



D/H ratios of methoxyl groups of the sedimentary organic matter of Lake Holzmaar (Eifel, Germany): A potential palaeoclimate/-hydrology proxy

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Abstract

Stable hydrogen isotope ratios (δD values) of methoxyl groups in lignin and pectin from a variety of plant types from different locations have been shown to mirror δD values of precipitation, with a mean uniform isotopic fractionation. Since δD in precipitation is mainly influenced by climatic conditions, including temperature, evaporation and precipitation amount, methoxyl groups of organic matter have been proposed as a potential palaeoclimate proxy. Here, we measured the δD values of the methoxyl groups of sedimentary organic matter derived from sediment core segments of Lake Holzmaar (Eifel, Germany). The sediment core covers the entire Holocene and part of the Late Glacial (until 13,650 years BP). Since the sedimentary organic matter was indicated by organic source proxies of predominantly phytoplanktonic origin, we considered the δD values of the methoxyl groups as a proxy for the δD value of the lake water. Presently and probably during most of the Holocene, the δD value of precipitation was primarily controlled by temperature ($2\text{--}4.5\text{‰}/^\circ\text{C}$) as well as in isotopic equilibrium with the δD value of the lake water. We used these modern temperature sensitivities of the Eifel region together with the measured δD values of the methoxyl groups of the sedimentary organic matter to evaluate temperature changes recorded for the Holocene. The resulting mean temperature variance was found to be consistently less than $1.8\text{--}4\text{ }^\circ\text{C}$ and is broadly in line with that reported from the NGRIP ice core for the same period. The transition from the Holocene to the Late Glacial period was accompanied with more negative δD values of the methoxyl groups ($\sim 13\text{‰}$ for the Younger Dryas). Besides the association with temperature we assumed a higher susceptibility of the δD value of Lake Holzmaar to evaporative enrichment during the Younger Dryas which could serve as an explanation for discrepancies reported for existing palaeoclimate/-hydrology records of the Eifel region. Our findings indicate that the δD values of methoxyl groups have great potential for assisting with palaeoclimate and palaeohydrology, particularly when the organic matter is well characterized and of uniform origin.

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1. INTRODUCTION

The relative abundance of oxygen and hydrogen isotopes within precipitation, expressed as $\delta^{18}\text{O}_{\text{precip}}$ and δD_{precip} values, respectively, are highly dependent on climatic conditions including temperature, evaporation as

well as source and amount of precipitation (Craig, 1961; Craig and Gordon, 1965; Gonfiantini, 1986; Gat, 1996). Frequently this has been used as a palaeoclimate proxy in natural archives able to preserve this climate signal, most prominently in ice cores (Dansgaard et al., 1971; Johnsen et al., 1992; NGRIP Members, 2004; NEEM Community, 2013). For non glacial regions additional archives are necessary to increase spatial coverage and for further understanding of how past climate evolved globally (Sachse et al., 2012). In this context, stable isotope studies of organic matter would seem appropriate, since water is the primary hydrogen source of photosynthesizing organisms and a variety of their biosynthetic products possess δD values reflecting that of their source water (Sachse et al., 2012). Several organic compounds have been identified as suitable for palaeoclimatic or palaeohydrologic studies, as, for example, n-alkanes (Rach et al., 2014), n-alkanoic acids (Feakins et al., 2014) and sugar biomarkers (Zech et al., 2014) all extracted from lake sediments or cellulose extracted from tree rings (Epstein et al., 1977; Yapp and Epstein, 1982; Feng and Epstein, 1994; Epstein, 1995; Treydte et al., 2009; Holzkämper et al., 2012).

δD values of methoxyl groups ($\delta D_{\text{methoxyl}}$) have recently been proposed as a potential palaeoclimate proxy (Keppler et al., 2007; Greule and Keppler, 2011; Gori et al., 2013; Feakins et al., 2013a). Methoxyl groups in plant material are either ether bonded, for example in lignin, or, ester bonded, for example in pectin. Lignin and pectin are important plant cell wall compounds in different quantities in all higher plants. The $\delta D_{\text{methoxyl}}$ signatures of lignin and pectin of the same plant sample are known to be similar (Greule and Keppler, 2011). $\delta D_{\text{methoxyl}}$ values can be measured by cleavage of the ether or ester moieties with hydroiodic acid (HI) to form the gaseous compound methyl iodide (CH_3I) whose δD value is measurable by gas chromatography pyrolysis isotope ratio mass spectrometry (GC-P-IRMS) (Greule et al., 2008; Feakins et al., 2013b). For the purposes of brevity this procedure is hereafter referred to as the ‘HI-method’. $\delta D_{\text{methoxyl}}$ values reflect the δD values of their source water (δD_{source}) and are modulated by a large uniform biosynthetic fractionation. The fractionation between δD_{source} and $\delta D_{\text{methoxyl}}$ differs on plant type, as, for example, in wood and potato tubers with $-216 \pm 19\text{‰}$ and $-161 \pm 11\text{‰}$, respectively (Keppler et al., 2007; Keppler and Hamilton, 2008). For the purposes of this study we have assumed uniform fractionation between δD_{source} and $\delta D_{\text{methoxyl}}$ within a particular plant type.

This study evaluates the suitability of the measurement of $\delta D_{\text{methoxyl}}$ values for investigation of geological archives containing organic matter. For this we chose sedimentary organic matter from sediment core segments of Lake Holzmaar located in the Eifel region, Germany (Fig. 1). Lake Holzmaar was considered suitable, because a number of (palaeo-) limnology studies have been conducted (Raubitschek et al., 1999; Zolitschka et al., 2000; Baier et al., 2004; Sirocko, 2009; Messyasz et al., 2012) and the sedimentary organic matter characterized (Lücke et al., 2003). Furthermore, a high precision multi-proxy dating for the actual sediment core used in this study has been published (Sirocko et al., 2013). The sediments cover the

entire Holocene and date further back to Bølling–Allerød interstadial (13,650 years BP).

Ideally, $\delta D_{\text{methoxyl}}$ values are measured for a particular plant type, for example wood (Keppler et al., 2007; Gori et al., 2013; Feakins et al., 2013a), fruit (Greule and Keppler, 2011) and vegetable species (Keppler and Hamilton, 2008). This thus ensures that the fractionations between δD_{source} and $\delta D_{\text{methoxyl}}$ of each specific plant type is known (Greule and Keppler, 2011). A major challenge in this study is that the methoxyl groups of the sedimentary organic matter are likely from different compound classes produced by mixed vegetation, such as autochthonous aquatic and allochthonous terrestrial. Therefore here we attempt to characterize the origin of the sedimentary organic matter of Lake Holzmaar using organic source proxies inferred from C/N ratios determined in this and additional proxies of previous studies.

2. STUDY SITE

2.1. Lake Holzmaar and sediment core samples

Lake Holzmaar formed within a small maar crater which erupted more than 25,000 years ago and is part of the West Eifel Volcanic Field (Brauer, 1994; Fig. 1). It became a very effective sediment trap for its catchment area and is presently still filled with water. The maar lake is approximately circular shaped with maximum depths of 20 m and a maximum diameter of ~ 320 m. Dam constructions during the late Middle Ages created an additional shallow embayment (Zolitschka, 1998). The draining stream Sammetbach enters and leaves the maar lake through the embayment. The mean residence time of the water body is approximately 1 year (Sirocko, 2009) or less (Zolitschka, 1998). Lake Holzmaar is currently suggested to be meso- to eutrophic (Baier et al., 2004).

The sediment core of Lake Holzmaar in this study was provided by the ELSA Project (Eifel Laminated Sediment Archive; <http://www.uni-mainz.de/FB/Geo/Geologie/elsa/index.php>) and was drilled in 1998 by Niederreiter technology. Exact coordinates of the coring site are provided in Table 1.

Fifty-one sediment samples were taken from the HM1 core of Lake Holzmaar (referred as SHM-1 to 51) for the measurement of the $\delta D_{\text{methoxyl}}$ values of the sedimentary organic matter. Every sample represented approximately 1 cm of sediment of the core. Only fine laminated sediment and no coarse grained or obvious event layers were collected. Samples were lyophilized and ground prior to analysis. Sample details are provided in Table 2.

2.2. Age control

The age versus depth correlation of the sediment of Lake Holzmaar used in this study was established by Sirocko et al. (2013) (Fig. 2). Briefly, until 9950 years BP the age model is based on varve counting. Older laminations are not complete annual varves due to missing diatom layers of the summer season (Zolitschka et al., 2000; Sirocko et al., 2013). Thus, the remaining downcore section has

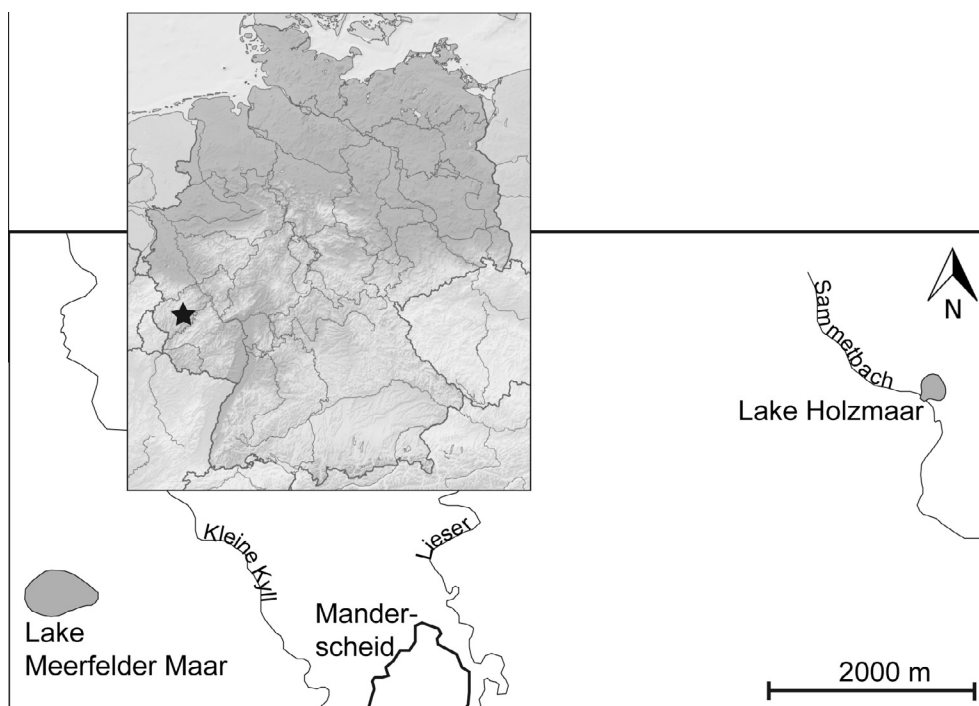


Fig. 1. Map of Eifel Maar sampling site of Lake Holzmaar and its location, indicated by the star, in Germany.

