Clim. Past, 10, 1843–1855, 2014
www.clim-past.net/10/1843/2014/
doi:10.5194/cp-10-1843-2014

Water pH and temperature in Lake Biwa from MBT′/CBT indices during the last 280 000 years

T. Ajioka[1], **M. Yamamoto**[1,2], **K. Takemura**[3], **A. Hayashida**[4], **and H. Kitagawa**[5]

[1]Graduate School of Environmental Science, Hokkaido University, Kita-10, Nishi-5, Kita-ku, Sapporo 060-0810, Japan
[2]Faculty of Environmental Earth Science, Hokkaido University, Kita-10, Nishi-5, Kita-ku, Sapporo 060-0810, Japan
[3]Institute for Geothermal Science, Kyoto University, Noguchihara, Beppu, Ohita 874-0903, Japan
[4]Department of Environmental Systems Science, Doshisha University, 1–3 Tatara-Miyakodani, Kyotanabe, Kyoto 612-0321, Japan
[5]Graduate School of Environmental Studies, Nagoya University, Nagoya 464-8601, Japan

Correspondence to: T. Ajioka (ajioka@ees.hokudai.ac.jp)

Received: 25 February 2014 – Published in Clim. Past Discuss.: 26 March 2014
Revised: 15 August 2014 – Accepted: 24 August 2014 – Published: 17 October 2014

Abstract. We generated a 280 000 yr record of water pH and temperature in Lake Biwa, central Japan, by analysing the methylation index (MBT′) and cyclisation ratio (CBT) of branched tetraethers in sediments from piston and borehole cores. Our aim was to understand the responses of precipitation and air temperature in central Japan to the East Asian monsoon variability on orbital timescales. Because the water pH in Lake Biwa is determined by phosphorus and alkali cation inputs, the record of water pH should indicate the changes in precipitation and temperature in central Japan. Comparison with a pollen assemblage in a Lake Biwa core suggests that lake water pH was determined by summer temperature in the low-eccentricity period before 55 ka, while it was determined by summer precipitation in the high-eccentricity period after 55 ka. From 130 to 55 ka, the variation in lake pH (summer precipitation) lagged behind that in summer temperature by several thousand years. This perspective is consistent with the conclusions of previous studies (Igarashi and Oba, 2006; Yamamoto, 2009), in that the temperature variation preceded the precipitation variation in central Japan.

1 Introduction

The East Asian monsoon governs the climate of East Asia (Wang et al., 2003), and East Asian monsoon variability on orbital timescales has been the topic of many studies, which have revealed that it has responded to precession; however, the timing of monsoon variability continues to be debated. Kutzbach (1981) hypothesised that the Asian monsoon responds to insolation changes at low latitudes, which are regulated by precession. According to this hypothesis, the summer monsoon is maximal when Northern Hemisphere summer insolation is maximal in the precession cycle. Indeed, oxygen isotope records from cave stalagmites in China have demonstrated that summer monsoon variability was pronounced at the precession cycle and maximal at the July–August precession (e.g. Wang et al., 2001, 2008; Yuan et al., 2004; Dykoski et al., 2005). However, some proxy records are not consistent with this hypothesis. Clemens and Prell (2003) reported that Indian summer monsoon variability showed both precession and obliquity cycles and was maximal at the November perihelion on the precession band. The pollen record in the north-western Pacific off central Japan shows that the East Asian monsoon has been strongest at the October–November perihelion in a precession cycle (Heusser and Morley, 1985; Igarashi and Oba, 2006). Thus, the conclusions have varied according to the proxy record used.

Lake sediments provide a good, widely available palaeoclimate archive. Proxies applicable to lake sediments include pollen and diatom fossils, δD of long-chain n-alkanes, lignin, biogenic opal, and pigments, among others. In Lake Biwa, sediment cores have been investigated using pollen fossils (Miyoshi et al., 1999; Nakagawa et al., 2008), lignin

Published by Copernicus Publications on behalf of the European Geosciences Union.

(Ishiwatari and Uzaki, 1987; Ishiwatari et al., 2009; Ohira et al., 2013), diatom frustules (Kuwae et al., 2004), biogenic opal (Xiao et al., 1997), pigments (Ishiwatari et al., 2009), and δD of long-chain n-alkanes (Seki et al., 2012). Although palaeoclimate information is available from these proxy records, more records generated by other new proxies are necessary to better understand the response of the East Asian monsoon to orbital forcing.

Glycerol dialkyl glycerol tetraethers (GDGTs) in natural environments include isoprenoid and branched GDGTs (Appendix; Nishihara and Koga, 1987; Sinninghe Damsté et al., 2000), which are produced by Archaea (De Rosa and Gambacota, 1988) and Bacteria (Sinninghe Damsté et al., 2000, 2011; Weijers et al., 2006), respectively. Branched GDGTs contain cyclopentane rings and/or additional methyl branches (Sinninghe Damsté et al., 2000; Weijers et al., 2006). Weijers et al. (2007b) reported that the relative abundance of branched GDGTs in soils reflects soil pH and mean annual air temperature (MAAT). Additionally, the cyclisation ratio of branched tetraethers (CBT) is correlated with soil pH, and the methylation index of branched tetraethers (MBT and MBT′) is correlated with both soil pH and MAAT (Weijers et al., 2007b; Peterse et al., 2012; Ajioka et al., 2014). This response to pH and temperature is speculated to be an adaptation of the lipid membrane for sustaining its fluidity and permeability (Weijers et al., 2007b). Based on these empirical relationships, the MBT/CBT palaeotemperature index was proposed (Weijers et al., 2007b). This index has been applied successfully in marine sediments from the Congo River fan (Weijers et al., 2007a).

The MBT/CBT index has been also applied to lake sediments for palaeotemperature reconstruction (e.g. Niemann et al., 2012), but most applications in lake sediments were unsuccessful (e.g. Tierney and Russel, 2009; Tyler et al., 2010; Zink et al., 2010; Wang et al., 2012). Tierney and Russel (2009) argued that the unrealistic estimated MAATs are attributable to in situ production of branched GDGTs in lake water. Tierney et al. (2010) noted that the correlation between MBT/CBT from sediments and MAAT for 46 lakes in East Africa differed from that of the global soil set and proposed a calibration applicable in lake environments. Ajioka et al. (2014) investigated the distribution of GDGTs in soils and river and lake sediments in the Lake Biwa drainage basin and showed that the distribution of branched GDGTs in the lake sediments was different from that in the catchment soils, suggesting in situ production of branched GDGTs in the lake. They also found, in contrast to the conclusion of Tierney et al. (2010), that the relationships among soil pH, MAAT, and MBT′/CBT in soils are not different from those of lake water pH, temperature, and MBT′/CBT in lake sediments, implying that the soil calibration is applicable without modification to the study of lake sediments to obtain lake water temperature and pH.

In this study, we investigated branched GDGTs in sediments from borehole BIW08-B and piston core BIW07-6 in

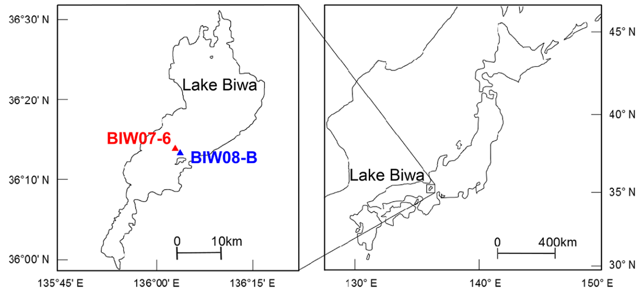

Figure 1. Map showing the study sites.

Lake Biwa, central Japan, to reconstruct lake water pH and temperature during the last 280 000 yr. We then evaluated the variability of the East Asian summer and winter monsoons based on estimated summer precipitation and winter lake water temperature.

2 Materials and methods

2.1 Environmental setting of Lake Biwa

Lake Biwa in central Japan is at an elevation of 84 m and is surrounded by mountains ca. 1000 m high. With an area of 674 km^2 and a watershed area of 3850 km^2, Lake Biwa is the largest lake in Japan (Fig. 1). More than 118 rivers flow into the lake, and the Seta River discharges from it. The climate of the area is affected by the East Asian monsoon (Yoshino, 1965): summer monsoon brings warm and humid conditions and winter monsoon brings snowfall to the northern part of the area and dryness to the southern part.

The MAAT is 14.7 °C at Hikone Meteorological Observatory (elevation of 87 m; from 1981 to 2010; Japan Meteorological Agency, available at http://www.jma.go.jp/jma/index.html). Water temperature and pH data were obtained from the Lake Biwa Environmental Research Institute (http://www.pref.shiga.lg.jp/biwako/koai/hakusyo/index.html).

