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Water pH and temperature in Lake Biwa from MBT′/CBT indices during the last 282 000 years

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Abstract

We generated a 282 000-year 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 to understand the responses of precipitation and air temperature in central Japan to the East Asian monsoon variability on the orbital timescale. Because water pH in Lake Biwa is determined by phosphorus input driven by precipitation, the record of water pH should indicate changes in summer precipitation in central Japan. The estimated pH showed significant periodicity at 19 and 23 ka (precession) and at 41 ka (obliquity). The variation in the estimated pH agrees with variation in the pollen temperature index. This indicates synchronous variation in summer air temperature and precipitation in central Japan, which contradicts the conclusions of previous studies. The variation in estimated pH was also synchronous with the variation of oxygen isotopes in stalagmites in China, suggesting that East Asian summer monsoon precipitation was governed by Northern Hemisphere summer insolation on orbital timescales. However, the estimated winter temperatures were higher during interglacials and lower during glacials, showing an eccentricity cycle. This suggests that the temperature variation reflected winter monsoon variability.

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 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 of central Japan shows that the East Asian monsoon has been strongest at the October–November perihelion in precession cycles (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. Additionally, the MBT′/CBT and TEX$_{86}$ indices of glycerol dialkyl glycerol tetraethers (GDGTs) have been applied recently to lake sediments for palaeotemperature reconstruction (e.g. Powers et al., 2004; Niemann et al., 2012). In Lake Biwa, sediment cores have been investigated using pollen fossils (Miyoshi et al., 1999; Nakagawa et al., 2008), lignin (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).

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 Acidobacteria (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). 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), but most applications in lake sediments have been 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 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 Lake Biwa, central Japan, to reconstruct lake water pH and temperature during the last 282 000 years. 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 1981–2010) (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/).

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 created using calendar ages converted from radiocarbon dates of 13 terrestrial plant remains and radiogenic ages of five volcanic ash layers (Fig. 3a; Takemura et al., 2010; Kitagawa, personal communication, 2014), and the average sedimentation rate was found to be 0.4 m ka^{-1}. The sediment was stored at 4 °C for 0.5 years. 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 ka.

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) in 2008 (Fig. 1). The sediments consisted of

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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; Sato, personal communication, 2014). The age–depth model for core BIW08-B was created from the radiogenic ages of 18 volcanic ash layers (Fig. 3b; Takemura, personal communication, 2014), and the average sedimentation rate was found to be 0.3 m ka^{-1}. The sediment was stored at 4 °C for 0.5 years. Then, 152 samples (2.5 cm thick) were collected from 13 m (43 ka) to 88 m (282 ka), and the samples were immediately freeze-dried. The average sampling interval was $\sim$ 1.9 ka.

2.3 Analytical method

Lipids were extracted (3×) from a freeze-dried sample using a DIONEX ASE-200 at 100 °C and 1000 psi for 10 min with 11 mL CH_2Cl_2/CH_3OH (6 : 4 v/v) and 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 analyzed 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 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 ionization (APCI) MS in positive ion mode. The spectrometer was run in full scan mode (m/z 500–1500). Compounds were assigned from 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} GDGT; 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 ionization 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} GDGT. The standard deviation of a replicate analysis was 3.0 % of the concentration for each compound. The BIT index was calculated as per 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 as per 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 as per Weijers et al. (2007b) and Peterse et al. (2012):

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

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

The pH and MAAT were calculated according to the following equations based on the dataset 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 analytical accuracy of CBT and MBT′ was 0.034 and 0.015, respectively, in this study.

3 Results

The concentrations of isoprenoid and branched GDGTs varied between 0.01 and 2.55 and between 0.05 and 12.58 µg g^{-1}, respectively (Fig. 4). CBT-based pH ranged from 6.0 to 7.6 (Fig. 4). 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/). The CBT-based pH values of the core sediments are lower than those in the present lake water. CBT-based pH was maximal at 6, 25, 45, 75, 100, 120, 137, 162, 202, 216, 245, 253, and 280 ka and minimal at 16, 30, 52, 91, 112, 131, 154, 184, 206, 226, 251, and 268 ka. The intervals between these peaks averaged 23 ka. MBT′/CBT-based temperature ranged from 4 to 11 °C and was lower during glacials and higher during interglacials (Fig. 4). 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 in (~ 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/).

