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1 **The paleolimnologist's guide to compound-specific stable isotope analysis – an**  
2 **introduction to principles and applications of CSIA for Quaternary lake sediments**

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32 **ABSTRACT**

33 The stable isotope composition of key chemical elements for life on Earth (e.g., carbon,  
34 hydrogen, nitrogen, oxygen, sulfur) tracks changes in fluxes and turnover of these elements

35 in the biogeosphere. Over the past 15 to 20 years, the potential to measure these isotopic  
36 compositions for individual, source-specific organic molecules (biomarkers) and to link them  
37 to a range of environmental conditions and processes has been unlocked and amplified by  
38 increasingly sensitive, affordable and wide-spread analytical technology. Paleoenvironmental  
39 research has seen enormous step-changes in our understanding of past ecosystem  
40 dynamics. Vital to these paradigm shifts is the need for well-constrained modern and recent  
41 analogues. Through increased understanding of these environments and their biological  
42 pathways we can successfully unravel past climatic changes and associated ecosystem  
43 adaption.

44 With this review, we aim to introduce scientists working in the field of Quaternary  
45 paleolimnology to the tools that compound-specific isotope analysis (CSIA) provides for the  
46 gain of information on biogeochemical conditions in ancient environments. We provide  
47 information on fundamental principles and applications of novel and established CSIA  
48 applications based on the carbon, hydrogen, nitrogen, oxygen and sulfur isotopic composition  
49 of biomarkers. While biosynthesis, sources and associated isotope fractionation patterns of  
50 compounds such as *n*-alkanes are relatively well-constrained, new applications emerge from  
51 the increasing use of functionalized alkyl lipids, steroids, hopanoids, isoprenoids, GDGTs,  
52 pigments or cellulose. Biosynthesis and fractionation are not always fully understood.  
53 However, although analytical challenges remain, the future potential of deeper insights into  
54 ecosystem dynamics from the study of these compounds is also emerging.

55 **KEYWORDS:** stable isotopes, global, paleoclimatology

## 56 **1 INTRODUCTION**

57 The key elements that form organic matter on Earth, carbon, hydrogen, oxygen and nitrogen,  
58 occur in the form of two (C, H, N) or three (O) stable isotopes as determined by the number of  
59 neutrons in their nuclei, with the lighter isotope dominating. Each chemical reaction during the  
60 formation of organic matter and each phase transition (e.g., evaporation) changes the isotope  
61 distribution of the product (organic molecule, water vapour) by discriminating against the  
62 heavier (C, H, O) or, in some cases, lighter (N) isotopes. Thus, as these elements, and others  
63 such as sulfur, pass through biogeochemical cycles, their isotopic composition in a specific  
64 molecular and environmental context carries information on where they originally came from  
65 and how they got there. The determination of stable isotope ratios in an organic molecule  
66 therefore provides a tool to investigate and understand modern-day elemental cycling, thereby  
67 aiding our ability to reconstruct the variability of past element fluxes and the associated  
68 environmental drivers (for an introduction to stable isotope geochemistry see, e.g., Galimov,

69 1985; Hoefs, 2004). On a global scale, isotope distributions of carbon, oxygen and hydrogen  
70 vary over time, depending on the amounts of carbon dioxide and water stored in the major  
71 reservoirs, ocean water, atmosphere and polar ice caps or, on geological time scales, in rocks.  
72 Over the past five decades, stable carbon and oxygen isotope data from marine carbonates  
73 and ice cores, for example, has been fundamental in improving our understanding of the  
74 biogeosphere's response to external and internal forcing and associated changes in elemental  
75 fluxes such as the transfer of carbon from the atmosphere to the ocean. More recently, isotope  
76 analysis of individual biological compounds, i.e. compound-specific isotope analysis (CSIA)  
77 has allowed geoscientists to zoom in on processes involving organic matter transformation on  
78 much smaller scales and to study element cycling within individual ecosystems, from primary  
79 producer to ultimate microbial degrader and mineralisation. The improved understanding of  
80 how certain ecosystem changes can modify the isotopic fingerprint of organic molecules in  
81 sedimentary archives has resulted in the development of CSI-based proxies that document  
82 the adaption of the biosphere to the variability of key environmental parameters such as  
83 temperature or moisture supply. Some CSI proxies in fact respond to changes in these  
84 parameters directly, such as the hydrogen and oxygen isotope composition of meteoric water  
85 that is reflected in the isotope composition of biomarkers synthesized through the uptake of  
86 water and a carbon substrate (e.g., leaf-wax lipids, cellulose; Sauer et al., 2001a; Wolfe et al.,  
87 2001, 2007; Sachse et al., 2012). Many of the concepts, methodologies and  
88 paleoenvironmental proxies have originally been developed and applied in marine research,  
89 due to the fact that the global ocean is the most extensive ecosystem on Earth, with relatively  
90 well understood ecological boundary conditions, as compared to lakes, which feature specific  
91 ecological conditions that rarely match from one lake to another. However, since analytical  
92 facilities have become more widely available and the calibration of CSI data for applications  
93 in diverse lacustrine systems more affordable, an increasing number of lacustrine  
94 paleoenvironmental research projects now include CSIA, supporting established palynological  
95 or bulk geochemical data and thereby also bridging the (still existing) gaps between the  
96 various scientific communities.

97 This review aims to introduce CSIA as a prospective and increasingly popular tool to scientists  
98 in the field of paleolimnology who are practitioners of paleolimnology rather than specialized  
99 biogeochemists, involved in interdisciplinary studies and aiming for an improved  
100 understanding of the basic principles that control the proxy data they are dealing with or might  
101 want to produce themselves. The rapid expansion of diverse applications of CSIA has  
102 produced a plethora of research outputs, including recent reviews (i.e., Castañeda and  
103 Schouten, 2011; Sessions, 2016; Diefendorf and Freimuth, 2017) that provide detailed  
104 information on either individual isotopes or specific compound classes in both marine and

105 terrestrial settings. Here we provide an encompassing overview of CSIA (C,N,H,S) from an  
106 extensive spectrum of compounds for reconstructing Quaternary environmental change  
107 specifically from limnic settings, guiding the reader towards a more focused literature base  
108 with key case studies (summarized in Table 1). We include an introduction into the  
109 biosynthesis of the relevant biomarkers since isotope fractionation during biosynthesis is a  
110 key factor with regard to the ultimate stable isotope distribution in an organic molecule, in  
111 addition to the environmental factors driving the isotopic composition of the substrates used  
112 by primary producers. The desire for an improved understanding of proxy variability and  
113 sensitivity links paleoenvironmental sciences to studies of biogeochemical processes in  
114 modern ecosystems and food webs. Some of the CSI applications introduced here, for  
115 example, those using amino acids, pigment or sulfur-containing compounds, still are at the  
116 stage of development where further study of modern biogeochemical processes alongside  
117 pioneering paleoenvironmental research and methodological advances will help to develop  
118 their full potential, which also means that there are merits still to be gained. We thus hope our  
119 approach will help investigators new to the field to understand the relevance and power of  
120 isotope-based proxies and potentially inspires new ventures into one of the most dynamic  
121 realms of paleoenvironmental sciences.

122 In the following, we first provide an overview of the fundamental principles of isotope  
123 fractionation in biogeochemical cycles, followed by sections that introduce and discuss  
124 specific compound classes for which environmental proxies are well established (e.g., alkyl  
125 lipids) and less well-known compound classes or individual compounds (e.g., cellulose), with  
126 information on their various sources and CSIA applications. Although bulk elemental isotope  
127 analyses ( $\delta^{13}\text{C}$ ,  $\delta^{15}\text{N}$ ) provide useful paleoenvironmental information, particularly in  
128 combination with compound-specific isotopes, we will not review this area as it is well covered  
129 by other recent contributions (e.g., Sessions, 2016; Diefendorf and Freimuth, 2017).

## 130 **2 STABLE ISOTOPE DISTRIBUTION, FRACTIONATION AND ANALYSIS**

### 131 **2.1 Isotopes in the biogeosphere**

132 Photosynthetic and chemoautotrophic primary producers form the ultimate base of aquatic  
133 and terrestrial food chains, transforming molecular or elemental inorganic substrates (e.g.,  
134  $\text{CO}_2$ ,  $\text{CH}_4$ ,  $\text{NH}_3$ ,  $\text{H}_2$ ) and water into biomass. Biochemically speaking, life on Earth is essentially  
135 composed of carbon, hydrogen, oxygen, nitrogen and phosphorous, with a bulk stoichiometry,  
136 e.g., of the most important autotrophic producers of biomass, marine algae, of  
137  $\text{C}_{106}\text{H}_{263}\text{O}_{110}\text{N}_{16}\text{P}$  (Redfield, 1958). Each autotrophic organism taps into specific reservoirs of  
138 the elements required in which the heavier stable isotopes, i.e.  $^{13}\text{C}$ ,  $^2\text{H}$ ,  $^{18}\text{O}$ ,  $^{15}\text{N}$ , are present  
139 in specific proportions. These proportions vary for each reservoir, depending on physical  
140 conditions and variable exchange with other reservoirs (e.g., proportions of  $\text{CO}_2$  with heavy

141 carbon and/or oxygen atoms in the atmosphere or the ocean vary across glacial-interglacial  
142 cycles, depending on temperature and evaporation rates; e.g., Hayes et al., 1999). Once a  
143 substrate has been taken up by an organism it will be fully or partially incorporated into organic  
144 molecules by enzymes. Enzymatic activity discriminates against the heavier (C, H, O) or, in  
145 case of nitrogen, lighter isotopes of reactants, leading to a different relative abundance of the  
146 light and heavy isotopes of the product, i.e. the isotope fractionation factor  $\epsilon$  (Hayes et al.,  
147 1989; Popp et al., 1989), discussed in more detail below. Hydrogen and nitrogen are also  
148 frequently exchanged between the compound that is biosynthesized and the operating  
149 enzyme. For example, during the biosynthesis of major lipid compound classes in a  
150 photosynthetic organism, enzymatic reactions involving nicotinamide adenine dinucleotide  
151 phosphate (NADPH) lead to repeated addition of isotopically light hydrogen (i.e.  $^1\text{H}$  rather than  
152  $^2\text{H}$ ) to the synthesized lipid (e.g., Smith and Epstein 1970; Luo et al., 1991; see also Fig. 1).

153 Thus, the isotope composition of an element in biomass from primary production reflects the  
154 specific isotope composition of the reservoir and substrate and, through the fractionation factor  
155 between original substrate and synthesized biomass, the level and pathway of metabolic  
156 processing. Heterotrophic organisms consuming biomass of a certain isotope composition will  
157 again increase the fractionation factor to a certain extent when incorporating organic  
158 compounds into their own body tissue, either directly (little fractionation) or through further  
159 metabolic processing (additional fractionation; see, e.g., DeNiro and Epstein, 1978; Peterson  
160 and Fry, 1987).

161 Reactions between reduced inorganic sulfur and organic compounds in sediments are  
162 considered to be important for organic matter preservation. The fractionation of sulfur is a  
163 useful tracer of sulfurization reactions post-deposition, which often occur in the presence of  
164 strong pore water isotopic gradients, typically driven by microbial sulfate reduction, active  
165 during deposition and sedimentation (Habicht and Canfield, 1997; Kraal et al., 2013). Prior  
166 studies have looked at bulk sedimentary OM to understand fractionation as a function of  
167 sulfidization reactions between authigenic sulfide, and residual organosulfur compounds  
168 (Amrani and Aizenshtat, 2004; Riedinger et al., 2017; Pärn et al., 2018). However, enhanced  
169 ability to measure compound-specific sulfur isotopic compositions of volatile organosulfur  
170 compounds, co-eval pore water, sulfides forming, and the residual organic matter has greatly  
171 enabled our ability to understand the processes that govern sulfur cycling and diagenetic  
172 processes in both modern and ancient sediments.

## 173 **2.2 Compound-specific isotope analysis (CSIA)**

174 Compound-specific isotope analysis (CSIA) provides the opportunity to trace the basic  
175 elements (C, H, N, S) through primary biosynthetic processes, food web dynamics and

176 heterotrophic microbial degradation to burial in the sedimentary archive (Matthews and Hayes,  
177 1978). Quantifying these elemental fluxes underpins reconstructions of environmental  
178 dynamics and is key to the field of paleoenvironmental science. In recent years, applications  
179 of CSIA proxies to paleoenvironmental studies have gained increasing traction as our  
180 understanding of the biological and physical/chemical controls of isotopic fractionation  
181 improves (e.g., through studies of isotope fractionation in modern systems and mesocosm  
182 experiments). At the same time, analytical facilities are becoming more sensitive, automated  
183 and economical and therefore more widely available.

184 CSIA has now been successfully used to reconstruct changes in organic matter sources as  
185 well as to record the response of organisms to changes in temperature and moisture supply,  
186 air mass handling, shifts in food webs and diets, phytoplankton community shifts, water  
187 chemistry, redox chemistry, carbon cycling, methane cycling, vegetation change, and  
188 paleohydrology (see Table 1 for references).

189 Many CSIA methods start with common lipid extraction techniques such as microwave-  
190 assisted extraction (MAE), accelerated solvent extraction (ASE), ultrasonication, or Soxhlet  
191 extraction, using a range of organic solvent combinations and in some cases an added  
192 aqueous buffer. The protocols mainly differ in the processing of the total lipid extract (TLE) in  
193 order to purify the various target compounds, which typically includes separation of polar and  
194 non-polar compounds or of aliphatic hydrocarbons, aromatic hydrocarbons and alcohols (e.g.,  
195 Sauer et al., 2001b). Individual compounds are commonly identified by gas chromatography–  
196 mass spectrometry (GC-MS) through their specific mass spectra and analysed by gas  
197 chromatography-isotope ratio mass spectrometry, with either a combustion or thermal  
198 conversion interface (GC-C-IRMS, GC-TC-IRMS; Hayes et al., 1989; Freeman et al., 1990;  
199 Hilkert et al., 1999), and by high-performance liquid chromatography-isotope ratio mass  
200 spectrometry (LC-IRMS; Boschker et al., 2008) to determine their isotopic composition. The  
201 latter is expressed as the divergence of the ratio of the heavier isotope over the lighter isotope  
202 from the equivalent ratio in a standardised reference material ( $\delta$ -annotation) as shown for  
203 carbon below (Eq. 1):

$$204 \quad \delta^{13}\text{C} = \left( \frac{(^{13}\text{C}/^{12}\text{C})_{\text{sample}}}{(^{13}\text{C}/^{12}\text{C})_{\text{standard}}} - 1 \right) * 1000 \quad \text{Equation 1}$$

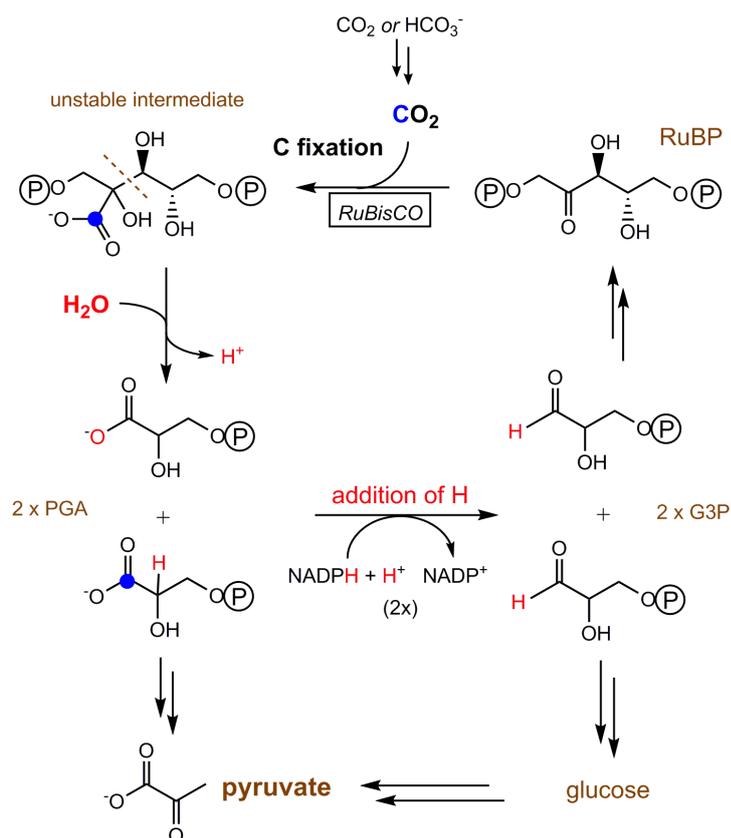
205 The international reference standards are Vienna Peedee Belemnite (VPDB) for  $^{13}\text{C}$ , Vienna  
206 Standard Mean Ocean Water (SMOW) for  $^2\text{H}$ , atmospheric  $\text{N}_2$  (AIR) for  $^{15}\text{N}$  and Vienna  
207 Canyon Diablo Troilite (V-CDT) for  $^{34}\text{S}$ . A comprehensive compilation of CSIA methodologies,  
208 including details on instrumentation, has been published by Jochmann and Schmidt (2011).

209 **2.3 Isotopic fractionation: from substrate to compound**

210 The basics of isotope fractionation apply to organic compounds biosynthesised by organisms  
211 across the phylogenetic tree in virtually every aquatic and terrestrial environment. Responsible  
212 for the variable isotopic composition of organic molecules is biochemical processing during  
213 biosynthesis, which discriminates against the heavier carbon, hydrogen and oxygen isotopes  
214 and lighter nitrogen isotope and results in the more processed molecules being isotopically  
215 lighter (i.e. depleted in  $^{13}\text{C}$ ,  $^2\text{H}$ ,  $^{18}\text{O}$ ) or heavier (enriched in  $^{15}\text{N}$ ) compared to less processed  
216 molecules. An example for such a process is enzymatic carbon chain elongation, which leads  
217 to long-chain *n*-alkyl compounds produced by higher plants being depleted in the heavy  
218 carbon and hydrogen isotopes compared to short-chain *n*-alkyl compounds, even within the  
219 same plant (Diefendorf and Freimuth, 2017, and references therein). Typically, plants are  
220 responsible for a fractionation factor ( $\epsilon$ ) of -10 to -30 ‰ for carbon and -100 to -170 ‰ for  
221 hydrogen between substrate and *n*-alkyl compounds (Collister et al. 1994; Chikaraishi et al.,  
222 2004; Hou et al., 2007; Sachse et al., 2012; Sessions, 2016). An exception to the general  
223 depletion of the heavy isotope in products of enzymatically controlled reactions has been  
224 observed in some microbes, with inverse hydrogen isotope fractionation, i.e. enrichment of  $^2\text{H}$ ,  
225 widely occurring in lipids of aerobic heterotrophs (Zhang et al., 2009; Osburn et al., 2016;  
226 Kümmel et al., 2016).

227 Prior to fractionation during biosynthesis, however, it is the isotopic composition of the  
228 substrates providing the key elements for primary production, e.g.,  $\text{CO}_2$ ,  $\text{HCO}_3^-$ ,  $\text{H}_2\text{O}$  and  $\text{NO}_3^-$   
229 for photoautotrophs, that determines the baseline isotopic composition of an organic  
230 compound, and this is where information on paleoenvironmental conditions can be gained.

231 Atmospheric  $\text{CO}_2$  is taken up by the vast majority of primary producers through photosynthetic  
232 carbon fixation, a process that strongly fractionates against  $^{13}\text{C}$  (e.g. Körner et al., 1991;  
233 Diefendorf and Freimuth, 2017). For land plants, water availability is one of the parameters  
234 that significantly influences fractionation rates during carbon fixation as it exerts a strong  
235 control on plant stomatal conductance, which in turn influences biosynthetic fractionation  
236 during photosynthesis. Variability of  $\delta^{13}\text{C}$  values of compounds from higher plants is likely to  
237 represent water availability, at least qualitatively, when  $\delta^{13}\text{C}$  values are determined for time  
238 intervals when vegetation changes were minimal and where no major shifts in atmospheric  
239  $\text{CO}_2$  took place (Diefendorf and Freimuth, 2017). Interpreting changes in *n*-alkane  $\delta^{13}\text{C}$  values  
240 as precipitation indicators has been established as a paleoclimatic tool in certain settings (see  
241 Kohn, 2010 and references therein).

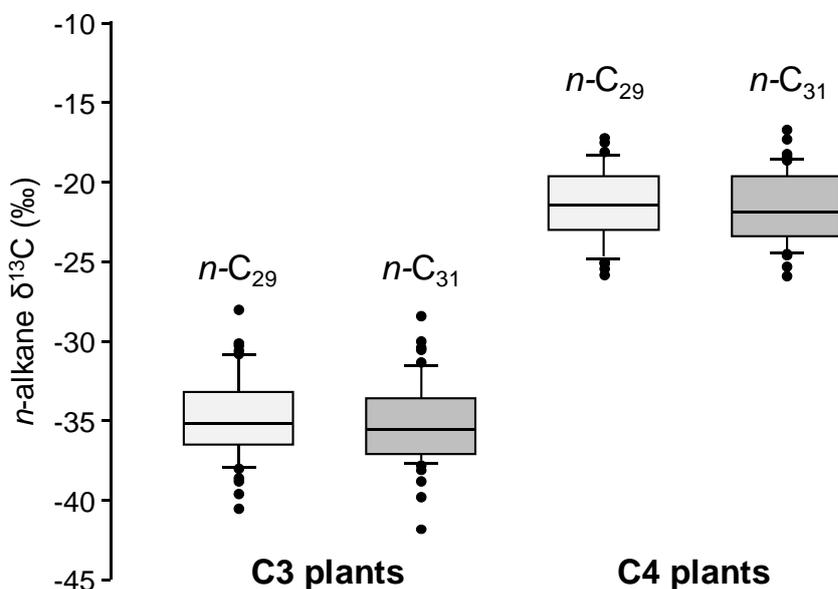


242

243 **Figure 1:** Fixation of carbon dioxide through the Calvin cycle during photosynthesis and  
 244 biosynthesis of pyruvate, the starting material for the biosynthesis of many of the compounds  
 245 discussed in this review (after Calvin and Benson, 1948; Sachse et al., 2012; Berg et al.,  
 246 2015). CO<sub>2</sub> and meteoric water are taken up by the photosynthesizing organism for  
 247 carboxylation and hydrolysis of Ribulose 1,5-bisphosphate (RuBP). This process produces two  
 248 molecules of 3-phosphoglycerate (PGA) and discriminates against the heavy isotopes (blue  
 249 dot: added carbon from CO<sub>2</sub>; added hydrogen atoms in red). PGA can be turned into pyruvate  
 250 either through a 10-step mechanism (not shown) or via the biosynthesis of simple sugars such  
 251 as glucose (shown on the right), the first step of which is the formation of glyceraldehyde-3-  
 252 phosphate (G3P). Five out of six G3P molecules produced from three initial RuBP molecules  
 253 are needed to recover three RuBP molecules while one G3P molecule can be used for the  
 254 formation of glucose. Thus, six CO<sub>2</sub> molecules are taken up for the formation of one sugar  
 255 molecule.

