### Chapter 19 Climate Signals in Stable Isotope Tree-Ring Records



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**Abstract** In this chapter we introduce the climate signal in stable isotope tree-ring records, with the emphasis on temperate forests. The development of the subdiscipline is recapped followed by an exploration of isotope dendroclimatic records by geography and, broadly, by isotopic species. Whilst there are still questions to be answered around signal strength and age-related effects in different environments and in different species, the proxy is now contributing to palaeoclimatology in a far greater way than in the days of the first hints of 'isotope tree thermometers'. We include two summary tables. Table 19.1 exemplifies the range of climate information available from stable carbon isotope time series and Table 19.2 explores oxygen isotope proxy signals. Due to the greater complexity seen in stable carbon isotope interpretations we explore response groupings with example references given

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for each category of proxy response. Finally, we summarize the state of the art in isotope dendroclimatology and discuss possible future directions.

#### 19.1 Introduction

Our understanding of the climate variability of the last two thousand years has been significantly aided by large, network tree-ring reconstructions, the dendroclimatic contribution to which is based almost exclusively on ring width and density data (e.g. PAGES 2k Consortium 2013, 2017; Neukom et al. 2019; Esper et al. 2014; Luterbacher et al. 2016). However, the increase in proxy data availability, for example of temperature reconstructions (Wilson et al. 2016; Mann et al. 1999; Helama et al. 2002; McCarroll et al. 2013; Linderholm et al. 2014; Dorado-Liñán et al. 2012, 2015; Klippel et al. 2019) has been accompanied by an understanding of the vital need for more information, at greater spatial resolutions, for more regions and including more variables than warm season temperatures (Smerdon and Pollack 2016; Gouirand et al. 2008; Frank et al. 2010). There is a particular need for additional tree-ring data from areas spatially underrepresented in climate proxy databases, in order to capture the regional signature of past climate variability (Smerdon and Pollack 2016). A key drive is an emerging picture of significant differences in the magnitude and dynamics of forced and internal climate variability which requires stronger regional detail through high-resolution regional reconstructions of multiple climate variables (e.g. Gagen et al. 2016; Smerdon and pollack 2016; Young et al. 2019).

Tree-ring width and density-based dendroclimatology has, in the last ten years, coalesced around four key efforts. To: (a) improve reconstructions of large scale changes to explore the hemispheric temperature signature of climate change, (b) to expand the geographic reach of regional temperature reconstructions to explore the dynamics of forced and internal variability, (c) to increase the breadth and depth of our understanding of the temporal variations in proxy records and the statistical fingerprints of different reconstruction methods and, (d) to expand the non-temperature (e.g. hydroclimate) potential of the tree-ring archive. Stable isotope measurements from tree rings, both annual and non-annual, contain valuable climatic, physiological and environmental information that can contribute to these research drives (McCarroll and Loader 2004). Here we review the research frontier in stable isotope dendroclimatology and explore the subject's contribution to palaeoclimate science.

# 19.1.1 The Development of Stable Isotope Measurements from Tree Rings

A cluster of studies carried out in the 1970s (Libby and Pandolfi 1974; Epstein and Yapp 1976; Libby et al. 1976; Yapp and Epstein 1977), began the process of exploring

what environmental information could be accessed by measuring isotopic variations in tree rings (see also Chap. 1). These early studies explored a range of isotope species and, whilst the methods were evolving, the earliest and most critical studies were of relevance to the exploration of both the water and carbon isotopes. Early tree-ring isotope time series were based largely on samples from a single tree, which required a huge time and monetary cost to produce and used a variety of measurement methodologies, analyzing pools of years together and often not extracting samples to cellulose before measurement. However, without the quantitative knowledge of how plant functions fractionate isotopes as they moved through the metabolic pathways of photosynthesis, and physically around the plant, and how sensitive these fractionations are to temperature changes, the tantalizing evidence for a new climate proxy was effectively stalled until the underlying fractionation theoretical frameworks were in place. When this happened in the 1980s and 1990s (e.g. Farquhar et al. 1982, 1989b; Francey and Farquhar 1982; Marshall and Monserud 1996) we were able to state unequivocally that stable isotope ratios measured from tree rings provided a usable environmental archive for the first time (see Chaps. 9, 10 and 13).

Early isotopic investigations on blocks of whole wood showed relatively little similarity in common isotopic signal (see Craig 1954; Farmer and Baxter 1974; Pearman et al. 1976; Libby and Pandolfi 1974). Whole wood contains varying amounts of resins and waxes, as well as lignin and cellulose (see Chap. 5). Without extracting and separating such components prior to analysis, it is difficult to obtain a common environmental signal not masked by noise from the isotopically heterogeneous resins, waxes and lignin. This problem was worked through by Epstein and Yapp (1977) and Wilson and Grinsted (1977). From this point onwards, it gradually became the working norm to extract tree-ring samples from wood to cellulose (or cellulose nitrate for  $\delta D$  in order to ensure that only non-exchangeable hydrogen is analyzed (Epstein and Krishnamurthy 1990) and Chap. 11), prior to the analysis of stable isotope ratios (Bradley 1985). Wilson and Grinsted (1977) established the methodology for cellulose extraction, based on the works of Green (1963), the so called 'Jayme-Wise' method. It is this method, or the alternative Brendel method (Brendel et al. 2000) that are generally used to extract whole wood tree-ring samples to cellulose still, often in fast batch processing systems to reduce lab time (Loader et al. 1997). Andreu-Hayles et al. (2019) summarizes the state of the art in isotope dendroclimatology preparation options (see also Chap. 5).

There is evidence that, with non-resinous species in particular, using whole wood can increase the efficiency of sample processing and still retain common signal coherence (Loader et al. 2003). The use of whole wood in isotopic tree-ring studies was encouraged by the revelation that there is a high degree of coherence between  $\delta^{13}$ C derived from cellulose and that from (resin-extracted) whole wood, with an offset between 1.5 and 3% (e.g. Loader et al. 2003) with variability between tree taxa. As the majority of climate reconstructions derived from stable isotope time series do not use absolute isotopic values, such an offset does not have consequences for reconstruction accuracy, and analyzing resin-extracted whole wood can heavily reduce lab time. A suite of studies has now developed climate reconstructions from

stable carbon isotope series based on whole wood measurements (e.g. Verheyden et al. 2005; Harlow et al. 2006).

Multiyear and multi-tree pooling methodologies have once again become popular, following increased knowledge about the between-tree levels of isotopic variability for commonly samples tree species (see Chaps. 4 and 6). These methods considerably increase time efficiency and reduce costs while providing comparable results to single tree studies, if certain conditions are met (Dorado-Liñán et al. 2011; Woodley et al. 2012).

For several decades after the palaeoclimatic potential of the stable isotope treering proxies was first explored following the establishment of the models describing isotopic fractionation in C3 plants (e.g. Burk and Stuiver 1981; Farquhar et al. 1982), the literature remained dominated by single site studies with results from a few tree cores, with relatively low sample replication (Ramesh et al. 1986; Buhay and Edwards 1995; Anderson et al. 1998; Gagen et al. 2004, 2006; McCarroll and Pawellek 1998, 2001). Such studies offered exciting evidence of a strong, new climate proxy (McCarroll and Loader 2004) but its exploitation was limited by the time and costs associated with mass spectrometric analysis. The 2000s were thus marked by methodology developments that could be explored with low sample numbers, rather than large replication climate reconstructions from stable isotope dendroclimatology. There were hints of relatively simple age-related trends in carbon isotope time series (Gagen et al. 2007, 2008) and, eventually, in oxygen (Duffy et al. 2017, 2019; Büntgen et al. 2020) as compared to ring width proxies. Aspects remain to be explored, however, because there are mixed results from different species and sites (Treydte et al. 2006; Esper et al. 2010; Brienen et al. 2017). Non-climatic trends in multi-tree stable carbon isotope time series also revealed information on changing plant carbon water relationships (Gagen et al. 2011a; Andreu-Hayles et al. 2011) useful to future climate projections where an accurate estimate of physiological forcing from the biosphere is needed. Methods for pre-reconstruction corrections for the effects of the changing stable isotopic composition of atmospheric CO<sub>2</sub> (McCarroll and Loader 2004) and for the bulk rise in atmospheric CO<sub>2</sub> amount (McCarroll et al. 2009) were developed (see Chaps. 17 and 25).

Advances in analysis increased the sample replication that could be achieved in a reasonably equipped stable isotope dendroclimatology lab, by an order of magnitude (see Chap. 7) (Loader et al. 1997, 2017; Brendel et al. 2000; Gagen et al. 2012). By the 2010s isotope dendroclimatic reconstructions often had sample replications equivalent to studies using ring width or density data (Gagen et al. 2011b; Young et al. 2012a, b, c; Loader et al. 2013). However, the time and cost of producing these climate reconstructions, using stable isotope mass spectrometry, was astronomical in comparison to equivalent growth proxy times series based on ring width measurements. Moreover, the general dependence on a laboratory process that involves physically cutting each ring to be analyzed has limited the exploitation of the stable isotope tree-ring proxies at a time when they have much to contribute.

