Examining the Mid- Brunhes Event in the Terrestrial Arctic: an Organic Geochemical Record from Lake El'gygytgyn, Russia

Mary Helen Habicht

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EXAMINING THE MID- BRUNHES EVENT IN THE TERRESTRIAL ARCTIC: AN ORGANIC GECHEMICAL RECORD FROM LAKE EL’GYGYTGYN, RUSSIA

A Thesis Presented

by

M. HELEN HABICHT

Submitted to the Graduate School of the University of Massachusetts Amherst in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

September 2015

Department of Geosciences
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M. HELEN HABICHT

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This thesis is the culmination of two years of work that I am very proud of. However, I must acknowledge the people without whom this accomplishment would have been nearly impossible. I must begin by recognizing the many excellent teachers and mentors I have had along the way, especially: Mr. Walter Erhardt at the Battle Creek Area Math and Science Center for the frank introduction to failure; Dr. Thom Wilch at Albion College for the endless encouragement and understanding; Dr. Carrie Menold at Albion College for exposing me to the nuances of scientific research; Dr. Isla Castañeda for immersing me in the subject of organic geochemistry; and Dr. Julie Brigham-Grette for inspiring me to bring passion to all aspects of my life. To all the Geoscience faculty and staff at UMass who have helped and mentored me over the past two years, thank you. Your encouragement and assistance is truly appreciated.

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Dan, for getting me back in the pool
Ben, for maintaining my sanity
Mom, for showing me resilience
Dad, for teaching me to do my best and have fun

I am ever grateful for your presence in my life.
Love.
ABSTRACT

EXAMINING THE MID- BRUNHES EVENT IN THE TERRESTRIAL ARCTIC: AN ORGANIC GECHEMICAL RECORD FROM LAKE EL’GYGTYGN

SEPTEMBER 2015

M. HELEN HABICH, B.A., ALBION COLLEGE
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Directed by: Assistant Professor Isla S. Castañeda

Multi-proxy analysis of lake sediments provides information on changes in environmental and climatic conditions over geologic time. Biomarker proxies combined with sedimentological characteristics provide an excellent approach for reconstructing past climate change. This method is applied in this study to produce a paleoclimate record from Lake El’gygytgyn in the Far East Russian Arctic (67.5 oN, 172 oE). Analysis of branched glycerol dialkyl glycerol tetraethers (brGDGTs) produces temperature reconstructions and measurements of $n$- alkanes (plant leaf waxes) provide a sense of aridity changes at the site over the interval of 340-730 ka. The combination of organic geochemical proxies and sedimentological measurements provides a robust record of climatic change and lake environmental parameters during the Mid- to Late Pleistocene. The glacial and interglacial cycles of the Pleistocene are punctuated by the Mid- Brunhes Event (MBE), a climatic transition at ~430 ka. Numerous records, particularly from the Southern Hemisphere have indicated increased amplitude of climatic cycles after 430 ka, This study provides evidence of an MBE signal in the terrestrial Arctic. Proxy data from the Lake El’gygytgyn core indicates increased climatic variability after 430 ka.

Paleoclimate temperature reconstructions based on brGDGTs produce warmer
interglacial periods and cooler glacial periods in the post-MBE interval, suggesting the terrestrial Arctic experienced increased amplitude glacial and interglacial cycles post-MBE. $n$-Alkane average chain length values indicate a shift toward wetter conditions, particularly during interglacial periods after the MBE. It is possible that changes in Antarctic bottom water production and associated variability in North Pacific upwelling and sea surface temperatures are responsible for translating the signal of the MBE from the Southern Hemisphere to Lake El’gygytgyn and the Arctic.

Analysis of brGDGTs during this study led to the discovery of a suite of novel compounds. These have been loosely identified as H-shaped brGDGTs with m/z 1048, 1034, and 1020. The presence of these compounds has since been noted in a variety of globally distributed marine and lacustrine samples. The relatively high abundances and ubiquitous nature of these compounds make their use as biomarkers promising.
This thesis represents four semesters (Fall 2013- Spring 2015) of research carried out in the department of Geosciences at the University of Massachusetts –Amherst, and builds on the significant work carried out by a team of international scientists over many years. The sediments that I analyzed were collected in 2009 by Dr. Julie Brigham-Grette and many others as an International Continental Scientific Drilling Program (ICDP) project. This massive undertaking was the culmination of two decades of planning, political logistics, and orchestration of several international scientific groups.

After the successful collection of 318 meters of core and subsequent sampling at the University of Bremen, the working and archive halves of the core sections were sent to the National Lacustrine Core Repository, LacCore, at the University of Minnesota. The cores were excellently curated, and it was there that I and fellow students Ben Keisling and Greg de Wet, went to sample the cores in September 2013. This thesis presents results of biogeochemical analysis of samples during 2014 under the supervision of Dr. Isla Castañeda in the UMass Biogeochem Lab.

My research was funded by NSF Grant #1204087 to Dr. Julie Brigham-Grette, Dr. Isla Castañeda, and Dr. Steve Burns (all at UMass), titled “Characterizing Arctic Climate Extremes from the Pliocene to the Present: the view from Lake El’gygytgyn, western Beringia.” Funding for research detailed in Chapter 3 of this thesis, “Structure and significance of H- shaped branched GDGTs in Lake El’gygytgyn (Russia) sediments” came from the Elsevier Research Scholarship 2014.
My work focuses on identifying a signal of the Mid-Brunhes Event (MBE) climatic transition and reconstructing climatic variability in the Arctic over the interval of 340-730 ka. Many records have noted increased amplitude of glacial-interglacial climate cycles after the MBE. The presence of the MBE as a global climatic event has been disputed, and this may be in part due to the lack of long, continuous terrestrial records from the Northern Hemisphere. The Lake El’gygytgyn sediment record provides a solution to this problem as it is continuous and covers the last 3.6 Ma. Studies of the Arctic are also critical as the region is currently undergoing rapid and unprecedented climate change.

All unpublished data presented in this manuscript will be archived with ScholarWorks at UMass, and following publication, with the National Oceanic and Atmospheric Administration (NOAA) National Climatic Data Center Paleoclimate database.
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CHAPTER 1
INTRODUCTION

1.1 Overview

Our capacity for understanding current climate and predicting future climate change depends on our knowledge of past climate. The Arctic is currently undergoing unprecedented environmental change at extremely rapid rates. This environmental evolution includes increased temperatures, changes in precipitation, and changes in atmospheric circulation (IPCC, 2014). The Arctic is particularly sensitive to global climate change because of strong feedback mechanisms involving marine, atmospheric, cryosphere, and terrestrial processes (IPCC, 2014), so it is essential to understand the paleoclimate history of this region. Reconstructing past Arctic climate provides insight about important climate change variables, thus creating context for current and future changes.

Lake sediments are valuable paleoclimate archives of terrestrial settings. Lakes often have abundant organic matter that can be used to infer paleoclimatic changes. Ancient organic molecules that have been preserved in sediment, also known as biomarkers, come from specific organisms and provide information on past lake ecological and environmental conditions. Two types of biomarkers are used in this study: branched glycerol dialkyl glycerol tetraethers and \( n \)-alkanes. Branched glycerol dialkyl glycerol tetraethers (hereafter brGDGTs) are membrane lipids presumed to be produced by bacteria, whose distributions and abundances can be calibrated to reconstruct past annual air temperature and pH (Weijers et al., 2007). Their use as a paleoclimate proxy is
relatively novel and has been successful in numerous globally distributed studies (Loomis et al., 2012; Peterse et al., 2014; Shanahan et al., 2013b; Sun et al., 2011). BrGDGTs are used in this study to reconstruct relative temperature changes in the terrestrial Arctic. Aliphatic hydrocarbons or \( n \)-alkanes are compounds produced by plants and form the waxy barrier on leaves. Different lengths of these carbon chains are attributed to various types of plants, and their distributions in sediments can be used as a proxy for environmental changes (Bush and McInerney, 2015; Cranwell et al., 1987; Eglinton and Hamilton, 1967; Ficken et al., 2000; Meyers, 2003). BrGDGTs and plant leaf waxes are discussed in more detail in sections 1.3.1 and 1.3.2, respectively.

This project tests the hypothesis that biomarkers and other proxy data in a sediment core from Lake El’gygytgyn, NE Russia record a signal of the Mid- Brunhes Event (MBE), a climatic transition \(~430\) ka. Numerous globally distributed records have indicated that after the MBE, the amplitude of glacial- interglacial climate cycles increased (Augustin et al., 2004; Becquey and Gersonde, 2002; Berger and Wefer, 2003; Blain et al., 2012; Jansen et al., 1986; Tzedakis et al., 2009; Wang et al., 2003; Yin and Berger, 2010a) (Figure 1). However, the mechanism producing the event and the geographic extent of the MBE are unconfirmed.

Lake El’gygytgyn is a 3.6 Ma old meteorite impact crater (Layer, 2000) located in a previously unglaciated region of northeast Siberia. Sediment cores drilled in 2009 comprise 318 m of sediment and provide a continuous record of the past 3.6 Ma. This core is the longest record of the terrestrial Arctic. Previous multi-proxy analysis of Lake El’gygytgyn sediments have shown a regionally representative signal of climate changes and indicated global teleconnections (Brigham-Grette et al., 2013; Melles et al., 2012),
both of which make this lake core an excellent place to examine the MBE in the terrestrial Arctic. The research in this thesis builds upon this initial proxy work of Melles et al. (2012) and Brigham-Grette et al. (2013) and provides a record of relative temperature change and environmental evolution based on brGDGTs and n-alkanes from 340-730 ka.

1.2. Lake El’gygytgyn

Lake El’gygytgyn is located 100 km north of the Arctic Circle in northeastern Russia (67.5°N, 172°E) (Figure 2). The lake lies in a meteorite impact crater formed 3.58 ± 0.04 Ma (Layer, 2000). Lake El’gygytgyn is 170 m deep, has a diameter of 12 km, and a surface area of 110 km² (Nolan and Brigham-Grette, 2007). The lake is relatively round, with a basin-like shape and lies within a small catchment with an area of 293 km² (Nolan and Brigham-Grette, 2007). This small catchment area allows for all climatic signals recorded in the sediment to result from the close surroundings. The sediment record is continuous and covers the last 3.6 Ma with centennial- to millennial-scale temporal resolution (Melles et al., 2012).

Lake El’gygytgyn is a cold, monomictic lake with summer temperatures of ~3 °C (Nolan and Brigham-Grette, 2007). The lake is oligotrophic to ultra-oligotrophic due to 9 months of lake-ice cover per year (Nolan and Brigham-Grette, 2007). Lake El’gygytgyn experiences complete water column overturning during the ice-out season and has low primary productivity levels (Nolan and Brigham-Grette, 2007). The combination of these factors produce well oxygenated bottom waters throughout the year (Melles et al., 2012).
Today, the Lake El’gygytgyn region has mean annual air temperature of -10 °C with mean July temperatures of 8 °C and average winter lows of -35 °C (Nolan and Brigham-Grette, 2007). Mean annual precipitation is approximately 200 mm/year (Nolan and Brigham-Grette, 2007). Re- analysis data indicate the climatology of the basin is representative of much of the Arctic (Nolan and Brigham-Grette, 2007). The climatology of the region currently maintains sparse tundra vegetation species such as hummock and moss as well as intermittent prostrate willows and dwarf birch (Brigham-Grette et al., 2013). However, pollen data indicate that the lake was surrounded by boreal forest during intervals of its history (Brigham-Grette et al., 2013; Melles et al., 2012). There are two primary atmospheric circulation patterns that affect Beringia: The Siberian High and the Aleutian Low (Mock et al., 1998; Nolan et al., 2013) (Figure 2). Nolan et al. (2013) analyzed modern synoptic weather patterns in the region. Their results indicate a strong seasonality in modern weather patterns around Lake El’gygytgyn (Nolan et al., 2013). Summer weather is generally typified with weak low pressure systems over the Arctic Ocean or Siberia, and winter weather is dominated by strong high pressure over the Arctic Ocean and strong low pressure over the Pacific (Nolan et al., 2013).

Lake El’gygytgyn was drilled in winter 2009 from a lake ice platform (Melles et al., 2011). A 318 m long composite sequence representing the last 3.6 Ma was recovered in International Continental Drilling Program (ICDP) core 5011-1. The core was investigated by non-destructive scanning and logging technologies. Core chronology was developed based on magnetostratigraphy (Haltia and Nowaczyk, 2013) and tuning of proxy data with marine isotope stratigraphy (Lisiecki and Raymo, 2005) and summer insolation at 65 °N (Laskar et al., 2004) (Nowaczyk et al., 2013). Lake El’gygytgyn
provides a continuous record of the terrestrial Northern Hemisphere spanning the interval of the MBE and thus is an ideal record to test for the presence of this event at a high-latitude continental site.

1.3 Lipid Biomarkers

Organic matter preserved in sediments can provide a direct indication of environmental conditions at the time of deposition. Therefore, these compounds are significant to paleoclimate studies. Numerous individual organic compounds and a variety of classes of these organic molecules (lipids) found in sediments can be linked to a specific organism or biological process, and are therefore referred to as “biomarkers” (Peters et al., 2005). Biomarkers may be preserved in geologic material for up to billions of years, so they may be used to provide a basis of environmental and climatic conditions throughout much of Earth’s history. This study utilizes an organic geochemical approach based on brGDGTs and \( n \)-alkanes to examine the paleoclimate history surrounding the MBE in the terrestrial Arctic.

