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Temperature-induced fractionation of oxygen isotopes of diatom frustules and growth water in Lake Sihailongwan in Northeast China

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Diatom oxygen isotopes have been widely applied in quantitative reconstruction of the paleoclimate and paleoenvironment, but have rarely been reported in China. In the present study, Lake Sihailongwan in Northeast China was selected for detailed investigation of oxygen isotopic fractionation between diatom frustules and lake water induced by growth temperature. This study involved a 2-year period of field monitoring of the lake water temperature at multiple depths and biweekly collections of traps for both sediment and water at shallow and bottom depths (7 and 49 m below the lake surface, respectively), diatom separation and purification of the trap sediments, and oxygen isotope measurement for diatom silica and lake water samples. The conditioned experiment conducted herein demonstrated that the laboratory device, methods and techniques used in this study were capable of generating reliable data for the typical oxygen isotope composition of diatom frustules. The data obtained revealed a prominent linear relationship between the oxygen isotope composition of the modern diatom and lake temperature during growth. The fractionation coefficient was about –0.185‰/°C–0.238‰/°C in the temperature range of 3.6–24°C, which is consistent with the observations from various aquatic environments and laboratory culture with different diatom taxa. These findings provide strong support for the dominant control of the growth temperature on the oxygen isotope fractionation between the diatom frustules and ambient water. A notable difference in the fractionation coefficient was observed between the surface and bottom diatom oxygen isotopes, suggesting that various depositional processes and taphonomic effects influenced the surface and bottom trap samples. Another factor leading to this difference may be that enrichment by evaporation and dilution by rainfall have a stronger influence on the surface. Overall, the results presented here demonstrate significant progress in evaluation of diatom oxygen isotopes in China and draw attention to the differences between surface and bottom diatom oxygen isotope compositions.

diatom silica, oxygen isotope, isotopic fractionation, Lake Sihailongwan, Northeast China

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Diatom oxygen isotope signatures have increasingly been applied as a quantitative climatic proxy in paleoclimate reconstructions of marine and lacustrine sedimentary records [1–3]. Theoretically, the oxygen isotope composition of diatom frustules is dependent on the isotopic composition of ambient water and temperature during their growth, similar to foraminifer tests that are used for paleoclimate study. Diatoms can survive in various aquatic environments and under different climate conditions, such as salty and fresh water bodies in warm and cold climates, and thus have great potential for use in quantitative reconstructions of paleoclimate change. However, such studies have rarely been conducted in China.

Early studies [4] suggested that the temperature fractionation coefficient of diatom oxygen isotopes with temperature was –0.5‰/°C, which is close to the coefficient

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derived from abiotic silica [5,6]. However, marine diatom studies conducted at high latitudes [7] have demonstrated that the previous conclusions [4,8] overestimated the effect of temperature on isotopic fractionation. A study of oxygen isotopes of laboratory cultured diatoms [9] demonstrated that the coefficient of temperature-induced fractionation was –0.2‰/°C, and that there was no significant difference between species. The results of a systematic monitoring study of lacustrine diatoms in northern Germany [10] were nearly identical to those obtained using laboratory cultured diatoms [9]. The temperature fractionation coefficient obtained has consistently been –0.198‰/°C for various size grades of diatoms, providing additional evidence of an equal fractionation effect of temperature for different diatom species. However, the available data are still rather limited in terms of both aquatic and phyletic coverage. Therefore, the mathematical correlations obtained from previous studies must be verified to ensure their applicability in other lakes, particularly in regions with different climates. Furthermore, there are notable differences in the mathematical equations generated from recently conducted studies, and advanced understanding of this issue depends largely on more systematic monitoring of natural aquatic environments.

In addition, the oxygen isotope compositions of different lakes vary from one region to another and even between lakes in the same region. This is also true for diatom colonies with respect to their dominant species and assemblage, which implies that there is a difference in the ecological and thus climatic significance of the diatom oxygen isotopes. Accordingly, it is necessary to mathematically specify the fractionation effect of temperature on diatom oxygen isotopes and to clarify the climatic/environmental implications for a given lake.

Lake Sihailongwan is a maar in Northeast China that is characterized by a continuous sedimentary sequence with well-developed varves [11]. Significant progress has been made in modern limnological studies of the lake and the records of organic elements and isotopes, pollen and inorganic geochemistry of the sedimentary sequence [12–16]. These records indicate an excellent correlation with global climate change over the past 16 ka and demonstrate great potential for a high resolution study of the paleoclimate record. More specifically, the sediment of Lake Sihailongwan contains abundant diatoms, providing a good chance for a diatom oxygen isotope study. For these reasons, Lake Sihailongwan was selected for this study, in which an attempt was made to establish the relationship between diatom isotope composition and water temperature during growth. To accomplish this, systematic field monitoring of the modern lake and collections of both lake water and sediments were conducted. It is expected that the results presented here will provide a basis for future applications in paleoenvironmental and paleoclimatic reconstructions in a quantitative manner.

