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Multiple stable isotopes from oak trees in southwestern Scotland and the potential for stable isotope dendroclimatology in maritime climatic regions

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Abstract

Across much of Europe, Eurasia and N. America there exist networks of long tree-ring chronologies which, under favourable circumstances, may be used to provide a record of palaeoclimate information. A proportion of these tree-ring archives, primarily those collected for archaeological dating purposes, represent a significant and largely untapped palaeoenvironmental archive. Such records may be unsuitable for palaeoclimatic reconstruction based solely upon their physical characteristics (ring width and density) owing to weak or poorly expressed climatic forcing. This is especially true of oak chronologies from maritime regions. This study explores the potential for extracting a climate signal from such chronologies by comparing the stable isotope ratios of C, H and O from the rings of common oak (*Quercus robur*) trees in southwestern Scotland, with local and regional meteorological data. Summer (growing season) climate influences all three isotopes and the relationships identified are consistent with published empirical and mechanistic studies. The climate signal appears strongest in O and weakest in H. The C and O series, in combination, explain 31% of the variance in July–August mean temperature measured locally and 26% when compared with a homogenised gridded dataset for the period AD1957-2002. Over longer timescales the combination of C and O isotopes may also preserve a significant low-frequency signal (July–August $r^2=0.57$, 9-year running mean AD1879–1998). These findings demonstrate the potential of stable isotope dendroclimatology for investigating climatic change from oak chronologies in maritime regions.

Keywords: Stable isotope; Dendroclimatology; Oak; Carbon; Hydrogen; Oxygen

1. Introduction

Analysis of the absolutely dated annual growth increments of trees provides a powerful method for the reconstruction of late Holocene environmental change. Where trees can live for many hundreds, or even thousands of years, continuous long-timeseries can be

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constructed (Ferguson, 1970; Lara and Villalba, 1993; Hantemirov and Shiyatov, 2002; Cook et al., 2006). For the majority of shorter-lived species, chronologies can be objectively developed using living, archaeological and sub-fossil samples through synchronisation (cross-dating) to develop continuous, long-timeseries extending back beyond the lifetime of living trees (Hollstein, 1980; Pilcher et al., 1984; Becker, 1993; Grudd et al., 2002; Eronen et al., 2002; Wilson et al., 2004; Griggs et al., 2007).

In regions where tree growth is controlled by a single or simple combination of environmental variables, and where this relationship can be robustly calibrated and verified, it is possible to exploit variations in the physical and chemical characteristics of each growth ring to infer the nature of past environmental change. This has been successfully accomplished for conifers growing at the boreal and altitudinal treelines where temperature typically dominates tree growth and also in moisture-limited areas where water controls ring-width formation (Fritts, 1976; Grudd et al., 2002; Gunnarson and Linderholm, 2002; Helama et al., 2002; Naurzbaev et al., 2002; Saurer et al., 2002; McCarroll et al., 2003; Luckman and Wilson, 2005; Büntgen et al., 2006; Gagen et al., 2007). Such studies have made a significant contribution to our understanding of past climate variability.

Many tree-ring timeseries originate from non-conifer species and are consequently unsuitable for conventional X-ray densitometric analysis. Across much of central and western maritime Europe, highly replicated oak chronologies have been constructed, which extend back for centuries and in some regions for millennia (Kelly et al., 2002). These records were constructed primarily for the purposes of historical dendrochronology (tree-ring dating) rather than dendroclimatology. Although cross-dating over large areas clearly demonstrates that each chronology *must* preserve some climatic information (i.e., the common signal observed relating to a common forcing which is presumed to be climatic), this signal has rarely been demonstrated to be strong enough to extract a quantifiable climate signal and has thus prevented their wider application as palaeoclimatic archives. Ring-width measurements are, in essence, proxy estimates of inter-annual variability in net tree growth. Where trees are growing under conditions where a single climate parameter is not strongly growth limiting, which is generally the case for oak growing under maritime conditions, then the statistical relationship between climate parameters and ring width may be difficult to characterise precisely or too weak to be useful.

Stable isotope dendroclimatology differs from this approach because the variations in the stable isotope ratios of carbon, oxygen and hydrogen are not proxy measures of net growth, but are directly controlled by a range of external and internal factors that are reasonably well understood (Farquhar et al., 1982; Francey and Farquhar, 1982; Edwards and Fritz, 1986; Farquhar and Lloyd, 1993; Roden and Ehleringer, 2000; Roden et al., 2000; Treydte et al., 2001; Barbour et al., 2001; Waterhouse et al., 2002; Barbour, 2007). The potential therefore exists for applying stable isotope methods to areas where the ring width–climate relationship is weak or poorly defined through analysis of the dated tree rings as a chemical archive of plant response to external forcing. The main controls on stable isotope ratios in trees are stomatal conductance, assimilation rate, photon flux, meteoric (source) water variability and leaf water enrichment. These factors are externally influenced by photon flux (sunshine), leaf temperature, vapour pressure deficit and air mass properties, which may be directly correlated with more widely available meteorological parameters such as air temperature, relative humidity and antecedent precipitation (McCarroll and Loader, 2004, 2005).

