



Evaluation of glycerol dialkyl glycerol tetraether proxies for reconstruction of the paleo-environment on the Qinghai-Tibetan Plateau



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ABSTRACT

The uplift of the Qinghai-Tibetan Plateau has a great effect on local and global climate changes. Here we report the late Holocene climate change in the northern plateau by using a 3490-year sediment core record from Kusai Lake. Glycerol dialkyl glycerol tetraethers (GDGTs) collected from the core were examined in combination with other paleo-environmental proxies. The reconstructed mean annual air temperatures (MAAT) using branched GDGT (membrane lipids of certain bacteria) proxies are higher than the measured MAAT, but much closer to measured summer air temperatures, suggesting a possibility of a bias of the reconstructed MAAT towards summer temperatures. The pH values derived from a branched GDGT proxy show a negative correlation with TOC (a lake productivity indicator in arid regions). Furthermore, both CBT-pH and TOC show temporal cyclic changes, which suggest that the branched GDGT derived pH index may be useful in reconstructing paleo-pH values in a lacustrine system. Lastly, the composition of isoprenoid GDGTs (membrane lipids of archaea) shows a major shift around 1400 BP, which is in line with a large increase in sediment soluble salts at this time, but lags behind the onset of salt mineral precipitation by 600 yr, suggesting that change in archaeal community composition and salt mineral precipitation may require different threshold values of salinity. The results of this study demonstrate that useful paleo-climatic and paleo-environmental information can be extracted from the GDGTs preserved in lake sediments.

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1. Introduction

The Qinghai-Tibetan Plateau, the highest plateau on Earth, plays an important role in the evolution of Asian monsoon (Kutzbach et al., 1997; An et al., 2001, 2012). The continuous uplift of the plateau since 50 My ago has affected Asian climate and global atmospheric circulation patterns (Ruddiman and Kutzbach, 1991; Kutzbach et al., 1993; Wu and Zhang, 1998; An, 2000). Many important climatic events have taken place in the Qinghai-Tibetan Plateau since the Holocene (Colman et al., 2007; X. Liu et al., 2009; An et al., 2012), a period that is also linked to human activity (May-

ewski et al., 2004). These climate changes are recorded both regionally and globally (Shindell et al., 2001; Macklin and Lewin, 2003; Leemans and Eickhout, 2004). Hence, studying Holocene climatic fluctuations on the Qinghai-Tibetan Plateau is critical for the understanding of either contribution or response of local regions to the global climate system, as well as for evaluating the influence of anthropogenic activities on recent climate change.

In the last two decades, ice cores (Thompson et al., 2000; Zhao et al., 2012), loess deposits (An et al., 2001; Lu et al., 2004), and lake sediments (Shen et al., 2005; Liu et al., 2008; Zhu et al., 2008) have been used as archives to reconstruct paleoclimate changes on the Qinghai-Tibetan Plateau by employing various geochemical proxies, such as total organic carbon (TOC), tree-ring, alkenone and pollen records, $\delta^{18}\text{O}$ and chironomids (Thompson et al., 2000; Esper et al., 2002; Z. Liu et al., 2006; Zhang et al., 2007; X. Liu et al., 2009; Herzschuh et al., 2009). In comparison to ice cores and loess deposits, lakes have a greater sensitivity to climate variations and can provide a superb record of paleo-climatic conditions (Castañeda

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and Schouten, 2011). However, lacustrine records are also complicated because lake sediments may be derived from multiple sources including eolian transport, soil and local vegetation, in addition to the in situ lake production (allochthonous source). Thus, some of these traditional proxies may not be directly applicable to lakes and may complicate interpretations (Huang et al., 2002). Furthermore, some of the organisms, from which certain organic proxies are derived, may be absent or poorly preserved and cannot be used to generate continuous climate records (Zink et al., 2001; Powers et al., 2004; Woltering et al., 2011). For these reasons, it is desirable to seek other indicators for paleo-climate reconstruction using lake sediments.

In the last 10 years, a group of organic proxies, derived from glycerol dialkyl glycerol tetraethers (GDGTs) of bacteria and archaea, have been applied to paleo-environmental studies (Castañeda and Schouten, 2011; Schouten et al., 2013). Isoprenoid glycerol dialkyl glycerol tetraethers (iGDGTs) are membrane lipids of archaea, of which crenarchaeol has been recognized as a biomarker for aquatic (Sinninghe Damsté et al., 2002; Brochier-Armanet et al., 2008; Pester et al., 2011) and soil (Leininger et al., 2006) Thaumarchaeota. These archaea are abundant in oceans, lakes and soils (Auguet and Casamayor, 2008; Kan et al., 2011; Sinninghe Damsté et al., 2012a). Branched GDGTs (bGDGTs) are suggested to be produced by some anaerobic soil bacteria and are distributed ubiquitously in terrigenous environments (Weijers et al., 2006). Based on their respective sources of bGDGTs (terrigenous) and iGDGTs (aquatic bodies), a proxy for estimating the terrigenous input to oceans and lakes, called branched and isoprenoid tetraether (BIT) index, was proposed (Hopmans et al., 2004). In general it is believed that a high BIT value should indicate a high terrigenous contribution to an aquatic environment. However, there have been debates about the usefulness of the BIT index. For instance, high BIT values can also result from in situ production of bGDGTs in lakes (Sinninghe Damsté et al., 2009; Tierney and Russell, 2009). BIT values in the high elevation/arid regions of Tibet in NW China are usually lower than most global soil values (Wang et al., 2012; Xie et al., 2012), and in the Qinghai Lake region of the Qinghai-Tibetan Plateau, BIT in the soil is actually lower than that in near shore lake sediments (Wang et al., 2012). Thus, in these cases this proxy may not indicate a terrigenous input. In addition, the BIT index can be influenced by large changes in crenarchaeol concentration (Fietz et al., 2011; Smith et al., 2012; Sinninghe Damsté et al., 2012b). Additionally, CBT (cyclisation ratio of branched tetraether) and MBT (methylation ratio of branched tetraether) indices were developed to quantitatively calculate soil pH and mean annual air temperature (MAAT) (Weijers et al., 2007), based on the observation that the degrees of the methylation and the cyclisation of bGDGTs are related to these environmental conditions. Likewise, recent studies have developed the ACE (the archaeol and caldarchaeol ecometric) index for estimating paleo-salinity (Turich and Freeman, 2011; Wang et al., 2013).

These GDGT derived proxies have provided possibilities to obtain paleo-environmental information in lacustrine systems (Bechtel et al., 2010; Tyler et al., 2010; Zink et al., 2010; Castañeda and Schouten, 2011; Fawcett et al., 2011; Niemann et al., 2012; Schouten et al., 2013). However, the MBT/CBT derived MAAT (Weijers et al., 2007) have been shown to be very different from actually measured temperatures for some lakes (Blaga et al., 2010; Zink et al., 2010; Loomis et al., 2011; Pearson et al., 2011; Tierney et al., 2012). It is assumed that in situ production of branched GDGTs in lakes is responsible for the differences (Blaga et al., 2010; Pearson et al., 2011; Tierney et al., 2012). Recently several specific lacustrine based calibrations have been proposed to reconstruct temperature and pH based on bGDGT distributions (Blaga et al., 2010; Tierney et al., 2010; Zink et al., 2010; Pearson et al., 2011; Sun et al., 2011). To accurately interpret these reconstructed

paleo-environmental conditions for lacustrine systems, it is critical to determine the origin of bGDGTs (soil derived vs. in situ production within lake).