1 Regional physiography

Lake Sihailongwan is located at 42°17′N and 126°36′E in the Longgang Volcanic Field in Jingyu County, Jilin Province, China. The lake is nearly perfectly circular and is encompassed by mountainous walls ranging from 10 to 119 m above the lake surface. The lake surface is 675–680 m above sea level and has an area of 0.4 km^2 and a maximum depth of about 50 m at the center. The total area of the catchment is 0.7 km^2. The basin is closed, with no outlets or inlets of flow.

The Sihailongwan region is located in the middle temperate climate zone on the margin of the East Asian monsoon, which is characterized by warm and rainy summers and cold and dry winters. The weather record at Jingyu for 1960–2008 indicates that the mean annual temperature of the study area is 2.5°C and the average annual rainfall is 780 mm, 85% of which occurs from May to October. Normally, the lake surface is completely frozen in early December, and the ice cover lasts for about 5 months until complete melt out in late April. The lake surface ice has been found to be covered with snow for most of the freezing period, implying a poor photic condition beneath the ice. Therefore, diatom productivity should be negligible during this period, because diatom growth requires sunlight for photosynthesis. The Sihailongwan region is densely covered with conifer-broad leaf mixed forest and soil erosion is rather weak.

2 Sample collection and laboratory methods

To evaluate the relationship between the oxygen isotopes of diatoms and water temperature during growth in Lake Sihailongwan, a field study was conducted to monitor the lake temperature at multiple depths and collect trapped sediments and paired lake water samples. Following collection of the samples, the diatoms were separated from the sediment and purified. In addition, the oxygen isotopes of the diatoms and the paired lake water samples were measured.

2.1 Monitoring of lake water temperature and trap harvest

Monitoring of the lake water temperature and trap sediment collection were conducted from May 2006 to May 2008. Based on the results of a previous study [17] and seasonal variations in the lake surface level, the traps were deployed at a depth of 7 m and at 1 m above the lake floor (about 49 m deep) in the center of the lake. The traps at each water depth consisted of four sets, and each set was constructed using three non-transparent PVC (polyvinyl chloride) cylindrical tubes with a diameter to height ratio of 15 to 78 cm. The mooring system of the traps included a surface buoy, a trap set and a weight anchor, which were connected by a guide rope. The distance between the trap sets was no less than 10 m. A total of 8 trap sets were deployed for both depths. The trap sediment was harvested biweekly from spring soon after the ice cover melted until early winter before the lake surface was completely frozen. In addition, lake water samples paired with the trap sediments were collected for isotope analysis. Trap sediments with paired lake water samples were also collected once during the freezing period for some years. Sediment and paired lake water samples were sealed and kept frozen in a freezer until laboratory analysis.

The lake water temperature was monitored using an auto-thermal recorder with five sensors that was deployed in the lake center, which were mounted at 0, 2, 5 or 7, 22, and 37 or 46 m of the water depths, respectively. The data recorded had a 2 h resolution and were used to obtain the daily mean, ten-day mean and biweekly mean temperatures (Figure 1(a)).

2.2 Diatom separation and purification

Diatom separation of the trap sediment samples was conducted according to the procedure described by Morley et al. [18], with some modifications. The major steps involved in the separation included the removal of organic matter by the addition of H_2O_2, removal of carbonate by HCl, removal of large sized minerogenic detritus using a 200 mesh sieve, removal of clay-sized particulates using the gravitation method, and separation of the diatoms in the samples using heavy liquid. With the aid of microscopic examinations, the last step may be repeated if the concentration of the impurities is high [19]. In general, the required purity of the diatom samples is greater than 95%; however, if this level of purity is not present, the concentration of the mineral detritus should be evaluated and its effect on the measured diatom oxygen isotope value should be calibrated [2,20]. Microscopic observation indicated that all of the diatom samples to be used for oxygen isotope analysis had a purity $\geqslant$ 96%; thus, the effects of the impurities could be neglected in this study.

2.3 Methods of oxygen isotope analysis for diatom frustules and lake water

Diatom frustules are composed of opal, a noncrystalline form of SiO_2 with some exchangeable oxygen ($SiO_2 \cdot nH_2O$). Frustules contain two types of chemical bonds, internal Si–O tetrahedral and external Si–OH structures. The internal Si–O–Si is quite stable, but the external Si–OH can be exchanged with water, even under low temperature conditions [21]. To obtain the typical oxygen isotope compositions bounded in the Si–O–Si structure, the oxygen in the outer layer must be removed.

