Response of vegetation in central Japan to precession during the last 147,000 years: A lignin record from Lake Biwa core BIW08-B

Fukashi Ohira[1], Masanobu Yamamoto[1,2,*], Keiji Takemura[3], Akira Hayashida[4]

[1] Graduate School of Environmental Science, Hokkaido University, Kita-10, Nishi-5, Kita-ku, Sapporo 060-0810, Japan.

[2] Faculty of Environmental Earth Science, Hokkaido University, Kita-10, Nishi-5, Kita-ku, Sapporo 060-0810, Japan.

[3] Institute for Geothermal Science, Kyoto University, Noguchihara, Beppu, Ohita 874-0903, Japan.

[4] Faculty of Science and Engineering, Doshisha University, 1-3 Tatara Miyakodani, Kyotanabe, Kyoto 612-0321, Japan.

*Corresponding author; Phone/Fax: +81-11-706-2379, E-mail: myama@ees.hokudai.ac.jp (M. Yamamoto)

ABSTRACT

To understand the responses of terrestrial vegetation in central Japan to global climate changes, we generated a record of lignin composition from core BIW08-B in Lake Biwa, central Japan, during the last 147,000 years by TMAH-pyrolysis-GC/MS. Lignin abundance was intermittently elevated and associated with a high ratio of cinnamyl (C) to vanillyl (V) phenols (C/V ratio) of lignin, suggesting episodic inflows

of herbaceous plant-derived organic matter into Lake Biwa. The largest inflow occurred during the last deglaciation. Variation in the ratio of syringyl (S) to vanillyl (V) phenols (S/V ratio), which is a contribution index of angiosperms against gymnosperms, showed a precession-like cycle, was consistent with a pollen record from Lake Biwa, and showed a pattern similar to the S/V record from an offshore marine site in the northwestern Pacific. The variation reflected the regional replacement of cool-temperate deciduous broadleaf forests, subalpine conifer forests, and Japanese cedar forests in central Japan caused by the repetition of warmer, dry and cooler, wet climates on a precession cycle.

Keywords: lignin, vegetation, TMAH pyrolysis, glacial, Lake Biwa, central Japan, late Pleistocene, BIW08-B

1. Introduction

Central Japan is located near the atmospheric and oceanic boundaries between the subarctic and subtropical regimes. Paleoenvironmental change in this region is therefore sensitive to latitudinal shifts of these boundaries in the northwestern Pacific region. Marine records have demonstrated that the oceanic subarctic boundary in the northwestern Pacific has been displaced in response to the Earth's precession (e.g., Aizawa et al., 2004; Koizumi et al., 2004; Yamamoto et al., 2004; Oba et al., 2006) and millennial forcing (e.g., Yamamoto et al., 2005b; Isono et al., 2009) and have also shown that the atmospheric boundary has shifted in response to orbital and millennial forcing (e.g., Tada et al., 1999; Irino and Tada, 2000, 2002; Nagashima et al., 2007, 2011; Takahara et al., 2010).

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 and some long-term records have demonstrated how the vegetation of central Japan changed in response to glacial–interglacial cycles (e.g., Tsukada, 1988; Miyoshi et al., 1999; Igarashi and Oba, 2006; Nakagawa et al., 2008; Hayashi et al., 2010a, b; Takahara et al., 2010).

Lake Biwa is located in central Japan, which includes, from warmer to cooler regions, warm-temperate evergreen broadleaf forests, cool-temperate deciduous broadleaf forests, and subarctic coniferous forests (Fig. 1). Vegetation around Lake Biwa is thus sensitive to changes in climate. Fuji (1984) investigated variations in pollen assemblages in a Lake Biwa core. Subsequent studies demonstrated glacial–interglacial variations in pollen assemblages in Lake Biwa during the late Pleistocene and Holocene (Higuchi and Inouchi, 1991; Miyoshi et al., 1991; Hayashi et al., 2010a, b).

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: the p-hydroxy, vanillyl, syringyl, and cinnamyl groups (Hedges and Mann, 1979) (Fig. 2). The vanillyl group is abundant in gymnosperms,

whereas the syringyl group is specific to angiosperms. The cinnamyl group is abundant in the non-woody tissues of vascular plants and grasses (Hedges and Mann, 1979; Goñi and Hedges, 1992). 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), Lake Baikal, Siberia (Orem et al., 1997; Ishiwatari et al., 2005), and also in marine cores (Yamamoto et al., 2005a; 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. Ishiwatari and Uzaki (1987) attributed the decreasing trend of lignin abundance with increasing depth in a Lake Biwa sediment core to degradation of lignin during diagenesis. The time resolution of lignin records has generally been lower than that of other records because the time and effort required for conventional lignin analysis have hindered this work.

Pyrolysis–gas chromatography–mass spectrometry with in situ methylation with tetramethylammonium hydroxide (TMAH-pyrolysis-GC/MS) has been used recently for analysis of macromolecules such as lignin (e.g., Clifford et al., 1995; Hatcher et al., 1995). TMAH-pyrolysis-GC/MS yields lignin phenols that are equivalent to those produced by conventional alkaline CuO oxidation (Hatcher et al., 1995; Yamamoto, 2000). In this method, organic matter is pyrolyzed in the presence of TMAH, and the pyrolysates are transformed to a methyl ester, a methoxy benzene, and so forth. The derivatized pyrolysates are then analyzed with on-line GC/MS. This method enables more rapid analysis with a small amount of sample (~0.1 mg C) compared with the conventional alkaline CuO oxidation method.

In this study, we generated a record of lignin composition from core BIW08-B from Lake Biwa by TMAH-pyrolysis-GC/MS through the last 147,000 years to understand the responses of terrestrial vegetation in central Japan to global climate changes.

2. Materials and methods

2.1. Study area

Located in central Japan at an elevation of 84 m, Lake Biwa is surrounded by mountains that are approximately 1,000 m high. Lake Biwa is the largest lake in Japan. It has an area of 674 km^2 and a watershed area of 3,850 km^2 (Fig. 1). More than 118 rivers flow into the lake, but only one, the Seta River, discharges from it. The climate of this area is strongly affected by the East Asian monsoon. The East Asian summer monsoon provides warm and humid conditions, whereas the winter monsoon brings snowfall to the northern part of this area and dryness to the southern part.

