Estimates of Arctic land surface temperatures during the early Pliocene from two novel proxies

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ABSTRACT

During the Pliocene (2.6 to 5 Ma ago) atmospheric CO_2 levels have been estimated as similar to or slightly above present levels (Tripati et al., 2009; Pagani et al., 2010), and yet Earth's climate was considerably different. Recent evidence suggests that although global temperatures were 2–3 °C warmer than pre-industrial, Arctic warming may have been amplified during the Pliocene. Thus precise temperature records of this interval are required to assess the sensitivity of Earth's climate to persistent levels of CO_2 between 365 and 415 ppm.We present records of two independent proxies for terrestrial growing-season temperatures at the Early Pliocene Beaver Pond site on Ellesmere Island. $\delta^{18}O$ values of cellulose from well-preserved peat constrain the $\delta^{18}O$ values of meteoric water to −20.7 ± 0.3‰, which we combined with $\delta^{18}O$ values of aragonitic freshwater molluscs found within the peat in order to calculate mollusc growth temperatures. This approach results in an average growing-season temperature of 14.2 ± 1.3 °C. Temperatures were independently derived by applying carbonate 'clumped isotope' thermometry to mollusc shells from the same site, indicating an average growing-season temperature of 10.2 ± 1.4 °C. A one-way ANOVA indicates that the differences between the two techniques are not significant as the difference in mean temperatures between both methods is no different than the difference between individual shells using a single technique. Both techniques indicate temperatures ~11–16 °C warmer than present (May–Sept temperature = −1.6 ± 1.3 °C) and represent the first thermodynamic proxy results for Early Pliocene Ellesmere Island.

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1. Introduction

An increasing number of studies, including the most recent Intergovernmental Panel on Climate Change (IPCC) report, have highlighted the early Pliocene climate as an example of climate conditions that could result from elevated atmospheric CO_2 driven by anthropogenic emissions (Jansen et al., 2007). Models of Pliocene climate suggest temperatures ~2–3 °C warmer globally and 7–15 °C warmer in the Arctic relative to today (Haywood et al., 2009; Sloan et al., 1996) which is within the range projected for the end of this century (Jansen et al., 2007). The Pliocene configuration of the continents was more similar to today than other periods of climatic warmth, and estimated Pliocene CO_2 levels of ~365–415 ppm were similar to or slightly above present levels (Pagani et al., 2010; Tripati et al., 2009). Therefore, the Pliocene is, in many respects, an accessible example of near-future temperatures (Haywood et al., 2009; Jansen et al., 2007). However, accurate and detailed constraints on polar temperatures in the Early Pliocene are needed to test Pliocene model predictions, but have been limited to-date. New reconstructions of Pliocene Arctic temperatures are particularly needed, as such data would constrain the extent to which global warming is amplified at high latitudes and help assess the Earth System Sensitivity of global and Arctic climate to changing levels of CO_2 (Lunt et al., 2010).

Fossil forest sites in the Canadian Arctic, which contain well-preserved plants, vertebrates and invertebrates, are amenable to the use of two novel proxies to constrain Pliocene polar temperature. The Beaver Pond locality (78º 33′ N; 82º 25′ W) on Ellesmere Island, Canada, so named because of the abundance of beaver-gnawed sticks found at the site (Rybczynski, 2008), is particularly well characterized and is unique in having abundant well-preserved remains of both plants and animals. The study site is located in Central Ellesmere Island near the head of Strathcona Fiord (Fig. 1). Stratigraphically the site lies within the Beaufort Formation, a

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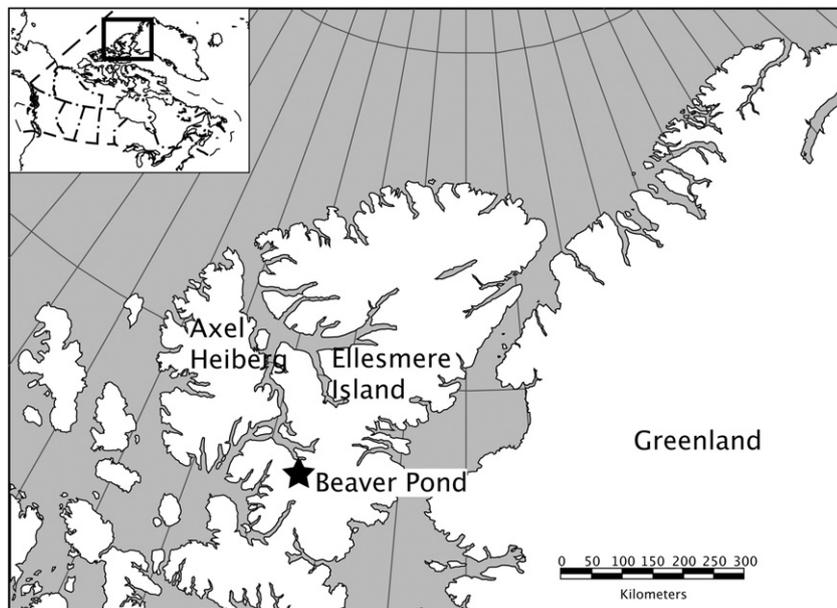E-mail address: csank@ltrr.arizona.edu (A.Z. Csank).

Fig. 1. Map showing the Beaver Pond locality at the head of Strathcona Fiord in central Ellesmere Island.

predominantly fluvial unit that forms part of the Sverdrup Basin (Fyles, 1989).

The Beaver Pond section is composed of cross-bedded sand layers and arkosic gravels intercalated with fossiliferous peat, suggesting a fluvial depositional setting. Sand layers are cross-bedded in the coarser layers and planar bedded in the finer layers; both layers contain abundant plant macrofossils. Sand layers containing discontinuous lenses of peat indicate peat-forming units likely occurred within a braided river system. The gravel units probably represent gravel bars at the river bends or between channels. Peat deposits likely formed between channels and in the river flood plain. The Beaver Pond deposit itself is a thick peat layer that likely represents an oxbow lake deposit formed when a beaver dam was built across one of the channels. The entire sequence is capped by glacial deposits of Pleistocene age.