Currently, extraction of the typical oxygen isotope composition (strongly bound oxygen in the internal layer) of diatom frustules is attained through stepwise fluorination (SWF) [1,2] or some modified methods such as the heating-fluorination method [22,23]. A controlled isotope exchange method (CIE) [21] is sometimes used in the case of insufficient amount of samples. The oxygen produced is then converted into CO_2 for isotopic measurement. Very recently, a high-temperature carbon reduction method (iHTR) [24] developed, which uses a specialized device to disintegrate the outer layered oxygen under low temperature (~1050°C) and produce CO for the internal layered oxygen through C–Si exchange in the reduction chamber at higher temperatures (⩾1550°C up to 2200°C) without the use of fluoric reagent.

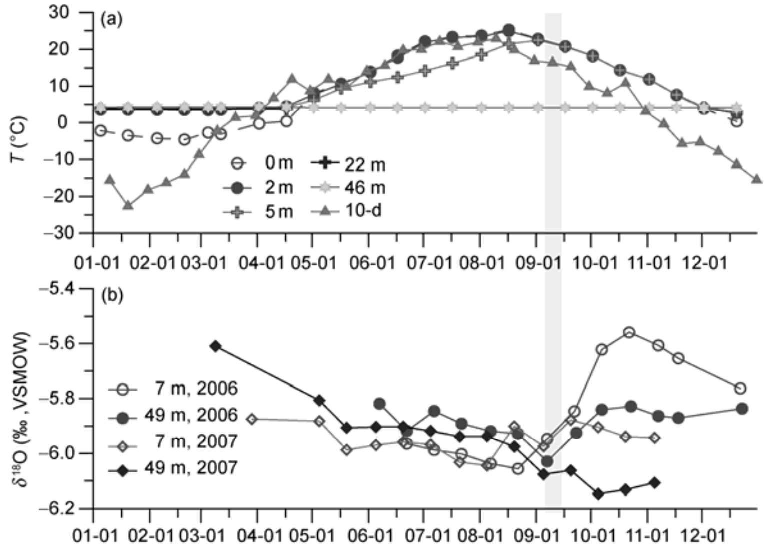

Figure 1 Lake water temperature and air temperature of Lake Sihailongwan and oxygen isotope composition of the lake water. (a) Biweekly mean temperature in 2008. The 10-d (day) mean air temperature was obtained based on daily records from the Jingyu Weather Station. (b) Water oxygen isotope compositions of Lake Sihailongwan at depths of 7 and 49 m during 2006–2007.

The CO is then measured through a directly connected mass spectrometer. The greatest advantage of the iHTR method is much less amount of the sample to be required. However, the diffusion effect of oxygen isotopes in the diatom frustules at high temperatures (>1000°C) must still be evaluated. In this study, the conventional SWF method was employed.

Laboratory analyses were conducted in the Silicate Oxygen Isotope Laboratory of the Institute of Geology and Geophysics, Chinese Academy of Sciences. The reliability of the analytical line was tested through detailed calculations and modification of the device during conditioned experiments of stepwise fluorination using BrF_5 as the reagent (see next section). Subsequently, a two-step fluorination method was used for the diatom oxygen extraction. In the first step, the outer layer of oxygen is removed using a controlled quantity of BrF_5 equal to about 30% of the theoretical amount required for complete reaction. The second step uses BrF_5 at an amount three times greater than the amount required to ensure that all of the oxygen in the frustules is released. The oxygen generated is then converted to CO_2 through the reaction in a connected heated graphite lamp, after which it is collected for isotope measurement using MAT-252. For samples with a larger mass, 15 mg of the sample amount was used, otherwise 7 mg of sample was used, which is the minimal amount required to obtain a reliable result. During early stages of the experiment, each batch of six samples contained one standard diatomite established in our lab and one international standard NBS28 (quartz), while in later stages every batch contained one standard diatomite and every two batches contained one NBS28. The oxygen isotope values are expressed in the δ-notation against the V SMOW scale (Vienna Standard Mean Ocean Water) [25] as

$$\delta^{18}\mathrm{O}=\left[\left(\frac{^{18}\mathrm{O}}{^{16}\mathrm{O}_{\mathrm{sample}}}\bigg/\frac{^{18}\mathrm{O}}{^{16}\mathrm{O}_{\mathrm{standard}}}\right)-1\right]\times 1000‰.$$

