Arctic Environmental Change across the Pliocene-Pleistocene Transition

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Arctic environmental change across the Pliocene-Pleistocene Transition

A Thesis Presented

By

BENJAMIN ANDREW KEISLING

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

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Department of Geosciences
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I am proud of the work I present here, and I claim the mistakes and errors (which are many) as wholly mine. Any credit for the good bits, though, is mine only to share. I offer it to the myriad teachers and mentors I have had throughout my life, but especially to: Dr. Robert Jacobel at St. Olaf College for an invaluable introduction to scientific research; Dr. Knut Christianson, now at University of Washington (*lykke til!*), for his inhuman patience; Dr. Isla Castañeda, for immersing me in the fascinating world of organic geochemistry; and Dr. Julie Brigham-Grette, for encouraging me to cultivate the sides of myself that do not find an outlet in the physical sciences. To all the Geoscience professors at UMass who have coached and mentored me for two years, thank you for your encouragement and support – it is deeply felt.

And, a hearty thanks to those who make it all worthwhile:

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TL, for keeping me rooted.

PGW, for teaching me to write
PAK, for teaching me to speak
and KEK, for keeping me laughing.

I love you (!)
ABSTRACT

ARCTIC ENVIRONMENTAL CHANGE ACROSS THE PLIOCENE-PLEISTOCENE TRANSITION

MAY 2015

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Environmental change in the Arctic proceeds at an unprecedented rate. The Pliocene epoch (5-2.65 million years ago) represents an analog for future climate conditions, with $pCO_2$ and continental configurations similar to present. Yet conditions in the Pliocene Arctic are poorly characterized because of sparse sampling. The records that do exist indicate periods of extreme warmth, as well as the first expansion of large ice-sheets in the Northern Hemisphere, took place from the end of the Pliocene into the early Pleistocene. Understanding these deposits and their implications for our future requires developing a sense of climatic evolution across the Plio-Pleistocene transition and especially during the intensification of Northern Hemisphere Glaciation (iNHG) ~2.7 million years ago. Here we reconstruct environmental change in the Arctic using a suite of organic geochemical proxies in a sedimentary archive recovered from Lake El'gygytgyn, Arctic Northeast Russia. We use the distribution of branched glycerol dialkyl glycerol tetraethers (brGDGTs) and the hydrogen isotopic composition ($\delta D$) of plant leaf-waxes ($n$-alkanes) to reconstruct relative temperature change across the interval spanning 2.8 to 2.4 million years ago. Our work demonstrates that, following the first major glaciation of the Northern Hemisphere, it took multiple glacial cycles for the Arctic
to become synchronized with the climatic changes recorded in the deep ocean. This work has implications for understanding the role of sea-level, sea-ice, vegetation and carbon-cycle feedbacks in a changing Arctic.
PREFACE

This thesis crowns four semesters of study (2013-2015) in the Geosciences department at the University of Massachusetts – Amherst, but my research builds on many years of work by others. The sediments I analyzed for this study were collected in 2009 by an international research team jointly led by Dr. Julie Brigham-Grette; their recovery was, in turn, the culmination of decades of scientific inquiry, political deliberation, and logistical ballet.

After a successful field campaign to Lake El’gygytgyn and subsequent sampling of the recovered cores at the University of Bremen, the working and archive halves of each core section were sent to the National Lacustrine Core Repository, LacCore, at the University of Minnesota. It was there that M.S. student Helen Habicht, Ph.D. student Greg de Wet, and I met to sample the cores in September 2013. This thesis presents results from analyses that were carried out on these samples during 2014 under the supervision of Dr. Isla Castañeda in the Biogeochemistry Laboratory.

My research was partially funded by NSF Grant #1204087 to Dr. Brigham-Grette, Dr. 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.” Additional funding for salary and tuition in my second year of study came from an NSF Graduate Research Fellowship (Grant #1451512).
My work focuses on the establishment of the modern Arctic as Earth moved from the globally warm Pliocene epoch into the colder, more variable Pleistocene. The Pliocene epoch has garnered intense interest because global $pCO_2$ levels and climatic boundary conditions were very similar to today; thus, a comprehensive description of the Pliocene environment may be, in some sense, prophetic. It is now apparent that the Arctic responds more intensely to climatic changes than any other region on earth. However, as more studies have focused on understanding the Pliocene Arctic, contradictions have surfaced: for instance, proxy-based temperature estimates are systematically higher than the warmth predicted by climate-model simulations. This mismatch undermines confidence in both methods, and delays confident projection of future climate relevant to, and necessary for, global society.

Part of the problem has been a lack of continuous sequences of Pliocene age from the Arctic. Many deposits represent a snapshot in time and space, and are difficult to correlate regionally or globally. In contrast, models predict environmental conditions across the globe for a discrete period of time, but require known boundary conditions that are poorly constrained for the Pliocene (i.e. the size of the Greenland Ice Sheet or atmospheric $pCO_2$).

My thesis, comprising three chapters, addresses this need by providing the first quantitative temperature reconstruction across the Plio-Pleistocene transition from the terrestrial Arctic based on organic geochemical proxies. In Chapter 1, I review existing knowledge of Pliocene climate, with a focus on the high latitudes and the mechanisms of
climatic change that are thought to have influenced the climatic deterioration from the warm Pliocene into the cool Pleistocene. Chapter 2 takes the form of a manuscript, to be submitted this spring to a peer-reviewed journal, based on the data I produced under the supervision of Dr. Castañeda. Chapter 3 highlights gaps in our understanding of the proxies and processes that are implicated in Chapter 2, and represents directions of inquiry that I hope to pursue in the future.

All unpublished data presented in this manuscript will be archived with ScholarWorks at UMass, and following publication, with the PANGAEA Data Publisher for Earth & Environmental Science.
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CHAPTER 1
INTRODUCTION

1.1 Pliocene Climate

The polar ice sheets contain enough water to raise global sea level by ~70 meters (Bamber et al. 2013, Fretwell et al. 2013). Observations indicate the Antarctic and Greenland Ice Sheets are both losing mass at an accelerating rate, contributing to the ongoing rise in global sea level (Shepard et al. 2013, Rignot et al. 2011, Hay et al. 2015). If such trends continue, they will have disastrous impacts on coastal populations. Still, polar ice sheets are not the only part of the climate system currently undergoing major changes (IPCC 2013). Today, human impacts have pushed the earth system beyond the known envelope of natural variability in numerous realms, including sea-ice extent and surface temperatures (IPCC 2013, Steffen et al. 2015). As these so-called “boundary conditions” evolve, the climate system may respond in ways that we have not seen in recorded history.

Fortunately, the geologic record is rich with natural experiments: times when the earth’s boundary conditions changed in similar ways to what we see today. These intervals represent potential analogues for future climate. The most recent epoch of elevated atmospheric carbon dioxide concentrations (\(\rho\text{CO}_2\), measured in parts per million by volume, p.p.m.v.) and higher global temperatures is the Pliocene warm period, 5-2.65 Million years ago (Ma) (Bartoli et al. 2011). The Pliocene is relatively well-represented in global geological records, and a broad base of knowledge about conditions during this
time exist (Haywood and Valdes, 2004, Dowsett et al. 1994, Salzmann et al. 2011). However, the abundance of research on the Pliocene has also borne out significant paradoxes and contradictions. Here I review existing knowledge of Pliocene climate relevant to the study at hand.

1.2.1 Marine Conditions

A major debate in Pliocene oceanography concerns conflicting evidence regarding tropical ocean dynamics. Although tropical sea surface temperatures (SSTs) were not much different from present globally, multiple sites in the Pacific suggest a more profound warming in the Eastern Equatorial Pacific (EEP) relative to the Western Equatorial Pacific (WEP) (Wara et al. 2005). This would have resulted in a deepening of the thermocline; a reduction in the upwelling of cool, nutrient-rich deep waters along the East Pacific margin; and the abatement of the Walker Circulation, which is driven by a strong West-East SST gradient in the modern ocean (Fedorov et al. 2010, Ravelo et al. 2007, Ravelo et al. 2004). This configuration is similar to oceanic conditions during strongly positive El-Niño-Southern Oscillation (ENSO) modes, prompting some workers to suggest that the Pliocene was characterized by a fundamentally different tropical oceanography (Wang and Fielder 2006, Wara et al. 2005). On the other hand, high-resolution isotope measurements on corals demonstrate that Pliocene ENSO was similar in frequency and magnitude to modern ENSO, and revisited SST records show that temperatures in the EEP and WEP evolved in tandem throughout the Pliocene, tracking the general global cooling during this time (Watanabe et al. 2011, Zhang et al. 2013, O’Brien et al. 2014). Irregardless of changes in spatial gradients, records globally agree
that the tropics were modestly (<2ºC) warmer than presently during the Pliocene (Herbert et al. 2010).

Beyond the tropics, temperature changes were more substantial. The ongoing Pliocene Research, Interpretation and Synoptic Mapping (PRISM) project seeks to provide both boundary conditions and a target for global climate model simulations of the Pliocene (e.g. Dowsett et al. 1994). A three-dimensional data synthesis of ocean temperatures during the Pliocene shows mean annual temperature anomalies of ~2º in the extra-tropics (15º-30º latitude), 3º in temperate latitudes, 4º in the North Pacific and >8º in the North Atlantic (Dowsett et al. 2009, Figure 1). Summer temperature estimates for the subpolar North Atlantic are up to 18º warmer than present, and there is no evidence for perennial sea ice at sites as far north as 80.5º during the Pliocene (Robinson et al. 2009).

In summary, while tropical ocean circulation may have been fundamentally different during the Pliocene, tropical SSTs were within a few degrees of modern averages (Herbert et al. 2010, Dowsett et al. 2009). In contrast, SSTs were markedly elevated at high latitudes, resulting in a reduced equator-to-pole (meridional) temperature gradient. Various mechanisms have been proposed to explain the increased heat transport required to maintain warm polar climates in the absence of tropical warmth, but few have been substantiated by data, and this remains a significant uncertainty in modeling the Pliocene (e.g. Ravelo and Andreasen 2000, Abbot and Tziperman 2008, Dowsett et al. 2013).
One difficulty in synthesizing Pliocene records is that they can represent multiple time periods in global history with potentially different boundary conditions (Dowsett et al. 2013, Salzmann et al. 2013). Robinson et al. 2009, for example, suggest that alkenone- and planktonic foraminifera-based temperature estimates from the polar North Atlantic are biased toward warm periods with high primary production, as lateral transport of alkenones and extensive carbonate dissolution are documented for their sites at other time periods. In developing a synthesis of ocean temperatures during the Pliocene, the PRISM effort looked for the warmest temperatures within a time-window, in order to characterize a “super-interglacial,” exceptionally warm Pliocene climate state (Dowsett et al. 1994). Yet, different physical mechanisms have spatially distinct anomaly signatures (Fedorov et al. 2013, Lawrence et al. 2013), which may be obscured by this approach.

In addition, some sea-surface temperature (SST) records from the Pliocene show large-amplitude variability. This is surprising, because the Pliocene probably lacked the strong ice-albedo feedback that was salient in driving the high-amplitude climate changes of the Pleistocene (Broccoli & Manabe 1987). Although high amplitude SST variations are seen at some sites (Lawrence et al. 2009), these are not a ubiquitous feature of Pliocene oceanography (e.g. Haug et al. 2005, Herbert et al. 2010). In fact, recent work on Pliocene climate sensitivity found that, after accounting for a diminished ice-albedo feedback, Pliocene climate changes for a given pCO2 forcing were the same as the Pleistocene (Martinez-Boti et al. 2014).
1.2.2 Terrestrial Climate

In the terrestrial Arctic during the Pliocene, the treeline extended to the Arctic Ocean, hosting abundant *Picea* (Spruce) and *Pinus* (Pine) forests (Salzmann et al. 2011). Offshore cores containing abundant *Tsuga* (Hemlock) pollen document 4º-10º warming in Norway, Iceland, and Subarctic Canada, with biomes presently existing at 45ºN extending to 67ºN during the Pliocene (Willard et al. 1994). Three independent proxy temperature estimates (based on tree-ring oxygen isotopes, branched glycerol dialkyl glycerol tetraethers, and pollen analysis) from Pliocene deposits in Arctic Canada (78ºN) suggest that temperatures were ~19ºC warmer than present there (Ballantyne et al. 2010) some time during the Mid-Pliocene (3.4±0.5 Ma). These deposits also contain bone fragments from prehistoric camels, whose range apparently extended into the High Arctic at that time. Though sparse, terrestrial deposits from the Pliocene Arctic illustrate its profound difference from the modern Arctic: low-albedo vegetation covered a continuous North American landmass, extending in some places to the edge of the Arctic ocean, supporting large and varied animal life not particularly adapted to cold conditions. The extent of climatic variability in the Pliocene Arctic has not been documented, due to a lack of records, but terrestrial records from lower latitudes demonstrate both gradual and abrupt changes occurred during the Pliocene (Wilson et al. 2014, Bolton et al. 2010, Becker et al. 2005). Unfortunately, because most records are discontinuous and difficult to date precisely, temporally correlating such changes to test mechanistic linkages remains difficult. Moreover, in the Arctic Ocean, low sedimentation rates and widespread dissolution (Polyak et al. 2011) prohibit correlation between records necessary for documenting the transient evolution of Pliocene climate. In order to bridge
this gap, well-dated, high-sedimentation-rate sites with good preservation from both the terrestrial and marine realms are necessary, but remain elusive.

Precise dating of terrestrial deposits is difficult, complicating regional correlations, but some workers have tried to align periods of enhanced warmth with sea-level transgressions. The Gubik formation from Northern Alaska contains deposits from at least three sea-level high stands during the Late Pliocene, termed the Colvillian (~2.8 Ma, + 40 m), the Bigbendian (~2.6 Ma, + 40 m), and the Fishcreekian (~2.1-2.4 Ma, +30 m) transgressions (Miller et al. 2010). Pollen grains preserved in the Gubik formation document the advance of the treeline nearly to the Arctic Ocean during sea-level highstands, implying substantial warmth accompanied these three periods (Nelson and Carter, 1991). Larger fossils (sea otter bones) in the Gubik formation also suggest the absence of seasonal sea-ice at 70ºN during the Bigbendian and Fishcreekian transgressions, implying substantially warmer conditions than present (Brigham-Grette and Carter, 1992).

Other deposits in the circumarctic document periods of high sea-level and elevated warmth. For example, the Kap København formation in Northeast Greenland documents higher sea level, summer warming of 10-15ºC, and seasonally ice-free conditions, which would require substantial retreat of the summer sea-ice margin and imply disintegration of a large portion of the Greenland Ice Sheet (Funder et al. 2004). These deposits have been dated to ~2.5 Ma based on amino acid racemization ratios, reversed paleomagnetism in the fine-grained marine portions of the sequence, and the
first and last appearances of ostracodes and small mammals known from Alaskan Neogene deposits (Funder et al. 2004). Brigham-Grette and Carter (1992) suggested the Fishcreekian transgression known from Alaskan deposits may be correlative with the Kap Københaven formation based on the amino acid racemization ages of both deposits. However, multiple sea-level changes known from global records fall within the age uncertainties of both deposits (Röhling et al. 2014). Determining which of these sea-level highstands was caused by the disintegration of the Greenland Ice Sheet, and the planetary conditions that led to such a collapse, is a chief goal of Pliocene paleoclimate. Yet the nature of discontinuous deposits makes it difficult to piece together cause and effect, hindering progress in this realm.

