



# Abnormal positive $\delta^{13}\text{C}$ values of carbonate in Lake Caohai, southwest China, and their possible relation to lower temperature

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## ABSTRACT

Carbon source inputs,  $\text{CO}_2$  exchange between atmosphere and lake water, as well as lacustrine productivity are commonly served as the main controls on  $\delta^{13}\text{C}$  values of authigenic carbonates in lake sediments. Generally,  $\delta^{13}\text{C}$  values of recent carbonates in most lakes are lower than  $+5\text{‰}$  (all values reported here with respect to the PDB standard), and rather few reach up to  $+13\text{‰}$ . Extreme positive  $\delta^{13}\text{C}$  values up to  $+23.10\text{‰}$  are reported in authigenic carbonate in Lake Caohai, southwest China, and some  $\delta^{13}\text{C}$  values are the most positive values in the previously reported surface water carbonate  $\delta^{13}\text{C}$  values in lakes. Simultaneously, there are two intervals of large carbonate  $^{13}\text{C}$  enrichment during the past 500 years, namely 1670–1714 AD and 1788–1881 AD.

On the basis of combination with the oxygen isotopic composition of carbonate and Drought/Flood index proxies (D/F), carbon source inputs,  $\text{CO}_2$  exchange between atmosphere and lake water can not cause this extreme carbonate  $^{13}\text{C}$  enrichment. In addition, the inconsistent between organic matter content and  $\delta^{13}\text{C}$  values of carbonate, lower organic matter  $\delta^{13}\text{C}$  values, as well as the weak/negative correlation between  $\delta^{13}\text{C}$  values of organic matter and carbonate during these two intervals confirmed that lacustrine productivity is also not the dominant factor that controls abnormal positive carbonate  $\delta^{13}\text{C}$  values. Temperature variations in Lake Caohai during the past 500 years were reconstructed from co-analysis of  $\delta^{18}\text{O}$  values of carbonate and organic matter cellulose, and periods of abnormal positive  $\delta^{13}\text{C}$  values of carbonate correspond well with the lower temperature periods. The 1670–1714 AD and 1788–1881 AD cold periods were synchronous with the coldest intervals of Little Ice Age (LIA), and also consistent with the Maunder and Dalton sunspot minimum, respectively. Considering these geochemical data together, although there is no direct effect between temperature and carbonate  $\delta^{13}\text{C}$  values, the lower temperature restrains the degradation of organic matter, and bacteria have the chance to participate the carbon isotopic fractionation of organic matter, thus generating the methane ( $\text{CH}_4$ ) gas, which has the extreme lower  $\delta^{13}\text{C}$  values up to  $-60\text{‰}$ , resulting in the extreme enrichment  $^{13}\text{C}$  in carbonates due to the preferential synthesis of  $^{12}\text{CH}_4$ . The important inputs of bacteria to sedimentary sequence during the periods of 1670–1714 AD and 1788–1881 AD have been further verified by the carbon isotopic fractionation between carbonate and organic matter. Therefore, this mechanism may be responsible for abnormal positive  $\delta^{13}\text{C}$  values in Lake Caohai. Abnormal positive  $\delta^{13}\text{C}$  values of carbonate in Lake Caohai may be indirectly ascribed to the lower temperature, and more attention should be paid to the carbon isotopic composition of carbonates in Lake Caohai in future research. Particular factors affecting carbonate carbon isotopic composition should be taken into account in order to avoid misinterpreting palaeoclimatic reconstructions.

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## 1. Introduction

Lacustrine sediments have become one of the most valuable archives for reconstructing past environmental changes (e.g. Wan et al., 2003; Jin et al., 2009). This is because they have numerous advantages such as extensive distribution, varied sedimentation rates, preservation of continuous climate record, sensitive to

regional/global climate, and containing many chemical, isotopic and biological proxies. In particular, since the pioneering works of Stuiver (1970) and McKenzie (1985), carbon isotopic composition of carbonates from lake sediments are now commonly and routinely applied as an indicator for environmental reconstruction (Stuiver, 1970; McKenzie, 1985). Lacustrine productivity, the isotope composition of in-flowing water, as well as CO<sub>2</sub> exchange between atmosphere and lake water, are generally considered as the main factors controlling the carbon isotopic composition of lacustrine authigenic carbonate (Li and Ku, 1997; Mayer and Schwark, 1999; Valero-Garces et al., 1999; Leng and Marshall, 2004; Teranes and Bernasconi, 2005; Xu et al., 2006a; Rosqvist et al., 2007; Chen et al., 2008). However, knowledge about the true causes of carbon isotopic variations in carbonate is far from complete, because they may be influenced by a wide range of factors, such as hydrological, hydrochemical and limnological conditions, and some factors are interlinked (Leng and Marshall, 2004). For instance,  $\delta^{13}\text{C}$  value of authigenic carbonate from lake sediments is insensitive to temperature variations, but temperature can cause hydrological and limnological changes, which will produce change of carbonate  $\delta^{13}\text{C}$  values (e.g. Li and Ku, 1997; Xu et al., 2006a).

In general, under isotopic equilibrium with the atmospheric CO<sub>2</sub> ( $\delta^{13}\text{C} = -7\text{‰}$ ), lake water  $\delta^{13}\text{C}$  would have a value between  $-0.2\text{‰}$  and  $+2.2\text{‰}$  (Mayer and Schwark, 1999; Leng and Marshall, 2004), and carbonate  $\delta^{13}\text{C}$  would have a value between  $+0.8\text{‰}$  and  $+3.2\text{‰}$ , because the  $\delta^{13}\text{C}$  value of calcite is 1‰ more positive than the corresponding  $\delta^{13}\text{C}$  value of the dissolved inorganic carbon (DIC) (Emrich et al., 1970; Mook et al., 1974; Leng and Marshall, 2004; Lamb et al., 2007). In some saline environments, carbonate  $\delta^{13}\text{C}$  value can reach  $+5\text{‰}$  (Valero-Garces et al., 1999). Lacustrine sediments with high carbonate  $\delta^{13}\text{C}$  values often occur in concentrated evaporating brines, anoxic sediments and some Andean lakes (Turner and Fritz, 1983; Stiller et al., 1985; Nissembaum et al., 1988; Talbot, 1990; Valero-Garces et al., 1999; Gu et al., 2004; Pueyo et al., 2011) (Fig. 1). Extreme  $^{13}\text{C}$  enrichments as high as  $+34.9\text{‰}$  in dissolved inorganic carbon (DIC) and as high as  $+13\text{‰}$  in carbonate have been found (Stiller et al., 1985; Valero-Garces et al., 1999). In addition, an increasing number of records illustrate that carbon isotopic composition of carbonate in lakes was not determined exclusively by lacustrine productivity, carbon source inputs or/and equilibrium with atmospheric CO<sub>2</sub>, especially some abnormal positive values, which may influence the interpretation of carbon

isotope record of carbonate (e.g. Stiller et al., 1985; Talbot and Kelts, 1986; Schwab et al., 1999; Valero-Garces et al., 1999; Lamb et al., 2000; Rosqvist et al., 2007). For example, in some Andean Altiplano lakes, carbonate  $\delta^{13}\text{C}$  values show up to  $+13\text{‰}$ , and degassing of carbon dioxide and residence time are considered as the main mechanisms for  $^{13}\text{C}$  enrichment (Valero-Garces et al., 1999). In Lake Apopka, methanogenesis can cause pore water  $\delta^{13}\text{C}$  values up to  $+26.4\text{‰}$  (Gu et al., 2004). Recently, some depleted  $\delta^{13}\text{C}$  values of lacustrine authigenic carbonate have been studied and explained, in particular within some hypertrophic lakes, and bacteria (Hollander and Smith, 2001; Teranes and Bernasconi, 2005) as well as isotopic disequilibrium (Fronval et al., 1995; Teranes and McKenzie, 1999; Wu et al., 2004) may be responsible for such depleted carbonate  $^{13}\text{C}$ . In contrast, the mechanism of abnormal positive  $\delta^{13}\text{C}$  values and their controlling factors are not well understood and remain inadequate.

