



Invited review

Seasonal temperature and precipitation recorded in the intra-annual oxygen isotope pattern of meteoric water and tree-ring cellulose



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ABSTRACT

Modern and ancient wood is a valuable terrestrial record of carbon ultimately derived from the atmosphere and oxygen inherited from local meteoric water. Many modern and fossil wood specimens display rings sufficiently thick for intra-annual sampling, and analytical techniques are rapidly improving to allow for precise carbon and oxygen isotope measurements on very small samples, yielding unprecedented resolution of seasonal isotope records. However, the interpretation of these records across diverse environments has been problematic because a unifying model for the quantitative interpretation of seasonal climate parameters from oxygen isotopes in wood is lacking. Towards such a model, we compiled a dataset of intra-ring oxygen isotope measurements on modern wood cellulose ($\delta^{18}\text{O}_{\text{cell}}$) from 33 globally distributed sites. Five of these sites represent original data produced for this study, while the data for the other 28 sites were taken from the literature. We defined the intra-annual change in oxygen isotope value of wood cellulose [$\Delta(\delta^{18}\text{O}_{\text{cell}})$] as the difference between the maximum and minimum $\delta^{18}\text{O}_{\text{cell}}$ values determined within the ring. Then, using the monthly-resolved dataset of the oxygen isotope composition of meteoric water ($\delta^{18}\text{O}_{\text{MW}}$) provided by the Global Network of Isotopes in Precipitation database, we quantified the empirical relationship between the intra-annual change in meteoric water [$\Delta(\delta^{18}\text{O}_{\text{MW}})$] and $\Delta(\delta^{18}\text{O}_{\text{cell}})$. We then used monthly-resolved datasets of temperature and precipitation to develop a global relationship between $\Delta(\delta^{18}\text{O}_{\text{MW}})$ and maximum/minimum monthly temperatures and winter/summer precipitation amounts. By combining these relationships we produced a single equation that explains much of the variability in the intra-ring $\delta^{18}\text{O}_{\text{cell}}$ signal through only changes in seasonal temperature and precipitation amount ($R^2 = 0.82$). We show how our recent model that quantifies seasonal precipitation from intra-ring carbon isotope profiles can be incorporated into the oxygen model above in order to separately quantify both seasonal temperature and seasonal precipitation. Determination of seasonal climate variation using high-resolution isotopes in tree-ring records makes possible a new understanding of the seasonal fluctuations that control the environmental conditions to which organisms are subject, both during recent history and in the geologic past.

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1. Introduction

Multiple empirical studies have shown the oxygen isotopic composition of meteoric water ($\delta^{18}\text{O}_{\text{MW}}$) to be highly correlated with various climate parameters on local, regional, and global scales (e.g., Araguás-Araguás et al., 1998; Bowen, 2008; Dansgaard, 1964; Lachniet and Patterson, 2006, 2009; Rozanski et al., 1992, 1993). One fate for meteoric water is uptake by plant roots and incorporation into plant tissues; in fact, meteoric water exerts

fundamental control on the oxygen isotope signature of plant tissues (Deniro and Epstein, 1979). Because trees are long-lived and tree fossils are abundant in the fossil record, workers have long sought to gain physiological (Gessler et al., 2009; Offermann et al., 2011) or environmental information from the oxygen isotope composition of both modern (Brienen et al., 2012; Knorre et al., 2010; Loader et al., 2010, 2007; McCarroll and Loader, 2004; Poussart et al., 2004; Rinne et al., 2013; Saurer et al., 2008; Treydte et al., 2006; Young et al., 2015) and ancient wood (Jahren and Sternberg, 2002, 2003, 2008; Richter et al., 2008a; Wolfe et al., 2012). Cellulose has been the substrate of choice because it is resistant to degradation (e.g., Griffith et al., 2008; Jahren and