In order to further examine the applicability of these GDGT derived proxies to paleo-environmental reconstruction for lake systems, we studied the relationship between the distribution of GDGTs and environmental conditions in a 3490-year sediment core of Kusai Lake from the northern Qinghai-Tibetan Plateau, NW China. Our results show that the GDGT derived proxies are applicable to the reconstruction of paleo-environmental conditions in the Kusai Lake region if the origin of GDGTs can be identified and resulting estimates of paleo-environmental conditions can be cross checked by other geochemical proxies.

2. Materials and methods

2.1. Site description and sample collection

Kusai Lake (35°37′–35°50′N, 92°38′–93°15′E, 4475 m a.s.l.) is a saline lake located in the largest, almost uninhabited Hoh Xil region of the northern Qinghai-Tibetan Plateau, NW China (Fig. 1). The lake is 254.4 km² in area with a catchment area of ca. 3700 km². The maximum water depth is ca. 50 m in the northwestern region of the lake. This endorheic lake is fed by Kusai River at its southwestern margin and has no outflow. The mean annual evaporation of the lake (ca. 1600 mm) is in excess of the mean annual precipitation (ca. 250 mm), resulting in an arid climate and modern-day salinity of 28.54 g/l. Its high altitude setting results in a low mean annual air temperature (MAAT) of ca. –4.5 °C (based on the Wudaoliang meteorological station, situated ca. 60 km to the south of Kusai Lake). However, there is a strong seasonal variation in temperature, ranging from –13 °C in winter to 5 °C in summer. Daily temperature range is also large. In a typical winter day, temperature can vary from –20 °C at night to 2 °C in the middle of the day. The vegetation around Kusai Lake is dominated by desert Chenopodiaceae and *Artemisia* (X. Liu et al., 2009).

In June 2010, a 5 m sediment core was obtained from the southeastern region of Kusai Lake at 35°43′18.4″N and 92°55′11.8″E at a water depth of 14.5 m using UWITEC coring equipment. Two soil samples (0–5 cm in depth) from the lake region were also collected. In the laboratory the core was sliced at 2 cm intervals and alternate sub-samples (4 cm depth intervals) were collected for GDGT extraction, and total organic carbon (TOC) and total organic nitrogen (TON) analyses. Sediment pore water was obtained after centrifugation of each subsample and analyzed for pH, conductivity, and major cations and anions. Selected sediment subsamples were analyzed for pH, concentration of soluble salts, and mineralogy.

2.2. Age model

An age model was established based on 10 sediment subsamples evenly distributed along the length of the core by using accelerator mass spectrometry (AMS) ¹⁴C dating of bulk organic carbon at Beta Analytic Inc. (Miami, Florida, USA) and the Rafter Radiocarbon Laboratory of the National Isotope Centre, GNS Science in New Zealand. The radiocarbon ages were converted to calendar years before 1950 (cal yr BP) using the Calib6.1 program (Reimer et al., 2009). Linear interpolation between two calendar year ages was used to obtain the ages of all sediment subsamples.

2.3. Porewater chemistry

Porewater pH and conductivity were measured with a pH meter (SevenGo Pro, Mettler Toledo, Switzerland) and a conductivity me-

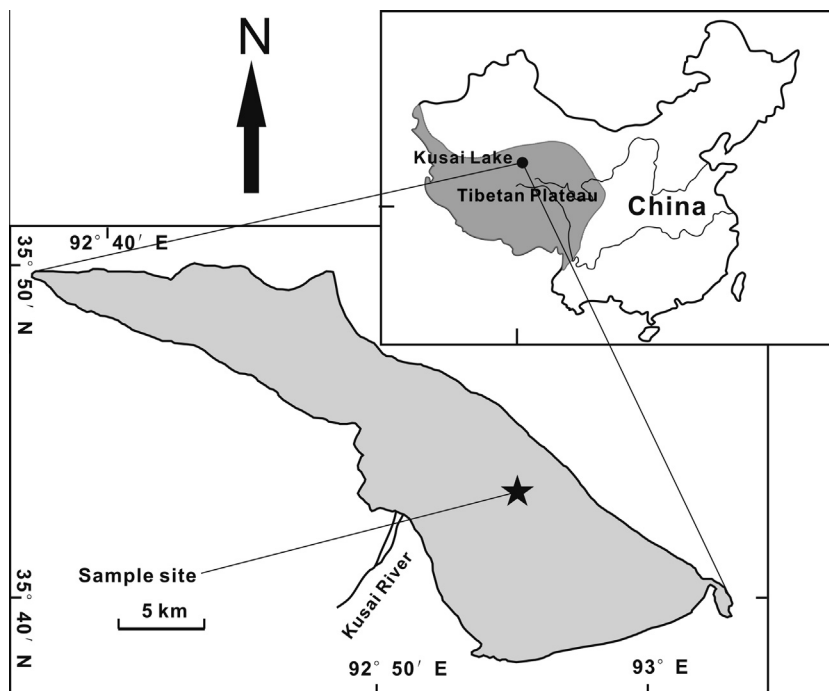


Fig. 1. Location map of Kusai Lake (35°37'–35°50'N, 92°38'–93°15'E, 4475 m above sea level) and the coring site.

ter (DDS-307A, SHKY, China), respectively. Anion concentrations were determined with ion chromatography with Dionex DX-500 (AS14A column, and 10 μ M Na₂CO₃/NaHCO₃ as an eluent, Dionex, USA). Cation concentrations were determined with direct current plasma emission spectrometry (DCP-OES, Beckman, USA). Salinity was calculated by summing the total numbers of cations and anions.

2.4. pH and concentrations of soluble salts of the Kusai Lake sediments

Aliquots of the soil samples and 16 lake sediment subsamples were separated from pore water by centrifugation, sieved to collect 2 mm size fraction and dried at room temperature. Ten grams of these sieved and dried soil and sediment samples were analyzed for pH and concentrations of soluble salts. Measurements were made at the Service Testing and Research (STAR) lab of the Ohio State University, USA by the conventional methods (Thomas et al., 1996; Whitney, 1998).

2.5. Sediment mineralogy by X-ray diffraction

X-ray diffraction was performed on six representative sediment subsamples. These six subsamples covered the range of sediment color and pore water chemistry. The mineralogy was identified by using a Scintag X1 powder diffractometer system with CuK α radiation, a variable divergent slit and a solid state detector. Sediment samples were air dried overnight and ground to powder. To facilitate comparison among the samples, a similar amount of powdered sediment material from each sample was packed into the well of low background quartz XRD slide (GemDugout, Inc., Pittsburgh, PA, USA). The routine power was 1400 W (40 kV, 35 mA). Samples were scanned from 2–70 two-theta with a 0.02 step size and a count time of 2 s per step. After background subtraction, the search-match software was preliminarily used to identify a list of possible minerals. Further identification was aided

by manually matching three strongest reflections of each mineral with those in the database.

