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Temporal changes in the phytoplankton community of the southern basin of Lake Baikal over the last 24,000 years recorded by photosynthetic pigments in a sediment core

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Abstract

Photosynthetic pigments and other indicators of phytoplankton were analyzed in a dated undisturbed sediment core obtained from the southern basin of Lake Baikal to reveal temporal changes in the phytoplankton community in the lake through the last glacial/post-glacial transition. The sedimentation age of the core spans the last 24 ¹⁴C ka. Chlorophyll *a*, its derivatives, carotenoids and total organic carbon (TOC) started to increase after 15 ¹⁴C ka, and the onset of biogenic silica occurred at 10 ¹⁴C ka. This indicated that the post-glacial growth of diatoms was preceded by that of other phytoplankton groups. In the record of the pigments and TOC, a temporary decrease was observed in the period 11.5–10.5 ¹⁴C ka, corresponding to the Younger Dryas cold period. The similarity found between the depth profiles of pyropheophytin *a* and steryl chlorin esters formed through predation of phytoplankton by zooplankton and that of TOC suggested the important contribution of fecal pellets to sedimentary organic matter in the lake.

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1. Introduction

Temporal changes in the primary productivity of a lake ecosystem are commonly and conveniently deduced from the total organic carbon (TOC) or biogenic silica (BGS) contents of corresponding sediments. Sedimentary records of photosynthetic pigments have been studied as more direct and general indicators of the phytoplankton population to elucidate the response of a lake phytoplankton system to environmental changes (Watts et al., 1975; Griffiths and Edmonton, 1975; Griffiths, 1978; Züllig, 1981; Engstrom et al., 1985; Swain, 1985; Sanger, 1988; Soma et al., 1995; Wetzel, 2001). Recent developments in high-performance liquid chromatography have made it possible to analyze photosynthetic pigments readily and precisely (Mantoura

and Llewellyn, 1983; Goodwin and Britton, 1988; Wright, 1984; Wright and Jeffery, 1997).

We have applied this approach to sediments from Lake Baikal and have been able to detect chlorophyll derivatives and carotenoids from recent (Soma et al., 1996; Tani et al., 2001) or surficial (Soma et al., 2001a) sediments of this deep, oxic and oligotrophic lake. Using a dated sediment core obtained from the southern basin of the lake, representing the last glacial/post-glacial transition, we have shown that the profile of photosynthetic pigments changed significantly during this period (Tani et al., 2001). However, since the sediment core was taken at a site close to the southern coast with rather a steep slope, it was uncertain whether the core was representative of pelagic conditions in the lake.

Significant amounts of steryl chlorin esters (SCEs), formed through grazing of phytoplankton by zooplankton (Harradine et al., 1996; King and Wakeham, 1996; Talbot et al., 1999a,b, 2000), were found to be preserved in a long sediment core from Lake Baikal (the

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BDP98 core spanning 2.8 Ma), demonstrating that SCEs can usefully serve as stable paleolimnological indicators of phytoplankton community structure in lake ecosystems (Soma et al., 2001b). However, comparison between SCEs and other sedimentary pigments was not possible, because most pigments were not preserved in such ancient sediments from Lake Baikal.

In this report, we describe our investigation of a dated undisturbed sediment core which is considered to be more representative of the pelagic southern basin of Lake Baikal, covering the period of the last glacial/post-glacial transition and allowing us to examine the relationships among various photosynthetic pigments originating from different phytoplankton with a time resolution of 200–300 years. It will be shown that the sedimentary profiles of photosynthetic pigments such as carotenoids and chlorophyll derivatives including SCEs, as well as that of TOC during this period, are significantly different from that of BGS, which essentially reflects the diatom population. The importance of phytoplankton predation by zooplankton for the accumulation of organic matter in the bottom sediment and the relationship between sedimentary carotenoids and SCEs will also be discussed.

2. Materials and methods

2.1. Sediment core

A gravity core, Ver.99 G-6 (360 cm), collected at the southern basin of Lake Baikal (52°05'20"N, 105°50'24"E, water depth 200 m) on 7 July 1999, was used for analysis. A supplementary short core, Ver.99 M-6 (35 cm), was obtained by a multiple corer, which took surficial sediment with overlying water. The core samples were sliced into 3–5-cm sections for the gravity core and 2-cm sections for the short core immediately after sampling, and each slice was transferred to a plastic bag. The sliced sediment samples were then stored at –80 °C until analysis.

2.2. Analysis of photosynthetic pigment

Photosynthetic pigments in the sediment samples were analyzed by the method described previously (Soma et al., 1996) using a Shimadzu LC-10 liquid chromatography system with photodiode array (PDA) absorbance detection. For the reference compounds, commercially available chlorophyll *a*, chlorophyll *b*, pheophytin *a*, pheophytin *b*, pyropheophytin *a* and β -carotene were used. Concentrations of steryl chlorin esters transformed from chlorophyll *a* (SCEs-*a*) were determined as the sum of the pheophytin *a* derivatives eluted after pyropheophytin *a* in the HPLC analysis (Eckardt et al., 1991, 1992; King and Repeta, 1991;

Prowse and Maxwell, 1991) by assuming their absorption coefficients at 400 nm were the same as that of pyropheophytin *a*. The concentration of the steryl ester of pyropheophorbide *b* (SCE-*b*) eluted after pyropheophytins *a* and *b* in the reverse-phase HPLC analysis (Talbot et al., 1999b) was also determined by assuming its absorption coefficient at 440 nm was the same as that of pheophytin *b*.

After extraction of pigments, the residual sediment was oven-dried and suspended in pure water with ultrasonication, followed by determination of particle size distribution by wet-sieving (<45 μ m, 45–75 μ m, 75–212 μ m and > 212 μ m).

2.3. Biogenic silica and total organic carbon

BGS was extracted using 2 M Na₂CO₃ solution at 85 °C for 5 h after treatment of the oven-dried samples in 10% H₂O₂ for 30 min and 2 M HCl for 30 min (Mortlock and Floeich, 1989). The concentration of dissolved Si was determined by an atomic absorption spectrometer (Perkin-Elmer AAS 3300) with an N₂O-acetylene high-temperature burner system. TOC was determined by a TOC analyzer (Shimadzu, TOC5000A-SSM5000A) after treatment in 2 M HCl overnight followed by three washes with pure water.

2.4. ¹⁴C age

¹⁴C age was measured for five layers of core G-6 at 0–3 (G6–1), 78–83 (G6–25), 158–163 (G6–41), 238–243 (G6–57) and 308–313 cm (G6–71) using an accelerator mass spectrometer (AMS) at the National Institute for Environmental Studies (NIES-TERRA; Kume et al., 1997; Yoneda et al., 1998).

