Centennial-scale compound-specific hydrogen isotope record of Pleistocene–Holocene climate transition from southern New England

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[1] Northeastern North America experienced major climate shifts during the Pleistocene–Holocene transition. However, there have been no high-resolution isotopic records of climate change from this region. Here, we present a centennial-scale record of climate change during the transition based on D/H ratios of behenic acid (C_{22} n-acid) or δD_{BA} from a sediment core in Blood Pond, Massachusetts. Surface calibrations from a transect of 19 lakes in eastern North America show that δD_{BA} values track mean annual atmospheric temperature variations. The abrupt climate events observed in Blood Pond records show remarkable similarity with Greenland ice core $\delta^{18}O$ records during the Pleistocene. During the early Holocene, the northeastern North America δD_{BA} record was more variable than Greenland, possibly due to the close proximity of the Laurentide ice sheet, and impact of freshwater outbursts as the ice sheet rapidly retreated. **Citation:** Hou, J., Y. Huang, W. W. Oswald, D. R. Foster, and B. Shuman (2007), Centennial-scale compound-specific hydrogen isotope record of Pleistocene–Holocene climate transition from southern New England, *Geophys. Res. Lett.*, *34*, L19706, doi:10.1029/2007GL030303.

1. Introduction

[2] The Pleistocene–Holocene transition is characterized by abrupt climatic fluctuations around North Atlantic Ocean [e.g., *Stuiver et al.*, 1995; *Hughen et al.*, 1996]. However, the spatial variations in the timing, amplitude, and phasing of the abrupt events are less understood on the adjacent continents. This is particularly true for the northeastern North America where the driving forces for climate were particularly complex, comprising a combination of changes in North Atlantic sea surface temperature, Laurentide ice sheet (LIS) extent, atmospheric composition, and insolation [e.g., *Webb et al.*, 1993]. Centennial-scale quantitative records from the northeastern North America are thus extremely important for better understanding marine-terrestrial-atmosphere-cryosphere connections and regional climatic responses.

[3] Existing paleoclimate records from the northeastern North America are mainly based on paleoecological approaches, such as assemblages of pollen [e.g., *Peteet et al.*, 1990; *Webb et al.*, 1993; *Shuman et al.*, 2002] and Chironomidae (midge) [e.g., *Cwynar and Spear*, 2001;

Walker et al., 1997] from lake sediments. However, the possibility of transient vegetation responses to short-term, small-magnitude climate variations [e.g., *Davis and Botkin*, 1985], and the non-analogue conditions for Chironomidae [e.g., *Kurek et al.*, 2004] could increase the difficulty of using pollen and Chironomidae data to assess abrupt (<centennial-scale) climate variability.

[4] Compound-specific hydrogen isotope analyses of aquatic lipids in sediments [e.g., *Sauer et al.*, 2001; *Huang et al.*, 2002, 2004; *Dawson et al.*, 2004] offer a new way to quantify past climate variations. The technique is especially useful for regions like northeastern North America where the lake sediments lack carbonate deposit. Organic compounds produced by algae and macrophytes track lake water isotopic variations [e.g., *Huang et al.*, 2002, 2004; *Hou et al.*, 2006; *Sauer et al.*, 2001], which in regions of high precipitation-evaporation (P-E) ratio, mimic precipitation isotopic variations. For example, the low resolution record of D/H ratios of behenic acid (C_{22} n-acid) or δD_{BA} tracks general climate variation for the past 16,000 yr at Blood-Pond [*Hou et al.*, 2006]. The objectives of this study are: (1) to establish a transfer function between δD_{BA} and surface air temperature; (2) to quantify the temperature variations of the abrupt climate events during the Pleistocene–Holocene transition; and (3) to integrate with other isotopic records and pollen data to probe the mechanisms of abrupt climate events in northeastern North America.

