

## Paleotemperature variations at Lake Caohai, southwestern China, during the past 500 years: Evidence from combined $\delta^{18}\text{O}$ analysis of cellulose and carbonates

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The oxygen isotopic values of aquatic plant cellulose and carbonates in Lake Caohai sediments were measured using a continuous flow isotopic ratio mass spectrometer (CF-IRMS). Because of predictable oxygen isotopic fractionation between cellulose and its source water, the oxygen isotopic composition of paleo-lake water has been established quantitatively. Combined oxygen isotopic values of cellulose and carbonates were used in the 'Craig' equation to determine paleotemperatures and their variation in the lake during the past 500 years. Results show that the paleotemperature trend correlates well with meteorological records from Weining. There are four notable cold intervals at Lake Caohai over the past 500 years, namely 1540–1570AD, 1670–1715AD, 1780–1870AD and 1900–1930AD, and the former three cold intervals have been observed in the conventional Little Ice Age (LIA). These cold periods at Lake Caohai correspond well with those recorded from tree ring, peat, and ice core data from adjacent regions, particularly temperature those inferred from  $\delta^{18}\text{O}$  of peat cellulose from Hongyuan Southwestern China. The trend in paleotemperature variations at Lake Caohai are also consistent with both the change of Indian summer monsoon, derived from  $\delta^{18}\text{O}$  values of a stalagmite in Dongge, and a recorded shift in solar activity. The findings of this study illustrate that coupled analysis of  $\delta^{18}\text{O}$  values of cellulose and carbonates from lake sediments may be used as a paleotemperature proxy. These results also provide further evidence of the existence of LIA in southwestern China.

**temperature variations, Little Ice Age (LIA), carbonate oxygen isotopic composition, cellulose oxygen isotopic composition, Lake Caohai**

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Data from ancient lake sediments and especially their stable isotope archives play an increasingly important role in the study of past global climate change. Stable oxygen isotopes of lake sediments have been extensively applied in paleoclimate/paleoenvironment research since the pioneering works of Urey (1947) and McCrea (1950) emphasized the

potential for oxygen isotope compositions to be used as a paleotemperature thermometer (Urey, 1947; McCrea, 1950; Urey et al., 1951; Epstein et al., 1953). Numerous studies have proposed that carbonates precipitate generally in oxygen isotope equilibrium with lake water (Craig, 1965; Talbot, 1990; Frogley et al., 1999; Leng and Marshall, 2004; Anderson et al., 2005). Therefore, the oxygen isotope composition of carbonates is mainly controlled by both the oxygen isotope composition of paleo-lake water and the tem-

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perature of carbonate precipitation. On the basis of this information, a great number of studies have established the quantitative relationship among these parameters. Many researchers have used the 'Craig' equation, which is described as follows (Craig, 1965):

$$T(^{\circ}\text{C}) = 16.9 - 4.2(\delta_{\text{c}} - \delta_{\text{lw}}) + 0.13(\delta_{\text{c}} - \delta_{\text{lw}})^2.$$

In this equation,  $\delta_{\text{c}}$  denotes  $\delta^{18}\text{O}$  values of carbonates relative to the PDB international standard, and  $\delta_{\text{lw}}$  denotes  $\delta^{18}\text{O}$  values of paleo-lake water relative to the SMOW international standard.

Since the oxygen isotope composition of carbonates is chiefly influenced by both the oxygen isotope composition of paleo-lake water and temperature, the interpretation of oxygen isotope of carbonates remains debatable. For instance, Lister and Henderson suggested that carbonate  $\delta^{18}\text{O}$  in Lake Qinghai is determined by the balance between precipitation and evaporation. They further pointed out that evaporation/precipitation conditions are mainly affected by variations in Asian monsoon intensity (Lister et al., 1991; Henderson and Holmes, 2009). However, Xu et al. (2006a) inferred that carbonate  $\delta^{18}\text{O}$  in Lake Qinghai is primarily influenced by temperature. The discrepancy between these studies is driven by the difficulties in separating the relative impacts of paleotemperature and paleo-fluid composition on the oxygen isotope composition of carbonate.

Based on the 'Craig' equation, the reconstruction of temperature variations should rely on the reconstruction of the oxygen isotope composition of paleo-lake water. Factors that influence oxygen isotope composition of lake water include the oxygen isotope composition of atmospheric precipitation and input water, evaporative intensity, and hydrological conditions (Talbot, 1990; Frogley et al., 1999; Leng and Marshall, 2004; Anderson et al., 2005). Thus, the reconstruction of oxygen isotope composition of paleo-lake water is complex and carbonate  $\delta^{18}\text{O}$  may not be an ideal temperature indicator for some lakes. In hydrologically closed lakes with a long residence time, for example, lake water  $\delta^{18}\text{O}$  is principally controlled by precipitation/evaporation ratios, and carbonate  $\delta^{18}\text{O}$  can be used to reflect the hydrological balance (Frogley et al., 1999; Leng and Marshall, 2004; Henderson and Holmes, 2009).

