

Lignin and fatty acid records in Lake Baikal sediments over the last 130 kyr: A comparison with pollen records

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Abstract

A 10 m sediment core from Academician Ridge in Lake Baikal was analyzed for its molecular composition using on-line TMAH (tetramethylammomium hydroxide) thermochemolysis. Major products are lignin phenols, *n*-C₁₄ to C₃₀ fatty acids (alkanoic acids), cutin acids, hydroxy acids and aliphatic dicarboxylic acids. Lignin phenols are abundant in warmer periods (the interglacial: marine isotope stage (MIS) 5e and MIS 1), but extremely low in the other (colder) periods. This result coincides well with pollen records reported for a core near the present site, where an expansion of coniferous forests in sub-stage 5e and MIS 1 was implied. Normal C₂₄–C₃₀ alkanolic acids, important components of plant wax esters, are abundant in 5e and MIS 1 and are present in significant amounts in the other (colder) periods, unlike the lignin phenols. A high abundance of *n*-C₂₄ to C₃₀ alkanolic acids relative to lignin phenols in the Bølling–Allerød warm period suggests an enhanced development of herbs.

It is implied from comparison of the sedimentary lignin phenol record with fossil pollen records and lignin phenol analysis of modern pollen that the ratio of cinnamyl phenols to vanillyl phenols may serve as an indicator of pollen contribution to sedimentary organic matter.

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1. Introduction

Many studies have been carried out to decipher sedimentary records in Lake Baikal, south-central Siberia (central Asia) by researchers in the fields of geology, paleoclimatology, paleolimnology, geochemistry and related sciences. These studies have revealed that the hydrodynamic systems and

productivity of the lake are sensitive to orbitally forced climatic changes because of its location in the continental interior in the middle latitudes (e.g., Williams et al., 1997; Kashiwaya et al., 2001).

We have been involved in organic geochemical studies of Lake Baikal cores, the major interest being characterization of organic matter preserved in the sediments and the application of organic molecules to a study of biological response to climate change. In a previous paper (Ishiwatari et al., 2005), we characterized the organic matter composition of sediments from the northern basin over the last glacial/interglacial period and showed that lignin phenols, *n*-C₁₄ to C₂₈ ω-hydroxyalkanoic

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acids and total cutin acids relative to total organic carbon (TOC) in the interglacial (Holocene) were 5–6 fold higher than in the glacial. In addition, our results indicated that lake palaeoproductivity, estimated using organic carbon of phytoplanktonic origin in the northern basin was $<20 \text{ g C m}^{-2} \text{ yr}^{-1}$ in the glacial (before 18 ka) and was high ($50\text{--}120 \text{ g C m}^{-2} \text{ yr}^{-1}$) in the Holocene. Orem et al. (1997) reported the lignin phenol composition in three cores from the lake and discussed the terrestrial vegetation history over the past 90 kyr from lignin phenol records. They observed that lignin phenol concentrations in cores from the Buguldeika Bay and Selenga River sites in the central basin were significantly higher than those at Academician Ridge. This result was explained by an enhancement in the input of terrestrial organic matter reflecting the proximity of the former two sites to riverine inflow. The core site at the Academician Ridge is remote from rivers.

Although fossil pollen analysis of lake sediments is a common technique for studying terrestrial vegetation around a lake, we have increasingly been recognizing the importance of a study of vegetation-derived organic matter (e.g., lignin phenols) in providing important information on terrestrial palaeoenvironment. In particular, the organic geochemical approach would be a key to drawing a picture of carbon cycles in the past. A number of geochemical studies of plant tissue, including stems, leaves and herbs have revealed that both woody and non-woody tissues of gymnosperms (ferns and conifers) produce vanillyl phenols by chemical degradation, but not syringyl phenols (e.g., Hedges et al., 1982). Non-woody tissue (leaves, needles, bark and stems) from vascular plants can be distinguished from woody tissue by the higher yield of cinnamyl phenols. Woody and non-woody tissue from angiosperms (herbs and hardwood) characteristically produces syringyl phenols, and the former generally produces more syringyl phenols than the latter.

These characteristic compositions of lignin phenols in higher plants have been used as a proxy for vegetation analysis to the study of paleoenvironments. Several comparative studies of lignin phenols and other organic compounds with fossil pollen records have been carried out. Orem et al. (1993) referred to pollen records in a study of palaeoenvironment during the Holocene of Lake Baikal using lignin phenol data. Leopold et al. (1982) measured pollen and lignin records in postglacial ($\sim 13 \text{ ka}$)

sediments from Lake Washington. Although lignin records are not necessarily consistent with pollen records, they considered that the apparent inconsistency was caused by the difference in the mode of transportation between pollen grains and lignin phenols. They concluded that lignin phenols reflected the composition of vascular plants that grew around the lake, so classes and distributions of local vegetation would be detected that were not evident from pollen remains.

However, studies are still not sufficient to allow a picture of vegetational palaeoenvironment to be drawn. It was revealed that pollen characteristically produces cinnamyl phenols (Keil et al., 1998; Hu et al., 1999). Keil et al. (1998) observed a high ratio of *p*-coumaric acid to ferulic acid (Pc/Vc: ~ 10) in the sediment fraction with a grain size of $38\text{--}100 \mu\text{m}$, where pollen grains were abundantly present in Washington continental margin sediments. The high Pc/Vc ratios and high C/V ratios for pollen were also observed for fresh gymnosperm pollen samples (Keil et al., 1998; Hu et al., 1999). These observations indicate a possibility that estimates of vegetational composition from lignin phenol compositions of gymnosperm needles in sediments are strongly biased (Hu et al., 1999).

Long-chain ($>C_{20}$) *n*-alkanoic acids occur in higher plant leaf wax and have been used as an indicator of higher plant contributions to sediments. However, the usefulness and limit of these acids as a proxy for palaeovegetation remains unclear. Therefore, a comparative study of the analysis of organic compounds and pollen records is still important for better use of organic compounds for understanding past environments.

This paper had two main objectives: To (1) evaluate lignin phenols and fatty acids (*n*-acids) obtained using TMAH chemical degradation as proxies for palaeovegetation and palaeoenvironment and (2) describe and discuss palaeoenvironmental changes in Lake Baikal over the past 130 kyr by comparing and integrating the data for these compounds with pollen records.

2. Materials and methods

2.1. Sediment samples

A 10 m long core (Ver 98-1, St-6) was taken in 1998 at the Academician Ridge ($53^{\circ}41'39''\text{N}$, $108^{\circ}21'01''\text{E}$) at a water depth of 335 m. The ridge divides the north and central basins of Lake Baikal.

The core was expected to preserve geological records without considerable disturbance by turbidites, because the ridge tends to escape fluvial influences. Many sediment cores have been taken from this location and investigated (e.g., Horiuchi et al., 2000; Kashiwaya et al., 1999; Oda et al., 2000; Williams et al., 1997).

The core is composed of both a gravity (pilot) core of ~180 cm (for upper sections), and a piston core of ~900 cm (for lower sections). The core covers marine isotope stage (MIS) 1 to a part of MIS 7 (Oda et al., 2002). Stratigraphy and lithology of the core were obtained from Ikehara (personal communication) and Oda et al. (2002). The lithology of sections of MIS 1 to a part of MIS 6 is presented in Fig. 2. The sediments essentially display a pattern of alternating layers of diatom-rich ooze or mud and layers of diatom-barren silty clay. It is commonly observed in Lake Baikal sediments that diatom-rich ooze was deposited in interglacial periods and diatom-barren clay was formed in glacial periods (e.g., Kashiwaya et al., 1999; Williams et al., 1997). The interval 32–84.5 cm interval of the piston core was disturbed, probably as a result of a slow trigger (Oda et al., 2002).

2.2. Bulk analysis

The core was cut at every 2.3 cm for sub-samples and stored at -20°C . The sub-samples were freeze-dried for determination of water content, and total organic carbon (TOC or C_{org}), total nitrogen (total N or N_{total}) and stable carbon isotopic composition of the TOC were then determined, as follows.

