



Postglacial climate reconstruction based on compound-specific D/H ratios of fatty acids from Blood Pond, New England

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[1] We determined hydrogen isotope ratios of individual fatty acids in a sediment core from Blood Pond, Massachusetts, USA, in order to reconstruct climate changes during the past 15 kyr. In addition to palmitic acid (C₁₆ *n*-acid), which has been shown to record lake water D/H ratios, our surface sediments and down core data indicate that behenic acid (C₂₂ *n*-acid), produced mainly by aquatic macrophytes, is also effective for capturing past environmental change. Calibration using surface sediments from two transects across eastern North America indicates that behenic acid records δ D variation of lake water. Down core variations in δ D values of behenic acid and pollen taxa are consistent with the known climate change history of New England. By evaluating the hypothesis that D/H fractionations of long chain even numbered fatty acids (C₂₄-C₃₂ *n*-acids) relative to lake water provide independent estimates of relative humidity during the growing season, we find that differences between lake-level records and isotopically inferred humidity estimates may provide useful insight into seasonal aspects of the hydrologic cycle. Combined analyses of D/H of short and long chain fatty acids from lake sediment cores thus allow reconstructions of both past temperature and growing season relative humidity. Comparison of δ D records from two lakes in New England provides critical information on regional climate variation and abrupt climate change, such as the 8.2 ka event.

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1. Introduction

[2] Organic matter preserved in lacustrine sediments contains important paleoenvironmental in-

formation [Meyers, 2003]. For example, compositions of lipid biomarkers provide information on changes in biological inputs [e.g., Coolen *et al.*, 2004; D'Andrea and Huang, 2005], and carbon,

hydrogen and oxygen isotopic ratios of organic matter allow reconstruction of lake biogeochemistry and paleoclimatic conditions [Meyers and Ishiwatari, 1993; Edwards, 1993; Krishnamurthy et al., 1995; Lamb et al., 2004]. Important progress has been made in the past decade on compound-specific isotope analysis which allows the determination of carbon and hydrogen isotope ratios of individual organic compounds [Hayes et al., 1990; Burgoyne and Hayes, 1998; Anderson et al., 1997; Huang et al., 1999, 2001, 2002, 2004; Sauer et al., 2001; Sessions et al., 2002]. Because organic substances in lake sediments are often derived from multiple sources including aquatic and terrestrial plants, as well as microbes [Cranwell, 1982; Huang et al., 1999; Meyers and Ishiwatari, 1993], measuring isotope ratios of individual lipid compounds minimizes the complications due to multiple sources of organic matter and the effect of selective diagenesis.

[3] Compounds of aquatic sources are of particular interest for compound-specific hydrogen isotope analysis because of their potential to record lake water D/H ratios which respond strongly to climatic changes (e.g., temperature change). However, lipid compounds exclusively biosynthesized by aquatic organisms are rare in lake sediments. In order to validate the ability of a lipid compound to record lake water D/H ratios, one of the most effective tests is to study modern lake water and surface sediments [Huang et al., 2002, 2004; Sauer et al., 2001]. For example, hydrogen isotope ratios of C₂₇ and C₂₈ sterols from surface sediment of lakes and oceans have been shown to record those of lake and ocean water [Sauer et al., 2001]. Huang et al. [2002] demonstrated that hydrogen isotope ratios of palmitic acid (PA, C₁₆ n-acid) isolated from lake sediments captured the lake water composition, and recorded the late Quaternary climate changes. Ester-bound palmitic acid has been shown to better record hydrogen isotope ratios of lake water than free palmitic acid [Huang et al., 2004]. Although none of these lipid compounds is an exclusive biomarker of aquatic organisms, they faithfully record lake water D/H ratios because contributions from other organisms with different isotopic fractionation factors are small in lake sediments. In addition to lipids attributable to aquatic sources, lake sediments also contain compounds derived from terrestrial plants, such as long chain leaf waxes [Huang et al., 1999; Meyers, 2003]. Organic matter of terrestrial plants can track the D/H ratios of water

available to plants during the growing season, but can also become enriched in D/H ratios under conditions of lower effective moisture due to combined soil evaporation and transpiration effects [Yapp and Epstein, 1982]. We hypothesize therefore that higher plant biomarkers, such as long chain C₂₄ to C₃₂ fatty acids, may be used to reconstruct of past changes in precipitation/evaporation ratios (P/E). Therefore a combined study of D/H ratios of both aquatic and terrestrial lipids in the northeastern U.S. where independent paleoclimate records (e.g., pollen, lake levels, chironomids) are abundant may provide important test of the paleotemperature and paleoprecipitation information contained within the D/H ratios of individual compounds.

[4] Among various lipids in lake sediments, fatty acids have advantages over other compounds particularly for paleoclimate study. Fatty acids (1) are abundant in lake sediments, (2) are relatively easy to isolate and purify, thus minimizing coelution in GC, and (3) contain compounds from both aquatic and terrestrial sources. Because fatty acids of different chain length appear in the same fraction during sample preparation, isotopic analyses on these compounds can often be performed simultaneously, reducing the time for sample processing and isotopic analyses. The possibility of multiple source organisms for short-chain fatty acids may add isotopic heterogeneities, but the overall impact on the hydrogen isotopic records from lake sediments appears to be small on the basis of our surface sediment calibrations [Huang et al., 2002, 2004].