The isotopic method is time-consuming and expensive, so the greatest advantage is likely to be gained by applying it to those sites and samples where either the standard physical proxies (ring width or maximum relative density) do not perform well or where additional environmental information may be provided by the isotopes. Across much of the United Kingdom, oak ring widths do not generally correlate well with climatic parameters and so isotopes may provide additional climatic information. This study will assess the climatic sensitivity of carbon, oxygen and hydrogen isotopes in absolutely dated latewood cellulose of oak tree rings from southwestern Scotland. If these methods can be demonstrated to provide a reliable record from such dendroclimatologically “complacent” regions (Fritts, 1976), then the stable isotope approach may offer potential for the wider dendroclimatic exploitation of the long European oak chronologies.

2. Methods

Samples of *Quercus robur* were collected from an area of ancient woodland, on a gentle southwest slope, near Lochwood in southwestern Scotland (55°16′N 03°26′W 175 m asl). Mean annual temperature is 7.0 °C with average annual precipitation of 1536 mm and relative humidity 85.5% for the period AD1961–1990. The forest comprises old growth oak and beech (closed canopy) with some evidence of past management (pollarding) and limited regeneration in forest openings.

Local soils are shallow Brown Earths (clay: 6%, silt 41%, fine sand 53%) ~60 cm in depth overlying a blocky substrate. The site was originally sampled by Pilcher and Baillie (1980).

Samples were collected using a 4 mm diameter increment borer, and prepared for measurement and cross-dating using standard dendrochronological methods (Stokes and Smiley, 1968). A site chronology was independently developed, which cross-dates against the original Pilcher and Baillie (1980) chronology (Baille–Pilcher *t*-value of 14.7, Gleichläufigkeit 77%, 270 years overlap), updating the record to AD2002. Four mature trees showing minimum disturbance were selected for isotopic analysis and additional core material obtained using a 12-mm diameter increment borer. These "isotope samples" were absolutely dated against the master chronology prior to cutting, cellulose purification and analysis.

The latewood fraction of each dated tree-ring was isolated as thin slivers using a scalpel and the material from each of the four trees carefully *pooled* prior to cellulose extraction. Although pooling reduces the amount of additional information that may be obtained from analysis of individual cores (McCarroll and Loader, 2005; Loader et al., 2007), this approach was necessary because the site forms part of a larger pan-European network (ISONET) with associated common sampling protocol (Isotope timeseries developed from core material of four trees, pooled annually). Each pooled sample was purified to α-cellulose (Loader et al., 1997). To ensure complete homogeneity within the pool each α-cellulose sample was then transferred to a 2 ml microcentrifuge tube and further homogenised in cold deionised water using a Hielscher ultrasonic probe (60 s (5-second pulses) at 50% power) to yield a homogenised fibrous sample and freeze-dried for 48 h prior to mass spectrometry.

For carbon isotope analysis 0.30–0.35 mg of dry α-cellulose were weighed into tin foil cups and combusted over chromium(III) oxide and copper(II) oxide at 1000 °C. For oxygen isotope analysis 0.30–0.35 mg cellulose were weighed into silver foil cups and pyrolised over glassy carbon at 1090 °C. Combustion and pyrolysis were conducted using a Europa ANCA GSL elemental analyser interfaced with a Europa 20/20 isotope ratio mass spectrometer. Isotope ratios are expressed as per mille deviations using the delta notation (δ) relative to VPDB (carbon) and VSMOW (oxygen) standards (Coplen, 1995). Analytical precision for repeat analysis of a standard laboratory cellulose is typically 0.1 and 0.3‰ for carbon and oxygen isotopes respectively ($n=10$). To ensure comparability between laboratories and analytical cycles 15 standards are run per 100 sample "burns".

Carbon and oxygen isotopes can be analysed on the α-cellulose, but for hydrogen isotopic analysis, the samples require equilibration or nitration (Ramesh et al., 1988; Schimmelman, 1991; Feng et al., 1993) prior to mass spectrometry to remove exchangeable hydroxyl bound hydrogen that constitutes *ca.* 30% of the hydrogen within the α-cellulose monomer. For this study α-cellulose was nitrated by a method modified after Ramesh et al. (1988), followed by dissolution in dry acetone and subsequent reprecipitation of the pure product in cold deionised water. The nitrated cellulose samples were freeze-dried for 48 h. For hydrogen isotope analysis 1 mg of dry nitrated cellulose was weighed into a silver foil cup and pyrolised at 1400 °C using a high temperature elemental analyser (TC-EA) interfaced with a ThermoFinnnegan MAT253 mass spectrometer. Hydrogen isotope ratios (δD) are reported as per mille deviations relative to the VSMOW standard. Analytical precision based upon replicate analysis of IAEA CH-7 polyethylene was 1‰ ($n=10$).

Although still a matter for further research, it has been suggested that following an initial "juvenile" phase, stable isotopes in tree rings require little or no additional de-trending prior to climatic analysis (McCarroll and Loader, 2005). For carbon isotopes, however, two non-climatic factors influential to isotopic fractionation during the last century require quantification/removal before the timeseries can be analysed for its palaeoclimatic signal. Many carbon isotopic timeseries are characterised by a decrease in $\delta^{13}C$ values after AD1850, which accelerates from *ca.* AD1950 to present. This trend reflects the increasing contribution of isotopically depleted CO_2 in the atmosphere as a consequence of industrialisation (Freyer, 1979a,b) and can be mathematically removed from the dataset by adjusting $\delta^{13}C_{plant}$ for the change in $\delta^{13}C_{atmosphere}$ determined from ice core and direct measurements (McCarroll and Loader, 2004, 2005; M. Leuenberger, Pers. Comm.).

