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1 **Hydrological and ecological changes in Western Europe between 3200**  
2 **and 2000 years BP derived from lipid biomarker  $\delta D$  values in Lake**  
3 **Meerfelder Maar sediments**

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6 O. Rach<sup>1,2\*</sup>, S. Engels<sup>3</sup>, A. Kahmen<sup>4</sup>, A. Brauer<sup>5</sup>, C. Martín-Puertas<sup>5,6</sup>, B. van  
7 Geel<sup>7</sup>, D. Sachse<sup>1</sup>

8

9 <sup>1</sup>GFZ German Research Centre for Geosciences, Section 5.1,

10 Geomorphology, Organic Surface Geochemistry Lab, Telegrafenberg, D-

11 14473 Potsdam, Germany

12 <sup>2</sup>Institute for Earth- and Environmental Science, University of Potsdam, Karl-

13 Liebknecht-Strasse 24-25, 14476 Potsdam (Germany)

14 <sup>3</sup>Centre for Environmental Geochemistry, School of Geography, University of

15 Nottingham, University Park, Nottingham (UK)

16 <sup>4</sup>Botany – Department of Environmental Sciences, University of Basel,

17 Schönbeinstrasse 6, 4056 Basel (Switzerland)

18 <sup>5</sup>GFZ German Research Centre for Geosciences, Section 5.2 Climate

19 Dynamics and Landscape Evolution, Telegrafenberg, 14473 Potsdam

20 (Germany)

21 <sup>6</sup>Department of Geography, Royal Holloway, University of London, Egham,

22 Surrey TW20 0EX, United Kingdom.

23 <sup>7</sup>Institute for Biodiversity and Ecosystem Dynamics, University of Amsterdam,

24 Science Park 904, 1098 XH Amsterdam (Netherlands)

25

26 \* Corresponding author's email address: [oliver.rach@gfz-potsdam.de](mailto:oliver.rach@gfz-potsdam.de)

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29 **Highlights**

30 - We present a high-resolution late Holocene biomarker  $\delta D$  record from

31 W Europe

- 32 - Terrestrial biomarker  $\delta D_{\text{terr}}$  records minor hydrological changes  
33 between 3.2-2.0 cal ka BP  
34 -  $\delta D_{\text{terr}}$  data are in agreement with other paleoecological data  
35 - We observe significant effects of aquatic lipid source changes on the  
36  $\delta D_{\text{aq}}$  record  
37 - Multiproxy approaches are essential to avoid hydrological  
38 misinterpretations  
39  
40

#### 41 **Keywords**

42 Holocene; Climate dynamics; Paleoclimatology; Western Europe; Continental  
43 biomarkers; Organic geochemistry; Stable isotopes; Vegetation dynamics  
44  
45  
46

#### 47 **Abstract**

48 One of the most significant Late Holocene climate shifts occurred around  
49 2800 years ago, when cooler and wetter climate conditions established in  
50 western Europe. This shift coincided with an abrupt change in regional  
51 atmospheric circulation between 2760 and 2560 cal years BP, which has  
52 been linked to a grand solar minimum with the same duration (the Homeric  
53 Minimum). We investigated the temporal sequence of hydroclimatic and  
54 vegetation changes across this interval of climatic change (Homeric climate  
55 oscillation) by using lipid biomarker stable hydrogen isotope ratios ( $\delta D$  values)  
56 and pollen assemblages from the annually-laminated sediment record from  
57 lake Meerfelder Maar (Germany).

58 Over the investigated interval (3200 to 2000 varve years BP), terrestrial lipid  
59 biomarker  $\delta D$  showed a gradual trend to more negative values, consistent  
60 with the western Europe long-term climate trend of the Late Holocene. At ca.  
61 2640 varve years BP we identified a strong increase in aquatic plants and  
62 algal remains, indicating a rapid change in the aquatic ecosystem  
63 superimposed on this long-term trend. Interestingly, this aquatic ecosystem

64 change was accompanied by large changes in  $\delta D$  values of aquatic lipid  
65 biomarkers, such as  $nC_{21}$  and  $nC_{23}$  (by between 22-30‰). As these variations  
66 cannot solely be explained by hydroclimate changes, we suggest that these  
67 changes in the  $\delta D_{aq}$  value were influenced by changes in *n*-alkane source  
68 organisms. Our results illustrate that if ubiquitous aquatic lipid biomarkers are  
69 derived from a limited pool of organisms, changes in lake ecology can be a  
70 driving factor for variations on sedimentary lipid  $\delta D_{aq}$  values, which then could  
71 be easily misinterpreted in terms of hydroclimatic changes.

72

73

## 74 **1. Introduction**

75 Late Holocene climate was characterized by a gradual long-term cooling trend  
76 recognized globally (Marcott et al., 2013; Wanner et al., 2008), but also by  
77 superimposed short-term climatic variations occurring over the lifetime of a  
78 few generations and with strong impact on regional climate and society. For  
79 example, a relatively abrupt cooling and increased humidity 2800 years ago in  
80 the North Atlantic-European region (Swierczynski et al., 2013; Wirth et al.,  
81 2013) were interpreted from peat bog records in the Netherlands (van Geel et  
82 al., 1996; van Geel et al., 1999), glacial advances, and increased lake levels  
83 throughout Europe (e.g. Magny, 1993; Engels et al., 2016a). This change  
84 (Movius, 2013) coincided with a significant shift in the western Europe  
85 landscape that marked the onset of the Subatlantic period (Litt et al., 2001).  
86 The climate change 2800 years ago has been related to the occurrence of a  
87 grand solar minimum (Magny, 1993; Martin-Puertas et al., 2012b; van Geel et  
88 al., 1996; van Geel et al., 1999), the Homeric Minimum, which occurred  
89 between 2750-2550 cal years BP recognized in both  $^{14}C$ -tree rings (Reimer et  
90 al., 2009) and  $^{10}Be$ -Greenland ice core records (Reimer et al., 2009; Vonmoos  
91 et al., 2006). Martin-Puertas et al. (2012b) recently reconstructed changes in  
92 solar variability during the time interval from 3300 to 2000 years BP by  
93 analyzing changes in  $^{10}Be$  accumulation rates in the annually laminated  
94 (varved) sediment record of lake Meerfelder Maar (MFM). The authors  
95 compared the reconstructed changes in solar variability to changes in

96 windiness (reconstructed from varve thickness) using the sediment record.  
97 The study showed a sharp increase (over less than a decade) in both the  
98 climatic and solar proxies at  $2759 \pm 39$  varve years BP and a reduction  $199 \pm$   
99 9 years later, indicating that atmospheric circulation reacted abruptly and in  
100 phase with the grand solar minimum and hence showing empirical evidence  
101 for a solar-induced “Homeric Climate Oscillation” (HCO).  
102 The HCO has been suggested to be the trigger for human migrations during  
103 the transition from Bronze Age to Iron Age (Scott et al., 2006; van Geel et al.,  
104 1996). Archeological and paleoecological studies from different locations in  
105 Europe (e.g. the Netherlands and Germany) also provide evidence for an  
106 increase in human activity and reorganization of prehistoric cultures around  
107 that time (Kubitz, 2000; van Geel et al., 1996), most likely favored by a rise in  
108 human population density after the climate deterioration (van Geel and  
109 Berglund, 2000). Although wetter conditions have been inferred for the HCO,  
110 it yet remains elusive if these wetter conditions were associated to major  
111 changes in rainfall intensity and/or lower evapotranspiration and the possible  
112 relation to the observed vegetation changes in western Europe. Furthermore,  
113 the exact temporal succession of regional hydrological and environmental  
114 changes during this period is unknown due to the lack of highly-resolved  
115 hydrological records in western Europe.  
116 In this study we analyze high-resolution lipid biomarker hydrogen isotope  
117 ratios of a Late Holocene sedimentary sequence from lake MFM in western  
118 Germany to test its potential for elucidating the nature of hydrological changes  
119 during the HCO. Stable hydrogen isotope ratios (expressed  $\delta D$  values) of  
120 sedimentary lipid biomarkers (i.e. *n*-alkanes), which can be traced back to  
121 their biological sources (Eglinton and Eglinton, 2008; Killips, 2005; Peters et  
122 al., 2007; Sachs et al., 2013), have become an important paleohydrological  
123 proxy over the last ca. 15 years. This has resulted in new insights into  
124 hydroclimate dynamics over different geological timescales (Aichner et al.,  
125 2010; Atwood and Sachs, 2014; Feakins et al., 2014; Rach et al., 2014;  
126 Sachs et al., 2009; Schefuss et al., 2011; Smittenberg et al., 2011; Tierney et  
127 al., 2010; Tierney et al., 2008; Zhang et al., 2014). Rach et al. (2014)

128 demonstrated that *n*-alkane  $\delta D$  analyzes are a suitable proxy for  
129 reconstructing regional hydrological changes during major and abrupt climate  
130 shifts during the Late-Glacial that are recorded in the varved sediments of lake  
131 MFM.

132 Our specific objectives for this study are (1) to reconstruct hydroclimate  
133 variations for central-western Europe during a period of changing  
134 environmental conditions (3200-2000 varve years BP) using lipid biomarker  
135 stable isotope data, and (2) to combine this record with a high-resolution  
136 aquatic and terrestrial vegetation reconstruction in order to evaluate possible  
137 effects of vegetation change on the biomarker stable isotope record.

