Understanding the transfer of contemporary temperature signals into lake sediments via paired oxygen isotope ratios in carbonates and diatom silica: Problems and potential

David B. Ryves a,⁎, Melanie J. Leng b, c, Philip A. Barker d, Andrea M. Snelling b, c, 1, Hilary J. Sloane b, Carol Arrowsmith b, Jonathan J. Tyler e, 2, Daniel R. Scott a, Alan D. Radbourne b, 3, N. John Anderson a

a Geography and Environment, Loughborough University, Loughborough LE11 3TU, UK
b NERC Isotope Geosciences Facilities, British Geological Survey, Keyworth, Nottingham NG12 5GG, UK
c Centre for Environmental Geochemistry, School of Biosciences, Sutton Bonington Campus, University of Nottingham, Loughborough LE12 5RD, UK
d Lancaster Environment Centre, Lancaster University, Lancaster LA1 4YQ, UK
e Department of Earth Sciences, University of Oxford, Oxford OX1 3AN, UK

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ABSTRACT
Although the oxygen isotope composition (δ18O) of calcite (δ18O_{calcite}) and, to a lesser extent, diatom silica (δ18O_{diatom}) are widely used tracers of past hydroclimates (especially temperature and surface water hydrology), the degree to which these two hosts simultaneously acquire their isotope signals in modern lacustrine environments, or how these are altered during initial sedimentation, is poorly understood. Here, we present a unique dataset from a natural limnological laboratory to explore these issues. This study compares oxygen and hydrogen isotope data (δ18O, δ2H) of contemporary lake water samples at ~2-weekly intervals over a 2-year period (2010–12) with matching collections of diatoms (δ18O_{diatom}) and calcite (δ18O_{calcite}) from sediment traps (at 10 and 25 m) at Rostherne Mere (maximum depth 30 m), a well-monitored, eutrophic, seasonally stratified monimictic lake in the UK. The epilimnion shows a seasonal pattern of rising temperature and summer evapo- rative enrichment in 18O, and while there is a temperature imprint in both δ18O_{diatom} and δ18O_{calcite}, there is significant inter-annual variability in both of these signals. The interpretation of δ18O_{diatom} and δ18O_{calcite} Values is complicated due to in-lake processes (e.g. non-equilibrium calcite precipitation, especially in spring, leading to significant δ18O_{calcite} depletion), and for δ18O_{diatom}, by post-mortem, depositional and possibly dissolution or diagenetic effects. For 2010 and 2011 respectively, there is a strong temperature dependence of δ18O_{calcite} and δ18O_{diatom} in fresh trap material, with the fractionation slope for δ18O_{diatom} of ca. −0.2‰/°C. In agreement with several other studies. The δ18O_{diatom} data indicate the initiation of rapid post-mortem secondary alteration of fresh diatom silica (within ~6 months), with some trap material undergoing partial maturation in situ. Diatom δ18O of the trap material is also influenced by resuspension of diatom frustules from surface sediments (notably in summer 2011), with the net effect seen as an enrichment of deep-trap δ18O_{diatom} by about +0.7‰ relative to shallow-trap values. Contact with anoxic water and anaerobic bacteria are potentially key to initiating this silica maturation process, as deep-trap samples that were removed prior to anoxia developing do not show enrichment. Dissolution (perhaps enhanced by anaerobic bacterial communities) may also be responsible for changes to δ18O_{diatom}, that lead to increasing, but potentially predictable, error in inferred temperatures using this proxy. High resolution, multi-year monitoring can shed light on the complex dynamics affecting δ18O_{diatom} and δ18O_{calcite} and supports the careful use of sedimentary δ18O_{diatom} and δ18O_{calcite} as containing valuable hydroclimatic signals especially at a multi-annual resolution, although there remain substantial challenges to developing a reliable geothermometer on paired δ18O_{diatom} and δ18O_{calcite}. In particular, δ18O_{diatom} needs cautious

⁎ Corresponding author.
E-mail address: D.B.Ryves@lboro.ac.uk (D.B. Ryves).
1 Present address: School of Geography, University of Nottingham, Nottingham NG7 2RD, UK.
2 Present address: Department of Earth Sciences and Sprigg Geobiology Centre, University of Adelaide, SA 5005, Australia.
3 Present address: Centre for Ecology and Hydrology, Environment Centre Wales, Deiniol Road, Bangor, Gwynedd LL57 2UW, UK.

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interpretation where silica post-mortem secondary alteration is incomplete and diatom preservation is not perfect, and we recommend dissolution be routinely assessed on diatom samples used for isotopic analyses.

1. Introduction

The oxygen isotope composition of diatom silica ($\delta^{18}O_{\text{diatom}}$) and endogenic calcite ($\delta^{18}O_{\text{calcite}}$), is controlled by three factors: both the temperature and $\delta^{18}O$ of the water in which they form, and (potentially) both diagenetic and disequilibrium effects. Individually, $\delta^{18}O$ of diatom silica or calcite are often used as tracers of past lake water temperature and hydrological balance, an approach that is potentially strengthened when applied together (Lamb et al., 2005; Swann et al., 2010; Dean et al., 2013). Nevertheless, both proxies share the fundamental limitation that they respond to both temperature change and the $\delta^{18}O$ of lake water ($\delta^{18}O_{\text{lake}}$) in which they form. Additionally, diagenesis (e.g. dissolution) and non-equilibrium effects may affect the signals themselves (Teranes et al., 1999a; Moschen et al., 2006; Smith et al., 2016). Analysing the two in tandem can explore some of these issues, allowing for an independent temperature prediction (a geothermometer). Although this has been explored with sedimentary data (Rozanski et al., 2010), no studies, as far as we are aware, have done so in modern environments. Such a geothermometer would have great potential for application in a range of lakes where both diatoms and calcite are preserved in the same sedimentary samples.

Questions remain concerning the degree to which processes occurring during signal acquisition and subsequent alteration can bias the interpretation of $\delta^{18}O_{\text{diatom}}$ and $\delta^{18}O_{\text{calcite}}$ as environmental proxies. For $\delta^{18}O_{\text{diatom}}$, species-specific (vital) offsets during valve silicification have been reported (e.g. Swann et al., 2007), although this is not always the case (Bailey et al., 2014), whereas there is some evidence of post-mortem alteration of the $\delta^{18}O_{\text{diatom}}$ signal preserved in the frustule, both through diatom dissolution (Smith et al., 2016), and, independent of this, rapid post-mortem dehydroxylation of fresh diatom silica (Dodd and Sharp, 2010; Dodd et al., 2012; Tyler et al., 2017). Under certain conditions, calcite can precipitate out of isotopic equilibrium with...
formation waters (Teranes et al., 1999a), whereas the role of subsequent calcite dissolution on δ18Ocalcite is unknown.

Despite the uncertainties that plague the interpretation of δ18Odiatom and δ18Ocalcite as paleoclimatic proxies, only a handful of studies have integrated contemporary seasonal measurements of limnological conditions (such as temperature, pH) and lake δ18O composition with direct measurement of the δ18O signal of in-situ endogenic calcite or diatom silica (Moschen et al., 2006; Li and Han, 2010; Dean et al., 2015). Here, we combine seasonal limnological monitoring with analyses of δ18O in both contemporary diatom silica and calcite soon after their genesis in the water column, and before longer term diagenetic alteration and temporal blurring of the signals as they become incorporated into the sediment archive. This provides the opportunity to examine the production of these signals in more detail, and how they correspond to and capture information about the contemporary lake system, as a means to calibrate the δ18O signal from palaeoenvironmental studies of sedimentary records (see Teranes et al., 1999a; Moschen et al., 2006; Dodd et al., 2012).

The purpose of this study was two-fold. Firstly, to assess the correspondence between the surface lake isotope composition and the signal contained within endogenic calcite and planktonic diatom diatoms over two-weekly to seasonal timescales. Secondly, to examine the relationships between physical limnology (e.g. stratification and mixing), hydroclimatology (seasonal change and short-term events, e.g. river flood inputs), and the isotope composition of the hydrological system (rainfall, groundwater, lake water, inflow, outflow), to determine the main drivers of water column isotope variability in a well-characterised lake. In combination, these objectives provide a means to explore the reliability of sedimentary δ18Odiatom and δ18Ocalcite as palaeohydroclimatic (temperature) proxies at seasonal scales in such a system. As a case study, we use a temperate, strongly stratifying, productive lake in the UK (Rostherne Mere, Cheshire) as a natural laboratory in which to explore the isotope systematics manifested in the modern calcite and diatom silica, with high-frequency (two-weekly to monthly) and seasonal sediment traps and water sampling over a two-year period, and generate an isotopic dataset that is unique (as far as we are aware). We also assess the implications of the results for the reliable application of δ18Odiatom and δ18Ocalcite as palaeoenvironmental proxies in their own right, and examine some of the challenges that exist to developing a geothermometer to infer past lake surface temperature from paired δ18Odiatom and δ18Ocalcite data from the same sediment samples.