Flora includes macrofossils of bryophytes and vascular plants. The bryophytes consist mostly of extant species (Matthews and Ovenden, 1990), whereas the vascular plants contain some extinct forms including a larch (*Larix groenlandii*) (Ballantyne et al., 2006; Tedford and Harington, 2003). Other vascular plants include spruce (*Picea*), pine (*Pinus*), cedar (*Thuja*), alder (*Alnus*), and birch (*Betula*) (Ballantyne et al., 2010; Matthews and Ovenden, 1990). The rich mammal fauna, as diverse as that of the modern Arctic tree-line, consists of beaver (*Dipoides*), rabbit (*Hypolagus*), a small canine (*Eucyon*), shrew (*Arctisorex*), bear (*Ursus abstrusus*), wolverine (*Plesiogulo*), badger (*Arctomeles*) and a hipparionine horse (*Plesiohipparion*). Biostratigraphic age control based on first appearances of these species provides an Early Pliocene (4–5 Ma) age for the site (Tedford and Harington, 2003). The age is primarily based on the species *Ursus abstrusus* that in North America dates from 3.5 to 5 Ma ago and *Plesiohipparion* that dates between 4 and 5 Ma ago (Tedford and Harington, 2003).

Although it is unusual to see carbonates preserved in peat deposits, the overall fluvial depositional setting offers some insight into why this is possible at this site. Ovenden (1993) states that the assemblages of bryophytes found at the site are indicative of species that existed in neutral to slightly acidic treed fens. Fen environments are fed by ground water and/or streams and thus are much higher in pH than ombrotrophic bogs (Vitt et al., 1993). Additionally, at least one of the species used in our study (*Gyraulus albus*) is tolerant of slightly acidic low carbonate environments (Boycott, 1936; Dussart, 1979; White et al., 1999). The molluscs likely lived among the aquatic vegetation of the fen. Hydrologically a fen environment fed by groundwater is not as susceptable to large seasonal fluctuations in the $\delta^{18}O$ values of the source water (White et al., 1999; Zanazzi and Mora, 2005).Turner et al. (2010) note that groundwater-influenced channel fens and oxbow lakes in the Yukon tend to show slightly depleted values weighted towards winter snow melt, however, these groundwater fed systems exhibit little to no evaporative enrichment in $\delta^{18}O$ values during the summer months leading to fairly consistent annual $\delta^{18}O$ values.

Previous attempts to estimate early Pliocene temperatures in this region used non-thermodynamically based proxies. Estimates of summer temperatures based on beetle assemblages are 10 ± 2 °C warmer than present (Elias and Matthews, 2002). Transfer functions based on $\delta^{18}O$ values of wood cellulose have been interpreted to reflect mean annual temperatures ~14–19 °C warmer than present (Ballantyne et al., 2006; Ballantyne et al., 2010). Estimates based on plant macrofossils and molecular techniques indicate mean annual temperatures ~19 °C warmer than present (Ballantyne et al., 2010). These temperature calculations rely upon empirical transfer functions, whereas, our study relies upon the thermodynamically controlled isotopic distributions within carbonate minerals and between those minerals and co-existing water.

2. Methods

We use two approaches, using carbonate stable isotope values, to provide both independent estimates of temperature and baseline $\delta^{18}O$ values for Arctic meteoric water during the Pliocene. First, we use $\delta^{18}O$ values of cellulose of aquatic moss derived from peat as a proxy for the $\delta^{18}O$ value of meteoric water (Ménot-Combes et al., 2002; Sauer et al., 2001; Zanazzi and Mora, 2005). These reconstructed lake water $\delta^{18}O$ values are compared with $\delta^{18}O$ values of well-preserved freshwater molluscs found within the peat to calculate paleotemperatures using the temperature-dependent partitioning of $^{18}O/^{16}O$ ratios between calcium carbonate and water (Dettman et al., 1999; Grossman and Ku, 1986). A second technique, carbonate 'clumped isotope' thermometry, examines the proportion of ^{13}C and ^{18}O that are bound to each other within the carbonate mineral lattice. The basis for the clumping of these heavy isotopes into bonds with each other is thought to be the thermodynamically controlled exchange of stable isotopes among isotopologues of calcium carbonate, or carbonate ions in solutions from which carbonate minerals precipitate (Eagle et al., 2010; Eiler, 2007; Ghosh et al., 2006; Schauble et al., 2006; Tripati et al., 2010). The equilibrium constant for the reaction: $Ca^{12}C^{18}O^{16}O_2 + Ca^{13}C^{16}O_3 \Leftrightarrow Ca^{13}C^{18}O^{16}O_2 + Ca^{12}C^{16}O_3$ (Reaction 1; or its equivalent for dissolved inorganic carbon species) forms the theoretical basis for carbonate clumped isotope thermometry, with the

doubly substituted species of CO_2 (or heavy isotope, mass-47, "clump") produced during acid digestion slightly more stable than the other isotopologues. Thus, a progressively more random distribution of heavy isotopes among all possible isotopologues is preferentially favored with increasing temperatures (Schauble et al., 2006). Abundances of mass-47 isotopologues are reported using Δ_{47} (Eiler and Schauble, 2004). The Δ_{47} value is defined as the difference in per mil between the measured 47/44 ratio of the sample and the 47/44 ratio expected for that sample if its stable carbon and oxygen isotopes were randomly distributed among all isotopologues, referred to as stochastic distribution.