1.3.1 Branched GDGTs

Branched glycerol dialkyl glycerol tetraethers are membrane lipids, likely produced by bacteria, ubiquitous in soils globally (Weijers et al., 2007) (Figure 3). The distribution of brGDGTs, expressed by their degree of methylation (methylation index of branched tetraethers; MBT) and cyclization (cyclization index of branched tetraethers; CBT) in soils has been found to correlate with mean annual air temperature (MAAT) and soil pH (Weijers et al., 2007). CBT is a proxy for soil pH and is based on the negative correlation between the relative number of cyclopentane moieties of brGDGTs and the
pH of the growth environment (Weijers et al., 2007). MBT, based on the number of methyl branches, is primarily a function of temperature, but is also negatively correlated to soil pH. To reconstruct MAAT, soil pH is first calculated from CBT, and then this value is used to correct the MBT value for the effect of soil pH. Recently, De Jonge et al. (2013) found that the dependence of MBT on CBT is an artifact of incomplete separation by HPLC of the brGDGT isomers of hexamethylated brGDGTs and the authors developed a new method for complete separation of the isomers. However, the new method is currently unpublished (Hopmans et al., in prep) and this study utilizes the original method of Weijers et al. (2007).

Branched GDGTs are increasingly used as a proxy to reconstruct past temperature and pH variability in studies from a variety of environments and climates (Loomis et al., 2012; Pearson et al., 2011; Peterse et al., 2014; Shanahan et al., 2013b; Sun et al., 2011). Initially, brGDGTs were presumed to be exclusively produced in soils, and subsequently washed into lakes or marine environments via erosion by rivers and streams (Hopmans et al., 2004). Recent research has suggested that they may also be produced in situ in lakes and rivers (Bechtel et al., 2010; Buckles et al., 2014; De Jonge et al., 2015; Loomis et al., 2014, 2012; Schoon et al., 2013; Tierney et al., 2010; Tierney and Russell, 2009; Weber et al., 2015; Zell et al., 2013; Zhu et al., 2011)). The source of brGDGTs at Lake El’gygytgyn is unconfirmed, but it is suspected that the main source is from in situ production within the water column of the lake. This is because Lake El’gygytgyn is surrounded by permafrost with a shallow active layer with low concentrations of brGDGTs (Bischoff et al., 2013), yet the lake sediments have relatively high concentrations of brGDGTs (D’Anjou et al., 2013). Thus, it is likely that much of the
brGDGT production must occur either throughout the water column or within the lake sediments. There are numerous regional and global calibrations for calculating MAAT from MBT/CBT ratios in soils and lakes (Loomis et al., 2012; Pearson et al., 2011; Peterse et al., 2012; Sun et al., 2011; Tierney et al., 2010; Weijers et al., 2007; Zink et al., 2010). The relationships between MBT/CBT, temperature, and pH vary widely between different studies, so a large range of reconstructed absolute temperatures are produced when applying different calibrations to the same data; however, relative trends remain the same (Figure 7). BrGDGT sources and calibrations are discussed in more detail in section 2.5.1.

1.3.2 Plant leaf waxes (n-alkanes)

Aliphatic hydrocarbons (n-alkanes) are organic compounds produced by plants as leaf waxes (Figure 4)(Eglinton and Hamilton, 1967). They are widespread in lacustrine sedimentary archives and can be derived from autochthonous and allochthonous sources (Didyk et al., 1978; Eglinton and Hamilton, 1967). Principally, the sources of n-alkanes in lake sediments are algae and plants that live in the lake and vascular plants that reside around it. These compounds are useful indicators of local environmental changes. Short chain n-alkanes (C_{15}-C_{21}) are attributed to algae and photosynthetic bacteria (Cranwell et al., 1987; Meyers, 2003), submerged and emergent aquatic plants are the main producers of mid-chain (C_{21}, C_{23}, and C_{25}) n-alkanes (Ficken et al., 2000), and long chain compounds (C_{25}-C_{33}) are characteristic of higher terrestrial plants (Cranwell et al., 1987; Eglinton and Hamilton, 1967). Various n-alkane indices based on the molecular distributions of each sample can provide environmental information. These ratios include
the terrestrial to aquatic ratio (TAR) (Bourbonniere and Meyers, 1996), the average chain length (ACL) (Poynter and Eglinton, 1990), and the carbon preference index (CPI) (Bray and Evans, 1961). The CPI can provide information on the preservation or degradation in the system as well as source organism distributions. The TAR index can indicate organic matter (OM) sources, distinguishing contributions of terrestrial OM from aquatic. The ACL can be used to assess hydrologic variability as it is sensitive to both temperature and aridity (Bush and McInerney, 2015 and references therein).

1.3.3 Other algal biomarkers

Numerous organic compounds produced by algae make useful biomarkers. The carbon number, position of methyl groups, and double bonds in sterols and stanols may be indicative of certain groups of organisms (Volkman, 1986; 2003). For example, dinosterol is produced by dinoflagellate (Pyrrophyta) species (Boon et al., 1979; Robinson et al., 1984; Volkman, 2003), and has been used for examining past changes in dinoflagellate productivity at Lake El’gygytgyn (e.g. D’Anjou et al., 2013). Tetrahymanol, a biomarker for bacterivorous ciliates may be used to infer the presence of a stratified water column (Castañeda and Schouten, 2011 and references therein). The presence of long chain \( n \)-alkyl diols in sediments may indicate input from algae in marine and lacustrine settings (Castañeda et al., 2009 and references therein) and these compounds can be used to reconstruct aquatic primary productivity at a site, which is associated with changes in climatic and environmental variability (Rampen et al., 2012). Finally, pentacyclic triterpenes, such as arborinol, are derived from higher order terrestrial plants (Jacob et al., 2005). Arborinol may be used to reconstruct a record of
vegetation and forest cover at the study site (Jacob et al., 2005) and has been previously identified in Lake El’gygytgyn sediments (D’Anjou et al., 2012). However, other studies have proposed arborinol to be of a microbial origin instead of being sourced from higher plants (Jaffé and Hausmann, 1995). See Figure 4 for structures of compounds discussed in this section.

1.4 Thesis Outline

This thesis is divided into four chapters. Chapter one provides a general introduction to the setting of Lake El’gygytgyn, the MBE, and the proxies used in this study. Chapter two comprises a manuscript detailing the MBE signal at Lake El’gygytgyn. Chapter three provides a brief summary of an organic geochemical project identifying a new compound (H- shaped brGDGTs) found in the Lake El’gygytgyn sediment core. Finally, chapter four presents a summary of conclusions and suggestions for future work on this project.
CHAPTER 2
EXAMINING THE MID- BRUNHES EVENT IN THE TERRESTRIAL ARCTIC:
AN ORGANIC GEOCHEMICAL RECORD FROM LAKE EL’GYGGYTGN

2.1 Abstract

The glacial-interglacial cycles of the Pleistocene are punctuated by a climatic transition at ~ 430 ka, the Mid-Brunhes Event (MBE). After the MBE, numerous records have indicated increased amplitude climatic cycles, with especially warm interglacials occurring after 430 ka. This study provides an Arctic paleoclimate record based on organic biomarkers in sediments from Lake El’gygytgyn, Russia spanning 340 ka - 730 ka. Analysis of branched glycerol dialkyl glycerol tetraethers (brGDGTs) produces temperature reconstructions and measurements of n-alkanes (plant leaf waxes) average chain length (ACL) provide a sense of hydrologic variability through changes in aridity at the site. Temperature reconstructions based on brGDGTs indicate the Arctic experienced the warmest interglacial periods during the post-MBE interval, although interglacials prior to the event are also quite warm. Glacial periods prior to the MBE are relatively mild and become more extreme during the post-MBE interval. ACL values indicate arid glacial periods and wet interglacial periods with a shift toward increased wetness after the MBE. The combination of this data provides a robust record of climatic change and variability in lake environmental parameters during the Mid-Pleistocene. Statistical analysis of the combined data sets indicates greater climatic variability during the post-
MBE interval (after 430 ka), suggesting the terrestrial Arctic experienced climatic cycles of greater amplitude after the event.

2.2 Introduction

The climate of the Pleistocene (2.58 Ma – 11.7 ka) is characterized by the strong alternation between cold (glacial) and warm (interglacial) periods. This global climatic variation is punctuated by two major changes. First, the Mid Pleistocene Transition (MPT), which began at 1250 ka and was complete by 700 ka, over which the period of climate cycles changed from 41 ka to 100 ka and global ice volume increased (Clark et al., 2006; Imbrie et al., 1993; Ruddiman et al., 1989). Next, was the Mid Brunhes Event (MBE), a climatic transition at ~430 ka, after which the amplitude of glacial-interglacial cycles increased (Jansen et al., 1986). The MBE occurs in the transition between Marine Isotope Stage (MIS) 12 and MIS 11 at ~430 ka (Meckler et al., 2012) and divides the mild, early- to mid- Pleistocene interglacials from the warmer mid- to late- Pleistocene interglacials (Figure 8). In this study, pre- and post- MBE intervals are defined as 866-430 ka and 430- 0 ka respectively. Earth’s climate prior to the MBE is characterized by cooler interglacials (Augustin et al., 2004), less radiative forcing from greenhouse gases including carbon dioxide and methane (Jouzel et al., 2007; Lüthi et al., 2008; Siegenthaler et al., 2005), and less global ice volume (Lisiecki and Raymo, 2005). After the MBE, numerous records including Antarctic ice cores (Augustin et al., 2004) and benthic oxygen isotopes (Lisiecki and Raymo, 2005) indicate increased variability in temperature, greenhouse gases, and global ice volume. Increased amplitude of glacial-interglacial cycles after the MBE has been noted in many records, particularly from the
Southern Hemisphere (Augustin et al., 2004; Becquey and Gersonde, 2002; Berger and Wefer, 2003; Jansen et al., 1986; Tzedakis et al., 2009; Wang et al., 2003).

Paleo-investigations of marine and terrestrial sequences throughout the Northern Hemisphere have provided conflicting evidence for the presence of an MBE signal (Blain et al., 2012; Candy et al., 2010; Cronin et al., 2014; Fawcett et al., 2011; Holden et al., 2011; Meckler et al., 2012; Sarkar and Gupta, 2014; Yin and Berger, 2010b). While many paleoclimate records show increased glacial and interglacial amplitudes following the MBE (Blain et al., 2012; Cronin et al., 2014; Fawcett et al., 2011; Lang and Wolff, 2011), others indicate warmer interglacials but note no change in the glacial amplitude (Lambert et al., 2008) or find no evidence of an MBE signal (Candy et al., 2010) (Figure 5). Thus, the presence of the MBE as a global climatic transition is disputed (Blain et al., 2012; Candy et al., 2010). In their analysis of the British terrestrial sequence, Candy et al. (2010) demonstrated that interglacials during the middle Pleistocene were equally as warm as those occurring in the late Pleistocene, and suggest that the MBE is not a global climate event, but rather is constrained to the higher latitudes of the Southern Hemisphere. Candy and McClymont (2013) investigated proxy records in the North Atlantic. They found that SST records from the North Atlantic latitudes 40° to 56° N show no statistical difference between the magnitudes of interglacial temperature during MIS 19-13 and MIS 11-1 (Candy and Mcclymont, 2013). In their analysis of a stalagmite from Borneo, Meckler et al. (2012) determine that although hydroclimate and temperature vary between interglacials in their record, they do not change across the MBE. It is postulated that the MBE is only seen in the high latitudes due to the effects of polar amplification and that this signal did not penetrate into the deep tropics (Meckler et
al., 2012). In contrast, Lang and Wolff (2010) found that many records in their global analysis show increased amplitude glacial cycles, with warmer interglacial periods and cooler glacial periods predominating the post-MBE interval. The inconsistency of an MBE signal preserved in records from the Northern Hemisphere may be due to a shortage of long, continuous, high-resolution terrestrial records (Candy et al., 2010; Tzedakis et al., 2009).

Hypotheses as to the mechanism producing the MBE cite orbital forcing and carbon dioxide concentrations (Berger and Yin, 2012; Jouzel et al., 2007; Yin and Berger, 2010b), ocean circulation changes (Alonso-Garcia et al., 2011; Berger and Wefer, 2003; Caley et al., 2012; Jouzel et al., 2007), and ice sheet dynamics (Holden et al., 2011). The prevailing hypothesis comes from a modeling study by Yin (2013). She finds that changes in insolation and associated feedbacks with the location of the polar front, salinity, and sea ice formation impacted Antarctic bottom water (AABW) formation, leading to generally cooler interglacials in the pre-MBE interval (Yin, 2013).

Constraining the geographic extent of the MBE is critical to understanding this major change in earth’s climate and in providing context for present and future climatic evolution in the terrestrial Arctic. Here, we investigate the MBE in the terrestrial Arctic using an organic geochemical approach toward sediments from Lake El’gygytgyn, Russia located 100 km north of the Arctic Circle (Figure 2). The sediment core, comprising 3.6 million years of accumulation was drilled in spring 2009 (Melles et al., 2011) and represents the longest continuous high-resolution record of the terrestrial Arctic, proving to be an unparalleled record for examining climatic change. Significant work has already been completed on the Lake El’gygytgyn core, providing numerous records of
environmental conditions through the Pleistocene and Pliocene (e.g. Brigham-Grette et al., 2013; Melles et al., 2012). Previous studies of the lake sediments have shown considerable teleconnections with Antarctic records (Brigham-Grette et al., 2013; Coletti et al., 2014; Melles et al., 2012), fostering a sense of the communication between the hemispheres and potential for recording the MBE climatic transition in the Northern Hemisphere. MIS 11 (the first interglacial after the MBE) has been coined a “super interglacial” at Lake El’gygytgyn with sediments indicating extremely high diatom and terrestrial plant productivity during this period (D’Anjou et al., 2013; Melles et al., 2012; Vogel et al., 2013), thus suggesting enhanced interglacial intensity in the terrestrial Arctic after the MBE. In addition, analysis of sediment hue, a proxy for wetness at Lake El’gygytgyn, indicates significantly wetter conditions during MIS 11 and 9 than throughout other Pleistocene interglacials (Wei, 2013).

