Late Quaternary climate and environmental reconstruction based on leaf wax analyses in the loess sequence of Möhlin, Switzerland

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Abstract: We present the results of leaf wax analyses (long-chain n-alkanes) from the 6.8 m deep loess sequence of Möhlin, Switzerland, spanning the last ∼70 kyr. Leaf waxes are well preserved and occur in sufficient amounts only down to 0.4 m and below 1.8 m depth, so no paleoenvironmental reconstructions can be done for marine isotope stage (MIS) 2.

Compound-specific δ2Hwax analyses yielded similar values for late MIS 3 compared to the uppermost samples, indicating that various effects (e.g., more negative values due to lower temperatures, more positive values due to an enriched moisture source) cancel each other out. A pronounced ∼30 ‰ shift towards more negative values probably reflects more humid conditions before ∼32 ka. Radiocarbon dating of the n-alkanes corroborates the stratigraphic integrity of leaf waxes and their potential for dating loess–paleosol sequences (LPS) back to ∼30 ka.

Kurzfassung: Wir präsentieren die Ergebnisse von Blattwachsanalysen (langkettige n-Alkane) aus einer 6.8 m mächtigen Löss-Sequenz bei Möhlin, Schweiz, welche bis etwa 70 ka zurückreicht. Nur bis 0.4 m Tiefe und unterhalb von 1.8 m sind die Blattwachse gut und in ausreichender Menge erhalten, so dass Aussagen bezüglich der Umweltbedingungen während der marinen Isotopenstufe (MIS) 2 nicht gemacht werden können. Die Muster der n-Alkane zeigen für alle Proben einen dominanten Input von Gras-Alkanen, jedoch ist es nur anhand der n-Alkane nicht möglich, die Existenz von Koniferen vor allem während des MIS 3 auszuschliessen. Komponenten-spezifische δ2Hwax Analysen zeigen für MIS 3 ähnliche Werte wie für die obersten Proben aus der Sequenz. Offensichtlich heben sich mehrere Effekte gegenseitig auf (z.B. negativere Werte aufgrund niedrigerer Temperatur, positivere Werte aufgrund angereicherter Feuchtigkeitsquellen). Ein auffälliger ∼30 ‰ Wechsel zu negativeren Werten...
1 Introduction

Vast parts of Switzerland were repeatedly covered by glaciers (Graf, 2009). This explains the lack of widespread thick loess deposits as they exist, for example, in southeastern Germany, southeastern and eastern Europe (Haase et al., 2007). Nevertheless, there are a few sites in Switzerland where loess has been found (Gouda, 1962; Preusser et al., 2011; Gaar and Preusser, 2017), and they might have potential for palaeoenvironmental reconstruction. One of these sites is the Möhliner Feld in northwestern Switzerland (Fig. 1). Until recently, there was a subdued ridge considered to be a terminal moraine of the most extensive glaciation (MEG; >300 ka) in the Swiss Alps (Gutzwiler, 1894; Penck and Brückner, 1909; Keller and Krayss, 2011). However, the ridge cannot be linked to the MEG, because till containing Alpine material is only found 30 m below the surface and covered by gravel and loess (Preusser et al., 2011; Gaar and Preusser, 2017). While the till can be attributed to the MEG, although no numerical age control is available, the ridge has to be interpreted as a loess dune, not as a moraine, as it consists of loess (Gaar and Preusser, 2017). The dune might have been deposited by strong winds, called the “Möhlin jet”. The jet nowadays mostly occurs in winter, when the air fills up the Swiss Plateau and overflows the eastern Jura Mountains. This results in a dry wind with a speed of up to 10 m s$^{-1}$ (Schüepp, 1982; Müller, 2001; Gaar and Preusser, 2017). In 2011, a rotary drill core was recovered from the ridge, consisting entirely of loess sediment down to 6.8 m depth. According to luminescence dating (OSL and IR50), most of the loess was deposited during marine isotope stage (MIS) 2 and late MIS 3, while the lowermost part of the sequence probably dates back to MIS 4 (Gaar and Preusser, 2017).

