Experimental determination of the temperature dependence of oxygen-isotope fractionation between water and chitinous head capsules of chironomid larvae

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Abstract Oxygen-isotope values of invertebrate cuticle preserved in lake sediments have been used in palaeoenvironmental reconstructions, generally with the assumption that fractionation of oxygen isotopes between cuticle and water (α_{cuticle–H₂O}) is independent of temperature. We cultured chironomid larvae in the laboratory with labelled oxygen-isotope water and across a range of closely controlled temperatures from 5 to 25 °C in order to test the hypothesis that fractionation of oxygen isotopes between chironomid head capsules and water (α_{chironomid–H₂O}) is independent of temperature. Results indicate that the hypothesis can be rejected, and that α_{chironomid–H₂O} decreases with increasing temperature. The scatter in the data suggests that further experiments are needed to verify the relationship. However, these results indicate that temperature-dependence of α_{chironomid–H₂O} should be considered when chironomid δ¹⁸O is used as a palaeoenvironmental proxy, especially in cases where data from chironomids are combined with oxygen-isotope values from other materials for which fractionation is temperature dependent, such as calcite, in order to derive reconstructions of past water temperature.

Keywords Oxygen isotopes · Chironomids · Temperature-dependent isotope fractionation · Palaeoenvironments · Limnology

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Introduction

Oxygen-isotope records from lake sediments are valuable sources of palaeoclimatic information. Although authigenic carbonate is the material most commonly analysed, other minerals and biomolecules have also been used in lakes that do not precipitate carbonate or as complementary sources of data in those that do (Leng and Marshall 2004). The remains of aquatic invertebrates provide a promising source of material for oxygen-isotope analyses (Schimmelmann and DeNiro, 1986; Schimmelmann et al. 1986) and determinations have been undertaken on beetle exoskeletons (van Hardenbroek et al. 2012), cladoceran remains (Verbruggen et al. 2011; Schilder et al. 2015) and the larval head capsules of chironomids (Wooller et al. 2004; Verbruggen et al. 2010a,b). Several studies using specimens collected in the field have demonstrated a strong positive correlation between the oxygen-isotope ratio of host water ($\delta^{18}$O$_{H_{2}O}$) and invertebrate cuticle ($\delta^{18}$O$_{cuticle}$) (van Hardenbroek et al. 2012; Mayr et al. 2015; Verbruggen et al. 2011; Chang et al. 2018; Lasher et al. 2017). These investigations covered a wide range of geographical areas and a correspondingly wide range of $\delta^{18}$O$_{H_{2}O}$ in the water bodies concerned, and the results have shown that the oxygen-isotope ratio of the host water appears to be the dominant control on $\delta^{18}$O$_{cuticle}$. This was previously noted by Wooller et al. (2004), who found a linear relationship between $\delta^{18}$O measured in chitinous head capsule and estimated annual average $\delta^{18}$O$_{H_{2}O}$ of precipitation for four sites in eastern USA, Greenland and Baffin Island. By assuming that fractionation between chironomid head capsules and water was independent of temperature, they derived an initial estimate of the “biological fractionation factor” between chironomid and water of $\alpha_{\text{chironomid-H}_{2}\text{O}} \approx 1.028$. (For a given substance, in this case chironomid head capsules, the fractionation factor $\alpha_{\text{chironomid-H}_{2}\text{O}}$ is defined as the ratio between $^{18}$O/$^{16}$O in chironomid head capsules and water respectively, but can be accurately approximated from $\delta^{18}$O values as $(1000+\delta^{18}$O$_{\text{chironomid}})/(1000+\delta^{18}$O$_{\text{H}_{2}\text{O}}$). As chitin is the dominant constituent in the cuticle of chironomid head capsules, the assumption made by Wooller et al. (2004) has been extrapolated in the literature to imply that fractionation between chitin and water is independent of temperature. However, neither the original assumption nor the extrapolation has been tested experimentally. The strong relationship between $\delta^{18}$O$_{\text{chironomid}}$ and $\delta^{18}$O$_{\text{H}_{2}\text{O}}$ was confirmed experimentally by Wang et al. (2009), who cultured chironomid larvae in waters with near-constant $\delta^{18}$O$_{\text{H}_{2}\text{O}}$ close to $-15.1 \%e$ and $+6.5 \%e$ in triple-replicated treatments at a constant temperature of 23 °C. By also controlling the $\delta^{18}$O of the food provided to the cultured larvae, Wang et al. demonstrated that 69% of the oxygen atoms in the larvae were derived from the host water, and 31% from food. Subsequent studies have suggested that a proportion of chitin oxygen may also be derived from isotopically invariant atmospheric oxygen (Nielson and Bowen, 2010; Soto et al. 2013), although this source has not been included in estimates of fractionation in our study.

