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North American transect of stable hydrogen and oxygen isotopes in water beetles from a museum collection

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Abstract Museum collections contain a wealth of insect remains originating from a wide geographic range, which can be used to investigate their utility as a proxy for environmental isotope ratios. Chitinous remains of insects such as beetles (Coleoptera) are chemically stable and their stable isotope composition is strongly related to that of environmental water in the period of cuticle formation. We present a dataset of chitin δD and $\delta^{18}O$ in two genera of water beetles from a museum collection containing 40 locations for

Helophorus (water scavenging beetles) and 48 locations for *Hydroporus* (predaceous diving beetles) that were selected from latitudes 27–82°N in North America. Only two genera were used to minimize inter-sample variation caused by species-specific differences in metabolic effects, feeding strategy, habitat, and life cycle. The isotopic composition of water beetle exoskeletons had a strong latitudinal trend (North–South) from -160 to $+65$ ‰ for δD and from 7 to 34 ‰ for $\delta^{18}O$, paralleling gradients of isotopes in precipitation. Strong relationships were observed between isotopic composition of beetles and modelled July precipitation ($0.71 < R^2 < 0.82$, $p < 0.001$). The relationship between δD and $\delta^{18}O$ in the beetle samples had a systematic offset from the global meteoric water line, which was likely caused by metabolic effects during chitin formation. The offset between δD values in beetles and in modelled precipitation was 33 ‰ larger, on average, for *Hydroporus* compared with *Helophorus*, suggesting fractionation of hydrogen isotopes during passage through the food chain. This trophic level effect was not observed for stable oxygen isotopes. Furthermore, the observed deviations between isotopic composition of water beetles and modelled precipitation at collection sites were not constant and indicated local hydrological deviations from modelled precipitation. The largest deviations were observed for sites in the Southern US and the Arctic that are highly evaporative and at sites in the Rocky Mountains and Coastal Mountains that were fed by snow melt. Our results indicated that the isotopic

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composition of water beetles from a museum collection was systematically related to δD and $\delta^{18}O$ values of precipitation at the collection site.

Keywords Water beetles · Stable isotopes · Chitin · Hydrology

Introduction

The composition of stable oxygen isotopes ($\delta^{18}O$) and stable hydrogen isotopes (δD) of environmental water varies widely and systematically across the globe (Bowen et al. 2005; Dansgaard 1964). A strong relationship has been observed between stable isotopes in environmental water and temperature (Dansgaard 1964), which has led to the wide application of $\delta^{18}O$ and δD in palaeoclimatology, including the stable isotope analysis of various compounds that preserve well in lake sediments. Compounds that are chemically inert after synthesis have been used to infer past $\delta^{18}O$ of lake water, including authigenic and biogenic carbonates (Eicher and Siegenthaler 1976; Von Grafenstein et al. 1999a), biogenic silica (Barker et al. 2001), aquatic cellulose (Wolfe et al. 2007), and chitin (Wooller et al. 2004). $\delta^{18}O$ of carbonates is, however, not only affected by lake water $\delta^{18}O$, but also directly by a temperature-dependent fractionation, and $\delta^{18}O$ of biogenic silica and aquatic cellulose can be contaminated by terrestrial material (Leng and Barker 2006; Sauer et al. 2001). In contrast, $\delta^{18}O$ and δD of chitinous remains of lacustrine invertebrates do not appear to be affected by temperature or terrestrial contamination. Wooller et al. (2004) were among the first to demonstrate that $\delta^{18}O$ of lacustrine invertebrates is related to $\delta^{18}O$ of regional precipitation, using chironomid remains in surface sediments from four lakes in North America. In a more extensive study of 31 lakes along a North–South transect in Europe, Verbruggen et al. (2011) found a strong relationship between $\delta^{18}O$ of modelled local precipitation and $\delta^{18}O$ of remains of both chironomids and Cladocera. A stronger relationship was observed in the same study between $\delta^{18}O$ of lake water and $\delta^{18}O$ of invertebrate remains, indicating that the isotope composition of lake water strongly influences $\delta^{18}O$ of chitinous invertebrate remains. Using culturing experiments with chironomid larvae, Wang et al. (2009) showed that approximately 69 % of the oxygen and approximately 31 % of hydrogen in the larval biomass was derived from environmental water.

