



# Natural forcing of the North Atlantic nitrogen cycle in the Anthropocene

Xingchen Tony Wang<sup>a,b,1</sup>, Anne L. Cohen<sup>c</sup>, Victoria Luu<sup>a</sup>, Haojia Ren<sup>d</sup>, Zhan Su<sup>b</sup>, Gerald H. Haug<sup>e</sup>, and Daniel M. Sigman<sup>a</sup>

<sup>a</sup>Department of Geosciences, Princeton University, Princeton, NJ 08544; <sup>b</sup>Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena, CA 91125; <sup>c</sup>Department of Marine Geology and Geophysics, Woods Hole Oceanographic Institution, Woods Hole, MA 02540; <sup>d</sup>Department of Geosciences, National Taiwan University, 106 Taipei, Taiwan; and <sup>e</sup>Climate Geochemistry Department, Max Planck Institute for Chemistry, 55128 Mainz, Germany

Edited by Donald E. Canfield, Institute of Biology and Nordic Center for Earth Evolution, University of Southern Denmark, Odense M., Denmark, and approved August 28, 2018 (received for review January 18, 2018)

**Human alteration of the global nitrogen cycle intensified over the 1900s. Model simulations suggest that large swaths of the open ocean, including the North Atlantic and the western Pacific, have already been affected by anthropogenic nitrogen through atmospheric transport and deposition. Here we report an ~130-year-long record of the <sup>15</sup>N/<sup>14</sup>N of skeleton-bound organic matter in a coral from the outer reef of Bermuda, which provides a test of the hypothesis that anthropogenic atmospheric nitrogen has significantly augmented the nitrogen supply to the open North Atlantic surface ocean. The Bermuda <sup>15</sup>N/<sup>14</sup>N record does not show a long-term decline in the Anthropocene of the amplitude predicted by model simulations or observed in a western Pacific coral <sup>15</sup>N/<sup>14</sup>N record. Rather, the decadal variations in the Bermuda <sup>15</sup>N/<sup>14</sup>N record appear to be driven by the North Atlantic Oscillation, most likely through changes in the formation rate of Subtropical Mode Water. Given that anthropogenic nitrogen emissions have been decreasing in North America since the 1990s, this study suggests that in the coming decades, the open North Atlantic will remain minimally affected by anthropogenic nitrogen deposition.**

North Atlantic | nitrogen cycle | Anthropocene | atmospheric deposition

The global nitrogen (N) cycle has been altered dramatically by human activities since the Industrial Revolution. The dominant natural N input to the biologically available (fixed) N reservoir is by N<sub>2</sub>-fixing organisms that break the triple bond of molecular nitrogen (N<sub>2</sub>) to produce ammonium (NH<sub>4</sub><sup>+</sup>) for incorporation into their biomass. The invention of the Haber-Bosch process in the early 20th century enabled humans to produce fixed N on an industrial scale, mostly for fertilizer. The rises in global population and food demand over the last century have greatly increased the rate of industrial N<sub>2</sub> fixation (~110 Tg N/y at present) (1). Further, fossil fuel burning and other human activities emit nitrogen oxides (NO<sub>x</sub>) and ammonia (NH<sub>3</sub>) into the atmosphere, through which they are transported before being deposited. In sum, the rate of human generation of fixed N is currently ~200 Tg N/y, similar to the rate of natural N<sub>2</sub> fixation (200–250 Tg N/y) (2). The majority of anthropogenically fixed N is eventually transferred into the environment, through emission and volatilization or leaching and runoff. As a result, terrestrial ecosystems and the coastal ocean have experienced nutrient enrichment over the past several decades (3–6).

It is less clear whether the open ocean N cycle has also been affected by human activities. Modeling studies suggest that large regions of the open ocean (e.g., the western halves of the North Pacific and North Atlantic) have already been significantly affected by anthropogenic atmospheric nitrogen (AAN) through atmospheric transport and deposition (7–9). However, very few atmospheric and oceanographic measurements allow for the assessment of the current effect of human activities on the open ocean N cycle, let alone its history.

The isotopic composition of N is a promising tool for reconstructing AAN inputs to the marine environment. The AAN reaching the open ocean has an <sup>15</sup>N/<sup>14</sup>N (or δ<sup>15</sup>N, where δ<sup>15</sup>N =

$[(^{15}\text{N}/^{14}\text{N})_{\text{sample}} / (^{15}\text{N}/^{14}\text{N})_{\text{air}}] - 1$ ) that is lower than the other N sources to sunlit surface waters, making the N isotopes a tracer of this AAN input (10). At Bermuda, an average δ<sup>15</sup>N of close to –5‰ appears to apply to total AAN deposition (11–15). On an annual basis, the natural N input to the Sargasso Sea (the subtropical North Atlantic region surrounding Bermuda) is dominated by the upward mixing of nitrate from the shallow subsurface (the thermocline), with a minor contribution by in situ N<sub>2</sub> fixation. Both of these inputs have a higher δ<sup>15</sup>N than that of AAN (2.5‰ and –1‰, compared with –5‰) (16–18). Under the nutrient-poor conditions that characterize the Sargasso Sea, phytoplankton completely consume the N supply, transmitting its δ<sup>15</sup>N to the organic matter produced in its surface waters. Thus, an increase in AAN inputs relative to natural N sources should be evidenced by a decrease in the δ<sup>15</sup>N of this organic matter.

Scleractinian corals that live in the surface ocean deposit calcium carbonate skeleton annually as they grow. They acquire their N from the environment, with feeding on zooplankton and other components of the particulate organic matter in surface waters likely dominating their N nutrition under the low-nutrient conditions of Bermuda's offshore reefs (19). A small portion of the coral's organic tissue is used to build the coral skeleton and is subsequently trapped in and protected by its mineral matrix (20). This protection preserves the organic matter against the diagenetic loss and exogenous N contamination that introduce uncertainty into non-fossil-bound archives of organic matter (21).

## Significance

Human activities have altered the global nitrogen cycle through nitrogen fertilizer usage and fossil fuel burning. It has been suggested that even the remote open ocean is influenced by anthropogenic nitrogen through atmospheric transport and deposition. However, the magnitude and timing of the anthropogenic N effect on the open ocean remain elusive, mainly because of very limited long-term measurements. Here we provide an ~130-year coral record of N cycle dynamics from the subtropical North Atlantic. This record shows minimal influence of anthropogenic N deposition, in contrast to published model simulations, suggesting that previous estimates of anthropogenic N deposition on the open ocean were too high.