The borehole core BIW08-B (100.3 m long) was collected in 2008 by drilling offshore of Okishima in Lake Biwa (35°13′41.15″N, 136°03′21.19″E) at a water depth of 53 m (Fig. 1; Takemura et al., 2010). The sediments consist of dark-gray massive silty clay from 0 to 89 m, sandy silt containing abundant sand and plant debris from 89 to 99 m, and dark-gray massive silty clay from 99 to 100.3 m (Fig. 3; Sato et al., submitted). The results of analysis for top 44 m are reported in this paper. An age–depth model of top 44 m was created using radiometric ages of 14 volcanic ash layers (Fig. 4; Takemura et al., 2010; Takemura et al., in preparation). The average sedimentation rate was 0.3 m/ky. The sediment was stored at 4°C for one-half year. A total of 80 samples (2.5 cm thick) were collected from the upper 44 m (0–147 ka) of the core, and the

samples were immediately freeze dried. The average sampling interval was ~1.8 ka.

2.2. Organic carbon analysis

Each homogenized sample (ca. 4 mg) was placed in an Ag capsule, HCl was added, and the sample was kept overnight. The capsule was dried once, HCl was again added, and the capsule was then dried at 100°C for 12 h. Vanadium pentoxide (ca. 6 mg) was added to the dried samples, and they were wrapped in an Ag capsule. The Ag capsule was then wrapped with a Sn capsule.

Total organic carbon (TOC) content was determined using a EuroVector (Milan, Italy) elemental analyzer EA3011 (single furnace model). Helium was used as the carrier gas under conditions of constant flow at 120 ml/min and pressure of 80 kPa. The oven temperature was 115°C, the furnace temperature was 1020°C, and the analytical time was 385–390 sec.

2.3. Lignin analysis

Pyrolysis gas chromatography-mass spectrometry with in situ methylation with tetramethylammonium hydroxide (TMAH-pyrolysis-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-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 sec 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 minutes. The mass spectrometer was run in the full scan ion-monitoring mode (m/z 50-650). Electron impact spectra were obtained at 70 eV. Identification of lignin phenols was achieved by comparison of their mass spectra and retention times with those of authentic standards. Concentrations of lignin phenols were obtained according to the following equation:

$$Conc_A = W_{IS} (Area_A/RF_A)/(Area_{IS}/RF_{IS})/W_{SD}$$

where $Conc_A$ is the concentration of compound A (μg/g), W_{IS} is the weight of interbnal standard (μg), $Area_A$ is the peak area of compound A on the ion chromatogram of 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 (μg). W_{IS} was 2 μg in this study. The response factors of lignin phenols (RF_{LG}) and internal standard (RF_{IS}) were determined by the analysis of the authentic standards (lignin phenols and n-nonadecanoic acid) according the following formula:

$$RF_{LG} = Int_M/Int_{50\text{-}650}$$

$$RF_{IS} = Int_{74}/Int_{50\text{-}650}$$

where Int_M is the intensity of molecular ion in the mass spectrum of ligninphenol, 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 were listed in Table 1. 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 vanyllyl phenol [$(Ad/Al)_v$ ratio], respectively.

3. Results

3.1. Total organic carbon (TOC) content

TOC varied between 0.5 and 4.1%, with an average of 1.1% (Fig. 5). A single organic carbon peak was observed at 13.7 ka. TOC was higher in late MIS 5e to 5d, late MIS 5c, the MIS 5a/4 boundary, and late MIS 2 to MIS1 than in other periods (Fig. 5).

3.2. Lignin abundance

Σ8 (mg/10g sediment), which is the total amount of eight lignin phenols belonging to the vanillyl, syringyl, and cinnamyl groups (Fig. 2), varied between 0.02 and 2.71, with an average of 0.19 (Fig. 5). Λ (mg/100mg TOC), which is the total amount of the eight lignin phenols in 100 mg of TOC, varied between 0.02 and 0.66, with an average of 0.14 (Fig. 5). Lignin concentration (Σ8) tended to decrease downward in the study core and reached levels beneath the detection limit below 44 m (~147 ka). This tendency is consistent with that found in a previous lignin study of a sediment core from Lake Biwa (Ishiwatari and Uzaki, 1987), which attributed the trend to degradation of lignin during diagenesis.

193 Σ8 and Λ were intermittently elevated (Fig. 5). Between 17.5 and 11.3 ka (five
194 samples; peak at 13.7 ka), both Σ8 and Λ were significantly high. Smaller peaks in Σ8
195 and Λ were also found at 133.8, 123.9–123.2, 94.3–92.4, 77.9, and 37.8 ka (Fig. 5).
196
197 *3.3. Lignin composition*
198 The ratio of acid to aldehyde of vanillyl phenols [$(Ad/Al)_v$] increases systematically
199 as lignin is degraded by aerobic fungi, and the ratios of highly degraded lignin exceed
200 ~0.4 in the alkaline CuO oxidation method (Goñi et al., 1993). The TMAH procedure is
201 more sensitive for calculation of $(Ad/Al)_v$ ratios than is the alkaline CuO oxidation
202 procedure (Hatcher et al., 1995). The sensitivity of $(Ad/Al)_v$ ratios for expressing the
203 extent of fungal degradation with the TMAH procedure is ~15 times higher than that
204 with the CuO oxidation method (Hatcher et al., 1995; Filley et al., 2000). Fresh,
205 moderately degraded, and highly degraded lignins have $(Ad/Al)_v$ ratios of ~0.5, ~3, and
206 7–12, respectively, with the TMAH procedure (Yamamoto et al., 2005a). In core
207 BIW08-B, the $(Ad/Al)_v$ ratio ranged from 0.3 to 4.5, with an average of 1.9 (Fig. 5),
208 which suggests that the lignin was not highly degraded but rather slightly or moderately
209 degraded by aerobic microbes. Relatively high values were observed in late MIS-6,
210 early MIS-5e, late MIS-5b, late MIS-3, at the MIS-2/1 boundary, and in late MIS-1 (Fig.
211 5).
212 The ratios of syringyl (S) to vanillyl (V) phenols (S/V ratio), which is a contribution
213 index of angiosperms against gymnosperms (Hedges and Mann 1979), ranged from 0.10
214 to 0.53, with an average of 0.27. The values fell within the range of a mixture of
215 angiosperms (mean values of leaf and branch are 0.71 and 0.90, respectively; Shuichi
216 Yamamoto, unpublished data) and gymnosperms (mean values of leaf and branch are

0.07 and 0.07, respectively; Shuichi Yamamoto, unpublished data). The S/V ratio showed maximal peaks at early MIS-5e, early MIS-5c, late MIS-5b to early MIS-5a, the MIS-4/3 boundary, middle MIS-3, and early MIS-1 (Fig. 5).

