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A biomarker record of Lake El'gygytgyn, far east Russian Arctic: investigating sources of organic matter and carbon cycling during marine isotope stages 1–3

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Paleoenvironmental archives in Arctic regions serve as sensitive recorders of past climate change where summer temperatures hover near freezing and small climate variations may exhibit strong threshold-crossing environment responses. Lake El'gygytyn (Far East Russian Arctic) is a high-latitude crater impact lake that contains a continuous sediment record influenced by neither glaciation nor glacial erosion since the time of impact at 3.58 Ma. Prior research on sediments collected from Lake El'gygytyn suggest times of permanent ice cover and anoxia corresponding to global glacial intervals, during which the sediments are laminated and are characterized by the co-occurrence of high total organic carbon, microscopic magnetite grains that show etching and dissolution, and negative excursions in bulk sediment organic matter carbon isotope ($\delta^{13}\text{C}$) values. Here, we investigate the abundance and carbon isotopic characteristics of lipid biomarkers recovered from Lake El'gygytyn sediments spanning marine isotope stages 1–3, to identify key sources of organic matter (OM) to lake sediments, to establish which compounds and thus OM sources drive the negative $\delta^{13}\text{C}$ excursion exhibited by bulk sediment OM, and to explore if there are molecular and isotopic signatures of anoxia in the lake during glaciation. We find that during marine isotope stages 1–3, direct evidence for water column anoxia is lacking. A $\sim 4\%$ negative excursion in bulk sediment $\delta^{13}\text{C}$ values during the local Last Glacial Maximum (LLGM) is accompanied by more protracted, higher magnitude negative excursions in *n*-alkanoic acid and *n*-alcohol $\delta^{13}\text{C}$ values that begin 20 kyr in advance of the LLGM. In contrast, *n*-alkanes and the C_{30} *n*-alkanoic acid do not exhibit a negative $\delta^{13}\text{C}$ excursion at this time. Our results indicate that the C_{24} , C_{26} and C_{28} *n*-alkanoic acids do not derive entirely from terrestrial OM sources, while the C_{30} *n*-alkanoic acid at Lake El'gygytyn is a robust indicator of terrestrial OM contributions. Overall, our results strongly support the presence of a nutrient-poor water column, which is mostly isolated from atmospheric carbon dioxide during glaciation at Lake El'gygytyn.

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1 Introduction

Arctic lakes provide evidence of climate-sensitive environmental changes in terrestrial and aquatic ecosystems through accumulated sediment, which partially documents conditions of life and erosion within the lake basin. Arctic regions are particularly important recorders of past climate because summer temperatures in these regions hover near freezing, thus small changes in climate may cause large changes in environmental response (Vincent and Laybourn-Parry, 2008). Lake El'gygytgyn (67°30' N, 172°5' E; Fig. 1) is a 12 km wide 175 m deep crater impact lake dated to 3.58 ± 0.04 Ma (Layer, 2000) that contains a continuous record of sedimentation (Brigham-Grette et al., 2007) validated through seismic surveys (Gebhardt et al., 2006). Like much of Beringia, the crater and surrounding region have not been glaciated or subject to glacial erosion since impact (Brigham-Grette et al., 2004). Thus unlike many Arctic lakes that contain discontinuous, glacially-disturbed sediment archives, Lake El'gygytgyn may provide a long term, continuous record of climate and ecosystem change in the high Arctic from Pliocene to the present. In order to interpret this record, it is essential to understand how the ecology of the lake and its surroundings are expressed in the sedimentary record of the lake. Studies of Lake El'gygytgyn pilot cores spanning the past 250 kyr have revealed large cyclical changes in sedimentary geochemistry such as total organic carbon (TOC), isotopic measurements of total organic carbon ($\delta^{13}\text{C}_{\text{TOC}}$), and magnetic susceptibility (Melles et al., 2007; Nowaczyk et al., 2007). These changes are closely tied to regional climate variables, thought to be largely regulated by the extent and timing of ice cover at the lake (Melles et al., 2007). However, the degree to which variations in aquatic productivity, water column anoxia, or methanogenesis may have impacted the sedimentary record is not well understood. This study seeks to explore the shifting biogeochemical conditions within the lake during marine isotope stages (MIS) 1–3 in relation to changing ice cover and the associated impacts to carbon cycling and changes in availability of atmospheric gases to the lake water.

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Previous studies have linked the large changes in bulk geochemistry with permanent (year-round) ice cover during glacial intervals that, with reduced potential for re-supply of atmospheric oxygen, might have led to severe water column anoxia. For example, Nowaczyk et al. (2007) proposed that extreme shifts in magnetic susceptibility might represent dissolution of magnetite grains during anoxia. This interpretation is supported by the co-occurrence of laminated sediments, suggesting minimal bioturbation due to anoxic conditions (Melles et al., 2007), and inspection of microscopic magnetite grains that show etching and dissolution (Murdock et al., 2012).

This study examines bulk, molecular and isotopic characteristics of Lake El'gygytgyn sediments spanning the past 90 kyr, in an effort to better understand sources of OM to lake sediments, to constrain which compounds and OM sources exhibit $\delta^{13}\text{C}$ characteristics similar to the TOC record, and to seek molecular and isotopic evidence for anoxia. Bulk sedimentary $\delta^{15}\text{N}$ values are employed as a possible proxy for denitrification and anoxic intensity. Lipid biomarkers are identified to constrain contributions of terrestrial and aquatic OM to lake sediments. Compound-specific $\delta^{13}\text{C}$ analysis of *n*-alkanes, *n*-alkanoic acids, and *n*-alkanols are used to investigate the source of a strong negative isotopic shift in the bulk sediment $\delta^{13}\text{C}$ during glacial intervals. Specifically, two questions are posed: (1) is there specific evidence for anoxia in the water column during glacial intervals at Lake El'gygytgyn?, and (2) what organic matter source(s) drive the ^{13}C -depleted bulk sediment isotopic signature during the interpreted glacial intervals?

2 Methods

2.1 Sampling

Sediment core LZ1029 was recovered from a floating platform in 2003 from 175 m water depth using a gravity corer and a 3 m long percussion piston corer, which captured a composite sequence of several overlapping sections (Swann et al., 2010; Juschus et

al., 2009). The section used for this study, LZ1029-7 is 2.91 m in length. This study also references previously published data from nearby pilot cores PG1351 and LZ1024, collected in 1998 and 2003, respectively (Brigham-Grette et al., 2007; Melles et al., 2007; Juschus et al., 2007). LZ1029 is located at the same site as PG1351, while LZ1024 is approximately 2 km southwest closer to the center of the lake.

2.2 Core LZ1029 chronology

Core LZ1029-7 spans approximately the past 63 ka. The chronology, as presented in Murdock et al. (2012), was established by correlation to the other sections of composite core LZ1029 (-5, -8, -9) and core PG1351 based on sedimentology and stratigraphic markers (e.g. turbidites) and similar trends in TOC (Fig. 2a) and bulk $\delta^{13}\text{C}$. The age model for core PG1351 is based on the IRSL dating of the core sediments and the magnetic susceptibility record tuned to July insolation at 70° N, supported by other geochemical, pollen, and diatom data (Forman et al., 2007; Frank et al., 2012; Nowaczyk et al., 2002, 2007). Core LZ1024 is slightly longer than core PG1351 and extends to approximately 340 ka BP (Juschus et al., 2009, 2007).