2. Study site and sampling

2.1. Rostherne Mere

Rostherne Mere (53°20′N, 2°24′W; Fig. 1), one of the Shropshire-Cheshire meres (Reynolds, 1979), is a relatively deep (31 m maximum depth), small (lake area 49 ha), freshwater, monomictic and eutrophic lake. The lake is of glacial origin, and has been deepened by dissolution of underlying salt-bearing strata (Reynolds, 1979) and lies within till, which supplies the lake with bicarbonate ions through inflows and groundwater. The mere is unusually deep for its area (surface area to maximum depth [A0/Zmax] is 0.016), with some topographic protection from westerly winds, and generally stratifies from mid-April to late November or early December (Scott, 2014; Radbourne et al., 2017). Naturally strong monomictic stratification has been exacerbated by eutrophication, especially over the 20th century, when the two catchment sewage treatment works (STWs) were overwhelmed by a growing surrounding population (Carvalho et al., 1995).

Most of the lake’s 9 km² catchment area is drained by Rostherne Brook (Fig. 1), the only significant surface inflow, although deep and shallow groundwater must also contribute to the water balance (Carvalho et al., 1995). Lake water outflow is to the east via Blackburn’s Brook (Fig. 1). The lake is eutrophic, with a high bicarbonate alkalinity (mean values from 2010 to 12; 1900 μM L⁻¹) and high concentrations of phosphorus (mean TP; ~7 μM L⁻¹), nitrogen (mean TN; ~87 μM L⁻¹) and silica (spring maximum ~72 μM Si L⁻¹). Lake net primary production is high (NEP ~130 g C m⁻² year⁻¹ in 2011–12 with individual algal blooms > 20 g m⁻² dry weight; Reynolds, 1979; Scott, 2014). Planktonic diatoms typically bloom in spring (notably Asterionella formosa, Stephanodiscus neoaeastrea and S. parvus) and autumn (Aulacoseira granulata, Cyclostephanos dubius and C. tholiformis; Radbourne, 2018), while cyanobacteria (Microcystis) dominate in summer (Reynolds, 1978; Livingstone and Reynolds, 1981; Moss et al., 2005; Hargreaves et al., 2013; Radbourne et al., 2017). Under the strong stratification, respiration of the sinking algal crop from the spring and early summer turns the hypolimnion anoxic within only a few weeks (Scott, 2014). Given the lake’s large volume relative to surface inflow and outflow, Rostherne Mere has a relatively long water residence time (~1.6 years, as calculated from the outflow method; Carvalho, 1993; 2.4 ± 0.25 years using the runoff method; Moss et al., 2005) though more recent data from 2016 suggest it may be < 1 year (Radbourne, 2018). Lake level responds rapidly to increased inflow during periods of high rainfall, and usually falls over summer due to high evaporation. Lake level typically varies by ~1 m over an annual cycle.

Rostherne Mere has been monitored (physical, chemical, biological) for over 100 years (e.g. Tattersall and Coward, 1914; Grimshaw and Hudson, 1970; Reynolds, 1978). There was a renewal of scientific interest following the diversion of sewage from the lake in 1991 (e.g. Carvalho et al., 1995; Krivtsov et al., 2001; Moss et al., 2005). The lake currently hosts an on-lake automated water quality and weather monitoring station (AWQMS), as part of the UK Lake Ecological Observatory Network (UKLEON; http://www.ceh.ac.uk/our-science/projects/uk-lake-ecological-observatory-network-ukleon), continuing the long-term monitoring of seasonal stratification at Rostherne which has been ongoing since autumn 2005.

2.2. Lake profile temperature data

Thermistors were installed in the lake (at the AWQMS; Fig. 1) and measured temperature continuously at 12 depths (every 2 m) from 0.5 m to ~24 m, recording a value every 15 min. These data were averaged to give daily values for each 2 m depth point and processed within Surfer 8 to map lake water isotherms over time. Mixing depth was estimated as the depth of the thermocline, the depth at which the vertical change in temperature was greatest (typically falling by > 1 °C per m), and stratification and overturn periods defined by when the thermocline appeared in spring and disappeared in late autumn/early winter.

2.3. Water sampling

During regular visits to the lake, from February 2010 to May 2012, water samples for oxygen and hydrogen isotope analyses were collected from the centre of the lake at the AWQMS site (Fig. 1) using 30 mL polypropylene bottles. These were rinsed twice with lake water prior to complete filling. Sampling was carried out, on average, every 2–3 weeks throughout the year, except during winter months (January, February) when up to monthly visits were made. On every visit, samples were collected from 0.5 m water depth and the inflow (Rostherne Brook), and less frequently, from 12 m and 24 m water depth using a Ruttner water sampler (1.5 L), as well as the outflow, and groundwater from a spring at Harper’s Bank (Fig. 1). Samples from 0.5 m depth were taken to avoid any surface water boundary effects.

An automatic Teledyne-ISCO water sampler was also installed, collecting water from the littoral zone (~1–2 m depth; 10 m from the shore) near to the boathouse (Fig. 1) every 2 weeks during summer 2010, to test if automatic water collection for isotope analyses and on-site storage could be used to reduce the frequency of trips to the lake. Over two periods in summer 2010 (6 and 8 weeks), 750 mL samples
were collected in 1 L bottles to which were added 20 mL of analytic-grade liquid paraffin to prevent evaporation. These samples were stored within the ISCO sampler at ambient temperature and collected at the end of the two periods.

2.4. Sediment trapping

Systematic and high-frequency monitoring of the lake and settling particles began in spring 2010, although some sediment trapping with open traps was carried out prior to this (from autumn 2005; Table 1). Sediment traps were installed in the central pelagic area (∼28–30 m water depth, Fig. 1) using both open-tube and fully automatic and programmable rotating-carousel sequencing traps (model Technicap PPS 4/3; Radbourne et al., 2017). The first sequencing trap was installed in May 2010 at 10 m depth (“shallow”), and a second (“deep”) sequencing trap in April 2011 at 25 m water depth. As the thermocline is shallower than 10 m for much of the stratified period, both upper and lower traps integrate the bulk of pelagic diatom silica and calcite production (i.e. summer production) within the lake.

Open-tube traps are composed of an array of 3 or 4 plastic tubes (450 mm length, 72 mm internal diameter) with a trapping ratio (length/diameter) of 6.25. Open-tube traps were set at ∼8–10 m (shallow) and 22 m (deep) until May 2010, after which both open-tube traps were set to collect at 22 m. These were emptied after different time periods, from 2 weeks up to ~1 year. Once both shallow and deep sequencing traps were installed in May 2010, the open-tube trapping interval was set to every ~3 (occasionally 4) months. Additionally, open traps (at 8 m and 22 m) were set for various periods starting in autumn 2005 until 2010, allowing some comparative analyses of the isotope composition of calcites and diatom silica prior to the systematic monitoring period.

The sequencing traps (trapping area 0.05 m², trapping ratio 5.2) were programmed to collect seston in 12 × 250 mL polypropylene bottles at ~2-week intervals for 10 months a year (March to December), and monthly in January and February (when productivity was at its lowest). Sequencing traps were reset every ~6 months as dictated by the trapping interval used (~April and September). Sediment trap samples were stored in polypropylene bottles and kept frozen until analysis.

3. Analytical methods and data analysis

3.1. Stable isotope analyses

We use the standard definition for δ18O, where

\[ \delta^{18}O_{\text{sample}} = \left( \frac{^{18}O_{\text{sample}}/^{16}O_{\text{sample}} - ^{18}O_{\text{standard}}/^{16}O_{\text{standard}}}{^{18}O_{\text{standard}}/^{16}O_{\text{standard}}} \right) \times 1000 \]

Water isotopes (δ18O, δ2H) were analysed in batches at the NERC Stable Isotope Facility, British Geological Survey (BGS). Polypropylene bottles have been tested for secure storage for >1 year at BGS. Samples were taken directly from the ISCO bottles using a long syringe to sample well below the paraffin layer, but were otherwise analysed according to standard methods. δ18O measurements were carried out using the CO2 equilibration method with an Isoprime 100 mass spectrometer plus Aquaprep device. δ18O measurements were made using an online Cr reduction method with a EuroPyrOH-3110 system coupled to a Micromass Isoprime mass spectrometer. Isotope measurements were normalised against internal standards calibrated against the international standards V-SMOW2 and V-SLAP2. Errors were ±0.05‰ for δ18O and ±1.0‰ for δ2H.

