Tree-ring δ²H values from lignin methoxyl groups indicate sensitivity to European-scale temperature changes

T. Anhäuser, Birgit Sehls, Werner Thomas, Claudia Hartl, Markus Greule, Denis Scholz, Jan Esper, Frank Keppler

1. Introduction

High-resolution tree-ring series are valuable climate archives fundamentally contributing to the understanding of past and current climate variability (Büntgen et al., 2011; Esper et al., 2019, 2002). Dendrochronological climate proxies are commonly used to reconstruct regional temperature variability derived, for instance, from tree-ring width (TRW) or maximum late wood density (MDX) from trees growing at or close to the altitudinal or latitudinal treeline (Esper et al., 2016; for hydroclimate see: Ljungqvist et al., 2020). Alternative proxies potentially suitable for climate reconstructions are tree-ring stable hydrogen and oxygen isotope ratios (expressed as δ²H and δ¹⁸O values) since these partly reflect stable isotopes of the local precipitation (δ²H⁰precip and δ¹⁸O⁰precip) (Augusti et al., 2008; Hartl-Meier et al., 2014; Hilasvuori et al., 2009; Liu et al., 2015; McCarroll and Loader, 2004; Pauly et al., 2018; Sternberg, 2009; Tang et al., 2000; Treydte et al., 2006; Voelker et al., 2014). Both δ²H⁰precip and δ¹⁸O⁰precip values are sensitive tracers of hydroclimate as they integrate a combination of (i) meteorological conditions in the moisture source area, (ii) changes during the meridional atmospheric vapor transport (particularly water volume loss, but also potential mixing of different air masses), and (iii) local temperature (Araguas-Araguas et al., 2000; Bowen et al., 2019;...
Danskgaard, 1964; Rozanski et al., 1993). Both stable water isotopes are therefore widely used proxies for a number of climate archives including ice cores, speleothems or lake sediments. Considering the global distribution of trees, suitable stable isotope proxies may therefore be particularly helpful in improving the spatial coverage of reconstructed stable water isotopes values. Furthermore, reconstructions of $\delta^2$Hprecip and $\delta^{18}$Oprecip values are able to complement commonly used tree-ring proxies (reflecting regional climate changes) with an additional stable isotope proxy (reflecting large-scale hydro-climatic changes).

When aiming to reconstruct stable water isotopes using tree-ring archives the compound of choice is commonly cellulose (e.g., Pauly et al., 2018; Treydte et al., 2006) since isotope signatures can differ among individual wood compounds (Cullen and Grierson, 2006; Wilson and Grinsted, 1977). However, cellulose incorporates hydrogen and oxygen atoms partly from leaf-water that experienced an evaporative $^2$H and $^{18}$O enrichment prior to biosynthesis (Anderson et al., 2002; Roden et al., 2000; Roden and Ehleringer, 1999; Sternberg, 2009; Voelker et al., 2014) potentially complicating the reconstruction of the initial source water $^2$H and $^{18}$O values. This has particularly been proven challenging for cellulose-derived $^2$H values as they are additionally controlled by plant physiological variability affecting internal fractionation processes (Augusti et al., 2008, 2006; Waterhouse et al., 2002). Moreover, to circumvent interferences with exchangeable hydrogen atoms, hydroxyl hydrogens must first be either replaced with nitro groups by nitration (DeNiro, 1981; Epstein et al., 1976; Yapp and Epstein, 1982) or equilibrated with water of known isotopic composition (Feng et al., 1993; Schimmelmann, 1991). The extraction procedures prior to stable hydrogen isotope analyses are therefore time consuming, particularly when aiming for a sufficient replication that allows statistical evaluation of the accompanied $^2$H and $^{18}$O variability among high resolution tree-ring series (McCcrar and Loader, 2004).

Another wood component that has been increasingly suggested for the investigation of $^2$H values in tree wood are lignin methoxyl groups (expressed as $\delta^2$HLM values; Anhäuser et al., 2017b, 2017a; Keppler et al., 2007; Riechelmann et al., 2017). Methoxyl groups (R-OCH$_3$) in wood are predominantly ether-bonded in lignin including hydrogen atoms that do not exchange with other hydrogen containing organic compounds or surrounding water. $^2$HLM values of wood can therefore readily be measured as methyl iodide (CH$_3$I) upon treatment with hydroiodic acid providing, when compared to cellulose $^2$H analysis, a fast and straightforward extraction method (Greule et al., 2008). Lignin, formed within the xylem tissue, is mainly derived from three precursor compounds: p-coumaryl, coniferyl and sinapyl alcohol (Boerjan et al., 2003). Contrary to cellulose, lignin methoxyl groups are therefore not suggested to incorporate hydrogen atoms derived from leaf water. Support for this distinction is given by Gori et al. (2013) observing only a minor common variability ($r^2 = 0.24$, 0.15 and 0.38 with $n = 76$, 149 and 73, respectively) between $^2$H values of cellulose and lignin methoxyl measured on identical tree-ring series. Thus, even though cellulose and lignin methoxyl groups share a common source of hydrogen atoms (soil water), subsequent biochemical pathways define cellulose-derived $^2$O and $^2$H values primarily as a proxy for leaf water stable isotopes (Anderson et al., 2002; Roden et al., 2000; Roden and Ehleringer, 1999; Sternberg, 2009; Voelker et al., 2014) and $^2$HLM values as a proxy for xylem water $^2$H values (Feaksin et al., 2013).

