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Short-lived juvenile effects observed in stable carbon and oxygen isotopes of UK oak trees and historic building timbers



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ABSTRACT

Stable carbon (δ^{13} C) and oxygen (δ^{18} O) isotope ratios were measured on the latewood α -cellulose of individual oak (Quercus robur L, Q. petraea Liebl.) samples from living trees and historic building timbers. This represents the type of material available to produce long tree-ring chronologies for north-western Europe including the UK and Ireland. Results from the juvenile rings, those located closest to the pith, were compared with results from equivalent sections (representing the same calendar years) from independent master isotope chronologies that do not contain any juvenile wood, allowing any juvenile offsets and trends to be separated from those caused by environmental change. Oak timbers from archaeological sources are often relatively short (< 100 years). Therefore, removing the first 50 rings, as is typical for Pinus sp., would severely constrain the material available for chronology construction. The aim of this study was to determine the magnitude and duration of juvenile effects, including the detection of trends, offsets and their influence upon signal strength. The results show clearly that juvenile effects for oak from central England are very small and short-lived and that removing merely the first five rings closest to the pith is sufficient to avoid them. This result greatly increases the potential for building long and well-replicated stable isotope chronologies using archived oak samples from historic building timbers, allowing high-resolution climate reconstructions to be produced for the highly-populated regions, where oak is abundant and which are currently under-represented in regional palaeoclimate reconstructions.

1. Introduction

In the climatically-temperate, low-altitude, mid-latitude regions of Europe, where deciduous oak trees (*Quercus robur* L, *Q. petraea* Liebl.) are common, ring widths have been measured and cross-dated to produce very long dendrochronologies, principally for archaeological dating and radiocarbon calibration (Baillie, 1973; Pilcher et al., 1984; Kelly et al., 1989; Becker, 1993; Friedrich et al., 2004). Although the series from which they are compiled share common environmental information that permits dendrochronological cross-dating, the absence of a single, stable, growth-limiting climate variable means that unfortunately, climate signals preserved in the ring widths are generally weak, difficult to characterise and rarely meet the strict calibration and verification criteria required for the reliable reconstruction of past climate (NRC, 2006; McCarroll et al., 2015). Stable isotopes of carbon and oxygen within the latewood cellulose of oak tree-rings, however, have been shown to contain stronger climate signals than tree-ring width (Loader et al., 2008). It has therefore been argued that it may be possible to use stable isotopes to reconstruct past changes in both: summer sunshine and/or temperature (Etien et al., 2009; Hilasvuori and Berninger, 2010); and the oxygen isotope ratios of summer rainfall, which in some areas are strongly correlated with total summer rainfall amount (Masson-Delmotte et al., 2005; Danis et al., 2006; Rinne et al., 2013; Young et al., 2015; Labuhn et al., 2016). Reliable reconstructions of past climate from samples collected and archived across the distribution of oak could therefore greatly improve regional and hemispheric-scale palaeoclimate reconstructions, which are currently strongly biased towards high-latitude and high-altitude sites (Luterbacher et al., 2016; Wilson et al., 2016).

The climate of the past few hundred years can be reconstructed using samples taken from living oak trees. However, extending records back further requires the use of oak building timbers and sub-fossil material. Oak building timbers are relatively abundant in the historic building and archaeological records and many have already been cored

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and securely dated (e.g. Miles, 2006). Cores can, with great care, be sub-sampled for isotopic analysis by removing a thin slice whilst retaining the original measurement surface as a dendrochronological archive. In order to obtain true annual resolution, stable isotope analysis is conducted on the latewood rather than the whole ring (McCarroll et al., 2017), because in ring-porous species such as oak the earlywood is formed primarily from reserves. Although there are long, slow-grown series of oak available for extensive periods, the rings are often very narrow with little latewood, presenting a serious challenge for the development of stable isotope chronologies.

An important consideration when using a combination of living trees and building timbers to develop isotope chronologies is the effect of juvenile wood, which in this context refers to the inner rings, closest to the pith. In the living trees, which are cored at breast height, the rings near the pith were formed when the tree was young. In timbers, where the vertical position on the tree cannot be defined, the age of the tree when the near-pith rings formed is unknown.

Growth or response to environmental variables of juvenile wood may be atypical when compared to more mature rings (Loader et al., 2007). In developing isotope chronologies for palaeoclimate reconstruction it is common practice to exclude the inner rings to avoid potential 'juvenile effects' (Tans and Mook, 1980; Loader et al., 2003; Sidorova et al., 2009; Hafner et al., 2014; Kress et al., 2014; Liu et al., 2014; Young et al., 2015). The number of rings excluded from analysis is commonly set at 30 (Labuhn et al., 2014) or even as high as 50 (Gagen et al., 2008). Applying such a protocol to build short chronologies using living oak trees, with hundreds of rings, is not problematic. It would, however, be a serious constraint for the construction of isotope chronologies from historic oak building timbers, which rarely contain so many suitable rings. Analysis would be restricted to the largest timbers or would rely on combining many short fragments from smaller timbers, an approach which is highly resource-intensive. Given such restrictions, many of the best-replicated historic tree-ring archives would struggle to provide sufficient usable material to build robust chronologies beyond the last few hundred years.

1.1. The 'juvenile effect' in tree-ring stable isotopes

Some of the earliest studies of stable isotopes in tree-rings reported anomalous values in the rings closest to the pith (Craig, 1954; Jansen, 1962). Typically, a rising trend in carbon isotope values and increasing inter-series coherence with tree-ring number (cambial age) has been observed (Freyer, 1979a, 1979b; Francey, 1981; Freyer and Belacy, 1983; Leavitt and Long, 1985). Studies that have focussed specifically on juvenile effects or age-related trends have tended to concentrate on stable carbon isotopes (e.g. Bert et al., 1997; Duquesnay et al., 1998; Arneth et al., 2002; Raffalli-Delerce et al., 2004; Li et al., 2005; Gagen et al., 2007, 2008; Buhay et al., 2008; Daux et al., 2011; Young et al., 2011a; Helama et al., 2015). A more limited body of research has also been undertaken on stable oxygen isotopes (e.g. Raffalli-Delerce et al., 2004; Treydte et al., 2006; Young et al., 2011a; Labuhn et al., 2014; Kilroy et al., 2016) and hydrogen isotopes (Mayr et al., 2003).