2.3 Bulk sediment analysis

The TOC and magnetic susceptibility records for core LZ1029 are described in Murdock et al. (2012). TOC $\delta^{13}\text{C}$ values were determined on acidified (1 N H_2SO_3 , evaporated to dryness at 60°C for 12 h) sediment samples by online combustion using a Costech elemental combustion system (ECS140 EA) interfaced to a Thermo Delta V isotope-ratio mass spectrometer (EA-irMS). Bulk sediment $\delta^{15}\text{N}$ values were determined on the same instrument, using samples that were not acidified. Analyses were run in triplicate and are reported relative to the Vienna Pee Dee Belemnite (VPDB) standard in per mil (‰) notation for $\delta^{13}\text{C}$, and relative to atmospheric nitrogen ($\delta^{15}\text{N} = 0\text{‰}$) for $\delta^{15}\text{N}$ values. Instrument precision was evaluated with replicate analyses of standard reference materials (ammonium sulfate: USGS25 and IAEA-N1). Throughout sample analysis,

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17 replicates of USGS25 ($\delta^{15}\text{N} = -30.4\text{‰}$) yielded an average value of -30.3‰ with one standard deviation of $\pm 0.3\text{‰}$ and 20 replicates of IAEA-N1 ($\delta^{15}\text{N} = 0.4\text{‰}$) yielded an average of 0.45‰ with one standard deviation of $\pm 0.24\text{‰}$.

2.4 Lipid analysis

14 samples (4.7–11.8 g) were selected for biomarker analysis from core LZ1029. All analyses were conducted at the UMass Biogeochemistry Laboratory, except as noted. Freeze dried and homogenized sediment (with a C_{36} *n*-alkane internal standard added) was extracted with a 9 : 1 dichloromethane (DCM): methanol (MeOH) (vol:vol) in an accelerated solvent extractor (Dionex ASE 200). Total lipid extracts were separated by column chromatography into neutral (4 ml DCM:isopropyl alcohol) and acid (8 ml 2% formic acid in DCM) fractions using aminopropyl columns. The neutral fraction was further separated by silica gel column chromatography into four fractions: hydrocarbons (4 ml hexane); aldehydes/ketones (4 ml DCM); alcohols and sterols (4 ml 3 : 1 hexane:ethyl acetate); and more polar compounds (4 ml MeOH). The acid fractions and an external isotope mass balance standard (heniocosanoic acid) were methylated with BF_3 -methanol to convert *n*-alkanoic acids to fatty acid methyl esters (FAMES), which were purified on a silica gel column. The alcohol fractions along with two external isotope mass balance standards (nonadecanol and octacosanol) were derivatized with *N,O*-bis(trimethylsilyl)trifluoroacetamide (BSTFA) to convert alcohols to trimethylsilyl (TMS) ethers. A known mass of C_{36} *n*-alkane was added to FAME and TMS-alcohol fractions for quantification. Identical lot numbers of BF_3 -MeOH and BSTFA were used in derivatization of standards and analytes, to correct for the isotopic contribution of carbon atoms added during derivatization.

FAMES, *n*-alkanes and TMS-esters of *n*-alkanols were identified on a HP 6890 series GC – mass selective detector (GC-MSD) equipped with a 5% phenyl methyl siloxane column (HP-5MS, 30 m \times 0.25 mm i.d., film thickness 0.25 μm). Positive identification was achieved by comparing mass fragmentation patterns and relative retention times

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with those from a mass spectral database and published literature. FAMEs, *n*-alkanes and TMS-esters of *n*-alkanols were quantified using a Hewlett Packard (HP) 6890 series gas chromatograph – flame ionization detector (GC-FID) equipped with a 5% phenyl methyl siloxane capillary column (30 × 0.25 mm i.d., film thickness 0.25 μm).

5 Temperature programs for all fractions and instrument runs are reported in Table 1. Quantification was achieved using the mass of a known internal quantification standard (C₃₆ alkane).

Compound-specific δ¹³C analysis of FAMEs, *n*-alkanes and TMS-esters of *n*-alkanols were conducted at Yale University's Earth System Center for Stable Isotopic Studies. Samples were analyzed on a Thermo Scientific (Trace GC Ultra 2000)-combustion interface GC coupled to a Thermo Scientific Finnigan MAT 253 stable-isotope ratio mass spectrometer (GC-irMS) and equipped with a DB-1 column (60 m × 250 μm i.d., 0.25 μm film thickness). Results are expressed as δ notation, where: δ¹³C = [(R_{sample}/R_{standard}) - 1] × 1000; R = ¹³C/¹²C, and the standard is

15 VPDB (δ¹³C = 0‰). δ¹³C values are corrected for the addition of carbon atoms on derivatization. Instrument precision was determined with replicate analysis of a known isotope external standard (C₃₆ *n*-alkane) measured relative to VPDB. For the *n*-alkane (13 replicates) and *n*-alkanol fractions (15 replicates), the average values were within one standard deviation (< 0.66‰) of the known δ¹³C_{C36} value (-29.88‰). FAME replicates (14) consistently displayed values outside one standard deviation (average δ¹³C_{C36} = -30.54‰, Std. dev. = 0.25‰). Therefore, FAME values were reevaluated by correcting the internal standard to the known δ¹³C_{C36} value and adjusting other values in each sample accordingly, an average adjustment of +0.658‰. The fractionation effects associated with FAME and TMS-alcohol derivitization were calculated using known external standards (Hayes, 1993).

25 Following analysis by GC, GC-MS, and GC-IRMS, the alcohol fraction was un-derivatized by shaking with ultrapure water and extracting the water 4 times with DCM. A known quantity of an internal standard (a C₄₆ GDGT) was added. These fractions were subsequently filtered through a 0.45 μm PTFE syringe filter in 99 : 1

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hexane:propanol and analyzed on an Agilent 1260 HPLC coupled to an Agilent 6120 MSD, for identification and quantification of glycerol dialkyl glycerol tetraethers (GDGTs) following the methods following the methods of Hopmans et al. (2000), with minor modifications (Schouten et al., 2007). Separation was achieved on a Prevail
5 Cyano column (150 mm × 2.1 mm, 3 mm) using 99 : 1 hexane:propanol (vol:vol) as an eluent. After the first 7 min, the eluent increased by a linear gradient up to 1.8 % iso-propanol (vol) over the next 45 min at a flow rate of 0.2 ml min⁻¹. Scanning was performed in selected ion monitoring (SIM) mode.

3 Results

3.1 Bulk geochemical data

As reported in Murdock et al. (2012), TOC concentrations in core LZ1029 range from 0.2–1.8 % (Fig. 2). TOC concentrations in LZ1029 are similar to those reported for core PG1351 (Melles et al., 2007) throughout much of the record from modern through MIS 3, with highest TOC concentrations found in a narrow range sediments corresponding to the LLGM. TOC $\delta^{13}\text{C}$ values in core LZ1029 range from -25.0‰ to -32.6‰ (Fig. 3). The lowest $\delta^{13}\text{C}$ values correspond to samples with the highest TOC concentrations. However, TOC $\delta^{13}\text{C}$ values begin to decline at approximately 43 ka, ~ 20 kyr in advance of the % TOC increase observed at the LLGM. Bulk sediment $\delta^{15}\text{N}$ values in core LZ1029 range between 1.5‰ and 4.5‰, increasing from ~ 3–3.5‰ in the lower portion of the core to approximately 4.5‰ between 35–30 ka (Fig. 4). This high is followed by a rapid decrease in $\delta^{15}\text{N}$ values to approximately 2‰ during the LLGM, with a slight increase in $\delta^{15}\text{N}$ values to approximately 2.5‰ after 17 ka. These changes in $\delta^{15}\text{N}$ values mirror those in % TOC and magnetic susceptibility (Fig. 4), and are similar to the TOC $\delta^{13}\text{C}$ record. The correlation coefficients between $\delta^{15}\text{N}$ and TOC and bulk
25 $\delta^{13}\text{C}$ are $R^2 = 0.30$ and 0.13, respectively.

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3.2 Abundance and isotopic composition of lipid biomarkers

3.2.1 *n*-alkanes

Core LZ1029 contains a suite of *n*-alkanes ranging from 21 to 33 carbons in length. Total *n*-alkane concentrations range from 7.8 ng g⁻¹ TLE in the lower portion of the core to 70.7 ng g⁻¹ TLE in the most recent sample, displaying a gradual increase around 43 ka to a 20.1 ng g⁻¹ TLE peak during the LLGM (Fig. 2d). Figures 2 and 3 display a few representative compounds for simplicity of presentation; full data are available in the Supplemental Information. The C₂₉ and C₃₁ *n*-alkanes are the most abundant throughout much of core LZ1029, but C₂₁, C₂₃ and C₂₅ are more abundant during the LLGM (see C₂₅ *n*-alkane, Fig. 2d). The relative abundance of the C₂₃ to C₂₉ *n*-alkanes generally follows trends in %TOC with highest values confined to the LLGM, while C₃₁ and C₃₃ display a distinctly different pattern, displaying maxima in concentrations prior to the LLGM around 32 ka (see C₂₉ and C₃₁ *n*-alkanes, Fig. 2d).

