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Climate signals in $\delta^{13}C$ of wood lignin methoxyl groups from high-elevation larch trees

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A B S T R A C T

In this study, a barely used method to measure $\delta^{13}C$ values from lignin methoxyl groups ($\delta^{13}C_{methoxyl}$) of tree-rings is applied to high alpine larch trees to test their potential as a climate proxy. Thirty-seven larch trees (*Larix decidua* Mill.) were sampled at a tree line site near Simplon Village in the Valais/Switzerland. Samples were used to measure tree-ring width, and from five individuals, $\delta^{13}C_{methoxyl}$ was determined at annual resolution from 1971 to 2009, and at pentadal resolution from 1747 to 2009.

The physiological tree responses to increasing atmospheric CO_2 concentration since 1850 and the corresponding decrease in $\delta^{13}C$ (Suess effect) were corrected using a range of published discrimination factors and approaches. One of these approaches considers a flexible correction factor, which minimizes the residuals with target climate data.

Testing the response of the new $\delta^{13}C_{methoxyl}$ proxy to climate revealed significant correlations with June to August temperatures, ranging from $r = 0.56$ to 0.75 for annually and from $r = 0.41$ to 0.87 for pentadally resolved data depending on the correction methods. Tree-ring width also shows significant correlations with June to August temperature. These results demonstrate the potential of $\delta^{13}C_{methoxyl}$ to serve as a summer temperature proxy in high-elevation alpine environments.

1. Introduction

Over recent decades, there have been numerous studies using stable carbon and oxygen isotope ratios from tree-rings (e.g., Daux et al., 2011; Esper et al., 2015; Hafner et al., 2011; Konter et al., 2014; Kress et al., 2010; Reynolds-Henne et al., 2007; Treydte et al., 2001; Wang et al., 2011). In particular, the carbon isotope composition from tree-rings has been established as a suitable palaeoclimate proxy in the Northern hemisphere (e.g., Becker et al., 1991; Kress et al., 2010; Leavitt et al., 1995; Treydte et al., 2007). $\delta^{13}C$ is sensitive to air humidity and soil water changes at dry sites such as the inner Alpine valleys (Giuggiola et al., 2015; Kress et al., 2010; Treydte et al., 2001). Summer irradiance and temperature changes seem to have a stronger influence on the $\delta^{13}C$ at humid sites (McCarroll and Loader, 2004), e.g., at higher elevation sites at the boundaries of the upper species distribution (Hafner et al., 2011; Reynolds-Henne et al., 2007). These differences are mainly related to variations in stomatal conductance, controlled by soil and air moisture and determining the tree's water-use efficiency (Frank et al., 2015; McCarroll and Loader, 2004; Saurer et al., 2014). For these isotope studies, fewer trees are typically used, as time-series development is expensive and the high-frequency climate signals are stronger compared to tree-ring width (TRW) and maximum latewood density data (MXD) (Daux et al., 2011; Hafner et al., 2011; Hartl-Meier et al., 2015).

Most studies used cellulose to determine $\delta^{13}C$ in of tree-rings, but also $\delta^{13}C$ of lignin and whole wood have been measured to compare the potentially changing climate signals retained in these wood components (e.g., Borella et al., 1998; Loader et al., 2003; Sidorova et al., 2008; Wilson and Grinsted, 1977). An alternative approach is the measurement of $\delta^{13}C$ of lignin methoxyl groups ($\delta^{13}C_{methoxyl}$), an approach originally developed by Keppler et al. (2004) and optimized by Greule et al. (2009). While this method does not require the time consuming cellulose extraction, the amount of sample material is generally higher compared to measurements based on cellulose and whole wood. Furthermore, methoxyl groups are chemically stable and are not exposed to any exchange after formation (Greule et al., 2009). The method was recently tested in two studies for its applicability to serve as a climate proxy (Gori et al., 2013; Mischel et al., 2015). Gori et al. (2013) compared $\delta^{13}C$ values from whole wood, cellulose and the lignin methoxyl groups of *Picea abies* sampled at three south-alpine locations (900–

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1900 m above sea level). The results indicated a constant offset and a high correlation of $\delta^{13}C$ among the different wood components. However, the resulting $\delta^{13}C$ time series do not contain a distinct climate signal from any of the three different wood components at the sampling sites. This could be due to species and site specific conditions. A second study (Mischel et al., 2015) investigated $\delta^{13}C_{methoxyl}$ values of *Pinus silvestris* trees from a middle range mountain site in Germany and compared these data with $\delta^{13}C$ values from whole wood and α-cellulose. The $\delta^{13}C$ series from the different wood components correlate significantly with each other and with climate variables such as temperature, precipitation, vapour pressure deficit and infiltration. These partly heterogeneous results on $\delta^{13}C_{methoxyl}$ data as a climate proxy necessitate further investigations.

Here, we applied the method established by Keppler et al. (2004) and Greule et al. (2009) to thoroughly test the potential of $\delta^{13}C_{methoxyl}$ from larch trees (*Larix decidua* Mill.) as a palaeoclimate proxy in a high-elevation, temperature-constrained environment.

2. Materials and methods

2.1. Study area

The study site is located near Simplon Village in the Simplon region in southern Switzerland (Fig. 1). The region bridges over the southern main mountain range of the western Alps including the NNW–SSE-oriented Simplon valley. It is one of the lowest passes in the Alps at 2005 m above sea level (asl).

Simplon Village and the sampling site are located south of the pass, which acts as a climate divide between the dry inner alpine Rhône valley in the north, and the Mediterranean influenced climate in the south (Müller, 2005). Annual mean temperature at Simplon Village in 1495 m asl is 5.3 °C (1971–1996), and annual precipitation 1247 mm (1961–2009) (www.meteoswiss.ch). The seasonal precipitation distribution shows a bimodal pattern with highest precipitation sums in spring (May) and autumn (October) and lower amounts in winter (January and February) and summer (July) (Müller, 2005).

2.2. Sampling and TRW measurements

Thirty-seven larch trees (*Larix decidua* Mill.) were sampled in September 2010 at 2150 m asl (46°13 N, 8°04 E) close to the tree line on a southwest-exposed slope (Fig. 1). The sampling site is characterized by a typical, subalpine larch forest of low stand-density with shrubs and herbs as understory. Two to three 5-mm increment cores were sampled at breast height considering trees of all age classes (Nehrbass-Ahles et al., 2014; Speer, 2010). The resulting 78 cores were cut perpendicular to the wood fibers using a microtome (Gärtner and Nievergelt, 2010) to generate a plane surface for a better visibility of the tree-rings. TRW was measured with an accuracy of ±0.01 mm using a LINTAB measuring table equipped with TSAP-Win software. Cross dating of the individual TRW series was performed visually and verified using the COFECHA software (Holmes, 1983). Tree age-related growth trends were eliminated by calculating residuals from individually fitted negative exponential functions after power transformation (Cook and Peters, 1997) and variance stabilization (Frank et al., 2007) was performed with a 300 year spline with the software ARSTAN (Cook, 1985).

2.3. $\delta^{13}C$ values of wood lignin methoxyl groups

Five of the 37 trees and one core of each of these five trees were selected for annually resolved $\delta^{13}C$ measurements of wood lignin methoxyl groups over the period 1971–2009. The years before 1971 were analyzed in blocks of five years, i.e., thin sections of the five tree cores were cut with a microtome (Gärtner and Nievergelt, 2010) and blocks of five consecutive tree-rings cut from these sections for one isotopic measurement. The pentadal blocks were analyzed to test not only the year-to-year but also the long-term variability of the proxy record. For the measurement of $\delta^{13}C_{methoxyl}$, the cut wood pieces of 0.4 to 3.7 mg were weighed into crimp glass vials (1.5 ml) using a Satorius Research R200D microbalance (±0.01 mg).