[5] The objectives of the present study are (1) to further test the utility of various fatty acids as paleoclimate proxies; (2) to reconstruct paleoclimate changes for the past 15 kyr from Blood Pond, New England by combined isotope and pollen stratigraphy; and (3) to compare this record with our previous published data on Crooked Pond, to better understand the influence of hydrology on δD records of fatty acids. We are particularly interested in the δD values of a middle chain fatty acid, behenic acid (BA, C₂₂ n-acid), which has not been discussed in our previous papers [Huang et al., 2002, 2004]. Ficken et al. [2000] have shown that the middle chain (C₂₀ to C₂₄) n-alkyl lipids have exceptionally high abundance in submerged and emergent aquatic macrophytes relative to terrestrial higher plants. This compound hence has the potential to

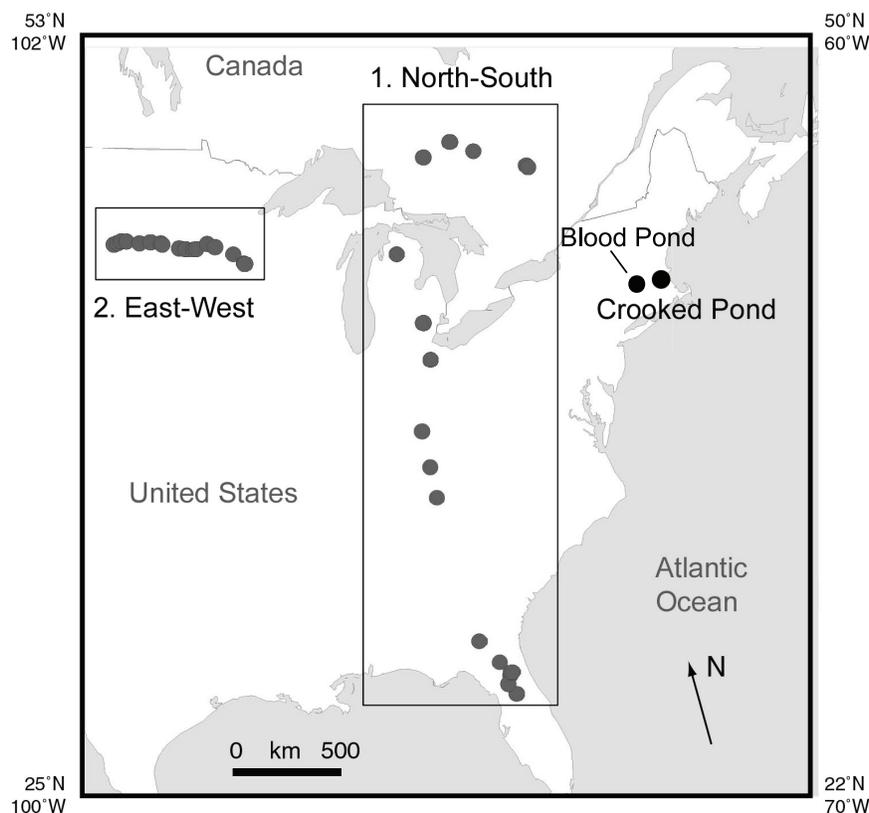


Figure 1. Sampling sites ($n = 33$) for lake surface sediments along north-south and east-west transects and the locations of Blood Pond and Crooked Pond, Massachusetts.

record the D/H ratio of lake water. Moreover, the records provide new insights on the range and intensity of abrupt climate events such as the Younger Dryas and 8.2 ka events.

2. Sample and Methods

2.1. Sample Collection

[6] Samples for surface calibration have been described in previous papers [Huang *et al.*, 2002, 2004]. Briefly, lake water and surface sediment samples were collected from sites across eastern North America along two transects: (1) from Ontario to Florida and (2) from South Dakota to Wisconsin (Figure 1). Water samples were collected from lake centers, at approximately 50 cm below the surface. Surface sediments (0–2 cm) were collected using an Ekman dredge or a short gravity corer. Sediment samples were kept at 0°C immediately after sampling, and frozen once returned to Brown University.

[7] Blood Pond (42.081°N, 71.961°W, 212.1 m a.s.l.) is a kettle pond located in the south-central

Massachusetts town of Dudley. The lake surface area is about 0.08 km², with a 0.96 km² watershed. The water depth was 3.6 m when coring took place in 2001. There is an outlet drains to the south, flowing into the Quinebaug River. Plants in the watershed include oak, clethra, white pine, and red maple, with alder and highbush blueberry in a swampy area on the pond edge. We used a 7-cm-diameter plastic tube fitted with a piston to collect the upper sediments (180 cm) and a 4.5-cm-diameter modified Livingstone sampler to collect lower sediments in 1-m-long drive lengths. The lower drives were extruded horizontally in the field, and the sediment cores were wrapped in plastic wrap and aluminum foil. The upper core was extruded vertically in the laboratory at 1-cm intervals. The lower drives were sliced into 2-cm intervals. Pollen has been studied in detail throughout the core (W. W. Oswald *et al.*, Post-glacial changes in spatial patterns of vegetation across southern New England, submitted to *Journal of Biogeography*, 2005; hereinafter referred to as Oswald *et al.*, submitted manuscript, 2005). Samples for isotope analyses were selected at 6 cm interval between two neighboring samples.