In this study we examine temperature variability during MIS 11 and the period surrounding the MBE and construct a paleoclimate record with ~3ka timestep spanning the interval of 340 to 730 ka. Proxies utilized in this record include the methylation and cyclization of branched tetraethers (MBT/CBT) to reconstruct past temperature (Weijers et al., 2007) and multiple ratios of plants leaf wax n-alkanes providing information on environmental parameters.

### 2.3 Methods and Background Information

#### 2.3.1 Study site

Lake El’gygytgyn is located in the Chukotka Peninsula of the Far East Russian Arctic (67°30’ N, 172°5’E) (Figure 2). The lake was created by a meteorite impact 3.58 ±
The catchment has a diameter of 18 km and an area of 293 km² (Nolan and Brigham-Grette, 2007). A network of streams carries runoff into the lake and the Enmyvaam River provides an outlet to the Bering Sea (Nolan and Brigham-Grette, 2007). Today, Lake El’gygytgyn is 170 m deep, 12 km wide, and has a volume of 14.1 km³ (Nolan and Brigham-Grette, 2007). The lake is monomictic and oligotrophic, with summer temperatures not exceeding 4°C (Nolan and Brigham-Grette, 2007). Annual overturning occurs in late summer, and lake ice formation begins by October and persists through June (Nolan and Brigham-Grette, 2007).

Modern air temperatures at Lake El’gygytgyn range from -46°C in the winter to +26°C in the summer, with a mean annual air temperature of -10.3°C (Nolan and Brigham-Grette, 2007). There is typically very little precipitation at the site, with the cumulative annual precipitation from between 2002 to 2007 ranging from 70 to 200 mm (Nolan, 2012). The area around Lake El’gygytgyn is affected by winds from dominantly north or south (Nolan and Brigham-Grette, 2007). There are two main atmospheric circulation patterns that affect the area: the Siberian High and the Aleutian Low (Mock et al., 1998; Nolan, 2013) (Figure 2). The summer weather at the lake is characterized by a weak Aleutian pressure systems, and winter is predominated by a strong Siberian High systems and weaker low pressure systems in the Pacific (Nolan et al., 2013). Precipitation in these seasons results from the dominant pressure system and is relatively equally distributed between summer and winter (Nolan, 2012). Modern vegetation at the lake is characterized as tundra, with lichen and herbaceous taxa dominating (Lozhkin et al., 2006). The closest modern forest is composed of conifers and lies ~150 km south west of the lake (Lozhkin et al., 2006).
Lake El’gygytgyn was drilled from an ice platform on International Continental Scientific Drilling Project (ICDP) expedition number 5011-1 in winter 2008/2009 (Melles et al., 2011). Three cores of lake sediment and impact rock: A, B, and C were drilled in the center of the lake at ~170 m water depth. Core A recovered 132 m of sediment at 92% recovery, Core B recovered 106.6 m at 98% recovery, and Core C recovered 273.8 m at 63% recovery (Melles et al., 2012). The three cores were combined to create a composite core, which is 318 m long and covers the past 3.6 Ma. The Lake El’gygytgyn age model is based on magnetostratigraphy (Haltia and Nowaczyk, 2013) and is tuned to the global benthic stack and regional insolation (Melles et al., 2012; Nowaczyk et al., 2013).

2.3.2 Core sampling

The composite Lake El’gygytgyn sediment core is curated at the national lacustrine core facility (LACCORE) at the University of Minnesota. Subsamples were taken at 1 cm resolution in Fall 2013, but for this study, the sampling resolution is ~3 kyr. Mean sedimentation rates during the last 1.0 Ma were ~4 cm ka⁻¹ (Nowaczyk et al., 2013), thus each 1 cm sample in this study interval integrates approximately 250 ka. Samples were kept frozen until selection for biomarker analysis.

2.3.3 Sample extraction and preparation

138 sediment samples (1-6 grams) were selected for analyses at a coarse sampling resolution of approximately one sample per 3 kyr for the 390 kyr study interval. Additional samples were taken for the period of MIS 11 to provide higher resolution (~1
ka) through this interval. Sediment samples were freeze-dried, homogenized, and then extracted with a dichloromethane (DCM)/methanol (MeOH) (9:1, v/v) mixture using a Dionex Accelerated Solvent Extractor (ASE 200). The total lipid extract (TLE) from each sample was separated into apolar (9:1 DCM/hexane v/v) and polar (1:1 DCM/MeOH v/v) fractions using alumina oxide column chromatography. The polar fractions were then split in half. One half was filtered for analysis of branched glycerol dialkyl glycerol tetraethers (brGDGTs) via high performance liquid chromatography-mass spectrometry (HPLC-MS). The other half was saved for derivitization and characterization of polar lipids.

2.3.4 Branched GDGT analysis and quantification by HPLC-MS

Splits of the polar fractions were filtered through 0.45µm PTFE syringe filters in 99:1 hexane/isopropanol (v/v). A C₄₆ GDGT internal standard was added. Samples were analyzed on an Agilent 1260 HPLC coupled to an Agilent 6120 Quadrupole MSD. Separation of compounds was carried out on a 150 mm long, 2.1 mm diameter Prevail Cyano 3µm column. Scanning was performed in selected ion monitoring (SIM) mode. Identification and quantification of brGDGTs were achieved following the methods of Hopmans et al. (2000) and Schouten et al. (2007).

2.3.5 n-alkane identification and quantification by GC-FID

Gas chromatography-flame ionization detection (GC-FID) was used to identify and quantify n-alkanes in the apolar fraction. The GC-FID was an Agilent 7890A GC with equipped with two Agilent 7693 auto injectors and two FIDs. The GC-FID columns were Agilent HP-5 columns (60 m x 320 µm internal diameter and 0.25 µm film
thickness). Helium was used as the carrier gas. The GC-FID method for analysis of apolar fractions begins at a temperature of 70 °C, ramps at 10 °C/minute to 130 °C, ramps again at 4 °C/minute until it reaches 320 °C, and then holds the final temperature for 10 minutes. *n*- Alkanes were quantified using an external calibration curve where squalane was injected at multiple concentrations ranging from 2 to 100 ng/μl.

2.4 Results

2.4.1 BrGDGTs

All samples analyzed contained brGDGTs, although in a few samples, the compound abundances were too low to provide reliable MBT/CBT reconstructions. brGDGT concentrations range from 0. μg g sed⁻¹ to 1.56 μg g sed⁻¹ with a mean of 0.11 μg g sed⁻¹ (Figure 6). MBT values range from 0.12 to 0.44 with a mean of 0.22 (Figure 6). CBT values range from 0.09 to 1.5 with a mean of 0.6 (Figure 6). See Table 2 for definitions of these indices.

2.4.2 *n*-alkanes

The C₁₇ to C₃₅ *n-* alkanes are present the Lake El’gygytgyn samples. Concentrations of total *n-* alkanes range from 0.54 to 403.67 ng g sed⁻¹ with a mean value of 26.95 ng g sed⁻¹. Concentrations of short-chain (C₁₇ to C₂₃) *n-* alkanes range from 0.03 to 174.34 ng g sed⁻¹ with an average of 6.98 ng g sed⁻¹ (Figure 6). Concentrations of long-chain (C₂₇ to C₃₃) *n-* alkanes range from 0.4 to 153.45 ng g sed⁻¹ with an average of 13.15 ng g sed⁻¹ (Figure 6). The carbon preference index (CPI) values for C₂₃ to C₃₃ *n-* alkanes ranges between 0.33 and 10.4 with an average of 4.3. The terrestrial to aquatic *n-*
alkane ratio (TAR) has values between 1.33 and 27.74 with an average of 7.24. Neither of these ratios seem to have a distinguishable pattern for glacial or interglacial cycles, and so have not been included in the figures. The average chain length (ACL) of \( n \)-alkanes in samples from this study ranges from 24.9 to 30.3 with an average of 27.7 (Figure 6). Higher ACL values generally correspond to glacial periods in the record. See Table 2 for definitions of, and references for indices discussed above.

2.5 Discussion

2.5.1 Biomarker Reconstructions

BrGDGTs are membrane lipids presumably produced by Acidobacteria bacteria ubiquitous in soils globally (Sinninghe Damsté et al., 2011; Weijers et al., 2007) (Figure 3). The distribution of brGDGTs, expressed by their degree of methylation (Methylation Index of Branched Tetraethers; MBT) and cyclization (Cyclization Index of Branched Tetraethers; CBT) in soils is correlated with mean annual air temperature (MAAT) and soil pH (Weijers et al., 2007). CBT provides a proxy for pH as there is a negative correlation between the relative number of cyclopentane moieties of brGDGTs and the pH of the growth environment (Weijers et al., 2007). MBT is a function of temperature, but is also negatively correlated with pH. Temperature may be reconstructed by first calculating pH from CBT and then using this value to correct the MBT for the effect of pH (Weijers et al., 2007).

BrGDGTs have been utilized as a paleo proxy for temperature and pH in a variety of environments (D’Anjou et al., 2013; Loomis et al., 2012; Peterse et al., 2014; Sun et al., 2011) Initially, it was thought that these compounds are produced only in soils, and
their presence in aquatic sediments is a result of erosion (Hopmans et al., 2004). More recently, it has been suggested that these compounds are produced \textit{in situ} in lakes and rivers (e.g. (Bechtel et al., 2010; Buckles et al., 2014; De Jonge et al., 2015; Loomis et al., 2014, 2012; Schoon et al., 2013; Tierney et al., 2010; Tierney and Russell, 2009; Weber et al., 2015; Zell et al., 2013; Zhu et al., 2011). The source of brGDGTs at Lake El’gygytgyn is not known, but production within the water column of the lake is suspected. This is because the lake is surrounded by permafrost (Bischoff et al., 2013), making brGDGT production in the soils unlikely.

Temperature changes at Lake El’gygytgyn were examined using the MBT/CBT temperature proxy. Originally developed as a soil based paleotemperature/pH proxy (Weijers et al., 2007), more recent work has shown a significant correlation between brGDGTs in lakes and mean annual air temperature (Bechtel et al., 2010; Blaga et al., 2008; Loomis et al., 2012; Pearson et al., 2011; Shanahan et al., 2013b; Sun et al., 2011, 2011; Tierney et al., 2010; Tierney and Russell, 2009; Zink et al., 2010). Early attempts to apply the same MBT/CBT calibration developed for soils to lacustrine sediments, lead to the conclusion that these calibrations do not accurately reconstruct absolute temperatures when applied to lake sediments (Pearson et al., 2011; Tierney et al., 2010), and produce temperatures that are much lower than measured air or water temperatures. Several studies have attempted to make empirical calibrations for brGDGTs in lakes (Loomis et al., 2012; Pearson et al., 2011; Tierney et al., 2010). Subsequent studies have focused on lake specific calibrations with both the MBT/CBT index as well as various fractional abundances of brGDGTs. The relationships between MBT/CBT, temperature,
and pH vary widely between different various calibrations (Table 1), producing a large range of reconstructed temperatures, but generally the same trends (Figure 7).

Application of MBT/CBT in lakes is complicated. It is noted that without a modern, site-specific calibration and without knowing the direct source (autochthonous or allochthonous) of the brGDGTs in the lake sediments, it is difficult to determine which calibration is most appropriate to apply. However, it is likely that there is some production of brGDGTs in the water column at Lake El’gygytgyn, so a lacustrine calibration may be the most suitable. Some studies have found that brGDGTs may be more abundant in lake sediments than in surrounding soils and the distributions of the compounds in soils are different from those in the lacustrine sediments (Bechtel et al., 2010; Buckles et al., 2014; Loomis et al., 2014; Tierney and Russell, 2009; Weber et al., 2015). Tierney and Russell (2009) found that the degree of methylation and cyclization varied between soil and aquatic samples and produced differing pH values. However, the pH produced by CBT values of brGDGTs in the lake sediments was in agreement with that of the lake water (Tierney and Russell, 2009), suggesting that brGDGTs in the water column produce a lake specific signal. Temperature reconstructions using brGDGTs in lake sediments more accurately reproduce lake temperatures as opposed to soil temperatures (Bechtel et al., 2010; Buckles et al., 2014; Loomis et al., 2014). Therefore, application of a lacustrine calibration is imperative.

The calibration from Chinese and Tibetan lakes by Sun et al. (2011) produces temperatures in closest agreement with summer temperature reconstructions from Lake El’gygytgyn based on pollen in the sediments (Figure 7). Mean temperature of the warmest month (MTWM) based on pollen yields maximum temperatures for MIS 11 of
16 °C (Melles et al., 2012), while maximum temperatures produced from brGDGTs are
~17 °C (Figure 10). Given that pollen is a land based temperature proxy, and brGDGTs
may, to some extent, represent an aquatic temperature signal, this correspondence is
robust. However, the Sun et al. (2011) calibration is only appropriate if the brGDGTs are
providing a summer temperature signal at Lake El’gygytgyn. MBT/CBT temperature
reconstructions and July insolation at 67° N show significant correspondence (Figure 9),
indicating the brGDGTs may indeed be representing a summer signal.