For the present study, we analyzed long-chain $n$-alkanes, i.e., leaf waxes, in the drill core from Möhlin in order to evaluate their potential for paleovegetation reconstruction. Moreover, we applied compound-specific $\delta^{2}H$ analyses on the most abundant $n$-alkanes ($n$-C$_{29}$ and $n$-C$_{31}$) to reconstruct paleoclimate and hydrology. In addition, we performed radiocarbon dating on some $n$-alkanes to test the stratigraphic integrity of the leaf waxes.

2 Leaf waxes – a novel tool in Quaternary research

Long-chain $n$-alkanes ($>n$-C$_{25}$) are produced by higher terrestrial plants (de Bary, 1871; Eglinton and Hamilton, 1963, 1967; Kunst, 2003; Shepherd and Wynn Griffiths, 2006; Samuels et al., 2008). They are straight, saturated carbon–hydrogen chains ($C_{n}H_{2n+2}$), stable over geological timescales (Eglinton and Eglinton, 2008; Schimmelmann et al., 2006) and thus preserved in various sedimentary archives. Their homologue pattern depends on the type of vegetation (Cranwell, 1973; Marseille et al., 1999; Schwark et al., 2002) and can provide information about whether deciduous trees or grasses were dominant in the research area, whereas deciduous trees produce mainly $n$-C$_{27}$ and grasses predominantly $n$-C$_{31}$ and $n$-C$_{33}$ (Zech et al., 2010; Schäfer et al., 2016b; Schwark et al., 2002). Although controversy exists as to whether this approach can be used universally to reconstruct paleovegetation (Bush and McInerney, 2013; Wang et al., 2015), there is good evidence that leaf wax patterns can be used on a local (Schwark et al., 2002) and regional (Schäfer et al., 2016a) scale in Europe. Schwark et al. (2002) investigated $n$-alkanes in a lake in southern Germany and found a remarkable accordance of pollen records and $n$-alkanes. Schäfer et al. (2016a) measured leaf wax patterns along a transect from southern to northern Europe in grasslands, deciduous forests and coniferous forests. They analyzed samples from litter and two depths of the uppermost soil horizon. The results of the Schäfer et al. (2016a) study are that (1) the chain lengths correlate significantly along the transect with the grassland and deciduous vegetation, (2) $n$-alkanes from conifer forests show the understorey and (3) a correction for degradation of the $n$-alkanes is needed to get reliable information about the vegetation. $n$-Alkane patterns are thus a particularly valuable tool for the reconstruction of
paleov egetation when pollen are absent, which is often the case in loess—paleosol sequences (LPS).

The compound-specific isotopic composition of \( n \)-alkanes (\( \delta^2 H_{\text{wax}} \)) is increasingly used as a tool for the reconstruction of past climate conditions. Liu and Huang (2005) measured \( \delta^2 H_{\text{wax}} \) in a Chinese loess—paleosol sequence and showed that it recorded past climate changes. In principle, \( \delta^2 H_{\text{wax}} \) reflects the isotopic composition of precipitation (\( \delta^2 H_{\text{precip}} \)) (Sachse et al., 2012), which in turn depends on (and is thus a proxy for) climate (temperature, precipitation amount, evaporation) and geographical location (latitude, altitude, continentality, moisture source) (Dansgaard, 1964). Additional factors that need to be taken into account when interpreting \( \delta^2 H_{\text{wax}} \) records are biosynthetic fractionation, evaporative enrichment, vegetation period, degradation and type of vegetation (Sessions et al., 1999; Sachse et al., 2006; M. Zech et al., 2011, 2015; Kahmen et al., 2013; Gao et al., 2014; Hepp et al., 2015; Tipple et al., 2013). Evapotranspiration leads to an enrichment, depending mainly on relative humidity (M. Zech et al., 2013; Farquhar et al., 2007). Biosynthetic fractionation is often assumed to be \( \sim 160\% \) (Sachse et al., 2012).

Compound-specific radiocarbon analyses on sedimentary \( n \)-alkanes is a new tool in geochronology (Häggi et al., 2014; Haas et al., 2017; Zech et al., 2017). It allows us to test the synsedimentary nature, and thus the stratigraphic integrity of leaf waxes, and can complement other dating methods, for example based on luminescence.