It is clear that if paleo-lake water  $\delta^{18}\text{O}$  can be constrained, then temperature of carbonate precipitation is readily estimated. Some researchers have attempted to establish the quantitative relationship between Sr/Ca ratios of ostracod shells and paleo-lake water  $\delta^{18}\text{O}$ , and have used such data to reconstruct paleotemperature variations during the past 900 years in Lake Daihai (Shen et al., 2001, 2002). However, differences between the results obtained from laboratory experiments and natural observations have prevented a historical reconstruction of lake water  $\delta^{18}\text{O}$ . One potential method for isolating temperature signal is to reconstruct paleo-lake water  $\delta^{18}\text{O}$ . Fortunately, cellulose in organic matter can provide a direct record of lake water oxygen isotope composition. Numerous studies have illustrated that

oxygen isotopic fractionation between cellulose and its source water is constant, which allows the direct and predictable inference of paleo-lake water  $\delta^{18}\text{O}$  from measured cellulose  $\delta^{18}\text{O}$  (Edwards and McAndrews, 1989; Rozanski et al., 2010). Therefore, a combined analysis of oxygen isotope composition of cellulose and carbonates may help identify past temperature records. Based on this approach, we measured paired  $\delta^{18}\text{O}$  values of cellulose and carbonates from Lake Caohai to reveal temperature variations during the last 500 years. Results from this comparative study suggest that co-analysis of  $\delta^{18}\text{O}$  values in cellulose and carbonates may be an effective proxy index for paleotemperature reconstruction.

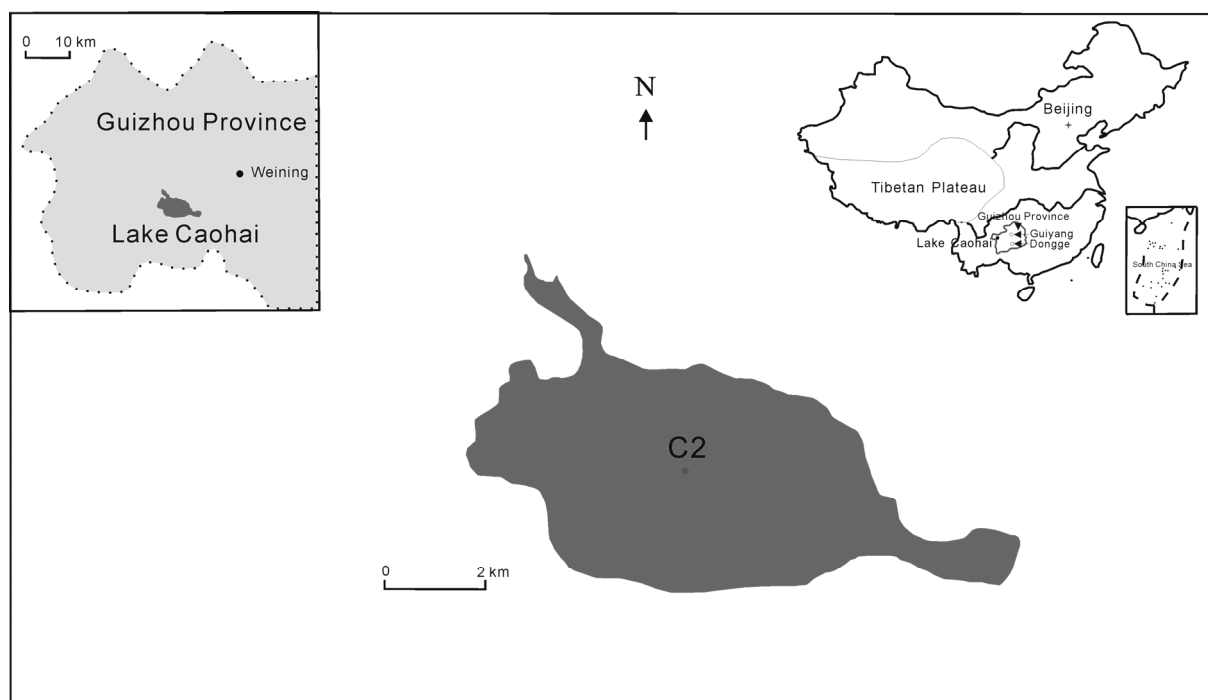
## 1 Study area

Lake Caohai (26°49'–26°53'N, 104°12'–104°18'E), is a Tibetan lake located in southwestern Weining County, Guizhou Province, southwestern China. It is approximately 350 km west of Guiyang City and 400 km northwest of the famous Dongge stalagmite, which has been frequently cited in reconstruction of the Asian summer monsoon (Figure 1). Freshwater Lake Caohai is shallow, and has a water level of 2171 m. It has an average length of 14.2 km, and a maximum width of 6.2 km (average width of 1.76 km). The maximum depth of the lake is 5.0 m (average depth of 2.4 m). Lake Caohai is dominantly supplied by groundwater and precipitation, and is hydrologically closed. This region is typically dominated by the Indian summer monsoon. Mean annual precipitation at Lake Caohai is about 951 mm, and 88% of the total annual precipitation occurs between May and October. Salinity of the lake water is 134 mg/L, and is classified as bicarbonate sodium group II water. Thus, the lake water is weakly alkaline and hard (i.e. with high content of dissolved minerals) (Wang and Dou, 1998). Abundant organic matter deposited in Lake Caohai makes this lake highly suitable for cellulose extraction and research into cellulose oxygen isotopes.