256 Most plants fix carbon directly through the Calvin cycle of photosynthesis (Fig. 1), requiring  
 257 stomatal gas exchange with the atmosphere for CO<sub>2</sub> uptake in the process, i.e. during daytime.  
 258 As the first metabolic product contains three carbon atoms (3-phosphoglycerate) these plants  
 259 are called C<sub>3</sub> plants. Under arid conditions, however, some plants fix CO<sub>2</sub> temporarily through  
 260 the Hatch-Slack pathway by forming oxaloacetate, a molecule containing four carbon atoms,  
 261 before shifting it into bundle sheath cells where the CO<sub>2</sub> is released to facilitate the Calvin

262 cycle (for details see Berg et al., 2015). This allows the plants to shift stomatal gas exchange  
 263 for CO<sub>2</sub> uptake into the night and, thus, minimise water loss. Again, with reference to the first  
 264 metabolic product, plants following this strategy are called C4 plants. They mainly represent  
 265 tropical grasses, including maize, for example. Importantly, the C4 metabolic adaption  
 266 discriminates less strongly against <sup>13</sup>C, leading to a difference in fractionation ( $\Delta^{13}\text{C}$ ) between  
 267 terrestrial C3 and C4 plants that is significantly greater than 10 ‰, with bulk  $\delta^{13}\text{C}$  values of C3  
 268 plants ranging from -22 to -37 ‰ (average of -27 ‰) and of C4 plants from -9 to -15 ‰ (average  
 269 of -12 ‰; O’Leary, 1988; Kohn, 2010). Therefore,  $\delta^{13}\text{C}$  values of bulk organic matter and  
 270 individual terrestrial lipids such as leaf wax-derived long-chain *n*-alkyl compounds (see Fig. 2  
 271 for *n*-alkane  $\delta^{13}\text{C}$ ) can generally be used to reconstruct spatiotemporal changes in C3 and C4  
 272 vegetation, in particular, the relative abundance of tree and shrub-dominated vegetation  
 273 compared to grasslands (e.g., Huang et al., 2001; Castañeda et al., 2007; Sinninghe Damsté  
 274 et al., 2011a; Magill et al., 2013; Freeman and Pancost, 2014; Garcin et al., 2014; Johnson et  
 275 al., 2016). However, apart from the above-mentioned modifying influence of water availability,  
 276 interspecies differences in isotope fractionation and leaf wax production associated with  
 277 changes in the plant community will also have to be considered, alongside past variations in  
 278 the  $\delta^{13}\text{C}$  value of atmospheric CO<sub>2</sub> (Garcin et al., 2014; Diefendorf and Freimuth, 2017).



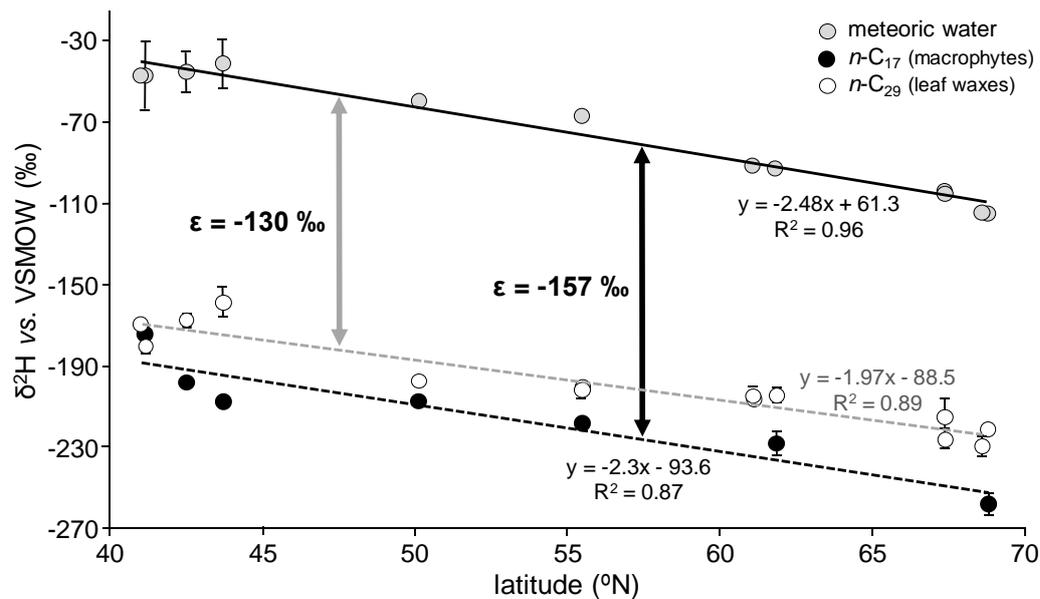
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280 **Figure 2:** Box and whisker diagram of CSI data of plant-wax derived C<sub>29</sub> and C<sub>31</sub> *n*-alkanes of  
 281 C3 and C4 plants illustrating their potential for reconstructions of vegetation changes in tropical  
 282 settings (modified from Castañeda and Schouten, 2011, data from Castañeda et al., 2009).

283 Aquatic primary producers use dissolved carbon dioxide (CO<sub>2[*aq*]</sub>) or, under CO<sub>2[*aq*]-limited  
 284 conditions, bicarbonate (HCO<sub>3</sub><sup>-</sup>) as inorganic carbon sources for photosynthesis (Lucas, 1983;  
 285 Prins and Elzenga, 1989). In freshwater lakes, CO<sub>2[*aq*]</sub> is typically not limited and derives to</sub>

286 variable extent from heterotrophic respiration in the water column or sediment and exchange  
287 with the atmosphere (Cole and Prairie, 2009). This means that freshwater photoautotrophs,  
288 which are C3 plants, and terrestrial C3 plants partly use the same inorganic carbon substrate,  
289 resulting in bulk organic carbon isotope ratios (bulk  $\delta^{13}\text{C}_{\text{org}}$ ) of freshwater algae that are  
290 indistinguishable from those of terrestrial C3 plants (Meyers and Teranes, 2001; Lamb et al.,  
291 2006 and references therein).

292 The primary source of hydrogen for biosynthesis in photosynthetic organisms is environmental  
293 water, and the major determinant of the  $\delta^2\text{H}$  value of lipids is the  $\delta^2\text{H}$  value of the source water  
294 used by the organism (Yapp and Epstein, 1982; Sternberg, 1988; Sessions et al., 1999;  
295 Sachse et al., 2012; Rach et al., 2017). Water vapour contained by a specific air mass  
296 becomes isotopically depleted in  $^2\text{H}$  as more water precipitates, i.e. with distance from the  
297 evaporation centre as well as with cooling and increasing altitude (Craig, 1961; Darling et al.,  
298 2005). The basic application of  $\delta^2\text{H}$  values in environmental archives is, therefore,  
299 paleohydrology, i.e. the reconstructions of changes in the moisture content of the air mass  
300 delivering precipitation or an altogether change in the trajectory and source of the air mass  
301 (air mass tracking). Higher plants take up meteoric water (through soil water; Sachse et al.,  
302 2012), and evaporation processes during plant respiration (e.g., loss of leaf water)  
303 subsequently modify the isotopic composition of the water before it is used in biosynthetic  
304 reactions (e.g. Kahmen et al., 2013a, 2013b; Rach et al., 2017).  $\delta^2\text{H}$  values derived from lipids  
305 of terrestrial plants will therefore reflect a combined precipitation and evapotranspiration signal  
306 (Sachse et al., 2004, 2012). By contrast, submerged aquatic macrophytes and algae use water  
307 from the surrounding water column as their hydrogen source. This means that, e.g., in a lake  
308 system with no significant fluvial inflow of water from distant areas, the  $\delta^2\text{H}$  values of lipids  
309 from submerged macrophytes and algae will mainly reflect the average  $\delta^2\text{H}$  value of local  
310 precipitation (Sachse et al., 2004; Fig. 3), unless it is modified by elevated lake water  
311 evaporation rates under more arid climate regimes. In this case, the difference between the  
312  $\delta^2\text{H}$  values of macrophyte-derived mid-chain and terrestrial long-chain *n*-alkanes ( $\Delta^2\text{H}$ ) can  
313 potentially be used to assess changes in lake water evaporation (Mügler et al., 2008; Aichner  
314 et al., 2010a) although this approach still needs further testing (Aichner et al., 2010a; Rao et  
315 al., 2014). Nevertheless, many studies have illustrated the generally strong relationship  
316 between modern-day climate and  $\delta^2\text{H}$  in lipids in settings with pronounced hydrological  
317 gradients (e.g., Huang et al., 2004; Sachse et al., 2004; Nieto-Moreno et al., 2016).



318

319 **Figure 3:** Correlation between the  $\delta^2\text{H}$  values of lake water from a European N-S transect and  
 320 the  $\delta^2\text{H}$  values of the  $\text{C}_{17}$  and  $\text{C}_{29}$   $n$ -alkanes from macrophytes and terrestrial plants in the  
 321 catchments, illustrating the close control of lake water isotopic composition on leaf wax  $\delta^2\text{H}$   
 322 values (modified from Sachse et al., 2004).

323 The main nitrogen substrates for eukaryotic algae are nitrate ( $\text{NO}_3^-$ ) and ammonium ( $\text{NH}_4^+$ ),  
 324 while prokaryotic cyanobacteria can directly fix dissolved nitrogen ( $\text{N}_{2(\text{aq})}$ ; Harvey, 1940, 1953;  
 325 Stal, 2015; Glibert et al., 2016). There is little to no fractionation involved in biological nitrogen  
 326 fixation (Hoering and Ford, 1960; Minagawa and Wada, 1984), allowing phytoplankton  
 327 communities dominated by cyanobacteria to be differentiated from eukaryote-dominated  
 328 communities. As  $\text{N}_2$  can be fixed in both terrestrial and aquatic environments, nitrogen from  
 329 both of these sources contribute to the lacustrine nitrogen cycle. Isotopic fractionation can  
 330 occur during many of the transformations nitrogen undergoes, including  $\text{N}_2$  dissolution,  
 331 nitrification and denitrification, nitrate and ammonium assimilation, and ammonia volatilisation  
 332 (Collister and Hayes, 1991; Talbot, 2001). Thus, the absolute  $\delta^{15}\text{N}$  value of the substrates  
 333 provides limited environmental information compared to the absolute  $\delta^{13}\text{C}$  and  $\delta^2\text{H}$  values of  
 334 atmospheric and dissolved  $\text{CO}_2$  and meteoric water, respectively. Instead, information on  
 335 environmental change may be gained from the difference in the isotope values of source  
 336 amino acids, retaining the isotope composition of the initial substrate, and trophic amino acids,  
 337 determined by fractionation along each trophic step, with implications for changes in the  
 338 lacustrine food web structure (see Section 3.2 for details).

339 The transfer of sulfur between different reservoirs typically involves a change in the oxidation  
 340 state, which is mediated either through abiologically or biologically induced processes  
 341 (Strauss, 1997; Farquhar et al., 2000). The main source of sulfur in sediments is derived from

342 sulfate in the overlying water column or pore waters via downward diffusion in the sediments.  
343 Typically, sulfate is reduced to sulfide by bacterial sulfate reduction (BSR), active just below  
344 the sediment-water interface, leading to sedimentary sulfide typically depleted with respect to  
345  $^{34}\text{S}$  (e.g., Jørgensen, 1978; Habicht et al., 1998). Isotopic fractionation between sulfate in the  
346 water, sulfide, and organic sulfur compounds is fundamentally a function of the availability of  
347 sulfate to be reduced and the efficiency of the bacterium present (i.e. large amounts of easily  
348 metabolizable organic matter aids the sulfate reduction process; e.g. Kaplan et al., 1963;  
349 Canfield and Thamdrup, 1994; Habicht and Canfield, 1997). Favourable conditions for BSR  
350 and an open source of sulfate can result in large isotopic fractionation between sulfate and  
351 the sulfide product. In the context of restricted settings, such as lakes, sulfate is not readily  
352 replenished and may undergo seasonal variation resulting in variations in the range of isotopic  
353 fractionation of the sulfate and the product sulfide (i.e. Urban et al., 1999; Zerkle et al., 2010;  
354 Oduro et al., 2013, discussed later). Furthermore, the bio-mediated uptake of sulfur into  
355 organosulfur compounds in organic matter leads to variable enrichment of  $^{34}\text{S}$  with respect to  
356 sulfide phases formed, as well as variability of  $^{34}\text{S}$  across different organic sulfur compounds  
357 present (Andreae, 1990; Kharasch, 2013). Typically, studies have focussed on the isotopic  
358 variation between original sulfate, the sulfide and bulk organic matter. Utilisation of compound-  
359 specific analysis in the examples discussed here is able to better deduce the physical and  
360 biochemical processes that lead to sulfur fractionation in sediments.

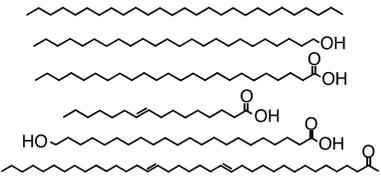
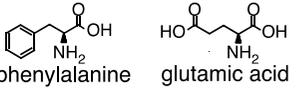
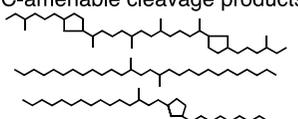
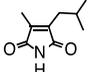
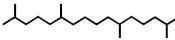
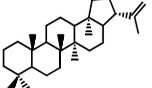
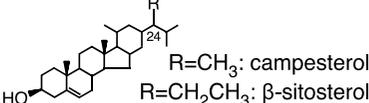
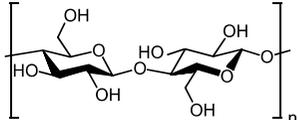
361 The basic physiological and substrate-related drivers of isotopic fractionation in primary  
362 producers during diagenesis are thus relatively well constrained. However, as illustrated by  
363 many examples in the remaining sections of this review, a range of environmental and source-  
364 specific factors such as temperature, seasonality and salinity or vegetation change and  
365 associated changes in evapotranspiration can further modify the isotopic composition of  
366 organic compounds. These need to be understood in order to improve the interpretation of  
367 CSI data variability in environmental archives. On the other hand, new proxies can be  
368 developed that target additional and more specific aspects of ecosystem change, once such  
369 causal relationships are established, and it is this improved understanding of isotope  
370 fractionation in modern biogeochemical cycles that brings to light the potential of CSIA in future  
371 paleoenvironmental studies. The compounds most frequently studied for their CSI values in  
372 paleoenvironmental research are alkyl lipids. Therefore, these compounds also provide many  
373 examples of the complex relationship between environmental factors, diverse sources and  
374 compound-specific carbon and hydrogen isotope ratios, some of which are presented in the  
375 following. A more comprehensive introduction to alkyl lipid CSI applications is provided in  
376 Section 3.1.

377 The  $\delta^{13}\text{C}$  values of alkyl lipids are susceptible to more specific and often local factors. Eley et

378 al. (2016) demonstrate that *n*-alkane  $\delta^{13}\text{C}$  values of C3 and C4 plants from a temperate  
379 saltmarsh show a significant variability of  $\delta^{13}\text{C}$  values, with differences between C3 species of  
380 up to 10 ‰ and pronounced intra-species differences across the growing season. In a tropical  
381 wetland setting, Yamoah et al. (2016) observe large-scale variability in *n*-alkane  $\delta^{13}\text{C}$  values,  
382 with long-chain compounds becoming isotopically enriched during drier periods. The authors  
383 attribute this finding to a shift in the main substrate from dissolved  $\text{CO}_2$  to isotopically heavier  
384 bicarbonate rather than changes in the overlying vegetation and enhanced C4 plant input.  
385 Significant differences in the  $\delta^{13}\text{C}$  value between mid- and long-chain compounds have been  
386 reported, with the reason behind the offset remaining elusive. An apparently climatically  
387 controlled systematic offset of up to 6 ‰ between suberin-derived  $\text{C}_{22}$  *n*-fatty acid and leaf  
388 wax-derived long-chain fatty acids in Late Quaternary lake sediments (see supplement to  
389 Holtvoeth et al., 2017) could either point to an age-offset between lipids from leaf litter and  
390 soils (root material) or to differences in  $\text{CO}_2$  uptake by plants for the formation of leaf and root  
391 tissue under variable climatic regimes and different rates of microbial respiration in the soil.  
392  $\text{C}_{22}$   $\omega$ -hydroxy acid found in Miocene lake sediments is reported to be depleted by 4-5 ‰  
393 relative to the long-chain  $\omega$ -hydroxy acids (Huang et al., 1996). In this case, the authors  
394 hypothesised this compound to derive from anoxic bacterial biomass. The examples above  
395 illustrate the need for an improved understanding of carbon isotope fractionation in natural  
396 systems. A detailed review of environmental factors that can influence the  $\delta^{13}\text{C}$  values of fatty  
397 acids has recently been published by Reiffarth et al. (2016).

398 The range of factors that can further modify the  $\delta^2\text{H}$  values of alkyl lipids is even more complex.  
399 Additional environmental and physiological variables such as secondary hydrogen exchange  
400 reactions and effects of algal growth rates or metabolic differences can influence the isotopic  
401 fractionation between hydrogen in environmental water in aquatic and terrestrial lipids (see  
402 review by Sachse et al., 2012). Extensive growth experiments have shown that C3 and C4  
403 grasses not only discriminate significantly different against  $^{13}\text{C}$  but also differ in the  $\delta^2\text{H}$  values  
404 of their *n*-alkanes by 40 ‰, on average (Gamarra et al., 2016). This could be attributed to the  
405 metabolic differences in the way NADPH is produced, i.e. in the bundle sheaths in C4 grasses  
406 rather than in the chloroplasts in C3 grasses, with the NADPH then providing the hydrogen for  
407 lipid biosynthesis (Gamarra et al., 2016). Studying the leaf wax *n*-alkane hydrogen isotope  
408 distribution of riparian trees, Oakes and Hren (2016) describe significant interspecies variation  
409 of  $\delta^2\text{H}$  values that can exceed 50 ‰ throughout the growing season. Similarly, Tipple and  
410 Pagani (2013) found differences in the correlation between precipitation and *n*-alkane  $\delta^2\text{H}$   
411 values between tree species. However, such interspecies differences appear to be averaged  
412 out in the soil as *n*-alkanes from soil samples did show a good correlation between  
413 precipitation and CSI  $\delta^2\text{H}$  values. On the other hand, short-term fluctuations in  $\delta^2\text{H}$  of the leaf

414 wax C<sub>28</sub> *n*-fatty acid reported from the sedimentary record of an Alpine lake may be due to  
415 local factors such as length of growing season, amount of snowfall or anthropogenic  
416 modification of the local vegetation (Wirth and Sessions, 2016), factors that are not always  
417 well constrained. Ladd et al. (2017) investigated the influence of growth rate and temperature  
418 on the  $\delta^2\text{H}$  value of algal lipids (fatty acids and brassicasterol) in an oligotrophic and a  
419 eutrophic lake. Although the authors found significant variability in the  $\delta^2\text{H}$  values of fatty acids  
420 throughout the growing season the average  $\delta^2\text{H}$  value of the C<sub>16</sub> *n*-fatty acid matched the  $\delta^2\text{H}$   
421 value of the lake water and was also preserved in the surface sediment. An in-depth  
422 discussion of the factors that can modify  $\delta^2\text{H}$  values of *n*-alkanes exceeds the objectives of  
423 our introduction to CSIA and we therefore refer to the very detailed recent review on this matter  
424 provided by Sessions (2016).

Compound class	Structures	Application / Indicative for...	Isotope-Proxies	Analytical Technique	Refs.
Alkyl lipids: n-alkanes, n-fatty acids, n-alcohols, unsaturated fatty acids, hydroxy acids, alkenones (structures top to bottom)		meteoric water source / air mass tracking, seasonality, evaporation rates, climate change vegetation change (C3 vs. C4 plants) compound source (terrestrial, aquatic, bacterial) potentially: salinity	$\delta^2\text{H}$ $\delta^{13}\text{C}$ $\delta^2\text{H}, \delta^{13}\text{C}$ $\delta^2\text{H}$	GC-IRMS	1 - 4 5 - 7 4 8 9
Amino acids	 phenylalanine glutamic acid	food web structure, trophic level compound source	$\delta^{15}\text{N}$ $\delta^{13}\text{C}, \delta^{15}\text{N}$	GC-IRMS	10, 11 12
Glycerol-dibiphytanyl- glycerol tetraethers (GDGTs)	GC-amenable cleavage products* 	terrestrial vs. aquatic sources (brGDGTs, iGDGTs)	$\delta^2\text{H}, \delta^{13}\text{C}$ $\delta^{13}\text{C}$	GC-IRMS SWIM-IRMS	13 - 15 16
Chlorins Maleimides	 maleimide	photic zone euxina source	$\delta^{15}\text{N}$ $\delta^{13}\text{C}$	GC-IRMS	17 18 19, 20
Isoprenoids	 crocetane	paleoenvironment autotrophy vs. heterotrophy	$\delta^2\text{H}$ $\delta^{13}\text{C}$	GC-IRMS	21 22, 23
Hopanoids	 diploptene	bacterial autotrophy vs. heterotrophy methanotrophy	$\delta^{13}\text{C}$	GC-IRMS	24 25
Steroids	 R=CH <sub>3</sub> : campesterol R=CH <sub>2</sub> CH <sub>3</sub> : $\beta$ -sitosterol	meteoric water source, hydrology change, salinity compound source (e.g., terrestrial, aquatic)	$\delta^2\text{H}$ $\delta^{13}\text{C}, \delta^2\text{H}$	GC-IRMS	26, 27 28
Sulfurised compounds	 dibenzothiophene	S cycling in active redox zones pathways of DMS formation VOCS production and release	$\delta^{34}\text{S}$	MC-ICPMS	29 30 31 32
Cellulose		source (terrestrial vs. aquatic) carbon cycling, lake-water balance	$\delta^{18}\text{O}$ $\delta^{13}\text{C}$	GC-IRMS	33 34

426 **Table 1:** Overview of compound classes, representative structures and isotope applications  
427 with key references (reviews where applicable). References are: 1. Sauer et al. (2001); 2.  
428 Nichols et al. (2009); 3. Sachse et al. (2012); 4. Sessions (2016); 5. Huang et al. (2001); 6.  
429 Sinninghe Damsté et al. (2011a); 7. Garcin et al. (2014); 8. Reiffarth et al. (2016); 9. Schouten  
430 et al. (2006); 10. Chikaraichi et al. (2009); 11. Ohkouchi et al. (2017); 12. Larsen et al. (2015);  
431 13. Wuchter et al. (2004); 14. Weijers et al. (2010); 15. Lengger et al. (2014); 16. Pearson et  
432 al. (2016); 17. Boreham et al. (1994); 18. Popp and Hayes (1978); 19. Grice et al. (1996a,  
433 1996b); 20. Wolfe et al. (2001); 21. Grice et al. (2005); 22. Koopmans et al. (1996); 23.  
434 Whiteside and Grice (2016); 24. Coolen et al. (2008); 25. Talbot et al. (2014); 26. Sauer et al.  
435 (2001); 27. Schwab and Sachs (2011); 28. Chikaraishi et al. (2005); 29. Amrani et al. (2013);  
436 30. Raven et al. (2014); 31. Oduro et al. (2013); 32. Greenwood et al. (2018); 33. Edwards  
437 and McAndrews (1989); 34. Street-Perrot et al. (2018). \*for intact molecules see Figures 9  
438 and 10.

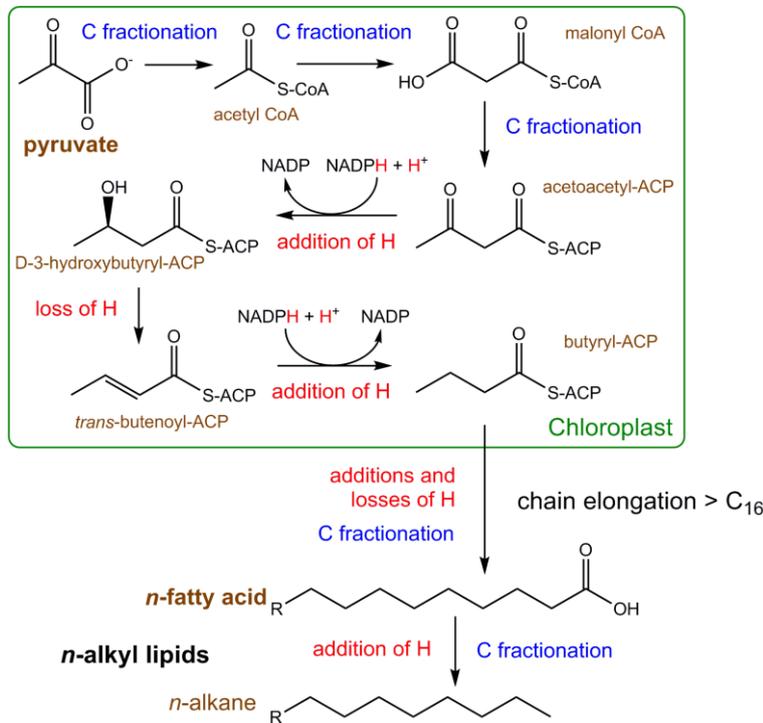
### 439 **3 SOURCES AND CSI APPLICATIONS OF BIOMARKER COMPOUND CLASSES**

#### 440 **3.1 Alkyl lipids (*n*-alkanes, *n*-fatty acids, *n*-alcohols, alkenones)**

441 Alkyl lipids of variable carbon chain lengths are ubiquitous building blocks in the formation of  
442 organic tissue. They form the hydrophobic part of cell membrane lipids in bacterial, plant and  
443 animal tissue (e.g., phospholipids, glycolipids, sphingolipids), function as storage fats  
444 (triacylglycerides, steryl esters) or contribute to protective layers such as the wax ester and  
445 cutin layers on the outer surfaces of plant cells, mainly on leaves, or suberin on the inside of  
446 plant cells, mainly in roots. This wide functional range of alkyl lipids involves different levels of  
447 biosynthetic processing, an understanding of which greatly improves the interpretation of CSI  
448 values from the various compounds found in a TLE. It also increases the range of paleo-  
449 environmental information to be gained, and we therefore briefly introduce the basics of alkyl  
450 lipid biosynthesis in the following.