3 Material and methods

The drill core from Mühlin is described in detail in Gaar and Preusser (2017). In brief, the core consists of loess down to 6.8 m but is decalcified and overprinted by pedogenesis down to 1.6 m depth and from 5.9 to 6.2 m. We sampled the core in continuous 20 cm intervals for leaf wax analyses.

3.1 Leaf wax analyses

Approximately 40 g of each sample was extracted with an accelerated solvent extractor using dichloromethane / methanol (9/1). The total lipid extract was dried and passed over pipette columns with an aminopropyl-coated silica gel as the stationary phase. Nonpolar compounds, including \( n \)-alkanes, were eluted with hexane and then spiked with 5\( \alpha \)-androstane. The long-chain \( n \)-alkanes (\( n \)C\(_{25} \)--\( n \)C\(_{35} \)) were analyzed using a GC-FID (gas chromatography–flame ionization detector) at the Department of Soil Science at TUM-Weihenstephan, Freising, Germany. The Thermo Scientific Trace 1310 was equipped with a Zebron ZB-5HT column and operated in splitless injection mode. The He carrier gas flow was set constantly to 1.2 mL min\(^{-1} \), and the GC temperature was first held at 50°C for 1 min, ramped to 250°C at 30°C min\(^{-1} \) and then to 340°C at 7°C min\(^{-1} \), and held for 11 min.

The most abundant \( n \)-alkanes, \( n \)C\(_{29} \) and \( n \)C\(_{31} \), were later targeted at the Geographical Institute, University of Bern, for compound-specific \( \delta^2 H \) analyses. Using an IsoPrime 100 mass spectrometer, coupled to an Agilent 7890A GC via a GC5 pyrolysis–combustion interface operating in pyrolysis mode with a Cr (ChromeHD) reactor at 1000°C. Each sample was measured three times. Precision of the measurements was checked by analyzing a standard \( n \)-alkane mixture with known isotopic composition twice every six runs. The H\(_3^+ \) factor was 3.4 and stable. The results are given in delta notation (\( \delta^2 H \)) versus Vienna Standard Mean Ocean Water (VSMOW).

3.2 \( n \)-Alkane patterns

The total \( n \)-alkane concentration (µg g\(^{-1} \) dry weight, \( A_{\text{tot}} \)) is here defined as the sum of \( n \)C\(_{25} \) to \( n \)C\(_{35} \). The odd-over-even predominance (OEP; Eq. 1) was calculated after Hoefs et al. (2002) and is an indicator for degradation: values smaller than 5 are considered to be strongly degraded (Zech et al., 2010; Schäfer et al., 2016a) and must thus be interpreted with care.

\[
\text{OEP} = \frac{n \text{C}_{27} + n \text{C}_{29} + n \text{C}_{31} + n \text{C}_{33}}{n \text{C}_{26} + n \text{C}_{28} + n \text{C}_{30} + n \text{C}_{32}}
\]

Changes in the average chain length (ACL; Eq. 2) of the measured \( n \)-alkanes indicate whether deciduous trees and shrubs (shorter ACL) or grasses and herbs (longer ACL) were the dominant plant type (Poynter et al., 1989).

\[
\text{ACL} = \frac{27 \cdot n \text{C}_{27} + 29 \cdot n \text{C}_{29} + 31 \cdot n \text{C}_{31} + 33 \cdot n \text{C}_{33}}{n \text{C}_{27} + n \text{C}_{29} + n \text{C}_{31} + n \text{C}_{33}}
\]

Because degradation can influence the ACL, one needs to correct for those effects (Zech et al., 2010). We performed a correction after Schäfer et al. (2016a) (Eq. 3–6), which results in the semi-quantitative %grass content for the samples.

\[
\text{Tree endmember} = 0.09 \cdot \ln(\text{OEP}) + 0.66
\]

\[
\text{Grass endmember} = -0.17 \cdot \ln(\text{OEP}) + 0.75
\]

\[
\text{Ratio} = \frac{n - C_{31} + n - C_{33}}{n - C_{27} + n - C_{31} + n - C_{33}}
\]

\[
\% \text{Grass} = \frac{\text{grass endmember} - \text{tree endmember}}{\text{grass endmember} - \text{tree endmember}}
\]