Seston samples were freeze dried and subsampled for loss-on-ignition following standard methods (Dean Jr., 1974) to estimate organic content (550 °C for 2 h, error ±2%) and carbonate content (925 °C for 4 h, error <4%). Calcite crystals are known to form endogenically within the upper water column as a result of algal photosynthesis (Livingstone and Reynolds, 1981; Scott, 2014; Radbourne, 2018), in agreement with the calcite saturation index (CSI; Fig. 2). Here, we use

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**Table 1**

Values of δ18O for open trap diatom and authigenic calcite samples (relative to both VPDB and VSMOW-SLAP; Coplen, 1995) collected prior to monitoring began in 2010 at Rostherne Mere. Multiple open tubes deployed in the same trap array allow for some estimation of within-sample variability for δ18O calcite values (increasing analytical error slightly).

| Date in | Date out | No. days | Trap depth (m) | Sample δ18OVPDB | Sample δ18OVSMOW | Calcite δ18O error (tube replicates) |
|---------|----------|----------|---------------|-----------------|-----------------|-------------------------------------|
| 18/11/2005 | 6/10/2006 | 322 | 25 | −7.2 | 23.59 | 0.09 |
| 17/11/2006 | 5/10/2007 | 322 | 25 | −6.7 | 24.04 | 0.25 |
| 22/11/2007 | 3/10/2008 | 316 | 25 | −7.2 | 23.55 | 0.3 |
| Average error = 0.13 |

| Date in | Date out | No. days | Trap depth (m) | Sample δ18OVPDB | Sample δ18OVSMOW | Calcite δ18O error (tube replicates) |
|---------|----------|----------|---------------|-----------------|-----------------|-------------------------------------|
| 7/10/2005 | 18/11/2005 | 42 | 8 | +29.5 |
| 14/11/2008 | 20/11/2009 | 371 | 25 | +29.7 |

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the formulation CSI = pHm − pHc, where pHm is pH measured in the water and pHc is pH of the water when in equilibrium with calcite (APHA, 2005; Scott, 2014). Fig. 4 shows that calcite production occurs in spring and summer periods when algal production is high (with algal communities dominated by diatoms in spring and autumn, and cyanobacteria in summer; Radbourne, 2018). At Rostherne Mere, from 2010 to 12, only trap samples collected during the stratified period contained enough material for isotopic analyses of calcite (Table 2, Fig. 2). Identification of tridonal crystals under SEM inspection and yields of CO2 from isotope analysis (see below) demonstrated that the material collected in the traps was calcium carbonate (calcite).

Samples with high carbonate (> 10% CaCO3 by dry weight) and sufficient material were selected for bulk oxygen and carbon isotope analyses of carbonates (δ18O, δ13C), with the average ratio of organic to total carbon (OC:TC) in analysed samples of 0.57 ± 0.2. The samples were immersed in 5% sodium hypochlorite solution (10% chlorox) for 24 h to oxidise the reactive organic material. Samples were then washed three times in distilled water, dried at 40 °C, and ground in an agate mortar and pestle. The isolated material was reacted with anhydrous phosphoric acid in vacuo overnight at 25 °C. The liberated CO2 was separated from water vapour under vacuum and collected for analysis. Measurements were made on a VG Optima mass spectrometer. All δ18O values were converted to the V-SMOW scale using the within-run laboratory standard diatomite, BFCmod. In detail, samples are run as CO2 against the V-PDB standard through in-house reference material calibrated through NBS-19, and converted to V-SMOW using Coplen et al. (1983), then normalised to δ18O BFC (+28.9 ± 0.3‰; n > 1000; Chapligin et al., 2011). For a given number of samples analysed, an additional 20% of standards are run and 10% are replicates. Errors (1SD) for δ18Odiatom were 0.3‰.

Separate assessments of diatom species composition and assemblage dissolution were made on cleaned trap samples under phase-contrast light microscopy (× 1000) which also revealed when different diatom taxa bloomed (Radbourne et al., 2017; Radbourne, 2018). Dissolution was assessed using the proportion of valves showing no visible signs of dissolution compared to the total number counted, reported as the F index (Ryves et al., 2001; Ryves et al., 2013). F values vary between 0 (all valves partially dissolved) and 1 (all valves pristine).

3.2. Temperature data and isotope calculations

The isotope composition of diatoms and calcite from the traps represent discrete time periods over which they were formed. Average temperatures in the upper water column (where diatoms were growing and calcite was precipitating; Raubitschek et al., 1999) over the period represented by the individual trap samples were calculated using the thermistor data, with averages calculated over the upper 0–4 m and 0–6 m water column (Raubitschek et al., 1999). Endogenic calcite crystals precipitated at the same time as the trap sample in which they were deposited (Fig. 2), but as individual diatom valves might have been formed earlier and stayed in suspension several days before sinking into the traps (see Miklasz and Denny, 2010), temperatures were calculated using a one-week offset. Furthermore, whereas silica precipitation in diatoms is thought to occur during photosynthesis, it may also proceed during dark conditions (Werner, 1977; Martin-Jezequel et al., 2000), so we used both average daytime (0600 to 1800) water temperatures as well as 24 h averages. There are thus two temperatures for each calcite isotope value (integrating over two depths: 0–4 m and 0–6 m), and eight for diatoms (integrating temperatures over two depths, two trapping periods, and daylight/24 h). The differences between these values are small, but for shorter sampling periods (i.e. sequencing trap samples) at certain times of rapid lake temperature change, they may be significant.

Theoretical temperature values derived from δ18Ocalcite and δ18Odiatom compositions were calculated using the lake surface (0.5 m) δ18O for that sampling period (no δ18O gradient was observed in the upper 6 m; Fig. 4) and compared to measured temperatures as above. A number of different fractionation factor-temperature relationships are available in the literature for both δ18Ocalcite (e.g. Kim and O’Neil, 1997; Coplen, 2007) and δ18Odiatom (see below). The empirically-derived fractionation factor of Kim and O’Neil (1997) has been applied across a
δ2H
δ18O
GMWL
Lake 0.5 m
Lake 6 m
Lake 12 m
Lake 18 m
Lake 24 m
Inflow
Spring
Outflow

Fig. 3. Correlation of δ18O and δ2H for the Rostherne Mere system. Lake water samples are shown by filled circles for 0.5 m, 6 m, 12 m, 18 m and 24 m water depths. Catchment waters are indicated: Rostherne Brook inflow (green circles), Harper’s Bank Spring groundwater (orange triangles), outflow (red triangles). The GMWL (global meteoric water line), local meteoric water line (LMWL) and local evaporation line (LEL) are plotted. Linear regressions between measured δ18O and δ2H for the different water types, and regression equations for the LMWL and LEL are given. See Fig. 1 for sampling locations within the lake.

Wide range of temperatures, and is the most appropriate model to use here for δ18Ocalcite (see Eq. (1), Section 5.3.2). In contrast, the spectrum of published silica-water fractionation factors (e.g. Fig. 6b) do not represent true fractionation factors but combinations of different end members representing fresh biogenic silica-water and quartz-water equilibria. Several published fractionation factors were applied to the δ18Odiatom data, namely Juillet-Leclerc and Labeyrie (1987), Shemesh et al. (1992), Dodd and Sharp (2010) and Moschen et al. (2005). The best fit for δ18Odiatom under all possible temperature sets, as defined above, was found using Moschen et al. (2005; Eq. (3), Section 5.3.2), with all other models producing estimates with substantial errors (with r² < 0.6 for predicted ~ observed temperature for all other models). We appreciate that this does not represent the true silica-water fractionation factor, but we apply this fractionation factor to explore how diagenetic effects impact the temperature signal in the diatom silica host.

4. Results

4.1. The stable isotope composition of the lake- and catchment waters

The δ2H and δ18O of the catchment waters (surface and groundwater inflow to the lake) lie along a local meteoric water line (LMWL) (this study). This is offset but parallel to the global meteoric water line (GMWL; Fig. 3), which varies regionally with humidity. In contrast, the lake water isotope composition deviates from the LMWL along a local evaporation line (LEL), due to lake water evaporation in the spring and summer months. As expected, surface and shallow lake waters (< 6 m) show the most enrichment in δ2H and δ18O. Evaporative enrichment of the lake water is a function of the relatively long water residence time (~1–2 years), and the strong lake water stratification over the summers which preclude mixing of the evaporated water (high δ2H and δ18O) with deeper (fresher, lower δ2H and δ18O) waters for ~8 months of the year.

4.2. Seasonal patterns of stratification and lake water δ18O

The development of seasonal stratification is typical of warm monomictic lakes, though the lake is stratified longer than most lakes at ~8 months of the year (due to its high relative depth and sheltered position, likely enhanced by high algal productivity in spring absorbing radiation). Stratification at Rostherne usually develops in April, starts to break down in October with complete overturn in late November or early December, with almost all pelagic production occurring while the lake is stratified. In 2011, stratification had established by the end of March following an exceptionally cold winter, when (unusually) the lake completely froze in January and February.

Rostherne Brook δ18O values are generally between ~7 and ~6‰ (probably representing an average shallow water composition of mixed annual rainfall). There are occasional excursions to higher (October 2010, December 2011) or lower values (March 2010) coinciding with significant rainfall events (Fig. 4). The degree to which rainfall amount and δ18O values are transmitted into the inflow depends largely on antecedent moisture conditions in the catchment. Greater evaporative transpiration in summer across the vegetated catchment reduces the amount of discharge generated from summer rainfall, while in autumn or winter, reduced evaporative transpiration and high catchment soil moisture levels from preceding rainfall result in efficient, rapid, and highly variable river runoff. There is no clear systematic rise in river δ18O over the summer months in either year, despite the clear summer evaporative signal in the lake, which again suggests the intrusion of shallow ground water (or the low impact of evaporation rate relative to flow rate in the lotic environment).

