**A 700-year macrophyte productivity record inferred from isotopes of
macrophyte remains and bulk carbonates in Lake Koucha, northeast
Qinghai-Tibetan Plateau**

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Abstract

The isotopic composition of total organic carbon (TOC) in lakes has been widely used to interpret paleoclimatic changes and the depositional environments of lake sediments. However, the main factors that affect the carbon isotopes of TOC may vary in different lake sediment records, limiting the ability of organic carbon isotopes to explain biogeochemical and environmental changes, especially in lakes with a large number of aquatic plants. In this study, the $\delta^{13}\text{C}$ values of macrophyte remains and bulk carbonate in a sedimentary core from Lake Koucha were investigated to evaluate their paleoenvironmental implications. We found that the bulk carbonate was dominated by authigenic carbonates formed in the lake and that their $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values can be used to reconstruct environmental changes in the Lake Koucha area. The macrophyte productivity derived from the carbon isotopic offset between the macrophyte remains and the bulk carbonate ($\epsilon_{\text{remains-BC}}$) in the Lake Koucha area agree well with total solar irradiance (TSI) records inferred from $\Delta^{10}\text{Be}$ and temperature records based on tree rings from the Qinghai-Tibetan Plateau. Although

the distribution of macrophytes is related to water depth according past studies and our observations in the field, our findings suggest that changes in macrophyte productivity may be primarily driven by temperature changes in the Lake Koucha area.

Keywords: Macrophyte remains, Carbon isotope, Productivity, Temperature, Lake Koucha, Tibetan Plateau

1. Introduction

The Tibetan Plateau (TP) is one of the most sensitive regions to global climate change, and it involves complex interactions between the mid-latitude westerly circulation and the subtropical Asia monsoon circulation, acting as a bridge between high- and low-latitude climatic processes. In recent decades, the paleoenvironmental/paleoclimatic changes on the TP across different time scales have been widely studied using various natural archives, such as ice cores (Yao et al., 1996; Thompson et al., 1997, 2003), tree rings (Shao et al., 2005; Liu et al., 2009; Yang et al., 2014) and lake sediments (Lister et al., 1991; Shen et al., 2005; Liu et al., 2006; Colman et al., 2007; Zhao et al., 2013; An et al., 2012; Woszczyk et al., 2014). Among these, lake sediment sequences have been the most frequently used because of the large number of lakes on the TP that provide potential records for paleoclimatic reconstructions, especially for late Holocene (Xu et al., 2006a, 2014; Zhao et al., 2010; He et al., 2013a, b; Wang et al., 2013; Chen et al., 2015).

The use of stable C isotopes to investigate past lake levels, temperatures, primary productivity, nutrient dynamics and moisture availability is well documented in lakes in this area (Mischke et al., 2008; Herzsuh et al., 2010a, b; Liu et al., 2013; Woszczyk et al., 2014; Qiang et al., 2005; Xu et al., 2006a, 2014; Li and Liu, 2014). Bulk organic matter in lake sediment is derived from plants and organisms with different $\delta^{13}\text{C}$ values that live in the lake and its watershed. Consequently, the bulk organic matter contains an integrated isotopic signal that reflects the collective paleoclimate and paleoenvironmental variations (Meyers, 2001). The carbon isotope ratios ($\delta^{13}\text{C}$) of lacustrine carbonates are primarily a function of the $\delta^{13}\text{C}$ values of the

dissolved inorganic carbon (DIC) in the lake and the isotopic fractionation between DIC and precipitated carbonate (Deines et al., 1974; Buchardt and Fritz, 1980). In general, three predominant factors control the carbon isotopic composition of lake DIC: the isotopic composition of inflowing waters, CO₂ exchange between the atmosphere and the lake water, and the photosynthesis/respiration of aquatic plants within the lake (Herczeg, 1987; Hollander and Mckenzie, 1991; Zhang et al., 1995; Miyajima et al., 1997; Wang and Veizer, 2000). Therefore, paleoclimatic or paleoenvironmental interpretations of the carbon isotopic composition of authigenic carbonate and sedimentary TOC may be different because the isotopic signals in authigenic carbonate and TOC may be affected by multiple factors, such as the carbon isotopic signals from different sources, such as atmosphere CO₂, the input of terrestrial plants, the decomposition of aquatic plants, etc., in lakes on the TP or in other regions (Talbot and Livingstone, 1989; Piovano et al., 2004; Leng and Marshall, 2004; Mischke et al., 2008; Herzsuh et al., 2010a, b; Lei et al., 2010; Liu et al., 2013; Woszczyk et al., 2014; Qiang et al., 2005; Xu et al., 2006a, 2014; Li and Liu, 2014).