## 2 Sampling and methods

### 2.1 Sampling

Sediment core C2 was retrieved from the central part of Lake Caohai at approximately 2 m water depth in October 2007, using a self-designed gravitational sediment sampler fitted with a polymethyl tube with an internal diameter of 59 mm. The sediment core was perfectly preserved, since the suspended layer was not disturbed and the interface water was clear during coring. The core had a length of 142 cm, which was subsequently sectioned at continuous 1–2 cm intervals, and sealed in plastic bags to minimize contamination and oxidation. A total of 99 samples were collected. Lake water, aquatic plants, terrestrial plants, as well as



**Figure 1** Geographical location of Lake Caohai and coring site, C2.

catchment carbonates were also sampled at the study site. Sediment samples were divided into two portions for subsequent pretreatment and measurement. One set of the samples was used for cellulose extraction. Another set of samples was dried using a vacuum freeze drier (FD-IA-50). Subsequently, the dried samples were crushed and ground to homogenous powder (passing through 120  $\mu\text{m}$  sieves) for geochemical analysis. Terrestrial plant remains were picked out from the sediment core samples for radiocarbon  $^{14}\text{C}$  dating using the accelerator mass spectrometry (AMS).

## 2.2 Method of cellulose extraction

Analysis of the oxygen isotopic composition of cellulose requires samples to be almost pure cellulose. Wolfe et al. (2007) have summarized the research advances based on oxygen isotope analysis of cellulose, and have pointed out that cellulose extraction is critical for the development of paleoclimate research. Generally, methods for cellulose extractions are based on wood and peat samples, and are also recommended for lake sediment samples (Green, 1963; Hong et al., 1999; Sauer et al., 2001; Wolfe et al., 2005; Kitagawa et al., 2007). However, Cellulose extraction from lake sediments is difficult because of the generally lower contents of organic matter compared with wood and peat samples. Wolfe et al. (2005) developed several processes for cellulose extraction, including solvent extraction, bleaching, alkaline hydrolysis, leaching and heavy-liquid separation, based on methods used on tree rings. However, these methods, especially the heavy-liquid separation, pre-

sent challenges for cellulose extraction from lake sediments with low organic content (Wolfe et al., 2005). In the present study, we conducted repeated experiments, based on a newly developed process using four-step effective steps that included (1) alkaline-washing with 5% NaOH, (2) acid-washing with 5% HCl, (3) bleaching by glacial acetic acid and sodium chlorite mixed solution and (4) alkaline-washing with 17.5% NaOH solution. Results from infrared spectra of samples prepared in this manner suggested that spectrograms were consistent with that of the standard  $\alpha$ -cellulose, indicating that this procedure is simple and feasible to purify samples for further isotope analysis (Zhu and Chen, 2009b). Thus, this method was used to extract cellulose from sediment core C2 in Lake Caohai.

## 2.3 Experimental methods

Oxygen isotope values of cellulose were determined using a Finnigan Delta Plus Isotope Ratio Mass Spectrometer (IRMS) coupled with a Thermal Chemical Elemental Analyzer (TC/EA). About 0.4 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 standard IAEA-C3 cellulose with a known  $\delta^{18}\text{O}$  value of 32.20‰ was measured every 10 samples to monitor analytical precision and to calibrate samples. The parallel standard and sample results showed that analytical precision was better than 0.30‰. Cellulose oxygen isotope ratios are reported relative to the international VSMOW standard.

Stable oxygen isotope values of carbonates were ana-

lyzed using a GV IsoPrime stable isotope ratio mass spectrometer (CF-IRMS) equipped with an online carbonate preparation system. Samples were reacted with anhydrous phosphoric acid at a temperature of 90°C, and reaction gases were cryogenically purified to remove water and other gases. Purified CO<sub>2</sub> was introduced into the mass spectrometer for oxygen isotope measurements. Three known δ<sup>18</sup>O values from standards were used to monitor results and precision. Results from replicate samples indicated that the analytical precision was better than 0.15‰. Carbonate oxygen isotope ratios are reported relative to the international VPDB standard.

Samples of 0.5 g were used to measure carbon isotope composition of organic matter. The samples were first pre-treated with HCl (0.5 mol/L) and placed in a water bath for 2 hours at 60°C to remove carbonate materials, and rinsed repeatedly with distilled water to reach neutral pH. Then the samples were dried at 50°C for 24 hours using a drying oven. δ<sup>13</sup>C values of organic matter were measured on an Elemental Analyzer Coupled with Finnigan Delta Plus Isotope Ratio Mass Spectrometer. Analytical precision was better than 0.1‰. Organic matter carbon isotope ratios are reported relative to the international VPDB standard.

All isotopic composition of samples mentioned in this paper is expressed as “δ” values, representing deviations in per mil (‰) from a standard:

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

In this equation,  $R$  is the <sup>18</sup>O/<sup>16</sup>O ratio of the sample.

Elemental analyses of TOCC and C/N ratios were measured by the elemental analyzer (PE2400 Series II) with an error less than 5%.

The specific activity of <sup>137</sup>Cs was measured at 661.6 keV by γ-spectrometry using a Multichannel Analysis System (Canberra S-100) and low-background germanium detector. The analytical error was better than 10%. All measurements were conducted at the State Key Laboratory of Environmental Geochemistry, Chinese Academy of Sciences in Guiyang City.

The pretreatment method of terrestrial plants was similar to that used in the organic carbon isotope analysis. The plant material was converted to CO<sub>2</sub>, which was used for <sup>14</sup>C dating by accelerator mass spectrometry (AMS) at the Scottish Universities Environmental Research Centre AMS Facility. The radiocarbon age was calibrated to calendar years using the INTCAL 98 curve (Stuiver et al., 1998) and the University of Oxford Radiocarbon Accelerator Unit calibration program (OxCal3).

