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Climate reconstruction from paired oxygen-isotope analyses of chironomid larval head capsules and endogenic carbonate (Hawes Water, UK) - Potential and problems

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ABSTRACT

Temperature and the oxygen isotopic composition ($\delta^{18}O$) of meteoric water are both important palaeoclimatic variables, but separating their influences on proxies such as the $\delta^{18}O$ of lake carbonates is often problematic. The large temperature variations that are known to have occurred in the northern mid-latitudes during the Late Glacial make this interval an excellent test for a novel approach that combines oxygen-isotope analyses of chironomid larval head capsules with co-occurring endogenic carbonate. We apply this approach to a Late Glacial lake sediment sequence from Hawes Water (NW England). Oxygen-isotope values in chironomid head capsules show marked variations during the Late Glacial that are similar to the oxygen isotope record from endogenic carbonate. However, summer temperature reconstructions based on the paired isotope values and fractionation between chironomids and calcite yield values between −20 and −4 °C, which are unrealistic and far lower than reconstructions based on chironomid assemblages at the same site. The composition of a limited number of samples of fossil chironomid larval head capsules determined using Pyrolysis gas-chromatography mass spectrometry indicates the presence of aliphatic geopolymers, suggesting that diagenetic alteration of the head capsules has systematically biased the isotope-derived temperature estimates. However, a similar trend in the isotope records of the two sources suggests that a palaeoclimate signal is still preserved.

1. Introduction

Variations in the oxygen isotopic composition of lake sediments provide an excellent means of past climate reconstruction. Analyses are most commonly undertaken on endogenic or biogenic carbonate (Leng and Marshall, 2004), although other lacustrine materials have also been used, including biogenic silica (Leng and Barker, 2006), aquatic cellulose (Wolfe et al., 2007; Heyng et al., 2014) and chitin (Wooller et al., 2004). Oxygen isotopes have an advantage over many other climate proxies in that their distribution is governed by well-understood physical principles and in favourable cases they can be used to make quantitative reconstructions with well-defined uncertainties. For lacustrine carbonates however, the interpretation of oxygen-isotope records is confounded by the fact that $\delta^{18}O_{carbonate}$ is controlled both by water temperature and water isotope composition, as well as possible departures from isotopic equilibrium (Leng and Marshall, 2004). Deconvolving the signature into its individual components is difficult without independent estimates of either past water temperature or $\delta^{18}O_{lakewater}$, which may not be available. Moreover, although carbonate-precipitating lakes are not uncommon, most

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lakes in acidic catchments do not precipitate carbonates and in these cases other materials must therefore be used to construct oxygen-isotope records.

The chitinous remains of chironomid larvae (Insecta: Diptera: Chironomidae) provide an alternative and promising means for inferring past $\delta^{18}O_{lakewater}$. The fractionation of oxygen-isotopes between chitin and water has been thought to be negligibly affected by temperature (Mayr et al., 2015). If this assumption were true, $\delta^{18}O_{chironomid}$ values could be used to estimate $\delta^{18}O_{lakewater}$ without the need for an independent estimate of water temperature. Lombino et al. (2021) have recently provided evidence for a small temperature dependence of oxygen-isotope fractionation between chironomid head capsules and water. In either circumstance, there exists the potential to combine $\delta^{18}O_{chironomid}$ and $\delta^{18}O_{carbonate}$ values from the same levels in a stratigraphic sequence in order to reconstruct past water temperature. Although paired $\delta^{18}O_{chironomid}$ and $\delta^{18}O_{carbonate}$ analyses have previously been reported from a Quaternary sediment sequence (Verbruggen et al., 2010), no attempt has yet been made to undertake quantitative temperature reconstructions using such an approach, nor to evaluate its validity. In this study, we undertook such paired analyses from the Late Glacial sediments of Hawes Water, a small hardwater lake in NW England, in order to reconstruct the $\delta^{18}O_{lakewater}$ and lake water temperature. For evaluation of this new approach, Hawes Water has the advantage of previously-published and methodologically-independent estimates of palaeotemperature, undertaken using transfer-functions based on the species compositions of chironomid assemblages (Marshall et al., 2002; Jones et al., 2002; Bedford et al., 2004; Lang et al., 2010), against which the results of our isotope-based calculations can be compared.

The Late Glacial, which is taken here to refer to the interval between the onset of warming at the end of Greenland Stadial 2 (GS-2) and the start of the Holocene (~14.7–11.7 ka BP), was a time of rapid, high-amplitude change in temperature in the boreal mid- and high latitudes (Lowe et al., 2008) and thus represents an excellent testing ground for our approach. Temperature reconstructions from chironomid assemblages indicate that during the Late Glacial interstadial mean July air temperatures in north-west England were between ~11 and 14 °C, falling to between ~7 and 10 °C during the Younger Dryas stadial and then rising again to between ~11.5 and 15 °C in the Early Holocene (Brooks and Langdon, 2014). These substantial temperature changes should be mirrored in the oxygen-isotope ratios of both endogenic carbonates and chironomid chitin. To be judged successful, any isotope-based method of temperature reconstruction should be capable of accurately matching the transfer function results for summer air temperatures. There is additional evidence that the Late Glacial climate was characterized by changes in atmospheric circulation (e.g. Bakke et al., 2009; Lane et al., 2013). As oxygen isotopes in meteoric waters are sensitive tracers of atmospheric circulation (e.g. Hammarlund et al., 2002), concomitant reconstruction of lake water $\delta^{18}O$ from paired chironomid and carbonate values might provide new information for comparison with previous studies.

2. Study site, materials and methods

2.1. Hawes Water and the late glacial sediment record

Hawes Water (54°10′58″N, 2 48′10″W) is a small, oligotrophic, monomictic lake (area 0.08 km^2, max depth ~12 m, 8 m a.s.l.) situated within a Carboniferous limestone catchment in north-west England (Marshall et al., 2002, 2007) (Fig. 1). The surface catchment area is small and boggy and the principal inputs to the lake are groundwater flow from the Carboniferous limestone as well as rainwater falling onto the lake and its catchment. The lake has a residence time of <1 year (Wiik et al., 2015). Although NW England was ice-covered during the last glacial, the Hawes Water catchment was free of ice by the Late Glacial (Jones et al., 2002). The weighted mean annual $\delta^{18}O$ of precipitation (2003–2005) is −6.8‰ VSMOW, with slightly higher (−6.1‰) values during summer over the same period. Summer epilimnion waters (−5.3‰, 1998–2005) show slight evaporative enrichment with respect to rainfall and modern calcite precipitates in oxygen-isotope equilibrium with those waters (Marshall et al., 2007). Marshall et al. (2007) also present results of several years of monitoring of the lake and its environment and note that in summer the temperature difference between lake waters and the air above averages 2.3 °C.