Recent studies have shown that the TOC content is primarily controlled by aquatic plants, and aquatic plant macrofossils can be well preserved in lake sediments because of the low temperatures in many lakes on the eastern TP (Lin et al., 2002; Aichner et al., 2010; Herzsuh et al., 2010b; Qiang et al., 2013; Liu et al., 2013). $\delta^{13}\text{C}_{\text{TOC}}$ and carbonate $\delta^{13}\text{C}$ values were used to reconstruct variations in primary productivity and lake nutrients, respectively, since the early Holocene in Lake Koucha (Mischke et al., 2008; Herzsuh et al., 2010a, b). Isotopic analyses ($\delta^{13}\text{C}$ and $\delta^{15}\text{N}$) of fossil aquatic plants (*Potamogeton pectinatus*) have been used to study lake nutrient variability in Lake Koucha and Lake Luanhaizi on the northeast TP (Herzsuh et al., 2010a, b). In addition, a recent study has shown that the $\delta^{13}\text{C}$ values of *Potamogeton pectinatus* may have the potential to indicate variations in water depth (Qiang et al., 2013). However, the climatic and environmental significance of the $\delta^{13}\text{C}_{\text{TOC}}$ and carbonate $\delta^{13}\text{C}$ values from these lakes have not been well evaluated until now.

In this study, we present isotopic analyses of aquatic macrophyte remains, bulk carbonate and total organic matter from Lake Koucha on the northeast TP. The aims of this study were to evaluate $\epsilon_{\text{remains-BC}}$ ($\delta^{13}\text{C}_{\text{macrophyte remains}} - \delta^{13}\text{C}_{\text{bulk carbonate}}$) as a potential proxy for macrophyte productivity and its relationship with hydrological and climatic changes in Lake Koucha.

2. Studied sites

Lake Koucha (34.0°N; 97.2°E), situated on the northeastern Tibetan Plateau, is a freshwater lake with a maximum depth of 7.0 m. The lake lies at an elevation of 4530 m on the southern flank of the Bayan Har Mountains, an eastern range of the Tangelashan (Fig. 1). The lake occupies a glacially eroded, wide depression in the southern foreland of the Bayan Har Mountains. The region was entirely covered by a local ice cap during the penultimate glaciation, according to the published data (Zhou and Li, 1998; Heyman et al., 2011). Therefore, glacial drift sediments are widespread around the lake and mainly comprise locally derived erosion products of Triassic black quartz arenites. Large erratic boulders of granite are exposed in places and were likely transported over ~40 km from the central Bayan Har Mountains to the lake site. Several small streams feed the lake. The catchment area of the open-basin lake is approximately 88 km², which is only five times the size of the lake itself (18 km²). A single outflowing stream is one of the upper tributaries of the Yellow River.

The climate is dominated by the Asian monsoon system. Regional instrumental data collected by a weather station over the last 50 years reveal cool temperatures during summer and precipitation mainly occurring between June and September (Maduo weather station at 98.22°E, 34.91°N, 4273 m asl; $T_{\text{July}}=7.8^{\circ}\text{C}$, $T_{\text{ann}}=-4.0^{\circ}\text{C}$, $P_{\text{ann}}=321$ mm). The mean annual precipitation at a weather station 20 km to the south of the lake (Qingshuihe, 4415 m asl) is 511 mm, and the mean annual temperature is -4.8°C , according to the published data of Fan et al. (2004). The annual potential evapotranspiration is relatively low, with a value of approximately 700 mm (Ling, 1999).

The lake itself is densely populated by aquatic macrophytes, primarily

Potamogeton pectinatus, to a depth of 4 m, according to published data (Herzschuh et al., 2009). No submerged macrophytes were observed in water depths exceeding 4 m. In shallower areas with a water depth less than 0.8 m, mats were intermixed with *Batrachium bungei* (a water crowfoot species). The marginal lake vegetation is dominated by emergent Cyperaceae species (Mischke et al., 2008; Herzschuh et al., 2010a, b). The vegetation around Lake Koucha is dominated by dense *Kobresia* meadows. At higher elevations in the nearby Bayan Har Mountains, vegetation grades into sparse alpine vegetation. Areas above ~5000 m are free of vegetation (Herzschuh et al., 2009).

3. Materials and methods

A 41-cm-long core (KCC14-3) was drilled in the northern part of the lake (34.0108°N and 97.2422°E, water depth 2.5 m) in late April 2014 using Livingstone coring equipment. This coring site is near the position of another core (34.0122°N and 97.2404°E) described by Mischke et al. (2008) (Fig. 1). The new core consists of sandy marl with quantities of fossil aquatic plants. The entire core was sub-sampled at continuous 0.5 cm intervals for use in this study.

