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Re-examination of the temperature-dependent relationship between $\delta^{18}O_{diatoms}$ and $\delta^{18}O_{lake\ water}$ and implications for paleoclimate inferences

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Abstract The oxygen isotope composition ($\delta^{18}O$) of diatoms is commonly used for paleoclimate reconstruction. There is, however, no consensus regarding the equilibrium isotopic fractionation factor between diatom silica and the water in which it is precipitated. We re-examined the temperature-dependent relationship between $\delta^{18}O_{diatoms}$ and $\delta^{18}O_{lake\ water}$ from Lake Annecy (France). A temperature coefficient of $-0.16‰/°C$ ($R^2 = 0.51$) was determined, supporting findings from previous calibration studies. However, regression lines obtained from different calibration studies, though displaying similar slopes, were shifted. In this manuscript, we propose that several factors, including selected variables (temperature, $\delta^{18}O_{lake\ water}$), analytical techniques, the impact of diagenetic processes and biological effects, may influence the silica-water fractionation factor for diatom silica. The similar magnitude of the diatom-temperature coefficients determined across studies is promising, supporting its use as a valuable tool for interpreting variations in $\delta^{18}O$ values from fossil lacustrine diatoms in temperate lakes. With respect to paleoclimatic applications, the temperature-dependent relationship yielded uncertainties of $\pm3°C$ on reconstructed temperatures and $\pm0.5‰$ on $\delta^{18}O_{lake\ water}$.

Keywords Diatoms · Oxygen isotopes · Fractionation factor · Lake

Introduction

The oxygen isotope composition ($\delta^{18}O$) of biological remains is now widely used to reconstruct past lacustrine temperatures and hydrologic conditions (Leng and Marshall 2004; Gasse 2005). The $\delta^{18}O$ of carbonate and biogenic silica depends primarily upon the ambient water temperature and the isotopic composition of the water in which carbonate and biogenic silica precipitated in isotopic equilibrium. If one of the variables, i.e. water temperature, can be estimated by independent methods, the 'unknown' isotopic composition of the water can then be calculated using the isotopic fractionation factor between the water and the mineral of interest. Measurements of carbonates are commonly utilized to determine $\delta^{18}O$ values (Ito 2001; von Grafenstein 2002). For biogenic silica, $\delta^{18}O$ records are generally based upon the oxygen isotopic composition of diatoms ($\delta^{18}O_{diatoms}$) (Leng and Barker 2006). Diatoms secrete opal

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(SiO_2, nH_2O) (Round et al. 1990) and are assumed to precipitate in isotopic equilibrium with lake water (Juillet-Leclerc and Labeyrie 1987; Brandriss et al. 1998; Moschen et al. 2005). Because diatoms are photosynthetic algae, they record the seasonal variability of the water temperature and the $\delta^{18}O_{water}$. During the last decade, $\delta^{18}O_{diatoms}$ records have increased in number and have been used either to assess past temperature changes (Shemesh and Peteet 1998; Rietti-Shati et al. 1998; Rosqvist et al. 1999) or to determine trends in lake moisture balance or moisture source region (Rietti-Shati et al. 2000; Barker et al. 2001, 2007; Leng et al. 2001, 2005; Rioual et al. 2001; Shemesh et al. 2001; Lamb et al. 2005; Haug et al. 2005; Morley et al. 2005; Polissar et al. 2006; Hernandez et al. 2008). However, if only measured values of $\delta^{18}O_{diatoms}$ are used, caution must be exercised when quantifying past lake temperatures and $\delta^{18}O_{lake\ water}$ because there is no consensus regarding the isotopic fractionation factor between diatom silica and the water in which it precipitated.

Few calibrations between the temperature-dependent relationship for $\delta^{18}O_{diatoms}$ and $\delta^{18}O_{water}$ are available, and those were performed using different $\delta^{18}O$ analytical procedures. In addition, several approaches were employed to overcome the possible contribution of exchangeable oxygen on measured $\delta^{18}O_{diatoms}$. Biogenic silica contains hydroxyl and unstable silanol groups that are likely to exchange with oxygen atoms from the atmosphere or from the solutions with which they are in contact after formation (Labeyrie and Juillet 1982). The first calibration study (Juillet-Leclerc and Labeyrie 1987) performed on marine diatoms in surficial sediments ($n = 18$) used controlled isotopic exchange (CIE) to fix the $\delta^{18}O$ value of exchangeable oxygen, followed by a conventional oxygen extraction technique (Clayton and Mayeda 1963). The technique yielded a fractionation coefficient of −0.29‰/°C. Using a part of this calibration data set, data for low temperatures from 1.5 to 8°C, Shemesh et al. (1992) calculated a higher fractionation coefficient of −0.49‰/°C ($n = 6$). Schmidt et al. (1997, 2001) used living, cultured, and sedimentary marine diatoms ($n = 55$) and three different methods, vacuum heating and CIE followed by the conventional oxygen extraction technique and a stepwise fluorination. No temperature-dependent relationship between $\delta^{18}O_{diatoms}$ and $\delta^{18}O_{water}$ was determined.

