Environmental modulations of nutrient conditions in the Labrador Sea reconstructed from nitrogen isotopes in a six-hundred-year-old crustose coralline alga

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Abstract

The climatological impacts on biogeochemical processes in the polar North Atlantic remain poorly understood, as there exist both biological and physical mechanisms that drive nutrient availability in the region. Here, we present nitrogen isotope measurements (δN) from a six-hundred-year-old coralline alga to elucidate historic and modern trends in Labrador Sea nitrate utilization, defined as the degree of biological nitrate assimilation relative to nitrate supply. Prior to the Little Ice Age (LIA), periods during which utilization became complete corresponded to neutral modes of the Atlantic Multidecadal Oscillation (AMO), which we argue promoted the oceanographic conditions favorable for simultaneous phytoplankton growth and reduced nitrate input. More recently, nitrate utilization became complete during periods characterized by reduced deep-water convection in the Labrador Sea, suggesting a reduced inflow of equatorially-sourced nitrate driven by a weakening of the Labrador Current. Such nutrient rerouting may have implications for socioeconomically-important fisheries and carbon sequestration throughout the region.

Climate-modulated nutrient conditions along the Labrador Shelf: Evidence from nitrogen isotopes in a six-hundred-year-old crustose coralline alga

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Key Points:

- Nitrogen isotopes from a crustose coralline alga are argued to record ocean circulation and nutrient utilization along the Labrador Shelf
- Past periods of increased polar inflow waters and nutrient utilization are linked to negative modes of the Atlantic multidecadal oscillation
- An anomalously long phase of low nutrient input since ~1870 is linked to the weakening of the Atlantic meridional overturning circulation

Abstract

The impacts of climate change on north Atlantic nutrient chemistry remain poorly understood, as there exist a multitude of rapidly changing biological and physical drivers of nutrient conditions throughout the region. Here, we present nitrogen isotope measurements derived from a six-hundred-year-old crustose coralline alga ($\delta^{15}N_{algal}$) to elucidate historical and contemporary trends in nitrate utilization and circulation patterns along the Labrador Shelf. Prior to the early 1900s, we argue that intervals during which utilization approached completion were controlled by reduced nitrate advection linked to an increased proportion of nitrate-poor polar waters and subdued Atlantic influence, as expected from concurrent negative modes of the Atlantic multidecadal oscillation. While nitrate conditions should have recovered in recent years, our record suggests that high utilization persisted since ~1870, which we also attribute to reduced Atlantic advection, likely associated with the twentieth-century anthropogenic weakening of the Atlantic meridional overturning circulation. These results highlight the role of ongoing climate-induced circulation changes in modulating nutrient distributions throughout the subpolar north Atlantic, which may have implications for other environmental phenomena such as fisheries and oceanic carbon storage.

1 Introduction

High-latitude regions suffer the greatest impacts of modern-day climate change (Pithan & Mauritsen, 2014). One effect of this change is enhanced sea-ice melt along the Labrador Shelf (Halfar et al., 2013), which is driving an unprecedented increase in primary productivity relative to the past several hundred years (Chan et al., 2017). While such a dramatic change in productivity should intuitively lead to the greater depletion of upper-ocean nutrients, multiple simultaneous environmental changes throughout the region make this relationship complex. This is because nutrient availability in the subpolar north Atlantic is not only a function of biological activity, but also of physical oceanographic processes that regulate nutrient supply.

The Labrador Sea in the subpolar north Atlantic receives considerable scientific attention because deep-water convection in the region is thought to be historically important for driving the strength of the Atlantic meridional overturning circulation (AMOC) (Buckley & Marshall, 2016; Kuhlbrodt et al., 2007). Paleoceanographic investigations suggest that convection in the Labrador Sea has been at an anomalously weak state over the last ~150 years, most likely due to anthropogenic warming and freshwater forcing (Caesar, Rahmstorf, Robinson, Feulner, & Saba, 2018; Thibodeau et al., 2018; Thornalley et al., 2018). Recent observations further suggest that convection in the Labrador Sea has been virtually shut off (Lozier et al., 2019), which has weakened the influence of nitrate-rich Atlantic inflow along north-western Atlantic coast (Thibodeau et al., 2018; Thibodeau, De Vernal, Hillaire-Marcel, & Mucci, 2010). Such a reorganization of upper-ocean circulation patterns may therefore also have implications for primary productivity, regionally important fisheries (Stock et al., 2017) and oceanic carbon storage (Takahashi et al., 2009). Due to the absence of long-term observational data, however, paleo-proxies are required to contextualize these contemporary changes and their effects on nitrate delivery.

Along the coastal Labrador Shelf, nitrate is supplied during winter via vertical mixing (Harrison et al., 2013; Harrison & Li, 2007; Henson, Dunne, & Sarmiento, 2009) and advection from the eastern subpolar region (Loder, Petrie, & Gawarkiewicz, 1998). Advective supply relies on the Labrador Current, which sources waters from the eastern region of the subpolar Atlantic, Baffin Bay and Hudson Strait (Figure 1a and 1b). Eastern subpolar waters are comprised of Arctic outflow, sourced from the East Greenland Current, and Atlantic inflow, sourced from the North

Atlantic Current, an extension of the Gulf Stream. However, previous field surveys indicate that the nitrate derived from the Hudson Strait only impacts the northern-most tip of the shelf (Drinkwater & Harding, 2001). As such, nitrate supply along the mid-shelf region is primarily affected by vertical mixing and open-ocean advection, which today is mostly completely consumed in the upper ~20 m of the water column during the phytoplankton growing season (Figure 1c and 1d).

The degree of nitrate consumption relative to supply, known as utilization (Altabet and Francois, 1994), imprints an isotopic fingerprint on biologically assimilated nitrogen. This is due to kinetic fractionation processes that result in the preferential assimilation of ^{14}N-nitrate in virtually all photosynthetic organisms that have been studied (e.g., Altabet & Francois, 1994; Mariotti et al., 1981), including macro-benthic algae (Swart, Evans, Capo, & Altabet, 2014). During the contemporary phytoplankton growing season along the Labrador Shelf, utilization approaches completion and the isotopic composition of biologically assimilated nitrogen is therefore expected to approximate that of the initial source (e.g., Altabet & Francois, 1994; Mariotti et al., 1981). This utilization-induced fractionation makes the isotopic composition of geologically preserved nitrogen useful for reconstructing nutrient utilization in a variety of past marine settings (Altabet and Francois, 1994), including the subpolar north Atlantic (Straub et al., 2013).