The ratio 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 0.04 to 1.44, with an average of 0.36. The C/V ratio showed maximal peaks at late MIS-6, early MIS-5b, mid MIS-3 (~38 ka), and at the MIS-2/1 boundary (Fig. 5).

4. Discussion

4.1. Terrestrial versus aquatic organic matter

A linear relationship exists between TOC and Σ8 in sediments from core BIW08-B (r = 0.90; Fig. 6). The intercept and slope of the regression line are 0.85 and 1.31, respectively. There are two potential sources of organic carbon, i.e., terrestrial organic carbon derived from land and aquatic organic carbon produced in the lake. 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 (TROC) and aquatic organic carbon (AQOC) are computed by the following formulae, respectively.

TROC (%) = 1.31 x Σ8 (mg/10g)

AQOC (%) = TOC (%) – TROC (%).

TROC ranged from 0 to 3.4%, with an average of 0.2% (Fig. 5). AQOC ranged

241 from 0.2 to 1.4%, with an average of 0.9% (Fig. 5). TROC showed maximal peaks at
242 the same periods as did TOC. AQOC showed maxima in MIS-5d, late MIS-5c, late
243 MIS-5a to early MIS-4, and at the MIS-2/1 boundary. The calculated AQOC does not
244 show a clear glacial–interglacial pattern (Fig. 5). Variation in AQOC is not consistent
245 with that in diatom abundance in core BIW95-4 (Kuwae et al., 2004). Diatoms are one
246 of the primary producers in Like Biwa, and an increase in diatom production supplies
247 more organic matter and diatom frustules. The supply of organic matter contributes
248 directly to AQOC, but the supply of diatom frustules dilutes AQOC, canceling the
249 variation in AQOC. Thus, AQOC is not sensitive to environmental changes in Lake
250 Biwa.

251 Between 17.5 and 11.3 ka (five samples; peak at 13.7 ka), TOC, Σ8, and Λ were
252 significantly high (Fig. 5). This peak interval was associated with a high C/V ratio (Fig.
253 5), suggesting a contribution from herbaceous plants. Ishiwatari et al. (2009) reported a
254 5-cm-thick layer showing high TOC, Σ8, and C/V ratio in core BIW95-5 from central
255 Lake Biwa at 10.8 ka (conventional age) and concluded that the terrigenous organic
256 matter originated from surface soils including peat-like material and was likely
257 transported by flooding. Our record showed that the peaks of Σ8 at 133.8, 123.9–123.2,
258 94.3–92.4, 77.9, and 37.8 ka were also accompanied by elevated C/V ratio (Fig. 5). This
259 suggests that herbaceous organic matter repeatedly flowed into Lake Biwa.

260 Figure 7 shows changes in C/V and the ratio of herb pollen to tree and herb pollen
261 [herb/(herb + tree)] reported by Hayashi et al. (2010a, b) from the BIW95-4 and
262 Takashima-oki cores retrieved near the study site. The C/V and herb/(herb + tree) pollen
263 ratios generally do not show good agreement aside from late MIS-2, which shows
264 higher values of both C/V and herb/(herb + tree) pollen. As discussed above, C/V

reflects intermittent inflow events of herbaceous organic matter. On the other hands, herb pollen abundance possibly reflects a different aspect of the contribution of herbaceous organic matter. Pollen can be delivered by both riverine and eolian transportations. Since eolian transport is not affected by intermittent riverine inflows, we suppose that the herb/(herb + tree) pollen ratio reflects vegetation around Lake Biwa more accurately.

4.2. Changes in the contributions of gymnosperms and angiosperms

The S/V ratio, which is a contribution index of angiosperms against gymnosperms (Hedges and Mann 1979), showed maximal peaks at early MIS-5e, early MIS-5c, late MIS-5b to early MIS-5a, the MIS-4/3 boundary, middle MIS-3, and early MIS-1 (Fig. 5). These maxima corresponded to maxima of deciduous broadleaf trees such as *Quercus*, *Lepidoblanus*, *Ulmus/Zelkova*, and *Fagus* (angiosperms) that showed in pollen records from a 1,400-m borehole core (Miyoshi et al., 1999) and the BIW95-4 and Takashima-oki cores (Fig. 8A; Hayashi et al., 2010b) from central Lake Biwa. Also, minima of the S/V ratio roughly corresponded to maxima of *Cryptomeria* (gymnosperm) from MIS-6 to early MIS-3 and with maxima of pollen of pinaceous conifer trees such as *Abies*, *Picea*, *Pinus*, and *Tsuga* (gymnosperm) from late MIS-3 to MIS-2 (Fig. 8A). This correspondence indicates that the S/V ratio reflects vegetation in the watershed of Lake Biwa and indicates the relative contribution of angiosperms to gymnosperms.

The correspondence to pollen assemblages indicates that a higher S/V ratio reflects a warmer climate with cool-temperate deciduous boadleaf forests (angiosperms) and that a lower S/V ratio reflects a cooler climate with subalpine conifer forests

289 (gymnosperms). From MIS-6 to early MIS-3, Japanese cedar, *Cryptomeria*, forests
290 (gymnosperms) also played a major role: a higher S/V ratio reflects a drier climate with
291 less *Cryptomeria*, and a lower S/V ratio reflects a wetter climate with more *Cryptomeria*.
292 Variation in the S/V ratio in Lake Biwa thus reflects variation in both air temperature
293 and precipitation and suggests a precession-controlled repetition of warmer, drier and
294 cooler, wetter climates.

