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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Key Points:

- A reduction in the strength of the Labrador Current has limited nitrate supply to the Labrador Shelf over the last 130 years
- Prior to the industrial-era weakening of the Labrador Current, nitrate concentrations in the region were likely driven by the AMO
- Rerouting of oceanic nutrients in the North Atlantic may have implications for regional fisheries and atmospheric carbon sequestration

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 ($\delta^{15}N$) 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 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.

Plain Language Summary

Key oceanic nutrients in the North Atlantic are supplied from equatorial latitudes via surface currents. However, multiple lines of evidence suggest that ocean circulation in this region has weakened over the last 150 years, likely as a direct consequence of anthropogenic climate warming. Using geochemical evidence, we investigate the physical and biological mechanisms responsible for regulating nutrient concentrations in the Labrador Sea, and show that ocean circulation has played a crucial role in both the past and present. Importantly, we demonstrate that the ongoing circulation weakening has resulted in an anomalously low supply of nutrients to the region, which may have implications for future marine ecosystems and oceanic carbon uptake.

1 Introduction

Due to multiple positive feedbacks, polar regions suffer the greatest impacts of modern-day climate change (Pithan & Mauritsen, 2014). One example of this is the recent unprecedented increase in Labrador Shelf productivity relative to the past few hundred years, which has been attributed to anomalously high sea-ice melt in the area (Chan et al., 2017). While such a dramatic change in productivity should intuitively have consequences on regional biogeochemistry, the fate of nutrients under simultaneous rapid climatic warming and increased productivity is convoluted. This is because nutrient dynamics in the polar North Atlantic are not only a function of biological activity, but also of physical oceanographic conditions that regulate nutrient supply.

The supply of nitrate to the polar North Atlantic is controlled by the advection of nitrate-rich equatorial waters via the upper limb of the Atlantic meridional overturning circulation (AMOC) (Pelegrí, Csanady, & Martins, 1996; Whitt, 2019; Williams et al., 2011) and vertical mixing (Harrison et al., 2013; Harrison & Li, 2007; Henson, Dunne, & Sarmiento, 2009). Several lines of evidence indicate that the AMOC has been at an anomalously weak state over the last ~150 years. This is likely due to warming-induced meltwater input, which prevents the inflow of equatorial waters from sinking in a process known as deep-water convection (Caesar, Rahmstorf, Robinson, Feulner, & Saba, 2018; Rahmstorf et al., 2015; B. Thibodeau et al., 2018; Thornalley et al., 2018). The most recent oceanographic observations further demonstrate that convection in the Labrador Sea has been virtually shut off, and that the eastern subpolar region now contributes almost entirely to this process (Lozier et al., 2019). Because the AMOC both responds to and drives climatic variability in ways that are not yet fully understood, paleoceanographic data are crucial to assessing the downstream effects of the weakened circulation, such as the potential alteration of nutrient budgets in the polar North Atlantic. These biogeochemical changes may additionally have ecological implications for socioeconomically-important fisheries in the region (Stock et al., 2017), as well as effects on atmospheric carbon sequestration (Takahashi et al., 2009).

Present-day nitrate concentrations in surface waters along the Labrador Shelf vary seasonally. In the spring, photosynthetic organisms consume most of the nitrate throughout the upper ocean (Figure 1), which allows the isotopic composition of their organic nitrogen to approximate that of the regional nitrate pool (Altabet & Francois, 1994). During fall and winter months, nitrate is then resupplied via vertical mixing (*Harrison and Li*, 2007; *Henson et al.*, 2009; *Harrison et al.*, 2013). Due to the preferential assimilation of the light isotope, the $\delta^{15}N$ signature (the ratio of $^{15}N/^{14}N$ relative to a standard) of organic nitrogen produced by photosynthetic organisms is affected by the level of nitrate utilization, or the degree of biological uptake relative to nitrate supply. When nitrate utilization is low, preferential assimilation of the light isotope results in lower organic $\delta^{15}N$ values. Under the above-mentioned condition of mostly-complete nitrate consumption, however, it is impossible for organisms to discriminate against the heavy isotope and so the offset between the $\delta^{15}N$ of organic matter and seawater nitrate is minimized (Altabet & Francois, 1994).

