Oxygen isotopes recorded in lacustrine diatoms from southwestern Greenland:
First results based on a laser fluorination method

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This is to certify that I have examined this copy of a master's thesis by

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and have found that it is complete and satisfactory in all respects,
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Abstract

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Late Holocene changes in atmospheric circulation patterns are reconstructed for coastal southwestern Greenland using the first diatom oxygen isotope record ($\delta^{18}O_{si}$) from a lake in Greenland. Diatom $\delta^{18}O_{si}$ is used to estimate the isotopic composition of lake water ($\delta^{18}O_{w}$), which, in this through-flow lake near Sisimiut, reflects the isotopic composition of precipitation ($\delta^{18}O_{p}$). $\delta^{18}O_{w}$ reveals changes in atmospheric circulation patterns over the past c. 3.5 ka. Similar shifts are seen in Greenland ice cores, and suggest eastward and westward migrations of the Baffin Trough over the past c. 2.5 ka. Although this sediment record is restricted to the Late Holocene, it constitutes a first step towards resolving Greenland paleoclimate on a local and regional scale. Our method to measure $\delta^{18}O_{si}$ utilizes a remotely-controlled laser to volatilize the silica-bound oxygen of diatom frustules in a fluorinated atmosphere prior to conventional mass spectrometry. This novel technique yields robust measurements of diatom $\delta^{18}O_{si}$ and improves the safety and efficiency of $\delta^{18}O_{si}$ analysis.

Table of Contents

List of Figures

List of Tables

Acknowledgements

Introduction

Paleoclimate studies in Greenland have focused greatly on ice cores (e.g., Dansgaard *et al.*, 1993; O'Brien *et al.*, 1995) that provide valuable insight into hemispheric-scale paleoclimate, particularly mean annual air temperature (e.g., Dahl-Jensen et al., 1998) and precipitation (e.g., Alley *et al.*, 1993; Kapsner *et al.*, 1995). Comparatively little is known about the nature of climate variability on smaller spatial scales (e.g., Barlow et al., 1997; Levesque *et al.*, 1997; MacDonald *et al.*, 2000; McGowan *et al.*, 2003). Recently deglaciated terrain in Greenland has abundant lakes that provide archives of the regional and local heterogeneity of Greenland paleoclimate on land during the Holocene (e.g., MacDonald *et al.*, 2000; Anderson and Leng, 2004). Existing lake records indicate a thermal maximum during the early to mid-Holocene (e.g., Fredskild, 1985; Eisner *et al.*, 1995; Willemse and Törnqvist, 1999; Bennike, 2000; Wagner *et al.*, 2000; McGowan *et al.*, 2003; Andresen *et al.*, 2004), but the magnitude, timing, and geographic variation of climatic changes during the optimum are still in question (e.g., Kaufman *et al.*, 2004). Climate over the past *c*. 4 ka may be more complex and regionally variable due to shifts in the North Atlantic Oscillation (Appenzeller *et al.*, 1998), and the location of the Baffin Trough (Williams and Bradley, 1985; O'Brien *et al.*, 1995; Barlow *et al.*, 1997; McGowan *et al.*, 2003), but atmospheric circulation and precipitation patterns are not well defined by existing records (e.g., Kapsner *et al.*, 1995; MacDonald *et al.*, 2000; McGowan *et al.*, 2003).

The isotopic composition of oxygen ($\delta^{18}O_{si}$) in lacustrine biogenic silica ($BSiO_2$) has recently emerged as a valuable proxy to estimate quantitatively changes in temperature, precipitation patterns, and/or evaporation that influence climate in terrestrial ecosystems (e.g., Shemesh and Peteet, 1998; Rioual *et al.*, 2001; Jones *et al.*, 2004; Leng and Marshall, 2004; Rosqvist *et al.*, 2004). $BSiO_2$ in lake sediments is derived primarily from diatoms, which are photosynthetic algae that secrete internal frustules composed of silica ($SiO_2 \cdot nH_2O$). Numerous lakes in Greenland have abundant diatoms (e.g., Foged, 1977; 1989; Schmidt *et al.*, 1997; Cremer *et al.*, 2001a; 2001b; Leng and Anderson,

2003; Morley *et al.,* 2005), presenting a valuable opportunity to utilize $\delta^{18}O_{si}$ analysis to better constrain the magnitude and spatial variability of paleoclimatic changes on land during the Holocene. We present the first $\delta^{18}O_{si}$ record from Greenland from a short sediment core extracted from a through-flow lake approximately 60 km southwest of Sisimiut to reconstruct changes in precipitation patterns in this area for the past *c.* 3.5 ka. We utilize a new laser fluorination technique to measure the isotopic composition of silica-bound oxygen, and illustrate the capability of the method to yield robust diatom $\delta^{18}O_{si}$ results.

Paleoclimatic interpretation of $\delta^{18}O_{si}$

Although the isotopic composition of oxygen in biogenic carbonates is a well-established paleoclimate proxy (e.g., Stuiver, 1970), biogenic carbonates do not typically form in through-flow lakes (e.g., Shemesh and Peteet, 1998; Lamb *et al.,* 2004; 2005). Through-flow lakes are valuable in the study of past precipitation patterns, because waters in these types of lakes generally reflect the isotopic composition of precipitation (e.g., Gat, 1996). Unlike biogenic carbonates that exhibit species-specific isotopic fractionation and other 'vital' effects (Leng and Marshall, 2004), systematic disequilibrium processes do not appear to exist for isotopic fractionation in diatoms (e.g., Shemesh *et al.,* 1995; Rietti-Shati *et al.,* 1998; Rosqvist *et al.,* 1999; Moschen *et al.,* 2005). In addition, diatom frustules show minimal isotopic change due to post-depositional diagenesis (e.g., Shemesh *et al.,* 1992), hence their isotopic composition is maintained after burial.