2.2 Samples

Piston core BIW07-6 (18.42 m long) was taken from the central part of Lake Biwa (35°13′59.02″ N, 136°02′51.89″ E; water depth of 55 m) in 2007 (Fig. 1; Takemura et al., 2010). The sediments in the core consisted of homogenous dark-grey silty clay (Fig. 2). The age–depth model for core BIW07-6 was generated from 6 well-dated, widespread ash layers and 13 accelerator mass spectrometry (AMS) ^{14}C ages of plant wood fossils (partly reported in Kitagawa et al., 2010) analysed at 3 AMS facilities during the past decade: the Center for Chronological Research at Nagoya University (Laboratory code NUTA2; Nakamura et al., 2000, 2004), the W. M. Keck Carbon Cycle Accelerator Mass Spectrometry Laboratory (UCIAMS; Southon et al., 2004a, b), and the Korean Institute of Geoscience and Mineral

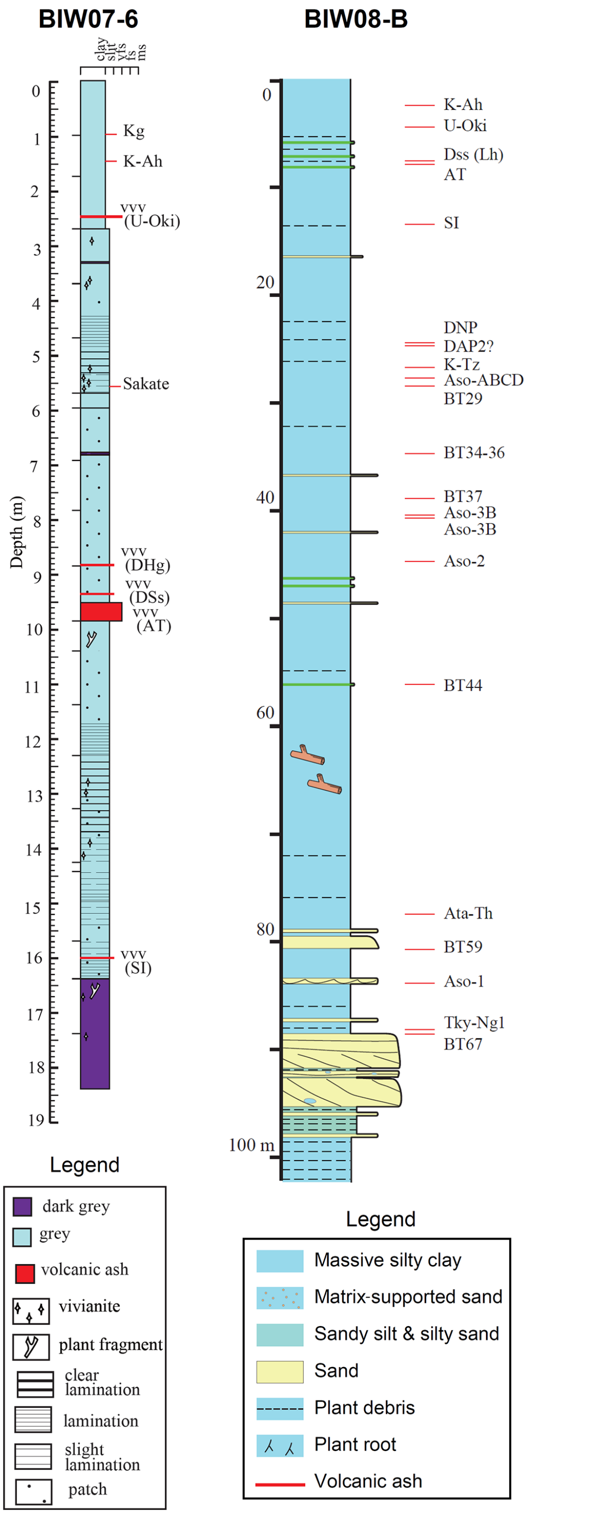

Figure 2. Lithologic columns of **(a)** core BIW07-6 and **(b)** borehole core BIW08-B (Takemura et al., 2010).

Table 1. Age controls of core BIW07-6.

Depth (m)	Source	^{14}C (BP, 1 SD)	Model age (cal BP, 2 SD)	Remarks
0.980	Kg		3150 ± 12	[1]
1.115	SOh	3650 ± 30	4086–3887	[2]
1.450	K-Ah		7350 ± 80	[3]
2.501	U-Oki		10 286 ± 45	[4]
3.510	^{14}C (wood)	11 855 ± 40	13 844–13 486	[5]
3.700	^{14}C (wood)	12 400 ± 45	14 940–14 110	[6]
4.010	^{14}C (wood)	12 865 ± 45	15 880–15 000	[5]
5.380	^{14}C (wood)	14 510 ± 80	17 940–17 235	[5]
5.630	Sakate		19 484 ± 112	[4]
6.130	^{14}C (wood)	18 050 ± 90	22 005–21 555	[5]
6.620	^{14}C (wood)	19 010 ± 100	23 275–22 310	[5]
7.160	^{14}C (wood)	20 440 ± 110	24 815–23 955	[5]
8.530	^{14}C (wood)	23 760 ± 170	29 160–28 033	[5]
9.870	AT		30 009 ± 189	[4]
11.560	^{14}C (wood)	27 950 ± 280	32 965–31 470	[6]
12.030	^{14}C (wood)	28 760 ± 320	34 495–32 265	[6]
15.360	^{14}C (wood)	36 530 ± 820	42 970–40 090	[5]
17.660	^{14}C (wood)	41 200 ± 1500	48 642–42 855	[6]
18.340	^{14}C (wood)	42 570 ± 1270	49 190–44 295	[6]

[1] Tani et al. (2013); [2] Fukuoka and Matsui (2002); [3] Kitagawa and van der Plicht (1998); [4] Staff et al. (2012); [5] Kitagawa et al. (2010); [6] Kitagawa (personal communication, 2014).

Resources (KIGAM; Hong et al., 2010) (Table 1). The ^{14}C ages were converted to calendar ages using the IntCal13 data set (Reimer et al., 2013). The average sedimentation rate was found to be 0.4 m ky^{-1} (Fig. 3). The sediment was stored at 4 °C for 0.5 yr. Then, 137 samples (1 cm thick) were collected from 0.30 m (0.6 ka) to 18.29 m (46 ka) and immediately freeze-dried. The average sampling interval was ∼ 0.3 ky.

Borehole core BIW08-B (100.3 m long) was collected from its site (35°13′41.15″ N, 136°03′21.19″ E; water depth of 53 m) in 2008 (Fig. 1). The sediments consisted of dark-grey massive silty clay from 0 to 89 m, sandy silt containing abundant sand and plant debris from 89 to 99 m, and dark-grey massive silty clay from 99 to 100.3 m (Fig. 2; Takemura et al., 2010). The age–depth model for core BIW08-B was generated from 17 dated widespread ash layers, 2 AMS ^{14}C age of plant wood fossils analysed at KIGAM (Hong et al., 2010), and 9 dated anhysteretic remanent magnetisation (ARM) events (Table 2). The ^{14}C ages were converted to calendar ages using the IntCal13 data set (Reimer et al., 2013). Ages of the ARM events were determined through the age model of core BIW07-6, based on the correlation of the ARM variations observed in Lake Biwa sediments (Hayashida et al., 2007). The average sedimentation rate was found to be 0.3 m ky^{-1} (Fig. 3). The sediment was stored at 4 °C for 0.5 yr. Then, 152 samples (2.5 cm thick) were collected from 13 m (43 ka) to 88 m (280 ka), and the samples were immediately freeze-dried. The average sampling interval was ∼ 1.9 ky.

Table 2. Age controls of core BIW08-B.

