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I, Zachary L Mergenthal, hereby submit this original work as part of the requirements for the degree of Master of Science in Geology.

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Preliminary investigation of n-alkanes and alkenones in East Greenland lacustrine sediment: Implications for possible Holocene climate reconstructions

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Preliminary investigation of \textit{n}-alkanes and alkenones in
East Greenland lacustrine sediment: implications for
possible Holocene climate reconstructions

By

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Abstract

This study reports a reconstruction of Holocene lacustrine paleotemperatures and paleovegetation for the Scoresby Sund region 70.5° north latitude in east Greenland using long-chain alkenones and n-alkanes. Long-chain alkenones (LCAs) are biomarkers, which are produced by haptophyte algae that can provide information on regional paleoclimate conditions. C37 LCAs were analyzed using the alkenone unsaturation index, Uk37, along with published lacustrine alkenone temperature calibrations. LCAs were identified in only 1 lake (Snoopy Lake) out of 4 lakes that were examined within Scoresby Sund. At Snoopy Lake, the coldest temperature of the Holocene was measured at 9,700 YBP while the warmest temperature was measured at 7,300 YBP, corresponding with the mid-Holocene climate optimum. Late Holocene warming indicated by the Snoopy Lake Uk37 record is inconsistent with other temperature records from Greenland. We suspect this difference in Uk37 predicted temperatures is related to extrinsic factors that modify the haptophyte Uk37 proxy rather than warmer than expected absolute temperatures in eastern Greenland. Terrestrial leaf wax lipids, n-alkanes, were also analyzed in order to infer changes in vegetation caused by changes in climate. Increasing concentration of long-chain n-alkane values indicate rapid expansion of terrestrial plants 8,000 years before present, followed by decreasing abundance towards present. This vegetation pattern is consistent with other regional records of the Holocene Thermal Maximum and the Little Ice Age. The similarities between our temperature reconstruction for the Early Holocene and other records suggest that something fundamental changed during the latter part of the Holocene effecting the alkenone unsaturation. Future work needs to characterize extrinsic factors that modify Uk37 proxies and methods to identify when reconstructed temperatures are biased.
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1.0) INTRODUCTION

Projections of future climate change predict a warming of as much as 6.5°C in the next 80 years (IPCC, 2007). However, much of this warming is projected to occur in the arctic (IPCC, 2007) resulting in significant melting of the Greenland ice sheet and the potential for reorganization of ocean currents. The models used to predict possible future climate change are based on observed interactions within modern climate systems but also rely heavily on the knowledge of past climate change events. The Arctic only has limited paleoclimate records that extend back through the Holocene and have been summarized by Kaufman et al. (2004). For example one time of interest is the so-called Holocene Thermal Maximum (HTM) defined as the time when the highest temperatures were recorded. Based on the limited archives of Holocene climate in the arctic, Kaufman et al. (2004) compiled a map of spatial and temporal variations of the initiation and termination of the HTM (Figure 1). The map illustrates regional uncertainties in the arctic, specifically in eastern Greenland. In order to resolve some of these uncertainties, additional paleoclimate records are required from many proxies, locations, and at many temporal scales. These new climate records could provide a more complete understanding of past, present, and future climatic change.

Direct measurements of paleoclimate conditions are not possible as instrumental records only extend to 1,8xx AD. Proxy records are not a directly measurements of past conditions but rather represent a second order response to climate change. Commonly utilized proxy records include pollen (Srivastava, 1970), tree rings (Fritts, 1966), marine (Wall et al., 1976) and lacustrine sediment (Meyers et al., 1999), ice cores (Dansgaard et al., 1993), and speleothems (Wilson et al., 1979). Paleoclimate proxies may respond to extrinsic factors other than targeted climatic variables posing challenges for proxy reconstructions and this has been discussed in
To reduce uncertainties in paleoclimate reconstructions, it is advantageous to develop and produce many proxy reconstructions within a given region. To this end, this study investigates Holocene climate conditions of eastern Greenland using the alkenone unsaturation index, Uk37, in a region that has limited proxy reconstructions. The UK37 proxy (Brassell et al., 1986) has been utilized successfully in western Greenland to capture high-frequency Holocene temperature changes (D’Andrea et al., 2011).

The enhanced response in arctic regions associated with modern climate change conditions (IPCC, 2007) suggest that past climate change events also occurred with an enhanced response in arctic regions. The response of arctic environments to past climate change, has provided archives of paleoclimate conditions in records such as lakes, glacial deposits, and glaciers (Figure 2 and 3). Lake derived proxies are ideal for high-resolution paleoclimate reconstructions because of the often continuous sedimentation and high sedimentation rates (compared to marine environments). In non-glaciated drainage basins, relatively low rates of sedimentation coupled with low organic productivity (both lacustrine and terrestrial) provide a long term record of Holocene climate in 1-2 meters of sediment (Honsaker, 2011). Organic material incorporated into lacustrine sediment provides dates through radiocarbon analysis as well as potential paleoclimate proxy records.

Biomarkers are organic compounds produced by lacustrine and terrestrial plants as well as algae and are often incorporated into sediment. These molecules contain information pertaining to the environmental and climatic conditions at their time of production. The use of biomarkers in conjunction with other proxy records has contributed new details about paleoclimate conditions that formerly were indistinguishable (Zheng et al., 2009; Jansen et al.,
2010; Mügler et al., 2010; Seki et al., 2011). Previously, biomarkers were commonly used to support other proxy records, but are now often used as stand alone reconstructions of paleoclimate conditions (Toney et al., 2010; D'Andrea et al., 2011). Biomarker records of Holocene paleoclimate exist for several lakes in west Greenland (D'Andrea et al., 2005; D'Andrea et al., 2011, Theroux et al., 2010), but to date, no such record exists for eastern Greenland.

Comparing proxy records of paleoclimate conditions between western and eastern Greenland, specifically the Scoresby Sund region, indicates differences in climate between east and west Greenland during the Holocene (Figure 3). A biomarker reconstruction from west Greenland indicates highly variable summer temperatures and a cooling trend beginning at 3,000 YBP and continuing to present day (D'Andrea et al., 2011). The Renland ice core indicates low temperature variability and a cooling trend through the Holocene (Johnsen et al., 1992). A lacustrine diatom record from the eastern coast of Greenland indicates warmer than present conditions from 10,000 YBP to 2,000 YBP followed by a cooling trend from 2,000 YBP to present day (Cremer et al., 2001). Are these differences among records a true reflection of Holocene climate conditions or an artifact of challenges associated with comparing different proxy records? The goal of this study is to investigate the record of Holocene climate in eastern Greenland lakes for comparison with other proxies in eastern Greenland and with records from western Greenland. This study focuses on reconstructing paleotemperatures from eastern Greenland with the lacustrine biomarker proxy Uk37 used in western Greenland (D'Andrea et al., 2011), that relies on $C_{37}$ long-chain alkenones produced by haptophyte algae (Zink et al., 2001; Sun et al., 2007; Toney et al., 2010; Theroux et al., 2010). D'Andrea et al. (2011) found that haptophyte algae in western Greenland reach peak bloom conditions during July, and that
reconstructions using these algae dominantly represent peak bloom conditions. Furthermore, this study aims to reconstruct the variability in lacustrine and terrestrial paleovegetation using \(n\)-alkanes (Zhang et al., 2006; Castañeda et al., 2009; Jansen et al., 2010) to compare to the lacustrine temperature records. Therefore, this study provides a lacustrine reconstruction of summer time temperatures and changes in paleovegetation in the Scoresby Sund region of East Greenland for the past 9,500 calendar years.
Figure 1
Reported by Kaufman et al. (2004) to represent the spatial and temporal variability of reconstructed paleoclimate conditions. a) and b) represent the initiation and termination of Holocene Thermal Maximum conditions, respectively.
Figure 2
Map of Greenland with locations of other Holocene paleoclimate records. Red circle: biomarker temperature reconstruction. Blue circle: ice core locations. Yellow circle: diatom record. A: D'Andrea et al., 2011 used C\textsubscript{37} alkenones to reconstruct temperature. B: a δ\textsuperscript{18}O record from the Renland ice core (Johnsen et al., 1992) C: This study D: A diatom study by Cremer et al., 2001. The blue, red and purple dotted lines represent the East Greenland Current (EGC), the Irminger Current (IC), and the West Greenland Current (WGC), respectively. The EGC brings cold arctic water south along the coast of Greenland, while the IC brings warm Atlantic water north. The EGC and IC mix, forming the WGC at the southern tip of Greenland, and the mixed ocean water continues up the West coast.
Figure 3
Paleoclimate conditions as depicted by three different records. **A:** (site A in figure 2) The D'Andrea et al. (2011) Uk37 temperature reconstruction. **B:** (site B in Figure 2) The Johnsen et al. (1992) δ^{18}O record from the Renland Ice Core. **D:** (site D in Figure 2) The Cremmer et al. (2001) record of lacustrine diatoms.
2.0) BACKGROUND

