. For example, consistently lower $\delta^{15}N$ of foraminifera with dinoflagellate symbionts relative to those without has been ascribed to the retention of low-$\delta^{15}N$ metabolic ammonium by the symbionts (Ren et al. 2012b), a mechanism supported by tracer experiments using isotopically labeled N sources (Uhle et al. 1999, LeKieffre et al. 2020). Additionally, symbiont-barren

foraminifera typically occupy deeper habitats (Ren et al. 2012b, Smart et al. 2018), where the $\delta^{15}N$ of the particulate organic matter available for feeding is typically higher (Altabet 1988, Altabet et al. 1991, Robinson et al. 2020). The more varied (intermediate to high) $\delta^{15}N$ of foraminifera with other (i.e., non-dinoflagellate) symbionts or microbial associations might be explained by the temporary or weaker nature of photosymbiotic activity (e.g., facultative versus obligatory; Hemleben et al. 1989, Takagi et al. 2019), their specific diets or dwelling depths (Ren et al. 2012b, Smart et al. 2018, Li et al. 2019), and/or the ability to directly assimilate ammonium from seawater (as demonstrated for *Globigerina bulloides* in culture; Bird et al. 2020).

The relationship between foraminifera and their diet is made apparent by the close seasonal coupling of foraminifera $\delta^{15}N$ with particulate organic matter (more so than with nitrate). In both the subtropical North Atlantic and the sub-Antarctic region, foraminifera $\delta^{15}N$ appears to follow the rise and fall of mixed-layer particulate organic matter $\delta^{15}N$ associated with spring bloom nitrate drawdown (which raises the $\delta^{15}N$ of nitrate and particulate N_{org}), late-summer ammonium recycling (which lowers the $\delta^{15}N$ of particulate N_{org} more than that of nitrate), and winter particle decomposition (raising $\delta^{15}N$ again) (Smart et al. 2018, 2020). The ability of the latter two N cycling processes to bias reconstructions of nitrate $\delta^{15}N$ from foraminifera depends on the relative contributions of late-summer and winter assemblages to the annual flux of shells to the seafloor. In the modern sub-Antarctic region (where spring and early-summer production dominate the sinking flux; e.g., Honjo et al. 2000), this potential bias appears to be relatively minor ($\leq$1‰), and its capacity for change in the past is likely constrained by the underlying control of nitrate and ammonium to the mixed layer on annual or longer timescales (Smart et al. 2020). Water-column $\delta^{15}N_{DB}$ measurements from the sub-Antarctic region indicated that the impact of ammonium is not limited to foraminifera, and again the bias in sedimentary records appears minimal (Robinson et al. 2020). Existing data also indicate that the annually averaged $\delta^{15}N$ offset between a given foraminifera species and the nitrate consumed in the surface ocean may vary between the subtropical and subpolar environments, possibly reflecting differences in the reliance of autotrophic biomass on new versus recycled N sources (Smart et al. 2018, 2020) (**Figure 3**). Nonetheless, more data are needed to quantify species-specific $\delta^{15}N$ relationships across a range of ocean environments.

On the second question, of $\delta^{15}N_{FB}$ fidelity, comparison between tissue (i.e., whole-organism biomass) and shells of planktic foraminifera caught in surface-ocean net tows indicates an approximately 1:1 relationship with minimal $\delta^{15}N$ offset (Smart et al. 2018, 2020) (**Figure 4*b***). The lack of mineral-bound versus biomass $\delta^{15}N$ offset in foraminifera (and corals; Muscatine et al. 2005) may stem from a common N source and/or similar molecular composition between the organic compounds active in biomineralization and those used in general cell functioning (unlike with diatoms). This strong correlation exists despite differing integration times of tissue (hours to days) and shells (weeks to months) and is consistent across contrasting nutrient regimes (subtropical and subpolar).

On the third question, of preservation, the available data indicate only a slight increase (~0.6‰) in $\delta^{15}N_{FB}$ between tows or traps in the upper ocean and on the seafloor despite a concurrent reduction in N content (Ren et al. 2012b, Smart et al. 2018), although these trends may not hold for all species or settings (Li et al. 2019). While diagenetic alteration of $\delta^{15}N_{FB}$ cannot be ruled out as an explanation for the minor observed offset, the more likely explanations reflect either the loss or gain of carbonate fractions, such as the absence of more thinly calcified shells and/or more susceptible shell components and associated increased importance of gametogenic calcification (shell thickening or chamber addition, which can occur shortly before reproduction and sinking) (Smart et al. 2018, Li et al. 2019). Nonetheless, the apparently minor difference between living foraminifera and fossil shells is encouraging for downcore reconstructions.