2. Samples and Methods

[5] Blood Pond (42.081°N, 71.961°W, 212.1 m above sea level) is a kettle pond located in Massachusetts (Figure 1). The lake is mainly recharged by ground water and precipitation, with a southerly overflow outlet. The sediment core was collected in 2001, and samples for isotope analyses were selected at 6 cm intervals. Chronology for the core is provided by AMS-^{14}C dating of bulk organic matter which were converted to calendar years before present (cal yr B.P.) using OxCal 3.9 [*Hou et al.*, 2006]. The preparation of the samples and the measurement of hydrogen isotopes have been described previously [*Hou et al.*, 2006]. Briefly, lipids were extracted from freeze-dried sediment using an Accelerated Solvent Extractor 200 (Dionex). Acid fractions were isolated, methylated, and purified. A HP 6890 GC interfaced to a Finnigan Delta[+] XL stable isotope spectrometer through a high-temperature pyrolysis reactor was used for hydrogen isotopic analysis. The precession (1σ) of triplicate analyses was <±2‰. The accuracy was routinely checked by measuring laboratory isotopic standards every six measurements. Temperature changes of precipitation were also reconstructed based on pollen assemblages in

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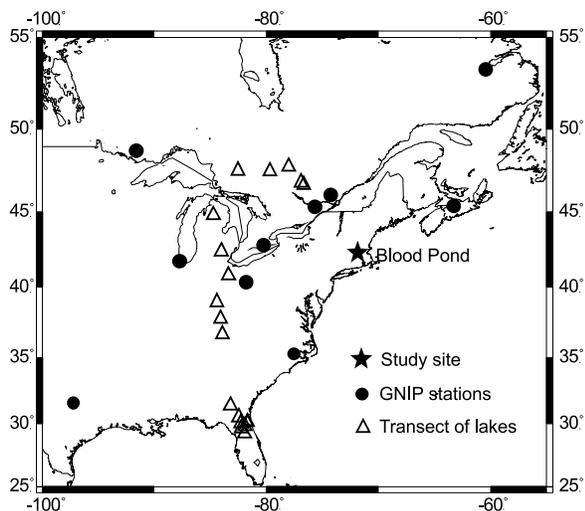[3]Department of Geography, University of Minnesota, Minneapolis, Minnesota, USA.

Figure 1. Map showing the location of Blood Pond (star), the GNIP stations (circles), and lakes along north–south transect (solid triangles).

the same sediment core using the modern analog technique described by *Webb et al.* [2003].

3. Results and Discussions

3.1. Relationship Between δD_{BA} and Surface Air Temperature

[6] D/H ratios of C_{22} *n*-acid (δD_{BA}) from lake surface sediment track lake water D/H ratios along lake transects in eastern North America [*Hou et al.*, 2006]. However, the relationship between the δD_{BA} values and surface air temperature (T) has not been established. Here, we establish the relationship between δD_{BA} and T along the N–S transect (Figure 1; see *Huang et al.* [2004] for details of the transect) across a temperature gradient (2 to 23°C) in eastern North America (Figure 2, left),

$$\delta D_{BA} = 4.3T - 208.4, \ R^2 = 0.96, \ p < 0.001 \quad (1)$$

[7] Based on this relationship, a 1°C change in T corresponds to ~4.3 ± 0.2‰ variation in δD_{BA}. To validate this relationship, we determined the relationship between T and precipitation δD value (δD_P) using the data from Global Network of Isotopes in Precipitation (GNIP) stations in eastern North America (Figure 1) [*Rozanski et al.*, 1993]. The δD_P data show a linear correlation with T (Figure 2, right),

$$\delta D_P = 5.2T - 113.0, \ R^2 = 0.97, \ p < 0.001 \quad (2)$$

This suggests that 1°C change in T corresponds to a change of ~5.2 ± 0.2‰ in δD_P. The apparent isotopic fractionation (α) for C_{22} *n*-acid relative to lake water is constant along the transect [*Hou et al.*, 2006]:

$$\alpha = 0.8681 = \frac{1000 + \delta D_{BA}}{1000 + \delta D_P} \quad (3)$$

or

$$0.8681(1000 + \delta D_P) = 1000 + \delta D_{BA} \quad (4)$$

Substituting (1) and (2) into (4), we obtain 4.5 (±0.2) T + 770 ≈ 4.3 (±0.2) T + 792. This suggests that the relationship between δD_{BA} and T is consistent with that between δD_P and T, when the D/H fractionation during the biosynthesis of behenic acid is taken into consideration.

3.2. δD_{BA} Fluctuations and Climatic Implications

[8] δD_{BA} values from Blood Pond sediments show pronounced variations during the Pleistocene–Holocene transition (Figure 3, also see auxiliary material).[1] D/H ratios increased by ~20‰ between 16 and 14.8 ka. The Bølling and Allerød warm periods were indicated by higher δD values at 14.8–14.4 ka and 14.2–13.7 ka, which were separated by one sample with low δD_{BA} value. The most significant δD variations were observed at the beginning and the end of Younger Dryas chronozone (YD). YD was indicated by lower δD_{BA} values with some fluctuations. The lowest δD_{BA} value occurred around 12.3 ka. The δD_{BA} records show similar fluctuations with $\delta^{18}O$ records from GISP2 ice core and Crawford Lake during late Pleistocene (Figure 3). During early Holocene, δD values showed more frequent fluctuations with smaller amplitudes, occurred at 10.9, 10.6, 10.3 to 10.1, 9.7, 9.3 and 8.9 ka, respectively. Although δD_{BA} values in the transect show strong correlation with T (Figure 2, left), δD_{BA} variations with small magnitude (<10‰) and defined by a single sample could be attributed to other factors in addition to temperature, such as P-E ratios, hydrological balance of lake water, seasonal shifts in precipitation. We will focus on major downcore δD_{BA} shifts to avoid over-interpreting the data as temperature changes.

3.2.1. Late Pleistocene (16–13.2 ka)

[9] Surface air temperature increased by ~5°C between 16 and 14.8 ka. The warmest period of the Late Pleistocene occurred between 14.8 and 14.4 ka, coinciding with the Bølling period (B). The Allerød period (A) is about 2°C cooler than Bølling. Warmth during the B-A periods inferred from the δD_{BA} data matches the warming pattern found in Greenland. Three short cold periods defined by single samples show similar temperature amplitude as those from GISP2 $\delta^{18}O$ (Oldest Dryas, Older Dryas, and Intra Allerød cold period (IACP), Figure 3), although variation in P/E ratios and seasonal changes in precipitation may affect the δD_{BA} changes. The onset of the Bølling period, and the step-change during B-A periods at Blood Pond appear to lead the GISP2 temperature changes by about 100 to 300 years. This may not reflect a real difference in phasing, as the chronological inaccuracies in Blood Pond records (100–350 year uncertainties, Figure 3) and/or the reservoir effect in Blood Pond could readily lead to observed chronological differences.

3.2.2. Younger Dryas Chronozone (13.2–11.6 ka)

[10] The most significant temperature shifts in the record occurred at the beginning and end of the YD. The beginning of YD (13.2–13 ka) is marked by ~5.6°C decline in temperature. Temperatures fluctuated during the YD, with
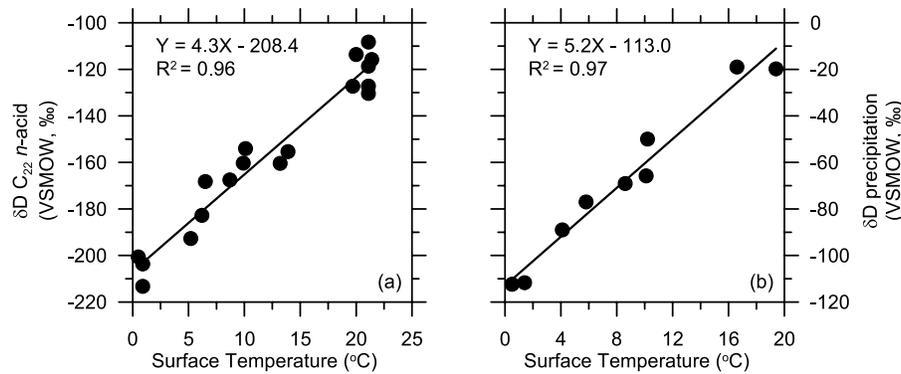