2.6. TOC and TON analysis

Samples were acidified with 1 N HCl, rinsed repeatedly with deionized water and dried at 80 °C. About 0.02 g dried material from each subsample was weighed with a Super Micro balance with a precision of 0.1 μ g (Mettler Toledo UMT2, USA) and analyzed for TOC and TON with a 2400 Series II CHNS/O Analyzer (Perkin Elmer, Waltham, MA, USA). The accuracy and precision of the analyzer were \leq 0.3% and \leq 0.2%, respectively.

2.7. Lipid extraction and analysis

Sediment samples (ca. 5 g) were freeze dried, homogenized with a mortar and pestle and ultrasonically extracted with methanol (2 \times), DCM:methanol (1:1, v:v; 2 \times), and DCM (2 \times). The supernatants from these six extractions were combined as total lipid extracts (TLEs) and dried under a gentle flow of N₂. TLEs were separated into the non-polar and the polar fraction over a silica gel column using eluent hexane:DCM (9:1, v:v) and DCM:methanol (1:1, v:v), respectively. After drying under N₂, the polar fraction was redissolved in hexane:isopropanol (99:1, v:v) and filtered through a 0.45 μ m PTFE syringe filter prior to analysis.

GDGTs were analyzed using an Agilent 1200 series high performance liquid chromatography-atmospheric pressure positive ion chemical ionization mass spectrometer (HPLC-APCI-MS) according to previously published methods (Hopmans et al., 2000; Schouten et al., 2007). Injection volume was 5 μ l and separation of different GDGTs was achieved on an Alltech Prevail Cyano column (150 mm \times 2.1 mm, 3 μ m) maintained at 30 °C. Hexane:isopropanol (99:1, v:v) was used as an eluent in isocratic elution for 5 min. The amount of the isopropanol in the eluent was linearly increased to 1.8% in 45 min at a flow rate of 0.2 ml/min during the gradient elution stage. GDGTs were monitored in the selected ion

monitoring (SIM) mode at specific mass/charge ratios (m/z) to increase sensitivity. The GDGTs were then quantified by integrating the area of the $[M+H]^+$ peaks and by comparing with the peak area of the C_{46} internal standard (Huguet et al., 2006; Zhang et al., 2012).

bGDGTs and iGDGTs (Fig. 2) were used to calculate several indices. The iGDGTs have isoprenoid carbon chains and 0–4 cyclopentane rings. Particularly, crenarchaeol (GDGT VIII) contains one cyclohexane moiety in addition to four cyclopentane moieties and GDGT VIII' is the regio-isomer of crenarchaeol. The bGDGTs have branched alkyl chains containing 4–6 methyl substituents and 0–2 cyclopentane rings. The BIT index was defined according to the following formula (Hopmans et al., 2004):

$$\text{BIT} = (\text{Ia} + \text{IIa} + \text{IIIa}) / (\text{Ia} + \text{IIa} + \text{IIIa} + \text{VIII}) \quad (1)$$

MBT and CBT indices were defined as follows (Weijers et al., 2007):

$$\text{MBT} = (\text{Ia} + \text{Ib} + \text{Ic}) / (\text{Ia} + \text{Ib} + \text{Ic} + \text{IIa} + \text{IIb} + \text{IIc} + \text{IIIa} + \text{IIIb} + \text{IIIc}) \quad (2)$$

$$\text{CBT} = -\log((\text{Ib} + \text{IIb}) / (\text{Ia} + \text{IIa})) \quad (3)$$

Roman numerals correspond to the structures shown in Fig. 2. Paleo pH values of Kusai Lake were calculated using a calibration equation (Tierney et al., 2010) developed for lakes with a high coefficient of determination ($R^2 = 0.83$) and large pH range (4.3–10.8):

$$\text{pH} = 10.32 - 3.03 \times \text{CBT} \quad (4)$$

Paleo-temperatures were calculated according to a calibration developed for global lakes (Sun et al., 2011):

$$T = 6.803 - 7.062 \times \text{CBT} + 37.090 \times \text{MBT} \quad (5)$$

3. Results

3.1. Chronology

The ten sediment subsamples define a correlation between the ^{14}C age and depth for this core (Table 1; Fig. 3A). This correlation reveals that Kusai Lake has a ^{14}C reservoir effect of 3030 years, which is similar to that observed for other saline lakes on the Qinghai-Tibetan Plateau (Morrill et al., 2006; Liu et al., 2008; X. Liu et al., 2009). After subtracting this reservoir effect from the ^{14}C ages, this core covers a time span of ca. 3490 years, from approximately 3430 yr before present (BP, 1950 A.D.) to the year 2010. Based on this age model, the average time resolution of the sediment core is ca. 25 calendar years. This age model is parallel to the one for a different core collected from an adjacent site of Kusai Lake in 2006 (X. Liu et al., 2009) (Fig. 3B).

3.2. Porewater chemistry

Porewater pH values range from 8.0–9.1, with an average of 8.8 ± 0.2 standard deviation (S_D). Conductivity of pore water varies

