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Transfer and early diagenesis of biogenic silica oxygen isotope signals during settling and sedimentation of diatoms in a temperate freshwater lake (Lake Holzmaar, Germany)

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Abstract

We have investigated the transfer of oxygen isotope signals of diatomaceous silica ($\delta^{18}O_{diatom}$) from the epilimnion (0–7 m) through the hypolimnion to the lake bottom (~20 m) in freshwater Lake Holzmaar, Germany. Sediment-traps were deployed in 2001 at depths of 7 and 16 m to harvest fresh diatoms every 28 days. The 7 m trap collected diatoms from the epilimnion being the main zone of primary production, while the 16 m trap collected material already settled through the hypolimnion. Also a bottom sediment sample was taken containing diatom frustules from approximately the last 25 years. The $\delta^{18}O_{diatom}$ values of the 7 m trap varied from 29.4‰ in spring/autumn to 26.2‰ in summer according to the temperature dependence of oxygen isotope fractionation and represent the initial isotope signal in this study. Remarkably, despite the short settling distance $\delta^{18}O_{diatom}$ values of the 7 and the 16 m trap were identical only during spring and autumn seasons while from April to September $\delta^{18}O_{diatom}$ values of the 16 m trap were roughly ~1.5‰ enriched in ^{18}O compared to those of the 7 m trap. Isotopic exchange with the isotopically lighter water of the hypolimnion would shift the $\delta^{18}O_{diatom}$ value to lower values during settling from 7 to 16 m excluding this process as a cause for the deviation. Dissolution of opal during settling with intact organic coatings of the diatom cells and near neutral pH of the water should only cause a minor enrichment of the 16 m values. Nevertheless, opal from the bottom sediment was found to be 2.5‰ enriched in ^{18}O compared to the weighted average of the opal from the 7 m trap. Thus, resuspension of bottom material must have contributed to the intermediate $\delta^{18}O_{diatom}$ signal of the 16 m trap during summer. Dissolution experiments allowed further investigation of the cause for the remarkably enriched $\delta^{18}O_{diatom}$ value of the bottom sediment. Experiments with different fresh diatomaceous materials show an increase of opaline ^{18}O at high pH values which is remarkably reduced when organic coatings of the cells still exist or at near neutral pH. In contrast, high pH conditions do not affect the $\delta^{18}O_{diatom}$ values of sub-fossil and even fossil opal. IR analyses show that the ^{18}O enrichment of the sedimentary silica is associated with a decrease in Si–OH groups and the formation of Si–O–Si linkages. This indicates a silica dehydroxylation process as cause for the isotopic enrichment of the bottom sediment. Silica dissolution and dehydroxylation clearly induce a maturation process of the diatom oxygen isotope signal presumably following an exponential behaviour with a rapid initial phase of signal alteration. The dynamics of this process is of particular importance for the quantitative interpretation of sedimentary $\delta^{18}O_{diatom}$ values in terms of palaeothermometry.

1. Introduction

The oxygen isotope composition of the carbonaceous shells of foraminifera, ostracods and molluscs as well as of authigenic carbonates from marine and lacustrine sediments has been successfully used for palaeoclimate research. However, in the sediments of many non-alkaline and productive lakes such carbonaceous materials do not exist. These lakes, on the other hand, often provide the continuous, high-resolution sedimentary records that are necessary for consistent regional climate reconstructions.

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Their sediments frequently contain large amounts of biogenic silica derived from diatoms. These algae (Bacillariophyceae) are almost ubiquitous in freshwater lakes, of proven autochthonous origin and build siliceous skeletons that are well identifiable and often well preserved in greater amounts in lacustrine sediments.

Because the oxygen isotope composition of these diatom skeletons depends on the water temperature during diatom growth (Labeyrie, 1974; JuilletLeclerc and Labeyrie, 1987) sedimentary diatomaceous silica may provide an alternative approach for quantitative temperature reconstructions. Recent studies with diatom cultures (Brandriss et al., 1998) and planktonic assemblages of freshwater diatoms harvested directly from a lake ecosystem (Moschen et al., 2005) determined the temperature dependence of the oxygen isotope composition of diatomaceous opal for water temperatures between 5 and 25 °C with −0.2‰/°C at high accuracy and precision. Still, uncertainties remain with respect to the magnitude of fractionation against ^{18}O as determined by different analytical approaches. Nevertheless, if the oxygen isotope composition of sedimentary diatomaceous silica were known together with the corresponding oxygen isotope value of the host water, a quantitative temperature reconstruction should be possible (Leng and Marshall, 2004).

However, Schmidt et al. (1997) found significant differences between the oxygen isotope fractionation determined from fresh marine diatoms harvested with plankton nets and the respective results for diatoms retrieved from marine surface sediments. Furthermore, in a subsequent study Schmidt et al. (2001) concluded that the oxygen isotope composition of marine sedimentary diatomaceous silica does not solely reflect the sea surface temperature and that biogenic opal undergoes an ^{18}O enrichment during sedimentation. Consequently, a quantitative interpretation of sedimentary diatomaceous silica oxygen isotope values requires knowledge about processes that might modify the initial isotope signal during settling, sedimentation and aging of diatom skeletons. The aim of this study, therefore, was to focus on the transfer of the diatomaceous silica oxygen isotope signal from the place of its formation in the epilimnion to the surface sediments of a freshwater lake with respect to possible mechanisms of signal alteration like dissolution, isotope exchange or silica maturation.

2. Study site

The study was carried out in Lake Holzmaar (50°7′N, 6°53′E; 425 m a.s.l.), a small meso- to eutrophic soft-water lake situated in the mountainous Westeifel Volcanic Field, Germany. The lake developed in a small maar crater, is mainly groundwater fed, and has only a limited surface inflow and outflow. The diameter of the lake is 250–315 m with a surface area of 0.058 km^2 and a maximum depth of 20 m (Fig. 1). The small catchment area is drained by the Sammetcreek which flows in and out of the lake. During summers with low precipitation the creek falls dry temporarily. The maximum elevation in the catchment area is 477 m a.s.l. (Fig. 1B). Mean daily air temperatures recorded at Lake Holzmaar vary between −7 °C in January and about 25 °C in July. The mean annual precipitation at the nearby meteorological station Manderscheid operated by the national meteorological service (DWD) amounts to 975 mm (see also Table 1).

From May to September a stable stratification develops in the water body resulting in a thermocline at a depth of about 7 m. During the period of stratification, strong pH changes (temporarily up to pH 11) are observed in the lake's epilimnion as well as oxygen super-saturation and a seasonal succession of various diatom assemblages. Simultaneously anoxic conditions develop in the lake's hypolimnion extending from bottom to a depth of approx. 8 m (Lücke, 1998). Growth of diatom assemblages occurs mainly in the epilimnion and is exposed to a strong thermal gradient throughout the seasonal cycle (Raubitschek et al., 1999).

3. Materials and methods

3.1. Sampling and separation of diatom frustules

Water samples for the determination of the oxygen isotope composition of lake water and dissolved silicon analyses were taken biweekly (14 days) at the lake's deepest part at 2 m depth intervals from the surface to the bottom. Water temperatures were measured accordingly. Also precipitation, the Sammetcreek at the inflow into Lake Holzmaar, and a small spring directly discharging into the lake were sampled biweekly.