2.5. Corals

Anthozoan corals in the phylum Cnidaria are a diverse group of metazoans that first emerged in the late Cambrian (~500 Ma) but were not prolific reef builders until the Devonian (~410 Ma). This group offers the unique opportunity to reconstruct past ocean biogeochemical dynamics at high temporal resolution (annual to subannual) for decadal to millennial timescales (Williams 2020, Thompson 2022).

2.5.1. Coral foundations. A distinct advantage of corals as environmental archives is that their accretionary skeletons can be accurately dated using radiometric techniques (Adkins et al. 2002, Fairbanks et al. 2005), which eliminates the need for stratigraphic correlations, for example, in sedimentary records (Robinson et al. 2014). There are two primary groups of Anthozoan corals used in paleoceanographic reconstruction: scleractinian (i.e., hard corals) and proteinaceous corals. Most shallow-water hard corals have evolved to form a nutritional symbiosis with Symbiodiniaceae algae, which allows them to acquire nutrients autotrophically through their algal symbionts or by heterotrophically feeding on detritus and other organisms (Houlbrèque & Ferrier-Pagès 2009), as well as directly from the water column through uptake of dissolved N_{org} (Goreau et al. 1971). However, this symbiosis, along with water chemistry constraints on calcified skeleton formation, limits the global distribution of scleractinian hard corals to the environmental conditions of the warm, shallow, oligotrophic waters of the tropics (Kleypas et al. 1999). Conversely, proteinaceous corals are found in all the world's oceans, from surface waters to depths greater than 8,600 m (Cairns 2007). The distribution of these deep-water corals is determined largely by hard-bottom substrate availability, current strength, and associated properties such as food availability, temperature, O_2 levels, and carbonate chemistry (Williams 2020). Most proteinaceous corals are omnivorous suspension feeders that lack autotrophic symbionts and instead heterotrophically feed on a wide variety of food sources, including plankton, particulate organic matter, and dissolved organic matter (Williams 2020). Deep-water proteinaceous corals tend to grow slower and live longer than their shallow-water counterparts (Robinson et al. 2014).

The utility of both hard and proteinaceous coral skeletons as fossil-bound N archives ($\delta^{15}N_{CS}$) lies in their production of a calcium carbonate (hard) or protein carbonate (proteinaceous) skeleton in accretionary growth bands over hundreds to thousands of years. Once deposited, these bands are not metabolically reworked and therefore preserve geochemical records of ocean conditions at the time of growth (Williams 2020, Thompson 2022). In hard corals, calcification of the skeleton is biologically driven, controlled simultaneously by the transport of calcium and bicarbonate ions that form carbonate crystals and the deposition of the skeletal organic matrix that encourages crystal nucleation (Allemand et al. 1998). The skeletal organic matrix is made up of a combination of proteins, polysaccharides, lipids, and chitin (Young 1971, Young et al. 1971) and is preserved within the carbonate crystalline structure (Yamazaki et al. 2013). Proteinaceous deep-sea coral skeletons, on the other hand, are made of cross-linked, fibrillar protein structures, often interlaced with or layered between calcium carbonate structural components that make this biological archive one of the most durable and diagenetically resistant proteinaceous materials known (Strzepek et al. 2014). While the N measured in proteinaceous corals is not encapsulated within the carbonate mineral, similarity in C:N ratios, $\delta^{13}C$ values, $\delta^{15}N$ values, and amino acid abundances between modern and fossil proteinaceous coral skeleton specimens suggests that isotopic signatures are well preserved on at least millennial timescales (Sherwood et al. 2005, Glynn et al. 2019).

2.5.2. Coral ground truthing. Early ground-truthing work found that $\delta^{15}N_{CS}$ showed a very consistent and linear relationship with changes in ambient water-column N (Marion et al. 2005,

Erler et al. 2015, Wang et al. 2015) and could, therefore, be used to faithfully track N dynamics. Subsequent work identified that, for hard corals near reef margins in the oligotrophic ocean, $\delta^{15}N_{CS}$ varies with the $\delta^{15}N$ of nitrate (i.e., the dominant N source), with consistent offsets in absolute values (Wang et al. 2016). Since $\delta^{15}N_{CS}$ values are not altered during assimilation into the skeleton (Hoegh-Guldberg et al. 2004, Muscatine et al. 2005), the offsets must be due to other physiological processes. Proposed explanations are symbiont-driven recycling of urea (Wang et al. 2016) and/or changes in coral trophic strategies (Erler et al. 2015). Due to these potential offsets, Wang et al. (2016) concluded that interpretation is simplest in regions dominated by nitrate or a single N source. Further ground truthing is needed for corals that exist with multiple dominant N sources.

