Chapter 10
Environmental, Physiological and Biochemical Processes Determining the Oxygen Isotope Ratio of Tree-Ring Cellulose

Xin Song, Andrew Lorrey, and Margaret M. Barbour

Abstract Analysis of the oxygen isotope ratio of tree-ring cellulose ($\delta^{18}O_{cell}$) is a promising tool for reconstructing past climatic variations and their influence on terrestrial ecosystems, but control mechanisms of $\delta^{18}O_{cell}$ are multi-faceted, involving a number of fractionation steps along the oxygen transfer pathway from precipitation water to the site of cellulose formation. The goal of the current chapter is to provide an overview of the current knowledge concerning fractionation mechanisms related to $\delta^{18}O_{cell}$. The review is organized by using the currently widely-used $\delta^{18}O_{cell}$ model as a reference context, and is focused on three main determinants of $\delta^{18}O_{cell}$: source water isotope ratio ($\delta^{18}O_{sw}$), leaf water isotope enrichment ($\Delta^{18}O_{lw}$), and biochemical fractionations downstream of $\Delta^{18}O_{lw}$. For each component, we summarize environmental, physiological, and/or biochemical processes underlying ^{18}O fractionations, and provide explanations of how these processes are critically relevant for linking $\delta^{18}O_{cell}$ to climatic factors in real-world scenarios. We identify knowledge gaps in mechanistic controls of $\delta^{18}O_{cell}$, and highlight opportunities for more research to improve upon the existing model.

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10.1 Introduction

Stable oxygen isotope composition of tree ring cellulose ($\delta^{18}O_{cell}$) has been demonstrated to reflect a suite of biotic and abiotic factors (i.e. air temperature, precipitation, relative humidity, leaf temperature, transpiration) during the period of tree growth. There is widespread interest in the employment of $\delta^{18}O_{cell}$ as a reconstructive proxy to these various factors, and such interest spans a range of research areas including paleoclimatic studies (Anchukaitis and Evans 2010; Saurer et al. 2012; Voelker et al. 2014; Zeng et al. 2017), plant ecophysiology (Helliker and Richter 2008; Brooks and Coulombe 2009; Ulrich et al. 2019), and environmental sciences (Savard 2010; Wagner and Wagner 2006; Guerrieri et al. 2011).

Central to many of the $\delta^{18}O_{cell}$-based applications is a solid understanding of the isotopic fractionation mechanisms underlying $\delta^{18}O_{cell}$. Over the last 30 years, plant scientists have made significant progress in characterizing physiology- and biochemistry-related fractionation processes and their influences on $\delta^{18}O_{cell}$. These efforts have led to an accumulation of knowledge about $\delta^{18}O_{cell}$-associated mechanisms, and consequently the development of a process-based model which can be mathematically expressed as the following (Roden et al. 2000; Barbour and Farquhar 2000):

$$\delta^{18}O_{cell} = \delta^{18}O_{sw} + (1 - p_{ex})\Delta^{18}O_{lw} + \varepsilon_o \tag{10.1}$$

where p_{ex} is the fraction of oxygen in the cellulose molecule that exchanges with water at the site of cellulose synthesis, and ε_o is the biochemical fractionation factor associated with the exchange of oxygen atoms between carbonyl group and the tissue water. $\Delta^{18}O_{lw}$ refers to isotope enrichment of bulk leaf water above source water and can be approximated as isotopic difference between leaf and source water or $\delta^{18}O_{lw} - \delta^{18}O_{sw}$.

In this chapter, we will review the current knowledge of the factors/processes affecting stable isotope compositions in tree ring cellulose, by using the tree-ring isotope model (Eq. 10.1) as a reference context. We will focus on the three main determinants of $\delta^{18}O_{cell}$ as represented by the mechanistic model: source water isotope ratio, leaf water isotopic enrichment, and biochemical fractionation at the site of sucrose production and cellulose synthesis. For each of the components we will present current understanding as well as highlight knowledge gaps that remain to be answered with future research. Further, recent evidence for the presence of biochemical fractionation during phloem loading and transport, a process not represented by the current model, will also be discussed.

10.2   Oxygen Isotope Ratio of Source Water ($\delta^{18}O_{sw}$)

10.2.1 $\delta^{18}O_{sw}$ and Climatic Signals

Source water is here defined as water in the soil available to be taken up by roots. Previous studies have produced convincing evidence that root uptake and subsequent xylem transport of the source water do not alter the original $\delta^{18}O$ signature (i.e., no occurrence of isotopic fractionation during these processes; Wershaw et al. 1966; Dawson and Ehleringer 1991; Dawson 1993). As such, it is now common practice for researchers to analyse stem xylem water when determining $\delta^{18}O_{sw}$.

In a general sense, the ultimate "source" of the source water originates from local precipitation. Hence, in situations where $\delta^{18}O_{xw}$ information is not available, use of $\delta^{18}O$ of precipitation ($\delta^{18}O_{ppt}$) as a proxy for $\delta^{18}O_{sw}$ is an alternative. The past several decades have seen great efforts to document natural variation in $\delta^{18}O_{ppt}$ in space and time (Bowen 2018). As a result, GIS-based, data-driven models (i.e., isoscape models) are now available enabling prediction of $\delta^{18}O_{ppt}$ at any given site on the Earth with high accuracy (Bowen and Revenaugh 2003). The availability of isoscape-type $\delta^{18}O_{ppt}$ data has provided a convenient and effective means for researchers to constrain $\delta^{18}O_{sw}$ with $\delta^{18}O_{ppt}$ under different field settings (Bowen 2010).