451 All alkyl lipids produced by primary producers, i.e. mainly photosynthesizing organisms, are  
452 based on *de novo* biosynthesis of fatty acids and formed using environmental water and either  
453 atmospheric CO<sub>2</sub> or, in case of aquatic organisms, dissolved CO<sub>2</sub> and bicarbonate (HCO<sub>3</sub><sup>-</sup>) as  
454 sources for hydrogen and carbon, respectively. Fatty acid biosynthesis follows the acetogenic  
455 pathway, using pyruvate derived from the breakdown of sugars (e.g., glucose) to first form an  
456 acetyl molecule bound to the co-enzyme A (acetyl CoA), then combining it with malonyl CoA  
457 to form a 4-carbon unit (acetoacetyl-ACP), with the reducing agent nicotinamide adenine  
458 dinucleotide phosphate (NADPH) replacing an oxygen atom by a hydrogen atom (Fig. 4).  
459 Repeated reactions with malonyl CoA and NADPH extend the molecule by two CH<sub>2</sub> units at  
460 each step. This process typically ends with the formation of C<sub>16</sub> and C<sub>18</sub> fatty acids and results

461 in a characteristic dominance of even over odd fatty acid chain lengths in most organisms (for  
 462 further details on fatty acid biosynthesis see, e.g., Sachse et al., 2012).



463  
 464 **Figure 4:** The “acetogenic pathway” of fatty acid biosynthesis, using pyruvate produced  
 465 through the Calvin-Benson cycle after CO<sub>2</sub> uptake. Addition and loss of C or H during reactions  
 466 as well as reactions between molecules discriminate against <sup>13</sup>C and <sup>2</sup>H, i.e. fractionation  
 467 occurs at each of these steps; ACP = acetyl carrier protein, CoA = co-enzyme A, NADPH =  
 468 nicotinamide adenine dinucleotide phosphate (partial scheme modified from Sachse et al.,  
 469 2012).

470 The C<sub>16</sub> and C<sub>18</sub> n-fatty acids, also known as palmitic and stearic acid, respectively, are basic  
 471 building blocks for a vast range of molecular structures, in particular, membranes. They are  
 472 modified according to specific requirements such as membrane fluidity through further  
 473 enzymatic processing, inserting, e.g., double bonds into the carbon chain (unsaturated fatty  
 474 acids), adding alkyl branches or further functional groups (branched fatty acids, hydroxy acids)  
 475 or forming cyclopropane units (cyclopropane fatty acids). Higher plants apply further  
 476 enzymatic processing in epidermal cells to extend the chain lengths of palmitic or stearic acid  
 477 for the formation of hydrophobic epicuticular wax esters and biopolyesters such as cutin and  
 478 suberin in the protective layers of leaves and roots (Millar and Kunst, 1997). The activity of  
 479 fatty acid elongase adds two CH<sub>2</sub> units to the starting molecule (C<sub>16</sub>, C<sub>18</sub> n-fatty acid) at each  
 480 step, resulting again in the dominance of even- over odd-numbered fatty acid chain lengths in  
 481 plant biomass. n-Alcohols and n-alkanes are formed through stepwise enzymatic reduction  
 482 and decarboxylation of n-fatty acids (e.g., Coursolle et al., 2015). Because of the removal of

483 an aldehyde (-CHO) *n*-alkanes are one carbon atom shorter than the original fatty acid, leading  
484 to a strong odd over even dominance among *n*-alkanes. Several calcifying and non-calcifying  
485 marine and lacustrine haptophytes produce long-chain alkenones, with chain lengths of 37 to  
486 40 carbon atoms and 2 to 4 double bonds, using the same chain-elongating process as land  
487 plants initially, followed by desaturation steps (Rontani et al., 2006), during which first di- and  
488 then tri-unsaturated alkenones are formed (Kitamura et al., 2018) as opposed to all double  
489 bonds being formed at once.

### 490 **3.1.1 Sources**

#### 491 *3.1.1.1. n-Alkanes, n-fatty acids, n-alcohols*

492 Generally, individual *n*-alkyl lipids are not species-specific. However, as different groups of  
493 organisms produce different types of homologous series of alkyl lipids, peaking at different  
494 chain lengths, shifts in chain-length distributions observed in a sedimentary archive can point  
495 towards changes in the major lipid sources and, hence, towards ecosystem adaption to  
496 environmental change. Long-chain *n*-alkyl lipids (> C<sub>24</sub>) are almost exclusively produced by  
497 land plants as part of the cuticular wax layer that protects leaves from disease and ultraviolet  
498 light, and functions as a barrier to inhibit water loss (e.g., Eglinton and Hamilton, 1967;  
499 Volkman et al., 1998; Jetter et al., 2000; Diefendorf and Freimuth 2017 and references  
500 therein). Although lower concentrations of these compounds also occur in waxes on the  
501 surface of other parts of plants, leaf waxes are commonly assumed to be the dominant source  
502 of long-chain *n*-alkyl lipids delivered to lake sediments (e.g., Gamarra and Kahmen, 2015;  
503 Diefendorf and Freimuth, 2017). By contrast, alkyl lipids produced by bacteria and aquatic  
504 taxa are mainly membrane lipids or storage fats and are dominated by the short-chain  
505 compounds, typically by C<sub>16</sub> and C<sub>18</sub> fatty acids as well as alcohols. Storage fats frequently  
506 include unsaturated compounds with chain lengths up to 20 or 22 carbon atoms, such as the  
507 essential poly-unsaturated fatty acids eicosapentaenoic acid (EPA) and docosahexaenoic  
508 (DHA). However, these biologically highly desirable and labile compounds are usually not  
509 preserved in sedimentary records. *n*-Alkanes in aquatic algae and bacteria are dominated by  
510 the C<sub>17</sub> or C<sub>19</sub> homologues (e.g., Gelpi et al., 1970; Sachse and Sachs, 2008) while some  
511 macrophytes tend to produce a mid-chain range of *n*-alkanes (C<sub>21</sub> - C<sub>25</sub>; e.g., Ficken et al.,  
512 2000; Aichner et al., 2010b). Depending on the investigated setting, a fairly robust marker for  
513 the supply of *n*-alkanes from peat moss (*Sphagnum* spp.) is the C<sub>23</sub> *n*-alkane (see review on  
514 *n*-alkane distributions by Bush and McInerney, 2013), although root material of some sedges  
515 can be another wetland-related source (Ronkainen et al., 2013). Mid-chain alkyl compounds  
516 (C<sub>22</sub> and C<sub>24</sub> *n*-fatty acids, hydroxy acids, diacids and *n*-alcohols) characterize the alkyl fraction  
517 of suberin, an important biopolyester in root material (Molina et al., 2006, Pollard et al., 2008).  
518 They can thus indicate soil organic matter supply (Holtvoeth et al., 2016, 2017). Next to

519 differences in *n*-alkyl chain lengths between species, there are also differences in the overall  
520 amounts of plant wax that are produced by land plants. Van den Bos et al. (2018), for example,  
521 showed that the concentration of the most abundant *n*-alkane homologues in *Betula pendula*  
522 (birch) exceeded 100 µg/g dry leaf material, whereas *Quercus robur* (oak) contained  
523 concentrations of around 10 µg/g per homologue or less. Diefendorf et al. (2011) and  
524 Diefendorf and Freimuth (2017) show that conifers typically produce significantly smaller  
525 amounts of *n*-alkanes than broad-leaved species.

### 526 3.1.1.2. *n*-Alkenes

527 Occasionally, mid-chain mono-unsaturated alkenes maximising at C<sub>25</sub> and C<sub>27</sub> are preserved  
528 in lake sediments (Jaffé et al., 1996; van Bree et al., 2014). Investigating their origin, van Bree  
529 et al. (2014) found these compounds in sinking particles collected in a shallow sediment trap  
530 in Lake Challa, but they were absent in terrestrial organic matter sources in the catchment,  
531 which suggests an origin in the oxygenated water column of the lake. Analysing the carbon  
532 isotope composition of the C<sub>25:1</sub> and C<sub>27:1</sub> *n*-alkenes, van Bree et al. (2014) were able to confirm  
533 an aquatic origin for these compounds as their δ<sup>13</sup>C values were consistent with the expected  
534 range for algal biomass in Lake Challa. However, the exact source of the mid-chain *n*-alkenes  
535 still has to be identified.

### 536 3.1.1.3 Long-chain alkenones

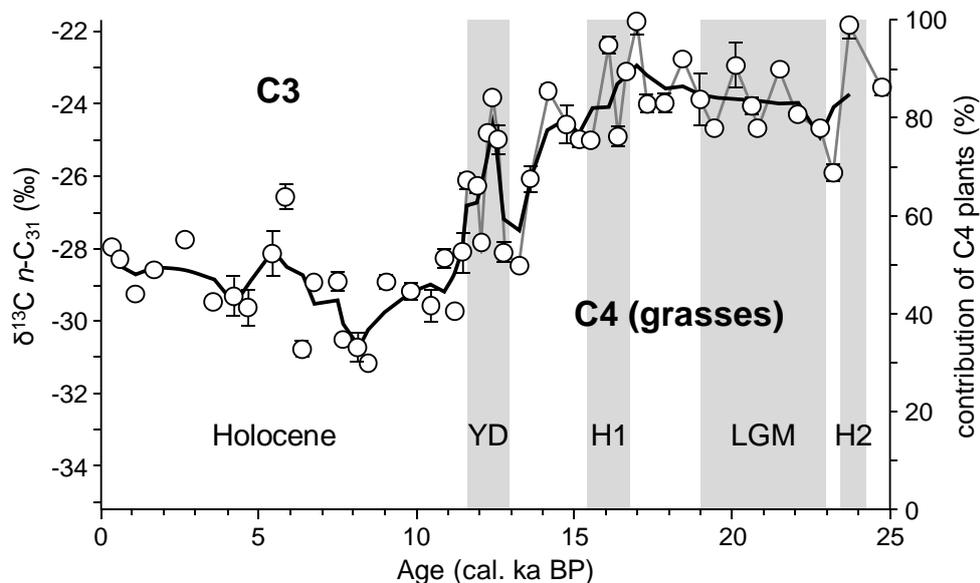
537 Long-chain alkenones are produced by several calcifying and non-calcifying haptophyte  
538 species in marine and saline lacustrine environments (Volkman et al., 1980a,b; Marlowe et  
539 al., 1984; Li et al., 1996; Thiel et al., 1997) and serve as energy storage lipids in these algae  
540 (e.g., Eltgroth et al., 2005). They have also been found in freshwater systems (Cranwell, 1985;  
541 Zink et al., 2001). However, in contrast to marine settings, the source of alkenones in lakes is  
542 generally not well defined as lacustrine haptophyte species show great biodiversity that  
543 significantly varies between lakes (Theroux et al., 2010; Toney et al., 2010). One of the non-  
544 calcifying haptophyte species found in saline lakes is *Chrysotila lamellosa* (Sun et al., 2007)  
545 while other alkenone producers appear genetically related to the coastal species *Isochrysis*  
546 *galbana* (Coolen et al., 2004a; D'Andrea et al., 2006; Theroux et al., 2010). For freshwater  
547 systems, Zink et al. (2001) speculate that also other, not yet identified non-haptophyte algae  
548 may produce alkenones. Nevertheless, alkenones can be abundant alkyl lipids in lake  
549 sediments (e.g., Zink et al., 2001; D'Andrea and Huang, 2005; Toney et al., 2011), they are  
550 relatively resistant towards diagenetic degradation (Sikes et al., 1991; Prah et al. 2000, 2003;  
551 Freitas et al., 2017) and can thus be targeted as an algal biomarker by CSIA.

### 552 3.1.2 Applications

553 First and foremost, the isotopic composition of an individual alkyl compound can identify or

554 confirm its presumed source, with the largest differences in biosynthetic isotope fractionation  
 555 ( $\epsilon$ ) separating terrestrial and aquatic plant matter sources as well as distinguishing between  
 556 C3 and C4 plants (review by Castañeda and Schouten, 2011) or pointing to methanotrophic  
 557 bacterial sources (e.g., Summons et al., 1994). Variability in the isotopic composition of a  
 558 specific compound over time typically reflects ecosystem response to a wide range of potential  
 559 environmental drivers, including changes in hydrology, seasonality, temperature, and nutrient  
 560 supply that affect species distribution and diversity. Accordingly, CSI data are ideally combined  
 561 with further proxy data to narrow down the key system drivers. For example, palynological  
 562 data may complement CSI proxy records by identifying changes in plant abundance or  
 563 diversity that reflect the adaptation of the vegetation to changes in hydrology or temperature  
 564 (e.g., Huang et al., 2006; Tierney et al., 2010).

565 Many studies applying CSIA focus on *n*-alkanes as they are easy to isolate from the TLE, do  
 566 not require further sample preparation or correction for added carbon or hydrogen during  
 567 derivatisation and their source is relatively specific, with their main source in sedimentary  
 568 archives being cuticular plant waxes. Thus, *n*-alkane CSI data interpretation can focus on a  
 569 limited number of reasonably well understood environmental drivers. For example, Sinninghe  
 570 Damsté et al. (2011a) used the  $\delta^{13}\text{C}$  values of the  $\text{C}_{31}$  *n*-alkane in sediments of Lake Challa  
 571 (Mt. Kilimanjaro) to reconstruct glacial-interglacial vegetation change from C4 grass-  
 572 dominated savannah to C3 vegetation in response to hydrological changes in East Africa over  
 573 the past 25 ka (Fig. 5).

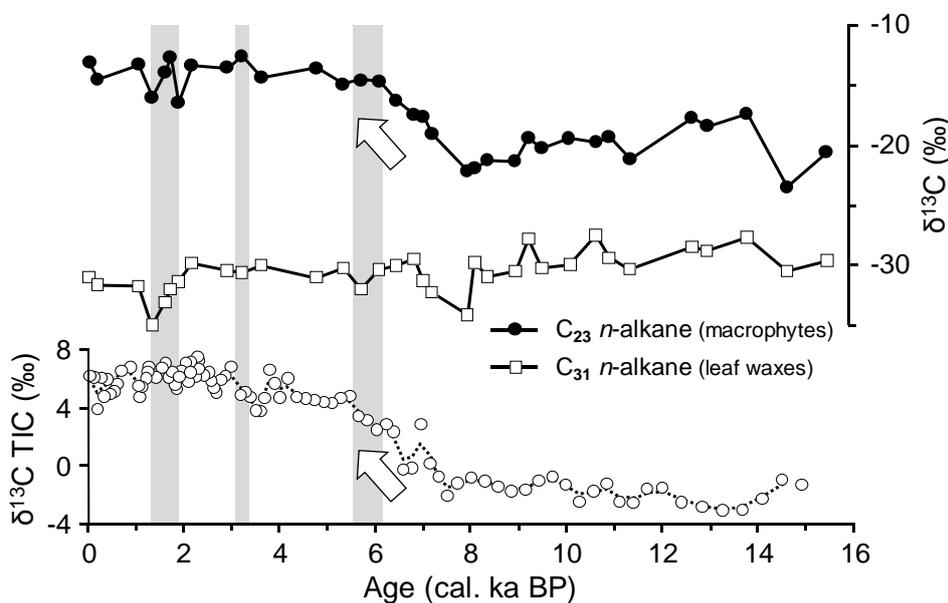


574

575 **Figure 5:** Reconstruction of changing proportions of C3 and C4 vegetation based on  $\delta^{13}\text{C}$   
 576 values of the  $\text{C}_{31}$  *n*-alkane in sediments of Lake Challa, East Africa for the past 25 ka, revealing  
 577 the transition from C4 grass savannah during the last glacial to mixed C3/C4 vegetation in the

578 Holocene (black line: 3-point moving average, H1/H2 = Heinrich event 1/2, LGM = last glacial  
579 maximum, YD = Younger Dryas; modified from Sinninghe Damsté et al., 2011a).

580 In Lake Koucha on the eastern Tibetan Plateau, Aichner et al. (2010b) found  $\delta^{13}\text{C}$  values of  
581 macrophyte-derived  $\text{C}_{23}$  *n*-alkanes (mainly from *Potamogeton*) diverging from the  $\delta^{13}\text{C}$  values  
582 of the terrestrial  $\text{C}_{31}$  *n*-alkane but following an equivalent shift towards heavier values in bulk  
583 inorganic carbon (TIC)  $\delta^{13}\text{C}$  values, which the authors interpreted as evidence for dissolved  
584  $\text{CO}_2$  limitation due to enhanced productivity at least in the littoral zone of the lake (Fig. 6). This  
585 coincided with a shift from a macrophyte-dominated saline ecosystem to a phytoplankton-  
586 dominated freshwater ecosystem as indicated by other biomarkers and micropaleontological  
587 data.



588

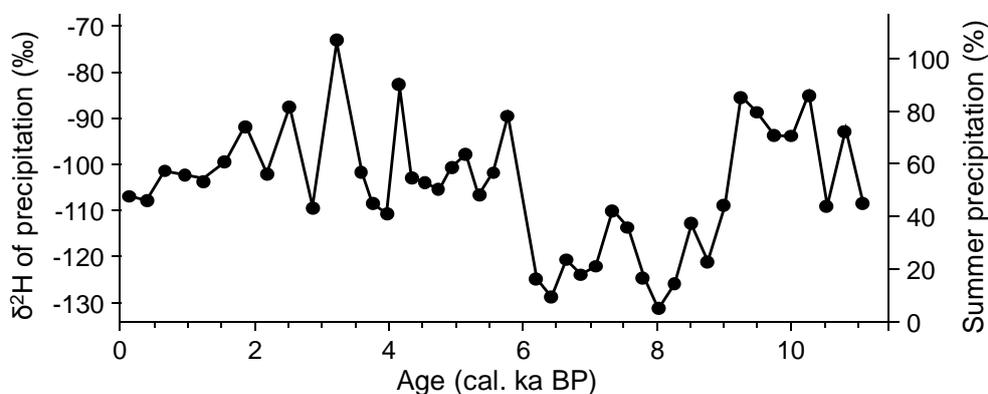
589 **Figure 6:** CSI data of the  $\text{C}_{23}$  *n*-alkane from macrophytes and the terrestrial  $\text{C}_{31}$  *n*-alkane  
590 compared to the  $\delta^{13}\text{C}$  values of bulk TIC in Lake Koucha (eastern Tibetan Plateau), suggesting  
591  $\text{CO}_2$  limitation due to enhanced productivity after 7 cal ka BP (grey bars: cold periods, dashed  
592 line: 3-point running average; modified from Aichner et al., 2010b).

593 The widened scope and an improved understanding of isotope fractionation affecting *n*-alkyl  
594 lipids in modern ecosystems has led to a rapid increase in studies targeting a wider range of  
595 alkyl lipids for the gain of more specific paleoenvironmental information in recent years. An  
596 increasing number of studies apply *n*-alkyl lipid  $\delta^2\text{H}$  values for paleohydrological  
597 reconstruction, illustrating the substantial promise of this novel method (Sachse et al., 2012).

598 Rach et al. (2014) studied the precisely dated varved sediment record from Lake Meerfelder  
599 Maar (Germany) to reconstruct changes in hydroclimate over Western Europe at the onset of  
600 the Younger Dryas, using *n*-alkane  $\delta^2\text{H}$  values. By comparing the  $\delta^2\text{H}$  records of the terrestrial

601  $C_{29}$  *n*-alkane and the aquatic  $C_{23}$  *n*-alkane (assumed to derive from macrophytes such as  
 602 *Potamogeton* sp.) the authors were able to differentiate between the effects of temperature  
 603 changes, aridification, and moisture source changes and could confirm a 170-year delay  
 604 between atmospheric cooling in Greenland and hydrology change over Western Europe,  
 605 which is also backed by palynological data from the site. A later study by Rach et al. (2017) of  
 606 the Holocene section of the same sedimentary record focussed on the Subboreal-Subatlantic  
 607 climate transition around 2.8 ka and found terrestrial *n*-alkane  $\delta^2H$  values to confirm the  
 608 establishment of cooler and wetter conditions, potentially associated with a change in  
 609 atmospheric trajectories. A sediment record spanning the same time interval obtained from  
 610 the Netherlands (Engels et al. 2016; van den Bos et al., 2018) shows an opposite  $\delta^2H$ -trend  
 611 around this time, which could be explained by a change in the atmospheric circulation pattern  
 612 resembling the negative phase of the North Atlantic Oscillation. Notably, Rach et al. (2017)  
 613 also observe a large change in  $\delta^2H$  values of aquatic lipid biomarkers ( $C_{21}$  and  $C_{23}$  *n*-alkane)  
 614 of up to 30 ‰, which the authors assume to result not just from hydrological change but also  
 615 from ecosystem change as it coincides with a strong increase in aquatic plants and algal  
 616 remains in the palynological record.

617 The combination of  $\delta^2H$  and  $\delta^{13}C$  values of the  $C_{29}$  *n*-alkanes in a Norwegian peatland was  
 618 used to reconstruct Holocene changes in the seasonality of rainfall, one of the more elusive  
 619 factors determining CSI data outside the monsoon regions (Nichols et al., 2009; Fig. 7).

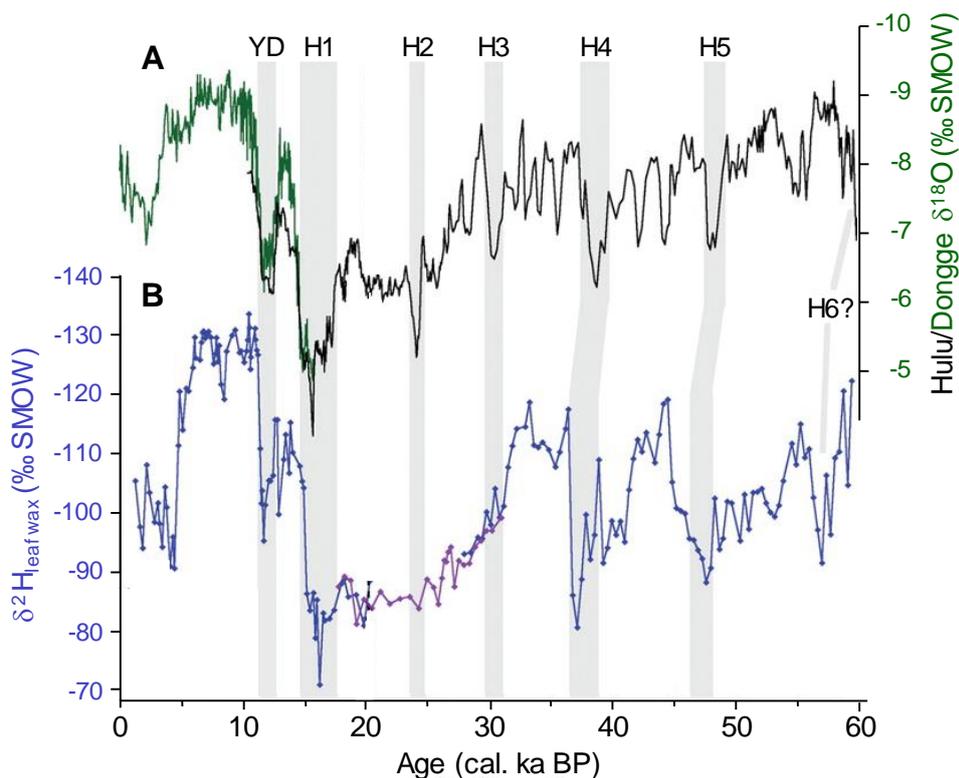


620

621 **Figure 7:** Seasonality of precipitation in NW Norway during the Holocene, expressed as the  
 622 proportion of summer precipitation and reconstructed from *n*- $C_{29}$  alkane  $\delta^2H$  values (modified  
 623 from Nichols et al., 2009).

