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Plant water δD and $\delta^{18}\text{O}$ of tundra species from West Greenland

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A B S T R A C T

Stable hydrogen and oxygen isotope ratios (δD and $\delta^{18}\text{O}$) of archived plant tissues can be used in paleoenvironmental reconstructions, assuming a well-grounded understanding of the environmental drivers of stable isotope variation in plant waters. Previous plant water calibration studies have focused on lower latitudes, but given the importance of arctic climate reconstructions, it is necessary to understand the drivers of isotope fractionation in plants that are unique to high latitudes. Here, we present δD and $\delta^{18}\text{O}$ values of plant waters from the Kangerlussuaq area in West Greenland. We use the evaporation line created by the xylem waters to estimate the hydrogen and oxygen isotope values of local meteoric source water and find values that are lower than modeled estimates. We also apply the modified Craig-Gordon leaf water model, using local climate parameters and xylem water values to model leaf water values. We find that measured plant water values are generally in good agreement with model estimates, and discrepancies are likely explained by plant microclimates that are warmer and drier than average air measurements. This study extends stable isotope calibrations to arctic regions and provides a new estimate of average precipitation water isotopes values, which in turn inform plant proxy-based paleoclimate studies in the Arctic.

INTRODUCTION

The stable isotope compositions of hydrogen and oxygen (δD and $\delta^{18}\text{O}$) in precipitation are determined by the transportation and consequent fractionation of water through the global hydrologic cycle (Craig, 1961; Craig and Gordon, 1965; Gibson et al., 1993; Edwards et al., 2004). As plants take up water and incorporate it into their tissues, they record the isotope ratio of local precipitation, modified by evaporative enrichment and biosynthetic fractionation (Barbour, 2007; Sachse et al., 2012). With the intermediary steps properly constrained, the compound-specific isotopic composition of plant materials (biomarkers) preserved in archives such as lake sediments can be used to reconstruct the history of hydrologic change in the surrounding area (e.g., Hou et al., 2008; Castañeda et al., 2009; Feakins et al., 2014). This analytical tool is being increasingly ap-

plied to climate reconstruction in the Arctic (Thomas et al., 2012; Balascio et al., 2013). Arctic climate is currently warming more severely and more rapidly than the rest of the planet (Overpeck et al., 1997; Hassol, 2004; Kaufman et al., 2004) and, with the Arctic's large stores of organic carbon and the presence of the Greenland Ice Sheet (GrIS), is a major driver of global climate (Bond et al., 1993; Alley et al., 2010). However, although the isotopic content of Greenland natural waters has been studied for decades (Friedman, 1953; Dansgaard, 1961, 1964), data coverage is still sparse for the island and for arctic areas in general. Reconstructing the climate history of Greenland may be especially influenced by proximity of the GrIS, which does not directly affect other modern arctic ecosystems.

To be able to derive information about precipitation and hydrology from plant tissues, it is necessary to understand fractionation during the incorporation of meteoric

water into plant tissues (Dawson and Ehleringer, 1993; Sachse et al., 2012). This process involves several steps that fractionate the water isotopes and that must be constrained in order to estimate the original precipitation isotope values from plant material isotope values, including (1) the origin of plant source water, which may be a mix of surface and soil or ground waters but which ultimately derives from meteoric water; (2) the movement of source water to sites of biosynthesis in a plant's leaves and out of leaves via transpiration; and (3) the formation of organic molecules—that is, biosynthesis. In modern systems, precipitation is often modeled using the Online Isotopes in Precipitation Calculator (OIPC; Bowen and Revenaugh, 2003; Bowen, 2008). The modified Craig-Gordon model, which originally described evaporative fractionation in open water bodies, is used to model the heavy isotope enrichment of leaf water from xylem water (Craig and Gordon, 1965; Flanagan et al., 1991; Flanagan, 1993). The Craig-Gordon model combines the effects of equilibrium fractionation during the phase change from liquid water to vapor inside the leaf and kinetic fractionation during diffusion of water vapor out of the leaf and into the surrounding air. The model requires estimates of factors such as relative humidity and leaf temperature, which may be impacted by high-latitude conditions such as near-continuous sunlight during the growing season. Fractionation imparted during biosynthesis is influenced by plant type and photosynthetic pathway (Sachse et al., 2012). Plant biomarker archives preserved in lake sediments are being used to provide paleoclimate records for the Arctic, and changes in their stable hydrogen and oxygen isotope ratios yield information on hydrologic changes over time (Balascio et al., 2013; Shanahan et al., 2013). However, interpretation of shifts in precipitation regimes from biomarker records requires a thorough understanding of the relationship between hydrogen and oxygen isotope ratios in plant biomarkers and their source waters, and therefore characterizing the nature of the drivers of stable hydrogen and oxygen isotopes in arctic plant waters is a key part of understanding the history of arctic hydrology regimes.

The goals of this study are to report on stable isotope ratios of plant waters from a highly studied area and to test meteoric source water estimates and the Craig-Gordon model against field measurements of plant waters from an arctic area where conditions are different from more typical study sites in temperate areas. We address two major questions relating to the intermediate steps between precipitation isotope values and plant tissue isotope values for Kangerlussuaq-area plants: (1) What is the isotopic value of plant source water, and how does it compare with measurements and model estimates of other local waters? and (2) How do local climate variables and the Craig-Gordon model apply to isotope frac-

tionation of plant waters in an arctic environment? The Arctic has a much briefer growing season than lower latitudes and one that is marked by nearly continuous sunlight as well as typically more arid conditions (Billings and Mooney, 1968). As part of the effort to properly constrain the variables incorporated into a single biomarker δD or $\delta^{18}O$ value, it is important to understand both the applicability of modeled precipitation and the impacts of an arctic environment on leaf water evaporation. The area where this study was conducted, Kangerlussuaq in West Greenland (Fig. 1), is already the site of several paleolimnology studies (Aebly and Fritz, 2009; Anderson et al., 2009, 2012) and has provided highly informative lake sediment cores dating back to more than 8000 yr before present (B.P.) (Willemse and Törnqvist, 1999; Anderson et al., 2008; D'Andrea et al., 2011; Olsen et al., 2012). It is also the site of ongoing plant ecology investigations (e.g., Post and Pedersen, 2008) and has a long history of study, making it an ideal location to examine the stable isotope composition of arctic plants given its modern ecological context and applicability to arctic paleohydrology.

MATERIALS AND METHODS

Study Area and Sample Analysis

The town of Kangerlussuaq (67°01'N, 50°42'W) lies at the head of the Søndre Strømfjord, one of the longest fjords in West Greenland. The climate along the Søndre Strømfjord is a gradient largely determined by proximity to the Atlantic Ocean at the west end or to the Greenland Ice Sheet (GrIS) at the east, and the Kangerlussuaq area has an arctic continental climate characterized by a relatively lower precipitation range and higher temperature range compared to coastal regions at the same latitude (Böcher, 1949). The Sandflugtdalen ("Flying Sand Valley"; Fig. 1) spans ~30 km from Kangerlussuaq to the edge of the GrIS and mostly comprises low hills of exposed rock or glacial outwash and floodplain terraces (Storms et al., 2012). Deglaciation of the Søndre Strømfjord began around 10–11 kyr B.P., coupled with the advance of tundra vegetation (Anderson et al., 2008; Leng et al., 2012), and reached the Kangerlussuaq area around 8 kyr B.P. (Bennike and Björck, 2002). Today, Kangerlussuaq receives a mean annual precipitation of ~140 mm, and the mean annual temperature is $-5.7^{\circ}C$ (data from the Danish Meteorological Institute, DMI). According to various proxy records from local lakes, the climate of the Kangerlussuaq area during the past 8000 years has varied significantly (Aebly and Fritz, 2009; D'Andrea et al., 2011).