Table 1
Geographical, morphometrical and limnological characteristics of Lake Holzmaar after Sirocko (2009) and Scharf and Menn (1992).

Parameter	In	Lake Holzmaar
Coring site latitude		50°07.163' N
Coring site longitude		6°52.734' E
Elevation	[m.a.s.l.] ^a	425
Mean depth	[m]	8.8
Maximum depth (z_{\max})	[m]	20
Reduced depth (z_{red}) ^b	[m]	15.5
Diameter	[m]	272
Lake surface area	[m ²]	58,000
Water volume	[m ³]	478,000
Catchment area	[m ²]	2,058,000
Water retention time	[years]	1
Trophic state		Meso- to eutrophic

^a m.a.s.l. = meters above sea level.

^b Reduced depth of theoretically mixing caused by wind according to Berger (1971).

been interpolated with the Ulmener Maar and Laacher See Tephra. This interpolation is supported by calibrated ¹⁴C dates of twigs. The age versus depth correlation for the section older than Laacher See Tephra (9.56–10.0 m) was extrapolated by assuming the same sedimentation rate as before and is in agreement with the independent age model that Zolitschka et al. (2000) established for an equivalent sediment core of Lake Holzmaar. Using the inverted slope as sedimentation rate reveals the temporal coverage of every sediment sample. Each sediment sample from the Late Glacial to around 3200 years BP covered ~15 years.

Resolution increased to ~6 years for the most recent period. All ages are reported in years or kilo years (kyr) BP.

3. ANALYTICAL TECHNIQUES

3.1. Determination of total carbon and total nitrogen

Contents of carbon and nitrogen were determined in duplicate after dry combustion at 950 °C with a VarioEL elemental analyzer (Elementar Analysensysteme, Hanau, Germany). Prior to analysis, subsamples were acidified (10% HCl) in order to establish if they contained inorganic carbon. Since no reaction was observed, inorganic carbon was negligible and the measured carbon was therefore considered equivalent to the total organic carbon (TOC). TOC and total nitrogen (TN) are expressed as dry weight (wt%).

3.2. Conversion of ester and ether bonded methoxyl groups to CH₃I using HI

Methoxyl groups of SHM were converted to methyl iodide (CH₃I) by the 'HI-Method' (for detailed description see Greule et al., 2008). Briefly, HI (0.5 mL, 55–58%) was added to the sample material in crimp glass vials (1.5 mL) which were sealed with crimp caps containing polytetrafluoroethylene (PTFE) – lined butyl rubber septa. The sealed vials were placed in an oven and heated at 130 °C for 30 min. This treatment cleaves the methyl moiety from methoxyl groups of organic matter and forms gaseous CH₃I which accumulates in the vial headspace. At the end of the heating period the vials were allowed to equilibrate at room temperature for at least another 30 min. In

Table 2
 $\delta D_{\text{methoxyl}}$ values and further parameters of SHM samples.

Sample	Depth [m]	Age ^a [years BP]	TOC [wt%]	C/N	Amount ^b [mg]	$\delta D_{\text{methoxyl}}$ ^c [‰ versus VSMOW]
SHM-1	0.01	2	5.3	8.1	182	-227 ± 4
SHM-2	0.20	33	4.3	7.7	220	-228 ± 4
SHM-3	0.40	67	4.9	7.7	241	-242 ± 5
SHM-4	0.60	100	2.9	7.3	352	-218 ± 5
SHM-5	0.80	216	2.2	6.7	398	-206 ± 4
SHM-6	1.01	298	2.3	8.1	281	-207 ± 4
SHM-7	1.20	427	2.7	7.4	276	-199 ± 5
SHM-8	1.40	513	3.6	7.4	261	-210 ± 4
SHM-9	1.60	580	2.1	6.8	359	-186 ± 2
SHM-10	1.80	620	2.6	6.9	276	-194 ± 2
SHM-11	2.00	720	3.2	7.7	235	-211 ± 2
SHM-12	2.20	847	3.9	8.4	225	-209 ± 2
SHM-13	2.40	987	8.2	9.0	97	-223 ± 3
SHM-14	2.60	1168	8.7	9.8	78	-220 ± 4
SHM-15	2.80	1342	9.5	10.0	57	-222 ± 2
SHM-16	3.01	1503	10.2	9.4	64	-221 ± 5
SHM-17	3.20	1701	12.5	11.3	58	-226 ± 1
SHM-18	3.40	1939	5.9	8.5	127	-232 ± 3
SHM-19	3.60	2139	8.6	10.5	52	-227 ± 2
SHM-20	3.80	2398	9.7	10.1	57	-230 ± 1
SHM-21	4.01	2610	10.2	10.3	50	-220 ± 2
SHM-22	4.21	2745	14.0	12.8	43	-218 ± 3
SHM-23	4.41	2818	n.a.	n.a.	56	-230 ± 4
SHM-24	4.61	3267	16.2	10.1	210	-243 ± 5
SHM-25	4.80	3670	14.4	10.8	93	-228 ± 2
SHM-26	5.00	4141	7.6	9.6	190	-225 ± 4
SHM-27	5.20	4553	9.1	10.0	168	-226 ± 3
SHM-28	5.40	4839	4.9	7.8	264	-217 ± 3
SHM-29	5.60	5258	7.4	9.1	244	-228 ± 4
SHM-30	5.80	5601	6.4	9.0	218	-227 ± 4
SHM-31	6.01	5792	6.1	8.9	258	-228 ± 4
SHM-32	6.20	6176	8.6	9.1	210	-234 ± 3
SHM-33	6.40	6566	7.4	8.9	168	-237 ± 3
SHM-34	6.60	6913	8.5	9.6	194	-228 ± 4
SHM-35	6.80	7310	8.9	12.3	162	-238 ± 2
SHM-36	7.00	7595	11.0	11.5	92	-237 ± 3
SHM-37	7.20	8027	8.7	11.7	187	-235 ± 3
SHM-38	7.40	8449	8.2	10.9	226	-237 ± 2
SHM-39	7.60	8898	7.6	8.9	237	-239 ± 3
SHM-40	7.80	9420	3.8	8.6	330	-228 ± 6
SHM-41	8.00	9812	n.a.	n.a.	382	-233 ± 3
SHM-42	8.20	10278	4.8	9.4	204	-233 ± 4
SHM-43	8.40	10744	3.8	8.1	344	-233 ± 3
SHM-44	8.60	11164	3.6	7.9	392	-222 ± 2
SHM-45	8.80	11530	3.0	6.8	361	-230 ± 4
SHM-46	9.01	11913	6.1	13.5	237	-243 ± 3
SHM-47	9.20	12260	2.6	7.1	449	-239 ± 6
SHM-48	9.40	12626	4.0	10.4	120	-242 ± 3
SHM-49	9.60	12918	0.9	11.4	799	-243 ± 7
SHM-50	9.80	13283	5.1	13.6	192	-240 ± 3
SHM-51	10.00	13649	5.0	13.3	224	-253 ± 3

^a Derived from age model (Sirocko et al., 2013).

^b Mean amount of 3 subsamples.

^c Mean value with standard deviation ($n = 12, 1\sigma$).

order to more accurately assess the analytical precision, three subsamples of every homogenized SHM sample were prepared by the ‘HI-method’. The amount of the sediment necessary for the ‘HI-Method’ was dependent on organic

matter content of the sample and hence sample size varied between 50 and 800 mg (Table 2).

To avoid possible corrosion due to residual HI in the vial, the samples treated with the ‘HI-Method’ can be

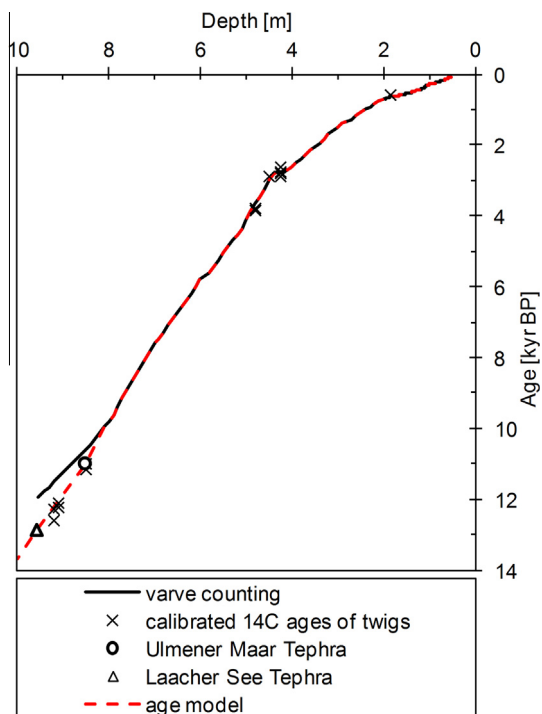


Fig. 2. Age model of sediment core HM1 of Lake Holzmaar (Sirocko et al., 2013).

neutralized using KOH as noted by Feakins et al. (2013a). However, this was found not necessary as the analytical procedure employed in this study requires small injection volumes into the GC (see Section 3.3).

3.3. Isotope ratio mass spectrometry for determination of δD of CH_3I

Determinations of $\delta D_{\text{methoxyl}}$ values of the organic matter in SHM samples were accomplished by compound specific GC-P-IRMS (for detailed description see Greule et al., 2008). Briefly, an A200S autosampler (CTC Analytics, Zwingen, Switzerland) injected a headspace sample (90 μL) into a Hewlett Packard HP6890 GC (Agilent Technologies, Santa Clara, CA, USA), which was interfaced with a Delta^{PLUS}XL isotope ratio mass spectrometer (ThermoQuest Finnigan, Bremen, Germany) via a high temperature conversion reactor [ceramic tube (Al_2O_3), length 320 mm, 0.5 mm i.d., reactor temperature 1450 $^\circ\text{C}$]. High-purity hydrogen with a δD range from -195‰ to -225‰ was used as the monitoring gas [Alphagaz 2, Hydrogen 6.0 (AirLiquide, Düsseldorf, Germany)] and normalized to a single CH_3I working standard (see Section 3.4). Every SHM subsample ($n = 3$) was measured four times consecutively.

