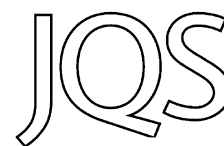


The 8.2-ka BP event in north-eastern North America: first combined oxygen and hydrogen isotopic data from peat in Newfoundland



T. J. DALEY,^{1*} K. E. BARBER,² P. D. M. HUGHES,² N. J. LOADER,³ M. LEUENBERGER⁴ and F. A. STREET-PERROTT³

¹School of Geography, Earth and Environmental Sciences, Plymouth University, Plymouth PL4 8AA, UK

²Palaeoenvironmental Laboratory, Geography and Environment, University of Southampton, Highfield, Southampton SO17 1BJ, UK

³Department of Geography, College of Science, Swansea University, Singleton Park, Swansea SA2 8PP, UK

⁴Climate and Environmental Physics, Physics Institute, and Oeschger Centre for Climate Change Research, University of Bern, CH-3012 Bern, Switzerland

Received 8 January 2016; Revised 27 April 2016; Accepted 6 May 2016

ABSTRACT: Finding direct evidence for atmospheric circulation change in terrestrial records of Holocene climate variability remains a fundamental challenge. Here we present the first combined stable oxygen and hydrogen isotopic palaeorecord from a peatland core in Newfoundland, Canada. *Sphagnum* cellulose samples were isolated from a core from Nordan's Pond Bog, Newfoundland, and analysed for δD values. Combined with existing $\delta^{18}O$ data, the resulting $\delta D/\delta^{18}O$ bi-plot correlates directly with existing measurements of the modern (late 20th century) isotopic composition of precipitation from GNIP stations in Nova Scotia and Labrador, implying a close relationship between the estimated isotopic composition of source water used by the mosses and that of the source precipitation. We use the relative variations between the two isotope records to test the hypothesis that atmospheric circulation changed in the millennium following the 8.2-ka BP climate event. The data reveal a secondary complex isotopic response ~ 200 years (8250–8050 a BP) after a primary oxygen isotopic event that is widespread in the north Atlantic region. This secondary event is characterized by a divergence in oxygen and hydrogen isotope records that can most plausibly be explained by the augmentation of precipitation moisture from a more distant and more continental vapour source.

Copyright © 2016 The Authors. *Journal of Quaternary Science* Published by John Wiley & Sons Ltd.

KEYWORDS: 8.2 ka; hydrogen; isotopes; Newfoundland; North Atlantic; *Sphagnum*.

Introduction

Ensemble model-simulated projections for 21st-century climate in the North Atlantic region suggest future warming may be mitigated in part by a decrease in the heat transfer from low to higher latitudes associated with slow down in Atlantic Meridional Overturning Circulation (AMOC) (Hofmann and Rahmstorf, 2009; Collins *et al.*, 2013). Changes in the surface oceanic heat gradient between low and high latitudes will impact upon the gradient in atmospheric temperature, thereby influencing the strength and position of the northern mid-latitude atmospheric jetstream circulation (hereafter jet) (Tang *et al.*, 2014; Francis and Vavrus, 2015). In this context, quantification of the impact of past changes in the northern mid-latitude atmospheric jet in response to oceanic circulation changes is valuable for constraining model simulations of similar scenarios in future climate projections (LeGrande and Schmidt, 2009; Tindall and Valdes, 2011; Holmes *et al.*, 2016).

The most compelling evidence for past changes in the northern atmospheric jet has been interpreted from the Greenland ice core records, where the multitude of independent indicators is sufficient to provide a convincing record (Dawson *et al.*, 2003; Vinther *et al.*, 2003; Alley and Ágústsdóttir, 2005; Jouzel *et al.*, 2007; Steffensen *et al.*, 2008). While oxygen isotope records from sedimentary sequences have enabled reconstruction of the hydrological cycle and comparison between different archives (Marshall *et al.*, 2007; Domínguez-Villar *et al.*, 2009; Holmes *et al.*, 2010, 2016; Kaislahti Tillman *et al.*, 2010; Daley *et al.*, 2011; Roland *et al.*, 2015), the additional information afforded by a

combined record of oxygen and hydrogen data is significant, not least for the ability to detect changes in the source of moisture (Dansgaard, 1964; Merlivat and Jouzel, 1979; Sonntag *et al.*, 1983; Rozanski *et al.*, 1993; Jouzel *et al.*, 2007; Pfahl and Sodemann, 2014; Steen-Larsen *et al.*, 2014). This insight is afforded by variations in the rate of kinetic fractionation of the isotopomers of hydrogen and oxygen in water and which are expressed as variations in the deuterium excess (d), given by the formula $d = \delta D - 8(\delta^{18}O)$. Deuterium excess data have already demonstrated their interpretative value in modern instrumental studies (Pfahl and Wernli, 2008; Daley *et al.*, 2012; Steen-Larsen *et al.*, 2014) and through analyses of ice cores (Jouzel *et al.*, 2007; Steffensen *et al.*, 2008), but they also now have a potential role in disentangling the causes of what can often be large variations in mid-latitude isotopic records that are rarely related to a single driver such as atmospheric temperature or the amount of precipitation alone (Araguás-Araguás *et al.*, 2000; Daley *et al.*, 2012; Young *et al.*, 2015; Holmes *et al.*, 2016). Variations in d relate most strongly to variations in atmospheric conditions over the vapour source region (Dansgaard, 1964; Merlivat and Jouzel, 1979; Gat, 1980; Sonntag *et al.*, 1983; Rozanski *et al.*, 1993). Past changes in d may therefore indicate changes in the source area for local precipitation. Traditionally, relatively high positive values of d (>10) have been used to diagnose moisture originating from surface evaporation in an environment with relatively low humidity and/or high wind speeds and/or relatively high ocean temperatures. Values <10 have indicated a moisture source that was humid and/or with relatively low surface water temperatures. Previous research estimated that a 10% increase in relative humidity over the ocean decreased d by $\sim 6\text{‰}$ (Rozanski, 1985). Recently, however, it has been demonstrated that the

*Correspondence: T. J. Daley, as above.

E-mail: tim.daley@plymouth.ac.uk

effect of wind speed over the sites of oceanic evaporation is a relatively minor contributory factor compared with relative humidity in the labelling of d in meteoric waters (Pfahl and Sodemann, 2014; Steen-Larsen *et al.*, 2014). Furthermore, Pfahl and Sodemann (2014) have demonstrated that relative humidity dominates any signal from the surface ocean temperatures. Indeed, they suggest that palaeorecords of variations in d should now be interpreted as variations driven primarily by relative humidity changes at the site of moisture source. Ice core records are the only source of combined oxygen and hydrogen isotopic measurements of palaeoprecipitation (e.g. Jouzel *et al.*, 2007) but they are limited to high-latitude and high-altitude locations and so there remains a gap in evidence from the mid-latitudes with which to test ideas of atmospheric circulation change.

The 8.2-ka BP climate event provides an ideal test case for a first comparison between hydrogen and oxygen records from a mid-latitude *Sphagnum* moss archive given that it was the most severe climatic event in the Holocene and appears to have had most pronounced impact in the northern mid- to high latitudes (Alley and Ágústssdóttir, 2005; Rohling and Pälike, 2005; Thomas *et al.*, 2007; Daley *et al.*, 2011; Morrill *et al.*, 2013). The 8.2-ka BP event was a circum-North Atlantic region cold event lasting ~150 years approximately 8200 years ago and occurred in response to changes in the salinity balance of the North Atlantic Ocean (Barber *et al.*, 1999). An injection of meltwater from the catastrophic flood of Glacial Lake Agassiz-Ojibway provided the trigger that initiated an oceanic-atmospheric response, the spatial parameters of which are already well reproduced in numerical model experiments (LeGrande *et al.*, 2006; LeGrande and Schmidt, 2008; Tindall and Valdes, 2011; Holmes *et al.*, 2016). The most pronounced isotopic excursion reported thus far was found in a peat core from Newfoundland (Daley *et al.*, 2009). Progressively reduced values for the isotopic excursion were observed with increasing distance from the Labrador Sea (Marshall *et al.*, 2007; Domínguez-Villar *et al.*, 2009; Daley *et al.*, 2011; Holmes *et al.*, 2016). While the spatial pattern of the climate event has been reproduced well by model experiments, the duration of the event has remained a challenge for those models to simulate (Daley *et al.*, 2011; Tindall and Valdes, 2011). Recent work has demonstrated that data model comparisons offer the best similarity where sustained re-routing of freshwater is applied, thereby extending the salinity imbalance and associated disruption of AMOC (Carlson *et al.*, 2009; Clarke *et al.*, 2009; Holmes *et al.*, 2016). Daley *et al.* (2011) combined nine oxygen isotopic records from multiple terrestrial archives in the North Atlantic region, including ice cores, speleothems, lakes and peatlands, to identify a singular primary event of ~150 years duration. Several of the records exhibited some evidence for a second anomaly. This seemed to agree with reports of two sea-level jumps (Hijma and Cohen, 2010) and two episodes of surface North Atlantic freshening (Ellison *et al.*, 2006). The prevalence of any secondary isotopic anomaly was, however, not universally registered, nor did it relate to proximity of the site to the region of the flood or to characteristics of latitude or longitude that might indicate a specific atmospherically transmitted response. When synchronized by the start date of the primary isotopic anomaly in each record, there was no evidence for a broad second event (Daley *et al.*, 2011). The oceanic response in the period around 8.2 ka BP was also characterized by a southward extension in the northern North Atlantic sea-ice boundary (Müller *et al.*, 2009). In the modern day, much of the precipitation in the Atlantic Provinces of Canada is delivered by 'nor'easters' or precipitation from a north-easterly

