



## Glacial–interglacial productivity and environmental changes in Lake Biwa, Japan: A sediment core study of organic carbon, chlorins and biomarkers

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### ABSTRACT

Temporal changes in paleoproductivity of Lake Biwa (Japan) over the past 32 kyr have been studied by analyzing bulk organic carbon and photosynthetic pigments (chlorins) in the BIW95-5 core. Primary productivity was estimated on the assumption of  $C/N_{org}$  values of 8 for autochthonous organic matter (OM) and 25 for allochthonous OM and using an equation developed for the marine environment. The estimate indicates that primary productivity ranges from 50 to 90  $g\ C\ m^{-2}\ yr^{-1}$  in the Holocene, while it is  $\sim 60\ g\ C\ m^{-2}\ yr^{-1}$  on average in the last glacial. Pheophytin *a* and pheophorbide *a* are the major chlorins. A downcore profile of chlorin concentration normalized to autochthonous organic carbon (OC) shows a decreasing trend. Chlorin productivity was corrected by removal of the effect of post-burial chlorin degradation. The temporal profile of chlorin productivity thereby obtained resembles that from autochthonous OC.

The difference in primary productivity between the Holocene and the glacial for the lake is markedly smaller than that for Lake Baikal situated in the boreal zone. This difference between the two lakes is probably caused by the difference in their climatic conditions, such as temperature and precipitation. Precipitation at Lake Biwa is relatively large during the glacial and the Holocene because of the continuous influence of the East Asian monsoon. Lake Baikal precipitation is generally small as a result of control by the continental (Siberia) climate regime. In addition, a significant difference in productivity between the glacial and the Holocene for Lake Baikal may be essentially controlled by the hydrodynamic systems in the lake.

Lake Biwa terrigenous OM input events occurred at least five times over the period 11–32 kyr BP, suggesting enhanced monsoon activity. Molecular examination of the layer with a large input of terrigenous OM during the Younger Dryas indicates that concentrations of terrigenous biomarkers such as *n*- $C_{27}$ – $C_{31}$  alkanes, lignin phenols, cutin acids,  $\omega$ -hydroxy acids and  $C_{29}$  sterols are high, suggesting that soil OM with peat-like material entered the lake as a result of flooding. An enhanced sedimentation rate in the last 3000 years might have been partially caused by agricultural activity around the lake.

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### 1. Introduction

A number of studies have reported temporal variations in organic carbon and organic compounds in lake sediments in relation to changes in paleoproductivity (e.g. Ishiwatari et al., 2005; Mayer and Schwark, 1999; Williams et al., 1993; Yoon et al., 2006). Knowledge of past primary productivity in a lake is important for understanding the history of its biogeochemical cycles in the distant past. Large and ancient lakes such as Lake Baikal and Lake Biwa are important, since they preserve records not only of local, but also of global, environmental changes. However, quantitative studies of lake paleoproductivity are scarce. Even then, in these

studies, terrigenous OM is often ignored in the estimation of lake paleoproductivity, although the contribution of terrigenous OM to total OM in lake sediments is generally higher than that in the marine environment (e.g. Williams et al., 1993; Prokopenko et al., 1999).

In quantitative studies, the methodology established in the field of paleoceanography has been applied to lakes (e.g. Ishiwatari et al., 2005; Qiu et al., 1993; Williams et al., 1993). In our previous study (Ishiwatari et al., 2005), we used the equation for estimating paleoproductivity that was established by Müller and Suess (1979), where paleoproductivity is expressed as a function of sedimentary organic carbon (OC) content, dry bulk density and linear sedimentation rate. In our previous study of Lake Baikal, we used algal derived OC instead of total sedimentary OC (Ishiwatari et al., 2005). The differentiation of algal OC from terrigenous OC was made from

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evaluation of the C/N values of sedimentary OM. Algal derived biomarkers (e.g. chlorins, carotenoids) are candidates for tracing autochthonous OM. Chlorophylls are essential photosynthetic pigments of all phytoplankton and chlorins are their transformation products. Therefore, chlorins have been used as a measure of algal productivity and as a proxy for marine primary productivity (e.g. Harris et al., 1996). In this approach, the effect of diagenetic change on chlorins for estimating past primary productivity should be calibrated. The second approach towards quantifying terrigenous bulk OM input is to determine terrigenous biomarkers, such as lignin phenols, cutin acids, C<sub>29</sub> sterols and higher plant *n*-alkanes and to obtain conversion factors of biomarkers to terrigenous bulk OM (Prah et al., 1994; Ishiwatari et al., 2009).

Lake Biwa is the largest freshwater lake in Japan, located in the central part of the mainland. It is situated in a temperate zone and receives relatively large precipitation with a moderate temperature. Abundant nutrients and detritus are supplied to the lake, supporting a relatively high primary productivity. Many organic geochemical studies have been conducted for molecular characterization, diagenetic changes and paleoenvironments by way of 200 and 800 m sediment cores (e.g. Kawamura and Ishiwatari, 1984; Ishiwatari and Uzaki, 1987; Ogura et al., 1990; Meyers et al., 1993). These studies have revealed good preservation of OM records responding to environmental changes related to global climatic change over the last 430 kyr.

Meyers and Horie (1993) reported a vertical profile of OC concentration, C/N ratio values and carbon isotopic composition of OM ( $\delta^{13}\text{C}_{\text{org}}$ ) in Lake Biwa sediments, deposited since 15 kyr ago, with relatively high resolution (20 cm/sample corresponding to 200–300 yr/sample). They concluded that the sedimentary OM is predominantly from aquatic production and the shift in  $\delta^{13}\text{C}_{\text{org}}$  (from  $-21\text{‰}$  to  $-25\text{‰}$ ) observed in the glacial–postglacial boundary was interpreted to be due to a shift in atmospheric  $p\text{CO}_2$ . Inouchi et al. (1995) reported a vertical profile of total carbon concentration over the last 30 kyr, with time resolution of 150–200 yr/sample. They recognized a broad peak in total carbon concentration over 1.5–7 kyr BP. However, no quantitative study of the lake paleoproductivity has been reported.

Lake Biwa sediments have also been studied by many authors in fields such as paleomagnetism, paleoclimatology, palynology and paleolimnology. Using quartz as an indicator of aeolian dust, Yamada et al. (2004) claimed to have identified a millennial-scale oscillation influenced by the Asian winter monsoon and the Westerlies in sediments since the last glacial. Hayashida et al. (2007) studied the paleomagnetic record in a core covering the last 40 kyr and claimed that the abundance of fine grained magnetite increases during interstadial (warm) periods, suggesting enhanced precipitation. The Younger Dryas was not clearly evidenced. Miyoshi et al. (1999) examined the fossil pollen record in a 250 m core and disclosed glacial/interglacial changes of vegetation in Japan over the past 430 kyr. Kuwae et al. (2002, 2004) conducted a study of fossil diatom records from a 140 m core and disclosed the close relationship between diatom productivity and climate. They claimed that sections with higher diatom concentration correspond to periods of warmer and wetter conditions and that those with lower concentration correspond to periods of colder/drier conditions. They claimed that variations in diatom productivity in the lake relate to summer monsoon intensity. Applying a newly developed method of pollen-based quantitative reconstruction of the climate in Japan to a long term (past 450 kyr) pollen record, Nakagawa et al. (2006, 2008) disclosed that continental (Siberian) and oceanic (northwest Pacific) air mass temperatures respond to the 100 kyr orbital rhythm and, moreover, that the land–ocean tem-

perature gradient and the vigor of the East Asian monsoon oscillate at the 23 kyr insolation cycle.