The difference in the oxygen isotope value between diatom frustules and growing water is expressed as $\Delta^{18}O_{\text{diatom-water}}$, or simply $\Delta^{18}O_{\text{Si-W}}$, which is defined as below. ‰

$$\Delta^{18}\mathrm{O}_{\text{diatom-water}}=\delta^{18}\mathrm{O}_{\text{diatom}}-\delta^{18}\mathrm{O}_{\text{water}}.$$

Duplications indicated that the analytical errors were commonly <0.5‰. When the error was larger than this, the experiment was repeated or the result was discarded if the sample was no longer available. Oxygen isotope analysis of the lake water samples was performed in the Stable Isotope Laboratory of the Institute of Geology and Geophysics, Chinese Academy of Sciences with an analytical error ⩽0.1‰.

3 Results and discussion

3.1 Seasonal variations in lake temperature and oxygen isotope composition of the lake water

The temperature data recorded with a resolution of one point/2h were integrated into a form of biweekly mean values on the day of the trap sediment harvest (Figure 1(a)) and were used as the mean growing temperatures for the corresponding diatom samples. During the ice-free period, the lake water temperatures at depths of 0 and 2 m were nearly identical (Figure 1(a)) and very close to the air temperature with a time lag of about 20 d. The highest half-month temperature occurred in late July for air and in early-middle August for the lake water at depths of 0 and 2 m. At a depth of 5 m, the temperature was always >3°C, and the temperature at this depth began to increase at the same time as temperatures at the 0 and 2 m depths during spring. The maximum temperature at 5 m was obtained during early September, about one month later than at 0 and 2 m. At 22 m, the temperature remained at 4°C constantly throughout the year. Temperatures at the lake surface (0 m) were <0°C from middle-late December to early May, indicating freezing of the lake center.

In general, the oxygen isotope composition of the lake water was rather stable throughout the year (Figure 1(b)), varying with an amplitude of 0.5‰ ($\delta^{18}O$ = –5.6‰ to –6.1‰) annually and about 0.2‰ ($\delta^{18}O$ = –5.8‰ to –6.0‰) from May to September. The largest variation occurred from September to December, when the temperature fell and the lake surface froze. In 2006, the $\delta^{18}O$ value of the surface lake water (7 m in depth) increased from early September until mid-October, suggesting that there was a stronger evaporation effect relative to precipitation during this season. From mid-late October, the $\delta^{18}O$ value fell because of freezing fractionation of the surface and the influx of snowfall into the lake, which typically has a markedly lower oxygen isotope composition than rainwater. The bottom water showed a similar variation pattern; however, the $\delta^{18}O$ of the bottom water continued to increase slightly as the surface water temperature decreased after mid October. These findings may indicate continued circulation mixing between the surface water and bottom water, as the surface generated 4°C water when the temperature fell and the oxygen isotopes of the surface water was heavier than the bottom water. In 2007, the $\delta^{18}O$ of the surface water showed only a slight increase in early September, which was soon followed by a rapid decrease. This more likely reflects heavy rainfall input during that period and the start of the freezing period.

Overall, the seasonal changes in the oxygen isotope composition of the lake water were affected by seasonal distribution of the rainfall, thermally driven circulation and freezing fractionation associated with the mixing processes. It should be noted that the surface water is heavier in oxygen isotopes in summer, but lighter during fall and winter when compared with the bottom water. The annual difference in the $\delta^{18}O$ of the lake water may have been caused by differences in the amount and isotopic composition of rainfall and the intensity of evaporation between years. However, this difference appeared rather small (<0.3‰).

3.2 Conditioned experiment of stepwise fluorination and characteristics of diatom oxygen isotope composition

To understand the structural composition of the diatom oxygen isotopes and determine if the analytical device could be used for oxygen extraction using the stepwise fluorination method, a conditioned experiment was designed in which eight steps were adopted and six samples were used, including three modern diatom samples from Lake Sihailongwan top sediment, two Paleogene diatomite samples, and one standard quartz sample, NBS28. The results obtained are shown in Figure 2.