Although the Pliocene presents an ideal case study of future climate, the inconsistencies in marine and terrestrial records outlined here only partially capture the uncertainties related to global conditions during this interval. In order to place Chapter 2 in perspective, it is specifically insightful to review the history of land ice, sea ice, and pollen analysis in the Arctic.

1.2.2.1 Land-Ice History

Although the Pliocene is generally characterized as a stable warm period (IPCC, 2013), major changes to the earth system occurred during this epoch. Chiefly, the global benthic oxygen isotope stack (henceforth δ^{18}O; Lisiecki and Raymo 2005) indicates that large changes in ice volume occurred over the last five million years. Understanding these variations is critical to understanding ice-sheet stability in a warming world (Alley
et al. 2010, Shepard et al. 2013). At 2.7 Ma, the amplitude of changes in δ¹⁸O increases markedly, in concert with the first major synchronous deposition of ice-rafted debris (IRD) in the North Pacific and North Atlantic basins (Kleiven et al. 2002, Jansen & Sjøholm 1991, Bailey et al. 2013), suggesting widespread, voluminous ice-sheets occupied the Northern Hemisphere for the first time, a phenomenon that had ostensibly been impossible earlier in Earth’s history because of the relatively high values of atmospheric pCO₂ (Zhang et al. 2013).

However, despite a proposed threshold for Northern Hemisphere Glaciation of 280 ppm pCO₂, there is evidence for land-ice in the Arctic throughout the Cenozoic (DeConto et al. 2008, Eldrett et al. 2007; Tripati et al. 2007; Moran et al. 2006; Knies et al. 2014). However, the presence of extensive ice sheets prior to 2.7 Ma is still controversial. The distinction is critical, because while glaciers can grow in isolated high-altitude or high-accumulation environments even in the present-day tropics, ice sheets require favorable climatic conditions over a large geographic region, and trigger dramatic feedbacks that affect the surficial and solid earth (Gasson et al. 2012, Abe-Ouchi et al. 2013). Though the presence of subglacially sculpted ice-rafted debris (or dropstones) in Eocene sediments is intriguing (Eldrett et al. 2007, Tripati et al. 2007), these cannot confirm the presence of extensive, climate-altering ice sheets, especially considering that these dropstones can also be attributed to seasonal or perennial sea-ice (Darby et al. 2014) or perhaps carried in the roots of fallen trees (Vogt et al. 2012).
De Schepper et al. (2013) describe three periods prior the globally recognized intensification of Northern Hemisphere Glaciation (iNHG), during which glacial advances are recorded at multiple sites in the Northern Hemisphere. The first of these occurred ~4.9 Ma. The change in benthic oxygen isotopes (Lisiecki et al. 2005) suggests up to 50 meters of eustatic sea-level fall or ~2º C of deep-ocean cooling. At least some ice on land reaching the sea is likely, because IRD records from both the Irminger Basin (St. John et al. 2002) and the Norwegian Sea (Jansen et al. 1991; Kleiven et al. 2002) show a coincident increase in glacially-derived debris. The first appearance of diatoms uniquely associated with glacial periods occurs in the North Pacific around ~5 Ma, but there is no evidence for ice-rafted debris at the same site during this time (Lagoe et al. 1993). Pillow basalts dated to ~4.7 Ma in Iceland (Geirsdottir et al. 2011) imply that the Icelandic land surface was glaciostatically depressed by a large ice-mass, allowing for the formation of underwater volcanic deposits that were subsequently uplifted when the ice-sheet disintegrated.

Another potential glacial event occurred ~4.0 Ma. Although the change in benthic oxygen isotopes implies only limited ice-growth or deep-sea temperature change (less than 30 m or ~1.5º C), the evidence for large ice-sheets on land in the Northern Hemisphere is more robust than at 4.9 Ma. A glacial diamict spanning east and southeast Iceland (e.g. covering >25% of the Icelandic landmass, >25,000 km² extent) is interbedded with basalts that constrain its age to 4.0 Ma (Geirsdottir 2011). Dropstones are found for the first time in the North Pacific at both the Bowers Ridge, north the Alaskan Peninsula (Takahashi et al, 2011) and in the Chinook Trough, south of the
Alaskan Peninsula (Krissek et al. 1995). In addition, pulses of ice-rafted debris are found off the coasts of Greenland, Iceland, and Norway (Jansen et al. 1999; Kleiven et al. 2002; St. John et al. 2002; Geirsdottir 2011).

A final large glaciation potentially occurred between ~3.5 and 3.3 Ma. The substantial change in benthic oxygen isotopes suggests up to 70 meters of global ice volume change or a deep-sea cooling of 3° over ~10,000 years (Lisiecki et al. 2005). Ice-rafted debris increases relative to the 4.0 Ma event across the North Pacific (Takahashi et al, 2011; Lagoe et al. 1993; Krissek et al. 1995) and accumulation rates of IRD in the North Atlantic increase to values more characteristic of Pleistocene glaciations (De Schepper et al. 2014). At least three extensive till sheets dated to this interval have been reported in the literature. The Zhuravlinean Till in Chukotka, Northeast Russia, dates to 3.5-3.2 Ma (Andreev et al. 2014). A till sheet dated to 3.3 Ma covers most of the Icelandic landmass (Geirsdottir 2011). In James Bay Lowland, Canada, a glacial diamict <50 m thick is exposed (Gao et al. 2012). Magnetostratigraphy of the overlying sediments suggests an age for the diamict between 3.5-3.3 Ma. Furthermore, pebbles in the till show evidence of deep crescentic gouges and parallel grooves, suggestive of physical weathering in a subglacial environment (Gao et al. 2012). Because this deposit records flowing ice at 52ºN latitude, it implies an ice-cap existed further north, with lobes of fast-flowing ice extending into subarctic latitudes.

It is intriguing to note that a deposit on Ellesmere Island (79ºN) suggesting summer temperatures ~19º warmer than modern (Ballantyne et al. 2010) and containing
the bones of prehistoric camels has been dated at 3.4±0.5 Ma using beryllium isotopes (Rybczynski et al. 2013). This is a reminder that early Pliocene glaciations occurred in an Arctic much different that the one we know today. Geochemical provenance of ice-rafted debris from the North Atlantic suggests that the first input of material derived from North America did not occur until 2.64 Ma (Bailey et al. 2013), but this work did not focus on the period prior to the intensification of Northern Hemisphere glaciation (at 2.73 Ma). Thus, it cannot be ruled out that an ice cap grew on the North American continent ~3.5-3.3 Ma and may have been extensive enough to reach the coast. Together, all these records suggest hemispherically synchronous glacial advance ~600,000 years before the onset of Pleistocene glacial-interglacial cycles and occurred in the context of a warmer, forested Arctic.

Although the evidence reviewed here for medium-sized (10-60 m eustatic sea-level equivalent) ice sheets during the early Pliocene is compelling, the character of these glaciations seems distinct from glacial advances in the more recent Pleistocene. During the last glacial maximum (LGM), when global sea levels were ~120 m lower than present, the North American continent hosted an enormous ice sheet accounting for up to 100 m of eustatic sea-level fall (Gregoire et al. 2012; Wickert et al. 2013). This suggests a high sensitivity of the North American continent to climatic changes and ice-sheet nucleation. Conspicuously, ice growth on North America did not occur until ~1 million years after the first major glaciation ~4.8 Ma in Greenland, Scandinavia and Iceland (De Schepper et al. 2013). Incomplete sampling could make North America seem less susceptible to Pliocene glaciation. Because topographic relief in Scandinavia and
Greenland is much greater than in North America, it would have been easier for glaciers to nucleate at high elevation and deliver icebergs to the nearby coast, where they can calve and release ice-rafter debris offshore. However, tidewater glaciers are ubiquitous in Alaska and British Columbia today, and later glacial advances unambiguously occurred in the circum-North Atlantic and circum-Pacific (e.g. at 3.5-3.3 Ma, De Schepper et al. 2013). Thus, the inconsistency might not concern sampling but rather have to do with a different mechanism for glaciation that, in contrast to conditions in the late Pleistocene (i.e. LGM), did not favor nucleation of ice-sheets in North America. Yet after iNHG, regular, large-amplitude glaciations occurred in North America. Determining which components of the climate system changed to permit this shift is a primary goal of Chapter 2.

1.2.2.2 Bering Straight History

The Bering Straight provides the only connection from the North Pacific into the Arctic basin today, and constitutes an important freshwater contribution to the saline basin (Woodgate & Aagaard 2005). Paleontological evidence indicates that the Bering straight first flooded ca. ~5.5 Ma (Demske et al. 2002), but the exceptionally shallow shelf (~50m below sea level today) experienced periodic inundation and exposure throughout the Plio-Pleistocene. During periods of globally (eustatic) or regionally (isostatic) high sea level, the Bering Straight is open, permitting exchange between North Pacific and Arctic water masses. During periods of low sea level, a land bridge is exposed, restricting exchange between basins.
Closure of the Bering Strait can lead to more erratic climate behavior (Hu et al. 2012, Hu et al. 2014). When the Strait is open, freshwater perturbations to the North Atlantic can be dissipated by mixing into the North Pacific. When the Strait is closed, the same perturbations recirculate to the North Atlantic via the Arctic Ocean and cause a prolonged disturbance to the overturning circulation there (Hu et al. 2012). In addition, the reduced northward freshwater flux under closed Strait conditions leads to a saltier Arctic Ocean, potentially muting the strong halocline present there today (Keigwin et al. 2007). The strong halocline in the Arctic Ocean controls to an array of important processes, including sea-ice formation, stratification, and productivity (Aagaard and Carmack 1989, Wadley and Bigg, 2002, Cooper et al. 1997). Thus, the exposure history of the Bering Strait is inexorably linked to many other features of the Arctic climate system.

1.2.2.3 Sea Ice History

The northern most part of the globe, which receives near-direct, continuous sunlight during the summer months, is occupied by the Arctic Ocean. Because of the low albedo and high heat content of seawater, the Arctic Ocean can serve as an important capacitor for the high-latitude climate system, absorbing solar energy in summer and releasing it to the atmosphere in winter in the form of latent and/or sensible heat. However, because of the extreme cold temperatures and restricted nature of the Arctic basin, sea-ice is common in the Arctic Ocean (Vihma 2014). Sea-ice forms in the winter, when the cold atmosphere and strong halocline foster rapid cooling of a relative fresh surficial layer of seawater surface skein of water, which forms ice once it has reached its
(salinity-dependent) freezing point (Wadhams 2013). This sea-ice persists into the summer, strongly influencing the reflectivity of the circum-Arctic, and serving as a positive feedback for sea-ice production the following winter (Eisenman & Wettlaufer 2009). Thus, changes in Arctic temperatures or ocean circulation can become magnified via the production of sea-ice, and the positive feedbacks involved make sea-ice susceptible to large changes on both observational and geological timescales (Wang & Overland 2009).

Dropstones found in the central Arctic Ocean argues for the presence of some perennial sea ice in the Arctic basin as early as the Eocene (Darby et al. 2014). However, there is emerging evidence that these may be rafted by other materials, for example fallen trees, which were ubiquitous in the circumarctic during the Eocene (Vogt et al. 2012, Sluijs et al. 2006). Biomarker-based evidence indicates the onset of modern sea-ice cover in the Arctic basin occurred ~2.6 Ma, coincident with the intensification of Northern Hemisphere glaciation (Knies et al. 2014). Except for the circumstantial evidence presented above for periods of Pliocene warmth when high-latitude coastlines were ice-free, little is known about the variability of sea-ice cover through the Plio-Pleistocene (Polyak et al. 2010, Brigham-Grette & Carter 1992).

1.2.2.4 Pollen Records

Making paleoclimatic inferences based on the distribution of pollen in sediments is a well-established technique, even in the sparsely sampled Arctic (Colinvaux 1967). Nevertheless, pollen can be carried long distances by wind, remobilized from catchment
sediments, and difficult to distinguish at the species-level, complicating paleoclimate interpretations from pollen assemblages (Ritchie, 1995, Gajewski, 2006). However, when used in concert with other methods, it can provide a powerful tool for environmental reconstruction.

Pollen biome reconstructions rely on mapping the modern spatial distribution of analog species to determine tolerable climatic regimes for each species (i.e. mean temperature of the warmest month (MTWM) or mean annual precipitation (MAP)). By considering the overlap between all pollen types present in a sample, estimates of probable climatic conditions can be proposed (Gavin et al. 2003). To carry out this analysis, one must assume that all the types of pollen present in a sample were living in the same time and place, e.g. subject to the same climate. Yet because of the transport processes involved, the types of pollen present in a sample may not represent species that meet this requirement. Indeed, often the bioclimatic ranges of all pollen types present in a sample do not completely overlap, and as such, reconstructions have high error in terms of absolute temperature and precipitation (Gavin et al. 2003).

Considering species individually can provide an additional layer of climatic information. For example, *Pinus pumila* requires deep snow during the winter to survive (Anderson et al. 2010); *Larix* spores indubitably indicate the presence of larch near a site, as the palynomorphs are not subject to eolian transport and readily degrade (Lozhkin 2007); and the time-transgressive appearance of different pollen types can indicate the retreat or advance of different biomes through a catchment (Lozhkin 2013). In the latter case, the progression of *Betula-Alnus-Pinus* is characteristic of recent interglacials in Arctic deposits, representing the establishment of deciduous forest at high northern
latitudes, and when culminating in a spectrum dominated by tree pollen, a re-advance of the boreal treeline (Lozhkin 2013).

1.2.2.5 Biomarker Records

The remains of living organisms can become entombed in sedimentary archives and evade degradation for millions of years. Compounds that can be traced back to specific source organisms, or a group of organisms, are called biomarkers (Peters 1993). Biomarkers can be widely distributed or specific to a single species, and can be transformed by post-depositional processes (Bianchi & Canuel 2011). Lipid extraction from sediments releases a suite of biomarkers that can be employed for paleoclimate reconstruction (Castañeda & Schouten 2011, and references therein).

Of particular interest to the present study are biomarkers that can be used in tandem with already published pollen records. N-alkanes are saturated hydrocarbon chains formed by linked carbon atoms ringed by hydrogen atoms (Figure 4). Long chain-length $n$-alkanes (i.e. 25-35 carbons, $C_{25}$-$C_{35}$) are diagnostic of terrestrial higher plants, and individual plants produce characteristic patterns of long-chain $n$-alkanes: for example, Sphagnum produces $C_{23}$ alkanes in abundance, whereas some grasses mainly produce $C_{31}$ or $C_{33}$ alkanes (Bush et al. 2013). Thus, $n$-alkane distributions can in some sense be used to reconstruct changes in vegetation, similar to pollen distributions, although for long chain-length $n$-alkanes each compound represents a mix of sources (Bush et al. 2013).