Later, two studies with freshwater diatoms, one using cultured algae ($n = 10$; Brandriss et al. 1998) and the other using diatoms in the lake water column ($n = 15$; Moschen et al. 2005), showed similar fractionation coefficients of −0.19 and −0.20‰/°C, respectively. Although Moschen et al. (2005) used the iHTR technique (inductive High Temperature carbon Reduction) recently calibrated by Lücke et al. (2005), Brandriss et al. (1998) used, prior to the conventional oxygen extraction, a simple dehydration technique from which a possible contribution of exchangeable oxygen to $\delta^{18}O_{diatoms}$ values was suspected.

Here, we re-examine the temperature-dependent relationship between $\delta^{18}O_{diatoms}$ and $\delta^{18}O_{water}$ using a new calibration with water, living diatoms, and in situ temperatures from Lake Annecy (France). CIE, followed by the new IR laser-fluorination technique, allowed analysis of small samples (0.3–1.6 mg) (Crespin et al. 2008). Lake Annecy was selected because it is an open, temperate lake characterized by a relatively short water residence time (~ 3.8 years) and because the lake's water displays a low $\delta^{18}O$ enrichment of 1.2‰ compared with precipitation (Danis 2003). Long-term climatic, physical, chemical, isotopic, and biological data were also available for Lake Annecy.

Study site

Lake Annecy (45°54′N, 6°08′E, 447 m a.s.l.) is located in the French Alps (Fig. 1), and is a peri-alpine lake of glacial origin, a remnant of the last glaciation (Benedetti-Crouzet 1972) with a catchment area of 280 km². Lake Annecy is one of the largest lakes in France, 14.6 km long and between 0.8 and 3.1 km wide, with a surface area of 26.5 km², a volume of 1.12 km³, a maximum depth of 65 m, and a mean depth of 41.5 m. It is divided into two basins, north and south, and mainly fed by rivers (Eau-Morte, Ire, Laudon, and Bornett), a sub-lacustrine source, and precipitation. The Laudon River is the only inflow for the northern basin and represents 12% of the total inflow to the lake. The Thiou river is the only outlet from the lake (Fig. 1). Data and simulations have provided evaporation rates ranging from 540 to 665 mm year⁻¹ for Lake Annecy (Danis et al. 2003). The average evaporation rate is 600 mm year⁻¹, and the average evaporated volume is 16×10^6 m³ year⁻¹. River inputs represent a volume
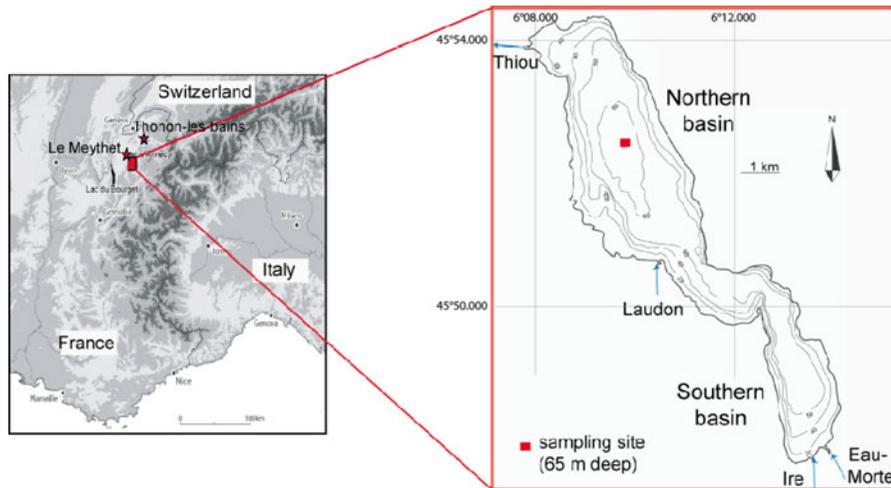
Fig. 1 Location and bathymetric map of Lake Annecy (*red square*) and weather stations (*red stars*): Lake Annecy (45°54′N, 6°08′E, 447 m a.s.l.), Le Meythet (45°54′N, 6°05′E, 458 m a.s.l.), Thonon-les-Bains (46.3°N, 6.4°E, 385 m a.s.l.)

of 220×10^6 m^3 year^{-1}. The ratio of these two volumes is 0.07, which reflects relatively low evaporation from the lake surface. As mentioned, the lake has a short water residence time (~ 3.8 years) (Danis 2003).