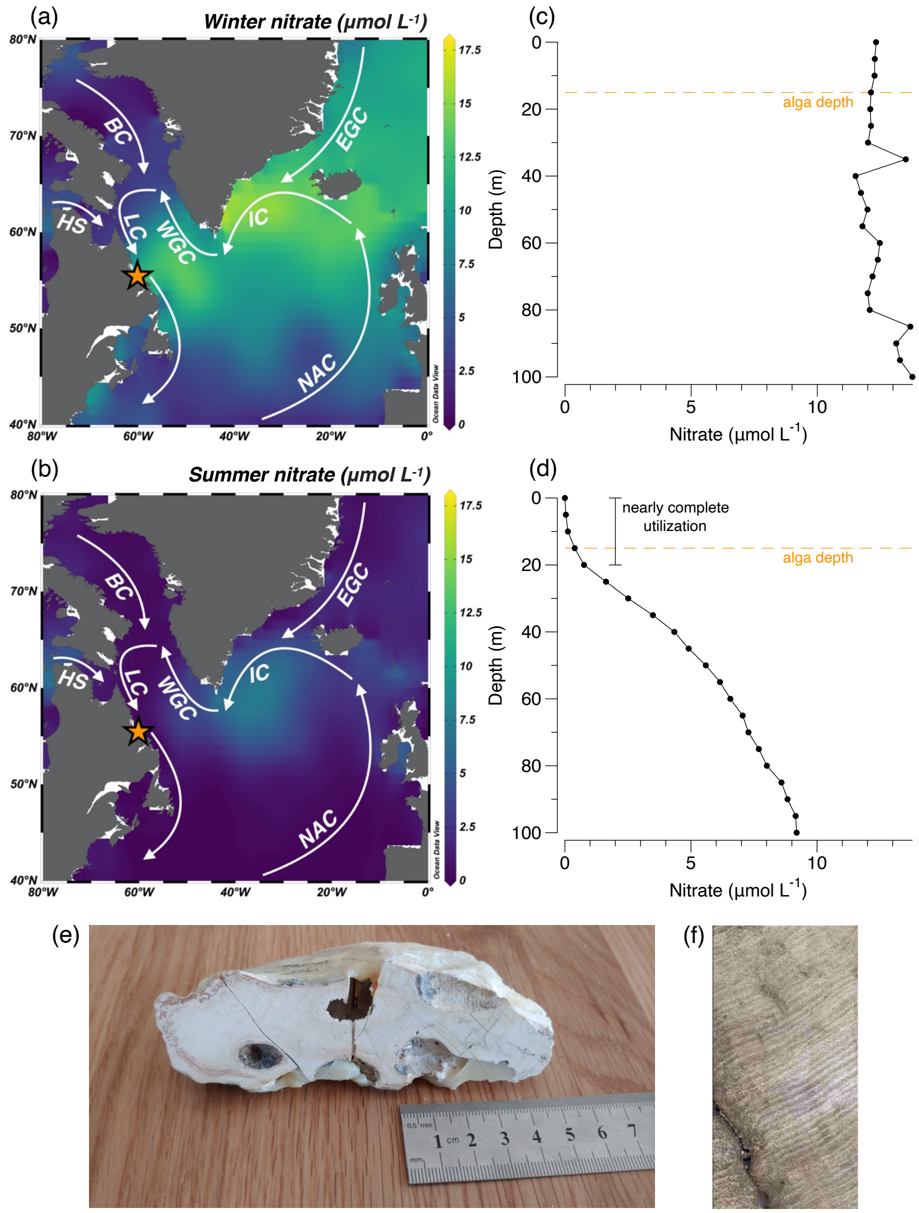

Fig. 1. Oceanographic setting and *C. compactum* specimen. (a, b) Surface maps of **(a)** winter and **(b)** summer nitrate distributions with a depiction of major north Atlantic circulation patterns. The study site is indicated by the orange star. Abbreviations: NAC: North Atlantic Current, IC: Irminger Current, EGC: East Greenland Current, WGC: West Greenland Current, LC: Labrador Current, BC: Baffin Current, HS: Hudson Strait outflow. These figures were generated with the help of Ocean Data View (Schlitzer, 2018) using inorganic nutrient data taken from the World Ocean Atlas (Garcia et al., 2013). **(c, d)** Depth profiles of **(c)** winter and **(d)** summer nitrate concentrations at 55.5 °N, 58.5 °W. **(e)** Cross-section of the *Clathromorphum compactum* specimen sampled in this study and **(f)** its growth bands.

Nitrogen is preserved in several geologically important marine organisms, such as foraminifera (Ren et al., 2009), corals (Muscatine et al., 2005; Sherwood, Lehmann, Schubert, Scott, &

McCarthy, 2011; Wang et al., 2014) and bivalves (Gillikin et al., 2017). Over the last few decades, crustose coralline algae have also emerged as promising paleoenvironmental archives due to their widespread distribution, significant longevity and annual banding patterns (Figure 1e and 1f), the latter of which allows for precise and high-resolution reconstructions of oceanographic changes in the recent geological past (e.g., Chan et al., 2017; Halfar et al., 2013; Moore et al., 2017). As such, the $\delta^{15}N$ of nitrogen retained in the organic-rich skeletons of coralline algae may offer a unique window into the history of marine nutrient dynamics on multicentennial timescales. Here, we present the first ~5-year-resolved $\delta^{15}N$ record derived from a 613-year-old crustose coralline alga, *Clathromorphum compactum* ($\delta^{15}N_{algal}$), and demonstrate its utility in reconstructing nitrate conditions along the rapidly changing Labrador Shelf throughout the last several centuries. Because a variety of factors may impact the isotopic composition of biologically assimilated nitrogen, we analyze our record in the context of several other high-resolution paleoenvironmental reconstructions to infer the most likely drivers of $\delta^{15}N_{algal}$ variations over the last several hundred years.

2 Materials and Methods

2.1 Specimen Collection and Age Model Development

A living *C. compactum* specimen was collected off the coast of Kingitok Island, Labrador, Canada (55.3983 °N; 59.8467 °W) at 15 m depth in 2011 via divers using SCUBA (Figure 1a-f). Following collection, the specimen was rinsed in freshwater and cross-sectioned perpendicular to the direction of growth. The cross-section was mounted on a plate using wax and polished with Allied High Tech diamond lapping film and water (30, 15, and 1 µm grains) until growth bands were clearly visible. Using high-resolution images of the specimen taken with a Nikon H600L Microscope (Figure 1f), bands were identified and assigned years to develop a growth chronology in Photoshop. Previous U-Th dating indicated that the age of the specimen was ~630 years old (Halfar et al., 2013), which was also verified by the number of growth bands counted.

2.2 Isotopic Analysis

A high-precision, computer-driven New Wave Research Micromill Sampling System attached to an x, y, and z stage was used to collect (mill) material from along the growth bands for $\delta^{15}N$

analysis. To remove external particulates before drilling, the specimen was sonicated 3 times for 5 minutes in Milli-Q water and then oven-dried for 24 hours. To verify the effectiveness of this Milli-Q cleaning technique, $\delta^{15}N$ values and %N were measured in replicate *C. compactum* samples exposed to our method and an oxidative cleaning technique designed for carbonate samples of much lower nitrogen content (Ren et al., 2009). While %N was consistently lower under oxidative cleaning, $\delta^{15}N$ values obtained from samples under both treatments remained within one standard deviation of each other (Table 1). These results may indicate that the additional nitrogen removed during oxidative cleaning was mostly derived from algal-fixed nitrogen rather than external contamination, as the removal of external contamination would be expected to also alter the $\delta^{15}N$.

Region	Sample Type	Treatment	Replicates	n	$\delta^{15}N$	$\delta^{15}N$ 1σ	%N	%N 1σ
Qikiqtarjuaq (Baffin Bay)	*C. compactum*	Oxidative	1	5	6.04	0.36	0.14	0.03
	C. compactum	Milli-Q	2	10	6.54	0.37	0.27	< 0.01
	Seawater NO_3 (≥100 m)	na	na	3	6.51	0.51	na	na
Labrador Shelf	*C. compactum*	Milli-Q	1	1	5.9	na	na	na
	Seawater NO_3 (100 m)	na	3	na	6	0.28	na	na

Table 1. Nitrogen isotope measurements from algal samples and seawater nitrate in two regions of nearly complete nitrate utilization. Nitrogen isotope measurements and concentrations were derived from Qikiqtarjuaq replicates under Milli-Q and oxidative (Ren et al., 2009) cleaning treatments. Experiments were performed on powder extracted from the full cross-section of the same skeletal chunk. For samples cleaned only with Milli-Q, two replicate powders (n = 5 for each powder) were used. Nitrogen isotope measurements of seawater nitrate for the Qikiqtarjuaq (Baffin Bay) and Labrador Shelf regions are taken from Lehmann et al., (2019) and Sherwood et al., (2011) respectively. Because both regions are subject to nearly complete nitrate consumption, the agreement between the isotopic composition of seawater nitrate and algal specimens supports the argument that *C. compactum* is likely recording marine nitrate utilization (see Section 3.1 for details).

Following the visible growth bands as much as possible, digitized drill paths were programmed on the Micromill screen. For each drill line, 5 to 6 150-µm-deep drill passes were made to obtain 7 mg of skeletal material. Samples were transferred and weighed in tin cups along with reference materials. The majority of samples were taken at 5-year increments with an average resolution of 3 to 6 years, except for regions of the skeleton where insufficient material required milling from more growth bands, increasing the resolution to between 7 to 20 years. Of the total 110 measurements reported here, 16 correspond to a time window of >7 years. Following the collection of each sample, pressurized air was used to remove residual sample powder. Then, the samples were analyzed using a Micromass Isoprime 100 isotope ratio mass spectrometer coupled to an Elementar Vario MicroCube elemental analyzer operated in continuous-flow mode at GEOTOP (Université du Québec à Montréal). Two internal reference materials (Leucine; $\delta^{15}N$ = -0.10 ± 0.24‰ and DORM 2; $\delta^{15}N$ = +14.95 ± 0.09‰) were used to normalize the results to the AIR scale based on international IAEA standards (N1, N2 and NO3). We measured a third internal standard (casein; $\delta^{15}N$ = -0.1 ± 0.15‰) to assess the normalization. Results are given in delta units (δ) in ‰ vs AIR. Overall analytical uncertainty (1σ) was calculated to be better than ± 0.2‰, based on the propagation of uncertainties of the normalization of internal reference materials and samples. Chromatographs produced from replication tests suggest that the algal carbonate underwent complete combustion. Specifically, an anomalous *m/z* 30 peak was not observed during any of the analyses, which would be expected from the production of $^{12}C^{18}O$ (~2% of CO isotopologues) in the case of incomplete combustion. In addition, N_2 peak tailing was not noticeably different between algal samples and organic standards, further assuring successful combustion.