Regarding climatic effects on $\delta^{18}O_{ppt}$, the pioneering work of Dansgaard (1964) has demonstrated that $\delta^{18}O_{ppt}$ can be influenced by several abiotic factors including altitude, latitude, distance from coast and amount of precipitation. Both the altitude and latitude effects are derived from the decreasing temperature as latitude and altitude increase, where the temperature influences the condensation rate and the equilibrium fractionation between vapour and liquid (Gat 1996). The distance from coast, known as the continental effect, is caused by a Rayleigh distillation process by which preferential precipitation of the heavier water isotopes (^{18}O and ^{2}H) leaves subsequent precipitation depleted as a weather system moves over land. The fourth effect noted by Dansgaard (1964), is the amount effect that is also caused by a Rayleigh process, resulting in a negative correlation between the amount of precipitation and its isotope composition, as typically observed in tropical regions.

The isotope processes described in Dansgaard (1964) suggest that $\delta^{18}O_{ppt}$ variation in space and time is mainly a function of two climatic variables; temperature and precipitation amount. It has been shown that temperature effect is often markedly present in the mid- and high-latitudinal regions whereas precipitation amount is more likely a significant controlling factor for low-latitudinal $\delta^{18}O_{ppt}$ variation (Bowen and Revenaugh 2003). Accordingly, $\delta^{18}O$ of tree rings, with $\delta^{18}O_{ppt}$ as one of its critical determinants, has also been shown by numerous studies to provide proxy information about precipitation amount in tropical ecosystems (Anchukaitis and Evans 2010; Brienen et al. 2012) and air temperature in boreal and temperate ecosystems (Rebetez et al. 2003; Etien et al. 2008). Modelled and measured $\delta^{18}O_{ppt}$ has also been included in mechanistic models of $\delta^{18}O_{cell}$ that couple variable climate measurements with environmental and ecophysiological parameters, which show

strong relationships for the inter-annual tree responses to vapour pressure deficit and relative humidity (Lorrey et al. 2016). On interglacial to glacial timescales, tree ring $\delta^{18}O_{cell}$ measurements are rare (Poussart 2004), but some species like New Zealand kauri offer this potential (Lorrey et al. 2018). Differences between interglacial and glacial oceanic $\delta^{18}O_{seawater}$ as a result of continental ice sheet expansion and eustatic sea level lowering drives $\delta^{18}O_{ppt}$ toward more negative values during glacial phases. This suggests an ice volume correction for $\delta^{18}O_{cell}$ may be required when tree rings outside of interglacial epochs are analysed.

10.2.2 Isotopic Transfer from Precipitation to Source Water

Other than studies that investigated the relationships between $\delta^{18}O_{cell}$ and $\delta^{18}O_{ppt}$-contained climatic factors, there are also studies performed to examine how $\delta^{18}O_{cell}$ is related to $\delta^{18}O_{ppt}$ itself (Saurer et al. 1997a; Barbour et al. 2001; Song et al. 2011). These studies generally showed good correlations between $\delta^{18}O_{cell}$ and $\delta^{18}O_{ppt}$, substantiating the role of $\delta^{18}O_{ppt}$ in controlling $\delta^{18}O_{cell}$. Notably, several large spatial-scale studies have presented data to show that $\delta^{18}O_{cell}$ is strongly correlated with amount-weighted average of $\delta^{18}O_{ppt}$ throughout the year ($\delta^{18}O_{ppt\_annual}$). Such observations indicate that source water utilized by trees during the period of tree-ring growth (i.e., the growing season) may not derive solely from water precipitated over the growing season, but rather is more likely from a combination of both growing and non-growing season precipitation water. As an example, Fig. 10.1 presents the results from a re-analysis of a published, world-wide collection of tree wood cellulose sampled from a number of *Quercus* and *Pinus* tree species (Barbour et al. 2001). As can be seen from Fig. 10.1(a), at this large, geographic scale $\delta^{18}O_{cell}$ was strongly positively correlated with the variation in $\delta^{18}O_{ppt\_annual}$, with a correlation coefficient of 0.79 (P < 0.001). By comparison, the correlation coefficient for the relationship between $\delta^{18}O_{cell}$ and growing-season averaged $\delta^{18}O_{ppt}$ (or $\delta^{18}O_{ppt\_grs}$) is only 0.61 (Fig. 10.1b), lower than the $\delta^{18}O_{cell}$ -$\delta^{18}O_{ppt\_annual}$ relationship. Further evidence in support of the notion that trees utilize a combination of both growing- and non-growing-season rainwater can be obtained from Sternberg et al. (2007) in which tree xylem water was directly sampled and analysed for $\delta^{18}O$ across a continental scale in the United States. For this study $\delta^{18}O$ of xylem water was found to be related more strongly to $\delta^{18}O_{ppt\_annual}$ than to $\delta^{18}O_{ppt\_grs}$ (see Fig. 10.2), in agreement with the pattern seen at the cellulose level.