2.1) Holocene background

The Holocene is noted for its significant departure from “ice-age” conditions during the late Pleistocene as seen in the Greenland and Antarctic ice cores (Dansgaard et al., 1993; Petit et al., 1999). Early Holocene conditions were warmer than present due to increased solar insolation (Miller et al., 2010). HTM conditions were slow to reach Greenland due to the influence of the Laurentide Ice Sheet, but once present, these conditions persisted for several thousand years (Kaufman et al., 2004). Although the Holocene is considered to be warm with respect to the last 200,000 years, many proxies for paleoclimate conditions indicate a cooling trend over the past 6,000 years (Johnsen et al., 1992; Vinther et al., 2008; Wagner et al., 2000; Wagner et al., 2002; Funder et al., 1978). However, the comparison between records indicates that climate conditions are regionally influenced, as indicated by the patterns in Figure 1.

The highest resolution record of Holocene climate conditions in Greenland comes from the Greenland ice cores, Camp Century, Dye-3, NGRIP, GRIP, and Renland which have been synchronized to the Greenland Ice Core chronology 2005 (GICC05; Vinther et al., 2008). These ice core records show a general cooling trend through the last 10,000 years, punctuated by a brief cold period around 8,200 years ago (8,200 year event; Alley et al., 1997). The Renland ice core is unique in that it is the only ice core from a small ice cap on the periphery of the Greenland ice sheet. Trends from the Renland ice core δ18O record indicate cooling conditions through the Holocene, with one brief cold temperature departure representing the 8,200 year event (Johnsen et al., 1992), similar to the other ice core records. The location of the Renland ice core, within the Scoresby Sund region of eastern Greenland, provides a regional record of climate conditions comparable to the high resolution ice core records from the summit of the Greenland ice sheet.
Changes in climate can be inferred by means other than ice cores. For example, plant species compositions can provide a qualitative record of climatic fluctuations. Funder et al. (1978) conducted a study of extant flora and lacustrine records of pollen in the Scoresby Sund region to track fluctuations in plant species through the Holocene. Three different floral assemblages were found in east Greenland: high arctic species, low arctic to sub arctic species, and ubiquitous species. The high arctic species have a southern limit just south of Scoresby Sund, while the low arctic species have a northern limit within the Scoresby Sund region. Pollen evidence indicates that Betula nana, an angiosperm that inhabits relatively warmer arctic regions, immigrated and expanded rapidly around 8,000 YBP. Today, Betula nana exists in a more retracted state. Therefore, pollen data indicate HTM conditions began in the Scoresby Sund region of east Greenland around 8,000 YBP.

Lacustrine sediment has been used in numerous Holocene climate change studies (Cremer et al., 2001; Wagner et al., 2001; Zink et al., 2001; Sun et al., 2007; Toney et al., 2010). Cremer et al. (2001) examined the ratio of planktonic and benthic diatom assemblages through time from Raffles SØ, a lake on Raffles Ø island off the coast of Scoresby Sund. This record along with increasing organic matter input suggests ice free conditions between 5,500 YBP and 1,800 YBP indicating a warm period during the Holocene. This is in contrast with other records of Holocene climate that indicate cooling during the same period (Johnsen et al., 1992; Wagner et al., 2001; D'Andrea et al., 2011).

The map of spatial and temporal patterns of HTM conditions (Figure 1; Kaufman et al., 2004) suggests that in the Scoresby Sund region, thermal maximum conditions were initiated between 6,000 and 9,000 YBP and terminated between 3,000 and 5,000 YBP. However, through
the Holocene, the Renland ice core $\delta^{18}O$ record indicates cooling conditions (Johnsen et al., 1992), pollen data suggests HTM conditions beginning around 8,000 YBP (Funder et al., 1978) and diatom assemblages indicate HTM conditions between 5,500 and 1,800 YBP (Cremer et al., 2001). These records demonstrate the incomplete understanding of climate conditions in the Scoresby Sund region during the Holocene.

### 2.2) Regional Climatic Context

Modern studies have shown the presence of a large latitudinal climate gradient in Greenland, separating high arctic conditions from sub arctic conditions; a significant climate gradient also exists between the east and west coasts. This longitudinal gradient is primarily driven by the East Greenland Current, which circulates cold high-arctic ocean water past the eastern coast of Greenland (Jennings et al., 2011) (*Figure 2*). The result of this constant flux of arctic water along the eastern coast of Greenland is sea ice that is sustained, even in summer months, at 72° N latitude. During peak summer melting, perennial sea ice cover retracts to about 170 km north of the Scoresby Sund inlet, while in the winter ice cover extends several hundred kilometers south of the Scoresby Sund inlet (http://nsidc.org/data/seaice_index/). This fluctuation in sea ice may influence the weather/climate of the Scoresby Sund region, resulting in regionally specific climate patterns.

### 2.3) Geographic Context

Four lakes were examined in the Scoresby Sund region of eastern Greenland, Quivit (71.17388 N, 28.97975 W), Raven (71.06601 N, 27.31106 W), Snoopy (70.977861 N, 22.293749 W), and Last Chance Lake (70.90646 N, 25.56951 W) (*Figure 4*). The lakes were
chosen along a transect from the east Greenland coast, inland to the Greenland Ice Sheet as representative of the Scoresby Sund region. The lakes were also chosen based on the absence of glacial influence in their drainage basins through the Holocene. It was hypothesized that the absence of glacial melt-water/sediment would increase the chances of continuous organic sedimentation needed for a complete biomarker record of Holocene climate patterns.
Figure 4

Top left: A map of Greenland with a red box denoting the area pertaining to the large image on the left, which includes the Scoresby Sund region. **Left:** The Renland ice core (Johnsen et al., 1992) location is denoted by a blue circle and the red circle marks the location the diatom study by Cremer et al., 2001. The green boxes denote the location of the lakes in this study. **Right:** A bathymetric map of one of the lakes in this study (Snoopy Lake; Honsaker, 2011), with a yellow circle representing the core location, and a red line representing the lakes modern watershed.
2.4) Geochemical paleoclimate reconstructions

2.4.1) n-Alkanes

n-Alkanes are present on the surface of most vascular plant leaves as part of the leaf wax coating (Eglinton and Hamilton, 1967). Due to the widespread presence of n-alkane producing plants, and the resistance of n-alkanes to degradation (as noted by the structure in Figure 5), these molecules are often preserved in the geologic record. Carbon chain-length and abundance of n-alkanes can yield information on biologic productivity, sediment source, sediment maturity, and climatic information (Bray and Evans, 1961; Castañeda et al., 2009).

