

Nutrient regime shift in the western North Atlantic indicated by compound-specific $\delta^{15}\text{N}$ of deep-sea gorgonian corals

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Despite the importance of the nitrogen (N) cycle on marine productivity, little is known about variability in N sources and cycling in the ocean in relation to natural and anthropogenic climate change. Beyond the last few decades of scientific observation, knowledge depends largely on proxy records derived from nitrogen stable isotopes ($\delta^{15}\text{N}$) preserved in sediments and other bioarchives. Traditional bulk $\delta^{15}\text{N}$ measurements, however, represent the combined influence of N source and subsequent trophic transfers, often confounding environmental interpretation. Recently, compound-specific analysis of individual amino acids ($\delta^{15}\text{N-AA}$) has been shown as a means to deconvolve trophic level versus N source effects on the $\delta^{15}\text{N}$ variability of bulk organic matter. Here, we demonstrate the first use of $\delta^{15}\text{N-AA}$ in a paleoceanographic study, through analysis of annually secreted growth rings preserved in the organic endoskeletons of deep-sea gorgonian corals. In the Northwest Atlantic off Nova Scotia, coral $\delta^{15}\text{N}$ is correlated with increasing presence of subtropical versus subpolar slope waters over the twentieth century. By using the new $\delta^{15}\text{N-AA}$ approach to control for variable trophic processing, we are able to interpret coral bulk $\delta^{15}\text{N}$ values as a proxy for nitrate source and, hence, slope water source partitioning. We conclude that the persistence of the warm, nutrient-rich regime since the early 1970s is largely unique in the context of the last approximately 1,800 yr. This evidence suggests that nutrient variability in this region is coordinated with recent changes in global climate and underscores the broad potential of $\delta^{15}\text{N-AA}$ for paleoceanographic studies of the marine N cycle.

compound-specific isotope analysis | deep-sea corals | nitrogen cycle | North Atlantic Oscillation | stable N isotopes

As evidence for anthropogenic climate change continues to amount (1), there is growing need for understanding its effects on the productivity of marine ecosystems. This understanding is critically dependent on long-term datasets derived from natural archives. Proxy data from sediment cores satisfies the need for long records, but detailed temporal resolution can be compromised by low sedimentation rates and bioturbation. Alternatively, long-lived, annually layered, biogenic archives such as corals and bivalves may be used to determine long-term (centuries to millennia) variability at a resolution comparable to that of modern observations. Biogenic archives have been used extensively for isotopic and trace element-based (e.g., $\delta^{18}\text{O}$, Mg/Ca) reconstructions of physical oceanographic variables such as temperature and salinity (2). In comparison, reconstructions of ecologically important variables such as nutrient source, primary productivity, and flux and composition of export production remain more difficult, due to lack of well preserved organic samples and geochemical complexity of organic material.

The $\delta^{15}\text{N}$ of organic material has long been used as a tracer of both trophic level of organisms and of the source of nitrogen (N) at the base of the food web (3). However, inability to distinguish

between these influences with measurements of bulk $\delta^{15}\text{N}$ can be a major barrier to interpretation. Recently, the common protein amino acids (AA) have been shown to fall into two groups with divergent isotopic enrichment behavior during trophic transfer. One group of “trophic” amino acids (Tr-AA) becomes strongly enriched in ^{15}N with each trophic transfer, while a second group of “source” amino acids (Src-AA) have $\delta^{15}\text{N}$ values that undergo little or no change (4, 5). The use of compound-specific $\delta^{15}\text{N}$ analysis of AA ($\delta^{15}\text{N-AA}$) to deconvolute the effects of trophic transfer on bulk $\delta^{15}\text{N}$ signals has been demonstrated in a number of environments (5–8). Here, for the first time, we apply $\delta^{15}\text{N-AA}$ measurements to a paleo-archive (coral) in order to resolve a major issue in the interpretation of bulk $\delta^{15}\text{N}$ records from a marine ecosystem. Specifically, we distinguish between temporal (decadal, centennial) change in fixed nitrogen source, versus change in export production trophic structure in the Scotia-Maine region of the Northwest Atlantic Ocean.

