

Potential application of biogenic silica as an indicator of paleo-primary productivity in East Antarctic lakes

JIANG Shan, LIU XiaoDong*, XU LiQiang & SUN LiGuang

Institute of Polar Environment, University of Science and Technology of China, Hefei 230026, China

Received February 26, 2011, accepted August 14, 2011

Abstract We collected two lake sediment cores (MC and DM) from the East Antarctic region for analysis of biogenic silica and other biogeochemical parameters (e.g., organic matter, C, N, S, H). Based on synthetically comparative research, we focused on the potential application of biogenic silica (BSi) for the reconstruction of paleo-primary productivity in the East Antarctic lakes. Analytical results showed that a large number of diatoms were well preserved in the freshwater lake sediments, and that concentrations of biogenic silica displayed notable fluctuations over different water depths. The content of biogenic silica had a consistent profile over water depth, and this pattern changed with organic matter, reflecting their potential as eco-environmental proxies. Low levels of BSi and organic matter indicated reduction of lake algal production, and corresponded to decreased lake primary productivity. Due to the fragile ecosystem state and limited contribution of terrestrial organic matter in the East Antarctic lakes, the contents of biogenic silica in the lacustrine sediments can sensitively indicate the evolutionary history of paleo-primary productivity. Overall, BSi is an ideal proxy for the reconstruction of past eco-environmental change recorded in the lacustrine sediments on East Antarctica.

Keywords East Antarctica, lacustrine sediments, BSi, paleo-primary productivity, organic matter

Citation: Jiang S, Liu X D, Xu L Q, et al. Potential application of biogenic silica as an indicator of paleo-primary productivity in East Antarctic lakes. *Adv Polar Sci*, 2011, 22: 131–142, doi: 10.3724/SP.J.1085.2011.00131

0 Introduction

Lake sediments are good materials to infer paleo-climatic and paleo-environmental change. These sediments can be used to record abundant information about climate, vegetation and human activity over time. At present, lake sediments have been used widely to study past global changes^[1–2].

Due to the fragile characteristics of lake ecosystems in Antarctica, even slight changes in environmental conditions would result in great fluctuations of lacustrine ecology and biogenic production. These variations are likely to be recorded in the lacustrine sediments^[3–4].

Multiple biogeochemical proxies (e.g., pigments, nutrient elements, amino acid, isotopes) from lake

sediments can be used to reconstruct paleo-primary productivity^[5–6]. In recent years, studies on biogenic silica (BSi) in lake sediments have drawn more attention from researchers in this field^[7]. Biogenic silica (compared to silica crystals), is a type of amorphous silicon. It mainly derived from diatom frustules in water, and a small amount also originated from plant silicate phytoliths, sponge spicules, radiolaria and chrysophyta^[8]. Silicon is the second most abundant element. Compared with oxygen, nitrogen and carbon, the biogeochemical cycle of silicon is slow, while its sedimentary rate is rapid. Thus, silicon can be preserved in the form of biogenic silica in sediments^[9]. BSi is a measurement of silica produced by diatoms and chrysophytes, and is a reasonably

Jiang Shan (female, Doctor student, polar paleoecological research, email: jscyc@mail.ustc.edu.cn)

*Corresponding author(email: ycx@ustc.edu.cn)

good proxy for the production of those algal species. In addition, because change in lake productivity has a close relationship with nutrient concentration and surface temperature in the water, BSi in lake sediments may reflect change in historical climate conditions^[10]. Numerous studies from high latitudes, such as Lake Baikal in Russia^[11–12], mid-latitudes, such as Lake Pipa in Japan^[13], and low latitudes, such as Huguangyan Maar lake in the Leizhou peninsula in China^[14], as well as Arctic lake sediments^[15], have shown that high BSi values correspond to warm and humid climate conditions. These values strongly contrast those of low level BSi generated from cold and dry climates. The above results suggest that variation in diatom productivity is closely related to climate change. Thus, the BSi recorded in lacustrine sediments can be used to indicate paleoclimatic changes. Even with the possibly negative influence of post-depositional dissolution processes and sedimentary rates^[12], BSi continues to be an ideal proxy for reconstruction of past eco-environmental changes in lakes^[10].

A multi-proxy analysis, combined with chronology results, is helpful for high-resolution reconstruction of paleo-climate, paleo-precipitation and paleo-salinity changes, as well as glacial advance and retreat patterns^[16]. However, as an important proxy for primary productivity, the application of BSi is still limited for sediments from high latitude Antarctic lakes. In this study, we investigated biogenic silica in two lake sediment cores from the Larsemann Hills. Combined with other biogeochemical proxies, we discuss the potential application of biogenic silica to paleo-environmental reconstruction, especially on historic changes of lake primary productivity in East Antarctica.

1 Study area

The Larsemann Hills constitute an ice-free area of approximately 40 km², located on the Ingrid Christensen Coast of Princess Elizabeth Land in Eastern Antarctica (69°12'S–69°28'S, 76°E–76°30'E) (Figure 1). The Larsemann Hills have a continental Antarctic climate, which is colder and drier than the maritime Antarctic. More than 150 freshwater lakes are located in this area. The sediments are particularly well suited for paleolimnological studies, since there is no significant bioturbation and a limited season of open water when wind-induced mixing

might encourage resuspension.

The two sediment cores investigated in this study were recovered from Mochou Lake and Daming Lake around Zhongshan Station on the Mirror Peninsula (Figure 1). These two lakes were formed by glacial erosion, and predominantly are fed by snow-melt water and local precipitation.

Based on the physico-chemical data of Mochou Lake reported by Li et al.^[4], the altitude is 8 m (a.s.l.). The maximum depth is about 4 m, the surface area is 0.005 km², and the catchment area is 0.127 km². Lake water is lost mainly through evaporation and outflow in the summer. Although Mochou Lake is still considered to be oligotrophic, the concentrations of nutrient elements are much higher than other lakes in the Larsemann Hills. In Mochou Lake, the concentrations of nutrient elements, species and biomass are much higher than those of other lakes in the Larsemann Hills, and inorganic matter mainly exists in the form of NH₄-N and PO₄-P. The dissolved oxygen is saturated, and the water body is weak acid to weak alkaline. Na⁺ and Cl⁻ are the dominant species of cation and anion, respectively^[17]. With respect to Daming Lake it is a shallow lake with a maximum water depth of 4 m and an altitude of 30 m above sea level (a.s.l.). The lake is weakly brackish and remains ice covered for 9–10 months of the year. According to limnological data^[18], weak seasonal thermal, salinity and nutrient stratification occur under the ice cover when the upper part of the water column is cooled and diluted by melting ice. In winter, under the ice, oxygen is consumed by the biota and weak anoxia can persist.