Transitions in sediment source and/or biologic productivity can be demonstrated through changes in the average chain length (ACL) of n-alkanes. For example, terrestrial plant species typically produce n-alkanes with chain lengths between C_{23}-C_{31}, submerged plants produce n-alkanes with chain lengths between C_{19}-C_{23}, and aquatic plants produce n-alkanes with chain lengths between C_{13}-C_{19} (Bray and Evans, 1961; Castañeda et al., 2009). Increasing terrestrial productivity and increasing terrestrial input are both represented by a higher ACL. Although decreased lacustrine productivity can also result in higher ACL due to the absence of C_{13}-C_{19} n-alkanes in the overall equation. The difference between these two signals lies in n-alkane abundance. If n-alkane abundance increases with the increase in ACL this is likely the result of increased terrestrial input or productivity. A decrease in n-alkane abundance associated with an increase in ACL is likely the result of decreased lacustrine activity.

Carbon preference index (CPI) can be used to analyze the maturity of sediment or the presence of a hydrocarbon source. For example, modern n-alkanes show a predominance of odd-chain length molecules (CPI >3), while n-alkanes from a petroleum source are typically represented by a slight predominance of odd- to even-chain molecules (CPI ~1; Bray and Evans, 1961). This relationship of odd-over-even dominance through time is related to the preferential
production, and degradation of odd-chain length molecules.

2.4.2) Alkenones

The well-established Uk37 proxy (Brassell et al., 1986; Sikes et al., 1993; Müller et al., 1998; Brassell et al., 2004; Eglinton et al., 2008; Sicre et al., 2008; Huguet et al., 2011) for reconstructing sea surface temperature based on long-chain alkenones has been modified for lacustrine environments (Wang et al., 1998; Zink et al., 2001; Sun et al., 2007; D’Andrea et al., 2011). This method relies on a group of phytoplankton known as haptophyte algae, which produce alkenones. Haptophyte algae produce C_{37} alkenones in three different states of unsaturation, C_{37:2}, C_{37:3}, and C_{37:4} depending on the temperature at which the algae has been living (Figure 6). Paleotemperatures can be estimated by comparing relative differences in the degree of alkenone unsaturation to lake water temperature in modern calibration studies (Zink et al., 2001; D'Andrea et al., 2011).

In the absence of C_{37:4} molecules, the alkenone unsaturation index Uk'37 (Equation 4) is the best ratio for temperature approximation (usually in marine environments). However, haptophyte algae in most lacustrine environments produce a high abundance of C_{37:4} alkenones, which necessitates the use of the alkenone unsaturation index Uk37 (Equation 3). The difference in C_{37:4} alkenone abundances between environments is thought to be caused by the different alkenone producing haptophyte species present in each environment (Theroux et al., 2010). Theroux et al. (2010) also speculates that the decreased salinity in lacustrine environments, compared to marine environments, results in a more pronounced C_{37:4} alkenone response by lacustrine haptophyte algae.

Individual haptophyte communities may have unique proportions of C_{37:2}, C_{37:3}, and C_{37:4} unsaturation with respect to temperature. Therefore site specific temperature calibrations may be
important in lacustrine studies (Zink et al., 2001; Toney et al., 2010; Theroux et al., 2010; Castañeda et al., 2011) if haptophyte communities vary between lakes with different extrinsic conditions. It is not uncommon for individual lakes to require different temperature calibrations (Prahl and Wakeham, 1987; Prahl et al., 1988; Volkman et al., 1995; Versteegh et al., 2001; Rontani et al., 2004; Chu et al., 2005; Sun et al., 2007; D’Andrea, 2008; Liu et al., 2008). Zink et al. (2001) studied several lakes in northern Europe and North America to test a more universal temperature calibration for lacustrine environments. In the absence of site specific calibrations, the Zink et al. (2001) calibration provides a good first approximation of temperature values.
**Figure 5**
n-Alkanes are composed of carbon-carbon single bonds linked in a straight chain. The C$_{25}$ n-alkane above is named for the 25 carbons linked together in its structure. This straight chain structure provides n-alkanes with the strength and stability to resist diagenetic breakdown in the geologic record.

**Figure 6**
Alkenones fall into a group of molecules known as ketones because of the presence of a carbonyl group (carbon to oxygen double bond) attached to a carbon chain at the number two carbon position. The alkenones pictured above contains 37 carbon atoms and would therefore be referred to as C$_{37}$ alkenones. The structure of a C$_{37}$ alkenone is shown above with varying states of unsaturation. These three variations of the C$_{37}$ alkenone are produced by haptophyte algae and the relative abundance of unsaturation state can be used to calculate temperatures at which the algae were growing.

*Modified from Castañeda et al., 2011*
3.0) METHODS

3.1) Core sediment sampling

Four lakes, Quivit, Raven, Snoopy, and Last Chance Lake were cored in order to better understand climate activity during the Holocene. These lakes were chosen based on geomorphic evidence that suggested they remained free of glacial influence through the Holocene, thus providing a continuous biomarker record.

Cores were sampled at 2 cm intervals to obtain a high resolution snapshot of Holocene climate conditions. In top 25 cm of the Snoopy Lake core preliminary radiocarbon dates (Honsaker, 2011) indicated modern sediment, so samples were collected every 5 cm. Samples were dried at 60º C for 24-48 hours. Dried samples were homogenized by mortar and pestle.

3.2) Loss on Ignition

Loss on ignition (LOI) was performed at the same intervals as biomarker sampling, following the methods outlined by Heiri et al. (2001). Approximately one cubic centimeter of core material was placed into clean ceramic crucibles in an oven at 110ºC overnight to dry. Dry samples were fired at 550ºC for one hour and 1000ºC for one hour. Sample weights were recorded after the 110ºC, 550ºC, and 1000ºC burn in order to calculate dry sample weight, organic material and carbonate material, respectively.

3.3) Lipid extraction and separation

Lipids were extracted from lacustrine sediment using an accelerated solvent extractor (Dionex ASE 350) with dichloromethane (DCM)/methanol (MeOH) (4:1, v/v) over three extraction cycles at 10.34MPa (1400psi) and 100ºC. The total lipid extracts were evaporated
with a gentle stream of nitrogen and transferred to 8 ml vials using DCM/MeOH (1:1, v/v).

The total lipid extract was separated into neutral and acid fractions using flash column chromatography with 0.5 g of aminopropyl bonded silica gel (stored at 70°C). The neutral and acid fractions were eluted with 8 ml of DCM/isopropyl alcohol (IPA) (2:1, v/v) and 8 ml of MeOH, respectively. The neutral fraction was further separated with silica gel flash column chromatography into the hydrocarbon, ketone, and polar fractions. Silica gel columns were constructed using Pasteur pipettes with 0.5 cm of pyrex wool and 0.70 g of activated (200°C for two hours) silica gel. The hydrocarbon fraction, ketone fraction, and polar fraction were separated using 4 ml of hexanes, 8 ml of DCM, and 8 ml of MeOH, respectively. Separations were verified with standards and test samples from the Snoopy Lake core prior to analysis.

