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ORIGINAL PAPER

Leaf wax δ^2H and varve-thickness climate proxies from proglacial lake sediments, Baffin Island, Arctic Canada

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Abstract We present a multiproxy paleoclimate record using leaf wax hydrogen isotopes (δ^2H_{wax}) and varve thickness from Arctic proglacial lake sediments. We also provide one of the first evaluations of the utility of δ^2H_{wax} as a paleoclimate proxy in Arctic proglacial lakes. We compare varve thickness and δ^2H_{wax} at sub-decadal resolution from 1948 to 2004 AD, and at sub-centennial resolution from 1450 to 2004 AD. Varve thickness and δ^2H_{wax} both contain large interannual variability and are anti-correlated during the late twentieth century, suggesting that both proxies respond rapidly, but by different mechanisms, to catchment-scale forcings. At longer time scales, varve thickness exhibits a strong response to Little Ice Age cooling (1661–1827 AD in this record) but does not show evidence for twentieth century warming recorded throughout the Arctic. δ^2H_{wax} does record regional-scale temperature changes, with more ^{2}H-depleted values during the Little Ice Age and an abrupt change to more ^{2}H-enriched values in the twentieth century. This corresponds well with a recent Arctic-wide temperature reconstruction in which the seventeenth century is the coldest interval, and the twentieth century is the warmest interval. Our results suggest that δ^2H_{wax} is a promising proxy that can be applied at high resolution in proglacial Arctic lakes.

Keywords Arctic climate · Baffin Island · Biomarker · Compound-specific isotopes · Holocene · Leaf wax · Proglacial lake · Varve

Introduction

Arctic proglacial lake sediments are excellent archives for high-resolution paleoclimate reconstructions due to high sedimentation rates and frequent presence of varves. Paleoclimate reconstructions from these sediments have primarily relied on varve thickness, because extremely low productivity precludes the presence of subfossil algae or midge remains, and high minerogenic sedimentation rates dilute terrestrial proxies such as pollen. The quantitative relationship between varve thickness and specific climate variables (temperature, precipitation, seasonal variations) is not always straightforward. Thus, developing new climate proxies for use in proglacial lake sediments is

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important for understanding past Arctic climate variability.

Paleohydrological proxies that rely on compound-specific hydrogen isotopes measured in sediment archives are showing promise for application around the world (Liu and Huang 2005; Schefuß et al. 2005; Jacob et al. 2007; Tierney et al. 2008; Nichols et al. 2009), including the Arctic (Pagani et al. 2006; Wilkie et al. 2010). The development of continuous flow gas chromatography-isotope ratio mass spectrometry (GC-IRMS; Burgoyne and Hayes 1998; Hilkert et al. 1999) allows for measuring compound-specific isotopes from organic-poor sediments. This opens up opportunities for generating high-resolution paleoclimate records from Arctic lake sediments.

Precipitation isotopes are potentially powerful climate proxies because they are directly influenced by climatic variables such as precipitation source and amount and atmospheric temperature (Rozanski et al. 1993). Furthermore, modern precipitation isotopes are rather well understood and can be calculated for any location as a function of climatological and spatial factors, with some error due to spatial and temporal limitations of empirical datasets (Bowen and Revenaugh 2003). Two isotopic methods are currently widely used to infer Arctic paleoclimate: direct measurements of precipitation δ^2H and δ^{18}O preserved in ice cores (e.g. Jouzel et al. 1997), and δ^{18}O measurements of lake sediment carbonate (e.g. Anderson et al. 2007). Ice-core and carbonate-lake-sediment archives have limited spatial extent, however, so a more broadly applicable isotopic proxy would be useful for expanding our spatial understanding of paleoclimate change. Leaf waxes (*n*-alkanes and *n*-alkanoic acids), which are a component of the protective coating produced by almost all land plants, are ubiquitous and well preserved in sediment archives (Eglinton and Eglinton 2008). Sedimentary *n*-alkane and *n*-alkanoic acid δ^2H is systematically offset from precipitation δ^2H (δ^2H_{precip}; Sachse et al. 2012). This offset can be constrained in modern settings and applied to paleoclimate records, allowing *n*-alkane and *n*-alkanoic acid δ^2H to be used as a proxy for environmental water isotopes (Huang et al. 2004; Sachse et al. 2004; Hou et al. 2008; Rao et al. 2009). Additional environmental and physiological processes, including vegetation type, leaf wax biosynthetic pathways, and evaporation from both soil and leaf, can influence the leaf wax δ^2H value (Sachse et al. 2012). Despite the complexities inherent in leaf wax δ^2H (δ^2H_{wax}) as a climate proxy, δ^2H_{wax} has been successfully used to reconstruct Pleistocene paleohydrology at low and mid latitudes (Schefuß et al. 2005; Hou et al. 2006; Tierney et al. 2008), and Paleogene paleohydrology at high latitudes (Pagani et al. 2006). Recently, researchers have begun to apply δ^2H_{wax} in Pleistocene high-latitude settings (Wilkie et al. 2010).

Here, we present a δ^2H_{wax} record based on C_{26} *n*-alkanoic acid that spans 1436–2004 AD from proglacial Ayr Lake on Baffin Island, eastern Arctic Canada. We also present a varve-thickness record from the same lake. Varve thickness is an annually resolved paleoclimate proxy that has been applied with success in proglacial lakes throughout the Arctic (Bird et al. 2009; Cook et al. 2009; Thomas and Briner 2009). We analyzed δ^2H_{wax} at sub-centennial resolution through the entire record, and at sub-decadal resolution from 1948 to 2004 AD. The purpose of this study is twofold: (1) To assess the utility of δ^2H_{wax} as an Arctic climate proxy by comparing it to varve thickness and a regional temperature reconstruction, And (2) To use this proxy to reconstruct past climate.

We suggest that varve thickness and δ^2H_{wax} are well suited for direct comparison. Lake sediments integrate leaf waxes from plants in the region surrounding the lake, carried to the sediments by wind and water (Sachse et al. 2012). Varve thickness also integrates processes occurring at catchment scale, including temperature and precipitation variability and glacier melt (Hodder et al. 2007). Thus, although δ^2H_{wax} is mainly controlled by source-water δ^2H and varve thickness is controlled by physical processes, both proxies are likely driven by similar catchment-scale climate and transport processes. We present one of the first δ^2H_{wax} records from an Arctic lake, and demonstrate that δ^2H_{wax} is a promising proxy for Pleistocene paleoclimate in the Arctic, including in low-organic-matter proglacial lakes.

Setting

Ayr Lake (70.459° N, 70.086° W, 68 m above sea level) is located between Clyde Inlet and Eglinton Fiord on northeastern Baffin Island (Fig. 1). The 115 km^2 lake rests in a deep valley incised into crystalline bedrock that spans the glaciated mountain range along the northeastern coast of Baffin Island.