2.3 Spectral Analysis

Cross-wavelet coherence and phase-relationship analyses were conducted using the Cross Wavelet and Wavelet Coherence toolbox in MatLab R2020a provided by A. Grinsted. For technical specifications of squared-wavelet coherence and phase-direction calculations, see Grinsted et al., 2004. Significance is reported at the 95% confidence level against red noise, which was determined via 300 Monte Carlo simulations. "In-phase" relationships describe those that represent positive correlations between variables and "antiphase" relationships describe negative correlations. To achieve equally spaced $\delta^{15}N_{algal}$ values, five-year interpolations were calculated from the raw data and used for spectral analysis.

3 Results and Discussion

3.1 Potential Drivers of $\delta^{15}N_{algal}$

Our record spans from 1392 to 2005. During this period, $\delta^{15}N_{algal}$ values generally followed an increasing trend from -0.3 to 7.9‰ (Figure 2). $\delta^{15}N_{algal}$ initially increased by ~7‰ from 1392 to the late 1500s prior to a transition to relatively constant average values, during which there were 4 notable periods characterized by values typically reaching maximum values of ~6 to 7‰ spaced by approximately 100 years. Beginning around 1870, $\delta^{15}N_{algal}$ increased by an average of ~2.9‰, with high values persisting throughout the remainder of the study period. Here, we propose that this algal record has documented changes in seawater nitrate utilization over the past six centuries.

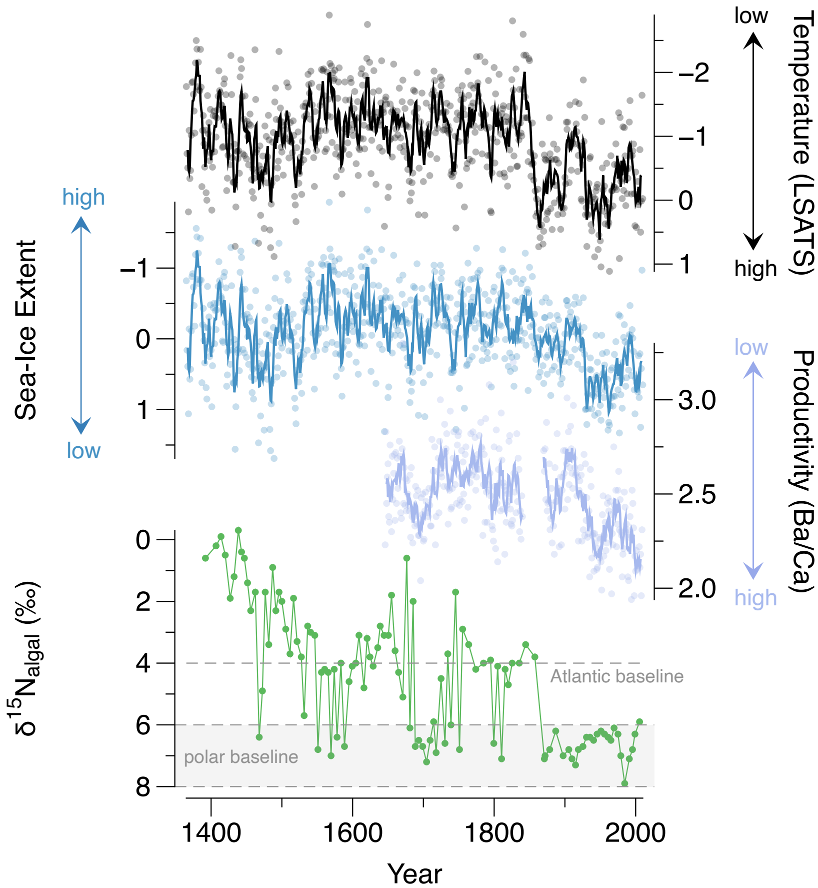

Fig. 2. Environmental changes in the Labrador Shelf archived in coralline algae. (top to bottom) Temperature reconstructed from the Labrador Sea Algae Time Series (LSATS) reported in Moore et al. (2017); historical algal-derived index of regional sea-ice extent taken from Halfar et al. (2013); algal Ba/Ca ([(µg g^{-1})/(µg g^{-1}) × 10^{-5}]), negatively correlated with primary productivity (Chan et al., 2017); and our coralline algal nitrogen isotope record (analytical uncertainty <0.2‰). Lines for temperature anomalies, sea-ice extent and Ba/Ca represent five-year-smoothed means of the data. The approximate Atlantic (4‰) and polar (Baffin Bay; 6 to 8‰) seawater nitrate $\delta^{15}N$ baselines are marked on the bottom panel. Phases of nearly complete utilization could be consistent with $\delta^{15}N_{algal}$ values falling within this range regardless of the relative proportion of Atlantic versus polar waters feeding the Labrador Current. However, we conservatively consider only the upper-bound (polar) isotopic range as coherent with nearly complete utilization (see Section 3.1 for details).

Recent culture experiments indicate that, like many marine autotrophs, coralline algae assimilate nitrate during their growth (Hanson, Slaymark, Kamenos, & Thibodeau, 2020). Further, our most recent $\delta^{15}N_{algal}$ measurements match the isotopic signature of ambient seawater nitrate along the Labrador Shelf (Sherwood et al., 2011) (Table 1). Throughout the shelf and larger Labrador Sea region, nitrate is the most critical nutrient for regulating primary productivity (Harrison & Li, 2007), and so the observed agreement between $\delta^{15}N_{algal}$ and the $\delta^{15}N$ of the local nitrate pool is expected if driven by the degree of nitrate utilization (e.g., Altabet & Francois, 1994; Mariotti et al., 1981). This agreement is also confirmed by measurements of $\delta^{15}N_{algal}$ and nearby seawater nitrate at higher latitudes (Lehmann et al., 2019) (Table 1), further verifying that $\delta^{15}N_{algal}$ likely tracks the isotopic composition of seawater nitrate. However, several other biological and biogeochemical processes may impact the $\delta^{15}N$ of seawater nitrate and therefore might also affect our record.

At coastal locations such as our study site, terrestrial nutrient runoff could impact the degree of nutrient utilization and/or the baseline isotopic composition of seawater nitrogen. However, annual runoff is only 600 – 700 mm along the shelf (Rollings, 1997), which is many orders of magnitude diluted by the Labrador Current, traveling at a coastal velocity of 0.8 Sv (Lazier & Wright, 2002). While runoff could play a role in the coastal nutrient budget, its relative influence suggests a negligible contribution and is therefore not likely to account for large changes in $\delta^{15}N_{algal}$ values.

Isotopic variations driven by chemical transformations of seawater nitrate, such as removal reactions (i.e., reduction via denitrification) and input reactions (i.e., atmospheric dinitrogen fixation), would impart isotopically heavier and lighter signals on the $\delta^{15}N$ of seawater nitrate respectively. However, *in-situ* water-column denitrification is unlikely as near-zero oxygen concentrations are required to favor such an anaerobic metabolism (Dalsgaard, Thamdrup, Farías, & Revsbech, 2012) whereas high ambient oxygen concentrations (~8 mL L^{-1}) exist along the Labrador Shelf (Garcia et al., 2013). While sedimentary denitrification might be possible along the shelf, this process typically does not induce isotopic fractionation in the water-column nitrogen pool due to complete consumption in pore waters (Lehmann, Sigman, & Berelson, 2004). One exception to this has been noted along the eastern Bering Sea Shelf in the polar north Pacific, where benthic denitrification coupled to the partial nitrification of ammonia yields a net increase in the $\delta^{15}N$ of seawater nitrate (Granger et al., 2011). As these waters are advected to Baffin Bay, such $\delta^{15}N$ variations may be relevant for our record. Yet, nitrification first requires the conversion of organic nitrogen to ammonia, and so both nitrification and benthic dentrification should also be linked to productivity. If productivity had historically been driven by sea-ice extent in this region, such as it presently is throughout much of the Arctic (e.g., Arrigo, van Dijken, & Pabi, 2008), this would not be a reasonable mechanism as multicentury Arctic sea-ice reconstructions do not show the centennial-scale variability that is observed in our record. However, additional paleoenvironmental reconstructions throughout the eastern Arctic would be helpful for resolving past variations in productivity and nitrogen cycling in this region.

