Compound-Specific Hydrogen Isotopes of Lipid Biomarkers in Lake El’gygytgyn, Ne Russia

Kenna M. K. Wilkie

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COMPOUND-SPECIFIC HYDROGEN ISOTOPES OF LIPID BIOMARKERS IN LAKE EL'GYGYTGYN, NE RUSSIA

A Dissertation Presented

by

KENNA M. K. WILKIE

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

DOCTOR OF PHILOSOPHY

May 2012

Geosciences
COMPOUND-SPECIFIC HYDROGEN ISOTOPES OF LIPID BIOMARKERS IN LAKE EL’GYGYTGYN, NE RUSSIA

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by

Kenna M. K. Wilkie

Approved as to style and content by:

Julie Brigham-Grette, Chair

Steven T. Petsch, Member

Stephen J. Burns, Member

David Finkelstein, Member

Jim Holden, Member

R. Mark Leckie, Department Head
Department of Geosciences
DEDICATION

For Grandpa
ACKNOWLEDGMENTS

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ABSTRACT

COMPOUND-SPECIFIC HYDROGEN ISOTOPES OF LIPID BIOMARKERS IN LAKE EL’GYGTYGYN, NE RUSSIA

MAY 2012

KENNA M.K. WILKIE, B.S., UNIVERSITY OF ALBERTA
M.S., SIMON FRASER UNIVERSITY
Ph.D., UNIVERSITY OF MASSACHUSETTS AMHERST

Directed by: Professor Julie Brigham-Grette

Recent successful drilling operations at Lake El’gygytgyn, NE Russia have recovered sediment cores back to 3.6Ma, representing the longest time-continuous sediment record of past climate change in the terrestrial Arctic. Analysis of the hydrogen isotopic ratio (δD) of specific organic biomarkers allows reconstruction of past hydrological conditions, thereby providing a powerful tool for reconstructing past Arctic climate changes. Compound specific isotopic analysis of sedimentary lipids from this remote basin provides new insights into the climate evolution of the Arctic, capturing the mechanisms and dynamics of the last two glacial-interglacial transitions, potentially enhancing the accuracy of modeled future climate change projections and presenting an opportunity to estimate past polar amplification of climate change. The results of this research document the first continuous, high fidelity continental record of reconstructed δD in precipitation from terrestrial plant leaf waxes in the High Arctic spanning the last 120 ka. The hydrogen isotopic composition of lipid biomarkers were determined from
previously obtained Lake El’gygytgyn sediment cores and compared with other multi-proxy evidence of past climate change within the lake basin. The modern isotope hydrology and controls on the δD lipid signal were first established within the El’gygytgyn Basin from modern precipitation, stream and lake waters, ice cover as well as modern vegetation, water column and lake bottom surface sediments in order to provide a modern context to properly constrain and interpret paleoclimatic proxy data. Reconstructed δD records of paleoprecipitation and temperature at Lake El’gygytgyn lead other northern hemisphere climate records (e.g. North Greenland Ice Core Project, NGRIP δ¹⁸O records) and are in phase with other continental and Antarctic climate records, suggesting early high northern latitude continental warming prior to established glacial-interglacial transitions. The data set generated here leads to multiple avenues of future work and provides critical insights into Arctic paleoclimate and paleohydrology, contributing to our understanding of high latitude environmental change over geological timescales. Collectively, the results of this dissertation research will provide a context for paleoclimate reconstructions and future organic geochemical and stable isotope analysis. Future application of compound-specific H isotope analyses to long drill cores (recovered in 2009; ~315m of sediment) will potentially provide a quantitative high-resolution record of paleoclimatic and paleoenvironmental changes spanning the last 3.6 Ma.
# TABLE OF CONTENTS

**ACKNOWLEDGMENTS**.............................................................................................................................................v

**ABSTRACT** ..........................................................................................................................................................vii

**LIST OF TABLES** ...............................................................................................................................................xii

**LIST OF FIGURES** .................................................................................................................................................xiii

**CHAPTER**

1. **INTRODUCTION**............................................................................................................................................. 1
   1.1 Overview ......................................................................................................................................................... 1
   1.2 Thesis Outline .................................................................................................................................................. 4
   1.3 Initial survey of El’gygytgyn Core LZ1029-7: Bulk organic geochemical and stable isotope analysis ........................................ 6
   1.3.1 Methods ....................................................................................................................................................... 7
   1.3.2 Chronology ................................................................................................................................................ 8
   1.3.3 Results and Discussion ................................................................................................................................. 9
   1.3.4 Conclusions .................................................................................................................................................12

1.4 References .......................................................................................................................................................14

2. **MODERN ISOTOPE HYDROLOGY AND CONTROLS ON δD OF PLANT LEAF WAXES AT LAKE EL’GYGTGYN, NE RUSSIA** ................. 22
   2.1 Abstract .........................................................................................................................................................22
   2.2 Introduction ..................................................................................................................................................22
   2.3 Study area: Location and climate .....................................................................................................................26
   2.4 Methods .......................................................................................................................................................27

   2.4.1 Sample collection .................................................................................................................................27
   2.4.1.1 Water samples .................................................................................................................................27
   2.4.1.2 Modern vegetation samples ............................................................................................................27
   2.4.1.3 Sediment traps and Sediment core tops .......................................................................................28

   2.4.2 Analytical Methods ............................................................................................................................29

   2.4.2.1 Water isotopic analysis ....................................................................................................................29
   2.4.2.2 Compound-specific isotopic analysis (CSIA) .............................................................................29
CONTINUOUS TERRESTRIAL ARCTIC RECORD OF RECONSTRUCTED PALEOTEMPERATURE 120KA TO PRESENT, LAKE EL’GYGYTGYN, NE RUSSIA

3.1 Abstract
3.2 Introduction
3.2 Methods

3.2.1 Location, climatic setting and chronology
3.2.2 Analytical methods
3.2.3 Data handling and calculations

3.2.3.1 Isotope mass balance correction
3.2.3.2 Application of net “apparent” fractionations

3.3 Results
3.4 Discussion
3.5 Conclusions
3.6 References
4. CONCLUSIONS AND FUTURE WORK..................................................................................................................... 98

4.1 Conclusions ......................................................................................................................................................... 98
4.2 Future Work......................................................................................................................................................... 101

4.2.1 Compound concentrations and OM cycling within Lake El’gygytgyn ......................................................... 101
4.2.2 Aquatic vs. Terrestrial sourced δD as an aridity proxy .......... 104
4.2.3 Multi-proxy comparison of δDAQ with δ¹⁸Odiatom for reconstructing δlake water ........................................ 105
4.2.4 Additional work ................................................................................................................................................. 106

4.3 References ......................................................................................................................................................... 108

APPENDIX: DATA TABLES........................................................................................................................................... 113

BIBLIOGRAPHY.......................................................................................................................................................... 114
<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Table 2.1</td>
<td>Mean values ($\delta^{18}O$, $\delta^D$, $d$-excess) for H$_2$O sample sets</td>
<td>61</td>
</tr>
<tr>
<td>Table 2.2</td>
<td>Concentrations and $\delta^D$ values for selected $n$-alkanoic acids with the El'gygytgyn Basin</td>
<td>67</td>
</tr>
<tr>
<td>Table 3.1</td>
<td>$\delta^D$ values for the methyl contribution from derivitization agent (BF$_3$ in MeOH)</td>
<td>94</td>
</tr>
</tbody>
</table>
LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Figure 1.1: Depth-age model developed for 3 m core LZ1029-7 based on linear interpolation of ages between tie points between cores LZ1029-5/8/9 and PG1351. a) High resolution scanned image of core LZ1029-7 prior to sampling. b) Depth-age model for core LZ1029-7. Correlation between cores was based on sedimentology and stratigraphic markers (e.g. turbidites, ash layer) and fluctuations in the TOC and bulk δ¹³C data.</td>
<td>19</td>
</tr>
<tr>
<td>Figure 1.2: Total organic carbon (TOC) concentrations and bulk δ¹³Corg compositions of sediment from a) core LZ1029-7 and b) core PG1351. Blue curves denote TOC (%); red curves show bulk δ¹³Corg (% VPDB).</td>
<td>20</td>
</tr>
<tr>
<td>Figure 1.3: a) Chromatograms of representative sections from the alkane fractions from core LZ1029-7. b) TOC and bulk δ¹³Corg data from core LZ1029-7 plotted vs. age (yr BP).</td>
<td>21</td>
</tr>
<tr>
<td>Figure 2.1: Location of Lake El'gygytgyn (red star) in NE Russia (from GeoMappApp.com).</td>
<td>61</td>
</tr>
<tr>
<td>Figure 2.2: Location of the sediment traps deployed in Lake El'gygytgyn in 2003, streams and the δD of sampled stream water. View to the NE with 5x vertical exaggeration. Dots indicate measured δD of stream waters collected summer 2003. Red line denotes watershed, streams are indicated in light blue lines. Contours indicate lake bathymetry.</td>
<td>62</td>
</tr>
<tr>
<td>Figure 2.3: Isotopic response of the lake water to changes in residence time and variable δDp of input (precipitation). Pink line denotes reconstructed δD of precipitation from δ¹⁸Ocellulose (Sidorova et al., 2008) based on Anderson et al. (2002). Blue curves show modeled response of δDlake with various residence times (10, 50, 100 and 300 years).</td>
<td>63</td>
</tr>
<tr>
<td>Figure 2.4: δ¹⁸O/ δD bi-plot of H₂O samples from modern precipitation (snow, rain), streams, lake water profiles, surface waters, and ice cover.</td>
<td>63</td>
</tr>
<tr>
<td>Figure 2.5: Relationship between δ¹⁸O and δD of precipitation with temperature within the El'gygytgyn Basin.</td>
<td>64</td>
</tr>
</tbody>
</table>
Figure 2.6: Hydrogen isotope composition of water from Lake El’gygytgyn at various depths, sampled in different months (May and August, 2003; November 2008). .................................................................65

Figure 2.7: Concentrations and δD values of n-alkanoic acids measured in modern vegetation samples from within the El’gygytgyn Basin. ..........................65

Figure 2.8: Concentrations of n-alkanoic acids with water column depth in sediment traps and lake surface sediments (note log scale). δD_{wax} values are plotted for lake surface sediments only as concentrations of n-alkanoic acids in sediment traps were insufficient for compound-specific δD analysis. ........................................................................66

Figure 2.9: Concentrations of n-alkanoic acids normalized to total yield of n-alkanoic acids by water column depth in Lake El’gygytgyn. b) Large moat formed by ice melt 500 m to the north of the southern shore on June 17, 2003 - approximately 1/3 way through sediment trap deployment. (From Melles et al., 2005). Note extent of snow and lake ice cover during typical summer month. C) Sediment traps deployed May 31, 2003 and recovered July 19, 2003. (From Melles et al., 2005). ........................................68

Figure 2.10: Conceptual diagram of major factors controlling the modern isotope hydrology at Lake El’gygytgyn. .................................................................68

Figure 3.1: Comparison of global climate records. (A) δ^{18}O records from Sanbao (orange; Wang et al., 2008), and Hulu Caves (brown; Wang et al., 2001). For comparison, the Hulu δ^{18}O record is plotted 1.6‰ more negative to account for the higher δ^{18}O values in the Hulu record compared to the Sanbao record (cf. Wang et al., 2008). (B) the North Greenland Ice Core Project (NGRIP) δ^{18}O record on the GICC05 timescale indicative of Greenland air temperature fluctuations (NGRIP dating group, 2006) (C) 3-point moving average MBT/CBT-derived air temperatures for the Mangshan loess plateau (Peterse et al., 2011) (D) the reconstructed δD of precipitation from leaf wax lipids record from Lake El’gygytgyn, NE Russia and summer insolation at 65°N (grey; Laskar et al., 2004) (E) the δD_{wax} record from Lake Tanganyika, SE Africa indicating past changes in aridity, (Tierney, et al. 2008) (F) 3-point moving average composite Red Sea relative sea-level reconstruction (RSL*) (Rohling et al., 2009) (F) the EPICA Dome C δD record indicative of Antarctic air temperature changes (Jouzel et al., 2007) ........................................................................................................95
Figure 3.2: a) Cross correlation of El’gygytgyn δD$_{\text{recon \ ppt}}$ with other global climate records. b) Lead/lag correlations of El’gygytgyn δD$_{\text{recon \ ppt}}$ and Antarctic δD, NGRIP δ$^{18}$O, Sanbao/Hulu cave δ$^{18}$O records and reconstructed continental air temperatures from Mangshan loess plateau, China (Peterse et al., 2011).................................96

Figure 3.3: Synoptical scale circulation features and locations of sites discussed in text. Dots represent locations of Lake El’gygytgyn (orange), Mangshan loess plateau (red), Sanbao and Hulu caves (yellow), Lake Tanganyika (beige), Dome C EPICA ice core (blue), and NGRIP ice core (grey). Basemap © 2011 Google.................................................................97

Figure 4.1: Concentrations of aquatic (blue) and terrestrially (green) sourced $n$-alkanoic acids, their δ13C values and % TOC (black) in Lake El’gygytgyn sediments. Light grey and dark grey lines denotes summer and winter insolation at 67°N, respectively. .......110

Figure 4.2: a) Comparison of aquatic sourced δD (δD$_{AQ}$; blue curve) with terrestrially sourced dD values (δD$_{TER}$; green curve). b) ΔδD$_{AQ-TER}$ (black curve) compared with the relative percent Poaceae pollen. Higher values of ΔδD$_{AQ-TER}$ correspond with cooler temperatures, increased aridity, and expansion of grass and tundra.................................................................111

Figure 4.3: El’gygytgyn δ$^{18}$O$_{\text{diatom}}$ record (far left panel; black curve) from Chapligin et al., 2012. The El’gygytgyn δD$_{AQ}$ record is plotted in blue and the δD$_{TER}$ from terrestrial leaf waxes is plotted in green. δD$_{lipid}$ data is plotted on the same axis.................................112
CHAPTER 1
INTRODUCTION

1.1 Overview

Our ability to make accurate predications about the future evolution of climate and related environmental changes in the Arctic and beyond depends on our capacity to understand the role of the Arctic region in modulating past periods of change under different climate forcing conditions (Fitzpatrick et al., 2010). Currently, the Arctic region is experiencing environmental change at unprecedented rates with not only marked changes in temperature but regional climate change patterns that include changes in precipitation and atmospheric circulation variability. The Arctic region is particularly sensitive to the effects of global climate change through strong feedback mechanisms involving marine, atmospheric, cyrosphere and terrestrial processes, making the paleoclimatic history of this region especially informative (IPCC, 2007; Manabe and Stouffer, 1980; Serreze et al., 2009; Hansen et al., 2006; Miller et al, 2010; White et al., 2010). Reconstructing past Arctic climates helps to reveal key processes of climate change, including the response to elevated greenhouse-gas concentrations, and provides insights into future climate behaviour (Miller et al., 2010). In particular, variations in hydrological processes in the Arctic have major implications not only for arctic terrestrial and marine ecosystems, but also for the cryosphere and global ocean dynamics (ACIA, 2005; Miller et al., 2010).
Water isotopes are powerful tracers of hydrologic and biogeochemical processes, allowing climatological reconstructions on spatial and temporal scales (Shanley et al., 1998). While the analysis of stable water isotopologues (H$_2^{18}$O and HDO) in ice cores (e.g. Petit et al., 1999, EPICA 2004) and speleothems (e.g. Wang et al., 2001; Yuan et al., 2004) has become the standard in reconstructing isotopic composition of paleo-precipitation, they are often limited in geographical extent. Recognizing the regionalization of climate (past and future) highlights the critical need for analysis of the isotopic signal recorded in terrestrial archives from low to high latitudes (IPCC, 2007; Sturm et al., 2010; Miller et al., 2010). Proxy data gathered from dispersed, regionally available continental settings can “fill in the gaps” and potentially capture regional feedbacks and expected spatial variability to hemispheric forcings.

Lake sediments contain valuable paleoclimate archives in continental settings because they can provide continuous high-resolution time series of multiple geochemical and microfossil proxies (Sauer et al., 2001; Meyers, 2003; Leng and Marshall, 2004). Lakes often contain abundant organic matter that can provide unique paleoclimatic and paleoenvironmental records through the preservation of molecular biological markers (biomarkers). Although limnological paleoisotopic studies have predominately focused on lacustrine carbonate to provide information on paleoclimate conditions such as temperature, moisture balance or circulation patterns, these studies are frequently hampered by inappropriate water chemistry (yielding carbonate dissolution), detrital carbonate input and difficulties in isolating purely autochthonous sedimentary material (review by Leng and Marshall, 2004).
Compound specific hydrogen isotopic study of sedimentary lipid biomarkers circumvents these issues, providing a highly selective means of isolating material of specific origin and allowing high-resolution paleoclimatic and paleoenvironmental reconstructions.