Author contributions: X.T.W., A.L.C., G.H.H., and D.M.S. designed research; X.T.W., A.L.C., and V.L. performed research; X.T.W., V.L., and H.R. contributed new reagents/analytic tools; X.T.W. and Z.S. analyzed data; and X.T.W. and D.M.S. wrote the paper.

The authors declare no conflict of interest.

This article is a PNAS Direct Submission.

Published under the PNAS license.

Data deposition: The data in this paper are available from the Biological and Chemical Oceanography Data Management Office (<https://www.bco-dmo.org/dataset/683097>).

<sup>1</sup>To whom correspondence should be addressed. Email: xingchen@caltech.edu.

This article contains supporting information online at [www.pnas.org/lookup/suppl/doi:10.1073/pnas.1801049115/-DCSupplemental](http://www.pnas.org/lookup/suppl/doi:10.1073/pnas.1801049115/-DCSupplemental).

Thus, coral skeletal  $\delta^{15}\text{N}$  (CS- $\delta^{15}\text{N}$ ) can provide a natural record of the AAN effect on the ocean surrounding Bermuda (10).

The Bermuda Islands are located 1,000 km downwind of the North American continent, which appears to represent the dominant source of anthropogenic N deposition at Bermuda (12, 22). AAN deposition has led to a 20th century decline in the sediment  $\delta^{15}\text{N}$  of remote watersheds in the United States and Canada (23, 24) as well as in the nitrate  $\delta^{15}\text{N}$  of Greenland ice cores (25, 26). If low- $\delta^{15}\text{N}$  AAN from North America is currently an important source of N supply to the remote North Atlantic surface ocean, the corals from Bermuda should also record a  $\delta^{15}\text{N}$  decline over the 20th century.

Here we report a 134-y-long, annually resolved CS- $\delta^{15}\text{N}$  record (AD 1880–2014) from the outer reef of Bermuda (Fig. 1A), which we use to test the hypothesis that AAN has affected the N supply to the open subtropical North Atlantic surface ocean (7, 27, 28). In the summer of 2014, a 60-cm-long core was collected from a living brain coral of the species *Diploria labyrinthiformis* at a depth of 3 m on Hog Reef at the northern end of the Bermuda pedestal (Fig. 1 and *SI Appendix*, Fig. S1). This site is on the outer rim reef, roughly 10 km north of the islands of Bermuda and thus remote from local island N input. Plankton  $\delta^{15}\text{N}$  at this site is similar to that of the open ocean at the Bermuda Atlantic Time Series Study (BATS) (29–31), confirming that this site is a good candidate to record the effect of AAN on the open North Atlantic. In addition, to extract information from further back in time, CS- $\delta^{15}\text{N}$  was measured in available intervals from a previously acquired core through a fossil *Diploria labyrinthiformis* extending back to approximately AD 1780; this coral is from John Smith's Bay (JSB) to the south of the island (Fig. 1A).

## Results and Discussion

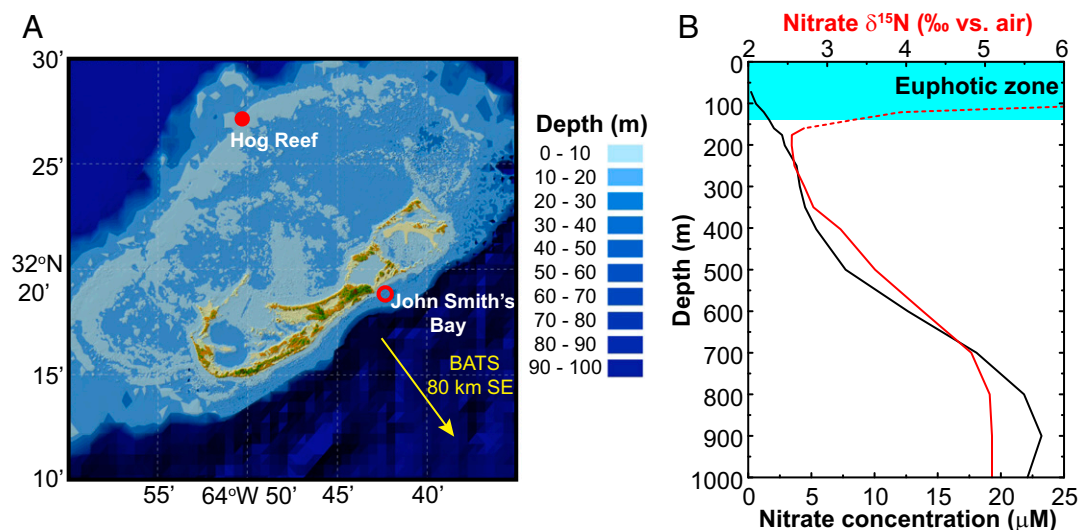
**Minimal Influence of AAN Deposition on the North Atlantic.** The average CS- $\delta^{15}\text{N}$  in the Hog Reef coral core is 4.17‰, with a SD of 0.26‰ (Fig. 2A). This is 1.6–1.7‰ higher than the thermocline nitrate  $\delta^{15}\text{N}$  of the surrounding ocean (Fig. 1B), consistent with both prior work on Bermuda (29) and the global correlation between the  $\delta^{15}\text{N}$  of the N supply to surface waters and CS- $\delta^{15}\text{N}$  (19). Despite the low- $\delta^{15}\text{N}$  of AAN deposition at Bermuda (12, 13, 15, 22), the CS- $\delta^{15}\text{N}$  record is remarkably stable. There appears to be a long-

term decline in CS- $\delta^{15}\text{N}$  of 0.6‰ from the early 20th century to the 1980s, with several superimposed decadal oscillations of 0.5–0.6‰ (see smoothed record in Fig. 3). One might argue that the long-term  $\delta^{15}\text{N}$  decline, although weak, was caused by increasing AAN deposition. However, since the 1980s, CS- $\delta^{15}\text{N}$  has increased back to the earlier 20th century values, a change that has not been observed in terrestrial or ice core  $\delta^{15}\text{N}$  records (Fig. 2C). This suggests that factors other than AAN have dominated variations in Bermuda CS- $\delta^{15}\text{N}$  over this time period. The decadal variability aside, the stability of CS- $\delta^{15}\text{N}$  across the entire record suggests that the AAN can only have been a minor contributor to the N supply to the remote North Atlantic surface ocean over the 20th century.