For determination of TOC and total N, an aliquot was wetted and treated with HCl vapour in a desiccator overnight to remove inorganic (carbonate) carbon. The HCl vapour was removed completely under vacuum and the sample was pulverized and subjected to C and N analysis with a Fisons NA1500NCS elemental analyzer. Carbon isotopic composition of TOC ($\delta^{13}\text{C}_{\text{TOC}}$) was determined using the following procedure. An HCl-treated, dried and pulverized aliquot was subjected to treatment in a Fisons NA1500NCS elemental analyzer. The isotope composition of the CO_2 produced was determined using a Finnigan Delta S mass spectrometer. The $\delta^{13}\text{C}$ values are reported relative to the PDB (Peedee Formation Belemnite) standard. The analytical precision was within 0.2‰.

2.3. TMAH thermochemolysis

Lignin phenols and *n*-alkanoic acids were analyzed using an on-line TMAH (tetramethylammonium hydroxide) thermochemolysis procedure. The details of the procedure will be published elsewhere (cf. Yamamoto and Ishiwatari, 2005). Briefly, in a typical procedure, the dry finely powdered whole sediment sample (<20 mg) was added to a pyrofoil (foil for pyrolysis) and weighed precisely; a measured amount of TMAH reagent (in methanol) and internal standard (e.g., *n*- C_{19} alkanolic acid) were added. After evaporation of the methanol, the pyrofoil was wrapped and heated at 590°C for 20 s in a Curie point pyrolyzer (JHP-3: Japan Analytical Industry Co.). The reaction temperature was maintained at 270°C . The products were introduced into a HP-5 GC column (30 m \times 0.32 mm; film thickness of 0.25 μm) via an interface (heated at 290°C) between the pyrolyzer and gas chromatograph (Varian 3400 GC), and analyzed using mass spectrometry (MS; Finnigan INCOS 50). The gas chromatography (GC) column was initially kept at 50°C for 5 min, heated from 50°C to 310°C at $6^{\circ}\text{C}/\text{min}$ and maintained at 310°C for 20 min. Mass spectra (electron ionization mode) were obtained over the range m/z 50–600 at a scan rate of 0.5 s/decade. The average coefficient of variation for the triplicate analysis of lignin phenols was $\pm 8.2\%$ for a dry sediment sample (5 mg of a sub-surface sediment section from Lake Baikal core 323-PC1 (Ishiwatari et al., 2005), with TOC content $28.5 \text{ mg g}^{-1} \text{ ds}$ (dry sediment)).

For a series of samples (ca. 100) from core Ver 98-1, St-6, sample size for TMAH analysis was determined by TOC content. Aliquots of 8–9 mg were used for samples with TOC $> 10 \text{ mg g}^{-1} \text{ ds}$, while 16–17 mg were used for TOC content $< 10 \text{ mg g}^{-1} \text{ ds}$. Analytical reproducibility for lignin phenols was tested using Ver 98-1, St-6 samples with different TOC contents. The average coefficient of variation for V, S/V, C/V was $\pm 26\%$, $\pm 17\%$, and $\pm 20\%$ for the samples with higher TOC content ($> 10 \text{ mg g}^{-1} \text{ ds}$; $n = 4$), $\pm 49\%$, $\pm 62\%$, $\pm 65\%$ for samples with 5–10 $\text{mg TOC g}^{-1} \text{ ds}$ ($n = 3$) and $\pm 67\%$, $\pm 66\%$, $\pm 60\%$ for those with $< 5 \text{ mg TOC g}^{-1} \text{ ds}$ ($n = 6$), respectively. Hence, the analytical reproducibility of lignin phenols in the TOC-poor samples was low. Although the analytical error is large compared with that for a traditional CuO oxidative degradation method, we consider that lignin phenol composition in sediment samples can be

characterized using this TMAH analysis. Risks of error in interpretation of features in temporal changes in lignin phenol composition are compensated for to a certain extent by the large number of TMAH analyses. In particular, we interpreted carefully the analytical results for lignin phenols from TOC-poor samples (mostly sediments deposited in glacial periods).

3. Results

3.1. Age model

Fig. 1 displays the depth–age relationship for core Ver 98-1, St. 6. AMS ^{14}C ages for the three shallow sections were adopted from those determined for core Ver 96-2, St. 3 (Oda et al., 2000). The location of core Ver 96-2, St. 3 ($53^{\circ}41'52''\text{N}$, $108^{\circ}21'06''\text{E}$, water depth 320 m) is close to our coring site. The three sections in core Ver 98-1, St. 6 were adopted from comparison of the profile of water content of core Ver 96-2, St. 3 with that of our core. Oda et al. (2000) assumed that the age of the 108 cm depth section in core Ver 96-2, St. 3, where willow (*Salix*) pollen starts to increase, is 16.0 ka. The 108 cm section in core Ver 96-2, St. 3 was assumed to correspond to 94 cm depth in our core, where TOC, lignin phenols and other organic biomarkers begin to increase, on the basis of comparison of the water content profiles for both cores. The AMS ^{14}C age of the sediment surface was assumed to be 1.2 ka because AMS ^{14}C ages of total

organic matter of surface sediments in Lake Baikal range from 0.5 to 1.5 ka (Nakamura and Oda, 1998). The ^{14}C age of the TOC-minimum layers observed at a depth of ~ 80 cm was assumed to be 13.5 ka (without correction of reservoir effect) from the similarity in TOC profile for a core from the southern basin of Lake Baikal (Tani et al., 2002).

For the sections deeper than ~ 100 cm (before ~ 18 ka), an age–depth relationship was obtained on the basis of interpretation of the curves of bio-organic SiO_2 (BioSi) abundance in core Ver 96-2, St. 3 (Oda et al., 2000), core BDP 96-2 (Prokopenko et al., 2001), and the depth profile from X-ray CT scanning of our core (Ver 98-1, St. 6) reported by Oda et al. (2002), and correlation with the chronostratigraphy of Martinson et al. (1987) for oxygen isotopes of benthic foraminifera in marine sediments.

A number of previous studies have demonstrated that the fluctuations in BioSi abundance and water contents are strongly correlated with warm and cold periods, where high BioSi and water contents are caused by enhanced abundance of diatoms in warm (interglacial) periods, while they are low due to low diatom abundance in cold (glacial) periods (e.g., Williams et al., 1997; Oda et al., 2002; Prokopenko et al., 2001; Kashiwaya et al., 1999).

The age for each sampling depth was obtained by linear interpolation between age control points, assuming uniform sedimentation rate. The relationship between core depth and marine isotope stages (MIS) could therefore be safely established.

3.2. Bulk organic matter

Fig. 2 gives vertical profiles of bulk parameters (water content, TOC), TOC/Total N (atomic TOC/ N_{total} i.e., “TOC/ N_{total} ” hereafter) and $\delta^{13}\text{C}_{\text{TOC}}$ for core Ver 98-1, St. 6, together with the lithology and the marine isotope stages. TOC concentration ranges from $3 \text{ mg g}^{-1} \text{ ds}$ to $28 \text{ mg g}^{-1} \text{ ds}$. Their values are high in both 0–80 cm and 560–620 cm depth ranges. These sections correspond to MIS 1 (Holocene) and 5e, respectively. TOC concentrations are relatively low in MIS 3, 4 and 5a–5d.

The shape of the TOC profile in the top 100 cm of the core is markedly different from that of water content (a presumed proxy of BioSi). This difference indicates a possibility of TOC sources other than diatoms, i.e., other phytoplankton and sources outside the lake. Another feature is a rather steady profile of TOC concentration during MIS 3–5d.

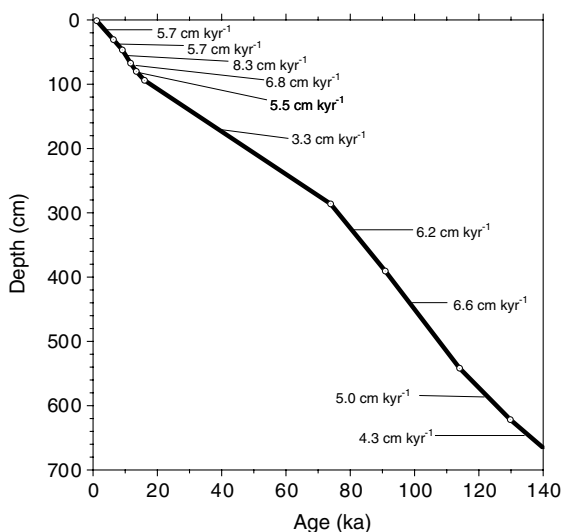


Fig. 1. Depth–age relationship for core Ver 98-1, St. 6.

