Bacterial Lipids in Holocene Sediments from Baffin Island: Insights into temperature reconstructions in Arctic Environments

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Defense Date: April 5th, 2019

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Abstract

This research study assesses the validity of bacterial branched glycerol dialkyl glycerol tetraethers (brGDGTs) for temperature reconstructions in Arctic settings from a sediment core extracted from Brother of Fog lake, Baffin Island. The distribution of brGDGTs in lake sediments have been shown to correlate with mean annual air temperature (MAAT) and serve as a proxy for paleotemperature reconstructions. This study aims to reconstruct temperature variability over the Holocene (~11500 years) and the applicability of this proxy for high latitude lakes. The results show a large bias within the brGDGT-inferred temperature reconstruction when applying the Russell et al. 2018 calibration. Due to the unintended nature of the temperature reconstruction, multiple cofounding variables were accounted for to understand the environmental influences on the formation of brGDGTs. Overall, this research shows the potential effects that anoxic water columns have on brGDGT temperature signals from lacustrine sediment cores extracted from Brother of Fog Lake in Baffin Island.

Keywords: Paleoclimate, Arctic, Temperature, Proxy, Baffin Island

TABLE OF CONTENTS

I.   Introduction to study

This honors thesis tests the applicability of a novel geochemical temperature proxy in a lake sediment record from the Canadian Arctic spanning the Holocene (past ~11500 years before present). This research is part of the ongoing NSF-funded project "Predicting Arctic Change through Ecosystem Molecular Proxies" (PACEMAP), which seeks to advance our understanding of how the Arctic will respond to climate change through paleoclimate research. Specifically, this interdisciplinary project aims to validate and apply ecosystem and climate proxies present in soils and lakes on Baffin Island, and to reconstruct past climate through the analysis of sediment cores. This thesis project focuses on one of the target lakes of the PACEMAP project; Brother of Fog Lake. The goal of this study is to extract and analyze organic bacterial cell membrane lipids called branched glycerol dialkyl glycerol tetraethers (brGDGTs) from a sediment core (18BRO-25) extracted from Brother of Fog Lake. Though the distribution of brGDGTs in sediments has been empirically shown to be related to environmental air temperature (e.g. Weijers et al., 2007b; Tierney et al., 2010; Russell et al., 2018), the exact nature of this relationship is complex and may be influenced by other environmental factors such as bacterial brGDGT source, dissolved oxygen concentration, etc. (e.g. Weber et al., 2018; Colcord et al., 2015; Loomis et al., 2014). This study examines the efficacy of the brGDGT proxy from a lake sediment record from Baffin Island, where previous research (e.g. Axford et al., 2009; Crump et al., 2017; Pendleton et al., 2019) has shown a strong pattern of early Holocene warmth followed by cooling during the past ~8-6 ka (thousands of years before present). Although previous scientific research performed on brGDGTs confirms the utility of these biomarkers as temperature proxies in the Arctic (Colcord et al., 2015; de Wet et al., 2016), relatively few comparisons with other proxies from the same

1

lake have been made to date. Following the conclusion of lab analyses, the goal is to compare

my Holocene brGDGT temperature reconstruction to other proxy data from Brother of Fog lake

as well as other paleoclimate records from the region. This research will contribute to our

knowledge of past Arctic temperature variability in order to predict the ecological effects of

future climate change while concluding the applicability and drawbacks of this proxy on high

latitude lake environments.

Research Question

What do brGDGT based paleotemperature estimates from a lacustrine sediment core

reveal about Holocene climate change at Brother of Fog Lake? Does the reconstruction match

previously known patterns of climate variability on Baffin Island and the Arctic over the same

time scale? What other factors may be influencing brGDGT distributions beyond temperature?

Through utilizing sediment core records and comparing my findings with previous pollen data,

how do brGDGTs help us to reconstruct temperature in the geologic record, and does this

biomarker accurately capture known Holocene climate variability in the Arctic? On a broad

scale, what predictions does this temperature proxy produce about past climate variability, and

how can this be used in our understanding of future climate change?

II.   Background/Literature Review

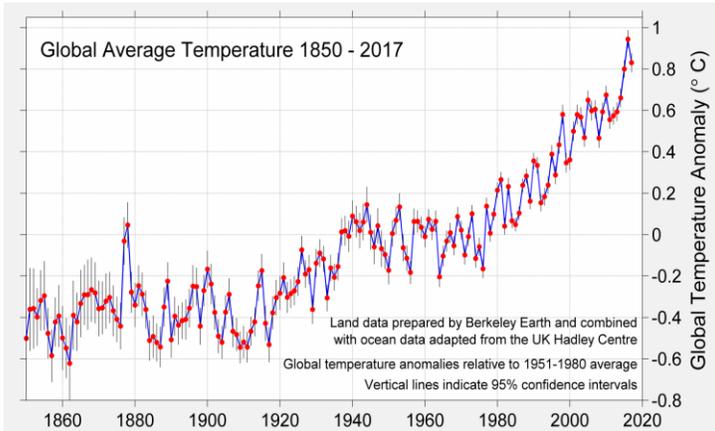### i.   *Climate change, Arctic Amplification*

Figure 1. Global average temperature from 1850-2017 (Berkeley Earth; UK Hadley Centre)
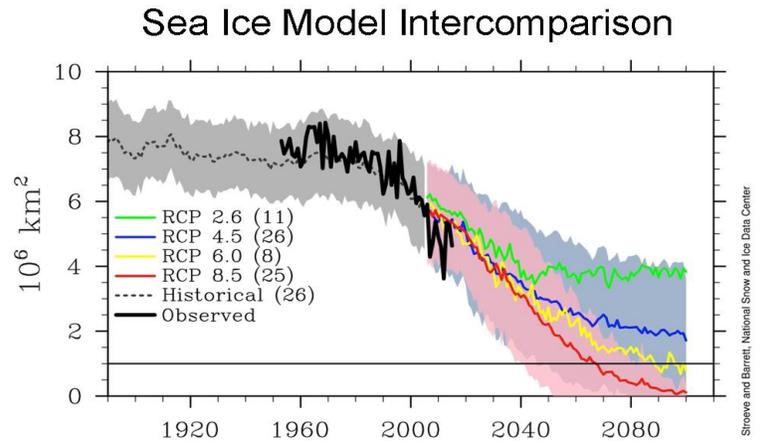

Figure 2. Sea ice model inter-comparison from 1900-2080 showing multiple RCP scenarios ranging from 2.6-8.5 alongside historical and observed data (IPPC, 2013)

The Arctic has become a point of concern regarding global climate change because of increased climatic vulnerability associated with strong positive feedback loops that are specific to the region (Serreze et al., 2011. Over the past decades, we have observed summer warming in the Arctic outpacing the global average of warming (Pendleton et al., 2019). Climate models that assess different future emissions scenarios project that surface temperatures will increase by 1.1 to 6.4 ℃ by the end of this century (Solomon et.al, 2007) with mean annual surface air temperature variance at 60-90°N rapidly increasing at twice the global average (Figure 1; Overland et al., 2016). Climate models also suggest a vast decrease in sea ice extent, with complete melting occurring under Representative Concentration Pathway (RCP) Scenario 8.5 within the next couple of decades (Figure 2;IPPC, 2013). Although the Arctic makes up less than

5 percent of the Earth surface, it contains extremely sensitive feedback loops (Miller et al. 2010) that exacerbate regional warming (Serreze et al., 2011). For example, the phenomenon of arctic amplification occurs when there is a reduction in ice extent resulting in a change of albedo leading to decreased reflectivity, thus heightening the overall effects of warming across the Arctic. Local Arctic climate perturbations exert a strong influence on global climate via changes in atmospheric and ocean circulation (Kerwin et al 2004; McGuire et al., 2006; Dethloff et al., 2006). For example, an increase in freshwater runoff due to melting ice sheets in the Arctic is potentially disruptive to the thermohaline circulation, which can significantly affect poleward heat transport (Soloman et al., 2017). Paleoclimate research attempts to improve our understanding of the sensitivity of the climate system by providing context for observed modern changes through the reconstruction of relevant climate parameters back through time.

ii. Proxy records – how we contextualize climate change

Climate change is one of the largest global threats to our environment, and the scientific research surrounding this issue allows for an enhanced understanding of potential effects on various ecosystems. Paleoclimate reconstructions provide critical insight into the mechanisms governing long term climate change (Russell et al., 2018; Braconnot et al., 2012) . In order to do so, proxy records are used to inform climate models and apply to the current state of our environment through which we observe changes. Proxy records cover a wide range of climatic information and are extracted from natural archives such as tree rings, ice cores, speleothems, soil deposits, and sediment cores (Dewey et al., 2010). For example, Briner et al. (2016) assessed 47 records from a recently published database of Holocene paleoclimate time series and compared them with previous records in the Arctic, performing a multi-proxy synthesis of Arctic

Canada and Greenland. This thesis focuses specifically on bacterial membrane lipids preserved in a lacustrine sediment core from Baffin Island. Arctic lake sediments are useful archives because (1) they are widely distributed across high latitudes; (2) local human activity has had little impact on most Arctic lakes; (3) many records span thousands of years (Pienitz et al., 2004). Furthermore, reconstructions of past Arctic climatic conditions provide a platform for mitigation and adaptation strategies as we approach the future effects of climate change (Cook, 2009).