Isotopic values of *n*-alkanes C₂₇-C₃₃ are consistently lower than TOC δ¹³C values through core LZ1029 (see C₂₉ and C₃₁ *n*-alkanes, Fig. 3b), but do not parallel the approximately 6‰ negative excursion observed in the TOC δ¹³C record during the LLGM. C₂₇-C₃₃ δ¹³C values are relatively constant at approximately -34‰ throughout the core, displaying lower δ¹³C values in one sample at 38 ka but no obvious isotope excursion during the LLGM. In contrast, C₂₅ *n*-alkane δ¹³C values are approximately 2‰ lower during the LLGM (Fig. 3b).

3.2.2 FAMEs

Core LZ1029 contains a suite of *n*-alkanoic acids ranging between 14 and 32 carbon atoms in size with the C₂₆ FAME being the most abundant. Total FAME concentrations range from 8.6 ng g⁻¹ TLE in the lower portion of the core to 34.9 ng g⁻¹ TLE during the LLGM and peak at 43.0 ng g⁻¹ TLE in the most recent sample (Fig. 2c). Odd carbon-number FAMEs are much less abundant than even-numbered FAMEs,

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and methyl-branched iso- and anteiso-fatty acids are detected only in the sample with the highest %TOC. Short- (C_{16} - C_{18}) and mid-chain (C_{20} - C_{22}) FAMES reach maximum abundance during the LLGM, similar to TOC concentrations, while long-chain FAMES (C_{24} - C_{30}) increase in abundance well before the LLGM (see C_{16} , C_{20} , C_{26} , and C_{30} *n*-alkanoic acids, Fig. 2f; other *n*-alkanoic acids in Supplemental Information).

Isotope analysis of *n*-alkanoic acids from LZ1029 reveals complex patterns in $\delta^{13}C$ values. The record of the C_{30} *n*-alkanoic acid $\delta^{13}C$ values is most similar to that of *n*-alkanes, with nearly constant values close to -34‰ throughout much of the core; an approximately 2‰ increase in $C_{30}\delta^{13}C$ values is observed prior to and during the LLGM (Fig. 3c). The $\delta^{13}C$ values of the C_{16} and C_{18} *n*-alkanoic acids are similar to TOC $\delta^{13}C$ values throughout the core, and an approximately 6‰ negative excursion beginning approximately 43 ka and peaking during the LLGM (see C_{16} *n*-alkanoic acid, Fig. 3c). This is paralleled by an approximately 4‰ negative excursion in $\delta^{13}C$ values of mid-chain (C_{20} and C_{22}) *n*-alkanoic acids, and an approximately 8‰ negative excursion in $\delta^{13}C$ values of long-chain (C_{24} , C_{26} and C_{28}) *n*-alkanoic acids (see C_{20} and C_{26} *n*-alkanoic acids, Figure 3c); for both mid- and long-chain *n*-alkanoic acids, $\delta^{13}C$ values prior to excursion are similar to the C_{30} $\delta^{13}C$ values and reach minimum values during the LLGM that are lower than the TOC $\delta^{13}C$ record. C_{15} iso- and anteiso- fatty acids (BAMEs) $\delta^{13}C$ values were only obtained on samples from within the LLGM, and are similar to C_{16} , C_{18} and TOC $\delta^{13}C$ values (Fig. 3c).

3.2.3 Alcohols and sterols

LZ1029 contains a suite of mainly even-numbered *n*-alkanols from C_{22} to C_{28} , as well as the odd numbered C_{21} *n*-alkanol. The C_{24} *n*-alkanol is most abundant throughout most of the core. Total *n*-alkanol concentrations range from 4.7 ng g^{-1} TLE at 12 ka to 15.6 ng g^{-1} TLE at 6.5 ka, peaking at 13.6 ng g^{-1} TLE during the LLGM (Fig. 2c). Similar to total *n*-alkanoic acid concentrations, total *n*-alcohols begin to increase at approximately 43 ka with a peak in abundance during the LLGM. It is notable that the

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2004). BIT values in Lake El'gygytyn are generally high, indicating increased inputs of branched GDGTs relative to crenarchaeol, and range from 0.39 to 0.94 with the lowest values of the record noted during the LLGM (Fig. 5e).

4 Discussion

5 In this study, the term Local Last Glacial Maximum (LLGM; approximately 20–25 ka) is used to refer to the period of most extreme changes in bulk geochemistry data, including shifts in magnetic susceptibility, TOC, and bulk $\delta^{13}\text{C}$. “Local” is meant to differentiate this region from other areas of the Arctic impacted by glacial activity, given that regional cooling in the area of Lake El'gygytyn may or may not have been entirely
10 synchronous with glacial activity in other parts of the Arctic.

Lake El'gygytyn is an unusual lake in that the sediment record for the past 200 kyr is characterized by higher TOC concentrations (Melles et al., 2007; Murdock et al., 2012) and biomarker concentrations in sediments from glacial periods. In contrast, many lake records, including Lake Baikal (Prokopenko and Williams, 2004), exhibit high TOC dur-
15 ing interglacial periods, which is consistent with conditions of higher productivity during warmer climate intervals. Furthermore, the interval studied here (MIS 1–3) seems to differ from earlier sections of the El'gygytyn record. In contrast to our results, D'Anjou et al. (2012) note that in the interval from MIS 9–12, increased concentrations of all biomarkers occur during the interglacial periods (MIS 9 and MIS 11) rather than during
20 the glacials. Thus, MIS 2 (the LLGM) may be somewhat anomalous in comparison to earlier glacials. The increased TOC at Lake El'gygytyn during the LLGM may result from increased primary productivity (Snyder et al., 2012), increased OM preservation, decreased dilution of TOC from inorganic inputs to the lake sediments, or some combination of these three. Previous research on Lake El'gygytyn sediments has not
25 resolved this, but some intriguing observations are noted. Foremost, times of elevated TOC concentrations are also characterized by negative excursions in TOC $\delta^{13}\text{C}$ values and increased OM C/N ratios (Melles et al., 2007). One interpretation of this is

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an increase in the delivery and burial of terrestrially-derived OM during glaciation, as terrestrial OM is characterized by higher C/N ratios and lower $\delta^{13}\text{C}$ values than typical aquatic primary production; this is supported by the continuous record of pollen deposition in Lake El'gygytgyn sediments (Lozhkin et al., 2007), indicating production and delivery of terrestrial OM from the landscape during both glacial and interglacial intervals. However, this interpretation is difficult to reconcile with a perennially ice-covered lake, and tools such as molecular markers and their isotopic characteristics are needed to refine OM sources and carbon cycling at Lake El'gygytgyn. The high %TOC in Lake El'gygytgyn sediments noted during the LLGM also coincides with unexpectedly high biogenic silica values as well as a diatom assemblage indicating higher nutrient status compared to the Holocene (Snyder et al., 2012). Snyder et al. (2012) suggest that changes in lake circulation, by either occasional circulation of an ice covered lake or by circulation-induced seasonal nutrient pulses under transparent ice cover, could explain the high contributions of nutrient-favoring diatoms during the LLGM.

4.1 Division of LZ1029 record into Intervals A, B, C

Prior research (e.g. Melles et al., 2007; Minyuk et al., 2007; Nowaczyk et al., 2007) has argued that the magnetic susceptibility, inorganic geochemical and biogeochemical records from Lake El'gygytgyn correspond well with Pleistocene Marine Isotope Stages. This holds true for core LZ1029, in which changes in rock magnetic properties and % TOC are synchronous with MIS boundaries (Murdock et al., 2012). However, close inspection of LZ1029 TOC $\delta^{13}\text{C}$ values and molecular abundances and isotopic compositions presented here suggests changes in OM sources and carbon cycling at Lake El'gygytgyn that precede, for example, the sharp increase in %TOC at the start of MIS 2. As such, we divide our record into three intervals A, B and C (Figs. 2–4).