Stable carbon isotope values of lignin methoxyl groups were measured as CH_3I released upon treatment of the dried wood samples with hydriodic acid (HI) (Greule et al., 2009). The acid (0.25 ml,

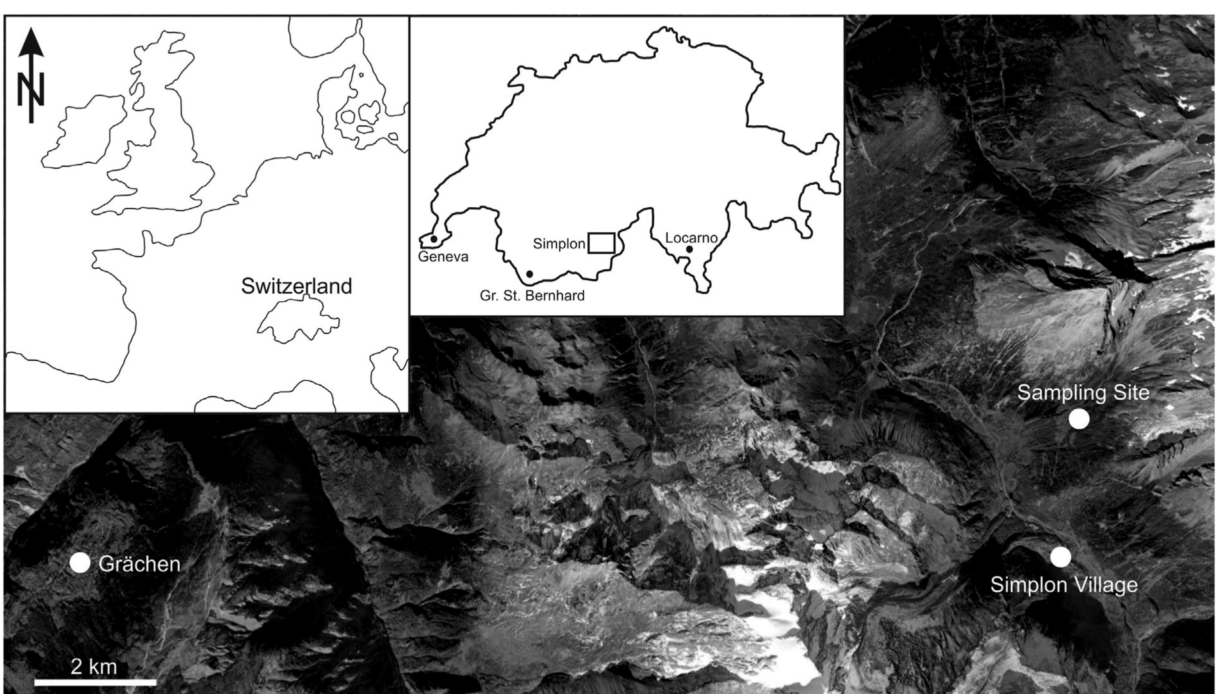

Fig. 1. Location of the Simplon region and meteorological stations in Switzerland (modified after Google earth).

55–58%) was added to the sample in the glass vial. The vials were sealed with crimp caps containing PTFE lined butyl rubber septa (thickness 0.9 mm) and incubated for 30 min at 130 °C. After heating, the vials were allowed to equilibrate at room temperature (22 ± 0.5 °C, air-conditioned room) for at least 30 min before 10–90 μl from the headspace was directly injected into the gas chromatography–combustion–isotope ratio mass spectrometry (GC-C-IRMS) system.

Measurements were performed with an HP 6890 N gas chromatograph (Agilent, Santa Clara, CA, USA) equipped with an A200S autosampler (CTC Analytics, Zwingen, Switzerland), coupled to a Delta^{PLUS}XL isotope ratio mass spectrometer (ThermoQuest Finnigan, Bremen, Germany) via an oxidation reactor and a GC Combustion III interface. For further details of the GC-IRMS measurements, refer to Greule et al. (2009).

The isotope signatures were measured relative to a high purity CO_2 reference working gas (Air Liquide, Düsseldorf, Germany). All $\delta^{13}C$ values are expressed relative to the international VPDB standard using a CH_3I working standard. The $\delta^{13}C$ value of CH_3I was calibrated against international reference substances (IAEA-CH-6, IAEA-CH-7, NBS-22) using an offline elemental analyzer (EA)/IRMS system (*Iso-Analytical Ltd., Sandbach, UK*). The calibrated $\delta^{13}C$ value in ‰ vs. VPDB for CH_3I was -69.27 ± 0.05 ‰ ($n = 15$, 1σ). This working standard was measured after every fourth sample injection. The analytical precision was <0.3 ‰.

As this procedure represents solely a 1-point calibration, it has to be pointed out that the $\delta^{13}C$ data might be affected by an additional error ("scale compression"). CH_3I working standards with distinct isotopic signatures spanning the full range of measured $\delta^{13}C$ values were not available for this study to eliminate or minimize this error. The authors are aware that international comparability of stable isotope abundance measurements ideally requires a 2-scale anchor calibration with accepted isotope abundance values as recommended by the IUPAC guidelines (Coplen, 2011).

2.4. Meteorological data

The response of the $\delta^{13}C_{methoxyl}$ and the TRW records to climate was assessed by comparison with monthly resolved data of temperature, precipitation (1866–2009), and cloudiness (1966–2009) of the meteorological station in Grächen (46°12′ N, 7°50′ E, 1605 m asl) and precipitation data of the station in Simplon Village (46°12′ N, 8°03′ E, 1495 m asl; Fig. 1) for the annually resolved period 1971–2009.

The Grächen data were used because the station is located 15 km west of Simplon Village (Fig. 1) and provides continuous monthly time series from 1866 to 2009. The nearby weather station in Simplon Village only provides temperature data from 1971 to 1996 and precipitation data from 1971 to 2009. The June–August (JJA) temperature data from the Grächen station are consistent with the data from the station of Simplon Village as well as with those from the stations Great St. Bernhard (2472 m asl), Geneva (420 m asl) and Locarno (366 m asl) (Fig. 2).

To estimate the combined effects of low water availability and high evaporative demand on $\delta^{13}C_{methoxyl}$ and tree growth, we also calculated and applied the drought index (DRI) of Bigler et al. (2006):

$$DRI = P - PET \quad (1)$$

with P being the monthly precipitation and PET the potential evapotranspiration according to Thornthwaite (1948). The index was calculated based on temperature and precipitation data from Grächen.

2.5. Correction of $\delta^{13}C_{methoxyl}$ values

Due to the anthropogenic burning of fossil fuel, the CO_2 concentration in the atmosphere increased from 280 ppmv at AD 1800 to 400 ppmv today (Francey et al., 1999) (NOAA Mauna Loa CO_2 Data, www.co2now.org). Since the fossil CO_2 has a lighter carbon isotopic composition than the atmosphere, the $\delta^{13}C$ value of the atmosphere decreased from −6.4 ‰ (in 1850) to a current value of −8.3 ‰ (http://scrippsco2.ucsd.edu/data/mlo.html), the so-called Suess effect (Keeling, 1979). This change in source $\delta^{13}C$ has to be corrected for to investigate the climatic signal in tree-ring $\delta^{13}C$ values. This was here done using the atmospheric $\delta^{13}C$ data listed at www.climexp.knmi.nl and in McCarroll and Loader (2004).