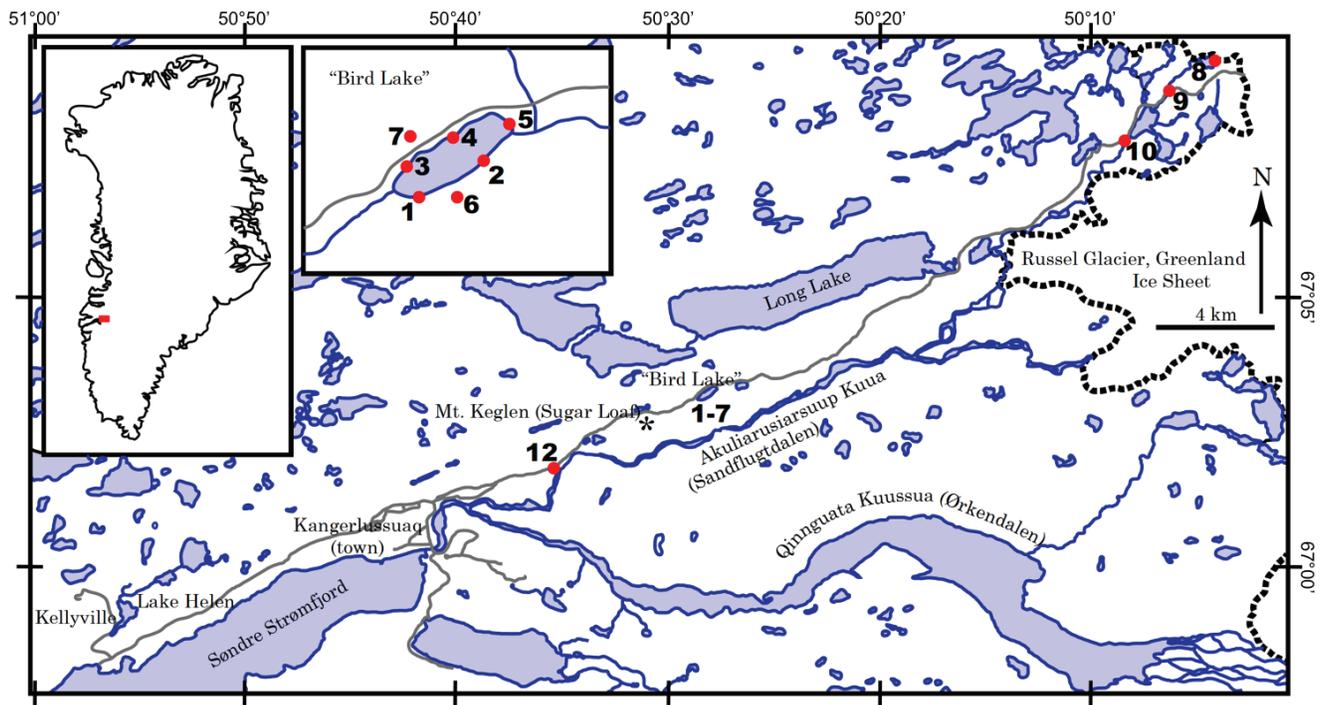


FIGURE 1. Map of Greenland (inset) and Kangerlussuaq study area, with site locations. Sites in red, road in gray.

Local vegetation is polar tundra or steppe (Böcher, 1949; Peel et al., 2007) and belongs to the Low Arctic classification (Bliss and Matveyeva, 1992). It is dominated by dwarf shrubs (*Betula nana*, *Empetrum hermaphroditum*, *Rhododendron lapponica*, *R. tomentosum*, *Salix glauca*, and *Vaccinium uliginosum*) with abundant forbs, graminoids (e.g., *Calamagrostis lapponica* and *Eriophorum angustifolium*), and horsetails (*Equisetum arvense*), as well as mosses and lichens. Although the study area is well north of the natural range limit for trees, there is a stand of several species of small trees of unknown provenance east of the town of Kangerlussuaq, including *Alnus* sp., *Betula* sp., *Picea* sp., *Pinus* sp., and *Populus* sp. Otherwise, trees are not present in or native to the local area.

Leaf and stem samples were collected from multiple plant species along the Sandflugtdalen between 18 July and 3 August 2014 (Fig. 1, Table 1). Most samples (Sites 1–5) were collected around the margin of a small lake directly east of Mount Keglen, ~11 km northeast of Kangerlussuaq, and ~11 km from the nearest margin of the GrIS. Samples were also collected from a north-facing hill slope (Site 6) and a south-facing slope (Site 7) within the lake watershed. Additional samples were collected from tundra adjacent to the GrIS: at the moraine edge (Site 8) and at a distance of ~1 km from the GrIS (Sites 9 and 10). Samples were also collected from the trees near Kangerlussuaq (Site 12). Species and isotope results are reported in Appendix Table A1. Plant

samples were clipped in the field and placed immediately into precleaned 8 mL glass vials with polytetrafluoroethylene-lined (PTFE-lined) caps and sealed with PTFE tape. For larger plants with exposed stems, leaf and stem samples were collected from the same stem, and stem samples were clipped near to the main stem to avoid fractionation effects. Separate stem samples were not collected for smaller plants because the stems were buried in moss and litter and covered by soil moisture. When whole plants were sampled (e.g., for horsetails and grasses), the entire aboveground plant was collected in a vial. Whole plant measurements were not included in the comparisons of leaf and xylem water values. Once collected, all samples were kept cool and out of direct light for transportation and storage until analysis. Samples were first extracted under vacuum following the method described by West et al. (2006) and then analyzed via wavelength-scanned cavity ring down spectroscopy (Picarro L1102-i water isotope analyzer) at the Stable Isotope Laboratory at the University of Utah. Activated charcoal chips were added to the extracted waters before analysis to remove any secondary compounds in the water samples, and appropriate corrections were made (Schmidt et al., 2012). Anomalously positive plant water values (outliers) or leaf water values lower than corresponding xylem values from the same plant were discarded (3 samples). Samples were measured in conjunction with three in-house standards, which yielded average uncertainty of $\pm 1.2\%$ standard deviation (on a

TABLE 1

Locations and collection dates of plant water samples, with hourly mean temperature (T, °C) and relative humidity (RH, %) from the Kangerlussuaq weather station at the time of sample collection.

Site	Location	Coll. Date	Latitude	Longitude	Mean T	RH
1	Bird Lake	18-Jul-2014	67°03.114'N	050°28.605'W	12.9	68
2	Bird Lake	18-Jul-2014	67°03.216'N	050°27.942'W	16.5	52
3	Bird Lake	18-Jul-2014	67°03.203'N	050°28.592'W	17.7	43
4	Bird Lake	19-Jul-2014	67°03.285'N	050°28.251'W	9.8	63
5	Bird Lake	19-Jul-2014	67°03.327'N	050°27.750'W	13.3	51
6	Bird Lake, N-facing slope	19-Jul-2014	67°03.115'N	050°28.171'W	17.9	44
7	Bird Lake, S-facing slope	19-Jul-2014	67°03.307'N	050°28.385'W	18.3	44
8	Subglacier portal	20-Jul-2014	67°09.391'N	050°03.988'W	6.6	77
9	River	20-Jul-2014	67°08.823'N	050°06.271'W	14.5	50
10	River	3-Aug-2014	67°07.926'N	050°08.484'W	7.9	65
12	Trees	3-Aug-2014	67°01.821'N	050°35.565'W	14.7	45

minimum of four measurements) or better for δD measurements and $\pm 0.2\text{‰}$ or better for $\delta^{18}O$.

Climate data were compiled from the DMI record of hourly measurements at Kangerlussuaq (Station 4231). For the analyses presented here, we use hourly weather data at the times of sample collection in 2014 as well as July averages from 1977 to 2013. Most of the samples were collected in July, with non-July samples being collected on 3 August, and the comparison of time-of-collection climate measurements with averaged data allows for an assessment of the assumptions typically necessary for biomarker proxy-based studies. The 37-year average temperature for July is 10.9 °C, with average minimum and maximum temperatures of 2.1 °C and 21.0 °C. Average air pressure is 101 kPa. Average relative humidity is 62%, with average minimum and maximum values of 24% and 98% (during precipitation events).