295 Figure 8B shows the S/V ratios in core BIW08-B and in core MD01-2421 from the
296 northwestern Pacific off central Japan (Yamamoto et al., 2005a). These two records
297 showed good agreement, except in MIS-6 to MIS-5d in MD01-2421 (Fig. 8B). In core
298 MD01-2421, the S/V record is generally consistent with the pollen record (Igarashi and
299 Oba, 2006), but a mismatch between S/V and the pollen record exists around MIS-5e in
300 core MD01-2421. Paleogeographical reconstructions displayed that the Kanto Plain,
301 which is the sediment source region of core MD01-2421, was covered by sea-water in
302 MIS-5e to a large extent (the Shimosueyoshi Transgression), as well as to a lesser extent
303 in early MIS-1 (the Jomon Transgression) (e.g., Kaizuka et al., 2000). The long-distance
304 transportation of lignin particles due to marine transgression could result in preferential
305 degradation of more labile syringyl phenols compared with vanillyl phenols (Yamamoto
306 et al., 2005a). This is also potentially the reason that the S/V variation at site
307 MD01-2421 was different from that in BIW08-B around MIS-5e. The general
308 agreement of the S/V ratios at these locations implies that the S/V ratio is a robust proxy
309 for terrestrial vegetation on a regional rather than a local scale.

310 The variation in S/V showed a precession-like cycle and corresponded to the June
311 21 variation in insolation at 65°N (Laskar et al., 2004; Fig. 8B). The variation was
312 nearly synchronous with the Hulu-Sanbao $\delta^{18}O$ record (Wang et al., 2001, 2008). This

correspondence is consistent with the viewpoint that variation in summer air temperature (variation in the abundance of the angiosperm *Quercus*) in central Japan was linked to intensification of the East Asian summer monsoon and that maxima of gymnosperm *Cryptomeria* pollen lagged the July 21 insolation at 65°N and the Hulu-Sanbao monsoon maxima by ~8 kyr (Fig. 9; Igarashi and Oba, 2006; Yamamoto, 2009).

Variation in air temperature in central Japan since MIS-6 was investigated by Igarashi and Oba (2006). The pollen assemblage in core MD01-2421 demonstrated that variation in the pollen temperature index, T_p (= 100 x $T_w/[T_c + T_w]$, where T_w is the sum of temperate taxa and T_c is the sum of subalpine taxa), was dominated by 23-kyr periods. The variation in T_p was synchronous with the Hulu-Sanbao $\delta^{18}O$ record (Fig. 9). This correspondence suggests that variation in summer air temperature in central Japan was linked to variation of the East Asian summer monsoon (Yamamoto, 2009).

Precipitation in Japan and China during early summer is determined principally by the position of the Baiu Front (an early summer rain front) that develops at the atmospheric boundary between warm, moist air masses flowing from the south and cold air masses from the north (Yoshino, 1965). If displacement of the Baiu Front corresponds to the precessional cycle, *Cryptomeria japonica*, which favors high precipitation, may have dominated in periods during which the Baiu Front developed over central Japan (Yamamoto, 2009).

The out-of-phase variation in air temperature and precipitation caused the repetition of warmer, dry and cooler, wet climates in central Japan on a precessional cycle, inducing replacement among cool-temperate deciduous broadleaf forests, subalpine conifer forests, and Japanese cedar forests. This perspective is key to a better

337 understanding of the regional response of the East Asian summer monsoon to orbital
338 forcing, and it should be tested based on additional pollen and lignin records from East
339 Asia.
340
341 **5. Conclusions**
342 The relative abundance of lignin was intermittently elevated and associated
343 with a high C/V ratio, suggesting that herbaceous plant-derived organic matter
344 repeatedly flowed into Lake Biwa. The largest inflow occurred during the last
345 deglaciation. Variation in S/V ratio showed a precession-like cycle and corresponded to
346 variation in northern hemisphere summer insolation. The out-of-phase variation in air
347 temperature and precipitation caused the repetition of warmer, dry and cooler, wet
348 climates in central Japan on a precessional cycle, inducing replacement among
349 cool-temperate deciduous broadleaf forests, subalpine conifer forests, and Japanese
350 cedar forests.
351
352 **Acknowledgements**
353 We would like to thank all of the members of BIW08 drilling project, K. Ohnishi,
354 T. Ajioka, N. Suzuki, K. Takahashi (Hokkaido University), S. Yamamoto (Soka
355 University), R. Hayashi (Lake Biwa Museum), and H. Kitagawa (Nagoya University)
356 for their valuable input. This study was carried out under Grants-in-Aid for Scientific
357 Research (A) of JSPS, Nos. 19204050 (to KT) and 19204051 (to MY).
358
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494 Table 1. Response factors of ligninphenols

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

495

496

Figure captions

Fig. 1. Maps showing (A) the modern vegetation of Japan (compiled by Igarashi and Oba, 2006) and (B) the locations of the BIW08-B and MD01-2421 cores. A: subarctic coniferous forests, B: pan-mixed forests, C: cool-temperate deciduous broadleaf forests, D: warm-temperate evergreen forests.

Fig. 2. 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.

Fig. 3. Lithologic column of BIW08-B (Sato et al., submitted).

Fig. 4. Age–depth model of core BIW08-B (Takemura et al., in preparation).

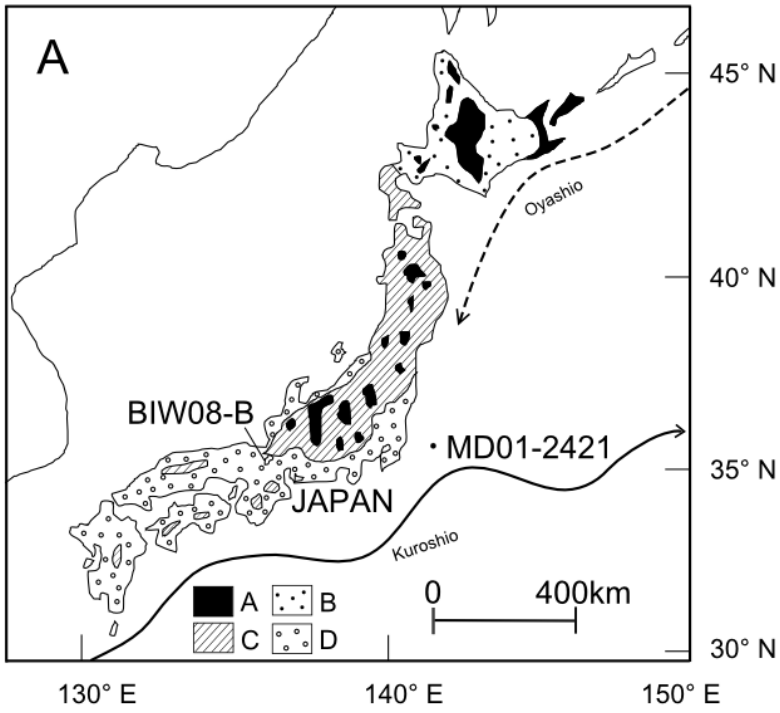
Fig. 5. Changes in total organic carbon (TOC) content, Σ8, Λ, S/V, C/V, $(Ad/Al)_v$, and terrestrial and aquatic organic matter contents (TROC and AQOC, respectively) in core BIW08-B during the last 147,000 years.