Arctic cyanobacteria fix atmospheric dinitrogen at similar rates to their low-latitude counterparts, which suggests that fixation may play an important role in high-latitude nitrogen cycling (Harding et al., 2018). Arctic fixation could lower the isotopic composition of seawater nitrate, feed into the East Greenland Current and Baffin Current and, eventually, enter the Labrador Shelf (Figure 1a and 1b). However, fixation should be related to temperature and sea-ice variability due to the requirement of open-ocean conditions for both cyanobacterial growth and Arctic throughflow (Yamamoto-Kawai, Carmack, & McLaughlin, 2006) and so the absence of centennial-scale variability, which is characteristic of $\delta^{15}N_{algal}$ values, in Arctic sea-ice reconstructions argues against such a mechanism. Further, the lack of a clear relationship between elevated temperatures, lower ice extent and lower $\delta^{15}N_{algal}$ throughout the record argues against *in-situ* fixation driving our record (Figure 2). In fact, the last ~130 years in our record reflect simultaneously the warmest, lowest-ice conditions and the highest $\delta^{15}N_{algal}$ values. As such, dinitrogen fixation is not a likely control on $\delta^{15}N_{algal}$.

Two plausible driving mechanisms of $\delta^{15}N_{algal}$ variability remain: changes in the relative proportion of Atlantic- and polar-sourced waters feeding the Labrador Current and/or changes in the relative degree of nitrate utilization. The Labrador Current is fed by waters derived from the polar Baffin Bay and from the north-eastern Atlantic (Figure 1a and 1b). Today, north-eastern Atlantic waters carry upper-ocean nitrate with a $\delta^{15}N$ value of ~4‰ (Marconi, Weigand, & Sigman, 2019), whereas nitrate derived from the upper ocean of the polar Baffin Bay is characterized by $\delta^{15}N$ values between ~6 to 8‰ (Lehmann et al., 2019). While such baseline nitrate isotopic compositions may have changed through time, GEOTRACES studies indicate that 4‰ is already among the lowest value observed in the entire contemporary north-eastern Atlantic

(Marconi et al., 2019), with only a few patches of lighter nitrate (~2 to 3‰) occuring predominately in some western regions (Marconi et al., 2015). As such, it is not likely that the average north-eastern Atlantic nitrate inflow source could be lighter than 4‰ without global-scale perturbations to the oceanic nitrogen cycle. In Baffin Bay, nitrate is mostly derived from the north Pacific, which could be subject to upstream denitrification and result in isotopically heavier seawater nitrate (Cline & Kaplan, 1975; Sigman et al., 2005). However, denitrification has been variable over the last century in the north Pacific, first decreasing until the 1990s and then subsequently increasing due to anoxia (Deutsch et al., 2014). The lack of this variability in our $\delta^{15}N_{algal}$ record over the last century thus indicates that any influence of Pacific denitrification on Baffin Bay nitrate is not translated to the nitrate along the Labrador Shelf. As such, it is reasonable to consider 4‰ (Atlantic) and ~6 to 8‰ (polar) as the lower and upper isotopic bounds of seawater nitrate in the source waters that feed the Labrador Current (Figure 2).

If utilization remained complete over the last 600 years, source-water variability could therefore be responsible for $\delta^{15}N_{algal}$ values within the 4 to 8‰ range, which would represent two extreme proportioning scenarios: a Labrador Current composed of entirely Atlantic-derived waters, or of entirely polar-derived waters. As such, $\delta^{15}N_{algal}$ values outside of this range would suggest additional fractionation mechanisms at play, likely implicating a change in nitrate utilization given the unlikelihood of the other known mechanisms described above. During each period of high $\delta^{15}N_{algal}$, the isotopic signature falls within the range of source-water nitrate values (Figure 2), which could be consistent with nearly complete nitrate utilization (e.g., Altabet & Francois, 1994; Mariotti et al., 1981). However, here we conservatively define "nearly complete utilization" by considering only the upper range of allowable $\delta^{15}N_{algal}$ values; i.e., when $\delta^{15}N_{algal}$ approximates the isotopic range of polar source waters (6 to 8‰). Importantly, by our definition these intervals would also correspond to a circulation regime dominated by polar-sourced waters, rather than Atlantic-sourced waters, along the Labrador Shelf. Yet, several intervals characterized by $\delta^{15}N_{algal}$ values lower than the $\delta^{15}N$ of Atlantic nitrate suggest that nitrate utilization did not always approach completion. Thus, the central questions that this study aims to address are: 1) how did nitrate utilization come to approach completion along the modern Labrador Shelf and 2) what drove periodic phases of increased polar influence and nearly complete utilization in the past?

3.2 Drivers of Nitrate Utilization along the Labrador Shelf

Nearly complete utilization may be caused by increased biological uptake, reduced nitrate supply or a combination of both. Over the last century, productivity reconstructed from algal Ba/Ca (Chan et al., 2017) has been highly variable while $\delta^{15}N_{algal}$ values remained relatively constant (Figure 2). This implies that nitrate utilization during this interval was at least partially controlled by changes in nitrate supply driven by advective and mixing processes, rather than exclusively by changes in biological uptake. Because changes in the Labrador Current, an advective nitrate source, are associated with changes in regional deep-water formation, the historical variability of regional convection may help to inform past variations in the Labrador Current's coastal inflow and its impact on nitrate supply to the Labrador Shelf. Deep-water formation is typically discussed in terms of its relationship with broader climatic fluctuations; notably, the North Atlantic Oscillation (NAO) and Atlantic Multidecadal Oscillation (AMO), which are connected to temperature and circulation patterns in the north Atlantic (e.g., Seip et al., 2019). While recent work indicates that the AMO may not be an oscillation per se, and may be more appropriately termed "Atlantic multidecadal variability" (Mann, Steinman, & Miller, 2020), here we use the original AMO language to be consistent with previous authors that have generated paleo-reconstructions of its behavior.

The NAO describes the sea-surface pressure gradient between the Icelandic Low and Azores High systems such that positive values (NAO+) correspond to increased pressure differences and negative values (NAO-) correspond to decreased pressure differences (Hurrell, 1995). During NAO- conditions, the advection of nitrate-rich Atlantic slope waters to the shelf is enhanced (Petrie, 2007). The AMO describes Atlantic multidecadal sea-surface temperature (SST) variations. Like the NAO, it is typically discussed in terms of an index, where positive values (AMO+) represent multidecadal-scale positive SST anomalies and negative index values (AMO-) represent multidecadal-scale negative SST anomalies in the north Atlantic (Schlesinger & Ramankutty, 1994). In the Labrador Sea, the AMO- mode is associated with increased cooling and sea-ice extent (Day, Hargreaves, Annan, & Abe-Ouchi, 2012; Miles et al., 2014) along with decreased productivity (Chan et al., 2017), while the AMO+ condition is characterized by the opposite. A recent synthesis of observational data, modeling studies and paleoclimate reconstructions suggests that the AMOC is responsible for driving this multidecadal variability throughout the Atlantic, with AMO+ conditions corresponding to a strong AMOC and AMO- conditions corresponding to a weak AMOC (Zhang et al., 2019). Numerical simulations additionally demonstrate that this variability has been significantly associated with the strength of the AMOC on 100-year periodicities throughout the last 1400 years (Knight, Allan, Folland, Vellinga, & Mann, 2005), reminiscent of the approximate pacing of phases of nearly complete nitrate utilization present in the $\delta^{15}N_{algal}$ record (Figure 2). Below, we illustrate the relevance of the NAO and AMO in modulating nitrate conditions along the Labrador Shelf, and how the twentieth-century weakening of the Labrador Current's Atlantic component has disrupted these historical dynamics.