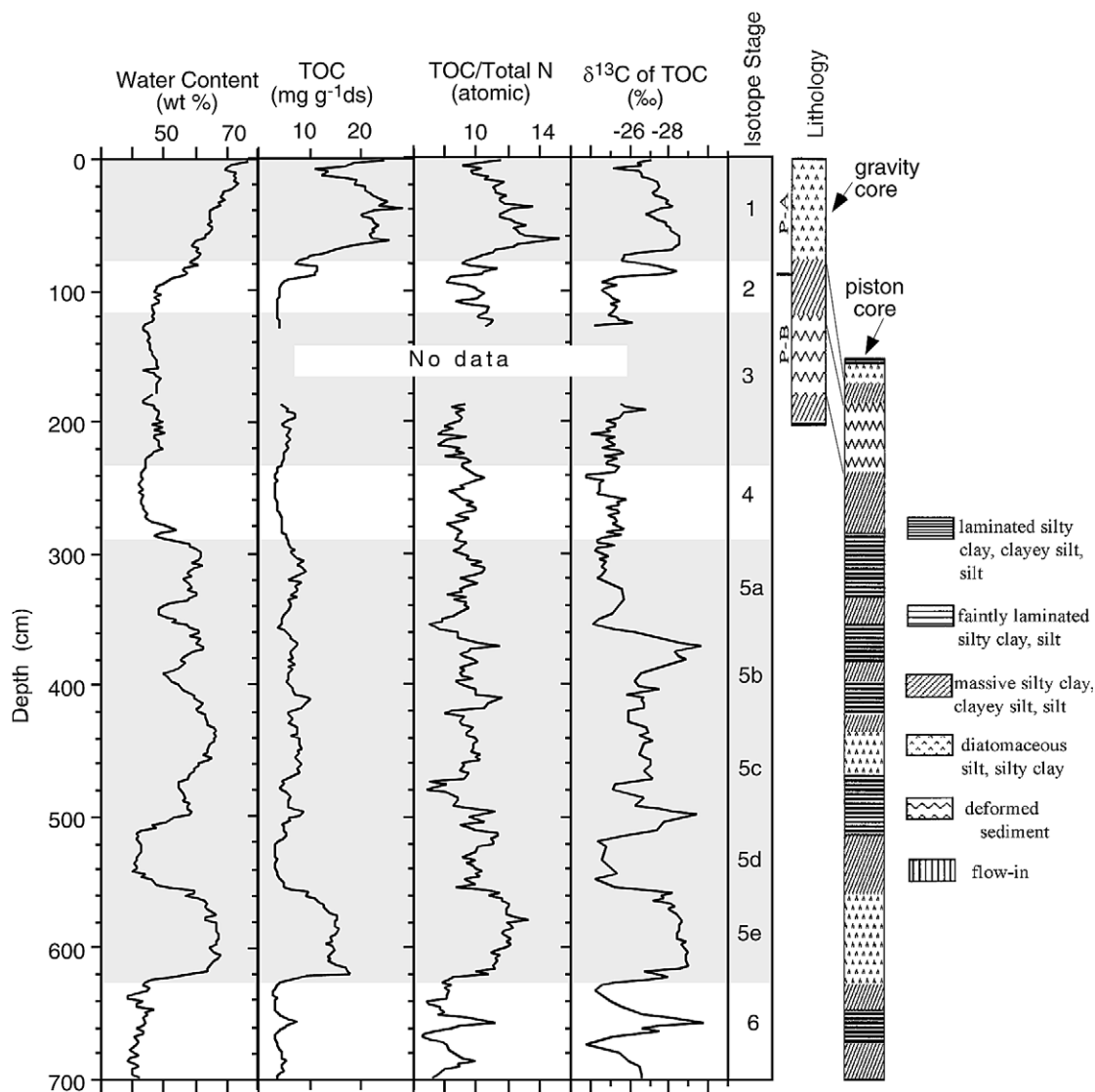


Fig. 2. Bulk parameters vs. depth.

The N_{total} contents range from 0.3 to 2.1 mg g^{-1} ds; the profile (not shown) resembles that of TOC, suggesting that the sources of both elements are essentially common. TOC/ N_{total} ratios range from 7 to 15, tending to higher values in warmer periods (MIS 1 and 5e) and lower in the other (colder) periods.

The $\delta^{13}\text{C}_{\text{TOC}}$ values range from -30‰ to -25‰ ; the profile resembles that of TOC/ N_{total} , with low values in the sections where TOC/ N_{total} is high. Exceptions are the early stage of 5c and the transition from 5b to 5a, where values are low when TOC/ N_{total} values are moderate.

3.3. TMAH thermochemistry products

Lignin phenols and $n\text{-C}_{14}$ to C_{30} alkanolic acids (determined as methyl esters) are obtained in considerable amounts from all the samples. Lignin phenols consist of vanillyl phenols (vanillin: Vh, acetovanillone: Vo, vanillic acid: Va; total: V), syringyl phenols (syringaldehyde: Sh, acetosyringone: So, syringic acid: Sa; total: S), and cinnamyl phenols (*p*-coumaric acid: Pc, ferulic acid: Vc; total: C). The *p*-hydroxy phenols (*p*-hydroxybenzoic acid, *p*-hydroxybenzaldehyde and *p*-hydroxyacetophenone), *m*-hydroxybenzoic acid and 3,5-dihydroxy-

benzoic acid (DHBA) are also present in the TMAH products. The *p*-hydroxy phenols are excluded from “lignin phenols” because these phenols can arise from non-lignin sources (Hedges et al., 1982; Requero et al., 1991). In addition, since reproducibility of analysis for *p*-hydroxybenzaldehyde and *p*-hydroxyacetophenone is low, analytical results for these compounds are not shown.

The amounts of lignin phenols and *n*-C₁₄ to C₃₀ alkanolic acids are generally high from the samples with high TOC concentrations, while they are considerably lower for TOC-poor samples. Cutin acids (8,16-, 9,16- or 10,16-dimethoxy C₁₆ acid, 7- or 8-methoxy C₁₆ diacid and 9,10,18-trimethoxy C₁₈ acid), ω -hydroxyalkanoic acids (C₁₄–C₂₈) and α,ω -aliphatic dicarboxylic acids (C₁₄–C₂₈) are present in extremely small amounts in almost all samples.

These acids were not quantified due to their low abundance.

3.3.1. Lignin phenols

The absolute concentrations of lignin phenols are expressed as μg of vanillyl, syringyl and cinnamyl phenols per g of dry sediment (V + S + C or V + S in $\mu\text{g g}^{-1}\text{ds}$; Fig. 3). The relative concentrations are expressed as μg of vanillyl and syringyl phenols per 100 mgTOC (V + S in μg per 100 mgTOC), corresponding to lambda (λ ; Hedges and Parker, 1976), or μg of vanillyl, syringyl and cinnamyl phenols per 100 mgTOC (V + S + C in μg per 100 mgTOC), corresponding to Λ (Hedges and Mann, 1979; Fig. 4).

