Oxygen and hydrogen isotope ratios in tree rings: how well do models predict observed values?

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Abstract

We have measured annual oxygen and hydrogen isotope ratios in the α-cellulose of the latewood of oak (*Quercus robur* L.) growing on well-drained ground in Norfolk, UK. We compare the observed values of isotope ratios with those calculated using equations that allow for isotopic fractionation during the transfer of oxygen and hydrogen from source water taken by the tree to cellulose laid down in the cambium. The equations constitute a model in which isotopic fractionation occurs during evaporative enrichment within the leaf and during isotopic change between carbohydrates and water in the trunk during cellulose synthesis. From the relationship between isotope ratios in precipitation and α-cellulose, we deduce that the source water used by the tree comprises a constant mixture of groundwater and precipitation, chiefly from the months of May, June and July of the growth year. By selection of isotopic fractionation factors and the degree of isotope exchange within the trunk, we are able to model the observed annual values of oxygen isotope ratios of α-cellulose to a significant level ($r = 0.77$, $P < 0.01$). When we apply the same model to hydrogen isotope ratios, however, we find that, although we can predict the average value over the time series, we can no longer predict the year-to-year variation. We suggest that this loss of environmental signal in the hydrogen isotopes is caused by differences in the kinetic isotope effects of the biochemical reactions involved in the fixation of hydrogen in different positions of the glucose molecule. Owing to these effects, the hydrogen isotope ratios of cellulose can vary in a way not anticipated in current models and hence may induce non-climatic 'noise' in the hydrogen isotope time series.

1.   Introduction

Numerous investigations over the past two decades have demonstrated the great
potential of stable isotopes in tree rings (carbon, oxygen and hydrogen) as a record of
continental environmental information ([1] and references therein). Tree rings offer
advantages over other sources of proxy environmental data, such as ice cores and lake
sediments, owing to unambiguous dating of tree rings to precise years. Ring widths
and x-ray absorption measurements have been very successfully used for climatic
reconstruction in 'marginal' areas such as Siberia [2] and the southwestern USA [3].
In these areas tree growth is influenced by a single dominant factor such as summer
temperature or precipitation. In temperate regions, however, where growth can be
influenced by several factors, the relationship between ring widths and climate is
much weaker; in contrast, isotope ratios display high correlations with climatic
parameters in these regions [4-6]. This paper focuses on relationships between
oxygen and hydrogen isotopes in tree rings and environmental parameters, and on our
theoretical understanding of the factors that cause isotopic fractionation of these
elements during the processes that ultimately produce cellulose in the annual growth
rings.

The source of oxygen and hydrogen atoms in the cellulose of annual growth rings of
trees is atmospheric precipitation. Hence the isotopic composition of these growth
rings is regarded as a valuable terrestrial source of information for the reconstruction
of isotopic ratios of precipitation. However, the isotope ratios ($^{18}O/^{16}O$ and D/H) of

the precipitation are modified during the complex processes that occur within the tree leading to the formation of cellulose. Some of the processes that result in isotopic fractionation (such as evaporative enrichment in the leaf – see below) are themselves dependent upon environmental parameters such as the relative humidity. There is

5 indeed much evidence for relationships between climatic parameters and oxygen and hydrogen isotopes in tree rings [1].

Early investigations tended to concentrate on spatial relationships over continental distances, where variations in environmental variables were relatively large. Burk and

10 Stuiver [7] reported a close relationship between mean annual temperature and $^{18}O/^{16}O$ in cellulose for trees growing along the western coast of North America. The following year Yapp and Epstein [8] reported a similar close relationship between average annual temperature and D/H in cellulose for trees from a wide area of the North American continent. More recently, interest has focused on the temporal

15 relationships between isotopes and climate parameters with the intention of using the long-term isotope record available in tree rings to reconstruct palaeoenvironmental parameters in a particular area. Studies from individual sites have found significant relationships between cellulose D/H and temperature [9-12] and humidity [9-11], and also between cellulose $^{18}O/^{16}O$ and temperature [13-15] and relative humidity [13,14].

