



The environmental water of the middle Eocene Arctic: Evidence from δD , $\delta^{18}O$ and $\delta^{13}C$ within specific compounds

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ABSTRACT

The extensive vertical exposure (>150 m) of terrestrial sediments on Axel Heiberg Island, which contain thick fossiliferous lignites, presents an exceptional opportunity to follow the establishment and re-establishment of Arctic *Metasequoia* forests during the middle Eocene. We compared δD values in *n*-alkanes of chain length 23, 25, 27 and 29 with $\delta^{18}O$ values in phenylglucosazone (P-G) derived from α -cellulose; we also analyzed %-abundance of ferns, gymnosperms and angiosperms using pollen and spores isolated from each lignite. Our results showed that forest composition was altered upon uplift, as gymnosperms became more abundant within the relatively well-drained upland sediments. This was also reflected in the small (1‰), but significant, increase in the $\delta^{13}C$ value of TOM from lowland to upland environments. However, neither the δD values of *n*-alkanes nor the $\delta^{18}O$ in P-G were statistically different in the upland sediments, as compared to the lowland sediments; from this we inferred that the oxygen isotope signature of environmental water available to the forests for plant growth was relatively uniform throughout the time of the fossil forests. The δD value of environmental water implied by both *n*-alkanes and P-G ranged from –168 to –131‰ and was considerably enriched compared to all environmental water samples available from the modern Arctic region (<–180‰). In addition to indicating a warmer Eocene Arctic, subject to meteoric transport patterns different from today's, these results argue against the presence of an Eocene polar ice cap.

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1. Introduction

Evidence from plant fossils and paleogeographic studies indicates that a lush deciduous conifer forest existed well above the Arctic Circle during the middle Eocene (~45 Ma; Fig. 1; Basinger, 1986; Ricketts and McIntyre, 1986). The Buchanan Lake Formation, which crops out extensively on Axel Heiberg Island, contains more than 30 lignite layers comprised of exceptionally preserved fossil wood, forest litter and amber, many of which are meters in thickness and are horizontally continuous for kilometers (Jahren, 2007). With few exceptions, prior analyses of Axel Heiberg sediments come from the area around the “K–L–M” lignites, a ~5 m thick section within the ~150 m sequence of Buchanan Lake sediments (e.g., Williams et al., 2003). Here we report the results of novel compound-specific analyses across the full sedimentary record of the Arctic middle Eocene, as recovered from Axel Heiberg Island. We present the first detailed and complete stratigraphic section described for the Buchanan Lake Formation and include the first data detailing the isotopic composition of specific compounds with successive establishment of fossil forests

throughout the section. We interpret the results we see in terms of the contrasting ecosystems of meanderplain (lowland) forests, compared with alluvial fan (upland) forests, and the larger hydrological patterns of the Arctic middle Eocene.

2. Field site

The sediment of the Buchanan Lake Formation has been placed within the middle Eocene, based on the recognition of brontothere fossils associated with the upper strata (Eberle and Storer, 1999). Unfortunately, a refined estimate of the time represented by the 150+ m of vertical terrestrial deposits is extremely difficult, because of the large uncertainties associated with terrestrial sedimentation rates. The sequence represents sediment accumulation within a narrow intermontane basin (Fig. 2). The principal controls on sedimentation were differential uplift and elevation of source terrane along tectonic strike leading to aggradation on an alluvial plain (Ricketts, 1991); because the basin is small and tectonically-controlled, very high rates of sedimentation may apply (Blatt et al., 1980). For these reasons, most researchers have concluded that the sediments of the Buchanan Lake Formation represent geologically rapid cycles of forest establishment, coarser sediment deposition, and forest re-establishment. Tarnocai et al. (1991) examined silica content within paleosols near the top of the section, and

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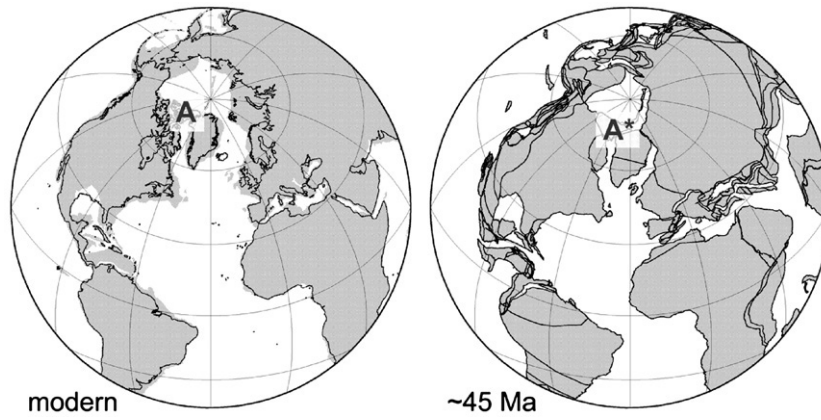


Fig. 1. Lambert azimuth map projections showing the location of the fossil forest site at present (A; 79°55'N) and during the time when the trees were alive (A'; ~45 Ma; 78.6 ± 1.6°N). Drawn using www.ods.de/ods.

concluded a soil development time of 10^3 to 10^4 yr, assuming that the silica resulted from a concentration of plant phytolith material. Based on the supposition of 50 paleosols, Ricketts (1991) ventured an estimate of 0.5 million years as the total accumulation rate of the Buchanan Lake

Formation. Given the above, we estimate that the 150+ vertical meters of sediment on Axel Heiberg Island constitute the remains of at least thirty distinct episodes of Arctic forestation that were established and re-established on thousand-to-ten-thousand year cycles.