The majority of detailed studies investigating non-climatic, age-related trends have been conducted on conifers, growing slowly in regions close to their ecological limits. Gagen et al. (2008), for example, studied the juvenile effect in carbon isotopes in Scots pine trees (*Pinus sylvestris* L.) growing at the boreal treeline, north of the Arctic Circle in Fennoscandia and concluded that a non-climatic trend was detectable for up to 50 years. Evidence from deciduous trees is sparse, however, Labuhn et al. (2014) and Raffalli-Delerce et al. (2004) report juvenile trends in *Quercus spp.*, although the latter was only in one from a sample of four trees. Duquesnay et al. (1998) identified juvenile trends in Beech (*Fagus sylvatica* L), Daux et al. (2011) found no juvenile effect in carbon isotopes of larch trees (*Larix decidua* Mill) in France and this conclusion has been supported by measurements on larch in the UK (Kilroy et al., 2016).

Although there is very limited information available on the nature and duration of juvenile effects in oaks, it has become common practice to assume that they exist and sample accordingly. Measuring the stable isotopes in all available rings and applying curve-fitting methods to remove age trends is a realistic option (Buhay et al., 2008; Gagen et al., 2008), however, it has not been widely adopted. One of the great advantages of stable isotopes in tree-rings is that, in many cases, they appear to contain no long-term trends and thus require no statistical detrending, thereby avoiding the potential loss of low-frequency climate signals that can apply to other tree-ring proxies (Gagen et al., 2007; Young et al., 2011a; Loader et al., 2013). De-trending by statistical curve-fitting to remove juvenile effects would remove this advantage. Measuring the isotope values and discarding those that are identified as juvenile (Raffalli-Delerce et al., 2004; Li et al., 2005; Gagen et al., 2007; Labuhn et al., 2014) also is not an attractive option, given the effort and cost involved in isotope analysis, and cannot be applied when wood from several trees is pooled prior to isolation of cellulose and mass spectrometry. The most common approach, for all species, is to simply not use the rings close to the pith. However, given the large uncertainty in the length of the juvenile effect, ranging from absent (Daux et al., 2011; Kilroy et al., 2016), about 20 years (Arneth et al., 2002; Raffalli-Delerce et al., 2004; Daux et al., 2011), around 30 to 50 years (Bert et al., 1997; Duquesnay et al., 1998; Li et al., 2005; Gagen et al., 2007, 2008; Labuhn et al., 2014), or even potentially much longer (Treydte et al., 2006; Esper et al., 2010; Helama et al., 2015), there is little clear guidance available on how many 'juvenile' rings should be avoided.

The purpose of this study is to investigate potential juvenile effects in oak, using a combination of living oak trees and historic building timbers that typify the material available to produce long isotope chronologies for the central England region of the UK. The central aim is to define the number of juvenile rings that need to be removed in order to produce reliable chronologies for palaeoclimate reconstruction. The isotope ratios of carbon and oxygen obtained from the latewood cellulose of individual samples, that contain the earliest formed tree rings, are compared with 'master chronologies' produced by combining the wood of several samples that have had the earliest rings removed, prior to isolation of cellulose and mass spectrometry. By compiling the differences in behaviour of individual samples from their equivalent parts of the master chronology it is possible to exclude the effects of environmental change, isolating only potential juvenile effects, allowing their magnitude and duration to be clearly defined.

2. Methods

The trees and historic building timbers used to produce the individual test series were sampled from across an area of central England (covering approximately 15,000 km², from c.52^oN–51^oN, 2^oW–1^oW). The ten test series are single cores from ten different trees and timbers. The master chronologies were constructed using trees and historic building timbers from sites across the UK (Supplementary Fig. 1). The average location of the master sites is 51.9^oN, 1.6^oW and the average of the test trees is 51.6^oN, 1.13^oW, which is a difference of c. 50 km.

Living trees were cored at a height of 1.2 m using standard methods and building timbers were obtained as sub-sampled cores from the Oxford Dendrochronology Laboratory archive. For the archived material, a softwood mount was glued to one edge of the core. A 1 mm thick slice was sawn from the top to preserve an archive record of the core and the newly sawn surface was sanded with progressively finer sanding belts on a bench-mounted linisher. Calendar dates were then marked off at decade intervals on the mount and the sample was again sectioned to about 4 mm thickness and re-sanded on the leading edge in preparation for stable isotope analysis.

All wood material was cross-dated (Stokes and Smiley, 1968) and compared with regional chronologies to assign precise ages. The latewood of each tree-ring was removed using a scalpel under a microscope as thin slivers (c.40 μ m thick). Samples were purified to α -cellulose

Table 1

A summary of ten tree-ring $\delta^{13}C$ and $\delta^{18}O$ series sampled from oak trees and historical building timbers (Quercus robur L, Q. petraea Liebl.) from Central England, UK.