This project tests the hypothesis that compound-specific hydrogen isotopes in lipid biomarkers record paleoclimatic and paleoenvironmental changes over the last ~120 ka at Lake El'gygytgyn, NE Russia. Lake El'gygytgyn is situated within a 3.6 Ma old meteorite crater (Layer, 2000) located in a previously unglaciated region of northeastern Siberia (67°30’N, 172°05’E; Glushkova and Smirnov, 2007; Figure 1). Sediment cores recovered as pilot work from the central part of the lake in 1998 and 2003, 13 m (core PG1351) and 16 m (core LZ1024) respectively, comprise the last ~340 ka BP (Nowaczyk et al., 2007, Melles et al, unpublished) and represent a unique continuous terrestrial record of Arctic climate change. Recent successful drilling (Spring 2009), recovered 315m of lake sediments spanning the last 3.6 Ma, representing the longest time-continuous terrestrial Arctic record of climate evolution since the warm mid-Pliocene (Andreev, et al., in prep.). Multi-proxy investigations of Lake El'gygytgyn sediments already recovered (PG 1351 and LZ1024) reveal periods of rapid climate change and a regionally robust climate signal with global teleconnections (Brigham-Grette et al., 2007 and references therein). The research in this thesis builds upon this initial framework and contributes towards greater understanding of Arctic paleoclimate and paleohydrology.
1.2 Thesis Outline

This research will utilize an integrated analytical approach (using organic and stable isotope geochemistry) to characterize and document signals of ecological, environmental and climatic change in the lake and its watershed. This will be accomplished by:

a) determining high-resolution total organic carbon (TOC) and bulk $\delta^{13}$C$_{org}$ records from $\sim$90 ka to present and developing compound targets and an analytical strategy (i.e. work flow model) for future organic geochemical investigation of El’gygytgyn sediments,

b) constraining the modern isotope hydrology by determining the $\delta$D and $\delta^{18}$O of modern precipitation, lake water and stream inflow at Lake El’gygytgyn and generating a model of the isotopic sensitivity of lake water with residence time,

c) obtaining compound-specific $\delta$D values from modern vegetation, sediment traps and the sediment-water interface to develop a modern base line and calculation of a multi-species net (apparent) fractionation between source water and leaf wax lipids. This fractionation value is fundamental in reconstructing past precipitation and paleohydrology based on $\delta$D values from leaf wax lipids,

d) obtaining compound-specific $\delta$D values from aquatic and terrestrial biomarkers from previously acquired sediment cores from Lake El’gygytgyn for the last 120 ka. The $\delta$D values from terrestrial plant leaf waxes can then be used to reconstruct the $\delta$D of past precipitation. The
reconstructed δD of precipitation can then be used to estimate past continental air temperatures at Lake El’gygytgyn spanning the last 120 ka and compared with other global records of past climate changes.

This thesis is presented/organized into four chapters. Chapter one provides a general introduction to compound specific hydrogen isotopic analysis, thesis outline and brief description of initial work and TOC and bulk δ13Corg analyses on a short 3 m core (LZ1029-7). For a detailed description of that work and its application the reader is directed to two other co-authored papers (Holland et al., *in prep*.; Murdock et al., *in prep*.). Chapter two comprises a manuscript combining objectives b and c (above) detailing the modern isotope hydrology and controls on the δD of plant leaf waxes at Lake El’gygytgyn. Chapter three presents the results of the downcore analysis of δD from terrestrial leaf waxes and reconstructed δD of precipitation over the last 120 ka. Temperature estimates were also calculated based on the reconstructed δDprecip and both reconstructed records were used to compare Lake El’gygytgyn with other global climate records and infer large-scale global teleconnections. Finally, chapter four presents a summary of conclusions and provides extended abstracts for future manuscripts based on data generated here.

The data set generated by these investigations leads to multiple avenues of future work. In brief, an additional 3 direct outcomes of this work will continue to be addressed in subsequent papers (*in prep*). These are outlined in the final chapter of this thesis under Future work. These include:
1) temporal variability in the principle sources of organic matter (OM) and OM cycling with Lake El'gygytgyn. Concentrations of compounds analyzed in this thesis are presented and discussed within a multi-proxy framework,

2) development of an aridity proxy within the El'gygytgyn basin.

Comparison of the δD values from aquatic and terrestrial sources provides a measure of ecosystem evapotranspiration with high values corresponding with greater aridity. This difference (i.e. ΔδD) is compared with other indicators of aridity such as the relative percentage of grass (e.g. Poacea) pollen over the last 120 ka,

3) examining the relationship between the resulting δD record from aquatic sources and the δ¹⁸O diatom record. Both proxies potentially record the stable isotopic signature of El'gygytgyn lake water and should be related through the local meteoric water line (i.e. δD = 7.35 δ¹⁸O − 9.62; Wilkie et al., *in prep.*, Chapter 2).

### 1.3 Initial survey of El'gygytgyn Core LZ1029-7: Bulk organic geochemical and stable isotope analysis

Previous research (e.g. Melles et al., 2007) shows that glacial-interglacial transitions over the past 250 kyr were characterized by sharp increases in TOC and fluctuations in bulk δ¹³C_{org} compositions. Total organic carbon and bulk δ¹³C_{org} analysis of sediment from 3m core LZ1029-7 (taken from the same location as PG1351; Melles et al., 2007; Brigham-Grette, 2005) provides a high-resolution archive of overall lake and watershed biological productivity and preservation
during the last two glacial-interglacial transitions (Figure 1). Initial analysis of this core was undertaken to guide further sampling for organic geochemical analyses. Representative samples were also collected to identify target compounds for use in compound specific isotopic analysis of Lake El'gygytgyn sediments (both $\delta^{13}$C and $\delta$D). These samples were also used to streamline the analytical method to be used on smaller samples collected from a longer sediment core (LZ1024; see below).

1.3.1 Methods

Sediment samples from core 1029-7 were freeze-dried, crushed and stored in combusted glassware (2 cm sampling resolution; 139 samples). Each sample was sub-sampled for both bulk organic carbon content (%TOC) and bulk $\delta^{13}$C$_{org}$ analysis. Samples were acidified with sulfuric acid prior to analysis to remove carbonate and dried at 60°C (~12 hrs). Total organic carbon concentrations were determined using a Costech ECS 4010 Elemental Analyzer (EA) (Costech, Valencia, CA). Bulk organic matter $\delta^{13}$C compositions were determined by online combustion using a Costech ECS 4010 EA interfaced to a Thermo Delta 5 isotope-ratio mass spectrometer. Analyses were run in triplicate and are reported relative to the Vienna PDB (VPDB) standard in per mil (‰) notation.

Soluble organic matter was extracted using an accelerated solvent extractor (ASE200, Dionex Corp., Sunnyvale, USA) with a dichloromethane (DCM)/methanol mixture (9:1) at 100°C and 1200 psi for three 15-min cycles. The resulting total lipid extract (TLE) was split equally into archive and working halves. The working half of the TLE was then separated into four fractions on a solid phase extraction
(SPE) column containing 0.5 g of DSC-NH2 stationary phase (Supelco) following the methods of Sessions (1999). Fractions collected were: alkanes (4 ml hexane), ketones (6 ml hexane/DCM 4:1), alcohols (7 ml DCM/acetone 9:1), and fatty acids (8 ml DCM/formic acid 4:1). The alcohol and ketone fractions were derivatized with N,O-bis (trimethylsilyl)-trifluoracetamide (BSTFA) to convert alcohols to trimethylsilyl ethers. The acid fraction was derivatized with BF3-Methanol to convert fatty acids to fatty acid methyl esters (FAMES). Each fraction was analyzed by GCMS to identify compounds of interest and to generate targets for future analysis.

Identification of compounds was conducted on a Hewlett Packard 6890 series gas chromatograph – mass selective detector (GC-MSD) equipped with a 5% phenyl methyl siloxane column (HP-5MS, 30m x 0.25mm i.d., film thickness 0.25 "m). Helium was the carrier gas and the inlet temperature was 300°C. The oven program for alkanes was 40°C (2 min), 20°C/min to 130°C, 4°C/min to 320°C (15 min). The oven program for FAMEs was 60°C (2 min), 6°C/min to 320°C (15 min). The oven program for alcohols was 60°C (2 min), 20°C/min to 160°C, 4°C/min to 320°C (15 min). Positive identification was achieved by comparing mass spectral fragmentation patterns and relative retention times with those from published literature.

1.3.2 Chronology

Chronology for this core was established by correlation to sister cores LZ1029-5/8/9 and to core PG1351 based on sedimentology and stratigraphic
markers (e.g. turbidites) (Figure 1.1). Although laminations observed in other short sister cores (e.g. Melles et al., 2007; Juchus, Wennrich and Melles, unpublished) were only weakly visible and/or absent in core LZ1029-7, similar trends in TOC % and bulk $\delta^{13}C_{org}$ are present and were used to provide additional tie points and further constrain the age-depth model (Figure 1.2). Ages were calculated by linear interpolation between correlation tie points. The chronology for core PG1351 was derived by tuning the magnetic susceptibility record to northern hemisphere insolation, supported by the biogenic silica, TOC and TiO$_2$ records as well as OSL dates yielding a basal age of 275 ka (Nowaczyk et al., 2002; Forman et al., 2007; Nowaczyk et al., 2007; Frank et al., in prep.). Development of an age model for LZ1029-7 sediments allows for direct comparison of multiple proxies both regionally and throughout the El'gygytgyn basin.

1.3.3 Results and Discussion

Total organic carbon (TOC) concentrations are very low, ranging from 0.2% to 1.9%. The range of TOC values is slightly smaller in core LZ1029-7 than observed in core PG1351 (ranges from 0.1% to 2.5%; Melles et al., 2007) however, the trends are very similar (Figure 1.2). Highest values of TOC occur during glacial periods when perennial ice cover and lake stratification may have resulted in anoxic/ low oxygen bottom waters, reduced degradation and increased preservation of OM (Melles et al., 2007). During these cold, dry climate modes (Melles et al., 2007), persistent ice cover excluded wind generated mixing as well as seasonal density-driven overturning by warming surface waters. Although extremely limited
terrestrial input at these times would be expected, aquatic productivity likely remained relatively high, which may also contribute to higher TOC values. TOC values are low during warmer, interglacial periods possibly due to greater OM degradation within a fully mixed, oxic water column extending to the sediment-water interface. Thus, fluctuations in the TOC record likely reflect the repeated movement of the redox boundary within the sediments and extending into the water column linked with degradation of OM (Lehmann et al., 2002; Melles et al., 2007). Alternatively, the amount of organic carbon in the lake sediments could be affected by dilution with greater inorganic or clastic input reducing the proportion of TOC in the sediments. However, a reduction of relative grain size, lower sedimentation rates and higher proportions of chlorite, suggest reduced weathering of clay minerals and lower detrital input during cold climate modes (Asikainen et al., 2007; Minyuk et al., 2007). Notably, only minor fluctuations in TOC values are observed from ~60 ka to 75 ka, in contrast with distinctly higher values during this interval in core PG1351. This may be due to lower preservation of LZ1029-7 as laminations noted within this interval in sister cores 1029-5/8/9/ and PG1351 were absent.

Fluctuations in TOC are accompanied by sharp transitions in bulk δ^{13}C_{org}, likely due to increased internal carbon cycling, abundant methane generation and methanotrophy (Melles et al., 2007). Large excursions in bulk δ^{13}C_{org} during glacial intervals along with higher TOC values suggest migration of the redox boundary into the water column and enhanced preservation of OM coupled with possibly greater bacterial methanogenesis. Bacterial methane oxidation would produce isotopically
light carbon within the lake, eventually resulting in overall reduction of bulk $\delta^{13}C_{\text{org}}$ values (Whiticar, 1999). Alternatively, perennial lake ice cover would restrict atmospheric CO$_2$ exchange, resulting in a continually depleted reservoir of CO$_2$ in the lake with ongoing primary production. Investigation of compound-specific $\delta^{13}C$ signatures will help to better identify and deconvolute the source(s) of the $\delta^{13}C_{\text{org}}$ depletion (Holland et al., in prep; Wilkie et al., in prep b).

Compound fractions were used to identify a suite of lipid biomarkers to be used as targets for future organic geochemical and stable isotope analysis. Initial focus on the alkane fraction was driven by potential use of these compounds for $\delta D$ analysis. However, although largely identifiable through GCMSD and GCFID analysis (Figure 1.3), their abundances were insufficient for compound-specific $\delta D$ analysis of both short and long chain compounds.

Initial interpretations from the alkane fraction include (Wilkie et al., 2007):

- $n$-alkanes show a distinct odd-over-even carbon preference (OEP; CPI = 3-5) in pre-and post-LGM samples suggesting a dominant terrestrial source of organic matter to the lake
- OEP is attenuated in LGM samples (LE120 and LE150; ~20ka and 25 ka BP respectively) suggesting increased autochthonous production and/or limited terrigenous input
- High values for both $n$-alkane CPI and ACL reflect significant input from higher plants during warm intervals (~10.7ka, ~15ka, ~34ka and ~66ka).
• These intervals are also characterized by high values (>0.5) of the Alkane Index (A.I.), reflecting grass-dominated terrestrial input to lake organic matter.

• The increase in the P_{aq} Index (aquatic macrophyte n-alkane proxy; Ficken et al, 2000) during the LGM suggests greater contribution from submerged/floating macrophytes to lake sediments during cold intervals.

1.3.4 Conclusions

These initial results from core LZ1029-7 are consistent with previous work demonstrating the duration of seasonal lake ice cover is the dominant control on changes in lake biogeochemistry and paleolimnology (e.g. Melles et al., 2007; Minyuk et al., 2007). Fluctuations in TOC values likely reflect preservation of organic matter due to dysoxic/anoxic conditions driven by lake ice cover and lake stratification. High TOC values corresponding with a strong negative shift in bulk δ^{13}C_{org} values suggests dysoxic to anoxic conditions favoring preservation of OM and bacterial processes involved in methane cycling. A dominant terrestrial source of OM (identified independently here through lipid analysis) throughout the lake sediment record is consistent with the abundance and continuous deposition of terrestrial pollen (Lozhkin et al., 2007). Higher terrestrial contribution to the TOC content in El'gygytgyn lake sediments during warm intervals is also consistent with greater detrital or clastic input and higher total pollen concentrations during these times (Lozhkin, 2007; Minyuk et al., 2007). Additional detailed analyses of the
various different compound classes (alkanes, alcohols and sterols and fatty acids) were subsequently undertaken by A. Holland (Holland et al., in prep) to elucidate the source(s) of organic matter driving the highly depleted bulk δ¹³C signal.
1.4 References


Figure 1.1: Depth-age model developed for 3 m core LZ1029-7 based on linear interpolation of ages between tie points between cores LZ1029-5/8/9 and PG1351. a) High resolution scanned image of core LZ1029-7 prior to sampling. b) Depth-age model for core LZ1029-7. Correlation between cores was based on sedimentology and stratigraphic markers (e.g. turbidites, ash layer) and fluctuations in the TOC and bulk δ¹³C data.
Figure 1.2: Total organic carbon (TOC) concentrations and bulk $\delta^{13}$C$_{org}$ compositions of sediment from a) core LZ1029-7 and b) core PG1351. Blue curves denote TOC (%); red curves show bulk $\delta^{13}$C$_{org}$ (‰ VPDB).
Figure 1.3: a) Chromatograms of representative sections from the alkane fractions from core LZ1029-7. b) TOC and bulk $\delta^{13}$C$_{org}$ data from core LZ1029-7 plotted vs. age (yr BP).
CHAPTER 2
MODERN ISOTOPE HYDROLOGY AND CONTROLS ON δD OF PLANT LEAF
WAXES AT LAKE EL’GYGYTGYN, NE RUSSIA

2.1 Abstract
Stable isotope data from lipid biomarkers and diatom silica recovered from lake sediment cores hold great promise for paleoclimate and paleohydrological reconstructions. However, these records rely on accurate calibration with modern precipitation and hydrologic processes. Here we investigate the stable isotopic composition of modern precipitation, streams, lake water and ice cover, and use these data to constrain isotope systematics of the Lake El’gygytgyn Basin hydrology. Compound specific hydrogen isotope ratios determined from modern vegetation are compared with modern precipitation and lake core top sediments. Multi-species net (apparent) fractionation values between source water (precipitation) and leaf wax lipids (mean value is -105±13‰) agree with previous results in arid environments and provide a basis for application of this proxy downcore. We conclude that although there may be some bias towards winter precipitation signal, overall leaf wax lipids record annual average precipitation within the El’gygytgyn Basin.