Earlier studies have mainly evaluated and quantified the spatial $^2$Hprecip-$^2$HLM relationship using numerous sampling sites across continental to global-scale transects (Anhäuser et al., 2017b; Keppler et al., 2007). Therein, $^2$HLM analysis was applied on homogenized tree-ring sections covering the most recently collected one or two decades. These studies suggested that $^2$HLM values reflect $^2$H values of the tree’s source water ($^2$Hsw) values as significant relationships between $^2$HLM and mean annual $^2$Hprecip values have been observed (implying that $^2$Hsw values reflect an annual integral of site-specific $^2$Hprecip values). As $^2$Hsw values were not measured in most of these studies, the estimated isotope fractionation was calculated between $^2$Hprecip and $^2$HLM (commonly expressed as the apparent isotope fractionation $\epsilon_{app}$). It was therefore suggested that $\epsilon_{app}$ reflects primarily the biosynthetic isotope fractionation ($\epsilon_{fas}$) during lignin methoxyl biosynthesis. Calculations of $\epsilon_{app}$ showed a broad agreement among various coniferous and deciduous tree-species ($n = 13$) with $\epsilon_{app}$ values of $-213 \pm 17\%$ except for Picea abies (L.) H. Karst. ($-237 \pm 19\%$; Anhäuser et al., 2017a). Other studies investigated site-specific $^2$HLM variability among tree species at single sites (Anhäuser et al., 2017a; Feaksin et al., 2013) showing maximum differences of $\leq 28\%$ among five trees (within a circumference of 200 m). Hence, the accompanied variability of $\epsilon_{app}$ (in the range of $\geq 17$ to $19\%$) was mainly assigned to inter-tree variability and defines the accuracy to reconstruct ‘absolute’ $^2$HLM values. Reconstructions of ‘absolute’ $^2$HLM values have therefore been considered suitable for wood samples covering anticipated large $^2$Hprecip changes (exceeding the accompanied $\epsilon_{app}$ Variability of $\geq 17$ to $19\%$) as recently observed in deep-time Eocene fossil wood specimens (Anhäuser et al., 2018).

Anhäuser et al. (2017a) suggested that relative temporal $^2$HLM changes, measured from multiple tree-ring series, may reflect relative temporal $^2$Hprecip changes much more accurately since the characterized main noise of $\epsilon_{app}$ (inter-tree variability) is minimized (Anhäuser et al., 2017a). Earlier studies conducted preliminary investigations of inter-annually resolved $^2$HLM tree-ring series (Gori et al., 2013; Mischel et al., 2015; Riechelmann et al., 2017). However, a detailed evaluation of the temporal $^2$HLM-$^2$Hprecip relationship was not possible either due to lacking site-specific instrumental $^2$HLM data (Gori et al., 2013; Mischel et al., 2015; Riechelmann et al., 2017) or potentially insufficient tree-ring series length of two decades (Mischel et al., 2015). To evaluate in detail the significance of $^2$HLM to reflect $^2$Hprecip at high resolution and its potential for climate reconstructions, this study investigates tree-ring $^2$HLM variability in the vicinity (< 2 km) of a GNIP and DWD station located at Hohenpeißenberg (Germany). Nine cores from four Fagus sylvatica L. specimens were used to perform inter-annually resolved $^2$HLM measurements with a common period of overlap 1916–2015. The data allowed also to assess the co-variance among radii and different trees and to evaluate potential non-climatic influences such as tree age. Subsequently, the $^2$HLM tree-ring series were compared to site-specific $^2$Hprecip Reference data as well as local climate data. Moreover, this study evaluates, for the first time, the influence of large-scale temperature changes and atmospheric circulation modes, such as the North Atlantic Oscillation (NAO), on tree-ring $^2$HLM values.

2. Study site and local climate

The study was conducted around the Hoher Peißenberg Mountain near the Hohenpeißenberg municipality in Germany (47° 48′N, 11° 01′E; ~800 m a.s.l.; Fig. 1). The site is located in the northern Alpine foothills consisting of molasse deposits (marlstones and calcareous gravels) and is further characterized by eutric cambisols, no permafrost and deciduous broadleaf forest.

Mean annual temperatures (MAT) during the 1916–2015 period ranged from 4.8 to 8.5 °C with a mean value of 6.6 °C and monthly temperatures varying between −1.4 °C (January) and 15.2 °C (July) (Fig. 2a, b). For the same time period, total annual precipitation ranged between 780 and 1570 mm with an average of 1160 mm, whereby half of the total annual precipitation falls between May and August. Precipitation in December, January and February falls primarily as snow. Monthly resolved $^2$Hprecip data are available from 1971 to 2008 from the nearby GNIP station (Fig. 2c, d). Weighted mean annual $^2$Hprecip values show an average value of −75‰ with a seasonal range from −107 (February) to −52‰ (August). Long-term climate trends of the 1916–2015 period at Hohenpeißenberg show that MATs increased significantly by 0.12 °C per decade ($r = 0.56$, $p < 0.001$, $n = 100$),
whereby neither significant changes in annual nor seasonal precipitation are observed (considering meteorological seasons). For the 1971–2008 period, weighted mean annual $\delta^{2}$Hprecip values correlate highly significantly with MAT ($r = 0.52$, $p < 0.001$), but show neither a significant correlation with annual ($r = -0.05$, $p = 0.62$, $n = 36$) nor with seasonal precipitation amount ($r$ ranging from $-0.32$ to $0.20$, $p > 0.05$).

3. Material and methods

3.1. Tree-ring material

Twenty Fagus sylvatica trees were sampled in spring and autumn 2016. To assure maximum age coverage, individuals with large circumferences were chosen (2.0 to 4.5 m). We took two to three cores per
tree at breast height (~1.2 m above ground) with a 5-mm increment borer yielding a total number of 52 cores (core lengths ranged from 400 to 600 mm). After collection, increment cores were cut perpendicularly to the wood fibers using a core-microtome to ease ring identification (Gärner and Niervegt, 2010). Tree-ring width (TRW) was measured for all cores with an accuracy of 0.01 mm using a LINTAB measuring table equipped with TSAP-Win Software (both Rinntech, Heidelberg, Germany). Cross-dating accuracy was assessed visually and statistically using the program COFECHA (Holmes, 1983).

