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1 **The stable isotope composition of organic and inorganic fossils in lake sediment records:**  
2 **current understanding, challenges, and future directions.**

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36  
37 **Abstract**

38  
39 This paper provides an overview of stable isotope analysis (H, C, N, O, Si) of the macro-  
40 and microscopic remains from aquatic organisms found in lake sediment records and their  
41 application in (palaeo)environmental science. Aquatic organisms, including diatoms,  
42 macrophytes, invertebrates, and fish, can produce sufficiently robust remains that  
43 preserve well as fossils and can be identified in lake sediment records. Stable isotope  
44 analyses of these remains can then provide valuable insights into habitat-specific

45 biogeochemistry, feeding ecology, but also on climatic and hydrological changes in and  
46 around lakes. Since these analyses focus on the remains of known and identified  
47 organisms, they can provide more specific and detailed information on past ecosystem,  
48 food web and environmental changes affecting different compartments of lake  
49 ecosystems than analyses on bulk sedimentary organic matter or carbonate samples. We  
50 review applications of these types of analyses in palaeoclimatology, palaeohydrology, and  
51 palaeoecology. Interpretation of the environmental 'signal' provided by taxon-specific  
52 stable isotope analysis requires a thorough understanding of the ecology and phenology of  
53 the organism groups involved. Growth, metabolism, diet, feeding strategy, migration,  
54 taphonomy and several other processes can lead to isotope fractionation or otherwise  
55 influence the stable isotope signatures of the remains from aquatic organisms. This paper  
56 includes a review of the (modern) calibration, culturing and modeling studies used to  
57 quantify the extent to which these factors influence stable isotope values and provides an  
58 outlook for future research and methodological developments for the different examined  
59 fossil groups.

60

61 **Keywords:** Stable isotopes; Lake sediment; Organic remains; Inorganic remains; Diatoms;  
62 Invertebrates; Ostracods

63

## 64 **1. Introduction**

65

66 Stable isotope analysis provides a versatile tool for investigating lake sediment records  
67 based on the link between stable isotope ratios and a range of environmental and  
68 biological processes, including climate change, hydrology, biogeochemical cycling, and  
69 consumer-diet interactions in food webs (Leng and Henderson 2013). Stable carbon and  
70 nitrogen isotope analysis of bulk sedimentary organic matter (SOM) is often used in  
71 palaeoenvironmental records as SOM is easy to sample and relatively straightforward to  
72 measure (Meyers et al. 2001). Some sediments require chemical pre-treatment to remove  
73 carbonates, which in itself can affect the stable isotope composition of SOM (Brodie et al.  
74 2011a, b). The information provided by SOM is always an integrated signal of catchment  
75 and in-lake processes, which can make it hard to interpret variations in its isotope  
76 composition. For example, an understanding of changes in  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  values of SOM

77 requires detailed information from the catchment as they are dependent on, amongst a  
78 range of factors, the composition and amount of input from terrestrial vegetation,  
79 anthropogenic nutrient input, lake volume, littoral-to-profundal ratio of the lake basin,  
80 productivity, groundwater inputs and stratification (e.g., Meyers and Ishiwatari 1993).

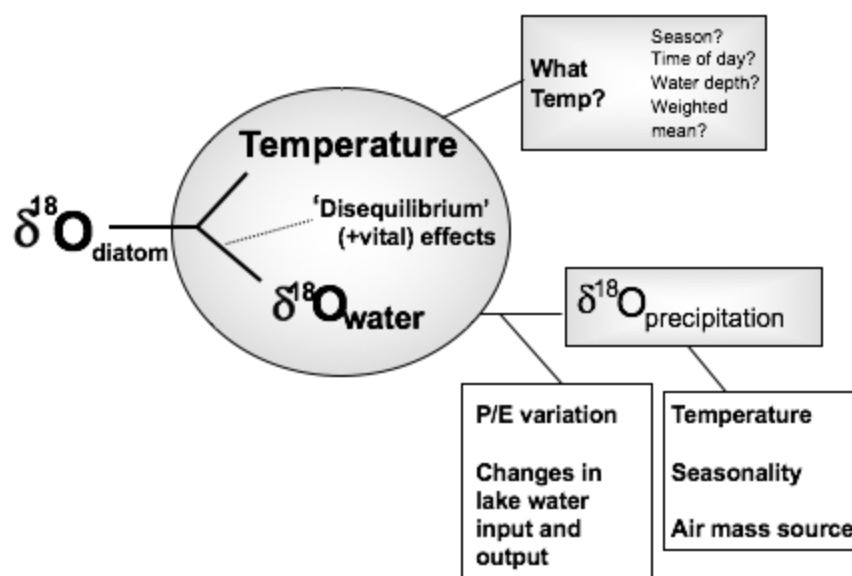
81 Stable isotopes of endogenic (bulk) carbonates are also widely used in  
82 palaeohydrology and palaeoclimatology. Changes in mineral  $\delta^{18}\text{O}$  values are interpreted in  
83 terms of changes in precipitation and temperature (Leng and Marshall 2004, Leng and  
84 Barker 2006). The  $\delta^{13}\text{C}$  values of endogenic carbonates are a complex sum of processes  
85 taking place in the lake and its catchment, including temperature and productivity-  
86 dependent fractionation, dissolved inorganic carbon (DIC) inflow, methanogenesis and  
87 methane oxidation,  $\text{CO}_2$  dissolution and outgassing and lake stratification (Siegenthaler  
88 and Eicher 1986; Hollander and Smith 2001; Leng and Marshall 2004; Schwalb et al. 2013).

89 To complement stable isotope data derived from analyses of SOM or carbonates, it has  
90 become more common to analyse the stable isotope composition of identifiable fossil  
91 remains separated and manually picked from lake sediments (e.g. diatoms, invertebrates,  
92 plant macrofossils), or to analyse stable isotopes of specific compounds chemically  
93 isolated from the sediments (e.g., lipids, amino acids, pigments). These approaches offer  
94 the great benefit of targeting specific organism groups or chemical biomarkers, which can  
95 reflect particular habitats or locations in a lake, or provide valuable information about  
96 their functional roles in an ecosystem. Targeting specific remains and compounds also  
97 means that it is easier to understand and test how the stable isotope composition is  
98 affected by biogeochemical and taphonomic processes over time.

99 In this review, we provide an overview of approaches based on stable isotopes  
100 measured on taxon-specific samples. We include the isotope systems H, C, N, O, Si,  
101 measured on diatoms, calcareous and chitinous invertebrate remains, fish remains, and  
102 plant macrofossils. We discuss their palaeolimnological applications and provide an  
103 overview of the current understanding of taphonomy and ecology that is required to  
104 interpret sedimentary records.

## 105 106 **2. Diatoms** 107

108 Diatoms are unicellular, eukaryotic, micro-organisms, which are ubiquitous in nature. As  
 109 such, diatom silica is an interesting sediment component for isotope measurements in  
 110 lake (Leng and Barker 2006) and marine (Swann and Leng 2009) environments, where the  
 111 oxygen ( $\delta^{18}\text{O}_{\text{diatom}}$ ), silicon ( $\delta^{30}\text{Si}_{\text{diatom}}$ ), carbon ( $\delta^{13}\text{C}_{\text{diatom}}$ ) and nitrogen ( $\delta^{15}\text{N}_{\text{diatom}}$ ) isotope  
 112 compositions can all be used as proxies for environmental change.  $\delta^{18}\text{O}_{\text{diatom}}$  tends to be  
 113 used as a measure of temperature/water composition variation (Fig. 1),  $\delta^{30}\text{Si}_{\text{diatom}}$  as a  
 114 proxy for nutrient availability and utilisation (Fig. 2), and  $\delta^{13}\text{C}_{\text{diatom}}$  and  $\delta^{15}\text{N}_{\text{diatom}}$  for  
 115 nutrient cycling/source investigation (Leng and Henderson 2013).



116

117 **Fig. 1:** Controls on the stable oxygen isotope composition of biogenic silica

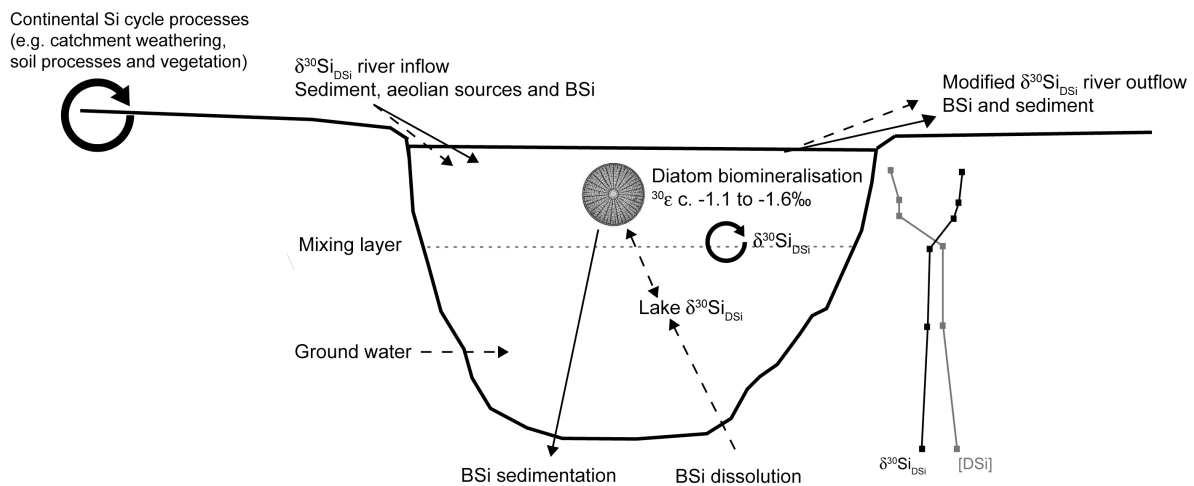
118

119 Compared to  $\delta^{18}\text{O}_{\text{diatom}}$  studies, the application of  $\delta^{30}\text{Si}_{\text{diatom}}$ ,  $\delta^{13}\text{C}_{\text{diatom}}$  and  $\delta^{15}\text{N}_{\text{diatom}}$   
 120 techniques are in their relative infancy, with only a few studies being applied in lacustrine  
 121 systems (Alleman et al. 2005; Street-Perrott et al. 2008; Swann et al. 2010; Hurrell et al.  
 122 2011; Hernández et al. 2011, 2013; Opfergelt et al. 2011; Chen et al. 2012; Barker et al.  
 123 2013; Cockerton et al. 2015; Webb et al. 2016; Panizzo et al. 2016, 2018a, b). There are  
 124 several reviews of the use of isotopes in biogenic (including diatom) silica (including Leng  
 125 and Barker 2006; Swann and Leng 2009; Leng et al. 2009; Leng and Henderson 2013;  
 126 Sutton et al. 2018), which highlight, in detail, the many issues associated with such  
 127 analyses. These will be further elucidated upon here and include issues such as equilibrium  
 128 fractionation, sample purification, post mortem maturation of diatom silica, and

129 standardisation and inter-laboratory calibrations. Given that more recent advances have  
 130 been made in  $\delta^{30}\text{Si}_{\text{diatom}}$  applications in lacustrine settings, in addition to the body of  
 131 literature on  $\delta^{18}\text{O}_{\text{diatom}}$ , we focus this review on these two proxies.

132 Diatom silica is a structurally complex mineral for  $\delta^{18}\text{O}_{\text{diatom}}$  (see section 2.4 below)  
 133 measurement due to a hydrous component. O isotope extraction generally adopts  
 134 fluorination (offline) techniques, with measurement via gas-source isotope ratio mass  
 135 spectrometry (IRMS), a technique which can also be used to measure  $\delta^{30}\text{Si}_{\text{diatom}}$  (Leng and  
 136 Sloane 2008). However, the use of multi-collector inductively-coupled-plasma mass  
 137 spectrometry (MC-ICP-MS) is becoming increasingly more dominant for  $\delta^{30}\text{Si}_{\text{diatom}}$  analyses  
 138 due to the reduced sample size needed ( $\sim 1$  mg), while carbon and nitrogen (for  $\delta^{13}\text{C}_{\text{diatom}}$   
 139 and  $\delta^{15}\text{N}_{\text{diatom}}$ ) are measured on very small quantities of organic material hosted  
 140 (occluded) within the structure (Webb et al. 2016).

141



142  
 143

144 **Fig. 2:** A schematic drawing of Si cycling in a lake system; solid arrows correspond to  
 145 particulate fluxes and dashed lines to dissolved phases or transformation processes. The  
 146 range in fractionation factors ( ${}^{30}\epsilon$ ) associated with the production of biogenic silica (in this  
 147 case, diatoms) from freshwater archives are also provided. Typical water column profiles  
 148 (for both lacustrine and oceanic settings) of DSi concentrations [DSi] and  $\delta^{30}\text{Si}_{\text{DSi}}$  (‰)  
 149 signatures are drawn, highlighting the effects of biological uptake in surface waters (e.g.,  
 150 lower [DSi] and higher  $\delta^{30}\text{Si}_{\text{DSi}}$ ). Reference to water column mixing is also made, which  
 151 depending on the limnological characteristics of individual sites, can compositionally  
 152 “reset” surface water  $\delta^{30}\text{Si}_{\text{DSi}}$  (e.g., on a seasonal basis).

153

154 Silicon has three naturally occurring stable isotopes  $^{28}\text{Si}$ ,  $^{29}\text{Si}$  and  $^{30}\text{Si}$  with a mean  
155 abundance of 92.2%, 4.7% and 3.1% respectively. The isotope composition of any sample  
156 ( $x$ ), for  $^{29}\text{Si}$  or  $^{30}\text{Si}$  ( $n$ ), is expressed in delta notation ( $\delta$ ), compared to the reference  
157 standard NBS28, using the following equation:

$$158 \quad \delta^n\text{Si}_x (\text{‰}) = \left( \frac{[(^n\text{Si}/^{28}\text{Si})_x - (^n\text{Si}/^{28}\text{Si})_{\text{standard}}]}{(^n\text{Si}/^{28}\text{Si})_{\text{standard}}} \right) \times 1000$$

159 An overview of the key processes affecting  $\delta^{30}\text{Si}$  in lakes are shown in Fig 2. These include  
160 processes in a catchment (weathering, soil development, vegetation cover) and in a lake  
161 (productivity, water supply, stratification, sedimentation, dissolution) and will be  
162 discussed in more detail below.

163

### 164 *2.1 Interpreting stable oxygen and silicon isotopes of diatom opal*

165

166  $\delta^{18}\text{O}_{\text{diatom}}$  has been used as a proxy for climate and hydrological change in many studies  
167 (Leng and Barker 2006) and the mineral-water fractionation has been estimated  
168 previously from analyses of diatoms from freshwater (and marine) sediments, coupled  
169 with estimates of the temperatures and isotope compositions of coexisting waters during  
170 silica formation (Labeyrie 1974; Juillet-Leclerc and Labeyrie 1987; Matheney and Knauth  
171 1989). There are very few calibration studies (e.g., Labeyrie and Juillet 1982; Wang and  
172 Yeh 1985; Juillet-Leclerc and Labeyrie 1987; Shemesh et al. 1995), and published estimates  
173 of the average temperature dependence for typical ocean temperatures range from  $-0.2$   
174 to  $-0.5 \text{ ‰ per } ^\circ\text{C}$  (Juillet-Leclerc and Labeyrie 1987; Shemesh et al. 1992; Brandriss et al.  
175 1998). However, in lake studies the oxygen isotope composition of diatom silica is often  
176 more sensitive to changes in “non-temperature” aspects of climate, such as amount or  
177 source of precipitation (Barker et al. 2001; Shemesh et al. 2001) and evaporation  
178 (Hernández et al. 2008).

179 In a pioneering study, Schmidt et al. (1997) suggested that there is no regular  
180 correlation between temperature and the oxygen isotope fractionation between modern  
181 diatoms and the water in which they biomineralise. This led to the hypothesis that the  
182 temperature-dependent oxygen isotope fractionation preserved in biogenic opaline  
183 sediments may, in some environments, have been established during diagenesis (see

184 below) rather than acquired during growth, a subject open to recent investigation  
185 (Menicucci et al. 2017; Tyler et al. 2017).