2.2 Introduction
Hydrogen isotope ratios (δD) of lipid biomarkers are emerging as a new paleoclimatic and paleohydrological proxy (e.g. Sauer et al., 2001; Huang et al,
2002; Jacob et al., 2007; Feakins and Sessions, 2010; Castaneda and Schouten, 2011, see references therein). The hydrogen in organic matter derives from meteoric waters, which have δD values that are strongly controlled by climatic variables such as temperature, elevation and water vapour source (Craig, 1961; Dansgaard, 1964; Gonfiantini, 1986; Gat, 1996). The isotopic composition of meteoric waters is also controlled by continental and “latitudinal effects” (Dansgaard, 1964; Craig, 1961; Gonfiantini, 1986; Gat, 1996; Bowen and Revenaugh, 2003; Kurita et al., 2004) which are reflected in the δD of plant leaf waxes (δD_{wax}) (Sachse et al., 2006; Smith and Freeman, 2006; Hou et al., 2008; Liu and Yang, 2008, Polissar and Freeman, 2010). Changes in δD_{wax} in the geological record have been interpreted as shifts in precipitation δD (δD_p) (e.g. Liu and Yang, 2008; Tierney et al., 2008) or in evapotranspiration (Schefuß et al., 2005; Sachse et al., 2006; Jacob et al., 2007).

Qualitatively, a positive δD shift interpreted as an increase in δD_p or an increase in evapotranspiration would indicate drier conditions in either case. However, while δD_{wax} is dependent on the δD of the source water, interpretations can be complicated by biosynthetic fractionations, plant life form (e.g. tree, shrub, grass) and water use, evapotranspiration from soil and leaf water and relative humidity (Craig and Gordon, 1965; Sessions et al., 1999; Liu and Yang, 2008; Smith and Freeman, 2006).

In general, abundance and composition of biomarkers can serve to identify past ecosystems and environmental parameters during their formation (Meyers, 2003). Fatty acids such as long-chain even carbon-numbered n-alkanoic acids (e.g. >24 carbon chain length) typically originate from leaf waxes of terrestrial plants
(Eglinton and Hamilton, 1967; Cranwell, 1974; Cranwell et al., 1987; Sachse et al., 2006). In contrast, short-chain \(n\)-fatty acids, (i.e. <22 carbon atoms), are abundant as major constituents of cell membranes and waxes in many organisms, and are generally used as aquatic biomarkers (Cranwell, 1974; Cardoso et al., 1983; Cranwell et al., 1987; Meyers and Ishiwatari, 1993). Aquatic photosynthetic organisms in lakes obtain hydrogen from lake water to produce their organic compounds whereas terrestrial plants utilize hydrogen within the leaf water, which is subject to evapotranspiration (Leaney et al., 1985; Huang et al., 2004; Sachse et al., 2004; Zhang and Sachs, 2007). Thus, two isotopically distinct source waters are used for the biosynthesis of aquatic versus terrestrial biomarkers (Sachse et al., 2006). Lake water hydrogen isotopic variations are driven by \(\delta D_P\), lake hydrology, and the residence time of the lake water (i.e. Leng and Marshall, 2004; Jacob et al., 2007). Large, well-mixed lakes with long lake water residence times, such as modern Lake El’gygytgyn, will ‘average out’ short-term seasonal variations in precipitation and stream input isotopic compositions, and will reflect mean annual precipitation (Leng and Marshall, 2004; Nolan and Brigham-Grette, 2007). Leaf wax lipids derived from terrestrial plants instead record the isotopic ratio of soil water, which is ultimately recharged by precipitation. Snowmelt is typically the dominant annual hydrological event in Arctic watersheds (Kane et al., 1992) and within the El’gygytgyn Basin soil water is annually recharged by snowmelt (Nolan and Brigham-Grette, 2007; Nolan et al., in prep b).

Proxy use of \(\delta D_{wax}\) for paleoclimatic reconstructions depends on establishing a “net (or apparent) fractionation” between meteoric water and lipid \(\delta D\) values
(\(\varepsilon_{\text{wax/w}}\)). Prior studies have shown a net fractionation for terrestrial plants in more humid climates up to \(-160\%\) (Chikaraishi and Naraoka, 2003; Sachse et al., 2006; Sessions, 2006; Smith and Freeman, 2006; Hou et al., 2007b), and lower average net fractionation in more arid climates (approx. \(-95\%\)) (Hou et al., 2008; Feakins and Sessions, 2010). These values may be offset due to transpiration (i.e. enrichment of leaf water) in semi-arid to arid environments that act to reduce \(\varepsilon_{\text{wax/w}}\), possibly after passing some threshold beyond which \(\varepsilon_{\text{wax/w}}\) remains insensitive to increasing aridity (Feakins and Sessions, 2010).

In addition to variable isotopic fractionations, large interspecies variability has been found at the individual plant scale (e.g. Chikaraishi and Naraoka, 2003; Liu and Huang, 2005), particularly in highly arid sites (Feakins and Sessions, 2010). Several studies have linked this variability to life form (e.g. tree, shrub, grass) (Liu et al., 2006; Liu and Yang, 2008), leading to concern for the potential to bias paleoclimatic reconstructions given inevitable vegetation shifts in response to climatic change. However, Feakins and Sessions (2010) find a strong correlation between \(\delta D\) of source water and the average \(\delta D_{\text{wax}}\) value at a site suggesting catchment-scale average \(\delta D_{\text{wax}}\) values reliably record regional climate despite a large spread in values between individuals. This is in good agreement with calibration studies using core-top sediments (e.g. Huang et al., 2004, Sachse et al., 2004, Hou et al., 2008) that show much better correlations to climate than studies of individual plants.

Here we establish local relationships between the \(\delta D\) of modern vegetation, sediment traps and the \(\delta D\) in modern El’gygytgyn lake sediments as the context for
reconstruction of El’gygytgyn Basin paleohydrology (described elsewhere). These studies are supplemented by isotopic analysis of samples of modern meteoric water, including winter and summer precipitation, streams, lake water and ice cover which provide insight into the modern isotope hydrology. This approach enables us to: (i) determine the net fractionation (\(\epsilon_{\text{wax/w}}\)) between modern vegetation and source water within the El’gygytgyn Basin, (ii) assess the delivery of organic matter and target compounds for \(\delta D\) analysis, (iii) establish a framework for separating variations in the isotopic composition of lake water from changes in the isotopic composition of precipitation in the \(\delta D_{\text{wax}}\) paleohydrological proxy.

2.3 Study area: Location and climate

Lake El’gygytgyn is situated within a 3.58 ± 0.04 Ma old meteorite crater (Layer, 2000) located in a previously unglaciated region of northeastern Siberia (67° 30’N, 172° 05’E; Glushkova and Smirnov, 2007; Figure 2.1). The crater rim elevations vary between 600 and 930 m, while the lake surface lies at 492 m above sea level. The crater is approximately 18 km in diameter with a total watershed area of 293 km\(^2\) (110 km\(^2\) is lake surface) and the lake is 12 km wide and 175 m deep with a volume of 14.1 km\(^3\) (Nolan and Brigham-Grette, 2007). Water temperatures in this cold monomictic, ultra oligotrophic lake are <4°C and the lake is fed by 50 streams draining from within the crater rim (Cremer et al., 2005; Nolan and Brigham-Grette, 2007). Shallow lagoons with seasonal water temperatures >6°C are dammed by gravel berms surrounding the lake edge (Nolan and Brigham-Grette, 2007). Mean annual air temperature measured from 2002-2008 was -10.4°C
and total precipitation rose from 35 cm a\(^{-1}\) to about 55 cm a\(^{-1}\) over this period with roughly equal rates between winter and summer precipitation (Nolan and Brigham-Grette, 2007; Nolan et al., *in prep b*).

The El’gygytgyn Basin is located in a zone of hypoarctic tundra (Yurtsev, 1973) and modern vegetation within the basin is dominated by lichen and discontinuous herbaceous taxa (Kohzevnikov, 1993; Minyuk, 2005; Lozhkin et al., 2007). *Salix* and Poaceae species comprise the dominant woody and non-woody taxa, respectively and modern tree line is located ca. 150 km to the south and west of the lake (Lozhkin et al., 2007).

### 2.4 Methods

#### 2.4.1 Sample collection

##### 2.4.1.1 Water samples

Lake water and precipitation samples were collected during the 2003 El’gygytgyn Field Expedition in 30 ml Nalgene bottles and stabilized with one drop mercuric chloride (Juschus et al., 2005a). Water from incoming streams and the Enmyvaam outflow were likewise collected and all water samples were stored at 4°C at the Geoscience Dept., UMass Amherst until analysis. Precipitation samples were also collected over the winter 2008-2009 (Table 2.1).

##### 2.4.1.2 Modern vegetation samples

Herbarium samples of typical modern plants growing close to the lake were sampled in summer 2003. All plants were collected during the growing season.
This procedure was accomplished in order to establish a standard pollen collection of the local vegetation at Lake El’gygytgyn (Minyuk, 2005). Seven representative herbarium samples (courtesy P. Minyuk, NESRI, RAS Magadan) were subsampled, lyophilized, ground with a mortar and pestle and sent to the Geoscience Dept., UMass Amherst for lipid and isotopic analysis.

2.4.1.3 Sediment traps and Sediment core tops

Sediment traps were also deployed during the spring Field Expedition, 2003 (Figure 2.2). Each sediment trap consisted of a base plate made of plastic with a steel rod to fix the trap in vertical position at the rope. Four plastic tubes with a diameter of 46 mm were screwed to the bottom of this plate. The rope was anchored at the lake bottom with a bag filled with pebbles and kept up in the water column by buoys fixed beneath the base of the lake ice (Juschus et al., 2005b). Unfortunately, sediment traps were only recovered at one location during the 2003 Expedition yielding only 6 samples.

Samples of the sediment water interface were also collected during the spring 2003 Field Expedition. Coring was carried out from a floating platform with a gravity corer; attention was paid to horizontal preservation of the sediment water interface. Twelve of these samples were selected for biomarker analysis of which four samples were selected for further preparation for compound specific isotopic analysis. Additionally, a sample from the upper 0-2 cm of a 16m long sediment core (LZ1024) was also isolated and prepared for analysis. These samples represent modern sedimentation in the lake.
2.4.2 Analytical Methods

2.4.2.1 Water isotopic analysis

The oxygen and hydrogen isotopic compositions of the water samples were analyzed at the Alfred Wegner Institute (AWI) Potsdam, Germany with a Finnigan MAT Delta-S mass spectrometer equipped with two equilibration units for online determination following the methods of Meyer et al. (2000). The stable isotope ratios \( r_o = \frac{^{18}O}{^{16}O} \) and \( r_h = \frac{D}{^{1}H} \) are measured for both sample and reference and the final \( \delta^{18}O \) and \( \delta D \) values are calculated relative to Vienna Standard Mean Ocean Water (V-SMOW) in permil (Gonfiantini, 1978):

\[
\delta = \frac{r_{\text{sample}} - r_{\text{VSMOW}}}{r_{\text{VSMOW}}} \times 10^3
\]

The water samples show a long-term standard deviation of <0.10‰ (1σ) for \( \delta^{18}O \) and <0.8‰ for \( \delta D \), respectively.

2.4.2.2 Compound-specific isotopic analysis (CSIA)

The method for vegetation, sediment traps and all sediment samples is identical. Samples were freeze-dried, crushed and stored in combusted glassware. Soluble organic matter was extracted using an accelerated solvent extractor (ASE200, Dionex Corp., Sunnyvale, USA) with a dichloromethane/methanol mixture (9:1) at 100°C and 1200 psi for three 15-min cycles. Given the relatively low amount of organic C in the samples (Melles et al., unpublished), the maximum amount of sediment available was used (between ~7 g - 12 g dry sediment). The total lipid extract (TLE) was separated into neutral and carboxylic acid fractions on
a solid phase extraction (SPE) column containing 0.5 g of DSC–NH2 stationary phase (Supelco). A neutral fraction was eluted with 4 ml hexane:DCM (1:1) and archived for future analysis. Fatty acids were eluted with 8 ml of 2% formic acid in DCM and were subsequently derivatized as methyl esters (FAME) with BF$_3$MeOH. Compounds (i.e. FAMES) were identified and quantified using a Hewlett Packard 6890 series gas chromatograph – mass selective detector (GC-MSD) and a Hewlett Packard 6890 series gas chromatograph – flame ionization detector (GC-FID), respectively, and with comparisons to external standard mixtures. Both the GC-MSD and GCFID were equipped with 5% phenyl methyl siloxane columns (30m x 0.25mm i.d., film thickness 0.25μm). The GC oven temperature programs were also identical for both instruments: 60 °C (2 min), 15 °C/min to 315 °C (15 min) with helium as the carrier gas and the inlet temperature set at 320°C.

The δD of individual lipids were determined at the ESCSIS facility at Yale University using a Thermo Finnigan MAT 253 mass spectrometer with a gas chromatograph combustion interface (GCC) with a high-temperature pyrolysis furnace operated at 1440°C (Hilkert et al., 1999) coupled with a Thermo TraceGC GC-MS equipped with a DB-5ms column (30m, ID:0.32 mm, film thickness: 0.5 μm, Agilent) . The gas chromatography (GC) temperature program was: 80 °C (2 min) to 120 °C at 12 °C/min and then to 320 °C at 6°C/min (held 16 min). For δD analysis, each sample was analysed in triplicate and the H$_3^+$ factor was determined daily prior to standard calibration and sample analysis. The results are reported using standard delta notation (i.e. δD values) in permil (‰) units. Isotope ratios were normalized relative to a co-injected standard mixture containing C$_{14}$ n-alkane to condition the
furnace and C\textsubscript{15} and C\textsubscript{38} \textit{n}-alkanes as compounds of known isotopic values (obtained from A. Schimmelmann, Indiana University). Instrument performance was also determined daily by measuring a suite of 5 FAMEs with a co-injected standard mixture (\textit{n}C\textsubscript{14}, \textit{n}C\textsubscript{15}, \textit{n}C\textsubscript{38}) of known isotopic values. The mean precision for replicate analyses of the standard compounds was typically better than 5\%\textsubscript{o} (1s).

2.4.3 Data handling

2.4.3.1 Isotope mass balance correction

Fatty acid δD values were measured on methyl ester derivatives. A \textit{n}-C\textsubscript{14} acid standard was derivitized with BF\textsubscript{3}MeOH (same lot number as used with samples) to calculate the δD contribution from the three H atoms added during the methylation reaction with BF\textsubscript{3} in MeOH. The bulk δD of this \textit{n}-C\textsubscript{14} fatty acid standard (-240.4\%\textsubscript{o} ± 1.5\%\textsubscript{o}; \textit{n}= 5) was determined prior to derivitization offline by Thermal Conversion Elemental Analysis (TCEA, ESCSIS Yale University). Derivitized standard was measured in triplicate to yield an average δD value for the methyl contribution from the derivitization agent (-172.2\%\textsubscript{o} ± 2.5\%\textsubscript{o}). This value was used to correct the measured δD values of fatty acid methyl esters for the added hydrogen atoms by mass balance.

2.4.3.2 Calculation of net “apparent” fractionations

Isotopic fractionations between two measured substrates, δD\textsubscript{a} and δD\textsubscript{b} are reported as enrichment factors. Enrichment factors are reported in permil notation, implying a factor of 1000 (Cohen et al., 2007). Here we present the “net (or
apparent) fractionation” ($\varepsilon_{\text{wax/w}}$) between the $\delta D$ of leaf wax ($\delta D_{\text{wax}}$) and the $\delta D$ of source water ($\delta D_w$), commonly used in the plant leaf wax literature, where:

\[
\varepsilon_{\text{wax/w}} = (\alpha)_{\text{wax/w}} - 1 = \frac{\delta D_{\text{wax}} + 1}{\delta D_w + 1} - 1
\]

Although $\varepsilon_{\text{wax/w}}$ is typically calculated relative to $\delta D$ of mean annual precipitation, this inherently assumes that the isotopic composition of the source water ($\delta D_w$) is identical to local $\delta D$ values of precipitation ($\delta D_{\text{precip}}$). In this study, the water available for plant uptake is largely spring snowmelt carried in streams and draining through the shallow active layer (see section 4.1; Nolan et al., in prep b), therefore we used the empirically determined average $\delta D$ for stream water. We also calculate the net fractionation between plant leaf wax and annual average precipitation in the basin ($\varepsilon_{\text{wax/precip}}$) for comparison.

