Long chain alkenones in Greenland lake sediments: Low $\delta^{13}C$ values and exceptional abundance

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Abstract

Long chain alkenones (LCAs) are a key class of biomarkers for certain members of the algal class Prymnesiophyceae (i.e., prymnesiophytes). They are ubiquitous in ocean sediments where they are extensively used for paleotemperature reconstruction, but are rare in lake sediments. Here, we report the discovery of LCAs (C_{37}–C_{39}) throughout a sediment core from one lake and in surface sediments of five lakes located in west Greenland. LCA concentrations in the surface sediments are one to two orders of magnitude greater than those reported for other lacustrine surface sediments around the world. The presence of C_{38} methyl ketones distinguishes Greenland LCA distributions from those found in other saline lakes in cold regimes. LCAs are present in five lakes with elevated salinity, but absent from five freshwater lakes in the study region. Using the published temperature calibration for lake sediments, alkenone unsaturation indices (U^K_{37} and $U^{K'}_{37}$) in the surface sediments of the Greenland lakes appear to record late spring/early summer temperature when algal blooms occur, supporting the use of lacustrine alkenones as a paleotemperature proxy. The LCAs have exceptionally low $\delta^{13}C$ values, ranging from −40‰ to −42‰, and are depleted by 3–10‰ relative to short chain fatty acids and sterols in the same samples. These $\delta^{13}C$ values are the lowest reported for alkenones in a natural setting and have important implications for tracing the alkenone producers in lakes.
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1. Introduction

Long-chain alkenones (LCAs, C_{37}–C_{39}) are ubiquitous in ocean sediments throughout the world and are important biomarkers for reconstruction of past sea surface temperatures (Brassell et al., 1986; Brassell, 1993; Marlowe et al., 1984; Prahl and Wakeham, 1987; Volkman et al., 1995). The compounds, often dominated by tetraunsaturated forms, have been found in lacustrine sediments from at least 17 lakes around the world, lo-

cated in England (Cranwell, 1985), Antarctica (Volkman et al., 1988), China (Li et al., 1996; Sheng et al., 1999; Wang and Zheng, 1998), Turkey (Theil et al., 1997), Norway (Innes et al., 1998), Gemany, Russia, USA (Zink et al., 2001) and South America (Theissen et al., 2005). Recent advances highlight the potential of lacustrine, biomarker-based paleothermometry (Powers et al., 2004; Zink et al., 2001). For example, Zink et al. (2001) showed that there exists a consistent relationship between environmental temperature and distributions of alkenone unsaturation in lake sediments.

Paleoclimate studies of ice cores from the Greenland ice sheet reveal climatic variations reflecting large scale, hemispheric climate processes (Alley et al., 1997;

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Dahl-Jensen et al., 1998). However, regional climate variability at low altitude around the perimeter of the ice sheet is more sensitive to oceanic–atmospheric changes such as the North Atlantic oscillation (Box, 2002; Hurrell, 1995), but is poorly constrained (Anderson and Leng, 2004). Lake sediments offer unique archives for understanding Holocene climate history and regional variations at low elevation in west Greenland, especially if alkenone paleothermometry can be applied to disentangle temperature from precipitation effects in paleolimnological proxy records. This work represents the first organic geochemical study of west Greenland lakes.

2. Samples and analytical methods

2.1. Study sites and samples

The Søndre Strømfjord region (Fig. 1) between the western edge of the Greenland ice sheet and the Davis Strait hosts ~20,000 lakes, most of which are dilute and oligotrophic. However, there is a small number of oligosaline lakes at the head of the Søndre Strømfjord with salinity of approximately 2–4 psu. The lack of hydrologic outflow from the lakes, coupled with locally negative effective precipitation (precipitation minus evaporation) has resulted in evaporative concentration of salts. These lakes are ~170 m above sea level and ~110 m above the regional marine limit, precluding seawater entrapment during isostatic uplift as a possible source of salinity. The dominant salts are $NaCO_3$, $NaHCO_3$ and $MgHCO_3$, which are delivered to the lakes by eolian transport from nearby sand sheets and by input from erosion within the lake catchments (Anderson et al., 2001). The lakes are calcium-depleted relative to