The climate is semi-continental. Data for 2000–2008 from the Météo France Le Meythet station, 45°54′N, 6°05′E, 458 m a.s.l., show a mean annual precipitation of 1,200 mm year^{-1} and mean monthly atmospheric temperatures varying from 2.0 to 7.8°C in winter and from 15.7 to 20.2°C in summer.

The lake is oligotrophic, and due to effective environmental management, was prevented from becoming eutrophic in the 1970s. Most of the time the lake is warm monomictic, with the winter surface water temperature rarely <4°C (Balvay 1978). The lake is completely mixed during winter. Lake Annecy is stratified from April/May to November/December, with a thermocline located between 10 and 16 m water depth. Water and atmospheric temperatures reflect epilimnic temperatures (Fig. 2).

Epilimnic (3 m depth) and hypolimnic (30 and 65 m depth) $\delta^{18}O_{\text{lake water}}$ mean monthly values have similar variations, ranging between -9.29 ± 0.16 and -8.56 ± 0.05‰ vs. V-SMOW for the December 2000/June 2002 period. Surface waters (epilimnion), where diatoms grow (Round et al. 1990), display little $\delta^{18}O$ variation at monthly to pluri-annual scales. From January 2000 to December 2002 the mean annual $\delta^{18}O_{\text{precipitation}}$ value was 8.93 ± 2.14‰ vs.
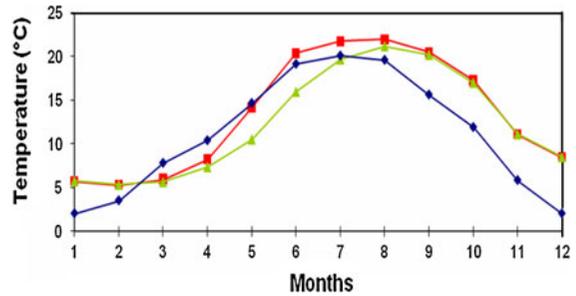

Fig. 2 Mean monthly atmospheric temperatures (°C, *blue curve*; Météo France data between 2000 and 2008, Le Meythet station), and mean monthly lake water temperatures at 3 m (°C; *red curve*) and 10 m depth (°C; *green curve*) (SILA monthly measurements between 2000 and 2005)

V-SMOW (Thonon-les-Bains station; 46.3°N, 6.4°E, 385 m a.s.l.; GNIP network, IAEA). Due to low evaporation (Danis 2003) $\delta^{18}O_{\text{lake water}}$ values (between -9.13 ± 0.18 and -8.91 ± 0.22‰) are within the range of $\delta^{18}O_{\text{precipitation}}$ mean annual values for the December 2000 to June 2002 period.

Materials and methods

Sampling

Living freshwater diatoms and water samples ($n = 11$) were collected seasonally between October 2006 and August 2008 in the northern basin where

Table 1 Samples, sampling date, epilimnion depth (m), sampling depth (m), associated water temperature (°C) and $\delta^{18}O_{lake\ water}$ values

Samples	Sampling date	Epilimnion (m)	Sampling depth (m)	Associated lake water temperature (°C)	$\delta^{18}O_{lake\ water}$ (‰ vs. VSMOW)
A1	Oct 2006	0–14	Over 30 m	16.00	−8.51
A2	Oct 2006	0–14	10	17.30	−8.31
A3	Oct 2006	0–14	10	17.30	−8.32
B1	Feb 2007	Non-stratified	10	6.10	−8.62
C1	April 2007	0–5	12	15.20	−8.71
C2	April 2007	0–5	3	15.75	−8.77
F1	Nov 2007	0–16	10	10.45	−8.38
F2	Nov 2007	0–16	3	10.50	−8.41
H2	June 2008	0–10	3	16.30	−8.83
I1	July 2008	0–10	25	13.00	−8.66
J2	Aug 2008	0–10	3	21.24	−8.22

the lake is deepest (65 m) (Table 1). Samples were collected in the epilimnion ($n = 8$; A2, A3, B1, C2, F1, F2, H2, J2) between 3 and 12 m depth and in the hypolimnion ($n = 2$; C1, I1). Only sample A1 was collected with a plankton net from 0 to 30 m depth, thus mixing the epi- and hypolimnion.

Water and plankton were pumped through a hose to obtain samples at selected depths. For each sample, the temperature was measured in situ with a multi-parameter probe (Sea and Sun Technology). Plankton samples were filtered through a 5-µm net prior to storage in plastic bottles with a few drops of nitric acid to eliminate zooplankton.