Sediment samples were treated with 6 M HCl at 80 °C until dryness to remove inorganic carbon. The acid-pretreated samples containing about 0.4 mg of organic carbon were heated at 900 °C for 8 h with 0.5 g of Cu, 1 g of CuO and a small piece (ca. 0.5 mm × 5 mm × 0.01 mm) of Ag foil in a sealed quartz tube to convert organic carbon to CO₂. The CO₂ thus produced was purified cryogenically using liquid N₂ and a mixture of CH₃OH and dry ice in a vacuum line, and then converted to graphite on an iron powder catalyst (1 mg) by reduction with H₂ at 470 °C for 2 h.

¹⁴C/¹²C ratios were corrected into the conventional ¹⁴C ages by δ^{13} C values determined by ¹²C and ¹³C measurements of AMS (Stuiver and Polach, 1977). Furthermore, the age calibration was conducted using a calibration program, OxCAL ver. 3.5 (Bronk Ramsey, 1995), and the latest calibration curve (INTCAL98: Stuiver et al., 1998) for four results except for G6–71 (303–308 cm). Because the consensus calibration data beyond 24,000 calBP have not been reported, we used a dataset of varved sediments from Lake Suigetsu for

preliminary calibration of G6–71 (Kitagawa and van der Plicht, 2000).

3. Results and discussion

3.1. AMS ^{14}C age of core G-6

The conventional ^{14}C ages for core G-6 together with $\delta^{13}\text{C}$ values are listed in Table 1. The average sedimentation rates were 17.5 cm/kyear (1.5–80.5 cm), 12.0 cm/kyear (80.5–160.5 cm), 13.9 cm/kyear (160.5–240.5 cm) and 20.5 cm/kyear (240.5–306.5 cm) based on the conventional ^{14}C age (Fig. 1a). Since the age of the lowest part of core G-6 corresponded to about 24.8 ^{14}C ka, the age of core G-6 spanned the transition from the last glacial to post-glacial period.

The top layer of core G-6 was lost during sampling. By comparing depth profiles of water contents, particle size distributions, TOC and BGS in multiple core M-6 with those in the upper part of gravity core G-6 carefully, we estimated the length of the missing top sediment layer of G-6 to be about 10 cm. From the estimated length of the missing layer and extrapolation of the ^{14}C data for the sedimentation rate of the upper part of core G-6 (Table 1), the apparent ^{14}C age of the surficial sediment at the sampling point was 1192 year BP. Nakamura and Oda (1998) reported that the apparent AMS ^{14}C ages of the surficial sediments (0–2 cm) were normally within the range 0.5–1.5 ^{14}C ka

throughout Lake Baikal. This age discrepancy for surface sediments in Lake Baikal may include an offset between atmospheric and lacustrine ^{14}C ages, the so-called reservoir effect. Because any reservoir effect in Lake Baikal has not been evaluated, we tentatively corrected the ^{14}C ages for a reservoir age of 1192 year BP and converted them to calBP (Table 1). Therefore this report uses the conventional ^{14}C age without any corrections, unless otherwise noted.

Water content gradually increased upward (Fig. 1b), and fine particles (<45 μm) dominated (more than 80%) the sediment throughout core G-6 (Fig. 1c). These findings suggested an absence in this core of turbidite layers with a high content of coarse sand, which sometimes characterize bottom sediments of Lake Baikal (Kuzumin et al., 2000). Thus core G-6 offered an unperturbed sedimentary record with a time resolution of 200–300 years.

3.2. Profiles of chlorophyll derivatives, TOC and BGS in the sediment core

A typical HPLC chromatogram of an extract from core G-6 is shown in Fig. 2. We denote the summed concentration of chlorophyll *a* and its derivatives as total chlorophyll *a* (Fig. 3a). Chlorophyll *a* (Fig. 3b) and its derivatives, including pheophorbide *a* methyl ester (Fig. 3c), pheophytin *a* (Fig. 3d), pyropheophytin *a* (Fig. 3e) and steryl chlorin esters (SCEs-*a*; Fig. 3f), were detected in core G-6 in accordance with previous studies

Table 1
AMS dating obtained for core G-6

Sample (Lab. Code. No)	Depth (cm)	$\delta^{13}\text{C}$ (‰)±error (1 σ)	Conventional ^{14}C age (BP)±error (1 σ)	Calibrated age ^{a,b}	Calibrated age ^{a,c}
				calBP [probability (%)]	calBP [probability (%)]
G6–1 (TERRA-b011300a07)	0–3	–25.2±3.5	1851±182	791–501 (68.2)	
G6–25 (TERRA-b011300a08)	78–83	–24.6±3.9	6377±129	6170–6146 (5.0) 6112–6071 (7.6) 6060–6041 (3.2) 6030–6010 (3.4) 6002–5858 (33.5) 5830–5750 (15.5)	
G6–41 (TERRA-b011300a09)	158–163	–23.2±3.6	13,023±153	14,076–13,774 (42.4) 13,702–13,507 (25.8)	
G6–57 (TERRA-b011300a10)	238–243	–19.9±2.9	18,999±205	21,574–20,769 (68.2)	21,663–21,454 (15.3) 21,291–21,170 (8.8) 21,113–20,858 (20.0) 20,628–20,349 (24.1) 25,193–24,465 (68.2)
G6–71 (TERRA-b011300a15)	308–313	–21.4±2.0	22,174±249		

^a The ^{14}C ages were corrected for the reservoir age (1192 years; see text) and calibrated with the program OxCAL ver. 3.5 (Bronk Ramsey, 1995).

^b The latest calibration curve (INTCAL98; Stuiver et al., 1998) was used.

^c A dataset of varved sediments from Lake Suigetsu (Kitagawa and van der Plicht, 2000) was used.

