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Palaeogeography, Palaeoclimatology, Palaeoecology 214 (2004) 347–358

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Methanogenesis in Eocene Arctic soils inferred from $\delta^{13}C$ of tree fossil carbonates

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Received 9 July 2003; received in revised form 7 July 2004; accepted 21 July 2004

Abstract

We report on the carbon and oxygen stable isotope composition of fossil tree material collected at the White Mountain locality of the Buchanan Lake Formation on Axel Heiberg Island in the High Arctic of Canada. The fossils are Middle Eocene in age and have been permineralized with carbonate. Microscopic examination of fossils revealed them to be the remains of *Metasequoia* stems, composed of secondary carbonate (calcite) and original wood intermingled at the cellular level. Because the specimens show little compression, crushing, or tissue degradation, we believe that carbonate permineralization occurred soon after burial, and therefore provides insight into Eocene carbon cycling at the locality. The carbon isotope signature of the carbonate suggests that methanogenesis resulted in a ^{13}C-enriched CO_2 pool that equilibrated with soil water and gave rise to unusually ^{13}C-enriched $CaCO_3$. Tree fossil carbonate exhibited strikingly high $\delta^{13}C$ values (+4.0 to +7.4‰) compared to published Phanerozoic pedogenic carbonate $\delta^{13}C$ values. These $\delta^{13}C$ values, in conjunction with fractionation factors (α) previously determined for carbonate precipitation and methanogenic pathways, indicate an Eocene soil CO_2 pool containing 80–95% CO_2 produced as a by-product of acetate-fermentation methanogenesis. Because methane in the atmosphere is a powerful greenhouse gas, we suggest that methane emissions from Axel Heiberg soils contributed to the relatively warm Arctic climate during the Middle Eocene.

Keywords: Eocene; Arctic; Paleosol; Carbon isotope; Methanogenesis

1. Introduction

The fossiliferous sediments of the Middle Eocene (Lutetian/Uintan; 41.3–47.5 Ma; Harrison et al., 1999) Buchanan Lake Formation are best known from Napartulik, Axel Heiberg Island, Nunavut, Canada (Fig. 1). Although the plant-rich sediments

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doi:10.1016/j.palaeo.2004.07.030

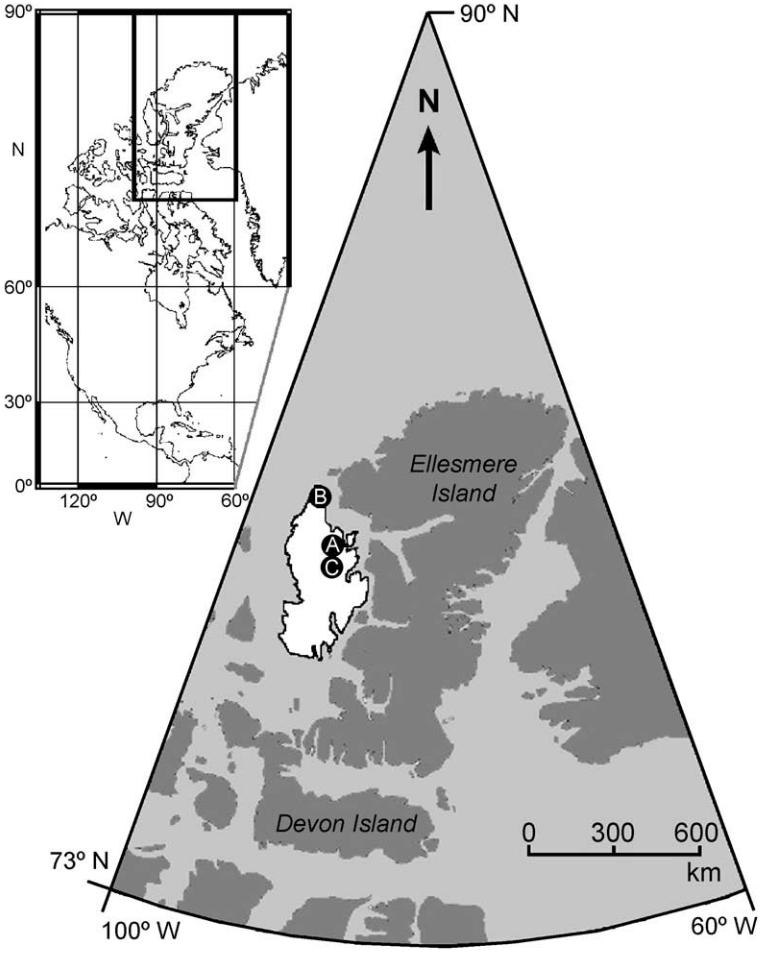

Fig. 1. Map of Axel Heiberg Island (shown in white) with White Mountain (A), Svartevaeg Cliffs (B), and Napartulik (C) fossil localities identified.

