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Silicon isotope composition of diatoms as a paleoenvironmental proxy in Lake Huguangyan, South China

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ABSTRACT

Silicon is essential for the growth of diatoms, which utilize dissolved silicic acid in lake water and form opaline silica ($SiO_2{\cdot}nH_2O$). During the uptake of dissolved silicic acid, there is a preferential incorporation of light silicon isotope (^{28}Si) into biogenic silica, resulting in the enrichment of heavy silicon isotope (^{30}Si) in dissolved silicic acid. The silicon isotope composition of diatom silica ($\delta^{30}Si_{diatom}$) may thus record changes in the percentage utilization of dissolved silicic acid by diatoms, which can be then related to other aspects of climate/environment. With the aim of exploring the potential of $\delta^{30}Si_{diatom}$ as an indicator of lacustrine environment, here we made the first measurements of $\delta^{30}Si_{diatom}$ in the sediment core from Lake Huguangyan, a closed crater lake in China. The result shows that $\delta^{30}Si_{diatom}$ varies from −0.6‰ to 1.1‰ and displays broad similarities to variations in contents of biogenic silica and organic carbon throughout the sediment core. $\delta^{30}Si_{diatom}$ is a reliable paleotemperature proxy in Lake Huguangyan, which is supported by good correlation between $\delta^{30}Si_{diatom}$ and available temperature records. Heavier $\delta^{30}Si_{diatom}$ indicates greater dissolved silicic acid utilization at higher temperature while lighter $\delta^{30}Si_{diatom}$ reflects decreased utilization at lower temperature. The most negative $\delta^{30}Si_{diatom}$ values in the sediment core occur between AD 1580 and 1920, which suggests AD 1580–1920 was the coldest period in Lake Huguangyan over the past 2000 years, thus providing evidence for the existence of the LIA in tropical South China.

There are few means by which to reconstruct the history of temperature changes in tropical terrestrial region. $\delta^{30}Si_{diatom}$, in this study, has proven to be a new promising paleotemperature proxy in lacustrine sediments, and may play important role in reconstructing past temperature changes at low latitude in the future. Detailed investigations on the silicon isotopes of diatoms in more lakes would be desirable in further research.

1. Introduction

Diatoms, present in most lake sediments, are photosynthetic algae that secrete a shell composed of opaline silica ($SiO_2{\cdot}nH_2O$) (Round et al., 1990; Leng and Barker, 2006; Lamb et al., 2007). The oxygen and silicon isotope compositions ($\delta^{18}O$ and $\delta^{30}Si$) of diatom frustules, which grow in water body, generally record the temperature and isotope compositions of the water at the time of formation (Juillet-Leclerc and Labeyrie, 1987; Shemesh et al., 1992; Brandriss et al., 1998; Lamb et al., 2007). In recent 10 years, the oxygen isotope composition of diatom silica ($\delta^{18}O_{diatom}$) in lacustrine sediments is increasingly utilized to infer changes in temperature or the oxygen isotope composition of lake water which is then related to climate/hydrology (Rosqvist et al., 1999, 2004; Hu and Shemesh, 2003; Jones et al., 2004; Lamb et al., 2005; Leng and Barker, 2006; Mackay, 2007). In contrast to large amounts of investigations on $\delta^{18}O_{diatom}$, the published data on silicon isotope composition of diatom silica in lacustrine sediments are very limited. Only few silicon isotopic studies on diatom silica in lake water and its sediments were reported so far (Ding et al., 1996; Alleman et al., 2005). This is probably because of the dangerous and challenging measurement procedures of $\delta^{30}Si_{diatom}$, which requires the use of a fluorinating gas, and also because of the neglect of the potential of $\delta^{30}Si_{diatom}$ as an indicator of lacustrine environment.

Silicon has three stable isotopes in different abundance, ^{28}Si (92.23%), ^{29}Si (4.67%) and ^{30}Si (3.10%) (Ding et al., 1996; Hoshi et al., 1997), and is essential for the growth of diatoms. Diatoms utilize dissolved silicic acid (H_4SiO_4) in lake water and form opaline

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silica ($SiO_2 \cdot nH_2O$). During the uptake of dissolved silicic acid, there is a preferential incorporation of light silicon isotope (^{28}Si) into biogenic silica and a discrimination against heavy silicon isotope (^{30}Si). De La Rocha et al. (1997) quantitatively investigated the fractionation between diatom silica and dissolved silicic acid through laboratory-based culturing experiments. The extent of the isotopic fractionation was calculated as a fractionation factor, α, defined as:

$$\alpha = R_{\mathrm{diatom}}/R_{\mathrm{dsa}} \tag{1}$$

where R_{diatom} and R_{dsa} are the ratios of ^{30}Si to ^{28}Si in diatom silica and dissolved silicic acid respectively. De La Rocha et al. (1997) found that the value of α was about 0.9989, and it did not vary measurably with temperature in the range from 12 °C to 22 °C or among different diatom species. Through investigation on the silicon isotope compositions of water and biogenic opal in Lake Tanganyika, Alleman et al. (2005) gives further support to the non-species, non-temperature dependent character of the silicon isotope fractionation by diatoms in fresh water. Thus, the use of $\delta^{30}Si_{\mathrm{diatom}}$ is greatly simplified because of the lack of interspecific variation. It is not necessary to pick monospecific diatoms from lacustrine sediments, which is virtually impossible because of the small size of diatoms.