### 3 Results

The age model of core C2 was established on the basis of combined results from the <sup>14</sup>C and <sup>137</sup>Cs dating. Variations of <sup>137</sup>Cs activity versus depth in sediment core C2 are

shown in Figure 2(a). The peak <sup>137</sup>Cs activity occurred at the depth of 12.5 cm, with a depth sedimentation rate of 0.28 cm/yr. In this study, only one terrestrial plant sample was found with higher C/N ratio in the sediment core, and it was used for <sup>14</sup>C dating. The chronology of sample C2-62 was about 237 yr BP (AMS No. SUERC21791) (Figure 2(b)), with an average depth sedimentation rate of 0.26 cm/yr, based on derivation from <sup>137</sup>Cs activity.

In addition, two sediment samples taken at the depths of 94 and 100 cm were used to extract cellulose for <sup>14</sup>C dating, but the <sup>14</sup>C dating result was not obtained, possibly because of a low content of modern carbon in the organic matter composition of Lake Caohai, which is unsuitable for <sup>14</sup>C dating.

The sediment accumulation rate in Lake Caohai is assumed to be relatively stable as a result of good preservation conditions, few human impacts, and sampling location in the central part of lake. An age-depth model of sediment core C2 was established based on sampling depth and depth sedimentation rate (Figure 2(b)). The 142 cm-long sediment core represents the deposited record over the past 500 years, with an average temporal resolution of about 5 years.

Variations in δ<sup>18</sup>O values of cellulose and carbonates in Lake Caohai are shown in Figure 3. δ<sup>18</sup>O values of cellulose varied widely between 8.69‰ and 24.35‰, with a mean value of 16.52‰. From 1500–1750AD, cellulose δ<sup>18</sup>O values show a decreasing trend, while an increasing trend is evident after 1750AD. δ<sup>18</sup>O values of carbonates display similar variations with cellulose δ<sup>18</sup>O, varying between

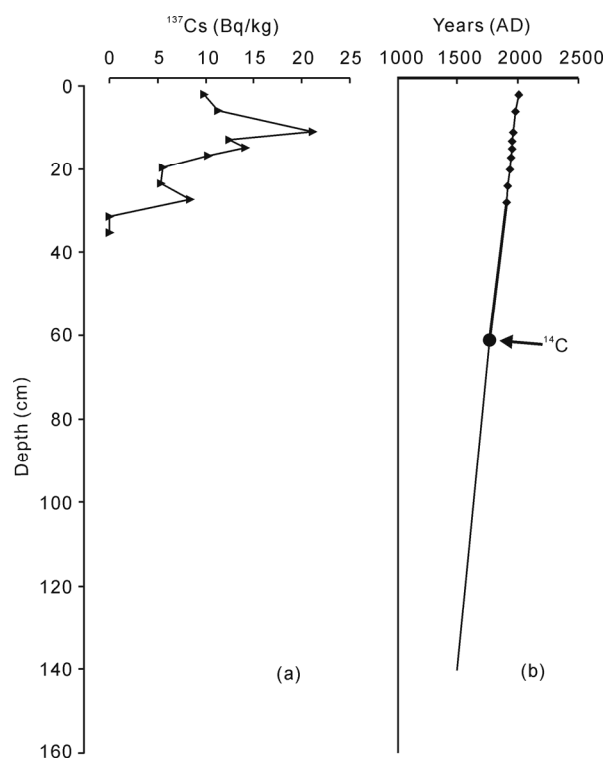
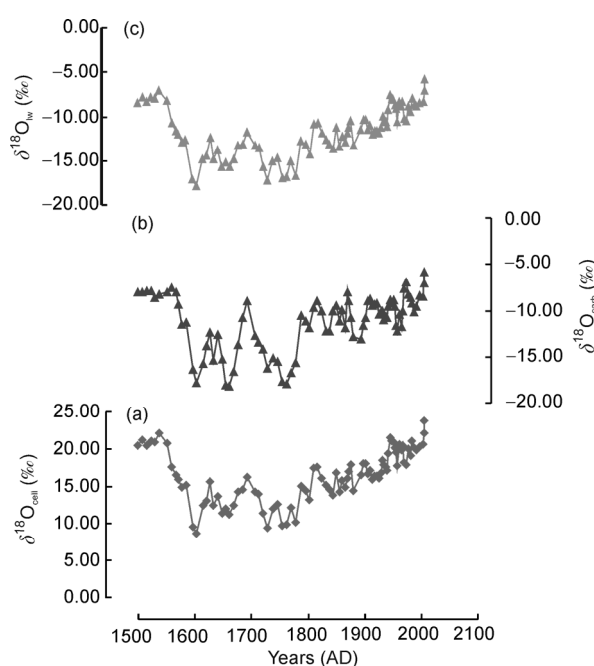
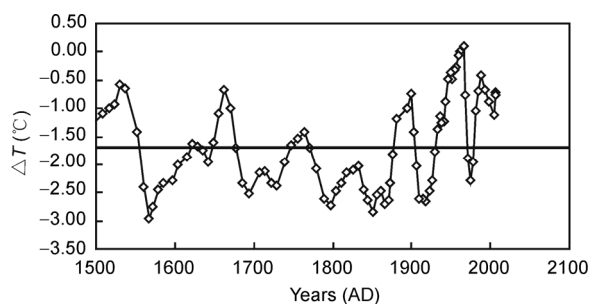


Figure 2 Diagram of <sup>137</sup>Cs activities and age-depth model of core C2.

