JOURNAL OF GEOPHYSICAL RESEARCH: BIOGEOSCIENCES, VOL. 118, 184–194, doi:10.1002/jgrg.20021, 2013

Differing source water inputs, moderated by evaporative enrichment, determine the contrasting $\delta^{18}O_{CELLULOSE}$ signals in maritime Antarctic moss peat banks

Jessica Royles,[1,2] Louise C. Sime,[2] Dominic A. Hodgson,[2] Peter Convey,[2] and Howard Griffiths[1]

Received 31 May 2012; revised 18 December 2012; accepted 22 December 2012; Published 25 February 2013.

[1] Oxygen isotope palaeoclimate records, preserved in moss tissue cellulose, are complicated by environmental influences on the relationships between source water inputs and evaporative conditions. We carried out stable isotope analyses of precipitation collected from the maritime Antarctic and cellulose extracted from co-located *Chorisodontium aciphyllum* dominated moss peat bank deposits accumulated since 1870 A.D. Analyses of stable oxygen and hydrogen isotope composition of summer precipitation on Signy Island (60.7°S, 45.6°W) established a local meteoric water line (LMWL) similar to both the global MWL and other LMWLs, and almost identical to the HadAM3 isotope-enabled global circulation model output. The oxygen isotopic composition of cellulose ($\delta^{18}O_C$) revealed little temporal variation between four moss peat banks on Signy Island since 1870. However, $\delta^{18}O_C$ followed two patterns with Sites A and D consistently 3‰ enriched relative to $\delta^{18}O_C$ values from Sites B and C. The growing moss surfaces at Sites A and D are likely to have been hydrated by isotopically heavier summer precipitation, whilst at Sites B and C, the moss banks are regularly saturated by the isotopically depleted snow melt streams. Laboratory experiments revealed that evaporative enrichment of *C. aciphyllum* moss leaf water by 5‰ occurred rapidly following saturation (ecologically equivalent to post-rainfall or snow melt periods). In addition to the recognized source water-cellulose fractionation extent of 27 ± 3‰, such a shift would account for the 32‰ difference measured between $\delta^{18}O$ of Signy Island precipitation and cellulose.

Citation: Royles, J., L. C. Sime, D. A. Hodgson, P. Convey, and H. Griffiths (2013), Differing source water inputs, moderated by evaporative enrichment, determine the contrasting $\delta^{18}O_{CELLULOSE}$ signals in maritime Antarctic moss peat banks, *J. Geophys. Res. Biogeosci.*, *118*, 184–194, doi:10.1002/jgrg.20021.

1. Introduction

[2] The oxygen isotope composition ($\delta^{18}O$) of plant material is determined by both the isotopic composition of the leaf water ($\delta^{18}O_L$) during organic matter synthesis and fractionation processes that occur during subsequent metabolic inter-conversion [*Barbour*, 2007]. Primary isotopic inputs represent source water ($\delta^{18}O_{SW}$) and atmospheric water vapor ($\delta^{18}O_{WV}$), whilst evaporative water loss to the atmosphere is dependent upon relative humidity and air temperature, and isotopic exchange occurring between leaf water and organic molecules determines $\delta^{18}O_L$ at the site of cellulose synthesis [*Barbour et al.*, 2005; *Helliker and Griffiths*, 2007; *Kahmen et al.*, 2011]. For ombrotrophic moss peat banks, locally abundant across the maritime Antarctic region [*Gimingham and Smith*, 1971], rain and snow are the dominant water sources for growth, and thus, the isotopic composition of precipitation ($\delta^{18}O_P$) is critical to $\delta^{18}O_L$.

[3] When water evaporates and forms clouds, the isotopically heavier isotopologues ($H_2^{18}O$, $HD^{16}O$) tend to remain in the liquid phase; therefore, vapors are ^{18}O depleted with respect to the liquid phase [*Gat*, 1996]. When precipitation forms, the heavier isotopologues tend towards the condensed aqueous phase, and consequently, precipitation is isotopically enriched relative to residual cloud water vapor; temperature and rainout effects result in snowfall being further depleted, relative to rain [*Dansgaard*, 1964; *Gat*, 1996]. The Global Meteoric Water Line (GMWL) [*Craig*, 1961] describes the relationship between the stable hydrogen (δ^2H) and oxygen ($\delta^{18}O$) isotopic composition of global precipitation formed under equilibrium conditions [equation (1)].

$$\delta^2 H = \left(8 \times \delta^{18} O\right) + 10 \quad (1)$$

[4] Precipitation becomes progressively more isotopically depleted at high latitudes due to the preferential rainout of the heavy isotopologues as clouds move towards the poles [*Ciais et al.*, 1995; *Noone*, 2008]. Observations and model

[1]Department of Plant Sciences, University of Cambridge, Cambridge, UK.
[2]British Antarctic Survey, Cambridge, UK.

Corresponding author: J. Royles, Department of Plant Sciences, University of Cambridge, Downing Street, Cambridge CB2 3EA, UK. (jesyle@bas.ac.uk)

2169-8953/13/10.1002/jgrg.20021

outputs both suggest that the mid-latitude oceans of the Southern Hemisphere provide the main evaporative sources for Antarctic precipitation [*Noone*, 2008; *Werner et al*., 2001].

[5] The isotopic composition of precipitation may not fall along the GMWL, and rather along a local meteoric water line (LMWL) due to the difference between the mass-dependent kinetic fractionation factors of oxygen and hydrogen isotopes. The extent of this deviation from the GMWL is quantified through "deuterium excess" (d) [*Dansgaard*, 1964] (equation (2)):

$$d = \delta^2 H - \left(8 \mathrm{x} \delta^{18} O\right) \quad (2)$$

[6] As well as being used to identify the extent of evaporative recycling, deuterium excess is dependent upon the freezing history of water due to the difference in mass, and consequently the diffusion coefficients, between $^1H^2H^{16}O$ and $^1H_2^{18}O$ [*Gat*, 1996; *Lacelle*, 2011; *Souchez et al*., 2000]. Freeze-thaw processes can alter d, with the slope of a "freezing line" (d plotted against $\delta^{18}O$) dependent upon the freezing rate, the percentage of freezing, and the thickness of the boundary layer [*Lacelle*, 2011; *Souchez et al*., 2000].

[7] Bryophytes absorb and lose water more readily than vascular plants [*Sveinbjörnsson and Oechel*, 1992], so in the absence of roots, the availability of water sources abstracted from precipitation, fog, dew, and water vapor are critical for growth [*Jonsson et al*., 2008]. Most water conduction occurs within the external capillary component of the bryophyte hydraulic system [*Proctor*, 2000]. Desiccation tolerance allows many bryophytes to be successful in unpredictable, intermittently drought-ridden areas as photosynthesis occurs when conditions are locally humid or following rehydration [*Longton*, 1988; *Proctor*, 2000].

[8] Cellulose is a degradation-resistant structural carbohydrate which remains well preserved for millennia in tree rings [*McCarroll and Loader*, 2004; *Sternberg*, 2009] and peat banks [*Kaislahti Tillman et al*., 2010a]. The isotopic composition of cellulose ($\delta^{18}O_C$) is enriched biochemically by 27 ± 3‰ compared with the oxygen isotopic composition of water at the site of cellulose synthesis [*Da Silveira et al*., 1989; *De Niro and Epstein*, 1979; *Sternberg*, 2009; *Zanazzi and Mora*, 2005]. Interpretation of oxygen isotope paleoclimate records preserved in cellulose is complex, due to the multiplicity of factors influencing the measured $\delta^{18}O_C$, and the species and tissue specificity of how environmental changes are reflected in $\delta^{18}O_C$ [*Kaislahti Tillman et al*., 2010b; *Moschen et al*., 2009]. For example, evaporative isotopic enrichment of leaf water after a rain event or isotopic exchange between atmospheric water vapor and tissue water under conditions of high external relative humidity can result in an offset between the isotopic composition of source water ($\delta^{18}O_{SW}$) and the water at the cellulose synthesis site so that $\delta^{18}O_C$ ceases to reflect directly $\delta^{18}O_{SW}$ [*Helliker and Griffiths*, 2007; *Sternberg*, 2009]. Initial models that invoked $\delta^{18}O_C$ preserved in tree rings as a direct paleo-thermometer [*Libby et al*., 1976] have been further developed, with seasonal precipitation inputs [*Ogée et al*., 2009], leaf temperature [*Helliker and Ritcher*, 2008], and the leaf-to-atmosphere vapor pressure deficit all critical determinants of $\delta^{18}O_C$ [*Kahmen et al*., 2011].

[9] Despite these potential complexities, modern $\delta^{18}O_C$ analyzed from a *Sphagnum* peat bank at the temperate Walton Moss, UK (54.99°N, 2.76°W) tracked $\delta^{18}O_P$, and thus, the preserved $\delta^{18}O_C$ provided a good indication of the $\delta^{18}O_P$ over time, along with an estimate of summer wetness [*Daley et al*., 2010]. Similarly, $\delta^{18}O_C$ of bog plants in Switzerland represented a smoothed precipitation signal [*Ménot-Combes et al*., 2002], illustrating the importance of bog micro-topography to the isotopic composition of the leaf water, through evaporative enrichment of the source water, and subsequently the composition of the cellulose [*Aravena and Warner*, 1992]. Along an altitudinal transect in Poland, the stable isotope composition of surface water was the primary determinant of the $\delta^{18}O$ values of peat-forming plants growing at the surface of mires [*Skrzypek et al*., 2010]. Thus, the vast global expanses of peatland, which have mainly developed since the Last Glacial Maximum [*Yu et al*., 2010], have the potential to provide significant information, through $\delta^{18}O_C$ values, about the isotopic composition of source waters. Here we further examine this potential through the first $\delta^{18}O_C$ analysis of unusual moss peat formations that have developed across the maritime Antarctic region over at least the past 5500 years [*Björck et al*., 1991; *Fenton*, 1982].