Tree code	Location	Living or timber	Series length (years)	Calendar period (AD)	δ ¹³ C (‰)		δ ¹⁸ Ο (‰)	
					Mean	Range	Mean	Range
BAD83	Baddesley Clinton	Timber	50	1711–1760	- 24.88	2.75	28.01	3.37
HVL3	Ludgershall	Timber	50	1721–1770	- 24.29	3.05	29.13	3.42
HN10a	Oakhouse Drive Cottages	Timber	41	1726–1766	-24.78	2.85	28.74	3.60
MM51	Mapledurham Mill	Timber	50	1740–1789	-24.24	3.49	28.77	4.27
MAP1	Mapledurham	Living	50	1761–1810	-23.28	2.67	30.35	4.73
OOP1	Blenheim Park	Living	40	1791–1830	- 24.85	3.45	28.63	3.13
MAP71	Mapledurham	Living	50	1816–1865	-24.50	3.37	29.42	4.88
MAP78	Mapledurham	Living	49	1824–1873	- 24.57	1.89	29.34	4.14
HWK110	Hardwick Estate	Living	50	1838–1887	-24.80	2.01	28.91	4.58
BDM01	Broadmoor	Living	50	1958-2007	- 24.89	3.57	30.56	5.11

using standard methods (Green, 1963; Loader et al., 1997), homogenised and then freeze dried for 48 h at -50 °C < 50 mbar. Between 0.30 and 0.35 mg of α -cellulose were weighed into silver capsules for pyrolysis over glassy carbon at 1400 °C and simultaneous measurement of carbon and oxygen isotope ratios using a Flash HT elemental analyser interfaced with a Thermo Delta V isotope ratio mass spectrometer. The analytical precision determined from a standard laboratory α -cellulose (Sigma Aldrich UK (No. C-8002 Lot. 92F-0243)) was 0.15‰ for δ^{13} C and 0.3‰ for δ^{18} O ($\sigma_{n-1} n = 10$) (Loader et al., 2016). This method has been shown to provide a precise and cost effective approach to carbon and oxygen isotopic analysis of cellulose (Young et al., 2011b).

Test samples were processed individually. The master chronologies comprise the chronology described by Young et al. (2015) supplemented with the latewood of 10 trees, all from Central England, which was pooled and processed prior to the isolation of cellulose. Between CE 1700 and 2012 the master chronologies have a minimum sample depth of 13 trees and an average sample depth of 32 trees (Supplementary Fig.2). Each sample was ultrasonically homogenised to ensure a wellmixed and representative cellulose product of combined material from multiple trees (Laumer et al., 2009). Carbon and oxygen isotope ratios are reported in per mille (‰) using the usual delta (δ) notation relative to the VPDB (δ^{13} C) and VSMOW (δ^{18} O) standards (Coplen, 1995). Prior to statistical analyses the carbon isotope ratios were corrected for changes in the isotope ratios in atmospheric carbon dioxide by simple addition as described by McCarroll and Loader (2004). Carbon isotopes from UK oaks do not appear to require any further correction for the direct effect of increases in the amount of carbon dioxide in the atmosphere (McCarroll et al., 2009; Young et al., 2012). Oxygen isotope values require no numerical pre-treatment.

Identifying the magnitude and duration of the juvenile effect in individual trees is difficult because the effect of tree age cannot easily be separated from the effect of environmental changes that may have occurred when rings close to the pith were formed. A common approach, therefore, is to take several trees and arrange them according to cambial age, rather than calendar year and examine the average behaviour. The rationale behind this approach is that averaging by ring number rather than calendar year effectively removes the influence of environmental change. However, this is only true if the sample is sufficiently large and comprises trees of very different age (Esper et al., 2002; Gagen et al., 2008). Such a sampling scheme should result in a mean curve that rises (or falls) during the juvenile phase (where present) and subsequently remains perfectly flat. In reality it is difficult to obtain a sample that is sufficiently large and disparate in age. Therefore, even in the best-replicated studies, the average retains some variability that is an artefact of environmental change. In such circumstances it remains difficult to separate, with confidence, the effects of age and environment.

In this study the problems of sample size and heterogeneity of age structure are overcome by adopting a novel approach, based on comparing isotope series from ten individual trees or timbers with master chronologies for both carbon and oxygen isotopes. Critically, the master chronologies were produced entirely from wood that is non-juvenile so that the average isotope results from the individual juvenile trees may be compared with those from the equivalent sections of the master chronologies. The isotope series from each individual juvenile tree can now be compared with the master chronology by calendar age (Supplementary Figs. 2, 3 and 4). The advantage is that the influence of environmental changes is present in both the individual series and the equivalent master chronology segment, but only the individuallymeasured trees contain juvenile wood. Differences between the individual trees and their equivalent sectors of the master chronologies can then be compiled to produce sets of data that represent the average difference in behaviour of juvenile and non-juvenile wood compared over the same calendar years, effectively isolating the effect of tree age from environmental change.

This approach is applied here to investigate three potential problems of juvenile wood and specifically to define how many juvenile rings need to be removed to ensure that a mean isotope record is not influenced by juvenile effects. The three potential problems of trends, offsets and signal strength are addressed.

3. Results

Summary statistics for the individual stable isotope time series are presented in Table 1 and the full data sets are included in the Supplementary material (Tables 1 to 4). The average behaviour of the individual trees when aligned by cambial age (ring number) and of the equivalent sections of the master chronology (controls) are presented in Fig. 1. It is clear that the oxygen isotope results from the individual (juvenile) samples and controls are very similar, even for the rings very close to the pith. The mean carbon isotope ratios of the first five rings are slightly higher than the control but the control values lie very close to or within the 95% confidence intervals around the mean.

Rising or falling trends that last for up to a few decades are to be expected in any of the palaeoclimate proxies derived from tree rings, including stable isotopes, because the environmental (climatic) controls are not constant through time. Here, trends due to environmental changes are separated from juvenile trends by comparing the average behaviour of the isotope ratios in the juvenile wood with the average behaviour in the equivalent sections of the master chronology.