To harvest fresh diatoms, sediment-traps were deployed at water depths of 7 and 16 m near the lake's centre. Sediment-trap samples were collected every month (28 days) to ensure that enough diatomaceous silica was collected even at times with low diatom productivity. The 7 m trap collects the settling materials from the main growth zone of the planktonic algae, i.e., the epilimnion of the lake. In contrast, the 16 m trap accumulated all materials which would normally reach the lake's bottom and be buried in the sediment. A bottom sediment sample of the upper 15 cm containing diatom frustules grown during approximately the last 25 years was taken using a clamshell bottom sampler.

Pure diatomaceous silica samples from trap material and from the bottom sample were obtained by SPLITT fractionation (Rings et al., 2004). This method is based on the different sinking velocities of particles in a liquid suspension that is gently pumped through a narrow channel in a laminar flow. Before separation of diatom frustules from minerogenic matter freeze-dried samples were suspended in de-ionised water. Organic matter was removed using a hydrogen peroxide digestion (H_2O_2; 15%) for three times at 60 °C for 8 h at a time. Possibly remaining carbonates were removed by a mild hydrochloric acid treatment for 8 h (100 µl of HCl 32%/20 ml sample suspension).

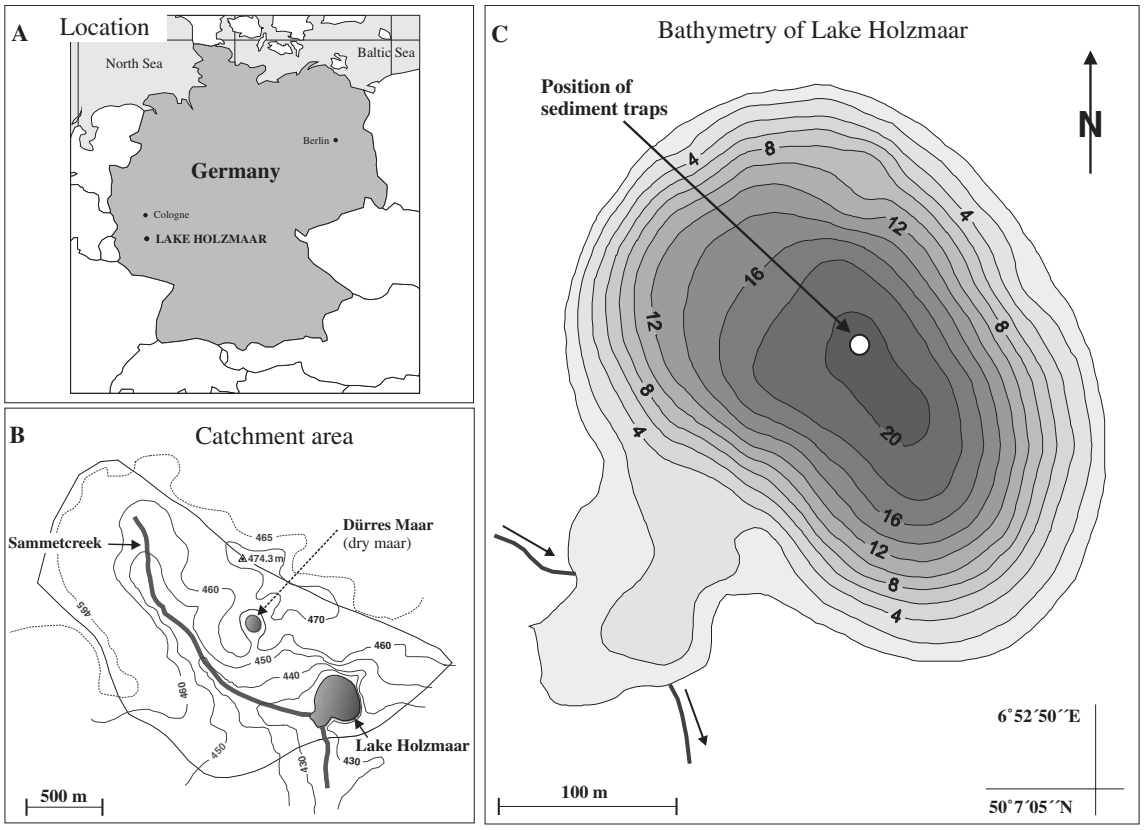

Fig. 1. Lake Holzmaar. Location (A), catchment area (B), bathymetry and sediment-trap positions (C).

Table 1
Geographical data, present-day range of water-chemical and limnological data of Lake Holzmaar and local climate data (1985–2001) from the nearby Station Manderscheid (50°6′N; 6°48′E, 403 m a.s.l.)

Parameter		Epilimnion (mean)	Hypolimnion (mean)
Elevation [m a.s.l.]	425		
Maximum depth [m]	20		
Lake surface [km^2]	0.058		
Catchment area [km^2]	2.06		
Mean annual air temperature [°C]	8.4		
Mean January air temperature [°C]	0.3		
Mean July air temperature [°C]	17.0		
Mean annual precipitation [mm]	975		
Water temperature [°C]		12.5[a]	4.9[a]
pH		8.3[a]	7.7[a]
O_2 [mg/L]		12.7[a]	0.8[a]
Nitrate [mg/L]		19.8	16.5
Phosphate [µg/L]		2.7	2.4
Silicon [mg/L]		1.9	2.9
Calcium [mg/L]		12.1	12.6
Potassium [mg/L]		1.9	2.0
Magnesium [mg/L]		7.0	7.2
Sodium [mg/L]		18.1	19.0

[a] Measured at 11:00 am.

Subsequently the samples were rinsed in de-ionised water and wet-sieved to obtain sediment size classes of 20–80, 10–20 and 5–10 µm. These size classes which were selected according to the size distribution of freshwater diatoms were treated in the SPLITT channel separately. The quality of the separation procedure was checked for each sample by light microscopy (for details, see Rings et al., 2004).

3.2. Diatom cultivation

Two freshwater diatoms (*Cyclotella meneghiniana* and *Fragilaria crotonensis*), both abundant in recent diatom assemblages of Lake Holzmaar, were cultured under steady-state conditions in a fermentation system (chemostat) using continuous, near natural light. During steady-state, the flow rate of the cultivation medium into the culture vessel determines the specific diatom growth rate and is held constant. Diatoms are harvested continuously from the algal suspension in the culture vessel (5 L) to balance the inflowing medium. The oxygen isotope composition of the de-ionised water used for preparation of the culture medium represents the source value for the oxygen isotope fractionation occurring during formation of the silica frustules at the set water temperature. Fractionation is assumed to proceed at isotopic equilibrium. Samples of culture medium were taken from every bottle of medium that was prepared. The average $\delta^{18}O_{water}$ value of all bottles of medium used was $-7.6 \pm 0.1‰$ vs. V-SMOW.

To prepare opal samples for laboratory experiments 5 L of sample suspension containing ~2 g of living diatom cells were filtered through a 0.45 µm filter. To remove organic matter the samples were digested three times in hydrogen peroxide (15%) at 60 °C for 8 h at a time. The treated

samples were repeatedly washed with de-ionised water and freeze-dried. No other cleaning steps were necessary to obtain pure diatom opal samples.