The objectives of this study were to present the OM record of Lake Biwa sediments (BIW95-5 core) at high resolution (centennial: 30–170 yr/sample) for the last glacial–postglacial periods (ca. 32 kyr) and to highlight the importance of the approach for the evaluation of the variability in organic parameters and lake paleoproductivity in response to global and regional climatic and environmental changes. The core is dated via four tephra layers described below (Takemura et al., 2000).

## 2. Materials and methods

### 2.1. Sediment samples and age model

Lake Biwa (surface elevation 84.4 m) is 63.49 km long and 22.8 km wide (max. width) and covers an area of 674 km<sup>2</sup>, with a maximum water depth of 104 m and an average of 48 m. The watershed area is 3850 km<sup>2</sup> (Kuwae et al., 2004). The lake receives a mean annual precipitation of 1570 mm and the mean annual temperature is 14.3 °C (10 yr average for 1991–2000; calculated from the data of Hikone Meteorological Observatory). The trophic status is oligotrophic–mesotrophic (Otsuki et al., 1981).

A 15 m piston core (BIW95-5) was collected in 1995 near the center (35°15.00'N, 136°03.00'E; water depth 67 m; ca. 4 km off shore) (Fig. 1). In addition, two short piston cores (BIW95-A, 83 cm and BIW95-B, 64 cm) were collected at the same site. The long piston core is generally composed of homogeneous gray clay with seven volcanic ash layers (Table 1 and Fig. 2). The detailed lithology of this core was reported by Takemura et al. (2000). Other bulk sediment characteristics, e.g. paleomagnetic parameters, were reported by Ali et al. (1999).

Fig. 2 displays the depth–age relationship for core BIW95-5. Age control points are volcanic ashes of Kawagodaira (Kg: 2.8–

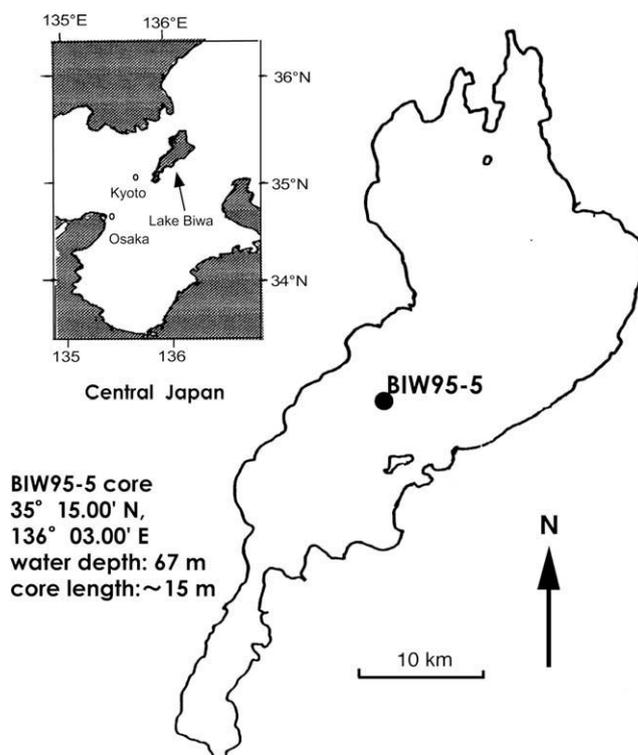


Fig. 1. Map of Lake Biwa (Japan) with sampling point.

**Table 1**  
Age control points (volcanic ash layers) for core BIW95-5.

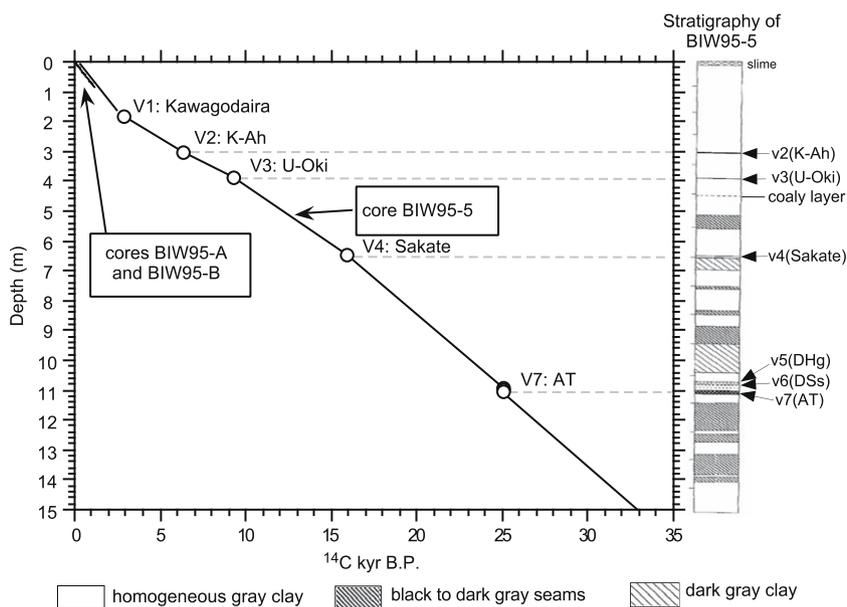
Ash no. <sup>a</sup>	Ash name		Composite depth <sup>b</sup> Av. (m) m	<sup>14</sup> C age <sup>c</sup> kyr BP	Calendar age <sup>d</sup> yr BP
	Short	Full			
V1	Kg	Kawagodaira	2.11	2.8–2.9	3000
V2	K-Ah	Kikai-Akahoya	3.32	6.3	7300
V3	U-Oki	Ulreung-Oki	4.18	9.3	10,750
V4	Sakate	Volcanic ash	6.78	15.9	15,420
V5	DHg	Daisen tephra	10.55		
V6	DSs	Daisen tephra	11.05		
V7	AT	Aira-Tn Tephra	11.22–11.34	25	27,700

<sup>a</sup> Volcanic ash number adopted in this study.

<sup>b</sup> Combination of BIW95-5 (piston core) and BIW95-A (piston core).

<sup>c</sup> From Takemura et al. (2000).

<sup>d</sup> From Yamada (2004).



**Fig. 2.** Age model for cores BIW95-A, BIW95-B and BIW95-5. Stratigraphy of BIW95-5 quoted from Takemura et al. (2000). V1, V2, V3, V4 and V7 are volcanic ash layers.

2.9 <sup>14</sup>C kyr BP), K-Ah ash layer (6.3 <sup>14</sup>C kyr BP), U-Oki ash layer (9.3 <sup>14</sup>C kyr BP), Sakate ash layer (15.9 <sup>14</sup>C kyr BP) and AT ash layers (24.3–24.7 <sup>14</sup>C kyr BP). Since calendar years for the control points are different depending on the model for the relationship between <sup>14</sup>C year and calendar year, we use <sup>14</sup>C year in this paper. The age for each sampling depth was obtained by linear interpolation between age control points, assuming uniform sedimentation rates.

The two short cores stored at 5 °C were cut into 2.0 cm sections. Subsamples from core BIW95-A were used for dry bulk density, TOC (total organic carbon) and total N (total nitrogen) measurements. Subsamples kept in a wet state were used for measurement of chlorins and lipids. Core BIW95-5 was divided into 2.4 cm sections which were stored at –20 °C in glass bottles. Water content was determined from the difference between original wet weight and that measured after freeze drying. Dry bulk density was calculated by dividing the freeze-dried sediment weight by the inner volume of the cube ( $2.4^2 \times 2.0 \text{ cm}^3$ ).