fresh lakes in the region due to $CaCO_3$ precipitation. The oligosaline lakes of this study range in depth from ~12 to 33 m. The photosynthetic zone of the shallowest lake SS6 (12 m) may reach the water–sediment interface, while in the deeper lakes (BrayaSø, 22 m; HundeSø, 33 m; LimnæaSø, 28 m; and Lake E, 20 m) photosynthesis occurs to a depth of ~12 m. Climate near the head of Søndre Strømfjord exhibits mean summer temperature of 9.3 °C and mean winter temperature of −18 °C (for the period 1961–1990; Box, 2002), and receives less than 150 mm yr^{-1} of precipitation. Permafrost is continuous in the region and vegetation comprises dwarf-shrub tundra with *Betula nana* (dwarf birch), *Salix glauca* (glaucous willow), *Vaccinium* spp. *Empetrum nigrum* (crowberry) and various herbs and grasses.

Surface sediment samples (0–1 cm depth from sediment–water interface) from BrayaSø, HundeSø and LimnæaSø were retrieved with a gravity corer from the deepest part of each lake. Lake E, SS49 and SS86 sediments were retrieved with a Russian peat corer and were provided by N. John Anderson and Sheri Fritz. SS6 short core samples and surface samples from freshwater lakes SS32, SS50, SS66 were retrieved with a gravity corer and were provided by N. John Anderson.

2.2. Experimental methods

Samples were freeze dried and homogenized using a mortar and pestle. They were extracted with dichloromethane (DCM) using an Accelerated Solvent Extractor ASE200 (Dionex). Extracts were separated into acid and neutral fractions using Supelco Supelclean™ LC-NH₂ solid phase extraction (SPE) tubes (Huang et al., 2004). The neutral fraction was further separated into aliphatic (hexane elution), ketone (DCM), and alcohol
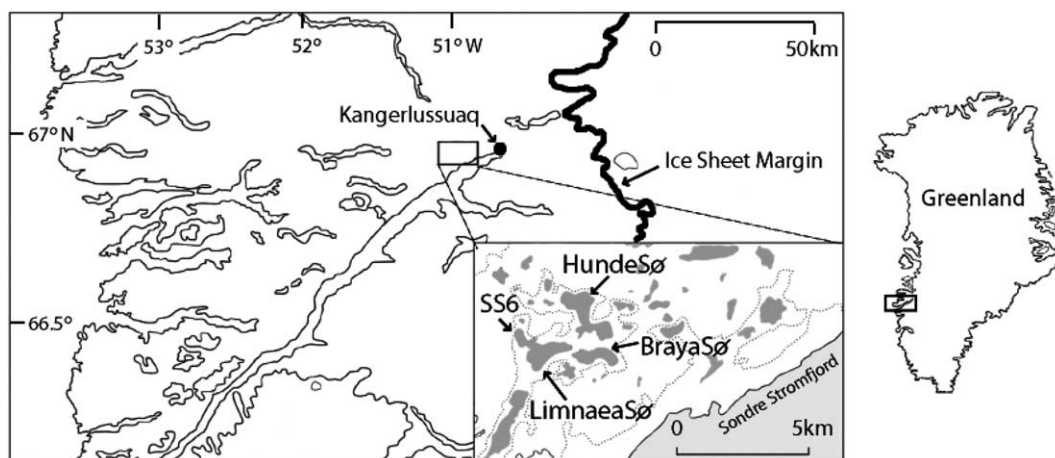

Fig. 1. Study area at head of Søndre Strømfjord, west Greenland. Labeled lakes contain high concentrations of alkenones in sediments. Lake E is located ~10 km northwest of HundeSø.