The isotopic composition of biogenic silica ($\delta^{18}O_{si}$) is driven by the temperature (T_w) and isotopic composition ($\delta^{18}O_w$) of lake water (Shemesh *et al.,* 1992). Empirical data suggest a fractionation factor (α) of 1.041±0.00445 (1.5-25ºC; Juillet-Leclerc and Labeyrie, 1987), with a temperature-dependence of -0.2‰/ºC (Moschen *et al.,* 2005). The isotopic composition of lake water is determined by precipitation ($\delta^{18}O_p$) and lake hydrology, namely the inflow to outflow ratio (Gat, 1995). Mean residence time of the

lake water should be long enough for $\delta^{18}O_w$ to average out seasonal variations in $\delta^{18}O_p$, and short enough to minimize fractionation due to evaporation. If these conditions are met, the isotopic composition of lake water ($\delta^{18}O_w$) closely approximates the annual average isotopic composition of precipitation ($\delta^{18}O_p$) (Gat, 1995; 1996; Criss, 1999; Leng and Marshall, 2004). Variations in $\delta^{18}O_p$ depend on changes in air temperature (+0.67‰/°C for high latitudes; Dansgaard, 1964; Dahl-Jensen *et al.*, 1998), variations in atmospheric circulation that shift air mass trajectory and moisture source (Rioual *et al.*, 2001; Shemesh *et al.*, 2001a; 2001b; Rosqvist *et al.*, 2004), or a combination (Rietti-Shati *et al.*, 1998; Shemesh and Peteet, 1998; Jones *et al.*, 2004).

To interpret changes in $\delta^{18}O_{si}$, one must consider all environmental factors that contribute to its value, including T_w and factors that affect $\delta^{18}O_w$. To assess the magnitude of changes in $\delta^{18}O_w$ that would result from various fluctuations in climate and lake hydrology, we have performed sensitivity tests similar to those reported by Shemesh and Peteet (1998). The isotopic buildup in a through-flow lake at steady state is given by:

$$\delta^{18}O_w = \delta^{18}O_{in} + (\delta^{18}O_{atm} - \delta^{18}O_{in} + \varepsilon/h)/(1 + F_{in}/E*(1-h)/h) \qquad \text{(Equation 1)}$$

where $\delta^{18}O_w$, $\delta^{18}O_{in}$, and $\delta^{18}O_{atm}$ are the compositions of lake water, inflow, and atmospheric moisture, respectively (Gat, 1995; 1996). Epsilon (ε) is equal to $(\alpha-1)*1000+\Delta\varepsilon$ where α is the temperature-dependent fractionation factor of water (Criss, 1999) and $\Delta\varepsilon$ is equal to $C_k(1-h)$ where C_k is the kinetic constant (15‰ for ^{18}O; Gat, 1996). The water flux into the lake (e.g., precipitation, groundwater, streams), the evaporative flux, and the relative humidity are given by F_{in}, E, and h, respectively. The terms most likely to respond to a shift in climate are $\delta^{18}O_{in}$, ε, h, and F_{in}/E, as these variables are temperature-dependent (Shemesh and Peteet, 1998).

Although Greenland air temperatures have likely varied by no more than 2.5°C during the Holocene (Johnsen *et al.*, 1992; Larsen *et al.*, 1995; O'Brien *et al.*, 1995;

Dahl-Jensen *et al.,* 1998; Willemse and Törnqvist, 1999), we examine the response of $\delta^{18}O_{in}$, ε, h, and F_{in}/E to temperatures ranging from 0-20°C to identify the maximum effect of each parameter on $\delta^{18}O_w$. Results indicate that even severe changes in air temperature (i.e., 10°C), relative humidity (i.e., 80%), and the ratio of inflow to evaporative fluxes (i.e., 60%) are expected to alter $\delta^{18}O_w$ by no more than 1.0‰ individually (Table 1). Of course, these variables do not change independently in natural systems. Some effects will cancel each other out, such as cooler temperature decreasing evaporation (Shemesh and Peteet, 1998), and some will compound, such higher temperature increasing humidity and altering the F_{in}/E ratio. However, even when extreme changes in climate and lake hydrology are combined, they change $\delta^{18}O_w$ by less than ~1.5‰ (Table 1). The only factor that can change $\delta^{18}O_w$ by more than 1.5‰ is a shift in the isotopic composition of precipitation (i.e., $\geq 5\%$ change in $\delta^{18}O_p$). Fluctuations in $\delta^{18}O_w$ that are at least 1.5‰ therefore primarily reveal changes in precipitation patterns (e.g., storm track trajectory, moisture source). Smaller variations may reflect a combination of climatic and hydrological factors and are thus more difficult to interpret.

Table 1.   Select results of sensitivity tests.

Change in environmental parameter(s)	Resulting change in $\delta^{18}O_w$
10^oC change in air temperature	0.95‰ between 0 and 20°C
Decrease in air temperature from 4 to 2^oC	+0.21‰
Change in relative humidity from 0.1 to 0.9	0.003‰ at 0^oC; 0.38‰ at 20^oC
60% change in flux in	0.76‰ between 0 and 20°C
Increase in air temperature from -2 to $+1^oC$, change in relative humidity from 0.02 to 0.6, and 50% change in F_{in}/E ratio	0.98‰
Increase in air temperature from 0 to 5^oC, change in relative humidity from 0.2 to 0.6, and 50% change in F_{in}/E ratio	1.06‰
Increase in air temperature from 0 to 10^oC, change in relative humidity from 0.2 to 0.8, and 30% change in F_{in}/E ratio	1.32‰
Keeping all else constant, 5% change in $\delta^{18}O_p$	1.50‰ between 0 and 20°C

Study site

      Koko Lake (our informal name) is located along the coast of southwestern Greenland, approximately 60 km southeast of Sisimiut and 50 km north of the fjord of Kangerlussuaq (Danish: Søndre Strømfjord; 66 °49'N, 52 °36'W; elevation 36 m; Figure 1). Sisimiut is characterized by a moist low-arctic maritime climate, with mean annual and mean July temperatures of –6 and +6.3°C, respectively (Leng and Anderson, 2003). Precipitation is 383 mm/year, most of which falls in the summer and peaks in August (*c.* 60 mm). Koko Lake is 1.5 km long and 4.5 km wide, and our maximum measured water depth is 75 m. Several small streams drain into the lake from the south and east, and Koko Lake drains northwest into a lower lake. Residence time is on the order of 10 yr, using average annual Sisimiut precipitation and approximated lake volume (2.025×10^8 m^3) and drainage area (50×10^6 m^2). August lake water pH is 5.5-6.3 and surface water temperature is 12.9-13.8°C. Local vegetation is discontinuous dwarf shrub tundra dominated by *Betula nana*, with scattered fens near the lakeshore.