624 Although *n*-alkanes are well established as target compounds for CSIA they frequently are a  
 625 minor TLE fraction compared to *n*-fatty acids or *n*-alcohols (see, e.g., Cranwell, 1981; Otto  
 626 and Simpson, 2005; Berke et al., 2012; Holtvoeth et al., 2016), which can provide valuable  
 627 alternative data when the amount of sample material and extractable *n*-alkanes are too low

628 for CSIA. Tierney et al. (2008), for example, applied hydrogen isotope ( $\delta^2\text{H}$ ) analysis of the  
 629 leaf wax-derived  $\text{C}_{28}$  *n*-fatty acid to sediment cores from Lake Tanganyika (East Africa) to  
 630 reconstruct variations in precipitation patterns over the past 60,000 years in order to better  
 631 understand the processes that control climate in the tropics. Their data show that this  
 632 understudied region experienced abrupt paleohydrological changes coeval with orbital and  
 633 millennial-scale events recorded in Northern Hemisphere monsoonal climate records (Fig. 8).  
 634 These results provide sound evidence for a strong control of Indian Ocean surface  
 635 temperatures and winter Indian monsoon on precipitation in southeast Africa.



636  
 637 **Figure 8:** The close correlation of the  $\delta^2\text{H}$  values of leaf wax-derived  $\text{C}_{28}$  *n*-fatty acid in  
 638 sediments of Lake Tanganyika (B) with the  $\delta^{18}\text{O}$  records of the Hulu and Dongge caves (A)  
 639 reveal the close linkage between Northern Hemisphere monsoon variability and East African  
 640 hydrology over the past 60,000 years (YD = Younger Dryas, H1-6 = Heinrich events 1-6;  
 641 modified from Tierney et al., 2008).

642 A study by Berke et al. (2012) on sediments of the past 14 kyrs from Lake Victoria combines  
 643  $\delta^{13}\text{C}$  data of the  $\text{C}_{29}$  *n*-alkane and, due to the relatively low abundance of *n*-alkanes,  $\delta^2\text{H}$  data  
 644 of the  $\text{C}_{28}$  *n*-fatty acid with a biomarker-based temperature proxy ( $\text{TEX}_{86}$ ; Section 3.3) in order  
 645 to reconstruct hydrologically controlled changes in the catchment, in particular, changes in the  
 646 proportion of C3 and C4 plants. The data are then compared to equivalent data from other  
 647 African settings, specifically,  $\delta^2\text{H}$  data of the  $\text{C}_{28}$  *n*-fatty acid from Lakes Challa (Tierney et al.,

648 2011), Tanganyika (Tierney et al., 2008) and Malawi (Konecky et al., 2011) and of the C<sub>29</sub> *n*-  
649 alkane from higher plants of the Congo Basin (Schefuß et al., 2005) and the Zambezi River  
650 catchment (Schefuß et al., 2011). Berke et al. (2012) find their reconstruction in good  
651 agreement with other African records and illustrated the spatiotemporal propagation of drier  
652 and cooler conditions across East and North Africa after a warm and humid early Holocene  
653 as well as the influence of monsoonal moisture supply in periods of maximum seasonal  
654 contrast between Northern and Southern Hemisphere insolation. Notably, the authors observe  
655 a mismatch between their *n*-alkane  $\delta^{13}\text{C}$  values and palynological data which they attribute to  
656 different source vegetation for leaf waxes and pollen from around the lake, underscoring the  
657 value of multiproxy approaches. The  $\delta^2\text{H}$  values of the *n*-fatty acids, on the other hand, should  
658 be independent of this as they are determined by the  $\delta^2\text{H}$  value of meteoric water rather than  
659 interspecies differences in biosynthetic processing. Accordingly, the  $\delta^2\text{H}$  values of the *n*-fatty  
660 acids do indeed appear coherent with the changes in the amount of precipitation and  
661 associated biome adaption postulated by Berke et al., (2012).

662 Due to the strong control of meteoric water isotope composition over leaf wax  $\delta^2\text{H}$  values that  
663 is particularly pronounced in regions with distinct seasonal changes in moisture source a  
664 similar approach was taken by Cisneros-Dozal et al. (2014) for a reconstruction of North  
665 American monsoon intensity during the late Pleistocene (540 - 360 ka BP). In the sediments  
666 of a paleolake in the southwestern US,  $\delta^2\text{H}$  values of the C<sub>28</sub> *n*-fatty acid reflect the changing  
667 intensity of monsoonal moisture supply from the Gulf of Mexico and the Gulf of California,  
668 which is seasonally alternating with moisture supply from the cooler North Pacific Ocean. The  
669 CSI data resolves the orbitally controlled monsoon variability during interglacials, specifically,  
670 during marine isotope stage 11, and thus provides the mechanism driving equivalent changes  
671 in pollen, bulk  $\delta^{13}\text{C}$  and GDGT-based temperature data from the same record.

672 Studying the isotopic composition of *n*-alkyl lipids that are part of tissue types other than  
673 cuticular waxes widens the application of CSI data considerably towards aquatic ecosystems  
674 as well as towards other terrestrial OM sources such as soil OM (suberin-derived alkyl  
675 compounds). In fact, soil OM is the larger carbon reservoir compared to living biomass by a  
676 factor of ~2 (Post et al., 1977). The amounts and isotopic composition of suberin-derived  $\alpha,\omega$ -  
677 diacids or C<sub>22</sub> and C<sub>24</sub>  $\omega$ -hydroxy acids can provide evidence for the dynamics of the soil  
678 carbon pool (Mendez-Millan et al., 2010) ascribed to changes in vegetation cover or land use  
679 change and, thus, support established CSIA of leaf wax *n*-alkanes tracking changing  
680 proportions of C3 and C4 plants. Even within a pure C3 river catchment, Alewell et al. (2016),  
681 for example, were able to distinguish between contributions to river sediment from different  
682 OM sources (forest, agricultural land) using CSI data and concentrations of *n*-fatty acids. In  
683 order to investigate the links between the isotopic composition of the major limnic carbon

684 pools, i.e. dissolved inorganic and organic carbon (DIC, DOC),  $\text{CO}_{2(\text{aq})}$ , particulate organic  
685 carbon (POC) and algal and bacterial biomass, on the one hand, and lake water  $p\text{CO}_2$ , food  
686 web structure and nutrient regime in lakes of different trophic status, on the other hand, de  
687 Kluijver et al. (2014) combined bulk substrate isotope values with CSI data of algal and  
688 bacterial fatty acids and glucose. This approach revealed complex interdependencies  
689 between carbon pool dynamics and isotope values, with nutrient level being a major factor. In  
690 order to assess aerobic methanotrophic bacterial production that is responsible for relatively  
691 low methane outgassing in Lake Kivu, Morana et al. (2015) interpreted  $\delta^{13}\text{C}$  values of *n*-fatty  
692 acids, mono-unsaturated and branched fatty acids alongside  $\delta^{13}\text{C}$  values of methane, DIC and  
693 POC from water column profiles. Studying methane production in and outgassing from surface  
694 sediments of West, Central and North European lakes, Stötter et al. (2018) found correlations  
695 between in-lake methane concentrations and the relative abundance of  $^{13}\text{C}$ -depleted mono-  
696 unsaturated fatty acids in the sediments that appeared to derive mainly from methane-  
697 oxidising bacteria. However, the authors also find that oxygen availability at the sediment-  
698 water interface is a major factor affecting the abundance of these compounds. Thus, although  
699 reconstructing changes in methane outgassing from lakes would contribute significantly to the  
700 understanding of methane cycling in the past, the extension of such approaches into the  
701 paleorecord remains a challenge. Glucose has a low preservation potential, for example, and  
702 disentangling the sources of microbial biomarkers from communities living in the water column  
703 or *in situ* will be an issue. However, in any such attempt, CSIA will provide an essential tool  
704 due to the strong fractionation resulting from the consumption of microbial methane, whichever  
705 biomarker from a methanotrophic organism one would be studying. We would like to point out  
706 the research opportunities that follow from the relations described above between  
707 environmental factors and the isotope composition of certain lipids and glucose in soils and  
708 modern aquatic ecosystems since the potential of many of these relations for  
709 paleoenvironmental proxy development has yet to be explored.

710 CSIA of long-chain alkenones from incubation experiments with the dominant marine  
711 haptophyte species, *Emiliana huxleyi* and *Gephyrocapsa oceanica*, and the coastal species  
712 *Isochrysis galbana* demonstrated that the  $\delta^2\text{H}$  value of the alkenones is generally determined  
713 by the  $\delta^2\text{H}$  value of the water and, to a significant extent, by salinity (e.g., Englebrecht and  
714 Sachs, 2005; Schouten et al., 2006; M'boule et al., 2014; Weiss et al., 2017). Haptophyte  
715 growth rate is another modifying factor (Schouten et al., 2006; M'boule et al., 2014). The  
716 concept of alkenone  $\delta^2\text{H}$  values tracking salinity was applied, e.g., by van der Meer et al.  
717 (2007) to sedimentary alkenones in the eastern Mediterranean where the alkenone  $\delta^2\text{H}$  value  
718 strongly correlates with enhanced freshwater supply during sapropel formation. In a Holocene  
719 sediment core from an estuarine site on the west coast of Florida, alkenone  $\delta^2\text{H}$  values also

720 appear to have varied to some extent with salinity (van Soelen et al., 2014), however, such  
721 relation was not seen, e.g., in alkenones in suspended particles and surface sediment from  
722 the Chesapeake Bay estuary on the east coast of the US (Schwab and Sachs, 2011). A shift  
723 in haptophyte species distribution along with change in salinity is one of the likely reasons for  
724 the weak or absent correlation between alkenone  $\delta^2\text{H}$  values and salinity in brackish coastal  
725 settings. In North American saline lakes, Nelson and Sachs (2014) observe a correlation,  
726 particularly, of the  $\delta^2\text{H}$  value of the  $\text{C}_{37:4}$  alkenone in the surface sediment with lake water  $\delta^2\text{H}$ ,  
727 although this appears weaker than in the marine realm. As far as we are aware at the time of  
728 writing, the applicability of alkenone  $\delta^2\text{H}$  for reconstructions of salinity changes in a lacustrine  
729 setting has yet to be tested, ideally, for an extant lacustrine environmental archive where the  
730 evolution of both salinity and algal species can also be determined by other means.

731 Schouten et al. (2001) and D'Andrea and Huang (2005) determined the  $\delta^{13}\text{C}$  values of  
732 alkenones in sediments of Antarctic and Arctic saline lakes and found further  $^{13}\text{C}$  depletion in  
733 the alkenones relative to other biomarkers such as fatty acids, sterols and steranes, with  $\delta^{13}\text{C}$   
734 values of the alkenones of  $-35\text{‰}$  (Schouten et al., 2001) to  $-42\text{‰}$  (D'Andrea and Huang,  
735 2005). These offsets are not straightforwardly explained and low growth rates and high  
736 concentrations of dissolved  $\text{CO}_2$  due to the low water temperatures in the investigated settings  
737 remain hypothetical causes for enhanced fractionation during alkenone biosynthesis.  
738 D'Andrea and Huang (2005) again refer to the uncertain source of the alkenones in Arctic  
739 lakes but point out the possibility that the isotopic fingerprint of the alkenones may relate to  
740 specific ecological conditions. Similarly, a  $1\text{‰}$  shift in alkenone  $\delta^{13}\text{C}$  values in mid-Holocene  
741 sediments from a restricted estuary (Charlotte Harbour, Florida) may also derive from a shift  
742 in species distribution and an associated change in fractionation as isotopic change in DIC  
743 could be ruled out based on  $\delta^{13}\text{C}$  values of carbon from foraminifera (van Soelen et al., 2014).  
744 We are currently not aware of CSIA of alkenones in pure freshwater systems, for which the  
745 potential of such application for paleoenvironmental reconstructions remains to be explored.

## 746 **3.2 Amino acids**

### 747 **3.2.1 Sources**

748 Amino acids are biologically ubiquitous compounds present in all organisms, both in the form  
749 of proteins (polypeptides, i.e. chains of amino acids) and as precursors and intermediates in  
750 the biosynthesis of other essential biomolecules, such as porphyrins, neurotransmitters in  
751 animals, and lignin in plants. Heterotrophic organisms typically cannot biosynthesise all amino  
752 acids they require, i.e. some amino acids have to be assimilated through food sources. These  
753 are known as essential amino acids or source amino acids. By contrast, nonessential amino  
754 acids are synthesised by heterotrophs through enzymatically controlled addition of ammonia  
755 ( $\text{NH}_3^+$ ) to metabolic intermediates, commonly pyruvate, oxaloacetate,  $\alpha$ -ketoglutarate, in a

756 process called transamination (for details see, e.g., Lengeler et al., 1999; Chikaraishi et al.,  
 757 2009). Like many enzymatically controlled biosynthetic reactions, transamination and  
 758 deamination (removal of ammonia) inherit isotope fractionation (Gaebler et al., 1966) and, in  
 759 this case, result in <sup>15</sup>N enrichment of the nonessential (or trophic) amino acids (McClelland  
 760 and Montoya, 2002; Chikaraishi et al., 2007). Thus, the nitrogen isotopic composition of  
 761 essential and nonessential amino acids in heterotrophic organisms is determined by the  
 762 source (essential amino acid) and by the level of metabolic processing (nonessential amino  
 763 acid). Phenylalanine (Phe), for example, is an essential amino acid in mammals and  
 764 undergoes few metabolic steps in which fractionation could occur, therefore, δ<sup>15</sup>N<sub>Phe</sub> values  
 765 represent those of the diet, and ultimately the base of the food web. Phe is therefore referred  
 766 to as a source group amino acid. On the other hand, glutamic acid (Glu) plays a central role  
 767 in amino acid biosynthesis, and so δ<sup>15</sup>N<sub>Glu</sub> values reflect the amount of N metabolic cycling  
 768 between the base of the food web and the consumer tissue, and is referred to as a trophic  
 769 group amino acid (McClelland and Montoya, 2002; O'Connell, 2017).

770 It is thus possible to estimate the trophic position of organisms in aquatic and terrestrial  
 771 ecosystems using an equation based on the differing trophic <sup>15</sup>N enrichments of Glu and Phe,  
 772 of approximately 8 ‰ and 0.4 ‰, respectively (Eq. 2):

$$773 \quad T_{L_{\text{Glu-Phe}}} = \frac{\delta^{15}\text{N}_{\text{Glu}} - \delta^{15}\text{N}_{\text{Phe}} - \beta}{7.6} + 1 \quad \text{Equation 2}$$

774 where β is the difference between Glu and Phe at the base of the food web being studied  
 775 (Chikaraishi et al., 2009; Chikaraishi et al., 2010; Yamaguchi et al., 2017). This method has  
 776 benefits over using a bulk method, as the δ<sup>15</sup>N values of these amino acids provide an internal  
 777 trophic position measure, without the need to measure the flora and fauna contributing to the  
 778 diet (Chikaraishi et al., 2007, 2009).

### 779 **3.2.2 Applications**

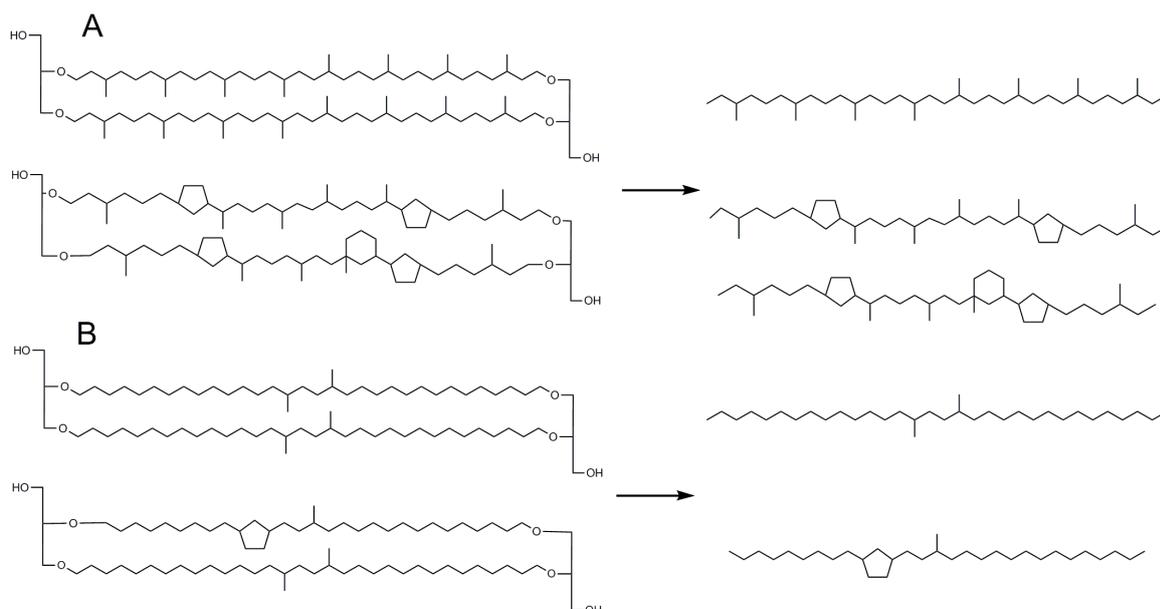
780 CSIA of amino acids has developed into a tool to improve our understanding of nitrogen  
 781 transfer in modern aquatic food webs (e.g., Uhle et al., 1997; McClelland and Montoya, 2003;  
 782 McCarthy et al., 2007; Yamaguchi et al., 2017). An increasing number of studies successfully  
 783 apply nitrogen as well as carbon CSIA of amino acids to track amino acid production in the  
 784 limnic water column as well as microbial processing during sinking and in surface sediments  
 785 (e.g., Carstens et al., 2013). In paleolimnological contexts, the application of CSIA of amino  
 786 acids has so far been limited due to the relatively low preservation potential of amino acids  
 787 and the uncertainties associated with nitrogen fractionation affecting individual amino acids  
 788 during and after entering the sedimentary record. Carstens et al. (2013) observe an early  
 789 diagenetic decrease of amino acid-bound nitrogen relative to the total nitrogen from 38 to 10

790 % in the top 6 cm of sediment in two Swiss lakes as well as changes in the  $\delta^{15}\text{N}$  values of  
791 amino acids that are also likely to result from *in situ* microbial processing rather than changing  
792 inputs over time. Further evidence for heterotrophic alteration of selected amino acids from  
793 detrital organic matter leading to a scattered amino acid  $\delta^{15}\text{N}$  pattern is provided in a critical  
794 review of amino acid nitrogen CSIA in environmental contexts by Ohkouchi et al. (2017), with  
795 the authors concluding that understanding how exactly microbial activity alters amino acid  
796  $\delta^{15}\text{N}$  patterns “remains a frontier area of CSIA-AA applications”. Thus, while amino acid  $\delta^{15}\text{N}$   
797 values may provide information on both organic matter sources and microbial degradation,  
798 these processes will have to be understood before any proxy can be reliably applied.

### 799 **3.3 Glycerol-dibiphytanyl-glycerol tetraethers (GDGTs)**

#### 800 **3.3.1 Sources**

801 Isoprenoidal etherlipids, in particular archaeol and hydroxyarchaeol (diethers) or glycerol  
802 dibiphytanyl glycerol tetraether lipids (iGDGTs, Fig. 8A) are the predominant membrane lipids  
803 of archaea (Langworthy, 1982, 1977; Langworthy et al., 1972; Schouten et al., 2013). Archaea  
804 are widespread in mesophilic settings: marine and lake sediments (MacGregor et al., 1997;  
805 Vetriani et al., 1998), soils (Hershberger et al., 1996; Leininger et al., 2006), and the ocean  
806 (DeLong, 1992; Fuhrman and Davis, 1997; Karner et al., 2001). Isotopic fractionation has  
807 been studied on only a small proportion of cultured organisms (Könneke et al., 2012; van der  
808 Meer et al., 2001). The membranes of some bacteria can also consist of diether lipids and  
809 tetraether lipids, containing non-isoprenoidal, sometimes methylated, hydrocarbon chains  
810 (glycerol dialkyl glycerol tetraetherlipids or branched GDGTs, (brGDGT, Fig. 8B; Sinninghe  
811 Damsté et al., 2011b, 2014; Weijers et al., 2006). Sources of brGDGTs comprise  
812 microorganisms thriving in lacustrine and riverine environments (Blaga et al., 2010; Tierney  
813 and Russell, 2009; De Jonge et al., 2014), peats (Weijers et al., 2006) and soils (Weijers et  
814 al., 2007).



815

816 **Figure 9:** Glycerol-dibiphytanyl-glycerol tetraether lipids (GDGTs) and cleavage products; A:  
 817 common isoprenoidal GDGTs (iGDGTs) and biphytanes, B: common branched GDGTs  
 818 (brGDGTs) and branched and cyclic alkanes (modified from Schouten et al., 1998).

819  $\delta^{13}\text{C}$  values of GDGTs are most commonly measured after chemical degradation to  
 820 biphytanes and branched alkanes (Schouten et al., 1998; Fig. 9), but can also be determined  
 821 for intact molecules by a spooling-wire microcombustion device interfaced with an isotope-  
 822 ratio mass spectrometer (SWiM-IRMS; Pearson et al., 2016) or possibly by high-temperature  
 823 GC-IRMS (Lengger et al., 2018). Analytical challenges in the determination of the stable  
 824 hydrogen isotopic composition are large and only a limited amount of CSI studies focusing on  
 825 GDGTs have been carried out, so far (e.g., Kaneko et al., 2011).

### 826 3.3.2 Applications

827 The applicability of carbon isotopes of GDGTs for lacustrine environmental reconstructions  
 828 still has to be tested. However,  $\delta^{13}\text{C}$  values of GDGTs have been the subject of a significant  
 829 number of studies of modern environments that work towards the development of GDGT-  
 830 based paleoenvironmental proxies. These include stable isotope probing experiments aiming  
 831 to study origin and metabolism of GDGTs (Wuchter et al., 2003; Lengger et al., 2014), and the  
 832 determination of natural  $\delta^{13}\text{C}$  values of GDGTs. GDGTs are highly abundant in lakes, and  
 833 their distributions are well studied as they are used in paleothermometers such as  $\text{TEX}_{86}$  and  
 834 MBT (Castañeda and Schouten, 2011). Some are produced *in situ* in the lakes, while others  
 835 are exogenous and derived from surrounding soils or riverine influx. Provided sources and net  
 836 carbon isotope fractionation factors for archaeal, planktonic iGDGTs such as crenarchaeol are  
 837 further constrained,  $\delta^{13}\text{C}_{\text{biphytane}}$  could potentially be used as a paleo-DIC proxy in lakes, as  
 838 suggested for marine settings (Hoefs et al. 1997, Kuypers et al. 2001, Pearson et al. 2016).

839 Bacterial brGDGTs, on the other hand, have been reported to be depleted by 1 ‰ in  $^{13}\text{C}$   
840 compared to the bulk organic carbon in a peat (Weijers et al., 2010); consistent with a  
841 heterotrophic lifestyle. However, in lakes (sediments and water column), brGDGTs were found  
842 to be varying with  $\delta^{13}\text{C}$  of POM, but strongly depleted in  $\delta^{13}\text{C}$  in anoxic bottom waters, with  
843 values of -43 to -47 ‰ (10 ‰ depleted compared to TOC, Weber et al., 2015) and -42 ‰  
844 (Weber et al., 2018). Weber et al. (2018) attributed this depletion to uptake of  $^{13}\text{C}$ -depleted  
845 organic carbon ultimately derived from biogenic methane by the source bacteria living in and  
846 below the redox transition under hypoxic and methanotrophic conditions. Thus,  $\delta^{13}\text{C}$  values of  
847 brGDGTs in lake sediments can shed light on organic matter sources and lake  
848 biogeochemistry.