assigned to the Buchanan Lake Formation occur at a number of localities throughout Axel Heiberg and Ellesmere islands, the best and most complete forest preservation occurs at Napartulik. Buchanan Lake sediments at Napartulik contain the spectacular in situ remains of hundreds of *Metasequoia* (Dawn Redwood) trees. These lowland Taxodiaceae-dominated forests grew at a paleolatitude of 77°N under alternating conditions of total winter darkness and continuous summer light. Studies associated with this site have resulted in a number of monographs on the evolutionary and biogeographic history of some of the taxa, as well as a number of papers dealing with the paleoecology of the site (e.g., Francis, 1991; Greenwood and Basinger, 1994; LePage, 2001; LePage and Basinger, 1995; Williams et al., 2003a). The forest-bearing sediments are spatially extensive and contain large quantities of mummified litter, stumps, boles, roots, seeds, cones, rhizomes, soil-organic matter, and fossilized resin. The preservation of these fossils indicates little diagenesis beyond drying (Jagels et al., 2001) and presents a unique opportunity to apply stable isotope techniques usually reserved for much geologically younger specimens. For example, cellulose extracted from Napartulik fossils has been analyzed for δD and δ^{18}O value (Jahren and Sternberg, 2002; Jahren and Sternberg, 2003); silica phytoliths from Napartulik paleosols have been analyzed for δ^{18}O value (Kodama et al., 1992).

Here we use the carbon stable isotope composition of carbonate and organic carbon within tree fossils to infer soil carbon cycling processes during the Middle Eocene. The fossils were recovered from a bimodal fine-and-coarse-grained unit sitting atop a thick, framework-supported conglomerate unit at the White Mountain site, located just north of the Napartulik site, within the Buchanan Lake Formation of Axel Heiberg Island (Fig. 1 and Ricketts, 1994). These *Metasequoia* tree fossils are composed of intertwined undecomposed wood and secondary carbonate (Fig. 2A–C). While mummified wood is common in strata of the Buchanan Lake Formation, the fossils at the White Mountain locality are striking because most pieces have been permineralized with carbonate, showing little distortion of the original morphology of the wood (Fig. 2). The individual growth rings occlude varying amounts of organic matter (5–55% by mass) and preserve the original anatomical details of the wood. The co-occurrence of organic carbon and carbonate indicates that the fossils have preserved part of the original carbon sequestered during the life of the tree as well as carbon that was cycled within the ecosystem, allowing for insight into both processes via stable isotope measurements.

2. Materials and methods

Three specimens of carbonate-permineralized fossil wood from the White Mountain locality ("Fossils A, B, and C"; Fig. 2) were chosen for stable isotope analysis because the secondary carbonate in these fossils formed particularly well-defined rings. Previous isotopic studies have shown that growth rings preserve a more temporally uniform carbon isotope signature than fine carbonate in the same settings (Pendall et al., 1994). Moreover, permineralized rings have been shown to be less subject to dissolution than disseminated carbonate (Chadwick et al., 1987). Examination

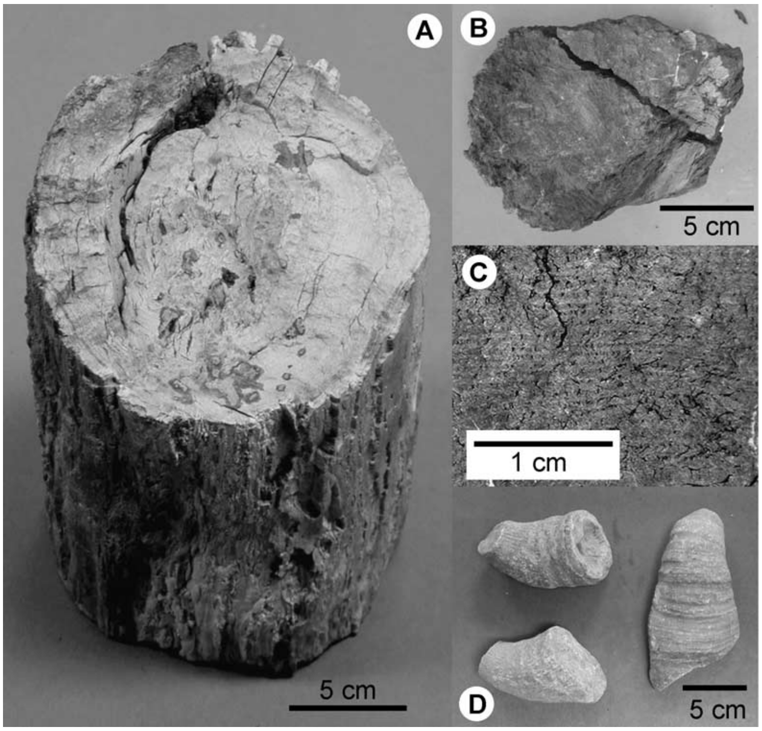

Fig. 2. *Metasequoia* fossils permineralized with carbonate: Fossils A, B, and C are from the White Mountain locality on Axel Heiberg Island. Secondary carbonate is finely intermingled with fossil wood and specimens have not been distorted or crushed, indicating that permineralization occurred soon after burial. Permian marine carbonate fossils from Svartevaeg Cliffs within the Sverdrup Basin of the Princess Margaret range (D) were analyzed for comparison to the Buchanan Lake Formation tree fossil carbonates.