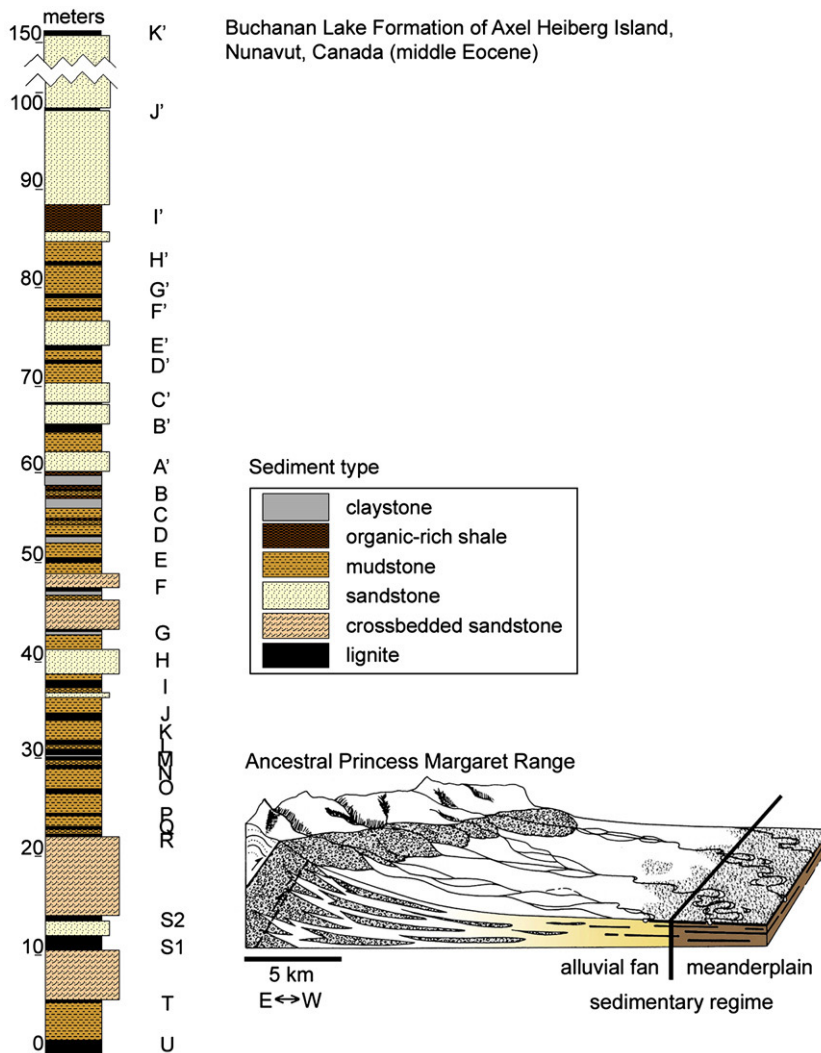


Fig. 2. Stratigraphic column of sedimentary units within the Buchanan Lake Formation of Axel Heiberg Island, Nunavut, Canada. The strata are middle Eocene in age (Eberle and Storer, 1999) and include a rotating sequence of claystones, shales, mudstones, sandstones and lignites, ranging from a few cm to > 10 m in thickness. The sequence shows two distinct sedimentary regimes associated with the Ancestral Princess Margaret Range: the lower portion of the column (below A'; <60 m) resulted from terrestrial deposition within a lowland meanderplain, the higher (above layer A'; 60 m and above) portions of the column correspond to relatively upland deposition within an alluvial fan (after Ricketts, 1991).

The depositional environment interpreted from sediment facies has historically been separated into two regimes (Ricketts, 1991): the coals (0–60 m) and the “prime” layers (60+ m; always labeled with a “prime” symbol). The “prime” layers (A' to K') are dominated by sandstones, often exhibiting crossbedding, with thick lignites interspersed. Because of the large grain size associated with the deposits, the “prime” portions of the section represent forests established within the alluvial fan, or relatively upland, sedimentary environment. The coals, rich with fining-upward mudstones and claystones interbedded with lignites, represent forests established within the meanderplain, or relatively lowland, sedimentary environment (Fig. 2). Because these changes in facies are continuous over several exposed kilometers, we believe the cause of change from lowland to upland regime was controlled by tectonic uplift of the basin, in agreement with previous structural characterizations of the area (Ricketts, 1994).

The extensive vertical exposure and exquisite preservation of the lignitic material within the Buchanan Lake Formation presents us with an excellent opportunity to look at trends in isotopic signatures within a successively re-establishing forests, changing from a floodplain (lowland) environment to an upland environment, as we move from the base of the section to the top, sampling each available lignite. We find evidence of a conifer forest, dominated by *Metasequoia*, with a diverse angiosperm and fern understory within each fossiliferous layer, but have further characterized the relative abundance of each group via palynological analysis. Because these forests thrived under an Arctic light regime for tens of thousands of years, the water source and availability to both upland and lowland forests present enigmatic environmental variables. Thus we have used oxygen and hydrogen isotopes in specific compounds to compare the environmental water within the upland forests to those which established within the lowland meanderplains, and to further characterize the entire region's paleohydrology.

3. Analytical approach and laboratory methods

We exploited several specific compounds in order to estimate the isotopic composition of environmental water available to the forests established within what are now the Buchanan Lake sediments. In order to reconstruct the δD signature of water available to support photosynthesis within leaves, we performed hydrogen isotope analysis upon *n*-alkanes of chain length 23, 25, 27 and 29. Similarly, in order to reconstruct the $\delta^{18}O$ signature of environmental water available to trees, we performed oxygen isotope analysis on phenylglucosazone (P-G), a compound derived from fossil cellulose with superior predictive power for $\delta^{18}O$ value of xylem water. Finally, we determined the $\delta^{13}C$ of both bulk terrestrial organic matter (TOM) and cuticle isolates within the lignite, in order to gain insight into the ecological status of the plant organisms. For *n*-alkane extraction, we used TOM isolated from lignite layers; for phenylglucosazone derivation, we used cellulose isolated from suitable fossil wood found within 17 lignite layers. Each dataset represents both upland and lowland depositional environments, as discussed above.

The lignites exploited for *n*-alkane analysis were composed of forest floor detritus (primarily leaves) from the fossil forest. While these leaves were alive, lipid biosynthesis incorporated meteoric water drawn into the plant at the root and transported by the stem to the leaf. After biosynthesis and excretion through the endoplasmic reticulum, lipids are deposited onto the leaf surface where they comprised essential components of the cuticular waxes that protect the plant against ultraviolet radiation, water saturation, and restrict the loss of moisture (Samuels and Kunst, 2003). This process would have involved minimal evapotranspiration effects due to the high paleohumidity of the site (Jahren and Sternberg, 2003; Jahren and Sternberg, 2008), but may have been subject to isotopic exchange with atmospheric water vapor. Although we tested a variety of terpenoid

lipids, we found that *n*-alkanes derived from acetate precursors were the optimal hydrogen isotopic carrier substances for comparisons across the entire sample set. *N*-alkanes are also the compound class least susceptible to hydrogen isotopic exchange over geological timescales (Sessions et al., 2004).