direction during the cyclonic rotation of Atlantic depressions, which are themselves controlled by the latitudinal position of the atmospheric jet (Woollings *et al.*, 2012). An early Holocene extension in sea-ice extent should have noticeably altered the average conditions in the blend of Newfoundland-bound Atlantic moisture, if it is assumed that most of the precipitation would have come from a North Atlantic source. That change should be detectable in the records of the *Sphagnum* mosses. It is reasonable to hypothesize that the influence of the nor'easters may have been noticeably reduced through reduction of the surface area of ocean available for moisture sourcing or through migration of the jet and associated storm tracks (*sensu* Woollings *et al.*, 2012; Loader *et al.*, 2013). Available oceanic moisture would be limited to an alternative, more distant source. This process would be evidenced by a change in the deuterium excess and by a relative decrease in $\delta^{18}\text{O}$ values if the distance from vapour source to site of precipitation were greater than that which is observed in the modern day. In this study, therefore, we used combined hydrogen and oxygen isotopic data from the same sub-samples of *Sphagnum* cellulose from a peatland in Newfoundland to test directly the hypothesis that deuterium excess (and therefore atmospheric circulation) changed in the millennium following the 8.2-ka BP event.

Understanding the hydrogen isotopic signal of the source water in *Sphagnum* cellulose

Sphagnum cellulose isotopic values are modified from the source water (precipitation) isotopic composition by local environmental processes and by the biochemical processes occurring to produce cellulose (Ménot-Combes *et al.*, 2002; Daley *et al.*, 2010). First, isotopic values may be modified by any evaporation of precipitation waters on the surface of the bog before use of the water by the plant. Secondly, isotopic values are modified by biochemical fractionation during cellulose synthesis.

The processes leading to the oxygen isotopic labelling of *Sphagnum* cellulose are relatively well understood. *Sphagnum* $\delta^{18}\text{O}$ values have been shown to more closely approximate that of the source precipitation than bog surface waters based on long-term surface monitoring of several sites in Europe (Daley *et al.*, 2010). The close linkage between the oxygen isotopic composition of *Sphagnum* cellulose and its meteoric source water has been applied in subsequent palaeoclimatic studies (Kaislahti Tillman *et al.*, 2010; Roland *et al.*, 2015). Several studies have detected differences in *Sphagnum* isotopic values associated with microtopographical variations and distance from the water table (Brenninkmeijer *et al.*, 1982; Daley *et al.*, 2010; Loader *et al.*, 2016). The study by Daley *et al.* (2010) alongside earlier pioneers (Brenninkmeijer *et al.*, 1982; Aravena and Warner, 1992) also observed similar scales of variation between surface samples during individual sampling experiments. While evaporation undoubtedly influences surface variability, extended monitoring over 2 years demonstrated that any topographic control on variation in $\delta^{18}\text{O}_{\text{Sphagnum}}$ values was not consistent through time, partly because this difference was enhanced in summer bog waters (when most sampling in these studies has taken place) relative to spring or autumn waters in a way that was not consistently captured by the mosses. This longer-term pattern is probably due to temporary suspension of photosynthesis under dry conditions, when the evaporative effect would be greatest (Williams and Flanagan, 1996). The limited effect of this local spatial fractionation signal over the longer-term records implies that there remains reliability in the decadal-synthesized signal in peatland

palaeorecords, while recognizing that there still remains a challenge to characterize and quantify the evaporative influence (Loader *et al.*, 2016).

Biochemical fractionation affects oxygen and hydrogen to different extents due to the different pathways followed during cellulose synthesis (Estep and Hoering, 1981; Sternberg and DeNiro, 1983; Sternberg *et al.*, 1986; Yakir and DeNiro, 1990; Sternberg and Ellsworth, 2011). For both elements, the cellulose synthesis process involves reactions that take place in light conditions (photosynthesis) and those that occur during biosynthesis later on in the pathway (Yakir and DeNiro, 1990). Cellulose synthesis of oxygen atoms exhibits a nearly constant enrichment of ~27‰ relative to source water in plants from all photosynthetic modes and under a range of environmental conditions (DeNiro and Epstein, 1979, 1981; Sternberg *et al.*, 1986; Yakir and DeNiro, 1990; Waterhouse *et al.*, 2013). Enrichment results from isotopic fractionation during hydration of carbonyl groups of the intermediates of cellulose synthesis (DeNiro and Epstein, 1981). Any temperature-dependent effect is likely to be limited although may be present (Sternberg and Ellsworth, 2011). Plants of all photosynthetic modes have a stage in which oxygen passes through a carbonyl stage, which explains the occurrence of 27‰ in all plant types (Sternberg *et al.*, 1984a,b; Yakir and DeNiro, 1990).

Hydrogen fixation in cellulose, by contrast, is not the same for all plants. This difference results partly from the variable extent of biochemical fractionation occurring in different biosynthetic pathways (Estep and Hoering, 1980, 1981; Yakir and DeNiro, 1990). Hydrogen in cellulose is derived entirely from hydrogen in leaf water (Yapp and Epstein, 1982). Fractionation is regulated by two sets of processes: those occurring in the leaf during photosynthesis (leading to strong depletion in the cellulose) and subsequent processes of

cellulose synthesis from the intermediates (leading to enrichment) (Estep and Hoering, 1981; Yakir and DeNiro, 1990; Luo and Sternberg, 1991). The photosynthetic depletion relates to preferential hydration of nicotinamide adenine dinucleotide phosphate (NADP) with protium rather than deuterium to form NADPH (Yakir and DeNiro, 1990). Subsequent enrichment occurs during exchange with hydrogen in heterotrophic cellulose synthesis (Estep and Hoering, 1981; Yakir and DeNiro, 1990; Luo and Sternberg, 1991).

The fractionation factor that describes the isotopic discrimination in the formation of cellulose from water is defined as:

$$\alpha = ((\delta_{\text{cellulose}}/1000) + 1)/((\delta_{\text{source water}}/1000) + 1) \quad (1)$$

In modern Patagonian *Sphagnum*, α_D has been determined as 0.922 and reflects a greater net photosynthetic depletion of *Sphagnum* with respect to source waters (Pendall *et al.*, 2001). Strong depletion of *Sphagnum* δ_D relative to vascular plants has also been reported from sites in Europe (Brenninkmeijer *et al.*, 1982). Investigation of the fractionation of hydrogen in *Sphagnum* cellulose has been limited, although the studies above indicate that a strong depletion signal may be present in the genus (Loader *et al.*, 2016). It is possible that this may reflect the simple physiology of *Sphagnum* reflecting limited post-photosynthetic exchange of intermediates used in cellulose synthesis.