The discrimination against ^{30}Si during biogenic silica formation progressively results in the enrichment of ^{30}Si in dissolved silicic acid. In a closed system with a finite pool of dissolved silicic acid, variations in the silicon isotope compositions of diatom silica and dissolved silicic acid follow the Rayleigh model (Fig. 1) (De La Rocha et al., 1997, 1998). Obviously, increased utilization of dissolved silicic acid results in more positive $\delta^{30}Si_{\mathrm{diatom}}$ values, while decreased utilization results in more negative $\delta^{30}Si_{\mathrm{diatom}}$ values. Therefore, $\delta^{30}Si_{\mathrm{diatom}}$ may reflect changes in the percentage utilization of dissolved silicic acid by diatoms, which can be then related to other aspects of climate/environment. De La Rocha et al. (1998) have successfully use $\delta^{30}Si_{\mathrm{diatom}}$ to demonstrate that the percentage utilization of dissolved silicic acid by diatoms in the Southern Ocean during the last glacial period was strongly diminished relative to the present interglacial. However, investigation on the silicon isotope composition of diatom silica in lacustrine sediments is scarce until now. With an aim of exploring the potential of $\delta^{30}Si_{\mathrm{diatom}}$ as an indicator of lacustrine environment, here we, for the first time, investigated the downcore variations in $\delta^{30}Si_{\mathrm{diatom}}$ in lacustrine sediments from Lake Huguangyan, a closed crater lake in South China.

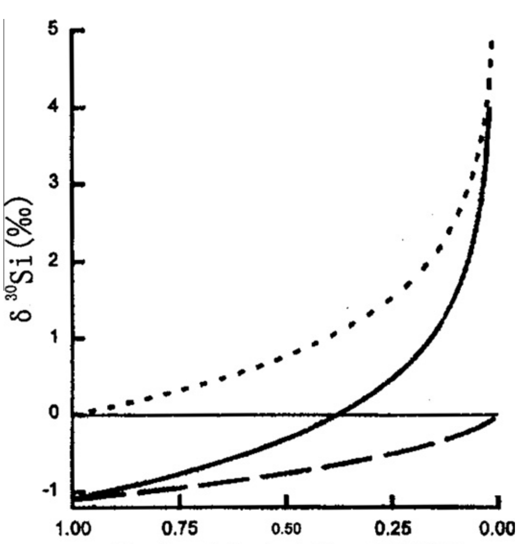

Fig. 1. $\delta^{30}Si$ variations during opal precipitation by diatoms according to the Rayleigh model. Curves depict changes in $\delta^{30}Si$ of dissolved silicic acid (dotted line), biogenic silica produced at each instant during the depletion of dissolved silicic acid (solid line), and accumulating biogenic silica (dashed line) (De La Rocha et al., 1997).

2. Study site

Lake Huguangyan (21°9′N, 110°17′E) is a closed crater lake, located on the Leizhou Peninsula, South China (Fig. 2A). It has a surface area of c. 2.3 km^2, a watershed area of c. 3.5 km^2, a mean depth of c. 12 m, and a maximum depth of c. 22 m (Chu et al., 2002). The regional climate is strongly influenced by the southeast monsoon, with lesser influence by the southwest monsoon (Fig. 2A). Thus it is obviously seasonal. More than 85% of the mean annual precipitation of 1600 mm falls between April and October, when warm–humid air from the southeast and southwest predominates. From November to March, cold–dry air from the north prevails and there is less precipitation. The mean annual temperature is c. 23 °C, and the mean annual evaporation is c. 1770 mm. There is neither inflow stream nor outflow stream. The lake water mainly comes from the rainfall on the lake, the surface runoff and the underground water from the catchment. Available hydrological data from the Management Bureau of Lake Huguangyan show that Lake Huguangyan has a very small fluctuation of the water level during AD 1960–2004, with interannual variations less than 1.5 m. The lake water is weakly alkaline with a pH 7.6. Ca^{2+}, Mg^{2+} and HCO_3^- are the dominant cations and anions in lake water.

The crater basin was created from basaltic phreatomagmatic eruptions (Liu, 1999; Chu et al., 2002). The tephra ring is 10–58 m above the lake surface and consists of pyroclast (Chu et al., 2002). K/Ar dated basalts from the volcanoclastic breccia of the crater rim have yielded an age of about 127 ka, suggesting lake formation at roughly that time (Fong, 1992; Yancheva et al., 2007). The catchment is well covered by evergreen sub-tropical forest.