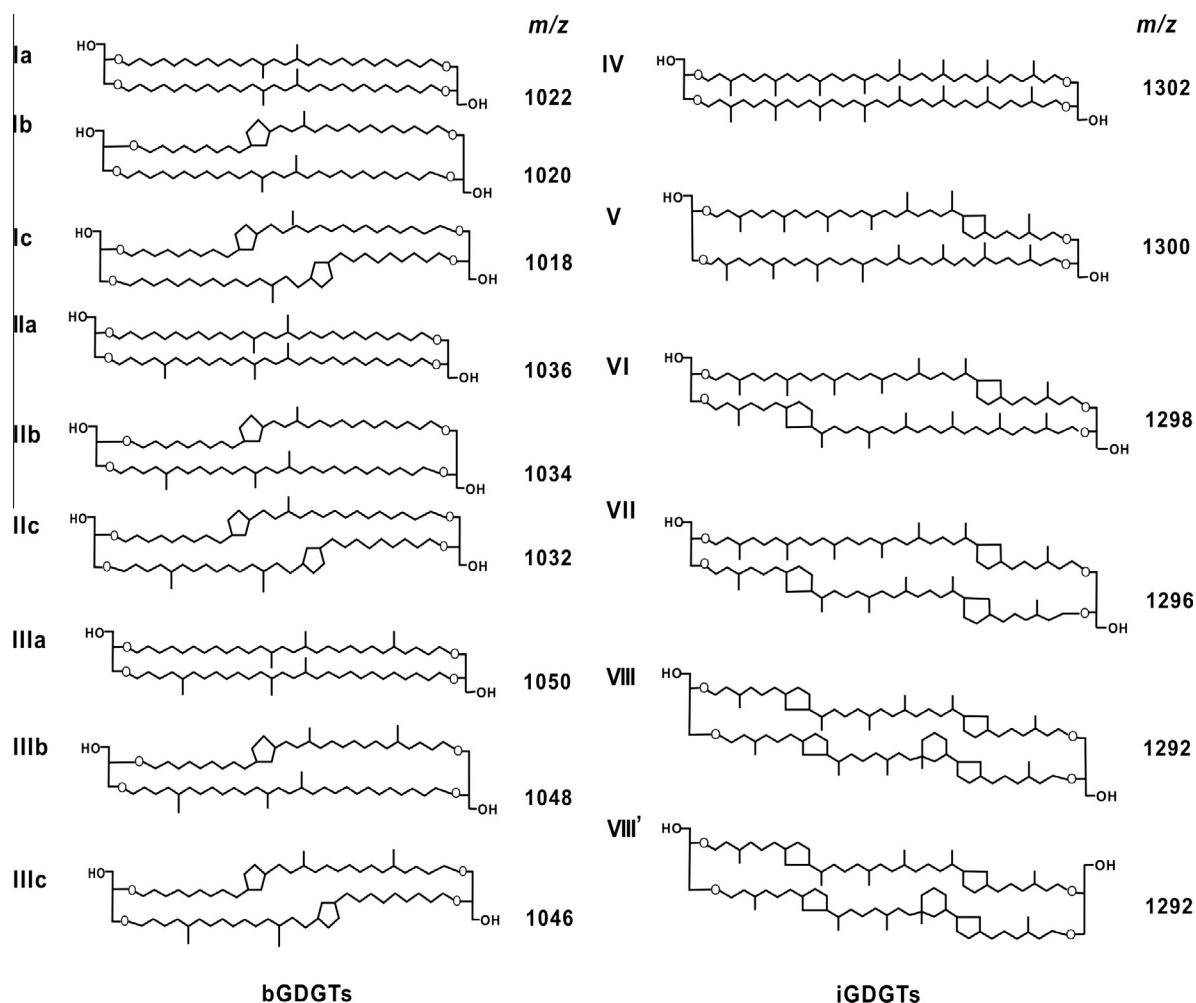


Fig. 2. Structures of the glycerol dialkyl glycerol tetraethers (GDGTs) analyzed in this study. Lipid groups I, II, III are bGDGTs; lipid IV–VIII are iGDGTs.

Table 1
 ^{14}C AMS ages analyzed on TOC and calibrated ages for Kusai Lake.

Depth (cm)	^{14}C age/yr BP (1σ)	$\delta^{13}\text{C}\text{‰}$	Reservoir corrected ^{14}C age by 3030 yr	Calendar age/cal yr BP (2σ)
34	3255 ± 25		225 ± 25	269–308 (289)
60	3390 ± 30	–22.7	360 ± 30	421–499 (460)
100	3585 ± 25	–23.6	555 ± 25	523–562 (543)
130	3910 ± 30	–23.2	880 ± 30	729–832 (781)
232	4540 ± 30	–22.5	1510 ± 30	1326–1421 (1340)
264	4520 ± 30	–22.6	1490 ± 30	1306–1416 (1361)
350	5080 ± 25	–23.8	2050 ± 25	1945–2069 (2007)
380	5200 ± 40	–23.1	2170 ± 40	2055–2318 (2187)
414	5440 ± 40	–23.2	2410 ± 40	2345–2542 (2444)
493	6202 ± 25	–23.9	3172 ± 25	3360–3446 (3403)

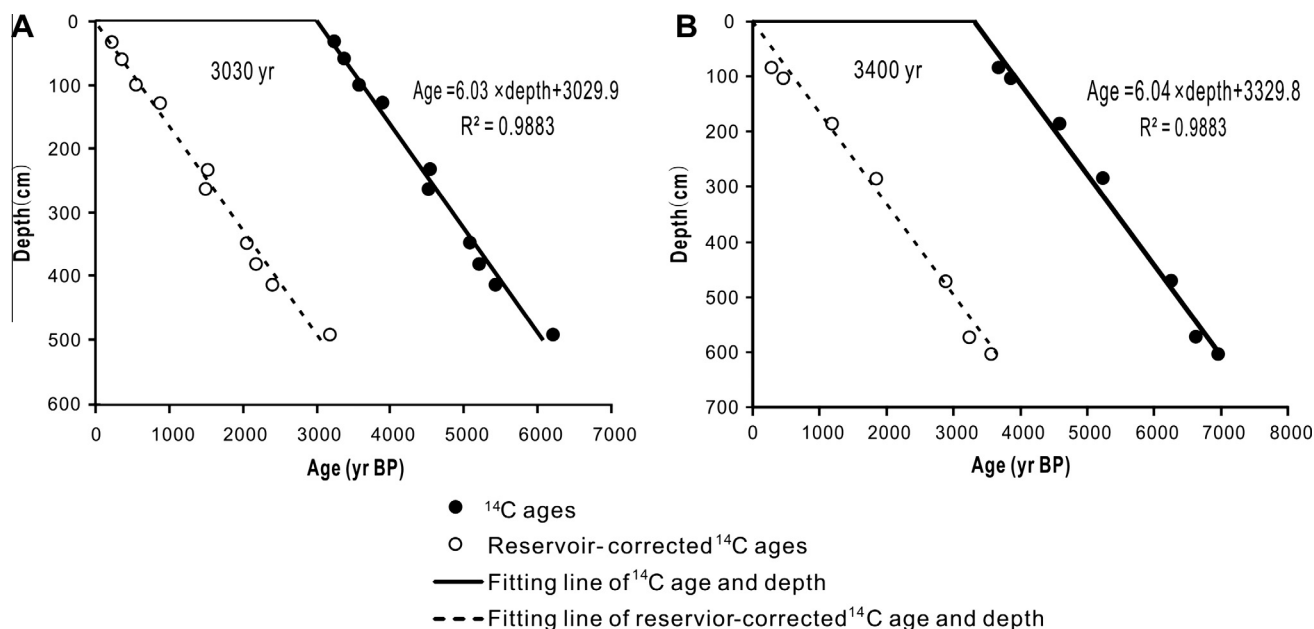


Fig. 3. (A) An age-depth model for the Kusai Lake sediment core of 500 cm in length. This model was developed based on ten calibrated radiocarbon ages of bulk organic carbon and it shows the radiocarbon ages and reservoir corrected ^{14}C ages vs. depth (after subtraction of 3030 yr from the ^{14}C ages). (B) An age model for another Kusai Lake core of 606 cm in length from a previous study (X. Liu et al., 2009) for comparison.

from 11.76–43.04 ms/cm. The calculated salinity, by summing the total numbers of cations and anions, varies from 4.90–23.46 g/l. Both pore water conductivity and salinity show an overall increasing trend from the bottom of the core to the top with a large jump at ca. 200 cm (Fig. 4A and B).

3.3. Sediment pH, soluble salts, and mineralogy

The measured pH values for the sediment subsamples range from 8.9–9.4, which are similar to the measured porewater pH values (8.0–9.1), but higher than the measured pH of 7.7–8.4 for the two soil samples collected from the surrounding region of Kusai Lake. The concentrations of sediment soluble salts, measured by conductivity after dissolution of these salts into distilled water, show a similar depth trend to the porewater salinity and conductivity profiles (Fig. 4C).