In addition, paleotemperature reconstructions based on biomarkers can complement pollen-based biome reconstructions. Two powerful techniques of interest to
the present study are (1) the use of \( n \)-alkane \( \delta D \) to reconstruct precipitation isotopes (Sauer et al. 2001), and (2) the use of branched glycerol dialkyl glycerol tetraether (brGDGT) distributions to directly reconstruct soil temperature and pH (Weijers et al. 2007). These methods are detailed and applied in Chapter 2 for reconstruction of paleoenvironment across the Plio-Pleistocene transition.

### 1.3 Summary

Pliocene boundary conditions are similar enough to present to warrant considering the period as an analog for the future. Yet, it is prudent to consider that there may have been significant structural climate changes as well (i.e. persistent positive ENSO-like conditions in the tropical Pacific, large oscillations in global sea level). The potential societal impacts of such changes are large and costly (i.e. fishery collapse and displacement of coastal populations); thus resolving uncertainties related to Pliocene climate and oceanography is a timely endeavor. Research on the Pliocene has revealed that many elements of the climate system were in flux during this period, and of critical interest is the role of various feedbacks in promoting and/or delaying those transitions. For example, the latitude of the treeline influences regional albedo, as does the extent sea-ice and land-ice, and high sea level allows for greater heat and freshwater transport through the Bering straight. As has been outlined here, questions remain about the transition from the globally warm Pliocene into the colder, more variable Pleistocene; uncertainties are especially dire for the terrestrial realm. The record presented in Chapter 2 attempts to address this gap, so that we may refine our understanding of the mechanisms that guided climatic evolution during this epoch.
CHAPTER 2
ENVIRONMENTAL CHANGE ACROSS THE PLIOCENE-PLEISTOCENE TRANSITION

2.1 Introduction

We live on a planet that has experienced extreme climatic changes during its history. Yet human society flourished during the past 10,000 years, a period of relative climatic quiescence termed the Holocene. To accurately predict future climate change, we must understand how climate has evolved over longer periods of geologic time. Analog periods are especially important for viewing observed climate phenomena against the backdrop of natural variability, and determining the extent to which ongoing changes are unprecedented. Reconstructions of climate over the Holocene or the last glacial cycle have the advantage of high-resolution, and in some cases, continuous sampling (e.g. Balascio et al. 2013, Praetorius and Mix, 2014). Such records permit robust assessment of the role of various climate forcings in driving past climate change, and determination of leads and lags in the climate system (Marcott et al. 2013, Shakun et al. 2012). However, as global carbon atmospheric carbon dioxide concentrations ($pCO_2$) increase beyond the envelope of natural variability during these well-studied intervals (~400 ppm today compared to ca. 180-280 ppm over the last 800 ka (Augustin et al. 2004)), analogs must be sought farther back in the geological record.

The Pliocene was a globally warm epoch ca. 5-2.65 million years ago (Ma) when global $pCO_2$ was 350-450 ppm (Zhang et al. 2013, Martínez-Botí et al. 2015), and has
been proposed as a good analog for future warming (Thompson and Fleming, 1996). In light of this, the aim of this study is to reconstruct how climate in the Arctic evolved during the transition from the warm Pliocene into the glaciated Pleistocene (2.82-2.41 Ma, this study). Of additional interest are thresholds passed in the climate system during this interval. The most pronounced of these is the intensification of Northern Hemisphere glaciation (iNHG) ~2.73 Ma, which has been studied extensively in marine records (Fig. 1). Haug et al. (2005) analyzed sediments from the North Pacific and found a complex series of oceanographic changes occurred across iNHG. Both alkenone and planktonic δ¹⁸O-based sea surface temperature (SSTs) warmed abruptly by 7-9°C at 2.73 Ma (during glacial Marine Isotope Stage (MIS) G6), followed by a permanent drop in biogenic opal accumulation and a steady increase in the background magnetic susceptibility of ice-rafted debris. Based on modern seasonality of production for these two SST proxies, they infer an early fall warming took place across the North Pacific at 2.73 Ma. They also used a coupled ocean-atmosphere model to show that at least two equilibria exist for the subarctic North Pacific: one characterized by a destratified, mixed water column, and the other by a permanent halocline causing thermal isolation of surface waters from the deeper ocean (as is true today (Aagaard et al. 2006)). They posit that a switch from the destratified equilibrium to the stratified case occurred at ~2.73 Ma, transforming the subarctic North Pacific into a major source of winter moisture for the Northern Hemisphere.

Woodard et al. (2014) argue that a similar threshold was crossed in Pacific bottomwater characteristics across this transition. They measured planktonic δ¹⁸O and benthic Mg/Ca to reconstruct geochemical and physical properties of North Atlantic and
North Pacific water masses across iNHG. They found that concurrent with iNHG, geochemical and physical gradients that were established through the Late Pliocene suddenly collapsed. These results suggest incursions of North Atlantic-sourced deep water began bathing the deep Pacific at $\sim 2.9$ Ma. Yet, other SST records from the North Atlantic and North Pacific imply a gradual, rather than threshold, transition from the warm Pliocene into the heavily glaciated Pleistocene. Lawrence et al. (2009) use the lead of alkenone-derived SSTs over benthic $\delta^{18}$O to infer slow but steady glaciation of high northern latitudes from 3.5–2.7 Ma. They argue for the establishment of a permanent Greenland Ice Sheet (GIS) between 3.5-2.5 Ma, based on a cooling of $\sim 5^\circ$C at Site 982 during this interval, and consistent with the onset of ice-rafted debris accumulation in the same core at $\sim 2.5$ Ma. Venti et al. (2013) use a similar method to show that subtropical Pacific SSTs in the Kuroshio Current Extension are lower than would be expected from direct CO$_2$ or insolation forcing across iNHG. They posit that around 2.7 Ma, enhanced wind stress increased evaporative cooling of the subtropical North Pacific, producing a moisture source capable of delivering more precipitation to high latitudes. In contrast to records from the North Atlantic and North Pacific, the record from Venti et al. (2013) indicates warming of $\sim 3^\circ$C from 3.0-2.7 Ma. These reconstructions highlight that while there is considerable evidence for both gradual cooling trends and crossed oceanographic thresholds across iNHG, a coherent story of the climatic changes that primed and then drove the earth system through the periodic glaciations of the Pleistocene remains elusive.

Although the oceans are a major component of the climate system, northern landmasses were the also dramatically affected by the growth of large ice sheets during
the Pleistocene. Thus, the paucity of terrestrial records from this time period is a major hurdle to improving our understanding of iNHG. Unfortunately, high-resolution, continuous terrestrial sections of Pliocene age are sparse. They are exceptionally rare in the high latitudes, where repeated exfoliation of the landscape by Pleistocene ice sheets has removed many sedimentary sequences. In 2009, an expedition recovered a sediment core from Lake El’gygytgyn (hereafter Lake E), Russia, which spans the last \( \sim 3.6 \) Ma. This record provides a unique view of environmental change preceding, during, and following iNHG from the Arctic. Although pollen-based estimates of environmental change have been published for Lake El’gygytgyn (Melles et al. 2012, Brigham-Grette et al. 2013), these are regional in nature and subject to large errors based on the modern analogue approach (Andreev et al. 2014). Organic geochemical proxies provide an independent means of examining terrestrial temperature and hydrological change (e.g., Weijers et al. 2007, Tierney et al. 2008, Feakins et al. 2012, Pautler et al. 2014) and may provide a more local signal in a lacustrine environment (Buckles et al. 2014, Loomis et al. 2014).

Here we apply two proxies that have previously been used to reconstruct temperature on Arctic sediments, as well as a suite of biomarkers for terrestrial and aquatic productivity and environmental conditions. Firstly, we use the methylation of branched tetraethers/cyclization of branched tetraethers (MBT/CBT ratio) based on branched glycerol dialkyl glycerol tetraethers (brGDGTs) (Weijers et al. 2007, Peterse et al. 2012). Secondly, we measure the deuterium to hydrogen ratio on terrestrial higher plant leaf waxes (\( n \)-alkane \( \delta^D \)). We use these in conjunction with a suite of other
(in)organic geochemical climate proxies to investigate environmental change in the Siberian Arctic across the Pliocene-Pleistocene transition.

Comparison with other data, including published work from Lake El’gygytgyn (Brigham-Grette et al. 2013, Melles et al. 2012) and the benthic δ¹⁸O isotope stack of Lisiecki and Raymo (2005), guide our interpretations. While the former enables us to more critically assess the strengths and shortcomings of each of the proxies applied, the latter represents mean global conditions and incorporates two slow components of the climate system, the deep ocean and ice sheets (Lisiecki and Raymo, 2005). As Lake El’gygytgyn is situated in the high Arctic, we expect that the environmental changes occurring across the PlioPleistocene transition will be pronounced compared to the oceanographic changes that have been documented for this interval. Placing our Arctic record in the context of global records yields insight to the evolution of ice-sheets as earth moved into an “icehouse” world (Raymo and Ruddiman, 1992).

2.2 Study area and regional setting

Lake El’gygytgyn is located in northeastern Siberia (67.5ºN, 172ºE). The lake was created by a bolide impact ∼3.6 million years ago (Ma), resulting in a small catchment with a high degree of topographic relief (Layer, 2000, Nolan and Brigham-Grette, 2006). The lake and its catchment are roughly circular, with diameters of ∼12 km and ∼18 km, respectively (Fig. 2). The lake is ice-covered for ∼10 months of the year, with most inflow during the early June freshet, delivered by 50 small creeks that ring the lake (Nolan and Brigham-Grette, 2006). Outflow is through the shallow Enmyvaam River, which flows ephemerally to the south-southeast during the summer (Fedorov et al. 2013).
The lake escaped the periodic glaciations of the Plio-Pleistocene, perhaps due to
its extremely arid climate (Barr and Clark, 2011). As such, it accumulated a continuous
sedimentary record through the Late Pliocene and into the Pleistocene (Brigham-Grette et
al. 2013). In 2009, the International Continental Drilling Program recovered 318 meters
of composite core from Lake El’gygytgyn (Brigham-Grette et al. 2013, Melles et al.
2012). Three separate drives comprise the composite core, which were correlated based
on their lithological properties (Gebhardt et al. 2013). The age model is based on a three-
tiered system of tie points: primarily, on twelve magnetic reversals dated by the official
geomagnetic polarity timescale; secondarily, by tuning the elemental ratio of
silica/titanium and hue angle to the benthic δ¹⁸O stack; and lastly, by tuning of magnetic
susceptibility and total organic carbon (% TOC) to Northern Hemisphere summer
insolation (Haltia and Nowaczyk 2014, Nowaczyk et al. 2013). The uncertainty in
absolute age are 3-15 kyr, with higher uncertainties during the Pliocene portion of the
record (Nowaczyk et al. 2013). However, correlation between the lake core, benthic
oxygen isotopes, and Northern Hemisphere summer insolation should be more precise, as
the age of the lake sediments has been tuned to these records.

Lake El’gygytgyn sits between two prominent atmospheric pressure centers in the
Northern Hemisphere, the Siberian High and the Aleutian Low. Although their position
and strength show significant interannual variability, their mean position causes extreme
windiness at the lake (Fig. 1) (Mock et al. 1998). Aloft, the persistent “East Asian
Trough” in the jet stream brings southerly flow to the Lake (Mock et al. 1998). In
summer, the Pacific subtropical high sits over the northeastern Pacific, bringing
predominately southerly surface flow to the lake (Mock et al. 1998). Historical
observations of atmospheric circulation patterns are consistent with weather station data spanning 2002, which showed winds were predominantly south-easterly and north-westerly (Nolan et al. 2013). Precipitation data from the same year showed that the lake is extremely arid (< 200 mm yr$^{-1}$), with precipitation occurring approximately equally in summer and winter. Although the Siberian High and Aleutian Low are persistent features of the climatology, they are subject to change as the jet stream kinks and migrates, and the mean climatology at Lake El’gygytgyn may have shifted over time as a consequence.

The imposition of large ice masses in the Northern Hemisphere has dramatic consequences for atmospheric pressure centers (Bromwich et al. 2004). Studies of the last glacial maximum indicate an intensified Aleutian Low, and a potential splitting of the jet stream aloft, so that more southerly-sourced air would be advected over the lake (Bromwich et al. 2004). Katabatic flow off of the ice sheets would produce localized anticyclonic circulation, the effects of which would be felt if ice-sheets nucleated near the lake (Mock et al. 1998). Also during the last glacial maximum, the sea-ice margin was almost certainly farther south and more persistent through the summer (Kocis et al. 2013).

The nearby Bering Sea experiences dramatic seasonal changes due to sea-ice cover. In March, the sea-ice margin extends to $\sim$55ºN, but by September the ice-edge has retreated $\sim$3300 km to $\sim$80ºN (NSIDC 2014). This leads to enhanced productivity in the summer months, accompanied by a significant warming, from 1ºC in winter to 12ºC in summer (Haug et al. 2005). Surface flow in the Bering Sea is driven by the clockwise North Pacific Gyre, which forces westerly flow through and along the Aleutian Islands. Most of this water returns to the Pacific via the deep Kamchatka Strait, but at shallow
depths (<150 m), some water is routed through the Bering Strait (Aagaard et al. 2006). Flow through the Strait is driven by a persistent gradient in sea-surface height, attributed to topographic differences between the basins and a difference in salinity between the fresh North Pacific (average salinity 32.5 psu) and the saltier Arctic Ocean (average salinity 34.8 psu) (Aagaard et al. 2006). The net effect is a 0.8 Sverdrup flow from the Bering Sea into the Arctic Ocean, through the relatively shallow and narrow Bering Strait (Aagaard et al. 2006). Critically, lower global sea level during glacial periods exposed the Bering Shelf and eliminated northward flow into the Arctic Ocean, resulting in a higher degree of continentality at the lake, more mercurial overturning circulation in the North Atlantic, and isolation of the Arctic Basin from fresh, warm Pacific water (Barr and Clark 2011, Hu et al. 2012, Aagaard et al. 2006). The evolution of each of these features is relatively poorly constrained across iNHG, but previous work provides important benchmarks that can assist our interpretations (e.g. Polyak et al. 2010, Miller et al. 2010, Alley et al. 2010, Knies et al. 2014).

2.3 Sampling and methods

2.3.1 Sample preparation

Core sampling was conducted in September 2013 at LacCore (University of Minnesota, USA). 5-7 cm³ sediment samples were collected at one-centimeter intervals from the working half of each core section where possible, and the archive half where necessary. For this study, we analyzed samples every ~10 cm throughout the composite core, resulting in a climate reconstruction with ~2 kyr resolution (mean sample spacing = 2.3 kyr, median = 1.3 kyr). For comparison between this record and other published
datasets, all timeseries were re-interpolated onto 2.5 kyr spacing. The results presented here were tested for interpolations between 2-4 kyr to confirm that interpretations are robust within the range of reasonable data coverage (Fig. 3).