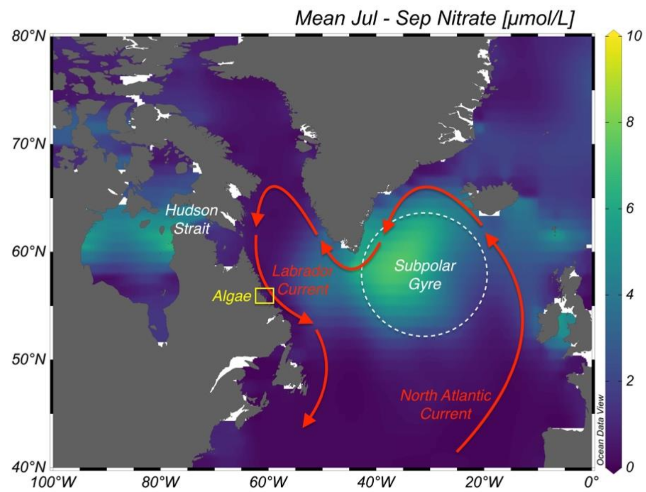

Figure 1: Modern oceanography and nitrate distribution in the Labrador Shelf region. Mean July – September surface nitrate distributions and the major surface currents involved in the supply of nitrate to our study site (yellow box). This figure was generated with the help of Ocean Data View (Schlitzer, 2018).

The isotopic composition of organic nitrogen is well-preserved within marine carbonate archives such as foraminifera (*Ren et al.*, 2009), corals (Muscatine et al., 2005) and bivalves (Gillikin et al., 2017). As such, nitrogen isotope measurements derived from carbonate-bound organic matter have contributed invaluably to advancing our understanding of past biogeochemical and climatic cycles. In the past decade, coralline algae have emerged as important paleoclimate archives, as annual growth bands characteristic of certain species allow for the reconstruction of high-resolution oceanographic processes in the recent geological past (e.g., *Halfar et al.*, 2013; *Chan et al.*, 2017; *Moore et al.*, 2017). Here, we present the first-ever 613-year-old, ~5-year-resolved $\delta^{15}N$ record derived from a crustose coralline alga (*Clathromorphum compactum*) extracted from the Labrador Shelf (Figure 1). *C. compactum* produces a carbonate skeleton, similar to other marine archives, and should therefore preserve the isotopic composition of ancient organic nitrogen within the organism. This notion is supported by our most recent algal-bound $\delta^{15}N$ measurements, which approximate the $\delta^{15}N$ of Labrador Sea nitrate (6 to 7‰; Marconi, Weigand, & Sigman, 2019; Sherwood, Lehmann, Schubert, Scott, & McCarthy, 2011), as would be expected during the mostly-complete nitrate consumption characteristic of the contemporary period (Figure 2). Here, we use this novel record in combination with other high-resolution paleoclimatological data to deconvolve the historic contributions of atmospheric and oceanic circulation patterns to nitrate supply in the Labrador Sea. Our record captures important intervals in Earth's recent climate history, such as the Little Ice Age (LIA) and the contemporary period of anthropogenic climate forcing.

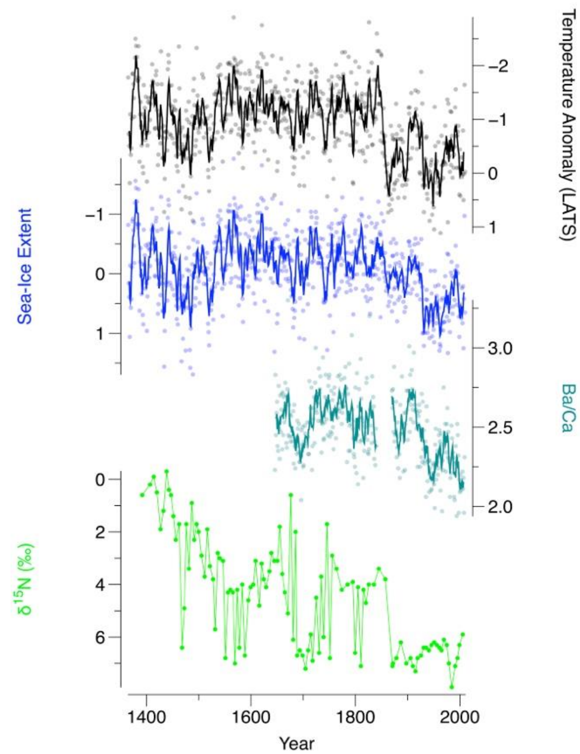

Figure 2: Local forcing archived in coralline algae. (top to bottom) Temperature reconstructed from the Labrador Algae Time Series (LATS) reported in (Moore et al., 2017); historical algal-derived inverse index of regional sea-ice extent (Halfar et al., 2013); algal Ba/Ca ([(μg g^{-1})/(μg g^{-1}) x 10^{-5}]), inversely representative of productivity (Chan et al., 2017); and nitrate utilization reconstructed via the isotopic composition of algal-bound nitrogen. Lines for LATS, sea-ice extent and Ba/Ca represent five-year-smoothed averages of the data.