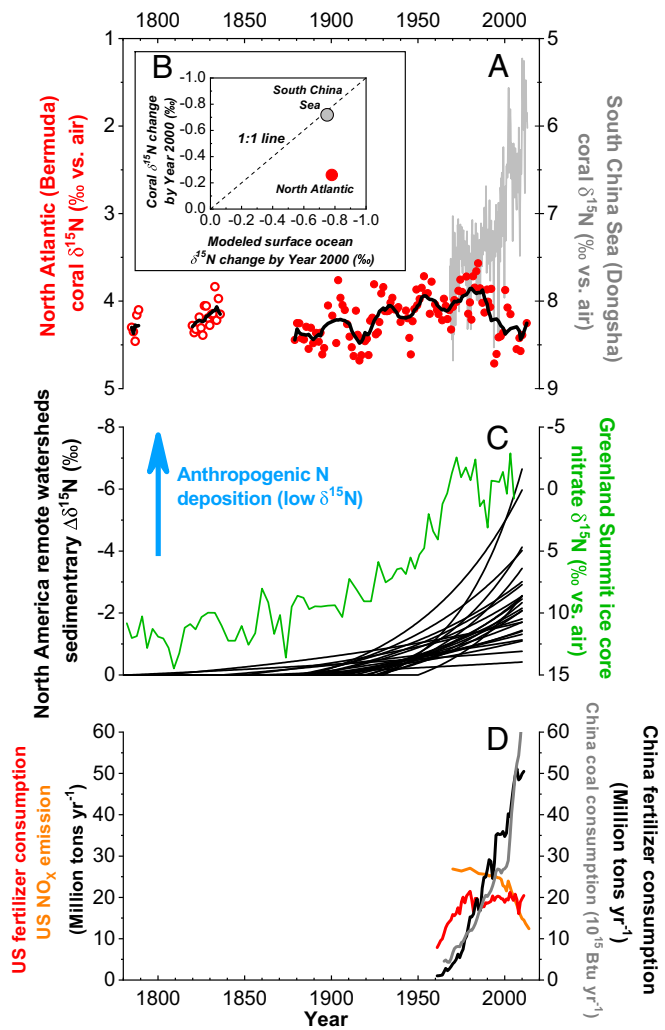
AAN deposition can lower the  $\delta^{15}\text{N}$  of ocean ecosystems and thus corals in two related ways. First, in each year, AAN deposition represents a N input to the euphotic zone (the photosynthetically active upper layer) that is lower in  $\delta^{15}\text{N}$  than the nitrate supply from below and in situ  $\text{N}_2$  fixation, thus working to lower the  $\delta^{15}\text{N}$  of organic N produced by phytoplankton (Fig. 4A). Second, operating over multiple years, the lowered  $\delta^{15}\text{N}$  of organic N sinks into the shallow subsurface and is remineralized, gradually lowering the  $\delta^{15}\text{N}$  of the subsurface nitrate (Fig. 4A). This subsurface nitrate is the dominant annual supply of fixed N to the surface ocean, and thus, its  $\delta^{15}\text{N}$  decrease is communicated back to the surface ocean ecosystem. We first address the  $\delta^{15}\text{N}$  of subsurface nitrate in the Sargasso Sea and then consider the annual N isotope budget of its euphotic zone (the sunlit surface layer).

In the modern Sargasso Sea, the subsurface nitrate  $\delta^{15}\text{N}$  at 200 m depth is 2.5‰ (Fig. 1) (16, 18), lower than the mean ocean nitrate  $\delta^{15}\text{N}$  of 5‰ (32). It has been suggested that  $\text{N}_2$  fixation in the euphotic zone and subsequent sinking and remineralization of the resulting organic N is dominantly responsible for the deviation of thermocline nitrate  $\delta^{15}\text{N}$  from the mean ocean value (33, 34). However, because AAN at Bermuda has an even lower  $\delta^{15}\text{N}$  than newly fixed N, it could not be ruled out that AAN is an important contributor to the low  $\delta^{15}\text{N}$  of the nitrate in the Sargasso Sea thermocline (11). Similarly, it has been suggested that the low nitrate  $\delta^{15}\text{N}$  (of  $\sim 3$ ‰) in the Mediterranean Sea (35) is dominantly due to anthropogenic inputs (36).

However, the modern CS- $\delta^{15}\text{N}$  is similar to the CS- $\delta^{15}\text{N}$  in the late 19th century. Moreover, the fossil coral from the south shore of



**Fig. 1.** Sampling sites and modern oceanographic context. (A) Bathymetric map of the Bermuda pedestal showing the location of the Hog Reef coral used in this study (collected alive in July 2014) and a fossil coral at John Smith's Bay (collected in 2001). The direction of BATS is indicated by the yellow arrow. Map modified from ref. 29, with permission from Elsevier. (B) Average depth profiles of nitrate concentration and  $\delta^{15}\text{N}$  at BATS based on 18 cruises since 2005 (18). The thermocline nitrate  $\delta^{15}\text{N}$  below the euphotic zone is 2.5‰, lower than the deep nitrate  $\delta^{15}\text{N}$  of 5.0‰. The upward increase in nitrate  $\delta^{15}\text{N}$  into the euphotic zone is caused by nitrate assimilation and does not reflect the  $\delta^{15}\text{N}$  of the nitrate supply to the euphotic zone as a whole (18).