2 Sampling and methods

The MC (85 cm) and DM (63 cm) cores were recovered from Mochou Lake and Daming Lake, respectively (Figure 1). In order to avoid the influence of human disturbance on the sedimentary environment, the coring site at MC was far away from the pumping region, where is an important source of cooling water for Zhongshan Station. The detailed lithological profile of MC has been described by Liu et al.^[19]. Based on lithological characteristics of the MC core, the bottom sediment unit (between 85 and 74 cm) was distinctly different from the top 70 cm sediment layer. The former mainly consists of black

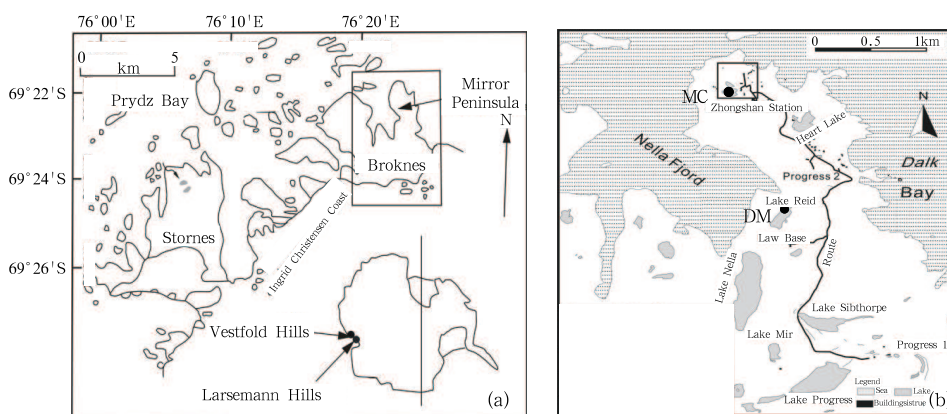


Figure 1 Study area showing the sites at Mochou and Daming lakes.

organic mud, which has a strong and unpleasant odour, most likely from hydrogen sulphide accumulated in the sediments, as a result of anoxia. However, the latter is dominated by relatively fresh and greenish organic matter, which mainly originates from crudely laminated algal and microbial mats. The middle sediment unit, between 74 and 70 cm, shows transitional lithological characteristics. This is the result of the sedimentary marine-freshwater transition that is evident in all regional lakes below an altitude of 8 m (e.g. [20]). Additionally, in the bottom 11 cm of sediments, some gravels were found to be rounded. However, a few clasts present in the top 70 cm sediment layer were subrounded or weakly rounded, indicating relatively short transportation processes and/or hydrodynamically weak sedimentary environments. The sedimentary change was consistent with the history of the Holocene sea-level fluctuation in the study area^[21–23]. In this study, we focused on the fresh water sediments above 70 cm. The lithology of the DM core was consistent with the description by Hodgson et al.^[18]. The surface 13 cm of sediments were not compressed, and mainly were composed of lake algae. The sediments between 13 and 17 cm became increasingly compressed, and their main components were still lake algae. However, gravel abundance increased gradually, and sediments from 17 to 63 cm were predominantly composed of gravels with a small amount of lake algae. Unlike the sedimentary conditions of low altitude Mochou Lake, Daming Lake experienced no submersion since the Last Glacial Period.

At present, there are many approaches to measuring the content of BSi^[20,24–25]. In our study, we used

modified alkali solvent extraction methods^[26–28]. The detailed procedures for these methods are described as follows. We transferred 100 mg of each freeze-dried sediment sample into a 10 mL polyethylene centrifuge tube, and then added H₂O₂ (10%). After letting the samples stand undisturbed for 30 min, we added HCl (1 mol·L⁻¹), and then oscillated them for half an hour. Then, 5 mL deionized water were added and then centrifuged for 8 min at a speed of 4 000 r·min⁻¹. The supernatant was removed and then dried overnight at 60°C in the oven. This procedure was followed in order to briefly dry the samples. Then, BSi was dissolved by treating the samples with 8 mL Na₂CO₃ (2 mol·L⁻¹) for 5 h at 85°C in a water bath, with complete sample agitation every hour. Then, the samples were centrifuged. Aliquots of 2.0 mL supernatant were removed, to which 5 mL HCl (1:1) and deionized H₂O were added. BSi was measured on these aliquots by Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES), and the relative standard deviation (RSD) was controlled within 2%.

Total nitrogen (TN), total carbon (TC), total sulfur (TS) and total hydrogen (H) were determined by a C/N/S/H elemental analyzer (vario EL III) with a RSD less than 1%. The potassium dichromate oxidation-chemical volumetric method was used to measure total organic carbon (TOC) with a RSD of 0.5%. The SEM analysis for diatoms was conducted on a FEI Sirion 200 schottky field emission scanning electron microscope at the University of Science and Technology of China. The samples were broken, mixed, and fixed on a sample holder, and coated with gold.

3 Results and discussion

3.1 Preservation of diatoms

In general, the majority of the biogenic silica originated from diatoms, as well as sponge spicules and the silicon minerals^[29]. Some sedimentary samples at different depths were scanned using the electron microscope. As seen in Figure 2, under the condition of relatively low magnification (less than 5 000 fold), we could observe a great proportion of algal residue (e.g., MC-43, MC-69). When the microscope was magnified more than 10 000 times, the structures of the diatom were observed

clearly (e.g., MC-5, MC-25, MC-59), suggesting that the diatoms were well preserved in the sediments. In fact, the diatom species preserved in lakes are well studied, and they typically are used to discuss historical records of climate variations in Antarctic lakes. For example, Hodgson et al.^[18] suggested that there were abundant diatoms in Daming Lake, and the species and abundance displayed clear change over water depths. The well preserved diatoms in the sediments of Daming and Mochou lakes provide the potential to measure pigment and BSi contents.

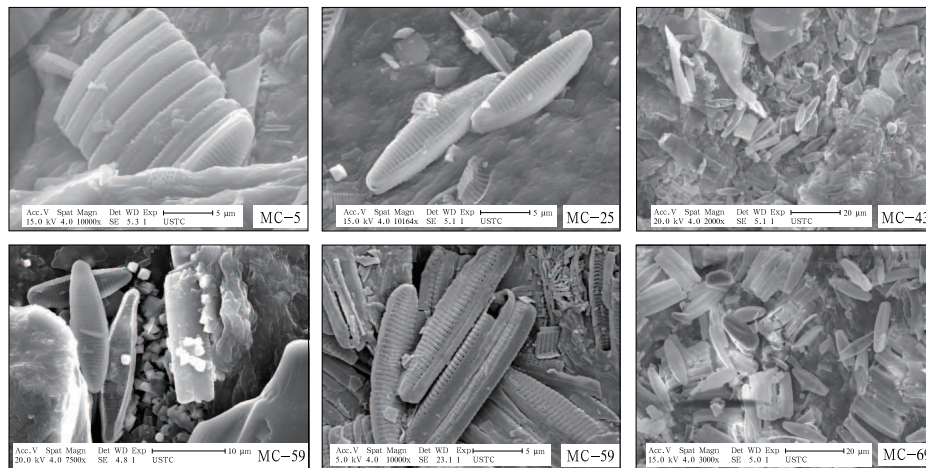


Figure 2 SEM photos of diatom samples from Mochou Lake sediments. The sample number in the diagram stands for the sampling depth.