3.3 Radiocarbon dating

For radiocarbon analyses of the \( n \)-alkanes, four samples were selected and the nonpolar fraction passed over two pipette columns filled with AgNO\(_3 \) impregnated silica gel and zeolite, respectively. The zeolite was dissolved in HF, and the purified \( n \)-alkanes were recovered via liquid–liquid extraction with n-hexane. Finally, the purified \( n \)-alkanes were transferred with dichloromethane into tin capsules. The \( ^{14} \text{C} \) measurements were performed on the MICADAS accelerator mass spectrometer, coupled to an element analyzer (Ruff
et al., 2010; Salazar et al., 2015), at the LARA AMS Laboratory, University of Bern (Szidat et al., 2014). 14C results are reported as fraction modern carbon (F14C) and were corrected for constant and blank contamination (Salazar et al., 2015; Haas et al., 2017). The blank contamination was 0.4 µg C for a single tin capsule with a F14C value of 0.734 ± 0.19. The calibrated radiocarbon ages were calculated using OxCal (Ramsey, 2009) and IntCal13 (Reimer et al., 2013).

4 Results

Most samples from Mõhlin are characterized by a dominance of odd, long-chain (>nC25) n-alkanes typical for leaf waxes; additionally, other compounds and an unresolved matrix complex occur in variable amounts (Fig. 2).

However, samples from 0.4 to 1.6 m depth have very low concentrations and quantification of the target compounds is difficult. Total n-alkane concentrations for these samples can only be estimated as <0.4 µg g−1, and the OEP values are less than 5, indicating enhanced degradation. These samples are therefore not plotted in Fig. 3. All other data are illustrated in Fig. 3, Table 1 and the supplement table (Wüthrich et al., 2017b).

The two uppermost samples have n-alkane concentrations of 1.2 and 0.4 µg g−1, OEP values of 8.3 and 7.5, and ACL values of 30.1, respectively. Samples from depths of 1.6 to 6.8 m have highly variable n-alkane concentrations, ranging from 1 to 5.3 µg g−1. Their OEP values range from 9.9 to 18.6, and their ACL is between 30.5 and 31.1. The uppermost two samples and the samples below 1.6 m depth had sufficient amounts of nC29 and nC31 for compound-specific δ2H analyses. δ2Hwax values range from −215.1 to −143.5 ‰ and from −210.4 to −146.9 ‰, respectively. Down-core patterns are very similar and correlate well with an R value of 0.68.

All four samples selected and purified for radiocarbon dating yielded sufficient carbon masses for AMS analyses (Table 4.1). Fraction modern (F14C) ranges from 0.023 to 0.055, yielding calibrated 2σ ages between 26.4 and 38.0 cal kyr BP. As we did measure the whole n-alkane fraction and not single compounds, a contamination of post-sedimentary, especially short-chain and even-numbered, n-alkanes is possible, leading to too-young ages. But as three samples are in very good agreement with the ages published by Gaar and Preusser (2017), a contamination can most probably be excluded for the uppermost three samples.

5 Discussion

5.1 Chronology

The uppermost IR50 (infrared stimulated luminescence at 50°) and OSL (optically stimulated luminescence) ages from Gaar and Preusser (2017) suggest that at least the upper ~1 m of Mõhlin sequence was deposited ~19 ka, i.e., MIS 2, and just before final deglaciation of the Swiss Plateau (Wirsig et al., 2016; Wüthrich et al., 2017a). Soil formation and decalcification down to 1.6 m depth must have occurred during the Late Glacial and Holocene. The next three IR50 and OSL ages from depths of 3.4 to 5 m document rapid sedimentation between 34 and 31 ka, i.e., late MIS 3. Our radiocarbon ages from depths of 2.0 and 3.4 m are slightly younger (26.4 to 30.0 cal kyr BP) but are in reasonable agreement in view of the limitations and uncertainties related to both the luminescence and the radiocarbon dating methods. The radiocarbon age from 5.8 m depth is 31.7 to 38.0 cal kyr BP and with only 0.023 F14C even closer to the lower limit of radiocarbon dating. Nevertheless, the age is also in good agreement with the OSL and IR50 ages of 31.0 and 41 kyr, respectively, from the same depth, so all of these ages document rapid loess accumulation during late MIS 3 (Fig. 3).