20

It is clear from empirical measurements that the relationship between isotope ratios in tree ring cellulose and climatic parameters is complex, and depends, among other things, upon the environmental conditions under which the trees grow. In order to obtain the maximum environmental information from oxygen and hydrogen isotope

25 ratios in tree rings a complete understanding is required of the complex processes that

determine these ratios. To this end we report here a study of the behaviour of $^{18}O/^{16}O$

and D/H isotope ratios in cellulose of individual annual growth rings of oak (*Quercus*

robur). In particular we examine the extent to which the calculated values of

cellulose isotope ratios correspond to observed values. It should be noted that the

5   year-to-year variation in $^{18}O/^{16}O$ and D/H values of source water taken by individual

trees growing naturally, and hence of cellulose in annual growth rings, are much less

than the range of isotope ratios usually encountered in greenhouse studies and studies

in which trees are sampled over a wide geographical area. As a consequence, small

effects that have so far been ignored in constructing models of isotopic fractionation

10   are likely to be more apparent. Our study highlights significant differences, which

might be caused by such an effect, in the behaviour of oxygen and hydrogen isotopes

in cellulose.

15

Oxygen and Hydrogen Isotopic Fractionation:

The Craig-Gordon equation [16] for isotopic fractionation was derived for a simple

system of evaporation at open water surfaces. It has since been adapted and expanded

20   to model the relationship between the oxygen and hydrogen isotope ratios of leaf

water (δ_l) and source water (δ_s) [17,18]. The simplest expression [14] of this

relationship is given by Equation 1:

$$\delta_l \ = \ \delta_s + (\varepsilon_e + \varepsilon_k)(1\text{-}h) \qquad (1)$$

25

In this model it is assumed that an isotopic steady state has been reached in the leaf and that source water and atmospheric water vapour are in isotopic equilibrium. It is also assumed that there is no isotopic fractionation during uptake of water by the roots and transport to the leaf [19]. The terms ε_e and ε_k are the equilibrium and kinetic

5   fractionation factors respectively for diffusion of water vapour through the stomata, and h is the relative humidity. In line with Roden and co-workers [20], the term leaf water is used to indicate the water at the site of evaporation (which is appropriate for the site of carbohydrate synthesis in the chloroplast), and not bulk leaf water, which is enriched to a lesser extent [21,22]. Equation 1 predicts that the degree of isotopic

10   enrichment in the leaf depends on the value of relative humidity experienced by the leaf. Temperature should also independently influence the isotopic ratios in leaf water by the effect on meteoric water. More comprehensive versions of this model, which allow also for diffusion through the leaf boundary layer (affected by air velocity), have been developed by others [18,20,21]. In order to use these models,

15   however, knowledge of vapour pressure and wind speed at the leaf surface, and vapour pressure in intercellular air space is required. Such detailed information is not normally available in studies where annual growth rings of trees growing under natural conditions are used as a source of past environmental information. In these cases the only parameters likely to be available over extended periods are air

20   temperature and the relative humidity measured at a nearby meteorological centre.

Carbohydrates synthesized in the leaf will inherit the evaporatively enriched isotopic signal of the leaf water. If it is assumed that the cellulose is then formed from these carbohydrates without further isotopic modification, the values of oxygen and

25   hydrogen isotope ratios in the cellulose are given by Equation 2:

$$\delta_{cell} = \delta_s + (\varepsilon_e + \varepsilon_k)(1-h) + \varepsilon_n \qquad\qquad (2)$$

where ε_n is the appropriate biochemical fractionation factor for oxygen or hydrogen.

Equation 2 carries the implication of two main environmental influences on the value

of δ_{cell}. The first is temperature, through its effects on meteoric water [23] and hence

δ_s, and the second is relative humidity, through its influence on evaporative

enrichment of leaf water. It should be noted that Equation 2 is valid for both oxygen

and hydrogen and predicts that isotopes of these two elements will behave in a

proportional fashion.

The equation is, however, unlikely to be directly applicable to free-growing trees

owing to a number of factors. First, it does not take into account the probable post-

photosynthetic exchange of oxygen and hydrogen between carbohydrates and the

xylem water during cellulose formation in the trunk, a process for which there is

increasing evidence [24-26]. Second, it does not address the possibility of a mixed

origin for the tree's source water, which may be a mixture of recent precipitation and

groundwater drawn up by deeply penetrating roots. Other uncertainties in the

equation include the appropriate values for the fractionation factors.