Our analysis focuses on specimens of the deep-sea gorgonian coral *Primnoa resedaeformis* with a two-part endoskeleton of calcite and proteinaceous “gorgonin.” The diagenetically stable gorgonin (9) is deposited in discrete annual growth rings, permitting annually resolved sampling over the decadal to centennial life spans of individual colonies (10, 11). Whereas the calcite is synthesized from dissolved inorganic carbon at depth, the gorgonin derives from particulate organic matter (POM), which the corals feed on, having been recently biosynthesized and exported from surface waters. In this regard, gorgonian corals act like “living sediment traps,” which can be used for $\delta^{15}\text{N}$ -based reconstructions of changes in euphotic zone nutrients and export production back through time in open and/or remote regions of the ocean (12–14).

Specimens were collected from the outer Northeast Channel, on the upper continental slope southwest of Nova Scotia, Canada (Fig. 1). Here, climate forcing associated with the North Atlantic Oscillation (NAO) (15) drives the ebb and flow of subpolar and subtropical slope water masses (16–19). During negative modes of the NAO, cold (6°C), fresh (34.9 psu), and nutrient-poor ($\sim 15 \mu\text{M NO}_3^-$) Labrador Slope Water (LSW) is advected along slope, from the Grand Banks of Newfoundland to southwestward of Georges Bank (Fig. 1). During positive modes of the NAO, LSW retreats northeastward and is replaced by relatively warm

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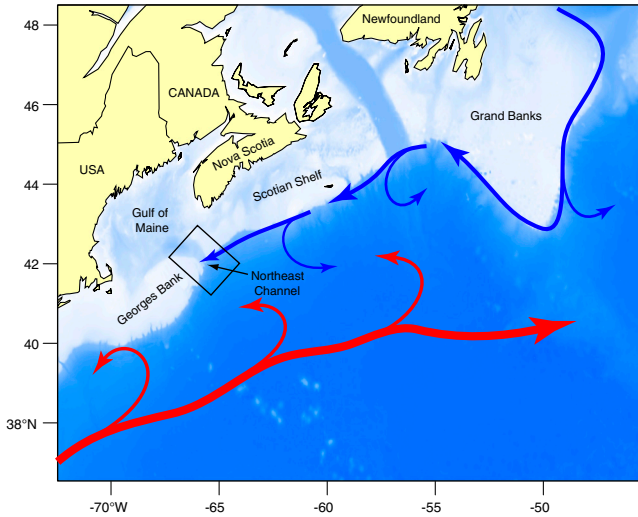


Fig. 1. Map of the study area with location of Northeast Channel. Blue arrows mark the approximate position of the Labrador Current, which transports Labrador slope water (LSW) southward, along-slope. Red arrows show the location of the Gulf Stream. Warm slope water (WSW) occupies the region between the Gulf Stream and continental shelf edge. Temperature and nitrate data were extracted from the 2 × 2 degree grid centered over the Northeast Channel, from 150 to 250 m water depth, where interannual variability is most pronounced (18). Temperature data are from the Bedford Institute of Oceanography hydrographic database. Nutrient data are from the Biochem database of Fisheries and Oceans Canada (44).

(10°C), saline (35.2 psu) and nutrient-rich (~23 μM NO₃⁻) Warm Slope Water (WSW) associated with the Gulf Stream. Modal shifts in slopewater regime may impact the δ¹⁵N of export production through (i) changes in the δ¹⁵N of nitrate (δ¹⁵N_{NO₃⁻}), which averages 1‰ higher in LSW than in WSW (Fig. 2), and (ii)