186  $\delta^{30}\text{Si}_{\text{diatom}}$  is a relatively underused technique in lacustrine systems, with few studies  
187 published despite silicon cycling in lakes being a key component of the continental silicon  
188 cycle. However, the field is growing, with contemporary studies examining the  $\delta^{30}\text{Si}$   
189 signature of lake surface waters and diatom opal as a means to validate the technique for  
190 palaeolimnological applications (Opfergelt et al. 2011; Panizzo et al. 2016). The method  
191 has traditionally been more widely applied in oceanographic settings as a means to  
192 reconstruct past biogeochemical cycling, with conventional interpretation of the method  
193 as a diatom silica utilisation or water mass/circulation proxy, the latter particularly when  
194 coupled with  $\delta^{13}\text{C}_{\text{diatom}}$  and  $\delta^{15}\text{N}_{\text{diatom}}$  or  $\delta^{30}\text{Si}$  from other silicifying organisms (i.e. sponge  
195 spicules and radiolarians) (Abelmann et al. 2015; Beucher et al. 2007; De La Rocha et al.  
196 1998; Hendry and Brzezinski 2014; Hendry et al. 2016; Horn et al. 2011; Maier et al. 2013;  
197 Panizzo et al. 2014).

198 Lake water dissolved silica (DSi)  $\delta^{30}\text{Si}$  signatures ( $\delta^{30}\text{Si}_{\text{DSi}}$ ) are essentially a product of  
199 upstream catchment processes (e.g., weathering, erosion and soil processes, and  
200 vegetation), regulated by regional climate systems, and within-lake biogeochemical  
201 processes (e.g., diatom utilisation and dissolution; see section 2.2) (De la Rocha et al.  
202 2000; Frings et al. 2016; Opfergelt and Delmelle 2012; Panizzo et al. 2018b). In instances of  
203 more extreme climatic variability, particularly in tropical catchments, lake water budgets  
204 can be considerably altered so that there are large opposing (seasonal) variations in  
205 overall lake water DSi concentrations and  $\delta^{30}\text{Si}_{\text{DSi}}$  signatures (with increasing compositions  
206 of  $\sim 0.5$  ‰ during dry season periods; Cockerton et al. 2013). This can be further  
207 compounded at sites where groundwater inputs are considerable (Street-Perrott et al.  
208 2008). Within-lake biomineralisation can significantly alter the outflowing concentration  
209 and composition of DSi and  $\delta^{30}\text{Si}_{\text{DSi}}$  (respectively). As such, lakes have been found to act as  
210 a key buffer within the continental Si cycle (in addition to the soil-vegetation system)  
211 (Frings et al. 2014).

212 Studies of  $\delta^{30}\text{Si}_{\text{DSi}}$  and  $\delta^{30}\text{Si}$  of diatom opal ( $\delta^{30}\text{Si}_{\text{diatom}}$ ) therefore act as a tracer of  
213 biogeochemical processes in nature. Early studies were conducted at lake sites with basalt  
214 and volcanic geology, where Si weathering, riverine DSi fluxes and biomineralisation  
215 potential are high (e.g., Alleman et al, 2005; Street-Perrott et al. 2008; Opfergelt et al.



216 2011; Chen et al. 2012; Cockerton et al. 2015). In lacustrine systems these techniques are  
217 applied to investigate variations in water column mixing (e.g. DSi supply) and diatom  
218 bloom duration (e.g. DSi utilisation), which are all regulated by intrinsic (e.g. water column  
219 mixing, stratification, ice-cover duration) and extrinsic processes (e.g. climate and riverine  
220 source water changes) (Fig. 2; Alleman et al. 2005; Street-Perrott et al. 2008; Opfergelt et  
221 al. 2011; Panizzo et al. 2016, 2017, 2018a, b).

222

## 223 *2.2 Fractionation and vital effects of diatom opal*

224

225 As with other organisms, diatoms are assumed to be precipitated in isotope equilibrium as  
226 predicted by thermodynamic fractionation. However, it has been widely shown in  
227 carbonates that offsets from oxygen (and carbon) isotope equilibrium may arise in  
228 response to variations in kinetic or metabolic processes within and between individual  
229 taxa, e.g., changes in growth rates, nutrient availability or rates of calcification/silicification  
230 (Duplessy et al. 1970; Wefer and Berger 1991; Spero and Lea 1993, 1996; Spero et al. 1997;  
231 Bemis et al. 1998). For biogenic carbonates, such as ostracods (see section 3 below), the  
232 impact of vital effects can be overcome by selecting species-specific samples for isotope  
233 analysis. This is not feasible for diatoms due to their small size. A number of culture (Binz  
234 1987; Brandriss et al. 1998; Schmidt et al. 2001), sediment trap (Moschen et al. 2005) and  
235 down core studies (Sancetta et al. 1985; Juillet-Leclerc and Labeyrie 1987; Shemesh et al.  
236 1995; Bailey et al. 2014) in lacustrine (and marine) systems do not show any oxygen  
237 isotope vital effect exists in diatoms. While data in Brandriss et al. (1998) display a 0.6 ‰  
238 difference between two laboratory cultured diatom taxa and Shemesh et al. (1995) found  
239 a 0.2 ‰ offset between two different size fractions of diatoms, offsets of this magnitude  
240 are within the range of reproducibility routinely achieved when analysing  $\delta^{18}\text{O}_{\text{diatom}}$ .

241 Early studies on the fractionation of diatom opal during valve dissolution suggested a  
242  $-0.55$  ‰ enrichment of  $\delta^{30}\text{Si}_{\text{diatom}}$  (Demarest et al. 2009) although this has since been  
243 challenged, to suggest an absence of dissolution fractionation effects, based on analyses  
244 of marine (Wetzel et al. 2014) and lacustrine sedimentary diatoms (Panizzo et al. 2016).  
245 More complex, and still in dispute to a certain degree, are the isotope fractionations  
246 associated with diatom biogenic silica production. When diatoms take up DSi (in the form  
247 of silicic acid,  $\text{Si}(\text{OH})_4$ ) during biomineralisation they actively discriminate against the

248 heavier ( $^{30}\text{Si}$ ,  $^{29}\text{Si}$ ) isotopes in favour of the lighter isotope ( $^{28}\text{Si}$ ), leading to the enrichment  
249 of the residual pool ( $\delta^{30}\text{Si}_{\text{DSi}}$ ) (De La Rocha et al. 1997). Evidence from *in-vitro* and *in-situ*  
250 studies from marine diatoms suggests that this per mille enrichment factor ( $^{30}\epsilon_{\text{uptake}}$ ) is  
251 independent of temperature,  $p\text{CO}_2$  and nutrient availability (De La Rocha et al. 1997;  
252 Fripiat et al. 2011; Milligan et al. 2004; Varela et al. 2004). The general consensus for  
253  $^{30}\epsilon_{\text{uptake}}$  is  $-1.1 \pm 0.4$  ‰ (refer to Frings et al. 2016 for the latest compilation of data) with  
254 good agreement with more recent *in-situ*, contemporary studies from freshwater diatoms  
255 (published values ranging between  $-1.1$  and  $-1.6$  ‰; Alleman et al. 2005; Opfergelt et al.  
256 2011; Panizzo et al. 2016; Sun et al. 2013) (Fig. 2). However, Sutton et al. (2013) have  
257 challenged this consensus reporting species-dependent  $^{30}\epsilon_{\text{uptake}}$  ranging from  $-2.09$  to  
258  $-0.54$  ‰ (based on cultured polar and sub-polar marine diatom strains). While such  
259 evidence has not (to date) been replicated, these studies highlight the ongoing challenges  
260 in applying  $\delta^{30}\text{Si}$  approaches to down core reconstructions and reinforce the value of  
261 modern day, lake site-specific calibrations of the method (as per Panizzo et al. 2016).

262

### 263 2.3 Sample purification

264

265 Much effort is placed on diatom purification prior to isotope analysis (e.g., van Bennekom  
266 and van der Gaast 1976; Shemesh et al. 1995; Schleser et al. 2001; Morley et al. 2004;  
267 Rings et al. 2004; Lamb et al. 2005; Tyler et al. 2007; Brewer et al. 2008; Mackay et al.  
268 2011) as high sample purity is required for  $\delta^{18}\text{O}_{\text{diatom}}$  and  $\delta^{30}\text{Si}_{\text{diatom}}$  analysis. This is because  
269 oxygen and silicon are both common elements in many other components found in lake  
270 sediments (including clay, silt, tephra and carbonates) and a high proportion of these can  
271 introduce significant isotopic offsets.  $\delta^{13}\text{C}_{\text{diatom}}$  and  $\delta^{15}\text{N}_{\text{diatom}}$  are usually measured on  
272 occluded (within the frustule) organic matter and therefore external organic matter, a  
273 contaminant, is removed using chemical oxidation (for further information consult  
274 Robinson et al. (2004), Singer and Shemesh (1995) and references therein).

275 In most instances, standard chemical (oxidation) and physical separation approaches  
276 (sieving, heavy density liquids) work well for samples with a high proportion of diatom  
277 silica ( $>10$  %). However, more complex and time consuming methods are required to clean  
278 relatively diatom poor ( $<10$  %) material, where sample sizes are small or where the  
279 contaminant is similar in size and density to the diatom silica. These include SPLIT

280 (gravitational split-flow lateral-transport), micromanipulation, and chemical mass balance  
281 modelling. SPLITT is an approach similar to heavy density separation (Giddings 1985),  
282 whereby individual particles within a sample are separated under laminar flow of water on  
283 the basis of their density, size and shape (Schleser et al. 2001; Rings et al. 2004; Leng and  
284 Barker 2006). Micro-manipulation is an alternative approach: where a device is attached  
285 to an inverted microscope, with a micro-injector system used to extract individual non-  
286 diatom particles from a sample (Snelling et al. 2013). Although time-consuming this  
287 technique is routinely used in other fields (e.g., cryptotephra, Lane et al. 2014), and may  
288 be the only option, in some cases, to remove contaminants that are chemically and  
289 physically similar to diatoms. In instances where all other methods are unsuccessful in  
290 removing sample contaminants, mass balance chemical modelling can be applied. Here,  
291 whole-rock geochemistry and electron-optical imaging provides a method for the  
292 identification, quantification and subsequent removal of (e.g. via an offset correction  
293 factor) the effects of different types of contamination (Lamb et al. 2005; Brewer et al.  
294 2008; Mackay et al. 2011). This approach can also work with multiple contaminants so  
295 long as they are well characterised (Wilson et al. 2014). Purity is routinely demonstrated in  
296 publications either visually (e.g., scanning electron microscopy) or quantitatively, via  
297 estimations of sample contamination  $<1\%$  (e.g.,  $\text{SiO}_2:\text{Al}_2\text{O}_3 <1$ ).

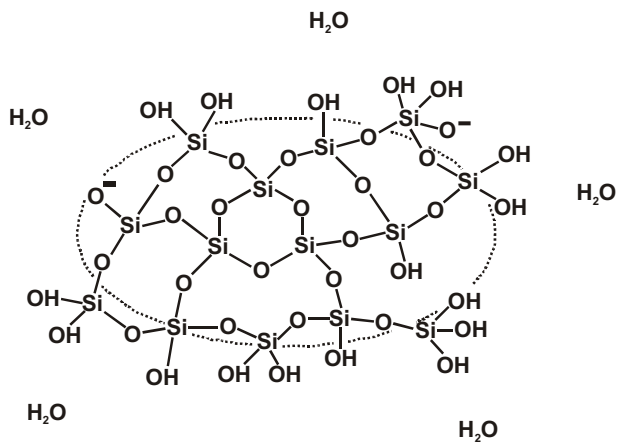
298

#### 299 *2.4 The hydrous layer and maturation of oxygen isotopes in biogenic silica*

300

301 Biogenic silica has an amorphous structure containing Si-O-Si bonds, Si-OH bonds and  
302 crystallization water (Knauth and Epstein 1982). These oxygen-bearing compounds (-OH  
303 and H<sub>2</sub>O) can exchange freely with their environmental lake water (Fig. 3), for example  
304 with sedimentary pore water during the burial of diatoms (Mopper and Garlick 1971;  
305 Kawabe 1978; Mikkelsen et al. 1978; Schmidt et al. 1997; Brandriss et al. 1998; Moschen  
306 et al. 2006) or with laboratory water used in diatom cleaning preparation techniques  
307 (Tyler et al. 2017). The hydrous layer must be removed prior to  $\delta^{18}\text{O}$  measurements due to  
308 its ready exchangeability (most notable in modern diatoms), which makes it a complex  
309 mineral to analyse (Leng and Sloane 2008). Secondary processes, such as diagenesis, can  
310 also alter  $\delta^{18}\text{O}_{\text{diatom}}$  due to the presence of this hydrous layer.

311



312

313 **Fig. 3:** *Schematic illustration of the nature of amorphous hydrated silica (from Leng and*  
 314 *Marshall 2004)*

315

316 The influence of silica condensation on the isotope composition of sedimented opal,  
 317 as a result of isotope exchange, has been described by Schmidt et al. (2001). Diatom silica  
 318  $^{18}\text{O}$  enrichment is attributed to biogenic silica maturation (dehydroxylation i.e. reduction  
 319 of Si–OH groups) following the removal of organic coatings (Moschen et al. 2006).  
 320 Similarly, secondary processes are likely to affect sedimentary diatomaceous silica  
 321 (especially the hydrous parts), although the vast proportion (c. 90%) of diatom valve  
 322 oxygen is bound to silicon in  $\text{SiO}_4$  tetrahedrons (forming the structurally bound oxygen)  
 323 which should be more resistant to alteration (refer to reviews of Leng and Henderson,  
 324 2013; Swann and Leng, 2009). Furthermore, the absence of trends in  $\delta^{18}\text{O}$  signatures  
 325 through time would suggest progressive silica maturation does not occur and it is likely  
 326 that there is a very slow progression of the maturation process after a fast initial phase of  
 327 signal alteration. Therefore, some of the diatom  $\delta^{18}\text{O}$  composition is acquired soon after  
 328 the formation of biogenic silica, during early diagenesis in the water column and later  
 329 during early sediment burial (Dodd and Sharp 2010). Interestingly, the conflating effects of  
 330 temperature on  $\delta^{18}\text{O}$  recorded by palaeo-diatom silica could be reduced or removed via  
 331 maturation in deep lacustrine environments with nearly constant temperatures as re-  
 332 equilibration of diatom silica occurs, thereby providing direct information on the  $\delta^{18}\text{O}$  of  
 333 the water (Dodd and Sharp 2010).

334

335 *2.5 Methods and inter-laboratory calibrations*

336

337 There are several techniques for the dehydration and release of O<sub>2</sub> from biogenic silica for  
338  $\delta^{18}\text{O}$  analysis. However, only one silica standard is universally available (NBS28 quartz)  
339 distributed by the IAEA, Vienna. Additional standards to calibrate the  $\delta^{18}\text{O}$  values of  
340 biogenic silica were introduced through an inter-laboratory comparison (Chapligin et al.  
341 2011) by eight participating laboratories using their individual bespoke methods and IRMS.  
342 The standard materials (diatoms, phytoliths and synthetically-produced hydrous silica)  
343 were analysed in accordance to a prescribed protocol. Despite procedural differences at  
344 each laboratory (controlled isotopic exchange, stepwise fluorination, inductive high-  
345 temperature carbon reduction and inert gas flow dehydration; Chapligin et al. 2011; Leng  
346 and Henderson 2013), all methods were in reasonable agreement, with a standard  
347 deviation (SD) range for  $\delta^{18}\text{O}$  between 0.3 ‰ and 0.9 ‰.

348 There are several methods published for the liberation of  $\delta^{30}\text{Si}$  from biogenic silica,  
349 these include both acid and alkaline dissolution/fusion, Si separation using cation  
350 exchange, selective co-precipitation, and gas-source versus plasma-ionization (high and  
351 low resolution) mass-spectrometric techniques (Reynolds et al. 2007). Three standards  
352 were used for a  $\delta^{30}\text{Si}$  inter-laboratory comparison exercise using a variety of chemical  
353 preparation methods and mass spectrometric techniques. The standard reference  
354 materials used were IRMM-018 (a SiO<sub>2</sub> standard), Big-Batch and Diatomite (natural  
355 diatomites). All analyses were compared with the international Si standard NBS28  
356 (RM8546) and were in reasonable agreement (within  $\pm 0.22$  ‰ ( $1\sigma$ ) for  $\delta^{30}\text{Si}$ ) showing little  
357 statistical difference between the mean values obtained by each laboratory, with the  
358 notable exception of the IRMM-018. Overall, they concluded that all the methods have  
359 similar precision and differences are limited to 0.2 ‰ in mean  $\delta^{30}\text{Si}$  values for a given  
360 sample between laboratories (or differences of 0.13 ‰ in mean  $\delta^{29}\text{Si}$ ). On the basis of this  
361 study, the reference standard Diatomite, is routinely reported to demonstrate analytical  
362 precision (consensus value of  $+1.26$  ‰  $\pm 0.2$  ‰, 2 SD; Reynolds et al. 2007).