3.4. Isotopic data treatment

All measured δD values were normalized to a single CH_3I working standard which was calibrated against international reference substances (IA-R002, IAEA-CH7,

NBS-22) using an offline EA-IRMS (Elemental analyzer/isotope ratio mass spectrometry) instrument (Iso-Analytical Ltd., Sandbach, UK). The calibrated δD value of the CH_3I working standard was $-179.0 \pm 2.9\text{‰}$ ($n = 15$, 1σ ; Greule et al., 2008). The working standard was measured after every fourth sediment sample injection. Furthermore, all δD values were corrected for area dependence which was calculated at regular intervals by injecting varying volumes of the working standard. Such a correction is, for example, also recommended for compound-specific $\delta^{18}\text{O}$ analyses (Zech and Glaser, 2009). The H_3^+ factor was estimated on a daily basis with a range of 1.93–2.04 ppm/nA for the measurements of SHM samples. All δD values are reported in the conventional delta notation, which expresses the deviation in per mil [‰] to the standard ‘Vienna Standard Mean Ocean Water’ (VSMOW) by the equation:

$$\delta D = \frac{D/H_{\text{SAMPLE}}}{D/H_{\text{V-SMOW}}} - 1$$

4. RESULTS AND DISCUSSION

4.1. Analytical results

4.1.1. Total organic carbon and total nitrogen of SHM samples

The TOC of the SHM samples ranged from 0.9 to 16.2 weight% (wt%) with a mean value of 6.6 wt%. The highest TOC contents were observed around 3300 years BP (Table 2; Fig. 3a). The mean TN of the sediment samples was 0.7 wt%, with a range from 0.07 to 1.6 which closely mirrored the profile of the TOC content (data not shown). This leads to a fairly constant TOC/TN ratio, referred to as C/N ratio, with a mean value of 9.4 and a range of 6.7–13.6 (Fig. 3b).

4.1.2. $\delta D_{\text{methoxyl}}$ values of SHM

$\delta D_{\text{methoxyl}}$ values of SHM samples are shown in Table 2 and presented graphically against age in Fig. 3d. Each data point is the mean value obtained from four consecutive measurements of each of the three subsamples ($n = 12$). The mean standard deviation for all SHM samples was 3.3‰ ($n = 51$) ranging from -254‰ to -184‰ with a mean of -227‰ . The results obtained display robust and reproducible $\delta D_{\text{methoxyl}}$ measurements by the technique employed. The oldest sample (SHM-51), within Bølling–Allerød interstadial, had the most negative $\delta D_{\text{methoxyl}}$ value. Moreover, together with the subsequent five samples (SHM-46 to 50), moving into late Younger Dryas stadial, the most negative consecutive values were found. Then at the onset of the Holocene (between SHM-45 and 46) until around 6100 years BP (SHM-32) a distinct increase to less negative values, between -238‰ and -233‰ , was noted, with the exception of three values around 11,200, 9400 and 6900 years BP. From around 5800 to 1000 years BP $\delta D_{\text{methoxyl}}$ values remained relatively constant, but approximately 5–10 ‰ less negative. However, exceptions of even less negative values at around 4800, 2700 and 2600 years BP and one very negative value at 3200 years BP, a value comparable to that of the Younger Dryas samples, were

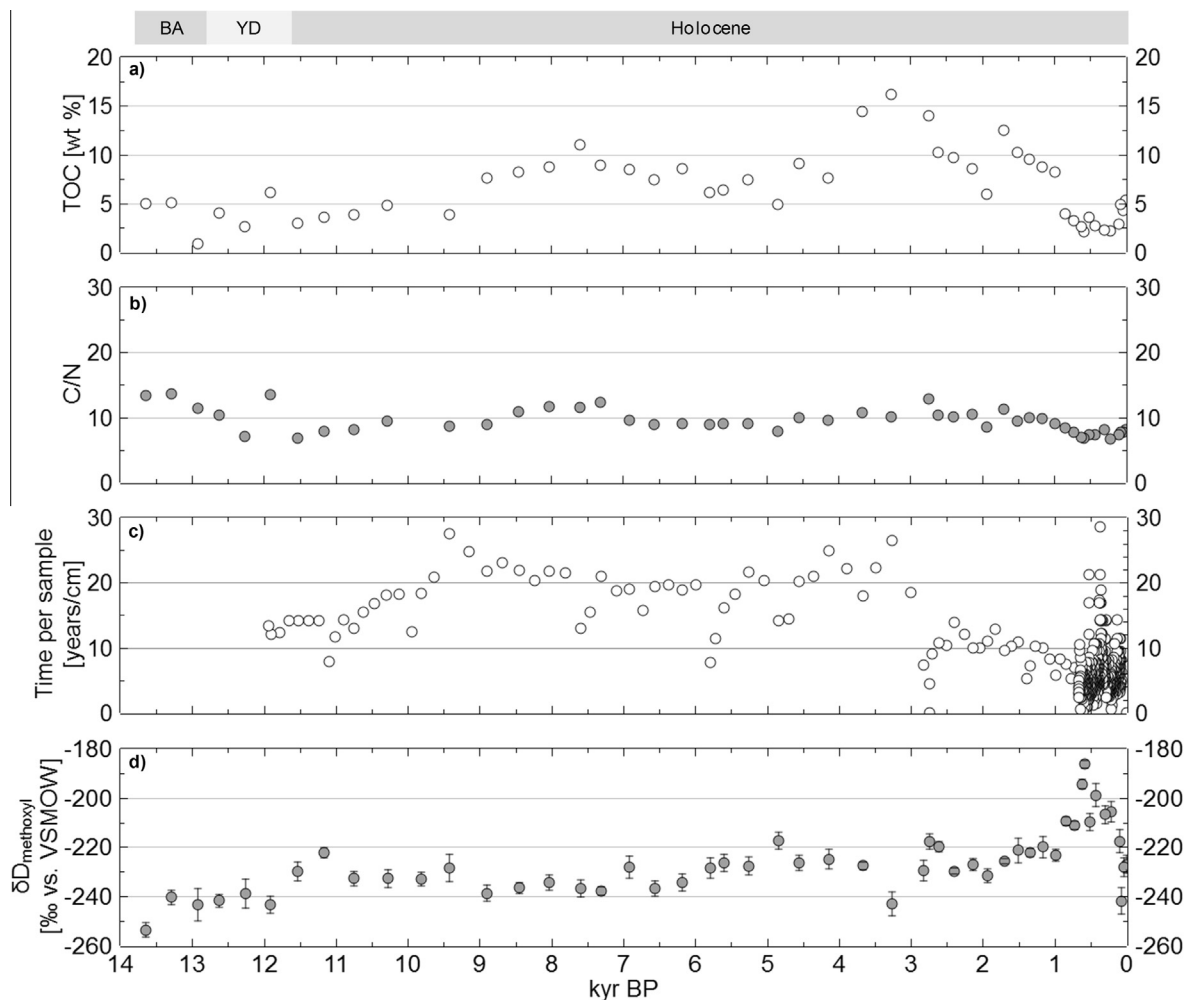


Fig. 3. Estimated parameters of SHM samples plotted against age in kyr BP as derived from Sirocko et al. (2013). (a) TOC = total organic carbon, (b) C/N = total organic carbon over total nitrogen as proxy for organic matter source, (c) sample specific temporal coverage derived from varve counting (Sirocko et al., 2013), and (d) $\delta D_{\text{methoxyl}}$ with standard deviations ($n = 12, 1\sigma$). Pollen zones are shown at the top and are based for the Eifel on Litt and Stebich (1999); BA = Bølling–Allerød interstadial, YD = Younger Dryas stadial.

observed. A major change within a short time period was seen for the $\delta D_{\text{methoxyl}}$ values of the youngest SHM samples. Here, values between 900 and 100 years BP showed an almost symmetrical peak, with a steep rise yielding the most positive value at 580 years BP followed by a steep fall into more recent times.

4.2. Formation of $\delta D_{\text{methoxyl}}$ in sedimentary organic matter

To interpret $\delta D_{\text{methoxyl}}$ values of the sediment samples it is essential to characterize the origin of the sedimentary organic matter. C/N ratios of lacustrine sediments have been reported as a useful tool for this purpose (Frenette et al., 1998; Meyers and Lallier-Vergès, 1999). Land plants and macrophytes possess significantly higher C/N ratios than lacustrine phytoplankton (Meyers and Ishiwatari, 1995; Albuquerque and Mozeto, 1997). A range from 5 to 10 is considered indicative of phytoplankton and 20 or higher of land plants and macrophytes. However, it should be pointed out that even samples with a ratio of up to 13

might still be indicative of phytoplankton, due to preferential loss of the nitrogen rich fraction of deposited organic matter (Herczeg, 1988).