The Δ_{47}–temperature relationship for most modern biogenic carbonates measured to date (Came et al., 2007; Eagle et al., 2010; Ghosh et al., 2006; Huntington et al., 2009; Tripati et al., 2010) generally adheres to the inorganic calcite calibration reported by Ghosh et al. (2006). Two studies have calibrated the carbonate clumped isotope thermometer in aragonitic molluscs (Came et al., 2007; Huntington et al., 2009) and found evidence for a Δ_{47}–temperature calibration that is similar to inorganic calcite. As a result, we apply the inorganic calibration of Ghosh et al. (2006) to aragonitic molluscs from the Beaver Pond site to estimate temperature. However, as this is a new proxy, the full scope of potential kinetic isotope effects on carbonates has not yet been resolved. We note that there may be some evidence of kinetic isotope effects in certain biogenic carbonates (e.g. surface-dwelling coral, fish otoliths), although the growth temperatures of these calibration materials were poorly constrained (Ghosh et al., 2006; 2007; Tripati et al., 2010).

2.1. Methods: stable isotope analysis

Mollusc shells were separated from the peat and washed in an ultrasonic bath containing deionized water before being air-dried and examined to ensure no matrix was contained within the shells. Initially three gastropod shells (G. albus) were crushed with a mortar and pestle and analyzed as whole samples. Subsequent samples of mollusc shells, four gastropods (two G. albus and two Lymnae sp.) and two bivalve shells (Pisidium sp.) were sub-sampled using a Dremel dental drill fixed in place under a binocular microscope. Carbonate was sampled along growth banding for three of the specimens, for seasonal analysis, while bulk analyses were conducted on the remaining two specimens (Table 1). Samples were analyzed for $\delta^{18}O$ values using a Kiel-III carbonate preparation device directly coupled to a Thermo Finnigan MAT 253 mass spectrometer in dual inlet mode, with an analytical precision of 0.1‰. $\delta^{18}O_{aragonite}$ was calibrated and corrected to VPDB using the standard NBS-19. Initial (bulk) analyses were carried out at the Saskatchewan Isotope Laboratory (SIL), University of Saskatchewan and additional samples were analyzed using an identical set up located at the Environmental Isotope Laboratory at the University of Arizona.

Moss fragments from the aquatic species (Scorpidium scorpioides) were isolated from the peat using a binocular microscope and tweezers to select only individuals of the desired species and washed in deionized water. The moss stems were subsequently processed to α-cellulose using the sodium chlorite bleaching method outlined by Leavitt and Danzer (1993). Moss fragments were placed in heat-sealed mesh pouches immersed in a solution consisting of 1 L deionized water, 15 g of sodium chlorite and 10 mL of acetic acid. The solution with samples was heated to 70 °C and left over night with another 10 g of sodium chlorite added every 4 h during the subsequent day. Samples were left in solution at 70 °C until lignin was completely removed as indicated by the samples turning completely white. Deionized water heated to 70 °C was used to rinse the samples followed by a rinse in 20 °C deionized water. 10 mL of 10% sodium hydroxide was added to the samples that were subsequently heated to 80 °C for 2 h, samples were removed from solution and rinsed with deionized water. This step ensures removal of all sugars and hemicellulose from the samples. The samples were rinsed in deionized water one final time and placed in a vacuum oven at 40 °C to dry for 12 h. $\delta^{18}O_{cellulose}$ values of moss were determined at the SIL using a Thermo Finnigan TC/EA coupled to a Thermo Finnigan Delta Plus

Table 1

Summary table of all stable isotope measurements. Uncertainties in the temperature calculation are based on the standard errors of both the stable isotope determination of calcite and the standard error of the meteoric water value inferred from moss cellulose. Average of all molluscs is determined as the average calculated from each individual mollusc.

Species	Sample type[a]	$\delta^{18}O$ aragonite VSMOW	Temp. (°C)[b]
Gyraulus albus	Sub-sampled	11.45	11.4 ± 0.4
		10.82	14.2 ± 0.4
		10.57	15.3 ± 0.4
		11.38	11.7 ± 0.4
		11.19	12.5 ± 0.4
		10.32	16.4 ± 0.4
		10.40	16.1 ± 0.4
		10.48	15.7 ± 0.4
Gyraulus albus	Average	10.83	14.2 ± 0.7
	Sub-sampled	12.15	8.4 ± 0.4
		11.92	9.4 ± 0.4
		13.03	4.7 ± 0.4
		12.71	6.1 ± 0.4
		13.21	4.0 ± 0.4
		12.57	6.7 ± 0.4
		11.81	9.9 ± 0.4
		12.30	7.8 ± 0.4
Lymnae sp.	Average	12.46	7.1 ± 0.5
	Sub-sampled	9.61	19.6 ± 0.4
		9.58	19.8 ± 0.4
		9.95	18.1 ± 0.4
		10.17	17.1 ± 0.4
		9.56	19.9 ± 0.4
		9.33	20.9 ± 0.4
		9.73	19.1 ± 0.4
Lymnae sp.	Average	9.70	19.2 ± 0.8
	Sub-sampled	10.02	17.8 ± 0.4
		10.16	17.1 ± 0.4
Pisidium sp.	Bulk	11.59	10.5 ± 0.4
Gyraulus albus	Bulk	10.67	14.7 ± 0.4
Gyraulus albus	Bulk	10.50	15.2 ± 0.4
Gyraulus albus	Bulk	10.55	15.0 ± 0.4
Average all molluscs		10.80 ± 0.31	14.2 ± 1.3

[a] 'Sub-sampled' indicates that the shells were sampled at irregular intervals along a growth whorl. 'Bulk' indicates that analyses were carried out on entire shells that were powdered homogenized and analyzed.
[b] Temperatures are determined using Eq. (2). Uncertainty in the temperature determinations represents the cumulative errors in the inferred water determination and the analytical precision of the $\delta^{18}O$ measurements on both the moss cellulose and the aragonite.