The branched and isoprenoid tetraether (BIT) index ranged from 0.83 to 0.99 (Fig. 4). BIT values exceeded 0.95 in most intervals, but BIT values lower than 0.9 were found at 243, 215, 115, 30, and 6–0 ka (Fig. 4).

The methane index (MI) ranged from 0.1 to 0.9 (Fig. 4). The MI value was maximal at 257, 232, 199, 137, 91, 52, and 15 ka and minimal at 242, 215, 178, 115, 73, and 20 ka (Fig. 4). The average interval between these peaks was 40 ka.

4 Discussion

4.1 CBT-based pH and its controlling factor

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 sulphuric 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 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. Evaporation of lake water increases water pH (Wetzel, 2001), but pollen records in Lake Biwa cores suggest moist environments throughout the last 430 ka (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/). 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/). Thus, we conclude that photosynthesis in the lake water is the major factor controlling water pH in Lake Biwa.

4.2 Changes in precipitation during the last 282 ka

Spectral analysis revealed that the variation in CBT-based pH during the last 282 ka has significant periodicities at ∼ 41 ka (obliquity) and at ∼ 23 and ∼ 19 ka (precession) (Fig. 5a). The strong precession signal agrees with that postulated by the hypothesis that the monsoon is regulated by insolation variation at low latitudes (Kutzbach, 1981). Cross-spectral analysis indicated that the CBT-based pH delayed behind precession minimum by $56 \pm 11^\circ$ (3.6 ± 0.7 ka) at 23 ka band (Fig. 6).

Variation in CBT-based pH was synchronous with variation of warm pollen species in cores BIW95-4 and Takashima-oki BT in Lake Biwa (Fig. 7; Hayashi et al., 2010a, b) and the Tp value, warm/(warm+cool) pollen ratio, in marine core MD01-2421 off of central Japan (Figs. 6 and 7; Igarashi and Oba, 2006). This suggests that summer precipitation varied synchronously with summer temperature in central Japan. Igarashi and Oba (2006) reported that variation in the Tp value preceded the abundance of *Cryptomeria*, which they assumed as a proxy of summer precipitation, by several thousand years, and pointed out a time lag between orbital-timescale air-temperature and precipitation variations (Fig. 6). Yamamoto (2009) interpreted that this time lag was caused the latitudinal shift of the Baiu Front (early summer rain front). Clemens et al. (2010) stressed that the East Asian summer monsoon was synchronised with the Indian summer monsoon (Fig. 6). However, our new record of CBT-based pH was synchronised with the Tp record, implying synchronous variation of precipitation and temperature. Changes in the intensity of the East Asian summer monsoon induced changes in both summer precipitation and air temperature. The variation in CBT-based pH was also synchronous with that of δ^{18}O in stalagmites in China (Figs. 6 and 7; Wang et al., 2001, 2008). This correspondence indicates that both records reflect variation in the East Asian summer monsoon.

4.3 Changes in winter air temperature during the last 282 ka

In Lake Biwa, MBT′/CBT-based temperatures from surface sediments agree with the water temperature in winter (Ajioka et al., 2014), indicating that the MBT′/CBT reflects the water temperature in winter. Variation in the estimated winter temperature is consistent with that 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). Spectral analysis the MBT′/CBT-based temperatures indicates the eccentricity cycle rather than the obliquity or precession cycle (Fig. 5b). The 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/, Japan Meteorological Agency; available at http://www.jma.go.jp/jma/index.html) and reflects the intensity of the Asian winter monsoon. Thus, this result suggests that the East Asian winter monsoon in the climate of central Japan exhibits a strong eccentricity cycle.

Kuwae et al. (2004) reported that the abundance of planktonic diatom frustules in a core from Lake Biwa varied in response to glacial-interglacial changes and interpreted that the abundance variations reflected changes in precipitation. Their variation is different from our precipitation record but similar to our temperature record (Fig. 8). Kuwae et al. (2004) suggested that the diatom flux was influenced not only by precipitation, but also by water ventilation which is controlled by winter temperature and snowfall. We, however, suppose that the diatom record reflects temperature change rather than precipitation changes because warmer climate generally enhances chemical weathering, which produces more dissolved silica that can be used for diatom production in the lake (Kilham, 1971).

