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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.

Pliocene Ellesmere Island.

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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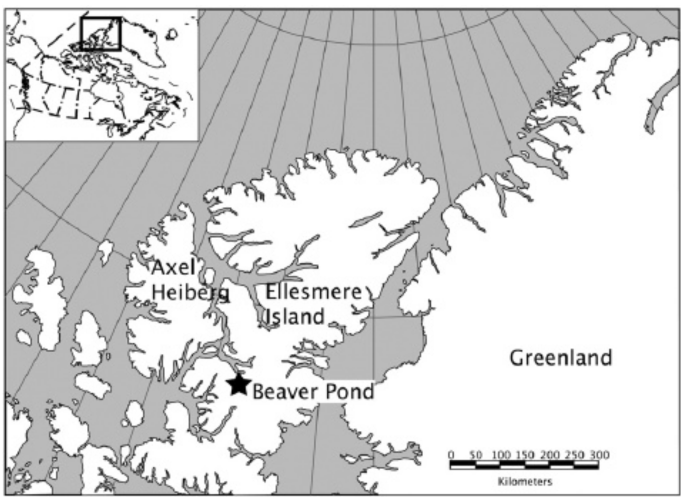

Fig. 1. Map showing the Beaver Pond locality at the head of Strathcona Fiord in central Ellesmere Island.

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 floodplain. 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 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

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; Whiteet al., 1999). The molluscs likely lived among the aquatic vegetation of the fen. Hydrologically a fen environment fed by groundwater is not as susceptible to large seasonal fluctuations in the $\delta^{18}O$ values of the 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; Tripatiet 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

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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; Huntingtonet al., 2009; Tripatiet 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 (Ghoshet 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

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
	Average	10.83	14.2 ± 0.7
Gyraulus albus	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
	Average	12.46	7.1 ± 0.5
Lymnae sp.	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
	Average	9.70	19.2 ± 0.8
Lymnae sp.	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 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 ThermoFinnigan TC/EA coupled to a ThermoFinnigan Delta Plus

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

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