The weak paleosol preserved between 5.9 and 6.2 m depth must have developed earlier although probably still during MIS 3, because it developed into loess deposited during MIS 4 based on OSL and IR50 ages of 68.1 and 58.1 kyr, respectively. Our radiocarbon age from 6.8 m depth is only 28.7–32.2 cal kyr BP and very likely underestimates the real sedimentation age of the loess at this depth. The F14C of the sample is only 0.038 and the smallest amounts of contamination (in the lab or from other compounds) can readily explain the discrepancy between the luminescence and radiocarbon ages. Another possibility might be incorporation of root-derived n-alkanes by roots from plants growing after deposition, as suggested, for example, by Gocke et al. (2014). But a post-sedimentary production of roots can most probably be excluded, as shown by Häggi et al. (2014), Zech et al. (2017) and Haas et al. (2017).

In general, our radiocarbon results are in reasonable agreement with the ages of Gaar and Preusser (2017) and corroborate the MIS 3 to MIS 4 transition with high sedimentation rates postulated for other time periods by Gocke et al. (2014) and Zech et al. (2017). The uppermost sample from 6.8 m depth is older than 28 ka and therefore about 6 ka before the MIS 3 to MIS 2 transition, which is also indicated by a much shallower MIS 3 lacustrine horizon compared to MIS 2 at the LARA site.
Table 1. Radiocarbon data and ages for the four selected samples.

<table>
<thead>
<tr>
<th>Sample label</th>
<th>Sample code</th>
<th>Carbon mass (µg)</th>
<th>F¹⁴C</th>
<th>Age range (2σ) (cal kyr BP)</th>
</tr>
</thead>
<tbody>
<tr>
<td>M11</td>
<td>BE-3951.1.1</td>
<td>54</td>
<td>0.0547 ± 0.0040</td>
<td>26.4–28.7</td>
</tr>
<tr>
<td>M18</td>
<td>BE-3952.1.1</td>
<td>42</td>
<td>0.0486 ± 0.0040</td>
<td>27.4–30.0</td>
</tr>
<tr>
<td>M31</td>
<td>BE-3953.1.1</td>
<td>80</td>
<td>0.0229 ± 0.0037</td>
<td>31.7–38.0</td>
</tr>
<tr>
<td>M36</td>
<td>BE-3954.1.1</td>
<td>88</td>
<td>0.0378 ± 0.0038</td>
<td>28.7–32.2</td>
</tr>
</tbody>
</table>

Figure 3. n-Alkane dates for the Möhlin loess sequence. OSL and IR50 (italic) ages have previously been published in Gaar and Preusser (2017); radiocarbon ages are given in bold letters.

orate that radiocarbon analyses of n-alkanes are a promising new tool for dating LPS back to ∼30 ka (Häggi et al., 2014; Haas et al., 2017; Zech et al., 2017). Moreover, the stratigraphic integrity and synsedimentary nature of the long-chain n-alkanes could be confirmed for the uppermost 6 m.

The OSL, IR50 (Gaar and Preusser, 2017) and our radiocarbon ages show that the major part of the sequence was developed between 35 and 30 kyr and that older deposits are probably influenced by erosion. The paleosol might show a hiatus. Our interpretation is thus mainly valid for the time between 35 and 30 ka, when the rapid loess accumulation occurred.

5.2 Paleovegetation

The uppermost two samples from depths of 0.2 and 0.4 m have a relatively low ACL compared to most other samples from the profile. This indicates more input of n-alkanes from deciduous trees and shrubs; however, concentrations are also lower, and lower OEP values show enhanced degradation (Fig. 4). The plot also illustrates that changes in the alkane ratio (the same is true for the ACL) are partly an artefact of degradation. However, the sample from 0.4 m depth plots furthest below the grass endmember, which is numerically expressed as lowest %grass (Fig. 3). This possibly reflects the remnant leaf wax signal from the natural potential vegetation at Möhlin during the Holocene, i.e., mainly deciduous trees, whereas the site is used today as grassland.