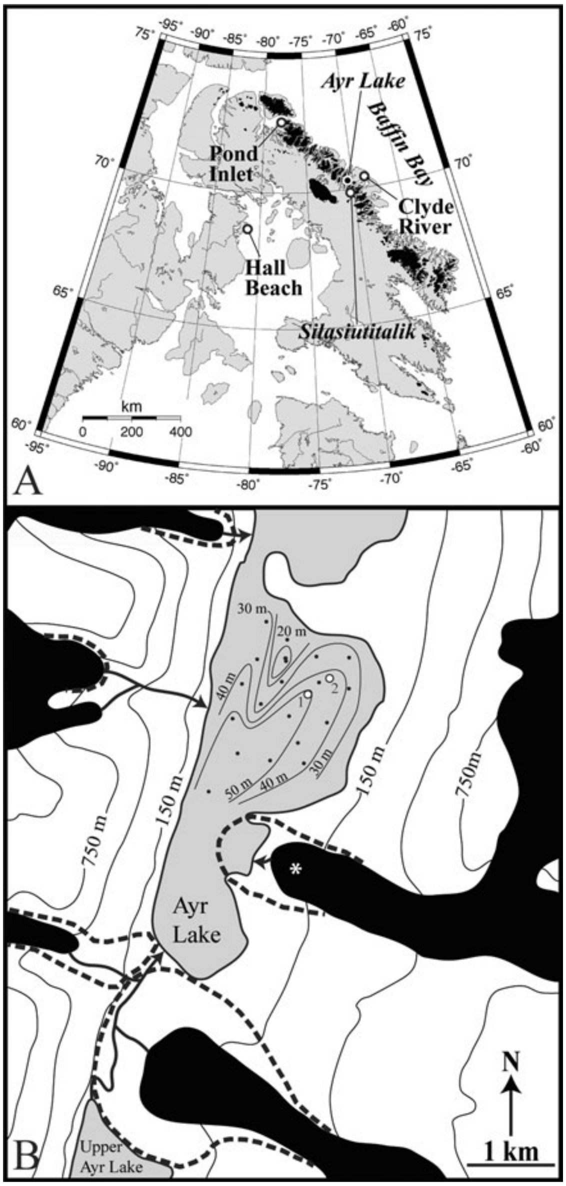

Fig. 1 **a** Baffin Island region showing sites mentioned in text. **b** Ayr Lake southern basin bathymetry and surrounding catchment. Glaciers shown in *black*, lakes shown in *gray*, major Little Ice Age moraines shown with *thick dashed lines*. Contour interval is 300 m. Core sites 1 and 2 are *white circles*; bathymetry data points are *black dots*. The glacier that likely calved into Ayr Lake during the Little Ice Age is labeled with an *asterisk*

The catchment of Ayr Lake has an area of 1,300 km^2, 36% of which is glaciated (based on aerial photographs take in 1958). At the southern end of Ayr Lake, near the western side of the glaciated mountain range, a peninsula nearly isolates a 3.7 km^2 basin from the main lake basin. Our core sites are located in this southern basin, which has a maximum depth greater than 50 m and a catchment area of 517 km^2, 44% of which is glaciated. Upstream of Ayr Lake, the Ayr valley bottom is covered by tundra grasses, herbs, and shrubs. The Ayr valley is windier than adjacent areas of Baffin Island, as evidenced by windswept lake ice during several May field seasons, and by accounts of local residents (J. Qillaq, pers. comm.). Winds are funneled from the west into the long, narrow valley, over the tundra-covered valley bottom and eventually over Ayr Lake itself.

Clyde River, the closest town with a weather station (in operation since 1946; Environment Canada 2011), is on the coast of Baffin Bay, east of the mountain range and 80 km northeast of our core sites in Ayr Lake. A secondary weather station, in operation since early September 2010, is located at Silasiutitalik, at the head of Clyde Inlet, 50 km south of the southern basin of Ayr Lake, but on the same side of the mountain range (Fig. 1; Kangiqtugaapik (Clyde River) Weather Station Network 2011). Weather at Silasiutitalik is probably more representative of Ayr Lake weather, but the record length is limited, and so we utilize both instrumental records in this study.

Modern sediment sources to the southern basin of Ayr Lake include inflow streams from several icefield outlet glaciers, an inflow stream from Upper Ayr Lake (informal name), and rockfall from steep catchment walls. There are currently no glaciers that calve directly into Ayr Lake, although based on the position of moraines deposited during the Little Ice Age (LIA), at least one glacier used to calve into the southern basin (Fig. 1). The glaciers in the Ayr Lake catchment have retreated up to 1 km from their LIA extents. A single outflow stream is located at the northern end of Ayr Lake, 48 km from our coring site.

Because temperatures remain below freezing from September to late May (Fig. 2; Environment Canada 2011), ice covers the lake for ~9 months of the year and is ~2 m thick by the end of winter. A moat around the edge of the lake begins to form in late June or July and the lake is usually ice-free for the months of July, August, and September. Modern sediment input to the lake is therefore confined to the summer months from late June to September. Similarly, plant growth occurs during the summer months when plants are not temperature or light limited. Leaf waxes are abraded from the surface of the leaves by wind and water and