[10] In order to assess the maritime Antarctic influences on $\delta^{18}O_C$, current precipitation and cellulose from moss peat banks on Signy Island were used to address the relationships between source water, environmental conditions, and moss cellulose composition since 1870 A.D. Temporally, the $\delta^{18}O_C$ signal was relatively constant across this period, but there were significant spatial variations between local moss banks. First, a local meteoric water line (LMWL) was developed for Signy Island, South Orkney Islands, Antarctica, which was used to test the isotopic composition of precipitation simulated by the HadAM3 isotope-enabled general climate model [*Tindall et al*., 2009] from 1871 A.D. to 2000 A.D. [*Yoshimura et al*., 2009]. Whilst we have recently suggested that the Signy Island moss peat accumulation rate has increased due to an extended growing season [*Royles et al*., 2012], the aim of this current study was to identify the water sources for moss growth, as preserved in $\delta^{18}O_C$. Laboratory experiments on *Chorisodontium aciphyllum* were also used to determine the evaporative enrichment of source water during likely periods of cellulose synthesis, in order to assess the extent that the oxygen isotopic composition of *Chorisodontium aciphyllum* provides a useful proxy for past water sources.

2. Site Description

[11] Signy Island (Figure 1; 60.7°S, 45.6°W) lies at the confluence of the Scotia and Weddell Seas. The seasonal climate of the island, characteristic of the maritime Antarctic, is dependent upon the warm and cold air masses associated with the two seas [*Holdgate*, 1964]. Small (5 km × 3 km), low-lying, and mid-oceanic with relatively thin, low-density ice cover across the center, Signy Island is very sensitive to minor fluctuations in summer temperature as even a small increase in temperature could result in substantial ice melt and increase the area of ice-free land [*Appleby et al*., 1995; *Smith*, 1990].

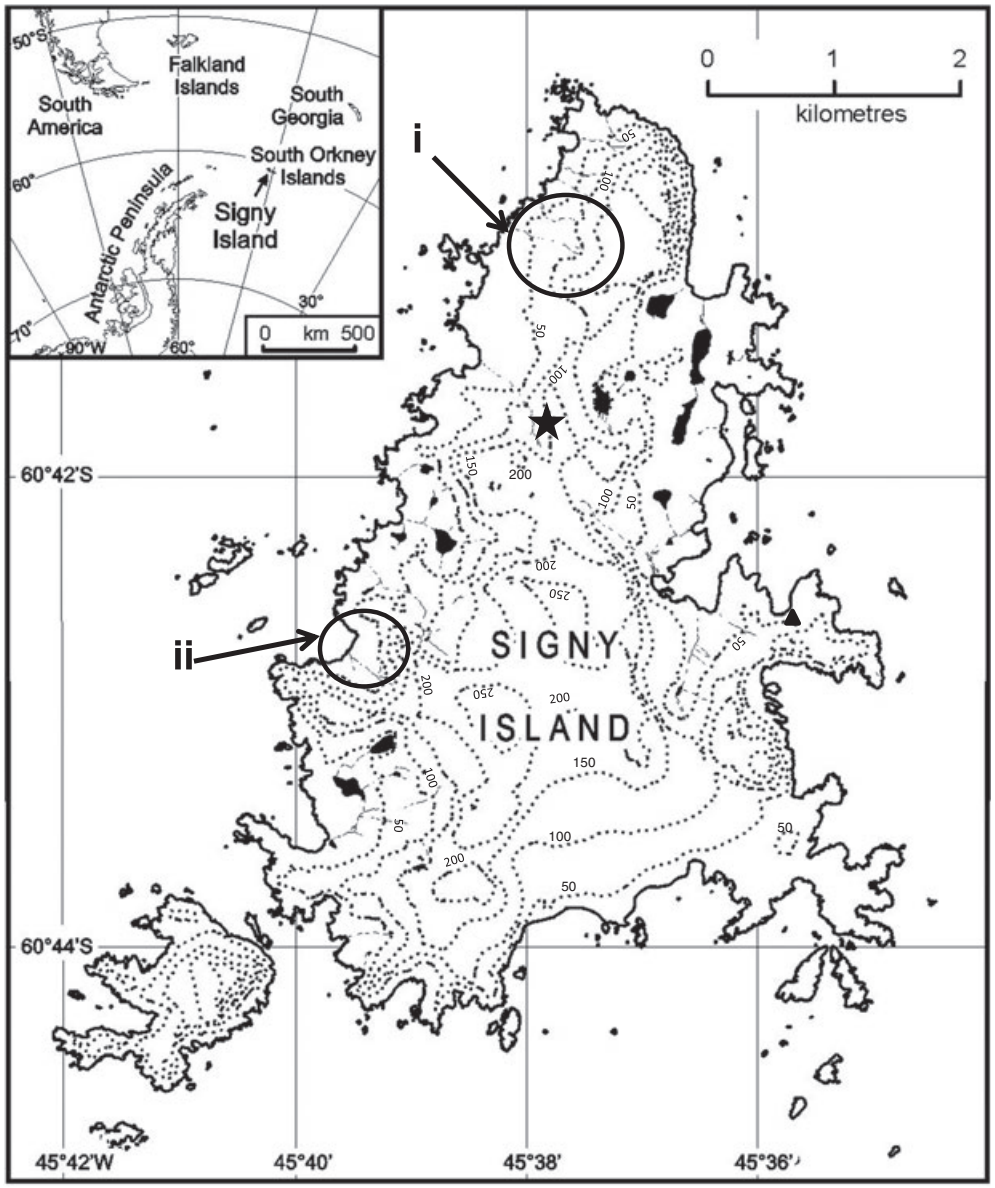

Figure 1. Location of Signy Island (60°43′S, 45°38′W) within the Antarctic Peninsula region. Region (i) Moss Braes (Sites A, B, and D); Region (ii) Port Jebsen (Site C), rain gauge (triangle), and meteorological station (star). Contour lines represent altitude in meters above sea level.

[12] Year-round meteorological data were recorded on Signy Island between 1947 and 1995, and an ongoing record has been maintained at Orcadas station (Laurie Island), 51 km east of Signy Island, since 1903. Summer monthly mean air temperatures range from 0 to 3°C with an annual precipitation of around 400 mm [*Guglielmin et al*., 2012] falling across 280 days per year [*Walton*, 1982]. The island receives strong prevailing west-north-westerly winds [*Noon et al*., 2002]. Over a 3 year period, only 1 month had average cloud cover under 6 oktas (75%) [*Walton*, 1982].

[13] Over the past 60 years on Signy Island, rapid environmental changes have been evident. Ice cover on the low-lying island reduced by 45% between 1950 and the late 1980s [*Smith*, 1990] and has continued to do so. Simultaneously, the annual extent of ice-free days on two freshwater lakes has increased by 2 months, whilst mean annual lake water temperatures have increased by 0.9°C [*Quayle et al*., 2002; *Quayle et al*., 2003] and mean annual air temperatures have increased by 2 ± 1°C over the past 50 years (Figure 2) [*Turner et al*., 2005].

[14] Moss peat banks over 2 m deep and up to 5000 years old, predominantly composed of *Chorisodontium aciphyllum*, cover over 0.34 km^2 of the ice-free land on Signy Island [*Fenton*, 1980; *Fenton and Smith*, 1982]. Within the moss peat banks, permafrost is present, currently below an active layer of approximately 300 mm depth [*Cannone et al*., 2006; *Gugliemin et al*., 2008].

3. Materials and Methods

3.1. Sample Collection

[15] One core of moss peat up to 1680 mm deep was extracted from each of four moss peat banks (Figures 1 and 3 and Table 1) across Signy Island during the September

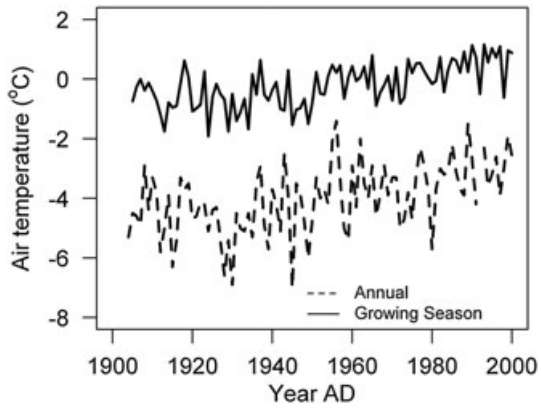

Figure 2. Mean annual (solid line) and growing season (November–March; dashed line) air temperatures measured at Orcadas station, 50 km east of Signy Island [*Colwell*, 2002].