363 While there are no inter-calibration studies on  $\delta^{30}\text{Si}_{\text{DSi}}$  in freshwaters, one was  
364 recently undertaken on marine waters, tackling challenges associated with the purification  
365 and instrumental precision of waters with low silicic acid concentrations ( $9 \mu\text{mol L}^{-1}$ )  
366 (Grasse et al. 2017). Overall consensus for high ( $113 \mu\text{mol L}^{-1}$ ) and low concentration

367 seawaters was obtained between all laboratories ( $+1.25 \pm 0.06$  and  $+1.66 \pm 0.13$  ‰  
368 respectively), although some small and significant differences between data were  
369 obtained, which the authors attribute to the complex pre-concentration methods  
370 (Triethylamine Molybdate; De la Rocha et al. 1996; MAGIC; Georg et al. 2006; or via Mg-  
371 induced co-precipitation with purified ammonia; Zhang et al. 2014) and purification steps  
372 involved, as well as instrument bias of the different laboratories (e.g., Neptune MC-ICP-  
373 MS, Nu Plasma MC-ICP-MS and MAT 252 IRMS) (Grasse et al. 2017).

374 Diatom silica occluded organic matter is mainly derived of pleuralins, silaffins and  
375 long chain polyamines. The  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  analysis of these compounds from diatoms is  
376 thought to be a better representation of the carbon and nitrogen cycle rather than bulk  
377 organic matter (Hecky et al. 1973; Kroger and Poulson 2008; Bridoux et al. 2010). There is  
378 no universally accepted method for  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  analysis of occluded organic matter in  
379 diatom silica (Leng and Swann 2010). These methods are more popular in  
380 palaeoceanography with few published studies in (palaeo)limnology (Webb et al. 2016).  
381 The advantages are: the C and N isotope composition within the diatom cell walls is not  
382 affected by post depositional degradation and therefore potentially preserves an  
383 unaltered signal of surface water conditions during diatom growth (Brenner et al. 1999;  
384 Ficken et al. 2000) and avoids the generally heterogeneous nature of SOM (Hurrell et al.  
385 2011).

386

## 387 *2.6 Future directions*

388

389 Understanding the isotope composition of diatom silica lags behind work on carbonates  
390 by decades, probably because of the ongoing issues of contamination, the hydrous layer  
391 and associated maturation of diatom silica. Within the community, research continues in  
392 better understanding diatom species-specific fractionation effects for  $\delta^{18}\text{O}_{\text{diatom}}$  and  
393  $\delta^{30}\text{Si}_{\text{diatom}}$ . In particular, lacustrine case studies are needed because until now data on  
394 fractionation factors are predominantly derived from *in-vitro* and *in-situ* experiments of  
395 marine diatom strains. The potential for expanding  $\delta^{30}\text{Si}_{\text{diatom}}$  applications in lacustrine  
396 systems has been highlighted here, however a solid understanding of contemporary  
397 source water and biogenic opal endmembers (e.g. seasonal variability) is essential in order

398 to best trace biogeochemical pathways (e.g. changes in DSi supply versus diatom  
399 utilisation). In the natural environment, open-system models have been applied to lakes  
400 to interpret diatom fractionation processes (Chen et al. 2012; Opfergelt et al. 2011;  
401 Panizzo et al. 2016, 2017; 2018b) although closed-system approaches have also been  
402 adopted to explain isotope evolution at certain sites (Cockerton et al. 2015). Modern-day  
403 calibration studies are needed to best define the most appropriate system and would best  
404 constrain any potential for a lake system to periodically shift to a closed-system approach  
405 (e.g. during extended periods of ice cover or lake stratification). Furthermore, changes in  
406 catchment chemical weathering rates on glacial-interglacial timescales will alter DSi fluxes  
407 to lake basins and regulate their isotope composition (e.g., Cockerton et al. 2015; Frings et  
408 al. 2016). The coupling of  $\delta^{30}\text{Si}_{\text{diatom}}$  reconstructions with organic-bound  $\delta^{15}\text{N}_{\text{diatom}}$  and  
409  $\delta^{13}\text{C}_{\text{diatom}}$ , in addition to stable isotopes of different silicifiers (e.g., sponge spicules), could  
410 therefore be further explored as a means to independently constrain the supply of  
411 nutrients and their utilisation over such timescales.

412

413

### 414 **3. Biogenic carbonates**

415

416 The shells of ostracods and aquatic molluscs have often been used in palaeolimnological  
417 studies. Ostracods are small (generally microscopic) aquatic crustaceans that are common  
418 in lakes. They secrete carapaces made of two low-Mg calcite valves, which are often  
419 abundant and well preserved in lake sediments. Ostracods grow by moulting their shells,  
420 up to 8 times following hatching from eggs until maturity. Shell formation occurs rapidly,  
421 over the course of a few hours to days, and once the shell is formed there is no further  
422 addition of calcite (Holmes 1992). Aquatic molluscs, in contrast, are macroscopic and grow  
423 incrementally; they thus provide a more time-averaged record of their environment,  
424 although carbonate formation may be markedly seasonal (Leng et al. 1999; Leng and  
425 Lewis, 2016). Many mollusc species produce aragonitic shells although some may be  
426 composed of calcite. Ostracod and mollusc shells are regularly used as sources of  
427 carbonate for oxygen and carbon isotope analyses in palaeolimnological reconstructions  
428 (Holmes 1996; Holmes and Chivas 2002; Leng and Lewis, 2016). Charophytes are complex  
429 algae that are often abundant in shallow, alkaline, fresh to saline lakes (Schneider et al.

430 2015). Charophyte photosynthetic activity can promote the precipitation of calcium  
431 carbonate as encrustations around the thallus and associated with the female  
432 reproductive bodies known as gyrogonites, the two components being readily  
433 distinguished under a light microscope. Dense beds of charophytes can have significant  
434 impacts on the  $\delta^{13}\text{C}$  of DIC within lakes as a result of bicarbonate utilization for  
435 photosynthesis (Pentecost et al. 2006). Whilst the carbonate deposits associated with  
436 charophytes are not strictly fossils in the same sense as ostracod or mollusc shells, the  
437 encrustations often make up a large component of the carbonate sediments formed in  
438 freshwater alkaline lakes (Soulié-Märsche et al. 2010), leading to the formation of so-  
439 called *Chara*-marl, and so are considered briefly here. Ostracods shells and *Chara* remains  
440 tend to be most abundant in lakes situated on carbonate rocks, or those that are in  
441 hydrologically-closed or near-closed basins.

442 The oxygen isotope composition of lacustrine carbonate is controlled by water  
443 temperature and water isotope composition, as for endogenic calcite (Leng and Marshall  
444 2004), together with offsets from isotopic equilibrium, which are discussed further below.  
445 The carbon isotope composition of lacustrine carbonate is determined primarily by the  
446 carbon isotope composition of DIC: offsets from carbon isotope equilibrium appear to be  
447 negligible although, for reasons outlined below, they are difficult to assess.

448 The interpretation of oxygen and carbon isotope signatures derived from lacustrine  
449 carbonate depends on the climatic and hydrological characteristics of the lake and its  
450 catchment, meaning that an understanding of the modern isotope systematics of the site  
451 is beneficial. Species vary in their preferred habitat within a lake and also in their life cycle,  
452 with some species calcifying in specific seasons (Decrouy et al. 2011). For molluscs,  
453 whereas many taxa are gill-breathing, the fact that some are lung breathing may have an  
454 impact on the isotope composition of their shells. Knowledge of an individual species'  
455 physiology, ecology and life cycle is therefore also important when interpreting isotope  
456 signatures (Shanahan et al. 2005).

457 There are a number of advantages to using shells as opposed to endogenic  
458 carbonate for stable isotope analyses. First, the use of shells assures that the carbonate  
459 was formed in water and avoids possible inclusion of detrital material with contrasting  
460 isotope composition into the sample analysed. Second, the analysis of shells means that  
461 constraints can be placed on the timing and location of carbonate formation within a lake.



462 Ostracods provide a specific temporal and spatial ‘snapshot’ of water conditions and  
463 circumvent the problem of averaging. Moreover, the fact that some species have seasonal  
464 preferences and inhabit defined zones (e.g., deep benthic versus littoral) within a lake  
465 means that isotopic records derived from species with known life cycles and ecologies may  
466 provide seasonal and habitat-specific information (von Grafenstein et al. 1999b). For  
467 molluscs, whole-shell analyses provide a more time-averaged signal, since the shells grow  
468 incrementally, although non-continuous growth throughout the year may mean that that  
469 this signal is still seasonally biased (Leng and Lewis, 2016). Conversely, the isotope analysis  
470 of individual growth increments, which is analytically feasible for some larger taxa, may  
471 provide information about seasonal or inter-annual variability in environment (e.g., Leng  
472 et al. 2009; Dettman et al. 1999), although this may not be possible when the short-term  
473 changes in temperature or the isotope composition of water/DIC composition are small  
474 (Shanahan et al. 2005). Thirdly, analysis of shells provides some certainty over the  
475 mineralogy of the material being analysed. For ostracods, it is low-Mg calcite; for molluscs,  
476 often aragonite. Because aragonite is thermodynamically unstable and recrystallization  
477 leads to the ‘resetting’ of the isotopic signature (Leng and Marshall, 2004), it is important  
478 to assess the degree of preservation of aragonitic mollusc shells, for example using X-ray  
479 diffraction to confirm the presence of aragonite. These advantages also bring some  
480 problems, however. The time- and space-specific character of an ostracod isotope  
481 signature may not record the ‘average’ conditions within a lake that are generally required  
482 in palaeolimnological reconstructions. Furthermore, because the calcification of ostracod  
483 and mollusc shells is under strong biological mediation, isotopic fractionation may not  
484 conform to expectations derived from investigations of inorganic carbonate. For  
485 charophytes, different isotopic signatures may be recorded depending on where on the  
486 plant the carbonate formed (Pentecost et al. 2006). In short, care is required in the  
487 interpretation of such signatures.

488

### 489 *3.1 Oxygen and carbon isotope records from lakes*

490

491 Although the fundamental controls on isotope composition of carbonate are well  
492 understood and quantifiable in some instances, the palaeoclimatic and  
493 palaeoenvironmental interpretation of isotope records from lake sediments depends

494 strongly on the characteristics of individual lakes including their climatic setting, depth,  
495 volume, hydrology, aquatic vegetation and catchment properties (Holmes 1996). Oxygen  
496 isotope values derived from ostracod or mollusc shells, or marl, have been used in  
497 reconstructions of air temperature and the oxygen isotope composition of rainfall (von  
498 Grafenstein 2002; von Grafenstein et al. 1999a), effective moisture (Hodell et al. 1991;  
499 Street-Perrott et al. 2000; Holmes et al. 2010; Hodell et al. 1995), meltwater influx  
500 (Dettman et al. 1995) and changes in river routing within the lake's catchment (Schwalb et  
501 al. 1994). Carbon isotopes are often more difficult to interpret but have been used to  
502 reconstruct lake/catchment carbon cycling, productivity, and methanogenesis (Bridgwater  
503 et al. 1999; Anadón et al. 2006; Li and Liu 2014; Schwalb et al. 2013), although many  
504 studies report only the oxygen isotope results (e.g., Hodell et al. 1991; von Grafenstein et  
505 al. 1999a; Holmes et al. 2010; Hodell et al. 1995).

506

### 507 *3.2 Disequilibrium*

508

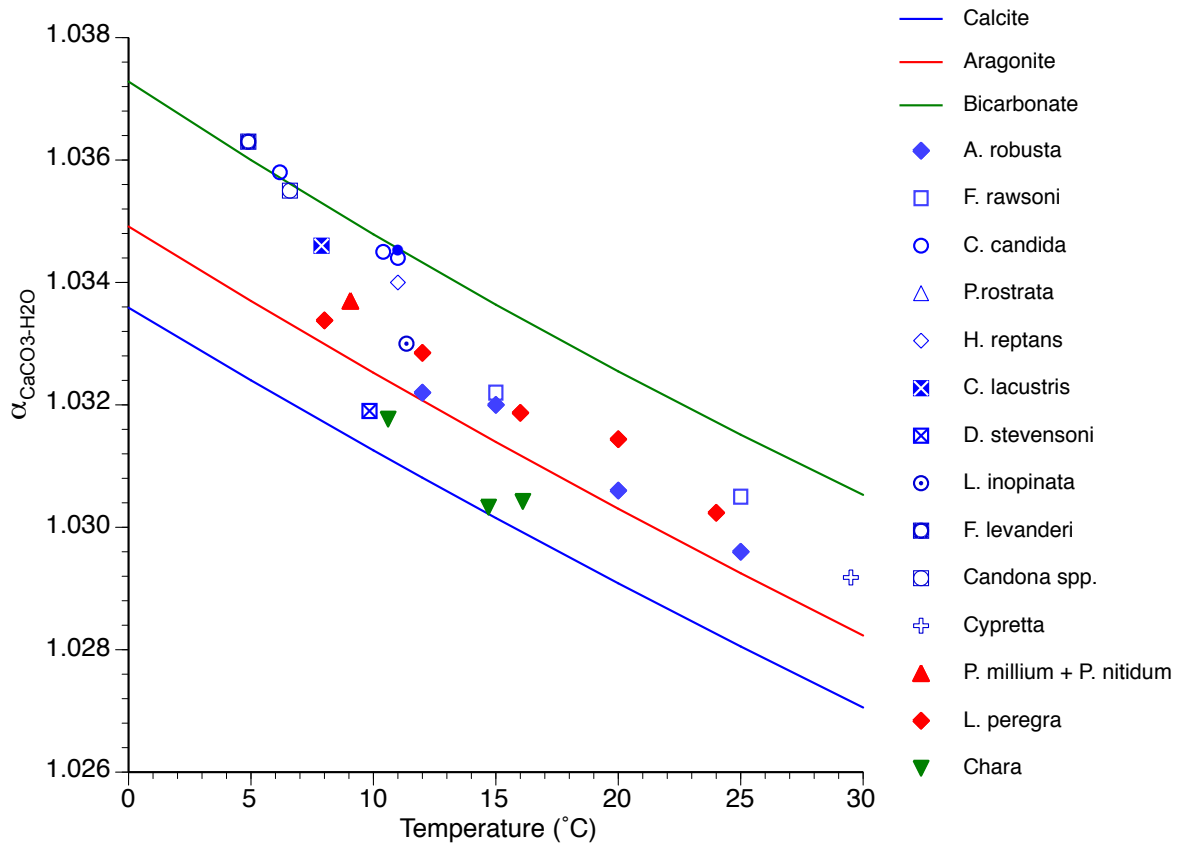
509 Despite early suggestions that ostracod calcite is precipitated in isotopic equilibrium with  
510 the host water (Durazzi 1977, albeit for marine taxa) it is now well established that  
511 significant offsets exist, especially for oxygen. Similar offsets have been shown for some  
512 mollusc taxa (e.g., White et al. 1999; Shanahan et al. 2005). Knowledge of such offsets is  
513 needed if ostracod or mollusc shell isotope values are to be used in quantitative  
514 environmental reconstruction (von Grafenstein et al. 1999a; Decrouy 2012; Devriendt et  
515 al. 2017). Moreover, offsets have provided insights into calcification mechanisms (Keatings  
516 et al. 2002; Shanahan et al. 2005; Decrouy 2012; Devriendt et al. 2017), although the  
517 mechanism behind the observed offsets from oxygen and carbon isotope equilibrium  
518 remains incompletely understood. Charophyte isotope records are potentially complicated  
519 by differences in isotopic signatures between stem encrustations and calcified remains of  
520 gyrogonites, which also vary depending on the strength of water flow (Andrews et al.  
521 2004; Pentecost et al. 2006).