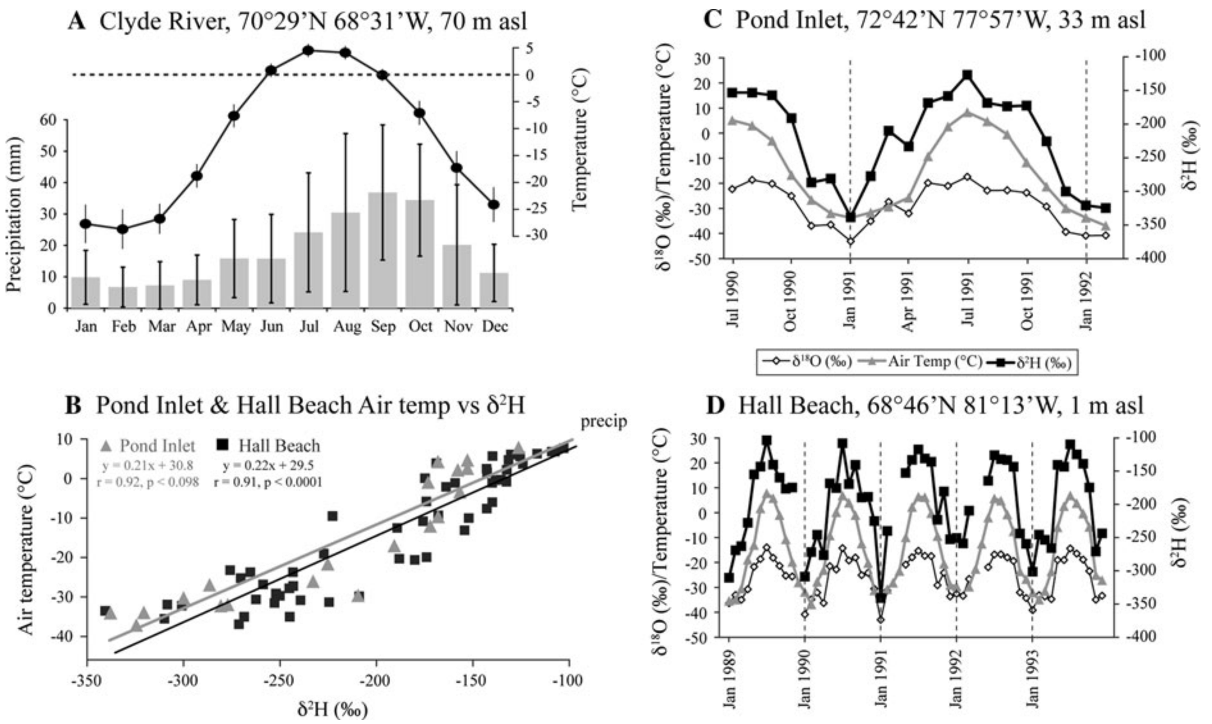

Fig. 2 **a** Average monthly precipitation and temperature at Clyde River, Baffin Island from 1946 to 2006 AD. Large 1σ *error bar*s for precipitation reflect the high inter-annual variability. **b** Comparison of monthly temperature and δ^2H_{precip} at Pond Inlet and Hall Beach. **c** Monthly temperature and precipitation isotopes measured from July 1990 to February 1992 at Pond Inlet, Baffin Island, 410 km north of Ayr Lake. **d** Monthly temperature and precipitation isotopes measured from January 1989 to December 1993 at Hall Beach, Melville Peninsula, 450 km west of Ayr Lake (IAEA/WMO 2010)

are transported to the lake by wind and by stream flow, mainly during the summer growing season (Eglinton and Eglinton 2008). Modern vegetation in northeastern Baffin Island is composed of herbs and heath (Ericaceae, Cyperaceae, and *Oxyria digyna*), grasses (Poaceae) and shrubs (e.g. *Salix*; Fréchette and de Vernal 2009). Pollen studies in this region indicate that long-distance pollen transport accounts for a low percentage of pollen assemblages (<5%), at least in Holocene lake sediments (Fréchette and de Vernal 2009). Thus, long-distance transport of leaf waxes is likely also rare on this part of Baffin Island. Despite the mid-Arctic environment, vegetation is abundant enough to produce leaf waxes that are deposited in measurable quantities in lake sediments.

Modern precipitation isotopes

We examine precipitation isotopes at the two Global Network of Isotopes in Precipitation (GNIP) stations closest to Ayr Lake: Pond Inlet and Hall Beach (Fig. 1). Pond Inlet is located on the northeastern side of Baffin Island, 410 km north of Ayr Lake and east of the glaciated mountain range that extends along the length of the island. Hall Beach is on the Melville Peninsula, 450 km west of Ayr Lake and on the west side of the Baffin Island mountain range. There are no GNIP stations located in the mountain range, which would be the most representative of precipitation falling in the Ayr Lake catchment. The existing GNIP records are short and discontinuous (all available precipitation isotope data are shown in Fig. 2; IAEA/WMO 2010), but the seasonal variability is still evident. Hall Beach precipitation is approximately 20–30‰ enriched in ^2H relative to Pond Inlet precipitation. This is partially driven by strong latitudinal temperature gradients; Pond Inlet is 400 km farther north than Hall Beach. Using the regional relationship between temperature and δ^2H_{precip}, the average temperature difference between these sites (1.7°C) can explain only 8‰ of the δ^2H_{precip} difference. Thus, different precipitation sources at these two sites may explain the remaining 12–22‰ δ^2H_{precip} difference between Pond Inlet and Hall Beach. At both sites, seasonal δ^2H_{precip} variability is extreme, and is strongly coupled to the pronounced seasonal temperature changes (Fig. 2). Summer precipitation is up to 200‰ more enriched in ^{2}H (−110 to −140‰ at Hall Beach, −140 to −160‰ at Pond Inlet) than winter precipitation (−250 to −300‰ at Hall Beach, −300 to −340‰ at Pond Inlet; IAEA/WMO 2010).

Methods

Sediment coring

In May 2009 three sediment cores with intact sediment–water interfaces were recovered from Ayr Lake using a Universal Coring system. Core site locations (Fig. 1) were chosen in deep water (>40 m) and away from the steep valley walls and lateral moraines to reduce the chance of erosion by turbidity flows and increase the probability of continuous deposition. A 63-cm-long core (09AYR2) and a 136-cm-long core (09AYR5) were collected at core site 1 at a water depth of 51 m (70.269°N, 70.617°W). A 23-cm-long core (09AYR6) was collected at core site 2 at a water depth of 43 m (70.271°N, 70.611°W). The surface cores were kept vertical and dewatered for at least 24 h before being packed with foam for shipment. Once at the laboratory, the cores were split lengthwise, photographed, and described before being placed in cold storage.

Lamination analysis

The sediment was prepared for thin sections at the University at Buffalo following methods similar to Lamoureux (1994) and Francus and Asikainen (2001). Thin sections were made at Texas Petrographics Services, Inc. in Houston, TX, and then scanned using a transparency scanner at 1,600 dpi. Laminated couplets were identified, marked and counted in Adobe Illustrator and lamination thicknesses were measured perpendicular to the laminations using ImageJ software. The number of isolated sand grains >0.30 mm in maximum diameter was counted per lamination using ImageJ software.

Plutonium dating

We used plutonium ($^{239+240}$Pu) concentrations to determine if the Ayr Lake laminations are varves by pinpointing the onset and peak of $^{239+240}$Pu deposition in 1952 and 1963 AD, respectively (Ketterer et al. 2004a). Dried aliquots (0.5 g) of the top 32 cm of core 09AYR2 were analyzed for $^{239+240}$Pu concentrations at the Northern Arizona University Department of Chemistry using ICP-MS analysis following the methods of Ketterer et al. (2004b). Sediments were analyzed at 2 cm intervals from 0 to 10 cm, 1 cm intervals from 10 to 15 cm, 0.5 cm intervals from 15 to 21 cm, 1 cm intervals from 21 to 22 cm, and 2 cm intervals from 22 to 32 cm ($n = 28$).

Lipid biomarker analysis

Extraction and purification

Cores 09AYR2 and 09AYR5 were subsampled for lipid biomarker analysis. The surface of core 09AYR2 was sampled every 1–3 laminations. Below lamination #57, 1-cm-thick samples encompassing 2–5 laminations each were collected at regularly spaced intervals down to the base of the sequence. Free lipids were extracted from freeze-dried samples weighing 0.75–4.50 g using an Accelerated Solvent Extractor 200 (Dionex) using 9:1 (v:v) dichloromethane (DCM):methanol. Cis-11-eicosenoic acid (5 µg) was added to each sample extract as an internal standard. The carboxylic acid fraction was isolated from the total extracts using solid phase extraction (Aminopropyl Bond Elute®) with 4% acetic acid in diethyl ether as the eluent, and was then methylated using anhydrous 5% HCl in methanol. The methylated carboxylic acid fractions were further purified using silica gel flash column chromatography with DCM as the eluent, to remove hydroxyl-carboxylic acids.

Gas chromatography

Fatty acid methyl esters were first analyzed using a Hewlett-Packard 6890 gas chromatograph (GC), fitted with a 30 m fused silica column (HP-1MS, 0.32 mm i.d., 0.25 µm film thickness), a flame ionization detector (FID), a split/splitless injector (operated in splitless mode), and an HP7683 auto-sampler. Helium was used as the carrier gas, with a flow rate of

1.7 ml min^{-1}. The temperature program was isothermal at 60°C for 1 min, followed by heating at 20°C min^{-1} to 220°C, and then heating at 6°C min^{-1} to 315°C, where it was held for 15 min. Leaf wax concentrations were determined using the peak areas obtained from the GC-FID results.