There is however also increasing evidence that trees respond physiologically to the increasing CO_2 concentration in the atmosphere (Feng and Epstein, 1995; Kürschner, 1996; McCarroll et al., 2009; Saurer et al., 2003; Treydte et al., 2009; Wang et al., 2011). This physiological response depends on the relative increase of the internal leaf CO_2 concentration (c_i) compared to the increase in atmospheric CO_2 concentration (c_a). If c_i increased at the same rate as c_a ($c_a - c_i$ = constant), this would

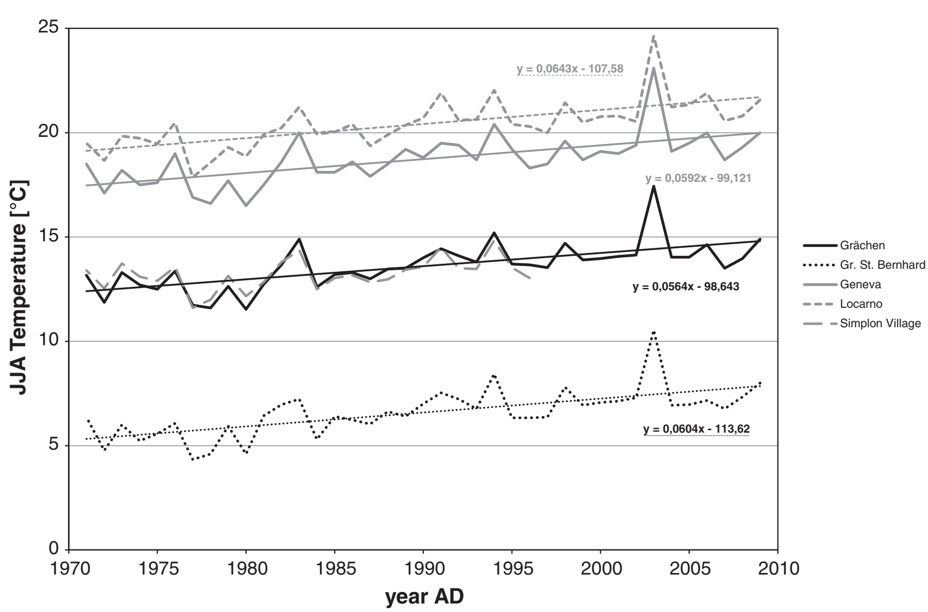

Fig. 2. JJA temperatures recorded in Grächen, Great St. Bernhard, Geneva, and Locarno from 1971 to 2009 and Simplon Village from 1971 to 1996. Data source: www.meteoswiss.ch.

result in a strong discrimination against ^{13}C within the leaf, and thus lower $\delta^{13}C$ would be obtained. If, however, plants actively responded to an increase in c_a, by reducing stomatal conductance to save water and maintain CO_2 uptake, then c_i increases would be reduced (proportionally, i.e., c_i/c_a = constant), and no change in discrimination and tree-ring isotopes would be observed (Farquhar et al., 1989; Saurer et al., 2004; Treydte et al., 2009). Note that the physiological responses are still controversial and seem to be different for different species and locations (Feng and Epstein, 1995; Gessler et al., 2014; Kürschner, 1996; McCarroll et al., 2009; Treydte et al., 2009). We chose to apply the following suite of corrections to evaluate the related uncertainties.

First, we corrected the tree-ring $\delta^{13}C_{methoxyl}$ data for the Suess effect only. We then accounted for potential effects of discrimination changes under elevated CO_2 concentration by adding correction factors derived from (i) Kürschner (1996), indicating a discrimination change of 0.0073 ‰/ppmv CO_2; (ii) Feng and Epstein (1995), indicating 0.02 ‰/ppmv CO_2; and (iii) Treydte et al. (2009), indicating a flexible factor and 0.012 ‰/ppmv CO_2 in their study.

The PIN-correction (Pre-industrial normalization; correcting $\delta^{13}C$ values with respect to 1850 AD) of McCarroll et al. (2009) was not considered because our sampling design (annual resolution 1971–2009; pentadal resolution 1771–2009) of $\delta^{13}C$ is not applicable to this correction method (D. McCarroll, personal communication). Further, the $\delta^{13}C_{methoxyl}$ data were detrended with a 10-year (annual resolution) and 10-point (pentadal resolution) fast Fourier transformation (FFT) filter, using the software Origin®, to emphasize high-frequency variance in the data.

3. Results

3.1. Tree-ring width

The 78 sampled cores contained in 18,538 tree-rings, the inter-series correlation calculated using the COFECHA software reached $r = 0.74$. This inter-series correlation is the average correlation of each series with the mean of all remaining series (Holmes, 1983). The five cores selected for the $\delta^{13}C_{methoxyl}$ analyses contain 1203 tree-rings and inter-series correlation at $r = 0.68$. The TRW record of all series spans 445 years with a minimum replication of five trees, and the five cores used for isotope analyses span 239 years with a minimum replication of four trees. The mean TRW records of all and the five selected cores correlate at $r = 0.89$ ($p < 0.001$), indicating that the sub-samples used for $\delta^{13}C_{methoxyl}$ analysis represents the common signal of the site chronology (Fig. 3). Hence, the chronology of all sampled trees was used to assess the climate response in TRW and compared with the $\delta^{13}C_{methoxyl}$ records.

3.2. $\delta^{13}C_{methoxyl}$ values, correction of the Suess effect and physiological response

The raw $\delta^{13}C_{methoxyl}$ series of the five trees do not show a clear common pattern during the annually resolved period 1971–2009 (Fig. 4a), as reflected by the insignificant inter-series correlation of $r = 0.14$ ($p > 0.05$; Table 1). In comparison, the TRW series of the same five trees inter-correlate at $r = 0.66$ ($p < 0.001$; Fig. 4c). The annually resolved $\delta^{13}C_{methoxyl}$ series of the period 1971–2009 were averaged over five-year blocks for comparison with the earlier $\delta^{13}C_{methoxyl}$ data before 1971 that were measured at pentadal resolution. The resulting low-resolution $\delta^{13}C_{methoxyl}$ series contain more variance in common reflected by an inter-series correlation of $r = 0.50$ ($p < 0.001$; Table 1). The TRW of the pentadally resolved series inter-correlate at $r = 0.62$ ($p < 0.001$; Fig. 4d). Importantly, the raw $\delta^{13}C_{methoxyl}$ records do not significantly correlate with the corresponding TRW records (Table 1).

After correction of the Suess effect (atmospheric correction, $\delta^{13}C_{methoxyl\ atmo}$), the $\delta^{13}C_{methoxyl}$ values appear more enriched towards present (Fig. 5), and the inter-series correlation of the annually resolved data increases to $r = 0.23$ ($p > 0.05$). The inter-series correlation of the pentadally resolved data, however, decreases to $r = 0.28$ ($p > 0.05$). The $\delta^{13}C_{methoxyl}$ values become even more enriched after correcting for the physiological tree response following Kürschner (1996) (+K), Feng and Epstein (1995) (+Fe) and Treydte et al. (2009) (+opt) considering JJA temperatures as the best-correlating climate parameter and season. This procedure resulted in corrections of 0.032 ‰/ppmv CO_2 for the annual resolved and 0.036 ‰/ppmv CO_2 for the pentadally resolved $\delta^{13}C_{methoxyl}$ data. These optimum correction factors are determined by changing this factor from −0.05 to +0.05 ‰/ppmv CO_2 in steps of 0.001 ‰. The correlations of these differently corrected $\delta^{13}C_{methoxyl}$ series to JJA temperature are tested for the highest one, which results in the used correction factors. Applied to our data the optimum correction is higher than the fixed corrections from Kürschner (1996) at 0.0073 ‰/ppmv CO_2 and Feng and Epstein (1995) at 0.02 ‰/ppmv CO_2, as well as the corrections by Treydte et al. (2009) at 0.012 ‰/ppmv CO_2 and Wang et al. (2011) at 0.016 ‰/ppmv CO_2.