3.3 Periodic Phases of Nearly Complete Nitrate Utilization

The five phases of nearly complete nitrate utilization interpreted from high $\delta^{15}N_{algal}$ values over the last 600 years may either be driven by increases in primary productivity or decreases in nitrate supply. Light attenuation modulated by sea-ice demise is the main driver of productivity along the past and present Labrador Shelf (Chan et al., 2017; Harrison et al., 2013). As such, and because direct productivity reconstructions are not available until after 1600, we infer indirect productivity changes from paleo-reconstructed sea-ice cover for earlier time intervals in our record (Halfar et al., 2013). Coherence of decreased sea-ice extent (and thus, inferred increased productivity) with increased $\delta^{15}N_{algal}$ values until 1500 supports a productivity-driven change in nitrate utilization (Figures 3 and 4). However, $\delta^{15}N_{algal}$ leads sea-ice extent, suggesting that productivity could not have controlled nitrate utilization during this brief first phase (~1470). Furthermore, a significant antiphase association between the sea-ice proxy and $\delta^{15}N_{algal}$ during phase 2 (~1550 – 1590) indicates that increased sea-ice extent (and thus, inferred decreased productivity) occurred in tangent with increased $\delta^{15}N_{algal}$ values. Because decreased productivity should normally result in lower nitrate utilization, and thus lower $\delta^{15}N_{algal}$ values, such a relationship discredits productivity as the main driver of nitrate utilization during this interval.

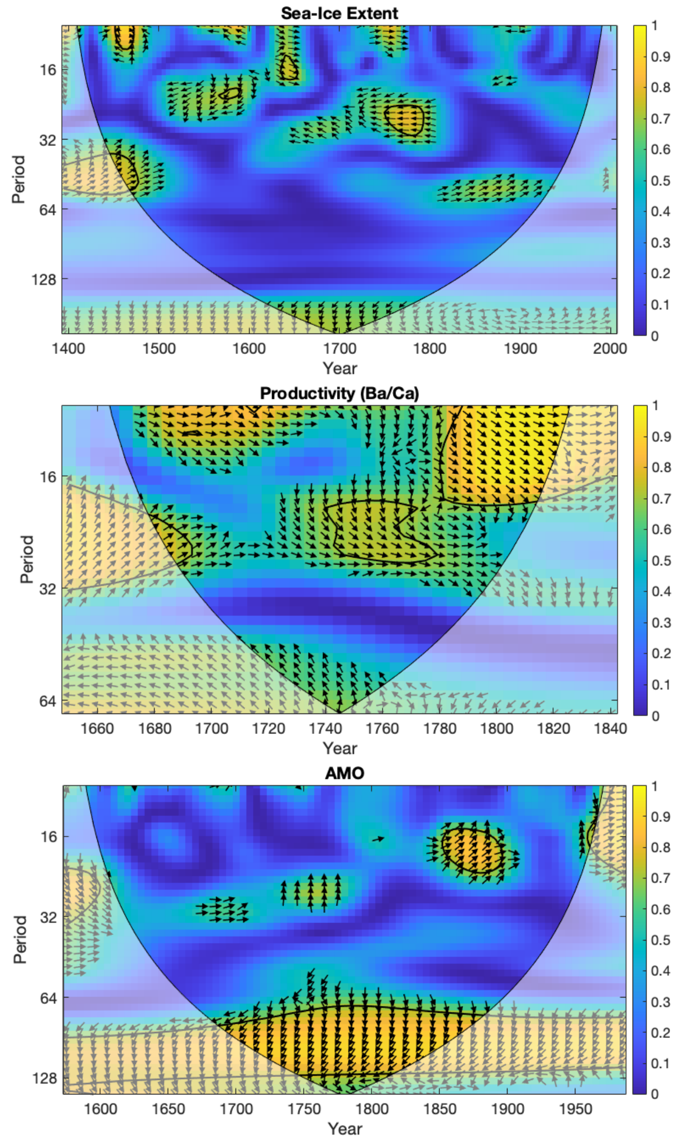

Fig. 3. Cross-wavelet coherence and phase relationships between paleo-records and $\delta^{15}N_{algal}$. Significant overlaps in spectral power between signals at the 95% confidence level against red noise are represented within the black contours. Arrows indicate phase relationships, where leftward-pointing represents an antiphase relationship, rightward-pointing represents an in-phase relationship, downward-pointing represents the titular time series leading our record and upward-pointing represents the opposite. The areas in which edge effects may interfere with analyses are depicted by the shaded regions. All analyses were performed in MatLab R2020a using default options in the Cross Wavelet and Wavelet Coherence toolbox provided by A. Grinsted. For specifications of the relevant calculations, the reader is referred to the original publication (Grinsted et al., 2004). Sea-ice, productivity and AMO paleo-reconstructions are from Halfar et al. (2013), Chan et al. (2017) and Gray et al. (2004) respectively.

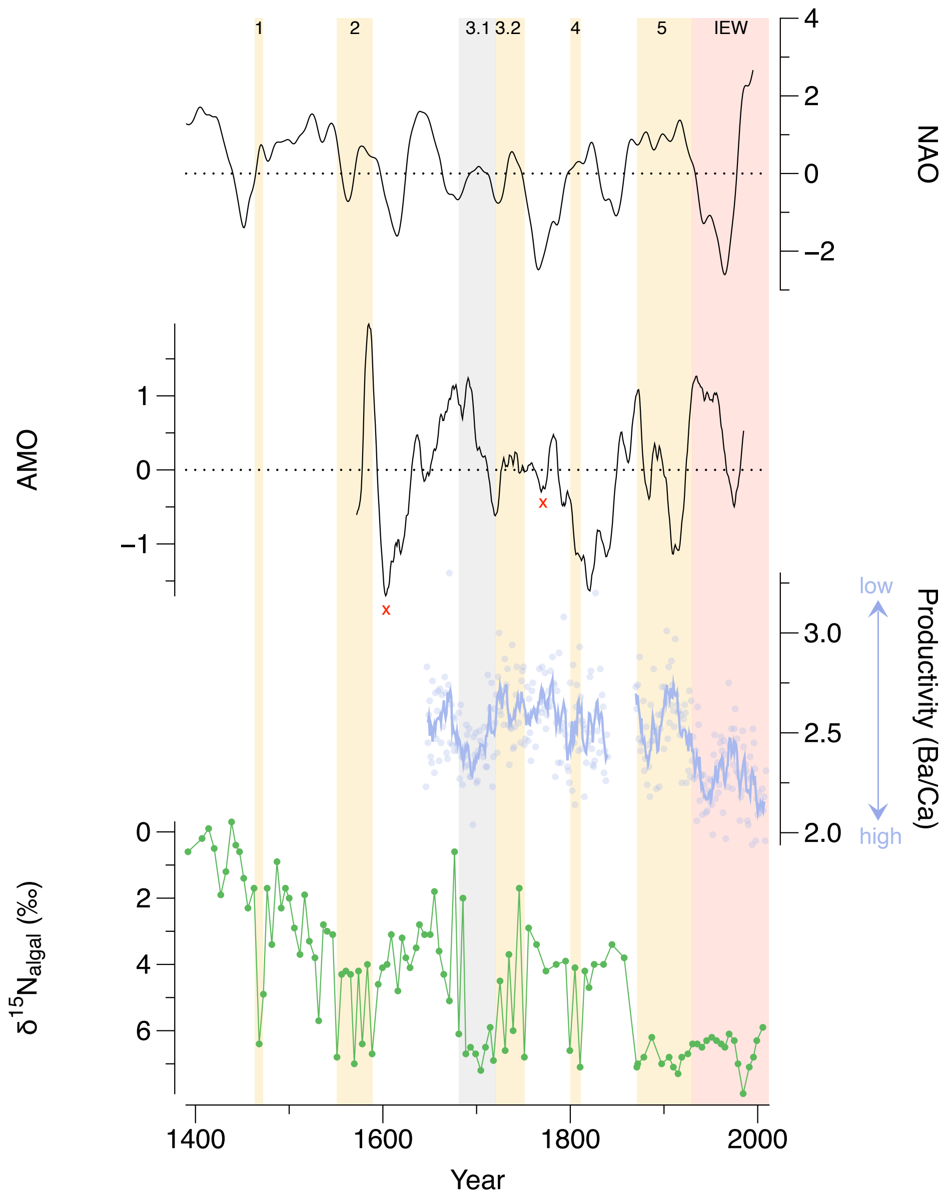

Fig. 4. Climate variability, productivity and nitrate utilization. Phases of nearly complete utilization, corresponding to a circulation regime dominated by polar-sourced waters with relatively high $\delta^{15}N_{nitrate}$ along the Labrador Shelf, are highlighted by the vertical shaded regions. Phase 3.1 (grey interval) corresponds to an interval of increased primary productivity, whereas the red interval represents the industrial-era weakening of the Labrador Current. Red x marks denote negative AMO excursions that did not trigger large increases in nitrate utilization, which are hypothesized to have been offset by the concurrent negative NAO excursions (see Section 3.3). NAO, AMO and productivity paleo-reconstructions are from Trouet et al., (2009), Gray et al., (2004) and Chan et al., (2017) respectively. See the legend of Figure 2 for a full description of the Ba/Ca data.