Lignin phenol concentrations (V + S + C or V + S in μg per 100 mgTOC) in the Holocene sedi-

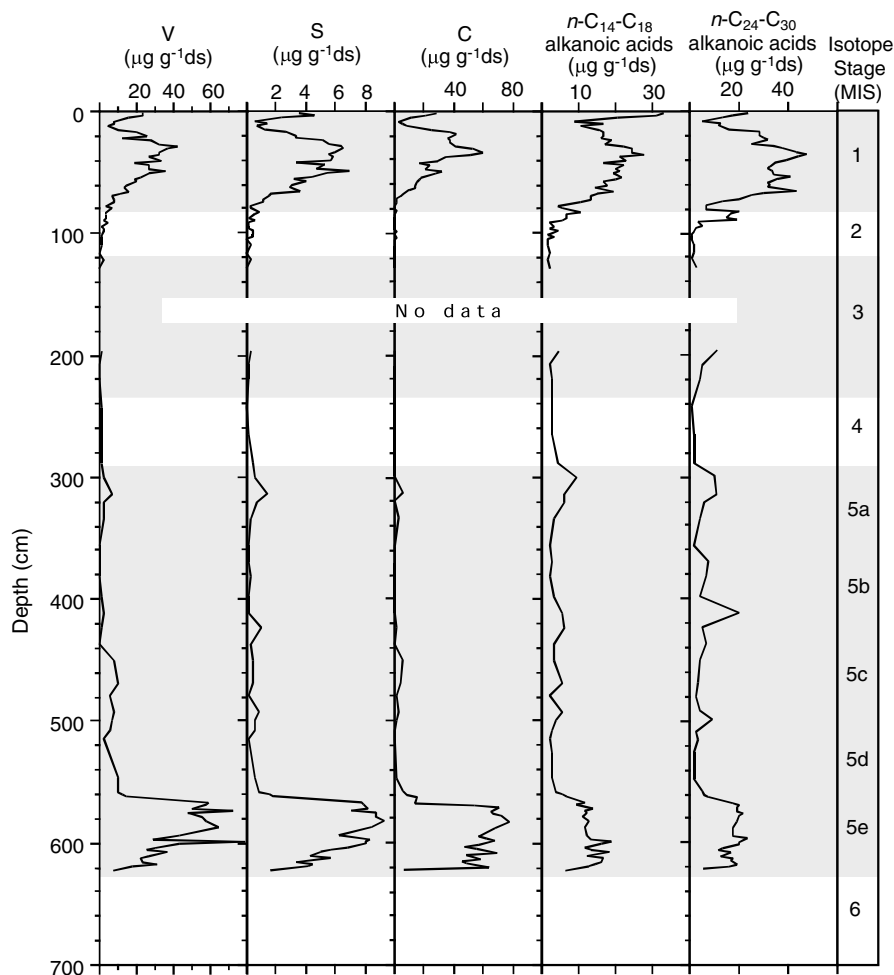


Fig. 3. Abundance of lignin phenols and alkanolic acids vs. depth.

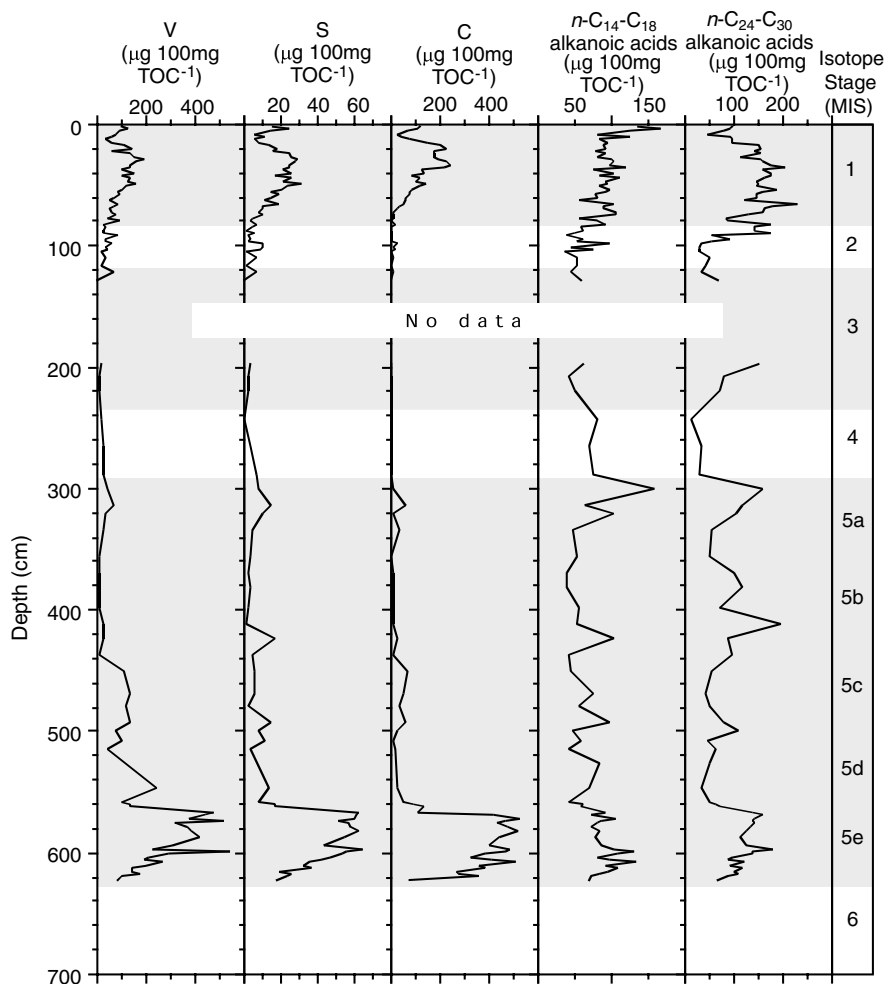


Fig. 4. TOC-normalized concentrations of lignin phenols and alkanolic acids vs. depth.

ments range from 50 to 409 or 44 to 219 (μg per 100 mgTOC; average 223 ± 108 or 117 ± 46), respectively. These values are higher than those reported previously by Orem et al. (1997) for the Academician Ridge sediment core (e.g., $V + S + C = 44 \pm 18 \mu\text{g}$ per 100 mgTOC). Lignin phenol concentrations for the MIS 2 sediments range from 15 to 92 for $V + S + C$ (average 50 ± 24) and from 15 to 88 for $V + S$ (average 41 ± 19), respectively. These $V + S + C$ values are similar to those reported by Orem et al. (1997, 44 ± 42 for 23–92 ka). The lignin phenol concentrations for other sites in Lake Baikal reported previously are generally higher than for Academician Ridge sediments: $V + S + C = 305 \pm 118 \mu\text{g}$ per 100 mgTOC for the Holocene and 84 ± 40 for 19–89 ka for Selenga River Delta sediments, $V + S + C = 326 \pm 56 \mu\text{g}$ per 100 mgTOC for Holocene and 298 ± 205 for

26–84 ka for Buguldeika Bay sediments (Orem et al., 1997); $V + S = 612 \pm 163 \mu\text{g}$ per 100 mgTOC for Holocene and 98 ± 45 for last glacial for Northern Basin sediments (Ishiwatari et al., 2005).

Absolute concentrations of lignin phenols for the interglacial (5e and MIS 1) for our core are considerably (4–40 times) higher than those for colder periods (5d–5a and MIS 4–MIS 2; Fig. 3). TOC-normalized concentrations are also high for the interglacial (5e and MIS 1) and low for colder periods (5d–5a and MIS 4–MIS 2) (Fig. 4).