According to the ^{137}Cs data, the top of core KCC14-3 may have been disturbed when the core was collected because of the large number of aquatic plants living on the lake bottom (Table 1). The total organic carbon of two macrophyte remains (*Potamogeton*) was measured for radiocarbon dating via acceleration mass spectrometry (AMS) at the Xi'an AMS Center, China (Table 1). The two radiocarbon dating samples were chemically treated according to the standard acid-alkali-acid procedure based on the laboratory's analytic standard pretreatment protocols. The reservoir effect (1812 ± 22 years) due to old carbon was determined from the ^{14}C age of the surface macrophyte remains. The radiocarbon ages of other ^{14}C measurements were then corrected using the corresponding reservoir ages (Table 1). The reservoir-corrected radiocarbon ages of the samples were converted to calendar ages (Table 1) using the software Calib601 (Reimer et al., 2009). The age-depth relationship was established using a linear interpolation between calibrated calendar

ages between the depth of 36 cm and the assumed ‘zero’ age (AD 2013) at the top of the core. Each 1-cm-thick sample represents approximately 16 years of sedimentation, and this sedimentation rate is similar to the sedimentation rate of another 180-cm core (14 years/cm) (Mischke et al., 2008), which was collected near position of the core KCC14-3.

The wet sediments were all freeze-dried. The macrophyte remains were separated from the sedimentary samples for the carbon isotope measurements. The dried sediment without aquatic plants was ground in an agate mortar, sieved through a 200-mesh screen and homogenized. Then, the selected plant samples and portions of the ground sediment were treated with 2 M HCl for 24 h at room temperature to remove carbonates. Subsequently, the samples were rinsed to a pH of approximately 7 with deionized water and dried at 40°C. The dried samples (including plants and sediments) were combusted for 4 h at 850°C in evacuated sealed quartz tubes in the presence of 1 g of CuO, 1 g of Cu and Pt foil. The carbon dioxide was then cryogenically purified. The isotopic ratios of the purified CO₂ were measured using a Finnigan MAT 251 gas source mass spectrometer at the Institute of Earth Environmental, Chinese Academy of Sciences (IEECAS). The isotopic ratios are reported using delta (δ) notation in per mil (‰) relative the V-PDB standard for C. The overall precision of the δ¹³C analyses was better than 0.2‰ (Liu et al., 2013).

Another portion of the ground samples were analyzed for ¹³C/¹²C and ¹⁸O/¹⁶O at IEECAS using an isotope ratio mass spectrometer (MAT-252) with an automated carbonate preparation device (Kiel II). The results are expressed in delta (δ) notation relative to the V-PDB standard. Repeated analyses of the laboratory standard carbonates with known δ¹³C and δ¹⁸O values were performed daily to ensure instrumental accuracy. The analytical error of the laboratory standard was approximately ±0.1‰ for both δ¹³C and δ¹⁸O values.

4. Results

The δ¹³C values of the bulk carbonate (δ¹³C_{BC}) show large variations, from values as low as 1.79‰ to as high as 9.28‰ (Fig. 2a). The δ¹³C_{BC} values were

relatively stable during the period ~ 1290-1420 AD (varying from 4.72‰ to 6.07‰) (Fig. 2a). The highest $\delta^{13}\text{C}_{\text{BC}}$ values occurred in the period ~ 1420-1750 AD, with the greatest values (9.28 ‰) occurring in ~ AD 1500. After ~ AD 1750, the $\delta^{13}\text{C}_{\text{BC}}$ values increased to 6.44‰ in ~ AD 1910, decreased to 1.79‰ in ~ AD 1980, and finally increasing again since ~ AD 1980 (Fig. 2a). The $\delta^{18}\text{O}$ values of the bulk carbonate ($\delta^{18}\text{O}_{\text{BC}}$) displayed a mean of -6.53‰ and generally ranged from approximately -7.99‰ to -5.19‰ (Fig. 2b). The $\delta^{18}\text{O}_{\text{BC}}$ values in core KCC14-3 initially decrease, reaching a minimal value of -7.99‰ in ~ AD 1340, then increase until ~ AD 1390, and finally decrease again until ~ AD 1420 (Fig. 2b). During the last 700 years, the mean $\delta^{18}\text{O}_{\text{BC}}$ values (approximately -6.42‰) were high during the period of ~ AD 1420 to 1720, with peaks at ~ AD 1450 and AD 1500 (Fig. 2b). The $\delta^{18}\text{O}_{\text{BC}}$ values have decreased and exhibited larger fluctuations in the period from ~ AD 1720 to 1980, reaching a minimal value of -7.68‰ in ~ AD 1980. Since ~ AD 1980, the values have continued to decrease (Fig. 2b).