5 Conclusions

We analysed the MBT′/CBT indices in sediment cores retrieved from Lake Biwa to reconstruct changes in summer precipitation and winter temperature in central Japan during the last 282 ka. Summer precipitation varied in response to obliquity and precession and was higher when summer insolation was maximal. The periodicity and timing of the variation are consistent with those in summer temperature records from central Japan and summer precipitation records from China. This suggests that summer precipitation and temperature co-varied under the control of East Asian summer monsoon variability. This perspective contradicts the conclusions of previous studies (Igarashi and Oba, 2006; Yamamoto, 2009) that the temperature variation preceded the precipitation variation in central Japan. Winter temperature varied in response to eccentricity and was higher during interglacials, presumably reflecting the variability of the East Asian winter monsoon in the north-western Pacific area.

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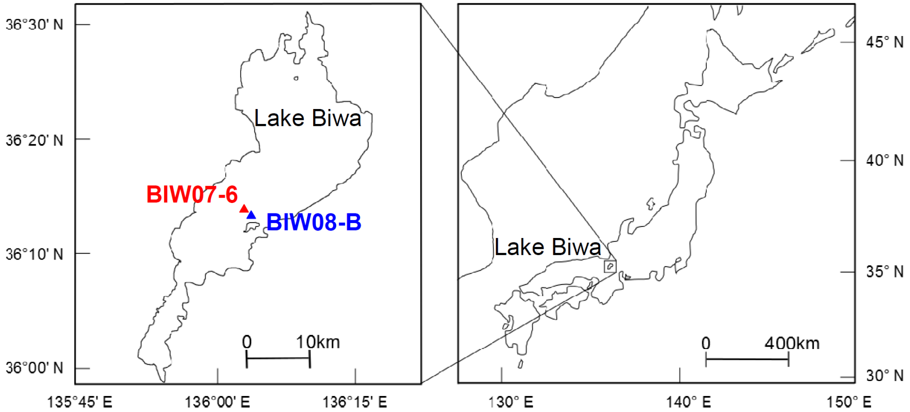

Fig. 1. Map showing the study sites.

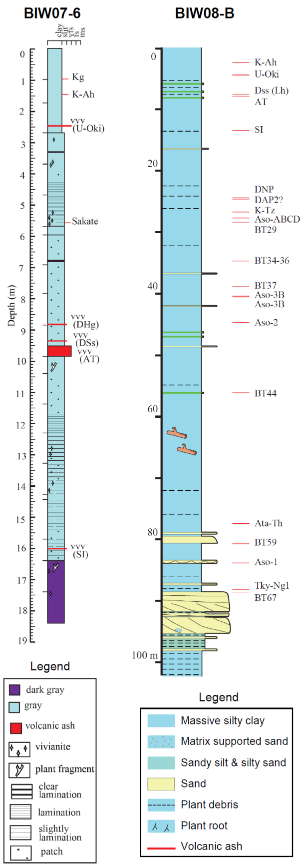

Fig. 2. Lithologic columns of **(a)** core BIW07-6 (Takemura et al., 2010) and **(b)** borehole core BIW08-B (Sato, personal communication, 2014).