Oxygen atoms in carbohydrates are able to exchange with xylem water during

cellulose synthesis in the cambium *via* reversible hydration at carbonyl groups of

triose phosphates [25,26]. Equation 2 can be modified [20,24] to allow for this

exchange, giving Equation 3.

$$\delta^{18}O_{cell} = (1-f_o)[\delta^{18}O_s+(\varepsilon_e+\varepsilon_k)(1-h)+ \varepsilon_o] + f_o(\delta^{18}O_s+\varepsilon_o) \qquad (3)$$

where f_o is the fraction of oxygen atoms exchanging with the xylem water, and ε_o is

the biological fractionation factor for oxygen, which has the same value for processes

5   within the leaf and trunk.

Carbon-bound hydrogen atoms in carbohydrates are also able to exchange with xylem

water *via* enolization at carbonyl groups [24,27]. Modification of Equation 2 to allow

for this yields Equation 4.

10

$$\delta D_{cell} = (1-f_H)[\delta D_s+(\varepsilon_e+\varepsilon_k)(1-h)+\varepsilon_a] + f_H(\delta D_s+\varepsilon_h) \qquad (4)$$

where f_H is the fraction of hydrogen atoms exchanging with the xylem water; ε_a is the

biological fractionation factor associated with NADPH during carbohydrate formation

15   in the leaf; ε_h is the fractionation factor for exchange of carbon-bound hydrogen

atoms with water. Equations 4 is equivalent to one derived by Roden and co-workers

[20].

The main purpose of this study is to determine the extent to which measured values of

20    $\delta^{18}O_{cell}$ and δD_{cell} may be modelled using Equations 3 and 4, taking into account (i)

differing amounts of post-photosynthetic exchange during cellulose synthesis and (ii)

the degree of mixing of recent precipitation and groundwater to provide the water

used by the tree.

25

2.   Site and Trees

Two oak trees (*Q. robur)* (SP10 and SP19) were sampled for isotope measurement. They grow in an open stand in well-drained sandy soil in Sandringham Park,

5   northwest Norfolk, in eastern England about 5 km from the coast. A full description of the site has been given previously [6]. Groundwater samples were taken directly from springs at several locations at the site. Records of temperature from the central England temperature series (since 1895) and humidity (since 1920) were obtained as previously described [6,28]. Isotope ratios of precipitation (δ_{mw}) are available since

10   1982 from the station at NERC Centre for Ecology and Hydrology, Wallingford (Berkshire), 180 km to the southwest of the site.

3.   Methods

15   Wood samples for isotopic analysis were taken from each tree using a 12 mm diameter increment borer. The annual growth rings were assigned unambiguously to individual years by matching the ring width time series for each tree against the master ring width chronology for the site based on 25 cores from 11 trees [6,29]. The late (summer) wood was manually removed under magnification in thin shavings

20   from each annual ring using a scalpel. The early wood was discarded from the analysis because it is known that early wood is formed at least in part from photosynthates produced in the previous year [25]. α-Cellulose was separated from the slices [30] and values of $\delta^{18}O_{cell}$ determined by the method of Field and colleagues [31] based on pyrolysis with mercury(II) chloride. Values of δD_{cell} were measured

25   after nitration of the α-cellulose to trinitrocellulose, using a mixture of nitric and

phosphoric acids [32]. This procedure is necessary in order to remove the oxygen-bound hydrogens, which are readily exchangeable with environmental water. The crude trinitrocellulose was purified by dissolution in the minimum volume of acetone and subsequent precipitation from cold water [33].

5

Isotope ratios are presented using the standard 'delta' notation where the oxygen and hydrogen isotope values in a sample ($\delta^{18}O$ and δD respectively) are expressed as the measured isotope ratio in the sample relative to that in a standard in parts per mille (‰):

10
$$\delta = (R_{sample}/R_{standard} - 1)1000‰.$$

The international standard for oxygen and hydrogen is Vienna Standard Mean Ocean Water (VSMOW). For cellulose, the isotope ratios for oxygen and non-exchangeable hydrogen are represented as $\delta^{18}O_{cell}$ and δD_{cell} respectively. Standard deviations for replicate measurements of a standard sample of α-cellulose are 0.2‰ and 2‰ for

15   oxygen and hydrogen respectively.