For each individual tree, and equivalent section of the master chronology, simple linear trends were examined using the relationship between stable isotope ratio and ring number (Pearson's correlation coefficient). 30-year and 20-year correlation windows were applied, starting with ring 1, adjacent to the pith, and then shifted sequentially by one year until the end of the segment. For example, a tree that has a 50-year segment length has the correlation measurement repeated 21 times using the 30-year window and 31 times using the 20-year window. If there are strong juvenile effects that persist for more than two or three decades (e.g. Daux et al., 2011), statistically significant



Fig. 1. Mean isotope ratios of the ten individual trees (filled circles, solid line) aligned by ring number, with 95% confidence limits (grey lines), compared with the mean of the ten equivalent sections of the master chronology (open circles, dashed line). Note that the variability of the mean of the master chronology segments is muted because each segment effectively represents the mean of at least ten trees (pooled).

trends would be expected in the early windows for the individual trees but not in those of the master chronology controls.

The average correlation coefficients for the individual trees and the master chronology segments, which here act as a control, are plotted in Fig. 2, with 95% confidence limits. Although the average absolute correlation coefficient for the individual (juvenile) trees is slightly higher than the control for both isotopes in the earliest windows, none of the mean values are statistically significant and even the largest difference, between the first 20-year window for carbon (r = -0.32, p = 0.17) and the equivalent control (r = 0.05, p = 0.83) is not statistically significant (z-test for two correlation coefficients, z = -1.11, p = 0.27). The most consistent trends occur in the carbon isotope

ratios, where the earliest correlation windows give mean correlation coefficients that are negative and 95% confidence limits that fall below zero. When the windows are shifted, so that just the first three or four rings are excluded, the correlation coefficients are close to zero and thereafter they follow closely the correlation profile of the control. In the earliest windows the oxygen isotopes give low positive correlation coefficients, but they are far from statistically significant.

These results suggest that two or three-decade long juvenile trends do not occur in either isotope series. The first few rings of the carbon isotope series tend to be slightly but consistently higher (approximately 1‰), which imparts a negative trend when they are included, but excluding just the two or three rings closest to the pith is sufficient to remove the effect entirely, bringing age-related trends in these samples very close to zero. If the correlation coefficients are replaced with the slope coefficients the results are nearly identical (Supplementary Fig. 5).

If juvenile tree-rings have isotope ratios that are anomalously low or high, the inclusion of juvenile rings in a mean (or pooled) chronology could result in an offset in the mean isotope ratios. To test this, isotope results obtained from each individual tree are compared with the equivalent sections of the master chronology. Isotopic off-sets between individual trees are expected (Leavitt and Long, 1984; Leavitt, 2010), so isotope ratios of individual trees are not expected to have the same mean as the master chronology. The important question is whether the magnitude of any offset changes systematically with ring number, which would be the expectation if there was a strong juvenile effect. This is tested by comparing the difference between ring 1 and the equivalent calendar year in the master chronology with the average difference for the remainder of the series, then repeating this procedure for each consecutive ring up to ring 30. The results for all ten trees can then be compiled to show the average behaviour of the juvenile rings, together with 95% confidence limits around the mean.

The results show that the carbon isotope ratios in the five youngest rings of the individual trees are slightly offset (less depleted) relative to the equivalent sectors of the master, but in all but one case (ring 5) the 95% confidence limits cross zero (Fig. 3). The oxygen isotope results show a small negative offset in rings 1 to 3 and 6 to 8 but throughout the series the 95% confidence limits cross zero, so the offsets are not statistically significant. For both isotopes it is clear that the variability of the offsets, as shown by the 95% confidence limits, declines over the first few years. These results indicate that average juvenile offsets in both isotopes are very small, variable and short-lived.

Although studies of the juvenile effect in tree-ring isotopes are

Fig. 2. Mean correlation coefficients (Pearson's r) for 20year and 30-year windows run sequentially through the isotope series. Test series (ten-tree mean) are filled circles joined by solid lines, with solid grey 95% confidence limits around the mean. Equivalent master series controls (tenseries mean) are open circles with dashed lines. The horizontal dashed black lines represent the positive and negative critical values for a correlation coefficient (two tail, p = 0.05).





Fig. 3. Mean difference between each ring and the equivalent ring in the master chronology expressed relative to the average of those differences for the rest of the sequence. For a 50-year sequence, for example, the point at ring number ten represents the mean differences of the tenth ring in each individual sample from the equivalent rings (same calendar year) in the master chronology expressed relative to the average difference between each sample and the equivalent master segment for rings 11 to 50. The dashed lines are 95% confidence limits around the mean.

normally confined to the impact on slope and offset, the availability of a master chronology allows us to consider whether the potential signal quality is also affected. When tree-ring isotope values are compiled to produce a mean chronology (by measuring individual values or by pooling), the aim is to enhance the common environmental signal whilst cancelling some of the individual noise. A stronger correlation between individual trees will lead to a stronger common signal (Wigley et al., 1984).

A running 20-year correlation (Pearson's r) was calculated between each tree and the equivalent section of the master, starting with rings one to twenty and removing one juvenile ring at each step. The mean correlation coefficient together with 95% confidence intervals is plotted (Fig. 4) together with the critical threshold for statistical significance (one tail p = 0.05). The results clearly show that the common signal in oxygen is much stronger than in carbon. For oxygen the mean correlation values are consistently high, and far exceed the critical value even if no rings are removed. For carbon isotopes, removing four rings is sufficient to raise the mean correlation above the critical threshold.

4. Discussion and conclusions

The inner rings of trees and timbers are often avoided when developing stable isotope chronologies, due to concerns that juvenile effects might cause spurious trends or offsets in the mean chronology or that the climate signal might be weakened. Our results suggest that for the oak material studied here, sourced from central England and comprising both living trees and historic building timbers, these concerns are unwarranted. Juvenile effects in both carbon and oxygen isotopes appear to be very small in magnitude and very short in duration.