3.3. Dissolution experiments

The chemical stability of diatom frustules was tested by dissolution experiments with various diatomaceous silica materials. Material of the freshwater species *C. meneghiniana* and *F. crotonensis*, both grown in laboratory cultures, of a mid-Holocene diatomaceous opal sample from Lake Holzmaar containing frustules of various diatom species (varve dated at 5420 BP) and of the marine diatom *Ethmodiscus rex* from a Weddell Sea sediment (approx. 4 My) were used for these experiments. In a first experiment, approximately 20 mg of cleaned organic free diatom frustules of *C. meneghiniana* were stored in closed bottles for periods of 2, 7, 14, 28 and 62 days at room temperature in 50 ml of de-ionised water at two pH conditions (<0.1 mg dissolved silicon/L; $\delta^{18}O_{water}$ −7.2‰; the pH of the de-ionised water was 5.6 and set to pH 9.0 with NaOH). Further, an untreated sample of *F. crotonensis*, still containing the cell and its organic coatings, the sub-fossil Holzmaar sample and the *E. rex* sample were stored for two days in de-ionised water at the same two pH conditions (pH 5.6 and 9.0). For each experiment, a sample not exposed to in de-ionised water was used as the control.

3.4. Oxygen isotope analysis

The oxygen isotope composition of the diatomaceous silica was determined using inductive high-temperature carbon reduction (iHTR) and isotope ratio mass spectrometry. The novel iHTR method is based on a multi-step thermal dehydration procedure immediately followed by the reduction of SiO_2 with graphite powder at a temperature of 1550 °C (Lücke et al., 2005). The opal sample was stoichiometrically mixed with graphite powder, placed into a vacuum reaction vessel and evacuated. Water molecules, hydroxyl-groups and weakly bound oxygen contained in the opal were volatilised stepwise under high vacuum at temperatures of up to 1050 °C and pumped away instantaneously. Following this dehydration procedure the opal was decomposed at 1550 °C and the liberated oxygen was quantitatively converted to carbon monoxide (CO). The CO was analysed offline with an isotope ratio mass spectrometer (Optima, Micromass Ltd., UK). Oxygen isotope ratios are reported in the commonly used δ-notation as per mil [‰] deviation from V-SMOW calibrated against the NBS28 quartz standard. The adopted value for the NBS28 standard was 9.6‰ V-SMOW and precision for the laboratory standard (diatomaceous earth) used was ±0.14‰ (1σ) for $n = 19$. Samples were analysed up to four times with precision better than ±0.15‰ (1σ).

Diatomaceous silica from both the sediment-trap material and the lake bottom sediment was separated into three size classes (20–80, 10–20 and 5–10 μm). The oxygen isotope composition of each size class was measured separately. The mean oxygen isotope composition of a respective sample ($\delta^{18}O_{diatom}$) was calculated from the three individual biogenic silica oxygen isotope values of these size classes weighted by the mass of diatomaceous silica separated in each size class.

The oxygen isotope composition of water samples ($\delta^{18}O_{water}$) was measured using an on-line water–gas equilibration system (AP2002, Analytical Precision Ltd., UK). Oxygen isotope ratios of water are reported as per mil deviation from V-SMOW and calibrated against international water standards. Precision for $\delta^{18}O_{water}$ is better than ±0.12‰ (1σ).

The epilimnic water temperature was calculated from the measured water temperatures at the lake surface and at depths of 2, 4 and 6 m according to the formula $T_{epilimnion} = (T_{H_2O}\ (0\ m) + 2{\cdot}T_{H_2O}\ (2\ m) + 2{\cdot}T_{H_2O}\ (4\ m) + 2{\cdot}T_{H_2O}\ (6\ m))/7$. Thereby T_{H_2O} (0 m) represents the water temperature from the surface to a depth of one meter, T_{H_2O} (2 m) the temperature from one to three meter and so on. To calculate the mean epilimnic water temperature of the 28 days trap deployment period, $T_{epilimnion}$ from the beginning, the middle and the end of each 28 days period were used. The oxygen isotope composition of the epilimnic water body was calculated accordingly.

3.5. Structural investigations

Infrared spectroscopy (IR) was used for structural investigations of diatomaceous opal separated either from the culture material, from sediment-trap material harvested in Lake Holzmaar and the sub-fossil opal from the lake sediments. IR analyses were performed using KBr as matrix material and approx. 250 μg of silica pressed into sample pellets. Pellets were analysed in a Perkin-Elmer PE 780 infrared spectrometer and scanned in the 4000–370 cm^{-1} range.

4. Results

4.1. Temperature and oxygen isotope composition of water

During the year 2001 variations of the isotope composition of precipitation were in accordance with air temperature variations at Lake Holzmaar. Lowest $\delta^{18}O_{precipitation}$ values of −10.0 to −12.0‰ occurred in winter months, highest values of −4.0 to −5.0‰ during summer months. The respective mean $\delta^{18}O_{precipitation}$ value was −7.6‰ ($n = 79$) with a weighted average of −7.8‰ which is in good accordance with the long-term weighted average of −7.8‰ at the nearby meteorological DWD station Trier-Petrisberg (IAEA, 1992). In the Sammetcreek and the small spring no seasonal variation was observed. During the period of investigation the average $\delta^{18}O_{water}$ value of the Sammetcreek was −8.2‰ ± 0.2‰ ($n = 84$; min. −8.5‰, max. −7.8‰) while that of the spring was −8.3‰ ± 0.1‰ ($n = 64$; min. −8.5‰, max. −8.1‰). These values can be

taken as an approximation for the isotope composition of the main inflows into the lake.

During full mixing in winter and early spring the mean oxygen isotope composition of the whole water body of Lake Holzmaar was −8.0‰ (Fig. 2B). This value reflects the isotopic composition of the lake's main water sources. Simultaneously, a water temperature of approx. 4.5 °C prevailed throughout the whole water body (Fig. 2A). Temperature increases from early spring onwards resulting in a strong thermal stratification between the warm oxygen-rich epilimnion and the cold anoxic hypolimnion from May to September. During summer the epilimnic water temperature reaches values of 22–23 °C whereas the hypolimnic water merely reaches 5.0–5.5 °C. The rising temperature of the epilimnic water body resulted in surface-water evaporation and, thus, the surficial water layers of Lake Holzmaar become gradually enriched in ^{18}O (Fig. 2B). From April onwards the epilimnic $\delta^{18}O_{water}$ values increase steadily and reach maximum values of approx. −6.2‰ during August and September. Because of the stratification of the lake water body, oxygen isotope changes in the hypolimnion only take place during winter overturn (Fig. 2B).

4.2. Oxygen isotope composition of diatomaceous silica

The oxygen isotope composition of all analysed diatomaceous silica samples from the sediment-traps are summarised in Table 2. The $\delta^{18}O_{diatom}$ values of the diatomaceous silica harvested from the 7 m trap range from 26.2‰ to 29.4‰. The $\delta^{18}O_{diatom}$ values of the diatomaceous silica from the 16 m trap range from 27.1‰ to 29.8‰. The $\delta^{18}O_{diatom}$ value of the lake bottom sediment is 30.0 ± 0.2‰ ($n = 14$). The bottom sample contains frustules of various diatom species and represents approx. 25 years of sedimentation.