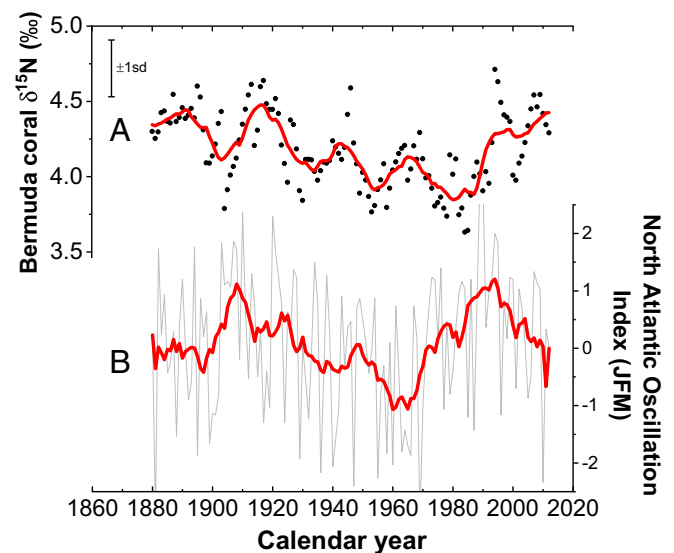
**Fig. 2.** The Bermuda CS- $\delta^{15}\text{N}$  record and its comparison with other records. (A) The Bermuda CS- $\delta^{15}\text{N}$  record (red circles and black line, the latter being a 10-y running mean), with the CS- $\delta^{15}\text{N}$  record from Dongsha Atoll in the South China Sea shown for comparison (gray line) (10). The Bermuda CS- $\delta^{15}\text{N}$  record was compiled from two coral cores: the continuous coral core from Hog Reef (AD 1880–2014; solid red circles) and the fossil coral core from the John Smith’s Bay (AD 1780–1840; open red circles). Due to a problem in core archiving, only short intervals in the bottom part of the John Smith’s Bay coral were available for CS- $\delta^{15}\text{N}$  analysis. (B) Comparison of CS- $\delta^{15}\text{N}$  changes to modeled surface ocean  $\delta^{15}\text{N}$  changes (28) in the North Atlantic and South China Sea over the 20th century. (C) Greenland Summit ice core nitrate  $\delta^{15}\text{N}$  record (green line) (25) and power functions (black lines) fitted to  $\delta^{15}\text{N}$  records from 24 remote North American watersheds (23). The watershed  $\delta^{15}\text{N}$  records were normalized to each record’s preindustrial value (23). In both A and C,  $\delta^{15}\text{N}$  decreases upward, so that interpreted greater AAN importance is upward. (D) US N fertilizer consumption and  $\text{NO}_x$  emissions (red and orange lines), compared with China fertilizer consumption and coal consumption, the latter intended as a rough indicator of combustion N sources (black and gray lines). Data in D were compiled by the Earth Policy Institute.

Bermuda (John Smith’s Bay; Fig. 1A) going back to approximately AD 1780 confirms this low  $\delta^{15}\text{N}$  (Fig. 2A), suggesting that the low nitrate  $\delta^{15}\text{N}$  in the thermocline water has been a persistent feature of the Sargasso Sea since before the Industrial Revolution. Because anthropogenic perturbation of the atmospheric reactive N cycle was very limited before the Industrial Revolution (7, 25), the stability of Bermuda CS- $\delta^{15}\text{N}$  argues that natural processes such as  $\text{N}_2$  fixation in the surface ocean, not AAN deposition, are the dominant drivers of the low  $\delta^{15}\text{N}$  in the nitrate of the modern Sargasso Sea

thermocline. Qualitative expectations are that relatively rapid AAN deposition would be needed over many years to significantly change the  $\delta^{15}\text{N}$  of thermocline nitrate, due to the substantial burden of fixed N in the thermocline and its continuous exchange with the rest of the ocean’s vast nitrate reservoir (“mixing” in Fig. 4A). Thus, this finding is not particularly surprising.

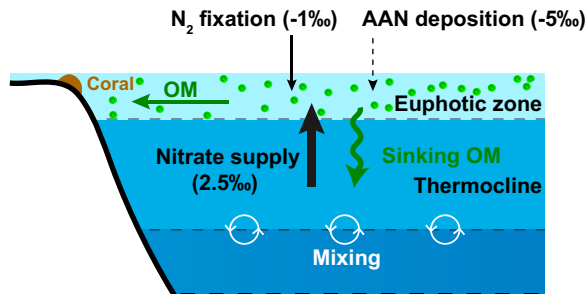
In comparison with the  $\delta^{15}\text{N}$  of thermocline nitrate, the annual N isotope budget of the euphotic zone is more directly affected by a given rate of AAN deposition, and yet the stability of CS- $\delta^{15}\text{N}$  argues that it also changed little over the 20th century. A simple isotope mixing calculation of this budget indicates that the 0.2‰ decrease in Bermuda CS- $\delta^{15}\text{N}$  from the early 20th century to the year 2000 translates to only a 2% increase in the annual fixed N supply to the Sargasso Sea euphotic zone due to rising AAN deposition (*SI Appendix, Fig. S2*). One potential caveat in this calculation is that the rate of  $\text{N}_2$  fixation in the North Atlantic might have decreased over the 20th century in response to increasing AAN input. In our isotope mixing model, when including suppression of  $\text{N}_2$  fixation that perfectly compensates for AAN deposition, AAN deposition represents a maximum of 5% of total fixed N supply to the euphotic zone for the year 2000 (*SI Appendix, Fig. S2*). Thus, it appears that compensation by  $\text{N}_2$  fixation is not dominantly responsible for the stability of the Bermuda CS- $\delta^{15}\text{N}$  record; rather, AAN deposition increases must have been small relative to the nitrate supply from below (Fig. 4A).

The lack of a clear decline in CS- $\delta^{15}\text{N}$  at Bermuda was not expected. A model study of the effect of the recent history of AAN deposition rate on the  $\delta^{15}\text{N}$  of the organic N produced in the upper ocean predicts a decline of 0.8‰ from the early 20th century to the year 2000 in the Sargasso Sea (28), greater than the observed 0.2‰ decline in the Bermuda CS- $\delta^{15}\text{N}$  record over this time period (Fig. 2B). The 0.8‰ decline in the model occurred despite the inclusion of  $\text{N}_2$  fixation suppression by AAN; a larger  $\delta^{15}\text{N}$  decline would have been simulated without it (28). The Bermuda record also contrasts with a CS- $\delta^{15}\text{N}$  record from Dongsha Atoll in the South China Sea (10), which shows a  $\delta^{15}\text{N}$  decline of 0.7‰ by the year 2000 (Fig. 2A); the South China Sea CS- $\delta^{15}\text{N}$  change is consistent with the model-based prediction

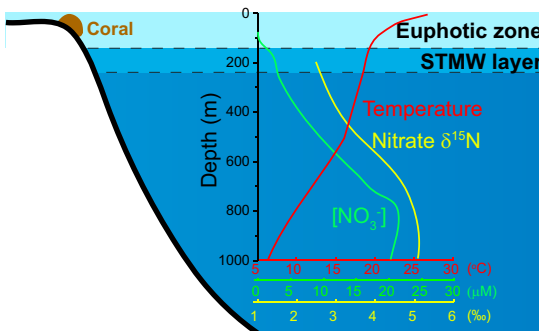


**Fig. 3.** Decadal variation in the Bermuda CS- $\delta^{15}\text{N}$  record and the history of the North Atlantic Oscillation. (A) The Bermuda CS- $\delta^{15}\text{N}$  data (black circles) and its 10-y running mean (red line). (B) The station-based North Atlantic Oscillation (NAO) index (light gray line) and its 10-y running mean (red line) (57). The CS- $\delta^{15}\text{N}$  record shows maximum positive correlation ( $r = 0.70$ ) with NAO when CS- $\delta^{15}\text{N}$  lags NAO by roughly a decade (*SI Appendix, Fig. S3*).