## 2.2. Bulk OM analysis

TOC (or  $C_{\text{org}}$ ) and total N (or  $N_{\text{total}}$ ) were determined after drying and powdering. TOC and total N were analyzed using a Fisons NA1500NCS elemental analyzer.

## 2.3. Chlorins

The sum of chlorophyll *a*, and its transformation products (pheophytin *a*, pyropheophytin *a*, pheophorbide *a* and pyropheophorbide *a*) for cores BIW95-5 and BIW95-B is expressed as “chlorins”.

Wet samples (1 g) were weighed into 10 ml glass centrifuge tubes. Pigments were extracted (3×) using 8 ml acetone with sonication in a Branson Sonifier for 15 min. After centrifugation for 10 min, the supernatant was decanted. Sonication and centrifugation were repeated (3×) and the supernatant collected in a 50 ml centrifuge bottle. The extracts were concentrated to 0.5 ml under  $N_2$ . The resultant solution was redissolved in 2 or 3 ml MeOH after addition of 30 μl IPCA (0.5 M tetra-*n*-butylammonium phosphate), and 5 μl of the internal standard (mesoporphyrin IX dimethyl ester; 48.9 mg 100 ml<sup>-1</sup> in benzene). The solution was centrifuged (3000 rpm, 15 min) and filtered with a GL-chromatodisc (pore size 0.2 μm, GL Science Co.) and used for instrumental analysis.

High performance liquid chromatography (HPLC) was performed in the reversed phase mode using an Inertsil ODS-2 15 cm × 4.6 mm (i.d.) column. Solvent mixtures and reagents were slight modified from the method of Bidigare et al. (1985). The elution gradient was programmed from 100% solvent A (80% MeOH, 20% 0.005 M tetra-*n*-butylammonium phosphate in water) to 100% solvent B (70% MeOH, 30% acetone) and isocratic elution

for 30 min at 1.2 ml min<sup>-1</sup>. Before the next injection, the column was re-equilibrated with the initial solvent for 10 min. Pigment peaks were quantified with a Hitachi model F1000 spectrofluorometer at excitation and emission wavelengths of 410 and 665 nm, respectively. Chromatograms with quantified data were stored using a Shimadzu Chromatopac model C-R7A.

Commercial chlorophyll *a*, pheophytin *a*, pheophorbide *a* were obtained from Wako Pure Chemicals Co., while pyropheophorbide *a* was from the Tama Biochemicals Co. The response factors of chlorophyllide *a* and pyropheophytin *a* were assumed to be the same as for pheophorbide *a* and pheophytin *a*, respectively.

#### 2.4. Sterols

The analytical procedure was slightly modified from that of Matsumoto et al. (2001). Wet samples (5 g) were weighed into 50 ml glass centrifuge bottles. MeOH (30 ml) was added and the mixture sonicated in a Branson Sonifier for 5 min and centrifuged at 2500 rpm for 10 min. The supernatant was collected. Sonication and centrifugation were repeated twice and the supernatants pooled in a 200 ml flask and concentrated to near dryness. To the sediment residue, benzene/MeOH (6/4 v:v, 30 ml) was added and the mixture sonicated for 10 min and centrifuged. The supernatant was added to the same 200 ml flask. These procedures were repeated (3×). The combined extracts were concentrated to 1 ml under N<sub>2</sub> and transferred to a 10 ml glass ampoule. The extract was concentrated to near dryness, 0.5 M NaOH/MeOH (5% water) was added and the ampoule closed and heated at 95 °C (2 h) to saponify the extract. The saponified extract was transferred to a separation funnel (200 ml) and 0.5 M NaOH solution (30 ml) was added. The mixture was extracted with *n*-hexane/diethyl ether (9:1, 30 ml) and agitated for 2 min. This extraction procedure was repeated (3×) to collect the neutral lipid extract.

The neutral extract was concentrated to near dryness, redissolved in a small volume of solvent and separated into four fractions (aliphatic hydrocarbons, aromatic hydrocarbons, aliphatic ketones and alcohols/sterols) by subsequent elution with *n*-hexane, *n*-hexane/benzene (3:1) benzene and benzene/MeOH (4:1) using a silica gel column. The alcohol/sterol fraction was concentrated to near dryness under N<sub>2</sub> and transferred to a 1 ml glass ampoule. An internal standard (30 μl *n*-C<sub>25</sub>H<sub>52</sub> in cyclohexane) was added and the fraction derivatized with *N,O*-bis(trimethylsilyl)acetamide (BSA, 70 μl) by heating the closed vial at 75 °C for 30 min.

Sterols were analyzed by using gas chromatography (GC) with a Hewlett-Packard 5890 series II gas chromatograph equipped with on-column injector and flame ionization detector. The derivatives were separated on a J & W Scientific DB-5 fused silica column (30 m × 0.32 mm i.d.; 0.25 μm film thickness). He was the carrier gas. The GC oven temperature was programmed as follows: 50–120 °C at 30 °C min<sup>-1</sup>, to 310 °C (held 30 min) at 6 °C min<sup>-1</sup>. Concentrations were calculated by comparing peak areas with that of the co-injected *n*-alkane C<sub>25</sub>H<sub>52</sub>. Sterols were also analyzed using gas chromatography–mass spectrometry (GC/MS). For quantifying concentrations, *m/z* 129 was used for 22-dehydrocholesterol, cholesterol, brassicasterol, campesterol, stigmasterol and β-sitosterol, *m/z* 215 for cholestanol and stigmastanol and *m/z* 271 for dinosterol.

#### 2.5. TMAH analysis of lignin phenols and alkanolic acids

Lignin phenols and alkanolic acids (*n*-C<sub>14</sub>–C<sub>30</sub>) were analyzed using an on-line TMAH (tetramethylammonium hydroxide) thermochemolysis procedure (Ishiwatari et al., 2006). Briefly, dry finely powdered sediment (<20 mg) on a pyrofoil was weighed precisely and a measured amount of TMAH (in MeOH) and an internal stan-

dard (e.g. *n*-C<sub>19</sub> alkanolic acid) were added. After the MeOH had evaporated, the pyrofoil was wrapped up and heated at 590 °C for 20 s in a Curie point pyrolyzer (JHP-3: Japan Analytical Industry Co.). The temperature of the reaction chamber was maintained at 270 °C. For GC/MS, the TMAH products were injected into a HP-5 GC column (30 m × 0.32 mm; film thickness 0.25 μm) via an interface (heated at 290 °C) between the pyrolyzer and gas chromatograph (Varian 3400) and analyzed using MS (Finnigan INCOS 50). The GC column temperature program was 50 °C (5 min) to 310 °C (held 20 min) at 6 °C min<sup>-1</sup>. Mass spectra (electron ionization mode) were obtained in the range 50–600 *m/z* at a scan rate of 0.5 s.