Compared to deeper sections of LZ1029, Interval A (~ 17 ka–present) is characterized by lower %TOC, lower absolute concentrations of long-chain FAMES, alcohols and *n*-alkanes, relatively greater abundance of long-chain *n*-alkanes and FAMES, and relatively similar $\delta^{13}\text{C}$ values for all measured FAMES and for all *n*-alkanes. Tree and shrub

pollen (Lozhkin et al., 2007) is relatively high during this interval. This interval includes MIS 1 and extends into MIS 2.

Interval B (~ 43 ka–17 ka) is characterized by high absolute concentrations of *n*-alkanoic acids, *n*-alkanes and *n*-alkanols, as well as the only detectable quantities of sterols and methyl-branched fatty acids found in this study. The base of Interval B is defined by the increase in absolute FAME concentrations compared to those deeper in the core, and by the progressive ¹³C depletion of *n*-alkanols and the C₁₄–C₂₈ *n*-alkanoic acids paralleling TOC δ¹³C values. The C₃₀ *n*-alkanoic acid and *n*-alkanes show little to no negative shift in δ¹³C values during this interval. The uppermost portion of Interval B includes the LLGM, characterized by the most negative lipid δ¹³C values, the greatest absolute concentrations of *n*-alkanes, alcohols, FAMES and crenarchaeol, relatively higher concentrations of shorter-chain versus longer-chain *n*-alkanoic acids and *n*-alkanes, as well as the lowest calculated BIT index values. The changes in lipid abundance and isotopic composition observed throughout Interval B suggests that the LLGM is the terminal part of a broader time interval of environmental change in and around the lake that is not captured in the bulk %TOC and C/N records. Pollen during Interval B derives almost exclusively from herbaceous plants, mainly grasses (Lozhkin et al., 2007).

Interval C (~ 63 ka–43 ka) is similar to Interval A in that it is characterized by lower %TOC and relatively low concentrations of FAMES, alcohols, and *n*-alkanes. Lipid δ¹³C values are similar to those found in Interval A, with no divergence in δ¹³C values between different *n*-alkanoic acids. However, short-chain FAMES are relatively most abundant within this interval, and the pollen record suggests slightly lesser contributions from trees and shrubs compared to Interval A (Lozhkin et al., 2007).

4.2 Sources of organic matter

Bulk sedimentary geochemistry data from Lake El'gygytgyn pilot cores display synchronous shifts between glacial and interglacial intervals. In particular, increased TOC

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during the LLGM has been interpreted as a signal of increased preservation of organic matter during times of decreased oxygen in the water column due to interannual ice cover (Melles et al., 2007). Compound-specific analysis helps to separate the various sources contributing to the organic matter, and how these sources have changed through time. Our results indicate that sedimentary organic matter at Lake El'gygytgyn mostly falls into two source categories: terrestrial and aquatic, with only minor contributions from microbial sources.

Terrestrially-derived OM is represented by the suite of *n*-alkanes as well as the C₃₀ *n*-alkanoic acid as these compounds are known components of leaf waxes, and is possibly suggested by the suite of branched GDGTs (see below for caution in interpreting sources of GDGTs). This interpretation is strengthened by the $\delta^{13}\text{C}$ values of *n*-alkanes and the C₃₀ *n*-alkanoic acid which remain nearly constant through Intervals C, B and A (Fig. 3). These constant $\delta^{13}\text{C}$ values require lipid synthesis from a carbon source that does not change in $\delta^{13}\text{C}$ across this time interval, i.e. atmospheric CO₂.

Aquatic OM, considered here as primary production occurring within the lake, is most clearly represented by the C₁₄-C₂₂ FAMES, the sterols and the C₃₂ 1,15-*n*-alkyl diol. While the C₂₄-C₂₈ FAMES and *n*-alkanols have commonly been assigned a terrestrial source in previous research at other sites, $\delta^{13}\text{C}$ analysis of FAMES and alcohols reveals that this is not entirely the case at Lake El'gygytgyn. The $\delta^{13}\text{C}$ values of the C₂₀-C₂₂ *n*-alkanoic acids show an approximately 8‰ negative excursion during Interval B (see C₂₀*n*-alkanoic acid, Figure 3c), indicating a similar negative shift in the $\delta^{13}\text{C}$ value of the inorganic carbon source supporting aquatic primary production. During this time, the C₂₄, C₂₆ and C₂₈*n*-alkanoic acids show an approximately 4‰ negative excursion at this time, while the $\delta^{13}\text{C}$ values of the C₃₀ *n*-alkanoic acid remain nearly constant (see C₂₆ and C₃₀ *n*-alkanoic acids, Fig. 3c). Thus, the $\delta^{13}\text{C}$ values of the C₂₄-C₂₈ *n*-alkanoic acids can be interpreted as roughly equal contributions from a terrestrial source (that has a nearly constant $\delta^{13}\text{C}$ value) and from an aquatic source (that experiences an approximately 8‰ negative excursion during Interval B). This occurrence is consistent with other literature confirming numerous (if infrequent) microalgal and bacterial

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sources of long-chain *n*-alkanoic acids (Bobbie and White, 1980; Logan and Eglinton, 1994; Schouten et al., 1998; Volkman et al., 1980). It is not clear if this aquatic source for the C₂₄-C₂₈ FAMES persists throughout the LZ1029 record, with a $\delta^{13}\text{C}$ value for this source shifting through time, or if it is just confined to Interval B, when changes in lake ecology may be accompanied by C₂₄-C₂₈ *n*-alkanoic acid-producing aquatic organisms; both scenarios are supported by available data. Thus, our results demonstrate that caution must be applied when assigning sources of long-chain FAMES in sediments, and it should not be assumed that these compounds derive from mainly from terrestrial sources. Similar caution must be applied in interpreting the source of *n*-alkanols. Our results show a substantial (10–15‰) negative excursion in C₂₂-C₂₈ *n*-alkanol $\delta^{13}\text{C}$ values during Interval B (see C₂₄ and C₂₈ *n*-alkanols, Fig. 3d); while these *n*-alkanols are commonly assigned a terrestrial source, the negative excursion in $\delta^{13}\text{C}$ values requires an aquatic contribution at least during Interval B. Additionally, the approximately 3‰ negative excursion in the C₂₅ *n*-alkane $\delta^{13}\text{C}$ values indicate that this compound may partly have an aquatic source as well, at least during the LLGM.

Microbially-derived OM is not an abundant source of OM in Lake El'gygytgyn sediments. Bacteria produce many of the same fatty acids as aquatic organisms, thus making it difficult to distinguish between the two sources. Two fatty acids diagnostic of bacteria, C₁₅ iso- and C₁₅ anteiso- FAMES (Kaneda, 1991), were present at low concentrations during the LLGM (21 ka). Markers of microbial methane cycling such as diplopterol and hydroxyarchaeol were not detected. Crenarchaeol concentrations are very low throughout most of the record, with exception of the LLGM.

