



Lakewater paleothermometry from Deep Lake, Minnesota during the deglacial–Holocene transition from combined $\delta^{18}\text{O}$ analyses of authigenic carbonate and aquatic cellulose

William M. Buhay^{a,*}, Brent B. Wolfe^b, Antje Schwalb^c

^a Department of Geography, University of Winnipeg, 515 Portage Avenue, Winnipeg, Manitoba R3B 2E9, Canada

^b Department of Geography and Environmental Studies, Wilfrid Laurier University, Waterloo, Ontario N2L 3C5, Canada

^c Institut für Umweltgeologie, Technische Universität Braunschweig, Langer Kamp 19c, D-38106 Braunschweig, Germany

ARTICLE INFO

Article history:

Available online 7 December 2011

ABSTRACT

Carbonate, cellulose, and bulk organic isotope data from varved sediments of Deep Lake (Minnesota) provide a record of paleohydrologic and paleoclimatic change during the deglacial–Holocene transition from 12,000 to 7500 cal BP. Deep Lake became enriched in ^{18}O in response to increased influence of maritime tropical moisture from the Gulf of Mexico between 12 000 and 9500 cal BP culminating in regional expansion of *Pinus* and *Quercus*, and then again as a result of increased aridity with the establishment of more zonal circulation and prairie vegetation by 8500 cal BP. Summer lake water temperatures simultaneously increased during the deglacial–Holocene transition, as suggested by decoupling of carbonate $\delta^{18}\text{O}$ and cellulose-inferred lake water $\delta^{18}\text{O}$ values between 11,000 and 9500 cal BP, and then declined briefly around 8600 cal BP, possibly in response to the cooling event associated with the final drainage of Glacial Lakes Agassiz and Ojibway into the Labrador Sea. Although the carbonate–cellulose paleothermometer generated unrealistically high values, these can readily be explained by imposing kinetic effects that occur during rapid carbonate precipitation and conservative estimates of a seasonal lag effect in the synthesis of cellulose with respect to carbonate. These new results suggest that climatic variations during the deglacial–Holocene transition in northwestern Minnesota were driven mainly by changes in large-scale atmospheric circulation and that Lake Agassiz played a comparatively minor role except during its final drainage.

© 2011 Elsevier Ltd and INQUA. All rights reserved.

1. Introduction

Carbonate materials in lake sediments have been widely utilized as oxygen isotope ($\delta^{18}\text{O}$) archives of paleohydrologic and paleoclimatic information. Their oxygen isotope compositions are influenced primarily by both lake water oxygen isotope composition and lake water temperature. The latter is controlled by the isotope composition of source waters (precipitation, surface runoff and subsurface input), modified by secondary evaporative isotopic enrichment (von Grafenstein et al., 1999; Anderson and Abbott, 2001; Wolfe et al., 2003; Leng and Marshall, 2004). Thus, changes in climate, atmospheric circulation patterns, hydrological conditions, catchment characteristics, lake water temperature and other factors can lead to changes in lake sediment carbonate $\delta^{18}\text{O}$ records and, consequently, these stratigraphic profiles may be challenging to

interpret (Yu et al., 1997; Smith and Hollander, 1999; Hammarlund et al., 2002; Anderson et al., 2005).

In some previous studies, it has been necessary to assume that water temperature remained relatively constant, allowing the carbonate $\delta^{18}\text{O}$ sediment profiles to be interpreted solely on the basis of shifting lake water oxygen isotope composition. Although valid in cases where benthic ostracodes are presumed to have calcified at relatively invariant or near constant bottom lake water temperatures (e.g., Schwalb et al., 1994; Xia et al., 1997; Hammarlund et al., 1999; von Grafenstein et al., 1996, 1999; von Grafenstein, 2002; Danis et al., 2003; Dettman et al., 2005), other studies that utilize authigenic carbonate formed in the epilimnion require assumptions regarding lake water temperature or isotopic composition that are not easily tested (Anderson et al., 1997; Yu et al., 1997; Leng et al., 2001; Hammarlund et al., 2002; Leng and Marshall, 2004; Liu et al., 2009).

In contrast, the oxygen isotope composition of aquatic cellulose is systematically enriched by about 27–28‰ compared to its ambient water independent of temperature (DeNiro and Epstein, 1981;

* Corresponding author.

E-mail address: b.buhay@uwinnipeg.ca (W.M. Buhay).

Edwards and McAndrews, 1989; Sternberg, 1989; Yakir, 1992; Sauer et al., 2001; Wolfe et al., 2001, 2007). This constant isotopic enrichment allows direct inference of lake water $\delta^{18}\text{O}$ ($\delta^{18}\text{O}_{\text{lw}}$) from measured cellulose $\delta^{18}\text{O}$ ($\delta^{18}\text{O}_{\text{cell}}$) of aquatic origin in lake sediments. Although $\delta^{18}\text{O}_{\text{lw}}$ records inferred from cellulose oxygen isotope measurements are not immune to complexities that influence lake water oxygen isotope composition, this is a paleolimnological approach that has been applied in many settings to extract paleo-hydrologic and paleoclimatic information (Wolfe et al., 2001, 2007; Buhay et al., 2009; Jonsson et al., 2010; St. Amour et al., 2010). Additionally, as recently demonstrated by Rozanski et al. (2010), the coupling of authigenic carbonate $\delta^{18}\text{O}$ and aquatic cellulose $\delta^{18}\text{O}$ represents a powerful new method for quantitative reconstruction of both paleohydrology and paleotemperature from lake sediments.

This paper combines sedimentology, new isotopic and elemental data from undifferentiated organic matter and isolated aquatic cellulose, and previously reported bulk carbonate isotope results (Hu et al., 1997, 1999) from the varved sediments of Deep Lake, Minnesota. This integration is used to refine the paleohydrology and to estimate the epilimnion paleotemperature of Deep Lake in the context of profound climate changes that occurred in central North America between 12,000 and 7500 cal BP.

Previous work by Hu et al. (1997) showed a marked ^{18}O – depletion in bulk carbonate between 10,500 and 9900 cal BP that interrupted an overall ^{18}O – enrichment trend from 12,000 to 9100 cal BP. The decrease in $\delta^{18}\text{O}$ was attributed to decreased summer temperature and increased precipitation originating from the cold and ^{18}O – depleted glacial meltwaters of Lake Agassiz, which had expanded at about this time due to ice re-advancement (Marquette) over the lake's eastern outlets (Lowell and Teller, 1994; Hostetler et al., 2000; Leverington et al., 2000; Leverington and Teller, 2003; Teller and Leverington, 2004; Teller et al., 2005; Breckenridge, 2007; Breckenridge and Johnson, 2009). However, pollen studies at

Deep Lake (Hu et al., 1997) and elsewhere in the region (Minnesota, Manitoba, northern Illinois) show that *Pinus* (Bartlein et al., 1984; Schwab and Dean, 2002; Wright et al., 2004; Teller et al., 2008; Teed et al., 2009), *Quercus* (Strong and Hills, 2005; Yansa et al., 2007; Teller et al., 2008; Gonzales and Grimm, 2009) and *Ulmus* (Yansa et al., 2007; Teller et al., 2008; Gonzales and Grimm, 2009) continued to increase during this interval at the expense of *Picea*, indicating that the inferred climatic change did not result in a reversal to *Picea*-dominated forest. The effects of glacial Lake Agassiz on regional climate in the northern Great Plains thus remain open for alternative interpretations (Bartlein and Whitlock, 1993; Hu et al., 1999; Yu and Wright, 2001; Dean et al., 2002; Schwab and Dean, 2002; Yansa and Ashworth, 2005; Henne and Hu, 2010).