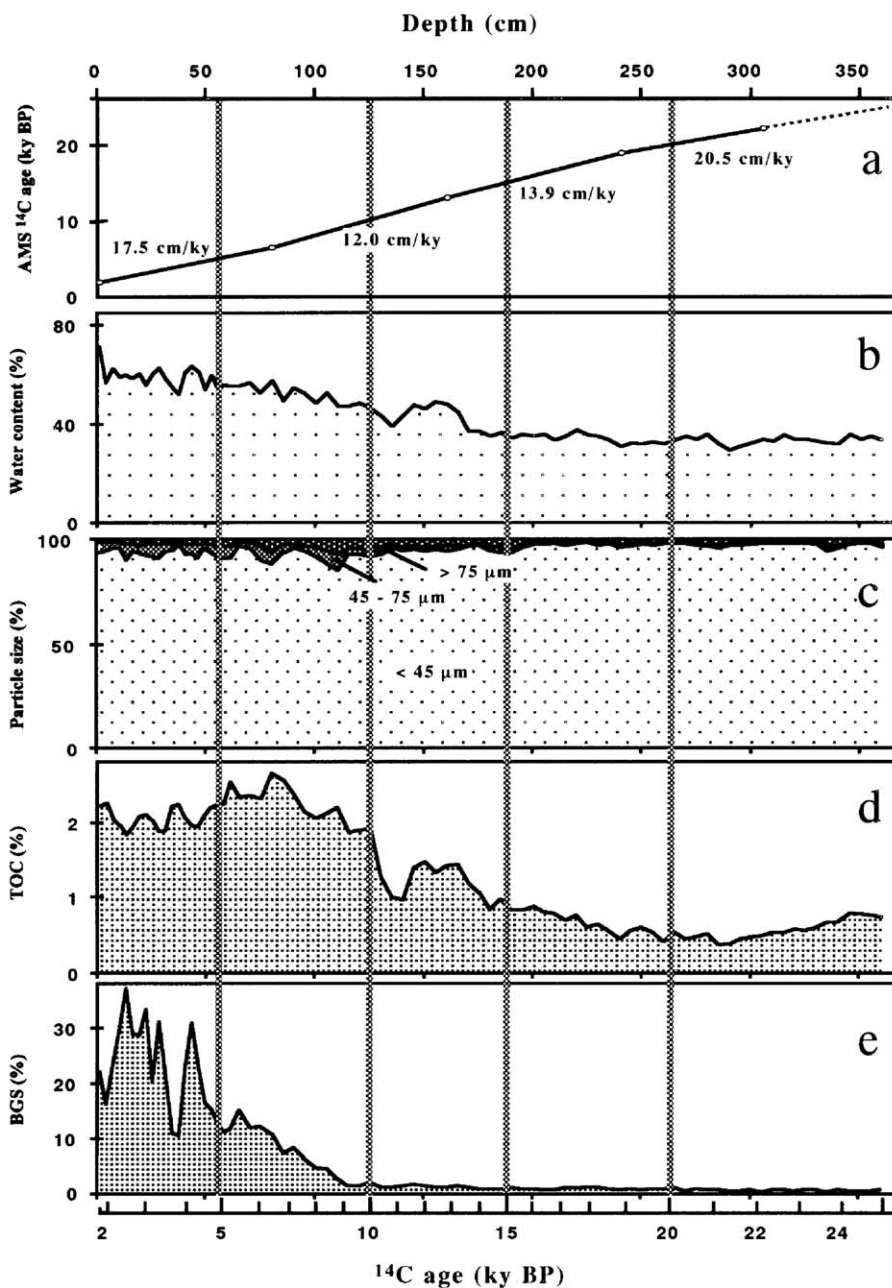


Fig. 1. Depth profiles of fundamental parameters in core G-6. a; sedimentation rate, b; water content, c; particle size distribution, d; TOC and e; BGS.

of Lake Baikal sediments (Soma et al., 1996; Tani et al., 2001). SCEs-*a* are sterol esters of pyropheophorbide *a*, in which the phytol moiety of pyropheophytin *a* is replaced by sterol moieties, and are formed as a result of predation of phytoplankton by zooplankton and excreted in fecal pellets (Harradine et al., 1996; King and Wakeham, 1996; Talbot et al., 1999a, b, 2000). The presence of SCEs in Lake Baikal sediment has already

been reported briefly (Naylor and Keely, 1998; Tani et al., 2001). SCEs-*a* have also been found in a long sediment core from Lake Baikal (BDP98; Soma et al., 2001b).

The chlorophyll *b* derivatives, pheophytin *b* and pyropheophytin *b*, were detected (Figs. 2 and 3g) together with a smaller amount of the sterol ester of pyropheophorbide *b* (SCE-*b*; Fig. 3h), which was eluted

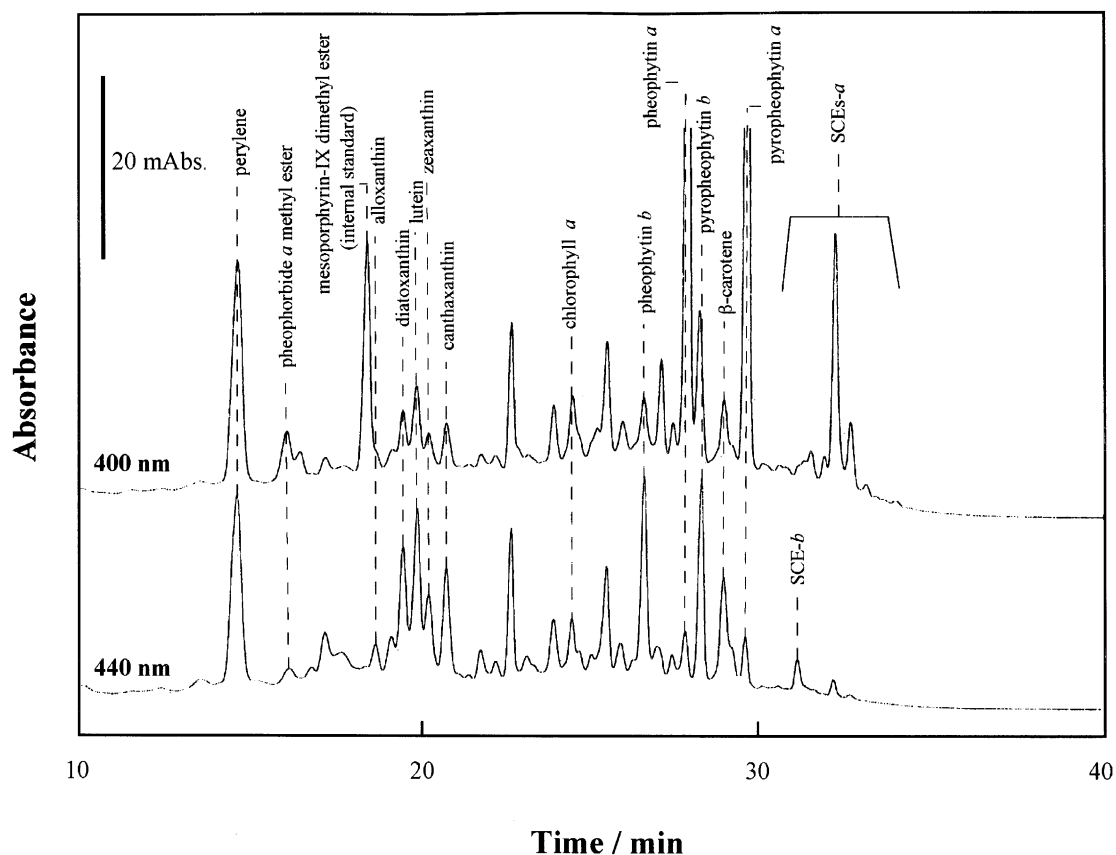


Fig. 2. Typical HPLC chromatograms of an extract of core G-6 at a depth of 42–45 cm.

after pyropheophytins *a* and *b* (Talbot et al., 1999b). SCE-*b* has been found in deeper sediments of Lake Baikal (Soma et al., 2001b). Total chlorophyll *b* (pheophytin *b* + pyropheophytin *b* + SCE-*b*; Fig. 3g) was an order of magnitude less than total chlorophyll *a* (Fig. 2a) throughout core G-6.