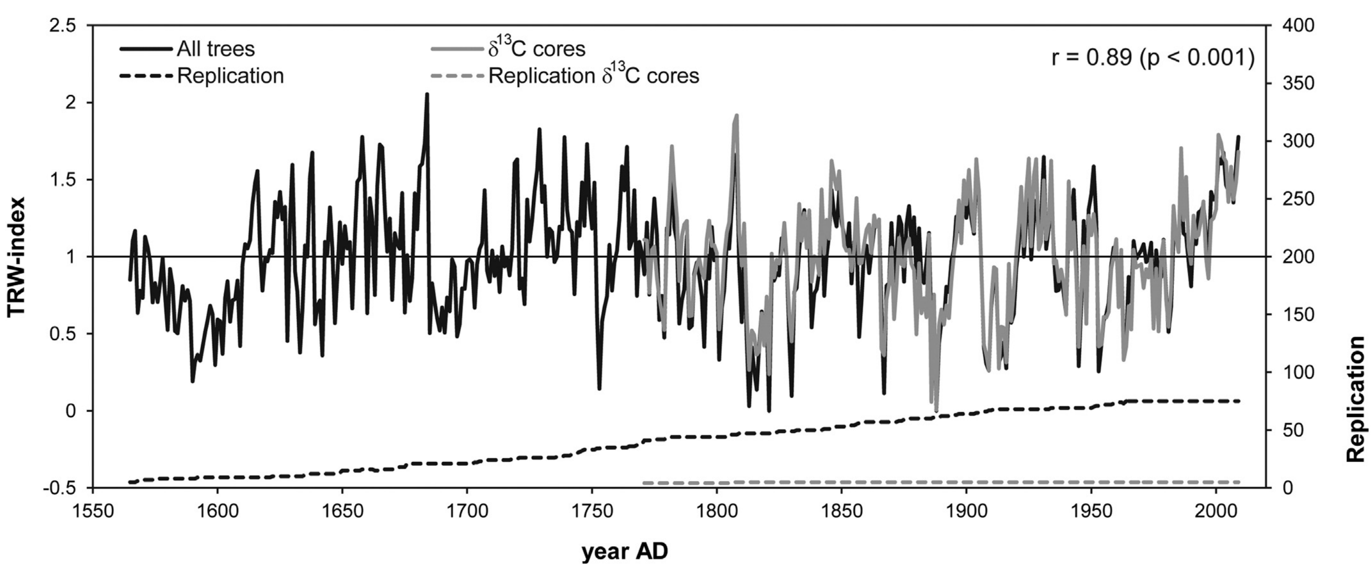

Fig. 3. TRW records of all trees, and the five trees selected for $\delta^{13}C_{methoxyl}$ analyses. Individual records were detrended using negative exponential functions, and the records were truncated at a minimum replication of 5 trees for TRW of all trees and 4 samples for TRW of the five cores used for the $\delta^{13}C$ analyses.

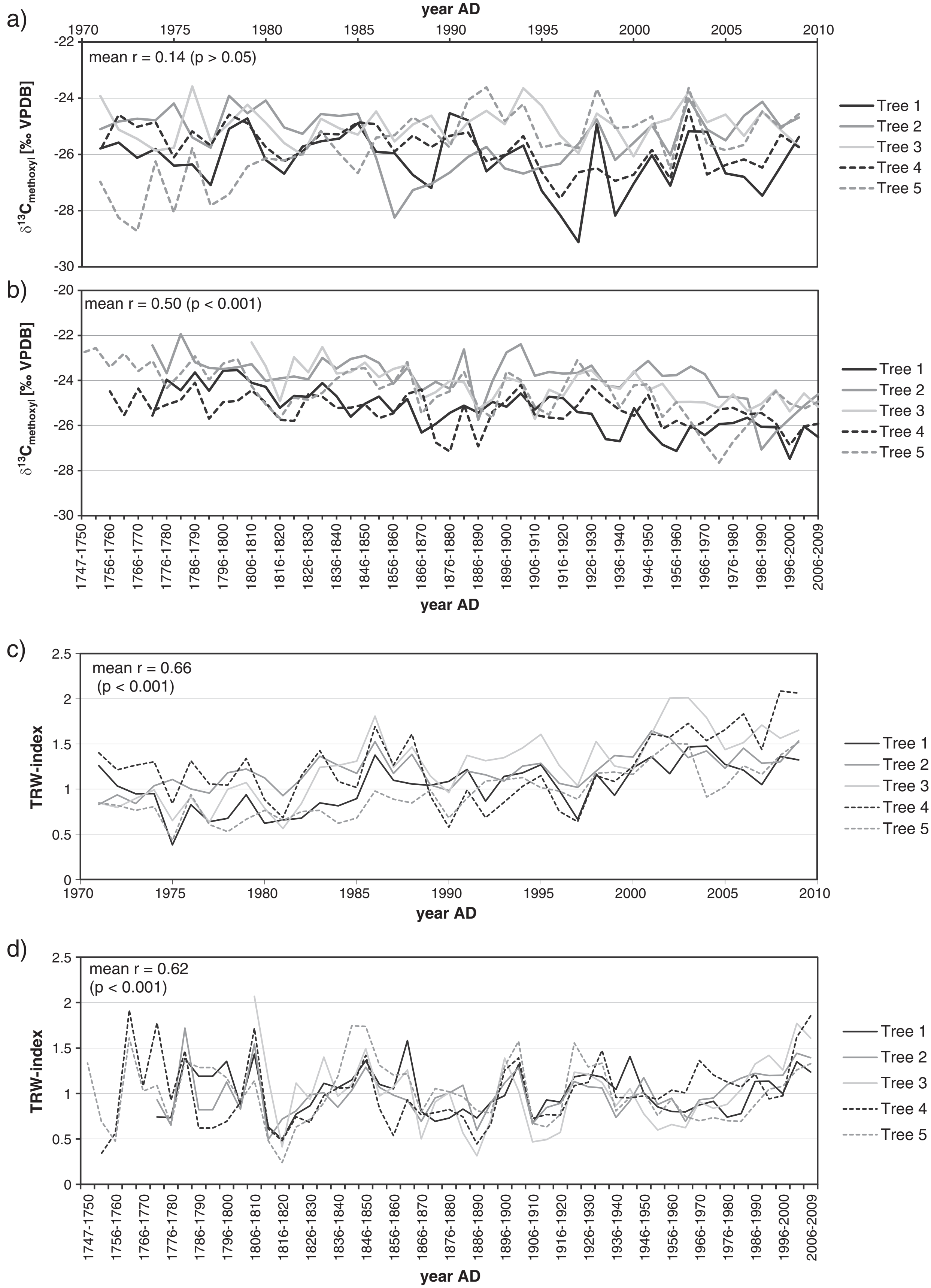

Fig. 4. Individual $\delta^{13}C_{methoxyl}$ records of (a) the annually resolved period 1971–2009 and (b) the pentadally resolved period 1747 to 2009. Individual TRW records of the $\delta^{13}C_{methoxyl}$ cores for (c) the annually resolved period 1971–2009 and (d) the pentadally resolved period 1747 to 2009.

Table 1
Mean inter-series correlation (mean of the correlations of each series with each series) of annually resolved records and those derived from measurements of pentadal blocks. Correlation with TRW record and with JJA temperature are shown for all $\delta^{13}C_{methoxyl}$ records (raw values and corrected and detrended records). Correlation coefficients with $p < 0.001$ are shown in bold, $p < 0.01$ are underlined, and $p < 0.05$ are shown in italics. The degrees of freedom were reduced for calculation of the correlation coefficient between the $\delta^{13}C_{methoxyl}$ (mean of the five series) and the TRW record as well as JJA temperature, due to lag-1 autocorrelation in both time series.

	Raw $\delta^{13}C_{methoxyl}$	$\delta^{13}C_{methoxyl}$ atmo	$\delta^{13}C_{methoxyl}$ atmo + Kürschner	$\delta^{13}C_{methoxyl}$ atmo + Feng	$\delta^{13}C_{methoxyl}$ atmo + optimum	$\delta^{13}C_{methoxyl}$ high frequency
Annual resolution (1971–2009)						
Mean inter-series correlation $n = 39$	0.14	0.23	*0.31*	0.46	**0.58**	0.27
Correlation with TRW chronology $n = 39$	0.29	**0.62**	**0.62**	0.66	**0.79**	0.44*
JJA temperature $n = 39$	0.40	**0.66**	**0.71**	**0.74**	**0.75**	**0.56***
Pentadal resolution						
Mean inter-series correlation $n = 41–51$ (1806–2009)–(1756–2009)	**0.50**	0.28	*0.32*	**0.52**	**0.73**	*0.29*
Correlation with TRW chronology $n = 48$ (1771–2009)	0.08	**0.57**	**0.71**	**0.54**	**0.66**	**0.67***
JJA temperature $n = 29$ (1866–2009)	−0.20	0.59	**0.75**	**0.86**	0.87	*0.41**

* Correlations were the $\delta^{13}C_{methoxyl}$ as well as the TRW record and JJA temperature were detrended with a 10-year and 10-point FFT filter, respectively.