For the δ2HLM analysis, four trees with no obvious disturbance influence, i.e., growth release or suppression, were selected (referred to as F1, F2, F3 and F4; Fig. 1 and Table 1). To better assess intra-tree variability, we choose three cores of F1 and two cores of F2, F3 and F4 (termed F1.1, F1.2, F1.3 and so on). The four selected trees were either located at moderate east-facing slopes (<10°), such as F1 and F2, or in flat terrain, such as F3 and F4. The longest tree-ring series of the four trees date back to 1905 (F1.2), 1844 (F2.2), 1890 (F3.1) and 1896 (F4.1) and were used to determine the ‘pith offset’ (number of missing innermost rings). The corresponding shortest tree-ring series for each tree dated back to 1912 (both F1.1 and F1.3), 1858 (F2.1), 1916 (F3.2) and 1916 (F4.2). Consequently, each tree provides a minimum of two radii that covered the 1916–2015 common period whereby two radii older than 1916 are provided by F2 (extending back to 1844 and 1858). Over the full periods, tree rings were carefully dissected at the tree ring border (latewood/earlywood transition) with a scalpel under a magnifier to subsequently allow annually resolved δ2HLM measurements. All dissected tree-ring samples yielded a minimum weight of 1 mg.

### Table 1

<table>
<thead>
<tr>
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<th>Last year</th>
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<tr>
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<td>F1.3</td>
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<td>2015</td>
</tr>
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<td>1858</td>
<td>2015</td>
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<td>F2.2</td>
<td>8</td>
<td>1844</td>
<td>2015</td>
</tr>
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<td>47°48’21.78”N</td>
<td>F3.1</td>
<td>7</td>
<td>1890</td>
<td>2015</td>
</tr>
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<td>11°2’25.85”E</td>
<td>F3.2</td>
<td>33</td>
<td>1916</td>
<td>2015</td>
</tr>
<tr>
<td>F4</td>
<td>47°48’22.90”N</td>
<td>F4.1</td>
<td>6</td>
<td>1896</td>
<td>2015</td>
</tr>
<tr>
<td></td>
<td>11°1’17.52”E</td>
<td>F4.2</td>
<td>26</td>
<td>1916</td>
<td>2015</td>
</tr>
</tbody>
</table>

3.2. Instrumentation and analytical uncertainty of δ2HLM analysis

The δ2HLM value of wood can be measured as CH3I released upon treatment of the samples with hydroiodic acid (HI) by the method described by Greule et al. (2008). Briefly, HI (0.25 ml; puriss. p.a., 55–60%, not stabilized, purchased from Sigma-Aldrich, Seelze, Germany, or Gillingham, UK, respectively) was added to the annually dissected tree-rings (1 to 10 mg, not homogenized) in a crimp glass vial (1.5 ml; IVA Analysentechnik, Meerbusch, Germany). The vials were sealed with crimp caps containing PTFE lined butyl rubber septa (1.5 ml; IVA Analysentechnik, Meerbusch, Germany). The calibration for δ2HLM values was used as carrier gas at a constant flow rate of 0.6 ml/min.

A tank of high purity hydrogen gas (H2, hydrogen 5.0, Linde, Höllriegelskreuth, Germany) with a δH value ranging from −195 to −225‰ (vs. V-SMOW, range provided by the supplier) was used as the working reference gas. The H3+ factor, determined daily during the measurement period, was between 1.9 and 2.4 ppm/nA.

All δ2HLM values were normalized by a two-point linear calibration (Paul et al., 2007) using δ2H values of two CH3I working standards relative to V-SMOW. The δ2H values of the CH3I working standards were calibrated against international reference substances (VSMOW2 [δ2H/VSMOW = 0.0 ± 0.3‰] and SLAP2 [δ2H/VSMOW = −427.5 ± 0.3‰]) using an elemental analyser-isotopic ratio mass spectrometer (IsoLab, Max Planck Institute for Geochemistry, Jena, Germany). The calibrated δ2H values in ‰ versus V-SMOW for the two CH3I working standards were −173.0 ± 1.5‰ (n = 9, 1σ) and −66.2% ± 1.2‰ (n = 8, 1σ). All samples were measured in triplicate followed by consecutive injections of both working standards. Standard deviations (1σ) of the triplicate measurements averaged ±1.4‰ (ranging from < ± 0.1 to 13.9‰). Additional uncertainty is introduced by the ‘external precision’ (also referred to as the chemical replication uncertainty). To estimate this uncertainty, we cut tree rings (n = 68) parallel to growth direction to obtain three tree-ring subsamples of the same cambial age (each comprising early and late wood). These subsamples enabled three separate HI treatments and subsequent δ2HLM analysis. The standard deviation of the three subsamples (n = 68) averaged ±2.7‰ (1σ) and was used as estimator for the ‘external precision’. Using Gaussian error propagation, the overall analytical uncertainty of the δ2HLM determination averaged ±3.6‰ (ranging from ±3.3 to ±14.4‰ with n = 1086).

3.3. δ2HLM covariance assessment and calibration

Coherency among the nine δ2HLM tree-ring series was assessed over the 1916–2015 common period using Pearson’s correlation coefficient (r), inter-series correlation (Rbar) and expressed population signal (EPS; Wigley et al., 1984). Calculations of these metrics were performed using the ‘dplR’ library in R programming (Bunn, 2008). Rbar was further employed to assess the internal coherency over time by estimating Rbar over 31-year segments. Furthermore, to test whether any anomalous tree-ring δ2HLM series causes a drastic decrease in internal coherency, we estimated modified Rbar values by consecutively removing one of the nine radii. To visualize the long-term δ2HLM coherence of the four F. sylvatica trees, we calculated for each series the annual δ2HLM deviation to its mean value of the 1961–1990 period and averaged the resulting index δ2HLM series for each tree to produce four mean δ2HLM series. To identify potential non-climatic trends of δ2HLM values of juvenile tree-rings, we compared linear trends among differently old trees over a common time period. First year autocorrelation (Lag-1) has been calculated to determine the influence of the previous year on δ2HLM.

At humid sites, such as Hohenpeißenberg, soil water drawn during the tree’s growth period rather reflects an accumulation of multiple precipitation events fallen during and prior the growth period potentially even including winter precipitation (Allen et al., 2019). To estimate the temporal integral of the source water for the F. sylvatica trees, we calculated Pearson’s correlation coefficients between tree-ring δ2HLM and δ2Hprecip (GNP) for the 1971–2008 period using a variety of monthly, seasonal and annual mean values. Moreover, we also included δ2Hprecip signatures of months of the preceding fall as well as ‘shifted’ annual values, such as previous September to current August. Whenever


δ²Hprecip values were averaged, individual δ²Hprecip values were weighted by precipitation amount to obtain representative mean values.