The appearance of the lignites sampled ranged from dry, loose, light brown ashy material (e.g., H layer) to dark brown, moist, planar fragments (e.g., F' layer). Samples were pulverized in a shatterbox for 1–2 min; ~12 g of each powdered sample was then packed into cells of a Dionex Accelerated Solvent Extractor 200. Because the samples were organic-rich, each sample was extracted three times with a mixture of dichloromethane and methanol (1:1) at 150 °C and 1500 psi. The resulting total lipid extract was separated using column chromatography on silica gel by elution with hexane (saturated hydrocarbons), hexane-dichloromethane (1:1, aromatic hydrocarbons) and dichloromethane-methanol (1:1, polar compounds). Following further separation by an additional column chromatography step using silica gel impregnated with 5% AgNO₃, fractions enriched in *n*-alkanes (hexane eluate) were quantified using gas chromatography with flame ionization detection (GC-FID). Each ‘alkane’ fraction was concentrated in an appropriate volume of hexane, from which an aliquot of 1 μ L was injected for each analysis. The amount of carbon in each *n*-alkane peak and each sample was then estimated using an external quantification standard, cholestane; or an internal quantification standard, 3-methylheneicosane (ai-C₂₂). Gas Chromatography-mass spectrometry analyses confirmed the identity of compounds that had been quantified by GC-FID.

H-isotopic analyses were conducted using a ThermoFinnigan Delta Plus XP Gas Chromatography–Pyrolysis–Isotope Ratio Mass Spectrometry system (GC–P–IRMS) following the methods, calibration and quality control protocols developed by Sessions et al. (1999a) and Schimmelmann et al. (2004). The analyses were not generally sample-limited; each sample was analyzed in triplicate using C₁₁, C₁₆ and C₂₀ fatty acid methyl esters as co-injected internal H-isotopic standards (FAME). Isotopic measurements for hydrogen are presented in standard delta-notation relative to Vienna Standard Mean Ocean Water (VSMOW). Details of all individual analyses and analytical uncertainties associated with δD measurements are available within Byrne (2005). Averaged over the period of all the analyses, the accuracy of δD measurements, determined by root-mean-square error in 15 reference *n*-alkanes in an external standard injected daily, was found to be 6.7 ± 2.7%.

Exceptionally-preserved fossil wood was isolated within 17 lignite layers, and identified as *Metasequoia*-type from thin section under optical microscope. Cellulose was extracted from whole fossil wood, and analyzed for $\delta^{18}O$ value using methods developed for Axel Heiberg samples and described within Jahren and Sternberg (2003, 2008). An aliquot (0.3 g) of the purified cellulose was used for hydrolysis and phenylglucosazone synthesis using methods described within Sternberg et al. (2007), and phenylglucosazone (P-G) was successfully purified from 12 of the lignite layers. The resultant compound lacks the oxygen attached to the second carbon of the cellulose–glucose moieties (C–O₂). This oxygen is subject to variable isotopic fractionations relative to other cellulose oxygen atoms and superimposes a biological signal upon the isotopic climate signal of cellulose (Sternberg et al., 2006, 2007). Thus phenylglucosazone, which lacks C–O₂, most accurately reflects the $\delta^{18}O$ value of water supplied to the tree during wood synthesis (Sternberg et al., 2007).

We used standard elemental analysis (EA–IRMS) to measure the $\delta^{13}C$ value of homogenized TOM from 22 lignites, and compared it to cuticle fragments of *Metasequoia* identified macroscopically, and isolated under microscope (after Arens and Jahren, 2000; Jahren et al., 2001; Arens and Jahren, 2002; Jahren et al., 2005) from 22 layers. In order to characterize the composition of the forest as preserved by each lignite, %-abundance of ferns, gymnosperms and angiosperms were determined from fossil pollen. Palynological samples were

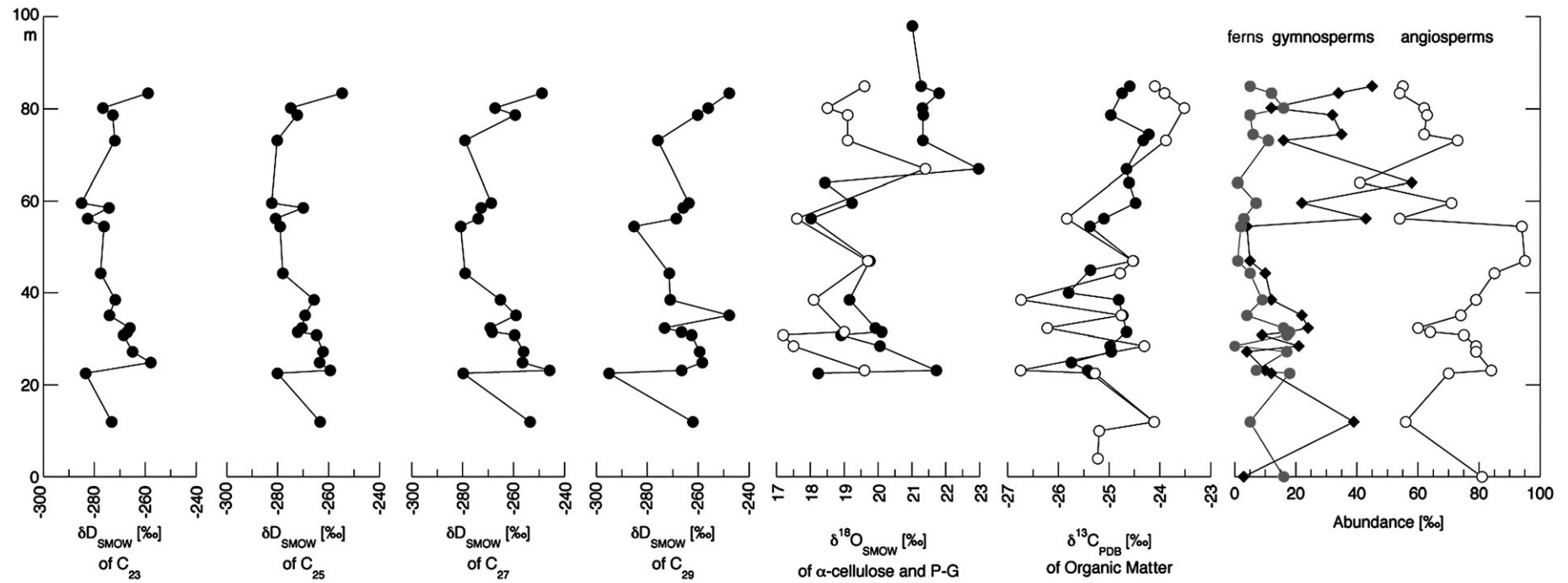


Fig. 3. The stable isotope composition of specific compounds vs. the stratigraphic position of sampled layers. From left to right: the hydrogen isotope composition of *n*-alkanes C₂₃; C₂₅; C₂₇; C₂₉ (error estimation discussed within Byrne, 2005); the carbon isotope composition of *Metasequoia* leaf cuticle (○) and bulk terrestrial organic matter (●) (values are subject to an analytical error of ±0.1‰); the oxygen isotope composition of α-cellulose (●) and phenylglucosazone (P-G) (○), isolated from fossil *Metasequoia* wood (values are subject to an analytical error of ±0.2‰). Also included are %-abundance determinations for fern (●), gymnosperm (◆) and angiosperm (○) flora.