4.3. Diatomaceous silica dissolution experiments

In order to evaluate possible isotope effects during dissolution processes of diatom frustules, laboratory

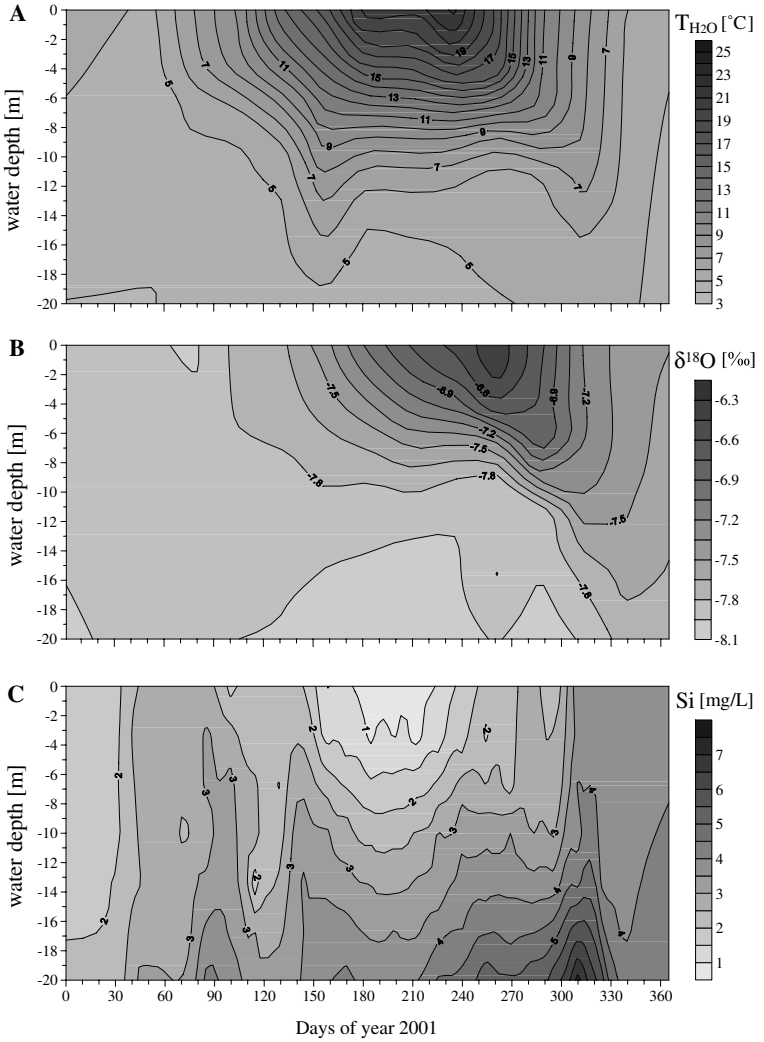

Fig. 2. Thermoisopleths of water temperatures [°C] (A), contour lines of $\delta^{18}O_{water}$ variations [‰ vs. V-SMOW] (B) and respective contour lines of dissolved silicon [mg/L] (C) in the water body of Lake Holzmaar in 2001 (contouring method used for interpolation between measurements was griging).

Table 2
Oxygen isotope composition of diatomaceous silica samples from sediment-trap materials from Lake Holzmaar

Date of sampling	7 m trap $\delta^{18}O_{diatom}$ [‰ vs. V-SMOW]			16 m trap $\delta^{18}O_{diatom}$ [‰ vs. V-SMOW]		
	20–80 μm	10–20 μm	5–10 μm	20–80 μm	10–20 μm	5–10 μm
13/02/01	29.2 ± 0.13	29.4 ± 0.16	29.0 ± 0.11	29.5[a]	29.3 ± 0.11	[b]
13/03/01	28.5 ± 0.12	28.3 ± 0.05	28.5 ± 0.05	28.3[c]		
10/04/01	[b]	27.8 ± 0.14	28.0[a]	28.0[a]	28.5 ± 0.28	28.6[a]
08/05/01	27.7 ± 0.05	27.1 ± 0.06	27.1 ± 0.04	28.8 ± 0.42	28.8 ± 0.17	27.9 ± 0.12
06/06/01	26.2[a]	26.4 ± 0.13	26.4 ± 0.02	28.6[a]	28.4 ± 0.08	[b]
03/07/01	27.1 ± 0.11	27.4 ± 0.11	27.5 ± 0.19	[b]	28.4 ± 0.11	28.4[a]
31/07/01	26.8[a]	26.6 ± 0.07	26.8 ± 0.02	28.0 ± 0.09	[b]	[b]
28/08/01	28.7[a]	26.9 ± 0.05	27.1 ± 0.10	27.1[a]	28.6 ± 0.08	27.1[a]
25/09/01	26.8[a]	26.8 ± 0.24	26.7 ± 0.10	28.9 ± 0.03	28.5 ± 0.03	28.4 ± 0.03
23/10/01	27.6[a]	27.5[a]	27.9 ± 0.10	27.6 ± 0.11	27.3 ± 0.05	27.1[a]
20/11/01	28.6[a]	28.7[a]	[b]	28.7[a]	28.6 ± 0.13	[b]

Sediment-traps were deployed at depths of 7 and 16 m in the centre of the lake and emptied every 28 days.
[a] One oxygen isotope measurement; mass of opal not sufficient for repeated measurements.
[b] Mass of opal not sufficient for an oxygen isotope measurement.
[c] Only one oxygen isotope measurement on opal from all three size classes; mass of opal not sufficient for three individual measurements.

experiments were performed using various diatomaceous silica materials. The different materials show different reactions during storage in de-ionised water. The storage of cleaned diatom frustules from the freshwater species *C. meneghiniana* (culture material) in water of pH 9.0 led to considerable silicon dissolution and a substantial enrichment of 6.8‰ in the oxygen isotope composition of the frustules (Table 4). In contrast, the storage of an untreated sample of *F. crotonensis* (culture material) which was not treated with H_2O_2 prior to the storage in water of pH 9.0 revealed a strongly reduced reaction. However, at near neutral pH conditions no difference between the $\delta^{18}O_{diatom}$ value of the exposed samples and the control was observed even after relatively long storage times of up to 62 days. The storage of diatomaceous silica from the sub-fossil Lake Holzmaar sediment and the fossil *E. rex* under high pH conditions did not lead to considerable silica dissolution or to a modification in the oxygen isotope composition of these materials. The results of the laboratory dissolution experiments are summarised in Table 4.

5. Discussion

5.1. Signal transfer during settling and sedimentation

The oxygen isotope composition of the diatomaceous silica separated from the 7 m trap material varies significantly with season (Fig. 3A). Low $\delta^{18}O_{diatom}$ values coincide with high epilimnic water temperatures during summer, high $\delta^{18}O_{diatom}$ values coincide with seasons of low water temperatures. The relation between water temperature and oxygen isotope fractionation during diatomaceous silica precipitation is described by a strictly linear correlation ($R^2 = 0.88$) leading to a temperature coefficient of −0.2‰/°C (Moschen et al., 2005). The $\delta^{18}O_{diatom}$ values of the three different diatom size classes which presumably represent different taxonomical groups have been analysed separately for most of the sediment-trap samples. These values do not differ significantly (Table 2) and, therefore, a species-specific vital effect could not be detected (Moschen et al., 2005). Nutrient supply as indicated by variations of dissolved silicon (Fig. 2C) or the degree of competition with other classes of algae does also not affect the oxygen isotope composition of the diatomaceous silica. Therefore, it can be assumed that in Lake Holzmaar the diatomaceous silica was precipitated in isotopic equilibrium and that the $\delta^{18}O_{diatom}$ value of the 7 m trap depends entirely on water temperature and the isotopic composition of the lake water.