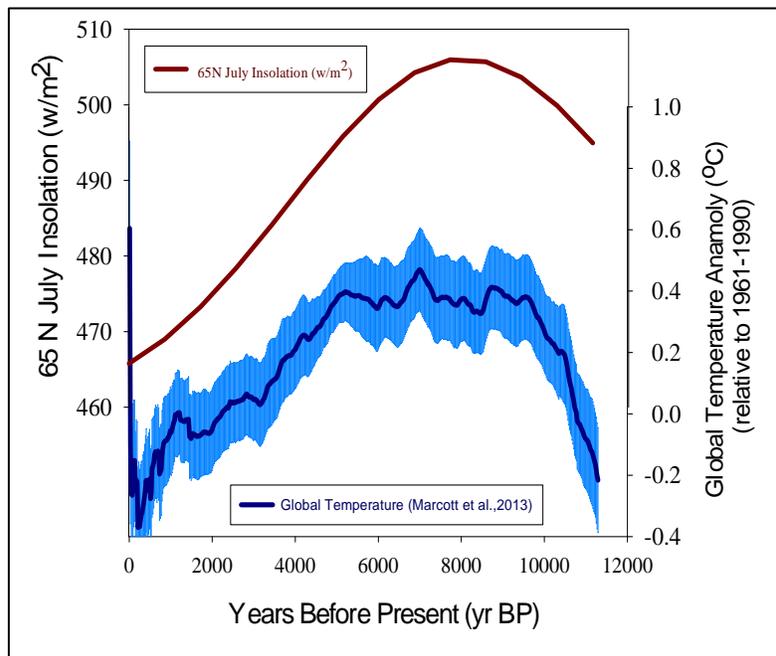### *iii.   Arctic Climate change over the Holocene*

Figure 3. Top: 65 N July insolation over the Holocene. Bottom: global temperature reconstruction Source: Marrcott et al.(2013)
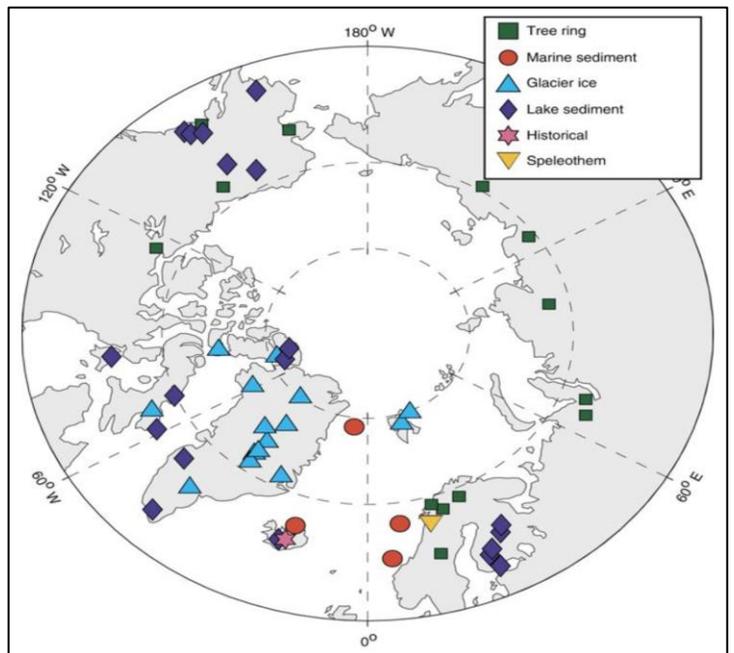

Figure 4. This figure shows the location and archive type of proxy temperature records from the Arctic. Source: Kaufman et al. (2014)

Paleoclimate research within the Arctic is particularly important due to the variability of warming across different areas calculated changes in solar insolation resulted in increased fluxes

of global temperatures (Figure 3). Due to Arctic Amplification, the magnitude of climate change at high latitudes is significantly higher resulting in large climate signals (Briner et al., 2016). Temperature trends over the Holocene are mainly controlled mainly by declining solar insolation at high latitudes (Figure 3). Although when previous studies assessed Holocene Arctic climate change, they showed strong spatial and temporal heterogeneity in the expression of the "Holocene Thermal Maximum" and Neoglacial cooling around the Arctic. (Kaufman et al., 2014). Kaufman et al. (2014) point out the necessity for further research surrounding data errors for climate modeling in the Arctic. In Figure 4, Kaufman et al. (2014) research points out the proxies that have been assessed throughout study sites across the Arctic through the application of tree rings, marine sediment, glacier ice, speleothems, and historical records (Figure 4). Although a portion of the study sites yielded warmer early or middle Holocene and a cooler late Holocene, overall temperature trends vary between sites (Kaufman et al., 2014). For example, pollen-derived temperature estimates for the western Arctic show an average anomaly of $1.6 \pm 0.8°C$ during the Holocene (Kaufman et al., 2014), but chronomid-based estimates for Baffin Island range from $2 \pm 1°C$ (Francis et al., 2006) to $5.0 \pm 1.5°C$ (Axford et al., 2009). Further research conducted with quantitative proxies that possess higher temporal resolution will allow for a clearer understanding of exact temperature measurements in the Arctic in conjunction with previous paleoclimate reconstructions.

iv.   BrGDGT Proxy

Molecular approaches are promising
tools to assess past climate change (e.g.
Castaneda and Schouten, 2011).Over the past
decade, the utilization of temperature proxies
based on isoprenoidal and branched glycerol
dialkyl tetraether (iGDGTs and brGDGTs, e.g.
Shouten et al., 2002; Tierney et al., 2008;
Bendle et al., 2010; Berke et al., 2012; Loomis
et al., 2017) have been applied with geological
archives including lake sediments (Loomis et
al., 2007), river fan deposits (Weijers et al.,
2007a), loess (Peterse et al., 2011), and peat
(Zheng et al., 2017).BrGDGTs are membrane-
spanning lipids produced by bacteria that include straight alkyl core chains with four to six
methyl groups (Sinninghe Damaste et al., 2000, 2011). Notably, brGDGTs demonstrated the
effect of soil pH and air temperature on the degree of cyclization and methylation of 9 brGDGTs
(Figure 5), expressed as the cyclisation ratio of branched tetraethers (CBT) and the methylation
index of branched tetraethers (MBT) (Weijers at al., 2007). Further improvement of the proxy
with only 7 of the soil brGDGTs allowed for a better transfer function for pH and MAAT
(MBT'/CBT; Peterse et al., 2009). Improvements in the chromatographic separation of brGDGT
isomers led to modified MBT and CBT indices producing new regressions for MAAT in soils
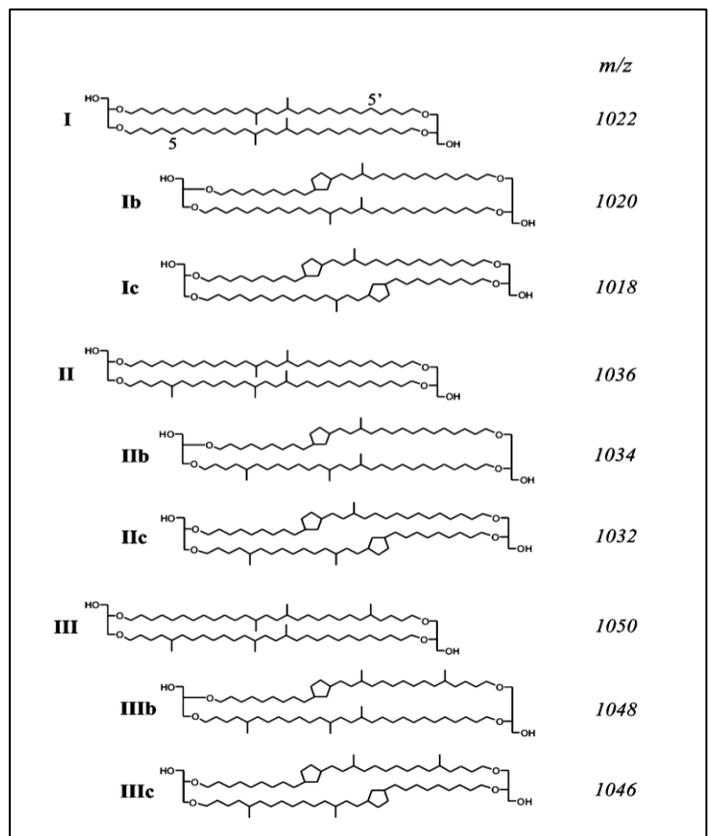

