Biomarker characterization of the North Water Polynya, Baffin Bay: implications for local sea ice and temperature proxies

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Abstract. The North Water Polynya (NOW, Inuktitut: Sarvarjuaq; Kalaallisut: Pikialasorsuaq), Baffin Bay, is the largest polynya and one of the most productive regions in the Arctic. This area of thin to absent sea ice is a critical moisture source for local ice sheet sustenance and, coupled with the inflow of nutrient-rich Arctic Surface Water, supports a diverse community of Arctic fauna and indigenous people. Although paleoceanographic records provide important insight into the NOW’s past behavior, it is critical that we better understand the modern functionality of paleoceanographic proxies. In this study, we analyzed lipid biomarkers, including algal highly branched isoprenoids and sterols for sea ice extent and pelagic productivity and archaeal glycerol dibiphytanyl glycerol tetraethers (GDGTs) for ocean temperature, in a set of modern surface sediment samples from within and around the NOW. In conjunction with previously published datasets, our results show that all highly branched isoprenoids exhibit strong correlations with each other and not with sterols, which suggests a spring or autumn sea ice diatom source for all highly branched isoprenoids (HBIs) rather than a combination of sea ice and open-water diatoms as seen elsewhere in the Arctic. Sterols are also highly concentrated in the NOW and exhibit statistically higher concentrations here compared to sites south of the NOW, consistent with the order of magnitude higher primary productivity observed within the NOW relative to surrounding waters in spring and summer months. Finally, our local temperature calibrations for GDGTs and OH-GDGTs reduce the uncertainty present in global temperature calibrations but also identify some additional variables that may be important in controlling their local distribution, such as nitrate availability and dissolved oxygen. Collectively, our analyses provide new insight into the utility of these lipid biomarker proxies in high-latitude settings and will help provide a refined perspective on the past development of the NOW with their application in downcore reconstructions.

1 Introduction

Arctic and Antarctic polynyas are key sites for deep water formation (Kuhlbrodt et al., 2017), ice sheet moisture (Smith et al., 2010), and enhanced productivity that can sequester atmospheric CO₂ (Arrigo and van Dijken, 2004). As global temperatures continue to climb, further reductions in sea ice are projected along Arctic coastlines (Barnhart et al., 2015; Onarheim et al., 2018), calling the future status of polynyas into question. Polynyas will cease to exist where seasonal sea ice vanishes or transitions to marginal sea ice zones, which will both result in cascading negative effects on regional and global environments (Meredith et al., 2019; Moore et al., 2021). One way to alleviate some uncertainty about the future status of polynyas is by reconstructing changes in sea ice extent and productivity in the recent geologic past to understand how polynyas have responded to past climate change. In this light, the Holocene instability of coastal polynyas has recently been shown in the Barents Sea (Knies et al., 2018), eastern Greenland (Syring et al., 2020), and northern Baffin Bay (Jackson et al., 2021; Ribeiro et al., 2021) using lipid biomarker climate proxies, such as IP₂₅ (sea ice) and sterols (open-water productivity), along with other proxies such as microfossils and bulk geochemistry. Improved understanding of the modern distributions of biomarkers and the influencing environmental factors within dynamic Arctic regions is
critical for supporting downcore interpretations (e.g., Smik and Belt, 2017; Belt et al., 2019; Kolling et al., 2020).

Here, we focus on the North Water Polynya (NOW, Inuktitut: Sarvarjuaq; Kalaallisut: Pikialasorsuaq), which is the largest polynya (85 000 km²) and one of the most productive regions in the Arctic (Barber et al., 2001; Klein et al., 2002). The latent heat NOW forms when an ice bridge consolidates at the head of Smith Sound, which restricts the passage of Arctic ice floes but allows throughflow of nutrient-rich Arctic Surface Water (ASW) into Baffin Bay through Nares Strait (Fig. 1, Melling et al., 2001). This throughflow and open water fuels high local productivity, which supports a diverse community of Arctic fauna, including higher-trophic-level seabirds and marine mammals (Stirling, 1980; Tremblay et al., 2002). Due to the rich biodiversity, the region has also supported intermittent human occupation for at least 4400 years (Grønnow and Sørensen, 2006; Raghavan et al., 2014), with modern Inuit inhabitants continuing to rely on the NOW for their food security and subsistence economy today (Hastrup et al., 2018). Given that stable ice arches fail to form as reliably as they once did (Vincent, 2019; Moore et al., 2021), the NOW is becoming geographically and seasonally less defined (Ryan and Münchow, 2017).

In this study, we aim to characterize the NOW through the distribution of lipid biomarkers archived in marine seafloor surface sediments that encompass its modern area in Baffin Bay using both new and previously published data (Kolling et al., 2020). We focus on different lipid classes that inform us about seasonal sea ice extent, surface productivity, and ocean temperature. Our assessment of these biomarker proxies against modern instrumental data (i.e., satellite-derived sea ice extent and in situ environmental datasets) provides a key baseline for interpreting the presence and extent of the NOW in the geologic past (Georgiadis et al., 2020; Jackson et al., 2021). On a broader scale, our work is also critical for the community’s general understanding of these lipids’ environmental relationships at high northern latitudes where some proxy datasets are currently sparse (e.g., Tierney and Tingley, 2014, 2018). For example, existing biomarker temperature calibrations are often global in scale and feature high uncertainties at the low end of the temperature spectrum (Kim et al., 2010, 2012). However, uncertainty can be substantially reduced by filling in high-latitude regions and isolating their distinct characteristics with local calibrations (Tierney and Tingley, 2014, 2018; Harning et al., 2019). While some of our biomarker datasets are limited in size, they provide an important first step for the continued refinement of these proxies at high latitudes.

2 Study area

Ocean circulation in Baffin Bay is cyclonic, involving the northward-flowing West Greenland Current (WGC) and the southward-flowing Baffin Current (BC) (Fig. 1). The warm and saline WGC carries a mixture of Atlantic Water from the Irminger Current and Polar Water from the East Greenland Current, whereas the BC is comprised of low-salinity Arctic Surface Water (ASW) that enters Baffin Bay from the Arctic Ocean through the Canadian Arctic Archipelago (CAA) channels. The ASW is modified by mixing with terrestrial-derived freshwater and by sea ice processes en route to Baffin Bay (Tang et al., 2004; Münchow et al., 2006, 2015; Azetsu-Scott et al., 2010). The present-day depths of the CAA channels govern the composition of inflowing ASW (Jones et al., 2003); Nares Strait has a sill depth of 220 m that allows passage of both the Polar Mixed Layer (containing high-nutrient Pacific Water from Bering Strait) and some of the halocline
layer that has been mixed with the underlying Atlantic layer of the Arctic Ocean (Azetsu-Scott et al., 2010). Lancaster and Jones Sounds have shallower sill depths that exclude all but the most carbonate-undersaturated Polar Mixed Layer (Azetsu-Scott et al., 2010). These Arctic outflows join the BC and form the upper 100 to 300 m of surface water in Baffin Bay, except where the WGC dominates in the southeast (Tang et al., 2004).