$-11.22‰$  and  $-5.83‰$ , with a mean value of  $-11.16‰$ . There is a strong positive correlation between  $\delta^{18}\text{O}$  values of cellulose and carbonates, yielding a correlation coefficient of 0.86. The  $\delta^{18}\text{O}$  values of lake water during the past 500 years were reconstructed based on the oxygen isotope fractionation between cellulose and its source water, discussed in detail below (Figure 3). Temperature variations inferred from the combination of cellulose and carbonate  $\delta^{18}\text{O}$  values, using the ‘Craig’ paleotemperature equation and standards, were reconstructed during the last 500 years, as indicated in Figure 4. Based on these results, it is apparent that paleotemperature at Lake Caohai varied greatly, and those four cold intervals occurred during the past 500 years, specifically 1540–1570AD, 1670–1715AD, 1780–1870AD and 1900–1930AD.



**Figure 3** Evolution of  $\delta^{18}\text{O}$  values of cellulose (a), carbonates (b) and paleo-lake water (c) in sediment core C2 at Lake Caohai during the past 500 years.  $\delta^{18}\text{O}$  values of paleo-lake water were reconstructed from cellulose using oxygen isotopic fractionation ( $\alpha=1.028$ ).



**Figure 4** Reconstructed paleotemperature variations at Lake Caohai during the past 500 years. The vertical line represents the average value of temperature.

## 4 Discussions

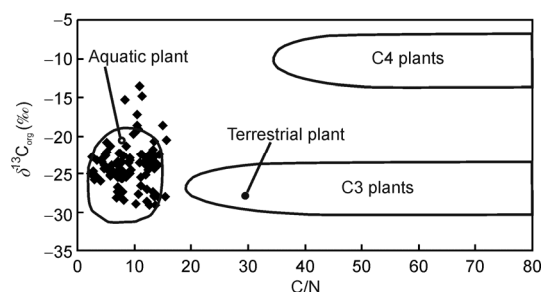
### 4.1 Source of organic matter in Lake Caohai

When using cellulose  $\delta^{18}\text{O}$  for paleoclimate reconstruction, the source of organic matter must be identified, since oxygen of terrestrial cellulose is not derived from lake water (Wolfe et al., 2007). Previous studies have revealed that C/N ratios can be used effectively to distinguish the source of sedimentary organic matter (Meyers and Ishiwatari, 1993; Meyers, 1997; Dean, 1999). Generally, algae contain low amounts of fiber, but are rich in proteins, and therefore have atomic C/N ratios less than 10. In contrast, terrestrial plants are rich in fiber, but low in proteins, and hence have atomic C/N ratios greater than 20 (Meyers and Ishiwatari, 1993; Meyers, 1997). In addition,  $\delta^{13}\text{C}$  values are entirely different between aquatic and terrestrial plants. Therefore, the combination of C/N ratios and carbon isotope values of organic matter ( $\delta^{13}\text{C}_{\text{org}}$ ) may be an effective method to distinguish the source of organic matter from lake sediments (Meyers and Ishiwatari, 1993; Meyers, 1997). Meyers (1997) has identified three distinctive suites of C/N ratios and  $\delta^{13}\text{C}_{\text{org}}$  values of plants to distinguish sources of organic matter in lake sediments (Figure 5).

As shown in Figure 5, Lake Caohai data plot within the field of aquatic plants, and are significantly different from fields of C3/C4 land plants, indicating a greater contribution of aquatic plants as the source of sedimentary organic matter at Lake Caohai, relative to terrestrial sources (Zhu et al., 2011). In addition, the single modern aquatic macrophyte sampled from Lake Caohai had a C/N ratio and  $\delta^{13}\text{C}$  value of 8.9 and  $-21.78‰$ , respectively, and modern terrestrial plant sample had a C/N ratio and  $\delta^{13}\text{C}$  value of 29.3 and  $-27.56‰$ , respectively. The C/N ratios and  $\delta^{13}\text{C}$  values of organic matter in the sediment core are similar to the aquatic algae, and are rather different from the terrestrial plant sample, providing additional evidence that organic matter from Lake Caohai is derived from aquatic sources.

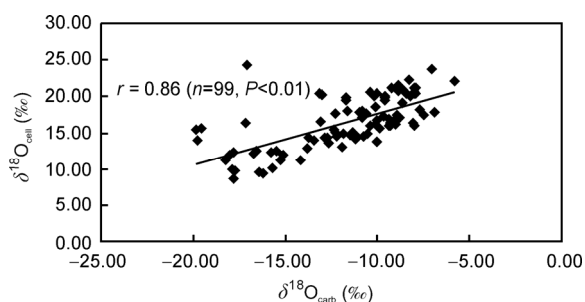
### 4.2 Source of carbonate in Lake Caohai

Under natural conditions, carbonates in lake sediments may



**Figure 5** C/N ratios and  $\delta^{13}\text{C}_{\text{org}}$  values of sedimentary organic matter, and aquatic and terrestrial plants at Lake Caohai (general C/N ratios and  $\delta^{13}\text{C}_{\text{org}}$  ranges for aquatic plants and C3/C4 land plants cited from Meyers (1997)).