A seasonal bias has been noted in brGDGT distributions in modern lakes from
mid- to high- latitudes. Sun et al. (2011) combined data from Chinese and Tibetan lakes
with existing published data to compare sites between 68 °N to 54°S (Bechtel et al., 2010;
Blaga et al., 2008; Tierney et al., 2010; Tyler et al., 2010; Zink et al., 2010) and found the
relationship between temperature and the MBT/CBT index was most robust during
summer. Pearson et al. (2011) also examined temperature and MBT/CBT, generating an
empirical relationship between brGDGTs in lake surface sediments and summer
temperatures in a transect of lakes from Arctic Scandinavia to Antarctica. Shanahan et al.
(2013b) examined numerous lakes on Baffin Island, and found significant relationships
between mean summer temperature and MBT/CBT derived temperature reconstructions,
which they attributed to increased productivity in the summer and conductivity due to
increased temperatures, light, and reduced ice cover. The authors suggest that the
interpretation of brGDGT data in sediment cores should remain consistent because the
season of highest productivity is most likely always going to occur during the summer
months (Shanahan et al., 2013b). This is because of the favorable conditions created by
warmer temperatures and reduced ice cover (Shanahan et al., 2013b). Currently, Lake
El’gygytgyn is only ice free for ~2 months (July and August), thus restricting most primary productivity to these times (Nolan and Brigham-Grette, 2007). If brGDGTs are produced during the highest productivity season, then they are likely recording a summer biased temperature at Lake El’gygytgyn.

The MBT/CBT paleothermometer produces strong temperature variations for glacials and interglacials in this study as well as capturing smaller temperature changes, as in interstadials MIS 11.b and MIS 9.b (D’Anjou et al., 2013) (Figure 8). This demonstrates the sensitivity of the MBT/CBT method to reconstruct past temperature variability. Although there is some visual correlation between the global benthic stack and reconstructed temperatures (Figure 8 and Figure 9), there is no statistical correlation. Interestingly, some of the other records from Lake El’gygytgyn, including geochemical proxies (Melles et al., 2012) and pollen reconstructions (Vogel et al., 2013), show good correspondence with the benthic stack during MIS 11. Insolation appears to correlate very well with the reconstructed temperatures (Figure 8 and Figure 9), but again does not have any statistical significance. The lack of statistical correlation may be due to issues with the Lake El’gygytgyn age model, as there are several places (e.g. MIS 11, 14, and 16) where there are visible offsets between the brGDGT temperature reconstructions and both the global benthic stack and the local insolation record (Figure 9). Given Lake El’gygytgyn’s high latitude, it is logical that the insolation would have a strong effect on temperature. This would be particularly amplified during the summer when the Arctic receives nearly continuous sunlight, and therefore strongly influence the brGDGT temperatures if they are indeed being produced during that season. Given the visual correspondence between insolation, the similarity to pollen temperature reconstructions
for mean temperature of the warmest month as well as modeled temperature results for
MIS 11, and MBT/CBT temperature reconstructions with the Sun et al. (2011) calibration
(Figure 8, 9, an 10), data will hereafter be plotted using that calibration. Unfortunately,
there is no regional calibration available for the Arctic, and the Sun et al. (2011)
calibration is the only one in existence for Eurasia, making it the geographically closest
available calibration and providing additional support for its application to this study. It
should also be noted that although the reproducibility of the data is excellent, with an
analytical error of <1 °C, the Sun et al. (2011) calibration has an uncertainty of +/- 5.24
°C. Therefore, caution should be taken before interpreting MBT/CBT temperature
reconstructions as absolute temperatures.

Aliphatic hydrocarbons (n-alkanes) are organic compounds produced by plants as
leaf waxes (Figure 4). They are widespread in lacustrine sedimentary archives and can be
derived from autochthonous and allochthonous sources (Didyk et al., 1978; Eglinton and
Hamilton, 1967). Principally, the sources of n- alkanes in lake sediments are algae and
vascular plants that live in the lake and vascular plants that reside around it. These
compounds are useful indicators of local environmental changes. Short chain n-alkanes
(C_{15}-C_{21}) are attributed to algae and photosynthetic bacteria (Cranwell et al., 1987;
Meyers, 2003), submerged and emergent aquatic plants are the main producers of mid-
chain (C_{21}, C_{23}, and C_{25}) n-alkanes (Ficken et al., 2000), and long- chain compounds
(C_{25}- C_{33}) are characteristic of higher terrestrial plants (Cranwell et al., 1987; Eglinton
and Hamilton, 1967). Various n- alkane indices based on the molecular distributions of
each sample can provide environmental information, such as relative organic matter
contributions of terrestrial and aquatic plants, or relative changes in temperature and/or aridity. See Table 2 with formulas for indices discussed in the sections above.

2.5.2 Glacial-interglacial diversity

The Pleistocene Epoch is characterized by the strong alternation between cold glacial periods and warm interglacial periods. This fluctuation has a period of ~100 ka over the past 800 ka (Imbrie et al., 1993) and has been noted records from a variety of environments. Although the glacial-interglacial repetitions form a general pattern, analysis of numerous records has shown there are differences between each of the climatic cycles (Lang and Wolff, 2011). For example, the diversity of glacial and interglacial periods is evident in the EPICA Dome C ice core (Figure 1) (Jouzel et al., 2007). The differences between interglacial periods are particularly noticeable, with generally longer, cooler interglacials predominating prior to the MBE (430 ka) and the more recent ones being warmer and shorter (Augustin et al., 2004; Jouzel et al., 2007). In the EPICA Dome C record, the mean annual peak temperatures for pre-MBE interglacials are 0.5-1.5 °C colder than the last millennium, whereas the post-MBE interglacials were 2-4.5 °C warmer (Augustin et al., 2004). The diversity of each glacial and interglacial are due to different climate forcing regimes with a variety of internal and external forcing mechanisms (Lang and Wolff, 2011). Orbital forcing parameters are thought to produce much of the variability in climatic cycles. Jouzel et al. (2007) determined that when obliquity and precession parameters are in phase, strong interglacials result and when they are antiphase, their effects lead to weaker interglacials. Yin and Berger (2010) note that for MIS 1, 5, 9, 15, 19, and 21, precession and obliquity are approximately in phase,
but for the interglacials of MIS 7, 11, and 17, obliquity precedes precession, and they are nearly anti-phase. Therefore, interglacial warm periods may still occur when the orbital forcing is opposite. In fact, MIS 11, one of the most extreme interglacials of the Pleistocene has weak astronomical forcing (Berger and Wefer, 2003). Thus, orbital forcing cannot entirely account for the diversity of interglacial periods before and after the MBE (Yin and Berger, 2010).

Greenhouse gas concentrations are also thought to produce significant changes in the amplitude of climate cycles. During the last 800 ka, atmospheric CO₂ has fluctuated significantly. CO₂ concentration varies with the glacial and interglacial cycles, and is always lower during glacial periods and elevated during interglacials (Augustin et al., 2004; Lüthi et al., 2008) (Figure 1). CO₂ levels are strongly correlated with temperature throughout all climate cycles during this period (Lüthi et al., 2008). However, atmospheric CO₂ levels are lower during interglacials in the pre-MBE interval. After the MBE, CO₂ levels are significantly higher for interglacial periods (Tzedakis et al., 2009). Interestingly, peak CO₂ concentration occurs during MIS 9 and reaches 300 ppm (Petit et al., 1999) although MIS 9 is not the warmest interglacial during the post-MBE interval. This is in contrast to MIS 11, which had CO₂ concentrations ~20 ppm lower than MIS 9, but was nearly as warm (Jouzel et al., 2007).

Further investigation of the variability of climate cycles indicates that there are differences in amplitude, length, and profile for each of the them (Lang and Wolff, 2011). However, Lang and Wolff’s (2011) stack of paleoclimate records indicates an overall pattern of increased interglacial extremity after the MBE, with MIS 5 and 11 standing out
as the strongest interglacials of the last 800 ka and MIS 13 as the weakest, and with the
most severe glacial periods occur predominantly after the MBE.

Proxy data produced in this study, by D’Anjou et al. (2013) and Castañeda et al.
(unpublished data) reconstructs glacial- interglacial cycles over the period of 0- 730 ka
(Figure 8). Each peak in the temperature reconstructions appears to correspond to a
precessional cycle. This demonstrates the importance of orbital forcing on the climate of
the terrestrial Arctic, and indicates that the predominant signal in this portion of the
record may be more representative of regional changes in insolation and temperature than
global climatic variability. Strong insolation forcing effects on climate in the northern
high latitudes were also noted by Prokopenko et al. (Prokopenko et al., 2001) in biogenic
silica records of productivity in Lake Baikal. A strong climatic response to precession
and obliquity insolation forcing has been noted in numerous proxy records (Caley et al.,
2011; Chen et al., 2014; Hao et al., 2012; Tabor et al., 2015) as well as modeling studies
(Huybers, 2011; Khodri et al., 2005). During the mid- to late- Pleistocene, global climate
cycles of ice volume and CO₂ fluctuated with a period of 100 kyr (Lisiecki and Raymo,
2005; Lüthi et al., 2008). It has been suggested that these cycles may be controlled by
several obliquity cycles (Huybers, 2006) or by the variability of precession cycles
(Raymo, 1997). Ruddiman (2006) also suggests a mechanism for control of 100 kyr CO₂
and ice volume cycles by precession and obliquity variations.

Previous analysis of the Lake El’gygytgyn core has produced records of glacial-
interglacial variability in the terrestrial Arctic. Sediment facies analysis identifies three
facies: A, B, and C (Melles et al., 2012) (Figure 8). Facies A is a grey, laminated facies
found only in glacial periods after 2.6 Ma. Facies B is the predominant sediment facies at
the lake and comprises the majority of accumulated sediment and represents both glacial and interglacial periods. Finally Facies C, a reddish laminated facies occurs only during the most extreme or “super” interglacial stages at Lake El’gygytgyn (Melles et al., 2012). The first appearance of Facies C during the period of this study occurs at MIS 11, and subsequently again at MIS 9 (Figure 8). Facies C occurs during MIS 11c, while peak temperatures produced in this record occur during 11e (i.e. Railsback et al., 2015) (Figure 8). The second occurrence of Facies C, at the beginning of MIS 9, corresponds to a period when reconstructed temperatures are relatively cold (12 °C) (D’Anjou et al., 2013). The highest reconstructed temperature in the Lake El’gygytgyn record for 0-800 ka is 21.69 °C (Castañeda, unpublished data) and occurs in MIS 7 when Facies C is not present.

Additional proxy data based on sediment geochemistry and produced by Melles et al. (2012) includes the silica to titanium ratio (Si/Ti), the manganese to iron ratio (Mn/Fe), magnetic susceptibility, and percent total organic carbon (%TOC) (Figure 8). Si/Ti represents aquatic diatom productivity in the lake. High primary production at Lake El’gygytgyn is associated with interglacial periods, presumably due to longer ice-free seasons and increased nutrient supply from the catchment (Melles et al., 2012). Magnetic susceptibility and manganese to iron (Mn/Fe) ratios are indicative of bottom water oxygenation (Melles et al., 2007). High values for these indices imply well-oxygenated bottom waters, while low values indicate a stagnant water column with very low oxygen concentrations in the bottom waters (Melles et al., 2007). Low bottom water oxygenation is a result of persistent cold temperatures and perennial lake ice (Melles et al., 2012). Percent total organic carbon (%TOC) indicates primary productivity and OM
preservation in sediments and increases in %TOC likely reflect high primary production, but less decomposition due to anoxic bottom waters in winter (Melles et al., 2012) The %TOC values at Lake El’gygytgyn are low, ranging from 0.1 to 3% during the study interval. High Si/Ti ratios, Mn/Fe ratios, magnetic susceptibility, and high %TOC occur in the Lake El’gygytgyn record during interglacial periods (Melles et al., 2012). However, high %TOC is not always associated with interglacials. Extremely high values for these proxies are associated with coined “super interglacial” periods (including MIS 11) throughout the record (Melles et al., 2012) which are signified by Facies C, high productivity, and high temperature.

2.5.3 MIS 11

MIS 11 is globally recognizable in the marine sediment record through an abrupt transition from high to low benthic foraminifera oxygen isotope (δ¹⁸O) values at ~430 ka (the MIS 12/11 boundary) and prolonged low values of δ¹⁸O throughout the interglacial (Lisiecki and Raymo, 2005). The transition from MIS 12 to 11 (Termination V) was of larger magnitude that previous glacial-interglacial changes (Augustin et al., 2004). MIS 11 had similar orbital configurations and greenhouse gas concentrations to the present interglacial, and so has been selected as a possible analog for comparison to modern climate conditions and changes (Augustin et al., 2004; Loutre and Berger, 2003). Indeed, MIS 11 is one of the most extreme interglacial periods of the last 800 ka (Lang and Wolff, 2011) and is the first interglacial after the MBE. Its weak astronomical forcing make its extreme warmth and length a paradox (Berger and Wefer, 2003). Relatively moderate atmospheric CO₂ concentrations and low insolation forcing may have
contributed to the long duration of MIS 11 (Raynaud et al., 2005). The characteristics of the “super” interglacial (Melles et al., 2012) have been expressed globally with marine sediment cores from the North Atlantic (Lawrence et al., 2009; Voelker et al., 2010) and the Arctic (Cronin et al., 2014) and in Asian lacustrine sequences from Lake Baikal, indicating a prolonged interglacial of ~30 kyr (Prokopenko et al., 2010).