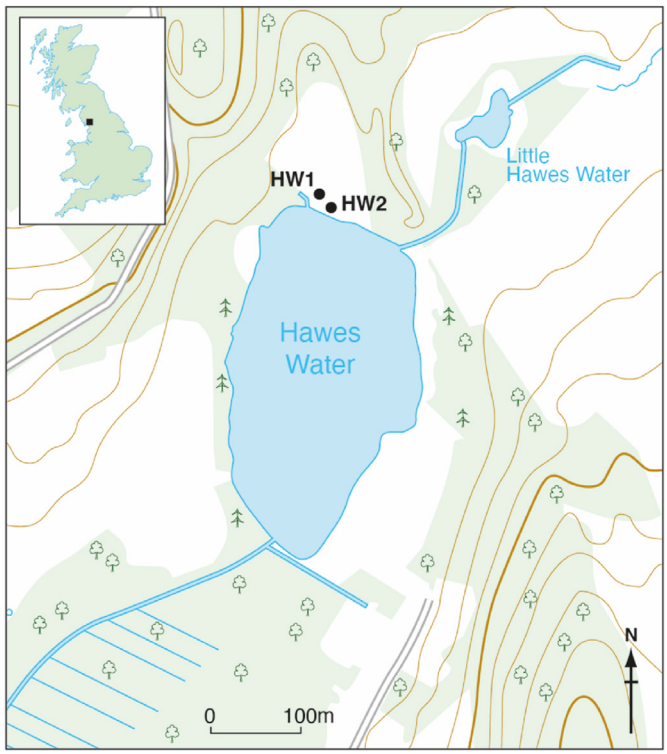

Fig. 1. Location of the coring sites at Hawes Water. Inset shows the location of the lake in NW England.

This study is based on data derived from three cores (HW1/1 and HW1/2, which are referred to collectively as HW1 below, and HW2), all taken within a few meters of each other from the marl benches slightly landward of the northern margins of the present lake (Fig. 1). These benches formed under shallow water when lake-levels were higher during the Late Glacial. Between about 1.0 and 1.3 m of characteristic tri-partite Late Glacial and early Holocene sediment (marl-clay-marl) is present in each sequence, overlying blue clays deposited at the end of the last glacial. Marl sediments are overlain by fen peat, which formed when lake levels fell during the very early Holocene (Jones et al., 2011). The Late Glacial carbonate sediments formed endogenically within the lake, with no evidence for input of detrital carbonate from the catchment (Marshall et al., 2002). As part of this study, Core HW2 (107 cm long) was recovered for chironomid oxygen-isotope analyses using a large-diameter 'Russian' corer: carbonate oxygen-isotope analyses were also undertaken on this material. Complementary published data are available from parallel, ~120 cm long cores HW1/1 and HW1/2: carbonate oxygen-isotopes were undertaken on the former (Jones et al., 2002; Marshall et al., 2002) and chironomid-inferred temperatures determined on the latter

(Bedford et al., 2004). The two datasets were placed on a common depth scale to allow for minor differences in depth, as described in Bedford et al. (2004). Cross correlation of the HW1 sequence with HW2 was achieved by sequence-slotting (see Supplementary Material) of the carbonate oxygen-isotope data from the two cores.

2.2. Chronology and late glacial environment at Hawes Water

Previously-published lithological information, pollen, $\delta^{18}O_{carbonate}$ and chironomid-inferred temperatures on HW1/1 and HW1/2 were compared by Lang et al. (2010) with the oxygen-isotope event stratigraphy for the NGRIP ice core (Lowe et al., 2008) in order to develop a chronology for the Late Glacial sequence at Hawes Water, with confirmation of a late glacial age provided by two radiocarbon dates on terrestrial plant macrofossils (Marshall et al., 2002) (Fig. 2). The studied sequence begins with marl corresponding to the Late Glacial interstadial, overlying clays deposited during Greenland Stadial 1. There is an initial rise in $\delta^{18}O_{carbonate}$ in the marl that was abruptly followed by a temporary reversal (marked "A" on Fig. 2) before the $\delta^{18}O_{carbonate}$ rise was resumed. Over the same interval, there was an increase in head capsules from thermophilic chironomid taxa (Bedford et al., 2004). The published pollen record indicates open grassland during this interval (Jones et al., 2002; Bedford et al., 2004), which marks the transition from the glacial into the Late Glacial interstadial (Greenland Interstadial 1a to 1e). Marl continues above this, with high $\delta^{18}O_{carbonate}$ values that are interrupted by 3 marked negative excursions (labelled "B", "C" and "D" on Fig. 2). There is a large but progressively decreasing number of thermophilic chironomid taxa and pollen indicative of juniper scrub in the earlier part and birch woodland in the later part of the interval, which coincides with the Late Glacial interstadial. The uppermost part of the marl shows a sharp lowering of $\delta^{18}O_{carbonate}$ values and a return to pollen indicative of open grassland vegetation coupled with a shift to fewer thermophilic and more cold-tolerant chironomid taxa. The overlying clay, which displays low $\delta^{18}O_{carbonate}$ values, an abundance of cold-tolerant chironomid taxa and pollen indicative of open ground to tundra vegetation, coincides with the Younger Dryas stadial (Greenland Stadial 1). An increase in $\delta^{18}O_{carbonate}$ values in the upper part of the clay, a shift to pollen indicative of open ground and an increase in warm-water chironomid taxa mark the transition to the Early Holocene, which is accompanied by a return to marl sedimentation, a rise in $\delta^{18}O_{carbonate}$ values and a change to grassland pollen. Above this, marl sediments are replaced by Early Holocene fen peat.