3.2 Biogeochemical proxies in Mochou Lake sediments

The changes in TN, TC, TS, H, TOC and BSi are plotted in Figure 3 versus water depth and age. All the curves show the same pattern of change, indicating a common source. Correlation analyses suggest that TN, TC, H have strong positive correlations with TOC (Table 1). The values of TOC and TC are approximate, indicating low content of inorganic carbon, such as carbonate. Thus, total C, N and H were mainly derived from organic matter. Although TS and TOC showed the positive correlation at the 0.01 level (Table 1), the low correlation coefficient suggests that the sulfur content in the sediments may have been susceptible to influence of post-depositional oxidation conditions, except for the significant effect of organic matter inputs. This is supported by the fact that the catchment of the Mochou Lake lacks land vegetation, and the process of soil formation is very

limited due to low biological activity and poor chemical weathering^[4]. Thus, input of organic matter from terrestrial plants and nutrients washed out from terrestrial soils are insignificant. In Mochou Lake, the organic matter in the sediments is mainly composed of relatively fresh brown-green algae^[6]. Bird et al.^[30] suggested that post-depositional decomposition and microbial degradation of sedimentary organic matter were very weak, perhaps due to the extremely low temperatures in East Antarctica. Combined with observations on lithology and field study (exposed bedrock was found around the lake, where there was almost no vegetation cover), we presumed that the organic matter in the lake sediments mainly originated from endogenous material, namely dead algae^[16]. This hypothesis is supported by the following analyses on carbon and nitrogen isotopes, and organic geochemical parameters in the sediments. The vertical depth profile curves of TN and TOC are very similar, implying that

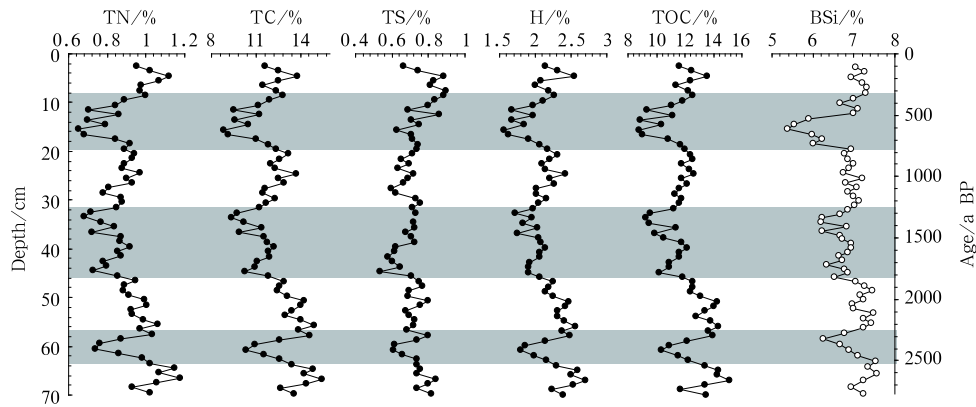


Figure 3 Profiles of biogeochemical proxies versus water depth and chronology in Mochou Lake lacustrine sediments. The age data on the right are redrawn from the reference 19.

Table 1 Correlations between TN, TC, TS, H, TOC and BSi in Mochou Lake lacustrine sediments

	TN	TC	TS	H	TOC	BSi	S2
TN	1.000						
TC	0.927	1.000					
TS	0.581	0.441	1.000				
H	0.923	0.977	0.441	1.000			
TOC	0.916	0.982	0.425	0.957	1.000		
BSi	0.742	0.768	0.282	0.749	0.776	1.000	
S2	0.916	0.866	0.353	0.846	0.871	0.755	1.000

Note: All the correlations are significant at the level of 0.01, with the exception of the correlations between BSi, S2 and TS, which are at the 0.05 level.

these two proxies can be used to indicate the change of lake algal abundance in Mochou Lake. Thus, changes of TOC and TN have clear eco-environmental implications, and their high values are consistent with the high algal growth and high primary productivity of the lake.

3.3 Source of sedimentary organic matter in lacustrine sediments

The direct influence of modern human activity on sedimentary organic matter should not be ignored. Several stations have been built around the study area since 1986 (e.g., Zhongshan Station, Progress 1 and 2, Law Base). Thus, the study samples are likely to be subject to frequent anthropogenic influences. For instance, as an important source of cooling water for Zhongshan Station, the outlet water into Mochou Lake might contain some human-derived organic components, and this could pollute the lake water and the deposited sediments in Mochou Lake, especially in the surface sediment samples. In order to avoid human impacts of outwater on sedimentary composition in the MC core, the coring site of

MC was far away from the pumping site (Figure 1). Indeed, according to studies of human impacts on freshwater lakes in the Larsemann Hills, prior to 1986, local human impact was virtually nil^[31]. Thus, the environmental changes associated with human activities have been very sudden. Based on the result of chronology of the MC core^[19], the adjacent 1 cm samples represent approximately 40 years intervals. Since the Zhongshan Station was built only 20 years ago, the anthropogenic pollution may not have caused serious influence on the chemical composition of lacustrine sediments below the surface. In order to further confirm this result, we identified the source of organic composition and assessed the possibility of anthropogenic pollution and post-depositional degradation on sedimentary organic matter, based on analyses of carbon, nitrogen isotope compositions and organic geochemical parameters.