MIS 11 was unique in the polar regions. Antarctica experienced temperatures 2 °C warmer than pre-industrial temperatures (Jouzel et al., 2007), and a boreal forest extended across Greenland (Vernal and Hillaire-Marcel, 2008). Large lakes in Siberia were productive and record warmer air and lake temperatures than today. Temperature estimates based on pollen indicate Lake Baikal was 2 °C warmer (Prokopenko et al., 2010) and Lake El’gygytgyn may have been 4 °C warmer than present (Lozhkin and Anderson, 2013). MBT/CBT temperature reconstructions from this study indicate similar warmth to the pollen reconstructions from Lake El’gygytgyn, with peak temperatures of 17 °C during MIS 11 (Figure 9). Planktic foraminifera assemblages suggest summer sea surface temperatures (SSTs) in the Arctic Ocean may have been 8-10 °C warmer than present (Cronin et al., 2014). MIS 11 is also exceptional in the Arctic because Beringian glaciers advanced while sea level was still high (Brigham-Grette, 2001), implying that parts of Beringia were rapidly glaciated as high latitude insolation dropped, but prior to the sea level falling in response to ice sheet growth in the lower latitudes.

In many paleoclimate records MIS 11 values gradually increase to peak temperatures in the middle of the interglacial at ~ 413 ka (Lang and Wolff, 2011). This record paints a different picture. Sampling resolution of 1 ka throughout MIS 11 provides a well-defined record of temperature variation throughout the interglacial. MBT/CBT
reconstructed temperatures reach an abrupt peak early in the interglacial during MIS 11e (Figure 10), with temperatures transitioning quickly from 6 °C at the end of MIS 12 at ~430 ka to peak temperatures of 17°C at the beginning of MIS 11 at ~425 ka (Figure 10). This warmth is not sustained throughout the interglacial, but instead immediately begins to drop off. This behavior is in contrast to the length and shape of MIS 11 reconstructed through analysis of biomarkers at Lake El’gygytgyn (D’Anjou et al., 2013). D’Anjou et al. (2013) interpreted a long, sustained interglacial in the terrestrial Arctic with high concentrations of numerous aquatic and terrestrial biomarkers. Primary productivity at Lake El’gygytgyn is strongly enhanced during MIS 11 as inferred from high Si/Ti ratios (Melles et al., 2012) (Figure 10). Substantial spruce pollen is evident in MIS 11 sediments (Melles et al., 2012) suggesting the presence of forest cover around or near the lake. Climate reconstructions based on pollen indicate mean temperature of the warmest month (MTWM) peaking at ~ 15 °C and annual precipitation (PANN) of ~700 mm (Melles et al., 2012) (Figure 10). This increase in precipitation during MIS 11 is also evident in Wei et al. (2013) work using sediment hue (iron oxide staining) as a proxy for wetter conditions. Interestingly, reconstructions based on pollen in Lake El’gygytgyn sediments have a different interglacial profile than the brGDGT reconstructions (Figure 10). Both the MTWM and PANN suggest sustained warmth and elevated precipitation throughout MIS 11 (Melles et al., 2012). Analysis of pollen assemblages, and geochemical properties of Lake El’gygytgyn sediments, by Vogel et al. (2013), also indicates relatively stable climate conditions throughout MIS 11 with MTWM ranging from 10-15 °C and PANN ranging from 300-600 mm. However, the authors note that there are two periods of deviation from the average during this interglacial: a warming
from 425-424 ka and a cooling between 424 and 420 ka (Vogel et al., 2013). These deviations correspond with the peak temperature of 17°C at 424 ka and subsequent cooling reconstructed in this record from brGDGTs. However, the rebounding and sustained climate after 420 ka reconstructed by Vogel et al. (2013) does not correspond with the continued temperature decline recorded by the brGDGTs. A long (~30 kyr), warm MIS 11 is also noted in the Lake Baikal record (Prokopenko et al., 2010) and in ice core records (Augustin et al., 2004).

Other records from the Arctic have shown similar climatic behavior to the abrupt temperature drop off reconstructed in this study. Caisse's (2012) record of diatom productivity in the Bering Strait indicates peak diatom accumulation rates early in MIS 11 (Figure 10) when SSTs were not particularly warm, but there was intense upwelling and sea level was high causing flooding in the Bering Strait. During peak MIS 11 (411-400 ka), diatom assemblages indicate warm SSTs, with highly stratified water, occasional sea ice, and reduced upwelling, but overall lower productivity (Caisse, 2012).

SSTs throughout the Pacific Ocean were elevated during MIS 11 (Figure 10). The tropical Pacific experienced warm interglacial temperatures of ~30°C, a degree warmer than the average for Pleistocene interglacials (de Garidel-Thoron et al., 2005; Li et al., 2011; Medina-Elizalde and Lea, 2005). In the mid-latitudes of the Pacific Ocean, SST reconstructions based on alkenones also indicate higher temperatures for MIS 11 than previous interglacial periods (LaRiviere et al., 2012). Alkenone UK37 SST reconstructions for higher latitude sites indicate a peak temperature of ~11°C during MIS 11, suggesting MIS 11 was warmer than prior interglacials (Martínez-Garcia et al., 2010). Biogenic silica counts in sediments from the North Pacific indicate decreased upwelling.
at this time (Haug et al., 1995; Jaccard et al., 2010). These warm temperatures and decreased upwelling during MIS 11 may be related to a minima in Antarctic bottom water production (AABW) causing changes in the thermohaline circulation and ocean ventilation (Hall et al., 2001). AABW production is responsible for bringing cold water into the Pacific Ocean, and minima in this production would result in warmer interglacial SSTs and varied thermohaline circulation (Hall et al., 2001).

2.5.4 The MBE

Numerous globally distributed records have noted increased extremity in glacial and interglacial cycles after the MBE (Augustin et al., 2004; Becquey and Gersonde, 2002; Berger and Wefer, 2003; Blain et al., 2012; Jansen et al., 1986; Tzedakis et al., 2009; Wang et al., 2003), although the geographic extent of the MBE signal has not been fully constrained. This record provides evidence of an MBE signal in the terrestrial Arctic expressed as increased variability in proxy data and biomarkers in Lake El’gygytgyn sediments after 430 ka. Sedimentological proxy data from Lake El’gygytgyn (Melles et al., 2012) is separated into pre- (866-430 ka) and post- (430–0 ka) MBE intervals for statistical analysis (Figure 8). This encompasses six interglacials pre- and post- MBE and five glacial before and after the event. Box-plot analysis of this proxy data for glacial and interglacial periods from 0-866 ka indicates increased variability in glacial and interglacials after 430 ka (post- MBE) (Figures 10-13). This increased variability is representative of higher amplitude climatic cycles post- MBE. Most parameters examined exhibited statistically significant differences at the 95% confidence level between the pre- and post- MBE glacial and interglacials, as determined from a two sample Student’s t-
test ($p < 0.05$).

Statistical analysis indicates that Si/Ti data, interpreted as recording productivity changes in Lake El’gygytgyn (Melles et al., 2012), has slightly higher mean and median values for glacial and interglacial periods before the MBE, but increased overall variability after the event (Figure 11). This suggests that there may have been warmer interglacial periods with long ice-free seasons and high nutrient supplies allowing for increased primary productivity in the lake. High concentrations of dinosterol, a proxy for dinoflagellate productivity, during MIS 11 and 9 provide evidence for greater primary productivity during these intervals (D’Anjou et al., 2013). The glacial cycles after the event have some low outliers in Si/Ti levels, indicating possible increased glacial extremity post-MBE.

The response of %TOC to glacial and interglacial periods is not consistent throughout the study interval (Holland et al., 2013; Melles et al., 2012, 2006). Some interglacial periods have much higher %TOC than glacials. For example MIS 11 has higher %TOC than either of the surrounding glacial periods, while other interglacial periods have lower %TOC than surrounding glacials. However, despite the non-linear response of %TOC to glacial and interglacial climates, the average %TOC in sediment is higher, the median value is higher and there is greater climatic amplitude after the MBE (Figure 14). Some of these low %TOC interglacials may be the result of significant organic matter decomposition when bottom waters were well oxygenated (Melles et al., 2012). Both Mn/Fe ratios and magnetic susceptibility have higher mean and median values as well as increased variability for glacial and interglacial periods after the MBE (Figure 12 and Figure 13), implying increased oxygenation during higher amplitude
climate cycles. Warmer interglacials during the post-MBE interval would result in less ice cover at the lake allowing for better oxygenation of the water column.

Statistical analysis of MBT/CBT temperature reconstructions from 0-730 ka indicates lower mean and median temperatures than the pre-MBE mean and median temperatures and greater variability of the data in the post-MBE interval (Figure 15). This absence of very cold temperatures in the pre-MBE record may be due to lower (3 ka) sampling resolution, generating an artificially high mean and median temperature for data in the pre-MBE interval. It could also be the case that it was relatively warm at Lake El’gygytgyn during these periods. Paleoclimate records from Lake Baikal corroborate warm conditions in this region prior to the MBE and indicate that glacial periods were not severe (Prokopenko et al., 2006, 2001). The highest reconstructed temperatures based on brGDGTs occur in interglacials during the post-MBE interval, and there is a greater spread in the data for these periods, implying that the amplitude of interglacial cycles increased. The mean and median temperatures of glacial periods decreased in the post-MBE interval. This may be an artifact of the warm reconstructed glacial temperatures in the pre-MBE interval or it may be indicating more extreme glacial cycles after the event.

During interglacial periods throughout the record, values for the $n$-alkane indices (CPI, TAR, ACL,) suggest organic matter in the sediments is largely derived from terrestrial sources and is well preserved throughout the record. This is supported by the tree pollen data from MIS 11, and percent trees and shrubs data, which is suggestive of forestation in the catchment area during interglacials (Lozhkin and Anderson, 2013; Melles et al., 2012). $n$-Alkanes are present in almost all samples in varying abundance throughout the record. Although there are periods when the lake likely had perennial ice
cover (Melles et al., 2007), there are still \( n \)-alkanes present in these samples. This may be because aquatic biota can still thrive and produce \( n \)-alkanes under the ice as long as sunlight can penetrate the ice cover, while high sensitivity of terrestrial plants to decreased temperature makes the habitat inhospitable (Melles et al., 2006). It is also possible that terrestrial \( n \)-alkanes are still entering the lake through a lagoon/moat system created around the lake during the summer months (Nolan and Brigham-Grette, 2007).

Statistical analysis and boxplots of \( n \)-alkane data provide valuable information on organic matter preservation and relative changes in aquatic and terrestrial plant productivity.

The CPI is frequently used as an indicator of OM preservation. OM in aquatic sediments is generally considered to be highly degraded if the CPI values are below 1 (Bray and Evans 1961). CPI values for \( n \)-alkanes in this record are mostly greater than 1, with only two data points with values less than 1. The average CPI value is 4.3. There is no evidence for increasing degradation down core as the CPI values are lower and less variable in the younger section of the record (Figure 16) and CPI values for this portion of the core are similar to those during the Pliocene, which average ~4 (Keisling, 2015). Therefore, progressive degradation of OM in Lake El’gygytgyn sediments through time is unlikely.

The TAR is used to determine OM contributions from vascular plants in the watershed vs. contributions from plants of aquatic origin. A TAR value greater than 1 is indicative of greater terrestrial plant contribution, while values less than 1 are attributable to greater aquatic plant OM. The minimum TAR value in this record is 1.33, suggesting that terrestrial plant input is always greater than that of aquatic. However, after the MBE, mean and median TAR values for glacial and interglacials decrease, which may be
representative of increased aquatic productivity (Figure 17). Across the entire record, concentrations of $C_{17}$- $C_{23}$ $n$-alkanes average of 6.77 ng/g sed, while $C_{27}$-$C_{33}$ $n$-alkane concentrations have a mean of 12.96 ng/g sed. This pattern is also repeated in the $n$-alkanol concentrations. Short chain length $n$-alkanols ($C_{18}$- $C_{24}$) have an average concentration of 6.1 ng/g sed, while long chain lengths ($C_{26}$-$C_{34}$) have an average concentration of 7.29 ng/g sed. This is also representative of generally greater OM contributions from terrestrial plants.

The ACL is used to assess aridity and temperature changes (Bush and McInerney, 2015). Leaf surface temperature is important in determining ACL values (Rommerskirchen et al., 2003). Increasing the ACL increases the melting point of the leaf waxes, so plants synthesize longer chain lengths to prevent leaf wax melting in extreme temperatures (Rommerskirchen et al., 2003). High ACL values have been found to correlate with warmth and humidity in the Central United States (Bush and McInerney, 2015), while ACL was found to be associated with higher temperature at Lake Malawi (Castañeda et al., 2009). Higher ACL values have also been found to correlate to aridity (Poynter et al., 1989; Schefuβ et al., 2003; Liu and Huang, 2005). The evidence for a correlation between aridity and ACL is mixed, and the predominant driver of ACL (temperature or aridity) seems to vary by region. Calvo et al. (2004) note increased ACL values in the Pleistocene during cool dry times in a record from the Tasman Sea, but Castañeda et al. (2009) found increased ACL values during warm, wet periods at Lake Malawi throughout the late Pleistocene. There is no statistical correlation with MBT/CBT reconstructed temperatures and ACL values during the study interval. Therefore, ACL is likely representative of aridity at Lake El’gygytgyn, although temperature cannot be
entirely ruled out based on the insignificance of the correlation. ACL values throughout
the record have an average of 27.7. However, particularly low values of 25-26 tend to
occur throughout the record during interglacial periods, suggesting an increase in
precipitation (Figure 6). Boxplots indicate higher median values for ACL in the pre-
MBE interval, suggesting a shift to wetter interglacials after the event (Figure 18). ACL
values are higher overall during glacial periods, reflecting increased aridity in these
intervals. Reconstructed annual precipitation based on pollen during MIS 11 indicates
elevated precipitation during this period (Melles et al., 2012). Wei et al. (2014) analysis
of sediment hue also indicates increased wetness at Lake El’gygytgyn during interglacial
periods 11 and 9 following the MBE. Low ACL values during these interglacials provide
supporting evidence for increased precipitation during post- MBE interval (Figure 10).