522

#### 523 *3.2.1 Oxygen*

524

525 Evidence from field collections of ostracods under closely monitored conditions (e.g., von  
526 Grafenstein et al. 1999b; Keatings et al. 2002a; Decrouy et al. 2011) as well as *in vitro*  
527 cultures (Xia et al. 1997a; Chivas et al. 2002) have shown that their shells are precipitated  
528 out of oxygen isotope equilibrium with the host water (Fig. 4). The offsets from equilibrium  
529 are almost invariably positive, up to +3 ‰ or more. Several investigations have shown that  
530 the magnitude of the offset varies taxonomically, with members of the same genus, or  
531 even sub-family or family, sharing similar offset values (see table 10.1 in Decrouy 2012).  
532 Adults and juveniles and males and females of the same species usually show offsets of  
533 the same magnitude (Chivas et al. 2002; Decrouy 2012; von Grafenstein et al. 1999b). The  
534 two culturing studies cited above suggest that offsets are greater at higher temperature.  
535 Decrouy et al. (2011) have demonstrated that there are some differences in the magnitude  
536 of the vital offset *within* taxa from different localities, suggesting that water chemistry, in  
537 addition to taxonomy, may also play a role. Devriendt et al. (2017) have confirmed these  
538 observations based on a comprehensive meta-analysis of studies undertaken over a very  
539 large range of water types, and have argued that they can be explained by a carbonate ion  
540 effect. At high pH, a greater proportion of the DIC is present as the  $\text{CO}_3^{2-}$  ion rather than as  
541  $\text{HCO}_3^-$ , which dominates in lower pH waters: the degree of fractionation between water  
542 and the  $\text{CO}_3^{2-}$  ion is less than that with  $\text{HCO}_3^-$ , and since ostracod shells are formed from  
543 DIC, they will have lower  $\delta^{18}\text{O}$  values in higher pH waters (Devriendt et al. 2017). Positive  
544 offsets from oxygen isotope equilibrium have been observed in some mollusc taxa (White  
545 et al. 1999; Shanahan et al. 2005) although some species appear to precipitate their shells  
546 in isotopic equilibrium (Leng et al. 1999).  
547



548

549

550 **Fig. 4.** Fractionation factors between selected ostracod and mollusc species and water.  
 551 Fractionation between bicarbonate (Beck et al. 2005), synthetic calcite (Kim and O'Neil  
 552 1997) and synthetic aragonite (Kim et al. 2007) is also shown. Key to taxa and sources: *A.*  
 553 *robusta* – *Australocypris robusta* (Chivas et al. 2002); *F. rawsoni* – *Fabaeformiscandona*  
 554 *rawsoni* (Xia et al. 1997a); *C. candida* – *Candona candida* (Keatings, 1999; von Grafenstein  
 555 et al. 1999b); *P. rostrata* – *Pseudocandona rostrata*; *H. reptans* – *Herpetocypris reptans*  
 556 (Keatings et al. 2002); *C. lacustris* – *Cytherissa lacustris*; *D. stevensoni* – *Darwinula*  
 557 *stevensoni*; *L. inopinata* – *Limnocythere inopinata*; *F. levanderi* – *Fabaeformiscandona*  
 558 *levanderi*; *Candona* spp. (von Grafenstein et al. 1999b); *C. brevisaepta* - *Cypretta*  
 559 *brevisaepta* (J. A. Holmes, unpublished); *P. millium* + *P. nitidum* - *Pisidium millium* +  
 560 *Pisidium nitidum* (Keatings 1999); *L. peregra* - *Lymnaea peregra* (White et al. 1999); *Chara*  
 561 – charophyte stem encrustations (Andrews et al. 2004).

562

563

564 The offsets from isotopic equilibrium must be corrected for if calculations of past water  
 565 temperature or past water isotope composition are to be derived from the oxygen isotope

566 values of ostracod shells, otherwise significant errors may arise (von Grafenstein 2002;  
567 Devriendt et al. 2017).

568

### 569 3.2.2 Carbon

570

571 Assessing offsets from carbon isotope equilibrium in shells is more difficult because the  
572  $\delta^{13}\text{C}$  composition of DIC, the source of carbon for calcification, varies significantly at the  
573 micro scale meaning that there may be a weak relationship between the  $\delta^{13}\text{C}$  at the site of  
574 calcification and that within the main lake, which is the value that is typically measured.  
575 This is much more so than for oxygen isotopes, which tend to be relatively more  
576 homogenous within a lake. For example, the DIC within sediment pores may be  $^{13}\text{C}$ -  
577 depleted as a result of mineralisation of SOM. In methane-producing lakes, however, the  
578 formation of  $^{13}\text{C}$ -enriched co-genetic  $\text{CO}_2$  may have the opposite effect (Durand et al.  
579 1984), which may lead to very high  $\delta^{13}\text{C}$  values in the shells of infaunal ostracods  
580 (Bridgwater et al. 1999). Interestingly, the opposite (very low ostracod  $\delta^{13}\text{C}$  values) can be  
581 observed when methane is oxidized close to the sediment-water interface and  $^{13}\text{C}$ -  
582 depleted carbon is added to pore water DIC that is then available for incorporation into  
583 ostracod shells (Schwalb et al. 2013). Close to the leaves of submerged macrophytes that  
584 utilise  $\text{HCO}_3^-$ , DIC may also be  $^{13}\text{C}$ -enriched as a result of preferential uptake of  $^{12}\text{C}$  by  
585 plants for photosynthesis (Kelts and Talbot 1990). Hence, organisms co-existing in different  
586 micro-environments within a lake, or calcifying at different seasons, may have markedly  
587 contrasting  $\delta^{13}\text{C}$  values (Bridgwater et al. 1999). For molluscs, contrasts can be seen  
588 between gill-breathing and lung-breathing species, which may relate to differences in  
589 physiology or life history (Shanahan et al. 2005). Variations in  $\delta^{13}\text{C}$  values between  
590 different taxa are therefore often regarded as habitat effects rather than offsets from  
591 equilibrium *sensu stricto* (Heaton et al. 1995).

592

### 593 3.3 Sample preparation and shell cleaning

594

595 Shells destined for isotope analysis need to be well preserved (cf. section 3.4, below) and  
596 free from detrital contamination. Various methods have been used to remove

597 contamination from ostracod shells, especially organic material, which may interfere with  
598 isotope determinations. However, the potential of these techniques to modify the primary  
599 isotope composition of the shell as well as to remove any contaminant has not been fully  
600 assessed. Five techniques have been used to remove contaminants, namely simple manual  
601 cleaning with a fine paint brush and (usually) methanol, roasting *in vacuo*, heating in an  
602 oxygen plasma and chemical oxidation with sodium hypochlorite (clorox) or hydrogen  
603 peroxide (Keatings et al. 2006). For each technique, a variety of conditions (treatment  
604 times, temperatures, reagents strengths) has been used. Keatings et al. (2006) compared  
605 treated and untreated (manually cleaned) valves of the same carapace of late Pleistocene  
606 lacustrine ostracods and showed that in most instances, the mean impact of the cleaning  
607 techniques over manual cleaning was small, although treatment other than simple  
608 mechanical cleaning typically increased within-sample variability. Roberts et al. (2018)  
609 confirmed that treatment can cause changes in both oxygen and carbon isotope values,  
610 but concluded that hydrogen peroxide treatment would be preferable if treatment were  
611 required, since this reagent does not appear to have a significant impact on the isotope  
612 composition. Despite the relatively small changes imparted by each of the treatment  
613 methods, the increase in variability that may result suggests that anything other than  
614 simple mechanical cleaning should only be undertaken if absolutely necessary (i.e. to  
615 remove detrital contamination that could not otherwise be eliminated). The potential  
616 impact on variability needs to be borne in mind if single-shell samples are analysed  
617 (section 3.5) and, moreover, implications of cleaning for trace elements must be taken into  
618 account in cases where 'tandem' isotope and trace-element determinations are  
619 undertaken on the same shells, as in Chivas et al. (1993) and Xia et al. (1997b). Similar  
620 methods have been employed for the removal of organic material from mollusc shells  
621 destined for isotope analyses: modifications to techniques involving heating and or  
622 grinding are required in order to prevent inversion of aragonite to calcite (White et al.  
623 1999; Dettman et al. 1999). Marl samples, including those dominated by charophyte  
624 carbonate, are commonly treated by heating or chemical oxidation to remove organic  
625 matter (e.g., Apolinarska and Hammarlund 2009).

626

#### 627 3.4 *Signal preservation and diagenetic alteration*

628

629 An advantage of analysing shell calcite over endogenic calcite is that diagenetic alteration  
630 can usually be detected. For ostracods, early diagenetic alteration can usually be detected  
631 by the presence of etching, opaque rather than transparent or translucent appearance,  
632 and obscured or altered surface ornament (Keatings et al. 2002b). Ideally, shells showing  
633 signs of such alteration should be excluded from analyses. However, in some cases pristine  
634 material may not be preserved in sediment sequences, meaning that ostracod specimens  
635 that have undergone some degree of alteration need to be analysed. Limited attention has  
636 been paid to the impacts of early diagenesis on isotope signatures. Keatings et al. (2002b)  
637 found no clear evidence of an impact of preservation on the oxygen isotope signature of  
638 late Pleistocene lacustrine ostracods from a Jamaican hardwater lake: evidence for the  
639 absence of an impact on carbon isotopes was less conclusive. The potential for alteration  
640 increases for older material. Bennett et al. (2011) showed that isotope values, especially  
641 for oxygen, of Carboniferous non-marine ostracods from Scotland primarily reflected the  
642 degree of diagenetic alteration rather than a palaeoenvironmental signature and warned  
643 of the potential for cryptic diagenesis to alter the shells and their isotope values. However,  
644 Bajpai et al. (2013) derived plausible palaeoenvironmental signatures from both the  
645 oxygen and carbon isotope values from Late Cretaceous non-marine shells from peninsular  
646 India, some pristine and others showing signs of alteration. For aragonitic mollusc shells,  
647 recrystallization to calcite can effectively 'reset' the isotopic signature: mineralogical  
648 assessment of shells destined for isotope analyses is therefore often undertaken (e.g.,  
649 Leng et al. 1999).

650

### 651 3.5 Measurement of multiple versus single-shell samples

652

653 Adult ostracod shells weigh anything from a few micrograms for a single shell of small or  
654 weakly calcified taxa, such as species belonging to the genera *Limnocythere*, *Darwinula*  
655 and *Cypria*, to several hundred micrograms for large and well-calcified taxa belonging to  
656 genera such as *Sclerocypris*, although many taxa have shells in the tens of micrograms  
657 range (J. A. Holmes, unpublished). Juveniles are not only smaller than adults of the same  
658 species but also less well calcified, meaning that they weigh substantially less. Dual-inlet  
659 mass spectrometers are therefore able to measure isotope ratios for single shells of adults  
660 of many ostracod species (Chivas et al. 1993). Most stratigraphic studies of ostracods have

661 used single, multiple-shell, monospecific samples, where the number of shells analysed is  
662 determined not by the material requirements of the instrument, but by the need to obtain  
663 a sample that is representative of 'average' conditions within the lake and over the time  
664 interval represented by the increment of sediment from which the shells are recovered.  
665 However, there is increasing interest in undertaking analyses of multiple single shells at  
666 individual stratigraphic intervals in a lake-sediment sequence. Such an approach has the  
667 advantage of providing information about short-term variability within the lake as well as  
668 allowing any analytical outliers to be identified, although it does of course increase  
669 analytical costs. Pilot studies of large numbers of shells from a few intervals can be used to  
670 determine optimum sample size (Escobar et al. 2010). Such an approach has been used to  
671 assess short-term changes in effective moisture in NW India (Dixit et al. 2015) and in  
672 Mayan lakes from Central Mexico (Escobar et al. 2010), and variations in meltwater input  
673 in Lake Huron (Dettman et al. 1995). Despite the fact that a single mollusc shell typically  
674 integrates a longer time interval than a single ostracod shell, and would typically provide  
675 sufficient material for an isotope determination, similar issues have arisen with the isotope  
676 analysis of single mollusc shells, especially for species that have short life spans  
677 (Apolinarska et al. 2015).

678

### 679 *3.6 Other isotopes and future developments*

680

681 Further work is needed to compare oxygen-isotope signatures in different minerals or  
682 biomolecules. Theoretically, comparison of signatures in calcite or biogenic silica, in which  
683 oxygen-isotope fractionation is temperature dependent (section 3.2.1), with those in  
684 materials such as cellulose or chitin, which show temperature-independent fractionation  
685 (section 4.2.2), should lead to quantitative reconstructions of water temperature.  
686 However, existing studies show that this does not always work in practice. For example,  
687 Rozanski et al. (2010) attributed unrealistically-high estimates of temperature from  
688 coupled calcite and cellulose oxygen isotope analyses for an eastern European lake to  
689 kinetic effects during rapid carbonate formation. Comparison of  $\delta^{18}\text{O}$  values of diatom  
690 silica and endogenic calcite in Lake Pinarbasi, Turkey, show contrasting trends in spite of  
691 their mutual dependence on the water  $\delta^{18}\text{O}$  and lake-water temperature. The most likely  
692 explanation for this divergence is difference in seasonality of biological productivity



693 mediated by the strongly continental climate of the Anatolian plateau. The endogenic  
694 calcite  $\delta^{18}\text{O}$  is thought to be temporally limited to a few summer months and the diatom  
695 silica  $\delta^{18}\text{O}$  provides seasonally-specific water isotope composition in the spring and  
696 autumn and, at least in the record in question, captures periods of heavy snow through  
697 the spring thaw (Leng et al. 2001). Further investigations are needed to indicate the  
698 circumstances in which lake water temperature can be reconstructed from  $\delta^{18}\text{O}$  offsets  
699 between calcareous/siliceous and organic remains.

700 Ostracod shells have been used in analyses of other isotopes in a limited number of  
701 studies, including  $^{87}\text{Sr}/^{86}\text{Sr}$  (Janz and Vennemann 2005; Holmes et al. 2007) and U-series  
702 (for dating) (Bischoff et al. 1998). The chitinous shell linings, which remain after dissolving  
703 the calcium carbonate with a 5 % HCl solution, can be used for measuring  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  to  
704 provide insights in the position of ostracods in the aquatic food web (Fig. 6). Future  
705 developments require additional calibration work to improve understanding of the  
706 mechanisms behind vital offsets and their quantification for additional species, especially  
707 for oxygen isotopes. Future work may also lead to the use of 'novel' isotope systems like  
708 Ca (Oehlerich et al. 2015) and clumped isotope analysis (Mering 2015) on biogenic  
709 carbonates.

710

#### 711 **4. Organic remains of aquatic plants and animals**

712

713 Many organisms living in lakes produce organic structures that are remarkably robust to  
714 degradation once buried in lake sediments. These remains are composed (partly) of  
715 flexible polymers that are difficult to break down including chitin, keratin, lignin, collagen,  
716 and cellulose. These polymers are bonded or otherwise associated with proteins, calcium,  
717 carbonate, or other compounds to provide strength (Leschine 1995; Nation 2002;  
718 Kornitłowicz-Kowalska and Bohacz 2011; Jex et al. 2014). We will focus on identifiable  
719 organic remains of some of these organisms, including invertebrates, aquatic macrophytes  
720 and fish. We will review how taxon-specific analysis of stable isotopes on these remains  
721 are used in palaeolimnological studies to understand changes in carbon cycling, food web  
722 structure, eutrophication, hydrology and climate.

723

#### 724 4.1 Chitinous invertebrate remains

725

726 Invertebrates are ubiquitous in lakes and their exoskeleton fragments and resting eggs are  
727 preserved in lake sediments for tens of thousands of years (e.g., Engels et al. 2010).  
728 Remains of a wide range of invertebrates can be identified using microscopy and the  
729 composition of fossil invertebrate assemblages can be indicative of ecological and  
730 environmental conditions (Frey 1964). The exoskeleton fragments from various insect  
731 orders (e.g., Coleoptera, Diptera, Ephemeroptera, Trichoptera), crustaceans (e.g.,  
732 Cladocera, Ostracoda), and mites (Oribatida) are commonly found in lake sediments, as  
733 are the resting stages of Cladocera and moss animals (Bryozoa).

734 Robust organic remains of many invertebrate groups consist predominantly of  
735 chitin cross-linked with protein (Stankiewicz et al. 1996; 1998). In suitable conditions they  
736 can remain relatively unchanged over thousands of years (Miller 1991; Verbruggen et al.  
737 2010a). Isotope analyses of these remains can therefore be used to reconstruct past  
738 changes in the isotope composition of the formerly living organisms (Wooller et al. 2004;  
739 Verbruggen et al. 2011). The chemical composition of these remains means that they  
740 contain relatively large amounts of hydrogen, carbon, oxygen, some nitrogen, and to a  
741 lesser extent sulphur. Isolating the small remains from sediments and preparing them for  
742 stable isotope analysis can be time consuming, but efficient protocols are available (Wang  
743 et al. 2008), which can be adapted depending on the chemical pre-treatment steps  
744 required (e.g., Heiri et al. 2012). Using a 200-micrometre mesh (instead of the commonly  
745 used 90 to 100-micrometre mesh) can decrease processing time by 30 to 58 % because of  
746 the disproportionately large gain in sample mass from larger fragments (van Hardenbroek  
747 et al. 2010a). Using large mesh sizes may cause the loss of smaller fragments, which could  
748 lead to systematic bias against particular taxa and body parts – and subsequently against  
749 certain habitats, or feeding habits.

750 The amount of sample required for stable isotope analysis depends on the  
751 chemical element being analysed, the relative abundance of the element in the  
752 invertebrate remains as well as on the analytical equipment used. The carbon content of  
753 chitinous invertebrate remains is relatively high, followed by oxygen, nitrogen, and  
754 hydrogen (Table 1). The elemental composition (% by weight) of invertebrate remains is  
755 generally 40-50 %C, 25-30 %O, 7-10 %N, and 5-6 %H. Interestingly, the nitrogen content of

756 Bryozoa remains ( $12.7 \pm 1.7$  %N) is consistently higher than that of other invertebrates. A  
 757 lower carbon and nitrogen content has been observed in the carapaces of Cladocera ( $18.3$   
 758  $\pm 2.7$  %C and  $2.8 \pm 0.7$  %N, respectively). At present it is unclear what causes the  
 759 differences between taxa and different types of remains; further analysis of the chemical  
 760 composition of the remains is required.