The Craig-Gordon Model

The Craig-Gordon model describes isotope fractionation during evaporation from an isolated, open body of water (Craig and Gordon, 1965). It was modified to describe evaporative fractionation during transpiration from a leaf (Flanagan et al., 1991; Flanagan, 1993) and has been found to be a remarkably robust model for explaining water isotope fractionation in plants (Roden and Ehleringer, 1999; Roden et al., 2000; Smith and Freeman, 2006; Horita et al., 2008; Kahmen et al., 2013; Tipple et al., 2014). The modified Craig-Gordon model states

$$R_{lw} = \alpha^* \left[\alpha_k R_{xw} \left(\frac{e_i - e_a}{e_i} \right) + \alpha_{kb} R_{xw} \left(\frac{e_s - e_i}{e_i} \right) + R_a \left(\frac{e_a}{e_i} \right) \right], \quad (1)$$

where R_{lw} , R_{xw} , and R_a are the D/H (i.e., HDO/H₂O) or ¹⁸O/¹⁶O molar ratios of leaf water, xylem water, and water vapor in air, respectively. In this equation, α^* is the equilibrium fractionation factor relating to the movement from liquid to vapor phases for the heavy and light isotopes; α_k is the kinetic fractionation factor relating to diffusion from the evaporation site; and α_{kb} represents the kinetic fractionation factor in the leaf surface boundary layer. Lastly, e_i , e_s , and e_a are the partial pressures of water vapor in the leaf intercellular space, at the leaf surface, and in atmospheric air, respectively. The equilibrium fractionation factor α^* is temperature-dependent and has been determined most recently by Horita and Wesolowski (1994), with separate equations for D/H and ¹⁸O/¹⁶O. The kinetic fractionation factor, α_k , has been empirically determined for both D/H and ¹⁸O/¹⁶O by Cappa et al. (2003), where for D/H, $\alpha_k = 1.01636$, and for ¹⁸O/¹⁶O, $\alpha_k = 1.03189$.

Boundary layer effects are shown to have an effect of 2–6‰, which is near analytical error for hydrogen isotope measurements but significant for oxygen isotope measurements (Flanagan, 1993). Thus, boundary layer effects can usually be safely ignored when considering hydrogen isotopes (e.g., in studies of leaf wax lipids), but are important for oxygen isotopes. The boundary layer fractionation factor α_{kb} is calculated as α_k raised to the 2/3 power (Flanagan, 1993). Leaf surface vapor pressure can be calculated using the equations of Ball (1987), which require an estimate of stomatal conductance and

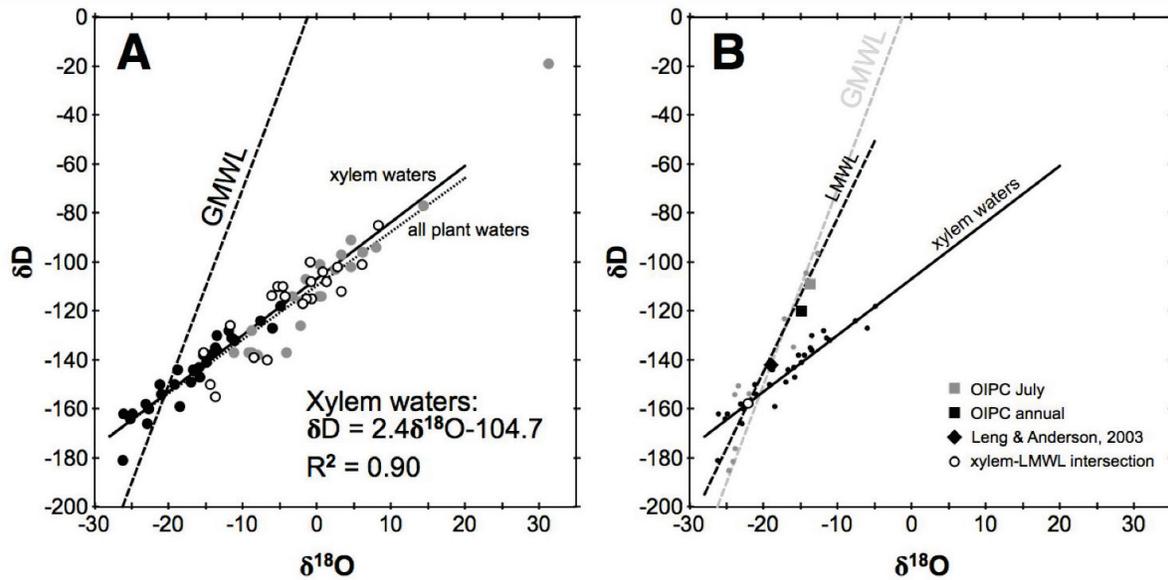


FIGURE 2. Measured plant waters and modeled or estimated precipitation δD versus $\delta^{18}O$ values, plotted against the global meteoric water line (GMWL). (A) All data, including stem waters (black circles), leaf waters (gray circles), and whole plant waters (hollow circles), as well as linear regressions for all plant waters (dotted line) and for xylem waters alone (solid line). (B) Local evaporation line (LEL; linear regression in black solid line) for xylem waters from this study (black circles), and local meteoric water line (LMWL; linear regression in black dashed line) for precipitation data from Lindborg et al. (2016) (gray circles); intersection point for LMWL and xylem water LEL (open circle), as well as earlier precipitation estimate by Leng and Anderson (2003; black diamond) and OIPC modeled estimates for July and annual precipitation (gray and black squares, respectively).

leaf transpiration (Roden and Ehleringer, 1999; Roden et al., 2000).

The δD value of leaf water (δD_{lw}) is proportional to R_{lw} via the equation

$$\delta D_{lw} = \frac{R_{lw}}{R_{std}} - 1, \quad (2)$$

where δD is expressed in per mil (‰), reported relative to standard mean ocean water (SMOW). Thus, δD_{lw} is a function of the δD value of source (xylem) water (δD_{xw}), the equilibrium isotope effect of the liquid-vapor transition, the kinetic isotope effect due to diffusion, and isotopic exchange between leaf air and the atmosphere. A similar statement can be made for the $\delta^{18}O$ value of leaf water. This definition assumes that the leaf air space is saturated with water vapor and that liquid and vapor have the same temperature. These conditions are both typically satisfied for the air space inside a leaf, where intercellular air is in equilibrium with cell water (Flanagan, 1993).

It has been shown that water is not fractionated by root uptake (Washburn and Smith, 1934; White et al., 1985; Dawson and Ehleringer, 1991, 1993), meaning that xylem water from mature, non-photosynthesizing stems should

have the same isotopic composition as plant source water, assuming no evaporative loss. Whether and how this belowground source water correlates to the isotopic composition of local precipitation is examined below for plants in West Greenland, as this linkage is often assumed to be direct in paleohydrologic interpretations of plant-derived δD and $\delta^{18}O$ values. Assuming that the precipitation is in equilibrium with water vapor in the air, an assumption not necessarily valid for arid areas, we can use the equilibrium relationship between vapor and liquid ratios to apply the δD and $\delta^{18}O$ values of local precipitation as substitutes for R_a . Stable isotope values of precipitation were obtained using the OIPC model (Bowen, 2008), the local evaporation line formed by lake waters (Leng and Anderson, 2003), and the intersection of xylem waters measured in this study with a local meteoric water line (discussed below).