Figure 5. *Sstructures of branched glycerol diakyl tetraethers Source: Dang et al .(2017); Yang et al. (2015)*

(De Jonge et al. 2014). Although brGDGTs were thought to be produced only in soil environments, subsequent research revealed the presence of a novel "mixed" hexamethylated brGDGTs identified in lake environments and not in soils of the surrounding watershed, suggesting the manifestation in situ production of brGDGTs in lake environments (Tierney and Russell, 2009; Tierney et al., 2010; Zink et al., 2010; Buckles et al., 2014; Loomis et al., 2011, 2012, 2014a, 2014b; Pearson et al., 2011; Li et al., 2016). Since this discovery, several temperature calibrations have been introduced that calculate brGDGT-inferred temperatures in different locations across the globe (Blaga et al., 2010; Pearson et al., 2011; Sun et al., 2011; Loomis et al., 2012; Foster et al., 2016; Vandergoes et al., 2016). A recent study measured globally distributed soil samples and observed the relationship between mean annual air temperature (MAAT) in conjunction with the methylation index of branched tetraethers (MBT) and the cyclisation ratio of branched tetraethers (CBT). Due to the influence of soil pH on CBT, this calculation can correct the effect of pH on the MBT. De Jonge et al. (2014a) and Hopmans et al. (2016) formulated a CBT and MBT index that includes 5-methyl but excludes 6-methyl isomers. Further research conducted by Russell et al. (2018) assessed the separation of 5- and 6-methyl isomers and formulated a temperature calibration specific for lacustrine environments (Russell et al., 2018). Overall, temperature calibrations based upon MBT'$_{5'ME}$ provided greater accuracy of temperature reconstructions in lake sediments (Russell et al., 2018).

Previous research on the brGDGT proxy in lakes across Baffin Island (Shanahan et al., 2013) showed that brGDGTs exhibit significant relationship with temperature when warm-season temperatures are considered, in contrast to isoprenoid GDGTs (Iso GDGTs). The presence of Iso GDGTs, membrane lipids, are formulated by Archaea including Thaumarchaeota, Crenarchaeota, and Euryarchaeota rather than Acidobacteria specific to

brGDGTs (Weijers et al., 2006a, 2009; Sinninghe Damste et al., 2001). Although brGDGTs have become an important tool for continental temperature reconstructions, there are drawbacks with their application due to biases introduced by multiple biological sources, and the fact that global calibration does a poor job in cold regions. In research conducted by Weber et al. (2015), they found that there was a significant correlation between brGDGT-based surface sediment temperatures with summer bottom water temperatures in study lakes located in southwestern Greenland that were experiencing anoxic bottom waters (Weber et al., 2018). This data suggests the importance of evaluating individual lake systems and being aware of potential sources of measured brGDGTs (Weber et al., 2018). The presence of increasing ratio of Iso GDGTs-0/Crenarcheol found in the lacustrine sediment core has been shown to correlate with the emergence of methanogens in the lake water column which can in turn influence the source of brGDGTs and temperature signal due to methanogensis (Naeher et al., 2013). Thus, in order to formulate an accurate and precise temperature reconstruction from the brGDGT proxy, it is crucial to constrain the physical and chemical properties of the system (Tierney and Russell, 2009; Blaga at al., 2010; Tinerney et al., 2012; Wang et al., 2012; Weber et al., 2015).

v. *Previous work on Baffin Island*

As previously discussed, Arctic regions are notably sensitive to shifts in climate. Thus, furthering our understanding of how this region has responded to climate forcing throughout the Holocene, particularly during the warmest intervals, will help us to confine its response to future climate change. Baffin Island has become a pertinent study area for paleoclimate research (Figure 6). Previous studies in the Arctic were able to obtain intact lacustrine sediments within glaciated terrains where ice

Figure 6. *Google Earth imagery of Baffin Island. Source: Google Earth*

sheets were minimally errosive (Axford et al., 2009; Miller et al., 2010).

Current temperature proxies used to recreate the thermal maximum for the Holocene in the Eastern Canadian Arctic remain contentious (Briner et al., 2007). Previous studies have included the use of sedimentology, chironimids, and pollen proxies to reconstruct Holocene climate located in Baffin Island (Briner et al., 2006; Briner et al., 2007; Francis et al., 2006; Frechette et al., 2006). For example, research conducted in Baffin Island analyses in situ ^{14}C inventories in rocks from various locations which compared within the context of temperature records from ice cores retrieved from Greenland show summer warmth of the past century exceeds any century in ~115,000 years (Pendleton et al., 2019). In recent years, new approaches

have increased our understanding of the Holocene in the eastern Canadian arctic (Briner et al.,

2016). Lake sediments from Baffin Island express an increasing amount of geochemical training

sets such as the brGDGT proxy allow for significant quantitative assessments of past

environmental variables (Briner et al., 2016; Kerwin et al., 2004; Shanahan et al., 2013).
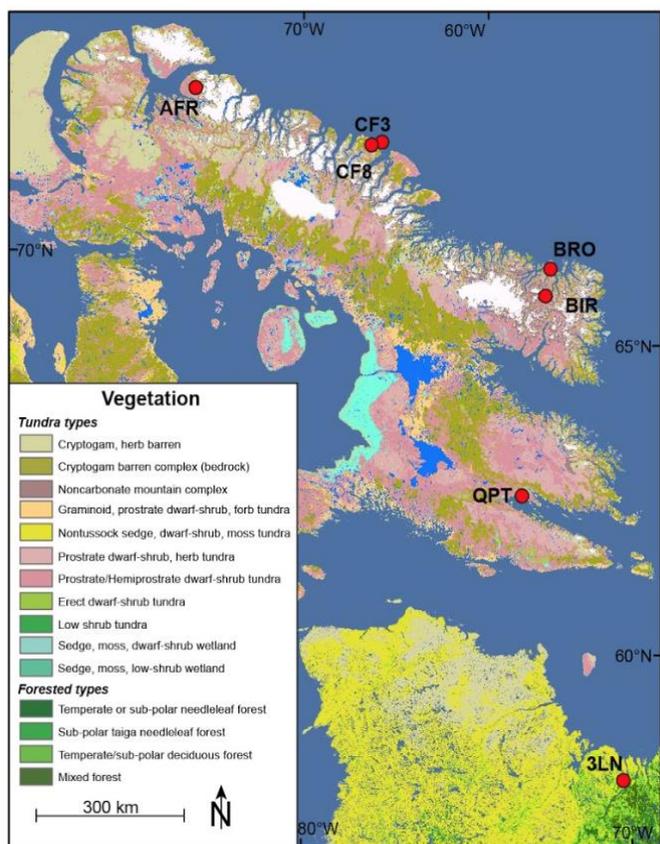
III. Methods
i. *Location*