Sea ice covers nearly all of Baffin Bay in winter, except in the southeast due to the warmth and salinity of the WGC (Fig. 1). Sea ice begins to form in September and reaches maximum coverage in March and is thickest along the Baffin Island coast where the ASW flow is concentrated (Fig. 1, Tang et al., 2004). In contrast, the NOW has low concentrations of thin sea ice, even during winter months. Consolidation of an ice arch at the head of Smith Sound initiates the formation of the polynya, which is further stimulated by northerly winds and currents that remove newly formed sea ice (Ingram et al., 2002; Bi et al., 2019) and sensible heat from WGC upwelling on the Greenland side (Melling et al., 2001; Ingram et al., 2002). Baffin Bay sea ice concentrations decrease between April and August, beginning in the NOW region before propagating southward and creating a generally ice-free Baffin Bay by June (Bi et al., 2019). The Pacific Water, a major component of the ASW, has twice the nitrogen and phosphorus and 7 times the silica of Atlantic Water (Jones et al., 2003). The high nutrient content of incoming ASW, along with higher light levels and stratification in the NOW, fuels high seasonal phytoplankton productivity (Lewis et al., 1996; Ingram et al., 2002; Tremblay et al., 2002). Productivity is an order of magnitude higher in the NOW than in adjacent areas of Baffin Bay, making it one of the most important areas for new production in the Arctic (Tremblay et al., 2002).

3 Background on lipid biomarkers

3.1 HBIs

Highly branched isoprenoids (HBIs) are unsaturated hydrocarbons (Fig. S1) biosynthesized by a narrow range of marine diatoms (see review by Belt, 2018). The mono-unsaturated HBI termed IP25, first discovered in Canadian Arctic sea ice (Belt et al., 2007), has developed into an important proxy for seasonal sea ice due to its production during spring blooms (Brown et al., 2011; Limoges et al., 2018; Amiraux et al., 2019) of Arctic sea ice diatoms (Brown et al., 2014). The di-unsaturated HBI II likely also has an Arctic sea ice diatom source based on distinctly heavy stable carbon isotopic composition, in addition to similar concentration profiles to IP25 across Arctic marine surface sediment (Belt et al., 2008; Cabedo-Sanz et al., 2013; Brown et al., 2014; Limoges et al., 2018). IP25 and HBI II below the limit of detection have often been interpreted to reflect either a lack of seasonal sea ice cover or permanent and thick sea ice that blocks sunlight penetration needed for sea ice diatom photosynthesis. However, this is currently only an assumption, and no targeted investigations aimed at clarifying the production or deposition of IP25 under perennial sea ice cover have been carried out (Belt, 2018).

Other HBIs, such as the tri-unsaturated isomers HBI III and IV, have been attributed to biosynthesis by open-water phytoplankton (Belt et al., 2000, 2008, 2015, 2017; Rowland et al., 2001). The PIP25 index has been used to differentiate between open-water and thick sea ice conditions inferred from IP25 and HBI II in the Arctic and develop semi-quantitative sea ice reconstructions (Cabedo-Sanz et al., 2013; Smik et al., 2016; Köseoğlu et al., 2018):

\[
\text{PIP25} = \frac{\text{IP25}}{\text{IP25} + (\text{phytoplankton biomarker} \times c)},
\]

where the balance factor \(c\) is a ratio of mean IP25 and mean phytoplankton biomarker concentrations (e.g., HBI III). Certain sterols (see Sect. 3.2) can also be used as the phytoplankton biomarker in lieu of HBI III (e.g., Müller et al., 2011). Although in some regions high concentrations of HBI III have also been associated with highly productive marginal ice zones (Barents Sea, Belt et al., 2019), marine fronts (North Iceland Shelf, Harning et al., 2021), and sea ice (Amiraux et al., 2019, 2021; Koch et al., 2020) that may complicate PIP25-derived indices, recent compilations of Arctic surface sediments show that PIP25-based indices broadly correlate with spring and autumn sea ice concentrations (Xiao et al., 2015; Kolling et al., 2020).

3.2 Sterols

Sterols are ubiquitous components in eukaryotic organisms (Fig. S2, Volkman, 1986) and, similar to HBI III and IV, have become common complementary biomarkers in IP25 and PIP25 datasets. Although these biomarkers have often been attributed to specific sources, such as pelagic phytoplankton (brassicasterol, e.g., Navarro-Rodriguez et al., 2013), di-noflagellates (dinosterol, e.g., Boon et al., 1979), and vascular plants (campesterol and β-sitosterol, e.g., Huang and Meinschein, 1976), they are now known to derive from multiple sources that complicate their source specificity. For example, brassicasterol and dinosterol are also produced by sea ice algae (Nichols et al., 1990; Belt et al., 2013, 2018) and pennate diatoms (e.g., Volkman et al., 1993; Rampen et al., 2010), and campesterol and β-sitosterol can be produced by diatoms and vascular plants (Belt et al., 2013, 2018; Rampen et al., 2010). Hence, the abundance of these sterols within marine sedimentary records is more broadly reflective of general marine productivity (e.g., Köseoğlu et al., 2019). In the CAA, where terrestrial biomass is low (Gould et al., 2003), we further assume that the contribution of terrestrial-derived campesterol and β-sitosterol is minimal compared to that produced in the ocean.
3.3 GDGTs

Isoprenoid glycerol dibiphytanyl glycerol tetraethers (GDGTs) are cell-membrane-spanning lipids biosynthesized by archaea (Fig. S3, Pearson and Ingalls, 2013), including ammonia-oxidizing Thaumarchaeota (Schouten et al., 2002; Könneke et al., 2005; Pitcher et al., 2011; Besseling et al., 2020). Thaumarchaeota can modify the number of cyclopentane moieties (cyclization) in GDGTs in response to in situ temperature variability, a process known as homeoviscous adaptation (e.g., Elling et al., 2015). Thus, correlations are found between the degree of GDGT cyclization in global surface sediment datasets and upper-ocean temperature. These degrees of cyclization are commonly reported with various versions of the tetraether index of tetraethers consisting of 86 carbons (TEX$_{86}$) index (Schouten et al., 2002, 2013; Kim et al., 2010, 2012).