RESULTS

Precipitation and Local Evaporation Line

Table A1 reports leaf and xylem water stable isotope values, and Figure 2, part A, shows plant waters (leaf, xylem, and whole plant) for all samples plotted against the global meteoric water line (GMWL, which has the

equation $\delta D = 8 \times \delta^{18}O + 10$). Leaf waters are significantly D- and ^{18}O -enriched relative to paired xylem waters. Plant water δD and $\delta^{18}O$ values strongly correlate (linear regression $R^2 = 0.91, p < 0.0001$), excluding one outlying point for the introduced trees (*Alnus* sp.). A regression line of the plant water values forms a local evaporation line (LEL; Fig. 2, part A) with a lower slope (2.2) compared to the GMWL, as expected (Allison et al., 1985). A regression of xylem waters alone gives a slope of 2.4 ($R^2 = 0.90, p < 0.0001$), and regression of leaf waters alone gives a slope of 2.6 ($R^2 = 0.88, p < 0.0001$). Assuming that xylem waters are not isotopically fractionated from soil waters (White et al., 1985; Dawson and Ehleringer, 1991, 1993), xylem water values can serve as a proxy for soil waters. Although soil water LEL slopes are typically lower than surface water LEL slopes, 2.4 is lower than most soil water slopes and much lower than model predictions for soil waters at high latitudes (Gibson et al., 2008).

Xylem water values, which represent plant source waters, are generally more negative than OIPC modeled July or annual precipitation values (Fig. 2, part B), and there is no correlation between xylem water values and proximity to the GrIS. There is also no correlation between xylem or leaf water values and species. Leng and Anderson (2003) analyzed lake water isotope values from several lakes along the length of Søndre Strømfjord and utilized the intersections of the lake evaporation lines with the GMWL to estimate a $\delta^{18}O$ value of -19‰ and a δD value of -142‰ for local average precipitation (Fig. 2, part B). The xylem water data here clearly comprise a similar LEL, and instead of intersecting it with the GMWL, we are able to utilize precipitation data from the Kangerlussuaq area recently made available by Lindborg et al. (2016). The stable isotope values of local snow and rain events form a local meteoric water line (LMWL) for Kangerlussuaq, which is similar to but not the same as the GMWL (Fig. 2, part B). This is in addition to the two climate stations on the west coast of Greenland for which isotope measurements are available: Thule and Grønødal (now Qaanaaq and Kangilinnuit), which are ~ 1300 km northwest and ~ 700 km south of Kangerlussuaq, respectively (IAEA/WMO, 2016). In order to derive a more accurate estimate of average meteoric source water for local vegetation, we can use the intersection of the xylem water LEL from this study and the Kangerlussuaq LMWL. The point of intersection between the lines (XW-LMWL intercept) gives isotope values of $\delta^{18}O = -22.1\text{‰}$ and $\delta D = -158\text{‰}$, which are significantly more negative than the estimate generated by Leng and Anderson (2003) or OIPC-modeled values (Table 2). However, two pieces of evidence support this new precipitation estimate. First,

TABLE 2

Stable isotope values of estimated local precipitation with corresponding equilibrium atmospheric vapor values.

	$\delta^{18}O_p$	δD_p	$\delta^{18}O_a$	δD_a
OIPC, July	-13.7	-109	-24.1	-187
OIPC, Annual	-14.9	-120	-25.2	-197
Leng and Anderson (2003)	-19.0	-142	-29.3	-217
XW-LMWL intercept	-22.1	-158	-32.4	-232

we examine the deuterium excess. Deuterium excess (d) is the deviation of a water sample from the GMWL, defined as $d = \delta D - 8 \times \delta^{18}O$, and more positive d values are typically the result of (A) colder, drier air at the time of initial evaporation from sea water and/or (B) additional moisture recycling over land (Merlivat and Jouzel, 1979; Aemisegger et al., 2014; Pfahl and Sodemann, 2014). The d value for our precipitation estimate is 19‰, which is in good agreement with the available evidence. Deuterium excess is higher for winter precipitation (Pfahl and Sodemann, 2014), which comprises a large proportion of soil waters via snow and ice melt. Deuterium excess values increase with decreasing temperature for both Thule and Grønødal (IAEA/WMO, 2016). The XW-LMWL intercept also lies within the range of values for winter precipitation events (Lindborg et al., 2016). Second, using this precipitation value and average July climate variables and assuming an equilibrium relationship between water and vapor give atmospheric vapor values of $\delta^{18}O = -32.4\text{‰}$ and $\delta D = -232\text{‰}$, which are in good agreement with isotope values recently reported for late summer (August) water vapor samples over seawater at the Kangerlussuaq harbor and three lakes in the same study area (Feng et al., 2016). Therefore, we utilize this new precipitation value as a reasonably confident estimate of average local meteoric water.

Applying the Craig-Gordon Model to Greenland Plant Waters

Stomatal conductance of water vapor varies with photosynthetic rate within a plant as well as between species in the same environment, and therefore we have used three different estimates. Therefore, we have used three separate estimates for stomatal conductance in the model results reported here—one each for *S. glauca* and *B. nana*, and a general tundra shrub value for the other species. Stomatal conductance ranges between 0.15 and 0.70 mol m⁻² s⁻¹ for *S. glauca* plants

in alpine areas (Bowman and Conant, 1994; Dudley, 2006; Dudley and Galen, 2007). Lower stomatal conductance rates ($0.020\text{--}0.40\text{ mol m}^{-2}\text{ s}^{-1}$) were found for the similar species *Salix arctica* in the Arctic (Dawson and Bliss, 1989b; Jones et al., 1999), including Greenland (Bredahl et al., 2004), and arctic plants generally have lower stomatal conductances than alpine plants (Dawson and Bliss, 1989a). Although there are no conductance or transpiration measurements available for the plants analyzed here, $0.30\text{ mol m}^{-2}\text{ s}^{-1}$ is considered a reasonable value for *S. glauca* and is employed in the model (Roden and Ehleringer, 1999). For *B. nana*, we use a stomatal conductance value of $0.10\text{ mol m}^{-2}\text{ s}^{-1}$, based on recent measurements of the species in the field (Pattison and Welker, 2014), including at Kangerlussuaq (Cahoon et al., 2016). For the remaining species, we apply a generalized, conservative estimate of $0.20\text{ mol m}^{-2}\text{ s}^{-1}$ for stomatal conductance, based on mean conductance values for several common arctic shrubs, including *V. uliginosum* (Oberbauer and Oechel, 1989), and maximum conductance estimates for tundra shrubs (Schulze et al., 1994; Körner, 1995). The effect of variation in stomatal conductance is minimal for δD values (typically $<1\text{‰}$), but can be important for modeling $\delta^{18}\text{O}$ values.

Leaf temperature, which controls fractionation within the leaf, rarely equals air temperature and depends on variable factors such as sun exposure. Based on observations of *S. arctica* and other species at 75°N latitude in the Canadian Arctic (Wilson, 1957) and at 83°N latitude in North Greenland (Mølgaard, 1982), a difference of $+4\text{ }^\circ\text{C}$ is used for average leaf temperature here. However, this may be a conservative estimate as recent work from Arctic Alaska has shown average leaf temperatures to be $\sim 10\text{ }^\circ\text{C}$ higher than ambient air for several tundra shrub species, including *B. nana* and *V. uliginosum* (Gersony et al., 2016). Average air temperature for July in Kangerlussuaq is $10.9\text{ }^\circ\text{C}$, but this likely underestimates the temperature in the microclimates surrounding tundra vegetation, especially on sunny or partly cloudy days without precipitation. On sunny days, temperatures at the ground surface and within or under shrubs in West Greenland can be up to $30\text{ }^\circ\text{C}$ warmer than ambient air (Böcher, 1949; Wilson, 1957; Hansen, 1973), although recent work has reported much more modest increases of $1\text{--}2\text{ }^\circ\text{C}$ in *B. nana* shrub canopies (Cahoon et al., 2016). Elevated ground surface temperatures also lower the relative humidity within the vegetation microclimate (Böcher, 1949).