Figure 7. Map of Baffin Island with the location of targeted lakes of PACEMAP. BRO stands for Brother of Fog Lake. Source: Raynolds and Walker (2016); North American Land Change Monitoring System (2013)
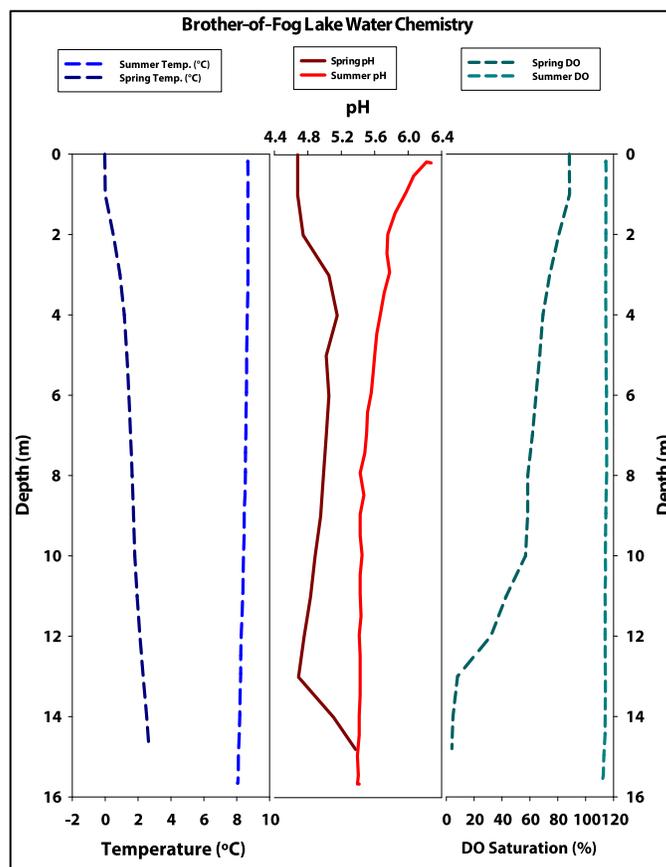

Figure 8. Vertical profiles showing summer and spring temperatures, pH, and dissolved oxygen content in Brother of Fog Lake.

Brother of Fog Lake (67°11.5'N, 63°15'W; 192,275 m^2) is located at an altitude of

400 m near the settlement of Qikiqtarjuaq in eastern Baffin Island (Figure 7). The

lake is 16 meters deep in its depocenter, has a catchment area of 0.64 km^2, and the

shore line is ~1.68 km long. The temperature remains similar in depth while the spring

dissolved oxygen content declines implying the presence of anoxia in the water column.

The pH levels in the spring are around 4.8 while the summer pH concentrations are

around 6.4 (Figure 8).

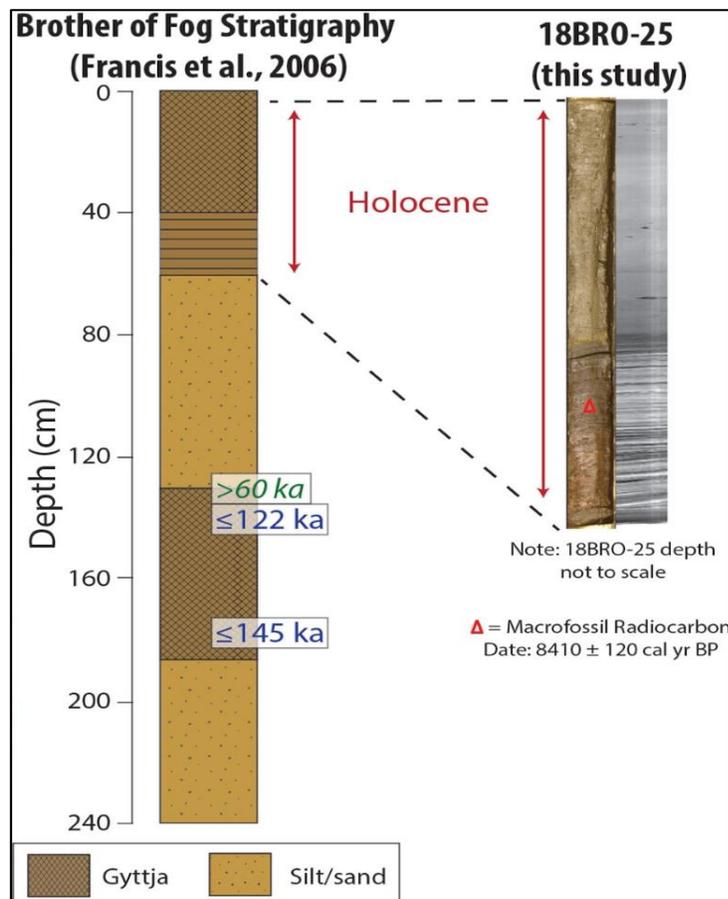<p style="text-align:center">ii.   Sediment Coring</p>

A number of sediment cores were collected from Brother-of-Fog Lake in May of 2018 using a modified Nesje coring system (Nesje, 1992) operated from the lake ice. This study focused on core 18BRO-25, which was collected from 15.55m water depth, with an intact sediment/water interface and 80 cm of sediment upon recovery. The core was kept cold but above freezing for the duration of fieldwork and then stored at 4°C until processing. Core 18BRO-25 was split longitudinally with a vibrating Dremel saw and described in the dedicated ancient DNA clean lab at the Trace and Environmental DNA (TrEnD) Lab at Curtin University. The working half was subsampled for DNA and organic geochemistry analysis using sterilized tools (cleaned in a 10% bleach solution and UV irradiated). The archive half was preserved for core scanning. The sediment core contains ~42.5 cm of a grayish brown gyttja at the top followed by strongly laminated gray-black sediments down the core (Figure 9).

iii.   *brGDGT extraction and GDGT analysis*

After sub-sampling at Curtin University, samples for organic geochemical analysis were processed in the Organic Geochemistry laboratory at the University of Colorado, Boulder. Lipids were extracted from a total of 36 freeze-dried and homogenized samples via an Accelerated Solvent Extractor (ASE), using dichloromethane (DCM): methanol (MeOH) (9:1, v:v) at 100°C and 2000 psi. The mean mass of the sediment extracted was 2 gr, with a range of 0.45 to 3.9 gr. Each sediment sample was extracted twice to ensure complete recovery of extractable lipids.

Total lipid extracts (TLEs) were dried under nitrogen and three standards were added to the TLE: 4.2 ug of a $C_{20,1}$ n-acid, 1 ug of a C_{36} *n*-alkane, and 1 ug of C_{46} GDGT standard. Samples were then dissolved in 9:1 DCM:MeOH and an aliquot of 10% kept for brGDGT analysis. Prior to injection on the HPLC, samples were dissolved in 500 ul of 99:1 Hexane:Isoprophyl alcohol (Hexane:IPA, v:v), sonicated for 10 minutes, and mixed with a vortex device before filtration with a 0.45 um Millex-FH Syringe Filter (Millipore).

The samples were then analyzed on a Thermo Scientific Ultimate 3000 high performance liquid chromatograph (HPLC) interphase to a Q Exactive Focus Orbitrap-Quadrupole MS via atmospheric pressure chemical ionization (APCI- MS). Samples were analyzed on positive ionization mode with the following conditions: probe heater temperature, 425 °C; capillary temperature, 263 °C; sheath gas flow rate, 50 AU; auxiliary gas flow rate, 13 AU; spray voltage, 3.50 kV. HPLC methodology was derived from previous research conducted on brGDGTs (De Jonge et al., 2014b, Hopmans, et al., 2014). The isocratic flow was augmented to 30% B for the first 20 minutes then 45% B in 25 minutes followed by 100% completed in 20 minutes.

iv.   *brGDGT indices*

Branched GDGTs were originally thought to be produced within soil and peat environments, but recent work has shown the strong differentiation between fractional abundances of brGDGTs in aquatic environments from catchment soils (Russell et al., 2018). The following calibrations applied to the brGDGTs extracted from Brother of Fog Lake were as followed:

MBT'$_{5ME}$ = (Ia + Ib + Ic) / (Ia + Ib + Ic + IIa + IIb + IIc + IIIa + IIIb + IIIc)

CBT'$_{5ME}$ = -log [(Ib + IIb) / (Ia + IIa)]

In the study area, the lake is ice covered ~ 9 months per year, so the distribution of brGDGTs is expected to resemble mean summer temperature, as previously shown by Pearson et al. (2011) in Arctic lakes. The MBT'$_{5ME}$ lake temperature calibration of Russell et al. (2018) was selected because it is only one of two published lake calibration efforts that utilize the separation of the 5- and 6-methyl isomers of brGDGTs II and III, and is applicable to non-alkaline lakes. The mean annual air temperature equation was derived from this following equation:

MAT (Russell et al., 2018) = 1.21 + 13.42 x MBT'$_{5ME}$

In conjunction with Russell et al. 2018 lacustrine calibrations, the cyclisation ratio of branched tetraethers (CBT') index was proven to be strongly correlated with surface water pH, so the calibration utilized for pH is derived from this calculation:

CBT' (Tierney et al., 2010; Loomis et al., 2014b) = -Log ((Ic + Iia' + IIIa' + IIIb' + IIIc') / (Ia + IIa + IIIa))

Surface Water pH (Russell et al., 2018) = 8.95 + 2.65 x CBT'

Each of these equations was applied to the extracted brGDGTs from the sediment core with supplemental calibrations from both soil and lacustrine equations included as well (De Jonge et al., 2014b, Pearson et al., 2011). Due to the dissimilar locality of the Russell et al. 2018 calibration, it is important to remain cautious when observing absolute temperature reconstruction in an Arctic setting.