2008 and October 2009 austral summers. An adapted ice corer (82.5 mm in diameter; based on *Nørnberg et al.* [2004]) was used to extract cores from the center of the extensive Sites A (200 m^2) and D (100 m^2) moss peat banks, as permafrost was encountered at 300 mm depth. A moss peat monolith (500 × 100 × 100 mm) was removed from the center of the Site B hummock (1 m^2) which, at 340 mm in depth, was not frozen. At Site C (20 m^2), two monolith tins (500 × 100 × 100 mm) were used at a non-frozen eroded, exposed edge of the moss peat bank to remove vertical sections of moss peat 900 mm in length. The cores extended from the green growing surface to the underlying rocky substrata. The cores were transported frozen to the UK for analysis where they were hand sliced once longitudinally, with one half then divided into 5–7 mm transverse sections. Samples for radiocarbon dating were extracted from the preserved longitudinal half and used to develop age-depth models as detailed in *Royles et al.* [2012]. The age-depth models were generated independently for each core, with high-resolution dating utilizing the "bomb-spike" in atmospheric $^{14}CO_2$ since 1960 completed on the particularly well-preserved Site B core.

[16] Water was extracted by cryogenic vacuum distillation from 1 g sub-samples of the transverse core sections [*Ehleringer et al.*, 2000; *West et al.*, 2006]. This "core water" was a mixture of the internal and external tissue water associated with each core sub-sample at the time of collection.

[17] Precipitation was collected daily at Signy Island research station (60.71°S, 45.59°W) between January and March, and October and December, 2009. Both the type (rain/snow) and volume of precipitation were recorded. Water samples were sealed in 12 ml vials and then stored and transported back to the UK at +4°C.

3.2. Analyses of Water Samples

[18] Both the oxygen ($\delta^{18}O$) and deuterium ($\delta^{2}H$) isotope signals were determined directly from the precipitation and core-water samples using cavity ring down spectroscopy (CRDS) [*Lis et al.*, 2008]. Water samples were transferred into 2 ml glass vials with pierceable septa within their caps and analyzed using a L1102-*i* Isotopic Water Liquid Analyzer (Picarro, Sunnyvale CA, USA) at the Godwin Laboratory,

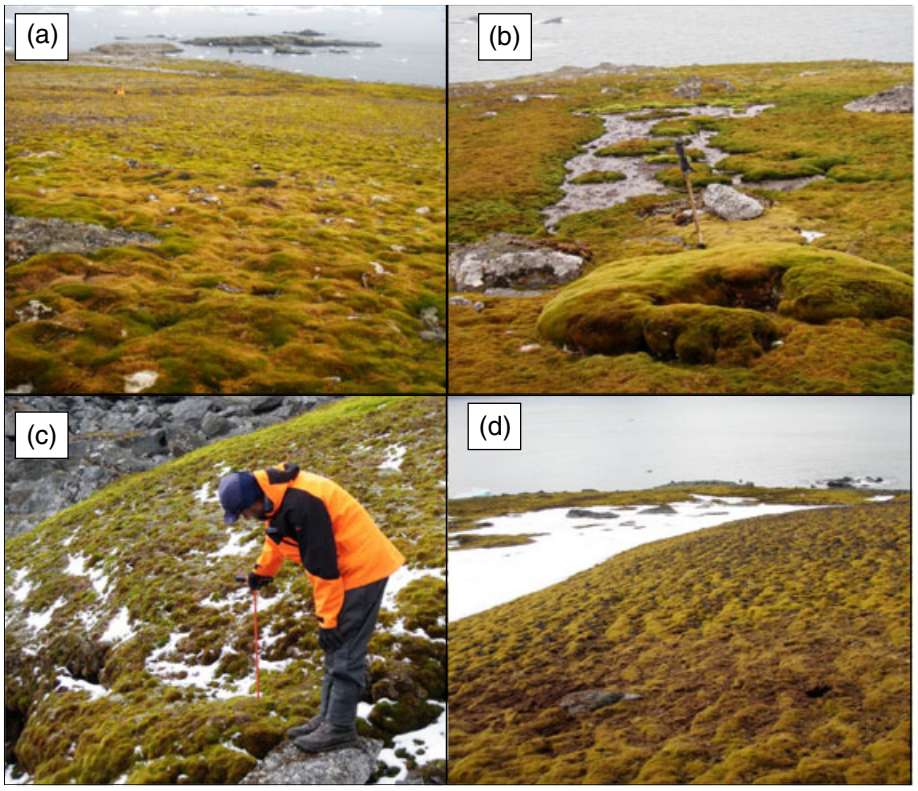

Figure 3. Photographs of Signy Island moss banks (a) Site A (approximately 200 m^2), (b) Site B (small central hummock, approximately 1 m^2, with 1 m high ski pole for scale), (c) Site C (approximately 20 m^2), and (d) Site D (approximately 100 m^2). See Table 1 for details.

Table 1. Physical Parameters Describing the Four Peat Core Extraction Sites on Signy Island[a]

Site ID	Location	Latitude (°S)	Longitude (°W)	Elevation (m asl)	Max Core Length (mm)	Area of Moss Bank (m^2)	Description of Site
A	Moss Braes (Region i)	60.69	45.63	62	1000	200	South facing extensive *Chorisodontium aciphyllum* bank
B	Moss Braes (Region i)	60.68	45.63	52	340	1	Isolated hummock above meltwater stream mainly *C. aciphyllum*
C	Port Jebsen (Region ii)	60.71	45.65	46	900	20	Extensive, mixed, undulating moss bank sloping west
D	Moss Braes (Region i)	60.68	45.62	112	1580	100	High site, between a hollow with permanent snow cover and an area of dead, black, wind-eroded moss

[a]Regions i and ii Refer to Figure 1.

University of Cambridge. $\delta^{18}O$ and $\delta^{2}H$ were calculated to the VSMOW scale using within-run laboratory standards (SPIT, SPIT-2, BOTTY) alongside the international standards SLAP, VSMOW, and GISP. Each sample was analyzed nine times, with the mean of the final six analyses calculated as the sample value. Within these runs, a precision of $\pm<0.1$‰ (1SD) for $\delta^{18}O$ and $\pm<1$‰ (1SD) for $\delta^{2}H$ was achieved (data not shown).

[19] Some organic contaminants of water samples can interfere with CRDS analysis [*West et al*., 2010] so all output spectra were processed using "ChemCorrect" software (Picarro, Sunnyvale CA, USA) [*Picarro*, 2010]. No signs of contamination were identified in any of the samples analyzed. To further verify the isotopic measurements of the water, a random selection of 40 samples were additionally analyzed by an independent method: equilibration of the water sample with gaseous CO_2. A 1 ml sub-sample of water was equilibrated with 1 ml of pure CO_2 gas in a sealed vial (Labco, High Wycombe, UK) for 48 h prior to direct measurement of the isotopic composition of the CO_2 using an Isotope Ratio Mass Spectrometer (IRMS) (SIRA, VG Isotech, modified by Pro-Vac Services Ltd, Crewe, UK) with laboratory standards interspersed throughout the unknown samples. The measured $\delta^{18}O$ value was standardized relative to VSMOW using the known water standards BAS-LO ($\delta^{18}O = -31.44$‰ VSMOW), BAS-HI ($\delta^{18}O = -8.73$‰ VSMOW), and SWK ($\delta^{18}O = -0.97$‰ VSMOW). There was no significant difference in the $\delta^{18}O_{VSMOW}$ values determined by the two methods (CRDS and equilibration; paired *t*-test, t = 0.41, df = 39, p = 0.68).

3.3. Local Meteoric Water Lines

[20] Data from the five global network of isotopes in precipitation (GNIP) stations within 2000 km of Signy Island (Vernadsky (65.25°S, 64.27°W, 1050 km from Signy Island, record spans 1964–2008), Rothera (67.57°S, 68.13°W, 1300 km, 1996–2009), Halley (75.50°S, 26.65°W, 1800 km, 1965–2009), Ushuaia (54.78°S, 68.28°W, 1500 km, 1981–2002), and Punta Arenas (53.00°S, 70.51°W, 1750 km, 1990–2009)) [*IAEA and WMO*, 2006] were used to plot Local Meteoric Water Lines (LMWLs) using the amount-weighted mean monthly $\delta^{18}O$ and $\delta^{2}H$ precipitation values from throughout the recording periods for each station. The amount weighting is used to counteract the "amount effect", which is an isotopic depletion associated with an increase in the amount or intensity of rain, most frequently associated with tropical and monsoon affected regions [*Daansgard*, 1964]. In addition to the GNIP stations, two of which are in South America (Punta Arenas and Ushuaia) and the remaining three in Antarctica, *Fernandoy et al*. [2011] calculated a northern Antarctic Peninsula LMWL from precipitation samples collected between February 2008 and March 2009 at Base General Bernardo O'Higgins Riquelme (63.32°S, 57.90°W, 950 km).

3.4. Cellulose Extraction

[21] From each transverse, moss peat core slice approximately 0.2 g of *Chorisodontium aciphyllum* dry organic matter was removed for cellulose extraction. Cellulose was extracted following a method developed for extraction of α-cellulose from wood [*Loader et al*., 1997]. In preparation for $\delta^{18}O_C$ analysis, 1 mg samples of dry α-cellulose were transferred into individual pressed silver capsules (5.25 mm × 3.2 mm) (Elemental Microanalysis Ltd., Okehampton, UK). $\delta^{18}O_C$ analysis was completed at the Godwin Laboratory, University of Cambridge following standard procedures [*Kornexl et al*., 1999; *Werner et al*., 1996] using a Thermo Finnigan 253 Stable Isotope Ratio Mass Spectrometer (Thermo Fisher Scientific, Waltham, MA, USA) with High Temperature Conversion Elemental Analyser (TCEA) (Thermo Fisher Scientific, Waltham, MA, USA). Two laboratory standards, α-cellulose ($\delta^{18}O = 27.7$‰) and CC31 ($\delta^{18}O = 31.85$‰), and an international standard, NBS 127 ($\delta^{18}O = 8.6$‰), were used to calibrate the oxygen isotope ratio of the high purity CO reference gas. ISODAT operating software (Thermo Fisher Scientific, Waltham, MA, USA) was used to calculate the sample values relative to this reference gas value, and thus, $\delta^{18}O_C$ was anchored to the VSMOW scale. This normalization method can cause analytical error of up to 0.5‰ to be introduced, dependent upon the relative difference between the $\delta^{18}O$ values of the reference gas and the samples [*Paul et al*., 2007]. In order to correct for any instrument drift, standards were measured at the beginning, middle, and end of each run ($\delta^{18}O$ CC31 (n = 5): mean = 31.85‰, SD = 0.16‰; $\delta^{18}O$ α-cellulose (n = 5): mean = 27.78‰, SD = 0.14‰).