Fig. 6. Plot of total organic carbon content (TOC) against total lignin concentration (Σ8) in BIW08-B samples.

Fig. 7. Changes in C/V in core BIW08-B and in the ratio of herb pollen to herb and tree pollen [Herb/(Herb + Tree)] in the BIW95-4 and Takashima-oki cores.

521

522 **Fig. 8.** Changes in (A) the relative abundances of deciduous broadleaf tree, Japanese
523 cedar *Cryptomeria*, and pinaceous tree pollen to total tree pollen in the BIW95-4 and
524 Takashima-oki cores and (B) S/V ratio in the BIW08-B and MD01-2421 cores.
525 Insolation on June 21 at 65°N is shown for comparison (Laskar et al., 2004). Pollen data
526 refer to Hayashi et al. (2010a, b).



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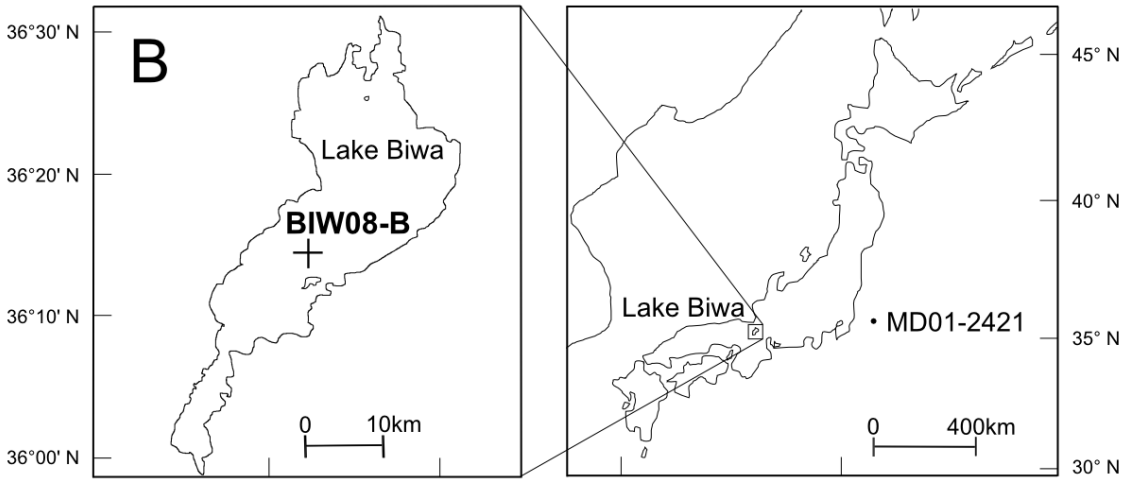


528

529

530 Fig. 1

531

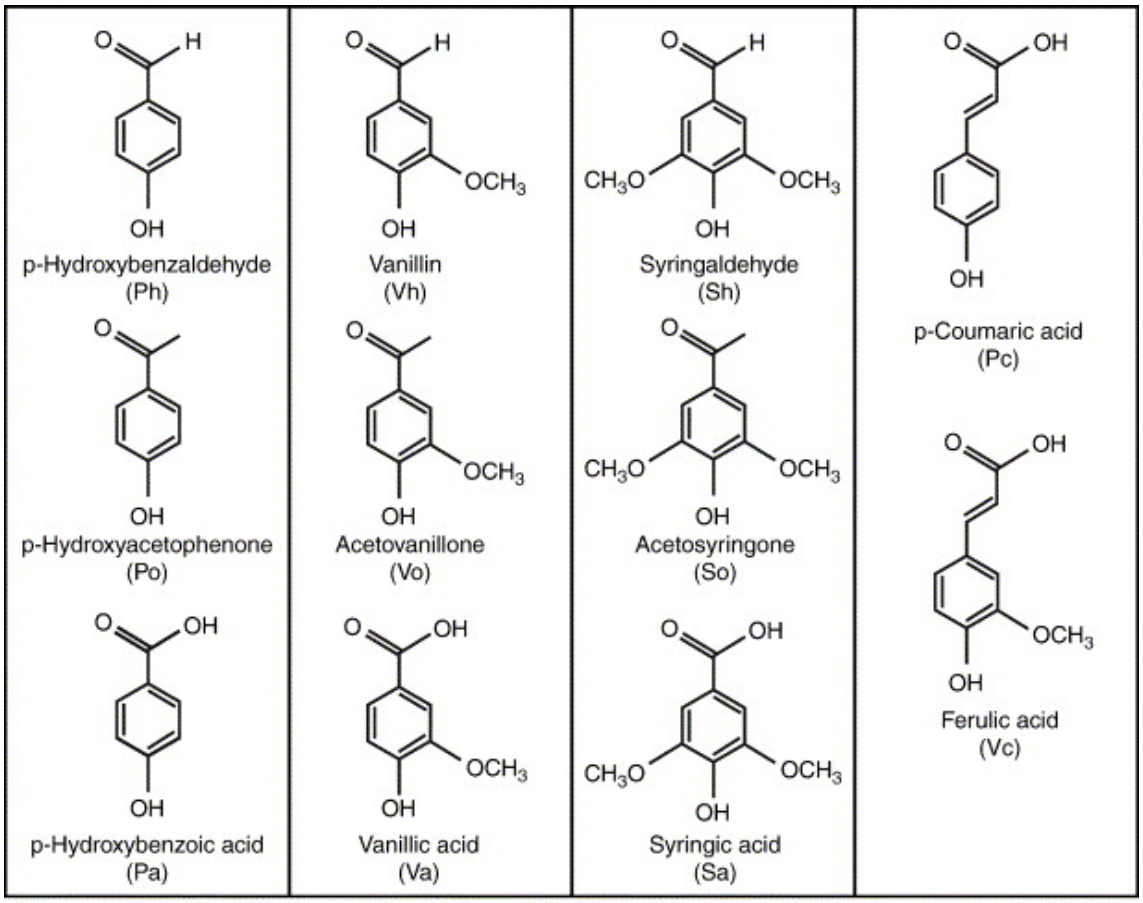

p-Hydroxybenzaldehyde
(Ph)
Vanillin
(Vh)
Syringaldehyde
(Sh)
p-Coumaric acid
(Pc)
p-Hydroxyacetophenone
(Po)
Acetovanillone
(Vo)
Acetosyringone
(So)
p-Hydroxybenzoic acid
(Pa)
Vanillic acid
(Va)
Syringic acid
(Sa)
Ferulic acid
(Vc)
p-Hydroxy phenols
Vanillyl phenols
Syringyl phenols
Cinnamyl phenols

Fig. 2.