Field and laboratory methods

A 56.5-cm-long sediment core (KL-2) was raised from 9 m water depth in a small basin of Koko Lake with a gravity corer in early August 2005. The core was photographed, described, and subsampled at 2-cm-intervals. Water depth was measured by dropping a weighted measuring line into lake water at 44 locations, and a bathymetric profile was generated using Matlab-based contouring functions (Figure 2). Subsamples from seven sediment slices were processed for geochemical analyses. Organic carbon (%OC), inorganic carbon (%IC), and nitrogen (%N) were measured with a CHNOS elemental analyzer (Elementar vario EL III). Thirteen subsamples from an adjacent core (KL-1; 34 cm long) were processed for $BSiO_2$ content. $BSiO_2$ was extracted by alkaline dissolution (Mortlock and Froelich, 1989) and concentrations were determined with an inductively-coupled argon optical emission spectrometer (Perkin Elmer Optima 3300 DV). All geochemical values are presented as percent by weight. Seven water samples were collected, and their stable isotopic compositions ($\delta^{18}O_w$ and δ^2H_w) were measured on a Finnigan MAT Delta-S mass spectrometer. Chronological control is provided by two bulk sediment radiocarbon dates (2205 ± 35 yr BP at 12.5-14.5 cm; 3365 ± 35 yr BP at 38.5-40.5 cm) that were pretreated according to an acid-base-acid protocol to remove inorganic and adsorbed carbon (PALE, 1994) and submitted to Lawrence Livermore National Laboratory for dating. Biogenic silica analysis and sediment processing for $\delta^{18}O_{si}$ analysis took place at the University of Washington; isotopic analyses and other geochemical measurements took place at the Alfred Wegener Institute for Polar and Marine Research, Potsdam.

Sediment processing for $\delta^{18}O_{si}$ analysis

Diatoms were isolated from bulk sediment following Morley et al. (2005): (1) treatment with 30% H_2O_2 (room temperature for 24 h; 90°C for 2 h) to oxidize organic matter and 5% HCl (room temperature for 12 h) to remove carbonates; (2) sieving (at 10,

20, 45, 63, and 90 μm) to obtain the desired size fraction; (3) differential settling (repeatedly centrifuging for 4 min at 1500 rpm and pipetting off "light" diatom layer); and (4) heavy liquid separation (2.1 specific gravity sodium polytungstate solution; centrifuging 20 min at 2500 rpm). Split-flow thin fractionation (SPLITT; Rings *et al.,* 2004), which typically follows heavy liquid separation, was not needed because KL-2 samples were exceptionally pure. After sieving, each size fraction was inspected visually at 400x. The 10-20 μm fraction of each sample was chosen for analysis because it consistently contained the highest abundance and lowest diversity of diatom frustules (~95-99% *Aulacoseira* spp.).

Isotopic measurement

Although $\delta^{18}O_{si}$ analysis has great potential to provide quantitative paleoclimatic information, the method has been underutilized due to the difficulty of the analysis (e.g., Schmidt *et al.,* 1997; Lamb *et al.,* 2004; Morley *et al.,* 2005). Analytical procedures are based on either: 1) high temperature carbon reduction of silica to liberate oxygen as CO (e.g., Lücke *et al.,* 2005; Moschen *et al.,* 2005); or 2) oxidation by fluorine or halogen fluorides to yield O_2 that is converted to CO_2 prior to isotopic measurement (e.g., Clayton and Mayeda, 1963; Juillet-Leclerc and Labeyrie, 1987; Jones *et al.,* 2004; Lamb *et al.,* 2005). The laser fluorination system: 1) greatly simplifies the fluorination procedure by using a laser to vaporize the sample; 2) enhances its efficiency so that very small diatom samples (mg to sub-mg range) can be analyzed; 3) eliminates the uncertainty involved in converting the extracted O_2 to CO_2; and 4) improves safety by isolating the fluorination line and remotely controlling the operation.

The laser fluorination method is divided into two distinct phases: (A) heating the purified diatom sample with a defocused CO_2 laser (5.5 W) in a melting chamber to remove adsorbed H_2O and form a silicon bead; and (B) heating the silicon bead with a focused CO_2 laser (4.0 W) in a BrF_5 atmosphere in a reaction chamber to convert SiO_2 to SiF_4 and release O_2. The reaction chamber is heated prior to Step B to remove adsorbed H_2O and it is pre-fluorinated with BrF_5 gas. Non-oxygen components of the released gas

are condensed in a liquid nitrogen cold trap, and the O_2 is adsorbed in a molecular sieve cooled with liquid nitrogen. The extracted O_2 is then desorbed and analyzed in a PDZ Europa 20-20 mass spectrometer for its isotopic composition referenced to an O_2 gas standard (13.4‰). The standard gas is calibrated against international standard quartz (NBS28). Multiple beads of a single diatom sample are analyzed to ensure stable values. The long-term reproducibility is 0.25‰ (H. Meyer, unpublished data). Further details of the laser fluorination method including software, safety principles, long-term standard measurements and tests of the routine will be published elsewhere.

Results

Isotopic systematics of modern lake system

Three Koko Lake inflow samples collected August 2, 2005 average -14.2±0.1‰ for $\delta^{18}O$ and -109.0±0.8‰ for $\delta^{2}H$ (standard deviations: 0.41 and 1.72, respectively). The outflow is isotopically similar ($\delta^{18}O$ -13.8±0.1‰; $\delta^{2}H$ -108.1±0.8‰). Surface ($\delta^{18}O$ -13.8±0.1‰; $\delta^{2}H$ -107.7±0.8‰) and deep waters (58.5 m depth; $\delta^{18}O$ -13.7±0.1‰; $\delta^{2}H$ -107.8±0.8‰) are indistinguishable. These waters, as well as a local rain sample ($\delta^{18}O$ -17.2±0.1‰; $\delta^{2}H$ –130.0±0.8‰), plot along the global meteoric water line (GMWL; Figure 3A), indicating minimal isotopic effects of evaporation.