761

762 **Table 1:** *Elemental composition (% by weight) with 1 standard deviation (SD) of*  
 763 *invertebrate remains in surface and down core sediments (n = number of data points).*  
 764 *Data from van Hardenbroek et al. (2010b, 2012, 2013b, 2014, 2018, van Hardenbroek,*  
 765 *Heiri and Wooller unpublished data, Perga unpublished data).*

	%C	SD	n	%N	SD	n
Chironomidae head capsules	46.4	5.4	247	8.6	1.3	247
Cladocera ephippia	44.4	5.4	380	8.8	1.8	379
Cladocera carapaces	18.3	2.7	28	2.8	0.7	28
Bryozoa statoblasts	45.7	3.9	168	12.7	1.7	167
Ephemeroptera mandibles	39.0	10.0	19	7.5	3.0	19
Ostracoda shell lining	41.7	7.6	11	10.4	2.1	11
Trichoptera frontoclypeus/mandible)	42.5	9.5	20	8.1	1.7	20
Sialis (frontoclypeus/mandible)	47.0	3.7	13	10.0	1.2	13
Chaoborus (mandible)	45.3	7.4	22	8.8	1.4	22
Coleoptera (elytron)	43.1	2.8	14	8.2	1.0	14

	%O	SD	n	%H	SD	n
Chironomidae head capsules	29.6	1.8	27	5.6	0.3	27
Cladocera ephippia	28.6	2.6	77	5.5	0.5	77
Bryozoa statoblasts	25.5	3.9	48	5.2	1.1	48

766

767

768 For  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  analyses an Elemental Analyser IRMS (EA-IRMS) setup is  
 769 commonly used, whereas  $\delta^{18}\text{O}$  and  $\delta\text{D}$  analysis often rely on a Thermal Conversion /  
 770 Elemental Analyzer (TC/EA)-IRMS setup. With this equipment, analyses are typically based  
 771 on tens to hundreds of invertebrate remains. A reduction of the sample size is possible  
 772 using Laser Ablation nano Combustion Gas Chromatography (LA/nC/GC)-IRMS (Schilder et  
 773 al. 2018) or Spooling-Wire Microcombustion (SWiM)-IRMS (Zhao et al. 2017), allowing  $\delta^{13}\text{C}$   
 774 analysis of individual invertebrate remains. The Supplementary Table provides an  
 775 overview of mean weight of individual remains, to allow better estimates of the minimum  
 776 number of remains required for stable isotope measurements. The mean weight of

777 remains in down core samples is seemingly smaller than that of remains in surface  
778 sediments (Supplementary Table). Material from surface and down core samples  
779 originates from different sites and includes different species, making it difficult to make  
780 conclusive statements about differences between remains in surface and down core  
781 samples in the Supplementary Table without more work on the taphonomy of  
782 invertebrate remains.

783

#### 784 *4.2 Dietary and environmental isotopes reflected by chitinous remains*

785

786 Analyses of the isotopic offsets between aquatic invertebrates, their food and their  
787 chitinous remains focussed on different organism groups such as marine crustaceans,  
788 freshwater crustaceans and aquatic insects. Much of this work started in the 1980s mainly  
789 with marine decapods (Schimmelman and DeNiro 1986a, b; Schimmelman 2011).  
790 However, results based on marine crustaceans may not be representative for chitinous  
791 microfossils of many freshwater invertebrate taxa. This is because calcium carbonate  
792 forms an important component of the exoskeleton of many crustaceans (Greenaway  
793 1985; Willis 1999), but calcium may be less relevant in some planktonic freshwater  
794 crustaceans (Jeziorski and Yan, 2006) and the cuticles of other freshwater invertebrates  
795 groups (e.g., aquatic insects, Willis 1999) do not contain calcium carbonate. Many  
796 experimental studies assessing the relationships between isotope sources and isotopic  
797 contents of invertebrates have selectively isolated and analysed chitin or chitin-derived  
798 compounds (Schimmelman and DeNiro 1986a, b; Schimmelman 2011) and this needs to  
799 be considered when using this information for interpreting stable isotope studies based on  
800 whole chitinous remains (including proteins, lipids, etc.) of aquatic invertebrates.

801

##### 802 *4.2.1 Carbon and nitrogen isotopes*

803

804 Carbon and nitrogen in chitin of heterotrophic organisms originates from their diet  
805 (DeNiro and Epstein 1978, 1981; Schimmelman 2011). Metabolic activities and life stage  
806 may also influence the isotope composition for some elements and organism groups  
807 (Schimmelman 2011). Chitinous remains of aquatic invertebrates in lake sediments do  
808 not only consist of chitin but include other organic components such as proteins or lipids

809 (e.g. Verbruggen et al. 2010a). The exact composition of fossilising exoskeleton parts may  
810 differ between organism groups but also within the same organism, between different  
811 types of structures (e.g., Jeziorski et al. 2008). Ideally, the relationship between the  
812 isotope composition of diet, bulk tissue and fossilizing structures is therefore established  
813 for each organism group and isotope pair of interest before developing down core isotope  
814 records. Experiments and environmental measurements constraining these relationships  
815 for C and N are presently available for planktonic cladocerans, chironomid larvae and  
816 bryozoans. Laboratory experiments with *Chironomus* (Chironomidae) larvae showed that  
817 there are only very minor offsets (reported here as  $\Delta$  values) between the  $\delta^{13}\text{C}$  values of  
818 the food and chironomid biomass ( $\Delta^{13}\text{C}$  of ca.  $-1.5$  to  $+1.5$  ‰ in most cases; Goedkoop et  
819 al. 2006; Wang et al. 2009; Heiri et al. 2012; Frossard et al. 2013). In contrast, observed  
820 offsets between foods and body tissue for  $\delta^{15}\text{N}$  were more pronounced ( $\Delta^{15}\text{N}$   $-1.5$  to  $+3.4$   
821 ‰; Goedkoop et al. 2006; Wang et al. 2009; Heiri et al. 2012). For fourth instar larvae,  
822 head capsule  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  values were very similar to but on average ca. 1 ‰ lower than  
823 the isotope composition of the remaining larval tissue (Heiri et al. 2012; Frossard et al.  
824 2013).

825 The  $\delta^{13}\text{C}$  values of the exoskeleton of the cladocerans *Daphnia* and *Bosmina* were  
826 shown to be very similar to the values for the bodies: offsets are  $-0.8 \pm 0.2$  ‰ and  $1.4 \pm$   
827  $0.7$  ‰ for *Daphnia* and *Bosmina*, respectively (Perga 2010). Lower  $\delta^{15}\text{N}$  values for *Daphnia*  
828 exoskeletons were observed compared with the whole bodies (by as much as  $7.9 \pm 0.5$  ‰;  
829 Perga (2010). This offset was very consistent along a gradient of *Daphnia*  $\delta^{15}\text{N}$  values,  
830 however, and a strong relationship between  $\delta^{15}\text{N}$  values of *Daphnia* exoskeletons and the  
831 entire organisms was found. The fossilizing sheaths of resting eggs (ephippia) of *Daphnia*  
832 *pulicaria* are very similar in their isotope composition to the *Daphnia* they originated from,  
833 with mean offsets of  $+0.2$  and  $-1.5$  ‰ for  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$ , respectively (Schilder et al.  
834 2015a). Experimental results indicate that the  $\delta^{13}\text{C}$  values of *Daphnia* are also close to the  
835 isotope composition of the available food, with offsets between food and *Daphnia* of  $0.5 \pm$   
836  $0.3$  ‰ ( $\Delta^{13}\text{C}$ ) and  $+3.4 \pm 0.3$  ‰ ( $\Delta^{15}\text{N}$ ) and between food and ephippia of  $0.7 \pm 0.2$  ‰  
837 ( $\Delta^{13}\text{C}$ ) and  $1.8 \pm 0.4$  ‰ ( $\Delta^{15}\text{N}$ ) (Schilder et al. 2015a).

838 Experimental results indicate that  $\delta^{13}\text{C}$  values of chitinous resting stages  
839 (statoblasts) of the bryozoans *Plumatella* and *Lophopus* are similar as those of both their

840 food and soft tissue parts of these organisms: statoblasts have between 0 to 1.7 ‰ lower  
841  $\delta^{13}\text{C}$  values than the living colonies (van Hardenbroek et al. 2016). In a survey of lakes in  
842 Northwest and Central Europe, median  $\delta^{13}\text{C}$  values of bryozoan colonies of *Cristatella*  
843 *mucedo*, *Pectinatella magnifica* and *Plumatella* were observed to be closely related with  
844 the isotope composition of the statoblasts for most sites (offsets generally between  $-3$  to  
845  $+4.5$  ‰; van Hardenbroek et al. 2016). The seemingly large variability of offsets recorded  
846 in the above study suggests that, in field situations, food sources can change between the  
847 formation of fossilising structures and the formation of new soft tissue. Chitinous  
848 fossilising invertebrate structures are formed within a period of 1-2 weeks (Candy and  
849 Kilby 1962; Nation 2002) and their stable isotope values will largely represent food sources  
850 in this period and shortly before. In the limited studies comparing living invertebrates and  
851 their fossilising structures, the  $\delta^{13}\text{C}$  values of fossilising structures are within one standard  
852 deviation of the mean  $\delta^{13}\text{C}$  values of living chironomids and cladocerans (Morlock et al.  
853 2017; Schilder et al. 2017). This strongly suggests that  $\delta^{13}\text{C}$  values of samples of fossilising  
854 structures are representative for mean  $\delta^{13}\text{C}$  values of the invertebrates at longer (annual  
855 to decadal) time scales. The large number of sedimentary remains required for regular EA-  
856 IRMS measurements will not normally allow detection of short-term (weekly to seasonal)  
857 variability in stable isotope values found in living invertebrates (but see Zhao et al. 2017  
858 and Schilder et al. 2018). Future studies should quantify the impact of tissue turnover time  
859 and the sources of material incorporated during the formation of chitinous structures on  
860 the stable isotope composition of these remains. This would be similar to stable isotope  
861 studies on turnover time of different tissues in other aquatic organisms such as fish (e.g.,  
862 Pinnegar and Polunin 1999; Hanisch et al. 2010).

863         When quantifying offsets between soft tissues and fossilising structures, controlled  
864 laboratory experiments give more consistent results than field studies. Culturing  
865 experiments have demonstrated that variability in these offsets is generally low: 0.2–0.9  
866 ‰ for  $\delta^{13}\text{C}$  and 0.3–0.5 ‰ for  $\delta^{15}\text{N}$  (Perga 2010; Heiri et al. 2012; Frossard et al. 2013;  
867 Schilder et al. 2015a). Information from such controlled experiments is crucial as it  
868 demonstrates that variability  $> 0.9$  ‰ ( $\delta^{13}\text{C}$ ) and  $> 0.5$  ‰ ( $\delta^{15}\text{N}$ ) is most likely related to  
869 environmental processes rather than natural variability in offsets between soft tissues and  
870 fossilising structures.

871

#### 872 4.2.2 Oxygen and hydrogen isotopes

873

874 Less information, compared with C and N, is available that documents the relationship  
875 between the stable O and H isotope composition of aquatic invertebrates, their fossilizing  
876 remains, and their diet and source water. Available evidence from lakes indicates that  
877 most of the O in aquatic invertebrates originates from lake water (56 to 84 %; Wang et al.  
878 2009; Nielson and Bowen 2010; Soto et al. 2013; Schilder 2015a) with smaller  
879 contributions from dietary O. The exact proportions vary between the available  
880 experiments and therefore may also vary between different organism groups, tissue types  
881 and chemical compounds. Schilder et al. (2015a) demonstrated that changing the oxygen  
882 isotope composition of the water influenced  $\delta^{18}\text{O}$  values of *Daphnia* ephippia, which were  
883 on average  $0.8 \pm 0.4$  ‰ lower than for the entire *Daphnia*. Limited evidence from this  
884 culturing experiment also suggested no significant temperature-dependent fractionation  
885 between  $\delta^{18}\text{O}$  values of water and  $\delta^{18}\text{O}$  values of *Daphnia* tissues (Schilder et al. 2015a). A  
886 close relationship between  $\delta^{18}\text{O}$  of aquatic invertebrate remains and lake water has also  
887 been confirmed by environmental surveys demonstrating a high correlation between  $\delta^{18}\text{O}$   
888 values of chitinous invertebrate remains in lake sediments and lake water  $\delta^{18}\text{O}$  (Fig. 5 and  
889 Wooller et al. 2004; Verbruggen et al. 2011; Lombino 2014; Mayr et al. 2015; Chang et al.  
890 2016, 2017; Lasher et al. 2017).

891 The greatest proportion of H in freshwater invertebrate biomass and chitinous  
892 remains apparently originates from the diet of these organisms (Solomon et al. 2009;  
893 Wang et al. 2009; Soto et al. 2013; Belle et al. 2015b). Based on controlled experiments,  
894 estimates of the amount of H in freshwater invertebrate tissue originating from water  
895 range from 20 to 47 % (Solomon et al. 2009; Wang et al. 2009; Soto et al. 2013). Belle et al.  
896 (2015b) reported offsets between chironomid larval bodies and fossilizing head capsules of  
897  $-24 \pm 7$  ‰. In a field study of bryozoan colonies in 23 lakes, median  $\delta\text{D}$  values of the  
898 fossilizing statoblasts of the colonies were relatively close to the median  $\delta\text{D}$  values of their  
899 soft tissues for *Plumatella* (observed offsets  $-34$  to  $+16$  ‰) but distinctly more negative ( $-$   
900  $75$  to  $-16$  ‰) for *Cristatella* (van Hardenbroek et al. 2016). This finding might be related to  
901 differences in food type, mobility and seasonality of resting stage production between the

902 examined bryozoan groups. The H-isotope composition of many food types available in  
903 lakes (e.g., algae and organisms feeding on these) will be related to the isotope  
904 composition of the lake water. Therefore,  $\delta D$  values of aquatic invertebrate remains will in  
905 many cases be related to lake water  $\delta D$  values, even if food sources play a major role in  
906 determining aquatic invertebrate  $\delta D$  values (see, e.g., van Hardenbroek et al. 2016).

907 The observed variability in offsets between soft tissues and fossilising structures can  
908 be as large as 50‰ for  $\delta D$  in field studies due to natural variability. Controlled laboratory  
909 experiments are required to evaluate what part of this variability is due to changes in the  
910 environment (food supply, temperature, isotope composition of lake water) and what part  
911 is the inherent natural variability in the offset between soft tissues and fossilising remains.  
912 Limited data from controlled studies suggests that natural variability in this offset may be  
913 as small as ca. 0.4‰ for  $\delta^{18}O$  (Schilder et al. 2015a) and ca. 7‰ for  $\delta D$  (Belle et al. 2015b).  
914 This implies that variations  $> 0.4$  ‰ for  $\delta^{18}O$  and  $> 7$  ‰ for  $\delta D$  will in many instances be  
915 related to environmental processes and could be interpreted in palaeoenvironmental  
916 records.

917

#### 918 *4.3 Effects of chemical treatment and taphonomy*

919

920 Chitinous invertebrate remains for isotope analysis are isolated from sediments by a  
921 combination of mechanical and chemical treatments (van Hardenbroek et al. 2010a).  
922 Sediments are usually first chemically treated by exposing the samples in a 5 to 10 % KOH  
923 solution to facilitate sieving and eliminate easily degradable organic material. For C and O  
924 isotopic analysis it is essential that carbonates are eliminated prior to isotope analysis by  
925 exposing the samples to acids (e.g., low concentration HCl solution or fumigation  
926 Verbruggen et al. 2010a; Heiri et al. 2012; Belle et al. 2014) or a buffered  $NH_4Cl$  solution  
927 (Verbruggen et al. 2010b). Commonly used chemical pre-treatment methods apparently  
928 do not strongly affect the  $\delta^{13}C$  values of chitinous and fossilizing structures (head capsules)  
929 of chironomid larvae. In contrast, the oxygen isotope composition of chironomid cuticles  
930 can be strongly affected by strong alkali or acid treatments (Verbruggen et al. 2010a;  
931 Lombino 2014) and such treatments can lead to selective removal of protein or chitin from  
932 the cuticles. Furthermore, acid solutions can promote oxygen exchange between the



933 solution and the cuticles (Verbruggen et al. 2010b). Less information is available on the  
934 effects of chemical pre-treatments on the fossilizing structures of other chitinous  
935 invertebrates and on the N- and H-isotope composition of remains. Treatment with 10 %  
936 KOH solution has no apparent effect on the C, O and N isotope composition of the  
937 ephippia sheaths of *Daphnia pulicaria* (Schilder et al. 2015a).

