Environmental evolution recorded by multi-proxy evidence in Lake Chenghai sediments, Yunnan Province during recent 100 years

ZHU Zhengjie^{1,2,3}, CHEN Jing'an^{1*}, REN Shicong², and ZENG Yan¹

¹ The State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang 550002, China

² Chongqing Key Laboratory of Exogenic Mineralization and Mine Environment, Chongqing Institute of Geology and Mineral Resources, Chongqing 400042, China

³ Chongging Research Center of State Key Laboratory of Coal Resources and Safe Mining, Chongging 400042, China

* Corresponding author, E-mail: chenjingan@vip.skleg.cn

Received August 20, 2011; accepted August 22, 2012 © Science Press and Institute of Geochemistry, CAS and Springer-Verlag Berlin Heidelberg 2013

Abstract Lacustrine sediments can provide potential information about environmental changes in the past. On the basis of high-resolution multi-proxy analysis including carbon and nitrogen contents of organic matter, C/N ratios, inorganic carbon contents, and carbon and oxygen isotopic composition of carbonate, together with precise ¹³⁷Cs dating, the environmental evolution of Lake Chenghai, Yunnan Province, during the past 100 years has been investigated. It is shown that the carbonate in Lake Chenghai is authigenic, and the organic matter is mainly derived from aquatic plants and algae, instead of terrestrial-source materials. The environmental evolution of Lake Chenghai can be diverged into three periods with the contrasting characteristics during the past 100 years. Before 1940, the stable carbon and oxygen isotope values, the poor correlation between them and the lower carbon and nitrogen contents of organic matter suggested that Lake Chenghai was open, and the lake water was oligotrophic during that period. During 1940–1993, the negative δ^{13} C values and the gradual increase of carbon and nitrogen contents of organic matter and C/N ratios indicated that the eutrophication was aggravated. The closeness of Lake Chenghai and human activities may be responsible for this eutrophication. After 1993, notable increases in carbon and oxygen isotopic values of carbonate, carbon and nitrogen contents of organic matter, C/N ratios and inorganic carbon contents demonstrated that the increase of lacustrine productivity and the serious eutrophication were resulted from strong human activities. Therefore, the multi-proxy in Lake Chenghai sediments has reliably recorded the natural environmental evolution and the impacts from human activities.

Key words Lake Chenghai; carbon; oxygen; isotope; source; human activity; eutrophication

1 Introduction

Lacustrine sediments, as an archive of environmental changes in the past, have numerous advantages such as variable sedimentation rate, continuous climate record and extensive distribution (Wan Guojiang et al., 2003; Jin Zhangdong et al., 2009). Among the various indicators of lacustrine sediments, stable isotopes have become one of the most effective methods for reconstructing environmental changes in the past. Due to the limits of sedimentation rate, sampling precision and dating, research on high-resolution, especially annual-resolution environment/climate changes mainly focused on ice cores and tree rings, and there have been reported few studies on lacustrine sediments, particular in recent 100 years. Lake Chenghai, located in Yunnan Province, Southwest China, now as a closed lake, has reliably recorded regional environment/climate changes. Its high sedimentation rate (1 cm/a) (Chen Jing'an et al., 2002; Wan Guojiang et al., 2005) and many changes in its environments over the last century also enable this lake to be an ideal lacustrine setting to study environmental changes in the past, and is also helpful to distinguish natural impacts from and human ones. Information on the natural evolution and human impacts on lakes is highly helpful for understanding the current status and predicting future development of the lake systems (Wu Jinglu et al., 2004), which is of vital importance for formulating measures to prevent further eutrophication of lakes. Additionally, Lake Chenghai is of great importance for its functions as water supply, fisheries, agriculture and breeding industry. When the direct measurements of the environmental data are not available, therefore, it is urgent to carry out paleolimnological studies to understand its past.

In this study, a 108 cm-deep sediment core from the central part of Lake Chenghai was drilled, and carbon and nitrogen contents of organic matter, C/N ratios, inorganic carbon contents as well as carbon and oxygen isotopic composition of carbonate in annual resolution over the past 100 years were measured. The aims of this study are to trace the historical eutrophication of Lake Chenghai over the last century, and also to understand the interactions between nature and human impacts.

2 Study area

Lake Chenghai is located approximately 18 km south of Yongsheng County, Yunnan Province, China $(26^{\circ}27'-26^{\circ}38'N, 100^{\circ}38'-100^{\circ}41'E)$ (Fig. 1), which was formed in the Early Pleistocene. The water level of Lake Chenghai is 1503 m. It has a length of 19 km, and an average breadth of 4 km, covering a surface area of 77 km². The lake has the maximum depth of 35.1 m, with the average depth of 25.7 m, and a volume area of 20×10^8 m³. Lake Chenghai is a tectonic-fault depression and also a lake covering a small catchment area. Now, no water has flown from it, thus becoming a hydrologically closed lake. As a result, the lake level and composition of lake water and sediments are sensitive to environmental change. In addition, as the eutrophication history of Lake

