Implications for the branched tetraether membrane lipid temperature proxy in Arctic paleoclimate reconstruction—Evidence over the Holocene from Baffin Island lacustrine sediment

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Abstract

This thesis aims to assess the validity of bacterial branched glycerol dialkyl glycerol tetraethers (brGDGTs) temperature reconstructions in Arctic lake settings from a Holocene (~11,700 BP) lacustrine sediment core from Baffin Island, Eastern Canadian Arctic. The distribution of brGDGTs in peats, soils, and lake sediments has been shown to correlate with mean annual air temperature (MAAT) and this proxy has been widely applied to sedimentary archives for paleotemperature reconstructions. However, the production and distribution of brGDGTs are impacted by confounding environmental variables that are currently not well understood. Here I study the distribution of brGDGTs preserved in a high-Arctic lake setting and apply the most up-to-date brGDGT-inferred temperature reconstruction calibrations. This thesis specifically investigates the role of changing oxygen levels on reconstructed brGDGT paleotemperatures. Comparisons with other soil and lacustrine samples from Baffin Island suggest that brGDGTs in Upper Gnarly are primarily sourced from within the lake over the Holocene, and estimated temperatures from surface sediments using recently published lake-specific calibrations compare favorably with measured summer air and water temperatures from the region. The downcore reconstruction from Upper Gnarly exhibits a trend opposite of what is expected with a cool Early Holocene followed by warming towards the present. Importantly, two intervals of cooler reconstructed temperatures are observed during intervals of supposed suboxia in the lake. Overall, my results present further evidence that suboxic conditions generate a cold-bias in brGDGT paleotemperature reconstructions, and ultimately need to be considered in future research in paleotemperature reconstruction in high-Arctic lake settings.

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Preface

Looking back over my journey in my undergraduate degree at the University of Colorado Boulder, I would have never seen myself conducting research in the organic biogeochemistry field. Freshman year, I entered with a major in Geological Sciences as I loved anything pertaining to geosciences. After the first few introductory courses in geology, I was ready to tackle the program; however, I began to feel restricted as my growing interest in the environmental field combated with the foreshadowed future careers in industry and resource extraction, so I switched over to Environmental Studies.

Luckily, I took a course called “Global Change: The Recent Geologic Record” with the wonderful Julio Sepúlveda that introduced to me the concepts of past glacial and interglacial periods, climate records, and climate reconstruction. The course opened my eyes to diverse avenues of climate research that merged all geosciences. The same course introduced me to Greg de Wet, who one winter’s day in INSTAAR, approached me and introduced me to the PACEMAP project and a unique opportunity to conduct research on an Arctic lake sediment core. Now a year and half later, I have done it… I have learned so much, not only about climate reconstruction, Arctic lakes, bacterial membranes, organic geochemistry (here I was thinking “IPA” meant India Pale Ale and not isopropyl alcohol), but more importantly, I learned a lot about myself. Thank you for the memories and the learning opportunity!

Acknowledgments

I would like to thank my thesis advisors Gregory de Wet, Julio Sepúlveda, Dale Miller, and Gifford Miller for their support and encouragement throughout this tedious and awesome project. I would like to acknowledge the NSF-funded PACEMAP Project for allowing me to conduct research on their lake core, especially one with such a great name like Upper Gnarly. I would like to thank Greg, Nadia Dildar, and everyone at the Organic Geochemistry Lab at CU Boulder for guiding and teaching me the skills to conduct my research.

Julio, thank you for your encouragement in this subject and your continual support both in school and in life; you are a sage of wisdom. I have never met a better teacher than you.

Greg, I would like to thank you individually for approaching me with this unique opportunity. I cannot say how much your patience, guidance, enthusiasm, and friendship helped me through everything. You are one of the best people I have ever met.

Dale, shout out to you for tolerating me for two years. It probably felt like I was never leaving. Jokes aside, thank you for supporting me through everything. You have helped me from the start with a plan of action and wise words. Thank you for your calming presence.

I would like to thank Extra Strength Advil for giving me the strength to finish this thesis. And I would like to thank my dog, Tobin, for often being the only family member to greet me late in the night at 1:00 a.m. when I came back home from school, and for wishing me good luck every day with tail wags of encouragement. Shout out to my friends Kelsie, Caitlynn, and Ben for being there and helping me through the bouts of tears and fatigue. Shout out to Anne Marie Panetta for being an inspiration as well as watching me grow over these few years.

Introduction

This undergraduate honors thesis aims to assess and reconstruct paleoclimate through a novel geochemical temperature proxy from a lacustrine sediment record spanning the Holocene (past ~11,700 years BP) from Baffin Island in the Eastern Canadian Arctic. This research is part of the on-going NSF-funded project "Predicting Arctic Change Through Ecosystem MoleculAr Proxies" (PACEMAP). PACEMAP seeks to understand and quantify past and future climate and ecosystem change in the Eastern Canadian Arctic by utilizing novel molecular techniques to reconstruct temperature, hydroclimate, and vegetation over multiple interglacial periods. This thesis project specifically focuses on an Arctic paleotemperature reconstruction for the Holocene for central eastern Baffin Island and primarily utilizes a temperature reconstruction proxy derived from organic bacterial cell membrane lipids known as branched glycerol dialkyl glycerol tetraethers (brGDGTs).

Throughout Earth's geological history, the icy regions of our planet have served as a buffer for the global climate system, influencing and stabilizing the globe's ocean circulations, global average temperature, and albedo feedbacks (IPCC, 2018). Now as the atmosphere is inundated with increasing rising concentrations rates of anthropogenically-sourced greenhouses gases, Arctic regions are changing (IPCC, 2018). As the Arctic continues to experience unprecedented warming, it is critical for environmental scientists and communities dependent on this ecosystem to understand how the Arctic region will respond to higher temperatures. Past warm interglacial periods that were comparatively warmer than pre-anthropogenic temperatures, including the Early Holocene, serve as useful analogues for future warmth and can provide valuable insights into the Arctic's response to higher temperatures. Paleoclimate reconstructions provide fundamental understanding of long-term global climate change (Braconnot et al., 2012;

Otto-Bliesner et al., 2013). Therefore, it is invaluable to continually assess various Arctic modern and paleotemperature reconstruction techniques in their validity in reproduction and application in various environmental settings.

In the last two decades, relatively novel geochemical techniques in paleoclimate reconstruction have become an important research focus, specifically in glycerol dialkyl glycerol tetraethers (GDGTs) and branched GDGTs and their application as temperature and soil pH proxies in soils and sediments (e.g. Naafs et al., 2017a, 2017b; Russell et al., 2018). Although the distribution of brGDGTs has been established to be empirically related to MAAT and environmental pH, this relationship is complex and could be confounded by other environmental factors such as bacterial brGDGT source, Arctic seasonality, dissolved oxygen concentration, etc. (Weijers et al., 2007; Tierney et al., 2010; Loomis et al., 2014; Russell et al., 2018; Weber et al., 2018). Though previous research utilizing these biomarkers in global soils and modern lake settings expands the applicability of the brGDGT proxy (Naaf et al. 2017a, 2017b; Russell et al., 2018), there are relatively few studies examining this biomarker proxy in Arctic settings (Shanahan et al., 2013). This research will contribute to the larger applicability of the proxy in Arctic paleotemperature reconstruction as well as compare it to other proxy data from similar Arctic lake settings and cores from the PACEMAP project.

This thesis focuses on three primary research questions. Below I list the research questions with corresponding objectives and steps needed in order to address the research questions for the greater goal of assessing the brGDGT proxy applicability in Arctic paleotemperature reconstructions for PACEMAP

- What do the downcore brGDGT paleotemperature reconstructions illustrate about Holocene climate change at Baffin Island?

    - I extracted brGDGTs from a Baffin Island Holocene lake sediment core from and reconstructed paleotemperature trends over the Holocene utilizing a novel geochemical brGDGT temperature proxy by applying the most up-to-date brGDGT-based calibrations.
    - Upper Gnarly's Holocene paleotemperature reconstruction was assessed against other global Holocene temperature reconstructions from various temperature proxies and compared to Holocene Arctic solar insolation trends.
- Do Upper Gnarly's paleotemperature reconstructions match other downcore temperature reconstructions and climate produced from other downcore Arctic and Baffin Island lake sediment cores that span the same relative Holocene timescale?
    - The data was compared against other PACEMAP Baffin Island lake temperature reconstructions to assess the validity of the Upper Gnarly record.
    - Fractional abundances from Upper Gnarly were compared to modern Baffin Island lake water column brGDGTs and other Baffin Island downcore fractional abundances in order to assess the suite of brGDGTs.
- How are brGDGT distributions affected by supposed intervals of suboxic conditions in Upper Gnarly during the Holocene?
    - I assessed the suggested suboxic intervals (based on visual stratigraphy) in Upper Gnarly through the application of redox proxies and determine if the data are indicative of lower oxygenation levels.
    - The brGDGT distributions were compared across suboxic intervals in Upper Gnarly with other Baffin lake records that display similar stratigraphy.

- I evaluated sources of brGDGTs and other lake in-situ factors that could affect the temperature reconstruction.

Background

In the following sections I will discuss the relevant background needed to understand Arctic climate change over the Holocene and previous work on Baffin Island as well as the pertinent geochemical groundwork in temperature reconstruction and for the brGDGT temperature proxy.

Arctic climate change over the Holocene

In the past 800,000 years, climate scientists have recorded over 11 different interglacial periods. These past warm interglacial periods can serve as useful analogues for future warming, and are especially pertinent for the Arctic regions as changes in northern high Arctic latitudes respond more rapidly to climatic fluctuations due to arctic amplification (Serreze and Barry, 2011). But deciphering the complexity that is Earth's global system is no small feat; there are myriad confounding variables that cause the global climate system to warm or cool that span geologic timescales, i.e. carbon burial, atmosphere carbon dioxide concentrations, greenhouse gas effect, changing tectonic settings, volcanic activity (e.g. Crawley and Berner, 2001; Retallack, 2003; Ganino and Arndt, 2009; Miller et al., 2013). One of the greatest drivers of global climatic variability are orbital forcings like precession, obliquity, and eccentricity. The cyclical fluctuations of continental ice sheets are greatly instigated by the changing level of received solar insolation in the Arctic which fluctuates from shifts in Earth's orbit (Miller et al., 2013).

The Holocene (~11,700 years BP to today) marks the transition in the Quaternary Period where Earth shifted out of the Last Glacial Period (LGM) around 115,000 - 11,700 years BP. The early Holocene serves as a useful analogue for future warmth from anthropocentric global warming in Arctic regions because approximately 11,000 years BP 70°N June solar insolation was 45 W/m squared greater than today (Kaufman et al., 2004) with average summer temperatures reconstructed to be + 1.6 °C with a range of 0.5 to 3.0°C (Miller et al., 2013). The peak in solar insolation in the Arctic around 10-12,000 years BP is the primary driver of a warm interval called the Holocene Thermal Maximum (HTM) (Kaufman et al., 2004). Reconstructions from terrestrial and marine archives record peak Holocene summertime warmth to be greater than instrument-measured 20th century Arctic temperatures (Kaufman et al., 2004). The majority of paleoenvironmental records from the HTM record summer temperatures, which is relevant to brGDGT proxy paleotemperature reconstruction at Baffin Island because the brGDGTs preserved in Arctic lake records are thought to be primarily produced in summer months (Shanahan et al., 2013). Multiple lines of evidence from macrofossils and pollen around the Arctic and stable isotope analysis of foraminifera suggest that after the initial peak of HTM, the Arctic entered into an interval of neoglaciation with an initial summer temperature decrease of 1-2°C (Jennings et al., 2002; Miller et al., 2013). Estimates for initial neoglaciation cooling are placed around 4-6,000 yrs BP; thus, brGDGT and other temperature proxy reconstructions should show a cooling trend in the Arctic around that interval.

Proxy records—How we contextualize climate change

Anthropogenic global climate change is the greatest threat to the health and versatility of the Earth's environments and ecosystems (IPCC, 2018). Consequently, our understanding as a scientific and global community on how the numerous and complex ecological, hydrological, and climatic systems will respond to change will largely depend on precise and accurate climate modeling predictions. Current models for future climate projections are calibrated using observed climate measurements from the past 40 years; however, various geologic archives record past environmental responses to climate change and can provide an unparalleled opportunity to assess climate model performance outside our limited climate observations (Braconnot et al., 2012). There are paleoclimate archives which directly record past atmospheric concentrations and temperature like ice cores (e.g. Legrand & Mayewski, 1997) and boreholes (e.g. Beltrami et al., 2011), but the majority of paleoclimate records are indirect archives of past environmental and climate parameters that serve as estimates for paleotemperature and/or paleoenvironmental reconstructions (Braconnot et al., 2012). Proxies envelope a large spectrum of preserved physical characteristics that contain a diverse range of geochemical data, stable isotope compositions, hydrologic change, and phylogenetic change. For example, paleoenvironmental proxies can be extracted from modern or preserved biological or geologic archives like corals (e.g. Fairbanks et al., 1997; Druffel, 1997), tree rings (e.g. McCarroll & Loader, 2004), fossilized leaves (e.g. Uhl and Mosbrugger, 1999; Royer et al., 2005), and speleothems (e.g. McDermott et al., 2006). Climate proxies can be generated from geochemical analysis of planktonic foraminifera (e.g. Crundwell et al., 2008), lacustrine and marine diatoms (e.g. Smol et al., 2000), volcanic tephra (e.g. Larson et al., 2001), and Arctic and Antarctic lake sediments (e.g. Pienitz et al., 2004).

