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## A high-resolution hydrogen isotope record of behenic acid for the past 16 kyr in the northeastern United States

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#### ABSTRACT

D/H ratios of leaf lipids from lacustrine aquatic macrophytes have been shown to record precipitation  $\delta D$  values, which can reflect precipitation-weighted mean annual temperature (MAT) in the northeastern United States. Here we report a high-resolution hydrogen isotopic record from Little Pond, Massachusetts, USA, which we compare with other paleoclimate data from the region, including a similar  $\delta D$  record from Blood Pond, Massachusetts. Together the two datasets provide a >16 ka record of  $\delta D$  variability in the region, affording new insights into Holocene climate history. First, the long-term trends in  $\delta D$  correlate significantly with regional temperatures inferred from alkenone records from nearby areas of the North Atlantic and lake-level inferred changes in precipitation and evaporation. The long-term  $\delta D$  trends reflect a period of maximum regional warmth at ca. 8-6 ka after the collapse of the Laurentide Ice Sheet. Second, unlike the positive relationship between temperature and  $\delta D$  observed over the long-term and during early events like the Younger Dryas, we find that a series of warm and dry events at 4.9-4.6, 4.2-3.9, 2.9-2.1, and 1.3-1.2 cal kya BP coincide with negative  $\delta D$  excursions from the long trends. These events were likely driven by summer drought dynamics.

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#### 1. Introduction

Paleoclimate reconstructions from New England in the northeastern United States provide major reference for evaluating modern climate change and climate forcings. Such efforts include pollen (e.g., Webb et al., 2003; Shuman et al., 2007; Oswald et al., 2010; Williams et al., 2010; Marsicek et al., 2013), chironomid assemblages (Cwynar and Spear, 2001; Francis and Foster, 2001), alkenone ratios (Sachs, 2007), lithological characteristics (Shuman et al., 2001; Newby et al., 2009; Hubeny et al., 2011) and organic biomarker hydrogen isotopes (e.g., Huang et al., 2002; Shuman et al., 2006; Hou et al., 2007, 2012). These records reveal rich information on past precipitation and temperature at different time scales, including both long-term climate trends and multi-century

variability. For example, early-Holocene warming led to peak

Major paleoclimate questions remain, particularly about the patterns and causes of the multi-century climate variability (Newby et al., 2014; Shuman and Marsicek, 2016). Although stable isotope records from ice cores and speleothems can provide detailed paleoclimate records on time scales from decades to millennia (e.g., Grootes and Stuiver, 1997; Wang et al., 2004, 2008; Vinther et al., 2009), New England is devoid of such paleoclimate archives. In the recent years, hydrogen isotope records from sedimentary lipids have shown major advantage in recording high resolution temperature and precipitation regime changes in this region (Huang et al., 2002; Shuman et al., 2006; Hou et al., 2007, 2012). When compared with multiple, quantitative climate signals from pollen, alkenones, and lake-level studies (Sachs, 2007; Newby et al., 2014;

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temperatures during ca. 9000-5500 cal yr BP and was followed by subsequent long-term cooling (Marsicek et al., 2013; Sachs, 2007; Shuman and Marsicek, 2016). Effective moisture increased as the temperatures declined (Marsicek et al., 2013; Newby et al., 2014; Shuman and Marsicek, 2016), and a series of multi-century coolwet/warm-dry fluctuations punctuated the long trends since ca. 6 ka (Sachs, 2007; Newby et al., 2014; Shuman and Marsicek, 2016).

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Shuman and Marsicek, 2016), the integrated paleoclimate data would provide an important framework for considering the influences of different climate forcings, such as orbitally-forced insolation trends (e.g., Shuman and Donnelly, 2006), the Laurentide Ice Sheet (Shuman et al., 2006; Hou et al., 2007, 2012), and solar activity (e.g., Nichols and Huang, 2012).

Recent studies demonstrate that  $\delta D$  values of mid-chain length leaf lipids (e.g., behenic acid  $\delta D$  ( $\delta D_{BA}$ )) from aquatic macrophytes preserved in lake sediments are useful proxies for lake water  $\delta D$ values (Hou et al., 2006, 2007), and can therefore capture the different isotopic signatures integrated by the lake water. Lakes with abundant aquatic plant inputs are particularly attractive, because terrestrial plants also produce small amounts of mid-chain leaf waxes and could potentially interfere with aquatic plant isotopic signals (Gao et al., 2011). To deal with this problem, Gao et al. (2011) developed a model for selecting the most suitable lakes for hydrogen isotopic reconstruction (see Methods section for more details). We produce a new high-resolution, Holocene-length, behenic acid  $\delta D$  ( $\delta D_{BA}$ ) record from Little Pond, located in the town of Royalston, central Massachusetts, USA. Then, using existing data from Blood Pond, also located in central Massachusetts (Hou et al., 2006, 2007), we produce a composite isotopic record in New England for the past 16 kyr.

To understand the climate signals embedded in the Little Pond  $\delta D_{BA}$  record, we statistically decomposed the time series and compared both the raw data series and the different spectral components with two regional datasets: an ensemble of multiple quantitative precipitation minus evaporation (P-E) reconstructions based on lake-level records from eastern Massachusetts (Newby et al., 2014; Shuman and Marsicek, 2016), and the nearest Holocene-length alkenone-derived sea-surface temperature (SST) record from the Scotian margin (Sachs, 2007). The P-E and SST records are significantly correlated at centennial scales with each other and with pollen-inferred precipitation and temperature reconstructions, and thus represent well-validated climate signals for the region (Marsicek et al., 2013; Shuman and Marsicek, 2016). Using these datasets, we evaluate 1) how the isotopic variations correspond to the temperature and moisture variations, and 2) how the variations relate to the different climate forcings in this region at different time scales. Thus, the comparisons presented here further test and expand a multifaceted framework for understanding the climate history of the North Atlantic region as expressed in New England, and reveal different interacting temperature and moisture dynamics at multi-millennial and multicentury scales.