Stable carbon and nitrogen isotopes, and elemental C/N ratios have been used effectively to evaluate the sources of organic compositions in lake sediments^[32]. The values of $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ in Mochou sediments varied

from -11.0‰ to -9.1‰ , and from 2.9‰ to 4.2‰ , respectively. In addition, both isotopes showed small fluctuations (Figure 4). In comparison with data of high-latitude plants and other lake sediments, the $\delta^{13}\text{C}_{\text{org}}$ values of Mochou Lake sediments are extremely high. In fact, algae in the moats, shallow water or lakes with seasonal ice-cover commonly have very high $\delta^{13}\text{C}_{\text{org}}$ ($\sim -10\text{‰}$) in East Antarctica^[33–34]. This is likely caused by the CO_2 -diffusion limited environment that results from high primary productivity in summer. Nevertheless, Antarctic phytoplankton growing in such environmental conditions have low $\delta^{15}\text{N}$ values, generally varying from -5‰ to 6‰ ^[35], and the fluctuations of $\delta^{15}\text{N}$ can reflect the variation of the organic matter in both N_2 -fixing plants and non- N_2 fixing algae. If anthropogenic organic components have significantly influenced Mochou Lake sediments, the values of $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ can change sensitively in the subsurface sediment samples. According to data previously reported, sewage generally has significantly high $\delta^{15}\text{N}$, but low $\delta^{13}\text{C}$ values^[36]. For example, the $\delta^{13}\text{C}$ of surface sediments adjacent to the sewage outfall was as below as -22‰ at the McMurdo Station in Antarctica, and this result also was found at other sewage discharge points^[36] or in the sedimentary organic composition impacted by human activities^[37–38]. However, the $\delta^{13}\text{C}$ values in the upper MC sediments remained at high levels (about -10‰), suggesting that the predominant factor controlling $\delta^{13}\text{C}$ variations is likely to be algal production, and the effect of the anthropogenic organic input was negligible. Assuming that the anthropogenic organic component could contribute to the entire variation of $\delta^{13}\text{C}_{\text{org}}$ in the MC sediments, we employed the sim-

ple two end-member mixture model (algae and anthropogenic sources) for our analysis. The calculated results showed that less than 10% of the organic component was from anthropogenic sources. In fact, the variation of sedimentary $\delta^{13}\text{C}_{\text{org}}$ in the Mochou Lake was related closely to the high algal productivity condition, and the $\sim 2\text{‰}$ difference throughout the $\delta^{13}\text{C}_{\text{org}}$ profile was largely due to the change of historical primary productivity over the past 3 000 years (to be addressed in detail in a future paper). The extremely high $\delta^{13}\text{C}_{\text{org}}$ values of Mochou Lake sediments appear to be related to the intensified photosynthesis of algae, and the fluctuation of $\delta^{13}\text{C}_{\text{org}}$ down the depth profile is likely caused by change of historical primary productivity of the lake. With increasing algal biomass and sufficient solar radiation, intensified algal photosynthesis allows dissolved inorganic carbon to be diffused into algal cells at maximum speed and then assimilated. This could lead to a significant weakening of the isotopic fractionation between the carbon substrates and the organic products, which would result in more ^{13}C assimilated into plants and higher $\delta^{13}\text{C}_{\text{org}}$ values in lacustrine sediments. Conversely, natural lake algae generally are depleted in ^{15}N relative to human-derived organic matter^[39]. Waste water typically has a $\delta^{15}\text{N}$ of 10‰ – 22‰ , and even treated sewage also has relatively high $\delta^{15}\text{N}$ ($\sim 10\text{‰}$)^[40]. As shown in Figure 4, there was no significant change between $\delta^{15}\text{N}$ values in the upper and lower samples. The $\delta^{15}\text{N}$ values in the uppermost samples did not reach peak levels throughout the MC sediment core, and the values remained very low ($\sim 4\text{‰}$). This finding is consistent with the results of $\delta^{13}\text{C}$. Thus, we suggested that the input of the anthropogenic organic component should have weak effects on MC sediments,

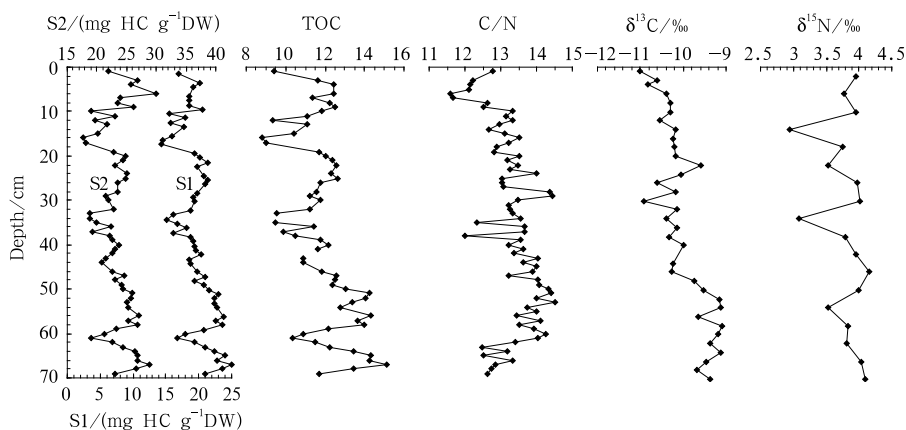


Figure 4 Changes of organic matter proxies including S1, S2, TOC, C/N, $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ in Mochou lacustrine sediments.

and that variations of $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ reflect characteristics of organic components from natural sources.

In the MC lacustrine sediments, the C/N ratios exhibited a small range, varying from 11.6 to 14.5, with a mean of 13.2. The C/N ratios indicated that the organic matter was predominantly characteristic of an autochthonous source^[41]. The lower C/N in the near-surface samples indicated enhanced contributions of organic matter derived from lake aquatic sources. Following the procedure reported by Sanei and Goodarzi^[42], organic matter parameters (e.g., S1, S2) were obtained using Rock-Eval six analyses (Vinci Technologies, Rueil-Malmaison, France). S1 represented the quantity of free “volatile” hydrocarbons; and S2 indicated the quantity of the higher molecule, kerogen-derived hydrocarbons released by the thermal cracking of organic matter. According to the Rock-Eval analysis, S1 is a good indicator of the labile portion of algal-derived organic matter, which is known to decompose easily. However, the S2 compounds originated from lake algae are more resistant to degradation during early diagenesis. Thus, the quantity of S2 may serve as a more suitable indicator of algal productivity in aquatic sediments than that of S1^[42–44]. Correlation analyses showed that S2 and TOC in MC sediments were highly correlated ($r=0.86$, $n=60$), and this correlation did not change significantly in the upper 6 cm of the samples ($r=0.84$, $n=4$). These results suggested that the organic matter in the MC sediments was mainly derived from lake algae, and the effects of both post-depositional microbial degradation and anthropogenic source were minor.