In contrast to the inflow stream, patterns of δ18O within the lake water column show clear seasonality, reflecting climatic effects as well as stratification and mixing. At the start of the year (January/February) when the lake is mixed, there is no significant differentiation within the 30 m water column in terms of δ18O values, which all lie within the analytical uncertainty (~0.05‰). Quickly after stratification is established (~April), however, the upper water column (surface and 6 m depth) becomes isotopically enriched in δ18O (i.e. higher δ18O values) from seasonal evaporation, while the lower water column (12 m and deeper) maintains δ18O values similar to the mixed winter period (Fig. 4). δ18O values peak in September 2010 in the surface waters (ca. ~5‰), thereafter declining concomitantly with declining water temperatures as the lower lake water column is mixed with the surface waters. In January 2011, when the lake is completely mixed, δ18O values throughout the water column (0–24 m) have an average of ~5.52‰ (~0.08‰).

This seasonal pattern was repeated in 2011, although the increase in δ18O was less rapid, and the peak occurred later in the year (October or November 2011), followed by a rapid δ18O decrease into winter (Fig. 4). This appears to reflect the pattern of stratification; in 2011, the maximum water temperature was reached later in the summer, and stratification itself was longer and more stable. Mixing of the lake to 12 m in November 2011 did not have a noticeable effect on δ18O, perhaps because of increased Rostherne Brook inflow with higher δ18O or inter-annual isotopic “memory” of the lake. There is a noticeable trend to increasing δ18O over the two study years (winter 2010 values are around ~5.5‰, and ~5.2‰ in winter 2011), which is more striking than variations in the inflow. As groundwater δ18O does not change, this might result from the cumulative effect of lake water evaporative enrichment over consecutive years, since deep lake water samples also show an increase. Alternatively it might reflect a shift in regional precipitation δ18O over this time.

The discharge and hydrochemistry of Rostherne Brook is not clearly reflected in the lake δ18O as the lake water volume acts as a buffer (as seen in Fig. 4), although a full characterisation of inflow δ18O is difficult without high-frequency monitoring, given the highly variable stream discharge. Individual outflow samples are a good measure of surface water conditions in the lake, and thus an efficient means to sample a lake (in terms of δ18O) where access to the open water may be an issue. Indeed, at Rostherne Mere, the very good agreement between littoral ISCO and central lake δ18O values (Fig. 4e) demonstrates that the upper water column is well mixed spatially across the lake, and thus near-
littoral sampling for isotope characterisation of upper lake water (i.e. the mixed epilimnion) would be effective. Furthermore, this method of sample collection, and specifically the use of a paraffin layer to stop post-sampling evaporation, can be successfully used for remote sampling and storage onsite, even after 2 months within the sampler by the lake at ambient summer temperatures. This approach could improve isotopic monitoring of water bodies that are too remote or otherwiselogistically challenging to sample frequently in person.

4.3. Comparison of lake water, δ¹⁸Ocalcite and δ¹⁸Odiatom of annual and seasonal samples

Calcite δ¹⁸O (relative to V-PDB and V-SMOW; Tables 1 and 2) and diatom silica δ¹⁸O (relative to V-SMOW) from sediment traps (collection from 2 weeks, up to ~1 year) are shown in Tables 1–3 and Fig. 5, which also shows trap samples in comparison to surface lake water δ¹⁸O. Table 1 shows the values for samples collected before regular monitoring of the lake began in 2010 (including replicate tube collections in open trap arrays), while Tables 2 and 3 present data collected during the high-resolution monitoring programme from 2010 to 2012.

Calcite δ¹⁸O in trap samples recovered from different tubes from the same deep, open traps collecting for a year from 2006, 2007 and 2008 all differ by <0.5‰ (average difference within three sets of replicate tubes 0.13‰; Table 1), substantially less than the inter-annual variation in average δ¹⁸Ocalcite of about 1‰. These longer-term calcite trap data are consistent (in average and intra-trap range) with the 3-monthly summer values from 2010 and 2011, which are ca. −7.4‰ and −6.7‰ respectively, an inter-annual increase in δ¹⁸O that parallels changes in surface water δ¹⁸O from 2011 to 12. These data suggest that multi-year variation in δ¹⁸Ocalcite in the modern system is ≤1‰ (Fig. 5a).

Seasonal or annual samples conceal greater variation on shorter timescales. Through 2010, δ¹⁸Ocalcite exhibits systematically higher values by ~2‰ from June to November (Fig. 5a). This trend is not seen...
in 2011, with the exception of an unusually low value in the 3-month open trap in May–June 2011 (Fig. 5a). Values of samples recovered from deep and shallow open traps are within the sampling error (Table 1, Fig. 5a), although this difference is larger (~0.5‰) when compared to the two 14-day trap samples covering the same time period in summer 2011 (though a tendency for higher or lower δ18O compared to the two 14-day trap samples covering the same time periods, δ18O diatom shows considerable variation, for example, between sequential two-weekly samples (Fig. 5b). On a seasonal scale, however, there is a clear trend in δ18O values among 2-weekly and 3-monthly trap samples. This is most strongly evident in the deep-trap samples from 2011, where δ18O diatom is higher in the early growth period (May 2011; ca. +30.7‰) before falling to +29.2‰ by September, with the shallow-trap 2-weekly samples following a similar trend, though with greater variability (Fig. 5b).

In contrast to δ18O calcite, there is evidence that there is a depth effect on δ18O diatom, with a consistent isotopic enrichment of 18O in deeper trap samples (Table 3 and Fig. 5b), for both the two-weekly and 2 & 4-month integrated samples (compare October 2005, May 2011 and July 2011). The slope of δ18O diatom isotopic depletion (i.e. lower δ18O diatom values) seen over 2011 is similar between deep and shallow traps but average values differ by ~0.7‰ (deep traps: +30.1‰, shallow +29.4‰; Fig. 5b) but up to +2.2‰ between the deep and shallow open trap in spring 2011 (Fig. 5b). Somewhat surprisingly, the shallow trap 3-monthly integrated δ18O diatom value in spring 2011 does not overlap with any of the four two-weekly δ18O diatom collected over the same period at the same depth (arrowed datapoint in Fig. 5b). Both these observations are discussed below.

4.4. Calculated vs measured temperatures from δ18O data

Fig. 7 and Tables 2 and 3 show the δ18O-inferred temperature against measured lake water temperature for all available δ18O calcite (n = 21) and δ18O diatom (n = 14) from empirically-derived fractionation relationships using the equations of Kim and O’Neil (1997; δ18O calcite) and Moschen et al. (2005; δ18O diatom). As too few values from the shallow trap data at Rostherne (n = 5, Fig. 6b) are available to calculate a reliable surface water fractionation factor, the fractionation factor of Moschen et al. (2005) was chosen, which is from a similar study (using sub-seasonal trap samples) from a eutrophic, temperate lake (Holzmaar, western Germany) that also stratifies strongly. The comparability of these systems (and hence we argue, processes involved) is supported by the good agreement between the Rostherne and Holzmaar δ18O diatom data (Table 3, Fig. 6b), although there is some inevitable bias introduced. Nonetheless, all models applied for both δ18O calcite and δ18O diatom (for all temperature sets) apparently overestimate lake water temperature, on average by < 5 °C for δ18O calcite and by < 1.5 °C for δ18O diatom (for the best fit temperature and time, δ18O calcite average overestimate 6 °C, δ18O diatom average overestimate 1.85 °C; Tables 2 and 3), compared to the annual temperature range of ~16 °C in the lake. The data for δ18O calcite imply non-equilibrium calcite precipitation in all cases, with average values around ~1.5‰ lower than expected (Fig. 6a). This offset is systematic, however, and we argue that our data do show a temperature effect contained within δ18O calcite and δ18O diatom which we explore further below.

5. Discussion

5.1. Differences between δ18O calcite and δ18O diatom in deep and shallow traps

5.1.1. δ18O calcite

Several assumptions are made in interpreting sedimentary lacustrine calcite δ18O values (in traps or sediment cores) as a reliable record of ambient water δ18O at the time of formation. It is often assumed, but rarely demonstrated, that endogenic calcites precipitate in equilibrium with ambient water (Leng and Marshall, 2004), but more recent work (Coplen, 2007; Ðaëron et al., 2019) suggests that isotopic equilibrium may only occur during very slow precipitation, which is often not the case in lake systems, especially under eutrophic conditions (Fronval et al., 1995; Teranes et al., 1999a; Teranes et al., 1999b; Bluszcz et al., 2009; Rozanski et al., 2010). Diagenetic processes (e.g. calcite dissolution) have also been shown to impact isotopic compositions, while sediment resuspension can incorporate calcite deposited from previous time periods (and also possibly diagenetically altered by dissolution;
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Microscopic examination of trap material, sieve fractions analysed and our understanding of sedimentation dynamics (Radbourne, 2018) allows us to discount the presence of significant quantities of biogenic calcite and catchment (detrital) calcite entering traps during stratification, but non-equilibrium precipitation (see Section 5.3.1) and calcite dissolution (discussed below) may have significant impacts.