of fossils in transection revealed them to be stem material from conifer trees of probable *Metasequoia* type based on the presence of uniseriate ray cells irregularly interspersed with ordered tracheids (Fig. 3 and Wilson and White, 1986). Estimates of the minimum number of growth rings in the samples indicated that the trees were at least 50–75 years of age when they died. X-ray diffraction showed the carbonate rings to be composed exclusively of calcite. Petrographic examination of thin sections from specimens revealed that secondary carbonate replacement has preserved the microscopic anatomy of the wood and resulted in micron-scale intermingling of carbonate with the original wood material; the intricate morphology of the plant fossil secondary carbonate contrasted sharply with the homogeneous texture apparent in Princess Margaret range Permian carbonate of Axel Heiberg Island (Fig. 3). The specimens showed very little compression, crushing, or tissue degradation, indicating that the permineralization occurred soon after burial, prior to any crushing or flattening processes commonly associated with most Napartulik plant fossils. Based on these observations, we concluded that the permineralization occurred rapidly in a subsoil or shallow aqueous environment, prior to deformation associated with burial. Therefore, the secondary carbonate of the fossils formed during active pedogenesis within the soil or as the result of very shallow groundwater interacting with the soil environment or through some combination. We expect that the ultimate source of carbon for carbonate precipitation was most likely microbially cycled organic matter, given the large amount of organic matter contributed annually to the carbon-rich soils supporting the *Metasequoia* deciduous ecosystem (Francis, 1991; Williams et al., 2003a). The nearest potential source of parent-material carbonate is within the Princess Margaret range, located ~40 km west of the fossil location. In order to evaluate the stable isotope composition of this potential carbonate influence, we have analyzed marine carbonate from the Permian succession at Svartevaeg Cliffs within the Sverdrup Basin of the Princess Margaret range (Figs. 1 and 2D, and LePage et al., 2003).

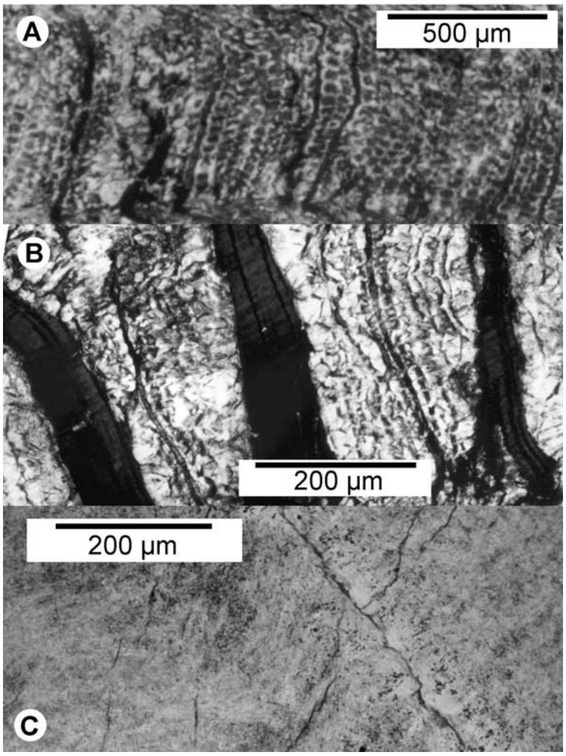

Fig. 3. Petrographic thin sections of specimens analyzed for stable isotope composition; photographs were taken with crossed polars. Examination of transections of tree fossils using petrographic microscopy revealed irregularly spaced uniseriate ray cells composed of the original wood material interspersed with rounded tracheids that have been replaced by secondary carbonate (A). Fossils A, B, and C all showed groups of tracheids and adjacent ray cells composed of the original wood material separated by carbonate-replaced tracheids (B). The thickness of the cell walls suggests that the original wood material is best preserved in the late-wood portion of the fossils. In contrast, thin sections of Permian marine carbonate from the Princess Margaret range appeared homogeneous in texture at similar magnification (C).

Fossilized wood and secondary carbonate were sampled from the three specimens along transects spanning the longest axis of each fossil using dentistry picks and chisels. Transect paths were chosen to maximize wood content and to sample across the maximum number of carbonate rings possible. Approximately 5 g of the organic woody tissue was sampled at each point in the transect. These samples were then ground and thoroughly acidified in 1 M HCl for 72 h to remove carbonate. Carbonate samples (5 g each) from tree fossils and from Permian marine fossils were ground to a fine powder using a mortar and pestle. Organic samples were analyzed in triplicate using a Eurovector automated combustion system; combustion also resulted in a quantification of %C in each sample (all values ±1% C analytical