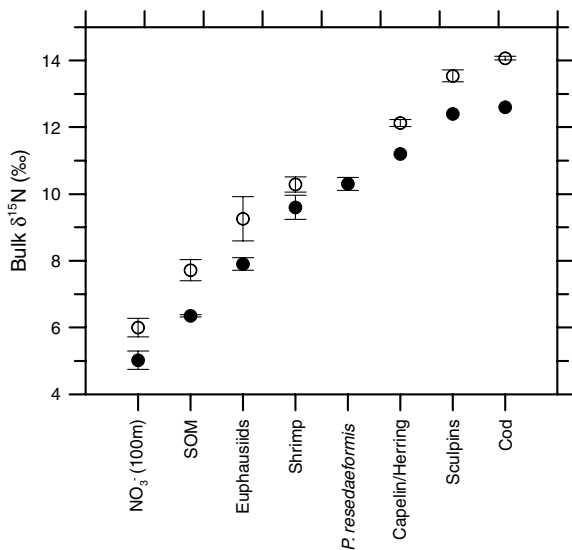


Fig. 2. Differences in the δ¹⁵N of NO₃⁻ (δ¹⁵N_{NO₃⁻}), sedimentary organic matter (SOM; reflects the long-term average for sinking particles), invertebrates (whole body), and fish (muscle), from (●) Scotian Shelf/Gulf of Maine (WSW influenced) and (○) Newfoundland and Labrador (LSW influenced) regions. The δ¹⁵N_{NO₃⁻} data are from this study. Data for Gulf of Maine SOM (45), Georges Bank fish and invertebrates (29), tissue samples of Northeast Channel *P. resedaeformis* (13), outer Newfoundland and Labrador shelf and slope SOM (46), fish and invertebrates (Bonavista corridor and Hawke Channel) (30) were compiled from the literature. Specimens of *P. resedaeformis* from comparable LSW-influence off Newfoundland have not been measured. Error bars are standard errors of the mean (where *n* > 2).

physical oceanographic-driven changes in phytoplankton and zooplankton community structure (20–22). To resolve this fundamental ambiguity in distinguishing nutrient sources from trophic effects, we present detailed bulk δ¹⁵N records supplemented with measurements of δ¹⁵N-AA.

Results

The alternating presence of LSW and WSW at the Northeast Channel is evident in the subsurface (150–250 m depth) temperature record, which is positively correlated with the NAO index at lags of 1–2 yr (Fig. 3) (16, 19). Prior to 1970, both NAO and temperature persisted in a mostly negative/cold regime culminating with the 1960s, the coldest decade of the instrumental record. Since the early 1970s, NAO and temperature have shifted to a mostly positive/warm regime. Although too sparse for meaningful time-series statistics, subsurface nitrate concentration data show a similar pattern of low values in the 1960s, followed by higher values from 1970 onward. While NAO index, temperature, and nitrate increased over the twentieth century, the bulk δ¹⁵N record from *P. resedaeformis* significantly decreased by about 1‰ over the same period, with most of the decline occurring after 1970