Heterotrophic plasticity: the ability of an organism to switch from acquiring nutrition primarily photoautotrophically to primarily heterotrophically or by a combination of both

How coral physiological processes and trophic plasticity affect $\delta^{15}N_{CS}$ values is relatively unknown. Corals have heterotrophic plasticity (Conti-Jerpe et al. 2020) and can regulate their heterotrophy across environmental gradients (Houlbrèque & Ferrier-Pagès 2009, Fox et al. 2019, Ferrier-Pagès et al. 2021, Wall et al. 2021). Thus, if corals were to change their N assimilation preference through time, this could confound $\delta^{15}N_{CS}$ interpretation (Erler et al. 2015, Rangel et al. 2019). Amino acid C isotope fingerprinting on coral polyp tissue has been used to explore the trophic plasticity in corals (e.g., Fox et al. 2019, Wall et al. 2021), which may help shed light on the degree of intra- and interspecies variation in heterotrophic feeding by symbiont-containing hard corals.

One feeding study investigated the fidelity of $\delta^{15}N_{CS}$ in recording varying N sources and found a slow (>3-month) N-tissue turnover time in metabolically active coral tissues, indicating that comparatively fast changes in N sources will not be recorded within the skeleton (Rangel et al. 2019). Consistent with this finding, Great Barrier Reef $\delta^{15}N_{CS}$ records failed to detect severe but brief bleaching events (Erler et al. 2020b). Conversely, recent work to disentangle multiple nutrient sources successfully identified dynamic trends (Duprey et al. 2020, Marion et al. 2021), suggesting that $\delta^{15}N_{CS}$ has potential to trace variations in source N dynamics at ecologically relevant timescales. As this field grows and corals of varying species and habitats are used to build $\delta^{15}N_{CS}$ time series, their biological and trophic plasticity will need to be quantified and accounted for.

Tornabene et al. (2017) analyzed $\delta^{15}N_{CS}$ in a suite of modern and fossil hard corals with and without symbionts across a range of diagenetic states and showed that early Miocene (18–20 Ma) corals exhibited the same N isotopic ratio offset identified in modern corals. These results suggest that the $\delta^{15}N_{CS}$ proxy can successfully be used in the ancient fossil coral record as well as modern systems.

While ground truthing of proteinaceous coral $\delta^{15}N_{CS}$ is limited, several lines of encouraging data suggest similar high fidelity of proteinaceous coral records to environmental variation in N cycling. Gold corals (*Kulamanamana haumeaae*) from the Hawaiian Islands had modern $\delta^{15}N_{CS}$ values of approximately 2.3‰, which aligned well with the $\delta^{15}N_{CS}$ range of present-day thermocline NO_3^- ($\delta^{15}N_{NO3} = 1.5–2.4‰$) and sinking particulate N ($\delta^{15}N_{PNsink} = 2.3–3.6‰$) at Station ALOHA (Sherwood et al. 2014) (**Figure 3**). Similarly, Sherwood et al. (2005) found that *Primnoa* spp. $\delta^{15}N_{CS}$ (and $\delta^{13}C_{CS}$) values from northeast Pacific shelf waters, northwest Atlantic slope waters, the Sea of Japan, and a Southern Ocean Pacific sector seamount were strongly correlated with regional surface apparent O_2 utilization metrics of surface productivity, suggesting strong coupling between proteinaceous coral $\delta^{15}N_{CS}$ values and biophysical processes in surface waters. Isotopic records in metabolically active polyp tissue closely mirrored $\delta^{15}N_{CS}$ for three proteinaceous deep-sea coral genera from widely divergent oceanographic environments (McMahon et al. 2018). However, a subset of amino acids—often termed trophic amino acids for their known fractionation during metazoan trophic transfers—were consistently ^{15}N depleted relative to polyp tissue, suggesting that some differential trophic partitioning occurs between

polyp tissue and proteinaceous skeleton biosynthesis. Overall, these observations suggest that the geochemical signals recorded in coral polyp tissue and proteinaceous skeleton are likely robust, at least for gorgonin-based proteinaceous corals.