IV. Results
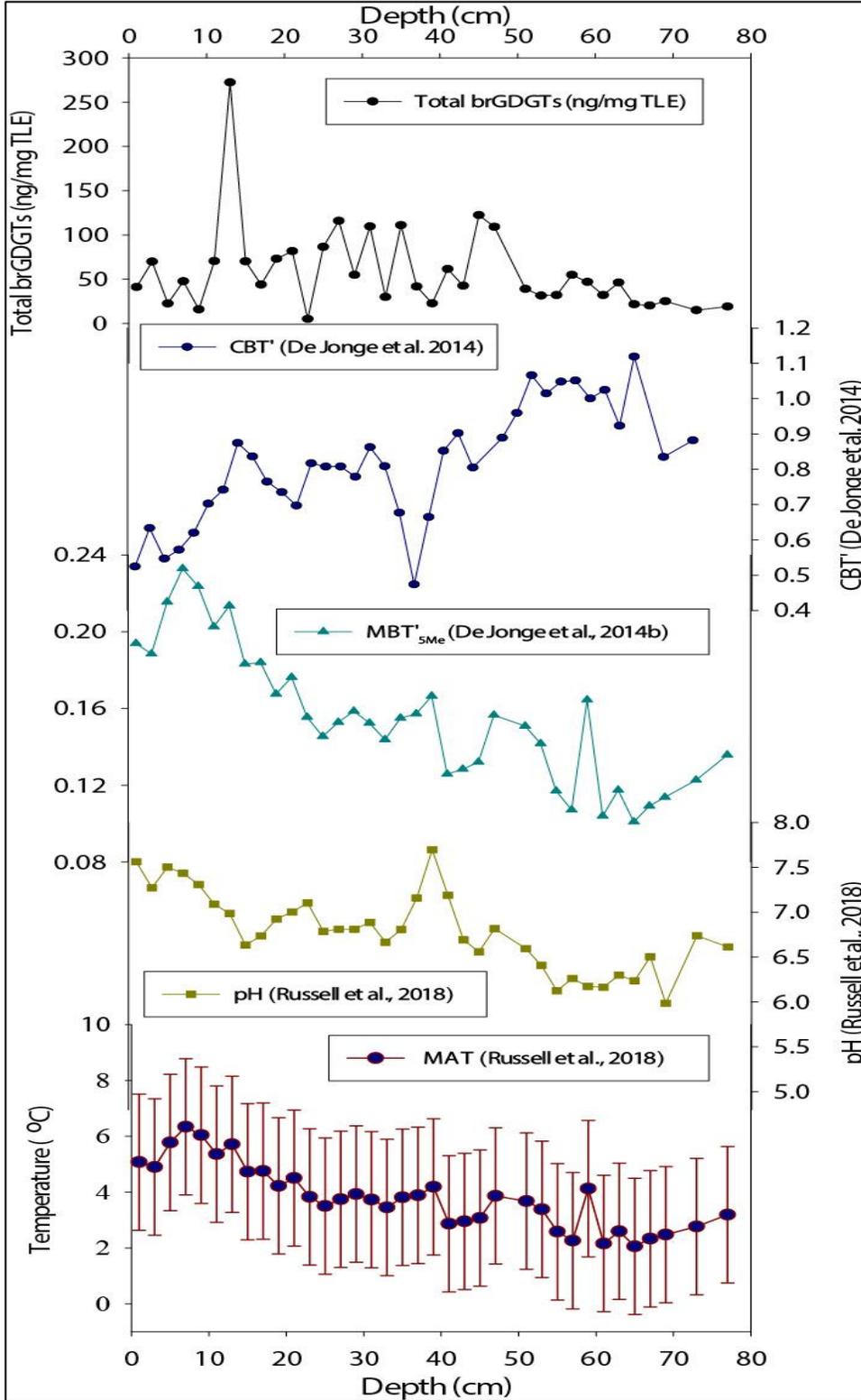

Figure 10. *Results from the BRO sediment core showing total brGDGT concentration, CBT' and MBT'$_{5ME}$ indices, pH, and temperature reconstruction.*
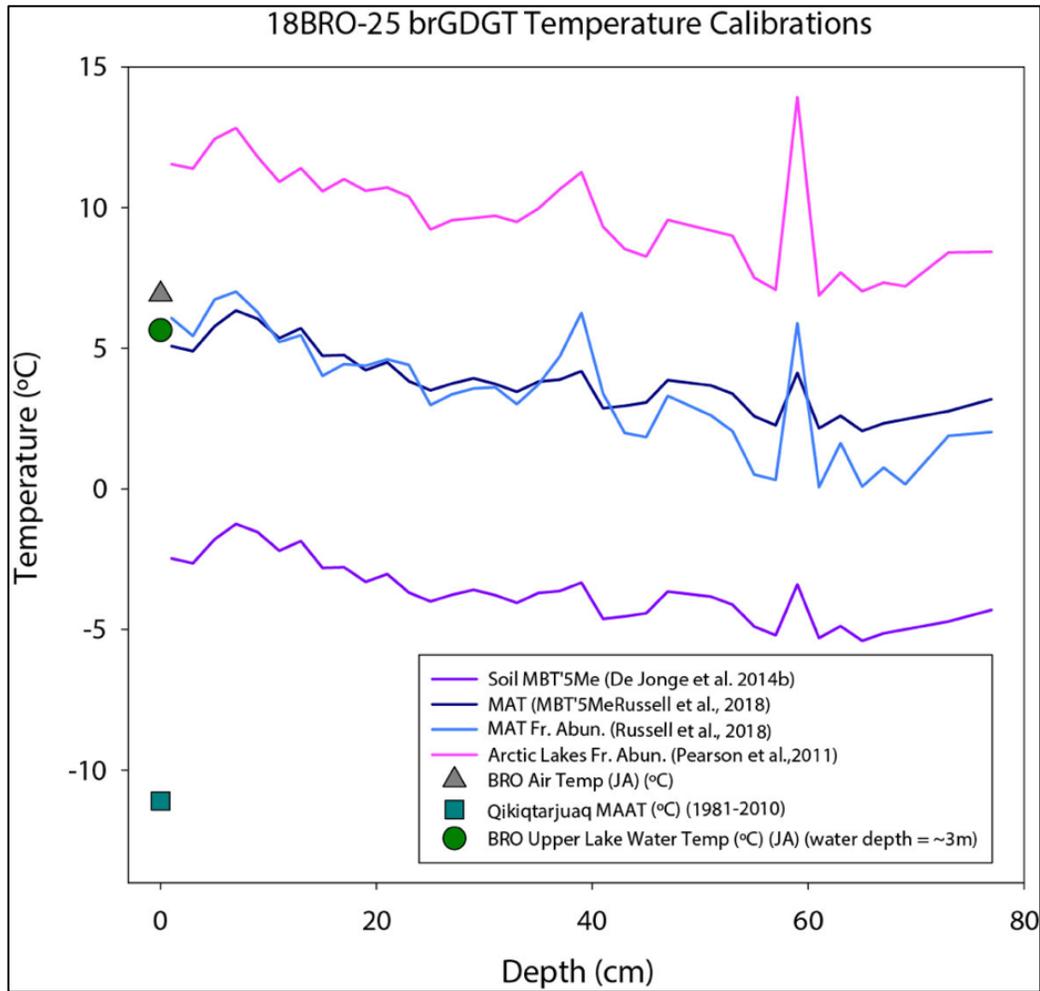
Figure 11. *Results from BRO sediment core showing different calibrations from De Jonge et al.2014, Russell et al. 2014, and Pearson et al. 2011 as well as BRO air temperature, Qikiqtarjuaq MAAT, and BRO upper lake water temperature.*

36 sediment samples from core 18BRO-25 generated concentrations of brGDGTs for temperature estimates. The total lipid extract from the samples yielded a mean of 9.5 mg, with a range of 0.6 to 35.2 mg. The total brGDGT concentrations ranged from 9.4 to 272.3 ng/g, with a mean of 61.02 ng/g sediment extracted.