XL mass spectrometer in continuous flow mode via a Conflo III interface with an analytical precision of 0.2‰, and standard deviation on repeat measurements of 0.3‰. $\delta^{18}O_{cellulose}$ values were calibrated and corrected to VSMOW using the IAEA 601 and 602 benzoic acid standards as well as an internal cellulose standard.

Nine precipitation samples were collected from Strathcona Fiord, Ellesmere Island Canada in July, 2004. Samples were collected using a bucket and then transferred to 50 mL nalgene bottles. Bottles were filled to the top to eliminate headspace and the tops were sealed tightly and then wrapped with electrical tape. $\delta^{18}O$ values of moss were determined at the SIL using a Thermo Finnigan TC/EA coupled to a Thermo Finnigan Delta Plus XL mass spectrometer in continuous flow mode via a Conflo III interface with an analytical precision of 0.2‰, and standard deviation on repeat measurements of 0.3‰. $\delta^{18}O$ values were calibrated and corrected to VSMOW using Standard Light Antarctic Precipitation (SLAP) and VSMOW.

2.2. Methods: 'clumped isotope' measurements

CO_2 analyte was obtained from carbonate samples by reacting 10 mg carbonate samples in H_3PO_4 on a custom-built automated online vacuum system described in Passey et al. (2010). Reactions were carried out at 90 °C for 20 min, and CO_2 was immediately trapped at liquid nitrogen temperatures as it evolved. Each sample was then

cryogenically purified in dry ice/ethanol and liquid nitrogen traps, and purified on a gas chromatograph to remove hydrocarbon contaminants according to the scheme outlined in Ghosh et al. (2006) and modified as detailed in Passey et al. (2010). Sample gasses were analyzed at the California Institute of Technology for masses 44 through 49 (inclusive) on a Thermo-Finnigan MAT 253 gas source isotope ratio mass spectrometer in dual inlet mode for 8 acquisitions of 10 cycles, each with an integration time of 8 s and a total analysis time of approximately 3 h (including pressure balance, background measurement and peak-centering routines). Measurements were made with a stable 16-volt signal at mass 44, with peak centering, background measurement and pressure-balancing before each acquisition (Huntington et al., 2009; Passey et al., 2010).

Data for this study were collected between June 12 and 14, 2009. On every day of machine use, gasses heated to 1000 °C were analyzed to define the stochastic distribution of isotopologues as described in Eiler and Schauble (2004). Heating of gasses to 1000 °C is necessary to drive the sample gasses to the stochastic distribution. Carbonate standards run during this time period consisted of an analysis of two separate extractions of a marble, yielding an average Δ_{47} value of $0.345 \pm 0.003‰$, and two extractions of a vein calcite 102-GC-AZ01 ($\Delta_{47} = 0.669 \pm 0.002‰$). The long-term mean Δ_{47} values for 17 analyses of the marble standard analyzed at 90 °C on the same system is $0.352‰ \pm 0.019‰$, (Ghosh et al., 2006; Passey et al., 2010).

The error in Δ_{47} of CO_2 extracted once ($n = 1$) from a carbonate sample ranged from 0.006 to 0.013‰ (one standard error), (Table 2). This uncertainty is calculated as one standard error of the mean Δ_{47} value, determined from eight acquisitions of the same gas. The external precision for carbonate sample Ell 1a (*Lymnaea* sp.), from which measurements were taken from four separate extractions, was 0.006‰ (Table 2). This uncertainty is calculated as one standard error of the mean Δ_{47} value determined from multiple CO_2 samples extracted from separate aliquots of the same material, and analyzed for eight acquisitions each.

2.3. Methods: moss isotopes

Variations in the $\delta^{18}O$ of aquatic mosses reflect the composition of meteoric waters in which they grow. When oxygen is fixed into cellulose, the isotopic ratio of cellulose is controlled by the isotopic value of the environmental water in the cell enriched by a biologic fractionation factor of 27–29‰ (DeNiro and Epstein, 1981; Epstein et al., 1977; Yakir and DeNiro, 1990). Thus, $\delta^{18}O$ of cellulose can be considered a record of cellular water at the site of fixation. However, in terrestrial plants, leaf water $\delta^{18}O$ becomes enriched by evaporation of cellular water from the leaf (Roden et al., 2000). Aquatic plants do not undergo evaporative enrichment on their own and instead form

cellulose in equilibrium with surrounding water (DeNiro and Epstein, 1981; Ménot-Combes et al., 2002; Sauer et al., 2001; Zanazzi and Mora, 2005). Mosses lack both a vascular system and stomata, thus fractionation occurs as a function of diffusion and biological fractionation during cellulose synthesis. Therefore, cellulose $\delta^{18}O$ in aquatic plants should reflect the $\delta^{18}O$ value of meteoric water, after removing effects of fractionation factors associated with cellulose synthesis and diffusion. There is a linear relationship between source water $\delta^{18}O$ and cellulose $\delta^{18}O$ (Eq. (1)) (Sauer et al., 2001). The intercept of this equation is indistinguishable from the reported theoretical fractionation during cellulose synthesis of 27–29‰ (Yakir and DeNiro, 1990).

$$\delta^{18}O_{cellulose} = 0.882 \delta^{18}O_{water} + 28.3‰ \qquad (1)$$

In this study, we evaluated moss isotopic values from previously published field studies and examined the overall relationship between $\delta^{18}O$ of cellulose and $\delta^{18}O$ of water (Fig. 2). The relationship established by Sauer et al. (2001) (Eq. (1)) holds true even when moss $\delta^{18}O$ values from other studies are incorporated into the regression, with Eq. (1) plotting within the confidence limits of a regression line that incorporates two additional moss isotope studies (Ménot-Combes et al., 2002; Zanazzi and Mora, 2005).
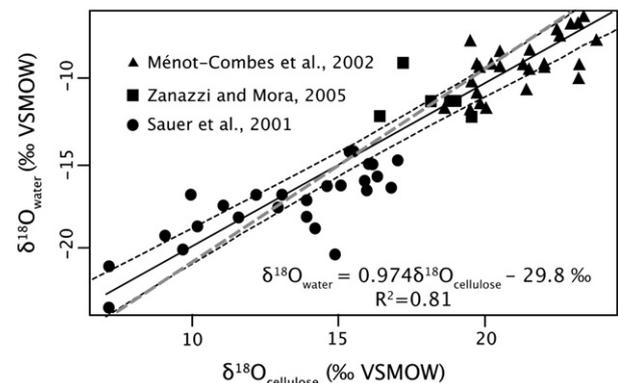
2.4. Methods: mollusc stable isotopes