Stored meteoric water in soil and regolith that interacts with tree roots (Sprenger et al. 2016) has an isotopic composition related to multiple precipitation events, including rainfall from the growing season and pre-growing season dormancy intervals. This highlights the fact that trees utilise a heterogeneous precipitation resource from both the current and past seasons. Recently, capitalizing on a four-year collection of isotope compositions of precipitation, soil and tree xylem water, Brinkmann et al. (2018) conducted a rigorous, quantitative evaluation of the residence time of
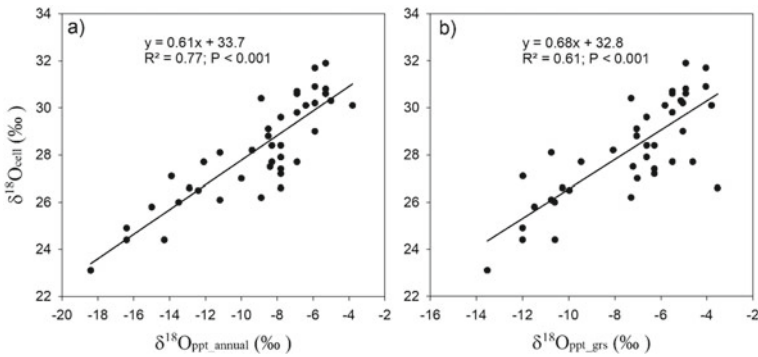
Fig. 10.1 The relationships between $\delta^{18}O$ of tree-ring cellulose ($\delta^{18}O_{cell}$) and annual-weighted ($\delta^{18}O_{ppt\_annual}$; **a**), and growing-season-weighted ($\delta^{18}O_{ppt\_grs}$; **b**) $\delta^{18}O$ of precipitation. The $\delta^{18}O_{ring}$ data presented in this figure were obtained from Barbour et al. (2001). Each of the $\delta^{18}O_{ring}$ data points represents integration of 3–10 year of tree-ring isotope signal in the late 1990s. $\delta^{18}O_{ppt\_annual}$ and $\delta^{18}O_{ppt\_grs}$ were calculated based on the site information (latitude, longitude and elevation) presented in Barbour et al. (2001), using the online precipitation isotope calculator at http://www.waterisotopes.org (Bowen and Revenaugh 2003). The criterion set out in Song et al. (2011) was used to define growing-season months for each sampling site. For more information about this world-wide collection of $\delta^{18}O_{ring}$ data refer to Barbour et al. (2001)

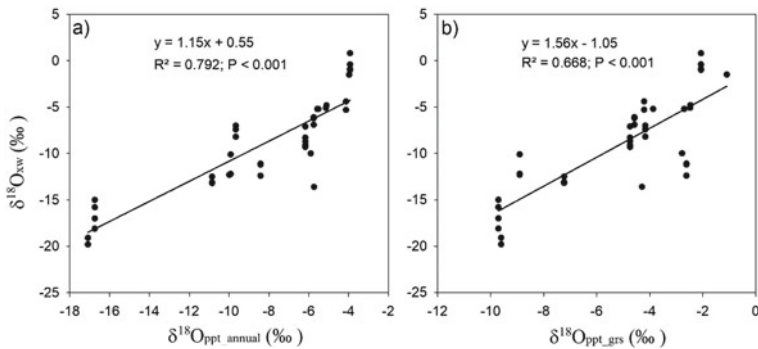**Fig. 10.2** The relationships between $\delta^{18}O$ of stem xylem water ($\delta^{18}O_{xw}$) and annual-weighted ($\delta^{18}O_{ppt\_annual}$; **a**), and growing-season-weighted ($\delta^{18}O_{ppt\_gs}$; **b**) $\delta^{18}O$ of precipitation across a wide range of sites in the United States. (**a**) is an adaptation from Fig. 1 of Sternberg et al. (2007). For (**b**), $\delta^{18}O_{ppt\_grs}$ values were calculated based on the site information presented in Sternberg et al. (2007), using the online precipitation isotope calculator at http://www.waterisotopes.org (Bowen and Revenaugh 2003). The criterion set out in Song et al. (2011) was used to define growing-season months for each sampling site

precipitation in the soil of a temperate forest. Their results showed that the residence time of soil water can be months or even years long, depending on the relative strengths of the precipitation input and the amount of water removal through evapotranspiration and infiltration. A significant finding of the Brinkmann et al. (2018)

is that contributions of growing season and non-growing season precipitation are of similar magnitude as far as the total water supply of temperate trees is concerned. This finding is consistent with the pattern seen at the spatial scale that demonstrates strong correlations of $\delta^{18}O_{cell}$ or $\delta^{18}O_{xw}$ with $\delta^{18}O_{ppt\_annual}$.