Chemical treatment of diatom samples

Freshwater diatoms were cleaned with a mixture of 20 ml of $HClO_4$ (70%) and 20 ml of HNO_3 (65%) in a water bath at 50°C for 20 min. The treatment was repeated at least five times. Samples were successively rinsed with distilled water by decantation and centrifugation (Crespin et al. 2008). For purity control, samples were mounted on glass slides with Naphrax and examined under 1,000× magnification with oil immersion using a Nachet NS400 light microscope. Taxonomic identification of diatom assemblages was determined following the species concept used by Round et al. (1990). In each sample, a minimum of 200 valves was identified.

Measurements of oxygen isotopic composition

Prior to oxygen analysis, a CIE for opal-A described by Juillet-Leclerc and Labeyrie (1987) was utilized to fix the exchangeable oxygen isotopic composition. The CIE was processed twice using two water samples of known $\delta^{18}O$ values on a 29-sample holder that included ten standards. Samples were kept under vacuum or in a desiccator until they were loaded into the sample chamber of the IR-laser fluorination line. The CIE exchange procedure is particularly suitable for small samples (0.3–1.6 mg) (Crespin et al. 2008).

$\delta^{18}O_{diatoms}$ values were obtained using the IR laser fluorination technique (Crespin et al. 2008). Molecular O_2 was extracted in a laser extraction line with a 30 W CO_2 IR laser. The oxygen isotopic composition of the diatoms was measured with a dual inlet mass spectrometer (ThermoQuest Finnigan Delta Plus). For samples smaller than 1.6 mg the extracted oxygen was concentrated into an auto-cooled 800-µl micro-volume directly connected to the dual-inlet system.

Results are expressed in standard δ-notation, relative to Vienna Standard Mean Ocean Water (V-SMOW) where R represents $^{18}O/^{16}O$ and:

$$\delta = \left[\left(R_{sample}/R_{standard} \right) - 1 \right] \times 1000(‰) \tag{1}$$

Measured $\delta^{18}O$ values of the samples were corrected on a daily basis using a quartz lab standard ($\delta^{18}O_{"Boulangé\ 50-100µm"} = 16.36 \pm 0.09‰$; Alexandre et al. 2006). Additionally, three aliquots of biogenic

silica lab standard MSG 40 were run per measurement session to verify the effectiveness of the CIE procedure. Replicate analysis of the international standard NBS 28 during the calibration period gave an average value of 9.62 ± 0.23‰ ($n = 23$).

The oxygen isotopic composition of the non-exchangeable oxygen ($\delta^{18}O_{diatoms}$) and the percentage of exchangeable oxygen (X) in each diatom sample were calculated using Eq. 2:

$$\delta^{18}O_{diatoms} = \left[100\delta^{18}O_{measured\ 1\ or\ 2} \right. \\ \left. - X\left(\delta^{18}O_{exchanged\ 1\ or\ 2}\right) \right] \Big/ \left(100 - X\right) \tag{2}$$

where $\delta^{18}O$ values ($\delta^{18}O_{measured\ 1\ or\ 2}$) were measured and $\delta^{18}O_{exchanged\ 1\ or\ 2}$ values were calculated according to Juillet-Leclerc and Labeyrie (1987). The uncertainty associated with the calculation of $\delta^{18}O_{diatoms}$ was ±0.5‰, as estimated using a Monte–Carlo simulation. The complete procedure was described in Crespin et al. (2008).

Measurements of $\delta^{18}O_{lake\ water}$ were obtained using an Equilibration Device/DeltaPlus mass-spectrometer (Thermo-Finnigan), with a precision of ±0.05‰. All measurements were conducted at the CEREGE Stable Isotopes Laboratory.

Results

Temperatures and $\delta^{18}O_{lake\ water}$

For the time period studied, Lake Annecy was stratified between April/May and November/December, resulting in a thermocline located between 10 and 16 m depth. Lake water temperatures obtained for samples A2, A3, B1, C2, F1, F2, H2, J2 were epilimnic temperatures measured in situ. For hypolimnic samples, the associated lake water temperature is the one measured at the base of the epilimnion (samples A1, C1, and I1). Measured epilimnic temperatures ranged from 6.1 to 21.24°C and $\delta^{18}O_{lake\ water}$ values for the same period varied between -8.83 and -8.22‰ vs. V-SMOW (Table 1).

Diatom assemblages

Living diatoms in the sampled water column were mainly composed of oligotrophic planktonic species

(Table 2). The dominant species were *Fragilaria crotonensis*, which represented more than 50% of the total flora in samples A1, A2, A3, B1, C1, C2, F1, and F2, associated with *Cyclotella cyclopuncta* and *C. bodanica*. Samples B1 and I1 were characterized by *Asterionella formosa* (>30%). In sample J2, the diatom flora was more diversified, with the dominant planktonic *C. cyclopuncta* associated with benthic species such as *Achnanthidium minutissimum* and *Encyonopsis microcephala*. In all samples, Chrysophyceae represented <1% of the counts. Diatom size varied between 4 and 90 μm. *Fragilaria crotonensis* was the longest species with sizes ranging between 55 and 98 μm. However, its average size rarely reached 80 μm.