Table 1
Stable isotope analyses of carbonate from Axel Heiberg Island

Carbonate specimen	$\delta^{13}C$ (‰)	$\delta^{18}O$ (‰)
White Mountain Fossil A (n=20)	7.3	−22.0
	5.8	−22.1
	6.8	−22.2
	5.7	−22.4
	6.6	−22.6
	7.4	−22.3
	6.4	−22.5
	6.5	−22.4
	6.8	−22.2
	7.3	−21.9
	6.3	−23.1
	6.3	−22.6
	6.6	−22.1
	6.7	−22.9
	6.4	−22.3
	7.1	−22.2
	7.2	−22.2
	6.9	−22.7
	7.0	−22.6
	6.8	−22.3
Mean±σ[a]	6.7±0.5	−22.4±0.3
White Mountain Fossil B (n=15)	7.7	−21.7
	7.5	−21.6
	7.7	−21.6
	7.7	−21.7
	7.6	−21.8
	7.7	−21.6
	7.3	−21.6
	7.7	−21.7
	6.7	−21.5
	7.3	−21.6
	7.5	−21.9
	6.1	−21.6
	7.1	−21.4
	7.1	−21.5
	7.7	−22.1
Mean±σ[a]	7.4±0.5	−21.7±0.2
White Mountain Fossil C (n=9)	4.2	−20.5
	4.3	−20.4
	3.7	−20.7
	4.0	−20.4
	4.0	−20.4
	4.0	−20.3
	4.0	−20.3
	3.8	−20.1
	3.9	−20.2
Mean±σ[a]	4.0±0.2	−20.4±0.2
Permian marine carbonate (n=6)	1.0	−6.2
	1.0	−6.1
	0.9	−8.2
	0.6	−8.4
	0.7	−8.4
	−1.2	−9.2
Mean±σ[a]	0.5±0.8	−7.8±1.3

[a] σ represents the standard deviation seen in n isotopic measurements for the sample.

uncertainty). Carbonate subsamples were analyzed in triplicate by reaction in evacuated vessels with 5–10 cm^3 of 100% phosphoric acid for 24 h at 25 °C (McCrea, 1950). Resultant purified CO_2 gas was analyzed for $^{13}C/^{12}C$ in the case of organic samples and carbonates, and for $^{18}O/^{16}O$ in the case of carbonates, using an Isoprime SIRMS at the Johns Hopkins University. Precision associated with measurements was within ±0.1‰ in all cases; isotopic variability between replicate samples was observed to be within 0.1‰ for both carbon and oxygen isotopes. All results are reported in standard isotopic δ-notation

Table 2
Stable isotope and TOC analyses of fossil wood from Axel Heiberg Island

Fossil wood specimen	$\delta^{13}C$ (‰)	%C (by mass)
White Mountain Fossil A (n=11)	−23.8	63
	−23.6	58
	−23.9	61
	−23.3	62
	−24.0	60
	−23.5	63
	−23.8	61
	−23.8	57
	−24.1	58
	−24.2	59
	−24.0	63
Mean±σ[a]	−23.8±0.3	60±2.2
White Mountain Fossil B (n=5)	−23.9	59
	−23.1	57
	−22.7	58
	−24.0	58
	−23.8	57
Mean ± σ[a]	−23.5±0.5	58±0.8
White Mountain Fossil C (n=5)	−23.9	62
	−24.2	57
	−23.8	59
	−23.5	58
	−23.6	61
Mean±σ[a]	−23.8±0.3	59±2.1

[a] σ represents the standard deviation seen in n isotopic measurements for the sample.

(‰) relative to the Vienna Peedee belemnite standard (VPDB):

$$\delta(‰) = \left[\left(\frac{R_{\text{sample}}}{R_{\text{standard}}}\right) - 1\right]1000. \quad (1)$$

3. Results

Stable isotope analyses of tree fossil carbonate yielded a narrow range of $\delta^{13}C_{VPDB}$ and $\delta^{18}O_{VPDB}$ values (Table 1). The mean oxygen isotope values of carbonate sampled across Fossils A, B, and C were all within 2 ‰: Fossil A $\delta^{18}O_{cc}$=−22.4±0.3‰ (mean ± σ [standard deviation], n=20); Fossil B $\delta^{18}O_{cc}$=−21.7±0.2‰ (mean ± σ, n=15); Fossil C $\delta^{18}O_{cc}$=−20.4±0.2‰ (mean ± σ, n=9). The mean carbon isotope values of carbonate showed more variability across the three fossils, but all mean $\delta^{13}C_{cc}$ values were within 3.4‰: Fossil A $\delta^{13}C_{cc}$=+6.7±0.5‰ (mean ± σ, n=20); Fossil B $\delta^{13}C_{cc}$=+7.4±0.5‰ (mean ± σ, n=15); Fossil C $\delta^{13}C_{cc}$=+4.0 ± 0.2 ‰ (mean ± σ, n=9). Carbon stable isotope values of the fossil wood occluded in Fossils A, B, and C showed very low variability (Table 2), the mean $\delta^{13}C_{om}$ value of all fossils was within 0.3‰: Fossil A $\delta^{13}C_{om}$=−23.8±0.3‰ (mean ± σ, n=11); Fossil B $\delta^{13}C_{om}$=−23.5±0.5‰ (mean ± σ, n=5); Fossil C $\delta^{13}C_{om}$=−23.8±0.3‰ (mean ± σ, n=5). No spatial trends across transects were observed for any measured isotopes.