849  $\delta^{13}\text{C}$  values of iGDGTs produced by archaea can also be used to study present and past  
850 settings of anaerobic oxidation of methane. GDGTs with unusually negative  $\delta^{13}\text{C}$  values have  
851 been found mostly in methane seep environments and euxinic water columns, and are strong  
852 evidence for anaerobic methanotrophs (ANME; Hinrichs et al., 1999, 2000; Wakeham et al.,  
853 2004; Niemann and Elvert, 2008). Recently, these have been used for the first time to trace  
854 anaerobic oxidation of methane in sediments of a freshwater wetland (Segarra et al., 2015).

855 In summary, there are several potential applications for  $\delta^{13}\text{C}$  values of GDGTs as proxies in  
856 lacustrine and freshwater environments. These range from establishing the presence of  
857 anaerobic methane oxidising archaea, to constraining paleo-DIC and organic matter sources.

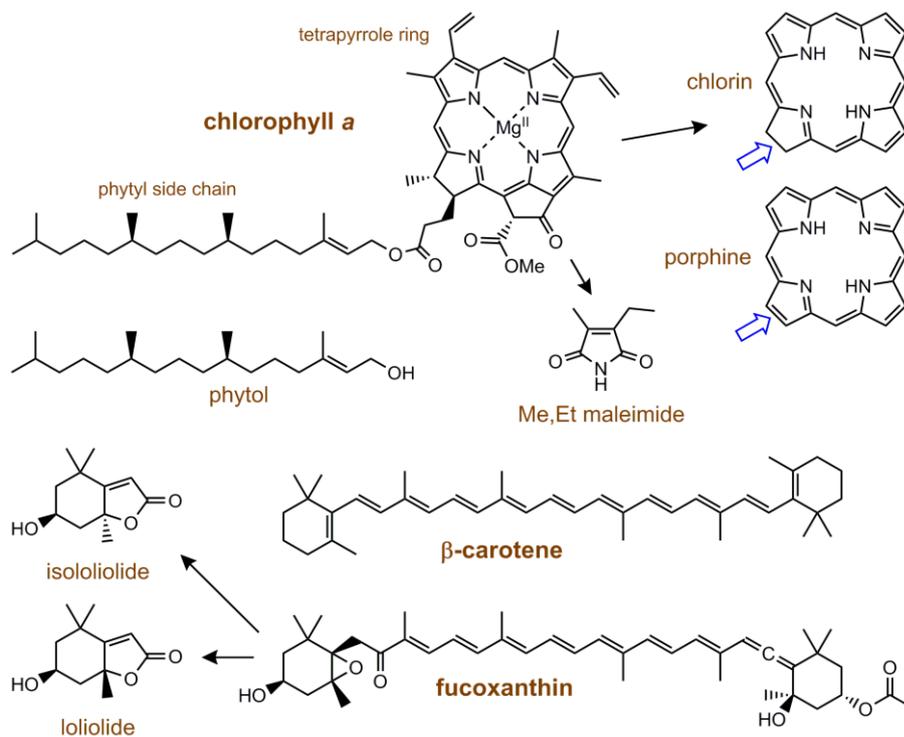
### 858 **3.4 Pigment transformation products**

859 Key compounds for photosynthesis, chlorophylls and bacteriochlorophylls are the most  
860 abundant pigments on the planet. Their transformation products, chlorins, porphyrins, and  
861 maleimides can be preserved in lacustrine and marine sediments. Another important group of  
862 pigments in plants and microbes are carotenoids. Pigments contain chromophore groups,  
863 typically conjugated double bonds that absorb portions of the visible solar spectrum and give  
864 molecules their distinctive colours. Many of the pigments integrate oxygen functional groups  
865 that provide sites for microbial degradation, making these compounds particularly sensitive to  
866 post-depositional alterations. The major forms of stabilizing alterations are complete  
867 aromatization of the chlorophyll tetrapyrrole ring to lead to porphyrins and hydrogenation of  
868 carotenoids carbon-carbon double bonds to form isoprenoid alkanes (Fig. 10).

869 The various chlorophylls differ principally in the alkyl sidechains attached to the central  
870 tetrapyrrole ring. The most important sidechain of chlorophyll *a*, the most common  
871 photosynthetic pigment, is the ester-linked diterpenoid alcohol, phytol (Fig. 10, see Fig. 11 for  
872 biosynthesis). As chlorophylls absorb red wavelengths of solar energy, aquatic phototrophs  
873 have evolved different carotenoid compounds as accessory pigments to broaden the range of

874 wavelengths useful for photosynthesis (c.f. Swain, 1985; Sanger, 1988). Many of the  
 875 accessory pigments are characteristic of different photoautotrophs and this can be used to  
 876 help identify past sources, synthesis, taphonomy, and freshness of organic matter in limnic  
 877 records (Naeher et al., 2013).

878 Chlorophylls undergo minor to major transformations within the water column and in the  
 879 sediment. These continue during diagenesis and lead to the formation of porphyrins and  
 880 maleimides (Grice et al., 1996, 1997; Pancost et al., 2002). The reactivity of pigments makes  
 881 them sensitive indicators of changes in aquatic environments. For example, the diagenetic  
 882 conversion of chlorophyll to pheophytin is enhanced by acidic conditions, as shown by  
 883 Guilizzoni et al. (1992) when employed in the reconstruction of the progressive acidification of  
 884 lakes in the Central Alps.



885

886 **Figure 10:** Molecular structures of common pigment types and representative degradation  
 887 products in limnic settings. Chlorophyll a is the dominant chlorophyll and primary  
 888 photosynthetic pigment. Secondary pigments such as carotenoids (e.g.,  $\beta$ -carotene,  
 889 fucoxanthin) are present in various amounts in plants and algae as well as dinoflagellates.  
 890 Pigments are rarely preserved intact whereas degradation products such as chlorin,  
 891 porphyrins (parent structure: porphine) and maleimides from chlorophylls or  
 892 loliolide/isololiolide from fucoxanthin are frequently observed in lake sediments and can be  
 893 used as indicators for photoautotrophs.

### 894 3.4.1. Chlorins and porphyrins

895 **3.4.1.1 Sources**

896 Chlorins are broadly defined as chlorophylls and their phaeopigment derivatives central to  
897 photosynthesis (Fig. 10) and thus inherently linked to primary producers (Sanger, 1988). As  
898 they quickly degrade in light and oxygen, chlorins extracted from water or surface sediments  
899 are thought to be derived from synthesis at or close to the collection site, reducing the influence  
900 of transport. Degradation of chlorins during diagenesis and transport biases limnic sediments  
901 toward autochthonous sources, although chlorins are also synthesized by land plants (Sanger,  
902 1988). Chlorins contain four nitrogen atoms to each molecule (Fig. 10), offering the opportunity  
903 for compound-specific  $\delta^{15}\text{N}$  analysis.

904 Intensively studied since the 1930s (e.g., Treibs, 1936) porphyrins are aromatic organic  
905 compounds that consist of carbon and nitrogen and sometimes contain a metal atom such as  
906 magnesium at their centre (e.g., chlorophyll). Whereas chlorins comprise the immediate  
907 diagenetic products of chlorophylls, geoporphyrins result from long-term diagenesis (cf. Callot  
908 et al., 1990). They have vanadium or nickel in their centre and can be preserved in a wide  
909 range of sediments for hundreds of millions of years (Eglinton et al., 1985; Callot and Ocampo,  
910 2000).

911 **3.4.1.2 Applications**

912 The nitrogen isotopic composition of chlorins has been determined from contemporary waters  
913 and cultured algae (Sachs and Repeta, 1999; York et al., 2007), as well as from late  
914 Quaternary marine and limnic sediments (Sachs and Repeta, 1999; 2000; Higgins et al.,  
915 2010), e.g., to provide insights into the marine N-cycle in the Mediterranean sapropel  
916 formation. These studies, however, relied upon phaeopigments (Sachs and Repeta, 1999,  
917 2000) or on the coalescence of several chlorin fractions (Higgins et al., 2010). Coupled  $\delta^{13}\text{C}$   
918 and  $\delta^{15}\text{N}$  from chlorins extracted from last glacial-interglacial transition sediments of Lake  
919 Suigetsu, Japan (Tyler et al., 2010) emphasize both the potential (e.g., the response of aquatic  
920 primary productivity to post-glacial environmental change) and further work needed for chlorin-  
921 specific isotopes as tracers in lake sediments.

922 Where ancient sediments are concerned,  $\delta^{15}\text{N}$  measurements of diagenetic products of  
923 chlorins are more prevalent, e.g. metalloalkylporphyrins (Hayes et al., 1987; Ohkouchi et al.,  
924 2006 for nitrogen fixation/assimilation) and maleimides (Grice et al., 1996a; Pancost et al.,  
925 2002; see Section 3.4.3).

926 **3.4.2 Aromatic carotenoids and maleimides**

927 **3.4.2.1 Sources**

928 Carotenoids are usually yellow- to red-coloured lipids formally derived from the irregular  $\text{C}_{40}$

929 isoprenoid lycopene carbon skeleton by hydrogenation, dehydrogenation, cyclization and  
930 oxidation reactions (Pfenning, 1978). Biosynthesized *de novo* by all photosynthetic bacteria,  
931 eukaryotes, halophilic (high salt) archaea, and a large variety of non-photosynthetic  
932 organisms, over 600 different carotenoid structures have been identified in modern organisms  
933 (Goodwin, 1976; Liaaen-Jensen, 1979; Summons and Powell, 1986). In aquatic sedimentary  
934 environments, the only significant biological sources for aromatic carotenoids are green and  
935 purple sulfur bacteria, anoxygenic photoautotrophic prokaryotes that inhabit the sulfide-rich,  
936 light-limited, and oxygen depleted bottom waters of some lakes and ocean basins (Grice et  
937 al., 1996a; Koopmans et al., 1996; Schaeffer et al., 1997).

938 Maleimides are the oxidation products mainly of the tetrapyrrole nuclei from chlorophyll and/or  
939 bacteriochlorophyll related pigments (Fig. 10) and potentially from other sources, e.g.,  
940 cytochromes (Paoli et al., 2002) and phycobilins from cyanobacteria and rhodophytes (Glazer  
941 et al., 1976; Brown et al., 1990), possibly by a transformation pathway involving the oxidation  
942 of vinylic chlorophyll substituents and the formation of an aldehyde intermediate during early  
943 diagenesis under anoxic conditions (Pickering and Keely, 2011; Naeher et al., 2013).  
944 Bacteriochlorophyll (bchl) pigments *c*, *d*, and *e* (1 and 2; M = Mg, R3 = farnesyl) are exclusively  
945 made by green sulfur bacteria (Pfennig, 1978).

#### 946 **3.4.2.2. Applications**

947 Although their multiple double bonds make them reactive compounds that should be  
948 interpreted cautiously, source-specific chlorophyll-derived pigments (e.g., carotenoids and  
949 maleimides) can be robustly preserved in sediments thousands to millions of years old (as  
950 reviewed in Brocks and Summons, 2005), yielding unparalleled information for  
951 paleolimnological reconstructions, including details on lake evolution, redox transitions,  
952 changing patterns of aquatic primary productivity, and environmental conditions.

953 The presence of aromatic carotenoids (or bchl derived porphyrins) in lakes provides evidence  
954 of anoxygenic photosynthesis in contemporary environments and in sediments, a vast array  
955 of diagenetic aromatic components have been identified (Grice et al., 1997; Koopmans et al.,  
956 1996) that are derived from green sulfur bacteria (e.g. aromatic compounds isorenieratene/  
957 chlorobactene with a 2,3,6 methyl aromatic substitution pattern) or from okenone from purple  
958 sulfur bacteria (e.g. with a 2, 3, 4 methyl aromatic substitution pattern; Brocks and Summons,  
959 2005.) These carotenoids and bchl-derived porphyrins serve as a marker for photic zone  
960 euxinia in the past. (Grice et al., 1996a,b; Koopmans et al., 1996; Hartgers et al., 1995; Grice  
961 et al., 1997; Grice et al., 2005a; Ocampo et al., 1985; Whiteside and Grice, 2016).

962 Furthermore, changes in primary producers can be inferred from the types of pigments that  
963 are present in sediments. For example, progressive eutrophication of Esthwaite Water in the

964 English Lake District is recorded by increases in the concentrations of the carotenoids  
965 indicative of cyanophytes (Griffiths, 1978). Similarly, in other lake settings, relative abundance  
966 changes of bchl *a* relative to bchls *c* and *d* indicate development-related changes in the  
967 structure of the bacterial community, leading to increased competition for light or nutrients  
968 (Abella et al., 1980; Parkin and Brock, 1980; Rodrigo et al., 2000). Differences in the  
969 proportions of bchl *e* and bchls *c* and *d* indicate if brown or green species of green sulfur  
970 bacteria dominate in lakes of different depths and where different light regimes and chemical  
971 conditions prevail (Vila and Abella, 1994). Wilson et al. (2004) looked at the impact of  
972 stratigraphic resolution of sediment depth profiles of bchls *c* and *d*, as revealed by  
973 methanolysis, in Kirisjes Pond, Antarctica, and a finely laminated microbial mat from Les  
974 Salines de la Trinitat, Spain and showed that bacterial communities are highly sensitive to  
975 changing conditions and respond quickly. With regard to primary productivity sources on  
976 longer timescales, Kimble et al (1974) demonstrated that the major extractable tetraterpane  
977 in the ~50 million-year-old lacustrine Green River Formation is the  $\beta$ -carotene derivative  
978 perhydro- $\beta$ -carotene, suggesting that algal photosynthesis was the primary source of organic  
979 matter to this paleolimnologic system.

980 A recent modern calibration study for past biogeochemical cycling of redox-stratified lakes  
981 by Fulton et al. (2018) observed distinctive  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  values of pigments and nutrients in  
982 the water column and surface sediments of Fayetteville Green Lake (New York, USA), which  
983 they attribute to seasonally variable populations of cyanobacteria, purple sulfur bacteria and  
984 green sulfur bacteria at the chemocline. Informed by these data, and  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  values for  
985 pyropheophytin and bacteriochlorophyll from the Black Sea deposited during its transition to  
986 a redox-stratified basin ~7.8 ka, the authors proposed an isotopic mixing model for nutrient  
987 evolution that shows pigment decomposition to a common porphyrin derivative can produce  
988 non-specific sedimentary isotope signatures. This model underlines the need for caution and  
989 further refinement in paleobiogeochemical interpretations from basins with diverse microbial  
990 populations near a shallow chemocline.

991 Most maleimide studies have looked at the oxidation products of porphyrins in crude oil (e.g.,  
992 the Quirke et al., 1980 investigation of the Cretaceous Boscan crude oil) and petroleum source  
993 rocks (e.g., studies by Grice et al., 1996, 1997 on the Australian Permian Kupferschiefer and  
994 Mid-Triassic Serpiano shales that used Me,*n*-Pr and Me,*i*-Bu maleimides and the Me,*i*-  
995 Bu/Me,*Et* ratio as indicators for Chlorobi and hence, for the occurrence of photic zone euxinia  
996 across the end-Permian extinction). In a recent study, Naeher et al. (2013) linked Me,*i*-Bu  
997 maleimide to the presence of photic zone euxinic and anoxic conditions in Swiss lake Rotsee  
998 during the last 150 years and throughout the Romanian Black Sea history, including the limnic  
999 phase. A further need remains for the detection and characterization of maleimides in recent

1000 lake bodies and sediments to determine their partly unidentified precursors, their formation  
1001 processes during chlorophyll/bacteriochlorophyll degradation and importance in terms of  
1002 environmental conditions, particularly the impact of oxygen. In a recent study towards this end,  
1003 (Naehler et al., 2013) proposed Me,Me and Me,Et indices as novel proxies for estimating the  
1004 degree of organic matter degradation, which are applicable for longer timescales than e.g. the  
1005 chlorin index.

1006 Carotenoid and maleimide diagenetic products are easily distinguished by CSIA. For example,  
1007 bacterially derived green sulfur products are ca. 15 ‰ more enriched in <sup>13</sup>C than phytoplankton  
1008 biomarkers (e.g., steranes, hopanoids and steroids) due to the assimilation of CO<sub>2</sub> by the  
1009 reversed TCA cycle (Quandt et al., 1977) rather than the C<sub>3</sub> carbon fixation pathway. Purple  
1010 sulfur bacteria differ from green sulfur bacteria in that they fix CO<sub>2</sub> by the C<sub>3</sub> pathway and are  
1011 typically depleted in <sup>13</sup>C due to assimilation of the lighter carbon that characterises the deeper  
1012 water column (Hollander et al., 1993; Schaeffer et al., 1997).

### 1013 **3.4.3 Biomarkers derived from porphyrin pigments**

#### 1014 **3.4.3.1 Regular and irregular isoprenoids**

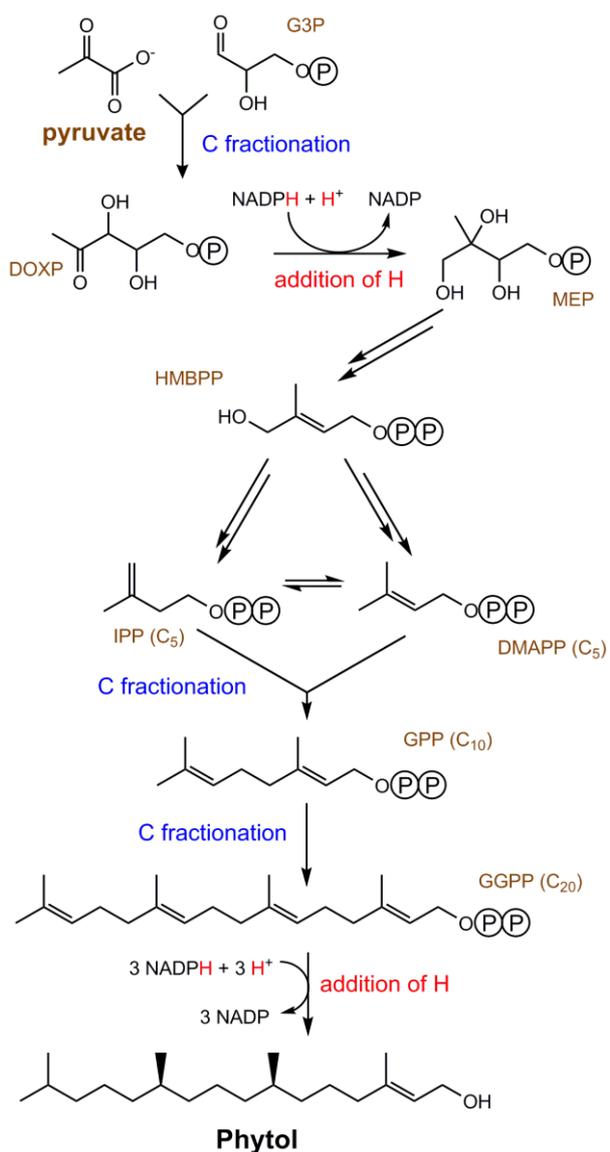
1015 Pristane (Pr) and phytane (Ph), are C<sub>19</sub> and C<sub>20</sub> regular isoprenoid alkanes, respectively, that  
1016 are largely derived from the phytyl side chain of chlorophyll *a* (Fig. 10, phytol biosynthesis in  
1017 Fig. 11) in many photosynthetic organisms, as well as from bacteriochlorophylls *a* and *b* of  
1018 purple sulfur bacteria (Pfenning, 1978). Tocopherols are also precursors of pristane in plants  
1019 (Goossens et al., 1984). Studies from Dead Sea Basin halites and other hypersaline  
1020 sediments reveal other sources to be ether-linked membrane lipids of halophiles (Ph) and the  
1021 C<sub>21</sub> to C<sub>25</sub> regular isoprenoids (Grice et al., 1998). The C<sub>15</sub> regular isoprenoid farnesane is  
1022 largely derived from the side chain of bacteriochlorophylls *c*, *d*, *e* in green sulfur bacteria  
1023 (Pfenning, 1978). Other sources for phytane include methanotrophic bacteria (Freeman et al.,  
1024 1990).

1025 The C<sub>20</sub> irregular isoprenoids crocetane (structure in Table 1) and pentamethylcosane (PMI)  
1026 have been detected in sediments (e.g., Thiel et al., 1999; Barber et al., 2001; Greenwood and  
1027 Summons, 2003), modern cultures and microbes (Summons et al., 1996). Crocetane can be  
1028 a thermally formed product of either archaeal biphytane or isorenieratene from green sulfur  
1029 bacteria (Maslen et al., 2009). PMI is derived from methanotrophic archaea that live in  
1030 symbiosis with sulfate-reducing bacteria, allowing the oxidation of methane under strict anoxic  
1031 conditions (Schouten et al., 1997).

#### 1032 **3.4.3.2 Applications**

1033 The δ<sup>13</sup>C of crocetane can reveal whether it stems from a precursor that was biosynthesized  
1034 by green sulfur bacteria indicative of photic zone euxinia, (values of 11 and -6 ‰) that use the

1035 reverse tricarboxylic acid (TCA) cycle (Summons and Powell, 1986) or by archaea engaging  
 1036 in the anaerobic oxidation of methane (AOM; Orphan et al., 2001; values of -150 ‰). Although  
 1037  $\delta^{13}\text{C}$  of crocetane has not been measured in Quaternary lake sediment records, a novel study  
 1038 by Tulipani et al. (2015) used relative abundances of methyltrimethyltridecylchromans  
 1039 (MTTCs) and  $\delta^{13}\text{C}$  values with other biomarker parameters as indicators of riverine freshwater  
 1040 incursions (i.e., a freshwater lens) into Middle to Late Devonian paleoreefs (Canning Basin,  
 1041 Western Australia), characterised by prevailing anoxia, persistent photic zone euxinia (Spaak  
 1042 et al., 2018) and water column stratification.



**Figure 11:** The mevalonate-independent pathway (“DOXP/MEP pathway”) for the biosynthesis of phytol via the isoprenoid precursors dimethylallyl pyrophosphate (DMAPP) and isopentenyl diphosphate (IPP), starting with pyruvate produced through the Calvin cycle after CO<sub>2</sub> uptake (Fig. 1); DOXP = 1-deoxy-D-xylulose, G3P = glyceraldehyde-3-phosphate, GPP = geranyldiphosphate, GGPP = geranylgeranyldiphosphate, HMBPP = (*E*)-4-hydroxy-3-methyl-but-2-enyl pyrophosphate, MEP = 2-methyl-erythroyl-4-phosphate, NADPH = nicotinamide adenine dinucleotide phosphate (after Sachse et al., 2012).

1043

### 1044 3.5 Isoprenoid biomarkers of *Botryococcus braunii*

#### 1045 3.5.1 Sources

1046 Three races of the unicellular green microalga *Botryococcus braunii* are reported (A, B and L),  
 1047 and are characterized by their hydrocarbon lipids. The B race makes C<sub>30</sub> to C<sub>37</sub> branched  
 1048 isoprenoidal hydrocarbons called botryococcenes, giving rise to the isoprenoidal biomarkers

1049 botryococcane (e.g. Maxwell et al., 1968; Metzger and Largeau, 1999; Grice et al., 1998) and  
1050 a range of cyclic botryococcenes (Metzger et al., 1985) and polymethylatedsqualenes  
1051 (Summons et al., 2002). Botryococcane is biosynthesized by the mutual action of separate  
1052 and distinct squalene synthase enzymes (Niehaus et al., 2011), whereas the L race  
1053 biosynthesise a C<sub>40</sub> isoprenoid hydrocarbon, lycopa-14(E),18(E)-diene (Grice et al., 1998 and  
1054 references therein). B-race biomarkers are indicative of freshwater to brackish lakes and  
1055 saline seas (e.g. Maxwell et al., 1968; Metzger and Largeau, 1999; Grice et al., 1998;  
1056 Summons et al., 2002) from varying latitudes (Tyson, 1995).