In general, the $\delta^{13}\text{C}$ values of macrophyte remains ($\delta^{13}\text{C}_{\text{remains}}$) exhibit a constant falling trend with fluctuations (varying from -6.96‰ to -2.12‰) in the period ~ 1290-1540 AD (Fig. 2c), but the $\delta^{13}\text{C}$ values of total organic carbon ($\delta^{13}\text{C}_{\text{TOC}}$) show a constant rising trend (from -19.32‰ to -14.74‰) during this period (Fig. 2d). The $\delta^{13}\text{C}_{\text{remains}}$ values then increase with little fluctuation, reaching a peak value of -2.39‰ in ~ AD 1660, before decreasing with fluctuations until ~ AD 1760 (Fig. 2c). In contrast, the $\delta^{13}\text{C}_{\text{TOC}}$ values exhibit the opposite trend (from -17.17‰ to -14.51‰) during the period ~ AD 1540-1760 (Fig. 2d). After ~ AD 1760, the $\delta^{13}\text{C}_{\text{remains}}$ values continue to increase, reaching a maximum value of -2.93‰ at ~ AD 1920, then decreasing until the present (Fig. 2c). However, the $\delta^{13}\text{C}_{\text{TOC}}$ values still show the opposite varying trend compared to the $\delta^{13}\text{C}_{\text{remains}}$ data, changing from -17.47‰ to -15.45‰ during the period ~ AD 1760-2010 (Fig. 2d).

5. Discussion

5.1. The source of the TOC in the sediment from core KCC14-3

Lacustrine sedimentary TOC consists of a mixture of organic materials from

sources within the lake (e.g., aquatic plants and microorganisms) and external sources (e.g., dust and different vegetation and soils types in the catchment). These sources may have clearly distinguishable isotopic signatures; therefore, changes in the sources of TOC may be reflected in the stable isotope composition of the sedimentary TOC (Meyers, 1994; Lücke and Brauer, 2004).

A large number of macrophyte remains (Potamogeton) were preserved in core KCC14-3. Thus, the macrophyte remains appeared to be the main source of the sediments in Lake Koucha. However, the trends in the $\delta^{13}\text{C}_{\text{TOC}}$ values were the opposite of those in the $\delta^{13}\text{C}_{\text{remains}}$ values in core KCC14-3 during the last 700 years in Lake Koucha (Fig. 2). A correlation analysis shows that the $\delta^{13}\text{C}_{\text{remains}}$ values are negatively correlated with the $\delta^{13}\text{C}_{\text{TOC}}$ values throughout the core except for a single abnormal period ($p < 0.01$, $r = -0.51$; Fig. 3). These results suggest that the aquatic macrophytes may not be the main source of the TOC in sediments in core KCC14-3 in Lake Koucha. We observed that a large number of Myriophyllum were present together with Potamogeton and other macrophytes at the bottom of Lake Koucha in our field observation (appendix-1). The lake bottom was covered with a large number of macrophyte according to the lake bottom photo (appendix-1). The biomass of aquatic plants on the lake bottom is much higher than the terrestrial biomass in Lake Koucha (Aichneer et al., 2010a). Therefore, the source of the TOC in sediments was not primarily dominated by the terrestrial biomass in Lake Koucha (Aichneer et al., 2010a).

The results from a 5.6-m core suggested that Lake Koucha might be macrophyte-dominated before 8 cal ka BP. After that time, the lake became phytoplankton dominated, corresponding to a shift from a saline to a freshwater system at approximately 7.2 cal ka BP (Mischke et al., 2008). In addition, biomarker and compound-specific $\delta^{13}\text{C}$ evidence proved the presence of a variety of algal and bacterial markers, such as hopanoids and isoprenoids, of which phytane, pentamethylcosene (PMI), moretene and diploptene are particularly abundant in the same core from Lake Koucha since 7.2 cal ka BP (Aichner et al., 2010b). The $\delta^{13}\text{C}$ values of algae and bacteria or their specific compounds vary from -35.00‰ to -20.20‰

in the lakes on the TP (Aichner et al., 2010a; Qiang et al., 2013; Tuo et al., 2011; Liu et al., 2013; Lu et al., 2013). We conclude that the source of the TOC in the sediment is primarily controlled by the microalgae and bacteria; thus, the $\delta^{13}\text{C}$ signal of sedimentary TOC is also primarily controlled by the low $\delta^{13}\text{C}$ values of the microalgae and bacteria in Lake Koucha. However, we can only sample macrophyte remains because they are well preserved and cannot collect alga and bacteria because of poor preservation or their small size in the sediments from Lake Koucha. Therefore, macrophyte remains may be considered to be the ideal reference for paleoecological or paleoenvironmental investigations because submerged macrophytes are common in shallow lakes on the TP (Lin et al., 2002; Aichner et al., 2010a; Herzsuh et al., 2010b; Qiang et al., 2013).