Fossil wood within Fossils A, B, and C contained 57–63%C by mass (Table 2), which agreed with the well-established range in %C seen in modern plant tissues (Reichle et al., 1973) and in Napartulik fossil wood (Jahren and LePage, 1999). The $\delta^{13}C_{om}$ mean values of Fossils A, B, and C agreed within 1‰ with carbon isotope values found in Napartulik fossil wood (Jahren and LePage, 1999) as well as with Middle Eocene $\delta^{13}C_{om}$ values inferred from the isotopic composition of shallow-water carbonate fossils (Ekart et al., 1999). Comparison of the carbon and oxygen stable isotope values of Fossils A, B, and C with the values determined for carbonate fossils from the Permian succession at Svartevaeg Cliffs (Table 1) revealed large differences in both carbon and oxygen isotopic composition between the Eocene secondary carbonate and the Permian marine carbonate: Princess Margaret range carbonate fossils had mean $\delta^{13}C_{cc}$ value=+0.5 and mean $\delta^{18}O_{cc}$ value=−7.8‰ (n=6).

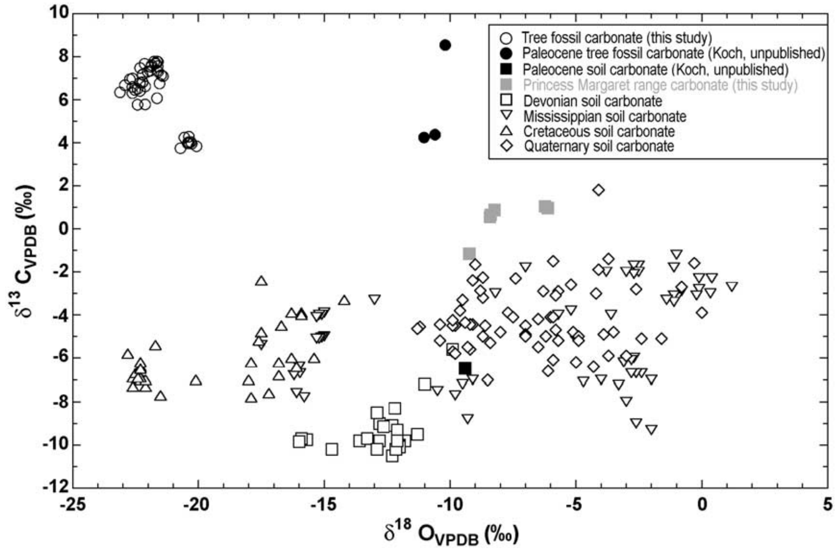

Fig. 4. Comparison of $\delta^{13}C$ and $\delta^{18}O$ values of Axel Heiberg Island tree fossil secondary carbonate with values of Late Devonian (Mora et al., 1996), Mississippian (Mora et al., 1996), Early Cretaceous (Lee, 1999; Lee and Hisada, 1999), and Quaternary (Amundson et al., 1996; Amundson et al., 1994; Wang et al., 1996)—age pedogenic carbonate. Also shown are the $\delta^{13}C$ and $\delta^{18}O$ values of Permian marine carbonate from the Princess Margaret range on Axel Heiberg Island as well as Late Paleocene tree fossil carbonates and pedogenic carbonate from the northern Bighorn Basin (P.L. Koch, unpublished).

Because of the isotopic dissimilarity between the secondary carbonate from the White Mountain locality and the marine carbonate of the Princess Margaret range, we concluded that the older marine carbonate did not chemically influence the Eocene carbonate found intertwined with tree fossil wood at the White Mountain locality.

Measurement of the stable isotope composition of organic carbon and carbonate carbon from the same point in the Earth's history can be used to estimate $p\mathrm{CO}_2$ of the paleoatmosphere (Ekart et al., 1999). However, obvious dissimilarities between our results and published analyses of Phanerozoic micritic pedogenic calcite argued against the application of this model to our data. When compared with carbon and oxygen isotope values reported for pedogenic carbonates of the last 400 Myr (Fig. 4), $\delta^{18}\mathrm{O}_{\mathrm{cc}}$ values of White Mountain tree fossils were low, reflecting the influence of depleted meteoric waters inferred for the region from fossil cellulose (Jahren and Sternberg, 2003). In comparison, terrestrial carbonates from the Late Paleocene (Tiffanian Ti-4; 57.48 Ma; Gingerich, 2001) in the northern Bighorn Basin had $\delta^{18}\mathrm{O}_{\mathrm{cc}}$ values ranging from $-11.0‰$ to $-9.4‰$ (Fig. 4 and P.L. Koch, unpublished). Carbon isotope values of carbonate from Fossils A, B, and C were conspicuously high; $\delta^{13}\mathrm{C}_{\mathrm{cc}}$ values of White Mountain tree fossils were up to 19‰ higher than reported carbon isotope values in pedogenic carbonate from the last 400 Myr (Fig. 4). However, the $\delta^{13}\mathrm{C}_{\mathrm{cc}}$ values of Fossils A, B, and C carbonate were similar to $\delta^{13}\mathrm{C}_{\mathrm{cc}}$ values of carbonate associated with Late Paleocene tree fossils from the northern Bighorn Basin in Wyoming, which were found to have $\delta^{13}\mathrm{C}_{\mathrm{cc}}$ value 10.7–15.0‰ higher than pedogenic carbonate of similar age (Fig. 4 and P.L. Koch, unpublished). These anomalous carbon isotope values led us to consider the possibility that the precipitation of secondary carbonate associated with these tree fossils was controlled by different processes than are commonly invoked in models of soil carbonate pedogenesis.