This thesis specifically focuses on an Arctic lacustrine sediment record. Arctic lake sediment records serve as useful archives in paleoclimatic reconstructions and proxy applications because (1) many records span thousands of years, (2) lacustrine settings are highly prominent in circumpolar regions, and (3) Arctic ecosystems are the first to show signs of environmental shifts (Pienitz et al., 2004; Braconnot et al., 2012). Regrettably, long-term monitoring data is particularly lacking in high latitude regions, so consequently, indirect proxy methods are needed to reconstruct past environmental and climatic data (Pienitz et al., 2004); additionally, climate model simulations tend to underestimate the degree of regional changes in the Arctic (Braconnot et al., 2012). Therefore, ultimately, this thesis aims to evaluate the proficiency and reliability of the brGDGT paleotemperature proxy in high-latitude Arctic settings with additional confounding environmental factors for temperature reconstruction.

Geochemical and molecular analyses in lacustrine and other settings

Advances in organic molecular proxies are laying new groundwork in efforts to contextualize and assess modern and past climate change (Castañeda & Schouten, 2011). However, greater efforts need to be made in developing proxies that are specialized for their applicability in particular terrestrial and aquatic ecosystems.

In paleoenvironmental and paleotemperature reconstructions, there are myriad bulk geochemical properties of organic matter (e.g. total organic content (TOC), carbon to nitrogen ratio [C:N], and carbon and nitrogen isotopes [d13C, d15N]) that are routinely analyzed (e.g. Meyers, 2003). Similarly, various organic geochemical proxies and compound-specific isotopic analyses are being increasingly utilized in recent years to: reconstruct ancient terrestrial and aquatic environments and parameters (e.g. hydrological variability, salinity, lake surface temperatures, lacustrine vegetation, and soil temperature and pH); study biogeochemical cycling; and examine the movement of allochthonous and autochthonous organic matter (Meyers, 1997; Killops and Killops, 2005; Peterse et al., 2005; Eglinton and Eglinton, 2008).

In molecular biogeochemical approaches to environmental and climate reconstructions, individual compounds or compound classes that are traceable back to a specific source organism or biological processes are used to relate past environmental settings (Peterse et al., 2005). These individual compounds and compound classes that are preserved in geological material are called biomarkers. Biomarkers are often structural fragments of parent organic compounds whose carbon skeleton can be structurally related back to their biogenic precursor. Biomarkers and other organic compounds contain clues preserved in their carbon skeletons about the past environmental settings in which they were produced (Killops and Killops, 2005). In the context of a lacustrine environment, examination of these compounds at molecular levels allows the separation of components terrestrial, aquatic, or sedimentary in origin, and thus ultimately allows for the examination of environmental conditions, including temperature, in the water column and surrounding watershed (Castañeda & Schouten, 2011).

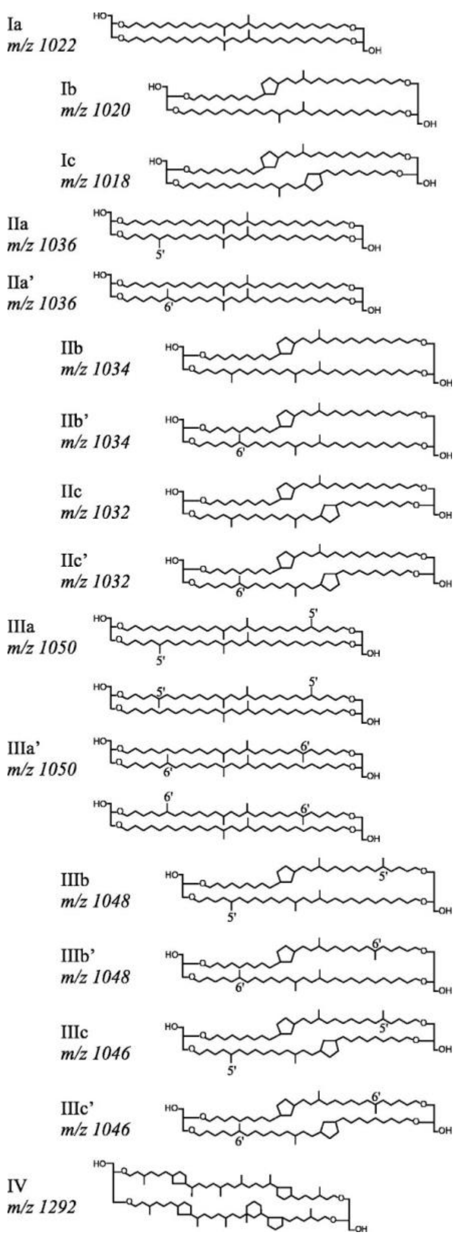
GDGTs and brGDGTs: The membrane lipids behind the proxy

Over the past two decades, research investigating the unique set of the organic molecular compounds GDGTs has been identified in the biogeochemical community as a useful approach in climate and environment reconstruction. These membrane-spanning lipids are at the foreground for geochemical and molecular research for modern and paleotemperature reconstruction because of their ubiquitous global distribution in a variety of environmental settings coupled with their application as temperature and pH proxies. Currently, there are two identified types of GDGT lipids found in nature: isoprenoidal glycerol dialkyl glycerol tetraethers (isoGDGTs), produced by archaea, and branched glycerol dialkyl glycerol tetraethers (brGDGTs), produced by bacteria.

IsoGDGTs are synthesized by a wide range of Archaea (de Rosa et al., 1977). IsoGDGTs are of notable interest because of their utilization in proxies for reconstructing surface temperatures in marine and lake settings (Schouten et al., 2002) and for quantifying inputs of soil organic matter to marine or lacustrine environments (Castañeda & Schouten, 2011; Schouten et al., 2013). Despite isoGDGTs' ability to be found in extreme extremophilic settings, they are also regularly found in the water column and sediments of lakes (e.g. Powers et al., 2005; Tierney et al., 2009; Blaga et al., 2009; Damsté et al., 2009). In this thesis, two specific isoGDGTs are analyzed (GDGT-0 and GDGT-4 "Crenarchaeol") for their applicability as a proxy for oxygenation levels in sediments.

BrGDGTs are selectively synthesized by bacteria and first identified by Damsté et al. (2000) in peat samples; however, there is still uncertainty in the source organism(s) of brGDGTs, but evidence suggests that bacteria members from the phylum Acidobacteria are at least one of the sources of these compounds (Damsté et al., 2011). Currently, brGDGTs are found ubiquitously in mesophilic settings like peats (e.g., Weijers et al., 2006a; Huguet et al., 2010, 2013), soils (e.g., Weijers et al., 2006a; Peterse et al., 2012), lake sediments (e.g., Blaga et al., 2009, 2010; Tierney et al., 2010; Pearson et al., 2011; Loomis et al., 2012), and shallow marine sediments (e.g., Weijers et al., 2006b; Donders et al., 2009).

The membrane lipids contain two straight C_{28} alkyl core chains with four to six methyl groups (i.e. the "branch" part of branched GDGTs) and one or two cyclopentyl moieties (Damsté et al., 2000, 2011). The brGDGTs and their isomers (6-methyl branched copy) can be further defined as tetramethylated brGDGTs (Ia-Ic), pentamethylated (IIa-IIc'), and hexamethylated (IIIa-IIIc') (*Fig. 1*). The alkyl core chains undergo internal cyclization, resulting in the presence of one or two cyclopentane moieties. It is generally thought that the composition of the brGDGTs lipid membrane varies in order to adjust the membrane permeability in variable environments (De Jonge et al., 2014b). The relative distribution of the fifteen brGDGTs (recently 10 with the identification of the novel IIIa" isomer by Weber et al. [2015]) can be expressed in the Methylation of Branched Tetraethers (MBT) and the Cyclisation of Branched Tetraethers (CBT) ratios. Particularly, CBT provides a proxy for soil pH as Weijers et al. (2006b) first observed in a global dataset of surface soils that the relative number of cyclopentane moieties in the brGDGTs is exponentially negatively correlated with soil pH. Likewise, the MBT is positively correlated with mean annual soil temperature, which is generally comparable to mean annual air temperature (Weijers et al., 2006b). More importantly, the CBT and MBT calibrations have been consequently refined and recalibrated based on environmental parameters and climatic conditions (i.e. aridity, locality, surface water temperature). Peterse et al. (2012) refined the MBT calibration based upon an extended soil dataset with the removal of brGDGT IIb and IIIc



Fig, 1. *Chemical structures of branched GDGTs (I-III) with isomers and Crenarchaeol GDGT (IV). The structures of the penta- and the hexamethylated brGDGTs (II-III) with cyclopentyl moiety(ies) indicated (De Jonge et al., 2014a).*

as the MBT' index. Subsequently, De Jonge et al., 2014a further refined the CBT to CBT' and the MBT' to include both 5-methyl and 6-methyl isomers; furthermore, De Jonge et al., 2014a found that removal of the 6-methyl isomers improved temperature calibrations and thus developed the CBT'_{5Me} and MBT'_{5Me} calibrations. The latest refined calibrations for MAAT using the MBT' and MBT'_{5Me} from De Jonge et al., 2014a was recalibrated by Russell et al. (2018) using soils from East African Lakes.

De Jonge et al. (2014b) concluded that separate quantification of the 6- and 5-methyl brGDGT is essential for accurate quantifications of brGDGTs in environmental samples, and the separation results in substantially improved MAAT and soil pH reconstructions (De Jonge et al., 2014b). Additionally, De Jonge et al. (2014b) found that temperature calibrations with the CBT'_{5Me} index no longer contribute significantly to MAAT reconstructions. Russell et al. (2018) found the CBT' index in the calculation of soil pH likely does not have a major effect on lacustrine brGDGT distributions and temperature calibrations, which is why pH calculation is not heavily focused on in this thesis. Furthermore, Russell et al. (2018) strongly recommends that lake-derived pH calibrations to be interpreted with caution as the degree of cyclization of brGDGTs in lakes are probably controlled by variables other than pH.

In CBT and MBT calibrations, several of the most common brGDGTs are selected as they are conjectured to have the largest influence on MAT and soil pH reconstructions due to relative quantity (De Jonge et al., 2014a). Despite this, further research needs to be made in quantifying the influences of minor brGDGT quantities in samples, as some subsidiary isomers could be indicators of distinct environmental influences or shifts, as previously theorized with the identification of the IIIa'' isomer and its potential relationship with anoxic settings in lacustrine sediments and modern water columns (Weber et al., 2015, 2018).

Redox proxies

Upon initial observations of Upper Gnarly's downcore stratigraphy, two large sections of thinly laminated dark brown to black sediment were identified and preliminarily noted as preserved intervals of lake water suboxia. Undisturbed, well-defined laminae preserved in lacustrine sediment cores can be inferred to have little to no active bioturbation from lake biota during preservation of sediment deposition. Accordingly, the presence of little to no bioturbation could indicate events of lowered available dissolved oxygen content in Upper Gnarly's water column during the Holocene (e.g. Taylor and Goldring, 1993). To affirm the presence of anoxic/suboxic conditions in Upper Gnarly Lake, I examined various redox proxies downcore.

For this reason, extensive effort was made to confirm these two observed intervals of suboxic conditions through multiple redox proxies. Previous work on Baffin Island by Camuti (2019) on Brother of Fog Lake on a lacustrine sediment core observed a large interval of suboxia for the late Holocene. Subsequently, Camuti (2019) concluded that oxygen depletion events in Arctic lake created a cold-bias in paleotemperature reconstructions produced by the brGDGT proxy, and ultimately concluded that downcore suboxic events must be considered in paleotemperature reconstruction. Therefore, the two suboxic intervals in 18UGN-03 help firstly, to determine if the effects of oxygen depletion in downcore paleotemperature reconstruction is ubiquitous in other Arctic localities, and secondly to assess the temperature reconstruction fluctuations between the oxic to suboxic transitions.

Below, I discuss the redox proxies used in the analysis of Upper Gnarly's suboxic intervals: (1) the ratio of manganese to iron (Mn/Fe), (2) the ratio of incoherent and coherent scattering (Inc/Coh) as determined by x-ray fluorescence core scanning, (3) and the ratio of Isoprenoidal GDGT 0/Crenarchaeol (GDGT-0/Cren). Previous work in a modern lake setting has shown that the sedimentary Mn/Fe ratio can be used as a high-resolution proxy to reconstruct bottom water oxygenation in lake settings (Naeher et al., 2013); additionally, other studies have observed that lower Mn/Fe ratios marked lower O_2 concentrations in the water column and higher ratios suggested higher O_2 concentrations (Wersin et al., 1991; Loizeau et al., 2001; Koinig et al., 2003; Dean and Doner, 2012; Melles, 2012; Naeher et al., 2013).

Sediments that are carbon-rich and are organic in origin, such as gyttja, have low average atomic masses, and consequently produce high incoherent (Inc) and low coherent (Coh) scattering (Fernandez 1992; Croudace et al. 2006). Previous work from Chawchai et al. 2016 assessed the validity of the Inc/Coh proxy for organic matter concentrations in multiple tropical lake settings. They found a strong correlation between the Inc/Coh ratio and total organic carbon (TOC) in lithologically variable sediment sequences. Incidentally, when organic-rich sediment layers were analyzed separately from the lithologic whole, the correlation becomes weak (Chawchai et al. 2016).