Eight mollusc shells were extracted from within the peat ensuring that the cellulose and the mollusc samples were contemporaneous. Four of the mollusc shells were of the species *G. albus*, two were *Lymnaeae* sp. and two were small *Pisidium* sp. clams. Three of the mollusc shells were sampled along growth bands to attempt to resolve a seasonal signal. Temperature calculations were carried out using the Grossman and Ku (1986) equation modified for use in freshwater molluscs (Dettman et al., 1999) (Eq. (2)) Where T is degrees in Kelvin and α is the fractionation between water and aragonite described by Eq. (3), such that,

$$1000 \ln(\alpha) = 2.559 \left(10^6 T^{-2} \right) + 0.715 \qquad (2)$$

and

$$\alpha_{aragonite-water} = \left(1000 + \delta^{18}O_{aragonite(VSMOW)} \right) \qquad (3)$$
$$/ \left(1000 + \delta^{18}O_{water(VSMOW)} \right).$$

Table 2
Summary of all 'clumped isotope' measurements, samples were all measured on individuals with no sub-sampled members. All errors are reported as standard error.

Species[a]	$\delta^{18}O$ aragonite VSMOW	$\delta^{18}O$ water VSMOW	[b]Δ_{47} (‰)	[c]Temp. (°C)
Lymnae sp.	8.43	−22.1	0.695 ± 0.006	14.7 ± 1.3
Lymnae sp.	8.41	−23.1	0.716 ± 0.008	10.5 ± 1.5
Lymnae sp.	8.38	−22.4	0.701 ± 0.009	13.3 ± 1.8
Lymnae sp.	8.47	−23.7	0.730 ± 0.008	7.8 ± 1.5
Gyraulus albus	9.47	−22.2	0.719 ± 0.011	9.8 ± 2.2
Pisidium sp.	11.05	−21.8	0.744 ± 0.013	5.3 ± 2.3
[d]Average all molluscs	9.03 ± 1.1	−22.6 ± 0.7	0.717 ± 0.007	10.2 ± 1.4

[a] Each measurement is from a different mollusc.

[b] ± Uncertainty in Δ_{47} values represents the internal precision of each measurement (one standard error).

[c] Uncertainty in Δ_{47} temperature values represents the error in temperature in °C propagated from the internal or external precision of the Δ_{47} measurement (one standard error).

[d] The ± values in the average row refer to the external precision of Δ_{47} measurements to one standard error.

Fig. 2. Illustrates the relationship of moss $\delta^{18}O_{cellulose}$ to $\delta^{18}O_{water}$ for three studies (Ménot-Combes et al., 2002; Sauer et al., 2001; Zanazzi and Mora, 2005) of moss isotopes. Gray dashed line indicates the line determined by the theoretical relationship established by Sauer et al. (2001) (Eq. (1)). Note that the relationship determined by Sauer et al. (2001) is indistinguishable from the relationship determined by adding additional moss isotope data. Scatter in the plot represents a standard error (SE) of 0.15‰.

$$\delta^{18}O_{water} = 0.974 \delta^{18}O_{cellulose} - 29.8‰$$
$$R^2 = 0.81$$

$\delta^{18}O_{aragonite}$ is the isotopic ratio in VPDB measured from the gastropod shells converted to VSMOW using the $\alpha_{SMOW-PDB}$ of 1.03091 (Gonfiantini et al., 1995). $\delta^{18}O_{water}$ is the isotopic ratio derived from the $\delta^{18}O_{cellulose}$ values of aquatic moss and calculated using (Eq. (1)). The uncertainty in the source water estimates is combined with the uncertainty in Eq. (2) in order to determine the uncertainty of the calculated temperature. White et al. (1999) conducted a combined laboratory and field study on the temperature relationship of biogenic aragonite from the freshwater gastropod *Lymnaea*. Based on their results they posited that there is no vital effect that is specific either to this freshwater, or to other, mollusc genera.