Depth (m)	Source	^{14}C (BP, 1 SD)	Model age (cal BP, 2 SD)	Remarks
0.00	Core top		-57 ± 0	[1]
1.12	^{14}C (wood)	1920 ± 60	1868 ± 160	[1]
2.09	SOh	3650 ± 30	4086–3887	[2]
2.18	^{14}C (wood)	4720 ± 110	5408 ± 324	[1]
2.45	K-Ah		7350 ± 80	[3]
3.28	U-Oki		$10\,286 \pm 45$	[4]
4.34	ARM-1 event		$13\,837 \pm 103$	[5][6]
4.97	ARM-2 event		$16\,586 \pm 155$	[5][6]
5.63	Sakate		$19\,484 \pm 112$	[4]
6.04	ARM-3 event		$23\,181 \pm 277$	[5][6]
7.61	DSs (Plinian)		$29\,247 \pm 270$	[1]
7.85	AT		$30\,009 \pm 189$	[4]
8.82	ARM-4 event		$31\,078 \pm 442$	[5][6]
9.84	ARM-6 event		$32\,720 \pm 803$	[5][6]
10.58	ARM-7 event		$34\,529 \pm 770$	[5][6]
12.58	ARM-8 event		$40\,594 \pm 1425$	[5][6]
13.32	SI		$42\,080 \pm 1250$	[1]
13.69	ARM-9 event		$42\,619 \pm 1329$	[5][6]
14.83	ARM-10 event		$44\,154 \pm 2028$	[5][6]
23.58	DNP		$82\,922 \pm 10\,758$	[6]
23.66	DMP2		$83\,039 \pm 10\,788$	[6]
26.81	KTZ		$96\,715 \pm 7080$	[6]
27.73	AsoABCD		$104\,263 \pm 5352$	[6]
28.41	Unnamed tephra		$108\,098 \pm 5505$	[6]
34.81	Unnamed tephra		$114\,925 \pm 5544$	[6]
38.99	Unnamed tephra		$120\,837 \pm 7675$	[6]
40.59	Aso-3b		$123\,619 \pm 9005$	[7]
44.67	Aso2		$142\,975 \pm 9059$	[7]
83.91	Aso1		$266\,000 \pm 28\,000$	[7]

[1] Kitagawa (personal communication, 2014); [2] Fukuoka and Matsui (2002); [3] Kitagawa and van der Plicht (1998); [4] Staff et al. (2012); [5] Hayashida et al. (2007); [6] Takemura (personal communication, 2014); [7] Matsumoto et al. (1991).

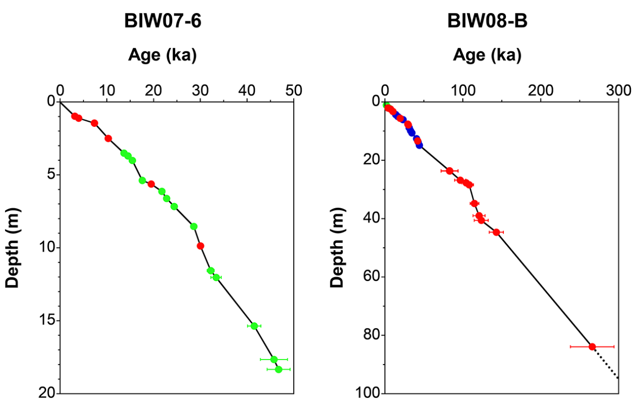

Figure 3. Age–depth models of cores BIW07-6 and BIW08-B. The red, green, and blue dots indicate volcanic ashes, ^{14}C of plant debris and total organic carbon, and ARM events, respectively (see Tables 1 and 2). Error bars indicate the 95 % confidence intervals (2σ).

2.3 Analytical method

Lipids were extracted (3 times) from a freeze-dried sample using a DIONEX Accelerated Solvent Extractor 200 at 100 °C and 1000 psi for 10 min with 11 mL CH_2Cl_2 / CH_3OH (6 : 4 v / v) and is concentrated. The extract was separated into four fractions using column chromatography (SiO_2 with 5 % distilled water; 5.5 mm × 45 mm): F1 (hydrocarbons) with 3 mL hexane; F2 (aromatic hydrocarbons) with 3 mL hexane / toluene (3 : 1 v / v); F3 (ketones) with 4 mL toluene; F4 (polar compounds) with 3 mL toluene / CH_3OH (3 : 1 v / v). An aliquot of F4 was dissolved in hexane / propan-2-ol (99 : 1 v / v) and filtered. The GDGTs were analysed using high performance liquid chromatography mass spectrometry (HPLC-MS) with a Shimadzu SIL-20AD system connected to a Bruker Daltonics micrOTOF-HS time-of-flight mass spectrometer. A Prevail Cyano column (2.1 × 150 mm, 3 µm; Alltech) at 30 °C was used, following the methods set out by Hopmans et al. (2000) and Schouten et al. (2007). The conditions were: flow rate of 0.2 mL min^{-1}, isocratic with 99 % hexane and 1 % propan-2-ol (5 min) followed by a linear gradient to 1.8 % propan-2-ol over 45 min. Detection was achieved using atmospheric pressure chemical ionisation (APCI) MS in positive-ion mode. The spectrometer was run in full-scan mode (m/z 500–1500). Compounds were assigned from a comparison of mass spectra and retention times with GDGT standards (from the main phospholipids of *Thermoplasma acidophilum* via acid hydrolysis) and values from a previous study (Hopmans et al., 2000). Quantification was achieved by integrating the summed peak areas in the $(M+H)^+$ and $(M+H+1)^+$ chromatograms and comparing them with the peak area from an internal standard C_{46} glycerol trialkyl glycerol tetraether (GTGT; Patwardhan and Thompson, 1999) in the $(M+H)^+$ ion chromatogram, according to the method set out by Huguet et al. (2006). The correction value for the ionisation efficiency between GDGTs and the internal standard was obtained by comparing the peak areas from *T. acidophilum* derived mixed GDGTs with that from C_{46} GTGT. The standard deviation of a replicate analysis was 3.0 % of the concentration for each compound. The branched and isoprenoid tetraether (BIT) index was calculated following Hopmans et al. (2004):

$$\begin{aligned}\mathrm{BIT} = {} & ([\mathrm{GDGT\ I}] + [\mathrm{GDGT\ II}] + [\mathrm{GDGT\ III}])/([\mathrm{GDGT\ I}] \\ & + [\mathrm{GDGT\ II}] + [\mathrm{GDGT\ III}] \\ & + [\mathrm{crenarchaeol}]).\end{aligned}$$

The methane index (MI) was calculated following Zhang et al. (2011):

$$\begin{aligned}\mathrm{MI} = {} & ([\mathrm{GDGT\text{-}1}] + [\mathrm{GDGT\text{-}2}] + [\mathrm{GDGT\text{-}3}])/([\mathrm{GDGT\text{-}1}] \\ & + [\mathrm{GDGT\text{-}2}] + [\mathrm{GDGT\text{-}3}] \\ & + [\mathrm{crenarchaeol}] + [\mathrm{crenarchaeol\ regioisomer}]).\end{aligned}$$

CBT and MBT′ were calculated following Weijers et al. (2007b) and Peterse et al. (2012):

$$\mathrm{CBT} = -\log([\mathrm{GDGT\ Ib}] + [\mathrm{GDGT\ IIb}])/([\mathrm{GDGT\ I}] + [\mathrm{GDGT\ II}]),$$

$$\mathrm{MBT}' = ([\mathrm{GDGT\ I}] + [\mathrm{GDGT\ Ib}] + [\mathrm{GDGT\ Ic}])/([\mathrm{GDGT\ I}] + [\mathrm{GDGT\ Ib}] + [\mathrm{GDGT\ Ic}] + [\mathrm{GDGT\ II}] + [\mathrm{GDGT\ IIb}] + [\mathrm{GDGT\ IIc}] + [\mathrm{GDGT\ III}]).$$

The pH and MAAT were calculated according to the following equations based on the data set of Lake Biwa watershed soils (Ajioka et al., 2014):

$$\mathrm{pH} = 7.90 - 2.08 \times \mathrm{CBT},$$

$$\mathrm{MAAT} = 1.28 - 5.77 \times \mathrm{CBT} + 26.4 \times \mathrm{MBT}'.$$

The standard deviations of CBT and MBT′ of replicated analyses averaged 0.034 and 0.015, respectively, in this study. The average root mean square errors for the calibration of pH and MAAT are 0.5 and 3.5 °C, respectively.

2.4 Previous results of GDGTs in lake surface and river sediments and soils in the Lake Biwa drainage basin

Ajioka et al. (2014) investigated the distributions of GDGTs in lake surface and river sediments and soils in the Lake Biwa drainage basin. MBT′ and CBT values are lower in lake surface sediments than in the soils from the catchment areas (Fig. 4). Among lake surface sediments, coarse-grained sediments have higher values (Fig. 4). River sediments have intermediate values between lake surfaces sediments and soils (Fig. 4). Based on this result, Ajioka et al. (2014) suggested that branched GDGTs in lake surface sediments are mostly produced in lake water, but there are some contributions of soil GDGTs in coarse-grained sediments in the lake. The relationships between CBT and soil pH and between MBT′/CBT and mean annual temperature in soil samples in the Lake Biwa drainage basin are not different from those in the global soil set (Peterse et al., 2012). If global and Lake Biwa soil calibrations are applied, the estimated pH values by CBT fit the winter pH values of lake water, but the application of lake calibration (Tierney et al., 2010) was not successful (Fig. 5). If global and Lake Biwa soil calibrations are applied, the temperatures estimated by MBT′/CBT fit the winter temperatures of lake water. Ajioka et al. (2014) thus suggested that the branched GDGTs in Lake Biwa sediments are produced in winter, CBT and MBT′ reflect winter pH and temperature of lake water, and soil calibration is applicable to Lake Biwa sediments.