The three identical diatom samples showed notably low $\delta^{18}O$ values in the first step of the fluorination when compared with subsequent steps (Figure 2). In the second step of fluorination, the $\delta^{18}O$ values of the generated oxygen increased remarkably, with two samples reaching the plateau value and another sample nearly reaching this value. Following the third step of fluorination, the $\delta^{18}O$ values of all the three diatom samples were very close, and they remained stable for a number of subsequent steps, indicating that the out-layered exchangeable oxygen of the diatom frustules had been completely removed through the first two steps. Accordingly, following removal of 25%–30% of the diatom mass (the amount of fluorinated diatom frustules in the first two steps), the typical oxygen isotope composition could be obtained. After the third step of fluorination, the $\delta^{18}O$ values displayed an increasing trend, demonstrating that lighter isotopes are kinetically more active than heavier isotopes and thus released more easily into the gaseous state. During the last fluorination step, only one diatom sample generated enough oxygen for mass spectrometric measurement and the isotopic value fell significantly. These results suggest that minerogenic impurity in the sample influenced the value because minerogenic substances have stronger Si–O bonds and have notably lower $\delta^{18}O$ values than diatom frustules.

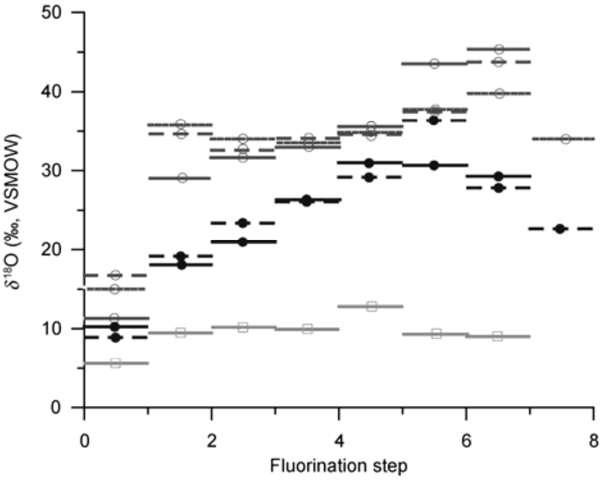

Figure 2 Conditioned stepwise fluorination. Open circles represent modern diatom samples from Lake Sihailongwan, solid circles indicate diatomite, and squares represent NBS28.

Diatomite samples displayed an increasing trend during the stepwise fluorination process, except during the last two steps. This phenomenon suggests that homogeneous diffusion of the Paleocene amorphous silica occurred during the long period of preservation after its formation, and that the stepwise release of oxygen followed the kinetic order of the isotopes. Microscopic observations indicated that the diatomite was partly crystallized into quartz, which led to some isotopic redistribution. A notable decrease in the $\delta^{18}O_{\text{diatomite}}$ during the last step also suggests that there was a small fraction of silicate minerals inside the diatomite samples. The standard quartz NBS28 was generally stable in $\delta^{18}O$ during the entire stepwise fluorination. Some small-amplitude variations during the stepwise processes were observed, but the reason for these variations is not clear.

In summary, the conditioned stepwise fluorinations showed a clear pattern in which the diatom $\delta^{18}O$ values were lower in the early steps, increased to a higher and stable plateau value, and then decreased to a lower value. These observations are consistent with the results of previous studies [26] and imply that the typical oxygen isotope composition of the diatom frustules can be determined through a two-step fluorination method. By removing the first two steps of fluorination for diatomite samples (the oxygen generated in the two steps was 28% of the total), the weighted $\delta^{18}O_{\text{diatomite}}$ was 27.83‰±0.4‰ and the $\delta^{18}O$ values of the three parallel diatom samples were 35.06‰, 34.83‰ and 36.04‰, respectively, with a mean value of 35.31‰±0.4‰. Independent measurement of the diatom sample revealed a value of 35.04‰, and the difference between these values was 0.27‰, which is better than the currently acceptable analytical error of ±0.5‰. These results provide strong evidence of the reliability of the method we used and the good quality of the results obtained in this study.

3.3 Diatom oxygen isotope composition of the modern Lake Sihailongwan and fractionation effect of growth temperature

Through separation and purification of the periodically harvested trap sediments, 31 diatom samples with a weight >7 mg were obtained, of which 18 samples produced reliable $\delta^{18}O$ values that were confirmed by duplicate or triplicate analysis. Based on the oxygen isotope composition of the paired lake water samples, the $\Delta^{18}O_{\text{diatom-water}}$ of each sample was calculated, and its relationship with the growth temperature is expressed in Figure 3. The sedimentary flux of biogenic silica showed no significant difference between surface and bottom traps, indicating that diatoms grow primarily in the photic zone; thus, the temperature at 2 m was used for both surface and bottom samples in the plot (Figure 3).