Whilst the first tree-ring network analyses using stable isotope data from multiple sites are emerging (e.g. Szejner et al. 2016; Young et al. 2019), exploitation of the full potential of the proxy is still held back by the maximum speed of mass spectrometry,

as the primary measurement method. At present a high-end stable isotope dendroclimatology lab uses some version of the following standard methodologies (see McCarroll and Loader 2004) to prepare samples for, and measure, stable isotopes of carbon, oxygen and hydrogen.

- 1. Dating via standard methods generally (see Loader et al. 2019 for an exception).
- 2. Physically isolating each ring, or a portion of each ring (e.g. latewood), by cutting.
- 3. Performing a variety of chemical extractions on individual samples, ranging from simple resin removal to full extraction to alpha-cellulose.
- 4. Drain, freeze dry, weigh out and individually 'wrap' samples.
- 5. Perform mass spectrometric analysis.

There is a pressing need to increase the speed, and reduce the cost, at which we can produce stable isotope tree-ring time series in order to reach the sample replication necessary for statistically high-quality networks of climate reconstructions.

The analysis method noted above typically achieves measurement precisions around 0.15% for  $\delta^{13}C$  and 0.3% for  $\delta^{18}O$  (on–1 n = 10) (Loader et al. 2016). In terms of increasing sampling speeds, at the very best step 1 is carried out by an ablating laser (Loader et al. 2017) and step 2 skipped in the analysis of non-resinous tree species. However, a more typical analysis time, from start to finish, is in the region of one week per 100 samples. Whilst the laborious nature of measuring stable isotopes by mass spectrometry is a limiting factor, there are other limitations to the reliance on this technique. Mass spectrometry typically requires a sample of the ring equivalent to approximately 2–300  $\mu$ g dry weight of alpha cellulose (Rinne et al. 2005). This can require a whole wood cut of several cubic mm of wood from each ring.

Stable isotope measurements are routinely reported using the delta notation (‰). This notation gives the ratio of the heavier to the lighter stable isotope relative to an isotope standard, in parts per mille. V-*SMOW* (Vienna Standard Mean Oceanic Water) is used as a standard for stable hydrogen and stable oxygen isotope measurements in tree-rings ( $\delta^2$ H and  $\delta^{18}$ O) and V-*PDB* (Vienna Pee Dee Belemnite) as the standard for  $\delta^{13}$ C analyses (see Chap. 8 for a full discussion of the relevant isotopic notations and standards).

### 19.2 Dendroclimatic Information from Stable Carbon isotope Time Series

The use of  $\delta^{13}$ C as a tree-ring proxy is based on a mechanistic framework for the leaf-level fractionations of  $^{13}C/^{12}C$ , which allows us to understand the relationships between climate and variations in the stable carbon isotope ratio of photosynthate. In Table 19.1 we give an overview of the range of climate information, which can be derived from stable carbon isotope time series. In plants, discrimination against the heavier carbon isotope at the point that ambient  $CO_2$  enters the leaf, and again

**Table 19.1** Common climate signals in stable carbon isotope measurements from the rings of trees. Work on carbon isotope dendroclimatology is wider ranging than that on the water isotopes. A summary of the common signals and their associated environments is given in this table

	Site and isotope	Context	Common signals
Less moisture stress—carbon isotope signal dominated by photon flux control over photosynthetic assimilation rate	Stable carbon isotopes (generally of latewood in conifers)	Stable carbon isotopes at high latitude, moist sites, generally in Boreal forest conifers	A photosynthetic proxy, not a growth proxy, variability is sensitive to (in addition to warm season temperature) cloud related hydroclimate e.g. summer % cloud cover (e.g. see Young et al. 2019) Summer temperature (often where sunshine data unavailable), in Russian Altai (Sidorova et al. 2013), Canadian Boreal forests (Gennaretti et al. 2017), Canada (Bégin et al. 2015). growing season relative humidity (Edwards et al. 2008)
More moisture stressed—carbon isotope signal dominated by hydroclimatic control of	Stable carbon isotopes in tropical wood	Moist tropical environments	Moist tropics, relationship between stable carbon isotope variability and light availability remains (Brienen et al. 2016; van der sleen et al. 2014)
rate of stomatal conductance to CO <sub>2</sub>	Stable carbon isotopes in temperate regions, high elevation forest	Where moisture is available throughout the growing season	Summer sunshine and solar radiation (Hafner et al. 2014; Dorado-Liñan et al. 2016), summer temperatures in Europe (Lipp et al. 1991; Esper et al. 2015), Asia (Liu et al. 2014; Treydte et al. 2009) and South America (Lavergne et al. 2018)
	Stable carbon isotopes in lower latitude drier environments	High elevation 'Mediterranean' type forest or American latitudinal equivalents. Moisture stress restricts stomatal conductance to CO <sub>2</sub> in the summer	Cool season temperature (Heinrich et al. 2013) Summer precipitation and drought (Leavitt and Long 1989a, b, Bale et al. 2011; Kress et al. 2010). Also spring relative humidity in Asia (Liu et al. 2018). Extreme precipitation events in spring and summer in Iberia (Andreu-Hayles et al. 2017)

(continued)

Schrag 2004; Anchukaitis et al. 2008; Pons and Helle

2011

Site and isotope Context Common signals Seasonally dry Seasonal drought signal tropics (Gebrekirstos et al. 2009: Brienen et al. 2016) Use of dendrochemical and stable isotope methods to try and identify the annual ring boundary (with varying degrees of success), (Leavitt and Long 1991; Poussart and Schrag 2005; Ohashi et al. 2009; Evans and

Table 19.1 (continued)

upon assimilation by the plant, depends on the internal leaf concentration of  $CO_2$  (ci) and on atmospheric  $CO_2$  concentration (ca) expressed as the ratio ci/ca (Farquhar et al. 1982, 1989b). Chapter 9 gives a full discussion of these fractionation and discrimination processes. In trees growing in climates which are not water limited, ci is regulated primarily by photosynthetic rate, controlled by variations in temperature and sunlight. In climates that are water limited, ci is more often regulated by stomatal conductance to  $CO_2$ , controlled by antecedent precipitation and relative humidity (Gebrekirstos et al. 2009; Brienen et al. 2016). Thus, at sites where the fundamental laws of dendroclimatology apply (Fritts 1976) stable carbon isotope measurements in tree rings, have successfully been used to reconstruct summer sunshine (e.g. Young et al. 2019) temperature (e.g. Payomrat et al. 2018) as well as hydroclimate proxies (e.g. Liu et al. 2004; Roden and Ehleringer 2007).

Dendroclimatic reconstructions based on stable carbon isotopes still represent a small fraction compared to those based on more readily measured variables such as tree-ring width and maximum latewood density. Although they have a higher production cost, stable carbon isotope measurements from tree rings also offer a record of changes in plant carbon–water relationships via Intrinsic Water Use Efficiency (iWUE) as it responds to changes in atmospheric CO<sub>2</sub> (i.e., Leavitt and Long 1986, 1988; Granda et al. 2017). We can summarize the proxy potential of stable isotope dendroclimatology:

- Stable carbon isotope tree-ring time series record the interaction between photosynthetic rate and stomatal conductance. As such they are not a growth proxy, their variability is sensitive to parameters including warm season temperature and sunlight as well as hydroclimate e.g. summer cloud cover at moist, high latitude sites.
- Age related trends in stable carbon isotope tree-ring time series are less complicated than in growth proxy series, and their impacts on signal strength are easier to mitigate via simple mathematical standardizations and juvenile cut-off points.

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• The capture of additional information in stable carbon isotope series related to changes in plant carbon—water relationships through time (e.g. Intrinsic Water Use Efficiency, discussed below and in Chap. 17), which add to the range of paleoenvironmental information available from tree-ring records.

Carbon isotopes in tree rings have some advantages of interpretation, in comparison to growth proxies, because the fractionation mechanisms controlling carbon isotope variability are known (Farquhar et al. 1982, 1989), the signal-to-noise ratio between trees is high (McCarroll and Pawellek 1998), they can preserve high-to-low frequency common climate signals and the number of samples required to build a statistically robust chronology is often lower than for other tree-ring proxies (Leavitt and Long 1986; McCarroll and Loader 2004). The proxy is an integration of (1) the stable isotope composition of atmospheric carbon dioxide, (2) the relevant regulation rates within trees (photosynthetic and stomatal conductance rates), and (3) the environmental variables, which influence those rates, including temperature, sunlight, relative humidity and precipitation (McCarroll and Loader 2004). All climate reconstructions based on carbon isotope measurements from tree rings are built upon the theory of how carbon dioxide is fractionated at the entrance to the stomatal pores and in the C3 photosynthetic pathway (Farquhar et al. 1982, 1989b). A suite of environmental variables influences these fractionation set points by exerting control over two rates – stomatal conductance to CO<sub>2</sub> (generally noted as gs) and photosynthetic assimilation rate (generally noted as  $A_N$ ). Sites at which stomatal conductance to CO<sub>2</sub> dominates the stable carbon isotope signal are usually restricted to dry, or moisture stressed, forests. In non-moisture-limited settings carbon isotope discrimination is generally controlled by photosynthetic rate, driven by temperature and/or sunlight (Farquhar et al. 1989a; McCarroll and Loader 2004). Unlike ring-width and density tree-ring proxies, carbon isotope series contain simpler age-related trends and, at some sites, do not require detrending, allowing low-frequency variability to be fully preserved in the final reconstruction (McCarroll and Loader 2004; Gagen et al. 2007). Comparisons between paleoclimate reconstructions based on ring width and carbon isotopes in some cases reveal similar (Esper et al. 2015; Bale et al. 2011) or even larger (e.g., Lavergne et al. 2018) variability in the carbon isotope series and increased signal capture at variable frequencies. However, this is not the case for all species and all sites (Esper et al. 2010, 2015; Helama et al. 2015; Brienen et al. 2017).