Sediment description and geochemical analyses

KL-2 sediment is silty, and transitions downcore from dark brown (Munsell 10YR 3/3; 0.0-28.0 cm) to dark olive grey/very dark grey (Munsell 5Y 3/2 and 5Y 3/1; 28.0-56.5 cm). Inorganic carbon averages 2.3% and gradually decreases from 2.7% at 6.5 cm to 2.0% at 54.5 cm (Figure 3B). Organic carbon varies between 1.4-2.3% with an average of 1.9%, and nitrogen is nearly constant (average 0.5%). Biogenic silica is consistently very high in KL-1, although percentages decrease from an average of 58.0% between 0-29 cm to 39.5% between 29-33 cm (Figure 4).

$\delta^{18}O_{si}$ and reconstructed $\delta^{18}O_{w}$

Samples from Koko Lake were analyzed only when the isotopic values of standards (NBS28 and Campolungo quartz) were within 2% of expected. Diatom samples were measured at eight depths in triplicate (three beads per sample; 24 total). Measured isotopic values from each bead were averaged to obtain a single value per sample, and standard error was calculated by dividing standard deviation by the number of measurements per sample. KL-2 $\delta^{18}O_{si}$ values fluctuate between 24.7-26.8‰ (standard error 0.0-0.2), and two 1.5-2.1‰ excursions occur in the upper 18.5 cm (Figure 3C).

The fractionation factor for oxygen between diatom silica and lake water (α) is calculated to be 1.0385 based on the difference between Koko Lake $\delta^{18}O_w$ (average -13.8‰) and surface sediment $\delta^{18}O_{si}$ (0-4.5 cm core depth; 24.7‰). This value is within the range of previous estimates (α:1.041±0.00445). Since the fractionation factor varies in different lake systems according to lake temperature, measured $\delta^{18}O_{si}$ rather than reconstructed $\delta^{18}O_w$ is usually shown and interpreted directly (e.g., Rioual *et al.*, 2001; Shemesh *et al.*, 2001b; Hu and Shemesh, 2003). We estimate $\delta^{18}O_w$ because we are interested in using $\delta^{18}O_w$ to track $\delta^{18}O_p$, and we have determined our lake-specific fractionation factor. Using α:1.0385, $\delta^{18}O_w$ values range from -11.7 to -13.8‰. In the upper 18.5 cm, there are two periods of relative isotopic enrichment (6.5-8.5 cm: -12.1‰ and 14.5-16.5 cm: -11.7‰), and three periods of relative isotopic depletion (0-6.5 cm: average -13.5‰; 8.5-12.5 cm: average -13.5‰; 16.5-18.5cm: -13.2‰; Figure 3D). $\delta^{18}O_w$ decreases slightly (1.0‰) between 18.5-44.5 cm.

Discussion and Conclusions

Non-glacial terrestrial paleoclimatic reconstructions from Greenland are based primarily on robust but qualitative interpretations from pollen records; few quantitative estimates of changes in temperature or precipitation patterns on land are available. The potential for thousands of through-flow, coastal lakes in Greenland to have abundant diatoms presents a valuable opportunity to utilize $\delta^{18}O_{si}$ analysis to trace past changes in lake water $\delta^{18}O_w$, hence $\delta^{18}O_p$, to create a spatial network of isotopic change across Greenland. Such an understanding will improve our understanding of local and regional-scale atmospheric circulation and precipitation patterns during the Holocene, a period characterized by dynamic and regionally-variable shifts in precipitation patterns (Edwards *et al.,* 1996; Hammerlund *et al.,* 1997; MacDonald *et al.,* 2000; Seppä and Hammarlund, 2000; McGowan *et al.,* 2003; Anderson and Leng, 2004).

Climate of coastal southwestern Greenland is primarily determined by meridional atmospheric and oceanic circulation patterns (Funder, 1989), and the location of the Baffin Trough, which today parallels the outer coast and controls summer temperatures and the dominant wind direction (Barlow *et al.*, 1997). A more eastward location of the Baffin Trough is associated with stronger subpolar westerlies that transport air masses originating in the Pacific Ocean across North America to western Greenland. An anomalous westward location is associated with weaker westerlies and enhanced meridional flow. Meridional flow drives relatively isotopically-depleted air masses towards Greenland from the North Atlantic, as opposed to more enriched air masses arriving from the west (Newell and Zhu, 1994).

Since Koko Lake water falls along the GMWL, confirming minimal isotopic effects of evaporation, and sediments contain very high concentrations of diatom frustules dominated by a single genus, it is an ideal site to utilize diatom $\delta^{18}O_{si}$ to study past atmospheric circulation patterns in a region with a paucity of data. In the upper 18.5 cm of core KL-2, fluctuations in reconstructed Koko Lake $\delta^{18}O_w$ are 1.5‰ or greater,

suggesting changes in $\delta^{18}O_p$ over the past *c.* 2.5 ka. Relatively depleted $\delta^{18}O_w$ values suggest enhanced meridional transport *c.* 1.0-0.0 ka (0-6.5 cm core depth), *c.* 1.9-1.6 ka (8.5-12.5 cm core depth), and after 2.2 ka (16.5-18.5 cm core depth). Similarly, periods of relative isotopic enrichment *c.* 1.3 ka (6.5-8.5 cm core depth) and after 2.2 ka (14.5-16.5 cm core depth) suggest eastward shifts of the Baffin Trough and intensified subpolar westerlies bringing more enriched air masses to southwestern Greenland from North America.

Greenland ice cores provide additional evidence for Late Holocene shifts in precipitation patterns, with increases in sea salt and terrestrial dust implying expansion of the north polar vortex or intensified meridional air flow 0.6-0.0 ka and 3.1-2.4 ka (O'Brien *et al.,* 1995). Similarly, diatom-inferred conductivity records from closed-basin lakes near the head of Kangerlussuaq reflect decadal to centennial shifts in effective precipitation that suggest shifts in the location of the Baffin Trough, but the magnitude of Late Holocene fluctuations is small compared to those that occurred prior to *c.* 4 ka (McGowan et al., 2003; Anderson and Leng, 2004). The mid-Holocene is noted elsewhere as a period of profound climatic change (e.g., Steig, 1999), but we are unable place KL-2 shifts in $\delta^{18}O_w$ into this longer-term perspective.