Further to this "industrial effect", it has been suggested that tree-ring carbon isotopic series may also incorporate an additional trend reflecting a change in the physiological response to increased atmospheric concentrations of CO_2 (Marshall and Monserud, 1996; Feng, 1998, 1999; Waterhouse et al., 2004) which may influence model stability in recent decades. Whilst a topic for continued debate, two methods have been proposed to adjust for this effect. The first implicitly assumes that all trees will behave in a similar manner and involves addition of a fixed correction to $\delta^{13}C$

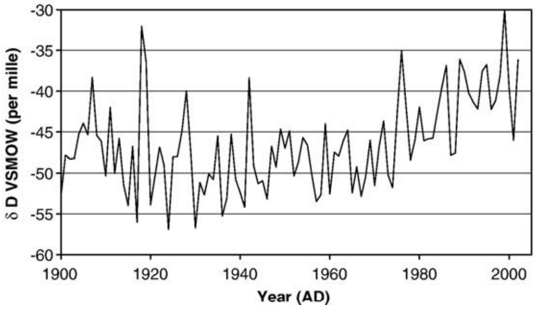

Fig. 1. Stable hydrogen isotope variability (AD1900–2002) from *Quercus robur* latewood cellulose nitrate. This record represents a pool of 4 trees.

per unit increase in atmospheric CO_2 concentration (Kürschner, 1996; Feng, 1999; Treydte et al., 2001). The second approach is based on converting tree-ring $\delta^{13}C$ into values for the internal concentration of CO_2 (c_i), and then attempting to estimate the values of c_i that would have been obtained under pre-industrial conditions within logical constraints. The technique, in theory at least, offers a more conservative approach for dealing with the CO_2 effect and in addition to this study has been successfully applied to tree-ring sequences growing under different climatic conditions in Finland (Gagen et al., 2007), Norway, Italy and Slovenia.

To assess the climatic sensitivity of the resulting isotopic timeseries, the data were compared using correlation analysis with monthly records of sunshine, temperature, precipitation and relative humidity from the nearby UK Meteorological Office station at Eskdalemuir (55° 20′ N 3° 12′ W 242 m asl AD1957–2002). The Eskdalemuir station has been designated by the UK Meteorological Office to be part of the Global Climatological Observing System (GCOS) surface network (GSN) for the UK (Jones and Lister, 2004). Composite correlation diagrams demonstrate the empirical relationship between each monthly record and the isotope timeseries. This record is too short to allow the sequence to be split into separate calibration and verification periods, but is used in this study to indicate the nature and magnitude of the correlation between stable isotopic and local meteorological variables over the 46-year calibration period. Replicate resampling methods such as the "jack-knife" technique (Quenouille, 1949, 1956) may be employed to obtain a measure of confidence on the calibration, but this approach was not explored as a part of this study. In addition to the data from Eskdalemuir, the isotopic data were compared to a 'gridded' temperature dataset to explore the stability of the relationships identified using local data through cross-calibration and independent verification (AD1850–2002) (Climatic Research Unit CRU 3.0T dataset: Brohan et al., 2006). Since the gridded timeseries represents data homogenised from multiple stations across a 5°×5° degree grid square (an area about the size of Ireland), some of the higher-frequency, site-specific signal may have been "lost", at the expense of more robust larger-scale, lower frequency trends. To explore these lower frequency trends further the data were smoothed using a 9-year running mean and compared with the equivalent low-frequency trends in the isotopic record.

3. Results and discussion

Three stable isotope timeseries were produced. For hydrogen isotopes (Fig. 1), the data cover the period AD1900–2002 with 4-tree coverage throughout. For oxygen (Fig. 2) and carbon (Fig. 3) isotopes, the pooled latewood series extends back to AD1749, but palaeoenvironmental interpretation will be restricted to the period with 4-tree coverage (AD1780–2002).

3.1. Climatic analysis

Pearson correlation coefficients were calculated between the isotope timeseries and monthly meteorological parameters from the Eskdalemuir weather station from AD1957–2002 (sunshine hours, relative humidity, precipitation and mean temperature) for the period October ($t-1$) to October (t), where t=the year of tree-ring formation. Results are presented as composite correlation diagrams (Figs. 4–6).

3.1.1. Hydrogen

The relationship between the hydrogen isotope timeseries and climate appears rather weak. There is a

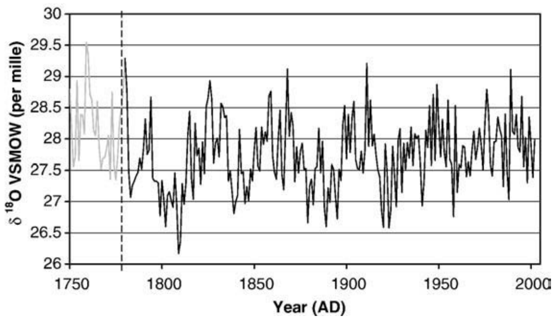

Fig. 2. Stable oxygen isotope variability (AD1750–2002) from *Quercus robur* latewood cellulose. This record represents a pool of 4 trees (AD1790–2002).