Correlation coefficients between δ²HLM tree-ring series and local climate parameters of Hohenpeißenberg were assessed for the common period of overlap (1916–2015) employing data of the nearby DWD station. To assess large-scale temperature influences on the Hohenpeißenberg tree-rings, spatial correlations between δ²HLM and the HadCRUT4.6 ensemble data (Morice et al., 2012) were conducted over the 1916–2015 period. Due to the prevailing westerlies across Europe, we focused on areas mainly west of Hohenpeißenberg (~48°N, 11°E). Thus, spatial correlations with land and sea surface temperature (CRU TS 4.01 and HadSST1, respectively) were conducted from North Africa to Scandinavia and from the Eastern North Atlantic to mid-Europe (range: 20°–80°N and 30°W–20°E) employing the KNMI climate explorer at 1° x 1° resolution (Royal Netherlands Meteorological Institute; http://climexp.knmi.nl). The reconstruction skill for δ²HLM tree-ring series and climate parameters was assessed by the Durbin-Watson statistics (DW) testing for lag-1 autocorrelation in the linear model residuals. Further verification statistics included the reduction of error (RE; Briffa et al., 1988) as well as the coefficient of efficiency (CE; Cook, 1994). Positive scores of both RE and CE value indicate reconstruction skill of the model (Cook, 1994).

The NAO, defined as the normalized sea-level pressure difference between the Icelandic Low and the Azores High, reflects the strength of westerly airflow over Europe is therefore an important control on European weather and climate (Hurrell, 1995). Recent studies showed an influence of the NAO on European stable water isotopes, particularly during winter (Baldini et al., 2008; Deininger et al., 2016; Field, 2010). For the common period of overlap (1916–2015), maximum and minimum δ²HLM values are comparable in magnitude with up to ~25‰ differences in F4. δ²HLM tree-ring series may also point to some hydrogen 'storage effects' inherent to all δ²HLM series. These auto-correlations may reflect an autocorrelation adopted from the δ²Hprecip values. An equivalent autocorrelation for the δ²Hprecip over the 1971–2008 period cannot be observed (r = 0.22, p > 0.1). However, a lack of autocorrelation in the δ²Hprecip data may not indicate an equivalent lack of autocorrelation for δ²HLM values. Whereas δ²Hprecip values are individually measured of monthly collected precipitation, the source water δ²H value reflects an integral of multiple precipitation events or even seasons reflecting a water body with a progressively changing δ²H value. Thus, it seems reasonable to assume an autocorrelation inherent to δ²HLM, which is transferred to the δ²HLM tree-ring series. Nonetheless, the autocorrelations observed for the δ²HLM tree-ring series may also point to some hydrogen 'storage effect' such as the incorporation of remobilized hydrogen during the lignin methoxyl groups biosynthesis.

When observing the mean δ²HLM series standardized for each tree (Fig. 3c), both the short-term (inter-annual) and long-term (multi-decadal) changes in δ²HLM values are comparable in magnitude with up to ~20‰. The long-term δ²HLM trends can broadly be grouped into four phases including (1) a decline of ~20‰ from 1858 to 1916 (covered only by F2), (2) a ~15‰ increase from 1916 to 1956 retained in all trees, (3) a decrease of ~10‰ until 1981, and (4) an increase by ~25‰ during the most recent decades. The most recent increase in δ²HLM values is most pronounced in F4.

### Table 2
Descriptive statistics of the nine δ²HLM tree-ring series of the four Fagus sylvatica trees.

<table>
<thead>
<tr>
<th>Series ID</th>
<th>Minimum</th>
<th>Maximum</th>
<th>Difference (Max. – Min.)</th>
<th>Mean with SD (1σ)</th>
<th>Autocorrelation (Lag-1)</th>
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<tbody>
<tr>
<td>F1.1</td>
<td>−294</td>
<td>−243</td>
<td>51</td>
<td>−269 ± 11</td>
<td>0.645</td>
</tr>
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<td>F1.2</td>
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<td>−266 ± 10</td>
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<tr>
<td>F1.3*</td>
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<td>−236</td>
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<td>−271 ± 11</td>
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<tr>
<td>F2.1</td>
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<td>F3.1</td>
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<td>−231</td>
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<td>41</td>
<td>−261 ± 15</td>
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* Nine years (1923–1931) are missing due to analytical problems.
Table 3
Pearson’s $r$ (with $n$) between the nine annually resolved $\delta^{2}H_{LM}$ tree-ring series (all statistically significant at $p < 0.001$). Color shading indicates $r$ values between radii of the same tree.

<table>
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<tr>
<th></th>
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<th>F1.3</th>
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</tbody>
</table>

Fig. 3. Characteristics of the $\delta^{2}H_{LM}$ tree-ring series. (a) Rbar statistics for 31-year segments (black solid line) and for the full 1916–2015 period (dashed line) (b) Annually resolved $\delta^{2}H_{LM}$ values of the four $F. sylvatica$ trees (F1, F2, F3 and F4) collected at Hohenpeißenberg (Germany). Each series reflects the mean $\delta^{2}H_{LM}$ series with $n = 2$ or 3. (c) Standardized tree-ring series of (b) using the mean $\delta^{2}H_{LM}$ value of the reference period 1961–1990.
of F2 (cambial age 81–termed as phase of F1 (cambial age 12
chronology development have been observed over century-scale time periods (Esper et al.,
accordance to re
series over the period 1916
\[\delta H_{LM}\] trends and tree age (cf. Table 4). The slopes of
\[\delta H_{LM}\] values, we consider only the first mechanism (soil water-related)
as influential because leaf water-derived hydrogen is not involved in lignin methoxyl group’s biosynthesis (Boerjan et al., 2003). Thus, as the juvenile \[\delta H_{LM}\] values of F1 presented in this study show a minor mean trend deviation (associated with increasing \[\delta H\] values), this indicates no impact of soil water-related juvenile effects, which would be associated with decreasing \[\delta H\] values. This may either point to a weak or nonexistent gradient of soil water \[\delta H\] values at Hohenpeißenberg or to a quickly developed root system of F. sylvatica trees within the first decade of growth. Nonetheless, future studies should take into account the potential influence of soil water evaporation rates on juvenile \[\delta H_{LM}\] values, in particular for more arid study sites than Hohenpeißenberg.