### 3. Results

#### 3.1. TOC and total N

TOC concentrations for most of the sediments range from ca. 10 mg g<sup>-1</sup> ds to ca. 20 mg g<sup>-1</sup> ds (dry sediment; Fig. 3a). Concentrations in the Holocene (shallower than 5.5 m depth) fluctuate around 20 mg g<sup>-1</sup> ds while those in the last glacial (below 5.5 m) fluctuate around 10 mg g<sup>-1</sup> ds. The vertical profile is similar to that in previous studies (e.g. Kawamura and Ishiwatari, 1984; Inouchi et al., 1995; Meyers and Horie, 1993; Yamada, 2004). Abrupt minima at ca. 11.3, 4.2 and 3.3 m correspond to the volcanic ash layers (Table 1). A strong TOC peak is observed at 4.77 m. Total N ranges from ca. 0.2 to 2.3 mg g<sup>-1</sup> ds (Fig. 3b), the profile being almost the same as that for TOC. A peak in total N occurs at 4.77 m and three minima in the volcanic ash layers.

#### 3.2. Chlorins

Chlorophyll *a*, pheophytin *a* and pyropheophytin *a* were observed, together with pheophorbide *a* and pyropheophorbide *a* in cores BIW95-5 and BIW95-B. Pheophytin *a* and pyropheophytin *a* comprise 60–70% of the chlorins in shallow sections (<20 cm) and the other chlorins are composed of chlorophyll *a* (12–19%) and chlorophyllide *a*, pheophorbide *a* and pyropheophorbide *a*. Below ca. 20 cm, pheophytin *a* plus pyropheophytin *a* comprise ca. 90% of the chlorins. The downcore pattern of chlorins shows higher values of 1–4.5 μg g<sup>-1</sup> ds in the upper 5 m sections corresponding to the Holocene and lower values (ca. 0.5 μg g<sup>-1</sup> ds) in the glacial (Fig. 3c). Extremely low concentrations occur in the volcanic ash layers (3.3 m and 11.3–10.8 m).

#### 3.3. OM accumulation

To quantify and obtain the true variability in sedimentary OM, we determined the mass accumulation rate (MAR) or flux of TOC and chlorins (Fig. 4). Determination of these MARs has not been reported for this lake. TOC-MAR or chlorin-MAR are calculated as the product of linear sedimentation rate (LSR), dry bulk density (DBD) and weight content of TOC or chlorins:

$$\begin{aligned} \text{TOC- or chlorin-MAR [g m}^{-2} \text{ yr}^{-1}] \\ = \text{LSR [cm (10}^3 \text{ yr)}^{-1}] \times \text{DBD [g cm}^{-3}] \\ \times \text{TOC or chlorins [mg or } \mu\text{g (g of dry sediment)}^{-1}] \end{aligned}$$

Linear sedimentation rates (LSRs) for the past 32 kyr are determined from the age model described above (Fig. 2). Five age control points are used. LSR for the uppermost 1.9 m sections is high (74.2 mm yr<sup>-1</sup>) and that for the other sections ranges from 28.7 to 48.8 mm yr<sup>-1</sup> (Fig. 4a). The LSR was assumed to be constant between each age control point. MAR ranges from 120 to 500 g m<sup>-2</sup> yr<sup>-1</sup>, giving maxima at around the last 3000 yr and at

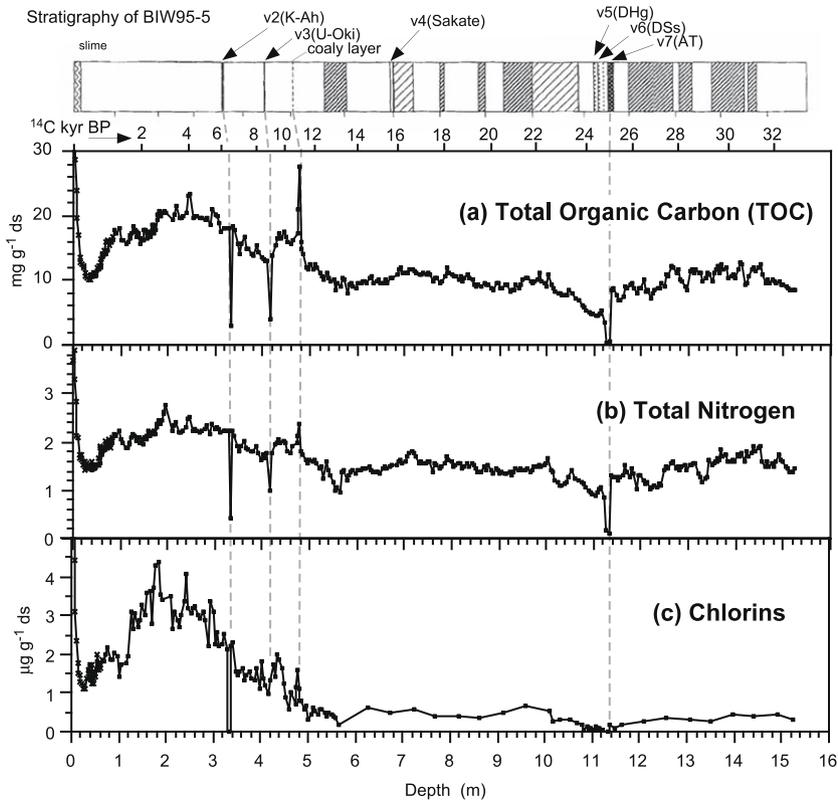


Fig. 3. (a) TOC, (b) total nitrogen and (c) chlorins in Lake Biwa sediments.

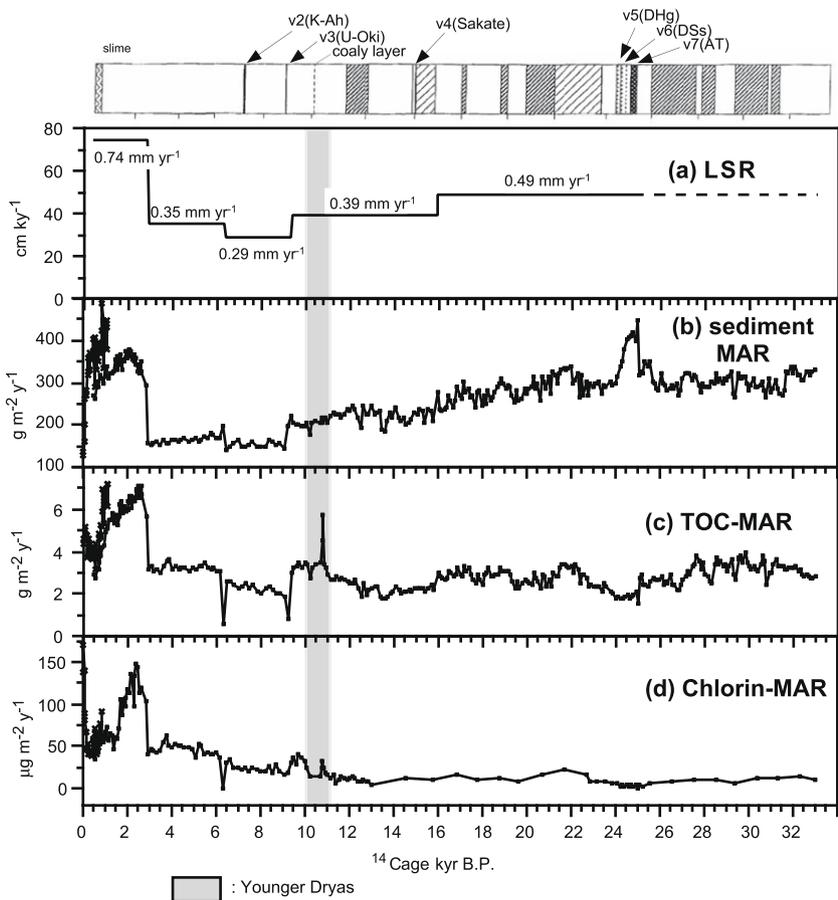


Fig. 4. (a) Linear sedimentation rate (LSR), (b) mass accumulation rate (MAR) of sediments, (c) total organic carbon MAR and (c) chlorin-MAR in Lake Biwa sediments.