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 1). 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, 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. 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. 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 and 20 years. Each sample consisted of 7 mg of skeletal material. Following sample collection, pressurized air was used to remove residual sample powder. Samples were weighed in tin cups to obtain the same amount of N_2 for all samples and reference materials. 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. Two internal reference materials ($\delta^{15}N$ = -0.10 ± 0.24‰ & +14.95 ± 0.09‰) were used to normalize the results to the AIR (IAEA-N1, IAEA-N2 & IAEA-N3) scale, and a third reference material ($\delta^{15}N$ = -0.1 ± 0.15‰) was analyzed as an unknown 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‰, which is based on the propagation of uncertainties of the normalization of internal reference materials and samples.

2.3 Spectral analysis

Cross-wavelet coherence and phase-relationship analyses were conducted using the Cross Wavelet and Wavelet Coherence toolbox in MatLab R2019a 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 $\delta^{15}N$ values, five-year interpolations were calculated from the raw data and used for spectral analysis. In cases where $\delta^{15}N$ data were analyzed against annually-resolved records, data points corresponding to the $\delta^{15}N$-interpolated year were used. Raw data were used in analyses between two annually-resolved records.

3 Results and Discussion

3.1 Data description and potential factors affecting algal $\delta^{15}N$ variability

Our record was determined to span from 1392 to 2005. During this period, algal $\delta^{15}N$ values generally followed an increasing trend from -0.3 to 7.9‰ (Figure 2). The $\delta^{15}N$ values initially increase ~7‰ from 1392 to the late 1500s prior to a transition to relatively constant average values, during which there are 4 notable periods characterized by values typically between 6 and 7‰ spaced by approximately 100 years. Beginning around 1871, another period of high $\delta^{15}N$ values is present, which persists throughout the remainder of the study period.

Nitrogen isotope ratios may be affected by changes in nitrogen fixation, denitrification and nitrate utilization, defined as the degree of biologically-assimilated nitrate relative to nitrate supply. Variations in the isotopic composition of algal nitrogen in the polar North Atlantic are likely controlled by changes in nitrate utilization (e.g., *Straub et al.*, 2013; *Thibodeau et al.*, 2017), as nitrogen-fixing diazotrophs are not found in polar surface waters (Bergman, Sandh, Lin, Larsson, & Carpenter, 2013), and high oxygen concentrations prevent the occurrence of water-column denitrification. Therefore, the two major drivers of our record are: 1) the relative degree of productivity, which controls the degree of biological uptake, and 2) nitrate supply, which controls the pool of biologically-available nitrate.

During each phase of high algal $\delta^{15}N$, the isotopic signature has approximated that of ambient seawater nitrate (Marconi et al., 2019; Sherwood et al., 2011), and so we consider such periods to reflect phases of nearly-complete nitrate utilization (Altabet & Francois, 1994) (Figure 2). While these phases may be driven by increased biological uptake, this interpretation is likely complicated due to changes in nitrate supply which may be associated with the considerable variability characteristic of the ocean-atmosphere system over the last 600 years (e.g., *Gray et al.*, 2004; *Trouet et al.*, 2009; *Moffa-Sánchez et al.*, 2014; *Thibodeau et al.*, 2018; *Thornalley et al.*, 2018). In fact, over the last century productivity reconstructed from algal Ba/Ca (Chan et al.,

2017) has been highly variable while algal $\delta^{15}N$ values remained relatively constant (Figure 2). This implies that nitrate utilization during this interval was at least partially controlled by forcings independent of biological mechanisms.