5.2. Evaluation of bulk carbonate-derived $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values

The $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values of bulk carbonate in lakes may contain a contribution from detrital carbonate derived from the local bedrock, as well as aeolian dust, which will affect the interpretation of environmental changes when the carbon and oxygen isotopic compositions of bulk carbonate are used in paleoenvironmental studies. These external contributions also affect the carbon and oxygen isotope ratios of bulk carbonate when compared with ostracod carbonate (Talbot, 1990; Li and Ku, 1997; Schwalb et al., 1999; Hammarlund et al., 2003; Dettman et al., 2005; Yang et al., 2005; Bright et al., 2006; Liu et al., 2014). Very few ostracod shells were present in certain sections of core KCC14-3 from Lake Koucha in this study; thus, the bulk carbonate was treated as authigenic carbonate in the isotopic analyses. Therefore, we must evaluate whether the isotopic signals of the bulk carbonate ($\delta^{18}\text{O}_{\text{BC}}$ and $\delta^{13}\text{C}_{\text{BC}}$) can be used to describe environmental changes in Lake Koucha.

Carbonate $\delta^{18}\text{O}$ values depend primarily on both the $\delta^{18}\text{O}$ value and the temperature of the host water, and carbonate $\delta^{13}\text{C}$ values are controlled primarily by dissolved inorganic carbon (DIC) in the ambient water (Lister et al., 1991; Liu et al., 2009; Li et al., 2012). The dominant inorganic carbon species in water is mainly controlled by pH, and HCO_3^- is predominant in water with pH values greater than 7.4

(Stumm and Morgan, 1981). Therefore, the dominant inorganic carbon species in the water DIC is likely HCO_3^- because the pH of the lake water is close to 9.8 in modern Lake Koucha (Mischke et al., 2008). A past study showed that the carbonate-bicarbonate (HCO_3^-) enrichment factors for carbon isotopes are approximately $1.0 \pm 0.2\text{‰}$ for calcite and $2.7 \pm 0.6\text{‰}$ for aragonite and are essentially constant throughout the range of temperatures (10 - 40°C) (Romanek et al., 1992). Therefore, the carbonate-DIC (HCO_3^-) enrichment factors should be in the range of 1.0‰ to 2.7‰ in Lake Koucha because the bulk carbonate is mostly calcite and aragonite in the lake (Zhang et al., 2011). The measured $\delta^{13}\text{C}$ value of the bulk carbonate in the surface sediment is approximately 5.07‰, and the $\delta^{13}\text{C}$ value of water DIC is approximately 3.29‰ according to unpublished data. Therefore, the carbon isotopic enrichment factor between bulk carbonate and DIC (HCO_3^-) is 1.78‰ in Lake Koucha, which is in the range of the carbonate- HCO_3^- enrichment factors (1.0‰ to 2.7‰) (Romanek et al., 1992). In addition, the calculated water temperature at which the carbonate formed can be determined using the paleotemperature equation of Leng and Marshall (2004):

$$T = 13.8 - 4.58 \Delta + 0.08 \Delta^2 \quad (1)$$

where T (°C) is the water temperature at which the carbonate formed, and Δ is the oxygen isotopic value difference between the carbonate and the water. If the majority of the bulk carbonate formed in the lake, the calculated water temperature should be close to the summer water temperature because carbonate primarily forms in summer on the TP (Leng and Marshall, 2004; Liu et al., 2009). In modern Lake Koucha, the $\delta^{18}\text{O}$ value of the bulk carbonate from the surface sediment is approximately -5.63‰, and the $\delta^{18}\text{O}$ value of the lake water is approximately -5.1‰. Based on these isotopic data, the calculated water temperature is approximately 16.2°C in Lake Koucha based on equation 1. This temperature is close to our observed average water temperature in July 2012 (approximately 15.8°C) in the lake. Therefore, we conclude that the bulk carbonate is dominated by authigenic carbonates formed in the lake and that their $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values can be used to indicate changes in the environment of Lake Koucha.