(ethyl acetate:hexane 1:3) fractions using a flash silica gel column. The acid fractions were methylated with 5% anhydrous HCl in methanol at 60 °C for 12 h. The alcohol fractions were derivatized using pyridine: *N*,*N*-bis(trimethylsilyl)-trifluoroacetamide (BSTFA;1:4). Compounds were analyzed using GC-FID for quantification, GC–MS for identification and GC-IRMS for isotopic analysis (Huang et al., 2004). The $^{13}C/^{12}C$ ratios were measured using an HP 6840^+ GC-pyrolysis system interfaced to a Finnigan Delta$^+$ XL stable isotope mass spectrometer. For fatty acids and sterols, the carbon isotope ratios were corrected for the carbon added during methylation and silylation, respectively (e.g., Huang et al., 2004). Organic compounds were identified by comparison of mass spectral data with previously reported standards and GC retention times (de Leeuw et al., 1980; Marlowe et al., 1984). LCA concentrations were determined from GC-FID analysis of the ketone fractions based on peak response relative to *n*-C_{36} as internal standard for SS6, or as external standard for the other lakes.

3. Results and discussion

3.1. Occurrence and abundance of LCAs

We found C_{37}–C_{39} LCAs in the surface sediments from all five oligosaline lakes (HundeSø, BrayaSø, LimnæaSø, SS6, and Lake E; Fig. 2) and in 14 sediment horizons throughout the upper 30 cm of SS6 sediment (representing the past ∼1100 years; Anderson and Leng, 2004). The concentrations are the highest reported for lacustrine surface sediments (Table 1). The C_{37} compounds comprise $C_{37:4}$ methyl ketone ($C_{37:4}$Me), $C_{37:3}$Me, and $C_{37:2}$Me; the C_{38} compounds include
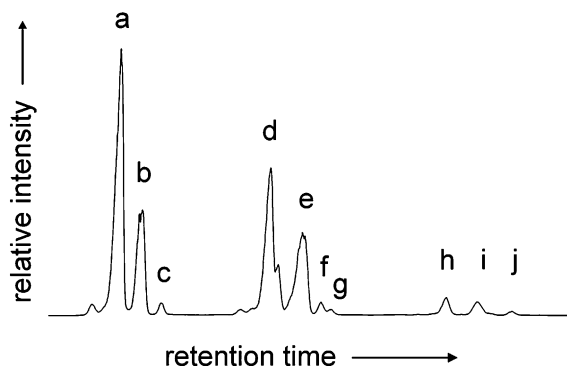

Fig. 2. Partial gas chromatogram of ketone fraction from SS6 lake sediment showing characteristic distribution of LCAs in west Greenland lake sediments. (a) $C_{37:4}$Me. (b) $C_{37:3}$Me. (c) $C_{37:2}$Me. (d) $C_{38:4}$Et and $C_{38:4}$Me. (e) $C_{38:3}$Et and $C_{38:3}$Me. (f) $C_{38:2}$Et. (g) $C_{38:2}$Me. (h) $C_{39:4}$Et. (i) $C_{39:3}$Et. (j) $C_{39:2}$Et.

$C_{38:4}$ ethyl ketone ($C_{38:4}$Et), $C_{38:3}$Et, $C_{38:2}$Et, as well as $C_{38:4}$Me, $C_{38:3}$Me and $C_{38:2}$Me; the C_{39} compounds contain $C_{39:4}$Et, $C_{39:3}$Et, and $C_{39:2}$Et. In all samples, alkenones of the same carbon number are dominated by the more unsaturated forms (i.e., tetraenoic > trienoic > dienoic).

The dominance of the tetraunsaturated isomers in west Greenland lake sediments is common for lacustrine LCAs (Cranwell, 1985; Theil et al., 1997; Wang and Zheng, 1998; Schouten et al., 2001; Zink et al., 2001). However, the distributions in the west Greenland lakes contain C_{38} methyl ketones which are absent from other LCA-containing, saline lakes in cold regimes (Volkman et al., 1988; Li et al., 1996; Theil et al., 1997; Wang and Zheng, 1998). The distributions appear similar to those found for marine sediments (e.g., Marlowe et al., 1984) and German (Zink et al., 2001) and English lake sediments (Cranwell, 1985). The similarity among the Greenland and German lake and marine sediment distributions is enhanced by the absence of C_{40} compounds from these systems.