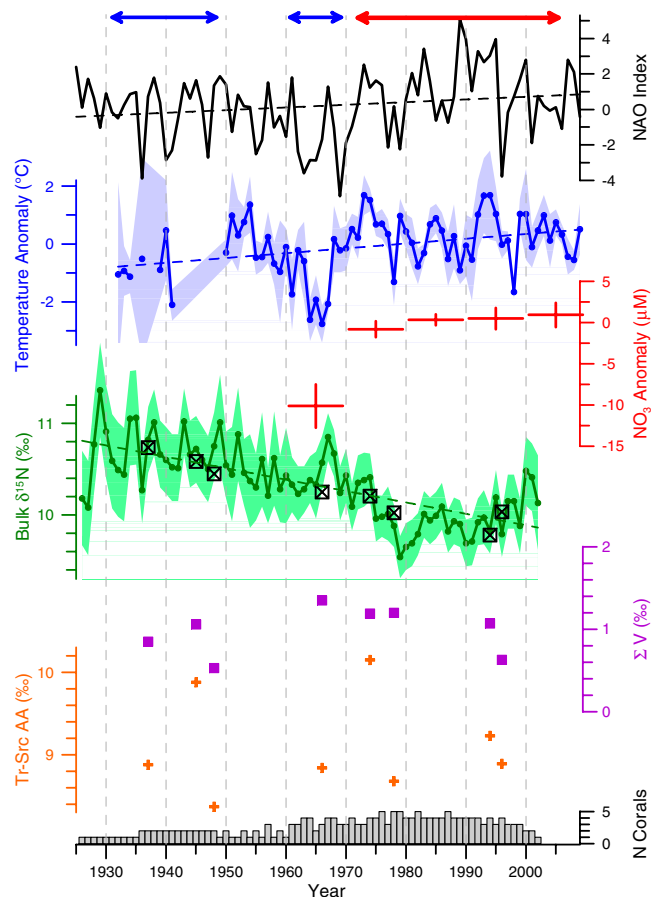


Fig. 3. Time series of the winter (December to March) station-based NAO index (15); temperature and nitrate (plotted as the annual means of monthly anomalies to reduce the effects of seasonal cycles); and annual mean bulk δ¹⁵N from six colonies of the deep-sea gorgonian *P. resedaeformis*. Shaded areas represent 95% confidence intervals around annual means. Dashed lines indicate long-term trends, where significant. Note the cold periods (blue bars) of the 1930s/1940s and 1960s and sustained warm period (red bar) since 1970. Bulk δ¹⁵N is most strongly correlated with NAO at a lag of 4 years (*r* = -0.19, *p* < 0.10) and with temperature at a lag of 3 years (*r* = -0.27, *p* < 0.05). Cross-correlation analysis technique is described in *SI Text*. Also shown are Σ*V* and a trophic index based on the broadest possible grouping of Tr-AAAs and Src-AAAs (see text for details). Squares in bulk δ¹⁵N plot show values of the eight individual samples used for δ¹⁵N-AA analysis.

Table 1. Linear regression statistics for time-series records of NAO, temperature, bulk $\delta^{15}\text{N}$, and compound-specific isotope analysis (CSIA) parameters

Parameter	Length of record (years AD)	N	Slope	St. Error	r^2	p -value
NAO index	1926–2001	76	0.020	0.010	0.05	0.056
Temperature index	1931–2001	59	0.019	0.007	0.12	0.008
Bulk $\delta^{15}\text{N}$ (all samples pooled)	1926–2001	76	-0.013	0.001	0.57	<0.001
Bulk $\delta^{15}\text{N}$ (samples for CSIA)	1937–1996	8	-0.014	0.002	0.91	<0.001
TL (Glu-Phe)	1937–1996	8	0.014	0.022	0.06	0.551
TL (TrAA*-SrcAA [†])	1937–1996	8	0.001	0.011	0.00	0.927
ΣV [‡]	1937–1996	8	0.001	0.005	0.02	0.734

To maintain consistency with the coral data, NAO, and temperature time series were clipped to the time period 1926–2001. $\delta^{15}\text{N}$ statistics include the pooled record from all specimens of *P. resedaeformis*, and the eight individual samples used for CSIA. Relative trophic level (TL) formulations include $\delta^{15}\text{N}$ differences in Glu and Phe only (Glu-Phe) and also the broadest possible groupings of trophic (Tr) and source (Src) AAs (TrAA-SrcAA).

*TrAA = average(Asp, Glu, Ala, Ile, Leu, Val and Pro)

[†]SrcAA = average(Gly, Lys, Ser, Phe, Tyr)

[‡] $\Sigma V = 1/n \sum \text{Abs}(\chi \text{AA})$, where χ (deviation) of each AA = [$\delta^{15}\text{N-AA} - \text{AVG}\delta^{15}\text{N}(\text{Ala, Asp, Glu, Ile, Leu, and Pro})$], and n = the total number of AAs used in the calculation.