3.4 BSi in Mochou Lake sediments and paleoenvironmental implications

For the MC sediment core, the content of BSi varied between 5% and 8%, and the average value was 6.9% ($n=69$), much lower than that in the surface sediments in Prydz Bay (4.89%–85.41%, averaging 30.90%)^[45]. A 56-lake dataset in east Antarctica suggests that diatom flora and species diversity are lower in Mochou Lake in the Larsemann Hills, and three taxa (*C. cf. molesta*, *P. abundans* and *S. inermis*) are the most abundant diatoms. These species usually appear in both freshwater and slightly brackish lakes of the Larsemann Hills^[46–47]. In addition to diatom species, the stomatocysts (i.e., chrysophytes) may be another important source of

BSi in this shallow freshwater lake^[47]. In future studies, measurements of absolute diatom contents and stomatocyst in sediment samples using organic pigment methods may allow for comparisons with BSi values, and may provide more detailed information on the sources of BSi in Mochou Lake.

Correlation analysis showed that BSi had a strongly positive correlation with some geochemical proxies for algal abundance (Table 1), indicating that the content of BSi in Mochou Lake was mainly controlled by the amount of lake algae. Thus, BSi could effectively reflect the historical change of lake primary productivity. Furthermore, the BSi only originated from lake algae, and it was buried in the sediments after the algae died. The close relationships between BSi and other geochemical parameters could further confirm that sedimentary organic matter was predominantly derived from natural products in the lake, and that anthropogenic organic input did not significantly influence organic matter compositions in MC sediments. The results of biogenic silica measurements in surface sediments of Prydz Bay showed that spatial variation of the biogenic silica was related closely to nutrients, chlorophyll a and primary productivity^[45]. Thus, the BSi was capable of reflecting change of primary productivity in the upper water column. As illustrated in Figure 3, changes of BSi and organic matter contents in the sediments revealed that there were at least three stages with low lake primary productivity (marked by shaded areas), corresponding to 64–57 cm, 46–32 cm and 22–10 cm, respectively. The change of algal abundance in the lake was interpreted to be related to climate conditions, solar variations and nutrient levels. With a warming climate, lake water tended to become warmer and more productive. The lake could create more suitable conditions for the growth of phytoplankton and zooplankton, finally leading to an overall increase in lake productivity from benthos to plankton. However, during climatic deterioration, the catchment area of Mochou Lake could be covered with more snow and ice, making it more difficult for plants to receive solar radiation and nutrient inputs. This would result in a decline of algal production, as well as limiting diatom propagation^[48]. Thus, the trough stages of BSi in the sediments of Mochou Lake likely corresponded to at least three periods of historically deteriorated climate conditions in the study area.

3.5 Change of biogenic silica in Daming Lake

Changes of TN, TC, TS, H and BSi contents versus depth in the DM sediment core are plotted in Figure 5. Like Mochou Lake, Figure 5 shows that the profiles of TN, TC, TS and H contents over depth had consistent trends. Their contents were relatively low in the sediments below 15 cm. They increased rapidly from 15 cm, and then remained higher in the upper 10 cm of sediments. The content of BSi also displayed a notable change versus depth. The sediments below 15 cm had BSi levels con-

sistently less than 2%, and the top 10 cm sediments had BSi contents of up to 12%–13%. Comparing the profiles of BSi and TN, TC, TS, H contents over depth in the Daming lacustrine sediments, they showed very similar change trends. Furthermore, Figure 6 shows that BSi had highly positive correlations with TN, TC, TS and H in the sediments, suggesting that all these proxies can be used to commonly indicate paleo-limnological changes in Daming Lake.

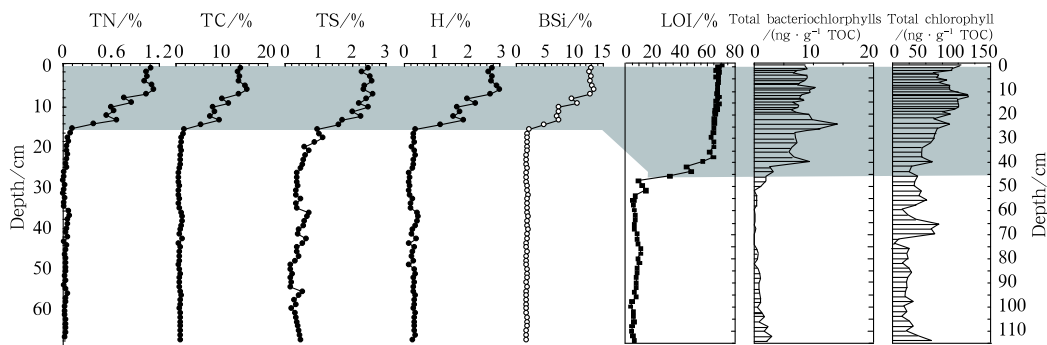


Figure 5 Changes of TN, TC, TS, H and BSi contents in the DM sediment core against depth. The LOI, total bacteriochlorophylls and total chlorophyll on the right are redrawn from the analytical data of reference 18 for a sediment core taken from the center of Daming Lake.

Based on a 115-cm sediment core taken from the center of Daming Lake, Hodgson et al.^[18] used multiple proxies, including TOC, carbon stable isotopes, fossil pigments and diatoms to reconstruct continuous paleo-environmental records. These records included historical climatic changes, salinity and lake water level over the past 40 000 years. Here, we have redrawn the data of loss-on-ignition (LOI), total bacteriochlorophyll and total chlorophyll in Figure 5. These three parameters are considered to be related to changes in lake primary productivity. As shown in Figure 5, the pigment contents and the LOI values, indicative of the change in organic matter, increased rapidly in the sediment layer between 55–40 cm, and they remained high in the upper 40 cm. The BSi, TN and other proxies analyzed in our DM core had the same trends. However, a sudden increase in these environmental proxies occurred at 15–10 cm in the DM core, which was very different from the critical depth of 40–55 cm reported by Hodgson et al.^[18]. The depth difference may be related to the coring position. The sediment core studied by Hodgson et al.^[18] was collected in the lake center, whereas the coring

site at DM in our study was closer to the lake shore. As mentioned above, the difference in light intensity, temperature and nutrient inputs may have affected the algae biomass and lake productivity. Based on field observations, algae grow more in the lake center, and thus the deposition of lake algae may be more rapid in the middle of the lake. Conversely, the clastic deposition rate was likely to have been faster near the lake shore. In addition, the different sediment compactions also may have caused the depth difference of environmental proxy changes in the different sediment cores. In spite of that, the lithology throughout these two cores still displayed consistent change characteristics. Thus, we suggest that the critical depths of both sediment cores should correspond to the same eco-environmental event. According to Hodgson et al.^[18], pigments increased within 50–40 cm, yielding date ranges between 17 000 and 11 000 a BP. During this period, seasonal meltwater input to the lake increased and the lake received more light intensity, leading to rapid enhancement of lake productivity. Meanwhile, favorable climatic conditions may have promoted algal growth in Daming Lake, and the increased productivity of the dia-

toms may have resulted in the high value of BSi. The relatively high content of BSi in the upper 10 cm of the sediments in the DM core was consistent with high levels of pigments obtained from Hodgson et al.^[18], suggesting that the sediments in the upper 10 cm of the DM core were likely deposited during the period of Holocene glacial retreat. According to Hodgson et al.^[18], Daming Lake became seasonally ice-free during summer at the beginning of the Holocene deglaciation, and warmer cli-

matic conditions occurred since $\sim 7\,400$ a BP. This would have resulted in a significant enhancement of lake productivity. The notably high values of BSi, TC, TN and TS in the top sediment layer of the DM core likely revealed the increased lake primary productivity due to the warming climatic conditions. This provides further evidence that biogenic silica is a good proxy for reconstructing change of paleoproductivity in Antarctic lakes.