be of both autochthonous and allochthonous origin. Authigenic carbonate can provide potentially important information about past environmental change, although this information may be complicated by the presence of allochthonous carbonate (Leng and Marshall, 2004). Therefore, it is necessary to identify the source of carbonates from lake sediments before they are used for paleoclimate interpretation. Previous studies have used mineralogical methods to distinguish carbonate sources. However, this method is not suitable in some lakes, particularly in some karstic lakes. In recent studies of Lake Chenghai, southwestern China, we put forward several lines of evidences to show that carbonate in that lake is authigenic. We included comparisons of  $\delta^{18}\text{O}$  values of surface carbonates and aquatic plant cellulose,  $\delta^{13}\text{C}$  values of dissolved inorganic carbon and carbonates, and comparisons of the ionic activity product (IAP) with the equilibrium constant (Zhu and Chen, 2009a). Applying this method in modern Lake Caohai, all the evidences indicate that present-day carbonates in Lake Caohai are authigenic. For instance, the average  $\delta^{13}\text{C}$  value of DIC is  $-3.96\text{‰}$ . Thus, 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. This is similar to a measured surface sediment sample (Zhu et al., 2013). The IAP of Caohai Lake water is routinely larger than 1 between  $10^\circ\text{C}$  and  $25^\circ\text{C}$ . Additionally, the carbon isotope value of carbonates from the catchment of Lake Caohai is  $0.50\text{‰}$ , which is similar to the value of marine carbonate. This value is also significantly different from values of core sediment carbonates in Lake Caohai, which vary between  $-14.25\text{‰}$  and  $23.10\text{‰}$ . This combined evidence suggests that carbonates in Lake Caohai are authigenic (Zhu et al., 2013). Therefore, carbonate-related proxies in Lake Caohai sediments can be used to deduce paleoenvironment information. Furthermore, the strong correlation between  $\delta^{18}\text{O}$  values of cellulose and carbonates (correlation coefficient of 0.86), shown in Figure 6, not only indicates the same paleoclimate implications, but also provides additional evidence that the two different isotopic archives are strongly related to the isotopic composition of lake water, probably because of the fact that they formed in the same lake water.



**Figure 6** Correlation between  $\delta^{18}\text{O}$  values of cellulose and carbonates at Lake Caohai.

### 4.3 Paleo-lake water $\delta^{18}\text{O}$ reconstruction and paleoclimate implications

Cellulose is a nearly ubiquitous component of plant tissues, and is frequently abundant in wood and peat. Cellulose also is a structural constituent of the cell walls of some algae, constituting 1%–10% of the dry weight of the organism. Within organic-rich lake sediments, cellulose may be preserved as disseminated residues such as identifiable algal cells, zooplankton fecal pellets and amorphous organic matter (Edwards and McAndrews, 1989; Wolfe et al., 2001, 2005; Rozanski et al., 2010). Cellulose is composed of carbon, hydrogen and oxygen. Hydrogen, carbon, and oxygen molecules linked on the cellulose carbon chain will undergo no further degradation in the decomposition process after death of the plants. Thus, the isotopic composition of cellulose can provide original information of the synthesis of cellulose, and possibly identify appropriate material for paleoclimate reconstruction.

Extensive field and laboratory studies have been carried out to investigate the relationship between oxygen isotope composition of cellulose and the water in which the plants grew (Epstein et al., 1977; DeNiro and Epstein, 1981; Yakir, 1992; Aucour et al., 1996; Abbott et al., 2000; Sauer et al., 2001; Wolfe et al., 2001). Most of these studies have shown that the oxygen isotope fractionation between cellulose and water is nearly constant, independent of water temperature, plant species and photosynthetic pathway of the organism, with a mean value of  $1.028 \pm 0.001$  (Epstein et al., 1977; DeNiro and Epstein, 1981; Yakir, 1992; Aucour et al., 1996; Abbott et al., 2000; Wolfe et al., 2001). As a result, the oxygen isotope composition of cellulose can reliably reflect original oxygen isotope composition of water. To better examine the use of cellulose isotopes as a proxy for past water isotopic composition, Sauer cultured aquatic mosses under different water isotopic composition water with constant water temperature (Sauer et al., 2001). Results of that study showed that new cellulose  $\delta^{18}\text{O}$  can precisely record water  $\delta^{18}\text{O}$ . The correlation coefficient between them is 0.9997, with an error less than  $0.2\text{‰}$ , which further supports the notion that cellulose  $\delta^{18}\text{O}$  can directly and quantitatively reconstruct past water  $\delta^{18}\text{O}$  with great precision. Taking these results into consideration, the oxygen isotope composition of cellulose appears to be faithfully record change in lake water  $\delta^{18}\text{O}$ . In this paper, we applied 1.028 as the oxygen isotope fractionation factor between cellulose and lake water, as numerous previous studies have recommended. Thus, the oxygen isotopic composition of paleo-lake water in Lake Caohai during the past 500 years was reconstructed (Figure 3).