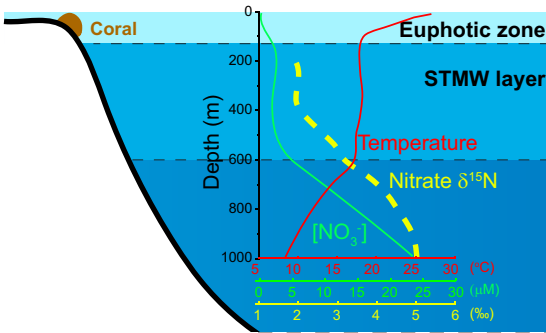
### A N budget in the modern Sargasso Sea



### B Positive NAO: Thin Subtropical Mode Water



### C Negative NAO: Thick Subtropical Mode Water



**Fig. 4.** (A) The euphotic zone fixed nitrogen budget in the modern Sargasso Sea and the depth profiles of temperature, nitrate concentration, and nitrate  $\delta^{15}\text{N}$  near Bermuda during phases of (B) positive NAO and (C) negative NAO. On an annual basis, AAN deposition (with a  $\delta^{15}\text{N}$  of  $-5\text{‰}$ ) represents less than 5% of N supply to the euphotic zone in the modern Sargasso Sea (*SI Appendix, Fig. S2*), with the vertical nitrate supply dominating the total fixed N supply and  $\text{N}_2$  fixation (with a  $\delta^{15}\text{N}$  of  $-1\text{‰}$ ) contributing a small fraction of N supply. The thermocline waters from which nitrate is supplied, in turn, exchange water with the deeper and higher-latitude waters, which is simplified in A as “mixing” with underlying deep water. During a positive phase of NAO (B), a thin STMW layer is generated in the subsurface, increasing the nitrate concentration and nitrate  $\delta^{15}\text{N}$  in the thermocline. During a negative phase of NAO (C), a thick STMW layer is generated in the subsurface, decreasing the nitrate concentration and nitrate  $\delta^{15}\text{N}$  in the thermocline. The temperature and nitrate concentration depth profiles are from ref. 51. The nitrate  $\delta^{15}\text{N}$  depth profile under positive NAO state is from Fig. 1, whereas the nitrate  $\delta^{15}\text{N}$  depth profile under negative NAO state (dashed yellow line) is based on a calculation (*SI Appendix, Figs. S4 and S5*).

for that region (Fig. 2B). In the South China Sea, the same isotope mixing model as applied to Bermuda suggests that by the year 2000, AAN deposition had increased the total N supply to the surface ocean by 17–23% (10) (*SI Appendix, Fig. S2*).

The difference of the Bermuda CS- $\delta^{15}\text{N}$  record from ocean model predictions raises the possibility that ocean models have overestimated open-ocean AAN deposition. In general, the variation in atmospheric N deposition across models, and thus the reliance of the community on model ensembles (37), points to the substantial uncertainties in the model estimates. In terms of systematic bias, overestimation of AAN deposition has been suggested and related to ocean/atmosphere cycling of both ammonium/ammonia and dissolved organic N (27), for which there is isotopic and chemical evidence at Bermuda (13, 14). The Bermuda CS- $\delta^{15}\text{N}$  record thus provides impetus for further investigation of the processes responsible for AAN delivery to the open ocean (27).

An alternative set of explanations for the discrepancy relates to oceanic transports of fixed N. Specifically, the global ocean models used for the simulations may underestimate the rate of nitrate supply to the euphotic zone from below, thus artificially raising the proportional importance of AAN deposition in the N budget of the euphotic zone. The existence of such a bias toward underestimating the subsurface nitrate supply is supported by a documented discrepancy between ocean models and observations for net primary productivity in the subtropical gyres of both the North Atlantic (at BATS) and the North Pacific (38). Such a bias might apply in the subtropical gyres but not in the South China Sea because the gyres do not experience the wind-driven upwelling that occurs in the South China Sea, so that more complex mechanisms of nutrient supply are proportionally more important in the gyres. Global ocean models are unlikely to adequately simulate these more complex mechanisms (17, 39).

The lack of clear CS- $\delta^{15}\text{N}$  decline in the Bermuda coral core also contrasts with the strong  $\delta^{15}\text{N}$  declines observed in remote North American terrestrial records ( $>3\text{‰}$  on average) and Greenland ice cores ( $>10\text{‰}$ ) (23, 25, 26) (Fig. 2C). On an annual basis, both terrestrial and marine ecosystems receive most of their fixed N from internal recycling (40, 41). In the ocean, circulation and mixing supply subsurface nitrate that itself is the product of remineralization of sinking organic N. On land, soil organic N is decomposed and remineralized, making the N available to plants (40, 42); the freshwater bodies from which the terrestrial  $\delta^{15}\text{N}$  records were generated also receive N from soil organic matter remineralization (23). The rate of this recycled N supply appears to be comparable between land and ocean (40, 43), so a land-to-ocean difference in this term is probably not the primary driver of the distinction in the AAN  $\delta^{15}\text{N}$  signal between the terrestrial  $\delta^{15}\text{N}$  records and the coral CS- $\delta^{15}\text{N}$  record (Fig. 2).

One cause for the greater response of the terrestrial (lake)  $\delta^{15}\text{N}$  records is probably simply their greater proximity to the anthropogenic N sources and thus their receipt of more AAN deposition (44). However, given the starkness of the distinction, it may have additional causes. For example, as discussed above, the  $\delta^{15}\text{N}$  of thermocline nitrate is buffered by continuous exchange with the global ocean nitrate reservoir and thus is expected to change only very gradually due to anthropogenic N accumulation in the subsurface (28). In soils, however, the source of the remineralized N flux from soil organic matter may be restricted to a small fraction of the total soil N, with the rest cycling so slowly as to be considered virtually unavailable (45). If so, the remineralized N flux to plants and runoff may decline in  $\delta^{15}\text{N}$  relatively rapidly as AAN accumulates in this small, actively cycled fraction of soil N. Putting aside this specific proposal, the contrast between the land and coral  $\delta^{15}\text{N}$  records promises to advance our understanding of the differences in N dynamics between land and ocean.