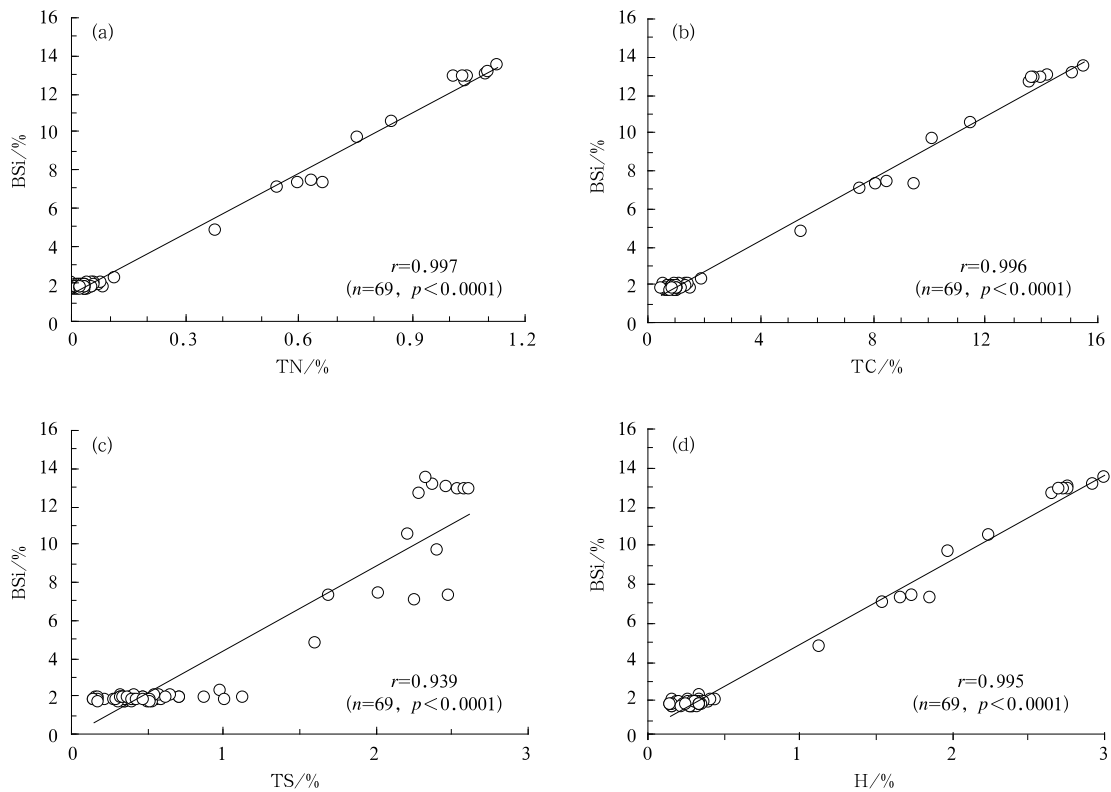


Figure 6 Correlations between TN, TC, TS, H and BSi in the Daming Lake sediments.

3.6 Advantages of BSi as a proxy for paleo-productivity in East Antarctic Lakes

In many lakes of East Antarctica, including Larsemann Hills, Vestfold Hills and McMurdo Dry Valley, diatoms are well preserved in the lacustrine sediments^[46,49–51], and they are important components of microbial communities in Antarctic and sub-Antarctic lakes^[52]. Many diatom species only exist in the extremely cold Antarctic^[53]. This is the case for some species present in the Larsemann Hills lakes^[46]. In high latitude regions, especially in the Antarctic, diatoms provide unique biogenic indicators for paleolimnological study.

Distribution of different diatom species in lacustrine sediments provide an important proxy for the reconstruction of past climatic variations, and up to now they have been successfully applied to the reconstruction of lake salinity, ice thickness, sea level and other paleo-environment information^[46]. However, the diatom species can not characterize the total primary productivity in lakes.

We analyzed productivity proxies, such as organic matter, pigments, and BSi in lake sediments from Ny-Ålesund, Arctic^[54]. Those proxies exhibited good correlations in the sediments with relatively low organic matter content (e.g., the period of Little Ice Age [LIA]).

The deteriorating climatic conditions could have caused the decrease in lake primary productivity and other biogeochemical indices. However, at the beginning of the 20th century, lake productivity increased significantly due to climate warming, and thus organic matter and pigments displayed higher contents in the upper sediments. However, at that time the BSi showed the opposite trend in these sediment samples^[54]. Axford et al.^[55] also found similar BSi variations in surface sediments from Arctic lakes, and suggested that the dilution effect brought by the large input of terrestrial organic matter could not be ignored. The above results show that BSi contents may be influenced by many factors in Arctic lakes. For example, the input of terrestrial organic matter derived from abundant mosses growing around the lakes may cause significant influence on the change patterns of BSi in the sediments. Under this condition, the profile of BSi content over depth in the lacustrine sediments could not reflect the true change of lake primary productivity. However, in the remote East Antarctic continent, the exposed bedrock and sparse vegetation around lakes may have limited the input of terrestrial organic matter into lakes, and thus the effect of exogenous organic matter on the distribution of BSi was likely negligible. Overall, BSi is an ideal proxy for the reconstruction of paleoproductivity recorded in the East Antarctic lakes.

4 Conclusions

Based on comparative research between BSi and other environmental proxies for the sediments of Mochou Lake and Daming Lake on East Antarctica, we can draw the following conclusions:

(1) In the DM and MC sediment cores, BSi showed the consistent change patterns with bio-geochemical proxies, such as organic matter. In addition, they exhibited strong positive correlations. This implied that the content of BSi, like TOC, pigments, and TN, was responsible for the historical change of lake algal biomass, and the high value indicated rapid growth of lake algae. Thus, the BSi level in the sediments could effectively indicate the fluctuation of historical lake primary productivity.