Nitrate in the North Atlantic is sourced from equatorial waters advected by the upper limb of the AMOC, which is redistributed by regional surface currents (Figure 1) (Pelegrí et al., 1996; Whitt, 2019; Williams et al., 2011). Because the Labrador Current is the main current responsible for transporting equatorial-derived nitrate to the Labrador Sea, variations in the strength of this current may also affect the supply of nitrate to the region. While nitrate could additionally be derived from the Hudson Strait (Sutcliffe, Loucks, Drinkwater, & Coote, 1983), such an outflow would also require a strong Labrador Current for the delivery of nitrate to the northeastern Labrador shelf (Figure 1). Terrestrial input may further compromise the otherwise-straightforward connection between the Labrador Current and regional nitrate supply. However, the Labrador coastline receives only 600 – 700 mm of runoff per year (Rollings, 1997) and, due to the Labrador Current's high velocity of 0.8 Sv (Lazier & Wright, 2002), terrestrial input is likely dramatically overprinted by marine sources. As such, most of the nitrate supply associated with upper-ocean advection is likely derived from the Labrador Current, which itself is ultimately reliant upon equatorial water masses (Pelegrí et al., 1996; Whitt, 2019; Williams et al., 2011).

The supply of nitrate is further complicated by upper-ocean stratification during summer months, which restricts the input of nutrients to the photic zone and thus sets the limit of available nitrate for biological assimilation (Harrison et al., 2013; Harrison & Li, 2007; Henson et al., 2009).

Because the degree of stratification is controlled by both upper-ocean warming and freshening, it is possible to qualitatively assess this phenomenon using proxy-based temperature reconstructions (Moore et al., 2017), which faithfully track instrumental temperature measurements over the last century (Table S1). Upper-ocean temperature and salinity anomalies (Cote et al., 2019) are significantly positively correlated (Table S1). This suggests that cold and fresh meltwater significantly impacts regional upper-ocean temperatures such that anomalously high stratification forced by large inputs of freshwater should also correspond to anomalously negative temperature excursions. Alternatively, anomalously high stratification forced by upper-ocean warming should correspond to anomalously positive temperature excursions. However, there is no indication of anomalous temperature conditions reflecting high stratification during phases of mostly-complete nitrate utilization, as the average magnitudes of temperature anomalies during these time periods are either below or close to average pre-1850 values (Figure S1). Because temperature anomalies are not themselves anomalous, upper-ocean stratification via excessive freshwater forcing or excessive upper-ocean warming cannot alone explain the existence of such phases.

The North Atlantic Oscillation (NAO) and Atlantic Multidecadal Oscillation (AMO) are two crucial climatic fluctuations associated with temperature and circulation patterns in the North Atlantic. The NAO describes the atmospheric pressure gradient between the Icelandic Low and Azores High systems, which is typically expressed by an index that assigns positive values (NAO+) to increased pressure differences and negative values (NAO-) to decreased pressure differences (Hurrell, 1995). The NAO+ mode facilitates the advection of Arctic-derived air masses to the Labrador Sea and thus cools the region, producing conditions favorable for extensive sea-ice formation (Drinkwater, 1996; Petrie, 2007; Prinsenberg, Peterson, Narayanan, & Umoh, 2011), whereas NAO- conditions are associated with the opposite characteristics. The AMO describes multidecadal sea-surface temperature (SST) variations characteristic of the North Atlantic basin. Like the NAO, it is typically discussed in terms of an index, where positive index values (AMO+) represent positive SST anomalies and negative index values (AMO-) represent negative SST anomalies (Schlesinger & Ramankutty, 1994). In the Labrador Sea, the AMO- mode is associated with increased cooling and sea-ice extent (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 persistently 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 nearly-complete nitrate utilization phases present in our record. Below, we illustrate the relevance of the NAO and AMO in modulating nitrate conditions in the Labrador Sea, and how recent declines in the AMOC following the LIA have disrupted these historic dynamics. A summary of these findings is available in the supplement (Table S2).