There is no evidence for any consistent difference in δ18Ocalcite between the shallow and deeper traps, despite being separated by some ~15 m (Fig. 5a). Whereas calcite dissolution occurs in the anoxic waters of some lakes (Oehlendorf and Sturm, 2001), trap flux data do not indicate significant loss of precipitated calcite between the two trap depths during the summer (Radbourne et al., 2017; Radbourne, 2018). Following the onset of stratification in early spring and the sedimentation of large algal blooms, the hypolimnion rapidly becomes anoxic from the lake floor and is deoxygenated within ~1 month (Scott, 2014). The calcite saturation index (CSI) at Rostherne from 2010 to 12 (Fig. 2; Scott, 2014) reveals that both deep and shallow traps sit in waters undersaturated with respect to calcite for much of the year (typically CSI ~ −1 in summer at 10 m depth, and between −1 and −2 at 24 m). Calcite dissolution is expected to lead to an enrichment of 18O (Bluszcz et al., 2009) as 18O is preferentially lost from the calcite matrix during dissolution. Our data suggest that any calcite dissolution occurring at Rostherne Mere during the sampling period did not impact δ18Ocalcite which are within the range of replicate open-tube traps at the same depth (in 2006–7; Table 1). If resuspension of calcite has occurred, the similarity of δ18O values between deep and shallow traps implies this has not had any noticeable effect on trap calcite δ18O (which also supports evidence that calcite is being formed in the same zone, i.e. the epilimnion).

5.1.2. δ18Odiatom

Diatom δ18O in 2011 differs significantly between deep (25 m) and shallow (10 m) traps, by between 0.7 and 2‰, which is beyond analytical error (Fig. 5b). Earlier work from monthly sediment trap studies in Lake Holzmahar, Germany (Moschen et al., 2006), also showed that δ18Odiatom values systematically increase by 2.5‰ between the shallow trap (7 m), deeper trap (16 m), and lake floor (20 m), which was linked to the resuspension of 18O-enriched surface sediment contaminating the traps. More recently, studies of short sediment cores from a shallow freshwater pond in New Mexico revealed that the δ18Odiatom signal changes rapidly after the death of the cell during initial maturation, becoming enriched in 18O (more positive δ18O) within months after sedimentation (Dodd et al., 2012). In contrast to the calcite data, resuspension of such 18O-enriched diatom silica may affect the Rostherne samples, as there is an offset (~1‰) between deep and shallow traps, similar to that found in Lake Holzmahar (Fig. 5b).

At Rostherne, the deeper trap did consistently collect slightly more material (organic, carbonate and mineral matter) than the shallow trap in summer 2011 (Radbourne et al., 2017), implying there was some sediment resuspension and focussing of previously sedimented material from shallower sediments lying above the thermocline, although most resuspension occurs during winter mixing periods. Whereas surface sediments were not analysed directly within this study, other studies have shown that surface sediment δ18Odiatom values are higher relative to fresh diatom silica or seston (Moschen et al., 2006), a result of post-mortem silica dehydroxylation (condensation) processes (Dodd et al., 2012; Dodd et al., 2017; Tyler et al., 2017). Alternatively, initial dissolution of fresh, reactive outer silica layers enriched in 18O may lead to higher δ18O of the residual silica, as has been observed in experimental phytolith dissolution (Prentice and Webb, 2016). However, in this study, samples from most deeper trap samples analysed for δ18Odiatom are no more dissolved than shallow trap assemblages (see Table 3).

Evidence for the alteration of δ18Odiatom values on the timescale of months, as proposed by Dodd et al. (2012) who found significant increase in δ18Odiatom within 6 months of diatom death, is provided by comparing material from the shallow open and sequencing traps for

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Bluszcz et al., 2009). Finally bulk sedimentary calcite may also include biogenically-formed calcite (e.g. produced by green algae such as Chara and Phacotus spp., or ostracod or mollusc shell; van Hardenbroek et al., 2018), or detrital calcite, washed in from geological deposits within the catchment, with very different isotopic signatures (e.g. Stansell et al., 2017). At Rostherne Mere, sufficient calcite for isotopic analyses was only found in traps from periods when the lake was stratified (during the main periods of endogenic calcite precipitation; Fig. 2; Table 2).
This alteration or maturation has been linked to dehydroxylation associated with the selective loss of isotopically-light silanol groups (Si-\(^{16}\)O\(^{-}\)) (Schmidt et al., 2001; Moschen et al., 2006; Dodd et al., 2017), which in turn should lead to the entrainment of exchangeable, silanol-derived \(O\) within the Si-O-Si matrix (Tyler et al., 2017). However, this was not observed by Dodd et al. (2012), who instead suggest that silica decomposition (perhaps by anaerobic bacteria) is key. It may therefore be that anoxic conditions and the presence of anaerobic bacteria (as in the hypolimnion of productive lakes or within surface sediments) after the death of the diatom cell initiates this rapid maturation and enrichment. Differences in ambient \(pH\) between the shallow and deep traps may alter silica dissolution-reprecipitation kinetics, although at Rostherne Mere, the maximum difference between \(pH\) at 10 m and 25 m is 1.2 \(pH\) units (in late summer 2011), and generally \(<1\) \(pH\) unit (typically \(pH\) \(\sim 7.6\) at 10 m and \(pH\) 6.8–7 at 25 m; Scott, 2014). The activity or metabolites of anaerobic bacteria may buffer the system, compared to one where dissolution processes are dominant, or the anaerobic conditions may affect dehydroxylation kinetics of silica through effects on \(-OH\) groups. Recent research has suggested that such maturation processes at temperatures typically found in aquatic sediments alter diatom \(\delta^{18}O\) values over long (~10\(^{5}\)-10\(^{6}\) years) timescales rather than months (Dodd et al., 2017). Further experimental work is needed to explore this issue further, but our current dataset cannot address this issue, which is beyond the scope of the present study.

The apparent lack of an enrichment effect in the deep-trap samples from spring 2010 (Fig. 5b) supports the conjecture that anaerobic conditions play a role in diatom silica oxygen isotope dynamics. These samples were in oxic water before or during early stratification, and were removed from the lake every 2 weeks for processing, which may have prevented this rapid maturation (Dodd et al., 2012). Regardless of the mechanism, as Moschen et al. (2006) argued, simple isotope exchange with ambient waters of the hypolimnion is not the most logical explanation for the enrichment, since deep water \(\delta^{18}O\) values during the stratified period (when diatoms are growing) are always lower than those in the epilimnion (Fig. 4e). Nevertheless, any consideration of secondary isotope exchange should take into account both the rate and total amount of oxygen exchange as well as the silica-water isotope fractionation during that process, both of which are likely to be temperature dependent. It is possible, for example, that at low temperatures (such as at the bottom of oceans and in the hypolimnia of stratified lakes), the rate of secondary alteration is low, meaning that the time required for alteration is much longer than in warmer conditions. In contrast, mineral-water oxygen isotope fractionation is usually inversely correlated to temperature, such that slow alteration at low temperatures might impart a larger effect on the isotope composition of modified silica. More work is needed to quantify these processes using a combination of structural and isotope analyses.

5.2. The role of diatom dissolution and species composition on \(\delta^{18}O_{\text{diatom}}\) values

At Rostherne Mere, there are distinct changes in diatom preservation (i.e. dissolution) within the trap samples, which may impact \(\delta^{18}O_{\text{diatom}}\) values. Diatom assemblages become more dissolved over time through spring and summer 2011 (\(F\) in spring for all traps was \(~0.82\) to 0.90; Table 3), early dissolution as the main mechanism of enrichment (Prentice and Webb, 2016) seems less likely as the sample with the lowest \(\delta^{18}O\) (an open trap sample) is also the most dissolved (\(F = 0.77\)). Sampling logistics may explain this difference, as the early sequencing trap samples (from April 2011) had longer to mature in situ compared to the open trap sample, which was removed from the lake after 3 months in June 2011 and frozen until analysis (with most diatom silica likely in the trap for < 2 months). In contrast, the sequencing trap samples remained in the lake within the carousel until the trap was reset in September 2011, thus the earlier samples had more time to alter (~5 months for the April 2011 sample), in agreement with findings from Dodd et al. (2012). Alterations in \(\delta^{18}O_{\text{diatom}}\) through dissolution may partly explain the resultant error in inferred temperature from samples of this trap type (see Fig. 7, discussed in Section 5.2 below).
in Section 5.1.2, resuspension of older sedimented material (which is likely more dissolved) probably drives this signal.