If $\alpha_{\text{chironomid-H}_{2}\text{O}}$ is indeed independent of temperature, it should be possible to reconstruct past values of $\delta^{18}$O$_{\text{H}_{2}\text{O}}$ directly from measurements of $\delta^{18}$O$_{\text{chironomid}}$ in fossil material, with obvious applications in palaeoclimate reconstruction. Wooller et al. (2004) noted similarities between chitin and aquatic cellulose in respect of oxygen-isotope fractionation from host water. Both have broadly similar fractionation factors (previous studies quote $\alpha$ values between about 1.023 and 1.028), suggesting similarity in the biochemical reactions by which oxygen derived from water is incorporated in the two polymers, despite the fact that cellulose is produced by plants and chitin by animals and fungi. Moreover, $\alpha_{\text{cellulose-H}_{2}\text{O}}$ is also generally regarded as temperature independent (Beuning et al. 1997). However, independence from temperature remains unproven for either biopolymer and results from culture experiments and field collections suggest there may in fact be temperature dependence of $\delta^{18}$O for Cladocera (Verbruggen et al. 2011; Schiller et al. 2015), and cellulose (Aucour et al. 1993). Clearly, temperature dependence needs either to be disproven or, if shown to be true, to be quantified in order for accurate reconstructions of $\delta^{18}$O$_{\text{H}_{2}\text{O}}$ to be made.

Here, we report the results of a laboratory culture study of the influence of temperature on oxygen-isotope fractionation between host water and the chitinous head capsules of chironomid larvae using culture experiments under conditions of constant $\delta^{18}$O$_{\text{H}_{2}\text{O}}$ and shared diet, leaving temperature as the variable to be investigated for its influence on $\delta^{18}$O$_{\text{chironomid}}$. 
Materials and methods

We reared larvae of the chironomid *Chironomus riparius* (Meigen 1804) from eggs (supplied by Huntington Life Sciences Ltd). This species was chosen based on its eggs being readily available. Eggs were reared in glass Erlenmeyer flasks, containing 2 L of bottled mineral water and 500 g of sand that was first combusted at 550 °C for six hrs to eliminate any organic matter that might have provided extraneous food sources. The flasks were placed inside isothermal cabinets set at nominal temperatures of 5, 10, 15, 20 and 25 °C. Duplicate experiments at each temperature (triplicate at 15 °C) were conducted concurrently in the same cabinet to minimize temperature differences between the replicates. The flasks were kept in complete darkness to inhibit photosynthetic activity and loosely sealed with aluminium foil to minimize evaporation. Typically, every other day, each flask was provided with 1.5 mL of a suspension of finely ground Tetramin fish food flakes. This was prepared weekly by blending 4 g of fish food flakes with 1 L of water and kept refrigerated. The isotopic composition of food was not measured but was assumed to be constant. Rationing was adjusted according to water quality and larval behaviour, because decomposition of uneaten food can lead to increased microbial activity and reduced dissolved oxygen concentration, which may subsequently hinder larval development. Water quality was maintained through regular partial water replacements by siphoning off one litre of water from each flask weekly and replacing it with stock mineral water stored at the relevant temperature. This ensured satisfactory dissolved oxygen concentration and optimal environmental conditions for growth and development. Experiment duration varied depending on larval growth rates but in all cases, experiments were terminated once the majority of larvae had reached their final instar.