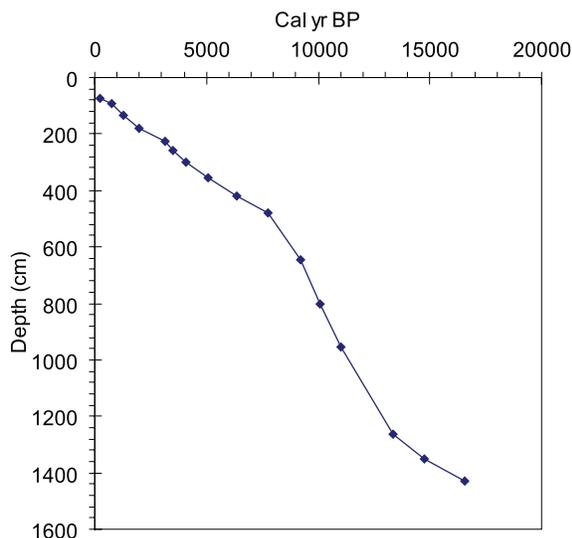


Figure 2. Age model for the sediment core from Blood Pond, Massachusetts. A total of twenty-one ^{14}C dates were obtained, but six were excluded due to age inversions (^{14}C date of a sample is younger than a sample above it).

2.2. Chronology

[8] Chronological control for samples from Blood Pond is provided by (1) radiocarbon dating of fifteen samples of bulk organic matter (Figure 2) and (2) pollen evidence (i.e., European settlement at 236 cal yr B.P. is evidenced by the increase in weedy taxa at 72 cm) verified via Pb-210 dating (Oswald et al., submitted manuscript, 2005). The ^{14}C dates were converted to calendar years before present (cal yr B.P.) using OxCal 3.9 [Bronk Ramsey, 2001].

2.3. Laboratory Analyses

[9] Sediment samples were freeze dried. Free lipids were extracted using an Accelerated Solvent Extractor ASE 200 (Dionex). Carboxylic acid fraction was isolated from the total extracts using solid phase extraction (Aminopropyl Bond Elute[®]) and then methylated using anhydrous 2% HCL in methanol. Hydroxyl acids were removed using silica gel column chromatography (DCM as solvent), in order to further purify the fatty acid methyl esters and avoid chromatographic coelution.

[10] Quantification and identification of compounds were carried out using GC and GC-MS, respectively. An HP 6890 GC interfaced to a Finnigan Delta+ XL stable isotope spectrometer

through a high-temperature pyrolysis reactor was used for hydrogen isotopic analysis [Huang et al., 2002, 2004]. The precision (1σ) of triplicate analyses was kept $<\pm 2\%$. The accuracy was routinely checked by an injection of laboratory isotopic standards between every six measurements. δD values obtained from individual acids (as methyl esters) were corrected by mathematically removing the isotopic contributions from added groups before reporting. The δD value of the added methyl group was determined by acidifying and then methylating (along with the samples) the disodium salt of succinic acid with a predetermined δD value (using TC/EA-IRMS) [Huang et al., 2002].

3. Results and Discussion

3.1. Surface Sediment Calibration for Behenic Acid (BA, C_{22} n-acid)

[11] Previous studies have demonstrated that surface sediment calibration is an effective approach to test a paleoclimate proxy [Bartlein et al., 1984; Huang et al., 2002, 2004; Sauer et al., 2001]. We have further examined behenic acid (i.e., C_{22} n-acid) using the same approach and the same set of samples as used in Huang et al. [2002], because middle chain n-alkyl lipids are particularly abundant in aquatic macrophytes [Ficken et al., 2000]. Figure 3a shows comparison between δD values of behenic acid from surface sediment and lake water from our two transects. The $\delta\text{D}_{\text{BA}}$ values (δD values of behenic acid) correlate highly with the $\delta\text{D}_{\text{water}}$ values in all 33 lakes:

$$\delta\text{D}_{\text{BA}} = 0.8185 \times \delta\text{D}_{\text{water}} - 140.01, \quad R = 0.898; P < 0.05. \quad (1)$$

[12] If only lakes from the south-north transect are used (Figure 3b), the regression becomes

$$\delta\text{D}_{\text{BA}} = 0.8681 \times \delta\text{D}_{\text{water}} - 136.40, \quad R = 0.938; P < 0.05. \quad (2)$$

[13] Sessions and Hayes [2005] derived the exact equations to calculate fractionation factors for hydrogen isotope without approximations commonly used for carbon and oxygen isotopes. Lake water is the only source for aquatic plants to biosynthesize behenic acid, so a single component isotope fractionation ($\delta\text{D}_{\text{Product}} = \alpha \times \delta\text{D}_{\text{Source}} + \epsilon$) can be applied (where $\epsilon = (\alpha - 1) \times 1000$). Using this equation (1), we obtain a fractionation factor (α) of 0.8185 from the slope, and of 0.8599 from the intercept. From equation (2), we obtain a