138

## 139 **2. Lipid biomarkers as paleoclimate proxies**

### 140 *2.1 Sedimentary n-alkanes as biomarkers for aquatic and terrestrial* 141 *organisms*

142 Straight-chained hydrocarbons such as *n*-alkanes are increasingly applied for  
143 paleoclimate reconstruction. Different *n*-alkane homologues are produced by  
144 bacteria, aquatic as well as terrestrial plants (Aichner et al., 2010; Baas et al.,  
145 2000; Cranwell et al., 1987; Eglinton and Hamilton, 1967; Ficken et al., 2000;  
146 Gelpi et al., 1970). As such, *n*-alkanes can be used to obtain information on  
147 their biological sources. While not species-specific, different groups of source  
148 organisms can be distinguished based on *n*-alkane chain length: *n*-alkanes  
149 with 17 to 19 ( $nC_{17}$  -  $nC_{19}$ ) carbon atoms (short-chain) are predominantly  
150 synthesized by aquatic algae but also by bacteria (Cranwell et al., 1987; Gelpi  
151 et al., 1970; Sachse and Sachs, 2008). Mid-chain *n*-alkanes ( $nC_{21}$  -  $nC_{25}$ ) are  
152 mainly synthesized by submerged aquatic plants (Aichner et al., 2010; Baas  
153 et al., 2000; Ficken et al., 2000). Long-chain *n*-alkanes ( $nC_{27}$  -  $nC_{31}$ ) are major  
154 components of the leaf waxes of terrestrial higher plants (Eglinton and  
155 Hamilton, 1967; Massimo, 1996), although conifers produce significantly  
156 smaller amounts of *n*-alkanes than broad-leaved species (Diefendorf et al.,  
157 2011). Some terrestrial plants also produce significant amounts of  $nC_{25}$ ,  
158 making source assessment for this compound more difficult, but in general

159 aquatic or terrestrial sources can be distinguished from *n*-alkane abundances  
160 in sediments (Gao et al., 2011).

161

## 162 *2.2. Climatic and environmental influences on $\delta D$ values of aquatic and* 163 *terrestrial biomarkers*

164 The observation that  $\delta D$  values of aquatic ( $\delta D_{aq}$ ) and terrestrial ( $\delta D_{terr}$ ) plant  
165 derived lipid biomarkers record the  $\delta D$  values of the organisms' source water  
166 (Garcin et al., 2012; Huang et al., 2004; Sachse et al., 2012; Sachse et al.,  
167 2004; Sauer et al., 2001) has fueled the application of  $\delta D$  measurements as a  
168 paleohydrological proxy. The major determinant of the  $\delta D$  values of aquatic  
169 and terrestrial lipid biomarkers is the  $\delta D$  value of the source water used by the  
170 organism (Sachse et al., 2012). Photosynthetic lacustrine aquatic organisms,  
171 such as submerged aquatic macrophytes and algae use lake water as a  
172 hydrogen source to synthesize *n*-alkanes. In a closed lake system (in  
173 temperate climates), which is only fed by precipitation and characterized by a  
174 low precipitation/ evaporation ratio, the hydrogen isotope composition of lake  
175 water can be interpreted as an integrated signal of precipitation  $\delta D$  (Aichner  
176 et al., 2010; Sachse et al., 2012). In particular, for MFM, being a maar with  
177 steep catchment walls (sheltered from the wind) an effect of evaporation on  
178 lake water is unlikely. For a neighboring maar lake (Holzmaar) a long-term  
179 study of lake water has shown that  $\delta^{18}O$  values vary only around 1‰ and  
180 follow the seasonal temperature evolution (Moschen et al., 2005). Thus, in  
181 such a lake system sedimentary  $\delta D_{aq}$  values provide an integrated  
182 precipitation  $\delta D$  signal (Sachse et al., 2004).

183 Higher land plants on the other hand directly take up precipitation water  
184 (through soil water) (Sachse et al., 2012). However, transpirative processes in  
185 the leaf of the plant modify the isotopic composition of water (i.e. increased  
186 enrichment in D under drier conditions) before hydrogen is being fed into  
187 biosynthetic reactions (Kahmen et al., 2013a; Kahmen et al., 2013b; Sachse  
188 et al., 2012). As a consequence, sedimentary  $\delta D_{terr}$  values also record  
189 changes in ecosystem evapotranspiration (Kahmen et al., 2013b; Sachse et  
190 al., 2004).

191

192 *2.3. Species-specific differences and their influence on aquatic and terrestrial*  
193 *lipid  $\delta D$  values*

194 In addition to the isotopic composition of source water, it has been  
195 demonstrated that changes in vegetation type (of terrestrial plants) as well as  
196 aquatic lipid source organisms can also significantly affect the isotope  
197 composition of terrestrial and aquatic lipids (Sachse et al., 2012).  
198 For example, major differences in the net or apparent fractionation ( $\epsilon_{l/w}$ ), i.e.  
199 the isotopic difference between the source water ( $\delta D_w$ ) and lipid ( $\delta D_l$ ) (equ. 1),  
200 have been observed among different plant functional types (Gao et al., 2014;  
201 Sachse et al., 2012).

202

$$(1) \quad \epsilon_{l/w} = \frac{(D/H)_l}{(D/H)_w}$$

203

204 Since  $\epsilon_{l/w}$  represents the sum of physical and biochemical fractionation  
205 processes, it is currently unclear to what extent individual parameters are  
206 responsible for the observed differences. For example, major differences in  
207 the biosynthetic fractionation ( $\epsilon_{bio}$ ) between various species as well as  
208 differences in leaf-morphology, transpiration and water use efficiency between  
209 grasses and broadleaf-woody plants have been shown to affect  $\epsilon_{l/w}$  (Kahmen  
210 et al., 2013b; Liu et al., 2006; McInerney et al., 2011; Sachse et al., 2012).  
211 On the other hand,  $\epsilon_{l/w}$  in aquatic algae and cyanobacteria can also be  
212 influenced by water salinity and growth rate, possibly related to biochemical  
213 processes as shown for *n*-alkanoic acids (Sachs, 2014), the biosynthetic  
214 precursors of *n*-alkanes (Eglinton and Eglinton, 2008; Sachse et al., 2012;  
215 Sessions et al., 1999). In addition, significant differences in  $\epsilon_{bio}$  have been  
216 observed among different algae (Zhang and Sachs, 2007). For example,  
217 under similar conditions in batch cultures, two different groups of green algae  
218 (Chlorophyceae and Trebouxiophyceae) produced  $C_{16}$  *n*-alkanoic acids, which  
219 differed in their  $\delta D$  values by 160‰ (Zhang and Sachs, 2007). Less  
220 information is available for submerged aquatic plants, but studies on modern



221 aquatic plants and lake surface sediments have suggested the  $\epsilon_{\text{bio}}$  for aquatic  
222 macrophytes (i.e. *Potamogeton*) may be significantly smaller (-82‰) (Aichner  
223 et al., 2010) than observed for algae (-157‰) (Sachse et al., 2004).  
224 Therefore, if various algae and other water plants produce the same  
225 unspecific biomarker (e.g. short- to mid-chain *n*-alkanes) and the aquatic  
226 ecosystem (i.e. species composition) changes, the sedimentary *n*-alkane  $\delta\text{D}$   
227 record could be affected. In a similar way, major vegetation changes can  
228 affect the  $\delta\text{D}_{\text{terr}}$  signal (Nelson et al., 2013). Despite these complications,  $\delta\text{D}$   
229 values of aquatic and terrestrial lipids from sedimentary archives can be used  
230 to reconstruct changes in hydroclimate over time, if constraints on the  
231 processes discussed above, i.e. information about the terrestrial and aquatic  
232 producers of the studied lipids, are available (Aichner et al., 2010; Atwood and  
233 Sachs, 2014; Rach et al., 2014).

234

235 Therefore, for a robust paleoclimatic interpretation it is important to  
236 understand the interplay between hydrological and vegetation change and  
237 their effect on sedimentary lipid biomarker  $\delta\text{D}$  records. The here studied time  
238 interval was characterized by long and short-term climatic change as well as  
239 vegetation changes and this provides a testing ground to study the above  
240 discussed processes and their influence on biomarker  $\delta\text{D}$  values. Therefore,  
241 we compare a high-resolution  $\delta\text{D}_{\text{aq}}$  and  $\delta\text{D}_{\text{terr}}$  record from lake MFM in  
242 western Germany to lake and catchment ecosystem development, inferred  
243 from a new pollen-based vegetation reconstruction, as well as published  
244 sedimentary proxy data from MFM, such as varve thickness and Ti influx  
245 (Martin-Puertas et al., 2012b).