While the n-alkanes between 0.6 and 1.6 m are strongly degraded and too low in concentration to robustly infer any paleoenvironmental conditions during MIS 2, high concentrations and good preservation allow this for the rest of the sequence. The positive trend in the ACL from depths of ∼6 to 2 m indicates an increase of grass-derived n-alkane input during late MIS 3. However, the observed trend in ACL is probably an artefact of degradation. This is illustrated in the endmember again (Fig. 4), in which all these samples plot very close to the grass endmember. Accordingly, %grass (Fig. 3) does not show much of a trend and no major vegetation changes seem to be documented in the n-alkane patterns for the lower part of the profile between 1.8 and 6.8 m depth, i.e., during MIS 4 and MIS 3. This example shows that it is imperative to not over-interpret ACL and to account for degradation, even when preservation is generally good.

Our results suggest that the n-alkanes preserved at Möhlin during MIS 3 and possibly MIS 4 were mainly produced by grasses and herbs and that deciduous trees and shrubs
played a minor role, if any. Based on $n$-alkanes only, however, one cannot rule out that conifer trees grew at the research site. $n$-Alkane concentrations in conifer needles are mostly about an order of magnitude lower than in deciduous trees or grass, with the exception of *Juniperus*. Hence $n$-alkane proxy records are quite insensitive for detecting conifer vegetation (Diefendorf et al., 2011; Tarasov et al., 2013; Schäfer et al., 2016b). Open conifer forest during parts of MIS 3 have been reported from peat sequences at Gossau (Schlüchter et al., 1987; Preusser et al., 2003) and Niederwangen (Drescher-Schneider et al., 2007), both located a few dozen kilometers to the east of Möhlin. Similar vegetation may have prevailed at Möhlin, with the long-chain $n$-alkanes having only recorded thinly recorded grasses, i.e., the understory of the open conifer forest.

5.3 Paleoclimatology

The $\delta^{2}H_{\text{wax}}$ values from the uppermost two samples (ranging from $-167$ to $-205 \%\epsilon$; Fig. 3) are perfectly in the range observed in topsoil samples from central Europe (Schäfer et al., unpublished data) and in agreement with what can be expected based on theoretical considerations. Assuming a constant metabolic fractionation of $-160 \%\epsilon$, $\delta^{2}H_{\text{leaf water}}$ for the uppermost two samples ranges from $-8.7$ to $-53.4 \%\epsilon$. This is close but tends to be a little bit higher than today’s $\delta^{2}H_{\text{precip}}$ in Möhlin, which has a value of $\sim -40 \%\epsilon$ in summer (Bowen et al., 2005; Bowen, 2008). As spring and possibly also winter precipitation, which is more depleted than summer precipitation, may have been used by the plants as well, some evapotranspirative enrichment certainly occurred.

The $\delta^{2}H_{\text{wax}}$ values below 1.8 m depth are relatively constant around $-180 \%\epsilon$, i.e., similar to the values from the uppermost two samples. Most conspicuously, a sudden drop occurs just below 5 m depth to values as low as $-215 \%\epsilon$ (Fig. 3). $\delta^{2}H_{\text{wax}}$ then increases again in the lowermost meter of the Möhlin sequence. The observed $\delta^{2}H_{\text{wax}}$ pattern strongly resembles the pattern from the LPS Bobingen, Germany, 200 km northeast of Möhlin (R. Zech et al., 2015). Here, $n$-alkanes are $\sim -200 \%\epsilon$ in sediments dated to latest MIS 3 ($\sim 30$ ka) and MIS 2, and values drop to $<-220 \%\epsilon$ below, before they increase again in the lowest part of the profile dated to $\sim 45$ ka.