### 2.4.3.3 Model parameters

In order to assess the sensitivity of the lake basin to changes in the lake water residence time and changing $\delta D_p$ and $\delta^{18}O_p$ over time, we constructed an isotope mass balance model of the lake (Figure 2.3).

\[
\delta_{\text{lake}(i+t)} = \delta_{\text{lake}(i)} + \left(\frac{\delta_{\text{in}(i)} - \delta_{\text{lake}(i)}}{\tau}\right) \cdot \Delta t
\]

where $\delta_{\text{lake}(i)}$ represents the initial $\delta$ value of the lake water, $\delta_{\text{in}}$ represents the isotopic composition of input or precipitation, $\tau$ and $t$ represent the lake residence time and timestep (here defined as 1 due to the annual resolution of the tree-ring timeseries), respectively. Initial lake conditions were assigned based on the present day mean $\delta D_{\text{lake}}$ (-155‰) and is similar to reconstructed input approximations. As
long term records of past $\delta D_p$ are lacking in this region, we used $\delta^{18}O$ data from tree ring cellulose in Northern Siberia (Sidorova et al., 2008) to reconstruct the isotopic ratios of past precipitation for input to our model. In order to derive isotope ratios of precipitation from $\delta^{18}O_{\text{cellulose}}$, we used the relationship between source water (here assumed to be precipitation) and $\delta^{18}O_{\text{cellulose}}$ described in Anderson et al (2002). We assigned a mid-range value of 0.6 for the fraction of leaf water not subject to evaporation ($f$) (e.g. Saurer et al., 1997) and a relative humidity ($h$) of 78%. Average relative humidity was determined from the automated weather station data collected at Lake El’gygytgyn 2002-2008 (Nolan et al., in prep b). Conversion of $\delta^{18}O_{\text{reconstructed precip}}$ to our proxy model input, $\delta D_{\text{in}}$ where $\delta D_p = \delta D_{\text{in}}$, was accomplished by applying our LMWL equation established above (i.e. $\delta D = 7.35 \delta^{18}O - 9.6$).

2.5 Results

2.5.1 $\delta D$ and $\delta^{18}O$ values of water samples

Precipitation collected in summer 2003 (rain), winter 2008/2009 (snow), streams, lake ice and lake water profile samples were analysed for their oxygen and hydrogen isotopic compositions (Figure 2.4). Mean $\delta^{18}O$ and $\delta D$ values for the different hydrological components are overall lower than previously reported values for the El'gygytgyn basin (Table 2.1; Schwamborn et al., 2006). Snow samples $\delta^{18}O$ values ranged from -33.9‰ to -14.1‰ (mean: -23.16‰) and $\delta D$ values from -271.0‰ to -100.5‰ (mean: -179.9‰) (Table 2.1). Rain $\delta^{18}O$ values range from -15.91‰ to -12.37‰ (mean -14.29‰) and $\delta D$ values range from -
127.5‰ to -98.1‰ (mean -114.8‰) (Table 2.1). Summer precipitation shows much lower deuterium excess (d-excess) values (mean d-excess = -0.5‰) than winter precipitation and is offset from the GMWL consistent with observations by Schwamborn et al. (2006). The mean d-excess values for both snow and stream samples (5.4‰ and 6.7‰ respectively) are similar while lake water d-excess values are lower. Annual average precipitation is calculated partitioning precipitation into a 60% winter contribution and 40% summer input (annual average δ18O=-19.3‰, δD=-152.9‰) based on Nolan and Brigham-Grette (2007). These proportions are derived from measurements of water equivalency made in a single year but are thought to be representative for modern climate (Nolan and Brigham-Grette, 2007).

The δD-δ18O relationship in winter precipitation samples follows close to the global meteoric water line (GMWL; Craig, 1961) and defines a linear relationship of:

$$\delta D = 7.35 (\pm 0.24) \delta^{18}O - 9.62 (\pm 5.64)$$

$$n = 35; R^2 = 0.97$$

where n is the number of data points and $R^2$ is the coefficient of determination (Figure 2.4). Streams, lake ice and lake water profile samples also display similar linear relationships, close to the GMWL and consistent with a circum-polar regression complied from the International Atomic Energy Agency/World Meteorological Organization (IAES/WMO) Global Network of Isotopes in Precipitation (GNIP) database ($\delta D = 7.26 \delta^{18}O - 5.98; R^2=0.99$; Lacelle, 2011; IAEA/WMO, 2006). Summer precipitation defines a Local MWL (LMWL) different from the GMWL ($\delta D = 6.80 \delta^{18}O - 22.3; R^2=0.95$) indicating kinetic fractionation (Figure 2.4). These results are consistent with previous observations
within the El’gygytgyn basin (Schwamborn et al., 2006) and in northern Siberia (Meyer et al., 2002, Sugimoto et al., 2003; Kurita et al., 2004; Opel et al., 2011).

The isotopic composition of precipitation and temperature are strongly correlated at mid- and high latitudes (Dansgaard, 1964), occurring because the degree of rain-out from the atmosphere through condensation is highly correlated with the condensation temperature (see Jouzel et al., 1997 for review). Figure 2.5 shows the δD-T and δ¹⁸O-T relationships for the El’gygytgyn basin for both winter and summer precipitation (n= 26). Positive spatial relationships (δ¹⁸O = 0.43 T - 18.5, R² = 0.68; δD = 3.1 T - 143.7, R² = 0.64) are observed between the isotopic compositions of precipitation and air temperature. Temperatures used are ‘precipitation temperature’ (i.e. surface air temperature during a precipitation event) as isotopic values are discrete, not weighted means. The slope coefficients of the δ-T relationships presented here are similar to the spatial δ¹⁸O-mean air temperature (MAT) relation for Taymyr and Lena data (δ¹⁸O = 0.59 MAT -11.47, R² = 0.91; Boike et al., 1997) and data from 47 European IAEA/WMO stations to the west (δ¹⁸O = 0.59 MAT - 14.35; Rozanski et al., 1992). However, the slope coefficient for δD-T relationship at El’gygytgyn is lower than previously reported by Rozanski et al. (1992) (4.5‰ °C⁻¹) and from the Siberian Network of Isotopes in Precipitation (δD_winter= 5.6 T_DJF-77.9; R² = 0.93; δD_summer= 5.1 T_JJA -157.3; R²= 0.55; Kurita et al., 2004).

Spatial variations in the isotopic composition of stream water samples were observed. Stream δ¹⁸O values ranged from 24.23‰ to -16.68‰ (mean-18.91‰) and δD values ranged from -179.5‰ to -127.8‰ (mean -144.9‰; Table 3.1).
Relatively enriched values cluster predominantly along the south facing and western slopes (Figure 2.2). Most negative $\delta^{18}$O values and $\delta$D values were found along the eastern side of the crater, in streams with relatively high gradients (Figure 2.2). Decreasing $\delta^{18}$O and $\delta$D values broadly correlate with higher relief ($R^2=0.44$), with the exception of the shortest stream (Stream 37). There is a general trend toward increasing $\delta^{18}$O and $\delta$D values over the course of the summer sampling interval ($R^2=0.33$).

Sampled profiles of the lake water show small ($\delta^{18}$O: $\sim1.5\%$, Chapligin et al., 2012; $\delta$D: $\sim11\%$, Figure 2.6) seasonal variations in the upper 2 m surface waters. These variations are likely due to spring (May) input from streams carrying isotopically depleted snowmelt and evaporative enrichment during summer (August) (Chapligin et al., 2012). Below 2 m water depth, the lake is well mixed with an average $\delta$D value of $-155.1\pm0.7\%$.

### 2.5.2 Modern vegetation samples

We report abundances and hydrogen isotope ratios for $C_{20}$, $C_{24}$, $C_{26}$, $C_{28}$, and $C_{30}$ $n$-alkanoic acids from representative samples of modern vegetation from within the Lake El’gygytgyn basin (Figure 2.7). Despite the small sample set ($n=7$), we observe a large interspecies variation in the distribution of compounds with some species producing relatively high concentrations of short-chain compounds typically associated with aquatic organisms (i.e. $nC_{20}$ and $nC_{22}$ acids; Cranwell et al., 1987; Ficken et al., 2000). The average chain length ($ACL = \sum(C_n \cdot n)/\sum C_n$, where $n= 20, 22, 24, 26, 28, 30$) for modern vegetation varied between species, ranging from 24 to 27
Concentrations are normalized per g of total lipid extract (TLE). The highest concentrations of C$_{30}$ n-alkanoic acid were found in the *Douglasia ochotensis* and *Rumex sp.* samples whereas lowest concentrations were observed in *Artemisia* and *Bryophyta sp.* High concentrations of nC$_{28}$ acid were found in the *Bryophyta sp.* but concentrations of all other n-alkanoic acids were very low or below detection limit.

For all plants yielding measurable n-alkanoic acids, δD values are reported in Table 2.2. We observe differences in n-alkanoic acid chain length abundances for different species as well as isotopic offsets between different chain lengths in some species. Thus, a mass-weighted mean δD value (δD$_{\text{wax}}$) was calculated to provide a common basis for comparison (Table 2.2). This allows comparison of the δD of different species regardless of chain length abundances. Within lake sediments, only nC$_{30}$ acid can be attributed solely to a terrestrial source (Holland et al., *in prep*) therefore, we also compared δD$_{\text{wax}}$ values with the δD values of nC$_{30}$ acid (i.e. δD$_{30}$).

The hydrogen isotope compositions of C$_{30}$ n-alkanoic acid (δD$_{30}$) strongly correlate with the concentration-weighted δD$_{\text{wax}}$ values ($r^2=0.97$) confirming δD$_{30}$ values are representative of integrated δD values for terrestrial leaf waxes from plants within the Lake El’gygytgyn watershed (ranging between -227.5‰ and -260.5‰). Net fractionation values calculated between plant leaf wax (i.e. nC$_{30}$ acid) and two different source waters (stream water, ε$_{\text{wax/streams}}$ and annual average precipitation, ε$_{\text{wax/precip}}$) are similar but show slightly higher values with annual average precipitation (mean ε$_{\text{wax/precip}}$ = -107.4 ±12‰; Table 2.2).
2.5.3 Sediment traps and lake sediments

Concentrations of even chain \( n \)-alkanoic acids (\( nC_{20}, C_{22}, C_{24}, C_{26}, C_{28}, \) and \( C_{30} \)) varied widely between sediment traps and samples of the upper 0-2 cm of lake sediments (Figure 2.8). Sediment traps show variable distributions of compounds and concentrations with water depth with highest concentrations of all compounds at 90 m water depth (Figure 2.8). Individual compounds were normalized by total yield of \( n \)-alkanoic acids to show changes in the relative proportions of compounds (normalized to total yield of \( n \)-alkanoic acids) with water depth (Figure 2.9). The upper surface waters show high percentages of \( C_{20}, C_{22}, C_{24}, \) and \( C_{26} \) acids with a marked decline of \( C_{22} \) acid by 50 m depth. The shortest chain \( n \)-alkanoic acid, \( nC_{20}, \) decreases with depth. Below 50m, \( C_{30} \) and \( C_{22} \) acids appear to co-vary, whereas \( C_{24}, C_{26}, \) and \( C_{28} \) follow a similar general trend down to 130 m water depth. Concentrations of \( C_{24} \) and \( C_{26} \) increase at the deepest sediment trap (146 m water depth), yielding higher percentages of these compounds near the lake bottom than in surface waters. Abundances of all compounds in all sediment traps were too low for \( \delta D \) analysis.

High concentrations of all compounds were observed in the upper 0-2 cm of lake sediments, increasing in concentrations with increasing lake water depth (note log scale, Figure 2.8). The distribution of all compounds is consistent across all samples as indicated by calculated values of average chain length (ACL = \( \sum (C_n n) / \sum C_n, \) where \( n= 20, 22, 24, 26, 28, 30 \)) (Table 2.2). The hydrogen isotope compositions of sedimentary \( n \)-alkanoic acids are also reasonably consistent across samples (i.e. sedimentary \( \delta D_{30} \) values varied by \( \sim 10\%_0; \) within 2\( \sigma \) analytical error).
Net fractionation values calculated between terrestrially sourced nC30 acid and the different source water signals (stream water, ε30/streams or annual average precipitation, ε30/precip) are similar but show slightly higher values with annual average precipitation (mean ε30/streams = -114.0 ± 13‰; mean ε30/precip = -105.4 ±13‰; Table 2.2).

2.6 Discussion

2.6.1 Modern isotope hydrology

The isotopic composition of modern precipitation and various components of the hydrological system provide the basis for applying paleoclimatic interpretations to stable isotope compositions of sediment archives (Schwamborn et al., 2006). Here we outline the modern isotope hydrology from precipitation to stream runoff to lake water and discuss the major controls on each component. Each of these components affects the hydrogen isotope composition ultimately recorded in the δD values from leaf wax lipids (Figure 2.10).

Precipitation regimes are influenced by air temperature, proximity to moisture sources and trajectories of weather systems over landmasses. Consequently, the δ18O and δD values in local precipitation (i.e. δD_p) are highly variable and the slope values of local meteoric precipitation often deviate from the GMWL. Spatially, lower slope values are located in areas with local orographic effects and continental climatic regimes, while higher slope values are from sites with maritime climates (Lacelle, 2011). East Siberian Arctic winter precipitation exhibits a wide range of stable isotopic compositions (e.g. Kurita et al., 2004) and
although the values presented here are not weighted means, the range of variation (e.g. $\Delta \delta^{18}O$ values = 17‰ and $\Delta \delta^D$ values = 19‰) is similar to that previously reported within the El’gygytgyn Basin (Schwamborn et al., 2006). Modern winter precipitation at Lake El’gygytgyn closely follows the $\delta^D$ and $\delta^{18}O$ values of precipitation from other Arctic sites in the GNIP database. The values of the slope (7.35) and the y-intercept (-9.62) are lower than the GMWL but very close to the GNIP-based circum-polar regression, indicating a nearly unaltered precipitation signal from the original moisture source during winter months. In contrast, summer precipitation shows a clear kinetic fractionation of isotopes with lower slope and d-excess values. This may be related to enhanced evaporation occurring during summer months in typical tundra settings due to the water surplus on the land surface and continuous 24hr net radiation (Ohmura 1982; Boike, 1997). Reprecipitated moisture derived from recycled water masses from the land surface may also be included (Sugiomoto et al., 2003; Kurita et al., 2004; Schwamborn et al., 2006).

The seasonal contrast in modern precipitation may also be explained by the strong seasonality in the dominant weather patterns. Modern synoptic weather patterns identified from National Centers for Environmental Prediction (NCEP) global reanalysis data show strong low pressure systems over the Aleutians during winter and broad high pressure system to the south and east with weaker lows to the north during the summer (Nolan et al., in prep a). Strong Aleutian Lows during winter tend to bring cold Arctic air from the east and north to the lake, whereas summer synoptic weather patterns bring warm continental air from the south and
west (Nolan et al., *in prep a*). Thus, these dominant weather patterns affect both the seasonal temperature change and source of moisture delivery to Lake El’gygytgyn. Seasonal air temperature changes affect the saturation vapour pressure of air masses and subsequently the degree of rainout, yielding decreasing precipitation isotope ratios with decreasing temperatures and along trajectories of atmospheric vapour transport. These trajectories deliver winter precipitation from a proximal moisture source (i.e. E. Siberian, Chukchi and Bering seas) and recycled moisture from the Siberian land surface to the south and west during the summer months. Furthermore, Nolan et al. (*in prep a*) suggest that these weather patterns have been relatively stable with time and are likely representative of this and other interglacial periods.

Input to the lake via streams draining from the crater rim is predominantly driven by winter snowmelt and shows spatial variations in isotopic composition according to stream gradient and slope aspect (Figure 2.2). Stream samples are more $^{18}$O and D depleted than overall summer precipitation isotope ratios with values closer to mean annual precipitation ($\delta D_p$). This suggests that stream waters carry a large winter precipitation signal offset by some input of isotopically enriched summer precipitation and/or evaporative enrichment of the soil water. Water tracks, characteristic of permafrost terrain and immature drainage systems, are common on El’gygytgyn slopes with rapid drainage of moisture through the active layer in early spring/summer (Nolan and Brigham-Grette, 2007; Nolan et al., *in prep b*). The residence time of the water in the soil typically produces a dampening of the seasonal variations observed in precipitation (Buhay and Edwards, 1995; Anderson
et al., 2002), however, this residence time is exceedingly short within the El’gygytgyn Basin. Therefore, stream water effectively represents the soil moisture in the basin, draining rapidly and recharged annually by snowmelt. Soil moisture data collected from different depths within the El’gygytgyn Basin (to base of active layer; 2002-2008) shows peak soil moisture in early spring prior to peak soil temperatures and with individual summer precipitation events having only a minor effect on soil moisture content (Nolan et al., in prep b). Deep permafrost in this region (~500 m; Yershov, 1998; Schwamborn et al., 2006) precludes deep groundwater input and streams are therefore representative of soil moisture recharged by winter precipitation draining through the shallow active layer during the short summer season.

Streams with south facing and western slopes display relatively enriched isotope ratios. Lower gradients for these slopes, longer transit times and seasonally greater net incoming solar radiation likely resulted in $^{18}\text{O}$ and D enrichment of these stream waters due to evaporation. These streams were also sampled late in the summer season, well after peak discharge and when flow in many of the smaller streams was reduced ($<1\text{ m}^3\text{s}^{-1}$) and is often just a trickle (Nolan and Brigham-Grette, 2007). Thus, despite summer sampling during maximum expected evaporative enrichment, the isotopic ratios of stream samples appear biased towards more negative winter precipitation isotope ratios though offset by some minor evaporative enrichment.