prepared from each lignite after the methods of Bos et al. (2004) with an overnight treatment in hydrogen fluoride (HF) to remove the clastic material, and twice (before and after HF) in sodium pyrophosphate.

4. Results

Stable isotope values of *n*-alkanes, α -cellulose, phenylglucosazone (P-G), organic matter and %-abundance of flora are depicted according to position in the stratigraphic column in Fig. 3. Sixty meters represents the stratigraphic height of the change from lowland sediments to upland sediments, as depicted in Fig. 2. Therefore, all data below the line, represent components of the lowland forest ecosystem, whereas data above the line reflect the environment of the upland forest ecosystem. An unpaired two-tailed *t*-test and equal variance analysis (Table 1) revealed statistically different stable isotope values between lowland and upland sediments for $\delta^{18}\text{O}$ in α -cellulose and for $\delta^{13}\text{C}$ in terrestrial organic matter (TOM). In addition, %-abundance of both gymnosperms and angiosperms were significantly different within the lowland sediments, as compared to the “prime” layers. However, neither the δD values of *n*-alkanes nor the $\delta^{18}\text{O}$ in P-G were statistically different in the upland sediments, as compared to the lowland sediments. Based on these observations, we envisioned a change in the middle Eocene forests of Axel Heiberg correlated with the tectonic uplift of the basin, and the onset of upland sedimentation. The most obvious change was a change in the relative abundance of major types of flora: %-abundance of gymnosperms in upland forests were double that found within lowland forests, similarly %-abundance of angiosperms decreased by one-third upon transition to upland forests. The %-abundance of fern spores showed no significant difference, thus we concluded that forest composition was altered upon uplift, as gymnosperms became more abundant within the relatively well-drained upland sediments. This was also reflected in the small (1‰), but significant, increase in the $\delta^{13}\text{C}$ value of TOM from lowland to upland environments: conifers leaves have been shown to be enriched in ^{13}C relative to angiosperm leaves (Warren et al., 2001).

We observed that the $\delta^{18}\text{O}$ value of α -cellulose changed significantly upon conversion from lowland to upland environment, while the $\delta^{18}\text{O}$ value of P-G did not. Phenylglucosazone (P-G) is derived from α -cellulose by removing the oxygen atom attached to the second carbon atom of the cellulose–glucose moieties ($\text{C}-\text{O}_2$); we have shown that the isotopic fractionation of this oxygen atom differs from that of the other oxygen atoms by at least 9‰, relative to plant-available water (Sternberg et al., 2006).

Our work further showed that the magnitude of the isotopic fractionation associated with $\text{C}-\text{O}_2$ was related to the biosynthetic pathway used for cellulose construction: for example, plants remo-

bilizing storage compounds exhibited very different oxygen isotope fractionation than those using lipid precursors. When we derive P-G from α -cellulose we lose $\text{C}-\text{O}_2$ and thus lose the information about biosynthesis, leaving an improved indicator of environmental water $\delta^{18}\text{O}$ value (Sternberg et al., 2007). Therefore, because the $\delta^{18}\text{O}$ value of P-G did not change significantly upon conversion from lowland to upland forest (Fig. 3), we inferred that the oxygen isotope signature of environmental water available to the forests for plant growth also did not change upon uplift. Because all cellulose was extracted from *Metasequoia* fossil wood, the significant change in the $\delta^{18}\text{O}$ value of α -cellulose (3‰) implied a change in the metabolic functioning of the *Metasequoia*, probably the establishment of an upland ecotype. There is much work still to be done in order to quantify general relationships between biosynthetic processes and the oxygen isotope signature of $\text{C}-\text{O}_2$, however, this work demonstrates the likelihood of ecotypic specialization within *Metasequoia*, contemporaneous with a change in floral composition and sedimentary environment.

Within the lignites, we observed a very strong odd-over-even carbon number predominance for the waxy C_{23-33} *n*-alkanes as is characteristic of flora. The general predominance of *n*- C_{29} accords with the finding of Yang et al. (2005b), who observed that C_{29} predominance reflects the whole-leaf signature of *Metasequoia* spp., as opposed to leaf surfaces alone where C_{25} predominates. Within our samples, C_{29} is followed in abundance by C_{27} , C_{31} , C_{25} , C_{23} and C_{33} . Based on these observations, we can constrain the possible biological origins of the hydrocarbons. Given that there are comparatively few *n*-alkanes with a chain length $<\text{C}_{20}$, we conclude that cyanobacteria and other bacteria were minor contributors and that diagenetic and catagenetic alteration was minimal, consistent with the exceedingly mild thermal history of this deposit (Ricketts, 1991). Accordingly, microbial and abiotic contributions to the *n*-alkane hydrogen isotopic signal were negligible. The paucity of short-chain *n*-alkanes and bacteriohopanes reflect a limited bacterial presence, or rather, a plant source that overwhelmingly dominates any bacterial signal. Sessions et al. (1999a) noted that *n*-alkanes generally become more enriched in deuterium with longer chain lengths, a trend that is observed, but muted, in our data. For all the above reasons, we take the δD of *n*-alkanes within the lignites as a signal of the δD of environmental water available for plant growth at the site during the middle Eocene. Similar to our analyses of P-G, we found that the δD of *n*-alkanes did not change significantly upon conversion from lowland to upland forest (Fig. 3). These two independent lines of evidence showed that the isotope value of environmental water did not change upon uplift, and therefore represented a regional signal of water input to the area, as opposed to a local isotopically-heterogeneous input. Based on this, we used the δD of *n*-alkanes and the $\delta^{18}\text{O}$ value of P-G to reconstruct the isotopic composition of regional environmental water supplied to the Axel Heiberg forests during the middle Eocene.