There is also evidence that the Pacific Ocean experienced changes due to the
MBE, although the responses to the MBE vary by location (Figure 8). Statistical analysis
of records from the tropics (Li et al., 2011), mid (LaRiviere et al., 2012), and high
latitudes (Martínez-Garcia et al., 2010) of the Pacific Ocean was performed. The records
used cover the interval of 0-866 ka and were divided into pre- and post- MBE glacial and
interglacial intervals. A Student’s t-test performed at the 95% confidence interval
confirmed that the pre- and post- MBE glacials and interglacials were significantly
different. Ocean Drilling Program site 1143 in the South China Sea experienced overall
cooler but more variable glacial and interglacial periods with more extreme warm and
cool outliers (Figure 19). At ODP site 1208 in the mid- latitudes of the western Pacific
Ocean, interglacial SSTs became warmer on average and more variable, while glacial
SSTs became slightly warmer on average, but with fewer warm outliers and more cold
outliers (Figure 20). In the high latitudes of the North Pacific, at ODP site 882, both
glacial and interglacial temperatures increased and became more variable after the MBE
(Figure 21). This warming in the North Pacific is in contrast to records from the Arctic
Ocean. Polyak et al. (2013) note a sharp rise in polar foraminifera species in the Arctic
Ocean toward MIS 11 and suggest that perennial sea ice may have begun to predominate
in the Arctic around the time of the MBE. They postulate that the MBE is expressed there
as an intensification of glacial periods in the Northern Hemisphere (Polyak et al., 2013).

In summary, the bulk geochemical and biomarker data from Lake El’gygytgyn
indicate a clear response to the MBE in the terrestrial Arctic. The proxy data has greater
variability (i.e. amplitude) in the climate cycles post- MBE. This is most obvious in the
analysis of interglacial periods. Pre- MBE interglacials are characterized by lower
%TOC, Mn/Fe values, and magnetic susceptibility, indicating less organic matter
production and/or preservation and poor bottom water oxygenation, respectively. These
lower values suggest lower temperatures during pre- MBE interglacials. Although the
mean and median Si/Ti values, representing productivity, are slightly higher in the pre-
MBE interval, there are more high and low outliers in the post- MBE interval, thus
supporting the signal of increased amplitude cycles after the event. The temperature
reconstructions record a similar pattern of lower mean and median values, but greater
variability post- MBE, suggesting that the warmest interglacials and coldest glacial
occurred after the MBE. Analysis of $n$-alkane ACL suggests overall increased
precipitation at Lake El’gygytgyn during the post- MBE interglacials.
2.5.5 Mechanisms for a high-latitude response to the MBE

The mechanism behind the MBE and glacial-interglacial variability is unconfirmed, although numerous hypotheses have been brought forth. A prevailing hypothesis comes from a study by Yin (2013) who uses model simulations to show that feedbacks between sea ice, temperature, evaporation, and salinity in response to changes in insolation caused vigorous Antarctic Bottom Water (AABW) formation and Southern Ocean ventilation prior to the MBE. This increased overturning and bottom water formation was in response to changes in eccentricity in austral winter and changes in obliquity during austral summer, not a systematic change in forcings (Yin, 2013). The effect of insolation forcing was amplified when CO₂ forcing was added to the model (Yin, 2013). These variations of insolation and interglacial responses all led to a cooler deep ocean during the pre-MBE interglacials (Yin, 2013).

Strong connections between the northern and southern hemisphere climates have been found through the similarities between the Lake El’gygytgyn record and the ANDRILL 1B record, as noted by Melles et al. (2012). The coupling of the two hemispheres is indicated through the excellent correspondence between “super interglacials” in the Lake El’gygytgyn record (Melles et al., 2012) and diatomite layers in the ANDRILL 1B record (McKay et al., 2012), which reflect a diminished West Antarctic Ice Sheet (WAIS) and open water in the Ross Embayment (Pollard and DeConto, 2009). Melles et al. (2012) hypothesized that these periods of correlation between the two hemispheres are a result of a reduction in AABW formation. The authors suggest that a change in AABW production and Southern Ocean ventilation would affect thermohaline circulation, and reduce upwelling in the North Pacific, thereby
producing a stratified water column and warm SSTs during super interglacials (Melles et al. (2012). In support of this, particularly low AABW inflows to the southwest Pacific during MIS 11 are noted by Hall et al., (2001), while reduced upwelling in the Pacific is indicated by low BSi concentrations in ODP site 882 sediments covering this interval (Haug et al., 1995; Jaccard et al., 2010).

The two dominant pressure patterns over Lake El’gygytgyn are the Siberian high and Aleutian low (Mock et al., 1998). Warm SSTs in the North Pacific could cause changes in these pressure patterns resulting in increased air temperatures and elevated precipitation over Russia (Melles et al., 2012). This mechanism would have operated in the post-MBE interval. Vigorous AABW production proposed by Yin (2013) would make this process impossible during the pre-MBE interval. The changes in temperature and precipitation created by manipulation of the Siberian high and Aleutian low would have affected the Lake El’gygytgyn climate and created a signal of the MBE in the sediment record. The lack of super interglacials during the mid-Pleistocene prior to the MBE is likely a result of the vigorous AABW production proposed by Yin (2013). Decreased AABW production after the MBE led to warmer deep-ocean and the mechanism for expression of the MBE at Lake El’gygytgyn.

2.5.6 Conclusions

Biogeochemical analysis of the Lake El’gygytgyn sediment core reveals a number of details about Pleistocene climate variability and the expression of the MBE in the terrestrial Arctic. Statistical analysis of temperature reconstructions based on brGDGTs over the interval of 0-730 ka suggests that the terrestrial Arctic experienced both warmer
interglacial periods and colder glacial periods during the post-MBE interval. During the pre-MBE interval, interglacials and glacials are both relatively warm, but the climate cycles seem to increase in amplitude after the MBE. Temperature reconstructions for MIS 11 are of particular interest, as they suggest an early peak of 17 °C at 425 ka, with an abrupt decline afterward continuing through the duration of the interglacial. This is in contrast with other records, which have reconstructed later peak temperatures and relatively sustained warmth throughout the interglacial. Analysis of \( n \)-alkanes over the interval of 340-730 ka indicates an overall shift toward more precipitation after the MBE, particularly during interglacial periods. Analysis of other proxy data from the Lake El’gygytgyn core suggests that these interglacials may also have had increased productivity. Given that an MBE signal is present in most proxy records from Lake El’gygytgyn, we conclude that the continental Arctic experienced a climatic shift due to the event. Therefore, we believe that the MBE was not restricted to the high latitudes of the Southern Hemisphere. We suggest that the expression of an MBE signal in the Arctic may be due to changes in insolation forced AABW production (i.e. Yin, 2013). Following previous studies of Lake El’gygytgyn we suggest that these changes were translated northward via reduced upwelling in the Pacific Ocean (i.e. Galbraith et al., 2007) increasing SSTs and manipulating the positions of the Siberian High and Aleutian Low (i.e. Mock et al., 1998; Nolan et al., 2013).

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CHAPTER 3

STRUCTURE AND SIGNIFICANCE OF H- SHAPED BRANCHED GDGTS IN LAKE EL’GYGYTGYN (RUSSIA) SEDIMENTS

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3.1 Abstract

A sediment core spanning the last 3.6 Ma was drilled from Lake El’gygytgyn, Russia. This unique core represents the longest continuous paleoclimate record of the terrestrial Arctic and is the focus of numerous ongoing studies. Lake El’gygytgyn sediments contain branched glycerol dialkyl glycerol tetraethers (brGDGTs) and temperature reconstructions via the methylation index of branched tetraethers and cyclization of branched tetraethers (MBT/CBT proxy) have been successful and are continually utilized to investigate temperature changes across the Plio- Pleistocene record (D’Anjou et al., 2013; Holland et al., 2013; Keisling, 2015, de Wet et al., in review). In the process of brGDGT analysis, a series of late eluting peaks with m/z values of 1048, 1034, and 1020 were noted in high performance liquid chromatography- mass spectrometry (HPLC-MS) chromatograms. These unknown compounds appear to be abundant and ubiquitous throughout the Lake El’gygytgyn record and have also been noted in globally distributed samples from marine and lacustrine settings. MS/MS analysis using high- resolution accurate mass spectrometry suggests these compounds are H- shaped brGDGTs. Continued compound identification and structural analysis is ongoing. The abundant and pervasive nature of these compounds make their prospective use as biomarkers promising.
3.2 Introduction to GDGTs

Glycerol dialkyl glycerol tetraethers (GDGTs) are membrane lipids found in soils, sediments, and water. These compounds were initially thought to be exclusively produced by archaea living in extreme conditions, but subsequent research has refuted this assumption (Schouten et al., 2013). Samples from diverse environments have been analyzed in numerous studies, and indicate that GDGTs have a wide structural diversity, a multitude of source organisms, and are found ubiquitously in an array of diverse environments (Schouten et al., 2013 and references therein). Studies have identified GDGTs in oceans, lakes, and their sediments, and in soils and peats (Schouten et al., 2013). There are numerous known glycerol ethers, and new compounds of this type continue to be identified (i.e. Liu et al., 2012). The more commonly known groups of glycerol ether lipids include isoprenoidal GDGTs and branched GDGTs (Figure 3). Additionally, related compounds such as isoprenoidal H- shaped GDGTs, hydroxylated analogues of isoprenoidal GDGTs (OH- GDGTs) and derivative compounds lacking one glycerol moiety, called glycerol dialkanol diethers (GDDs) have recently been identified (Liu et al., 2012). Isoprenoid GDGTs generally comprise GDGTs with 0-3 cyclopentane rings, cyclohexane bearing crenarcheol, and its regioisomer and are produced by archaea in a variety of settings (Schouten et al., 2000). Isoprenoidal H- shaped GDGTs are informally designated as GDGTs whose alkyl chains are bridged by a covalent C-C bond (Liu et al., 2012). Branched GDGTs are non- isoprenoidal glycerol tetraethers with 13, 16 dimethyl or 5, 13, 16 trimethyl octasanyl moieties (Damsté et al., 2000) and their
molecular configuration implies a bacterial origin (Sinninghe Damsté et al., 2000; Weijers et al., 2006). Both isoprenoidal and branched GDGTs have been found to record environmental parameters and have been developed into biomarker proxies. These include the tetraether index consisting of 86 carbon atoms (TEX$_{86}$), a sea surface temperature proxy based on isoprenoid GDGTs (Schouten et al., 2002) and the methylation index of branched tetrathers/ cyclization index of branched tetraethers (MBT/CBT proxy) for reconstructing mean annual air temperature and pH (Weijers et al., 2007). These proxies have been utilized in a variety of settings.

3.3 Mystery Peaks in Lake El’gygytgyn sediments

The Lake El’gygytgyn sediment core is presently the focus of numerous ongoing investigations over the interval of 0-3.6 Ma. Lake El’gygytgyn sediments contain brGDGTs and temperature reconstructions at this site via the MBT/CBT proxy (Weijers et al., 2007) have been successful across multiple intervals of the record (e.g. D’Anjou et al., 2013; Holland et al., 2013) and continue to be utilized in numerous studies to investigate Plio-Pleistocene Arctic temperature variability. At present, over 1,000 samples from the Lake El’gygytgyn drill core have been analyzed for brGDGTs (This study; Castañeda et al., in prep; de Wet et al., in review; Keisling et al., in prep; D’Anjou et al., 2013; Holland et al., 2013).

In the process of GDGT analysis, a series of late eluting peaks were noted in high performance liquid chromatography-mass spectrometry (HPLC-MS) chromatograms (Figure 22). Interestingly, these peaks were sometimes significantly larger than the secondary group of brGDGTs (Ib, IIb, and IIIb) brGDGT peaks, but were generally much
smaller than the main brGDGTs (Ia, IIa, and IIIa). These unknown compounds also appear to be present in globally distributed marine and lacustrine sites including ODP 660A offshore NW Africa (Castañeda et al., in prep), a marine sediment core offshore southern Tanzania (Castañeda et al., in prep) at several small lakes in southwest Greenland and Iceland (de Wet et al., in prep), and at Basin Pond, Maine (USA) (Miller et al., in prep). In summer 2014, I applied for funding through the Elsevier Research Scholarship. I received funding to travel to the Royal Netherlands Institute for Sea Research (NIOZ) to work with Drs Ellen Hopmans and Stefan Schouten on identification of the unknown compounds.

3.4 Structural identification of H-shaped brGDGTs

Prior to travel to the Netherlands, several hundred polar fractions from the Lake El’gygytgyn core were compiled into four concentrated samples to provide ample material to analyze. Upon arrival at NIOZ, aliquots of these samples were analyzed on several different instruments. First, the samples were analyzed by ultra-high performance liquid chromatography- mass spectrometry (UHPLC-MS). This analysis revealed three unknown compounds associated with m/z ratios 1048, 1034, and 1020, and that each of the unknown compounds has multiple isomers (Figure 22).