Most SHM samples were found to have a C/N ratio of 10 or less (Fig. 3b). Several values of almost 14 indicated a larger, but not dominant contribution from land plants/macrophytes. Thus, the sedimentary organic matter had a predominantly phytoplanktonic source, a finding in agreement with existing studies. Lücke et al. (2003) conducted a much more detailed study of the sedimentary organic matter at a higher mean time resolution than that done in this study. They found a prevailing autochthonous source and suggested that any allochthonous contribution could be neglected. In that study C/N ratios were also estimated and these are in general agreement with the pattern found here. Parameters additionally determined by Lücke et al. (2003) included $\delta^{13}\text{C}$ of bulk organic matter ($\delta^{13}\text{C}_{\text{bom}}$) and accumulation rates of inorganic and organic matter. $\delta^{13}\text{C}_{\text{bom}}$, used to distinguish between the organic matter of phytoplankton and land plants/macrophytes, also

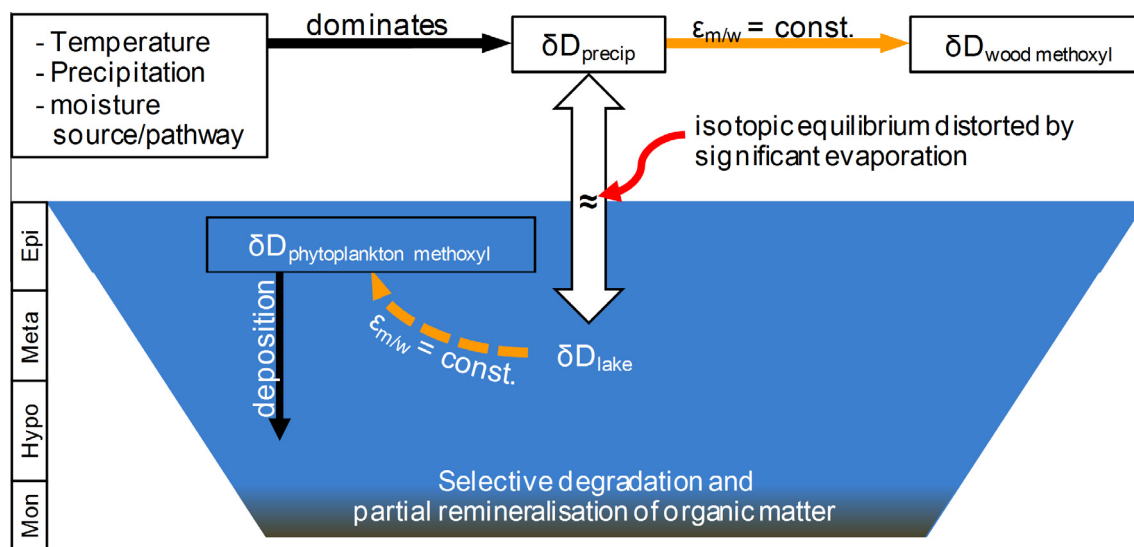


Fig. 4. Scheme of $\delta D_{\text{methoxyl}}$ formation of phytoplankton in Eifel maar lakes. The orange arrows represent fractionations of δD as estimated, for example, for wood (solid arrow) and as assumed for phytoplankton (dashed arrow). An exemplary thermal lake stratification is shown on the left side: Epi = Epilimnion, Meta = Metalimnion, Hypo = Hypolimnion, Mon = Monimolimnion. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

suggested a predominantly phytoplanktonic organic matter source. Moreover, for Lake Holzmaar it was used as a proxy for lacustrine palaeoproductivity, based on a decreasing ^{13}C discrimination of dissolved CO_2 with increasing lacustrine productivity (Herczeg and Fairbanks, 1987; Herczeg, 1988; Hollander and McKenzie, 1991). Further evidence is also provided as neither the accumulation rates of inorganic or organic material or the C/N ratios showed a convincing correlation with $\delta^{13}\text{C}_{\text{bom}}$. However, the origin of the sedimentary organic matter might not be representative of a certain compound containing methoxyl groups. But nevertheless as the majority of the SHM samples (35 of 51) indicated an exclusively phytoplanktonic origin of the sedimentary organic matter of Lake Holzmaar the methoxyl groups must be of aquatic origin. Consequently we consider it unlikely that the other remaining samples (indicating a minor contribution of terrestrial organic matter) should solely have contributed terrestrial-derived methoxyl moieties to the sedimentary organic matter whilst the aquatic-derived contribution would have suddenly stopped or became less evident. Nevertheless, this issue will need to be investigated in more detail in future studies when making $\delta D_{\text{methoxyl}}$ measurements of organic matter samples of unknown origin.

If the methoxyl groups of sedimentary organic matter in Lake Holzmaar are assumed to be predominantly phytoplanktonic in origin, it is possible to confine their source organic compound. Lignin from phytoplankton can almost certainly be excluded as source of methoxyl groups since non-vascular plants do not produce it. Hitherto, lignin has only been reported for *Calliarthron cheilosporioides*, an intertidal red alga (Martone et al., 2009). As opposed to lignin, pectin or pectin-like organic substances have been reported for phytoplankton like cyanobacteria (Desikachary, 1959; Wolk, 1973), as well as for green algae (Green and Jennigs, 1967; Prescott, 1968; Gooday, 1971;

Sikes, 1978; Painter, 1983; Domozych et al., 2007; Eder and Lütz-Meindl, 2008). The present phytoplanktonic environment of Lake Holzmaar is known to include cyanobacteria and green algae (Messyasz et al., 2003, 2006). Whereas cyanobacteria are generally abundant in the epilimnion and very dominant in the metalimnion between July and September, green algae grow preferentially in the epilimnion and are more pronounced during July and August. Both chlorophyll-a and dissolved oxygen, considered as indicative of phytoplanktonic activity in general, have been shown to peak within the metalimnion during May and September (Sirocko, 2009; Messyasz et al., 2012).

Consequently, it would seem logical both to assume a similar formation of the predominantly phytoplankton-derived sedimentary organic matter and also the inter-annually timing and the location of growth. Therefore, the main fraction of methoxyl groups in SHM samples would have originated in the upper water column and been derived from pectin-comprising phytoplankton, predominantly in the metalimnion during spring and late summer (Fig. 4). Presently during these growth periods Lake Holzmaar is thermally stratified (Messyasz et al., 2003). Thus, assuming a nearly constant fractionation between δD_{source} and $\delta D_{\text{methoxyl}}$, as has recently been shown for methoxyl groups of wood and vegetables (Keppler and Hamilton, 2008; Keppler et al., 2007; Greule and Keppler, 2011; Feakins et al., 2013a), changes in $\delta D_{\text{methoxyl}}$ of SHM samples should indicate changes in δD of the ambient lake water (δD_{lake}).

4.3. Proxy for palaeoclimate/hydrology

Methoxyl groups of SHM samples are suggested to reflect the isotope signature of δD_{lake} . Thus, it is important to discuss the development of δD_{lake} and its palaeoclimatic/hydrologic implications. In principle, the water balance

of closed basins is mainly controlled by the input of precipitation (directly on the lake surface and inflows via the catchment area and the subsurface) and loss due to evaporation. Consequently δD_{lake} is controlled by both these parameters (Dansgaard, 1964; Craig and Gordon, 1965; Gonfiantini, 1986; Gat, 1996; Gibson et al., 1998, 2005). In humid climates, such as in the present Eifel region, precipitation usually exceeds evaporation. The small catchment area of Lake Holzmaar possesses a homogeneous δD_{precip} . Thus, δD_{precip} and δD_{lake} should be in isotopic equilibrium, as can be seen for late summer (Sachse et al., 2004; Fig. 5a), and probably also for most of the Holocene exhibiting a predominant humid climate.

Monthly resolved temperature and precipitation data¹ from 1981 to 2010 together with interpolated δD_{precip} data from 1981 to 1999 are presented in Fig. 5a. These data reveal the dominant influence of local air temperature ($R^2 = 0.98$) and a minor importance of the precipitation amount ($R^2 = 0.40$) on δD_{precip} in the Eifel region. This leads to an inter-annual temperature sensitivity of $2.03\text{‰}/\text{°C}$ for δD_{precip} . Since the $\delta D_{\text{methoxyl}}$ values of trees and potato tubers (Keppler et al., 2007; Keppler and Hamilton, 2008) reflected the weighted mean annual δD_{precip} values we also considered the relation between the mean annual air temperature and the weighted mean annual of δD_{precip} .² Interestingly, the mean annual relationship of both values indicates a higher temperature sensitivity of $4.39\text{‰}/\text{°C}$ (Fig. 5b). This suggests that long term temperature changes (associated with climate) affect δD_{precip} differently in comparison to short term temperature changes (associated with season). Most SHM samples comprise sedimentary organic matter deposited on decadal time-scales, i.e., an averaged sedimentary organic matter from a certain growing period. Hence, $\delta D_{\text{methoxyl}}$ values of SHM samples are likely affected by the long term temperature sensitivity. However, the dataset showing the higher temperature sensitivity of $4.39\text{‰}/\text{°C}$ shows a lower correlation which might be explained by the much lower temperature variation of 1.9°C during the measured time period. To account for the seasonal and annual temperature sensitivity we applied a range of $2\text{--}4.5\text{‰}/\text{°C}$ for a first evaluation of the palaeotemperature significance of the $\delta D_{\text{methoxyl}}$ values for the Holocene.

During the Late Glacial period studied, Lake Holzmaar was exposed to more arid conditions especially during the Younger Dryas where intensified evaporation is indicated for the Eifel region (Rach et al., 2014) and thus potentially led to a disequilibrium between δD_{precip} and δD_{lake} (Fig. 4). Therefore, since δD_{lake} was likely affected by an evaporative enrichment during the Younger Dryas, the $\delta D_{\text{methoxyl}}$ values would also incorporate an evaporative signature.

The estimated mean fractionations between δD_{source} and $\delta D_{\text{methoxyl}}$ for wood and potato tuber samples showed uncertainty values of $\pm 19\text{‰}$ and $\pm 11\text{‰}$, respectively

¹ Data obtained from Deutsche Wetterdienst station Manderscheid-Sonnenhof, 6 km southwest of Lake Holzmaar (Fig. 1), 390 m a.s.l.

² Data obtained from GNIP station Koblenz, 65 km northwest of Lake Holzmaar.