3. Results and discussion

3.1. Inferred $\delta^{18}O$ of meteoric water

The $\delta^{18}O$ values of cellulose obtained from the Pliocene moss averaged $10.1 \pm 0.24‰$ VSMOW ($n = 8$), implying a water $\delta^{18}O$ value of $-20.7 \pm 0.3‰$ (Eq. (1)). Water $\delta^{18}O$ values calculated using clumped isotope-derived temperatures combined with mollusc $\delta^{18}O$ support a slightly lower (though similar) value of $-22.6 \pm 0.7‰$ VSMOW ($n = 7$). Water $\delta^{18}O$ values determined from moss cellulose likely represent values for the moss growing season, and are thus possibly biased more towards June and July than the isotopic values determined from 'clumped isotopes' that would reflect water $\delta^{18}O$ values for the period of mollusc calcification. Moss-derived water $\delta^{18}O$ values contain more of a summer signal and are ~3–5‰ enriched compared to modern Arctic summer precipitation on Ellesmere Island measured in July 2004 ($\delta^{18}O = -25.4‰ \pm 0.5‰$ VSMOW; $n = 9$). Estimates of Pliocene water $\delta^{18}O$ are also higher than values reported by GNIP (the global network for isotopes in precipitation) for summer precipitation on Ellesmere Island (-24 to $-28‰$) (IAEA/WMO, 2006), and much higher than annually averaged precipitation for Ellesmere Island (approx. $-30.8 \pm 6.7‰$) (IAEA/WMO, 2006). Both proxies yield Pliocene values that are similar to modern annual GNIP water values from Alaska and the Yukon ($-20.8 \pm 2.3‰$; Barrow, Mayo and Whitehorse stations) (IAEA/WMO, 2006). Values of meteoric water calculated in this study are similar to values of meteoric water calculated for the Paleocene and Eocene at the same location (Jahren et al., 2009; Richter et al., 2008; Tripati et al., 2001). Meteoric water values for the Eocene derived from mollusc shells are enriched relative to modern and have $\delta^{18}O$ values that range from -16 to $-23‰$ (Eberle et al., 2010; Jahren et al., 2009; Tripati et al., 2001). Richter et al. (2008) estimated modern values of annual precipitation isotopes for Axel Heiberg Island not much different from their estimated Eocene values of $-21.9‰$ using the Bowen and Wilkinson (2002) online precipitation isotope calculator. However, these inferred values are high when compared to both the IAEA and our measurements of modern precipitation. Based on this they argued that the gradient of values of $\delta^{18}O$ of meteoric water remained unchanged over much of the Cenozoic (Richter et al., 2008), however, this is unlikely given the results presented here which show a 3–5‰ enrichment in $\delta^{18}O$ of Pliocene Arctic water. Jahren et al. (2009) also demonstrated a difference in δD of Eocene meteoric water and modern of ~40‰ and suggests that the latitudinal gradient in precipitation isotopes was likely different. Recent modeling studies of Eocene isotopes in precipitation have indicated that when the latitudinal temperature gradient is reduced there is a corresponding change in the latitudinal gradient of isotopes in precipitation (Speelman et al., 2010). Thus the difference in isotopic ratios between the present and the Pliocene instead likely reflects either local, regional or global changes in the hydrologic cycle, which in turn could record differences in the temperature of precipitation, in Rayleigh fractionation associated with distillative condensation during vapor transport, and possibly in the season of precipitation (i.e., the ratio of summer to winter precipitation). Furthermore if we consider that a reduction in ice

volume during the Pliocene caused $\delta^{18}O$ values of meteoric water to be globally depleted by ~1‰ (Lear et al., 2000) and that the latitudinal temperature gradient was reduced (Ballantyne et al., 2010), then our estimates of a 3–5‰ enrichment in $\delta^{18}O$ of Arctic water suggest that the latitudinal gradient in $\delta^{18}O$ of meteoric water was also diminished in the Pliocene. Studies of other Pliocene sites from a range of latitudes and the use of isotope-enabled models would provide further insight into these changes.

3.2. Temperature estimates from independent proxies

Temperatures calculated based on the difference in $\delta^{18}O$ of meteoric water, inferred from moss cellulose, and co-existing mollusc carbonate average $14.2 \pm 1.3\,°C$ (Fig. 3). Temperatures calculated based on 'clumped isotope' thermometry average $10.2 \pm 1.4\,°C$ (Fig. 3). We infer these temperatures to equal mean mollusc growing season temperatures. Fig. 3 presents results obtained from all gastropod shells measured in this study. Sub-sampled shells were sampled at intervals along their growth transect and thus have a spread of values representing seasonal variations (either in $\delta^{18}O$ of meteoric water or temperature). Bulk values represent whole shells that were powdered and measured. Temperatures were calculated from $\delta^{18}O$ values of both sub-sampled and bulk mollusc samples using the Grossman and Ku (1986) equation and the $\delta^{18}O$ value of meteoric water, inferred from moss cellulose. Temperatures are independently derived using the stochastic 'clumped isotope' technique and indicated as Δ_{47} (Fig. 3). To assess the differences between methods we conducted a t-test grouping the data based on the method used and found that there are no significant differences between the stable isotope and 'clumped isotope' results ($t = 2.02$; $p = 0.07$). We also conducted a one-way ANOVA, grouping the sub-sampled stable isotope results as one group, the bulk results as another and the 'clumped isotope' results as a third group, again finding no significant difference ($F = 1.26$; $p = 0.30$). If we run the ANOVA analysis using each individual mollusc as a group then we do find significant differences, however, the difference between the 'clumped isotope' individuals and the stable isotope individuals is no greater than the difference between two individuals in the sub-sampled isotope group. There is no difference between the two techniques for the species *G. albus*, however, there are differences between the results obtained from both *Lymnaea* sp. and *Pisidium*. Although both *G. albus* and *Lymnaea* sp. grow throughout the year, both species experience much slower growth during the winter months and rapid growth between April and August (Dussart, 1979; White et al., 1999). However, these
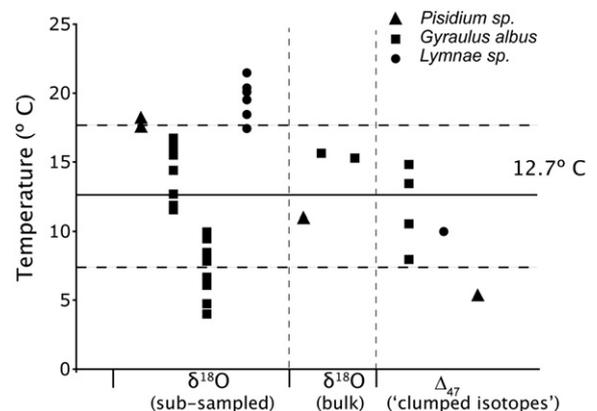