3. SIGNIFICANT INSIGHTS FROM FOSSIL-BOUND NITROGEN ISOTOPE RECORDS

3.1. Reconstructing Changes in the Nitrogen Inventory and Its Relationship with Oxygen

The total amount of reactive N in the ocean is controlled primarily by one source (N_2 fixation) and two sinks (water-column and sedimentary denitrification) (Brandes & Devol 2002, Gruber 2004), each with distinct isotope effects that can be leveraged to reconstruct their changing contributions through time. In today's open ocean, N_2 fixation occurs where nitrate is often limiting but other essential nutrients (phosphate and iron) and energy (e.g., sunlight) are plentiful (e.g., Karl et al. 2002, Voss et al. 2013). N_2-fixer biomass is remineralized in subsurface waters to ammonium and ultimately nitrate, with a $\delta^{15}N$ near 0‰ (e.g., Carpenter et al. 1997). Denitrification has the opposite effect of preferentially removing ^{14}N-bearing nitrate from the ocean, with a large isotope effect (15–25‰; e.g., Mariotti et al. 1981), elevating the $\delta^{15}N$ value of the remaining nitrate (Cline & Kaplan 1975). Major ocean denitrification occurs in oxygen minimum zones in the intermediate-depth waters of the eastern tropical Pacific and the Arabian Sea (i.e., water-column denitrification) (e.g., Cline & Kaplan 1975, Paulmier & Ruiz-Pino 2009) and in the pore fluids of continental shelves and slopes globally (i.e., sedimentary denitrification) (Liu & Kaplan 1984, Devol 1991). Sedimentary denitrification, while proportionally more important to the budget, has little impact on global ocean nitrate $\delta^{15}N$ due to complete nitrate conversion (Brandes & Devol 1997). Based on these understandings of the present modern N budget, both bulk sediment and fossil-bound $\delta^{15}N$ have been used to explore or infer changes in nutrient dynamics, oxygenation, ocean fertility, and circulation through time.

Evaluation of N fixation in the paleoceanographic record was historically hampered by diagenesis and/or contamination of bulk $\delta^{15}N$ records. Fossil-bound $\delta^{15}N$ enables reconstructions from low-flux and marginal sea environments, such as the oligotrophic oceans. In the (sub)tropical Atlantic and Pacific, $\delta^{15}N_{FB}$ values are substantially higher during glacial intervals relative to interglacials (e.g., the subtropical gyre record in **Figure 5*b***). This is best explained by an ice-age reduction in N_2 fixation (Atlantic: Ren et al. 2009, Meckler et al. 2011, Straub et al. 2013a; Pacific: Ren et al. 2012a, 2017b; Wang et al. 2017). Over the last eight major ice-age cycles, $\delta^{15}N_{FB}$ in the South China Sea is strongly coherent with sea level, implying a tight relationship between N_2 fixation at the site and the cyclic expansion and contraction of the continental shelves, and thus benthic denitrification (Ren et al. 2017b). Lower sea levels reduced the shallow-water phosphorus excess generated by shelf denitrification (Gruber & Sarmiento 1997) and thus weakened the competitive advantage of N_2 fixers (Tyrrell 1999) in the region. More recently, proteinaceous coral $\delta^{15}N_{SC}$ records showed that recent increases in N_2 fixation in the modern instrumental record in the North Pacific Subtropical Gyre were the continuation of a much larger, centennial-scale trend linked to Northern Hemisphere climate change since the end of the Little Ice Age (Sherwood et al. 2014). In this way, fossil $\delta^{15}N$ records support the long-hypothesized coupling between production and removal of fixed N that stabilizes the ocean N inventory through time (Tyrrell 1999, Deutsch et al. 2004).

Together with geochemical models, fossil-bound $\delta^{15}N$ is also helping to reconcile disparate ocean oxygenation histories related to denitrification (Studer et al. 2021). Bulk sedimentary $\delta^{15}N$