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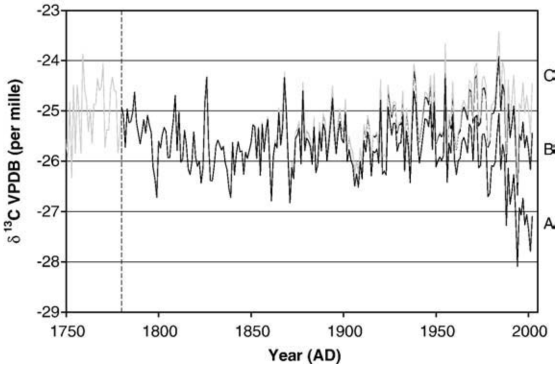

Fig. 3. Stable carbon isotope variability (AD1750–2002) from *Quercus robur* latewood cellulose. This record represents a pool of 4 trees (AD1790–2002). The black line (A) depicts the raw $\delta^{13}C$ data, the medium grey line (B) has been corrected mathematically for post industrial changes in atmospheric $\delta^{13}C_{atmosphere}$ (the "industrial effect"). The light grey line (C) shows the carbon isotope data corrected objectively for changes in plant response as a consequence of increasing atmospheric CO_2 concentrations (McCarroll et al. submitted for publication).

tendency for higher positive correlations with summer (July) parameters (temperature and sunshine) and negative correlations with precipitation and relative humidity, reflecting isotopic (evaporative) enrichment during the growing season (Fig. 4). The positive correlations with precipitation amount from January to June (significant for March) might also be related to the degree of soil moisture recharge that can influence plant source water signals through rainout-related amount effects or air mass characteristics (Epstein and Yapp, 1976; IAEA, 1981; Yapp and Epstein, 1982). A composite signal of water source/recharge coupled with summer enrichment has been observed previously for oxygen and hydrogen isotopes (Robertson et al., 2001; Waterhouse et al., 2002).

The strongest correlation obtained was with July temperature (r=0.45). It is notable that the hydrogen isotope results display a strong and significant (r=0.71, p<0.001) increase of about 13‰ over the period for which local meteorological data are available, and this is not reflected in any of the measured climate variables. The reason for this trend is not clear, but may reflect changes in air mass dominance. When this trend is removed through differencing, the relationship with climate variables remains weak. The strongest correlations between the detrended hydrogen isotope and meteorological parameters are for mean temperature of July (0.45) and relative humidity of August (−0.43). Further study of the assimilation pathways, mechanisms and environmental controls on hydrogen isotopes in tree rings is likely required in order to understand and exploit these timeseries more completely.

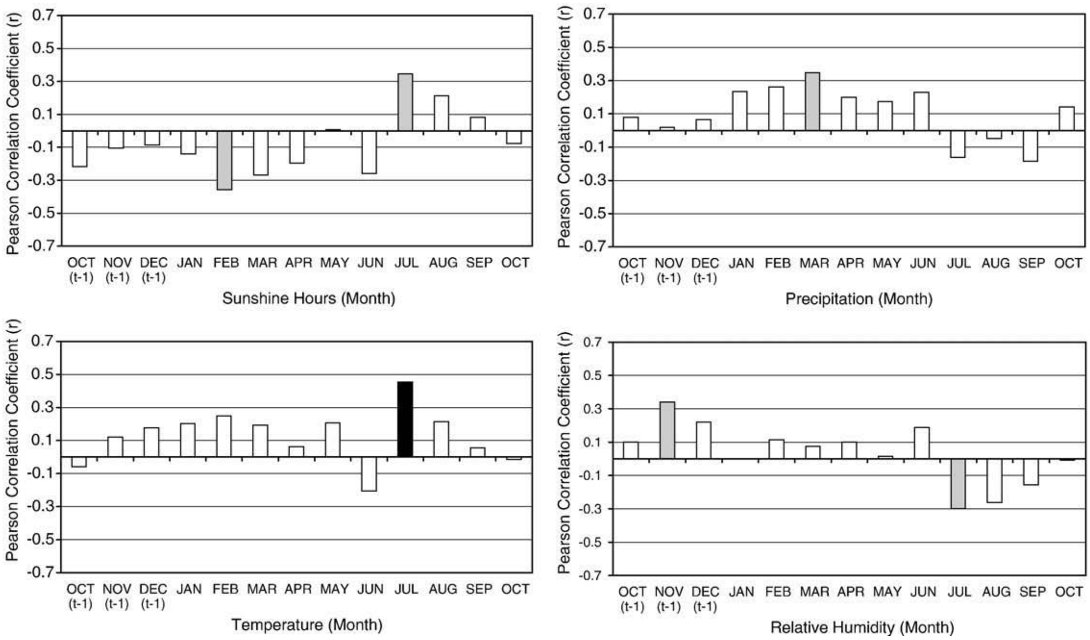

Fig. 4. Composite correlation diagram showing the Pearson correlation (r) between monthly meteorological parameters from Eskdalemuir and hydrogen isotope data from Lochwood, southwestern Scotland (AD1957–2002). Grey shaded bars represent correlations significant at 95% confidence level, black shaded bars represent correlations significant at the 99% confidence level.