In contrast to work on treeline conifers (Gagen et al., 2008), we find no evidence for juvenile trends or offsets that persist for decades. For



Fig. 4. Mean running 20 yr correlation between each tree and the equivalent section of the master chronology. Dotted lines are the 95% confidence limits around the mean. The horizontal dashed line is the one-tail critical value for significance of Pearson's correlation coefficient with a sample size of twenty.

the carbon isotopes, in the oak trees we studied, it is only the first four or five rings that show any evidence of a juvenile offset or trend, and even that is negligible (< 0.5% on average). For the oxygen isotopes, juvenile trends and offsets are similarly small and last for, at most, ten years. The 'juvenile' effects in oaks from the central England region appear to be so negligible that they would effectively have no effect on mean isotope chronologies produced for palaeoclimatic reconstruction, when averaged with 10–20 trees of mixed age. Avoiding the first five rings, closest to the pith, is certainly sufficient to avoid any detectable influence in a mean chronology based on ten trees.

The decline in carbon isotope ratios in the rings closest to the pith is particularly unexpected, and in the opposite direction to that which would occur, for example, due to recycling of respired carbon dioxide (Schleser and Jayasekera, 1985), or to increasing hydraulic resistance with rising tree height (McDowell et al., 2002). Declining δ^{13} C implies a trend towards less fractionation, which means rising internal concentrations of CO₂, which might be caused by either a rise in stomatal conductance or a decline in photosynthetic rate (or both). The slight rise in δ^{18} O would imply a slight increase in evaporative enrichment, so rising stomatal conductance seems the most likely driver. In this case the cause of rising stomatal conductance would have to be a fall in hydraulic resistance rather than a rise in air humidity, because the latter would cause oxygen isotope ratios to decline. One possible explanation is that water supply to the leading branch, at the highest point on the tree, is slightly constricted but that with the addition of just a few rings the extra hydraulic resistance is relieved. Experiments are now underway to test this hypothesis, which cannot be tested using the data collected for the present study.

The results presented here suggest that it is possible to build reliable stable isotope chronologies using a combination of living trees and building timbers sourced from across much of the central England region of the UK, without the constraint of avoiding large numbers of rings close to the pith. Avoiding the first five rings is sufficient. This greatly reduces the work required to source, date and prepare the archaeological building timber samples required to extend well replicated isotope records beyond the last few hundred years, when living trees are available. Building long and well-replicated isotope chronologies will facilitate the production of high-resolution palaeoclimate reconstructions from oaks in England. We recommend that similar tests be applied to oak timber archives, collected for archaeological dating purposes, elsewhere across the temperate climatic regions of the lowaltitude mid-latitudes, where deciduous oak trees, and people, are abundant but reliable palaeoclimate records are currently sparse.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx. doi.org/10.1016/j.chemgeo.2017.09.007.

References

- Arneth, A., Lloyd, J., Santruckova, H., Bird, M., Grigoryev, S., Kalaschnikov, Y.N., Gleixner, G., Schulze, E.D., 2002. Response of central Siberian scots pine to soil water deficit and long term trends in atmospheric CO₂ concentration. Glob. Biogeochem. Cycles 16, 1.
- Baillie, M.G.L., 1973. A recently developed Irish tree-ring chronology. Tree-Ring Bull. 33, 15–28.
- Becker, B., 1993. An 11, 000-year German oak and pine dendrochronology for radiocarbon calibration. Radiocarbon 35, 201–213. http://dx.doi.org/10.2458/azu_js_rc. 35.1560.
- Bert, D., Leavitt, S.W., Dupouey, J.-L., 1997. Variations of wood Δ¹³C and water-use efficiency of *Abies alba* during the last century. Ecology 78, 1588–1596. http://dx.doi. org/10.1890/0012-9658(1997)078[1588:VOWCAW]2.0.CO;2.
- Buhay, W.M., Timsic, S., Blair, D., Reynolds, J., Jarvis, S., Petrash, D., Rempel, M., Bailey, D., 2008. Riparian influences on carbon isotopic composition of tree rings in the Slave River Delta, Northwest Territories, Canada. Chem. Geol. 252, 9–20. http://dx.doi. org/10.1016/j.chemgeo.2008.01.012.
- Coplen, T.B., 1995. Discontinuance of SMOW and PDB. Nature 375, 285-285. http://dx. doi.org/10.1038/375285a0.
- Craig, H., 1954. Carbon-13 variations in sequoia rings and the atmosphere. Science 119, 141–143. http://dx.doi.org/10.1126/science.119.3083.141.
- Danis, P.A., Masson-Delmotte, V., Stievenard, M., Guillemin, M.T., Daux, V., Naveau, P., von Grafenstein, U., 2006. Reconstruction of past precipitation δ^{18} O using tree-ring cellulose δ^{18} O and δ^{13} C: a calibration study near lac d'Annecy, France. Earth Planet. Sci. Lett. 243, 439–448. http://dx.doi.org/10.1016/j.epsl.2006.01.023.
- Daux, V., Edouard, J.L., Masson-Delmotte, V., Stievenard, M., Hoffmann, G., Pierre, M., Mestre, O., Danis, P.a., Guibal, F., 2011. Can climate variations be inferred from treering parameters and stable isotopes from *Larix decidua*? Juvenile effects, budmoth outbreaks, and divergence issue. Earth Planet. Sci. Lett. 309, 221–233. http://dx.doi. org/10.1016/j.epsl.2011.07.003.
- Duquesnay, A., Bréda, N., Stievenard, M., Dupouey, J.L., 1998. Changes of tree-ring δ¹³C and water-use efficiency of beech (*Fagus sylvatica* L.) in north-eastern France during the past century. Plant Cell Environ. 21, 565–572. http://dx.doi.org/10.1046/j.1365-3040.1998.00304.x.
- Esper, J., Cook, E.R., Schweingruber, F.H., 2002. Low-frequency signals in long tree-ring chronologies for reconstructing past temperature variability. Science 295, 2250–2253. http://dx.doi.org/10.1126/science.1066208.
- Esper, J., Frank, D.C., Battipaglia, G., Büntgen, U., Holert, C., Treydte, K., Siegwolf, R., Saurer, M., 2010. Low-frequency noise in 8¹³C and 8¹⁸O tree ring data: a case study of *Pinus uncinata* in the Spanish Pyrenees. Glob. Biogeochem. Cycles 24, 1–11. http:// dx.doi.org/10.1029/2010GB003772.
- Etien, N., Daux, V., Masson-Delmotte, V., Mestre, O., Stievenard, M., Guillemin, M.T., Boettger, T., Breda, N., Haupt, M., Perraud, P.P., 2009. Summer maximum temperature in northern France over the past century: instrumental data versus multiple proxies (tree-ring isotopes, grape harvest dates and forest fires). Clim. Chang. 94, 429–456. http://dx.doi.org/10.1007/s10584-008-9516-8.
- Francey, R.J., 1981. Tasmanian tree rings belie suggested anthropogenic ¹³C/¹²C trends. Nature 290, 232–235. http://dx.doi.org/10.1038/290232a0.
- Freyer, H.D., 1979a. On the ¹³C record in tree rings. Part I. ¹³C variations in northern hemispheric trees during the last 150 years. Tellus 31, 124–137. http://dx.doi.org/ 10.1111/j.2153-3490.1979.tb00889.x.
- Freyer, H.D., 1979b. On the ¹³C record in tree rings. Part II. Registration of microenvironmental CO₂ and anomalous pollution effect. Tellus 31, 308–312. http://dx. doi.org/10.1111/j.2153-3490.1979.tb00909.x.