It is worth pointing out that the close linkage between precipitation water and source water notwithstanding, $\delta^{18}O_{ppt}$ inherently represents an approximation to $\delta^{18}O_{sw}$ regardless of the temporal scale over which it is integrated. In some cases, there is evidence that rapid uptake of meteoric rainfall (via increased soil moisture availability) corresponds to incremental growth of trees (Wunder et al. 2013), suggesting in some cases there may be low $\delta^{18}O_{ppt}$ residence time prior to incorporation in $\delta^{18}O_{cell}$. On the other hand, the transfer of the isotope signal from precipitation to the plant-available source water pool may not be a straightforward process, but instead, could be complicated by several factors. For example, after infiltrating into the soil, the precipitation signal can be damped or even masked after mixing with the existing soil water, and there is potential for precipitation and soil water to mix with short- and long-residence stem water, and/or precipitation may be further altered by extreme events such as tropical cyclones that often bring in large amount of water with distinctively low $\delta^{18}O$ values (Miller et al. 2006), or by evaporative enrichment of soil water or the influence of the ground water (Cernusak et al. 2016; Sprenger et al. 2016). In addition, $\delta^{18}O_{ppt}$ is known to be seasonally variable for many regions (Bowen 2018), which means the season of growth response that dominates incremental ring addition (and therefore $\delta^{18}O_{cell}$) may require consideration. Furthermore, according to the recently proposed "two-water worlds" theory, it is possible that in some circumstances the precipitation signal may not be present in $\delta^{18}O_{xw}$ at all, i.e., after soil pores are filled with tightly-bound water from early rainfall events, the subsequent, recurrent precipitation would only act as the so-called "mobile water" contributing mainly to the soil water flow, without interacting much with the plant-accessible pore water (Brooks et al. 2010). Nevertheless, the "two-water worlds" theory suggests that substantial energy will need to be overcome during root uptake of the tightly-bound water, and thus is incompatible with water movement along water potential gradients within the soil–plant–atmosphere continuum (Bowling et al. 2017). Because of these complications, we recommend caution in the use of $\delta^{18}O_{ppt}$ to parameterize $\delta^{18}O_{sw}$ in applications where very precise information about $\delta^{18}O_{sw}$ is needed.

10.3   Oxygen Isotope Enrichment of Leaf Water ($\Delta^{18}O_{lw}$)

10.3.1   The Craig-Gordon Model and Humidity Effect

During plant transpiration, the heavier $H_2^{18}O$ evaporates and diffuses more slowly through the stomata than does $H_2^{16}O$, leaving leaf water enriched in ^{18}O. Early studies of leaf water enrichment usually treated the leaf as a single, well-mixed and

isotopically uniform water pool such that $\Delta^{18}O_{lw}$ is the same as ^{18}O enrichment of water at the evaporative sites within the leaf ($\Delta^{18}O_e$). At steady state, $\Delta^{18}O_e$ can be well described by the Craig-Gordon model, as the following (Craig and Gordon 1965; Farquhar et al. 2007):

$$\Delta^{18}O_e = \varepsilon^+ + \varepsilon^k + \left(\Delta^{18}O_v - \varepsilon^k\right)\left(\frac{e_a}{e_i}\right) \qquad (10.2)$$

where ε^+ and ε^K are temperature dependent equilibrium fractionation factor for the water evaporation and the cumulative kinetic fractionation factor of water vapor diffusing out of the leaf respectively, $\Delta^{18}O_v$ denotes ^{18}O enrichment of atmospheric water vapour relative to the source water, and $\frac{e_a}{e_i}$ is the ratio of the water vapor mole fraction in the air relative to that in the intercellular air spaces within the leaf.

With regard to tree-ring isotope modelling, atmospheric water vapor is often assumed to be in isotopic equilibrium with the source water. This assumption has been examined in several studies that employed either isotope ratio infrared spectrometry for making high-frequency, in-situ measurement of $\delta^{18}O$ of water vapour ($\delta^{18}O_v$) throughout the year (Lee et al. 2006), or a novel, epiphyte-based proxy for estimating a $\delta^{18}O_v$ signal that integrates over the growing season (Helliker and Griffiths 2007; Helliker 2014). The results of these studies, albeit obtained through remarkably different types of methods, showed consistent evidence supporting the general validity of the equilibrium assumption. In the case of equilibrium, $\Delta^{18}O_v$ is equivalent to $-\varepsilon^+$. In such a case, Eq. 10.2 can be further simplified to:

$$\Delta^{18}O_{lw} = \left(\varepsilon^+ + \varepsilon^k\right)\left(1 - \frac{e_a}{e_i}\right) \qquad (10.3)$$

Note that ε^k is dependent on weighted diffusional fractionations through the stomata and leaf boundary layer, so a weak negative dependence of ε^K on stomatal conductance (g_s) is expected. Further, ε^+ may also be slightly (but in a positive manner) influenced by g_s, given that a lower g_s is generally associated with an elevation in leaf temperature. Nevertheless, in natural conditions both ε^+ and ε^K can vary only in a very limited range, and Eq. 10.3 essentially demonstrates that $\Delta^{18}O_{lw}$ is strongly related to $\frac{e_a}{e_i}$ in a negative manner. The $\frac{e_a}{e_i}$ term in Eq. 10.3 can be further approximated by the ambient relative humidity (RH) if tree canopies are generally assumed to be aerodynamically coupled to the ambient environment. Such an approximation in turn gives rise to the expectation that $\Delta^{18}O_e$ and by extension $\delta^{18}O_{cell}$ should contain a record of RH.