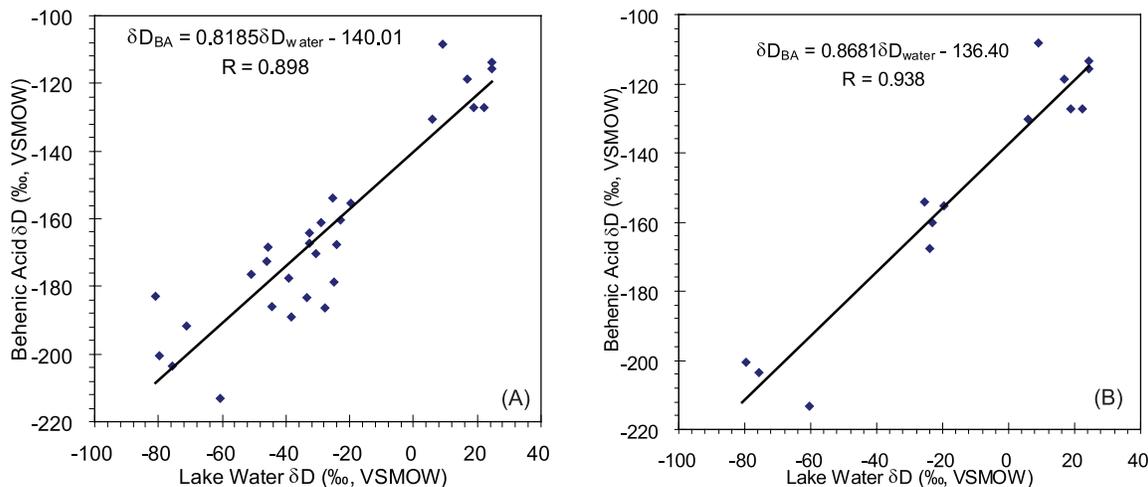


Figure 3. (a) Correlation between δD values of behenic acid (BA, C_{22} n -acid) from surface sediments and δD values of lake water ($n = 33$; VERSUSMOW is Vienna standard mean ocean water) of both transects. (b) Correlation between δD_{BA} and $\delta D_{lake\ water}$ of lakes in the north-south transect.

fractionation factor (α) of 0.8681 from the slope, and of 0.8636 from the intercept.

[14] Theoretically, the fractionation factor calculated from slope and from intercept should be equivalent. However, in practice, small difference is inevitable. The potential causes for the difference may be (1) the lipid compounds are not completely derived from a simple group of organisms and (2) the isotopic fractionation factor is slightly different for the various organisms that are sources of behenic acid. When only the north-south transect of samples is used, the regression is better than using samples from both transects, and fractionation factors derived from the slope and intercept are virtually identical. Our north-south transect is located a region with high precipitation/evaporation ratio (P/E), whereas the east-west transect encompasses large regional differences in P/E. Since our surface sediment samples probably represent deposition in the last 10s of years, the lake water from our east-west transect may be more susceptible to short-term changes, resulting in more variable D/H ratios and lower correlation with δD_{BA} .

[15] The maximum discrepancy in the fractionation factor for behenic acid between α_{slope} (0.8185) and $\alpha_{intercept}$ (0.8599) is only 0.0414 in our transects of 33 lake samples. This is very small when compared with previously published data. For example, bulk aquatic plant lipids had a difference of 0.313 (α_{slope} 0.546 versus $\alpha_{intercept}$ 0.859) [Sternberg, 1988], phytoplanktonic sterols differed by 0.053 (0.748 versus 0.801) [Sauer *et al.*, 2001], and free palmitic

acid had a difference of 0.106 (0.939 versus 0.833) [Huang *et al.*, 2002]. Our result is close to that for ester-bound palmitic acid, which differed by 0.026 (0.850 versus 0.824) [Huang *et al.*, 2004]. We therefore conclude that δD_{BA} is also an excellent biomarker to record lake water D/H ratios. In particular, for lakes with abundant submerged and emergent aquatic macrophytes (such as Blood Pond, which is surrounded by a large swampy area), δD_{BA} may be especially suitable for paleoclimate reconstructions.

3.2. Comparison of Hydrogen Isotope Records of Behenic Acid and Palmitic Acid With Pollen Stratigraphy

[16] The δD_{BA} and δD_{PA} values show similar down core variations (Figure 4). However, absolute values and ranges of variation of δD of behenic acid are somewhat different from those of palmitic acid. δD_{PA} ranges from -193.9 to -158.6‰ , while δD_{BA} ranges from -164.5 to -139.6‰ . Average hydrogen isotope ratios of palmitic acid are more depleted than those of behenic acid. The differences in absolute δD values result from different isotopic fractionation effects during biosynthesis of their producers.

[17] δD records of both palmitic and behenic acid suggest a gradual temperature increase from 15 000 to 13 000 cal yr B.P. The warming was accompanied by increasing pollen percentages of spruce (*Picea*) and subsequently pine (*Pinus*). Changes in fossil chironomid assemblages from lakes in maritime Canada and northern New England also