Chenghai has been described in detail (Wu Jinglu et al., 2003, 2004; Wan Guojiang et al., 2005) and its sedimentation rate is high (Chen Jing'an et al., 2002; Wan Guojiang et al., 2005; Zhu Zhengjie, 2009), all these factors make this lake become an ideal lacustrine setting to study environmental changes in the past by using geochemical proxies. This region is influenced by the southwesterly monsoon, and the precipitation is characterized by seasonal variations. Mean annual precipitation at Lake Chenghai is about 300-400 mm (Wang Suming et al., 1998), and more than 80% of the total annual precipitation falls between June and October. Vegetation in the catchment is predominated by C3 plants, such as Yunnan pine trees and shrubs. Bedrocks in the lake catchment include sandstones, dolomitic limestones and shales. The lake water is alkaline (pH: 9.25) with an average salinity of 1 g/L (Table 1), approaching the lower-limit ion concentrations of salt lakes, and its total P and N concentrations are 0.048 and 0.57 mg/L, respectively (Wu Jinglu et al., 2004). Phytoplanktons in Lake Chenghai are dominated by blue-green algae, including Anabaena, Microcystis and Oscillatoria (Wu Jinglu et al., 2004; Wan Guojiang et al., 2005). According to documentary records, approximately in 1940, a number of people had been settled in the lake catchment for living. Since the 1980s, the environment of Lake Chenghai has been seriously contaminated owing to the rapid development of agriculture and industry.



Fig. 1. Geographical location of Lake Chenghai (black blank rectangle) and sampling sites (black circle).

SiO ₂	Ca ²⁺	Mg^{2+}	K^+	Na ⁺	HCO ₃ -	CO3 ²⁻	SO4 ²⁻	Cl	NO ₃ ⁻	NO ₂ ⁻
0.37	9.33	63.62	11.83	171.42	548.5	101.83	3.39	22.47	0.97	0.05
$\mathrm{NH_4}^+$	DO	COD	P_2O_5	Fe ³⁺	Fe ²⁺	TFe	Total ion	рН	${\delta^{18}O_{lw}}^{*}$	Salinity*
0.02	1.92	2.03	0.21	0.0005	0.0002	0.0007	960.78	9.25 ¹	-1.53	50
${\delta^{18} O_{cell}}^{*}$	${\delta^{18}O_p}^*$	${\delta^{13}C_{DIC}}^{*}$								
22.86‰	-8.20‰	-1.63‰								

Table 1 Geochemical features of Lake Chenghai (mg/L)

Data sources: * This study; others from Wang Suming, 1998.

3 Sampling and methods

Sediment core B was retrieved in the central part of Lake Chenghai in 2006 by means of a self-designed gravitational sediment sampler coupled with a polymethyl tube (59 mm in inner diameter) (Li Jian et al., 2011). The aquatic and terrestrial plants were also sampled. The sediment core was perfectly preserved, since the suspended layer was not disturbed and the interface water was clear during coring. The core with a length of 108 cm was sectioned at 1 cm interval immediately and put into plastic bags in the field. Sediment samples were dried by means of a vacuum freeze drier (FD-IA-50). Before grinding terrestrial plant remains were picked out from the sediment core for radiocarbon ¹⁴C dating by accelerator mass spectrometry (AMS) at the Scottish Universities Environmental Research Centre AMS Facility, and then all dry sediment samples were ground as fine as 120-mesh homogenous powder. Then, the sediment core samples were divided into two portions for subsequent analysis.

One portion of the samples was used for the measurement of ¹³⁷Cs activity. ¹³⁷Cs activities were determined by gamma-spectrometry on a Canberra S-100 multi-channel spectrometer coupled with a GC5019 H-PR Ge coaxial detector (efficiency 50%) or a GCW3022 H-PR Ge well detector (efficiency 30%). The ¹³⁷Cs activity was determined in terms of its emissions at 661.6 keV. The analytical precision was better than 5%.

Samples for the measurement of C/N ratios were treated with HCl (1 mol/L) and placed in water bath for two hours at 60°C to remove carbonates, then rinsed repeatedly with distilled water for four times. Total carbon (TC) contents and C/N ratios were measured by using an elemental analyzer (PE2400 Series II) with an error less than 5%. Total inorganic carbon (TIC) contents were determined by the chemical volumetric method with the analytical precision being better than 5% (Li Younian, 1983; Chen Jing'an et al., 2002). Total organic carbon (TOC) contents were calculated as the difference between TC and TIC. The δ^{13} C and δ^{18} O values of carbonates were analyzed on a GV IsoPrime stable isotope ratio mass spectrometer (IRMS) connected with an online carbonate preparation system. The isotopic composition of samples is defined as delta (δ) notations in parts per thousand:

$$\delta_{\text{sample}}$$
 (‰) = [($R_{\text{sample}}/R_{\text{standard}})$ -1]×1000

where *R* represents the ${}^{13}C/{}^{12}C$ and ${}^{18}O/{}^{16}O$ ratios of a sample, and the isotopic ratios were reported relative to the PDB standard. Analytical precision is better

than 0.1% for the δ^{13} C values of carbonates, and 0.15% for the δ^{18} O values of carbonates. A number of duplicate samples were also measured and the results showed that the precisions were less than the limit of measurement accuracy. All the measurements were performed at the State Key Laboratory of Environmental Geochemistry, Chinese Academy of Sciences in Guiyang, the capital city of Guizhou Province, Southwest China.