The last proxy for anoxic and suboxic conditions is the ratio of Isoprenoidal GDGT 0/Crenarchaeol (GDGT-0/Cren). GDGT-0 is the most commonly occurring GDGT and occurs in all major groups of archaea. The presence of GDGT-0 is linked to methanotrophic archaea in sites with active anaerobic oxidation of methane (Schouten et al., 2013). Recently, research by Naeher et al. (2014) found that GDGT-0 is the predominant isoGDGT produced by methanogens, and concluded that methanogens were the predominant source of GDGT-0 under eutrophic conditions in lake water columns. Additionally, Naeher et al. (2014) found that branched GDGTs and Crenarchaeol are partly derived from surface soils, so any subsequent GDGT-0 contributions in the sediment samples were methanogenic in origin. GDGT-0/Cren ratio values >2 are indicative of the presence of methanogens (Naeher et al., 2014). Ultimately, the presence of methanogens indicates lowered to extreme suboxic conditions in lake water columns, thus potentially influencing brGDGT source and distribution throughout the water column, and consequently biasing brGDGT temperature calibrations.

Although the aforementioned redox proxies will assess events of lowered oxygenation levels in the past, it is impossible to quantify past lake column oxygenation levels. To further clarify terminology, this thesis references “oxic” conditions as fully saturated dissolved oxygen concentrations, “anoxic” as no detectable oxygen concentrations, and “suboxic” as the large range of between zero to hundred percent oxygen saturation. In the biogeochemistry field, the ranges and intervals of what is considered to be suboxic or anoxia is widely contested as certain organisms vary greatly in the need for available oxygen for production.

Previous work on Baffin Island, Eastern Canadian Arctic

The Arctic circumpolar region of our planet is currently undergoing an extensive transformation in its biosphere, hydrosphere, and cryosphere as previously discussed. Despite the growing awareness of Arctic change, the remoteness of suitable sites and the short history of coverage in high-latitude regions by monitoring systems has yielded an incomplete and relatively sparse documentation compared to climate change documentation in mid- to equatorial latitudes (Overpeck et al., 1997). However, Baffin Island (*Fig. 2*) has been an area of growing interest to climate scientists and geologists because of uncommon preserved sediment records that predates the LGM and the oldest stratigraphically intact ice core by 80,000 years from the Greenland Ice Sheet (e.g. Axford et al., 2009; Andersen et al., 2004; Miller et al., 2010). Particularly, these records are exceptional for Arctic regions as the LGM Laurentide Ice Sheet eroded large remnants of terrain in the northern Canadian regions and consequently destroyed sedimentary records predating ~26,000 years BP (Briner et al., 2008; Miller et al., 2010). Well-preserved geologic records and sediment archives are critical for paleoclimate reconstruction and proxy research. Previous work on Baffin Island glaciation and ice mass loss includes research by Steig et al. (1998), Gardener et al. (2011), and Pendleton et al. (2017) with further investigation on Holocene climate and glaciation by Miller et al. (2005) and Briner et al. (2008). Continued research in Baffin Island includes paleoecology and vegetation reconstruction on Baffin Island by pollen, diatom, and algal concentration and assemblages (e.g. Wolfe et al., 2000) and radiocarbon dating of pollen and macrofossils (e.g. Frechette et al., 2006). Previous studies in interglacial and Holocene temperature reconstruction include geochemical and chironomid analysis and proxy application (e.g. Francis et al., 2006; Thomas et al., 2011), and pollen assemblage proxies (e.g. Kerwin et al., 2004).

Fig. 2. *Satellite imagery of Earth's circumpolar region focusing on Greenland and the northern Canadian Arctic. Baffin Island, Nunavut is outlined is outlined in yellow. Upper Gnarly Lake (UGN) is represented by an orange circle (Source: Google Earth)*

Methods

Lake location and site description

Upper Gnarly Lake (informal name; 67°13.3'N; 63°00.0'W) is a small arctic lake situated on Baffin Island in the Eastern Canadian Arctic (*Fig. 3*). The lake resides on northeast-jutting peninsula northwest of Duck Island and Padloping Island, and approximately 1.54 km away from Baffin Bay with the closest settlement located approximately 56 kms away in Qikiqtarjuaq, Nunavut, Canada. The lake resides in a catchment valley between two raised mountain complexes, residing at an elevation of ~375 meters. The modern climate is maritime arctic; the mean July temperature is 5.3°C (41.5°F), and the mean January temperature is -25.4°C (-13.7°F). Mean annual precipitation is 203.3 mm (8.00 in), 85.24 percent occurring as snow, recorded by Environment Canada from 1981-2010 in Qikiqtarjuaq. Upper Gnarly Lake is meters in ~0.1 km squared in surface area with a lake perimeter of ~1.31 km. Vegetation type is subpolar to polar shrubland, lichen, and moss (Commission for Environmental Cooperation; Raynolds and Walker, 2016)

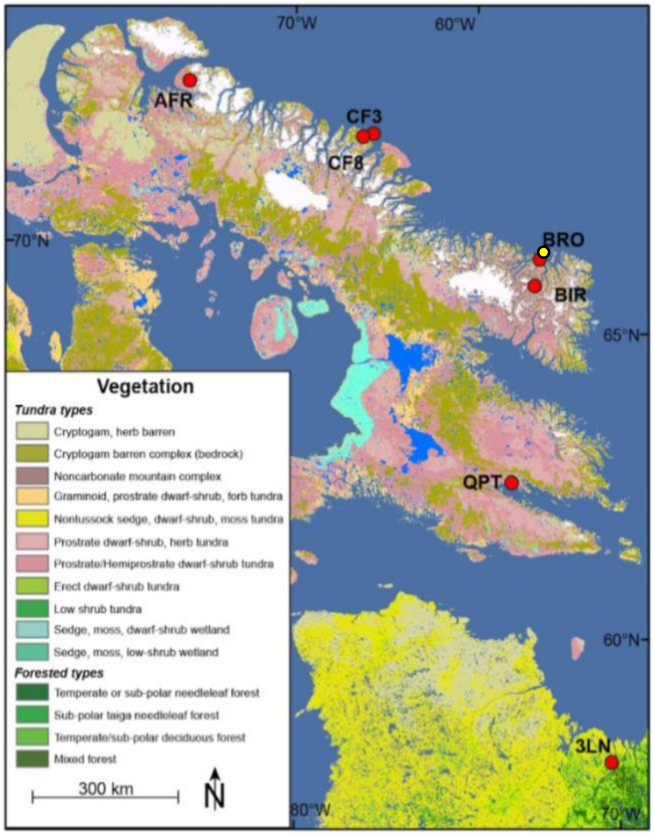


Fig. 3. *Vegetation map of Baffin Island with the location of several PACEMAP target lakes. Locations are represented by red circles. Upper Gnarly (UGN) is represented by a yellow circle. Source: North American Land Change Monitoring System (2013); Raynolds and Walker (2016)*

Upper Gnarly is northeast of other targeted PACEMAP lakes (Gnarly Lake, Brother of Fog Lake) with Gnarly Lake being the closest in proximity, approximately 1.47 km away. No lake water column chemistry such as water pH, water temperature, and dissolved oxygen

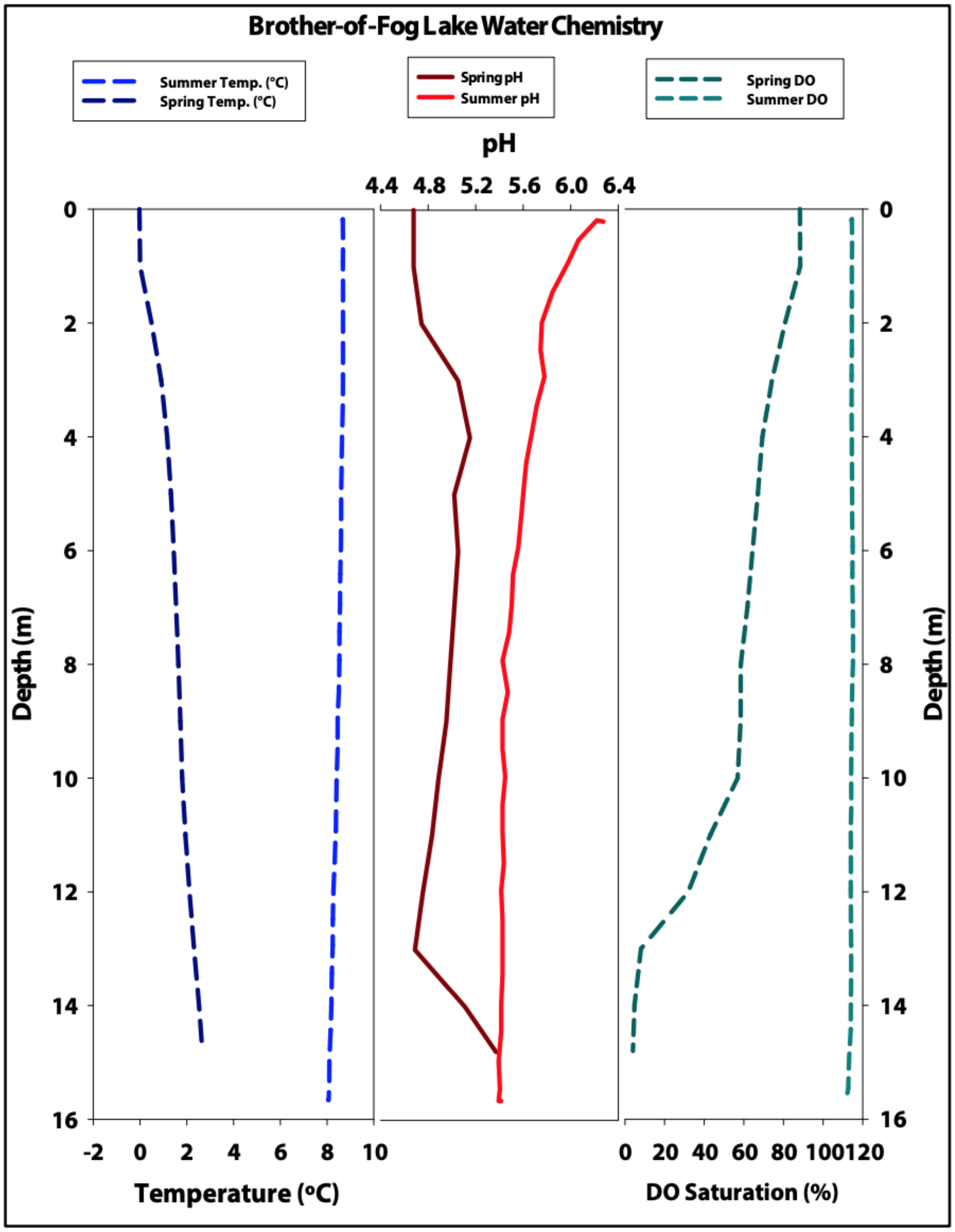


Fig. 4. *PACEMAP Brother of Fog Lake vertical water column profiles exhibiting measured spring and summer temperature, pH, and dissolved oxygen saturation (Camuti, 2019).*

saturation was recorded at Upper Gnarly. Water column chemistry was conducted at Brother of Fog Lake, approximately 6.77 km away from Upper Gnarly. Brother of Fog Lake (BRO) has a similar altitude (400m), shore line (~1.68 km), and maximum depth (16m). Given the lack of modern water chemistry data at Upper Gnarly, Brother of Fog can serve as a point of comparison to Upper Gnarly. In Brother of Fog, water temperature stayed relatively the same throughout water column depth, spring and summer water pH fluctuated between 4.5 to 6.3, with summer pH presumably less acidic due to dilution from maximum meltwater runoff (*Fig. 4*). Summer dissolved oxygen content remains consistent and fully saturated. The absence of strong temperature stratification in BRO's water column suggests that the lake is well-mixed in summer months (July/August); however, spring dissolved oxygen declines down the water column thus implying suboxia in the water column at depth in spring months, likely deriving from decreased water column mixing from lake ice cover.

Sediment coring and core description

Cores were collected cores from Upper Gnarly in May of 2018 using a modified Nesje coring method (Nesje 1992). This thesis focuses on core 18UGN-03 which was collected from the lake's deepest basin (12.41m water depth). Sediment core 18UGN-03 was collected in "hole 6" residing at (67°13'N; 62°59'W). Upon recovery, the sediment/water interface was intact and undisturbed with 131 cm of lacustrine sediment. Core pipe length totaled 135 cm. The core was packaged and secured for transport back to the University of Colorado, Boulder (UCB).

Core 18UGN-03 was split longitudinally with a Geotek Core splitter at the University of Colorado Boulder using methanol-rinsed sheet metal. A detailed core description was completed within 0.5 hour of splitting. 18UGN-03 was transported to the University of Massachusetts, Amherst for core imaging and scanning. The core was imaged and scanned for magnetic susceptibility using a Geotek Multi-sensor core scanner. An x-radiograph and high-resolution elemental data were collected using an Itrax X-ray Fluorescence (XRF) core scanner. PACEMAP sediment cores are currently stored in Core Processing Lab cold storage at 4℃ at UCB. Sediment samples were extracted from 18UGN-03 in one-centimeter length increments and subsequently weighed. *Fig. 5* below depicts stratigraphic column and core description.

