Late Pleistocene variation in lignin and fatty acids from core TKN-2004 in a small mountain basin in central Japan

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We generated a record of lignin and fatty acid compositions from the TK-2004 core in Takano Basin, central Japan, during 39–162 ka by TMAH-thermochemolysis-GC/MS. We tested lignin and fatty acid compositions in the sediments of a small lake (1.88 km^2 watershed) as a paleovegetation proxy to understand the responses of terrestrial vegetation in central Japan to global climate change. Variation in terrestrial organic carbon contents estimated by C/N and $\Sigma 8$ was parallel to the total organic content (TOC) variation, suggesting that the inflow of terrestrial organic matter was a major factor determining the TOC. The ratio of mid-chain C_{20}–C_{24} *n*-fatty acids to short-chain C_{14}–C_{18} *n*-fatty acids (MFA/SFA ratio) and the ratio of cinnamyl to vanillyl phenols (C/V ratio) of lignin gradually increased from mid-MIS 6 to early MIS 3. The increase in both parameters suggested increase in the contribution of submerged and floating plants as the flats were expanded in the lake margin. The ratio of syringyl to vanillyl phenols (S/V ratio) corresponded to the pollen vegetation index. This correspondence indicated that the S/V ratio reflected the relative abundance of angiosperms to gymnosperms in the Takano Basin. The consistency of the S/V ratio at the site of core TKN-2004 and the other two locations suggests that the S/V ratio in a small basin is a robust proxy for terrestrial vegetation on a regional scale.

Keywords: lignin, vegetation, TMAH thermochemolysis, glacial, Takano Basin, central Japan, Late Pleistocene

INTRODUCTION

Central Japan is located near the atmospheric and oceanic boundaries between subarctic and subtropical regimes. Paleoenvironmental change in this region is sensitive to latitudinal shifts of these boundaries. Climate records from central Japan and the adjacent areas are thus useful to the understanding of hemispheric climate changes in the past (e.g., Oba *et al.*, 1991; Tada *et al.*, 1999; Yamamoto *et al.*, 2004; Nakagawa *et al.*, 2008).

Pollen studies have demonstrated a remarkable difference in vegetation on the Japanese Islands between the Holocene and the last glacial maximum (LGM) (compiled in Tsukada, 1985; Takahara *et al.*, 2000). At the LGM, boreal coniferous forests occupied the modern cool-temperate deciduous broadleaf and mid-temperate conifer forest zones (NE Japan), and temperate coniferous forests occupied the modern warm-temperate evergreen forest zone (SW Japan). This difference in vegetation can be attributed to the lower air temperature and precipitation of the LGM (Tsukada, 1985). Although continuous

records of pollen are scarce, spliced records from on-land cores are available for the last glacial cycle (e.g., Tsukada, 1988). Some long-term records of pollen and spores have demonstrated how the vegetation of central Japan changed in response to glacial–interglacial cycles (e.g., Miyoshi *et al.*, 1999; Igarashi and Oba, 2006; Nakagawa *et al.*, 2008; Takahara *et al.*, 2010).

Lignin is an abundant, stable phenolic macromolecule uniquely found in the cell walls of vascular land plants. Alkaline CuO oxidation of lignin yields four groups of structurally related products that contain the p-hydroxyl, vanillyl, syringyl, and/or cinnamyl groups (Hedges and Mann, 1979; Goñi and Hedges, 1992) (Fig. 4). The relative abundance of the vanillyl, syringyl, and cinnamyl groups, therefore, is often used as an index of paleovegetation. Lignin has been investigated in sediment cores from Lake Biwa, Japan (Ishiwatari and Uzaki, 1987; Ishiwatari *et al.*, 2009) and Lake Baikal, Siberia (Orem *et al.*, 1997; Ishiwatari *et al.*, 2005), and also in marine cores (Yamamoto *et al.*, 2005; Inagaki *et al.*, 2009). These studies have shown glacial–interglacial and longer-term variations in lignin abundance and composition, which are attributable to diagenesis, vegetation changes, and sea-level changes.

Fatty acids are common biomarkers in environmental
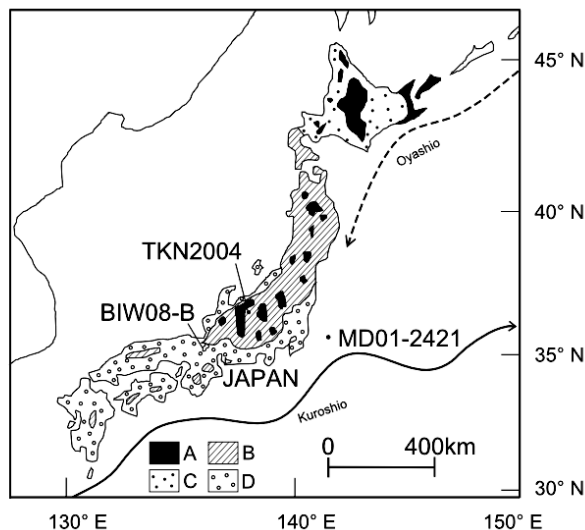
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Fig. 1. Map showing the modern vegetation of Japan (compiled by Igarashi and Oba, 2006) and the locations of cores TKN-2004, BIW08-B, and MD01-2421. A, subarctic conifer forests; B, cool-temperate deciduous broadleaf forests; C, pan-mixed forests; D, warm-temperate evergreen forests.

samples. Short-chain C_{14}–C_{18} *n*-fatty acids (SFA) are derived mainly from aquatic organisms, whereas long-chain C_{26}–C_{30} *n*-fatty acids (LFA) are derived predominantly from vascular plants (Kvenvolden, 1967). Mid-chain C_{20}–C_{24} *n*-fatty acids (MFA) are abundant in submerged and floating freshwater aquatic macrophytes (Ficken *et al.*, 2000). Abundances of short-, mid-, and long-chain fatty acids are hence useful in identifying the source of organic matter and estimating the contributions from different source organisms.