Assessment of the RH influence on $\Delta^{18}O_e$ has been included in numerous studies in a variety of plants (Farquhar et al. 2007). Some studies showed evidence of a RH signal in $\delta^{18}O_{cell}$ (Ramesh et al. 1986; Saurer et al. 1997b; Porter et al. 2009; Lorrey et al. 2016), whilst many others reported no significant relationship between $\delta^{18}O_{cell}$ and RH. The mixed results at the tree-ring level are not surprising given that $\delta^{18}O_{cell}$ is subject to the control of isotope signatures of two different water pools ($\delta^{18}O_{sw}$ and

$\Delta^{18}O_{lw}$; refer to Eq. 10.1). In view of the "dual control" nature, we can reasonably infer that the $\Delta^{18}O_e$-contained RH signal could be better revealed in circumstances where $\delta^{18}O_{sw}$ remains relatively constant and thus does not add a confounding factor, i.e., in deep-rooted trees that mainly utilize deep soil water or ground water; whereas when $\delta^{18}O_{sw}$ variation is considerable and becomes a dominant source of variation in $\delta^{18}O_{cell}$, the leaf-level signal may become dampened or even completely masked, resulting in a lack of significant correlation between $\delta^{18}O_{cell}$ and RH (see Tsuji et al. (2006) and Cintra et al. (2019) for examples illustrating this point).

It is worth pointing out that the above inference inherently assumes that RH as a climatic factor is only related to variation in $\Delta^{18}O_e$ but not with $\delta^{18}O_{sw}$. Clearly, this assumption is an over-simplification of the complex dynamics between isotopes and climates in nature, and thus may not be valid in some circumstances. For example, in regions where the "amount effect" dominates, a decrease in RH could act to increase $\delta^{18}O_{cell}$ not only because of its effect on enriching $\Delta^{18}O_{lw}$, but also because a lower RH (or drier atmosphere) is usually accompanied with a reduction in precipitation, which, in the event of the "amount effect" corresponds to higher $\delta^{18}O_{sw}$ values. In such a case, the amount-effect caused variation in $\delta^{18}O_{sw}$ (and the associated variation in RH) essentially acts to strengthen the $\delta^{18}O_{cell}$-RH link instead of confounding it; this is in contrast with the general case as pointed out in the preceding paragraph. This type of response has been observed for some tree species in monsoon-affected East Asia or tropical ecosystems (Xu et al. 2015; Zeng et al. 2015).

As far as detection of a leaf water signal in $\delta^{18}O_{cell}$ is concerned, plant physiologists have demonstrated the value of removing the influence of $\delta^{18}O_{sw}$ by expressing cellulose isotope signatures as enrichments above the source water (i.e., $\Delta^{18}O_{cell} = \delta^{18}O_{cell} - \delta^{18}O_{sw}$). Expressing Eq. 10.1 in the form of $\Delta^{18}O_{cell}$ notation yields the following:

$$\Delta^{18}O_{cell} = (1 - p_{ex})\Delta^{18}O_{lw} + \varepsilon_o \qquad (10.4)$$

From Eq. 10.4 it can be seen that $\delta^{18}O_{sw}$ is no longer a parameter influencing $\Delta^{18}O_{cell}$. Therefore we should expect that $\Delta^{18}O_{cell}$ is related to $\Delta^{18}O_{lw}$ or $\Delta^{18}O_{lw}$−contained RH signal in a more clear-cut manner, without relying on whether there is significant $\delta^{18}O_{sw}$ variation or not. However, counter to this theoretical expectation, in neither of the two studies that analysed large-scale collection of tree-ring datasets was $\Delta^{18}O_{cell}$ observed to exhibit strongly negative correlation with RH (Helliker and Richter 2008; Song et al. 2011; Fig. 10.3a, b). Such an inconsistency with what is predicted by theory (i.e. Equations 10.3 and 10.4) has prompted the suggestion that assumptions implicit in models where tree canopies are aerodynamically coupled to the ambient environment (such that e_a/e_i is equal to RH) are invalid (Helliker and Richter 2008). Subsequent calculations based on inverting of Eq. 10.4 led to the unexpected finding of boreal-to-subtropical convergence of photosynthesis-weighted tree leaf temperatures toward ca. 21 °C (Helliker and Richter 2008).

Of interest, a similar absence of a negative association between RH and $\Delta^{18}O$ of tree-stem cellulose was also observed in a more recent study performed across
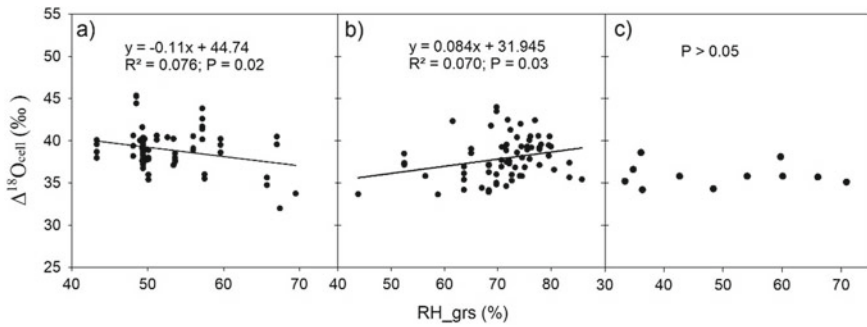
Fig. 10.3 The relationships between $\Delta^{18}O_{cell}$ and relative humidity (RH) across geographic scales. Data presented in (**a**) and (**b**) were obtained from Helliker and Richter (2008) and Song et al. (2011) respectively. (**c**) was Δ adapted from Fig. 3 of Cheeseman and Cernusak (2017). $^{18}O_{cell}$ values in (**a**) and (**b**) were derived from tree-ring cellulose samples while in (**c**) were from tree-branch cellulose samples. Data in (a) and (b) spanned a wide range of latitudes at the continental and global scale respectively; data in c) spanned an aridity gradient in the northeastern part of Australia. RH values shown in (**a**) and (**b**) represent growing-season averaged values and in (**c**) were averaged from site averages of 9 a.m. and 3 p.m. measurements and thus also likely represent the conditions during which the majority of photosynthesis occurs