This paper reports  $\delta^{13}\text{C}$  values up to  $+23.10\text{‰}$  in authigenic carbonate in Lake Caohai located in southwest China, with two intervals of large carbonate  $^{13}\text{C}$  enrichment during the past 500 years: 1670–1714 AD and 1788–1881 AD. Geochemical evidence is used to evaluate the mechanism of carbonate  $^{13}\text{C}$  enrichment, including Drought/Flood index, inorganic carbon content,  $\delta^{18}\text{O}$  values of carbonate and cellulose, organic matter content,  $\delta^{13}\text{C}$  values of organic matter as well as carbon isotopic fractionation between carbonate and organic matter. The results show that generation of methane by acetate fermentation is the most likely mechanism and the lower temperature may be indirectly responsible for abnormal positive carbonate  $\delta^{13}\text{C}$  values in Lake Caohai during these two intervals. This study is not intended to neglect the importance of other factors determining carbonate  $\delta^{13}\text{C}$  values in lake sediments, but rather is intended to highlight that some not typical and indirect factors should be considered, such as bacteria and temperature.

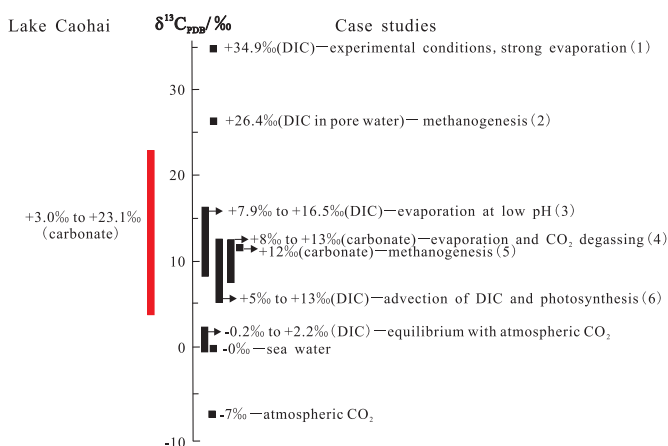
## 2. Regional setting

Lake Caohai ( $26^{\circ}49' - 26^{\circ}53'\text{N}$ ,  $104^{\circ}12' - 104^{\circ}18'\text{E}$ ) is a mountain, shallow and freshwater lake, situated in southwest Weining County, Guizhou Province, southwest China, approximately 350 km west of Guiyang (Fig. 2a). Lake Caohai is supplied by groundwater and precipitation, and is hydrologically closed. The water level of Lake Caohai is 2170 m. It has an average length of 14.2 km, with an average breadth of 1.76 km. The maximum depth of the lake is 5.0 m, with an average depth of 2.4 m. The lake surface area is about 25 km<sup>2</sup> and the catchment area is about 380 km<sup>2</sup>.

Geochemical data of lake water are presented in Table 1. The salinity of lake water is 134 mg/L, and the lake water is weak alkaline and high in hardness (Zhang et al., 2005). The lake is not eutrophic with low total phosphorus and nitrogen of lake water and sediments. Vegetation in the catchment is predominantly C3 plants, including evergreen plants and laurisilvae. Bedrock of the catchment mainly consists of shale and dolomite. Aquatic plants in Lake Caohai are submerged plants, including *Potamogeton lucens*, *Ottelia acuminata*, *Myriophyllum spicatum*. This region is influenced by the subtropical southwest monsoon. Mean annual precipitation at Lake Caohai is about 951 mm, and 88% of the total annual precipitation falls between May and October (Wang and Dou, 1998).

## 3. Materials and methods

In October 2007, a sediment core C2 was retrieved in the central part of Lake Caohai at 2 m water depth using a self-designed gravitational sediment sampler equipped with 59 mm internal diameter polymethyl tube (Fig. 2), and lake water, aquatic plants as well as catchment carbonates were also sampled. Lake water samples were



**Fig. 1.** High carbonate  $\delta^{13}\text{C}$  values in Lake Caohai and a compilation of high DIC  $\delta^{13}\text{C}$  values reported in the literature. Data sources: (1) Laboratory conditions (Stiller et al., 1985). (2) Lake Bosumtwi (Talbot and Kelts, 1986) and Lake Apopka (Gu et al., 2004). (3) Dead Sea brines (Stiller et al., 1985). (4) El Peinado and San Francisco lakes (Valero-Garces et al., 1999). (5) Lake Tilo and Lake Bosumtwi (Lamb et al., 2000; Rosqvist et al., 2007) (6) Lake Apopka (Gu et al., 2004).

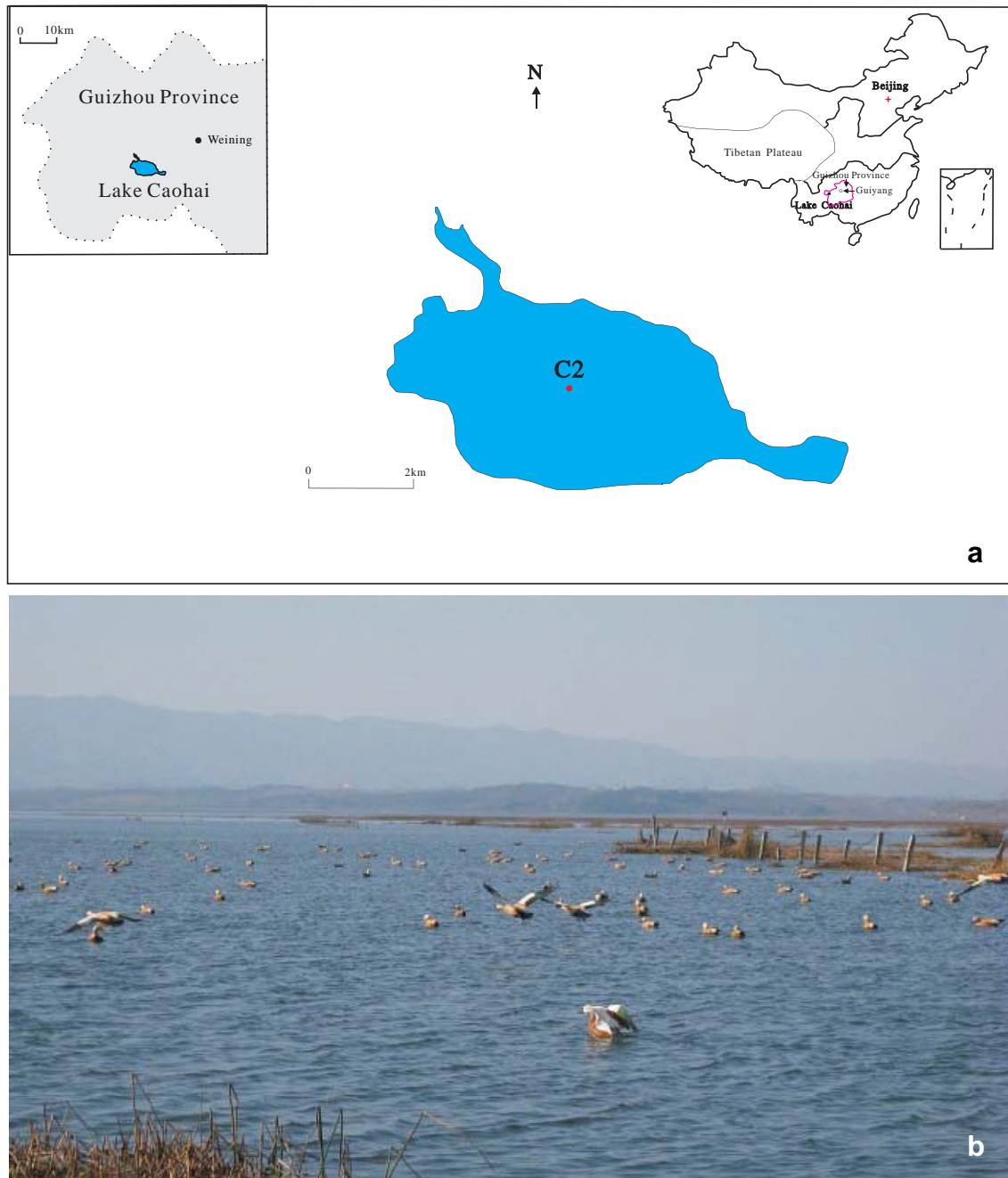


Fig. 2. (a) Geographical location of Lake Caohai and coring site of C2. (b) Ground photo of Lake Caohai.