In general, the oxygen isotope values of lacustrine carbonates are influenced by the temperature and, more importantly in closed lakes, the isotopic composition of the water at the time when the carbonates precipitated in lakes (Leng and Marshall, 2004; Xu et al., 2006; Mischke et al., 2010; Liu et al., 2009). Therefore, the oxygen isotopic records of lake sedimentary carbonates are assumed to indicate changes in the lake's E/P ratio (effective precipitation) or hydrologic balance (Lister et al., 1991; Benson et al., 2002), but the $\delta^{18}\text{O}$ values of lake carbonates have also been used as an indicator of temperature in some studies (Von Grafenstein et al., 1996; Xu et al., 2006). Although Lake Koucha is not a closed lake, the measured lake water $\delta^{18}\text{O}$ value (-5.10‰) is much higher than that of the water flowing into the lake from rivers ($\delta^{18}\text{O}$: -11.23‰). Therefore, the oxygen isotope composition of the lake water in Lake Koucha is strongly influenced by evaporation. The carbon isotope composition of the carbonates have rarely been fully exploited as proxies because their interpretation is considered difficult to assess, and the $\delta^{13}\text{C}$ values of carbonates have been mainly used to indicate variations in temperature (increasing temperature caused strong CO_2 exchange between lake water and atmosphere) or primary productivity in lakes on the TP (Qiang et al., 2005; Xu et al., 2006a, 2014; Li and Liu, 2014). However, the CO_2 exchange between lake water and atmosphere is not enough to cause the enriched $\delta^{13}\text{C}_{\text{BC}}$ values as high as 9.28‰, but high primary productivity may result in such enriched values in core KCC14-3. Therefore, we assumed that the changes in the bulk carbonate $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values in Lake Koucha are mainly related to changes in effective moisture (lake level) and primary productivity, respectively.

5.3. The offset between $\delta^{13}\text{C}_{\text{remain}}$ and $\delta^{13}\text{C}_{\text{BC}}$ ($\epsilon_{\text{remains-BC}}$) values as a proxy of macrophyte productivity

The $\delta^{13}\text{C}$ values of submerged macrophytes are assumed to reflect productivity-related carbon limitation under alkaline aquatic conditions (Papadimitriou et al., 2005). The main factors that influence the isotopic signature of macrophytes with special consideration to Potamogeton are (1) the isotopic signature of the DIC source and (2) the growth-rate-related fractionation during photosynthesis

(Herzschuh et al., 2010a, b). The physiological mechanism of HCO_3^- uptake of submerged macrophytes has been investigated in many studies (e.g., Lucas 1983; Maberly and Madsen, 1998). Across the range of temperatures commonly encountered by aquatic plants, the $\delta^{13}\text{C}_{\text{HCO}_3^-}$ will be 7-12‰ enriched compared to $\delta^{13}\text{CO}_2(\text{aq})$ (Zhang et al. 1995). In addition, the HCO_3^- may be the dominant water DIC species because of the high lake water pH in Lake Koucha (Stumm and Morgan, 1981). Therefore, the enriched $\delta^{13}\text{C}$ values of modern macrophyte remains compared to other terrestrial or emergent aquatic plants are related to the macrophyte's ability to utilize HCO_3^- as a carbon source in Lake Koucha. Consequently, HCO_3^- uptake is expected to play an important role in controlling the carbon isotope composition of aquatic plants in Lake Koucha, and this explains the enriched $\delta^{13}\text{C}$ values of macrophyte remains in the core KCC14-3. $\delta^{13}\text{C}_{\text{DIC}}$ values should increase with increasing primary productivity because many aquatic plants use the HCO_3^- in lakes for photosynthesis. Additionally, much more carbonate will form with increasing photosynthesis in the lake water, and the $\delta^{13}\text{C}_{\text{DIC}}$ values in the lake water will also increase in association with the precipitation of carbonates. Indeed, HCO_3^- -limited conditions tend to be associated only with the high productivity in dense plant stands, which can shift the $\delta^{13}\text{C}$ values of bulk carbonates and aquatic plants toward higher values. The modern data set has yielded a significant relationship between $\epsilon_{\text{fossil Potamogeton}}^{\text{DIC}}$ and measured HCO_3^- levels, and the transfer function has been applied to ancient $\epsilon_{\text{fossil Potamogeton}}^{\text{ostracod}}$ values to quantify past HCO_3^- concentrations in Lake Koucha (Herzschuh et al., 2010a). The result from another study suggested that $\epsilon_{\text{fossil Potamogeton}}^{\text{carbonate/DIC}}$ values can be used as the indicator of *Potamogeton pectinatus* growth rate, which can be interpreted in terms of primary productivity (Herzschuh et al., 2010b).