Next, MS/MS analysis using high-resolution accurate mass spectrometry was performed using an UHPLC coupled to an Orbitrap MS to gain more information about the structural nature of the compounds. The UHPLC-MS used in this analysis was a Thermo Scientific Q-Exactive UHPLC-MS (Quadrupole-Orbitrap hybrid MS) with Ion Max source with a positive ion APCI probe. Methods for this analysis are detailed in
Hopmans et al. (in prep). The working title of their publication is “The effect of improved chromatography on GDGT based paleoproxies”, and will be submitted to Organic Geochemistry.

The mass spectra analysis of the unknown compounds suggests they are H-shaped compounds due to their fragmentation patterns, while their mass distribution suggests they are branched GDGTs (Figure 23, Figure 24, and Figure 25). The mass distributions are the same as brGDGTs 1048, 1034, and 1020. H-shaped isoprenoid GDGTs have been identified by Liu et al. (2012), and one of these compounds elutes earlier in the run with isoprenoid GDGTs 1302 and 1292. The H-shaped brGDGTs are late eluting (after the other brGDGTs), suggesting their similar molecular configurations. The fragmentation pattern of the mass spectra indicates that there is a bond somewhere connecting the hydrocarbon chains, similar to the informally designated H-shaped isoprenoid GDGTs of Liu et al. (2012). This bond between the chains causes the compounds to be more stable and avoid fragmentation. There are few remaining options for chemical fragmentation of these compounds.

After the basic identification of H- 1048, 1034, and 1020, the remaining aliquots of the large, concentrated Lake El’gygytgyn polar fractions were run on a preparatory HPLC. This allowed for the separation of the H-shaped compounds from the other GDGTs. After this compound isolation, continued structural analysis will be performed. Ongoing work to characterize the structure of the late eluting H-shaped GDGTs includes ether cleavage via HI and subsequent analysis by high-temperature GC-MS with supersonic ion beam ionization at Shell Global in the Netherlands.
3.5 Potential of H- shaped brGDGTs as biomarkers

An H- shaped GDGT with a [M+H]$^+$ of 1020 was previously reported by Liu et al. (2012) in offshore marine sediments from the Mediterranean Sea, Pacific, and Atlantic Oceans, however, they do not specify that it is an H- shaped brGDGT. To our knowledge this is the first report of the H-brGDGTs with m/z ratios 1048, 1034, and 1020 as well as the first report of the presence of these compounds in lacustrine sediments. Although these compounds may be globally distributed, Lake El’gygytgyn sediments appear to be unique in that they contain several of these late eluting compounds (m/z 1048, 1034, and 1020) whereas many of the other sites contain only one (m/z 1020). From our initial observations, it also appears that the late eluting compounds may be more abundant in older (early Pleistocene and Pliocene) samples at Lake El’gygytgyn and ODP 660A (NW Africa) than in younger (late Pleistocene and Holocene) samples.

The H- shaped compounds are quite abundant and ubiquitous throughout the Lake El’gygytgyn sedimentary record. To investigate the paleoclimate potential of these compounds, their distributions and concentrations will be compared to those of the brGDGTs, and other biomarker data from the same samples.
CHAPTER 4
FUTURE EFFORTS

4.1 Abstract

This thesis presents the results of biogeochemical analysis of sediments from Lake El’gygytgyn, Russia. The results were used to determine that the terrestrial Arctic experienced increased amplitude climate cycles after the Mid-Brunhes Event. Further investigations of the biogeochemistry of Lake El’gygytgyn sediments can be undertaken to build upon this study or examine other periods of particular interest throughout the record. Future investigations of this record are critical to further our understanding of past climatic variability and to place current and future changes in context.

4.2 Future Work

4.2.1 High resolution records of periods of interest

Investigations of the biomarker record of the Lake El’gygytgyn sediment core in this and other ongoing studies have progressed knowledge and understanding of the terrestrial Arctic’s response to global and regional climatic changes. Continued proxy and biomarker analysis can be used to target areas of particular interest such as “super interglacials” throughout the record, the Mid-Pleistocene Transition, and early stages of lake formation. Additional work will eventually be combined into a robust and accurate 3.6 Ma synthesis record based on numerous organic biomarkers.
The biogeochemical analysis conducted in this study for the interval of 340 to 730 ka demonstrates the ability of biomarkers in the lake to record global climatic changes. Temperature reconstructions based on brGDGTs produce values similar to other proxy reconstructions at the lake and indicate the presence of a MBE signal in the sedimentary record. $n$-Alkanes in the sediment also capture shifts in climate parameters in the terrestrial Arctic, such as hydrologic variability. The biomarker record suggests long duration of MIS 11, but reconstructed interglacial temperatures reach an early peak of $\sim 17 \, ^{\circ}C$ and indicate prolonged decline from there. The record also demonstrates increased climatic variability after 430 ka, the accepted time of the MBE. The most successful periods of reconstruction are those with high sampling resolution (1000 yr resolution), while periods of data with lower sampling resolution (3000 yr resolution) are much noisier. The lower sampling resolution makes it difficult to determine the response time of the lake system to rapid climate shifts and transitions through glacial and interglacial cycles and may contribute to the lack of cold temperatures reconstructed in the pre- MBE interval. This demonstrates the need to focus future biomarker analyses on measuring changes at a fine scale.

4.2.2 Field work for a site- specific calibration

Additional field work is necessary to collect modern samples for validation and site specific calibration of the brGDGT measurements. This will impact the continued development of the MBT/CBT temperature proxy. Currently, numerous global (Pearson et al., 2011; Peterse et al., 2012; Sun et al., 2011; Weijers et al., 2007) and regional (Loomis et al., 2012; Sun et al., 2011; Tierney et al., 2010; Zink et al., 2010) calibrations
exist for soils and lakes. These multiple calibrations create similar responses of brGDGTs to temperature changes, but can only be interpreted as capturing relative temperature changes. Additional sampling of soils, surface sediment cores from the catchment area, lake core tops, and sediment traps in the water column paired with modern meteorological data could result in a site-specific calibration of MBT/CBT. This would allow for improved accuracy in temperature reconstructions, with the possibility of determining absolute temperatures for the paleoclimate record and provide a new regional calibration for the scientific community to use in high latitude regions. This work will also implicate the development of the proxy itself. The producing organism for brGDGTs is thought to live in soils (Weijers et al., 2007), but continued investigation has suggested the compounds may also be produced in situ in lakes and rivers (Bechtel et al., 2010; Loomis et al., 2012; Tierney et al., 2010; Zhu et al., 2011). Sampling of soils, lake core tops, and water column of Lake El’gygytgyn will provide insight about the production of GDGTs and their source organism.

4.2.3 \( \delta^{13}C \) analysis of brGDGTs

The source organisms of brGDGTs are, at present, unknown (Weijers et al., 2014). Higher abundances of these and structurally similar compounds have been noted in acidic soils and in many species of Acidobacteria, indicating Acidobacteria may be a source (Sinninghe Damsté et al., 2011; Weijers et al., 2014, 2007). However numerous organisms may contribute to brGDGT accumulation in sediments, and there is strong evidence to suggest brGDGTs are produced not only in soils, but in the water column or in lake sediments (Buckles et al., 2014; Loomis et al., 2014). Not knowing the source
environment of brGDGT production makes the interpretation of brGDGT based records more difficult.

A potential solution for determining sources of brGDGTs uses compound specific isotopes (Weber et al., 2015). The carbon isotopic signature can be measured on brGDGTs after separation of their ether bonds (Schouten et al., 2013). The isotopic signature of the core lipids reflects the composition of the source carbon and any fractionation due to the source organism (Schouten et al., 2013 and references therein). During research on H-shaped brGDGTs at NIOZ (see Chapter 3), concentrated fractions of GDGTs 1302 and 1292 as well as all of the brGDGTs were isolated. These samples comprise organic material throughout the entire 3.6 Ma record. Compound specific δ\textsuperscript{13}C analysis of these different compound fractions would provide a baseline sense of brGDGT distributions in Lake El’gygytgyn sediments. Analysis of individual samples throughout the record could then produce a time series for comparison with the average. Examination of changes in carbon isotopes would improve understanding of variability in compound production location (in soils or in the lake) and possible producer community changes, such as during periods of anoxia throughout the record.

4.2.4 δD of plant leaf wax \textit{n-} alkanes

Temperature reconstructions for this paleoclimate study are currently only based on brGDGTs, resulting in a record that is perhaps less robust and accurate than desirable. Analysis of δD of plant leaf wax \textit{n-}alkanes would provide a second proxy to examine both temperature and hydrologic variability at the lake. The hydrogen in plant tissues is derived from environmental waters, which in turn are influenced by temperature, weather
patterns, and hydrologic balance (Smith and Freeman, 2006). Changes in leaf wax δD often indicate differences in evapotranspiration (Schefuß et al., 2005) or a change in δD of precipitation over a site (Liu and Yang, 2008); a negative change in leaf wax δD for either of these situations would reflect increasingly wet conditions (Castañeda and Schouten, 2011). At Lake El’gygytgyn and other sites of polar latitude, temperature is expected to be the dominant control on δD of plant leaf waxes (Thomas et al., 2012; Wilkie et al., 2013), but a change in the dominant moisture source could also influence δD values, especially on glacial-interglacial timescales when boundary conditions i.e. sea ice extent and seasonality of precipitation are expected to change (Shanahan et al., 2013a; Thomas et al., 2012). Unfortunately, of the 140 samples analyzed in this study, only 11 contain n-alkanes abundant enough for δD analysis. Interestingly, n- alkanols seem relatively more abundant and may provide a solution to this problem as δD may also be measured on these compounds.

4.2.5 Analysis of algal lipids

Analysis of algal lipids in the polar fraction would provide useful information on environmental parameters at Lake El’gygytgyn. Long chain n-alkyl diols have recently been developed into a temperature proxy (Rampen et al., 2012) as well as providing information about algal productivity. Dinosterol, a biomarker for dinoflagellates, and can be used as an indicator of primary productivity in the lake (Castañeda and Schouten, 2011 and references therein). Primary productivity can be affected by environmental changes such as temperature, wind, and ice cover. Comparison between algal lipids and n-alkanes would provide a stronger sense of how environmental changes affect algae and
plant productivity in and around the Lake El’gygytgyn. Fifty samples with 9 ka resolution throughout the record were analyzed by gas chromatography- mass spectrometry (GC-MS) and gas chromatography- flame ionization detection (GC-FID). $n$- Alkanols were found in abundance for all samples. Occasional samples had small abundances of dinosterol an indicator of diatom productivity, and arborinol, a proxy indicative of forest cover (Jacob et al., 2005) or microbial activity (Jaffé and Hausmann, 1995). Further work should include assessment of additional compounds in the polar fractions and analysis of all samples throughout the study interval.

4.3 Conclusions

Biomarkers in the Lake El’gygytgyn record have the ability to record regional and global climatic changes. Branched GDGT temperature reconstructions using the MBT/CBT temperature proxy capture glacial- interglacial changes and indicate increased amplitude climate cycles after the MBE. Investigations of $n$- alkane ratios also provide information on environmental changes in and around the lake over the study interval. Given the length and continuity of the Lake El’gygytgyn record, future analysis will provide information on climate change during intervals rarely captured in terrestrial sedimentary archives and improve understanding of the expression of climate change through proxy records. Future work will contribute knowledge of paleoclimate variability over the past 3.6 Ma in the sensitive Arctic region. This will enhance our comprehension of global climate change and the extent of anthropogenic effects, as well as providing context for future climate evolution.
<table>
<thead>
<tr>
<th>Calibration</th>
<th>Minimum value</th>
<th>Maximum value</th>
<th>Mean Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weijers et al. (2007)</td>
<td>-11.15</td>
<td>10.03</td>
<td>-0.60</td>
</tr>
<tr>
<td>Pearson et al. (2011)</td>
<td>6.80</td>
<td>25.70</td>
<td>14.10</td>
</tr>
<tr>
<td>Loomis et al. (2012)</td>
<td>0.19</td>
<td>18.32</td>
<td>8.24</td>
</tr>
<tr>
<td>Sun et al. (2011)</td>
<td>2.90</td>
<td>18.70</td>
<td>10.80</td>
</tr>
<tr>
<td>Peterse et al. (2012)</td>
<td>-1.80</td>
<td>11.50</td>
<td>4.80</td>
</tr>
<tr>
<td>Zink et al. (2010)</td>
<td>2.40</td>
<td>12.20</td>
<td>8.30</td>
</tr>
<tr>
<td>Tierney et al. (2010)</td>
<td>-2.33</td>
<td>18.85</td>
<td>7.36</td>
</tr>
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</table>