25 kyr BP. The peak at 25 kyr BP corresponds to the fallout of AT volcanic ash (Fig. 4b). TOC-MAR ranges  $0.5\text{--}7\text{ g m}^{-2}\text{ yr}^{-1}$  and exhibits similar values of  $2\text{--}3\text{ g m}^{-2}\text{ yr}^{-1}$  from 32 to 3 kyr BP, except for abrupt minima and a maximum. It exhibits a broad maximum at 3000–1000 yr BP (Fig. 4c). Chlorin-MAR (Fig. 4d) ranges from 0 to  $170\text{ }\mu\text{g m}^{-2}\text{ yr}^{-1}$  and exhibits maxima at the surface and 3000–1500 yr BP. Chlorin-MAR is low at ca. 1000 yr BP and during the glacial.

#### 3.4. Contribution of terrigenous OM

TOC/ $N_{\text{total}}$  ratio (weight ratio, “C/N”, used hereafter) fluctuates between 7 and 9, with several exceptions at volcanic ash layers and other sections as described below. C/N values in the Holocene (above 5.5 m) are slightly higher than those in the glacial (Fig. 5a). C/N is commonly used to evaluate the source of TOC (algal derived vs. terrigenous OM). Meyers (2003) considers  $C/N_{\text{org}}$  of fresh algal OM to be 4–10. However, it is not easy to obtain a precise relative contribution of terrestrial vs. algal organic carbon from C/N values, because uncertainty must exist in the C/N ratio of the terrestrial end member when a single C/N value is used as the end member. In fact, terrestrial higher plants give a wide range of C/N values (17–550; e.g., Meyers and Ishiwatari, 1993; Meyers and Lallier-Vergès, 1999).

In order to estimate inorganic N within  $N_{\text{total}}$ , we plot total N concentration vs. TOC concentration. In the plot, we eliminate data points in several volcanic ash layers where the TOC content is

extremely low. The plot gives a good straight line, with an intercept for total N at  $0.48\text{ mg g}^{-1}\text{ ds}$ . Thus, we assume the presence of inorganic N of  $0.48\text{ mg g}^{-1}\text{ ds}$  for the whole sediment. Then,  $C/N_{\text{org}}$  (wt) values were calculated by subtracting  $0.48\text{ mg g}^{-1}\text{ ds}$  from each  $N_{\text{total}}$  value. Thus, average  $C/N_{\text{org}}$  values are  $10.5 \pm 1.3$  ( $n = 360$ ; Fig. 5b). In the next step, percentages of autochthonous (algal derived) organic carbon (%  $C_{\text{au}}$ ) in samples are calculated from the following equation on the assumption that  $C/N_{\text{org}}$  (wt) of algal derived OM [ $(C/N)_{\text{algal}}$ ] is 8 and that of terrigenous OM [ $(C/N)_{\text{terr}}$ ] is 25, which are adopted from our previous study (Ishiwatari et al., 2005):

$$\% C_{\text{au}} = [(C/N)_{\text{terr}} - (C/N)_{\text{sample}}] / [(C/N)_{\text{terr}} - (C/N)_{\text{algal}}] \times 100$$

The %  $C_{\text{au}}$  values calculated range from 33 to 100 ( $85 \pm 8\%$ ,  $n = 261$ ), excluding volcanic ash layers (Fig. 5c). Thus, we consider that the OM in the Lake Biwa core is essentially autochthonous (algal derived).

A temporal variation in chlorins/TOC (Fig. 5d) indicates that the values in the Holocene are two to four times higher than in the glacial. This might indicate that the production of algal derived OM was considerably higher in the Holocene than in the glacial. However, it should be taken into account that microbial and chemical degradation of chlorins may have caused a temporal decrease in chlorins/TOC (Sun et al., 1993a,b; Leavitt and Carpenter, 1990). In order to check whether the vertical profile of chlorins can be explained in terms of degradation, we examined the temporal variation in the chlorins/ $C_{\text{au}}$  ratio. A rate for chlorin degradation was

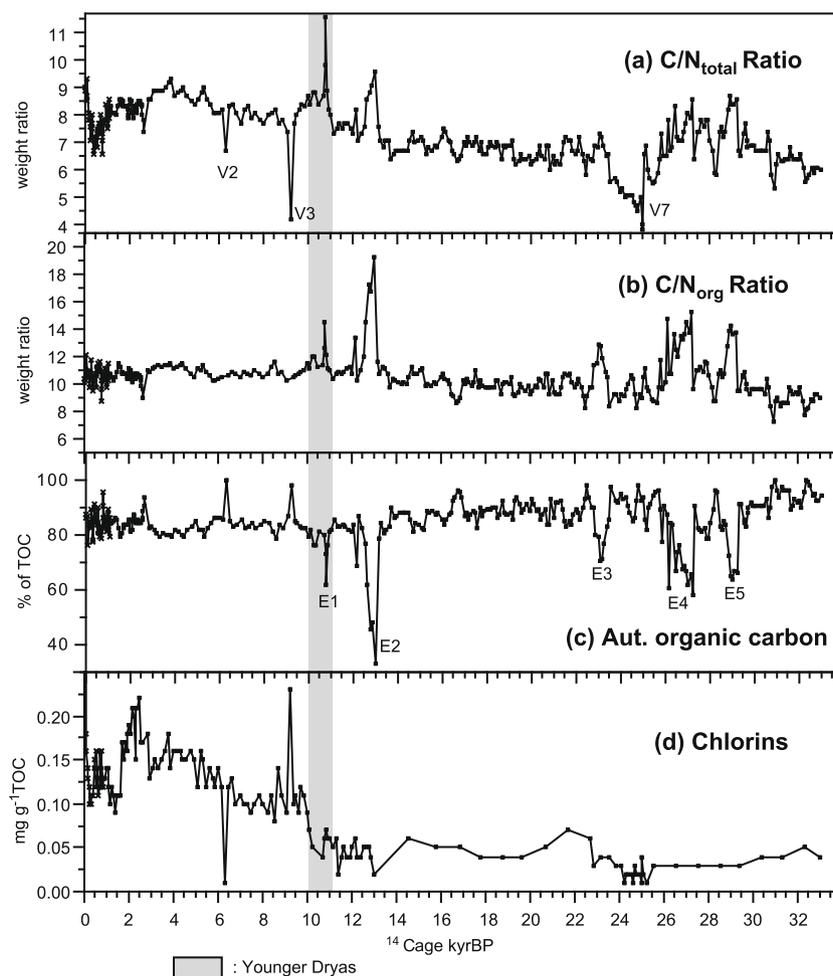


Fig. 5. (a) TOC/total N ratio, (b) TOC/organic N ratio, (c) autochthonous (algal derived) carbon in TOC and (d) TOC-normalized chlorins in Lake Biwa sediments.

calculated on the assumption that chlorin degradation reaction follows apparent first-order kinetics:

$$(\text{chlorins}/C_{\text{au}})_t = (\text{chlorins}/C_{\text{au}})_0 \times \exp[-kt]$$

where  $(\text{chlorins}/C_{\text{au}})_t$  = normalized total chlorins at time  $t$ ;  $t$  = year after sedimentation of chlorins (=0 at sediment surface) and  $k$  = first-order rate constant. The best fit least squares solution was obtained. In the calculation, the data points at the volcanic ash layers U-Oki (9.3 kyr BP) and around 25 kyr BP were omitted because chlorin/ $C_{\text{au}}$  values in these layers are unusually low, probably because of the presence of a high inorganic N content. The calculation gave the following results:

$$(\text{chlorins}/C_{\text{au}})_t = 18.2 \times \exp[-0.061t] \quad (r^2 = 0.57)$$

Half life = 11.4 kyr, where  $t$  =  $^{14}\text{C}$  age (kyr BP).