A visibly stronger discrepancy in \[\delta H_{LM}\] trends among the different trees can be observed for F4 at the end of our chronology (Fig. 3c). Comparing this discrepancy to F3, having a similar age as F4 (7 years apart; Table 1), suggests an influence not related to tree age. Similar conclusions can be drawn considering the moving Rbar values (Fig. 3a). The indicated coherency decrease occurs in the central part of our chronology, which only partly overlaps with the juvenile phase of F1. Consequently, deviations in the temporal \[\delta H_{LM}\] trends seem not primarily associated with juvenile growth phases or tree age in general, but may also be associated with temporal disturbances of \[\delta H_{LM}\] among the four tree sampling sites. A plausible mechanism would be a changing relationship between \[\delta H_{precip}\] and \[\delta H_{sw}\] over time in the nearby tree environment, such as changing soil and hydrological properties (leading to varying source water accumulation). A better understanding of such occasional temporal trend deviations in \[\delta H_{LM}\] may improve sampling strategies. Trees with potential temporal disturbances in the \[\delta H_{sw}\]–\[\delta H_{LM}\] relationship may justifiably be excluded when producing a mean \[\delta H_{LM}\] chronology subsequently leading to an improved overall coherency. Nonetheless, the \[\delta H_{LM}\] values of the nine tree-ring series generally show strong coherency and no major influence related to tree age. Therefore, we developed a chronology (without conducting any detrending or correction method) for the common period 1916–2015 by calculating for each of the nine tree-ring series the annual \[\delta H_{LM}\] deviation to the mean of the 1961–1990 period. Subsequently, by integrating all nine \[\delta H_{LM}\] series, a mean chronology was calculated with 95% confidence intervals to account for the internal variability (Fig. 5).

### 4.3. Relationship between \[\delta H_{LM}\] chronology and local \[\delta H_{precip}\] and climate

For the 1971–2008 period, correlations between the \[\delta H_{LM}\] chronology and \[\delta H_{precip}\] signatures are insignificant when using single months except for June (\(r = 0.43, p < 0.01\); Fig. 6a). Correlations partly increase in magnitude when using averaged \[\delta H_{precip}\] values of

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**Table 4**

Statistics of the linear regression analysis of the four mean \(\delta H_{LM}\) tree-ring series over the period 1916–1956 (as shown in Fig. 4). Series are ordered in accordance to reflected growth phase.

<table>
<thead>
<tr>
<th>Series</th>
<th>(r (p &lt; 0.05))</th>
<th>Slope with 95% CI</th>
<th>Cambial age covered</th>
</tr>
</thead>
<tbody>
<tr>
<td>F2</td>
<td>0.39</td>
<td>0.24 ± 0.18</td>
<td>81–121 (mature)</td>
</tr>
<tr>
<td>F3</td>
<td>0.63</td>
<td>0.34 ± 0.14</td>
<td>27–67 (intermediate)</td>
</tr>
<tr>
<td>F4</td>
<td>0.50</td>
<td>0.31 ± 0.17</td>
<td>27–67 (intermediate)</td>
</tr>
<tr>
<td>F1</td>
<td>0.67</td>
<td>0.49 ± 0.18</td>
<td>12–52 (juvenile)</td>
</tr>
</tbody>
</table>

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**Fig. 4.** Linear regression analysis of the four mean \(\delta H_{LM}\) tree-ring series over the period 1916–1956. During this period, trees differ in age. Statistics of linear fits are given in Table 4.
the previous fall, previous winter, spring and summer ($r = 0.40, 0.42, 0.53,$ and $0.45$, respectively; $p < 0.01$). Highest $r$ values are, however, found when using annual integrals, such as January until December with $r = 0.66$ ($p < 0.001$) or previous September to current August with $r = 0.73$ ($p < 0.001$; Fig. 6a and Supplemental Fig. S3). The observed pattern of the estimated correlation coefficients ($r$ values increase when extending the temporal integral of $\delta^{2}H_{\text{precip}}$ values) clearly indicates that tree's source water rather reflects an accumulation of multiple months to seasons and agrees with earlier findings (Allen et al., 2019; Ehleringer and Dawson, 1992; Feng and Epstein, 1995; Tang et al., 2000). Recent investigations supported this particularly for $F. sylvatica$ because they primarily use water from deeper soil layers (40 to 50 cm; Goldsmith et al., 2019) with $\delta^{2}H$ values less prone to changes induced by single precipitation events. Furthermore, tree-ring growth of $F. sylvatica$ typically starts in April and ceases in August (Čufar et al., 2008; Michelot et al., 2012) or September (Kraus et al., 2016). Precipitation falling after the latest late wood formation may therefore only contribute to the tree source water of the following year. Hence, the $\delta^{2}H_{\text{LM}}$ chronology not only correlates best with the ‘shifted’ annual values (previous September to current August), but this time period is also supported by considerations in source water accumulation and tree-ring growth. Conclusively, the $\delta^{2}H_{\text{LM}}$ chronology is considered to reflect primarily mean annual $\delta^{2}H_{\text{precip}}$ Values (previous September to current August) for the 1971–2008 period of data overlap. For the remaining years of the full 1916–2015 period, care has to be taken when the relative contribution of seasonal precipitation to the annual amount changes. In that case, $\delta^{2}H_{\text{LM}}$ would reflect a more seasonally pronounced $\delta^{2}H_{\text{precip}}$ signature. However, even though this induces some noise into the $\delta^{2}H_{\text{precip}}$-$\delta^{2}H_{\text{LM}}$ relationship, we consider this influence as negligible for Hohenpeißenberg since neither annual nor seasonal precipitation amount changed significantly over 1916–2015 (cf. Section 2).