The mineralogy of the Kusai Lake sediments is mainly composed of quartz, calcite, albite, kaolinite, aragonite and biotite. For the six analyzed samples covering the entire length of the core, the dominant minerals are similar, but their relative abundances vary with depth. Halite was detected at the depth of 226 cm, which approximately corresponds to the depth at which large increases of pore water conductivity and salinity, and sediment soluble salt concentration were observed (Fig. 4A–C). These salinity profiles are consistent with a previous mineralogical study (Yao et al.,

2011), which shows that salt minerals anhydrite and halite were observed in the upper portion of the core (Fig. 4D and E).

3.4. Distribution of GDGTs and relationship with paleo-salinity

All GDGT abundance data as well as calculated indices including CBT, MBT, BIT, MBT/CBT-temperature and CBT-pH are available in the Supplementary Table S1. The distributions of bGDGTs and iGDGTs were examined by cluster analysis (Supplementary Fig. S1) according to the compositions of these GDGTs in each sediment subsample following a method previously published (Wei et al., 2011). The depth profile of iGDGTs shows a major shift in relative distribution at ca. 1400 yr BP (Fig. 4F), while bGDGTs do not show any obvious change with time (Fig. 4G). Group 2 iGDGTs replaces Group 1 when salinity reaches 15.6 g/l (Fig. 4B). Specifically, Group 2 has a higher concentration of crenarchaeol (a higher number of cyclopentane rings) and lower concentration of GDGT-IV (no cyclopentane rings) than Group 1. Interestingly, all salinity indicators show a large increase at the same time, ca. 1400 yr BP (Fig. 4B–D). However, the onset of salt mineral precipitation occurred approximately 600 years before the major shift of iGDGTs composition (Fig. 4D–F).

3.5. C/N values and the BIT index

TOC contents of the core sediment subsamples range from 0.41–5.30% (Fig. 5) and TON from 0.07–0.88%. Except for the upper-

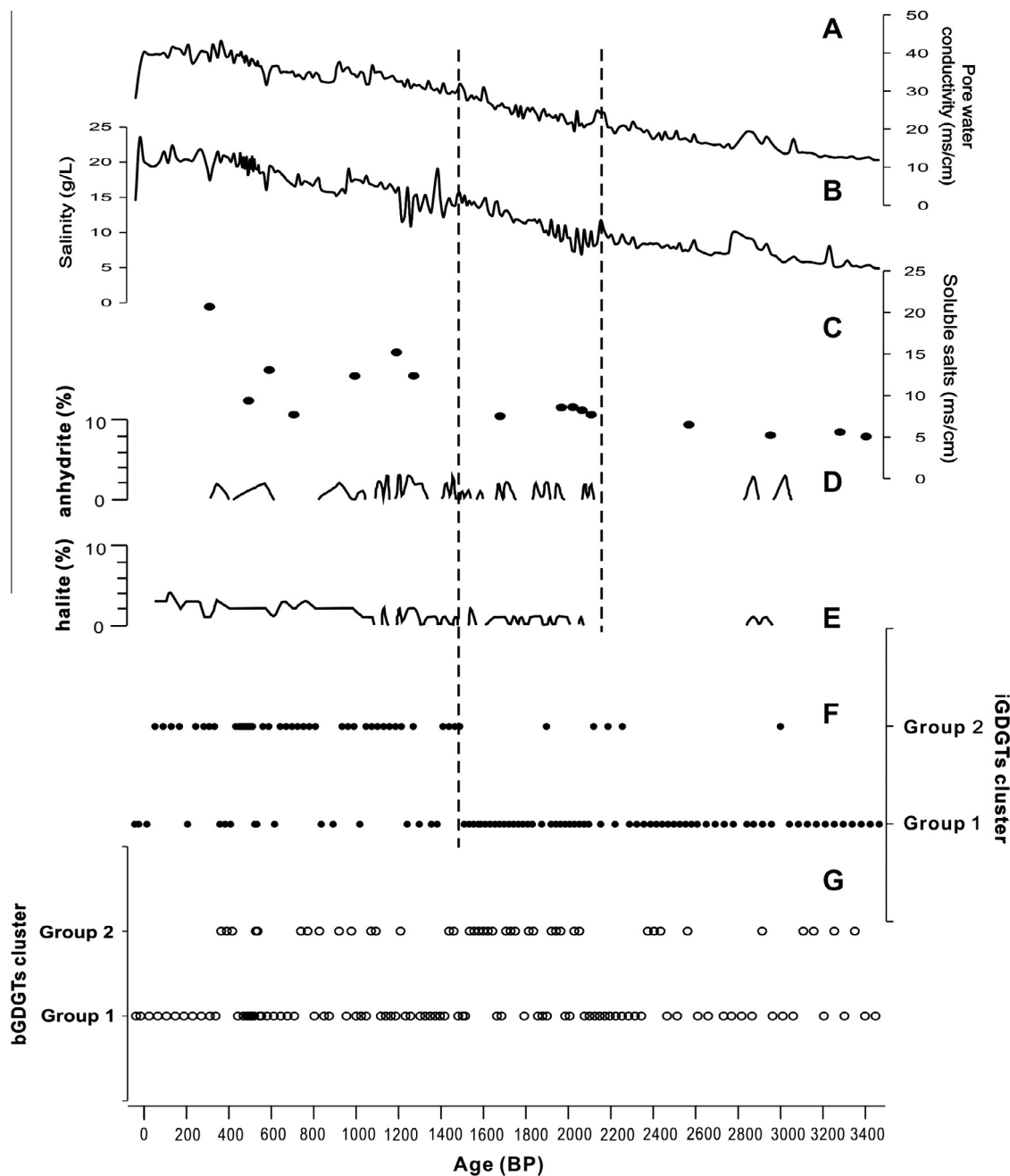


Fig. 4. Age profiles of pore water conductivity (A), salinity (B), sediment soluble salts (expressed in conductivity unit, C), relative abundances of two salt minerals halite (D) and anhydrite (E) from a previous study (Yao et al., 2011), and two groups of iGDGTs (F) and bGDGTs (G) identified by cluster analysis, respectively. The major shift in iGDGT composition was observed at 1400 yr BP, but the salt minerals emerged at 600 years earlier (2000 yr BP). The right vertical dash line denotes the onset of salt mineral precipitation. The left vertical dash line denotes a major shift in iGDGT composition. See text for discussion.

most five samples, the TOC and TON profiles are similar to those reported previously for an adjacent core of Kusai Lake (X. Liu et al., 2009). The high TOC and TON contents in the uppermost five sediment subsamples may be due to an accumulation effect of decayed organic matter from the overlying water column and were therefore excluded from further analysis. The calculated C/N values are generally low, varying from 3.69–7.92.