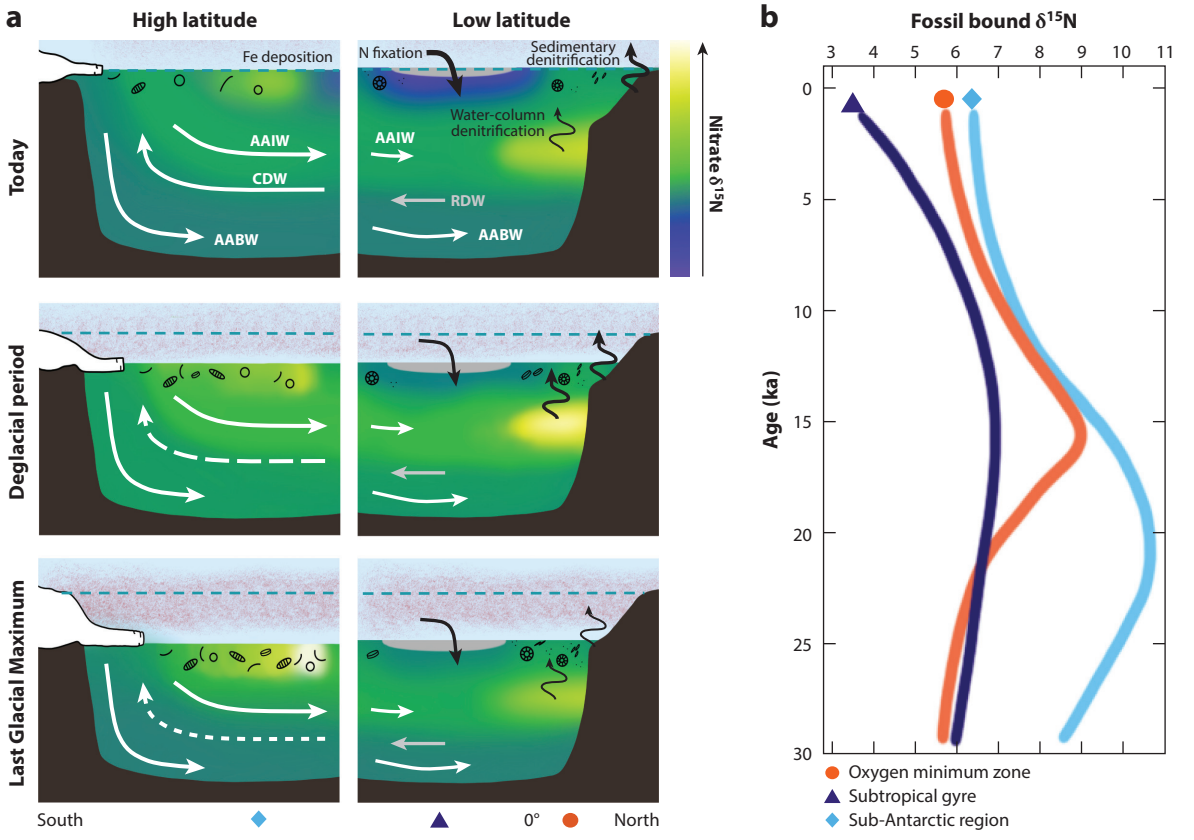

Figure 5

(*a*) Idealized longitudinal cross sections of the $\delta^{15}N$ of nitrate across high- and low-latitude ocean basins today (*top*, 0 ka), during the last deglacial period (*middle*, 12 ka), and during the Last Glacial Maximum (*bottom*, 20 ka). The dashed teal line indicates modern sea level. Phytoplankton symbols indicate relative primary productivity. The diamond, triangle, and circle at the bottom indicate approximate sample locations for the trends shown in panel *b*. (*b*) Paleoceanographic fossil-bound $\delta^{15}N$ trends for an oxygen minimum zone, a subtropical gyre, and a sub-Antarctic region. Abbreviations: AABW, Antarctic Bottom Water; AAIW, Antarctic Intermediate Water; CDW, Circumpolar Deep Water; RDW, regional deep water.

records, supported by other oxygenation proxies, provide significant evidence for reduced suboxia during ice ages (e.g., Galbraith et al. 2013). This was explained by the greater solubility of O_2 in colder waters and faster ventilation of the thermocline (Galbraith et al. 2004) and/or more complete nutrient consumption in the glacial sub-Antarctic region (Robinson et al. 2005, Martínez-García et al. 2014), leading to a reduced supply of nitrate to support the production and subsequent decay of sinking organic matter, reducing O_2 consumption in middepth waters (Robinson et al. 2005). On the other hand, more complete Antarctic zone nutrient drawdown and the isolation of the deep ocean in the ice-age mode of overturning circulation would have raised O_2 consumption in deep waters (e.g., Anderson et al. 2019, Jacobel et al. 2020), which gradually mix or upwell into overlying middepth waters. Records of $\delta^{15}N_{FB}$ from the eastern equatorial Pacific do not show a glacial–interglacial difference, only a transient deglacial rise in $\delta^{15}N_{FB}$ (oxygen minimum zone record in **Figure 5*b***), implying that competing middepth versus deep-ocean effects on O_2 concentration are nearly balanced but possibly offset in time (Studer et al. 2021).