**Influence of the North Atlantic Oscillation on the Sargasso Sea N Cycle.** The clearest variation in the Bermuda CS- $\delta^{15}\text{N}$  record is the 0.5–0.6‰ oscillation on roughly decadal time scales, which

appears to be related to the North Atlantic Oscillation (NAO) (Fig. 3), as supported by the magnitude-squared coherence between the two records (*SI Appendix, Fig. S3*). The biogeochemistry of the North Atlantic has been shown to be strongly affected by the NAO (46–49). There is evidence that Bermuda reef metabolism is sensitive to the NAO through open ocean productivity and organic matter transport to the reef (50). However, the proposed mechanism for this connection involves changes in mixing-driven nitrate supply to the sunlit surface waters around Bermuda, which would involve an immediate response to the NAO driver (50). In contrast, the strongest correlation of the CS- $\delta^{15}\text{N}$  record with the NAO index (with a correlation coefficient of 0.7) is achieved with a lag in CS- $\delta^{15}\text{N}$  of roughly a decade (*SI Appendix, Fig. S3*).

The correlation and lag between the Bermuda CS- $\delta^{15}\text{N}$  record and the NAO are best explained by the formation Subtropical Mode Water (STMW) north of Bermuda, which has been shown to be affected by the NAO and in turn to affect the nutrient dynamics of the subtropical North Atlantic through thermocline ventilation (51) (Fig. 4 B and C). In a negative NAO state, a thick layer of STMW forms north of Bermuda and is transported southward. This relatively thick STMW layer is characterized by a temperature of 18 °C and a low nitrate concentration of 2–3  $\mu\text{M}$  from 100 m down to 600 m (Fig. 4C). Its low nitrate concentration allows the remineralization of a given amount of low- $\delta^{15}\text{N}$ , recently fixed N from the euphotic zone to cause a greater decrease in the  $\delta^{15}\text{N}$  of the thermocline nitrate. As a result, the negative NAO state should encourage a decline in the  $\delta^{15}\text{N}$  of the thermocline nitrate supply to the euphotic zone. In contrast, in a positive NAO state, with less STMW formed, the thermocline should occupy a narrower depth range (Fig. 4B). As a result, deeper, denser water with high nitrate  $\delta^{15}\text{N}$  and concentration should approach the euphotic zone, increasing the  $\delta^{15}\text{N}$  of the nitrate supply and thus causing the recent rise in CS- $\delta^{15}\text{N}$  (Fig. 3A). The lag between NAO state and CS- $\delta^{15}\text{N}$  can be explained by the decadal time scales of (i) the gradual thickening of the thermocline and (ii) the ingrowth of nitrate from the remineralization of newly fixed N. A strong positive relationship between the nitrate concentration and the nitrate  $\delta^{15}\text{N}$  is observed spatially in the modern North Atlantic thermocline (34), supporting the plausibility of the proposed mechanism. Regardless of whether this specific explanation is incorrect, the correlation of the decadal variation in the Bermuda CS- $\delta^{15}\text{N}$  with NAO argues that the former is driven by natural processes, rather than by AAN changes.

**Implications for the Future North Atlantic.** Our findings have implications for the future of the effect of AAN on the North Atlantic. The primary anthropogenic atmospheric N source to the North Atlantic is the United States, in which anthropogenic N emission rates have leveled off (Fig. 2D), starting in the 1980s with the Clean Air Act. If N emissions from the United States have indeed plateaued or peaked, given their undetectable role

over the 130-y period of the Bermuda CS- $\delta^{15}\text{N}$  record, the open North Atlantic N cycle will remain minimally affected by AAN deposition for the foreseeable future.

## Materials and Methods

**Coral Samples and Age Model.** The coral samples used in this study are from the pedestal of the Bermuda islands in the North Atlantic subtropical gyre. A core was collected from a living brain coral (*Diploria labyrinthiformis*) in July 2014 at a site (Hog Reef) 10 km offshore to the north of the islands at a water depth of 3 m (Fig. 1A and *SI Appendix, Fig. S1*). In the laboratory, a 1-cm-thick slab was cut from the coral core and rinsed three times with deionized water and dried. The slab was scanned by X-ray computed tomography to determine the maximum growth axis, and an age model was developed by counting annual growth bands on the images. Along the growth direction, powder samples were collected from the slab at 2-mm increments (representing  $\sim 8$  mo of growth). The Hog Reef coral core extends back to approximately AD 1880.

To extract information from further back in time, a 230-y-old coral (*Diploria labyrinthiformis*) from JSB to the south of the island was used (Fig. 1). Although this core has previously been used to generate continuous records of climate parameters (52), due to a problem in sample archiving, only two bottom segments of the coral were available for our work. Unlike the Hog Reef site, the JSB site is close to shore ( $\sim 400$  m). Thus, current effects from human activities on the island are possible. However, this would not have applied before the Industrial Revolution, when the population in this part of the island was much smaller than today.

**Nitrogen Isotope Analysis.** The  $\delta^{15}\text{N}$  analysis on the coral powder samples followed the protocol described in ref. 29. Briefly, 10–15 mg of coral powder is soaked in 10 mL of sodium hypochlorite (10–15% available chlorine) in 15-mL centrifuge tubes on an orbital shaker for 24 h. The sample is rinsed three times with deionized water and dried at 60 °C. The sample is weighed into a precombusted 4-mL borosilicate glass vial and dissolved by reaction with 4M HCl. After dissolution, an aliquot of 1 mL freshly combined persulfate oxidizing reagent is added, and the sample is autoclaved for 1.5 h. After autoclaving, the sample is centrifuged, and the clear supernatant is transferred to another precombusted 4-mL borosilicate glass vial, in which the pH of the supernatant is adjusted to near 7 with HCl and NaOH solutions. The resulting nitrate concentration of the sample solution is analyzed by chemiluminescence (53), and the  $\delta^{15}\text{N}$  of the nitrate is measured by conversion to  $\text{N}_2\text{O}$  with the denitrifier method (54) followed by extraction, purification, and isotopic analysis of the  $\text{N}_2\text{O}$  product (55, 56). Glutamic acid reference materials USGS40 (US Geological Survey 40) and 41 are used in each batch of analyses to correct for the combined reagent and operational blanks, which is typically less than 2% of the total N content in an oxidized sample. An in-house coral standard (CBS-1) provides a metric for reproducibility both within an analysis batch and across batches; based on CBS-1, the analytical precision (1SD) of the protocol is 0.2‰ (29).