3.2 Pre-LIA and LIA: Historic atmospheric and oceanographic drivers of nitrate utilization

Phases of nearly-complete nitrate utilization interpreted from high $\delta^{15}N$ values may either be driven by increases in productivity or decreases in nitrate supply. Because productivity reconstructions are not directly available prior to the third phase, the historic sea-ice index (Halfar et al., 2013) is used to investigate paleo-productivity, as it has been previously demonstrated that the latter is controlled by the former (Chan et al., 2017). Cross-wavelet coherence analysis suggests that decreased sea-ice extent (and thus, increased productivity) briefly corresponded to increases in $\delta^{15}N$ values until 1500, which would be expected from a productivity-driven change in nitrate utilization (Figure 3a). However, $\delta^{15}N$ leads sea-ice index values, suggesting that productivity could not have controlled nitrate utilization during this interval. Furthermore, a significant antiphase association between the sea-ice index and $\delta^{15}N$ during phase 2 indicates that increased sea-ice extent (and thus, decreased productivity) occurred in tangent with increased $\delta^{15}N$ values. Because decreased productivity should normally result in lower nitrate utilization and thus lower $\delta^{15}N$ values, such a relationship discredits productivity as the main driver of nitrate utilization during this interval. In the 1600s, reconstructions of productivity become available from algal Ba/Ca data (Chan et al., 2017). The onset of phase 3 (~1680-1720; hereafter, 3_1) occurs in concert with an increase in productivity reconstructed from algal Ba/Ca (Figure 2). However, edge effects characteristic of the wavelet analysis between Ba/Ca and $\delta^{15}N$ prevent a complete statistical comparison of these variables during this period (Figure S2), and sea-extent reconstructions do not support a significant relationship between productivity and $\delta^{15}N$ (Figure 3a). Moreover, elevated $\delta^{15}N$ values are maintained well into a period of low productivity following phase 3_1 (Figure S2), and so nitrate supply was likely important for driving the first three phases.

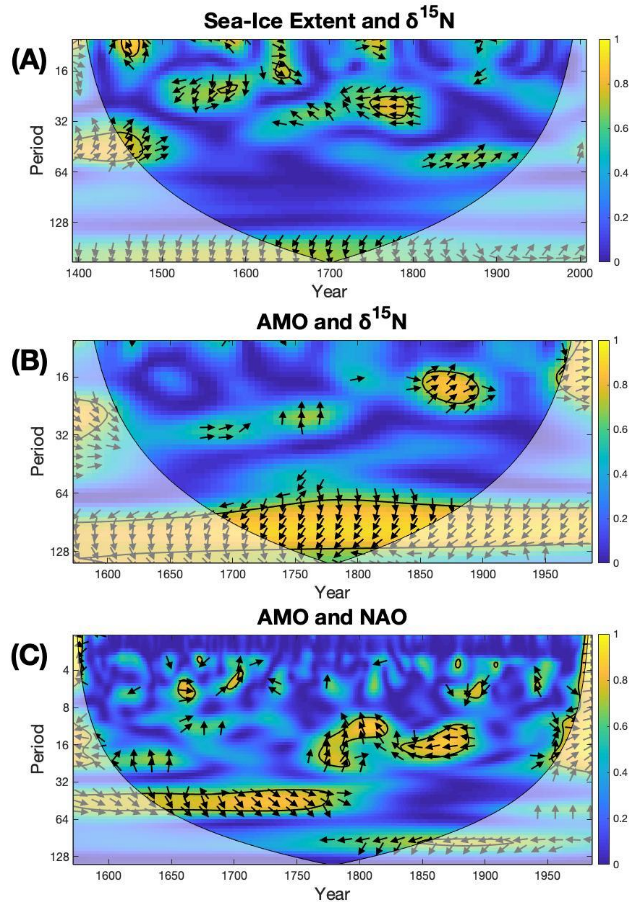

Figure 3: Cross-wavelet coherence and phase relationships between (a) sea-ice extent and $\delta^{15}N$, (b) AMO and $\delta^{15}N$ and (c) AMO and NAO. Significant overlaps in spectral power between signals at the 95% confidence level against red noise are represented within the black contours. Arrows indicate phase relationships, where leftward-pointing represents an antiphase relationship, rightward-pointing represents an in-phase relationship, downward-pointing represents the first series (written on the left side of the title) leading the second series 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 R2019a 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).

With the exception of phase 3_1, phases of nearly-complete nitrate utilization preceding and during the LIA correspond to relatively neutral NAO and AMO modes reconstructed from tree and speleothem archives (Gray et al., 2004; Trouet et al., 2009) (Figure 4a and 4b), with the AMO persistently significantly influencing nitrate utilization on periodicities of approximately

100 years (Figure 3b). Because nitrate utilization is a function of both biological assimilation and physical nitrate supply, such neutral modes could support conditions favorable for complete utilization. Specifically, a positive-mode AMO is associated with sea-ice reductions in the Labrador Sea and therefore likely drives increases in productivity and nitrate assimilation, but also corresponds to strong AMOC conditions, and thus a strong Labrador Current, responsible for supplying nitrate to the region. Conversely, a negative-mode AMO corresponds to sea-ice expansion and therefore likely lowers productivity, but its reliance upon a weak AMOC may result in reduced nitrate supply. Thus, the effects of high-amplitude variations in the AMO on nitrate utilization could be subdued due to the nature of both extremes producing equal effects on both productivity and nitrate supply. As such, we suggest that nitrate utilization was maximized during “Goldilocks” conditions of relatively neutral AMO forcing, also corresponding to neutral NAO forcing, characteristic of the first three phases. Such conditions allow for the occurrence of sufficient biological uptake while simultaneously weakening nitrate supply derived from the Labrador Current.