In the 1600s, reconstructions of productivity become available from algal Ba/Ca data (Chan et al., 2017). The onset of phase 3 (Phase 3.1; ~1680) occurred in concert with an increase in productivity reconstructed from algal Ba/Ca (Figures 3 and 4). However, edge effects characteristic of the wavelet analysis between Ba/Ca and $\delta^{15}N_{algal}$ prevent a robust statistical comparison of these variables during this period, and sea-ice extent reconstructions do not support a significant relationship between productivity and $\delta^{15}N_{algal}$ (Figure 3). Moreover, elevated $\delta^{15}N_{algal}$ values were maintained well after Ba/Ca recovered to its pre-3.1 levels, until ~1750. Phase 4 (~1800 – 1810) is characterized by low productivity indicated by the significant antiphase association between the sea-ice proxy and $\delta^{15}N_{algal}$ (Figure 3). Further, significant relationships between Ba/Ca and $\delta^{15}N_{algal}$ occurred in-phase during this interval. Since the Ba/Ca proxy is negatively correlated with productivity, this also indicates that periods of low productivity corresponded to periods of high nitrate utilization. Finally, during phase 5 (~1870 onward), nitrate utilization was entirely uncorrelated with both sea-ice extent and Ba/Ca-reconstructed productivity (Figure 3). As such, biological uptake appears to be generally unimportant for controlling utilization throughout these phases, implicating changes in nitrate supply as important for driving variations in the record.

Changes in nitrate supply may be associated with ocean circulation patterns and therefore could be sensitive to larger climatic variations. Specifically, a negative-mode AMO is linked to weak AMOC conditions (Zhang et al., 2019) and a weak Atlantic inflow, which could result in an increased proportion of relatively nitrate-poor polar waters at the shelf. Indeed, phases of nearly complete utilization correspond to negative excursions in the paleo-reconstructed AMO (Gray et al., 2004) (Figure 4). Such a relationship is further supported by the significant antiphase correlation between the AMO and $\delta^{15}N_{algal}$ on periodicities of ~100 years (Figure 3), in good agreement with the approximate pacing of phases of nearly complete utilization. Interestingly, the relationship between the AMO and $\delta^{15}N_{algal}$ is the opposite of that previously documented between the AMO and productivity at this site (Chan et al., 2017). Positive-mode AMO conditions were argued to drive increased heating in the northern hemisphere and sea-ice melt along the shelf (Day et al., 2012; Miles et al., 2014), which was linked to enhanced phytoplankton growth (Chan et al., 2017). The notion that negative AMO conditions appear to be associated with large increases in nitrate utilization therefore provides further evidence that biological uptake is not a major driver of our record and offers an explanation for the anticorrelation detected between $\delta^{15}N_{algal}$ values and paleo-reconstructed productivity (Figure 3).

The antiphase relationship between the AMO and $\delta^{15}N_{algal}$ also argues against stratification as a driver of increased nitrate utilization. A negative-mode AMO would promote cold conditions and ice growth along coastal shelf waters (Day et al., 2012; Miles et al., 2014), which would generally be expected to enhance mixing. As such, a reduction in advected nitrate modulated by the AMOC-induced weakening of the Labrador Current's Atlantic component is the most likely driving mechanism of these five phases. However, two negative AMO excursions following phases 2 and 3 failed to trigger additional periods of nearly complete utilization (Figure 4). These intervals also correspond to pronounced negative NAO modes (Trouet et al., 2009). Therefore, we hypothesize that these negative NAO conditions facilitated the advection of higher-nitrate Atlantic slope waters to the shelf (Petrie, 2007), thereby preventing large declines in nitrate supply otherwise expected from the concurrent negative AMO.

Interestingly, persistently high nitrate utilization characteristic of the contemporary period (~1930 to present) appears to be insensitive to high-magnitude AMO fluctuations (Figure 4). During this interval, the AMOC underwent an intense weakening (Caesar et al., 2018; Rahmstorf et al., 2015), likely driven by anthropogenic climate forcing, concomitant with strong reductions in Labrador Sea convection (Thornalley et al., 2018) and a migration of nitrate-rich Atlantic waters away from the coast (Thibodeau et al., 2018; Thibodeau et al., 2010). As such, this recent shift in the Labrador Current likely also reduced advective nitrate supply to the shelf, and is the most plausible mechanism for the anomalously prolonged phase of increased polar-sourced waters and nearly complete utilization characteristic of the last 150 years.

3.4 Environmental Implications

While previous studies have commented on the relationships between AMOC strength, nutrient supply and productivity in the north Atlantic, such studies have historically invoked upper-ocean stratification as the main mechanism responsible for these associations (Osman et al., 2019; Schmittner, 2005). However, recent modeling efforts argue that advection, rather than mixing, is the dominant control on nitrate supply to the subpolar north Atlantic region (Whitt & Jansen, 2020). Our findings support this claim at the Labrador Shelf, further highlighting the importance of upper-ocean circulation in routing nitrate away from the coast. Additionally, our study lends new field evidence to the previously proposed hypothesis that biogeochemical changes along the coastal north-western Atlantic may be associated with the larger-scale AMOC decline characteristic of the industrial era (Claret et al., 2018). While previous nutrient reconstructions based on coral compound-specific $\delta^{15}N$ measurements at the more-southern Gulf of Maine argue for an enhanced supply of nitrate coincident with the onset of the industrial era (Sherwood et al., 2011), we show the opposite trend occurring at the Labrador Shelf. The increased nitrate supply to the Gulf of Maine was attributed to an increased presence of nitrate-rich subtropical Atlantic waters, which is also a direct consequence of the recent changes to the Labrador Current (Sherwood et al., 2011; Thibodeau et al., 2018). However, these subtropical waters bend eastward to feed the North Atlantic Current prior to recirculating and joining the Labrador Current, and therefore do not directly enter the coastal Labrador Shelf (Figure 1a and 1b). Thus, the industrial-era changes to the Labrador Current have resulted in differential impacts along the Labrador Shelf and the Gulf of Maine regions. While the Labrador Shelf has lost nitrate due to the increased proportion of nitrate-poor polar waters that comprise the Labrador Current's coastal inflow, the Gulf of Maine has gained nitrate due to an increased influence of nitrate-rich subtropical Atlantic waters. The ecological and biogeochemical consequences of such nutrient reorganizations in the north Atlantic are not fully understood and should be subject to further research. For example, changing nitrate distributions may alter the locations and extent of primary productivity, which ecological models suggest strongly affect the vulnerable and socioeconomically important Atlantic cod (Ehrnsten, Bauer, & Gustafsson, 2019). In addition to the possible impacts on regional fisheries, changes in primary productivity may have implications for the future potential of oceanic carbon storage in the region (Takahashi et al., 2009). Thus, numerous environmental challenges may be exacerbated by ongoing anthropogenic disturbances to the north Atlantic.

4 Conclusions

Here, we have described mechanisms that drove changes in circulation patterns and nitrate utilization along the Labrador Shelf over the last 600 years. We show that changes in nitrate uptake driven by productivity did not trigger periodic intervals of nearly complete nitrate utilization observed in our record, and rather suggest that the increased proportion of nitrate-poor polar waters associated with negative AMO excursions drove the occurrence of such intervals on approximately centennial timescales. Additionally, we suggest that the reduction in the strength of the AMOC via its weakening of Atlantic inflow likely contributed to a persistently low supply of nitrate to the

Labrador Shelf, resulting in an anomalously prolonged phase of nearly complete utilization since ~1870, which should have otherwise ended in the early 1900s. In contrast to past cycles of nitrate supply, nutrient conditions will not likely recover due to the ongoing reduction of Atlantic influence at the shelf. Our study thus adds to the abundant body of evidence illustrating the intense sensitivity of the high-latitude north Atlantic region to modern climate change.