C_{38} methyl ketones have been found in cultured marine coccolithophorids belonging to *Emiliania huxleyi* and *Gephyrocapsa oceanica* (Conte et al., 1994; Brassell et al., 2004), but have not been definitively found in cultures of the Isochrysidaceae family (e.g., *Isochrysis galbana*; Conte et al., 1994). Partial 18S ribosomal DNA sequences recovered from sediments of Ace Lake, Antarctica suggest that the alkenones in this lake were produced by prymnesiophytes most closely related to *Isochrysis galbana* (Coolen et al., 2004). The presence of C_{38} methyl ketones in Greenland lake sediments but not in Ace Lake sediments may be due to the presence of different prymnesiophytes. We hypothesize that the Greenland prymnesiophytes are close relatives of *Emiliania huxleyi* and *Gephyrocapsa oceanica*, in contrast to the Ace Lake prymnesiophytes. Combined with the literature reports of alkenone distributions in different environments (reviewed by Brassell et al., 2004), alkenone distributions in Greenland lake sediments and DNA evidence from Ace Lake (Coolen et al., 2004) suggest that C_{38} methyl ketones may be specific to the close relatives of *Emiliania huxleyi* and *Gephyrocapsa oceanica*. More work is needed to test this hypothesis.

3.2. Temperature and salinity relationships

The U_{37}^{K} and $U_{37}^{K'}$ indices for LCAs in the surface sediment of the Greenland lakes are given in Table 1. Zink et al. (2001) developed an empirical relationship between alkenone unsaturation indices and summer average water temperature (*T*) using German lake sediment and water filtrates (Table 1). The similarity of the distributions in Greenland and German lakes provides a basis for applying the German lake calibrations ($U_{37}^{K} = 0.02T - 0.121$, $r^2 = 0.89$; $U_{37}^{K'} = 0.211T - 0.725$,

Table 1
Lakes with alkenones in surface sediment

Location	Lake	Concentration (μg/gTOC)	U_{37}^{K} [a]	$U_{37}^{K'}$ [a]
Greenland	SS6	11,100	−0.68	0.11
Greenland	BrayaSø	82,700	−0.61	0.085
Greenland	HundeSø	50,300	−0.66	0.072
Greenland	LimnæaSø	47,100	−0.61	0.089
Greenland	Lake E	5900	−0.60	0.087
Germany	Lake Constance[b]	69	−0.18	0.28
Germany	Waldsee[b]	32	−0.25	0.33
Germany	Olzreuter See[b]	111	−0.25	0.33
Germany	Lake Steisslingen[b]	12	−0.27	0.38
Germany	Lake Stechlin[b]	143	−0.37	0.2
Germany	Brieter Luzin[b]	52	−0.39	0.2
Germany	Schmaler Luzin[b]	202	−0.29	0.3
Germany	Hausee[b]	205	−0.25	0.33
Germany	Tollensesee[b]	69	−0.38	0.25
Germany	Dagowsee[b]	n.a.	−0.08	0.38
Germany	Gr. Wummsee[b]	25	−0.33	0.21
USA	Brush Lake[b]	203	−0.57	0.18
Turkey	Lake Van[c]	4911	−0.65	0.19
China	Qinghai Lake[d]	443	n.a.	0.20

n.a., not available.

[a] $U_{37}^{K} = (37:2 - 37:4)/(37:4 + 37:3 + 37:2)$; $U_{37}^{K'} = (37:2)/(37:3 + 37:2)$.

[b] Zink et al. (2001).

[c] Theil et al. (1997).

[d] Li et al. (1996).