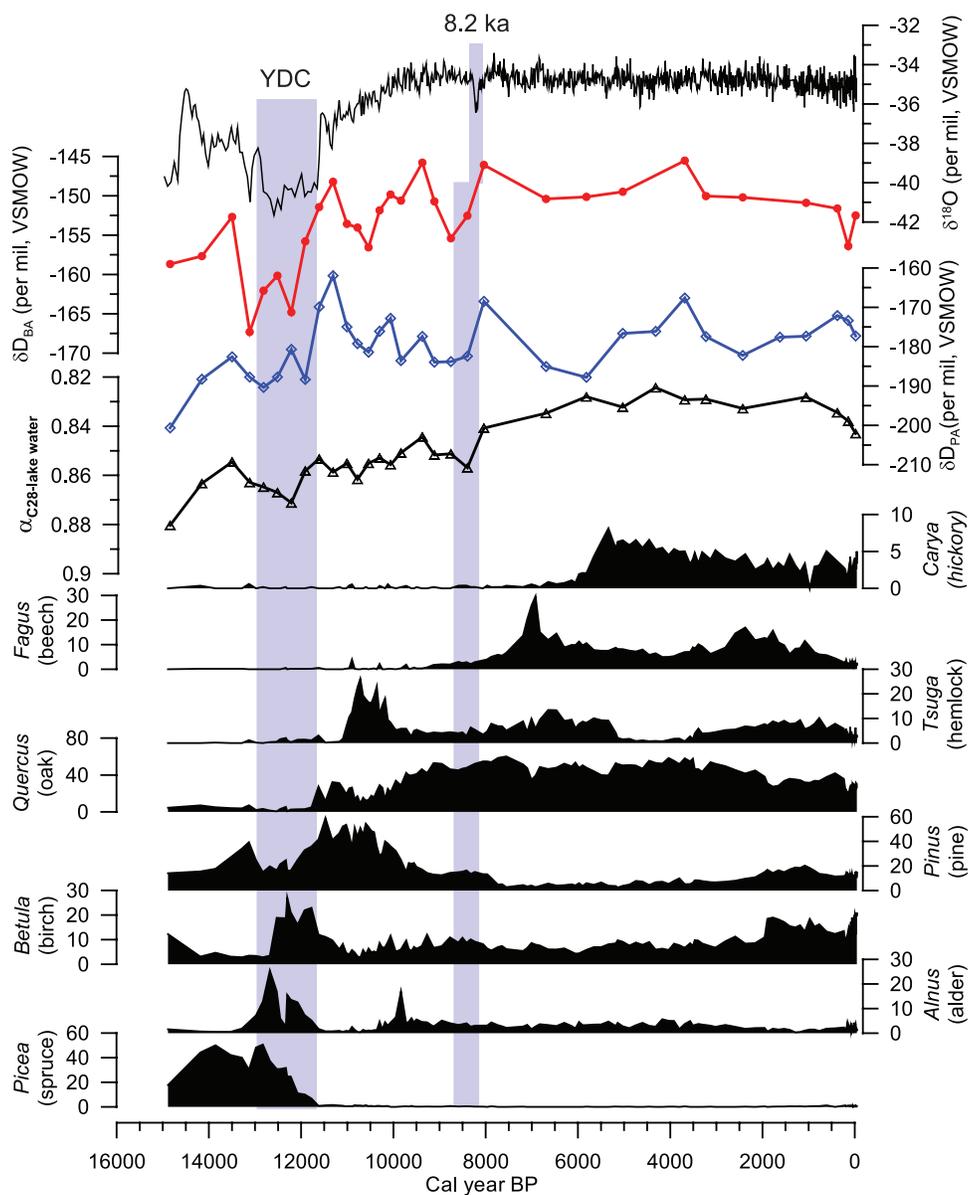


Figure 4. Hydrogen isotope records of behenic acid (δD_{BA}), palmitic acid (δD_{PA}), fractionation factor of C_{28} *n*-acid relative to lake water ($\alpha_{C_{28}\text{-lakewater}}$) from Blood Pond, Massachusetts. The pollen records from the same sediment core provide vegetation information. The GISP2 $\delta^{18}O$ record is shown for comparison. Shaded columns indicate the Younger Dryas chronozone (YDC) and the 8.2 ka cool event.

indicate that summer lake-water temperature rose until about 13 000 cal yr B.P. [Cwynar and Levesque, 1995].

[18] The Younger Dryas chronozone (YDC) [Shuman et al., 2002a; Stuiver et al., 1995], which appears between ~13 000 and 11 700 cal yr B.P. according to our age model, was the coldest period since 15 000 cal yr B.P. (Figure 4). Both Greenland isotope records [Stuiver et al., 1995] and chironomid records from maritime Canada and northern

New England [Cwynar and Levesque, 1995] recorded the YDC as the coldest postglacial period. At Crooked Pond [Huang et al., 2002], hydrogen isotope ratios of palmitic acid decline by 20‰ at 12 900 cal yr B.P., indicating that conditions during the YDC were $>5^{\circ}C$ cooler than before (on the basis of the global relationship between surface air temperature and δD for mean annual precipitation, $-5.6\text{‰}/^{\circ}C$ [Dansgaard, 1964]). At Blood Pond, the temperature change at the YDC derived from hydrogen isotope records of palmitic acid and

behenic acid ranges from 3 to 5 °C (the small difference between the two compounds may be due to mixing the contributions of organisms with small fractionation differences). The temperature estimates are close to the temperature variation estimated from chironomids in Maritime Canada and Maine [Cwynar and Levesque, 1995], pollen data in Massachusetts [Huang et al., 2002], and from nitrogen and argon isotopes from the Greenland ice core [Severinghaus et al., 1998]. This cold period was accompanied by increased abundance of boreal taxa such as *Picea*, *Alnus* and *Betula*, and lower abundance of *Pinus* and *Quercus* around Blood Pond (Figure 4). At the end of the YDC, the isotopic records indicate rapid warming (Figure 4), which is again consistent with the isotopic records from Crooked Pond [Huang et al., 2002], regional pollen and chironomid records [Cwynar and Levesque, 1995; Shuman et al., 2002b], and the Greenland ice core isotopic records [Stuiver et al., 1995]. Moreover, the YDC in our study site was not a uniformly cold period. There were some fluctuations, including a warm (~2°C) reversal occurred during the later part of the YDC. Pollen data (and to some extent, Greenland ice core data) also appear to record corresponding variations.