(Table 1). Moreover, interannual variability in bulk $\delta^{15}\text{N}$ was significantly and inversely correlated with NAO and temperature at mutually consistent temporal lags (Fig. 3 and *SI Text*).

The more time-consuming analysis of $\delta^{15}\text{N-AA}$ was performed on a subset of samples isolated from two of the longest-lived specimens. As expected from prior literature, $\delta^{15}\text{N-AA}$ values clearly fall into two groups (Fig. 4). The Tr-AA are substantially enriched in $\delta^{15}\text{N}$ versus the Src-AA, reflecting both autotrophic base metabolic patterns, as well as subsequent trophic transfers (4–8, 23). We note that within the Src-AA, Thr appears to constitute an outlier, with very negative values. While this is in contrast with the fundamental “source” designation, in fact similar observations for Thr (only) have been made in other animals (24), together suggesting that Thr displays a unique behavior and probably does not belong in the Src-AA grouping (25). The overall patterns in *P. resedaeformis* are very similar to those observed in pure plankton samples (4, 7), indicating that the basic photoautotrophic patterns are well preserved during POM transit and trophic incorporation into coral gorgonin. This qualitative observation is confirmed by the ΣV , a parameter tied to microbial resynthesis and alteration of $\delta^{15}\text{N-AA}$ patterns (7). The ΣV values in *P. resedaeformis* all fall in the range expected for fresh

biomass (i.e., live phytoplankton and zooplankton; 0.53 to 1.35), and further there is no significant trend in ΣV in our samples (Table 1 and Fig. 3).

Based on previous studies, the difference between $\delta^{15}\text{N}$ of the Tr-AA and Src-AA provides an internally normalized indication of relative trophic position, unaffected by changes in source nutrients (4, 5). We used two different formulations to test for changes in relative trophic level. The first calculates the difference in $\delta^{15}\text{N}$ between glutamic acid (Glu) and phenylalanine (Phe), the most common trophic level formulation based on the observation that Glu and Phe exhibit, respectively, the most and least trophic N-isotope fractionation (4). However, a formulation relying on only two AAs can be highly susceptible to diagenetic alteration or error in any single value (7). Our second formulation therefore calculates the difference in the averages of the broadest possible groupings of trophic [aspartic acid (Asp), Glu, alanine (Ala), isoleucine (Ile), leucine (Leu), valine (Val), proline (Pro)] and source [glycine (Gly), lysine (Lys), serine (Ser), Phe, tyrosine (Tyr)] AAs (7). In both formulations, regression over the record indicates no significant trend (Table 1) and the data are remarkably consistent [less than $\pm 1\%$, or well within typical instrumental error for $\delta^{15}\text{N-AA}$ values; see *Materials and Methods* and Fig. 3]. For two data points (1945 and 1975), however, values are elevated by about 1‰. These points may indicate trophic position elevation for average exported POM during these years but do not indicate any longer-term trend that might be correlated to bulk ^{15}N values.

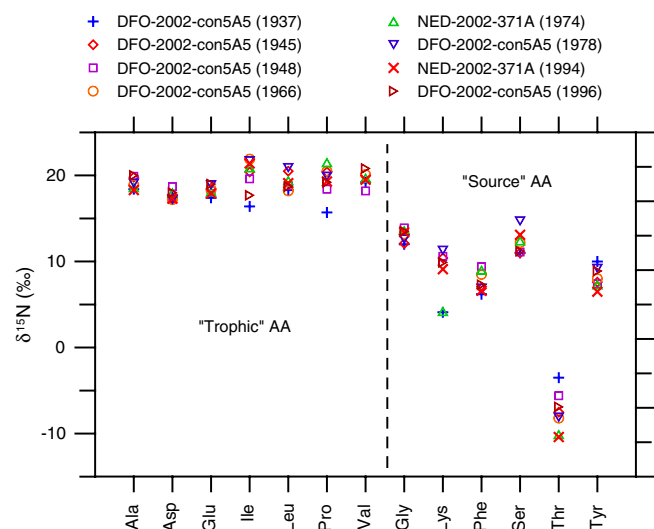


Fig. 4. Measured $\delta^{15}\text{N}$ of individual amino acids (AAs) in eight different samples isolated from two different specimens of *P. resedaeformis*. Trophic-AA (those that enrich strongly with trophic transfer) and Source-AA (those that are largely stable) refer to the two amino acid categories discussed in the text; individual AA abbreviations are as defined in text.