Evidence from a latitudinal transect in the western Atlantic Ocean demonstrates that GDGTs are most likely produced and exported to the seafloor from 80–250 m water depth (Hurley et al., 2018), which compares well to archaea abundance maxima at 200 m water depth in the Pacific Ocean (Karner et al., 2001). Considering that Thaumarchaeota are chemolithoautotrophs that perform ammonia oxidation (conversion of ammonia to nitrite), they are typically more abundant around the primary nitrate maximum near the base of the photic zone (Church et al., 2010; Francis et al., 2005; Hurley et al., 2018) and are most productive when there is minimized phytoplanktonic competition over ammonia (Schouten et al., 2013). In the higher latitudes, the latter occurs during the less productive dark winter months when photosynthesis for sea surface species is inhibited, which may explain the seasonal winter temperature bias of GDGTs observed in this latitudinal band (Herfort et al., 2006; Rueda et al., 2009; Rodrigo-Gámiz et al., 2015; Harning et al., 2019). Although the temperature relationship of TEX$_{86}$-based indices deviates from the linear global temperature calibrations and features higher uncertainty at the cold end of the spectrum (Schouten et al., 2002; Kim et al., 2010, 2012), regional calibrations have proven useful for reducing estimate uncertainty (Harning et al., 2019) that may be at least partially attributed to changes in community composition (e.g., Elling et al., 2017). Moreover, new indices based on hydroxylated isoprenoid GDGTs (Fig. S3, OH-GDGTs, e.g., RI-OH and RI-OH’ indices, Lü et al., 2015), also produced by planktic Thaumarchaeota (Elling et al., 2017; Bale et al., 2019), have been suggested to improve upon TEX$_{86}$-based proxies in the polar oceans (Fietz et al., 2013, 2020; Huguet et al., 2013). This is because the addition of one hydroxyl group may further reduce membrane rigidity at lower temperatures (Huguet et al., 2017). In addition to temperature, recent studies have shown that several other environmental and geochemical factors can influence the degree of GDGT cyclization, such as growth phase (Elling et al., 2014), ammonia oxidation rates (Hurley et al., 2016), and oxygen concentrations (Qin et al., 2015) but not likely salinity (Wuchter et al., 2004, 2005; Elling et al., 2015). Although the effects of these environmental parameters on OH-GDGT cyclization have not been rigorously tested, emerging evidence suggests that salinity, sea ice, seasonality, and terrestrial input may be complicating factors in some oceanic settings (Fietz et al., 2013; Kang et al., 2017; Lü et al., 2019; Park et al., 2019; Wei et al., 2020; Sinninghe Damsté et al., 2022).

4 Materials and methods

4.1 Marine surface sediment samples

We analyzed marine surface sediment samples ($n = 13$) collected from box core ($n = 12$) and trigger core tops ($n = 1$) collected during the 2008 CSS $Hudson$ and 2015 and 2017 CSS $Anundsen$ research cruises that range in water depth from 267 to 2373 m b.s.l. (Table 1). As each sample integrates the upper 1 to 2 cm of sediment, they likely reflect the several most recent decades or centuries of time depending upon site-specific sedimentation rates and mixing by bioturbation. Therefore, each sample reflects time averages of biomarker production in and out of the polynya. Marine surface sediment samples collected on these cruises and others over the past few decades have previously been analyzed for HBIs and select sterols (i.e., brassicasterol and dinosterol) as part of larger pan-Arctic datasets (Stoynova et al., 2013; Kolling et al., 2020). To generate larger datasets where possible, we compare our new dataset ($n = 13$) with a subset of samples ($n = 70$) previously published by Kolling et al. (2020). To avoid environmental settings that may be disproportionally impacted by terrestrial and/or glacier runoff, we exclude samples collected from within fjords (e.g., Kangigtaagapik, formerly Clyde Inlet) and bays (e.g., Disko Bugt). Moreover, while the International Hydrographic Organization defines the southern limit of Baffin Bay as 70°N (International Hydrographic Organization, 1953), we extend our range into Davis Strait to 67°N to provide greater breadth for the environmental gradients.

4.2 Bulk geochemistry

At the University of Colorado Boulder’s Earth Systems Stable Isotope Laboratory, freeze-dried and decalcified marine surface sediment subsamples ($n = 9$, Table 1) were analyzed for bulk elemental (% CaCO$_3$, % TC, % TN) and stable isotope ($\delta^{13}$C relative and $\delta^{15}$N) geochemistry on a Thermo Delta V elemental analyzer (EA) interfaced to an isotope ratio mass spectrometer (IRMS) and computed for elemental C/N values. $\delta^{13}$C values are expressed relative to Vienna Pee Dee Belemnite (VPDB) and $\delta^{15}$N relative to air. Only 9 of the total 13 samples were analyzed for bulk geochemistry as there was not enough mass in the remaining 4 for additional lipid biomarker analyses (see Sect. 4.3).
4.3 Lipid biomarkers

At the University of Colorado Boulder’s Organic Geochemistry Laboratory, freeze-dried marine surface sediment sub-samples (~1–4 g, n = 13) were extracted twice on a Dionex accelerated solvent extractor (ASE 200) using dichloromethane (DCM): methanol (9 : 1, v/v) at 100°C and 2000 psi. A 25% aliquot of the total lipid extract (TLE) was taken for GDGT analysis. The remaining 75% of TLE was then separated into five fractions (F1–F5) using silica column chromatography after elution with 1/2 dead volume (DV) hexane (F1), 2 DV hexane:DCM (8 : 2, v/v) (F2), 2 DV DCM (F3), 2 DV DCM:ethyl acetate (EtOAc) (1 : 1, v/v) (F4), and 2 DV EtOAc (F5). Each of these extractions contained 500 ng of the following internal standards: 3-methylheneicosane (F1), 3-Terphenyl-d14 (F2), docosanoic acid (F3), 1-nonadecanol (F4), and 2-Me octadecanoic acid (F5).

From F1, we focus on highly branched isoprenoid (HBI) IP25 (C25:1), HBI II (C25:2), HBI III (C25:3), and HBI IV (C25:3) biomarkers. HBIs were analyzed via gas chromatography–mass spectrometry (GC-MS) on a Thermo Trace 1310 gas chromatograph interfaced to a TSQ Evo 8000 triple quadrupole mass spectrometer and fitted with an Agilent DB-1MS GC column (60 m × 0.25 mm × 0.25 µm) following modified methods and operating conditions of Belt et al. (2012). We used an ion source temperature of 250°C rather than 300°C to prevent excessive fragmentation during ionization, which yields larger molecular ions that facilitated compound identification both in full scan (FS) and selected reaction monitoring (SRM) modes (e.g., Boudinot et al., 2020). The identification and quantification of IP25 (m/z 350, Belt et al., 2007), HBI II (m/z 348, Belt et al., 2007), and HBI III and IV (m/z 346, Belt et al., 2000) was based on their respective mass spectra compared to that of the internal standard (3-methylheneicosane, m/z 310.6). To account for the varying response factors of different lipid classes and to make our sample set comparable with other published HBI datasets, we corrected the concentrations based on our internal standard (3-methylheneicosane) by the response factor of a five-point external HBI dilution series comprised of 7-hexynonadecane (7-HND) and 9-octylheptadec-8-ene (9-OHD) (Fig. S4, Belt et al., 2012).

From F4, we focus on a series of diagnostic sterols, namely brassicasterol (24-Methylcholesta-5,22E-dien-3β-ol), dinosterol (4α,23,24-Trimethyl-5α-cholesta-22E-en-3β-ol), campesterol (24-Methylcholesta-5-en-3β-ol), and β-sitosterol (24-Ethylcholesta-5-en-3β-ol). Before analyses, each sample was derivatized with N,O-bis(trimethylsilyl)trifluoroacetamide (BSTFA; 25 µL) and pyridine (catalyst, 25 µL at 70°C for 20 min.). Sterols were analyzed using the same GC-MS system described above but with an Agilent DB-5MS GC column (60 m × 0.25 mm × 0.25 µm) and under the following operating conditions: initial temperature of 80°C (held for 2 min), ramp 20°C min−1 (2.5 min), and ramp 5°C min−1 (68 min, held for 30 min). Mass spectrometric analyses were carried out in full scan (FS) and selected reaction monitoring (SRM) modes. Individual sterols were identified based on their respective mass spectra (Boon et al., 1979) and then quantified by comparing their response factor to that of the internal standard (1-nonadecanol, m/z 284.5). To account for the different response factor of sterols and to make our sample set directly comparable with Kolling et al. (2020), we corrected the concentrations based on our internal standard (1-nonadecanol) by the response factor of a five-point external dilution series of cholesterol (Fig. S4).