Our results indicate that terrestrial OM is the main OM source to Lake El'gygytgyn throughout the past ~60 ka, which is consistent with findings from other Siberian lakes (Ouellette, 2003; Rodgers, 2005); and supporting the continuous accumulation of pollen in Lake El'gygytgyn sediments throughout this record (Lozhkin et al., 2007). The high %TOC and high lipid yield during the LLGM indicate that, surprisingly, the LLGM corresponds to the time of maximum terrestrial OM delivery to the sediments, possibly via ephemeral ice-free moats along the lake margin or intermittent streams

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carrying terrestrial organic matter from the basin. Interestingly, the C_{31} and C_{33} n -alkanes achieve their peak concentrations well before the LLGM (38 ka), while maxima in the C_{23} - C_{29} n -alkane concentrations are synchronous with the TOC maximum (see C_{25} , C_{29} and C_{31} n -alkanes, Fig. 2d). These trends suggest changes in terrestrial OM and thus terrestrial ecology, and hint that the peak in TOC is derived from multiple sources contributing increased organic carbon at different times. It remains unclear why, or how, terrestrial OM inputs can remain dominant throughout this time interval, including times such as the LLGM when the lake was perennially ice-covered, and when extremely cold and dry conditions should have limited terrestrial primary production on the landscape surrounding Lake El'gygytgyn. In comparison to other lakes, TOC values are very low. Consequently, terrestrial inputs are significant only in that absolute concentrations consistently exceed aquatically sourced material, which may be explained by the ultra-oligotrophic nature of Lake El'gygytgyn and does not suggest that there is a large export from the terrestrial ecosystem to the lake.

Aquatic sources are secondary to terrestrially-derived OM throughout the record, but are greatest during Interval B and specifically the LLGM. This is supported by the increase in the absolute abundance of C_{14} - C_{28} FAMES, including the partial aquatic source of the C_{24} - C_{28} FAMES as described above, as well as the occurrence of sterols and 1,15-diols during this interval.

In marine environments, the BIT Index provides a proxy for aquatic versus soil organic matter input to sediments (Hopmans et al., 2004). Branched GDGTs are thought to be produced by anaerobic soil bacteria, which are commonly found in soils and peats, but the source organism(s) presently remain known (Weijers et al., 2007). The compound crenarchaeol, is produced by marine and lacustrine Thaumarchaeota, and provides an aquatic endmember. BIT values range from 0 to 1: a value of 0 indicates a purely aquatic source while a value of 1 represents source from soil organic matter (Hopmans et al., 2004). However, use of the BIT Index in lacustrine systems is not straightforward, as it appears that branched GDGTs are produced in-situ in the water columns of many lakes (e.g. Tierney et al., 2012; Sinninghe Damsté et al., 2009;

Tierney et al., 2010; Tierney and Russell, 2009; Zink et al., 2010; Blaga et al., 2009; Bechtel et al., 2010). Furthermore, several studies have noted that changes in the BIT Index can be mainly driven by changes in crenarchaeol concentrations (Castañeda and Schouten, 2011 and references therein). This is the case at Lake El'gygygtyn, which is generally characterized by high BIT values of 0.9 to 1, but lower BIT values of around 0.4 are noted during the LLGM (Fig. 5e). This drop in the BIT Index during the LLGM is driven by a significant increase in the concentration of crenarchaeol but concentrations of branched GDGTs also increase at this time (Fig. 5c). Overall, high BIT values and generally higher concentrations of branched GDGTs relative to crenarchaeol (with the exception of the interval around the LLGM) could be interpreted as indicating mainly terrestrial inputs to Lake El'gygygtyn. This scenario is feasible since peat exists within the watershed of the lake and since other terrestrial biomarkers are relatively abundant while aquatic biomarkers, such as those of primary producers, are generally absent in this oligotrophic lake. However, the possibility that branched GDGTs could be produced in-situ, in the water column of Lake El'gygygtyn, cannot be ruled out especially given the evidence for in-situ production of branched GDGTs in many lakes. Further investigations are required to address this issue.

4.3 Production vs. preservation of organic matter

Bulk geochemical investigations from previous studies (e.g. Melles et al., 2007) supported the interpretation that high TOC during the LLGM is a function of increased preservation of organic matter (rather than increased production) due to a lack of oxygen during times of perennial lake ice cover. Values for the carbon to nitrogen ratio (C/N) from adjacent core PG1351 increase during the LLGM, suggesting either an increase in terrestrial input or more likely severe nitrogen limitation due to ice cover and stratification (Melles et al., 2007), as supported by bulk $\delta^{15}\text{N}$ results in this study (below).

Biomarker concentration results from this study also support increased LLGM preservation of organic matter. Increased absolute concentrations of terrestrial organic

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matter during the LLGM are more likely caused by increased preservation than increased terrestrial export productivity from a frozen landscape to an ice-covered lake. Terrigenous/aquatic ratios (C_{30}/C_{20} FAMES) display a decrease during the LLGM, suggesting an increase in aquatic contribution (Fig. 2g) and indicating that increased productivity of aquatic OM may also play a role during the LLGM. Higher aquatic productivity during the LLGM is also supported by diatom analysis (Snyder et al., 2012). A more gradual increase in TLE-normalized concentrations of all compound classes from both terrestrial and aquatic sources (*n*-alkanes, alcohols and FAMES) during Interval B prior to the LLGM suggests that oxygen in the water column did not disappear suddenly, as is evoked by the sudden and sharp TOC transition, but gradually weakens over the course of Interval B (Fig. 2e–f). The magnitude and timing of the TOC peak at the LLGM must largely reflect preservation of additional organic matter other than the compounds evaluated in this study. This occurrence may reflect a threshold of dissolved oxygen, below which a much greater proportion of the organic matter in the lake is preserved. Alternatively, the sharp TOC peak may represent the progression of the oxycline above the sediment-water interface, thus exposing a portion of the water column to anoxic processes.

4.4 Temperature change at Lake E

The MBT/CBT Index (Weijers et al., 2007), calculated from branched GDGTs, provides a proxy for mean annual soil temperature, which in many cases is similar to mean annual air temperature. Applying the global soils calibration of Weijers et al. (2007) yields temperatures ranging from -12.4 to -4.9 °C whereas applying the lakes calibrations of Pearson et al. (2011) and Tierney et al. (2010) yields temperatures ranging from 6.6 to 10.6 °C and -5.2 to 3.5 °C, respectively (Fig. 5b). Relative temperature changes in MBT/CBT derived temperature at Lake El'gygytgyn reveal cooler temperatures during the LLGM (Fig. 5), as expected. Modern air temperatures at Lake El'gygytgyn range from -40 °C in winter to $+26$ °C in summer with a mean annual temperature of -10.3 °C, while the temperature of the water column ranges from 0 to 4 °C (Nolan

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and Brigham-Grette, 2007). Given the wide variability in modern temperatures at Lake El'gygytyn it is not clear which of the available MBT/CBT calibrations, if any, is the most appropriate to apply, especially if a seasonal bias in branched GDGT production exists.

Due to the current lack of a modern calibration study at Lake El'gygytyn, we note that absolute temperatures reconstructed by the MBT/CBT proxy, in addition to the overall amplitude of temperature shifts, cannot be trusted; however, the data can be interpreted in terms of relative changes in MBT/CBT data (warming and cooling) (also see D'Anjou et al., 2012). It has been noted that site specific temperature calibrations are likely required when applying GDGT-based temperature proxies to lakes (Castañeda and Schouten, 2011 and references therein) and thus a modern study of Lake El'gygytyn and its watershed is required to determine where the branched GGTs are produced and if MBT/CBT based MAATs represents the annual mean temperature or a rather a seasonal temperature.

4.5 What source(s) drive the negative shifts in TOC $\delta^{13}\text{C}$?

Negative shifts in TOC $\delta^{13}\text{C}$ values during the LLGM in Lake El'gygytyn sediments suggest that a highly depleted aquatic carbon end member (isotopic composition unknown) exists that is not present or abundant during warmer periods. The resulting TOC $\delta^{13}\text{C}$ signature is a mixture between this highly depleted lacustrine OM and some contribution of relatively enriched terrestrial OM. The considerable LLGM ^{13}C -depletion in OM at Lake El'gygytyn differs from nearby Lake Elikchan (Latitude $60^{\circ}45' \text{N}$), which experiences glacial ^{13}C -enrichment (Rodgers, 2005), but this difference might be explained by the latitude difference, duration of ice cover, and access to atmospheric CO_2 (Lozhkin and Anderson, 2011). Over the period of time covered in this study, the isotopic composition of terrestrial OM inputs does not change significantly (Köhler et al., 2010; Smith et al., 1999), as supported by the isotopic trend of the C_{30} *n*-alkanoic acid (Fig. 3c). Therefore, it is assumed that changes in TOC $\delta^{13}\text{C}$ reflect changes in the isotopic composition of aquatic organic matter and/or the changing ratio between

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aquatic and terrestrial carbon sources. At first glance, a possible contribution to a depleted TOC $\delta^{13}\text{C}$ signature could be methane oxidation in the upper water column, which would require depleted oxygen in a portion of the water column. However, previous studies have postulated that due to the existence of an established community of non-migrating salmonid species (Nolan and Brigham-Grette, 2007) and the persistence of vivianite from fish bones (Minyuk et al., 2007), it is likely that the upper water column has remained oxygenated through several glacial/interglacial cycles.