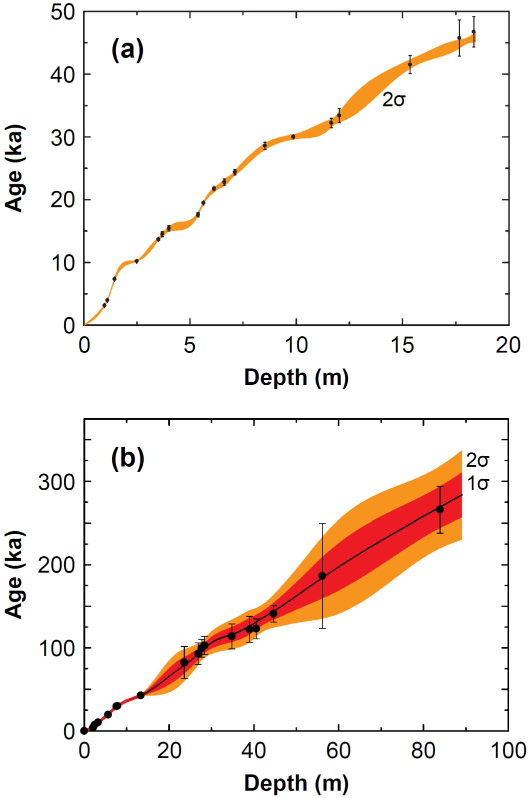

Fig. 3. Age–depth models of **(a)** core BIW07-6 (Kitagawa, personal communication, 2014) and **(b)** borehole core BIW08-B (Takemura, personal communication, 2014). The red and orange areas show the 64 % and 95 % confidence intervals, respectively. The black circles with 95 % error bars are radiometric and model-obtained ages of volcanic ash layers used as age constraints for construction of the age models.

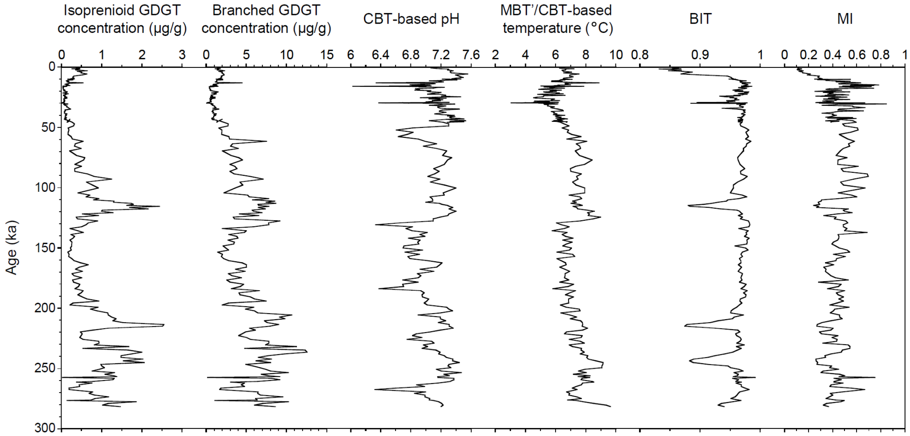

Fig. 4. Variations in the concentrations of isoprenoid and branched GDGTs, CBT-based pH, MBT′/CBT-based temperature, BIT, and MI in cores BIW07-6 and BIW08-B during the last 282 000 years.

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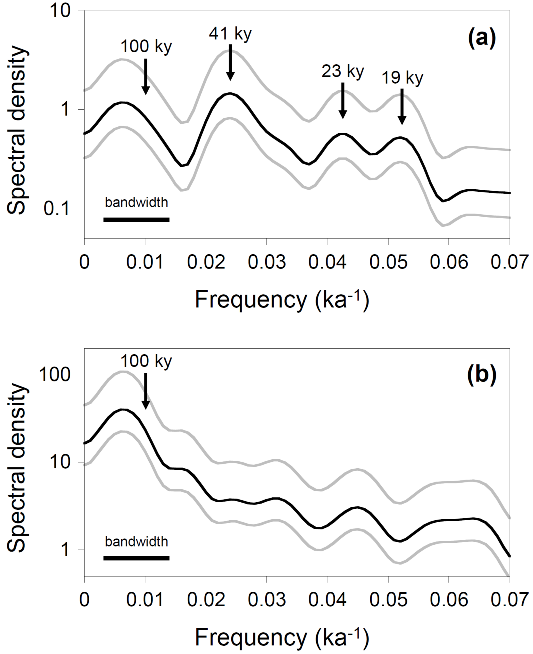

Fig. 5. Power spectra of the variations in **(a)** CBT-based pH and **(b)** MBT′/CBT-based temperature in sediment cores BIW07-6 and BIW08-B for the last 282 000 years. The grey lines indicate upper and lower limits of the 80 % confidence level. The spectral analysis was conducted using the Blackman–Tukey method provided in the Analyseries software package (Paillard et al., 1996).