immediately injected with a few drops of  $\text{HgCl}_2$  solution and sealed in 60 ml bottles. The suspended layer was not disturbed and the interface water was clear when coring, implying that the sediment core was well preserved. The core with the length of 149 cm was

**Table 1**  
Geochemical features of lake water in Lake Caohai.

$\text{Ca}^{2+}$ (mg/l)	$\text{Mg}^{2+}$ (mg/l)	$\text{K}^+$ (mg/l)	$\text{Na}^+$ (mg/l)	$\text{Cl}^-$ (mg/l)	$\text{SO}_4^{2-}$ (mg/l)
45.62	9.52	5.96	10.89	50.52	49.49
$\text{HCO}_3^-$ (mg/l)	$\text{CO}_3^{2-}$ (mg/l)	TN(mg/l) <sup>a</sup>	TP(mg/l) <sup>a</sup>	$\delta^{13}\text{C}_{\text{DIC}}\text{‰}^a$	$\delta^{18}\text{O}_{\text{lw}}\text{‰}^a$
4.29	3.61	0.25	0.007	-3.96	-6.08

Data sources.

<sup>a</sup> This study. Others from Zhang et al. (2005).  $\text{CO}_3^{2-}$  and  $\text{HCO}_3^-$  were measured by titration using HCl. Cations and anions were determined by ICP-AES.

sectioned at 1–2 cm intervals and put into plastic bags and sealed in situ in the field for transport to the laboratory. Each subsample was dried using vacuum freeze drier (FD-IA-50), then terrestrial plant remains were picked out from the sediment core for radiocarbon  $^{14}\text{C}$  dating using Accelerator Mass Spectrometer (AMS) at the Scottish Universities Environmental Research Centre AMS Facility. Based on the dry weight sediments, the mass depth was calculated. Before geochemical analysis, all dry sediment samples were ground to homogenous powders smaller than 124  $\mu\text{m}$ .

Total inorganic carbon contents (TIC) were determined by chemical volumetric method with an analytical precision better than 5% (Li, 1983; Chen et al., 2002). Precisely 3 g subsamples were reacted with 20 ml 0.5 M HCl for 5 min with the temperature of 100 °C, and the remaining HCl was accurately titrated with

0.25 M NaOH, thus the inorganic carbon can be calculated. Elemental analyses of total carbon (TC) were measured by the elemental analyzer (PE2400 Series) with an error less than 5%. TOC contents were calculated as the difference between TC and TIC.  $\delta^{13}\text{C}$  value of DIC was determined by the acidification with anhydrous phosphoric acid to produce  $\text{CO}_2$ . After being purified cryogenically in a vacuum line, the  $\text{CO}_2$  was transferred in a Finnigan MAT-252 for measurement of carbon isotopic ratio. For carbonate stable isotopic analysis, samples were wet sieved to smaller than 20  $\mu\text{m}$ . As to measurement of stable isotopes of carbonate and organic matter, parallel measurement for each of the sample was carried out to monitor the analytical precision and to calibrate the samples for analytical results.  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values of carbonates were analyzed using a GV IsoPrime stable isotope ratio mass spectrometer (IRMS) coupled with an online carbonate preparation system. Samples reacted with anhydrous phosphoric acid with the temperature of 90 °C, and reaction gases were cryogenically purified to remove water and other gases. Purified  $\text{CO}_2$  was introduced into the mass spectrometer for carbon and oxygen isotopic measurement. Samples for determination of carbon isotopic composition of organic matter were pretreated with HCl (1 M) and placed in water bath for 2 h at 60 °C to remove carbonates, then rinsed repeatedly with distilled water for four times.  $\delta^{13}\text{C}$  values of organic matter were analyzed on the Finnigan Delta Plus isotope ratio mass spectrometer coupled with an Elemental Analyzer (EA). The carbon in the sample was oxidized at 1000 °C to form  $\text{CO}_2$ , which is measured for  $\delta^{13}\text{C}$  values in the mass spectrometer.

Cellulose extraction from lake sediments and aquatic plants has been used following the method of Hong et al. (2000). Oxygen isotope composition of cellulose was determined using a Finnigan Delta Plus Isotope Ratio Mass Spectrometer (IRMS) equipped with a Thermal Chemical Elemental Analyzer (TC/EA). About 1 mg of cellulose sample was loaded in a silver capsule and dropped by the auto-sampler into the pyrolysis furnace of the TC/EA. The oxygen in the sample forms carbon monoxide gas, which is measured for  $\delta^{18}\text{O}$  in the IRMS. The isotopic composition of samples is defined as delta ( $\delta$ ) notations in parts per thousand:

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

where  $R$  is the  $^{13}\text{C}/^{12}\text{C}$  and  $^{18}\text{O}/^{16}\text{O}$  ratio of a sample and isotopic ratios were reported relative to the international PDB standard except cellulose oxygen isotope, which is relative to SMOW standard. Based on the parallel measurement, analytical precision is better than 0.1‰ for  $\delta^{13}\text{C}$  values of DIC, carbonate and organic matter, 0.15‰ for  $\delta^{18}\text{O}$  values of carbonate, and 0.30‰ for cellulose  $\delta^{18}\text{O}$  values. All the measurements were conducted at the State Key Laboratory of Environmental Geochemistry, Chinese Academy of Sciences in Guiyang.

#### 4. Results

Sediment samples in core C2 without clear lamination consist of homogeneous silty clay. Dating of Lake Caohai sediments is difficult due to the lack of terrestrial plants and the abundant aquatic plants. In this study, only one terrestrial remain with higher C/N ratio in this sediment core was picked out for  $^{14}\text{C}$  dating. The dating model of core C2 was established on the basis of linear extrapolation. Due to the compaction effects, the depth sedimentation rate in surface sediments is largely different from the bottom sediments (e.g. Chen et al., 2002; Xu et al., 2006a). Therefore, mass depth is generally adopted to calculate sedimentation rate instead of depth. The radiocarbon age was calibrated using the University of Oxford Radiocarbon Accelerator Unit calibration program (OxCal3). The chronology of C2-62 (lab # SUERC21791) was about 237a BP with the mass depth of 29.36 g/

**Table 2**

Carbonate content,  $\delta^{13}\text{C}$ ,  $\delta^{18}\text{O}$ , organic matter content and  $\delta^{13}\text{C}$ , cellulose  $\delta^{18}\text{O}$  values from Lake Caohai sediment samples.