3.2. High-Resolution Records of Nitrogen Dynamics in the Anthropocene

Anthropocene: the current geologic age, defined by human activity's dominant influence on Earth's environment

Since the industrial revolution in the early 1800s, the world has seen a rapid increase in emissions from fertilizer usage and combustion of fossil fuels and a concurrent increase in atmospheric transport and deposition of bioreactive N into the ocean (Galloway et al. 2004, Duce et al. 2008, Ren et al. 2017a). This increase in N input to the oceans has altered numerous biological (e.g., productivity, biodiversity, and disease) and environmental (eutrophication, hypoxia, and climate) processes (Devlin & Brodie 2005, Furnas et al. 2005, Wooldridge & Done 2009, De'ath & Fabricius 2010, Fowler et al. 2013). Records of $\delta^{15}N_{CS}$ provide a mechanism to disentangle isotopically diagnostic N dynamics in the Anthropocene (Ren et al. 2017a, Duprey et al. 2020) thanks to the high-resolution annual banding in coral skeletons, corals' sessile lifestyle, and corals' prevalence in near-coastal locations that sit at the terrestrial, marine, and atmospheric interfaces.

Several recent examples show the utility of $\delta^{15}N_{CS}$ to trace N fluxes from coastal riverine inputs, one of the dominant sources of N pollution to the oceans (Fowler et al. 2013). Marion et al. (2021) illustrated that annual-resolution $\delta^{15}N_{CS}$ records reflect the cascading effects of multiple N transformations during the passage of river particulate organic matter through anthropogenic catchment processes to the ocean, tied to episodic flood pulses following large precipitation events over multidecadal timescales (**Figure 6**). Duprey et al. (2020) linked a collapse in coral communities within Hong Kong during the 1990s to increases in agricultural and sewage-derived nutrients that led to eutrophication, which was reflected in increased $\delta^{15}N_{CS}$ values. Erler et al. (2020a) assembled a composite coral record spanning more than 300 years that showed a consistent and significant decline in $\delta^{15}N_{CS}$ values toward the present day on the Great Barrier Reef. Contrary to the findings by Duprey et al. (2020), who found that changes in $\delta^{15}N$ came directly from river

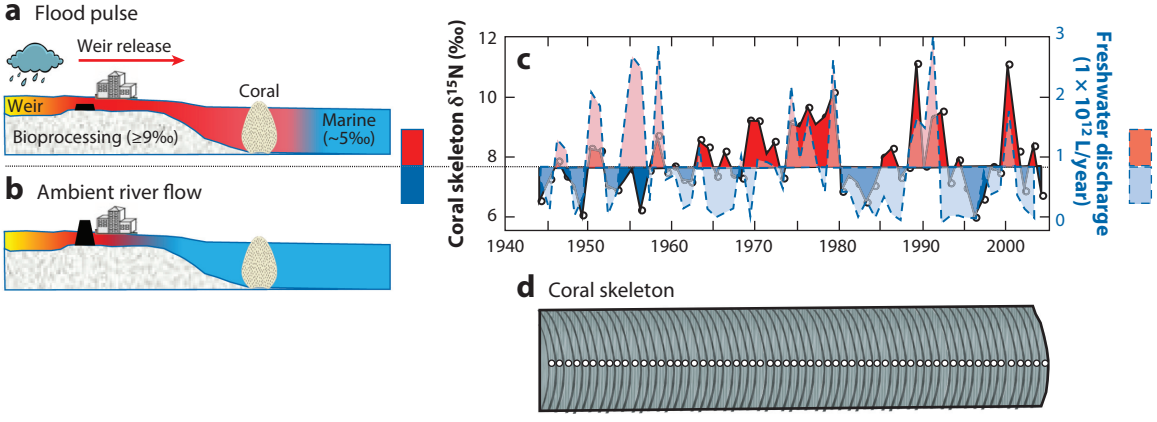

Figure 6

Conceptual models showing a proposed two-end-member mixing system between high riverine $\delta^{15}N$ values (≥9‰) resulting from microbial processing in a flood-controlled weir system and comparatively low offshore marine particulate organic matter $\delta^{15}N$ values (~5‰) in the southern Great Barrier Reef. (*a*,*b*) Flood pulses and ambient river flow in the weir system. Following heavy precipitation events, the ^{15}N-enriched reservoir waters from the weir are discharged as low-salinity flood pulses (panel *a*) into the coastal waters, causing enrichment of organic fractions in nearshore coral skeletons (panel *b*) relative to ambient flow conditions. (*c*) Illustration of the strong relationship between composite annual mean time series of coral skeleton $\delta^{15}N$ values (*solid lines*) and river discharge (*dashed lines*) in the southern Great Barrier Reef (data from Marion et al. 2021). Shaded areas indicate values greater (*red*) or less (*blue*) than the mean $\delta^{15}N$ (7.8‰) and mean river discharge (0.8×10^{12} L/year) (data from Marion et al. 2021). White circles indicate annual sampling of the coral carbonate skeleton-bound $\delta^{15}N$ values. (*d*) Schematic cross section of a coral skeleton, showing annual banding that can be sampled to produce high-resolution $\delta^{15}N$ time series. White dots indicate a hypothetical annual sampling plan. Panels *a*–*c* adapted with permission from Marion et al. (2021).

outputs, Erler et al. (2020a) determined that the changes in the Great Barrier Reef were from increased relative and absolute amounts of N from N_2 fixation in the region. Research on ancient fossil corals have helped put these recent Anthropocene changes into a broader geologic context (e.g., Tornabene et al. 2017, Glynn et al. 2019).