$r^2 = 0.68$) to Greenland lakes. Employing the calibrations, Greenland U_{37}^{K} data yield water temperature estimates ranging from ∼2 to 5.5 °C and $U_{37}^{K'}$ data yield water temperature estimates ranging from ∼10 to 11.5 °C (Fig. 3). Measured surface water temperature from BrayaSø ranged from 0 °C in early June to ∼17 °C in mid-July, 2000 (Anderson and Brodersen, 2001), bracketing the temperatures calculated using the calibrations of Zink et al. (2001). The major algal bloom in the Greenland lakes takes place during this period, as
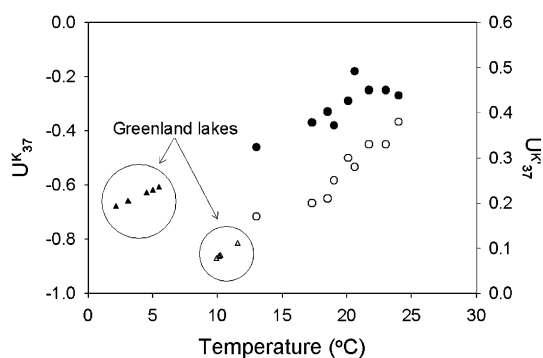
sunlight increases and lake turnover supplies nutrients to the photic zone. The U_{37}^{K} temperature calibration provides estimates similar to temperatures immediately following ice melt (early June) while the higher $U_{37}^{K'}$ estimates resemble the measured temperatures a week or two later.

U_{37}^{K} (due to inclusion of $C_{37:4}$) may be influenced by environmental variables other than temperature. Previous workers reported strong correlation between water salinity and production of $C_{37:4}$ in the North Atlantic and Nordic Seas ($r^2 = 0.699$, Rosell-Melé et al., 2002; $r^2 = 0.78$; Sicre et al., 2002). However, application of these salinity calibrations to the west Greenland lakes yields salinity estimates ranging from ∼18 to 35 psu, an order of magnitude higher than the actual salinity (2–4 psu). It has been noted that the apparent salinity dependence in the North Atlantic and Nordic Seas may be an artifact of temperature dependence on $C_{37:4}$ production, given the co-variability of salinity and temperature in these waters (Sicre et al., 2002; Sikes and Sicre, 2002). Bendle and Rosell-Melé (2004) suggested that the complexity of water masses and differing relative contributions of different prymnesiophytes in the North Atlantic and Nordic Seas may be responsible for the difficulty met when applying U_{37}^{K} and $U_{37}^{K'}$ temperature calibrations in the region. Although the relationship is still not fully understood, evidence is mounting that salinity does not exert a significant control on $C_{37:4}$ production.

Fig. 3. Estimated lake water temperatures for west Greenland lakes based on U_{37}^{K} (filled symbols) and $U_{37}^{K'}$ (empty symbols) temperature calibrations of Zink et al. (2001). German lake data are plotted as circles; Greenland lake data as triangles.

The *occurrence* of LCAs (and by inference, the presence of prymnesiophytes) in the Greenland lakes does appear to depend on salinity. Mean conductivity for the oligosaline lakes in this region is an order of magnitude higher than for freshwater lakes (2387 and 136 μS cm^{-1}, respectively; Anderson et al., 2001). While unusually high concentrations of alkenones are present in the surface sediment of the oligosaline lakes, surface sediments from five nearby freshwater lakes (SS32, SS49, SS50, SS66 and SS86) are devoid of LCAs. Their absence from the freshwater lakes and presence in lakes of slightly elevated salinity (∼10% of seawater) implies a salinity threshold for the occurrence of LCA-producing prymnesiophyte algae. Alkenones were not found in surface sediments of 36 freshwater lakes in eastern North America (Huang et al., 2004). Indeed, reports of LCA occurrence have been for marine capture basins (Volkman et al., 1988) or lakes in evaporative settings lacking outflow (Li et al., 1996; Theil et al., 1997; Wang and Zheng, 1998; Zink et al., 2001) with salinity ranging from ∼6 to 21.6 psu. Furthermore, LCAs were found in Younger Dryas sediments from Lake Steisslingen, Germany (Zink et al., 2001) in concentrations almost as high as in the Greenland lakes, but were absent or negligible elsewhere in the core. Dry conditions associated with the Younger Dryas may have increased lake salinity during this time (Zink et al., 2001), providing a habitat for alkenone-producing prymnesiophytes.