Freeze-dried, homogenized samples were extracted using a Dionex Accelerated Solvent Extraction (ASE 200) system with a mixture of methylene chloride (DCM):methanol (9:1, v:v). Total lipid extracts (TLEs) were dried under a stream of N₂ and separated into apolar, ketone, and polar fractions by sequential elution over activated Al₂O₃ using DCM:hexane (9:1, v:v) (apolar fraction), DCM:hexane (1:1, v:v) (ketone fraction), and DCM:methanol (1:1, v:v) (polar fraction).

2.3.2 brGDGT analysis

One half of each polar fraction was filtered through 0.45 µm PTFE filters in hexane:isopropanol (99:1, v:v), dried under a stream of N₂, and dissolved in 100 µl hexane:isopropanol containing 0.1 µg of a C₄₆ GDGT internal standard. All GDGTs were quantified with respect to the C₄₆ standard, assuming equal ionization efficiency for all compounds. GDGTs were analyzed using an Agilent 1260 High Performance Liquid Chromatograph (HPLC) coupled to an Agilent 6120 Mass Selective Detector (MSD), equipped with a Prevail Cyano column (150 mm × 2.1 mm × 3 µ) run in selected ion monitoring (SIM) mode for the major brGDGT protonated molecules [M+H]⁺. GDGTs were eluted by 99:1 hexane:isopropanol for 7 minutes, then by a linear solvent gradient culminating in 1.8% hexane:isopropanol after 32 additional minutes following the methods of Hopmans et al. (2000) and Schouten et al. (2007).
Weijers et al. (2007) proposed the MBT/CBT proxy for mean annual air temperature (MAAT) based on the distribution of brGDGTs, which they found to be globally ubiquitous in soils and peat. Subsequent studies refined this relationship (defining the MBT index) (Peterse et al. 2012) and extended it to lacustrine environments (e.g., Pearson et al. 2011, Sun et al. 2011). brGDGTs are comprised of two ether-linked dialkyl chains containing zero to two methyl branches (prefixes I, II, and III) and zero to two cyclopentane moieties (suffixes a, b, and c) (Fig. 4). Although the source organisms are unknown, the compounds are thought to form the cellular membrane of certain bacteria (e.g., Sinninghe Damsté et al. 2011). Despite total uncertainty about the mechanism of production and cellular role of these compounds, the MBT and CBT indices have proven useful across a range of environments for reconstructing past temperature and soil pH. The indices proposed by Weijers et al. (2007) are as follows:

\[
CBT = -\log \frac{[Ib] + [Ilb]}{[Ia] + [IIa]}
\]  
(1)

\[
MBT = \frac{[Ia + Ib + Ic]}{[Ia + Ib + Ic] + [IIa + IIb + IIc] + [IIIa + IIIb + IIIc]}
\]  
(2)

Following the original study of Weijers et al. (2007), subsequent work found major discrepancies between the original calibration and measured MAAT, especially in lakes. To remedy this, two lines of inquiry relevant to the present study have been explored: refinement of the global MBT/CBT calibration using additional soil and lacustrine samples and improved chromatography (e.g. Peterse et al. 2012, De Jonge et al. 2014) and development of in situ calibrations based on the relative abundances of branched GDGTs or the MBT/CBT indices in lacustrine environments (e.g. Sun et al. (2011), Pearson et al. (2011), Loomis et al. (2012), Zink et al. (2010), Tierney et al.
The latter have the advantage of greatly reduced residual errors and thus more robust estimates of absolute (and relative) temperatures down-core. However, they require collection of soil or peat samples throughout a catchment and, ideally, sub-annually resolved sediment trap samples from the lake(s) in question. In remote regions, this can be prohibitively difficult or expensive, so, as in this case, a calibration must be selected from the published literature and extrapolated to the environment in question. Here, we apply the global lakes calibration of Sun et al. (2011) (see discussion):

$$MAAT = 3.949 - 5.593 \times CBT + 38.213 \times MBT'. \quad (3)$$

Lake El’gygytgyn is surrounded by permafrost with a shallow active layer (<0.5 m) and low concentrations of brGDGTs (Bischoff et al. 2013). Yet despite the small and barren watershed, brGDGTs are abundant in Lake El’gygytgyn sediments (D’Anjou et al. 2013). Several authors have found evidence for in situ production of brGDGTs within lakes, either within the water column or in the sediments themselves (Buckles et al. 2014, Loomis et al. 2014, Weber et al. 2015). Thus, we assume the brGDGTs at Lake El’gygytgyn to be produced in situ rather than washed in from the catchment.

In addition, Shanahan et al. (2013) found that MBT/CBT-derived temperatures inferred from lake sediments across Baffin Island reflected mean summer temperatures. At Lake El’gygytgyn, ice-cover for 10 months of the year restricts most primary production to the warmest months. Thus, we suspect that if brGDGTs are indeed produced within the lake, they will reflect warm season temperature (mean summer temperature, MST). For this study, we choose to apply the calibration of Sun et al. (2011). Sun et al. (2011) studied lakes on the arid Tibetan Plateau, representing some of the geographically closest samples that have been analyzed for brGDGT distributions.
In support of our assumptions, reconstructed MST from core-top (Holocene) sediments agree with pollen-based mean temperature of the warmest month (MTWM) estimates and observed summer temperatures (Brigham-Grette et al. (2013), unpublished data). Nevertheless, it is informative to consider multiple calibrations, especially considering that much work remains to be done to understand the sources of brGDGTs in lacustrine settings, and the sensitivity of brGDGT producing organisms within Lake El’gygytgyn to various environmental parameters (Fig. 7). Thus, recognizing the limitations of the current lacustrine brGDGT calibrations with respect to our dataset, the results presented here should not be interpreted in terms of absolute temperature. However, relative changes in temperature are robust.

2.3.3 n-alkane analysis

For n-alkane analyses, apolar fractions were first injected on an Agilent 7890A dual gas chromatograph-flame ionization detector (GC-FID) with two Agilent 7693 autosamplers equipped with 5 % phenyl methyl siloxane columns (HP-5, 60 m × 0.32 mm × 0.25 µm). The oven program ramped from 70°C to 130°C at a rate of 10°C min⁻¹, then ramped from 130°C to 320°C at a rate of 4°C min⁻¹, and held the final temperature for 10 min. Quantification was achieved via an external calibration curve of a sequence of squalane mixtures with concentrations ranging from 1 ng/µl to 100 ng/µl. N-alkanes were identified on the same samples by a Hewlett Packard 6890 gas chromatograph coupled to an Agilent 5973 Mass Selective Detector equipped with a 5 % phenyl methyl siloxane column (HP-5MS, 60 m × 0.25 mm × 0.25 µm), with an identical oven program to the GC-FID. Samples with sufficiently high n-alkane concentrations for isotope
analysis were separated into saturated and unsaturated fractions by elution over activated 
AgNO₃ columns with hexane (saturated fraction) and ethyl acetate (unsaturated fraction). 
Saturated fractions were dissolved in 100 µl of ethyl acetate, re-quantified by GC-FID, 
and re-dissolved in 3-30 µl ethyl acetate to achieve a concentration of 350 ng/µl for the 
C₂₉ n-alkane.

δD measurements were achieved by gas chromatograph - pyrolysis - isotope ratio 
mass spectrometry (GC-P-iRMS). A Thermo Trace GC Ultra equipped with a column 
was coupled to a reactor operated at 1450°C, which was connected to a Thermo Delta V 
Advantage iRMS. The oven program held 70°C for 2 minutes, ramped at 20°C min⁻¹ to 
145°C, then ramped at 4°C min⁻¹ to 320°C and held for 13 minutes. Molecular 
deuterium/hydrogen ratios are reported in δD notation relative to the Vienna Standard 
Mean Ocean Water (VSMOW) and calculated following Polissar and D’Andrea (2014). 
All samples were run in triplicate, and each instrument run began and ended with three 
injections of a lab internal standard and three injections of a standard mixture containing 
C₁₆ - C₃₀ n-alkanes (Schimmelman A5 standard) with known δD values ranging from -9 
to -254 ‰ versus VSMOW. Each sample run was bracketed by three injections of H₂ gas 
of known isotopic value. Instrument drift was corrected for when necessary by linearly 
interpolating the isotopic offset of the laboratory standard injected between each set of 
triplicate analyses.

n-alkanes are hydrocarbon chains that form the waxy surface of many terrestrial 
plant leaves, and can be short-chained (e.g. C₁₇, characteristic of aquatic organisms) or 
long-chained (e.g. C₃₃, diagnostic of terrestrial higher plants) (Eglinton and Hamilton, 
1967). n-alkanes are resistant to diagenesis over tens of millions of years (e.g. Andersen
et al. 2001) and common in sedimentary records (Peters 1993). Additionally, the deuterium to hydrogen ratio (D/H) of their chemical structure reflects the D/H of precipitation, which depends on the extent of Rayleigh distillation of a precipitating water mass (Dansgaard, 1964, Pierrehumbert, 2002). At high latitudes, $\delta^D$ is strongly correlated with temperature (Thomas et al. 2012, Pautler et al. 2014, Shanahan et al. 2013), and can thus provide a complementary measure to GDGT-based temperature reconstructions.

2.3.4 Biomarker analysis

After brGDGT analysis, half of the polar fractions of 67 samples were analyzed for $n$-alkanols, dinoflagellate sterols and stanols. These samples were derivatized using bistrimethylsilyltrifluoroacetamide (BSTFA) with acetonitrile as a catalyst (1:1, v:v) and held at 70ºC for 30 minutes prior to analysis by GC-FID and GC-MS. The instruments and oven programs for biomarker analysis are identical to those described in section 3.3. Compounds were identified by their characteristic mass fragmentation patterns and comparison with published literature (e.g. Peters 1993).

2.4 Results

2.4.1 BrGDGTs

2.4.1.1 Concentrations

Between 2.77 and 13.65 (median 5.89) grams of sediment ($g_{sed}$) were extracted for each sample, resulting in brGDGT concentrations ranging from 0.09 to 10.22 (median 1.45) $\mu g/g_{sed}$. Crenarchaeol concentrations ranged from 0.0007 to 3.82 (median 0.10) $\mu g/g_{sed}$ (Fig. 3). 69 samples were run in duplicate 5-8 months after the first injection.
The median of the absolute value (and range) of reproducibility for BIT, MBT, and CBT were 0.003 (-0.061 to 0.022), 0.005 (-0.025 to 0.027), and 0.017 (-0.18 to 0.023), respectively (Fig. 5). The median (and range) differences in MBT and CBT between injections represent analytical uncertainty and translate to MAAT uncertainties of -0.1°C (-0.1 to 1.0) and 0.2°C (-1.0 to 1.0), respectively.

All nine brGDGTs were present in all samples analyzed (Figure 6). 12 samples have exceptionally high fractional abundances of brGDGT Ib ranging from 0.16 to 0.56 (Fig. 6). These samples occur between 2650 and 2661 kyr, with peak abundances of Ib occurring at 2656 kyr. The median (and range) of concentrations for these twelve samples is 5.49 (3.94 to 6.91) µg/gsed, representing some of the highest in the dataset. These samples systematically had the worst reproducibility, with differences in MAAT of up to 1.94°C. This is much higher than the standard lab accuracy of the HPLC-MS, and >3 standard deviations outside the replicate error for other samples. These 12 samples are discussed directly in Section 5.7.

2.4.1.2 Paleoclimate Reconstruction: MIS G3-G11, 2.82-2.65 Ma

MIS G10 and G11 are seen in pollen (MTWM) and brGDGT (MST) records as a ∼4°C amplitude temperature change, corresponding to a 0.5 ‰ change in benthic oxygen isotopes (Fig. 9). MIS G8 and G9 are distinct in the pollen and MBT/CBT reconstructions, in contrast with a plateau in benthic oxygen isotopes. However, MIS G7 is a mild interglacial in the MBT/CBT and pollen records, in contrast with the exceptionally low values of the benthic oxygen isotope stack. Glacial stage G6, corresponding to the first major excursion of the benthic oxygen isotope stack (∼1 ‰)
and iNHG, appears in our record as an exceptionally cold glacial with one sample indicating a temperature decrease of 10°C. This transition is also marked in the pollen record by a change from \(\sim13ºC\) at G7 to \(\sim9ºC\) at G6. Both records are in-phase with the sharp increase in benthic oxygen isotope values across iNHG.

MIS G9 has high percentages of Pinus and Picea pollen, indicating dense forest cover around the lake, which is common in the earlier part of the record (Andreev et al. 2014) and implies that the treeline extended to the Arctic Ocean. Pollen biome reconstruction indicates high precipitation (500 mm/yr) during this time (Brigham-Grette et al. 2013). The pollen assemblage changes little between G9 and G7, indicating stable conditions, as reconstructed by both temperature proxies and the precipitation reconstruction (Andreev et al. 2014). The later parts of G9 and G7 also appear as Facies “C,” and coincide with increases in aquatic biomarkers dinosterol and dinostanol, and a suite of \(n\)-alkanols, otherwise, biomarker concentrations are low during this interval (Fig. 9). A sharp decrease in precipitation and MST, and a gradual decline in MAAT, occurs at the end of MIS G7. Biomarker concentrations are low through MIS G6, and the percentage of tree and shrub species crashes, with the new assemblage suggesting tundra-like conditions at the lake. Pollen concentrations and average chain length (Fig. 8) are also exceptionally low during this interval, further substantiating the disappearance of woody vegetation from the catchment during G6 (Andreev et al. 2014).

Both MST and MAAT temperature reconstructions are steady through MIS G4 and G5 at near-glacial values \(\sim9ºC\) (Fig. 9). However, there is evidence for two discrete periods of warmth during this time, substantiated by increases in MST/MAAT, increases in precipitation, and pollen spectra changes (Fig. 9). The progression from \textit{Betula-Alnus-}
Pinus/Picea/Larix indicates deciduous forest returning to the catchment and, especially when Picea and Larix are present, the re-advance of the treeline into the catchment (Andreev et al. 2014). This progression is seen clearly for the first time at MIS G5 (Fig. 9), and is repeated at MIS G4 and MIS G3. The brief interglacial MIS G3 is punctuated by a period of extreme warmth in our record, driven by brGDGT distributions unlike anything seen in modern calibration studies (e.g. Peterse et al. 2012). 12 samples spanning ~12 kyr showing elevated temperatures (18-34°C). These sediments correspond to another brief appearance of super-interglacial Facies “C,” high-precipitation conditions at the lake, and pollen assemblages similar to those seen earlier in the Pliocene, with Pinus-Picea-Larix dominated dense forest. Andreev et al. (2014) found exceptionally high concentrations of pollen grains in this interval and inferred that conditions were much warmer and wetter between 2.665-2.646 Ma. Aquatic and terrestrial biomarker concentrations are high during this interval, but there is no substantial change in n-alkane concentrations or average chain length (Fig. 8).