- Freyer, H.D., Belacy, N., 1983. ¹³C/¹²C records in northern hemispheric trees during the past 500 years—anthropogenic impact and climatic superpositions. J. Geophys. Res. 88, 6844. http://dx.doi.org/10.1029/JC088iC11p06844.
- Friedrich, M., Remmele, S., Kromer, B., Hofmann, J., Spurk, M., Felix, K., Christian, K., Manfred, O., 2004. The 12,460-year Hohenheim oak and pine tree-ring chronology from central Europe—a unique annual record for radiocarbon calibration and paleoenvironment reconstructions. Radiocarbon 46, 1111–1122.
- Gagen, M., McCarroll, D., Loader, N.J., Robertson, I., Jalkanen, R., Anchukaitis, K.J., 2007. Exorcising the 'segment length curse': summer temperature reconstruction since AD 1640 using non-detrended stable carbon isotope ratios from pine trees in northern Finland. The Holocene 17, 435–446.
- Gagen, M., McCarroll, D., Robertson, I., Loader, N.J., Jalkanen, R., 2008. Do tree ring 8¹³C series from *Pinus sylvestris* in northern Fennoscandia contain long-term nonclimatic trends? Chem. Geol. 252, 42–51. http://dx.doi.org/10.1016/j.chemgeo. 2008.01.013.
- Green, J.W., 1963. Methods of Carbohydrate Chemistry, 3rd ed. Academic Press, New York, NY.
- Hafner, P., McCarroll, D., Robertson, I., Loader, N., Gagen, M., Young, G., Bale, R., Sonninen, E., Levanič, T., 2014. A 520 year record of summer sunshine for the eastern European alps based on stable carbon isotopes in larch tree rings. Clim. Dyn. 1–10. http://dx.doi.org/10.1007/s00382-013-1864-z.
- Helama, S., Arppe, L., Timonen, M., Mielikäinen, K., Oinonen, M., 2015. Age-related trends in subfossil tree-ring 8¹³C data. Chem. Geol. 416, 28–35. http://dx.doi.org/10. 1016/j.chemgeo.2015.10.019.
- Hilasvuori, E., Berninger, F., 2010. Dependence of tree ring stable isotope abundances and ring width on climate in Finnish oak. Tree Physiol. 30, 636–647. http://dx.doi. org/10.1093/treephys/tpq019.
- Jansen, H.S., 1962. Depletion of carbon-13 in young Kauri tree. Nature 196, 84–85. http://dx.doi.org/10.1038/196084a0.
- Kelly, P.M., Munro, M.A.R., Hughes, M.K., Goodess, C.M., 1989. Climate and signature years in west European oaks. Nature 340, 57–60. http://dx.doi.org/10.1038/ 340057a0.
- Kilroy, E., McCarroll, D., Young, G.H.F., Loader, N.J., Bale, R., 2016. Absence of juvenile effects confirmed in stable carbon and oxygen isotopes of European larch trees. Acta Silvae Ligni 111, 27–33.
- Kress, A., Hangartner, S., Bugmann, H., Büntgen, U., Frank, D.C., Leuenberger, M., Siegwolf, R.T.W., Saurer, M., 2014. Swiss tree rings reveal warm and wet summers during medieval times. Geophys. Res. Lett. 41, 1732–1737. http://dx.doi.org/10. 1002/2013GL059081.Received.
- Labuhn, I., Daux, V., Girardclos, O., Stievenard, M., Pierre, M., Masson-Delmotte, V., 2016. French summer droughts since 1326 CE: a reconstruction based on tree ring cellulose δ¹⁸O. Clim. Past 12, 1101–1117. http://dx.doi.org/10.5194/cp-12-1101-2016.
- Labuhn, I., Daux, V., Pierre, M., Stievenard, M., Girardclos, O., Féron, A., Genty, D., Masson-Delmotte, V., Mestre, O., 2014. Tree age, site and climate controls on tree ring cellulose δ^{18} O: a case study on oak trees from south-western France. Dendrochronologia 32, 78–89. http://dx.doi.org/10.1016/j.dendro.2013.11.001.
- Laumer, W., Andreu, L., Helle, G., Schleser, G.H., Wieloch, T., Wissel, H., 2009. A novel approach for the homogenization of cellulose to use micro-amounts for stable isotope analyses. Rapid Commun. Mass Spectrom. 23, 1934–1940. http://dx.doi.org/10. 1002/rcm.
- Leavitt, S.W., 2010. Tree-ring C-H-O isotope variability and sampling. Sci. Total Environ. 408, 5244–5253. http://dx.doi.org/10.1016/j.scitotenv.2010.07.057.
- Leavitt, S.W., Long, A., 1984. Sampling strategy for stable carbon isotope analysis of tree rings in pine. Nature 311, 145–147. http://dx.doi.org/10.1038/311145a0.
- Leavitt, S.W., Long, A., 1985. The global biosphere as net CO₂ source or sink: evidence from carbon isotopes in tree rings. In: Caldwell, D.E., Brierly, J.A., Brierly, C.L. (Eds.), Planetary Ecology. Van Nostrand Reinhold Company, New York, pp. 89–99.
- Li, Z.H., Leavitt, S.W., Mora, C.I., Liu, R.M., 2005. Influence of earlywood-latewood size and isotope differences on long-term tree-ring δ¹³C trends. Chem. Geol. 216, 191–201. http://dx.doi.org/10.1016/j.chemgeo.2004.11.007.
- Liu, Y., Wang, Y., Li, Q., Song, H., Linderhlom, H.W., Leavitt, S.W., Wang, R., An, Z., 2014. Tree-ring stable carbon isotope-based May–July temperature reconstruction over Nanwutai, China, for the past century and its record of 20th century warming. Quat. Sci. Rev. 93, 67–76. http://dx.doi.org/10.1016/j.quascirev.2014.03.023.
- Loader, N.J., McCarroll, D., Gagen, M.H., Robertson, I., Jalkanen, R., 2007. Extracting climatic information from stable isotopes in tree rings. In: Dawson, T.E., Siegwolf, R.T.W. (Eds.), Stable Isotopes as Indicators of Ecological Change. Academic Press, London, pp. 27–45.
- Loader, N.J., Robertson, I., Barker, A., Switsur, V., Waterhouse, J.S., 1997. An improved technique for the batch processing of small wholewood samples to α -cellulose. Chem. Geol. 136, 313–317.
- Loader, N.J., Robertson, I., McCarroll, D., 2003. Comparison of stable carbon isotope ratios in the whole wood, cellulose and lignin of oak tree-rings. Palaeogeogr. Palaeoclimatol. Palaeoecol. 196, 395–407.
- Loader, N.J., Santillo, P.M., Woodman-Ralph, J.P., Rolfe, J.E., Hall, M.A., Gagen, M., Robertson, I., Wilson, R., Froyd, C.A., McCarroll, D., 2008. Multiple stable isotopes from oak trees in southwestern Scotland and the potential for stable isotope dendroclimatology in maritime climatic regions. Chem. Geol. 252, 62–71.
- Loader, N.J., Street-Perrott, F.A., Mauquoy, D., Roland, T.P., van Bellen, S., Daley, T.J., Davies, D., Hughes, P.D.M., Pancotto, V.O., Young, G.H.F., Amesbury, M.J., Charman, D.J., Mallon, G., Yu, Z.C., 2016. Measurements of hydrogen, oxygen and carbon isotope variability in sphagnum moss along a micro-topographical gradient in a southern Patagonian peatland. J. Quat. Sci. 31, 426–435. http://dx.doi.org/10.1002/ jos.2871.
- Loader, N.J., Young, G.H., McCarroll, D., Wilson, R.J., 2013. Quantifying uncertainty in