$\delta^{18}O_{diatoms}$ values

For all samples, $\delta^{18}O_{measured\ 1}$, $\delta^{18}O_{measured\ 2}$, the percentage of exchangeable oxygen (X), and $\delta^{18}O_{diatoms}$ values are presented in Table 3. Each sample was analyzed at least twice. The reproducibility of the $\delta^{18}O_{measured}$ values ranged from ±0.01 to 0.55‰. Samples with reproducibility lower than ±0.55‰ (1σ) were removed. Calculated $\delta^{18}O_{diatoms}$ values varied from 26.60 to 29.53‰ and had a long-term calibrated precision of ±0.5‰ (Crespin et al. 2008).

Relationship between $[\delta^{18}O_{diatoms} - \delta^{18}O_{lake\ water}]$ and temperature

$[\delta^{18}O_{diatoms} - \delta^{18}O_{lake\ water}]$ values for each sample are presented in Table 3. Assuming that diatom frustules form in isotopic equilibrium with lake water, the relationship between $\delta^{18}O_{diatoms}$ and $\delta^{18}O_{lake\ water}$ can be expressed for a given range of temperature in the form of the following temperature-dependent relationship:

$$\left[\delta^{18}O_{diatoms} - \delta^{18}O_{lake\ water} \right](‰\ \text{vs. VSMOW}) \\ = a\,t(°C) + b \tag{3}$$

where a is the fractionation coefficient, t is the lake water temperature, and b is a constant.

From the $\delta^{18}O$ data set and for the measured temperature range of 6.1–21.24°C, the equation becomes (Fig. 3):

Table 2 Absolute (*n* counted valves/sample) and relative abundances (%) of diatom species in water column samples from Lake Annecy collected between October 2006 and August 2008

Species	Samples																					
	A1	%A1	A2	%A2	A3	%A3	B1	%B1	C1	%C1	C2	%C2	F1	%F1	F2	%F2	H2	%H2	I1	%I1	J2	%J2
Achnanthidium minutissimum																					15	4.85
Amphora pediculus															1	0.36					14	4.53
Asterionella formosa	2	0.8					103	35.9	27	7.0	22	6.0			4	1.5			160	38.3	12	3.9
Brachysira neoexilis																						
Cocconeis placentula euglypta					1	0.4																
Cymbella silesiaca																					6	1.9
Cyclotella bodanica	3	1.3	10	3.9	1	0.4	30	10.5	14	3.6	16	4.4	1	0.3			12	3.8	48	11.5		
Cyclotella cyclopuncta	96	40.3	35	13.7	63	23.4	4	1.4					2	0.6	5	1.8	289	92.6	42	10.0	180	58.3
Cyclotella ocellata													3	1.0	4	1.5	1	0.3			25	8.1
Cyclotella stelligera															1	0.4						
Encyonopsis microcephala					2	0.7															21	6.8
Eunotia sp.																					6	1.9
Fragilaria crotonensis	135	56.7	210	82.4	197	73.2	144	50.2	340	88.3	324	89.0	292	94.2	251	91.6			163	39.0	22	7.1
Gomphonema angustum																					19	6.1
Mastogloia smithii																					2	0.6
Navicula gregaria																					2	0.6
Navicula lanceolata													1	0.3								
Pseudostaurosira brevistriata													2	0.6								
Staurosira construens					4	1.5																
Staurosirella pinnata	2	0.8			1	0.4			4	1.0	2	0.5			2	0.7						
Stephanodiscus medius							4.0	1.4					9	2.9	6	2.2	10	3.2	5	1.2		
Synedra ulna							2.0	0.7											2	0.5	6	1.9
Σ	238	0	255	0	269	0	281	0	385	0	364	0	310	0	274	0	312	0	418	0	309	0

Table 3 Samples, sampling date, $\delta^{18}O_{measured\,1}$ and $\delta^{18}O_{measured\,2}$ values, percentage of exchangeable oxygen (X), calculated $\delta^{18}O_{diatoms}$ values, $\delta^{18}O_{lake\,water}$ values, and $(\delta^{18}O_{diatoms} - \delta^{18}O_{lake\,water})$ values (‰ vs. V-SMOW)