246

### 247 **3. Study site**

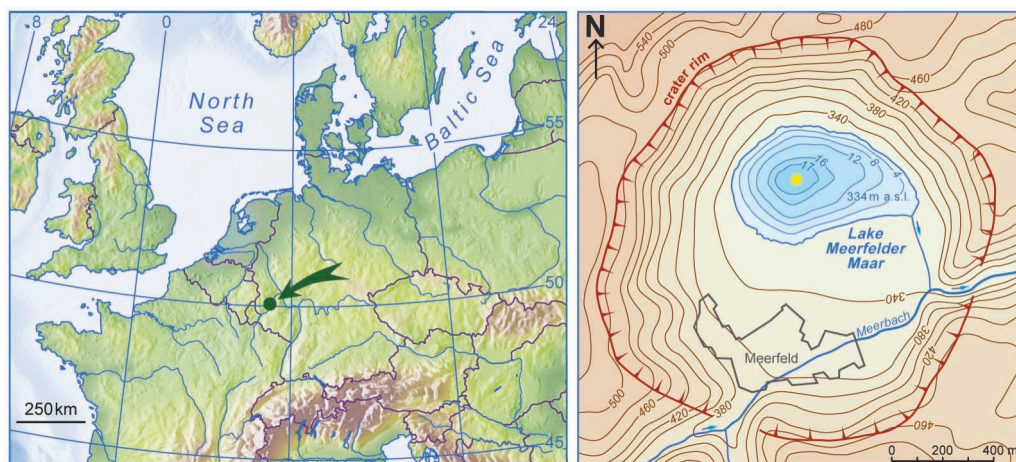
248 Lake Meerfelder Maar ( $50^{\circ} 06' 2.87'' \text{ N}$ ;  $06^{\circ} 45' 27.13'' \text{ E}$ ) is located in  
249 western Germany as a part of the West-Eifel Volcanic Field (Fig. 1). The lake  
250 is situated in a volcanic crater which was formed by a phreatomagmatic  
251 eruption 80,000 years ago (Zöller, 2009).

252 The modern lake is situated at 336.5 m a.s.l. and the lake surface is around  
253 0.248 km<sup>2</sup>, covering the northern part (ca. 1/3) of the maar crater surface (Fig.  
254 1). The maximum water depth is 18m. The southern part of the crater is filled  
255 in by a shallow delta plain, deposited from a stream (Meerbach) passing  
256 through the crater rim in the south. The lake is eutrophic and due to its  
257 particular morphological situation within a deep maar crater, Lake MFM is  
258 wind-sheltered, favoring the preservation of fine seasonal layers within the  
259 sediment sequence (Brauer et al., 1999a; Brauer et al., 2008).

260 The climate of the region is influenced by its proximity to the North Sea coast  
261 (ca. 250 km) with a mean annual air temperature of 8.2 °C and mean annual  
262 precipitation of 950 mm, peaking in winter (Martin-Puertas et al., 2012a).

263 Seven sediment cores were collected in 2009 from the deepest area of Lake  
264 MFM using a UWITEC piston core, with a maximum distance between sites of  
265 20 m. The sediment cores, labeled as MFM09-A to MFM09-G, were split,  
266 imaged, described and an overlapping sediment profile was constructed  
267 (Martin-Puertas et al., 2012a). For the present study the uppermost core  
268 MFM09-A was selected for sampling. We studied a meter long sequence from  
269 230 to 330 cm depth, which covers the interval from 2000 to 3200 varve years  
270 BP (Martin-Puertas et al., 2012b). The MFM chronology (MFM2000) has been  
271 established by varve counting from ca. 1500 cal years BP back to 14,200 cal  
272 years BP along 7.85 m of sediments with a cumulative counting error of less  
273 than 5% and is supported by 51 radiocarbon dates (Brauer et al., 2000). This  
274 independent but floating chronology was anchored to the calendar year time  
275 scale by adopting the age of the regional (Eifel) Ulmener Maar Tephra (UMT)  
276 for the MFM record (Brauer et al., 1999b; Brauer et al., 2000). The UMT is  
277 dated at 11,000 ± 110 cal years BP in the Lake Holzmaar (HZM) varve  
278 chronology by multiple count sequences and <sup>14</sup>C based-correction (Zolitschka  
279 et al., 2000). The proximity of Lake HZM to MFM (10 km) provides the  
280 opportunity to compare both records, showing a good agreement between the  
281 chronologies (Litt et al., 2009). For the study interval, an age error estimate  
282 has been provided by combining varve counting, radiocarbon dating and  
283 sediment <sup>10</sup>Be accumulation rates (Martin-Puertas et al., 2012b). All ages in

284 the following text are rounded on 5 years to avoid interpretations on a  
285 temporal accuracy level, which is not supported by the current age model.



286  
287 **Fig. 1:** Map of western Europe with the study locations. Coloured dots mark  
288 the study (left) and coring (right) site at MFM.

289

## 290 4. Methods

### 291 4.1 Biomarker extraction, identification and quantification

292 A 1.0-m-long core section, which included the time interval of the HCO, was  
293 sampled in consecutive 1-cm-thick slices, resulting in a total of 100 samples.  
294 Due to differences in sedimentation rate, the temporal resolution of the  
295 samples varies between 4 and 45 years per sample.

296 To remove remaining water, all samples were freeze-dried and subsequently  
297 homogenized. A Dionex accelerated solvent extraction system (ASE 350) with  
298 a dichloromethane (DCM): methanol mixture (9:1) at 100°C and 103 bar was  
299 used for the extraction of lipid biomarkers from freeze-dried samples in the  
300 biomarker laboratory at the University of Potsdam. The total lipid extracts  
301 (TLE) were separated into three fractions (aliphatic (F1), aromatic (F2) and  
302 alcohol/ fatty acid (F3)) by solid phase extraction (SPE). The separation was  
303 achieved using 2g silica gel as the stationary phase and hexane,  
304 hexane:DCM (1:1) and DCM as the respective mobile phases. Activated  
305 copper in a pipette column was used to remove elemental sulfur from the F1  
306 fraction. The aliphatic fraction was dominated by *n*-alkanes ( $nC_{21}$ - $nC_{31}$   
307 homologues) and alkenes. Fractions F2 and F3 contained mainly ketones,  
308 alcohols and fatty acids. To avoid coelution of alkanes and alkenes during

309 isotope measurement, the F1 fraction was further purified using silver nitrate  
310 ( $\text{AgNO}_3$ ) impregnated silica gel in a pipette column with hexane and  
311 dichloromethane as the mobile phase for the elution of alkanes and alkenes,  
312 respectively.

313 *n*-Alkane identification and quantification was performed using a gas  
314 chromatograph (GC 7890-A, Agilent, Santa Clara, USA) coupled to a flame  
315 ionization detector (FID) and a mass selective detector (MSD) (MS 5975-C,  
316 Agilent, Santa Clara, USA) coupled via an electronic split interface. The  
317 quantification was performed through the FID by comparing compound peak  
318 area to the peak area of the internal standard (5 $\alpha$ -androstane). Compound  
319 identification was achieved using the MSD and comparison with library and  
320 literature mass spectra. The GC temperature program used for *n*-alkane  
321 quantification contained the following specifications: injection at 70°C (hold for  
322 2 minutes), then heating up to 140°C with a ramp of 12°C per minute directly  
323 followed by a heating to 320°C with a ramp of 2°C per minute. The final  
324 temperature of 320°C was held for 15 minutes. The PTV injector started at  
325 50°C and was heating up to 350°C with a ramp of 14°C per second.

326

#### 327 *4.2 Stable isotope measurement and evaluation*

328 Compound-specific hydrogen isotope ratios of the *n*-alkanes were measured  
329 on a Delta-V-Plus Isotope Ratio Mass Spectrometer (IRMS) (Thermo Fisher,  
330 Bremer, Germany) coupled to a Trace Gas Chromatograph Ultra (Thermo  
331 Fisher, Bremer, Germany) at the Swiss Federal Institute of Technology Zurich  
332 (ETH Zurich). The following GC-temperature program was used: start at 90°C  
333 (held for 2 minutes), heating up to 150°C with 10°C per minute, heating from  
334 150°C to 320°C with 4°C per minute; the final temperature was held for 10  
335 minutes. Each sample was injected three times. For conversion of the  
336 measured  $\delta\text{D}$  values to the VSMOW scale a standard containing  $n\text{C}_{16}$  to  $n\text{C}_{30}$   
337 alkanes (Mix A4 obtained from Arndt Schimmelmann, Indiana University) with  
338 known  $\delta\text{D}$  values was measured in triplicate at the beginning and the end of  
339 each sequence. All measured  $\delta\text{D}$  values were corrected to the VSMOW scale  
340 using a linear regression function (with a specific slope and intercept) derived

341 from measured vs. real Mix A4 standard values. The mean standard deviation  
342 of all A4 standard measurements (n=441) was 2.1‰, while the mean  
343 standard deviation of all sample *n*-alkane measurements (n=492) was 1.4‰.  
344 To avoid misinterpretation of the measured  $\delta D$  values only baseline separated  
345 peaks with areas over 20Vs have been used for interpretation. The H3<sup>+</sup> factor  
346 was determined before each sequence and remained constant at  $3.63 \pm 0.39$   
347 during the 4 weeks measurement period.