All the samples show a higher abundance of branched GDGTs than isoprenoid GDGTs and the resulting BIT values range between 0.72–0.89, averaging $0.81 \pm 0.04S_D$. Total bGDGTs concentrations show a positive correlation with TOC ($R = 0.549$, $p = 0.0001$) (Fig. 5), better than the correlation between iGDGTs and TOC ($R = 0.425$, $p = 0.0001$) (not shown).

3.6. Paleo-pH estimate using the CBT index

CBT values range between 0.35 and 0.86 with an average of $0.67 \pm 0.10S_D$, and MBT values range from 0.17–0.38 with an average of $0.25 \pm 0.04S_D$. The calculated pH values using Eq. (4) range from 7.5–9.2 with an average of $8.1 \pm 0.3S_D$ (Fig. 6). The calculated pH (9.2) for the youngest sediment is in agreement with the measured pH value (9.3) for the Kusai lake water. For the rest of the sediment core, no independent estimates of paleo-pH values were available, because pore water pH and sediment-pH represent modern-day values and are expected to be different from paleo-pH values. However, the CBT derived pH is negatively correlated with TOC ($R = -0.454$, $p = 0.0001$) (Fig. 6).

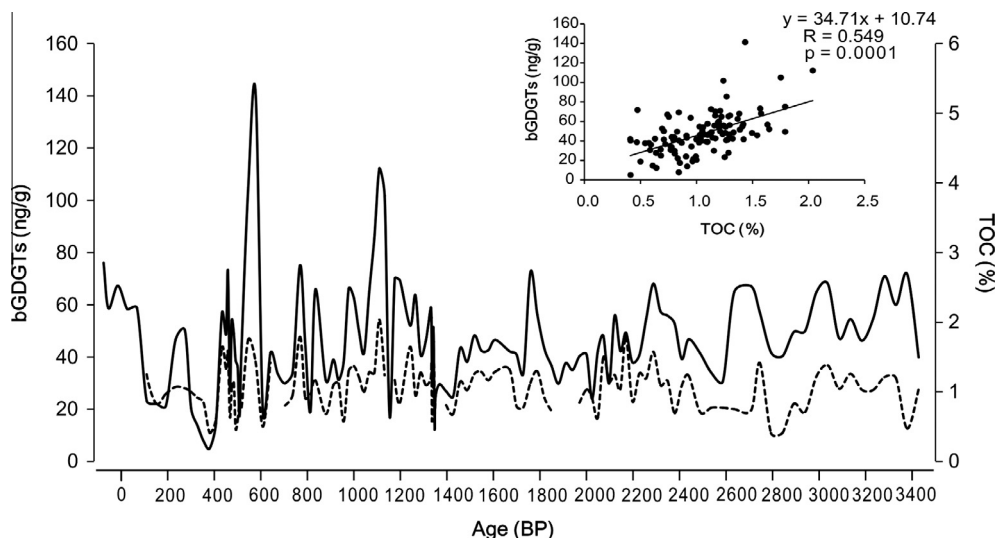


Fig. 5. Depth profiles of TOC content and bGDGT concentrations of the Kusai Lake sediment core. The inset is a scatter plot showing a positive correlation between total bGDGTs and TOC.

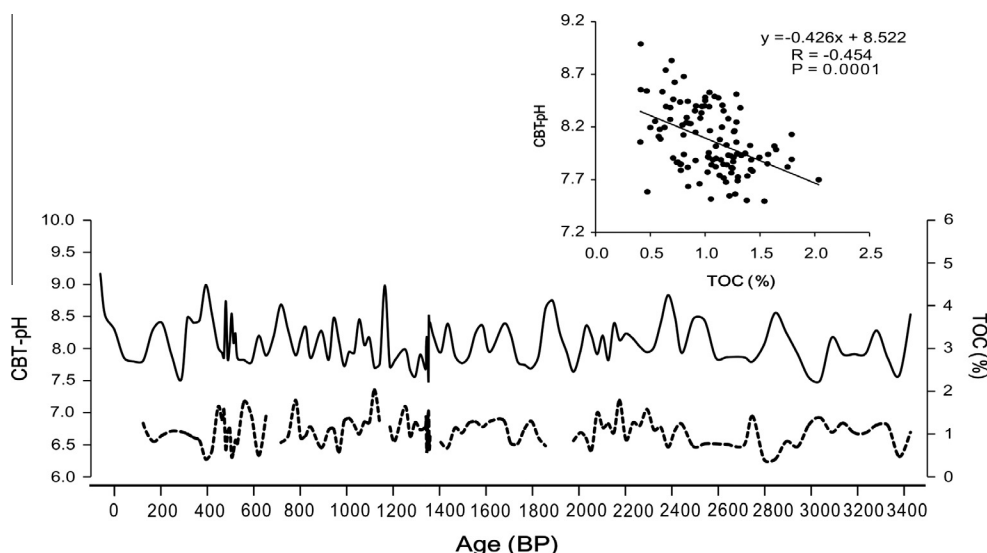


Fig. 6. A comparison between the CBT-pH and TOC profiles during the last 3490 years. The inset is a scatter plot showing a negative correlation between the CBT-derived pH and TOC.

Program Redfit35 (Schulz and Mudelsee, 2002) was applied to detect periodicities of this 3490 yr pH record. Power spectrum analysis reveals two significant periodicities centering at 160 and 107 yr at the 90% confidence level (Fig. 7A). Interestingly, TOC shows a similar periodicity (95 yr) at the 90% confidence level (Fig. 7B).

3.7. Paleo-temperature estimate using the MBT/CBT index

The MBT/CBT derived temperature values vary from 8.5–15.8 °C in the past 3490 yr (Fig. 8), and the temperature for the top sediment sub-sample of the core is estimated to be 14.7 °C, which is much higher than the measured mean annual air temperature in this region (−4.5 °C). The difference between the estimated and measured temperatures is beyond the standard error of the global lake calibration (± 5.24 °C) (Sun et al., 2011). Furthermore, the range of the MBT/CBT derived temperatures (7.3 °C) is much greater than those estimated based on other proxies (i.e., 2–4 °C) for the Qinghai-Tibetan Plateau (Yang et al., 2003; Liu et al., 2011).

4. Discussion

4.1. Relationship between the distribution of iGDGTs and paleo-salinity

The replacement of Group 1 iGDGT by Group 2 (higher concentrations of crenarchaeol and lower concentrations of GDGT-IV than Group 1) in response to increased salinity suggests that change in archaeal membrane composition may be an important mechanism for these organisms to adapt to a changing environment (Valentine, 2007). Liposomal and culture studies of archaea have shown that an increasing number of cyclopentane rings in the dibiphytanyl chains could make the membrane packing tighter and more rigid (Gabriel and Chong, 2000; Benvegnu et al., 2004; Chong et al., 2012). A tighter and more rigid membrane present in Group 2 could conceivably play a beneficial role in protecting cells from an external saline environment.