The trends in TOC (Fig. 1d), BGS (Fig. 1e) and chlorophyll derivatives (Fig. 3a–g) from past to present show that all of those indicator substances increased in recent times starting between 15 and 10 ¹⁴C ka. This is consistent with the increased lake productivity during the post-glacial period. Fig. 4 shows the relative concentrations of chlorophyll *a* and its derivatives in core G-6. Pheophorbide *a* methyl ester was relatively high in the uppermost layer of the sediment (22–30% at 0–9 cm) and then immediately decreased with depth (to less than 10%). Pheophytin *a* exhibited a gradual decrease in relative abundance with depth. In contrast, pyropheophytin *a* and SCEs-*a* increased with depth and their abundance relative to total chlorophyll *a* exceeded 70%. These changes in the relative concentrations of individual chlorophyll *a* derivatives may reflect the long-term stabilities of these derivatives in the sediments of Lake Baikal, i.e., SCEs-*a* > pyropheophytin *a* > pheo-

phytin *a* >> pheophorbide *a* methyl ester. This order of stability corresponds to the lipophilicities of these derivatives, i.e., their order of reverse-phase HPLC elution. This suggests that a faster post-depositional loss of less lipophilic derivatives, i.e. pheophorbide *a* methyl ester, occurred in the sediment, whereas lipophilic derivatives, i.e. pyropheophytin *a* and especially SCEs-*a*, were relatively preserved. The relative stability of SCEs has been demonstrated in a laboratory experiment (Talbot et al., 1999a) and in sediments (Prowse and Maxwell, 1991; Soma et al., 2001b). Soma et al. (2001b) showed that SCEs-*a* and pyropheophytin *a* were dominant chlorophyll *a* derivatives in deeper layers of sediment in Lake Baikal, whose age spanned 2.8 million years. The present study has shown that pyropheophytin *a* and SCEs-*a* are the dominant chlorophyll *a* derivatives in Lake Baikal sediments whose ages exceed 10–15 ¹⁴C ka. Thus pyropheophytin *a* and SCEs-*a* are more appropriate biogenic indicators for reconstructing the long-term history of phytoplankton productivity in Lake Baikal.

Table 2 shows the correlation between TOC and individual chlorophyll *a* derivatives throughout core G-6. Notably, SCEs-*a* and pyropheophytin *a* showed the

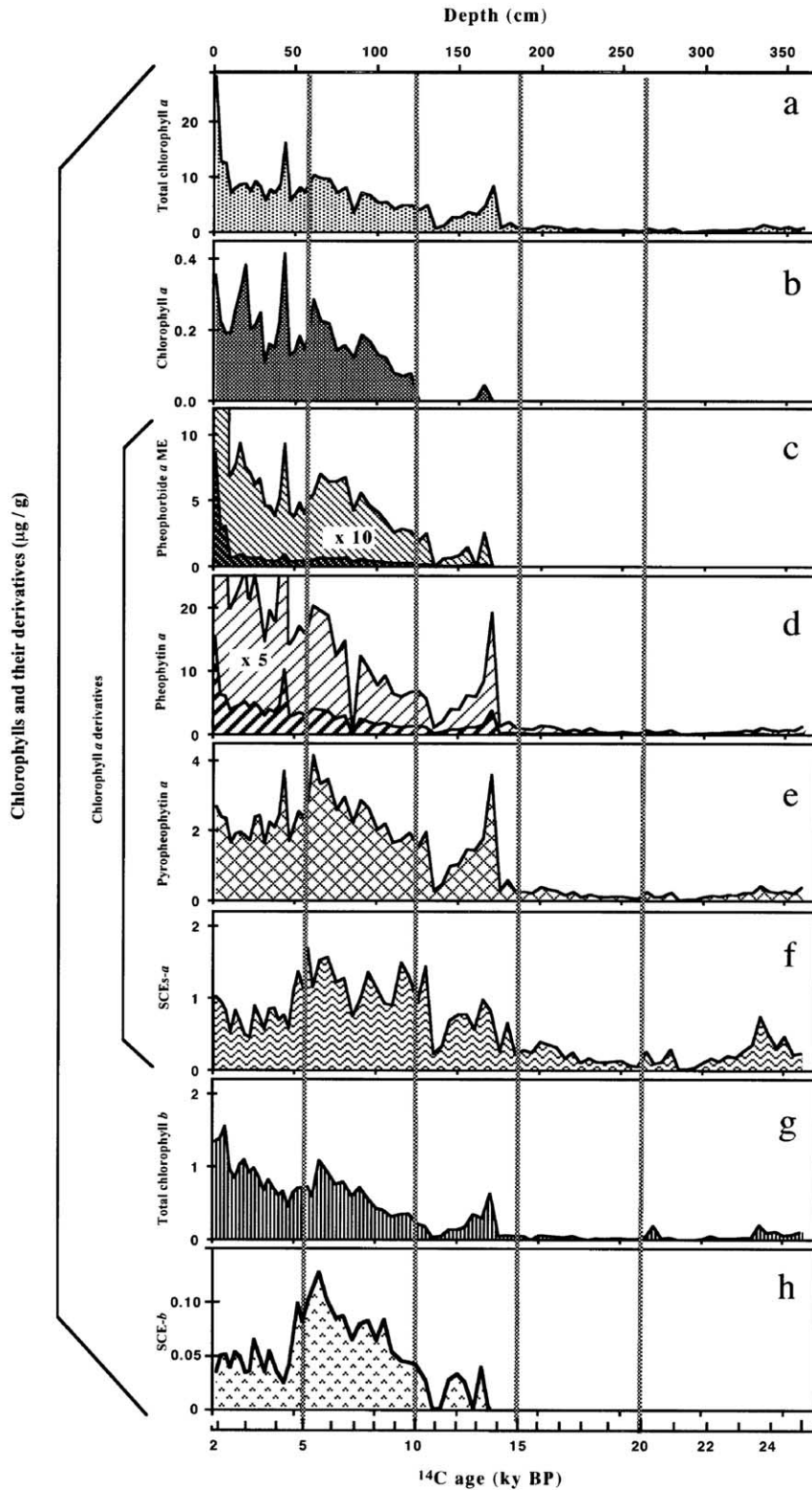


Fig. 3. Depth profiles of chlorophyll derivatives in core G-6. a; total chlorophyll *a*, b; intact chlorophyll *a*, c; pheophorbide *a* methyl ester, d; pheophytin *a*, e; pyropheophytin *a*, f; SCEs-*a*, g; total chlorophyll *b* and h; SCE-*b*.