348

#### 349 *4.3 Palynological analysis*

350 Two plastic containers of 35x260 mm were pressed into cores MFM09A2DR  
351 and MFM09A2UR to a depth of 10 mm. The sediment in the plastic containers  
352 was subsequently subsampled with a 3 samples/ centimeter resolution for the  
353 sediments older than 2765 varve years BP and a 2 samples/ centimeter  
354 resolution for the sediments younger than 2765 varve years BP. These  
355 sampling intervals correspond to a temporal resolution of 1-29 years per  
356 sample. Ninety-one samples were prepared for the analysis of pollen and  
357 spores at the University of Amsterdam following the protocols of Faegri et al.  
358 (1990) and Moore et al. (1991). Standard tablets with *Lycopodium* spores  
359 were added to the sample during laboratory processing to estimate pollen and  
360 spore concentrations and influx numbers (Stockmarr, 1971). Pollen, fern  
361 spores, fungal spores, and other palynomorphs (including remains of  
362 freshwater algae) were identified using a light microscope with 400x  
363 magnification (1000x when necessary). Keys and illustrations by Moore et al.  
364 (1991) and Beug (2004) as well as a reference collection were used for pollen  
365 identification. The identification of algal remains and other non-pollen  
366 palynomorphs (NPPs) follows van Geel (1978). A pollen percentage diagram  
367 was calculated using a pollen sum ( $\Sigma$ -pollen) that includes arboreal pollen and  
368 pollen of upland herbs and the average  $\Sigma$ -pollen is 572 (range: 443-698). The  
369 percent-abundances of all pollen, spores and NPPs are calculated in relation  
370 to  $\Sigma$ -pollen. Concentrations of individual taxa were calculated by multiplying  
371 the number of encountered pollen by the ratio of the number of added  
372 *Lycopodium* spores and the number of spores encountered during analysis.

373 This number was then divided by the volume of material used in the analysis  
374 to derive taxon-specific pollen concentrations. A percent-abundance diagram  
375 was plotted using TILIA v 1.17.6; concentration- and influx-diagrams were  
376 plotted using C2. Details on the taxa important for the interpretation of our *n*-  
377 alkane data are presented in section 5.3 (pollen data), whereas overview  
378 diagrams of the arboreal taxa (percentages, concentrations and influx) (Fig.  
379 S1) and the aquatic taxa (expressed as percentages in relation to  $\Sigma$ -pollen)  
380 (Fig. S2) can be found in the Supplementary Information.

381

382

## 383 **5. Results**

### 384 *5.1 n-Alkane concentrations*

385

386 In total 100 samples were analyzed for their *n*-alkane content. Eighteen  
387 samples did not contain enough material for *n*-alkane analysis. In the  
388 remaining 82 samples the concentration of all identified *n*-alkanes ( $nC_{21}$  to  
389  $nC_{31}$ ) ranged from 0.34 to 69.42  $\mu\text{g/g}$  dry weight of sediment. The most  
390 abundant *n*-alkane homologue in all samples was  $nC_{29}$  with an average  
391 concentration of 26.5  $\mu\text{g/g}$  sediment dry weight per sample (range 3.0-  
392 69.1  $\mu\text{g/g}$ ). The compound with the lowest concentration was always  $nC_{21}$  with  
393 3.9  $\mu\text{g/g}$  on average (range 0.34 -14.3  $\mu\text{g/g}$ ). Other *n*-alkanes ( $nC_{23}$ ,  $nC_{25}$ ,  $nC_{27}$   
394 and  $nC_{31}$ ) had average concentrations between 4.2 to 20.5  $\mu\text{g/g}$  sediment dry  
395 weight. The average chain-length (ACL) varied between 26.0 and 28.8.

396 The average influx values ( $\mu\text{g}$  normalized per varve year) of short- and long-  
397 chain *n*-alkanes showed significant variations. Before the HCO,  $nC_{21}$  and  $nC_{23}$   
398 showed average influx values of 0.35 and 0.27  $\mu\text{g/ year}$ , while the  $nC_{25}$  to  $nC_{31}$   
399 homologues showed average influx values between 0.46 and 1.34  $\mu\text{g/year}$ ,  
400 respectively (Fig 2B). The influx of  $nC_{21}$  and  $nC_{23}$  increased rapidly to 0.68  
401 and 1.03  $\mu\text{g/ year}$  after 2785 varve years BP, while the influx values of  $nC_{25}$  to  
402  $nC_{31}$  also increased to average values between 2.10 and 6.28  $\mu\text{g/year}$  (Fig  
403 2B). The average *n*-alkane influx values for  $nC_{21}$  and  $nC_{23}$  decreased abruptly  
404 to average values of 0.12 and 0.15  $\mu\text{g/ year}$  after the HCO (Fig 2B). The  $nC_{25}$

405 to  $nC_{31}$  homologues also decreased to average influx values between 0.37  
406 and  $1.42\mu\text{g}/\text{year}$ .  $nC_{21}$  showed maximum influx values during the first part of  
407 the HCO (2750 – 2660 varve years BP), while long-chain  $n$ -alkanes had their  
408 maximum influx rates in the second part of the HCO (2700 – 2610 varve years  
409 BP) (Fig 2B). Influx rates of  $nC_{23}$  showed local maxima both in the first half of  
410 the HCO (at 2740 varve years BP) as well as in the second half of the HCO  
411 (at 2610 varve years BP) (Fig 2B).

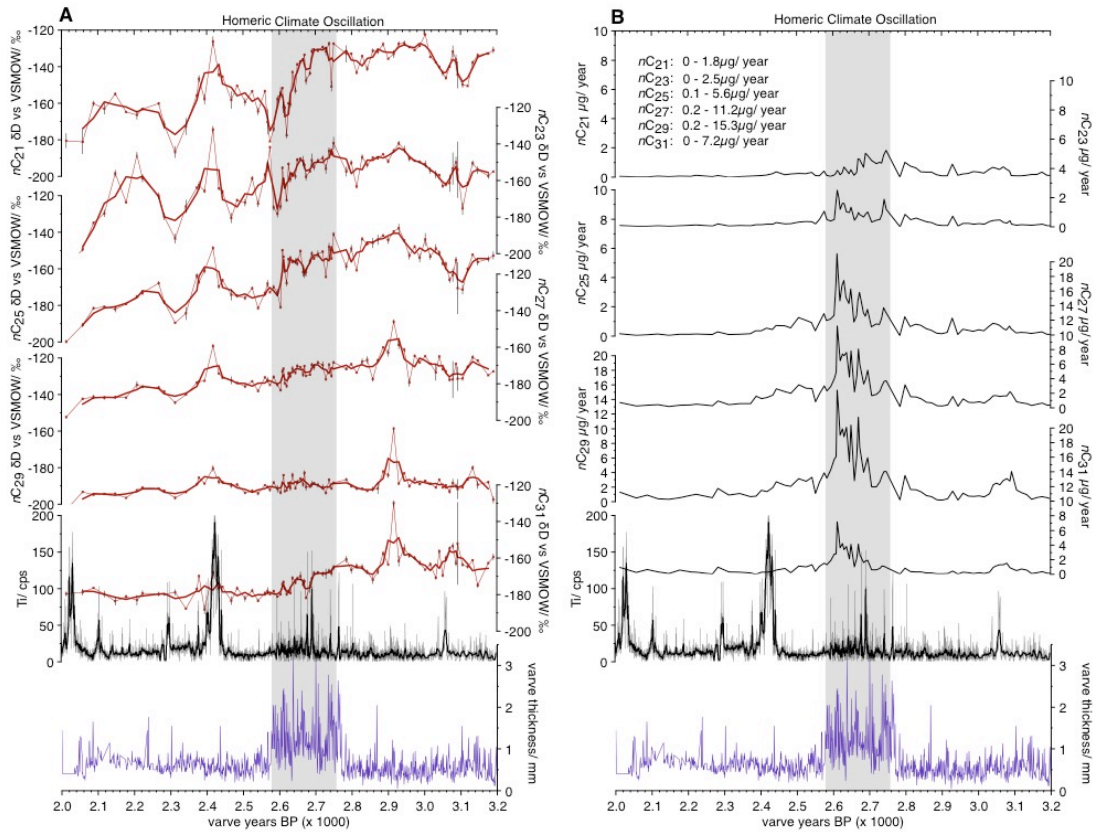
412

### 413 *5.2 Stable hydrogen isotope composition ( $\delta D$ values) of the $n$ -alkanes*

414 All 82 samples were analyzed for compound specific stable hydrogen isotope  
415 ratios, expressed as  $\delta D$  values. The  $n$ -alkane  $\delta D$  values showed a  
416 decreasing trend during the analyzed period (Fig 2A). Generally, the  $\delta D$   
417 values of all  $n$ -alkanes were more positive before the HCO than after (Fig 2A).  
418 However, there were major differences in the magnitude of variation between  
419  $n$ -alkanes of different chain-length. Short and mid-chain  $n$ -alkanes ( $nC_{21}$ - $nC_{25}$ )  
420 generally showed higher variability in their  $\delta D$  values than long-chain  $n$ -  
421 alkanes. Before the HCO,  $nC_{21}$   $\delta D$  values were on average  $-135 \pm 2\text{‰}$   
422 (arithmetic mean from 3190 to 2785 varve years BP with respective 95%  
423 confidence interval) while after the HCO the average  $\delta D$  value changed to -  
424  $160 \pm 5\text{‰}$  (arithmetic mean from 2540 to 2015 varve years BP). Applying the  
425 epsilon equation (Sessions and Hayes, 2005) for accurate calculations of  
426 differences in  $\delta$ -values results in a difference of about 30‰ for  $nC_{21}$   $\delta D$  values  
427 before and after the HCO. The average  $\delta D$  values of  $nC_{23}$  and  $nC_{25}$  for the  
428 same period changed from  $-153 \pm 3\text{‰}$  and  $-152 \pm 3\text{‰}$  to  $-171 \pm 7\text{‰}$  and  $-176$   
429  $\pm 4\text{‰}$ , respectively (difference 22 and 28‰) (Fig 2A).