Based on these results, we concluded that the $\epsilon_{\text{remains}}^{\text{DIC}}$ values can be used to trace changes in macrophyte productivity in Lake Koucha. Because $\delta^{13}\text{C}_{\text{DIC}}$ values cannot be measured directly in lake sediments, $\delta^{13}\text{C}_{\text{BC}}$ values can be used in paleolimnological studies as an alternative ($\epsilon_{\text{CaCO}_3\text{-HCO}_3^-}$: ~1‰, Romanek et al., 1992) though the dependence of fractionation on temperature and calcite precipitation rate

may obscure the original $\delta^{13}\text{C}_{\text{DIC}}$ signal to some extent (Hollander and McKenzie, 1991). The $\delta^{13}\text{C}_{\text{BC}}$ values were not corrected because these effects are an order of magnitude smaller than the total $\delta^{13}\text{C}_{\text{BC}}$ range in core KCC14-3 from Lake Koucha. In addition, the reliability of $\delta^{13}\text{C}_{\text{BC}}$ values as a proxy of former $\delta^{13}\text{C}_{\text{DIC}}$ values is likely severely reduced in dense charophyte swards when pH raises to >11 , allowing atmospheric CO_2 to directly combine with the OH^- ions of water, which results in strong isotopic disequilibrium between charophyte carbonate and HCO_3^- , as was observed by Pentecost et al. (2006). However, a previous study showed that such phases do not appear to have been present in Lake Koucha since the early Holocene (Herzschuh et al., 2010b), and the $\delta^{13}\text{C}_{\text{BC}}$ values can be used as a reliable proxy of former $\delta^{13}\text{C}_{\text{DIC}}$ values in Lake Koucha. Therefore, the offset between the $\delta^{13}\text{C}_{\text{remains}}$ and $\delta^{13}\text{C}_{\text{BC}}$ values ($\epsilon_{\text{remains-BC}}$) can be treated as a proxy for macrophyte productivity in Lake Koucha. The high $\epsilon_{\text{remains-BC}}$ values indicate high macrophyte productivity in the Lake Koucha area.

As shown in Figure 4, the macrophyte productivity was high before $\sim$ AD 1420, as indicated by relatively high $\epsilon_{\text{remains-BC}}$ values (average value of -9.83‰). Subsequently, the macrophyte productivity sharply decreased, reaching the lowest value in the period $\sim$ AD 1450-1480. Then, the macrophyte productivity increased from $\sim$ AD 1480 incrementally until $\sim$ AD 1895 along with fluctuations in the area of Lake Koucha. However, the macrophyte productivity was very low, as indicated by the low average $\epsilon_{\text{remains-BC}}$ values (about -10.78‰) in the period $\sim$ AD 1420-1890, which correspond to the cold climate of the ‘Little Ice Age’ (LIA). After $\sim$ AD 1890, the macrophyte productivity sharply increased, as indicated by increasing $\epsilon_{\text{remains-BC}}$ values in this area.

Recent studies have shown that the distribution of macrophytes is strongly associated with water depth in lakes on the TP (Liu et al., 2013; Qiang et al., 2013), and the *Potamogeton* usually grows in shallow water areas with water depths of less than 10 m in lakes on TP, according to previous studies (Herzschuh et al., 2010b; Liu et al., 2013; Qiang et al., 2013) and our own field observation. Therefore, macrophyte productivity may be affected by the water depth of the lakes, and the productivity of

this species may decrease with increasing water depth. Therefore, the changes in macrophyte productivity derived from $\epsilon_{\text{remains-BC}}$ values were compared with changes in effective moisture (related to lake level) derived from $\delta^{18}\text{O}_{\text{BC}}$ values in core KCC14-3 to avoid the uncertainty in the age model. In general, Figure 4 shows that the $\delta^{18}\text{O}_{\text{BC}}$ values exhibit trends opposite those in the macrophyte productivity indicated by $\epsilon_{\text{remains-BC}}$ values in core KCC14-3. The low $\delta^{18}\text{O}_{\text{BC}}$ values indicate increased lake levels corresponding to high macrophyte productivity indicated by high $\epsilon_{\text{remains-BC}}$ values in Lake Koucha (Fig. 4). Obviously, the relationship between lake level and macrophyte productivity based on isotopes was inconsistent with the hypothesis that macrophyte productivity decreases with increasing water depth based on our observations of modern Lake Koucha. Therefore, while the distribution of macrophyte productivity may be controlled by water depth, the carbon isotope composition of these species or their productivity may not be primarily affected by water depth in Lake Koucha. In addition, past studies have suggested that the primary productivity is also related to temperature and that high temperatures should result in increased primary productivity in the lakes (Xu et al., 2006; An et al., 2012; Li and Liu, 2014). The result from a culture experiment showed that the $\epsilon_{\text{Potamogeton pectinatus-DIC}}$ values increased with increasing culture temperature due to changes in the DIC content (Lin, 2008). Therefore, we considered that the macrophyte productivity may be related to the temperature of Lake Koucha. As shown in Figure 4, the varied pattern of macrophyte productivity recorded by $\epsilon_{\text{remains-BC}}$ values in core KCC14-3 from Lake Koucha generally corresponds to changes in reconstructed total solar irradiance (TSI) records inferred from $\Delta^{10}\text{Be}$ (Bard et al., 2000) and temperature derived from tree rings dating back to 1310 AD on the northeastern TP (Liu et al. 2009). The macrophyte productivity generally increased with increasing total solar irradiance, and the macrophyte productivity was low when TSI was weak (Fig. 4). However, we found that macrophyte productivity recorded by $\epsilon_{\text{remains-BC}}$ values in core KCC14-3 from Lake Koucha do not perfectly mirror the temperature changes recorded by tree rings from the northeastern TP (Fig. 4). The difference between these two records can be attributed to dating uncertainties in our record. Therefore, we