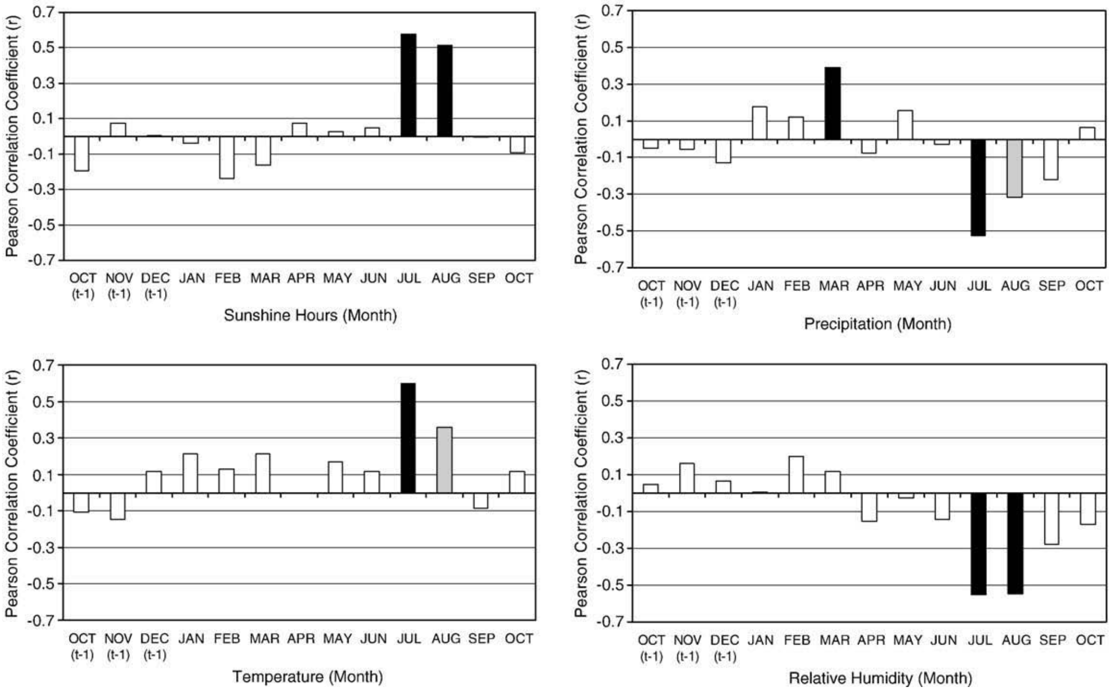

Fig. 5. Composite correlation diagram showing the Pearson correlation (r) between monthly meteorological parameters from Eskdalemuir and oxygen isotope data from Lochwood, southwestern Scotland (AD1957–2002). Grey shaded bars represent correlations significant at 95% confidence level, black shaded bars represent correlations significant at the 99% confidence level.

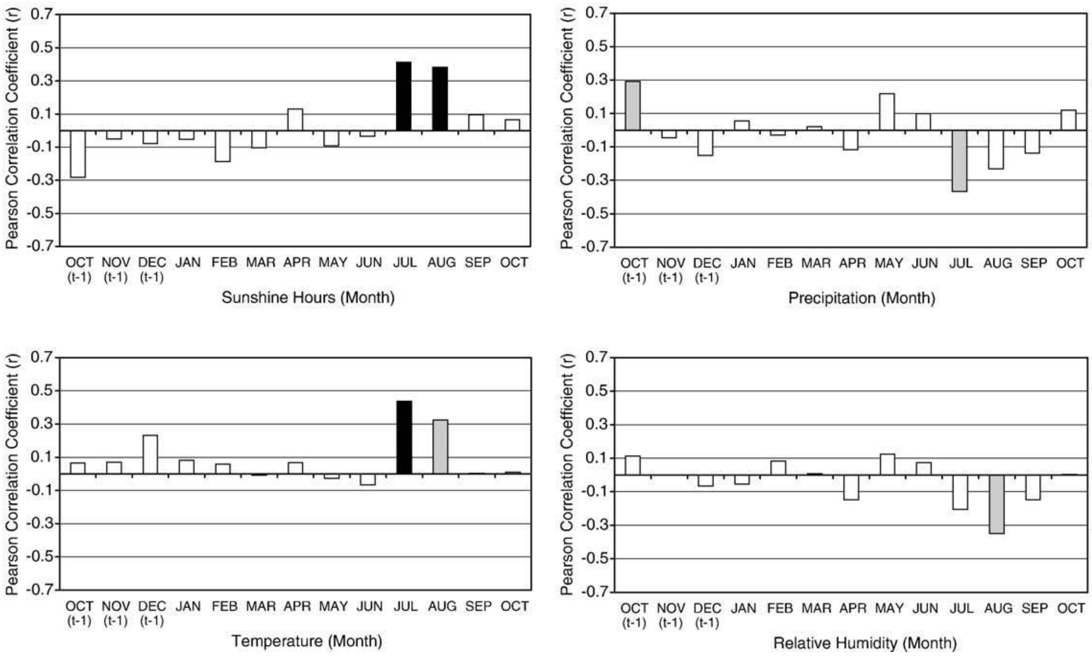

Fig. 6. Composite correlation diagram showing the Pearson correlation (r) between monthly meteorological parameters from Eskdalemuir and corrected carbon isotope data from Lochwood, southwestern Scotland (AD1957–2002). Grey shaded bars represent correlations significant at 95% confidence level, black shaded bars represent correlations significant at the 99% confidence level.

3.1.2. Oxygen

The climate signal in the oxygen isotope results appears much stronger than that in the hydrogen isotopes. Highly significant correlations with summer months (July and August) confirm that the oxygen isotope signal preserved in the latewood is influenced significantly by the climate of the summer during which it was formed (Fig. 5). The positive correlation results suggest a tendency towards higher isotope values with increasing temperatures, greater sunshine, lower precipitation and lower relative humidity, which in western European summers associate generally with the pressure types relating to warm, mainly dry periods with light winds (typically anti-cyclonic systems) (Lamb, 1972). The structure of, and agreement between the individual correlation diagrams for temperature and relative humidity are indicative of a system similar to those proposed through mechanistic models that link source waters (which carry a temperature signal) with humidity related evaporative enrichment in the leaf (Edwards and Fritz, 1986; Saurer et al., 1998; Roden and Ehleringer, 2000; Roden et al., 2000).