2. Regional setting

Deep Lake (47.6836°N, 95.4001°W, Fig. 1) is a hydrologically closed basin with a surface area of approximately 0.04 km² and a maximum depth of 21 m. Located in northwestern Minnesota, near the current prairie-forest border and the triple-junction of diverse competing air masses (Arctic, Gulf of Mexico, Pacific), Deep Lake is ideally situated to record hydrologic and climatic changes associated with the deglacial–Holocene transition. Recovered Deep Lake sediments consist of easily identifiable varved couplets composed of light-coloured precipitated calcite alternating with dark-coloured clastic and organic debris (Hu et al., 1999).

3. Materials and methods

Sediment samples for bulk organic and cellulose elemental and isotope analyses were obtained from three overlapping cores from Deep Lake correlated by varves and from the same depth intervals as for carbonate carbon and oxygen isotope analyses where sufficient

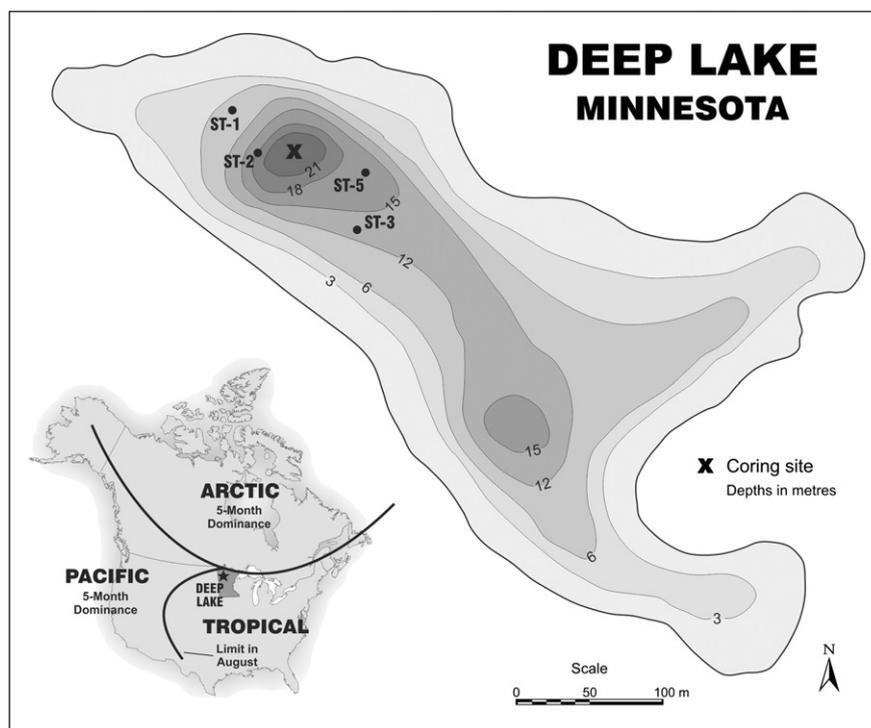


Fig. 1. Deep Lake (47.6836°N, 95.4001°W) has a maximum depth of 21 m, surface area of about 0.04 km², and is a hydrologically-closed basin. Deep Lake is strategically located near the triple-junction of competing cold, dry air from the Arctic, warm, moist air from the Gulf of Mexico, and mild, dry air from the Pacific which contribute to strong seasonality and variation in the isotopic composition of precipitation (Bryson and Hare, 1974; Simpkins, 1995). The X symbol indicates the location of the sediment core (Hu et al., 1999). The four recovered sediment trap (ST-1, ST-2, ST-3, ST-5) locations are also indicated.

sediment was available (Hu et al., 1997, 1999). In May 2009, sediment traps were deployed at five sites (Fig. 1) to collect settling material at 5–6 m water depth. Four of the traps were later recovered in September 2009. These samples were also subjected to elemental analysis as well as carbonate and cellulose carbon and oxygen isotope analyses. Epilimnion temperatures were measured in Deep Lake weekly from May to August, 2009, using a YSI metre. Water samples were also collected in May 2009 at the four sediment trap sites (1 m depth).

All samples were treated with 10% HCl to remove carbonate material, rinsed repeatedly with distilled water, and oven-dried (>40 °C). Following the carbonate removal and drying, the sediment samples were sieved (<500 µm) to eliminate macrofossil plant debris of possible terrestrial origin. Organic carbon and nitrogen elemental content and carbon isotope composition were determined on the fine-grained fraction at the University of Winnipeg Isotope Laboratory (UWIL) using an elemental analyzer (EuroVector EA) attached to a continuous-flow isotope-ratio mass spectrometer (Elementar Americas IsoPrime). Additional sample treatment involved solvent extraction, bleaching and alkaline hydrolysis to remove non-cellulose organic constituents, oxyhydroxide leaching to remove possible inorganic oxygen sources, and sodium polytungstate heavy liquid separation to isolate the sediment cellulose from remaining minerogenic material (Wolfe et al., 2001, 2007). The carbon and oxygen isotope composition of cellulose was analyzed using the UWIL Elementar Americas IsoPrime. Subsamples of the material collected in the four recovered sediment traps were sent to the Saskatchewan Isotope Laboratory (SIL) for bulk carbonate carbon and oxygen isotope analyses. Carbonate carbon and oxygen isotope compositions were determined on the trap sediments using a Kiel

Carbonate Device coupled with a Thermo Scientific MAT 253. The four water samples were also sent to SIL and analyzed using a Picarro L1102i Isotopic Liquid Water Analyzer.

Isotope results are expressed as “ δ ” values, which represent deviations in per mil (‰) from the VPDB standard for carbon and carbonate oxygen and the VSMOW standard for cellulose oxygen such that $\delta_{\text{sample}} = [(R_{\text{sample}}/R_{\text{standard}}) - 1] \times 10^3$ where R is the $^{13}\text{C}/^{12}\text{C}$ or $^{18}\text{O}/^{16}\text{O}$ ratio in the sample and standard. Results of $\delta^{18}\text{O}$ analyses are normalized to -55.5‰ for Standard Light Antarctic Precipitation (SLAP; see Coplen, 1996). The $\delta^{13}\text{C}_{\text{org/cell}}$ and $\delta^{18}\text{O}_{\text{cell}}$ values have analytical uncertainties of $\pm 0.1\text{‰}$ and $\pm 0.2\text{‰}$, respectively (based upon a standard:sample ratio of 1:3; duplicate and triplicate sample repeats were run on every 5th and 10th samples, respectively). Sediment trap $\delta^{18}\text{O}_{\text{carb}}$ values have an analytical uncertainty of $\pm 0.11\text{‰}$. The water sample oxygen isotope values have an analytical uncertainty of $\pm 0.1\text{‰}$.