Methods

A 9-m-long peat core (NDN02/1) was collected from Nordan's Pond Bog in 2002 (Fig. 1) using a large-bore Russian corer (Hughes *et al.*, 2006). Hydrogen isotope analyses were undertaken on aliquots of the same *Sphagnum*

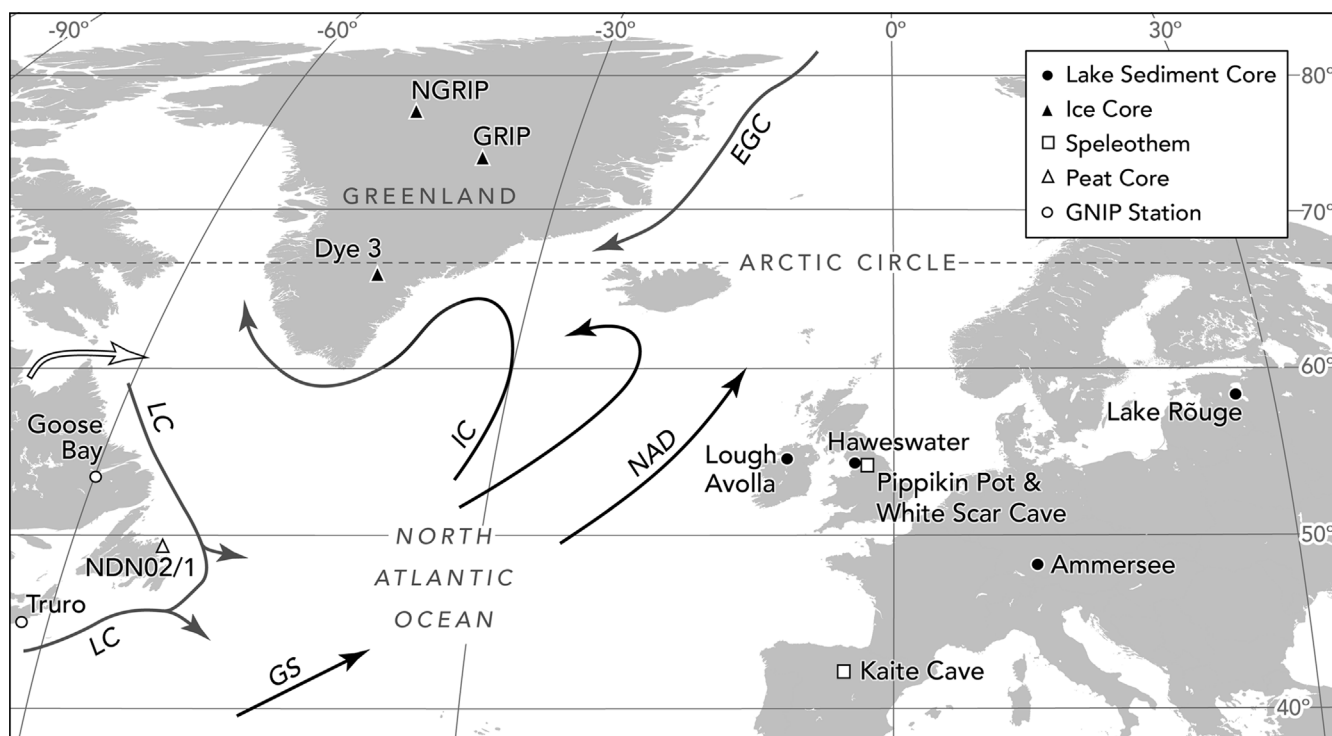


Figure 1. Map of the North Atlantic region showing modern ocean surface currents, Glacial Lake Agassiz outflow, NDN02/1 site location (open triangle), Global Network of Isotopes in Precipitation (GNIP) monitoring stations at Goose Bay, Labrador and Truro, Nova Scotia (open circles), and published reference site locations for existing high-resolution records. Solid circles = lake sediment cores, solid triangles = ice cores, open squares = speleothem sites. Dark arrows indicate warm surface ocean currents: GS = Gulf Stream, NAD = North Atlantic Drift, IC = Irminger Current. Grey arrows indicate cool surface ocean currents: EGC = East Greenland Current, LC = Labrador Current. Thick open arrow indicates routing of final drainage of glacial Lake Agassiz.

cellulose sub-samples previously reported for oxygen isotope analyses (Daley *et al.*, 2009). The cellulose sub-samples had previously been prepared from *Sphagnum* leaves that were isolated from the peat matrix using a stacked sieve system and density-separation procedure (Daley *et al.*, 2009, 2010). Four adjacent cellulose samples at 8-cm separation were selected at ~1000-year intervals based on the published chronology (Daley *et al.*, 2011) to provide a broad stratigraphic framework of $\delta D_{Sphagnum}$ values throughout the Holocene. Sample resolution was increased to one sample every 4 cm from ~8400 to 8000 a BP and contiguous 1-cm samples were analysed across the primary isotopic event observed in the oxygen isotope stratigraphy, providing sub-centennial and decadal resolution, respectively, such that hydrogen sample resolution equalled that of the oxygen record through 576–708 cm (7594–8812 a BP).

We used an online equilibration method for the measurements of $\delta D_{Sphagnum}$ values because of the benefits offered in terms of the rapidity of the process, the small sample sizes necessary, the limited fractionation effects and the avoidance of dangerous chemical procedures (Filot *et al.*, 2006; Loader *et al.*, 2015). The procedure used is described in detail in Filot *et al.* (2006) and is summarized here. Samples of 0.5–0.7 mg of dry alpha cellulose were weighed into tin capsules and wrapped loosely to allow water vapour to enter while remaining closed enough to prevent sample loss. Samples were then placed into an equilibration chamber and subjected to a continuous flow of a standard 'Meerwasser' water vapour of known isotopic composition [$+1\text{‰}$ vs. Vienna Standard Mean Ocean Water (VSMOW)] at 110°C and a flow rate of $7.8\text{ }\mu\text{L min}^{-1}$ delivered by a helium carrier gas stream at 40 mL min^{-1} . After 540 s the water supply was stopped and the sample transferred into an AS128 autosampler and then the pyrolysis reactor after only a few seconds. Pyrolytic conversion took place at 1450°C over a glassy carbon granulate on a 2-mm layer of silver wool and 20-mm bed of quartz wool in a thermo-chemical elemental analyser. Pyrolysis products were separated using a 1-m GC column then carried by a ConFlow II open split unit to a Thermo Finnigan Delta plus XL isotope ratio mass spectrometer. Results are given in standard delta notation relative to VSMOW. Repeat measurements of three separate cellulose standards (Merck; IAEA; Sigma) indicated measurement error was limited to $\sim 5\text{‰}$. The D/H ratio of non-exchangeable carbon-bound hydrogen was estimated from the bulk hydrogen isotope data using a mass balance relationship (Filot *et al.*, 2006).

Results and discussion

$\delta D_{Sphagnum}$ values for core NDN02/1 from Nordan's Pond Bog are presented as a time series alongside $\delta^{18}\text{O}_{Sphagnum}$ values (Daley *et al.*, 2009) using the age–depth model from Daley *et al.* (2011) in Fig. 2. The grey bars in the figure represent the 2σ range on repeat sample measurements. Age error estimates are reported here based on the maximum and minimum ages from the published CLAM age depth model (Daley *et al.*, 2011). With the exception of the early Holocene event, $\delta D_{Sphagnum}$ values show variation centred on $\sim -120 \pm 10\text{‰}$ with no general increasing or decreasing trend. $\delta D_{Sphagnum}$ values through the early Holocene event exceeded the range of variability found throughout the rest of the record, albeit with a lower sampling resolution from $\sim 7950 (\pm 50)$ a BP to present.

At $\sim 8450 (\pm 50)$ a BP, $\delta D_{Sphagnum}$ values fell $\sim 15\text{‰}$ in ≤ 55 years, stabilized for ~ 40 years then dropped a further $\sim 22\text{‰}$ in approximately 10 years to an isotopic minimum

$\sim 8350 (\pm 40)$ a BP. The subsequent recovery was very rapid ($\sim 30\text{‰}$ in ~ 20 years). $\delta D_{Sphagnum}$ values oscillated for the following ~ 100 years then recovered to $-130 \pm 5\text{‰}$ for the next ~ 200 years.

Good general correspondence between the hydrogen and oxygen isotopic records is observed. Both datasets show relatively high values at the base of the record, a strong isotopic depletion with a minimum at $\sim 8350 (\pm 40)$ a BP, higher and generally rising values between $\sim 7800 (\pm 60)$ a BP and $\sim 4200 (\pm 90)$ a BP, followed by a fall to lower values centred on $\sim 3500 (\pm 55)$ a BP rising to higher values again $\sim 2200 (\pm 40)$ a BP. Lower correspondence between the two records is observed in the upper section of the core. Between $\sim 1000 (\pm 55)$ and $\sim 600 (\pm 50)$ a BP, $\delta^{18}\text{O}_{Sphagnum}$ values exhibit a relatively low-magnitude isotopic decline. This corresponds to a large decline in $\delta D_{Sphagnum}$ values. In the top four samples, $\delta D_{Sphagnum}$ values again show relatively higher variability than the equivalent $\delta^{18}\text{O}_{Sphagnum}$ values for these levels.