4.   Results and Discussion

20   *Climate Relationships:*

We investigated the relationship between isotope ratios and climatic parameters using a single time series for each isotope, generated by calculating an average value for each year from the two trees, in order to increase the signal-to-noise ratio. We have

25   previously shown that trees on this site show the strongest relationships between

latewood $\delta^{18}O_{cell}$ and temperature and relative humidity for the months of July and

August [29]. Values of the correlation coefficient (r) for $\delta^{18}O_{cell}$ against average July

and August temperature and relative humidity are reproduced in Table 1 together with

corresponding values for δD_{cell}, which have not been reported previously. Values of r

5   in Table 1, although significant ($P<0.01$), are not particularly high and are lower than

those obtained for the carbon isotopes from the same site [6]. However, the values

are similar to those obtained from previous studies investigating temporal variations

in oxygen and hydrogen isotope ratios in tree rings at annual resolution [9-11,13,15].

10

Modelling Oxygen Isotopes:

In order to compare observed and modelled values of annual isotope ratios in

latewood from 1982 - 1994, the period during which $\delta^{18}O_{cell}$ and $\delta^{18}O_{mw}$ are both

15   available, we changed the above strategy of using a mean isotope time series derived

from the time series of individual trees. As we have isotope values from only two

trees, averaging two annual values will not necessarily improve the agreement

between observed and calculated values for that year; on the contrary, where, for a

particular year, the observed values of $\delta^{18}O_{cell}$ differ significantly, an average will

20   reduce or destroy the closeness of match between observed and calculated values for

one of the individual trees. We decided, therefore, to use the results from a single tree

(SP19) to test the model. SP19 was chosen because $\delta^{18}O$ values from this tree

correlated more highly with those of meteoric water ($r = 0.82$, $P < 0.001$) than did

SP10 ($r = 0.22$, $P > 0.01$). Examination of the individual values in the $\delta^{18}O_{cell}$ time

25   series for the two trees between 1982 and 1994 indicated that there were two years in

which the $\delta^{18}O_{cell}$ values differed significantly, sufficient to lower the value of r for

SP10 compared with that for SP19. We think that this discrepancy is more likely to

arise from experimental error in the isotopic measurements for the two aberrant years,

than from a difference in environmental response between the trees. In support of this

5   interpretation the $\delta^{18}O_{cell}$ values of the two trees show a higher correlation over the 87

year period from 1895 – 1981 ($r = 0.51$, $P < 0.001$) than over the 13 years from 1982

– 1994 ($r = 0.44$, $P > 0.1$), indicating that the trees are behaving similarly over the

long term.

10

Table 2 shows the correlation coefficients r between latewood $\delta^{18}O_{cell}$ for SP19 and

$\delta^{18}O_{mw}$ for specified months between 1982 and 1994 (the period during which

continuous records of isotope ratios of precipitation are available from CEH

Wallingford). For this particular tree the strongest relationship ($r = 0.82$; $P<0.001$) is

15   with the mean values $\delta^{18}O_{mw}$ for the months May-July (calculated as a weighted

average from the precipitation of each month). Precipitation at earlier times during

the year seems also to have some influence, as evidenced by the values of r for

December, January and March. We have previously shown that the predominant

influence on an 'eastern England' $\delta^{18}O_{cell}$ chronology (derived from the two trees at

20   Sandringham and a further two trees growing on a wet site approximately 3 km to the

south southwest) are the values of $\delta^{18}O_{mw}$ of the preceding December and January

[29]. The difference in relationship between $\delta^{18}O_{mw}$ and the $\delta^{18}O_{cell}$ time series for

SP19 and that for the mean of four trees can be explained as follows. In taking an

average for the isotope ratios of individual trees to produce a mean time series, the

25   particular influences relating to each tree are also averaged. The mean time series

will therefore represent that of a hypothetical tree growing under average growth

conditions. At the wet site, we argue [29] that water may take several months to

move through the saturated zone to reach the rhizosphere, and hence water taken up

by the tree during the period of latewood formation is likely to be dominated by the

5   previous winter's precipitation. At the dry site (Sandringham) precipitation is likely

to reach the rhizosphere much more rapidly, and hence during the period of latewood

formation, water taken up by the roots will be dominated by more recent (May-July)

precipitation. The relationship between isotope ratios in cellulose and precipitation

therefore depends crucially on the conditions in which a tree grows.