3.4) n-Alkane Characterization and Quantification

The hydrocarbon fraction was analyzed for n-alkanes by gas chromatography (GC)-mass spectroscopy (MS)-flame ionization detection (FID) using an Agilent Technologies (AT) 7890A GC system connected to an AT 5975C inert MSD with triple axis detector. A fused silica capillary column (Agilent HP-5; 30 m, 0.25 mm diameter, 0.25 μm film thickness) was used with helium as the carrier gas and flow rate of 1.5 ml/min. Column effluent was split 1:1 with a AT Microfluidics Two-Way Splitter with helium make-up gas at 3.8 psi. The sample was injected in pulsed-splitless mode on a Multimode Inlet at 60°C and held for one minute, ramped at 6°C/min to 320°C and held for 15 minutes. Prior to quantification, a known aliquot of each fraction was spiked with the internal standard 1,1' binaphthyl at a final concentration of 10 μg/ml. Compounds were quantified via GC with flame ionization detection (FID). Compound peak areas were normalized to those of 1,1' binaphthyl and converted to abundance using
response curves for $n$-C$_7$ to $n$-C$_{40}$ alkanes ranging in concentration from 0.1 to 100 μg/ml with Chemstation software. Average chain length (ACL) and carbon preference index (CPI) were determined using the following Equations 1 and 2.

3.5) Alkenone Characterization and Quantification

Alkenone characterization and quantification was measured with the AT GC-MS-FID system described above. Samples were injected into a silica capillary column (J&W DB-1; 60 m, 0.32 mm diameter, 0.10 μm film thickness) with helium as the carrier gas at a flow rate of 1.5 ml/min. Samples were injected at 60°C and held for 1 minute, ramped to 290°C at 30°C/min, ramped to 300°C at 5°C/min, and followed by a ramp to 325°C at 2°C/min and held for 15 minutes (modified from Toney et al., 2010). Prior to quantification a known aliquot of each sample was spiked with $n$-C$_{36}$ at 3 ng/ml of hexanes. Quantification was determined by integrating the FID chromatograms using Chemstation software relative to external alkane standards $n$-C$_{29}$, $n$-C$_{30}$, $n$-C$_{31}$, $n$-C$_{33}$, $n$-C$_{35}$, and $n$-C$_{38}$ ranging in concentration from 0.5 to 100 μg/ml.

3.6) Temperature from Alkenones

Paleotemperatures were reconstructed using alkenone abundances (Brassell et al., 1986; D’Andrea et al., 2011; Huang et al., 2004; Toney et al., 2010; Zink et al., 2001). Alkenones are molecules produced by haptophyte algae as a part of their cell membranes and the alkenone unsaturation index is modified based on temperature to maintain membrane fluidity (Castañeda et al., 2011). The degree of unsaturation in these molecules influences the viscosity the cell membrane. The Uk37 proxy uses the relative abundances of C$_{37}$:2, C$_{37}$:3, and C$_{37}$:4 unsaturated
molecules by comparing the ratio of the difference between C\textsubscript{37:4}, C\textsubscript{37:3} and C\textsubscript{37:2} to the total sum of C\textsubscript{37} alkenones and compares this degree of unsaturation to temperature measured in modern calibration studies (Equation 3; Brassell et al., 1986). The Uk'37 index (Equation 4) is also used in paleoclimate proxies but this proxy does not incorporate the C\textsubscript{37:4} alkenone. When the C\textsubscript{37:4} alkenone is present, the Uk37 index is more reliable than the Uk'37 index for temperature reconstruction. Regional or haptophyte species specific temperatures calibration curves are applied to the Uk37 (Uk'37) number in order to derive a quantitative temperature value. In this case, the exact species of haptophyte is unknown, so two regional calibrations (D'Andrea et al., 2011 and Zink et al., 2001) were applied to the Uk37 data for comparison.
Average Chain Length (ACL) is a parameter used to distinguish between higher plants (Bray and Evans, 1961). ACL has also been shown to vary with increasing temperature or aridity (Rommerskirchen et al., 2003; Peltzer et al., 1989).

\[
ACL = \frac{(19n-C_{19} + 21n-C_{21} + 23n-C_{23} + 25n-C_{25} + 27n-C_{27} + 29n-C_{29} + 31n-C_{31})}{(n-C_{19} + n-C_{21} + n-C_{23} + n-C_{25} + n-C_{27} + n-C_{29} + n-C_{31})}
\]

**Equation 1**

*Modified from Bray and Evans 1961*

Carbon Preference Index (CPI) is a parameter used to examine odd over even predominance in long-chain n-alkanes (Bray and Evans, 1961). CPI can be used to distinguish between well preserved terrestrial molecules and petroleum sources. CPI values >3 indicate terrestrial origin, while values ~1 indicate a hydrocarbon source.

\[
CPI = 0.5 \left[ \frac{(n-C_{19} + n-C_{21} + n-C_{23} + n-C_{25} + n-C_{27} + n-C_{29} + n-C_{31})}{(n-C_{18} + n-C_{20} + n-C_{22} + n-C_{24} + n-C_{26} + n-C_{28} + n-C_{30})} + \frac{(n-C_{19} + n-C_{21} + n-C_{23} + n-C_{25} + n-C_{27} + n-C_{29} + n-C_{31})}{(n-C_{20} + n-C_{22} + n-C_{24} + n-C_{26} + n-C_{28} + n-C_{30} + n-C_{32})} \right]
\]

**Equation 2**

*Modified from Bray and Evans 1961*

\[
U_{37}^{k} = \frac{[37:2] - [37:4]}{[37:2] + [37:3] + [37:4]}
\]

**Equation 3**

\[
U_{37}^{k'} = \frac{[37:2]}{[37:2] + [37:3]}
\]

**Equation 4**

*Equations 3 and 4 from Brassell et al. (1986)*
4.0) RESULTS

Snoopy Lake is the only lake out of the four lakes sampled in this study to contain $C_{37}$ alkenones useful in reconstructing paleotemperatures. Therefore we focus here on Snoopy Lake (450 m a.s.l.), located 1.5 km to the west of the Istrovet Ice Cap within the Liverpool Land area of Scoresby Sund (Figure 4). A north/south trending fault to the east of Snoopy Lake separates this drainage basin from the influence of glacial melt water, resulting in the source area for sediment in Snoopy Lake to be constrained only to its drainage basin and eolian sources. Snoopy Lake covers an area of 177,000 sq. m, has a maximum depth of 20 m and a drainage basin that covers an area of 423,000 sq. m. On August 30th 2010 the water temperature was measured to be 8.8°C. Future studies will attempt to determine why lakes with similar extrinsic factors do not contain alkenones.

4.1) Core Description

The Snoopy Lake core is dominated by a tangled mat of lacustrine plant fibers (Figure 7). This organic mat is found all the way through the core, with a few zones of slightly lower abundance and one small zone of complete absence. Based on visual stratigraphy, the core was divided into five dominant units, and they are reported here from the base up. Unit 5 (108-113 cm) is more visually distinct than any of the other units and is characterized by brown silts and clays. No organic matter is present within this unit. A notable shift on sediment color and composition, olive colored silt and clay matrix to a light brown clay dominated matrix, occurs at 110.5-112.5 cm of unit 5. Unit 4 (95.5-108 cm) was divided into three sub groups, A, B, and C, based on slight changes within the unit. The lithology of 4A and 4C resembles that of unit 2, but 4B marks a transition to a dark brown silty matrix with densely concentrated organic fibers. Unit
3 (87-95.5 cm) marks a transition to light brown silts and clays with less organic plant fibers present than units above and below. Unit 2 (64-87 cm) is an organic rich silt with a higher concentration of plant material than unit 1. Unit 1 (0-64 cm) is a massive unit composed of organic rich silt and plant fibers.