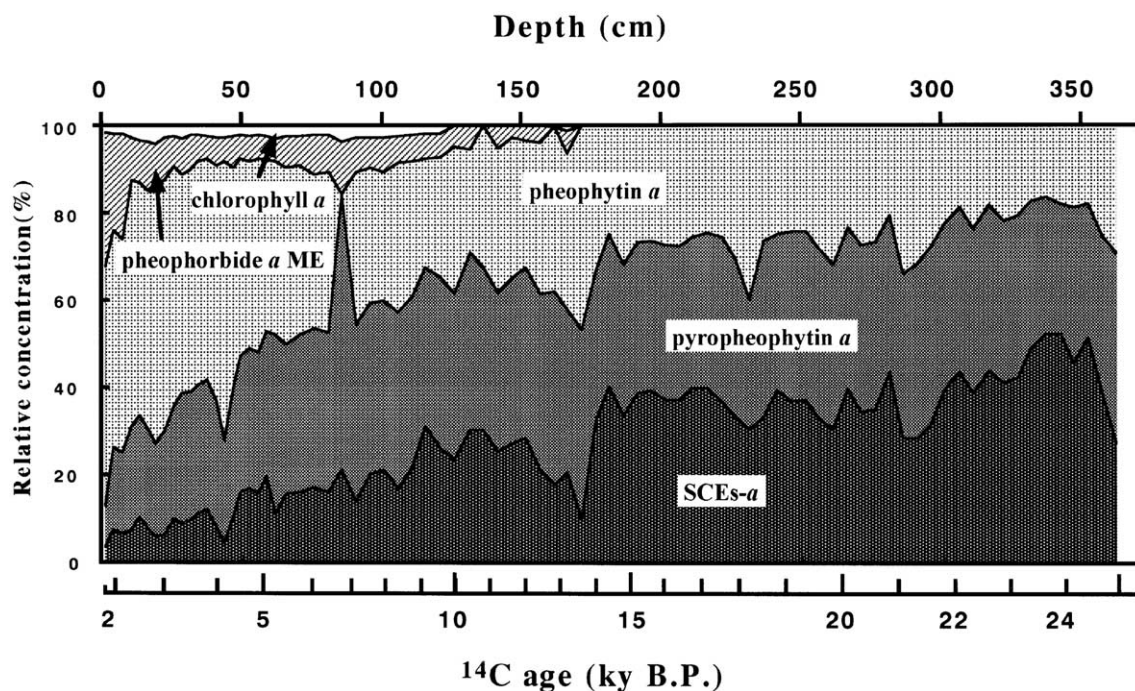


Fig. 4. Relative concentrations of chlorophyll *a* derivatives in core G-6.

Table 2

Correlation coefficients between TOC and chlorophyll *a* derivatives in core G-6 ($n=81$)

	TOC	Chlorophyll <i>a</i>	Pheophorbide <i>a</i> ME	Pheophytin <i>a</i>	Pyropheophytin <i>a</i>	SCEs- <i>a</i>
TOC	1.00					
Chlorophyll <i>a</i>	0.80	1.00				
Pheophorbide <i>a</i> ME	0.41	0.56	1.00			
Pheophytin <i>a</i>	0.67	0.87	0.82	1.00		
Pyropheophytin <i>a</i>	0.91	0.81	0.40	0.73	1.00	
SCEs- <i>a</i>	0.84	0.58	0.31	0.51	0.86	1.00

highest positive correlations with TOC ($R=0.84$ and 0.91 , respectively). Fig. 5 shows the higher correlation between TOC and sum of SCEs-*a* and pyropheophytin *a*. Since SCEs-*a* and pyropheophytin *a* are the main products formed from phytoplankton chlorophyll *a* by the grazing process (Harradine et al., 1996; Talbot et al., 1999a), these results indicate that the extent of grazing of phytoplankton by zooplankton and the succeeding fecal transportation are closely related to the accumulation of TOC, as well as chlorophyll derivatives in the sediment of Lake Baikal. Rapidly sinking fecal pellets carry the pigments out of the photic zone where otherwise photo-oxidation would completely degrade chlorophyll derivatives to colorless compounds within a few days (Carpenter et al., 1986; Nelson, 1993; Sun et al., 1993), and thus augment the accumulation of SCEs in the sediment, aided by their post-depositional stability (Soma et al., 2001b).

The data for BGS and TOC are plotted in Fig. 6. The data after 6^{14}C ka, where BGS accumulation was high (Fig. 1e), and those before, are distinguished by different symbols. After 6^{14}C ka, TOC showed negative dependence on BGS with a correlation coefficient $R=-0.84$. BGS also showed a negative correlation with SCEs-*a* ($R=-0.71$) and pyropheophytin *a* ($R=-0.43$). While BGS and TOC have been considered to indicate increased biological activity during the Holocene in Lake Baikal (Qiu et al., 1993; Carter and Colman, 1994; Horiuchi et al., 2000), the negative correlation between BGS and TOC indicates that the contribution of diatom residues to TOC was small, whereas the contribution due to dilution of TOC by BGS was significant. This suggests that, although diatoms are known to be the dominant algae in Lake Baikal at present (Kozhova and Izmet'eva, 1998), most of the BGS sedimentation was not accompanied by effective sedimentation of organic

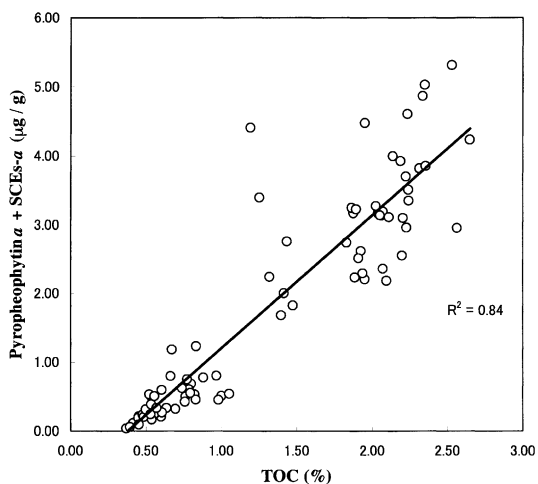


Fig. 5. Relationship between TOC and pyropheophytin *a* + SCEs-*a* in core G-6.

carbon produced by diatoms. A negative correlation between BGS and TOC in the surficial sediments of Lake Baikal has been reported previously (Williams et al., 1993).

BGS started to increase after about 10 ¹⁴C ka, while the chlorophyll *a* derivatives and TOC started to increase significantly as early as 15 ¹⁴C ka (Figs. 1d, 1e and 3b–f). The latter indicators decreased temporarily once between 11.5 and 10.5 ¹⁴C ka and then increased

again (Figs. 1d and 3b–f). The partial dissolution of BGS (diatom frustules; Ryves et al., 2001) might affect the amount of residual sedimentary BGS. However, since the TOC level was high and stable between 10 and 5 ¹⁴C ka, it is unlikely the more significant change in BGS during this period was due to the changes in the amount of BGS dissolved.