The oxygen isotope composition of the diatomaceous silica from the 16 m trap also varies with season, but differences between highest and lowest $\delta^{18}O_{diatom}$ values were significantly smaller compared to the 7 m trap (Fig. 3A). During seasons with relatively low water temperatures, differences between the $\delta^{18}O_{diatom}$ values from the two sampling depths were relatively small to negligible. In contrast, the warming up of the surficial water layers from April onward resulted in $\delta^{18}O_{diatom}$ values from the 16 m trap being continuously ~1.5‰ more enriched in ^{18}O than the $\delta^{18}O_{diatom}$ values from the 7 m trap. A temporal lag (settling) between the 7 and the 16 m trap (Table 3) could not explain this difference since the annually weighted mean $\delta^{18}O_{diatom}$ values of 27.5‰ (7 m) and 28.5‰ (16 m) remain different.

One possible explanation for this observation could be diatom growth below a depth of 7 m that would lead to the formation of ^{18}O enriched biogenic opal due to lower water temperatures. However, since the maximum depth of the photic zone is approx. 7 m major diatom productivity in Lake Holzmaar takes place in the upper few metres of the water body (Raubitschek et al., 1999). Therefore, a large diatom production in the hypolimnion of Lake Holzmaar can be excluded.

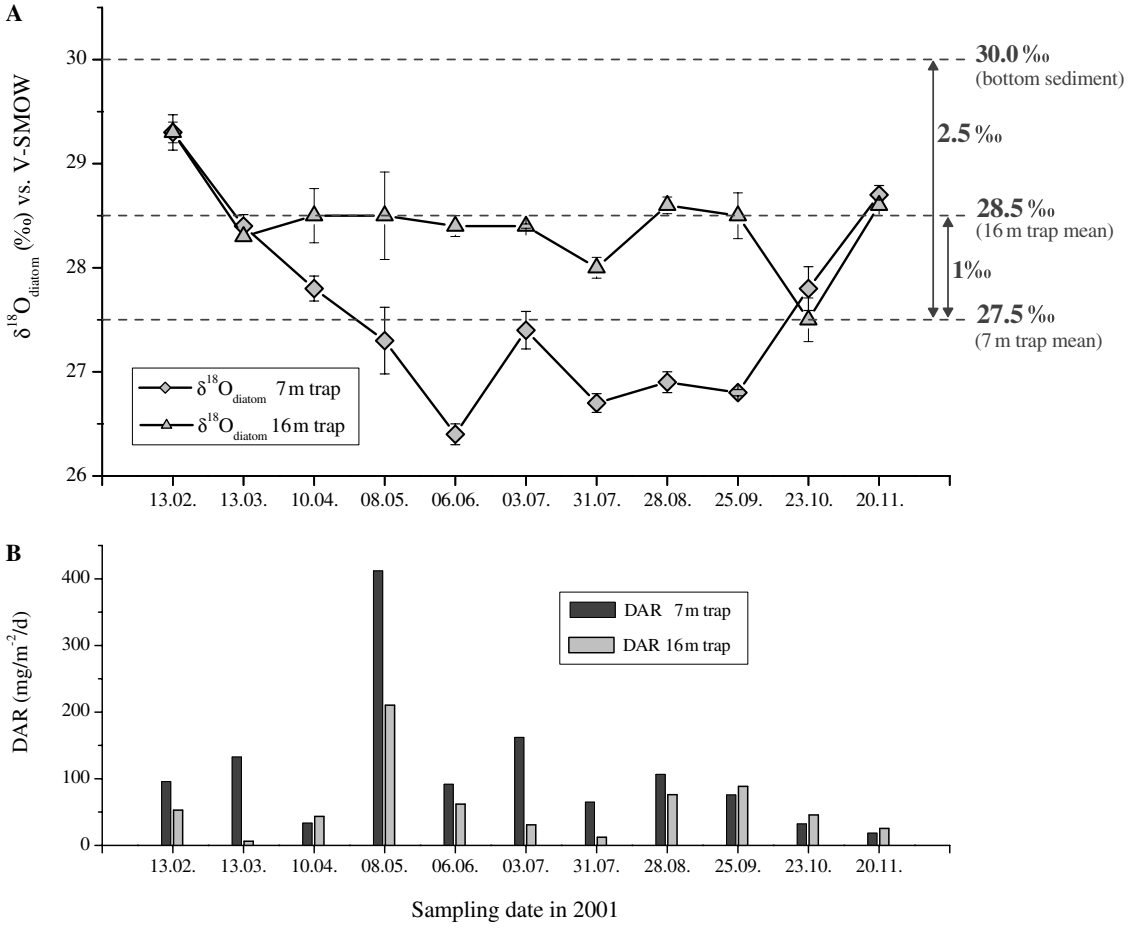

Fig. 3. Oxygen isotope composition of diatomaceous silica from sediment-trap material harvested in 2001 in Lake Holzmaar in 7 m (diamonds) and 16 m trap (triangles) (A) and diatom accumulation rate (DAR) in 7 m (dark-gray bars) and 16 m trap (grey bars) (B).

Table 3
Weighted mean oxygen isotope composition of diatomaceous silica samples from Lake Holzmaar, diatomaceous silica accumulation rate (DAR) and total sediment accumulation rate (SAR)

Date of sampling	$T_{epilimnion}$ [°C]	$\delta^{18}O_{water}$(epil.) [‰]	Weighted $\delta^{18}O_{diatom}$ [‰]		DAR [mg/m^{-2}/d^{-1}]		SAR [mg/m^{-2}/d^{-1}]	
			7 m	16 m	7 m	16 m	7 m	16 m
13/02/01	3.7	−8.1	29.3 ± 0.17	29.3 ± 0.10	95.7	52.9	2336	4227
13/03/01	4.7	−8.2	28.4 ± 0.11	28.3[a]	132.7	6.2	4647	9967
10/04/01	6.3	−8.3	27.8 ± 0.12	28.5 ± 0.26	33.4	43.5	2014	4766
08/05/01	8.7	−8.3	27.3 ± 0.32	28.5 ± 0.42	411.9	210.3	1608	3976
06/06/01	11.7	−8.1	26.4 ± 0.10	28.4 ± 0.10	91.7	62.0	2541	3331
03/07/01	14.6	−7.8	27.4 ± 0.18	28.4 ± 0.02	162.1	30.8	1701	2121
31/07/01	17.4	−7.5	26.7 ± 0.09	28.0 ± 0.1[b]	64.9	12.3	3542	3507
28/08/01	19.0	−7.2	26.9 ± 0.10	28.6 ± 0.71	106.6	76.1	2785	3354
25/09/01	15.9	−7.0	26.8 ± 0.03	28.5 ± 0.22	75.8	88.5	3069	4068
23/10/01	13.2	−7.0	27.8 ± 0.21	27.5 ± 0.21	32.3	45.7	1248	2174
20/11/01	9.9	−7.3	28.7 ± 0.09	28.6 ± 0.05	18.5	25.4	1303	3583

Sediment-traps were deployed at depths of 7 and 16 m in the centre of the lake and emptied every 28 days. Mean epilimnic water temperatures and $\delta^{18}O_{water}$ values are given for the 28 days sampling interval (for calculation of mean values see method section). Oxygen isotope ratios are reported as per mil [‰] deviation from V-SMOW.