[22] Using the age-depth curve developed for each core [*Royles et al*., 2012], the depth from which each $\delta^{18}O_C$ sample was extracted was converted to an equivalent year of assimilation, thus normalizing inter-core comparisons for the spatial and temporal variations in accumulation rate. The accumulation rates over the past 200 years at Sites B and C were approximately 2 mm yr^{-1}, compared with approximately 1 mm yr^{-1} at Site A and 0.5 mm yr^{-1} at Site D.

[23] The degree of humification of the moss peat subsamples was assessed following standard procedures [*Blackford and Chambers*, 1993; *Chambers et al*., 2011]. The percentage of light, of a wavelength of 540 nm, transmitted

through diluted moss filtrate was measured in three successive aliquots at each sample depth using a Biowave WPA S2100 Diode Array Spectrophotometer (Biochrom, Cambridge, UK).

3.5. Modeled Isotopic Composition of Precipitation

[24] HadCM3 is a global non-flux-adjusted coupled atmosphere-ocean general circulation model (GCM) that provides a good representation of global climate, atmospheric circulation, and heat transport, by incorporating both an oceanic (HadOM3) and an atmospheric (HadAM3) component on a $2.5° \times 3.75°$ latitude-longitude grid [*Tindall et al*., 2009]. An isotopic sub-model that describes the behavior of $^1H_2^{18}O$ and $^1H^2H^{16}O$ was incorporated into HadCM3 to allow simulation of the isotopic composition of precipitation [*Sime et al*., 2009; *Tindall et al*., 2009]. As part of the GNIP-SWING project (Stable Water Isotope Intercomparison Group [*Yoshimura et al*., 2009]), HadAM3 outputs of annual and monthly isotopic precipitation composition were generated for a location at 60°S, 45°W (the Signy Island coordinates) from 1871 to 2000 A.D.

3.6. Isotopic Composition of *Chorisodontium aciphyllum* Tissue Water

[25] Three small clumps ($10\,cm \times 10\,cm$) of actively growing *Chorisodontium aciphyllum* were collected during the October 2009 austral summer (J. Royles, Signy Island, Antarctica) and transported to the UK at +4°C. To maintain moss growth in the UK, the clumps were kept in transparent plastic boxes at +4°C under a constant light source and the air was humidified with de-ionized (DI) water as required.

[26] Immediately prior to experimentation, the green shoots of moss stalks covering a basal area of $10\,cm^2$ were cut from the clump, immersed briefly in DI water ($\delta^{18}O_{VSMOW} = -9.0 \pm 0.2‰$) and gently blotted to remove excess water but retain the external water directly associated with the leaves. The moss shoots were placed within the Whole Plant Chamber (LI6400-17, LiCor, Lincoln, NE, USA) attached to the LI6400-XT open gas exchange system (LiCor, Lincoln, NE, USA). Within the chamber, the shoots were illuminated using the RGB Light Source (LI6400-18, LiCor, Lincoln, NE, USA) with $500\,\mu mol\,m^{-2}\,s^{-1}$ light intensity and left to photosynthesize for fixed periods (0, 30, 60, 300 min), after which the moss was weighed (FW) and placed within a sealed vial (Labco, High Wycombe, UK). At 1 minute intervals throughout the period of photosynthesis, the instantaneous assimilation rate was automatically recorded. Any remaining water associated with each moss tissue sample (both internal and external water, collectively called "moss water") was isolated by cryogenic vacuum distillation [*Ehleringer et al*., 2000; *West et al*., 2006], and the tissue samples were re-weighed to establish dry weight (DW). The oxygen isotope composition of the moss tissue water ($\delta^{18}O_{TW}$) was determined by equilibration with CO_2 (section 3.2). The relative water content (RWC) of the moss tissue at the end of the photosynthetic period was determined ($RWC = 100 * (FW - DW) / DW$).

4. Results

4.1. Isotopic Composition of Signy Island Precipitation

[27] The precipitation at the five GNIP stations closest to Signy Island was slightly depleted in deuterium compared to the GMWL (Figure 4). The Signy LMWL was almost identical to that measured during an overlapping period at Base General Bernardo O'Higgins Riquelme on the northern tip of the Antarctic Peninsula [*Fernandoy et al*., 2011]. Unlike the GNIP station measurements, the isotopic composition values for the Signy Island precipitation were not weighted by amount (i.e., the impact of the proportional volume of water lost from any given cloud formation) and they reflected only the summer precipitation during one calendar year (2009). However, despite the limited data, the local meteoric water line for Signy fitted within the LMWL range of the surrounding GNIP stations. The Signy LMWL had a very similar gradient to both the Rothera and Halley LMWLs, despite the monthly isotopic values for both Rothera and Halley being seasonally variable and the Signy LMWL being generated from summer precipitation alone.

[28] Summer precipitation on Signy Island fell as both snow and rain, with all those samples with a $\delta^{18}O_P$ value more negative than -12‰ falling as snow (Figure 5a). For both rain and moss peat, core-water $\delta^{18}O$ values ranged from −5 to −10‰, although the LMWL was significantly different from the moss peat core-water line (Wilcoxon signed rank test, $V = 9045$, p-value < 0.001: Figure 5a). There was a significant difference between the deuterium excess values of precipitation and the moss peat core water, with the core-water *d* values tending to be more negative than those of precipitation (Figure 5b; Wilcoxon test, $W = 6050$, $p < 0.0001$).

[29] The mean monthly isotopic precipitation composition of our HadAM3 isotopic simulation was in good agreement with the measured Signy LMWL (Figure 5c); indeed, the two lines are almost indistinguishable despite their different origins and timescales. The model output represents the period between 1871 and 2000 A.D., and although there is a 15‰ range of annual δ^2H values and a 1.5‰ range in annual $\delta^{18}O$ values, the ratio between the two values had a range of only 0.2‰, with no significant trend over time. In comparison, the measured LMWL is derived from analysis of daily precipitation samples collected during the austral summer months of 2009.

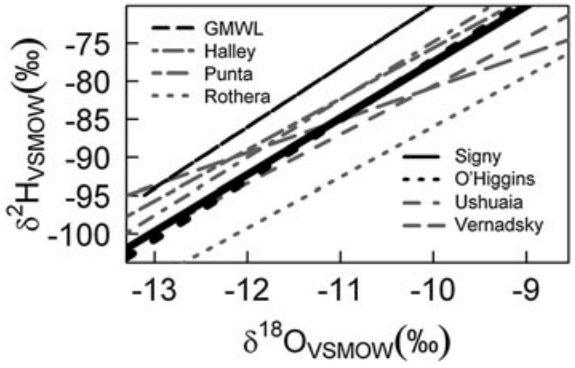

Figure 4. Measured local meteoric water line (LMWL; δ^2H_{VSMOW} as a function of $\delta^{18}O_{VSMOW}$) for Signy Island summer precipitation (–) plotted with LMWLs generated from the weighted-mean monthly precipitation at local GNIP stations, Base General Bernardo O'Higgins Riquelme (O'Higgins), and the GMWL (GMWL – –, O'Higgins - - - (bold), Ushuaia – -, Vernadsky – –, Halley - – -, Punta Arenas - –, Rothera - - -).