Similarly, Nielson and Bowen (2010) showed that approximately 69 % of oxygen and 38 % of hydrogen in lacustrine brine shrimps was derived from environmental water and approximately 10 % of oxygen and 26 % of hydrogen from their diet. Furthermore, Solomon et al. (2009) indicated that 6–39 % of hydrogen in various freshwater invertebrates is derived from environmental water. Together, these experiment-based studies suggest that invertebrate $\delta^{18}O$ is largely determined by $\delta^{18}O$ of environmental water, whereas it is expected that invertebrate δD is affected to a large extent by sources other than environmental water. δD of food is one of these sources, and the results of Nielson and Bowen (2010) suggest that δD of food is more important than δD of environmental water in determining δD of lacustrine brine shrimps.

Beetles (Coleoptera) have highly sclerotized chitinous elytra (wing covers) that are very robust and often preserve well in sediment records (Elias 2006), allowing the analysis of stable oxygen and hydrogen isotope composition of their remains (Schimmelmänn et al. 1993). A number of studies have compared stable isotope values of local precipitation or environmental water with $\delta^{18}O$ or δD in beetles and discussed the potential for palaeoclimatic applications (Gröcke et al. 2006; Miller et al. 1988; Schimmelmänn et al. 1993). Several of these studies analysed beetles that were taxonomically heterogeneous and did not constrain habitat and feeding type of the beetles.

In this study, we used museum specimens of aquatic beetles, which allowed us to select only a few species of beetles from two genera, minimizing the inter-sample variation caused by species-specific differences in metabolic effects, feeding strategy, habitat and life cycle. The use of museum specimens also allowed us to select specimens originating from a large geographical and climatic range, with minimal travel expenses. An important drawback of museum specimens is that they were collected over nearly a century for investigations focussed on taxonomic and biodiversity rather than stable isotope study. Accordingly, no information is available about the stable isotope composition of the environmental water or the local precipitation of the collection sites. Although this limits the application of museum specimens to infer climatic information, it can be partly overcome by comparing isotopes in beetles with modelled isotopic values of local precipitation (Bowen et al. 2005; Gröcke et al. 2006; Verbruggen et al. 2011).

We selected beetle specimens that originated from locations along a latitudinal gradient in North America, to test if the strong and systematic spatial patterns of stable oxygen and hydrogen isotopes in local precipitation observed by Dansgaard (1964) could also be observed in beetles from a museum collection and to investigate if these patterns are similar for $\delta^{18}\text{O}$ and δD .

Materials and methods

Water beetle samples

Forty specimens belonging to nine different species in the genus *Helophorus* and 48 specimens belonging to seven different species in the genus *Hydroporus* were taken from the Canadian National Collection of Insects (Agriculture and Agri-Food, Ottawa, Canada). The beetle specimens were originally collected between 1913 and 1994. The specimens were selected from locations on a latitudinal transect from 27 to 82°N in North America in order to follow expected shifts in isotope values with latitude. Detailed information about the specimens, collection location and isotopic composition can be found in the Electronic Supplementary Material Table 1.

Sample pre-treatment and analysis

First, all samples and an internal chitin standard (Sigma) were rinsed with a solution of 2:1 chloroform:methanol to remove waxes, and boiled for 24 h in a 1 M NaOH solution to remove proteinaceous material rich in exchangeable hydrogen groups. An important concern with regard to the analysis of hydrogen isotopes of chitinous cuticles is the potential for exchange with hydrogen from the surrounding environment (Schimmelmann and Miller 2002). In this study we reduced the effect of exchangeable hydrogen on inter-sample variability by air equilibrating all samples and an internal chitin standard with the same hydrogen pool in laboratory air moisture (Wassenaar and Hobson 2003). All samples were allowed to equilibrate for at least 96 h with atmospheric water vapour in the laboratory air (McMaster University, Hamilton, ON, Canada). Hydrogen of the laboratory air moisture was monitored daily throughout the period of sample analysis (20–29 June 2006) by