### 1057 **3.5.2. Applications.**

1058 Biomarkers derived from *Botryococcus* are more enriched in <sup>13</sup>C compared to other  
1059 phytoplankton biomarkers in both sediments (Huang et al., 1995; Grice et al., 1998; Huang et  
1060 al., 1999; Audino et al., 2001; Summons et al., 2002) and culture (Summons et al., 1996).  
1061 Potential explanations include (1) isotopic fractionation associated with photosynthesis may  
1062 not be fully expressed due to limiting internal pCO<sub>2</sub> in these microalgae, (2) the thick outer  
1063 walls may limit the CO<sub>2</sub> diffusion rates, thereby enriching biomass in <sup>13</sup>C (Boreham et al.,  
1064 1994), and (3) *Botryococcus braunii* utilize a <sup>13</sup>C-rich bicarbonate source (Huang et al., 1999  
1065 and references therein). Sediments recovered from the last glacial maximum have  
1066 *Botryococcus* biomarkers (Huang et al., 1999) that are significantly enriched in <sup>13</sup>C (δ<sup>13</sup>C =  
1067 5%). These values are attributed to low atmospheric pCO<sub>2</sub> and accompanying depletion of  
1068 dissolved CO<sub>2</sub> causing these microalgae to assimilate isotopically heavier bicarbonate from  
1069 their lacustrine environment. The δ<sup>2</sup>H of lipids (e.g., alkadienes, botryococcenes,  
1070 heptadecenes, fatty acids, and phytadiene) from *Botryococcus braunii*, closely follow the δ<sup>2</sup>H  
1071 of the assimilated water (Zhang et al., 2007), and have been used alongside n-alkanes in  
1072 lacustrine oil shales (torbanites) of Permian to Carboniferous age to disentangle dual-source  
1073 systems in tropical and glacial environments (Dawson et al., 2004).

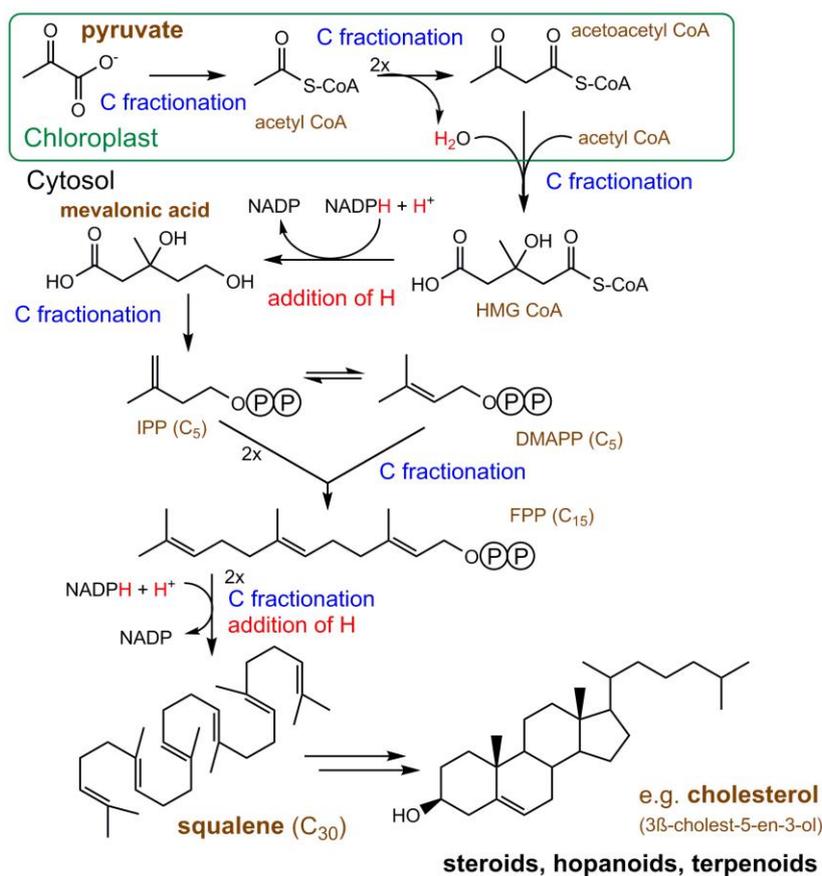
## 1074 **3.6 Bacterial hopanes and hopenes**

### 1075 **3.6.1 Sources**

1076 Bacterial hopanes and hopenes are a class of pentacyclic triterpenoids that comprise  
1077 membrane lipids produced by bacteria (Rohmer et al., 1984). Although only about ~10% of  
1078 bacterial types produce bacteriohopanoids, it is generally not possible to link a given hopanoid  
1079 to a specific bacterial source (Pearson et al., 2007). The use of compound-specific isotopes,  
1080 however, offers tremendous power for distinguishing among potential bacterial sources of  
1081 hopanes and hopenes (Freeman et al., 1990). Hopanoid-producing bacteria in limnic settings  
1082 include photo- and chemoautotrophs, and heterotrophs able to grow on a wide variety of  
1083 carbon sources (Freeman, 1990; Pancost and Sinninghe Damsté, 2003; Sessions, 2016).  
1084 Bacterial hopanoids have long been considered functional analogues of eukaryotic sterols

1085 (Rohmer et al., 1984), although the specifics of their roles in membranes remain the subject  
1086 of extensive investigation (e.g. Poralla et al., 1984; Welander et al., 2009; Blumenberg et al.,  
1087 2012; Eickhoff et al., 2013; Ricci et al., 2017).

1088 Bacteria produce hopanoids from squalene via the mevalonic pathway of squalene  
1089 biosynthesis as shown in Figure 12, starting with pyruvate and followed by cyclization of  
1090 squalene to form the C<sub>30</sub> compounds 17 $\beta$ ,21 $\beta$ (H)-hop-22(29)-ene (diploptene; Table 1) and  
1091 diplopterol, and may build upon the diploptene structure via adenosylhopane to synthesize  
1092 diverse C<sub>35</sub> bacteriohopanepolyols (BHPs, Rohmer, 1993; Bradley et al., 2010). Modifications  
1093 to the hopanoid structure (methylation at C-2 or C-3, unsaturation within the ring structure,  
1094 side-chain length and composition) have traditionally been interpreted as indicators of specific  
1095 bacterial lineages (e.g. Summons et al., 1999; Talbot et al., 2014). However, further research  
1096 indicates it is increasingly likely that the specific distribution of hopane and BHP structures  
1097 reflects environmental conditions or metabolic processes rather than, or in addition to,  
1098 phylogeny (e.g. Ricci et al., 2014; Osborne et al., 2017). Source attribution may yet prove  
1099 more specific for some compounds (e.g. 35-aminobacteriohopane-30,31,32,33,34-pentol in  
1100 Type I methanotrophic bacteria; Neunlist and Rohmer, 1985; Talbot et al., 2003; but see van  
1101 Winden et al., 2012; Rush et al., 2016) or some settings (e.g. hop-17(21)-ene and 2-  
1102 methylhop-17(21)-ene in methanotrophic *Sphagnum* symbionts; van Winden et al., 2010).  
1103 Nonetheless, elucidating the relationships between bacterial hopanoid synthesis and  
1104 environmental conditions will further enhance the information that can be derived from these  
1105 compounds.



1106

1107 **Figure 12:** The “mevalonic pathway” for the biosynthesis of squalene, starting with pyruvate  
 1108 produced through the Calvin cycle after CO<sub>2</sub> uptake (Fig. 1); CoA = co-enzyme A, DMAPP =  
 1109 dimethylallyl pyrophosphate, FPP = farnesyl pyrophosphate, HMG = 3-hydroxy-3-  
 1110 methylglutaryl, IPP = isopentenyl diphosphate, NADPH = nicotinamide adenine dinucleotide  
 1111 phosphate (after Sachse et al., 2012).

1112 In marine and freshwater nitrogen cycling, anaerobic oxidation of ammonium (anammox) to  
 1113 dinitrogen gas (N<sub>2</sub>) with nitrate as an electron acceptor is an important microbial process  
 1114 performed exclusively by anammox bacteria. A stereoisomer of bacteriohopanetetrol (BHT),  
 1115 BHT II, has been unequivocally identified in culture enrichments of anammox bacteria and  
 1116 oxygen minimum zone waters, microbial hotspots responsible for fixed nitrogen removal  
 1117 (Sáenz et al., 2011; Rush et al., 2014). Given the residence time in geological sediments, the  
 1118 BHT isomer is a potential biomarker for past anammox activity (Matys et al, 2017; and potential  
 1119 expansion of OMZs in warmer worlds of Earth’s deep past), which has heretofore eluded  
 1120 detection through ladderane fatty acid abundances in sediments older than 140 ky  
 1121 (Jaeschke et al., 2009).

1122 Carbon isotopic analysis of hopanes and hopenes is by far the most commonly exploited  
 1123 isotope system for bacterial hopanoids (Pancost and Sinninghe Damsté, 2003). In order to  
 1124 deconvolve bacterial hopane and hopenes sources, studies often focus on the stable carbon

1125 isotopic compositions of C<sub>29</sub> to C<sub>31</sub> 17β,21β(H)-hopanes and hopenes (e.g. Aichner et al.,  
1126 2010b; Davies et al., 2016; Zheng et al., 2014). Analysis of functionalized hopanols (e.g.  
1127 diplopterol) can be accomplished through derivatization with BSTFA (e.g. Hollander and  
1128 Smith, 2001), however a correction must be applied to account for carbon added with the  
1129 trimethyl silica moiety (Jones et al., 1991). Although δ<sup>2</sup>H analyses promise to provide  
1130 substantial further information (Osburn et al., 2016; Zhang et al., 2009), few environmental  
1131 studies measuring δ<sup>2</sup>H in hopanoids have been conducted to date (Sessions 2016; Li et al.,  
1132 2009). As the topic of stable hydrogen isotopes in paleoenvironmental research has been  
1133 thoroughly discussed in a recent review (Sessions, 2016), this section focuses on stable  
1134 carbon isotopes.

### 1135 **3.6.2. Applications**

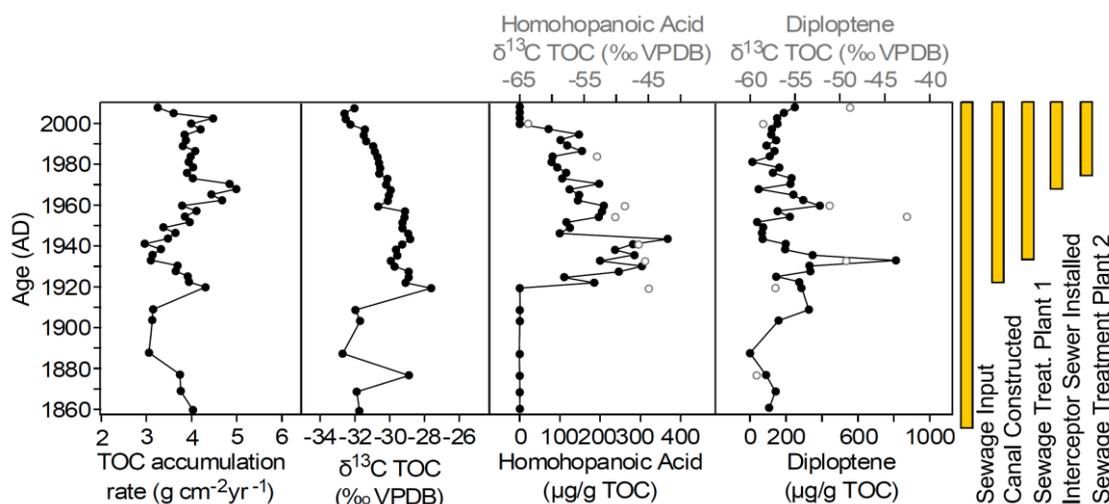
1136 Because carbon source and biosynthetic pathway can have substantial impacts on hopane  
1137 and hopene carbon isotopic composition, the carbon isotopic composition of hopanes and  
1138 hopenes is often used to differentiate photoautotrophic and heterotrophic bacterial sources  
1139 from chemoautotrophic and methanotrophic bacterial sources. This can provide valuable  
1140 insight into lacustrine carbon cycling, sources of sedimentary organic carbon, cryptic changes  
1141 in bacterial community composition, and changes in water column structure. For example,  
1142 Hollander and Smith (2001) demonstrated a striking increase in recycling of carbon associated  
1143 with the post-1900 AD extreme eutrophication of Lake Mendota through the carbon isotopic  
1144 composition of hopanol in tandem with other markers of lacustrine primary producers. A similar  
1145 approach, using compound-specific carbon isotope analyses of hopanes as well as other  
1146 sedimentary lipids (steranes, pristane, phytane) in the ~50 million year old lacustrine Green  
1147 River Formation clearly demonstrated protracted meromixis and abundant chemoautotrophic  
1148 and methanotrophic bacteria (Collister et al., 1992).

1149 Many studies that seek qualitative assessment of intensive methane cycling in wetlands and  
1150 lakes utilize carbon isotope analyses of hopanes. Incorporation of biogenic methane-derived  
1151 carbon into bacterial biomass results in hopanes with substantial depletions in <sup>13</sup>C (Summons  
1152 et al., 1994; Jahnke et al., 1999; but see also Sakata et al., 2008; and Kool et al., 2014).  
1153 Although absence of <sup>13</sup>C-depletion in hopanes and hopenes is inadequate to exclude methane  
1154 cycling, the presence of hopanes or hopenes with carbon isotopic compositions of < -40 ‰ is  
1155 often explained as at least a partial contribution from methanotrophic bacteria (e.g., Freeman  
1156 et al., 1990; Schoell et al., 1994). This is particularly true in wetland deposits where hopanes  
1157 are more depleted in <sup>13</sup>C than ~-34 ‰ are rarely observed (van Winden et al., 2012; Pancost  
1158 et al., 2000). For example, in a study of Holocene wetland deposits, Zheng et al. (2014)  
1159 observed that increased diploptene concentrations with lower δ<sup>13</sup>C<sub>diploptene</sub> (from ~-32 ‰ to -42  
1160 to -50 ‰ around 6.4 to 4 thousand years ago) coincided with decreased abundances of lipids

1161 derived from methanogens and locally dry conditions. Zheng et al., (2014) attribute this  
1162 combination of observations to increased efficiency of aerobic methane oxidation and bacterial  
1163 incorporation of methane-derived carbon under drier conditions. Consequently, drier phases  
1164 had a two-fold impact on wetland methane emissions through decreased methanogenesis as  
1165 well as more efficient aerobic methanotrophy. These findings provide a mechanism linking  
1166 changes in wetland water balance and the Asian monsoon with the mid-Holocene decrease  
1167 in atmospheric methane concentrations, findings which have been robust to further study over  
1168 a longer timescale (18kyr; Huang et al., 2018). For glacial-interglacial cycles, Talbot et al.  
1169 (2014) showed the highest abundance of highly specific BHP biomarkers for aerobic methane  
1170 oxidation, 35-aminobacteriohopane-30,31,32,33,34-pentol (aminopentol) from the Congo  
1171 River Basin correlated with warm intervals. CSIA for BHPs indicate aminopentol was likely  
1172 supplied by terrestrial watershed or gas hydrates/subsurface reservoirs. This study is a  
1173 demonstration of the large potential of aminoBHPs to trace and, once better calibrated and  
1174 understood, quantify past methane sources and fluxes.

1175 In lacustrine settings, methane incorporation into bacterial biomass is greatest in localized  
1176 areas of diffusive methane flux, rather than plant-mediated or ebullition (Davies et al., 2016).  
1177 Even so, several studies have effectively documented changes in incorporation of methane  
1178 derived carbon in hopanoids as a function of climatic conditions (water balance, temperature)  
1179 or anthropogenic factors (eutrophication). Elvert and colleagues (2016) demonstrate that the  
1180 Holocene Thermal Maximum is associated with enhanced methane processing in a North  
1181 American Arctic thermokarst lake. Aichner et al. (2010b), as part of a broad paleolimnologic  
1182 investigation of Lake Koucha in the eastern Tibetan Plateau, observe an increase in the  
1183 concentration of  $^{13}\text{C}$ -depleted hopanoids, including diploptene (-45.5 to -62.7 ‰), beginning  
1184 around 7,000 cal BP. The authors attribute this increase in both bacterial contribution to  
1185 sedimentary organic matter and incorporation of methane-derived carbon into bacterial  
1186 biomass to lake freshening. Naeher et al. (2014) utilize the previously determined  
1187 eutrophication history of Lake Rotsee, Switzerland to examine trends in biomarkers  
1188 associated with methane cycling. This analysis indicated that increased primary productivity  
1189 and stratification led to an increase in the concentrations of  $^{13}\text{C}$ -depleted diploptene (-60 to -  
1190 43 ‰) and homohopanoic acid (-64 to -45 ‰), although the two compounds' concentrations  
1191 and isotopic compositions exhibit a complex relationship, suggesting a larger role for methane  
1192 oxidizing bacteria from the 1930s onward in Lake Rotsee (Fig. 13). While some lake hopanoid  
1193 CSIA datasets indicate active incorporation of methane-derived carbon for long timescales  
1194 (e.g., Street et al., 2012), this is not the case for all lakes (e.g., Huang et al., 1999; Sarkar et  
1195 al., 2014).

1196 Despite the insights afforded by CSIA of bacteriohopanoids into relative changes in the  
 1197 intensity of assimilatory methane oxidation, diverse sources of uncertainty and the  
 1198 idiosyncratic natures of lakes and wetlands impede efforts to devise a generalizable or  
 1199 quantitative proxy for assimilatory methane oxidation or methane emissions. Consequently,  
 1200 much additional work remains to be done to refine the use of hopanoid carbon isotopes to  
 1201 assess past changes in limnic carbon cycling.



1202  
 1203 **Figure 13:** Homohopanoic acid and diploptene reflect changes in methane cycling as a  
 1204 function of anthropogenic impacts on Lake Rotsee, Switzerland (modified from Naeher et al.,  
 1205 2012; 2014). Persistent nutrient inputs associated with sewage inputs, coupled with water  
 1206 balance and sedimentation impacts of canal construction triggered eutrophication and  
 1207 stratification. This increased organic matter supply combined with anoxia drove increases in  
 1208 bacterial productivity (hopanoid concentrations) and incorporation of biogenic methane into  
 1209 bacterial biomass (carbon isotopic composition of hopanoids).

### 1210 3.7 Steroids

#### 1211 3.7.1 Sources

1212 Sterols, the biological precursors of steranes commonly found in sedimentary rocks, are a  
 1213 diverse group of polycyclic isoprenoids (tetracyclic triterpenoids) characteristic of Eukarya  
 1214 (Rohmer et al., 1979; Volkman, 1986). Sterols represent a significant fraction of the lipid pool  
 1215 in marine algae (Jones et al. 1994), and play a key structural role in organisms, including  
 1216 control of cell membrane fluidity, cell signaling, phagocytosis, and stress tolerance (Bloch,  
 1217 1991; Castoreno et al., 2005; Volkman, 2005). Like hopanoids, sterols are biosynthesized  
 1218 following the same mevalonate pathway that produces the C<sub>30</sub> isoprenoid squalene (Figure  
 1219 12, section 3.6). Biosynthesis continues with the epoxidation of squalene (C<sub>30</sub>) to  
 1220 oxidosqualene, followed by a subsequent cyclization to two intermediate molecules  
 1221 (protosterols), cycloartenol and lanosterol, respectively (e.g., Volkman, 2005; Summons et al.,

1222 2006). A series of enzymatic oxidation and decarboxylation steps leads to the formation of  
1223 animal and fungal steroids (e.g., cholesterol [C<sub>27</sub>] and ergosterol [C<sub>28</sub>]) from lanosterol, and  
1224 the formation of plant sterols (e.g., sitosterol [C<sub>29</sub>]) from cycloartenol. In contrast to hopanoids,  
1225 the biosynthesis of sterols is oxygen-dependent (e.g., Summons et al., 2006). Although  
1226 Eukarya are the primary producers of sterols, a limited number of steroid structures have also  
1227 been reported in a small number of bacteria, including cyanobacteria (e.g., Pearson et al.  
1228 2003; Volkman 2003, 2005). A recent study, however, indicates that the potential for bacterial  
1229 sterol synthesis may occur more widely than previously thought (Wei et al., 2016).

1230 The diversity of sterols is determined by the number of carbon atoms in their skeleton (e.g.,  
1231 C<sub>26-30</sub>), the position of hydroxyl (alcohol) functional groups in the ring system, the position of  
1232 unsaturations (double bonds) in the ring structure and side chain, and differences in ring  
1233 and/or side-chain alkylations (e.g., Volkman, 1986; Volkman, 2005). While some sterols can  
1234 be considered characteristic of a given algal class, many of them are widely distributed and  
1235 less diagnostic. For instance, 24-norcholesterol (C<sub>26</sub>) has been reported in some diatom and  
1236 dinoflagellate species (Rampen et al., 2007); cholesterol (C<sub>27</sub>) is typically found in red algae  
1237 and metazoa (Volkman, 1986, 2003; Volkman et al., 1998; Kodner et al., 2008); 24-  
1238 methylcholesterol (C<sub>28</sub>) is present in chlorophyll-c containing algae (dinoflagellates,  
1239 coccolithophores, diatoms) and prasinophytes (Volkman, 1986, 2003; Volkman et al., 1998;  
1240 Kodner et al., 2008; Rampen et al. 2010); 24-ethylcholesterol (C<sub>29</sub>) is found in green algae,  
1241 prasinophytes, diatoms and land plants (Volkman, 1986, 2003; Volkman et al., 1994, 1998;  
1242 Kodner et al., 2008; Rampen et al. 2010); 24-*n*-propyl-cholesterol (C<sub>30</sub>) is present in  
1243 Chrysophytes and pelagophytes (Moldowan, 1984; Volkman et al., 1998). Additionally, 23,24-  
1244 dimethyl-cholesterols are present in dinoflagellates and haptophytes, while 4-methylsterols  
1245 and 4,23,24-trimethylcholesterol (dinosteranes) derive mostly from dinoflagellates (de Leeuw  
1246 et al., 1983; Summons et al., 1987; Withers 1987; Mansour et al., 1999).