10

Fig. 1 shows the relationship between $\delta^{18}O_{cell}$ and average May-July $\delta^{18}O_{mw}$. In

agreement with Equation 3, there is a good linear relationship ($r = 0.82$, $P<0.01$).

However, Equations 3 and 4 predict that the regression line should have a gradient of

1, for both oxygen and hydrogen, assuming that the precipitation is the source water

15   taken up by the roots. Yapp and Epstein [8,34] obtained gradients close to 1 for the

relationship between δD_{cell} and δD_{mw} for trees across North America. The observed

slope in Fig. 1, however, is considerably less (0.59). This suggests that the oak tree

ring isotopes are recording $\delta^{18}O_{mw}$, but that the relationship is damped. Saurer and

co-workers [14] also observed gradients significantly lower than 1 for the regression

20   line of $\delta^{18}O_{cell}$ vs. $\delta^{18}O_{mw}$ (May-August average) for beech trees growing in two sites

in Switzerland. They accounted for the gradient by assuming that the source water

sampled by the tree derives from a mixture of precipitation from preceding months,

weighted for mixing in the soil. In the case of the oak tree examined in the present

study, the simplest explanation is that during the period of formation *the tree is*

25   *sampling both groundwater of constant $\delta^{18}O$ via its deep roots and precipitation via*

shallower roots in the ratio of ca. 40:60. The assumption that the isotope ratio of
groundwater is constant is supported by observations by Hemming (unpublished
work) in which the isotopic ratios of the groundwater over an eight month period, at a
site with similar characteristics to Sandringham, showed no significant variation

5   despite large variations in the isotopic ratios of the precipitation over the same period.
If it is assumed that a 40:60 mixture of groundwater and precipitation is sampled
during formation of latewood, then $\delta^{18}O_s = 0.6\delta^{18}O_{mw} + 0.4\delta^{18}O_{gw.}$ The $\delta^{18}O$ value of
groundwater was measured as -7.3±0.1‰ (n=3).

10   We can now use Equation 3, in which $\delta^{18}O_s$ is defined as above, to calculate values of
$\delta^{18}O_{cell}$ and compare these with the observed (Fig. 2). Values of ε_e and ε_k are taken
respectively as 9.5‰ [35], and 28.5‰ [20], and values of *h* are for 10.00h GMT.
Values of ε_o are reported as falling within the range of 27 ±3‰ [36] and f_o within the
range of 0.40 - 0.45 [20,24]. In order to test the sensitivity of the model to values of

15   ε_o and f_o we varied these parameters within the ranges of 24-32‰ and 0-0.50
respectively. Fig. 2 shows the best fit that was obtained with observed values of
$\delta^{18}O_{cell}$, in terms of both mean value and variance. This occurred when $\varepsilon_o = 30‰$ and
$f_o = 0.46$ (observed mean and variance are 30.1‰ and 0.7 respectively; calculated
values are 29.9‰ and 1.4 respectively; correlation coefficient between observed and

20   calculated values is 0.77, *P*<0.01). Although these values of ε_o and f_o are at or just
beyond the extremes of values in the literature, they do provide a better fit the
observed values of $\delta^{18}O_{cell}$ than do values of ε_o and f_o set within the mid range of
literature values. This is illustrated in Fig. 2 for $\varepsilon_o = 27‰$ and $f_o = 0.42$ (calculated
mean and variance are 27.3‰ and 1.6 respectively). For comparison, Fig. 2 also

shows calculated values of $\delta^{18}O_{cell}$ when $\varepsilon_o = 27‰$ and $f_o = 0$. In this case both

calculated mean (32.1‰) and variance (3.0) are significantly higher than observed.

The calculated values of $\delta^{18}O_{cell}$ from Equation 3 are also dependent upon the time of

5 day at which relative humidity values are measured. Fig. 3 shows calculated values

of $\delta^{18}O_{cell}$ for relative humidity measured at 10.00h, 13.00h and 18.00h GMT, with ε_o

set at 30‰ and f_o set at 0.46. The best fit with observed values of $\delta^{18}O_{cell}$ is for the

relative humidity at 10.00h. Values of relative humidity from 13.00h give poorer

agreement with the observed isotope ratios than do the 10.00h and 18.00h values.