Albeit preliminary and limited to the Late Holocene, Koko Lake data illustrate the potential of utilizing $\delta^{18}O_{si}$ analysis to resolve local and regional patterns of climatic change in Greenland during the Holocene. KL-2 $\delta^{18}O_{si}$ data constitute the first such record used to estimate changes in lake $\delta^{18}O_w$ from Greenland, and initial results illustrate the capability of the laser fluorination method. Improved chronology and sampling resolution of future studies will facilitate the identification of short-term fluctuations in the sediment record, and will allow more direct comparisons to be drawn between ice core and existing lacustrine records. Deeper sediment cores will allow the assessment of early to mid-Holocene climatic fluctuations, such as the Holocene thermal maximum, and multi-proxy analyses will help assess the likelihood of temperature and precipitation patterns suggested by changes in $\delta^{18}O_{si}$. Obtaining $\delta^{18}O_{si}$ data from a dense grid of

suitable sites across Greenland will provide stronger constraints on mechanisms of local and regional climatic change on land in the past *c*. 10 ka than can be obtained from qualitative lake records alone, and it will improve our understanding of precipitation patterns in the terrestrial realm of Greenland during the Holocene. The KL-2 $\delta^{18}O_{si}$ record constitutes a first step in this direction, and sets the stage for future work at this lake and beyond.
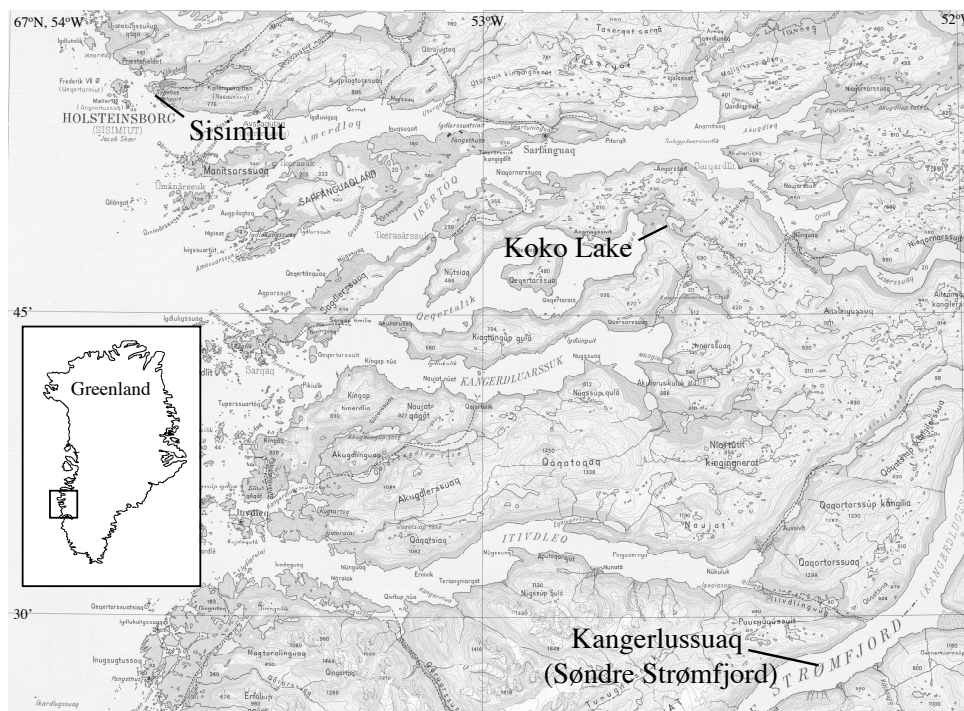
Figure 1. Map of southwestern Greenland showing site locations.
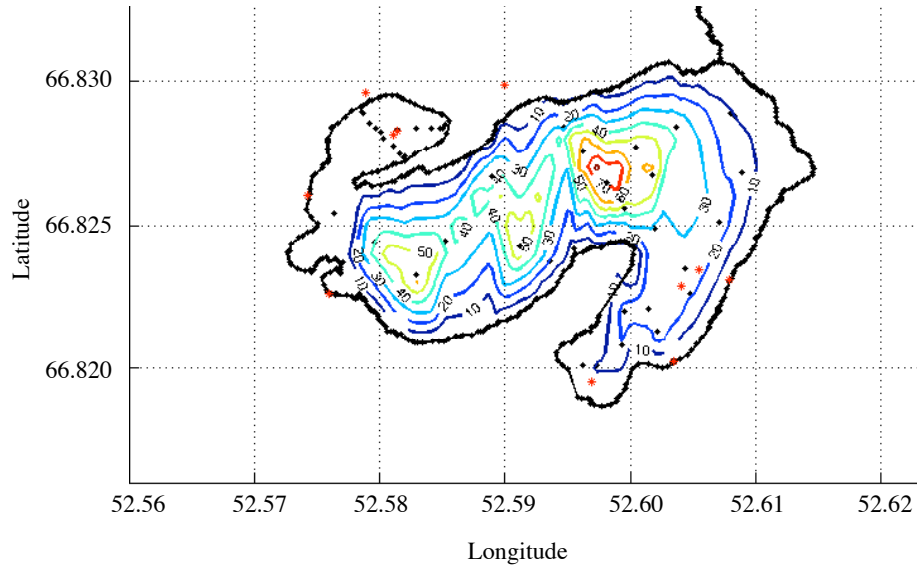
Figure 2. Bathymetric map of Koko Lake (depths are in meters).
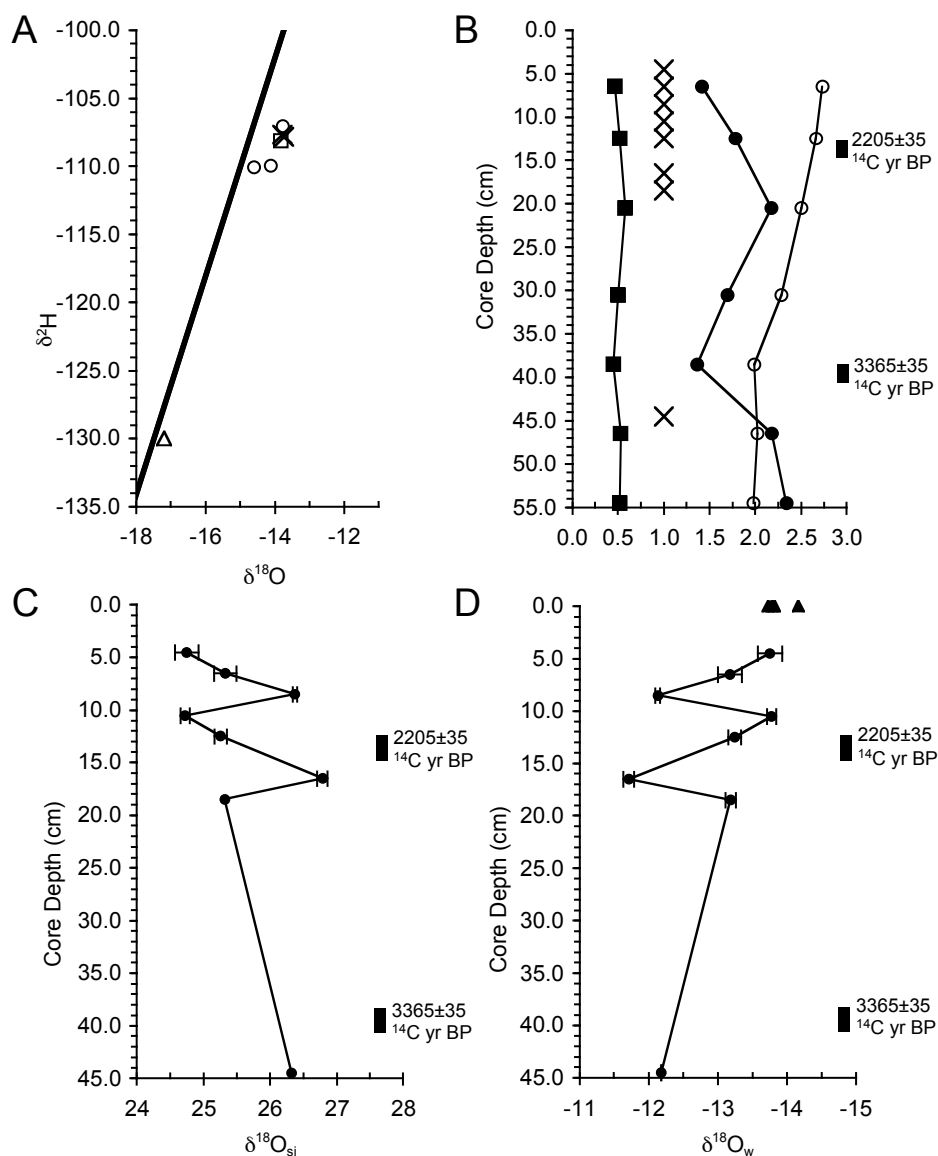
Figure 3. (A) Modern Koko Lake isotopic data (solid line: GMWL, $\delta^2H=8\delta^{18}O+10‰$ SMOW); open triangle: modern rain sample; open circles: inflows; open square: outflow; cross: surface and deep lake water); (B) KL-2 geochemical data (%IC: open circles; %OC: solid circles; %N: solid squares; crosses indicate where diatom $\delta^{18}O_{si}$ measurements were made); (C) KL-2 $\delta^{18}O_{si}$ vs VSMOW (average of three samples and standard error); (D) $\delta^{18}O_w$ vs VSMOW (average of three samples and standard error for $\delta^{18}O_{si}$ measurements; triangles: modern lake water $\delta^{18}O_w$). Each sample in (B-D) constitutes a 2-cm slice of core; data points are plotted at core-depth bottom. Note changes in scale.