It is important to take into consideration the spatial size when we obtain climate signal from sediment archives. Pollen studies can isolate the climate signal from the non-climate noise by selecting the appropriate spatial and temporal scale for quantitative paleoclimate reconstruction (Bradshaw, 1994). Pollen is delivered to lake sediments by both rivers and winds. Aeolian transport induces the fractionation of pollen composition with increasing transportation distance (Erdman, 1969). The number of pollen particles is highly variable among different species (Erdman, 1969). The composition of pollen in sediments obtained from a small lake thus does not necessarily reflect the bulk composition of pollen produced in the watershed (Prentice, 1986). Therefore, sediments from lakes that have larger catchment basins are recommended for pollen studies because pollen composition reflects the regional pollen rain in the catchment basin and is not unduly influenced by vegetation in the immediate vicinity of the sampling site (Prentice, 1986).
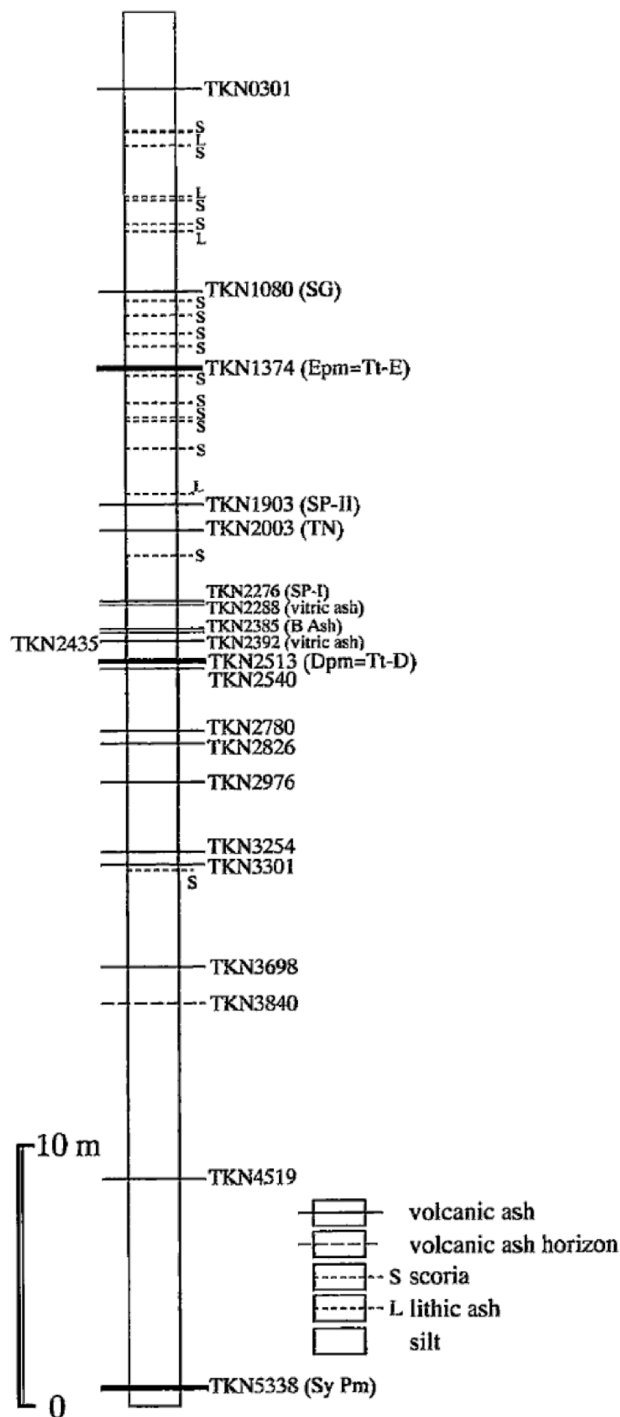

Fig. 2. Lithologic column of core TKN-2004 (Tawara et al., 2006).

Unlike pollen, lignin is expected to be delivered to lake sediments mainly by rivers because lignin is a constituent of plant tissues, which do not easily undergo aeolian transport. The composition of lignin thus reflects the lignin produced in the watershed. This finding suggests
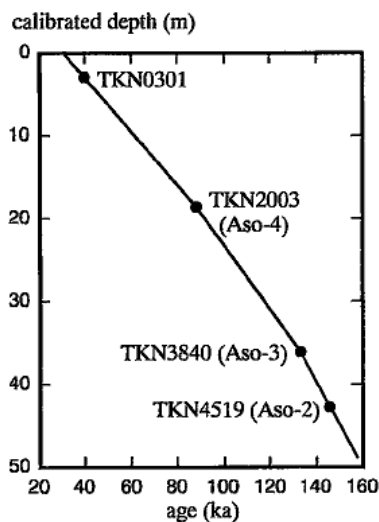
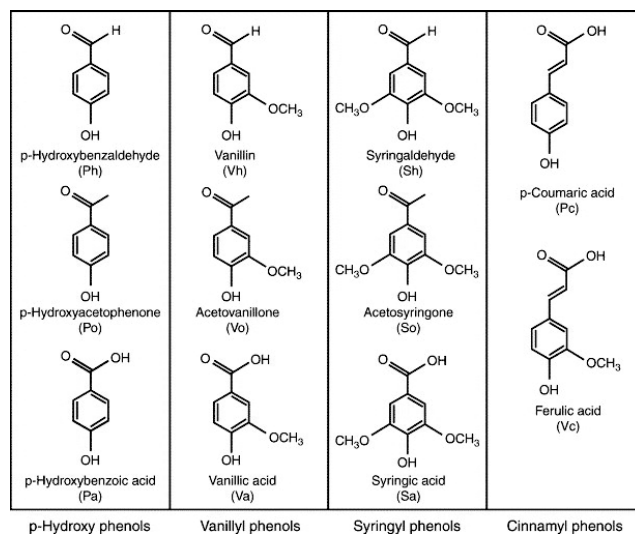Fig. 3. Age-depth model of core TKN-2004 (Nagahashi et al., 2007).

Fig. 4. The degradation products of lignin by alkaline CuO oxidation (Hedges and Parker, 1976; Hedges and Mann, 1979). The hydroxy groups are converted to methoxy groups in TMAH pyrolysate.

that the lignin composition is potentially useful in quantitatively reconstructing paleovegetation. Comparison of lignin and pollen records from different locations in the same vegetation zone will contribute to tests of lignin as a proxy for paleovegetation.