Fig. 3. Paleotemperature calculations from Pliocene molluscs, *Pisidium* sp., *G. albus* and *Lymnae* sp. $\delta^{18}O$ (sub-sampled) represents multiple measurements from the same individuals with the variability in values being the result of sampling along growth whorls. $\delta^{18}O$ (bulk) represents bulk aragonite values from single shells. Δ_{47} ('clumped isotope') represents 'clumped isotope' thermometry of mollusc shells. The average temperature of 12.7° is plotted along with 1σ error bars.

studies used species collected in the British Isles. Pip (1992) noted that in Manitoba, Canada both species of mollusc generally hibernate for the entire period of ice cover and exhibit most growth during the months of May to September, which is consistent with a study by Caquet (1993) showing that *Lymnaea* exhibits almost no growth between September and May. Additionally as this would have been high enough latitude to experience complete darkness during the winter months, it is unlikely that either species grew during the winter. Both species generally only live one to two years (Dussart, 1979; Pip, 1992). Pip (1992) reports that these molluscs are born between June and September and then over-winter as sub-adults before growing to full size. That there is no difference between temperatures calculated from $\delta^{18}O$ and temperatures determined from Δ_{47} from *G. albus* could suggest that *G. albus* grows primarily during the same period as the moss whereas the greater difference between $\delta^{18}O$ and Δ_{47} temperature results determined from *Lymnaceae* and *Pisidium* could suggest that these two species exhibit a longer growing season than the moss (Fig. 3). Thus the differences between the two techniques could simply be an artifact of the fact that the moss $\delta^{18}O$ value represents average water $\delta^{18}O$ values of the moss growing season (likely summer) and not the average $\delta^{18}O$ values of the mollusc growing season. Although Zanazzi and Mora (2005) indicate that water in fen environments has little seasonal variation in isotopic values. Turner et al. (2010) suggest that there is a tendency for more depleted values during the 2 months of snow melt in the spring and if some species of molluscs start growing early in the season their $\delta^{18}O$ values may biased towards more depleted winter precipitation. To test this we can use the meteoric water $\delta^{18}O$ value determined from the 'clumped isotope' results ($-22.6 \pm 0.7‰$), which should represent the average water value of the period of mollusc calcification, instead of the moss-inferred water $\delta^{18}O$ value to calculate temperatures from the *Lymnaea* and *Pisidium*. If we do this, the average *Lymnaea* temperature of 11.8 ± 0.2 °C is much closer to the clumped isotope value of 9.8 ± 2.2 °C suggesting that it may be that moss and *Lymnaea* growth periods do not overlap.

Three mollusc specimens were sampled at up to eight points along the growth whorl of the gastropod in two of these three mollusc samples with calculated temperatures ranging between 12.7 and 21.7 °C (7.5–16.4 °C if the $\delta^{18}O$ water value inferred from 'clumped isotopes' is used) suggesting spring–summer temperatures are predominantly recorded (Fig. 4). The third sub-sampled mollusc has temperatures ranging between 5.4 and 10.8 °C (-2.9–2.8 °C if the $\delta^{18}O$ water value inferred from 'clumped isotopes' is used). Because all molluscs were sampled from near the center of the shell this could represent an individual that was born late in the year and grew mostly in the fall and spring as *G. albus* can have two generations, one born in the spring and another born in the fall (Dussart, 1979). 'Clumped isotope' results and 'bulk' sample results likely do contain more of a winter signal than the sub-sampled gastropods because there would be some influence from the minor amount of carbonate formed during the winter on the temperatures calculated using calcite from the entire shell. These values are 14.3 ± 4.5 °C (average of all results) warmer than the modern (May–Sep) temperatures for Eureka, Ellesmere Island, of -1.6 ± 1.3 °C (Environment Canada, 2008). May to September temperatures were used because these months represent a standard growing season and cover the period when molluscs have their highest growth rates (Dussart, 1979; Pip, 1992).

Without detailed information on the growing season of Pliocene molluscs or information on the seasonal variation of water $\delta^{18}O$, we are unable to use these data to determine seasonal variation in temperature. If we assume low variability in water $\delta^{18}O$ during the period of calcification, we can then use the intra-shell variability in $\delta^{18}O$ combined with our inferred water $\delta^{18}O$ values ($-20.7‰$) in order to estimate maximum and minimum temperatures during the season of calcification. Maximum and minimum growing season temperatures of 21.7 °C and 5.4 °C are calculated.
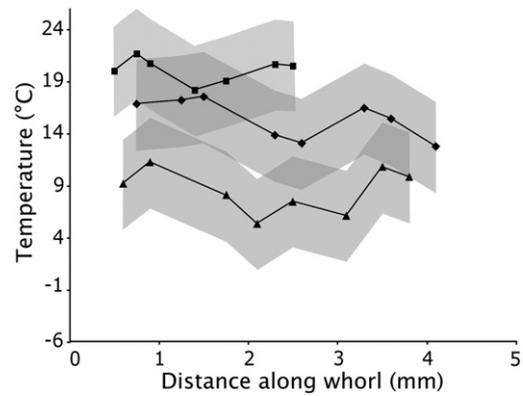

Fig. 4. Paleotemperature calculations from three Pliocene molluscs that were sampled at intervals along a growth whorl indicating seasonal variability in single individuals. Temperatures were calculated using Eq. (2) and the meteoric water value determined from moss stable isotopes with gray shading indicating a range of temperatures inherent in the standard deviation of Eq. (1).