The highest mean inter-series correlations is revealed in the optimum corrected reaching $r = 0.58$ ($p < 0.001$) for the annually resolved and $r = 0.73$ ($p < 0.001$) for the pentadally resolved series (Table 1). Low mean inter-series correlations were found in the high-pass filtered (10-year and 10-point, see Methods) data, reaching $r = 0.27$ ($p > 0.05$) in the annually resolved and $r = 0.29$ ($p < 0.05$) in the pentadally resolved time series (Table 1). Application of the optimum correction also changed the correlation between $\delta^{13}C_{methoxyl}$ and TRW from $r = 0.29$ to $r = 0.79$ ($p < 0.001$) at annual resolution. For the pentadally resolved data, the highest $\delta^{13}C_{methoxyl}$/TRW correlation ($r = 0.71$, $p < 0.001$) is recorded in the data corrected considering Kürschner (1996) (Table 1).

3.3. Climate signals in TRW and $\delta^{13}C_{methoxyl}$ records

While the annually resolved TRW chronology correlates best with mean temperatures of May–July (MJJ) ($r = 0.68$, $p < 0.001$) and June–August (JJA) ($r = 0.64$, $p < 0.001$), the Suess effect corrected

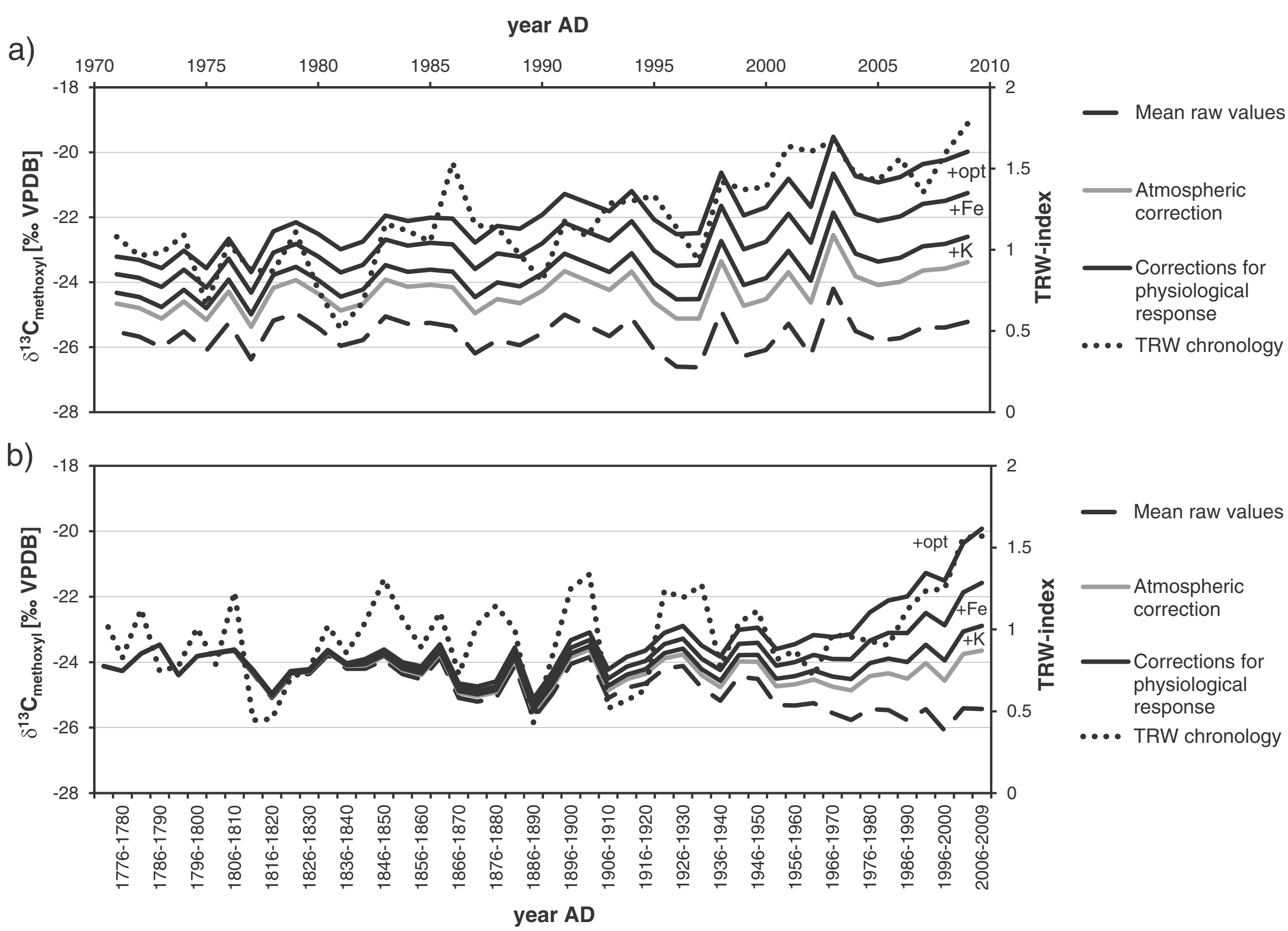

Fig. 5. Effect of the correction of the physiological response to the increased atmospheric CO_2 concentration and the change in the atmospheric $\delta^{13}C$ value (a) are the annually resolved records, (b) the pentadally resolved records. Mean raw values indicate the raw $\delta^{13}C_{methoxyl}$ record, "Atmospheric correction" refers to the correction of the Suess effect only, and +K, +Fe, and +opt are combined correction of the Suess effect and an increase in the discrimination of 0.0073 ‰/ppmv CO_2 for +K (Kürschner, 1996), 0.02 ‰/ppmv CO_2 for +Fe (Feng and Epstein, 1995), and self-derived values of 0.032 ‰/ppmv CO_2 (a) and 0.036 ‰/ppmv CO_2 (b) for +opt (Treydte et al., 2009). The detrended TRW records of all trees are plotted for comparison.