Figure 2. Correlation between (left) D/H ratios of behenic acid (C_{22} n-acid) or δD_{BA} and surface air temperature (T) along the north–south transect in eastern North America, and (right) mean annual δD of precipitation (δD_P) and surface air temperature (T) for GNIP stations in eastern North America (1961–1987, data from *Rozanski et al.* [1993]).

the lowest temperature occurring at ∼12.3 ka. The YD ended abruptly at 11.6 ka, ∼5.4°C increase in less than 200 years. The δD_{BA}-inferred temperature variations from Blood Pond can be compared with carbonate $\delta^{18}O$ variation from Crawford Lake in Ontario [*Yu and Eicher*, 1998] (Figure 3), White Lake in New Jersey [*Yu*, 2006], and with opal $\delta^{18}O$ change from Linsley Lake in Connecticut [*Shemesh and Peteet*, 1998]. The $\delta^{18}O$-inferred temperature

variation in Crawford Lake and White Lake was ∼6 and 8°C [*Yu and Eicher*, 1998; *Yu*, 2006]. The opal $\delta^{18}O$-inferred temperature change in Connecticut was ∼6°C [*Shemesh and Peteet*, 1998]. Temperature changes during the YD have also been estimated using Chironomidae assemblages from lakes in the White Mountains of New Hampshire [*Cwynar and Spear*, 2001] and from pollen data in New England [e.g., *Huang et al.*, 2002] and New York
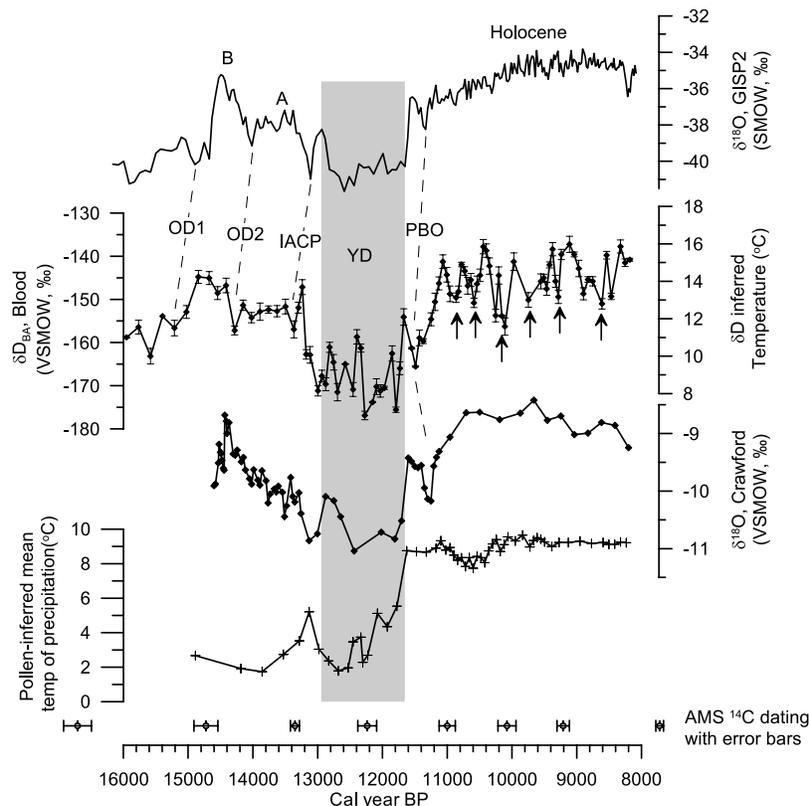