Our data show that there is a major switch in iGDGT composition after Kusai Lake starts precipitating anhydrite and halite (Fig. 4D–F). This switch is in line with the large increase in soluble

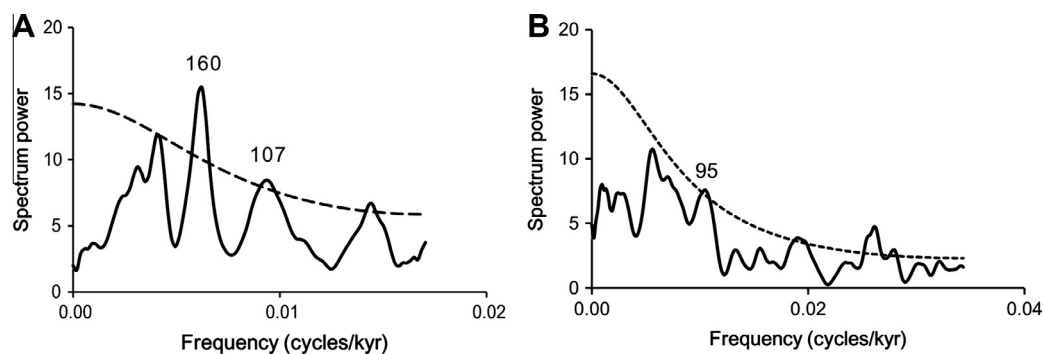


Fig. 7. Power spectrum analysis for the CBT-pH record (A) and TOC record (B) from the Kusai Lake sediment core over the last 3490 years. Numbers on top of the curves indicate the periodicities and the dashed lines show the 90% significance level.

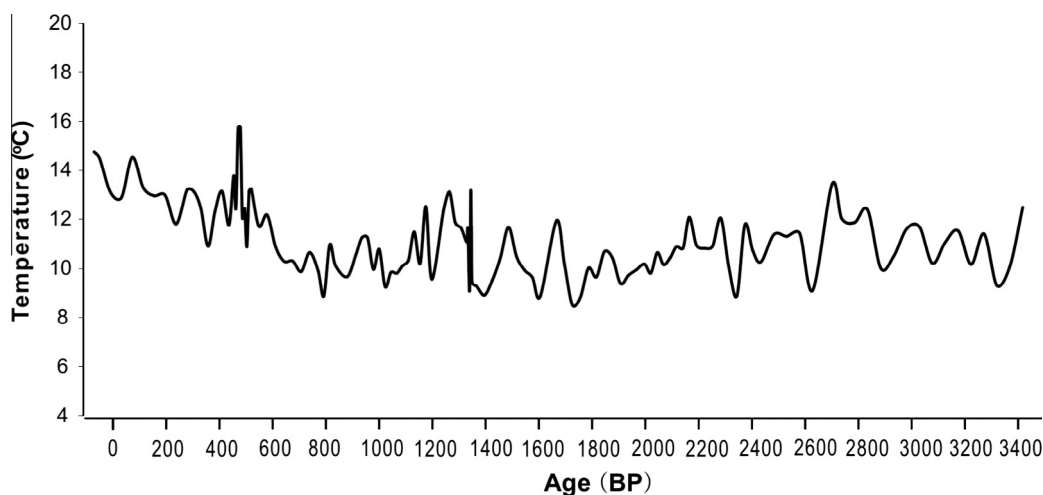


Fig. 8. The MAT/CBT derived MAAT for the past 3490 yr of Kusai Lake region.

salt concentration (Fig. 4C and F) but lags behind the onset of salt precipitation by 600 yr. This time lag suggests that change in archaeal community composition and salt mineral precipitation may require different threshold values of salinity. Although it is currently unknown what organisms are responsible for such a switch in iGDGT composition, it is likely that archaeal community composition underwent change as salinity increased at ca. 1400 BP. Indeed, changes in archaeal community composition in response to salinity increase have been observed previously and this archaeal community composition–salinity relationship forms the basis for the recently proposed ACE index (Turich and Freeman, 2011; Wang et al., 2013). These studies found that the abundance of archaeol (a compound common in halophilic archaea but also present in other archaea) relative to caldarchaeol (a compound not present in halophilic archaea) increases with increased salinity, which can be quantified by the ACE index that can potentially serve as a paleo-salinity indicator.

4.2. Origin of bGDGTs in Kusai Lake

C/N ratio and carbon isotopes are commonly combined to reflect the contribution of terrigenous organic matter to marine or lacustrine sedimentary record (Hedges et al., 1997; Schubert and Calvert, 2001). Terrigenous higher plants tend to have higher C/N ratios and more depleted ^{13}C values than aquatic algae and microorganisms (Hedges et al., 1997). In the Kusai Lake region, vegetation is dominated by desert Chenopodiaceae and *Artemisia* which belong to dicotyledons and should have C/N ratios of 15–20 (Ngai and Jefferies, 2004). All the calculated C/N ratios for the Kusai Lake

sediments are < 10, suggesting that lacustrine algae are the main sources of the organic matter in the lake (Krishnamurthy et al., 1986; X. Liu et al., 2009). The positive correlation between total bGDGT concentration and TOC (Fig. 4) suggests that most of the bGDGTs in the Kusai lake sediments also originated from autochthonous production within the lake. This conclusion appears to be inconsistent with the high BIT values (averaging at 0.81 ± 0.04) calculated for the Kusai lake sediments. However, high values of BIT do not necessarily suggest a terrigenous input. In fact, in the Qinghai lake region, BIT in soils is lower than that in near shore lacustrine sediments (Wang et al., 2012), so high BIT values may instead suggest a lacustrine source of organic matter which is then consistent with the low C/N ratios. In addition, BIT values in the high elevation/arid regions of China/Tibet are usually lower than most global soil values (Wang et al., 2012; Xie et al., 2012). High BIT values have been observed in many lacustrine systems (Blaga et al., 2009; Sinninghe Damsté et al., 2009; Tierney et al., 2010), apparently as a result of autochthonous production of branched GDGTs in the lake water column (Castañeda and Schouten, 2011 and references therein). Hence, we conclude that bGDGTs in Kusai Lake were produced within the lake and the BIT index is not a good indicator of terrigenous input.

4.3. Reconstruction of paleo-pH in Kusai Lake

The estimated pH values from the CBT index should represent lake water pH since the bGDGTs were mainly produced within the lake. Because of the lack of independent paleo-pH record through time, it is difficult to evaluate the validity of the CBT

derived pH index. However, two lines of evidence suggest that this CBT index is applicable to Kusai Lake and may be used to reconstruct the paleo-pH record of Kusai lake water.