Samples	Sampling date	$\delta^{18}O_{measured\,1}$ (‰) Mean	SD	n	$\delta^{18}O_{measured\,2}$ (‰) Mean	SD	n	X (%)	$\delta^{18}O_{diatoms}$ (‰ vs. VSMOW)	Analytical uncertainty	$\delta^{18}O_{lake\,water}$ (‰ vs. VSMOW)	Analytical uncertainty	$[\delta^{18}O_{diatoms} - \delta^{18}O_{lake\,water}]$ (‰ vs. VSMOW)
A1	Oct 2006	23.56	0.26	2	31.24		1	15.98	28.86	1.60	−8.51	0.50	37.37
A2	Oct 2006	24.16	0.01	2	31.29	0.44	2	14.09	29.11	1.60	−8.31	0.50	37.42
A3	Oct 2006	23.82	0.20	2	31.07	0.01	2	15.08	28.81	1.60	−8.32	0.50	37.13
B1	Feb 2007	25.75	0.05	2	30.38	0.01	2	9.63	28.95	1.60	−8.62	0.50	37.57
C1	April 2007	24.80	0.07	2	29.61	0.07	2	10.01	28.03	1.60	−8.71	0.50	36.74
C2	April 2007	23.43	0.15	2	29.23	0.21	2	12.08	27.24	1.60	−8.77	0.50	36.01
F1	Nov 2007	25.89	0.10	2	31.06	0.35	3	11.51	29.53	1.60	−8.38	0.50	37.90
F2	Nov 2007	25.96	0.01	2	30.90	0.06	2	11.21	29.43	1.60	−8.41	0.50	37.85
H2	June 2008	23.91	0.08	2	29.10	0.32	4	10.79	27.32	1.60	−8.83	0.50	36.15
I1	July 2008	24.17	0.06	2	30.70	0.03	2	13.58	28.64	1.60	−8.66	0.50	37.30
J2	Aug 2008	23.63		1	28.25	0.06	2	9.61	26.60	1.60	−8.22	0.50	34.82

Analytical uncertainties were obtained from a long term calibration previously published (Crespin et al. 2008). $\delta^{18}O_{measured\,1}$ and $\delta^{18}O_{measured\,2}$ values calculated with $\delta^{18}O_{H_2Oliquid\,1} = -8.14 \pm 0.05$‰ and $\delta^{18}O_{H_2Oliquid\,2} = 40.37 \pm 0.05$‰
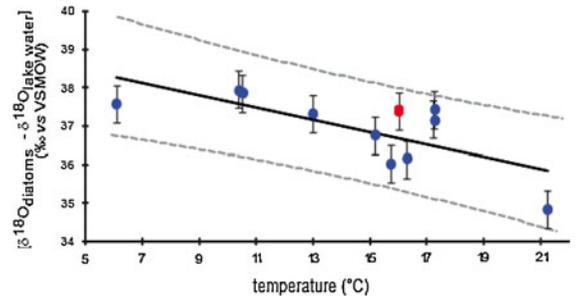

Fig. 3 Relationship between $(\delta^{18}O_{diatoms} - \delta^{18}O_{lake\,water})$ and water temperature. The *black line* is the regression line ($R^2 = 0.51$, p value = 0.014). *Dotted curves* express a 90% confidence interval. *Error bars* represent the analytical uncertainty (± 0.5‰) obtained from Crespin et al. (2008)

$$[\delta^{18}O_{diatoms} - \delta^{18}O_{lake\,water}]\,(\text{‰ vs.V-SMOW})$$
$$= -0.16\,(\pm 0.09)t(^{\circ}C) + 39.25\,(\pm 1.4)\,(R^2 = 0.51) \tag{4}$$

or

$$t(^{\circ}C) = 245.3 - 6.25[\delta^{18}O_{diatoms} - \delta^{18}O_{lake\,water}]$$
$$(\text{‰ vs. V-SMOW}) \tag{5}$$

The slope of the regression line (i.e. the temperature-coefficient) was -0.16 ± 0.09‰/°C ($R^2 = 0.51$). When sample A1 (red dot on Fig. 3), which represents integrated sampling depths (0–30 m), was removed, the temperature-coefficient was similar (-0.17 (± 0.10) ‰/°C; $R^2 = 0.56$).