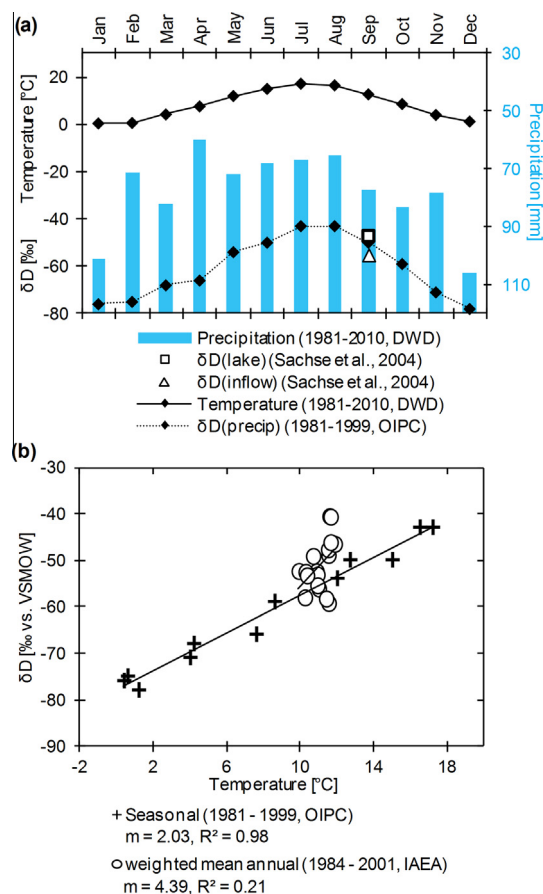


Fig. 5. δD_{precip} and its potential influential parameters, (a) inter-annually development of δD_{precip} derived from the Online Isotopes in Precipitation Calculator (OIPC). Temperature and precipitation data were derived from DWD (Deutscher Wetterdienst) station in Manderscheid-Sonnenhof, (b) inter-annually and weighted mean annual temperature sensitivity of δD_{precip} derived from OIPC and the GNIP station Koblenz (IAEA/WMO, 2006), respectively.

(Keppler et al., 2007; Keppler and Hamilton, 2008). This uncertainty has most certainly the largest impact on reconstructing δD_{source} values from compound-specific δD values (Polissar and D'Andrea, 2014) and thus should also be evaluated for the $\delta D_{\text{methoxyl}}$ values of the SHM samples. The above mentioned relatively high uncertainties in the fractionation are likely due to (i) the simplified assumption for the majority of the samples that δD_{source} equals δD_{precip} , (ii) δD_{precip} values were interpolated using the Online Isotopes in Precipitation Calculator³ (OIPC) and therefore included large error bars (mean standard deviation $\pm 11\text{‰}$, cf. Fig. 6) and (iii) the $\delta D_{\text{methoxyl}}$ values of the tree samples using a saline water source (circles in Fig. 6) indicate the lowest fractionations which deviate the most from the estimated mean fractionation. An influence of salinity, leading to lower fractionations, has already been reported

³ Accessible at <http://www.waterisotopes.org/>, employing the IAEA database and interpolation algorithms developed by Bowen and Wilkinson (2002) and refined by Bowen and Revenaugh (2003) and Bowen et al. (2005).

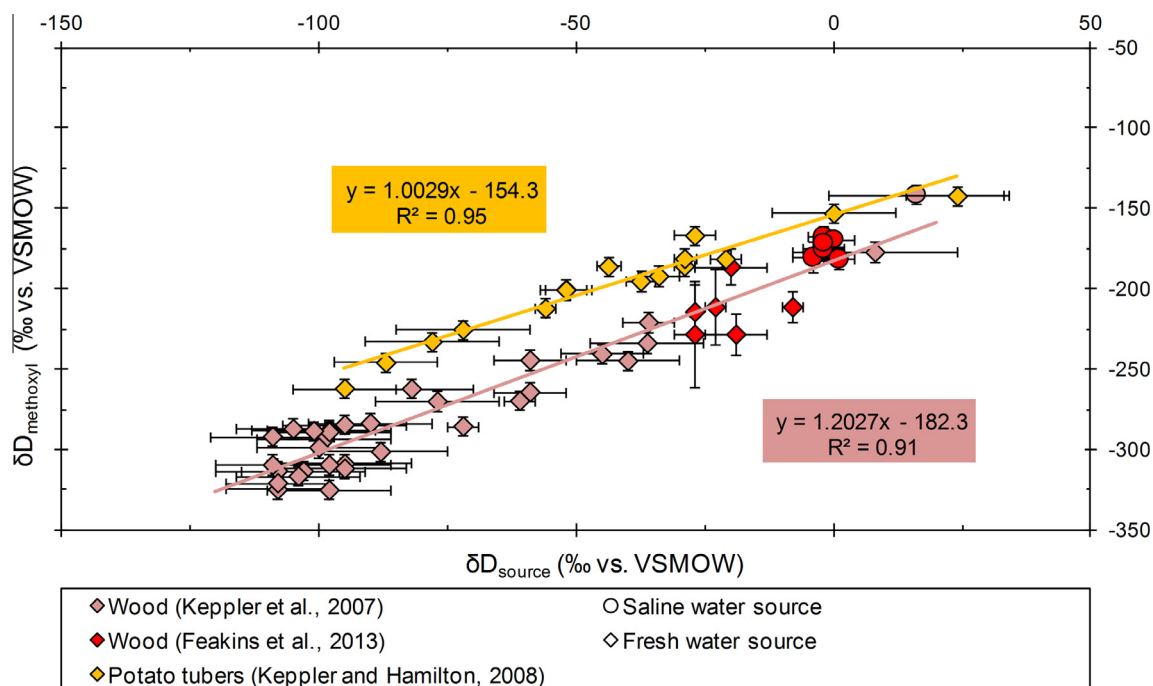


Fig. 6. $\delta D_{\text{methoxyl}}$ of organic matter (wood and potato tubers) versus δD_{source} (Keppler and Hamilton, 2008; Keppler et al., 2007; Feakins et al., 2013a). δD_{source} of wood and potato tubers were derived from the OIPC. δD_{source} of Feakins et al. (2013a) was derived from the xylem water.

for other organic compounds, such as lipids in cyanobacteria (Sachse and Sachs, 2008) and marine algae (Schouten et al., 2006; Sachs and Schwab, 2011). Consequently, the uncertainties in the fractionation might indicate a maximum value and are possibly considerably lower if the 'true' δD_{source} is known and samples with a potential influence of salinity are not included. However, a quantitative uncertainty in fractionation between δD_{lake} and $\delta D_{\text{methoxyl}}$ of phytoplankton has not yet been established.

4.4. Interpretation of $\delta D_{\text{methoxyl}}$ values of SHM

4.4.1. Holocene

The observed $\delta D_{\text{methoxyl}}$ values measured for samples from the late middle ages and the beginning of the modern age (SHM-1 to 12) are difficult to interpret as a temperature signal when modern temperature sensitivities of 2–4.5‰ per 1 °C were applied. These data would suggest an unexpected rise and fall in temperature of ~ 10 °C within a relatively short period of time with respect to the whole archive (Fig. 3d). This positive isotopic anomaly which covers a stratigraphic range of around 2 m and several centuries cannot be caused by a single event but rather may be associated with a change in organic matter and/or the hydrological conditions. A sediment core from the nearby Schalkenmehrener Maar which showed a significant increase of flood events during an equivalent time period was attributed to the 'Little Ice Age', where cold and snowy winters led to strong snow melts in spring (Sirocko, 2009). Other evidence indicate that this period had increased amounts of precipitation in general (Pfister, 1999; Glaser,

2001, 2008). Even though in Lake Holzmaar these flood events are not as obvious as in Schalkenmehrener Maar, the weather extremes of the 'Little Ice Age' may have altered the hydrological conditions and subsequently the inter-annually development of δD_{lake} . This may have especially affected samples SHM-1 to 12, since individually they have a low temporal coverage and hence would have had a lesser chance of smoothing out weather extremes (Fig. 3c). However such an explanation is considered inappropriate since increased precipitation, leading to the 'rain out' effect

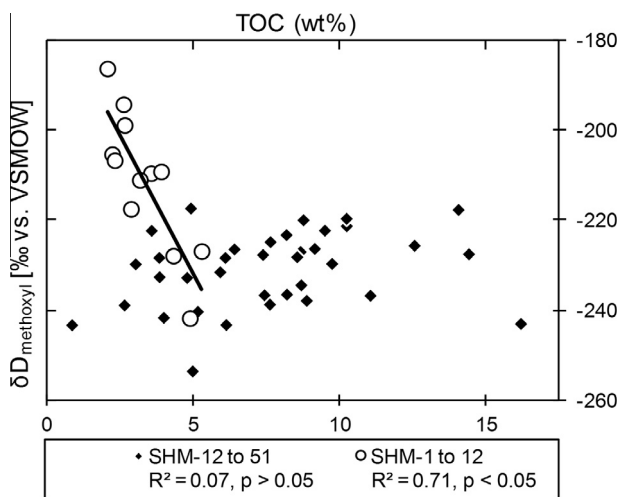


Fig. 7. Total organic carbon versus $\delta D_{\text{methoxyl}}$ of SHM.

should have led to more negative δD_{lake} anomalies. An interfering contribution of terrestrial vegetation is on the one hand not indicated by the C/N ratios (Fig. 3b), but on the other hand likely by considering the sediment accumulation rates for this period, which are ~ 10 -fold higher as for most of the Holocene (Zolitschka, 1998). Water sources of terrestrial vegetation are prone to an evaporative enrichment of δD_{precip} and thus could reasonably explain this positive anomaly. A further interesting aspect was found when we studied the correlation pattern between $\delta D_{\text{methoxyl}}$ and TOC of the SHM samples in more detail. Whereas the entire dataset showed no significant correlation between these two parameters, samples SHM-1 to 12 displayed a significant inverse correlation indicating dependence of $\delta D_{\text{methoxyl}}$ on TOC (Fig. 7). This might show that during sample preparation other organic compounds, with less negative δD values than methoxyl groups, reacted with HI to form CH_3I . Such interferences have previously been reported for methoxyl-free carbohydrates (Goto et al., 2005, 2006). Indeed, Greule and Keppler (2011) pointed out that a contribution of CH_3I from methoxyl-free carbohydrates should be considered when the lignin and pectin content of any sample was less than 3% of its total organic matter. Although such proportions are rarely found in terrestrial organic matter this possibility cannot be excluded for SHM. Interestingly, since only the youngest samples were shown to have a correlation with TOC this might reveal the role of selective degradation of organic matter. Since samples SHM-1 to 12 were in an early stage of

degradation, they could have been affected by the aforementioned phenomena leading to increased δD values. Hence it would appear that selective degradation would seem to be in favor of the $\delta D_{\text{methoxyl}}$ proxy over time. However, as $\delta D_{\text{methoxyl}}$ values for this period are very likely affected by terrestrial and/or geochemical influences we decided to exclude samples SHM-1 to 12 for our palaeoclimate interpretations discussed below.