5. Calculation of δD and $\delta^{18}\text{O}$ values of Eocene environmental water

Using published relationships, we calculated the oxygen and hydrogen isotope value of the environmental water available to forests throughout the time period preserved in Lake Buchanan formation sediments (Fig. 4). Several estimates of the hydrogen isotope fractionation between the δD of environmental water and the δD of vascular plant *n*-alkanes have been proposed (Table 2). Analyses of sediments have yielded widely divergent fractionations between *n*-alkanes of terrestrial or mixed origin and ambient water (Sauer et al., 2001; Huang et al., 2004; Sachse et al., 2006). The *n*-alkane data presented in Fig. 3 come from vascular terrestrial plants within a litter layer dominated by gymnosperm contributions. No difference in the hydrogen isotopic fractionation factor, however, has been observed between terrestrial angiosperm and gymnosperms (Chikaraishi and Naraoka, 2003; Bi et al., 2005). Presently, the most applicable values

Table 1

Significance (*p*-value) of difference between upland (<60 m) and upland (>60 m) sedimentary environment

Substrate	δD	$\delta^{18}\text{O}$	$\delta^{13}\text{C}$	% flora
C_{23} <i>n</i> -alkane	>0.050			
C_{25} <i>n</i> -alkane	>0.050			
C_{27} <i>n</i> -alkane	>0.050			
C_{29} <i>n</i> -alkane	>0.050			
α -cellulose		0.028		
P-G ^a		>0.050		
TOM ^b			0.006	
Cuticle			n.d. ^c	
Fern				>0.050
Gymnosperm				0.013
Angiosperm				0.006

^a Phenylglucosazone.

^b Terrestrial organic matter.

^c Insufficient measurements above 60 m to justify *p*-value calculation.

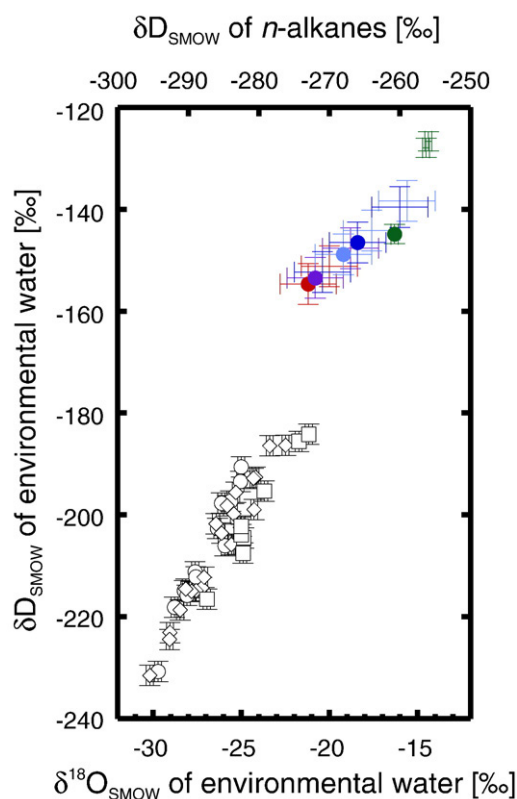


Fig. 4. Mean value of δD in long-chain n -alkanes (x_2 -axis) vs. value of δD in environmental water predicted using the average of α -values reported by Chikaraishi and Naraoka (2003); Smith and Freeman (2006) (y -axis); color-coded: ● = C_{23} ; ● = C_{25} ; ● = C_{27} ; ● = C_{29} . Samples are separated by lowland (●) and upland (no symbol) depositional environment; error = 4‰, the maximum propagated. The green points represent the mean predictions of $\delta^{18}O_{\text{environmental water}}$ from the $\delta^{18}O$ value of phenylglucosazone (x_1 -axis) using the relationship defined within (Sternberg et al., 2007). Samples are separated by lowland (●) and upland (no symbol) depositional environment; values are subject to an analytical error of $\pm 0.2\%$. The $\delta D_{\text{environmental water}}$ (y -axis) values for these data were calculated using the Meteoric Water Line with a slope of 9.5, as determined within (Jahren and Sternberg, 2003). Black data represent measured $\delta^{18}O$ (x_1 -axis) vs. measured $\delta D_{\text{environmental water}}$ (y -axis) from the modern Axel Heiberg site: □ = soil water; ○ = ice pack; ◇ = stream water; error bars represent analytical uncertainty of $\delta^{18}O$ ($= 0.2\%$) and δD ($= 2.0\%$) measurements.

for the alkane-environmental water fractionation factors are those reported by Chikaraishi and Naraoka (2003) and Smith and Freeman (2006), with $\alpha = \frac{R_{n\text{-alkane}}}{R_{\text{environmental water}}}$ ranging from 0.835 to 0.884 ($R = D/H$) specifically for terrestrial vascular plants. We note that preliminary studies of conifers grown under continuous light meant to simulate arctic environments during the PETM yielded n -alkane fractionations that were very low (Yang et al., 2005a), compared to those presented

above. However, further study is necessary to confirm what these studies suggest to be the strong influence of continuous light on both carbon and hydrogen fractionation during n -alkane synthesis. Chikaraishi et al. (2004b) observed different “classes” of hydrogen fractionation due to different biosynthetic pathways, and concluded that water efficiency and evapotranspiration are only minor factors, which argues against the existence of a wholly unique fractionation under continuous light.

Using the midpoint of the ranges discussed above ($= 0.860$), we reconstructed the δD value of environmental water. The range in average δD of our n -alkanes per stratigraphic layer is -285 to -253% . Therefore, using the above estimate of α , calculated $\delta D_{\text{environmental water}}$ ranges from -168 to -131% . This value overlaps with the range of $\delta D_{\text{environmental water}}$ estimates made using the $\delta^{18}O$ of phenylglucosazone (P-G; Fig. 4). We note that P-G, a product of wood synthesis, gives generally more enriched predictions than do n -alkanes, which can be explained by considering the timing of tissue synthesis. The n -alkanes studied are produced as leaf compounds, and therefore reflect environmental water during deciduous leaf construction, early in the short growing season. Wood construction is performed relatively late in the growing season, and at a more constant rate year round. Therefore, we see that n -alkanes are isotopically depleted in source water, compared to wood compounds, as is expected from the environmental difference between early precipitation inputs vs. year round averages. We note that relatively large uncertainties in fractionation factor arise from the 40‰ variability seen both between and within plant leaves (Sessions et al., 1999b; Sessions, 2006) and temper our claims regarding the δD value of Eocene environmental water accordingly.