In this study, we generated a record of lignin and fatty acid compositions from core TKN-2004 in Takano Basin of central Japan by TMAH-thermochemolysis-GC/MS during 39–162 ka. We tested lignin and fatty acids in the sediments of a small lake (1.88 km^2 watershed) as a paleovegetation proxy to understand the responses of terrestrial vegetation in central Japan to global climate change.

MATERIALS AND METHODS

Study area

Takano Basin is located at an altitude of 720–730 m in central Japan and is surrounded by low ridges ~900 m high. A small stream called the Takano River flows northeastward through the basin, dendritically eroding lacustrine sediment. Late Pleistocene sediments of the Takano Formation were deposited in this small deposition formed by faulting along the margins of the basin (Kimura, 1987). The area of the basin bottom surface is 0.95 km^2. The area of the watershed of the Takano River is 1.88 km^2, only twice the basin bottom area. The present potential vegetation around Takano Basin is cool-temperate deciduous broadleaf forest and is situated in between warm-temperate evergreen forest and subalpine conifer forest (Tsukada, 1985). Vegetation around Takano

Basin is thus sensitive to climate change.

A borehole core TKN-2004 (53.88 m long) was retrieved in 2004 by scientific drilling at a relict of the terrace in the Takano Basin at 36°32′55″ N, 138°02′07″ E (Fig. 1). The sediments are lacustrine deposits and consist of pale-brown to reddish-brown weathered clayey silt from 0 to 2.31 m, dark-gray clayey silt from 2.31 to 35.70 m, and dark-gray silt from 35.70 to 53.87 m (Fig. 2), associated with many marker tephra beds. An age–depth model was created using four volcanic ash layers by Nagahashi et al. (2007) (Fig. 3). The average sedimentation rate was 0.33 m/ky. A total of 98 samples were collected and analyzed approximately every 50 cm (~1.5 ky) from 2.7 m (38.6 ka) to 53.5 m (162.0 ka).

The total organic carbon (TOC) content and the ratio of TOC to total nitrogen (C/N ratio) in sediments from the core TKN-2004 were reported by Tawara et al. (2006). Major element composition and some pollen data were reported by Ito et al. (2010).

Lignin and fatty acid analysis

Lignin and fatty acids were analyzed following the methods of Yamamoto et al. (2001) and Yamamoto et al. (2005) modified after S. Yamamoto (2000), respectively. Pyrolysis gas chromatography mass spectrometry with in situ methylation with tetramethylammonium hydroxide (TMAH-thermochemolysis-GC/MS) was carried out using a Japan Analytical Industry JHP-5 Curie point pyrolyzer that was directly connected to the injection port of a Hewlett Packard 5973 gas chromatograph mass selective detector. The column used was a Chrompack CP-

Compound	Diagnostic ion	Response factor
Ph	136 (M$^+$)	0.224
Po	150 (M$^+$)	0.197
Pa	166 (M$^+$)	0.120
Vh	166 (M$^+$)	0.228
Vo	180 (M$^+$)	0.291
Va	196 (M$^+$)	0.154
Sh	196 (M$^+$)	0.215
So	210 (M$^+$)	0.182
Sa	226 (M$^+$)	0.157
Pc	192 (M$^+$)	0.143
Vc	222 (M$^+$)	0.128
n-nonadecanoic acid	74 (McLafferty rearrangement)	0.205

Sil5CB (length, 30 m; i.d., 0.25 mm; thickness, 0.25 μm). The sediment sample (*ca*. 20 mg) was placed on a Ni–Co pyrofoil plate with 30 μL of 5% TMAH in methanol and 20 μL of internal standard solution (0.1 g/L *n*-nonadecanoic acid in hexane). After drying, the sample was wrapped in pyrofoil. The sample was heated at 590°C for 20 s in the pyrolyzer, and the generated compounds were transferred to the GC splitless injection system at 300°C with a helium carrier gas. The oven temperature was programmed from 70°C to 310°C at 4°C/min after the initial hold time of 1 min, and then it was held isothermally at 310°C for 30 min. The mass spectrometer was run in the full scan ion-monitoring mode (*m/z* 50–650). Electron impact spectra were obtained at 70 eV. The lignin phenols were identified by comparing their mass spectra and retention times with those of authentic standards (Fig. 4). Concentrations of lignin phenols and fatty acids were obtained according to the following equation:

$$\text{Conc}_A = 2 \times (\text{Area}_A/\text{RF}_A)/(\text{Area}_{IS}/\text{RF}_{IS})/W_{SD},$$

where Conc$_A$ is the concentration of compound A, Area$_A$ is the peak area of compound A on the ion chromatogram for its molecular ion, Area$_{IS}$ is the peak area of internal standard (*n*-nonadecanoic acid) on the ion chromatogram of *m/z* 74, RF$_A$ and RF$_{IS}$ are the response factors of compound A and internal standard, and W$_{SD}$ is the sample weight. The response factors of lignin phenols (RF$_{LG}$) and internal standard (RF$_{IS}$) were determined by analysis of the authentic standards (lignin phenols and *n*-nonadecanoic acid) according the following formula:

$$\text{RF}_{LG} = \text{Int}_M/\text{Int}_{50-650}$$

$$\text{RF}_{IS} = \text{Int}_{74}/\text{Int}_{50-650},$$

where Int$_M$ is the intensity of molecular ion in the mass spectrum of lignin phenol, Int$_{74}$ is the intensity of *m/z* 74 fragment ion in the mass spectrum of *n*-nonadecanoic

acid, and Int$_{50-650}$ is the sum of ion intensities from *m/z* 50 to *m/z* 650. The response factors of lignin phenols and *n*-nonadecanoic acid obtained by this way are listed in Table 1. The response factor of *n*-nonadecanoic acid was applied for other fatty acids. The standard deviations in replicate analysis (five times) were 10%, 7%, 15%, and 8% of the concentration for total syringyl phenol (S), total vanillyl phenols (V), total cinnamyl phenol (C), and total eight lignin (Σ8; S+V+C), respectively, and they were 0.01, 0.03, and 0.06 for S/V and C/V ratios and the ratio of acid to aldehyde of vanillyl phenol [(Ad/Al)$_v$] ratio, respectively. The standard deviations in three duplicate analyses averaged 13% of the concentration for total fatty acids.