Since the sedimentation rate of Lake Holzmaar increased after ~ 3000 years BP (Fig. 3c), subsequent $\delta D_{\text{methoxyl}}$ values have been merged to approximately coincide with the mean time resolution of the earlier periods of the Holocene. This procedure helps avoid over interpretation of recent high-variance deviations in the context of the past several thousand years (Marcott et al., 2013).

Fig. 8 shows the mean $\delta D_{\text{methoxyl}}$ value including the standard deviation for each SHM sample plotted as the deviation to the overall mean $\delta D_{\text{methoxyl}}$ value of the Holocene. Single $\delta D_{\text{methoxyl}}$ values might overestimate a potential climate signal since the $\delta D_{\text{methoxyl}}$ values are additionally affected by an uncertainty of fractionation (as evaluated in Section 4.3). Hence, a moving average (3 data points) of the $\delta D_{\text{methoxyl}}$ deviations was established in order to compare the long term trend with the $\delta^{18}\text{O}$ values from the NGRIP ice core. The long term trend of the Holocene shows a reduced variance of the $\delta D_{\text{methoxyl}}$ values that does not exceed $\pm 8\text{‰}$ suggesting a temperature variance of lower than $1.8\text{--}4\text{ °C}$ when modern temperature sensitivities of $2\text{--}4.5\text{‰/°C}$ are applied. Thus, the reduced variance is in

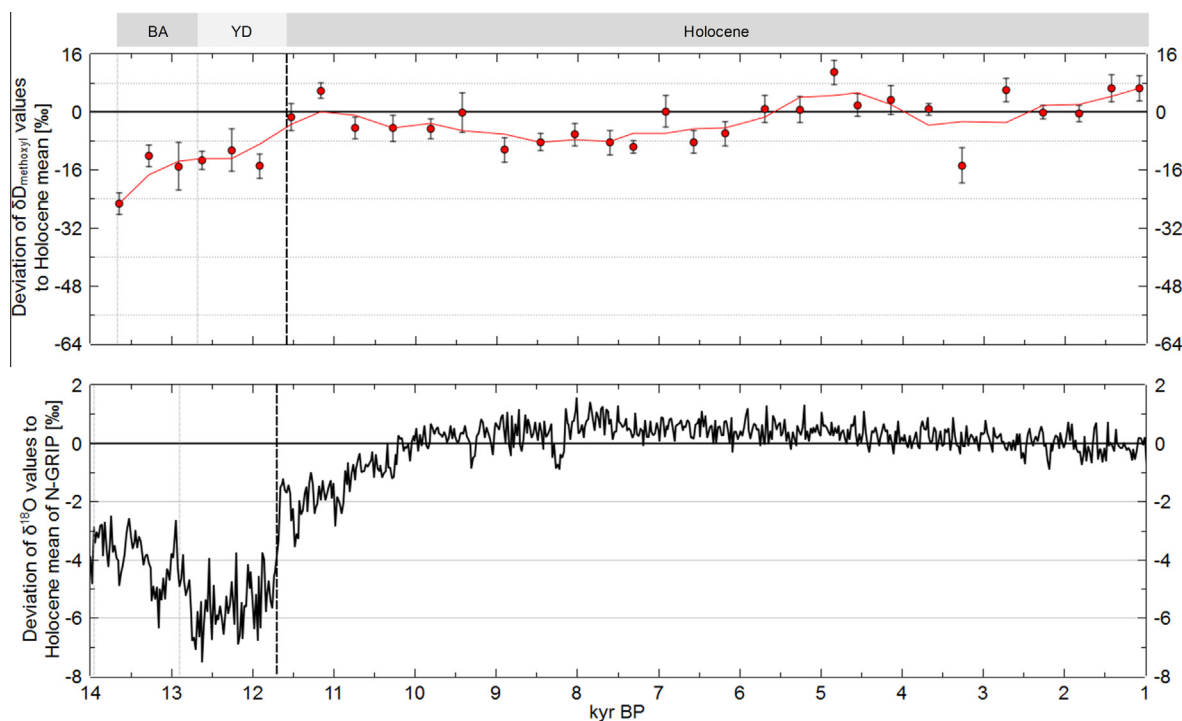


Fig. 8. $\delta D_{\text{methoxyl}}$ of SHM and $\delta^{18}\text{O}$ values of NGRIP ice core (NGRIP Members, 2004). For a better comparison, both isotope values are shown as the deviation to their Holocene mean value and the scales are displayed according to the relationship of the meteoric water line, i.e., $\delta D = 8 \cdot \delta^{18}\text{O}$. Top: Pollen zones for the Eifel region after Litt and Stebich (1999), BA = Bolling–Allerød interstadial, YD = Younger Dryas stadial, Note: stadial/interstadial transitions in Greenland as indicated by major changes in $\delta^{18}\text{O}$ are often earlier defined as for Mid-Europe by Litt and Stebich (1999).

agreement with the known fairly stable climate conditions during the Holocene. In the early Holocene $\delta^{18}\text{O}$ values of the NGRIP record are about 2‰ more negative as the Holocene mean and become progressively less negative until they reach their maximum at the Holocene Climatic Optimum (around 8000 years BP) and are followed by a slight trend to more negative isotope values from 8000 to 1000 years BP. These minor trends cannot be observed for the $\delta\text{D}_{\text{methoxyl}}$ values. Nevertheless, on a multi-centennial scale the $\delta\text{D}_{\text{methoxyl}}$ values of the Holocene are broadly in line with the reconstruction of NGRIP. This suggests that the most influential parameter for the $\delta\text{D}_{\text{methoxyl}}$ values of SHM during the Holocene was temperature and is preserved over geological time-scales.

4.4.2. Late glacial

The Late glacial period, especially the Younger Dryas shows consistently more negative $\delta\text{D}_{\text{methoxyl}}$ values of $\sim 13\text{‰}$ with respect to the Holocene mean (Fig. 8). Even though the timing of this decline is in good agreement with the NGRIP record, the magnitude is less pronounced. Moreover, the transition Allerød/Younger Dryas is not

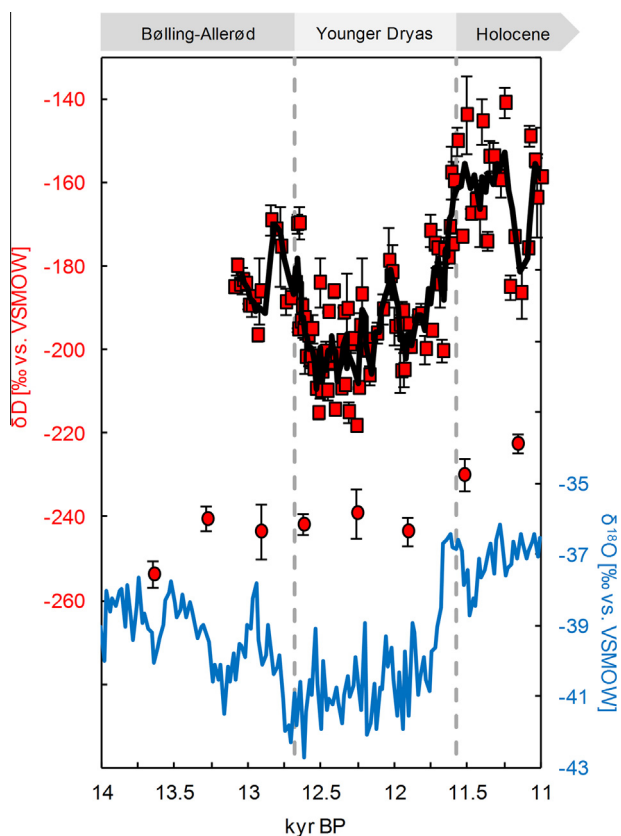


Fig. 9. $\delta\text{D}_{\text{nC23}}$ values (red squares) of Lake Meerfelder Maar (Rach et al., 2014) and $\delta\text{D}_{\text{methoxyl}}$ values (red circles) of Lake Holzmaar (this study) both derived from Late Glacial sediment segments. $\delta\text{D}_{\text{nC23}}$ values are further shown with a moving average (3 data points). $\delta^{18}\text{O}$ values from the NGRIP ice core are shown at the bottom (blue line). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

obvious for the $\delta\text{D}_{\text{methoxyl}}$ record. Based on the arid climate of the Younger Dryas including intensified evaporation (Rach et al., 2014) we considered the additional influence of an evaporative enrichment of $\delta\text{D}_{\text{lake}}$ potentially leading to a disequilibrium between $\delta\text{D}_{\text{precip}}$ and $\delta\text{D}_{\text{lake}}$ of Lake Holzmaar. To specifically evaluate our proxy for this period we compared it to a similar approach conducted by Rach et al. (2014) who estimated δD values of the nC_{23} alkanes from a Late Glacial sediment segment of the nearby Lake Meerfelder Maar⁴ (Fig. 9). The nC_{23} alkanes are biomarkers for aquatic plants and their δD value ($\delta\text{D}_{\text{nC23}}$) reflects $\delta\text{D}_{\text{lake}}$ with a mean uniform fractionation (Aichner et al., 2010), a finding similar to that suggested for the $\delta\text{D}_{\text{methoxyl}}$ values of SHM. The general offset between both these $\delta\text{D}_{\text{lake}}$ proxies is most likely the result of the larger fractionation of δD during the biosynthesis of the methoxyl groups. It is questionable if a detailed comparison of both proxies is appropriate since the mean time resolution is considerably lower for the $\delta\text{D}_{\text{methoxyl}}$ record. However, it seems likely that neither the major decline of $\sim 38\text{‰}$ at the onset of the Younger Dryas nor the major increase of $\sim 30\text{‰}$ at the termination of the Younger Dryas, as can be seen for the $\delta\text{D}_{\text{nC23}}$ values, is indicated by the $\delta\text{D}_{\text{methoxyl}}$ values (Fig. 9). Rach et al. (2014) explain the decline at 12,850 years BP with the temperature drop of the Younger Dryas as well as a decline of North Atlantic surface water δD values and at 12,680 years BP with a change in moisture pathway. The increase around 11,600 years BP is explained by the sudden establishment of a wetter, more humid climate at the beginning of the Holocene. Since Lake Meerfelder Maar and Lake Holzmaar are in close vicinity (Fig. 1) we consider that they were supplied by precipitation with the same $\delta\text{D}_{\text{precip}}$ signature. The major hydrological difference between both maars during the Late Glacial was most likely the water volume since nowadays Lake Holzmaar is about four times smaller than Lake Meerfelder Maar. Consequently, it would seem plausible that the $\delta\text{D}_{\text{methoxyl}}$ record does not equivalently show the decline at the onset of the Younger Dryas noted in the $\delta\text{D}_{\text{nC23}}$ record because of the higher susceptibility of $\delta\text{D}_{\text{lake}}$ of Lake Holzmaar to an evaporative enrichment which would have negated the declines in $\delta\text{D}_{\text{precip}}$. Further this would also explain the less pronounced transition of the $\delta\text{D}_{\text{methoxyl}}$ values at the termination of the Younger Dryas when compared with the $\delta\text{D}_{\text{nC23}}$ or NGRIP record. Consequently, the $\delta\text{D}_{\text{methoxyl}}$ values could be explained qualitatively by considering the climatic conditions during the Younger Dryas and its impact on the hydrological setting of Lake Holzmaar.