For comparison to Eocene values, modern environmental water samples collected from Axel Heiberg Island were analyzed for $\delta^{18}O$ and δD using classical methods (Epstein and Mayeda, 1953; Coleman et al., 1982; Morrison et al., 2001) and are reported relative to VSMOW; soil water was extracted using vacuum techniques described within Mora and Jahren (2003). All reconstructions of fossil forest $\delta D_{\text{environmental water}}$ were enriched in deuterium and oxygen relative to values obtained from the site for modern soil water ($n=8$; average = -200%), stream water ($n=25$; average = -205%) and ice pack ($n=12$; average = -208%) across the 1999–2001 field seasons (Fig. 4). Soil water at plant rooting depth is isotopically invariant throughout the year, within mesic environments (Mora and Jahren, 2003). Today, the δD value of precipitation in the Axel Heiberg locale is approximately -220% (Bowen and Ravenaugh, 2003) or $-213 \pm 7\%$ (Global Network of Isotopes in Precipitation, 2001) as measured at Resolute Bay ($74.72^\circ N$ and $-94.98^\circ E$). Therefore, the observed and predicted δD values of environmental water fall into two distinct ranges: $< -200\%$ for modern Axel Heiberg Island; $> -168\%$ for the Arctic fossil forest.

One outstanding and important question is whether or not extensive snow and ice fields were present on Axel Heiberg during the Eocene? In order to comment, we examined the modern isotopic

Table 2
D/H fractionation in plant n -alkanes

Plant type	Species	ϵ (n -alkane–water) mean, range[δD ‰]	Source
Gymnosperms (C3)	<i>Cryptomeria japonica</i>	121, 91–152	Chikaraishi et al. (2004a)
Gymnosperms (C3)	<i>Chamaecyparis obtusa</i> , <i>Pinus thunbergii</i> , <i>Cryptomeria japonica</i>	116, 103–129	Chikaraishi and Naraoka (2003)
Angiosperms (C3)	<i>Acer argutum</i> , <i>Acer carpiniifolium</i> , <i>Acer palmatum</i> , <i>Albizia julibrissin</i> , <i>Artemisia princeps</i> , <i>Benthamedia japonica</i> , <i>Camellia sasanqua</i> , <i>Manihot utilissima</i> , <i>Phragmites communis</i> , <i>Plantago asiatica</i> , <i>Prunus jamasakura</i> , <i>Quercus acutissima</i> , <i>Quercus mongolica</i> , <i>Quercus dentata</i> , <i>Taraxacum officinale</i>	117, 90–114	Chikaraishi and Naraoka (2003)
Angiosperms (C4)	<i>Miscanthus sinensis</i> , <i>Saccharum officinarum</i> , <i>Sorghum bicolor</i> , <i>Zea mays</i> , <i>Zoysia japonica</i>	132, 120–144	Chikaraishi and Naraoka (2003)
Freshwater (CAM ^a)	<i>Hydrilla verticillata</i> , <i>Potamogeton perfoliatus</i> , <i>Vallisneria asiatica</i>	135, 118–152	Chikaraishi and Naraoka (2003)
Marine (CAM)	<i>Binghamia californica</i> , <i>Gelidium japonicum</i> , <i>Undaria pinnatifida</i>	155, 121–189	Chikaraishi and Naraoka (2003)
Gymnosperms (C3)	<i>Larix</i> sp., <i>Metasequoia</i> sp., <i>Taxodeum</i> sp.	^b , 43–87	Yang et al. (2005a)

^a Reported as C3 within Chikaraishi and Naraoka (2003); however $\delta^{13}C$ bulk = -14.6 to -16.5% .

^b No mean value reported.

patterns of continental snow and ice fields with latitude. We compiled data from a glacier inventory database (National Snow and Ice Data Center, 1999, recently updated 2005) for the presence of snow and ice fields at various latitudes and altitudes. We are interested in low elevation environments, similar to the low-lying floodplains of the Axel Heiberg fossil forest (modern elevation=200 m; reconstructed elevation <100 m), although we did not place any altitudinal limit on our data compilation. However, we did confine our search to the Northern hemisphere, citing the similarity between Eocene plate position and modern continental configuration. At elevations consistent with the floodplain of the fossil forest, ~200 m and below, modern snow and ice fields appear primarily at latitudes $\geq 75^\circ$ and above. A single exception is the rough terrain within Kate's Needle Creek in British Columbia, Canada where glaciers meet the ocean at $\sim 57^\circ\text{N}$ latitude; we consider this a thoroughly dissimilar environment to the relatively flat topography of the fossil forest landscape.

We used the Bowen–Wilkinson equation (Bowen and Wilkinson, 2002) to calculate the expected oxygen isotope ratios of precipitation ($\delta^{18}\text{O}$) at the latitudes (LAT) and minimum altitudes (ALT) of the snow and ice fields above designated by the analysis above:

$$\delta^{18}\text{O}[\text{‰}] = (-0.0051 \times \text{LAT}^2) + (0.1805 \times \text{LAT}) + (-0.002 \times \text{ALT}) - 5.247$$

The expected hydrogen isotope ratios of the precipitation (δD) was then calculated by using the linear relationship given by the global meteoric water line (GMWL) first established by Craig (1961):

$$\delta^{18}\text{O}[\text{‰}] = m\delta^{18}\text{O} + 10$$

Because our previous analyses of oxygen and hydrogen isotope ratios within fossil forest cellulose samples suggested that the local meteoric water line (LMWL) during the Eocene at Axel–Heiberg had a slope of 9.5 (Jahren and Sternberg, 2008) we calculated the expected δD based on $m=9.5$. The δD values of Eocene precipitation currently only sustain significant snow and ice fields with a minimum altitude of ~1000 m, which is a much greater altitude than the low-lying floodplain reconstructed for the Axel Heiberg forest during the Eocene (Ricketts, 1991). Based on the general similarity between Eocene and modern tectonic plate configurations, we believe that this lack of overlap implies a middle Eocene Arctic lacking in snowfall, and probably lacking sufficient accumulation for an ice pack or a glacier.