2.3. Analytical methods

The principal laboratory methods employed in this study were $\delta^{18}O$ analysis of chironomid head capsules by pyrolysis to CO over carbon at 1450 °C followed by gas-source mass spectrometry, and isotopic analysis of endogenic lake carbonate samples by

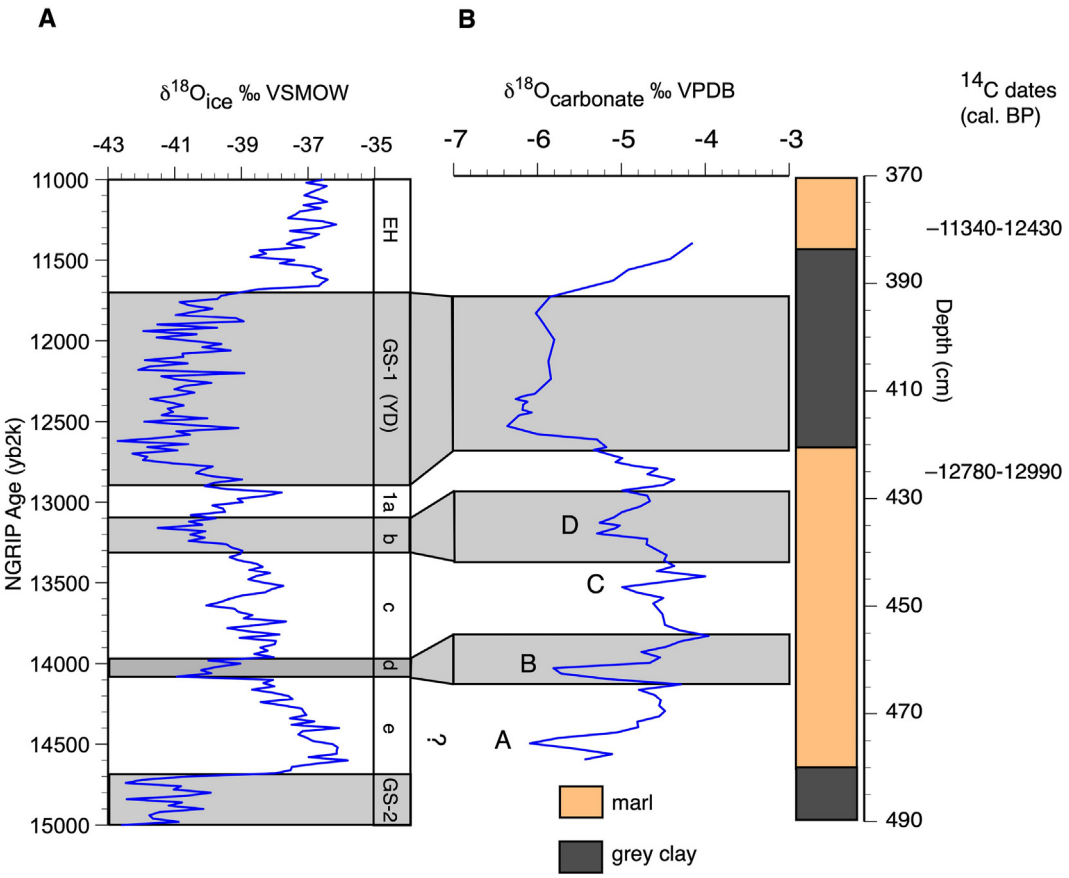

Fig. 2. Development of a chronology for the Hawes Water Late Glacial sediment sequence. **A**. Greenland ice core (NGRIP) oxygen-isotope record (North Greenland Ice Core Project members, 2004), with proposed correlation to HW1. Shading denotes NGRIP stadials. GS2 = Greenland Stadial 2; 1a to 1e inclusive = Greenland Interstadial 1a to 1e, which is equivalent to the Late Glacial Interstadial; GS-1 (YD) = Greenland Stadial 1, which is equivalent to the Younger Dryas Stadial; EH = Early Holocene. **B.** Late Glacial carbonate oxygen-isotope record from Hawes Water core HW1 (on its original depth scale). Events labelled "A" to "D" are negative oxygen-isotope excursions in the HW1 record (based on Marshall et al., 2002; Lang et al., 2010). Radiocarbon dates are from Marshall et al. (2002), calibrated here using Calib 8.20 (Stuiver and Reimer, 1993) and IntCal20 and expressed as 1 sigma ranges in calendar years BP.

conventional techniques. In addition, a few samples of chitin from head capsules were analyzed by flash pyrolysis followed by gas chromatography and mass spectrometry (Py-GC-MS). The original purpose of the Py-GC-MS analyses was to compare the effects of different pre-treatments of the head capsules on the molecular degradation of chitin, but this method later provided important evidence for alteration of the original chitin in the Hawes Water samples.

2.3.1. Isotope analysis of chironomid head capsules

Freeze-dried, 1 cm-thick sediment segments from selected intervals were washed through 210 μm and 90 μm mesh sieves with deionized water and sonicated to remove sediment particles. The stratigraphic resolution of the chironomid record was restricted by the abundance of chironomids; however, where possible, analyses were performed every 2 cm. Chironomid head capsules were picked from aliquots of sieved residue under a low-power (× 25 magnification) binocular microscope. Owing to limited availability of material, all the head capsules in each level were aggregated, regardless of species, and because of this species identifications were not determined. Based on experiments to determine minimum sample size and optimum methods for head capsule purification (Supplementary Material), 60 ± 10 μg of head capsule material from each sample was analyzed following pretreatment to eliminate impurities. The pretreatment process involved three steps applied sequentially to each sample of separated head capsules; firstly 2:1 dichloromethane:methanol, secondly 0.25 M HCl and thirdly 0.25 M NaOH for 24 h at 20 °C. The head capsules were further washed and sonicated at each stage in the treatment process to confirm that all particles of sediment had been removed. Oxygen-isotope analyses of treated chironomid remains were performed at Durham University Stable Isotope Biogeochemistry Laboratory (SIBL) using a Thermo TC/EA coupled to a ThermoFinnigan Delta V Advantage IRMS, via a ConFlo III interface. Oxygen-isotope ratios are expressed in standard delta units, as per mil (‰) deviations from the VSMOW standard. Results were calibrated against three international reference standards (IAEA-600, IAEA-601, IAEA-602). Sample analytical precision was better than ±0.64‰ (1 SD) based on analysis of three replicate samples from one level in the Hawes Water sequence that contained abundant chironomid head capsules.