Using the July average air temperature $10.9\text{ }^\circ\text{C}$ and assuming that precipitation is in equilibrium with atmospheric water vapor, we can calculate water vapor

stable isotope values ($\delta^{18}\text{O}_a$ and δD_a) from the variously estimated precipitation values ($\delta^{18}\text{O}_p$ and δD_p) for the area, including both annual and July OIPC modeled values, the precipitation value estimated using lake waters by Leng and Anderson (2003), and the new precipitation value estimated from the XW-LMWL intercept, described above. Using the XW-LMWL water vapor estimates and the climate parameters described above—as well 101 kPa atmospheric pressure, which was both July average and daily pressure at the Kangerlussuaq climate station during the time of sampling—we model leaf water $\delta^{18}\text{O}$ and δD values with the Craig-Gordon model and compare modeled and measured values. These comparisons exclude the outlying *Alnus* sp. leaf sample. We then compare leaf water δD and $\delta^{18}\text{O}$ values modeled using the climate data from time of collection (Table 1) and those using the July averages for air temperature and relative humidity ($10.9\text{ }^\circ\text{C}$ and 62%) with measured leaf water values (Fig. 3). Both sets of modeled data give similar results in comparison with measured leaf waters. The monthly average-based model values produce a linear regression with a stronger correlation to measured values ($R^2 = 0.69$ and 0.58 for July-based δD and $\delta^{18}\text{O}$ values, compared to $R^2 = 0.43$ and 0.30 , respectively), which is expected given the variation in the hourly data. Because of the similar correlation and better fit, we use the monthly averages to examine the effects of increased temperature and decreased humidity on leaf water values. Figure 4 shows that the precipitation estimates based on local waters, i.e., the Leng and Anderson (2003) and XW-LMWL values, produce modeled leaf water values that agree more closely with measured leaf water values than model values based on OIPC precipitation estimates. The δD regression slope is 1.5 , and $\delta^{18}\text{O}$ slope is 1.7 .

Considering that relative humidity decreases away from the fjord, with increasing proximity to the cold, dry winds originating on the GrIS, and that humidity decreases with increased microclimate temperatures in the plant canopy (Böcher, 1949), Figure 5, parts A and B, uses the XW-LMWL estimate for precipitation and show modeled leaf waters using the average July humidity (62%) as well as 10% greater and 10% and 20% less. Figure 5, parts C and D, shows leaf waters using the July average air temperature ($10.9\text{ }^\circ\text{C}$), as well as 10 and $20\text{ }^\circ\text{C}$ warmer, consistent with a warmer microclimate at the ground surface and within vegetation. Figure 6 shows the same precipitation-modeled leaf waters as Figure 4, but for the two species with the most samples (*B. nana* and *S. glauca*), and it demonstrates that the XW-LMWL precipitation estimate matches most closely with the measured xylem and leaf waters. Again focusing on *B. nana* and *S. glauca*, Figure 7, parts A and

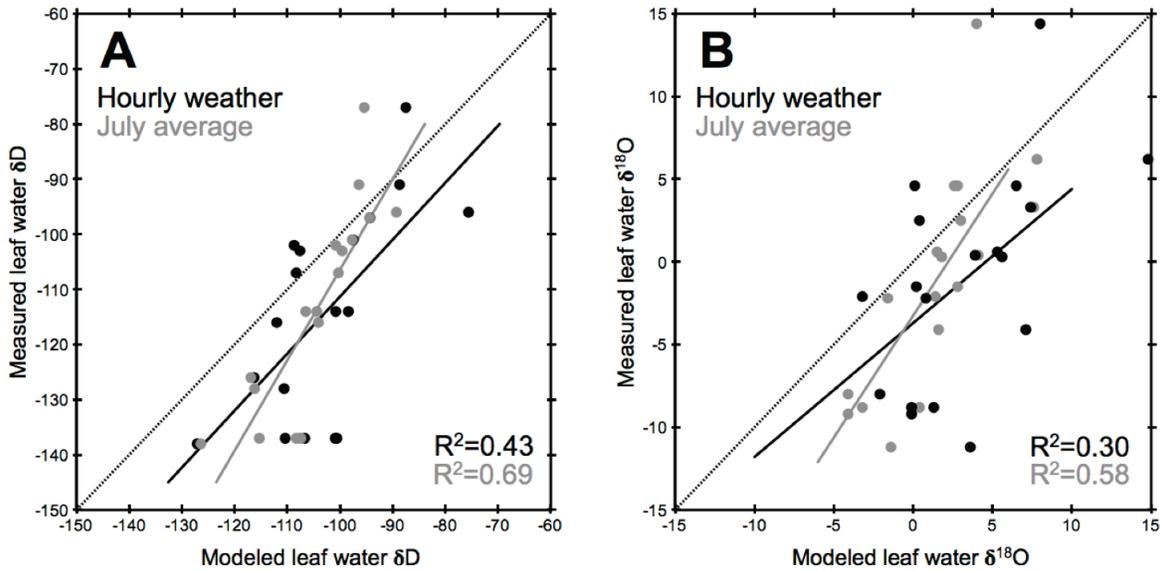


FIGURE 3. Modeled leaf water stable isotope values compared with measured leaf waters for (A) δD and (B) $\delta^{18}O$, using hourly weather measurements at the time of sample collection (black) and average July climate values (gray).

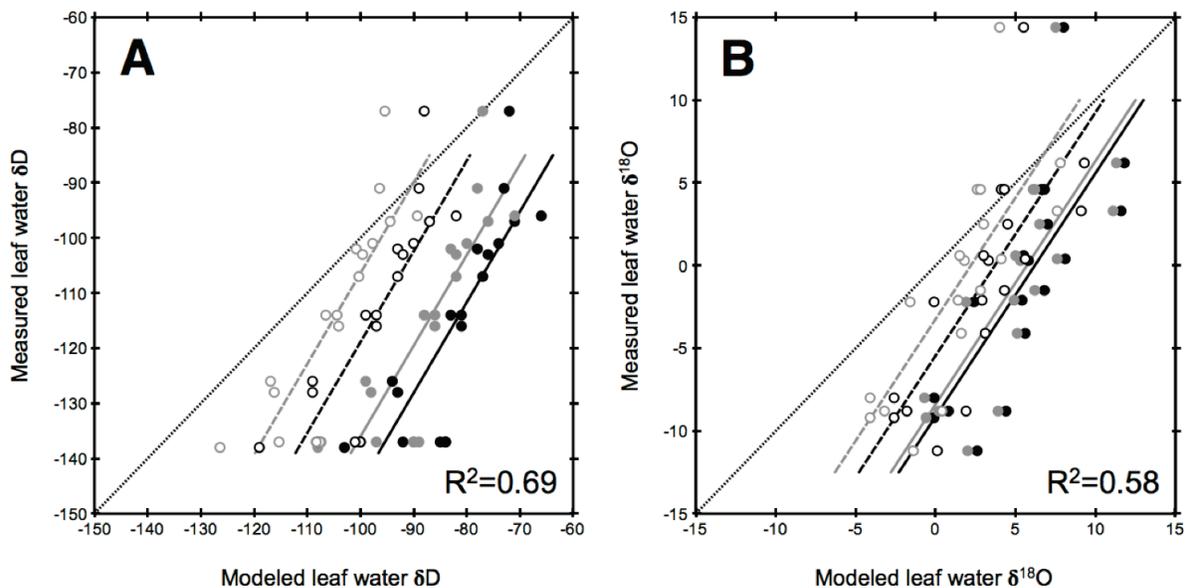


FIGURE 4. Modeled leaf water stable isotope values compared with measured leaf water values for (A) δD and (B) $\delta^{18}O$, using measured xylem waters and the variously calculated atmospheric vapor values: OIPC July average (black filled circles, solid black line), OIPC annual average (gray filled circles, solid gray line), Leng and Anderson (2003) estimate (black hollow circles, dashed black line), XW-LMWL intercept (grey hollow circles, dashed grey line). Corresponding lines represent linear regression lines.