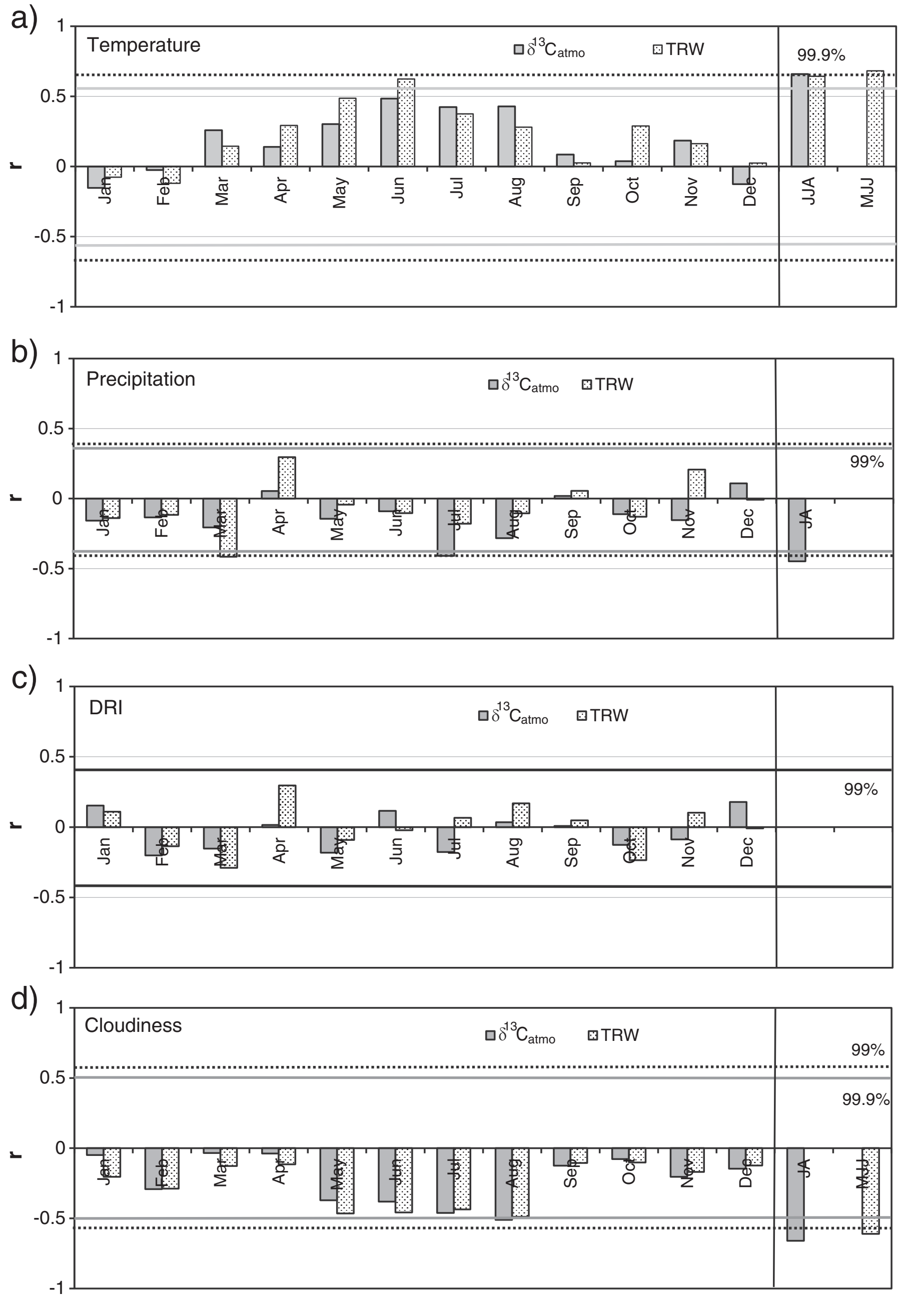

Fig. 6. Monthly correlation coefficients between the annually resolved $\delta^{13}C_{methoxyl\ atmo}$ record, the TRW record and temperature (a), precipitation (b), DRI (c), and cloudiness (d) for the current year together with the highest correlations for a combination of months for the period 1971–2009. Significance levels are given in each panel. If correlation coefficients for specific seasons are calculated (a, b, d), these are given after the reduction of the degrees of freedom due to lag-1 autocorrelation of the data series. Bold gray lines (a, b, d) indicate significance level for the correlation of the atmospheric corrected $\delta^{13}C_{methoxyl}$ record. Dotted black line (a, b, d) indicates significance level for the correlation of the TRW record. Solid black lines (c) indicate significance level for the TRW and atmospheric corrected $\delta^{13}C_{methoxyl}$ records.

$\delta^{13}C_{methoxyl\ atmo}$ record contains a clear JJA temperature signal ($r = 0.66$, $p < 0.001$) (Fig. 6a). Further, the $\delta^{13}C_{methoxyl\ atmo}$ data are negatively correlated with summer (JA) precipitation. The TRW or $\delta^{13}C_{methoxyl\ atmo}$ records show no significant correlation with the drought index (DRI), while the $\delta^{13}C_{methoxyl\ atmo}$ data reach correlations up to $r = -0.66$ ($p < 0.001$) with JA cloudiness and the TRW data $r = -0.61$ ($p < 0.01$) with MJJ cloudiness (Fig. 6d).

Highest correlations for both the pentadally resolved TRW and the atmospheric corrected $\delta^{13}C_{methoxyl}$ records were also found with summer temperatures (Fig. 7a), with the TRW data correlating at $r = 0.73$ ($p < 0.001$) to JJA temperature, and the $\delta^{13}C_{methoxyl\ atmo}$ data at $r = 0.59$ ($p < 0.01$) to JJA temperature. Spring (April–May) precipitation and DRI data correlate at $r = 0.56$ ($p < 0.01$) and $r = 0.57$ ($p < 0.01$), respectively, with the TRW data.

Highest correlations were found between JJA temperatures and the annually and pentadally resolved $\delta^{13}C_{methoxyl\ atmo}$ and TRW records, indicating that the climate parameter (temperature) and season (JJA) are most indicative. The following correlations were calculated using the $\delta^{13}C_{methoxyl}$ data corrected for tree physiological response with the factor resulting from the approach of Treydte et al. (2009). For the annually resolved $\delta^{13}C_{methoxyl}$ series, the correlation with JJA temperature increased to $r = 0.75$ ($p < 0.001$; Table 1, Fig. 8a) after application of the optimum correction. The strongest JJA temperature signal ($r = 0.87$; $p < 0.01$; Table 1; Fig. 8c) is observed for the optimum corrected,

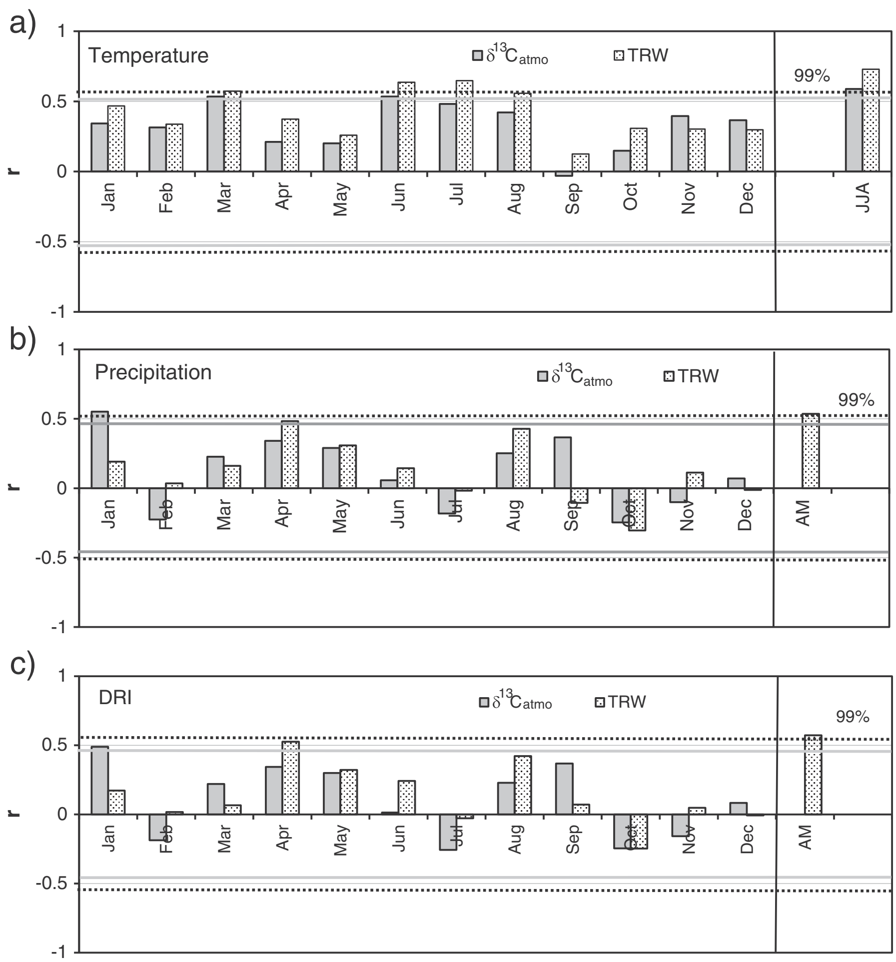

Fig. 7. Monthly correlation coefficients between the pentadally resolved $\delta^{13}C_{methoxyl\ atmo}$ record, the TRW record and temperature (a), precipitation (b), and DRI (c) for the current pentade together with the highest correlations for a combination of months for the period 1866–2009. Significance levels are given in each panel. If correlation coefficients for specific seasons are calculated (a, b, c), these are given after the reduction of the degrees of freedom due to lag-1 autocorrelation of the data series. Bold gray lines (a, b, c) indicate significance level for the correlation of the atmospheric corrected $\delta^{13}C_{methoxyl}$ record. Dotted black lines (a, b, c) indicate significance level for the TRW record.

pentadally resolved $\delta^{13}C_{methoxyl}$ data. However, the series corrected using other discrimination factors result in significant and only slightly lower summer temperature correlations: $r = 0.71$ (Kürschner, 1996) and $r = 0.74$ (Feng and Epstein, 1995) for the annually resolved series; $r = 0.75$ (Kürschner, 1996) and $r = 0.86$ (Feng and Epstein, 1995) for the pentadally resolved series (Table 1). Considering the 10-year and 10-point high-pass filtered $\delta^{13}C_{methoxyl}$ and summer temperature data, the correlations decrease to $r = 0.56$ for the annually and $r = 0.41$ for the pentadally resolved data but still reach significance at $p < 0.001$ and $p < 0.05$, respectively (Fig. 8b and d).