This implies that changes in the abundance of chlorins relative to  $C_{\text{au}}$  are controlled by microbial/chemical degradation. Therefore, we consider that realistic changes in paleoproductivity in the glacial can be drawn from reconstruction of chlorin content using the above equation.

### 3.5. Temporal variation in primary productivity

Primary productivity ( $P$ ,  $\text{g C m}^{-2} \text{yr}^{-1}$ ) was estimated using an equation developed by Müller and Suess (1979) for the marine environment:

$$P = (\% \text{ C} \times \text{DBD}) / (0.0030 \times S^{0.3})$$

where % C is the wt% of TOC in the sediment, DBD the dry bulk density ( $\text{g cm}^{-3}$ ) and  $S$  the sedimentation rate ( $\text{cm kyr}^{-1}$ ), respectively. The equation was established by comparison of accumulation rates of OC in open sea surface sediments with primary production rates. Williams et al. (1993) reported the estimation of primary productivity by applying the equation to surface sediments of Lake Baikal.

Their estimates are roughly consistent with modern observations (Meshcheryakova, 1993). Therefore, we assume that the equation is also applicable to other lake sediments (Ishiwatari et al., 2005). However, primary productivity was calculated by using algal derived organic carbon ( $C_{\text{au}}$ ) in the sediment instead of using TOC as proposed earlier. A problem with application of the equation to lake sediments is discussed below (Section 4.2).

Primary productivity estimated for Lake Biwa ranges from 30 to  $100 \text{ g C m}^{-2} \text{yr}^{-1}$  during the past 32 kyr, changing several times (Fig. 6a). For 32–25 kyr BP a broad peak (ca.  $70 \text{ g C m}^{-2} \text{yr}^{-1}$ ) with two minima (E4 and E5) occurs. For 24–13 kyr BP, productivity becomes low (ca.  $60 \text{ g C m}^{-2} \text{yr}^{-1}$ ) with two minima (E2 and E3). During 10–2 kyr BP in the Holocene, productivity becomes high ( $80\text{--}90 \text{ g C m}^{-2} \text{yr}^{-1}$ ) and then decreases after 2 kyr BP. Productivity becomes a minimum ( $\sim$ ca.  $40 \text{ g C m}^{-2} \text{yr}^{-1}$ ) around 0.5 kyr BP and then increases again to the present. The most recent primary productivity is estimated to be ca.  $50 \text{ g C m}^{-2} \text{yr}^{-1}$ , slightly lower than the modern value ( $60\text{--}70 \text{ g C m}^{-2} \text{yr}^{-1}$ ) reported as net productivity (Hayakawa, 2005).

Like the variation in carbon productivity (estimated from  $C_{\text{au}}$ ), “chlorin productivity” expressed as  $\text{mg total chlorins m}^{-2} \text{yr}^{-1}$  is higher in the Holocene and lower in the glacial (Fig. 6b). The difference in chlorin productivity between the Holocene and the glacial is greater than in the carbon productivity. The difference can be explained on the basis of selective decay of chlorins (Section 3.4). Fig. 6c shows temporal variations in chlorin productivity obtained by correction of the effect of post-burial degradation (expressed as “reconstructed chlorin productivity”). An approximately linear relationship exists between carbon ( $C_{\text{au}}$ ) productivity ( $Y$ ,  $\text{g m}^{-2} \text{yr}^{-1}$ ) and reconstructed chlorin productivity ( $X$ ,  $\text{mg m}^{-2} \text{yr}^{-1}$ ), expressed by the equation of  $Y = 4.3 \times 10^3 X$  ( $r^2 = 0.64$ ,  $n = 170$ ). Moreover, the temporal profiles of  $C_{\text{au}}$  and reconstructed chlorin productivity resemble closely that of fossil diatom valve flux from another Lake Biwa sediment core reported

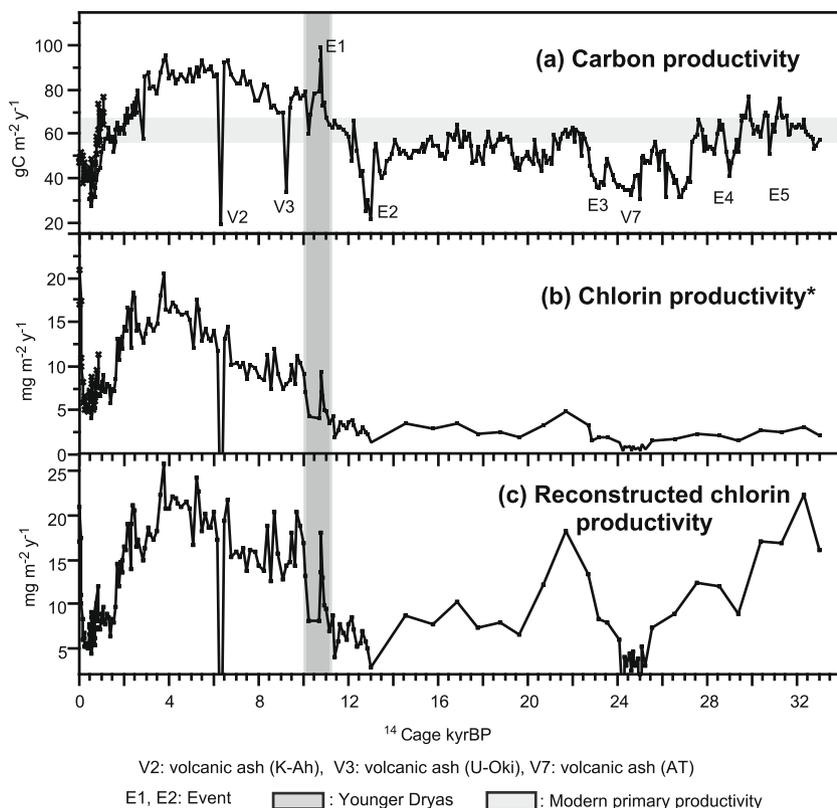


Fig. 6. Records of (a) carbon paleoproductivity, (b) chlorin productivity\* and (c) reconstructed chlorin productivity [\* effect of chlorin degradation not corrected for (see text)].