3.3. Changes in the Efficiency of the High-Latitude Biological Pump

Some of the strongest evidence for the Southern Ocean's role in regulating atmospheric pCO_2 comes from fossil-bound N isotope records of glacial–interglacial change. The reservoir of unused nutrients in the Southern Ocean surface today reflects relatively inefficient transfer of carbon from the surface ocean–atmosphere system to the deep ocean by the biological pump (e.g., Sigman et al. 2021). At present, the assimilation of major nutrients (silicate, nitrate, and orthophosphate) by Southern Ocean phytoplankton is thought to be limited by iron and/or light availability (Martin 1990, Mitchell et al. 1991), leaving unused nutrients and excess CO_2 in the surface ocean.

Elevated fossil-bound $\delta^{15}N$ records across diatoms, foraminifera, and corals during the Last Glacial Maximum imply that the demand for nitrate increased more than the supply (e.g., the sub-Antarctic record in **Figure 5*b***). A reduced supply of nutrients and CO_2 to the surface of the ice-age Southern Ocean and an increase in the demand for nutrients (related to a relief of iron limitation) have been inferred from the existing N isotope records and assigned a role in regulating atmospheric CO_2 concentrations in the past (Robinson et al. 2004, 2005; Robinson & Sigman 2008; Martínez-García et al. 2014; Studer et al. 2015; Wang et al. 2016; Ai et al. 2020). An important strength of these fossil-bound $\delta^{15}N$ interpretations is their relative consistency across biomineral or fossil types. These archives were targeted in the Southern Ocean in particular because some of the first evidence for alteration of bulk sedimentary $\delta^{15}N$ values came from the Southern Ocean (Altabet & Francois 1994) and because the Southern Ocean does not meet the shallow, high-accumulation-rate criteria generally used to justify the use of bulk $\delta^{15}N$ measurements (Robinson et al. 2012).

3.4. Evidence for Variable Organic Matter Preservation

Direct comparisons of fossil-bound $\delta^{15}N$ and bulk sedimentary $\delta^{15}N$ records are limited. Available comparisons show differences that indicate that variable alteration occurs in bulk sedimentary $\delta^{15}N$ values even in environments where bulk isotope measurements are considered to be reliable (e.g., highly productive waters) (e.g., Robinson et al. 2005, Straub et al. 2013b, Martínez-García et al. 2014, Studer et al. 2021). Comparisons of both $\delta^{15}N_{DB}$ and $\delta^{15}N_{FB}$ with bulk $\delta^{15}N$ records from sub-Antarctic-zone sites show distinct offsets between bulk and fossil-bound values that vary with changes in total sediment accumulation rate, pointing to variable preservation as a cause (Robinson et al. 2005, Martínez-García et al. 2014). While alteration is not unexpected in the Southern Ocean, understanding how preservation changes with time may improve proxy reconstructions beyond N isotope records. In the eastern equatorial Pacific, where sedimentary bulk N isotope records are typically considered reliable, $\delta^{15}N_{FB}$ records deviate from bulk sediment $\delta^{15}N$ records in the same sediment cores (Dubois et al. 2011, Studer et al. 2021), suggesting that higher and more variable bulk $\delta^{15}N$ values during interglacials are an artifact, potentially due to diagenetic alteration or terrestrial inputs (Studer et al. 2021). The latter example emphasizes the potential for alteration of bulk $\delta^{15}N$ records from high-accumulation-rate margins and the importance of digging deeper into controls on the fossil-bound proxies as they become increasingly critical for producing robust reconstructions of surface-ocean conditions in the past.