4. Discussion

4.1. $\delta^{13}C$ values of lignin methoxyl groups

The weak inter-series correlation of the annually resolved raw $\delta^{13}C_{methoxyl}$ data in comparison to other $\delta^{13}C$ studies (e.g., Konter et al., 2014; Kress et al., 2010; Treydte et al., 2001; Treydte et al., 2009) and the corresponding TRW series (Fig. 4) cannot yet be explained. Weak inter-series correlation but nevertheless high strength of the climate signal has also been reported for wood anatomical features such as vessel size records (Fonti et al., 2009). By contrast, the significant mean inter-series correlation for the pentadally resolved series is mainly caused by the dominating decrease in the long-term trend due to the Suess effect. This is confirmed by the decrease of the inter-series correlations after correction of the Suess effect (Table 1).

It has been demonstrated that the $\delta^{13}C$ values of lignin methoxyl groups contain a constant offset to the isotope values derived from cellulose or whole wood of the same tree-rings (Gori et al., 2013; Mischel et al., 2015), and both the intra- and inter-annual $\delta^{13}C$ variations are highly similar between lignin and cellulose based measurements (Wilson and Grinsted, 1977). Therefore, we can to the greatest possible extent exclude any miss-interpretation of the long-term tree-ring $\delta^{13}C$ response to CO_2 and climate due to the specific wood component measured in this study. We can, however, not exclude that the slightly higher discrimination factor used in the optimum correction applied to the pentadally resolved time series could be due to an age-related increasing trend in the $\delta^{13}C_{methoxyl}$ values comparable to the age-trend in TRW data (Esper et al., 2010). Such trends might lead to lower $\delta^{13}C_{methoxyl}$ values in young tree rings, although testing this hypothesis would require measuring $\delta^{13}C_{methoxyl}$ in many more, and differently aged trees.

The application of additional correction methods (Feng and Epstein, 1995; Kürschner, 1996; Treydte et al., 2009) results in increasing mean inter-series correlations due to the increasing long-term trend in the annually and pentadally resolved series. The alignment of the long-term trends in $\delta^{13}C_{methoxyl}$ and TRW records results in the highest correlations of $r = 0.79$, considering the optimum corrected annually resolved $\delta^{13}C_{methoxyl}$ record, and $r = 0.71$, considering the Kürschner (1996) corrected pentadally resolved $\delta^{13}C_{methoxyl}$ record (Table 1). However, also the high-pass filtered $\delta^{13}C_{methoxyl}$ and TRW records show significant correlations reaching $r = 0.44$ at annual and $r = 0.67$ at pentadal resolution.

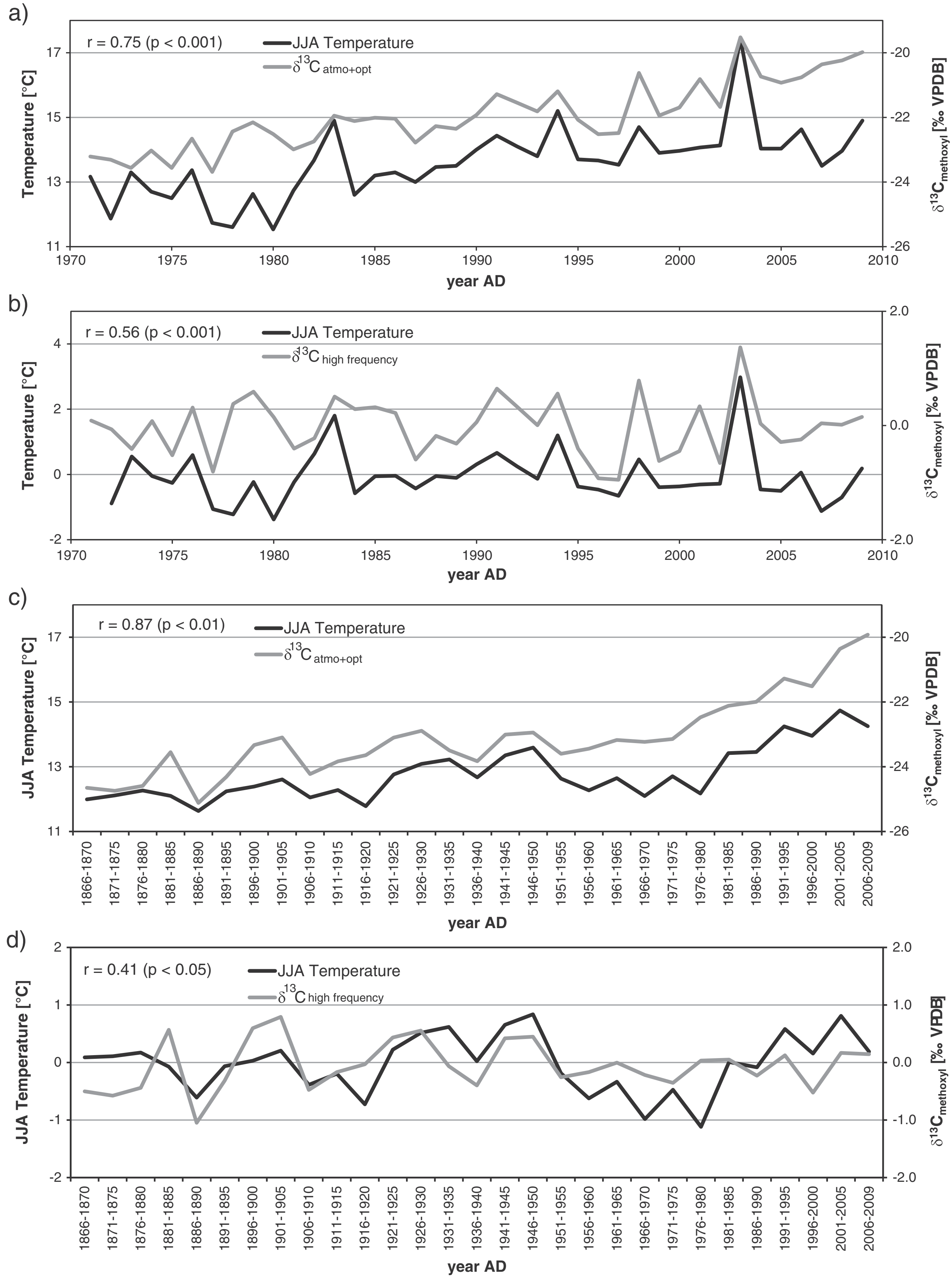

Fig. 8. June–August (JJA) temperature and (a) the annually resolved, optimum corrected $\delta^{13}C_{methoxyl}$ record (Treydte et al., 2009); (b) annually resolved $\delta^{13}C_{methoxyl}$ data detrended with a 10-year FFT filter both for the period 1971 to 2009; (c) pentadally resolved, optimum corrected $\delta^{13}C_{methoxyl}$ record; (d) pentadally resolved $\delta^{13}C_{methoxyl}$ data detrended with a 10-point FFT filter both for the period 1866 to 2009.