3. Field and laboratory work

Sediment cores were retrieved from the center part of Lake Huguangyan at a water depth of 17 m (Fig. 2B) in December 2004, using a gravity sampler. The water–sediment interface was not disturbed during coring and the sediment cores were perfectly preserved. They were immediately divided into 1.0–1.5 cm sections and put into plastic bags in the field.

Analysis of the silicon isotope composition of diatoms requires samples to be almost pure diatom silica. Contamination by silt and clay particles may considerably influence the $\delta^{30}Si_{\mathrm{diatom}}$ signal because the generally used fluorination techniques liberate silicon from all the components (including silt and clay) in the sediment. Consequently, sediment samples need to be cleaned prior to analysis. Based on repeated experiments of various cleaning procedures and comparison observation in light microscope, a continuous five-stage cleaning method was established especially for Huguangyan sediments on the basis of the four-stage method by Morley et al. (2004), including organic matter and carbonate removal by HCl–H_2O_2, coarse detrital minerals removal by sieving, clay removal by differential settling, diatom purification by heavy liquid floatation and impure material removal by sieving. This method has been successfully used to produce 88 diatom samples with >95 diatom content from 142 primary sediment samples in Lake Huguangyan (Li and Chen, 2007). Among the 88 diatom samples, only 60 samples have enough materials for the silicon isotope analysis.

Silicon isotope ratios were determined by the SiF_4 method (Ding et al., 1996; Ding, 2004). The SiO_2 was reacted with BrF_5 in a metal

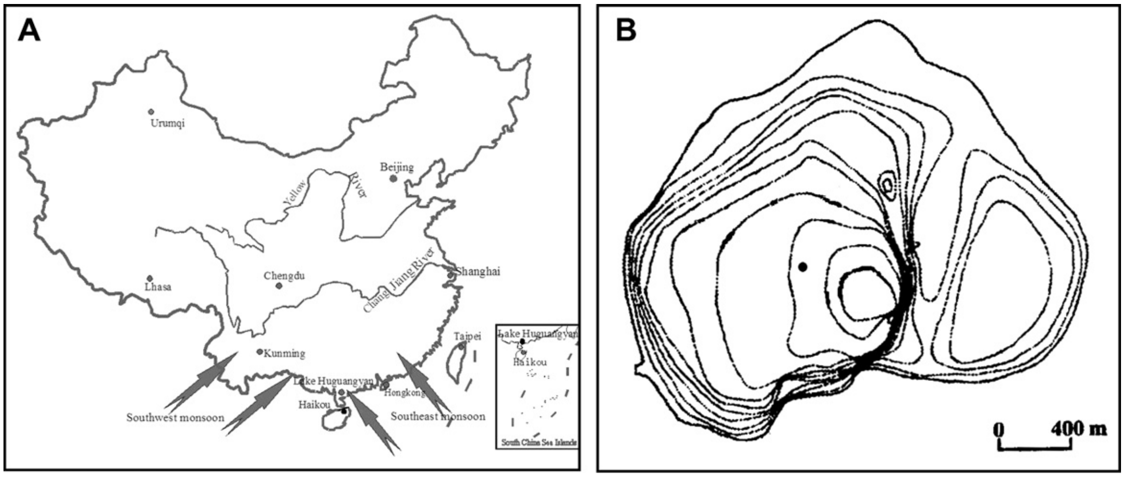

Fig. 2. Location and bathymetry of Lake Huguangyan with sampling site marked as solid circle. The interval of isobath curve is 2 m (Chu et al., 2002).

vacuum line to produce SiF_4. The SiF_4 was separated first from O_2, N_2, BrF_5 and BrF_3 by cryogenic separation using cold traps of dry ice–acetone melting temperature and liquid nitrogen temperature. Then the SiF_4 was purified by passing through a Cu tube containing pure Zn particles at 60 °C, where the remaining trace amounts of active fluorine compounds reacted with Zn to form ZnF_2 and $ZnBr_2$. Finally, the purified SiF_4 was collected for the silicon isotope analysis. δ^{30}Si were measured on a Finnigan MAT 253 mass spectrometer at the Key Laboratory of Isotope Geology, Ministry of Land and Resources. All results were reported as δ^{30}Si values relative to the standard NBS28:

$$\delta^{30}\text{Si}(\%) = ((R_{\text{sam}}/R_{\text{std}}) - 1) \times 1000 \tag{2}$$

where R_{sam} and R_{std} are the ratios of ^{30}Si to ^{28}Si in the sample and NBS28, respectively. Analytical precision on δ^{30}Si values is better than 0.1‰ (2σ).

Six terrestrial plant macrofossils were picked out from the sediment core to carry out radiocarbon dating on the accelerator mass spectrometry (AMS) at the Scottish Universities Environmental Research Centre AMS Facility. The calibrated age was determined from the University of Oxford Radiocarbon Accelerator Unit calibration program (OxCal3).