The duration of the primary early Holocene isotopic event for both records was similar if the primary event is considered to have been initiated from the point of inflexion in both records at 656 cm ($\sim 8450 \pm 50$ a BP). The most notable difference between the two records is in the presence of a second isotopic minimum that succeeds the primary event. In the $\delta^{18}\text{O}_{Sphagnum}$ data, a second minimum was centred on $\sim 8150 (\pm 40)$ a BP, was of roughly half the magnitude of the primary event and had a duration of ~ 200 years. In the $\delta D_{Sphagnum}$ data, we find no evidence for a contemporaneous secondary minimum. Rather, the secondary oxygen minimum is associated with $\delta D_{Sphagnum}$ values within 1σ of the mean for the record. During the period in which $\delta^{18}\text{O}_{Sphagnum}$ values are observed to fall, $\delta D_{Sphagnum}$ values show a general increasing trend. Comparison of the two isotopic tracers therefore suggests that a high-magnitude isotopic event occurred $\sim 8450 (\pm 50)$ a BP with a minimum centred on $\sim 8350 (\pm 40)$ a BP and had a total duration of ~ 150 years, consistent with the broader north Atlantic region isotopic anomaly. There followed a divergence in $\delta D_{Sphagnum}$ and $\delta^{18}\text{O}_{Sphagnum}$ values. This divergence lasted approximately 200 years and probably represented a sustained change in d (Fig. 2).

To estimate the isotopic composition of the cellulose source water (δ_{sw}) we applied the published cellulose–water enrichment factors of $\alpha_D = 0.922$ (Pendall *et al.*, 2001) and $\alpha^{18}\text{O} = 1.274$ (Daley *et al.*, 2010) to the $\delta_{Sphagnum}$ cellulose values. The resulting estimates overlay modern GNIP measurements of the isotopic composition of precipitation from Goose Bay, Labrador and Truro, Nova Scotia (IAEA/WMO, 2004) in the bi-plot in Fig. 3. Average seasonal values for modern GNIP data are presented in Table 1. The linear regression for both the measured meteoric waters (or regional meteoric water line, RMWL; $\delta D = 7.47 \delta^{18}\text{O} + 5.38$; $R^2 = 0.97$) and the NDN02/1-inferred palaeo-estimates ($\delta D = 8.26 \delta^{18}\text{O} + 5.77$; $R^2 = 0.61$) are remarkably similar (Fig. 3). The 95% confidence and prediction limits are given as dotted and dashed lines, respectively (Fig. 3). The close correspondence between δ_{sw} estimates and the RMWL suggests that δ_{sw} was equivalent to $\delta_{precipitation}$. The mean of d for the length of the record is 4.05 ($n = 51$). The minor offset of the palaeo-slope to the right of the RMWL may have two explanations. First, the offset may represent the relatively consistent time-integrated local evaporation effect on $\delta_{Sphagnum}$ values from which the estimates are derived. Or, secondly, it may represent consistently lower deuterium excess in cellulose relative to measured annual weighted $\delta_{precipitation}$ values because of the seasonality of *Sphagnum* moss growth. Annually, deuterium excess values vary through

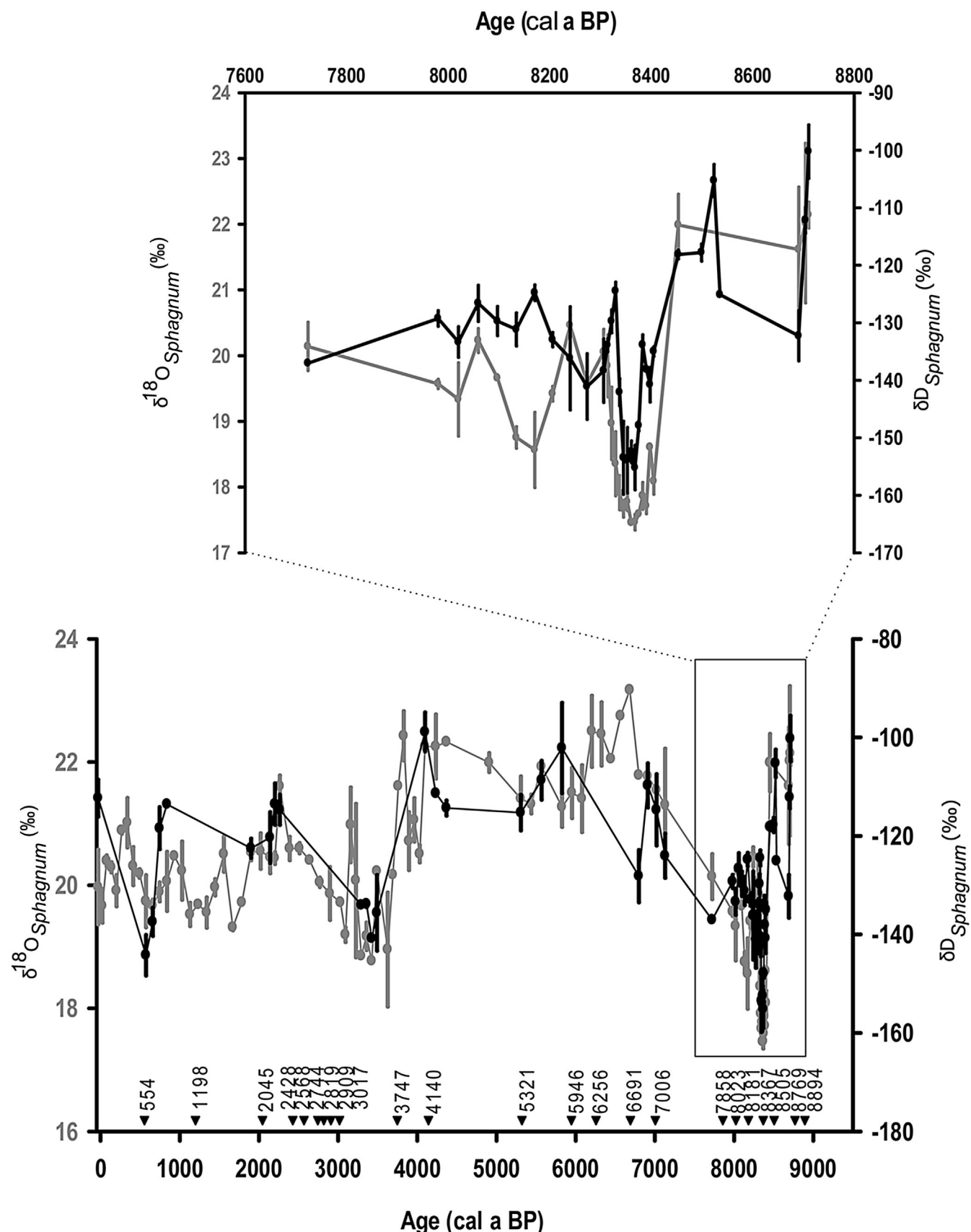


Figure 2. Combined records of $\delta D_{\text{Sphagnum}}$ values (black) and $\delta^{18}\text{O}_{\text{Sphagnum}}$ values (dark grey; Daley *et al.*, 2009) from NDN02/1. All values are given in delta notation relative to VSMOW. Chronology is that published in Daley *et al.* (2011). Dating control points are highlighted by black triangles. Values represent the best estimate based on the published CLAM age depth model (Daley *et al.*, 2011).

the year such that during summer months relatively low values of d are observed, reflecting warmer ocean water and higher relative humidity in the sites of moisture sourcing. In the winter, higher values of d are observed. In global

meteoric waters, this is observed as an inter-hemispheric variation over the year (Clark and Fritz, 1997; Gibson *et al.*, 2005; Pfahl and Sodemann, 2014; Steen-Larsen *et al.*, 2014). Given that *Sphagnum* would suspend growth in the absence