2.3.2. Isotope analysis of carbonate

Between 3 and 5 g aliquots of bulk sediment were treated with 100 mL 5% sodium hypochlorite overnight to remove organic material, wet-sieved through an 80 μm mesh to remove bioclastic material, rinsed in deionized water and then freeze dried in order to isolate endogenic carbonate for oxygen-isotope analyses. Standard analytical methods were employed as described for the Hawes Water material in Marshall et al. (2002) and Thomas (2014). In brief, samples of around 2 mg were then analyzed at the University of Liverpool stable isotope laboratory using a VG ISOCARB automated 'common acid bath' gas preparation system connected to a VG SIRA10 mass spectrometer. Oxygen-isotope ratios are expressed in standard delta units, as per mil (‰) deviations from the VPDB standard. VPDB to VSMOW conversion, where required, followed Kim et al. (2015). Analytical precision for carbonates based on the long-term measurement of standards was better than ±0.1‰ (1 SD).

2.3.3. Pyrolysis − gas chromatography − mass spectrometry (Py−GC−MS)

To monitor the effect of the combined purifications (extraction, acid and base treatment, see Supplementary Material) on their composition, modern chironomid head capsules and isolated fossil heads from three levels in the sequence (358 cm, 360 cm and 364 cm) were analyzed by Py-GC-MS. The selection of core levels from which to analyse fossil heads was dictated by the availability of remaining material following the completion of the oxygen-isotope analyses.

Pyrolysis was carried out in helium carrier gas on a Horizon Instruments Curie-Point pyrolyser. Samples (typically 1−2 mg) were pressed onto Ni/Fe Curie point wires and subsequently heated for 5 s at 590 °C. The pyrolysis unit was directly connected to a Carlo Erba GC8060 gas chromatograph through a splitless injector set at 280 °C, and the products were separated by a fused silica column (Varian, 25 m, 0.32 mm i.d.) coated with CP-Sil5 (film thickness 0.40 μm). The GC oven was initially kept at 40 °C for 1 min then heated at a rate of 7 °C min^{-1} to 320 °C and maintained at that temperature for 15 min. The column was coupled to a Fisons MD800 mass spectrometer (mass range *m/z* 45−650, ionization energy 70 eV, cycle time 0.7 s). Identification of the compounds was carried out from their mass spectra using a NIST library and/or by interpretation of the spectra, by their retention times and/or by comparison with data from the literature (Stankiewicz et al., 1996; Smith et al., 1988). Quantification was performed by peak integration using two main fragment ions of each compound. From the peak areas, relative contributions of each compound and groups of compounds were calculated using the correction factors reported by Menzel et al. (2005). Each day, prior to analysis of samples, a standard (ball-milled oak root, *Quercus robur* L.) was run in order to check pyrolysis, chromatography and mass spectrometry based on an array of compounds present, including polysaccharides, proteins, guaiacyl-lignin, syringyl-lignin, tannins, suberin, and triterpenoids. Each of these compounds has distinct features upon Py-GC-MS, thus allowing possible problems with the system to be traced. In case of maintenance or when too much sample was pyrolyzed (based, for example, on peak overload or high intensity), a blank was run (either only GC-MS running or running a pre-extracted Curie-point wire). For the chitin-derived pyrolysis products correction factors were determined by dividing the peak area of the whole peak by those obtained from the selected fragment ions using the pyrolysis-GC trace of chitin powder. The correction factors are: acetic acid (1.5), acetamide (1.0), 3-acetamido-3-methylfuran (2.2), 3-acetamido-4-pyrone (3.1), and 1,6-anhydro-2-acetamido-2-deoxyglucose (5.4).

3. Results and interpretation

3.1. Derivation of past water-temperature and lake water $\delta^{18}O$

Previous work has demonstrated a strong positive correlation between $\delta^{18}O_{chironomid}$ and $\delta^{18}O_{lakewater}$ (van Hardenbroek et al., 2018). Fig. 3 combines information from the field collections reviewed by van Hardenbroek et al. (2018, see their Fig. 5) with data from laboratory culture experiments by Wang et al. (2009) and Lombino et al. (2021). Wang et al. (2009) performed experiments at constant temperature (25 °C). Lombino et al. (2021) reared chironomid larvae in a range of cultures with temperatures from 5 to 25 °C and found a small temperature effect of about −0.1‰ $°C^{-1}$.

Although Fig. 3 reveals a strong relationship between $\delta^{18}O_{chironomid}$ and $\delta^{18}O_{H2O}$, the data also show considerable scatter ($r^2 = 0.80$). This scatter probably results from a number of factors that differ both within and between the individual studies, including inter-species effects as well as differences in temperature, sample preparation methods and analytical protocols. The best-fit line does not indicate a 1:1 correspondence between the isotope ratios in the chironomid head capsules and the water, but instead has a gradient of 0.83. This probably reflects the fact that in controlled culture experiments reported by Wang et al. (2009)