430 Long-chain  $n$ -alkanes generally showed smaller changes in their  $\delta D$  values.  
431 The average  $\delta D$  values of  $nC_{27}$  and  $nC_{29}$  changed from  $-169 \pm 2\text{‰}$  and  $-188 \pm$   
432  $2\text{‰}$  (before the HCO) to  $-182 \pm 3\text{‰}$  and  $-192 \pm 2\text{‰}$  (after the HCO) (difference  
433 15 and 4‰). The  $\delta D$  values of  $nC_{31}$  changed from  $-162 \pm 3\text{‰}$  to  $-179 \pm 2\text{‰}$   
434 (difference 20‰) (Fig 2A).

435



436

437 **Fig. 2:**  $\delta D$  values (A) (smoothing by 3-data running average) and annual flux  
 438 ( $\mu g/year$ ) (B) of  $nC_{21}$ - $nC_{31}$  alkanes and varve thickness as well as Titanium  
 439 content (smoothing by 100-data running average) (Martin-Puertas et al.,  
 440 2012b) of the studied core section.

441

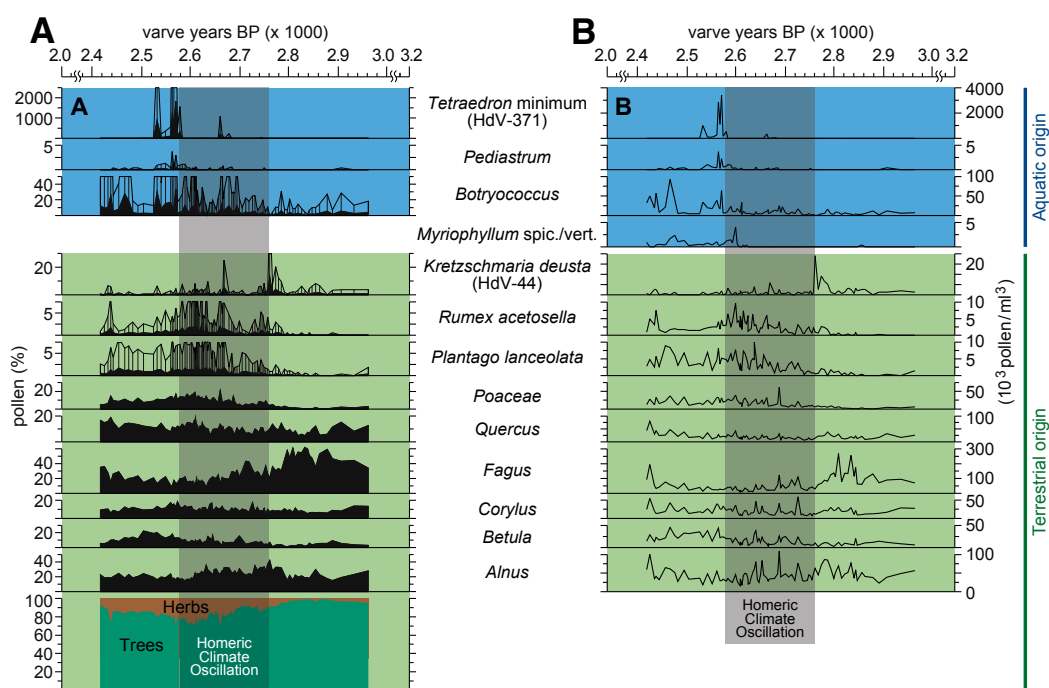
### 442 5.3 Pollen-data

443 The lower part of the pollen record (2945-2795 varve years BP) was  
 444 characterized by relatively high percentages of arboreal pollen (AP) of 95-  
 445 100% (Fig. 3). The pollen-assemblages were dominated by *Fagus* which  
 446 reached abundances  $>60\%$ , accompanied by relatively high abundances of  
 447 other deciduous tree taxa such as *Alnus* (15-30%), *Corylus* (5-15%) and  
 448 *Quercus* (5-15%). Pollen from non-arboreal taxa (NAP) were only present in  
 449 low abundances between 2945-2795 varve years BP, suggesting that the  
 450 vegetation around MFM consisted of a closed-canopy forest.

451 A sharp decrease in relative abundance of *Fagus* to values of around 40%  
 452 was observed at  $\sim 2795$  varve years BP (Fig. 3). Simultaneously, spores of  
 453 *Kretzschmaria deusta*, a parasitic fungus living on various tree species (van



454 Geel et al., 2013), showed an increase in abundance to values of 5%. An  
 455 increase in the relative abundance of *Alnus* as well as of several NAP-taxa  
 456 coincided with the decrease in *Fagus* (Fig. 3). Crop plants (e.g. Poaceae,  
 457 Cerealia) as well as *Plantago lanceolata* and *Rumex acetosella*-type all  
 458 started to increase after 2795 varve years BP. Remains (vegetative cell walls)  
 459 of the green algae *Botryococcus*, *Tetraedron minimum* and of the aquatic  
 460 macrophyte *Myriophyllum spicatum/verticillatum*-type showed an increase  
 461 around 2620 and 2595 varve years BP, respectively.  
 462



463  
 464 **Fig. 3:** Pollen and spores abundance of the major constituents of vegetation  
 465 in and surrounding MFM given in % (A) and pollen concentrations (B). Thinner  
 466 lines on top of the upper six plots in A marking exaggeration-lines (5-times).  
 467 Blue shaded areas marking aquatic organisms. Green areas are showing  
 468 terrestrial plants. The dark-green/ orange areas show the local tree/ herb  
 469 distribution in percentage.

470

## 471 6. Discussion

472 Our lipid biomarker stable hydrogen isotope record showed a long-term trend  
 473 to more negative  $\delta D$  values during the 3200 to 2000 varve years BP interval.  
 474 This is evident in all analyzed biomarkers, regardless of their biological origin

475 (Fig. 2). The decrease in lipid  $\delta D$  values possibly reflects the long-term  
476 cooling trend as a consequence of declining summer insolation in the  
477 Northern Hemisphere (Marcott et al., 2013; Renssen et al., 2009) in the way  
478 that a decrease in air temperature would lead to more negative precipitation  
479  $\delta D$  values (Dansgaard, 1964; Gat, 1996; Gat et al., 2000). However, we  
480 observed substantial differences in the magnitude of changes in  $\delta D$  values  
481 between aquatic and terrestrial plant derived lipid biomarkers:  $\delta D_{\text{aq}}$  values  
482 showed a rather abrupt decrease starting at around 2700 varve years BP, a  
483 change not observed for  $\delta D_{\text{terr}}$  values (except a slight decrease in  $nC_{31}$   $\delta D$   
484 values). This indicates that different processes controlled the observed  
485 changes for aquatic and terrestrial biomarkers. While different biosynthetic  
486 fractionation factors for aquatic and terrestrial plants can explain different  
487 absolute  $\delta D$  values, different magnitudes of change indicate either significant  
488 evapotranspirational or ecological changes. For example, cooler and more  
489 arid conditions could explain a stronger decrease in  $\delta D_{\text{aq}}$  compared to  $\delta D_{\text{terr}}$ ,  
490 as  $\delta D_{\text{terr}}$  values would reflect increasing plant transpiration (Kahmen et al.,  
491 2013b). However, there is no evidence for a substantial aridification during  
492 this period in western Europe. Rather, several studies suggest a shift to more  
493 humid conditions during this period (Martin-Puertas et al., 2012b; van Geel,  
494 1978; van Geel et al., 1996; van Geel et al., 2013). With our combined high-  
495 resolution lipid biomarker and palynological analysis we therefore explore  
496 ecological changes in the aquatic and terrestrial ecosystem in and around  
497 MFM to test if these changes may have influenced the magnitude of change  
498 in biomarker  $\delta D$  values.

499

### 500 *6.1. Changes in vegetation based on palynological records*

501 The palynological data provide first evidence for changes in the terrestrial  
502 ecosystem at ca. 2800 varve years BP. Our pollen record showed a decrease  
503 in relative pollen abundance of *Fagus* by half and a doubling of *Alnus*,  
504 accompanied by a general trend to increasing grass/herb vegetation in the  
505 catchment of MFM (Fig. 3A). The presence/increase of human-impact  
506 indicators such as *Plantago lanceolata* and *Rumex acetosella*-type provided

507 evidence for increased human impact (Behre, 1981) in the catchment of MFM.  
508 *Kretzschmaria deusta* spores increased in abundance from 2795 to 2765  
509 varve years BP, which could be a result of the temporary occurrence of this  
510 fungus on wounded trees that were present in the landscape after the clearing  
511 of parts of the forest (Kubitz, 2000; van Geel et al., 2013).