4 Results

4.1 Chronology

The sediment core in Lake Chenghai has no clear lamination with a high sedimentation rate according to the results of previous studies (Chen Jing'an et al., 2002; Wan Guojiang et al., 2005). Therefore, ¹³⁷Cs was used for sediment dating, which has been widely applied as a proper time-marker for estimating the dates of recent sediments (Wan Guojiang et al., 1987; Bai Zhanguo and Wan Guojiang, 1998). Generally, mass depth $(g \text{ cm}^{-2})$, 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 the decrease of sediment porosity with depth (Chen Jing'an et al., 2002; Xu Hai et al., 2006a). Although some factors such as redistribution may influence the shape of ¹³⁷Cs peaks, the deposition of ¹³⁷Cs maximum can not be easily modified (Wan Guojiang et al., 2003; Xu Hai et al., 2006a). As shown in Fig. 2, ¹³⁷Cs activity reaches its peak at the mass depth of 8 g/cm². This peak can be ascribed to the fallout from the Chernobyl disaster in 1986, which is in consistency with the conclusion drawn by Wu Jinglu et al. (2004). Otherwise, the peak of ¹³⁷Cs activity in 1964 and 1975 in Lake Chenghai can not be obtained. This may be attributed to the short half life of 137 Cs, and that of 137 Cs in 1964 and 1975 can not be detected. In addition, a terrestrial plant remain at the depth of 42 cm was picked out for ¹⁴C dating, and no dating result has been acquired, indicating that the depositional time of 42-cm sample is later than 1950 (years before present). Based on this ¹³⁷Cs peak and linear extrapolation methods, the average sedimentation rate of Lake Chenghai is about 0.40 g/cm²·a (1 cm/a), and sediment core B represents the sediment deposited from about 1900 to 2007. The age-depth model is shown in Fig. 3.

4.2 $\delta^{13}C$ and $\delta^{18}O$ values of carbonates

The stratigraphic patterns of δ^{13} C and δ^{18} O values of carbonates are plotted in Fig. 4. δ^{18} O values vary from -7.21‰ to -4.84‰, with an average value

of -5.97‰, but are relatively stable between 1900 and 1940. δ^{18} O values generally increase to the maximum in 1941 with a value of -4.84‰. A slight decrease in δ^{18} O occurred between 1941 and 1993, followed by a sharp increase in δ^{18} O from 1993 till the top of the core.



Fig. 2. The vertical profile of 137 Cs in the sediment core in Lake Chenghai.



Fig. 3. The age-depth model of the sediment core in Lake Chenghai.

 δ^{13} C values show similar patterns to the δ^{18} O values, but δ^{13} C values in the lower part of the core are characterized as being high between 1900 and 1920, reaching the maximum value of 1.54‰ in 1920. A distinct decrease in δ^{13} C occurred between 1941 and 1993, followed by a sharp increase in δ^{13} C to the top of the core. In comparison with δ^{18} O values in the whole core, δ^{13} C values show intensive fluctuations.

4.3 TIC, TOC, TN and C/N ratios

TOC varies between 0.22% and 1.87%, with an average value of 0.51%. Total nitrogen varies between 0.13% and 0.30%, with an average value of 0.17%. TIC varies between 0.83% and 1.38%, with an average value of 1.07%. C/N ratios vary between 1.5 and 7.5, with an average value of 3.3. The good correlation between TOC and TN suggests that organic mat-

ter in Lake Chenghai was derived from single plant (Fig. 5). During the period between 1900 and 1993, TOC and TN were stable. Later, TOC and TN increased sharply. C/N ratios show an increasing trend in the whole core, and also increase sharply after 1993. TIC shows similar variations to δ^{18} O values. The value was stable between 1900 and 1920, and then increased until 1940. A distinct decrease occurred between 1941 and 1960, followed by a sharp increase in δ^{13} C to the top of the core.

5 Discussion

5.1 The source of organic matter in Lake Chenghai

Previous studies revealed that C/N ratios can be effectively used to identify the source of organic matter (Meyers and Ishiwatari, 1993; Meyers, 1994, 1997; Dean, 1999; Chen Jing'an et al., 2002; Zhu Zhengjie et al., 2011). Generally, the atomic C/N ratios in algae are less than 10. In contrast, atomic C/N ratios in terrestrial plants are high, varying between 20 and 200 (Krishnaunurhy et al., 1986; Lamb et al., 2004). In addition, δ^{13} C values are significantly different between aquatic and terrestrial plants. Therefore, C/N ratios (C/N) and carbon isotope values of organic matter (δ^{13} C_{org}) are an effective method to distinguish the source of organic matter from lake sediments (Meyers and Ishiwatari, 1993; Meyers, 1994, 1997).