10 This may be explained by the fact that trees growing in dry conditions have a lower

rate of photosynthesis during the warmest part of the day. Under these conditions the

photosynthesis curve shows two peaks, one in the morning and another during the late

afternoon [37]. Therefore relative humidity measured for 10.00h probably gives a

better representation of conditions under which the majority of photosynthesis occurs

15 than values taken in the middle of the day.

Considering the large approximations that have been made, the model represented by

Equation 3 allows the calculation of $\delta^{18}O_{cell}$ values that are in good agreement with

observed values. In particular, the annual variation in $\delta^{18}O_{cell}$ is well predicted. This

20 gives confidence to our basic understanding of the mechanisms involved in oxygen

isotope fractionation.

Modelling Hydrogen Isotope Ratios:

Equation 4 was used to calculate values of δD_{cell}. Assuming that groundwater and precipitation mix in a ratio of 4:6, then $\delta D_s = 0.6\delta D_{mw} + 0.4\delta D_{gw}$, where δD_{gw} has the measured value of -50.1‰. Values of ε_e, ε_k, ε_a and ε_h are taken respectively as 82‰ [35], 25‰ [18], -171‰ and 158‰ [24]. Values of h are for 10.00h GMT. Different

5 values of f_H were entered into the equation, and the best fit, in terms of observed (-43.9‰) and calculated (-45.3‰) mean values of δD_{cell}, was with $f_H = 0.46$ (Fig. 4). Fig. 4 also shows calculated values of δD_{cell} when f_H is set at 0.40 and 0.50. The sensitivity of the model to values of f_H is apparent. A value for f_H of 0.46 is consistent with the range of 0.40-0.45 observed by Yakir and DeNiro [24], but is significantly

10 larger than 0.31 obtained by Roden et al. [20]. The fact that 'best fit' values of f_o and f_H in this study are both 0.46 is striking, and suggests that carbohydrate molecules exchange the same proportion of oxygen and carbon-bound hydrogen atoms with water.

15 The important thing to note in Fig. 4 is that, although the calculated mean value of δD_{cell} is close to the observed, *there is no significant correlation in behaviour over the period of analysis between calculated and observed values (r = 0.14, P > 0.1).* In contrast to oxygen isotopes, hydrogen isotopes appear to have lost the annual details of the environmental signal. This behaviour is quite unlike that of oxygen isotopes; it

20 is not predicted in current models and has not been previously reported. Indeed, using the same model as here, Roden and co-workers [20] obtained reasonable agreement between observed and calculated values of δD_{cell} for trees growing under greenhouse or field conditions. However, the range of natural variation in δD_{cell} in this study is much less than in that of Roden et al; and as agued above, a small effect that has

25 previously been ignored may be more apparent in our study. We suggest that the

failure to replicate annual variation in δD_{cell} over the 13 year period of study arises

from a factor not incorporated in current models. This results from the varying

abundance of the D isotope at different positions in the glucose ring caused by

differences in kinetic isotope effects (KIE) of chemical reactions involved in the

5   synthesis of glucose [38]. Thus the abundance of D at C3 of the PGA molecule

formed by carboxylation of RuBP differs from that formed from glyoxylate, owing to

the different KIEs of the enzyme-catalysed reactions involved. The resulting

abundance of D at C6 in glucose therefore depends upon the physiological state of the

plant [38]. Effects of this type will affect correlation of δD_{cell} with environmental

10   parameters in an unpredictable way and could explain the loss of environmental

signal as observed.

5.   Conclusions

15

In line with expectation, we find that oak trees growing in their natural environment

record information on growing season temperature and relative humidity in the

oxygen and hydrogen isotope ratios in the α-cellulose from the latewood of annual

growth rings. Values of oxygen isotopes in cellulose are well predicted by a model

20   that takes into account the origin of water used by the tree and isotopic fractionation

in leaf water and in the cambium during cellulose synthesis. However, the model

requires knowledge of the source water used by trees, which for the trees in this study

is a mixture of groundwater and precipitation. It follows that if the model is to be

used to derive oxygen isotope values in precipitation from isotope ratios of tree ring

25   cellulose, then knowledge of this mixing is required. This has implications when

using ancient timber samples for environmental reconstruction, as there may be little

or no information on the extent to which the trees from which the samples came

sampled groundwater. This suggests that shallow rooted trees, such as pine and

beech, may be more suitable than oak for reconstructing isotope ratios of

5   precipitation, as for these species, precipitation is likely to be a much greater

component of their source water than it is for oak. When an analogous model is

applied to hydrogen isotopes, it predicts the average value of δD_{cell} well but, unlike

the case for oxygen isotopes, the model does not predict the pattern of annual

variation. We suggest, that for hydrogen isotopes, the existing model may be

10   deficient in that it does not take into account changing intramolecular distributions of

hydrogen isotopes within the glucose unit. A more complete knowledge of this effect

may thus be necessary to obtain full environmental information from measurements of

δD_{cell}.