Sample number	Year/AD	$\delta^{13}\text{C}_{\text{carb}}\text{‰}$	$\delta^{18}\text{O}_{\text{carb}}\text{‰}$	$C_{\text{inorg}}\%$	$C_{\text{org}}\%$	$\delta^{13}\text{C}_{\text{org}}\text{‰}$	$\delta^{18}\text{O}_{\text{cell}}\text{‰}$
C2-1	2007	-3.31	-7.06	4.48	13.02	-15.31	23.8
C2-2	2006	-2.95	-5.83	1.91	14.33	-18.69	22.12
C2-3	2004	-4.26	-8.49	1.65	8.57	-13.51	20.63
C2-4	2001	-6.73	-13.12	1.54	6.52	-14.77	20.49
C2-5	1998	-4.01	-8.42	1.52	5.43	-19.14	20.36
C2-6	1993	-4.31	-9.56	1.28	5	-22.52	19.88
C2-7	1988	-7.69	-10.16	1.32	4.91	-23.59	20.14
C2-8	1985	-3.97	-9.25	1.48	4.21	-17.15	21.11
C2-9	1982	-1.44	-8.63	1.57	3.42	-25.02	19.11
C2-10	1979	1.26	-8.21	1.69	2.5	-25.62	19.99
C2-11	1975	0.96	-6.94	1.95	2.91	-25.57	17.91
C2-12	1971	0.36	-7.68	1.82	3.09	-23.43	18.16
C2-13	1968	-1.91	-10.03	2.87	3.85	-22.98	20.49
C2-14	1965	-4.57	-11.71	2.33	4.65	-19.74	19.87
C2-15	1962	-4.89	-10.41	1.47	6.24	-22.83	20.63
C2-16	1959	-6.43	-12.29	1.57	7.3	-24.59	17.71
C2-17	1957	-4.39	-11.68	1.44	7.12	-23.7	19.55
C2-18	1954	-3.39	-9.59	1.46	6.45	-23.38	20.1
C2-19	1952	-4.69	-8.85	1.63	6.6	-23.88	20.86
C2-20	1949	-2.9	-9.2	1.82	4.95	-25.46	21.11
C2-21	1946	-4.55	-8.83	1.71	5.62	-25.18	21.5
C2-22	1943	-5.53	-9.56	2.09	9.23	-23.22	19.43
C2-23	1941	-5.43	-10.85	1.18	9.64	-23.95	17.07
C2-24	1938	-5.21	-10.61	1.32	8.67	-23.35	17.65
C2-25	1935	-4.8	-10.99	1.33	8.26	-23.35	17.81
C2-26	1933	-3.84	-10.11	0.87	8.79	-24.07	18.54
C2-27	1930	-3.79	-10.02	0.82	7.87	-24.38	16.82
C2-28	1926	-2.67	-10.41	0.85	6.4	-22.7	16.1
C2-29	1922	-1.82	-9.17	0.53	7.46	-22.46	16.4
C2-30	1919	-2.67	-9.32	0.81	7.29	-21.85	16.34
C2-31	1915	-2.65	-9.41	1.13	7.11	-22.65	15.95
C2-32	1910	-2.45	-8.77	1.02	6.86	-22.13	17.19
C2-33	1906	-2.89	-9	0.79	7.04	-20.77	16.6
C2-34	1903	-3.95	-10.8	0.76	6.98	-22.91	18.03
C2-35	1899	-4.11	-11.64	0.6	6.07	-22.87	18.02
C2-36	1896	-5.86	-13.03	0.84	9.9	-23.85	20.31
C2-37	1894	-6.08	-13.11	1.27	9.74	-23.51	16.55
C2-38	1892	-8.12	-17.1	1.8	14.58	-18.62	24.35
C2-39	1890	-9.89	-19.52	2.11	16.53	-20.54	15.69
C2-40	1888	-14.25	-19.77	2.06	13.68	-28.02	14.02
C2-41	1886	-10.91	-17.13	1.59	10.44	-27.32	16.29
C2-42	1884	-12.97	-19.87	1.54	13.84	-27.97	15.4
C2-43	1881	4	-12.86	0.83	6.83	-27.94	14.4
C2-44	1877	12.09	-10.74	0.9	4.95	-27.84	17.83
C2-45	1873	18.04	-8.98	0.94	3.48	-28.63	16.94
C2-46	1870	20.94	-8.01	1.03	3.77	-29.14	16.04
C2-47	1866	9.9	-11.87	0.73	5.2	-29.13	14.9
C2-48	1862	17.45	-9.89	0.65	2.2	-28.99	15.69
C2-49	1856	14.96	-11.21	0.86	1.69	-28.57	14.24
C2-50	1851	14.51	-9.41	0.97	1.34	-27.76	16.85
C2-51	1845	18.09	-10	0.91	2.55	-26.64	13.81
C2-52	1839	12.06	-12.24	0.52	1.84	-27.01	14.53
C2-53	1832	15.12	-12.26	0.28	1.59	-27.68	15.11
C2-54	1825	23.04	-10.12	0.63	0.76	-28.15	16.11
C2-55	1818	22.52	-8.95	0.65	0.88	-24.56	17.52
C2-56	1811	23.1	-9.66	0.78	0.75	-23.87	17.39
C2-57	1804	19.08	-11.94	0.55	0.43	-24.3	13.15
C2-58	1797	6.27	-11.14	0.7	0.27	-25.34	14.45
C2-59	1788	2.95	-10.52	0.44	0.52	-25.15	15
C2-60	1779	0.25	-15.68	0.65	0.34	-25.46	10.12
C2-61	1771	-0.11	-16.7	0.6	0.3	-25.73	12.18
C2-62	1763	-0.25	-17.91	0.52	0.38	-22.93	9.86
C2-63	1755	-4.08	-17.74	0.68	0.22	-24.95	9.74
C2-64	1747	-3.11	-15.5	0.7	0.24	-24.67	12.56
C2-65	1739	-5.46	-15.13	0.73	0.2	-25.04	12.04
C2-66	1730	-2.71	-16.19	0.49	0.37	-24.4	9.46
C2-67	1722	-3.41	-14.15	0.78	0.22	-22.75	11.29
C2-68	1714	5.04	-13.43	0.73	0.46	-23.47	14.01
C2-69	1708	14.22	-12.71	0.7	0.68	-24.59	14.3
C2-70	1701	18.77	-13.65	0.63	0.99	-23.39	
C2-71	1694	16.99	-9.01	0.47	1.15	-23.57	16.24
C2-72	1686	13.5	-10.77	0.52	0.79	-23.64	14.52
C2-73	1678	7.46	-13.75	0.26	0.89	-21.3	14.28

Table 2 (continued)

Sample number	Year/AD	$\delta^{13}\text{C}_{\text{carb}}/\text{‰}$	$\delta^{18}\text{O}_{\text{carb}}/\text{‰}$	$\text{C}_{\text{inorg}}\%$	$\text{C}_{\text{org}}\%$	$\delta^{13}\text{C}_{\text{org}}/\text{‰}$	$\delta^{18}\text{O}_{\text{cell}}/\text{‰}$
C2-74	1670	2.59	-16.6	0.65	0.54	-20.84	12.46
C2-75	1662	-8.76	-18.22	0.71	0.51	-22.46	11.27
C2-76	1656	-10.62	-18.02	0.35	0.94	-22.35	11.99
C2-77	1649	-11.05	-15.26	0.21	1.16	-23.24	11.29
C2-78	1642	-7.82	-12.64	0.52	0.95	-22.24	13.7
C2-79	1635	-2.89	-15.45	0.55	1.14	-22.7	12.45
C2-80	1629	5.94	-12.34	0.32	1.79	-22.52	15.54
C2-81	1622	2.07	-13.8	0.61	1.29	-24.62	12.96
C2-82	1615	-7.31	-15.78	0.61	0.9	-23.86	12.39
C2-83	1609	-8.5	-17.83	0.64	0.78	-21.3	12.39
C2-84	1603	-7.86	-17.79	0.7	0.7	-22.57	8.69
C2-85	1597	-4.35	-16.4	0.64	0.61	-22.13	9.51
C2-86	1591	-1.83	-11.14	0.87	0.41	-23.23	
C2-87	1585	-1.58	-11.33	0.55	0.82	-24.79	15.09
C2-88	1578	-2.02	-11.51	0.69	0.63	-23.9	14.8
C2-89	1572	-0.92	-9.28	0.9	0.84	-25.31	15.95
C2-90	1567	-0.99	-8.05	1.35	1.16	-27.44	16.45
C2-91	1560	-1.07	-7.47	2.79	1.33	-25.51	17.55
C2-92	1552	-1.69	-7.97	3.61	0.85	-25.42	20.69
C2-93	1545	-1.81	-8.2	3.69	0.77	-24.97	
C2-94	1537	-1.65	-8.25	3.87	0.45	-25.98	22.18
C2-95	1531	1.8	-8.65	4.18	0.82	-26.71	20.97
C2-96	1523	3.49	-7.9	4.57	0.77	-27.44	21.13
C2-97	1516	3.31	-7.94	4.76	0.85	-25.51	20.48
C2-98	1508	3.29	-7.96	4.59	1.08	-24.97	21.22
C2-99	1500	3.27	-7.97	4.21	1.19	-24.54	20.46