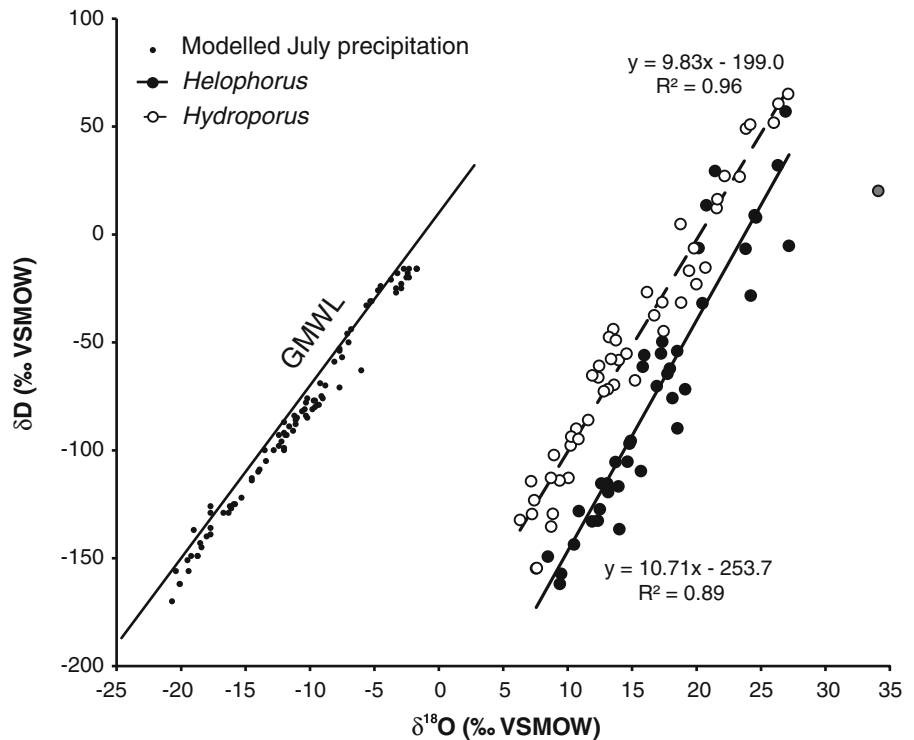
measuring a chitin reference material that followed the same processing as the samples. No changes in δD values were observed in the reference material during the period of analysis. Assuming that all samples received the same proportion of exchangeable hydrogen from lab moisture, no correction of δD values was applied. This technique resulted in an internally consistent data set which was indicated by the strong correlation between δD and $\delta^{18}\text{O}$ in beetle samples (Fig. 1) and allowed us to simultaneously measure hydrogen and oxygen isotopes on a large number of samples with small weight (50–100 μg).

Next, the material was weighed using a microbalance, transferred into 6 × 4 mm isotope-grade silver capsules, and crushed into small balls. Analyses were performed using a TC/EA connected to a Thermo-Finnigan Delta Plus XP isotope-ratio mass-spectrometer. All analyses were run without diluting the samples with helium gas in order to measure hydrogen and oxygen isotopes simultaneously. The results were internally calibrated against the chitin standard and C_{36} *n*-alkane, an isotopic reference material from Indiana University. ANU sucrose was used as an international isotopic reference material. Repeated measurement of the standards gave standard deviations (1 SD) of <0.4 ‰ ($\delta^{18}\text{O}$) and <5 ‰ (δD). When possible, replicate measurements of beetle samples were analyzed, yielding 1 SD uncertainty estimates of 0.47 and 3.1 ‰ for $\delta^{18}\text{O}$ and δD , respectively. All values are reported in the delta notation against Vienna Standard Mean Ocean Water (‰ VSMOW).

Climatic and modelled isotope data

Isotopic data for environmental water at the time of beetle collection were not available. Therefore, an approximation of isotope values in July precipitation at each sample site was modelled with the online isotope precipitation calculator (www.waterisotopes.org; Bowen and Revenaugh 2003; Bowen et al. 2005; Bowen and Wilkinson 2002). This tool uses the GNIP database (IAEA/WMO 2006) and interpolation algorithms to predict monthly isotope composition of precipitation for any latitude/longitude/altitude combination. In addition, we retrieved mean annual and mean monthly temperatures and precipitation amounts from the nearest weather stations, using 1971–2000 average values from the Canadian Weather Office (www.climate.weatheroffice.ec.gc.ca) and NOAA

Fig. 1 Linear regression of δD and $\delta^{18}O$ for *Helophorus* (solid circles) and *Hydroporus* (open circles). The global meteoric water line (GMWL) and modelled isotopic composition of July precipitation for the collection sites are included for comparison. One *Helophorus* outlier is shown in grey



(<http://ggweather.com/normals/>), see Electronic Supplementary Material Table 1.