3.1.3. Carbon

The carbon isotopic timeseries from Lochwood is characterised by a decrease in δ^{13}C values reflecting the impact of industrialisation on atmospheric $\delta^{13}CO_2$ (Fig. 3). This trend, which commences around AD1850 decreasing towards the present day was mathematically removed from the dataset by adjusting for measured changes in $\delta^{13}C_{atmosphere}$ (McCarroll and Loader, 2004, 2005; M. Leuenberger, Pers. Comm.). The pooled timeseries was then adjusted for changing response in atmospheric CO_2 concentration using the objective method described above that recalculates δ^{13}C based upon a pre-industrial level of c_i. The effect of the two corrections applied for changing atmospheric δ^{13}C and changing atmospheric CO_2 on the δ^{13}C timeseries is presented in Fig. 3.

The correlation coefficients resulting from these corrected data (Fig. 6) reveal a pattern very similar to that observed in the oxygen isotope record. This relationship primarily reflects the influence of higher temperatures, increased insolation, low humidity and reduced precipitation on the assimilation/stomatal conductance balance of the trees resulting in less negative isotope values. The relationships observed are not as strong as with oxygen isotopes, and this is perhaps to be expected in trees growing in this region where stomatal conductance and assimilation rate may rarely limit fractionation exclusively. These findings are in agreement with models relating the principal controls on carbon isotope fractionation with direct or associated climatic parameters (Farquhar et al., 1982; Treydte et al., 2001; Loader et al., 2003; McCarroll and Loader 2004).

The influence of the corrections upon the relationship between δ^{13}C and climate was explored further through a correlation analysis between the Eskdalemuir dataset and tree-ring δ^{13}C corrected for $\delta^{13}C_{atmosphere}$ and changing atmospheric CO_2 concentration. In almost all cases the correlation coefficient between isotopes and climate data increased from the raw data, through the δ^{13}C-corrected data, to the CO_2 concentration-corrected data (Fig. 7). Whilst the correction for atmospheric δ^{13}C is well accepted, the conservative "pre-industrial" correction for changing CO_2 concentration represents an emerging methodology. It should be noted that either with or without this second correction the structure of

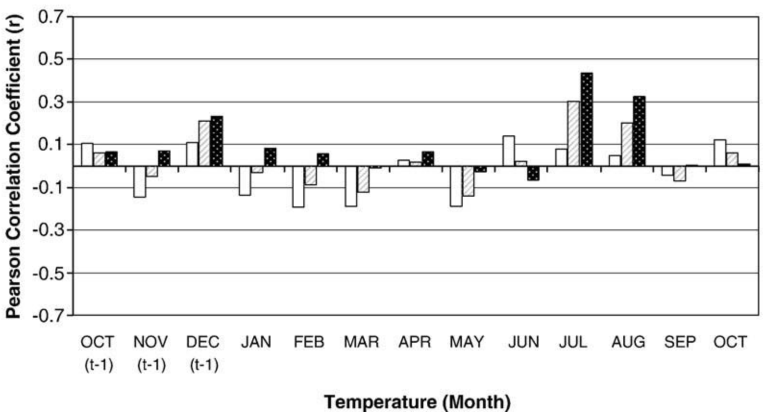

Fig. 7. Composite correlation diagram showing the Pearson correlation (r) between monthly meteorological parameters from Eskdalemuir and carbon isotope data from Lochwood, southwestern Scotland (AD1957–2002). White bars represent correlation coefficients obtained against raw carbon isotope data; grey bars against atmospheric δ^{13}C corrected data; black bars against δ^{13}C and CO_2 corrected data. Pearson product moment correlation coefficient confidence interval thresholds for 95% and 99% (n=46) are 0.291 and 0.376 respectively.

the plant response through time remains generally consistent, suggesting that the pre-industrial correction does not over-correct the dataset or adversely modify the signal obtained through standard correction of the "industrial effect" alone.

3.2. Potential for climatic reconstruction and preservation of lower frequency trends

One of the problems facing isotopic dendroclimatologists is the calibration and verification of isotopic variability with appropriate meteorological parameters. The primary (non-biochemical) controls on isotopic discrimination are related to assimilation rate, stomatal conductance and source water composition, which are rarely recorded. In the absence of reliable mechanistic models, isotope dendroclimatologists are therefore forced to compromise in developing regression-based models through comparison of the isotopic timeseries with standard meteorological data (typically temperature, humidity and precipitation) which may be closely related to, but not directly controlling, isotopic fractionation in trees. Comparison of the meteorological data from Eskdalemuir with the isotopic timeseries suggests that the local summer climate signal is important in controlling the inter-annual variability in tree-ring stable isotopes. Relationships were identified linking oxygen and carbon isotopes with summer (latewood) growing season conditions, with the dominant control occurring in July followed closely by August.