$\text{cm}^2$ , thereby the average mass sedimentation rate of Lake Caohai is about  $0.12 \text{ g/cm}^2 \text{ a}$ . The accumulation rate in Lake Caohai is regarded to be relatively stable as a result of good preservation conditions, limited human impacts, as well as the sampling in the central part of lake. In terms of this mass sedimentation rate, the dating model of sediment core C2 was established (Table 2).

Variations of  $\delta^{13}\text{C}$  values of sediment carbonate in Lake Caohai with chronology are shown in Table 2 and presented in Fig. 3. As

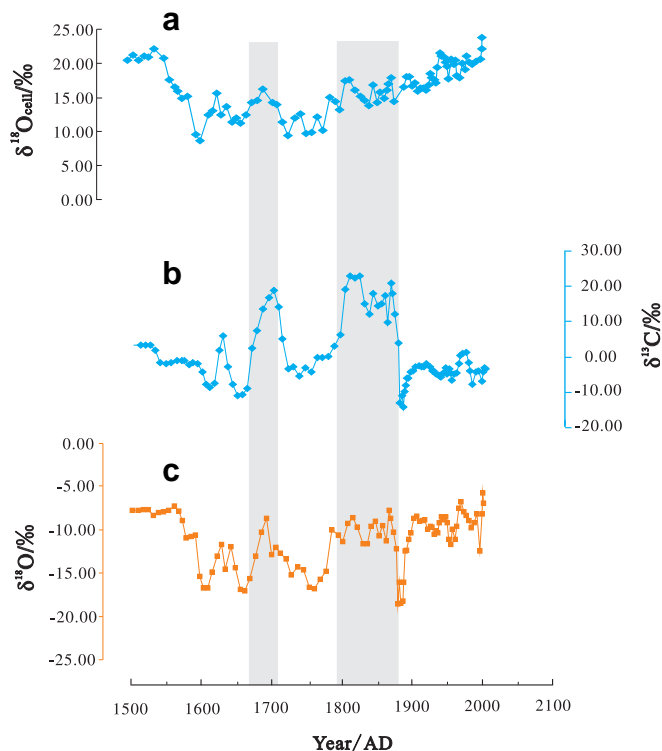


Fig. 3. Evolution of  $\delta^{18}\text{O}$  values of cellulose (a),  $\delta^{13}\text{C}$  (b),  $\delta^{18}\text{O}$  (c) values of carbonate and in Lake Caohai during the last 500 years.

indicated, carbonate  $\delta^{13}\text{C}$  values show several unusual features. Firstly, there is a wide range of carbon isotopic values, ranging from  $-14.25\text{‰}$  to  $+23.10\text{‰}$  with a mean value of  $0.61\text{‰}$ , much higher than the previous carbon isotopic variations. Secondly, there are two periods of extreme carbonate  $^{13}\text{C}$  enrichment during the past 500 years, namely 1670–1714 AD and 1788–1881 AD, and the most positive  $\delta^{13}\text{C}$  value reach  $+23.10\text{‰}$ . Given the occurrence of abnormal positive  $\delta^{13}\text{C}$  values of authigenic carbonate in Lake Caohai, three samples C2-56, C2-57 and C2-58 were selected for subsequent analysis using phosphoric acid pretreatment method to measure carbon isotopic values through MAT-252 mass spectrometer for further confirmation, and the results indicated that the abnormal positive carbonate  $\delta^{13}\text{C}$  values at Lake Caohai are in existence.

Carbonate  $\delta^{18}\text{O}$  values in Lake Caohai vary between  $-19.87\text{‰}$  and  $-5.83\text{‰}$ , with an average value of  $-11.66\text{‰}$  (Fig. 3).  $\delta^{18}\text{O}$  values of cellulose show a similar pattern with carbonate  $\delta^{18}\text{O}$ , varying between  $8.69\text{‰}$  and  $24.17\text{‰}$  with a mean value of  $16.45\text{‰}$ . TOC varies between  $0.21\%$  and  $16.53\%$ , with an average value of  $4.05\%$ . TIC varies between  $0.20\%$  and  $4.76\%$ , with an average value of  $1.36\%$ .  $\delta^{13}\text{C}$  values of organic matter display small variations as compared with carbonate  $\delta^{13}\text{C}$  value, varying between  $-13.51\text{‰}$  and  $-29.14\text{‰}$ , with an average value of  $-23.94\text{‰}$ . During the intervals of 1670–1714 AD and 1788–1881 AD, the TIC and TOC are very low.

## 5. Discussion

### 5.1. Sources of sedimentary carbonate

Under natural conditions, carbonates in lake sediments are composed of autochthonous and allochthonous carbonate. Allochthonous carbonates are derived from the weathering of parent rocks. Autochthonous carbonates are derived by primary precipitation through photosynthetic utilization of  $\text{CO}_2$  or chemical changes of lake water resulting in the calcium carbonate supersaturation, biogenic carbonates such as ostracods and molluscs, and post-depositional diagenetic carbonates (Kelts and Hsü, 1978; Chen et al., 2002; Leng and Marshall, 2004; Zhu and Chen, 2009; Leng et al., 2010). No biogenic carbonates are precipitated in Lake Caohai. Before analysis of carbonate-related indicators it is necessary to identify the source of carbonates from lake sediments. Recent studies have developed several lines of evidences to demonstrate carbonate is authigenic in Lake Chenghai, including combination with  $\delta^{18}\text{O}$  values of surface carbonate and aquatic plant cellulose,  $\delta^{13}\text{C}$  values of dissolved inorganic carbon and surface carbonate, and comparison the ionic activity product (IAP) with the equilibrium constant (Zhu and Chen, 2009). Applying this method in Lake Caohai, all the evidence illustrated that carbonate in Lake Caohai is authigenic. For instance, the average  $\delta^{13}\text{C}$  value of DIC is  $-3.96\text{‰}$ , thereby the calculated surface carbonate  $\delta^{13}\text{C}$  value would be  $-2.96\text{‰}$  in terms of the  $1\text{‰}$  difference between  $\delta^{13}\text{C}$  value of carbonate and its corresponding DIC (Emrich et al., 1970; Mook et al., 1974), similar with the measured surface sediment sample. The carbon isotopic composition of carbonate in Lake Caohai catchment is  $0.50\text{‰}$ , very different from the values of core sediment carbonates in Lake Caohai, in particular the abnormal positive  $\delta^{13}\text{C}$  values. Furthermore, if the carbonate in Lake Caohai is mainly allochthonous from catchment, stable  $\delta^{13}\text{C}$  values of the sediment carbonate would be expected due to the certain  $\delta^{13}\text{C}$  values of dolomite. Additionally, calcite was the only carbonate mineral identified by XRD. They are hypidiomorphic-granular or aggregate. All these observations demonstrate that carbonate in Lake Caohai is authigenic, rather than allochthonous. This conclusion is in consistent with the previous studies by mineral analysis (Chen et al., 2001). Therefore, carbonate-related proxies in Lake Caohai

sediments can be used to deduce the palaeoenvironmental information.