2.4.1.3 Paleoclimate Reconstruction: MIS 100-G2, 2.65-2.55 Ma

Glacial-interglacial variability is muted between 2.65-2.55 Ma (Fig. 10). Both temperature reconstructions indicate little change during MIS G2, though the disappearance of Picea and Pinus suggests cooling, opening and drying of the forested landscape (Tarasov et al. 2013). Facies “C” appears during MIS G1, but neither temperature reconstruction shows much change during this period. Yet, the pollen spectrum shows a modest re-advance of the treeline, with some Picea and Larix toward the end of the interval, when MST indicates a warming of ~4°C (Fig. 10). A subsequent
cooling of \( \sim 5^\circ C \) in the MBT/CBT record culminates in the first appearance of glacial facies “A,” although the MTWM shows little change during this time (Brigham-Grette et al. 2013). In general, pollen spectra and reconstructed MTWM during MIS 104-101 are remarkably stable, showing little temperature change and a stabilization of pollen distributions with few trees and shrubs (Fig. 10, Andreev et al. 2014). MST indicates a cooling of \( \sim 4^\circ C \) into glacial stage 102, where there is also a lone peak in Pinus pollen, though unaccompanied by the usual pollen progression indicating a return of a more forested biome (Andreev et al. 2014). Because Pinus pumila (whose pollen is not differentiable from other types of Pinus; Andreev et al. (2014)) requires deep snow to survive the winter, this isolated peak may suggest an increase in winter precipitation during this time. The muted temperature variability during these stages contrasts with moderate swings in benthic \( \delta^{18}O \). On the other hand, biomarker records indicate higher concentrations of aquatic biomarkers during interglacial stages, though these are not strongly correlated with reconstructed temperatures from the same samples. In contrast to \( n \)-alkanols and dinoflagellate sterols, \( n \)-alkanes show higher concentrations during glacial stages and low concentrations during interglacial periods (Fig. 10).

### 2.4.1.4 Paleoclimate Reconstruction: MIS 95-99, 2.55-2.4 Ma

MIS 99, 97, and 95 show strong glacial-interglacial cycles in MST and MAAT. MST across MIS 100 shows high-frequency temperature variability superimposed on a modest cooling; the MTWM temperatures, in contrast, show one discrete cold interval between two warmer, more stable interglacials (Fig. 11). MIS 99 is a modest interglacial in both reconstructions, but after this stage, the amplitude of glacial-interglacial change
begins to increase, with large changes \( \sim 6-8^\circ \text{C} \) in both temperature proxies. The appearance of glacial facies “A” at MIS 98 coincides with the lowest reconstructed temperatures for that interval, and two discrete appearances of glacial facies “A” during MIS 96 perhaps substantiate the multiple periods of cooling seen in MST (Fig. 11). Intriguingly, save for the exceptional warmth in MIS G3, interglacials 95 and 97 show warmer temperatures than the Late Pliocene (Fig. 9).

2.4.2 \textit{N}-alkanes

2.4.2.1 Concentrations

\textit{N}-alkanes are particularly abundant biomarkers in the samples studied. Chain lengths range from C\textsubscript{21} to C\textsubscript{35}. An odd-over-even predominance is seen in all samples, but \textit{n}-alkane distributions, as described by ACL, are variable. ACL varies between 29 and 26, or between 30 and 29 if only long chain-lengths are considered (ACL\textsubscript{27–33}). The ACL also shows higher-frequency variability. Variability is superimposed on a decreasing trend, from an ACL of 29 at 2.8 Ma to 27 at 2.4 Ma. ACL\textsubscript{27–33} shows the sample pattern (Fig. 8), with a decrease in average chain length through the Plio-Pleistocene. The variability in both records is more difficult to interpret, as there are multiple peaks in each glacial and interglacial stage that are not well-correlated with changes in local insolation or pollen changes. Although ACL and ACL\textsubscript{27–33} show no significant correlations with insolation or the benthic oxygen isotope stack, concentrations of long-chain \textit{n}-alkanes (here the sum of C\textsubscript{27}, C\textsubscript{29}, C\textsubscript{31}, and C\textsubscript{33}) are negatively correlated with mean July insolation \( (r^2=0.22, p<0.001, n=163) \). This correlation is not observed for short-chain (i.e. C\textsubscript{21}) \textit{n}-alkanes.
2.4.2.2 δD

We focus our δD analysis on C₂₉ and C₃₁ n-alkanes, which are generally derived from terrestrial plants at Lake El’gygytgyn (Holland et al. 2013). Concentrations of the C₂₉ and C₃₁ n-alkanes range from 0.16 to 4.73 µg/g_{sed} and 0.16 to 5.58 µg/g_{sed}, respectively. For δD analysis, a concentration of 0.35 µg/µl for the C₂₉ n-alkane was achieved by dissolving the purified n-alkanes in 5-30 µl of ethyl acetate.

~50 samples were prepared and run in triplicate for δD analysis. Analytical error was propagated following Polissar and D’Andrea (2014), resulting in a standard analytical error of ~5‰ (Figure 13). From 2.82-2.7 Ma, δD values are stable. Following iNHG at ~2.7 Ma, δD values vary from -290 to -250 ‰. δD values show a general trend of more positive values during interglacial stages and more negative values during glacial stages after 2.7 Ma.

2.4.3 Biomarker Analysis

Dinoflagellate-specific biomarkers dinosterol and dinostanol were present in many samples, and the sum of these is shown in Fig. 9, 10, and 11. Concentrations range from below detection limit to 0.82 µg/g_{sed} for dinosterol and below detection limit to 4.07 µg/g_{sed} for dinostanol, and up to 4.99 µg/g_{sed} for the summed compounds (Fig. 8). Significant correlation with the LR04 stack indicates that higher concentrations of summed dinoflagellate sterols occur during interglacial periods (r²=0.25, p<0.001, n=67). n-alkanols were also present and abundant in many sediments, ranging from C₂₂ to C₂₈, with a dramatic dominance of even chain lengths. Previous work demonstrates that these
$n$-alkanols represent a mix of terrestrial and aquatic sources at Lake El’gygytgyn (Holland et al. 2013), complicating their interpretation as biomarkers. Concentrations of even $n$-alkanols range from 1.05 to 9.97 $\mu$g/g_sed and are consistently higher during interglacial periods in our record, with notable exceptions during MIS 99 (low concentrations during an interglacial) and MIS 102 (low concentrations during a mild glacial).

2.5 Discussion

The Lake El’gygytgyn terrestrial sequence documenting the transition of high northern latitudes from the warm Pliocene into the frequently glaciated Pleistocene is the first of its kind. Our application of the MBT/CBT paleotemperature proxy corroborates past work, showing clear glacial-interglacial variability during the early Pleistocene (Fig. 12), documenting clear, predictable response of the Lake El’gygytgyn brGDGT-producing organisms to glacial-interglacial variability (e.g. MIS 95-99). In the earlier part of the record, inferred temperatures are variable but less well-correlated with other records of global change (e.g. MIS 100, G2). Comparison with terrestrial vegetation records (pollen and $n$-alkanes) reveals that across the Plio-Pleistocene transition, numerous proxies show an unexpected yet coherent response.

2.5.1 Age model considerations

Differences in the age models between records can introduce significant uncertainties when trying to link climatic changes across records. Although the age model of the Lake El’gygytgyn core has been tuned to the benthic $\delta^{18}$O isotope stack of Lisiecki and Raymo (2005), there is at least one significant difference between the two
records for the interval in question, based on the age assignment of magnetic reversals. Lisiecki and Raymo (2005) use an age of 2.608 Ma for the Matuyama/Gauss reversal corresponding to the glacial MIS 104, whereas Nowaczyk et al. (2013) use an age of 2.588 Ma, placing the reversal in the interglacial MIS 103. Thus, discrepancies between the two records around this time may be expected. For other time periods the ages of climatic transitions between the two records should not differ greatly, nor should our reconstructions differ from other parameters measured on the Lake El’gygytgyn sediments, as we apply the same, published age model (Nowaczyk et al. 2013). This is qualitatively confirmed by the agreement between our biomarker records and other published records of paleoproductivity (e.g. biogenic silica), which show a strong correlation (Gebhardt et al. 2013) (Fig. 3).

2.5.2 Production, preservation and normalization of biomarker records

Only a small portion of the organic matter produced by living organisms makes it into the sedimentary records. In lacustrine environments, the amount of organic matter settling on the lake floor is controlled by: the delivery of organic matter to the system by in situ production and fluvial or aeolian delivery; remineralisation within the water-column; and redox conditions at the lake-bottom (Bianchi and Canuel, 2011). Once deposited, sediments can be re-worked by undercurrents, mixed by bioturbation, or disturbed by mass movements (Bianchi and Canuel, 2011). Biomarker records reflect the combined influence of all these processes. An ideal biomarker record tracks solely changes in the production of an organic compound, which can be achieved by normalizing to a dataset that reflects the preservation of organic matter.
Distinguishing between production and preservation of organic matter is quantitatively difficult, but it can be sedimentologically and geochemically constrained. Because preservation is enhanced during periods of bottom-water anoxia, when bioturbation is low, laminated Facies can be assumed to also have enhanced preservation relative to non-laminated Facies. Three distinct Facies occur at Lake El’gygytgyn (Gebhardt et al. 2013). Facies “A” is a glacial Facies, first occurring at 2.6 Ma, characterized by gray to black finely laminated sediments and low magnetic susceptibility values, suggesting complete and persistent bottom-water anoxia and year-round ice-cover (Gebhardt et al. 2013, Brigham-Grette et al. 2013). Facies “B” is an interglacial Facies, representing most of the record in question, characterized by brownish massive sediments and high magnetic susceptibility, reflecting complete water-column oxygenation (Gebhardt et al. 2013; Brigham-Grette et al. 2013). Facies “C” contains reddish-brown finely laminated Facies and is associated with especially intense interglacial intervals, termed “super interglacials” at Lake El’gygytgyn (Gebhardt et al. 2013, Brigham-Grette et al. 2013). Super interglacials were characterized by high productivity and (at least) seasonal anoxia, resulting in the deposition of high-TOC, laminated sediments (Melles et al. 2012, 2006). Thus, the sedimentology can guide general assumptions about the character of organic matter in the sediments: Facies “C” will have high production and high preservation of OM; Facies “B” will have moderate production and low preservation of OM; and Facies “A” will have low production and high preservation of OM.

There are also geochemical methods for qualitatively distinguishing sources of production and the extent of preservation. Normalizing silica, which is produced mainly
by diatoms and has few terrestrial sources, to titanium, which is primarily derived from landscape erosion, can provide a way to track terrestrial and in situ contributions to sedimentation (Si/Ti). However, this is a qualitative indicator and cannot be used to normalize biomarker records, only guide interpretations. In some lakes, TOC (%) can reflect in-lake primary productivity, but this can also be influenced by terrestrial carbon sources and changes in preservation (Bianchi and Canuel, 2011). For the time period in question, TOC varies between 0 and 2 %, with higher values generally during interglacial periods (Melles et al. 2012) associated with Facies B. However, there are clear increases in TOC associated with Facies A and C, implying that the TOC record reflects both production and preservation of OM. In addition, changes in sedimentation rate (e.g. more clastic input) can influence TOC. As an alternative to TOC, biomarker amounts can be normalized to grams of sediment extracted ($\mu$g g$_{sed}^{-1}$), dry bulk density of the sediments (g cm$^{-3}$), and linear sedimentation rate (cm ka$^{-1}$) to produce a record of mass accumulation rate ($\mu$g cm$^{-2}$ ka$^{-1}$), which accounts for variability in sedimentation and sampling. However, this cannot directly account for changes in preservation. For this record, normalizing to MAR introduces two large spikes in the record, due to large excursions in sedimentation rate around 2.45 and 2.7 Ma (Fig. 3). While different normalizations slightly change the character of the time-series analyzed here, the general trends are robust for all normalizations (Fig. 3).

An additional method for differentiating allochthonous and autochthonous input in an aquatic setting was proposed using the BIT index, which traces the abundance of brGDGTs relative to crenarchaeol (Hopmans et al. 2004). However, it is now accepted that the BIT index is of little utility in lacustrine systems, where brGDGTs can be
produced within the water column and crenarchaeol can be washed in from the catchment (Castañeda and Schouten, 2011). The BIT record for our study shows large excursions, driven by changes in the concentration of both brGDGTs and crenarchaeol (Fig. 5). Without additional studies on Lake El’gygytgyn and the surrounding watershed, it is unclear what these variations represent.

2.5.3 brGDGTs

Although the distribution of branched GDGTs globally is strongly correlated with both mean annual temperature and pH, the calibration between MBT, CBT, and MAAT varies spatially. Because sufficient data to make a local calibration for Lake El’gygytgyn do not exist, we applied the calibration of Sun et al. (2011) to reconstruct summer temperatures (MST) at Lake E, as discussed previously (section 3.2). As long as changes in mean summer temperatures track changes in mean annual temperatures, and the seasonality of production does not vary, this interpretation is defensible.

BrGDGTs lose their polar headgroups relatively rapidly after deposition, but the core lipids can persist, unaltered, for millions of years (Weijers et al. 2007). This is clear from brGDGT concentrations measured on the sediments in this study (median: 1.45 \( \mu g/g_{sed} \)) compared to more recent sediments from the lake (median: 0.2\( \mu g/g_{sed} \) for MIS 9-11, D’Anjou et al. (2013)). BrGDGT concentrations are closely correlated to changes in the concentration of crenarchaeol ($r^2=0.49$, $p<0.001$, n=163). Crenarchaeol is a biomarker for the aquatic Thaumarchaeota (Pitcher et al. 2009), but has been measured in high concentrations in some arid soils (Dirghangi et al. 2013). Thus the covariance of these two proxies may simply reflect increased terrestrial input to the lake rather than
higher productivity. However, brGDGT concentrations are also highly correlated with biogenic silica accumulation rate, a proxy for diatom productivity \((r^2=0.31, p<0.001, n=163)\) (Fig. 3) (Meyer-Jacob et al. 2014). Normalizing to mass accumulation rate of brGDGTs yields a similar result (Figure 3). Together, this suggests that (presumably) bacterial, archael, and eukaryotic communities are responding similarly to environmental conditions in the catchment on glacial-interglacial timescales, with higher productivity associated with warm interglacial periods (Fig. 3).

### 2.5.4 MAAT Reconstruction

Reconstructed summer temperatures range from 0-30°C using the calibration of Sun et al. (2011). Other calibrations give different absolute temperature estimates and magnitudes of glacial-interglacial change (Fig. 7), but the brGDGT distributions in this study span a wide range of MBT/CBT values, resulting in high temperature variability on six published calibrations ((Weijers et al. 2007, Peterse et al. 2012, Loomis et al. 2012, Tierney et al. 2010, Sun et al. 2011, Zink et al. 2010)). The reconstruction spans nine warm interglacial periods (marine isotope stages (MIS) 95, 97, 99, 101, 103, G1, G3, G5, and G7). Here we are interested in the general character of glacial-interglacial transitions at Lake E, how they relate in amplitude to one another, and the character of the Plio-Pleistocene transition, all of which are robust regardless of the calibration applied (Fig. 7).