3.3. Carotenoid distribution in the core

Major carotenoids detected (Figs. 2 and 7), indicative of various phytoplankton taxa (Young, 1993; van den Hock et al., 1995; Jeffrey and Vesik, 1997), including diatoxanthin (diatoms, Dinophyta, and Chrysophyceae), lutein (green algae), canthaxanthin (cyanobacteria), zeaxanthin (cyanobacteria and green algae), alloxanthin (Cryptophyceae) and β -carotene (ubiquitous; Fig. 2), were in agreement with previous reports (Soma et al., 1996; Tani et al., 2001). Fig. 7 shows the depth profiles of these carotenoids in core G-6, where total carotenoids (Fig. 7a) represents the summed concentrations of all carotenoids. All the carotenoids except for alloxanthin increased in the sediment above the detection level after 15 ¹⁴C ka (Fig. 7b–g), demonstrating directly the contribution of the relevant algae to the increase in primary productivity. While alloxanthin, diatoxanthin and canthaxanthin are of definite phytoplankton origin, lutein, zeaxanthin and β -carotene are found not only in phytoplankton but also in higher land

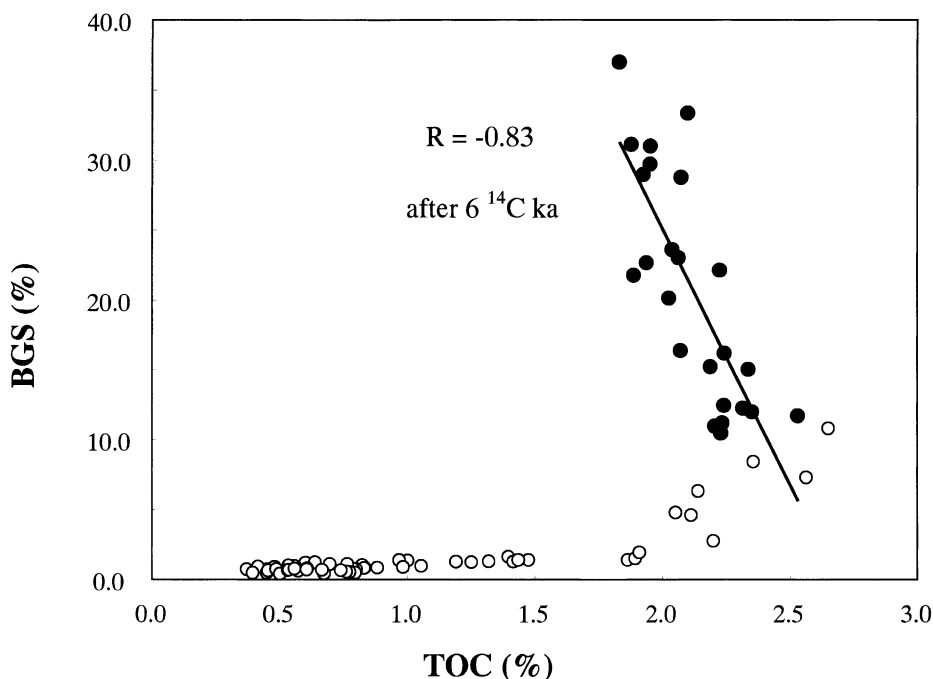


Fig. 6. Relationship between TOC and BGS in core G-6. ●; after 6 ¹⁴C ka, ○ before 6 ¹⁴C ka.

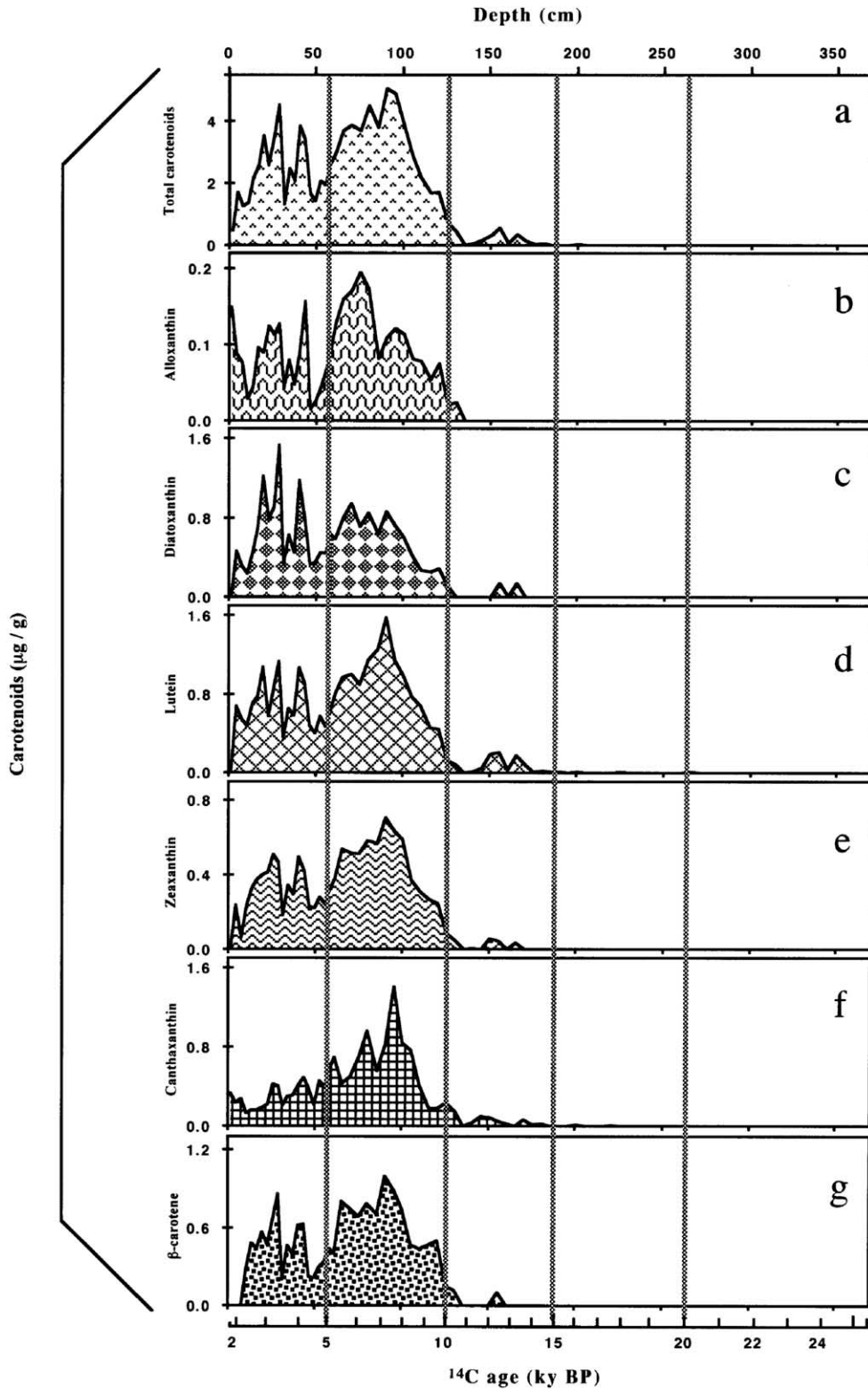


Fig. 7. Depth profiles of carotenoids in core G-6. a; total carotenoids, b; alloxanthin, c; diatoxanthin, d; lutein, e; zeaxanthin, f; canthaxanthin and g; β-carotene.

plants. However, carotenoids in leaves of higher land plant are generally considered to decompose on their way to the lake bottom (Swain, 1985; Sanger, 1988). Moreover, their depth profiles in core G-6 were similar to those of other carotenoids of phytoplankton origin (Fig. 7b–g). Accordingly, they are also attributed to the relevant phytoplankton.