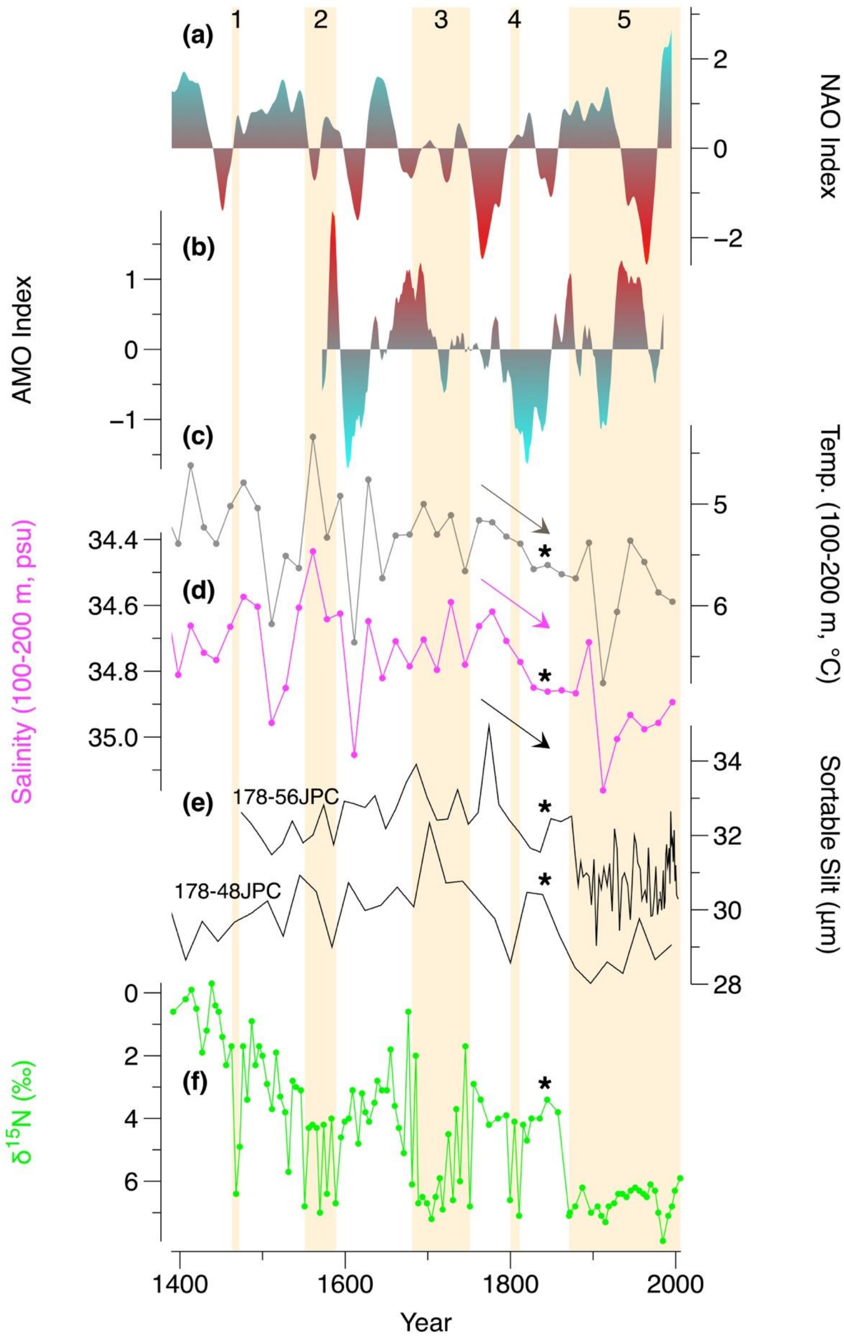

Figure 4: Ocean-atmosphere processes and their effects on the Labrador Sea. (a) NAO index reconstructed from tree and speleothem archives (Trouet et al., 2009); **(b)** AMO index reconstructed from tree-ring analysis (Gray et al., 2004); Labrador Sea convection reconstructed from **(c)** temperature and **(d)** salinity at 100 – 200 m depth (Moffa-Sánchez et al., 2014), and from **(e)** mean sortable silt (Thornalley et al., 2018); and **(f)** nitrate utilization. In NAO and AMO plots, colors correspond to cold (blue) and warm (red) conditions associated with each mode in the Labrador Sea region. The vertical shaded regions correspond to phases of nearly-complete