Vertical profiles of lignin phenol compositions (Fig. 5) indicate that S/V ratios for the interglacial (5e and MIS 1) are ~ 0.2 . S/V ratios decrease slightly upward for the last interglacial (5e), while they change little for MIS 1. C/V ratios are generally high for both 5e and MIS 1. High S/V and slightly high C/V values are observed for 5c–5a. However,

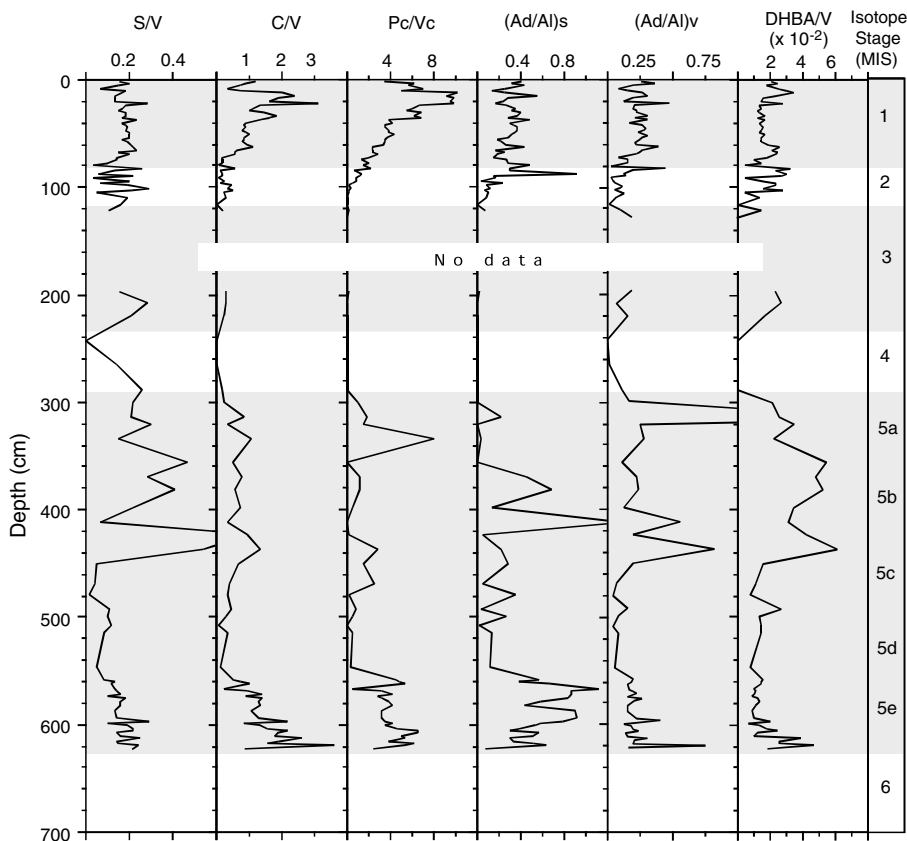


Fig. 5. Lignin phenol compositions vs. depth.

this observation is not conclusive and reexamination is needed, because the reliability of these data is low as described in Section 2.3. The vertical profile of Pc/Vc ratios is similar to that of C/V.

3.3.2. *n*-Alkanoic acids

The compositions of *n*-alkanoic acids exhibit a bimodal distribution, with maxima at C₁₆ and either C₂₆ or C₂₈, which are slightly different from those reported by Ishiwatari et al. (2005) where *n*-C₂₄ acid in many sections is more abundant than other acids in the higher molecular weight region. Absolute concentrations ($\mu\text{g g}^{-1}$ ds) of both *n*-C₁₄ to C₁₈ and *n*-C₂₄ to C₃₀ alkanolic acids are high in 5e and MIS 1, while they are low in the other MIS periods (Fig. 3). TOC-normalized concentrations for both *n*-C₁₄ to C₃₀ and *n*-C₂₄ to C₃₀ acids range from 50 to 160 μg per 100 mgTOC and 50–250 μg per 100 mgTOC. These concentrations in the interglacial are only slightly higher than those in the other periods. Moreover, they fluctuate considerably for the cold periods (5d to MIS 1; Fig. 4).

4. Discussion

4.1. TOC, C/N_{total} and $\delta^{13}\text{C}_{\text{TOC}}$ as palaeolimnological proxies

TOC content, C/N_{total} ratio and $\delta^{13}\text{C}_{\text{TOC}}$ are important parameters for reconstructing the palaeoenvironment of a lake and the surrounding land area. Sediment TOC content is used to estimate TOC mass accumulation rate and then to reconstruct aquatic palaeoproductivity. In this reconstruction procedure, C/N_{total} ratio and $\delta^{13}\text{C}_{\text{TOC}}$ are commonly used to evaluate the origin of the TOC because sedimentary organic matter (OM) is potentially a mixture from various sources (e.g., autochthonous (algal) vs. allochthonous (land higher plant); e.g., Meyers, 2003). The proportions of land plant OM relative to algal OM on a bulk basis is calculated using a simple mixing model.

The first point of discussion is that there is some uncertainty in the estimation of C/N_{total} ratios of

the two end members (autochthonous OM vs. allochthonous OM). In addition, it happens quite often that different C/N_{total} ratios are adopted by different authors for the two end members. For example, Meyers (2003) takes C/N_{total} of fresh algal OM as 4–10, with vascular land plant OM at ≥ 20 . Colman et al. (1996) used C/N_{total} of 25.7 for vascular plant OM and 8.57 for algal OM for Lake Baikal. We assumed C/N_{total} (weight) of allochthonous OM to be 8 and that of algal OM to be 25 (Ishiwatari et al., 2005). Prokopenko et al. (1999) ignored allochthonous OM for sedimentary OM having C/N_{total} (weight) of 12 or higher in Lake Baikal.

The second point of discussion is that the interpretation of $\delta^{13}C_{\text{TOC}}$ is not easy in the case of lake sediments, because the carbon isotopic composition of algal OM is usually indistinguishable from that of OM produced by C_3 higher land plants (e.g., Meyers, 1994; Ishiwatari et al., 2005). Furthermore, it is necessary to take into account for the interpretation of $\delta^{13}C_{\text{TOC}}$ that stable carbon isotopic composition is also controlled by other factors such as (1) C_4 and CAM plants as carbon sources, and (2) changes in carbon isotope fractionation during photosynthesis.

In our previous study of Lake Baikal sediments covering the past 37 kyr (Ishiwatari et al., 2005), $\delta^{13}C_{\text{TOC}}$ values essentially classified the OM into three groups:

The first occurs in the glacial, where the $\delta^{13}C_{\text{TOC}}$ values are heavy ($-24.0 \pm 0.8\text{‰}$) and λ values are low (~ 0.1). The OM is probably a mixture of algae, submerged plants and/or herbs.

The second occurs in the interglacial; the $\delta^{13}C_{\text{TOC}}$ values are low (-30‰ to -29‰) as are the λ values (~ 0.1). Hence, the OM of this group is probably of phytoplankton (diatom) origin.

The third group appears in the interglacial and is characterized by high and variable λ values (0.2–1.4) and low $\delta^{13}C_{\text{TOC}}$ values of -27‰ to -26‰ . The dominant OM in this group, with the high λ values (0.8 ± 0.4), probably originated from terrestrial higher plants, with other OM with lower λ values present consisting of a mixture of OM of terrestrial higher plant and algal origin.

The profile of $\delta^{13}C_{\text{TOC}}$ in MIS 2–1 and those at the end of MIS 6 to 5e resemble each other. However, no marked variation in $\delta^{13}C_{\text{TOC}}$ is apparent for 5c–5a. Since the abundance of BioSi fluctuates considerably (between 20 and 340 mg g^{-1} ds; Oda et al., 2000) in the 5c–5a sections, variations in $\delta^{13}C_{\text{TOC}}$ probably reflect the fluctuation of abun-

dance of phytoplankton, which is generally isotopically light in the lake.

In a previous study, we reported that TOC concentrations in Lake Baikal sediment (Northern Basin) in the Holocene were 7 times higher and C/N_{total} ratios 1.6 times higher than those in the last glacial (Ishiwatari et al., 2005). We consider that high C/N_{total} ratios in the Holocene were caused by an enhanced contribution of OM of terrestrial higher plant origin in the total OM, because there was a positive correlation between λ (lignin phenols/TOC) and C/N_{total} , and λ was more than 6 times higher than the values for the glacial.

In this study, we recognize that TOC concentrations, C/N_{total} ratios increase and $\delta^{13}C_{\text{TOC}}$ values decrease from the end of MIS 6 to 5e. These temporal variations resemble those reported previously for the last cold stage to MIS 1. The mechanisms causing these variations may be similar between the two periods – enhanced contribution of OM of terrestrial higher plant origin. However, Prokopenko and Williams (2003) proposed a hypothesis that a “biological pump” effect could explain the enhancement in C/N ratios in the interglacial. Although further work is necessary to find the cause of this enhancement of C/N_{total} ratios for sedimentary OM from Lake Baikal in the interglacial, we consider that its occurrence cannot be explained by the latter hypothesis.