Figure 4. KL-1 %BSiO$_2$. Each sample constitutes a 2-cm slice of core; data points are plotted at core-depth bottom.

Appendix A: Supplementary Data

Table 1. Description of all Koko Lake gravity cores collected during 2005 reconnaissance. Colors based on Munsell soil color chart.
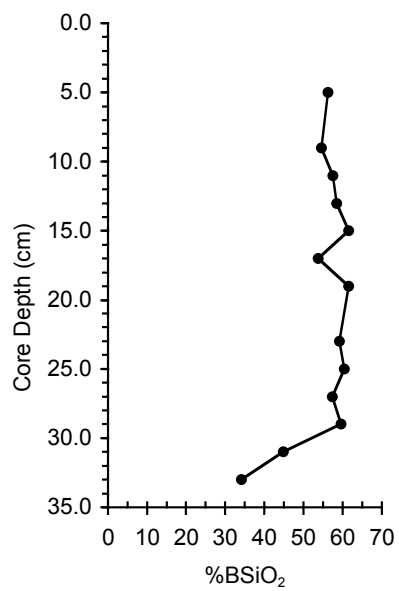
KL-1: Core depth (cm)	Sediment description
0.0-2.5	Unconsolidated, flocculated very dark greyish brown (10YR 3/2)
2.5-6.5	Massive olive (5Y 4/3)
6.5-12.5	Massive olive (5Y 4/3); abundant black (5Y 2.5/2) Mn and red (2.5YR 4/8) oxidized Fe particles
12.5-16.0	Massive olive (5Y 4/3); some Mn particles
16.0-18.5	Massive very dark grey (5Y 3/1); some Mn particles
18.5-29.0	Massive dark olive grey (5Y 3/2); some Mn particles
29.0-34.0	Massive olive grey (5Y 4/2); occasional Mn particles