Hydrogen isotope analyses

Hydrogen isotope analyses were performed using an HP 6890 GC, equipped with an AS 200 auto-sampler, interfaced via a high-temperature conversion interface to a Finnigan MAT Delta+ XL mass spectrometer. The temperature program was isothermal at 40°C for 1 min, followed by heating to 300°C at 10°C min^{-1}. Helium (UHP grade) was used as the carrier gas, operating at constant flow mode with a rate of 1.1 ml min^{-1}. Sample injections were performed in the splitless mode, and each sample was analyzed in triplicate. Compounds separated by GC column were converted to H_2 by a pyrolysis reactor at 1,445°C. Six pulses of hydrogen reference gas with a known δ^2H value were injected via the interface to the IRMS, for the computation of δ^2H values of sample compounds relative to Vienna Standard Mean Ocean Water. The average standard deviation of triplicate analyses was smaller than ±3‰. An external standard, composed of C_{16}, C_{18}, C_{22}, C_{24}, C_{26} and C_{28} *n*-alkanoic acids, injected twice after every sixth sample injection, also showed consistent δ^2H values throughout the analyses, with variability <±2‰. A correction was made on the fatty acid methyl esters to remove the isotopic contribution from the methyl group added during methylation using the formula:

$$\delta^2\mathrm{H}_{\mathrm{sample}} = [(2\mathrm{n}+2)\delta^2\mathrm{H}_{\mathrm{measured}} + 123.7\text{‰} \times 3]/(2\mathrm{n}-1) \quad (1)$$

where n is the number of carbons in the molecule and −123.7‰ is the δ^2H value for the added methyl group.

For this study, we use the hydrogen isotope values from the C26 *n*-alkanoic acid, which have smaller standard deviations, optimum peak sizes, and are significantly correlated with C_{22}, C_{24}, C_{28}, and C_{30} *n*-alkanoic acids (Supplemental Fig. 1). The C24 *n*-alkanoic acid has peak sizes similar to the C26 *n*-alkanoic acid (Supplemental Fig. 1), but both compounds have the same variability and are significantly correlated. Although middle-chain-length *n*-alkanoic acids (C22) are mainly produced by aquatic plants (Gao et al. 2011), there is little aquatic productivity in Ayr Lake because the water is turbid due to glacial inflows. Thus, the C22 *n*-alkanoic acid peak in Ayr Lake sediment samples is small, and δ^2H_{C22} is significantly correlated with δ^2H_{C26} (Supplemental Fig. 1), indicating that C22 *n*-alkanoic acids in this setting are probably made by terrestrial plants.

Results[1]

Sediment core description

The three sediment cores collected from Ayr Lake contain millimeter-scale rhythmically laminated sediments that are composed of siliclastic grains (Fig. 3a). The laminated couplets are composed of a dark olive-gray, medium-sand to silt lower layer that grades normally into an olive-gray fine-grained cap. The couplets are separated by sharp contacts. Within some of the couplets, dark olive-gray layers of very fine to medium sand are present. Laminations contain no evidence for erosional contacts.

In many of the laminations, normal gradation is interrupted by sub-laminations (graded laminations that are lacking defined clay caps; Fig. 3b) or massive fine to medium sand layers (Fig. 3c). The thickness of these sand layers range from 0.24 to 9.04 mm. Isolated subangular to subrounded grains, fine sand to granule in size, are found intermittently dispersed within many of the laminations. In a few instances, the isolated grains form a nearly continuous layer near the top of the lamination (Fig. 3d).

Chronology

The onset of $^{239+240}$Pu deposition (1952 AD) occurred at a depth of 16.0–16.5 cm (laminations 53 and 54) and the peak $^{239+240}$Pu deposition (1963 AD) occurred at a depth of 12.0–13.0 cm (laminations 40–42; Fig. 4). By assigning lamination 54 to 1952 AD, the lamination assigned to 1963 AD would be number 43, which is not within the 12.0–13.0 cm interval. There is

[1] All of the data from Ayr Lake presented in this study are available on-line through the World Data Center for Paleoclimatology (http://www.ncdc.noaa.gov/paleo/pubs/jopl2012arctic/jopl2012arctic.html).

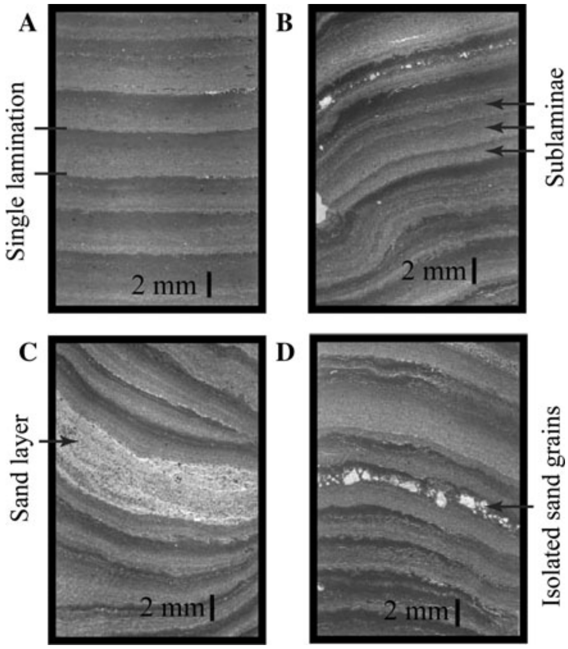

Fig. 3 Scanned thin sections of Ayr Lake sediments. **a** Horizontal laminations consist of normally graded silt and clay couplets. **b** Some couplets contain sublaminations that are identified by a thin clay top or by their isolated occurrence at just one core site. **c** Sand layers, perhaps deposited during rockfalls or other rare events, are present in some laminations. **d** Sand grains form discontinuous layers, or scattered single grains within a lamination. These isolated sand grains were deposited in autumn, as indicated by their presence in the upper, fine-grained portion of the couplet

therefore a single solution that fits the $^{239+240}$Pu data: lamination 53 likely was deposited in 1952 AD and lamination 42 likely was deposited in 1963 AD. Based on this correspondence between lamination number and the timing of $^{239+240}$Pu deposition (Fig. 4b), we conclude that the laminations are varves. The uppermost preserved lamination corresponds to 2004 AD, indicating that the four laminations deposited from 2005 to 2008 AD were destroyed during sample collection, similar to losses that occur at other lakes (Thomas and Briner 2009). Below varve 54, the chronology of all three cores is based on varve counting and correlation between cores (Fig. 4c).

Varves in each core were counted independently of each other and then correlated between cores using distinct maker beds (e.g. sand layers, varves with multiple sublaminations, and varves with isolated grains; Supplemental Fig. 2a). The number of varves between maker beds was counted and compared between cores. Discrepancies between varve counts were used to correct varve counts in each core for misidentified varves. Overall, 14 misidentified and missing varves in the three cores over the 569-varve record indicates a minimum error of 2.5% in the chronology (Fig. 4c). Additional errors may be present in the chronology due to the lack of overlap between cores for the entire record.