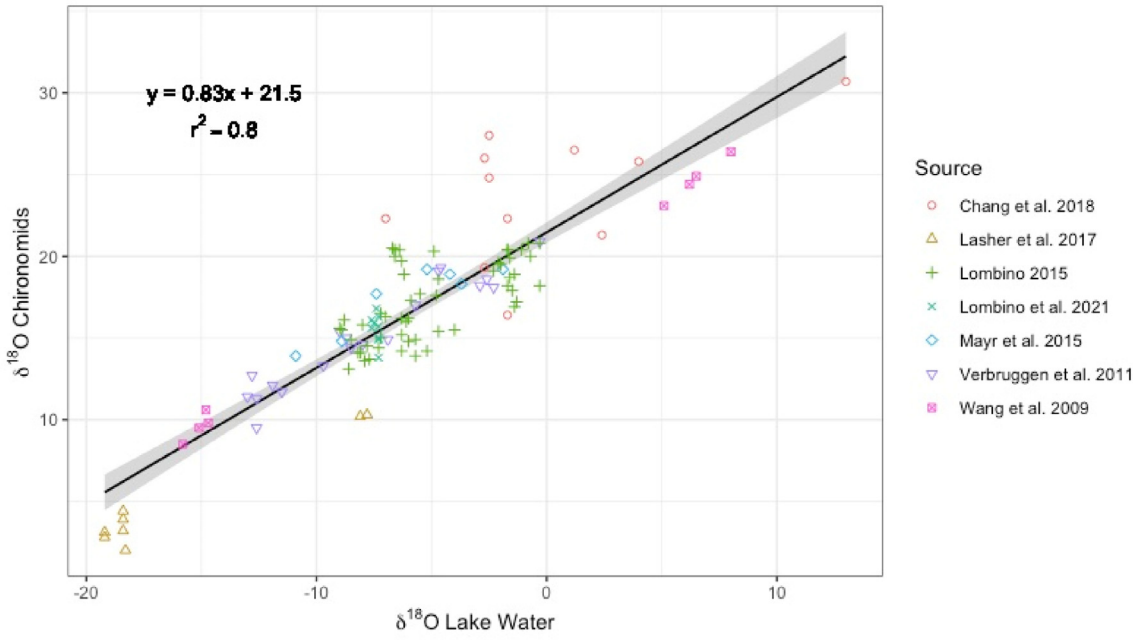

Fig. 3. $\delta^{18}O_{chironomid}$ versus $\delta^{18}O_{H2O}$ based on a range of field collections (Verbruggen et al., 2011; Lombino, 2015; Mayr et al., 2015; Lasher et al., 2017; Chang et al., 2018) and two culture experiments (Wang et al., 2009; Lombino et al., 2021). The ordinary least-squares regression line, with 95% confidence limits, was fitted through all of the data. Based on van Hardenbroek et al. (2018) with additions and modifications.

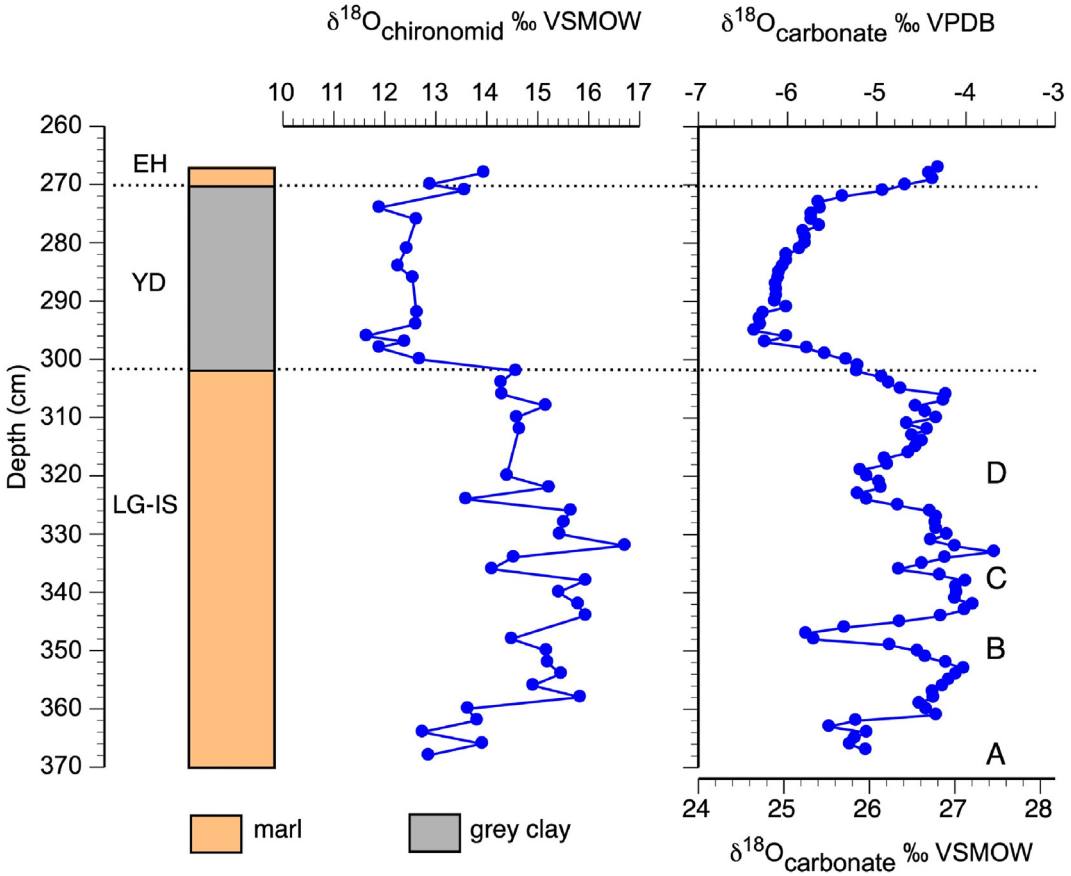

Fig. 4. Oxygen-isotope stratigraphy ($\delta^{18}O_{chironomid}$ and $\delta^{18}O_{carbonate}$) for core HW2 (on the original depth scale). Negative excursions in the $\delta^{18}O_{carbonate}$ record are labelled A to D. LG-IS = Late Glacial interstadial; YD = Younger Dryas stadial; EH = Early Holocene.