KL-2: Core depth (cm)	Sediment description
0.0-1.5	Unconsolidated, flocculated very dark greyish brown (10YR 3/2)
1.5-4.0	Massive dark brown (10YR 3/3); some Mn particles
4.0-6.5	Dark yellowish brown (10YR 3/6); abundant oxidized Fe particles
6.5-7.5	Massive dark brown (10YR 3/3)
7.5-7.7	Distinct oxidized Fe band
7.7-12.5	Massive dark brown (10YR 3/3); few Mn and oxidized Fe particles
12.5-14.0	Olive (5Y 5/3) band
14.0-28.0	Massive dark brown (10YR 3/3); some Mn and Fe oxide particles
28.0-48.0	Diffuse gradient from dark olive grey (5Y 3/2) to very dark grey (5Y 3/1); abundant Mn particles
48.0-51.0	Diffuse band of very dark grey (5Y 3/1) and Mn particles
51.0-56.5	Massive very dark grey (5Y 3/1) with few Mn particles

KL-3: Core depth (cm)	Sediment description
0.0-11.0	Massive, loose dark yellowish brown (10YR 3/4)
11.0-11.3	Massive dark brown (10YR 3/3)
11.3-11.5	Distinct band of Mn and oxidized Fe
11.5-24.0	Massive dark brown (10YR 3/3)
24.0-27.0	Distinct change to very dark grey (5Y 3/1)

KL-4: Core depth (cm)	Sediment description
0.0-14.0	Massive, loose dark yellowish brown (10YR 3/4)
14.0-17.5	Massive dark brown (10YR 3/3)
17.5-17.7	Distinct band of Mn and oxidized Fe
17.7-26.0	Massive dark brown (10YR 3/3)
26.0-30.0	Distinct change to very dark grey (5Y 3/1)

Table 2. Description of all Little Loon Lake gravity cores collected during 2005 reconnaissance. Colors based on Munsell soil color chart.

LL-1: Core depth (cm)	Sediment description
0.0-19.0	Gradual gradation from massive dark yellowish brown (10YR 3/4) to dark brown (10YR 3/3); abundant black (5Y 2.5/2) Mn particles
19.0-26.5	Massive grey (5Y 4/1); abundant Mn particles

LL-2: Core depth (cm)	Sediment description
0.0-23.0	Gradual gradation from massive dark yellowish brown (10YR 3/4) to dark brown (10YR 3/3); abundant black (5Y 2.5/2) Mn particles
23.0-24.0	Massive grey (5Y 4/1); abundant Mn particles

Table 3. Description of all Snowfly Lake gravity cores collected during 2005 reconnaissance. Colors based on Munsell soil color chart.

SF-1: Core depth (cm)	Sediment description
0.0-9.0	Unconsolidated, flocculated brownish orange (combination of 10YR 3/4 and 2.5YR 2.5/4)
9.0-27.0	Massive grey (10YR 3/1)

SF-2: Core depth (cm)	Sediment description
0.0-6.0	Unconsolidated, flocculated combination of orange (2.5YR 4/8) and grey (5Y 4/2)
6.0-7.8	Massive grey (5Y 4/1); abundant Mn particles
7.8-8.0	Lighter grey layer of gley (5Y 6/1)
8.0-10.0	Massive grey (5Y 4/1); abundant Mn particles
10.0-22.0	Massive grey (5Y 4/1)

SF-3: Core depth (cm)	Sediment description
0.0-3.0	Unconsolidated, flocculated (10YR 4/4)
3.0-5.0	Dark orange ozidized Fe-rich layer (5YR 5/8)
5.0-7.0	Massive grey (5Y 4/1)
7.0-12.0	Massive grey (5Y 4/1); abundant Mn particles
12.0-16.0	Massive grey (5Y 5/1); abundant Mn particles

SF-4: Core depth (cm)	Sediment description
0.0-1.0	Unconsolidated, loose dark yellowish brown (10YR 3/4)
1.0-4.5	Light brown (combination of 5Y 4/3 and 5Y 4/2)
4.5-7.0	Dark, very oxidized layer (2.5YR 3/4)

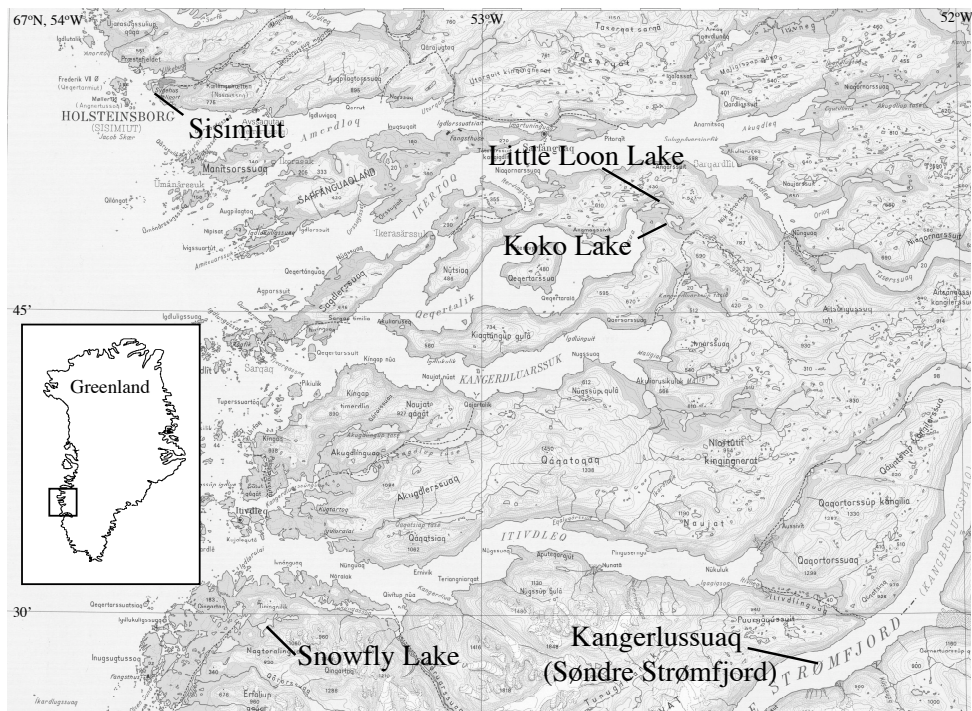| SF-5: Core depth (cm)	Sediment description
0.0-2.0	Unconsolidated, loose dark yellowish brown (10YR 3/4)
2.0-10.5	Brownish orange (combination of 5Y 4/3 and 10YR 4/3)
10.5-18.0	Massive grey (5Y 4/1)