It is firstly instructive to consider the correlation between the global benthic oxygen isotope record and our MBT/CBT based reconstruction. For 2.4-2.5 Ma, the records are positively correlated \((r^2=0.42, p<0.001, n=38)\). From 2.5-2.7 Ma, the two
records are not significantly correlated ($r^2=0.01$, $p=0.85$, $n=71$). Between 2.7-2.82 Ma, the records are again strongly correlated ($r^2=0.33$, $p<0.001$, $n=49$). A significant cooling ($\sim10^\circ C$) occurs across the Plio-Pleistocene transition, beginning at 2.74 Ma and ending at 2.72 Ma. These results are in agreement with previously published pollen-based biome reconstructions (Andreev et al. 2014). The correlation between pollen-based temperatures and brGDGT-based temperatures is significant throughout the record ($r^2=0.20$, $p<0.001$, $n=175$), and especially strong during the period when brGDGT-based temperatures are not well correlated with the LR04 record (2.6-2.7 Ma; $r^2=0.50$, $p<0.001$, $n=45$).

Facies change generally supports our temperature reconstructions. Previous modeling work demonstrates that a mean annual temperature reduction of $\sim4^\circ C$ is required to produce year-round ice cover at the lake, resulting in bottom water deoxygenation and the formation of glacial Facies “A” (Nolan and Brigham-Grette, 2006). The MBT/CBT reconstructed temperatures show reductions of at least 4$^\circ C$ before the occurrence of Facies “A” at three points in our record and for multiple calibrations (Fig. 7) (MIS 96, 98, and 104); the pollen reconstructed temperatures show a similar change for the most recent two occurrences, and little change for the third occurrence, during MIS 104. Thus, we find independent support from two proxies for this modeled threshold. However, there are numerous temperature decreases in our record (e.g. MIS G6) where Facies A is not observed. These may correspond to times when there was less annual ice cover, and the same magnitude temperature trop did not cross the permanent ice-cover threshold of (Nolan and Brigham-Grette, 2006). The relationship between temperature and Facies changes illustrates that the boundary condition of ice-cover at Lake El’gygytgyn has probably changed through time, which may undermine
assumptions about the production of brGDGTs. Although the reconstructed amplitude of temperature change from both pollen and brGDGTs is uncertain, these results suggest that the previous posited threshold for permanent lake-ice cover was not present for all of geologic time, and the first occurrence of Facies A at MIS 104 may indicate an increased sensitivity of the lake to climatic changes after this time.

Facies “C,” which occurs during the “super interglacials” of the Pleistocene, appears four times in our record. The first is during MIS G1, which is delayed by ~10kyr in the pollen and MBT/CBT records relative to the benthic oxygen isotope stack (Fig. 10). The second occurrence is MIS G3, which is characterized by high fractional abundances of brGDGT 1b, extremely warm reconstructed temperatures in our MBT/CBT record, and the recurrence of Picea pollen. The third and fourth occur during MIS G7 and G9, which are only moderately warm in the pollen and MBT/CBT records, and are cooler than later interglacials (e.g. MIS 95) which do now show Facies “C.” Thus, the mechanism for producing Facies “C” may not be solely based on warmth, and the character of “super interglacials” is highly variable: for instance, we observe delayed (MIS G1), extreme (MIS G3), and mild warmth (MIS G7, G9) all associated with Facies “C.” As Facies “C” is associated with high productivity and eutrophication, it may also appear during periods of increased nutrient delivery to the lake.

2.5.5 n-alkanes

Long-chain n-alkane concentrations are poorly correlated to the LR04 record, but indicate increased production during local insolation minima. For one interval, n-alkane concentrations are significantly correlated with the LR04 record, with higher
concentrations during cold glacial periods (e.g. 2.57-2.67 Ma, $r^2=0.26$, p<0.001, n=41). Otherwise, long-chain $n$-alkane concentrations seem to vary independently of glacial-interglacial changes and reconstructed temperatures (MST or MAAT). Average chain length (ACL) utilizing both the full range of measured $n$-alkanes and a limited range (Fig. 8) shows a decreasing trend through our record, which previous studies have associated with warmer and/or more arid conditions (e.g. Hughen et al. 2004). Interestingly, there are no strong correlations between ACL and both MAAT and MST. This suggests that aridity may play a more important role than temperature for driving $n$-alkane distributions within the catchment. This contrasts with findings from other periods at Lake El’gygytgyn. For example, Wilkie et al. (2013) found higher ACL during warm periods of the last 120 ka, and D’Anjou et al. (2013) found no significant relationship between ACL and temperature across MIS 9-11.

The rather chaotic variations in long-chain $n$-alkane concentrations are surprising, and indicate a complex vegetation response to environmental change across the Pliocene-Pleistocene transition. Although this is in keeping with the “stepped” transition from the Pliocene recorded by pollen and other proxies at Lake El’gygytgyn (Brigham-Grette et al. 2013), it is unexpected given the coherent response between bacterial, archaeal, and eukaryotic biomarkers described above.

The $\delta D$ of $C_{29}$ $n$-alkanes ($\delta D_{wax}$) supports MBT/CBT temperature reconstructions, especially in the interval 2.55-2.41 Ma (Fig. 13). $\delta D_{wax}$ variations indicate more isotopically enriched precipitation during interglacial intervals, and more depleted precipitation during glacial intervals (Fig. 14). Using the empirical relationship for the Yukon derived by Dansgaard (1964), a change of 30‰, as seen for glacial-interglacial
transitions during the interval 2.55-2.41 Ma, would correspond to a change in MAAT of 5-6°C, in keeping with MBT/CBT estimates (Fig. 14). Prior to 2.7 Ma, δD shows relatively little change, implying that the fractionation between source water and plant lipids was different during this time (Feakins and Sessions, 2010) or overprinting of the temperature signal from a moisture-source effect (Dansgaard 1964). Further work necessary to integrate the δDwax results into the paleoclimate reconstruction are outlined in Chapter 3.

2.5.6 Sea-level records, exposure of the Bering land bridge and sea-ice changes

Interpreting climatic changes in the Arctic across the Pliocene-Pleistocene transition is tricky, because many components of the climate system were in flux during this time. Although sea level was ∼20 ± 10 m at the peak of Pliocene warmth, sea level drops of ∼30 m occurred throughout the Pliocene, with increased amplitude (∼80-100 m) after iNHG (Röhling et al. 2014) (Fig. 12). The shallow Bering land bridge, which at present permits exchange of water masses between the Arctic and North Pacific ocean basins, would have restricted flow between the basins were sea level to drop 50 m below present. Substantial complications arise when one considers the potential effects of glacial isostatic adjustment (GIA) on relative sea level across Beringia. For example, the sea-level change associated with just the southern third of the Laurentide Ice Sheet across the Bering Strait is only ∼75 % of the ice-sheet’s global eustatic effect, due to the increased gravitational pull of the ice-sheet itself (Clark et al. 2002). Records from the last deglaciation imply that the local sea-level curve is identical to the global cure, e.g. no GIA effect due to the Laurentide Ice Sheet. However, this interpretation is severely data-
limited and subject to large uncertainties in radiocarbon reservoir age (Keigwin et al. 2006).

Prior to iNHG, it is assumed that most of the global eustatic sea-level variations were driven by changes in Antarctic ice volume (DeConto et al. 2008). Around \( \sim 2.7 \) Ma, as the Northern Hemisphere began to glaciate, Greenland was probably the first landmass to host an ice-sheet (DeConto et al. 2008). Some workers have suggested that North America did not host continental ice until at least \( \sim 2.64 \) Ma (Bailey et al. 2013). Although ice-volume changes in Greenland and Antarctica would be fully felt at the Bering Strait, high-latitude ice masses closer to the region would have a muted effect on local sea level there (e.g. Niessen et al. 2013). Thus, depending on the nucleation location of ice sheets during the Plio-Pleistocene, the effect on ocean circulation could be different.

Another component of the high-latitude climate system that underwent a dramatic transition during our period of interest is sea-ice (Knies et al. 2014). Unfortunately, Arctic sea-ice records across the Plio-Pleistocene lack the resolution to explore changes on glacial-interglacial timescales pertinent to this study. Certainly, by 2.5 Ma, sea-ice extent similar to the present day was possible, which in turn likely caused a dramatic reduction in the precipitable moisture during summer months (Knies et al. 2014). Indeed, pollen-based biome reconstructions at Lake El’gygytgyn show a dramatic decrease in mean annual precipitation at 2.7 Ma (Brigham-Grette et al. 2013).

Reconstructed \( p\text{CO}_2 \) through the Plio-Pleistocene transition lacks the resolution to assess the change in \( p\text{CO}_2 \) forcing for each glacial and interglacial stage, but there are some interesting characteristics to note (Martínez-Botí et al. 2015). The largest excursion
in the $p$CO$_2$ record occurs across iNHG, with $p$CO$_2$ dropping from $\sim$350 ppmv at MIS G7 to $\sim$250 ppmv at MIS G6, an interval across which we observe a $\sim$12 $^\circ$C cooling and coinciding with stratification of the North Pacific and an increase in ice-raftered debris in the North Atlantic (Lawrence et al. 2009, Fig. 12). During the period when our record is poorly correlated with the benthic oxygen isotope stack, $p$CO$_2$ shows muted variability, asynchronous with changes in benthic oxygen isotopes (Martínez-Botí et al. 2015). The resolution of the $p$CO$_2$ record is inadequate to assess the amplitude of $p$CO$_2$ forcing for MIS 95-99, which are the largest amplitude in our record and most coherent with changes in the benthic $\delta^{18}$O (Fig. 8). Similarly, the excursion in temperatures during MIS G3 is not sampled in the $p$CO$_2$ reconstruction, and cannot be confidently attributed to another known change in climate forcing, further questioning the validity of interpreting this excursion solely in terms of temperature.

Although insolation is also an important forcing of high-latitude climate change, our temperature records do not show a strong influence of insolation on the proxies of interest. In fact, during the time when the most temperature variability is observed (MIS 95-99), the changes in insolation are negligible. Yet, decreases in insolation are significantly correlated with increases in the concentration of long-chain $n$-alkanes, suggesting vegetation response to insolation at some scale. Ongoing work to increase the resolution of biome reconstructions across this interval (Anderson, pers. comm.) will make this possible in the future.

As our record shows, high latitude environmental change across the Plio-Pleistocene transition was complex and occurred in a series of steps. Yet, new biomarker records provide an opportunity to link some existing records of global change across this
interval and better characterize the mechanisms of climatic change active during this time. High precipitation in the Late Pliocene, as well as abundant *Pinus*, *Picea*, and *Larix* pollen argue for restricted seasonal sea-ice, which would have provided the high-latitude moisture source necessary for supporting this ecosystem (Brigham-Grette et al. 2013). Our record of temperature change shows a sharp cooling across iNHG, with a coincident drop in precipitation and dramatic deforestation. This would be consistent with the expansion of sea-ice and exposure of the Bering Land Bridge, resulting in a transition to a very arid continental climate at Lake E (e.g. Barr and Clark 2010). $pCO_2$ reconstructions support this, with $pCO_2$ falling to $\sim 240$ ppmv during this interval, well below the threshold for Northern Hemisphere glaciation. In contrast, sea level records are equivocal about the transition, with some records indicating a drop of $\sim 50$ m from the mean Pliocene highstand (Wang et al. 2010) and others indicating little change (Naish et al. 2009). During MIS G5-101, sea level records show little change, indicating that most of the variability in benthic oxygen isotopes is attributable to deep-ocean temperature change. Our temperature reconstructions generally show muted variability during this time. Although the veracity of reconstructed temperatures for MIS G3 is sketchy (see below), the return of *Picea* pollen during this interval reflects a re-advance of the treeline and increase in precipitation, potentially detailing an interval of sea-ice retreat. After this event, *Picea* is absent from the record and reconstructed precipitation remains low, arguing for the establishment of modern sea-ice conditions around 2.6 Ma. This contrasts with the findings of (Haug et al. 2005), who argued for an increase in precipitable moisture to the Northern Hemisphere at $\sim 2.7$ Ma. However, these findings may be consistent given the average circulation in the region (Mock et al. 1998, Bromwich et al.)
2004). Air masses advect over Lake El’gygytgyn primarily from the North during the summer, and so would have become arid following the expanding Arctic sea ice (Knies et al. 2014). Air masses advecting over the North Pacific primarily precipitate over North America, so ice accumulation in the winter months would be expected to take place on that continent following the oceanographic changes inferred by Haug et al. (2005).

In contrast, temperature reconstructions for MIS 99-95 show high-amplitude variability, in-sync with changes in benthic oxygen isotopes. At the same time, sea-level records show departures from the Pliocene mean sea-level during the intervening glacial stages, large enough in magnitude to cause the closure of the Bering Strait (Miller et al. 2005, Naish et al. 2009, Wang et al. 2010). Increased temperature change at the high latitudes for these glacial stages relative to others in the record is consistent with a strong ice-albedo feedback, due to the growth and decay of ice sheets on land. $pCO_2$ reconstructions, in contrast, are above the threshold for Northern Hemisphere glaciation during much of this time (Martinez-Botí et al. 2015). These highly resolved records now allow us to suggest that the close synchronicity between different components of the climate system observed for the last few glacial cycles (Augustin et al. 2004) did not develop instantaneously upon glaciation of the Northern Hemisphere.

Our results can be summarized as follows: a change in the seasonality of precipitation occurred a 2.7 Ma, owing to both secular changes in sea-ice extent and an abrupt change in North Pacific stratification. An open Arctic ocean at this time would have provided substantial moisture to summer precipitation systems, which bring air from the Arctic Ocean basin across the lake. As the sea-ice margin advanced from 3.0-2.5 Ma, this precipitation source would have been significantly restricted, leading to the dramatic
changes in Arctic biome distribution (e.g. retreat of the tree-line from the Arctic ocean margin) inferred from the Lake El’gygytgyn pollen record at 2.7 Ma (Brigham-Grette et al. 2013, Knies et al. 2014). The warming of North Pacific surface waters by 7-9ºC in late fall (Haug et al. 2005) would have provided a new moisture source for the Northern Hemisphere, which, when advected over the cool continental interior of eastern Beringia, led to the accumulation of ice. The modern-day presence of the Aleutian Low and Siberian high pressure systems dictates that most moisture evaporated from the North Pacific is advected first over Eastern Beringia and the Chukchi Sea, returning to Western Beringia as a south-westerly, arid flow (Mock et al. 1998). Thus, moisture from the warming North Pacific would likely not have reached Western Beringia and Lake El’gygytgyn (consistent with reconstructed aridity there (Brigham-Grette et al. 2013)), instead raining out preferentially over Eastern Beringia. The closure of the Bering Strait during intervening glacial periods would have caused a more sensitive overturning circulation in the North Atlantic (Hu et al. 2012), resulting in variable heat transport from the tropics to the Northern Hemisphere. We find evidence for increase glacial-interglacial temperature cycling during MIS 99-95, consistent with a strong ice-albedo feedback from the accumulation of ice on land, southerly retreat of low-albedo forest biomes, and stable sea-ice cover. This may help explain the abrupt climate changes recorded during early Pleistocene glacial cycles seen in tropical and sub-tropical records (Bolton et al. 2010, Becker et al. 2005, Wilson et al. 2014), because a closed Bering Strait decreases the stability of North Atlantic overturning (Hu et al. 2012). After a major glaciation at 2.7 Ma, sea-ice, land-ice, and vegetation were in transition, resulting in a variable response with transient periods of increased warmth and precipitation. However, by ~2.55 Ma,
positive feedbacks related to each of these climate system components were synchronized, resulting in the strong glacial-interglacial variability seen in multiple independent temperature proxies from Lake El’gygytgyn.