Meyers (1997) has provided three distinctive suites of C/N and $\delta^{13}C_{org}$ values in plants to distinguish the source of organic matter from lake sediments, as illustrated in Fig. 6. Lake Chenghai data plot within the field of aquatic plants, and are thoroughly different from those of C3/C4 plants (Zhu Zhengjie et al., 2011), indicating that sedimentary organic matter in Lake Chenghai is derived mainly from algae, and the import of organic matter from terrestrial plants is not important (Fig. 6). Otherwise, C/N ratios in organic matter from Lake Chenghai would fall within the field of algae whose C/N ratios vary between 4 and 10. Actually, the dominant species of algae in Lake Chenghai include Anabaena, Microcystis and Oscillatoria (Wan Guojiang et al., 2005). Furthermore, the single aquatic algae sampled from Lake Chenghai have the C/N ratio and δ^{13} C value of 6.9‰ and -26.68‰, respectively, and terrestrial plant has the C/N ratio and δ^{13} C value of 32.1‰ and -24.56‰, respectively, further suggesting that organic matter from Lake Chenghai is derived from algae.

5.2 The source of carbonate in Lake Chenghai

It is well-known that authigenic carbonate in lake sediments can provide potential information about environment/climate change in the past, and allochonous



Fig. 4. Vertical profiles of δ^{13} C and δ^{18} O values of carbonates, inorganic carbon contents, organic carbon and nitrogen, C/N ratios versus chronology in the sediment core in Lake Chenghai.

carbonate can also complicate this information (Leng et al., 2010). Thus, it is necessary to identify the source of carbonate in lake sediments. In the previous study, we provided several lines of evidence to prove that carbonate is authigenic in Lake Chenghai, in combination with δ^{18} O values of surface carbonate and aquatic plant cellulose, δ^{13} C values of dissolved inorganic carbon and carbonate, and in comparison with the ionic activity product (IAP) with the equilibrium constant (Zhu Zhengjie and Chen Jing'an, 2009). According to the results of other studies, the carbonate in Lake Chenghai is also of authigenic source. For instance, the carbonate contents in sediments increase with increasing water depth and further with increasing distance from the banks of Lake Chenghai (Wang Yunfei et al., 1989), supporting the view that sedimentary carbonates are autochthonous. In deep water of Lake Chenghai, the contents of calcite in sediments reach up to 10%, also supporting this conclusion (Wang Yunfei, 1993).



5.3 Implications of proxies

The δ^{13} C values of authigenic carbonates are controlled mainly by the δ^{13} C of DIC, since there is a relatively small temperature effect (0.0355‰/°C) (Talbot, 1990; Romanek et al., 1992; Gasse et al., 1996; Li and Ku, 1997; Mayer and Schwark, 1999; Nuemann et al., 2002; Leng and Marshall, 2004; Xu Hai et al., 2006b; Lamb et al., 2007; Rosqvist et al., 2007; Henderson and Holmes, 2009). In general, there are three predominant factors that influence the carbon isotopic composition of DIC, including the isotopic composition of the in-flowing water, CO₂ exchange between lake water and atmosphere, as well as photosynthesis/respiration of aquatic plants in the lake (Mook et al., 1974; Nuemann et al., 2002; Leng and Marshall, 2004; Xu Hai et al., 2006b). Atmospheric CO₂ and carbonate dissolution as well as organic matter degradation were the main DIC sources. The escape of lake water CO₂ to atmosphere can cause the enrichment of ¹³C (Li and Ku, 1997; Mayer and Schwark, 1999). Organic matter has negative $\delta^{13}C$ values and carbonate has positive $\delta^{13}C$ values. For instance, in some karstic regions, the $\delta^{13}C$ values of DIC are around +1‰ (Leng and Marshall, 2004). Under isotopic equilibrium with the atmospheric CO₂ $(\delta^{13}C = -7\%)$, lake water $\delta^{13}C$ values would vary between -0.2‰ and +2.2‰ (Mayer and Schwark, 1999), then carbonate δ^{13} C values would vary between +0.8‰ and +3.2‰, because the δ^{13} C value of calcite is 1‰ more positive than the corresponding δ^{13} C of the DIC (Mook et al., 1974; Leng and Marshall, 2004; Lamb et al., 2007). In some organic matter-rich lakes, the lacustrine productivity is considered as the main control to determine the carbon isotopic composition of carbonate (Teranes and Bernasconi, 2005).