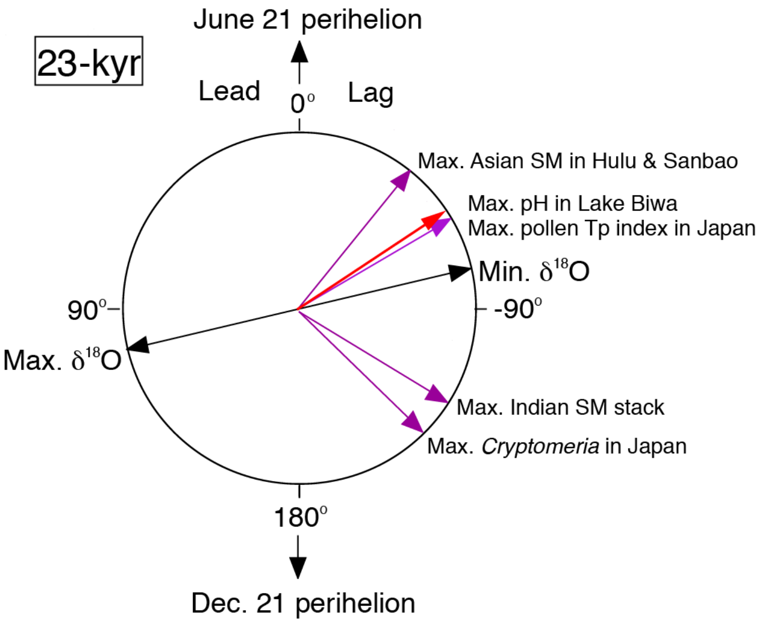

Fig. 6. Precession wheel showing the phases of the CBT-based pH from cores BIW07-6 and BIW08-B (this study), the maximum summer air temperature (maxima of pollen Tp index, Igarashi and Oba, 2006), the maximum summer precipitation in Japan (abundance maxima of *Cryptomeria japonica* in core MD01-2421, Igarashi and Oba, 2006), SPECMAP δ^{18}O maxima and minima (Imbrie et al., 1984, 1992), the maximum Indian summer monsoon (Indian SM stack by Clemens and Prell, 2003), and the maximum East Asian summer monsoon (Hulu and Sanbao stalagmite δ^{18}O minima, Wang et al., 2001, 2008). Positive and negative angles indicate phase leads and lags, respectively, relative to the precession minima (21 June perihelion). The spectral analysis was conducted using the Blackman–Tukey method provided in the Analyseries software package (Paillard et al., 1996).

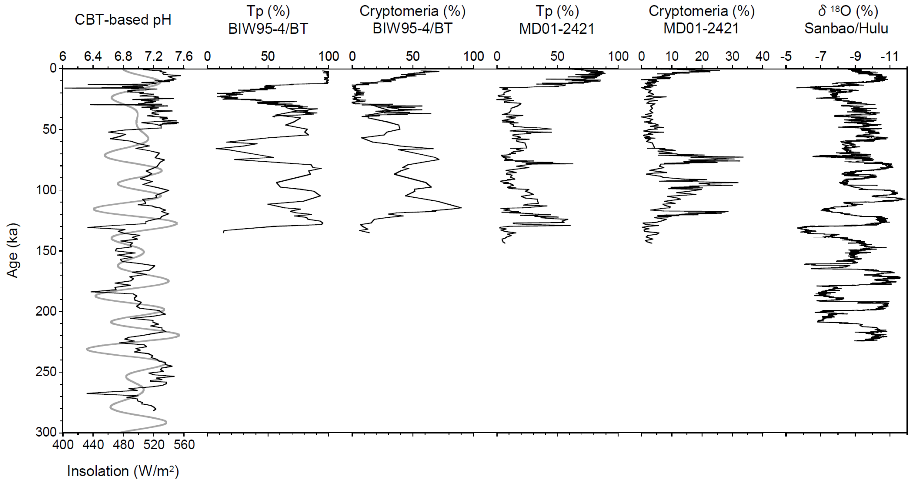

Fig. 7. Variations in CBT-based pH from cores BIW07-6 and BIW08-B (this study), Tp and *Cryptomeria* (%) from cores BIW95 and Takashima-oki BT in Lake Biwa (Hayashi et al., 2010a, b), Tp and *Cryptomeria* (%) from marine core MD01-2421 in the north-western Pacific off of central Japan (Igarashi and Oba, 2006), and δ^{18}O in stalagmites of Sanbao and Hulu caves in central China (Wang et al., 2001, 2008).