4.2) Loss On Ignition

Loss on ignition was examined at each location that alkenone samples were collected (Figure 8) (Table 1). Unit 5 contained less organic matter than any other unit in the core. Just above unit 5 the organic matter increases to about 31% and remains fairly consistent (+/- 3%) until about 60 cm. From 60 cm to the top of the core the organic matter fluctuates from higher to lower values with higher variability than in the lower sections of the core. A slight negative trend is observed in the top 60 cm of the core, where organic matter decreases from 30% to 26%. The percent of carbonate material was much less variable than organic matter. A slight positive trend was found from 113-76 cm, culminating in a peak between 76 and 78 cm where carbonate reaches 5.4%. Above 76 cm, a gradual negative trend was observed until carbonate reached 1% in the modern samples.

4.3) Radiocarbon

Radiocarbon dates were obtained from aquatic plants extracted from Snoopy core at depths of, 6, 23.3, 85.5, and 109 cm by Honsaker (2011) (Table 2). Radiocarbon ages were converted from $^{14}C$ years before present to calibrated years before present (cal. YBP) using Calib 6.0 with a 2 sigma range. The samples at 6 and 23.3 cm yielded modern ages, and the samples at 85.5 and 109 cm yielded ages of 5,638 cal. YBP and 9,716 cal. YBP, respectively (Figure 8). In
order to establish a more robust chronology of the core, five additional samples were collected, at 24, 43, 66, 76, and 100 cm; these additional samples will help establish a chronology of Snoopy Lake that will account for variables such as changes in sedimentation rate. Samples will be analyzed during the summer of 2012 and will be published as an addendum to this thesis.

4.4) n-Alkanes

*n*-Alkanes are present from *n*-C<sub>19</sub> to *n*-C<sub>33</sub> in the Snoopy Lake core as illustrated by Figure 8. *n*-Alkane concentration (Figure 9), suggests a decline in biologic productivity. Total *n*-alkane concentration declined from 33.5 µg/g at 109 cm to 13.2 µg/g at 7 cm. However, the concentration of *n*-alkanes significantly increases at 105 cm (1412.1 µg/g).

The transition from unit 4B to unit 4A marks a particularly high ACL value in the core (26.0) but both above and below this point the values drop sharply (Figure 9). The lowest ACL value in the core occurs in unit 3, which is shown by a decreasing trend from 25.8 at 95.5 cm to 24.3 at 88.5 cm. At 85.5 cm, the transition from unit 3 to unit 2, an abrupt increase in ACL to 25.6 occurs. The ACL trend in unit 2 peaked at 25.9 at 65.5 cm, transitioning into unit 1 where the ACL steadily decreased to 24.7 at 7 cm, which is considered to be a modern value based on the chronology of this core.

Unit 4C shows a zone of relatively stable CPI with values between 5 and 9, but in unit 4B and 4A CPI increases sharply to 24.2 and 23.1 at 102.5 cm and 97.5 cm, respectively (Figure 9). At the top of unit 4A CPI values drop to 5.02 and fluctuate only slightly until the middle of unit 1 where CPI reaches 34.4 at 23 cm. This brief peak is again followed by a decline to 13.4 at 19.5 cm. A modern CPI of 7.8 is observed at 7 cm. At 26.5 cm there is an absence of even chain *n*-alkanes, which caused the CPI for this sample to be undefined.
4.5.) Alkenone Trends

C$_{37}$ concentrations through the core range from 0.7 $\mu$g/g to 43.2 $\mu$g/g at 93 cm and 32.5 cm, respectively. The zone from 90-100 cm marks a decrease in alkenone concentration to about 1$\mu$g/g of sediment. From 90-82.5 cm, the concentration increased by an order of magnitude to 27.4 $\mu$g/g. The concentration remained relatively unchanged from 84-70 cm. Above this, the concentrations become highly variable, ranging from 33.54 $\mu$g/g at 69.5 cm to 5.74 $\mu$g/g at 7 cm with a negative trend from 70-0cm.

4.5.1) m/z 152

Toney et al. (2010) demonstrated the importance of GC-MS identification of alkenones before using GC-FID to quantify the compounds because of the presence of an unidentified compound that co-elutes with C$_{37}$ alkenones. In a study of 53 lakes, this unidentified molecule was reported in 19 lakes, including 12 lakes that did not contain alkenones. This unidentified molecule has a dominant ion peak at molecular weight 152 and will henceforth be referred to as m/z 152 following Toney et al. (2010). In the Snoopy Lake samples we also identified a molecule, with the same mass spectra described by Toney et al. (2010), that was found co-eluting with the alkenones in all samples (Figure 12), but varying in abundance relative to alkenone abundances. The presence of m/z 152 was less than 10% of the alkenones in most samples, based on relative ion-extracted peak areas. In the horizon between 85 and 100 cm, alkenone concentrations decreased substantially, to as low as 0.73 $\mu$g/g while the relative abundance of m/z 152 increased. This negative correlation between alkenones and m/z 152 has previously been observed (Toney, 2012; personal communication), but the origin, molecular structure, chemical composition, and role in the ecosystem are currently unknown (Toney et al., 2010)
4.5.2) Temperature Trends

Temperature values are calculated from C_{37} alkenones using the Uk37 number (Equation 3) and a temperature calibration based on haptophyte community. The exact species of haptophyte algae in Snoopy Lake is/are unknown; therefore two regional calibrations were applied to the Uk37 data for comparison (Zink et al., 2001; D'Andrea et al., 2011). The two temperature calibrations resulted in similar trends in the core but were offset by an average of 1.1°C. During the 2010 field season, Snoopy Lake temperature was measured to be 8.8°C at the end of August and the youngest reconstructed temperature using the Zink et al. (2001) calibration was 9.6°C, which is within the margin of error reported for analytical analysis (Toney et al., 2010). The youngest temperature from the D'Andrea et al. (2011) calibration was 10.5°C, outside of the accepted error of this analysis. Therefore the following trends are discussed in the context of the Zink et al. (2001) calibration due to the similarity in measured and reconstructed lake temperatures. At 113-105 cm the temperature remains close to 10°C but at 102.5 cm the temperature drops 2.5°C. Following this significant drop in temperature, alkenone concentrations decrease and m/z 152 becomes more dominant, resulting in unreliable temperature reconstructions from 100-85 cm (Figure 12B). Above 85 cm, alkenone concentrations rebound and m/z 152 abundance decreases to 10% or less of the total alkenone concentrations (Figure 12A). Temperatures fluctuate between 6.2°C and 10.0°C through the rest of the core and a warming trend is observed with time. From 85 cm to the top of the core the temperature increases about 2.3°C, with a modern temperature of 9.6°C compared to a measured temperature of 8.8°C.
Figure 7

Snoopy Lake core stratigraphy:

Left: Photograph of the Snoopy Lake core. Black arrows indicate previously processed radiocarbon samples (Honsaker, 2011), while red arrows indicate locations of radiocarbon samples yet to be processed. A significant percent of the core is composed of a tangled mat of macro organic fibers, likely of aquatic origin. Units 1-5 are described above. Right: Stratigraphic representation of the Snoopy Lake core.