The δ^{18} O of carbonate is controlled by both the δ^{18} O of lake water and temperature when the carbonate is precipitated. In arid and semi-arid lakes, minor temperature effect is observed, and the δ^{18} O of carbonate can provide information about the balance between precipitation and evaporation (effective moisture). The correlation between δ^{18} O and δ^{13} C of carbonate can also yield information about the hydrology of lakes. In hydrologically closed lakes, there is normally a strong covariance. In contrast, there is little or no correlation in open lakes (Talbot, 1990; Li and Ku, 1997; Chen Jing'an et al., 2008).



Fig. 6. C/N ratios and $\delta^{13}C_{org}$ values of sedimentary organic matter from Lake Chenghai (typical C/N ratios and $\delta^{13}C_{org}$ values for aquatic plants, C3/C4 land plants cited from Meyers, 1994, 1997).

In the aquatic plant-dominant lakes, TOC and TN are indicative of lake productivity (Meyers, 1997; Dean, 1999). The atomic TOC/TN ratios can reflect the proportions of terrestrial and autochthonous plants. Such studies revealed that the positive correlation between TOC and TIC is the result of carbonate precipitated by primary production (Mullins, 1998; Chen Jing'an et al., 2002).

5.4 Environmental evolution of Lake Chenghai over the last century

Based on the geochemical proxies including the carbon and nitrogen contents of organic matter, C/N ratios, inorganic carbon contents, and the carbon and oxygen isotopic compositions of carbonate (Fig. 4), the environmental evolution of Lake Chenghai can be divided into three intervals in the past 100 years.

5.4.1 1900-1940

The lake was oligotrophic. The δ^{13} C value of carbonate was +1‰, which is consistent with the value of exchange between atmospheric CO₂ and lake water DIC, applying that Lake Chenghai is steady. The poor correlation between carbon and oxygen isotopes of carbonate, lower carbon and nitrogen contents as well as C/N ratios of organic matter indicate that during this period Lake Chenghai was open, and the lake was oligotrophic.

5.4.2 1940-1993

The Lake was closed and eutrophic. The decrease of δ^{13} C value of carbonate suggests that the depleted ¹³C found its way into the DIC, and the degradation of algae may be the source of depleted ¹³C, since the δ^{13} C value of biocarbonate is much higher than the value of algae. The gradual increase of carbon and

nitrogen contents also indicates that the lake is eutrophic, and the good correlation between carbon and oxygen isotopes of carbonate shows that during this period the lake was hydrologically closed.

5.4.3 1993-2006

The lake was seriously eutrophic. The geochemical data during this period are characterized by a sharp increase.

As mentioned above, it is well known that there are two shift periods in environmental evolution in Lake Chenghai, i.e., during 1940 and 1993. Before 1940, Lake Chenghai was steady and the productivity was low. After this period, Lake Chenghai began to be closed, and the environment experienced obvious changes. According to the documentary records, about in the 1940, a number of people had been settled to the lake catchment for living, which may be the main factor leading to the increase of lake productivity. Therefore, the environment change of Lake Chenghai after 1940 was the result of both human activity and natural evolution. During the period between 1993 and 2006, all the geochemical data increased sharply, suggesting that Lake Chenghai was seriously and increasingly eutrophic, which may be ascribed to the intensive human activities due to the rapid development of agriculture and breeding industry. In Lake Chenghai, at present, the phytoplankta dominated by blue-green algae, including nabaena, Microcystis and Oscillatoria, lend a further support to the conclusion that Lake Chenghai is of serious eutrophication. This conclusion is also testified by the results of research on ²¹⁰Pb_{ex} (Wan Guojiang et al., 2005).



Fig. 7. The correlation between the δ^{18} O and δ^{13} C values of carbonate at Lake Chenghai during the different periods.

In addition, a sediment core from Lake Chenghai has revealed its environmental changes in the past in terms of the carbon and oxygen isotopic compositions of carbonate and pigments (Wu Jinglu et al., 2004). Due to the different sampling sites, the resolution of this study is different from what was obtained by Wu Jinglu et al. (2004). They proposed that during the period between 1911 and 1942, Lake Chenghai was meso-eutrophic, this conclusions is different from ours. This divergence was speculated to have been caused by the errors involved in low-resolution dating.