isotope dendroclimatology. The Holocene 23, 1221–1226. http://dx.doi.org/10. 1177/0959683613486945.

- Luterbacher, J., Werner, J.P., Smerdon, J.E., Fernández-Donado, L., González-Rouco, F.J., Barriopedro, D., Ljungqvist, F.C., Büntgen, U., Zorita, E., Wagner, S., Esper, J., McCarroll, D., Toreti, A., Frank, D., Jungclaus, J.H., Barriendos, M., Bertolin, C., Bothe, O., Brázdil, R., Camuffo, D., Dobrovolný, P., Gagen, M., García-Bustamante, E., Ge, Q., Gómez-Navarro, J.J., Guiot, J., Hao, Z., Hegerl, G.C., Holmgren, K., Klimenko, V.V., Martín-Chivelet, J., Pfister, C., Roberts, N., Schindler, A., Schurer, A., Solomina, O., von Gunten, L., Wahl, E., Wanner, H., Wetter, O., Xoplaki, E., Yuan, N., Zanchettin, D., Zhang, H., Zerefos, C., 2016. European summer temperatures since Roman times. Environ. Res. Lett. 11, 024001. http://dx.doi.org/10.1088/1748-9326/11/2/024001.
- Masson-Delmotte, V., Raffalli-Delerce, G., Danis, P.A., Yiou, P., Stievenard, M., Guibal, F., Mestre, O., Bernard, V., Goosse, H., Hoffmann, G., Jouzel, J., 2005. Changes in European precipitation seasonality and in drought frequencies revealed by a fourcentury-long tree-ring isotopic record from Brittany, western France. Clim. Dyn. 24, 57–69. http://dx.doi.org/10.1007/s00382-004-0458-1.
- Mayr, C., Frenzel, B., Friedrich, M., Spurk, M., Stichler, W., Trimborn, P., 2003. Stable carbon- and hydrogen-isotope ratios of subfossil oaks in southern Germany: methodology and application to a composite record for the Holocene. The Holocene 13, 393–402. http://dx.doi.org/10.1191/0959683603hl632rp.
- McCarroll, D., Gagen, M.H., Loader, N.J., Robertson, I., Anchukaitis, K.J., Los, S., Young, G.H.F., Jalkanen, R., Kirchhefer, A., Waterhouse, J.S., 2009. Correction of tree ring stable carbon isotope chronologies for changes in the carbon dioxide content of the atmosphere. Geochim. Cosmochim. Acta 73, 1539–1547. http://dx.doi.org/10.1016/ j.gca.2008.11.041.
- McCarroll, D., Loader, N.J., 2004. Stable isotopes in tree rings. Quat. Sci. Rev. 23, 771–801. http://dx.doi.org/10.1016/j.quascirev.2003.06.017.
- McCarroll, D., Whitney, M., Young, G.H.F., Loader, N.J., Gagen, M.H., 2017. A simple stable carbon isotope method for investigating changes in the use of recent versus old carbon in oak. Tree Physiol. http://dx.doi.org/10.1093/treephys/tpx030.
- McCarroll, D., Young, G.H., Loader, N.J., 2015. Measuring the skill of variance-scaled climate reconstructions and a test for the capture of extremes. The Holocene 25, 618–626. http://dx.doi.org/10.1177/0959683614565956.
- McDowell, N.G., Phillips, N., Lunch, C., Bond, B.J., Ryan, M.G., 2002. An investigation of hydraulic limitation and compensation in large, old Douglas-fir trees. Tree Physiol. 22 (11), 763–774.
- Miles, D., 2006. Refinements in the interpretation of tree-ring dates for oak building timbers in England and Wales. Vernac. Archit. 37, 84–96. http://dx.doi.org/10. 1179/174962906X158291.
- NRC, 2006. Surface Temperature Reconstructions for the Last 2,000 Years. National Academies Press, Washington, DC.
- Pilcher, J.R., Baillie, M.G.L., Schmidt, B., Becker, B., 1984. A 7,272-year tree-ring chronology for western Europe. Nature 312, 150–152. http://dx.doi.org/10.1038/ 312150a0.
- Raffalli-Delerce, G., Masson-Delmotte, V., Dupouey, J.L., Stievenard, M., Bréda, N., Moisselin, J.M., Munksgaard, B., 2004. Reconstruction of summer droughts using