Statistical analyses

Ordinary least square regressions on the isotope data were done with PAST v2.14 (Hammer et al. 2001). Regression lines were considered similar if their 95 % confidence intervals overlapped. Because the residuals of all regression lines were not normally distributed, the 95 % confidence intervals were calculated using bootstrapping with 2,000 replicates (Hammer 2012). One specimen of *Helophorus* originating from a water tank in New Mexico was considered an outlier based on its high δD and $\delta^{18}O$ values (Figs. 2, 3). Therefore, it was excluded from linear regressions.

Results

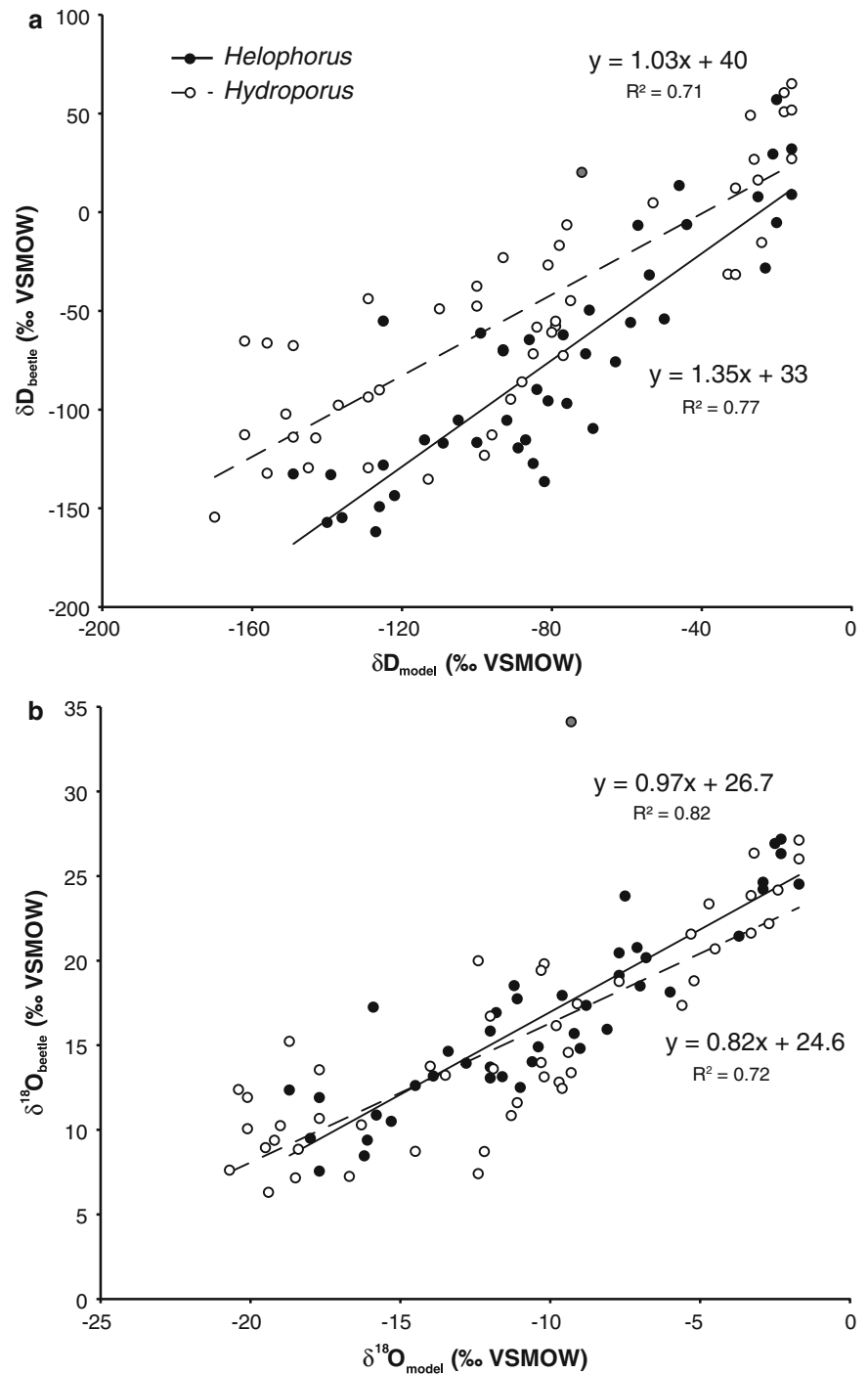
The isotopic values in both beetle genera ranged from -160 to $+65$ ‰ for δD and from 7 to 34 ‰ for $\delta^{18}O$ (Electronic Supplementary Material Table 1). A clear pattern could be observed in isotopic values of water beetles and modelled precipitation, with lowest values at