The effect of silica dissolution on $\delta^{18}O_{\text{diatom}}$ remains controversial, as the few studies that have examined this directly report conflicting results. Experimental diatom dissolution studies have yielded all possible outcomes in $\delta^{18}O_{\text{diatom}}$ values with increasing dissolution: no change (Schmidt et al., 2001), strong enrichment (by up to +7‰; Moschen et al., 2006) and more limited, but still significant, depletion (by up to −1.3‰; Smith et al., 2016). Work on phytoplankton has shown an initial increase in $\delta^{18}O$ during dissolution followed by a reduction (to original or lower values; Prentice and Webb, 2016), but the differences between the materials used (diatoms, phytoplankton), sample age and amount of dissolution in these experiments make direct comparisons problematic. Smith et al. (2016) used geologically aged diatom samples $\sim 10^5$– $10^6$ years in age, and all appreciably dissolved, whereas Moschen et al. (2006) only found significant change (enrichment) on fresh, cultured diatoms (with no change in samples aged from $\sim 5000$ years or 2.4 M year). Schmidt et al. (2001) dissolved fresh marine plankton, cultured diatoms and sediment trap material but found no change in $\delta^{18}O$ after up to 31% of silica loss (intriguingly, a diatom plankton assemblage was depleted in $^{18}O_{\text{diatom}}$, beyond analytical error despite losing only 2.4% of its silica). Substantial silica loss can occur before this is revealed by routine assessment under light microscopy. In dissolution experiments on mixed assemblages of freshly collected lacustrine diatoms, Ryves et al. (2001) found that even visually well-preserved assemblages (F index values $\sim 0.7$) could have lost substantial diatom silica (−30%). During such early dissolution, diatom silica may undergo internal reorganisation of the silica structure through accelerated maturation.

Our dataset cannot be used to determine if dissolution imparts a consistent enrichment or depletion of $^{18}O_{\text{diatom}}$ in samples, as other factors (e.g. variations in surface water $\delta^{18}O$ and temperature of water) also vary. However, within the sequencing trap samples, there is some evidence that dissolution leads to greater absolute error in inferred temperatures from diatom-silica data (Fig. 7). The relationship suggests a linear dependence of the error on assemblage dissolution (i.e., $1 - F$), and essentially disappears when sample preservation is excellent (F = 1; Fig. 7). We suggest this may be related to conditions that are fostered within this type of trap, where seston samples are isolated from the surrounding ambient lake water once the sample is collected, and anoxia and associated bacterial communities can rapidly develop. Given widespread diatom dissolution observed in contemporary marine, freshwater and saline systems and their sedimentary archives (e.g. Shemesh et al., 1989, Biddle and Azam, 1999, Ryves et al., 2003, 2006, Ryves et al., 2013) and the conflicting observations from experimental diatom dissolution work from Moschen et al. (2006), Schmidt et al. (2001) and Smith et al. (2016), and our own preliminary findings (Fig. 7), this is an area that clearly merits more thorough experimental investigation. We recommend this be carried out on a range of fresh material covering key assemblages commonly used for palaeoenvironmental inference in marine and freshwater systems. Given the potential impact of dissolution on $\delta^{18}O_{\text{diatom}}$-derived proxies suggested by our data (Fig. 7), we further recommend routine assessment of diatom dissolution in samples in the context of $\delta^{18}O_{\text{diatom}}$, especially where preservation and species composition change.

There is a complete turnover of planktonic diatom species during a typical seasonal succession at Rostherne Mere (Radbouthe, 2018), though given the relatively consistent silica-water isotope fractionation relationships published (Moschen et al., 2005; Tyler et al., 2008; Chaplin-Jones et al., 2012; Bailey et al., 2014; Fig. 6b), major species effects seem unlikely. There was insufficient material to carry out rigorous testing of the effect of diatom species or size in the present study.

5.3. Prospects and problems of using $\delta^{18}O_{\text{calcite}}$ and $\delta^{18}O_{\text{diatom}}$ for temperature inference

5.3.1. Inter-annual variability and non-equilibrium behaviour of calcite

The results of this study show that patterns within the isotope data for both $\delta^{18}O_{\text{diatom}}$ and $\delta^{18}O_{\text{calcite}}$ vary considerably from year to year, and that different drivers may dominate the signal within a mineral host in different years. The expected strong seasonal (i.e. temperature) effect is only seen in the calcite $\delta^{18}O$ series in 2010 and is not observed in 2011 (Fig. 5a), while the opposite is true for the diatom $\delta^{18}O$ data (although data are sparse in 2010 for diatom $\delta^{18}O$). This inter-annual variability highlights potential problems with developing a paired isotope approach for palaeoclimatic inference, as an annual temperature signal may not be consistently recorded in isotopic sedimentary proxies. Instead, in any given year, $\delta^{18}O$ data may be driven by factors with little or only an indirect relationship to climate, such as stratification pattern or changing nutrient status (e.g. affecting non-equilibrium precipitation dynamics of calcite $\delta^{18}O$ or seasonality of diatom production), where there may also be a mismatch in timing of the generation of the isotopic signal between proxies (i.e. different production periods of endogenic calcite from diatom silica). Our results suggest that sediment samples that integrate several years may give the most reliable isotopic climate signal, as high-resolution (and especially annual records, such as varves) may have any direct temperature signal overprinted by limnological or chemical processes occurring in a given year.

Our results also imply that calcite collected in traps did not precipitate under equilibrium conditions (Fig. 6a). This has been observed in calcites from other eutrophic lakes over seasonal (Sacrow See, Germany; Bluszcz et al., 2009; Baldeggersee, Switzerland; Teranes et al., 1999a) and longer term datasets (Lake Arresa, Denmark; Frövaln et al., 1995), as well as in systems recovering from eutrophication (Lake Gocia, Poland; Rozanski et al., 2010), and is well-known in Chara-precipitated carbonates, for example (Leng and Marshall, 2004). In all these cases, rapid precipitation of calcite related to intense algal photosynthesis resulted in calcite $\delta^{18}O$ values that were isotopically lighter, from kinetic fractionation effects, often associated with calcite supersaturation in the epilimnion and the production of larger calcite crystals (e.g. Baldeggersee, Lake Gocia). In the case of Lake Arresa and Baldeggersee, this was consistently observed from sediment samples spanning several decades as the lakes underwent eutrophication (Frovaln et al., 1995; Teranes et al., 1999b), whereas in contemporary sediment trap studies from Baldeggersee and Sacrow See (Teranes et al., 1999a; Bluszcz et al., 2009), disequilibrium fractionation in calcites from late spring samples (which dominated annual production) was most obvious. Daëron et al. (2019) suggest that the majority of calcites worldwide, including biogenic carbonates, precipitate out of equilibrium, whereas in a modelling study, Watkins et al. (2014) argue that the effect of mineral growth rate on calcite-water oxygen isotope fractionation is subtly dependent on both pH and temperature. Nevertheless, despite the prevalence of non-equilibrium isotope fractionation, the consistent slope of the temperature effect on calcite-water isotope fractionation between calibration studies suggests that it is actually the intercept of that relationship which varies to the greatest extent (Daëron et al., 2019). Our data from Rostherne Mere support this interpretation, since the slope of the regression in Fig. 6a (with or without the three adjusted points; see below) is parallel to that from Kim and O’Neil (1997) and Coplen (2007) derived from synthetic and stalagmite carbonates respectively, albeit with larger intercept offsets. This apparently systematic offset would then imply that $\delta^{18}O_{\text{calcite}}$ retains quantitative potential to infer past temperature and hydrological change.

Beyond the general systematic offset of lower $\delta^{18}O_{\text{calcite}}$ than would be predicted for equilibrium conditions, there also appear to be specific calcite samples that are especially isotopically light (Fig. 6a). A detailed study of seasonal calcite deposition within sediment traps and varves in
Table 2
Measured $\delta^{18}O$ for authigenic calcite trap samples from shallow and deep traps, arranged by collection length and then chronologically, from 2010 to 2011 (relative to both VPDB and VSMOW-SLAP; Coplen, 1995). Measured lake surface $\delta^{18}O$ and inferred temperatures are shown. Inferred temperatures use the equation of Kim and O'Neil (1997) that gave the best fit to a range of measured temperatures, including two depth intervals (upper 0–4 m and 0–6 m of the lake). For three calcite samples, measured $\delta^{18}O$ was adjusted (adj.) for depletion under rapid calcite precipitation (e.g. Teranes et al., 1999a). See Sections 4.4 and 5.3 for further discussion.