The detailed distributions of the carotenoids, however, were different. Diatoxanthin, which is contained in diatoms, Dinophyta and Chrysophyceae, was maximal after 4 ^{14}C ka, the period when BGS exhibited a marked increase (Fig. 7c). However, the other carotenoids showed a maximum before that time. Alloxanthin (Cryptophyceae) showed a maximum at 75 cm (6 ^{14}C ka; Fig. 7b), lutein (green algae) and zeaxanthin (cyanobacteria) at 88 cm (7 ^{14}C ka; Fig. 7d and 7e, respectively) and canthaxanthin (cyanobacteria) at 93 cm (7.5 ^{14}C ka; Fig. 7f). Notably, while the concentration of canthaxanthin was high at a depth of around 90 cm, it was low above 50 cm as compared with the other carotenoids.

3.4. Primary productivity after 15 ^{14}C ka during the post-glaciation

Amounts of residual photosynthetic pigments in lake sediment depend not only on their production in water but also their whole fate during transportation to the sediment (Carpenter et al., 1986; Nelson, 1989; Leavitt and Brown, 1988; Leavitt and Carpenter, 1990; Nelson, 1993; Wetzel, 2001) and during diagenetic modification within the sediment (Swain, 1985; Furlong and Carpenter, 1988; Villanueva et al., 1994). As described above, predation of phytoplankton by zooplankton and fecal transportation play important roles in the accumulation of organic carbon in the sediment of Lake Baikal. Grazing selectivity (Burkill et al., 1987) should bias phytoplankton-dependent carotenoid distributions in the sediment from those expected from the phytoplankton composition in water. Although the carotenoid distribution in the sediments may be a consequence of such complex processes in the water column and sediments, we can summarize the changes in the phytoplankton population of Lake Baikal during the post-glacial period from the variation of TOC, BGS and photosynthetic pigments with depth in core G-6, described above, assuming that all photosynthetic pigments in the sediment are of autochthonous phytoplankton origin.

After 15 ^{14}C ka, the lake productivity, which had previously been low, began to increase. During the period between 15 and 5 ^{14}C ka, algal groups such as green algae, cyanobacteria, Dinophyta, and Cryptophyceae, rather than diatoms, dominantly contributed to the primary productivity. The contribution reached maximum around 8 to 6 ^{14}C ka and then gradually diminished. In turn, diatoms gradually increased to reach a maximum after 4 ^{14}C ka and became the major primary producers.

The period during which the carotenoids, except for diatoxanthin, showed maximum concentrations coincides with the so-called climate optimum of the post-glacial period at 6000 to 7000 year BP (Parker, 2000). The increase in diatoms in Lake Baikal, which was reflected in core G-6 by increases in BGS and diatoxanthin (although several other algal groups also contain diatoxanthin), after the climate optimum has been reported previously (Qiu et al., 1993; Carter and Colman, 1994; Horiuchi et al., 2000; Karabanov et al., 2000). Karabanov et al. (2000) attributed this delay in the BGS increase to the delayed climatic optimum in the Lake Baikal region. Horiuchi (1996) reported that the sedimentary records of Lake Baikal indicated a period between 16 and 6 ^{14}C ka with high TOC and relatively low BGS. As the C/N ratio in this period was compatible with autochthonous phytoplankton origin, he considered algae other than diatoms had contributed significantly to primary production in Lake Baikal.

The change in SCE patterns within the post-glacial period was apparently not large, as was the case with SCE patterns in one interglacial period for the BDP98 core (Soma et al., 2001b). HPLC chromatograms of the SCE fraction in the post-glacial and last glacial periods are shown in Fig. 8. In the post-glaciation, SCE patterns showed one main SCE-*a* peak, which had been designated as “peak 5” in the previous report (Soma et al., 2001b) and a SCE-*b* peak (designated as “peak 1”; see the lower trace in Fig. 2 obtained by 440 nm detection) without C₃₀ stanol chlorin ester (designated as “peak 8”). A lack of “peak 8” would suggest that dinoflagellate grazing during the post-glaciation was negligible in Lake Baikal. The correlation coefficient between SCE-*b* and total SCEs-*a* in core G-6 during the post-glaciation was lower ($R=0.74$, $n=42$) than that in the BDP98 core at a depth of 90–95 m ($R=0.85$, $n=38$) where SCE-*b* was more abundant than in the other sections of the core, and the amount of SCE-*b* relative to total SCEs-*a* was 0.059 on average, being lower than that (0.287 in average) in the 90–95 m section of the BDP98 core. Therefore, the contribution of algae other than green algae was also significant for SCEs-*a* in Lake Baikal during the post-glaciation, consistent with the observation of various carotenoids in the corresponding section of core G-6. The depth profile of SCE-*b* shown in Fig. 3h exhibits a general trend common with that of lutein (Fig. 7d), although there were disagreements in the peak positions. While both SCE-*b* and lutein would have originated from green algae, this may be ascribed either to a difference in the lutein/chlorophyll *b* ratio in different green algal species (Yokohama, 1982) or to a difference in diagenetic behavior between SCE-*b* and lutein. More detailed study including identification of each SCE will be needed to confirm the close link between the compositions of carotenoids and SCEs-*a*.