**ACKNOWLEDGMENTS.** The authors thank G. P. Lohmann, R. Smith, A. Alpert, and J. Zhou for their assistance in the field. This work was supported by the National Science Foundation [Awards OCE-1060947 (to D.M.S.) and OCE-1537338 (to A.L.C. and D.M.S.)], the Grand Challenges Program of Princeton University (D.M.S.), a Schlanger Ocean Drilling Fellowship (to X.T.W.), and the Simons Foundation [Grant 497534 (to X.T.W.)].

- Battay W, Aneja VP, Schlesinger WH (2017) Is nitrogen the next carbon? *Earths Future* 5:894–904.
- Fowler D, et al. (2013) The global nitrogen cycle in the twenty-first century. *Philos Trans R Soc Lond B Biol Sci* 368:1–13.
- Hautier Y, et al. (2014) Eutrophication weakens stabilizing effects of diversity in natural grasslands. *Nature* 508:521–525.
- Deegan LA, et al. (2012) Coastal eutrophication as a driver of salt marsh loss. *Nature* 490:388–392.
- Cai W-J, et al. (2011) Acidification of subsurface coastal waters enhanced by eutrophication. *Nat Geosci* 4:766–770.
- Conley DJ, et al. (2009) Ecology. Controlling eutrophication: Nitrogen and phosphorus. *Science* 323:1014–1015.
- Duce RA, et al. (2008) Impacts of atmospheric anthropogenic nitrogen on the open ocean. *Science* 320:893–897.
- Doney SC, et al. (2007) Impact of anthropogenic atmospheric nitrogen and sulfur deposition on ocean acidification and the inorganic carbon system. *Proc Natl Acad Sci USA* 104:14580–14585.
- Kim I-N, et al. (2014) Chemical oceanography. Increasing anthropogenic nitrogen in the North Pacific Ocean. *Science* 346:1102–1106.
- Ren H, et al. (2017) 21st-century rise in anthropogenic nitrogen deposition on a remote coral reef. *Science* 356:749–752.
- Knapp AN, Hastings MG, Sigman DM, Lipschultz F, Galloway JN (2010) The flux and isotopic composition of reduced and total nitrogen in Bermuda rain. *Mar Chem* 120: 83–89.
- Altieri KE, Hastings MG, Gobel AR, Peters AJ, Sigman DM (2013) Isotopic composition of rainwater nitrate at Bermuda: The influence of air mass source and chemistry in the marine boundary layer. *J Geophys Res* 118:11304–11316.
- Altieri KE, Hastings MG, Peters AJ, Oleynik S, Sigman DM (2014) Isotopic evidence for a marine ammonium source in rainwater at Bermuda. *Global Biogeochem Cycles* 28: 1066–1080.
- Altieri KE, Fawcett SE, Peters AJ, Sigman DM, Hastings MG (2016) Marine biogenic source of atmospheric organic nitrogen in the subtropical North Atlantic. *Proc Natl Acad Sci USA* 113:925–930.
- Gobel AR, Altieri KE, Peters AJ, Hastings MG, Sigman DM (2013) Insights into anthropogenic nitrogen deposition to the North Atlantic investigated using the isotopic composition of aerosol and rainwater nitrate. *Geophys Res Lett* 40: 5977–5982.