The correction method of Treydte et al. (2009) performing correlation tests using a range of discrimination factors indicates that the correction of the Suess effect alone does not result in an optimal fit to the long-term trend of the target instrumental data. Obviously, some of the low-frequency signal is still suppressed by non-climatic trends, which is hypothesized to be related to the increase of atmospheric CO_2 concentration and plant physiological reactions via leaf internal ^{13}C discrimination changes (Feng and Epstein, 1995; Kürschner, 1996; McCarroll et al., 2009; Treydte et al., 2001; Treydte et al., 2009; Wang et al., 2011). The increase in the discrimination rate of 0.032 ‰/ppmv–0.036 ‰/ppmv CO_2 derived in this study is the highest among published values. A possible explanation for the wide range of CO_2-increase-related discrimination changes could be the fact that water-use efficiencies in different habitats and different tree species vary as well. Waterhouse et al. (2004) showed that pine trees act with higher water-use efficiency than beech and oak at a site in South Bedfordshire (England), while Kloeppel et al. (1998) found larches to have a lower water-use efficiency than evergreen conifers at the same site. Only recently, Saurer et al. (2014) confirmed variations in the water-use efficiency between conifers and deciduous species from several sites in Europe. It thus appears unlikely that the correction factor remains constant among tree species. We hypothesize that the relatively high discrimination of 0.032–0.036 ‰/ppmv CO_2 in this study is likely related to a less effective water-use efficiency of larch (Kloeppel et al., 1998). It has to be noted that the majority of studies with published discrimination factors used evergreen conifers (Feng and Epstein, 1995; McCarroll et al., 2009; Treydte et al., 2009; Wang et al., 2011). However, further work involving different tree species from different sites is needed to reduce uncertainty in the correction of $\delta^{13}C$ time series.

4.2. $\delta^{13}C_{methoxyl}$ and TRW response to climate

As expected, we found a clear summer temperature signal in TRW chronology from our high-elevation site. However, we also found significant temperature signals in $\delta^{13}C_{methoxyl\ atmo}$ and reduced correlations with warm season precipitation and cloudiness data. Also, the TRW chronology anti-correlated with the cloud cover observational data. The combined signals are likely related to the regional synoptic associations including a negative correlation between summer temperature and precipitation, as well as positive correlation between cloudiness and precipitation. Further, cloudiness affects solar irradiance and air humidity in connection with precipitation and evaporation. The correlations with these latter parameters are overall lower though, indicating temperature to be the main controlling factor of both TRW and $\delta^{13}C_{methoxyl}$. Drought signals are overall weak.

A similar pattern occurred in the pentadally resolved TRW and $\delta^{13}C_{methoxyl\ atmo}$ records. These time series contain the expected summer temperature signal, but TRW additionally correlates positively with spring precipitation and drought, which appeared surprising as no such correlation is seen in the annually resolved data. The positive correlations of the pentadally resolved records are likely driven by a long-term increase in spring precipitation, accompanying the long-term increase in summer temperature in the region. The correlations with temperature are also higher than those with precipitation and drought.

4.3. $\delta^{13}C_{methoxyl}$ as a climate proxy

The results of the differently corrected and detrended, annually and pentadally resolved $\delta^{13}C_{methoxyl}$ records indicate this novel parameter to be an appropriate proxy for summer (JJA) temperature at this high alpine site. Also the high-frequency $\delta^{13}C_{methoxyl}$ series show that not only the long-term trend supports correlation with summer temperatures but also that year-to-year and pentade-to-pentade variations are preserved in the $\delta^{13}C_{methoxyl}$ data (Fig. 8, Table 1). The correlation with summer temperature and the non-appearing drought signals indicate that methoxyl-based $\delta^{13}C$ data are likely more closely related to photosynthetic activity via the enzyme RuBisCo than to stomata conductance. This finding might be restricted to relatively cool and moist conditions at our high-elevation site. Stomatal conductance is relatively high and the carbon assimilation rate, stimulated by temperature and sunshine, seems to dominate the tree-ring $\delta^{13}C_{methoxyl}$ signal (Gagen et al., 2007; McCarroll and Pawellek, 2001).

The strength of tree-ring $\delta^{13}C$ from cellulose and whole wood as a climate proxy was investigated in several studies in the Alps (e.g., Daux et al., 2011; Gagen et al., 2006; Hafner et al., 2011; Kress et al., 2010; Treydte et al., 2001). These studies suggest that local hydroclimate conditions, particularly soil moisture and air humidity, have a strong influence on $\delta^{13}C$. For example, relative humidity and soil water content signals are revealed in tree-ring $\delta^{13}C$ of dry sites, whereas summer irradiance and temperature are controlling factors at humid sites (McCarroll and Loader, 2004). These local climate influences were also detected by Hafner et al. (2011), who analyzed $\delta^{13}C_{cellulose}$ in larch trees at the forest limit in the south-eastern Alps, indicating strong JA temperature ($r = 0.68$) and weaker JA precipitation signals ($r = -0.47$), similar to our findings. Reynolds-Henne et al. (2007) reported a correlation coefficient of $r = 0.56$ between $\delta^{13}C_{cellulose}$ and July temperatures, using oak and pine samples from moist sites (1412 mm) south of the main Alpine crest.

Due to the drier conditions in the Lötschental, a site only 30 km north of the Simplon region, Kress et al. (2010) and Treydte et al. (2001) found significant negative correlations to summer precipitation and positive correlations to summer temperature, which were combined to a drought index (Kress et al., 2010) leading to the highest correlations for this site. This drought index (DRI) was also tested in this study but did not lead to significant correlations with the $\delta^{13}C_{methoxyl}$ data. Only for the atmospheric corrected $\delta^{13}C_{methoxyl}$ record, a correlation of $r = -0.45$ ($p < 0.01$) was found for July/August precipitation. These contrasting results are likely related to the local synoptic climate. The Lötschental is a site valley of the inner alpine dry Rhône valley, reaching only 900 mm of annual precipitation (www.meteoswiss.ch). The sampling site in the Simplon valley is located on the southern site of the Simplon Pass, which is acting as a climate divide. The Simplon valley is more humid reaching 1247 mm of annual precipitation www.meteoswiss.ch), due to orographic rainfall on the southern side of the Alps. Therefore, the $\delta^{13}C$ values from the tree-rings at this site are more closely related to temperature and irradiance.

The studies based on tree-ring $\delta^{13}C_{cellulose}$ seem to confirm our findings based on $\delta^{13}C_{methoxyl}$, indicating that the applied lignin methoxyl group method in this study (Greule et al., 2009) represents a useful method for tree-ring stable isotope research and could potentially be used as a climate proxy required less preparation effort than cellulose $\delta^{13}C$. Further studies using $\delta^{13}C_{methoxyl}$ from different tree species and from different sites are needed to enhance our knowledge.

5. Conclusion

For the high-elevation larch trees studied here, the physiological response to increased atmospheric CO_2 concentration was corrected using different values for possible changes in discrimination. The optimum correction factor at our site derived after Treydte et al. (2009) resulted in a discrimination factor of 0.032 ‰/ppmv CO_2 for annually resolved and 0.036 ‰/ppmv CO_2 for pentadally resolved $\delta^{13}C_{methoxyl}$ time series. These values are higher than the discrimination factors in previous publications. The higher discrimination is probably related to a lower water-use efficiency of larch trees in comparison to evergreen conifer species.

A significant JJA temperature signal is preserved in TRW as well as $\delta^{13}C_{methoxyl}$ data, the latter to be an alternative climate proxy in high-elevation, alpine environments. Low and high-frequency variations are preserved in $\delta^{13}C_{methoxyl}$ data. Our findings fit quite well to the pattern established for $\delta^{13}C_{cellulose}$ as a temperature proxy at moist sites in the alpine region, where photosynthesis is the main influencing factor.

As this new method is less time consuming in preparation than the extraction of cellulose, it seems to be a useful alternative for palaeoclimate reconstruction purposes.

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