B, illustrates that with decreasing humidity, modeled leaf water values move from measured xylem water values to measured leaf water values, as expected. With increasing air temperature, modeled leaf water values are closer to those measured for *B. nana* (Fig. 7, part C) but not for *S. glauca* (Fig. 7, part D).

DISCUSSION

Precipitation Estimate

Using the XW-LMWL precipitation estimate, modeled leaf water values approach measured values more

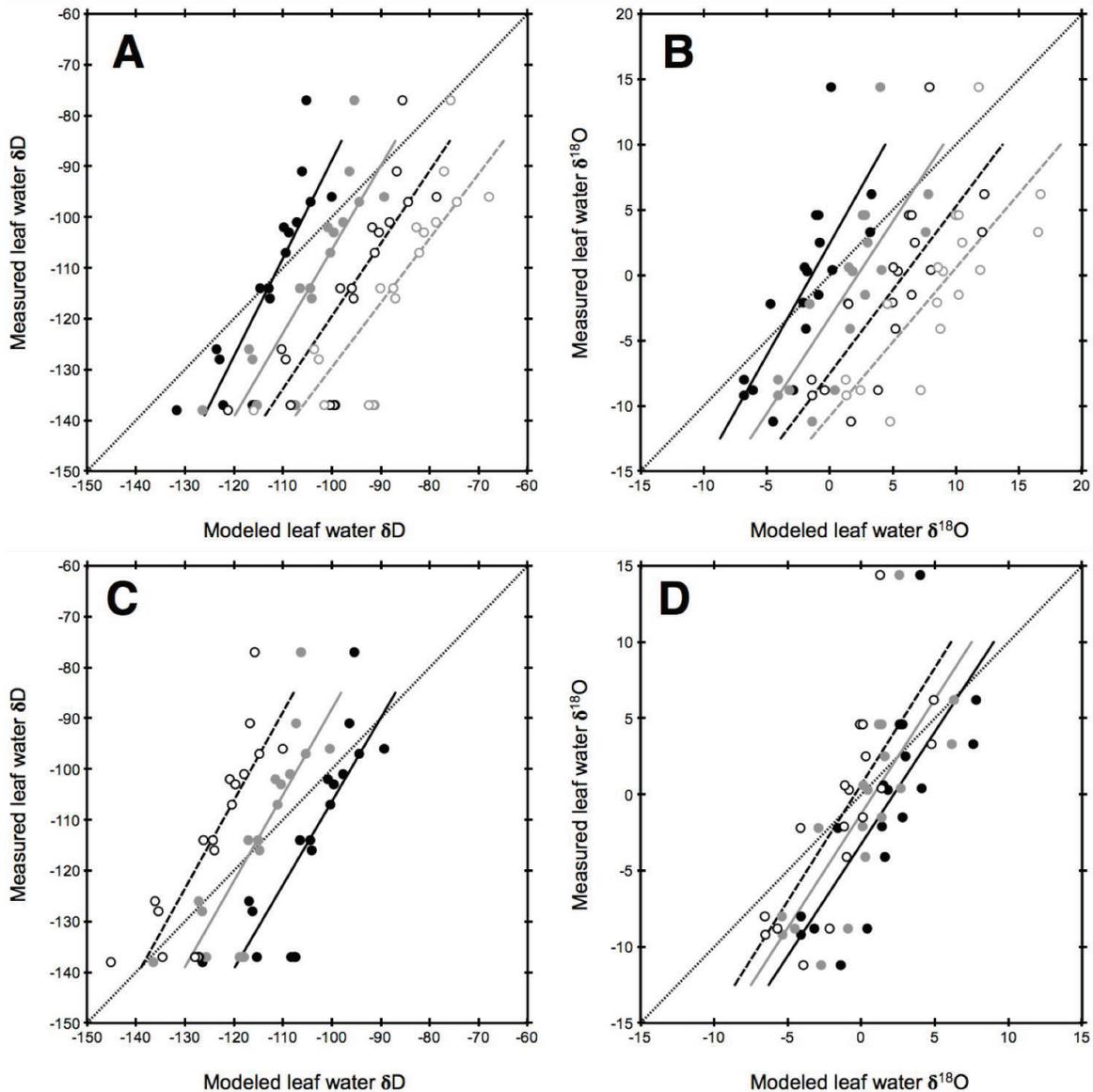


FIGURE 5. Modeled leaf water (A and C) δD values and (B and D) $\delta^{18}\text{O}$ values compared with measured values, using (A and B) different relative humidities: 72% (black filled circles, black solid line), 62% (gray filled circles, gray solid line), 52% (black hollow circles, black dashed line), and 42% (gray hollow circles, gray dashed line); or using (C and D) different air temperatures: 11 °C (black filled circles, black solid line), 21 °C (gray filled circles, gray solid line), and 31 °C (black hollow circles, black dashed line).

closely than using the annual or July OIPC modeled values (Figs. 4 and 6). Although there are only two stations reporting precipitation stable isotope data for the whole of West Greenland, and the OIPC estimates are least robust for arctic and Antarctic areas (Bowen and Revenaugh, 2003), it should be noted that the OIPC estimate for July is in excellent agreement with the measurements from summer rain events (Lindborg et al., 2016). That the precipitation value estimated here using plant waters is more negative than other estimates likely reflects a greater utilization by plants (and lakes) of

snow or soil frost melt (Oberbauer and Dawson, 1992; Sugimoto et al., 2002, 2003), which accumulates over the winter and has a lower delta value than summer precipitation. This is similarly supported by the high d value described above. Kangerlussuaq is within the region of continuous permafrost (Jørgensen and Andreasen, 2007), although local permafrost distribution is dependent on topography (Henkner et al., 2016). Glacial runoff also contributes water to the landscape and has a more negative isotope value than local meteoric waters. The $\delta^{18}\text{O}$ values of bulk meltwaters from the Imersuaq Glacier,

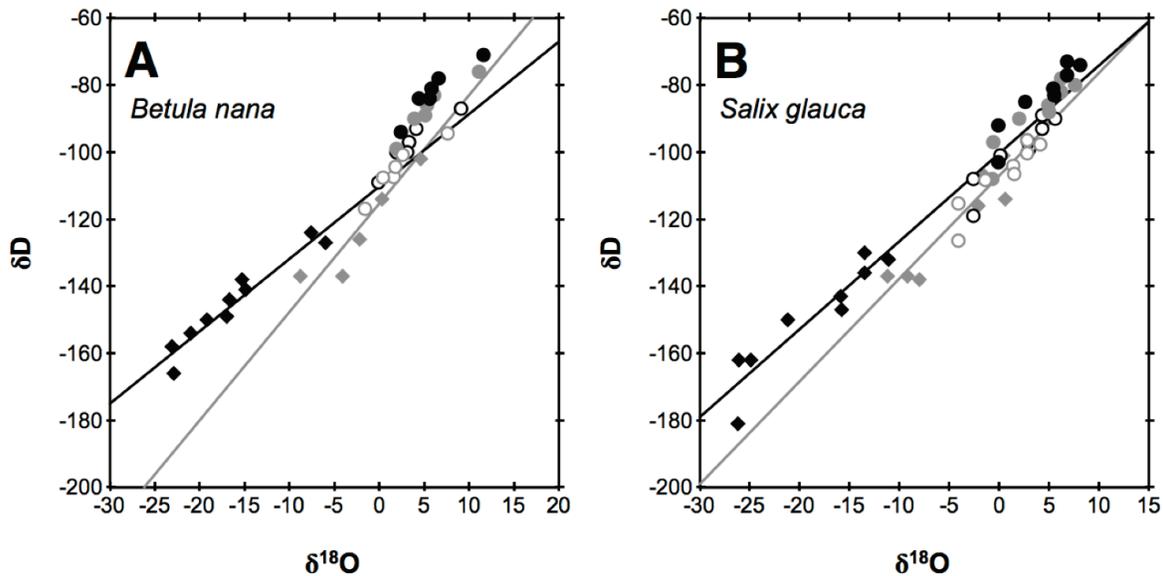


FIGURE 6. Measured xylem waters (black diamonds, black line) and leaf waters (gray diamonds, gray line) compared with modeled leaf water values for using the OIPC July (black filled circles), OIPC annual (gray filled circles) and Leng and Anderson (2003) precipitation values (black hollow circles), and the precipitation estimated using xylem waters (gray hollow circles) for (A) *Betula nana* and (B) *Salix glauca*.

south of Kangerlussuaq, were measured to be between -26‰ and -30‰ (Yde and Tvis, 2004). However, although plants growing directly adjacent to the river may access some amount of glacial meltwater (Sites 8–10 and 12), glacial melt is unlikely to contribute water to the closed-basin lakes or to plants not growing on or near river banks.