When comparing the $\delta^{2}H_{\text{LM}}$ chronology with temperature data of the nearby DWD station (covering the full period of 1916–2015), highly

![Fig. 5. $\delta^{2}H_{\text{LM}}$ chronology for the 1916–2015 common period. Chronology reflects the arithmetic mean of the annual $\delta^{2}H_{\text{LM}}$ deviations with respect to the 1961–1990 period of the nine individual tree-ring series and is shown with 95% confidence intervals (grey lines).](image)

![Fig. 6. Pearson’s correlations ($r$) between annually resolved mean $\delta^{2}H_{\text{LM}}$ chronology (cf. Fig. 5) and $\delta^{2}H_{\text{precip}}$ from 1971 to 2008 ($n = 36$) (a) as well as with temperature, precipitation and relative humidity from 1916 to 2015 ($n = 100$) (b) for Hohenpeißenberg (Germany). Grey horizontal lines mark significance level of 99.9%.](image)
significant correlations ($p < 0.01$) are found for numerous months (previous October, January, April, June, August) with $r$ values ranging from 0.26 to 0.39 and for all seasons except for fall of the current year with $r$ values ranging from 0.29 to 0.41 (Fig. 6b). Similar as observed for $\delta^2$H$_{\text{precip}}$, the highest correlation coefficient can, however, be noted for the ‘shifted’ annually averaged temperature (year defined from previous September to August) with $r = 0.56$ ($p < 0.001$). Precipitation amount as well as relative humidity show weak correlations with the $\delta^2$H$_{\text{LM}}$ chronology (Fig. 6b) and are mostly insignificant.

4.4. Relationship between the $\delta^2$H$_{\text{LM}}$ chronology and large-scale climate and the NAO

Besides changes in local climate, $\delta^2$H$_{\text{precip}}$ at the site of precipitation is controlled by a number of large-scale and remote hydro-climatic influences. This includes changing meteorological conditions in the moisture source area, meridional atmospheric transport and particularly a modified water volume loss, but also potential mixing with different air masses (Araguás-Araguás et al., 2000; Dansgaard, 1964; Rozanski et al., 1993). Stable water isotopes are therefore increasingly considered to indicate large-scale atmospheric phenomena rather than variations in local or regional climate state (Bowen et al., 2019) including atmospheric circulation modes such as the NAO index (Baldini et al., 2008; Deininger et al., 2016; Field, 2010).

As the $\delta^2$H$_{\text{LM}}$ chronology reflects best annually averaged $\delta^2$H$_{\text{precip}}$ values (previous-year September to current-year August), spatial correlations have been accordingly estimated between the Hohenpeißenberg $\delta^2$H$_{\text{LM}}$ chronology and mean annual surface temperatures (previous-year September to current-year August). The results show significance across Western Europe ($r$ ranging from 0.2 to 0.6 with $p < 0.1$; Fig. 7a). Highest correlations (with $r > 0.6$) are found for both land (northern Mediterranean) and numerous sea areas (western Mediterranean Sea, northwest North Sea, Gulf of Biscaya, parts of the eastern North Atlantic and the Arctic Sea). This shows that the $\delta^2$H$_{\text{LM}}$ chronology exhibits higher correlations with temperature anomalies of multiple remote areas than with local temperature anomalies at Hohenpeißenberg (Fig. 6b). A similar evaluation of temperature influences on the temporal variability of stable water isotopes was done by Field (2010) using data of 23 central European GNIP stations. Therein, spatial correlations between temperature and stable water isotopes showed a similar multi-centered structure with areas of highest correlations west of the used GNIP stations. Correlations between the $\delta^2$H$_{\text{LM}}$ chronology and the NAO index are insignificant regardless of the used monthly or averaged winter NAO index (Fig. 7b). Based on the found temporal integral of accumulated soil water at Hohenpeißenberg (previous September to current August; Fig. 6a), the lacking influence of the NAO on the $\delta^2$H$_{\text{LM}}$ chronology may not be surprise. Correlations between the NAO and stable water isotopes have mainly been reported during winter (Baldini et al., 2008; Field, 2010) including also the Hohenpeißenberg study site (Deininger et al., 2016). Overall, the $\delta^2$H$_{\text{LM}}$ chronology reflects climatic imprints commonly observed for central European stable water isotopes. Moreover, a lacking sensitivity for the NAO is further evidence that $\delta^2$H$_{\text{LM}}$ values record primarily an annual integration of $\delta^2$H$_{\text{precip}}$ values.

The main moisture source of precipitation of the northern Alpine foothills (including the Hohenpeißenberg study site) has been determined by Lagrangian moisture source diagnostics for the time period 1995–2002 (Sodemann and Zubler, 2010). This study concludes that the majority of annual northern Alpine precipitation originates from multiple sources including the eastern North Atlantic (~29%), continental Europe (~21%), the Western Mediterranean Sea (~16%), the North and Baltic Sea (~13%) and the Arctic and Nordic Seas (~5%). Consequently, even though our $\delta^2$H$_{\text{LM}}$ chronology shows highly significant correlations with large-scale and remote annual temperature changes, the involved stable water isotope mechanisms on Hohenpeißenberg $\delta^2$H$_{\text{precip}}$ values are more complex considering the multiple moisture source areas of northern Alpine precipitation and the associated numerous hydro-climatic influences therein. A dominant control on inter-annual variability of stable water isotopes comes from variations in the Rayleigh distillation (Gat, 1996). This process describes the progressive $^2$H depletion of the remaining atmospheric vapor as a result of consecutive rainouts along the air mass trajectory. Consequently, the Rayleigh distillation alters primarily as a function of the temperature gradient between the moisture source areas and the site of precipitation. Interestingly, northern Alpine moisture source areas (Sodemann and Zubler, 2010) overlap broadly with areas where temperature changes show the highest correlations with the Hohenpeißenberg $\delta^2$H$_{\text{LM}}$ chronology ($r > 0.6$; Fig. 7a). Therefore, the
positive correlation areas (Fig. 7a) may point to a potential linkage between rising temperatures in the moisture source areas and a less intense Rayleigh distillation leading to higher δ²H$_{\text{precip}}$ values at Hohenpeißenberg.