4. Results and discussion

4.1. Sedimentology

Deep Lake sediments deposited from 12,000 to 7500 cal BP consist of six discrete units (Fig. 2a). Siliclastic-dominated couplets deposited before about 11,000 cal BP are composed of light-coloured carbonate laminations with few diatoms, and dark-coloured organic laminations. Carbonate-dominated couplets deposited between 11,000 and 9500 cal BP and from 8900 to 8300 cal BP are characterized by light-coloured laminations containing micritic calcite, suggesting a mainly authigenic origin, and abundant diatoms. Dark-coloured laminations consist of diatoms and organic material. The

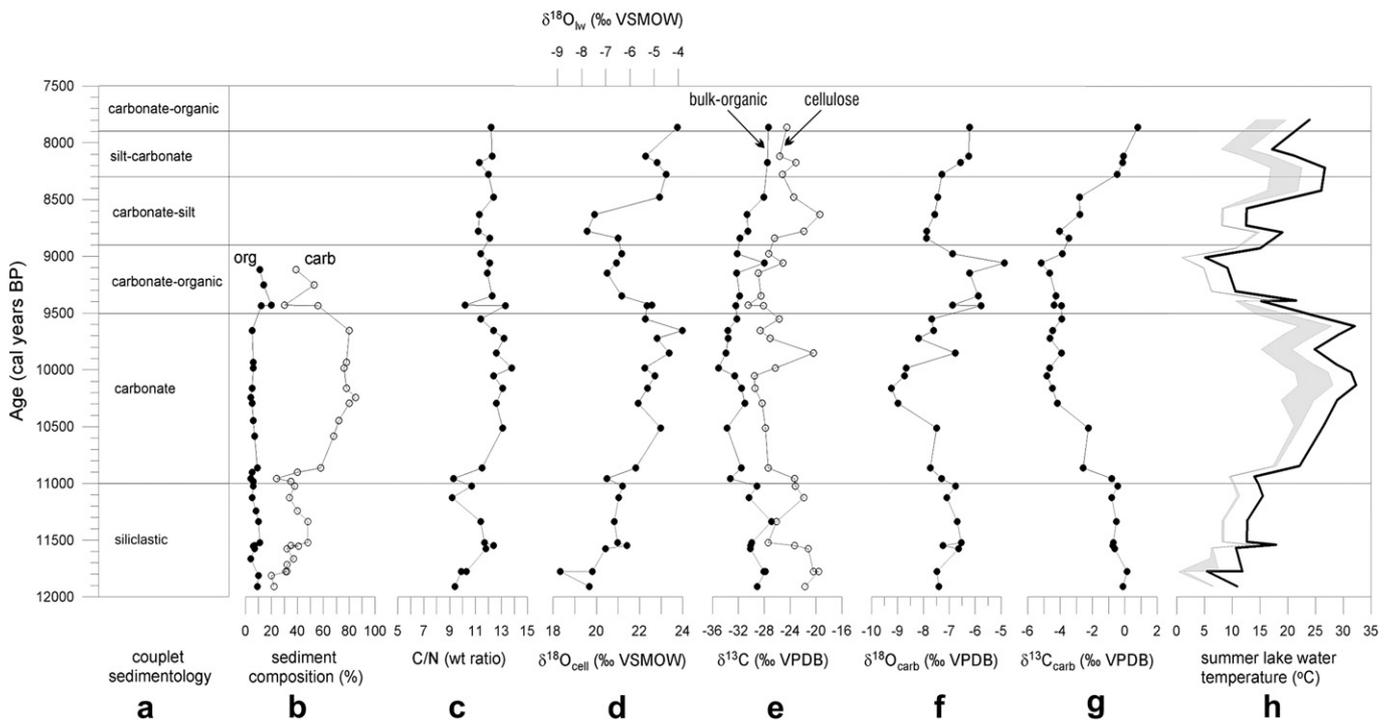


Fig. 2. Stratigraphic information and profiles for Deep Lake: a) couplet sedimentology, b) sediment composition, c) C/N weight ratio, d) cellulose $\delta^{18}\text{O}$ and cellulose-inferred lake water $\delta^{18}\text{O}$, e) bulk organic (solid circles) and cellulose (hollow circles) $\delta^{13}\text{C}$, f) carbonate $\delta^{18}\text{O}$ (from Hu et al., 1997, 1999), g) carbonate $\delta^{13}\text{C}$ (from Hu et al., 1997, 1999), and h) reconstructed summer lake epilimnion water temperature calculated from the calcite–water equilibrium equation [t (°C) = $13.8 - 4.58(\delta^{18}\text{O}_{\text{carb}} - \delta^{18}\text{O}_{\text{lw}}) + 0.08(\delta^{18}\text{O}_{\text{carb}} - \delta^{18}\text{O}_{\text{lw}})^2$] (Kim and O’Neil, 1997; black line) and data from d) and f). The shaded area in h) represents the range between the temperatures calculated assuming the average kinetic effect (3.8 °C) determined in Table 1 to account for rapid calcite precipitation (right of the shading) and those assuming carbonate–cellulose seasonal lag enrichments (left of the shading; see text). The Deep Lake varved sediment chronology is from Hu et al. (1997, 1999). It was anchored on a wood fragment calibrated AMS ^{14}C date of 8090 ± 0.085 ka (calibrated 8986 cal BP) and extended to 11,522 ka by varve counts. The chronology for the non-varved section was linearly interpolated between 11,522 and 12,610 ka (based on a *Picea* needle AMS ^{14}C date of $10,700 \pm 0.107$ ka).

carbonate content between 11,000 and 9500 cal BP, as determined by loss-on-ignition, increases from 20 to 40 per cent (Hu et al., 1997) to over 80 per cent (Fig. 2b). Between 9500 and 8900 cal BP, carbonate couplets are distinguished by a higher organic content (15–25%) compared to the couplets deposited prior to this interval (5–15%) and carbonate content decreases to 40–60 per cent (Fig. 2b). Couplets deposited between 8300 and 7900 cal BP consist of silt, carbonate with diatoms, and organic sediment with diatoms. After 7900 cal BP, couplets contain mainly laminations of light-coloured micritic carbonate with abundant diatoms and dark-coloured organic sediment.