TMAH-thermochemolysis-GC/MS yields lignin phenols that are equivalent to those produced by conventional alkaline CuO oxidation (Clifford *et al.*, 1995; Hatcher *et al.*, 1995; Yamamoto, 2000). The Σ8 and Λ values obtained by TMAH thermochemolysis are the same as those obtained by CuO oxidation, but the S/V ratio is lower, and the C/V and (Ad/Al)$_v$ ratios are higher in TAMH thermochemolysis than in CuO oxidation (Shuichi Yamamoto, unpublished data). Wysocki *et al.* (2008) recently reported 10 times lower Λ values in TMAH thermochemolysis than in CuO oxidation, but we suggest that this low yield was caused by the incomplete reaction of O–C cleavage at a low temperature condition (250°C).

RESULTS

Lignin abundance

Lignin was detected in a sufficient amount in the depth interval between 4.20 m (42.9 ka) and 42.80 m (141.4 ka). The intervals above 4.20 m and below 42.80 m yield a trace amount of lignin, but the amount was not enough to discuss its composition.

Between 4.20 m (42.9 ka) and 42.80 m (141.4 ka), Σ8 (mg/10 g sediment), which is the total amount of eight lignin phenols belonging to the vanillyl, syringyl, and cinnamyl groups (Fig. 2), varied between 0.01 and 3.90, with an average of 1.33 (Fig. 5). Λ (mg/100 mg TOC), which is the total amount of the eight lignin phenols in 100 mg of TOC, varied between 0.01 and 0.90, with an average of 0.31 (Fig. 5).

The values of Σ8 and Λ were high from MIS 5 to early MIS 5d, early MIS 5b, and mid-MIS 5a (Fig. 5). Higher Σ8 and Λ were found in the interval showing higher TOC and C/N (Fig. 5).

Lignin composition

The ratio of acid to aldehyde of vanillyl phenol [(Ad/Al)$_v$] increases systematically as lignin is degraded by aerobic fungi, and the ratios of highly degraded lignin exceed ~0.4 in the alkaline CuO oxidation method (Goñi
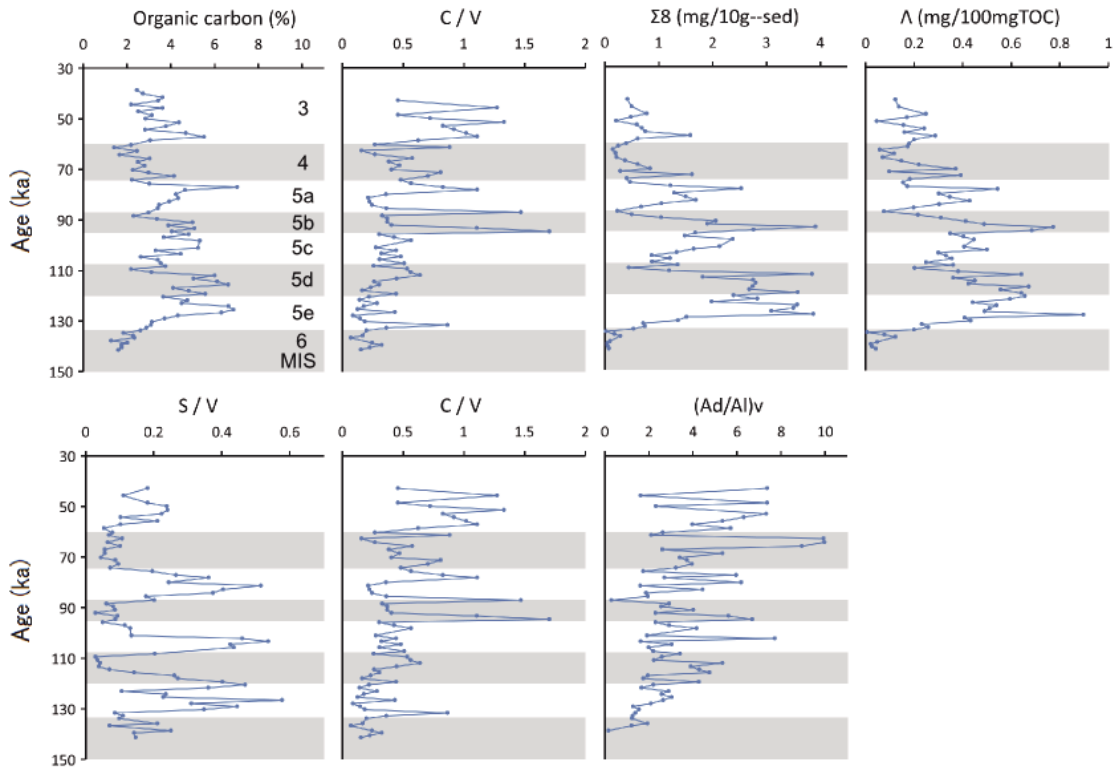
Fig. 5. Changes in total organic carbon (TOC) content C/N, $\Sigma 8$, Λ, S/V, C/V, and $(Ad/Al)_v$ in core TKN-2004 between 41 and 151 ka. TOC and C/N refer to Tawara et al. (2006).
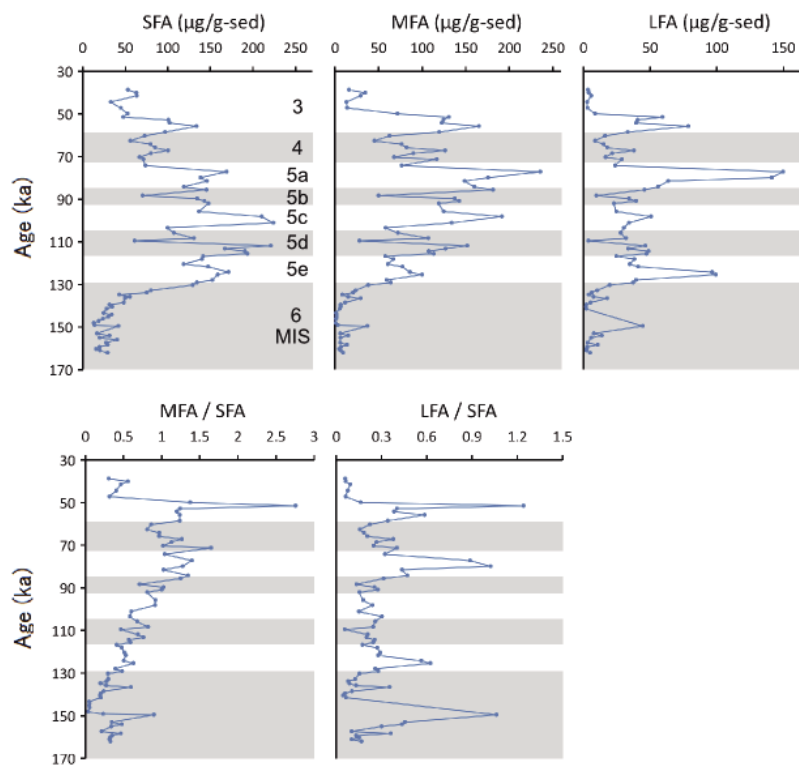