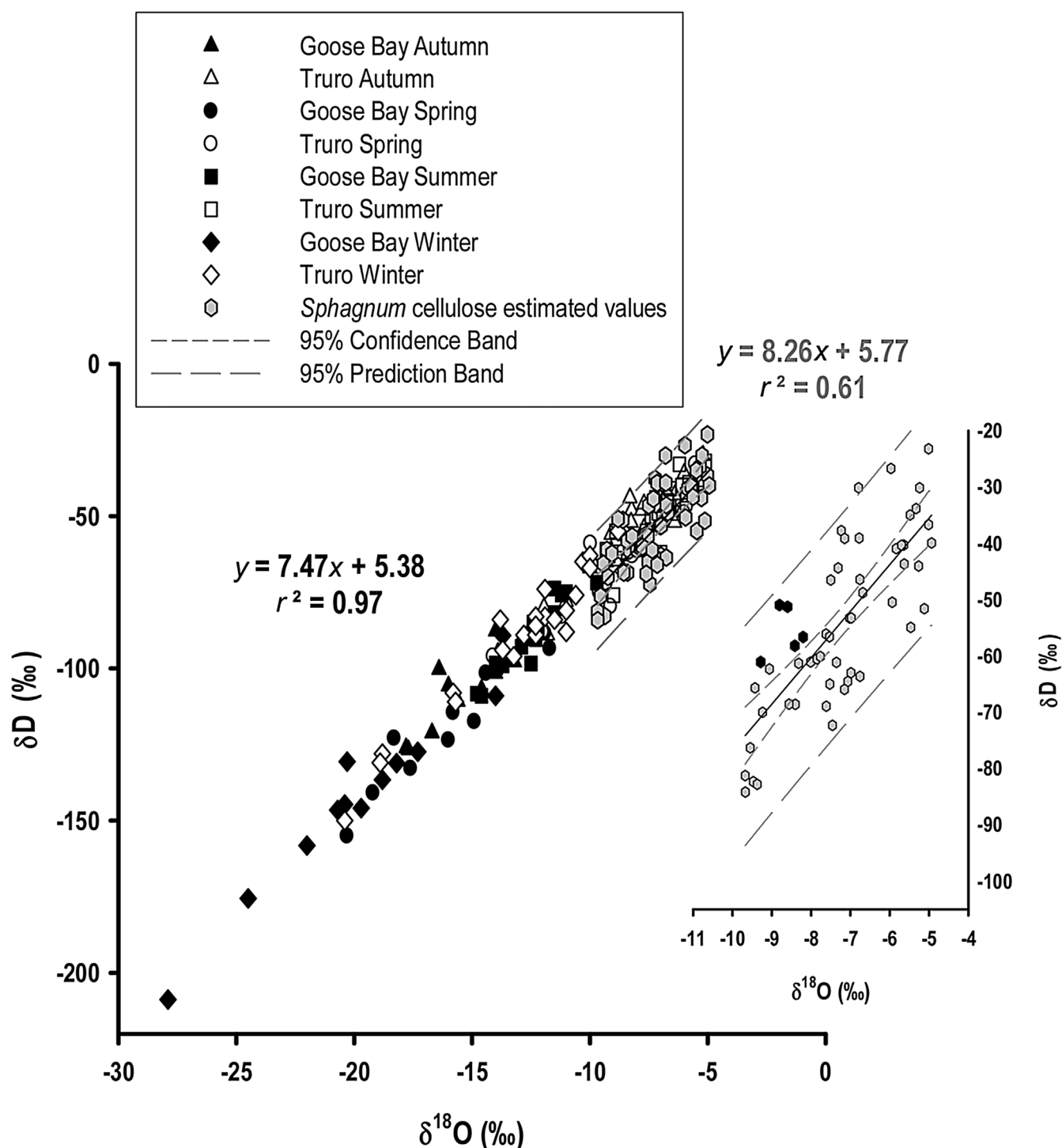


Figure 3. Comparison of Holocene *Sphagnum* source water reconstruction from NDN02/1 with modern GNIP precipitation data (IAEA/WMO, 2004) using $\alpha\delta^{18}\text{O}=1.0274$ (Daley *et al.*, 2010) and $\alpha\text{D}=0.922$ (Pendall *et al.*, 2001) for cellulose–water enrichment. GNIP variation in the isotopic composition of meteoric waters is given by season. Closed symbols = Truro; open symbols = Goose Bay. Cellulose palaeo-source water estimates = grey hexagons. Black hexagons in expanded insert = samples from the period 8350–8050 a BP with relatively high values of d .

of liquid water, either during periods of aridity or when unavailable (frozen) and that average temperatures in Newfoundland in the modern day are significantly below 0°C for at least 3 months of the year, there would be a natural bias in the record towards summer season cellulose synthesis. Modern climate data for 1971–2000 from Musgrave Harbour (49.450°N , 53.967°W ; altitude 3 m AOD; 43 km north-west of Nordan's Pond Bog) demonstrate the range of temperature seasonality. Mean monthly temperatures vary from a January maximum of -2.3°C and minimum of -9.8°C to a July maximum of 19.9°C and minimum of 10.8°C . Mean monthly maximum temperatures between 1971 and 2000 were below

Table 1. Seasonal weighted means of monthly isotopic data (‰) for Goose Bay (1961–1965) and Truro (1975–1983) (IAEA/WMO, 2004).

	Autumn	Winter	Spring	Summer
Goose Bay				
$\delta^{18}\text{O}$	-14.6	-19.8	-15.4	-12.4
σ	2.1	4.0	3.0	1.4
δD	-102.0	-142.0	-113.9	-89.2
σ	15.6	30.5	22.5	12.0
Truro				
$\delta^{18}\text{O}$	-8.5	-12.6	-8.8	-7.0
σ	1.9	3.3	2.4	1.3
δD	-56.7	-87.5	-62.2	-48.9
σ	15.3	24.4	18.3	11.2

0 °C for the winter months (December, January and February). This would, correspondingly, explain a plot with a slope consistent with meteoric waters, but a lower intercept. On balance, it is more likely that the small persistent offset, associated with a mean value for d slightly lower than RMWL

intercept (4.05; $n = 51$) and similarity in slope results from the seasonal growth bias. An evaporative effect would be expected to become more effective under higher surface air temperatures and be reflected in a local evaporative line with a lower slope angle.