11 sampling sites that spanned an aridity gradient in NE Australia (Cheeseman and Cernusak 2017; Fig. 10.3c). However, this observation cannot be fully explained by leaf-air temperature uncoupling, as along this same gradient a strongly negative correlation was observed between RH and leaf cellulose enrichment. In view of the different patterns between stem- and leaf-cellulose enrichment, Cheeseman and Cernusak (2017) proposed that the nil trend of stem cellulose enrichment along the RH gradient is a result of variation in the biochemical term "p_{ex}" (a topic that will be explored in more detail in the next section) and especially that p_{ex} is related to aridity. As of now, whether it is leaf temperature or p_{ex} that represents the true mechanism for the observed stem or tree-ring cellulose patterns remains to be further tested. Future studies explicitly designed to examine the relevant assumptions (as recently attempted by Helliker et al. (2018)) will hold the key to unravelling this uncertainty.

10.3.2 The Péclet Effect Model

The Craig-Gordon model has been shown to predict general trends in leaf water enrichment quite well. However, if examined more closely, measured bulk leaf water enrichment in many cases was found to be somewhat less enriched than that predicted by the Craig-Gordon equation (Walker et al. 1989; Flanagan et al. 1991). This has led to the realization that the Craig-Gordon equation may only predict the ^{18}O enrichment at the evaporative sites within the leaf water, but not the bulk leaf water. The latter instead can be highly heterogeneous, likely as a result of mixing processes within the leaf lamina involving both unenriched and enriched water. This process was

rigorously treated by Farquhar and Lloyd (1993), who introduced a Péclet effect into the leaf model to mathematically account for the ratio of advection of unenriched vein water via transpiration stream to back-diffusion of the enriched water from the evaporative site. With the incorporation of the Péclet effect, $\Delta^{18}O_{lw}$ model can be further modified into the following form:

$$\Delta^{18}O_{lw}- = \Delta^{18}O_e - \frac{1 - e^{-P}}{P} \tag{10.5}$$

where $\Delta^{18}O_e$, as aforementioned, refers to ^{18}O enrichment of evaporative site water and can be predicted by the Craig-Gordon model (Eq. 10.2) and $P = \frac{EL}{CD}$. E is leaf transpiration rate, L is the scaled effective pathlength (m) for water movement within the leaf lamina, C is the density of water ($55.56\ 10^3\ mol\ m^{-3}$) and D is the diffusivity of $H_2^{18}O$ in water (Cuntz et al. 2007). A detailed, theoretical analysis of Eq. 10.5 revealed that for plants experiencing similar atmospheric conditions (i.e., similar $\delta^{18}O_v$ and RH), there should be a negative correlation between $\Delta^{18}O_{lw}$ and stomatal conductance and/or transpiration rate (Barbour et al. 2000a). The demonstrated potential for $\Delta^{18}O_{lw}$ to record transpirative physiology in turn stimulated considerable interest among plant scientists to explore the use of plant oxygen isotopes as a phenotypic trait for various applications in crop breeding, forest management, and global change ecology (Barbour et al. 2000b; Brooks and Coulombe 2009; Cabrera-Bosquet et al. 2009; Battipaglia et al. 2013). For more details on this topic, the reader is referred to the "dual isotope" chapter (Chap. 16) of this book.

Although the Péclet effect is a theoretically sound concept, until now the available evidence in support of this concept remains limited. The standard procedure for experimentally testing the Péclet effect relies on examination of the relationship between transpiration rate (E) and the proportional difference between $\Delta^{18}O_{lw}$ and $\Delta^{18}O_e$ (f). A positive correlation between f and E is compatible with that predicted from the Péclet theory (Flanagan et al 1991; Barbour et al. 2000a), and consequently is used as a criterion by which to determine the validity of the Péclet concept. However, to date a significantly positive f–E relationship was only observed in some studies (Flanagan et al. 1994; Barbour et al. 2000a; Rippulone et al. 2008), but not in many others (Roden and Ehleringer 1999; Cernusak et al. 2003; Song et al. 2015; Roden et al. 2015).