[19] From the end of the YDC to 9000 cal yr B.P., temperature variations derived from the hydrogen isotopic records at Blood Pond show different patterns from the Greenland ice core isotopic records. Greenland ice core isotopic records show a gradual warming with small variability until 9000 cal yr B.P. However, two relative cool periods are indicated by the temperature records from Blood Pond and Crooked Pond [Huang et al., 2002]. The first cool period is coincident with high percentages of *Tsuga* pollen, while the second coincides with an *Alnus* pollen peak around 9800 cal yr B.P.

[20] The 8.2 ka event was a major, abrupt climate change event in the early Holocene [Alley and Agustsdottir, 2005; Alley et al., 1997]. It is believed that the strongest evidence of this cooler, drier and perhaps windier event should be recovered in eastern North America. However, so far evidence for a strong 8.2 ka event in eastern North America has been sparse. For example, Yu and Eicher [1998] found an oxygen isotope shift in carbonate toward colder values in a lake in southern Ontario, Canada. A lake in central Nova Scotia, Canada showed a short-lived shift to more minerogenic conditions at the time of the event, indicating ecological change in the lake [Spooner et al., 2002]. In New England, a sharp drop in loss-on-

ignition was detected in two lakes from New Hampshire [Kurek et al., 2004]. Shuman et al. [2004] showed that pollen data from North Pond (western Massachusetts) contain a reversal that may be attributed to the 8.2 ka event.

[21] There is no clear response of pollen record from Blood Pond to the 8.2 ka cold event. In contrast, δD records of palmitic acid and behenic acid clearly record this cold event (~9000–8000 cal yr B.P.). The estimated temperature variation based on our data is 1.7 to 2.8°C. This cooling is less than suggested by the Greenland ice core (5–7°C) [Alley and Agustsdottir, 2005; Severinghaus et al., 1998], but is consistent with the variation in a lake in southern Ontario, Canada [Yu and Eicher, 1998]. The 8.2 ka event at Blood Pond appears to have started earlier and lasted longer than at the Greenland summit. Similar longer-duration cold events have been reported in North America [Spooner et al., 2002] and Europe [Ariztegui et al., 2001; Heiri et al., 2003]. However, our dating control is based on linear interpolation between only a few ¹⁴C dates, and hence we cannot accurately determine the duration of the event without further detailed radiocarbon dating.

[22] A relatively cool period between 7000 and 5000 cal yr B.P. was revealed by the δD records from Blood Pond and such a cooling may be consistent with a transition from *Pinus* and *Quercus* dominated pollen assemblages to assemblages that contain abundant *Fagus*, *Tsuga*, and *Betula*. $\delta^{18}O$ records from the Greenland ice core also show slight cooling during the same period [Stuiver et al., 1995]. In the last millennium, declines in the δD values of behenic acid and the pollen percentages of multiple taxa (e.g., *Carya* and *Quercus*) suggest a cooling trend. This trend is consistent with pollen and hydrogen isotope records from Crooked Pond [Huang et al., 2002; Shuman et al., 2004]. Overall, our compound-specific D/H data provide a new paleoclimate proxy that is particularly sensitive to relatively short-term events, such as the 8.2 ka event.

3.3. δD Records of Long Chain Fatty Acids and Implication for Growing Season Relative Humidity Changes

[23] Long chain normal fatty acids (C₂₄ to C₃₂ *n*-acids) originate from the waxy coating of terrestrial plants which can be transported to lake sediments by wind and streams [Meyers, 2003]. Higher plants use soil water as their source water

for biosynthesis. As a result, the isotopic compositions of organic compounds derived from higher plants are affected by precipitation-evaporation ratios and plant evapotranspiration.

[24] We estimated the lake δD values for the past 15 kyr in Blood Pond using δD_{BA} , based on the regression established from surface sediments calibration. We then calculated the fractionation factor of long chain fatty acids relative to lake water. The assumption here is that lake water δD values are the same as the δD values of water used by terrestrial plants, which is the best we can do since we have no other means to reconstruct soil water δD values. Biosynthesis of leaf waxes from leaf water involves many biochemical steps with the possibility of hydrogen isotope fractionation [Buddenbaum and Shiner, 1977]. However, it is the overall fractionation rather than the fractionation associated with any one step that is of interest of us. We therefore calculated the overall hydrogen isotope fractionation using the following equation:

$$\alpha = [1000 + \delta D_{\text{long chain acid}}] / [1000 + \delta D_{\text{lake water}}]. \quad (3)$$

[25] An empirical relationship ($\alpha = -0.124h + 1.089$) between net hydrogen isotope fractionation factor and growing season relative humidity has been obtained from tree ring cellulose [Yapp and Epstein, 1982], indicating higher value of fractionation factor (α) under lower relative humidity. A quantitative relationship between hydrogen isotope fractionation of leaf waxes and relative humidity has not been established. However, study of a loess profile spanning the past 130 kyr by Liu and Huang [2005] has demonstrated that δD values of long chain leaf waxes during dry periods are 40 to 50‰ higher than during wet periods in the Chinese Loess Plateau. Therefore the impact of relative humidity on hydrogen isotopic fractionation must be in the same direction for both tree ring cellulose and leaf waxes.