The original hypothesis driving this study proposed that methanogenic archaea and methanotrophic bacteria would become abundant during periods of near permanent ice cover, and that compounds diagnostic of these organisms would display extremely depleted ^{13}C values suggesting methane cycling associated with water column anoxia. The largest contribution of depleted ^{13}C at Lake El'gygytyn was expected to derive from extreme depletion (near -60%) in fatty acids diagnostic of bacterial sources (BAMEs) within the short-chain fatty acids, which would indicate that bacteria in the lake were associated with methane cycling (Whiticar, 1999). However, methyl-branched BAMEs (C_{15} iso- and C_{15} ante iso-) were identified at sufficient concentrations to measure $\delta^{13}\text{C}$ in only one LLGM sample (21 ka), but displayed isotopic values similar to bulk $\delta^{13}\text{C}$ (-33.0% to -33.7% ; Fig. 3c). These results suggest the existence of bacteria associated mainly with processes other than methane cycling and/or existing only in the upper oxygenated portion of the water column.

The most isotopically-depleted compounds at Lake El'gygytyn were found within the mid-chain *n*-alkanoic acids (C_{20} and C_{22}), which are usually associated with aquatic organisms and vegetation (Meyers and Ishiwatari, 1993), submerged/emergent macrophytes, or bacteria. The mid-chain *n*-alkanoic acid $\sim 10\%$ carbon isotope excursion during Interval B (see C_{20} , Fig. 3c) suggests that aquatic organic matter was utilizing a pool of ^{13}C -depleted CO_2 in the water column that was not fully mixed with atmospheric CO_2 . Degradation and oxidation of OM released ^{13}C -depleted CO_2 to the water column, which without complete mixing with the atmosphere, was re-used to support new primary production during Interval B. Aquatic organic matter could be using CO_2 from a

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number of possible sources: dissolved atmospheric CO₂, oxidation of sinking degraded aquatic organic matter, dissolved inorganic carbon (DIC) from stream input, oxidation of dissolved or particulate organic carbon (DOC/POC) from stream input, or CO₂ from oxidation of methane (Meyers, 1997; Whiticar, 1999). During the LLGM, the depletion of aquatic lipids to -43.2‰ (e.g. C₂₀ FAME) suggests that these compounds derived in part from CO₂ from oxidized OM, either aquatic, terrestrial or methane, because only these CO₂ sources could drive the negative lipid δ¹³C signatures. With no molecular evidence for methanogenesis, a likely scenario for generating depleted aquatic lipid ¹³C is that aquatic primary producers were in large part using recycled CO₂ from oxidation of sinking organic matter rather than atmospheric CO₂. In a situation where there is little atmospheric CO₂ input (semi-permanent ice cover), δ¹³C of sinking organic matter using a combination of 1/3 recycled CO₂ and 2/3 atmospheric CO₂ could become progressively more negative (by ~ -10‰) until a ¹³C-enriched carbon source is made available. This speculation requires further modeling to address in full.

Results show another, somewhat surprising, contribution to the depleted bulk δ¹³C signal. Long-chain *n*-alkanoic acids (~ C₂₄ to C₃₃) are expected to follow the trend of similar chain-length *n*-alkanes, which display a relatively constant isotopic signature and suggest that terrestrial organic matter does not experience an isotopic shift over the timeframe of this study. However, only one long-chain *n*-alkanoic acid (C₃₀) displays the expected terrestrial trend and may be associated with a purely terrestrial source. Other long-chain *n*-alkanoic acids (C₂₄, C₂₆, C₂₈) show a ~ 5‰ depletion during the LLGM similar to aquatic compounds (see C₂₆ *n*-alkanoic acid, Fig. 3c and Supplement), which might be explained by an approximately equal mix of organic matter with a constant carbon source (terrestrial *n*-alkanoic acid C₃₀) and aquatic or bacterial organic matter with a carbon isotope excursion of ~ 10‰ over the course of Interval B (similar to the negative δ¹³C excursion observed in mid-chain *n*-alkanoic acids). An equal mix between these two sources would produce an excursion of approximately 5‰. This occurrence is consistent with other literature confirming numerous (if infrequent) microalgal and bacterial sources of long-chain *n*-alkanoic acids (Bobbie and

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White, 1980; Logan and Eglinton, 1994; Schouten et al., 1998; Volkman et al., 1980). Thus, our results demonstrate that caution must be applied when assigning sources of long-chain FAMES and it should not be assumed that these compounds derive from mainly from terrestrial sources.

5 4.6 Is there biogeochemical evidence for anoxia?

Previous studies (Melles et al., 2007; Nowaczyk et al., 2007) have posited that extremely low magnetic susceptibility values as well as finely laminated sediments support evidence for extreme water column anoxia during periods of interpreted glacial conditions. However, it cannot be determined from this evidence whether anoxia exists in the water column or strictly in the sediments. To explore another possible indicator for anoxia, and to test the original interpretation that magnetic susceptibility is a proxy for lake ice cover due to dissolution of magnetite grains under highly anoxic conditions, this study attempted to link the magnetic susceptibility record to the nitrogen cycle through bulk $\delta^{15}\text{N}_{\text{total}}$ to show evidence of anoxia through denitrification. However, the expected bulk $\delta^{15}\text{N}$ enrichment (denitrification) signal is not evident during the LLGM. Furthermore, bulk $\delta^{15}\text{N}$ actually appears to be anti-correlated with TOC during the LLGM (Fig. 4). There is perhaps an initial pulse of denitrification in response to anoxia at the beginning of Interval B, but this trend deteriorates resulting in relative ^{15}N -depletion during the LLGM, possibly related to ultra-oligotrophic conditions and a limitation of available nitrate in the lake and the surrounding frozen landscape. These results neither support nor preclude the existence of a significant anoxic portion of the water column during the LLGM at Lake El'gygytgyn.

Other evidence for anoxia might be found in the biomarker record with compounds that are often associated with anoxic conditions or methanogenesis such as tetrahymanol, loliolide/isolololide, archaeol, *sn*2-hydroxyarchaeol, crocetane, and 2,6,10,15,19-pentamethylcosane. None of the above compounds were identified in this study.

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If a portion of the water column becomes increasingly suboxic (and in the absence of appreciable sulfate), methanogenesis is expected to play a more dominant role in OM remineralization. With little evidence for methanogenesis at Lake El'gygytgyn, we look to the iron cycle to find an electron acceptor that may support anaerobic degradation of OM. Evidence exists for an Fe-reducing environment in both vivianite, which occurs throughout the core regardless of climate mode (Minyuk et al., 2007), and tentative magnetic identification of siderite (Murdock et al., 2012). It has been suggested that formation of vivianite associated with Fe-reduction requires anoxia only within diagenetic microenvironments of the sediment (Minyuk et al., 2007), but perhaps Fe-reduction becomes more dominant or widespread when other electron acceptors (i.e. O₂) are not available. More research is needed to determine whether this is the case (Murdock et al., 2012). As postulated by Nowaczyk et al. (2007), the extent of iron oxides may have implications for the unexpected patterns of magnetic susceptibility throughout the core.

5 Conclusions

There are five key points to note in conclusion of this study.

First, lipid abundance and isotopic trends do not strictly correspond with either MIS boundaries or the inferred regional LLGM. Instead, concentration and isotopic shifts are gradual and precede sharp changes in bulk geochemistry. It is apparent that there is a broader interval of molecular variability associated with the most recent cold period at Lake El'gygytgyn that is not reflected in bulk geochemistry. This work underlines the importance of further compound-specific study on Lake El'gygytgyn sediments to further constrain the interpretation of paleoenvironmental response to regional past climate variability.