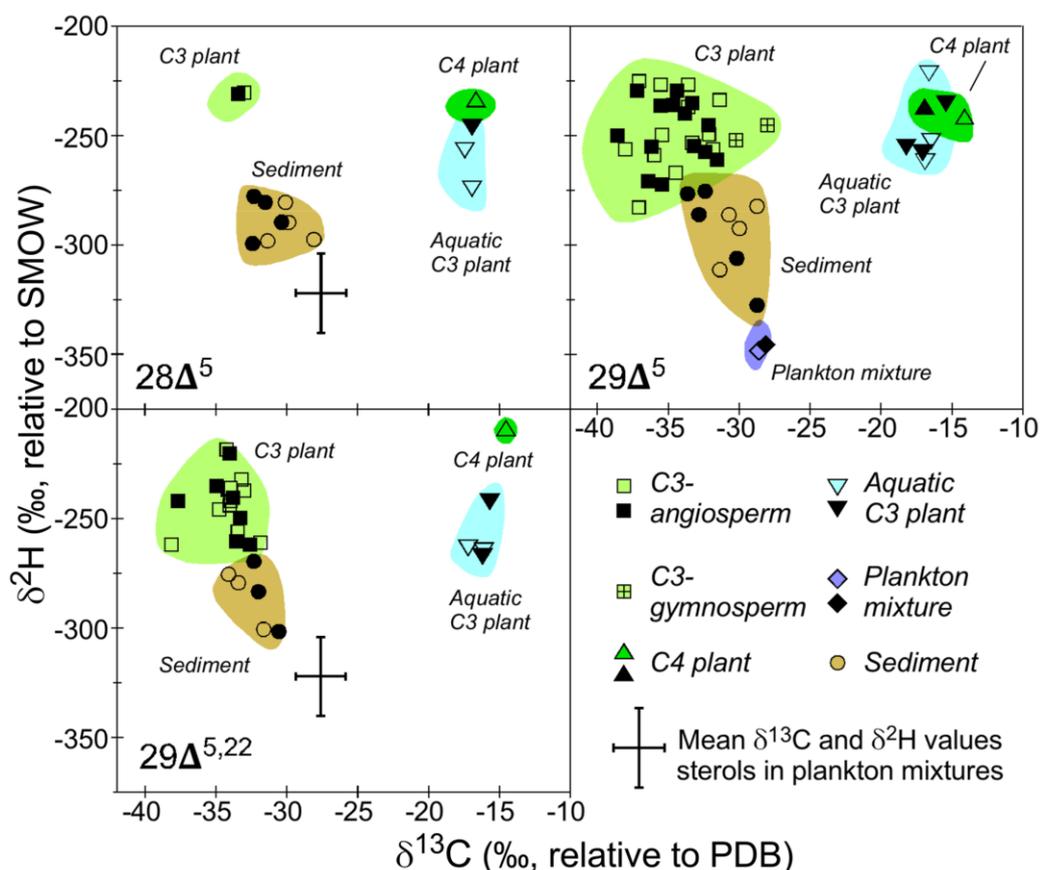
1247 The diagenesis of sterols leads to modifications in their molecular structure as a result of photo  
1248 oxidation, oxidation, reduction, dehydration, rearrangement, hydrogenation, and  
1249 aromatization (e.g., Mackenzie et al., 1982; Meyers and Ishiwatari, 1995; Peters et al., 2005).  
1250 These reactions result in the loss of double bonds and/or hydroxyl groups, and the generation  
1251 of stanols, stanones, sterenes, and aliphatic and aromatic steranes. Due to their broad  
1252 diversity, relative specificity, and stability in sediments, the distribution and abundance of  
1253 sterols and steranes preserved in sedimentary records have been long used in  
1254 paleoenvironmental reconstructions (e.g., Grantham and Wakefield, 1988; Meyers and  
1255 Ishiwatari, 1993; Hinrichs et al., 1999; Menzel et al., 2003; Knoll et al., 2007; Kasprak et al.,  
1256 2015; Brocks et al., 2017).

### 1257 **3.7.2 Applications**

1258 While sterols have been successfully applied in paleolimnological studies to trace changes in  
1259 algal and other organic matter sources (e.g., Aristegui et al., 1996; Matsumoto et al., 2003;  
1260 Tani et al., 2009) or redox changes (Matsumoto et al., 2003), few studies have explored the  
1261 full potential of the ecological and environmental information encoded in their stable isotopic  
1262 composition. The stable carbon isotope composition ( $\delta^{13}\text{C}$ ) of sterols, as well as other algal  
1263 lipids, is controlled by multiple biological and environmental factors, including the isotopic  
1264 composition of dissolved inorganic carbon (DIC), carbon transport mechanisms, isotopic  
1265 fractionation during carbon fixation and biosynthesis, growth rates, cell geometry, and nutrient  
1266 availability, among others (Pancost et al., 1999; Popp et al., 1999, Schouten et al., 1998,  
1267 Hayes, 2001; Pancost and Pagani, 2006, Cernusak, et al., 2013). Thus, if some of the factors  
1268 controlling their stable isotope composition can be constrained, the  $\delta^{13}\text{C}$  of sterols present in  
1269 aquatic environments can be used to, for instance, disentangle changes in biological sources  
1270 (e.g., algal vs. land plants; Matsumoto et al., 1982; Canuel et al., 1997; Neunlist et al., 2002;  
1271 Chikaraishi et al., 2005; Chikaraishi and Naraoka, 2005), the diagenetic transformation of  
1272 sterols to stanols (Neunlist et al., 2002), the possible sources of other algal lipids such as  
1273 alkenones (D'Andrea and Huang, 2005), and prevailing biogeochemical conditions (e.g.,  
1274 nutrient availability, carbon cycling, primary productivity, the concentration and isotopic  
1275 composition of inorganic carbon pools, changes in column stratification; Hollander and Smith,  
1276 2001; Villinski et al., 2008). A step forward in tracing the specific sources of organic matter  
1277 preserved in lacustrine environments is the paired analysis of carbon and hydrogen stable  
1278 isotopes in sterols ( $\delta^{13}\text{C}$ - $\delta^2\text{H}$ ). By using the  $\delta^{13}\text{C}$ - $\delta^2\text{H}$  sterols present in Lake Haruna, Japan,  
1279 Chikaraishi and Naraoka (2005) were able to disentangle the complexity of single and mixed  
1280 (aquatic vs. terrestrial) sources in this setting. For instance, while the  $\delta^{13}\text{C}$ - $\delta^2\text{H}$  values of  
1281 sedimentary 24-methylcholesta-5,22-dien-3 $\beta$ -ol corresponded well to those of planktonic  
1282 algae, the  $\delta^{13}\text{C}$ - $\delta^2\text{H}$  of sterols such as 24-ethylcholest-5-en-3 $\beta$ -ol indicated a mixture of  
1283 sources from terrestrial  $\text{C}_3$  plants and planktonic algae (Fig. 14). Overall, the results from this  
1284 study confirmed observations that  $27\Delta^{5,22}$ ,  $27\Delta^5$ ,  $27\Delta^0$ , and  $28\Delta^{5,22}$  sterols are algal products,  
1285 while  $28\Delta^5$ ,  $29\Delta^{5,22}$ , and  $29\Delta^5$  sterols can derive from multiple sources, thus allowing their more  
1286 reliable use in paleolimnological and paleoclimatic reconstructions.

1287 The  $\delta^{13}\text{C}$  of sterols, along with other algal and bacterial biomarkers preserved in lake  
1288 sediments, has also been utilized to develop eutrophication models over time (Hollander and  
1289 Smith, 2001). By studying the diversity, mass accumulation rate, and  $\delta^{13}\text{C}$  of biomarkers  
1290 present in sediment from Lake Mendota (south-central Wisconsin, USA), in addition to the  
1291 present-day isotopic dynamics in the lake water column, these authors produced  
1292 eutrophication models (from moderate to severe) that take into account changes in eukaryotic-

1293 and microbially-derived productivity over time. Notably, these models allow to explain how  
 1294 microbially-mediated carbon cycling processes can influence the  $\delta^{13}\text{C}$  record of bulk  
 1295 sedimentary organic carbon, and thus provide insight into interpreting carbon isotopic trends  
 1296 preserved in lacustrine records. Additionally, the presence of  $^{13}\text{C}$ -depleted sterols in sediment  
 1297 of Ace Lake in Antarctica was used to constrain the presence of aerobic methanotrophic  
 1298 bacteria and an active methane cycle in this setting during the Holocene (Coolen et al., 2004b).



1299  
 1300 **Figure 14:** Cross plots of  $\delta^{13}\text{C}$ - $\delta^2\text{H}$  of  $28\Delta^5$ ,  $29\Delta^{5,22}$ , and  $29\Delta^5$  sterols from the Lake Haruna  
 1301 environment. Open and filled symbols indicate the naturally occurring i.e. “free” sterols and  
 1302 bound forms, respectively (modified from Chikaraishi and Naraoka, 2005).

1303 More recently, along with other algal lipids such as alkenones (Section 3.2), the  $\delta^2\text{H}$  of sterols  
 1304 present in aquatic environments has increasingly been used as a proxy for the  $\delta^2\text{H}$  of  
 1305 environmental water ( $\delta^2\text{H}_{\text{water}}$ , see review by Sachse et al., 2012). Sauer et al. (2001b) first  
 1306 showed that the  $\delta^2\text{H}$  of 24-methylcholest-3-ol, 24-ethylcholest-5,22-dien-3-ol, and 4,23,24-  
 1307 trimethylcholesterol extracted from aquatic sediments exhibited a rather constant fractionation  
 1308 (around  $\sim 201 \pm 10\text{‰}$ ) with respect to environmental water. Since then, a growing body of  
 1309 research has demonstrated that, besides  $\delta^2\text{H}_{\text{water}}$ , biological factors such as biosynthetic  
 1310 pathways, secondary hydrogen exchange, growth rates, in addition to environmental factors

1311 such as salinity, temperature, and nutrient availability can influence hydrogen isotope  
1312 fractionation and the  $\delta^2\text{H}$  of sterols (Sessions et al. 1999, Li et al. 2009, Chikaraishi et al. 2004,  
1313 Zhang and Sachs 2007; Zhang et al., 2009; Sachse et al., 2012; Romero-Viana, 2013; Nelson  
1314 and Sachs, 2014). Over the past few years, the  $\delta^2\text{H}$  of source-specific sterols such as  
1315 dinosterol have also been shown to be controlled by salinity. The  $\delta^2\text{H}$  of dinosterol present in  
1316 suspended particles and surface sediment from the Chesapeake Bay (salinity range of 10–29  
1317 PSU) exhibits a  $^2\text{H}/^1\text{H}$  fractionation that decreases by  $0.99 \pm 0.23$  per unit increase in salinity  
1318 (Schwab and Sachs, 2011). While the exact mechanism controlling isotopic fractionation  
1319 under varying salinity remains elusive, the observed relationship in sterols and other lipids  
1320 supports qualitative to semi-quantitative reconstructions of past salinities from sedimentary  
1321 dinosterol  $\delta^2\text{H}$  values. For example, the  $\delta^2\text{H}$  of dinosterol preserved in sediments from a  
1322 brackish lake in Palau (Sachs et al., 2009; Richey and Sachs, 2016) and an endorheic lake in  
1323 Galápagos (Atwood and Sachs, 2014; Nelson and Sachs, 2016), have been used to infer  
1324 variations in salinity and precipitation associated with latitudinal shifts in the position of the  
1325 Intertropical Convergence Zone during the Late Holocene. The information embedded in the  
1326  $\delta^2\text{H}$  of sterols in sedimentary records, however, is gradually lost over geologic timescales due  
1327 to hydrogen exchange with increasing thermal maturity (Sessions, 2016).

### 1328 **3.8 Sedimentary cellulose**

#### 1329 **3.8.1 Sources**

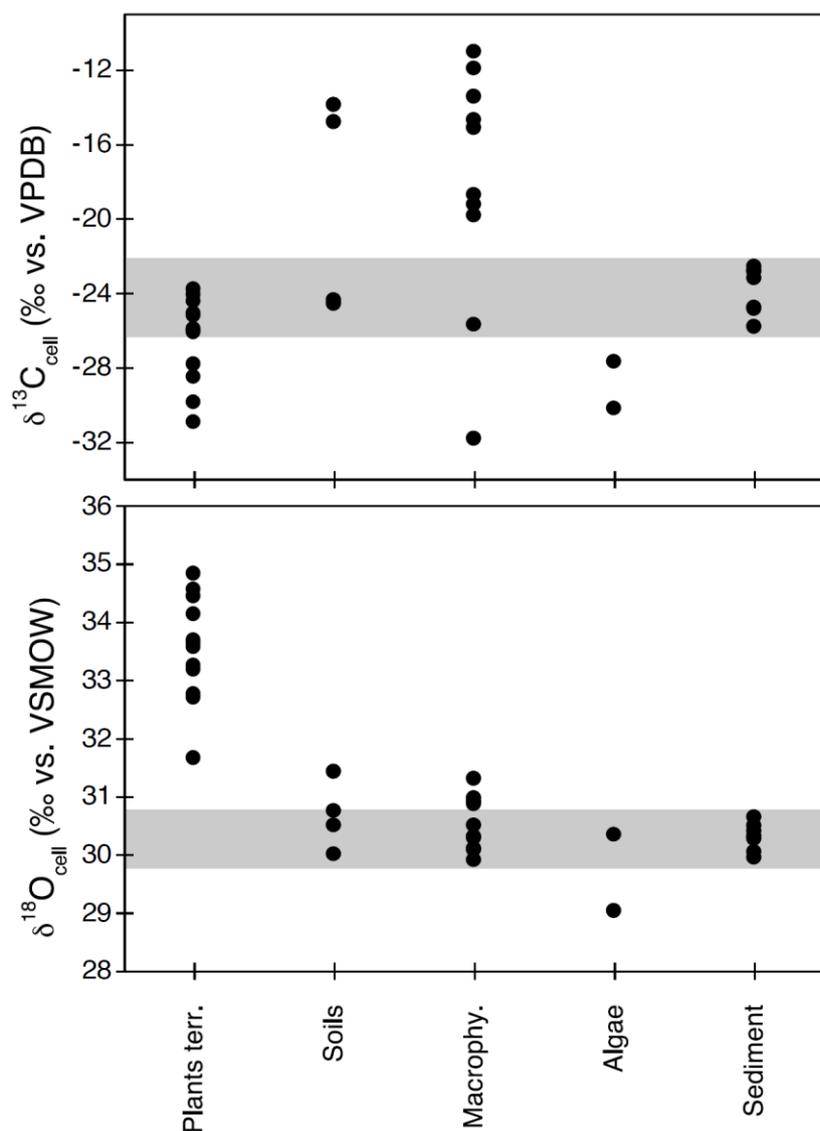
1330 Cellulose is a structural carbohydrate and plays an essential role for cell growth and  
1331 development of higher plants forming a major component of vascular plant organic matter  
1332 (Khezami et al., 2005). Non-vascular plants, such as bryophytes and some algae (Rho and  
1333 Litzky, 1979; Koyama et al., 1997), and bacteria (Ross et al., 1991) are also capable to  
1334 synthesize cellulose. Potential sources for sedimentary cellulose are therefore terrestrial  
1335 plants, soils, aquatic macrophytes, bacteria, and algae. Cellulose is biosynthesized from initial  
1336 photosynthates (trioses) converted to hexoses and condensed to form cellulose (Hayes,  
1337 2001). Cellulose microfibrils, consisting of bundles of cellulose molecules, are completely  
1338 embedded into a matrix of polysaccharides (hemicellulose) and small amounts of structural  
1339 proteins in cell walls (Showalter, 1993; Popper et al., 2011) and, thus, not easily accessible  
1340 for decomposing organisms.

#### 1341 **3.8.2 Applications**

1342 The isotopic composition of oxygen, carbon, and hydrogen in the molecular structure of  
1343 aquatic cellulose provides information on cellulose origin, the lacustrine carbon cycle and the  
1344 lake-water balance. Here, we focus on the determination of the oxygen isotope composition  
1345 of sedimentary cellulose ( $\delta^{18}\text{O}_{\text{cell}}$ ), which either can be of terrestrial (litter, plant debris, soil) or

1346 aquatic origin (aquatic macrophytes, algae, bryophytes). The  $\delta^{18}\text{O}$  value of aquatic cellulose  
1347 is closely linked to the host water isotopic composition (Sauer et al., 2001a; Sternberg et al.,  
1348 2007; Zhu et al., 2014a; Mayr et al., 2015), while terrestrial cellulose is generally more  $^{18}\text{O}$ -  
1349 enriched due to soil evaporation and leaf water transpiration (Roden et al., 2000). In many  
1350 cases, aquatic and terrestrial cellulose sources contribute to bulk sediment  $\delta^{18}\text{O}_{\text{cell}}$  values,  
1351 which is a challenge for paleoenvironmental interpretation. In this respect, multiple-proxy  
1352 approaches, including analyses of C/N ratios of bulk sediment and  $\delta^{13}\text{C}$  of cellulose, can give  
1353 valuable clues for interpretation (Heyng et al., 2014, c.f. Figure 15). Alternatively, identifiable  
1354 cellulose-containing microfossils can be extracted from the sediment and analysed. Hence,  
1355 some studies focus on cellulose extracted from aquatic moss remains in sedimentary  
1356 sequences (Mayr et al., 2013; Zhu et al., 2014b). In other cases, the environmental setting  
1357 precludes major terrestrial cellulose input, e.g. for lakes with very small or scarcely vegetated  
1358 catchments (Heyng et al., 2014).

1359 The  $\delta^{18}\text{O}$  values of cellulose, calcite and diatom opal from the Last Glacial to Holocene time  
1360 intervals of the sediment record of Polish Lake Gosciadz were analysed to disentangle host  
1361 water isotope variations from temperature changes (Rozanski et al., 2010). While at least two  
1362 unknowns, temperature and host-water  $\delta^{18}\text{O}$ , influence calcite and opal  $\delta^{18}\text{O}$  values,  $\delta^{18}\text{O}_{\text{cell}}$   
1363 was used to directly reconstruct host-water  $\delta^{18}\text{O}$  and thus resolve temperature- $\delta^{18}\text{O}$  equations  
1364 of the other proxies. A similar approach was used for a 6000-year long, Holocene record from  
1365 Lake Pupuke, New Zealand (Heyng et al., 2015). In that study,  $\delta^{18}\text{O}$  values of biogenic opal  
1366 and  $\delta^{18}\text{O}_{\text{cell}}$  were combined to reconstruct fluctuations of lake-water temperatures and  
1367 compared with independent temperature reconstructions using GDGTs. Both temperature  
1368 reconstructions matched comparatively well. In dry regions, the lake-water-isotope  
1369 composition is strongly influenced by evaporative heavy-isotope enrichment. Host-water-  
1370 isotope reconstructions from  $\delta^{18}\text{O}_{\text{cell}}$  can then provide information about past lake-water  
1371 balance and regional hydrology in such areas. Zhu et al. (2014b) used  $\delta^{18}\text{O}_{\text{cell}}$  of submerged  
1372 aquatic mosses from sediments of Laguna Potrok Aike to reconstruct lake-water  $\delta^{18}\text{O}$  of this  
1373 Patagonian steppe lake during the last deglaciation.



1374

1375 **Figure 15:** Stable isotope composition of cellulose from autochthonous and allochthonous  
 1376 sources and sediment from a modern survey at Lake Pupuke (Heyng et al., 2014). Shown are  
 1377  $\delta^{13}\text{C}_{\text{cell}}$  (upper) and  $\delta^{18}\text{O}_{\text{cell}}$  (lower) values from terrestrial plants, soils, aquatic macrophytes,  
 1378 lacustrine algae, and lake sediments (upper 30 cm). Grey bars indicate the range of Lake  
 1379 Pupuke's sediments. Note the  $^{13}\text{C}$  enrichment of aquatic macrophytes in that lake, while  
 1380 terrestrial plant cellulose is strongly  $^{18}\text{O}$  enriched compared to other sources and sediments.

### 1381 3.9 Organic sulfur compounds

#### 1382 3.9.1 Sulfur sources

1383 The use of stable isotopes to understand the biogeochemical cycling of sulfur in oceanic (Rees  
 1384 et al., 1978; Jørgensen et al., 2004; Böttcher et al., 2006), freshwater (Fry, 1986; Canfield et  
 1385 al., 2010; Zerkle et al., 2010), and terrestrial systems (Goldhaber and Kaplan, 1980; Habicht  
 1386 and Canfield, 2001) has principally focussed on the dynamics of inorganic sulfate, sulfide and  
 1387 their intermediate species. Organic sulfur compounds (OSCs) in sedimentary organic matter

1388 are predominantly incorporated via secondary processes (Werne et al., 2008). The major  
1389 sulfurization pathway involves an abiotic reaction of reduced inorganic sulphur species during  
1390 diagenesis (e.g., pore water HS<sup>-</sup>; or polysulfides, S<sub>x</sub><sup>2-</sup>) that is produced by microbial sulfate  
1391 reduction (Kaplan and Rittenberg, 1964; Fry et al., 1986). OSCs deposited from biological  
1392 sources (e.g., the amino acid cysteine), which are synthesized through direct reduction and  
1393 assimilation of dissolved sulfate, are very labile to diagenetic loss (Hedges, 1992; Hedges and  
1394 Keil; 1995), but may still contribute to sedimentary organic matter which commonly has δ<sup>34</sup>S  
1395 values that range between those of biotic (relatively high δ<sup>34</sup>S) and abiotic (lower δ<sup>34</sup>S) end  
1396 members (Canfield et al., 1998; Passier et al., 1999; Werne et al., 2003; Aizenshtat and  
1397 Amrani, 2004). Few studies (e.g., Amrani et al., 2009; Oduro et al., 2011, 2012) have looked  
1398 at the S isotope composition of OSC.

1399 Thermochemical sulfate reduction (TSR) can also contribute high concentrations of OSCs in  
1400 gas (i.e., high H<sub>2</sub>S) reservoirs. TSR is a high temperature redox process in which sulfates,  
1401 such as gypsum or anhydrite, are reduced and organic matter oxidised (Krouse et al., 1988;  
1402 Cross et al., 2004). TSR can significantly influence the δ<sup>34</sup>S of OSCs, which will gradually  
1403 inherit the δ<sup>34</sup>S value of the mineral sulfates utilised, these are typically relatively heavy  
1404 compared to OSCs from reduced S sources (Amrani et al., 2012).

1405 In recent years the advent and utilization of quadruple sulfur isotopes (<sup>32</sup>S, <sup>33</sup>S, <sup>34</sup>S, and <sup>36</sup>S)  
1406 has allowed for increased resolution and fingerprinting of the biological and abiotic processes  
1407 that govern sulfur cycling. The minor isotopes (<sup>33</sup>S, and <sup>36</sup>S) are subject to inorganic and  
1408 organic fractionation mechanisms that are similar to those for <sup>34</sup>S. Experimental studies have  
1409 shown that biological S metabolisms produce minor isotope patterns, with characteristics  
1410 attributed to differences in the individual step controls of the metabolic pathways (Farquhar et  
1411 al., 2003, 2007; Johnston et al., 2005, 2007, 2008; Ono et al., 2006). The incorporation of  
1412 minor isotopes into studies allows for fuller characterisation within biogeochemical systems  
1413 (at both the cellular and ecosystem level) and as such can be used to assess the contribution  
1414 of different pathways (enzymatic or biogeochemical) to the measured isotopic values.

### 1415 **3.9.2 Applications**

1416 Early biogeochemical applications of CSIA of sulfur-containing compounds have included  
1417 studies of the mechanism and timeframes of diagenetic organic sulfurization and cycling in  
1418 sediments, the characterisation of ocean-derived sulfur aerosols, exploration for oil and  
1419 mineral resources and other paleo-environmental reconstructions. Further details of the first  
1420 of these, as applied to modern settings, follow:

1421 *Diagenetic sulfurization pathways*

1422 A combination of syngeneic (water column) and diagenetic (sediment) S sources in immature  
1423 sediments from the Cariaco Basin were identified by  $\delta^{34}\text{S}_{\text{OSCs}}$  (Raven et al., 2015). These two  
1424 main organic sulfurization mechanisms consisted of:

1425 i) Reaction of dissolved  $\text{HS}^-$  with OM resulting in the intra-molecular addition of available S.  
1426 Difficulties in releasing intra-molecularly bound S make this a relatively irreversible  
1427 reaction. The incorporation of  $^{32}\text{S}$  would be kinetically favored, thus, leading to organic S  
1428 lower in  $^{34}\text{S}$  than  $\text{HS}^-$  and more similar to co-existing pyrite.

1429 ii) Reaction of OM with polysulfides ( $\text{S}_x^{2-}$ ) resulting in an intermolecular addition and  
1430 formation of  $\text{S}_x$ -bridges between different organic units. A reverse of this process could  
1431 subsequently release the  $\text{S}_x$ -bridges from the organic moiety, such that  $\delta^{34}\text{S}$  of this organic  
1432 S would be reflective of the equilibrium status of these reactions.

1433 Raven et al. (2015) considered pathway ii) to be most likely responsible for the relative  $^{34}\text{S}$   
1434 enrichment (e.g. Amrani and Aizenshtat, 2004) traditionally attributed to organic sulfurization  
1435 and the formation of the kerogen fraction.