Figure 3. δD_{BA} record and pollen-inferred temperature from Blood Pond during the transition from late Pleistocene to Holocene in comparison with $\delta^{18}O$ data from Greenland Ice Sheet Project 2 (GISP2), and carbonate $\delta^{18}O$ from Crawford Lake. The abbreviations indicate the corresponding periods: OD1, Oldest Dryas; OD2, Older Dryas; IACP, Intra-Allerød cold period; YD, Younger Dryas; PBO, Pre-Boreal oscillation; B, Bølling; A, Allerød. The arrows beside the δD_{BA} curve indicate the freshwater outburst from proglacial lakes. Calibrated ages from accelerator mass spectrometry radiocarbon (AMS ^{14}C) dating with errors are shown.

[*Webb et al.*, 2003]. The observed temperature decline in the Chironomidae records was ~5 to 6°C [*Cwynar and Spear*, 2001]; pollen data show ~8°C increase in January temperatures and ~4°C increase in July temperatures after the YD [*Huang et al.*, 2002; *Webb et al.*, 2003]. The Blood Pond pollen data were used to infer a 3°C decline in the mean temperature of precipitation at the beginning of the YD, and an 8°C increase at the end of YD (Figure 3).

3.2.3. Early Holocene (11.6–8 ka)

[11] A series of abrupt temperature excursions is evident in the early Holocene interval of the record. A temperature decrease of ~3°C follows a warming trend at the end of the YD (just before 11.5 ka). This cooling may represent the Preboreal Oscillation (PBO). After 11.5 ka, temperature increased ~6°C in ~400 years, which is also observed in the $\delta^{18}O$ record from Crawford Lake [*Yu and Eicher*, 1998], but was not seen in pollen-based climate reconstructions from northeastern North America and in the Greenland ice core records (Figure 3). In addition to PBO, some other potential cold periods are also revealed by the lower δD_{BA} record, around on 10.9, 10.6, 10.3 to 10.1, 9.7, 9.3 and 8.9 ka.

3.3. Comparison of Pollen and Isotope-Based Temperature Reconstructions

[12] Mean temperature of annual precipitation inferred from pollen assemblages in the same sediment core using the modern analog method [*Webb et al.*, 2003] show similar variations as inferred from the δD_{BA} especially for the YD (Figure 3, note the absolute values of pollen and δD inferred temperatures differ due to independent calibrations). However, there are discrepancies between pollen and δD_{BA} inferred temperatures. For example, between 15 and 13.5 ka, pollen data suggest lower temperature than inferred by δD_{BA} record. Despite similar sampling resolution, multiple fluctuations of δD_{BA} during the early Holocene are not observed in the pollen data (Figure 3). The discrepancies may result from misrepresentation of dry conditions as cool conditions by the pollen method, and/or the misrepresentation of dry conditions as warm conditions by the isotopic data (both δD_{BA} from Blood Pond and carbonate $\delta^{18}O$ from Crawford Lake). Although the northeastern North America is known for positive P-E ratio, which favors relatively small evaporative enrichment, a radical decrease in the P-E balance could enrich D/H ratios of lake water. The low lake level between 15 to 13.5 ka [*Shuman et al.*, 2001] may have enriched lake water D/H ratios, causing higher δD_{BA} values. Alternatively, the close proximity to the Laurentide ice sheet during the pre-YD period could alter the moisture source for precipitation, the precipitation seasonality. Local hydrologic factors could alter the residence time of the lake, the balance of groundwater and surface runoff into the lake, and/or the source of groundwater. More studies are needed to reconcile these discrepancies.