Varve thickness

Varve thickness from each core was normalized to account for average varve thickness differences at the different core sites (Supplemental Fig. 2c). To derive a composite varve-thickness record, the average varve thickness was calculated for the areas of overlap between cores, and the measurement from a single core was used in areas without overlap. The resulting composite varve chronology extends from 1435 to 2004 AD and contains three distinct intervals: 1435–1660 AD and 1828–2004 AD exhibit high variability, including multi-decadal variability and 2.6 and 2.2 mm average varve thickness, respectively; 1661–1827 AD contains lower variability and 1.6 mm average varve thickness (Fig. 5).

For the interval of overlap with the weather station record at Clyde River, we compared varve thickness to climate variables including monthly, seasonal and annual temperature, precipitation, and heating degree days. The correlation with all climate variables is weak and not significant. Summer temperature has been found to exert a significant control on varve thickness elsewhere on northeastern Baffin Island (Hughen et al. 2000; Moore et al. 2001; Thomas and Briner 2009), but Clyde River summer temperature is not significantly correlated with varve thickness ($r = 0.13$, $p = 0.35$).

Isolated sand grains

Throughout the record, 37% of varves contain isolated sand grains larger than 0.30 mm maximum diameter (Fig. 5). From 1435 to 1826 AD, 31% of varves have isolated sand grains with a maximum of nine grains per varve. From 1827 to 1911 AD, 70% of the varves contain isolated sand grains with a maximum of 32 grains per varve. The size of the isolated sand grains in the 1827 to 1911 AD interval increases from medium to very coarse sand, and the grains are confined to the upper clay portion of these varves. From 1912 to 2004 AD, the proportion of

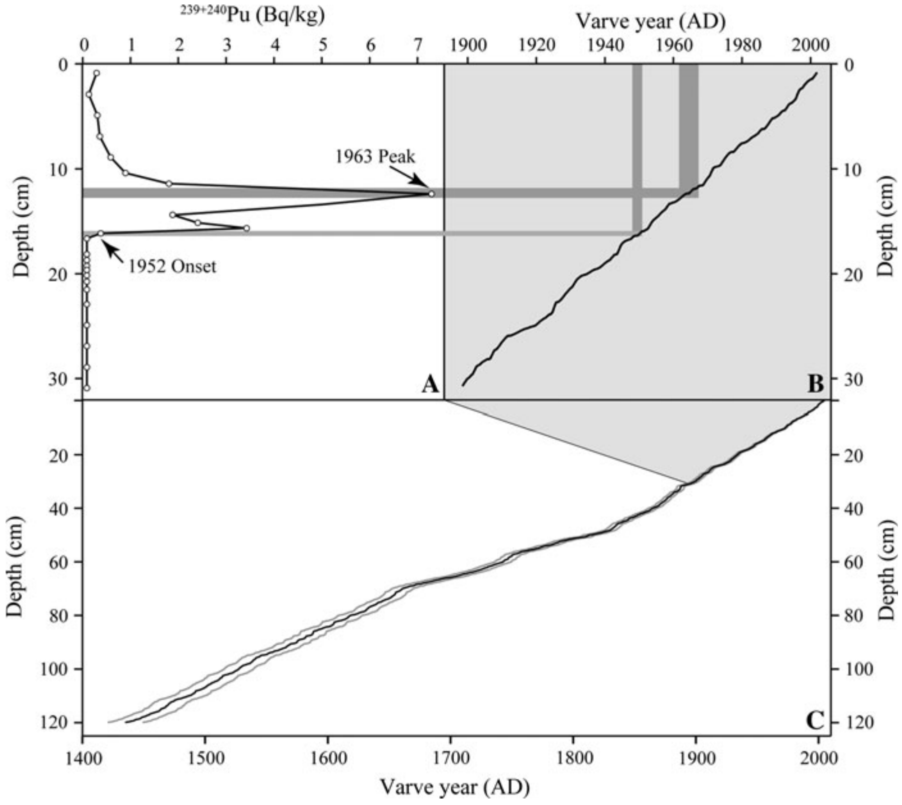

Fig. 4 Ayr Lake chronology. **a** $^{239+240}$Pu concentrations in core 09AYR2. **b** The correspondence of the onset and peak of $^{239+240}$Pu deposition with varve counts. **c** Age-depth model for the entire sediment core, including 2.5% minimum chronological error due to misidentified or missing varves

varves that contain isolated sand grains decreases to 37% with a maximum of six grains per varve.

Leaf wax hydrogen isotopes

We analyzed δ^2H_{wax} at two different time scales in this record: nearly annual and sub-centennial. On the nearly annual time scale, the variability among samples is up to 12‰ (Fig. 6). In the 55-year period of overlap with the instrumental record at Clyde River, the δ^2H_{wax} range is −239 to −259‰. Samples most enriched in ^{2}H are from 1948 to 1951 AD and the mid-1980s, and samples depleted in ^{2}H are from the mid-1950s, mid-1970s, and early 1990s. Similar to varve thickness, we compared δ^2H_{wax} to climate variables at Clyde River. The correlation with summer precipitation and temperature, the variables most likely to drive changes in δ^2H_{wax}, is not significant (precipitation: $r = 0.09$, $p = 0.56$; temperature: $r = 0.05$, $p = 0.76$). Leaf wax concentrations range from 0.75 to 4.75 μg g^{-1} sediment and contain trends similar to δ^2H_{wax} (Fig. 6). Higher concentrations of leaf waxes correspond to samples depleted in ^{2}H, and the two records are significantly correlated ($r = 0.42$, $p = 0.007$; Fig. 6d).

The sub-centennial record extends from 1450 to 2004 AD. Decadal averages were calculated for the high-resolution twentieth century δ^2H_{wax} data so that they would be at a resolution comparable to the rest of the record. In sediment from 1450 AD, δ^2H_{wax} is −254‰, declines to a minimum of −266‰ at 1821 AD and increases to an average of −258‰ between 1846 and 1940 AD (Fig. 5). During the second half of the twentieth century, leaf waxes are enriched in ^{2}H compared to the rest of the record (−246‰) and trend toward more negative values (−251‰) in the early twenty-first century.