| Sample code | Trap depth (m) | Trap type   | Date in       | Date out       | No. days | Sample $\delta^{18}O_{VPDB}$ (vs PDB) | Sample $\delta^{18}O_{VSMOW}$ (vs VSMOW-SLAP) | Lake surface $\delta^{18}O$ | Inf. temp (°C) | Best fit obs. temp (°C) |
|-------------|----------------|-------------|---------------|----------------|----------|--------------------------------------|-----------------------------------------------|---------------------|----------------|---------------------|
| RM67        | 8              | Open        | 18/05/2010    | 26/08/2010     | 100      | −7.42                                | +23.27                                        | −5.17               | 24.5           | 17.55               |
| RM138       | 8              | Open        | 05/07/2011    | 02/11/2011     | 120      | −6.58                                | +24.13                                        | −4.86               | 21.9           | 16.39               |
| RM75        | 10             | Sequencing  | 01/07/2010    | 15/07/2010     | 14       | −7.54                                | +23.15                                        | −5.12               | 25.4           | 19.25               |
| RM76        | 10             | Sequencing  | 15/07/2010    | 29/07/2010     | 14       | −7.36                                | +23.33                                        | −5.06               | 24.7           | 18.56               |
| RM77        | 10             | Sequencing  | 29/07/2010    | 12/08/2010     | 14       | −6.71                                | +24.00                                        | −5.03               | 21.7           | 18.21               |
| RM78        | 10             | Sequencing  | 12/08/2010    | 26/08/2010     | 14       | −7.39                                | +23.30                                        | −4.99               | 25.3           | 17.90               |
| RM79        | 10             | Sequencing  | 28/08/2010    | 11/09/2010     | 14       | −6.72                                | +23.99                                        | −5.06               | 21.6           | 16.83               |
| RM83        | 10             | Sequencing  | 23/10/2010    | 06/11/2010     | 14       | −6.06                                | +25.60                                        | −5.34               | 17.1           | 10.72               |
| RM83 (adj)  | 10             | Sequencing  | 23/10/2010    | 06/11/2010     | 14       | −5.16                                | +24.67                                        | −5.34               | 13.0           | 10.72               |
| RM99        | 10             | Sequencing  | 23/07/2011    | 06/08/2011     | 14       | −6.71                                | +24.00                                        | −4.90               | 22.4           | 18.49               |
| RM100       | 10             | Sequencing  | 06/08/2011    | 20/08/2011     | 14       | −6.34                                | +24.38                                        | −4.87               | 20.7           | 17.91               |
| RM107       | 10             | Sequencing  | 23/07/2011    | 06/08/2011     | 14       | −7.34                                | +23.35                                        | −4.93               | 25.3           | 18.49               |
| RM123       | 10             | Sequencing  | 21/09/2011    | 03/10/2011     | 14       | −6.35                                | +24.37                                        | −4.80               | 21.1           | 15.44               |
| RM166       | 25             | Open        | 18/05/2010    | 26/08/2010     | 100      | −7.31                                | +23.38                                        | −5.17               | 24.0           | 17.55               |
| RM136       | 22             | Open        | 01/04/2011    | 05/07/2011     | 95       | −7.97                                | +23.63                                        | −5.45               | 25.8           | 14.28               |
| RM136 (adj) | 22             | Open        | 01/04/2011    | 05/07/2011     | 95       | −7.07                                | +22.70                                        | −5.45               | 21.4           | 14.28               |
| RM137       | 25             | Open        | 05/07/2011    | 02/11/2011     | 120      | −6.70                                | +24.02                                        | −4.86               | 22.5           | 16.39               |
| RM74        | 22             | Sequencing  | 17/06/2010    | 01/07/2010     | 14       | −7.88                                | +22.80                                        | −5.24               | 26.4           | 18.48               |
| RM104       | 25             | Sequencing  | 06/08/2011    | 20/08/2011     | 14       | −7.90                                | +23.71                                        | −4.96               | 23.5           | 17.91               |
| RM113       | 25             | Sequencing  | 19/10/2011    | 02/11/2011     | 14       | −6.98                                | +24.65                                        | −4.81               | 24.1           | 12.19               |
| RM113 (adj) | 25             | Sequencing  | 19/10/2011    | 02/11/2011     | 14       | −6.08                                | +23.72                                        | −4.81               | 19.8           | 12.19               |
Table 3

| Sample code | Trap depth (m) | Trap type | Date in | Date out | No. days | Sample δ18O | Lake surface δ18O | Inf. temp (°C) | Best fit obs. temp (°C) | F index |
|-------------|---------------|-----------|---------|----------|----------|-------------|-----------------|----------------|-------------------|---------|
| RM-BSi92    | 10            | Sequencing| 16/04/2011 | 30/04/2011 | 14       | +30.5       | −5.43           | 8.6             | 10.97             | 0.82    |
| RM-BSi93    | 10            | Sequencing| 30/04/2011 | 14/05/2011 | 14       | +29.3       | −5.43           | 14.8            | 13.01             | 0.90    |
| RM-BSi97    | 10            | Sequencing| 25/06/2011 | 09/07/2011 | 14       | +29.1       | −5.06           | 17.3            | 16.33             | 0.85    |
| RM-BSi100   | 10            | Sequencing| 06/08/2011 | 20/08/2011 | 14       | +29.2       | −4.87           | 17.9            | 18.07             | 0.96    |
| RM-BSi136   | 22            | Open      | 01/04/2011 | 05/07/2011 | 95       | +30.8       | −5.32           | 12.4            | 12.90             | 0.82    |
| RM-BSi138   | 22            | Open      | 05/07/2011 | 02/11/2011 | 120      | +30.1       | −4.86           | 18.6            | 16.45             | 0.55    |
| RM-BSi54    | 24            | Open      | 03/02/2010 | 03/03/2010 | 28       | +29.4       | −5.46           | 14.0            | 14.25             | 0.85    |
| RM-BSi61    | 22            | Open      | 31/03/2010 | 14/04/2010 | 14       | +29.1       | −5.80           | 13.8            | 6.56              | 0.90    |
| RM-BSi62    | 22            | Open      | 14/04/2010 | 30/04/2010 | 16       | +29.5       | −5.79           | 11.7            | 9.04              | 0.85    |
| RM-BSi64    | 22            | Open      | 30/04/2010 | 17/05/2010 | 17       | +28.6       | −5.68           | 16.7            | 10.70             | 0.88    |
| RM-BSi123   | 25            | Sequencing| 21/09/2011 | 05/10/2011 | 14       | +29.4       | −4.80           | 22.6            | 15.20             | 0.22    |

As expected, given the systematically lower values of δ18Ocalcite, calculated δ18Ocalcite temperature overestimates observed temperature on average by ~5 °C (Fig. 6a), similar to the overestimation (+4.2 °C) from contemporary (sediment trap) δ18Ocalcite found for a freshwater
lake in central Poland (Rozanski et al., 2010), also using the equation of Kim and O’Neil (1997). Rozanski et al. (2010) suggested that kinetic fractionation effects during rapid calcite precipitation produced bulk calcite with systematically lower δ18O values than ambient water δ18O values, leading to this calculated temperature offset. At Rostherne Mere, this may also partly be an artefact of using the average temperature over the upper 4 m whereas calcite precipitation may be occurring in the uppermost 1–2 m in association with the densest phytoplankton blooms (Scott, 2014; Radbourne, 2018), where temperatures are slightly higher (e.g. the difference between average temperatures in the upper 4 m and at 1 m is about 1 °C, and higher in summer, with a maximum of 2.7 °C in 2009).

On the seasonal timescales of this study, there are many potential sources of error in inferring temperature from δ18Odiatom given the unresolved complexities in processes of silica precipitation, maturation and diatom taphonomy (dissolution and resuspension; Fig. 7) that additionally affect the δ18Odiatom signal, as discussed above (e.g. Moschen et al., 2006; Dodd and Sharp, 2010; Dodd et al., 2012; Smith et al., 2016). Nevertheless, the trend to lower δ18Odiatom in both the deep and shallow trap during spring/summer 2011 (though offset from each other; Fig. 5b) is in line with the fractionation expected as ambient upper lake temperatures rise over this period (~0.2‰ per 1 °C rise in temperature; Brandriss et al., 1998; Moschen et al., 2005; Crespin et al., 2010; Dodd and Sharp, 2010). Our shallow trap data are most comparable with the study of Moschen et al. (2005) at Lake Holzmaar, as expected given the similarities of the lakes and trapping approach (Fig. 6b). This study developed a δ18Odiatom-temperature relationship using diatoms from the 7 m shallow trap (as higher values of δ18Odiatom were observed in Holzmaar’s deep trap samples, as in Rostherne Mere), and we refer to these data in the discussion below.

It is likely that at both Rostherne and Holzmaar, diatom silica from the traps has not reached equilibrium with ambient (trap) water, as the silica-water fractionation relationship is not at equilibrium (Fig. 6b). Contrary to conclusions reported by Dodd et al. (2012), more recent research suggests that the maturation process of silica, by dehydroxylation of silanol and the formation of siloxane through condensation, may take decades or centuries rather than months (Dodd et al., 2017), progressively altering δ18Odiatom values. Using Eq. (5) below and considering the combined δ18Odiatom ~ δ18Ocalcite values, it might be possible to explore the extent to which this process has progressed, by estimating the amount of re-equilibrated silica in diatom samples. Given the range of factors involved in the kinetics of both diatom and calcite δ18O, and the few samples available here where both are measured, fuller investigation of this relationship is outside the scope of the present study.