512 The second substantial decline in tree pollen at 2695 varve years BP occurred  
513 about 100 years after the variations mentioned above (Fig 3A). This marks a  
514 second phase of ecosystem changes, which is additionally characterized by  
515 an increase of *Botryococcus* – green algae (Fig 3A). This second phase in  
516 ecological change could even have been caused by further increased human  
517 impact but climatic changes cannot be ruled out either.

518

## 519 *6.2. Environmental and hydroclimatic changes inferred from changes in lipid* 520 *biomarker abundance and $\delta D$ values*

521

### 522 *6.2.1 Terrestrial biomarker flux into the sediment*

523 At 2695 varve years BP, about 60 years after the increase in varve thickness  
524 (Fig 2) (Martin-Puertas et al., 2012b), our lipid biomarker record showed an  
525 increased influx of leaf wax *n*-alkanes into the sediment (Fig 2B). This  
526 doubling in lipid biomarker flux occurred simultaneous with an increase in  
527 Titanium counts, a proxy for surface runoff (Fig. 2) (Martin-Puertas et al.,  
528 2012b). At the same time, tree pollen decreased significantly (from 90-71%)  
529 and grass and other herbaceous pollen increased from 10 to 29% (Fig. 3A).  
530 We interpret these changes in the pollen record to reflect a shift toward a  
531 more open landscape, which might have led to increased erosion and flux of  
532 terrestrial material into the lake. This is supported by the observation that the  
533 influx of terrestrial biomarkers reached its maximum at the same time when  
534 the tree / herb pollen ratios showed their lowest value at ca. 2610 varve years  
535 BP. However, the onset of the tree pollen decline (from 96-86%) and  
536 increasing grass pollen (from 4 to 14%) occurred already 100 years earlier, at  
537 ca. 2800 varve years BP. Also, varve thickness increased likely because of

538 windier conditions already ca. 60 years before the increased terrestrial lipid  
539 biomarker influx at 2760 varve years BP.

540 The decadal resolution of our lipid biomarker and palynological data allows a  
541 detailed assessment of the temporal succession of proxy changes related to  
542 the HCO. We have to note that the different vegetation proxies presented here  
543 (alkanes, pollen) partly may reflect different source areas. While most of the  
544 *n*-alkanes likely were derived from vegetation growing on the lake shore,  
545 pollen assemblages may also include a signal from the upland vegetation  
546 surrounding the MFM crater. However, the specific catchment-conditions of  
547 lake MFM, with its steep crater walls and small catchment area, make it most  
548 likely that most pollen is derived from the catchment vegetation itself, and that  
549 the contribution of long distance transport is of minor importance (Engels et  
550 al., 2016b; Litt et al., 2009). The initial change in the pollen diagram observed  
551 at ca. 2800 varve years BP is not linked to additional transport of terrestrial  
552 material into the lake. Only at ca. 2700 varve years BP, when the largest  
553 vegetation change occurred, soil erosion increased. The first decrease in  
554 pollen concentrations at 2800 varve years BP may be due to decreased  
555 pollen production as a result of increased ecological stress, instead of  
556 changes in vegetation, which may have followed a few decades later.

557  
558

### 559 *6.2.2 Biomarker $\delta D$ values as recorders of hydroclimate*

560 In addition to the long-term trend to more negative  $\delta D$  values between 3200  
561 and 2000 varve years BP (Fig. 2A), evident in nearly all analyzed biomarkers  
562 (except *nC<sub>29</sub>*), aquatic and terrestrial lipid biomarker  $\delta D$  values showed their  
563 most substantial decrease (by between 30 and 4‰) during the HCO interval  
564 (Fig. 4).

565 While the 4-20‰ decrease in  $\delta D_{\text{terr}}$  values could have been caused by a  
566 combination of cooler conditions and lower plant transpiration (Craig, 1965;  
567 Flanagan et al., 1991; Kahmen et al., 2013b; Sachse et al., 2012) under the  
568 more humid conditions suggested by earlier studies (van Geel et al., 1996), it

569 remains difficult to explain the rapid decline in  $\delta D_{aq}$  values between 22-30‰,  
570 as these would not be affected by changes in terrestrial transpiration.  
571 While a decrease in air temperature would lead to more negative precipitation  
572  $\delta D$  values, the observed decrease of 22-30‰ in  $\delta D_{aq}$  would imply an  
573 unrealistic temperature decrease between 11 and 15°C during the HCO, when  
574 considering the modern temperature sensitivity of precipitation  $\delta D$  in this  
575 region (2‰/°C; (IAEA/WMO, 2006)). While no temperature reconstructions  
576 are available for the HCO, a temperature decrease between 0.5-1.5°C has  
577 been suggested for similar solar minima (Martin-Puertas et al., 2012b).  
578 Therefore, a potential 0.5-1.5°C decrease during the HCO would only have  
579 had a minimal effect on precipitation  $\delta D$  values. However, a decrease in  
580 temperature may also be associated to shifts in the moisture source region  
581 and/or changes in moisture source temperature, which may have exercised  
582 additional control on decreasing  $\delta D$  values. For example, Martin-Puertas et al.  
583 (2012b) suggested a reduced atmospheric pressure gradient between the  
584 subtropics and Iceland for the HCO, resembling a negative phase of the North  
585 Atlantic Oscillation (NAO), which today results in more negative winter  $\delta D_{precip}$   
586 values in parts of western Europe (Baldini et al., 2008). However, we do not  
587 observe an increase in  $\delta D$  values after the HCO, suggesting the observed  
588 change was not an excursion or phase but rather a shift of atmospheric  
589 conditions to a new regime.

590 While the relatively small changes in  $\delta D_{terr}$  can be largely explained by the  
591 proposed long-term hydroclimatic changes during this period, the abrupt  
592 changes in  $\delta D_{aq}$  of up to 30‰ over 180 years are difficult to reconcile with this  
593 scenario. Due to the absence of other proxy indicators suggesting  
594 hydroclimatic changes that could explain such a decline in  $\delta D_{aq}$ , we explore  
595 the possibility that factors additional to hydroclimate influenced  $\delta D_{aq}$ .

596

### 597 *6.2.3. The effect of lake ecosystem changes on $\delta D$ values of aquatic n-* 598 *alkanes*

599 Additional factors known to affect  $\delta D_{aq}$  include changes in water salinity, light  
600 intensity, growth rate and species changes (Sachs, 2014; Zhang and Sachs,

2007). MFM always was a freshwater lake, so that we can rule out salinity as a driver. Increased upland erosion and a subsequent delivery of nutrients into the lake may have resulted in increasing growth rates of aquatic organisms. However, for aliphatic lipids produced by algae D/H fractionation does not seem to change significantly with growth rate (Sachs, 2014), and no such data exist for aquatic plants.

However, palynological data indicate significant changes in the aquatic ecosystem at 2625 varve years BP, when the total amount of aquatic and swamp taxa pollen/ remains started to increase from virtually zero to a maximum of 1.5% at 2600 varve years BP (Fig. 4). Strikingly, this increase, as well as the change in species composition, was synchronous to the largest changes in  $nC_{21}$  and  $nC_{23}$  alkane  $\delta D$  values (Fig 4). These compounds are primarily synthesized by aquatic organisms, likely aquatic macrophytes (Aichner et al., 2010; Cranwell et al., 1987). A minor decrease was also observed for  $nC_{25}$   $\delta D$  (Fig 2) values, a compound that can originate from both aquatic as well as terrestrial sources (Baas et al., 2000; Eglinton and Hamilton, 1967; Ficken et al., 2000). Palynological analysis indicates the occurrence / increase of *Myriophyllum spicatum/verticillatum-type* (submerged aquatic plant), *Botryococcus*, *Pediastrum* and *Tetraedron minimum* (green algae) during and after the HCO (Fig. 3). The most abundant aquatic taxon identified from the microfossil record is *Botryococcus* (identified by vegetative cell walls). As such, the available palynological data indicate major changes in the aquatic ecosystem at 2625 varve years BP, coeval with the largest change in  $\delta D_{aq}$  values. Since  $nC_{21}$  and  $nC_{23}$  alkanes can be produced by a variety of different algae and submerged aquatic macrophytes (Aichner et al., 2010; Ficken et al., 2000; Gelpi et al., 1970; Parrish, 1988) it is possible that a change in the predominant aquatic organisms, characterized by different magnitudes of  $\epsilon_{bio}$ , was at least partly responsible for the observed changes. For the more ubiquitous  $nC_{16}$  alkanic acid differences in  $\epsilon_{bio}$  of up to 160‰ between different green algal taxa have been observed in culture studies (Zhang and Sachs, 2007). As such, if the spectrum of organisms producing  $nC_{21}$  and  $nC_{23}$  was relatively small, which is supported by the limited number

633 of pollen of aquatic taxa (Fig 3), it is conceivable that changes in the  
634 predominant  $nC_{21}$  and  $nC_{23}$  producers have resulted in a significant variation  
635 within the sedimentary  $\delta D_{aq}$  record.  
636 Therefore, we argue that the change in the  $\delta D$  values of the  $nC_{21}$  and  $nC_{23}$   
637 alkanes does not only reflect hydroclimatic changes, but that it was amplified  
638 as a result of a change in aquatic lipid sources. This also implies that without  
639 knowledge of the biosynthetic fractionation factors for the individual  $nC_{21}$  and  
640  $nC_{23}$  producers, a direct reconstruction of source water  $\delta D$  values is  
641 impossible. Arguably, the observed changes in the aquatic ecosystem were  
642 most probably initiated by the climatic and environmental changes. We  
643 suggest that the increasing influx of terrestrial material between 2695 and  
644 2610 varve years BP due to wetter conditions and decreasing tree cover (see  
645 section 6.2.1), delivered more nutrients into the lake, acting as a fertilizer for  
646 aquatic plants. The increase in abundance of aquatic organisms around 2640  
647 varve years BP occurred 60 years after the increase of terrestrial biomarker  
648 flux into the lake, possibly marking a threshold in the fertilization rate and  
649 triggering the diversification of the aquatic ecosystem.