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Sternberg, 2002) and can be extracted from heterogeneous lignin complexes (Green, 1963). Multiple studies have attempted to calculate the $\delta^{18}\text{O}_{\text{MW}}$ value from the $\delta^{18}\text{O}$ value of wood cellulose ($\delta^{18}\text{O}_{\text{cell}}$) using fractionations based on empirical datasets and experimental observations (Csank et al., 2013; Richter et al., 2008b; Saurer et al., 1997; Sternberg et al., 2007; Waterhouse et al., 2002; Yakir and DeNiro, 1990). Most of this work has been performed using whole leaf tissues or whole tree-rings due to the large amount of plant tissue required for classical isotope analysis (e.g., Sternberg, 1989). Recent advances in cellulose extraction techniques and mass spectrometry automation have allowed researchers to create high-resolution intra-ring profiles of $\delta^{18}\text{O}_{\text{cell}}$ based upon analyses of as little as 100 μg of cellulose (e.g., Dodd et al., 2008; Schollaen et al., 2014). However, a unifying relationship for interpreting observed patterns in $\delta^{18}\text{O}_{\text{cell}}$ extracted from across tree-rings is lacking. Multiple studies have shown that individual trees may have different $\delta^{18}\text{O}_{\text{cell}}$ absolute values, even when growing at the same site, under the same conditions (Reynolds-Henne et al., 2009; Richter et al., 2008b; Wang et al., 1998) and authors have concluded that the search for a single environmental signal to explain absolute $\delta^{18}\text{O}_{\text{cell}}$ values across all sites is futile (McCarroll and Loader, 2004). We have shown elsewhere that the relative change in the carbon isotope ($\delta^{13}\text{C}$) values measured from intra-ring profiles provides valuable quantitative paleoclimate information, despite the fact that absolute values of $\delta^{13}\text{C}$ in wood differed between individual trees at the same site (Schubert and Jahren, 2011). Here we sought to evaluate a similar approach for high-resolution intra-ring $\delta^{18}\text{O}_{\text{cell}}$ measurements.

Towards this, we present new intra-ring $\delta^{18}\text{O}_{\text{cell}}$ profiles from five widely distributed sites, and combine these new data with 28 other similar records from the literature to form a global dataset of intra-annual profiles of $\delta^{18}\text{O}_{\text{cell}}$ from 792 tree rings measured at 33 sites. We analyze the dataset to quantify a relationship between intra-annual changes in $\delta^{18}\text{O}_{\text{cell}}$ measured across tree rings and the intra-annual change in $\delta^{18}\text{O}_{\text{MW}}$ across all sites. We then use these data and a global dataset of monthly $\delta^{18}\text{O}_{\text{MW}}$ and climate data to produce an empirical relationship explaining the intra-annual $\delta^{18}\text{O}_{\text{cell}}$ patterns observed in tree rings worldwide. Last, we combine this result with our previous work that analyzed a global intra-ring carbon isotope dataset (Schubert and Jahren, 2011) in order to produce a set of equations for quantifying seasonal climate from recent and fossil, high-resolution, tree-ring records.

2. Materials and methods

2.1. Stable isotope analysis

We sampled four consecutive rings from each of five living trees for high-resolution intra-ring $\delta^{18}\text{O}_{\text{cell}}$ measurements. Given the consistency in the intra-annual $\delta^{18}\text{O}_{\text{cell}}$ pattern among closely spaced trees (e.g., Zhu et al., 2012), only a single tree was sampled at each site. However, four rings per sample were analyzed in order to attain an average intra-annual signal, as the $\delta^{18}\text{O}_{\text{cell}}$ pattern in individual tree rings within a tree can be variable from year-to-year (e.g., Schollaen et al., 2013). The trees grow at five sites within Hawaii, Japan, Alaska, and Norway (two sites), which together span more than fifty degrees of latitude, represent tropical to arctic ecosystems, and reflect a wide range of seasonal temperatures and precipitation amounts (Fig. 1). Five different genera are represented: three are evergreen (Site 1: *Sophora*; Site 4: *Picea*; and Site 5: *Tsuga*) and two are deciduous (Site 2: *Larix* and Site 3: *Metasequoia*) (Table 1). Using a razor blade, each tree ring was subsampled by hand into an average of ~14 subsamples/ring (minimum: Site 1, *Sophora*, 11 subsamples/ring; maximum: Site 5, *Tsuga*, 18 measurements/ring) to achieve the highest resolution