At sites where significant age-related trends do exist in stable carbon isotopes, treering density series, or their digital equivalent (McCarroll et al. 2002; Campbell et al. 2011; Wilson et al. 2014) are more suited to the reconstruction of past temperature variations because of their lower analysis costs. However, stable carbon isotopes offer additional advantages due to their increased frequency capture and as they appear be less prone to the 'divergence problem' (i.e., the loss of climate sensitivity in growth proxies, during recent decades, Jacoby and D'Arrigo 1995; Savard and Daux 2020).

### 19.2.1 Dendroclimatic Information from Stable Carbon Isotope Time Series in Temperate Regions

In temperate regions and high latitude forests, where adequate moisture is usually available throughout the growing season, stable carbon isotopes from tree rings have been successfully used to reconstruct past changes in summer sunshine and solar radiation (Hafner et al. 2014; Dorado-Liñan et al. 2016) and summer temperatures, further south into Europe (Lipp et al. 1991; Esper et al. 2015), Asia (Liu et al. 2014; Treydte et al. 2009) and South America (Lavergne et al. 2018). Temperature reconstructions at high latitude sites have traditionally been assessed based on tree-ring width and maximum density (Wilson et al. 2016, St. George and Esper 2019 and references therein). Heinrich et al. (2013) expanded the focus of European carbon isotope-based reconstructions of temperature to Turkey with an 850-year reconstructions of cool season (winter-to-spring) temperature, consistent with the atmospheric circulation patterns governing the cool season climatology of the region.

At higher latitude, moist, sites, stable carbon isotopes have proven a strong and reliable proxy for cloudiness and parameters related to summer sunshine hours (e.g., Gagen et al. 2011b; Loader et al. 2013; Young et al. 2010). However, the extension of successful reconstructions of sunshine from stable carbon isotopes into drier regions, below the high latitudes, also reflects the strength of the relationship between the variable and sunshine. Reconstructions include sunshine hours in the Alps (Hafner et al. 2014) and surface solar radiation in mountainous area of Spain (Dorado-Liñán et al. 2016). The strength of the carbon isotope 'palaeocloud' proxy is unsurprising given that the action of rubisco is far more strongly controlled by photon flux (sunlight) than temperature (Farguhar et al. 1982). At more mesic sites related climatic variables share influence over the carbon isotope signal and temperature can be reconstructed via its co variation with summer sunshine, solar radiation or vapor pressure deficit (McCarroll and Loader 2004; Treydte et al. 2009; Dorado-Liñán et al. 2016). Care must be taken not to extend this assumption to areas where summer sunshine and temperatures do not co vary, particularly at lower frequencies (e.g. Young et al. 2019). Emerging reconstructions of past cloudiness and summer sunshine are of crucial importance in current climate research since it may allow for an integrated assessment of the cloud-climate feedback, an important cause of the large spread in climate sensitivity between climate models (Dessler 2010; Flato et al. 2013).

At sites where summer moisture stress restricts stomatal conductance to  $CO_2$ , or where moisture stress is involved in the covariation of multiple climate variables (precipitation, temperature, cloudiness etc.) carbon isotope variability can be used to reconstruct summer precipitation and drought, in the USA (Leavitt and Long 1989a, b; Bale et al. 2011), and in central Europe (Kress et al. 2010) as well as spring relative humidity in Asia (Liu et al. 2018). Andreu-Hayles et al. (2017) used carbon isotopes to explore and corroborate extreme precipitation events in spring and summer in the Iberian Peninsula. This study also explored non stationarity in carbon isotopes, in this case shifts through time in the dominant climatic limiting factor (from control of carbon variability by spring precipitation to summer precipitation). Beyond the

reconstruction of specific climate parameters, carbon isotope variability in trees has also been used to reconstruct global modes of atmospheric circulation such as ENSO (Bale et al. 2011; Liu et al. 2014; Lavergne et al. 2018).

The carbon isotope proxy, in the temperate latitudes where tree rings excel in climate reconstructions, has clear potential to develop the continental scale network reconstructions that now dominate efforts with growth proxy time series (D'Arrigo et al. 2006a; Schneider et al. 2015; Stoffel et al. 2015; Wilson et al. 2016). Leavitt and Long (1989b) represent one such attempt, to reconstruct regional July drought variability across the north American southwest using a stable carbon isotope tree-ring network. To date, however, the regional networks of carbon isotopes chronologies, spanning several centuries, that do exist across North America and Europe, have predominantly been used to track changes in plant physiological responses such as Intrinsic Water Use Efficiency (i.e., Saurer et al. 2014; Frank et al. 2015; Shestakova et al. 2019).

As the palaeoclimate potential of well-replicated carbon isotope series was fully explored for the first time in the high latitudes (e.g. McCarroll and Pawellek 1998, 2001) the discipline has tended to focus on the conifer species, which dominate the northern forest zones. Whilst there are many species used to explore stable carbon isotope proxies in temperate forest, there are some taxa that have contributed most significantly to palaeoclimate products. These are *Fagus*, *Picea*, *Quercus*, *Abies*, *Larix* and *Pinus* (e.g. Saurer et al. 1997; Skomarkova et al. 2006; McCarroll and Loader 2004; Gagen et al. 2007; Churakova et al. 2019; Esper et al. 2015; Ferrio and Voltas 2005; Hafner et al. 2014; Helama et al. 2015; Holzkämper et al. 2012; Kirdyanov et al. 2008).

Stable carbon isotopes in tree rings from temperate regions offer an incomparable source of information to reconstruct climate variables that are unlikely to be accessible using other proxy records, such as summer cloudiness and non-age detrended temperature reconstructions, as well as having the potential to enhance our picture of climate variability in the southern hemisphere. The dominance of conifers in our understanding of carbon isotope variability should be useful as the discipline starts to focus on the underrepresented southern hemisphere, where preliminary results in conifers have shown the potential of carbon isotopes (Gebrekirstos et al. 2009).

### 19.2.2 Dendroclimatic Information from Stable Carbon Isotope Time Series in Northern and Boreal Regions

The limitation of photosynthetic assimilation rate by temperature and/or sunlight is common across northern latitudinal and boreal forests (see also Chap. 20). In those regions, moisture limitation is not as common as in lower latitudes and carbon isotope variability in trees is found to be driven primarily by the limitation of photosynthetic rate by photon flux. The capacity of stable carbon isotopes in Fennoscandian conifer

tree rings to track historical changes in sunlight and, where it covaries with cloudiness, summer temperatures too, has been consistently demonstrated (e.g. Gagen et al. 2011a; Loader et al. 2013; Young et al. 2010, 2019). Those reconstructions have not only described past changes in sunlight, but also revealed changes in atmospheric circulation patterns (Young et al. 2012b, 2019; Loader et al. 2013) providing the first attempt to better understand the largest source of uncertainty in modelling future changes in climate: the cloud-climate feedback (Dessler 2010; Flato et al. 2013; Boucher et al. 2013). Whilst the relationship between summer cloud and temperate was revealed, across the Fennoscandian boreal zone, as negative at interannual time scales, analysis of millennial length temperature and summer cloud cover reconstructions revealed the relationship to be positive at decadal time scales (Young et al. 2012b, 2019). Thus, warmer periods in the past were associated with increases in cloud cover at decadal time-scales, linked to the position of the polar vortex and the variability of the Arctic Oscillation (Young et al. 2012b, 2019; Loader et al. 2013). At these sites, cloudiness is likely modulating local summertime temperature at interannual time scales, but at longer timescales, cloud cover may respond to large-scale multidecadal temperature changes (Dessler 2010). Thus, assessments of the relationship between cloud cover and temperature at both hemispherical and millennial time-scales are needed to provide a more complete picture, spatially and temporally, of the cloud-climate feedback. In this context, carbon isotope records derived from subfossil wood (e.g. Helama et al. 2018) offer a promising opportunity for extending the Fennoscandia summer cloud reconstructions back in time to tease apart the high latitude cloud-temperature feedback further. This endeavor becomes more pressing the more we learn about how significantly clouds are involved in moderating or enhancing greenhouse gas induced warming in the past (Zhu et al. 2019).