Second, Lake El'gygytgyn demonstrates relatively high concentrations of both terrestrial- and aquatic-sourced lipid biomarkers during Interval B and especially during the LLGM. This is unusual in comparison to other lakes and likely suggests increased preservation due to perennial ice cover and lower O₂ concentrations due to restricted

exchange with the atmosphere rather than increased production of organic matter, although higher aquatic productivity cannot be discounted.

Third, *n*-alkanoic acid $\delta^{13}\text{C}$ values reveal aquatic contributions to long-chain C_{24} , C_{26} , and C_{28} compounds, indicating that these compounds cannot be used as markers of solely terrestrial contribution. Important for concurrent and subsequent Lake El'gygytgyn research, this finding suggests a terrestrial source for the C_{30} *n*-alkanoic acid and reveals a mixed aquatic/terrestrial source for other long-chain *n*-alkanoic acids (C_{24} , C_{26} , C_{28}) during the LLGM, which is consistent with an increase in aquatic contribution of organic matter during semi-permanent ice cover.

Fourth, direct evidence of methanogenesis is lacking throughout the our record of MIS 1–3, suggesting low-level rates/extents of methanogenesis in the lake that do not change significantly over time, even during perennial ice cover. Isotopic evidence from BAMEs suggests that much of the bacterial community exists under oxic conditions. Bulk $\delta^{15}\text{N}$ isotopic values do not require anoxic conditions in the water column. However, observations of extreme magnetic susceptibility shifts, laminated sediments, and even images from grain mounts providing hints of magnetite dissolution during the local LGM all suggest that anoxia cannot be confined only to the sediments.

Finally, isotope mass balance might place bounds on the contribution of oxidized methane or organic matter necessary to drive the $\sim 10\text{‰}$ excursion in *n*-alkanoic acid $\delta^{13}\text{C}$ values. Substantial depletion in aquatic lipids (assuming low levels of methane cycling) suggests considerable recycling of CO_2 from degraded organic matter back to aquatic primary producers with limited atmospheric CO_2 exchange. Continual cycling within this system could drive aquatic lipids to depleted values of -43‰ .

Several outstanding questions remain: How intense is water column anoxia? And, where is the oxycline? The results presented here could be compatible with a thin anoxic layer just above the sediment water interface, though it appears unlikely that a severe and significant anoxic layer throughout the water column persisted during the LLGM. Water column anoxia may not be an “on/off” switch, as the sudden shifts of magnetic susceptibility and TOC suggest, but a slow process that impedes degradation of

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organic matter (as shown by increased lipid concentrations relative to TOC) even before the sharp spike in TOC is apparent. Suboxic conditions may trigger methane cycling until limited by labile carbon, and followed by iron reduction, though more research is needed on this topic.

This work both assists in a greater understanding of the biogeochemical cycles occurring within Lake El'gygytgyn throughout various climate modes as well as expands on the body of compound-specific isotopic analysis in lake systems. Of particular interest to the Lake El'gygytgyn research community, this study confirms the complexity of interpreting glacial conditions within the El'gygytgyn water column. The expected anoxic indicators are not present, a finding that may support an interpretation of recycled carbon in an environment with reduced access to atmospheric carbon dioxide. Of interest to the lakes research community, Lake El'gygytgyn long-chain lipids (*n*-alkanoic acids C₂₄, C₂₆, and C₂₈) appear to represent a mixture of terrestrial and aquatic organic matter except for the C₃₀ *n*-alkanoic acid, which demonstrates a pure terrestrial source.

Supplementary material related to this article is available online at:
<http://www.clim-past-discuss.net/8/4625/2012/cpd-8-4625-2012-supplement.pdf>.

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Table 1. Temperature conditions for GC, GC-MS and GC-IRMS for the different compound classes examined in this study.

Fraction	Initial Temp	Hold Time	Ramp 1	Ramp 2	Ramp 3	Ramp 4	Final Temp hold
<i>n</i> -alkane (GC-FID)	60 °C	1 min	15 °C min ⁻¹ to 315 °C				15 min
<i>n</i> -alkanol (GC-FID)	60 °C	2 min	20 °C min ⁻¹ to 160 °C	4 °C min ⁻¹ to 320 °C			15 min
FAME (GC-FID)	60 °C	2 min	15 °C min ⁻¹ to 315 °C				10 min
<i>n</i> -alkane (GC-MS)	40 °C	0 min	6 °C min ⁻¹ to 320 °C				2 min
<i>n</i> -alkanol (GC-MS)	60 °C	0 min	20 °C min ⁻¹ to 160 °C				15 min
FAME (GC-MS)	40 °C	2 min	6 °C min ⁻¹ to 320 °C				2 min
<i>n</i> -alkane (GC-irMS)	115 °C	2 min	16 °C min ⁻¹ to 145 °C	12 °C min ⁻¹ to 200 °C	8 °C min ⁻¹ to 290 °C	3 °C min ⁻¹ to 325 °C	13.62 min
FAME (GC-irMS)	80 °C	2 min	12 °C to 145 °C	12 °C min ⁻¹ to 200 °C	8 °C min ⁻¹ to 290 °C	3 °C min ⁻¹ to 325 °C	11 min
<i>n</i> -alkanol (GC-irMS)	80 °C	2 min	20 °C min ⁻¹ to 200 °C	4 °C min ⁻¹ to 325 °C			15 min

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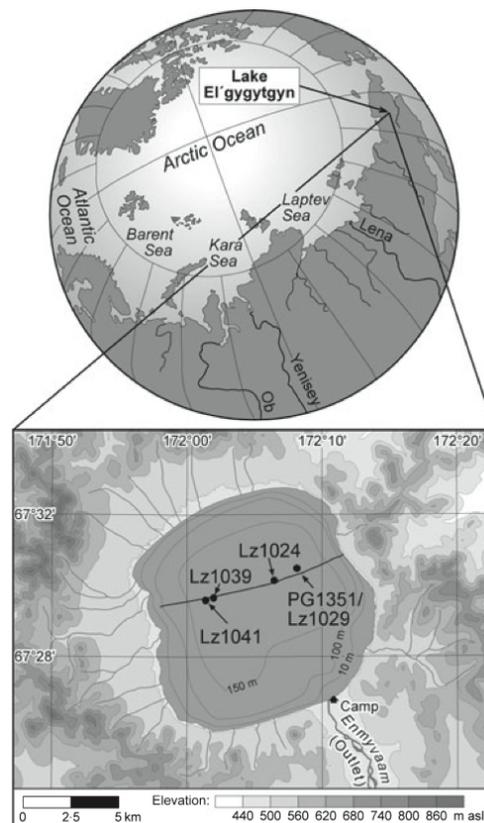


Fig. 1. Lake El'gygytgyn site location ($67^{\circ}30' \text{ N}$, $172^{\circ}5' \text{ E}$).