Specific activities of ^{210}Pb were determined using α-spectrometry through its granddaughter ^{210}Po, with ^{208}Po and ^{209}Po added as an internal yield tracer. Specific activities of ^{137}Cs were measured by γ-spectrometry using a Multichannel Analysis System (Canberra S-100) and low-background germanium detector. Contents of organic carbon were measured by the element analyzer (PE2400 SERIES II) after carbonate removal by HCl. Contents of biogenic silica were measured by flow injection spectrophotometry (molybdenum blue method) (Wang et al., 2000).

4. Results

The cored sediment in Lake Huguangyan consists of homogeneous greenish-gray gyttja without clear lamination. Here, ^{14}C, ^{210}Pb and ^{137}Cs are used to date the sediment core. Mass depth (g cm^{-2}), instead of depth (cm), is adopted to calculate sedimentation rate because sediment is usually compacted in the lower part of the sediment core, as confirmed by decreased sediment porosity with depth (Chen et al., 2005). The distribution pattern of ^{210}Pb$_{ex}$ in the sediment core (Fig. 3) indicates that the CIC model (Robbins and Edgington, 1975) can be used to calculate sedimentation rate. The result shows that the average sediment accumulation rate is 0.061 g cm^{-2} a^{-1}, which is supported by the distribution characteristics of ^{137}Cs in the sediment core. The peaks of ^{137}Cs occur from 1963 to 1976 (Fig. 3), which is well-known to be the main fallout period of global ^{137}Cs in the atmosphere. The accordance between ^{210}Pb$_{ex}$ and ^{137}Cs time markers indicates the stable sediment accumulation and good preservation conditions in Lake Huguangyan.

Linear interpolation between radiocarbon measurements from six terrestrial plant macrofossils is used to calculate sediment age, assuming that the sedimentation accumulation rate between the dated levels was linear. The average sedimentation rate in the upper part of the sediment core was 0.066 g cm^{-2} a^{-1} according to ^{14}C age of the plant macrofossils at depth of 54.5, 56 and 58 cm (Table 1). This is in good agreement with the ^{210}Pb and ^{137}Cs dating result. A decreased accumulation rate of 0.036 g cm^{-2} a^{-1} occurred in the lower part of the sediment core possibly as a result of less human influence.

Diatom samples for the silicon isotope analysis were confirmed in light microscope to be almost pure diatoms (Fig. 4). The influence of contaminants on the δ^{30}Si$_{diatom}$ signal was thus negligible. The δ^{30}Si$_{diatom}$ values vary substantially between −0.6‰ and 1.1‰ throughout the sediment core (Table 2). There is an obvious shift to the most negative δ^{30}Si$_{diatom}$ values during AD 1580–1920 (Fig. 5). Contents of biogenic silica (BS) vary from 4.0% to 13.8%, and contents of organic carbon (OC) between 1.25% and 4.88%. There are broad similarities among the records of δ^{30}Si$_{diatom}$, BS and OC in the sediment core (Fig. 5).

5. Discussion

During diatom growing, there is a preferential incorporation of light silicon isotope (^{28}Si) into biogenic silica, progressively resulting in the enrichment of heavy silicon isotope (^{30}Si) in remaining dissolved silicic acid. As described by De La Rocha et al. (1997), variations in the silicon isotope composition of diatom silica and dissolved silicic acid follow the Rayleigh model (Fig. 1) in a closed system with a finite pool of dissolved silicic acid. In natural lake system, there is continuous input of dissolved silicic acid from the catchment into lake water, so a model based on continuous flux of dissolved silicic acid into the system is more appropriate. In the continuous flux model, δ^{30}Si of both diatom silica and ambient dissolved silicic acid increases with increasing nutrient utilization until a steady state is reached between nutrients input and biological removal (De La Rocha et al., 1998). In Lake Huguangyan, δ^{30}Si$_{diatom}$ and BS display frequent fluctuations in the sediment core (Fig. 5), implying it is not at steady state. Dissolved silicic acid

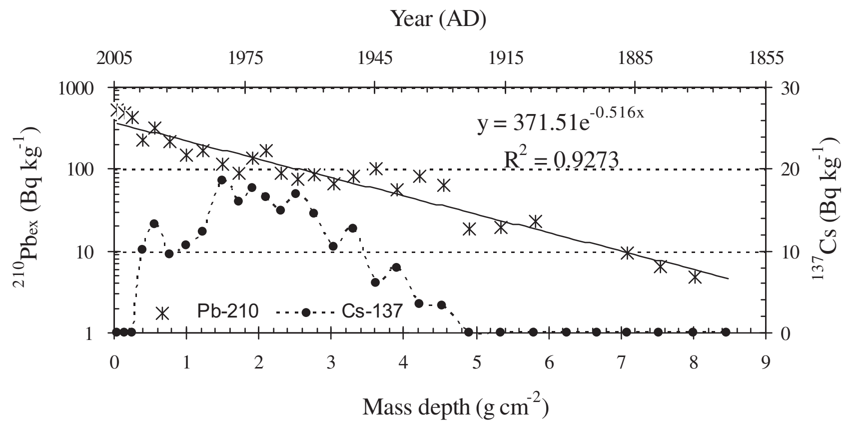

Fig. 3. Profiles of $^{210}Pb_{ex}$ and ^{137}Cs in the sediment core of Lake Huguangyan.