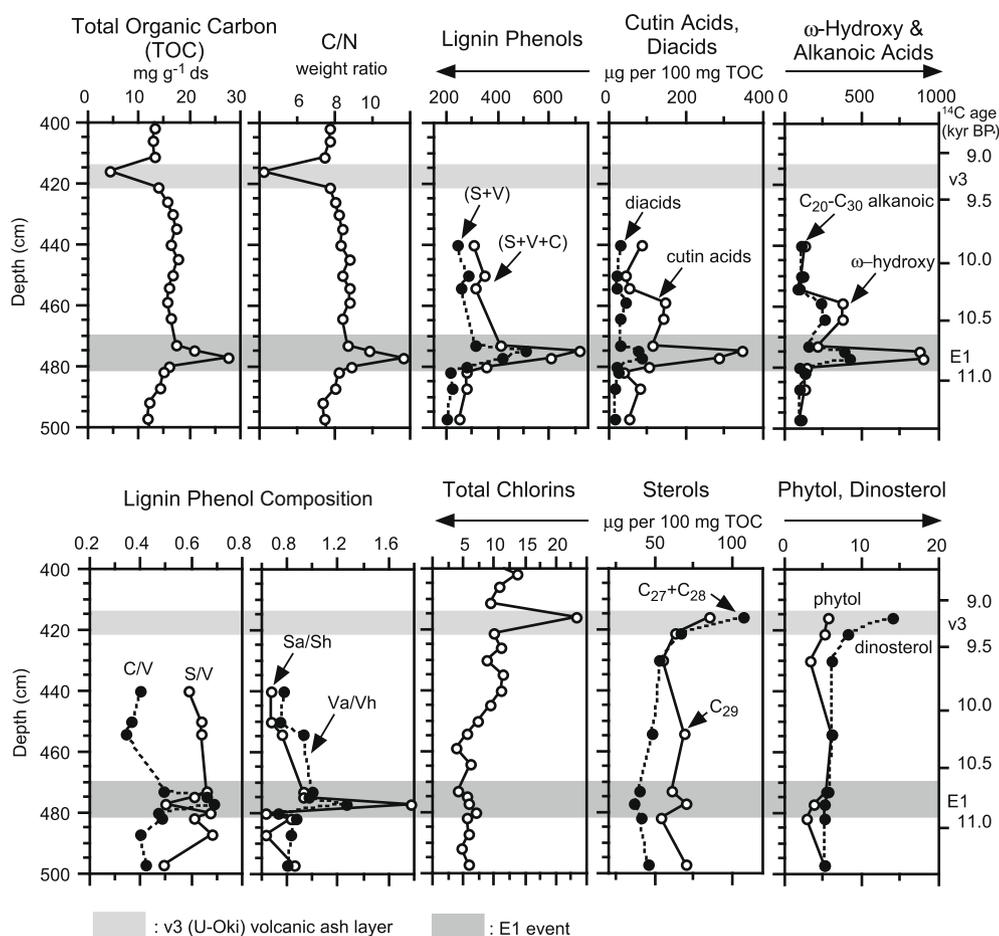


Fig. 7. Variation in biomarker parameters during 9–11  $^{14}\text{C}$  kyr BP.

by Kuwae et al. (2004), supporting strongly the reliability of temporal changes in estimated OM paleoproductivity. The average total diatom valve flux is ca.  $1 \times 10^7$  valves  $\text{cm}^{-2} \text{yr}^{-1}$  for the Holocene but ca.  $0.4 \times 10^7$  valves  $\text{cm}^{-2} \text{yr}^{-1}$  for the glacial (Kuwae et al., 2004).

### 3.6. Organic compound analysis of E1 layer

The E1 layer (ca. 5 cm thick), with high TOC concentration (21–28  $\text{mg g}^{-1} \text{ds}$ ) and high C/N value, occurs at ca. 10.8 kyr ( $^{14}\text{C}$  year) BP (Figs. 3 and 5). The high  $\text{C/N}_{\text{org}}$  value implies that the proportion of terrigenous OC in the TOC is high. This event is probably the same that observed by Meyers and Horie (1993) and Yamada (2004). Meyers and Horie (1993) observed an abrupt shift in  $\delta^{13}\text{C}_{\text{TOC}}$  value at the point corresponding to the E1 layer from ca.  $-21\text{‰}$  to ca.  $-25\text{‰}$ .

In order to obtain detailed information, we analyzed lipid biomarkers (sterols), lignin phenols, fatty acids, cutin acids from TMAH thermolysis in these and adjacent layers. The results in Fig. 7 reveal that the abundances of terrigenous biomarkers such as lignin phenols, cutin acids,  $\omega$ -hydroxy acids,  $\text{C}_{29}$  sterols (mostly ethylcholest-5-en-3 $\beta$ -ol and ethylcholesta-5, 22-dien-3 $\beta$ -ol) and  $n$ - $\text{C}_{27}$  to  $\text{C}_{31}$  alkanes (carbon preference index, CPI,  $4.2 \pm 0.2$ ) show strong peaks in this section. Therefore, we conclude that a large amount of terrigenous OM entered the lake. The relative concentration of terrigenous OC is estimated to be 40% vs. 20% in the other sections (Fig. 5c). Moreover, Va/Vh or Sa/Sh ratios (the acid/aldehyde ratio for vanillyl or syringyl phenol family) are high (1.3–1.8) in this layer, which is comparable to soil humic

substances (Ertel and Hedges, 1984). It is known that these ratios are generally low for fresh plant tissue and increase with oxidative microbial degradation (e.g. Hedges et al., 1988). Weight ratio values of total syringyl to total vanillyl phenols (S/V) are low and the ratio of cinnamyl phenols to total vanillyl phenols (C/V values) are high in the E1 layer, suggesting that the source of terrigenous OM is primarily non-woody material. Consequently, we conclude that the terrigenous OM in the E1 layer originates from surface soils with peat-like material and was probably transported via flooding. As shown in Fig. 6, it is suggested that carbon and chlorin paleoproductivity was enhanced at the E1 event as a result of input of nutrients from this terrestrial source.

## 4. Discussion

### 4.1. Factors controlling paleoproductivity of Lake Biwa: comparison with Lake Baikal

We reported (Ishiwatari et al., 2005) that the primary productivity of Lake Baikal (northern basin,  $55^\circ\text{N}$ ,  $109^\circ\text{E}$ ) situated in the boreal zone (Siberia) is considerably lower ( $<20 \text{ g C m}^{-2} \text{yr}^{-1}$ ) in the glacial than in the Holocene ( $50\text{--}120 \text{ g C m}^{-2} \text{yr}^{-1}$ ). Phytoplankton biomass in the glacial was estimated to be  $2 \text{ mg m}^{-3} \text{yr}^{-1}$  at 0–50 m water depth, in contrast to  $136 \text{ mg m}^{-3} \text{yr}^{-1}$  at present (Shimaraev et al., 1992).

The temporal profile of paleoproductivity of Lake Biwa in our study is markedly different from that of Lake Baikal, since carbon or chlorin paleoproductivity of Lake Biwa in the glacial is 1.5–2 times smaller than in the Holocene (Fig. 6). The high productiv-

ity of Lake Biwa during the glacial as compared with Lake Baikal might be predominantly associated with differences in climatic conditions (such as temperature and precipitation) in the two regions as described below, although lake size and water depth might also play an important role on the aquatic productivity. Lake Baikal has a big area of 31,500 km<sup>2</sup> (ca. 47 times larger than that of Lake Biwa) with a maximum water depth of 1637 m (16 times deeper than that of Lake Biwa). The marked contrast in paleoproductivity between the Holocene and the glacial periods for Lake Baikal is thought to have been caused by hydrodynamic systems which are sensitive to orbitally forced climatic changes (Prokopenko et al., 2001). According to Prokopenko et al. (2001), in the warm interglacial periods, the average temperature is high and the mesothermal density maximum layer becomes shallower. This phenomenon makes algae use nutrients effectively and be suspended for a longer time in the photic zone, resulting in high diatom productivity during the interglacial. In the glacial, on the other hand, it is difficult for diatoms to be sustained in the photic zone because of low thermocline temperature gradients and weak convection. Moreover, a deep mesothermal maximum layer prevents effective nutrient cycling and a long residence time of algae in the photic zone, resulting in low productivity during the glacial.