4.2. Evaluation of lignin phenols and n-alkanoic acids as palaeovegetation indicators

4.2.1. Lignin phenols

S/V and C/V ratios have been used to trace plant tissue sources in sediments (e.g., Hedges and Mann, 1979; Hedges et al., 1982; Hu et al., 1999). In a plot of S/V against C/V for Ver 98-1 St. 6 (Fig. 6), most S/V values are low (~ 0.2), indicating that lignin phenols originate predominantly from gymnosperms.

Here a question may arise as to whether the end member values reported by Hedges and Mann (1979) obtained using the CuO oxidation procedure can be used for comparisons with data from the TMAH thermochemolysis procedure. In a comparative study of the products obtained with the two procedures for Lake Baikal sediments, no marked difference in S/V ratio between the two procedures was observed (Yamamoto and Ishiwatari, 2005). Moreover, the values obtained with the CuO oxidation procedure (Orem et al., 1997) for 3 Holocene sediment samples from Academician Ridge show

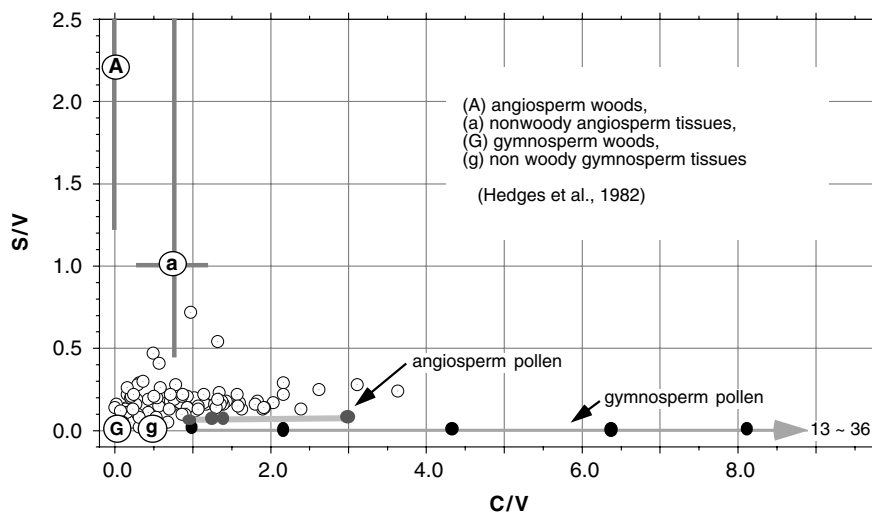


Fig. 6. S/V vs. C/V lignin compositional plot for sediments from core Ver 98-1, St. 6 examined in this study. Also illustrated are mean values and ranges for gymnosperms and angiosperms (Hedges et al., 1982). Data for modern pollen are cited in Table 1.

similar values (0.1–0.3) to ours. Therefore, we consider at present that there is no serious problem in using S/V ratio values obtained using the TMAH thermochemolysis procedure in the S/V vs. C/V diagram obtained using the CuO oxidation procedure.

The C/V ratio ranges from 0 to 4 (Figs. 5 and 6). The high values for core Ver 98-1, St. 6 imply that lignin phenols are considerably or predominantly derived from pollen, because high values for pollen were suggested by Keil et al. (1998) and Hu et al. (1999). Keil et al. (1998) observed that numbers of pollen grains, as well as high C/V and Pc/Vc ratio values, maximized in a particular grain size (38–250 μm) fraction of marine coastal sediment. In addition, modern pollen from gymnosperms [pine (*Pinus*), cedar (*Cedrus*) and spruce (*Picea*)] and angiosperms [oak (*Quercus*) and birch (*Betula*)] gives high C/V values (e.g., 1–36: Keil et al., 1998; Hu et al., 1999). In order to confirm the characteristics of the lignin phenol composition of modern pollen, we examined pollen from both gymnosperms and angiosperms. We obtained C/V values of 4–14 for pollen from gymnosperms [pine, cedar and fir (*Abies*)] and 0.9–1.3 for angiosperms (oak). S/V values for modern pollen from gymnosperms are reduced to 0 and for oak are 0.1–0.2, respectively. Table 1 and Fig. 6 compile data for published lignin phenol abundance and phenol ratios of modern pollen and our results. Most pollen from both modern gymnosperms and angiosperms produces high C/V and Pc/Vc ratio values, with gymnosperms seeming to produce higher C/V values than angiosperms.

Leaves and needles from modern gymnosperms and angiosperms do not give such high C/V values: they are 0.38–0.57 (average 0.49) for non-woody tissue from gymnosperms and 0.36–1.1 (average 0.76) for that from angiosperms, respectively (Hedges and Mann, 1979).

4.2.2. Straight chain C_{22} – C_{30} alkanolic acids

Straight chain alkanolic acids are major lipid components of most living organisms and their occurrence in recent sediments is well documented. Many studies attribute n - C_{22} to C_{32} alkanolic acids in sediments to an input of higher plant wax esters, while n - C_{12} to C_{18} acids are predominantly derived from aquatic source organisms such as phytoplankton (e.g., Cranwell, 1974, 1982; Ishiwatari et al., 1980; Simoneit, 1980; Tulloch, 1976). Therefore, a depth profile of n - C_{24} to C_{30} relative to n - C_{14} to C_{18} alkanolic acids in a lake sediment core should provide a record of the input of higher plant leaves relative to aquatic organisms.

As described in Section 3.3.2, the long-chain n -alkanoic acids in most of the core sections exhibit a maximum in the C_{26} – C_{28} region. In order to see detailed features of the depth variation in the long-chain acids, we calculated the average chain length (ACL) for n - C_{24} to C_{30} alkanolic acids in core Ver 98-1, St. 6 by the equation of $(\sum[C_i] \times i) / \sum[C_i]$ (for $i = 24$ – 30 where C_i = concentration of n -alkanoic acid containing i carbon atoms). The calculations indicate that ACL values in warm periods are high (26.6 ± 0.2 ($n = 22$) for sub-stage 5e,

Table 1

Lignin phenol abundance (mg 100 mg⁻¹ of total weight or mg 100 mgTOC⁻¹) and phenol ratios for modern pollen^a

Lignin phenols	<i>Pinus thunbergii</i> Parl.	<i>Pinus pumila</i> Regel.	<i>Pinus</i> sp.	<i>Cedrus deodara</i> Loud.	<i>Cedrus</i> sp.	<i>Abies mariesii</i> Mast.	<i>Abies</i> sp.	<i>Picea glauca</i>	<i>Picea mariana</i>	<i>Quercus acutissima</i> Carruth	<i>Quercus dentata</i> Thunb.	<i>Quercus</i> sp.	<i>Betula</i> sp.
	G ^b	G	G	G	G	G	G	G	G	A	A	A	A
<i>Individual phenols</i> (mg 100 mg ⁻¹)			c		c		c	c	c			c	c
Vanillin (Vh)	0.12	0.21	0.12	0.09	0.22	0.10	0.06	0.14	0.16	0.26	0.10	0.46	0.58
Acetovanillone (Vo)	0.03	0.03	0.25	0.02	0.07	0.05	0.02	0.03	0.05	0.06	0.03	0.17	0.07
Vanillic acid (Va)	0.06	0.06	0.07	0.03	0.13	0.10	0.05	0.08	0.28	0.04	0.03	0.79	0.17
Syringaldehyde (Sh)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.01	0.02	0.01
Acetosyringone (So)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.01	0.00	0.01
Syringic acid (Sa)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.03
<i>p</i> -Hydroxybenzaldehyde			1.35		0.38		0.53	2.53	1.99			1.61	1.28
<i>p</i> -Hydroxyacetophenone			0.22		0.07		0.11	0.34	0.34			0.07	0.10
<i>p</i> -Hydroxybenzoic acid			0.62		0.68		0.27	1.33	1.11			0.34	0.37
<i>p</i> -Coumaric acid (Pc)	2.68	2.29	5.70	0.07	0.56	1.00	0.10	8.87	6.41	0.21	0.14	1.64	0.68
Ferulic acid (Vc)	0.14	0.12	0.10	0.86	0.34	0.06	0.05	0.03	0.00	0.10	0.06	0.11	1.79
<i>Total phenols (mg/100 mg)</i>													
Vanillyl phenols (V)	0.21	0.30	0.44	0.14	0.42	0.24	0.14	0.25	0.49	0.37	0.16	1.43	0.82
Syringyl phenols (S)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.04	0.02	0.03	0.05
Cinnamyl phenols (C)	2.82	2.41	5.79	0.92	0.89	1.05	0.14	8.90	6.41	0.31	0.20	1.74	2.47
<i>p</i> -Hydroxyphenols (P)			2.19		1.12		0.90	4.20	3.44			2.02	1.75
V + S + C	3.03	2.71	6.23	1.06	1.31	1.30	0.28	9.15	6.90	0.72	0.38	3.19	3.35
<i>Phenol ratios</i>													
S/V	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.10	0.15	0.02	0.07
C/V	13.60	8.05	13.31	6.46	2.16	4.31	1.06	35.60	13.08	0.86	1.27	1.22	3.02
P/V			5.03		2.71		6.59	16.80	7.02			1.41	2.13
Pc/Vc	18.99	18.30	59.95	0.08	1.64	17.28	2.02	295.67		2.01	2.37	15.30	0.38
<i>Acid/aldehyde ratios</i>													
Va/Vh	0.46	0.29	0.55	0.30	0.59	1.01	0.79	0.57	1.75	0.16	0.29	1.71	0.29
Sa/Sh												0.00	2.03
Pa/Ph			0.46		1.80		0.51	0.53	0.56			0.21	0.29
References	This work	This work	Keil et al. (1998)	This work	Keil et al. (1998)	This work	Keil et al. (1998)	Hu et al. (1999)	Hu et al. (1999)	This work	This work	Keil et al. (1998)	Keil et al. (1998)