Acknowledgments, Samples, and Data

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References

Altabet, M. A., & Francois, R. (1994). Sedimentary nitrogen isotopic ratio as a recorder for surface ocean nitrate utilization. *Global Biogeochemical Cycles*. https://doi.org/10.1029/93GB03396

Arrigo, K. R., van Dijken, G., & Pabi, S. (2008). Impact of a shrinking Arctic ice cover on marine primary production. *Geophysical Research Letters*. https://doi.org/10.1029/2008GL035028

Buckley, M. W., & Marshall, J. (2016). Observations, inferences, and mechanisms of the Atlantic Meridional Overturning Circulation: A review. *Reviews of Geophysics*, *54*(1), 5–63. https://doi.org/10.1002/2015RG000493

Caesar, L., Rahmstorf, S., Robinson, A., Feulner, G., & Saba, V. (2018). Observed fingerprint of a weakening Atlantic Ocean overturning circulation. *Nature*, *556*(7700), 191–196. https://doi.org/10.1038/s41586-018-0006-5

Chan, P., Halfar, J., Adey, W., Hetzinger, S., Zack, T., Moore, G. W. K., … Hou, A. (2017). Multicentennial record of Labrador Sea primary productivity and sea-ice variability archived in coralline algal barium. *Nature Communications*. https://doi.org/10.1038/ncomms15543

Claret, M., Galbraith, E. D., Palter, J. B., Bianchi, D., Fennel, K., Gilbert, D., & Dunne, J. P. (2018). Rapid coastal deoxygenation due to ocean circulation shift in the northwest Atlantic. *Nature Climate Change*. https://doi.org/10.1038/s41558-018-0263-1

Cline, J. D., & Kaplan, I. R. (1975). Isotopic fractionation of dissolved nitrate during denitrification in the eastern tropical north pacific ocean. *Marine Chemistry*. https://doi.org/10.1016/0304-4203(75)90009-2

Dalsgaard, T., Thamdrup, B., Farías, L., & Revsbech, N. P. (2012). Anammox and denitrification in the oxygen minimum zone of the eastern South Pacific. *Limnology and Oceanography*. https://doi.org/10.4319/lo.2012.57.5.1331

Day, J. J., Hargreaves, J. C., Annan, J. D., & Abe-Ouchi, A. (2012). Sources of multi-decadal variability in Arctic sea ice extent. *Environmental Research Letters*. https://doi.org/10.1088/1748-9326/7/3/034011

Deutsch, C., Berelson, W., Thunell, R., Weber, T., Tems, C., McManus, J., … Van Geen, A. (2014). Centennial changes in North Pacific anoxia linked to tropical trade winds. *Science*. https://doi.org/10.1126/science.1252332

Drinkwater, K. F., & Harding, G. C. (2001). Effects of the hudson strait outflow on the biology of the Labrador Shelf. *Canadian Journal of Fisheries and Aquatic Sciences*. https://doi.org/10.1139/f00-210

Ehrnsten, E., Bauer, B., & Gustafsson, B. G. (2019). Combined Effects of Environmental Drivers on Marine Trophic Groups – A Systematic Model Comparison. *Frontiers in Marine Science*. https://doi.org/10.3389/fmars.2019.00492

Garcia, H. E., Boyer, T. P., Locarnini, R. A., Antonov, J. I., Mishonov, A. V, Baranova, O. K., … Johnson, D. R. (2013). World Ocean Atlas 2013. Volume 3: dissolved oxygen, apparent oxygen utilization, and oxygen saturation. *NOAA Atlas NESDIS 75*.

Garcia, H. E., Locarnini, R. A., Boyer, T. P., Antonov, J. I., Baranova, O. K., Zweng, M. M., … Johnson, D. R. (2013). World Ocean Atlas 2013, Volume 4 : Dissolved Inorganic Nutrients (phosphate, nitrate, silicate). In *NOAA Atlas NESDIS 76*.

Gillikin, D. P., Lorrain, A., Jolivet, A., Kelemen, Z., Chauvaud, L., & Bouillon, S. (2017). High-resolution nitrogen stable isotope sclerochronology of bivalve shell carbonate-bound organics. *Geochimica et Cosmochimica Acta*. https://doi.org/10.1016/j.gca.2016.12.008

Granger, J., Prokopenko, M. G., Sigman, D. M., Mordy, C. W., Morse, Z. M., Morales, L. V., … Plessen, B. (2011). Coupled nitrification-denitrification in sediment of the eastern Bering Sea shelf leads to 15N enrichment of fixed N in shelf waters. *Journal of Geophysical Research: Oceans*. https://doi.org/10.1029/2010JC006751

Gray, S. T., Graumlich, L. J., Betancourt, J. L., & Pederson, G. T. (2004). A tree-ring based reconstruction of the Atlantic Multidecadal Oscillation since 1567 A.D. *Geophysical*

Research Letters. https://doi.org/10.1029/2004GL019932

Grinsted, A., Moore, J. C., & Jevrejeva, S. (2004). Application of the cross wavelet transform and wavelet coherence to geophysical time series. *Nonlinear Processes in Geophysics*. https://doi.org/10.5194/npg-11-561-2004

Halfar, J., Adey, W. H., Kronz, A., Hetzinger, S., Edinger, E., & Fitzhugh, W. W. (2013). Arctic sea-ice decline archived by multicentury annual-resolution record from crustose coralline algal proxy. *Proceedings of the National Academy of Sciences*. https://doi.org/10.1073/pnas.1313775110

Harding, K., Turk-Kubo, K. A., Sipler, R. E., Mills, M. M., Bronk, D. A., & Zehr, J. P. (2018). Symbiotic unicellular cyanobacteria fix nitrogen in the Arctic Ocean. *Proceedings of the National Academy of Sciences of the United States of America*. https://doi.org/10.1073/pnas.1813658115

Harrison, W. G., Børsheim, K. Y., Li, W. K. W., Maillet, G. L., Pepin, P., Sakshaug, E., … Yeats, P. A. (2013). Phytoplankton production and growth regulation in the Subarctic North Atlantic: A comparative study of the Labrador Sea-Labrador/Newfoundland shelves and Barents/Norwegian/Greenland seas and shelves. *Progress in Oceanography*. https://doi.org/10.1016/j.pocean.2013.05.003

Harrison, W. G., & Li, W. K. W. (2007). Phytoplankton growth and regulation in the Labrador Sea: Light and nutrient limitation. *Journal of Northwest Atlantic Fishery Science*. https://doi.org/10.2960/J.v39.m592

Henson, S. A., Dunne, J. P., & Sarmiento, J. L. (2009). Decadal variability in North Atlantic phytoplankton blooms. *Journal of Geophysical Research: Oceans*. https://doi.org/10.1029/2008JC005139

Hurrell, J. W. (1995). Decadal trends in the North Atlantic oscillation: Regional temperatures and precipitation. *Science*. https://doi.org/10.1126/science.269.5224.676

Knight, J. R., Allan, R. J., Folland, C. K., Vellinga, M., & Mann, M. E. (2005). A signature of persistent natural thermohaline circulation cycles in observed climate. *Geophysical*

Research Letters. https://doi.org/10.1029/2005GL024233

Kuhlbrodt, T., Griesel, A., Montoya, M., Levermann, A., Hofmann, M., & Rahmstorf, S. (2007). On the driving processes of the Atlantic meridional overturning circulation. *Reviews of Geophysics*, *45*(2), RG2001. https://doi.org/10.1029/2004RG000166

Lazier, J. R. N., & Wright, D. G. (2002). Annual Velocity Variations in the Labrador Current. *Journal of Physical Oceanography*. https://doi.org/10.1175/1520-0485(1993)023<0659:avvitl>2.0.co;2

Lehmann, M. F., Sigman, D. M., & Berelson, W. M. (2004). Coupling the 15N/14N and 18O/16O of nitrate as a constraint on benthic nitrogen cycling. *Marine Chemistry*. https://doi.org/10.1016/j.marchem.2004.02.001

Lehmann, N., Kienast, M., Granger, J., Bourbonnais, A., Altabet, M. A., & Tremblay, J. (2019). Remote Western Arctic Nutrients Fuel Remineralization in Deep Baffin Bay. *Global Biogeochemical Cycles*. https://doi.org/10.1029/2018GB006134

Loder, J. W., Petrie, B., & Gawarkiewicz, G. (1998). The Coastal Ocean off Northeastern North America: A Large-Scale View. In A. Robinson & K. Brink (Eds.), *The Sea* (pp. 105–133). New York: Wiley.

Lozier, M. S., Li, F., Bacon, S., Bahr, F., Bower, A. S., Cunningham, S. A., … Zhao, J. (2019). A sea change in our view of overturning in the subpolar North Atlantic. *Science*. https://doi.org/10.1126/science.aau6592

Mann, M. E., Steinman, B. A., & Miller, S. K. (2020). Absence of internal multidecadal and interdecadal oscillations in climate model simulations. *Nature Communications*, *11*(49).