Lake Caohai is mainly influenced by the southwest monsoon, which indicates an inverse relationship between the amount and  $\delta^{18}\text{O}$  value of precipitation (Dansgaard, 1964; Zheng et al., 1983; Luo et al., 2008). In this case, cellulose  $\delta^{18}\text{O}$  in Lake Caohai can be interpreted as change in

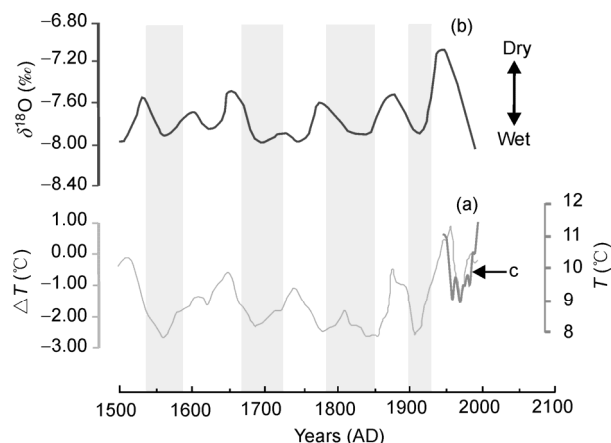
precipitation/evaporation ratios. In addition, assuming that the oxygen isotope composition of authigenic carbonate is entirely controlled by water temperature, and using the slope between  $\delta^{18}\text{O}$  of carbonates and water temperature of about  $-0.24\text{‰}/\text{°C}$  (Craig, 1965; Leng and Marshall, 2004), the range of  $12.39\text{‰}$  in  $\delta^{18}\text{O}$  would correspond to a temperature change of  $51\text{°C}$  during the past 500 years. Such a large temperature variation is obviously unrealistic for Lake Caohai, thereby demonstrating that temperature is clearly not the main control on  $\delta^{18}\text{O}$  values of authigenic carbonates in Lake Caohai during the past 500 years. Therefore, cellulose and carbonates  $\delta^{18}\text{O}$  in Lake Caohai seem to reflect the balance between precipitation and evaporation (Zhu et al., 2010), which is further verified by the strong positive correlation between  $\delta^{18}\text{O}$  values of cellulose and carbonates ( $r=0.86$ ,  $n=99$ ,  $P<0.01$ ) (Figure 6).

#### 4.4 Temperature variations at Lake Caohai during the past 500 years and comparisons

In summary, variations of  $\delta^{18}\text{O}$  values of cellulose and carbonates in Lake Caohai can only provide information about effective moisture, rather than temperature. Hence, the use of the ‘Craig’ paleotemperature equation has provided the theoretical basis for the temperature reconstruction. Coupled  $\delta^{18}\text{O}$  of cellulose and carbonates have strong potential for future paleotemperature reconstruction studies.

Based on the ‘Craig’ equation, for every  $1\text{°C}$  difference in temperature, there is an approximately  $0.24\text{‰}$  change in the  $\delta^{18}\text{O}$  of carbonates (Craig, 1965). On the basis of the slope  $0.24\text{‰}/\text{°C}$ , temperature differences among samples may be available. The surface sample (2007AD) was used as the time-marker. Thus, temperature variations at Lake Caohai over the past 500 years can be established (Figure 4). The reconstructed paleotemperatures correlate well with the temperature trend from meteorological records at Weining, implying that paired cellulose and carbonate  $\delta^{18}\text{O}$  values can be used as a proxy index for paleotemperature (Figure 7).

The long-term trend of temperature variations exhibits fluctuations and it is notable that there are four cold intervals recorded during the past 500 years, including 1540–1570AD, 1670–1715AD, 1780–1870AD and 1900–1930AD. Since high-resolution temperature data at Lake Caohai and southwestern China are mostly unavailable, we compared the four cold intervals from Lake Caohai with other records from adjacent regions in China, as discussed below. Increasing evidence suggests that the LIA was not a continuous cold period in China, in that a warm period occurred between the two cold intervals (Zhu, 1973; Yao and Thompson, 1992; Wang et al., 1998; Yao et al., 2001; Wang et al., 2003; Xu et al., 2006b, 2008). For instance, Zhu (1973) established paleotemperature variations for the first time in eastern China over the past 5 millennia through documentary records, and also pointed out that there were three cold intervals in the LIA, including 1470–1520AD,



**Figure 7** Temperature variations at Lake Caohai (10-year running mean) (a) compared with  $\delta^{18}\text{O}$  values of the stalagmite Dongge (b). Temperature variations after 1950AD are reconstructed from meteorological records at Weining (c).

1620–1720AD and 1840–1890AD. On the basis of synthesized data from documents, ice cores and tree rings, three cold intervals around 1450–1510AD, 1560–1690AD and 1790–1890AD were identified in the LIA (Wang et al., 2003).

The cold interval of 1540–1570AD may be the start of the LIA in China, which has been recorded in the Hongyuan peat, southwestern China (Xu et al., 2006b). During the Lake Caohai cold interval of 1670–1715AD, records from Lake Qinghai (Xu et al., 2008) and Dulan tree rings (Yao et al., 2001) registered the sharp decline in temperature, in agreement with the literature (Zhu, 1973). According to the document ‘History of Qing Dynasty’, it was very cold between the end of Ming and the beginning of Qing, which corresponded with the cold interval of 1670–1715AD. The Lake Caohai cold interval of 1780–1870AD is also in agreement with other records. This period was readily detected in the Hongyuan peat (Xu et al., 2006b), the Dunde ice core (Yao and Thompson, 1992) and historical literature records (Zhu, 1973). Wang et al. (2003) inferred that 1790–1890AD also was cold in China. The most recent cold interval of 1900–1930AD in the Lake Caohai record also corresponds to cold conditions inferred from peat cellulose  $\delta^{18}\text{O}$  at Hongyuan (Xu et al., 2006b). In conclusion, the four notable reconstructed cold intervals at Lake Caohai synchronized well with those recorded in ice cores, tree rings, peat and historical literature from adjacent regions, and suggests that coupled cellulose and carbonate  $\delta^{18}\text{O}$  appears to be a reliable paleotemperature indicator.