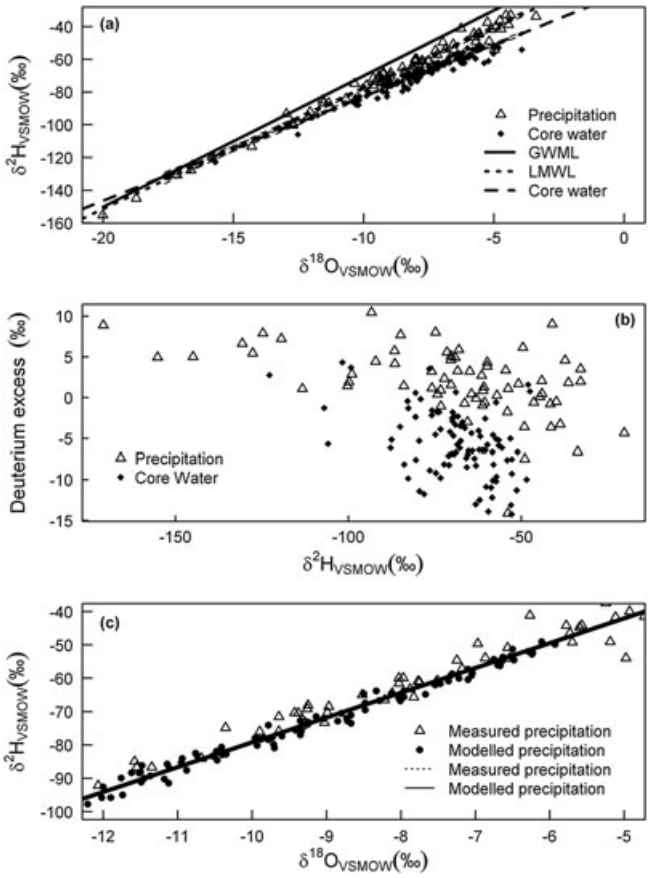

Figure 5. Isotopic analysis of liquid water sources collected on Signy Island. (a) Precipitation (Δ) used to generate the LMWL (dotted line; $y = 7.4\times - 3.45$, $F = 5319$, $df = 65$, $p < 0.0001$, $R^2 = 0.99$). Peat "core-water" line (♦, dashed line; $y = 6.35\times - 19.2$, $F = 3097$, $df = 136$, $p < 0.0001$, $R^2 = 0.96$) represents isotopic composition of water samples isolated from transverse moss peat core sections. GMWL plotted for comparison (solid line). (b) Deuterium excess (*d*) plotted as a function of δ^2H_{VSMOW} for both precipitation (Δ) and peat core water (♦). *d* is significantly different between the precipitation and core-water samples (Wilcoxon test, $W = 6050$, $p < 0.0001$). (c) δ^2H_{VSMOW} as a function of $\delta^{18}O_{VSMOW}$ for both mean monthly modeled (●, solid line, $y = 7.1\times - 7.9$) and measured (Δ, dashed line, $y = 7.4\times - 3.45$) Signy Island precipitation.

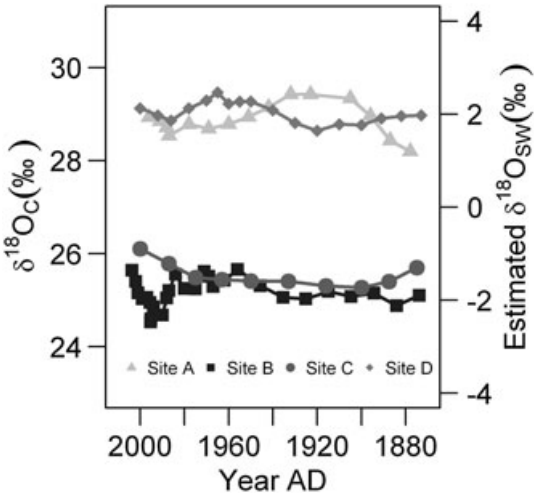

Figure 6. Oxygen isotope composition of cellulose ($\delta^{18}O_C$) and estimated composition of source water ($\delta^{18}O_{SW}$: $\delta^{18}O_C$: $\delta^{18}O_{SW} - 27‰$) for each peat core on Signy Island (Site A ▲, Site B ■, Site C ●, and Site D ♦) as a function of the year of cellulose synthesis plotted as running mean of six successive values over the period 1870–2009 A.D.

4.2. $\delta^{18}O_C$ of Signy Island Moss Peat Cores

[30] Throughout the analysis period, the $\delta^{18}O_C$ values measured at sites B and C were consistently 3‰ depleted compared to sites A and D (Figure 6), a difference substantially higher than the analytical error. The Site C core was taken from the edge of the bank, and although the Site B core was central within the small hummock, the hummock was only approximately 1 m in diameter. The smaller, more exposed hummock (B) showed the highest variations around the mean $\delta^{18}O_C$ value, relative to the sample taken from a promontory, which was part of a larger hummock (C: Figure 3c, cf. Figure 3b). The most consistent trend in $\delta^{18}O_C$ was measured at Site B where $\delta^{18}O_C$ increased from 24.5‰ to 25.5‰ between 1990 and 2000 A.D. In contrast to Sites B and C, moss samples from cores extracted out of the center of the extensive banks (A and D) had $\delta^{18}O_C$ values around 28‰ to 30‰, with maxima between 1900 and 1940 at Site A and 1970 at Site D. The higher uncertainty associated with the normalization method used to calibrate the $\delta^{18}O_C$ values [*Paul et al*., 2007] may perhaps have prevented observation of more discrete relationships within the data; however, there was no clear relationship between environmental signals (temperature, atmospheric CO_2 concentration, and precipitation all increased significantly) and inter-annual variations in $\delta^{18}O_C$ within cores across this post-industrial period (data not shown). In addition, there was no trend observed in humification index (data not shown) with transmission values consistent at approximately 65% throughout each core, suggesting that the degree of decomposition of moss peat material did not change significantly with age, depth, or between locations.

[31] If it is assumed that a fractionation of 27‰ occurred between leaf water and cellulose at the intracellular location of cellulose synthesis [*De Niro and Epstein*, 1979; *Sternberg et al*., 2006; *Zanazzi and Mora*, 2005], we can estimate the isotopic composition of tissue source water ($\delta^{18}O_{SW}$) during cellulose synthesis (Figure 6). For the extensive moss peat banks A and D, $\delta^{18}O_{SW}$ would, in theory, average +2‰, and for the exposed banks B and C, -2‰. Both of these values are more positive than measured precipitation as $\delta^{18}O_P$ was predominantly between -5 and -10‰.

[32] Laboratory experimental work investigated *Chorisodontium* $\delta^{18}O_{TW}$ and photosynthetic carbon assimilation as a function of RWC. When saturated (1350% RWC), $\delta^{18}O_{TW}$ was dominated by source water (−9‰) and assimilation rates, limited by diffusive CO_2 supply, were measured to a minimum of 20% of the maximum measured assimilation rate (Figures 7a and 7b). As tissues dried out, with a reduction in RWC to 400%, $\delta^{18}O_{TW}$ was evaporatively enriched to -4‰ (Figure 7a). The enriched signal was then maintained as the RWC continued to fall, which also facilitated maximum assimilation rates (Figure 7b).

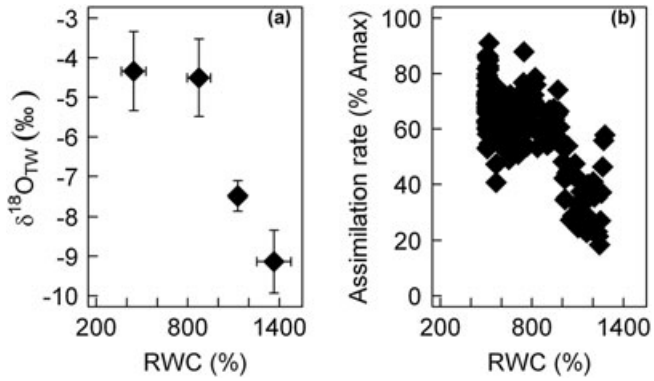

Figure 7. (a) Experimentally determined oxygen isotope composition of *Chorisodontium aciphyllum* tissue water ($\delta^{18}O_{TW}$) plotted as a function of tissue relative water content (RWC; n = 3), $\delta^{18}O_{SOURCE\text{-}WATER} = -9.0 \pm 0.2$‰ VSMOW. Error bars represent one standard error. (b) Running mean of three successive instantaneous *Chorisodontium aciphyllum* assimilation rate measurements, expressed as a percentage of the maximum measured assimilation rate, A_{MAX}, plotted against relative water content (RWC). Assimilation was measured at 1 min intervals, whilst the tissue dried from saturation.

Such optimal RWC values are consistent with those of the Signy Island moss peat banks [*Gimingham and Smith*, 1971] where, when air temperatures were 5°C, gross assimilation by *Chorisodontium* was measured to be 100 μg C g^{-1} ash-free dry weight per hour [*Davey and Rothery*, 1996].

5. Discussion

5.1. Signy Island Local Meteoric Water Line and Freezing Line

[33] The close similarity of the Signy Island LMWL to the GMWL suggests that little re-evaporation or recycling had occurred during precipitation formation [*Craig*, 1961], as would be expected given the low air temperatures (Figure 2). The Signy LWML was almost identical to that measured at Base General Bernardo O'Higgins Riquelme [*Fernandoy et al*., 2011], on the northern tip of the Antarctic Peninsula, which, though not a GNIP station, was the closest location to Signy with a complete annual cycle of isotope measurements in precipitation.

[34] Tested here for the first time, the measured isotopic composition of Signy Island precipitation was well captured by the HadAM3 model [*Sime et al*., 2009; *Tindall et al*., 2009]. The model output did not show any temporal trend in isotopic composition: although variation was evident in the isotopic composition of the precipitation, the ratio of δ^2H and $\delta^{18}O$, and consequently the modeled LMWL remained consistent back to the earliest output in 1871 A. D. Hence, it is likely that the precipitation source isotopic input has remained consistent over at least the past 140 years and possibly for much longer as the modeled LMWL remained constant throughout recent changes in the phase of the Southern Annular Mode [*Marshall*, 2003] and in wind intensity [*Russell et al*., 2006]. Given that local shifts in precipitation input during the growing season will have been dependent on ambient temperature (e.g., rain or snow), the relatively constant $\delta^{18}O_C$ isotopic compositions over 100 years found in the two contrasting types of moss bank (isolated vs. extensive) are consistent with the measured and modeled precipitation data.