5. CONCLUSIONS

We here present an initial assessment of the suitability of $\delta\text{D}_{\text{methoxyl}}$ values of organic matter from geological archives as a palaeoclimate/-hydrology proxy. In this instance we used sedimentary organic matter from Lake Holzmaar in the Eifel region (Germany). Ideally it would have been

⁴ 50°06'2,87" N; 06°45'27,13" E, ~ 9 km West of Lake Holzmaar and ~ 90 m lower in altitude.

preferential to have access to an archive containing a specific plant organic matter source, since it is known that fractionations between source water and methoxyl groups potentially differ for different plant types. However, using C/N ratios and the findings of Lücke et al. (2003) the samples studied are predominantly of a phytoplanktonic organic matter source. We made the assumption that the fractionation between source water and methoxyl groups from the sedimentary organic matter was constant and $\delta D_{\text{methoxyl}}$ could be used as a proxy for δD_{lake} . In the present Eifel region the temperature sensitivity of δD_{precip} is in the range of 2–4.5‰/°C and should also be in isotopic equilibrium with δD_{lake} . Thus, our assumption implied that for the predominant humid Holocene $\delta D_{\text{methoxyl}}$ should serve as a palaeoclimate proxy primarily controlled by temperature changes.

The first approach of using $\delta D_{\text{methoxyl}}$ values of sedimentary organic matter in a geological archive as a palaeoclimate proxy seems promising since the findings show clear similarities to major palaeoclimate features of existing records for the northern Hemisphere. The long term trend of the $\delta D_{\text{methoxyl}}$ values for the majority of the Holocene (1000–11,580 years BP) showed a reduced variance of $\pm 8\text{‰}$ and $\pm 1.8\text{--}4\text{ °C}$ when modern temperature sensitivities of the Eifel region are applied. The Late Glacial period, especially the Younger Dryas, was accompanied by intensified evaporation (Rach et al., 2014) potentially leading to disequilibrium of δD_{precip} and δD_{lake} . Hence, we assumed that an evaporative signature was incorporated in the $\delta D_{\text{methoxyl}}$ values. This assumption which seems reasonable since Lake Holzmaar is small in volume could also explain discrepancies to other palaeoclimate/-hydrology proxies for the Eifel region.

Even at this initial stage of research, the fluctuations of $\delta D_{\text{methoxyl}}$ values can be rationalized by considering palaeoclimatic and palaeohydrologic influences of the Holocene and Late Glacial period. Thus, we see great potential for the exploitation of the $\delta D_{\text{methoxyl}}$ values of organic matter from geological archives, more especially when well characterized samples are available. Additional organic deposits and geological archives, such as wood samples or peat cores, respectively, should also be considered suitable for investigation by this approach.

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REFERENCES

- Aichner B., Herzsich U., Wilkes H., Vieth A. and Böhner J. (2010) δD values of n-alkanes in Tibetan lake sediments and aquatic macrophytes. A surface sediment study and application to a 16 ka record from Lake Koucha. *Org. Geochem.* **41**, 779–790.
- Albuquerque A. L. S. and Mozeto A. A. (1997) C:N:P ratios and stable carbon isotope compositions as indicators of organic matter sources in a riverine wetland system (Moji-Guacu river, Sao Paulo-Brazil). *Wetlands* **17**, 1–9.
- Baier J., Lücke A., Negendank J. F. W., Schleser G.-H. and Zolitschka B. (2004) Diatom and geochemical evidence of mid-to late Holocene climatic changes at Lake Holzmaar, West-Eifel (Germany). *Quat. Int.* **113**, 81–96.
- Berger F. (1971) Zur Morphometrie der Seebecken. *Carinthia* **II**, 29–39.
- Bowen G. J. and Revenaugh J. (2003) Interpolating the isotopic composition of modern meteoric precipitation. *Water Resour. Res.* **39**, 13.
- Bowen G. and Wilkinson B. (2002) Spatial distribution of $\delta 18\text{O}$ in meteoric precipitation. *Geology* **30**, 315–318.
- Bowen G. J., Wassenaar L. I. and Hobson K. A. (2005) Global application of stable hydrogen and oxygen isotopes to wildlife forensics. *Oecologia* **143**, 337–348.
- Brauer A. (1994) *Weichselzeitliche Seesedimente des Holzmaares – Warvenchronologie des Hochglazials und Nachweis von Klimaschwankungen*. University of Trier.
- Craig H. (1961) Isotopic variations in meteoric waters. *Science* **133**, 1702–1703.
- Craig H. and Gordon L. I. (1965) Deuterium and oxygen-18 variations in the ocean and the marine atmosphere. In *Stable Isotopes in Oceanographic Studies and Palaeotemperatures* (ed. E. Tongioli). Laboratory of Geology and Nuclear Science, Pisa, Italy, pp. 9–130.
- Dansgaard W. (1964) Stable isotopes in precipitation. *Tellus* **16**, 436–468.
- Dansgaard W., Johnsen S. J., Clausen H. B. and Langway C. C. (1971) Climatic record revealed by the Camp Century ice core. In *The Late Cenozoic Glacial Ages* (ed. K. Turekian). Yale University Press, New Haven-London, pp. 37–56.
- Desikachary T. V. (1959) *Cyanophyta*. Indian Council of Agricultural Research, New Delhi.
- Domozych D. S., Serfis A., Kiemle S. N. and Gretz M. R. (2007) The structure and biochemistry of charophycean cell walls: I. Pectins of *Penium margaritaceum*. *Protoplasma* **230**, 99–115.
- Eder M. and Lütz-Meindl U. (2008) Pectin-like carbohydrates in the green alga *Micrasterias* characterized by cytochemical analysis and energy filtering TEM. *J. Microsc.* **231**, 201–214.
- Epstein S. (1995) The isotopic climatic records in the Alleröd–Bölling–Younger Dryas and post-Younger Dryas events. *Global Biogeochem. Cycles* **9**, 557–563.
- Epstein S., Thompson P. and Yapp C. J. (1977) Oxygen and hydrogen isotopic ratios in plant cellulose. *Science* **198**, 1209–1215.
- Feakins S. J., Ellsworth P. V. and da Sternberg L. da. S. L. (2013a) Lignin methoxyl hydrogen isotope ratios in a coastal ecosystem. *Geochim. Cosmochim. Acta* **121**, 54–66.
- Feakins S. J., Rincon M. and Pinedo P. (2013b) Analytical challenges in the quantitative determination of $^2\text{H}/^1\text{H}$ ratios of methyl iodide. *Rapid Commun. Mass Spectrom.* **27**, 430–436.
- Feakins S. J., Kirby M. E., Cheatham M. I., Ibarra Y. and Zimmerman S. R. H. (2014) Fluctuation in leaf wax D/H ratio from a southern California lake records significant variability in isotopes in precipitation during the late Holocene. *Org. Geochem.* **66**, 48–59.
- Feng X. and Epstein S. (1994) Climate implications of an 8000-year hydrogen isotope time series from Bristlecone pine trees. *Science* **265**, 1079–1081.
- Frenette J.-J., Vincent W. F. and Legendre L. (1998) Size-dependent C:N uptake by phytoplankton as a function of irradiance: ecological implications. *Limnol. Oceanogr.* **43**, 1362–1368.