Table 1
Radiocarbon dating results in Lake Huguangyan.

Sample ID	Lab ID	Material	$\delta^{13}C$ (‰ PDB)	^{14}C age (BP)	Calibrated age (BP)	Age used for calculation (BP)	Depth (cm)	Mass depth (g cm^{-2})	Sedimentation rate (g cm^{-2} a^{-1})
F-55	SUERC-8674	Terrestrial plant	−28.1	290 ± 18	265 ± 35	265	54.5	17.694	0.067
F-57	SUERC-8675	Terrestrial plant	−27.7	303 ± 20	280 ± 35	280	56.0	18.738	0.067
F-58-1	SUERC-8676	Terrestrial plant	−25	366 ± 23	370 ± 35	328	58.0	21.362	0.065
F-58-2	SUERC-8677	Terrestrial plant	−27.7	319 ± 20	300 ± 35				
F-58-3	SUERC-8678	Terrestrial plant	−29.2	351 ± 23	315 ± 35				
F-105	SUERC-8679	Terrestrial plant	−25	1273 ± 20	1275 ± 35	1275	116.0	45.480	0.036

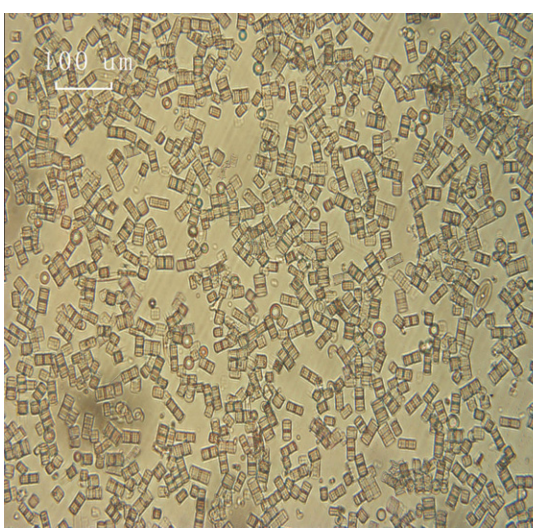

Fig. 4. Light microscope images of diatom sample used for the silicon isotope analysis.

in natural water comes mainly from weathering of igneous materials. $\delta^{30}Si$ of dissolved silicic acid supplied to lake water should be quite invariant in Lake Huguangyan since sources and routes of dissolved silicic acid are unlikely to be changed in this small closed crater lake with a catchment area of only 3.5 km^2. Increased utilization of dissolved silicic acid will result in an increase of the $\delta^{30}Si_{diatom}$ values according to the continuous flux model. Thus, $\delta^{30}Si_{diatom}$ in Huguangyan sediments may record changes in the percentage utilization of dissolved silicic acid by diatoms. This interpretation is supported by the broad similarities between $\delta^{30}Si_{diatom}$ and BS in the sediment core (Fig. 5). Higher BS generally

Table 2
$\delta^{30}Si_{diatom}$ values in the sediment core of Lake Huguangyan.

Sedimentation age (AD)	$^{30}Si_{diatom}$ (‰)	Sedimentation age (AD)	$^{30}Si_{diatom}$ (‰)
2003	1.1	1292	0.6
2001	0.8	1266	0.7
1999	0.7	1180	0.0
1989	0.7	1115	0.4
1976	0.2	1056	0.1
1970	0.0	1001	0.2
1963	0.2	921	0.7
1940	0.7	878	0.5
1932	0.7	858	0.4
1901	−0.4	724	0.6
1884	0.1	668	0.5
1839	−0.3	590	0.2
1798	0.3	576	0.0
1769	0.7	562	0.2
1722	−0.1	548	0.1
1676	−0.6	520	0.3
1603	−0.1	506	0.6
1588	0.4	491	0.0
1572	0.5	477	0.6
1556	1.0	463	0.5
1523	0.8	435	0.1
1508	0.6	379	0.2
1493	0.4	365	0.0
1456	0.3	336	0.1
1438	0.5	322	0.2
1420	0.8	308	0.2
1401	0.5	294	0.2
1360	0.3	280	0.5
1339	0.1	265	0.5
1316	0.6	238	0.3

indicates increased diatom production, which may be attributed to two possibilities. One is increased utilization of dissolved silicic acid; the other is increased nutrients input without increased