2.5.7 A 2.65 Ma event?

During MIS G3, the MBT/CBT proxy reconstructs astronomical mean annual air temperatures, occurring in a sharp but distinct “spike” with a ~15 kyr duration. Other proxies (\(n\)-alkane concentrations and ACL, \(n\)-alkanols and dinoflagellate sterols) do not change remarkably during this interval, although concentrations of branched and isoprenoidal brGDGTs reach their highest values. The lack of multi-proxy agreement suggests that this interval could represent a period of change in the microbial community responsible for producing GDGTs at Lake El’gygytgyn. For instance, an increase in methanogenesis and/or methanotrophy could have caused a new community of bacteria to flourish, overprinting the GDGT temperature signal and resulting in misleading reconstructions. Future analysis will focus on these anomalous samples.

It is possible that a coeluting compound (i.e. not a brGDGT) is present in these samples and spuriously influencing temperature estimates. A recently published new method for improved chromatographic separation of brGDGTs (De Jonge et al. 2014) may help clarify this. Alternatively, a number of new brGDGT isomers have recently been identified, one of which may be exclusive to lacustrine sediments (Weber et al. 2015). Although the chromatograms for samples during the 2.65 Ma do not seem to comprise multiple coeluting isomers (which appear as “humped” peaks), better chromatographic separation will also reveal the presence of these. Removal of the 1b
signal from these samples results in warm interglacial temperatures, of similar magnitude to other interglacials (Fig. 5).

One intriguing fact is the reoccurrence of *Picea* pollen corresponding precisely to the interval where we find elevated temperatures. In the pollen-biome reconstructions, the return of *Picea* indicates a substantial increase in mean annual precipitation, from ~200 mm/yr characteristic of the Pleistocene and Holocene, to ~600 mm/yr, more characteristic of peak Pliocene conditions (Brigham-Grette et al. 2013). Indeed, the progression of pollen species demonstrates that the treeline re-advanced from a presumably southerly position during this time, culminating in a probable reoccupation of the circum-arctic ocean by *Picea-Pinus-Larix* forests (Andreev et al. 2014). The occurrence of Facies “C” at this time argues against a re-worked or bioturbated signal, and instead implies that a climatic event drove a profound environmental change occurring over ~15 kyr at Lake El’gygytgyn. Indeed, other workers have found evidence for extreme climatic shifts following iNHG. Funder et al. (2004) describe a late Pliocene terrestrial sequence (ca. ~2.4-2.5 Ma) from Northeast Greenland that implies a 40m marine transgression and summer warming in excess of 15°C at that site. This suggests near-complete deglaciation of the Northern Hemisphere and the return of Pliocene-like conditions to the circum-Arctic. Intriguingly, the duration of the event they describe (10-20 kyr), as well as the progression of pollen species from broad-leaf shrubs (e.g. *Betula* and *Alnus*) to spruce forests (*Picea*) is similar to the climatic change we infer at MIS G3.

The potential for extreme warmth and rapid deglaciation following iNHG, as captured by these two records, is a hitherto poorly understood component of Plio-Pleistocene climatic change. Further work at these sites and others within the Arctic is
needed to corroborate or refute the existence and magnitude of such event(s). Future work on the isotopic composition of individual GDGTs will refine hypotheses of whether the bacterial community at the lake also shifted during this time, which may have amplified an actual warming in the GDGT record.

Because of the high brGDGT concentrations in these samples, it is likely this represents a change in production rather than preservation of brGDGTs. This section of the core is finely laminated, suggesting little bioturbation and implying these samples record a climatic change and were not subject to preferential degradation during deposition, which could bias fractional abundances. We note that there are four periods in our record identified as “super-interglacial” based on the sedimentological characteristics (Facies), and these all contain elevated concentrations of brGDGTs. However, there are three periods identified as “glacial” Facies, which also have fine laminations associated with anoxia at Lake E. These Facies do not show elevated concentrations of brGDGTs, as would be expected if changes in preservation were biasing the signal. Instead, high brGDGT concentrations seem to correlate with interglacial periods recorded in the benthic oxygen isotope stack, indicating increased accumulation of bacterial membrane lipids during interglacial periods, consistent with increased production.

2.6 Conclusions

Temperature reconstructions based on the distribution of brGDGTs in sediments from Lake El’gygytgyn, Arctic Northeast Russia, provide the some of the first quantitative estimates of environmental change across the Plio-Pleistocene transition in the terrestrial Arctic, and represent the first application of this proxy to the topic of
iNHG. An exceptionally strong cooling and drying is observed coincident with the first major glaciation of the Northern Hemisphere at 2.7 Ma. Temperature and vegetation change are closely linked to one another, but vary independently of global records from 2.7-2.55 Ma, suggesting that after an initial glaciation, the Arctic experienced a time of transition when the multiple positive feedbacks related to sea-ice and vegetation albedo were not synchronized. Near 2.55 Ma, the disappearance of large trees and increased amplitude of temperature change argue for strong positive feedbacks becoming synched with the global climate system, resulting in persistent sea-ice conditions (potentially for the first time in the history of the Arctic basin) and the establishment of tundra. Although this is consistent with global sea-level records and evidence for abrupt climatic change related to North Atlantic overturning variability in the early Pleistocene, $pCO_2$ records are not closely linked with the terrestrial changes we reconstruct. This may be related to the resolution of new $pCO_2$ records, or may indicate that the carbon cycle, which has important high-latitude components, had not yet synchronized with other parts of the climate system by 2.4 Ma.
3.1 Compound-specific isotope measurements for fingerprinting of lipid source history

3.1.1 δ\textsuperscript{13}C of branched GDGTs

The source organisms of the organic compounds that form the basis of this study (branched GDGTs) are, at present, unknown (Weijers et al. 2014). Higher abundances of brGDGTs in more acidic soils, as well as the presence of compounds structurally similar to brGDGTs in 13 species of Acidobacteria, suggest Acidobacteria as a source (Weijers et al. 2007, Sinninghe-Damstè 2011, Weijers et al. 2014). However, many organisms probably play a role in contributing to the pool of brGDGTs in sediments, and these organisms (or others) are now known to flourish in lakes as well (Loomis et al. 2014, Buckles et al. 2014, Weber et al. 2015). Therefore interpreting a brGDGT record from a lacustrine system is an inherently tricky endeavor.

One potential protocol for differentiating the sources of brGDGTs uses compound-specific isotopes (Weber et al. 2015). The carbon isotopic composition can be measured on brGDGT core lipids after cleavage of their ether bonds (Schouten et al. 2013). The carbon isotopic composition of the core lipids reflects the isotopic composition of source carbon, as well as the extent of biosynthetic fractionation by the source organism (Schouten et al. 2013, and references therein). For example, methane
producing and/or consuming organisms have been implicated in the production of isoprenoidal GDGTs (Naeher et al. 2014). Methanogenesis and methanotrophy utilize organic carbon, and are associated with a significant biosynthetic fractionation effect (Peters 1993). Thus, increased production of brGDGTs by organisms involved in methane cycling should influence the isotopic composition of core GDGT lipids.

Samples have already been prepared the in large concentrations required for isotope analysis as part of the procedure for other ongoing work (Habicht et al. pers. comm.). These samples, which use organic material from the entire Lake El’gygytgyn core (spanning 3.6-0 Ma), represent an “average” lipid profile, against which a time-series of brGDGT $\delta^{13}C$ can be compared. Of special interest would be periods of supposed anoxia (i.e. Facies A and C), when alternative redox pathways (e.g. methanogenesis) would have been energetically favored. Samples from the period 2.66-2.65 Ma, when bizarre brGDGT distributions are seen, should also be targeted for isotope analysis. Very little work on the $\delta^{13}C$ of brGDGT core lipids has been done to date, and even less has focused on using this proxy to vet paleoclimate reconstructions (Weber et al. 2015). Thus, this would be a straightforward but highly timely avenue to pursue in future work.

3.1.2 $\delta$D of n-alkanes

Although the independent temperature reconstructions based on pollen assemblages and brGDGT distributions described in Chapter 2 largely agree about the character of temperature change across the Pliocene-Pleistocene transition, discrepancies
remain (e.g. potential extreme warmth at MIS G3, magnitude of temperature change at MIS G6). Robust incorporation of a third temperature proxy may resolve these and help refine the posited relationship between sea-ice changes, vegetation changes, moisture availability, and temperature change in the Arctic during this time.

Although samples have been prepared and analyzed for this purpose, it is important to note that translation of \( n \)-alkane \( \delta^D \) values to a hydrological interpretation is not completely straightforward, especially at high latitudes (Feakins et al. 2012, Pagani et al. 2006). Today, the most deuterium-depleted precipitation falls at the poles (Jouzel et al. 2002), where moisture sources are often distal and rapid poleward cooling results in heavy rainout during transit. During past warm periods (i.e. the Pliocene) when the global meridional temperature gradient was reduced and local moisture sources were uncovered (Feakins and Sessions, 2010), the isotopic composition of rainfall could have been different.

Environmental water is directly incorporated into plant lipids, but subject to multiple independent fractionating steps that must be considered (Sachse et al. 2012). Different biosynthetic pathways between organisms can cause a biologically mediated fractionation effect (Diefendorf et al. 2011). Evapotranspiration leads to deuterium enrichment of leaf-water (Sessions et al. 1999). The unique characteristics of light in the Arctic enhance this effect: plants grown under continuous light are 40 \( \% \) enriched relative to plants grown under the same conditions, but under diurnal light conditions (Yang et al. 2009). This effect has subsequently been observed for numerous
environmental samples, whose fractionation from source water δD is much smaller than the global average (Yang et al. 2011, Shanahan et al. 2013). Wilkie et al. (2013) used modern samples to determine the local net apparent fractionation between alkyl lipids and source water at Lake E, but some consideration should be given to determine whether this might have changed over geologic time due to changes in vegetation type. As is generally the case, caution should be applied when extending this modern relationship to the Pliocene, when the vegetation is known to be substantially different (e.g. Andreev et al. 2014). Earlier studies (Wilkie et al. 2013) were performed on n-alkanoic acids, which may have different sources, and thus different apparent fractionation, compared to n-alkanes. Thus, additional work is necessary before interpreting an n-alkane δD record from Lake El’gygytgyn.

3.2 Effect of changing seasonality on proxy-based temperature estimates

Recent work in several lacustrine environments has revealed that branched GDGTs are produced seasonally (e.g. Loomis et al. 2014). This is in many ways unsurprising, as previous studies on a number of organic proxies have shown a strong seasonality of production (Herbert et al. 1998, Kim et al. 2008). Without site-specific seasonally-resolved datasets, it is difficult to assess seasonality of compound production, and in most cases, seasonal mean temperatures are so highly correlated with mean annual temperatures that the distinction is not informative for making paleoclimatic inferences. In other words, even if the reconstructed temperatures are systematically biased from the true temperatures, there will be a predictable relationship between the proxy estimates and the true temperature, and the relative changes reconstructed will reflect reality. For a
long paleoclimate record, however, changes in the seasonality of production could influence temperature estimates in different ways through time, which could mask or amplify actual changes in mean annual temperature, the variable which we are ultimately interested in accurately reconstructing. Due to the extreme annual changes in insolation and temperature in the Arctic, it is safe to assume that most biotic processes take place during the summer months. However, today Lake El’gygytgyn is ice-covered for 10 months of the year, potentially restricting productivity to two months, July and August (Nolan & Brigham-Grette 2006). Lake modeling suggests that a mean annual temperature decrease of 4ºC would promote year-round ice cover (Nolan & Brigham-Grette 2006), yet aquatic biomarkers are present throughout the entire record, even during the Last Glacial Maximum, when temperatures were at least 4ºC lower than present (Wilkie et al. 2013, Holland et al. 2013). It is presumed that during the LGM, exceptionally clear lake-ice permitted productivity to take place beneath the ice-cover during summer months, and a seasonal moat produced by wind-driven breakup of landfast ice around the lake perimeter facilitated deposition terrestrial sediments and biomarkers (Wilkie et al. 2013). Today, the lake is surrounded by permafrost with a shallow active layer (~0.5 m) (Schwamborn et al. 2012) with low organic matter content and low concentrations of brGDGTs (Bischoff et al. 2013). Given that branched GDGTs may be produced both within the lake catchment and within the lake itself, and that the seasonality of production is unknown for both environments, it is reasonable to expect that changes in seasonality of production may have occurred throughout the El’gygytgyn record, especially going as far back as the Pliocene.
Thus, an examination of how changing the seasonal production of GDGTs at Lake El’gygytgyn would affect temperature estimates is necessary (Supp. Figure 1). The modern temperature distribution can be approximated as a sinusoid, with winter minima of -25ºC and summer maxima of 10ºC. Here, I assume that brGDGTs are perfect recorders of temperature during their period of production and ignore all uncertainties related to calibration. For the modern case, modeled brGDGT production during ice-free months yields a mean temperature of 9.2ºC (compare to instrumental summer maximum temperature: 10ºC, measured brGDGT-based temperature on the Sun et al. 2011 global calibration: 11.6ºC for the Holocene). The same annual temperature cycle with brGDGT production over four ice-free months gives a mean temperature of 7.2ºC; six months of brGDGT production results in a temperature of 3.5ºC (Supp. Figure 1). Thus, simply changing ice cover can result in a substantial bias for temperature estimates.

Yet, the duration of ice-cover is not independent of temperature. If mean annual temperatures at the lake evolved in a similar fashion to the length of production season, it is possible these two effects would be effectively balanced in the brGDGT record, and a correction for the length of production season could be applied to normalize temperature estimates (no proxies exist to capture these signals, and no relevant modeling has been attempted). However, it is presently impossible to independently correct for either the change in ice-cover or seasonality of production. If ice-free conditions are necessary for brGDGT production, MST may also be warm-biased during cold periods (i.e. the last glacial maximum), because production would capture only the signal from the warmest, ice-free month(s). There are apparently many uncertainties and poorly constrained
parameters involved, but using some assumptions based on published work, some very basic modeling can provide a starting point for future efforts.

Using the estimate that a 4°C decrease in MAAT leads to year-round ice cover, and modern MAAT produces two months of ice-free lake conditions, we can estimate how ice-cover changes as a function of temperature (Supp. Figure 1). For this analysis, we limit the ice-free season (i.e. duration of brGDGT production) to range from 2 months in the Pleistocene to 6 months in the Pliocene, and use the assumption that 4°C of temperature change is required to augment the ice-free season by 2 months. Numerous assumptions, some of which are obviously spurious, are involved in this analysis. These include that ice-cover changes linearly with temperature, that brGDGT production is limited to the ice-free season, and that Late Pliocene mean summer temperatures were 8°C warmer than present at Lake El’gygytgyn and cooled linearly to present. This is not meant to be a precise assessment of seasonality changes over time, but rather an illustrative, highly presumptive example of the effects of seasonality on the brGDGT temperature proxy at Lake El’gygytgyn. Further, we consider only the long-term trend, not the glacial-interglacial aberrations that characterize the Plio-Pleistocene. Despite the shortcomings, this analysis indicates that in a Pliocene world with 8°C warmer summer temperatures and 6 months of brGDGT production, the brGDGT temperature estimate is only 2°C warmer than the Pleistocene estimate based on 2 months of brGDGT production.