- Gat J. R. (1996) Oxygen and hydrogen isotopes in the hydrologic cycle. *Annu. Rev. Earth Planet. Sci.* **24**, 225–262.
- Gibson J., Reid R. and Spence C. (1998) A six year isotopic record of lake evaporation at a mine site in the Canadian subarctic: results and validation. *Hydrol. Process.* **12**, 1779–1792.
- Gibson J. J., Edwards T. W. D., Birks S. J., St Amour N. A., Buhay W. M., McEachern P., Wolfe B. B. and Peters D. L. (2005) Progress in isotope tracer hydrology in Canada. *Hydrol. Process.* **19**, 303–327.
- Glaser R. (2001) *Klimageschichte Mitteleuropas. 1000 Jahre Wetter, Klima, Katastrophen*. Wissenschaftliche Buchgesellschaft, Darmstadt.
- Glaser R. (2008) *Klimageschichte Mitteleuropas. 1200 Jahre Wetter, Klima, Katastrophen. Mit Prognosen für das 21. Jahrhundert*. Wissenschaftliche Buchgesellschaft, Darmstadt.
- Gonfiantini R. (1986) Environmental isotopes in lake studies. In *Handbook of Environmental Isotope Geochemistry* (eds. P. Fritz and J. C. Fontes). Elsevier, pp. 113–168.
- Gooday G. (1971) A biochemical and autoradiographic study of the role of the Golgi bodies in thecal formation in *Platymonas tetrahele*. *J. Exp. Bot.* **22**, 959–971.
- Gori Y., Wehrens R., Greule M., Keppler F., Ziller L., La Porta N. and Camin F. (2013) Carbon, hydrogen and oxygen stable isotope ratios of whole wood, cellulose and lignin methoxyl groups of *Picea abies* as climate proxies. *Rapid Commun. Mass Spectrom.* **27**, 265–275.
- Goto H., Koda K., Tong G., Matsumoto Y. and Meshitsuka G. (2005) Formation of methyl iodide from methoxyl-free compounds by hydriodic acid treatment. *J. Wood Sci.* **51**, 312–314.
- Goto H., Koda K., Tong G., Matsumoto Y. and Meshitsuka G. (2006) Interference of carbohydrates in the determination of the methoxyl content of lignin in woody samples. *J. Wood Chem. Technol.* **26**, 81–93.
- Green J. and Jennigs D. (1967) A physical and chemical investigation of the scales produced by the Golgi apparatus within and found on the surface of the cells of *Chrysochromulina chiton* Parke et. *J. Exp. Bot.* **18**, 359–370.
- Greule M. and Keppler F. (2011) Stable isotope determination of ester and ether methyl moieties in plant methoxyl groups. *Isotopes Environ. Health Stud.* **47**, 470–482.
- Greule M., Mosandl A. and Keppler F. (2008) A rapid and precise method for determination of D/H ratios of plant methoxyl groups. *Rapid Commun. Mass Spectrom.* **22**, 3983–3988.
- Herczeg A. L. (1988) Early diagenesis of organic matter in lake sediments: a stable carbon isotope study of pore waters. *Chem. Geol.* **72**, 199–209.
- Herczeg A. L. and Fairbanks R. G. (1987) Anomalous carbon isotope fractionation between atmospheric CO₂ and dissolved inorganic carbon induced by intense photosynthesis. *Geochim. Cosmochim. Acta* **51**, 895–899.
- Hollander D. J. and McKenzie J. A. (1991) CO₂ control on carbon isotope fractionation during aqueous photosynthesis: a paleo-pCO₂ barometer. *Geology* **19**, 929–932.
- Holzschläger S., Tillman P. K., Kuhry P. and Esper J. (2012) Comparison of stable carbon and oxygen isotopes in *Picea glauca* tree rings and *Sphagnum fuscum* moss remains from subarctic Canada. *Quat. Res.* **78**, 295–302.
- IAEA/WMO. (2006) Global Network of Isotopes in Precipitation. The GNIP Database, Bundesanstalt für Gewässerkunde.
- Johnsen S., Clausen H., Dansgaard W., Fuhrer K., Gundestrup N., Hammer C., Iversen P., Jouzel J., Stauffer B. and Steffensen J. (1992) Irregular glacial interstadials recorded in a new Greenland ice core. *Nature* **359**, 311–313.
- Keppler F. and Hamilton J. T. G. (2008) Tracing the geographical origin of early potato tubers using stable hydrogen isotope ratios of methoxyl groups. *Isotopes Environ. Health Stud.* **44**, 337–347.
- Keppler F., Harper D. B., Kalin R. M., Meier-Augenstein W., Farmer N., Davis S., Schmidt H.-L., Brown D. M. and Hamilton J. T. G. (2007) Stable hydrogen isotope ratios of lignin methoxyl groups as a paleoclimate proxy and constraint of the geographical origin of wood. *New Phytol.* **176**, 600–609.
- Litt T. and Stebich M. (1999) Bio- and chronostratigraphy of the lateglacial in the Eifel region, Germany. *Quat. Int.* **61**, 5–16.
- Lücke A., Schleser G. H., Zolitschka B. and Negendank J. F. W. (2003) A lateglacial and Holocene organic carbon isotope record of lacustrine palaeoproductivity and climatic change derived from varved lake sediments of Lake Holzmaar, Germany. *Quat. Sci. Rev.* **22**, 569–580.
- Marcott S. A., Shakun J. D., Clark P. U. and Mix A. C. (2013) A reconstruction of regional and global temperature for the past 11,300 years. *Science* **339**, 1198–1201.
- Martone P. T., Estevez J. M., Lu F., Ruel K., Denny M. W., Somerville C. and Ralph J. (2009) Discovery of lignin in seaweed reveals convergent evolution of cell-wall architecture. *Curr. Biol.* **19**, 169–175.
- Messyasz B., Lücke A. and Schleser G. H. (2003) Dominance of cyanobacteria *Planktothrix rubescens* (D.C. ex Gom.) Anagn. et Kom. In *Lake Holzmaar, Germany – An Indication of the Trophic Status?* Act Bot. Warm. Masuriae 3, pp. 21–31
- Messyasz B., Czerwik-Marcinkowska J. and Lücke A. (2006) Ultrastructural observations on some species of cyanobacteria and green alga in the Lake Holzmaar. In *2nd Croatian Congress on Microscopy*. pp. 108–110.
- Messyasz B., Czerwik-Marcinkowska J., Lücke A. and Uher B. (2012) Differences in the ultrastructure of two selected taxa of phytoplankton in a thermally stratified Lake Holzmaar (Germany). *Biodivers. Res. Conserv.* **28**, 55–62.
- Meyers P. A. and Ishiwatari R. (1995) Organic matter accumulation records in lake sediments. In *Physics and Chemistry of Lakes* (eds. A. Lerman, D. Imboden and J. Gat). Springer, Berlin, pp. 279–328.
- Meyers P. and Lallier-Vergès E. (1999) Lacustrine sedimentary organic matter records of Late Quaternary paleoclimates. *J. Paleolimnol.* **21**, 345–372.
- NEEM Community (2013) Eemian interglacial reconstructed from a Greenland folded ice core. *Nature* **493**, 489–494.
- NGRIP Members (2004) High-resolution record of Northern Hemisphere climate extending into the last interglacial period. *Nature* **431**, 147–151.
- Painter T. (1983) Structural evolution of glycans in algae. *Pure Appl. Chem.* **55**, 677–694.
- Pfister C. (1999) *Wetternachhersage, 500 Jahre Klimavariationen und Naturkatastrophen*, Paul Haupt, Bern.
- Polissar P. J. and D'Andrea W. J. (2014) Uncertainty in paleohydrologic reconstructions from molecular δD values. *Geochim. Cosmochim. Acta* **129**, 146–156.
- Prescott G. W. (1968) *The Algae: A Review*. Houghton Mifflin Company, Boston, Massachusetts.
- Rach O., Brauer A., Wilkes H. and Sachse D. (2014) Delayed hydrological response to Greenland cooling at the onset of the Younger Dryas in western Europe. *Nat. Geosci.* **7**, 109–112.
- Raubitschek S., Lücke A. and Schleser G. (1999) Sedimentation patterns of diatoms in Lake Holzmaar, Germany (on the transfer of climate signals to biogenic silica oxygen isotope proxies). *J. Paleolimnol.* **21**, 437–448.
- Sachs J. P. and Schwab V. F. (2011) Hydrogen isotopes in dinosterol from the Chesapeake Bay estuary. *Geochim. Cosmochim. Acta* **75**, 444–459.

- Sachse D. and Sachs J. P. (2008) Inverse relationship between D/H fractionation in cyanobacterial lipids and salinity in Christmas Island saline ponds. *Geochim. Cosmochim. Acta* **72**, 793–806.
- Sachse D., Radke J. and Gleixner G. (2004) Hydrogen isotope ratios of recent lacustrine sedimentary n-alkanes record modern climate variability. *Geochim. Cosmochim. Acta* **68**, 4877–4889.
- Sachse D., Billault I., Bowen G. J., Chikaraishi Y., Dawson T. E., Feakins S. J., Freeman K. H., Magill C. R., McNerney F. a., van der Meer M. T. J., Polissar P., Robins R. J., Sachs J. P., Schmidt H.-L., Sessions A. L., White J. W. C., West J. B. and Kahmen A. (2012) Molecular paleohydrology: interpreting the hydrogen-isotopic composition of lipid biomarkers from photosynthesizing organisms. *Annu. Rev. Earth Planet. Sci.* **40**, 221–249.
- Scharf B. W. and Menn U. (1992) Hydrology and morphometry. In *Limnology of Eifel maar lakes* (eds. B. Scharf and S. Björk). E. Schweizerbart, Stuttgart, pp. 43–62.
- Schouten S., Ossebaer J., Schreiber K., Kienhuis M. V. M., Langer G., Benthien A. and Bijma J. (2006) The effect of temperature, salinity and growth rate on the stable hydrogen isotopic composition of long chain alkenones produced by *Emiliania huxleyi* and *Gephyrocapsa oceanica*. *Biogeosciences* **3**, 113–119.
- Sikes C. S. (1978) Calcification and cation sorption of *Cladophora glomerata* (Chlorophyta) 1, 2. *J. Phycol.* **14**, 325–329.
- Sirocko F. (2009) *Wetter, Klima, Menschheitsentwicklung. Von der Eiszeit bis ins 21. Jahrhundert*. Second., Konrad theiss, Stuttgart.
- Sirocko F., Dietrich S., Veres D., Grootes P. M., Schaber-Mohr K., Seelos K., Nadeau M.-J., Kromer B., Rothacker L., Röhner M., Krbetschek M., Appleby P., Hambach U., Rolf C., Sudo M. and Grim S. (2013) Multi-proxy dating of Holocene maar lakes and Pleistocene dry maar sediments in the Eifel, Germany. *Quat. Sci. Rev.* **62**, 56–76.
- Treydte K. S., Frank D. C., Saurer M., Helle G., Schleser G. H. and Esper J. (2009) Impact of climate and CO₂ on a millennium-long tree-ring carbon isotope record. *Geochim. Cosmochim. Acta* **73**, 4635–4647.
- Wolk C. (1973) Physiology and cytological chemistry blue-green algae. *Bacteriol. Rev.* **37**, 32–101.
- Yapp C. J. and Epstein S. (1982) Climatic significance of the hydrogen isotope ratios in tree cellulose. *Nature* **297**, 636–639.
- Zech M. and Glaser B. (2009) Compound-specific δ¹⁸O analyses of neutral sugars in soils using gas chromatography-pyrolysis-isotope ratio mass spectrometry: problems, possible solutions and a first application. *Rapid Commun. Mass Spectrom.* **23**, 3522–3532.
- Zech M., Tuthorn M., Zech R., Schlütz F., Zech W. and Glaser B. (2014) A 16-ka δ¹⁸O record of lacustrine sugar biomarkers from the High Himalaya reflects Indian Summer Monsoon variability. *J. Paleolimnol.* **51**, 241–251.
- Zolitschka B. (1998) A 14,000 year sediment yield record from western Germany based on annually laminated lake sediments. *Geomorphology* **22**, 1–17.
- Zolitschka B., Brauer A., Negendank J. F. W., Stockhausen H. and Lang A. (2000) Annually dated late Weichselian continental paleoclimate record from the Eifel, Germany. *Geology* **28**, 783–786.

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