Overall, we are therefore confident that the $\delta^{2}H_{\text{wax}}$ record from Möhlin is a local signal but also carries valuable regional information about paleoclimate changes. Interpretation in terms of changes in $\delta^{2}H_{\text{precip}}$ and evapotranspirative enrichment is, however, very challenging because disentangling these two major controls is not yet possible. To the best of our knowledge, there are no independent continuous records of $\delta^{2}H_{\text{precip}}$ in Europe during the last glacial. Luetscher et al. (2015) presented a $\delta^{18}O$ record from a northern Alpine speleothem, but it overlaps only slightly with ours and shows very little variation from 30 to 15 ka ($\sim 1 \%\epsilon$, $\delta^{18}O$, which is equivalent to $\sim 8 \%\epsilon$ $\delta^{2}H$). The only long continuous isotope records spanning the last 40 to 60 ky r currently come from an LPS in Crvenka, Serbia (R. Zech et al., 2013), which shows not much more than $10 \%\epsilon$ variability, and from marine cores offshore Portugal (Abreu et al., 2003) and in the Mediterranean Sea (Frigola et al., 2008). The marine $\delta^{18}O$ records (measured on foraminifera) show a minor trend towards more enriched values (corresponding to a $\delta^{2}H$ trend $<10 \%\epsilon$) from $\sim 60$ to 20 ka. Afterwards, during the last glacial termination and the Holocene, values become much more negative ($\sim 20 \%\epsilon$ $\delta^{2}H$). A comparison of these records suggests the following hypotheses: the sudden enrichment in $\delta^{2}H_{\text{wax}}$ after 32 ky r does not reflect a sudden change in the source, i.e., the North Atlantic. It might therefore document a sudden onset of more arid conditions and enhanced evapotranspiration.

The interpretation of the uppermost two samples is trickier: on one hand, the elevated $\delta^{2}H_{\text{wax}}$ of $nC_{29}$ in the uppermost two samples in Möhlin might document even more arid conditions than during MIS 3, because they do not show the more negative source values and thus may have experienced even more evapotranspirative enrichment, possibly caused by elevated temperatures and similar precipitation compared to MIS 3. On the other hand, $\delta^{2}H_{\text{wax}}$ of $nC_{31}$ is much more negative than $nC_{29}$. The reason for this might be different sources of $nC_{29}$ and $nC_{31}$. It makes a difference whether the alkanes are produced by grasses or deciduous trees: grasses produce their $n$-alkanes mainly in the intercalary meristem and are thus much less influenced by evaporative enrichment than deciduous trees and shrubs (Kahmen et al., 2013), which produce their $n$-alkanes mostly at leaf flush (Tipple et al., 2013) and are thus much more influenced by relative hu-
midity. Nevertheless, grasses produce also n-alkanes in their leaves (Gao et al., 2012) and also show evaporative enrichment to some degree. In older publications, it has been stated that nC_{29} is mainly produced by deciduous trees (Cranwell, 1973; Zech et al., 2010); the publication of Schäfer et al. (2016a) shows that both nC_{29} and nC_{31} are more or less equally produced by grasses and shrubs. However, relative to nC_{31}, Schäfer et al. (2016b) state that deciduous trees produce more nC_{29}. Thus the elevated amount of deciduous trees, recorded in the uppermost two samples, might show evaporative enrichment in nC_{29}. Also different biosynthetic fractionation of different plants might be a possible influence on the different values (e.g., Gao et al., 2014). As δ^{2}H_{wax} values of shrubs, trees and grasses are quite similar (Sachse et al., 2012), we think that evapotranspirative enrichment plays a more important role.

However, it is unclear how changes in atmospheric circulation, and thus source areas, have changed in the past and to which degree a temperature effect at the site of precipitation may have been relevant. If such a temperature effect was relevant on glacial–interglacial timescales and if the isotope record offshore Portugal reasonably reflected changes in the source signal, both effects would have canceled each other out explain the similar δ^{2}H_{precip} and δ^{2}H_{wax} values during the Holocene and the late MIS 3. Drawing robust paleoclimatological conclusions from δ^{2}H_{wax} records thus remains very difficult and independent δ^{2}H_{precip} records are needed to reconstruct changes in paleohumidity and evapotranspirative enrichment.