Both carbon and oxygen isotopes are strongly correlated with mean July ($r=0.44$ and $r=0.60$ respectively) and August ($r=0.37$ and $r=0.38$, respectively) temperature data at Lochwood, the pattern of significant correlations highlighting the period of maximum latewood formation. If we assume stationarity in response, there is the potential for combining the isotope timeseries to yield a record more closely related to the July–August period of latewood formation. To achieve this the isotope data were first standardised, and expressed as deviations from the AD1961–1990 mean, and then combined using a weighted average (McCarroll et al., 2003) based on the percentage variance explained by each isotope (relative weightings 55% and 45% for $\delta^{18}O$ and $\delta^{13}C$ respectively). Using this combined isotopic index the correlation with mean July–August temperature (r) increases to 0.59 (0.64 with 1986 isotopic outlier removed) (Table 1).

To ensure comparability between datasets, the combined isotopic index was compared with the homogenised gridded temperature data (Brohan et al., 2006). A composite correlation diagram produced for the equivalent (AD1957–2002) period (Fig. 8) demonstrates that the characteristic late summer inter-annual climate variability observed at Eskdalemuir is preserved in the gridded data. Comparisons are made with oxygen isotopes and both the $\delta^{13}C$ and CO_2 (pre-industrial)-corrected data to demonstrate the similarity between the two datasets and to illustrate the effect of these data treatments on the correlation distribution of the carbon isotopes. Inter-annual correlation against July–August mean temperature for this record is slightly lower ($r=0.50$ (0.59 with 1986 isotopic outlier removed)) than those recorded against the local Eskdalemuir data ($r=0.59$ (0.64 with 1986 isotopic outlier removed)) suggesting that some of the site-specific inter-annual variability is reduced during the compilation process. Since these meteorological data perhaps represent a more robust regional signal than an inter-annual record suitable for direct site calibration and verification, the two complete timeseries were smoothed using a 9-year centered running mean so that in addition to this inter-annual response, the lower frequency trends could be compared (Fig. 9).

The combined $\delta^{13}C$ and $\delta^{18}O$ (smoothed) dataset was split into two subsets of 60 years and based upon results obtained from the local data, correlated and independently verified against equivalent periods in July–August mean temperature calculated from the gridded data. Each model was tested using reduction of error (RE) and coefficient of efficiency (CE) statistics (National Research Council, 2007). The effect of

Table 1
Summary statistics for the correlation between the annually resolved carbon and oxygen isotope index and July to August temperature datasets for Eskdalemuir and regionally gridded (Brohan et al., 2006) data for the periods AD1957–2002 and AD 1851–2002 (complete record)

	No. observations (n)	July	August	July–August
Eskdalemuir	46	0.64 (0.69)**	0.37 (0.47)*	0.59 (0.64)**
Gridded data	46	0.60 (0.63)**	0.34 (0.45)*	0.50 (0.59)**
Gridded data	153	0.42 (0.43)**	0.39 (0.43)**	0.46 (0.49)**

Note: Figures in parentheses represent correlation coefficients calculated after removal of an isotopic outlier (AD1986). This adjustment is made for information only, all subsequent calculations including weighting and reconstructions are based upon the complete dataset. Correlations statistically significant at the *95% and **99% confidence levels.

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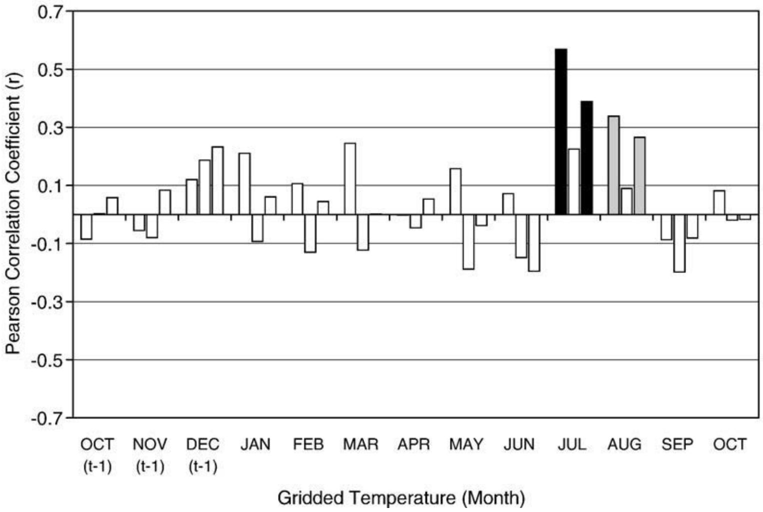

Fig. 8. Composite correlation diagram showing the Pearson correlation (r) between oxygen and carbon isotope timeseries and monthly gridded temperatures (Brohan et al., 2006) (AD1957–2002). Three datasets are presented per month; oxygen isotopes (left bar), carbon isotopes corrected for "δ^{13}C industrial effect" only (central bar), carbon isotopes corrected for "δ^{13}C industrial effect" and "pre-industrial" CO_2 concentration changes (right bar). Grey shaded bars represent correlations significant at 95% confidence level, black shaded bars represent correlations significant at the 99% confidence level.

filtering (smoothing) the data also changes effective sample size (n') and degrees of freedom which were calculated as described by Dawdy and Matalas (1964).

Both calibration models perform well (Table 2). Model 1, $r^2=0.47$ $n=60$ $n'=6.5$, is statistically significant at >80% (calibrated AD1939–1988), returns a positive reduction of error statistic ($RE_{verification}=0.58$), and also passes CE (0.14). Model 2, $r^2=0.56$ $n=60$ $n'=3.8$, is not significant above the 80% level, but has a positive RE statistic ($RE_{verification}=0.39$) the model does not pass the CE test, suggesting a lower skill of prediction. This may relate to differences in trend between the calibration and verification periods, but may also reflect that the number of trees contributing to this dataset is too low to capture significant low-frequency information over this time period.