For GDGTs, we focus on isoprenoid and hydroxylated isoprenoid GDGTs. A 25% aliquot of dry TLE samples was resuspended in hexane:isopropanol (99 : 1, v/v), son-
icated, vortexed, and then filtered using a 0.45 μm poly-
tetrafluoroethylene (PTFE) syringe filter. Prior to analysis
samples were spiked with 10 ng of the C46 GDGT internal
standard (Huguet et al., 2006). GDGTs were identified
and quantified via high-performance liquid chromatography–
mass spectrometry (HPLC-MS) following modified methods
of Hopmans et al. (2016) on a Thermo Scientific Ultimate
3000 HPLC interfaced to a Q Exactive Focus Quadrupole-
Orbitrap MS (Harning et al., 2019). GDGTs were identi-

For productivity biomarkers (HBIs and sterols), we com-
pared proxy data against the mean annual values and mean seasonal values where complete
datasets were available. Since winter and spring sea-
sonal data were either fragmentary or not available, the mean
annual datasets used in this study likely represent the ice-

To evaluate the degree of influence from non-thermal factors
on GDGT-derived indices, we compute the Ring Index for
each sample (RI, Zhang et al., 2016):

\[
RI = 0 \times [\text{GDGT-0}] + 1 \times [\text{GDGT-1}] + 2 \times [\text{GDGT-2}]
+ 3 \times [\text{GDGT-3}] + 4 \times [\text{cren.}] + 4 \times [\text{cren.}'],
\]

and compare with the global core top polynomial regression
for TEX86 values (Zhang et al., 2016):

\[
RITEX = -0.77(\pm 0.38) \times \text{TEX86} + 3.32(\pm 0.34)
\times (\text{TEX86})^2 + 1.59(\pm 0.10).
\]

Finally, for hydroxylated isoprenoid GDGTs, we explore two

\[
\text{RI-OH} = \frac{[\text{OH-GDGT-1}] + 2 \times [\text{OH-GDGT-2}]}
{[\text{OH-GDGT-1}] + [\text{OH-GDGT-2}]},
\]

\[
\text{RI-OH'} = \frac{[\text{OH-GDGT-0}] + [\text{OH-GDGT-1}] + [\text{OH-GDGT-2}]}
{[\text{OH-GDGT-0}] + [\text{OH-GDGT-1}] + [\text{OH-GDGT-2}]}. \]

\section{Results}

\subsection{Bulk geochemistry}

HBIs are present above the detection limit in all sediment
samples \((n = 13)\). IP25 is the most abundant HBI in the
dataset, followed by HBI II, HBI III, and HBI IV (Fig. 4a).
HBIs are generally more abundant at NOW sites compared
to sites outside this region, although \(t\)-test results show that
only HBI II and HBI IV are statistically different between
NOW and non-NOW sites when normalized to sediment
mass \((g, \text{Fig. 4a})\). When normalized to g TOC, the sample
set is reduced to nine, and there is no statistically significant
difference between NOW and non-NOW sites for any HBI
(Fig. S5a). Based on Pearson correlation analysis, each of
the HBIs strongly correlates with the others \((-0.74, \text{Fig. 5}),
which supports the similar spatial distribution of the four
HBIs throughout Baffin Bay (Figs. S6–S7).

\subsection{Sterols}

Sterols are present above the detection limit in all sediment
samples \((n = 13)\): β-sitosterol is the most abundant sterol in
the dataset, followed by campesterol, brassicasterol, and di-

\subsection{Statistical analyses and WOA18 instrumental
datasets}

For productivity biomarkers (HBIs and sterols), we com-
puted Pearson correlation matrices and \(p\) values to exam-
ine their statistical relationship with one another. To deter-
mine if sites within the NOW and outside the NOW are
statistically different in terms of the all studied biomark-
ers (HBIs, sterols, GDGTs and OH-GDGTs), we performed
\(t\) tests and computed corresponding \(p\) values. To assess and calibrate our GDGT-based proxies against modern climato-
logical fields, we use World Ocean Atlas 2018 (WOA18)
}

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Figure 2. WOA18 Annual 2007–2017 oceanographic variables from Baffin Bay against depth (m b.s.l.). Individual profiles are from each study site, where darker (lighter) colors reflect sites farther north (south) and dashed (solid) lines denote those within (outside) the modern limits of the NOW. Data from Garcia et al. (2018a, b), Locarnini et al. (2018), and Zweng et al. (2018).

trations to g TOC reduces the sample set to nine, NOW and non-NOW sites remain significantly different for all sterols (Fig. S5c). Based on Pearson correlation analysis, the sterols all strongly correlate with each other (>0.72), apart from dinosterol and β-sitosterol whose correlation is insignificant (Fig. 5). The strong correlations between sterols supports their similar spatial distribution throughout Baffin Bay (Figs. S8–S9).

5.4 PIP<sub>25</sub>

We calculated new Baffin Bay balance factors (c) for P<sub>HII</sub>IP<sub>25</sub> (3.19), P<sub>IV</sub>IP<sub>25</sub> (1.02), P<sub>R</sub>IP<sub>25</sub> (0.54), and P<sub>D</sub>IP<sub>25</sub> (0.63) based on a combination of the 70 previously published samples from Baffin Bay (Kolling et al., 2020) and this study’s sample set to reflect the balance factors for the combined datasets. Although HBI IV was quantified by Kolling et al. (2020), we note that the authors did not explore its potential as part of a PIP<sub>25</sub> index. For all four PIP<sub>25</sub> indices in our dataset (n = 13), we observe slightly higher mean values in non-NOW sites compared to NOW sites, although it is only statistically significant for the P<sub>D</sub>IP<sub>25</sub> index (Fig. 4e).

5.5 GDGTs and OH-GDGTs

GDGTs and OH-GDGTs are present above the detection limit in all sediment samples (n = 13). In terms of RI values, all samples plot below the global core top polynomial regression for TEX<sub>86</sub> (Fig. 6a). In terms of total fractional abundance, GDGTs (0.88 ± 0.03) dominate over their OH-GDGT counterparts (0.12 ± 0.03) (Fig. 6b). GDGTs and OH-GDGTs with no cyclopentane moieties are the most dominant (e.g., GDGT-0 and OH-GDGT-0), followed by crenarchaeol and then the GDGTs and OH-GDGTs with 1, 2, and 3 cyclopentane moieties (Fig. 6c–d). Spatially, the fractional abundance of GDGTs tends to be relatively low within the modern limits of the NOW, whereas the fractional abundance of OH-GDGTs is relatively high within the modern limits of the NOW (Fig. S11).