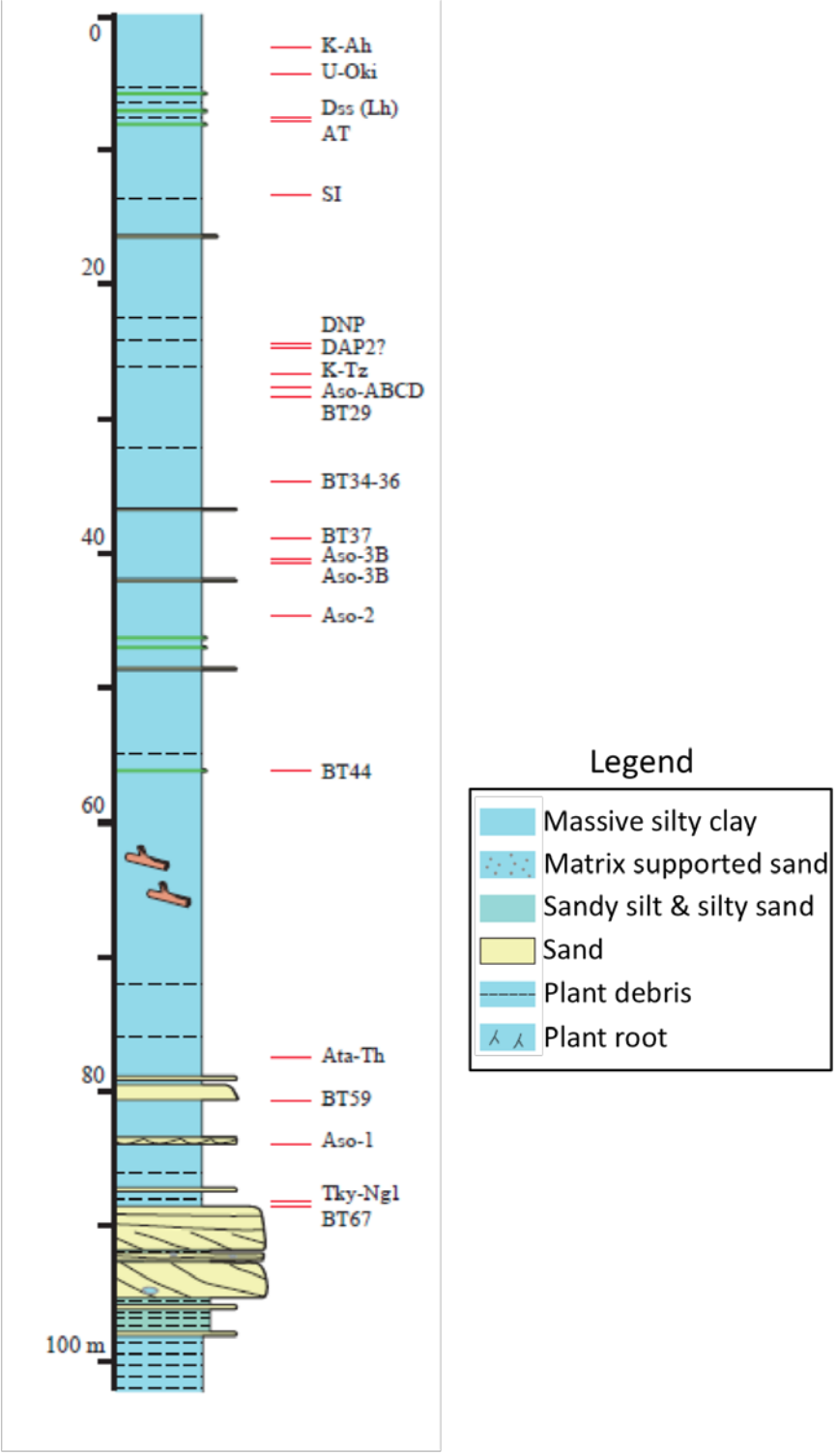

0
20
40
60
80
100 m
K-Ah
U-Oki
Dss (Lh)
AT
SI
DNP
DAP2?
K-Tz
Aso-ABCD
BT29
BT34-36
BT37
Aso-3B
Aso-3B
Aso-2
BT44
Ata-Th
BT59
Aso-1
Tky-Ng1
BT67
Legend
Massive silty clay
Matrix supported sand
Sandy silt & silty sand
Sand
Plant debris
Plant root