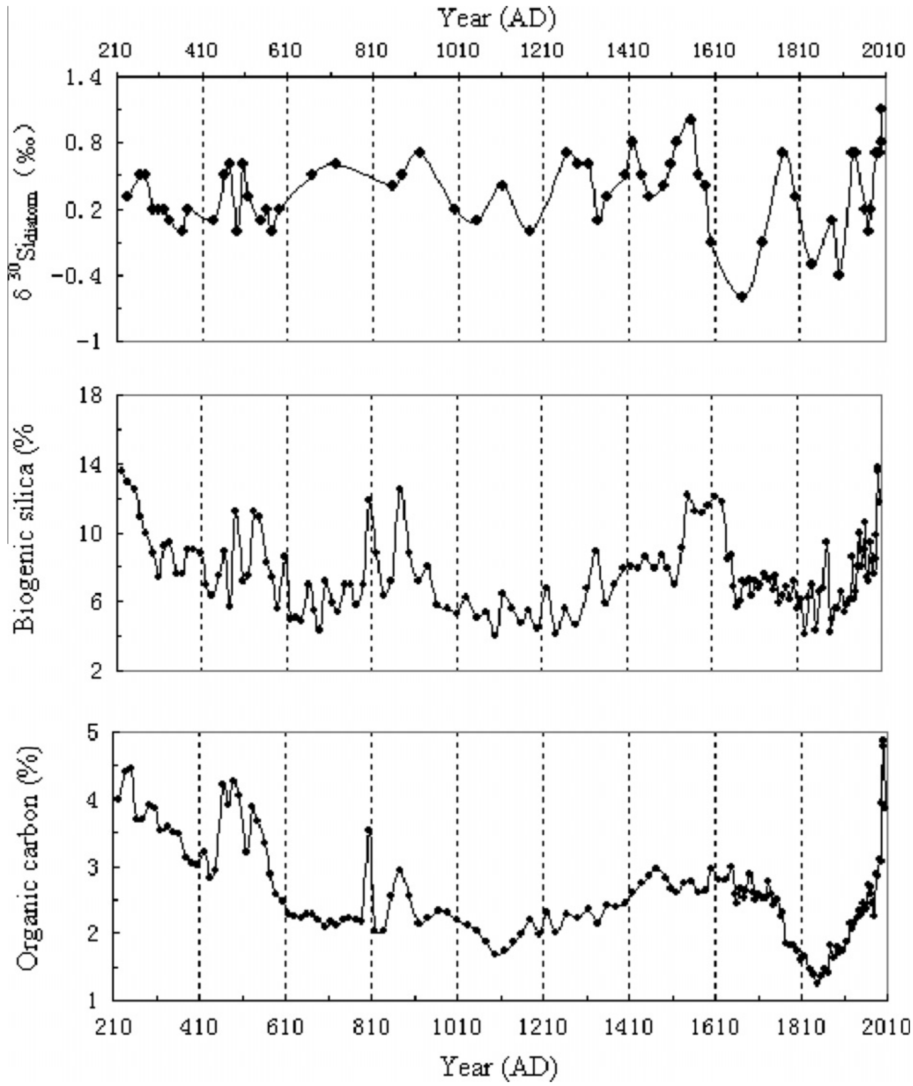

Fig. 5. Variations in $\delta^{30}Si_{diatom}$, BS and OC in the sediment core of Lake Huguangyan.

percentage utilization of dissolved silicic acid. The latter is obviously contrary to the fact that heavier $\delta^{30}Si_{diatom}$ occurs contemporaneously with higher BS (Fig. 5). It seems that diatom production responds primarily to changes in the extent of dissolved silicic acid utilization in Lake Huguangyan, although nutrients input should not be neglected. Heavier $\delta^{30}Si_{diatom}$ and higher BS indicate increased diatom production and increased dissolved silicic acid utilization in Lake Huguangyan.

Field investigations in ocean have confirmed the link between the dissolved silicic acid utilization and the silicon isotope composition of marine diatoms (De La Rocha et al., 2000; Varela et al., 2004; Cardinal et al., 2005, 2007), and $\delta^{30}Si_{diatom}$ in marine sediments has been successfully used as a proxy to reconstruct the history of marine relative silicic acid use by diatoms (De La Rocha et al., 1998; Brzezinski et al., 2002). With regard to silicon isotope fractionation between fresh water diatom and lake water, Alleman et al. (2005) have carried out systematic silicon isotopic determinations in fresh water and biogenic opal of Lake Tanganyika. Diatoms, collected simultaneously with the lake water during the survey, display relatively lighter $\delta^{29}Si$ than the surrounding water. The $\delta^{29}Si$ difference between the lake water and diatoms is -0.56 ± 0.1‰ in Lake Tanganyika (Alleman et al., 2005), which is consistent with the $\delta^{29}Si$ difference between the dissolved silicon and marine diatoms of -0.57 ‰ (calculated from the $\delta^{30}Si$ difference of -1.1‰ according to De La Rocha et al., 1997 and $\delta^{29}Si = \delta^{30}Si/1.934$). This confirms the non-species, non-temperature dependent character of the silicon isotope fractionation by diatoms as previously reported on marine diatoms (De La Rocha et al., 1997). The vertical profiles of dissolved silicon concentration and $\delta^{29}Si$ in water of Lake Tanganyika show a heavier isotopic signature in surface waters associated to low Si concentrations and inversely in deep waters, which is attributed mainly to a preferential ^{28}Si biological uptake by diatoms in surface waters. Alleman