3.3. Alkenone carbon isotope ratios

Schouten et al. (2001) found that alkenones from Ace Lake, Antarctica had low $\delta^{13}C$ values (−31.7‰ to −36.1‰; Table 2). They noted that ^{13}C-depleted LCAs could reflect: (1) low water temperature and therefore high CO_2 concentrations and low cell growth rates, acting to maximize carbon isotope fractionation (Popp et al., 1998), and/or (2) recycling of CO_2 from decomposition of organic matter within the lake. The $\delta^{13}C$ values of the LCAss in Greenland lake sediments are even lower than those from Ace Lake, ranging from −40.0‰ to −41.7‰, with $C_{37:4}$ consistently more negative than $C_{37:3}$ (Table 2). However, the $\delta^{13}C$ offset between $C_{37:4}$ and $C_{37:3}$ in the Greenland samples (0.4–1‰) is significantly smaller than that observed in the Black Sea (2–4‰, Freeman and Wakeham, 1991). Furthermore, alkenone $\delta^{13}C$ values are ∼3–10‰ lower than those of short chain alkanoic acids and sterols (primarily autochthonous lipids) within the same sediment samples. Depletion of ^{13}C in LCAs (by ∼2–9‰) relative to sulfur-bound C_{27}–C_{29} steranes was also reported for Ace Lake sediment (Schouten et al., 2001). Based on results from culture studies (Laws et al., 2001) it is unlikely that sterols produced by prymnesiophytes are isotopically enriched relative to alkenones as a result of biosynthetic isotopic fractionation. The $\delta^{13}C$ offset between LCAs

and sterols suggests that the prymnesiophyte contribution to total sedimentary sterols is small relative to the full range of primary producers.

If atmospheric CO_2 ($\delta^{13}C_{atmosphere} \sim -8‰$, yielding $\delta^{13}C_{CO_2}(aq) \sim -9‰$) is the sole carbon source for the alkenone producers in Greenland lakes, the observed $\delta^{13}C$ value of −41‰ for alkenones would require isotopic fractionation (ε_p) of ∼27‰ by alkenone producers (assuming maximum isotopic depletion of 5.4‰ for alkenones relative to algal biomass; Laws et al., 2001). At high $CO_2(aq)$ and low growth rate, a maximum ε_p of 25‰ has been observed in culture experiments with *E. huxleyi* (Popp et al., 1998). Values of $\delta^{13}C$ as low as −43.7‰ have been observed for various sterols in suspended particulate organic matter in the Southern Ocean and were tentatively attributed to slow growth rates and high CO_2 concentrations resulting from low water temperature (Popp et al., 1999).

In addition to CO_2 concentration and growth rate, carbon isotope fractionation also increases with the surface area to volume ratio (i.e., decreasing cell size) of a cell and as cell geometry becomes less spherical (Popp et al., 1998). The low $\delta^{13}C$ values of LCAs relative to other aquatic compounds may also suggest that the prymnesiophytes in Greenland lakes are smaller in size than other primary producers in the lakes. Small cell size, in addition to high $CO_2(aq)$ and slow growth rate, offers an appealing explanation for the low $\delta^{13}C$ values of alkenones, as it may account for the difficulty encountered in previous attempts to isolate lacustrine LCA producers (Li et al., 1996; Theil et al., 1997; Zink et al., 2001).

An alternative explanation for the low $\delta^{13}C$ values of alkenones relative to fatty acids and sterols is that dissolved atmospheric CO_2 is not the only carbon source for photosynthetic organisms. Salinity stratification, combined with a deep photic zone in the west Greenland lakes (Anderson et al., 2001), could create a habitat for autotrophic organisms directly above the chemocline, providing access to light for photosynthesis as well as recycled (^{13}C-depleted) CO_2, such as that produced by methane oxidation. LCA-producing prymnesiophytes may live in a habitat with greater access to the recycled CO_2 than other algae, leading to $\delta^{13}C$ values of alkenones that are lower than sterols and short chain alkanoic acids. However, $\delta^{13}C$ values of DIC in three of the Greenland lakes (HundeSø, BrayaSø and Limnæa-Sø) showed relative uniformity with water depth in May 1999, ranging from −1.1‰ to 0.8‰ (M. Leng, personal communication). If this homogenous DIC carbon isotope profile is representative of the entire algal growth season, then all submerged aquatic autotrophs in the lakes should utilize CO_2 having similar carbon isotope ratios. If this is the case, the $\delta^{13}C$ offset between alkenones and other autochthonous lipids is likely due to enhanced carbon isotope fractionation by alkenone-