The limited support for the Péclet theory may be viewed as an indication that the Péclet effect is insignificant in determining leaf water enrichment for many species. However, this indication is far from being conclusive, given that methodological issues common in the published experiments could have biased the results. For example, one methodological issue is related to the adoption by many early studies of a somewhat arbitrary procedure to determine isotopic steady state and $\delta^{18}O$ of leaf transpiration ($\delta^{18}O_E$) (Simonin et al. 2013); this could have led to uncertainty in estimating $\delta^{18}O_e$ and f, and by extension in assessing the f–E relationship (Loucos et al. 2015). Another methodological issue lies in that all currently available methods for measuring $\delta^{18}O_{lw}$ involve a step of destructive sampling of the leaf before isotopic

analysis. This dictates the need for collection of multiple leaves for generating a single f–E plot (i.e., each data point in the f–E plot corresponds to an individual leaf) (Cernusak and Kahmen 2013). Such a multi-leaf based approach is not ideal, because among-leaf variation in anatomical, morphological and physiological variables may be confounding factors that result in "noise" within the f–E plot (i.e., among-leaf variation *per se* results in much variation in f), potentially posing an obstacle to detecting the true Péclet signal.

Encouragingly, with the recent emergence of laser-based measurement instruments that permit online quantification of $\delta^{18}O_E$ at both steady and non-steady states, the above-mentioned first methodological issue can now be readily overcome (Song et al. 2015; Holloway-Phillips et al. 2016). Addressing the second issue will rest on development of new methods to allow for repeated determination of $\delta^{18}O_{lw}$ on a single leaf. In this context, we note that previous studies have attempted to indirectly estimate $\delta^{18}O_{lw}$ at different time points in a single castor bean leaf through repeated sampling and measurement of $\delta^{18}O$ of phloem sugar transported out of the leaf under different VPD conditions (Barbour et al. 2000a, Cernusak et al. 2003). The phloem-based "single-leaf" method is a novel attempt; nevertheless, this method has limitations in that: (1) it requires assumptions regarding the biochemical fractionation factor and/or time lags from isotopic transfer of leaf water to phloem organic matter, and (2) the method relies on a phloem-bleeding technique, yet this technique is only applicable to a few plant species. As such, future studies should focus on development of a method that would permit multiple direct measurements of isotopic signals from leaf water in a non-destructive manner, and also be generally applicable to different types of species.

Undoubtedly, continued mechanistic investigations will enlighten us as to whether the Péclet theory is a valid concept in different plant types. Nevertheless, it has been argued that the Péclet effect, even if present, is unlikely to exert a significant impact on $\delta^{18}O_{cell}$ when the effect is relatively small, because the transfer of the Péclet signal from leaf water down to tree-ring cellulose necessarily involves multiple steps that serve to further damp the original signal, to the point that the association of the Péclet effect to $\delta^{18}O_{cell}$ becomes weak or even negligible (Ogee et al. 2009). Furthermore, in many paleo-related contexts applying a single-value based correction (the so-called "damping factor") to the Craig-Gordon equation and the tree-ring model seems to serve the study purposes well (Saurer et al. 1997a; Saurer et al. 2016). In such cases there may be limited value of considering the more complicated Péclet correction. As such, we recommend that researchers carefully consider several factors including the strength of the Péclet signal and the scale and purpose of the planned investigation when it comes to deciding whether to include the Péclet correction for modelling $\delta^{18}O_{cell}$ in practice (Cernusak et al. 2016).

10.4 Biochemical Fractionation

10.4.1 Oxygen Isotope Exchange at the Sites of Sucrose Production and Cellulose Synthesis

Exchange of oxygen atoms between water and organic molecules can occur for oxygen in carbonyl groups via formation of short-lived gem-diol intermediates (Sternberg et al. 1986). Hydration of a carbonyl oxygen is closely coupled with subsequent dehydration and the oxygen atom retained in the organic molecule can be from either the original molecule or the reaction water (Sternberg 2009). Importantly, when this type of oxygen exchange reaction reaches equilibrium, the carbonyl oxygen will become ca. 27‰ more enriched in ^{18}O than the reaction water because of a biochemical fractionation effect (Sternberg and DeNiro 1983). This explains why ε_o (the biochemical fractionation factor) is treated as a constant of 27‰ in the tree-ring model (but see Sternberg and Ellsworth (2011) and Zech et al. (2014) for a slight temperature effect on ε_o).

According to the tree-ring model, carbonyl-water exchange of oxygen occurs during two distinct metabolic steps: the photosynthetic production of sucrose in the leaf and sucrose-cellulose conversion within the stem (Sternberg 2009). Of relevance to oxygen exchange at the leaf level, is the fact that all of the oxygen atoms in a sucrose molecule will pass through a carbonyl group at some point in the Calvin cycle leading to production of sucrose (Farquhar et al. 1998). For this reason, leaf sucrose is expected to be in equilibrium with the reaction water (i.e., leaf water). This expectation is well supported by published data proving that leaf soluble organic matter (a proxy for sucrose) is ca. 27% more enriched than leaf water in a diversity of plant species (Cernusak et al. 2003; Gessler et al. 2007, 2013; Barnard et al. 2007). The oxygen exchange at the site of cellulose synthesis is made possible by the requirement that sucrose be cleaved into carbonyl-containing hexoses (glucose and fructose) before it can be converted into cellulose. Further, it has been demonstrated that a proportion of hexose phosphate molecules also undergo futile cycling through triose phosphates before being incorporated to cellulose (Hill et al. 1995). This triose cycling process would expose more carbonyl oxygen to the local water (i.e., xylem water), allowing additional isotopic exchange.