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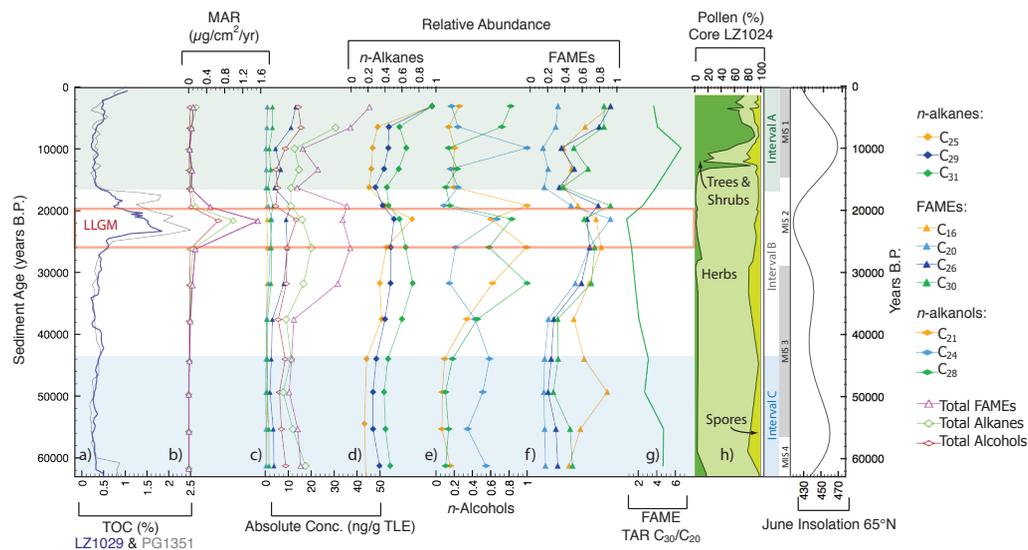


Fig. 2. Concentrations of alkanes, fatty acids and alcohols relative to TOC. Compound concentrations are represented in various configurations: **(b)** mass accumulation rates for compound groups, **(c)** absolute concentrations of representative FAMES and total *n*-alcohols, *n*-alkanes, and FAMES, **(d)** abundance of *n*-alkanes relative to the maximum value of each compound, **(e)** abundance of *n*-alcohols relative to the maximum value of each compound, **(f)** abundance of FAMES relative to the maximum value of each compound, **(g)** fatty acid terrigenous-aquatic geolipid ratio, and **(h)** pollen (core LZ1024; Lozhkin et al., 2007a).

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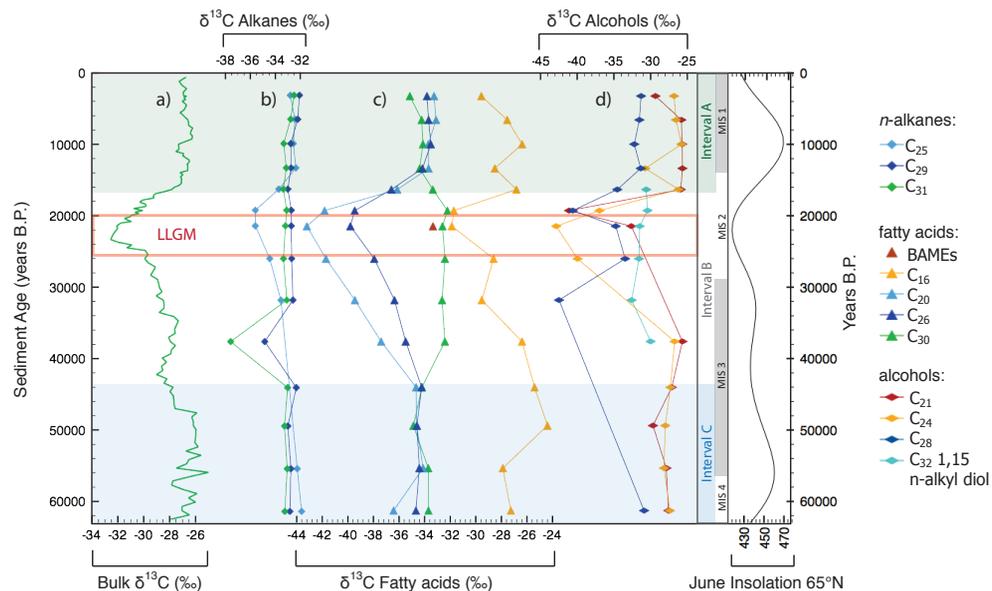


Fig. 3. (a) Bulk and compound-specific $\delta^{13}\text{C}$ values of representative (b) *n*-alkanes, (c) fatty acids, and (d) *n*-alkanols.

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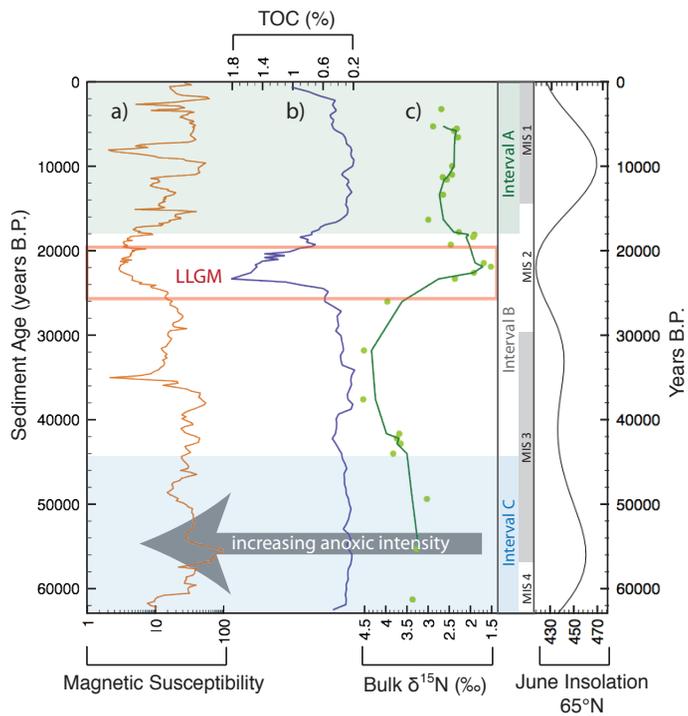


Fig. 4. (a) Magnetic susceptibility (Murdock et al., 2012) relative to (b) TOC (Murdock et al., 2012) and (c) Bulk $\delta^{15}\text{N}$. Note that the x-axis scale for TOC is reversed.

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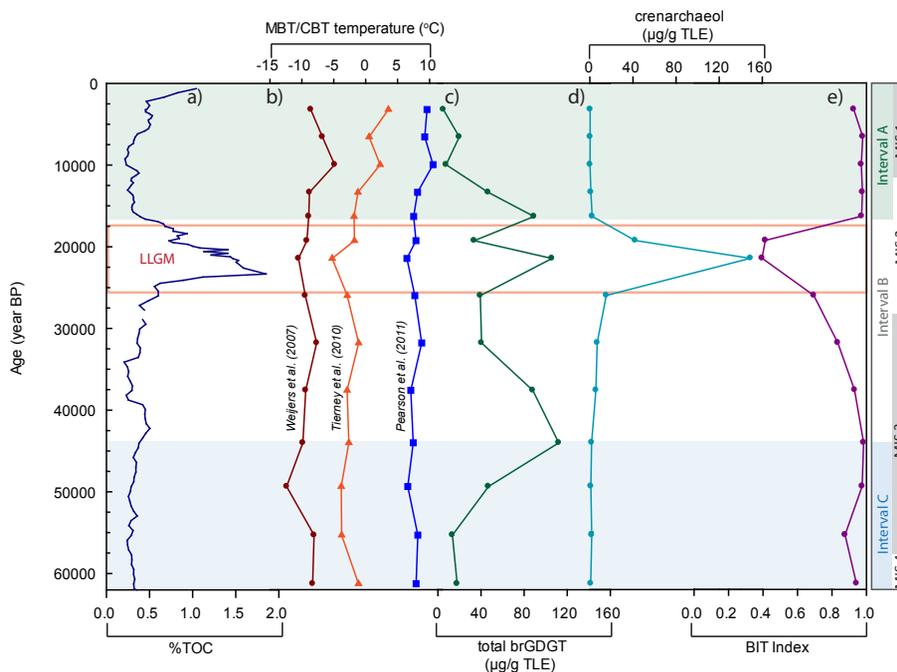


Fig. 5. Branched and isoprenoid GDGTs in Lake El'gygytgyn. The interval of the LLGM is highlighted. **(a)** %TOC (Murdock et al., 2012), **(b)** MBT/CBT derived temperatures applying the calibrations of Weijers et al. (2007; red circles), Tierney et al. (2010; orange triangles) and Pearson et al., (2011; blue squares). Note that the Weijers style calibration of Tierney et al. (2010) was applied. **(c)** Total branched GDGTs concentrations, **(d)** concentrations of the isoprenoid GDGT crenarchaeol, and **(e)** BIT Index values.

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