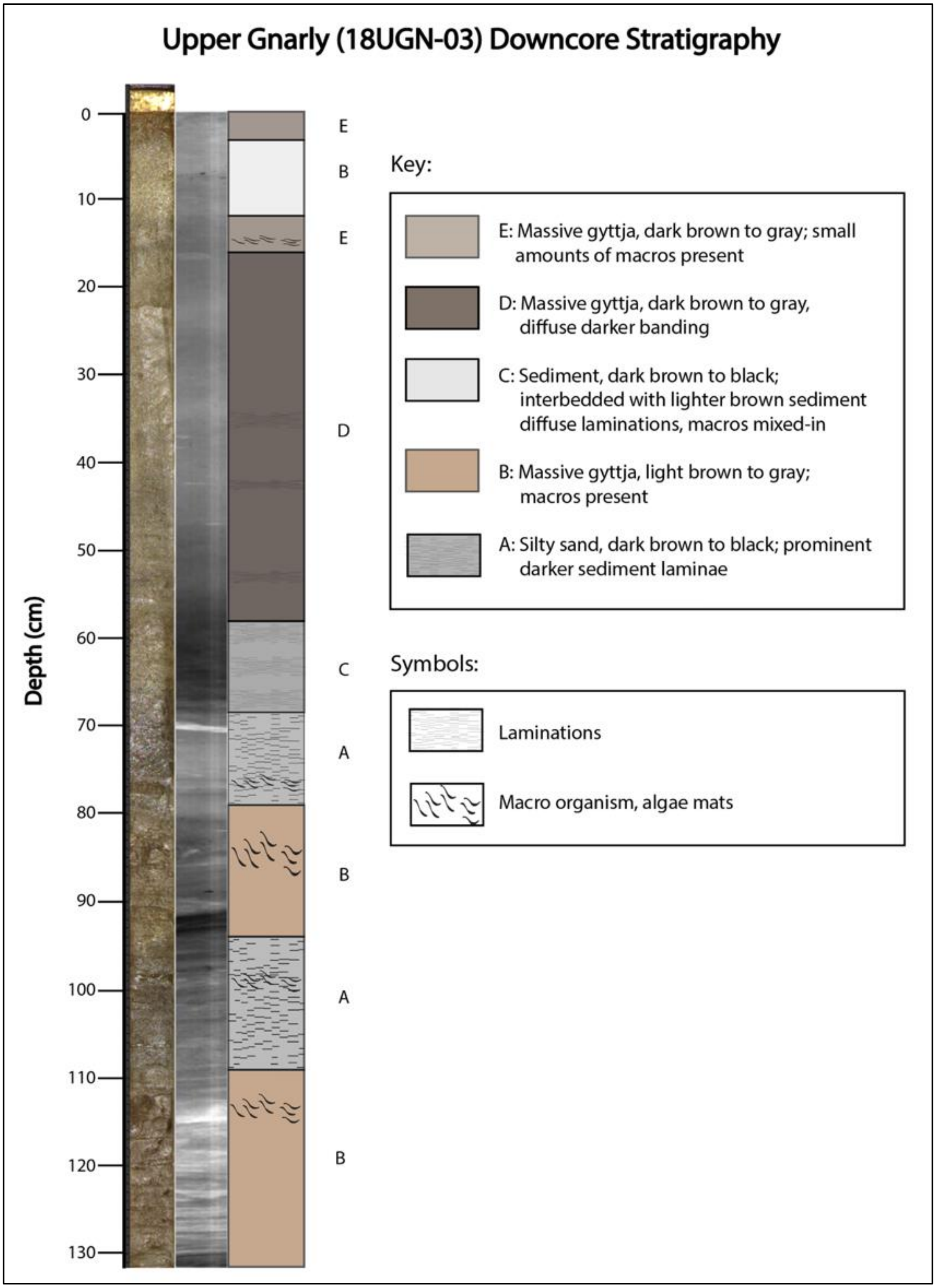


Fig. 5. *Lithostratigraphic units observed and described in core 18UGN-03 from Upper Gnarly Lake. Sediment size was estimated by observation; no grain size analysis was performed. A Geotek Multi-sensor core scanner image and an Itrax X-ray XRF image of 18UGN-03*

Bacterial lipid extraction and GDGT analysis

Samples for organic geochemical analysis were processed in the Organic Geochemistry Laboratory at UCB. Prior to lipid extraction, the homogenized soil samples were sub-sampled for Fourier Transform Infrared Spectroscopy (FTIRS) analysis at UCB. A total of 26 freeze-dried and homogenized samples (~0.21-0.48 grams) were extracted twice on a Dionex accelerated solvent extractor (ASE 200) using dichloromethane:methanol (9:1, v/v) at 100°C and 2000 psi for 40 minutes. ASE-extracted samples were then combined and concentrated to 4-ml volume of 100% TLE. The following standards were added to each sample: 10 µl of 100ng/µl C_{46} brGDGT standard; 20 µl of 0.05 µg/ml C_{36} *n-alkane* standard; 20 µl of 0.21 µg/ml C_{20},1 n-acid standard. The total lipid extracts (TLEs) were then kept for brGDGT analysis. For each 100% TLE sample, 10% TLE was archived, 85% for leaf wax analysis at the University of New York Buffalo, and 5% TLE was filtered for brGDGT analysis.

A 5% aliquot of the TLE was analyzed for brGDGTs in the Organic Geochemistry Laboratory at the University of Colorado Boulder. Dry samples were dissolved in 100 µl of hexane:isopropanol (99:1, v/v), sonicated, vortexed, and then filtered using a 0.45 µm polytetrafluoroethylene (PTFE) syringe filter. Branched GDGTs were identified and quantified via high performance liquid chromatography-mass spectrometry (HPLC-MS) following methods of Hopmans et al. (2016) on a Thermo Scientific Ultimate 3000 HPLC interphased to a Q Exactive Focus Orbitrap-Quadrupole MS. Samples were eluted on the HPLC with 18% solvent B for 25 minutes followed by a linear gradient to 35% B by 50 minutes, then another linear gradient to 100% solvent B by 100 minutes, followed by a return to 30% B by 110 minutes, where solvent A is 100% hexane and solvent B is hexane:isopropanol (99:1, v/v). brGDGTs were identified based on their molecular masses and diagnostic elution patterns (after Hopmans et al., 2016). Identification of the IIIa'' isomer peak followed procedure by Weber et al. (2018).

BrGDGT proxy: indices and calibrations

The ubiquitous presence of brGDGTs in soils has allowed for the development of proxies for modern and paleoreconstruction of climate and environmental parameters in a variety of settings. The MBT and CBT of brGDGTs are found to be controlled by MAAT and soil pH as previously aforementioned (Weijers et al., 2007).

In the past decade, numerous studies have evaluated the applicability of the CBT and MBT indices that comprise the MAAT and pH calibrations first published by Weijers et al., 2007, and subsequently altering the indices and calibrations for improved regressions in new environments gradients, ecological distributions, and geological archives (e.g. Weijers et al., 2007; Peterse et al., 2012; De Jonge et al., 2014a, 2014b; Naafs et al., 2017a, 2017b; Weijers et al., 2006b; Russell et al., 2018).

For this thesis, I applied a revised lacustrine paleotemperature calibration from Russell et al. (2018) with CBT and MBT' indices previously recalibrated by De Jonge et al. (2014a, 2014b) and soil-derived MAT calibrations developed by De Jonge et al. (2014b).

For the following indices, the roman numerals (I-III) refer to the brGDGTs indicated in *Fig. 1* and utilize chromatogram peak areas for all indices and calibration equations unless indicated otherwise. The following indices and were applied to brGDGTs extracted from 18UGN-03 samples:

For the calculation of soil pH, De Jonge et al. (2014b) refined index which includes the hexamethylated compounds and the 5-methyl and 6-methyl isomers as:

$$\mathbf{CBT'} = \frac{-\mathbf{log}\,(\mathbf{Ic} + \mathbf{IIa'} + \mathbf{IIb'} + \mathbf{IIc'} + \mathbf{IIIb'} + \mathbf{IIIc'})}{(\mathbf{Ia} + \mathbf{IIa} + \mathbf{IIIa})}$$

Additionally, De Jonge et al. (2014b) defined a CBT' index only upon 5-methyl isomers as:

$$\mathbf{CBT'_{5Me}} = -\boldsymbol{log}\left[\frac{(\mathbf{Ib} + \mathbf{IIb})}{(\mathbf{Ia} + \mathbf{IIa})}\right]$$

For MAAT calibrations, De Jonge et al. (2014b) redefined the MBT' index to include the 6-methyl isomers:

$$\mathbf{MBT'} = \frac{(\mathbf{Ia} + \mathbf{Ib} + \mathbf{Ic})}{(\mathbf{Ia} + \mathbf{Ib} + \mathbf{Ic} + \mathbf{IIa} + \mathbf{IIa'} + \mathbf{IIb} + \mathbf{IIb'} + \mathbf{IIc} + \mathbf{IIc'} + \mathbf{IIIa} + \mathbf{IIIa'})}$$

And defined an MBT' index excluding 5-methyl isomers as:

$$\mathbf{MBT'_{5Me}} = \frac{(\mathbf{Ia} + \mathbf{Ib} + \mathbf{Ic})}{(\mathbf{Ia} + \mathbf{Ib} + \mathbf{Ic} + \mathbf{IIa} + \mathbf{IIb} + \mathbf{IIc} + \mathbf{IIIa})}$$

Finally, De Jonge et al. 2014b developed a MAAT calibration based upon Index 1 which was generated from regression analysis as indicated below:

$$\mathbf{Index\ 1} = \boldsymbol{log}\left[\frac{(\mathbf{Ia} + \mathbf{Ib} + \mathbf{Ic} + \mathbf{IIa'} + \mathbf{IIIa'})}{(\mathbf{Ic} + \mathbf{IIa} + \mathbf{IIc} + \mathbf{IIIa} + \mathbf{IIIa'})}\right]$$

Previously generated MAAT calibrations have focused on temperature reconstructions based on peat-based calibrations (Naafs et al., 2017a), river particulate-based (De Jonge et al., 2014a), and global soil-based calibrations (Weijers et al., 2007; Peterse et al., 2012; De Jonge et al. 2014b). The following MAAT calibrations chosen for analysis derived from an lacustrine surface sediment calibration from East African lakes (Russell et al., 2018) and MAAT calibrations developed by De Jonge et al. (2014b). Residual mean standard error (RMSE) for each calibration are included. De Jonge et al. (2014b) temperature calibrations using the MBT'_{5Me} index with an RMSE of 4.8℃:

$$\mathbf{MAAT = -8.57 + 31.45 \times MBT'_{5Me}}$$

De Jonge et al. (2014b) calibration using Index 1 with an RMSE of 4.7℃:

$$\mathbf{MAAT = 5.05 + 14.86 \times Index\ 1}$$

Additionally, this thesis used novel lake calibrations from Russell et al. (2018) that utilize the aforementioned indices from De Jonge et al. (2014b). The following calibration excludes 6-methyl isomers and has an RMSE of 2.44℃:

$$\mathbf{MAAT = -1.21 + 32.42 \times MBT'_{5Me}}$$

Russell et al. (2018) calibration utilizing Index 1 with a RMSE of 2.47℃:

$$\mathbf{MAAT = 12.22 + 18.79 \times Index\ 1}$$

Russell et al. (2018) developed the new stepwise forward selection (SFS) calibration from a multivariate regression of brGDGT fractional abundances against MAAT, adding each brGDGT variable one at a time and found the following calibration with the least regression error and an RMSE of 2.14℃:

$$\mathbf{MAAT = 23.81 - 31.02 \times IIIa - 41.91 \times IIb - 51.59 \times IIb' - 24.70 \times IIa + 68.80 \times Ib}$$

Results

The sediment core 18UGN-03 was observed to have five distinctive stratigraphic sections, largely containing sections of massive gyttja and silty sand laminated sediment layers with thin, but notable algal mats and macro organisms (*Fig. 5*). From the 33 extracted sediment samples from core 18UGN-03, the total lipid extract (TLE) samples ranged from 1.32 mg to 10.09 mg and yield an average 5.64 mg per section analyzed. After TLE extraction and brGDGT chromatographic analysis, the total brGDGT concentrations of sediment samples ranged from 14.27 ng/g to 126.23 ng/g of sediment extracted and yield an average of 70.92 ng/g.

With the CBT' calibration for soil pH (De Jonge et al., 2014b), reconstructed pH averaged at 7.15 (RSME = 0.90. The soil pH calibration derived from the De Jonge et al. (2014) CBT'_{5Me} index yielded an average reconstructed pH of 5.55 (RMSE = 0.58). After applying the calibration by Russell et al. (2018) for surface water pH, pH averaged at 8.95 (RMSE = 0.80).

The average MBT' index used for MAAT reconstruction yielded 0.1085. The MBT' index continually increased from 0.0699 at 129 cm depth to 0.1179 at 4 cm depth. Notably, significant drops in MBT' from 0.0761 at 104 cm to 0.0806 at 69 cm depth. The average MBT'_{5Me} index was 0.1179 and generated MBT'_{5Me} values higher than the MBT' calibration. The MBT'_{5Me} calibration followed the same negative trend of decreasing MBT'_{5Me} values with core depth with a peak value of 0.1541 at 4 cm depth and the lowest value of 0.0766 at 129 cm depth; additionally, the MBT'_{5Me} showed two distinct valleys like MBT' calibration with 0.0857 at 69 cm depth and 0.0819 at 104 cm depth.