3 Results

The concentrations of isoprenoid and branched GDGTs varied between 0.01 and 2.55 and between 0.05 and 12.58 $\mu g\, g^{-1}$, respectively (Fig. 6). CBT-based pH ranged

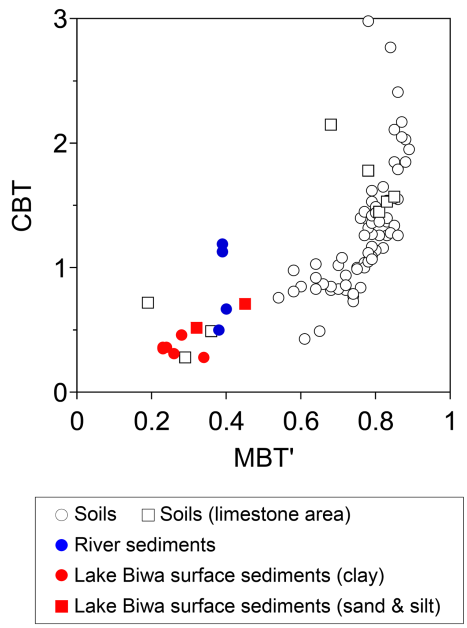

Figure 4. Plot of CBT against MBT′ for soils, river sediments, and Lake Biwa surface sediments (Ajioka et al., 2014).

from 6.0 to 7.6 (Fig. 6). The measured pH value in the surface water of Lake Biwa has an annual average of 8.1 and is lowest (∼ 7.6) in winter and highest (∼ 8.8) in summer, whereas the pH of the bottom water at a depth of 59 m ranges from 7.2 to 7.7 with an average value of ∼ 7.5 (off Minami-Hira: 35°11′39″ N, 135°59′39″ E; data from the Lake Biwa Environmental Research Institute, http://www.pref.shiga.lg.jp/biwako/koai/hakusyo/index.html). On the other hand, the measured pH of surface soils in the drainage basin ranged from 3.3 to 8.0 with an average of 5.0 (Ajioka et al., 2014), which is lower than that in lake water. The CBT-based pH values of the core sediments are lower than those in the present lake water. CBT-based pH was maximal at 279, 249, 210, 160, 133, 117, 78, 45, 25, and 6 ka and minimal at 264, 220, 178, 149, 123, 95, 52, 29, and 17 ka. MBT′/CBT-based temperature ranged from 4 to 11 °C and was lower during glacials and higher during interglacials (Fig. 6). The modern measured temperature of surface water in Lake Biwa has an annual average of 16.9 °C and is lowest (∼ 7.6 °C) in winter and highest (∼ 27.9 °C) in summer, whereas the temperature of bottom water at a depth of 59 m ranges from 7.2 to 8.2 °C with an annual average of ∼ 7.7 °C (off Minami-Hira; data from the Lake Biwa Environmental Research Institute, http://www.pref.shiga.lg.jp/biwako/koai/hakusyo/index.html).

The BIT index ranged from 0.83 to 0.99 (Fig. 6). BIT values exceeded 0.95 in most intervals, but BIT values lower than 0.9 were found at 240, 210, 114, 30, 29, and 0–6 ka (Fig. 6).

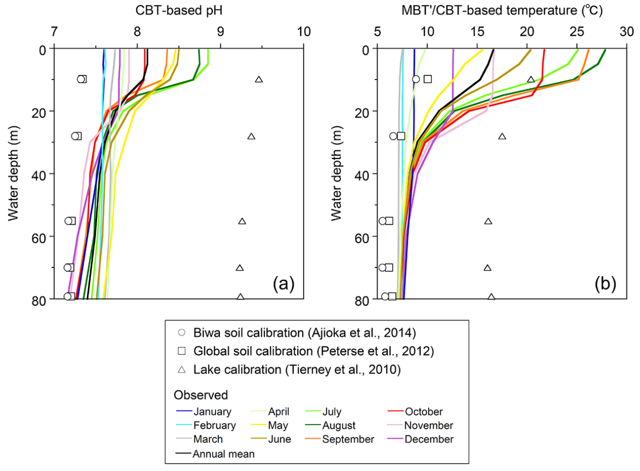

Figure 5. Reconstructed water pH **(a)** and MBT′/CBT-based temperature **(b)** for Lake Biwa surface clays (Ajioka et al., 2014).

The MI value ranged from 0.1 to 0.9 (Fig. 6). The MI value was maximal at 253, 226, 192, 133, 95, 52, and 15 ka and minimal at 237, 208, 174, 115, 76, and 20 ka (Fig. 6). The average interval between these peaks was 40 ky. Because of the high MI values (Zhang et al., 2011), we judge that TEX_{86} (tetraether index of tetraethers with 86 carbon atoms) is not reliable in Lake Biwa sediments.

4 Discussion

4.1 Factors controlling water pH in Lake Biwa

Lake water pH depends on the geology of the drainage basin, evaporation, the photosynthesis of phytoplankton and submerged plants, the respiration of organisms, and the decomposition of organic matter by microbes (Wetzel, 2001). In volcanic regions, lake water receives strong mineral acids, particularly sulfuric acid, which decreases pH to less than 4 (Wetzel, 2001). There is, however, no active volcano in the Lake Biwa watershed. Thus, this factor is not important for the pH of Lake Biwa water. In contrast, Ca^{2+} supplied from limestone increases lake water pH (Wetzel, 2001). In the Lake Biwa drainage basin, limestone is exposed only in the Mt. Ibuki area, and its contribution toward controlling lake water pH should be minor. However, if chemical weathering is enhanced, this may increase the flux of Ca^{2+} from the silicate rocks in the drainage basin. This is one of the potential factors affecting lake water pH in Lake Biwa. Evaporation of lake water increases water pH (Wetzel, 2001), but pollen records in Lake Biwa cores suggest moist environments throughout the last 430 ky (Miyoshi et al., 1999), so evaporation has not been a factor controlling lake water pH. Consumption of CO_2 by the photosynthesis of phytoplankton and submerged plants increases lake water pH (e.g. Talling, 1976). On the other hand, regeneration of CO_2 by the respiration of organisms and degradation of organic matter by microbes decreases lake water pH (Wetzel, 2001). Because of the balance of the CO_2 budget, the lake's surface water pH values range from 7.6 in winter to 8.8 in summer (data from the Lake Biwa Environmental Research Institute, http://www.pref.shiga.lg.jp/biwako/koai/hakusyo/index.html). A tripling of the concentration of chlorophyll from winter to spring in Lake Biwa increases lake water pH by 0.85 (data from the Lake Biwa Environmental Research Institute, http://www.pref.shiga.lg.jp/biwako/koai/hakusyo/index.html). These observations suggest that photosynthesis in the lake water is the second potential factor controlling water pH in Lake Biwa.

In Lake Biwa, photosynthesis is controlled mainly by the phosphorus concentration in the water (Ishida et al., 1982; Tezuka, 1985). The anthropogenic eutrophication of Lake Biwa induced high primary production, resulting in an increase in the pH of the lake water by more than 1 from the 1960s to the 1970s (Nakayama, 1981). The phosphorus concentration in the lake is determined by the inflow of phosphorus from the catchment soils, which is governed by precipitation in the watershed (Kunimatsu, 1993). At present, the East Asian summer monsoon brings most of the annual precipitation to the study area, exceptionally at high elevations in the northern part where snowfall brought by the East Asian winter monsoon is relatively important (http://www.jma.go.jp/jma/index.html). Therefore, summer precipitation in the watershed is a factor that controls photosynthesis and, consequently, the pH of the lake water. The phosphorus concentration may also be governed by air temperature because the dissolution of silicate depends on temperature in chemical weathering processes (White and Blum, 1995). Thus, both higher precipitation and higher temperature potentially increase the inflow of phosphorus to the lake, enhancing primary production, and thus raise the lake water pH. Increases in precipitation and temperature intensify chemical weathering. The chemical weathering increases the inflow of Ca^{2+} and phosphorus to the lake, with both raising lake water pH.