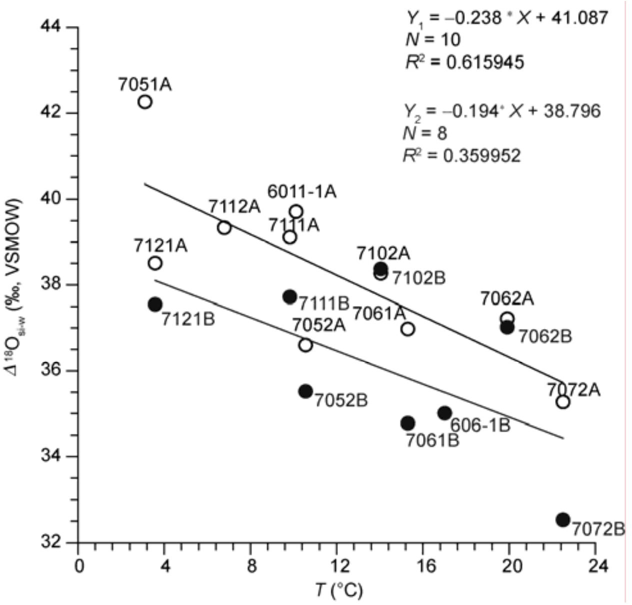

Figure 3 Plot of diatom oxygen isotope fractionation ($\Delta^{18}O_{\text{si-w}}$) versus water temperature at 2 m in Lake Sihailongwan. Open circles denote the surface sample (traps deployed at a depth of 7 m), solid circles are the bottom sample (1 m above the lake floor, i.e. 49 m in depth). Their regression equations are expressed as Y1 for surface and Y2 for bottom samples. A and B in the data point labels denote the surface and bottom samples, respectively.

It is clear that the $\Delta^{18}O_{\text{diatom-water}}$ of both surface and bottom samples decreased as the temperature increases in a linear fashion. The mathematical correlation of the $\Delta^{18}O_{\text{diatom-water}}$ with growth temperature for the surface samples is given as eq. (1):

$$\Delta^{18}O_{\text{diatom-water}} = -0.238T(°\text{C}) + 41.087. \qquad (1)$$

For the bottom samples, the linearly regressed relationship is expressed by the following equation:

$$\Delta^{18}O_{\text{diatom-water}} = -0.185T(°\text{C}) + 38.438. \qquad (2)$$

As shown in eqs. (1) and (2), at a temperature range of 3.6–24°C (based on the half-monthly mean), the temperature fractionation coefficient was between –0.185‰/°C and –0.238‰/°C, or about –0.2‰/°C. Even when all the diatom samples were combined, the linear relationship was still evident, and the temperature fractionation coefficient was –0.249‰/°C.

The coefficient of the temperature-induced oxygen isotopic fractionation between diatoms and lake water demonstrated in the modern Lake Sihailongwan (Figure 3) is very similar to that observed in studies of marine environments [7], laboratory cultured diatoms [9] and modern European lakes [10]. Because these studies cover a great variety of aquatic environments (fresh water or salty water) and species (single species or mixtures of diatom frustules in natural ecosystems), the consistency of the fractionation coefficients suggests that the temperature fractionation effect in diatom oxygen isotopes occurs in an inorganic fashion with no significant biogenic discrimination. These observations are particularly important and useful for diatom oxygen isotopes to be used as a paleothermometer.

The mathematical relationship between the diatom oxygen isotope composition and growth temperature obtained in this study (Figure 3), however, contained a large uncertainty and could not be used for quantitative reconstruction of paleotemperature in its present form. Therefore, it is necessary to further explore the factors that caused the uncertainty for a better understanding of the accurate implications of the diatom oxygen isotope composition. Comparatively, the correlation of the surface $\delta^{18}O_{\text{diatom}}$ value with the growing water temperature was significantly higher than that of the bottom samples, as the latter contained more scattered data points. This was likely because of the great water depth of Lake Sihailongwan, which results in a long time being required for sediment, including diatoms, to settle from the surface to the bottom. As a result, some diatoms growing in different periods or at different levels could be mixed during settling, which would cause some deviation in temperature from the value recorded at 2 m. Moreover, convergent deposition of the sediments in the lake margins toward the lake center can be expected, which would also carry some diatoms into the bottom traps. These factors are important taphonomic issues that deserve attention in future paleotemperature reconstructions using diatom oxygen isotopes. As pointed out in previous studies [22,27], the sedimentary processes, taphonomic effects, and isotopic exchange during deposition should not be neglected in marine environments, because of the great water depth and vertical heterogeneity of the water chemistry in such systems.