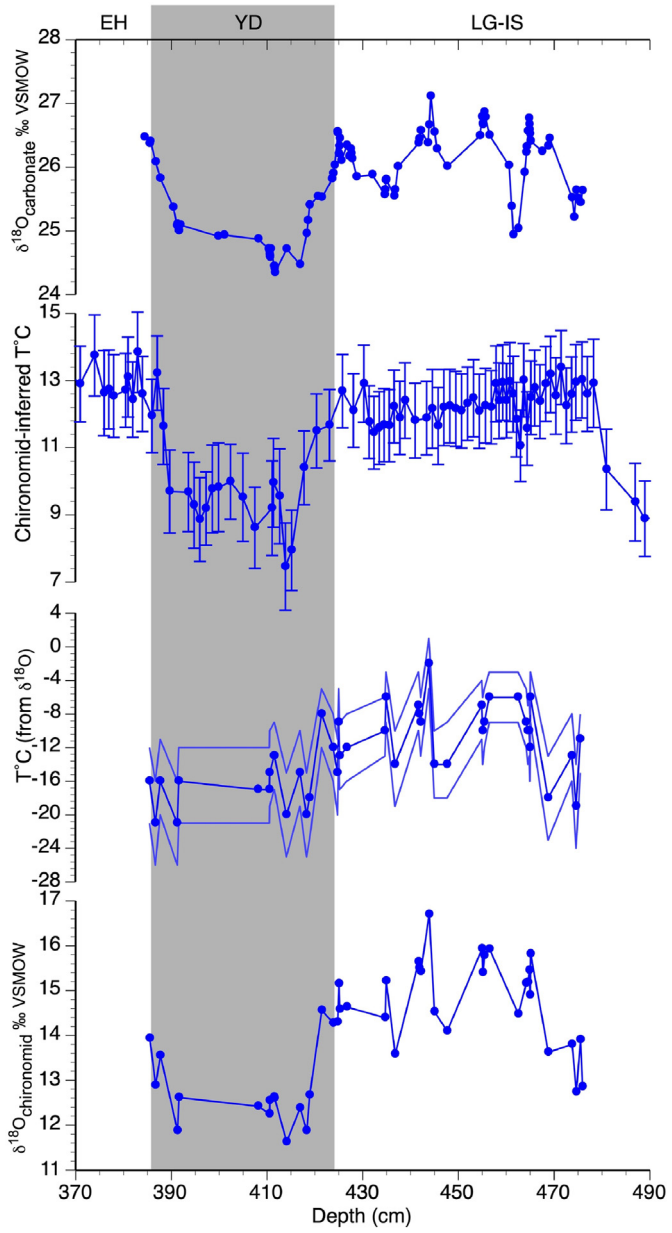

Fig. 5. $\delta^{18}O_{chironomid}$, temperature inferred from the chironomid oxygen isotopes and $\delta^{18}O_{carbonate}$ from core HW2 (plotted on the depth scale of HW1); chironomid-inferred temperatures (±1 SD) from core HW1/2 are from Bedford et al. (2004). Uncertainties (±1 SD) in the isotope-inferred palaeotemperature values (shown by pale lines) were propagated from the statistical uncertainties in equations (1) and (2) and analytical errors for $\delta^{18}O_{chironomid}$ and $\delta^{18}O_{carbonate}$ determinations. Note that $\delta^{18}O_{carbonate}$ values are shown relative to the VSMOW scale. LG-IS = Late Glacial Interstadial; YD = Younger Dryas Stadial; EH = Early Holocene. Transfer of HW2 data to the HW1 depth scale is explained in the Supplementary Data.

about 30% of oxygen atoms in chironomid chitin were derived from their food, while 70% were derived from the host water. Differences in the isotopic composition of food consumed by the larvae in the various studies may also, therefore, have contributed to the scatter in Fig. 3.

The calcite–water ($\alpha_{calcite\text{-}H2O}$) and chironomid–water ($\alpha_{chironomid\text{-}H2O}$) oxygen-isotope fractionations can be combined in order to derive an estimate of water temperature, assuming that the calcite and the chironomids formed under the same temperature and water $\delta^{18}O_{H2O}$. Chironomid larvae generally live on the sediment surface or amongst plants in relatively shallow water and grow during the warm season (late spring through to early autumn) (Tokeshi, 1995). At Hawes Water, calcium carbonate is currently precipitated within the upper 2 m of the water column, from mid-June to mid-August, when the surface waters become supersaturated with respect to calcite (Marshall et al., 2007). We can therefore be confident that the carbonate and chironomid larval head capsules formed under similar conditions of temperature and lake-water isotope composition.

We combine the equation for the temperature-dependence of oxygen-isotope fractionation between calcite and water (Kim and O'Neil, 1997) (equation (1)) with that between chironomid head capsules and water from Lombino et al. (2021) (equation (2)) in order to derive a fractionation between calcite and chironomid head capsules (equation (3)). We then use this relationship along with oxygen-isotope values from chironomid head capsules and co-occurring calcite in order to reconstruct past water temperature for the Hawes Water sequence.

$$1000 \ln \alpha_{calcite-water} = 18.03(\pm 0.36)\left(10^3 T^{-1}\right) - 32.42(\pm 1.22) \quad (1)$$

$$1000 \ln \alpha_{chironomid-water} = 6.29(\pm 1.86)\left(10^3 T^{-1}\right) + 1.16(\pm 6.46) \quad (2)$$

$$1000 \ln \alpha_{calcite-chironomid} = 1000(\ln \alpha_{calcite-water} - \ln \alpha_{chironomid-water}) = 11.74(\pm 1.89)\left(10^3 T^{-1}\right) - 33.58(\pm 6.58) \quad (3)$$

The value of $\alpha_{calcite\text{-}chironomid}$ for each pair of measurements is given by $(\delta^{18}O_{carbonate} + 1000)/(\delta^{18}O_{chironomid} + 1000)$, with both delta values on the VSMOW scale. This value can then be entered into Equation (3), suitably rearranged to give a value for T in kelvins, which can then be converted to °C. As a test of the accuracy and effectiveness of the method's application to fossil material, temperatures inferred from oxygen isotopes in this way can be compared with independent temperature reconstructions derived from the chironomid assemblages from Hawes Water (Bedford et al. 2004).

The Late Glacial $\delta^{18}O_{chironomid}$ record from Hawes Water core HW2 extends from the Late Glacial interstadial through the Younger Dryas stadial and into the earliest Holocene (Fig. 4). The record begins with low $\delta^{18}O_{chironomid}$ values, ~12.8‰ VSMOW reaching a maximum of ~16.8‰ before declining to ~14.5‰ immediately before the start of the stadial. $\delta^{18}O_{chironomid}$ values fall as low as 11.5‰ during the Younger Dryas before increasing to ~14‰ in the Early Holocene. The form of the $\delta^{18}O_{chironomid}$ record agrees closely with the $\delta^{18}O_{carbonate}$ record from HW2. The two records are largely coherent ($r^2 = 0.70$, $P < 0.05$, $n = 44$) and we note also that the negative excursions in the $\delta^{18}O_{carbonate}$ record (labelled "A" to "D" on Fig. 4) are also evident in the $\delta^{18}O_{chironomid}$ data. Despite broad similarity between the $\delta^{18}O_{chironomid}$ and $\delta^{18}O_{carbonate}$ records, we note that the overall amplitude of change over the Late Glacial is much larger for the former (~5‰) than the latter (~3‰).