[35] However, there was a significant difference between precipitation and core water from an isotopic perspective. The majority of the moss peat "core water" was frozen external water associated with the moss core when it was extracted from the surrounding moss peat bank. This water is likely to have had multiple opportunities for recharge and atomic (and thus isotopic) exchange/re-equilibration over the years since the moss peat was laid down, especially as the extent of the active layer on Signy Island has altered over time, and is currently increasing in depth by approximately 10 mm yr^{-1} [*Cannone et al*., 2006; *Gugliemin et al*., 2008] from the 300 mm measured in 2009. The range of absolute $\delta^{18}O$ values measured in core water was similar to that of Signy Island rain; however, the deuterium excess differed between precipitation and core water in a manner indicative of a mass-dependent freezing effect between $^1H^2HO$ and $^1H_2^{18}O$ [*Lacelle*, 2011; *Souchez et al*., 2000]. The slope of the freezing line is dependent upon the freezing rate, the percentage of freezing, and the thickness of the boundary layer, which, in combination, determine the proportion of heavy isotopologues in the water adjacent to the freezing front [*Souchez et al*., 2000]. Following Lacelle [2011], the slope of the Signy Island core-water $\delta^{18}O$-δ^2H relationship and the range of *d* values suggest that the core water went through at least one freeze-thaw cycle under equilibrium conditions after precipitation had percolated into the moss peat banks. The lowering of the MWL below the LMWL as a consequence of freezing has previously been measured within snow packs, with the slope of the MWL becoming progressively lower with each freeze-thaw cycle [*Zhou et al*., 2008]. Thus, it seems reasonable to conclude that the moss peat core water originated as precipitation with an isotopic composition along the measured LMWL. As the surface of the moss peat bank melted during the summer down to the base of the active layer, fresh precipitation percolated down and, as a consequence of a single freezing, or repeat freeze-thaw cycling within the moss peat bank, became relatively isotopically depleted in deuterium compared to the precipitation.

5.2. $\delta^{18}O_C$ of Signy Island Moss Peat Cores

[36] The lack of significant inter-annual intra-site variation in $\delta^{18}O_C$ in the face of measured increases in temperature, rainfall, and atmospheric CO_2 suggested a perhaps surprising insensitivity of the $\delta^{18}O_C$ signal to changes in gross climatic conditions, though this may also have been limited by the uncertainty in the isotope measurements. In contrast, the substantial 3‰ offset in $\delta^{18}O_C$ values between moss peat accumulated since 1900 at the smaller Sites B and C hummocks and extensive Sites A and D banks showed that the isotopic composition of the fixed cellulose was sensitive to some microclimatic or environmental differences between the locations. From Sites B and C, the core samples were necessarily extracted close to the edge of the hummocks, which were closely coupled to microclimate changes and likely to have gone through a higher number of diurnal and seasonal freeze-thaw cycles than the extensive Sites A and D banks, in which the centrally extracted moss peat core

would have been insulated on all sides and buffered from rapid temperature changes [*Walton*, 1982].

[37] With the Sites A and D cores having $\delta^{18}O_C$ values around 28.5‰ and Sites B and C around 25.5‰, the offsets to the median composition of measured Signy Island $\delta^{18}O_P$ were 36.5‰ and 33.5‰, respectively. This is substantially beyond the recognized 27‰ fractionation between source water and cellulose [*De Niro and Epstein*, 1979; *Sternberg et al*., 2006], and even the most isotopically enriched summer precipitation collected from Signy Island could not directly account for the measured $\delta^{18}O_C$. Despite 27‰ being accepted as the extent of oxygen isotope fractionation between source water and cellulose for vascular plants and submerged mosses, higher values have previously been measured in emergent plants, including mosses, with values up to +36.2‰ measured at a Burundian peat bog [*Aucour et al*., 1996] and +33.5‰ in wetlands at Lake Superior, USA [*Zanazzi and Mora*, 2005]. At both these locations, an isotopic enrichment of ~27‰ between water and cellulose was simultaneously measured in submerged plants, which, unlike the emergent plants, were not exposed to the wind and sub-saturation relative humidity of the atmosphere. Under these strongly evaporative conditions, the leaf water underwent isotopic enrichment prior to the standard biochemical enrichment during cellulose synthesis. Thus, the ~27‰ fractionation remains valid, but the leaf/chloroplast water with which atomic exchange occurs is enriched compared to the meteoric source water. Indeed, a greater degree of evaporative enrichment has been measured from the saturated surface of mosses than from the surface of an open pool, due to the very high evaporative leaf surface area and limited supply of leaf water [*Ménot-Combes et al*., 2002; *Nichols and Brown*, 1980].

[38] Over the period that the experimental tissue RWC (300–700%) was equivalent to the RWC measured under field conditions [mean = 400%, n = 7; *Gimingham and Smith*, 1971], the leaf water in *Chorisodontium aciphyllum* was measured to be 5‰ above that of the source water, a phenomenon that was previously demonstrated in similarly poikilohydric lichens [*Hartard et al*., 2009; *Lakatos et al*., 2007]. The experiments were carried out under controlled conditions; however, similar circumstances could frequently occur in the natural environment as precipitation is recorded on Signy Island on over 75% of days [*Walton*, 1982]. For example, during and immediately following a rain or melt event, mosses are fully saturated and the external water layer voluminous (as at the start of the experiments). However, as shown experimentally, little assimilation occurs under these conditions. After the rain ceases, there will be the initial period of rapid water loss, again as measured experimentally in *C. aciphyllum*, due to the difference between the water potential of the saturated moss and that of the drier atmosphere [*Lakatos et al*., 2007]. Over this relatively short period, evaporative enrichment of the leaf water occurs, and, as diffusion limitation reduces, the rate of assimilation can increase. A substantial proportion of the experimentally measured net assimilation occurred during the subsequent period of slow water loss, which, in a natural environment, would continue either until either the moss dries out too much to photosynthesize effectively, or further precipitation occurs and the cycle restarts. During this "optimal" photosynthetic period of gradual water loss, the homogeneous leaf water was consistently enriched by approximately 5‰ over that of the source water, and it is this enriched leaf water that is likely to have been the source water for metabolism and cellulose synthesis.

[39] Thus, the measured isotopic enrichment of up to 35‰ between precipitation (approximately -5 to -10‰) and cellulose (approximately 25 to 29‰) can be explained because of evaporative enrichment in tissue water of up to 5‰, prior to the standard 27 ± 3‰ fractionation during synthesis. Under constant source water conditions, high values of $\delta^{18}O_C$ are thought to reflect periods of strong evaporative enrichment allowing associated environmental conditions to be derived [*Farquhar et al*., 1997]. The absence of significant temporal variations within each moss bank over 150 years contrasts with the significant spatial variation between banks. We suggest that only minor changes in atmospheric evaporative demand have occurred since 1870 A.D., at least during periods of optimal assimilation and hydration during summer months. This contrasts with the significant impact of local microclimatic conditions and aspect, with systematic effects of moss bank topology, precipitation and snowmelt as source water inputs, and evaporative enrichment, occurring over this period.

[40] The different structures and locations of the four Signy Island moss banks may explain the absolute differences between the isotopic compositions of the cellulose. Sites A and D were large, extensive, ombrotrophic peat banks, above the flow of melt streams, and although they are snow covered during the winter, this melts early and the isotopically heavy summer rain is the dominant water source during the growing season. In addition, being part of a large bank, the colony microclimate effects known to influence the water status of *C. aciphyllum* [*Gimingham and Smith*, 1971; *Ochyra et al*., 2008] would help to maintain consistent conditions for optimal photosynthesis over a longer period of time than the meteorology alone may suggest [*Davey*, 1997]. In contrast, Site B was a small, isolated hummock, tightly coupled to the Signy Island climate within a low-lying area through which a snow melt stream runs for much of the summer. Thus, water at the more depleted end of the Signy Island precipitation range would continually wash through the moss during the growing season, despite the summer rain being relatively isotopically enriched. This depleted meltwater would percolate into the hummock, mixing and diluting water already present. Thus, the isotopic composition of the hummock water, and subsequently the cellulose, would be dependent upon the relative mix of rain and meltwater and any subsequent evaporative enrichment. It is similarly likely that there would be a significant contribution of isotopically depleted snow meltwater around Site C during cellulose synthesis, as the sample was taken from the edge of a promontory abutting rocks, adjacent to a meltwater flow.

[41] Although the link between $\delta^{18}O_C$ of *Chorisodontium aciphyllum* and $\delta^{18}O_P$ on Signy Island is less direct than the relationship previously measured in *Sphagnum* species [*Daley et al*., 2010; *Zanazzi and Mora*, 2005], the isotopic composition of Signy Island precipitation is consistent through freeze-thaw cycles with the measured isotopic composition of the moss peat core water, and, through a mixture of rainfall, snowmelt and evaporative enrichment, the isotopic composition of cellulose.

6. Conclusions and Implications

[42] The absolute difference in $\delta^{18}O_C$ measured between the sites suggested that *C. aciphyllum* was sensitive to the isotopic composition of source water input and local microclimate. The consistency of the $\delta^{18}O_C$ values over the past century contrasts with significant changes in temperature [*Quayle et al*., 2002], wind [*Russell et al*., 2006], rainfall patterns [*Kirchgaßner*, 2010; *Van den Broeke and Van Lipzig*, 2004], and moss assimilation proxy based on carbon isotope ratio composition [*Royles et al*., 2012], which have been measured on or close to Signy Island. However, the measured $\delta^{18}O_C$ proxy was consistent with the HadAM3 model output, which also suggested a relatively constant isotopic composition for precipitation since the 19th century. A stable hydrological supply and consistent water content of *C. aciphyllum* when growing in an extensive bank, as on Signy Island, were recognized as important factors in determining the development of these moss banks [*Gimingham and Smith*, 1971; *Ochyra et al*., 2008]. Since the majority of net carbon assimilation occurs consistently under optimal tissue water content for photosynthesis, assimilation and growth, the preserved ^{18}O cellulose signal provides a distinct spatial marker for individual moss bank hydrological inputs, rather than a long-term temporal marker of climatic conditions.