Fig. 3

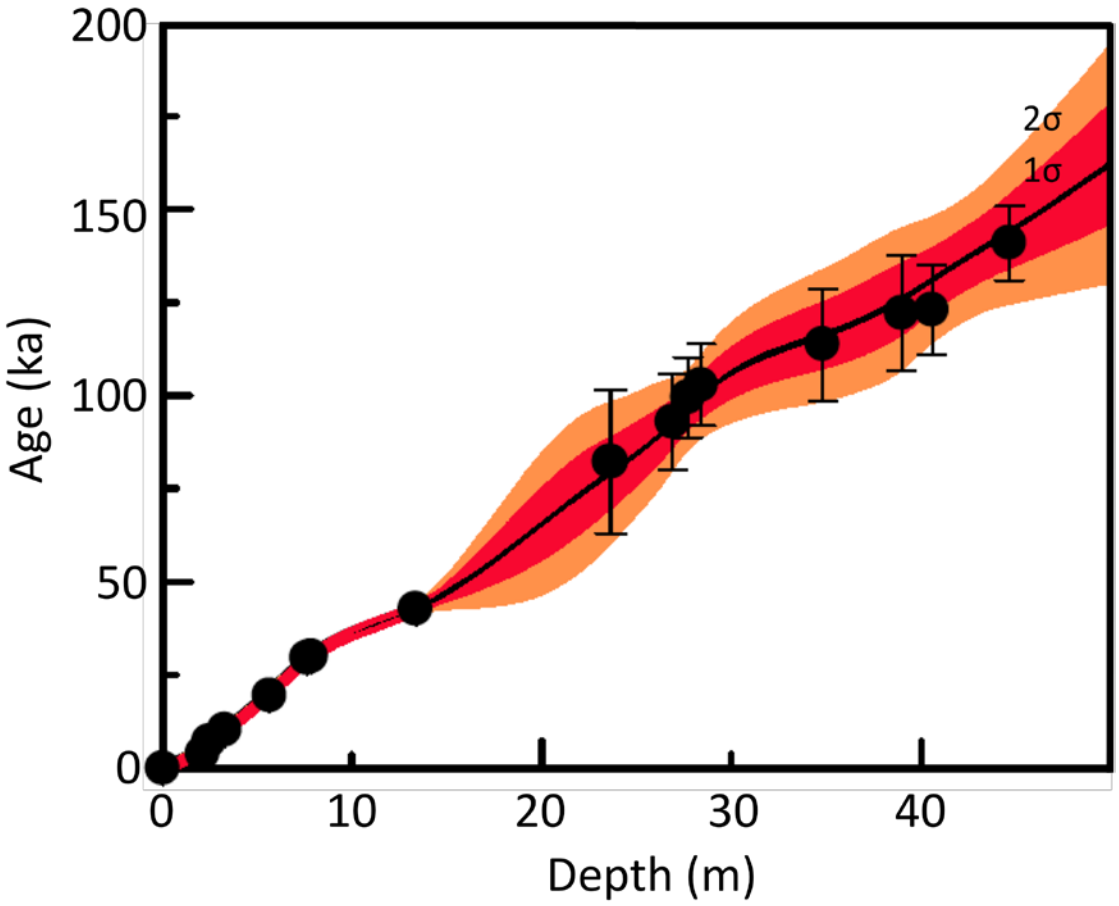
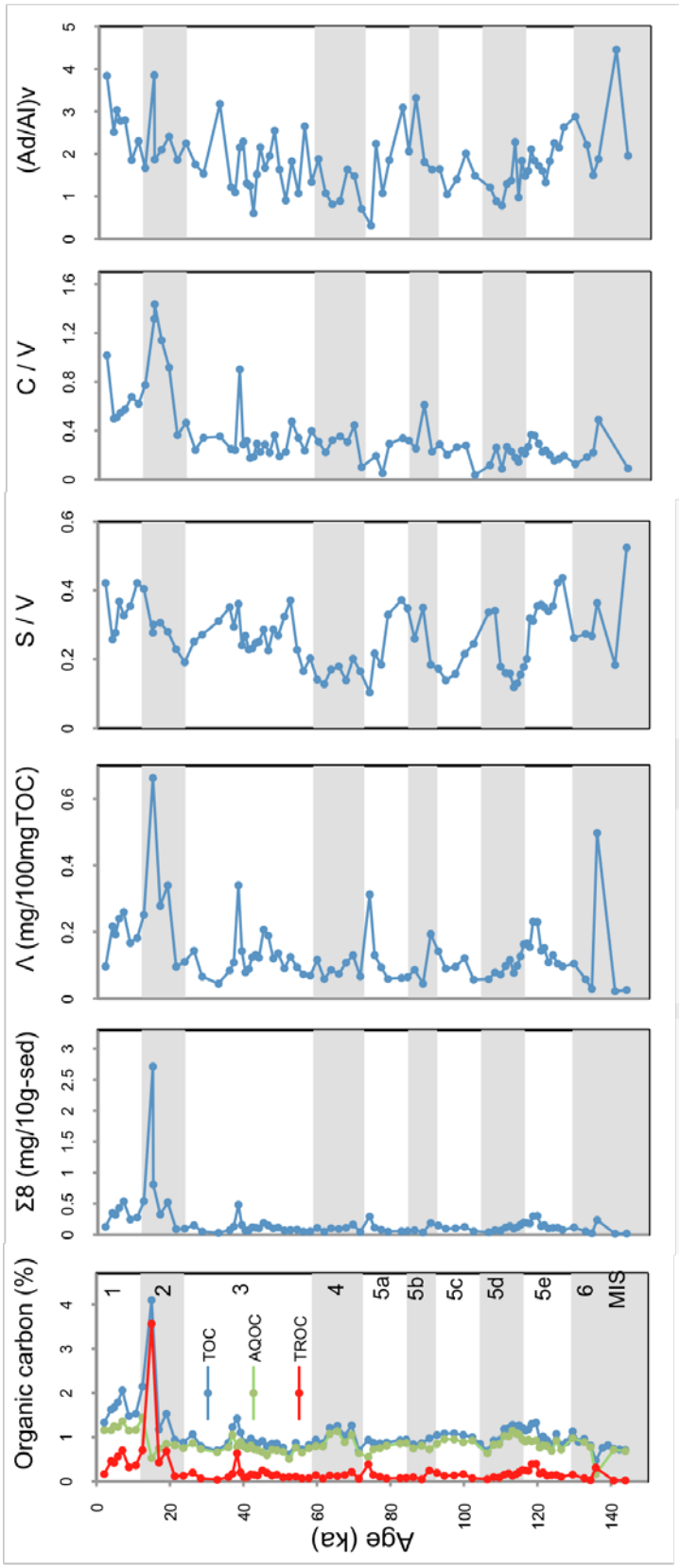


Fig. 4


(Ad/Al)v
C / V
S / V
Λ (mg/100mgTOC)
Σ8 (mg/10g-sed)
Organic carbon (%)
TOC
AQOC
TROC
1
2
3
4
5a
5b
5c
5d
5e
6
MIS
Age (ka)