[a] One oxygen isotope measurement on opal from all three size classes; mass of opal not sufficient for three individual measurements.

[b] Two oxygen isotope measurements on opal from 20 to 80 μm size class; mass of opal from smaller size classes not sufficient.

Dissolution of opal during settling of the diatom cells with intact organic coatings and at near neutral pH of the water should only cause a minor enrichment of the 16 m $\delta^{18}O_{diatom}$ values. Moreover, isotopic exchange between the diatomaceous opal and the ^{18}O depleted values of the hypolimnic water would drive the oxygen isotope

composition of the opal to even lower $\delta^{18}O$ values and cannot cause the enriched isotopic composition of the opal from the 16 m trap.

In the centre of small lakes with limited in and outflow a consistent sedimentation could be expected (Håkanson et al., 1989). Because of the steep slopes and the plane bottom of the basin of Lake Holzmaar, a morphometric sediment funnelling effect should be small. Assuming there is neither material input nor loss in the pelagic water body similar sedimentation rates should be attained at different depths. Contrary to this assumption the sediment accumulation rate (SAR) was considerably higher in the 16 m trap than in the 7 m trap (Table 3). Accordingly, erosion of shallower sediments from the lake's slopes and resuspended lake bottom material must have contributed to the sediment accumulated in the 16 m trap in addition to the vertically settling matter, at the same time masking the primary $\delta^{18}O_{diatom}$ signal of the 7 m trap. The relatively high mean $\delta^{18}O_{diatom}$ value of the bottom sediment of 30.0‰ which is considerably more enriched in ^{18}O than the $\delta^{18}O_{diatom}$ values of the opal harvested in both sediment-traps supports this assumption. We, therefore, conclude that bottom sediment material including diatom frustules is partly resuspended. Thereby the bottom oxygen isotope signal of 30.0‰ reaches the 16 m trap deployed just 3 m above the sediment surface. This causes the mixture of an older and enriched $\delta^{18}O_{diatom}$ signal originating from the lake bottom with the recent $\delta^{18}O_{diatom}$ signal originating from the epilimnion.

During seasons with a thermal stratification, the ^{18}O enriched bottom material could not be transported upwards into the epilimnion and, therefore, cannot affect the $\delta^{18}O_{diatom}$ signal of the opal from the 7 m trap. This led to the observed large isotopic offset between the diatomaceous silica samples from both traps from the end of April to mid September. During the rest of the season the opal of the 7 m trap is also enriched in ^{18}O due to increased fractionation at low water temperatures in spring and autumn. However, during times of complete mixing it cannot be excluded that bottom material including diatom frustules also reaches the 7 m trap because the isotopic composition of these older frustules will be indistinguishable from the frustules of diatom grown recently in the epilimnion. The interpretation as resuspension of bottom material influencing the 16 m trap also during summer months fits well the observation that during the last 60 years the sediments of Lake Holzmaar are not laminated, in contrast to the formation of varves during the entire Holocene (Kienel et al., 2005). This development is probably caused by the onset of summer resuspension.

While resuspension will have negligible effects for studies using varved sediments, it will considerably affect the time resolution that can be accomplished in studies on non-varved sediments. Moreover, it has strong implications for the design of further sediment-trap studies on the isotopic composition of diatomaceous opal in other lakes which should take such a process into consideration.

5.2. Processes of secondary ^{18}O enrichment

The weighted annually mean $\delta^{18}O_{diatom}$ value of the 7 m trap is 27.5‰, representing an integrated epilimnic isotope signal of the diatom vegetation period of a single year. In contrast, the $\delta^{18}O_{diatom}$ value of the bottom sediment is 30.0‰. Isotope exchange reactions with the isotopically lighter water of the hypolimnion during settling and sedimentation can be excluded as cause for this deviation since such an oxygen isotope exchange would shift the $\delta^{18}O_{diatom}$ value of the settling opal to lower values. Moreover, the short settling distance together with rapid diatom settling (spring bloom diatoms occurs simultaneously in material from 7 and 16 m trap, Fig. 3B) and the still existing organic coatings of the cells should be effective in preventing the dissolution of the frustules during settling. To explain the enriched $\delta^{18}O_{diatom}$ value of the bottom sediment as compared to the annually mean $\delta^{18}O_{diatom}$ value of the 7 m trap on the basis of a temperature shift would result in an unrealistic change of the water temperature during the last 25 years (Brandriss et al., 1998; Moschen et al., 2005). Also, a considerable change in the $\delta^{18}O_{water}$ value of Lake Holzmaar could explain the shift of 2.5‰ in the $\delta^{18}O_{diatom}$ value of the bottom sediment. However, since the mean $\delta^{18}O_{precipitation}$ pattern of the nearby meteorological station Trier-Petrisberg was almost constant during the last 20 years (IAEA, 1992) such an effect can be excluded. Another hypothesis to explain the relatively high $\delta^{18}O_{diatom}$ value of the bottom sediment would be a much higher amount of diatomaceous silica formed at low water temperatures and at relatively low $\delta^{18}O_{water}$ values during winter and early spring in earlier years. However, in recent years highest diatom flux rates appeared during summer and autumn (Table 3) (see also Raubitschek et al., 1999). The large difference of 2.5‰ between the weighted mean $\delta^{18}O_{diatom}$ value of the opal from the 7 m trap and the $\delta^{18}O_{diatom}$ value of the opal from the bottom sediment has, thus, to be attributed to other processes taking place largely at the sediment surface but not in the water column.

Causes of the observed ^{18}O shifts between diatom frustules harvested in the epilimnion and those derived from the lake's bottom sediment might be oxygen exchange reactions, partial silica dissolution or further condensation of the diatomaceous opal after the death of the cells. The surfaces of fresh diatom frustules have been found to be more reactive than those of sub-fossil and fossil frustules from sediments (Lewin, 1961). It has also been shown that the amount of loosely adsorbed water on fresh frustules was substantially higher than in fossil diatomite, suggesting that the surfaces of fresh frustules are far more hydrous than those of fossil silica (Hurd et al., 1981; Barker et al., 1994; Brandriss et al., 1998). In consequence of the reactive surface layers, frustules of freshly harvested diatoms are far more susceptible to oxygen isotope exchange than the

frustules of fossil diatoms from sediments (Juillet, 1980). Due to constantly low $\delta^{18}O_{water}$ values in the hypolimnion of Lake Holzmaar (Lücke et al., 1998; Moschen, 2004) the ^{18}O enrichment of the opal from the bottom sediment compared to the opal from the 7 m trap cannot be caused by isotope exchange reactions with ambient water, since isotope exchange would shift the $\delta^{18}O_{diatom}$ values to more negative values. Consequently, the results from Lake Holzmaar indicate rapid ^{18}O enrichment after sedimentation.