**Unit 1:** (0-64 cm) Organic rich silt and some plant fibers

**Unit 2:** (64-87 cm) Organic rich silt with higher concentration of plant material than above

**Unit 3:** (87-95.5 cm) Massive silt unit with plant material

**Unit 4A:** (95.5-100.5 cm) Olive silt and clay matrix with some plant material

**Unit 4B:** (100.5-103 cm) Organic rich silt dominated by plant fibers

**Unit 4C:** (103-108 cm) Olive silt and clay matrix with some plant material

**Unit 5:** (108-113 cm) Silt and clay with no plant fibers
Figure 8
Partial gas chromatograms of n-alkane abundance, determined by flame ionization detection. GL32, GL25, and GL27 are arranged in stratigraphic order according to the sampling locations. The internal standard is denoted by IS. The chromatograms indicate the distribution of the different n-alkane homologues through the core.
Figure 9
A comparison of the loss on ignition and geochemical data from the Snoopy core. A: Organic LOI, B: Carbonate LOI, C: C\textsubscript{37} alkenone concentration, D: Alkane concentration, E: Average Chain Length, F: Carbon Preference Index, G: Uk37 temperature reconstruction plotted with two different calibration curves.
Figure 10

Partial gas chromatograms of C_{37} alkenone abundance, determined by flame ionization detection. GL32, GL25, and GL27 are arranged in stratigraphic order according to the sampling locations. The chromatograms include C_{37} Alkenone peaks labeled as 4, 3, and 2, representing the number of double bonds in each molecule (the state of unsaturation). All x and y axes are scaled the same for ease of comparison.
Figure 11

C$_{37}$ alkenone data from Snoopy Lake. The black line represents C$_{37}$ alkenone concentration. The Blue line indicates Uk37 values calculated from the raw data. The red and green lines represent temperature reconstructions from the peak abundances in Figure 8. The interference by molecule m/z 152 as shown in the GL25 plot in Figure 12 rendered a zone of the core from 85-100 cm unusable for temperature reconstructions. The red temperature plot represents the Snoopy Lake Uk37 data applied to the Zink et al. (2001) temperature calibration and the green plot represents the Snoopy Lake Uk37 data applied to the D'Andrea et al. (2011) temperature calibration.
Figure 12
Mass spectroscopy partial gas chromatograms of Alkenone abundance. GL32, GL25, and GL27 are arranged in stratigraphic order according to the sampling locations. The chromatograms include C_{37} Alkenone peaks labeled as 4, 3, and 2, representing the number of double bonds in each molecule (the state of unsaturation). Ions 81, 95, and 152 have been plotted to show the changes in ionic composition through the core. Ions 81 and 95 belong to C_{37} alkenones, while Ion 152 is part of an unidentified molecule that has only been described previously in minor detail (Toney et al., 2010). All x and y axies are scaled the same for ease of comparison.
5.0) DISCUSSION

5.1) Vegetation History

Short-chain \( n \)-alkanes in the range of \( n-C_{13} \) to \( n-C_{19} \) are indicative of an algal, bacterial, and/or aquatic signal, \( n-C_{19} \) to \( C_{23} \) typically represent the submerged or lake marginal plant species, and \( n-C_{23} \) to \( C_{33} \) indicate the influence of higher terrestrial plants (Bray and Evans, 1961). The long-chain alkanes \( n-C_{19} \) to \( n-C_{33} \) found in the sediment from Snoopy Lake indicate terrestrial input from higher plants; the absence of short-chain \( n \)-alkanes (< \( n-C_{19} \)) indicates an oligotrophic environment (Zheng et al., 2009). Field observations of an oligotrophic lacustrine environment at Snoopy Lake support this finding. The physical stratigraphy of the core contains a large portion of aquatic plants/roots in units 1-4, but the absence of short chain \( n \)-alkanes in the core suggests that these plants are not producing \( n \)-alkanes. A decrease in total \( n \)-alkane concentration through time indicates a decline in biologic productivity of the basin through time.

Changes in ACL indicate variations in the relative input of terrestrial and submerged vegetation. Maximum ACL values in unit 4 followed by the stable decline in ACL values through time could represent the rapid expansion and steady decline of a specific group of vegetation. Pollen records indicate that around 8,000 YBP Betula nana immigrated and expanded rapidly but exists today in a more retracted state (Funder et al., 1978). Maximum ACL values indicate an increase in terrestrial biologic productivity, suggested by the rapid expansion of Betula nana (Funder et al., 1978) and the declining trend in ACL through time is supported by the declining presence of Betula nana in the Scoresby Sund region.

CPI values >3 are taken to represent young/well preserved \( n \)-alkanes while values ~1 indicate a mature source of \( n \)-alkanes, most likely from a hydrocarbon reservoir when observed in modern depositional environments like lakes (Bray and Evans, 1961). The CPI values in
Snoopy Lake span an order of magnitude and range from 2.9 to 34.4. These values of 3 and greater indicate a high degree of preservation and a modern vegetation source rather than a hydrocarbon seep. A large range such as this has been shown to exist in modern environments (Diefendorf et al., 2011), among different plant functional types.

The rapid fluctuation in the Snoopy Lake CPI, concomitant with the maximum ACL indicates a reorganization of plant communities with the potential for changes in plant functional types. These findings are supported by the pollen record (Funder et al., 1978) that indicates an introduction and rapid expansion of a new flora species around 8,000 YBP. A more detailed chronology of the Snoopy Lake sediment will allow for more precise comparisons between these sites.

5.2) Snoopy Lake Holocene lacustrine temperatures

The Uk37 temperature reconstruction from Snoopy Lake indicates a broad warming trend through the Holocene of about 3°C that does not agree with other reported records of Holocene climate activity (Johnsen et al., 1992; Cremer et al., 2001; D'Andrea et al., 2011). However, using the preliminary chronology to plot the Snoopy Lake data at the same time scale as the other records (Figure 13) reveals similar trends to the D'Andrea et al. (2011) data from about 6,000 YBP to 1,800 YBP, after which time the records diverge. D'Andrea et al. (2011) and Cremer et al. (2001) suggest a cooling trend during the last 1,800 years that is associated with Little Ice Age cooling, while the Snoopy Lake temperature reconstruction suggests warming trends through the last 1,800 years. D'Andrea et al. (2011) show a record of highly variable temperature conditions ranging from 4°C to 9.5°C with a slight cooling trend of 1°C during the last 3,000 years. The Snoopy Lake record not only shows an opposite temperature trend that
indicates warming of 2°C during this period, it also exhibits a dampened signal of variability of about 6.5°C to 10°C (Figure 13).

Bioturbation is a potential source of signal dampening in some lacustrine cores. The effects of bioturbation in Snoopy Lake are likely minimal, based on the presence of preserved bedding in a few horizons of the core. In the arctic, deep bioturbation is rare given the cold temperatures and short summer conditions, but it can not be precluded in some portions of the core, such as the upper 60 cm where homogeneous sediments are found. The reworking of lacustrine material would increase the amount of time averaging at each sample location, effectively dampening the signal of temperature. It is important to note that although temperature variability would decrease as a result of reworking, the broad, regional temperature trends would remain unchanged. The presence of non-varying geochemical signal resolution throughout the core coupled with stratified zones known to be free of bioturbation, indicate that bioturbation is not a factor in the dampened signal from the Snoopy Lake core.