5.5 The characterization of carbon isotopes of carbonate

In this study, during the time period between 1940 and 1993, the eutrophication of Lake Chenghai caused a decrease in δ^{13} C values of carbonate, and there was a negative correlation between them (r=-0.31, n=108, P<0.01), inconsistent with the conventional views that such an increase in productivity would produce higher $\delta^{13}C$ values of carbonate (Stuiver, 1970; Mayer and Schwark, 1999; Neumann et al., 2002; Leng and Marshall, 2004; Teranes and Bernasconi, 2005; Xu Hai et al., 2006b; Henderson and Holmes, 2009). There are several possible reasons which may explain this discrepancy. Firstly, isotopic disequilibrium may influence the carbon isotopic composition of carbonate to a certain degree. Several studies revealed that isotopic disequilibrium would lead to negative $\delta^{13}C_{carb}$ values during the process of eutrophication (Fronval et al., 1995; Teranes and McKenzie, 1999a; Teranes et al., 1999b; Wu Jinglu et al., 2003, 2004). However, our conclusion is that the carbon isotope of carbonate is in equilibrium with that of lake water (Zhu Zhengjie and Chen Jing'an, 2009), suggesting that isotopic disequilibrium is not the main factor leading to the negative correlation between $\delta^{13}C_{carb}$ values and organic matter contents in sediments from Lake Chenghai. Secondly, the input of bacteria in organic matter would cause negative $\delta^{13}C_{carb}$. Whereas, previous research showed no input of bacteria into organic matter (Zhu Zhengjie, 2009). Thirdly, the depleted ¹³C source affected the $\delta^{13}C_{carb}$, and this contribution enhanced with intensifying eutrophication. Actually, the source of CO₂ absorbed by algae would be altered with the change of lacustrine environment. During the initial stage of eutrophication, CO_2 absorbed by algae was derived from atmosphere. However, due to the strong eutrophication and rapid growth of algae, the balance between CO₂ in lake water and atmosphere would be destroyed, which would lead to the DIC being absorbed by algae derived from oxidation of organic matter, rather than atmospheric CO₂, thus giving rise to the negative $\delta^{13}C_{carb}$, since the δ^{13} C value of algae (-28‰) is much more negative than the value of atmospheric CO_2 (-7%). This seems to be the main factor that determines the variation of $\delta^{13}C_{carb}$ in Lake Chenghai. That is to say, the degradation of aquatic algae during the process of eutrophication is the primary factor leading to a decrease in δ^{13} C values of carbonate with increasing productivity in Lake Chenghai.

6 Conclusions

The conclusions we have drawn are given as follows:

(1) According to the multi-proxy analysis, the carbonate in Lake Chengai is authigenic. The source of organic matter in Lake Chenghai is derived mainly from algae, relative to terrestrial plants.

(2) Over the past one century, Lake Chenghai has undergone major changes in productivity and eutrophication due to natural evolution and human impacts. The multi-proxies including the carbon and nitrogen contents of organic matter, C/N ratios, inorganic carbon contents as well as the carbon and oxygen isotopic composition of carbonate have reliably recorded the historical environmental evolution of Lake Chenghai. The history of environmental evolution of Lake Chenghai during the last 100 years can be divided into three contrasting intervals. Before 1940 there were observed stable values of carbon and oxygen isotopes, the poor correlation between them and the lower carbon and nitrogen contents of organic matter, suggesting that Lake Chenghai during this time period is open, and the lake is oligotrophic. During the time period between 1940 and 1993, there is a slight increase in carbon and nitrogen contents of organic matter and C/N ratios, and an obvious decrease in δ^{13} C of carbonate, indicating that the eutrophication of Lake Chenghai is aggravated, which is considered as the result of the closeness of Lake Chenghai and the human impacts. After 1993, as shown by sharp increases in carbon and oxygen isotopic values of carbonate, the carbon and nitrogen contents of organic matter, C/N ratios and inorganic carbon contents, it is demonstrated that the lacustrine productivity is increased and the lake is of eutrophication. The rapid development of agriculture, breeding industries and intensive human activity may be responsible for present lacustrine productivity and eutrophication.

(3) The eutrophication of Lake Chenghai between 1940 and 1993 will induce a decrease in δ^{13} C values of carbonate, which is inconsistent with the conventional views that such an increase in productivity would produce higher δ^{13} C values of carbonate. We proposed that during the eutrophic periods, the degradation of blooming algae may be the main factor controlling the carbon isotopic composition of carbonate.

Acknowledgements The authors are grateful to the editors and reviewers for reviewing this paper, which contributed to an obvious improvement on the manuscript. This research project was financially supported jointly by the National Basic Research Program of China (Grant No. 2006CB403201) and the National Natural Science Foundation of China (Grant No. 40673068).