high latitudes and highest values at low latitudes. Strong and highly significant ($p < 0.001$) relationships were observed between δD and $\delta^{18}O$ in *Hydroporus* ($R^2 = 0.96$; Fig. 1) and *Helophorus* ($R^2 = 0.89$). The slopes of the regression lines in Fig. 1 are similar for *Helophorus* and *Hydroporus*, which is indicated by overlapping 95 % confidence intervals. Similarly, the 95 % confidence intervals of the slopes of regression lines for the global meteoric water line (GMWL) and modelled precipitation in Fig. 1 overlap. There is, however, a difference in the slope of regression lines for environmental water and beetles, the latter being steeper than the GMWL.

Furthermore, strong relationships ($p < 0.001$) were found between isotope values in modelled July precipitation and isotope values in water beetles (Fig. 2). These were slightly stronger for *Helophorus* ($R^2 = 0.82$ and 0.77 for $\delta^{18}O$ and δD , respectively) compared to *Hydroporus* ($R^2 = 0.72$ and 0.71 for $\delta^{18}O$ and δD , respectively). The regression lines for *Helophorus* in Fig. 2 appear to have steeper slopes than those for *Hydroporus*, although there is overlap between the 95 % confidence intervals of the regression slopes.

The difference (Δ) between isotope values in beetles and modelled July precipitation was calculated

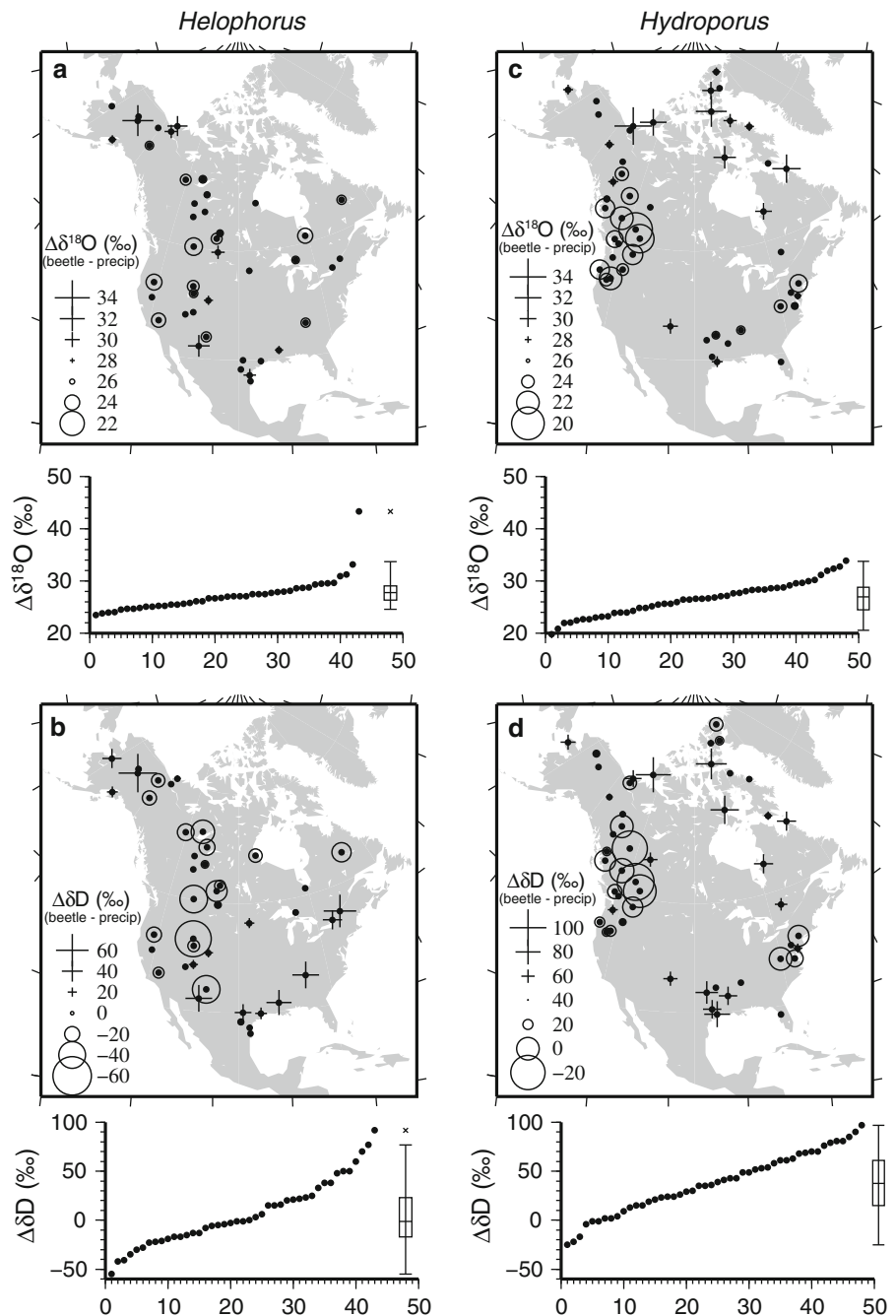
Fig. 2 Linear regression of isotopic composition of water beetles and modelled July precipitation for **a** δD and **b** $\delta^{18}O$. Closed circles represent *Helophorus*, open circles represent *Hydroporus*. One *Helophorus* outlier is shown in grey