5.3) Challenging the Uk37 record

The record produced by biomarkers in Snoopy Lake is inconsistent with other records of paleoclimate in the arctic (Figure 13), especially pertaining to the last 3,000 years. An overwhelming body of evidence supports a late Holocene cooling trend that is responsible for glacial advanced around the world (Johnsen et al., 1992; Cremer et al., 2001; Kaufman et al., 2004; Miller et al., 2010; Hall et al., 2010; Honsaker, 2011), and the Snoopy Lake record appears to be at odds with these records. Co-elution of m/z 152 with the C_{37} alkenones could result in varying degrees of influence through the core, skewing temperature reconstructions. Other factors such as species community changes, or extrinsic factors such as light and nutrients, that
control haptophyte growth, could influence alkenone ratios (Prahl et al., 2006; Placencia et al., 2010; Toney et al., 2010; Castañeda et al., 2011).

Disentangling the influence of $m/z$ 152 from alkenone abundance in the Snoopy Lake samples is challenging because we have limited knowledge about the source, structure, composition and standards for this compound. In this case $m/z$ 152 co-eluted with two alkenone peaks, $C_{37:4}$ and $C_{37:3}$. GC-MS analysis provided the means to identify $m/z$ 152 and alkenone responses separately by measuring abundance of molecular ions specific for alkenones and the unidentified compound. In this study, GC-MS was used for identification of compounds while GC-FID was used for quantification. Measuring the individual contributions of $m/z$ 152 and alkenones using GC-MS provides a qualitative approach to test if the $m/z$ 152 compounds are causing the higher than expected temperatures in sediments from 3,000 YBP to present. Contributions by the $C_{37}$ alkenones were determined by analyzing ion $m/z$ 95, while the contribution of the unknown molecule was measured using ion $m/z$ 152. Molecular ion contributions from $m/z$ 95 and $m/z$ 152 were examined on the $C_{37:4}$ and $C_{37:3}$ alkenone peaks using the ratio $m/z$ 95 / ($m/z$ 95 + $m/z$ 152). This ratio resulted in values between 0 and 1 (Table 5) that will be referred to as the influence factor (IF), with 0 representing no alkenone contribution and 1 representing no $m/z$ 152 contribution. The IF values are listed for the $C_{37:4}$ and $C_{37:3}$ alkenone peaks in Table 5. Relying on the information that increasing levels of unsaturation in $C_{37}$ alkenones indicates colder temperatures, the relative influence of the unknown molecule was assessed using a ratio of the two IFs ($C_{37:4}$ IF / $C_{37:3}$ IF) (Table 5). Values >1 indicate proportionally larger influence of the unknown molecule to $C_{37:3}$ resulting in a warmer than actual temperature reconstruction while values <1 indicate proportionally larger influence of the unknown molecule to the $C_{37:4}$ resulting in a colder than actual temperature.
reconstruction. Results of this total influence assessment indicate sample location where the contribution of m/z 152 resulted in warmer than actual temperatures and in some location colder than actual temperatures. In order for the contribution of m/z 152 to be responsible for the disparate temperature values at the top of the Snoopy Lake core, C_{37:4} IF / C_{37:3} IF values should be >1 and increasing towards the top of the core to account for the continued warming trend. However, this is not the pattern that is observed (Table 5) indicating that the contributions of m/z 152 are not the cause for an unreliable temperature reconstruction from Snoopy Lake. In fact, the apparent Uk37 temperature estimates are dampened by the m/z 152 contributions.

The Uk37 proxy was first developed in marine environments, which includes a relatively homogeneous global mixture of nutrients, while lake chemistry varies significantly between drainage basins. However, marine nutrient supply does vary, especially in zones of upwelling. For example, Placencia et al. (2010) examined the Peru-Chile margin where permanent upwelling supports phytoplankton communities large enough to deplete surface water nitrate concentrations which resulted in anomalously cold Uk'37 temperatures. In a laboratory culture experiment Prahl et al. (2006) demonstrated a change in Uk'37 values equivalent to a 3°C temperature decrease through nitrate and phosphate starvation. While these studies indicate factors other than temperature are responsible for changing alkenone ratios, nutrient starvation results in colder than actual temperature reconstructions, while the Snoopy Lake data represents warmer than actual conditions.

Light is another physiological factor influencing haptophyte growth and alkenone ratios. In a dark stress culture experiment Prahl et al. (2006) demonstrated an increase in Uk'37 values equivalent to a 1.3°C increase in temperature. This experiment was conducted by comparing a culture grown in a 12 hour light/dark cycle to a culture grown under 24 hours of darkness. This
finding indicates that dark stress leads to warmer than actual temperatures represented by the Uk37 values. Castaneda et al. (2011) suggested that dark stress may be especially important to ice-covered lakes. This influence could be pertinent to Snoopy Lake due to the duration of annual ice-cover, limiting light and inducing dark stress in the haptophyte algae present. D’Andrea et al. (2011) indicated haptophyte peak bloom conditions between mid June and mid but if haptophyte peak bloom occurs in Snoopy Lake during significant ice-cover, the Uk37 values would indicate warmer than actual temperatures, a trend that has been observed in the last 3,000 years at this location. However, if peak bloom conditions can not occur while lakes remain ice-covered, the prolonged ice cover conditions may delay haptophyte peak bloom until later in the summer. Changes in the timing of haptophyte peak bloom are not accounted for in temperature calibrations, and may result in unreliable temperature reconstructions. Furthermore, arctic regions receive 22-23 hours of daylight during June and July, which would cause a larger difference between in-situ measures of Uk37 values in ice free (nearly 24h of light) and ice-covered lakes (nearly 24 h of darkness). If, as indicated by other records of paleoclimate, the late Holocene was punctuated by a cold period that culminated in the Little Ice Age 150 YBP, then colder than present conditions would have prolonged ice cover on Snoopy Lake, resulting in a warmer than actual temperature reconstruction.

The Uk37 index was developed as proxy for reconstructing temperatures in marine environments, but through the development of the proxy, other environmental factors have been found to influence Uk37 values and the resulting temperature reconstructions. In this study an unidentified molecule was found co-eluting with C_{37} alkenones used to reconstruct temperature but the presence of this molecule was found not to be the cause of the major temperature discrepancies. Nitrate and Phosphate levels have also been found to influence Uk37 temperature
reconstructions (Prahl et al., 2006; Placencia et al., 2010) but nutrient starvation has been shown to lower Uk’37 values and the resulting temperatures. However, this is contradictory to the warmer than actual temperatures reported from Snoopy Lake indicating that nutrient starvation is not a factor causing the anomalous warm temperatures in this study. Another environmental factor that has been found to influence Uk’37 values is photic energy. Light starvation has been shown to increase Uk’37 values and the resulting temperatures (Prahl et al., 2006). The warmer than actual temperatures reported from haptophyte dark stress experiments agrees with the trends reconstructed from Snoopy Lake in the last 3,000 years. As climate progressively cooled towards the culmination of the Little Ice Age, ice cover would have remained for longer periods of time on Snoopy Lake, resulting in Uk37 values progressively warmer than actual conditions. While the influence of dark stress conditions can account for the anomalous temperature trends in the Snoopy Lake core, the data are inconsistent with other records of paleoclimate during the Holocene. Further work is needed on the Uk37 proxy for its use to become widespread in the arctic. However, this proxy provides the potential to reconstruct paleotemperatures from lacustrine environments around the world.
Figure 13
6.0) CONCLUSION