Last but not least, the OEP might also be influenced by climatic conditions: during MIS 3 it is lowest, when δ^{2}H_{wax} also has its lowest values. Higher humidity, expressed in lower δ^{2}H_{wax} values, might allow higher microbial activity and thus an enhanced degradation, which leads to a lower OEP.

### 6 Conclusions

Our investigations of long-chain n-alkanes from the Möhlin sequence reveal that they are well preserved and occur in sufficient amounts in the uppermost samples down to 0.4 m depth, as well as from 1.8 to 5.8 m depth, to use them for the reconstruction of paleovegetation and paleoclimate and for radiocarbon dating. From 0.6 to 1.6 m depth, concentrations are very low, probably related to Holocene pedogenesis and priming.

The n-alkane pattern of the uppermost samples reflects today’s grassy vegetation and possibly some leaf wax remnants of the natural deciduous forests that prevailed during most of the Holocene. No major vegetation changes are detected below 1.8 m depth. All samples indicate a dominant input of grass-derived leaf waxes and negligible contributions from deciduous trees and shrubs.

Compound-specific δ^{2}H analyses have yielded values for the uppermost samples that one can expect from today’s isotopic composition of the precipitation, the metabolic fractionation and some evapotranspirative enrichment. The δ^{2}H_{wax} values from 1.8 to 5 m depth, i.e., during late MIS 3, are not much different from today’s values, which might document that the source effect (more positive source water in the North Atlantic during the glacial) and the temperature effect (more negative precipitation during glacial times) cancel each other out. However, we cannot exclude that changes in evapotranspirative enrichment or in atmospheric circulation and thus source areas were also relevant. Independent records of δ^{2}H_{precip} would be necessary to quantitatively derive robust paleoclimatic information, particularly relative humidity and evapotranspirative enrichment. A very interesting feature in the δ^{2}H_{wax} pattern from Möhlin is a sudden shift of ~30‰ towards more negative values below 5 m depth. This shift is also observed in another LPS in the northern Alpine foreland and therefore probably a regional phenomenon. It might document a major change in paleohydrology, namely a shift from more humid to more dry conditions at ~32 ka. Nevertheless, independent δ^{2}H_{precip} records are needed for more robust paleoclimatic reconstructions.

Radiocarbon dating of the n-alkanes have yielded ages in reasonable agreement with published OSL and IR50 ages, although ages of ~30 kyr are close to the limit of radiocarbon dating of the n-alkanes. The synsedimentary nature and stratigraphic integrity of long-chain n-alkanes are thus corroborated, highlighting the great potential of this new tool for dating loess–paleosol sequences. The chronology of the Möhlin sequence shows that loess accumulation occurred during MIS 4 and started again ~34 ka, well before the onset of MIS 2.

Overall, our study shows the great potential of leaf wax analyses in LPS. More high-resolution records of leaf wax patterns and compound-specific δ^{2}H, complemented by larger numbers of radiocarbon dating, would be useful to investigate the regional variability of respective proxy patterns. Ideally, such studies should be accompanied by other sedimentological, palaeopedological and geochemical methods. Provenance analyses at Möhlin, for example, might help to investigate the proposed changes in wind direction and loess sources. Other leaf wax compounds, such as long-chain n-carboxylic acids or n-alkanols, or other biomarkers in general, could be used to corroborate and refine the vegetation reconstruction. Most importantly, the lack of independent δ^{2}H_{precip} records currently limits the possibility to robustly reconstruct past changes in relative humidity and evapotranspirative enrichment. A particularly promising path for future work is to further develop the biomarker-based “paleohygrometer”, which is based on a coupled δ^{2}H_{wax} and δ^{18}O_{sugar} approach. It allows us to disentangle changes in evapotranspiration and δ^{2}H_{precip} and has successfully been tested in topsoils (Tuthorn et al., 2015) and applied to organic-rich archives (M. Zech et al., 2013; Hepp et al., 2015).
Data availability. The dataset used in this paper can be found on the Pangaea database (Wüthrich et al., 2017b).

Competing interests. The authors declare that they have no conflict of interest.

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