## 5.2. General interpretation of the $\delta^{13}\text{C}$ record

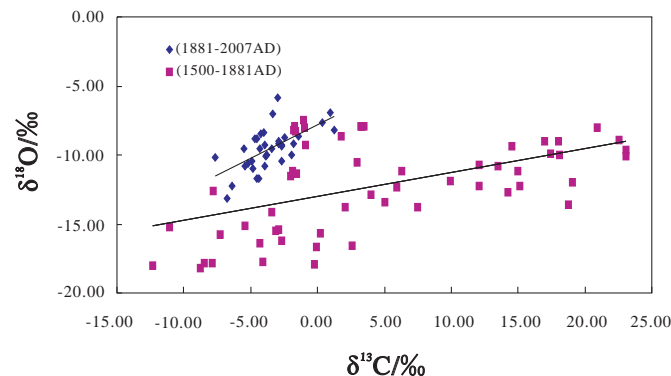
$\delta^{13}\text{C}$  values of authigenic carbonate in the lakes are mainly controlled by the carbon isotopic fractionation when they are precipitated and the  $\delta^{13}\text{C}$  values of DIC (Talbot, 1990; Romanek et al., 1992; Li and Ku, 1997; Mayer and Schwark, 1999; Leng and Marshall, 2004; Xu et al., 2006a). According to the research by Romanek et al., there is a relatively small temperature effect (0.0355‰/C) and carbonate precipitation rate effect (Romanek et al., 1992). Otherwise, the effect of DIC concentration is also very small through the experimental study (Spero et al., 1997). In consequence,  $\delta^{13}\text{C}$  of authigenic carbonate in lakes can provide information on the  $\delta^{13}\text{C}$  of DIC. Generally, factors predominantly influence carbon isotopic composition of DIC include the isotopic composition of the inflowing water,  $\text{CO}_2$  exchange between lake water and atmosphere, as well as photosynthesis/respiration of aquatic plants in the lakes (Leng and Marshall, 2004; Xu et al., 2006a). The increase of carbonate  $\delta^{13}\text{C}$  may be interpreted commonly as the increase of lake productivity/eutrophication, the strong evaporation as well as the long lake water residence time.

## 5.3. Mechanism of extreme enrichment of carbonate $^{13}\text{C}$ in Lake Caohai

A feature of the carbon isotopic data in Lake Caohai is the extreme enrichment  $^{13}\text{C}$  in primary carbonates. Below, several potential factors that can generate large carbonate  $^{13}\text{C}$  enrichment in Lake Caohai are discussed.

### 5.3.1. Evaporation effects

Generally, a strong net evaporation will also result in a large increase of the  $\delta^{13}\text{C}$  of DIC. Strong evaporation will enhance the preferential release of the light carbon into atmosphere, leading to the increase of the  $\delta^{13}\text{C}$  of DIC pool (Li and Ku, 1997; Lamb et al., 2000). For example, in laboratory conditions, strong evaporation can result in DIC  $^{13}\text{C}$  enrichment as high as +34.9‰ (Stiller et al., 1985). In addition, in some arid regions, both  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  are high and co-vary due to the evaporation effects (Li and Ku, 1997; Leng and Marshall, 2004). In Lake Caohai, net evaporation may influence carbonate  $\delta^{13}\text{C}$  to a certain extent, which was supported by the correlation between  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values of carbonate (Fig. 4). However, the oxygen isotopic composition of lake Caohai

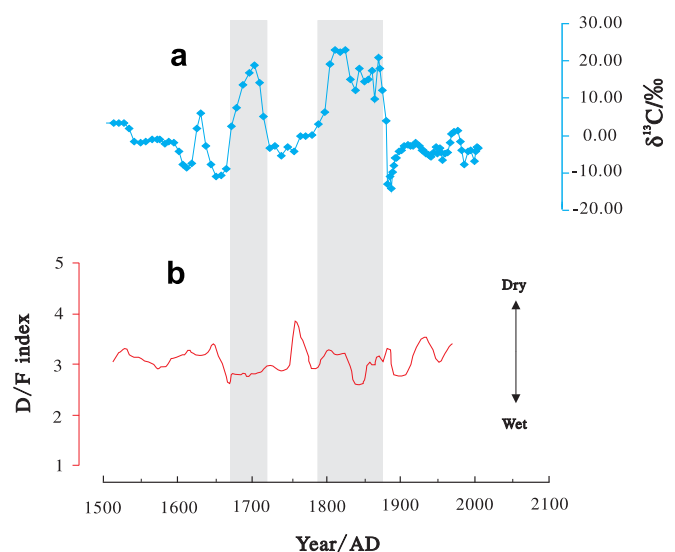


**Fig. 4.** Covariance of  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  in carbonate of sediment core in Lake Caohai during the past 500 years. Due to the effect of methanogenesis, the covariance of  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  has been separated into two populations. After 1881 AD, the good correlation between  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  of carbonate suggests that the same factor controlling them. Before 1881 AD, with the high values of  $\delta^{13}\text{C}$  and effects of bacteria, the correlation is poor.

water is  $-6.08\text{‰}$ , similar to the precipitation oxygen isotopic composition, suggesting no large evaporative enrichment. The wide range of carbonate  $\delta^{18}\text{O}$  values ( $14.04\text{‰}$ ) is much smaller than  $\delta^{13}\text{C}$  ( $37.35\text{‰}$ ), and the  $\delta^{18}\text{O}$  values are negative, with the mean value of  $-11.66\text{‰}$ . After 1881 AD, the strong correlation between  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values of carbonate may be ascribed to the same factor controlling them, such as an evaporation effect. Before 1881 AD, in particular within periods of the high carbonate  $\delta^{13}\text{C}$  values, heavier  $\delta^{13}\text{C}$  values without increasing  $\delta^{18}\text{O}$  values, indicating that others factors may play an important role.  $\delta^{13}\text{C}$  values of carbonate were compared with the D/F index of Guiyang, which have been reconstructed on the basis of historical documentary record (Zhang, 2004). An increase of D/F was defined to represent decreased precipitation or increased evaporation. As indicated in Fig. 5, abnormal positive  $\delta^{13}\text{C}$  values correspond with the wet periods. This evidence illustrates that evaporation effects cannot cause the extreme carbonate  $^{13}\text{C}$  enrichment.