concluded that the macrophyte productivity changes may be primarily controlled by temperature, but the distribution of this species is likely affected by internal lake dynamics, such as changes in lake level, which are related to climate changes in the Lake Koucha area.

6. Conclusions

In this study, the organic carbon isotopic compositions of macrophyte remains and bulk carbonate from a sedimentary core covering the last 700 years in Lake Koucha was investigated to evaluate its paleoclimatic/paleoenvironmental implications. We found that the bulk carbonate was dominated by authigenic carbonates formed in the lake and that their isotopic data can be used to reconstruct changes in the environment of Lake Koucha. The macrophyte productivity derived from the carbon isotopic offset between macrophyte remains and bulk carbonates ($\epsilon_{\text{remains}} - \text{BC}$) in Lake Koucha area agrees well with the total solar irradiance (TSI) records inferred from $\Delta^{10}\text{Be}$ and temperature records recorded by tree rings from the Qinghai-Tibetan Plateau. This result suggests that the changes in macrophyte productivity may be primarily controlled by temperature, but the distribution of this species is likely a function of internal lake dynamics (such as changes in lake level) that are indirectly caused by climatic changes in the Lake Koucha area.

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Captions

Table 1. The data of ^{137}Cs activity, AMS radiocarbon dates and calendar ages for the Lake Koucha sedimentary core (KCC14-3).

Figure 1. Map of Lake Koucha and its surrounding environment. The solid yellow five-pointed star on the map shows the location where the core KCC14-3 was collected.

Figure 2. The stable isotopic variations of bulk carbonate, macrophyte remains and total organic carbon (TOC) that were recorded in the core KCC14-3, which covers the past 700 years (a, bulk carbonate $\delta^{13}\text{C}$ values; b, bulk carbonate $\delta^{18}\text{O}$ values; c, macrophyte remains $\delta^{13}\text{C}$ values; d, TOC $\delta^{13}\text{C}$ values).

Figure 3. Correlation of TOC $\delta^{13}\text{C}$ values with Potamogeton remains $\delta^{13}\text{C}$ values from the Lake Koucha sedimentary core.

Figure 4. Comparison of b) macrophyte productivity derived from $\epsilon_{\text{remains-BC}}$ values in core KCC14-3 with a) bulk carbonate $\delta^{18}\text{O}$ values as a proxy for effective precipitation or lake level and c) the reconstructed total solar irradiance (TSI) records inferred from $\Delta^{10}\text{Be}$ (blue, [Bard et al., 2000](#)) and tree-ring temperature records from the northeastern Qinghai-Tibet Plateau (yellow, [Liu et al., 2009](#))

Appendix-1. A photograph of the lake bottom of Lake Koucha taken in April 2012.

Figure 1

Figure 2

Figure 3

Figure 4

Table 1

Lab. Code	Sample No.	Depth (cm)	Material	Measured ^{14}C age	Corrected by 1812 yr age (cal. yr BP) (Median Probability)
XA10601	KCC14-3-1AMS	0.5	macrophyte remains	1812 $\pm$ 22 BP	0
XA10602	KCC14-3-72AMS	36	macrophyte remains	2460 $\pm$ 20 BP	592
				^{137}Cs activity (Bq/kg)	
	KCC14-3-1	0.5		5.4	
	KCC14-3-9	4.5		1.4	
	KCC14-3-19	9.5		3.8	
	KCC14-3-29	14.5		0.7	