nitrate utilization. Arrows denote the post-LIA weakening of Labrador Sea convection and asterisks denote the potential pause in convection weakening.

3.3 Post-LIA: Deep-water convection and nitrate supply

In the late 1700s, the relationship between the NAO and AMO changes. A transient, higher-frequency interval of significance is recorded between the two signals, but variable phase relationships characteristic of this association argue against it being mechanistically important (Grinsted et al., 2004) (Figure 3c). During this time period, the NAO was at its most pronounced and long-lived negative mode, which corresponded to a reduction in Labrador Sea convection inferred from salinity and temperature reconstructions at 100 – 200 m depth (Moffa-Sánchez et al., 2014) (Figure 4c and 4d) and from mean sortable silt (Thornalley et al., 2018) (Figure 4e). Together, these trends support the previously-proposed hypothesis that the AMOC was weakened via freshwater forcing at the end of the LIA (Thornalley et al., 2018). This freshwater-induced reduction of Labrador Sea convection was likely driven by the strong negative NAO conditions during this interval (Figure 4a), which would be expected to limit the advection of Arctic-derived air masses to the Labrador Sea, warming the region and resulting in enhanced meltwater input (Drinkwater, 1996; Henson et al., 2009; Petrie, 2007; Prinsenberg et al., 2011). Because convection in the Labrador Sea requires the inflow of nitrate-rich equatorial waters, these circulation patterns could have also affected nitrate utilization trends.

Phase 4 was initiated during a period of low productivity, as shown by the significant antiphase association between the sea-ice index and $\delta^{15}N$ near the onset of phase 4 (Figure 3a). Further, significant relationships between Ba/Ca and $\delta^{15}N$ occur in-phase during this interval. Because the Ba/Ca proxy is inversely related to productivity, this indicates that periods of low productivity corresponded to periods of high nitrate utilization. As such, productivity cannot likely explain the occurrence of phase 4. However, this period is characterized by the onset of a statistically significant antiphase association between the AMO and NAO, which is the opposite of that observed during the LIA interval (Figure 3c). Further dissimilar to the LIA, the AMO stopped leading the NAO during the mid-19th century (Figure 3c), which indicates that a reorganization of ocean-atmosphere dynamics could have occurred during a brief resumption of Labrador Sea convection observed directly after phase 4. Phase 4 may therefore reflect a decreased supply of nitrate forced by a weaker equatorial inflow, while the decrease in nitrate utilization following phase 4 could be related to the resumption of equatorial nitrate supply driven by a reinvigorated Labrador Sea convection (Figure 4c – f).

The onset of the industrial revolution coincided with dramatic alterations in Labrador Sea oceanography. Over the last 150 years, the Labrador Sea region experienced notable changes in sea-ice extent, productivity, circulation strength and nitrate utilization. Interestingly, nitrate utilization remained mostly complete during this entire interval, making phase 5 the longest one present in our record. However, sea-ice extent and productivity exhibited considerable variability throughout phase 5 (Figure 2), which suggests that biological assimilation alone cannot explain its prolonged duration. This is supported by spectral analysis, which indicates that nitrate utilization was uncorrelated with both sea-ice extent (Figure 3a) and Ba/Ca-reconstructed productivity (Figure S2) throughout the interval. During phase 5, the AMOC underwent an intense weakening (Caesar et al., 2018; Rahmstorf et al., 2015) concomitant with strong reductions in Labrador Sea convection (B. Thibodeau et al., 2018; Thornalley et al., 2018) (Figure 4c and 4d) likely driven by anthropogenic climate warming. Absent from unknown oceanographic phenomena, the most likely explanation for phase 5 is therefore the limited input of nitrate driven by a weakening of the Labrador Current. Because the AMOC is expected to further weaken in the near future, the supply of nitrate to the Labrador Sea region may also continue to decline. Additionally, because most of the nitrate supplied to the Labrador Shelf is currently subject to nearly-complete consumption, a continued weakening of the AMOC may eventually limit productivity throughout larger areas of the region.