As already mentioned, the proportion of oxygen exchange with xylem water during the sucrose-cellulose conversion is termed p_{ex} in the tree-ring model. Regarding p_{ex}, the conventional assumption is that it is a rather invariable parameter, with a value close to 0.4 regardless of species or environmental conditions. Support for this assumption comes from a number of experimental and observational studies performed on a range of species and growth conditions (Sternberg et al. 1986; Yakir and Deniro 1990; Roden et al. 2000; Cernusak et al. 2005), over which average p_{ex} is ca. 0.42 (summarized by Cernusak et al. 2005). Nevertheless, several more recent studies have suggested that p_{ex} may exhibit considerable variation in association with variation in aridity (Cheeseman and Cernusak 2017), salinity (Ellsworth and Sternberg 2014), or turnover time (τ) of the sucrose pool available for cellulose synthesis

(Song et al. 2014). A relationship between p_{ex} and τ was suggested by Farquhar et al. (1998) through consideration of biochemical pathways leading to cellulose synthesis. When τ is small such that the sucrose pool turns over rapidly, there should be less opportunity for hexose phosphates to cycle through triose, potentially resulting in a smaller p_{ex} compared to the case of a slow turnover pool of sucrose. Further, it is known that τ is a parameter that can be readily influenced by plant growth environments, and hence the observed aridity- or salinity-dependence of p_{ex} may well be an indirect reflection of τ influence on p_{ex}. However, despite these plausible explanations, Waterhouse et al. (2013) demonstrated that position-specific isotopic exchange rates in cellulose cannot be fully accounted for by the carbonyl-exchange theory, with or without consideration of cycling via trioses. That is, our current understanding of the biochemical fractionation is incomplete and more research is needed to explore potential variations in p_{ex} and the associated mechanisms.

10.4.2 Oxygen Isotope Exchange During Phloem Loading and Transport of Sucrose

Lying between the above mentioned two metabolic steps is the sucrose translocation pathway, where sucrose is loaded into the minor-vein phloem of the leaf and subsequently transported downwards in phloem towards the cellulose synthesis site. The current tree-ring model assumes no isotopic effect during sucrose translocation. However, this assumption may be problematic, as both phloem loading and transport involve highly dynamic and complex mechanisms (i.e., multiple pathways during loading and the leakage-retrieval dynamics persisting throughout transport) (van Bel 2003), which may give rise to metabolic conversion of sucrose into carbonyl-containing intermediates and consequently to isotopic oxygen exchange (Barnard et al. 2007; Offermann et al. 2011; Gessler et al. 2013, 2014).

Indeed, several studies have documented significant leaf-to-phloem or phloem-basipetal isotopic gradients in sucrose (Gavrichkova et al. 2011; Offermann et al. 2011; Gessler et al. 2013), hinting at the possibility of biochemical fractionation during phloem loading and transport. In a field investigation involving five different species, Gessler et al. (2013) found that twig phloem-transported sucrose was significantly less enriched than its leaf counterpart in three evergreen species, but not in the other two deciduous species. Gessler et al. (2013) presented a detailed discussion of the anatomical and physiological variations in the studied species, and suggested that these variations may at least be partially responsible for species-specific variation in the extent of phloem-loading/transport associated oxygen exchange, in turn causing the observed variation in the isotopic difference between phloem sucrose and leaf water among species. The dataset presented in Gessler et al. (2013) does not allow for quantitative assessment of the contribution of bark photosynthesis (a critical confounding factor) to the $\delta^{18}O$ signature in phloem so that no definitive conclusion can be drawn yet regarding whether and to what extent carbonyl-oxygen

exchange during phloem loading/transport may influence the phloem-leaf isotopic difference in different species. Nevertheless, the observed isotopic effect during phloem loading/transport highlights knowledge gaps that need to be filled in order to put our understanding of the $\delta^{18}O_{cell}$-associated mechanisms on a firmer ground. To this end, future experimental studies should be performed not only to advance understanding of the biochemical/physiological mechanisms underlying the phloem-related oxygen exchange process, but also to quantify the mean and variation of the *apparent* fractionation factor associated with this process among different species and/or environmental conditions. This understanding should then be incorporated into the existing tree-ring isotope model, to improve our ability to interpret climatic and physiological signals from $\delta^{18}O_{cell}$ under various contexts.

10.5 Conclusions

The oxygen isotope composition of tree rings records environmental conditions, such as temperature and relative humidity, and to a lesser extent physiological and biochemical responses such as stomatal regulation of water loss and the balance between sources and sinks for carbohydrates. However, there are a number of gaps in our understanding that need to be addressed, the three most pressing being: (1) the relevance of the Péclet effect in leaves from different species; (2) the role of variability in the proportion of exchangeable oxygen during cellulose synthesis; and (3) isotope effects during phloem loading, unloading and transport. We envision that use of high-resolution isotope sampling/measurements techniques (see Chap. 7 for more details), combined with detailed physiological and environmental monitoring across a range of species and geographies would be helpful in resolving some of these uncertainties.

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