In terms of regressions against different environmental variables (e.g., temperature, salinity, dissolved oxygen, and

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nitrate), we find that the tested GDGT- (TEX\textsubscript{86} and TEX\textsubscript{L186}) and OH-GDGT-based indices (RI-OH and RI-OH\textsuperscript′) range in the strength of the correlation coefficients ($R^2$) and significance ($p$ values) (Figs. 7, S12–S14). Moreover, differences in the season and depth integration of the environmental variables also appear to influence the strength of their correlation (Figs. 7, S12–S14). For TEX\textsubscript{86}, the strongest significant temperature correlation is achieved with summer sea surface temperature (SST) in the upper 20 m of the water column ($R^2 = 0.21$ to 0.35, Fig. 7a). Although salinity and dissolved oxygen seem to have little confounding influence ($R^2 < 0.22$), we find a moderately strong but significant correlation between annual TEX\textsubscript{86} and nitrate concentrations above 5 m b.s.l. ($R^2 = 0.40$, Fig. S14). For TEX\textsubscript{L186}, the strongest significant temperature correlations ($R^2 > 0.40$) are found with annual temperature ($> 30$ m b.s.l., Fig. 7b). The influence of other environmental variables (e.g., salinity, dissolved oxygen, and nitrate) on TEX\textsubscript{L186} appears to be generally weak ($R^2 < 0.27$), although summer nitrate concentration correlations at 0–200 m b.s.l. are slightly higher and significant ($R^2 = 0.37$, Fig. S14). For RI-OH, the strongest significant temperature correlations are achieved with annual SST between 10 and 20 m b.s.l. ($R^2 = 0.44$ to 0.46). Autumn subsurface temperatures between 60 and 80 m b.s.l. also feature similarly significant correlations ($R^2 = 0.41$ to 0.42) (Fig. 7c). The influence of the other tested environmental variables on RI-OH appears to be generally weak ($R^2 < 0.27$), although summer and annual 0–20 m dissolved oxygen concentration correlations are slightly higher ($R^2 = 0.39$ and $R^2 = 0.36$, respectively, Fig. S13). Finally, for RI-OH\textsuperscript′, the strongest significant temperature correlations are achieved with annual 0–20, annual 0–30 m SST, and summer 0–100 m SST, although correlation coefficients for all are relatively low ($R^2 = 0.23$) (Fig. 7d). Based on our $R^2$ values, the influence of other environmental variables, namely annual and summer subsurface dissolved oxygen and nitrate below 100 m depth, appears to exert relatively greater influence than temperature on RI-OH\textsuperscript′ (Figs. S13–S14).

For the two indices that feature the strongest significant correlations with temperature ($R^2 > 0.40$), we derived individual linear temperature calibrations for Baffin Bay based on this study’s dataset ($n = 13$). The TEX\textsubscript{86} calibration ($R^2 = 0.45$) encompasses the surface and subsurface waters from 0–90 m b.s.l. and features a standard error (SE) of 0.13 °C (Fig. 8a):

$$\text{subT} = 10.573x + 6.636,$$

(8)

The RI-OH calibration ($R^2 = 0.46$) encompasses the surface waters from 0 to 20 m b.s.l. and features an SE of 0.26 °C (Fig. 8b):

$$\text{SST} = 27.982x - 31.524.$$  

(9)

6 Discussion

6.1 Spatial variability in surface productivity

A recent and expanded Arctic study by Kolling et al. (2020) explored the efficacy of using a variety of sedimentary HBIs (i.e., IP\textsubscript{25}, HBI II, and HBI III), sterols (i.e., brassicasterol and dinosterol), and their PIP\textsubscript{25}-derived indices to reconstruct sea ice extent and concentration and pelagic productivity by comparison to satellite data. For Baffin Bay, the main conclusions were that P\textsubscript{5}IP\textsubscript{25}, P\textsubscript{7}IP\textsubscript{25}, and P\textsubscript{11}IP\textsubscript{25} all exhibited strong correlations with modern spring and autumn seasonal sea ice concentration (Kolling et al., 2020). On the other hand, TR\textsubscript{25}, the recently proposed HBI proxy for spring phytoplankton bloom in the Barents Sea (Belt et al., 2019), did not exhibit a clear relationship with chlorophyll $a$ but instead paralleled spring, autumn, and winter sea ice extent.
Figure 4. Average concentrations (ng g SD$^{-1}$) and standard deviation of (a–b) HBIs, (c–d) sterols, and (e–f) PIP$_{25}$ indices for sample sets from this study ($n = 13$) and the subset of Kolling et al. (2020, $n = 70$). Standard deviations for each are shown in light gray. Sites within the NOW are purple, whereas sites outside the NOW are gray. Qualitative sea ice concentration limits in panels (e)–(f) are after Müller et al. (2011) for no sea ice (0 to 0.3), reduced sea ice (0.3 to 0.5), seasonal sea ice (0.5 to 0.7), and perennial sea ice (0.7 to 1). For all NOW and non-NOW comparisons, differences that are statistically different as defined by $t$ tests ($p$ value $< 0.05$) are denoted with an *. See Fig. S4 for complementary plots of biomarker concentrations normalized to TOC.

(Kolling et al., 2020). For this reason, we did not further explore the controls of chlorophyll $a$, which is a limited and discontinuous dataset in the Baffin Bay region (NASA MODIS), on the distribution of HBI III and HBI IV compounds that comprise the TR$_{25}$ proxy (e.g., Belt et al., 2019). However, we do further explore the ability of HBIs and PIP$_{25}$ indices to track sea ice extent throughout Baffin Bay and include another previously untested PIP$_{25}$ index (P$_{IV}$IP$_{25}$). Most importantly, we explore the ability of HBI and sterol biomarkers, including two additional sterols ($\beta$-sitosterol and campessterol) not analyzed by Kolling et al. (2020), to track the high surface productivity associated with the NOW. While it is common to report HBI and sterol concentrations relative to TOC, we note that only a subset of this study’s dataset ($n = 9/13$) and that of Kolling et al. (2020, $n = 51/70$) have corresponding TOC measurements. Given that the overall
pattern of HBI and sterol concentrations in the NOW compared to sites outside the NOW is the same whether concentrations are normalized to g sediment or TOC in both datasets (Figs. 4a–d and S5), we focus the following discussion on samples normalized to g sediment to present a larger combined dataset (n = 83). We note that while the methods to extract and separate biomarkers differ between Kolling et al. (2020) and this study, each method is routinely used and unlikely to result in any substantial dataset differences (e.g., Belt et al., 2014).