Water samples were taken regularly throughout the experiments to track changes in δ¹⁸O_H₂O and water chemistry. Stable isotope analyses were undertaken using a Picarro WS-CRDS system at the University of Liverpool. Results were normalized onto the VSMOW scale using internationally distributed standards with an internal precision < ±0.08 ‰. Electrical conductivity, dissolved oxygen concentration and pH were measured at approximately weekly intervals using Camlab Handylab 1 battery-powered hand-held meter attached to a data logger. Water temperature was measured hourly using Tinytalk (TK-0040) data loggers. At the end of each experiment, the contents of each flask were washed through a 1 mm mesh sieve and chironomid larvae picked from the retained residue using fine-tipped forceps before being frozen whole for storage. Only final instars were selected for isotope analyses. Following defrosting, head capsules were manually separated from larval bodies under a stereomicroscope (×25 magnification) using a mounted needle and fine-tipped forceps, taking care to remove as much of the digestive tract and muscle tissue as possible. The remaining outer portions of the head capsules were then subjected to chemical pre-treatment in three sequential steps: (1) 2:1 dichloromethane:methanol; (2) 0.25 M HCl and (3) 0.25 M NaOH, each for 24 h at 20 °C. This protocol had previously been found by experiment to maximize the elimination of non-chitinous material while minimizing the variability among replicated measurements of δ¹⁸O<sub>chironomid</sub> (Lombino 2015). Nevertheless, it is possible that some non-chitinous material survived the pre-treatment, as proteins and lipids are both present alongside chitin (Verbruggen et al. 2010a). Recognizing this possibility, we use the notation δ¹⁸O<sub>chironomid</sub> rather than δ¹⁸O<sub>chitin</sub> in describing our results. A minimum weight of 60 ± 10 μg was used for isotope analyses, equivalent to between 10 and 50 head capsules. The chironomid oxygen-isotope analyses were performed at the Stable Isotope Biogeochemistry Laboratory (SIBL, Durham University) using a TC/EA coupled to a Delta V Advantage IRMS, via a ConFlo III. Since chironomid material is rich in nitrogen compounds, the isotopic analysis should take into account the interference of N₂ gas generated from thermal combustion (Qi et al. 2011). The TCEA reactor was operated at 1400 °C with a 2 m GC column at a temperature of 60 °C in order to avoid nitrogen interference. All ion traces show that there was no interference between the nitrogen peak and carbon monoxide peak of the chironomid material. Analytical uncertainties were ≤ ± 0.64 ‰ (1SD) based on repeat analyses of three international reference standards (IAEA-600, IAEA-601, IAEA-602).
Results

Conditions during the experiments are assumed to have remained within the ecological tolerances of the C. riparius larvae since no significant mortality events occurred during the experiments, although eggs failed to hatch in one of the 25 °C cultures and only one analysis was available for 5 °C. In the failed culture, some eggs had already hatched and died by start of the experiment. Anoxic conditions in the small vials used for transportation, which would have been exacerbated at 25 °C, may have compromised the other eggs. The temperature, isotopic composition, pH and electrical conductivity showed little variation in each flask (Table 1): fluctuations in dissolved oxygen concentration were probably associated with changes in the rate of respiration by the chironomid larvae and the decomposition of uneaten food. Temperature had a strong influence on the rate of larval development, which is consistent with previous findings (Hauer and Benke 1991). In our study, there was a decrease in development rate of ~4 days °C⁻¹ between 5 and 25 °C.

The oxygen-isotope composition of the pretreated head capsules varied between +13.8 ‰ and +16.3 ‰ across the range of temperatures. This variability is around twice the reported analytical precision of ≤ ±0.64 ‰. On average, δ¹⁸Ochironomid values were ~1.3 ‰ lower in larvae reared at 25 °C than in larvae reared at 5 °C, with αchironomid–H₂O varying between 1.021 and 1.024 across the tested temperature range. There is a positive correlation between 1000 ln α¹⁸Ochironomid–H₂O and temperature (Fig. 1, r² = 0.53; p < 0.05; n = 9).

The best-fit relationship between α¹⁸Ochironomid–H₂O and temperature is:

\[ 1000 \ln \alpha_{\text{chironomid–H}_2\text{O}} = 8.45 \times (1000 \times T^{-1}) - 6.52 \]  

(1)

where T is temperature in Kelvin. The standard error of estimate for 1000 lnα¹⁸Ochironomid–H₂O is 0.6, which is comparable to the analytical uncertainty in measurements of δ¹⁸Ochironomid. We note that one of the

![Fig. 1 1000lnα¹⁸Ochironomid–H₂O as a function of inverse temperature. Error bars represent 1SD analytical uncertainty. Open symbol denotes an outlier that was excluded from Eq. 2](image)

Table 1 Water temperature and water composition of each culture experiment, along with the measured δ¹⁸Ochironomid values and chironomid-water fractionation factors (α-values)