First, the negative correlation between the CBT derived pH and TOC (Fig. 6) suggests that the CBT index is reliable index for paleo-pH reconstruction for Kusai, because such a systematic correlation would not be expected otherwise. This correlation can be interpreted in terms of common climatic and environmental factors which may have influenced both pH and TOC. TOC is a sensitive indicator of lake productivity in arid regions which is influenced by monsoon induced precipitation (X. Liu et al., 2009; An et al., 2011). Climatic changes on the Qinghai-Tibetan Plateau were largely controlled by Asian monsoon (Gasse et al., 1991; Shen et al., 2005). When the summer monsoon prevails, high precipitation and high nutrient level would lead to a high primary productivity in the lake. Concurrently, the lake water would lead to a pH decrease due to the dilution effect by neutral pH precipitation. Conversely, when the winter monsoon intensifies, low precipitation and low nutrient level would lead to a low primary productivity in the lake. Concurrently, the lake pH would lead to an increase of pH (to an alkaline value), likely due to increased evaporation relative to the amount of precipitation, which is accompanied by CO₂ degassing. Therefore, common climatic and environmental factors such as precipitation and nutrient input likely influenced both lake water pH and primary productivity but in opposite direction (Fig. 6). The small range of pH variations during the past 3490 yr of Kusai Lake ($8.1 \pm 0.3S_D$) suggests that there may be no extreme drought/flooding events in the region. Alternatively, algal photosynthesis (consuming CO₂) and respiration (producing CO₂) processes may have a buffering effect on the pH of Kusai lake water. However the interplay between these processes and monsoon driven precipitation is not well understood.

Second, the validity of CBT derived pH values and their correlation with TOC are further strengthened by the similar periodicities of both curves (Fig. 7). The periodic variations of paleo-pH and primary productivity in the Kusai Lake region during the past 3490 years are consistent with the Gleissberg cycle of solar activity (Gleissberg, 1971; Sonett et al., 1990; Yousef, 2006). Our observed periodicities fall within the range of the 80–120 year solar Gleissberg cycles (Yousef, 2006). The periodic oscillations of solar activity in the past 3490 years are probably the cause for the variations of precipitation (e.g., pH) and primary productivity in the Kusai Lake region and possibly elsewhere on the Qinghai-Tibetan Plateau. The mechanism that would cause this solar cyclicity to affect precipitation is probably due to changes in Asian summer monsoon intensity. When the solar irradiance is high, intensified Asian summer monsoon could result in high precipitation (X. Liu et al., 2009). This solar activity oscillation has been detected in the Qinghai-Tibetan Plateau and other areas in China. For example, Zhong et al. (2004) revealed a 97 yr cycle of mean grain size from a 4000 yr lake sediment record in the southern Tarim Basin. Xu et al. (2006) studied the oxygen isotopic composition of a 6000 yr peat cellulose record on the eastern Qinghai-Tibetan Plateau and observed multiple quai-100 yr periodicities. Liu et al. (2011) analyzed tree rings for the past 2485 years from the central eastern Tibetan Plateau, and obtained a 110 yr temperature cycle.

4.4. Late Holocene temperature record in the Kusai region

The overestimate of the MBT/CBT derived MAAT relative to the actual MAAT (14.7 °C vs. -4.5 °C) for the uppermost sediment subsample is consistent with previous reports in showing that GDGT-MAAT often overestimates actual annual temperatures (Peterse et al., 2009; Weijers et al., 2011a; Niemann et al., 2012; Wang et al., 2012). However, the estimated MAAT for the same sample (14.7 °C) is much closer to the maximal air temperatures measured

in summer (17 °C). These observations appear to suggest that bGDGT-producing bacteria would reflect seasonal rather than annual temperatures, which is consistent with the suggestion by Huguet et al. (2013). This seasonal bias may be particularly important for the arid/high elevation Qinghai-Tibetan Plateau region, where seasonal and even daily temperature fluctuations can be extreme (18 °C temperature range between winter and summer and 22 °C temperature range between winter day and night).

A potential seasonal bias of MBT/CBT derived temperature toward summer, rather than annual temperature, is supported by several recent soil studies (Rueda et al., 2009; Huguet et al., 2010; Weijers et al., 2011a). In particular, Weijers et al. (2011a) observed that the MAT/CBT derived MAAT in a peat bog (ca. 13 °C) was much higher than recorded annual air temperatures (5.5 °C), but close to porewater temperatures measured during the warmest months of the year (ca. 11 °C and 16 °C). However, the same group of authors (Weijers et al., 2011b) did not observe any seasonal trends in the concentrations and distributions of bGDGTs. To reconcile this inconsistency, Huguet et al. (2013) proposed a scenario where bGDGT-producing bacteria may be more active during warmer months. This scenario is supported by experimental data (Blume et al., 2002; Singh et al., 2010). Similarly, seasonal bias of MBT/CBT derived temperatures has also been reported for lakes (Pearson et al., 2011; Sun et al., 2011). Sun et al. (2011) presented two regressions (1) GDGT reconstructed air temperature in warm months vs. measured air temperature in warm months and (2) reconstructed mean annual air temperature vs. measured mean annual air temperature. Those authors found that the first regression showed a better correlation with a higher R^2 (0.62 vs. 0.52) and root mean square deviation (RMSE) (2.2 °C vs. 5.1 °C) than the second one. They ascribed this improvement of regression to more abundant and metabolically more active bGDGT-producing bacteria during the periods of the warmer season. Likewise, Pearson et al. (2011) used summer temperature data, rather than mean annual data, when they created a global calibration curve for lakes, based on an argument that mean annual temperature is not biologically relevant for those lakes that experience large seasonal fluctuations in temperature and long periods of ice cover. Tibetan lakes certainly belong to this category where there are large temperature fluctuations and long periods of ice covers.

However, it remains unclear how an enhanced activity of bGDGT-producing bacteria influences MBT and CBT, and estimated MAAT. Clearly, these observations call for a regional calibration for the Qinghai-Tibetan Plateau, preferably at higher temporal resolution than annual temperatures.

In addition to the magnitudes, the range of the MBT/CBT derived MAAT for the last 3490 yr of Kusai Lake (ca. 7 °C) (Fig. 8) is also greater than those (2–4 °C) estimated from other proxies for the Qinghai-Tibetan Plateau (i.e., based on tree rings, $\delta^{18}O$ and TOC) (Yang et al., 2003; Liu et al., 2011), but more comparable to temperature changes from the Last Glacial Maximum (LGM) to present (Hostetler and Clark, 2000; Tierney et al., 2008). The relatively low precision of the MBT/CBT calibration (RMSE = 5.24 °C) could possibly account for this large range of temperature fluctuations.

5. Conclusions

Our results show that the distribution of GDGTs in Kusai Lake sediments can be used to reconstruct palaeoclimate information once the origin of GDGTs is identified. Based on the low C/N values and positive correlation between bGDGT concentrations and TOC, we concluded that the bGDGTs in Kusai Lake were likely produced by heterotrophic bacteria within the lake. There is a large switch in iGDGT distribution in response to increased salinity of the lake and

this switch is likely a result of change in archaeal community composition. Meaningful lake water pH values can be extracted from the lake sediments, as evidenced by their negative correlation with TOC (a primary productivity indicator that is influenced by precipitation and pH). The reconstructed MAAT overestimates actual MAAT, but is much closer to measured summer maximal temperatures. These relationships suggest that GDGT derived MAAT is biased towards summer season, when bGDGT-producing bacteria may be more abundant and active than in colder seasons. A regional calibration should be established in order to more accurately reconstruct paleotemperatures of the Qinghai-Tibetan Plateau, which is characterized by drastic seasonal and daily temperature fluctuations.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.orggeochem.2013.06.002>.

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