(2) A great number of diatoms were well preserved in the freshwater lake sediments in East Antarctica. Throughout the depth profile, the BSi content showed notable variations, reflecting the fact that the significant

change of historical diatom productivity had occurred in the lakes. Historically, the primary productivity experienced at least three troughs during the past 3 000 years in Mochou Lake. However, in Daming Lake, the relatively high concentration of BSi in the upper 10 cm likely indicates increased lake primary productivity due to the Holocene climatic warming and glacial retreat.

(3) The content of BSi in Arctic lacustrine sediments is likely susceptible to the input of terrestrial organic matter, whereas the influencing factors on the variation of sedimentary BSi in the East Antarctic lakes are relatively simple. Thus, BSi is an ideal proxy for the reconstruction of past eco-environmental changes recorded in the lacustrine sediments of East Antarctica.

Acknowledgments We would like to thank the Chinese Arctic and Antarctic Administration, State Oceanic Administration for logistic field sampling support. We are appreciative to Dr Huang Tao for sampling DM sediment core in the field. This study was supported by the National Natural Science Foundation of China (Grant nos. 40876096, 41076123 and 40606003), the Open Research Funds from SOA Key Laboratory for Polar Science (Grant no. KP2007002) and a special fund for excellent PhD thesis of CAS. Thanks also are extended to several anonymous reviewers for their constructive comments which improved the manuscript.

References

- 1 Wang S M, Dou H S. *China Lake*. Beijing: Science Press, 1998: 580
- 2 Shen H Y, Li S J, Shu W X. Pigments in the lake sediments: environmental indicator. *Marine Geology & Quaternary Geology*, 2007, 27(3): 37–42
- 3 Hodgson D A, Noon P E, Vyverman W, et al. Were the Larsemann Hills ice-free through the Last Glacial Maximum? *Antarctic Science*, 2001, 13(4): 440–454
- 4 Li S K, Zhang Q S, Zhu L P. Landform development and environmental evolution since late Pleistocene in ice-free Antarctica. Beijing: Ocean Press, 1998
- 5 Kaufman D. An overview of late Holocene climate and environmental change inferred from Arctic lake sediment. *Paleolimnology*, 2009, 41(1): 1–6
- 6 Liu X D, Sun L G, Xie Z Q, et al. Geochemical evidence for the influence of historical sea bird activities on no worries lake sediments in the Zhongshan station area, East Antarctica. *Journal of Chinese Polar Research*, 2004, 16(4): 295–309
- 7 Smol J P, Birks H J B, Last W M (eds.). *Tracking environmental change using lake sediments. Volume 3: Terrestrial, algal, and siliceous indicators*. Dordrecht: Kluwer Academic Publishers, 2001: 400

- 8 Li J, Chen J A. An effective cleaning method for producing pure diatom samples from lake sediments. *Earth and Environment*, 2007, 35(1): 91–96
- 9 Birks H J B, Jones V J, Rose N L. Recent environmental change and atmospheric contamination on Svalbard as recorded in lake sediments-an introduction. *Paleolimnology*, 2004, 31(4): 403–410
- 10 Hu F S, Kaufman D, Yoneji S, et al. Cyclic variation and solar forcing of Holocene climate in the Alaskan subarctic. *Science*, 2003, 301(5641): 1890–1893
- 11 Colman S M, Peck J A, Karabanov E B, et al. Continental climate response to orbital forcing from biogenic silica records in Lake Baikal. *Nature*, 1995, 378(6559): 769–771
- 12 Swann G E A, Mackay A W. Potential limitations of biogenic silica as an indicator of abrupt climate change in Lake Baikal, Russia. *Paleolimnology*, 2006, 36(1): 81–89
- 13 Xiao J L, Inouchi Y, Kumai H, et al. Biogenic silica record in Lake Biwa of central Japan over the past 145,000 years. *Quaternary Research*, 1997, 47(3): 277–283
- 14 Wang W Y, Liu J Q, Peng P A. Determination and application of biogenic silica in lake sediments: An example from Huguangyan marr lake, southern China. *Geochimica*, 2000, 29(4): 327–330
- 15 Michelutti N, Douglas M S V, Wolfe A P, et al. Heightened sensitivity of a poorly buffered high arctic lake to late-Holocene climatic change. *Quaternary Research*, 2006, 65(3): 421–430
- 16 Sun L G, Xie Z Q, Liu X D, et al. *Ecological geology on Ice-free Antarctica*. Beijing: Science Press. 2006: 306
- 17 Li Z S, Wang J, Lei Z H. Hydrochemical properties of lakes in Larsemann Hills, Antarctica. *Chinese Journal of Polar Research*, 1997, 9(1): 71–77
- 18 Hodgson D A, Verleyen E, Sabbe K, et al. Late Quaternary climate-driven environmental change in the Larsemann Hills, East Antarctica, multiproxy evidence from a lake sediment core. *Quaternary Research*, 2005, 64(1): 83–99
- 19 Liu X D, Sun L G, Xie Z Q, et al. A preliminary record of the historical seabird population in the Larsemann Hills, East Antarctica, from geochemical analyses of Mochou Lake sediments. *Boreas*, 2007, 36(2): 182–197
- 20 Verleyen E, Hodgson D A, Milne G A, et al. Relative sea-level history from the Lambert Glacier region, East Antarctica, and its relation to deglaciation and Holocene glacier readvance. *Quaternary Research*, 2005, 63(1): 45–52
- 21 Verleyen E, Hodgson D A, Sabbe K, et al. Coastal oceanographic conditions in the Prydz Bay region (East Antarctica) during the Holocene recorded in an isolation basin. *Holocene*, 2004a, 14(2): 246–257
- 22 Verleyen E, Hodgson D A, Sabbe K, et al. Late Quaternary deglaciation and climate history of the Larsemann Hills (East Antarctica). *Quaternary Science*, 2004b, 19(4): 361–375
- 23 Liu S M, Zhang J. A study on the measurement of biogenic silica. *Marine Sciences*, 2002, 26(2): 23–26
- 24 Ye X W, Liu S M, Zhang J. The determination of biogenic silica and its biogeochemistry significance. *Advance in Earth Sciences*, 2003, 18(3): 420–426
- 25 Liu F, Zhao L B, Huang L F, et al. A methodological study on the determination of biogenic silica sourced from newly sedimentated diatom in Xiamen Inner-bay sediment. *Journal of Xiamen University (Natural Science)*, 2008, 47: 294–299
- 26 Mortlock R A, Froelich P N. A simple method for the rapid determination of biogenic opal in pelagic marine sediments. *Deep-Sea Research*, 1989, 36(9): 1415–1462
- 27 Liao B, Zhu J, Wu Y Y, et al. Determination method of biogenic silica in reservoir sediments. *Journal of Neijiang Teachers College*, 2006, 21: 226–229
- 28 Zhang L L, Chen M H, Xiang R, et al. Distribution of biogenic silica in surface sediments from southern South China Sea and its environmental significance. *Journal of Tropical Oceanography*, 2007, 26(3): 24–29
- 29 Conley D J, Schelske C L, Stoermer E F, et al. Modification of the biogeochemical cycle of silica with Eutrophication. *Marine Ecology-Progress Series*, 1993, 101(1-2): 179–192
- 30 Bird M I, Chivas A R, Radnell C J, et al. Sedimentological and stable-isotope evolution of lakes in the Vestfold Hills, Antarctica. *Palaeogeography Palaeoclimatology Palaeoecology*, 1991, 84(1–4): 109–130
- 31 Burgess J S, Spate A P, Norman F I. Environmental impacts of station development in the Larsemann Hills, Princess Elizabeth Land, Antarctica. *Journal of Environmental Management*, 1992, 36(4): 287–299
- 32 Gonnee M E, Paytan A, Herrera-Silveira J A. Tracing organic matter sources and carbon burial in mangrove sediments over the past 160 years. *Estuarine, Coastal and Shelf Science*, 2004, 61(2): 211–227
- 33 Burkins M B, Virginia R A, Chamberlain C P, et al. Origin and distribution of soil organic matter in Taylor Valley, Antarctica. *Ecology*, 2000, 81(9): 2377–2391
- 34 Doran P T, Wharton Jr R A, Lyons W B, et al. Sedimentology and geochemistry of a perennially ice-covered epishelf lake in Bunge Hills Oasis, East Antarctica. *Antarctic Science*, 2000, 12 (2): 131–140
- 35 Dunton K H. $\delta^{15}\text{N}$ and $\delta^{13}\text{C}$ measurements of Antarctic peninsula fauna: trophic relationships and assimilation of benthic seaweeds. *American zoologist*, 2001, 41: 99–112
- 36 Conlan K E, Rau G H, Kvittek R G. $\delta^{13}\text{C}$ and $\delta^{15}\text{C}$ shifts in benthic invertebrates exposed to sewage from McMurdo Station, Antarctica. *Marine Pollution Bulletin*, 2006, 52: 1695–1707
- 37 Botello A V, Mandelli E F, Macko S, et al. Organic carbon isotope ratios of recent sediments from coastal lagoons of the Gulf of Mexico, Mexico. *Geochimica et Cosmochimica Acta*, 1980, 44(3): 557–559
- 38 Gearing P J, Gearing J N, Maughan J T, et al. Isotopic distribution of carbon from sewage sludge and eutrophication in the sediments and food web of estuarine ecosystems. *Environmental Science and Technology*, 1991, 25: 295–301
- 39 Talbot M R. Nitrogen isotopes in palaeolimnology. In Last W M, Smol J P. (eds). *Tracking environmental change using lake sediments*. Kluwer Academic Publishers, 2001, 401–439