The palaeotemperatures reconstructed from the $\delta^{18}O_{chironomid}$ and $\delta^{18}O_{carbonate}$ values using the method described above are implausibly low, ranging between about −20 and −4 °C (Fig. 5). Comparison of the chironomid-isotope reconstructed temperatures with those inferred by transfer function from chironomid assemblages (Fig. 5) shows that the isotope-derived values are more variable than the faunal estimates, but still preserve — in a relative

way — the main features of the stadial-interstadial-stadial climatic sequence. However, the range in values from stadial to interstadial shown by the isotope-derived estimates is 14 °C, more than twice the faunal estimate of 6 °C.

The Py-GC-MS analyses (Table 1) show that the modern and fossil head capsules responded differently to pretreatment and, moreover, show contrasting composition. The modern heads became relatively enriched in chitin upon pretreatment, due to removal of fatty acids, whereas proteins were removed only to a relatively small extent. By contrast, the three fossil samples tested were relatively poorer in both proteinaceous material and chitin than the modern analogue. In addition, the fossil heads contained a relatively high abundance of aliphatic geopolymers, which were lacking from the modern specimens (Table 1).

4. Discussion

The chironomid-carbonate palaeothermometer is based on four assumptions: 1) $\delta^{18}O_{chironomid}$ is a reliable combined proxy for $\delta^{18}O_{H2O}$ and temperature, and that the contribution of each to the $\delta^{18}O_{chironomid}$ record can be reliably quantified; 2) both independent $\delta^{18}O$ archives formed simultaneously from waters with a common $\delta^{18}O_{H2O}$ and water temperature (i.e. in the same part of the water column and at the same time of year); 3) sample materials are free from contamination; and 4) sample materials are free from post-depositional alteration. The unrealistic sub-zero summer temperature estimates from Hawes Water $\delta^{18}O_{chironomid}$ imply that at least one of these assumptions is not valid. We now evaluate each of them in turn.

As discussed in 2.3 above, the relationship between $\delta^{18}O_{chironomid}$ and $\delta^{18}O_{H2O}$ is strong and has been confirmed through a number of field- and lab-based studies. The impact of temperature on $\alpha_{chironomid\text{-}water}$ in Lombino et al. (2021), however, represents only a single study and requires further confirmation. There is some evidence for temperature-dependent oxygen-isotope fractionation in cellulose, a biomolecule that shows similar isotopic behaviour to chitin (Beuning et al., 1997, 2002): both cellulose and chitin have previously been regarded as showing no temperature dependence in oxygen-isotope fractionation (Mayr et al., 2015; Wooller et al., 2004, 2008; Wolfe et al. 2001, 2007). However, even if we assume a constant $\alpha_{chironomid\text{-}H2O}$ value and then use this in conjunction with $\delta^{18}O_{carbonate}$ values, the reconstructed temperatures are still unrealistically low and show poor agreement with the chironomid-inferred temperature estimates. In short, our findings would be unchanged if this approach were taken.

The chironomids and carbonate are both very likely to have formed under the same conditions of water temperature and water-isotope composition (i.e. in the near-surface waters of the lake during late spring and summer). For the carbonate, this is confirmed by the detailed monitoring of Hawes Water (Marshall et al., 2007) summarized in 2.1 above. For the chironomids, there are numerous studies that confirm that the larval chitin forms in late spring to early autumn (Tokeshi, 1995). Although the larvae live in the surface sediments and plants, they tend to be confined to shallower water, with conditions of temperature and $\delta^{18}O_{H2O}$ similar to those for carbonate formation.

Sample contamination is unlikely to be a problem for either $\delta^{18}O_{chironomid}$ or $\delta^{18}O_{carbonate}$. The preparation method for carbonate at Hawes Water yields estimates for water temperature that are realistic for the modern lake when applied to contemporary carbonate (Marshall et al., 2007). For the chironomids, our evaluation of preparation methods suggests that this will not have led to any significant effect on the $\delta^{18}O_{chironomid}$ signal and the checks undertaken during sample preparation confirm the absence of sedimentary contamination (see Supplementary Material). This leaves only post-depositional alteration of the oxygen isotope ratios of one or both sample materials as a possible source of error. There is no evidence that post-depositional diagenesis of marl in Hawes Water has led to significant alteration of $\delta^{18}O_{carbonate}$ (Marshall et al., 2007), whereas chitin is an organic polymer that might be subject to degradation or other diagenetic processes.

The chemical composition of chitin is thought to remain largely unchanged for tens of thousands of years under favourable depositional environments (e.g. high sedimentation rates and anoxia) (Stankiewicz et al., 1997a, 1997b). However, the chromatographic screening of chironomid remains from Hawes Water shows they have lower proportions of both proteinaceous material and chitin than the modern analogue. Furthermore, the macromolecular structure of the tested chironomid remains from Hawes Water is characteristic of the formation of aliphatic (geo)polymers during diagenesis, via the polymerization of liberated lipid molecules (Baas et al., 1995; Cody et al., 2011; Gupta et al., 2009; Stankiewicz et al., 2000). Pretreatment had the effect of relatively enriching these geopolymers, whereas proteins and chitin became depleted (Table 1).

The conditions governing such geopolymerization are largely unknown and therefore the influence of the formation of geopolymers on the $\delta^{18}O_{chironomid}$ signature at Hawes Water is difficult to ascertain, but clearly diagenetic alterations have the potential to reset, or at least alter, the original $\delta^{18}O_{chironomid}$ signature. We combined the chironomid-inferred and isotope-derived temperatures presented above to estimate the amount of fractionation that may have occurred during diagenesis at each level in the core for which paired measurements are available. We emphasize that these estimates are based on the difference between the chironomid-inferred and isotope-derived temperatures: we did not attempt to estimate the degree of diagenetic fractionation based on the Py-GC-MS data, which are, in any case, only available from three sample levels. Instead, we use the compositional data as evidence that alterations consistent with diagenesis have occurred. The average inferred diagenetic fractionation using this approach is 1.0035 ± 0.0008 (1 SD); i.e. there is an inferred $+3.5 \pm 0.8$‰ change in $\delta^{18}O_{chironomid}$ values during diagenesis. We plot the calculated diagenetic fractionation against chironomid-inferred temperature in order to explore any influence of temperature on the diagenetic process (Fig. 6) and note that the data fall into two apparent

Table 1
Relative abundances of bio- and geopolymers in chironomid head capsules based on the abundances of their pyrolysis products. Sample numbers for fossil material from Hawes Water refer to sample depths in HW/2.