to test if geographical patterns could explain variations in Δ values. For this, a constant fractionation factor was assumed between environmental water and beetle tissue. Mean $\Delta\delta^{18}O$ values (reported ± 1 SD) were very similar for *Helophorus* and *Hydroporus*

(27.0 ± 2.2 ‰ and 26.6 ± 3.2 ‰, respectively). In contrast, mean $\Delta\delta D$ values of *Hydroporus* (38 ± 31 ‰) were 33 ‰ higher than mean $\Delta\delta D$ values of *Helophorus* (5 ± 31 ‰). Considered as a group, Δ values were normally distributed, but geographical

Fig. 3 Collection sites of **a**, **b** *Helophorus* and **c**, **d** *Hydroporus*. For each site, $\Delta\delta^{18}\text{O}$ (i.e. $\delta^{18}\text{O}$ beetle – $\delta^{18}\text{O}$ modelled July precipitation) and $\Delta\delta\text{D}$ (δD beetle – δD modelled July precipitation) are plotted. Beetle samples with Δ values lower than the mean Δ values are indicated with *circles*, beetle samples with Δ values higher than mean Δ values are shown as *plus signs*. The magnitude of Δ values corresponds with the *symbol size* as indicated in the *legend*. *Box-and-whiskers plots* below each map indicate minimum, 25th %, median, 75th % and maximum isotope values. One *Helophorus* outlier is indicated by *times symbol*



patterns indicate that Δ values reflect regional-scale climatic and hydrologic patterns. Sample locations with Δ values that were >1 SD lower than the mean Δ value are found predominantly in the Rocky Mountains and Coastal Mountains, whereas Δ values >1 SD higher than mean Δ values were found mostly in the Southern US and the Arctic (Fig. 3).

Discussion

δD and $\delta^{18}\text{O}$ in water beetles and environmental water

The slope of the regression line for δD and $\delta^{18}\text{O}$ values in beetle samples broadly reproduced the gradient in the

GMWL (Fig. 1). The similarity between gradients in stable isotopes of water beetles and stable isotopes of modelled July precipitation on a continental scale indicates that the δD and $\delta^{18}\text{O}$ values of environmental water from which water beetles derived their isotopic composition reflect δD and $\delta^{18}\text{O}$ values of precipitation at the collection location. We used the isotope composition of July precipitation, because in this month both beetle genera have emerged and are active (Larson et al. 2000; Smetana 1985) and we observed higher correlation coefficients between stable isotope values in beetles and modelled precipitation in July compared with other months (data not shown).