Paleobotanists noted that the preserved tree stumps lacked late wood, a relatively hard accretion that occurs in response to frost (Basinger, 1991), and have therefore interpreted a frost-free palaeoenvironment. However, they have also shown that the diameter of trachea within fossil wood is well below the threshold for frost embolism, implying the ability of these forests to survive frost conditions (Jagels et al., 2001). Multiple proxy data based on nearest living relatives for the period indicate that temperatures did not drop below freezing in the continental interiors (Greenwood and Wing, 1995), and models have attempted to explain this (e.g., Sewall and Sloan, 2004). Our data suggest the possibility of a global, spatially equable climate system during the middle Eocene, which enabled this ecosystem to thrive above the Arctic circle at temperatures warm enough to prevent the extensive buildup of ice and snow, even through three months of darkness.

6. Conclusions

Our analyses indicate an upland ecotype higher in gymnosperm abundance, compared to the lowland meanderplains, preserved by the lignite sequences of the Buchanan Lake Formation on Axel Heiberg Island. As the *Metasequoia* Arctic forest established and rapidly re-established through the middle Eocene, it effectively colonized all areas of the tectonically-active basin. Our study represents the first comparison of stable isotopes in *n*-alkanes, phenylglucosazone and isolated

cuticle from the same sedimentary substrate, and finds excellent agreement in stratigraphic pattern, revealing a coherent environmental water signal in both leaf wax and wood tissues. Furthermore, the oxygen and hydrogen isotopic composition of environmental water implied by our proxy analyses, point towards an Arctic Eocene subject to higher temperatures and different meteoric patterns, relative to today's Arctic, as well as a general paucity of polar ice.

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References

- Arens, N.C., Jahren, A.H., 2000. Carbon isotopic excursion in atmospheric CO_2 at the Cretaceous–Tertiary boundary: evidence from terrestrial sediments. *Palaios* 15 (4), 314–322.
- Arens, N.C., Jahren, A.H., 2002. Chemostratigraphic correlation of four fossil-bearing sections in southwestern North Dakota. In: Hartman, J.H., Johnson, K.R., Nichols, D.J. (Eds.), *The Hell Creek Formation and the Cretaceous–Tertiary Boundary in the Northern Great Plains: An Integrated Record of the End of the Cretaceous*. Geological Society of America Special Paper, Boulder, Colorado, pp. 75–93.
- Basinger, J.F., 1986. Our "tropical" Arctic. *Canadian Geology* 106, 28–37.
- Basinger, J.F., 1991. The fossil forests of the Buchanan Lake Formation (early Tertiary), Axel Heiberg Island, Canadian Arctic Archipelago: preliminary floristics and paleoclimate. In: Christie, R.L., McMillan, N.J. (Eds.), *Tertiary Fossil Forests of the Geodetic Hills, Axel Heiberg Island, Arctic Archipelago*. Geological Survey of Canada, pp. 39–65.
- Bi, X., Sheng, G., Liu, X., Li, C., Fu, J., 2005. Molecular and carbon and hydrogen isotopic composition of *n*-alkanes in plant leaf waxes. *Organic Geochemistry* 36, 1405–1417.
- Blatt, H., Middleton, G., Murray, R., 1980. *Origin of Sedimentary Rocks*. Prentice-Hall, Inc., Englewood Cliffs, New Jersey, 782 pp.
- Bos, J.A.A., Dickson, J.H., Coope, G.R., Jardine, W.G., 2004. Flora, fauna and climate of Scotland during the Weichselian Middle Pleniglacial – palynological, macrofossil and coleopteran investigations. *Palaeogeography, Palaeoclimatology, Palaeoecology* 204, 65–100. doi:10.1016/S0031-0182(03)00724-7.
- Bowen, G.J., Wilkinson, B.H., 2002. Spatial distribution of $\delta^{18}\text{O}$ in meteoric precipitation. *Geology* 30 (4), 315–318.
- Bowen, G.J., Ravenaugh, J., 2003. Interpolating the isotopic composition of modern meteoric precipitation. *Water Resources Research* 39 (10), 1299. doi:10.1029/2003WR002086.
- Byrne, M.C., 2005. A stable isotope stratigraphy of the Axel Heiberg fossil forest and its application to Eocene climate. Master's Thesis, Massachusetts Institute of Technology, Boston.
- Chikaraishi, Y., Naraoka, H., 2003. Compound-specific δD – $\delta^{13}\text{C}$ analyses of *n*-alkanes extracted from terrestrial and aquatic plants. *Phytochemistry* 63 (3), 361–371.
- Chikaraishi, Y., Naraoka, H., Poulson, S.R., 2004a. Carbon and hydrogen isotopic fractionation during lipid biosynthesis in a higher plant (*Cryptomeria japonica*). *Phytochemistry* 65, 323–330.
- Chikaraishi, Y., Naraoka, H., Poulson, S.R., 2004b. Hydrogen and carbon isotopic fractionations of lipid biosynthesis among terrestrial (C3, C4 and CAM) and aquatic plants. *Phytochemistry* 65, 1369–1381.
- Coleman, M.L., Shepherd, T.J., Durham, J.J., Rouse, J.E., Moore, G.R., 1982. Reduction of water with zinc for hydrogen isotope analysis. *Analytical Chemistry* 54, 993–995.
- Craig, H., 1961. Isotopic variations in meteoric waters. *Science* 133, 1702–1703.
- Eberle, J.J., Storer, J.E., 1999. Northernmost record of brontotheres, Axel Heiberg Island, Canada—implications for age of the Buchanan Lake Formation and brontothere paleobiology. *Journal of Paleontology* 73 (5), 979–983.
- Epstein, S., Mayeda, T., 1953. Variations of ^{18}O content of water from natural sources. *Geochimica et Cosmochimica Acta* 54, 1845–1846.
- Global Network of Isotopes in Precipitation, 2001. International Atomic Energy Agency and the World Meteorological Organization.
- Greenwood, D.G., Wing, S.L., 1995. Eocene continental climates and latitudinal temperature gradients. *Geology* 23 (11), 1044–1048.
- Huang, Y., Shuman, B., Wang, Y., Webb III, T., 2004. Hydrogen isotope ratios of individual lipids in lake sediments as novel tracers of climatic and environmental change: a surface sediment test. *Journal of Paleolimnology* 31, 363–375.
- Jahren, A.H., 2007. The Arctic forest of the middle Eocene. *Annual Review of Earth and Planetary Sciences* 35, 509–540.
- Jahren, A.H., Sternberg, L.S.L., 2003. Humidity estimate for the middle-Eocene Arctic rainforest. *Geology* 31 (5), 463–466.
- Jahren, A.H., Sternberg, L.S.L., 2008. Annual patterns within tree rings of the Arctic Middle Eocene (~45 Ma): Isotopic signatures of precipitation, relative humidity, and deciduousness. *Geology* 36 (2), 99–102. doi:10.1130/G23876A.1.
- Jahren, A.H., Arens, N.C., Sarmiento, G., Guerrero, J., Amundson, R., 2001. Terrestrial record of methane hydrate dissociation in the Early Cretaceous. *Geology* 29 (2), 159–162.