| Temperature (°C) | δ¹⁸O H₂O (% VSMOW) | pH | Dissolved oxygen (mg L⁻¹) | Electrical conductivity (μ S cm⁻¹) | Larval development (days) | δ¹⁸Ochironomid (% VSMOW) | αchironomid–H₂O |
|-----------------|-------------------|----|--------------------------|---------------------------------|--------------------------|------------------------|-------------------|
| 5.6 ± 0.4       | −7.4 ± 0.18       | 7.2 ± 0.2 | 7.3 ± 1.5                | 230 ± 12                          | 130                     | 16.8                  | 1.024             |
| 10.5 ± 0.4      | −7.6 ± 0.18       | 7.4 ± 0.2 | 7.1 ± 1.3                | 256 ± 18                          | 110                     | 16.1                  | 1.024             |
| 10.5 ± 0.4      | −7.5 ± 0.21       | 7.2 ± 0.2 | 7.2 ± 1.4                | 259 ± 25                          | 15.6                    | 1.023                  |
| 15.2 ± 0.4      | −7.5 ± 0.15       | 7.3 ± 0.1 | 6.4 ± 1.9                | 259 ± 16                          | 90                      | 15.9                  | 1.024             |
| 15.2 ± 0.4      | −7.3 ± 0.07       | 7.4 ± 0.2 | 6.7 ± 1.9                | 247 ± 18                          | 16.3                    | 1.023                  |
| 15.2 ± 0.4      | −7.4 ± 0.11       | 7.3 ± 0.2 | 6.2 ± 2.3                | 259 ± 14                          | 15.7                    | 1.023                  |
| 20.2 ± 0.3      | −7.3 ± 0.16       | 7.6 ± 0.1 | 6.8 ± 1.0                | 250 ± 7                           | 70                      | 15.0                  | 1.022             |
| 20.2 ± 0.3      | −7.3 ± 0.14       | 7.6 ± 0.0 | 6.8 ± 1.1                | 252 ± 8                           | 13.8                    | 1.021                  |
| 24.9 ± 0.5      | −7.3 ± 0.25       | 7.5 ± 0.2 | 6.1 ± 1.8                | 292 ± 17                          | 50                      | 14.9                  | 1.022             |
results at 20 °C appears to be an outlier. The reason for this is unknown but could be related to additional dietary contributions from microorganisms originating from the decomposition of excess food. Omission of this apparent outlier alters the gradient and intercept of the linear regression so that:

\[ 1000 \ln \alpha_{\text{chironomid--H}_2\text{O}} = 6.29 \times (1000 \times T^{-1}) + 1.16 \]  

with a stronger positive correlation between 1000/\ln \alpha_{\text{chironomid--H}_2\text{O}} and temperature \( (r^2=0.66; \ p<0.05; \ n=8) \). The standard error of estimate for 1000/\ln \alpha_{\text{chironomid--H}_2\text{O}} is reduced to 0.4.

**Discussion**

The systematic variability of \( \alpha_{\text{chironomid--H}_2\text{O}} \) implies that temperature plays a small but potentially important role in controlling \( \delta^{18}\text{O}_{\text{chironomid}} \) values. For water of a given isotopic composition, the rate of variation of \( \delta^{18}\text{O}_{\text{chironomid}} \) with temperature is approximately \(-0.1\% \degree\text{C}^{-1}\) for the relationships expressed in both Eqs. 1 and 2 above (although slightly higher for Eq. 1 than for Eq. 2: \(-0.11\) and \(-0.09\% \degree\text{C}^{-1}\), respectively), i.e. lower than for other minerals often used in palaeo-lacustrine settings, such as calcite \((-0.24\% \degree\text{C}^{-1}; \ \text{Kim and O’Neil 1997})\) and biogenic silica \((-0.2\) to \(-0.5\% \degree\text{C}^{-1}; \ \text{Brandriss et al. 1998; Juillet-Leclerc & Labeyrie 1987; Leng & Barker 2006})\). The cause of the variability in \( \alpha_{\text{chironomid--H}_2\text{O}} \) with temperature is unknown, although it may be related to the faster larval development at higher temperature.

Results from this investigation are compared with culture experiments of Wang et al. (2009) and Soto et al. (2013) (Fig. 2a). Both studies involved culturing chironomids under controlled water isotopic composition and temperature (23 °C and 24 °C respectively), but the species they used differed from our study (\textit{C. dilutus} and \textit{C. tentans} respectively; \textit{C. riparius} in our work). The two data points from Wang et al. (2009) fit well with the results from chironomids extracted from surface sediments, for which van Hardenbroek et al. (2018) report the relationship \( \delta^{18}\text{O}_{\text{chironomid}} = 0.89 \times \delta^{18}\text{O}_{\text{lake water}} - 22.5 \) (their Fig. 5). Figure 2a shows that the data from our study form a trend across the line joining the two data points from Wang