It is not clear whether branched GDGTs are produced in the water column or the sediment surface in Lake Biwa (Ajioka et al., 2014). If branched GDGTs are produced in the water column, the main production depth of branched GDGTs is unclear. Recently, Buckles et al. (2014) found a high abundance of intact branched GDGTs in the suspended particulates in the oxygen-deficient bottom water in Lake Challa. They suggested that the oxygen-deficient environment ($O_2 < 2\,mg\,L^{-1}$) provides favourable conditions for branched-GDGT production. In Lake Biwa, such conditions ($O_2 < 2\,mg\,L^{-1}$) exist in the bottom water above the sediment surface from autumn to early winter (http://www.pref.shiga.lg.jp/biwako/koai/hakusyo/index.html). It is thus likely that the branched GDGTs were produced mainly in the bottom water in Lake Biwa. However, this is merely speculation by analogy with the case of Lake Challa. This speculation

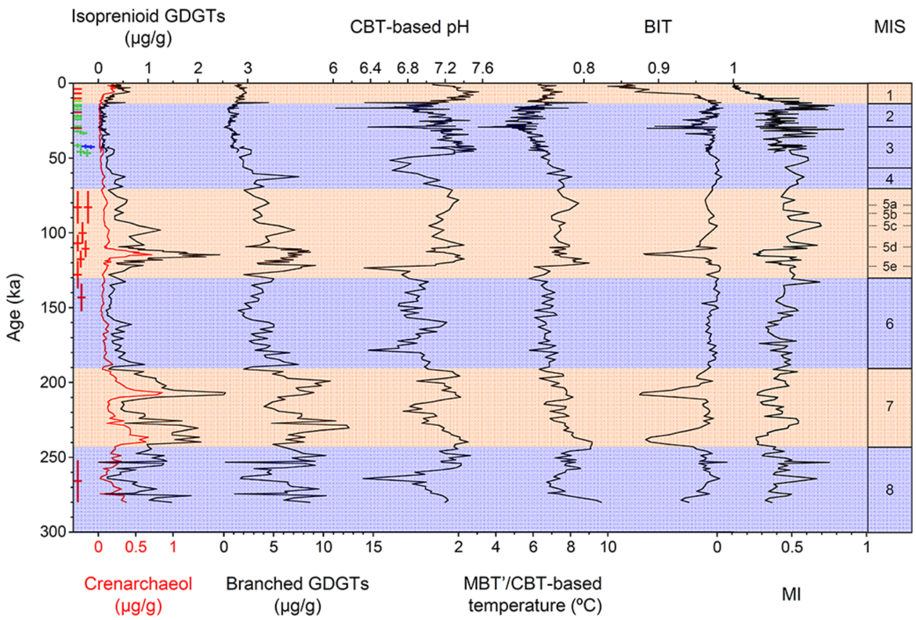

Figure 6. Variations in the concentrations of total isoprenoid and branched GDGTs and crenarchaeol, CBT-based pH, MBT′/CBT-based temperature and BIT and MI in cores BIW07-6 and BIW08-B during the last 280,000 years. Red, blue, and green bars indicate age controls with 95% confidence intervals of volcanic ashes, the ^{14}C of plant debris and total organic carbon, and ARM events, respectively.

should be tested using the original data of suspended and sinking particles in Lake Biwa.

4.2 Changes in lake water pH during the last 280 ky

The CBT-based pH during the last 280 ky showed a glacial–interglacial pattern with higher pH in interglacial periods (Fig. 6). The variation pattern in CBT-based pH was consistent with that of *Cryptomeria* pollen abundance and lagged behind that of the pollen temperature index, T_p ($= 100 \times T_w/[T_c+T_w]$, where T_w is the sum of temperate taxa and T_c is the sum of subalpine taxa), in cores BIW95-4 and Takashima-oki (BT) in Lake Biwa from 130 to 55 ka (Fig. 7; Hayashi et al., 2010a, b). Igarashi and Oba (2006) assumed that the abundance of *Cryptomeria* pollen could be used as a proxy for summer precipitation because the natural distribution of *Cryptomeria* corresponds to an area where precipitation is greater than 2000 mm per year. The correspondence between CBT-based pH and *Cryptomeria* pollen abundance indicates that both proxy records are robust records of precipitation.

The T_p is used as a proxy of summer air temperature (Igarashi and Oba, 2006). Igarashi and Oba (2006) reported that variation in the T_p value preceded the abundance of *Cryptomeria* pollen in core MD01-2421 off central Japan in the western North Pacific, indicating that the variation in summer air temperature preceded that in summer precipitation by several thousand years. Yamamoto (2009) argued that this time lag was caused by the latitudinal shift of the Baiu Front (an early summer rain front). Our new record indicates that CBT-based pH lagged behind the T_p record, implying that summer precipitation lagged behind summer air temperature, as suggested by pollen studies (Igarashi and Oba, 2006; Hayashi et al., 2010a, b).

However, the variation pattern in CBT-based pH was not consistent with that of *Cryptomeria* pollen abundance but with the T_p value in core BIW95-4/BT from 55 ka to the present (Fig. 7; Hayashi et al., 2010a, b). This correspondence suggests that the lake water pH was determined by summer temperature rather than summer precipitation in this period. Nakagawa et al. (2008) suggested that the response of the East Asian monsoon to summer insolation was different between low- and high-eccentricity periods, and that the response was not clear in the low-eccentricity (< 0.024) periods. The eccentricity was lower in the period from 55 ka to the present than the period from 130 to 55 ka. We speculate that higher-amplitude variations in summer insolation in the latter period induced higher-amplitude precipitation variations, which resulted in conditions in which precipitation controlled lake water pH. In contrast, lower-amplitude variations in the former period induced lower-amplitude precipitation variations. Alternatively, the other climatic forcing such as greenhouse gas forcing was relatively important, and temperature variation was a major factor controlling the variation in lake water pH.

The age uncertainty (2σ values (95 % confidence level)) of core BIW08-B ranges from 5 to 11 ky in MIS (marine isotope stage) 5 and 6 because of the large error of radiogenic ages of tephras (Table 2). However, the pollen composition (Tp and *Cryptomeria* abundance) in cores BIW95-4/BT nearby the

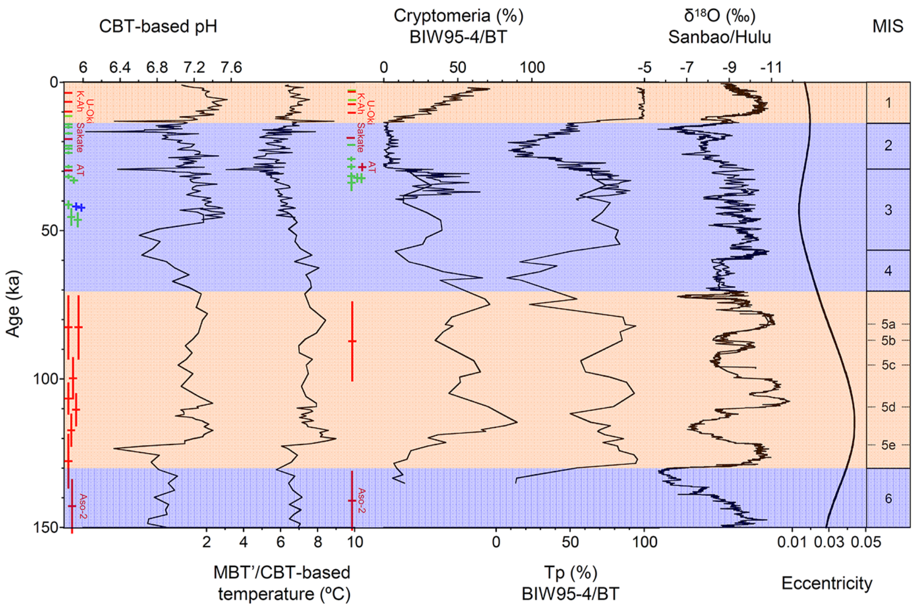

Figure 7. Variations in CBT-based pH and MBT′/CBT-based temperature from cores BIW07-6 and BIW08-B (this study); Tp and *Cryptomeria* (%) from cores BIW95-4 and BT in Lake Biwa (Hayashi et al., 2010a, b); the δ^{18}O of stalagmites in Sanbao and Hulu caves in China (Wang et al., 2001, 2008); and eccentricity during the last 150,000 years. Red, blue, and green bars indicate age controls with 95 % confidence intervals of volcanic ashes, the ^{14}C of plant debris and total organic carbon, and ARM events, respectively. The names of tephras that appeared commonly in BIW07-6/BIW08-B and BIW95-4/BT are shown in the panel.

study site has a variation consistent with that in marine core MD01-2421 from off the coast of central Japan in the western North Pacific. The age–depth model of core MD01-2421 was established by oxygen isotope stratigraphy using benthic foraminifera isotopes (Oba et al., 2006). The assumed synchronous vegetation change in central Japan, namely the correspondence of pollen assemblages between MD01-2421 and Lake Biwa cores, is evidence that the uncertainty of the age–depth models of Lake Biwa cores in MIS 5 and 6 was smaller than that indicated by the dating error of each tephra, and the ages of sediments were precise enough to discuss variation on orbital timescales.

Though caution must be exercised, due to this limitation of the age–depth model, comparison with Chinese stalagmite records revealed a regional perspective on the East Asian summer monsoon variability. In the period from 55 ka to the present, the variation in CBT-based pH was synchronous with that of δ^{18}O in stalagmites in China (Fig. 7; Wang et al., 2001, 2008). This correspondence suggests that summer temperature in central Japan varied synchronously with the δ^{18}O of the precipitated water in China.