Much work remains to be done to characterize the seasonality of brGDGT production at Lake El’gygytgyn, including comprehensive field studies to determine the modern sensitivity of brGDGT-producing organisms to environmental conditions. Yet,
this simple modeling might serve to clarify some enigmatic characteristics of the dataset emerging from Lake E. Mean brGDGT concentrations during the Pleistocene are 0.2 µg/gsed, whereas the Pliocene concentrations are 1.45 µg/gsed, which could be consistent with a longer season of production (D’Anjou et al 2013). Additionally, Pleistocene average temperatures are 9.2ºC (0-450 ka; Castañeda, personal comm.) whereas Pliocene average temperatures are 11.6ºC (2.4-2.8; this study), using the global calibration of Sun et al. 2010. The 2ºC Arctic warming predicted by the proxy grossly underestimates both model and proxy-based estimates of Arctic warmth during the Late Pliocene, which may have been as high as 19ºC (Ballyntyne et al. 2011) during the warmest intervals, and was probably 8ºC warmer on average at Lake El’gygytgyn (Brigham-Grette et al. 2013). Thus, this simple modeling exercise is both consistent with multiple lines of existing data and illustrates that the brGDGT temperature estimates spanning the Pliocene and Pleistocene at Lake El’gygytgyn tell a coherent story when the seasonality of production is considered (otherwise, interpretation of the continuous 3.6-0 Ma record is fraught). For the duration of this study (2.82-2.41 Ma), the changing seasonality would be a very minor influence on temperature estimates (Fig. 15). Thus, the differences predicted by the brGDGTs are more likely caused by independent, higher-frequency (glacial/interglacial) changes in temperature than by the secular evolution of lake-ice cover through the Plio-Pleistocene. This is not to say that lake ice does not respond on these timescales, as it is in fact known to (Nolan and Brigham-Grette, 2006). However, for considering how this record relates to other records from Lake El’gygytgyn (e.g. MIS 5e (Castañeda et al. in prep), MIS 11 (Habicht et al. in prep), MIS 31 (de Wet et al. in prep), MIS G2 (Salacup et al. in prep)) it is necessary to keep this process in mind.
3.3 The record from Lake Baikal

The continuous terrestrial sedimentary record of climatic change through the Plio-Pleistocene from Lake El’gygytgyn is singular in the Arctic, and almost unique Earth. While it thus represents an invaluable contribution to our knowledge of paleoclimate, it is also difficult to validate or verify hypotheses based on changes recorded at the lake, because so few records exist for comparison. One long terrestrial record of comparable temporal coverage and resolution comes from Lake Baikal (53ºN, 108ºE), which was cored by an international team in 1996 (Williams et al. 1997). Prokopenko et al. (2001) highlighted the time period from 2.8-2.5 Ma as representing a severe climatic deterioration in the Lake Baikal region. At ~2.7 Ma, the clay fraction increases from 20% to ~90% in the Lake Baikal record, coincident with a crash in diatom abundance from 70% to ~5%. The character of these changes is remarkably similar to the variations seen for the most profound Pleistocene glaciations, suggesting a pronounced cooling and glacial advance occurred in the Lake Baikal region during this time, as is seen at Lake El’gygytgyn (this study). Prokopenko et al. (2001) infer a return to warmer, more stable climatic conditions in continental Asia from 2.5-1.8 Ma based on low clay contents and moderate diatom abundances. Based on diatom and pollen assemblages in the Lake Baikal record, Demske et al. (2002) argue that the period ca. 2.8-2.6 Ma was warm and humid, whereas cooling and increased continentality at this site began around 2.3 Ma, ~400 ka after the Arctic had begun to cool and dry at Lake El’gygytgyn (Brigham-Grette et al. 2013, this study). Unfortunately, the changes we infer at Lake El’gygytgyn based on
high-resolution organic geochemical records at Lake El’gygytgyn (this study) are
difficult to compare with to the lower-resolution Lake Baikal record, due to the different
methods used and unavailability of datasets from Lake Baikal.

As Lake El’gygytgyn and Lake Baikal bracket the location of the Siberian High,
they are likely to be influenced concurrently by climatic changes that influence the
location and intensity of this pressure center. As the Siberian High has been implicated in
driving the transition to the strong glacial cycles of the Pleistocene (Ruddiman et al.
1989), attempts at more robust correlation of the two records are warranted. Future work
should explicitly consider teleconnections between the two sites to reconstruct changes in
atmospheric dynamics during the intense periodic glaciations of the Plio-Pleistocene.

There are a few conspicuous changes in diatom assemblages across the Plio-
Pleistocene transition which merit brief mention. Diatoms of the genus Thalassiobecki
siberica are solely present during the G3 interval, 2.65 Ma (Prokopenko et al. 2009). The
appearance and extinction of this diatom is thought to represent a significant
environmental change, perhaps related to increased precipitation (Demske et al. 2002).
Additional detailed study of this interval in the Lake Baikal record may help clarify the
substantial but equivocal changes in brGDGT distributions noted in the Lake
El’gygytgyn record during MIS G3 (this study).

3.4 In support of a Pliocene “Time-Slice” Approach

The Pliocene has been the subject of immense research focus since its
identification as a potential analogue for future climate (Thompson and Fleming, 1996).
The PRISM project catalogued temperature and vegetation estimates from all over the world, to provide both a target and starting point for global climate model simulations (Dowsett et al. 2009). This effort has lead to an abundance of geological data from the Pliocene, and revealed extraordinary deposits, especially at the high latitudes, chronicling extreme warmth and dramatically different climatic boundary conditions than present (Salzmann et al. 2011). Yet, comparisons with model simulations revealed that no climate model is able to recreate the spatial pattern of warming inferred from proxy records, and the models are especially inadequate at high latitudes (Salzmann et al. 2013). Consideration of additional climate mechanisms has lead to slight improvements, but the systematic under-prediction of high-latitude temperatures by climate models has lead some researchers to suggest that the proxy estimates are skewed (Salzmann et al. 2013). Exceptionally warm temperatures may not correspond to a Pliocene mean state, but rather capture extreme or anomalous “super-interglacial” intervals (Dowsett et al. 1994). High-latitude deposits may be especially biased toward these periods, because primary productivity is restricted during cooler periods (Robinson et al. 2009).

Reconstructed temperatures for the Plio-Pleistocene transition cover an enormous range of variability, from ~0°C to ~30°C (this study). Although the relationship between the reconstructed temperatures and true mean annual temperatures is not fully characterized for Lake El’gygytgyn, extremely variable climatic conditions bracketed iNHG in the Pliocene Arctic (Funder et al. 2004, Ballantyne et al. 2011, Brigham-Grette 2001). Temperatures vary by ~8°C between some glacial-interglacial intervals, and the character of different interglacial intervals in this study ranges from mild to extreme
warmth. Thus, age control for estimates of Late Pliocene warmth and sea-level is extremely important for correlation of different sections, and, if one puts full faith in the reconstructed temperatures, there may have been confined periods of extreme warmth during the Late Pliocene which are not characteristic of the mean Pliocene climate state. Records that document extreme warmth (Ballyntyne et al. 2010, Rybczynski et al. 2013) are invaluable for understanding the full gamut of climate variability under Pliocene boundary conditions, but may not be appropriate targets for modeling studies which seek to characterize a mean.

In light of this, our record supports the efforts of Haywood et al. (2013) to reconstruct Pliocene climate within a time-slice, using only records that can be robustly dated to the same interval. Although the time-slice they advocate (3.205 Ma) is slightly older than the time period covered by this study (2.4-2.8 Ma), our results reveal substantial high-latitude climate variability occurred during the later Pliocene. Potential correlation of our record with extreme warm periods during our interval of interest (i.e. those recorded in the Gubik and Kap København formations) indicates that similar efforts would be fruitful across the PRISM interval and the 3.205 Ma time-slice. In future work, the continuous nature of the Lake El’gygytgyn sediments will continue to enable us to better correlate Pliocene deposits across the Arctic and begin to piece together the causal mechanisms behind their origin.
Figure 1: Pliocene Sea Surface Temperature (SST) Anomalies for the Northern Hemisphere.

Lake El’gygytgyn and four marine sites mentioned in the text are labeled. The thick red line is the Pliocene reconstructed coastline. Two persistent sea-level pressure anomalies, which drive weather patterns across Beringia, are labeled: SH, Siberian High; AL, Aleutian Low. Black arrows indicated the general synoptic circulation. SST data are from Dowsett et al. 2009.
Figure 2: Detail map of Lake El’gygytgyn and the surrounding area. Inset map shows the location of Lake El’gygytgyn (small red box) and the bathymetry of the surrounding ocean. Note the wide, shallow shelf through the Bering Strait, which is exposed during times of low sea level, connecting Eastern Asia with Western North America. The detail map shows Lake El’gygytgyn and the surrounding watershed. Note the pronounced ridges that ring the lake, forming its small catchment. The deepest part of the lake (170m water depth) is labeled by the white contour, and the red dot indicates where the sediment core ICPD 5011-1 was extracted.
Figure 3: Illustration of the effects of interpolation and normalization on biomarker records.

A) Branched GDGT concentrations. Original measurements are shown by black dots, and three different interpolations (2 ka, 2.5 ka, 4 ka spacing) are shown with continuous lines. B) Normalization of brGDGT and crenarchaeol (cren) records by $g_{sed}$, %TOC, and MAR. Note that general trends are robust regardless of normalization method. C) Linear sedimentation rate, used to convert biomarker records to MAR. D) Dry bulk density (DBD), used to convert biomarker records to MAR (courtesy of V. Wennrich). E) %TOC (Melles et al. 2012). F) Biogenic Silica MAR and Silica/Titanium ratio (Brigham-Grette et al. 2013). All records have the same abscissa.
Figure 4: Branched glycerol dialkyl glycerol tetraether (brGDGT) structures, after Weijers et al. (2007). Red accents highlight the structural differences between these nine related compounds.
Figure 5: Indices used in this study and their associated analytical error.

A) Branched and Isoprenoid Tetraether Index, a proxy for terrigenous vs. aquatic organic matter (Hopmans et al. 2004). B) The methylation of branched tetraethers (MBT) index. C) The cyclization of branched tetraethers (CBT) index. D) Temperatures reconstructed by applying the Sun et al. (2011) MBT/CBT calibration to our dataset. Shown are reconstructed temperatures for the raw dataset (red), temperatures neglecting the compound brGDGT Ib (auburn) for the whole record, and temperatures neglecting the compound brGDGT Ib only for 2.666-2.651 Ma.
Figure 6: The fractional abundance of all nine branched GDGTs for all samples studied.

Note that the ordinate is not linear. High fractional abundance of brGDGT Ib results in a large temperature spike near 2650 ka. The most common brGDGTs are I (1022), II (1036), and III (1050).
Figure 7: The effect of different calibrations on brGDGT temperature estimates from 2.560-2.410 Ma.

Shown are the most recent three glacial-interglacial cycles (MIS 95-99; ordinate is identical to Figure 9). A) Absolute temperature estimates for six published calibrations for soils (Weijers et al. 2007, Peterse et al. 2012) and lakes (Loomis et al. 2012, Tierney et al. 2010, Sun et al. 2011, Zink et al. 2010). B) Relative temperature change for the same calibrations, calculated by subtracting the mean value from each of the datasets. Note that the Loomis et al. (2012) and Tierney et al. (2010) calibrations, which are based only on the major GDGTs I, II, and III, show the most variability and the largest amplitude of glacial-interglacial temperature change. The Sun et al. (2011) calibration sits in the middle of the calibrations in terms of the magnitude of reconstructed temperature change, but generally reconstructs the warmest absolute temperatures of all the calibrations shown.
Figure 8: Temperature and vegetation change across the Pliocene-Pleistocene transition at Lake El'gygytgyn.

A) Mean summer temperature estimated based on MBT/CBT, Mean Temperature of the Warmest Month (MTWM) based on pollen biome reconstruction (Brigham-Grette et al. 2013), and the Lisiecki-Raymo benthic oxygen isotope stack (Lisiecki and Raymo, 2005).

B) Average chain length of \( n \)-alkanes, calculated for all measured chain lengths (left ordinate) and a subset of chain length (right ordinate). C) Facies change throughout the record (Brigham-Grette et al. 2013), and the abundance of long-chain (C\(_{27}\)-C\(_{33}\)), odd-carbon-number \( n \)-alkanes. D) Percentage counts of individual pollen species.
Figure 9: Climatic change from MIS G9-MIS G3.

Figure 10: Climatic Change from MIS G3-MIS 101.

Figure 11: Climatic change from MIS 101-MIS 95.


A: \( C_{24} + C_{26} + C_{28} + C_{30} \) n-alkanes

B: Glacial Facies "A", Interglacial Facies "B", Super-Interglacial Facies "C"

C: Precipitation (mm/yr)

D: Biomarker Concentration (µg/g sed)
**Figure 12: Temperature records from Lake El'gygytgyn, compared with other reconstructions of global climatic change.**

Figure 13: C$_{29}$ n-alkane $\delta$D across the Pliocene-Pleistocene transition. $n$-alkane $\delta$D, in units of permil (‰), plotted along the left ordinate axes of each plot. A) brGDGT-based temperature reconstruction. B) The Lisiecki-Raymo benthic oxygen isotope stack (Lisiecki and Raymo, 2005). C) Mean July insolation (W/m$^2$) at 65ºN (Laskar et al. 2004).
Figure 14: Summary of brGDGT- and $n$-alkane- inferred environmental changes across the Pliocene-Pleistocene Transition.

A) brGDGT-based reconstructed temperatures. B) The Lisiecki-Raymo benthic oxygen isotope stack (Lisiecki and Raymo, 2005). C) Mean July insolation (W/m$^2$) at 65ºN (Laskar et al. 2004). D) $\delta_{D_{\text{wax}}}$ for C$_{29}$ $n$-alkanes.
Figure 15: Modeling brGDGT temperature estimates based on changing lake-ice cover and temperature at Lake E.

A) Modern daily temperatures estimated with a simple sinusoid (red) and shifted up by 8°C to approximate a Pliocene case (green). Red and green boxes indicate the duration of brGDGT production assumed to occur for the modern and Pliocene end-members, respectively. B) Modeled summer temperature at Lake El’gygytgyn (red) and modeled proxy temperature (blue), based on averaging the values of the sinusoidal function in (A) over the period of proxy production. The green boxes show actual brGDGT data from Lake El’gygytgyn averaged over the length of the box (0-500 ka, Castañeda et al. in prep; 2.4-2.8 Ma, this study) using the calibration of Sun et al. 2011. C) Duration of brGDGT production used in the model to produce the blue curve in (B).
Figure 16: Relationship between Arctic summer sea-ice cover (NSIDC, 2014) and Lake El'gygytgyn mean annual temperature (NCEP Reanalysis, Nolan et al. 2013).
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