Appendix A. We used a variant of the steady state Craig-Gordon (C-G) model and the mechanistic framework for leaf water (Roden et al. 2000, Barbour et al. 2004) to predict $\delta^{18}$O and $\delta$D and then calculated deuterium deviations ($\Delta d$) from the modeled $\delta^{18}$O and $\delta$D. Model estimates of $\Delta d$ were compared to measured $\Delta d$ values from leaf water and cellulose to help understand the driving factors controlling the $\Delta d$ variation. Fractionation factors differ between the two isotopes, but the structure of the leaf water model is the same for both. We predicted steady state isotopic variation, relative to source water, at the site of evaporation within a leaf [$\Delta e$ for either of $\Delta^{18}O_e$ or $\Delta D_e$,] according to the C-G model (Craig and Gordon 1965, Farquhar and Lloyd 1993):

$$\Delta e = \varepsilon^+ + \varepsilon_k + (\Delta_v - \varepsilon_k) \frac{e_a}{e_i}$$  \hspace{1cm} (A.1)

where $\varepsilon^+$ is the temperature-dependent equilibrium fractionation factor between liquid and vapor water (Cappa et al. 2003), $\varepsilon_k$ is the kinetic fractionation factor for water-vapor diffusion determined by the balance of stomatal and boundary layer conductance to water vapor, $\Delta_v$ is the isotope ratio of atmospheric water vapor ($R_v$) relative to source water ($R_s$) (i.e., $\Delta_v = ((R_v/R_s) - 1) \times 1000$), $e_a$ is the ambient vapor pressure and $e_i$ is the saturation vapor pressure at leaf temperature. Equation (A.1) predicts the enrichment above source water at the site of evaporation. However, water extracted from leaves includes a mixture of source water and water enriched by transpiration (Yakir et al. 1989). The isotopic signal recorded in photosynthates should reflect mixing of these pools in leaf lamina water, which can be described by the advection of [unenriched] xylem water into the leaf lamina being opposed by the diffusion of the
enriched $\Delta_c$ signal (Farquhar and Lloyd 1993). This advective/diffusive process can be described by a leaf’s Péclet number ($\phi$):

$$\phi = \frac{LE}{CD}$$  \hspace{1cm} (A.2)

where $E$ is the transpiration flux from the leaf (mmol m$^{-2}$ s$^{-1}$), $L$ is the effective pathlength for water through the leaf (m), $C$ is the molar concentration of water (55,500 mol m$^{-3}$) and $D$ is the diffusivity of heavy molecules in water (2.66 and 2.34 $\times$ 10$^{-9}$ m$^2$ s$^{-1}$ for molecules containing $^{18}$O and D, respectively (Wang 1954)). In the present study, $E$ was estimated as the product of stomatal conductance and the ratio of the leaf-to-atmosphere vapor pressure difference (i.e., $e_a - e_i$) over the barometric pressure. For the hardwoods and conifers investigated here, stomatal conductance was set to 0.2 and 0.1 mol m$^{-2}$ s$^{-1}$, respectively. Although these values are arbitrary, they are representative of the maximum values measured in the field for mature *Quercus macrocarpa* (Voelker et al. 2013) and *Pseudotsuga menziesii* (Woodruff et al. 2010) and should roughly correspond to the difference between angiosperms and conifers (Lammertsma et al. 2011). For the results presented here, we assumed $C$ and $D$ to be constant. We set $L$ to scale with transpiration rate following the empirical relationship in Song et al. (2013):

$$L = 0.094 E^{-1.20}$$  \hspace{1cm} (A.3)

This approximation of $L$ appears to work relatively well for hardwood and conifer species (Song et al. 2013), but the underlying mechanisms are not fully understood. Following Farquhar and Lloyd (1993), the Péclet number can be applied to $\Delta_c$ to estimate the isotopic enrichment of leaf lamina water above source (i.e., xylem) water ($\Delta_i$):
\[ \Delta_1 = \frac{\Delta_e (1 - e^{-\nu})}{\varphi} \] (A.4).

Once \( \Delta_l \) and \( \Delta_e \) were estimated for both isotopes, we calculated \( \Delta d = \delta D - (8 \times \delta^{18}O + 10) \) of leaf lamina bulk water (\( \Delta d_l \)) and at the sites of evaporative enrichment in leaves (\( \Delta d_{le} \)).

With the leaf water signal defined as above, the isotopic signal of plant cellulose (\( \delta_c \)) can be described after Roden et al. (2000) as:

\[ \delta_c = f (\delta_s + \epsilon_{it}) + (1 - f) (\delta_l + \Delta_l + \epsilon_A) \] (A.5)

where \( f \) is the proportion of atoms that exchange with source water during post-photosynthetic metabolism leading to cellulose synthesis (subscripts \( s \) = source water and \( l \) = leaf water). The values of \( f \) for \( ^{18}O \) and D were set to 0.42 and 0.35, respectively. For \( ^{18}O \) the fractionation factor associated with carbonyl-water interactions during sucrose synthesis (i.e. autotrophic, \( \epsilon_A \)) and cellulose synthesis (i.e. heterotrophic, \( \epsilon_H \)) were set equal to 27‰. For \( \delta D \), fractionation factors associated with carbohydrate metabolism, \( \epsilon_A \) and \( \epsilon_H \), were set to -171‰ and +158‰, respectively (Sternberg et al. 1986, Yakir and DeNiro 1990, Luo and Sternberg 1992).

For modeling leaf water from cellulose, the canopy integrated leaf temperature (\( T_l \)) was set to the mean daily May–August temperature.

Finally, the post-photosynthetic portion of the Roden et al. (2000) model can be applied such that cellulose \( \delta^{18}O \) and \( \delta D \) can be used to predict deuterium deviations in leaf lamina water (\( \Delta d_c \)). For modeling \( \Delta d_c \) from cellulose, Equation (A.5) was solved for \( \Delta l \) and then \( \delta_s \) was added to \( \Delta l \) to obtain each leaf water isotope value. For \( \delta^{18}O \) and \( \delta D \) this simplifies as:

\[ \Delta_1 = \frac{\delta_c - f(\delta_s + \epsilon_{it})}{1 - f} + \epsilon_A \] (A.6).
For modeling deuterium deviations at the sites of evaporative enrichment ($\Delta d_{ce}$), both components of $E$, $e_a - e_i$ and canopy-integrated stomatal conductance, may be unknowns. Nonetheless, for comparing $\Delta d_c$ versus $\Delta d_{ce}$, we calculated the difference between $\Delta e$ and $\Delta l$ using equations A.1-A.4 as described above and added this value to $\Delta l$ (as estimated from cellulose) to yield estimates of $\Delta e$ (as estimated from cellulose).

Evidence suggests that $\varepsilon_{H}$ varies with temperature (Sternberg and Ellsworth 2012), which would predict $\Delta d_c$ or $\Delta d_{ce}$ to be somewhat less negative than that predicted by the model described above at temperatures of cellulose synthesis lower than about 17.3° C and slightly more negative above 17.3° C. For studies using paleo cellulose, temperatures are likely to be poorly constrained so it would be difficult to incorporate this effect. Preliminary analyses using known growing season temperatures also suggested that slopes of $\Delta d_c$ or $\Delta d_{ce}$ vs. RH as well as the amount of variation predicted between these variables within or across sites did not change appreciably after incorporating this effect. As such the $\Delta d_c$ or $\Delta d_{ce}$ data we report here do not incorporate temperature effects on $\varepsilon_{H}$.

**LITERATURE CITED**