The average of MBT'$_{5ME}$ values was 0.155 while remaining continual throughout the core depths. For the CBT' values resulted in a mean of 0.82 with a decline occurring around 39 cm, followed by a sharp increase in the uppermost part of the core.

After applying the Russell et al. 2018 calibration, the top portion of the sediment core (1-29 cm) exhibited the highest temperatures (3.5-7°C). Below this, temperature values exhibited a steady drop in depth, with spikes in warming occurring at 39 cm and 59 cm.

The pH ranged between 5.6 and 7 with a peak occurring around 58 cm, without a clear trend throughout the core. The ratio between isoGDGT-0 and crenarchaeol (IsoGDGT-0/Crenarchaeol) ranged between 3.5 and 2,887, it remained relatively similar and low until about 45 cm, and then exhibited elevated values between 43 and 77 cm. The results range from values of 3.5 to 2,887.

A comparison of brGDGT-derived temperatures using multiple calibrations is shown in Figure 11. Pearson et al. (2011) calibration shows a higher temperature gradient in comparison with Russell et al. (2018) fractional abundance, MBT$_{5'ME}$, and De Jonge's soil MBT$_{5'ME}$ temperature calibrations. The Brother of Fog upper lake water temperature is relatively similar to the Russell et al. (2018) temperature reconstructions at the upper part of the core suggesting that it is capturing surface water temperature within the lake. The Qikiqtarjuaq average MAAT temperatures from 1981 to 2010 (-8 °C) is plotted well below each temperature calibration line.

V.   Discussion

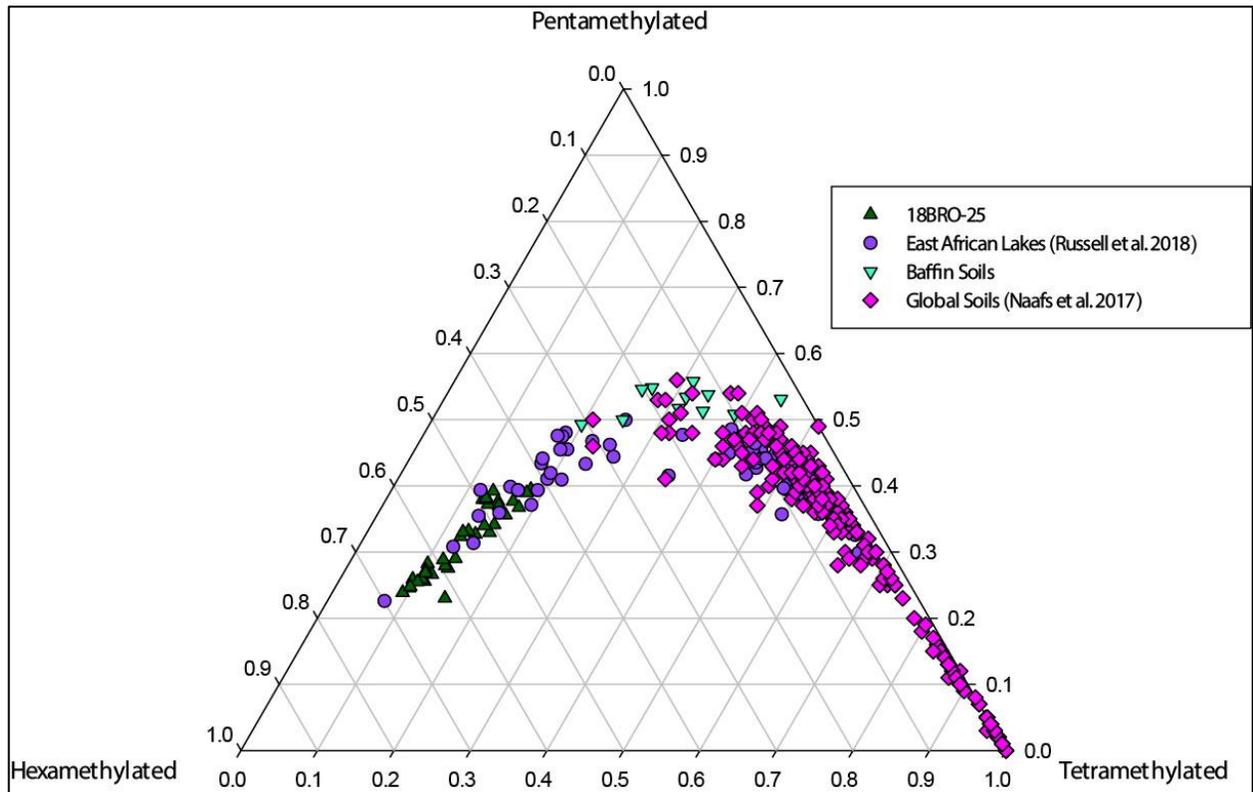### i.   *Sources of brGDGTs in Brother of Fog Lake*

Figure 12. *Ternary diagram comparing 18BRO-25, Russell et al. brGDGT abundance against Baffin and global soil data. Source: Naffs et al. (2017)*

The distribution of brGDGTs in the BRO sediment core suggest a differentiation of bacterial sources that are producing a bias signal in the temperatures. There is a research gap in overall fundamental knowledge surrounding the ecology of brGDGT-producing microbes in lakes, so it can be difficult to draw conclusions based upon the produced temperature configuration (Weber et al., 2018). The cross comparison of lake vs. soil brGDGTs in a ternary diagram allows for the differentiation of preference for tetramethylated, pentamethylated, hexamethylated brGDGTs in different environments (Figure 12). The comparison of 18BRO-25

20

data with soil signatures from Baffin Island, and the compiled data sets from Russell et al. (2018) and Naffs et al. (2017) shows a strong relationship between 18BRO-25 and lacustrine sediments, suggesting that 18BRO-25 data is predominantly aquatic in origin.

ii. brGDGT temperature reconstruction

The brGDGT inferred temperature reconstruction using the Russell et al. (2018) calibration resulted in a negative linear relationship between core depth and mean annual summer temperatures. The overall cooling trend down the 18BRO-25 core is not indicative of past warming during the Holocene, so it is pertinent to assess a set of variables and other research from proxy data conducted in Baffin Island. This data suggests that a multitude of environmental factors could be potentially influencing the formation of the brGDGT proxy.

The Russell et al. (2018) was conducted on a set of East African Lakes and was shown to have a significantly better correlation on the colder lakes than previous soil calibrations. The root mean square error was around 2.14°C, which is significantly better than soil calibrations (Figure 11). As previously stated, climate during the Holocene at high northern latitudes was influenced by changes in solar insolation, with expected warmer temperatures occurring during the early part of the record when the insolation anomaly was highest (Figure 4). Although this calculation is the most up to date lake derived brGDGT/temperature calculation; it does not directly apply to Arctic lake sediments.

iii.   *Comparison with modern environmental data at Baffin Island*

In order to fully assess the outcome of inferred-brGDGT temperatures, modern environmental data at Baffin Island and the BRO lake were compared against the down core record. The 2018 average summer temperature in Baffin Island during the month of July was around 7.05°C, with an average annual temperature of 3.13°C. The average of the combined calculated mean annual temperatures from the uppermost depths of the 18-BRO-25 core yielded 6.1°C. The brGDGT-inferred temperatures yielded from the Brother of Fog lake likely represent the mean summer average temperature due to ice lake coverage ~9 months out of the year (Dang et al., 2018; E.J. Pearson et al., 2011; Shanahan, Hughen, & Van Mooy, 2013). The average for the brGDGT-inferred temperatures for the top layer of the core show similar average temperatures from the 2018 July temperature in Baffin Island. The Brother of Fog lake water temperatures during the month of August 2018, spanned from 8.68°C at the top of the water column to -0.03°C towards the bottom. Although the temperatures derived from the brGDGT temperature reconstruction at the top of the core are similar to the modern temperatures taken around the lake, the uncertainty when moving down core is prevalent due to the source and environmental influences on the formation of brGDGTs.