Fig. 6. Changes in the concentrations of short-chain C_{14}–C_{18} n-fatty acids (SFA), mid-chain C_{20}–C_{24} n-fatty acids (MFA), and long-chain C_{26}–C_{30} n-fatty acids (LFA) in core TKN-2004 between 41 and 151 ka.
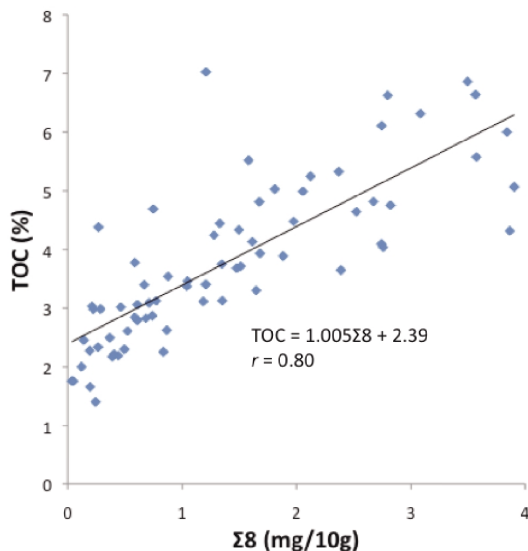
Fig. 7. Plot of total organic carbon content (TOC) against total lignin concentration (Σ8) in core TKN-2004 samples.

et al., 1993). The TMAH procedure is more sensitive for calculation of $(Ad/Al)_v$ ratios than is the alkaline CuO oxidation procedure (Hatcher *et al.*, 1995). The sensitivity of $(Ad/Al)_v$ ratios to fungal degradation with the TMAH procedure is ~15 times higher than that with the CuO oxidation method (Hatcher *et al.*, 1995; Filley *et al.*, 2000). Fresh, moderately degraded, and highly degraded lignins have the $(Ad/Al)_v$ ratios of ~0.5, ~3, and 7–12, respectively, with the TMAH procedure (Yamamoto *et al.*, 2005). In core TKN-2004, $(Ad/Al)_v$ ratio ranged from 0.3 to 10.0, with an average of 3.6 (Fig. 5), which suggests that lignin in most samples was fresh to moderately degraded, but the lignin in some samples was highly degraded by aerobic microbes. Highly degraded lignin was observed in late MIS 4 (Fig. 5). $(Ad/Al)_v$ ratio tended to increase upward (Fig. 5).

The ratios of syringyl (S) to vanillyl (V) phenols (S/V ratio), which is a contribution index of angiosperms against gymnosperms (Hedges and Mann, 1979), ranged from 0.02 to 0.58, with an average of 0.19. The values fell within the range of a mixture of angiosperms (mean values of leaf and branch are 0.71 and 0.90, respectively; Shuichi Yamamoto, unpublished data) and gymnosperms (mean values of leaf and branch are 0.07 and 0.07, respectively; Shuichi Yamamoto, unpublished data). A laboratory degradation of birch wood by a white-rot fungus, *Phelbia tremellosus*, linearly increased the $(Ad/Al)_v$ ratio and decreased the S/V ratio (Hedges *et al.*, 1988). There is, however, little correlation between S/V and $(Ad/Al)_v$ ratios ($r = -0.15$) in this core, implying that the variation of the S/V ratio was not significantly altered by aero-

bic degradation. The S/V ratio shows maximal peaks at mid-MIS 5e, the MIS 5d/5c boundary, and MIS 5a (Fig. 5).

The ratios of cinnamyl (C) to vanillyl (V) phenols (C/V ratio), which indicates the contribution of non-woody tissues and herbaceous plants (Hedges and Mann, 1979), ranged from 0.07 to 1.70, with an average of 0.48. The C/V ratio sensitively decreases by aerobic degradation of lignin (Hedges and Weliky, 1989; Opsahl and Benner, 1995). However, little correlation exists between C/V and $(Ad/Al)_v$ ratios ($r = -0.05$) in this core, implying that the variation of the C/V ratio was not altered by aerobic degradation. This C/V ratio tended to increase upward and showed maximal peaks at early and late MIS 5b, mid-late MIS 5a, and early MIS 3 (Fig. 5).

Normal fatty acids

Normal fatty acids showed trimodal homologous distribution with maxima at C_{16}, C_{22}, and C_{26}. Short-chain C_{14}–C_{18} *n*-fatty acids (SFA) are derived mainly from aquatic algae, whereas long-chain C_{26}–C_{30} *n*-fatty acids (LFA) are derived predominantly from vascular plants (Kvenvolden, 1967). Mid-chain C_{20}–C_{24} *n*-fatty acids (MFA) are abundant in submerged and floating freshwater aquatic macrophytes (Ficken *et al.*, 2000). The trimodal distribution of *n*-fatty acids suggests a contribution from aquatic plants, as well as aquatic algae and terrestrial plants.