[26] The variations of growing season relative humidity estimated from isotope fractionation factor can be compared with the Blood Pond pollen record and well-established climate scenarios (Figure 4). Growing season relative humidity increased in parallel with *Picea* and *Pinus* pollen percentages from 15 000 to 13 000 cal yr B.P. Subsequently, the D/H fractionation factor increases during the YDC, indicating lower growing season relative humidity (Figure 4). This finding is inconsistent with lake-level reconstructions for Crooked Pond and Makepeace Cedar

Swamp in eastern Massachusetts, which show a rise during the YDC [Newby *et al.*, 2000; Shuman *et al.*, 2001]. Our estimates of the growing season relative humidity are related to precipitation during the growing season of plants (spring and summer in New England), but are based on lake water δD values, which in New England derive mainly from winter precipitation [Shuman *et al.*, 2001]. It is possible that a P/E increase in winter and a P/E reduction in spring and summer occurred during the YDC, resulting in the observed discrepancy in isotope and lake level data. This hypothesis is reasonable given that cool summer conditions during the YDC may have reduced growing season humidity, even though Huang *et al.* [2002] inferred from isotope and pollen data that winter snow levels were high.

[27] From the end of YDC to 9000 cal yr B.P., the isotope data suggest that growing season relative humidity increased slightly (Figure 4). High *Pinus* pollen percentages during this interval have been used to infer drier than modern conditions [Deevey, 1939; Webb *et al.*, 1993] and are consistent with low lake levels throughout the region [Shuman *et al.*, 2004]. A subsequent increase in growing season relative humidity occurs rapidly at ca. 8200 cal yr B.P., and coincides with an increase in *Fagus* abundance. Pollen and lake level data have also been used to infer a rapid increase in moisture levels at this time [Shuman *et al.*, 2002a, 2002b]. The cool event around 8.2 ka also appears to have lower relative humidity on the basis of the fractionation factor of the long chain acids, a finding which is consistent with climate conditions in other regions [Alley and Agustsdottir, 2005]. However, the pollen data did not show clear evidence for the 8200 cal yr B.P. event (Figure 4), perhaps indicating that isotope ratios are a more sensitive proxy for detecting short climate events. After 8000 cal yr B.P., growing season relative humidity remained relatively high, with minor fluctuations around 5000 and 3000 cal yr B.P. This pattern is inconsistent with the lake-level reconstruction from Crooked Pond and other lakes in New England and Quebec [Shuman *et al.*, 2004], which suggests low effective moisture from ca. 5500–3000 cal yr B.P. Dry conditions from 5500–3000 cal yr B.P. have also long been inferred from pollen data [Deevey, 1939], but as noted regarding conditions during the YDC, growing season humidity may have been high even though soil moisture or winter precipitation levels were low.