Table 1: Minimum, maximum, and mean values for MBT/CBT calibrations.
<table>
<thead>
<tr>
<th>Equations and Indices</th>
<th>Summary</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon Preference Index (CPI)</td>
<td>[ \text{CPI} = \frac{(C_{23} + 2 \cdot (C_{25} + C_{27} + C_{29} + C_{31}))}{C_{33} + 2 \cdot (C_{24} + C_{26} + C_{28} + C_{30} + C_{32})} ]</td>
<td>Bray and Evans (1961)</td>
</tr>
<tr>
<td>Terrigenous to Aquatic Ratio (TAR)</td>
<td>[ \text{TAR} = \frac{(C_{27} + C_{29} + C_{31})}{(C_{17} + C_{19} + C_{21})} ]</td>
<td>Bourbonniere and Meyers (1997)</td>
</tr>
<tr>
<td>Average Chain Length (ACL)</td>
<td>[ \text{ACL} = \frac{17(nC_{17}) + 19(nC_{19}) + ... + 31(nC_{31}) + 33(nC_{33})}{nC_{17} + nC_{19} + ... + nC_{31} + nC_{33}} ]</td>
<td>Bush and McInerney (2013)</td>
</tr>
<tr>
<td>Methylation of Branched Tetraethers (MBT)</td>
<td>[ \text{MBT} = \frac{[I] + [Ib] + [Ic]}{([I] + [Ib] + [Ic]) + ([II] + [Iib] + [Iic]) + ([III] + [IIIb] + [IIIc])} ]</td>
<td>Weijers et al. (2007)</td>
</tr>
<tr>
<td>Cyclization of Branched Tetraethers (CBT)</td>
<td>[ \text{CBT} = - \log\left( \frac{[Ib] + [Iib]}{[I] + [II]} \right) ]</td>
<td>Weijers et al. (2007)</td>
</tr>
<tr>
<td>MBT/CBT MAAT Calibration (Soil)</td>
<td>[ T (°C) = 11.84 + 32.54 \cdot \text{MBT} - 9.32 \cdot \text{CBT} ]</td>
<td>Weijers et al. (2007)</td>
</tr>
<tr>
<td>MBT/CBT MAAT Calibration (Lake)</td>
<td>[ T (°C) = 6.803 - 7.062 \cdot \text{CBT} + 37.090 \cdot \text{MBT} ]</td>
<td>Sun et al. (2011)</td>
</tr>
<tr>
<td>GDGT Specific MAAT Calibration (Lake)</td>
<td>[ T (°C) = 50.47 - 74.18 \cdot f \text{GDGT III} - 31 \cdot 60 \cdot f \text{GDGT II} - 34 \cdot 69 \cdot f \text{GDGT I} ]</td>
<td>Tierney et al. (2010)</td>
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<tr>
<td>GDGT Specific MAAT Calibration (Lake)</td>
<td>[ T (°C) = 36.9 - (50.14 \cdot \text{fr.ab. III}) - (35.52 \cdot \text{fr.ab. II}) - (0.96 \cdot \text{fr.ab. I}) ]</td>
<td>Loomis et al. (2012)</td>
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<tr>
<td>GDGT Specific Summer Temperature Calibration (Lake)</td>
<td>[ T (°C) = 47.4 - (20.9 \cdot \text{GDGT I}) - (37.1 \cdot \text{GDGT II}) - (53.5 \cdot \text{GDGT III}) ]</td>
<td>Pearson et al. (2011)</td>
</tr>
<tr>
<td>MBT'/CBT MAAT Calibration (Soil)</td>
<td>[ T (°C) = 0.81 - 5.67 \cdot \text{CBT} + 31 \cdot \text{MBT}' ]</td>
<td>Peterse et al. (2012)</td>
</tr>
<tr>
<td>MBT Temperature Calibration (Lake)</td>
<td>[ T (°C) = 55.01 \cdot \text{MBT} - 6.055 ]</td>
<td>Zink et al. (2010)</td>
</tr>
</tbody>
</table>

Table 2: Equations and indices used in this study.
Figure 1: EPICA Dome C CO₂ record
Data from (Luthi et al., 2008) plotted with a vertical line marking the location of the MBE and horizontal lines indicating the change in amplitude of the climatic cycles after the event. Numbers across the top indicate the Marine Isotope Stages.
Figure 2: Location of Lake El’gygytgyn

Large map shows the location of Lake El’gygytgyn. The map is also labeled with the dominant atmospheric circulation patterns: the Siberian High (orange) and Aleutian Low (blue). Inset map shows the shape and size of Lake El’gygytgyn. The core location is indicated with the blue star and was taken from a depth of 170 m. This detail map shows Lake El’gygytgyn and the surrounding watershed. Note the pronounced ridges that ring the lake, forming its small catchment.
Figure 3: Branched GDGT structures and isoprenoid structures. Figure from Castañeda and Schouten (2011). These compounds are used for the calculation of MBT/CBT, the BIT index, and TEX$_{86}$. 
**Figure 4: Structures of selected lipid biomarkers discussed in the text.**
Structures shown include dinosterol, the $C_{30}$ 1, 15 $n$-alkyl diol, arborinol, tetrahymanol, and the $C_{29}$ $n$-alkane. Figure from Castañeda and Schouten (2011).
Figure 5: Global map of MBE studies.

Figure 6: Indices used in this study
A) Global benthic oxygen isotope stack ($\delta^{18}$O) (Lisiecki and Raymo, 2005). B) July insolation at 67°N (Laskar, 2004). C) Three point running mean of MBT/CBT temperatures (°C). from 288-730 ka (blue solid line) and raw data from D’Anjou et al. (2013) (red points) and this study (blue points). D) Three point running mean of $n$-alkane average chain length (green line) and raw average chain length values (green points). E) MBT values. F) CBT values. G) brGDGT concentrations (ug/g sed extracted). H) Concentration of long chain (C27-C33) $n$-alkanes (ng/g sed extracted). I) Concentration of short chain (C17- C23) $n$-alkanes (ng/g sed extracted). J) Lake El’gygytgyn sediment facies A- blue, B- gold, C- red (Melles et al., 2012). Dotted line marks location of the MBE ~430 ka.

**Figure 7: The effect of different calibrations on brGDGT temperature estimates.**

Data from this study plotted with multiple calibrations for soils and lakes (see legend) and peak temperatures from pollen reconstructions of MIS 11 (Melles et al., 2012), modeled temperature for MIS 11 (Coletti et al., 2014), mean July temperature at Lake El’gygytgyn (Nolan and Brigham- Grette, 2007), mean annual air temperature at Lake El’gygytgyn (Nolan and Brigham- Grette, 2007).
Figure 8: Temperature, vegetation, and geochemical variability from 0-800 ka.
A) Global benthic oxygen isotope stack ($\delta^{18}O$) (Lisiecki and Raymo, 2005). B) July insolation at 67°N (Laskar, 2004). C) Three point running mean of MBT/CBT temperatures (°C) from 288-730 ka (blue solid line) and raw data from D’Anjou et al. (2013) (red points) and this study (blue points). D) Three point running mean of n-alkane average chain length (green line) and raw average chain length values (green points). E) Lake Baikal percent biogenic silica (Prokopenko et al., 2001). F) EPICA Dome C CO2 record (Luthi et al., 2008). G) Pacific ocean sea surface temperature reconstructions from ODP site 1143 (Li et al., 2011) (aqua points), site 1208 (LaRiviere et al., 2012) (dark blue points) and site 882 (Martinex- Garcia et al., 2010) (light blue points). H) Lake El’gygytgyn Si/Ti ratio (Melles et al., 2012). I) Lake El’gygytgyn Mn/Fe ratio (Melles et al., 2012). J.) Lake El’gygytgyn %TOC (Melles et al., 2012). K) Lake El’gygytgyn magnetic susceptibility. L.) Lake El’gygytgyn sediment facies A- blue, B- gold, C- red (Melles et al., 2012).
Figure 9: Temperature correspondence to benthic stack and local insolation
Three point running average of MBT/CBT temperature reconstructions from D’Anjou et al. (2013) (red) and this study (blue) overlying the global benthic oxygen isotope stack (Lisiecki and Raymo (2005) (black) and local July insolation at 67°N (Laskar, 2004) (orange). Marine isotope stages and the location of the MBE are labeled along the top. Red ovals highlight intervals where there appears to be significant offsets between the records.
Figure 10: Climatic change surrounding MIS 11.
A) Global benthic oxygen isotope stack ($\delta^{18}$O) (Lisiecki and Raymo, 2005).  B) July insolation at 67°N (Laskar, 2004).  C) Three point running mean of MBT/CBT temperatures (°C) from 288-730 ka (blue solid line) and raw data from D’Anjou et al. (2013) (red points) and this study (blue points). Pink dot indicates reconstructed peak temperature at Lake Baikal (Prokopenko et al., 2010). D) Three point running mean of $n$-alkane average chain length (green line) and raw average chain length values (green points). E) Mean temperature of the warmest month pollen reconstructions from Lake El’gygytgyn (Melles et al., 2012). F) Average annual precipitation reconstructed from pollen from Lake El’gygytgyn (Melles et al., 2012). G) Si/Ti ratios for Lake El’gygytgyn sediments (Melles et al., 2012). H) Percent Biogenic silica from Lake Baikal (Prokopenko et al., 2001). I) Pacific ocean sea surface temperature reconstructions from ODP site 1143 (Li et al., 2011). J) ODP site 882 SST reconstructions (Martinez- Garcia et al., 2010). Gold dot indicates summer sea surface temperatures in the Arctic during MIS 11 (Cronin et al., 2014). K) ODP site 1208 SST reconstructions (LaRiviere et al., 2012). L) Lake El’gygytgyn sediment facies A- blue, B-gold, C- red. Marine Isotope Stages are labeled along the top and the location of the MBE ~430 ka is marked with a dotted line.
Figure 11: Silica/Titanium ratio boxplots.

Data from Melles et al. (2012) spanning the interval of 0-866 ka. This encompasses six interglacials and five glacial periods in the both the pre- and post- MBE intervals. The MBE is designated as occurring at 430 ka. Top panel: all data in the pre- and post- MBE intervals. Middle panel: pre- and post- MBE interglacial periods. Bottom panel: pre- and post- MBE glacial periods.
Figure 12: Manganese/Iron boxplots
Data from Melles et al. (2012) spanning the interval of 0-866 ka. This encompasses six interglacials and five glacials in the both the pre- and post- MBE intervals. The MBE is designated as occurring at 430 ka. Top panel: all data in the pre- and post- MBE intervals. Middle panel: pre- and post- MBE interglacial periods. Bottom panel: pre- and post-MBE glacial periods.
Figure 13: Magnetic Susceptibility boxplots.
Data from Melles et al. (2012) spanning the interval of 0-866 ka. This encompasses six interglacials and five glacials in the both the pre- and post- MBE intervals. The MBE is designated as occurring at 430 ka. Top panel: all data in the pre- and post- MBE intervals. Middle panel: pre- and post- MBE interglacial periods. Bottom panel: pre- and post-MBE glacial periods.
Figure 14: Percent Total Organic Carbon boxplots.
Data from Melles et al. (2012) spanning the interval of 0-866 ka. This encompasses six interglacials and five glacials in the both the pre- and post- MBE intervals. The MBE is designated as occurring at 430 ka. Top panel: all data in the pre- and post- MBE intervals. Middle panel: pre- and post- MBE interglacial periods. Bottom panel: pre- and post- MBE glacial periods.
Figure 15: MBT/CBT Temperature reconstruction boxplots.
Data from Castaneda et al. (unpublished), D’Anjou et al. (2013) and this study spanning the interval of 0-730 ka. The MBE is designated as occurring at 430 ka. Top panel: all data in the pre- and post- MBE intervals. Middle panel: pre- and post- MBE interglacial periods. Bottom panel: pre- and post- MBE glacial periods.
Figure 16: Carbon Preference Index boxplots
Data spanning the interval of 340-730 ka. The MBE is designated as occurring at 430 ka. Top panel: all data in the pre- and post- MBE intervals. Middle panel: pre- and post-MBE interglacial periods. Bottom panel: pre- and post- MBE glacial periods.
Figure 17: Terrigenous to Aquatic ratio boxplots
Data spanning the interval of 340- 730 ka. The MBE is designated as occurring at 430 ka. Top panel: all data in the pre- and post- MBE intervals. Middle panel: pre- and post-MBE interglacial periods. Bottom panel: pre- and post- MBE glacial periods.
Figure 18: Average Chain Length boxplots
Data spanning the interval of 340–730 ka. The MBE is designated as occurring at 430 ka. Top panel: all data in the pre- and post-MBE intervals. Middle panel: pre- and post-MBE interglacial periods. Bottom panel: pre- and post-MBE glacial periods.
Figure 19: ODP site 1143 boxplots
Data from Li et al. (2011) spanning the interval of 0-866 ka. The MBE is designated as occurring at 430 ka. Top panel: all data in the pre- and post- MBE intervals. Middle panel: pre- and post- MBE interglacial periods. Bottom panel: pre- and post- MBE glacial periods.
Figure 20: ODP site 1208 boxplots

Data from LaRiviere et al. (2012) spanning the interval of 0-866 ka. The MBE is designated as occurring at 430 ka. Top panel: all data in the pre- and post- MBE intervals. Middle panel: pre- and post- MBE interglacial periods. Bottom panel: pre- and post-MBE glacial periods.
Figure 21: ODP site 882 boxplots
Data from Martinez-Garcia et al. (2010) spanning the interval of 0-866 ka. The MBE is designated as occurring at 430 ka. Top panel: all data in the pre- and post-MBE intervals. Middle panel: pre- and post-MBE interglacial periods. Bottom panel: pre- and post-MBE glacial periods.
**Figure 22: UHPLC chromatogram**

UHPLC base peak chromatogram for a combined polar fraction from many samples throughout the Lake El’gygytgyn sediment core. The full suite of standard isoprenoid and branched GDGTs elute earlier in the run, while the H-shaped brGDGTs with m/z 1048, 1034, and 1020, and their isomers, are represented by the later eluting peaks. IS denotes the internal standard.
Figure 23: H- shaped brGDGT 1048 spectra and hypothesized structure.
Figure 24: H- shaped brGDGT 1034 spectra and hypothesized structure.
Figure 25: H-shaped brGDGT 1020 spectra and hypothesized structure.
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