In terms of HBIs, mean concentrations of all compounds are higher in sites within the NOW compared to sites outside the NOW in both datasets (Fig. 4a–b). However, only the concentration of HBI II is significantly different between NOW and non-NOW sites across the two datasets (Fig. 4a–b), while HBI IV is significantly different in this study (Fig. 4a) and HBI III is significantly different in Kolling et al. (2020) (Fig. 4b). For IP\textsubscript{25} and HBI II, the detection of each in all samples is consistent with the spring and autumn sea ice limits in Baffin Bay (Fig. S6, Cavalieri et al., 1996; Bi et al., 2019). We also observe a strong positive correlation between IP\textsubscript{25} and HBI II (Fig. 5a–b), which likely supports a common sympagic diatom source as observed elsewhere in the Arctic (Belt et al., 2008; Cabedo-Sanz et al., 2013; Brown et al., 2014; Limoges et al., 2018). Given the distinct oceanographic seasonal characteristics of the NOW (open water) and central Baffin Bay (seasonal sea ice), we expected higher IP\textsubscript{25} and HBI II concentration in the sites south of the NOW compared to sites within the NOW itself – a hypothesis inconsistent with our observations. One possibility is that these HBIs are produced earlier in the spring or later in the autumn when sea ice covers both the NOW and eastern coast of Baffin Island (Bi et al., 2019). Another possibility may be that the higher concentrations of IP\textsubscript{25} and HBI II within the NOW reflect the southward transport of drift ice through the open NOW, as well as the formation and export of thin sea ice from the NOW (Bi et al., 2019). While HBI III and IV are found in relatively low concentrations compared to IP\textsubscript{25} and HBI II (Fig. 4a–b), all four HBI’s distributions are highly correlated with one another and spatially similar (Figs. 5 and S6). This presents several possibilities. First, as observed in other regions of the Arctic such as the Barents Sea, increased concentrations of HBI III and IV are associated with populations of open-water (pelagic) phytoplankton in marginal ice zones (Smik et al., 2016; Belt et al., 2015, 2019). In this sense, the concentrations we observe in Baffin Bay are consistent with increased production of these HBIs during the spring transition from seasonal sea ice to open water in the NOW compared to sites outside that maintain seasonal sea ice cover during the summer. Alternatively, recent work that has monitored the production of various HBIs through the spring sea ice melt season in southwestern Baffin Bay shows that HBI III is produced under the sea ice before and concurrent with IP\textsubscript{25} and is therefore likely biosynthesized by sea ice (sympagic) diatoms in this region (Amiraux et al., 2019, 2021). Given that in both datasets HBI III and IV show weak or insignificant correlations with sterols (Fig. 5a–b), which are generally attributed to open-water phytoplankton (e.g., Köseoğlu et al., 2019), we argue that the latter scenario where HBI III and IV are produced by sympagic diatoms is most likely.

In terms of sterols, mean concentrations of all compounds were higher and statistically different for sites in the NOW compared to sites outside the NOW in both datasets (Fig. 4c–

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**Figure 5.** Pearson correlation coefficients between HBIs and sterols for (a) this study’s samples (n = 13) and (b) the subset of Kolling et al. (2020, n = 70). Positive correlations are displayed in blue, and negative correlations are shown in red. Both the color and size of the circle are proportional to the correlation coefficients. Insignificant correlations (p values > 0.01) are left blank.
We note that the non-NOW data for brassicasterol and dinosterol from Kolling et al. (2020) are proportionally higher than ours, which may reflect the incorporation of a greater diversity of oceanographic settings in Baffin Bay compared to ours. While a recent Holocene marine record from Petermann Fjord (northwestern Greenland) interprets campesterol and \( \beta \)-sitosterol as indicators of terrestrial input (Detlef et al., 2021), we note that all sterols are highly correlated in our dataset (Fig. 5a), which suggests a possible common source. Considering our bulk geochemistry data indicate a predominance of marine organic matter origin (Fig. 3a), the known production of all four sterols by marine diatoms (Belt et al., 2013, 2018; Rampen et al., 2010), and the low terrestrial biomass of surrounding landmasses (Gould et al., 2003), we suggest that in Baffin Bay, a marine source is most likely for brassicasterol, dinosterol, campesterol, and \( \beta \)-sitosterol. Although these sterols do not feature the same degree of source specificity as the HBIs do, the statistically higher concentrations of sterols in the NOW in both datasets is consistent with the high seasonal pelagic productivity that the NOW supports today (Fig. 4c–d). Moreover, studies based on nutrient concentrations of particulate matter in Baffin Bay show that primary productivity in the NOW is an order of magnitude higher than adjacent areas in Baffin Bay during spring/summer (Tremblay et al., 2002). Given the southward propagation of sea ice, and that the development of the NOW occurs at the transition between spring and summer (Bi et al., 2019), the sterols are likely recording a spring/summer season signal of pelagic productivity.

Finally, in terms of PIP25, all four indices (\( P_{III}P_{25} \), \( P_{IV}P_{25} \), \( P_{B}P_{25} \), and \( P_{D}P_{25} \)) for our samples were lower in sites within the NOW compared to sites outside the NOW (Fig. 4e). \( P_{B}P_{25} \) and \( P_{D}P_{25} \) values from Kolling et al. (2020) are higher in the NOW compared to non-NOW sites, while \( P_{III}P_{25} \) and \( P_{IV}P_{25} \) are consistent with ours (Fig. 4f). However, only the \( P_{D}P_{25} \) indices in both datasets are statistically different for sites in the NOW (Fig. 4e–f). The difference in \( P_{B}P_{25} \) and \( P_{D}P_{25} \) between datasets likely stems from the larger diversity of sites included in Kolling et al. (2020, \( n = 70 \)) compared to our smaller dataset (\( n = 13 \)).

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While the HBI-derived indices ($P_{III}IP_{25}$ and $P_{IV}IP_{25}$) feature overall higher values compared to those derived from sterols ($P_{B}IP_{25}$ and $P_{D}IP_{25}$) in both datasets, we caution against the application of the HBI-derived indices in Baffin Bay for sea ice concentration since these biomarkers may partly originate from sea ice diatoms (e.g., Amiraux et al., 2019, 2021), rather than a combination of sea ice and open-water diatoms. Moreover, these indices show no statistical difference between NOW and non-NOW sites (Fig. 4e–f). Looking at the only statistically different sterol-derived index (i.e., $P_{D}IP_{25}$) for both datasets, the trends are opposite, where this study shows higher concentrations of sea ice outside the NOW and Kolling et al. (2020) show higher concentrations of sea ice inside the NOW (Fig. 4e–f). This difference stems from the datasets’ dinosterol concentrations, which show less variability between NOW and non-NOW sites in our dataset compared to Kolling et al. (2020) (Fig. 4e–d), likely due to the inherently larger spatial coverage of the latter dataset. While it seems logical to therefore rely on the distribution of $P_{D}IP_{25}$ values from Kolling et al. (2020), the spatial variability of the dataset is inconsistent with late spring and summer sea ice cover in Baffin Bay, where the highest concentrations of sea ice are found off eastern and northeastern Baffin Island (Bi et al., 2019). Given the limited size of our dataset, which is consistent with these observations, we acknowledge that more work is needed to assess the utility of PIP indices in Baffin Bay.