4. LOOKING AHEAD

4.1. The Next Frontier: Compound-Specific Isotope Analyses of Fossil Material

Compound-specific isotope analysis (CSIA): measurement of isotope values of individual compounds (e.g., amino acids) from a heterogeneous biological sample

The typically low N content of fossil-bound archives has necessitated that much of the proxy development work focused on the total (bulk) N pool in a sample. Compound-specific isotope analysis (CSIA), which draws analytical power from the characterization of differential isotopic fractionation patterns of individual molecules (e.g., amino acids), offers a powerful suite of new tools to better characterize the highly heterogeneous biochemical content of organic matter, the taxonomic diversity of its sources, and the relative extent of physical, chemical, and biological alteration it experiences as it cycles through marine systems (Ohkouchi et al. 2017, Close 2019). As Hedges (2002, p. 25), a pioneer in marine organic geochemistry, put it, "the future of oceanographic research belongs in part to those who can learn to read these molecular messages."

In recent years, several powerful CSIA metrics have been developed that offered major breakthroughs in paleoceanography: (*a*) baseline inorganic N isotope values from source amino acids that exhibit minimal isotopic fractionation during trophic transfer, (*b*) microbial reworking of organic matter based on variance in $\delta^{15}N$ values of heavily fractionating trophic amino acids, and (*c*) trophic dynamics that are internally indexed to the N isotope baseline using offsets of trophic and source amino acids (McMahon & McCarthy 2016). These CSIA metrics have been applied to carbonate-bound paleoarchives (e.g., proteinaceous deep-sea corals and long-lived bivalves) to characterize shifting current systems on the Atlantic margin (Sherwood et al. 2011, Whitney et al. 2019), tease apart changes in ocean N fixation and trophic dynamics of export production in the central Pacific (Sherwood et al. 2014, McMahon et al. 2015), identify effects of long-term land-use change on Gulf of Mexico N cycling (Prouty et al. 2013), and assess the stability of mesophotic primary productivity in the western Pacific warm pool (Williams et al. 2017). CSIA presents a way forward to analyze specific fractions in groups where species are difficult to separate (e.g., diatoms and radiolarians) and a potential avenue for understanding physiological controls on species-specific offsets. However, to realize the full potential here, future ground-truthing studies must build on limited existing studies to constrain the relationships between the $\delta^{15}N$ of fossil-bound amino acids and that of metabolically active organismal tissue and environmental organic matter signals (Misarti et al. 2017, McMahon et al. 2018, Vane et al. 2018, Whitney et al. 2019).

4.2. Interspecies Comparisons

Within each archive reviewed here (diatoms, foraminifera, and corals), there exists a vast taxonomic diversity occupying a broad range of ecological and environmental niches. While certainly challenging, this interspecies diversity also presents the opportunity to create highly detailed reconstructions of specific components of the N system from multiple co-occurring species that reflect different depths, seasons, and/or N sources. Planktic foraminifera, with their relatively large size and often distinctive morphologies, lend themselves particularly well to the creation of multiple species-specific $\delta^{15}N$ records from the same sediment core. This approach is already yielding valuable insights into the changing seasonality (depth structure and nutrient conditions) of the upper ocean through major climate transitions (Ren et al. 2009, 2015). While species-specific diatom records are less likely to become a reality, the separation of pennate and centric forms has the potential to offer similar insights into upper-ocean conditions at the time of their peak abundance (Studer et al. 2015). Corals span a wide range of mixotrophy at both the genus (Conti-Jerpe et al. 2020) and individual (Fox et al. 2019) levels, which offers an opportunity to examine N drivers of past autotrophic and heterotrophic variability. To take full advantage of species-specific capabilities, additional ground truthing in the modern ocean and more culture studies are needed.

4.3. Deep Time

Fossil-bound $\delta^{15}N$ is poised to provide unprecedented insight into the marine N cycle on a multimillion-year timescale (Robinson et al. 2015, Kast et al. 2019). Older yet accessible deep-sea sediments tend to be recovered from low-accumulation-rate environments. As a consequence, the resulting bulk $\delta^{15}N$ records are immediately suspected of alteration. Recent work from samples of mixed planktic foraminifera taxa extends $\delta^{15}N_{FB}$ records back to 70 Ma (Kast et al. 2019). These records implicate tectonics as a modifier of the global N budget on these timescales, through its control on water-mass properties. In particular, the Paleocene–Eocene transition (57–50 Ma) exhibits a precipitous drop in $\delta^{15}N_{FB}$ (by 13–16‰ in the Pacific and 3–8‰ in the Atlantic) that precedes global cooling but coincides with the India–Asia collision. It is hypothesized that the associated closure of the Tethys Sea ended the formation of the saline, low-O_2 water mass that had encouraged high levels of water-column denitrification (and thus high nitrate $\delta^{15}N$) in Paleocene intermediate waters (Kast et al. 2019). Future efforts will expand our understanding of the global N cycle through Earth's history.

DISCLOSURE STATEMENT

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