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**Fig. 2**

**a** \( \delta^{18}\text{O}_{\text{chironomid}} \) versus \( \delta^{18}\text{O}_{\text{H}_2\text{O}} \) from Wang et al. (2009) (\textit{Chironomus dilutus}: open blue squares—whole larvae, reared at 23 °C; uncertainties are ± ISD of the replicate experiments), this study (\textit{Chironomus riparius}: filled blue squares—head capsules) and Soto et al. (2013) (\textit{Chironomus tentans}: green diamonds—larvae protein, reared at 24 ± 0.5 °C). For the present study each individual \( \delta^{18}\text{O}_{\text{chironomid}} \) value is plotted (Table 1) along with analytical uncertainty (± ISD), although error bars for the \( \delta^{18}\text{O}_{\text{H}_2\text{O}} \) are too narrow to be visible. **b** Data in (a) are plotted with additional data for cladocerans (open red circles, whole \\textit{Daphnia}, filled red circles, ephippia, reared at 12 and 20 °C each water composition.) from Schilder et al. (2015) and brine shrimp chitin (brown triangles, from Nielsen and Bowen 2010, reared at room temperature. Only those values for cultures reared with \( \delta^{18}\text{O}_{\text{food}} \) of 14 % are plotted here) are shown.
et al. (2009), with the data from rearing experiments at >20 °C plotting on or below that line and those from <20 °C plotting above. The trend of our data indicates the degree of scatter to be expected from variations in temperature over a 20 °C temperature range. On the other hand, the two groups of data from the study by Soto et al. (2013) lie respectively below and above the line. Although the measurement uncertainties for their data from the upper right in Fig. 2a are large enough to overlap the extrapolated Wang et al. (2009) line, this is not the case for their two data points at bottom left (Fig. 2a), whose deviations from the line far exceed the effect of the 1 °C difference in temperature that our experiments would predict. We do not have any explanation for this discrepancy other than the possibility that C. riparius (our study) and C. dilutus (Wang et al., 2009) share a common uptake of 72% of oxygen in chitin and associated tissue from environmental water, whereas Soto et al. (2013) estimate that C. tentans derives 87% from this source. We note that there are differences between the three studies in the preparation of chitinous material and in the techniques used to measure δ18Ochironomid, but these do not explain the differences in results. Our preparation and chitin purification steps removed both lipids and a substantial fraction of proteins from the larval head capsules, whereas Wang et al. (2009) analysed whole larvae without any chemical treatment and Soto et al. (2013) only extracted lipids from their samples. The results show agreement between the most and least treated larvae (our study and Wang et al., 2009) with deviation only for the intermediate treatment. All three studies used a high-temperature pyrolysis device to convert oxygen in chitin to CO gas for isotope ratio measurement. With respect to nitrogen interference from proteinaceous material, Soto et al. (2013) diverted the nitrogen produced by pyrolysis away from the source of the mass spectrometer, whereas this was not done by Wang et al. (2009) and this study. Qi et al. (2011) show that for δ18O measurements on keratin the results from the nitrogen diversion technique are on average about 3‰ above those on the same material without nitrogen diversion. Although a 3‰ downwards adjustment of the Soto et al. (2013) data would bring the data point at upper right in Fig. 2a into better alignment with the trend of the other studies, their point at lower left would be shifted even further away from the same trend. Further analytical research is required to ascertain the effects of nitrogen from proteinaceous material on TCEA oxygen isotope analysis.

Some support for the hypothesis of inter-specific differences as an explanation for the discrepancies between the three chironomid-based studies can be drawn from Fig. 2b, which includes additional data on chitinous material from the cladoceran Daphnia (Schilder et al. 2015) and the brine shrimp Artemia franciscana (Nielsen and Bowen 2010). In neither study was nitrogen diversion technique employed or nitrogen interference investigated. The brine shrimp were cultured at room temperature which, was presumably constant (Nielsen and Bowen, 2010), whereas the four treatments employed by Schilder et al. (2015) included a variation in temperature between 12 and 20 °C. The brine shrimp data define a trend that is approximately parallel to the chironomid line and the cladoceran data from Schilder et al. (2015) lie on this trend. The degree of scatter in the cladoceran data is consistent with their 8 °C temperature range. However, both data sets plot on a line that is markedly offset from that of chironomids (Fig. 2b), suggesting a significant difference in the fractionation of oxygen isotopes among the various chitin-forming animals. This difference, and the possibility of interspecific variation among chironomid species, both warrant further investigation.

**Conclusions**

The results from this investigation indicate that temperature exerts a modest but measurable influence on α18Ochironomid−H2O that is summarized in Eq. (2) and which should be taken into account in future studies using δ18Ochironomid as a proxy for lake water δ18O. As the present data set is small, further laboratory- and field-based calibration studies are needed to augment our findings and improve the estimates of coefficients in our equation. The variation of δ18Ochironomid with temperature, although small, may have significance when δ18Ochironomid values are used in palaeoenvironmental investigations. This is especially so in studies that combine δ18Ochironomid and δ18O\textsubscript{CaCO}_3 data from lakes in order to reconstruct water temperature (Verbruggen et al. 2010b).
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