4.2. Paleohydrologic reconstruction

As indicated by the low and constant C/N weight ratios for the sediment core samples (mean C/N = 9.7 ± 1.2 ; Fig. 2c) and the four sediment trap samples (mean C/N = 11.7 ± 0.8), the fine-grained organic fraction is autochthonous in origin (Meyers and Lallier-Vergès, 1999; Meyers, 2003; Das et al., 2008; Yamaguchi et al., 2010) supporting a direct calculation of lake water $\delta^{18}\text{O}$ ($\delta^{18}\text{O}_{\text{lw}}$) from cellulose $\delta^{18}\text{O}$ ($\delta^{18}\text{O}_{\text{cell}}$) (Fig. 2d; $\delta^{18}\text{O}_{\text{lw}} = 0.973 \delta^{18}\text{O}_{\text{cell}} - 27.2$, Rozanski et al., 2010). Interpretation of $\delta^{18}\text{O}_{\text{lw}}$ records requires differentiation of the isotopic composition of source water, reflecting the integrated signature of surface and subsurface inflow and precipitation, from hydrologic factors (i.e., mainly evaporative isotopic enrichment) that may subsequently modify the isotopic content of the lake water. Changing atmospheric circulation and moisture conditions during the deglacial–Holocene transition in this region have resulted in shifting precipitation $\delta^{18}\text{O}$ and evaporative ^{18}O -enrichment, both of which are manifested in the cellulose-inferred $\delta^{18}\text{O}_{\text{lw}}$ record. At nearby Pickerel Lake, South Dakota, ostracode $\delta^{18}\text{O}$ values during the deglacial–Holocene transition are higher compared to mid- and late Holocene values and are attributed to increased summer insolation and stronger summer monsoons carrying ^{18}O -enriched moisture from the Gulf of Mexico (Schwalb and Dean, 1998; Liu et al., 2003). Lake water ^{18}O -enrichment between 10,500 and 9500 cal BP (Fig. 2d) at the more northerly located Deep Lake is consistent with this interpretation and likely reflects maximum influence of Gulf-derived moisture. Evidence for increasingly warm and moist conditions developing between 12,000 and 9500 cal BP in the Deep Lake region are also provided by 1) the general decline in *Picea* beginning at 11,500 cal BP and brief increase in *Pinus* and *Quercus* pollen between 10,000 and 9500 cal BP (see Hu et al., 1997; Strong and Hills, 2005) and 2) bulk organic, cellulose and carbonate $\delta^{13}\text{C}$ trends to lower values likely indicating increasing influx of soil-derived ^{13}C -depleted dissolved inorganic carbon (DIC) (Fig. 2e, g).

Pinus pollen percentages decline markedly between 9600 and 9200 cal BP at the expense of herbaceous taxa (Hu et al., 1997, 1999; Wright et al., 2004) due to increased aridity related to a shift to more zonal atmospheric circulation (Bradbury et al., 1993; Hu et al., 1999; Yu and Wright, 2001; Dean et al., 2002) and a shift in precipitation seasonality (Henderson et al., 2010). In central Iowa, weighted mean values of modern precipitation $\delta^{18}\text{O}$ derived from a Gulf-Pacific source are 2–3‰ lower than moisture that originates exclusively over the Gulf of Mexico (Simpkins, 1995). Thus, reduced maritime influence from the Gulf of Mexico combined with greater moisture contribution from air masses derived from the Pacific following the *Pinus* maximum (10,000–9500 cal BP) may have led to more ^{18}O -depleted precipitation in the Deep Lake region and lower $\delta^{18}\text{O}_{\text{lw}}$ values between 9500 and 8600 cal BP. Alternatively, intrusions of dry, dense air from the west may have caused moist Gulf air to condense at higher altitudes, which would also lead to isotopic depletion in precipitation (Hu et al., 1999; Smith and Hollander, 1999). Therefore, lake water ^{18}O -enrichment after 8500 cal BP is attributed mainly to

a decline in regional effective moisture and an increase in regional temperature and lake water evaporation (Henderson et al., 2010). Drier conditions after 8500 cal BP are also consistent with ^{13}C -enrichment in the bulk organic matter, cellulose and carbonate (Fig. 2e and g), likely reflecting reduced influx of soil-derived ^{13}C -depleted DIC and productivity-driven ^{13}C -enrichment in the lakewater DIC.

4.3. Paleotemperature reconstruction

Comparison of cellulose-inferred $\delta^{18}\text{O}_{\text{lw}}$ (Fig. 2d) to $\delta^{18}\text{O}_{\text{carb}}$ (Fig. 2f) shows generally similar trends prior to 11,000 and after 9000 cal BP suggesting that $\delta^{18}\text{O}_{\text{carb}}$ may be largely controlled by changes in the oxygen isotope composition of the lake water, as initially proposed by Hu et al. (1997). However, a clear departure in these records occurs during the 11,000 to 9000 cal BP interval. In Fig. 2f, $\delta^{18}\text{O}_{\text{carb}}$ decreases by nearly 3‰ from 11,000 to 10,000 and then increases by almost 5‰ from 10,000 to 9000 cal BP. In Fig. 2d, however, cellulose-inferred $\delta^{18}\text{O}_{\text{lw}}$ increases by about 3‰ from 11,000 to 10,000 and then decreases by about 3‰ from 10,000 to 9000 cal BP. As noted above, Hu et al. (1997) interpreted the decreasing trend in the $\delta^{18}\text{O}_{\text{carb}}$ record between 11,000 to 10,000 cal BP to be mainly a result of increased precipitation derived from isotopically-depleted Lake Agassiz and decreased summer temperature. The cellulose-inferred $\delta^{18}\text{O}_{\text{lw}}$ reconstruction for Deep Lake is inconsistent with this interpretation as are isotopic analyses on ostracodes from the sediments of Pickerel Lake, which also display relatively ^{18}O -enriched values during this interval, and instead suggest that moisture was primarily derived from enhanced delivery of warm ^{18}O -enriched air masses forming over the Gulf of Mexico (Schwalb and Dean, 1998). Further, a simulation of the influence of Lake Agassiz on atmospheric circulation suggests substantially reduced precipitation in the vicinity of Deep Lake at 11,000 cal BP (Hostetler et al., 2000). An alternative explanation for the decreasing $\delta^{18}\text{O}_{\text{carb}}$ trend between 11,000 and 10,000 cal BP is an increase in summer lake water temperature (SLWT), which resulted in lower $\delta^{18}\text{O}_{\text{carb}}$ values due to reduced equilibrium isotope fractionation but did not impart an isotope effect on cellulose $\delta^{18}\text{O}$ because of the apparent insensitivity of cellulose-water oxygen isotope fractionation to temperature.