Discussion

Differences in nutrient processing histories underlie the distinct end-member $\delta^{15}\text{N}_{\text{NO}_3}$ signatures between WSW and LSW. The $\delta^{15}\text{N}_{\text{NO}_3}$ of WSW ($5.02 \pm 0.27\%$) is identical to the nominal mean ocean value of 5‰ (26), reflecting its origin in the nutrient-rich waters beneath the Gulf Stream (27, 28). The $\delta^{15}\text{N}_{\text{NO}_3}$ of LSW ($6.00 \pm 0.28\%$) reflects the low nutrient surface currents from which it is formed in the northern Labrador Sea. Because LSW is depleted in nutrients and not replenished by upwelling, the residual nitrate is enriched over that of WSW by 1‰. These end-member $\delta^{15}\text{N}_{\text{NO}_3}$ signatures reflect basin-scale circulation and likely did not vary significantly over the late Holocene.

The 1‰ difference in $\delta^{15}\text{N}_{\text{NO}_3}$ is remarkably well preserved through all levels of the food web at each of the different source water regions, from primary producers to top predators (Fig. 2). Based on an approximate 3‰ increase in bulk $\delta^{15}\text{N}$ with each step in trophic level (29, 30), *P. resedaeformis* (tissue $\delta^{15}\text{N} = 10.31 \pm 0.19$) likely feeds opportunistically on a mixture of sinking POM and small zooplankton, as previously noted (13). By this mechanism, $\delta^{15}\text{N}_{\text{NO}_3}$ signatures in the euphotic zone are trans-

mitted to and incorporated into the skeletal protein of deep-sea gorgonians.

Processes involved in the generation of coral N-isotopic signatures on the pathway from source nutrients to the gorgonin synthesis include (i) fixed-N uptake and growth of phytoplankton, (ii) microbial reworking/resynthesis and consumption during export and sinking of POM, and (iii) the assimilation of POM and zooplankton in the coral tissue and skeleton. Disentangling the factors involved in $\delta^{15}\text{N}$ fractionation during phytoplankton growth is simplified by the fact that nitrate utilization in the vicinity of the Northeast Channel is complete under the influence of both WSW and LSW, despite initial differences in nitrate concentrations in the two water masses (SI Text). Because the pool of nitrate is exhausted to completion, the accumulated phytoplankton biomass takes on the $\delta^{15}\text{N}$ of the source nitrate, regardless of the species involved in nitrate assimilation or the rate of growth (31, 32). Therefore, in this system, interannual variability in coral $\delta^{15}\text{N}$ may be attributed either to a change in $\delta^{15}\text{N}$ of source nitrate or to changes in trophic structure of the coral's food source.

The $\delta^{15}\text{N}$ -AA data provide two lines of evidence that there has been no significant change in the trophic structure of the coral's food source over the last century. First, the lack of a trend in the difference in $\delta^{15}\text{N}$ between Tr-AA and Src-AA provides strong evidence that there was no change in trophic level over the period from 1926 to 2001, in contrast to the significant trend observed in bulk $\delta^{15}\text{N}$ over the same time interval (Fig. 3). Second, the ΣV parameter strongly suggests that exported algal $\delta^{15}\text{N}$ -AA patterns at this location have been preserved in these corals with little diagenetic or microbial alteration. This increases confidence in the internal measure of trophic level, and further, the lack of any trend in ΣV also suggests potential change in POM diagenetic state is not a factor. Together, these data indicate that change in $\delta^{15}\text{N}_{\text{NO}_3}$ underlies the observed trends in the coral bulk $\delta^{15}\text{N}$ record, and its inverse correlation with NAO, temperature, and nitrate. We therefore interpret the change in coral bulk $\delta^{15}\text{N}$ over the twentieth century as a reflection of increasing presence of warm, nitrate-rich (lower $\delta^{15}\text{N}_{\text{NO}_3}$) WSW versus that of colder, nitrate-poor (higher $\delta^{15}\text{N}_{\text{NO}_3}$) LSW.