16. Knapp AN, Sigman DM, Lipschultz F (2005) N isotopic composition of dissolved organic nitrogen and nitrate at the Bermuda Atlantic Time-series Study site. *Global Biogeochem Cycles* 19:GB1018.
17. Fawcett SE, Lomas MW, Ward BB, Sigman DM (2014) The counterintuitive effect of summer-to-fall mixed layer deepening on eukaryotic new production in the Sargasso Sea. *Global Biogeochem Cycles* 28:86–102.
18. Fawcett SE, Ward BB, Lomas MW, Sigman DM (2015) Vertical decoupling of nitrate assimilation and nitrification in the Sargasso Sea. *Deep Sea Res Part I* 103:64–72.
19. Wang XT, et al. (2016) Influence of open ocean nitrogen supply on the skeletal delta N-15 of modern shallow-water scleractinian corals. *Earth Planet Sci Lett* 441:125–132.
20. Mass T, Drake JL, Peters EC, Jiang W, Falkowski PG (2014) Immunolocalization of skeletal matrix proteins in tissue and mineral of the coral *Stylophora pistillata*. *Proc Natl Acad Sci USA* 111:12728–12733.
21. Wang XT, et al. (2017) Deep-sea coral evidence for lower Southern Ocean surface nitrate concentrations during the last ice age. *Proc Natl Acad Sci USA* 114:3352–3357.
22. Hastings MG, Sigman DM, Lipschultz F (2003) Isotopic evidence for source changes of nitrate in rain at Bermuda. *J Geophys Res* 108:4790.
23. Holtgrieve GW, et al. (2011) A coherent signature of anthropogenic nitrogen deposition to remote watersheds of the Northern Hemisphere. *Science* 334:1545–1548.
24. Hobbs WO, et al. (2016) Nitrogen deposition to lakes in national parks of the western Great Lakes region: Isotopic signatures, watershed retention, and algal shifts. *Global Biogeochem Cycles* 30:514–533.
25. Hastings MG, Jarvis JC, Steig EJ (2009) Anthropogenic impacts on nitrogen isotopes of ice-core nitrate. *Science* 324:1288.
26. Geng L, et al. (2014) Nitrogen isotopes in ice core nitrate linked to anthropogenic atmospheric acidity change. *Proc Natl Acad Sci USA* 111:5808–5812.
27. Jickells TD, et al. (2017) A reevaluation of the magnitude and impacts of anthropogenic atmospheric nitrogen inputs on the ocean. *Global Biogeochem Cycles* 31:289–305.
28. Yang S, Gruber N (2016) The anthropogenic perturbation of the marine nitrogen cycle by atmospheric deposition: Nitrogen cycle feedbacks and the 15N Haber-Bosch effect. *Global Biogeochem Cycles* 30:1418–1440.
29. Wang XT, et al. (2015) Isotopic composition of skeleton-bound organic nitrogen in reef-building symbiotic corals: A new method and proxy evaluation at Bermuda. *Geochim Cosmochim Acta* 148:179–190.
30. Montoya JP, Carpenter EJ, Capone DG (2002) Nitrogen fixation and nitrogen isotope abundances in zooplankton of the oligotrophic North Atlantic. *Limnol Oceanogr* 47:1617–1628.
31. Fawcett SE, Lomas MW, Casey JR, Ward BB, Sigman DM (2011) Assimilation of upwelled nitrate by small eukaryotes in the Sargasso Sea. *Nat Geosci* 4:717–722.
32. Sigman DM, Altabet MA, McCorkle DC, Francois R, Fischer G (2000) The  $\delta^{15}\text{N}$  of nitrate in the Southern Ocean: Nitrogen cycling and circulation in the ocean interior. *J Geophys Res* 105:19599–19614.
33. Knapp AN, DiFiore PJ, Deutsch C, Sigman DM, Lipschultz F (2008) Nitrate isotopic composition between Bermuda and Puerto Rico: Implications for  $\text{N}_2$  fixation in the Atlantic Ocean. *Global Biogeochem Cycles* 22:GB3014.
34. Marconi D, et al. (2015) Nitrate isotope distributions on the US GEOTRACES North Atlantic cross-basin section: Signals of polar nitrate sources and low latitude nitrogen cycling. *Mar Chem* 177:143–156.
35. Pantoja S, Repeta DJ, Sachs JP, Sigman DM (2002) Stable isotope constraints on the nitrogen cycle of the Mediterranean Sea water column. *Deep Sea Res Part I* 49:1609–1621.
36. Mara P, et al. (2009) Isotopic composition of nitrate in wet and dry atmospheric deposition on Crete in the eastern Mediterranean Sea. *Global Biogeochem Cycles* 23:GB4002.
37. Lamarque JF, et al. (2013) Multi-model mean nitrogen and sulfur deposition from the Atmospheric Chemistry and Climate Model Intercomparison Project (ACCMIP): Evaluation historical and projected changes. *Atmos Chem Phys* 13:7997–8018.
38. Saba VS, et al. (2010) Challenges of modeling depth-integrated marine primary productivity over multiple decades: A case study at BATS and HOT. *Global Biogeochem Cycles* 24:GB3020.
39. Mahadevan A, Archer D (2000) Modeling the impact of fronts and mesoscale circulation on the nutrient supply and biogeochemistry of the upper ocean. *J Geophys Res* 105:1209–1225.
40. Gerber S, Hedin LO, Oppenheimer M, Pacala SW, Shevliakova E (2010) Nitrogen cycling and feedbacks in a global dynamic land model. *Global Biogeochem Cycles* 24:GB1001.
41. Voss M, et al. (2013) The marine nitrogen cycle: Recent discoveries, uncertainties and the potential relevance of climate change. *Philos Trans R Soc Lond B Biol Sci* 368:20130121.
42. Wang YP, Law RM, Pak B (2010) A global model of carbon, nitrogen and phosphorus cycles for the terrestrial biosphere. *Biogeosciences* 7:2261–2282.
43. Jenkins WJ (1988) Nitrate flux into the euphotic zone near Bermuda. *Nature* 331:521–523.
44. Galloway JN, et al. (2008) Transformation of the nitrogen cycle: Recent trends, questions, and potential solutions. *Science* 320:889–892.
45. Trumbore S (2009) Radiocarbon and soil carbon dynamics. *Annu Rev Earth Planet Sci* 37:47–66.
46. Palter JB, Sarmiento JL, Gnanadesikan A, Simeon J, Slater RD (2010) Fueling export production: Nutrient return pathways from the deep ocean and their dependence on the meridional overturning circulation. *Biogeosciences* 7:3549–3568.
47. Stanley RHR, Jenkins WJ, Doney SC, Lott DE, III (2015) The  $^3\text{He}$  flux gauge in the Sargasso Sea: A determination of physical nutrient fluxes to the euphotic zone at the Bermuda Atlantic Time-series Site. *Biogeosciences* 12:5199–5210.
48. Lomas MW, et al. (2010) Increased ocean carbon export in the Sargasso Sea linked to climate variability is countered by its enhanced mesopelagic attenuation. *Biogeosciences* 7:57–70.
49. Sherwood OA, Lehmann MF, Schubert CJ, Scott DB, McCarthy MD (2011) Nutrient regime shift in the western North Atlantic indicated by compound-specific  $\delta^{15}\text{N}$  of deep-sea gorgonian corals. *Proc Natl Acad Sci USA* 108:1011–1015.
50. Yeakel KL, et al. (2015) Shifts in coral reef biogeochemistry and resulting acidification linked to offshore productivity. *Proc Natl Acad Sci USA* 112:14512–14517.
51. Palter JB, Lozier MS, Barber RT (2005) The effect of advection on the nutrient reservoir in the North Atlantic subtropical gyre. *Nature* 437:687–692.
52. Goodkin NF, Hughen KA, Cohen AL, Smith SR (2005) Record of Little Ice Age sea surface temperatures at Bermuda using a growth-dependent calibration of coral Sr/Ca. *Paleoceanography* 20:PA4016.
53. Braman RS, Hendrix SA (1989) Nanogram nitrite and nitrate determination in environmental and biological materials by vanadium (III) reduction with chemiluminescence detection. *Anal Chem* 61:2715–2718.
54. Sigman DM, et al. (2001) A bacterial method for the nitrogen isotopic analysis of nitrate in seawater and freshwater. *Anal Chem* 73:4145–4153.
55. Casciotti KL, Sigman DM, Hastings MG, Böhlke JK, Hilkert A (2002) Measurement of the oxygen isotopic composition of nitrate in seawater and freshwater using the denitrifier method. *Anal Chem* 74:4905–4912.
56. Weigand MA, Foriel J, Barnett B, Oleynik S, Sigman DM (2016) Updates to instrumentation and protocols for isotopic analysis of nitrate by the denitrifier method. *Rapid Commun Mass Spectrom* 30:1365–1383.
57. Hurrell JW, Kushnir Y, Visbeck M (2001) Climate. The North Atlantic oscillation. *Science* 291:603–605.