We observed that the surface diatom samples often have a $\delta^{18}O$ value higher than the bottom samples harvested on the same day (Figure 3). This cannot be explained easily by the effect of thermodynamic fractionation, as the lake surface temperature is nearly always higher than that of greater depths during ice-free periods (see Figure 1). Although the diatoms deposited on the lake bottom are primarily from the surface level, some diatoms from deeper levels (growing with lower temperature) in the bottom samples should make an integrate growth temperature lower than the surface sample, and lead to a higher $\delta^{18}O$ value. However, this contradicts the observed results. One possible reason for this discrepancy is that the surface water was subject to isotopic enrichment by evaporation. As shown in Figure 1(b), the $\delta^{18}O$ of the surface water (at 7 m) was lower than that of deeper water in winter, nearly the same during summer, and higher from mid August or early September until December. After the lake was completely covered with ice, the $\delta^{18}O$ values of both levels tended to be the same. This phenomenon is consistent with the observations of the Holtzmaar in Germany [10]. These results suggest that evaporation-caused isotopic enrichment in the 0–2 m zone, which is the best photic and the primary growing zone of the diatoms, might have caused an enrichment of the diatom oxygen isotopes that exceeded the temperature effect.

The presence of fine grained minerogenic impurities associated with their concentration variations may affect the regression [20]. Therefore, improvement of diatom purification will be important for enhancement of the accuracy of diatom oxygen isotopes to be used as paleotemperature indicators.

Despite these uncertainties, the relationship between diatom oxygen isotope composition and growth temperature demonstrated in this study forms a concrete basis for its use in quantitative reconstructions of paleoclimate change. To understand the uncertainties associated with the mathematical relationship obtained in this study, it is necessary to pay attention to the ecological differences between surface and bottom samples and to minimize the influence of different habitats, such as planktonic and benthic environments. Furthermore, the climatic meaning of the diatom oxygen isotopes may vary individually with different circumstances. For example, the time resolution can be monthly, seasonal or yearly, and the blooming season may change from one lake to another. Generally, the time resolution is on a yearly basis, which requires detailed study of diatom flux distribution through a year. With detailed seasonal flux data, a sedimentary-flux-based mean value of the diatom oxygen isotope signature can be integrated, and a synthesized annual mean temperature can be obtained as a reference for the modern annual temperature. For some lake environments, however, the dominant diatom species may bloom in a short period once a year. Thus, the diatom oxygen isotope composition would indicate a water temperature for a specific season rather than a year.

4 Conclusions

Conditioned stepwise fluorination experiments indicated two oxygen isotopic components of diatom frustules with distinguished values, an exchangeable part with a lower δ^{18}O value that accounted for 25%–29% of the total oxygen yield, and a structurally stable part with a higher δ^{18}O value. The exchangeable part is released during the early stage of stepwise fluorination, and can be removed first through stoichiometrically controlled insufficient fluorination. The structurally stable oxygen isotope composition shows a plateau value, indicating the presence of a characteristic composition of oxygen isotopes in diatom frustules, which can be isolated by the two-step fluorination method. The diatom oxygen isotope compositions of the modern Lake Sihailongwan showed a linear relationship with growth temperature. In the range of 3.6–24°C, the temperature fractionation coefficient was about –0.2‰/°C, which is consistent with the results obtained from a variety of aquatic environments and species conducted by field monitoring or laboratory culture observations. These findings imply that diatom oxygen isotope fractionation may be dominated by growth temperature, suggesting that it has great potential for use as a paleo-temperature indicator. The notable difference between the surface and bottom samples observed in this study may result from different sedimentary processes. For the paleotemperature proxy of diatom oxygen isotopes to be practical for this region, more detailed monitoring of diatom flux and associated oxygen isotope composition through an entire year is required.

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1 Leng M J, Barker P A. A review of the oxygen isotope composition of lacustrine diatom silica for palaeoclimate reconstruction. Earth-Sci Rev, 2006, 75: 5–27

2 Han J, Chen H, Li D et al. Lacustrine diatom oxygen isotopes: A paleoclimatic proxy with great potential of broad application in terrestrial records (in Chinese). Quat Sci, 2006, 26: 634–642

3 Swann G E A, Leng M J. A review of diatom δ^{18}O in palaeoceanography. Quat Sci Rev, 2009, 28: 384–398

4 Labeyrie L. New approach to surface seawater palaeotemperatures using ^{18}O/^{16}O ratios in silica of diatom frustules. Nature, 1974, 248: 40–42

5 Kita I, Taguchi S, Matsubaya O. Oxygen isotope fractionation between amorphous silica and water at 34–93°C. Nature, 1985, 314: 83–84

6 Clayton R N, O'Neil J R, Mayeda T K. Oxygen isotope exchange between quartz and water. J Geophys Res-Solid Earth, 1972, 77: 3057–3067