938 Taphonomic changes in chitinous arthropod cuticles have mainly been studied for  
939 marine crustaceans, whereas much less information is available for lacustrine  
940 invertebrates. Major losses of chitin and protein have been observed during the first  
941 weeks of biodegradation of shrimp cuticle and other arthropod remains (Stankiewicz et al.  
942 1998; Schimmelmann et al. 1986). The C, N, O and H isotope composition was found to be  
943 preserved during partial degradation of chitin leading Schimmelmann et al. (1986) to  
944 conclude that chitin in ancient archaeological deposits can still be expected to faithfully  
945 carry the original isotopic signature. However, as mentioned above, experimental results  
946 based on decapod cuticles may not be representative for chitinous cuticles of other  
947 aquatic invertebrate groups. Perga (2011) studied the effects of degradation of cladoceran  
948 exoskeletons in in lake water and anoxic sediments. In degradation experiments with  
949 cladoceran exoskeletons changes in  $\delta^{13}\text{C}$  were very small (<1 ‰) and happened within the  
950 first three months (Perga 2011). No major changes in  $\delta^{15}\text{N}$  were observed if exoskeletons  
951 were incubated in sediments, but effects were larger in oxic or anoxic lake water (+2 to +5  
952 ‰). The chemical structure of chironomid head capsules isolated from 15,000-year old  
953 sediments was shown to be very similar to modern head capsules, suggesting that no  
954 extensive chitin or protein decomposition occurred in these structures after initial  
955 decomposition (Verbruggen et al. 2010a). Down core analyses demonstrated that  
956 chironomid head capsules from sediments 11,000-15,000 years old were still  
957 characterized by the centennial- to millennial-scale changes in  $\delta^{18}\text{O}$  values that  
958 characterized precipitation and lake water compositions in Europe, during the end of the  
959 last ice age (Verbruggen et al. 2010b; Lombino 2014).

960 In summary, available evidence indicates that pre-treatment and initial decomposition  
961 affects the isotope composition of different elements differently. Only very small sample  
962 pre-treatment effects are reported for  $\delta^{13}\text{C}$  values of invertebrate remains. More  
963 significant effects have been described for  $\delta^{18}\text{O}$  values, whereas little information is

964 available for  $\delta^{15}\text{N}$  and  $\delta\text{D}$  values. Similarly, some evidence indicates that effects of  
965 degradation may be more relevant for  $\delta^{15}\text{N}$  than  $\delta^{13}\text{C}$  values of invertebrate remains,  
966 whereas studies describing these effects for  $\delta^{18}\text{O}$  or  $\delta\text{D}$  values are lacking. Nevertheless, it  
967 appears that chitinous remains preserve well and (as far as evidence is available) retain  
968 their isotopic signature in lake sediments once initial stages of decomposition have been  
969 completed, which is also confirmed by the interpretable shifts in isotope composition  
970 reported for invertebrate remains in late Quaternary sediment records (see sections 4.4  
971 and 4.5 below).

972

#### 973 4.4 *Stable carbon and nitrogen isotope records based on chitinous invertebrate remains*

974

##### 975 4.4.1 *Impacts of land use, eutrophication, and food sources*

976

977 Section 4.2.1 discussed how  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  values of invertebrates and their remains  
978 closely reflect dietary composition, usually with a systematic offset. This makes it possible  
979 to provide information about the diet of invertebrates using the carbon and nitrogen  
980 isotope composition of their remains. Diets usually consist of a mixture of sources, each  
981 with its own isotope composition, and more nutritious or more easily digestible sources  
982 may therefore be assimilated preferentially (Kamjunke et al. 1999; Goedkoop et al. 2006).  
983 The food sources available to invertebrates also strongly depend on invertebrate feeding  
984 ecology and will differ for detritivores, grazers, filterer-feeders, or predators (Merritt et al.  
985 2008; Thorp and Rogers 2015), so it is crucial to understand the parent organism's modern  
986 habitat and ecology when interpreting stable isotope values (more detailed examples in  
987 van Hardenbroek et al. (2012, 2014)). Overall,  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  values of invertebrate  
988 remains and bulk sediment tend to follow the same trends in many lakes (Struck et al.  
989 1998; Wooller et al. 2008; Griffiths et al. 2010; van Hardenbroek et al. 2014; Kattel et al.  
990 2015), but significantly different  $\delta^{13}\text{C}$  profiles have also been reported (Perga et al. 2010;  
991 Schilder et al. 2017). Recent palaeolimnological studies that have measured taxon-specific  
992  $\delta^{13}\text{C}$  values of chironomid head capsules indicate that benthic invertebrates are sensitive  
993 to changes in available carbon sources (van Hardenbroek et al. 2014; Belle et al. 2017a,b;  
994 Schilder et al. 2017), including methane-derived carbon (see section 4.4.2).

995 Planktonic cladocerans are typically filter-feeding on particulate organic matter  
996 (POM) in the water column, predominantly consisting of algae and bacteria (Kamjunke et  
997 al. 1999) and their stable isotope composition follows that of their food sources during the  
998 annual cycle (Perga and Gerdeaux 2006; Morlock et al. 2017). As primary consumers,  
999 Cladocera are very sensitive to changes in primary productivity and the stable isotope  
1000 composition of their remains can be used to trace the impact of anthropogenic nutrient  
1001 enrichment of lakes and recovery from it (Perga et al. 2010; Frossard et al. 2014; van  
1002 Hardenbroek et al. 2014). In large lakes, there can be a strong relationship between  
1003 Cladocera  $\delta^{13}\text{C}$  values and the  $\text{CO}_2$  concentration in the lake water (Smyntek et al. 2012).  
1004 This is due to the strong relationship between algal carbon fractionation and dissolved  $\text{CO}_2$   
1005 availability (e.g., Hollander and McKenzie 1991; Laws et al. 1995). Based on this  
1006 mechanism, Perga et al. (2016) have shown that in three large, temperate lakes the  $\delta^{13}\text{C}$   
1007 values of Cladocera remains can be used as an indicator of past summer surface water  $\text{CO}_2$   
1008 concentrations. In smaller lakes, however, Cladocera are more likely to also incorporate  
1009 allochthonous or methanogenic (see section 4.4.2) carbon, which can compromise the  
1010 relationship between Cladocera  $\delta^{13}\text{C}$  values and  $\text{CO}_2$  concentrations.

1011 Bryozoa are another invertebrate group that produces resting stages (statoblasts),  
1012 which have been used for stable isotope analyses (van Hardenbroek et al. 2016). Bryozoa  
1013 are mostly sessile organisms, filter-feeding on suspended POM, which consists to a  
1014 considerable extent of algae and bacteria (Kaminski 1984). Bryozoan  $\delta^{13}\text{C}$  values generally  
1015 follow the trend in  $\delta^{13}\text{C}$  values of POM or, in down core studies, SOM (Turney 1999; van  
1016 Hardenbroek et al. 2014, 2018; Morlock et al. 2017; Rinta et al. 2016).

1017 The impact of urban and agricultural pollution to lakes can result in the increase of  
1018  $\delta^{15}\text{N}$  values of SOM of aquatic origin (Cabana and Rasmussen 1996; Laevitt et al. 2006). A  
1019 number of studies have found that  $\delta^{15}\text{N}$  of Cladocera remains and SOM are related (Struck  
1020 et al. 1998; Wooller et al. 2008), but the addition of nutrients can disturb this relationship.  
1021 In Lake Annecy, Perga et al. (2010) observed increasing  $\delta^{15}\text{N}$  values of SOM and *Bosmina*  
1022 carapaces during the 1960s and 1970s eutrophication. During re-oligotrophication  $\delta^{15}\text{N}$   
1023 values of SOM decreased again, but  $\delta^{15}\text{N}$  values of *Bosmina* remained high, possibly as a  
1024 result of a shift in their diet from algae to flagellates: changing the trophic position of  
1025 *Bosmina*. Griffiths et al. (2010) investigated the effect of marine-derived nutrients from

1026 sea-bird colonies on arctic lakes and showed that this input led to an increase in SOM  $\delta^{15}\text{N}$   
1027 values. Chironomid remains showed the same trend, albeit with greater variability,  
1028 whereas *Daphnia* remains did not show any change at all, indicating that both groups of  
1029 organisms can assimilate different sources of nitrogen, at least in the periods when the  
1030 fossilizing structures are formed.

1031 Aquatic food webs can be highly complex, with large spatial and temporal variations in  
1032 the quantity of carbon and nitrogen sources as well as the isotope composition of these  
1033 sources. Attempts to interpret sedimentary stable isotope records of invertebrate remains  
1034 to estimate the relative contribution of different dietary components (algae,  
1035 allochthonous OM, bacterial biomass) requires reliable estimates of the stable isotope  
1036 composition of these dietary components. This is challenging in modern food web studies,  
1037 and even more so in palaeoenvironmental applications. Emerging compound-specific  
1038 stable isotope analysis of microbial and algal compounds (e.g., Castañeda and Schouten  
1039 2011; Middelburg 2014; Taipale et al. 2015), combined with stable isotope analysis of  
1040 specific organic remains may hold the key to a substantial increase in understanding  
1041 trophic interactions over long timescales.

1042

#### 1043 4.4.2 Methane-fuelled food webs

1044

1045 Notably low  $\delta^{13}\text{C}$  values of invertebrates compared with  $\delta^{13}\text{C}$  values of algae and SOM  
1046 occur where  $^{13}\text{C}$ -depleted methane and methane oxidizing bacteria (MOB) provide carbon  
1047 sources for lacustrine food webs (e.g., Gebruk 1993; Bunn and Boon 1993; Jones et al.  
1048 2008; Devlin et al. 2015; Grey 2016). Filter-feeding and deposit-feeding invertebrates can  
1049 partially feed on MOB biomass (or on ciliates feeding on MOB) and their  $\delta^{13}\text{C}$  values  
1050 become lower with increasing contributions of methane-derived carbon.

1051 The  $\delta^{13}\text{C}$  values of some invertebrate groups and their remains in surface  
1052 sediments are systematically related to methane concentrations or fluxes in lakes, at least  
1053 in some regions and lake types. For example,  $\delta^{13}\text{C}$  values of Chironomini larval head  
1054 capsules and of *Daphnia* ephippia were negatively correlated to diffusive methane fluxes  
1055 in 17 lakes studied in Sweden and arctic Siberia (van Hardenbroek et al. 2013b). Also,  $\delta^{13}\text{C}$   
1056 values of *Daphnia* ephippia in 15 European lakes were found to correlate to lake methane

1057 concentrations (Schilder et al. 2015b) and  $\delta^{13}\text{C}$  values of Chironomini larvae in 6 lakes in  
1058 arctic Alaska were correlated to methane oxidation rates (Hershey et al. 2015). These  
1059 findings agree with the observation that, in small European lakes, the abundance of  $^{13}\text{C}$ -  
1060 depleted fatty acids in surface sediments, originating at least partially from MOB, also  
1061 increases with increasing  $\text{CH}_4$  concentrations (Stötter et al. 2018). This suggests that MOB  
1062 concentrations in these lakes also increase with  $\text{CH}_4$  concentrations. Sediment core studies  
1063 indicated higher uptake of methane-derived carbon in certain invertebrate groups (mainly  
1064 belonging to the chironomids and cladocerans) with increased primary productivity in  
1065 lakes. This was either driven by anthropogenic nutrient addition (Frossard et al. 2015;  
1066 Belle et al. 2016a, b; Rinta et al. 2016; Schilder et al. 2017), or triggered by warmer/wetter  
1067 climatic conditions (Wooller et al. 2012; van Hardenbroek et al. 2013b). Quantifying the  
1068 uptake of methane-derived carbon using isotope mixing models is possible, using the  $\delta^{13}\text{C}$   
1069 values of the two end member food sources, MOB and algae. POM/SOM has been used as  
1070 approximation for algae (Wooller et al. 2012; Belle et al. 2014, 2015b, 2016b; Schilder et  
1071 al. 2017), although this approach is associated with high levels of uncertainty due to  
1072 variations in  $\delta^{13}\text{C}$  values of methane and algal material between lakes.

1073 Measurements of  $\delta\text{D}$  values of invertebrates can also potentially be used to assess  
1074 the contribution of MOB to their diet, since methanogens also strongly discriminate  
1075 against the heavier D, and the resulting low  $\delta\text{D}$  values are transferred to certain taxa of  
1076 chironomid larvae (Deines et al. 2009; Belle et al. 2015b). In addition, in lakes with  
1077 significant contributions of methane to the lacustrine food web,  $^{14}\text{C}$  analyses of  
1078 invertebrate remains may in some situations be used to constrain the amount of old  
1079 carbon entering the food web: e.g., via methane from decomposing Pleistocene deposits  
1080 (Wooller et al. 2012; Elvert et al. 2016). However, in hard water lakes this approach is further  
1081 complicated by other old carbon sources such as carbonates derived from local bedrock.

1082 The stable isotope composition of invertebrates can vary seasonally in relation to  
1083 MOB availability, notably during autumn turnover when methane stored in the  
1084 hypolimnion is mixed (e.g., Grey et al. 2004; Kankaala et al. 2010; Yasuno et al. 2012). The  
1085  $\delta^{13}\text{C}$  values of invertebrate remains, however, are more likely to represent average values  
1086 of these seasonal variations (Morlock et al. 2017; Schilder et al. 2017, 2018; van  
1087 Hardenbroek et al. 2018). Likewise, spatial variation of methane production in lakes can

1088 lead to spatial variability of  $\delta^{13}\text{C}$  values of invertebrates (Deines and Grey 2006; Agasild et  
1089 al. 2013), which can also be observed in the remains (van Hardenbroek et al. 2012; Belle et  
1090 al. 2015a). Interesting examples of spatial variability of methane-derived carbon are  
1091 provided by Frossard et al. (2014, 2015), who observed an expansion (to shallower depths)  
1092 of the anoxic hypolimnion with ongoing eutrophication. As a result, chironomid head  
1093 capsule  $\delta^{13}\text{C}$  values became progressively lower, a process that was first observed in the  
1094 deepest cores, followed a few decades later in shallower cores.

1095

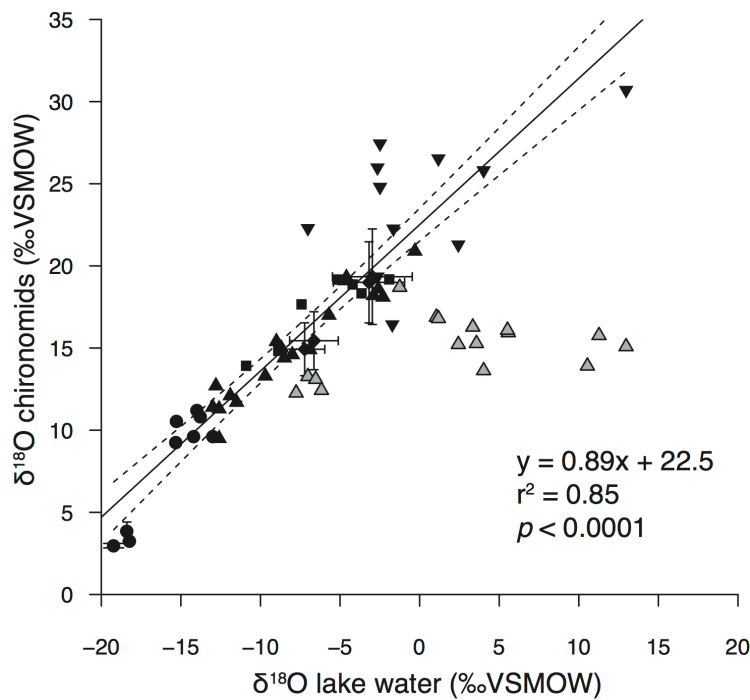
#### 1096 *4.5 Stable oxygen and hydrogen isotope records based on chitinous invertebrate remains*

1097

1098 The  $\delta^{18}\text{O}$  values of organic remains can provide information on the  $\delta^{18}\text{O}$  values of lake  
1099 water in which the organic remains were produced. Wooller et al. (2004) were the first to  
1100 measure  $\delta^{18}\text{O}$  values of chironomid head capsules in lake sediment records and  
1101 demonstrated that, within analytical error, chironomid  $\delta^{18}\text{O}$  values agree with the  
1102 expected  $\delta^{18}\text{O}$  values of modern regional precipitation. The relationship between  $\delta^{18}\text{O}$   
1103 values of lake water and chironomid remains has since been further validated and  
1104 explored via laboratory experiments (section 4.2.2) and field surveys. The field  
1105 relationship has been reproduced and further explored over larger transects and multiple  
1106 regions (Fig. 5), including Europe (Verbruggen et al. 2011; Lombino 2014), South America  
1107 (Mayr et al. 2015), Greenland (Lasher et al. 2017), and Australia (Chang et al. 2016, 2017).  
1108 In lakes with short residence times ( $\leq 1$  year), i.e. open basins, the relationship between  
1109 chironomid head capsules and lake water  $\delta^{18}\text{O}$  values is strong (Fig. 5). Here, chironomid  
1110  $\delta^{18}\text{O}$  values are enriched relative to lake water by  $\sim 22.5$  ‰. This relationship appears to  
1111 fail in closed basin lakes with long residence times. Sampled lake water from such lakes  
1112 may not reflect  $\delta^{18}\text{O}$  values of waters during the growing season due to evaporation  
1113 effects. In lakes where lake water – chironomid enrichment factors differ greatly from the  
1114 mean relationship demonstrated in open basins, an assessment of lake hydrology is  
1115 necessary to clarify what chironomid  $\delta^{18}\text{O}$  values are recording.