Small seasonal changes are also observable in the isotopic composition of the lake water. Profiles of the lake water column show seasonal enrichment of the
surface waters in summer and depleted surface waters in early spring. Although thermally stratified in winter, the lake is rapidly mixed following snowmelt and ice breakup in late May (Nolan and Brigham-Grette, 2007) with little variation below the upper surface waters. Isotopically depleted lake surface waters (2m depth, Figure 2.6) collected in late May are likely the combined result of melting lake surface snow and ice and input from streams carrying isotopically depleted snowmelt. Evaporative enrichment of the lake surface waters in summer (August) is small and likely very brief given vertical mixing due to strong winds (Nolan and Brigham-Grette, 2007) and has little to no influence on the overall isotopic composition of the lake (Chapligin et al., 2012).

The mean hydrogen isotope composition of the lake water (δD_{lake}) is largely controlled by the hydrogen isotope composition of precipitation (δD_p), duration of ice cover and the residence time of the lake. Input to the lake is a combination of direct precipitation on the lake surface and stream discharge. Streams account for 85% of water input to the lake (Fedorov et al., in prep) and prolonged or perennial ice cover prevents evaporative enrichment of surface waters. Accordingly, the average isotopic ratio of modern lake water is slightly more depleted in $^{18}$O and D when compared to mean annual precipitation values, reflecting either greater input from isotopically depleted snowmelt and/or a lag in response based on lake residence time to past changes in δD_p.

To assess the impact of this potential lag, lake water isotopic response was modelled by isotope mass balance (Figure 2.3). Variations in δD_p are reflected in the lake water isotopic response within decades ($\geq$10 yrs) but the magnitude of the
response is strongly attenuated by the residence time. Modern residence times for Lake El’gygytgyn are ~120 years (Fedorov et al., 2009; Fedorov et al., in prep) but could have been greater during ice covered, glacial conditions. Although the modelled $\delta D_{\text{lake}}$ does not record the full magnitude of minor fluctuations of $\delta D_p$, these results suggest $\delta D_{\text{lake}}$ does still respond to large magnitude changes in input on long glacial-interglacial timescales.

2.6.2 Climate signal preserved in plant leaf waxes

2.6.2.1 Modern vegetation

Modern vegetation within the El’gygytgyn Basin produced a range of $n$-alkanoic acids with variable concentrations and $\delta D$ values. Reconstructions of the $dD$ of meteoric water rely on a constant ‘net fractionation’ between lipid and meteoric water. Differences between plant species and vegetation type may affect the net fractionation (e.g. Chikaraishi and Naraoka, 2003; Smith and Freeman 2006; Hou et al., 2007), however within watersheds these differences are integrated and a representative multi-species net fractionation factor may be appropriate for paleohydrologic reconstructions (Feakins and Sessions, 2010). Modern vegetation within the El’gygytgyn Basin includes 249 identified species and approximately an additional 100 rare species (Kohzenikov, 1993; Minyuk, 2005), yet, despite the small sample set, the seven species analysed here appear to largely represent the modern vegetation contribution to modern lake sediments.

In order to evaluate how representative these 7 species are of all vegetation within the basin, we calculated an average distribution of compounds from modern
vegetation samples assuming an equal weighting of all species to produce a representative assemblage of $n$-alkanoic acids within the El'gygytgyn Basin (Figure 2.11). This modern vegetation distribution pattern was then compared with an average distribution of compounds from modern sediments calculated from all four sediment core tops. The two patterns are similar although as expected there are discrepancies given the relatively small sample set and the modern floristic diversity within the basin. The modern vegetation distribution pattern appears particularly sensitive to input from Bryophyta, as it produces $nC_{28}$ acid almost exclusively in high concentrations. Reducing the contribution from Bryophyta from the overall modern vegetation pattern, results in a distribution similar to that observed in modern lake sediments. This may be because Bryophyta may not be a significant portion of overall plant biomass in the basin or alternatively may not be a major contributor of terrestrially sourced $n$-alkanoic acids to the lake. Additionally, *Salix arctica* and *Artemisia spp.* are abundant on El'gygytgyn slopes and modification of their proportional contributions produces a nearly identical distribution of compounds to modern lake sediments (Figure 2.11). Minor differences may certainly be attributed to and accounted for with the further inclusion and proportional representation of the remaining vegetation types and species. This preliminary survey suggests that although the proportional contributions of each species to the overall pattern may change, these six species (excluding Bryophyta) are generally representative of the overall production and input of even-chain $n$-alkanoic acids from modern vegetation to the lake basin.
The hydrogen isotope composition observed in sampled vegetation may also be representative basin-wide. The range of interspecies δD variability observed around Lake El'gygytgyn is within other published ranges (e.g. Chikaraishi and Naraoka, 2003; Liu and Huang, 2005; Sachse et al, 2006, Hou et al, 2007; Feakins and Sessions, 2010) although, these authors note that there is significant scatter at the level of individual plants across a wide range of climatic conditions. Some studies have linked δD values to life form (e.g. tree, shrub, and grass; Smith and Freeman, 2006; Liu et al., 2006; Liu and Yang, 2008) however, no clear evidence for this was found in our study. Yet, despite a large spread between individuals, catchment scale average δD values generally do seem to reliably record the climate conditions of the region (e.g. Huang et al., 2004; Sachse et al., 2004; Feakins and Sessions, 2010) thereby allowing for a constant offset to be used for paleoenvironmental reconstructions.

Our calculated εwax/w values (Table 2.2) are also within published ranges (Liu and Yang, 2008 and references therein) with an overall average net fractionation between modern vegetation and stream water (εwax/streams) of -116.0 ± 12‰. However, this assumes that the source water available for plant uptake is directly represented by streams in the El'gygytgyn Basin (i.e. δw = δstreams). Average net fractionation between modern vegetation and annual average precipitation (εwax/precip) is slightly more positive (-107.0± 12‰). These values are similar to average net fractionations of -99 ± 8‰ reported from a North American transect of C28 n-alkanoic acids (Hou et al., 2008) and -94 ± 21‰ from long chain (C27, C29 and C31) n-alkanes in arid to semi-arid ecosystems (Feakins and Sessions, 2010). In a
global compilation, Liu and Yang (2008) report a high latitude effect with smaller $\varepsilon_{\text{wax}/w}$ values for woody plants versus grasses at high latitudes. Within the El'gygytgyn Basin, *Salix* and *Poaceae* comprise the dominant woody and non-woody taxa respectively (Minyuk, 2005; Lozhkin et al., 2007). We find no clear evidence of D/H fractionations related to life form and although limited, our data instead agrees with the average multi-species net fractionation ($-94\% \pm 21\%$) found by Feakins and Sessions (2010), despite the lack of grasses in their dataset. Both net fractionations ($\varepsilon_{\text{wax}/\text{streams}}$ and $\varepsilon_{\text{wax}/\text{precip}}$) determined here are very similar.

However, potential changes in the seasonality of precipitation and Arctic summer productivity (i.e. timing of biosynthesis with respect to peak snowmelt and runoff) suggests caution in application of $\varepsilon_{\text{wax}/\text{streams}}$ in paleohydrological reconstructions. These values could also be affected by inclusion of more plant samples and species given the large range of known $\delta$D diversity between individuals and the small sample set used here. Nevertheless, these results contribute towards establishing a constant net fractionation factor for arid environments and provide the basis for paleoclimatic reconstructions from sedimentary records of $\delta D_{\text{wax}}$.

### 2.6.2.2 Sediment traps

The abundances and distribution of compounds produced by vegetation directly affects the integrated signal captured in lake sediments and, thus, any sedimentary isotopic signature could be complicated by the inclusion of compounds from multiple sources with differing isotopic composition. Parallel compound-specific $\delta^{13}$C analysis shows that within El'gygytgyn sediments, $nC_{30}$ acid derives
from a strictly terrestrial source while other even long chain \( n \)-alkanoic acids derive from a mixed terrestrial and aquatic source (Wilkie et al, *in prep*; Holland et al., *in prep*). This same study further shows that \( nC_{20} \) and \( nC_{22} \) acids likely derive from an aquatic source, however production of these compounds in modern vegetation (*this study, see above*) initially suggests some contribution of a terrestrial source of these compounds to lake sediments. This explicitly requires intact delivery of these terrestrial sourced compounds to the lake bottom. Our results show the abundances of these compounds vary with depth in the water column, suggesting multiple processes in the water column influencing the ultimately integrated signal captured in lake sediments.

Even short chain \( n \)-alkanoic acids (e.g. \( nC_{14} \) – \( nC_{22} \)) typically produced by phytoplankton and/or bacteria (Cranwell et al., 1987; Gong and Hollander, 1997), are more labile and subject to rapid turnover in the water column (Lee et al., 2004; Jones et al 2008). Thus, the observed trend in \( nC_{20} \) acid is consistent with aquatic production in the upper surface waters and degradation with depth. Combined terrestrial inputs and aquatic production of even chain \( nC_{20} \) – \( C_{26} \) acids likely contributes a higher proportion of these compounds to surface waters, while the sharp decline by 50 m depth could reflect early degradation of the more labile shorter chain \( nC_{22} \) acid. Although \( nC_{24} \) and \( nC_{26} \) acids are typically attributed to terrestrial sources, some aquatic production (i.e. subaquatic/ floating macrophytes and filamentous algae similar to those observed in El’gygytgyn streams and lagoons; Figure 4.4) of these mid-chain fatty acids has been reported (Cranwell et al 1987; Ficken et al., 2000).
Relative abundances of \textit{nC}24 and \textit{nC}26 acids increase in the deepest water column sample, exceeding values observed in upper surface waters. This suggests either additional input at depth (e.g. delivery of terrestrial material from dense hyperpycnal flows from warming moat and lagoon waters), autochthonous production at intermediate to lower depths in the water column (>90 m water depth), and/or advantageous capture of a sinking organic debris entrained in and subsequently released by melting snow and lake ice. However, delivery of terrestrial sourced \textit{C}24 and \textit{C}26 acids by hyperpycnal flows is unlikely as this would also result in a concomitant increase in concentrations and relative proportions of \textit{nC}28 and \textit{nC}30 acids. While we cannot rule out autochthonous preferential production of \textit{nC}24 and \textit{nC}26 acids below 90 m water depth, capture of previously ice entrained sinking organic debris seems likely during the period of sediment trap deployment (late May to mid-July). Substantial lake ice persisted for most of the trap deployment, with extensive ice melting, development of leads and moat formation occurring throughout sample collection (Figure 2.9). Ice rafted fatty acids (IRFAs), possibly entrained during the previous fall freeze and accumulated over winter through aeolian deposition on lake snow and ice, would be released to the water column sporadically during lake ice melt and breakup. These settling plumes of IRFAs could explain the increase in total concentrations of all fatty acids at 90 m water depth, while shifting proportions with depth could reflect variable melt and release times of the ice over the site. The isotopic ratios of these IRFAs would still reflect their original biological sources regardless of transport and ice residence times though the signal from compounds of both aquatic and terrestrial sources
would be obscured. Further deployment and study of time-series sediment traps is required to fully assess modern water column processes and contributions to lake floor sediments.

2.6.2.3 Lake sediments

Lake sediments represent an integrated signal from the watershed and the carboxylic acids within them typically originate from multiple sources (Meyers, 2003). Concentrations of fatty acids in core top sediments increase exponentially towards the deepest part of the basin consistent with greater accommodation space and lower sediment supply resulting in less dilution of the organic signal. An age model developed on the deepest core from the central part of the lake (LZ1024, 170m water depth) yields an age of 200 yrs for the upper 0-1 cm. This resolution for the lake surface sediments means seasonal to interannual variations are lost and the ‘modern’ sediments are an integrated average of climate and deposition for the last 200 yrs. The consistent distribution of compounds across surface sediment samples regardless of water depth confirms a catchment-integrated organic signal reaching the lake bottom. Thus, the climatic signal from leaf waxes in lake surface sediments is a combined average for all vegetation changes in the catchment in the last 200 years (i.e. molecular abundances). Additionally, the sedimentary δD_wax also represents an integrated signal of precipitation for the last 200 years. Long-term δD_p records are lacking at this site, however the reconstructed estimates of δD_p from the northern Yakutia δ^{18}O_cellulose record (Sidorova et al., 2008) yields a 97-year average reconstructed δD_p of about -147‰. Net fractionations between core top
sediment and either streams (-100.8 ± 5.0‰) or precipitation (-94.5 ± 5.0‰) closely agree with $\varepsilon_{\text{wax/w}}$ values from modern vegetation (streams: $\varepsilon_{\text{wax/streams}} = -116.0 \pm 12‰$; precipitation: $\varepsilon_{\text{wax/precip}} = -107.4 \pm 12‰$). Calculation of these values inherently applies present day input to a time-integrated signal yet recalculation with the derived time-averaged $\delta D_p$ still yields near identical net fractionation values ($\sim -100‰$).

### 2.7 Conclusions

This study provides a detailed assessment of the stable isotopic composition of modern hydrology within the El'gygytgyn Basin and the controls on the $\delta D$ signature from plant leaf waxes within the El'gygytgyn Basin. Our results suggest different source regions for winter and summer precipitation, characterized by an unaltered isotopic signature from a northern and eastern moisture source in winter and a south-southwest continental moisture source including recycled moisture from the land surface. LMWL determined within the El'gygytgyn Basin is consistent with other circumpolar regressions (Kurita et al., 2004; Lacelle, 2011), though the local spatial $\delta$-T relationships are lower than previously reported. However, evaporative enrichment is not a strong control on $\delta D_{\text{lake}}$ and the lake responds relatively quickly to large magnitude changes in $\delta D_p$. Changes in the length of the residence time are reflected in the degree of dampening of the $\delta D_p$ driven signal, with longer residence times averaging out shorter term (e.g. decadal) changes. Inflow from streams in the basin represent soil water ($\delta_{\text{soil water}} = \delta_{\text{streams}}$) that is annually recharged by snowmelt, drained rapidly and relatively unaffected by
summer precipitation events. Enhanced evaporative enrichment on S-facing slopes causes $\delta_{\text{streams}}$ to more closely reflect annual average $\delta D_p$. Plants utilize waters this water within the active layer so $\delta D_{\text{wax}}$ should reflect $\delta_{\text{streams}}$. However, large interspecies variability and potential changes in seasonality of precipitation suggest caution in applying $\varepsilon_{\text{wax/streams}}$ in paleohydrological reconstructions. Therefore, it may be more prudent to use $\varepsilon_{\text{wax/precip}}$ for paleohydrological reconstructions (both values are within 1σ and agree with previously published ranges). Differences between samples are more likely due to randomly distributed net fractionations rather than a systematic offset between woody vs. grass samples (as predicted for high latitudes). However, larger sample sets including more species and multiple individuals within each genus are needed. In modern lake sediments: $\varepsilon_{C_{30}/\text{precip}} = -94.5 \pm 5\%_0$ which is determined only from terrestrial sourced $nC_{30}$ acid and represents catchment wide integrated signal (200 years of all basin vegetation and $\delta D_p$). Utilizing reconstructed (~100 year average) $\delta D_p_{\text{cellulose}}$ to calculate net fractionations for 200 yr-integrated lake sediments yields $\varepsilon_{30/\text{precip}} = -96 \pm 8\%_0$. This time averaged $\varepsilon_{30/\text{precip}}$ value provides a robust net “apparent” fractionation to be used in future paleohydrological reconstructions.
2.8 References


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Figure 2.1: Location of Lake El'gygytgyn (red star) in NE Russia (from GeoMappApp.com).

Table 2.1: Mean values (δ¹⁸O, δD, d-excess) for H₂O sample sets.

<table>
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<th>H₂O sample sets</th>
<th>δ¹⁸O (‰) vs. VSMOW</th>
<th>δD (‰) vs. VSMOW</th>
<th>d excess</th>
<th>δ¹⁸O (‰) OIPC a</th>
<th>δD (‰) OIPC a</th>
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<td>-163 b</td>
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<td>Lake profiles</td>
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<td>-154.9</td>
<td>3.4</td>
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</tbody>
</table>

a 95% confidence interval of model values determined from the Online Isotopes in Precipitation Calculator (OIPC), version 2.2 (Bowen and Revenaugh, 2003).

b Arithmatic mean of OIPC modelled monthly values for Siberian winter months (November -April)

c Arithmatic mean of OIPC modelled monthly values for Siberian summer months (June-August)
Figure 2.2: Location of the sediment traps deployed in Lake El’gygytgyn in 2003, streams and the δD of sampled stream water. View to the NE with 5x vertical exaggeration. Dots indicate measured δD of stream waters collected summer 2003. Red line denotes watershed, streams are indicated in light blue lines. Contours indicate lake bathymetry.
Figure 2.3: Isotopic response of the lake water to changes in residence time and variable $\delta D_p$ of input (precipitation). Pink line denotes reconstructed $\delta D$ of precipitation from $\delta^{18}O_{\text{cellulose}}$ (Sidorova et al., 2008) based on Anderson et al. (2002). Blue curves show modeled response of $\delta D_{\text{lake}}$ with various residence times (10, 50, 100 and 300 years).