The concentrations of SFA, MFA, and LFA were lower in early to mid-MIS 6, but they increased in late MIS 6 (Fig. 6). The concentrations were high and fluctuating throughout MIS 5. They decreased in MIS 4, increased again in early MIS 3, and dropped in mid-MIS 3. The ratio of MFA to SFA (MFA/SFA ratio) gradually increased from mid-MIS 6 to early MIS 3. The ratio of HFA to SFA (HFA/SFA ratio) was intermittently elevated at mid-MIS 6, early MIS 5e, MIS 5a, and early MIS 3.

DISCUSSION

Terrestrial versus aquatic organic matter

A linear relationship exists between TOC and Σ8 in sediments from core TKN-2004 (Fig. 7). The intercept and slope of the regression line are 2.39 and 1.005, respectively. The two major potential sources of organic carbon are terrestrial organic carbon derived from land plants and aquatic organic carbon produced in the lake. The latter "aquatic organic carbon" could include the organic carbon produced by terrestrial microorganisms. We thus assumed that the intercept represents the average organic carbon content produced in the lake and that the slope represents the relative abundance of lignin to terrestrial organic carbon. According to this assumption, terrestrial organic carbon content based on Σ8 (TROC-Σ8)
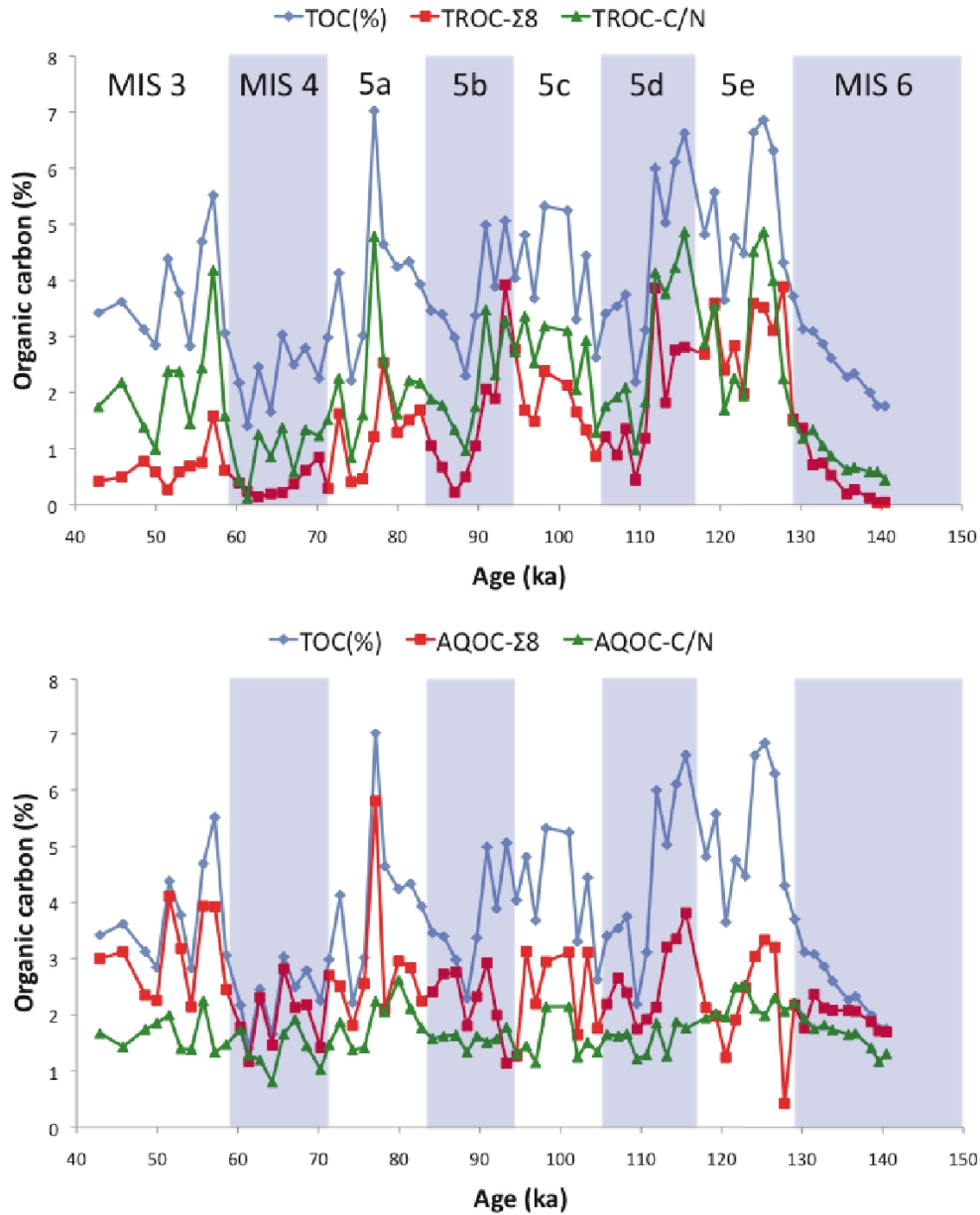
Fig. 8. TOC and terrestrial and aquatic organic matter contents based on Σ8 (TROC-Σ8 and AQOC-Σ8) and C/N (TROC-C/N and AQOC-C/N) in core TKN-2004.

and aquatic organic carbon content based on TROC-Σ8 (AQOC-Σ8) are computed by the following formulas, respectively.

$$\text{TROC-}\Sigma 8\ (\%) = 1.005\Sigma 8\ (\text{mg/10 g})$$

$$\text{AQOC-}\Sigma 8\ (\%) = \text{TOC}\ (\%) - \text{TROC}\ (\%).$$

TROC-Σ8 ranged from 0% to 3.9%, with an average of 1.3% (Fig. 8). AQOC-Σ8 ranged from 0.5% to 5.8%,

with an average of 2.4% (Fig. 8). TROC-Σ8 showed maximal peaks at the same period, as did TOC. AQOC-Σ8 showed maxima in early MIS 5e boundary, MIS 5e/5d boundary, MIS 5a, and early MIS 3.