A third composite model was then calculated based upon the 120-year dataset. Model 3 (AD1879–1998) explains 57% of the variance ($n=120$ $n'=6.5$) and is statistically significant at the 90% confidence level. The resulting model, when variance is scaled to the calibration period (Fig. 9), demonstrates a close association with the observed meteorological data, suggesting that this approach provides a useful and

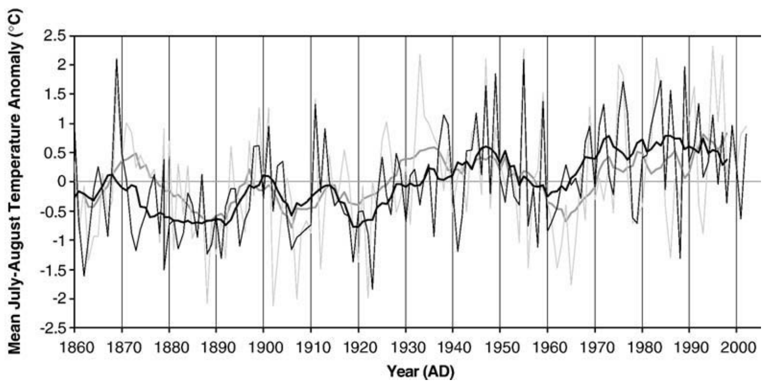

Fig. 9. Comparison of the low-frequency trends in July–August mean temperature anomalies (gridded data Brohan et al., 2006) (thin light grey line) and the combined δ^{13}C and δ^{18}O index (thin black line). Data are smoothed using a 9-year centered running mean (thick grey and black lines for temperature and isotopes respectively) and scaled to common variance for the calibration period (AD1879–1998). A good visual agreement is apparent at both high and low frequencies. The coefficient of variance (r^2) for the filtered data is 0.57 ($n=120$), which is significant at the 90% confidence level ($n'=5.7$).

Table 2
Summary statistics for the split-regression of the raw and filtered composite carbon and oxygen isotope timeseries against mean July–August temperature (Brohan et al., 2006) gridded dataset AD1879–1998

	Mean squared error (MSE)	Reduction of error	Coefficient of efficiency	r^2	n (n')
Model 1					
Calibration 1939–1998	0.25	0.47	–	0.47^{+}	60 (6.5)
Verification 1889–1938	0.11	0.58	0.14	–	–
Model 2					
Calibration 1889–1938	0.11	0.56	–	0.56	60 (3.8)
Verification 1939–1998	0.25	0.39	−0.29	–	–
Model 3					
Composite 1879–1998	0.06	0.57	–	0.57^{++}	120 (5.7)

Notes: Effective n (n') adjusted for the effect of filtering after Dawdy and Matalas (1964). Correlations statistically significant at the $^{+}$80% and $^{++}$90%. confidence levels. The steep rising trend observed in both the temperature and the isotopic datasets result in high autocorrelation, hence the low effective n values.

credible method for reconstructing past growing season conditions at high and low frequencies using stable isotopes in tree rings from maritime regions. Error in the reconstruction appears evenly distributed throughout the reconstruction, which from these data we believe to partly reflect the small number of trees comprising this record and uncertainties of the method rather than any prolonged or systematic divergence.

4. Conclusions

For all isotopes series examined in this study, an acceptable proportion of the variance preserved within the timeseries could be accounted for by meteorological forcing, the structure of which could be interpreted through our mechanistic understanding of the nature of isotopic fractionation during assimilation and wood formation. Based upon the local Eskdalemuir dataset, highest correlations were observed for oxygen and carbon isotopes against summer (July–August) climate variables that coincide with the period of maximum latewood formation in southwest Scotland. High temperatures, sunshine, low precipitation and low relative humidity were shown to drive more positive oxygen and less negative carbon isotope values supporting a standard “moisture–stress” relationship (source water/leaf water enrichment response in oxygen and stomatal conductance/assimilation rate response in carbon). The relatively low level of climatic sensitivity and strong temporal trend in the hydrogen isotopes limits the suitability of this record for climatic reconstruction using simple linear methods at present.

The results obtained demonstrate that it is possible to extract a strong and coherent summer climate signal using stable isotope methods from oak trees growing under maritime conditions where ring widths (and density) do not routinely yield useful climatic information. This study provides the impetus to revisit archived tree-ring material using stable isotope techniques to estimate past climates from maritime climatic regions. However, site selection, favourable timber preservation, a known sample provenance and high levels of replication remain factors critical in the success of any such study, particularly when working in the lower frequency domain.

Combination of the standardised carbon and oxygen isotope timeseries into a single index increases the correlation with meteorological data. This may simply reflect an increase in the signal:noise ratio, but could also reflect the constructive combination of stomatal conductance, assimilation rate, leafwater enrichment and source water variability to reinforce the climate signals observed (Scheidegger et al., 2000). Investigation of the lower frequency trends was accomplished by filtering the data, to reveal robust low-frequency climatic information relating to the latewood growing season (July–August). Despite the limitations of such a comparison of smoothed data, the resulting visual agreement and correlation coefficients appear to preserve a strong low-frequency climatic signal significant at the 90% confidence level for the period AD1860–2002.

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