Nonetheless, despite possible effects of rapid early maturation (Dodd et al., 2012; Dodd et al., 2017), the trend within the shallow trap δ18Odiatom data is consistent with changes in lake temperature over a seasonal cycle and shows a strong and significant relationship to surface temperature. The equation of Moschen et al. (2005) fits observed temperature extremely well with almost no offset, suggesting a similar point has been reached on the maturation continuum in both cases (Dodd et al., 2017): Tdiatom (°C) = 0.943(Tlake) - 0.044 (r² = 0.60, p = 0.036, n = 6). The best fit is with average daylight (0600–1800) temperatures in the upper 6 m, offset from the trap dates by 1 week (Table 3), reflecting the dominant process of light-driven biomineralisation of diatom silica within the mixed upper epilimnion, with an offset of about a week before senescent diatoms sediment into the upper trap at 10 m depth. There is clearly a blurring of this temperature signal as the seston moves down the water column, because the relationship is weaker, but still significant, in the deep-trap samples (r² = 0.45, p = 0.034, n = 8), leading to overestimation of epilimnion temperatures, like in other studies using surface-sediment data (Juillet-Leclerc and Labeyrie, 1987; Rietti-Shati et al., 1998). In the light of these results, we advise caution in using diatom silica δ18O data for systems where maturation and dissolution effects have not been considered or are unknown. Where the main purpose of applying δ18Odiatom analysis is for palaeotemperature inference, we recommend (1) that samples covering several years are used to reduce within-year variability; and (2) that other independent proxies of temperature are used to build a consensus (for example to generate an envelope of most likely temperature range).

Combining δ18Ocalcite with known surface lake water δ18O (δ18Olake) opens up the possibility to generate equations to estimate seasonal lake epilimnion temperature from known δ18Ocalcite and δ18Odiatom, if the separate relationships for each host against temperature are known (Rozanski et al., 2010), with similar seasonality in production of diatom silica and calcite. The equation of Kim and O’Neil (1997) is re-expressed by Leng and Marshall (2004):

\[
\text{T}_{\text{lake}} (°C) = 13.8 - 4.58 (\delta^{18}O_{\text{calcite}} - \delta^{18}O_{\text{lake}}) + 0.08 (\delta^{18}O_{\text{calcite}} - \delta^{18}O_{\text{lake}})^2
\]

(1)

To simplify subsequent substitution of the δ18Ocalcite term, we simplified Eq. (1) by ignoring the squared term, which did not reduce its predictive power. The fit to Rostherne data from Fig. 7b, without the squared term in Eq. (1), based on measured vs estimated temperature from Table 2, is Tcalcite = 1.060 Tlake + 4.388 (r² = 0.713, p < 0.0001), where Tlake is the average (summer) temperature of the 0–4 m layer, corresponding to the trap period (which gave the best correlation for calcite; Table 2). For further simplicity in generating a combined diatom-calcite geothermometer, assuming the slope between Tcalcite and Tlake = 1, rearranging this simplified Eq. (1) with respect to Tlake gives:

\[
\text{T}_{\text{lake}} (°C) = 9.41 - 4.58 (\delta^{18}O_{\text{calcite}} - \delta^{18}O_{\text{lake}})
\]

(2)

The relationship of Moschen et al. (2005) provides a means to isolate δ18Ocalcite if δ18Odiatom is known, with the best fit for the daylight 0–6 m layer (see above):

\[
\text{T}_{\text{diatom}} (°C) = 190.7 - 5.05 (\delta^{18}O_{\text{diatom}} - \delta^{18}O_{\text{lake}})
\]

(3)

Lake temperature data show that summer temperatures are 2.91 °C warmer on average in the upper 4 m compared to the daylight upper 6 m due to stratification (r² = 0.971 within the δ18Odiatom dataset), i.e. Tdiatom + 2.91 = Tlake in Eq. (2). Using this correction for Rostherne in Eq. (3) so that both proxies (δ18Ocalcite and δ18Odiatom) refer to the same lake temperature target, summer surface (0–4 m) lake water temperature can be estimated from δ18Odiatom as:

\[
\text{T}_{\text{lake}} (°C) = 187.79 - 5.05 (\delta^{18}O_{\text{diatom}} - \delta^{18}O_{\text{lake}})
\]

(4)

Rearranging for δ18Olake, substituting into Eq. (2) and simplifying gives an estimate for lake temperature (0–4 m) that does not rely on knowing δ18Ocalcite:

\[
\text{T}_{\text{lake}} (°C) = 10. \times (4.921 (\delta^{18}O_{\text{diatom}} - \delta^{18}O_{\text{calcite}}) - 172.27)
\]

(5)

Unfortunately, too few samples with both δ18Odiatom and δ18Ocalcite are available to test the geothermometer of Eq. (5) rigorously from our dataset, but it is clear that Eq. (5) will be very sensitive to errors in the difference of (δ18Odiatom - δ18Ocalcite), as an error of ±0.1‰ in (δ18Odiatom - δ18Ocalcite) will result in a temperature difference of ca. ±5 °C.

More fundamentally, our results suggest that a universally applicable diatom-calcite δ18O relationship for palaeoclimate inference will be very difficult to develop. Whereas there might be potential in exploring such a dual isotope geothermometer, our study shows that great caution must be exercised in any such attempts, particularly given the impact of disequilibrium fractionation on δ18Ocalcite values in lakes where calcite precipitation is rapid, and long-term diagenetic (dehydroxylation) changes that occur within diatom silica, which may override a temperature imprint. Before a diatom-calcite geothermometer can be developed and applied to sedimentary data in a given
lake, it is fundamental to understand contemporary δ¹⁸Odiatom and δ¹⁸Ocalcite dynamics and processes within that system, considering the range of possible factors affecting δ¹⁸O values from seston to sediment. Furthermore, calcite precipitation dynamics may vary as a lake trophic status changes (e.g. progressively isotopically lighter calcite may precipitate in lakes undergoing eutrophication; Fronval et al., 1995; Teranes et al., 1999b), an increasingly common trajectory for fresh-water lakes globally. This implies that, in such cases, monitoring of the contemporary isotopic system may not be an analogue for the lake under less eutrophic conditions in the past. Until these issues are addressed and quantified, although each proxy might individually contain palaeotemperature information, the prospect of developing an accurate and reliable geothermometer from paired δ¹⁸Odiatom and δ¹⁸Ocalcite will remain elusive.

6. Conclusions

High resolution and multiannual monitoring of both endogenic calcite and diatom deposition from sediment traps can be used to explore the environmental controls over oxygen isotope ratios in lacustrine water, biogenic silica and calcite. In a study of Rostherne Mere, both calcite and diatom δ¹⁸O were found to be out of isotopic equilibrium. For calcite, we suggest this is largely due to rapid calcite precipitation in meso-eutrophic systems, although there was no apparent effect of calcite dissolution, despite both shallow and deep traps lying in waters undersaturated with respect to calcite. Variations in δ¹⁸Odiatom are more complex, with evidence that there is a rapid alteration (and an enrichment of about +0.7‰; Fig. 5b) of the diatom silica frustule δ¹⁸O value within weeks after death and sedimentation. We speculate that this post-mortem maturation is linked to the time valves are exposed to anoxic conditions, and to the effects of anaerobic bacteria on the fresh silica matrix. Additionally, dissolution may result in changes to δ¹⁸O values, leading to significant, but potentially predictable, error in temperatures inferred using the diatom δ¹⁸O proxy. The intriguing findings presented here from the well-characterised natural laboratory of Rostherne Mere can form the basis for further work, for example through experimentation on fresh diatom material.

Monitoring for more than an annual cycle also shows that the seasonal cycle and inter-annual variations in lake water δ¹⁸O and temperature may not always be clearly recorded in lacustrine (endogenic) δ¹⁸Ocalcite and δ¹⁸Odiatom. Whereas our study does give some support to their use as palaeoclimatic proxies individually (with the caveats above), major obstacles in our understanding remain before paired diatom-calcite δ¹⁸O can be used directly as a robust geothermometer, even in a well-understood system such as Rostherne Mere. Although a temperature signal may be captured at the point of host formation of both δ¹⁸Odiatom and δ¹⁸Ocalcite, this imprint is subject to alteration and diagenesis almost immediately, in ways which are as yet incompletely understood. This is especially the case for diatom silica, which undergoes both rapid and potentially longer-term alteration affecting the quality of the δ¹⁸Odiatom signal as the fossil diatom assemblage dissolves and ages. Bridging this gap in understanding between processes occurring within the intact host at the timescale of weeks and months, and those occurring over longer timescales (from decades to geological timespans) as the signal is incorporated into the sedimentary archive, is key to developing these proxies further both individually, and potentially together, as palaeoclimatic tools.

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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