However, in the period from 143 to 55 ka, the variation in CBT-based pH lagged behind that of the δ^{18}O in stalagmites in China by several thousand years (Fig. 7). The mismatch between Japanese precipitation and Chinese stalagmite δ^{18}O records was reported by Yamamoto (2009) and Clemens et al. (2010). There are two possible interpretations of this phenomenon. First, precipitation in Japan and China during early summer is determined principally by the position of the Baiu Front that develops at the atmospheric boundary between warm, moist air masses flowing from the south and cold air masses from the north (Yoshino, 1965). The latitudinal shift of the Baiu Front in response to orbital forcing may have resulted in the difference in the response of precipitation between central Japan and China (Yamamoto, 2009). Second, synchronous variations in stalagmite δ^{18}O from Hulu Cave (Wang et al., 2001) and Sanbao Cave (Wang et al., 2008) in central China and from Dongge Cave (Yuan et al., 2004) in southern China suggest that the stalagmite δ^{18}O is not a simple index of local precipitation (Yamamoto, 2009). The negative shift of stalagmite δ^{18}O from Chinese caves is also synchronous with the rapid increase in air temperature in central Japan at glacial terminations, suggesting that the negative shift of stalagmite δ^{18}O was related in part to temperature increases in air masses derived from the summer monsoon. Heavy rains, which occur more frequently in warmer air masses, induce isotopically lighter water (Yamamoto, 2009). Clemens et al. (2010) argued, however, that winter precipitation contributed to stalagmite δ^{18}O. This question remains open. Our new result confirms the mismatch between the precipitation records in central Japan and Chinese stalagmite δ^{18}O records. This is an interesting topic for studies of the Asian monsoon.

In this study, we assume that the branched GDGTs produced in the lake contributed to sedimentary branched GDGTs in the study site. However, the spike of high CBT (low estimated pH) at 13 ka is exceptionally affected by the contribution of soil GDGTs (Fig. 6). Ohira et al. (2013) reported a spike of abundant lignin at the same layer in core BIW08-B. Because of low-CBT-based pH (3.3 to 8.0 with an average of 5.0; Ajioka et al., 2014) due to high CBT in the soils, the high CBT (low estimated pH) at 13 ka associated with high lignin abundance likely reflected the soil GDGT contribution.

4.3 Changes in MBT′/CBT -based winter lake water temperature during the last 280 ky

MBT′/CBT-based winter temperature showed a glacial–interglacial pattern (Fig. 6). The variation is consistent with the winter air temperature estimated from the pollen assemblage in Lake Biwa (Nakagawa et al., 2008). However, the MBT′/CBT-based temperatures (3 to 10 °C) are more realistic than the pollen-based temperatures (−10 to 5 °C; Nakagawa et al., 2008). The winter water temperature in Lake Biwa is controlled by winter cooling (data from the Lake Biwa Environmental Research Institute, http://www.pref.shiga.lg.jp/biwako/koai/hakusyo/index.html; Japan Meteorological Agency, available at http://www.jma.go.jp/jma/index.html) and reflects the intensity of the Asian winter monsoon. The rise of the MBT′/CBT-based winter lake water temperature lagged behind the rise of the Tp-based summer air temperature by ∼ 10 ky in Lake Biwa cores (Fig. 7). This suggests warmer summers and colder winters in MIS 5e, with a larger seasonal temperature variation in this period.

4.4 Changes in the microbial ecosystem of Lake Biwa during the last 280 ky

The BIT index was higher than 0.8 throughout the core (Fig. 6). Because most branched GDGTs are produced in the lake (Ajioka et al., 2014), this high BIT implies high bacterial production in Lake Biwa. The BIT record indicates negative spikes (< 0.9) at 240, 210, 114 and 6–0 ka, which correspond to the maximal peak of crenarchaeol concentration (Fig. 6). Because crenarchaeol is specific to Thaumarchaeota (Sinninghe Damsté et al., 2002), the production of Thaumarchaeota was enhanced in those periods. Although the reason that thaumarchaeotal production was enhanced in these specific periods is unclear, changes in the nutrient conditions are a possible cause of such an ecological change.

5 Conclusions

We analysed the MBT′/CBT indices in sediment cores retrieved from Lake Biwa to reconstruct changes in summer precipitation and temperature and in winter temperature in central Japan during the last 280 ky. Comparison with pollen assemblage in Lake Biwa cores suggests that lake water pH was determined by summer temperature in low-eccentricity periods, while it was determined by summer precipitation in high-eccentricity periods. From 130 to 55 ka, variation in lake pH (summer precipitation) lagged behind that in summer temperature by several thousand years. Thaumarchaeotal production was enhanced in specific periods in interglacials.

Appendix A

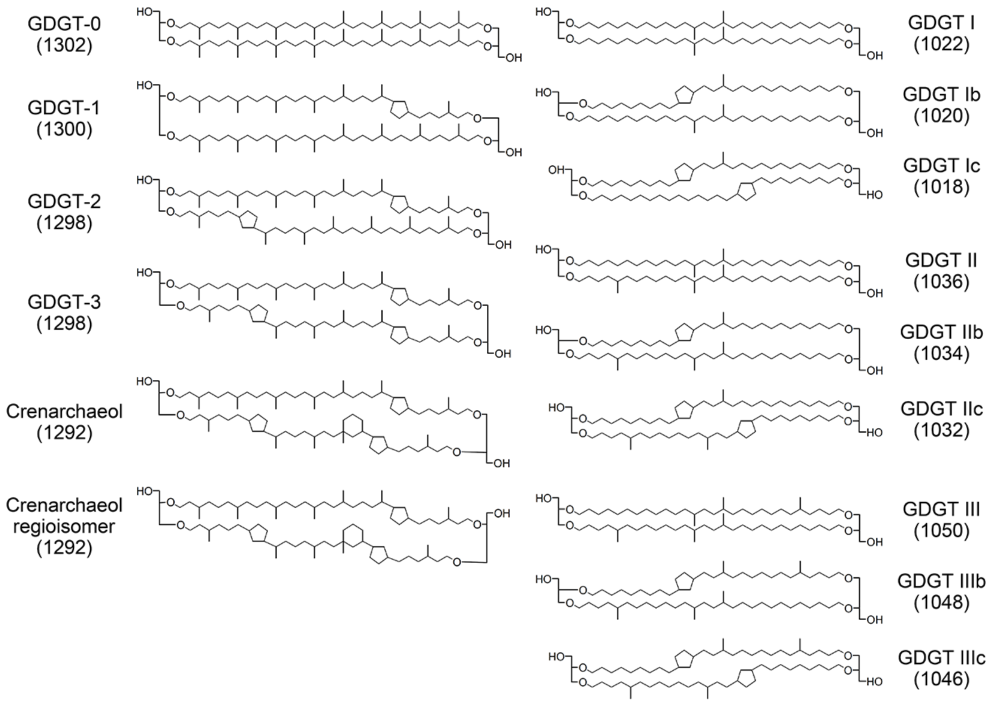

Figure A1. Structures of isoprenoid and branched GDGTs.

Acknowledgements. We would like to thank all of the members of the Lake Biwa drilling project, T. Okino, K. Ohnishi and F. Ohira (Hokkaido University) for analytical assistance and R. Hayashi (Lake Biwa Museum) for providing valuable information. Comments by two anonymous reviewers improved this manuscript. The study was carried out under Grant-in-Aid for Scientific Research (A) of JSPS no. 19204050 (to K. Takemura) and no. 19204051 (to M. Yamamoto).

Edited by: M.-T. Chen

References

Ajioka, T., Yamamoto, M., and Murase, J.: Branched and isoprenoid glycerol dialkyl glycerol tetraethers in soils and lake/river sediments in Lake Biwa basin and implications for MBT/CBT proxies, Org. Geochem., 73, 70–82, 2014.

Buckles, L. K., Weijers, J. W. H., Verschuren, D., and Sinninghe Damsté, J. S.: Sources of core and intact branched tetraether membrane lipids in the lacustrine environment: Anatomy of Lake Challa and its catchment, equatorial East Africa, Geochim. Cosmochim. Acta, 140, 106–126, 2014.

Clemens, S. C. and Prell, W. L.: A 350,000 year summer-monsoon multi-proxy stack from the Own Ridge, Northern Arabian Sea, Mar. Geol., 201, 35–51, 2003.

Clemens, S. C., Prell, W. L., and Sun, Y.: Orbital-scale timing and mechanisms driving Late Pleistocene Indo-Asian summer monsoons: Reinterpreting cave speleothem δ^{18}O, Paleoceanography, 25, 1–19, 2010.

De Rosa, M. and Gambacota, A.: The lipids of archaeabacteria, Prog. Lipid Res., 27, 153–175, 1988.