650

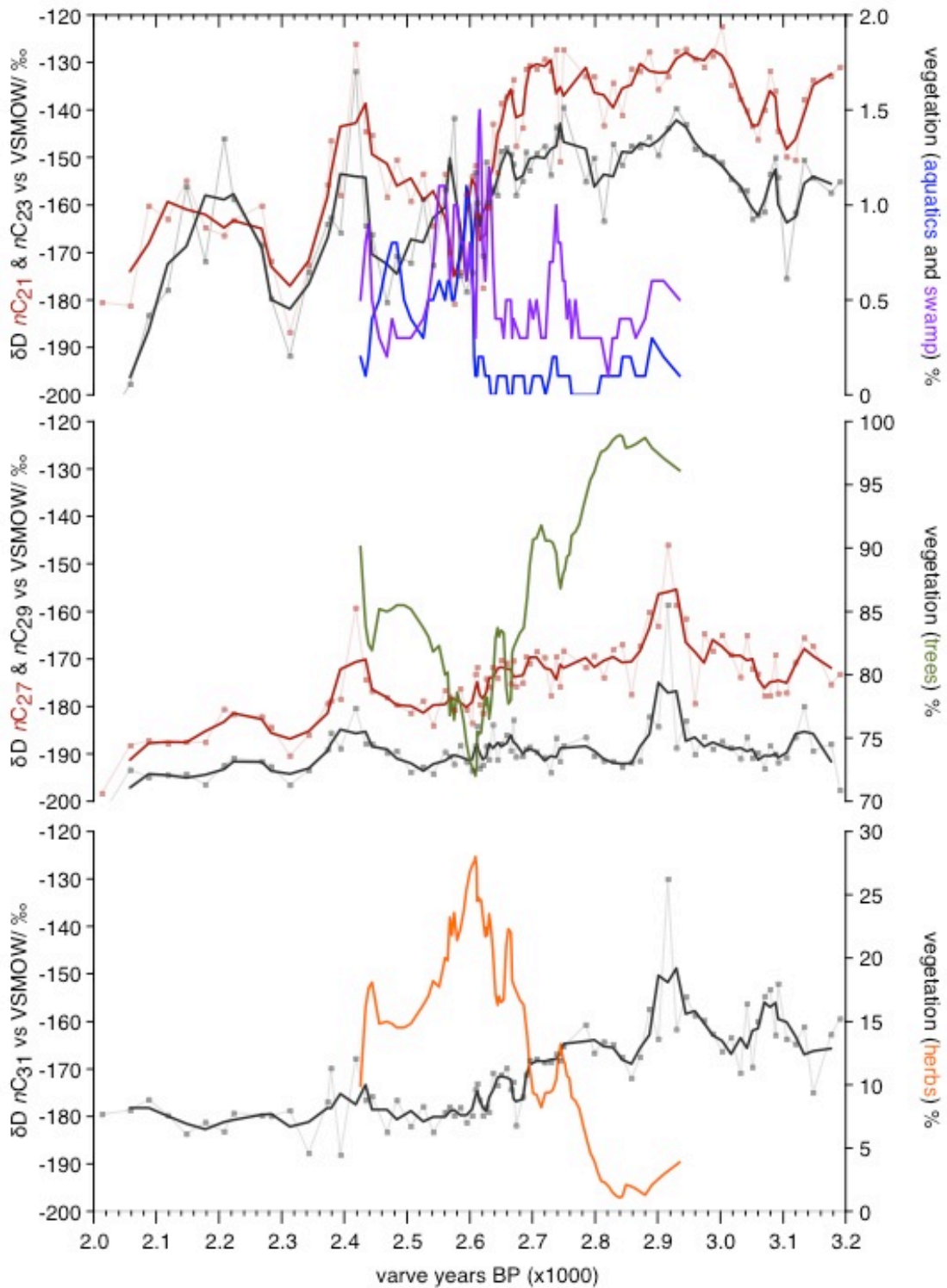
651 *6.2.4. The effect of vegetation changes on  $\delta D$  values of terrestrial  $n$ -alkanes*  
652  $\delta D$  values of the terrestrial plant derived  $nC_{27}$ ,  $nC_{29}$  and  $nC_{31}$   $n$ -alkanes  
653 decreased in total by 15, 4 and 20‰, respectively, during the HCO interval  
654 (difference between mean  $\delta D$  values from before and after the HCO) (Fig 2).  
655 While changes in  $nC_{27}$  and  $nC_{29}$   $\delta D$  values were gradual and can be  
656 explained by hydroclimatic changes (i.e. cooler and more humid conditions),  
657 the first larger and relatively abrupt decrease within the HCO of about 7‰  
658 observed for  $nC_{31}$  at 2685 varve years BP coincides with the onset of a 20%  
659 increase in grass and other herbaceous pollen (Fig 3) likely caused by an  
660 increase of human impact (Kubitz, 2000). As such, the change in  $\delta D$  values of  
661  $nC_{31}$  may have been amplified by changes in terrestrial vegetation and  
662 influenced not only by climatic but also by anthropogenic factors. While  $nC_{31}$   
663 is produced by different tree species (e.g. *Betula*, *Acer* (Diefendorf et al.,  
664 2011)) it is often found in higher concentrations in grasses (Massimo, 1996).

665 Therefore, the more negative  $\delta D$  values after 2680 varve years BP may  
666 reflect at least partly the increased amount of grass-derived  $nC_{31}$  into the lake  
667 sediment, as  $n$ -alkane  $\delta D$  values from grasses are usually found to be more  
668 negative (up to 30‰) compared to those from trees (Duan and He, 2011; Hou  
669 et al., 2007; Kahmen et al., 2013b; Liu et al., 2006; Sachse et al., 2012).

670 Based on the palynological data we suggest that the  $nC_{27}$  and  $nC_{29}$  alkanes in  
671 the MFM sediments were primarily produced by trees such as *Alnus*, *Betula*,  
672 *Salix*, *Fagus*, *Carpinus*, *Ulmus* and *Quercus*, species known to produce the  $n$ -  
673 alkanes (Diefendorf et al., 2011; Piasentier et al., 2000; Sachse et al., 2006).  
674 Interestingly,  $nC_{29}$   $\delta D$  values from the MFM sediments of the analyzed period  
675 were on average 18‰ more negative than  $nC_{27}$  and  $nC_{31}$   $\delta D$  values. This  
676 consistent offset possibly implies a different water source or a different  $\epsilon_{bio}$  for  
677 all or the major  $nC_{29}$  source organisms. The pollen record provides evidence  
678 for a high proportion of *Alnus* and *Salix* in the catchment area, taxa primarily  
679 adapted to wetter areas such as lake shores and riversides (Landolt and  
680 Bäumler, 2010; Lauber and Wagner, 2001). *Alnus* and *Salix* have been found  
681 to synthesize higher amounts of  $nC_{29}$  (Diefendorf et al., 2011; Sachse et al.,  
682 2006) and therefore the more negative  $nC_{29}$   $\delta D$  values may be due to the  
683 preferred location at the lakeshore within the crater, where higher relative  
684 humidity (due to the proximity of the water body) may have resulted in smaller  
685 leaf water isotope enrichment (Craig, 1965; Farquhar et al., 2007; Flanagan et  
686 al., 1991; Kahmen et al., 2011; Kahmen et al., 2013b).

687 Due to the wide variety of possible sources of the  $nC_{27}$  and  $nC_{29}$  alkanes, it is  
688 likely that these compounds had the highest integrative capacity and the  
689 occurrence or disappearance of single species did not significantly affect the  
690 sedimentary  $\delta D$  record. As such  $\delta D$  values of these compounds more  
691 faithfully recorded the long-term late Holocene hydroclimatic trend to cooler  
692 and wetter conditions. Nevertheless, while less susceptible to changes than  
693 species-poor assemblages, major environmental perturbances such as  
694 human impact on vegetation, wildfires, etc, can significantly affect diverse and  
695 species-rich plant assemblages to the extent that  $n$ -alkane records (and their  
696 stable isotope records) can be affected.





697

698 **Fig. 4:** Aquatic and terrestrial plant derived sedimentary *n*-alkane δD record  
 699 combined with reconstructed vegetation distribution. Vegetation data shown  
 700 as moving average over 3 data points. **(A)** Aquatic plant derived *n*-alkane δD  
 701 records (*n*C<sub>21</sub>, *n*C<sub>23</sub>) vs. vegetation population of aquatic and swamp taxa. **(B)**  
 702 Terrestrial plant (tree) derived *n*-alkane δD records (*n*C<sub>27</sub>, *n*C<sub>29</sub>) vs. tree

703 population. **(C)** Terrestrial plant (herbs) derived *n*-alkane  $\delta D$  record ( $nC_{31}$ ) vs.  
704 herb population.