Figure 1. Map of southwestern Greenland showing locations of sites explored and sampled during 2005 reconnaissance.
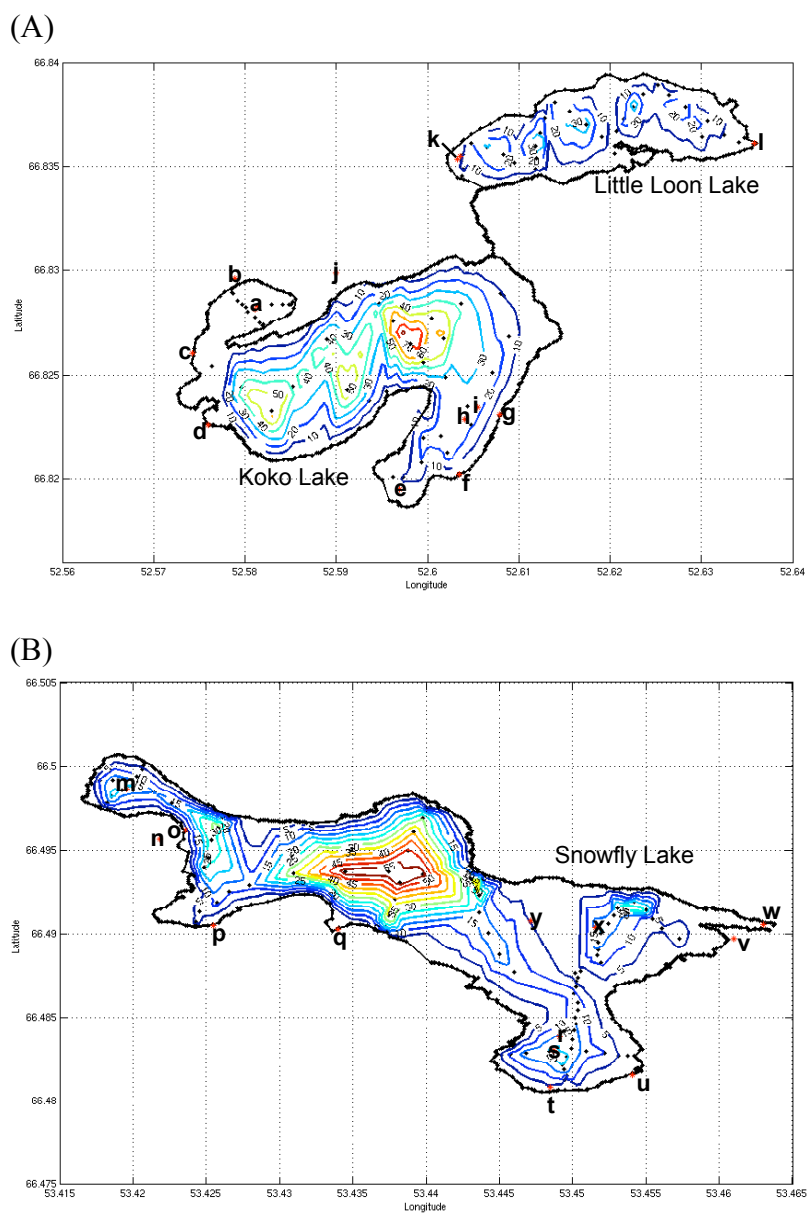
Figure 2. (A) Detailed bathymetric maps of Koko and Little Loon lakes: (a) cores KL-1 and KL-2 collected; (b-g) inflows; (h) core KL-3 collected; (i) core KL-4 collected; (j) shells collected from raised beach deposit; (k) cores LL-1 and LL-2 collected; (l) outflow to lower lake; (B) detailed bathymetric map of Snowfly Lake: (m) core SF-1 collected; (n) shells collected from beach deposit; (o-q) inflows; (r) core SF-3 collected; (s) core SF-2 collected; (t-u) inflows; (v) snow sample collected; (w) outflow from Snowfly Lake; (x) core SF-5 collected; (y) core SF-4 collected. Depths are in meters. See Appendix A, Tables 1-3 for core descriptions.

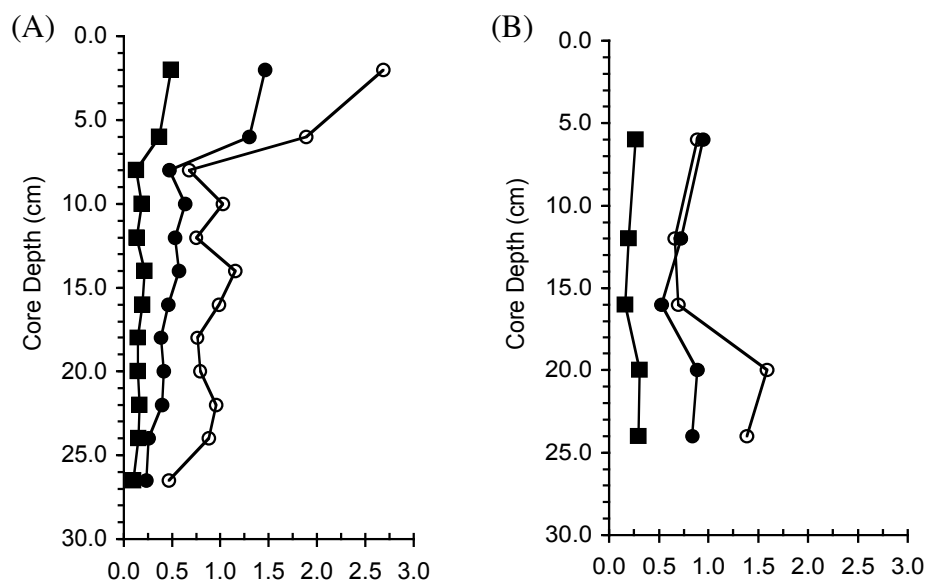Figure 3. Geochemical data from: (A) Little Loon Lake, core LL-1; and (B) Snowfly Lake, core SF-1 (solid squares: total nitrogen (%); solid circles: total organic carbon (%); open circles: total inorganic carbon (%)).

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