Discussion

Varve thickness and isolated sand grains as a paleoclimate proxy in Ayr Lake

The correlation between varve thickness and temperature during the instrumental period at multiple sites

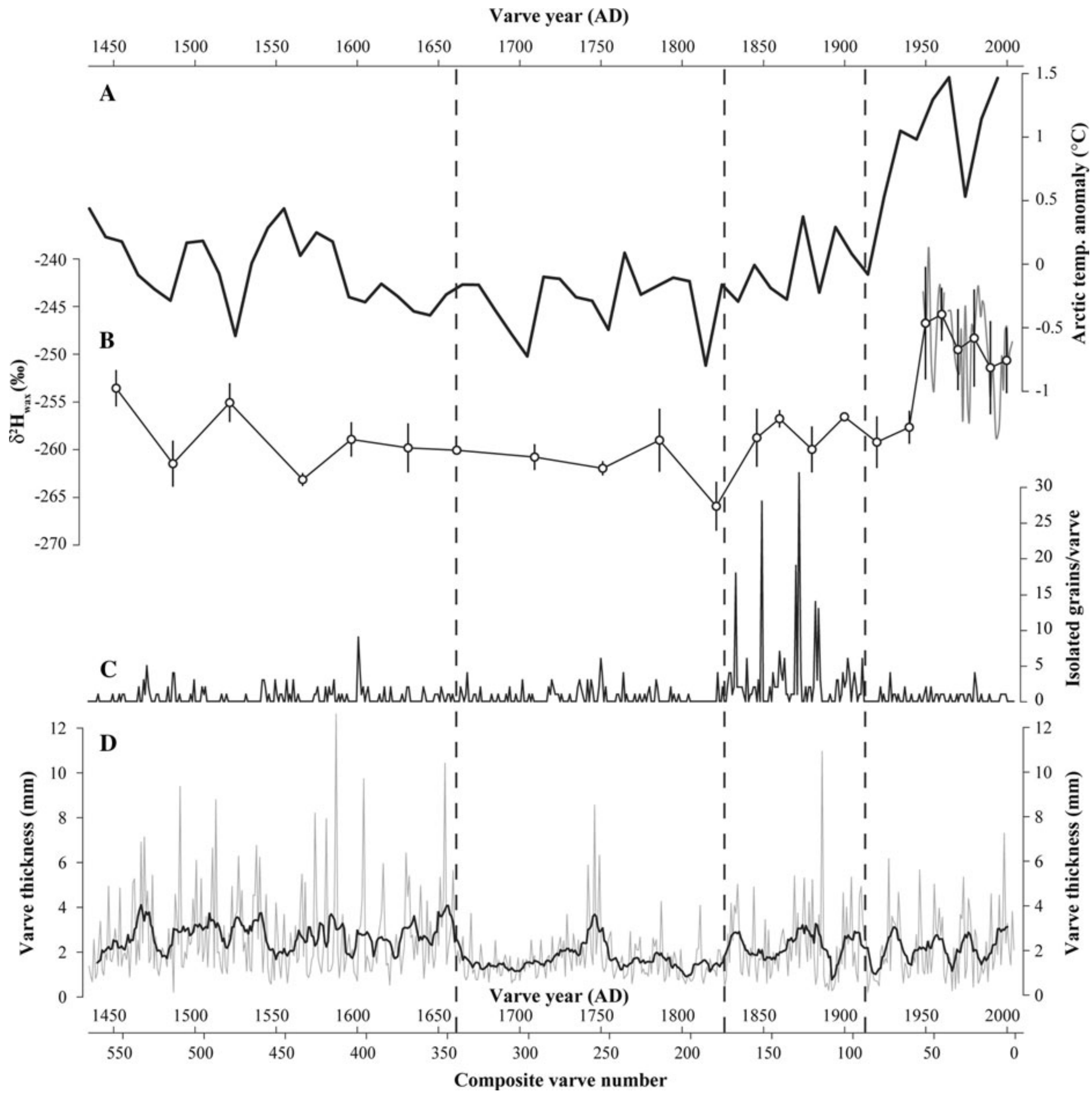

Fig. 5 **a** Arctic temperature anomaly relative to a 1961–1990 AD reference period (Kaufman et al. 2009). **b** Hydrogen isotope ratio of C26 *n*-alkanoic acid from Ayr Lake sediments. Decadal averages (*white circles*) were calculated using the high-resolution record from 1948–2004 AD (*gray line*). **c** Isolated sand grain counts per varve. **d** Ayr Lake composite varve thickness. *Gray line* is annual; *black line* is 10-year running mean

throughout the Arctic has been used to reconstruct paleoclimate (e.g. Hughen et al. 2000; Moore et al. 2001; Bird et al. 2009; Cook et al. 2009; Thomas and Briner 2009). The correlation between varve thickness and temperature is not always straightforward, however, because varve thickness integrates a complex combination of glacier, climate, fluvial, and geomorphological effects (Hodder et al. 2007). The lack of a significant correlation between Ayr Lake varve thickness and the Clyde River instrumental record could be a result of the climate signal being masked by the many other processes influencing varve formation. Alternatively, climate at Clyde River could be different from climate in the Ayr Lake catchment. Precipitation and temperature at Clyde River are moderated by Baffin Bay, whereas the southern basin of Ayr Lake

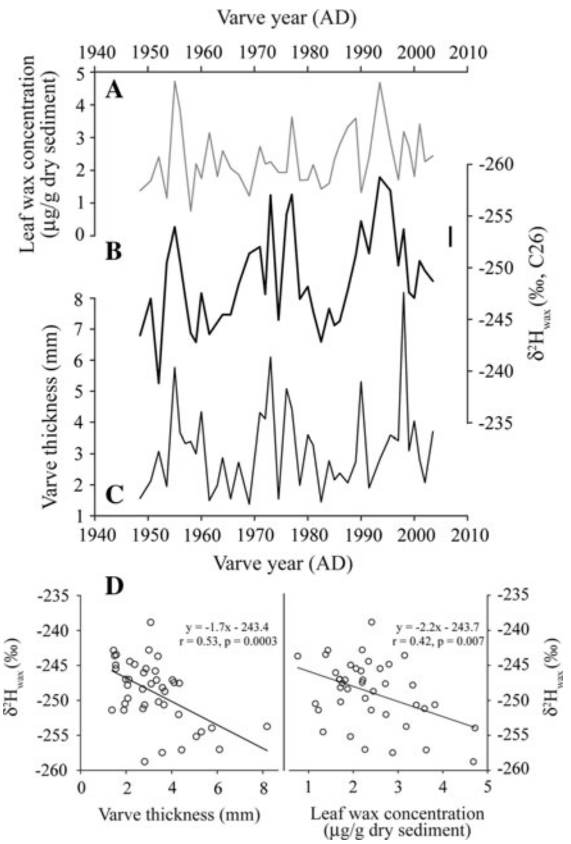

Fig. 6 Sub-decadal resolution leaf wax record from Ayr Lake for the period of overlap with the instrumental record at Clyde River. **a** C26 *n*-alkanoic acid concentration. **b** Hydrogen isotope ratio of C26 *n*-alkanoic acid; note *y*-axis is reversed. *Vertical black bar* on right is average 1σ error (±2‰) for all replicate C26 isotope analyses. **c** Ayr Lake varve thickness. **d** Scatter plots of δ^2H_{wax} versus varve thickness and leaf wax concentration

is isolated from this maritime influence by a >1,000 m-high mountain range. It is thus likely that the microclimates are different at these two sites. For example, a comparison of the 11-month temperature record at Silasiutitalik, at the head of Clyde Inlet, to the Clyde River Airport temperature record shows that growing season temperatures are approximately 3°C cooler on the coast than at the head of the fiord (Environment Canada 2011; Kangiqtugaapik (Clyde River) Weather Station Network 2011). Different local climates could conceivably result in a lack of correlation between Ayr Lake varve thickness and the Clyde River instrumental record.