iv.   Comparison with other Proxy Data

When assessing the brGDGT-inferred temperature data derived from Brother of Fog lake, previous research and data surrounding global temperatures and soils as well as nearby lake statistics present ambiguities.
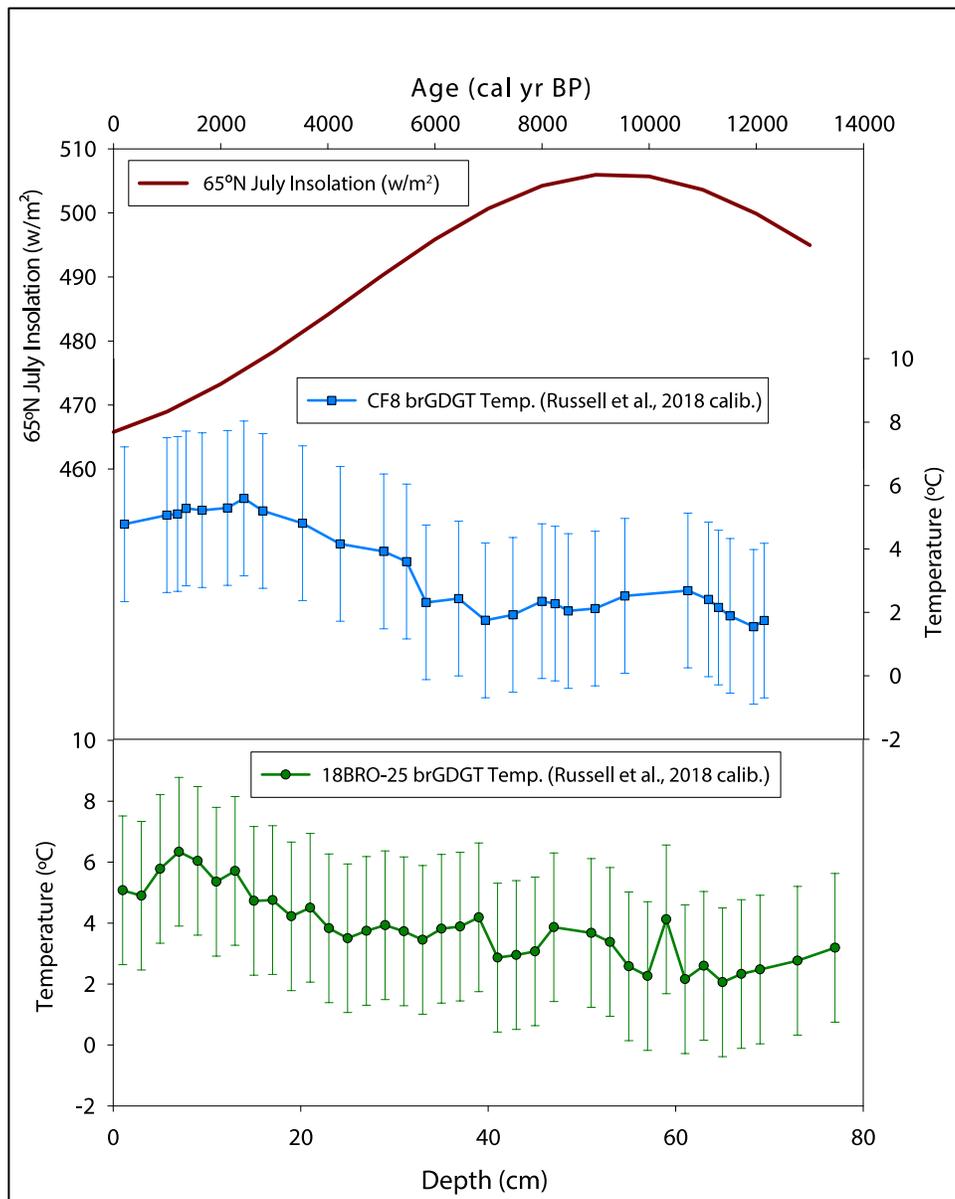

Figure 13. *Comparison graph of 65°N, CF8 lake brGDGT temperature, and 18BRO-25 brGDGT temperature with applied Russell et al. (2018) calibration.*

In an on-going study in a nearby lake in Baffin Island, a sediment core from lake CF8 assessed the usefulness of brGDGTs in formulating a temperature record (de Wet unpublished data). For this study, the same Russell et al. (2018) temperature calibration was applied. Similar to the results from the BRO sediment record, the CF8 data revealed a reduction in temperatures back in time (Figure 13). The comparison between proxy data in lake CF8 and BRO reveal similar in situ mechanisms for the brGDGTs that could be generating an artificial temperature response. Similar to the x-ray image of 18BRO-25, the CF8 core imagery shows patterns of strongly laminated sediments towards the bottom 30 cm. The CF8 temperature reconstruction also suggests an occurrence of anoxia in the water column similar to the observed temperature reconstruction in 18BRO-25.

The BRO data does not correlate with the solar insolation curve showing greater levels of insolation over the early Holocene (Fig. 12), neither with other Holocene temperature records (Marcott et al., 2013).

v. *Why is the brGDGT data different from what is expected?*

The unexpected nature of the derived temperature reconstruction over the Holocene

motivated the investigation of the role of other environmental parameters on the distribution and
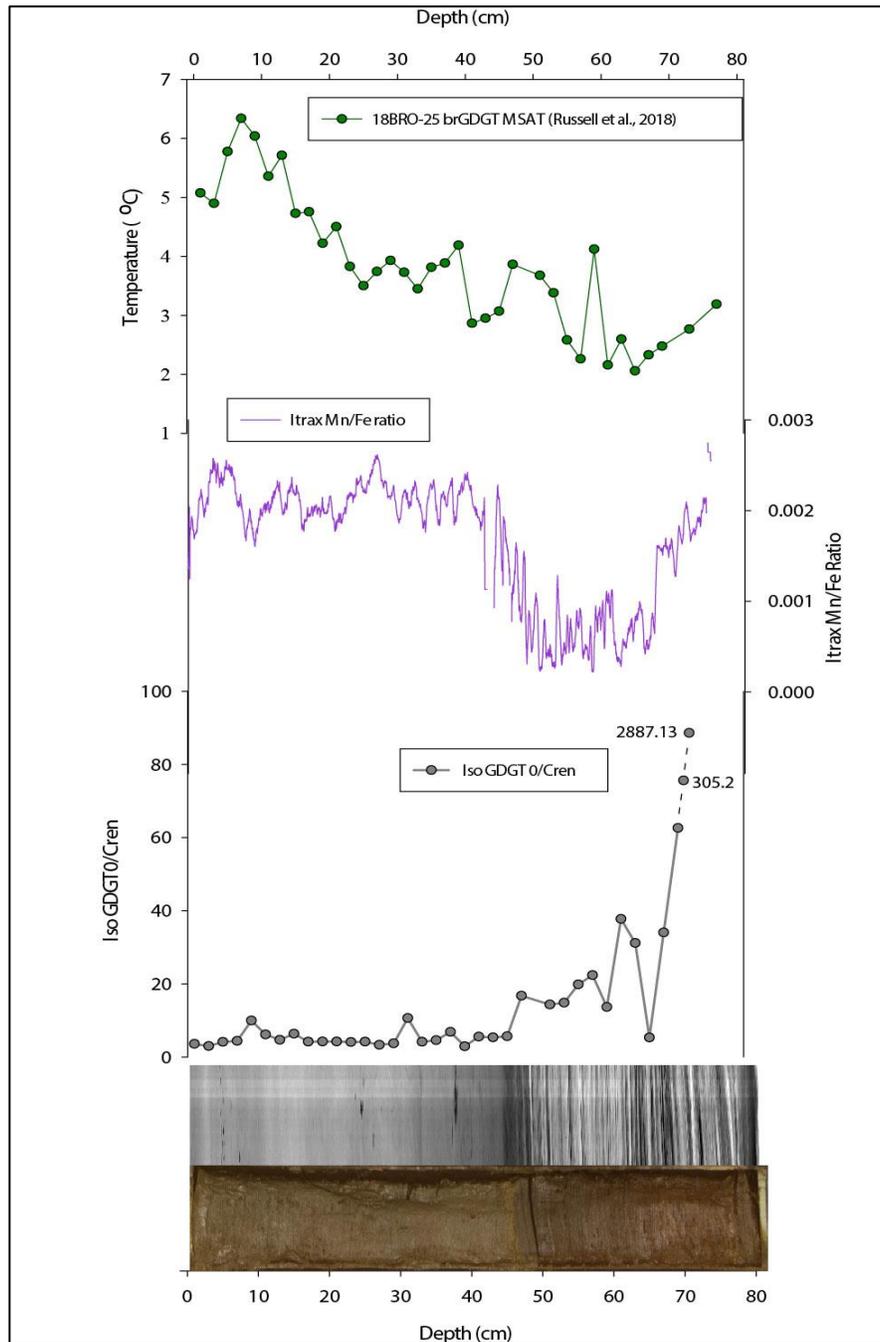
production of brGDGTs.