### 5.3.2. Lacustrine productivity effects

In some high productivity lakes, lacustrine productivity is often considered as the dominant influence on  $\delta^{13}\text{C}$  values of carbonate (Teranes and McKenzie, 1999; Teranes and Bernasconi, 2005). During the period of high productivity, the aquatic plants will use bicarbonate as their carbon source during photosynthesis due to the rapid consumption of aqueous  $\text{CO}_2$ . This process will not only result in an increase of  $\delta^{13}\text{C}$  value of DIC due to the preferential release of the  $^{12}\text{C}$  from the DIC pool during photosynthesis (Schelske and Hodell, 1991; Neumann et al., 2002), but also lead to an increase of  $\delta^{13}\text{C}$  value of organic matter (Meyers, 1997; Hodell and Schelske, 1998; Leng and Marshall, 2004; Xu et al., 2006a; Zhu et al., 2011), because the  $\delta^{13}\text{C}$  value of  $\text{HCO}_3^-$  is much more positive than  $\delta^{13}\text{C}$  value of aqueous  $\text{CO}_2$  (Meyers, 1997). Therefore, the increase of lacustrine productivity will cause both the increase of  $\delta^{13}\text{C}$  values of carbonate and organic matter (Meyers, 1997; Teranes and McKenzie, 1999; Neumann et al., 2002; Leng and Marshall, 2004; Teranes and Bernasconi, 2005; Xu et al., 2006a; Lu et al., 2010). Organic matter in Lake Caohai is derived from aquatic plants (Zhu et al., 2011), and total organic carbon is used to interpret as the result of variations of lake productivity (Meyers, 1997; Zhu et al., 2011). During the periods of extreme carbonate  $^{13}\text{C}$  enrichment, organic matter contents are very low, with the mean value lower than 1% (Fig. 6), indicating that productivity



**Fig. 5.** Comparison between D/F index (five-year running mean) of Guiyang (a) (see location in Fig. 2a) and carbonate  $\delta^{13}\text{C}$  values in Lake Caohai (b).

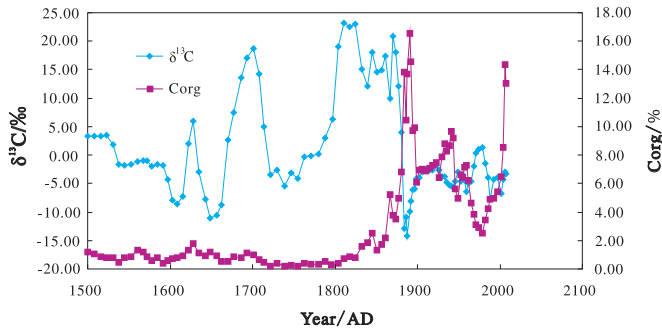


Fig. 6. Relationship between  $\delta^{13}\text{C}$  values of carbonate and organic matter content in Lake Caohai during the past 500 years.

during these two intervals is low, and lacustrine productivity may be not the factor determining the  $\delta^{13}\text{C}$  value of carbonate. Further support for the above interpretation can be derived from the data of  $\delta^{13}\text{C}$  values of organic matter. During the periods of 1670–1714 AD and 1788–1881 AD,  $\delta^{13}\text{C}$  values of organic matter are low (Fig. 7), and the correlation between  $\delta^{13}\text{C}$  values of carbonate and organic matter is also poor (Fig. 8). In addition to the productivity, eutrophication would also lead to heavier carbonate  $\delta^{13}\text{C}$  values. Limnological observations showed that Lake Caohai began to be polluted in the late 1980s (Zhang et al., 2005). Nutrient loadings P and N concentrations in Lake Caohai water are low (Table 1), suggesting that this lake is not eutrophic. Therefore, extreme carbonate  $^{13}\text{C}$  enrichment in Lake Caohai is not the result of lacustrine productivity or eutrophication.

### 5.3.3. Methanogenesis

As mentioned above, other factors would dominantly influence the abnormal positive carbonate  $\delta^{13}\text{C}$  values in Lake Caohai. Generally speaking, the largest carbon isotopic fractionations are associated with organic sources. Bacterial oxidation of organic compounds introduces  $\text{CO}_2$  with very low  $\delta^{13}\text{C}$  values in the DIC. In contrast, methanogenesis incorporates  $^{12}\text{CO}_2$  with very high  $\delta^{13}\text{C}$  values in the DIC. Therefore, considering these geochemical data together, abnormal positive carbonate  $\delta^{13}\text{C}$  values in Lake Caohai may be attributed to the large kinetic fractionation with the generation of methane, which has the extreme depleted  $\delta^{13}\text{C}$  value ( $-60\text{‰}$ ), causing a subsequent enrichment of  $^{13}\text{C}$  in DIC pool due to the large escape of  $^{12}\text{C}$  in  $\text{CH}_4$ . Similar mechanisms may occur in some lakes, especially organic-rich lakes, as suggested by a number of previous studies (Talbot and Kelts, 1986; Whiticar et al., 1986, 1999; Lamb et al., 2000; Rosqvist et al., 2007). In Lake Tilo and Lake Bosumtwi, methane-producing bacteria were thought to facilitate carbonate  $\delta^{13}\text{C}$  values to  $+12\text{‰}$  (Lamb et al., 2000; Rosqvist et al., 2007) and  $+10\text{‰}$  (Talbot and Kelts, 1986), respectively. In Lake

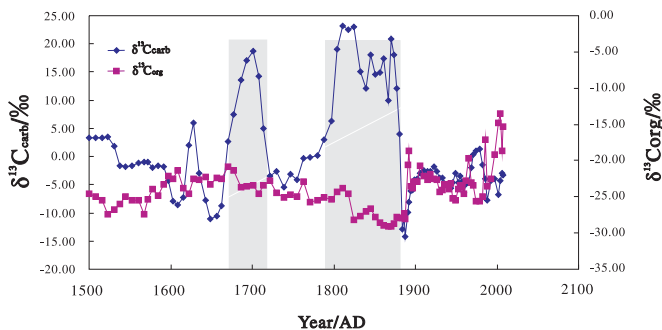


Fig. 7. Evolution of  $\delta^{13}\text{C}$  values of carbonate and organic matter in Lake Caohai. During the intervals of high carbonate  $^{13}\text{C}$  enrichment, organic matter  $\delta^{13}\text{C}$  values are very low.

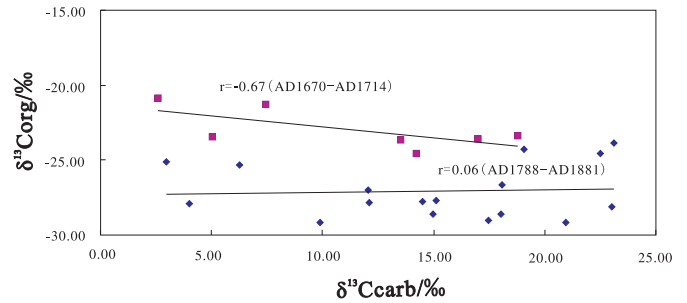


Fig. 8. Correlation between  $\delta^{13}\text{C}$  values of carbonate and organic matter during the two intervals with abnormal positive carbonate  $\delta^{13}\text{C}$  values in Lake Caohai over the past 500 years.

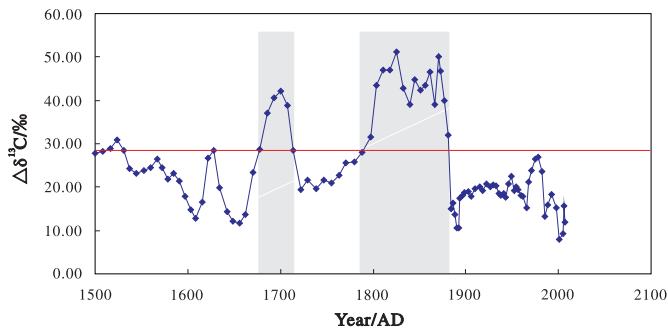
Apopka, methanogenesis can cause pore water  $\delta^{13}\text{C}$  values up to  $+26.4\text{‰}$  (Gu et al., 2004). Lake Caohai, a shallow lake with abundant organic matter deposited and anoxic water provides a good opportunity for bacterial fermentation to degrade organic matter. Whiticar et al. (1986) have concluded  $\text{CO}_2$  reduction is the basic methanogenic pathway in marine sediments (Equation (1)), whereas acetate fermentation dominates in freshwater environments (Equation (2)). Acetate fermentation is the most likely methane-producing mechanism to occur in Lake Caohai, as is common in lacustrine carbonates with anoxic waters and organic-rich sediments. Additionally, acetate fermentation is the process of  $\text{CO}_2$  production, which will constrain the carbonate precipitation.  $\text{CO}_2$  reduction is the process of  $\text{CO}_2$  assimilation, which will facilitate the precipitation of carbonate. The lower carbonate content ( $<1\%$ ) with higher carbonate  $\delta^{13}\text{C}$  values (Table 2) in 1670–1714 AD and 1788–1881 AD supports the above conclusion that acetate fermentation is the most likely methane-producing mechanism in Lake Caohai.