[43] **Acknowledgments.** J.R. is funded by NERC (NE/G523539/1, AFI11_05). J.R., L.C.S., P.C., and D.A.H. contribute to the BAS "Polar Science for Planet Earth" core research program, and this paper also contributes to the SCAR "Evolution and Biodiversity in Antarctica" program. We thank Jack Triest (BAS) for his role in the design and engineering of the peat corer and Julia Tindall for providing guidance and help with the HadAM3 simulations.

References

Appleby, P. G., V. J. Jones, and J. C. Ellis-Evans (1995), Radiometric dating of lake sediments from Signy Island (maritime Antarctic): Evidence of recent climate change, *Journal of Palaeolimnology*, *13*, 179–191.

Aravena, R., and R. G. Warner (1992), Oxygen-18 composition of *Sphagnum*, and microenvironmental water relations, *Bryologist*, *95*, 445–448.

Aucour, A.-M., C. Hillaire-Marcel, and R. Bonnefille (1996), Oxygen isotopes in cellulose from modern and Quatemary intertropical peatbogs: Implications for palaeohydrology, *Chemical Geology*, *129*, 341–359.

Barbour, M. M. (2007), Stable oxygen isotope composition of plant tissue: A review, *Functional Plant Biology*, *34*, 83–94.

Barbour, M. M., L. A. Cernusak, and G. D. Farquhar (2005), Factors affecting the oxygen isotope ratio of plant organic material, in *Stable Isotopes and Biosphere-Atmosphere Interactions*, edited by L. B. Flanagan, E. R. Ehleringer and D. E. Pataki, pp. 9–23, Elsevier, San Diego.

Björck, S., N. Malmer, C. Hjort, P. Sandgren, O. Ingolfsson, B. Wallen, R. L. Smith, and B. Jonsson (1991), Stratigraphic and paleoclimatic studies of a 5500-year-old moss bank on Elephant Island, Antarctica, *Arctic and Alpine Research*, *23*(4), 361–374.

Blackford, J. J., and F. M. Chambers (1993), Determining the degree of peat decomposition for peat-based palaeoclimatic studies, *International Peat Journal*, *5*, 7–24.

Cannone, N., J. C. Ellis-Evans, R. J. Strachan, and M. Guglielmin (2006), Interactions between climate, vegetation and the active layer in soils at two Maritime Antarctic sites, *Antarctic Science*, *18*(3), 323–333.

Chambers, F. M., D. W. Beilman, and Z. Yu (2011), Methods for determining peat humification and for quantifying peat bulk density, organic matter and carbon content for palaeostudies of climate and peatland carbon dynamics, *Mires and Peat*, *7*(7), 1–10.

Ciais, P., J. W. C. White, J. Jouzel, and J. R. Petit (1995), The origin of present-day Antarctic precipitation from surface snow deuterium excess data, *Journal of Geophysical Research*, *100*(D9), 18917–18927.

Colwell, S. (2002), READER Dataset, edited, British Antarctic Survey.

Craig, H. (1961), Isotopic variations in meteoric waters, *Science*, *133*(3465), 1702–1703.

Da Silveira, L., L. Sternberg, S. S. Mulkey, and S. J. Wright (1989), Ecological interpretation of leaf carbon isotope ratios: Influence of respired carbon dioxide, *Ecology*, *70*(5), 1317–1324.

Daansgard, W. (1964), Stable isotopes in precipitation, *Tellus*, *16*(436–468).

Daley, T. J., K. E. Barber, F. A. Street-Perrott, N. J. Loader, D. J. Marshall, S. F. Crowley, and E. H. Fisher (2010), Holocene climate variability revealed by oxygen isotope analysis of *Sphagnum* cellulose from Walton Moss, northern England, *Quaternary Science Reviews*, *29*(13–14), 1590–1601.

Dansgaard, W. (1964), Stable isotopes in precipitation, *Tellus*, *16*(4), 436–468.

Davey, M. C. (1997), Effects of short-term dehydration and rehydration on photosynthesis and respiration by Antarctic bryophytes, *Environmental and Experimental Botany*, *37*, 187–198.

Davey, M. C., and P. Rothery (1996), Seasonal variation in respiratory and photosynthetic parameters in three mosses from the Maritime Antarctic, *Ann Bot-London*, *78*, 719–728.

De Niro, M. J., and S. Epstein (1979), Relationship between the oxygen isotope ratios of terrestrial plant cellulose, carbon dioxide and water, *Science*, *204*(4388), 51–53.

Ehleringer, E. R., J. Roden, and T. E. Dawson (2000), Assessing ecosystem-level water relations through stable isotope ratio analyses, in *Methods in Ecosystem Science*, edited by O. E. Sala, R. B. Jackson, H. A. Mooney, and R. W. Howarth, pp. 181–198, Springer-Verlag, New York.

Farquhar, G. D., M. M. Barbour, and B. K. Henry (1997), Interpretation of oxygen isotope composition of leaf material., in *Stable Isotopes: Integration of Biological Ecological and Geochemical Processes*, edited by H. Griffiths, Taylor & Francis, Inc.

Fenton, J. H. C. (1980), The rate of peat accumulation in Antarctic moss banks, *Journal of Ecology*, *68*, 211–228.

Fenton, J. H. C. (1982), The formation of vertical edges on Antarctic moss peat banks, *Arctic and Alpine Research*, *14*(1), 21–26.

Fenton, J. H. C., and R. L. Smith (1982), Distribution, composition and general characteristics of the moss banks of the maritime Antarctic, *British Antarctic Survey Bulletin*, *51*, 215–236.

Fernandoy, F., H. Meyer, and M. Tonelli (2011), Stable water isotopes of precipitation and firn cores from the northern Antarctic Peninsula region as a proxy for climate reconstruction, *Cryosphere Discussions*, *5*, 951–2011.

Gat, J. R. (1996), Oxygen and hydrogen isotopes in the hydrologic cycle, *Annual Review of Earth and Planetary Science*, *24*(225–262).

Gimingham, C. H., and R. L. Smith (1971), Growth form and water relations of mosses in the Maritime Antarctic, *British Antarctic Survey Bulletin*, *25*, 1–21.

Guglielmin, M., M. R. Worland, and N. Cannone (2012), Spatial and temporal variability of ground surface temperature and active layer thickness at the margin of maritime Antarctica, Signy Island, *Geomorphology*, *155–156*, 20–33.

Gugliemin, M., J. C. Ellis-Evans, and N. Cannone (2008), Active layer thermal regime under different vegetation conditions in permafrost areas. A case study at Signy Island (Maritime Antarctica), *Geoderma*, *144*, 73–85.

Hartard, B., M. Cuntz, C. Maguas, and M. Lakatos (2009), Water isotopes in desiccating lichens, *Planta*, *231*, 179–193.

Helliker, B., and S. Ritcher (2008), Subtropical to boreal convergence of tree-leaf temperatures, *Nature*, *454*, 511–515.

Helliker, B. R., and H. Griffiths (2007), Toward a plant-based proxy for the isotope ratio of atmospheric water vapor, *Global Change Biology*, *13*(4), 723–733.

Holdgate, M. W. (1964), Terrestrial ecology in the maritime Antarctic, in *Biologie Antarctique*, edited by R. Carrick, M. W. Holdgate and J. Prevost, pp. 181–194, Hermann, Paris.

IAEA, and WMO (2006), Global network of isotopes in precipitation. The GNIP Database., edited, http://www.iaea.org/water.

Jonsson, A. V., J. Moen, and K. Palmqvist (2008), Predicting lichen hydration using biophysical models, *Oecologia*, *156*(2), 259–273.

Kahmen, A., D. Sachse, S. K. Arndt, K. P. Tu, H. Farrington, P. M. Vitousek, and T. E. Dawson (2011), Cellulose $\delta^{18}O$ is an index of leaf-to-air vapor pressure difference (VPD) in tropical plants, *Proceedings of the National Academy of Sciences*, *108*(5), 1981–1986.

Kaislahti Tillman, P., S. Holzkamper, P. Kuhry, A. B. K. Sannel, N. J. Loader, and I. Robertson (2010a), Long-term climate variability in continental subarctic Canada: A 6200-year record derived from stable isotopes in peat, *Palaeogeography Palaeoclimatology Palaeoecology*, *298*, 235–246.

Kaislahti Tillman, P. K., S. Holzkamper, P. Kuhry, A. B. K. Sannel, N. J. Loader, and I. Robertson (2010b), Stable carbon and oxygen isotopes in *Sphagnum fuscum* peat from subarctic Canada: Implications for palaeoclimate studies, *Chemical Geology*, *270*, 216–226.

Kirchgaßner, A. (2010), An analysis of precipitation data from the Antarctic base Faraday/Verdansky, *International Journal of Climatology*, *31* (3), 404–414.

Kornexl, B. E., M. Gehere, R. Hofling, and R. A. Werner (1999), On-line $\delta^{18}O$ measurement of organic and inorganic substances, *Rapid Communications in Mass Spectrometry*, *13*(16), 1685–1693.