Stable carbon isotopes in combination with other tree-ring variables have also been used to estimate July–August mean temperature in the Russian Altai for the last 200 years (Sidorova et al. 2013) and Canadian Boreal forests for the last millennium (Gennaretti et al. 2017). Bégin et al. (2015) reconstructed 200 years of June–August maximum temperature in northeast Canada by combining stable carbon and oxygen time series. Edwards et al. (2008) reconstructed growing season relative humidity for the last thousand years based on carbon isotopes from living and subfossil conifer species in boreal western Canada. In the highest Arctic environments methods have also been pioneered to explore carbon isotope variability in the annual stem growth increments of Arctic Bell Heather *Cassiope tetragona* (Rayback and Henry 2006) and *Salix* species (Schifman et al. 2012), with correlations to growing season precipitation in these strongly climate limited shrub species.

In addition to complexity of decoding the prime driver of isotopic fractionation in different climatic settings, carbon isotope records also experience common tree-ring proxy pitfalls such as non-linearities (Schleser et al. 1999) and changes in climate sensitivity through time (Daux et al. 2011; Andreu-Hayles et al. 2017). Non-linear responses to climate, and shifts or loss, of climate sensitivity are well-known issues in tree-ring growth, particularly at low latitude and high-altitude sites (Esper and Frank 2009; St. George and Esper 2019). Isotopic fractionation is an active mechanism that involves active physiological adjustments by the tree to changing environmental

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conditions. Non-linear responses due to shifts in the acclimation strategy to new conditions have been described in old boreal trees (Giguère-Croteaua et al. 2019) as water use efficiency changes in response to rising  $CO_2$  (see Chap. 17).

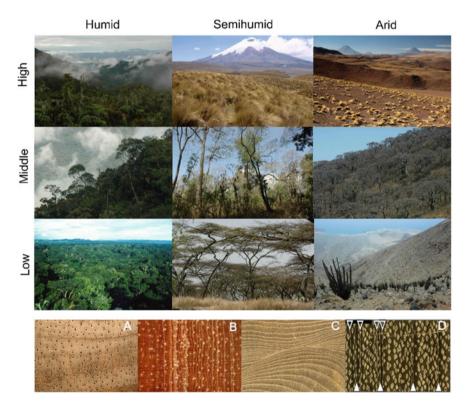
The regularity with which carbon isotope series from moist high latitude sites are interpreted as temperature proxies may be partly related to the scarcity of reliable instrumental records of sunlight and cloud cover. These parameters are sometimes not even considered as potential drivers of isotopic fractionation (e.g., Kirdyanov et al. 2008; Naulier et al. 2014). Where cloud data is available, the often-limited length of those records can prevent testing of the co variance of summer cloudiness with temperature on all time scales or the stability of the climate signal through time leading to assumptions about the linearity of the climate-carbon isotope relationship through time (e.g., Helama et al. 2018; Churakova et al. 2019). As a result, carbon isotopes have been interpreted as palaeotemperature records where temperature is in fact not the primary driver of carbon fractionation at the site (e.g. Gagen et al.2007). Where temperature and cloud cover co vary in the summer, which should be explored in the instrumental record wherever possible before regression-based reconstruction of either parameter from carbon isotope records is attempted (see Young et al. 2019 for an example), the reconstruction of one variable from the other is not necessarily problematic. Where cloud cover and temperature do not co vary in a region a divergence between the temperature reconstruction from carbon and independent temperature reconstructions will appear back in time (e.g. Gagen et al.2007). The identification of periods in which temperature and sunshine or cloud cover may have diverged might be the key to unequivocally identify the primary driver of carbon fractionation at such sites, or its non-stationarity through time. In this context, the atmospheric alteration caused by large volcanic eruptions may cause a large-scale cooling, which is detectable in temperature sensitive tree-ring records (D'Arrigo et al. 2013; Stoffel et al. 2015) but may not affect the photosynthetic capacity of the tree, which translates in non-significant changes in carbon isotopes (Gu et al. 2003; Battipaglia et al. 2007; Dorado-Liñán et al. 2016).

Tree-ring stable carbon isotopes in boreal forests offer perhaps the best opportunity to accurately constrain one of the main sources of uncertainty in the simulation of climate models: the cloud-climate feedback. By focusing on unequivocally identifying the main limiting factor of carbon fractionation and ensuring the stability of the climate signal, it should be possible to assess hemispheric relationships and feedbacks between cloud cover and temperature and vapor pressure deficit (VPD) providing critical information for the climate modelling community.

# 19.2.3 Dendroclimatic Information from Stable Carbon Isotope Time Series in the Tropics

Tropical forests hold about half of the planet's total terrestrial carbon biomass (Pan et al. 2011; Hunter et al. 2013). They home ecosystems spanning from humid to sub

humid to dry (Fig. 19.1). They are considered one of the major environments under threat from habitat loss and climate change (Holm et al. 2017) and the drive to find ways to develop tree-based climate proxies for the tropical forest regions of the world has a long history (Worbes 2002; Stahle 1999). Carbon isotope studies in tropical trees have much to contribute to tropical environmental science because of debates around the future behavior of the tropical forest carbon sink (Körner 2009; Lloyd and Farquhar 2008), and because proxy climate records for the tropics are still profoundly limited (see also Chap. 22). The scarcity of long instrumental climate records for the tropics, and the importance of the tropics in global climate dynamics (Chiang 2009), drives the motivation to expand the field of tropical isotope dendroclimatology. Settling questions around carbon dynamics in tropical trees requires a more detailed understanding of tropical plant carbon water dynamics (e.g. Loader et al. 2011) as well as detailed analyses of physiological and environmental drivers of tropical wood formation at daily, seasonal and multi-annual timescales (Steppe et al. 2015, Chap. 22). Whilst studies on tropical wood remain scarce, compared to temperate



**Fig. 19.1** Ecosystems included in the tropical area and pictures of wood with **A**) poorly visible rings, **B**) suppressed rings, **C**) wedging rings: **D**) false (empty triangle) and real rings. Examples are given for lowland, mid (forested) and upper (tree line) elevations. Modified from Brienen and Gebrekirstos (adapted from TRACE 2019, San Leucio Caserta)

and high-latitude regions, there is a common agreement about the need to integrate methodologies to explore tropical isotope dendroclimatology (Sass-Klaassen et al. 2016; Van der Sleen et al. 2017).

Tropical dendrochronology is a relatively new discipline in and of itself, because of the difficulties of cross dating tropical wood, caused by the lack of simple warmcool seasonality in the tropics. Cross dating tree rings visually is, at best, challenging and in 'ever wet' areas of the humid tropics impossible due to the lack of the climate seasonality needed to form an annual growth cycle in trees. Early studies focused on seasonally dry regions where the climate was capable of forcing a ring boundary. Coster (1927) and Berlage (1931) described annual growth rings in teak trees from tropical Indonesia, because the dry season provoked the cambial dormancy necessary for annual ring formation. This has been found to be the case across the seasonally dry tropics, including Australia (e.g. Buckley et al. 2010; D'Arrigo et al. 2006b; Heinrich et al. 2008; Pumijumnong and Eckstein 2011), tropical Africa (e.g. Therrell et al. 2006; Trouet et al. 2010) and the American tropics (e.g. Biondi 2001; Worbes 1999). Elsewhere ring boundaries have also been found to be caused by cambial activity cessation in flood periods within seasonally flooded Amazonian forests (e.g. Schöngart et al. 2002, 2004) or during salinity fluctuations in mangrove forests (e.g. Robert et al. 2011; Verheyden et al. 2004b). Whilst a number of tropical trees do grow annual rings, which can be cross dated (see Worbes 2002), there are many other problems facing the tropical dendrochronologists once they have found a species that at least grows annual rings. Indistinct ring boundaries are common, and many of the above studies mention low correlations with climate when calibration is attempted (generally with the short instrumental climate data typical for much of the global south). Tropical isotope dendroclimatology (Evans and Schrag 2004) emerged as a drive to resolve seasonality in tropical trees that lack visible tree-ring-boundaries by using seasonal stable isotope variability (e.g. Poussart and Schrag 2005).

An early endeavor was to utilize stable isotope variability to define the ring boundary in tropical trees (Leavitt and Long 1991). In Thailand Poussart and Schrag (2005) and later Ohashi et al. (2009) applied a version of this method seeking to use seasonal peaks and troughs in dendrochemical variables to identify non-visible tree ring boundaries isotopically. However, Poussart and Schrag (2005) seminal study achieving dendro isotope dating in the tropics has not been widely replicated. Tropical oxygen isotope dendroclimatology, or the combination of both isotopes (carbon and oxygen), has also been used to facilitate boundary identification in Costa Rica (Evans and Schrag 2004; Anchukaitis et al. 2008), Kenya (Verheyden et al. 2004a), Central Guyana (Pons and Helle 2011) and Brazil (Ohashi et al. 2015). These methods take advantage of the fact that in tropical areas where temperature and photoperiod are more or less constant through the year (Fromm 2013) a driver for periodic wood formation can be identified through changes in precipitation seasonality (Worbes and Junk 1999) or seasonal shifts in isotopic source water signal (Anchukaitis et al. 2008).