4. Discussion

Standard models of soil secondary carbonate formation involve the precipitation of calcium ions derived from weathering and carbonate ions resulting from the equilibration of soil organic-respired CO_2 with soil water. The soil environmental conditions commonly associated with this process are well-oxygenated, unsaturated, and high pH (~8) soil values. The presence of extensive organic matter and preserved plant fossils at Napartulik has led us to consider the possibility that the secondary carbonate in White Mountain fossils formed under the generally reducing conditions of soil saturation commonly associated with plant fossil preservation. Examination of the mineral fraction of Napartulik paleosols revealed the presence of lepidocrocite (γ-FeO(OH); C.J. Yapp, unpublished), a soil secondary mineral associated with periodically reducing environments (Schwertmann, 1987). In addition, Tarnocai and Smith (1991) described gray colors, silty textures, and coarse mottling in Buchanan Lake Formation paleosols—all features associated with hydromorphic soils (Fastovsky and McSweeny, 1987). Secondary carbonate does form in low pH, low oxygen, reducing modern soil environments, but its precipitation is associated with microsites in soil organic-matter aggregates, highlighting the potential importance of microbial activity (Rask and Schoenau, 1993). The porous structure of saturated conifer softwood provides an ample number of reducing microsites; the fine-scale replacement structures of secondary carbonates in White Mountain fossils may indicate that CaCO_3 precipitation preferentially occurred at or near such "hotspots" of microbial activity (Fig. 3).

Previous workers have described high $\delta^{13}\mathrm{C}$ values in Mesozoic soil Fe-carbonates; such sphaerosiderites have been linked to methanogenesis (Ludvigson et al., 1998). Fossil sphaerosiderites from Canada and Alaska with $\delta^{13}\mathrm{C}$ values as high as +10.8‰ (Ufnar et al., 2002; Ufnar et al., 2004) were used to infer high methane fluxes from high-latitude wetland soils during the mid-Cretaceous (Ludvigson et al., 2002). Given the unusually high $\delta^{13}\mathrm{C}$ values of carbonate found in the White Mountain fossils, these carbonates most likely resulted from $^{13}\mathrm{C}$-enriched CO_2 equilibration with soil water. Methane-producing soils have been shown to contain CO_2 with $\delta^{13}\mathrm{C}$ value much higher than the value expected due to plant and soil respiration (respiration has been shown to yield CO_2 that is isotopically similar to the plant material being respired; Quade et al., 1989). For example, Krüger et al. (2002)

measured δ^{13}C values ranging from −3.4‰ to −7.9‰ in CO_2 adjacent to plant roots with δ^{13}C value=−27.8‰ and with root tissue concentrations of biogenic CH_4 ranging from 14,300 to 24,700 ppmV. This ^{13}C-enriched soil CO_2 is one product of methane-producing pathways that also result in ^{13}C-depleted methane. Biogenic methane production ("methanogenesis") occurs in generally reducing terrestrial environments via two primary pathways: acetate fermentation,

$$CH_3COO^- + H^+ \rightarrow CH_4 + CO_2 \qquad (2)$$

and the reduction of CO_2,

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O. \qquad (3)$$

The isotopic fractionation factor α_b^a defined by

$$\alpha_b^a = \left(\frac{\delta^{13}C_a + 1000}{\delta^{13}C_b + 1000}\right), \qquad (4)$$

has been determined for the CO_2-reduction pathway ($\alpha_{CH_4}^{CO_2} = 1.045$; Sugimoto and Wada, 1993) and for the acetate fermentation pathway ($\alpha_{CH_4}^{acetate} = 1.021$; calculated using ε=21 and assuming unlimited acetate; Gelwicks et al., 1994). Using knowledge of these fractionation factors, the δ^{13}C value of CH_4 emitted from various environments has been used to assess the relative importance of methanogenesis pathways within ecosystems (e.g., Bilek et al., 1999; Hornibrook et al., 2000; Lansdown et al., 1992; Whiticar et al., 1986).

We expect that root respiration gave rise to the majority of CO_2 available for CO_2-reduction methanogenesis within the Eocene Arctic ecosystem. Because root respiration results in CO_2 that is isotopically similar to plant tissue (Quade et al., 1989), the δ^{13}C value of CO_2 available for CO_2-reduction methanogenesis was equal to the $\delta^{13}C_{om}$ value of White Mountain locality plant fossils. Acetate in soil pore-water has likewise been shown to be isotopically similar to plant tissues (measurements from an undisturbed ecosystem below 4-cm depth; Krüger et al., 2002). Therefore, we expect that the δ^{13}C value of White Mountain locality acetate was equal to the $\delta^{13}C_{om}$ value of White Mountain locality plant fossils. The isotopic composition of CO_2 generated as a result of acetate-fermentation methanogenesis can be determined using $\alpha_{CO_2}^{acetate} = 0.979$, which was calculated using Eq. (2) and $\alpha_{CH_4}^{acetate} = 1.021$. We hypothesize that the carbon that was incorporated into the carbonate of the White Mountain locality fossils resulted from the equilibration of a mixture of CO_2 available for CO_2-reduction methanogenesis and CO_2 resulting from acetate-fermentation methanogenesis with Eocene soil water. The carbon isotope composition of this CO_2 mixture can be calculated from the stable isotope composition of resulting carbonate using the classic fractionation factor determined for carbonate ($\alpha_{CaCO_3}^{CO_2} = 0.989$; Deines et al., 1974). After the δ^{13}C value of the CO_2 mixture that equilibrated with Eocene soil waters has been determined, a simple mass balance equation can be used to determine the relative contribution (f) of acetate-fermentation carbon dioxide to the soil CO_2 pool involved in soil water equilibration:

$$\delta^{13}C_{CO_2\ \mathrm{mixture}} = (1-f)\delta^{13}C_{CO_2\ \mathrm{available\ for\ reduction}} + (f)\delta^{13}C_{CO_2\ \mathrm{from\ acetate\ fermentation}}. \qquad (5)$$

Results from the calculations described above are presented in Table 3; separate results are presented for Fossils A, B, and C. Using the assumptions and relationships described above, we determined that 80–95% of the carbon in the CO_2 pool equilibrated with soil water at the White Mountain locality during the Middle Eocene was generated as a by-product of acetate-fermentation methanogenesis. This suggests that acetate fermentation was the dominant pathway of methanogenesis, in keeping with the widely cited observation that within temperate terrestrial environments, acetate fermentation accounts for ~70% of all methanogenesis (Whiticar et al., 1986). Hornibrook et al. (2000) have reported δ^{13}C values for CH_4 and other substrates from a temperate wetland and marsh system in southwestern Ontario, Canada. In environments best approximating the probable burial environment of the White Mountain locality Eocene tree fossils (i.e., at shallow depths in soils adjacent to wetland ponds), CH_4 production was found to occur primarily via acetate fermentation (Hornibrook et al., 2000).

Consideration of the organic material preserved at Napartulik may lend insight into the potentially large amount of acetate that was available for acetate fermentation on Axel Heiberg Island during the Middle Eocene. The paleosols of Napartulik contain

Table 3
Contribution of acetate-fermentation methanogenesis to CO_2 equilibrated with soil water during the Eocene

Specimen	$\delta^{13}C$ of plant fossil carbonate (mean$\pm\sigma$[a]; ‰)	$\delta^{13}C$ of CO_2 equilibrated with soil water[b] (‰)	$\delta^{13}C$ of CO_2 available for CO_2 reduction[c] (‰)	$\delta^{13}C$ of CO_2 resulting from acetate fermentation [d] (‰)	Percentage of equilibrated CO_2 resulting from acetate fermentation[e] ($f\times100\%$)
White Mountain Fossil A	6.7±0.5	−4.4±0.5	−23.8±0.3	−2.9±0.3	93±0.9
White Mountain Fossil B	7.4±0.5	−3.7±0.5	−23.5±0.5	−2.6±0.5	95±1.0
White Mountain Fossil C	4.0±0.2	−7.0±0.2	−23.8±0.3	−2.9±0.3	80±0.5

[a] As reported in Table 1: σ represents the standard deviation seen in n isotopic measurements for the sample, this deviation is propagated through the calculations.

[b] Calculated using α=0.989 (Deines et al., 1974).

[c] Assumed equal to $\delta^{13}C_{om}$ of fossil (Table 2 and Quade et al., 1989): σ represents the standard deviation seen in n isotopic measurements for the sample, this deviation is propagated through the calculations.

[d] Calculated using α=0.979 (Eq. (2) and Gelwicks et al., 1994).

[e] Calculated using Eq. (5).

thick O- and A-horizons that are rich in organic matter (Fig. 5). Net primary productivity (NPP) of one of the forests from Napartulik was calculated to be 550 g/m^2/year, with 58% of this mass as annual leaf contribution (Williams et al., 2003a; Williams et al., 2003b). This leaf contribution (320 g/m^2/year) is