7 Shemesh A, Charles C, Fairbanks R. Oxygen isotopes in biogenic silica: Global changes in ocean temperature and isotopic composition. Science, 1992, 256: 1434

8 Juillet-Leclerc A, Labeyrie L. Temperature dependence of the oxygen isotopic fractionation between diatom silica and water. Earth Planet Sci Lett, 1987, 84: 69–74

9 Brandriss M E, O'Neil J R, Edlund M B, et al. Oxygen isotope fractionation between diatomaceous silica and water. Geochim Cosmochim Acta, 1998, 62: 1119–1125

10 Moschen R, Lücke A, Schleser G H. Sensitivity of biogenic silica oxygen isotopes to changes in surface water temperature and palaeoclimatology. Geophys Res Lett, 2005, 32: L7708

11 Mingram J, Allen J R M, Bruchmann C, et al. Maar and crater lakes of the Long Gang Volcanic Field (N.E. China) – overview, laminated sediments, and vegetation history of the last 900 years. Quat Int, 2004, 123: 135–147

12 Schettler G, Liu Q, Mingram J, et al. Palaeovariations in the East-Asian Monsoon regime geochemically recorded in varved sediments of Lake Sihailongwan (Northeast China, Jilin Province). Part 1: Hydrological conditions and dust flux. J Paleolimnol, 2006, 35: 239–270

13 Schettler G, Mingram J, Negendank J F W, et al. Palaeovariations in the East-Asian Monsoon regime geochemically recorded in varved sediments of Lake Sihailongwan (Northeast China, Jilin Province). Part 2: A 200-year record of atmospheric lead-210 flux variations and its palaeoclimatic implications. J Paleolimnol, 2006, 35: 271–288

14 Schettler G, Liu Q, Mingram J, et al. East-Asian Monsoon variability between 15000 and 2000 cal. yr BP recorded in varved sediments of Lake Sihailongwan (northeastern China, Long Gang Volcanic Field).

Holocene, 2006, 16: 1043–1057

15 Parplies J, Lücke A, Vos H, et al. Late glacial environment and climate development in Northeastern China derived from geochemical and isotopic investigations of the varved sediment record from Lake Sihailongwan (Jilin Province). J Paleolimnol, 2008, 40: 471–487

16 Stebich M, Mingram J, Han J T, et al. Late Pleistocene spread of (cool-)temperate forests in Northeast China and climate changes synchronous with the north Atlantic region. Glob Planet Change, 2009, 65: 56–70

17 Raubitschek S, Lücke A, Schleser G H. Sedimentation patterns of diatoms in Lake Holzmaar, Germany (on the transfer of climate signals to biogenic silica oxygen isotope proxies). J Paleolimnol, 1999, 21: 437–448

18 Morley D W, Leng M J, Mackay A W, et al. Cleaning of lake sediment samples for diatom oxygen isotope analysis. J Paleolimnol, 2004, 31: 391–401

19 Li D, Han J, Sun H, et al. A novel improvement of diatom separation and purification with a focus on small size (in Chinese). Quat Sci, 2010, 30: 623–624

20 Morley D W, Leng M J, Mackay A W, et al. Late glacial and holocene environmental change in the lake baikal region documented by oxygen isotopes from diatom silica. Glob Planet Change, 2005, 46: 221–233

21 Labeyrie L D, Juillet A. Oxygen isotopic exchangeability of diatom valve silica: Interpretation and consequences for paleoclimatic studies. Geochim Cosmochim Acta, 1982, 46: 967–975

22 Schmidt M, Botz R, Stoffers P, et al. Oxygen isotopes in marine diatoms: A comparative study of analytical techniques and new results on the isotope composition of recent marine diatoms. Geochim Cosmochim Acta, 1997, 61: 2275–2280

23 Wang C H, Yeh H W. Oxygen isotopic compositions of DSDP Site 480 diatoms: Implications and applications. Geochim Cosmochim Acta, 1985, 49: 1469–1478

24 Lücke A, Moschen R, Schleser G. High-temperature carbon reduction of silica: A novel approach for oxygen isotope analysis of biogenic opal. Geochim Cosmochim Acta, 2005, 69: 1423–1433

25 Coplen T B. Reporting of stable hydrogen, carbon, and oxygen isotopic abundances. Pure Appli Chem, 1994, 66: 273–276

26 Matheney R K, Knauth L P. Oxygen-isotope fractionation between marine biogenic silica and seawater. Geochim Cosmochim Acta, 1989, 53: 3207–3214

27 Schmidt M, Botz R, Rickert D, et al. Oxygen isotopes of marine diatoms and relations to opal–A maturation. Geochim Cosmochim Acta, 2001, 65: 201–211