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Table 1 - Correlation coefficients (*r*) between oxygen and hydrogen isotope ratios of

tree ring cellulose and temperature for the years 1895 - 1994 and 13.00h GMT

relative humidity for the years 1920 - 1994.

	$\delta^{18}O$	δD
July - August temperature (1895-1994)	0.34*	0.37[#]
July - August relative humidity (1920-1994)	-0.48*	-0.46[*]

5   Significance levels: *$P<0.001$, [#]$P<0.01$.

Table 2 - Correlation coefficients (*r*) between oxygen isotope ratios of cellulose for

tree SP 19 and precipitation for specified months for the period 1982 - 1994.

Month	*r*	Month	*r*
October[a]	0.30	April	-0.02
November[a]	0.09	May	0.71[#]
December[a]	0.28	June	0.60[†]
January	0.53[‡]	July	0.52[‡]
February	0.01	August	-0.09
March	0.64[†]	May – June[b]	0.82*

10   [a] Previous calendar year. [b] Isotope ratios of precipitation for the months of May - June

for each year were calculated as a weighted means of the precipitation amount for the

individual months. Significance levels: *$P<0.001$, [#]$P<0.01$, [†]$P<0.05$, [‡]$P<0.1$

Figure Captions

Fig. 1. The relationship between oxygen isotope ratios in precipitation ($\delta^{18}O_{mw}$) and

5   in the α-cellulose ($\delta^{18}O_{cell}$) from latewood of *Quercus robur* SP19 from Sandringham

Park for the period 1982 - 1994. Isotope ratios in precipitation are an average for the

months of May-July, weighted for the amount of precipitation in each month. Error

bars on observed values of $\delta^{18}O_{cell}$ are for a standard deviation of 0.2‰

10

Fig. 2. Observed (●) and calculated values of oxygen isotope ratios ($\delta^{18}O_{cell}$) of α-

cellulose from latewood of *Quercus robur* SP19 from Sandringham Park. Calculated

15   values (Equation 3) are for different values of f_o, the fraction of oxygen atoms that

exchange with water in the trunk during cellulose synthesis, and ε_0, the biochemical

fractionation factor for oxygen:

$\varepsilon_0 = 27$‰, $f_o = 0$ ◇ ; $\varepsilon_0 = 27$‰, $f_o = 0.42$ △ ; $\varepsilon_0 = 30$‰, $f_o = 0.42$ ○.

Error bars on observed values of $\delta^{18}O_{cell}$ are for a standard deviation of 0.2‰

20

Fig. 3. Observed (●) and calculated values (Equation 3, $\varepsilon_o = 30$‰) of oxygen isotope

ratios ($\delta^{18}O_{cell}$) of cellulose in the latewood of *Quercus robur* SP19 from

Sandringham Park. The value of f_o is taken as 0.46 for each modelled value of $\delta^{18}O_{cell}$.

Calculated values are for the different times for which relative humidity is taken:

10.00h, ○; 13.00h, △; 18.00h, □. All times are GMT. Error bars on observed values

of $\delta^{18}O_{cell}$ are for a standard deviation of 0.2‰

5

Fig. 4. Observed (●) and calculated values of hydrogen isotope ratios (δD_{cell}) of

cellulose in the latewood of *Quercus robur* SP19 from Sandringham Park. Calculated

values (Equation 3) are for different values of f_H, the fraction of hydrogen atoms that

10   exchange with water in the trunk during cellulose synthesis:

$f_H = 0.40$ △ ; $f_H = 0.46$ ○ ; $f_H = 0.50$ □ .

Values of relative humidity are taken at 10.00h GMT. Error bars on observed values

of δD_{cell} are for a standard deviation of 2‰.