Dykoski, C. A., Edwards, R. L., Cheng, H., Yuan, D., Cai, Y., Zhang, M., Lin, Y., Qing, J., An, Z., and Revenaugh, J.: A high-resolution, absolute-dated Holocene and deglacial Asian monsoon record from Dongge Cave, China, Earth Planet. Sc. Lett., 233, 71–86, 2005.

Fukuoka, T. and Matsui, S.: Stratigraphy of pyroclastic deposits post-dating the AT tephra, Sanbe Volcano, Earth Science (Chikyu kagaku), 56, 105–122, 2002 (in Japanese).

Hayashi, R., Takahara, H., Hayashida, A., and Takemura, K.: Millennial-scale vegetation changes during the last 40,000 yr based on a pollen record from Lake Biwa, Japan, Quat. Res., 74, 91–99, 2010a.

Hayashi, R., Takahara, H., Yoshikawa, S., and Inouchi, Y.: Orbital-scale vegetation variability during MIS6, 5, 4, and 3 based on a pollen record from the Takashima-oki core in Lake Biwa, western Japan, Jap. J. Palynol. 56, 5–12, 2010b.

Hayashida, A., Ali, M., Kuniko., Kitagawa H., Torii, M., and Takemura, K.: Environmental magnetic record and paleosecular variation data for the last 40 kyrs from the Lake Biwa sediments, central Japan, Earth Planets Space, 59, 807–814, 2007.

Heusser, L. E. and Morley, J. J.: Pollen and radiolarian records from deep-sea core RC14-103: climatic reconstructions of northeast Japan and northwest Pacific for the last 90 000 years, Quat. Res., 24, 60–72, 1985.

Hong, W., Park, J. H., Sung, K. S., Woo, H. J., Kim, J. K., Choi, H. W., and Kim, G. D.: A new 1 MV AMS facility at KIGAM, Radiocarbon, 52, 243–251, 2010.

Hopmans, E. C., Schouten, S., Pancost, R., van der Meer, M. T. J., and Sinninghe Damsté, J. S.: Analysis of intact tetraether lipids in archaeal cell material and sediments by high performance liquid chromatography/atmospheric pressure chemical ionization mass spectrometry, Rapid Commun. Mass Spec., 14, 585–589, 2000.

Hopmans, E. C., Weijers, J. W. H., Schefuß, E., Herfort, L., Sinninghe Damsté, J. S., and Schouten, S.: A novel proxy for terrestrial organic matter in sediments based on branched and isoprenoid tetraether lipids, Earth Planet. Sc. Lett., 24, 107–116, 2004.

Huguet, C., Hopmans, E. C., Febo-Ayala, W., Thompson, D. H., Sinninghe Damsté, J. S., and Schouten, S.: An improved method to determine the absolute abundance of glycerol dibiphytanyl glycerol tetraether lipids, Org. Geochem., 37, 1036–1041, 2006.

Igarashi, Y. and Oba, T.: Fluctuations of monsoons and insolation in the northwest Pacific during the last 144 kyr from a high resolution pollen analysis of the IMAGES core MD01-2421, Quat. Sci. Rev., 25, 1447–1459, 2006.

Ishida, Y., Kimura, B., Nakahara, H., and kadota, H.: Analysis of major nutrient effecting *Uroglena americana* bloom in the northern Lake Biwa, by use of algal bioassay, Bull. Jap. Soc. Sci. Fish., 48, 1281–1287, 1982,

Ishiwatari, R. and Uzaki, M.: Diagenetic changes of lignin compounds in a more than 0.6 million-year-old lacustrine sediment (Lake Biwa, Japan), Geochim. Cosmochim. Acta, 51, 321–328, 1987.

Ishiwatari, R., Negishi, K., Yoshikawa, H., and Yamamoto, S.: Glacial-interglacial productivity and environmental changes in Lake Biwa, Japan: a sediment core study of organic carbon, chlorins and biomarkers, Org. Geochem., 40, 520–530, 2009.

Kitagawa, H. and van der Plicht, J.: Atmospheric radiocarbon calibration to 45 000 yr B.P.: Late Glacial fluctuations and cosmogenic isotope production, Science, 279, 1187–1190, 1998.

Kitagawa, H., Lim, J., Takemura, K., Hayashida, A., and Haraguchi, T.: Radiocarbon content of lignin-enriched fraction in core sediment from Lake Biwa, central Japan, Nucl. Instrum. Meth. B, 268, 1077–1079, 2010.

Kunimatsu, T.: Part D. The mass inflow from the catchment area to the lake. 1) Characteristics of contamination load in the catchment area, In the 10th anniversary symposium of Lake Biwa Research Institute-Results and future issues of Lake Biwa study, 192–204, 1993 (in japanese).

Kutzbach, J.: Monsoon climate of the Early Holocene: Climate experiment with the Earth's orbital parameters for 9000 years ago, Science, 214, 59–61, 1981.

Kuwae, M., Yoshikawa, S., Tsugeki, N., and Inouchi, Y.: Reconstruction of a climate record for the past 140 kyr based on diatom valve flux data from Lake Biwa, Japan, J. Paleolimnol., 32, 19–39, 2004.

Matsumoto, T., Uto, K., Ono, K., and Watanabe, K.: K-Ar age determinations for Aso volcanic rocks – concordance with volcanostratigraphy and application to pyroclastic flows –, Abstracts Fall Meet. in 1991, Volcanol. Soc. Japan, 73, 1991 (in Japanese).

Miyoshi, N., Fujiki, T., and Morita, Y.: Palynology of a 250-m core from Lake Biwa: a 430 000-year record of glacial-interglacial vegetation change in Japan, Rev. Palaeobot. Palynol., 104, 267–283, 1999.

Nakagawa, T., Okuda, M., Yonenobu, H., Norio, M., Toshiyuki, F., Gotanda, K., Tarasov, P., Yoshimune, M., Takemura, K., and

Shoji, N.: Regulation of the monsoon climate by two different orbital rhythms and forcing mechanisms, Geology, 36, 491–494, 2008.

Nakamura, T., Niu, E., Oda, H., Ikeda, A., minamia, M., Takahashi, H., Adachi, M., Pals, L., Gottdang, A., and Suya, N.: The HVEE Tandetron AMS system at Nagoya University , Nucl. Instrum. B, 172, 52–57, 2000.

Nakamura, T., Niu, E., Oda, H., Ikeda, A., Minamia, O., and Oda, T.: High precision ^{14}C measurement with the HVEE Tandetron AMS system at Nagoya University, Nucl. Instrum. Meth. B, 223/224, 124–129, 2004.

Nakayama, O.: Present state of eutrophication and fishery in Lake Biwa, Bull. J. Soc. Fish. Ocean., 38, 49–53, 1981 (in Japanese).

Niemann, H., Stadnitskaia, A., Wirth, S. B., Gilli, A., Anselmetti, F. S., Sinninghe Damsté, J. S., Schouten, S., Hopmans, E. C., and Lehmann, M. F.: Bacterial GDGTs in Holocene sediments and catchment soils of a high Alpine lake: application of the MBT/CBT-paleothermometer, Clim. Past, 8, 889–906, doi:10.5194/cp-8-889-2012, 2012.

Nishihara, M. and Koga, Y.: Extraction and composition of polar lipids from the archaebacterium, *Methanobacterium thermoautotrophicum*: Effective extraction of tetraether lipids by an acidified solvent, J. Biochem., 101, 997–1005, 1987.

Oba, T., Irino, T., Yamamoto, M., Murayama, M., Takamura, A., and Aoki, K.: Paleoceanographic change off central Japan since the last 144 000 years based on high-resolution oxygen and carbon isotope records, Global Planet. Change, 53, 5–20, 2006.

Ohira, F., Yamamoto, M., Takemura, K., and Hayashida, A.: Response of vegetation in central Japan to precession during the last 147,000 years: A lignin record from Lake Biwa core BIW08-B, Quat. Int., in press, 2013.

Patwardhan, A. P. and Thompson, D. H.: Efficient synthesis of 40- and 48-membered tetraether macrocyclic bisphosphocholines, Org. Lett., 1, 241–243, 1999.

Peterse, F., van der Meer, J., Schouten, S., Weijers, J. W. H., Fierer, N., Jackson, R. B., Kim, J. -K., and Sinninghe Damsté, J. S.: Revised calibration of the MBT-CBT paleotemperature proxy based on branched tetraether membrane lipids in surface soils, Geochim. Cosmochim. Acta, 96, 215–229, 2012.

Reimer, P. J., Bard, E., Bayliss, A., Beck, J. W., Blackwell, P. G., Ramsey, C. B., Buck, C. E., Cheng, H., Edwards, R. L., Friedrich, M., Grootes, P. M., Guilderson, T. P., Haflidason, H., Hajdas, I., Hatte, C., Heaton, T. J., Hoffmann, D. L., Hogg, A. G., Hughen, K. A., kaiser, K. F., Kromer, B., Manning, S. W., Niu, M., Reimer, R. W., Richards, D. A., Scott, E. M., Southon, J. R., Staff, R. A., Turney, C. S. M., and van der Plicht, J.: Intcal13 and Marine13 Radiocarbon Age Calibration Curves 0–50,000 Years Cal Bp, Radiocarbon, 55, 1869–1887, 2013.