tree-ring cellulose isotopes: a calibration study with living oaks from Brittany (western France). Tellus 56B, 160–174. http://dx.doi.org/10.1111/j.1600-0889.2004. 00086.x.

- Rinne, K.T., Loader, N.J., Switsur, V.R., Waterhouse, J.S., 2013. 400-Year May–August precipitation reconstruction for southern England using oxygen isotopes in tree rings. Quat. Sci. Rev. 60, 13–25. http://dx.doi.org/10.1016/j.quascirev.2012.10.048.
- Schleser, G.H., Jayasekera, R., 1985. Delta C-13-variations of leaves in forests as an indication of reassimilated CO₂ from the soil. Oecologia 65 (4), 536–542.
- Sidorova, O.V., Siegwolf, R.T.W., Saurer, M., Shashkin, A.V., Knorre, A.a., Prokushkin, A.S., Vaganov, E.a., Kirdyanov, A.V., 2009. Do centennial tree-ring and stable isotope trends of *Larix gmelinii* (Rupr.) Rupr. indicate increasing water shortage in the Siberian north? Oecologia 161, 825–835. http://dx.doi.org/10.1007/s00442-009-1411-0.
- Stokes, M.A., Smiley, T.L., 1968. An Introduction to Tree Ring Dating. University of Chicago Press, Chicago.
- Tans, P.P., Mook, W.G., 1980. Past atmospheric CO₂ levels and the C¹³/C¹² ratios in tree rings. Tellus 32, 268–283.
- Treydte, K.S., Schleser, G.H., Helle, G., Frank, D.C., Winiger, M., Haug, G.H., Esper, J., 2006. The twentieth century was the wettest period in northern Pakistan over the past millennium. Nature 440, 1179–1182. http://dx.doi.org/10.1038/nature04743.
- Wigley, T.M.L., Briffa, K.R., Jones, P.D., 1984. On the average value of correlated time series, with applications in dendroclimatology and hydrometeorology. J. Clim. Appl. Meteorol. http://dx.doi.org/10.1175/1520-0450(1984)023 < 0201:OTAVOC > 2.0. CO:2.
- Wilson, R., Anchukaitis, K., Briffa, K.R., Büntgen, U., Cook, E., D'Arrigo, R., Davi, N., Esper, J., Frank, D., Gunnarson, B., Hegerl, G., Helama, S., Klesse, S., Krusic, P.J., Linderholm, H.W., Myglan, V., Osborn, T.J., Rydval, M., Schneider, L., Schurer, A., Wiles, G., Zhang, P., Zorita, E., 2016. Last millennium northern hemisphere summer temperatures from tree rings: part I: the long term context. Quat. Sci. Rev. http://dx. doi.org/10.1016/j.quascirev.2015.12.005.

Young, G.H.F., Bale, R.J., Loader, N.J., McCarroll, D., Nayling, N., Vousden, N., 2012. Central England temperature since AD 1850: the potential of stable carbon isotopes in British oak trees to reconstruct past summer temperatures. J. Quat. Sci. 27, 606–614.

- Young, G.H.F., Demmler, J.C., Gunnarson, B.E., Kirchhefer, A.J., Loader, N.J., McCarroll, D., 2011a. Age trends in tree ring growth and isotopic archives: a case study of *Pinus* sylvestris L. from northwestern Norway. Global Biogeochem. Cycle 25, 1–6. http://dx. doi.org/10.1029/2010GB003913.
- Young, G.H.F., Loader, N.J., McCarroll, D., 2011b. A large scale comparative study of stable carbon isotope ratios determined using on-line combustion and low-temperature pyrolysis techniques. Palaeogeogr. Palaeoclimatol. Palaeoecol. 300, 23–28. http://dx.doi.org/10.1016/j.palaeo.2010.11.018.
- Young, G.H.F., Loader, N.J., McCarroll, D., Bale, R.J., Demmler, J.C., Miles, D., Nayling, N.T., Rinne, K.T., Robertson, I., Watts, C., Whitney, M., 2015. Oxygen stable isotope ratios from British oak tree-rings provide a strong and consistent record of past changes in summer rainfall. Clim. Dyn. http://dx.doi.org/10.1007/s00382-015-2559-4.