Quantitative reconstruction of SLWT from paired $\delta^{18}\text{O}_{\text{carb}}$ and cellulose-inferred $\delta^{18}\text{O}_{\text{lw}}$ samples using the calcite–water equilibrium equation (Kim and O’Neil, 1997) results in a wide range of values between 5 and 32 °C (± 5 °C) with an increase in SLWT during the deglacial–Holocene transition at roughly 11,000 cal BP (Fig. 2h). Reduced $\text{CO}_{2(\text{aq})}$ solubility due to warmer surface water temperatures in summer, perhaps enhanced by prolongation of the ice-free period, may partly account for the two-fold increase in carbonate content to over 80% between 11,000 and 9500 cal BP (Fig. 2b). An increase in carbonate content can also be observed in sediments from nearby Williams Lake (Schwalb et al., 1995) and Pickerel Lake (Schwalb and Dean, 1998) deposited around this time interval. An increase in SLWT during the deglacial–Holocene transition is also consistent with previously reported vegetation changes in the region (Bartlein et al., 1984; Hu et al., 1997; Strong and Hills, 2005) and coherent with simulated increases in regional temperatures during this time (Hostetler et al., 2000). Brief cooling occurred at 8700–8500 cal BP, which may be associated with the final drainage of glacial lakes Agassiz and Ojibway into the Labrador Sea (Hu et al., 1999; Teller et al., 2002). Given the uncertainties in the absolute sediment chronology, this short-lived cooling may relate to the widely reported 8200 cal BP cold event (Dean et al., 2002; Clarke et al., 2004, 2009; Hillaire-Marcel et al., 2007; Roy et al., 2011).

Table 1

Oxygen isotope data from four recovered sediment traps, and water, in Deep Lake, and calculated epilimnion temperatures from summer 2009. Epilimnion lake water oxygen isotope compositions ($\delta^{18}\text{O}_{\text{lw}}$) were calculated using $\delta^{18}\text{O}_{\text{lw}} = 0.973 \delta^{18}\text{O}_{\text{cell}} - 27.2$ (Rozanski et al., 2010). Epilimnion water temperature was calculated using the calcite–water equilibrium equation [t ($^{\circ}\text{C}$) = $13.8 - 4.58 (\delta^{18}\text{O}_{\text{carb}} - \delta^{18}\text{O}_{\text{lw}}) + 0.08 (\delta^{18}\text{O}_{\text{carb}} - \delta^{18}\text{O}_{\text{lw}})^2$] (Kim and O'Neil, 1997). Average calculated epilimnion temperature (15.7°C) is 3.8°C higher than the average measured epilimnion temperature (11.9°C), possibly due to kinetic effects associated with rapid calcite precipitation. Calculations also illustrate that close agreement between average calculated epilimnion temperature and average measured epilimnion temperature can readily be achieved by assuming that cellulose formed in lake water that was 1‰ higher than the lake water at the time of carbonate precipitation (see text).

Sample	$\delta^{18}\text{O}_{\text{carb}}$ (% VPDB)	$\delta^{18}\text{O}_{\text{cell}}$ (% VSMOW)	Cell-inferred $\delta^{18}\text{O}_{\text{lw}}$ (% VSMOW)	Measured $\delta^{18}\text{O}_{\text{lw}}$ (% VSMOW)	Epilimnion T measured ($^{\circ}\text{C}$)	Epilimnion T calculated ($^{\circ}\text{C}$)	Epilimnion T lag 1% ($^{\circ}\text{C}$)
ST-1	-4.5	23.7	-4.1	-8.4	12.9	15.5	10.9
ST-2	-5.3	23.4	-4.4	-8.5	11.4	17.8	13.2
ST-3	-4.9	22.9	-4.9	-7.9	11.9	13.8	9.3
ST-5	-5.6	22.6	-5.2	-7.4	11.5	15.6	11
Ave	-5.1	23.2	-4.7	-8.1	11.9	15.7	11.1

While the trends in reconstructed SLWT during the deglacial–Holocene transition are consistent with Deep Lake varve sedimentology, regional vegetation changes, other stratigraphic records and climate models, values higher than $\sim 25^{\circ}\text{C}$ are likely unrealistic given the average measured epilimnion lake water temperature during summer 2009 was 11.9°C . There are two possible explanations for the high SLWT values calculated using the carbonate–cellulose oxygen isotope paleothermometer. Rozanski et al. (2010) also encountered unrealistically high estimates of epilimnion temperatures for Lake Gosciuz, Poland, using the same approach. Results from modern process studies were used to suggest that kinetic-isotope depletion during rapid calcite precipitation led to average calculated epilimnion temperatures that were 4.2°C higher than average measured epilimnion temperatures. Based on the sediment trap data, the average calculated epilimnion temperatures are 3.8°C higher than the average measured epilimnion temperature (Table 1) – a result in close agreement with Rozanski et al. (2010).

The high SLWT values may also be due to a seasonal offset in the deposition of aquatic cellulose (autumn) compared to precipitation of authigenic carbonate (mid-late summer). While the sediment traps deployed in Deep Lake were not seasonally monitored, sediment trap studies at nearby Elk Lake indicate major algal production occurs during the spring and autumn when lake overturn results in nutrient replenishment (Nuhfer et al., 1993). The autumn and winter microlaminae of the varved deposits of Elk Lake, which are largely composed of organic matter, however tend to be more prominent than the spring overturn deposit which may even be missing in some years due to abrupt warming and stratification (Nuhfer et al., 1993). During the deglacial–Holocene transition, increased summer insolation may have further inhibited the formation of a spring overturn deposit, which may partly explain why the oldest varves at Elk Lake spanning 10,300 to 8300 cal BP are characterized by almost pure summer–winter microlaminae. A similar sequence of sedimentation at Deep Lake would lead to calculation of elevated SLWT because cellulose-inferred $\delta^{18}\text{O}_{\text{lw}}$ values would reflect additional ^{18}O -enrichment due to both isotopically-enriched rainfall and lake water evaporation captured in autumn aquatic production following mid-late summer carbonate precipitation. This seasonal offset may have been especially pronounced between 10,500 and 9500 cal BP due to maximum summer monsoonal activity, and after 8500 cal BP as a result of increased aridity. For example, lower and more reasonable SLWT values can readily be generated by employing a cellulose–carbonate lag enrichment of only 1‰ prior to 10,500 and between 9500 and 8500 cal BP, and 2‰ between 10,500 and 9500 and after 8500 cal BP, in accordance with the proposed greater seasonal isotopic offset in lake water composition during these latter two intervals (Fig. 2h).