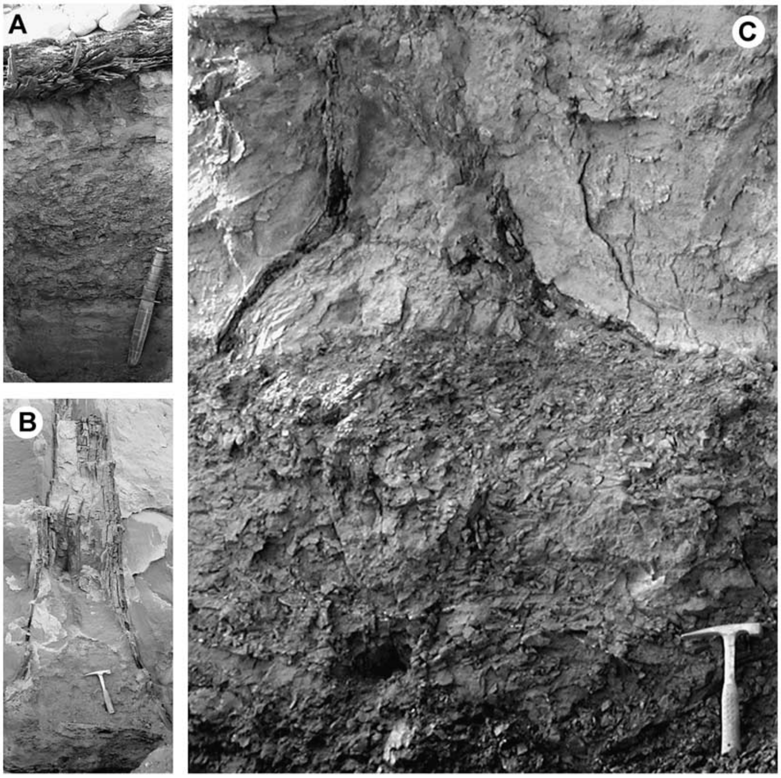

Fig. 5. Three paleosols of Napartulik with extensive organic horizons; paleosols often include autochthonous tree fossils (B and C). Pedon description resulted in taxonomic classification of the paleosols as Typic Humaquepts (A and B) and a Cumulic Humaquept (C).

similar to annual litterfall values observed in modern Cyprus swamp forests (328.5 g/m^2/year; Schlesinger, 1978). Given that plant tissues, including those analyzed from Napartulik, are composed of ~60% carbon, at least 192 gC/m^2/year was available for decomposition as annual leaf contribution to the soils of Napartulik. If a significant amount of the carbon annually available for decomposition was transformed to dissolved organic carbon (DOC), a large pool of acetate would accumulate. Decomposition field studies in deciduous ecosystems have shown that acetate carbon comprises as much as ~25% of the total DOC in the litter solution (Küsel and Drake, 1999). Taken together with Eq. (2), the observations above suggest that the maximum CH_4 release that could result from acetate-fermentation methanogenesis is 24 gC_{CH4}/m^2/year. This value is lower than, but comparable to, methane releases measured in other natural freshwater systems: 27.4–68.3 gC_{CH4}/m^2/year in a carbonate-forming boreal forest wetland (Rask and Schoenau, 1993); 26.6 gC_{CH4}/m^2/year in an acidic peat bog (Lansdown et al., 1992). If the maximum amount of acetate-fermentation methanogenesis was augmented, perhaps seasonally, by CO_2-reduction methanogenesis, ancient Axel Heiberg ecosystems may have contributed methane to the Eocene atmosphere in an amount comparable to the amount currently generated (per unit area) from temperate wetlands.

5. Conclusions

The existence of ice-free poles, brontotheres living at ~80°N latitude (Eberle and Storer, 1999) and the establishment of 28 distinct Taxodiaceae-dominated forest layers at Napartulik during the Middle Eocene are strong evidence for warmer temperatures at high latitudes, relative to today, that endured for a significant portion of the Early Cenozoic. Elevated atmospheric CO_2 levels have been suggested and may have contributed to a Middle Eocene greenhouse. Pedogenic carbonate studies yielded atmospheric pCO_2=1200 ppmV (=~3× modern levels) for the Middle Eocene (Ekart et al., 1999); isotopic studies of Middle Eocene pedogenic goethite yielded atmospheric pCO_2=2700 (±300) ppmV (=~7× modern levels; Yapp, 2004). GEOCARB results placed Middle Eocene atmospheric pCO_2 levels near 2× today's level (Berner and Kothavala, 2001). Stomatal indices based on fossil *Ginkgo* leaves indicated that the pCO_2 of the Eocene atmosphere approached 3× today's level (Retallack, 2001) or placed levels near those of the pre-industrial modern atmosphere (Royer et al., 2001), depending on the method used to interpret stomatal records. However, methane in the atmosphere has also been shown to be a powerful greenhouse gas (Lashof and Ahuja, 1990) and its oxidation is a significant source of stratospheric water vapor (Cicerone and Oremland, 1988). It has been suggested that during the Early Eocene, oxidation of wetland-liberated methane resulted in polar stratospheric ice clouds that prevented severe winter cooling in polar regions (Sloan et al., 1992). Annual emissions of methane from Arctic soils, as indicated by the carbon isotope relationships in Axel Heiberg tree fossil secondary carbonate, are a compelling candidate for the maintenance of relatively warm Eocene climate conditions.

Acknowledgments

This work was supported by NSF Grant OPP0323877 and by the Andrew W. Mellon Foundation. B.A. LePage thanks the Department of Earth and Environmental Science at the University of Pennsylvania for support during the collection of specimens. K. Charkoudian, W.M. Hagopian, and G. Mora assisted with laboratory work; we thank P.D. Gingerich, A.J. Kaufman, P.L. Koch, J.M. Lansdown, J.D. Møller, L.A. Stern, and C.J. Yapp for advice and helpful conversations. This manuscript was improved thanks to helpful suggestions from Y.I. Lee, G.A. Ludvigson, I.P. Montañez, G.J. Retallack, C.J. Williams, and two anonymous reviewers. This is PCSP Contribution #00802.

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