^a Pollen samples were provided by Dr. Kimiyasu Kawamuro, Forestry and Forest Product Research Institute, Japan.^b G: gymnorperm; A: angiosperm.^c mg 100 mg organic carbon⁻¹.

26.5 ± 0.1 ($n = 28$) for the Holocene and 26.5 ± 0.3 ($n = 7$) for B/A, and that the values are lower for colder periods [25.9 ± 0.3 for YD ($n = 4$), 25.7 ± 0.1 ($n = 8$) for LGM, 25.3 ± 0.1 ($n = 2$) for MIS 4 and 25.6 ± 0.31 ($n = 3$) for sub-stage 5d]. Temporal variations in ACL after the LGM are shown in Fig. 7.

Leaf waxes from a number of plants (land plants and aquatic plants) can be suggested as a candidate source for the long-chain *n*-alkanoic acids with maxima at C_{26} or C_{28} in the core. Those in modern or fossil angiosperm leaf waxes are known to maximize at C_{26} and/or C_{28} (e.g., Rieley et al., 1991; Logan et al., 1996; Matsumoto et al., 2003). According to Ficken et al. (2000), typical emergent aquatic plants have distributions dominated by C_{24} , and non-emergent (submerged and floating-leafed) plants

also display enhanced abundances of *n*- C_{22} – C_{24} homologues. Moss, sedge and lichen have distributions dominated by the C_{26} – C_{30} homologues (Ficken et al., 1998). Therefore, a predominance of angiosperms as terrestrial higher plants, and moss, sedge and lichen may cause higher ACL values in warmer periods, while aquatic macrophytes (submerged and floating-leafed) may contribute to lowering ACL values in cold periods, probably in combination with a recession in the terrestrial higher plants around the lake.

4.3. Palaeovegetational changes inferred from lignin phenols, *n*-alkanoic acids and pollen records

Fossil pollen in a core (Ver 96-2, St-3) from Aca-demician Ridge was analyzed by Oda et al. (2000).

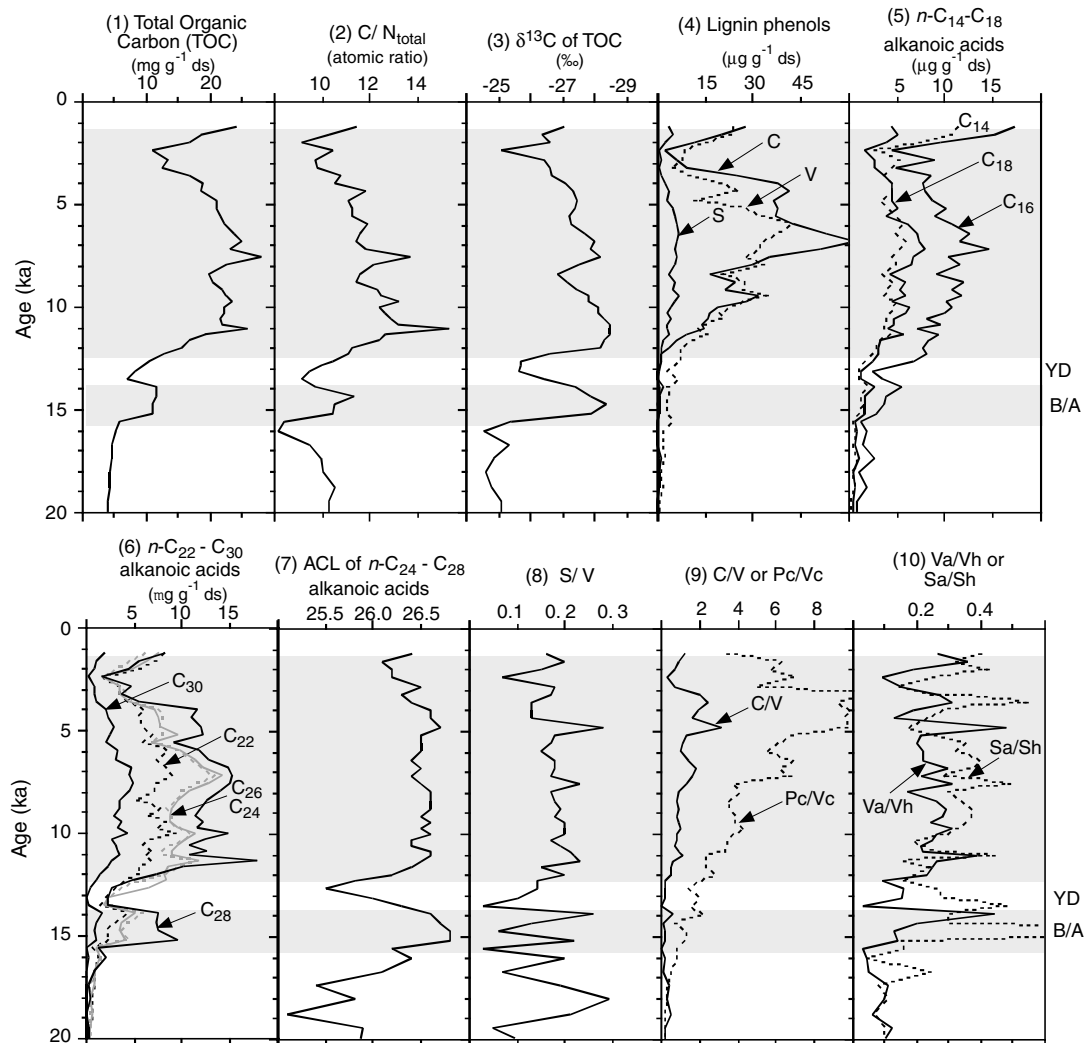


Fig. 7. Organic matter parameters vs. age over the past 20 kyr.

They divided pollen stratigraphy after 130 ka into five zones, including sub-zones. The zones correspond roughly to marine oxygen isotope stages (MISs). In the following, we describe reconstructions of palaeoenvironmental changes in the Lake Baikal area from biomarker records in combination with the pollen records.

4.3.1. Sub-stage 5e

Vertical profiles of lignin phenols (Figs. 3 and 4) indicate that absolute concentrations of V and S increase upward in sub-stage 5e and maximize around 122 ka, while the increase in C is more rapid than in V and S. The lignin phenol evidence suggests that gymnosperms predominated over angiosperms, and both gymnosperms and angiosperms spread extensively in 5e. This result corresponds well with the pollen records.