Marconi, D., Weigand, M. A., Rafter, P. A., McIlvin, M. R., Forbes, M., Casciotti, K. L., & Sigman, D. M. (2015). Nitrate isotope distributions on the US GEOTRACES North Atlantic cross-basin section: Signals of polar nitrate sources and low latitude nitrogen cycling. *Marine Chemistry*. https://doi.org/10.1016/j.marchem.2015.06.007

Marconi, D., Weigand, M. A., & Sigman, D. M. (2019). Nitrate isotopic gradients in the North

Atlantic Ocean and the nitrogen isotopic composition of sinking organic matter. *Deep Sea Research Part I*, *145*, 109–124.

Mariotti, A., Germon, J. C., Hubert, P., Kaiser, P., Letolle, R., Tardieux, A., & Tardieux, P. (1981). Experimental determination of nitrogen kinetic isotope fractionation: Some principles; illustration for the denitrification and nitrification processes. *Plant and Soil*. https://doi.org/10.1007/BF02374138

Miles, M. W., Divine, D. V., Furevik, T., Jansen, E., Moros, M., & Ogilvie, A. E. J. (2014). A signal of persistent Atlantic multidecadal variability in Arctic sea ice. *Geophysical Research Letters*. https://doi.org/10.1002/2013GL058084

Moore, G. W. K., Halfar, J., Majeed, H., Adey, W., & Kronz, A. (2017). Amplification of the Atlantic Multidecadal Oscillation associated with the onset of the industrial-era warming. *Scientific Reports*. https://doi.org/10.1038/srep40861

Muscatine, L., Goiran, C., Land, L., Jaubert, J., Cuif, J. P., & Allemand, D. (2005). Stable isotopes (δ13C and δ15N) of organic matrix from coral skeleton. *Proceedings of the National Academy of Sciences of the United States of America*. https://doi.org/10.1073/pnas.0408921102

Osman, M. B., Das, S. B., Trusel, L. D., Evans, M. J., Fischer, H., Grieman, M. M., … Saltzman, E. S. (2019). Industrial-era decline in subarctic Atlantic productivity. *Nature*. https://doi.org/10.1038/s41586-019-1181-8

Petrie, B. (2007). Does the North Atlantic Oscillation affect hydrographic properties on the Canadian Atlantic Continental Shelf? *Atmosphere - Ocean*. https://doi.org/10.3137/ao.450302

Pithan, F., & Mauritsen, T. (2014). Arctic amplification dominated by temperature feedbacks in contemporary climate models. *Nature Geoscience*. https://doi.org/10.1038/ngeo2071

Rahmstorf, S., Box, J. E., Feulner, G., Mann, M. E., Robinson, A., Rutherford, S., & Schaffernicht, E. J. (2015). Exceptional twentieth-century slowdown in Atlantic Ocean overturning circulation. *Nature Climate Change*, *5*(5), 475–480.

https://doi.org/10.1038/nclimate2554

Ren, H., Sigman, D. M., Meckler, A. N., Plessen, B., Robinson, R. S., Rosenthal, Y., & Haug, G. H. (2009). Foraminiferal isotope evidence of reduced nitrogen fixation in the ice age Atlantic ocean. *Science*, *323*(5911), 244–248. https://doi.org/10.1126/science.1165787

Rollings, K. (1997). *The hydrology of Labrador*. Retrieved from https://www.mae.gov.nl.ca/waterres/reports/hydrology_lab/index.html

Schlesinger, M. E., & Ramankutty, N. (1994). An oscillation in the global climate system of period 65-70 years. *Nature*. https://doi.org/10.1038/367723a0

Schlitzer, R. (2018). *Ocean Data View, https://odv.awi.de*.

Schmittner, A. (2005). Decline of the marine ecosystem caused by a reduction in the Atlantic overturning circulation. *Nature*. https://doi.org/10.1038/nature03476

Seip, K. L., Grøn, Ø., & Wang, H. (2019). The North Atlantic oscillations: Cycle times for the NAO, the AMO and the AMOC. *Climate*. https://doi.org/10.3390/cli7030043

Sherwood, O. A., Lehmann, M. F., Schubert, C. J., Scott, D. B., & McCarthy, M. D. (2011). Nutrient regime shift in the western North Atlantic indicated by compound-specific δ15N of deep-sea gorgonian corals. *Proceedings of the National Academy of Sciences of the United States of America*. https://doi.org/10.1073/pnas.1004904108

Sigman, D. M., Granger, J., DiFiore, P. J., Lehmann, M. M., Ho, R., Cane, G., & van Geen, A. (2005). Coupled nitrogen and oxygen isotope measurements of nitrate along the eastern North Pacific margin. *Global Biogeochemical Cycles*. https://doi.org/10.1029/2005GB002458

Stock, C. A., John, J. G., Rykaczewski, R. R., Asch, R. G., Cheung, W. W. L., Dunne, J. P., … Watson, R. A. (2017). Reconciling fisheries catch and ocean productivity. *Proceedings of the National Academy of Sciences of the United States of America*. https://doi.org/10.1073/pnas.1610238114

Straub, M., Tremblay, M. M., Sigman, D. M., Studer, A. S., Ren, H., Toggweiler, J. R., & Haug, G. H. (2013). Nutrient conditions in the subpolar North Atlantic during the last glacial period reconstructed from foraminifera-bound nitrogen isotopes. *Paleoceanography*, *28*(1), 79–90. https://doi.org/10.1002/palo.20013

Swart, P. K., Evans, S., Capo, T., & Altabet, M. A. (2014). The fractionation of nitrogen and oxygen isotopes in macroalgae during the assimilation of nitrate. *Biogeosciences*. https://doi.org/10.5194/bg-11-6147-2014

Takahashi, T., Sutherland, S. C., Wanninkhof, R., Sweeney, C., Feely, R. A., Chipman, D. W., … de Baar, H. J. W. (2009). Climatological mean and decadal change in surface ocean pCO2, and net sea-air CO2 flux over the global oceans. *Deep-Sea Research Part II: Topical Studies in Oceanography*. https://doi.org/10.1016/j.dsr2.2008.12.009

Thibodeau, B., Not, C., Zhu, J., Schmittner, A., Noone, D., Tabor, C., … Liu, Z. (2018). Last century warming over the Canadian Atlantic shelves linked to weak Atlantic Meridional Overturning Circulation. *Geophysical Research Letters*. https://doi.org/10.1029/2018GL080083

Thibodeau, Benot, De Vernal, A., Hillaire-Marcel, C., & Mucci, A. (2010). Twentieth century warming in deep waters of the Gulf of St. Lawrence: A unique feature of the last millennium. *Geophysical Research Letters*. https://doi.org/10.1029/2010GL044771

Thornalley, D. J. R., Oppo, D. W., Ortega, P., Robson, J. I., Brierley, C. M., Davis, R., … Keigwin, L. D. (2018). Anomalously weak Labrador Sea convection and Atlantic overturning during the past 150 years. *Nature*, *556*(7700), 227–230. https://doi.org/10.1038/s41586-018-0007-4

Trouet, V., Esper, J., Graham, N. E., Baker, A., Scourse, J. D., & Frank, D. C. (2009). Persistent positive north atlantic oscillation mode dominated the medieval climate anomaly. *Science*. https://doi.org/10.1126/science.1166349

Wang, X. T., Prokopenko, M. G., Sigman, D. M., Adkins, J. F., Robinson, L. F., Ren, H., … Haug, G. H. (2014). Isotopic composition of carbonate-bound organic nitrogen in deep-sea scleractinian corals: A new window into past biogeochemical change. *Earth and Planetary Science Letters*. https://doi.org/10.1016/j.epsl.2014.05.048

Whitt, D. B., & Jansen, M. (2020). Slower nutrient stream suppresses Subarctic Atlantic biological productivity in global warming. *Proceedings of the National Academy of Sciences*, 1–7. https://doi.org/10.1073/pnas.2000851117

Yamamoto-Kawai, M., Carmack, E., & McLaughlin, F. (2006). Nitrogen balance and Arctic throughflow. *Nature*. https://doi.org/10.1038/443043a

Zhang, R., Sutton, R., Danabasoglu, G., Kwon, Y. O., Marsh, R., Yeager, S. G., … Little, C. M. (2019). A Review of the Role of the Atlantic Meridional Overturning Circulation in Atlantic Multidecadal Variability and Associated Climate Impacts. *Reviews of Geophysics*. https://doi.org/10.1029/2019RG000644