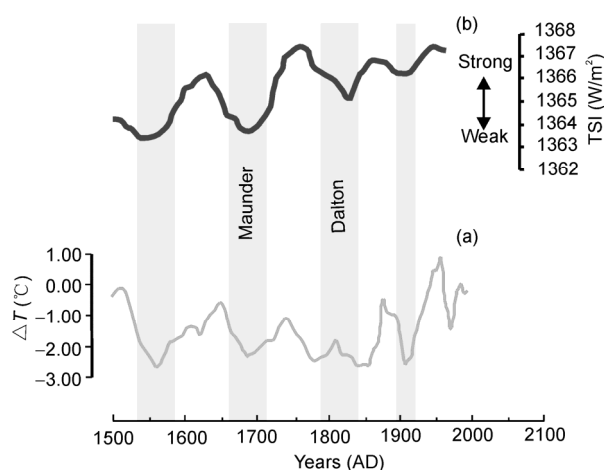
To further understand this paleotemperature indicator, we have compared inferred temperature variations at Lake Caohai with  $\delta^{18}\text{O}$  values of the stalagmite at Dongge and recorded solar activity. As shown in Figure 7, there is a close relationship between the profile of paleotemperature at Lake Caohai and the  $\delta^{18}\text{O}$  values of the stalagmite in Dongge (Wang et al., 2005). Previous studies have revealed that in southwestern monsoon regions, precipitation is in-

versely correlated with temperature, and that the main climate pattern is cold-humid/warm-dry, which closely agrees with our results.

A great number of studies have shown that solar activity is the dominant factor driving variations of Earth's temperature since the sun is our direct energy source of the Earth (Reid, 1991; Bard et al., 2000; Crowley, 2000; Chen et al., 2005; Wang et al., 2005; Muscheler et al., 2007; Tan et al., 2008; Zhang et al., 2008). Solar activity can be reconstructed from values of production of cosmogenic radionuclides. Cosmogenic radionuclide records, such as  $^{14}\text{C}$  and  $^{10}\text{Be}$  are generally considered as the most sensitive proxies for reconstructing variations of solar activity despite the fact that other factors such as geomagnetic field and climate may influence these records to some extent (Stuiver and Quay, 1980; Bard et al., 2000; Muscheler et al., 2007). As shown in Figure 8, comparisons of paleotemperature variations at Lake Caohai with the reconstructed total solar irradiance (TSI) inferred from  $^{14}\text{C}$  in tree rings and  $^{10}\text{Be}$  in ice cores during the past 500 years (Bard et al., 2000) result in a good correspondence. Thus, lower TSI relates to lower paleotemperature, and *vice versa*. The cold intervals of 1670–1715AD and 1780–1870AD at Lake Caohai coincide well with the Maunder minimum and Dalton minimum, respectively (Eddy, 1976). Consequently, temperature records reconstructed from combined  $\delta^{18}\text{O}$  analyses of cellulose and carbonates appear to be accurate, which will offer a new approach for paleoclimate research.

## 5 Conclusions

We reconstructed paleotemperature variations at Lake Caohai during the past 500 years, as inferred from paired aquatic plant cellulose and carbonate  $\delta^{18}\text{O}$  values, and application of the 'Craig' paleotemperature equation. Four notable cold



**Figure 8** Temperature variations (10-year running mean) at Lake Caohai (a) and total solar irradiance (TSI) (b) during the past 500 years. Grey shading denotes a cold interval. Maunder and Dalton minima are two sunspots number minimums in the LIA.

intervals during the past 500 years were identified as 1540–1570AD, 1670–1715AD, 1780–1870AD and 1900–1930AD, and synchronize well with records from ice cores, tree rings, peat and historical literature resources from adjacent regions. The earliest three cold intervals coincided well with the three coldest intervals of the conventional LIA. There is a close relationship among the temperature variations at Lake Caohai and  $\delta^{18}\text{O}$  values of a stalagmite at Dongge, and the trend of solar activity. The cold interval 1670–1715AD corresponds with the Maunder minimum, and the cold interval 1780–1870AD corresponds with the Dalton minimum. Such comparisons illustrate that the combination of cellulose and carbonate  $\delta^{18}\text{O}$  values can serve as a promising paleotemperature indicator. Our findings also provide additional evidence for the existence of LIA in southwestern China.

At present, the main paleotemperature indicator in lake sediments is carbonate/diatom oxygen isotopes. Both archives are largely dependent on both the temperature and the oxygen isotopic composition of the paleo-lake water in which they were precipitated, and it is difficult to distinguish their relative contributions. In addition, in monsoon-affected or low latitude regions, the oxygen isotopic composition of precipitation is mostly controlled by precipitation amount. Therefore, there are few proxy records for paleotemperature reconstruction from carbonate  $\delta^{18}\text{O}$  in these areas. This study has solidly confirmed that coupled  $\delta^{18}\text{O}$  analyses of cellulose and carbonates may be an effective paleotemperature indicator, and thus may play a significant role in future research of past global climate change.

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