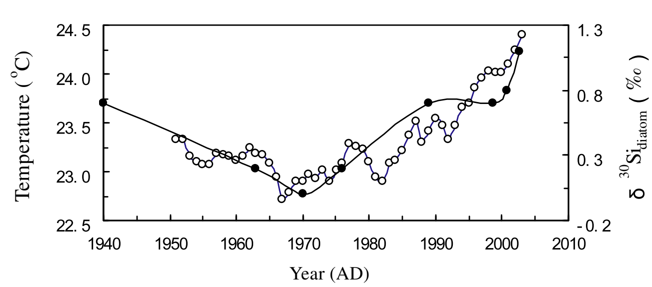

Fig. 6. Covariant trends between $\delta^{30}Si_{diatom}$ and the temperature records in Zhanjiang Weather Station. Filled circles represent $\delta^{30}Si_{diatom}$, and open circles stand for temperature.

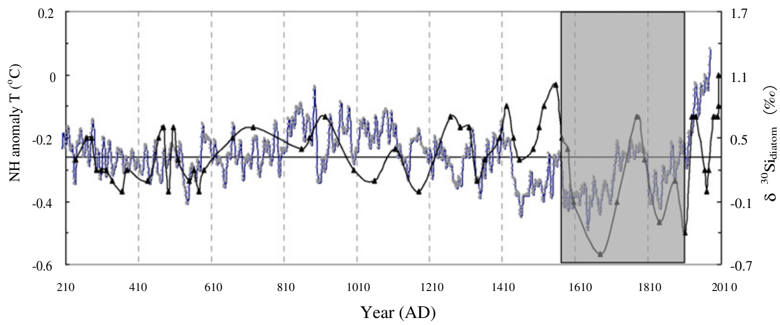

Fig. 7. Variations in $\delta^{30}Si_{diatom}$ and the northern hemisphere temperature (Mann and Jones, 2003) over the past 2000 years. Filled triangles represent $\delta^{30}Si_{diatom}$, and open circles stand for northern hemisphere temperature anomaly.

et al.'s study (2005), thus, provides the first evidence for that silicon isotopes are a relevant proxy to relative silicon utilization by diatoms in fresh water environments. Our investigation on the silicon isotope composition of diatom silica in the sediment core of Lake Huguangyan gives further support to $\delta^{30}Si_{diatom}$'s applicability for monitoring past changes in the percentage utilization of dissolved silicic acid by fresh water diatoms.

It is well-known that temperature and nutrients are two key factors controlling diatom growth in lake water. Increased percentage utilization of dissolved silicic acid by diatoms may occur in two situations. One is increased temperature; the other is reduced input of dissolved silicic acid. In Lake Huguangyan, high BS and OC occurs contemporaneously with heavier $\delta^{30}Si_{diatom}$ in the sediment core (Fig. 5), implying that the nutrients input is not reduced during high percentage utilization of dissolved silicic acid. Therefore, increased percentage utilization of dissolved silicic acid should be attributed mainly to increased temperature instead of reduced nutrients input in Lake Huguangyan. $\delta^{30}Si_{diatom}$ may thus have the potential of be a paleotemperature proxy. Heavier $\delta^{30}Si_{diatom}$ indicates greater dissolved silicic acid utilization at higher temperature while lighter $\delta^{30}Si_{diatom}$ reflects decreased utilization at lower temperature. Our inference is supported by good correlation between $\delta^{30}Si_{diatom}$ and the temperature records available from AD 1951 to the present in Zhanjiang Weather Station, 19 km to the northeast of Lake Huguangyan (Fig. 6). It is also supported by broad similarities between $\delta^{30}Si_{diatom}$ and the northern hemisphere temperature over the past 2000 years (Fig. 7).

As a whole, $\delta^{30}Si_{diatom}$ displays similar variations to the northern hemisphere temperature over the past 2000 years (Fig. 7), although they are at different resolutions and therefore difficult to compare in a statistical sense. In recent half century, $\delta^{30}Si_{diatom}$ showed a sharp increase and reached the most positive value of 1.1‰ in 2003, which was interrupted by a short interval of more negative $\delta^{30}Si_{diatom}$ values during AD 1963–1976 (Figs. 6 and 7). $\delta^{30}Si_{diatom}$ variations are in good agreement with the temperature records from AD 1951 to the present in Zhanjiang Weather Station. The temperature records show a marked warming in recent 50 years, which was interrupted by a relatively cold interval in AD 1965–1975 (Fig. 6). The good accordance between $\delta^{30}Si_{diatom}$ and the temperature records demonstrates that $\delta^{30}Si_{diatom}$ is a reliable temperature proxy in Lake Huguangyan.