Table 2
$\delta^{13}C$ values of representative organic compounds in Greenland lakes and Ace Lake, Antarctica[a]

Sediment sample	Alkenones		Alkanoic acids			Sterols	
	$C_{37:4}$	$C_{37:3}$	14	16	28	1[b]	2[b]
Greenland lakes							
BrayaSø	−41.7	−41.0	−35.0	−32.5	−30.4	−36.7	−36.3
	(.08)	(.01)	(s.m.)	(s.m.)	(s.m.)	(.18)	(.01)
HundeSø	−41.0	−40.0	−35.1	−32.4	−29.4	−37.2	−36.6
	(.01)	(.01)	(.17)	(.13)	(1.3)	(.18)	(3.4)
LimnæaSø	−40.8	−40.4	−37.2	−34.0	−32.4	−34.6	−36.3
	(.08)	(.04)	(.59)	(.04)	(.34)	(.48)	(.26)
Lake E	−41.4	−41.0	n.d.	n.d.	n.d.	n.d.	n.d.
	(.42)	(.30)					

	Alkenones	Steroids		
	$C_{37:4} + C_{37:3}$	C_{27} sterane	C_{28} sterane	C_{29} sterane
Ace lake, Antarctica[c]				
0–5 cm	n.d.	−28.6	n.d.	−29.2
		(0.5)		(0.7)
6.6–8.3 cm	−31.7	−28.2	−28.8	−28.3
	(0.3)	(0.2)	(0.2)	(0.1)
11.6–13.3 cm	−34.6	−27.9	−29.2	−28.5
	(0.3)	(0.2)	(0.4)	(0.1)
16.6–18.3 cm	−36.1	−30.3	−33.8	−30.6
	(0.4)	(0.3)	(0.1)	(0.1)
21.6–23.3 cm	−34.9	−30.4	−30.7	−30.1
	(0.9)	(0.3)	(0.3)	(0.1)

s.m., single measurement.
n.d., not determined.
[a] Greenland lake samples are surface sediments while Ace Lake (Antarctica) samples are down-core. $\delta^{13}C$ values are reported as ‰ relative to VPDB. Numbers in parentheses are standard deviation from duplicated measurements.
[b] (1) 5α-cholest-22E-en-3β-ol; (2) 5β-cholestan-3β-ol.

producing prymnesiophytes due to the combined effects of high $CO_2(aq)$, low growth rate and small cell size as discussed above.

4. Conclusions

The identification of alkenones in the sediments of five oligosaline lakes extends the known geographic range of these compounds to west Greenland. The sedimentary concentrations are the highest reported, suggesting that the Greenland lakes offer a favorable habitat for certain prymnesiophyte species. U_{37}^{K} and $U_{37}^{K'}$ water temperature estimates for the lakes, based on the calibrations of Zink et al. (2001), are in the range of measured lake water temperatures during the period of high aquatic productivity. Salinity calibrations from the North Atlantic and Nordic Seas, based on the proportion of $C_{37:4}$ in LCA distributions, provide incorrect salinity estimates for the Greenland lakes. Contributions from various unmineralized (i.e., lacking coccoliths) alkenone-producers such as those in the west Greenland lakes, or varying relative contributions from one or

more such organisms, could help explain the complexity of alkenone-based temperature calibrations in the North Atlantic and Nordic Seas. The highly negative $\delta^{13}C$ values for alkenones in west Greenland lakes represent the greatest isotopic depletion reported for these compounds from a natural setting. However, our data are insufficient to determine whether such low $\delta^{13}C$ values are due to enhanced carbon isotopic fractionation or utilization of ^{13}C-depleted carbon sources.

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