Our estimates of mean calcification temperature derived from both techniques of 10.2 and 14.2 °C (Fig. 3.) are generally similar to warm-month mean temperatures (WMMT) based on transfer functions derived from fossil beetle assemblages, also collected from the Beaver Pond locality (12.4 °C) (Elias and Matthews, 2002) (Table 3). However, the temperatures determined in our study are assumed to represent an average of the entire calcification period, hereafter referred to as growing season (and likely not solely reflecting summer). These data imply that summer temperatures may actually have been warmer than what has previously been reported (Elias and Matthews, 2002). $\delta^{18}O$ values of cellulose from wood collected at the Beaver Pond site on Ellesmere Island (Ballantyne et al., 2006) was used to reconstruct mean annual temperature (MAT). The tree-ring isotope-based temperature obtained from this earlier study was -5.5 ± 1.9 °C, or 14.2 ± 2.5 °C warmer than present (Ballantyne et al., 2006). This difference (Pliocene minus modern) is equivalent to the temperature difference calculated in our study using both proxies (14.3 ± 4.5 °C) and that of the beetle study of Elias and Matthews (2002) (10 ± 2 °C). These temperatures are also equivalent to WMMT calculated by Ballantyne et al. (2010).

In order to more closely compare to both the Elias and Matthews (2002) study, which is based on estimates of WMMT we can look at T_{max} (maximum calculated temperature) determined both from the stable isotopes of freshwater molluscs and moss (21.7 °C) and 'clumped isotopes' (14.7 °C) as analogous to temperatures recorded

Table 3

Comparison of results obtained in this study to results from previous non-thermodynamic temperature estimates for the Pliocene Beaver Pond locality. Note that our estimates confirm estimates from prior work. All errors are reported as standard error.

Pliocene growing season temperature	Difference from modern	
	T (°C)	ΔT (°C)
Freshwater mollusc shell $\delta^{18}O$	[a]14.2 ± 1.3	[a]15.9 ± 1.6
Freshwater mollusc shell Δ_{47} ('clumped isotopes')	10.2 ± 1.4	11.8 ± 1.5
Average this study	12.7 ± 1.9	14.3 ± 2.2
Pliocene warm month mean temperature		
Elias and Matthews (2002)	12.4	10 ± 2.0
Ballantyne et al. (2010)	14.4 ± 2.0	12 ± 2.0
Pliocene MAT		
Ballantyne et al. (2006)	-5.5 ± 1.9	14.2 ± 2.5
Ballantyne et al. (2010)	-0.5	19

The results presented are averages of all measurements for each technique.
[a] Temperatures calculated from freshwater mollusc $\delta^{18}O$ measurements uses the moss cellulose inferred water $\delta^{18}O$ values for temperature determination using Eq. (2).

during calcite formation during the warmest months, or WMMT. A difference from modern ΔWMMT of 14.1 ± 0.7 °C and 7.1 ± 1.3 °C can be inferred indicating that our estimates of WMMT are within the range of values determined by Elias and Matthews (2002) and Ballantyne et al. (2010). Elias and Matthews (2002) suggested that greater warming is evident during the winter months, meaning that differences from modern (ΔT) calculated for either growing season or mean annual temperatures are likely to appear greater than estimates of ΔWMMT. Ballantyne et al. (2006) confirmed this when they determined that their tree-ring isotope based reconstruction captured more of a winter signal than the beetle records of Elias and Matthews (2002) resulting in a higher estimate of ΔT.

Ballantyne et al. (2010) conducted a proxy comparison study of temperature estimates for the Beaver Pond locality updating and expanding upon the Ballantyne et al. (2006) study. Using three independent approaches, a study of the coexisting vegetation at the site and its relationship to climate, and stable isotope values of tree-ring cellulose and bacterial tetraethers, Ballantyne et al. (2010) inferred an MAT of -0.6 to -0.4 °C, or ~19 °C warmer than present. These inferred temperatures from three independent proxies are considerably warmer than the temperatures calculated by previous studies and in our own study (Table 3), however, as our study is representative of the period of calcification and is biased towards the period of maximum mollusc growth, we are not able to accurately compare our results to MAT. This large difference between the seasonally biased studies presented here and in Elias and Matthews (2002) and the mean annual temperature studies presented in Ballantyne et al. (2010) suggests that there was perhaps much greater warming, relative to modern, in Pliocene winter temperatures at high latitudes than in temperatures during the warmer months. The cause of greater winter warming could be related to a relatively ice-free Arctic Ocean during the Pliocene resulting in reduced albedo and allowing for maritime modulation of winter temperatures or to increased cloud cover during the winter months. Seasonal ice extent in the Arctic Ocean during the Pliocene is largely unknown (Zachos et al., 2008) and although a recent study by Abbot and Tziperman (2008) indicated that deep convective clouds can produce significant winter warming under ice-free conditions the climatic effects of both of these phenomena on Pliocene winter temperatures must be further investigated.

4. Summary and conclusions

The data we present provide constraints on the magnitude of Arctic Pliocene warmth, and on changes in Arctic hydrology associated with a warmer climate. Our temperature estimates (Table 3) indicate that the Pliocene climate of Ellesmere Island was similar to conditions experienced by modern boreal forests located ~15–20º further south. This is consistent with our surface water estimates (-20.7 to -22.6‰) that are also similar to $\delta^{18}O$ of water values from latitudes ~15–20º south of Strathcona Fiord. With mollusc growing season temperatures (inferred as May–Sept) on the order of 10.2–14.2 °C at paleolatitudes of 78° N, the Arctic Ocean was likely seasonally ice free (Haywood et al., 2009). Much greater estimates of ΔT are determined using proxies of MAT than proxies biased towards warmer months. This indicates that the difference between Pliocene and modern winter temperatures in the Arctic was greater than the difference between Pliocene and modern temperatures from warmer months. The Pliocene is a possible example of the temperatures that we may experience in the next century. Models of Pliocene climate are being constructed with an aim to improve model predictions of future climate by assessing the sensitivity of climate to forcings, such as, increased atmospheric CO_2 (Haywood et al., 2009; Jansen et al., 2007). Our study provides the first thermodynamically-based estimates of terrestrial Arctic surface-temperature and water $\delta^{18}O$ for the Pliocene, and the temperatures we estimate for Ellesmere Island provide some constraints on the magnitude of warming that might eventually occur in the Arctic if atmospheric CO_2 levels were stabilized at present levels.

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