Carbon isotopic fractionation between the carbonate and organic matter was considered to identify the important input of bacterial source in the sedimentary sequence. Presently, such studies have revealed that carbon isotopic fractionation between these two carbon sources may provide additional information about productivity and organic matter sources (Hayes et al., 1999; Teranes and Bernasconi, 2005).  $\Delta\delta^{13}\text{C}$  ( $\delta^{13}\text{C}_{\text{carb}} - \delta^{13}\text{C}_{\text{org}}$ ) was defined as the useful approximation of  $\epsilon_{\text{TOC}}$ . It is concluded that  $\epsilon_{\text{TOC}}$  values greater than  $32\text{‰}$  are indicative of significant inputs of bacteria to sedimentary sequences, and between  $28\text{‰}$  and  $32\text{‰}$  are the result of the mixed effects by the phytoplanktonic producers and bacteria (Hayes et al., 1999; Teranes and Bernasconi, 2005). In Lake Caohai, during the intervals of 1670–1714 AD and 1788–1881 AD with the extreme enrichment of carbonate  $^{13}\text{C}$ , all  $\Delta\delta^{13}\text{C}$  values are routinely larger than  $28\text{‰}$ , most greater than  $32\text{‰}$  (Fig. 9), demonstrating that significant bacteria have participated the carbon isotopic fractionation, which further supported the above conclusion.

### 5.3.4. Possible relation with temperature

From the above discussion, abnormal positive carbonate  $\delta^{13}\text{C}$  values are caused by the bacteria. Furthermore, there is a question: why would the methane-producing bacteria occur in these two intervals? Warm environments favour bacterial fermentation (Talbot and Kelts, 1986; Whiticar et al., 1986, 1999; Lamb et al., 2000). The oxygen isotopic composition of cellulose can serve as a sensitive proxy indicator of oxygen isotopic composition of lake



**Fig. 9.**  $\Delta\delta^{13}\text{C}$  values in Lake Caohai during the past 500 years. During the periods of 1670–1714 AD and 1788–1881 AD, most  $\Delta\delta^{13}\text{C}$  values are larger than 32‰, indicating methanogenesis.

water (e.g. Edwards and McAndrews, 1989; Jonsson et al., 2010). Thus the combination analysis of  $\delta^{18}\text{O}$  values of carbonate and cellulose may shed light on the information about temperature when using palaeotemperature equations (Jonsson et al., 2010; Rozanski et al., 2010). With this approach, temperature variations in Lake Caohai during the past 500 years have been established. However, by comparing temperature variations with carbon isotopic record, as plotted in Fig. 10, abnormal positive  $\delta^{13}\text{C}$  values of carbonate correspond well with lower temperatures. The two intervals 1670–1714 AD and 1788–1881 AD were normally observed in the conventional Little Ice Age (LIA). Climatic archives suggested that LIA occurred worldwide. According to the documents of the “History of Qinghai Dynasty”, it was very cold between the end of Ming and the beginning of Qing, corresponding with the cold intervals of 1670–1714 AD. 1788–1881 AD cold periods was also recorded by Hongyuan peats (Xu et al., 2006b), Dunde ice core (Yao and Thompson, 1992) and documentary records (Zhu, 1973). The 1670–1714 AD and 1788–1881 AD cold interval in Lake Caohai corresponded well with the Maunder and Dalton minimum in the LIA, respectively. Therefore, although there is no direct effect between temperature and carbonate  $\delta^{13}\text{C}$  values, the lower temperature restrains the degradation and growth of organic matter. In this case, bacteria have participated in the carbon

isotopic fractionation of organic matter, thus generating the methane gas ( $\text{CH}_4$ ), which has the lower  $\delta^{13}\text{C}$  value up to  $-60\text{‰}$ , resulting in the extreme enrichment  $^{13}\text{C}$  in carbonates due to the synthesis of  $^{12}\text{CH}_4$ . As a result, it is cautiously concluded that abnormal positive carbonate  $\delta^{13}\text{C}$  values in Lake Caohai may be the reflection of greater significant inputs of bacteria and indirect association with lower temperature. The carbon isotopic record from Lake Caohai challenges the widely accepted conclusion that  $\delta^{13}\text{C}$  values are sensitive only to changes in lacustrine productivity or evaporation effects, and acetate fermentation usually occurred in the warm periods.

## 6. Conclusions

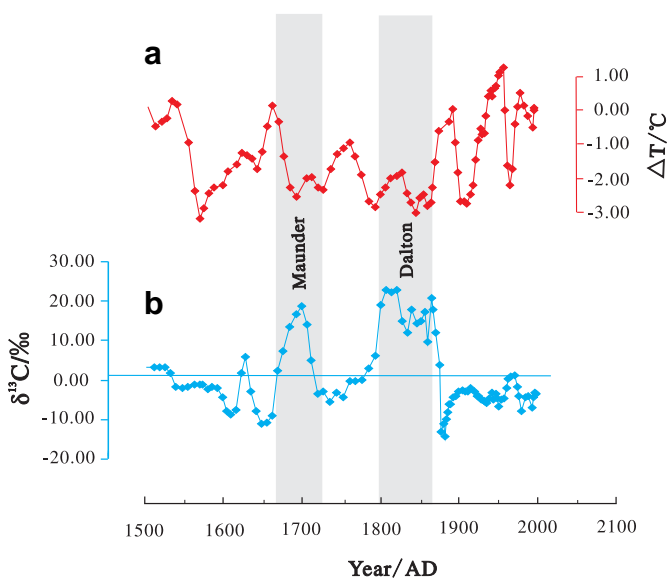
There are two intervals of abnormal positive carbonate  $\delta^{13}\text{C}$  values in Lake Caohai during the past 500 years, namely 1670–1714 AD and 1788–1881 AD, consistent with the two coldest periods in Little Ice Age, and also coincident with the Maunder and Dalton sunspot minimum, respectively. On the basis of various geochemical data, the evaporation and lacustrine productivity effects are excluded, and acetate fermentation is the most likely methane-producing mechanism to occur in Lake Caohai. Comparing temperature variations reconstructed from co-analysis of  $\delta^{18}\text{C}$  values of carbonate and organic matter cellulose, with abnormal positive  $\delta^{13}\text{C}$  values of carbonate, good correspondence between them was presented. Therefore, extreme enrichment  $\delta^{13}\text{C}$  values of carbonate in Lake Caohai may be indirectly ascribed to the lower temperature and bacterial biomasses may play a greater significance than generally accepted views to interpret lacustrine carbonate carbon isotopic records. In turn, this research indicates that some not typical forcing mechanisms should be considered when using carbonate carbon isotopic records for reconstruction of past climate changes despite the fact that the factors that influence carbonate carbon isotopes are well studied and explained. However, in order to adequately understand the extreme carbonate  $^{13}\text{C}$  enrichment in Lake Caohai, future research is necessary, requiring the detail sampling of DIC, pore water and bacterial experiments as well as sulfur isotopic analysis.

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**Fig. 10.** Comparison between temperature variations inferred from co-analysis of  $\delta^{18}\text{O}$  values of carbonate and cellulose (a), and  $\delta^{13}\text{C}$  values of carbonate in Lake Caohai during the past 500 years. The Maunder and Dalton minima are the two sunspot minimum in the LIA, denoting the two coldest intervals.



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