We observed a difference in the slope of the regression lines for δD and $\delta^{18}\text{O}$ when comparing environmental water and beetles (Fig. 1). This suggests that a stronger fractionation of hydrogen isotopes occurs in water beetles than in environmental water. Deuterium enrichment could happen by trophic discrimination (see “Offset between genera”), in metabolic processes, and during the synthesis of exoskeletons. For these processes, organic compounds derived from diet are important and the steeper regression slope for beetles in Fig. 1 may be an effect of deuterium-enriched diet. In order to investigate the importance of diet on water beetle δD , experimental studies are required that analyse stable isotopes of water beetles that are raised using water and food with different isotope composition.

The average beetle $\delta^{18}\text{O}$ values are offset from the modelled precipitation values by $27.0 \pm 2.2\%$ and $26.6 \pm 3.2\%$ on average for *Helophorus* and *Hydroporus*, respectively (Fig. 1). Offsets of a similar magnitude have been reported for other lacustrine invertebrates. Wooller et al. (2004) found an average offset of 28.5% between $\delta^{18}\text{O}$ of local precipitation and chironomids and Verbruggen et al. (2011) found average offsets between $\delta^{18}\text{O}$ of modelled precipitation and $\delta^{18}\text{O}$ of chironomids and Cladocera of 25.6 and 23.3% , respectively. The variation in offsets between different lacustrine invertebrates can be caused by differences in diet and metabolism (vital effects). For ostracods, it has been shown that $\delta^{18}\text{O}$ of their calcite valves has taxon-specific variations (von Grafenstein et al. 1999b). To our knowledge, no systematic studies exist that assess taxon-specific effects on the $\delta^{18}\text{O}$ and δD of chitinous remains of lacustrine invertebrates.

In addition to biochemical processes, $\delta^{18}\text{O}$ and δD of beetle chitin are affected by several hydrological

processes that affect the stable isotope composition of lake water at a site, which can deviate from the expected (modelled) isotope composition of environmental water. These processes include seasonal and annual variation in the isotope composition of precipitation (Dutton et al. 2005; Rozanski et al. 1993), moisture balance (Gibson et al. 2005, 2008), seasonal precipitation amounts (Shuman et al. 2006; Yu et al. 2002), snowpack volumes (Burnett et al. 2003), and atmospheric circulation patterns (Anderson et al. 2005; Smith and Hollander 1999). Because of these processes, stable isotopes of lake water and water beetles that live in it do not always reflect $\delta^{18}\text{O}$ and δD of local precipitation. It can be expected, however, that the relationship between stable isotopes in water beetles and the lake water in which they live is much stronger than the relationship between isotopes in water beetles and (modelled) precipitation. Indeed, Verbruggen et al. (2011) found stronger correlations between $\delta^{18}\text{O}$ of invertebrates and $\delta^{18}\text{O}$ of lake water than between invertebrate $\delta^{18}\text{O}$ and $\delta^{18}\text{O}$ of modelled precipitation in a study of 31 lakes along a latitudinal gradient in Europe.

For the sites in our study, we calculated the difference between isotope values in beetles and modelled precipitation (Δ). The Δ values had a standard deviation of 31.4% (δD) and 2.2% ($\delta^{18}\text{O}$) for *Helophorus* and 31.0% (δD) and 3.2% ($\delta^{18}\text{O}$) for *Hydroporus* from the mean Δ values (Fig. 3), which is small compared to the observed range of isotope values in this study. This suggests that the isotopic composition of water beetles from the majority of sites in this study was similar to the expected isotopic values of modelled July precipitation. This extensive dataset confirms earlier studies (Gröcke et al. 2006; Hobson et al. 1999b; Miller et al. 1988; Nielson and Bowen 2010; Schimmelmann et al. 1993; Verbruggen et al. 2011; Wooller et al. 2004) that investigated the relationship between δD or $\delta^{18}\text{O}$ in various freshwater and terrestrial invertebrates and isotopic values of (modelled) environmental water. For certain types of sites, however, the Δ values were >1 SD from the mean Δ value (Fig. 3). These sites were distributed unevenly, with some geographic regions showing anomalous concentrations of positive or negative Δ values. Relatively ^{18}O - and D-enriched values in beetles were observed at sites that included small and closed basins located in especially warm, arid areas in the Southern US and polar deserts in the Arctic (Fig. 3). Such sites

are expected to be highly evaporative and ^{18}O - and D-enriched (Gat 1995; Gibson 2002; Gibson and Edwards 2002). In contrast, relatively ^{18}O - and D-depleted values in beetles were mostly observed at locations that were fed by snow melt from the Rocky Mountains and Coastal Mountains (Fig. 3), which is depleted in ^{18}O and D (Gat 1995; Henderson and Shuman 2009). Where winter precipitation is a major component of the water budget, the δD and $\delta^{18}\text{O}$ values of surface waters, even in summer, remain lower than those of summer precipitation. Overall, the Δ values were not related to temperature at the collection locations, suggesting that hydrogen and oxygen isotopes of water beetles in this data set are not affected by a temperature-dependent fractionation during the formation of the elytra.