To put these data in a broader Holocene context, we also compared our twentieth century bulk $\delta^{15}\text{N}$ record with longer-term $\delta^{15}\text{N}$ measured over the 100- to 700-yr life spans of four fossil specimens of *P. resedaeformis* collected from the same location and depth in the Northeast Channel (Fig. 5). The average bulk gorgonin $\delta^{15}\text{N}$ of these fossils, sampled at the same temporal resolution as the modern corals (approximately annual), ranged from 10.8 ± 0.06 to $11.0 \pm 0.06\text{‰}$ (1 SE). Although the record is not continuous, all the fossil values fall within a very similar range, and from this perspective the decline during the twentieth century record appears striking. Assuming that the extent of nitrate utilization in surface waters has not changed, this strongly suggests that the more recent decline in $\delta^{15}\text{N}$ (implying a shift from LSW to WSW) is unique with respect to the last approximately 1,800 yr. Similarly, multiproxy evidence from sediment cores raised from the Scotian Shelf indicates near-constant temperatures for most of the past 1,600 yr, followed by sudden warming sometime within the last approximately 150 yr (33, 34). Our coral data more tightly constrain the timing of this change to the twentieth century, with most of the change occurring after 1970 when the NAO shifted to a sustained positive phase. With respect to the instrumental records, the decade of the 1960s would appear to represent an anomalous LSW-dominated period against a background of more WSW-dominated conditions. Analysis of longer-term proxy data reveals instead that LSW dominated through most of the late Holocene, and the recent shift to the WSW regime may be more similar to mid-Holocene hypsithermal conditions that ended approximately 2,500 yr ago (35).

This study demonstrates that $\delta^{15}\text{N}$ -AA can be used to independently track nitrate source and trophic history in a paleoarchive,

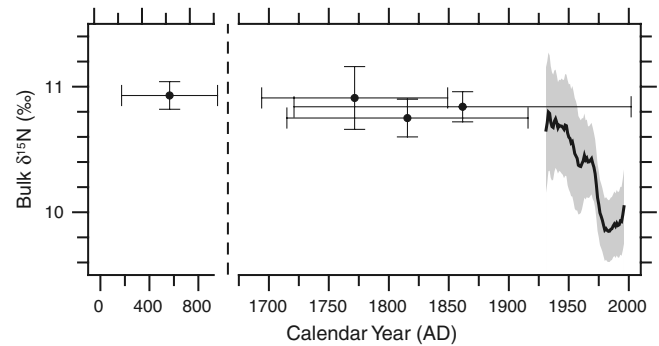


Fig. 5. Long-term trends in the bulk $\delta^{15}\text{N}$ of recent and fossil (pre-AD 1900) Northeast Channel corals. Fossil corals were sampled at approximately annual resolution, and dated with conventional ^{14}C and ^{210}Pb dating (SI Text); horizontal error bars integrate both dating error and specimen life-span. Vertical error bars and gray shaded region represent 95% confidence intervals. Note break in x-axis scale.

thus solving a major complication in all bulk $\delta^{15}\text{N}$ records. The fidelity of the $\delta^{15}\text{N}$ -AA patterns observed in this study indicates a broad range of new potential in coral-based paleoceanographic studies of the marine N cycle. Some examples of future potential include (i) the reconstruction of $\delta^{15}\text{N}$ of average exported production from the surface ocean, independent of complicating assumptions about any single species or biomarker (36); (ii) reconstruction of phytoplankton trophic structure through time; and (iii) a possible new tracer for variations in algal community structure, based on evolving studies of the tracer potential in compound-specific stable isotope patterns (37, 38).