Results from contemporary lake water $\delta^{18}\text{O}$ measurements of Deep Lake, and sediment trap cellulose and carbonate $\delta^{18}\text{O}$ analyses, provide additional support for a seasonal lag effect in the formation of

cellulose compared to carbonate. Cellulose-inferred lake water $\delta^{18}\text{O}$ values from the sediment traps are, on average, $\sim 3.4\text{‰}$ higher than the May 2009 lake water $\delta^{18}\text{O}$ measurements (Table 1). This indicates that cellulose production occurs later in the season, following an increase in lake water oxygen isotope composition due to evaporative isotopic enrichment and/or input of isotopically-enriched rainfall. Notably, imposing a lag ^{18}O -enrichment of only 1‰ on the Deep Lake sediment trap cellulose $\delta^{18}\text{O}$ data (i.e., assume sediment trap cellulose formed in lake water 1‰ higher than that of the sediment trap carbonate) generates close agreement between the average calculated epilimnion temperature (11.1°C) and the average measured epilimnion temperature (11.9°C ; Table 1). Thus, the lake water oxygen isotope composition that was contemporaneous with the precipitation of carbonate likely falls between the measured May 2009 lake water $\delta^{18}\text{O}$ values and the values inferred from the sediment trap cellulose $\delta^{18}\text{O}$ analyses. Further assessment of possible mechanisms to explain the SLWT results would require more intensive sampling to obtain seasonal carbonate, cellulose and lake water $\delta^{18}\text{O}$ data.

5. Conclusions

The paleohydrologic and paleotemperature record derived from multiple isotopic archives extracted from the varved sediments of Deep Lake, Minnesota, can be reconciled within the pre-existing framework of large-scale atmospheric circulation changes and resulting vegetation development during the deglacial–Holocene transition. The reconstructions suggest that glacial Lake Agassiz played a less important role in regional climate than previously thought, although the lake appears to possibly have had some impact during its final drainage (Bradbury et al., 1993; Hu et al., 1997, 1999; Dean et al., 2002). Overall, these isotopic records are consistent with an increase in maritime tropical moisture from the Gulf of Mexico and warming between 12,000 and 9500 cal BP. This was followed by a brief period of cooling, tentatively linked to the drainage of glacial lakes Agassiz and Ojibway, and a subsequent increase in temperature and aridity with the establishment of more zonal circulation by 8500 cal BP. The findings, like those of Rozanski et al. (2010), also highlight the strong potential for generating quantitative paleotemperature reconstructions from coupled $\delta^{18}\text{O}$ measurements of authigenic carbonate and aquatic cellulose in lake sediment records.

Acknowledgements

The authors wish to thank Weldon Hiebert for the professional location map and Sandra Timsic (University of Saskatchewan) for arranging the carbonate and water isotopic analyses. The authors also wish to thank two anonymous reviewers and the QI editors for their useful comments and suggestions which significantly improved the

paper. Finally, thank you Jim Teller for all your inspirational research on Lake Agassiz.