705

## 706 **7. Conclusions**

707 Our combined high-resolution hydroclimate and vegetation study based on  
708 lipid biomarker  $\delta D$  and palynological records from lake MFM provides detailed  
709 insights into the succession of climate and ecosystem change and  
710 emphasizes the advantages of a multiproxy approach for hydroclimate  
711 reconstructions during periods of ecological change. Specifically, our results  
712 indicate that:

713 (1) Between 3200 and 2000 varve years BP decreasing lipid biomarker  $\delta D$   
714 values reflect the overall late Holocene trend to cooler and/ or wetter  
715 conditions.

716 (2) Since lipid biomarker  $\delta D$  values remain more negative after the HCO,  
717 we suggest that this period does not only constitute a temporal climatic  
718 oscillation triggered by a grand solar minimum, but marks a transition  
719 phase resulting in the permanent establishment of cooler and wetter  
720 conditions and/or different atmospheric moisture pathways.

721 (3) Our data show that the local aquatic ecosystem composition did  
722 change significantly at 2640 varve years BP, ca. 60 years after the  
723 onset of changes in the terrestrial ecosystem. This is possibly induced  
724 by increased nutrient input due to enhanced soil erosion, which in turn  
725 was related to a decrease in vegetation caused by forest clearance.

726 (4) We argue that changes in the source organisms of aquatic *n*-alkanes  
727 (possibly associated with different degrees of biosynthetic hydrogen  
728 isotope fractionation) at the time of major (aquatic) ecosystem change  
729 caused significant changes in  $\delta D_{aq}$  values. Therefore, the appearance  
730 and/or disappearance of a single species can result in significant  
731 variations in sedimentary  $\delta D_{aq}$ , in particular for lake systems with a  
732 limited number of aquatic *n*-alkane source organisms. However, while  
733 *n*-alkane spectra of species-poor assemblages might be more  
734 susceptible to taxonomic turnover, even changes in species-rich

735 assemblages could significantly affect the *n*-alkane record. As such,  
736 changes in the aquatic lipid biomarker  $\delta D$  values during the study  
737 period do not only reflect hydroclimate changes but also reflect  
738 ecological change, in our case amplifying the climatic signal.

739 (5) In contrast, terrestrial higher plant derived leaf wax *n*-alkanes,  
740 produced by a number of different broadleaved tree species and  
741 derived from thousands of individual trees in the lake catchment, record  
742 an integrated signal of the terrestrial vegetation and, therefore a more  
743 reliable hydroclimate record.

744 Our data suggest the importance to consider the different integrative  
745 capacities of source specific vs. less specific lipid biomarkers and show that  
746 the combination with microfossil records can provide detailed insights into the  
747 succession of climatic and ecosystem changes in the lake catchment.

748

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750

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757

#### 758 **Author contributions**

759 O. Rach carried out the *n*-alkane extraction, analysis, stable isotope  
760 measurement, isotope data evaluation and wrote the paper. S. Engels and B.  
761 van Geel carried out the pollen analysis, pollen data evaluation and wrote the  
762 paper. A. Kahmen provided infrastructure for isotope measurement,  
763 contributed to the analysis, data evaluation and writing. A. Brauer was  
764 responsible for lake coring, data evaluation and writing. C. Martín-Puertas  
765 provided the chronology and stratigraphy, contributed to data evaluation and

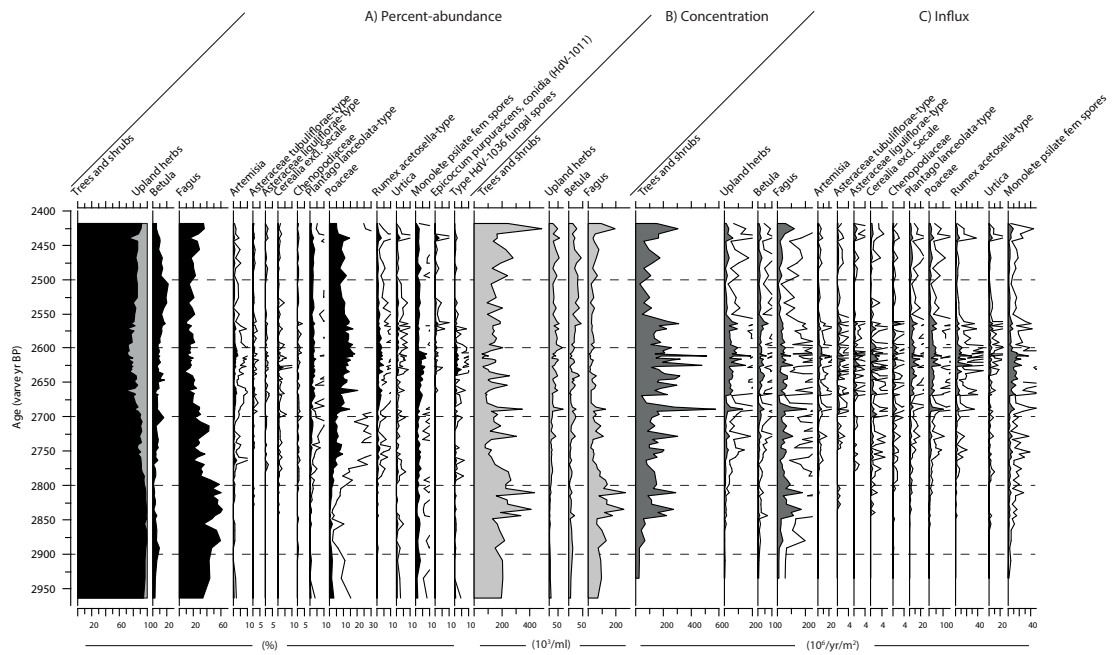
766 wrote the paper. Dirk Sachse conceived the research, acquired financial  
767 support and wrote the paper.

768

769 **Supplementary information**

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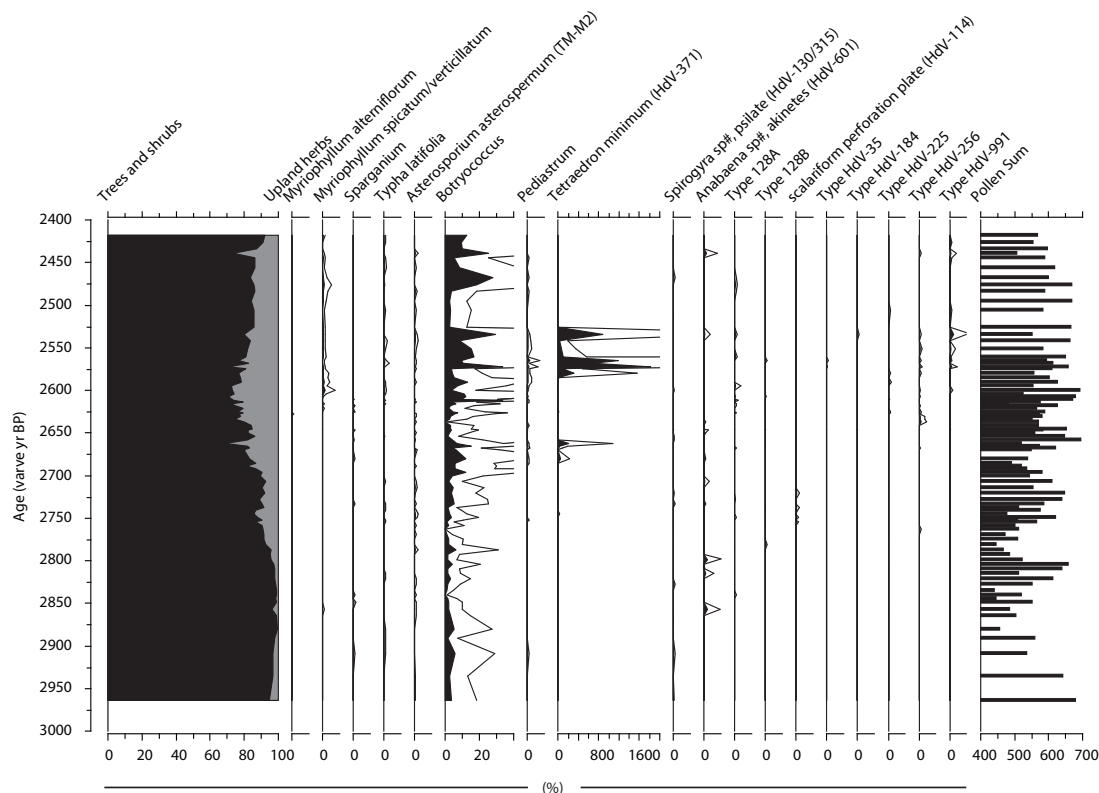
772

773 **Fig. S1:** Overview diagram on arboreal taxa (in percent - left, concentration –  
774 middle, influx - right)

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779 **Fig. S2:** Overview diagram on aquatic taxa (right part) and trees/ shrubs vs.  
 780 herbaceous taxa distribution (left) in percent

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782 **References**

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