4.5. Western European surface temperature changes as main control for the δ²H$_{\text{LM}}$ chronology?

To assess the temporal stability of the found large-scale temperature influence on central European stable isotopes, we attempt to reconstruct averaged surface temperatures changes of the area enclosing the highest spatial correlations ($r > 0.6$; 15°W - 20°E; 25–75°N; black box in Fig. 7a). We developed a linear regression model between the annually averaged (previous September to August) Western European surface temperature (WEST) anomaly and the δ²H$_{\text{LM}}$ chronology. The model reveals a significant correlation ($r = 0.72$; $p < 0.001$, DW = 1.4) with an elevated $r$ value when compared to any of the observed correlations shown in Fig. 7. When expressing the linear regression model, the following equation is obtained:

$$\Delta\text{Temperature}_{\text{WEST}}[^\circ\text{C}] \approx (\Delta\delta^{2}\text{H}_{\text{LM}}[^\%] + 0.75)/13.66[^\%/^\circ\text{C}]$$  \hspace{1cm} (1)

We subsequently compared the reconstructed and instrumental WEST anomalies at annual resolution (Fig. 8). To account for errors induced by the internal δ²H$_{\text{LM}}$ variability of the nine tree-ring series, we converted the annually estimated 95% confidence interval (error bars in Fig. 5) into temperature using Eq. (1). As an additional error assessment, we calculated the differences of the reconstructed and instrumental WEST anomalies that result at annual resolution (Fig. 8b). Differences between annually reconstructed and instrumental WEST anomalies differ in the range of −0.9 to +1.3 °C with an average absolute deviation of 0.3 °C ($n = 100$) (Fig. 8b). Hence, for the broad majority of annual reconstructions ($n = 84$), absolute deviations are < 0.5 °C, whereby the remaining absolute deviations in annual reconstructions are either between 0.5 and 1.0 ($n = 14$) and highest in 1956 and 1993.

When conducting a split calibration/verification on the linear model (Eq. (1)), a rather weak temporal robustness is indicated (1916–1965: CE = −1.52, RE = −0.73; 1966–2015: CE = 0.12, RE = −0.79). To explore this issue in more detail, we calculated a moving correlation for 31-year segments (blue line in Fig. 8c). The beginning of the chronology shows $r$ values ranging between 0.4 and 0.6 until the segment centered at 1940. After that, $r$ values decrease and remain distinctively lower (ranging between 0.2 and 0.4) until the segment centered at 1972. In the following, $r$ values increase again to values ranging between 0.5 and 0.8 until the end of the chronology. The phase of low moving correlations begins and ends rather abruptly also centering around 1956. This year, showing the highest deviation between reconstructed and instrumental WEST anomalies ($\Delta + 1.3$ °C; Fig. 8b), substantially lowers the overall performance of our linear model. Interestingly, during February 1956, central and western European weather was affected by an extreme abnormality in hemispheric circulation patterns (Andrews, 1956; Dizerens et al., 2017). Due to a long-lasting blocking of the westerlies, cold polar air continuously advec ted into Western and Central Europe resulting, for instance, in the coldest month ever recorded (−12 °C) at Hohenpeißenberg. Besides this severe temperature drop, such a reverse atmospheric circulation undoubtedly shifts moisture source areas and associated air mass trajectories of central European precipitation. As a result, δ²H$_{\text{precip}}$ values of 1956 may have been extraordinary causing a strong deviation from the commonly found association with WEST anomalies.

Fig. 8. a) Instrumental and reconstructed WEST anomaly (using Eq. (1)) for the time period 1916–2015 at annual resolution. Eq. (1) was also used to convert the annually estimated 95% confidence interval into temperature (grey lines) to account for errors induced by the internal δ²H$_{\text{LM}}$ variability of the nine tree-ring series b) Difference between reconstructed and instrumental WEST anomaly at annual resolution. c) Moving correlation between WEST anomalies and the δ²H$_{\text{LM}}$ chronology (using 31-year segments; blue line) along with the equivalent moving correlations when excluding the year 1956 (pale blue line). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
Calculating moving correlations between WEST anomalies and the δ²H_LM chronology without the year 1956 notably improves the temporal robustness of the linear model (pale blue line in Fig. 8c). Nonetheless, moving correlations remain systematically lower during the central part of our chronology. Besides extreme atmospheric events modifying the relationship between temperature and stable water isotopes, the reconstruction skill may additionally be influenced by inconsistencies between δ²H_precip and δ²H_LM values. Support for this is given as the period of low moving correlation broadly resembles the one observed for the moving Rbar value indicating a decrease in coherency among the nine δ²H_LM tree-ring series (both moving correlations are shown in Fig. 9). In fact, both parameters correlate significantly ($r = 0.77, p < 0.001$) suggesting that changes in the moving correlation are mainly controlled by the internal coherency (Rbar). We again created spatial correlations between large-scale temperature changes and the δ²H_LM chronology for three separate periods (Fig. 10). To assure comparability, we chose three equal periods (1916–1948, 1949–1982 and 1983–2015), whereby the second period also broadly isolates the observed period of the lowest moving correlations (Fig. 8c). Whereas the beginning and the end of our chronology (1916–1948 and 1983–2015, respectively) show significant correlations for large areas across Europe (Fig. 10a, c), the central part (1949–1982) appears almost insensitive to European temperature changes. At the same time, reversed relationships become apparent in northern Africa (Fig. 10b). Estimating Rbar values for each of these periods, indicates the lowest value for the central third (0.29) revealing a similar pattern as observed for the moving Rbar values. Thus, during the 1949–1982 period, the internal coherency of the δ²H_LM chronology seems insufficient to accurately record local δ²H_precip changes and is consequently unable to record the climatic imprint therein.