possible while obtaining sufficient material for cellulose extraction and stable isotope analyses. Cellulose was extracted from a total of 283 individual slices weighing between 1 and 3 mg using methods modified from Brendel et al. (2000), Gaudinski et al. (2005), and Evans and Schrag (2004). In brief, 80% acetic acid and 67.9% nitric acid were added in a 10:1 ratio, vortexed, and heated at 120 °C for 30 min. Samples were then washed twice with 99% ethanol and once with deionized water; 17% (w/v) NaOH was then added and the samples sat for 10 min. The NaOH was decanted and the samples were rinsed with a series of washes that included deionized water, acetic acid, ethanol, and acetone. The samples were then allowed to dry overnight at 50 °C. 0.45–0.55 mg of the resulting pure α -cellulose samples were weighed into silver capsules and analyzed for $\delta^{18}\text{O}_{\text{cell}}$. The $\delta^{18}\text{O}_{\text{cell}}$ measurements were made using a Delta V Advantage Isotope Ratio Mass Spectrometry (IRMS) instrument coupled to a High-Temperature Conversion Elemental Analyzer (Thermo Fisher, Bremen, Germany) configured with a zero-blank autosampler (Costech Analytical, Valencia, CA, USA). All $\delta^{18}\text{O}_{\text{cell}}$ values were normalized to the VSMOW-SLAP scale using two internal laboratory α -cellulose reference materials, calibrated using benzoic acid reference materials IAEA-601 (23.14‰) and IAEA-602 (71.28‰) (Brand et al., 2009). Three to six replicates of an α -cellulose quality assurance sample were analyzed as unknowns in each batch run. The standard deviation of all $\delta^{18}\text{O}_{\text{cell}}$ quality assurance samples was 0.15‰ ($n = 64$) with an average value within 0.02‰ of the calibrated value.

For two of the trees (*Picea* from Palmer, Alaska, USA, Site 4; *Tsuga* from Ås, Norway, Site 5), we also produced a high-resolution, intra-ring $\delta^{13}\text{C}$ record from the extracted cellulose. The samples were analyzed for $\delta^{13}\text{C}$ values using the Delta V Advantage IRMS instrument coupled to a Costech ECS 4010 Elemental Analyzer (Costech Analytical, Valencia, CA, USA) with the zero-blank autosampler. The analytical uncertainty associated with each measurement was <0.1‰.

2.2. Published tree-ring records

We augmented our dataset with a thorough survey of previously published data, including high-resolution intra-ring $\delta^{18}\text{O}_{\text{cell}}$ data from 19 studies from 28 sites (Fig. 1). The comprehensive dataset included high-resolution $\delta^{18}\text{O}_{\text{cell}}$ data from a total of 792 distinct rings from 33 sites spanning 112° of latitude (Table 1). We excluded studies that only sampled earlywood and latewood (i.e., 2 measurements per ring) (e.g., Sohn et al., 2013) and studies that were limited to high-resolution measurements across only one tree ring (e.g., Li et al., 2011). The resultant dataset was taxonomically diverse and included 13 angiosperm genera (*Carapa*, *Cordia*, *Fagus*, *Goupia*, *Hyeronima*, *Ocotea*, *Populus*, *Quercus*, *Rhizophora*, *Samanea*, *Sophora*, *Tachigali*, and *Tectona*) and 7 conifer genera (*Larix*, *Metasequoia*, *Picea*, *Pinus*, *Podocarpus*, *Sequoia*, and *Tsuga*) (Table 1).

2.3. International Atomic Energy Agency (IAEA) Global Network of Isotopes in Precipitation (GNIP) database

All long-term average monthly temperature (°C), precipitation (mm), and $\delta^{18}\text{O}_{\text{MW}}$ data were compiled from the IAEA GNIP database, unless noted. Because the database is regularly updated as new data are submitted and verified, the station names and data used for our analysis are provided in Supplementary Table 3. Taken in total, these sites span 158° of latitude ranging from 82.5 °N (Alert, Nunavut, Canada) to 75.6 °S (Halley Bay, Antarctica) (Fig. 1).

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