References

- Bai Zhanguo and Wan Guojiang (1998) Progress in the study of the soil erosion using radionuclides [J]. Advance in Earth Science. 13, 232–237 (in Chinese with English abstract).
- Chen Jing'an, Wan Guojiang, Wang Fushun, Huang Ronggui, Zhang Feng, and Schmidt R. (2002) Environmental records of carbon in recent lake sediments [J]. *Science in China* (Series D). 45, 875–884.
- Chen Jing'an, Wang Fushun, Wan Guojiang, Tang Degui, Zhang D.D., Huang Ronggui, Li Jian, and Xiao Tangfu (2008) δ¹³C-δ¹⁸O covariance: An effective indicator of hydrological closure for lakes [J]. Acta Geological Sinica. 82, 975–981.
- Dean W.E. (1999) The carbon cycle and biogeochemical dynamics in lake sediments [J]. *Journal of Paleolimnology*. 21, 375–393.
- Fronval T., Jensen N., and Buchardt B. (1995) Oxygen isotope disequilibrium precipitation of calcite in Lake Arres, Denmark [J]. *Geology*. 23, 463–466.
- Gasse F., Fontes J.C., Van C.E., and Wei K. (1996) Holocene environmental changes in Bangong Co basin (Western Tibet), Part 4: Discussion and conclusions [J]. *Palaeogeography, Palaeoclimatology, Palaeoecology*. **120**, 79–92.
- Henderson A.C.G. and Holmes J.A. (2009) Palaeolimnological evidence for environmental change over the past millennium from Lake Qinghai sediments: A review and future research prospective [J]. *Quaternary International.* **194**, 134–147.
- Jin Zhangdong, Yu Jiming, Wang Suming, Zhang Fei, Shi Yuewei, and You Chenfeng (2009) Constraints on water chemistry by chemical weathering in the Lake Qinghai catchment, northeastern Tibetan Plateau (China): Clues from Sr and its isotopic geochemistry [J]. *Hydrogeol*ogy Journal. 27, 2037–2048.
- Krishnamurthy R.V., Bhattacharya S.K., and Kusumgar S. (1986) Palaeoclimatic changes deduced from ¹³C/¹²C and C/N ratios of Kaeewa lake sediments, India [J]. *Nature*. **323**, 150–152.
- Lamb A.L., Leng M.J., Mohammed M.U., and Lamb H.F. (2004) Holocene climate and vegetation changes in the Main Ethiopian Rift Valley, inferred from the composition (C/N and δ¹³C) of lacustrine organic matter [J]. *Quaternary Science Reviews.* 23, 881–891.
- Lamb H.F., Leng M.J., Telford R.J., Ayenew T., and Umer M. (2007) Oxygen and carbon isotope composition of authigenic carbonate from an Ethiopian lake: a climate record of the last 2000 years [J]. *The Holocene*. 17, 515–524.
- Leng M.J. and Marshall J.D. (2004) Palaeoclimate interpretation of stable isotope data from lake sediment archives [J]. *Quaternary Science Re*views. 23, 811–831.
- Leng M.J., Jones M.D., Frogley M.R., Eastwood W.J., Kendrick C.P., and Roberts C.N. (2010) Detrital carbonate influences on bulk oxygen and carbon isotope composition of lacustrine sediments from the Mediterranean [J]. *Global and Planetary Change*. **71**, 175–182.
- Li H.C. and Ku T.L. (1997) δ^{13} C- δ^{18} O covariance as a paleohydrological indicator for closed-basin lakes [J]. *Palaeogeography, Palaeoclima*-

tology, Palaeoecology. 133, 69-80.

- Li Jian, Zhang Wei, Chen Jing'an, Zhu Zhengjie, Zeng Yan, Wang Jingfu, and Yang Yongqiong (2011) A newly developed sampler for collecting lake sediment cores [J]. *Earth and Environment.* **39**, 121–124 (in Chinese with English abstract).
- Li Younian (1983) Conventional Chemical Analysis Methods of Soil Agriculture [M]. Science Press, Beijing (in Chinese).
- Mayer B. and Schwark L. (1999) A 15,000-year stable isotope record from sediments of Lake Steisslingen, Southwest Germany [J]. *Chemical Geology*. 161, 315–337.
- Meyers P.A. (1994) Preservation of elemental and isotope source identification of sedimentary organic matter [J]. *Chemical Geology*. 114, 289–302.
- Meyers P.A. (1997) Organic geochemical proxies of paleoceanographic, paleolimnologic, and paleoclimatic processes [J]. Organic Geochemistry. 27, 213–250.
- Meyers P.A. and Ishiwatari R. (1993) Lacustrine organic geochemistry—An overview of indicators of organic matter sources and diagenesis in lake sediments [J]. *Organic Geochemistry*. **20**, 867–900.
- Mook W.G., Bommerson J.C., and Staverman W.H. (1974) Carbon isotope fractionation between dissolved bicarbonate and gaseous carbon dioxide [J]. *Earth and Planetary Science Letters*. 22, 169–176.
- Mullins H.L. (1998) Environmental change controls of lacustrine carbonate, Cayuga Lake, New York [J]. *Geology*. 26, 443–446.
- Neumann T., Stogbauer A., Walpersdorf E., Stüben D., and Kunzendorf H. (2002) Stable isotopes in recent sediments of Lake Arendsee, NE Germany: Response to eutrophication and remediation measures [J]. *Palaeogeography, Palaeoclimatology, Palaeoecology*. **178**, 75–90.
- Romanek C.S., Grossman E.L., and Morse J.W. (1992) Carbon isotope fractionation in synthetic aragonite and calcite: Effects of temperature and precipitation rate [J]. *Geochimica et Cosmochimica Acta*. 56, 419–430.
- Rosqvist G.C., Leng M.J., and Jonsson C. (2007) North Atlantic region atmospheric circulation dynamics inferred from a Late-Holocene lacustrine carbonate isotope record, northern Swedish Lapland [J]. *The Holocene*. **17**, 867–873.
- Stuiver M. (1970) Oxygen and carbon isotope ratios of fresh-water carbonates as climatic indicators [J]. Journal of Geophysical Research. 75, 5247–5257.
- Talbot M.R. (1990) A review of the palaeohydrological interpretation of carbon and oxygen isotopic ratios in primary lacustrine carbonates [J]. *Chemical Geology* (Isotopes Geoscience Section). 80, 261–279.
- Teranes J.L. and Bernasconi S.M. (2005) Factors controlling δ¹³C values of sedimentary carbon in hypertrophic Baldeggersee, Switzerland, and implications for interpreting isotope excursions in lake sedimentary records [J]. *Limnology and Oceanography.* **50**, 914–922.
- Teranes J.L. and McKenzie J.A. (1999a) Stable isotope response to lake eutrophication: Calibration of a high-resolution lacustrine sequence from Baldeggersee, Switzerland [J]. *Limnology and Oceanography*. 44, 320–333.
- Teranes J.L., McKenzie J.A., Bernasconi S.M., Lotter A.F., and Sturm M. (1999b) A study of oxygen isotopic fractionation during bio-induced calcite precipitation in eutrophic Baldeggersee, Switzerland [J]. *Geochimica et Cosmochimica Acta*. 63, 1981–1989.
- Wan Guojiang, Bai Zhanguo, Qing Hai, Mather J.D., Huang Ronggui, Wang Hairong, Tang Degui, and Xiao Baohua (2003) Geochemical records