Figure 2.4: $\delta^{18}O$/$\delta D$ bi-plot of H2O samples from modern precipitation (snow, rain), streams, lake water profiles, surface waters, and ice cover.
Figure 2.5: Relationship between $\delta^{18}$O and $\delta D$ of precipitation with temperature within the El'gygytgyn Basin.
Figure 2.6: Hydrogen isotope composition of water from Lake El’gygytgyn at various depths, sampled in different months (May and August, 2003; November 2008).

Figure 2.7: Concentrations and δD values of n-alkanoic acids measured in modern vegetation samples from within the El’gygytgyn Basin.
Figure 2.8: Concentrations of $n$-alkanoic acids with water column depth in sediment traps and lake surface sediments (note log scale). $\delta^{18}D_{\text{wax}}$ values are plotted for lake surface sediments only as concentrations of $n$-alkanoic acids in sediment traps were insufficient for compound-specific $\delta D$ analysis.
Table 2: Concentrations and δD values for selected n-alkanoic acids with the El’gygytgyn Basin

| Sample                      | Concentration (ug/g TLE) | ACL* | δD<sub>29</sub> | δD<sub>22</sub> | δD<sub>24</sub> | δD<sub>26</sub> | δD<sub>28</sub> | δD<sub>30</sub> | δD<sub>Δmax</sub> | ε<sub>C30/w</sub> | ε<sub>Δmax/w</sub> |
|-----------------------------|--------------------------|------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|
| Rumex sp.                   | 6.7 16.6 28.2 28.1 66.4 46.8 | 27   | -247.5 -262.6 -258.5 -263.1 -262.4 | -259.3 -260.5 | -134.0 -125.6 | -135.4 -127.0 |
| Saxifrage                   | 19.6 17.8 45.1 13.6 13.9 29.2 | 25   | -226.1 -229.6 -227.5 | -99.3 -90.6 | -96.8 -88.1 |
| Douglasia ochotensis        | 18.4 34.8 91.4 61.6 96.4 111.6 | 26   | -244.7 -234.1 -242.0 -243.3 -248.9 | -244.0 -243.8 | -116.1 -107.5 | -115.8 -107.3 |
| Poacea                      | 18.0 32.1 35.7 72.5 23.6 10.2 | 25   | -236.6 -236.3 -256.1 -238.6 | -245.4 | -117.8 -109.3 |
| Artemisia                   | 7.5 19.1 21.6 7.3 7.9 2.6  | 24   | -224.8 -245.7 -249.2 -253.3 -256.9 | -242.0 -246.5 | -113.7 -105.2 | -119.0 -110.5 |
| Bryophyta                   | 3.2 6.1 71.2 3.9 3.3 27    | 27   | -258.8 -245.4      | -117.7 -109.2 |
| Salix arctica               | 29.4 63.1 111.2 178.9 131.6 15.0 | 25   | -219.4 -222.8 -227.5 -247.2 -247.4 | -236.0 -238.3 | -106.8 -96.2 | -109.5 -100.8 |
| AVERAGE                     |                          |      | -242.2 -243.9 -114.0 -105.4 | -116.0 -107.4 |
| Sediment trap 30m water depth| 14.3 20.6 21.4 15.4 7.9 7.2 | 24   |                         |                  |
| Sediment trap 50m water depth | 8.2 8.7 10.2 8.1 4.3 5.6 | 24   |                         |                  |
| Sediment trap 90m water depth | 23.5 41.9 30.3 25.5 12.7 25.8 | 24   |                         |                  |
| Sediment trap 130m water depth | 6.0 7.7 4.7 3.5 4.2 25    | 25   |                         |                  |
| Sediment trap 146m water depth | 1.1 1.6 1.2 0.6 0.7 25 | 25   |                         |                  |
| Sediment water interface (0-1 cm) 159 m depth | 12.2 39.2 78.3 72.5 68.4 21.1 | 25   | -235.3 -246.2 -243.7 -241.6 -245 | -238.5 -243.0 | -107.2 -101.0 | -114.9 -106.4 |
| Sediment water interface (0-1 cm) 168 m depth | 136.6 412.0 818.3 776.6 626.8 230.1 | 25   | -253.2 -242.7 -236.1 -235.5 -236.8 | -228.2 -237.2 | -95.2 -88.9 | -108.1 -99.5 |
| Sediment water interface (0-1 cm) 170m depth | 1340.7 4273.0 9016.1 8819.4 7488.4 2660.2 | 25   | -254.5 -249.5 -239.1 -242.3 -243.5 | -232.8 -242.0 | -100.6 -94.3 | -113.8 -105.2 |
| Sediment core top (0-2 cm) LZ1024 170 m depth | 1879.8 5585.9 11258.1 10564.1 9172.4 3215.6 | 25   | -245.8 -244.1 -234.4 -231.1 -232.4 | -232.4 -234.8 | -100.2 -93.9 | -105.3 -96.7 |
| AVERAGE                     |                          |      | -233.0 -239.2 -100.8 | -94.5 -110.5 | -101.9 |

*ACL= Average Chain Length as defined in text.
Figure 2.9: Concentrations of $n$-alkanoic acids normalized to total yield of $n$-alkanoic acids by water column depth in Lake El'gygytgyn. b) Large moat formed by ice melt 500 m to the north of the southern shore on June 17, 2003 - approximately 1/3 way through sediment trap deployment. (From Melles et al., 2005). Note extent of snow and lake ice cover during typical summer month. C) Sediment traps deployed May 31, 2003 and recovered July 19, 2003. (From Melles et al., 2005).

Figure 2.10: Conceptual diagram of major factors controlling the modern isotope hydrology at Lake El’gygytgyn.
Figure 2.11: Average distribution of $n$-alkanoic acids from modern vegetation within the El'gygytgyn Basin (far left) and in core top sediments (far right). Modeled distributions are shown with varying proportions of vegetation species. Compounds are normalized to total yield of $n$-alkanoic acids.
CHAPTER 3
CONTINUOUS TERRESTRIAL ARCTIC RECORD OF RECONSTRUCTED PALEOTEMPERATURE 120KA TO PRESENT, LAKE EL’GYGYTGYN, NE RUSSIA

3.1 Abstract

Analysis of the hydrogen isotopic ratio (δD) of specific organic biomarkers allows reconstruction of past hydrological conditions, thereby providing a powerful tool for reconstructing past Arctic climate changes. However long millennial scale terrestrial paleoclimate archives that span multiple interglacials are rare in the Arctic due to widespread glacial erosion. Here we present the first continuous, high fidelity continental record of reconstructed δD in precipitation from terrestrial plant leaf waxes in the High Arctic spanning the last 120,000 years. Our data show a high latitude northern hemisphere signal that is in phase with Antarctic climate records and leads other northern hemisphere climate records. Data suggest that synoptic scale atmospheric circulation changes driven by northern hemisphere summer insolation and variability in sea surface temperatures may be the mechanism for propagating climatic changes from high to low latitudes.

3.2 Introduction

The Arctic is currently undergoing widespread and rapid environmental transformations (ACIA, 2005; IPCC, 2007), yet the diverse terrain, sparse coverage and incomplete high latitude monitoring networks have hampered our capacity to understand the role of this important region in global climate change (Fitzpatrick et
The unique sensitivity of the Arctic region to the effects of global climate change is expressed through strong feedback mechanisms involving marine, atmospheric, cyrosphere and terrestrial processes, making the paleoclimatic history of this region especially informative (IPCC, 2007; Manabe and Stouffer, 1980; Serreze et al., 2009; Hansen et al., 2006; Miller et al, 2010a; White et al., 2010). Variations in hydrological processes in the Arctic have major implications not only for arctic terrestrial and marine ecosystems, but also for the cryosphere and global ocean dynamics (ACIA, 2005; Miller et al., 2010b).

Reconstructing past Arctic climates helps to reveal key processes of climate change, including the response to elevated greenhouse-gas concentrations, and provides insights into future climate behaviour (Miller et al., 2010b). Paleoclimate proxy records provide opportunities to place recent Arctic warming within a longer term context to better understand the potential for future climate changes (Fitzpatrick et al., 2010; Miller et al., 2010a,b; White et al., 2010).

Terrestrial paleoclimate archives are rare in the Arctic due to widespread glacial erosion yet recognizing the regionalization of climate change (past and future) highlights the critical need for these long-term continental archives. Proxy data gathered from dispersed, regionally available continental settings can “fill in the gaps” and potentially capture regional feedbacks and validate expected spatial variability to hemispheric forcings. Analysis of the isotopic signal recorded in terrestrial archives from low to high latitudes can provide opportunities to trace feedbacks and processes involved in Arctic amplification and assess its contribution to global average temperature change (IPCC, 2007; Sturm et al., 2010; Miller et al,
Stable isotope data from lipid biomarkers recovered from lake sediment cores provides a powerful tool to reconstruct hydrologic and biogeochemical processes within continental settings. Lake El’gygytgyn in NE Russia is uniquely located within an unglaciated basin, thereby permitting the continued deposition of sediment throughout glacial-interglacial cycles. Compound specific hydrogen isotopic analysis of leaf wax lipids from El’gygytgyn sediments offers the opportunity to constrain the timing and magnitude of continental climatic changes in the Arctic.

Previous work has shown that the hydrogen isotope ratios from long-chain leaf wax lipids reflect the stable isotopic composition of annual precipitation within the El’gygytgyn Basin (Wilkie et al., in prep; Sachse et al., 2004; Sachse et al., 2006; Huang et al., 2004; Hou et al., 2008). Long-chain even carbon-numbered n-alkanoic acids (e.g. >24 carbon chain length) typically originate from leaf waxes of terrestrial plants (Eglinton and Hamilton, 1967; Cranwell et al., 1987). At Lake El’gygytgyn, sedimentary C$_{30}$ n-alkanoic acids derive from a solely terrestrial source (Holland et al., in prep) and their hydrogen isotope ratios ($\delta$D$_{30}$) are representative of integrated catchment-scale $\delta$D values for terrestrial leaf waxes (Wilkie et al., in prep). Changes in $\delta$D$_{30}$ values reflect changes in the isotopic composition of the source water (i.e. precipitation), with potential enrichment due to evaporation from soils (Smith and Freeman, 2006) and evapotranspiration from leaves (Sachse et al., 2004), which amplify the recorded signal in arid environments (Feakins and Sessions, 2010; Schefuß et al 2005). In high latitudes regions, depleted isotopic compositions of precipitation are strongly related to lower air temperatures (Dansgaard, 1964,
Jouzel et al., 1997); however, they can also be influenced by proximity to moisture sources (such as continentality and sea level changes) and trajectories of weather systems (Gat, 1996).

3.2 Methods

3.2.1 Location, climatic setting and chronology

To provide more insight into the nature of terrestrial Arctic climatic change and climatic forcing of hydrology, we present a reconstruction of precipitation changes in the El’gygytgyn basin in continental NE Russia. Lake El’gygytgyn is located in within a 3.58 ± 0.04 Ma old meteorite crater (Layer, 2000) in a previously unglaciated region of northeastern Siberia (67° 30’N, 172° 05’E; Glushkova and Smirnov, 2007). Elevations of the crater rim vary between 600 and 930 m, while the lake surface lies at 492 m above sea level. The crater is approximately 18 km in diameter with a total watershed area of 293 km² (110 km² is lake surface) and the lake is 12 km wide and 175 m deep with a volume of 14.1 km³ (Nolan and Brigham-Grette, 2007). Water temperatures in this cold monomictic, ultra oligotrophic lake are <4°C and the lake is fed by 50 streams draining from the crater rim (Cremer et al., 2005; Nolan and Brigham-Grette, 2007). Mean annual air temperature measured from 2002-2008 was -10.4°C and total precipitation rose from 35 cm a⁻¹ to about 55 cm a⁻¹ over this period with roughly equal rates between winter and summer precipitation (Nolan and Brigham-Grette, 2007; Nolan et al., in prep).

Chronological control has been determined elsewhere (Nowackyk et al., 2007; Frank et al., in prep). In brief, an age model was derived by tuning the
magnetic susceptibility record from core LZ1024 to northern hemisphere insolation, supported by the biogenic silica, total organic carbon (TOC) and TiO2 records as well as OSL dates from a well correlated sister core (Nowaczyk et al., 2002; Forman et al., 2007; Nowaczyk et al., 2007), yielding an age of 350 ka for the base of the 16.6 m long LZ1024 core (Frank et al., in prep). On the basis of our chronology, the upper 5.3 m of core LZ1024 corresponds to the last 120 ka. The average time resolution between the 170 samples is 400 years.

### 3.2.2 Analytical methods

Samples were freeze-dried, crushed and stored in combusted glassware. Soluble organic matter was extracted using an accelerated solvent extractor (ASE200, Dionex Corp., Sunnyvale, USA) with a dichloromethane/methanol mixture (9:1) at 100°C and 1200 psi for three 15-min cycles. Given the relatively low amount of organic C in the samples (Melles et al., unpublished), the maximum amount of sediment available was used (between ~7 g - 12 g dry sediment). The total lipid extract (TLE) was separated into neutral and carboxylic acid fractions on a solid phase extraction (SPE) column containing ~0.5 g of DSC-NH₂ stationary phase (Supelco). A neutral fraction was eluted with 4 ml hexane:DCM (1:1) and archived for future analysis. Fatty acids eluted with 8 ml of 2% formic acid in DCM and were subsequently derivatized as methyl esters (FAME) with BF₃:MeOH. Compounds (i.e. FAMES) were identified and quantified using a Hewlett Packard 6890 series gas chromatograph – mass selective detector (GC-MSD) and a Hewlett Packard 6890 series gas chromatograph – flame ionization detector (GC-FID),
respectively, and with comparisons to external standard mixtures. Both the GC-MSD and GCFID were equipped with 5% phenyl methyl siloxane columns (30m x 0.25mm i.d., film thickness 0.25μm). The GC oven temperature programs were also identical for both instruments: 60 °C (2 min), 15 °C/min to 315 °C (15 min) with helium as the carrier gas and the inlet temperature set at 320°C.

The δD of individual lipids were determined at the ESCSIS facility at Yale University using a Thermo Finnigan MAT 253 mass spectrometer with a gas chromatograph combustion interface (GCC) with a high-temperature pyrolysis furnace operated at 1440°C (Hilkert et al., 1999) coupled with a Thermo TraceGC GC-MS equipped with a DB5ms column (30m, ID:0.32 mm, film thickness: 0.5 μm, Agilent). The gas chromatography (GC) temperature program was: 80 °C (2 min) to 120 °C at 12 °C/min and then to 320 °C at 6°C/min (held 16 min). For δD analysis, each sample was analysed in triplicate and the H3+ factor was determined daily prior to standard calibration and sample analysis. The results are reported using standard delta notation (i.e. δD values) in permil (‰) units. Isotope ratios were normalized relative to a co-injected standard mixture containing C14 n-alkane to condition the furnace and C15 and C38 n-alkanes as compounds of known isotopic values (obtained from A. Schimmelmann, Indiana University). Instrument performance was also determined daily by measuring a suite of 5 FAMEs with a co-injected standard mixture (nC14, nC15, nC38) of known isotopic values. The mean precision for replicate analyses of the standard compounds was typically better than 5‰ (1σ).
3.2.3 Data handling and calculations

3.2.3.1 Isotope mass balance correction

Fatty acid δD values were measured on methyl ester derivatives. Three different production lots of BF$_3$MeOH were used over the course of this study. Aliquots from each lot number were used to derivitize a $n$-C$_{14}$ fatty acid standard to calculate the δD contribution from the three H atoms added during the methylation reaction with BF$_3$ in MeOH. The bulk δD of the $n$-C$_{14}$ fatty acid standard (-240.4‰ ± 1.5‰; n= 5) was determined prior to derivitization offline by Thermal Conversion Elemental Analysis (TCEA, ESCSIS Yale University). The nC$_{14}$ acid standard derivitized with each lot number was measured in triplicate to yield an average δD value for the methyl contribution from the derivitization agent (Table 3.1). These values were used to correct the measured δD values of fatty acid methyl esters for the added hydrogen atoms by mass balance.

3.2.3.2 Application of net “apparent” fractionations

Reconstruction of the past δD of precipitation ($\delta$D$_{\text{recon ppt}}$) relies on a constant net (apparent) fractionation between source water and leaf wax lipids within the El’gygytgyn watershed (-97 ± 6‰; Wilkie et al, in prep). Application of this net fractionation value to 170 samples downcore yields a reconstruction of the hydrogen isotope composition of annual precipitation ($\delta$D$_{\text{recon ppt}}$) spanning the last 120 ka. However, potential bias towards winter precipitation exists as the water available for plant uptake, source water, is directly represented by streams dominated by winter snowmelt in the El’gygytgyn Basin (Wilkie et al., in prep; Nolan
et al., in prep). Changing seasonal distribution of precipitation or large shifts in vegetation types may affect the net fractionation value and thus values of reconstructed δD of precipitation.