In summary, we have several recommendations for future lipid-based paleoenvironmental reconstructions in Arctic oceanographic settings. First, for complex oceanographic settings like Baffin Bay, we recommend the analysis of both sterols and HBIs to test the performance of various sea ice cover proxies and their ability to track local changes in sea ice and pelagic productivity. If possible, this would be best achieved through the analysis of modern surface sediments and sediment traps over an environmental gradient and through the seasons to capture proxy response to known variable changes (e.g., Navarro-Rodriguez et al., 2013; Smik and Belt, 2017; Koch et al., 2020). Second, continued research on sterol and HBI sources and seasonality of production is critical for the development of more refined sea ice and marine productivity reconstructions (e.g., Limoges et al., 2018; Amiraux et al., 2019, 2021). This is particularly necessary when combining $IP_{25}$, a known sea ice diatom proxy,
Figure 8. GDGT- and OH-GDGT temperature calibrations for this study’s dataset \((n=13)\). Shown are (a) TEX\textsubscript{86} versus annual 0–90 m sub\(T\); (b) RI-OH (OH-GDGTs) versus annual 0–20 m SST; (c) TEX\textsubscript{86} sub\(T\) estimates based on Iceland (blue, Harning et al., 2019), global (yellow, Kim et al., 2012), and Baffin Bay (purple, this study) calibrations against WOA18 annual 0–90 m sub\(T\) (black dashes, Locarnini et al., 2018); (d) RI-OH SST estimates based on global (blue, Lü et al., 2015) and Baffin Bay (purple, this study) calibrations against WOA18 annual 0–20 m SST (black dashes, Locarnini et al., 2018). Panels (e) and (f) show residuals of calibration estimates and WOA18 data for TEX\textsubscript{86} and RI-OH, respectively. The x axis refers to site number (see Fig. 1 and Table 1).

with less source-specific open-water proxies such as HBI III and sterols. Third, based on replicated Baffin Bay datasets, which show statistically higher sterol concentrations within the NOW compared to sites outside of its modern limits (this study, Kolling et al., 2020), we suggest that sterols are a key tool to characterize the presence or absence of the NOW in the recent geologic past. The complementary analysis of HBIs can then provide important context for sea ice changes and how said changes may have impacted pelagic productivity. Finally, the integration of additional paleoenvironmental proxy datasets, such as microfossils (e.g., foraminifera, diatoms, dinocysts) and bulk geochemistry, can lead to even more detailed reconstructions of past pelagic productivity and how that productivity relates to various environmental drivers (e.g., Jackson et al., 2021; Ribeiro et al., 2021).

6.2 Temperature calibrations

Temperature correlations for GDGTs first relied on empirical correlations between global surface sediments and the variability in biomarker structure (e.g., Schouten et al., 2002). Subsequent iterations and developments of TEX\textsubscript{86}-based indices removed some compounds (e.g., crenarchaeol stereoisomer for TEX\textsubscript{86}) for improved performance in certain latitudinal bands (Kim et al., 2012). Most recently, Bayesian statistics have been employed to generate spatially varying calibrations (i.e., BAYSPAR) that reach a compro-
mise between data-constrained global and regional calibra-
tions to capture regional oceanographic variability and site-
specific uncertainty more accurately (Tierney and Tingley, 2014). However, BAYSPAR does not include surface sed-
iment for sensitive oceanographic regions like Baffin Bay
(Tierney and Tingley, 2014). For this reason, developing lo-
cal correlation-constrained calibrations can be particularly
useful to capture the nuances of oceanographic variability in
regions where global dataset coverage is lacking or where the
temperature relationship deviates from global linear calibra-
tions (e.g., Harning et al., 2019; Park et al., 2019; Fietz et
al., 2020; Sinninghe Damsté et al., 2022). Moreover, explor-
ing the potential influence of additional environmental vari-
ables (e.g., salinity, DO, nutrients) will help us better under-
stand the mechanisms behind (and functionality of) this com-
monly applied paleotemperature proxy. Given the relatively
small sample size \( n = 13 \) and narrow temperature range of
our dataset (\( \sim 6^\circ \text{C}, \text{Fig. 2a} \)) compared to global compila-
tions (e.g., Kim et al., 2012; Lü et al., 2015), we acknowledge
that our conclusions in the following discussion are relatively
limited. However, as no previous GDGT and OH-GDGT ex-
ists from this region, it is an important first step in describing
depth, and understanding of their production in cultures (Elling et
al., 2017) indicate that planktic group 1.1a Thaumarchaeota
are likely the dominant producers. Therefore, the global re-
lation between TEX\textsubscript{86} and the RI (Fig. 6a, polynomial
black line) serves as a simple means to evaluate whether the
TEX\textsubscript{86}-based indices are influenced by additional nonther-
mal factors (Zhang et al., 2016). Even though our data ex-
hibit a correlation between TEX\textsubscript{86} and RI values \( (R^2 = 0.46) \)
with a slope like the global polynomial regression, all sam-
les plot below the lower 95 % uncertainty limit (Fig. 6a). A
recent study from the South China Sea found a similar rela-
tionship to ours, in that TEX\textsubscript{86} values were well correlated
with RI values but did not conform to the global polyno-
mial trend’s uncertainty (Wei et al., 2020). Wei et al. (2020)
posited that the shallow shelf environment (neritic zone) of
the South China Sea may result in the observed deviation from
the global polynomial TEX\textsubscript{86}-RI relationship, as shal-
low water Thaumarchaeota respond differently to tempera-
ture than the deep-dwelling communities (e.g., Kim et al.,
2015, 2016; Villanueva et al., 2015; Zhu et al., 2016; Jia et
al., 2017). While the depths of our sites are deeper than the
neritic zone \( (>200 \text{ m.b.s.l.}, \text{Table 1}) \), many are much shall-
ower than open-ocean sites used in the global calibrations
(Kim et al., 2010, 2012). One possibility is that the shallower
environment of northern Baffin Bay may result in a differ-
ent response of Thaumarchaeota to temperature and different
distribution of GDGTs than in the open ocean. In any case,
temperature seems to remain the dominant control on GDGT
cyclization in this region.

Our regression analysis against temperature, salinity, DO,
and nitrate further supports temperature as the dominant en-
vironmental control on GDGT distributions in Baffin Bay
for the seasons available in the WOA18 dataset. The lack of
WOA18 winter temperatures, in addition to the fragmentary
dataset for spring temperatures in Baffin Bay (Locarnini et
al., 2018), prevents us from assessing the impact of these in-
dividual seasons, which is unfortunate given that cold season
temperatures in other high-latitude settings exhibit a stronger
correlation with GDGT distributions (Herfort et al., 2006;
Rueda et al., 2009; Rodrigo-Gámiz et al., 2015; Harning et
al., 2019). However, the higher correlation between TEX\textsubscript{86}
and annual temperatures compared to summer and autumn
seasons (Fig. 7b) suggests a bias for Baffin Bay GDGT pro-
duction towards the cooler seasons. Although we explored
the relationship of the original TEX\textsubscript{86} index, we prefer to
rely on the low-temperature TEX\textsubscript{86}\textsuperscript{L} modification to assess
GDGT depth and season and temperature relationships. This
decision is supported by (1) generally low correlation co-
efficients for temperature and TEX\textsubscript{86}, except for summer
SST (Fig. 7a), and (2) the better correlations of TEX\textsubscript{86}\textsuperscript{L}
and lower water depths where ammonia oxidation likely occurs
(Fig. 6b, e.g., Hurley et al., 2018; Park et al., 2019). The mod-
erate correlation between TEX\textsubscript{86} and summer SST and the
lack of correlation between TEX\textsubscript{86}\textsuperscript{L} and SST from any sea-
son may indicate that the crenarchaeol stereoisomer, which
is included in the TEX\textsubscript{86} index but not in TEX\textsubscript{86}\textsuperscript{L}, may be
physiologically advantageous for surface dwelling Thaumar-
chaeota during the warmer summer months in Baffin Bay.
At least for one Thaumarchaeotal culture (Candidatus Ni-
trosotenuis uzonensis), temperature exerts a strong control
on the proportion of the crenarchaeol stereoisomer (Bale et
al., 2019). However, we also cannot rule out the possibility
of a yet unknown alternative biological source, as phylogeny
also exerts a secondary control (e.g., Bale et al., 2019).