Several studies also reveal strong correlations between stable carbon isotopes and climate in seasonal tropical trees. In tropical regions with a pronounced dry season, the limitation of stomatal conductance by moisture stress gives rise to robust climate

variability in tree-rings that is effectively a seasonal drought signal (Gebrekirstos et al. 2009; Brienen et al. 2016), providing the growth rings can be dated by traditional means. The signal is generally thought to be linked to water availability and precipitation amount provoking stomatal limitation of the internal partial pressure of carbon dioxide (Leavitt and Long 1991; Schubert and Timmermann 2015; Li et al. 2011). However, in moist environments the relationship between stable carbon isotope variability and parameters related to sunlight availability seems to hold true in the tropics as it does elsewhere (Brienen et al. 2016; van der Sleen et al. 2014).

In a recent review by van der Sleen et al. (2017) the theory, methods and results of tropical isotope dendroclimatology are reviewed and summarized (see also Chap. 22). Their review of 50 studies revealed a dominance of controls over stable carbon isotope variability by water availability, light and nutrient supply in tropical studies. Whilst oxygen isotope variability was dominated by source water signals with the potential for additional variables influencing fractionation, such as rooting depth and evaporative enrichment at the leaf (van der Sleen et al. 2017). The review also mentions the emerging importance of nitrogen isotope investigations, which can be used to explore the nitrogen cycle in complex tropical ecosystems.

### 19.2.4 Carbon Isotope Climate Sensitivity in Response to Increasing CO<sub>2</sub>

Intrinsic Water Use Efficiency (iWUE) is a useful variable for studying spatial and temporal changes in plant carbon–water relations and provides information on climate–vegetation feedbacks at broad geographical scales (Dekker et al. 2016; Lavergne et al. 2019). In the context of stable isotope tree-ring science, iWUE can be derived from  $\delta^{13}C$ . A detailed description and explanation of iWUE is given in Chap. 17.

Assessing changes in iWUE inferred from the stable carbon isotopes across treering networks reports an average global increase in tree iWUE of 0.1–0.3% per year over the last century (Peñuelas et al. 2011; Battipaglia et al. 2013; Saurer et al. 2014; Frank et al. 2015). Increases in iWUE are detected regardless of biome (Andreu-Hayles et al. 2011; Silva and Anand 2013), tree species (Martínez-Sancho et al. 2018; Lévesque et al. 2014) or tree status (Hereş et al. 2014; Voltas et al. 2013). Rises in iWUE seem generally to be more rapid during the second half of the twentieth century (up to >0.5% per year) (see Gagen et al. 2011b) at some sites. However, the rate of change is strongly site and species specific (e.g. Saurer et al. 2004). iWUE time series have been observed where increases are halted by active stomatal control in response to rising atmospheric CO<sub>2</sub> (Waterhouse et al. 2004; Gagen et al. 2011b; Bert et al. 1997; Saurer et al. 2004) and time series where 'spikes' of very large changes in iWUE occur against a background of a broadly passive response to rising CO<sub>2</sub> (Belmecheri et al. 2014). Increases in iWUE are still observed when solely accounting for the effect of increasing atmospheric CO<sub>2</sub> concentrations after

removing the climatic signal from stable carbon isotope series (Frank et al. 2015). This suggests that trees may have adapted allowing the CO<sub>2</sub> partial pressure within the stomatal cavities to rise in balance with atmospheric CO<sub>2</sub> concentration.

The species' and geographical variability in iWUE increases is unsurprising for two reasons, first, because of the range of carbon water economics that have evolved in trees, such that for some species it is beneficial to increase iWUE and for others less so (Lin et al. 2015). Second,  $CO_2$ -induced increases in iWUE can be a response to more than one change within the tree (Franks et al. 2013). Elevated  $CO_2$  does stimulate photosynthesis (Lloyd and Farquhar 2008), reduce stomatal conductance to a minor degree (Ehleringer et al. 1993; Farqhar et al. 1989) and allow trees to absorb the same amount of carbon with less water loss. However, FACE (Free Air  $CO_2$  Enrichment) experiments have found little stomatal response to increasing  $CO_2$  in mature trees (see Chap. 21 and 24). Reductions in stomatal conductance can also, however, be linked to increases in the costs of respiration (Clark et al. 2013; Wright et al. 2009), heat stress (Corlett 2011) and drought stress due to increasing transpiration as our climate dries out (Wright et al. 2009). Climatic drying is considered to be causal at several sites where an increase in iWUE does not translate in enhanced tree growth (Peñuelas et al. 2011).

Spatial variability in iWUE also assists with interpreting temporal changes in  $\delta^{13}$ C derived iWUE time series. Large changes in iWUE are found across regional aridity gradients, in particular in isohydric species (gymnosperms), which respond to water stress by strongly regulating transpiration to maintain near constant leaf water potentials when soil moisture drops (Brodribb et al. 2014). In such species, at arid sites, negative correlations are found between iWUE and metrics of water availability such as annual precipitation (*Pinus halepensis*, Ferrio and Voltas 2005), groundwater access (*Pinus sylvestris*, Song et al. 2016), or rooting depth (*Pinus sylvestris*, Santini et al. 2018). Differences in iWUE (from pooled analyses) may exceed 30% between aridity extremes (Santini et al. 2018). Strong latitudinal gradients, linked to hydroclimatic conditions, have been reported for iWUE across Europe, with increasing values southwards (Saurer et al. 2014). However, factors such as nutrient supply and interactions with climate influence the regional variability in iWUE, which may confound water availability effects across spatial scales (Silva et al. 2015).

A better understanding of how plant carbon water relationships change across environmental gradients is needed to improve predictions of how water and carbon balance within forest ecosystems are changing with climate (Saurer et al. 2014; Frank et al. 2015). The extent to which variation in iWUE translates into carbon—water changes at the ecosystem scale remains unclear. The complexities of changes in leaf area index and canopy structure under climate change, along with atmospheric boundary-layer feedbacks, challenge upscaling leaf-level information from tree rings to the whole ecosystem scale (Medlyn et al. 2017; Lavergne et al. 2019).

Outside the temperate regions, Rahman et al. (2019) summarize evidence for trends in tree growth and iWUE triggered by elevated  $CO_2$  against the background of climate change. The authors report that almost all studies show a consistent decrease of carbon discrimination over time, resulting in an increase in iWUE. Van der Sleen et al. (2014) estimate an increase of iWUE of 30–35% across the tropics in response

to elevated CO<sub>2</sub> but expect no similar increase in radial growth due to the impact of other factors in the nutrient-limited tropics. In a study of iWUE changes in non-annual ring forming trees in Borneo, Loader et al. (2011) found postindustrial increase in iWUE of similar magnitude as described by Van der Sleen et al. (2014). Rahman et al. (2019), reviewing iWUE histories in 81 species at 115 tropical sites, found increases in iWUE but no stimulated radial growth, as the negative effects of climate change overrode the fertilization potential of rising CO<sub>2</sub>.

Disentangling the iWUE/fertilization response in the tropics will take multi proxy ecophysiological studies of tropical wood formation, combining stable isotope, radiocarbon, wood anatomy and X-ray densitometry (De Mil et al. 2017). The climatic responses in these multiple proxies could then be combined to provide more robust long-term estimates of the response of tropical trees to past climate and improve model simulations of the impact of future climate change on tropical trees (De Micco et al. 2019).

### 19.3 Dendroclimatic Information from Stable Oxygen Isotope Time Series

## 19.3.1 Early Literature and Progress in Interpretations of $\delta^{I8}O$ Values in Tree-Rings

In the mid-1970s, trees were postulated to contain an 'isotopic thermometer' in the δ<sup>18</sup>O of tree-ring wood or extracted cellulose (Libby 1972; Libby and Pandolfi 1974). These early investigations were conducted on oak, cedar or spruce from temperate areas (Libby 1972; Libby and Pandolfi 1974; Libby et al. 1976; Gray and Thompson 1977). Following technical improvements in mass spectrometry, stable oxygen isotope tree-ring chronologies from sub-tropical to sub-arctic sites also began to be explored, revealing correlations with hydroclimate variables (including air humidity) and the isotopic signature of source water, whilst progress was also made in the mechanistic modeling of isotopes in soil and plant cellulose (Burk and Stuiver 1981; Edwards and Fritz 1986; Ramesh et al. 1986). In 2006 Treydte et al. published the first millennial length, annually resolved, well replicated stable oxygen isotope chronology, with results from seven Juniperus turcestanica from Northern Pakistan. This study also led the way in applying the standard statistical practices of traditional dendroclimatology - calibration/verification techniques—to a long, well replicated oxygen isotope tree-ring time series (Masson-Delmotte et al. 2005; Treydte et al. 2006).

Table 19.2 summarizes the range of climatic and environmental information, which can be derived from stable oxygen isotopes in tree rings. The climate signal in tree-ring stable oxygen isotopes arises from the influence of (a) meteorological processes before the water is incorporated into the tree (Chap. 18) and (b) the interaction between the atmosphere and the leaf (Chap. 10, see also Sects. 14.4.1 and 16.3).