- Jahren, A.H., Conrad, C.P., Arens, N.C., Mora, G., Lithgow-Bertelloni, C.R., 2005. A plate tectonic mechanism for methane hydrate release along subduction zones. *Earth and Planetary Science Letters* 236 (3–4), 691–704.
- Mora, G., Jahren, A.H., 2003. Isotopic evidence for the role of plant development on transpiration in deciduous forests of southern United States. *Global Biogeochemical Cycles* 17 (2) Art. No. GB1044.
- Morrison, J., Brockwell, T., Merren, T., Fourel, F., Phillips, A.M., 2001. On-line high-precision stable hydrogen isotopic analyses on nanoliter water samples. *Analytical Chemistry* 73, 3570–3575.
- Ricketts, B.D., 1991. Sedimentation, Eureka tectonism and the fossil forest succession on eastern Axel Heiberg Island, Canadian Arctic Archipelago. In: Christie, R.L., McMillan, N.J. (Eds.), *Tertiary Fossil Forests of the Geodetic Hills, Axel Heiberg Island, Arctic Archipelago*. Geological Survey of Canada, pp. 1–27.
- Ricketts, B.D., 1994. Basin analysis, Eureka Sound Group, Axel Heiberg and Ellesmere Islands, Canadian Arctic Archipelago. *Geological Society of Canada Memoir*, vol. 439, p. 119.
- Ricketts, B.D., McIntyre, D.J., 1986. The Eureka Sound Group of eastern Axel Heiberg Island: new data on the Eureka Orogeny, Current research, part B. *Geological Survey of Canada*, pp. 405–410.
- Sachse, D., Radke, J., Gleixner, G., 2006. δD values of individual n-alkanes from terrestrial plants along a climatic gradient: Implications for the sedimentary biomarker record. *Organic Geochemistry* 37 (4), 469–483.
- Samuels, A.L., Kunst, L., 2003. Wax biosynthesis and secretion in plants. *Progress in Lipid Research* 42, 51–80.
- Sauer, P.E., Eglinton, T.L., Hayes, J.M., Schimmelmann, A., Sessions, A.L., 2001. Compound-specific D/H ratios of lipid biomarkers from sediments as a proxy for environmental and climatic conditions. *Geochimica et Cosmochimica Acta* 65, 213–222.
- Schimmelmann, A., et al., 2004. D/H ratios in terrestrially sourced petroleum systems. *Organic Geochemistry* 35 (10), 1160–1195.
- Sessions, A.L., 2006. Seasonal changes in D/H fractionation accompanying lipid biosynthesis in *Spartina alterniflora*. *Geochimica et Cosmochimica Acta* 70 (9), 2153–2162. doi:10.1016/j.gca.2006.02.003.
- Sessions, A., Burgoyne, T.W., Schimmelmann, A., Hayes, J.M., 1999a. Fractionation of hydrogen isotopes in lipid biosynthesis. *Organic Geochemistry* 30, 1193–1200.
- Sessions, A.L., Burgoyne, T.W., Schimmelmann, A., Hayes, J.M., 1999b. Fractionation of hydrogen isotopes in lipid biosynthesis. *Organic Geochemistry* 30 (9), 1193–1200.
- Sessions, A.L., Sylva, S.P., Summons, R.E., J.M., H., 2004. Isotopic exchange of carbon-bound hydrogen over geological timescales. *Geochimica et Cosmochimica Acta* 68, 1545–1559.
- Sewall, J.O., Sloan, L.C., 2004. Less ice, less tilt, less chill: the influence of a seasonally ice-free Arctic Ocean and changing obliquity on early Paleogene climate. *Geology* 32, 477–480.
- Smith, F.A., Freeman, K.H., 2006. Influence of physiology and climate on δD of leaf wax n-alkanes from C3 and C4 grasses. *Geochimica et Cosmochimica Acta* 70 (5), 1172–1187.
- Sternberg, L.D.L., et al., 2007. Oxygen isotope ratios of cellulose-derived phenylglucosazone: an improved paleoclimate indicator of environmental water and relative humidity. *Geochimica et Cosmochimica Acta* 71, 2463–2473.
- Sternberg, L.S.L., Pinzon, M.C., Anderson, W.T., Jahren, A.H., 2006. Variation in oxygen isotope fractionation during cellulose synthesis: molecular and biosynthetic effects. *Plant, Cell and Environment* 29, 1881–1889.
- Tarnocai, C., Kodama, H., Fox, C., 1991. Characteristics and possible origin of the white layers found in the fossil forest deposits, Axel Heiberg Island. In: Christie, R.L., McMillan, N.J. (Eds.), *Tertiary fossil forests of the Geodetic Hills, Axel Heiberg Island, Arctic Archipelago*. Geological Survey of Canada Special Publication, Ottawa, Canada, pp. 189–200.
- Warren, C.R., McGrath, J.F., Adams, M.A., 2001. Water availability and carbon isotope discrimination in conifers. *Oecologia* 127, 476–486.
- Williams, C.J., Johnson, A.H., LePage, B.A., Vann, D.R., Sweda, T., 2003. Reconstruction of Tertiary *Metasequoia* forests II. Structure, biomass, and productivity of Eocene floodplain forests in the Canadian Arctic. *Paleobiology* 29 (2), 271–292.
- Yang, H., Equiza, M.A., Jagels, R., Pagani, M., Briggs, D.E.G., 2005a. Carbon and hydrogen isotopic compositions of deciduous conifers under a continuous-light environment: implications for the interpretation of the high-latitude plant isotope record at PETM. 2005 Salt Lake City Annual Meeting (October 16–19, 2005) Paper No. 186-3.
- Yang, H., Huang, Y., Leng, Q., LePage, B.A., Williams, C.J., 2005b. Biomolecular preservation of Tertiary *Metasequoia* fossil Lagerstätten revealed by comparative pyrolysis analysis. *Review of Palaeobotany and Palynology* 134, 237–256.