In the Lake Biwa region at present, average annual air temperature and precipitation are ca. 14 °C and ca. 1600 mm yr<sup>-1</sup>, respectively (Section 2.1). Fossil pollen studies inferred that mean air temperature during the glacial was 16–17 °C for the warmest month and -9 to -7 °C for the coldest, while precipitation from April to September was ca. 1000 mm (Nakagawa et al., 2008). These are essentially controlled by the activity of the East Asian monsoon (Nakagawa et al., 2008).

On the other hand, for Lake Baikal, both temperature and precipitation are low at present (average annual air temperature -1.6 °C and precipitation 340 mm yr<sup>-1</sup>) at the central part of the lake (Baikal Atlas, 1993). In the glacial, the air temperature was -8 °C (Sartanian, 24–11 kyr BP; Shimaraev et al., 1992). Precipitation during the glacial is unknown, but must have been much lower than in Lake Biwa, because the Lake Baikal area was under a strong influence of a continental (Siberian) air mass characterized by low humidity (Nakagawa et al., 2006).

In summary, the productivity in the glacial and the Holocene for Lake Biwa is essentially affected by East Asian monsoon activity. For Lake Baikal, the difference in productivity between the glacial and the Holocene must be controlled by both the continental (Siberia) climate regime and the hydrodynamic systems in the lake.

#### 4.2. Validity of equation for lake paleoproductivity

We reported a novel application of OM analysis to trace glacial/interglacial changes in lake paleoproductivity. The values obtained for both Lake Biwa and Lake Baikal during the glacial/interglacial periods seem to be reasonable, although further studies are necessary to establish the methodology (validity of the application of the equation for paleoproductivity originally established for the marine environment to the lake environment).

Here we raise one point which should be taken into account in applying the equation to lake sediments, that is, correction of excess water in calculating linear sedimentation rate (LSR). LSR is an important parameter in estimating paleoproductivity ( $P$ ), since  $P$  is inversely related to LSR in the equation as quoted in Section 3.5. For Lake Biwa, water content of the surface sediment is 84 wt% and decreases gradually with depth, becoming almost constant (ca. 59 wt%) at ca. 60 cm depth. Water content in the sections between 60 and 186 cm is  $59 \pm 1\%$  ( $n = 39$ ). Therefore, ca. 60 cm depth is regarded as the end of compaction. It is clear that the subsurface sediments are in a state of incomplete com-

paction. Therefore, we should subtract the water retained by incomplete compaction ("excess water") from the total water in the sediment to obtain an accurate linear sedimentation rate ( $S$  cm kyr<sup>-1</sup>). Thus, corrected LSR was calculated for each section (surface 60 cm) above the V1 volcanic ash layer (Kawagodaira: 2.85 kyr BP) for Lake Biwa. Revised values of carbon ( $C_{\text{au}}$ ) paleoproductivity obtained by using corrected LSR are 51–56 g C m<sup>-2</sup> yr<sup>-1</sup>, slightly (1–11%) higher than the uncorrected values of 47–52 g C m<sup>-2</sup> yr<sup>-1</sup>. Therefore, if the water content of the sediment is greater than ca. 60 wt%, correcting for excess water is recommended in order to obtain a precise LSR. For many marine sediments, compaction reaches a maximum within the upper 10 cm (Burdige, 2006).

#### 4.3. Geochemical and paleoenvironmental implications

##### 4.3.1. Terrigenous OM input events

The OM records suggest that the input of large amount of terrigenous OM to Lake Biwa, probably as a result of flooding, occurred at least five times during ca. 11–32 kyr: E1 (ca. 11 kyr BP), E2 (ca. 13 kyr BP), E3 (ca. 23 kyr BP), E4 (ca. 26–28 kyr BP) and E5 (ca. 29 kyr BP). The E1 event occurred during the Younger Dryas. A high C/N<sub>org</sub> value and low chlorins/TOC value for E2 layer implies a large contribution from terrigenous OM. Other peaks (E3–E4) with lower %  $C_{\text{au}}$  values also suggest enhanced terrestrial OM contribution, although low chlorin/TOC values are not observed. It is known that, during 32–24 kyr BP, millennial climatic oscillations occurred on a global scale (Dansgaard-Oeschger cycles). However, it is not certain whether the flooding events are related to these global climatic changes. Since the Lake Biwa region was under the influence of the East Asian monsoon, even in the glacial (Nakagawa et al., 2008), the flooding events are probably associated with significant precipitation under the summer monsoon.

##### 4.3.2. Possible cause for abrupt increase in sedimentation rate and burial of OM at ca. 3000 yr BP

The LSR and burial of OM increased abruptly at ca. 3000 yr BP. Thus, MAR of sediment, TOC and chlorins for sections above 2.11 m depth are approximately twice those of the lower sections (Fig. 4).

The high sedimentation rate might be associated with enhanced soil erosion and run-off, and agricultural activity around the lake. Paleogeographical studies indicate that the climate was cooler and humid, and that living conditions for humans became worse during 3000–2000 yr BP (Yasuda, 1990). Ca. 2300 yr ago (Yayoi period), agricultural techniques were imported from China and paddy-field rice cultivation began around the lake. Then, rice cultivation gradually expanded. This is evidenced by many remains of agriculture and villages found around the lake coast area (Lake Biwa Museum, 2008).

## 5. Conclusions

From studying vertical profiles of TOC, total N and photosynthetic pigments (chlorins) in Lake Biwa sediments deposited during the past 32 kyr, we reveal that:

- (i) TOC concentration ranges from ca. 10 to 20 mg g<sup>-1</sup> ds. The concentration in the Holocene fluctuates around 15–20 mg g<sup>-1</sup> ds, while TOC values are slightly lower during the glacial period. From C/N values, it is suggested that ca. 85% of TOC in the core is autochthonous (algal derived).
- (ii) The estimate indicates that primary productivity ranges from 50 to 90 g C m<sup>-2</sup> yr<sup>-1</sup> in the Holocene, while it is ca. 60 g C m<sup>-2</sup> yr<sup>-1</sup> on average in the last glacial. A temporal

change pattern in chlorin productivity obtained after correction of its post-depositional degradation agrees essentially with that of carbon productivity.

- (iii) The difference in primary productivity in Lake Biwa between the Holocene and the glacial exhibits a marked contrast to that of Lake Baikal, where productivity in the Holocene is three to eight times higher than in the glacial. This contrast between the two lakes may be associated with differences in climatic conditions such as temperature and precipitation. Precipitation at Lake Biwa is relatively large during the glacial to the Holocene because of the continuous influence of the East Asian monsoon. Precipitation for Lake Baikal is generally small because of controls by a continental (Siberia) climate regime. In addition, the difference in productivity between the glacial and the Holocene for Lake Baikal, may be controlled by the hydrodynamic systems in the lake.
- (iv) Large terrigenous OM input events to Lake Biwa occurred at least five times during ca. 11–32 kyr BP. These events suggest enhanced monsoon activity. Examination of biomarkers for an event occurring during the Younger Dryas may indicate that soil OM with peat-like material entered the lake via flooding.
- (v) An enhanced sedimentation rate in the last 3000 years may have been caused partially by agricultural activity around the lake.

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