Although free of glacial influence, Snoopy Lake was found to be oligotrophic based on field observation and the absence of \( n-C_{13} \) to \( n-C_{19} \) alkanes. A dense mat of lacustrine plant fibers was found tangled through the length of the core, with the exception of unit 5. As suggested by the presence of mid-chain length \( n \)-alkanes (\( C_{19} \) to \( C_{23} \)) this aquatic plant material could be a submerged plant species that grows in the shallow perimeter waters of the lake and is subsequently deposited in the deeper basins. The absence of short-chain \( n \)-alkanes and the presence of mid- to long-chain \( n \)-alkanes indicated that fluctuations in alkane concentrations represent changes in submerged and terrestrial plant communities, or changes in source material. ACL values fluctuate between 26.3 and 23.8 through the entire core indicating stable plant communities, but the decreasing ACL trend through time along with the decreasing \( n \)-alkane concentration indicate decreasing input of terrestrial material during the late Holocene. CPI values of 2.9 and greater support consistent source material and preclude the input of \( n \)-alkanes by petroleum sources. The decrease in \( n \)-alkane concentration and decrease of terrestrial input through time indicate the declining presence of terrestrial plants which supports cooling conditions during the late Holocene.

Four lakes were investigated for their potential to reconstruct temperature in East Greenland, but only one was found to support communities of haptophyte algae that produce alkenones suitable for temperature reconstruction (D'Andrea et al., 2011). This data is confirmed by other alkenone studies that suggest that these compounds are somewhat rare in lacustrine environments. The increasing temperature trend indicated for the last 3,000 years from the Snoopy Lake temperature reconstruction disagrees with other arctic records of paleoclimate conditions (Johnsen et al., 1992; Cremer et al., 2001; Kaufman et al., 2004; Miller et al., 2010; Hall et al., 2010; Honsaker, 2011; D'Andrea et al., 2011). Haptophyte communities subjected to
dark stress have been shown to produce Uk’37 values equivalent to warmer than actual conditions (Prahl et al., 2006). Lake ice-cover conditions resulting from cooling temperatures could lead to a variable influence of dark stress on haptophyte communities in the arctic. Cooling late Holocene conditions supported by the n-alkane data in this study could indicate an increase in the duration of summer ice-cover at Snoopy Lake. This increase in ice-cover duration could include the haptophyte algae peak bloom suggested to occur between mid June and mid July (D’Andrea et al., 2011). The increased duration of dark stress through the late Holocene could result in increasing temperatures reported by the Uk37 index, consistent with the trend reported in this study.

The broad climatic interpretations from Snoopy Lake indicate warm stable conditions during the early Holocene, followed by a cooling trend that is associated with fluctuations in plant communities as represented by n-alkanes. The biomarker records suggest a stabilization in climate and biosphere conditions around 5,600 YBP, demonstrated, in part, by the resurgence of C_{37} alkenone production during the same period that C_{37} alkenone production began in west Greenland lakes (D’Andrea et al., 2011). The west Greenland alkenone record and the Cremer et al. (2001) diatom record indicate cooling beginning at 1,800 YBP while the Snoopy Lake record indicates a continued warming trend. The disparate nature of the Snoopy Lake record in context with other records indicates challenges associated with lacustrine paleotemperature reconstructions from alkenones without further investigations into extrinsic controls on alkenone unsaturation.

Modern climate change is projected to impact arctic conditions at a greater magnitude than lower latitude regions, indicating the importance of arctic environments to paleoclimate reconstructions. Although the paleotemperature record from this study is obfuscated by
unidentified extrinsic factors, advancement of the Uk37 index with future work could provide a reliable record of temperature from Snoopy Lake. The influences of dark stress need to be examined more closely in arctic environments. For example, ice-covered lakes should be examined for the amount of light that penetrates the ice depending on its thickness, and if ice covered lakes can sustain haptophyte algae communities in peak bloom. If the influence of dark stress can be separated then it could be possible to obtain a reliable record of temperature. This study stresses the importance of future research on the extrinsic controls on alkenone paleotemperature based proxies. If these challenges can be minimized, then alkenones could be used as quantitative paleotemperature proxies at other lacustrine sites in the high arctic. These types of studies could then aid in the assessment of future climate change projections in arctic regions.
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Toney, personal communication, 2012


APPENDIX A

Data tables: 1-5
**Table 1**  
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Organic and carbonate loss on ignition from the Snoopy Lake core.

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14C radiocarbon ages from the Snoopy Lake core.

* denotes samples that have been collected but not yet processed.
Table 3

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| 85.5       | 18669215.72          | 10580766.44          | 1277625.82           | -0.570 | 8.56                        | 7.36                        |
| 88.5       | 3368651.68           | 1359032.32           | 0.00                 | -0.713 | 2.73                        | 0.59                        |
| 91         | 13495669.35          | 8337649.41           | 4871484.10           | -0.323 | 18.62                       | 19.05                       |
| 93         | 1727108.00           | 1463785.59           | 574286.03            | -0.306 | 19.31                       | 19.85                       |
| 95.5       | 22198460.43          | 15237396.30          | 4665878.61           | -0.416 | 14.81                       | 14.62                       |
| 97.5       | 2231746.31           | 12619114.48          | 772768.01            | -0.342 | 17.85                       | 18.15                       |
| 100        | 16290404.36          | 9053312.12           | 2669616.03           | -0.486 | 11.96                       | 11.31                       |
| 102.5      | 25723225.19          | 14610041.99          | 1563589.65           | -0.577 | 8.27                        | 7.03                        |
| 105        | 19136926.42          | 11734947.31          | 1947112.23           | -0.524 | 10.43                       | 9.54                        |
| 106.5      | 15545566.20          | 9670788.22           | 1339837.69           | -0.535 | 9.97                        | 9.01                        |
| 107.5      | 13545733.49          | 8102980.20           | 1349406.87           | -0.530 | 10.16                       | 9.23                        |
| 109        | 13777095.36          | 8322441.23           | 1203007.25           | -0.540 | 9.78                        | 8.79                        |

<sup>C<sub>37</sub> alkenone data reported from Snoopy Lake. The gray box indicated samples that yielded unreliable temperature reconstructions because of the presence of m/z 152 co-eluting with the alkenones.</sup>

<sup>a: 40.8 x Uk37 + 31.8  (D’Andrea et al., 2011)</sup>

<sup>b: (Uk37 + 0.725) / 0.0211  (Zink et al., 2001)</sup>
Table 5

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<th>m/z 95</th>
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<th>m/z 152</th>
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The influence of m/z 152

**a:** The m/z 95 contribution to the C37:4 peak

**b:** The ratio of m/z 95 to m/z 152 as denoted by the following equation:

\[
IF = \frac{m/z \text{ 95}}{(m/z \text{ 95} + m/z \text{ 152})}
\]

**c:** the ratio of C\(_{37:4}\) and C\(_{37:3}\) influence factors (IF) so that values >1 indicate warmer than actual temperatures and <1 indicate colder than actual temperatures with respect to the influence of m/z 152.
University of Cincinnati

Date: 6/19/2012

I, Zachary L Mergenthal, hereby submit this original work as part of the requirements for the degree of Master of Science in Geology.

It is entitled:
Preliminary investigation of n-alkanes and alkenones in East Greenland lacustrine sediment: Implications for possible Holocene climate reconstructions

Student's name: Zachary L Mergenthal

This work and its defense approved by:

Committee chair: Thomas Lowell, PhD
Committee member: Aaron Diefendorf, PhD
Committee member: Warren Huff, PhD

University of Cincinnati