**Table 19.2** Examples of oxygen isotope dendroclimatology studies across the boreal zone and high latitude areas of the northern hemisphere, the mid latitude temperate forest zone in northern and southern hemisphere and tropical forests. The examples are not exhaustive but provide an overview of available records and climate signals recorded in tree-ring oxygen stable isotopes in different biomes

Biome	Climate signal	Examples
Arctic tundra (high latitude)	Summer temperatures and North Atlantic Oscillation	Betula pubescens January-August (1950-1999, Xu et al.2021)
	(NAO)	Cassiope tetragona (Welker et al.2005)
Boreal forests (high latitude)	Summer season temperatures	Picea mariana warm season (1936–2004, Holzkämper et al. 2012) and summer (1000–2000, Naulier et al. 2015; 997–2006, Gennaretti et al. 2017); combined with $δ^{13}$ C (1800–2003, Bégin et al. 2015)
		Picea glauca (1780–2003, Porter et al. 2013)
		Pinus sylvestris (1736–2006, Seftigen et al. 2011)
	Spring and summer precipitation	Pinus sylvestris July (1600–2002, and summer (1736–2006, Seftigen et al. 2011); Picea mariana May (1936–2004, Holzkämper et al. 2012)
Temperate forests (mid latitude) Northern Hemisphere	Summer temperatures	Pinus sibirica 1901–2000, Loader et al. 2010), Quercus sp (1596–2000, Etien et al. 2008a); Larix decidua (1980–2010, Leonelli et al. 2017); with low cloud fog Sequoia sempervirens (1952–2003, Johnstone et al. 2013)
	Precipitation (different seasons)	Summer: Larix sibirica (2 centuries, Sidorova et al. 2013); Quercus sp. (1600–2000, Labuhn et al. 2014); Quercus robur (1613–2003, Rinne et al. 2013); Pinus ponderosa (1967–2002, Roden and Ehleringer 2007), Abies alba (1840–1997, Saurer et al. 2000)
		Spring/Summer: <i>Pinus sylvestris</i> (1600–2002, Andreu-Hayles et al. 2017)

(continued)

Table 19.2 (continued)

Biome	Climate signal	Examples
		October–September: <i>Pinus</i> sylvestris (1950–2009, Giuggiola et al. 2016)
		Winter: <i>Quercus robur</i> (Robertson et al. 2001)
	Summer season precipitation and temperature	Picea abies (1913–1995, Anderson et al.1998); Pinus sylvestris and Quercus petraea (1660–2002, Reynolds-Henne et al.2007); various? (1800–2000, Saurer et al. 2008); Quercus sp (1850–2012, Young et al. 2015)
	Summer drought, summer temperature, relative humidity (RH) and/or vapor pressure deficit (VPD)	Pinus sylvestris (1935–2005, Esper et al. 2018); Quercus petraea, Fagus sylvatica and Pinus sylvestris (1960–2007, Daux et al 2018); Quercus petraea (1900–2000, Etien et al. 2008a); Picea abies, Fagus sylvatica and Larix decidua (1970–2010, Hartl-Meier et al. 2015); Quercus sp (1600–2000, Labuhn et al. 2016); Quercus sp (1600–2000, Labuhn et al. 2016); Quercus sp (1600–2000, Masson-Delmotte et al. 2005); Quercus sp (1885–1996, Raffalli-Delerce et al. 2004); Quercus robur (1895–1994, Robertson et al. 2001); Quercus sp., Pinus sylvestris and Cedrus deodora (1900–2004, Treydte et al. 2007)
	Various warm season climate variables	Liriodendron tulipifera and Quercus rubra (1950–2014/2015 and 1980–2015, Levesque et al. 2019); Quercus sp (1200–2000, Loader et al. 2019)
Temperate forests (mid latitude) Southern Hemisphere	Summer temperature	Austrocedrus chilensis Sep-Marc (1890–1998, Roig et al. 2006)
		Nothofagus pumilio Dec–May (1952–2011, Lavergne et al. 2016)

(continued)

Table 19.2 (continued)

Biome	Climate signal	Examples
		Nothofagus pumilio Oct–Jan (1809–2013, Grießinger et al. 2018)
	Summer precipitation	Nothofagus pumilio Oct–Jan (1809–2013, Grießinger et al. 2018)
	Supper relative Humidity	Nothofagus betuloides Oct-Feb (1861–2015, Meier et al. 2020)
		Agathis australis May–Dec (1985–2002, Lorrey et al. 2016)
	Summer Vapour pressure (VP)	Agathis australis Oct–Dec (1985–2002, Lorrey et al. 2016)
Tropical forests (low latitude)	Precipitation, temperature, relative humidity or/and ENSO	Metrosideros polymorpha (Kahmen et al. 2011), Cedrela odorata (Brienen and Helle 2012), various (Zuidema et al. 2012, 2013), Polylepis tarapacana (Rodríguez-Catón et al. 2021), Hyeronima alcorneides (Evans et al. 2006), Pouteria sp. (Anchukaitis and Evans 2010), Cedrela montana (Volland et al. 2016)

At the meteorological scale, origin of the water vapor, temperature, evaporation and condensation processes are the dominant controlling factors. During condensation of water vapor the ambient air temperature determines the  $^{18}\text{O}/^{16}\text{O}$  ratio in meteoric water (Dansgaard 1964), resulting in a seasonal variation of the  $\delta^{18}\text{O}$  in precipitation water (Rozanski et al. 1993). During rain events some water evaporates at the plant and soil surfaces, leaving the remaining water enriched in  $H_2$  and  $^{18}\text{O}$  relative to the precipitation water. Water, infiltrating into the soil mixes with the residual soil water (Chap. 18). This mixing between infiltrated rain and residual soil water of different temporal origins (Allen et al. 2019) is reflected in tree rings mainly in temperate regions (Szejner et al. 2016), whereas in the tropics the  $\delta^{18}\text{O}$  values of tree rings corresponds to the wet season variables (Brienen and Helle 2012). During plant water uptake no measurable fractionation occurs. Differences in  $\delta^{18}\text{O}$  between xylem (source) water and soil water are due to a mixture of water absorbed from different soil depths with varying  $\delta^{18}\text{O}$  values (Sprenger et al., 2016). In Chap. 18 this topic is discussed in depth.

A detailed discussion about the variation in  $\delta^{18}O$  at leaf level is given in Chap. 10. Here, we present a summarizing overview. The  $^{18}O$  fractionation in the leaf is tightly linked to transpiration (E) and stomatal conductance (gs), both mainly controlled by air humidity with its  $\delta^{18}O$  value and leaf temperature. During transpiration the O isotope fractionation occurs as a result of the phase transition from liquid water to

the gaseous phase. As the lighter  $H_2^{16}O$  molecules evaporate more readily than the heavier ones the remaining leaf water pool becomes enriched in  $H_2^{18}O$  relative to the source water (Dongmann et al. 1974; Craig and Gordon 1965). The  $^{18}O$  enrichment is increased, with decreasing air humidity. To maintain the leaf water balance the transpired water is replenished with unenriched source water, leading to a reduction in the leaf water  $^{18}O$  enrichment, which is inverse proportional to the transpiration rate and gs. This inverse proportional relationship between E and gs is described as the Peclet effect (Farquhar and Lloyd 1993; Barbour 2007).

During photosynthetic assimilate production the  $\delta^{18}O$  signal of the leaf water is transferred to the assimilates. During the assimilate transport in the phloem, the  $\delta^{18}O$  of the assimilates is modified by a proportional oxygen exchange with the xylem water and at the sites of organic matter synthesis (Barbour 2007; Sternberg 2009; Gessler et al. (2014).

### 19.3.2 Dendroclimatic Information from Stable Oxygen Isotope Time Series in Temperate Regions

Traditional tree-ring parameters, such as tree-ring width or maximum latewood density have proved most useful where species ranges are strongly limited by a single climatic variable, such as summer rainfall or temperature, and it is these locations which dominate growth proxy climate reconstruction networks. In the past, stable-isotope studies have followed the same sampling strategy, starting at latitudinal or altitudinal limits to maximize the changes of accessing a strong common climate signal (Breshears et al. 2009; Loader et al. 2013). There is, however, increasing evidence, that stable oxygen isotope ratios in tree rings from temperate regions, where trees grow in favorable and moist climates, also carry strong climatic signals (Loader et al. 2019).

The strong source water signal in moist parts of the globe has steered the development of oxygen isotope dendroclimatology. Young et al. (2015) discuss such an example in UK oak that went on to reveal such strong climate signals in stable oxygen isotope variations that it led to the establishment of oxygen isotope dating of archaeological timbers, in sites where tree-ring growth was too complacent to allow for dendro dating via ring width variations (Loader et al. 2019). Similarly,  $\delta^{18}$ O measurements from subfossil wood (e.g. late glacial pines) is being explored as a method by which to reduce dating uncertainties in tree-ring width time series and radiocarbon dating (Pauly et al. 2018, 2020).

In the UK anticyclonic summers are dry and what precipitation does fall is enriched by short-lived, locally derived convective rain bearing clouds. This enriched source water signal is then further enhanced, in warm anticyclonic summers, by evaporative enrichment at the leaf, and thus high tree-ring stable oxygen isotope values in the wood. The opposite occurs in wet, cool cyclonic British summers where longer-lived Atlantic air masses, where many rainout events have depleted the source water, arrive

on UK shores and ultimately lead to the synthesis of photosynthate with low tree-ring oxygen isotope values (Young et al. 2015; Loader et al. 2019).