1116

1117



1118  
1119

1120 **Fig. 5:** Relationship between  $\delta^{18}\text{O}$  values of (lake) water and  $\delta^{18}\text{O}$  values of chironomid  
1121 head capsules from surface sediment samples. Plotted data points are from Verbruggen et  
1122 al. 2011 (closed triangles), Lombino 2014 (closed diamonds), Mayr et al. 2015 (closed  
1123 squares), Chang et al. 2016 (shaded triangles), Chang et al. 2017 (closed inverted  
1124 triangles), and Lasher et al. 2017 (closed circles). Error bars indicate 1 standard deviation  
1125 variability in replicate data from individual sites, where available. The linear regression  
1126 excludes data points from Chang et al. 2016, as these contain closed systems with high  
1127 evaporation, where the  $\delta^{18}\text{O}$  of sampled lake water may not be indicative of  $\delta^{18}\text{O}$  value of  
1128 water during chironomid growth.

1129

1130 Although chironomid larvae are often abundant in lake sediments, recalcitrant  
1131 organic structures of other aquatic organisms have also been used to measure  $\delta^{18}\text{O}$   
1132 values, including cladoceran ephippia (Verbruggen et al. 2011; Schilder et al. 2015a) and  
1133 elytra of aquatic beetle genera *Helophorus* and *Hydroporus* (van Hardenbroek et al.  
1134 2013a).

1135 Based on these demonstrated positive relationships between the  $\delta^{18}\text{O}$  values of  
1136 organic invertebrate remains and those of lake water (Fig. 5), a growing number of  
1137 palaeoecological and palaeoclimatic studies have used  $\delta^{18}\text{O}$  analyses of organic

1138 invertebrate remains as a palaeoclimatic proxy. Records have largely been developed from  
1139 sites from higher latitudes including Greenland (Wooller et al. 2004; Lasher et al. 2017),  
1140 Iceland (Wooller et al. 2008), Alaska (Wooller et al. 2012; Graham et al. 2016) and  
1141 Svalbard (Arppe et al. 2017; Luoto et al. 2018), but also from mid-latitudes (Verbruggen et  
1142 al. 2010b; Lombino 2014). These  $\delta^{18}\text{O}$  records do not only reflect temperature changes,  
1143 but a combination of drivers including (1) seasonality and source region of precipitation,  
1144 (2) the balance between inputs (precipitation, snow melt, inflow) and evaporation, and (3)  
1145 composition of invertebrate assemblages, their habitat and ecology. As a result, the  $\delta^{18}\text{O}$   
1146 records may in some situations be more variable than independent temperature  
1147 reconstructions (e.g., Wooller et al. 2004, 2008, 2012). In some records, however,  
1148 chironomid  $\delta^{18}\text{O}$  values closely follow minor climate oscillations (Verbruggen et al. 2011b;  
1149 Lombino 2014; Arppe et al. 2017). Chironomid  $\delta^{18}\text{O}$  has also been used to show the  
1150 reduction in freshwater availability attributed to the local extinction of woolly mammoth  
1151 on St. Paul Island (Graham et al. 2016).

1152 In contrast to the  $\delta^{18}\text{O}$  values from chironomids and other aquatic invertebrates, the  
1153  $\delta\text{D}$  values of these organisms have been found to be primarily controlled by the  $\delta\text{D}$  values  
1154 of diet rather than source water (section 4.2.2). Given this finding,  $\delta\text{D}$  values from  
1155 chironomids have found to be a valuable dietary biomarker, and used to trace the use of  
1156 terrestrial and methanogenic carbon by aquatic organisms (Deines et al. 2009; Karlsson et  
1157 al. 2012; Belle et al. 2015b; Mariash et al. in press, and see section 4.4.2).

1158

## 1159 4.6 *Other organic remains*

1160

### 1161 4.6.1 *Aquatic plant macrofossils*

1162

1163 Records of  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  of aquatic cellulose in lake sediments are widely available (e.g.,  
1164 Wolfe et al. 2007; Mayr et al. 2015; Street-Perrot et al. 2018) but are not discussed here. In  
1165 contrast, continuous, high-resolution sediment records of aquatic plant remains have only  
1166 in rare cases been analysed for their stable isotope composition. For example, Turney  
1167 (1999) found little variation in the  $\delta^{13}\text{C}$  values of terrestrial plant remains compared with  
1168  $\delta^{13}\text{C}$  of SOM in two kettle-hole lakes in the UK, while  $\delta^{13}\text{C}$  values of aquatic plant remains



1169 (*Potamogeton*) was more variable, possibly in response to changes in productivity. A  
1170 systematic study of the difference between  $\delta^{13}\text{C}$  values of *Potamogeton* and  $\delta^{13}\text{C}$  values of  
1171 DIC in lakes on the Tibetan Plateau and Yakutia (Herzschuh et al. 2010a), demonstrated  
1172 that this difference is dependent on the growth rate, which can be interpreted in terms of  
1173 productivity and applied to sediment records. Another study linked variations in  $\delta^{15}\text{N}$   
1174 values of aquatic macrophyte remains with N-limitation and productivity (Herzschuh et al.  
1175 2010b). When the organic matter produced within lakes by aquatic macrophytes and algae  
1176 is an important component of SOM, the stable isotope composition of SOM and algae (e.g.  
1177 *Botryococcus*) are strongly coupled, even on millennial time scales (Heyng et al. 2012). In a  
1178 study of 40 lakes on the Tibetan Plateau  $\delta^{13}\text{C}$  values of aquatic macrophytes correlated  
1179 positively with  $\delta^{13}\text{C}$  values of SOM, although much stronger correlations existed between  
1180  $\delta^{13}\text{C}$  values of *Potamogeton* and  $\delta^{13}\text{C}$  values of mid-chain n-alkanes, which are largely  
1181 produced by the macrophytes (Aichner et al. 2010). This study also demonstrated the  
1182 effect of terrestrial organic matter on  $\delta^{13}\text{C}$  of SOM and the importance of measuring  $\delta^{13}\text{C}$   
1183 values of different carbon sources to understand palaeolimnological records of SOM  $\delta^{13}\text{C}$   
1184 values (e.g., Gu et al. 2006; Das et al. 2008; Drew et al. 2008). The use of spooling-wire  
1185 microcombustion IRMS makes it possible to analyse very small samples of carbonised  
1186 terrestrial plant material (Urban et al. 2010, 2013). This approach could also be applied to  
1187 aquatic plant remains to disentangle the relative importance of terrestrial and aquatic  
1188 carbon sources in SOM.

1189 Stable oxygen isotopes of aquatic plant macrofossils have been studied in a similar  
1190 way as aquatic invertebrate remains (section 4.5), indicating a strong relationship between  
1191  $\delta^{18}\text{O}$  values of lake water and aquatic moss fragments (Zhu et al. 2014; Lasher et al. 2017).  
1192 Furthermore, stable oxygen isotope values of aquatic moss macrofossils and those of  
1193 purified cellulose are strongly correlated in some lakes, with a reported mean  $\delta^{18}\text{O}$  offset  
1194 from cellulose of  $\sim 2.7\text{‰}$  for aquatic vascular plants and  $\sim 1.3\text{‰}$  for aquatic mosses (Zhu et  
1195 al. 2014).

1196

#### 1197 4.6.2 Fish remains

1198

1199 Fish have crucial top-down impact on the structure of lake ecosystems, generally taking up

1200 the highest trophic positions in lacustrine food webs. Fish remains (e.g., scales, teeth,  
1201 bones and otoliths) can be preserved in lake sediments (e.g., Wooller et al. 2015) and the  
1202 assemblages in surface sediments broadly reflect the species in living fish communities  
1203 (Davidson et al. 2003). Fish remains contain organic and calcified moieties. The organic  
1204 fraction, mostly collagen, is derived from diet, whereas the calcified fraction can come  
1205 from both diet and DIC in lake water (Hoie et al. 2003). A good relationship between the  
1206  $\delta^{13}\text{C}$  values of scales and muscle tissue was found, with systematic offsets of ca. 2.5 to 4 ‰  
1207 and  $-1.5$  to  $0$  ‰ for  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$ , respectively (Perga and Gerdeaux 2003; Kelly et al.  
1208 2006). Decalcifying scales can improve this relationship (Perga and Gerdeaux 2003), but  
1209 has a minimal effect on  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  values (Ventura and Jeppesen 2010). Stable isotope  
1210 analysis of fish remains from lake sediments (Patterson et al. 1993; Wooller et al. 2015),  
1211 archived fish scale collections (Gerdeaux and Perga 2006), and fish remains from  
1212 archaeological settings (Häberle et al. 2016) hold great potential for investigating changes  
1213 in food chain length and trophic interactions in response to, for example, eutrophication,  
1214 non-native species introductions, fisheries and aquaculture.

1215

#### 1216 *4.7 Future directions*

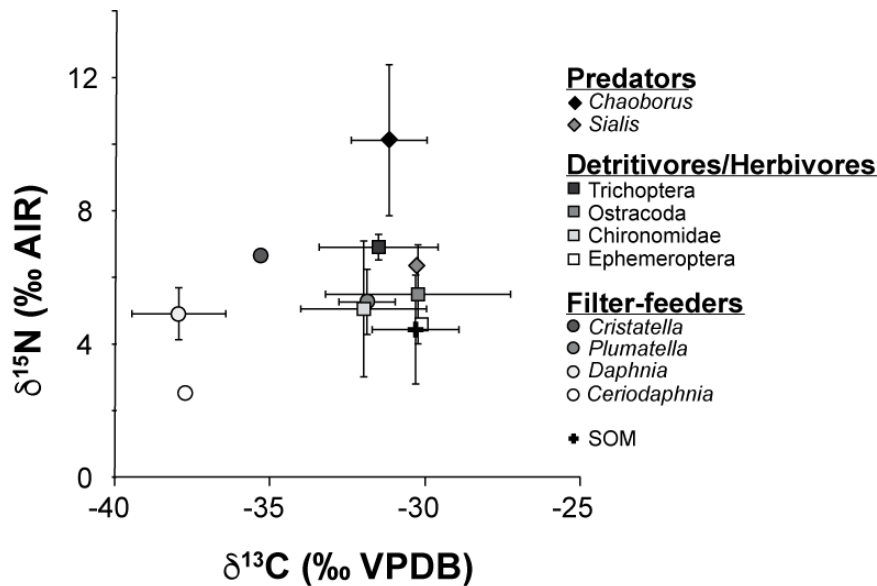
1217

1218 An increasing number of studies use stable isotope analyses on organic remains in  
1219 sediment records from arctic, boreal, and temperate regions. In contrast, subtropical and  
1220 tropical sediment records are almost completely absent, although the same pattern  
1221 applies to modern limnological studies (e.g., Iglesias et al. 2017; Sanseverino et al. 2012).  
1222 Other aspects that deserve further study are understanding drivers of spatial variability  
1223 within lake basins, for example by comparing shallow and deep-water cores (Frossard et  
1224 al. 2015), and by measuring the stable isotopes on components of the modern lake  
1225 (eco)system and catchment to better understand taphonomic processes and constrain  
1226 palaeolimnological interpretations (Morlock et al. 2017; Arppe et al. 2017). Related to this  
1227 is the continued need for controlled growth and feeding experiments, especially those that  
1228 investigate temperature-dependent fractionation (Schilder et al. 2015a).

1229 A novel direction is the use of dual  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  values from organic remains of  
1230 organisms, at different trophic positions throughout a sediment record, which allows the

1231 study of changes in food web structure over time. Initial work on invertebrate remains  
 1232 from surface sediments indicates that ranges of  $\sim 10$  ‰ for both  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  values can  
 1233 be observed (Fig. 6), similar to the ranges found in soft tissues of these organisms (e.g.,  
 1234 Jones and Grey 2011). Related to this is the potential for using  $\delta^{34}\text{S}$  values (e.g., Grey and  
 1235 Deines 2005) to understand trophic relationships as preserved in fossil assemblages.

1236



1237

1238

1239 **Fig. 6:**  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  values of invertebrate remains and SOM from surface sediments in  
 1240 Lake De Waay, The Netherlands (van Hardenbroek, Heiri, Schilder, Wooller unpublished  
 1241 data).

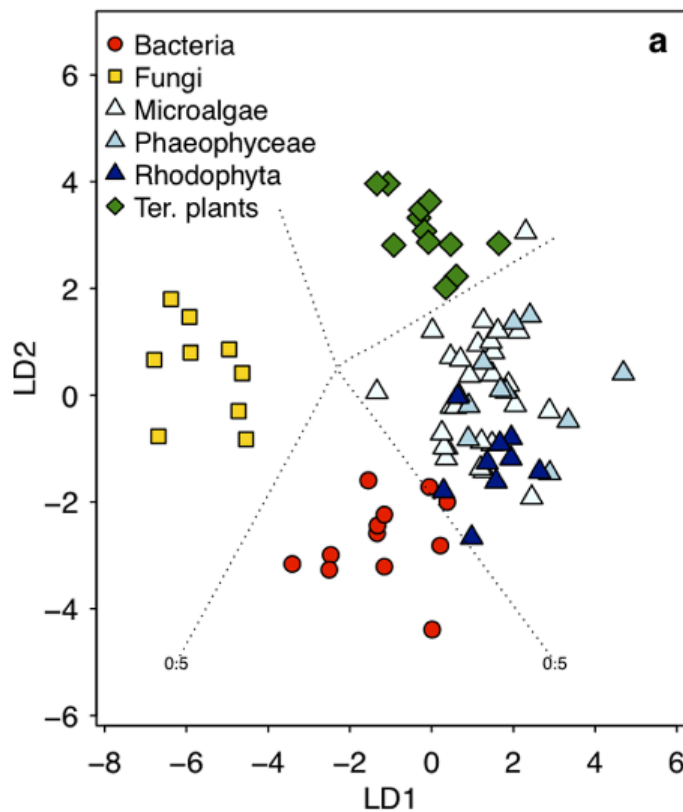
1242

1243 A further approach to understanding food web structure is by analysing stable  
 1244 carbon isotopes of essential amino acids in tissues (Larsen et al. 2009). These amino acids  
 1245 have specific stable isotope values, or isotope “fingerprints”, depending on the primary  
 1246 producer type that synthesised the essential amino acids: aquatic photosynthetic (derived  
 1247 from dissolved organic carbon), terrestrial photosynthetic (derived from atmospheric  
 1248 carbon dioxide) and microbial (Fig. 7). These fingerprints are independent of the isotope  
 1249 composition of the carbon source that was originally used to synthesise the essential  
 1250 amino acids and they are retained in consumer tissues (Larsen et al. 2009). These  
 1251 fingerprints can also be used in mixing model approaches to determine the proportional  
 1252 contribution of different primary production sources (e.g. terrestrial vs. aquatic vs.

1253 microbial) to consumers (Larsen et al. 2009; Larsen et al. 2013). This approach has been  
1254 tested in some marine ecosystems (Larsen et al. 2013; Arthur et al. 2014) and initial  
1255 palaeolimnological work is promising (Carstens et al. 2013).

1256

1257



1258

1259

1260 **Fig. 7:** Linear discriminant (LD) function analysis of the stable carbon isotope composition  
1261 of essential amino acids demonstrates the “fingerprinting” of a range of primary  
1262 production sources (from Larsen et al. 2013).

1263

1264

## 1265 **5. Stable isotope modelling in palaeolimnology**

1266

1267 Stable isotopes, for all their attractive qualities as environmental, ecological and  
1268 behavioural tracers, are at times rather blunt instruments: tissue isotope compositions are  
1269 influenced by a wide range of potential drivers, so that interpreting the cause(s)  
1270 contributing to any measured variation in isotope compositions can be challenging.

1271 Modern ecology and hydrology have greatly profited from explicit modelling of variations  
1272 in stable isotope composition due to known stressors, impacts, and processes, which can  
1273 help to separate realistic from unrealistic scenarios even in complicated situations with  
1274 overlapping variabilities due to seasonal changes, different drivers, and site- or taxon-  
1275 specific isotopic offsets. This type of modelling is mostly lacking when interpretations are  
1276 made in palaeolimnological studies, and some examples are outlined here that show how  
1277 approaches developed in modern modelling studies could be applied to palaeorecords.