Lacelle, D. (2011), On the $\delta^{18}O$, δD and D-excess relations in meteoric precipitation and during equilibrium freezing: Theoretical approach and field examples, *Permafrost and Periglacial Processes*, *22*, 13–25.

Lakatos, M., B. Hartard, and C. Maguas (2007), The stable isotopes of $\delta^{13}C$ and $\delta^{18}O$ of lichens can be used as tracers of microenvironmental carbon and water sources, in *Stable Isotopes as Indicators of Ecological Change*, edited by T. E. Dawson and R. Siegwolf, pp. 78–93, Academic Press, London.

Libby, L. M., L. J. Pandolfi, P. H. Payton, J. Marshall III, B. Becker, and V. Giertz-Siebenlist (1976), Isotopic tree thermometers, *Nature*, *261*, 284–290.

Lis, G., L. I. Wassenaar, and M. J. Hendry (2008), High-precision laser spectroscopy D/H and $^{18}O/^{16}O$ measurements of microliter natural water samples, *Analytical Chemistry*, *80*, 297–293.

Loader, N. J., I. Robertson, A. C. Barker, V. R. Switsur, and J. S. Waterhouse (1997), An improved technique for the batch processing of small whole-wood samples to a-cellulose, *Chemical Geology*, *136*, 313–317.

Longton, R. E. (1988), *Biology of Polar Bryophytes and Lichens*, Cambridge University Press, Cambridge.

Marshall, G. J. (2003), Trends in the southern annular mode from observations and reanalyses, *Journal of Climate*, *16*, 4134–4143.

McCarroll, D., and N. J. Loader (2004), Stable isotopes in tree rings, *Quaternary Science Reviews*, *23*, 771–801.

Ménot-Combes, G., S. J. Burns, and M. Leuenberger (2002), Variations of $^{18}O/^{16}O$ in plants from temperate peat bogs (Switzerland): Implications for palaeoclimatic studies, *Earth and Planetary Science Letters*, *202*, 419–434.

Moschen, R., N. Kuhl, I. Rehberger, and A. Lucke (2009), Stable carbon and oxygen isotopes in sub-fossil *Sphagnum*: Assessment of their applicability for palaeoclimatology, *Chemical Geology*, *259*, 262–272.

Nichols, D. S., and J. M. Brown (1980), Evaporation from a *Sphagnum* moss surface, *J Hydrol*, *48*, 289–302.

Noon, P. E., M. J. Leng, C. Arrowsmith, M. G. Edworthy, and R. J. Strachan (2002), Seasonal observations of stable isotope variations in a valley catchment, Signy Island, South Orkney Islands, *Antarctic Science*, *14*(4), 333–342.

Noone, D. (2008), The influence of midlatitude and tropical overturning circulation on the isotopic composition of atmospheric water vapor and Antarctic precipitation, *Journal of Geophysical Research*, *113*, D04102, DOI: 04110.01029/02007JD008892.

Nørnberg, T., M. E. Goodsite, and W. Shotyk (2004), An improvised motorized corer and sample processing system for frozen peat, *Arctic*, *57*(3), 242–246.

Ochyra, R., H. Bednarek-Ochyra, and R. I. L. Smith (2008), *Illustrated Moss Flora of Antarctica*, Cambridge University Press, Cambridge.

Ogée, J., et al. (2009), A single-substrate model to interpret intra-annual stable isotope signals in tree-ring cellulose, *Plant, Cell and Environment*, *32*(8), 1071–1090.

Paul, D., G. Skrzypek, and I. Forizs (2007), Normalization of measured stable isotopic compositions to isotope reference scales—A review, *Rapid Communications in Mass Spectrometry*, *21*, 3006–3014.

Picarro, I. (2010), ChemCorrectTM-Solving the problem of chemical contaminants in H_2O stable isotope research, *White Paper*,, http://www.picarro.com/assets/docs/Picarro_-_ChemCorrect_White_Paper.pdf

Proctor, M. C. F. (2000), The bryophyte paradox: Tolerance of desiccation, evasion of drought, *Plant Ecology*, *151*, 41–49.

Quayle, W. C., L. S. Peck, H. Peat, J. C. Ellis-Evans, and P. R. Harrigan (2002), Extreme responses to climate change in Antarctic lakes, *Science*, *295*, 645.

Quayle, W. C., P. Convey, L. S. Peck, J. C. Ellis-Evans, H. G. Butler, and H. J. Peat (2003), Ecological responses of maritime Antarctic lakes to regional climate change, *Antarctic Research Series*, *79*, 159–170.

Royles, J., J. Ogée, L. Wingate, D. A. Hodgson, P. Convey, and H. Griffiths (2012), Carbon isotope evidence for recent climate-related enhancement of CO_2 assimilation and peat accumulation rates in Antarctica, *Global Change Biology*, *18*(10), 3112–3124.

Russell, A., G. R. McGregor, and G. J. Marshall (2006), 340 years of atmospheric circulation characteristics reconstructed from and eastern Antarctic Peninsula ice core, *Geophysical Research Letters*, *33*, L08702.

Sime, L. C., E. W. Wolff, K. I. C. Oliver, and J. C. Tindall (2009), Evidence for warmer interglacials in East Antarctic ice cores, *Nature*, *462*, 342–345.

Skrzypek, G., P. Jezierski, and A. Szynkiewicz (2010), Preservation of primary stable isotope signatures of peat-forming plants during early decomposition—Observation along an altitudinal transect, *Chemical Geology*, *273*, 238–249.

Smith, R. I. L. (1990), Signy Island as a paradigm of biological and environmental change in Antarctic terrestrial ecosystems, in *Antarctic Ecosystems, Ecological Change and Conservation*, edited by K. R. Kerry and G. Hempel, pp. 32–50, Springer, Berlin.

Souchez, R., J. Jouzel, R. Lorrain, S. Sleewaegen, M. Stievenard, and V. Verbeke (2000), A kinetic effect during ice formation by water freezing, *Geophysical Research Letters*, *27*(13), 1923–1926.

Sternberg, L. (2009), Oxygen stable isotope ratios of tree-ring cellulose: The next phase of understanding, *New Phytologist*, *181*(3), 553–562.

Sternberg, L., M. C. Pinzon, W. T. Anderson, and A. H. Jahren (2006), Variation in oxygen isotope fractionation during cellulose synthesis: Intramolecular and biosynthetic effects, *Plant, Cell and Environment*, *29*, 1881–1889.

Sveinbjörnsson, B., and W. C. Oechel (1992), Bryophytes and lichens in a changing environment, in *Bryophytes and Lichens in a Changing Environment*, edited by J. W. Bates and A. M. Farmer, Oxford University Press, Oxford.

Tindall, J. C., P. J. Valdes, and L. C. Sime (2009), Stable water isotopes in HadCM3: Isotopic signature of El Nino–Southern Oscillation and the tropical amount effect, *Journal of Geophysical Research*, *114*, D04111.

Turner, J., S. R. Colwell, G. J. Marshall, T. A. Lachlan-Cope, A. M. Carleton, P. D. Jones, V. Lagun, P. A. Reid, and S. Iagovkina (2005), Antarctic climate change during the last 50 years, *International Journal of Climatology*, *25*, 279–294.

Van den Broeke, M. R., and N. P. M. Van Lipzig (2004), Changes in Antarctic temperature, wind and precipitation in response to the Antarctic Oscillation, *Annals of Glaciology*, *39*, 119–127.

Walton, D. W. H. (1982), The Signy Island terrestrial reference sites: XV. Microclimate monitoring, 1972–74, *British Antarctic Survey Bulletin*, *55*, 111–126.

Werner, M., M. Heimann, and G. Hoffmann (2001), Isotopic composition and origin of polar precipitation in present and glacial climate simulations, *Tellus Series B: Chemical and Physical Meteorology*, *53*(1), 53–71.

Werner, R. A., B. E. Kornexl, A. Rossmann, and H.-L. Schmidt (1996), On-line determination of $\delta^{18}O$ values of organic substances, *Analytica Chimina Acta*, *319*, 159–164.

West, A. G., S. J. Patrickson, and J. R. Ehleringer (2006), Water extraction times for plant and soil materials used in stable isotope analysis, *Rapid Communications in Mass Spectrometry*, *20*(8), 1317–1321.

West, A. G., G. R. Goldsmith, P. D. Brooks, and T. E. Dawson (2010), Discrepancies between isotope ratio infrared spectroscopy and isotope ratio mass spectrometry for the stable isotope analysis of plant and soil waters, *Rapid Communications in Mass Spectrometry*, *24*, 1948–1954.

Yoshimura, K., C. Sturm, and D. Noone (2009), Introduction of SWING-2/CEOP-ICCS activity paper presented at 6th International Scientific Conference on the Global Energy and Water Cycle and 2nd Integrated Land Ecosystem Atmosphere Processes Study Science Conference, Melbourne, Australia.

Yu, Z., J. Loisel, D. P. Brosseau, D. W. Beilman, and S. J. Hunt (2010), Global peatland dynamics since the Last Glacial Maximum, *Geophysical Research Letters*, *37*, LI3402.

Zanazzi, A., and G. Mora (2005), Paleoclimatic implications of the relationship between oxygen isotope ratios of moss cellulose and source water in the wetlands of Lake Superior, *Chemical Geology*, *222*, 281–291.

Zhou, S., M. Nakawo, S. Hashimoto, and A. Sakai (2008), The effect of refreezing on the isotopic composition of melting snowpack, *Hydrological Processes*, *22*, 873–882.