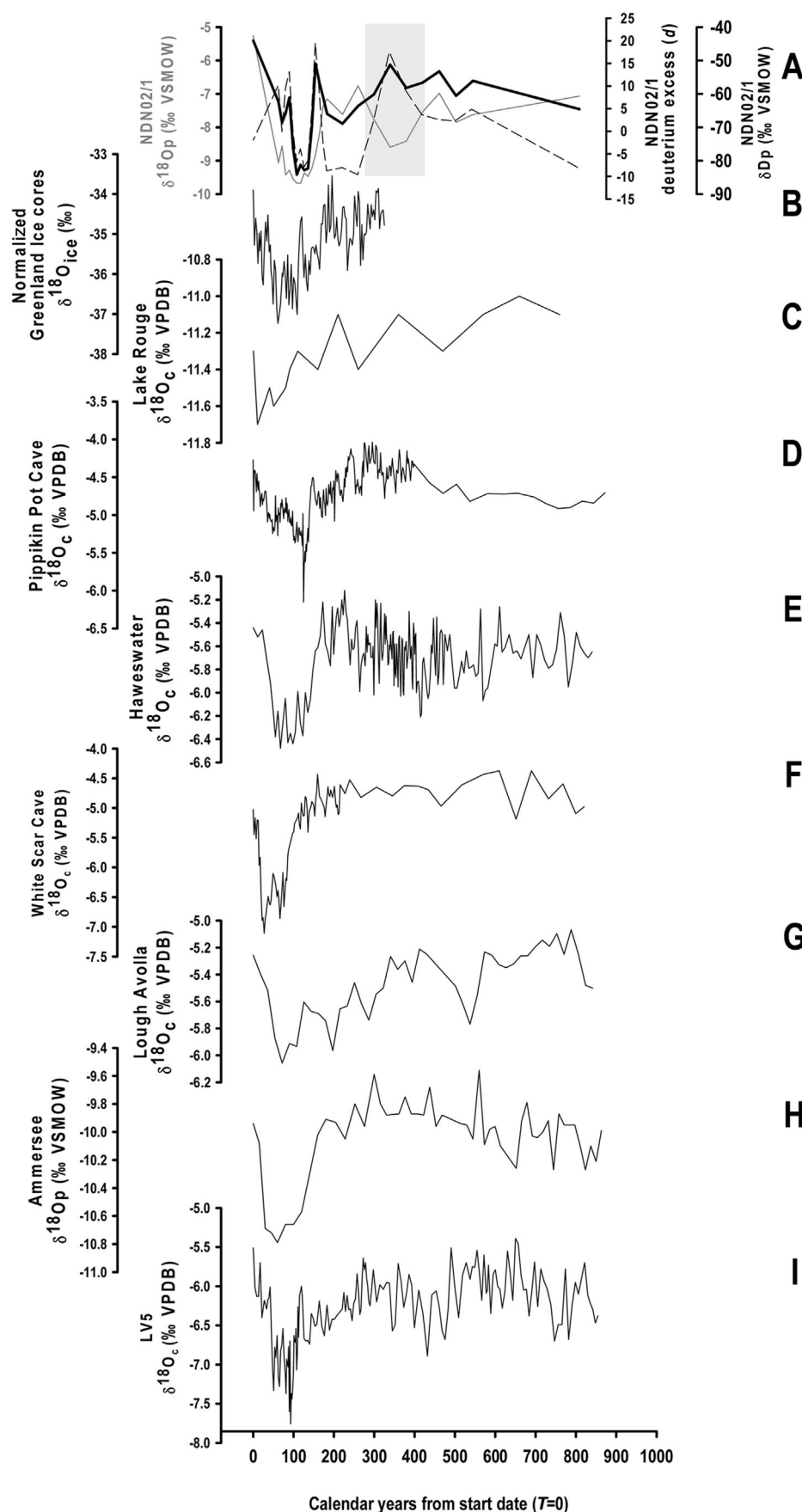


Figure 4. $\delta D_{\text{precipitation}}$ values (black), $\delta^{18}O_{\text{precipitation}}$ values (dark grey) and deuterium excess values (d ; dashed line) from NDN02/1 *Sphagnum* cellulose (top) compared with decadal-scale terrestrial isotopic time series for 9200–7400 a BP (BP = 1950 AD) for the North Atlantic region synchronized by start date ($T=0$; adapted from Daley *et al.*, 2011). The time from start of primary event progresses from left to right. (A) $\delta D_{\text{precipitation}}$ reconstruction (black line) with $\delta^{18}O_{\text{precipitation}}$ reconstruction (grey line) and d values (dashed line) from *Sphagnum* peat core NDN02/1, Newfoundland (Daley *et al.*, 2009). Grey shaded box indicates period of higher d values. (B) Greenland composite $\delta^{18}O_{\text{ice}}$ record (Thomas *et al.*, 2007). (C) Variation in lake-sediment $\delta^{18}O_{\text{calcite}}$ from Lake Røuge, Estonia (Veski *et al.*, 2004). (D) Sub-decadal variation in $\delta^{18}O_{\text{calcite}}$ from speleothem YD01, from Pippikin Pot Cave (Daley *et al.*, 2011). (E) Oxygen isotopic variation in lake-sediment calcite from Hawes Water, northern England (Marshall *et al.*, 2007). (F) Variation in $\delta^{18}O_{\text{calcite}}$ from annually banded speleothem WSC97-10-5, from White Scar Cave (Daley *et al.*, 2011). (G) Oxygen isotopic variation in lake-sediment calcite from Lough Avolla, western Ireland (Holmes *et al.*, 2016). (H) $\delta^{18}O_{\text{precipitation}}$ reconstruction from lake-sediment calcite from the Ammersee, Germany (von Grafenstein *et al.*, 1998). (I) Variation in $\delta^{18}O_{\text{calcite}}$ from speleothem LV5, northern Spain (Domínguez-Villar *et al.*, 2009).

In a recent review of the 8.2-ka BP event, Daley *et al.* (2011) compiled published isotopic records from sites around the North Atlantic region. The records were presented in calendar years since published start date for the event, given as $T=0$. Comparison of the new $\delta D_{\text{Sphagnum}}$ record with these existing reconstructions (Fig. 4) demonstrates that the secondary anomaly in $\delta^{18}\text{O}$ values in NDN02/1 (Daley *et al.*, 2009) is replicated neither in $\delta D_{\text{Sphagnum}}$ values nor more broadly and is associated with relatively high d values (Fig. 4). Only three mechanisms could explain this divergence. The first is that there was strong localized evaporation of the source water before cellulose synthesis. The second is that Nordan's Pond Bog, in effect, became more continental via increased distance between moisture source and the site. A third is that moisture from an evaporated, non-oceanic source contributed significantly to the source of the precipitation at Nordan's Pond Bog. A conclusion based on the first possibility would seem inconsistent with the broader evidence for a consistent slope to the reconstructed source water line and the integrated offset based on a predominance of *Sphagnum* growth in the summer months. Furthermore, the period 8250–8050 a BP was relatively cool (Leuenberger *et al.*, 1999; Hughes *et al.*, 2006; Thomas *et al.*, 2007). While it is possible that vapour pressure deficits may have increased in cool, dry air conditions (Alley and Ágústssdóttir, 2005), it seems unlikely that this was so sustained and so effective as to have produced the observed divergence in $\delta^{18}\text{O}$ and δD values. Further still, palaeoecological evidence from the core indicates that relatively wet bog surface conditions prevailed, suggesting minimal evaporation from the site (Hughes *et al.*, 2006; Charman *et al.*, 2009). Finally, localized evaporation cannot explain the decrease in $\delta^{18}\text{O}$ values. Instead, the second explanation would appear consistent with the observed extension of perennial sea ice in the North Atlantic and the decrease in $\delta^{18}\text{O}$ values (Müller *et al.*, 2009). The development of a longer pathway from water source to the peatland site is likely to have involved variation in the mean position or intensity of the northern atmospheric jet. Model simulations have demonstrated enhanced Atlantic anticyclonic activity during the 8.2-ka BP event (LeGrande and Schmidt, 2008; Clarke *et al.*, 2009; Tindall and Valdes, 2011), but none of which we are aware has run through the following millennium with similar temporal resolution. The enhanced temperature gradient between low and high latitudes induced by the slowdown in AMOC (Kleiven *et al.*, 2008) and extension of sea ice (Ellison *et al.*, 2006; Müller *et al.*, 2009) probably influenced the atmospheric jet such as to increase the intensity of zonal flow. However, it seems unlikely that a more intense and zonal atmospheric jet would enable the sourcing of oceanic moisture for Newfoundland precipitation from a more distant Atlantic source. A third possibility, then, is that the remaining bodies of continental water, which were continuing to drain into the North Atlantic via eastern North American routes (Jansson and Kleman, 2004), were now a source of moisture for Newfoundland precipitation. Higher levels of d (achieved by relatively high δD values compared with lower values of $\delta^{18}\text{O}$; Fig. 4A) would be associated with input of continentally sourced, re-evaporated moisture. Lower $\delta^{18}\text{O}$ values would also be expected with increased distance in the pathway from oceanic source to site. This third explanation would most plausibly fit the evidence from NDN02/1. The combined records from NDN02/1 would therefore suggest that in the period 8250–8050 a BP, following a primary isotopic anomaly registered widely in the North Atlantic region and known as the 8.2-ka BP event, the precipitation source moisture mix over Newfoundland was augmented by a more

distant, less humid and probably continental source. This variation was probably driven by increased atmospheric zonal flow induced by changes in the meridional atmospheric temperature gradient in the northern hemisphere.

Conclusions

Combined oxygen and hydrogen isotopic analyses on the cellulose of *Sphagnum* mosses from NDN02/1 in Newfoundland have revealed a complex climatic response to the final drainage of Glacial Lake Agassiz-Ojibway and subsequent routing of freshwater. Following a widespread regional climate event that lasted ~ 150 years, a secondary decrease in $\delta^{18}\text{O}$ values, which was not replicated regionally or in lower δD values from the same samples, most likely represented a sustained increase in deuterium excess. The most plausible explanation is that the mix of meteoric waters that provided precipitation to the peatland site was augmented by continentally derived moisture associated with increased zonal flow of the northern atmospheric jet. This first use of combined hydrogen and oxygen isotopic data from a peatland core demonstrates the interpretative value that can be gained from dual isotope analyses and provides a new tool for mid-latitude palaeoclimatic investigation. In so doing, it provides a contribution to the recent call for better reconstructions of Holocene atmospheric circulation change (Holmes *et al.*, 2016).