In the early decades of stable isotope dendroclimatology many studies focused on exploring the different signal strengths in the isotope and growth proxies (e.g. McCarroll and Pawellek 1998). Now multi parameter studies, bolstered by improved understanding of the mechanistic models of the isotope-climate system, allow for the reconstruction of more climate variables. Hartl-Meier et al. (2015) systematically assessed the climate response of tree-ring width,  $\delta^{13}$ C and  $\delta^{18}$ O from a temperate mountain forest in the Austrian pre-Alps. Variations in stem growth and isotopic composition of Norway spruce, common beech and European larch from dry, medium and moist sites were compared with records of sunshine, temperature, hydroclimate, and cloud cover. Results indicated uniform year-to-year variations in  $\delta^{13}$ C and  $\delta^{18}$ O across sites and species, but distinct differences in ring width according to habitat and species. Whilst the climate sensitivity of ring widths was generally weak, the  $\delta^{13}$ C and  $\delta^{18}$ O chronologies contained strong common signals. This pattern is often found in areas where stand dynamics impact growth proxies but isotopic variables are more simply related to climate. It is in such 'mesic' growth environments where the isotopes proxies may have most to contribute. As discussed, stable oxygen isotopes have revealed particularly high common signal strength and climate reconstruction potential throughout the geographical ranges of temperate tree species, rather than just on the periphery of their distributions (Cernusak and English 2015). These findings are also in line with studies from temperate sites across Switzerland (Saurer et al. 2008), in China (Liu et al. 2012; Xu et al. 2020), in the Tibetan Plateu (Oin et al. 2015; Bräuning 2006; Wernicke et al. 2015; Holmes et al. 2007; Grießinger et al. 2011), and in India (Ramesh et al. 1986).

In Europe a tree-ring isotope network study, ISONET, explored  $\delta^{18}O$  variability across 35 sites from Northern Fennoscandia to the Mediterranean. The ISONET time series revealed that the strongest twentieth century climatic signals were contained in tree-ring  $\delta^{18}O$  from sites across the Northwest (UK, France) and Central (Germany, Austria, Switzerland) European sites (Treydte et al. 2007). The close association of tree-ring  $\delta^{18}O$  with precipitation and temperature variables was postulated to be due to isotopic fractionation being a function of air mass sourcing (temperature of condensation) and air mass trajectory (Treydte et al. 2007; Rozanski et al. 1993).

Studies on individual sites within the ISONET network made use of the strong dependency of  $\delta^{18}O$  variation on moisture conditions and created robust multicentury precipitation and drought reconstructions for both the UK and France. Similarly, Rinne et al. (2013) developed a 400-year May–August precipitation reconstruction for Southern England from tree-ring  $\delta^{18}O$  of pedunculate oak. The analysis demonstrated a statistically robust signal back to 1697, and was robust over a larger area of the UK, later confirmed to cover the entire UK (Loader et al. 2019; Young et al. 2015), such is the strength of the source water signal in the UK's temperate oak. Critically UK oak stable oxygen isotope ratios retain both low- and high frequency precipitation variability (Rinne et al. 2013; Young et al. 2015). In northwestern Iberia, extremes in a centennial stable oxygen isotopic record tracked distinct seasonal hydroclimate conditions: wetter June-July periods were associated

with extremely low  $\delta^{18}O$  values, while extreme high  $\delta^{18}O$  values were associated with warm and dry conditions in the spring (Andreu-Hayles et al. 2017).

Lowland sites in France have also revealed strong hydroclimate reconstruction potential. Labuhn et al. (2016) developed a long, continuous cellulose  $\delta^{18}$ O chronology for France, using living oak trees and timber from historic buildings. They provide a regional reconstruction of summer drought covering more than six centuries, coherent with other proxies of summer climate from the region. Again, the trees show very strong inter-annual variability, and highly significant correlations with temperature, precipitation and drought during the twentieth century. The changes in coherence between two sites within their chronology, during earlier centuries, indicated that the response of the proxy to climate might be non-linear, or that the spatial patterns of climate in France have changed (Labuhn et al. 2016). Such findings are supported by other studies revealing the sensitivity of tree-ring  $\delta^{18}$ O to the combined effects of temperature and humidity, and therefore of drought (Raffalli-Delerce et al. 2004; Masson-Delmotte et al. 2005; Etien et al. 2008b; Labuhn et al. 2014, see also further discussions in Chap. 14). Temperate stable oxygen isotope time series from tree rings, particularly in oak species, are now strongly evidenced to retain a strong hydroclimate signal (Levesque et al. 2019; Roden and Ehleringer 2007; Szejner et al. 2016; Roden et al. 2011).

In Argentina, the  $\delta^{18}O$  tree-ring of *Nothofagus pumilio* and *Fitzroya cupressoides*, at relatively humid sites, was shown to be comparable and related to temperature (December through May) (Lavergne et al. 2016). The temperature signal encompassed a large area in southern South America geographically under the influence of the Southern Annular Mode (SAM). In light of the significant correlation between the oxygen and carbon isotope records at the site the correlation between  $\delta^{18}O$  and temperature was ascribed to the effect of temperature on isotopic enrichment of leaf water, more than to its effect on precipitation  $\delta^{18}O$  (Lavergne et al. 2017a). A modeling experiment later confirmed this interpretation (Lavergne et al. 2017b). Further South, at Perito Moreno glacier (Santa Cruz Province, Argentina), also a moist site, the  $\delta^{18}O$  of *Nothofagus pumilio* was found to be sensitive both to temperature and hydroclimate (Grießinger et al. 2018; Meier et al. 2020). Though changes in moisture source origin may have been involved via the SAM.

In a pioneering Antipodean study, Wilson and Grinsted (1978) were early to hypothesize that  $\delta^{18}O$  in wood could be used to reconstruct past temperature and the  $\delta^{18}O$  of source water. Whilst regional dendrochronology challenges, due to the variations in ring width coherence, may have slowed progress in creating long-term isotope series, a larger number of prominent New Zealand and Australia ecophysiological investigations explore  $\delta^{18}O$  (e.g. Barbour et al. 2002; Cernusak et al. 2005; Ellsworth et al. 2013). Brookman (2014) demonstrated that tree-ring  $\delta^{18}O$  in New Zealand conifers was a promising tool for regional hydroclimate reconstruction via a comparison of the  $\delta^{18}O$  records from *Agathis australis* and *Libocedrus bidwillii* from sites on South Island. Again, a hydroclimate signal dominated (air humidity, soil moisture deficit and rainfall amount) from previous autumn through the concurrent growth season. Isotope climate correlations were strong in several different species. In the North Island, Lorrey et al. (2016) also explored the palaeoclimate potential

of long-lived *Agathis australis* via  $\delta^{18}O$  in earlywood and evidenced statistically significant correlations with hydroclimate (October–December vapor pressure and May–December air humidity). The relationships were shown to be consistent with mechanistic  $\delta^{18}O$  simulations. These results suggested that *Agathis australis*  $\delta^{18}O$  has the potential to provide quantitative climate information to explore past ENSO activity in the region with sub-fossil chronologies having the potential to provide insights back into the late Quaternary.

#### 19.3.3 Dendroclimatic Information from Stable Oxygen Isotope Time Series at High Latitudes and in the Boreal Forest

At high latitudes in the Northern Hemisphere annually resolved  $\delta^{18}O$  chronologies have been developed across the Boreal zone. Buhay and Edwards (1995) carried out an early exploration of hydroclimate in Canada based on tree-ring water isotopes. They used an isotope model to account for the impact of fractionation on source water signal in different moisture environments allowing for a reconstruction resolved by hydroclimatic environment, over 275 years prior to the instrumental period. Birks and Edwards (2009) described changes in atmospheric circulation patterns for the North Pacific from water isotopes, showing the strongest relationship with temperature variations and a precipitation amount effect. Temperature variability for the last millennia has also been reconstructed using  $\delta^{18}O$  tree-ring records in Canada from Boreal-lake subfossil trees, revealing the speed of recent climatic warming at that latitude as well as a connection between the coldest periods of the nineteenth century and the volcanic eruptions and low solar activity associated with the late Little Ice Age (Naulier et al. 2015). Gennaretti et al. (2017) combined  $\delta^{18}$ O, δ<sup>13</sup>C and ring-width chronologies to develop an improved multi-proxy temperature reconstruction (using a Bayesian framework) for the same region. Annual temperature and  $\delta^{18}$ O meteoric water records have also been estimated using  $\delta^{18}$ O tree-ring reconstructions from Pleistocene subfossil wood in Nunavut (Csank et al. 2013). Further studies in the Northwestern Territories showed positive correlations between a tree-ring δ<sup>18</sup>O record and summer temperatures and negative relationships with summer humidity, also involving an oxygen isotope evaporative enrichment signal in warmer summers (Porter et al. 2009). Using longer  $\delta^{18}$ O records for the same site, a ~200-year spring-summer temperature reconstruction was generated (Porter et al. 2013). Further Canadian examples show the strength of Boreal  $\delta^{18}$ O for reconstructing source water dominated precipitation and temperature histories, where the two climate parameters co-vary (Holzkämper et al. 2012; Bégin et al. 2015). Even further north, in High Arctic environments, a significant correlation between the δ<sup>18</sup>O of birch trees growing in Southwestern Greenland and NAO was evidenced (Xu et al. 2021). Similarly, tree-ring cellulose of the shrub Cassiope tetragona in Ellesmere Island in Canada at 79 °N recorded Arctic and NAO variability (Welker et al. 2005). Rayback and Henry (2006) reconstructed 100 years of summer temperatures using cellulose material from tree rings of the shrub *Cassiope tetragona* in Ellesmere Island.