Despite the lack of significant correlation with the Clyde River record, longer-term trends in Ayr Lake varve thickness resemble climate records spanning the last millennium. The thinnest varves in Ayr Lake occur from 1661 to 1829 AD. This interval corresponds to the coldest centuries of the LIA throughout the Arctic (Fig. 5; Kaufman et al. 2009). Cooler temperatures would have caused less glacial runoff and shorter ice-free periods on Ayr Lake, reducing sediment deposition, and thus resulting in thinner varves. In addition, although there is no LIA moraine chronology from the Ayr valley, glaciers were most extensive throughout Baffin Island between 1650 and 1900 AD (Davis 1985; Miller et al. 2005; Briner et al. 2009).

The isolated-sand-grain record also provides insight into the glacier and climate history of Ayr Lake. Isolated sand grains could be derived from two main processes: (1) grains that saltate across lake ice and are deposited during seasonal lake-ice melt, or (2) grains that are deposited from icebergs. Icebergs were only present in Ayr Lake during the LIA when at least one glacier was calving into the southern basin of Ayr Lake (Fig. 1). However, for icebergs to move throughout the lake, there must also be periods each year when the lake is ice free. At present, Ayr Lake is only ice free for 3 months per year, and a small temperature drop during the LIA could have resulted in a much shorter ice-free summer season. We would therefore expect ice-rafted debris to be less prevalent throughout the Ayr Lake basin during the coldest decades of the LIA, a period of maximum glacier extent but also maximum lake-ice extent and duration.

Isolated sand grains were deposited at the highest rate from 1827 to 1911 AD, immediately following the interval with the thinnest varves and at a time when Arctic temperatures started to increase (Fig. 5; Kaufman et al. 2009). Simultaneous with the increased rate of sand-grain deposition, the size of the grains increased. Furthermore, the grains in this interval are concentrated in the late summer portion of the varves, indicating that the grains likely were transported to the core site after the lake became ice free. Thus, icebergs would be the most logical mechanism for transport of sand grains to the core site during this time period. These lines of evidence indicate that the increase in isolated sand grains from 1827 to 1911 AD was likely due to post-LIA decreased lake-ice cover extent and duration, and continued calving by at least one glacier into the southern basin of Ayr Lake. The significant decrease in sand-grain deposition rate after 1911 AD was probably due to glacier retreat out of Ayr Lake. Isolated sand grains are present throughout the record, but are smaller, less abundant, and occur in the lower, coarse part of the varves, which suggests that the grains were deposited early in the ice-free season. It is likely that these grains were transported onto the lake ice by wind, which we observed in May 2009, and then were deposited in the lake sediment during seasonal lake ice melt. In summary, the varve-thickness and isolated-sand-grain records suggest that climate in the Ayr Lake catchment was coolest from 1661 to 1829 AD, and warming starting in the mid-1800s AD caused up to 1 km of glacier retreat since that time.

Leaf wax hydrogen isotopes as a paleoclimate proxy in Ayr Lake

Controls on leaf wax hydrogen isotopes

The major source of water for plants in the Arctic, where permafrost precludes extensive groundwater systems, is precipitation, either as snowmelt or summer rain (Elberling et al. 2008). Thus, we hypothesize that δ^2H_{wax} in the Arctic is likely closely related to δ^2H_{precip}. Leaf wax synthesis occurs during the summer months when plants are neither temperature- nor light-limited. The apparent fractionation (ε) between leaf waxes and source waters varies with relative humidity (RH) and with potential evapotranspiration (Sachse et al. 2012). Long-term average growing season (June, July, August) RH at Clyde River is 80% (Environment Canada, 2011). The eleven-month dataset from Silasiutitalik at the head of Clyde Inlet suggests that growing season RH is slightly lower inland, around 75% (Kangiqtugaapik (Clyde River) Weather Station Network, 2011). The *n*-alkanoic acids synthesized by plants that grow at 70–80% RH have an ε of −100 to −120‰ relative to annual mean precipitation (Hou et al. 2008). The δ^2H_{wax} values from Ayr Lake sediments (−240 to −265 ‰) therefore suggest that source water δ^2H should range between -140 to -165‰ (assuming an ε of −100‰) and −120 to −145‰ (assuming an ε of −120‰). These calculated source water δ^2H values are within the range of measured summer δ^2H_{precip} values for both Pond Inlet and Hall Beach, although the values obtained with the larger ε are close to the maximum summer δ^2H_{precip} values for Pond Inlet. We therefore hypothesize that plants in this catchment utilize summer precipitation as their main water source (Fig. 2). Variability in summer δ^2H_{precip}, or utilization of small but varying amounts of winter precipitation, is likely driving variability in δ^2H_{wax} at Ayr Lake.

Using sedimentary δ^2H_{wax} as a paleoclimate proxy is successful partly because the leaf waxes are integrated from all plant types in an entire catchment. Thus, the potential effects of differing ε among plant individuals and species are minimized. Furthermore, sedimentary leaf wax-precipitation ε is constant along modern climatic gradients in multiple settings, despite changes in plant assemblages along the same gradients (Sachse et al. 2004; Hou et al. 2008; Rao et al. 2009). Changes through time in the type of plants producing leaf waxes can, however, influence the resulting δ^2H_{wax} (Sachse et al. 2012). Grasses (Poaceae), which are all C_3 at this latitude, tend to produce leaf waxes that are more depleted in ^2H relative to source water than other C_3 plants (Hou et al. 2007; Sachse et al. 2012). Therefore, any changes in the amount of grasses in the catchment could result in a depletion of ^2H in leaf waxes. Vegetation reconstructions based on pollen assemblages can help determine whether vegetation changes are an important factor. A centennial-resolution pollen record from southeastern Baffin Island indicates that plant composition was relatively constant in the late Holocene, and importantly, Poaceae remain relatively constant at 10% (Fréchette and de Vernal 2009). Changes in δ^2H_{wax} in this record are therefore likely driven by climatic changes, not vegetation changes.

Sub-decadal resolution δ^2H_{wax}

Leaf wax hydrogen isotopes exhibit a surprising amount of variability at the sub-decadal scale (Fig. 6). This high degree of variability indicates that leaf waxes are likely produced, transported and deposited in a relatively short period of time. This is in contrast to recent studies that find that leaf waxes can be stored in soils and deposited centuries after biosynthesis (Douglas et al. 2011). We contend that the large interannual variability would be obscured if leaf waxes in Ayr Lake sediments represented the integration of decades to centuries of leaf wax production. Furthermore, δ^2H_{wax} and varve thickness are significantly anti-correlated ($r = 0.53$, $p = 0.0003$; Fig. 6). This not only supports the notion that at least the majority of leaf waxes are deposited rapidly after they are produced, but also indicates that both proxies are experiencing similar climatic influences at similar times scales. Given these limited data, it appears that leaf waxes were deposited rapidly after synthesis, which seems reasonable in the windy Ayr valley. Further studies, including radiocarbon analyses of leaf waxes in Arctic lake sediments, will help clarify the lag between leaf wax formation and deposition in this type of setting.

