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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:

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

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 $\delta^{30}Si_{\text{diatom}}$ 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 $\delta^{30}Si_{\text{diatom}}$ values, while decreased utilization results in more negative $\delta^{30}Si_{\text{diatom}}$ values. Therefore, $\delta^{30}Si_{\text{diatom}}$ 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 $\delta^{30}Si_{\text{diatom}}$ 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

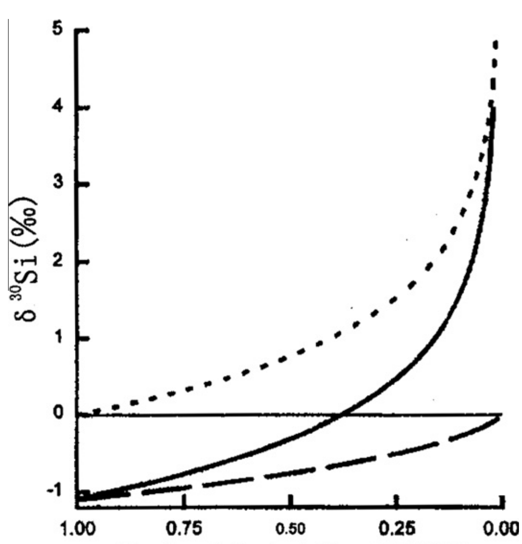

Fig. 1. $\delta^{30}Si$ variations during opal precipitation by diatoms according to the Rayleigh model. Curves depict changes in $\delta^{30}Si$ of dissolved silicic acid (dotted line), biogenic silica produced at each instant during the depletion of dissolved silicic acid (solid line), and accumulating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

scarce until now. With an aim of exploring the potential of $\delta^{30}Si_{\text{diatom}}$ as an indicator of lacustrine environment, here we, for the first time, investigated the downcore variations in $\delta^{30}Si_{\text{diatom}}$ in lacustrine sediments from Lake Huguangyan, a closed crater lake in South China.

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 $\delta^{30}Si_{\text{diatom}}$ 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