Comparing the climate-sensitive periods 1916–1948 and 1983–2015 in detail (cf. Fig. 10b and c) shows further that areas of highest correlations move partly eastwards with time leading to an enlarged coverage of European land masses and, consequently, indicates that local Hohenpeißenberg temperatures are only significant for the most recent 1983–2015 period. As δ²H_precip changes also integrate alterations in large-scale atmospheric circulation patterns, the eastward movement of areas of highest correlation may indicate an equivalent movement of moisture source areas and the associated air mass trajectories of northern Alpine precipitation during the 20th century (moving from the European shelf to Western and Central Europe). However, contrary to the year 1956, the indicated modification in atmospheric circulation patterns between these two periods seems to have no major impact on the linear model as indicated by the

![Fig. 9. Moving correlation between WEST anomalies and the δ²H_LM chronology (blue line) along with the moving Rbar value (red line). Both moving metrics use 31-year segments and correlate with $r = 0.77$. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)](image)

![Fig. 10. Spatial correlations between surface temperature changes and the δ²H_LM chronology for three time periods (a) 1916–1948, (b) 1949–1982 and (c) 1983–2015. Same data used as in Fig. 7a. Hohenpeißenberg study site is marked by black star.](image)
elevated moving correlations for both these periods (Fig. 8c).

Conclusively, the $\delta^{2}H_{\text{LM}}$ chronology reflects primarily annually $\delta^{2}H_{\text{precip}}$ values and, consequently, shows commonly observed climatic imprints for central European stable water isotopes (particularly large-scale and remote temperature changes; Field, 2010). Despite the complex evolution of northern Alpine $\delta^{2}H_{\text{precip}}$ changes, the $\delta^{2}H_{\text{LM}}$ chronology and the produced simple linear regression model suggest that the variance can mainly be explained by WEST anomalies ($r^{2} = 0.52$). Nonetheless, even though this model demonstrates potential of applying tree-ring $\delta^{2}H_{\text{LM}}$ values for reconstructing large-scale temperature changes, it also reveals its current constraints. The temporal robustness of the found temperature influence seems sensitive to low Rbar values but also to changing atmospheric circulation patterns occurring on short and long-term scales. Thus, besides an improved understanding of occasional temporal inconsistencies among tree-ring $\delta^{2}H_{\text{LM}}$ values, future studies may also involve a critical assessment of the influence of changing atmospheric circulation patterns on the relationship between large-scale temperatures and $\delta^{2}H_{\text{precip}}$ values. Alternatively, when combined with other temperature reconstructions, tree-ring $\delta^{2}H_{\text{LM}}$ values may also serve as proxy for synoptic climate changes such as reversed atmospheric circulation patterns and/or shifts in moisture source areas.

5. Conclusions

This study provides the first comprehensive investigation of the relationship between inter-annually resolved $\delta^{2}H_{\text{LM}}$ values, instrumental $\delta^{2}H_{\text{precip}}$ as well as local and large-scale climate data by using nine annually resolved F. sylvatica tree-ring series collected at Hohenefßenberg (Germany). Tree-ring $\delta^{2}H_{\text{LM}}$ series reveal valuable features when applied as a paleoclimatic proxy. This includes a strong overall internal coherency and no indication of non-climatic (age related) trends affecting the $\delta^{2}H_{\text{LM}}$ variability. A subsequently produced averaged $\delta^{2}H_{\text{LM}}$ chronology (integrating the nine tree-ring series covering the 1916–2015 period) was found to reflect primarily annual $\delta^{2}H_{\text{precip}}$ values averaged over the period previous-year September to current-year August. This finding agrees with considerations in local source water accumulation and seasonal tree-ring growth of F. sylvatica.

In line with the found association with $\delta^{2}H_{\text{precip}}$ values, the $\delta^{2}H_{\text{LM}}$ chronology shows similar climatic imprints as commonly observed for central European stable water isotopes values including a dominant influence of large-scale and remote temperature changes. In an attempt to reconstruct annual temperature anomalies averaged over Western Europe using the $\delta^{2}H_{\text{LM}}$ chronology, a linear model showed a significant relationship ($r = 0.72$, $p < 0.001$, $n = 100$). The temporal robustness of this linear relationship revealed, however, important insights when applying tree-ring $\delta^{2}H_{\text{LM}}$ values for climate reconstructions. The internal coherence among the tree-ring proxy data can vary over time and potentially prevents an accurate recording of the climate-sensitive $\delta^{2}H_{\text{precip}}$ values. Here, indication was found that persistently low moving Rbar values (using 31-years period) of lower than 0.4 obliterates the commonly observed relationship between Western European temperature changes and the $\delta^{2}H_{\text{LM}}$ chronology. Reconstruction models may therefore benefit from an improved understanding of the internal mechanisms controlling stable hydrogen isotope fractionation during lignin methoxyl biosynthesis. Future studies may also evaluate sub-annual variability of $\delta^{2}H_{\text{LM}}$ values. Such differences would induce noise in the $\delta^{2}H_{\text{precip}}$-$\delta^{2}H_{\text{LM}}$ relationship particularly when ratios between early- and latewood width differ over time.

Besides temporal inconsistencies in the $\delta^{2}H_{\text{precip}}$-$\delta^{2}H_{\text{LM}}$ relationship, our model also suggests that the large-scale temperature influence on $\delta^{2}H_{\text{precip}}$ requires a somewhat uniform mode of atmospheric circulation. Hence, tree-ring $\delta^{2}H_{\text{LM}}$ values may particularly powerful in combination with other temperature proxies such as TRW and MXD to differentiate between temperature and meteorological controls. Moreover, instrumental stable water isotope data usually covers only a few decades and are very sparse prior the 1960s (IAEA/WMO, 2020). Thus, besides a direct application for paleoclimatic and -hydrology reconstructions, tree-ring $\delta^{2}H_{\text{LM}}$ values may also be a valuable tool to decipher climatic controls on the inter-annual variability of $\delta^{2}H_{\text{precip}}$ values.

Data availability

$\delta^{2}H_{\text{LM}}$ measurements of the nine tree-ring core are available in the Supplemental Table S1. Other data used in this publication are available to the community and can be accessed by request to the corresponding author.

Declaration of competing interest

The authors declare no competing financial interests.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.palaeo.2020.109665.

References