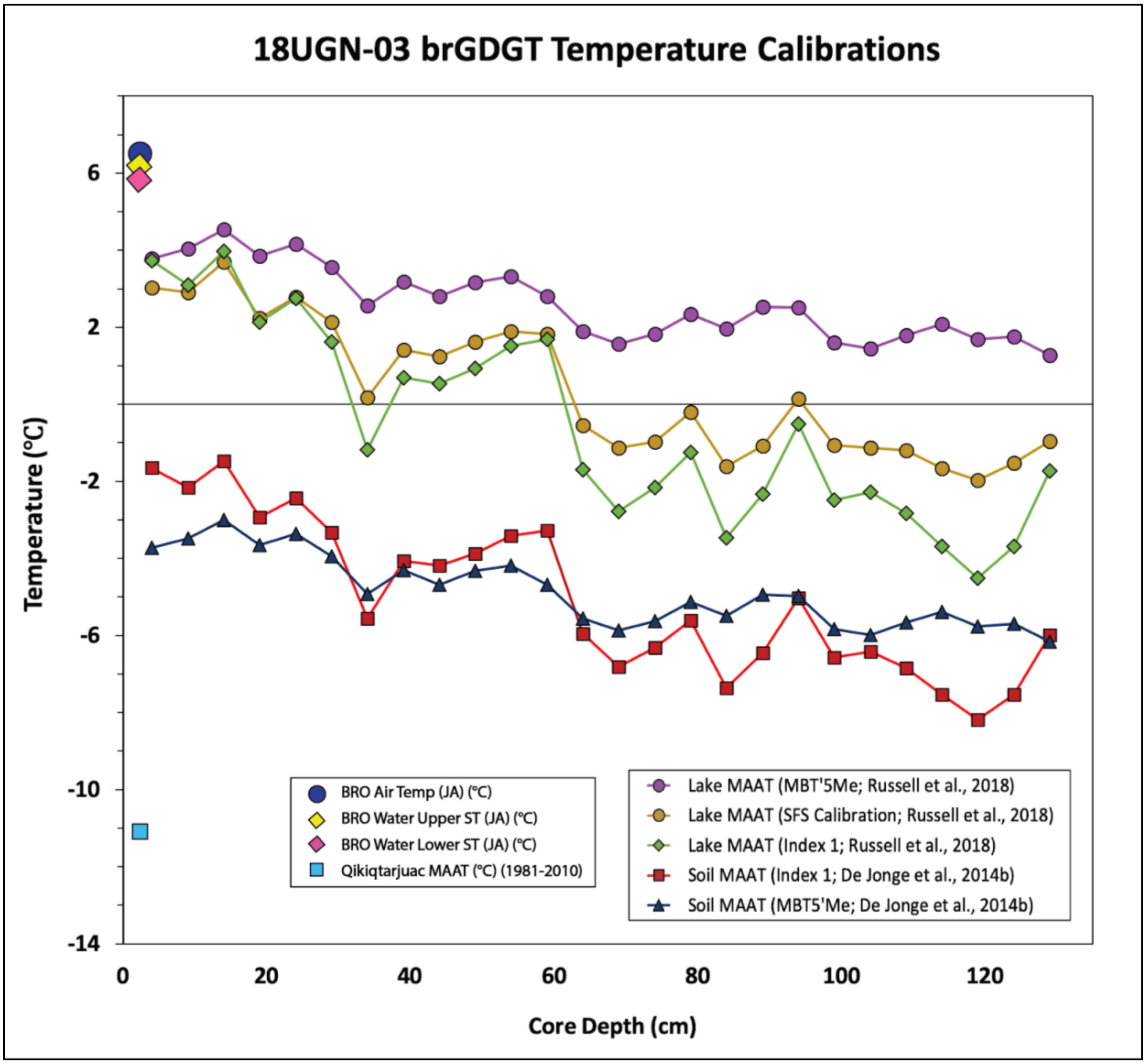


Fig. 6. *Results of the Holocene brGDGT paleotemperature reconstructions from Upper Gnarly comparing various brGDGT calibrations from De Jonge et al. (2014) and Russell et al. (2018). Modern climatic data is plotted for*

In 18UGN-03, the most abundant brGDGT was IIIa which yielded an average of 56.2% abundance throughout the core; notably, IIIa abundances generally increased downcore with a jump in abundance from ~54.2% at 59 cm depth to ~63.1% at 64 cm depth. The second most abundant brGDGT was IIa with an average 24.0% downcore followed by brGDGT Ia at 10.1% abundance (*Fig. 11*). The presence of the novel IIIa'' was identified in intervals of 9-24 cm depth and then 39-54 cm depth. Comparing brGDGT-derived temperature reconstructions (*Fig. 6*), the temperature record from the lake-derived MBT'_{5Me} Russell et al. (2018) calibration shows the highest temperature gradient when compared to the temperature records from the Russell et al. (2018) SFS calibration, Index 1 calibration, and De Jonge et al. (2014)'s Index 1 and MBT'_{5Me} calibrations. Modern lake data for BRO Lake mean summer air temperature of 6.35°C, BRO Lake mean summer upper surface temperature (ST) of 6.8°C, and BRO mean lower ST of 5.8°C all plot above all temperature records from the calibrations. MAAT for Qikiqtarjuac from 1981-2010 plotted at -11.1°C, and consequently is plotted well below all temperature calibrations.

Discussion

To discern the validity of a cold-bias in the brGDGT temperature reconstructions from suboxic conditions, I discuss various environmental factors in the following discussion sections. Modern temperature and brGDGT data from other Baffin sites are compared to the data in this thesis to better understand variation in regional Arctic climate change and in-lake factors.

BrGDGT sources in Upper Gnarly Lake

Analysis of the distribution of brGDGTs in Upper Gnarly sediment samples suggest that with the distribution in the suite of brGDGT production at Upper Gnarly there is a bias in temperature signals from bacterial sources. Currently, there is a fundamental gap in our understanding of what environmental and ecological factors influence the habitation of brGDGT-producing bacteria and what factors produce that change in brGDGT membranes (Weber et al., 2018). In the evaluation of current paleotemperature reconstruction calibrations, it is critical to consider brGDGT source production when creating new calibrations as brGDGT distributions change depending on bacteria production origin. For example, tetramethylated brGDGTs increase from lakes to soils to peats (Loomis et al., 2014b; Naafs et al., 2017a; Russell et al., 2018). Additionally, past analyses with global datasets evaluating brGDGT distribution shows that lake sediments often contain less tetramethylated brGDGTs and more hexamethylated compounds than their corresponding soil catchments (Loomis et al., 2014b, 2014a; Buckles et al., 2014) with water-logged soils reporting to have a brGDGT distribution more affiliated to lakes (Loomis et al., 2014). Notably, brGDGTs settling through the water column are comparable to brGDGT accumulation rates in surface sediments in a temperate setting (Loomis et al., 2014a). Considering this, brGDGT distributions in soil samples and water filtrates from BRO and CF8 are relatively analogous. Additionally, brGDGT fractional abundances of aquatic environments, particularly lake settings, can differ strongly from catchment soils indicating in-situ production of brGDGTs in lake settings (Tierney and Russell, 2009; Tierney et al., 2010; Zink et al., 2010; Buckles et al., 2014; Loomis et al., 2012, 2014a, 2014b; Pearson et al., 2011; Lei et al., 2016).

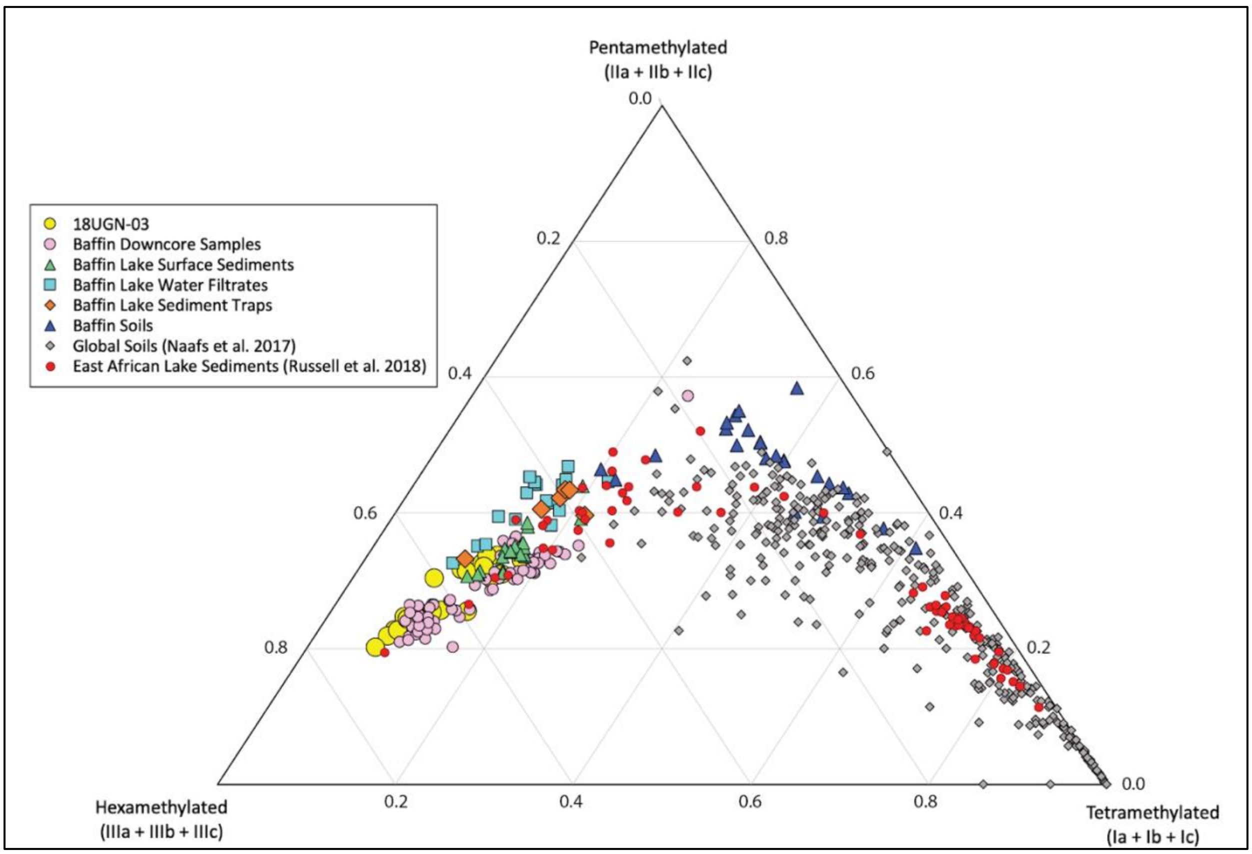


Fig. 7. *Ternary diagram comparing Upper Gnarly tetramethylated, pentamethylated, and hexamethylated brGDGTs against other downcore and modern Baffin Island lake samples, East African lake sediments from Russell et al. (2018, and global soils from Naafs et al. (2017)*

The cross comparison of lacustrine versus soil brGDGTs in a ternary diagram allows for sample differentiation and preference for tetramethylated, pentamethylated, and hexamethylated brGDGTs (*Fig. 7*). The distribution of brGDGTs downcore from 18UGN-03 appears most similar to other downcore (pink circles) and surface lake sediment samples (green triangles) from Baffin Island and overlaps with the lacustrine dataset of Russell et al. (2018) (red circles). The distributions throughout the entire 18UGN-03 are quite different from soil samples from Baffin Island (blue triangles) and the global soil dataset of Naafs et al. (2019) (gray diamonds). This suggests that the source of brGDGTs in Upper Gnarly sediments has not changed dramatically over the Holocene and does not appear to have been influenced greatly by soil bacteria. In the comparison of 18UGN-03 with other downcore lacustrine sediment samples, modern Baffin monitoring, and compiled datasets from Russell et al. (2018) lake sediments and Naafs et al. (2017b), 18UGN-03 brGDGTs are concluded to be dominantly produced in-situ in an aquatic setting.

BrGDGT production sources need to be considered in future lacustrine brGDGT temperature calibrations production locality and brGDGT source mixing is a large factor in addition to MAAT that influences the fractional abundance of brGDGTs, and ultimately the MBT indices that are used in temperature reconstruction.