The most negative $\delta^{30}Si_{diatom}$ values occur from AD 1580 to 1920 (Fig. 7). This implies that AD 1580–1920 is the coldest period in Lake Huguanguan over the past 2000 years. The lowest northern hemisphere temperature occurs almost in the same period, which is usually called 'Little Ice Age' (LIA). The LIA at earlier stage is referred to the cold period in Europe from AD 1550–1850 (Lamb, 1977). In recent years, the LIA has been increasingly recognized at widespread geographic locations (Keigwin, 1996; Verschuren et al., 2000; Lamoureux et al., 2001; Chen et al., 2005). This study provides evidence for the existence of the LIA in tropical South China.

From AD 210 to 1210, the $\delta^{30}Si_{diatom}$ values fluctuated mildly between 0.0‰ and 0.7‰, implying a relatively stable climate (Fig. 7). Three periods of temperature variations can be further identified: a cold period during AD 240–650 interrupted by two warm intervals in AD 240–280 and AD 460–510, a warm period between AD 650–1000, a return to cold period during AD 1000–1210. The former two periods are consistent with the variations in the northern hemisphere temperature. The last period seems to be not in phase with the northern hemisphere temperature changes, but it is consistent to a cold climate during AD 1000–1200 in the Tibetan Plateau, China (Yang and Braeuning, 2006). It is acceptable that regional temperature variation does not always follow the global temperature pattern.

From AD 1210 to 1580, The amplitude and rate of $\delta^{30}Si_{diatom}$ variations are obviously increased. It was first diminished from 0.6‰ to 0.1‰ in AD 1340, then increased sharply to 0.8‰ in AD 1420, followed by a rapid decline to 0.3‰ in AD 1460 and a steep increase to 1.0‰ in AD 1556, and finally declined until the LIA. This may represent the unstable climate during the transition to the LIA. The northern hemisphere temperature also shows similar change characteristics in this period (Fig. 7).

As a paleoenvironmental proxy, $\delta^{30}Si_{diatom}$ has two advantages over BS. Firstly, the $\delta^{30}Si_{diatom}$ signal can be better preserved in lacustrine sediments than BS. Diatom dissolution usually happens in sediments due to early diagenesis, so the original BS signal is changed. However, it has been observed that diatoms retain their $\delta^{30}Si$ signal even after dissolution of 26% of the opal in their frustules (De La Rocha et al., 1998). Demarest et al. (2009) also demonstrated that variation of <20% in the percentage of biogenic SiO_2 lost to dissolution will not result in analytically detectable shifts in $\delta^{30}Si_{diatom}$. In view of the problems of diatom dissolution at the sediment–water interface, the diatom silicon isotope analysis has become a potentially very important methodology to reconstruct paleoproductivity (Mackay, 2007). Secondly, $\delta^{30}Si_{diatom}$ reflects temperature changes more precisely than BS because it is less influenced by variations in the amount of nutrients input from the catchment into lake water.

6. Conclusions

The oxygen isotope composition of authigenic carbonate and diatom silica in lacustrine sediments has been routinely used as paleotemperature indicator at intermediate and high latitudes, where there is a Dansgaard relationship between $\delta^{18}O$ in precipitation ($\delta^{18}O_{precipitation}$) and temperature of approximately +0.6‰/°C (Dansgaard, 1964). However, the Dansgaard relationship is not common at low latitude because of the influence of the amount effect on $\delta^{18}O_{precipitation}$, thus there are less proxies suitable for the temperature reconstruction in tropical terrestrial region. In an initial attempt to explore the potential of $\delta^{30}Si_{diatom}$ as a paleotemperature proxy, we have made the first measurements of $\delta^{30}Si_{diatom}$ in lacustrine sediments in this study. Significant variation was found for $\delta^{30}Si_{diatom}$ (from −0.6‰ to 1.1‰) in the sediment core of Lake Huguangyan and $^{30}Si_{diatom}$ has proven to be a promising paleotemperature proxy. Heavier $\delta^{30}Si_{diatom}$ generally indicates greater dissolved silicic acid utilization at higher temperature while lighter $\delta^{30}Si_{diatom}$ reflects decreased utilization at lower temperature. The most negative $\delta^{30}Si_{diatom}$ values between AD 1580 and 1920 indicate the coldest period in Lake Huguangyan over the past 2000 years, confirming the influence of the Little Ice Age. The response of the silicon isotope composition of diatom to dissolved silicon utilization and climate changes, seems to be almost simultaneous. The diatom silicon isotope records may thus be very useful in studying the silicon cycle and the past climate changes in continent environment.

Here we, for the first time, presented the data on the downcore variations in $\delta^{30}Si_{diatom}$ and have glancingly discussed its correlations with BS, OC and temperature in Lake Huguangyan. Our understanding of the silicon isotopes of diatoms is far from comprehensive, but it serves to highlight the potential of $\delta^{30}Si_{diatom}$ as a new paleoenvironmental proxy in lacustrine sediments. Detailed investigations on the silicon isotopes of diatom silica in more lakes would be desirable in further research.

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