Acknowledgments. We thank Prof. Dan Charman, Dr Tom Roland and an anonymous reviewer for their helpful and kind comments on the manuscript. We acknowledge the support of NERC RAPID grant NER/T/S/2002/00460 to ISOMAP-UK, the NERC PRECIP grant under codes NE/G019851/1, NE/G020272/1, NE/G019673/1 and NE/G02006X/1 and grant NE/C50907/1. We thank Dr Marc Filot for support and assistance with the analysis of δD values in cellulose at UNIBE, Bern, Switzerland.

Abbreviations. AMOC, Atlantic Meridional Overturning Circulation; RMWL, regional meteoric water line; VSMOW, Vienna Standard Mean Ocean Water.

References

- Alley R, Ágústssdóttir A. 2005. The 8k event: cause and consequences of a major Holocene abrupt climate change. *Quaternary Science Reviews* **24**: 1123–1149.
- Araguás-Araguás L, Froehlich K, Rozanski K. 2000. Deuterium and oxygen-18 isotope composition of precipitation and atmospheric moisture. *Hydrological Processes* **14**: 1341–1355.
- Aravena R, Warner BG. 1992. Oxygen-18 composition of *Sphagnum*, and microenvironmental water relations. *Bryologist* **95**: 445–448.
- Barber DC, Dyke A, Hillaire-Marcel C *et al.* 1999. Forcing of the cold event of 8,200 years ago by catastrophic drainage of Laurentide lakes. *Nature* **400**: 344–348.
- Breninkmeijer CAM, van Geel B, Mook WG. 1982. Variations in the D/H and $^{18}\text{O}/^{16}\text{O}$ ratios in cellulose extracted from a peat core. *Earth and Planetary Science Letters* **61**: 283–290.
- Carlson AE, Clark PU, Haley BA *et al.* 2009. Routing of western Canadian Plains runoff during the 8.2 ka cold event. *Geophysical Research Letters* **36**: L14704.
- Charman DJ, Barber KE, Blaauw M *et al.* 2009. Climate drivers for peatland palaeoclimate records. *Quaternary Science Reviews* **28**: 1811–1819.
- Clark I, Fritz P. 1997. *Environmental Isotopes in Hydrogeology*. Lewis Publishers: Boca Raton, FL.
- Clarke GKC, Bush ABG, Bush JWM. 2009. Freshwater discharge, sediment transport, and modeled climate impacts of the final drainage of Glacial Lake Agassiz. *Journal of Climate* **22**: 2161–2180.
- Collins M, Knutti R, Arblaster JM *et al.* 2013. Long-term climate change: projections, commitments and irreversibility. In *Climate Change 2013: the Physical Science Basis*, Stocker TF, Qin D,

- Plattner G-K, Tignor M, Allen SK, Boschung J, Nauels A, Xia Y, Bex V, Midgley PM (eds). Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change. Cambridge University Press, Cambridge, UK.
- Daley TJ, Barber KE, Street-Perrott FA *et al.* 2010. Holocene climate variability revealed by oxygen isotope analysis of *Sphagnum* cellulose from Walton Moss, northern England. *Quaternary Science Reviews* **29**: 1590–1601.
- Daley TJ, Mauquoy D, Chambers FM *et al.* 2012. Investigating late Holocene variations in hydroclimate and the stable isotope composition of precipitation using southern South American peatlands: an hypothesis. *Climate of the Past* **8**: 1457–1471.
- Daley TJ, Street-Perrott FA, Loader NJ *et al.* 2009. Terrestrial climate signal of the '8200 yr B.P. cold event' in the Labrador Sea region. *Geology* **37**: 831–834.
- Daley TJ, Thomas ER, Holmes JA *et al.* 2011. The 8200yr BP cold event in stable isotope records from the North Atlantic region. *Global and Planetary Change* **79**: 288–302.
- Dansgaard W. 1964. Stable isotopes in precipitation. *Tellus* **16**: 436–468.
- Dawson AG, Elliott L, Mayewski P *et al.* 2003. Late-Holocene North Atlantic climate 'seesaws', storminess changes and Greenland ice sheet (GISP2) palaeoclimates. *Holocene* **13**: 381–392.
- DeNiro MJ, Epstein S. 1979. Relationship between the oxygen isotope ratios of terrestrial plant cellulose, carbon dioxide, and water. *Science* **204**: 51–53.
- DeNiro MJ, Epstein S. 1981. Isotopic composition of cellulose from aquatic organisms. *Geochimica et Cosmochimica Acta* **45**: 1885–1894.
- Domínguez-Villar D, Fairchild IJ, Baker A *et al.* 2009. Oxygen isotope precipitation anomaly in the North Atlantic region during the 8.2 ka event. *Geology* **37**: 1095–1098.
- Ellison CR, Chapman MR, Hall IR. 2006. Surface and deep ocean interactions during the cold climate event 8200 years ago. *Science* **312**: 1929–1932.
- Estep MF, Hoering TC. 1980. Biogeochemistry of the stable hydrogen isotopes. *Geochimica et Cosmochimica Acta* **44**: 1197–1206.
- Estep MF, Hoering TC. 1981. Stable hydrogen isotope fractionations during autotrophic and mixotrophic growth of microalgae. *Plant Physiology* **67**: 474–477.
- Filot MS, Leuenberger M, Pazdur A *et al.* 2006. Rapid online equilibration method to determine the D/H ratios of non-exchangeable hydrogen in cellulose. *Rapid Communications in Mass Spectrometry: RCM* **20**: 3337–3344.
- Francis JA, Vavrus SJ. 2015. Evidence for a wavier jet stream in response to rapid Arctic warming. *Environmental Research Letters* **10**: 014005.
- Gat JR. 1980. The isotopes of oxygen and hydrogen in precipitation. In *Handbook of Environmental Isotope Geochemistry*, Fritz P, Fontes JC (eds). Elsevier: Amsterdam; 21–47.
- Gibson JJ, Edwards TWD, Birks SJ *et al.* 2005. Progress in isotope tracer hydrology in Canada. *Hydrological Processes* **19**: 303–327.
- Hijma MP, Cohen KM. 2010. Timing and magnitude of the sea-level jump prelude the 8200-yr event. *Geology* **38**: 275–278.
- Hofmann M, Rahmstorf S. 2009. On the stability of the Atlantic meridional overturning circulation. *Proceedings of the National Academy of Sciences of the United States of America* **106**: 20584–20589.
- Holmes J, Arrowsmith C, Austin W *et al.* 2010. Climate and atmospheric circulation changes over the past 1000 years reconstructed from oxygen isotopes in lake-sediment carbonate from Ireland. *The Holocene* **20**: 1105–1111.
- Holmes JA, Tindall J, Roberts N *et al.* 2016. Lake isotope records of the 8200-year cooling event in western Ireland: comparison with model simulations. *Quaternary Science Reviews* **131**: 341–349.
- Hughes PDM, Blundell A, Charman DJ *et al.* 2006. An 8500 cal. year multi-proxy climate record from a bog in eastern Newfoundland: contributions of meltwater discharge and solar forcing. *Quaternary Science Reviews* **25**: 1208–1227.
- IAEA/WMO. 2004. Global Network of Isotopes in Precipitation, the GNIP database. isohis.iaea.org.
- Jansson KN, Kleman J. 2004. Early Holocene glacial lake meltwater injections into the Labrador Sea and Ungava Bay. *Paleoceanography* **19**: PA1001.
- Jouzel J, Stievenard M, Johnsen SJ *et al.* 2007. The GRIP deuterium-excess record. *Quaternary Science Reviews* **26**: 1–17.
- Kaislahti Tillman P, Holzkämper S, Kuhry P *et al.* 2010. Long-term climate variability in continental subarctic Canada: A 6200-year record derived from stable isotopes in peat. *Palaeogeography Palaeoclimatology Palaeoecology* **298**: 235–246.
- Kleiven HK, Kissel C, Laj C *et al.* 2008. Reduced North Atlantic Deep Water coeval with the glacial Lake Agassiz freshwater outburst. *Science* **319**: 60–64.
- LeGrande AN, Schmidt GA. 2008. Ensemble, water isotope-enabled, coupled general circulation modeling insights into the 8.2 ka event. *Paleoceanography* **23**: A3207.
- LeGrande AN, Schmidt GA. 2009. Sources of Holocene variability of oxygen isotopes in paleoclimate archives. *Climate of the Past* **5**: 441–455.
- LeGrande AN, Schmidt GA, Shindell DT, *et al.* 2006. Consistent simulations of multiple proxy responses to an abrupt climate change event. *Proceedings of the National Academy of Sciences of the United States of America* **103**: 837–842.
- Leuenberger MC, Lang C, Schwander J. 1999. $\delta^{15}\text{N}$ measurements as a calibration tool for the paleothermometer and gas-ice age differences: a case study for the 8200 BP event on GRIP ice. *Journal of Geophysical Research-Atmospheres* **104**: 22163–22170.
- Loader NJ, Street-Perrott FA, Daley TJ *et al.* 2015. Simultaneous determination of stable carbon, oxygen, and hydrogen isotopes in cellulose. *Analytical Chemistry* **87**: 376–380.
- Loader NJ, Street-Perrott FA, Mauquoy D *et al.* 2016. Measurements of hydrogen, oxygen and carbon isotope variability in *Sphagnum* moss along a micro-topographical gradient in a southern Patagonian peatland. *Journal of Quaternary Science* **31**: 426–435.
- Loader NJ, Young GHF, Grudd H *et al.* 2013. Stable carbon isotopes from Torneträsk, northern Sweden provide a millennial length reconstruction of summer sunshine and its relationship to Arctic circulation. *Quaternary Science Reviews* **62**: 97–113.
- Luo Y, Sternberg L. 1991. Deuterium heterogeneity in starch and cellulose nitrate of C₃ and C₄ plants. *Phytochemistry* **30**: 1095–1098.
- Marshall JD, Lang B, Crowley SF *et al.* 2007. Terrestrial impact of abrupt changes in the North Atlantic thermohaline circulation: Early Holocene, UK. *Geology* **35**: 639–642.
- Ménot-Combes G, Burns SJ, Leuenberger M. 2002. Variations of $^{18}\text{O}/^{16}\text{O}$ in plants from temperate peat bogs (Switzerland): implications for paleoclimatic studies. *Earth and Planetary Science Letters* **202**: 419–434.
- Merlivat L, Jouzel J. 1979. Global climatic interpretation of the deuterium-oxygen-18 relationship for precipitation. *Journal of Geophysical Research* **84**: 5029–5033.
- Morrill C, Anderson DM, Bauer BA *et al.* 2013. Proxy benchmarks for intercomparison of 8.2 ka simulations. *Climate of the Past* **9**: 423–432.
- Müller J, Massé G, Stein R *et al.* 2009. Variability of sea-ice conditions in the Fram Strait over the past 30,000 years. *Nature Geosciences* **2**: 772–776.
- Pendall E, Markgraf V, White JWC *et al.* 2001. Multiproxy record of Late Pleistocene–Holocene climate and vegetation changes from a peat bog in Patagonia. *Quaternary Research* **55**: 168–178.
- Pfahl S, Sodemann H. 2014. What controls deuterium excess in global precipitation? *Climate of the Past* **10**: 771–781.
- Pfahl S, Wernli H. 2008. Air parcel trajectory analysis of stable isotopes in water vapor in the eastern Mediterranean. *Journal of Geophysical Research* **113**: D20104.
- Rohling EJ, Pälike H. 2005. Centennial-scale climate cooling with a sudden cold event around 8,200 years ago. *Nature* **434**: 975–979.
- Roland TP, Daley TJ, Caseldine CJ *et al.* 2015. The 5.2 ka climate event: evidence from stable isotope and multi-proxy palaeoecological peatland records in Ireland. *Quaternary Science Reviews* **124**: 209–223.
- Rozanski K. 1985. Deuterium and O-18 in European groundwaters – links to atmospheric circulation in the past. *Chemical Geology: Isotope Geoscience Section* **52**: 349–363.
- Rozanski K, Araguás-Araguás L, Gonfiantini R. 1993. Isotopic patterns in modern global precipitation. In *Climate Change in*