BrGDGT temperature reconstructions

In this thesis, five brGDGT MAAT calibrations were tested with 18UGN-03 downcore lacustrine sediment samples. All temperature reconstructions from each calibration resulted in colder mean annual summer temperatures in the early Holocene. The temperature records from the Russell et al. (2018) calibration yields the most comparable to modern summer air and lake temperature values recorded at BRO Lake (*Fig. 6*). However, the negative linear relationship among all temperature calibrations contradicts evidence for past Early Holocene warming in the Arctic. This directly opposes evidence for a warm Early Holocene as average MAAT would have been greater in response to the larger amounts of solar insolation received by Arctic

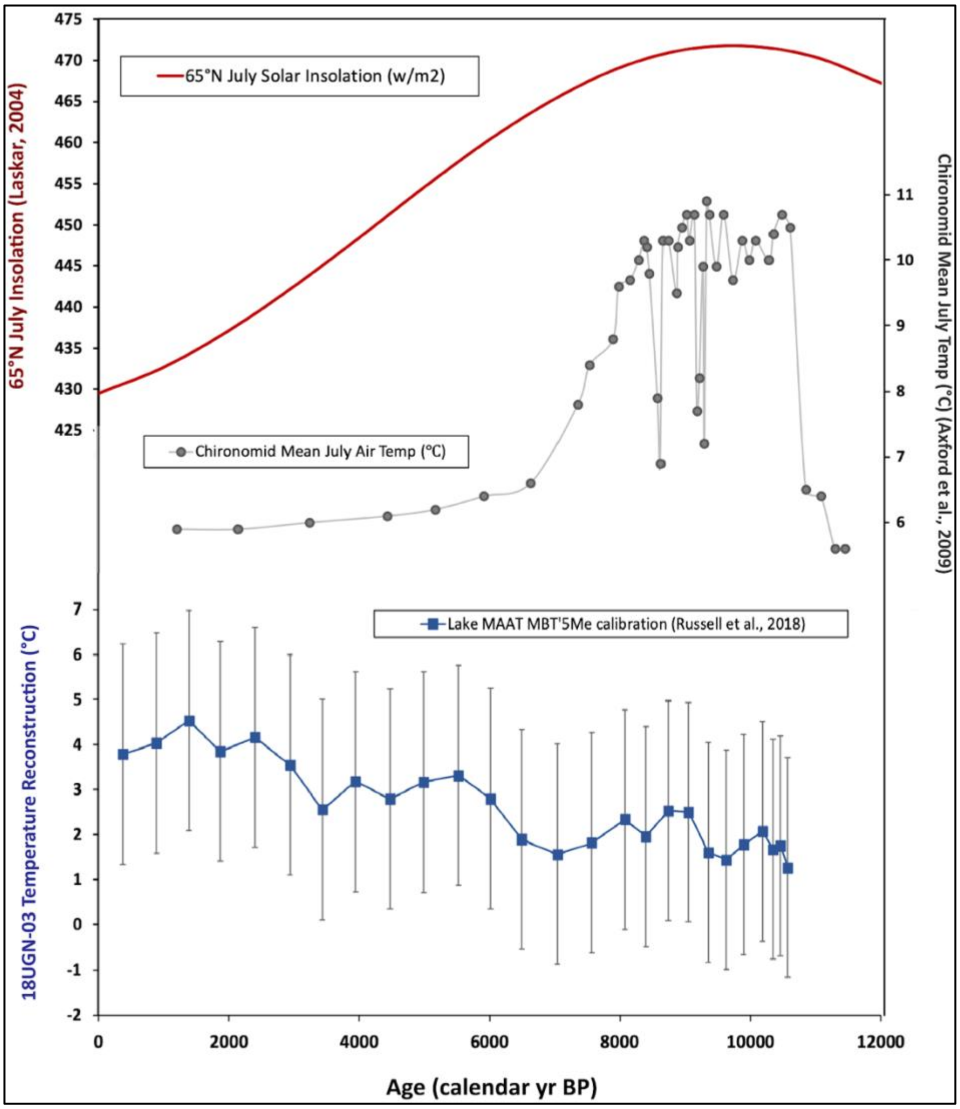


Fig. 8. *Comparison of Arctic solar insolation, Arctic temperature reconstruction derived from a chironomid proxy, and Upper Gnarly brGDGT temperature reconstruction. Arctic Holocene temperatures peaked around 10-12,000 BP (Kaufman et al., 2004)*

latitudes around the HTM (*Fig. 8*). This suggests there are multiple environmental or ecological factors contributing to the cold-bias reconstructions evident downcore (see “suboxic conditions as a cold-bias” section). The De Jonge et al. (2014b) temperature calibrations and MBT and CBT indices are based on globally distributed surface soils from Weijers et al. (2006b) and Peterse et al. (2012) with 16 surface soils (n= 239) sampled from regions relatively adjacent or in arctic latitudes. Russell et al. (2018) calibrations were calibrated on East African lake sediments, which were shown to have a better correlation to colder lakes than from other soil calibrations. Although the Russell 2018 calibration is the most updated lacustrine MAAT calibration, it is not directly calibrated for an Arctic lake setting. The East African lakes sampled vary in area, depth, oxygen saturation, ecological biota, and do not experience seasonal ice cover, and thus ultimately do not experience water column temperature stratification to the degree that Arctic lakes experience.

For further discussion, although Pearson et al. (2011) developed an Arctic lacustrine brGDGT MAAT calibration, this thesis did not test the validity of that calibration largely in part because the calibration was created before the brGDGT isomer separation was feasible. Additionally, this thesis did not test brGDGT calibrations based on the CBT and CBT' indices, nor evaluated the CBT index in for soil pH reconstruction. De Jonge et al. 2014b found that temperature calibrations with the CBT'_{5Me} index no longer contribute significantly to MAAT reconstructions. Subsequently, Russell et al. (2018) found the CBT' index in the calculation of soil pH likely does not have a major effect on lacustrine brGDGT distributions and temperature calibrations; furthermore, Russell et al. (2018) strongly recommends that lake-derived pH calibrations to be interpreted with caution as the degree of cyclization of brGDGTs in lakes are probably controlled by variables other than pH.

BrGDGT temperature comparison with modern data on Baffin Island

In order to assess the validity of the brGDGT temperature reconstructions in an Arctic lake environment, modern environmental data from Baffin Island must be compared to the reconstructed temperatures in the earlier section of 18UGN-03. The mean summer (July and August months) air temperature on Baffin Island was recorded at 6.35°C (*Fig. 6*). The first reconstructed temperature from 18UGN-03 from the first sampled depth of 4-5 cm is 3.78°C, which radiocarbon dating and BACON age model places that temperature reconstruction around 374.5 cal yr BP. Each of temperature records derived from each of the Russell et al. (2018) calibrations RMSE is in range with the 4-5cm depth reconstruction when compared to BRO's average summer air temperature of 6.35°C, BRO Lake mean summer upper surface temperature (ST) of 6.8°C, and BRO mean lower water temperature of 5.8°C. However, the MAAT recorded in Qikiqtarjuaq is substantially lower –11.1°C when compared to the temperature trends derived from the Russell et al. (2018) and De Jonge et al. (2014b) calibrations. Conversely, the modern recorded MAAT at Qikiqtarjuaq is obviously colder due to the extended winter season on Baffin Island, and brGDGT temperature reconstructions likely record summer temperatures (July/August) as brGDGT production is presumed to be higher in the water column (Pearson et al., 2011). Although the temperature records derived from the applied calibrations have large RMSE and do not match modern records, the temperature reconstructions are ultimately within a reasonable scope for past Arctic Baffin Island temperatures (*Fig. 6*).

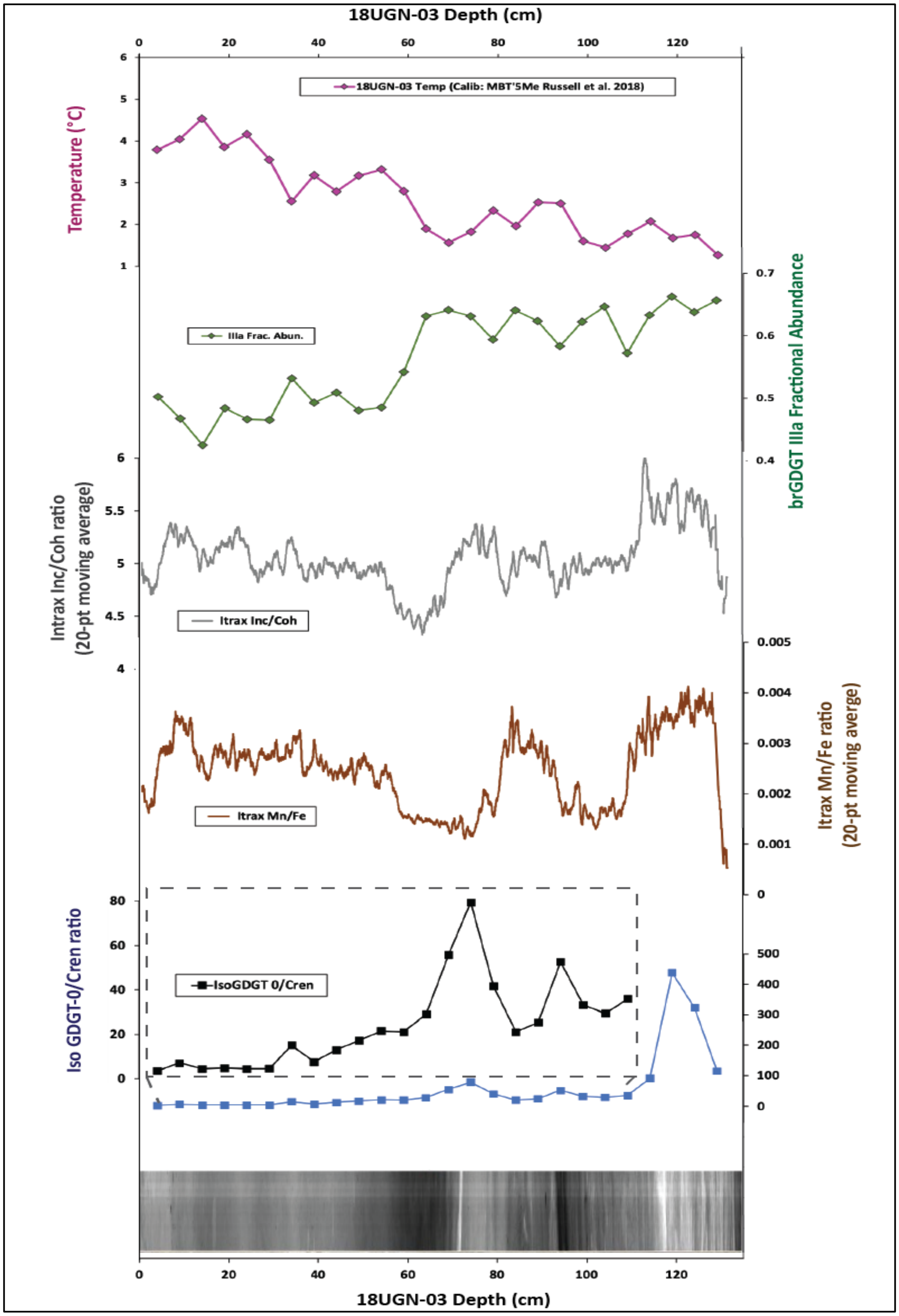


Fig. 9. *Comparison of Upper Gnarly downcore MAAT, brGDGT IIIa fractional abundance, Mn/Fe ratio values, Inc/Coh ratio values, and isoGDGT-0/Crenarchaeol ratio values. The trends represent changes over ~11,000 years with the two suboxic intervals identified as core depth 58-86 cm and 95-109 cm. The two suboxic intervals span ~5,900-8,500 BP and ~9,100-9,900 BP., respectively*

BrGDGT temperature comparison with proxy data and other Baffin sites

The 18UGN-03 temperature reconstructions do not correlate with summer solar insolation curve (Lasker, 2004) which shows that the Arctic received peak solar insolation around 9-10,000 yrs BP and a steady decline in insolation to the present. Chironomid proxy temperature reconstructions from Axford et al. (2009) correlates strongly mean summer temperatures with peak Holocene solar insolation; similarly showing responses in temperatures coincidently with warming and cooling after the HTM (*Fig. 8*). Additionally, temperature reconstructions from archive records and proxy data collected from 73 global distributed sites with archive data recording the last 11,300 years comparatively support Holocene temperature reconstructions trends like Axford et al. (2009) (see Marcott et al., (2013) and original authors within). The proxy temperature reconstructions from Axford et al. (2009) and Marcott et al. (2013) further demonstrates that the brGDGT temperature reconstructions calibrated from 18UGN-03 are anomalous, and consequently allude to other environmental or in-situ mechanisms resulting in the early Holocene cold-bias temperature response.

Applications of brGDGTs temperature reconstructions at similar sites on Baffin Island reveal similar cold-bias reconstructions for the early Holocene like 18UGN-03. At BRO lake (core 18BRO-25) and Lake CF8, temperature trends derived from the Russell et al. (2018) calibration reveal a reduction in summer temperature back through the Holocene (de Wet unpublished data; Camuti, 2019) (*Fig. 10*). Notably, records from BRO and CF8 indicate similar patterns of strongly laminated sediments in the bottom records of the cores that coincide with the cold-biased temperature reconstructions, as well as indications of suboxic conditions in those ranges similar to 18UGN-03. This will be further discussed in the sections below.