Now we can use the reconstructed δD of precipitation to estimate annual temperatures due to the strong relationship between mean annual temperature and the stable isotopic composition of precipitation at high latitudes. Estimates of mean annual air temperature were calculated using the empirically derived spatial relationship (δD=5.2T - 106.5; Kurita et al., 2004) for Russia.

3.3 Results

Here we show the first long terrestrial High Arctic record of reconstructed δD of precipitation from leaf wax lipids (Figure 3.1). δD_{recon ppt} values range from -112‰ to -202‰ (vs VSMOW) showing large amplitude variability over glacial-interglacial cycles and closely track orbitally induced Northern Hemisphere (NH) summer insolation at 65°N (Laskar et al., 2004). Transitions are sharp, similar to Chinese speleothem records, with more frequent Dansgaard-Oeschger (D-O) like events during stable climate states. Most depleted values occurred from 16.5 ka to 25.1 ka corresponding to Marine Isotope Stage (MIS) 2, from 66.8 ka to 71.0 ka corresponding to MIS 4 and from 88.7 ka and from 111.6 ka to 114.7 ka corresponding to MIS 5b and 5d, respectively (Figure 3.1). The record also shows depleted values at 12.2 ka corresponding to the Younger Dryas following a brief increase at ~16 ka possibly corresponding to the Antarctic Cold Reversal (ARC). δD_{recon ppt} values increased (up to -112‰) between 6 ka and 9.5 ka suggesting the
presence of a previously unidentified Holocene Thermal Maximum signal (Kaufman et al., 2004) in Lake El’gygytgyn sediments (Shilo et al., 2001). A step-like transition occurs within MIS 3, between two quasi-stable modes at ~45 ka, coincident with changing NH insolation and possibly corresponding to a large ice shelf advance in Kamchatka and into the Sea of Oskhosk (Nürnberg et al., 2011). Interglacial periods are characterized by higher $\delta D_{\text{recon ppt}}$ values, however values during the last interglacial (MIS 5e) are lower than Holocene or modern values.

Comparison of the El’gygytgyn $\delta D_{\text{recon ppt}}$ record with other global precipitation records shows strong visual similarities between the records (Figure 3.1). Cross correlation of the El’gygytgyn $\delta D_{\text{recon ppt}}$ record and the EPICA Dome C $\delta D$ record (Jouzel et al., 2007), show highest values ($r = 0.79$) with zero lag (Figure 3.2) suggesting that eastern Beringian climate responds in phase with Antarctic records. Similarly high cross correlation values ($r = 0.77$) between the El’gygytgyn $\delta D_{\text{recon ppt}}$ record and global sea level reconstructions (Rohling et al., 2009a) are also apparent and appear in phase (Figure 3.2). Cross correlation values between the El’gygytgyn $\delta D_{\text{recon ppt}}$ and NGRIP $d^{18}O$ records are lower ($r = 0.68$) with the Greenland record broadly lagging El’gygytgyn $\delta D_{\text{recon ppt}}$ by up to 2 ka. Likewise, Sanbao/ Hulu Cave $d^{18}O$ records also lag the El’gygytgyn $d_{\text{recon ppt}}$ record by ~1500 yrs (Figure 3.2) though the records are less well correlated ($r = 0.42$).

Mean annual surface temperatures were calculated from $\delta D_{\text{recon ppt}}$ values based on the spatial $dD$-$T$ relationship as defined by Kurita et al., (2004):

$$\delta D = 5.2 \, T_{\text{annual}} - 106.5 \quad (R^2 = 0.89)$$
Temperature estimates range from -1°C to -18°C over the last 120 ka. Average reconstructed Holocene temperatures (11.5 ka to present) were -4.1°C. Peak temperatures occurred during the HTM at 7 ka while the lowest temperatures in the record occurred at 23.7 ka during the Last Glacial Maximum (LGM). Estimated temperatures during the last interglacial (MIS 5.5) were similar to present although further analyses and extension of the El’gygytgyn δD_{recon ppt} record may be needed to capture the full range of variability in the last interglacial. The magnitude of temperature change at Lake El’gygytgyn (i.e. ΔT = 17°C) is slightly higher than the Mangshan loess plateau temperature reconstructions (ΔT = 14°C) and cross correlation analysis shows the records are highly correlated (r = 0.92) and in phase (Figure 3.2).

3.4 Discussion

The nature and timing of continental records of climate change are important for understanding teleconnections and mechanisms of past climate changes. Visual inspection of the El’gygytgyn δD record with other global climate records reveals a pervasive Antarctic signal at this high northern latitude that is parallel in timing with other continental and Antarctic records. This is supported by a lead/lag analysis between the various records (Figure 3.2). Our data show a high latitude northern hemisphere signal that is in phase with Antarctic climate records and leads (lags) other northern hemisphere climate records (i.e. NGRIP δ^{18}O record).

The El’gygytgyn δD_{recon ppt} closely follows NH summer insolation, suggesting that if the bipolar seesaw is driven by NH insolation and the isotopic signature of
precipitation reflects temperature at this latitude, then El'gygytgyn records should also lead Antarctic records (i.e. be in phase with Greenland records). That is, according to the bipolar seesaw model, one would expect better coherence and timing between other NH records and Lake El'gygytgyn and Greenland records should be in phase. However, the El'gygytgyn $\delta D_{\text{recon ppt}}$ record leads Greenland and Chinese speleothem records by $\sim 1.5$ to 2 ka. These leads could be due to inherent flaws in the event stratigraphy or a change in seasonality of the proxy signal. The discrepancy with the Greenland record is surprising given the high northern latitude of both locations, yet previous studies have described bias due to changing seasonality of precipitation in the isotopic temperature record in Greenland (Werner et al., 2000; Jouzel et al., 2003). Although both records are driven by NH insolation, perhaps the observed lag is associated with shifting global patterns of cyclogenesis and seasonality of precipitation (Figure 3.3). Significant reductions in Atlantic cyclogenesis and stronger Pacific cyclogenesis lead to low effective moisture transport and wintertime accumulation on the Greenland ice sheet during the LGM, resulting in a bias towards a summer precipitation signal during glacial intervals (Werner et al., 2000; Unterman et al., 2011). In contrast, the $\delta D$ signal in leaf waxes consistently reflects the mean annual isotopic composition of precipitation (Hou et al., 2008; Tierney et al., 2008; Feakins and Sessions, 2010).

Within the El'gygytgyn basin, seasonality effects are limited as winter snowmelt and summer precipitation yield an integrated source water signal for plants within the short High Arctic growing season (Wilkie et al., in prep; Nolan et al., in prep) with any potential bias targeted towards a winter precipitation signal.
Coeval timing of the El’gygytgyn $\delta^{13}D_{\text{recon ppt}}$ and continental air temperatures over the loess plateau, southeast Africa and Antarctica suggests globally pervasive common mechanism linking these sites. Assuming our lake chronology is correct, this suggests that El’gygytgyn precipitation reflects continental temperatures with atmospheric teleconnections linking high and low latitudes.

Our reconstructed El’gygytgyn record also reveals that temperature changes developed in phase with NH summer insolation throughout the record and that atmospheric warming occurs in phase with Antarctica. Recently, Laebelle et al. (2011) have produced an accumulation-weighted insolation signal as a temperature record in Antarctic ice cores that is in phase with summer insolation intensity in the NH. Our results show a 17°C temperature change over the last glacial-interglacial transition. The magnitude and timing of the temperature change at Lake El’gygytgyn is highly similar to the 20°C temperature change suggested by borehole temperatures (Johnsen et al., 1995; Cuffey et al., 1995) and gas diffusion thermometry (Severinghaus et al., 1999) in Greenland ice cores, as well as the continental air temperature record provided by the MBT/CBT proxy (derived from fossil branched tetraether membrane lipids from soil bacteria) from the Mangshan loess plateau (Peterse et al., 2011). The proxy air temperature record derived there is decoupled from the other climatic indicators and speleothem records with air temperatures leading precipitation changes (Peterse et al., 2011). Comparison of the reconstructed El’gygytgyn record with the independently dated speleothem $\delta^{18}O$ records from Sanbao and Hulu caves also shows a lag of East Asian summer monsoon (EASM) to increasing temperatures at this high latitude site. Previous
authors have also noted a better correlation of these Chinese speleothem records with Antarctic temperature (Rohling et al., 2009b; Barker and Knorr, 2007). Likewise, similar lags in Africa have been reported where deglacial warming after the LGM seems to coincide with temperature increase in Antarctic but where the onset of increasing precipitation matches with NH climatic changes (Gasse, 2000; Tierney et al., 2008). Our data suggest that the factors controlling atmospheric warming in these regions are pervasive and global in scale. We propose that our record corresponds well with the MBT/CBT records through synoptic scale atmospheric circulation patterns driving these signals at these sites.

Calculated temperatures for the upper (0-2 cm) lake core sediments are warmer than the present day mean annual air temperatures (-10.4°C; Nolan et al, in prep), although these upper lake sediments represent a 400 yr integrated average deposition that may not directly correspond with the most recent 8 yr meteorological data. Alternatively, this discrepancy reflects the combined influence of temperature and moisture source on the dD of precipitation. Although sea level and continentality have not varied significantly in the last 400 years, decadal variability in storm track trajectories and delivery of moisture through variations in the position and strength of the Aleutian Low (the dominant atmospheric pressure system in this region) may have impacted the resulting precipitation signal over Lake El’gygytgyn.

Global sea level reconstructions are also highly correlated and in phase with our record though the original sea level data were shifted by ~2 ka as discussed in Rohling et al. (2009a). Lower sea levels during glacial intervals would have a
lowering effect on the isotope ratios of precipitation through the increase in continence and exposure of the Bering Land Bridge (Brigham-Grette, 2001). Although the greatest change in sea level and exposure of continental shelf lies to the east of northern Chukotka, cyclonic flow associated with the synoptic scale Aleutian Low means that moisture source trajectories track counter-clockwise over this new land mass (e.g. Unterman et al., 2011) before delivery of moisture at El’gygytgyn. In addition, sea ice cover in the Bering Sea during glacial periods (Katsuki and Takahashi, 2005; Caissie et al., 2010) would further contribute to longer atmospheric vapour transport trajectories and lower isotope ratios of precipitation. This combined effect with lower temperatures during these periods may account in part for the greater amplitude of change in the El’gygytgyn δD record.

Questions remain to be addressed as to why a precipitation signal, driven by synoptic scale atmospheric circulation and transport processes, appears to reflect a more Antarctic and marine-like circulation lag feature? One possible answer lies in the dominant atmospheric circulation feature operating over the North Pacific and extending over Lake El’gygytgyn: the Aleutian Low.

Modern synoptic climatology provides insight into large-scale atmospheric circulation patterns that may function as global teleconnections and drive paleoclimatic responses (Mock et al., 1998; Kurita et al., 2004; Kokorowski et al., 2008). The dominant synoptic scale atmospheric feature controlling present day delivery of winter precipitation to Lake El’gygytgyn is the strength and position of the Aleutian Low, whereas summer synoptic patterns bring warm continental air
from the south and west (Nolan et al., in prep; Wilkie et al., in prep). These patterns affect both the seasonal temperature change and the source of moisture delivery to Lake El’gygytgyn yielding decreasing precipitation isotope ratios with decreasing temperatures and along trajectories of atmospheric vapor transport.

Synoptic features (e.g. Aleutian Low, Siberian High) can create variable spatial patterns of climatic responses that have been previously used to explain Beringian paleoclimatic variability associated with the YD (Kokorowski et al., 2008). Variability in these synoptic scale patterns is driven by changes in the Atlantic meridional overturning circulation (AMOC) and shifting position of the Intertropical Convergence Zone (ITCZ). These synoptic controls and associated response of Beringian climate during the YD may serve as conceptual model for other past glacial (cold) periods. Climatic changes associated with the YD may have been transmitted to the westernmost regions of Beringia via changes in westerly atmospheric flow caused by cooling of North Atlantic sea surface temperature (SST) (Kokorowski et al., 2008; Nagashima et al., 2010). Indeed, SSTs control latent heat flux into the atmosphere and ocean-basin SST gradients influence large-scale atmospheric circulation patterns. Cooler North Atlantic SST results in stronger winter and weaker summer monsoonal circulation (Sun et al., 2011). The net result produced drier conditions in Asia (Sun et al., 2011) and colder land-surface temperatures (Cohen et al., 2001). Reduction in AMOC and cooler Atlantic SST would also have restricted the flow of moisture across Eurasia (Karabanov et al., 1998). This region is also the source of modern summer precipitation at Lake El’gygytgyn, delivering re-precipitated moisture from the Eurasian land surface to
the El’gygytgyn Basin (Kurita et al., 2004; Schwamborn et al., 2008; Wilkie et al., in prep). Past restrictions in moisture flow from this potential source would result in lower δD values of precipitation and even more arid conditions at Lake El’gygytgyn, particularly during summer. Additionally, lower sea levels and exposure of the Bering Land Bridge would increase continentality in winter, particularly with more extensive sea ice cover, contributing to even lower δD values. Synoptic scale simulations of mean total precipitation and surface winds during wintertime LGM show strong northerly flow over Lake El’gygytgyn, likely amplifying lower isotope ratios of precipitation through both lower temperatures and delivery from an extreme northerly moisture source.

3.5 Conclusions

Our results show the first continuous long terrestrial High Arctic record of reconstructed δD of precipitation from leaf wax lipids. This high fidelity record is highly correlated and in phase (similar in timing) with other globally dispersed continental records and Antarctic ice core records. The apparent lag between El’gygytgyn and Greenland and Chinese speleothem records, particularly during the LGM to Holocene transition, may result from a shift in synoptic scale circulation and hydrological controls (effective moisture delivery) during this transitional phase. Coherent phasing and similar magnitude of the El’gygytgyn record with Antarctic and other continental temperature records, supports interpretation of a strong temperature signal with the isotopic data; however, global sea level and trajectories of moisture transport may also have contributed to the precipitation isotopic signal.
Our data suggests a globally pervasive climatic signal, driven by NH summer insolation. Possible mechanisms linking high and low latitudes and variable spatial patterns of climatic responses include synoptic scale reorganization of atmospheric teleconnections.
3.6 References


Table 3.1: $\delta D$ values for the methyl contribution from derivitization agent (BF$_3$ in MeOH)

<table>
<thead>
<tr>
<th>Analysis</th>
<th>Lot #</th>
<th>$\delta D$ (vs VSMOW) (%)</th>
<th>Average $\delta D$ (vs VSMOW) (%)</th>
<th>st dev</th>
<th>$\delta D_{CH3}$ * (vs VSMOW) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C14FA std 1_A</td>
<td>68139</td>
<td>-231.5</td>
<td></td>
<td></td>
<td></td>
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* $\delta D_{CH3}$ calculated by: $\delta D_{CH3} = \frac{\delta D_{FAME} (# of H_{FAME}) - \delta D_{CH3} (# of H_{FA})}{(# of H_{FA})}$
Figure 3.1: Comparison of global climate records. (A) $\delta^{18}O$ records from Sanbao (orange; Wang et al., 2008), and Hulu Caves (brown; Wang et al., 2001). For comparison, the Hulu $\delta^{18}O$ record is plotted 1.6‰ more negative to account for the higher $\delta^{18}O$ values in the Hulu record compared to the Sanbao record (cf. Wang et al., 2008). (B) the North Greenland Ice Core Project (NGRIP) $\delta^{18}O$ record on the GICC05 timescale indicative of Greenland air temperature fluctuations (NGRIP dating group, 2006) (C) 3-point moving average MBT/CBT-derived air temperatures for the Mangshan loess plateau (Peterse et al., 2011) (D) the reconstructed $\delta$D of precipitation from leaf wax lipids record from Lake El’gygytgyn, NE Russia and summer insolation at 65°N (grey; Laskar et al., 2004) (E) the $\delta$D_{wax} record from Lake Tanganyika, SE Africa indicating past changes in aridity, (Tierney, et al. 2008) (F) 3-point moving average composite Red Sea relative sea-level reconstruction (RSL*) (Rohling et al., 2009) (F) the EPICA Dome C $\delta$D record indicative of Antarctic air temperature changes (Jouzel et al., 2007).
Figure 3.2: a) Cross correlation of El’gygytgyn $\delta D_{\text{recon ppt}}$ with other global climate records. b) Lead/lag correlations of El’gygytgyn $\delta D_{\text{recon ppt}}$ and Antarctic $\delta D$, NGRIP $\delta^{18}O$, Sanbao/Hulu cave $\delta^{18}O$ records and reconstructed continental air temperatures from Mangshan loess plateau, China (Peterse et al., 2011).
Figure 3.3: Synoptical scale circulation features and locations of sites discussed in text. Dots represent locations of Lake El’gygytgyn (orange), Mangshan loess plateau (red), Sanbao and Hulu caves (yellow), Lake Tanganyika (beige), Dome C EPICA ice core (blue), and NGRIP ice core (grey). Basemap © 2011 Google.
CHAPTER 4

CONCLUSIONS AND FUTURE WORK

4.1 Conclusions

Initial steps of this thesis included an investigation of the basic biogeochemistry of Lake El’gygytgyn sediments using a short 3m core taken in 2003 (core LZ1029; taken in the same location as PG1351). This work provided a sound base for applying organic geochemical tracers in the study of climate conditions at Lake El’gygytgyn. Samples collected from core LZ1029-7 established a high-resolution bulk organic carbon and bulk $\delta^{13}C_{\text{org}}$ record for the last 94 ka (2 cm sampling resolution; 139 samples). These records were then used to guide further sampling for organic geochemical analyses. Representative samples from this data set were also used to identify target compounds to be used in compound specific isotopic analysis of Lake El’gygytgyn sediments (both $\delta^{13}C$ and $\delta D$) (Holland et al., in prep; Wilkie et al., in prep). Additionally, these samples were also used to develop and streamline the analytical method to be used on smaller samples collected from longer sediment cores (e.g. LZ1024; new cores drilled in 2009).