The xylem water LEL has a slope of 2.4, which is largely due to evaporation of water from the soil. It is much lower than predicted for a highly seasonal, high-latitude area and is similar to soil LELs from arid areas (Allison et al., 1983; Gibson et al., 2008). It is expected that soil water LELs are lower than surface water LELs, but whereas the Kangerlussuaq area surface waters fit with predictions (Leng and Anderson, 2003; Gibson et al., 2008), the xylem water LEL is still unusually low. Others have observed plant water LELs with slightly lower slopes than the soil water LEL for the same area (Busch et al., 1992), but this is explained by the inclusion of leaf water measurements with their higher rate of evaporative water loss through leaf transpiration (Allison et al., 1985). This does not explain the low slope observed in xylem waters alone. However, if plant waters partly reflect snow and soil frost melt, sublimation could contribute to D- and ^{18}O -enrichment in soil water sources before melt (Taylor et al., 2001; Moran and Marshall, 2009; Sokratov and Golubev, 2009). The possible contribution of heavy snow melt in this area and other arctic areas and the consequent

implications for local evaporations lines require further investigation.

Modeled versus Measured Leaf Water Values

The results presented here show that the Craig-Gordon model, using the XW-LMWL meteoric water estimate and average July climate values, does reasonably well estimating the evaporative enrichment in Kangerlussuaq leaf waters, with values falling across the 1:1 lines in the model-measurement comparisons (Figs. 4 and 5). Given the inclusion of unfractionated vein water in the total bulk leaf water, it is expected that measured leaf water values are slightly more negative than modeled leaf waters, although the two are correlated (Yakir et al., 1989, 1990; Flanagan and Ehleringer, 1991). Furthermore, diffusion of evaporatively enriched water through the leaf away from the evaporation sites around stomata, that is, the so-called Péclet effect, can also explain part of the remaining discrepancy (Barbour et al., 2004; Kahmen et al., 2011; Ferrio et al., 2012). This effect is moderated by the rate of transpiration, which in the Arctic can be driven by nearly continuous sunlight. During the month of July, Kangerlussuaq receives 24 to 19 hours of sunlight and 18 to 16 hours of light where the sun is greater than 6° above the horizon (solar twilight), excepting cloudy days. However, even with the near-continuous sunlight, diurnal temperature fluctua-

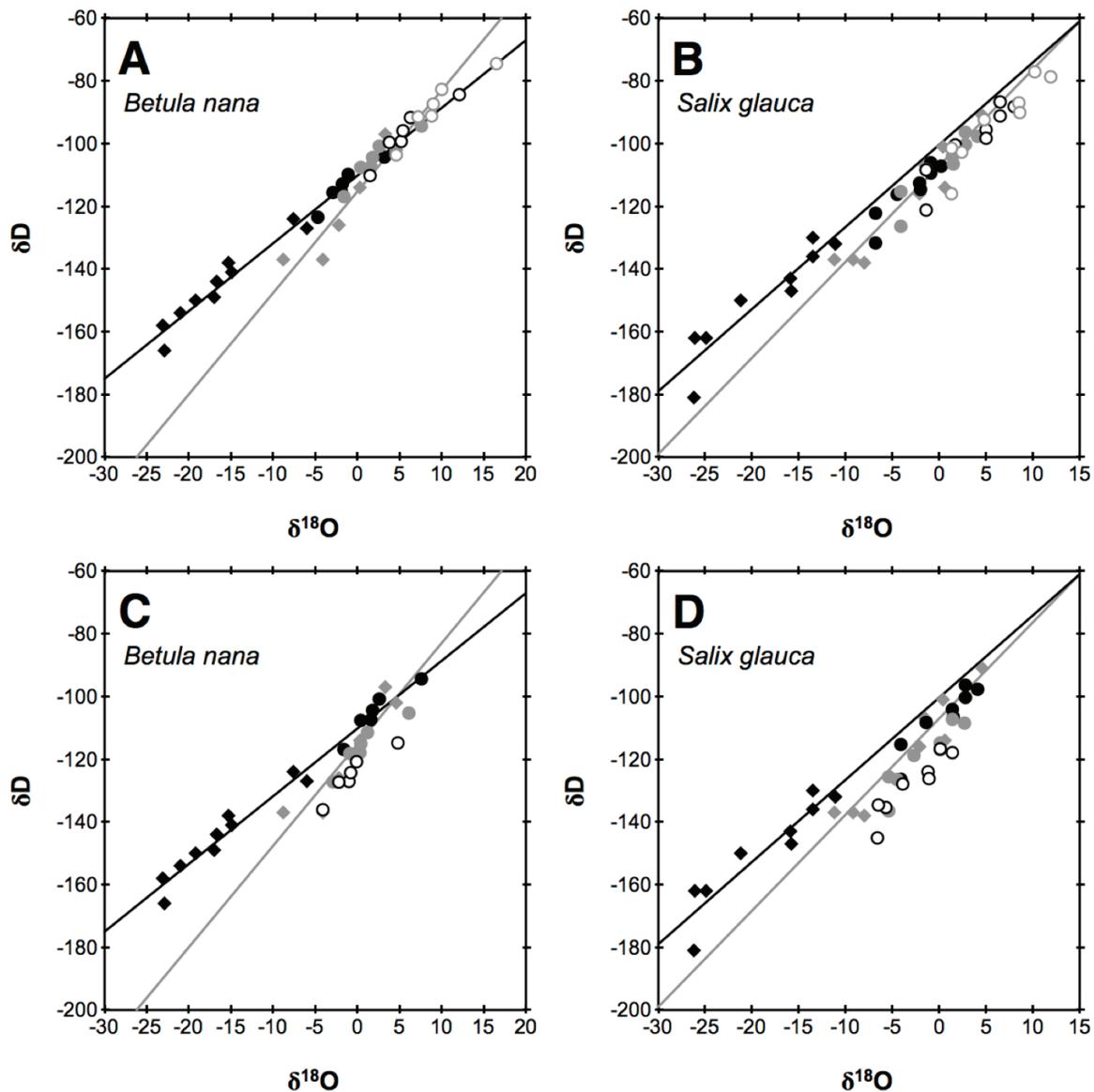


FIGURE 7. Measured xylem waters (black diamonds, black line) and leaf waters (gray diamonds, gray line) for (A and C) *B. nana* and (B and D) *S. glauca* compared with modeled leaf waters using (A and B) different relative humidities: 72% (black filled circles), 62% (gray filled circles), 52% (black hollow circles), and 42% (gray hollow circles); or using (C and D) different air temperatures: 11 °C (black filled circles), 21 °C (gray filled circles), and 31 °C (black hollow circles).