References

- Anderson, L., Abbott, M.B., 2001. Holocene climate inferred from oxygen isotope ratios in lake sediments, Central Brooks Range, Alaska. *Quaternary Research* 55, 313–321.
- Anderson, L., Abbott, M.B., Finney, B.P., Burns, B.P., 2005. Regional atmospheric circulation change in the North Pacific during the Holocene inferred from lacustrine carbonate oxygen isotopes, Yukon Territory, Canada. *Quaternary Research* 64, 21–35.
- Anderson, W.T., Mullins, T., Ito, E., 1997. Stable isotope record from Seneca Lake, New York: evidence for a cold paleoclimate following the Younger Dryas. *Geology* 25, 127–130.
- Bartlein, P.J., Webb III, T., Fleri, T., 1984. Holocene climate change in the northern Midwest: pollen derived estimates. *Quaternary Research* 22, 361–374.
- Bartlein, P.J., Whitlock, C., 1993. Paleoclimatic interpretation of the Elk Lake pollen record. In: Bradbury, J.P., Dean, W.E. (Eds.), *Elk Lake, Minnesota: Evidence for Rapid Climate Change in the North-central United States*. Geological Society of America Special Paper, vol. 276, pp. 275–293.
- Bradbury, J.P., Dean, W.E., Anderson, R.Y., 1993. Holocene climatic and limnology history of the north-central United States as recorded in the varved sediments of Elk Lake, Minnesota. In: Bradbury, J.P., Dean, W.E. (Eds.), *Elk Lake, Minnesota: Evidence for Rapid Climate Change in the North-central United States*. Geological Society of America Special Paper, vol. 276, pp. 309–328.
- Breckenridge, A., 2007. The Lake Superior varve stratigraphy and implications for eastern Lake Agassiz outflow from 10,700 to 8900 cal ybp (9.5–8.0 ^{14}C ka). *Palaeogeography, Palaeoclimatology, Palaeoecology* 246, 45–61.
- Breckenridge, A., Johnson, T., 2009. Paleohydrology of the upper Laurentian Great Lakes from the late glacial to early Holocene. *Quaternary Research* 71, 397–408.
- Bryson, R.A., Hare, R.K., 1974. The climate of North America. In: Bryson, R.A., Hare, R.K. (Eds.), *Climates of North America*. Elsevier, New York, pp. 1–47.
- Buhay, W.M., Simpson, S., Thorleifson, H., Lewis, M., King, J., Telka, A., Wilkinson, P., Babb, J., Timsic, S., Bailey, D., 2009. A 1000-year record of dry conditions in the eastern Canadian prairies reconstructed from oxygen and carbon isotope measurements on Lake Winnipeg sediment organics. *Journal of Quaternary Science* 24, 426–436.
- Clarke, G.K., Leverington, D.W., Teller, J.T., Dyke, A.S., 2004. Paleohydrology of the last outburst flood from glacial Lake Agassiz and the 8200 BP cold event. *Quaternary Science Reviews* 23, 389–407.
- Clarke, G.K., Bush, A.B.G., Bush, J.W.M., 2009. Freshwater discharge, sediment transport, and modeled climate impacts of the final drainage of Glacial Lake Agassiz. *Journal of Climate* 22, 2161–2180.
- Coplen, T.B., 1996. New guidelines for reporting stable hydrogen, carbon, and oxygen isotope-ratio data. *Geochimica et Cosmochimica Acta* 60, 3359–3360.
- Danis, P.A., von Grafenstein, U., Masson-Delmotte, V., 2003. Sensitivity of deep lake temperature to past and future climatic changes: a modeling study for Lac d'Annecy, France, and Ammersee, Germany. *Journal of Geophysical Research* 108 (D19), 4609–4621.
- Das, S.K., Routh, J., Roychoudhury, A.N., Val Klumo, J., 2008. Elemental (C, N, H and P) and stable isotope ($\delta^{15}\text{N}$ and $\delta^{13}\text{C}$) signatures in sediments from Zeekoevlei South Africa: a record of human intervention in the lake. *Journal of Paleolimnology* 39, 349–360.
- Dean, W.E., Forester, R.M., Bradbury, J.P., 2002. Early Holocene change in atmospheric circulation in the Northern Great Plains: an upstream view of the 8.2 ka cold event. *Quaternary Science Reviews* 21, 1763–1775.
- DeNiro, M.J., Epstein, S., 1981. Isotopic composition of cellulose from aquatic organisms. *Geochimica et Cosmochimica Acta* 42, 495–506.
- Dettman, D., Palacios-Fest, M., Nkotagu, H., Cohen, A., 2005. Paleolimnological investigations of anthropogenic environmental change in Lake Tanganyika: VII. Carbonate isotope geochemistry as a record of riverine runoff. *Journal of Paleolimnology* 34, 93–105.
- Edwards, T.W.D., McAndrews, J.H., 1989. Paleohydrology of a Canadian Shield lake inferred from ^{18}O in sediment cellulose. *Canadian Journal of Earth Sciences* 26, 1850–1859.
- Gonzales, L.M., Grimm, E.C., 2009. Synchronization of late-glacial vegetation changes at Crystal Lake, Illinois, USA with the North Atlantic Event Stratigraphy. *Quaternary Research* 72, 234–245.
- Hammarlund, D., Barnekow, L., Birks, H.J.B., Buchardt, B., Edwards, T.W.D., 2002. Holocene changes in atmospheric circulation recorded in the oxygen-isotope stratigraphy of lacustrine carbonates from northern Sweden. *Holocene* 12, 339–351.
- Hammarlund, D., Edwards, T.W.D., Björck, S., Buchardt, B., Wohlfarth, B., 1999. Climate and environment during the Younger Dryas (GS-1) as reflected by composite stable isotope records of lacustrine carbonates at Torreberga, southern Sweden. *Journal of Quaternary Science* 14, 17–28.
- Henderson, A.K., Nelson, D.M., Hu, F.S., Huang, Y., Shuman, B.N., Williams, J.W., 2010. Holocene precipitation seasonality captured by a dual hydrogen and oxygen isotope approach at Steel Lake, Minnesota. *Earth and Planetary Science Letters* 300, 205–214.
- Henne, P.D., Hu, F.S., 2010. Holocene climatic change and the development of the lake-effect snowbelt in Michigan, USA. *Quaternary Science Reviews* 29, 940–951.
- Hillaire-Marcel, C., de Vernal, A., Piper, D.J.W., 2007. Lake Agassiz Final drainage event in the northwest North Atlantic. *Geophysical Research Letters* 34, L15601.
- Hostetler, S.W., Bartlein, P.J., Clark, P.U., Small, E.E., Solomon, A.M., 2000. Simulated interactions of postglacial Lake Agassiz with the Laurentide Ice Sheet, 11 000 years ago. *Nature* 405, 334–337.
- Hu, F.S., Wright Jr., H.E., Ito, E., Lease, K., 1997. Climatic effects of glacial Lake Agassiz in the midwestern United States during the last deglaciation. *Geology* 25, 207–210.
- Hu, F.S., Slawinski, D., Wright Jr., H.E., Ito, E., Johnson, R.G., Kelts, K., McEwan, R.F., Boedigheimer, A., 1999. Abrupt changes in North American climate during early Holocene times. *Nature* 400, 437–440.
- Jonsson, C.E., Anderson, S., Rosqvist, G.C., Leng, M., 2010. Reconstructing past atmospheric circulation changes using oxygen isotopes in lake sediments from Sweden. *Climate of the Past* 6, 49–62.
- Kim, S.T., O'Neil, J.R., 1997. Equilibrium and non-equilibrium oxygen isotope effects in synthetic carbonates. *Geochimica et Cosmochimica Acta* 61, 3461–3475.
- Leng, M., Bernker, P., Greenwood, P., Roberts, R., Reed, J., 2001. Oxygen isotope analysis of diatom silica and authigenic calcite from Lake Pinarbasi, Turkey. *Journal of Paleolimnology* 25, 343–349.
- Leng, M., Marshall, J., 2004. Paleoclimate interpretation of stable isotope data from lake sediment archives. *Quaternary Science Reviews* 23, 811–831.
- Leverington, D.W., Mann, J.D., Teller, J.T., 2000. Changes in the bathymetry and volume of glacial Lake Agassiz between 11000 and 9300 ^{14}C yr BP. *Quaternary Research* 54, 174–181.
- Leverington, D.W., Teller, J.T., 2003. Paleotopographic reconstructions of the eastern outlets of Glacial Lake Agassiz. *Canadian Journal of Earth Science* 40, 1259–1278.
- Liu, W., Li, X., Zhang, L., An, Z., Xu, L., 2009. Evaluation of oxygen isotopes in carbonate as an indicator of lake evolution in arid areas: the modern Qinghai Lake, Qinghai-Tibet Plateau. *Chemical Geology* 268, 126–136.
- Liu, Z., Otto-Bliesner, B., Kutzbach, J., Li, L., Shields, C., 2003. Coupled climate simulation of the evolution of global monsoons in the Holocene. *Journal of Climate* 16, 2472–2490.
- Lowell, T.V., Teller, J.T., 1994. Radiocarbon vs. calendar ages of major lateglacial hydrological events in North America. *Quaternary Science Reviews* 13, 801–803.
- Meyers, P.A., 2003. Applications of organic geochemistry of paleolimnological reconstructions: a summary of examples from the Laurentian Great Lakes. *Organic Geochemistry* 34, 261–289.
- Meyers, P.A., Lallier-Vergès, R., 1999. Lacustrine sedimentary organic matter records of late Quaternary paleoclimates. *Journal of Paleolimnology* 21, 345–372.
- Nuhfer, E.B., Anderson, R., Bradbury, J.P., Dean, W.E., 1993. Modern sedimentation in Elk Lake, Clearwater County, Minnesota. In: Bradbury, J.P., Dean, W.E. (Eds.), *Elk Lake, Minnesota: Evidence for Rapid Climate Change in the North-central United States*. Geological Society of America Special Paper, vol. 276, pp. 75–96.
- Roy, M., Dell'Oste, F., Veillette, A., de Vernal, J., Hélie, J.-F., Parent, M., 2011. Insights on the events surrounding the final drainage of Lake Ojibway based on James Bay stratigraphic sequences. *Quaternary Science Reviews* 30, 682–692.
- Rozanski, R., Klisch, M.A., Wachniew, R., Gorczyca, Z., Goslar, T., Edwards, T.W.D., Shemesh, A., 2010. Oxygen-isotope geothermometers in lacustrine sediments: new insights through combined $\delta^{18}\text{O}$ analyses of aquatic cellulose, authigenic calcite and biogenic silica in lake Goszcz, central Poland. *Geochimica et Cosmochimica Acta* 74, 2957–2969.
- St. Amour, N.A., Hammarlund, D., Edwards, T.W.D., Wolfe, B.B., 2010. New insights into Holocene atmospheric circulation dynamics in central Scandinavia inferred from oxygen-isotope records of lake-sediment cellulose. *Boreas* 39, 770–782.
- Sauer, P.E., Miller, G.H., Overpeck, J.T., 2001. Oxygen isotope ratios of organic matter in arctic lakes as a paleoclimate proxy: field and laboratory investigations. *Journal of Paleolimnology* 25, 43–64.
- Schwalb, A., Locke, S.M., Dean, W.E., 1995. Ostracode $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ evidence of Holocene environmental changes in the sediments of two Minnesota lakes. *Journal of Paleolimnology* 14, 281–296.
- Schwalb, A., Dean, W.E., 1998. Stable isotopes and sediments from Pickerel Lake, South Dakota, USA: a 12ky record of environmental changes. *Journal of Paleolimnology* 20, 15–30.
- Schwalb, A., Dean, W.E., 2002. Reconstruction of hydrological changes and response to effective moisture variations from North Central USA lake sediments. *Quaternary Science Reviews* 21, 1541–1554.
- Schwalb, A., Lister, G.S., Kelts, K., 1994. Ostracode carbonate $\delta^{18}\text{O}$ - and $\delta^{13}\text{C}$ -signatures of hydrological and climate changes affecting Lake Neuchâtel, Switzerland, since the latest Pleistocene. *Journal of Paleolimnology* 11, 3–17.
- Simpkins, W.W., 1995. Isotopic composition of precipitation in central Iowa. *Journal of Hydrology* 172, 185–207.
- Smith, M.A., Hollander, D.J., 1999. Historical linkage between atmospheric circulation patterns and the oxygen isotopic record of sedimentary carbonates from Lake Mendota, Wisconsin, USA. *Geology* 27, 589–592.
- Sternberg, L.S.L., 1989. Oxygen and hydrogen isotope ratios in plant cellulose: mechanisms and applications. In: Rundel, P.W., Ehleringer, J.R., Nagy, K.A. (Eds.), *Stable Isotopes in Ecological Research*. Springer-Verlag, New York, pp. 124–141.
- Strong, W.L., Hills, L.V., 2005. Late-glacial and Holocene paleovegetational zonal reconstructions for central and north-central North America. *Journal of Biogeography* 32, 1043–1062.