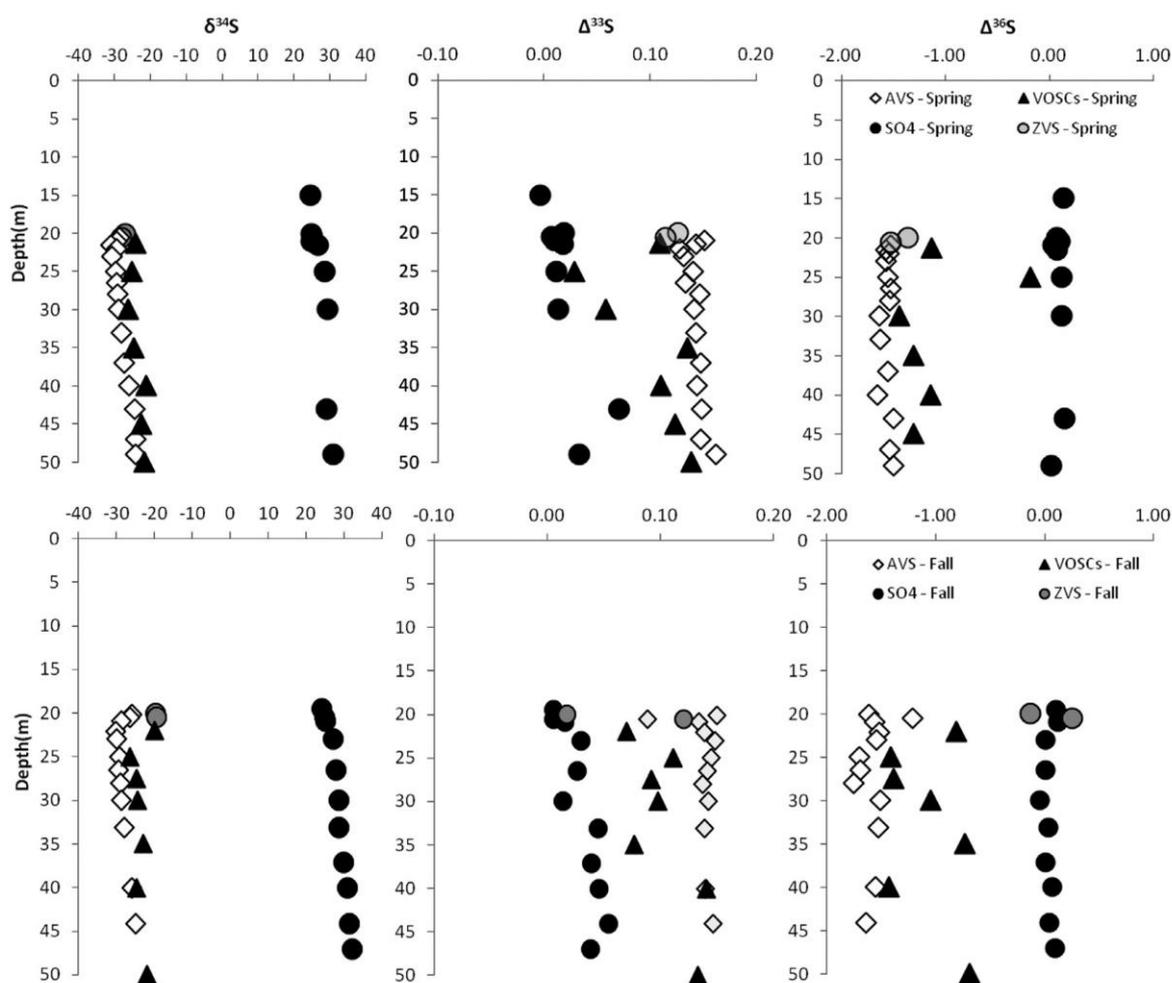
#### 1436 *Tracing organic sulfur cycling in modern lakes*

1437 Oduro et al. (2013) and Zerkle et al. (2010) utilized quadruple S isotope systematics and zero-  
1438 valent sulfur (ZVS), volatile organic sulfur compounds (VOSCs) and acid-volatile sulfur (AVS)  
1439 profiles as part of a multi-year study on the meromictic Fayetteville Green Lake (FGL, Fig. 16).  
1440 Stratification in the lake is mainly controlled via the inflow of highly saline groundwater,  
1441 resulting in a strongly developed chemocline, while the source of both organic and inorganic  
1442 sulfur is from high sulfate concentration in the water column. These conditions make the site  
1443 a natural analogue for ancient environments.

1444 Zerkle et al. (2010) showed that at the chemocline sulfide is enriched in  $^{34}\text{S}$  as a result of  
1445 sulfide oxidation via reaction with  $\text{O}_2$ , from the oxidized freshwater above, in spite of the high  
1446 population of phototrophic S-oxidizing organisms observed at the chemocline. They further  
1447 suggested that the production of product sulfur species, e.g., thiosulfate, sulfite, or zero-valent  
1448 sulfur, was a result of very fast turnover of S-intermediates by oxidation and/or  
1449 disproportionation processes around the chemocline. Their data also showed seasonal  
1450 variations in isotopic enrichment at the chemocline as a result of greater contribution from  
1451 phototrophic S-oxidation reactions under higher light availability in spring and summer. ZVS  
1452 in the chemocline in autumn is suggested to reflect production and re-oxidation by  
1453 phototrophic processes, including intercellular isotope exchange between  $\text{S}_0$ , polysulfides,  
1454 and sulfide, and further oxidation of ZVS to sulfate. Smaller fractionations between sulfide and

1455 zero-valent sulfur in April suggest a metabolic rate control on the extent of fractionation, similar  
1456 to that of sulfate-reducing prokaryotes.

1457 Oduro et al. (2013) built upon this study by quantifying VOSCs in the lake and highlighting the  
1458 various biotic and abiotic pathways available for methylated and non-methylated VOSCs  
1459 production and cycling in sulfidic freshwater environments (Fig. 16). These applications, while  
1460 focused on modern-day lakes, have implications for our abilities to identify such processes in  
1461 the preserved horizons of paleolakes and similar environments. While such studies of VOSCs  
1462 in the ancient rock record are limited due to issues of maturity, the overprints and alteration,  
1463 greater understanding of these processes in modern analogues may provide a new way to  
1464 fingerprint products of these processes that are identifiable in the rock record. Further, with  
1465 the development of new analytical techniques, greater machine resolution, the ability to  
1466 screen, and reduce, post-deposition organic contaminants, and better sample processing  
1467 (e.g., Brocks et al., 2008; Brocks and Hope, 2013) we can hope to soon be able to readily  
1468 identify these compounds in the rock record.



1469  
1470 **Figure 16:** Depth profiles of the multiple sulfur isotope composition of different sulfur species  
1471 (Sulfate –  $\text{SO}_4^{2-}$ , Acid Volatile Sulfur - AVS, Volatile Organic Sulfur Compounds – VOSCs, and

1472 Zero-Valent Sulfur – (ZVS) in Fayetteville Green Lake (FGL) for Spring, 2009 and Fall, 2008.  
1473 From Oduro et al., 2013, including data from Zerkle et al., 2010)

1474 In addition, the studies discussed above highlighted the role of simultaneous biological and  
1475 abiotic processes in freshwater environments that promote the formation of VOSCs and then  
1476 their diffusion to the atmosphere. Further characterization of these processes will aid in  
1477 improving estimate of the atmospheric sulfur budget in present and Recent times.

## 1478 **4 SUMMARY AND OUTLOOK**

1479 Over the past four decades, applications of CSIA have vastly expanded into multiple  
1480 paleoenvironmental applications using an extended range of isotopes and ever more  
1481 sophisticated analytical techniques. The study of carbon and hydrogen isotopes of  
1482 hydrocarbons such as *n*-alkanes is by now well-established as they are non-functionalized, of  
1483 well-understood origin and straightforward to analyse. However, there remain a number of  
1484 challenges, and particularly so for compounds where the biosynthetic pathway is not fully  
1485 understood, the source varies, or where there are analytical constraints.

### 1486 **4.1 General problems**

#### 1487 ***i) Biosynthesis***

1488 It has been observed that compounds produced through different biosynthetic pathways can  
1489 differ in their carbon isotope value by up to 20% within an individual organism (e.g., Summons  
1490 et al., 1994; Schouten et al., 1998; van der Meer et al., 1998). However, the exact mechanisms  
1491 leading to these isotopic differences are often not well-constrained (Hayes, 2001), which may  
1492 lead to ambiguous results unless biochemical studies improve our understanding of  
1493 differentiated fractionation within source organisms of biomarkers targeted by CSIA.

#### 1494 ***ii) Ecological factors***

1495 A key factor imposing carbon and hydrogen isotopic variation in land plants is water-use  
1496 efficiency, as observed in C3, C4 and CAM plants (Ehleringer et al., 1993), which is controlled  
1497 by local hydrology. In case of aquatic organisms, a range of ecological factors has been found  
1498 to inflict isotopic variation, including the partial pressure of CO<sub>2[*aq*]</sub> (*p*CO<sub>2[*aq*]</sub>), cell size and  
1499 geometry (Goericke et al., 1994; Popp et al., 1998), virus interactions and the growth rate of  
1500 phytoplanktonic cells (Laws et al., 1995; Bidigare et al., 1997; Chivall et al., 2014). These  
1501 findings highlight the need of culture studies, in particular, of lacustrine primary producers  
1502 since most of such investigations so far, like the ones cited above, have been aimed at marine  
1503 or coastal species.

#### 1504 ***iii) Source uncertainties***

1505 *In-situ* microbial biomass may add to and bias CSI data of supposedly aquatic or terrestrial  
1506 sources, and the distinction between genuine change in the isotopic composition of  
1507 sedimentary compounds and changing proportions of *in-situ* biomass often poses a challenge.  
1508 In this context, combining biomarker CSI and rDNA analyses in order to pin down the source  
1509 of specific microbial compounds appears highly promising (e.g., Coolen et al., 2004b).

1510 We have already pointed out some of the more specific challenges associated to isotope  
1511 analyses of the various compound classes discussed in Section 3. However, challenges  
1512 typically come along with opportunities, in this case, of further paleolimnological information  
1513 gained through extended approaches to CSIA, which we expand on in the following.

#### 1514 **4.2 Targeting the C and H of alkyl lipids – the easy, the tricky, and the prospective**

1515 Applications of CSIA of alkyl lipids as presented in Section 3.1 illustrate the great potential of  
1516 such measurements for the development of paleohydrological proxies in Quaternary  
1517 paleolimnology on a range of different time-scales, from the early Pleistocene to the Holocene.  
1518 However, these examples, as well as recent reviews (e.g., Eglinton and Eglinton, 2008;  
1519 Sachse et al., 2012; Reiffarth et al., 2016; Sessions, 2016; Diefendorf and Freimuth, 2017),  
1520 also indicate some gaps in our understanding of alkyl lipid stable isotopes. The fractionation  
1521 pathways of stable carbon isotopes and stable hydrogen isotopes, in particular, need to be  
1522 better understood in order to be able to arrive at robust reconstructions of paleohydrological  
1523 changes. Changes in species distribution in response to ecosystem adaption to environmental  
1524 change alone may be responsible for significant change in the  $\delta^2\text{H}$  values of non-species-  
1525 specific aquatic biomarkers (e.g., Rach et al., 2017). Laboratory-based growth experiments  
1526 as well as studies of isotope fractionation in modern ecosystems continue to expand the  
1527 knowledge of the biogeochemical fingerprint of the various OM sources and our understanding  
1528 of the origins and functions of alkyl lipids through time. Despite the many influences on the  
1529  $\delta^2\text{H}$  or  $\delta^{13}\text{C}$  values of alkyl lipids in environmental archives, much of the variability that results,  
1530 e.g., from seasonality or the patchiness of organic matter sources in the catchment of the  
1531 studied archive is averaged out due to intermediate storage of the compounds over extended  
1532 time intervals in soils and/or along transport across the catchment (e.g., Oakes and Hren,  
1533 2016). Still, the effects of changes in the source vegetation on CSI records are often  
1534 understudied and cannot be determined by isotope analysis alone (e.g., Hadley et al., 2008;  
1535 Rach et al., 2017). Studies combining independent indicators of vegetation change, such as  
1536 pollen or macrofossil analysis, and compound-specific stable isotope analyses can highlight  
1537 where factors other than climate played a role. Such information is especially needed when,  
1538 e.g.,  $\delta^2\text{H}$ -records of long-chain *n*-alkyl lipids are used to calculate terrestrial evaporation (e.g.,  
1539 Sachse et al., 2004; Rach et al., 2014) as this has been problematic in cases where vegetation  
1540 was diverse and showed spatiotemporal variability (e.g., Berke et al., 2012; Rao et al., 2014;

1541 Rach et al., 2017; van den Bos et al., 2018).

1542 Furthermore, the importance of the soil organic matter pool as a source of biomarkers in  
1543 sedimentary records is increasingly recognised. Systematically changing offsets, for example,  
1544 in  $\delta^{13}\text{C}$  values between suberin-derived mid-chain ( $\text{C}_{22}$ ) and cuticular long-chain lipids ( $>\text{C}_{26}$ )  
1545 have been reported (Holtvoeth et al., 2017). However, despite the apparent environmental  
1546 control, they cannot be interpreted unless the mechanisms behind the mismatch between  
1547 cuticular and suberin alkyl lipid CSI are understood. In this context, the transport pathways of  
1548 biomarkers from their source to the sediment archive are currently understudied. Specific  
1549 organic matter fractions are likely associated to certain grain size fraction in soils as well as  
1550 sediments (Baldock and Skjemstad, 2000; Gentsch et al. 2015; Wakeham and Canuel, 2016).  
1551 Therefore, the combination of paleohydrological and mineralogical data with source-sensitive  
1552 CSI data is advisable. Where possible, alkyl lipids and their isotope values from extant sources  
1553 should be investigated in order to reduce the uncertainty in the interpretation of CSI data from  
1554 environmental archives (e.g., Eley et al., 2016). Studies that use multiple *n*-alkyl compounds  
1555 (e.g., *n*-alkanes, *n*-alkanoic acids) or combine  $\delta^{13}\text{C}$  and  $\delta^2\text{H}$  measurements are still few but  
1556 will likely enhance our understanding of how alkyl lipids are ultimately preserved in geological  
1557 records (Sachse et al., 2012; Sessions, 2016; Diefendorf and Freimuth, 2017).

1558 Long-chain alkenones remain a challenge for CSI studies in lakes due to the biodiversity of  
1559 their source organisms and, therefore, the uncertainty associated to the ecological drivers of  
1560 lacustrine alkenone production and isotope fractionation during biosynthesis. Similar to the  
1561 marine biome, salinity appears to be a major factor affecting the  $\delta^2\text{H}$  value of lacustrine  
1562 alkenones, in addition to assumed effects of growth rate (e.g., Chivall et al., 2014). Thus,  $\delta^2\text{H}$   
1563 values of lacustrine alkenones may potentially be applied to lake systems that experienced  
1564 large climatically controlled changes in salinity throughout their evolution once the sources of  
1565 the alkenones have been ascertained. As phylogenetic shifts among the alkenone producers  
1566 are also likely to correlate with environmental changes, it appears advisable to combine CSI  
1567 with DNA studies of alkenone producers in both modern and ancient contexts, in particular,  
1568 with regard to alkenone producers in freshwater systems that are currently under-investigated.

#### 1569 **4.3 Propping up steroids and hopanoids**

1570 The  $\delta^{13}\text{C}$  and  $\delta^2\text{H}$  of algal sterols and steranes offers great potential for the reconstruction of  
1571 Quaternary ecosystems and environments. This includes changes in organic matter sources,  
1572 shifts in algal communities and productivity, as well as variations in the isotopic composition  
1573 of DIC and meteoric water, and salinity. However, the need for multiple purification steps prior  
1574 to analysis and for correction of the determined isotope ratio for derivatised carbon and  
1575 hydrogen atoms currently precludes a more routine use of sterols in high-resolution

1576 paleoenvironmental studies. Dinosterol has become the most commonly used sterol for CSI  
1577 analysis, particularly for  $\delta^2\text{H}$ , due to its biological specificity compared to other sterols. Several  
1578 new preparatory protocols using high performance liquid chromatography (HPLC) have been  
1579 developed for its purification from complex sterol/alcohol mixtures (e.g., Smittenberg and  
1580 Sachs, 2007; Atwood and Sachs; 2012; Nelson and Sachs, 2013).

1581 CSIA determined from hopanes will have continued utility in deconvolving modern and ancient  
1582 carbon cycling. Whereas bacterial inputs, especially with respect to inputs of methanotroph-  
1583 derived material (c.f. Talbot et al 2014; Raghoebarsing et al., 2005), as such do not  
1584 demonstrate that methanotrophy was actually taking place, significantly  $^{13}\text{C}$ -depleted  
1585 hopanoids are difficult to explain otherwise. Stable isotope probing and “pulse-chase”  
1586 experiments are likely to offer substantial advances in understanding the applications and  
1587 limitations of compound-specific isotope analysis of hopanoids (Crossman et al., 2001). CSIA  
1588 of derivatized BHPs improves our ability to analyze compounds with potentially greater  
1589 source/metabolic specificity; this will certainly fuel new and broader applications. For instance,  
1590 further work on applications of the BHT isomer as a potential biomarker for anammox activity  
1591 will greatly expand our knowledge of the complexity of nitrogen fixation processes in lacustrine  
1592 ecosystems. A better understanding of the drivers of hopanoid synthesis will improve  
1593 application of all hopanoid-based proxies. Coupling hopanoid CSIA with archaeal lipids is a  
1594 powerful approach to reconstructing prokaryotic roles in past ecosystems and response to  
1595 environmental change.

#### 1596 **4.4 Shedding light on pigments**

1597 Research into disentangling the complex array of factors that affect the synthesis,  
1598 transformation and sedimentation of pigment transformation products in the modern  
1599 environment is required to facilitate a more rigorous approach to interpreting isotope ratios in  
1600 pigments extracted from sediments. For example, we can anticipate that further work on  
1601 phaeopigments, such as limnic phaeophytin and pyropheophytin (Tyler et al., 2010),  
1602 especially in redox-stratified basins (Fulton et al., 2018), will improve paleoenvironmental  
1603 interpretations of chlorin-specific isotopic data. In addition, studies focused on environmental  
1604 conditions, including the impact of oxygen (particularly in the case of maleimides, c.f. Naeher  
1605 et al. 2013) can assist the development of novel proxies for estimating the degree of organic  
1606 matter degradation on a variety of timescales.

#### 1607 **4.5 Buttressing cellulose**

1608 Interpretation of sedimentary cellulose  $\delta^{18}\text{O}$  values for reconstructions of lake-water  $^{18}\text{O}$   
1609 (Section 3.6.2) has to consider that variable contributions of terrestrial cellulose can modify  
1610 the aquatic isotope signal. The choice of adequate sites with scarcely vegetated catchment is

1611 one option to overcome this potential bias. Methodological difficulties may have also biased  
1612 previous results (Beuning et al. 2002). The development of the CUAM method for cellulose  
1613 extraction (Wissel et al., 2008) therefore was a milestone for gaining pure cellulose from  
1614 sediments albeit its potential is not yet fully explored due to the scarcity of comparative studies.  
1615 The applicability of the method is sometimes limited by low content of cellulose in lacustrine  
1616 sediments, which is typically in the order of 0.1 wt% in productive lakes (Heyng et al., 2014).  
1617 Uncertainties still exist regarding the exact oxygen-isotope fractionation factors between  
1618 source water and cellulose, possibly due to methodological challenges. Reported fractionation  
1619 values vary between 25 ‰ and 32 ‰ according to different studies and preparation methods  
1620 (Wolfe, et al. 2001; Mayr et al. 2013, 2015). The occurrence of a temperature effect on oxygen-  
1621 isotope fractionation during cellulose formation is still discussed (Sternberg and Ellsworth,  
1622 2011; Mayr et al., 2013). A potential methodological extension is the recent development of  
1623 an analytical procedure for  $\delta^{18}\text{O}$  analyses on hemicellulose-derived sugar biomarkers (Zech  
1624 et al., 2014; Hepp et al., 2015).

#### 1625 **4.6 Sulfur on the horizon**

1626 Compound-specific  $\delta^{34}\text{S}$  analysis will help to illuminate the operation of organic sulfur cycles  
1627 of the past and present. A rapid transition is anticipated from the current practice of measuring  
1628 the bulk  $\delta^{34}\text{S}$  isotopic value of whole sediments or major organic fractions to measuring the  
1629  $\delta^{34}\text{S}$  composition of individual molecular species – similar to the uptake of compound specific  
1630  $\delta^{13}\text{C}$  and  $\delta^2\text{H}$  technologies. Further maturity of the technology for CSIA of sulfur-containing  
1631 compounds should lead to greater improvements in analytical performance (i.e., precision and  
1632 reproducibility  $<\pm 0.5$  ‰) and further targeted application leading to a better understanding of  
1633 the properties, interactions and fate of organic sulfur in lake basins.

#### 1634 **4.7 Stones unturned**

1635 Although the understanding of the various fractionation factors associated to amino acid  
1636 biosynthesis and metabolism is constantly improving, the fact that they also have a low  
1637 preservation potential in lacustrine sediments may limit their applicability for  
1638 paleoenvironmental studies. Still, as demonstrated by Carstens et al. (2013) for shallow  
1639 sediments (6 cm) of an oligotrophic and a eutrophic lake,  $\delta^{15}\text{N}$  values of amino acids did  
1640 preserve the different trophic status of the two lakes. Thus, for studies that aim to investigate  
1641 recent anthropogenic ecosystem change, e.g., in the context of industrialization or  
1642 urbanization, amino acid  $\delta^{15}\text{N}$  values may hold promising information on changes in nutrient  
1643 loading, while the limit of such an approach going back in time remains to be tested.

1644 Some compounds have been frequently observed but appear notoriously understudied. One  
1645 such example is loliolide and its epimer, iso-lololide. They represent the end pieces of the

1646 carotenoid pigment fucoxanthine (Fig. 10) and are formed in equal quantities during the  
1647 anaerobic degradation of the compound (Repeta, 1989), which is the main pigment in diatoms  
1648 but also occurs in dinoflagellates and haptophytes (Repeta and Gagosian, 1982; Klok et al.,  
1649 1984). Loliolide and iso-loliolide are frequently detected in marine sediments (Repeta and  
1650 Gagosian, 1982; ten Haven et al., 1987; Repeta, 1989; Hinrichs et al., 1999b; Menzel et al.,  
1651 2003) but have also been found in significant amounts in sediments of Lake Kivu (Al-Mutlaq  
1652 et al., 2008), Lake Malawi (Castañeda et al., 2009, 2011), Lake Challa (van Bree et al., 2018)  
1653 and Lake Ohrid (J. Holtvoeth, unpublished data). While they have been used as biomarkers  
1654 for diatoms for reconstructing changes in the marine (Hinrichs et al., 1999b) and limnic  
1655 phytoplankton community (Castañeda et al., 2009, 2011; van Bree et al., 2018), only Menzel  
1656 et al. (2003) determined the  $\delta^{13}\text{C}$  values of loliolide/iso-loliolide in eastern Mediterranean  
1657 sediments in order to find evidence for productivity changes during sapropel deposition. We  
1658 are not aware of any CSI study of these biomarkers in a lacustrine context where, e.g.,  
1659 changes in salinity,  $\text{CO}_2$  limitation or productivity could potentially be targeted through CSIA  
1660 of these algal compounds. The  $\delta^{13}\text{C}$  of the planktonic iGDGTs has also been reported to  
1661 contain some information about  $p\text{CO}_2$  in marine environments (Kuypers et al., 2002; Pearson  
1662 et al., 2016). As iGDGTs are also common in lake environments (Powers et al., 2004), they  
1663 could be exploited for this purpose.

1664 Finally, there is much scope for extending CSIA in future analytical technologies. These  
1665 include further applications of the relatively new analytical capability of compound-specific  $\delta^{34}\text{S}$   
1666 (Amrani et al., 2012), high-temperature GC-IRMS analysis of GDGTs (Lengger et al., 2018),  
1667 and the possible expansion of a variety of preparatory LC-MS techniques for purification of  
1668 steranes and hopanes. Also, the revolutionary ability to measure stable carbon and hydrogen  
1669 isotopes at specific molecular positions (Eiler et al., 2017) radically enhances the details of  
1670 the complex processes involved in the biosynthesis of molecules and usefulness as unique  
1671 environmental informants.

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