tions can be large (Böcher, 1949). Temperatures near the ground surface can be much higher than ambient air, up to 30°C greater (Sørensen, 1941; Böcher, 1949; Hansen, 1973), and with those warmer temperatures relative humidity at the surface can drop to 25%–30% (Böcher, 1949). Plants regulate their leaf temperatures for optimum photosynthesis (Helliker and Richter, 2008; Song et al., 2011), and it is likely that both leaf and microclimate temperatures in and around the tundra vegetation are warmer than the multi-year July mean of 10.9 °C. Thus, the modeled leaf water values may reflect an overly conservative estimate of air temperature. A 4 °C

difference between leaf and air temperature may also be an overly conservative estimate, as other studies have measured leaf temperatures 10–15 °C warmer than air temperature in tundra dwarf shrubs in Norway, Greenland, and Alaska (Biebl, 1968; Stoutjesdijk, 1970; Gersony et al., 2016). Wind strength coming from the GrIS is an additional factor that influences temperature and humidity, as it controls how far moist sea air reaches inland (Kopeck et al., 2014) and can reduce the leaf-to-air temperature difference by increasing evaporation. Wind direction may influence the relative humidity and the stable isotope values of atmospheric water vapor, but

winds generally come off the ice sheet during the summer. However, it should be noted that wind direction and its effect on moisture balance have been interpreted from records of varying lake levels in the Kangerlussuaq area over the last several thousand years (Perren et al., 2012), so this may be an important consideration for paleoclimate studies using plant tissue or biomarker archives. Overall, despite the variables considered above, the Craig–Gordon modeled values robustly replicate measured leaf water values and do so based on averaged, relatively low-resolution climate variables. This is an important consideration in the application to paleoclimate records, which, because of the time-averaged nature of sedimentary archives, cannot attain the high degree of temporal resolution (i.e., hourly or daily measurements of climate variables) available in modern ecological studies.

The findings here are important for interpreting climate and hydrology from leaf wax archives in the area and for comparison with other local precipitation records (McGowan et al., 2003). Sachse et al. (2012) found that for C_3 dicots, which include species measured here, the apparent fractionation for hydrogen isotopes between mean annual precipitation and the C_{29} n -alkane, one of the more commonly used plant biomarkers, was -113% . For Kangerlussuaq area plants, if the source precipitation δD value is 38% more negative than the OIPC modeled average annual value, applying a general apparent fractionation based on OIPC precipitation to local plant tissue (e.g., leaf wax lipids) measurements may significantly underestimate actual precipitation values. Our findings also reinforce the caveat that the climate signals recorded in plant biomarkers reflect a plant's microclimate and source water, which in turn correlate with, but are not necessarily the same as, general climate and hydrology conditions. However, the new estimate for plant source waters in the Kangerlussuaq area reported here and the confirmation of the Craig–Gordon model under summer arctic conditions will serve future isotopic studies of plant biomarkers in both living plants and in sediment archives.

CONCLUSIONS

We measured the δD and $\delta^{18}O$ values of plant waters, including stems and leaves, from tundra plants in the Kangerlussuaq area of West Greenland. The intersection of the xylem water LEL with a new LMWL based on recently reported local precipitation stable isotope values provides a new isotopic estimate of meteoric source water for plants, which is -22.1% for $\delta^{18}O$ and -158% for δD . This estimate is in good agreement with available evidence and

significantly lower than OIPC modeled values. Therefore, we recommend that any future analyses of hydrology using plants or plant materials in the Kangerlussuaq and Søndre Strømfjord area use precipitation values calculated from in situ measurements or the plant-derived values presented here. We also used xylem water stable isotope values to model evaporatively enriched leaf waters using the modified Craig–Gordon model. Modeled values are in good agreement with measured values when using precipitation isotope values based on in situ water measurements rather than modeled precipitation values. However, vegetation microclimate, with its elevated temperature and reduced humidity relative to ambient air, likely exerts a strong influence on leaf transpiration and thus heavy isotope enrichment in leaf waters. These factors should be taken into consideration in any future analyses of arctic plant waters and stable isotope measurements of plant tissues and biomarkers in Greenland and the Arctic. The findings reported here can serve as a basis for comparison and interpretation of stable isotope ratios in plant tissues and biomarkers from the Kangerlussuaq area.

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APPENDIX

TABLE A1

δD and $\delta^{18}O$ values for leaf, xylem, and whole plant (“plant”) waters. Whole plant samples were collected for grasses, *Equisetum arvense*, and plants where leaves were too small to separate from stems in the field.

Species	δD			$\delta^{18}O$		
	Leaf	Xylem	Plant	Leaf	Xylem	Plant
Site 1						
<i>Salix glauca</i>	-107	-136		-1.5	-13.5	
<i>Betula nana</i>	-102	-138		4.6	-15.3	
<i>Rhododendron tomentosum</i>	-103	-135		2.5	-13.7	
<i>Equisetum arvense</i>			-102			2.8
<i>Empetrum hermaphroditum</i>			-114			-4.3
lichen sp.			-115			-0.7
grass sp.			-110			-5.3
Site 2						
<i>Salix glauca</i>	-138	-181		-8.0	-26.2	
<i>Betula nana</i>	-126	-166		-2.2	-22.9	
<i>Rhododendron tomentosum</i>		-159			-18.5	
<i>Vaccinium uliginosum</i>			-108			-0.8
<i>Equisetum arvense</i>			-140			-6.7
<i>Calamagrostis lapponica</i>	-114			-3.3		
Site 3						
<i>Salix glauca</i>	-137	-150		-11.2	-21.2	
<i>Betula nana</i>		-141			-14.9	
<i>Rhododendron tomentosum</i>		-138			-14.5	
<i>Vaccinium uliginosum</i>	-128	-164		-8.8	-25.2	
<i>Empetrum hermaphroditum</i>			-104			0.8
<i>Equisetum arvense</i>			-155			-13.7
<i>Calamagrostis lapponica</i>			-137			-15.3
Site 4						
<i>Salix glauca</i>	-101	-132		0.4	-11.1	
<i>Betula nana</i>	-97	-127		3.3	-6.0	
<i>Rhododendron tomentosum</i>	-94			8.0		
<i>Vaccinium uliginosum</i>			-100			-0.9
<i>Equisetum arvense</i>						
<i>Eriophorum angustifolium</i>			-126			-11.7
<i>Calamagrostis lapponica</i>			-114			-6.1
Site 5						
<i>Salix glauca</i>	-91	-130		4.6	-13.5	
<i>Pedicularis</i> sp.			-101			6.1
<i>Betula nana</i>		-124			-7.6	
<i>Equisetum arvense</i>			-85			8.3
<i>Vaccinium uliginosum</i>		-131			-11.5	
<i>Rhododendron lapponica</i>	-77	-128		14.4	-11.9	

TABLE A1
Continued

Species	δD			$\delta^{18}\text{O}$		
	Leaf	Xylem	Plant	Leaf	Xylem	Plant
Site 6						
<i>Salix glauca</i>	-137	-162		-9.2	-26.1	
<i>Pedicularis</i> sp.			-112			3.3
<i>Betula nana</i>		-158			-23.1	
<i>Vaccinium uliginosum</i>			-108			1.3
<i>Equisetum arvense</i>			-139			-8.5
Site 7						
<i>Betula nana</i>	-137	-149		-4.1	-17.0	
Site 8						
<i>Salix glauca</i>	-116	-143		-2.1	-15.9	
<i>Betula nana</i>		-154			-21.0	
<i>Equisetum arvense</i>			-150			-14.4
<i>Vaccinium uliginosum</i>			-110			-4.6
<i>Rhododendron tomentosum</i>		-144			-18.8	
Site 9						
<i>Salix glauca</i>	-114	-147		0.6	-15.8	
<i>Betula nana</i>	-114	-144		0.3	-16.7	
<i>Equisetum arvense</i>			-115			-1.4
Site 10						
<i>Betula nana</i>	-137	-150		-8.8	-19.2	
<i>Equisetum arvense</i>			-117			-1.9
<i>Salix glauca</i>		-162			-24.9	
Site 12						
<i>Alnus</i> sp.	-19	-132		31.3	-11.1	
<i>Populus</i> sp.	-96	-118		6.2	-4.9	
<i>Betula</i> sp.		-160			-22.7	