Thin varves in Ayr Lake correspond to leaf waxes enriched in ^{2}H. This is difficult to interpret in terms of temperature, because cooler summer temperatures generally result in thinner varves (Thomas and Briner 2009) and should also result in ^{2}H-depleted precipitation, and ^{2}H-depleted leaf waxes. One potential explanation is that thin varves and ^{2}H-enriched leaf waxes are formed during years with less snowpack. Less snowpack would result in less springtime sediment delivery to Ayr Lake, and thin varves. Less snowpack would also reduce the snowmelt available to plants for leaf wax synthesis, and plants would utilize a higher proportion of ^{2}H-enriched summer precipitation. Furthermore, less snowmelt would transport fewer leaf waxes to the lake. This may explain the significant anti-correlation between leaf wax concentrations and δ^2H_{wax} (Fig. 6). During a season with a deep snowpack, thick varves would be deposited with a higher concentration of leaf waxes, and the plants would have greater access to ^{2}H-depleted source water for leaf wax synthesis. Given an ε of -100‰ and a δ^2H_{wax} range of -240 to -265‰, snowmelt could be 0–14% or 12–35% of the total precipitation utilized by plants, using the Pond Inlet and Hall Beach δ^2H_{precip} end members, respectively. In other words, in years when δ^2H_{wax} is -240‰ and varves are thin, plants may have utilized less than 12% snowmelt for their source water; in years when δ^2H_{wax} is -265‰ and varves are thick, plants may have utilized up to 14–35% snowmelt for their source water. Other explanations involving precipitation source area changes would not influence varve thickness, unless a change in source area also resulted in a change in precipitation amount and thus sediment delivery to the lake. More investigations will be required to decipher the mechanisms that are controlling this anti-correlation. Furthermore, the anti-correlation does not exist on sub-centennial time scales, indicating that other factors likely are driving δ^2H_{wax} on longer times scales.

Sub-centennial resolution δ^2H_{wax}

On sub-centennial time scales, δ^2H_{wax} exhibits patterns similar to regional temperature change (Fig. 5). Leaf waxes are most enriched in ^{2}H during the twentieth century, which corresponds to the warmest reconstructed interval in the past 2,000 years in the Arctic (Kaufman et al. 2009 and references therein). Furthermore, leaf waxes are most depleted in ^{2}H in the early nineteenth century, which corresponds to the coolest decades across the Arctic (Kaufman et al. 2009), as well as the maximum extent of glaciers on Baffin Island (Briner et al. 2009). We acknowledge that this early-nineteenth-century ^{2}H-depleted value is a single data point, and therefore do not interpret this further. Precipitation isotopes in this region are strongly influenced by temperature (Fig. 2; Rozanski et al. 1993), so δ^2H_{wax}, which ultimately is driven by δ^2H_{precip}, is likely strongly influenced by regional temperature change. The remarkable similarity between δ^2H_{wax} and regional temperature indicates that δ^2H_{wax} is a useful proxy to reconstruct temperature at decadal- to sub-centennial-resolution.

The statistical relationship between δ^2H_{precip} and air temperature at both Pond Inlet and Hall Beach is strong, and similar between the two stations (Fig. 2b). For every 1°C change in air temperature, there is a 4.5 and 4.7‰ change in δ^2H_{precip} at Pond Inlet and Hall Beach, respectively. Thus, if we assume that temperature is the only control on δ^2H_{wax}, the 12.6‰ average increase in δ^2H_{wax} in the late twentieth century (1950–2004 AD) relative to the rest of the record (1450–1950 AD) reflects a 2.7–2.8°C temperature increase. This estimate is $\sim$2°C higher than the Kaufman et al. (2009) Arctic-wide temperature reconstruction, which indicates an increase of 0.6°C for the same time intervals. This estimate of late twentieth century temperature increase is also $\sim$1–2°C higher than other paleoclimate reconstructions for Baffin Island based on varve thickness and chironomid assemblage data, which indicate late twentieth century warming of 0.6–1.6°C (Hughen et al. 2000; Thomas et al. 2008; Thomas and Briner 2009). Thus, although δ^2H_{wax} reflects sub-centennial-scale temperature variability, direct calculation of temperature change based on δ^2H_{wax} change is likely an overestimate compared with other currently available reconstructions. This may be due to changes in the precipitation source region: a shift to source regions farther south during the twentieth century could cause an enrichment of ^{2}H in precipitation at Ayr Lake. Alternatively, the large inferred temperature increase could also be explained if plants used 5–20% less winter precipitation for their source water after 1950 AD. A shift to less winter precipitation would also decrease the mean annual δ^2H_{precip}, although this would only be reflected in δ^2H_{wax} if the plants utilize year-round precipitation. Although temperature appears to be the dominant driver of seasonal δ^2H_{precip} variability, few studies have explicitly examined sources of precipitation to Baffin Island or plant utilization of seasonal precipitation. Thus, more research in these fields will enhance our ability to interpret δ^2H_{wax} records.

The LIA interval is more distinct in the Ayr Lake varve thickness record than in either the average Arctic temperature reconstruction (Kaufman et al. 2009) or in the δ^2H_{wax} record. The dramatic shift in varve thickness could be linked to a local threshold response to temperature change, such as an increase in lake-ice extent and duration, whereas the gradual trend toward ^{2}H-depleted values could be a reflection of gradual insolation-driven cooling (Kaufman et al. 2009).

Conclusions

This late Holocene δ^2H_{wax} record from Ayr Lake is one of the first of its kind in the Arctic, and suggests that δ^2H_{wax} has promise as an Arctic paleoclimate proxy. The significant anti-correlation between δ^2H_{wax} and varve thickness, especially on sub-decadal time scales, supports our hypothesis that leaf waxes and varve thickness are both driven, at least in part, by similar catchment-scale factors. At the same time, however, the anti-correlation between varve thickness and δ^2H_{wax} is difficult to explain in terms of temperature, and further research examining source water and the timing of leaf wax production and transport will be necessary to decipher the controls on leaf wax isotopes at this time scale. On sub-centennial time scales, δ^2H_{wax} is remarkably similar to other temperature reconstructions from the Arctic, with ^{2}H-depleted values during the coldest decades of the last two millennia, and ^{2}H-enriched values during the anomalously warm twentieth century. The fact that δ^2H_{wax} reflects regional changes on these time scales is probably because is δ^2H_{wax} is ultimately controlled by δ^2H_{precip}, which in this region is driven mainly by temperature changes (Rozanski et al. 1993).

Many questions remain about δ^2H_{wax} systematics in arctic systems. Our finding that leaf wax residence time in the Ayr Lake catchment may be quite short contrasts with evidence that leaf waxes can be retained for centuries in soils before being deposited in a lake (Douglas et al. 2011), and furthermore, terrestrial carbon residence time can be high in permafrost (Wolfe et al. 2004). Efforts to radiocarbon date leaf waxes in low-latitude settings have provided some insights into the residence times and different sources and pools of leaf waxes (Douglas et al. 2011), and this approach also could be a next step for Arctic lake sediments. In addition, tracking the source water that plants use to synthesize leaf waxes, and determining whether leaf wax production rate and source water δ^2H change through the growing season is essential to deciphering past changes in δ^2H_{wax}. Finally, a denser network of climate and precipitation isotope data, including information about storm tracks and precipitation source areas, would be extremely helpful when interpreting δ^2H_{wax} records.

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