in recent sediments of Lake Erhai: Implications for environmental changes in a low latitude-high altitude lake in Southwest China [J]. *Journal of Asian Earth Sciences.* **21**, 489–502.

- Wan Guojiang, Chen Jing'an, Wu Fengchang, Xu Shiqing, Bai Zhanguo, Wan Enyuan, Wang Changsheng, Huang Ronggui, Yeager K.M., and Santschi P.H. (2005) Coupling between ²¹⁰Pbex and organic matter in sediments of a nutrient-enriched lake: An example from Lake Chenghai, China [J]. *Chemical Geology*. **224**, 223–236.
- Wan Guojiang, Santschi P.H., Sturm M., Farrenkothen K., Lueck A., Werth E., and Schuler C. (1987) Natural (²¹⁰Pb, ⁷Be) and fallout (¹³⁷Cs, ^{239,240}Pu, ⁹⁰Sr) radionuclides as geochemical tracers of sedimentation in Greifensee, Switzerland [J]. *Chemical Geology*. 63, 181–196.
- Wang Suming and Dou Hongsheng (1998) *Lakes in China* [M]. Science Press, Beijing (in Chinese).
- Wang Yunfei (1993) Lacustrine carbonate chemical sedimentation and climatic-environmental evolution: A case study Qinghai Lake and Daihai Lake [J]. Oceanologia et Limnologia Sinica. 24, 31–36 (in Chinese with English abstract).
- Wang Yunfei, Hu Xiuying, and Zhang Xiuzhu (1989) Carbonate sediments in lakes of Yunnan, China [J]. Oceanologia et Limnologia Sinica. 20, 122–130 (in Chinese with English abstract).
- Wu Jinglu, Michael K.G., Jiang Xuezhong, Xia Weilang, and Wang Suming (2004) Sedimentary geochemical evidence of recent eutrophication of Lake Chenghai, Yunnan, China [J]. *Journal of Paleolimnology*. 32,

85-94.

- Wu Jinglu and Wang Suming (2003) Stable isotopic tracing of historic progressive eutrophication from Lake Chenghai, Yunnan in China [J]. *Quaternary Sciences.* 23, 557–564 (in Chinese with English abstract).
- Xu Hai, Ai Li, Tan Liangcheng, and An Zhisheng (2006a) Geochronology of a surface core in the northern basin of Lake Qinghai: Evidence from ²¹⁰Pb and ¹³⁷Cs radionuclides [J]. *Chinese Journal of Geochemistry*. 25, 301–306.
- Xu Hai, Ai Li, Tan Liangcheng, and An Zhisheng (2006b) Stable isotopes in bulk carbonates and organic matter in recent sediments of Lake Qinghai and their climatic implications [J]. *Chemical Geology*. 235, 262–275.
- Zhu Zhengjie (2009) Stable Carbon and Oxygen Isotopes in Lake Sediments and Li/Ca Ratios of Ostracod Shells and Paleoenvironmental Reconstructions [D]. Doctoral Thesis of Institute of Geochemistry, Chinese Academy of Sciences (in Chinese with English abstract).
- Zhu Zhengjie and Chen Jing'an (2009) Distinguishing the source of carbonates from lake sediments of Lake Chenghai, Yunnan Province [J]. *Journal of Lake Sciences.* 21, 382–386 (in Chinese with English abstract).
- Zhu Zhengjie, Chen Jing'an, Zeng Yan, Li Hang, Yan Hui, and Ren Shicong (2011) Research on the carbon isotopic composition of organic matter from Lake Chenghai and Caohai Lake sediments [J]. *Chinese Journal of Geochemistry*. **30**, 107–113.