Diatomaceous silica dissolution experiments performed with two freshwater species from our laboratory cultures indicate the possibility of secondary ^{18}O enrichment due to partial silica dissolution at high pH conditions (Table 4). However, at neutral pH conditions no difference between the $\delta^{18}O_{diatom}$ value of the exposed samples and the control was observed despite potential oxygen isotope exchange during silica dissolution and an observed minor dissolution of silica (up to 2 mg/L of dissolved silicon occurred). This corroborates findings by Schmidt et al. (2001) who also found only slight changes of $\delta^{18}O_{diatom}$ values in dissolution experiments performed at pH 7.8–8.0. A different situation arises if the frustules are stored in water of pH 9.0. After a relatively short storage time of 48 h a considerable amount of dissolved silicon was found in the water (~11 mg/L) and a substantial enrichment of 6.9‰ in the oxygen isotope composition of the frustules appeared (Table 4). The storage of a sample of freshly harvested cells of *F. crotonensis* from our laboratory culture which was not treated with H_2O_2 prior to the storage in water of pH 9.0 reveals a strongly reduced reaction. After 48 h an amount of approx. 1.5 mg/L of dissolved silicon was found in the water and an enrichment of only 1.6‰ in the oxygen isotope composition was observed. Despite the silica dissolution and enrichment in ^{18}O of both materials at high pH the considerably lower enrichment of the chemically untreated diatoms proves that organic coatings protect the frustules from dissolution in an effective way. In contrast to these findings, the storage of diatomaceous silica from the sub-fossil Lake Holzmaar sediment and the fossil *E. rex* under the same pH conditions did hardly lead to any detectable silica dissolution. Furthermore no modification in the oxygen isotope composition of the sub-fossil and even the fossil opaline material was observed (Table 4).

Dissolution of silicon from surface sediments is a common process in lakes, also leading to seasonally increasing concentrations of dissolved silicon at the base of the hypolimnion in Lake Holzmaar. We observed highest concentrations of dissolved silicon during summer and autumn at depths of 16–18 m (Fig. 2C). The corresponding mean pH values in the lake's hypolimnion range between 7.5 and 7.7 and are much lower than pH 9.0 in our diatom dissolution experiments. Nevertheless, the relatively high silicon concentration in the deepest part of the hypolimnion points to silica dissolution at the sediment surface and the possibly related isotope exchange effects would fit to the enriched sedimentary $\delta^{18}O_{diatom}$ value. It is, however, remarkable that in the *C. meneghiniana* experiment no isotopic enrichment could be detected despite an increase of dissolved silicon of up to 2 mg/L in the storage water indicating that dissolution is quite possible without detectable isotope effects.

Lower diatom accumulation rates (DAR) as observed in 16 m compared to 7 m depth (Fig. 3B) could also indicate a

Table 4
Oxygen isotope composition of different diatomaceous opaline materials (laboratory cultures and natural sediments) after storage in de-ionised water at different pH values (pH 5.6 and 9.0) at room temperature (22 °C)

Cyclotella meneghiniana (after removal of organic matter)	Silicon concentration of H_2O after opal storage [mg/L]	SD	Mean $\delta^{18}O$ [‰] vs. V-SMOW	SD	*n*
Control	—		26.3	0.09	4
7 days at pH 5.6	1.6	0.2	26.3	0.14	3
14 days at pH 5.6	2.0	0.2	26.3	0.10	3
28 days at pH 5.6	1.7	0.2	26.1	0.09	3
62 days at pH 5.6	1.6	0.2	26.3	0.07	3
2 days at pH 9.0	**10.6**	0.2	**33.2**	0.12	3
Fragilaria crotonensis (untreated culture material)					
Control	—		25.6	0.05	3
2 days at pH 5.6	<0.1	0.1	25.6	0.06	4
2 days at pH 9.0	**1.5**	0.1	**27.2**	0.08	3
Opal from Lake Holzmaar sediment (sub-fossil material, varve dated at 5420 BP)					
Control	—		32.7	0.14	5
2 days at pH 5.6	<0.1	0.1	32.5	0.07	4
2 days at pH 9.0	0.1	0.1	32.6	0.06	4
Ethmodiscus rex (fossil marine material of 2.4 Ma)					
Control	—		46.7	0.10	9
2 days at pH 5.6	<0.1	0.1	46.8	0.14	3
2 days at pH 9.0	<0.1	0.1	46.6	0.10	3

The silicon concentration of the used water is <0.1 ppm and the $\delta^{18}O_{water}$ value is −7.2‰ vs. V-SMOW.

silica dissolution process which occurs already during diatom settling. Since we have calculated accumulation rates, this difference cannot be explained by diluting the 16 m trap material with bottom sediment likely containing higher amounts of fine grained clay and silt settling preferably during winter month. Furthermore, scanning electron microscope inspection of diatom frustules separated from the 7 and 16 m trap material and also from the bottom sediment sample do not point to identifiable diatom frustules dissolution in recent Lake Holzmaar. One possible explanation other than dissolution for the lower DAR at a depth of 16 m compared to the DAR at 7 m during late spring and summer could be due to enhanced zooplankton feeding in the hypolimnion. High grazing losses during summer stratification at greater depth seems quite possible, since downward vertical migration during the lighted period of the day is common behaviour among cladocerans and copepods (Wetzel, 2001). It has been also shown, that diatom frustules constitute the major fraction of the contents of copepod fecal pellets and that the majority of the frustules had undergone extensive mechanical damage during ingestion by the copepods (Ferrante and Parker, 1977). Additionally, the rapid sinking velocity of zooplankton fecal pellets relative to individual diatom frustules corresponds to the observation, that silica dissolution only takes place at the sediment surface. Therefore, we assume considerable feeding of diatoms by zooplankton in the hypolimnion leading to a break up of frustules. This can easily produce a high amount of fragments smaller than 5 μm from the frustules that are generally small (mainly <20 μm) in Lake Holzmaar. This effect can explain the underestimation of DAR in the greater size classes (>5 μm) in the 16 m trap in comparison to the 7 m trap presumably less affected by feeding. Nevertheless as outlined earlier, a contribution of partial diatomaceous silica dissolution to the lower DAR at a depth of 16 m cannot be completely excluded.

To study a possible ^{18}O enrichment of diatomaceous silica, we performed IR spectroscopic analyses. According to Farmer (1974) the IR spectra of biogenic silica exhibit four vibration bands with two characteristic main bands at 1100 and 471 cm^{-1} which are attributed to SiO_4 tetrahedrons. An additional medium intensity band at 945 cm^{-1} corresponds to a Si–O stretching of Si–OH groups and the 800 cm^{-1} vibration band is typical for the inter-tetrahedral Si–O–Si bending vibration mode (Gendron-Badou et al., 2003). Beside the two characteristic main bands the analysed opal from the cultured *C. meneghiniana* and from the freshly harvested sediment-trap material show distinct vibration bands at 945 and 800 cm^{-1}, respectively (Fig. 4). In contrast the 945 cm^{-1} band is significantly weaker for the opal separated from the lake's surface sediment and particularly for the sub-fossil sedimentary opal from Lake Holzmaar, suggesting a much smaller number of Si–OH groups in their structure (Gendron-Badou et al., 2003) (Fig. 4). Consequently, a selective loss of isotopically light oxygen from the Si–OH groups may be responsible for the observed shift of 2.5‰ between the weighted mean $\delta^{18}O_{diatom}$ values of the 7 m trap and the lake's surface sediment. The results point to the conclusion that the decline of Si–OH groups in the siliceous structure of sub-fossil or even fossil sedimentary diatomaceous silica can be seen as an effect of dehydroxylation of unstable silicon–oxygen bonds which is accompanied by the loss of water molecules. Because of their lower bond energy it is feasible to suppose that during the dehydroxylation of the unstable silicon–oxygen bonds, water molecules with the isotopically lighter ^{16}O isotope are selectively released.