In terms of other tested environmental variables, corre-
lations between TEX\textsubscript{86}\textsuperscript{L} and salinity and dissolved oxygen
are generally poor \( (R^2 <0.3, \text{Figs. S12–S13}) \), consistent with
previous reports on the lack of relationship between GDGT
production and salinity (Wuchter et al., 2004, 2005; Elling et
al., 2015). The presence of a well-oxygenated water column
in Baffin Bay (Fig. 2c) likely has little influence on GDGT
cyclization, which has been reported to only occur in oxygen-
limited environments (e.g., Qin et al., 2015). The correlation
between TEX\textsubscript{86}\textsuperscript{L} and nitrate, while weak, is more pronounced
in the lowermost integrated depth \( (200 \text{ m b.s.l.}) \) (Fig. S14).
The main product of ammonia oxidation is nitrite, for which
we have no data in this region. However, since nitrite can
be subsequently oxidized to nitrate by bacteria (Kuypers et
al., 2018), we assume that nitrate provides indirect evidence
for both reactions. This provides evidence for a subsurface

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depth habitat of ammonia-oxidizing Thaumarchaeota in Baffin Bay, which supports our observations that TEX\textsubscript{15}L correlates best with annual sub\textit{T} (Fig. 8c).

Our complementary analysis of OH-GDGTs and environmental variables reveals several differences with the conclusions drawn for GDGTs in Baffin Bay and with OH-GDGTs elsewhere. First, the RI-OH′ index, which was developed as a modified version of RI-OH for low-temperature environments (Lü et al., 2015), does not perform as well as the RI-OH index in our dataset (Fig. 7c–d). Second, we find that RI-OH is best correlated with annual SST in the top 40 m of the water column ($R^2 = 0.46$), and with autumn in the subsurface (>50 m depth, Fig. 7c). The slightly stronger correlation between RI-OH and SST compared to sub\textit{T} is supported by Lü et al. (2019), who observed higher concentrations of OH-GDGTs in the upper portion of the water column compared to GDGTs in the East China Sea. Moreover, the slightly higher proportion of OH-GDGTs relative to GDGTs in our samples within the modern limits of the NOW (Fig. S11), where sea ice concentrations are low and sea surface primary productivity is high, suggests that these surface conditions may be conducive to their production in Baffin Bay. Additional studies have found that the ring composition of OH-GDGT often differs from GDGTs, which may suggest that these two lipid classes are sourced from different Thaumarchaeota subgroups or produced in different niches of the water column characterized by different environmental conditions (Liu et al., 2012).

In terms of additional environmental variables, only surface dissolved oxygen appears to exert a partial influence on OH-GDGT cyclization in the RI-OH index (Fig. S13c). However, when OH-GDGT-0 is considered in the RI-OH′ index, moderate correlations with dissolved oxygen (Fig. S13d) and nitrate appear within the subsurface waters (Fig. S14d). These latter observations conflict with our RI-OH temperature correlations that suggest a surface-dwelling producer of OH-GDGTs. Instead, this may suggest that OH-GDGT-0 is important for membrane functionality at these depths and/or for these environmental variables. Alternatively, OH-GDGT-0 may also have a different biological source in Baffin Bay, as at least for GDGTs, GDGT-0 can be produced by other groups of archaea (e.g., Pearson and Ingalls, 2013). Given the relatively low correlations between RI-OH′, which includes OH-GDGT-0, and temperature, our data further support the potential role of OH-GDGT-0 for membrane response to these non-thermal environmental variables in Baffin Bay. Although our data suggest that OH-GDGTs, reflected by the RI-OH index, are predominately a proxy for annual SST, more detailed studies on the biological producers, depth habitat, and response to environmental variables of OH-GDGTs will undoubtedly benefit future applications and interpretations of downcore OH-GDGT proxy records.

Following our evaluation of GDGT and OH-GDGT indices in terms of their ability to capture temperature, amongst other environmental variables, we present two temperature calibrations that can benefit future paleoceanographic reconstructions from Baffin Bay (Fig. 8). Like other regional TEX\textsubscript{15}L temperature calibrations in the greater North Atlantic region (e.g., Harning et al., 2019), our Baffin Bay TEX\textsubscript{15}L temperature calibration captures a subsurface signal (0–90 m b.s.l.) with a considerably lower SE (0.13 °C) compared to the latest global calibration (4.0 °C, Kim et al., 2012) despite the lower $R^2$ (0.45 vs. 0.87, respectively). While other subsurface depth calibrations are nearly as strong for 0–90 m b.s.l., which simply reflects the isothermal nature of temperature below ~80 m at our study sites (Fig. 2a), we choose to focus on the strongest for the sake of simplicity. The strength of our local TEX\textsubscript{15}L sub\textit{T} calibration is also supported by the fact that other regional (Harning et al., 2019) and global calibrations (Kim et al., 2012) overestimate the observed WOA18 temperature in Baffin Bay (Fig. 8c), with residuals as high as 5.8 °C for the Iceland calibration and 5.0 °C for the global calibration (Fig. 8e). In terms of the RI-OH SST calibration, the best of our knowledge there are no regional calibrations to compare with. However, comparison with the global calibration that features a SE of 6.0 °C (Lü et al., 2015) again reveals the power of reducing uncertainty with regional calibrations as ours from Baffin Bay features a smaller SE of 0.26 °C. While the global TEX\textsubscript{15}L calibration overestimates Baffin Bay temperatures by up to 5.0 °C, the RI-OH calibration overestimates local temperatures by less than 3.3 °C (Fig. 8d–f). In future studies, we suggest that these two calibrations may help quantify paleotemperature changes in Baffin Bay surface and subsurface waters. For other high-latitude locations that do not yet have local GDGT–temperature calibrations, our comparison between instrumental temperature and global calibration estimates caution against quantitative interpretations due to large overestimations. However, as the trends between regional and global calibrations are similar (Fig. 8c–d), qualitative interpretations remain valid.

### 7 Conclusions

As global climate change continues, the sustainability of Arctic polynyas is in jeopardy. While proxy reconstructions of polynyas prior to the instrumental period can shed light on key climate and environmental mechanisms that lead to polynya presence or absence, continued development of our understanding of those proxies is needed. Therefore, we evaluated a series of lipid biomarkers (HBIs, sterols, GDGTs, and OH-GDGTs) in surface sediment samples from Baffin Bay to characterize how these biomarkers capture sea ice and productivity conditions in the North Water Polynya (NOW) and inform the utility of commonly applied paleotemperature proxies in Baffin Bay. In conjunction with a similar study of lipid biomarker productivity proxies from the same region (Kolling et al., 2020), we draw the following conclusions.
Author contributions. JS and DJH designed the study, and JS and AEJ funded the study. DJH led the analyses of samples and developed GC-MS methods under the supervision of JS. BH and LW assisted with the extraction and purification of samples. DJH wrote the manuscript with discussion and contribution from all co-authors.

Competing interests. The contact author has declared that none of the authors has any competing interests.

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