Discussion

Present and previous calibrations are plotted in a $[\delta^{18}O_{diatoms} - \delta^{18}O_{lake\,water}]$ vs. temperature diagram (Fig. 4). The respective regression lines are parallel, i.e. have the same slope, but are clearly shifted. In other words, as seen in Eq. 3, although the fractionation coefficient a is similar, the constant b differs. For a given temperature of 10°C, shifts from the regression line obtained from freshwater diatoms in line a of the present study, to line b by Moschen et al. (2005), and line c by Brandriss et al. (1998) were, respectively, +2.4 and +3.2‰. The shift between line a, our calibration, and line d, the calibration obtained from marine sedimentary diatoms (Juillet-Leclerc and Labeyrie 1987), is −4.5‰. These shifts exceed the 90% confidence intervals calculated for

Fig. 4 The temperature-dependent relationships plotted in a [$\delta^{18}O_{diatoms} - \delta^{18}O_{lake\ water}$] vs. $t(°C)$ diagram: *a* this study, *b* Moschen et al. (2005), *c* Brandriss et al. (1998), *d* Juillet-Leclerc and Labeyrie (1987), and *e* Shemesh et al. (1992); *dotted lines* represent a 90% confidence interval for the *b* value calculated using XLstats. Fractionation coefficients are displayed
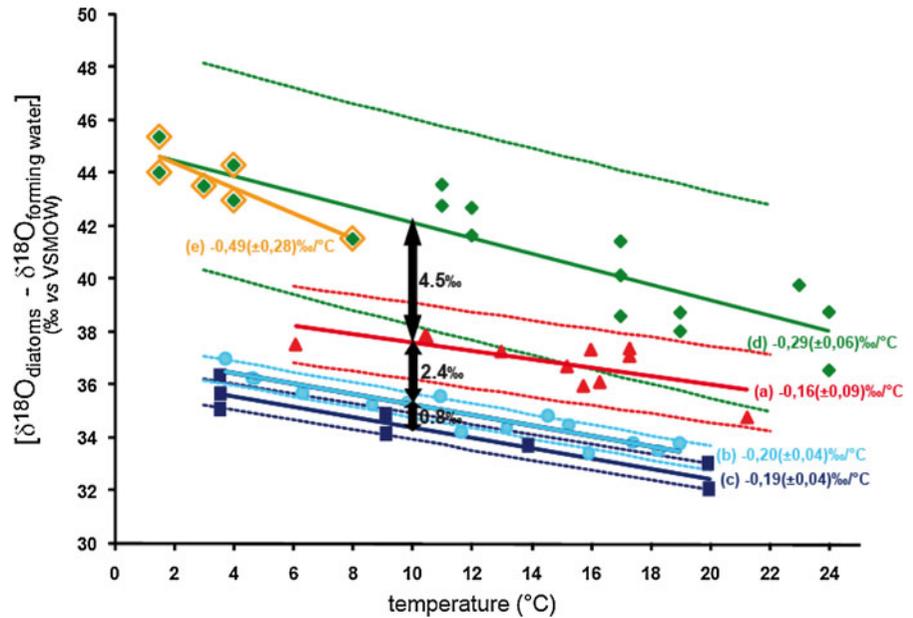
the constant *b* of each equation (dotted lines on Fig. 4): ±1.4‰ (line a), ±0.6‰ (line b), ±0.5‰ (line c), and ±0.9‰ (line d). We propose several factors that may account for the observed shifts:

1. Temperature and $\delta^{18}O_{water}$ values may have been under- or over-estimated. In fact, the calibration based on marine sedimentary diatoms (Juillet-Leclerc and Labeyrie 1987) used average values of measured temperature while $\delta^{18}O_{water}$ values were only measured for a few sites and were extrapolated for others, using the Craig and Gordon relationship (1965) (Juillet-Leclerc and Labeyrie 1987). In contrast, relationships deduced either from freshwater cultured (line c) or lacustrine diatoms (lines a and b) were obtained under controlled or in situ measured temperatures and $\delta^{18}O_{water}$.

2. Some techniques used to overcome the contribution of exchangeable oxygen to the measured $\delta^{18}O$ composition of diatoms may have been incomplete (Brandriss et al. 1998). The percentage of exchangeable oxygen in biogenic silica can vary from 4 to 7.7% (Crespin et al. 2008) to as much as 20% (Labeyrie 1979). The potential contribution to $\delta^{18}O_{diatoms}$ values can be estimated as follows: for a given $\delta^{18}O_{diatoms}$ value of 30‰, 5% of exchangeable oxygen with a $\delta^{18}O$ value of 0‰ would underestimate the $\delta^{18}O_{diatoms}$ value by 1.5‰; with 10% of exchangeable

oxygen with a $\delta^{18}O$ of 10‰, the underestimation of the $\delta^{18}O_{diatoms}$ value would be 2‰. Such contributions would need to be systematic to explain the line shifts.