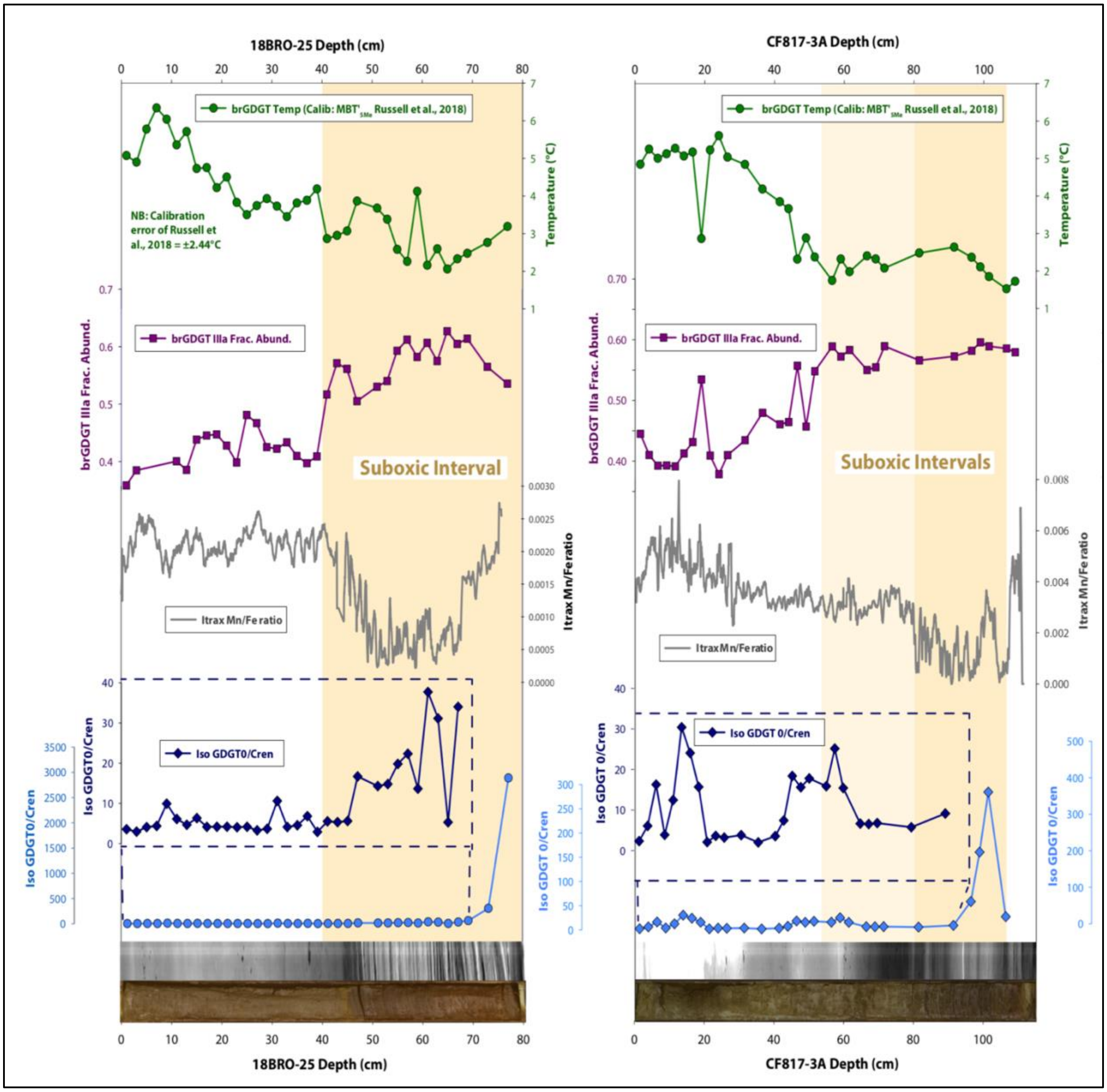


Fig. 10. *Side-by-side comparison of brGDGT MAAT temperature reconstructions derived from Russell et al. (2018) calibration compared to IIIa fractional abundance, Mn/Fe, Inc/Coh, GDGT-O/Cren ratio values. Suboxic intervals are identified by the yellow zones. (Source: de Wet unpublished, 2019)*

Suboxic conditions as a cold-bias

Although previous research has identified a link between suboxic to anoxic lake water conditions and changes in brGDGT distributions in modern environments (e.g. Weber et al., 2018), the impact of changing oxygen levels on brGDGTs in lacustrine sediment cores is less understood. In a recent study that utilized at a Holocene Arctic lake sediment core from Greenland, Kusch et al. (2019) could not explain the distribution of brGDGTs and associated anomalously cool Holocene brGDGT temperatures; they hypothesize that changes in deep bottom water oxygenation could have influenced brGDGT production. In this section, I discuss the resulting cold-bias in paleotemperature reconstructions from lowered oxygenation conditions.

Although Upper Gnarly's Mn/Fe ratios fluctuate greatly within a range from ~0.0015 to 0.004, there are distinctive patterns present in the early Holocene. Specifically, there are two intervals where the Mn/Fe ratio values lowered by ~0.001 from depth intervals of ~56-80 cm, and secondly ~90-110 cm (*Fig. 9*). As noted above, lower Mn/Fe ratios suggest reduced dissolved oxygen concentrations in lake water columns (Naeher et al., 2013). Additionally, Upper Gnarly shows lowered Inc/Coh ratios during those two suboxic intervals distinguished by the low Mn/Fe ratio values. There are apparent trends of decreasing Inc/Coh ratios coinciding with the on-set of perceived suboxic conditions from the Mn/Fe. In the first observed anoxic zone ranging from 109 cm to 95 cm, the Inc/Coh ratio gradually lowers from ~5.1 to ~4.6, respectively (*Fig. 9).* Before this suboxic event, the Inc/Coh is ~5.9 at a depth of 112 cm. In the second suboxic event, the Inc/Coh ratio reaches the lowest values for the entire core, but spans a smaller range of depth from ~52 to 62 cm. The Inc/Coh organic material proxy previously aforementioned suggests that in these two intervals of lowered Inc/Coh ratio, there was less organic matter that was preserved in the sediment record (Chawchai et al. 2016). Lower organic matter values can occur with lower levels of organic matter preservation in the lake sediments or lower levels of biological production in the water column (possibly from lowered dissolved oxygen levels in the water column or a general decline in temperature). However, I expect the lower Inc/Coh values at Upper Gnarly to be a result from lowered biological activity in the lake on the grounds that in anoxic conditions at the sediment/water interface there will be an increase in organic matter preserved in sediments as the organic matter cannot decay with the presence of high oxygen concentrations.

Lastly, the GDGT-0/Cren ratio, a proxy for methanogenesis in aquatic settings (Naeher et al., 2014), shows three distinct peaks of higher values: (1) ratio of ~438.3 around 119 cm core depth; (2) ~52.7 ratio at 94 cm depth; and (3) ~79.5 ratio at 74 cm depth. Although all GDGT-0/Cren ratios throughout 18UGN-03 are greater than the >2 ratio anoxia values assigned by Naeher et al. (2014), the three distinct ratio values are more indicative of the presence of extensive methanogenesis and associated low oxygen conditions in those intervals. Coincidentally, the ratios at the 74 cm and 94 cm core depth are within the suboxic intervals identified by lower Mn/Fe and Inc/Coh values. Broadly, changes in the ratio of GDGT-0/Cren do not always align with the changes in the Mn/Fe ratio values. It is possible there were singular events of heightened eutrophication preserved in the sediment (*Fig. 9*). But it is important to consider the recorded concentrations of GDGT-0 and Crenarchaeal in these three distinct events. That being said, the amounts GDGT-0 from ~6,490 to 11,000 years BP are on average ~49 percent higher than GDGT-0 amounts ~6,490 to 0 years BP with the highest ratio recording the largest quantity of GDGT-0 and with one of the lowest quantities of Crenarchaeal preserved in the core. The other two higher ratio peaks have relatively high concentrations GDGT-0, but moderate amounts of Crenarchaeal as compared to the collective group. In any event, caution must be advised when emphasizing one particular redox proxy over another as well as taking ratio amounts at face value. A singular value or ratio could indicate a unique ecological or hydrological change at one particular event in the lake's history, so it critical to examine the values and ratios against each other and within a larger trend.

As previously aforementioned, the initial observations of 18UGN-03's downcore stratigraphy, two large sections of thinly laminated dark brown to black sediment were identified and preliminarily noted as preserved intervals of lake water sub/anoxia (*Fig. 5*). The deeper anoxic section ranges from ~95-109 cm depth and the second section ranges from 58-86 cm depth. Each redox proxy (Mn/Fe, GDGT-0/Cren) with the organic matter proxy (Inc/Coh) shows strong evidence that preliminary interpretation of the dark, laminated intervals as representing suboxic conditions in 18UGN-03 are correct, and that two suboxic to anoxic events occurred in the early Holocene.

Although the application of Russell et al. (2018) brGDGT temperature calibration shows an overall cold-biased temperature reconstruction for Arctic lakes over the Holocene, specifically during the HTM; there are two particular dips in temperature that do not follow the gradual warming linear trend (*Fig. 8*). These two dips occur from 64-73 cm and 99-114 cm depth and exclusively occur in the aforementioned suboxic intervals. This provides further evidence that suboxic conditions within the lake water column will produce a cold-bias in brGDGT temperature reconstructions. It is even more important to note that the two troughs in the paleotemperature reconstructions are present in all the brGDGT temperature reconstructions with increases in temperature in-between the suboxic intervals (*Fig. 6*). In BRO and CF8, declining temperatures occur in observed suboxic intervals previously identified by Camuti (2019) and de Wet (2019) (*Fig. 10*).

Other in-situ mechanisms as a cold-bias

As previously discussed, a greater understanding of what environmental and ecological parameters influence the production of all 15 brGDGTs is needed (Weber et al., 2018) An observation made previously with the distribution of brGDGTs at BRO and CF8 recognized that brGDGT IIIa abundance increases downcore. The same observation occurs in 18UGN-03 as the fractional abundance of IIIa increases from 0.54 at 59 cm depth to 0.63 at 64 cm depth. Based on 18UGN-03 radiocarbon dating and the BACON age model, this shift in IIIa abundances occurs around ~6,000-6,400 year BP, which is around the presumed start for Holocene neoglaciation (*Fig. 8*) (Kaufman et al., 2004).

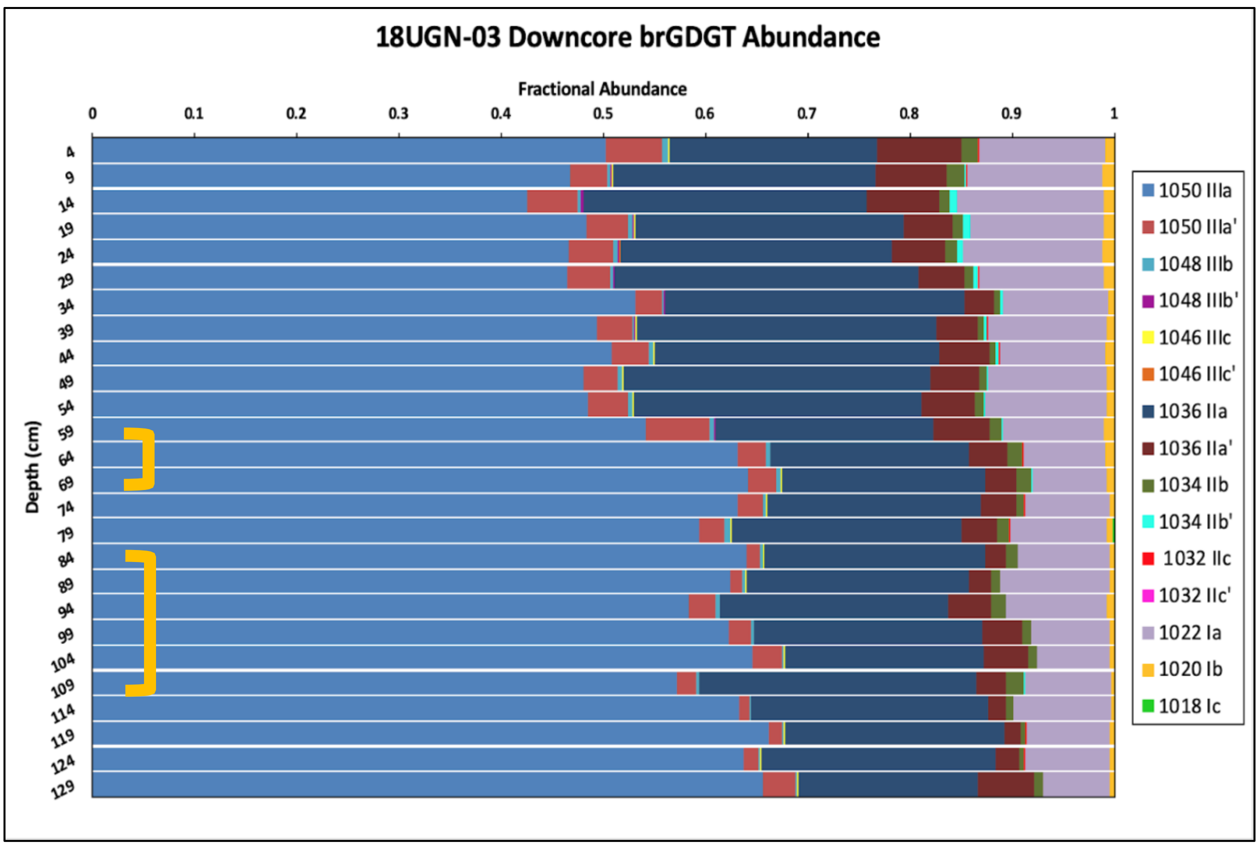


Fig. 11. *Comparison of the fractional abundances downcore at Upper Gnarly over the Holocene. The yellow bracket marks the intervals of lowered oxygen levels in the core.*