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MBT′/CBT indices

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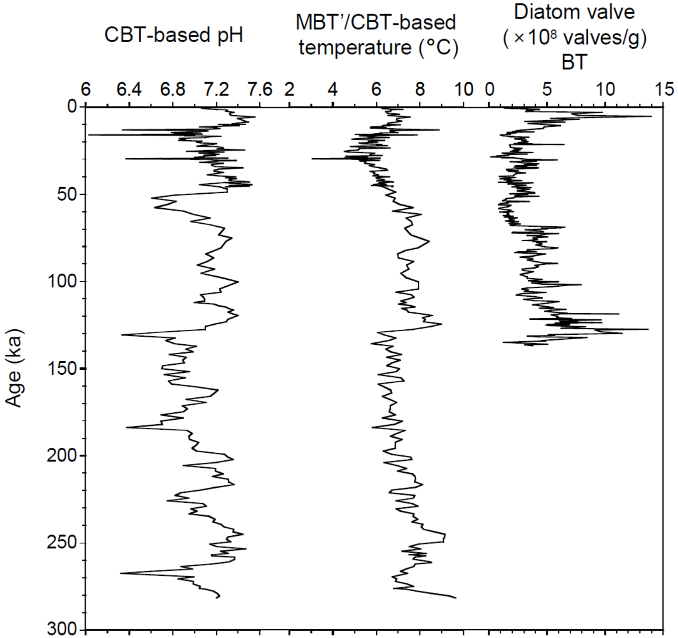

Fig. 8. Variations in CBT-based pH and MBT′/CBT-based temperature in cores BIW07-6 and BIW08-B (this study) and diatom valve concentration in core Takashima-oki BT (Kuwae et al., 2004).

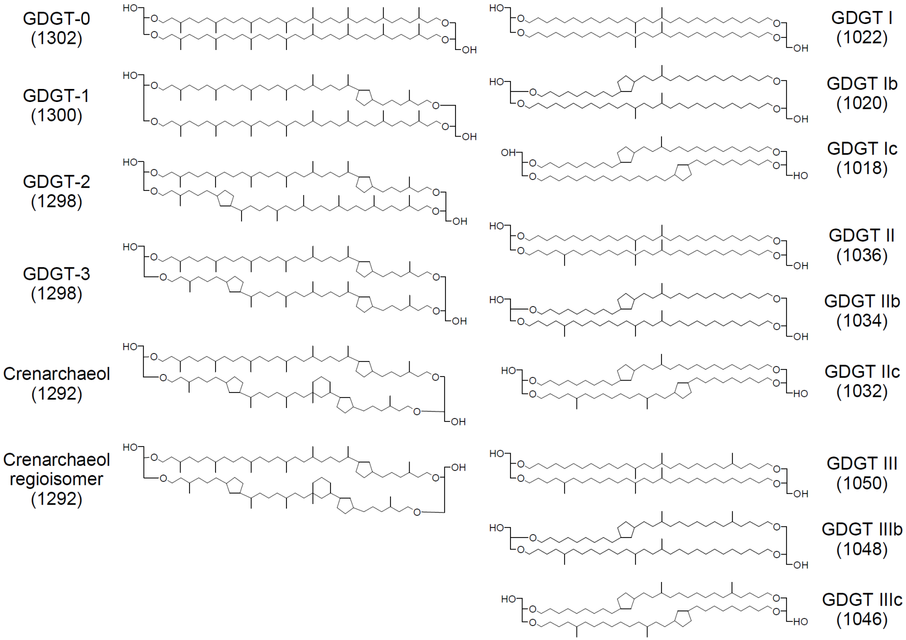

Fig. A1. Structures of isoprenoid and branched GDGTs.