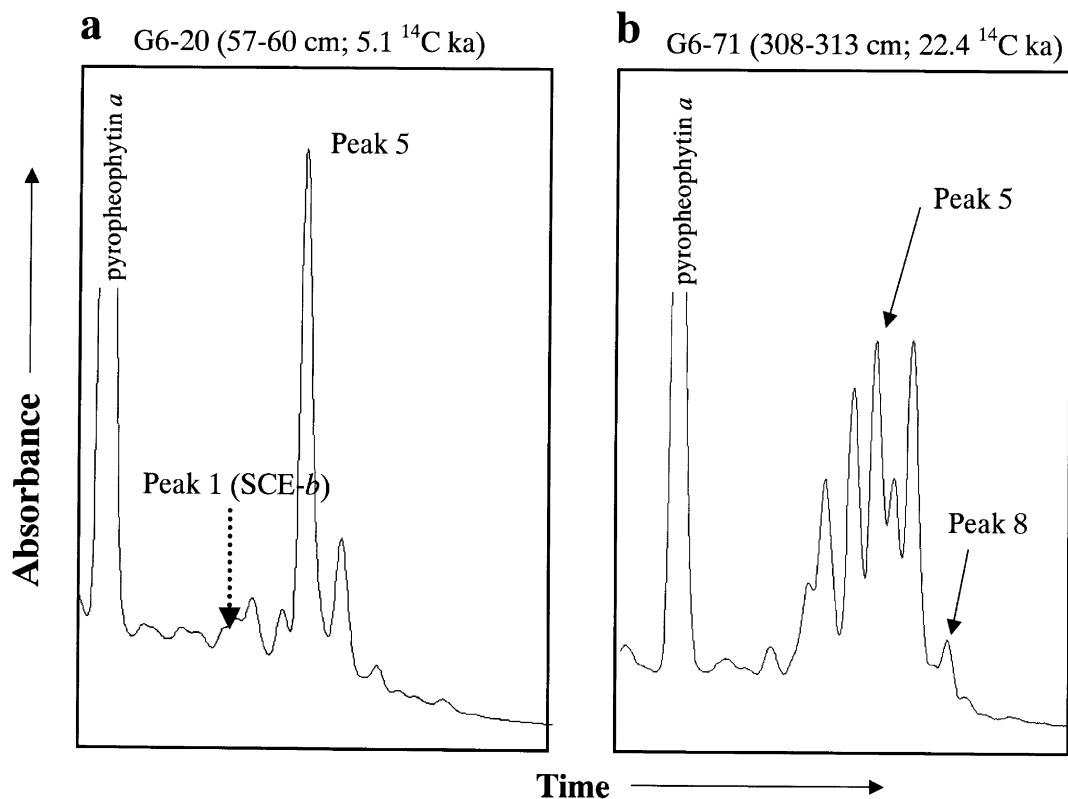


Fig. 8. HPLC chromatograms of SCE fraction in core G-6 detected at 400 nm absorbance in the post-glaciation (57–60 cm; 5.1 ^{14}C ka; a) and last glaciation (308–313 cm; 22.4 ^{14}C ka; b). The numbers of the SCE peaks are based on Soma et al. (2001b).

3.5. Primary productivity before 15 ^{14}C ka during the late last glaciation

In the sediment older than 15 ^{14}C ka, carotenoids were not detectable, while chlorophyll *a* derivatives such as pheophytin *a*, pyropheophytin *a* and SCEs-*a* were detected. This was due to the relative instability of sedimentary carotenoids among the residual photosynthetic pigments. SCEs-*a* reflected the autochthonous production. However, the amounts of total chlorophyll *a* and BGS as well as total carotenoids before 15 ^{14}C ka were almost negligible compared with those after 15 ^{14}C ka, while TOC remained at an appreciable level of about 0.6 wt%. The association of very low BGS and appreciable TOC in the Lake Baikal sediments was reported earlier and attributed to a relatively higher contribution of allochthonous input of organic matter to the lake (Horiuchi et al., 2000). The linear correlation between pyropheophytin *a* plus SCEs-*a* and TOC (Fig. 5) intersects TOC at about 0.4%, when the concentration of pyropheophytin *a* plus SCEs-*a* is 0. As the latter indicators are of autochthonous origin, this intersection may allow an estimate of allochthonous TOC, possibly during the last glacial period. This amounts to about 70% of TOC, indicating that autochthonous phyto-

plankton productivity in the last glacial period was still significant. It has been reported that during the last glaciation Lake Baikal was not completely frozen (Shimaraev et al., 1992) and its catchment was not completely barren, as indicated by pollen records in the sediment (see, for example, Horiuchi et al., 2000).

A nearly steady increase in the ratio of SCEs-*a* to total chlorophyll *a* with depth in the sediment core was observed (Fig. 4), regardless of the last glacial/post-glacial transition. Therefore the formation of SCEs-*a* through predation of phytoplankton by zooplankton would have operated in an essentially similar way during the glacial period. While carotenoids were not detectable in the sediment before 15 ^{14}C ka, there was a significant difference in the HPLC SCEs-*a* pattern for the late last glacial period (Fig. 8b) compared with that for the post-glacial period (Fig. 8a). This change in SCEs patterns suggests changes in the phytoplankton composition in Lake Baikal through the last glacial/post-glacial transition. The relative intensity of “peak 5” in the SCE patterns during the last glacial period was lower than in the post-glacial period. The SCE peak derived from a C_{30} stanol chlorin ester (“peak 8”) appeared, suggesting that dinoflagellates contributed to the accumulation of SCEs-*a* in the late last glacial period. SCE-*b*

(“peak 1”) was below the detection limit, and hence the contribution of green algae was negligible at this time.

3.6. *Manifestation of the Younger Dryas period (10.5–11.5 ¹⁴C ka) in the distribution of photosynthetic pigments in the sediment core*

It has been recognized that, in the northern hemisphere, the temperature started to increase after about 15,000 years BP, but decreased temporarily between 11,500–12,500 years BP, the so-called Younger Dryas period (Cronin, 1999). Colman et al. (1999) reported a temporary decrease in BGS in the BDP93 sediment core from Lake Baikal between 10 and 11 ¹⁴C ka and attributed this to the Younger Dryas cooling event. However, in previous studies using BGS as an indicator of primary productivity (Qiu et al., 1993; Carter and Colman, 1994; Horiuchi et al., 2000), the presence of the Younger Dryas has been seldom recognized, probably because of the increase in BGS (diatoms) that started in the late Holocene. In the present case the period was discernible not only from TOC but also from total chlorophyll *a* and total carotenoids. Most of the detected individual carotenoids showed the same trends. Thus it is suggested that the cold climate of the Younger Dryas period was imprinted in the record of sedimentary photosynthetic pigments in Lake Baikal. From the depth profile of magnetic susceptibility in the same sediment core sample from Lake Baikal as that described here, Sakai et al. (2001) noted the Younger Dryas period of 13–10 ¹⁴C ka.

When the ¹⁴C ages were calibrated after the reservoir effect correction (1192 years BP) (Table 1), the time period 10.5–11.5 ¹⁴Cka corresponds to 11,000–12,000 calBP. The calibrated age of this time without reservoir correction was 13,000–14,000 calBP. The calibrated age (11,000–12,000 calBP) with reservoir effect correction agrees well with the timing of the Younger Dryas cooling event found in other places (Strömberg, 1994; Goşlar et al., 1995; Hajdas et al., 1995; see for review, Cronin, 1999). More detailed studies of the factors controlling offset between atmospheric and lacustrine ¹⁴C ages, including the reservoir effect, in Lake Baikal will be needed for more accurate estimation of absolute age for such short-term climatic changes.

4. Conclusions

The present study has provided a good example of the type of information that the sedimentary record of photosynthetic pigments can provide about paleoenvironmental conditions that once prevailed in a lake as large, deep, oxic, oligotrophic and ancient as Lake Baikal. Grazing of phytoplankton by zooplankton was shown to play an important role in the transportation of

organic matter to the sediment of Lake Baikal. Photosynthetic pigments including carotenoids of clearly phytoplankton origin showed that a general increase in phytoplankton activity started as early as 15 ¹⁴C ka at the beginning of the post-glacial period, much earlier than the onset of the diatom record, represented by BGS. BGS increased appreciably after 10 ¹⁴C ka, and markedly after 5 ¹⁴C ka, while total carotenoids became maximal around the climatic optimum at 6–7 ¹⁴C ka. The record of photosynthetic pigments revealed a temporary decrease in algal activity during the Younger Dryas period. Whether these observations can be generally applied to all the basins of Lake Baikal remains to be determined.

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