Records of S/V ratios suggest a gradual increase in gymnosperms relative to angiosperms with time (Fig. 5). Moreover, a marked decrease in C/V ratio and Pc/Vc ratio with time suggests that lignin compositions changed from a gymnosperm pollen type to a gymnosperm woody/non-woody tissue type. In general, pollen grains are transported by winds before deposition because of their relatively small size. Pine pollen is one such representative which can be transported over long distances from regional catchment. On the other hand, plant remains and leaves are transported much less easily by winds and are carried predominantly by streams to be deposited away from the drainage basin and directly into the lake area. Therefore, the probable increase in plant tissue remains relative to pollen with time in 5e suggests an increase in terrestrial runoff from upstream regions in the drainage basin and/or from nearshore regions of the lake.

It is suggested from an upward decrease in both (Ad/Al)_v and DHBA/V ratios (3,5-dihydroxybenzoic acid over total vanillyl phenols), an indicator of oxidative degradation of lignin (Prahl et al., 1994), that angiosperm (possibly herb)-derived lignin remains in soil were carried into sediments early in 5e.

4.3.2. Sub-stage 5d to MIS 2

Here, absolute concentrations of lignin phenols (S, V, and C) are very low. This coincides with the pollen record, where concentrations are extremely low (≤ 1000 grains cm^{-3}) for these periods, except for 5c, 5a, and MIS 3 where pollen abundance is slightly higher (2000–12,000 grains cm^{-3} ; Oda et al., 2000). According to Oda et al. (2000), only

thin herbs are presumed to have existed on frozen soil (tundra) under cold and dry conditions in 5d, MIS 4 and MIS 2 (excluding deglaciation). There existed a weak growth of vegetation of shrubs [willow (*Salix*; predominant) and alder (*Alnus*) with birch and herbs] in 5c–5a and MIS 3 (slightly cool or slightly warm climate conditions).

Because of the extremely low lignin phenol concentrations in these periods, the reliability of the analytical data is poorer than that with for the interglacials (5e and MIS 1), as mentioned above in Section 2.1. In particular, the data are insufficient for proper characterization of lignin phenols for MIS 4–MIS 2 (before deglaciation). The composition for 5c–5a suggests mixtures of non-woody angiosperm tissue and pollen. These components are assumed to derive preferentially from soil erosion.

4.3.3. MIS 1

Large and rapid climatic changes, in particular Bølling–Allerød (B/A) warm periods and a Younger Dryas (YD) cold phase, occurred during the transition after LGM towards the Holocene (the last glacial–interglacial transition). Fig. 7 displays temporal variations in OM bulk parameters and various lignin phenol and *n*-alkanoic acid parameters during MIS 1. TOC concentration maximizes around 15 ka, which probably corresponds to a period of significantly warmer conditions (Bølling–Allerød Interstadials).

4.3.3.1. Last glacial–interglacial transition. Absolute concentrations of lignin phenols for both B/A and YD are low (Fig. 7). This is in accordance with considerably low pollen concentrations. S/V ratio fluctuates widely (0.1–0.3), which suggests the presence of mixed non-woody angiosperms and gymnosperms with a slight dominance of the former. C/V ratio is low (< 0.6) in the B/A. In the YD chronozone, S/V and C/V values are low (< 0.1 for the former and ~ 0.1 for the latter), suggesting a dominance of gymnosperm woody tissue.

It is worth noting that the abundance of *n*-C₂₄ to C₃₀ alkanolic acids (maximizing at *n*-C₂₈) is markedly high in the B/A, compared with that of lignin phenols. Abundance ratio values of *n*-C₂₄ to C₃₀ alkanolic acids to lignin phenols (V + S + C) are ca. 5 for B/A, while they are mostly < 1 for the Holocene. Because these acids are typical components of plant leaf waxes, and lignin contents of herbs are 2–3 times lower than in common gymnosperms and angiosperms (Takahashi and Yasuoka,

2002), these n -C₂₄ to C₃₀ alkanolic acids may have come predominantly from herbs.

Pollen records (Oda et al., 2000) indicate that pollen abundance increases after the LGM but still remains low ($8 \pm 5 \times 10^3$ grains g⁻¹ ds) in the B/A. The records suggest a predominance of broad leaved trees (willow) and herbs (chenopods) in the B/A. Total pollen abundance becomes low ($4 \pm 1 \times 10^3$ grains g⁻¹ ds) in YD, and a transition from willow to alder, birch and pine is suggested (Oda et al., 2000).

4.3.3.2. Holocene. Vertical profiles of lignin phenols (Fig. 7) indicate that absolute concentrations of V, S and C increase after the YD. V and S give two maxima around 9 ka and 7–4 ka, while C give high values around 9, 7 and 4 ka, with a maximum around 7 ka. V, S and C concentrations give a minimum at around 2–3 ka. These results imply that both gymnosperms and angiosperms expanded over the past 9–3 ka. The S/V ratio gives higher values shortly after the YD and then decreases gradually towards the present, suggesting that gymnosperms became dominant over angiosperms.

A gradual increase in C/V and Pc/Vc ratios after the YD to 2.5 ka suggests an increase in pollen-derived lignin relative to woody/non-woody tissue-derived lignin. This may have occurred in accordance with a gradual expansion of a pine forest (Oda et al., 2000). After ~3 ka, lignin phenol concentrations, C/V and Pc/Vc ratios declined and show low values towards the present. This means that lignin phenols changed from a pollen type to woody/non-woody tissue type in the last ~3 ka. This suggests changes in the terrestrial environment or surface conditions favourable for runoff by streams during this period.

Absolute concentrations of higher plant wax n -C₂₄ to C₃₀ alkanolic acids are high after the YD and maximize around a short period after the YD and between 11 and 6 ka, a period presumably corresponding to the hypsithermal interval. Their abundance minimized around 2 ka. These fluctuations are roughly in accord with lignin phenols except for the period 12–8 ka, where the acids are more abundant than the lignin phenols. This may be explained by the idea that n -C₂₄ to C₃₀ alkanolic acids are contributed more by deciduous trees and herbs than by conifers.

Pollen records indicate that pine and birch are dominant with some alder, willow and herbs in the early Holocene and later (after ~8 ka) a pine forest became predominant, with some birch and herbs present (Oda et al., 2000).

5. Conclusions

Analysis of lignin phenols and n -C₁₄ to C₃₀ alkanolic acids using on line TMAH thermochemolysis for a Lake Baikal sediment core have revealed features of organic matter composition and vegetational change in the Lake Baikal region in the past 130 kyr, with the following major conclusions:

1. Lignin phenols are abundant in sediments in the interglacial periods (5e and MIS 1) and extremely low in MIS 4–MIS 2 periods. These results correlate well with pollen records and suggest an expansion of coniferous forests in 5e and MIS 1.
2. High values of C/V (> 1.0) occur in the interglacial periods (5a and MIS 1). Comparison of lignin phenols with different types of fossil pollen indicates that these high ratios are caused predominantly by pollen. Previously published and data reported here on lignin phenols in modern pollen support this idea. The C/V ratio may serve as an indicator of pollen contribution to sedimentary organic matter.
3. Straight chain C₂₄–C₃₀ alkanolic acids are present in significant amounts throughout the core, while the abundance of lignin phenols is low in the glacial periods. A considerable portion of the n -C₂₄ to C₃₀ alkanolic acids in the glacial periods might be derived from herbs. A high abundance of n -C₂₄ to C₃₀ alkanolic acids in sediments in the Bølling–Allerød chronozone suggests that these acids originate predominantly from herbs.
4. Records of lignin phenols and n -alkanoic acids are roughly consistent with pollen records. Inconsistency between organic matter records and pollen records may exist because organic matter abundance differs according to plant species and parts, mode of transportation and diagenesis. Therefore, lignin phenol and n -alkanoic acids can provide important information not obtained from pollen remains. On line TMAH thermochemolysis allows rapid characterization of sedimentary organic matter and thus facilitates construction of temporally highly resolved temporal records of environmental change.

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