C/N ratio was also used for estimating TROC and AQOC (TROC-C/N and AQOC-C/N, respectively). Assuming that the C/N ratios of aquatic and terrigenous organic matter are 6 and 30, respectively (Bordowskiy, 1965), TROC-C/N and AQOC-C/N were calculated following the formula, respectively:
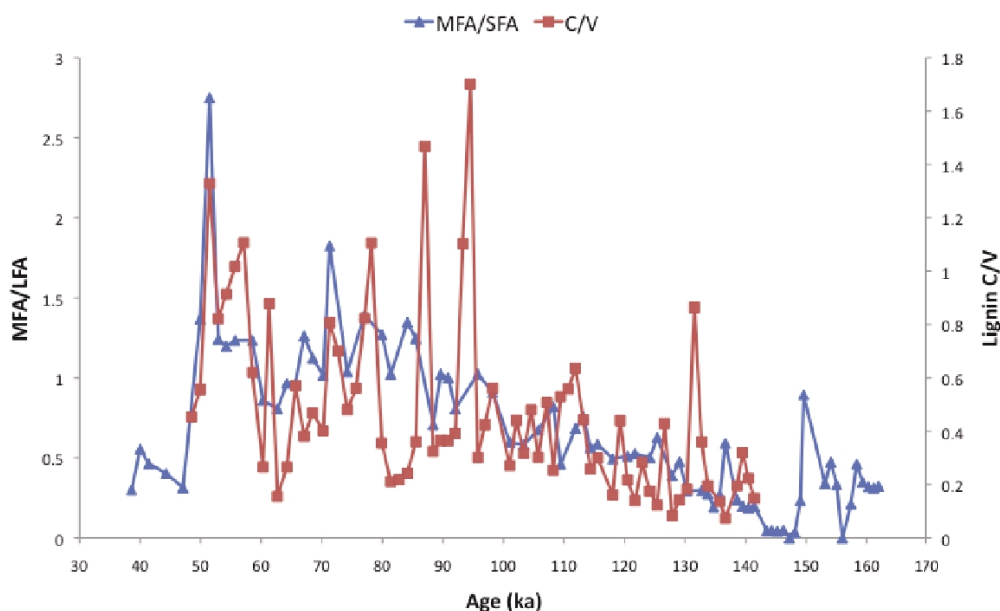
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Fig. 9. Changes in the ratio of mid-chain C_{20}–C_{24} n-fatty acids (MFA) to short-chain C_{14}–C_{18} n-fatty acids (SFA) and lignin C/V ratio in core TKN-2004.

$$\text{TROC-C/N (\%)} = 1.25 \times \text{TOC} \times \{1\text{-}6/(\text{C/N})\}$$

$$\text{AQOC-C/N (\%)} = \text{TOC} - \text{TROC-C/N}.$$

TROC-C/N ranged from 0% to 4.9%, with an average of 2.0% (Fig. 8). AQOC-C/N ranged from 0.8% to 2.6%, with an average of 1.6% (Fig. 8). TROC-C/N showed maximal peaks at the same period as TOC did. AQOC-C/N did not vary significantly.

TROC values estimated by C/N were higher than those estimated by Σ8, but the changing patterns are similar to each other (Fig. 8). Their variations are parallel to TOC variation. This observation suggests that the inflow of terrestrial organic matter is a major factor determining TOC. Tawara *et al.* (2006) attributed TOC variation in core TKN-2004 to either or both changes in primary production in the lake water and/or changes in the inflow of terrestrial plants. The results of this study showed that the TOC reflected the inflow of terrigenous organic matter into the lake.

Increased contribution of submerged and floating plants
The MFA/SFA ratio gradually increased from mid-MIS 6 to early MIS 3 (Fig. 9). This increase was accompanied by an increase in the lignin C/V ratio (Fig. 9). Because the MFA/SFA ratio is specifically high in submerged and floating plants (Ficken *et al.*, 2000), and the C/V ratio is high in the non-woody tissues of plants (Hedges and Mann, 1979), the increase in both parameters suggests

an increase in the contribution of submerged and floating plants. The middle and upper members of the Takano Formation consist of clayey sediments, suggesting that deep lake environments continued until 30 ka at the core site. Continuous sedimentation, however, could result in the shallowing of marginal areas. The increase in the MFA/SFA ratio and the lignin C/V ratio suggest that a gradual expansion of shallow coastal areas, where submerged and floating plants flourished, occurred in the margin of the lake.