#### 2. Samples and methodology

#### 2.1. Samples, study sites and chronology

For the Holocene temperature reconstruction, we collected a sediment core from Little Pond in Royalston, Massachusetts, USA (referred to as Little Pond Royalston in Oswald et al., 2007) (Fig. 1). Little Pond (42.68°N, 72.19°W, Elevation 301 m) is a small water body, that has a surface area of 4.0 ha and a maximum depth of 5.7 m. In Royalston, the long-term mean January temperature ranges from –12.3 to –0.2 °C, and the long-term July mean temperature from 13.5 to 27.7 °C (https://www.ncdc.noaa.gov/cdoweb/search; 1949–2015). Annual mean precipitation is ~1108 mm. The long-term mean January and July precipitation rates are ~85 mm/month and ~117 mm/month respectively (same source as temperatures). Little Pond is characterized by high aquatic productivity and abundant aquatic vegetation; the surrounding land-scape is mainly forested. The watershed contour of Little Pond is provided in Supplementary Material (Fig. S1). The pond has one

inlet and one outlet with an estimate of residence time of months to a few years based on previous study on New England lakes (Norton et al., 1989).

Modern moisture sources of our study site are estimated in Fig. S2A, based on detailed data from a recent publication by Puntsag et al. (2016). Basically, there are four principal sources of moisture for our study area, namely, south Atlantic, Northeastern Atlantic, Arctic, and western continental sources. These sources have mean  $\delta D$  values shown in Supplementary Table S1 and Fig. S2B. The study site reported in Puntsag et al. is at Hubbard Brook Experimental Forest, ~130 miles north of our site. We use the long-term isotopic data from Hubbard Brook Experimental Forest to approximate our isotopic values, by making a correction based on the modern offset between LPR and Hubbard Brook using the Online Isotopes in Precipitation Calculator (OIPC). Hysplit data in 2016 are also plotted to corroborate the moisture sources (Fig. S2C; Stein et al., 2015; Rolph, 2017).

The sediment core from Little Pond was collected in 2003, with a total length of ~7.8 m. The Little Pond age-depth model (Fig. S3) was generated using Bchron (Haslett and Parnell, 2008) and based on the chronological data reported by Oswald et al. (2007) (seven AMS 14C dates and pollen evidence for European settlement) plus an additional  $^{14}$ C date obtained for the depth of 712–713 cm (OS-82883;  $^{14}$ C age = 9940  $\pm$  45). The resulting sampling resolution was ~40 yr between 11 and 8 cal kyr BP, and ~80 yr between 8 cal kyr BP and present (about 10 yr resolution in the past 200 yr).

We statistically compared the details of the Little Pond record with the average P-E reconstruction from New Long Pond in Plymouth, Massachusetts (150 km SE of Little Pond), and Deep Pond in Falmouth, Massachusetts (175 km SE of Little Pond; Marsicek et al., 2013; Newby et al., 2014), and with the Uk'37 SST reconstruction from core OCE326-GGC30 from off the coast of Nova Scotia (Sachs, 2007), which was not significantly different, including its centennial details, from pollen-inferred growing-season temperatures from the region from Maine to New York (Shuman and Marsicek, 2016). Consistent with previous analyses, the SST record was linearly detrended to account for a warm-bias that causes Late-Pleistocene temperatures to be > 5 °C warmer than today in the raw data (see discussion by Shuman and Marsicek, 2016).

We also made a composite  $\delta D_{BA}$  record using our new data from Little Pond and the published  $\delta D_{BA}$  data from Blood Pond, south Massachusetts (Hou et al., 2007), which is ~80 km south of Little Pond, has a surface area of 8.5 ha, and reaches a maximum depth of 3.6 m. In Dudley, Massachusetts, where Blood Pond is located, the long-term mean January temperature ranges from -9.8 to 0.7 °C, and the long-term July mean temperature from 15.5 to 27.0 °C (source: http://www.ncdc.noaa.gov/cdo-web/;monthly normals for Charlton, MA; 1951–2016). Annual mean precipitation is ~1220 mm, which is evenly distributed throughout the year (same source as temperature). Temperatures are slightly warmer at Blood Pond than near Little Pond by around 1.9, 1.2, and 1.3 °C for the average high and low temperatures in January and the average low temperatures in July, respectively.

The existing Blood Pond  $\delta D_{BA}$  record (Hou et al., 2006, 2007, 2012) features about 90 yr resolution between 16 and 10 cal kyr BP and about 20 yr resolution from 10 cal kyr BP to 7.5 cal kyr BP (Fig. S3). To make the composite record from these two cores, we have aligned the Blood Pond record to the Little Pond record and reduced the Blood Pond  $\delta D_{BA}$  values by 5% in order to account for the slightly warmer temperature at that site. The  $\delta D$  of modern lake water from Blood Pond is also ~5% higher than that from Little Pond (Fig. 2A), which may reflect the slightly higher temperature, and/or different proportion of plant input sources (Gao et al., 2011). Applying such a small offset correction led to visually more consistent overlapping of the two records for the time interval of

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