Our data also specifically demonstrate a unique ability of this approach in determining the relative roles of top-down (consumer-driven) versus bottom-up (resource-driven) forcings on lower trophic level ecosystems in time and space (39). The lack of any trend in trophic level or POM diagenetic state indicates that the local plankton community along the upper continental slope was unaffected or perhaps more resilient to the “trophic cascade” thought to have occurred elsewhere on the Eastern Scotian Shelf and Labrador Sea in response to overexploitation of Atlantic cod and other groundfish species (40, 41). On the other hand, whereas nitrate concentration may be impacted by internal processes, nitrate source is externally forced; our results from the Scotian/Maine upper continental slope indicate that increasing nitrate levels were associated with externally driven shifts in nitrate source partitioning. Slopewater circulation in the Scotia-Maine region is linked with broader scale climate variability associated with the North Atlantic oscillation (16, 17, 19), which has trended toward the positive modal state over the same time period that global temperatures have increased most dramatically (1). We therefore conclude that changes in nitrate source partitioning may be tied to recent, human-caused changes in global climate. These results highlight the importance of novel and creative proxies like $\delta^{15}\text{N}$ -AA for investigating the links between climate change and ecosystem functioning beyond the last few decades of scientific observations.

Materials and Methods

Live and fossil specimens were collected by remotely operated vehicle (ROV), video grab, or scientific trawl, from approx. $42^{\circ}00'\text{N}$, $65^{\circ}36'\text{W}$, between 275 and 450 m water depth. Sections from the basal region of each colony were decalcified in 5% (v/v) HCl, and growth rings were sampled at 1 to 2 yr periodicity. Counting of growth rings and validation of their annual periodicity using bomb- ^{14}C are described elsewhere (11). Coral nitrogen isotope ratios ($\delta^{15}\text{N} = ((^{15}\text{N}/^{14}\text{N})_{\text{sample}} / (^{15}\text{N}/^{14}\text{N})_{\text{standard}} - 1) \times 1000$) were measured using continuous flow isotope ratio mass spectrometry (CF-IRMS) and standardized relative to atmospheric N_2 (AIR). Analytical error, based on sample replicates, was $<0.20\text{‰}$. Data processing is described in SI Text.

Individual AA isotopic analyses on coral gorgonin were made on acid hydrolysates (6 N HCl, 100 ml, 20 h) of approximately 1 mg homogenized material, following formation of isopropyl-TFA derivatives (7, 42). Derivatives were analyzed on a Thermo Trace Ultra GC, fitted with an Agilent DB-5 column (50 m × 0.32 mm i.d. × 0.52 μm film thickness), in line with an oxidation furnace and reduction furnace, and linked to a Finnigan Delta^{plus} XP mass spectrometer. All samples were derivatized with an accompanying AA standard for which authentic $\delta^{15}\text{N}$ values of each AA were determined offline, to monitor the accuracy of the instrument. Samples were injected in triplicate, bracketed by standards, and sample $\delta^{15}\text{N}$ values were corrected based on a running average of known standard values through a run. Reproducibility for individual AA values was typically better than 1‰.

Seawater samples for $\delta^{15}\text{N}_{\text{NO}_3}$ analyses were collected from three stations each off Nova Scotia (approximately 44.1°N, 58.7°W) and Labrador (54.7°N, 54.5°W) into prewashed (5% HCl and deionized water) 60 ml polyethylene bottles and frozen immediately upon collection. Measurement

of $\delta^{15}\text{N}_{\text{NO}_3}$ followed the bacterial denitrifier method (43), where nitrate is converted to nitrous oxide (N₂O) by denitrifying bacteria that lack N₂O reductase activity. Isotopic analysis (relative to AIR) was then performed on the N₂O gas by CF-IRMS. Analytical error, based on sample replicates, was 0.2‰.

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