Moving to consider the European context,  $\delta^{18}O$  records of *Pinus sylvestris* in Finland and Sweden also reveal hydroclimate sensitivity (Seftigen et al. 2011; Esper et al. 2018). In the Russian Altai, at the limit of the Boreal forest, summer temperature and precipitation signals were both preserved in  $\delta^{18}O$  chronologies of *Larix decidua* (Sidorova et al. 2013). High latitude Boreal forest has also formed the backdrop for ring width and densitometry-based dendroclimatology to develop networks reconstructions (e.g. Anchukaitis et al. 2017; Wilson et al. 2016) and so were a natural starting place for isotope dendroclimatology (e.g. McCarroll and Pawellek 1998, Robertson et al. 1997).

Trees are long lived in the Boreal and high-latitude forests and abundant subfossil material is available and well-preserved due to the cold environment. With the underlying isotope fractionation models described above and in Chaps. 10 and 18 suggesting that water isotopes in tree rings should sensitively record a source water signal in these moist, cool forests it is not surprising that tree-ring  $\delta^{18}$ O has proven to be a reliable hydroclimate proxy far into the northern forests. See also Chap. 20 for a discussion of relevant reconstructions.

### 19.3.4 Dendroclimatic Information from Stable Oxygen Isotope Time Series in the Tropics

A major research gap exists in the network of high-resolution proxy reconstructions for palaeoclimatology, in the terrestrial tropics (Evans and Schrag 2004). As discussed, this is in part due to the challenges of using traditional dendroclimatology in these regions (Worbes 2002). However, over the last two decades several authors have tried to address this research gap by exploring the source water signal and evaporative enrichment signal in cellulose  $\delta^{18}O$  from tropical trees to resolve both dating and climate signal (see Brienen et al. 2016; Rozendaal and Zuidema 2011; van der Sleen et al. 2017 for a review). In Chap. 22 we summarize major findings regarding the climatic information recorded in tree-ring  $\delta^{18}O$  from trees growing in tropical regions.

Away from the 'ever wet' regions, most parts of the tropics do experience precipitation seasonality, even with annually stable temperatures. Wet seasons are typified by  $\delta^{18}O$  depleted source water (Araguás-Araguás et al. 2000) with dryer periods seeing enriched source water. Moreover, even in regions with very little rainfall amount variability through the year, there is geographical source water variability, as the monsoon seasons shift through the year (Loader et al. 2011). Several studies have attempted to detect seasonality via source water variability as both a dating method in non-annual ring forming tropical trees, and a climate signal (Evans and Schrag 2004).

Kahmen et al. (2011) explored the mechanistic explanations for sensitivity of  $\delta^{18}O$  to climate in tropical tree rings. Using the mechanistic Péclet-modified Craig-Gordon model (PMGG) they reported that both air temperature and air humidity influenced tree that  $\delta^{18}O$ , integrated via VPD, along an aridity gradient of *Metrosideros polymorpha* in Hawaii. Xylem water  $\delta^{18}O$  decreased along the gradient whilst leaf and stem  $\delta^{18}O$  increased, suggesting that evaporative enrichment dominated the source water signal in Hawaii's coastal island environment.

In tropical rainforest environments of Central Guyana, Pons and Helle (2011) found  $\delta^{18}O$  cellulose patterns mimicked the source water annual isotope cycle well, with minima in both rainfall and cellulose at the start of the area's primary wet season. They tested their hypothesis with dual isotope measurements, which revealed that cellulose  $\delta^{13}C$  also showed low moisture stress at the same time as the minima in cellulose  $\delta^{18}O$ . Moreover, these revealing studies were successfully carried out in tropical trees with anatomically indistinct tree rings (Pons and Helle 2011).

In South America, in the western Amazon basin, Brienen and Helle (2012) reported a lower influence of temperature and vapor pressure variations on treering  $\delta^{18}$ O records from *Cedrela odorata*. Tree-ring  $\delta^{18}$ O correlated well with  $\delta^{18}$ O in precipitation, regional precipitation variability during the wet season and streamflow from Amazonian rivers. Non time stable relationships with ENSO parameters were also observed, as well as an increase in  $\delta^{18}$ O values over the twentieth century, shared with ice core records. Baker et al. (2015) reinforced the dominance of a source water signal in the Brienen and Helle (2012)  $\delta^{18}$ O Cedrela record via correlations with other  $\delta^{18}$ O tree-ring records from low altitude rainforest tree species, and with high altitude *Polylepis tarapacana* in the Bolivian Altiplano. The  $\delta^{18}$ O signature of Polylepis tarapacana chronologies along the South American Altiplano revealed a strong signal of December to March precipitation associated to the South American Summer Monsoon (Rodríguez-Catón et al. 2021). In Southern Ecuador, ENSO variability has also been shown to be recorded in  $\delta^{18}O$  tree-ring records of *Cedrela* montana (Volland et al. 2016). Good agreement with wet season precipitation was found in high-resolution  $\delta^{18}$ O records of *Tachigali myrmecophila* in Manaus, Brazil, in Cedrela odorata at 12 °S in the Amazonian and a 150-year Polylepis tarapacana tree-ring  $\delta^{18}$ O record from the Bolivian Altiplano at 22 °S (Ballantyne et al. 2011).

In Costa Rica variations in the tree-ring  $\delta^{18}O$  records from 16-year old *Hyeronima alcorneides* were found to be sensitive to tropical precipitation amount, especially during ENSO events (Evans et al. 2006). The  $\delta^{18}O$  cycles measured in two *Pouteria* trees, which did not have visible tree rings, and were assigned a calendar year via a radiocarbon age-depth model, showed enriched  $\delta^{18}O$  during warm ENSO wet seasons (Anchukaitis and Evans 2010). Annual cyclicity in  $\delta^{18}O$  has also been revealed in ring-less mangrove *Rhizophora mucronata* which also recorded sensitivity to the ENSO event in 1997 (Verheyden et al. 2004a).

In Central Java in Indonesia, Schollaen et al. (2013) reported that  $\delta^{18}$ O chronologies from rainforest teak (*Tectona grandis*) recorded precipitation signals during the dry and the rainy season. The  $\delta^{18}$ O teak tree-ring record also showed strong sensitivity to ENSO events driven by warmer sea surface temperatures over the central Pacific (Schollaen et al. 2015). In Indonesia and Thailand, high-resolution  $\delta^{18}$ O records from

cross dated tree rings of *Tectona grandis*, and ring-less *Samanea saman* grown at the same locality, show high correlations with instrumental data, reflecting the seasonal cycles of rainfall and air humidity (Poussart et al. 2004).

Tropical oxygen isotope dendroclimatology, to date, has revealed coherent correlations between various hydroclimate and source water signals and  $\delta^{18}O$  in tree-rings, often in trees with indistinct growth rings (e.g. Sano et al. 2009). These examples highlight opportunities to extend our understanding of past climate from trees to many parts of the tropics, from remote to highly populated areas where climate change may have direct and serious implications. Despite these promising single site studies, the environmental and physiological mechanisms controlling tropical isotopic signals between the atmosphere and soil, through the stem and canopy to the wood and into the cellulose of the tree-ring are highly complex, and more so in the tropics. The interplay between isotopic signals carried in the source water and those produced at the leaf level and during downstream enrichment and photosynthetic processes are still not well understood (Gessler et al. 2014). The mechanistic interpretation of  $\delta^{18}O$  in tropical trees remains therefore often problematic. Additional relevant discussions can also be found in Chaps. 13 and 22.

#### 19.4 Conclusions

The contributions of stable isotope dendroclimatology have increased tenfold, over recent decades, thanks to better analytical systems allowing greater sample throughput and replication, improved understandings of the mechanistic controls over the isotope signal and increased geographical and species coverage in example studies. Contributions to our understanding of the carbon—water-climate relationship in trees are now available from long, well replicated stable isotope tree-ring series across the old world, with pockets of emerging studies in previously underrepresented geographical areas. As global average temperatures continue to rise and we move into a '1.5-degree world' with increasing climate extremes, the additional glimpses into our pre anthropogenic climate that we obtain from tree-ring isotope records becomes ever more important. Coupled with the ability to explore how trees and woodland respond to changing climate and CO<sub>2</sub> levels in the atmosphere, the isotope dendro proxies are now a vital part of the palaeoenvironmental toolbox.

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