- 40 Costanzo S D, O'donohue M J, Dennison W C, et al. A new approach for detecting and mapping sewage impacts. *Marine Pollution Bulletin*, 2001, 42(2): 149–156
- 41 Meyers P A, Teranes J L. Sediment organic matter. In Last W M, Smol J P. (eds). *Tracking environmental change using lake sediments*. Kluwer Academic Publishers, 2001: 239–269
- 42 Sanei H, Goodarzi F. Relationship between organic matter and mercury in recent lake sediment: The physical-geochemical aspects. *Applied Geochemistry*, 2006, 21: 1900–1912
- 43 Outridge P M, Sanei H, Stern G A, et al. Evidence for control of mercury accumulation rates in Canadian High Arctic lake sediments by variations of aquatic primary productivity. *Environmental Science and Technology*, 2007, 41(15): 5259–5265
- 44 Stern G A, Sanei H, Roach P, et al. Historical interrelated variations of mercury and aquatic organic matter in lake sediment cores from a subarctic lake in Yukon, Canada: Further evidence toward the algal-mercury scavenging hypothesis. *Environmental Science and Technology*, 2009, 43(20): 7684–7690
- 45 Hu C Y, Yao M, Yu P S, et al. Biogenic silica in surficial sediments of Prydz Bay of the Southern Ocean. *Acta Oceanologica Sinica*, 2007, 29: 48–54
- 46 Sabbe K, Verleyen E, Hodgson D A, et al. Benthic diatom flora of freshwater and saline lakes in the Larsemann hills and Rauer islands, east Antarctica. *Antarctic science*, 2003, 15(2): 227–248
- 47 Sabbe K, Hodgson D A, Verleyen E, et al. Salinity, depth and the structure and composition of microbial mats in continental Antarctic lakes. *Freshwater Biology*, 2004, 49: 296–319
- 48 Wang J Q, Liu J L. Amino acids and stable carbon isotope distributions in Taihu Lake, China, over the last 15,000 years, and their paleoecological implications. *Quaternary Research*, 2000, 53(2): 223–228
- 49 Esposito R M M, Horn S L, McKnight D M, et al. Antarctic climate cooling and response of diatoms in glacial meltwater streams. *Geophysical Research Letters*, 2006, 33: L07406
- 50 Wagner B, Cremer H. Limnology and sedimentary record of Radok lake, Amery Oasis, East Antarctic. In Futterer D K, Damaske D, Kleinschmidt G, et al.(eds). *Antarctica: Contributions to global earth sciences*. Springer-Verlag, Berlin, Heidelberg, New York, 2006: 447–454
- 51 Ohtsuka T, Kudoh S, Imura S, et al. Diatoms composing benthic microbial mats in freshwater lakes of Skarvsnes ice-free area, east Antarctica. *Polar Bioscience*, 2006, 20: 113–130
- 52 Spaulding S A, Mcknight D M. Diatoms as indicators of environmental change in Antarctic freshwaters. In Stoermer E F, Smol J P (eds). *The diatoms: applications for the environmental and earth sciences*. Cambridge: Cambridge University Press, 1999: 245–263
- 53 Van de Vijver B, Beyens L, Lange-Bertalot H. The genus *Stauroneis* in the Arctic and Antarctic locations. *Bibliotheca Diatomologica*, 2004, 50: 311
- 54 Jiang S, Liu X D, Xu L Q, et al. The changes of pigments content and their environmental implication in the lake sediments of Ny-Ålesund, Svalbard, Arctic. *Chinese Journal of Polar Science*, 2010, 21(1): 60-70
- 55 Axford Y, Geirsdóttir, Miller G H, et al. Climate of the Little Ice Age and the past 2000 years in northeast Iceland inferred from chironomids and other lake sediment proxies. *Journal of Paleolimnology*, 2009, 41(1): 7–24