Schouten, S., Huguet, C., Hopmans, E. C., Kienhuis, M. V. M., and Sinninghe Damsté, J. S.: Analytical methodology for TEX_{86} paleothermometry by high performance liquid chromatography/atmospheric pressure chemical ionization-mass spectrometry, Anal. Chem., 79, 2940–2944, 2007.

Seki, O., Kawamura, K., and Ishiwatari, R.: Assessment of hydrogen isotopic compositions of n-fatty acids as paleoclimate proxies in Lake Biwa sediments, J. Quat. Sci., 27, 884–890, 2012.

Sinninghe Damsté, J. S., Hopmans, E. C., Pancost, R. D., Schouten, S., and Geenevasen, J. A. J.: Newly discovered non-isoprenoid dialkyl diglycerol tetraether lipids in sediments, J. Chem. Soc., Chem. Comm., 23, 1683–1684, 2000.

Sinninghe Damsté, J. S., Hopmans, E. C., Schouten, S., van Duin, A. C. T., Geenevasen, J. A. J.: Crenarchaeol: the characteristic core glycerol dibiphytanyl glycerol tetraether membrane lipid of cosmopolitan pelagic crenarchaeota, J. Lipid Res., 43, 1641–1651, 2002.

Sinninghe Damsté, J. S., Rijpstra, W. I. C., Hopmans, E. C., Weijers, J. W. H., Foesel, B. U., Overmann, J., and Dedysh, S. N.: 13,16-Dimethyl octacosanedioic acid (iso-diabolic acid): a common membrane-spanning lipid of Acidobacteria subdivisions 1 and 3, Appl. Environ. Microb., 77, 4147–4154, 2011.

Southon, J. and Santos, G. M.: Ion source development at KCCAMS, University of California. Radiocarbon, 46, 33–39, 2004a.

Southon, J., Santos, G., Druffel-Rodriguez, K., Druffel, E., Trumbore, S., Xu, X., Griffin, S., Ali., S., and Mazon, M.: The KECK Carbon cycle AMS laboratory, University of California, Irvine: Initial operation and background surprise, Radiocarbon, 46, 41–49, 2004b.

Staff, R. A., Nakagawa, T., Schlolaut, G., Marshall, M. H., Brauer, A., Lamb, H., Bronk Ramsey, C., Bryant, C. L., Brock, F., Kitagawa, H., van der Plicht, J., Payne, R. L., Smith, V. C., Mark, D. F., MacLeod, A., Blockley, S. P. E., Schwenninger, J. L., Tarasov, P., Haraguchi, T., Gotanda, K., Yonenobu, H., Yokoyama, Y., and Suigetsu 2006 project members.: The multiple chronological techniques applied to the Lake Suigetsu (SG06) sediment core, Boreas, 42, 33–39, 2012.

Takemura, K., Iwabe, C., Hayashida, A., Danhara, T., Kitagawa, H., Haraguchi, T., Sato, T., and Ishikawa, N.: Stratigraphy of marker tephras and sediments during the past 50,000 years from multiple sites in Lake Biwa, Japan, Daiyonkikenkyu (The Quaternary Research), 49, 147–160, 2010 (in Japanese).

Talling, S. J.: The depletion of carbon dioxide from lake water by phytoplankton, J. Ecol., 64, 79–121, 1976.

Tani, S., Kitagawa, H., Hong, W.., Park, J. H., Sung, K., and Park, G.: Age determination of the Kawagodaira volcanic eruption in Japan by ^{14}C wiggle-matching, Radiocarbon, 55, 748–752, 2013.

Tezuka, Y.: C:N:P ratios of seston in Lake Biwa as indicators of nutrient deficiency in phytoplankton and decomposition process of hypolimnetic particulate matter, Jpn. J. Limnol., 46, 239–246, 1985.

Tierney, J. E. and Russell, J. M.: Distributions of branched GDGTs in a tropical lake system: Implications for lacustrine application of the MBT/CBT paleoproxy, Org. Geochem., 40, 1032–1036, 2009.

Tierney, J. E., Russell, J. M., Eggemont, H., Hopmans, E. C., Verschuren, D., and Sinninghe Damsté, J. S.: Environmental controls on branched tetraether lipid distributions in tropical East African lake sediments: a new lacustrine paleothermometer?, Geochim. Cosmochim. Acta, 74, 4902–4918, 2010.

Tyler, J. J., Nederbragt, A. J., Jones, V. J., and Thurow, J. W.: Assessing past temperature and soil pH estimated from bacterial tetraether membrane lipids: evidence from the recent lake sediments of Lochnar, Scotland, J. Geophys. Res., 115, G01015, doi:10.1029/2009JG001109, 2010.

Wang, Y. J., Cheng, H., Edwards, R. L., An, Z. S., Wu, J. Y., Shen, C.-C., and Dorale, J. A.: A high-resolution absolute-dated late

Pleistocene monsoon record from Hulu Cave, China, Science, 294, 2345–2348, 2001.
Wang, G., Clemens, S. C., and Liu, P.: Contrasting the Indian and East Asian monsoons: implications on geologic timescales, Mar. Geol., 201, 5–21, 2003.
Wang, Y. J., Cheng, H., Edwards, R. L., Kong, X., Shao, X., Chen, S., Wu, J., Jiang, X., Wang, X., and An, Z.: Millennial- and orbital-scale changes in the East Asian monsoon over the past 224 000 years, Nature, 451, 1090–1093, 2008.
Wang, H., Liu, W., Zhang, C., Wang, Z., Wang, J., Liu, Z., and Dong, H.: Distribution of glycerol dialkyl glycerol tetraethers in surface sediments of Lake Qinghai and surrounding soil, Org. Geochem., 47, 78–87, 2012.
Weijers, J. W. H., Schouten, S., Geenevasen, J. A. J., David, O. R. P., Coleman, J., Pancost, R. D., and Sinninghe Damsté, J. S.: Membrane lipids of mesophilic anaerobic bacteria thriving in peats have typical archaeal traits, Environ. Microbiol., 8, 648–657, 2006.
Weijers, J. W. H., Schefuß, E., Schouten, S., and Sinninghe Damsté, J. S.: Coupled thermal and hydrological evolution of tropical Africa over the last deglaciation, Science, 315, 1701–1704, 2007a.
Weijers, J. W. H., Schouten, S., van Den Donker, J. C., Hopmans, E. C., and Sinninghe Damsté, J. S.: Environmental controls on bacterial tetraether membrane lipid distribution in soils, Geochim. Cosmochim. Acta, 71, 703–713, 2007b.
Wetzel, R. G.: Limnology: Lake and River Ecosystems, Third edition, Academic Press, San. Diego, USA, 1006 pp, 2001.
White, A. F. and Blum, A. E.: Effects of climate on chemical weathering in watersheds, Geochim. Cosmochim. Acta, 59, 1729–1747, 1995.
Xiao, J., Inouchi, Y., Kumai, H., Yoshikawa, S., Kondo, Y., Liu, T., and An, Z.: Biogenic silica record in Lake Biwa of central Japan over the past 145,000 years, Quat. Res., 47, 277–283, 1997.
Yamamoto, M.: Response of mid-latitude North Pacific surface temperatures to orbital forcing and linkage to the East Asian summer monsoon and tropical ocean-atmosphere interactions, J. Quat. Sci., 24, 836–847, 2009.
Yoshino, M. M.: Four stages of the rainy season in early summer over East Asia (part I), J. Meteorol. Soc. Jpn., 43, 231–245, 1965.
Yuan, D., Cheng, H., Edwards, R. L., Dykoski, C. A., Kelly, M. J., Zhang, M., Qing, J., Lin, Y., Wang, Y., Wu, J., Dorale, J. A., An, Z., and Cai, Y.: Timing, duration, and transitions of the last interglacial Asian monsoon, Science, 304, 575–578, 2004.
Zhang, Y. G., Zhang, C. L., Liu, X. L., Li, L., Hinrichs, K. U., and Noakes, J. E.: Methane Index: a tetraether archaeal lipid biomarker indicator for detecting the instability of marine gas hydrates, Earth Planet. Sc. Lett., 307, 525–534, 2011.
Zink, K. G., Vandergoes, M. J., Mangelsdorf, K., Dieffenbacher-Krall, A. C., and Schwark, L.: Application of bacterial glycerol dialkyl glycerol tetraethers (GDGTs) to develop modern and past temperature estimates from New Zealand lakes, Org. Geochem., 41, 1060–1066, 2010.