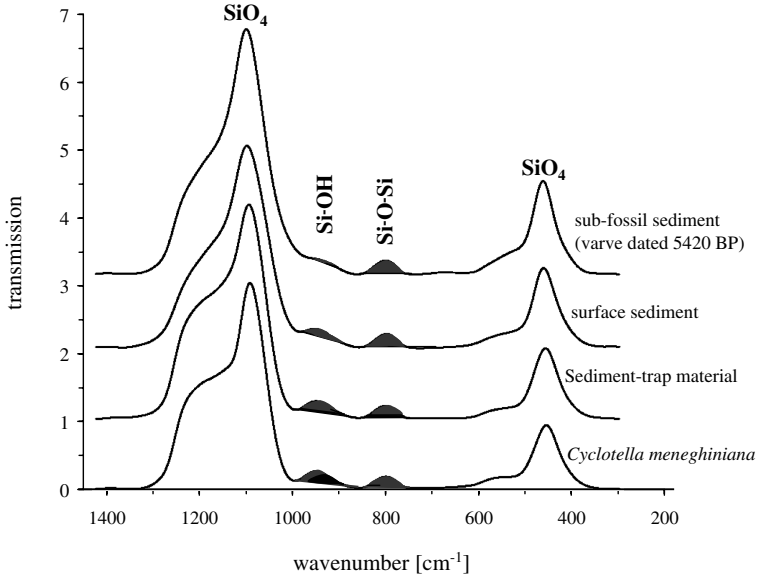

Fig. 4. Infrared absorption spectra of four different diatomaceous opaline materials from a laboratory culture and from Lake Holzmaar (trap and sediment). All transmission base lines fit y-axis and are aranged for reasons of comparison between samples.

Therefore, after sedimentation of diatom frustules a dehydroxylation process should initialize maturation of fresh phytoplankton opal (Schmidt et al., 2001; Gendron-Badou et al., 2003). Our results from Lake Holzmaar indicate that, beside a possible partial dissolution of isotopically light surficial opaline silica, a rapid opal maturation process taking place after sedimentation is responsible for enriched $\delta^{18}O_{diatom}$ values of the sedimentary opal. Both processes will be enhanced after the initial destruction of the organic matter from the soft parts and the organic coatings of the diatom cell. Even if we presently cannot distinguish between these processes it seems reasonable to assume that in pH neutral lakes like Lake Holzmaar the dissolution effect is comparably small while the maturation process is relatively more important for the alteration of the primary oxygen isotope signal in diatom opal. Our laboratory experiments additionally indicate that maturation initially occurs relatively fast and proceeds subsequently over longer time scales probably following exponential kinetics, thus, inducing a long-term trend of ^{18}O enrichment in sedimentary archives.

Such long-term trends of diatomaceous silica ^{18}O enrichment have not been described in any of the palaeoclimate studies based on the oxygen isotope composition of freshwater diatoms published so far (e.g., Rietti-Shati et al., 1998; Rosqvist et al., 1999; Barker et al., 2001; Hu and Shemesh, 2003; Jones et al., 2004; Lamb et al., 2005). However, a few of these studies present results that potentially provide an indication of a silica maturation process. Shemesh et al. (2001) detected a distinct depletion in $\delta^{18}O_{diatom}$ values occurring since the early Holocene in Swedish Lapland and attributed the continuous depletion trend in the $\delta^{18}O_{diatom}$ record to increased persistence of the polar Arctic continental air mass. They assume that deglaciation causes a slow-going shift in the isotopic composition of the lake water which is reflected in the diatom $\delta^{18}O$ record. In a second study in Swedish Lapland, Rosqvist et al. (2004) noted the occurrence of relatively abrupt successive transitions towards lower $\delta^{18}O$ values in a late Holocene $\delta^{18}O_{diatom}$ record superimposed on a general $\delta^{18}O_{diatom}$ depletion trend similar to the trend described by Shemesh et al. (2001). Both records fit well with each other and the general trend to depleted $\delta^{18}O_{diatom}$ values in both studies could also be an indication for slow-acting silica maturation processes.

6. Conclusions

Our results describe the transfer of temperature information stored as the oxygen isotope composition of diatom frustules in the epilimnion of Lake Holzmaar during settling through the hypolimnion to the lake surface sediments. In Lake Holzmaar during sedimentation of diatom frustules the epilimnic oxygen isotope signal is modified due to mixing with opal from older sediments as a result of resuspension processes which take place in the hypolimnion. This leads to a deviation between the isotopic signals from opal harvested with sediment-traps deployed in the epilimnion and hypolimnion during summer stratification. However, since other isotope effects on the settling frustules could not be detected, this has to be taken into account only with respect to the time resolution that can be reasonably accomplished for a respective archive. This effect should be negligible during times when varved sediments are formed.

At the sediment surface and within the surface sediments secondary processes take place leading to the enrichment of $\delta^{18}O_{diatom}$ values. We interpret the observed ^{18}O enrichment of the diatomaceous silica in the bottom sediment as an effect of silicon dissolution/biogenic silica maturation. Nevertheless, oxygen isotope exchange reactions cannot be completely excluded. A possible influence of silica condensation on the isotopic composition of sedimented opal was already discussed by Schmidt et al. (2001) and assigned to an isotope exchange reaction. Our laboratory experiments have shown that under high pH conditions partial silica dissolution and isotopic enrichment of up to 6.8‰ of cleaned fresh diatom frustules is initiated but is remarkably reduced when organic coatings of the diatoms still exist. Contrary to this observation with fresh opaline material, older diatom materials did not show any isotope reaction independent of pH. Based on IR structural analyses we were able to show that a weakening of the 945 cm^{-1} IR peak intensity corresponds to a reduction of Si–OH groups and coincides with the ^{18}O enrichment of the diatomaceous silica. This indicates a strong influence of dehydroxylation on the isotopic composition of the silica. It clearly shows that opal maturation through dehydroxylation is a major process leading to the observed shift of 2.5‰ between the average $\delta^{18}O_{diatom}$ value of the 7 m trap compared to the bottom sediment from Lake Holzmaar. Opal maturation effects can presently not be distinguished from silicon dissolution effects, but under pH neutral conditions like in Lake Holzmaar the former should be the more important one.

Although the oxygen isotope composition of sedimentary diatomaceous silica is affected by secondary processes, the predominant part of the oxygen should be bound to silicon in SiO_4 tetrahedrons. Since the relatively high activation energy for diatomaceous silica dissolution of approx. 13.8 kcal/mole is not much lower than the activation energy for quartz (15–18 kcal/mole) (Rimstidt and Barnes, 1980; Hurd et al., 1981) a temperature information recorded during diatom growth should be preserved even over long timescales. According to our results the progression of the silica maturation process with time should impose a non-linear, exponential trend leading to a successive isotopic enrichment in the sedimentary archive. However, most of the previously published $\delta^{18}O_{diatom}$ data sets from Holocene lacustrine sediments do not describe such an effect. This might be caused by a very slow progression of the maturation process after a rapid initial phase of signal alteration.

Our results clearly demonstrate that opal maturation and partial silica dissolution are of great importance for the palaeoclimatic interpretation of the oxygen isotope composition of sedimentary diatomaceous silica. If these processes are known and regular and if variations of the source value ($\delta^{18}O_{water}$) for the oxygen isotope fractionation are known, the temperature information which is recorded during diatom growth will be particularly useful as a quantitative palaeothermometer.

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