Figure 14. *Comparison of 18BRO-25 brGDGT MAT, Itrax Mn/Fe ratio, Iso GDGT 0/
Crenarchaeol ratio, and 18BRO-25 radiograph image.*

The Mn/Fe in the 18-BRO-25 core taken from Itrax core-scanning (de Wet unpublished data; Figure 14) shows a significant drop between ~45-70 cm, which roughly matches the interval with the lowest brGDGT-derived temperatures. Previous work has shown that the sedimentary Mn/Fe ratio could be used as a proxy to reconstruct bottom water oxygenation in lakes (Naeher et al., 2013). Thus, the low Mn/Fe ratio found in the ITRAX data in the lower depths of the BRO sediment core could indicate low oxygen conditions during that time.

The isoGDGT-0/crenarchaeol ratio shows high values near the bottom portion of the core (Figure 14). As previously discussed, values of this ratio > 2 are indicative of the presence of methanogens (Naeher et al., 2013). In a research study conducted by Naeher et al. (2013), the authors analyzed the distributions of brGDGTs in sediments of a lake environment where they found that GDGT-0 was the predominant isoGDGT under eutrophic conditions that supported the occurrence of methanogens. The appearance of methanogens means that the bottom waters must have been anoxic during that time period, potentially influencing the distribution and source of brGDGTs thus reflecting a bias temperature gradient following the Russell et al., 2018 applied calibration.
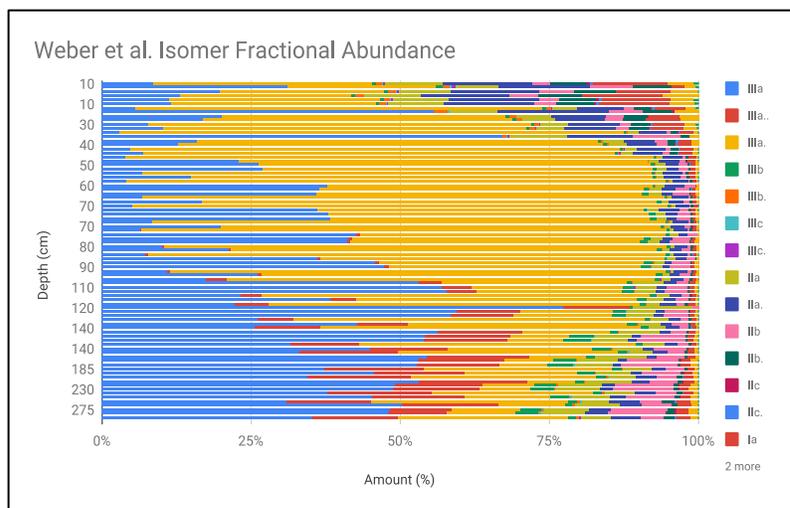
Figure 15. *Weber et al. brGDGT Isomer Fractional Abundance showing an increase in IIIa and decrease in IIIa' isomers with lake depth.*
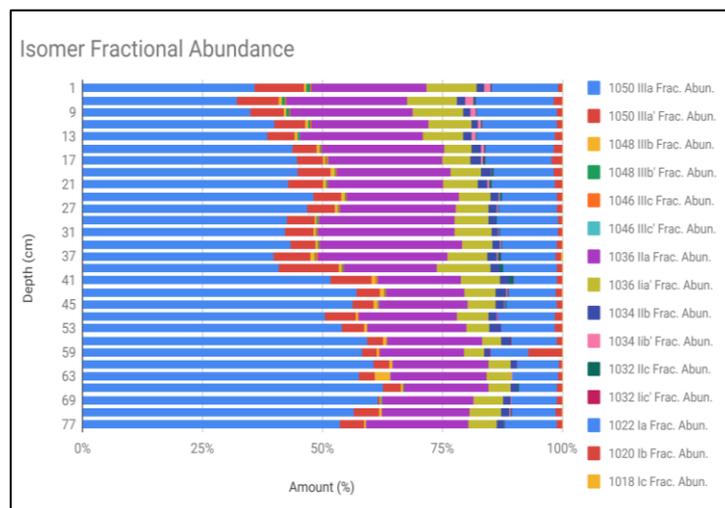
Figure 16. *18BRO-25 brGDGT Isomer Fractional Abundance showing an increase in IIIa and decrease in IIIa' isomers with core depth.*

In Weber et al. 2018, research surrounding bacterial sources of glycerol tetraether lipids in lakes shows a strong correlation with shallow depth lakes (<40 m) and ^{13}C-depleted with thermocline temperatures rather than surface water temperatures. Depletion of ^{13}C suggests a strong signal for methanogensis occurring in the water column. In the specified study lake, they found that there was a clear vertical segregation of IIIa' and IIIa'' isomers in the soil attributing this to the differences in redox requirements for the microorganisms (Weber et al., 2018; Figure 15). The IIIa' isomer percentage decreased as oxygen declined in the water column suggesting an oxic dependent variable. When assessing the fractional abundances of the isomers in the BRO sediment core, it is apparent that there is a decrease in the IIIa' isomer abundance (Figure 16). Ultimately, the authors found that the distribution of brGDGTs changes with depth, alongside oxygenation and composition of the bacterial community, thus showing that brGDGTs produced in anoxic waters are different from those produced on the surface (Weber et al., 2018).

Overall, the brGDGT-inferred temperature reconstruction is not in conjunction with previous Holocene climate, but show a similar composition to other lake sediment sampling thus indicating a change of in situ brGDGT formation in the water column. After assessing both environmental and chemical variables of the brGDGTs derived from Brother of Fog lake in Baffin Island, it is likely that the results of this research are being influenced by anoxia in the lake column. This data suggests that brGDGTs are influenced by variables outside of the previously assumed temperature indicator but also by the amount of oxygenation in the lake.

Conclusion

The evaluation of brGDGTs from a sediment core extracted from Brother of Fog lake, Baffin Island, yielded inferred temperatures that show a steady decline from the present towards ~11,000 years. The cold bias in the temperature reconstruction for the early Holocene does not correspond with climate trends over the Holocene from previous paleoclimate proxy data that indicate warming during this time, and is inconsistent with the maximum in solar insolation in the northern hemisphere during the early Holocene. Because the exact nature of the brGDGT proxy in relation to temperature is seemingly complex, this thesis sought increase our understanding of the physical and chemical variables that are potentially inhibiting an accurate paleoclimate reconstruction from this sediment core.

In order to explain the trends in our temperature reconstruction, selected proxies were analyzed to assess potential biases in the brGDGT proxy. Following this analysis, several confounding variables were identified that include:

1. **ITRAX data and the GDGT-0/crenarcheol ratio indicate the occurrence of anoxia in the lowermost part of the record.**

2. **Anoxia in the water column can influence the distribution of brGDGTs due to changes in derived bacterial community.**

Overall, the 18BRO-25 brGDGT temperature reconstruction was not indicative of warming trends over the Holocene thus alluding to anoxia in the water column that is shifting the source of brGDGT abundance from what was initially hypothesized. This research is essential when it comes to future research on the brGDGT proxy for temperature reconstructions because it shows that the conditions of paleolimnological proxies are not homogenous and require greater knowledge on the surrounding environment. The accuracy of the brGDGT proxy for temperature reconstruction in an Arctic lake setting will require greater temporal resolution and a calculated understanding of cofounding variables. With regards to the application of the brGDGT proxy, it will be important to strengthen further scientific investigation of anoxia in the lacustrine environment in order to produce accurate reconstructions of past climate change in the Arctic.

Suggestions for future research

For future research, it will be important to continue assessing the application of brGDGTs for temperature reconstruction in Baffin Island as well as the surrounding Arctic environment. A set of suggestions for research following the conclusion of this thesis include: (1) conducting research on other lakes in Baffin Island to understand the effects of anoxia on brGDGTs; (2) identifying the carbon isotope signature that would provide a stronger signal of methanogensis in the brGDGTs; (3) formulating a brGDGT temperature calibration specific to anoxic settings. Furthermore, it is essential in paleo-environmental reconstructions based on the brGDGT proxy to conduct a multi-proxy evaluation that permits accuracy within specified conclusions.

Acknowledgements

I would like to thank my thesis advisors, Greg De Wet, Dale Miller, and Julio Sepúlveda for their unwavering commitment to ensuring that I have all of the resources and guidance to be successful throughout this process. I would also like to thank INSTAAR at University of Colorado Boulder for the opportunity to work in the Organic Geochemistry lab for my research.

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