Bulk organic carbon content of Lake El’gygytgyn sediments (% TOC) shows that glacial-interglacial transitions are accompanied by sharp increases in TOC, suggesting better preservation at times of colder climate and presumably increased ice cover. This interpretation was strengthened by analysis of the bulk $\delta^{13}C_{\text{org}}$ that also showed sharp fluctuations at glacial-interglacial transitions, with highly depleted values occurring during glacial intervals. These have been tentatively
interpreted as variations in the oxygenation of lake water due to changes in annual lake ice extent, with more ice resulting in decreased oxygenation, increased internal carbon cycling, sediment anoxia, abundant methane generation and methanotrophy. Fluctuations in the TOC and bulk $\delta^{13}$C$_{org}$ data were also used to generate tie points between other short surface cores (cores 1029-5/9/8) and the longer better dated 13m core PG1351 to develop an age model for the upper 3 m of sediment. The large shifts in these initial bulk $\delta^{13}$C data highlighted the need for more detailed investigation to identify the source of these fluctuations, thus work was undertaken to identify and separate the various contributions to this signal through additional compound specific $\delta^{13}$C analyses (Holland et al., in prep).

Compound specific hydrogen isotopes offer a wealth of data and insights into the hydrological cycle and in paleoclimate reconstructions. Yet in order to properly constrain and apply this proxy, we must first understand and quantify modern isotope systematics and hydrology. The second focus of this thesis was towards this goal through analysis of the $\delta$D and $\delta^{18}$O compositions of a modern suite of precipitation, stream and lake water and lake ice cover samples. Modern precipitation shows strong seasonal cycle with strong Aleutian Lows delivering winter precipitation from the east and north, largely unaltered from the moisture source. In contrast, summer synoptic weather patterns bring warm continental air from the south and west and contain recycled moisture from the land surface. The stable isotopic compositions of stream waters vary spatially within the basin and carry a dominant winter snowmelt isotopic signature yet overall values reflect mean annual precipitation. Stream waters provide the main source water for plant uptake
and biosynthesis of photosynthetic products (e.g. leaf waxes), thus their isotopic signature is recorded in sedimentary plant lipid archives. Environmental variables, such as aridity, may substantially alter the isotopic composition of the source water while additional interspecies differences in physiology and biochemistry can complicate the final δD leaf wax signal. A multi-species net fractionation determined within the El’gygytgyn Basin between source water and plant leaf waxes attempts to broadly integrate these factors and appears to be consistent and reproducible in a range of arid to semi-arid environments (e.g. Feakins and Sessions, 2010). This finding is fundamental to application of the δD paleoprecipitation proxy to lake core sediments.

The next objective of this thesis was to analyse the δD of sedimentary lipid biomarkers from previously acquired lake core sediments. δD values were obtained for a suite of n-alkanoic acids (n-C20 to n-C30) with the longest and shortest carbon chain length compounds representing two distinct source end members: terrestrial and aquatic. δD values of n-C22 to n-C28 were consistently between these two end members, suggesting consistent sources of OM, or at least consistent n-acid yielding OM sources. The assignment of compounds into these two distinct end members is also supported by additional compound-specific δ13C analyses (Holland et al., in prep).

The δD values from terrestrial plant leaf waxes were then used to reconstruct the δD of past precipitation. This record is the first continuous, high fidelity continental record of reconstructed δD in precipitation from terrestrial plant leaf waxes in the High Arctic spanning the last 120,000 years. The reconstructed
El’gygytgyn $\delta D_{\text{precip}}$ record data shows a high latitude northern hemisphere signal that is in phase with Antarctic climate records and leads other northern hemisphere climate records. The apparent lead of El’gygytgyn climate records over NGRIP and independently dated Chinese speleothem records suggest continental warming in the northern hemisphere earlier than previously thought. The offset in magnitude and timing between El’gygytgyn and the northern hemisphere (i.e. NGRIP) and speleothem records may result from previously unrecognized continental warming at high latitudes and/or a shift in the seasonality of precipitation over Greenland during glacial-interglacial cycles. Synoptic scale atmospheric circulation changes driven by northern hemisphere summer insolation and variability in sea surface temperatures may be the mechanism by which climatic changes propagate from high to low latitudes.

The research carried out in this thesis lays the foundation for future analysis of long cores (obtained in 2009) from Lake El’gygytgyn. The work presented here provides a streamlined method for analysis of future samples, a modern context for paleoclimate reconstructions and future organic geochemical and stable isotope analysis and establishes and applies these proxies to Lake El’gygytgyn sediments over the last 120 ka.

4.2 Future Work

4.2.1 Compound concentrations and OM cycling within Lake El’gygytgyn

Principle sources of organic matter (OM) to the lake include input from terrestrial plants, autochthonous phytoplankton production, bacterial modification
and archaeal (methanogen and methanotroph) productivity. Variations in the contributions of these OM sources through time are resolved through analysis of diagnostic lipid biomarkers (e.g. n-alkanes, sterols, n-alkanoic acids) coupled to sedimentation and mass accumulation rates.

Vascular land plants and emergent macrophytes contain large proportions of C$_{24}$-C$_{30}$ n-alkanoic acids (Cranwell, 1974; Wiesenberg and Schwark, 2006) while contributions from aquatic algae and photosynthetic bacteria contain large proportions of short chain C$_{16}$-C$_{22}$ n-alkanoic acids. Within Lake El’gygytgyn, aquatic and terrestrial sourced end members can be recognized based on the $\delta^{13}$C signatures of n-C$_{20}$ and n-C$_{30}$ acids (Holland et al., in prep). Concentrations of both end members vary with time with collectively higher concentrations reflecting greater productivity or enhanced preservation or possibly both. However, enhanced preservation of OM due to lake stratification linked with decreased summer insolation (increased winter insolation) and increased or perennial ice cover, does not explain the contrasting sharp transitions observed in the bulk OM (TOC) record and gradually increasing concentrations of lipids prior to full glacial conditions (Figure 4.1). The discrepancy between the TOC record and n-alkanoic acids concentrations suggests that bulk organic carbon in Lake El’gygytgyn is dominated by input of refractory non-extractable kerogen and is less sensitive to changing lake stratification. Reactive OM degrades at similar rates under oxic and anoxic conditions (Kristensen and Holmer, 2001); however, the proportion of OM resistant to degradation is much higher under anoxic conditions (Borrel et al., 2011). Increasing n-alkanoic acid concentrations up to ~15 ka prior to full glacial
conditions may be suggestive of early high latitude climate deterioration and fluctuations in the redox boundary within the lake sediments and water column driven by increasing extent and duration of ice cover.

Concentrations of sedimentary n-acids closely track winter insolation over the last 55 ka, then more broadly between 60 ka and 120 ka and are anti-correlated with summer insolation. Glacial-interglacial transitions are broadly similar and characterized by increasing n-acid concentrations with increasing lake ice cover and tracking winter insolation. The transition from MIS 3 into the LGM is marked by a slow progression suggesting greater OM preservation coincident with climatic deterioration and increased ice cover and possibly lake stratification (e.g. Melles et al., 2007). Yet, this pattern is not replicated back in MIS 4 (~70 ka). Here bulk δ¹³C fluctuations are not represented or detected in the compound-specific δ¹³C signatures (Holland et al., in prep; Wilkie et al., unpublished). Compound concentrations appear decoupled in the period between 60 ka and 120 ka (encompassing both MIS 4 and 5) between terrestrial and aquatic sources (i.e. higher concentrations of terrestrial sourced lipids than aquatic) with possibly higher input from terrestrial sources during times of overall generally warmer climate (MIS 5 prior to MIS 4). This could be due to substantial vegetation shifts altering the sources of terrestrial OM yet comparison with pollen spectra over these time intervals (Lozhkin et al., 2007) does not support this interpretation. Alternatively, greater productivity during warmer conditions in the Late Pleistocene may have contributed to overall higher n-acid concentrations although peak concentrations generally correspond with summer insolation minima. The close
correspondence between lipid concentrations and winter insolation could also reflect greater aeolian transport during cooler more arid conditions that may be linked to the strength of the Aleutian Low, Siberian High and the East Asian Winter Monsoon (EAWM) (Yang et al., 2011; Wang et al., 2012).

Another alternative explanation for the offset between the terrestrial and aquatic endmembers in the older part of the record (i.e. prior to ~67 ka) is the selective degradation of the shorter chain aquatic sourced (nC$_{20}$) acids. In general, components from aquatic sources are more sensitive to bacterial degradative processes than are materials from terrestrial sources (Meyers and Ishiwatari, 1993). While the compound-specific d13C of these short chain n-alkanoic acids suggest an aquatic origin, the source of these compounds within the lake may derive from phytoplankton or microbial communities or both. Combining both compound specific δ$^{13}$C and δD datasets may further provide insights into methane cycling within the lake.

4.2.2 Aquatic vs. Terrestrial sourced δD as an aridity proxy

The hydrogen isotopic compositions of terrestrial plant leaf waxes (δD$_{TER}$) carry the isotopic signatures of source water (precipitation). Short chain even-numbered n-alkanoic acids derive from aquatic sources and therefore their δD signatures (δD$_{AQ}$) should reflect the isotopic composition of lake water. The difference between δD$_{AQ}$ and δD$_{TER}$ is represented by ΔδD$_{AQ-TER}$ (‰) and potentially represents net ecosystem evapotranspiration and may be a proxy for aridity (Sachse et al., 2004). High values of ΔδD$_{AQ-TER}$ persist during glacial intervals and
corresponds with higher amounts of Poaceae pollen (Fig. 2.2). The high content of Poaceae pollen points to development of discontinuous Arctic tundra in arid climatic conditions (Lozhkin et al., 2007). During glacial periods perennial ice cover would have at least partially isolated the lake, restricting or preventing atmospheric exchange and limiting input of isotopically depleted precipitation (Melles et al., 2007). Moat formation around the lake edge during glacial summers (Melles et al., 2007) would contribute isotopically enriched water to the ice covered due to greater evaporative enrichment in these shallow ponds under arid conditions. In contrast, interglacial periods are characterized by low values of $\Delta \delta D_{AQ-TER}$ suggesting the lake is open and ice free during summer months and the isotopic composition of the lake water reflects meteoric waters. Periods where $\delta D_{TER}$ and $\delta D_{AQ}$ are coupled yet offset (e.g. 75 ka to 110 ka; Fig. 2.2) suggest warmer, wetter climatic conditions with lake water reflecting the isotopic composition of precipitation, modified by evaporative enrichment and higher $\delta D_{AQ}$ values.

4.2.3 Multi-proxy comparison of $\delta D_{AQ}$ with $\delta^{18}O_{diatom}$ for reconstructing $\delta_{lake}$ water

This work focuses on examining the relationship between the resulting $\delta D$ record from aquatic sources and the $\delta^{18}O$ diatom record. Both proxies potentially record the stable isotopic signature of El’gygytgyn lake water and should be related through the local meteoric water line (i.e. $\delta D = 7.35 \delta^{18}O - 9.62$; Wilkie et al., in prep; see chapter 2). Yet initial visual inspection of the records reveals two broadly different signals (Fig 2.3; $\delta D_{AQ}$ vs $\delta^{18}O_{diatom}$ records). Proxy agreement may allow reconstruction of a LMWL through time whereas disagreement may provide
insights on lake ecology and sources of organic matter. Discrepancies between these records may relate to differences in organisms habitat, such as water column depth, community structure, life cycle vital effects and seasonality or timing of blooms (Leng and Marshall, 2004). Potential complications may arise through proper identification and assignment of an aquatic source to \( n-C_{20} \) acids as contributions from nonphotosynthesizing bacteria or terrestrial sources could alter or obscure the \( \delta D \) lake water signal (Li et al. 2009, X. Zhang et al. 2009). However, compound specific \( \delta^{13}C \) of \( n-C_{20} \) acids in Lake El'gygytgyn sediments shows a uniquely aquatic source within the main Lake El'gygytgyn water body of this compound (Holland et a., in prep). Alternatively, diatom production may occur in surrounding moats feeding into the lake. The \( \delta^{18}O_{\text{diatom}} \) appears to broadly correlate well with the \( \delta D_{\text{TER}} \) record over the last 70 ka, suggesting both signals track meteoric waters. If diatoms were produced in moats during full glacial summers, their isotopic composition would instead reflect that of the moat water and ultimately precipitation while lake waters are expected to differ given perennial ice cover and isolation.

4.2.4 Additional work

Additional future work may also include continued \( \delta D \) analysis of leaf wax lipids on El'gygytgyn samples obtained from cores drilled in 2009, thereby possibly extending the record back 3.6 Ma. However, care should be taken when applying a constant net fractionation over these long timescales and because \( n \)-alkanoic acids are more susceptible to degradation and alteration than the other types of lipid.
biomarkers (e.g., Meyers and Ishiwatari, 1993). Proxy work should be supported and interpreted within a fully multi-proxy framework with accompanying vegetative history and organic geochemical assessment of the sources of OM.

Further compound specific isotopic analysis of El'gygytgyn sediments may also contribute to investigating the geochemical cycling and redox conditions within Lake El'gygytgyn. This would entail a large synthesis of multiple proxies focusing on addressing processes and mechanisms involved in during early diagenesis of lacustrine sediments. The multidisciplinary approach combining organic and inorganic geochemical and rock-magnetic parameters gives evidence of the interrelation of the redox horizon glacial to interglacial conditions. Conceptual and predictive modeling of geochemical cycling of C, P, Fe and Mn may illustrate movement of the redox boundary (within sediments to water column) and diagenetic conditions.

Incorporation of an isotope component (i.e. reconstructed $\delta D_{\text{precip}}$) into regional and global circulation models can help support interpretation of isotopic climate archives. Climate models fitted with embedded stable water isotope diagnostics allow direct comparison of model output with the measured isotopic data from climate archives (see review in Sturm et al., 2010). These models can then be used to reveal dominant factors controlling temporal and spatial variability in moisture and heat transport in the region and help visualize global atmospheric teleconnections.
4.3 References


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Figure 4.1: Concentrations of aquatic (blue) and terrestrially (green) sourced $n$-alkanoic acids, their $\delta^{13}$C values and % TOC (black) in Lake El’gygytgyn sediments. Light grey and dark grey lines denotes summer and winter insolation at 67°N, respectively.
Figure 4.2: a) Comparison of aquatic sourced $\delta D$ ($\delta D_{AQ}$; blue curve) with terrestrially sourced $dD$ values ($\delta D_{TER}$; green curve). b) $\Delta \delta D_{AQ-TER}$ (black curve) compared with the relative percent Poaceae pollen. Higher values of $\Delta \delta D_{AQ-TER}$ correspond with cooler temperatures, increased aridity, and expansion of grass and tundra.
Figure 4.3: El’gygytgyn $\delta^{18}$O$_{\text{diatom}}$ record (far left panel; black curve) from Chapligin et al., 2012. The El’gygytgyn $\delta$D$_{AQ}$ record is plotted in blue and the $\delta$D$_{TER}$ from terrestrial leaf waxes is plotted in green. $\delta$D$_{\text{lipid}}$ data is plotted on the same axis.
APPENDIX

DATA TABLES

Wilkie_LZ1029_bulkdata_agemodel............................................. see Supplemental Content
Wilkie_LZ1029_F1concentrations_CPI............................................. see Supplemental Content
Wilkie_lake_isotope_model .......................................................... see Supplemental Content
Wilkie_LakeE-H2Oisotope-data......................................................... see Supplemental Content
Wilkie_LZ1024FAconcentrations....................................................... see Supplemental Content
Wilkie_LZ1024_DH_all................................................................. see Supplemental Content


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