Changes in the contributions of gymnosperms and angiosperms
The S/V ratio, which is a contribution index of angiosperms vs. gymnosperms (Hedges and Mann, 1979), showed maximal peaks at mid-MIS 5e, the MIS 5d/5c boundary, and MIS 5a (Fig. 10). The Tp value is the ratio of the pollen abundance of cool-temperate broadleaf trees to the sum of that of cool-temperate broadleaf plants and subarctic conifer trees (defined by Igarashi and Oba, 2006). In core TKN-2004, Tp was higher in MIS 5e, the MIS 5d/5c boundary, MIS 5a, and early MIS 3 (Fig. 10; Kanauchi *et al.*, 2007; Ito *et al.*, 2010). Variation in the S/V ratio corresponded to the Tp variation in core TKN-2004. This correspondence indicates that the S/V ratio reflected the vegetation in the Takano Basin, in turn indicating the relative contribution of cool-temperate broadleaf plants (angiosperms) compared with subarctic conifer trees (gymnosperms).
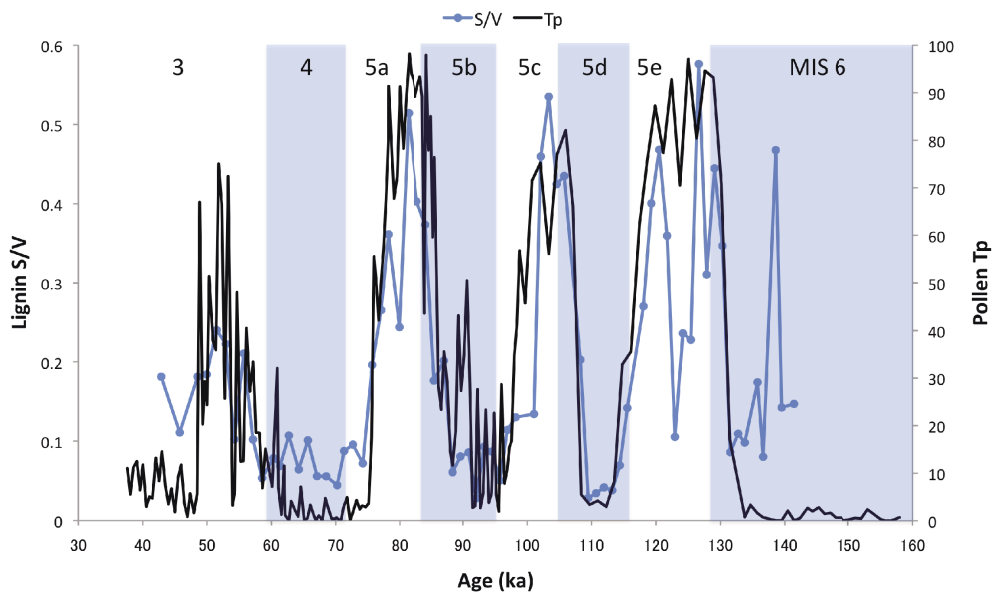
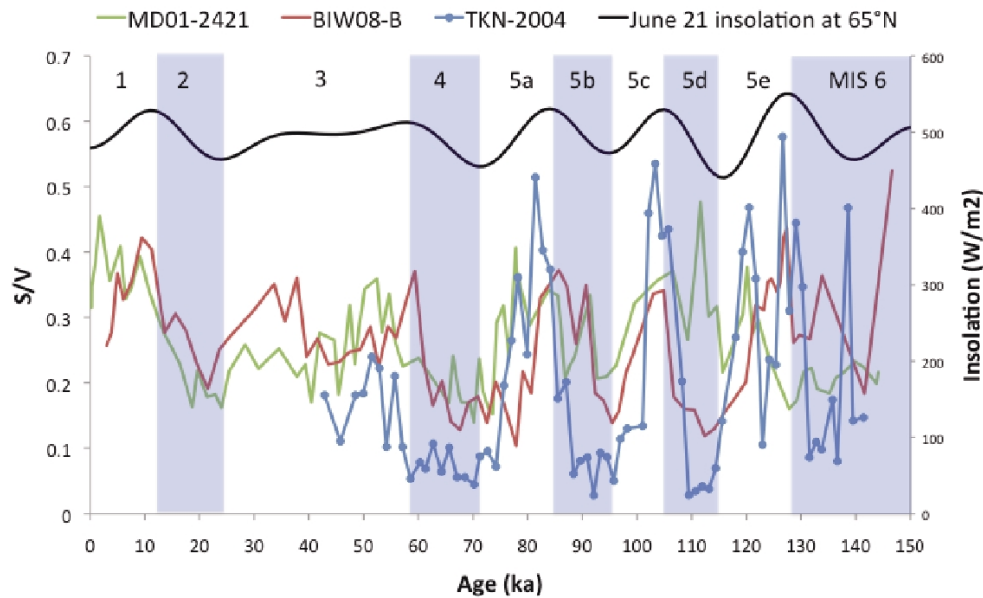Fig. 10. Changes in S/V ratio and Tp value in core TKN-2004. Tp values refer to Kanauchi et al. (2007).

Fig. 11. Changes in S/V ratio in cores TKN-2004, BIW08-B, and MD01-2421. Insolation on June 21 at 65°N was shown for comparison.

Figure 11 shows the S/V ratios in core TKN-2004 and other two cores, i.e., core BIW08-B from Lake Biwa in central Japan (Ohira *et al.*, 2014) and core MD01-2421 off central Japan in the northwestern Pacific (Yamamoto *et al.*, 2005). All of these records showed good agreement, except in the MIS 6 to MIS 5d in MD01-2421 (Fig. 11). The mismatch between S/V and pollen records around MIS 5e in MD01-2421 core was interpreted to mean that long-distance transportation of lignin particles caused by marine transgression could result in preferential degra-

dation of more labile syringyl phenols compared with vanillyl phenols (Yamamoto *et al.*, 2005). Alternatively, the mismatch could reflect hydrodynamic sorting caused by the resuspension and cross-shelf transport of particles (Goñi *et al.*, 1997). This mismatch is potentially the reason that the S/V variation at site MD01-2421 was different from that in other sites around MIS 5e. The general correspondence of the S/V ratios among these cores implies that the S/V ratio is a robust proxy for terrestrial vegetation not only on a local but also on a regional scale. Variation in S/V showed a precession-like cycle and corresponded to the June 21 variation of insolation at 65°N (Fig. 11).

Takano Basin is a small mountain basin only 1.88 km^2 in watershed area. The lignin composition in the sediments records the local vegetation within the basin. The S/V ratio in core TKN-2004 showed larger variation than that in the BIW08-B and MD01-2421 cores. This difference suggests that the S/V ratios in sediments of small basins are more sensitive to vegetation change because the forests within the watershed are easily replaced in response to climate change. Aside from the variation amplitude, the S/V ratio was generally consistent with regional vegetation, suggesting that the vegetation within the basin represents the vegetation of the surrounding area on a larger scale. This finding reminds us that mountainous small basins provide paleoclimate archives to investigate paleovegetation. Because small lakes are more numerous than large lakes, they will be useful for investigating the distribution of vegetation in space and time.

CONCLUSIONS

Variation in terrestrial organic carbon contents, estimated by C/N and Σ8, was parallel to the TOC variation, suggesting that the inflow of terrestrial organic matter was a major factor determining TOC.

MFA/SFA ratio and lignin C/V ratio gradually increased from mid-MIS 6 to early MIS 3. The increase in both parameters suggested an increase in the contribution of submerged and floating plants as the flats were expanded in the lake margin.

S/V ratio corresponded to the pollen vegetation index known as Tp. This correspondence indicated that the S/V ratio reflected the vegetation in Takano Basin and indicates the relative contribution of angiosperms to gymnosperms. The consistency of the S/V ratio in core TKN-2004 and the other two cores suggests that the S/V ratio is a robust proxy for terrestrial vegetation on a regional scale.

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