3. During early diagenesis, sedimentary diatoms might undergo partial dissolution of light silanol groups (Brandriss et al. 1998) and/or a structural change resulting in the formation of siloxane groups from silanol groups (Schmidt et al. 2001), leading to possible ^{18}O enrichment. Sedimentary diatoms have shown an ^{18}O enrichment of 3–10‰ relative to the $\delta^{18}O$ values of live diatoms in the water column of marine environments (Schmidt et al. 2001), and of 2.5‰ relative to $\delta^{18}O$ values obtained from diatoms in the water column of lakes (Moschen et al. 2006), which could partly explain the shift between the sedimentary marine diatom relationship (line d) and the freshwater diatom relationship (lines a, b, and c). Additionally, the absence of a temperature-dependent relationship demonstrated by Schmidt et al. (1997, 2001) was attributed to early diagenetic effects during silica maturation. Such biases, however, would have to be systematic to yield similar temperature coefficients. To elucidate this effect, an analysis of living diatoms sampled at different depths in the water column, as well as an analysis of fossil diatoms from a short core, are currently underway.

4. An effect of diatom size on $\delta^{18}O_{diatoms}$ was proposed by Swann et al. (2007). Moschen et al. (2005), however, demonstrated that for three different diatom size fractions, diatom-temperature coefficients ranged only from −0.195 to −0.216‰/°C, and suggested that such a size/species effect was likely negligible or within the range of $\delta^{18}O$ measurement reproducibility.

Although the factors mentioned above might partially explain the shifts seen between the lines representing the temperature-dependent relationships obtained from diatoms of different environments, further investigations are necessary to clearly constrain the related biases.

Figure 4 also shows similar fractionation in line slopes (or fractionation coefficients), in freshwater diatoms from Lake Annecy (line a) and Lake Holtzmaar (line b) (Moschen et al. 2005: −0.20(±0.04)‰/°C), and from freshwater cultured diatoms (line c) (Brandriss et al. 1998: −0.19(±0.04)‰/°C). The coefficient obtained for marine sedimentary diatoms is slightly higher, but close (line d), (Juillet-Leclerc and Labeyrie 1987: −0.29(±0.06)‰/°C).

Given the range in $\delta^{18}O_{diatoms}$ values of 26.60–29.53‰, and the diatom-temperature coefficient of −0.16‰/°C, the analytical uncertainty of ±0.5‰ on $\delta^{18}O_{diatoms}$ measurements would result in a reconstructed temperature uncertainty $< \pm3°C$. For a fixed temperature, the uncertainty on $\delta^{18}O_{lake\ water}$ would be ±0.5‰. Studies of a 200-year sedimentary record from Lake Annecy showed that $\delta^{18}O_{lake\ water}$ values obtained from $\delta^{18}O_{benthic\ ostracods}$ fluctuated between −8.6 and −9.9‰ (Leroux 2005; von Grafenstein et al. 2006), whereas epilimnic temperatures ranged from 5.5 to 22°C (Danis 2003). Under similar conditions, a $\delta^{18}O_{diatoms}$ record from Lake Annecy would enable one to reconstruct temperature variations rather than $\delta^{18}O_{lake\ water}$ fluctuations.

Conclusion

Our calibration between $\delta^{18}O_{diatoms}$, $\delta^{18}O_{lake\ water}$, and lake water temperature provided a diatom-temperature coefficient of −0.16‰/°C ($R^2 = 0.51$), similar to previously determined values. The diatom-temperature coefficient is in good agreement with those obtained from freshwater cultured diatoms

(Brandriss et al. 1998) and lacustrine diatoms (Moschen et al. 2005), supporting its use as a tool for interpreting variations of $\delta^{18}O$ values from fossil lacustrine diatoms in temperate lakes.

Important shifts between the temperature-dependent relationships obtained from lacustrine, marine, recent, or fossil diatoms, however, remain. Further investigations will be required to clearly identify the respective contribution of measurement uncertainty, temperature, the $\delta^{18}O_{water}$ estimation technique to overcome the contribution of exchangeable oxygen to $\delta^{18}O_{diatoms}$ values and impacts of early diagenesis.

Our ongoing research is focused on testing the relationship between sedimentary $\delta^{18}O_{diatoms}$, $\delta^{18}O_{lake\ water}$, and climate because diagenetic processes may influence the climatic signal patterns obtained from the sedimentary record (Schmidt et al. 2001; Moschen et al. 2006). Only one study, on lacustrine surface sediment samples spanning a large gradient across Western Europe, showed that the $\delta^{18}O_{diatoms}$ of sedimentary diatoms retains a regional-scale climate signal despite possible diagenetic effects (Tyler et al. 2008). Nevertheless, even if this study highlighted the great potential of $\delta^{18}O_{diatoms}$ from lake sediments as a proxy for past environmental changes, it also showed that relationships between $\delta^{18}O_{diatoms}$ and climate variables need to be re-examined, with good control over local lake water and atmospheric conditions at a single site. Lake Annecy offers a suitable experimental site for investigating these relationships, as it is well constrained, extensively monitored, and presents ideal hydro-isotopic conditions.

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