- Teed, R., Umbanhower, C., Camill, P., 2009. Multiproxy lake sediment records at the northern and southern boundaries of the Aspen Parkland region of Manitoba, Canada. *The Holocene* 19, 937–948.
- Teller, J.T., Boyd, M., Yang, J., Kor, P.S.G., Fard, A.M., 2005. Alternative routing of Lake Agassiz overflow during the Younger Dryas: new dates, paleotopography, and a re-evaluation. *Quaternary Science Reviews* 24, 1890–1905.
- Teller, J.T., Leverington, D.W., 2004. Glacial Lake Agassiz: a 5000-year history of change and its relationship to the $\delta^{18}\text{O}$ record of Greenland. *Geological Society of America Bulletin* 116, 729–742.
- Teller, J.T., Leverington, D.W., Mann, J.D., 2002. Freshwater outbursts to the oceans from glacial Lake Agassiz and their role in climate change during the last deglaciation. *Quaternary Science Reviews* 21, 879–887.
- Teller, J.T., Yang, Z., Boyd, M., Buhay, W.M., McMillen, K., Kling, H.J., Telka, A., 2008. Postglacial sedimentary record and history of West Hawk Lake crater, Manitoba. *Journal of Paleolimnology* 40, 661–688.
- von Grafenstein, U., 2002. Oxygen-isotope studies of ostracods from deep lakes. *Geophysical Monographs* 133, 249–266.
- von Grafenstein, U., Erlenkeuser, U.H., Brauer, A., Jouzel, J., Johnsen, S., 1999. A mid-European decadal isotope-climate record from 15500 to 5000 years BP. *Science* 284, 1654–1657.
- von Grafenstein, U., Erlenkeuser, U.H., Müller, J., Trimborn, P., Ales, J., 1996. A 200 year mid-European air temperature record preserved in lake sediments: an extension of the $\delta^{18}\text{O}$ p-air temperature relation into the past. *Geochimica et Cosmochimica Acta* 60, 4025–4036.
- Wolfe, B.B., Edwards, T.W.D., Elgood, R.J., Beuning, K.R.M., 2001. Carbon and oxygen isotope analysis of lake sediment cellulose: methods and applications. In: Last, W.M., Smol, J.P. (Eds.), *Tracking Environmental Change Using Lake Sediments: Physical and Chemical Techniques*, vol. 2. Kluwer Academic Publishers, Dordrecht, pp. 373–400.
- Wolfe, B.B., Edwards, T.W.D., Jiang, H., MacDonald, G.M., Gervais, B.R., Snyder, J.A., 2003. Effect of varying oceanicity on early- to mid- Holocene palaeohydrology, Kola Peninsula, Russia: isotopic evidence from treeline lakes. *The Holocene* 13, 153–160.
- Wolfe, B.B., Falcone, M.D., Clogg-Wright, K.P., Mongeon, C.L., Yi, Y., Brock, B.E., St Amour, N.A., Mark, W.A., Edwards, T.W.D., 2007. Progress in isotope paleohydrology using lake sediment cellulose. *Journal of Paleolimnology* 37, 221–231.
- Wright Jr., H.E., Stefanova, I., Tian, J., Brown, T.A., Hu, F.S., 2004. A chronological framework for the Holocene vegetational history of central Minnesota: the Steel Lake pollen record. *Quaternary Science Reviews* 23, 611–626.
- Xia, J., Haskell, B.J., Engstrom, D.R., Ito, E., 1997. Holocene climate reconstructions from tandem trace element and stable-isotope composition of ostracodes from Cold Water Lake, North Dakota, USA. *Journal of Paleolimnology* 17, 85–100.
- Yakir, D., 1992. Variations in the natural abundance of oxygen-18 and deuterium in plant carbohydrates. *Plant Cell and Environment* 15, 1005–1020.
- Yamaguchi, K.E., Oguri, K., Ogawa, N.O., Sakai, S., Hirano, S., Kitazato, H., Ohkouchi, N., 2010. Geochemistry of modern carbonaceous sediments overlain by a water mass showing photic zone anoxia in the saline meromictic Lake Kai-ike, southwest Japan: I. Early diagenesis of organic carbon, nitrogen, and phosphorus. *Palaeogeography, Palaeoclimatology, Palaeoecology* 294, 72–82.
- Yansa, C.H., Ashworth, A.C., 2005. Late Pleistocene Palaeoenvironments of the Southern Lake Agassiz Basin, USA. *Journal of Quaternary Science* 20, 255–267.
- Yansa, C., Dean, W., Murphy, E., 2007. Late Quaternary paleoenvironments of an ephemeral wetland in North Dakota, USA: relative interactions of ground-water hydrology and climate change. *Journal of Paleolimnology* 38, 441–457.
- Yu, Z., McAndrews, J.H., Eicher, U., 1997. Middle Holocene dry climate caused by change in atmospheric circulation patterns: evidence from lake levels and stable isotopes. *Geology* 25, 251–254.
- Yu, Z., Wright Jr., H.E., 2001. Response of interior North America to abrupt climate oscillations in the North Atlantic region during the last deglaciation. *Earth Science Reviews* 52, 333–369.