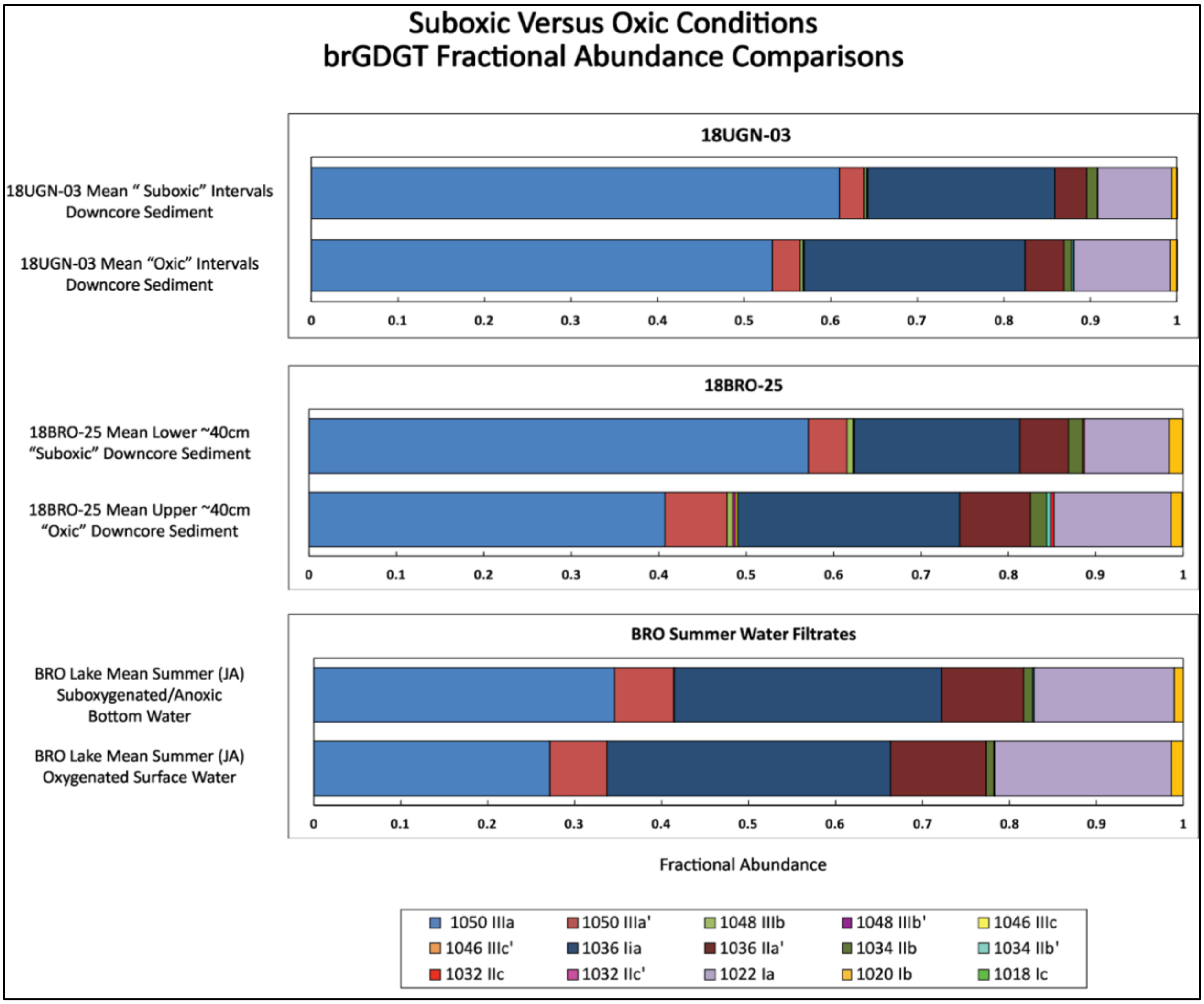


Fig. 12. *BrGDGT fractional abundances in oxic versus suboxic intervals in the Upper Gnarly core as compared to Brother of Fog (BRO) downcore oxic and suboxic intervals. Modern BRO lake brGDGTs water column abundances show a similar trend of brGDGT IIIa increasing in suboxic intervals as compared to the downcore comparisons.*

Additionally, there are distinct and consistent variations in the fractional abundances when comparing Upper Gnarly's oxic intervals with suboxic/anoxic intervals. The combined suboxic/anoxic intervals display notable patterns such as a decrease in IIa and Ia fractional abundances with a distinct increase in IIIa fractional abundance increases in collective (*Fig. 12*); likewise, both downcore samples from suboxic intervals in the BRO sediment record as well as modern water filtrates from low-oxygen lake water increased brGDGT IIIa abundances (*Fig.12*). Weber et al. (2018) conducted an analysis of fractional abundance in Lake Lugano, Switzerland

and found that fractional abundance of IIIa increased across the redox transition zone (RTZ) to higher values in anoxic lake water. Additionally, they found that brGDGT IIIa' was most abundant within oxygenated waters above the oxic-anoxic interface. In the lower part of the core, the abundance of brGDGT IIIa increases when temperature dips; conversely, lower IIIa abundance is correlated with higher temperature values (*Fig. 8*). This trend is also evident in reconstructions from the nearby Baffin lakes (*Fig. 10*). In all cases, it appears that higher brGDGT IIIa fractional abundances are associated with suboxic conditions. In *Fig. 13* which compares Upper Gnarly's brGDGT concentration with IIIa fractional abundance and the temperature reconstruction trend, there is a distinct dip in IIIa abundance from 64cm to 54cm depth. Based on the age model constructed from radiocarbon dating, IIIa decreases by 18 percent from ~6,490 to 5,521 years BP; this change occurs around the widely accepted range of neoglacial cooling in the Arctic. It is possible that brGDGT IIIa is an environmental or ecological threshold marker that indicates a substantial environmental or climatic shift in an Arctic environment.

Weber et al. (2018) determined that the type of deep water bacterial community influenced brGDGTs, especially in their anoxic bottom water setting. Additionally, Weber et al. (2018) noted that the presence of the novel brGDGT IIIa" was exclusively present in the anoxic water column zones, and remarked that presence of IIIa" is an indicator of anoxic water conditions. This thesis did find small concentrations of IIIa"; however brGDGT IIIa" was identified in the upper part of the core and not preserved in the two suboxic intervals downcore. This finding further complicates our understanding and perceptions of brGDGT production.

Ultimately, this thesis could not differentiate whether the overall early Holocene cold-bias and the specific suboxic interval cold-biases are brGDGT generation from a different suite of bacteria in the water column at those time intervals.

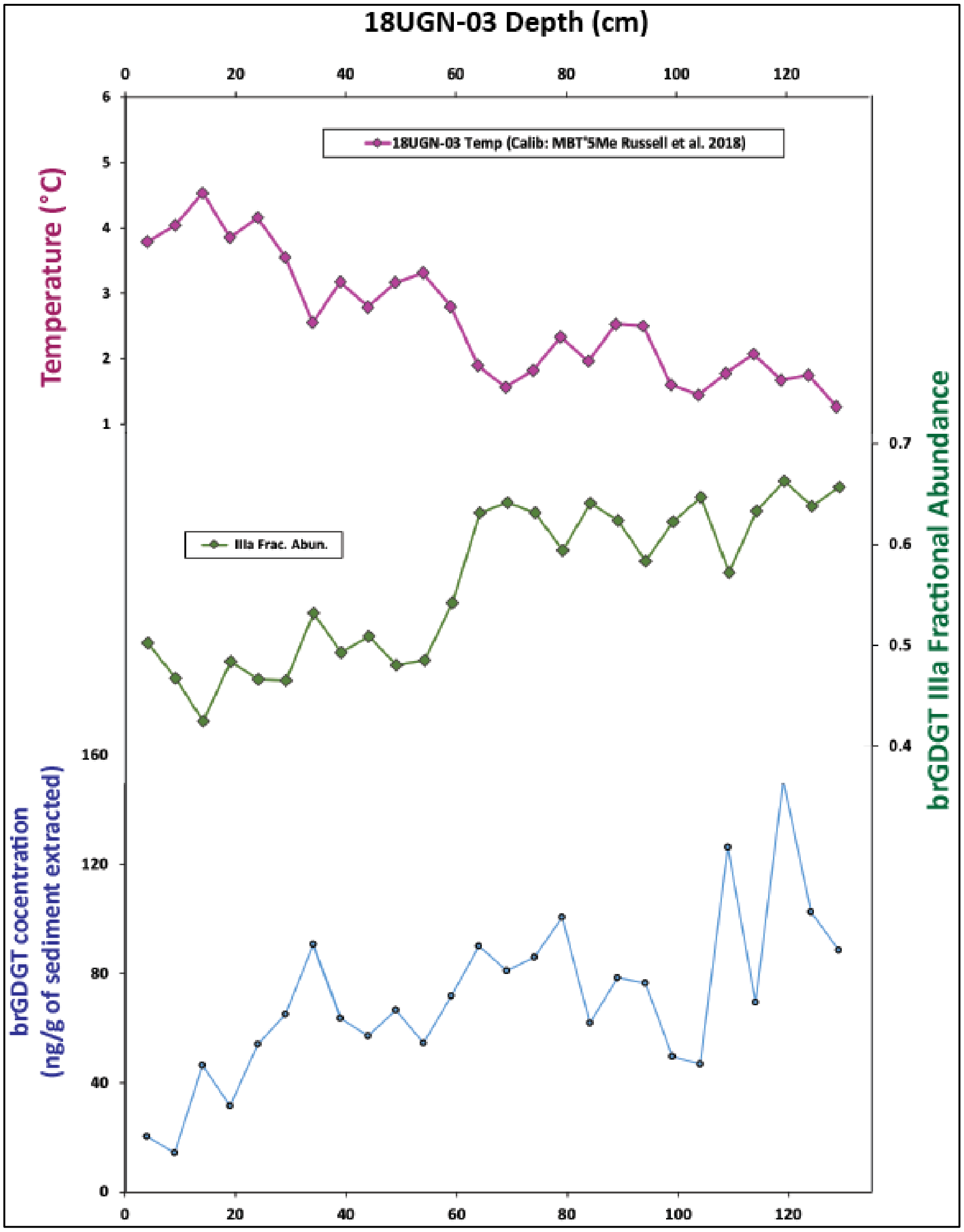


Fig. 13. *Comparison of Upper Gnarly's brGDGT concentrations, brGDGT IIIa fractional abundance, and the temperature calibrated from the reconstruction Russel et al. (2018) calibration over the Holocene. The fractional abundance of IIIa notably drops from 64cm to 54 cm depth, which correlates to a time span of ~6,490 to 5,521 years BP based on Upper Gnarly's radiocarbon dating.*

Conclusion

This thesis aimed to assess the validity of brGDGT paleotemperature reconstructions in Holocene Arctic lake core and to assess the role of changing oxygen levels in brGDGT paleotemperature reconstruction to understand better the environmental parameters that affect paleotemperature reconstruction in high-Arctic lake settings.

The evaluation of the brGDGT temperature reconstructions from a Holocene Baffin Island core do not reflect the recognized early Holocene warming from peak summer solar insolation, rather temperature reconstructions show a steady decline in temperature from present to ~11,000 yrs BP. De Jonge et al. (2014b) global soil calibrations yielded an overall cold-bias, colder than the temperature reconstructions derived from the Russell et al. (2018) lake calibrations. However, the temperatures from the Russell lake calibrations are within scope of summer Arctic temperatures when compared to modern climatic data recorded on Baffin Island. Upper Gnarly's brGDGT temperature reconstruction does match the general negative linear trend with temperature and core depth at other Baffin Island lake settings over the Holocene. In the analysis of suboxic to anoxic conditions, the Mn/Fe ratio, Inc/Coh ratio, and GDGT-0/Cren ratio denote two suboxic intervals present in Upper Gnarly that coincide with a intervals of cold-bias temperature reconstruction; additionally, the cold-bias present in 18UGN-03 is analogous with the temperature reconstruction in the previously identified suboxic/anoxic intervals in nearby Baffin Island lake records. Because the exact nature of the brGDGT production and distribution in lake water column is seemingly complex, it is lesser understood whether the increase in brGDGT IIIa fractional abundance in suboxic conditions is influenced by oxygenation concentrations or temperature; nonetheless, arctic seasonality, temperature, and oxygenation saturation play critical roles in brGDGT production and thus need to be investigated in greater detail in order to produce accurate past temperature and environmental reconstructions.

This thesis affirms the need for the application of a lacustrine temperature reconstruction calibration in lake settings; however, based on the temperature discrepancy and cold-bias present in suboxic conditions in Baffin Island and other Arctic downcore sediments, there is still a need for an arctic lake calibration addressing the physical, chemical, and environmental factors that influence brGDGT production specific for suboxic conditions in Arctic lakes.

Suggestions for Future Research

The application of paleoclimatology in the organic geochemistry field is constantly revising and developing temperature proxy calibrations. This thesis only looked at a singular application of the brGDGT-inferred temperature proxy in an Arctic lake. For future research, it is critical to continue assessing temperature reconstructions from brGDGTs proxies around Baffin Island and other high-latitude Arctic lake environments. Additionally, future research is needed in developing an Arctic-specific lake brGDGT-inferred temperature calibration. A limitation to this thesis is the singular application of a brGDGT temperature proxy for Holocene reconstruction; future research could include the application of an independent non-brGDGT temperature proxy for temperature reconstruction for temperature trend comparison, especially in events of the preserved suboxia.

By the publication of this thesis, there are eight 18UGN-03 samples that are currently being analyzed that further contribute to the data included here These samples were specifically taken around and within the transitions of the two suboxic events and will further elucidate the influence of suboxia on brGDGT distributions in Upper Gnarly sediments.

With the conclusion of this thesis, the following is a set of additional suggestions for future research: (1) evaluating brGDGT IIIa and other brGDGTs as environmental threshold markers in Arctic lake settings; (2) assessing the distribution of isomer IIIa" in lacustrine sediment records and identified suboxic/anoxic events; (3) quantifying the degree of suboxia created by methanogenesis organocarbon production by directly measuring the carbon isotopes of brGDGTs to determine the prevalence of methanogenesis (and presumed low oxygen conditions) during intervals of anomalously "cold" brGDGT paleotemperatures.

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