Offset between genera

Environmental water is the source of approximately 69 % of oxygen isotopes in aquatic invertebrates (Nielson and Bowen 2010; Wang et al. 2009) and 6 to 39 % of hydrogen isotopes (Solomon et al. 2009; Wang et al. 2009). Diet is another source that determines the isotopic composition of chitin (Schimmelmann and DeNiro 1986) and, furthermore, fractionation of hydrogen isotopes can occur as organic matter passes through the food chain (Birchall et al. 2005; Hedges et al. 2006; Hobson et al. 1999a). This could explain why the offsets between δD values of beetles and modelled precipitation are 33 % larger for *Hydroporus* than for *Helophorus* (Fig. 1), because predaceous *Hydroporus* has a higher trophic position than scavenging *Helophorus*. These results correspond with results of Schimmelmann and DeNiro (1986) who observed that chitin of totally predaceous arthropods shows 31 % more positive δD values compared to the chitin of predominantly herbivorous species, including filter feeders; the δD values of chitin from omnivorous arthropods fall in the middle. An effect of trophic position on δD has also been observed in analysis of bone collagen of fish and mammals and keratin of bird feathers (Birchall et al. 2005; Reynard and Hedges 2008; Soto et al. 2011), but experimental studies with monarch butterflies (Hobson et al. 1999b) and aquatic consumers (Solomon et al. 2009), showed negligible trophic enrichment. We found no evidence for trophic discrimination of oxygen isotopes, as the offset between $\delta^{18}\text{O}$ values of beetles and $\delta^{18}\text{O}$ of

modelled precipitation was the same for both genera (Fig. 1). This is in support of findings by Schimmelmann and DeNiro (1986), who did not observe a significant correlation between $\delta^{18}\text{O}$ values in arthropod chitin and trophic level.

Implications for palaeoclimate studies

The strong correlations between isotopic composition of water beetles and modelled local precipitation can also contain a climate signal, based on the widely-observed correlation between isotopic composition of local precipitation and temperature (Dansgaard 1964; Rozanski et al. 1993). The uncertainty about the isotopic composition of environmental water of the sites where beetles were originally collected, however, limits the potential to infer temperatures from this data set. Palaeoclimatological applications will be less affected by this issue if a single location is chosen, which is not prone to extreme evaporation or influx of snow melt and which has a relatively long residence time of the environmental water, thereby reducing the seasonal variability in isotopic composition of environmental water (Gasse 2005; Gat 1995). The results in this study suggest that the isotopic composition of water beetle remains from an undisturbed sediment record from a suitable location could provide information about changes in isotopic composition of local precipitation.

Conclusions

The strong correlation between δD and $\delta^{18}\text{O}$ values in water beetles and the systematic offset from the GMWL suggest that the chitinous exoskeletons of water beetles contain information about the isotopic composition of the environmental water in which they lived. This is supported by the strong correlation between the isotopic composition of water beetles and modelled July precipitation, indicating the potential to trace the geographical origin of water beetles based on their isotopic composition.

Furthermore, our data suggest that fractionation of isotopes during transfer to higher trophic levels occurs with stable hydrogen isotopes, whereas this was not observed for stable oxygen isotopes. Ideally, only remains of beetles from the same species or genus are used, to minimize noise in the data caused by inter-

species differences (e.g. diet, habitat, life cycle). This is especially important when comparing δD values of beetles from different sampling locations or stratigraphic horizons. For downcore analysis of beetle $\delta^{18}\text{O}$, it is less critical to reduce variation in water beetle taxa, as long as terrestrial beetles are excluded. In a single, hydrologically stable location, it should therefore be possible to reconstruct changes in past isotopic composition of environmental water and local precipitation using the isotopic composition of water beetle remains.

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