While previous studies have commented on the relationships between AMOC strength, nutrient supply and productivity in the North Atlantic, such studies have invoked upper-ocean stratification as the main mechanism responsible for these connections (Osman et al., 2019; Schmittner, 2005). However, our data suggest that stratification did not play a prominent role in driving nutrient supply to the Labrador Shelf during past and present phases of nearly-complete utilization (Figure S1), and rather highlight the importance of surface currents in rerouting nitrate throughout the region. The ecological and biogeochemical consequences of such nitrate rerouting 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 degree of phytoplankton productivity, which ecological models suggest strongly affects biomass production of the already-vulnerable and socioeconomically-important Atlantic cod (Ehrnsten, Bauer, & Gustafsson, 2019). In addition to the possible impacts on regional fisheries, changes in primary productivity may also have implications for the future potential of atmospheric carbon sequestration in the region (Takahashi et al., 2009). Thus, numerous environmental challenges may be exacerbated by anthropogenic disturbances to the physical and chemical oceanography of the North Atlantic.

4. Conclusions

Here, we describe mechanisms related to ocean-atmosphere dynamics that drove changes in nutrient biogeochemistry in the Labrador Sea over the last 600 years. We show that productivity alone cannot explain phases of nearly-complete nitrate utilization in the region, and rather suggest that neutral AMO forcing in the past promoted a "Goldilocks" state during which sufficient biological uptake coupled with changes in nitrate supply allowed for such phases to occur on centennial timescales. Additionally, we demonstrate that the modern reduction in the strength of the AMOC likely contributed to a persistently low supply of nitrate to the Labrador Shelf, resulting in an anomalously prolonged phase of nearly-complete utilization. Unlike the past, nitrate utilization will likely not recover due to the continued decline of Labrador Current strength expected from ongoing anthropogenic climate forcing. Our study thus adds to the abundant body of evidence illustrating the intense sensitivity of the polar North Atlantic region to modern warming.

Authors' Contributions

BW and BT designed the study. WA collected the alga. EK subsampled the specimen and developed the chronology. BT performed nitrogen isotope analysis. JMD conducted statistical analyses, interpreted the data and wrote the text with input from all authors.

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Figure Captions

Figure 1: Modern oceanography and nitrate distribution in the Labrador Shelf region. Mean July – September surface nitrate distributions and the major surface-ocean currents involved in the supply of nitrate to our study site (yellow box). This figure was generated with the help of Ocean Data View (Schlitzer, 2018).

Figure 2: Local forcing archived in coralline algae. (top to bottom) Temperature reconstructed from the Labrador Algae Time Series (LATS) reported in (Moore et al., 2017); historical algal-derived inverse index of regional sea-ice extent (Halfar et al., 2013); algal Ba/Ca ([(μg g^{-1})/(μg g^{-1}) x 10^{-5}]), inversely representative of productivity (Chan et al., 2017); and nitrate utilization reconstructed via the isotopic composition of algal-bound nitrogen. Lines for LATS, sea-ice extent and Ba/Ca represent five-year-smoothed averages of the data.

Figure 3: Cross-wavelet coherence and phase relationships between (a) sea-ice extent and $\delta^{15}N$, (b) AMO and $\delta^{15}N$ and (c) AMO and NAO. 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 first series (written on the left side of the title) leading the second series 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 R2019a 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).

Figure 4: Ocean-atmosphere processes and their effects on the Labrador Sea. (a) NAO index reconstructed from tree and speleothem archives (Trouet et al., 2009); **(b)** AMO index reconstructed from tree-ring analysis (Gray et al., 2004); Labrador Sea convection reconstructed from **(c)** temperature and **(d)** salinity at 100 – 200 m depth (Moffa-Sánchez et al., 2014), and from **(e)** mean sortable silt (Thornalley et al., 2018); and **(f)** nitrate utilization. In NAO and AMO plots, colors correspond to cold (blue) and warm (red) conditions associated with each mode in the Labrador Sea region. The vertical shaded regions correspond to phases of nearly-complete

nitrate utilization. Arrows denote the post-LIA weakening of Labrador Sea convection and asterisks denote the potential pause in convection weakening.