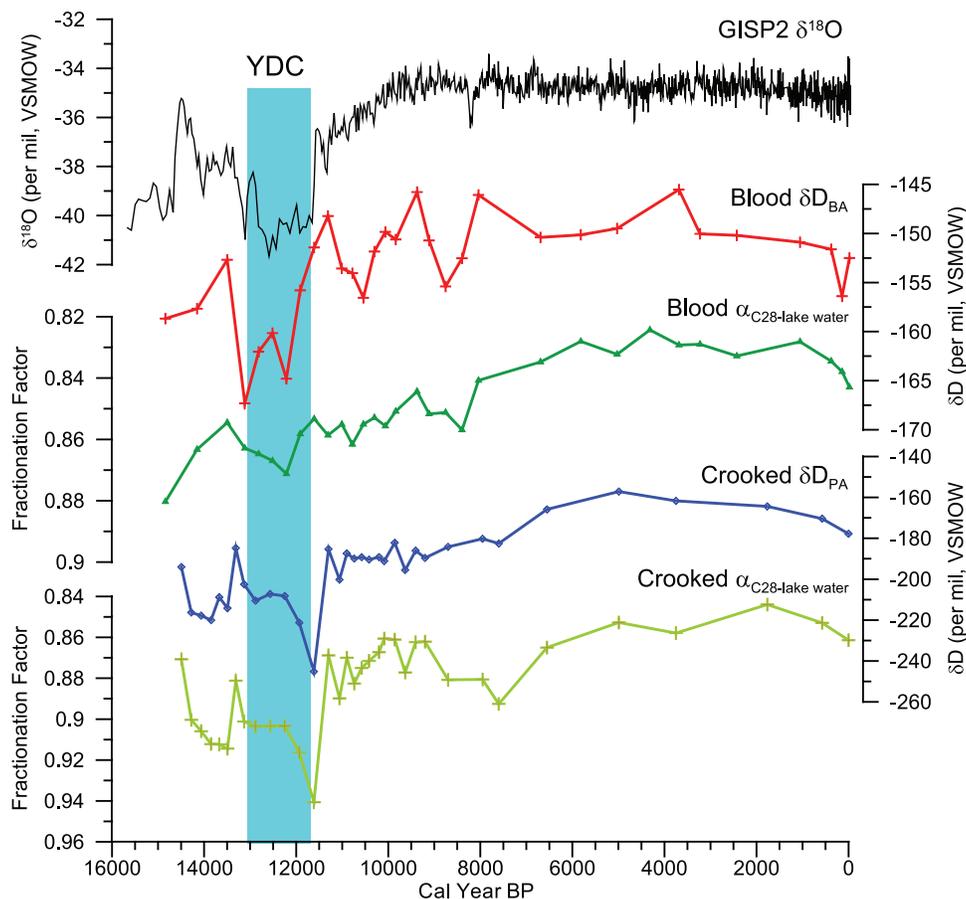


Figure 5. Comparison of isotope records from Blood Pond (Blood δD_{BA} , Blood $\alpha_{C28-lake\ water}$), Crooked Pond (Crooked δD_{PA} , Crooked $\alpha_{C28-lake\ water}$), and Greenland Ice Sheet isotope record (GISP2 $\delta^{18}O$). Blood Pond and Crooked Pond data show similar trends which slightly differ from the GISP2 record, probably suggesting climate differences between New England and the Greenland summit.

3.4. Comparison With δD Records From Crooked Pond

[28] Our previously published hydrogen isotope record from Crooked Pond, Massachusetts [Huang *et al.*, 2002] shows a similar general trend of climate variations to that from Blood Pond, particularly the clear climate cooling during the YDC (Figure 5). The mid-Holocene warm period and relatively cool late Holocene were also observed in our isotope data in both lakes, although the Blood Pond data show more variability. Down core variations of δD_{BA} and δD_{PA} from Blood Pond are very similar to those of δD_{PA} from Crooked Pond. The Crooked and Blood Pond fractionation factor reconstructions also show similar trends (Figure 5).

[29] However, there are a few differences between the records from the two lakes. First, δD_{PA} from Crooked Pond did not reveal a clear response to the cool event around 8200 cal yr B.P. Second, the full range of δD_{PA} variation (-245.1 to -157.1‰ ,

$\sim 88\text{‰}$) from Crooked Pond is larger than that of δD_{BA} (-167.3 to -140.7‰ , $\sim 27\text{‰}$) and δD_{PA} (-200.7 to -162.0‰ , $\sim 38\text{‰}$) from Blood Pond. The differences are likely due to (1) different sampling resolution for the two records and (2) different hydrological conditions at Crooked and Blood Ponds. Blood Pond is surrounded by a large area of shallow-water swamp, which is not present at Crooked Pond. There is intermittent inflow and a continuous outlet at Blood Pond, whereas Crooked Pond is hydrologically closed.

4. Conclusions

[30] Surface calibration using 33 lakes in eastern North America demonstrated that behenic acid (BA, C_{22} *n*-acid) captures lake water isotope ratios effectively. Correlation between lake water δD and δD_{BA} is significant ($\delta D_{BA} = 0.8185 \times \delta D_{lake\ water} - 140.01$, $R = 0.898$). Consistent fractionation factors derived from the slope and intercept of the equation

suggests that behenic acid is mainly produced by submerged and emergent macrophytes. Down core comparisons show that δD_{BA} is consistent with pollen record from the same sediment core. In Blood Pond, the down core variations in δD_{BA} and δD_{PA} are similar and appear to reflect primarily temperature changes for the last 15 kyr. In contrast, the isotopic fractionation factor variations of terrestrial plant leaf waxes (long chain acids) reflect growing season relative humidity. A contrast between isotope fractionation and lake level based moisture reconstructions is, however, significant with largest conflicts during the YDC and from 5500 to 3000 cal yr B.P. Limitations on reconstructing humidity using lake water isotopic values may impose some noise on the data, but the differences may be meaningful and useful indicators of the seasonality of moisture balance.

[31] Our isotope data are highly sensitive to abrupt climate changes, such as the YDC and the 8.2 ka event. On the basis of our data, the duration of 8.2 ka event in New England may be longer than on the Greenland ice sheet, although higher-resolution radiocarbon dating of Blood Pond sediments is needed to further constrain its exact duration. Hydrogen isotope ratios of long chain fatty acids also allowed us to estimate moisture balance changes during the YDC and the 8.2 ka event. Current pollen records from Blood Pond do not show the relatively short-term climate events such as 8.2 ka event. This suggests that our isotope approach is promising for high-resolution reconstruction of Holocene climate change in New England.

[32] Fatty acids are a particularly promising class of compounds for paleoclimatic and paleoenvironmental reconstructions because of the possibility of simultaneous reconstruction of both temperature and moisture balance changes. Fatty acids are relatively easy to isolate and purify during sampling preparation, minimizing coelution during gas chromatography–isotope ratio mass spectrometry analyses. Although palmitic and behenic acid are not exclusive biomarkers for aquatic plants, our surface sediment calibrations demonstrate that they do capture modern lake water conditions, and our down core studies suggest their D/H values record paleoclimatic changes.

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