	Modern heads		Fossil heads 358 cm		Fossil heads 360 cm		Fossil heads 364 cm	
	untreated	treated	Untreated	treated	untreated	treated	untreated	treated
Chitin	0.36	0.53	0.30	0.23	0.34	0.18	0.40	0.28
Fatty acids	0.17	0.01	0.01	0.04	0.02	0.05	0.01	0.05
Proteins	0.47	0.46	0.37	0.17	0.24	0.17	0.36	0.24
Aliphatic geopolymers	0.00	0.00	0.32	0.56	0.40	0.59	0.23	0.43

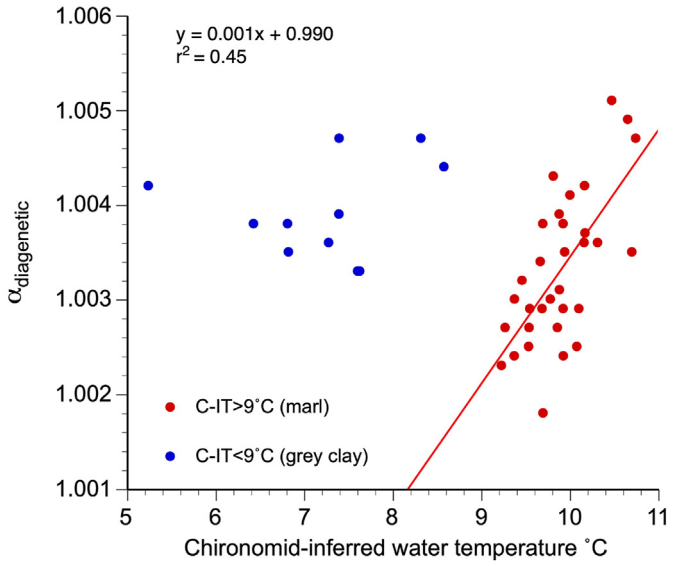

Fig. 6. Diagenetic fractionation factor ($\alpha_{diagenetic}$) versus chironomid-inferred water temperature (C-IT) for Hawes Water core HW2. Water temperature was determined by subtracting 2.3 °C from chironomid-inferred air temperature (Marshall et al., 2007). The regression equation and r^2 value relate only to C-IT values > 9 °C.

populations. For chironomid-inferred water temperatures <9 °C, there is no relationship between temperature and diagenetic fractionation whereas there is a strong positive relationship for chironomid-inferred water temperatures >9 °C. In general, the positive fractionation suggests a loss of ^{16}O during the geopolymerization process. The relationship with ambient temperature is difficult to explain, although we note that those levels for which a correlation between temperature and diagenetic fractionation exists are from marl sediments whereas the levels for which the correlation is absent are from clays. The positive diagenetic fractionation is consistent with early diagenesis, presumably mediated by bacteria within the marl: we speculate that this diagenetic process may have been delayed in the less permeable clays, which would account for the lack of correlation with ambient temperature at the time of deposition or shortly afterwards. The amount of diagenetic fractionation is sensitive to $\alpha_{chironomid\text{-}water}$, although different values of $\alpha_{chironomid\text{-}water}$ would not change the overall patterns observed, nor our interpretations of them.

The partial persistence of proteins after the treatments implies that they contribute to the $\delta^{18}O_{chironomid}$ values obtained, although their oxygen content is smaller than that of chitin. However, there is relatively less protein and chitin than geopolymer in the head capsule material following treatment. The diagenetic fractionation must therefore be associated with the formation of the geopolymer. Despite this, the coherence between the two independent $\delta^{18}O$ records (i.e. carbonate and chironomid head capsules) suggest that some form of environmental signal is still preserved even after diagenesis.

5. Conclusions

Previous work has shown that the oxygen-isotope composition of chironomid head capsules is determined primarily by the composition of the environmental water in which the chironomids lived, but is also dependent on temperature and on the oxygen isotopic composition of the dominant food source (van Hardenbroek et al., 2018: Lombino et al., 2021). We have shown, from a Late Glacial lake sediment record from Hawes Water, that a time series of oxygen-isotope values from chironomid head capsules strongly resembles records based on two other independent climatic proxies, namely the $\delta^{18}O$ of endogenic carbonate and temperatures inferred from chironomid assemblages using transfer functions. These similarities suggest that $\delta^{18}O_{chrinomid}$ records have considerable potential for future studies, especially in lakes that lack carbonate deposition or preservation, but in which other biomolecules are preserved. However, in our record the isotopic composition of the head capsules appears to have been altered during diagenesis, with this additional, unknown fractionation producing unrealistic results in temperature reconstructions. It is a matter for future research to establish whether such diagenesis is common in lake sediment settings. A possible relationship between sediment type and the extent of diagenetic alteration of chironomid head capsules that is evident in our data requires further investigation. While the apparently orderly diagenetic modification of the marl-encased head capsules militates for early diagenesis that is closely related to temperature, the discrepancy with the clay-encased material indicates that the rate of diagenesis is dependent on the sedimentary context and may be delayed and slowed in low-permeability materials. This implies that the present results are likely only to be mirrored in a general way in other lakes or water bodies, and that the diagenetic fractionation factors we have deduced should not be taken to apply to any sites other than Hawes Water. Nonetheless, our results do indicate that oxygen-isotope values of chironomid head capsules from Quaternary sequences should be interpreted with care, especially if the isotope data are to be used in quantitative reconstructions of past climate. Further testing of this 'combined isotope' approach could involve oxygen-isotope analyses of modern carbonate precipitates and head capsules from living chironomid larvae from a site in which water temperature and water isotope composition are closely monitored.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.quascirev.2021.107160.

Contributor roles

AL led the investigation and produced the initial draft of the manuscript. AL, DRG, JM, KN and ZT undertook the analytical work. SB and VJ supervised the work. TA and JH finalized the manuscript and led the data analysis. All authors contributed to drafting and finalizing the manuscript. Co-authors are listed alphabetically.

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