3.4. Overall Patterns of the Abrupt Climate Change in Northeastern North America

[13] Comparison of the Blood Pond δD_{BA} data with the GISP2 $\delta^{18}O$ record reveals similarity in the number and timing of abrupt climate events during the late Pleistocene (Figure 3). Five Greenland cold regimes have been centered around 14.8 (OD1), 14 (OD2), 13.2 (IACP), 12.3 (YD,

12.9–11.6) and 11.4 ka (PBO). Consistent with this, five cold periods are found in Blood Pond. The $\delta^{18}O$ data from Crawford Lake, Ontario and White Lake, New Jersey also suggest similar climate shifts [*Yu and Eicher*, 1998; *Yu*, 2006]. The similarity in the sequence of the climate events implies that repeated reversals during the late Pleistocene in the North Atlantic region is related to a common cause i.e., the changes in thermohaline circulation due to freshwater outbursts [*Clark et al.*, 2001].

[14] During the early Holocene, the linkage of the climate regimes of Greenland and northeastern North America appears to have weakened. There is more variability in the northeastern North America than in the Greenland, and the amplitude of the temperature increase after the PBO is larger in the northeastern North America records (~6°C) than in Greenland (~2°C). The GISP2 $\delta^{18}O$ data show a more gradual temperature increase until 10 ka (Figure 3). Melting of the Laurentide ice sheet (LIS) from 12 to 10 ka accelerated due to the elevated summer insolation in North Hemisphere [*COHMAP Members*, 1988]. The combination of the high insolation and rapidly retreating LIS may have resulted in a faster warming trend on the North American continent than in Greenland after the YD. Additionally, Blood Pond δD_{BA} values show six negative isotopic shifts, indicating cold events lasting decades to centuries which are not observed in the Greenland record (Figure 3). The timing of these events is close to the freshwater outbursts of relatively smaller magnitudes from Lake Agassiz, centered at ~10.6, 10.4, 10.3, 10.0, 9.5, and 9.2 ka [e.g., *Clark et al.*, 2001; *Teller et al.*, 2002]. The cold freshwater may influence northeastern North America by cooling coastal waters and the local atmosphere, rather than strongly affecting the thermohaline circulation and altering the climate around the North Atlantic basin, as has been suggested for the YD, PBO and 8.2 ka events [e.g., *Clark et al.*, 2001; *Alley and Agustsdottir*, 2005]. Therefore, the effect of these smaller freshwater outbursts on the Greenland ice sheet was minimal.

4. Conclusions

[15] D/H ratios of behenic acid (C_{22} *n*-acid) or δD_{BA} are strongly correlated to the surface air temperature (T) along a 19-lake transect in eastern North America. The temperature dependence of δD_{BA} is 4.3‰/°C. This is consistent with the relationship between isotopic precipitation and T in eastern North America (5.2‰/°C), when the isotopic fractionation of behenic acid ($\alpha = 0.8681$) is taken into consideration. In Blood Pond, isotope-inferred temperatures closely track pollen-inferred temperatures. Therefore, the general features of the δD_{BA} are robust, although some disagreement between pollen and isotopic values demonstrates the potential for different responses of lake water δD values and terrestrial vegetation to climate change. Abrupt climate events observed in the GISP2 ice core during the Late Pleistocene are also detected in δD_{BA} record from Blood Pond. This implies that climate change in both Greenland and northeastern North America during this time was related to a common cause, namely the changes in thermohaline circulation in North Atlantic Ocean due to freshwater outbursts. During the early Holocene, climate in northeastern North America showed greater variability than in Greenland,

possibly reflecting multiple climate forcing factors in northeastern North America versus a more uniform control by solar insolation above Greenland ice sheet. Multiple episodes of fresh water outbursts from Lake Agassiz may have induced a number of abrupt climate cooling events in northeastern North America during the early Holocene, each lasting several decades.

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