- Continental Isotopic Records*, Swart PK, Lohmann KC, McKensie JA, Savin S (eds). American Geophysical Union: Washington, DC; 1–36.
- Sonntag C, Rozanski K, Munnich KO *et al.* 1983. Variations of deuterium and oxygen-18 in continental precipitation and ground-water and their causes. In *Variations in the Global Water Budget*, Street-Perrott FA (ed.). D. Reidel: Dordrecht; 107–124.
- Steen-Larsen HC, Sveinbjörnsdóttir AE, Peters AJ *et al.* 2014. Climatic controls on water vapor deuterium excess in the marine boundary layer of the North Atlantic based on 500 days of in situ, continuous measurements. *Atmospheric Chemistry and Physics* **14**: 7741–7756.
- Steffensen JP, Andersen KK, Bigler M *et al.* 2008. High-resolution Greenland ice core data show abrupt climate change happens in few years. *Science* **321**: 680–684.
- Sternberg L, Ellsworth PF. 2011. Divergent biochemical fractionation, not convergent temperature, explains cellulose oxygen isotope enrichment across latitudes. *PLOS ONE* **6**: e28040.
- Sternberg LDL, DeNiro MJ. 1983. Biochemical implications of the isotopic equilibrium fractionation factor between the oxygen atoms of acetone and water. *Geochimica et Cosmochimica Acta* **47**: 2271–2274.
- Sternberg LO, DeNiro MJ, Johnson HB. 1984a. Isotope ratios of cellulose from plants having different photosynthetic pathways. *Plant Physiology* **74**: 557–561.
- Sternberg LO, DeNiro MJ, Ting IP. 1984b. Carbon, hydrogen, and oxygen isotope ratios of cellulose from plants having intermediary photosynthetic modes. *Plant Physiology* **74**: 104–107.
- Sternberg LDL, DeNiro MJ, Savidge RA. 1986. Oxygen isotope exchange between metabolites and water during biochemical reactions leading to cellulose synthesis. *Plant Physiology* **82**: 423–427.
- Tang Q, Zhang X, Francis JA. 2014. Extreme summer weather in northern mid-latitudes linked to a vanishing cryosphere. *Nature Climate Change* **4**: 45–50.
- Thomas ER, Wolff EW, Mulvaney R *et al.* 2007. The 8.2 ka event from Greenland ice cores. *Quaternary Science Reviews* **26**: 70–81.
- Tindall JC, Valdes PJ. 2011. Modeling the 8.2ka event using a coupled atmosphere–ocean GCM. *Global and Planetary Change* **79**: 312–321.
- Veski S, Seppä H, Ojala AEK. 2004. Cold event at 8200 yr BP recorded in annually laminated lake sediments in eastern Europe. *Geology* **32**: 681–684.
- Vinther BM, Johnsen SJ, Andersen KK *et al.* 2003. NAO signal recorded in the stable isotopes of Greenland ice cores. *Geophysical Research Letters* **30**.
- von Grafenstein U, Erlenkeuser H, Muller J, Jouzel J, Johnsen S. 1998. The cold event 8200 years ago documented in oxygen isotope records of precipitation in Europe and Greenland. *Climate Dynamics* **14**, 73–81.
- Waterhouse JS, Cheng S, Juchelka D *et al.* 2013. Position-specific measurement of oxygen isotope ratios in cellulose: isotopic exchange during heterotrophic cellulose synthesis. *Geochimica et Cosmochimica Acta* **112**: 178–191.
- Williams TG, Flanagan LB. 1996. Effect of changes in water content on photosynthesis, transpiration and discrimination against ^{13}C and $\text{C}^{18}\text{O}^{16}\text{O}$ in *Pleurozium* and *Sphagnum*. *Oecologia* **108**: 38–46.
- Woollings T, Gregory JM, Pinto JG *et al.* 2012. Response of the North Atlantic storm track to climate change shaped by ocean–atmosphere coupling. *Nature Geoscience* **5**: 313–317.
- Yakir D, DeNiro MJ. 1990. Oxygen and hydrogen isotope fractionation during cellulose metabolism in *Lemna gibba* L. *Plant Physiology* **93**: 325–332.
- Yapp CJ, Epstein S. 1982. A reexamination of cellulose carbon-bound hydrogen δD measurements and some factors affecting plant–water D/H relationships. *Geochimica et Cosmochimica Acta* **46**: 955–965.
- Young GHF, Loader NJ, McCarroll D *et al.* 2015. Oxygen stable isotope ratios from British oak tree-rings provide a strong and consistent record of past changes in summer rainfall. *Climate Dynamics* **45**: 3609–3622.