1278 This section will focus on the potential and pitfalls of modelling carbon and nitrogen  
1279 isotopes in modern and palaeo food webs and how this can contribute to the  
1280 interpretation of stable isotope records based on fossil remains in lake sediments. Recent  
1281 advances in the use of stable isotopes of oxygen and hydrogen in (palaeo)hydrological  
1282 modelling are only briefly highlighted, as the topic was reviewed recently (Jones et al.  
1283 2016a).

1284

### 1285 *5.1 Carbon and Nitrogen*

1286

1287 In a review of the use of stable isotopes in ecology, Boecklen et al. (2011) identify 46  
1288 separate sources of variation in stable isotope compositions (predominantly  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$   
1289 values) of organisms. In their review, the isotope composition of an organism is viewed as  
1290 an emergent property of that organism, influenced by the factors that are frequently the  
1291 subject of palaeontological investigation such as diet, trophic level, and environmental  
1292 variability (e.g., habitat and seasonality), but also by a large range of additional  
1293 physiological, ecological and biochemical factors that are often difficult to assess in  
1294 palaeoecological and palaeoenvironmental studies such as temporal and spatial variations  
1295 in stable isotope compositions of nutrients and food sources and physiological influences  
1296 on isotopic fractionation. Interpretations of stable isotope data are therefore vulnerable  
1297 to making overly simplified assumptions, and it is helpful to consider how sources of  
1298 uncertainty and variance can impact the validity of isotope-based ecological or  
1299 environmental interpretation before identifying possible solutions to deal with  
1300 uncertainty.

1301 In the simplest ideal case, the isotope composition of carbon and nitrogen in  
1302 consumers reflects the isotope composition of their prey. Where a consumer derives

1303 resources from two or more isotopically distinct prey sources, the relative importance of  
1304 those sources can be determined from a mass-balance based isotope mixing model (for  
1305 example, in the case of carbon derived from phytoplankton and methane, see section  
1306 4.4.2). Measuring stable isotopes on 'pure' algal or bacterial biomass is challenging in  
1307 modern food webs and culturing experiments (Templeton et al. 2006; Vuorio et al. 2006).  
1308 This hinders defining the isotope values of sources at the base of lake food webs and leads  
1309 to assumptions and uncertainties in mass-balance models. Compound-specific stable  
1310 isotope analysis of biomarkers typical for particular algal (n-alkanes, pigments, fatty acids,  
1311 amino acids) and bacterial groups (fatty acids, hopanols, amino acids), are now emerging  
1312 as palaeolimnological tools (Huang et al. 1999; Aichner et al. 2010; Castañeda and  
1313 Schouten 2011; Larsen et al. 2013; Middelburg 2014; Taipale et al. 2015; Elvert et al. 2016)  
1314 and will potentially address this issue.

1315         Mass-balance type models also assume the isotopic offset between diet and tissue  
1316 is known (see, e.g., McCutchan et al. 2003 and sections 4.2). More advanced Bayesian  
1317 mixing models such as SIAR (Parnell et al. 2013), mixSIR (Semmens et al. 2009) and FRUITS  
1318 (Fernandes et al. 2014) have been developed to incorporate uncertainties in diet-tissue  
1319 isotopic fractionation and to consider isotopic distributions of potential food sources.  
1320 However, mixing models are still simplifications of food webs with relatively limited  
1321 consideration of temporal or spatial variation in either isotope compositions or trophic  
1322 interactions. Model outputs should be interpreted with care to avoid oversimplification, as  
1323 highlighted by authors of isotopic mixing models and isotope metrics themselves (Layman  
1324 et al. 2012; Phillips et al. 2014), but can nevertheless provide estimates of the likelihood of  
1325 different scenarios, although it remains difficult to include temporal and spatial variability.

1326         Seasonality has a marked effect on biogeochemical cycles, associated nutrient  
1327 isotope compositions, food availability and food web structure (e.g., Woodland et al.  
1328 2012; Junker and Cross 2014; Visconti et al. 2014). Most isotope-based ecological analyses  
1329 either explicitly compare the isotope composition of the animal in question to a reference  
1330 baseline animal, assuming a constant isotopic baseline or infer that temporal change in  
1331 consumer isotope values reflects changes in the baseline isotope compositions. In all these  
1332 cases, short-term (e.g., seasonal) variability in isotope baselines can complicate  
1333 interpretations of consumer isotope data. This will be particularly pertinent for consumers  
1334 with high growth or metabolic rates such as chironomids, cladocerans, and

1335 ephemeropterans, where dynamic changes in baseline isotope values will be rapidly  
1336 incorporated into consumer tissues, although this is mediated to some extent because  
1337 many fossil specimens are needed for one stable isotope measurement, and therefore  
1338 represent a larger period of time. Woodland et al. (2012) built a time dynamic isotope  
1339 mixing model by coupling combined time-dependent functions of temporal baseline  $\delta^{13}\text{C}$   
1340 variation and functions predicting consumer isotope composition as a function of growth.  
1341 Relaxing assumptions of isotopic equilibrium, both in terms of consumer growth and  
1342 isotopic baselines, resulted in different and more realistic reconstructions of the  
1343 contribution of benthic resources to diets. Studies that quantify and model the isotope  
1344 variability in aquatic organisms are essential for understanding stable isotope records  
1345 from lake sediment cores, although few modern surveys are designed with  
1346 palaeoenvironmental applications in mind (e.g., von Grafenstein et al. 1999b; Dixit et al.  
1347 2015; Morlock et al. 2017; Schilder et al. 2017; section 4.5).

1348         When different locations and palaeolimnological studies are considered,  
1349 potentially confounding aspects of spatial/geographical variability, diagenesis and time  
1350 averaging are also added. Very quickly the number of potential variables that could be  
1351 drawn on to explain an observed temporal change either in means or distributions of  
1352 organism stable isotope compositions increases, leading to a range of possible scenarios  
1353 that could explain a measured isotopic response. One approach to quantitatively choosing  
1354 between alternative mechanisms responsible for measured isotopic variability is through  
1355 mechanistic modelling. For example, Magozzi et al. (2017) estimated spatial variations in  
1356 inter-annual ranges of  $\delta^{13}\text{C}$  values for phytoplankton, and show that these vary  
1357 systematically with latitude, at less than 1.5 ‰ in equatorial regions to >9 ‰ in highly  
1358 seasonal arctic systems. Estimates of spatial and temporal variability in isotopic baselines  
1359 can form the basis for more complex simulations of isotopic variability in food webs under  
1360 differing scenarios, and with differing sampling protocols.

1361         As a simple conceptual example, a time series of  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  values from benthic  
1362 insect remains from a sediment record within a small temperate lake can be assumed.  
1363 Changes in isotope composition and distributions through time are observed and the  
1364 question is what contributed to the observed change. A change in external conditions is  
1365 suspected (e.g., a change in the supply of terrestrial organic matter into the lake), but  
1366 uncertainty remains whether any other potential driving mechanisms (e.g., Boecklen et al.

1367 2011) or systematic changes in sampling associated with sedimentation could have  
 1368 contributed to the observed pattern. To set up a basic conceptual model of the isotopic  
 1369 systematics in the lake it is necessary to establish variables associated with isotope  
 1370 composition of nutrient inputs to the lake, pelagic production and benthic production.  
 1371 Each of these variables will have defined seasonal, inter-annual and longer-term  
 1372 variability, which can be varied in the model.

1373  
 1374  
 1375

**Table 2:** *Example of variables needed to derive a basic simulation of time series of lake sediment isotopic records.*

Nutrient input	Primary production	Benthic production	Taphonomy
<p>The number of isotopically distinct sources of carbon and nitrogen entering the lake.</p> <p>Proportional contribution of each nutrient source to primary production.</p> <p>The isotope composition of each source.</p> <p><b>Temporal variation in the above</b></p>	<p>Isotopic fractionation associated with primary production (with uncertainty) – can be linked to temperature and/or cell growth rate.</p> <p>Proportion of primary production formed in each season.</p> <p><b>Temporal variation in the above</b></p>	<p>Proportional contributions of detrital and pelagic organic matter to sediment.</p> <p>Contribution of methane to sediment organic matter.</p> <p><b>Temporal variation in the above</b></p>	<p>Time of year represented in the sample.</p> <p>Number of years assimilated into a single sample.</p> <p>Variability in sample time averaging.</p> <p>Differential loss of isotopically distinct fractions of production.</p>

1376  
 1377 Simple conceptual model systems building on variables suggested in Table 2 allow  
 1378 investigators to explore sensitivity of the measured output (the expected means or  
 1379 isotopic distributions of a population of invertebrates) to a range of variables, including  
 1380 seasonality, benthic vs. pelagic production, temperature-related differences in isotopic  
 1381 fractionation in phytoplankton, proportional methane contributions and terrestrial detrital  
 1382 matter input. In addition, the sensitivity of the system to naturally uneven sampling can be  
 1383 explored. Using this type of modelled time series in tandem with palaeoenvironmental  
 1384 records from lake sediments make it possible to test the likelihood of alternative scenarios



1385 and interpretations. This is not unlike studies that test models of fossil assemblage data  
1386 from sediment record to understand sensitivity or response of lake ecosystems to critical  
1387 transitions (e.g., Seddon et al. 2014; Doncaster et al. 2016).

1388

## 1389 *5.2 Oxygen and hydrogen*

1390

1391 An increasing number of palaeoenvironmental studies uses the systematic relationship  
1392 between climatic variables and  $\delta D$  and  $\delta^{18}O$  values measured from environmental water  
1393 (Dansgaard 1964; Gat 1996) to interpret proxies of palaeo lake water recorded in  
1394 sediment archives (Darling et al. 2006, Jones et al. 2016a; Swann et al. 2018). Mass-  
1395 balance models based on the linear resistance model of Craig and Gordon (1965) for the  
1396 isotope composition of evaporating water have been used to explain large proportions of  
1397 the variability in lake water isotopes, although the many steps between the isotope  
1398 composition of precipitation and the isotopic signal preserved in proxy records require a  
1399 thorough understanding of the 'proxy systems' and how they filter and adapt this  
1400 variability (Feng et al. 2016; Gibson et al. 2016; Jones et al. 2016b). Jones et al. (2016a)  
1401 suggest that such proxy system models (PSMs) could potentially be used to predict  
1402 'forward' modelled proxy time series. These predictions could then be tested against  
1403 output from General Circulation Models (GCMs) that have stable water isotope physics  
1404 included, although downscaling GCM output to make it compatible with local palaeo  
1405 records is challenging (e.g., Sturm et al. 2010). The inclusion of stable water isotopes in  
1406 GCMs now also allows quantitative validation of GCMs using water isotope data from  
1407 palaeoenvironmental records (especially when based on large, amalgamated data sets  
1408 that go beyond the local scale, as described by Horton et al. 2016). The water isotope  
1409 component of GCMs also creates opportunities for hypothesis-driven exploration of  
1410 palaeo climate data based on GCM output (e.g., Holmes et al. 2016). Further effort is  
1411 needed from the modelling, monitoring, and palaeo communities to quantifying the  
1412 physical processes in the atmosphere that drive spatial and temporal heterogeneity in  
1413 water isotopes. It might be challenging, however, to find 'well-behaved' lake systems due  
1414 to large variations and complexity of local hydrology (both spatially and temporally) that  
1415 affect the stable isotope composition of lake systems compared to marine systems.

1416

1417 **6. Concluding remarks**

1418

1419 This review shows the extraordinary potential for using stable isotope systems of H, C, N,  
1420 O, and Si from the macro- and microscopic remains of a wide range of organisms  
1421 commonly preserved in lake sediments. The stable isotope composition of these siliceous,  
1422 carbonate and organic components have been related to a range of ecological and  
1423 environmental variables and processes including evaporation, climate, nutrient cycling,  
1424 productivity, and methane cycling. Stable isotope measurements on fossil remains have  
1425 been used to reconstruct past changes in these variables and processes. Furthermore,  
1426 new approaches for reconstructing past environmental and ecosystem change (e.g.,  
1427 analysing changes in primary productivity or the structure of palaeo food webs) are  
1428 continuously being developed, expanding the range of applications for isotope analyses  
1429 based on macro- and microscopic remains in lake sediments. Our review has provided an  
1430 overview of the level of understanding of the driving variables for environmental proxies  
1431 based on isotope measurements. Complicating factors such as the effects of seasonality,  
1432 transport, sample preparation, offsets between different tissues, and of confounding  
1433 environmental variables, have also been highlighted. These factors remain a major  
1434 challenge for emerging but also established isotope based approaches analysing biotic  
1435 remains in lake sediments. An important aim of the review is therefore to also highlight  
1436 the importance of calibration studies, be it controlled experiments or in field surveys. Such  
1437 calibrations are essential to better understand the relationships between stable isotope  
1438 composition and ecological/environmental variables, and are crucial to interpret  
1439 variability measured in down core applications in terms of an ecological/environmental  
1440 'signal' or stochastic 'noise'. Modelling can be a valuable tool to increase our ability to  
1441 distinguish likely scenarios from unlikely ones. We have also touched on recent  
1442 methodological advances that have led to expanding the use of Si isotope measurements  
1443 on diatoms, or reducing the sample size needed for analysis of C isotopes on organic  
1444 samples, making it clear that technical developments are necessary to continue to  
1445 increase the stable isotope toolkit available to palaeolimnological studies.

1446

1447 **Author contributions**

1448

1449 MvH initiated the workshop on stable isotopes in fossils and organic compounds in lake  
1450 sediments, coordinated the review and manuscript, and drafted sections 1, 4.5, 4.6, 4.7  
1451 and 5.2; ML and VP drafted section 2; JAH drafted section 3; OH drafted section 4.2 and  
1452 4.3; MJW drafted section 4.4; CT drafted section 5.1. All co-authors participated in  
1453 workshop discussion groups, provided input for the manuscript, and suggested  
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1455

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1465

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2438



2439 **Supplementary Table:** Mean weight and standard deviation of individual invertebrate  
 2440 remains. Data are derived from surface and down core sediments after chemical  
 2441 processing with 10 % HCl and 10 % KOH (van Hardenbroek et al. 2010b, 2012, 2013; van  
 2442 Hardenbroek, Heiri and Wooller unpublished). Note that values are means for samples  
 2443 containing different sizes of remains, including head capsules from different larval instars.

	Surface samples			Down core samples		
	weight (µg)	SD	n	weight (µg)	SD	n
<b>Chironomid head capsules</b>						
<i>Chironomus anthracinus</i> -type	2.5	3.4	18			
<i>Chironomus plumosus</i> -type	2.8	2.7	14			
<i>Chironomus</i> spp.	2.1	2.1	81	1.2	0.4	30
<i>Dicrotendipes</i>	1.2	0.7	6			
<i>Endochironomus</i>	1.0	0.5	6			
<i>Glyptotendipes</i>	2.0	2.3	6			
<i>Microtendipes</i>	1.0	0.4	5			
<i>Polypedilum</i>	0.6	0.2	5			
<i>Sergentia</i>	0.9	0.3	1			
Chironomini (including all taxa)	1.6	2.2	241	1.0	0.4	76
<i>Corynocera ambigua</i>				1.3	0.1	7
Tanytarsini	0.6	0.5	122	0.5	0.2	39
Orthocladiinae	0.7	0.5	105	0.9	0.5	42
Diamesinae	1.9	0.9	3			
Tanypodinae	1.0	0.7	89	1.0	0.3	17
<b>Cladoceran ephippia</b>						
<i>Daphnia</i> spp.	2.8	2.9	148	2.8	2.7	51
<i>Simocephalus vetulus</i>	2.8	1.4	11			
<i>Ceriodaphnia</i> spp.	0.8	0.7	45			
<i>Leydigia</i>	1.1	0.8	5			
Chydorid	0.9	0.5	26			
<b>Bryozoan statoblasts</b>						
<i>Plumatella</i> spp.	1.2	0.7	116	0.6	0.3	23
<i>Cristatella mucedo</i>	30.3	28.1	66	21.0	8.1	15
<i>Lophopus crystallina</i>	4.6		1			
<i>Pectinatella magnifica</i>	18.1		2			
<b>Other remains</b>						
Ephemeroptera (mandible)	0.6	0.3	32			
Turbularia (cocoon)				1.2	0.2	18
Ostracoda (shell lining)	1.8	1.5	56			
Trichoptera (frontoclypeus/mandible)	2.2	3.7	32			
<i>Sialis</i> (frontoclypeus/mandible)	2.5	1.6	23			
<i>Chaoborus</i> (mandible)	1.5	1.0	37			
<i>Chaoborus</i> (thoracic horn)	0.9	0.2	7			

2444  
 2445  
 2446