543

544 Fig. 5

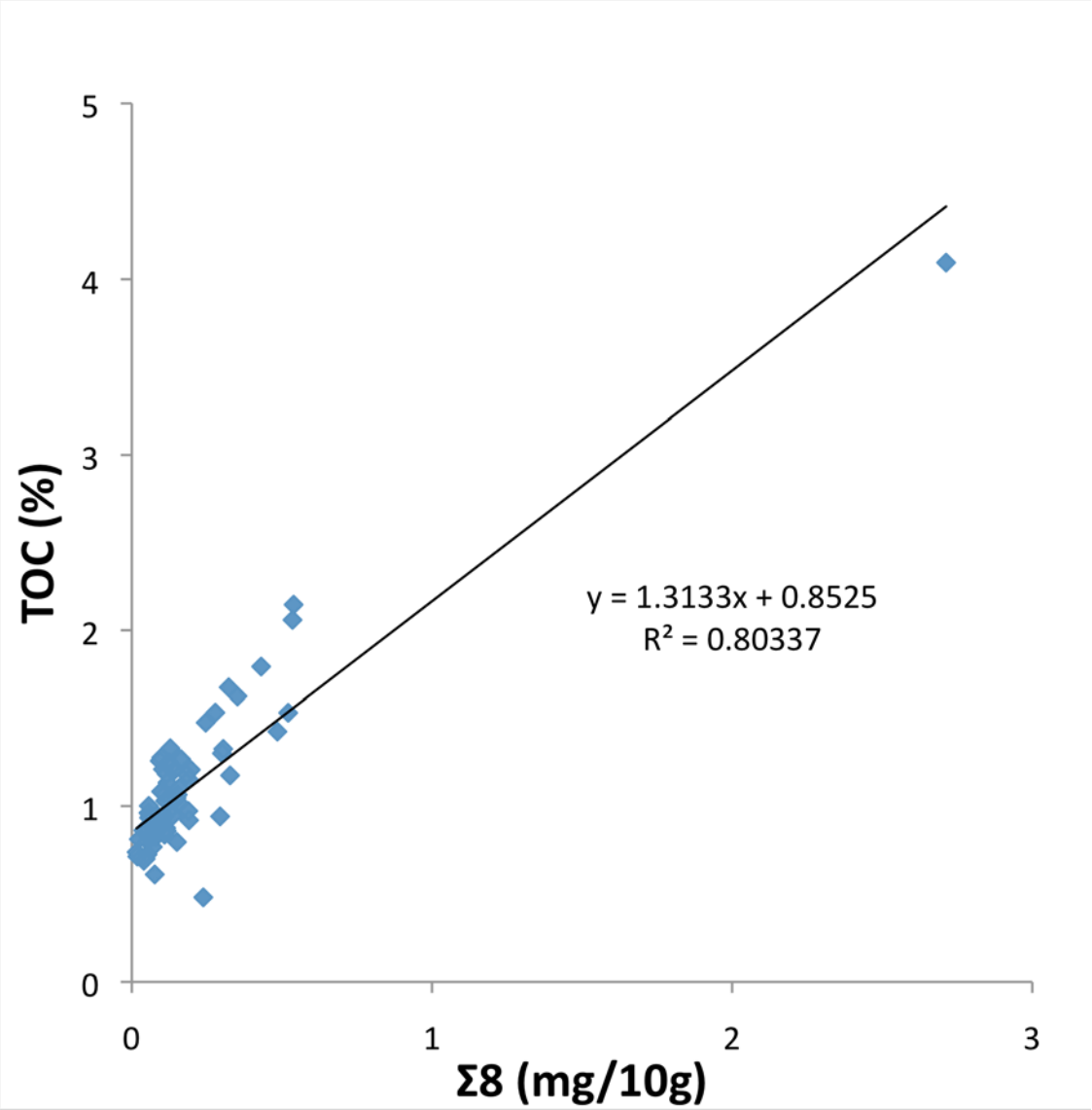
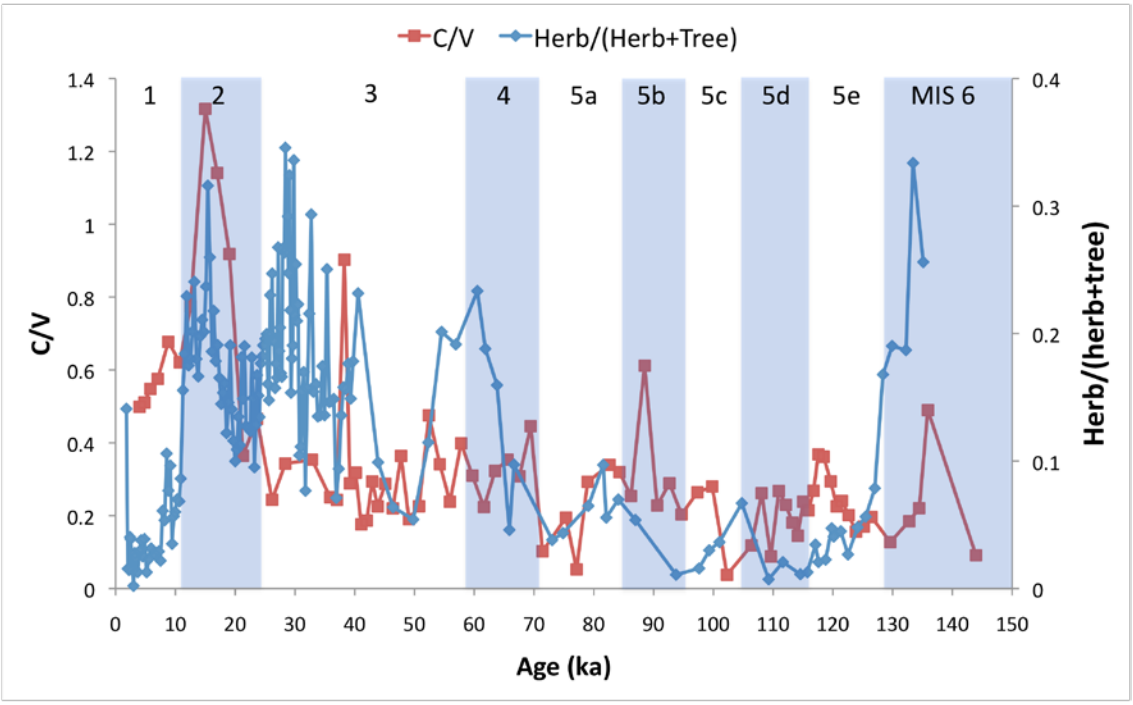


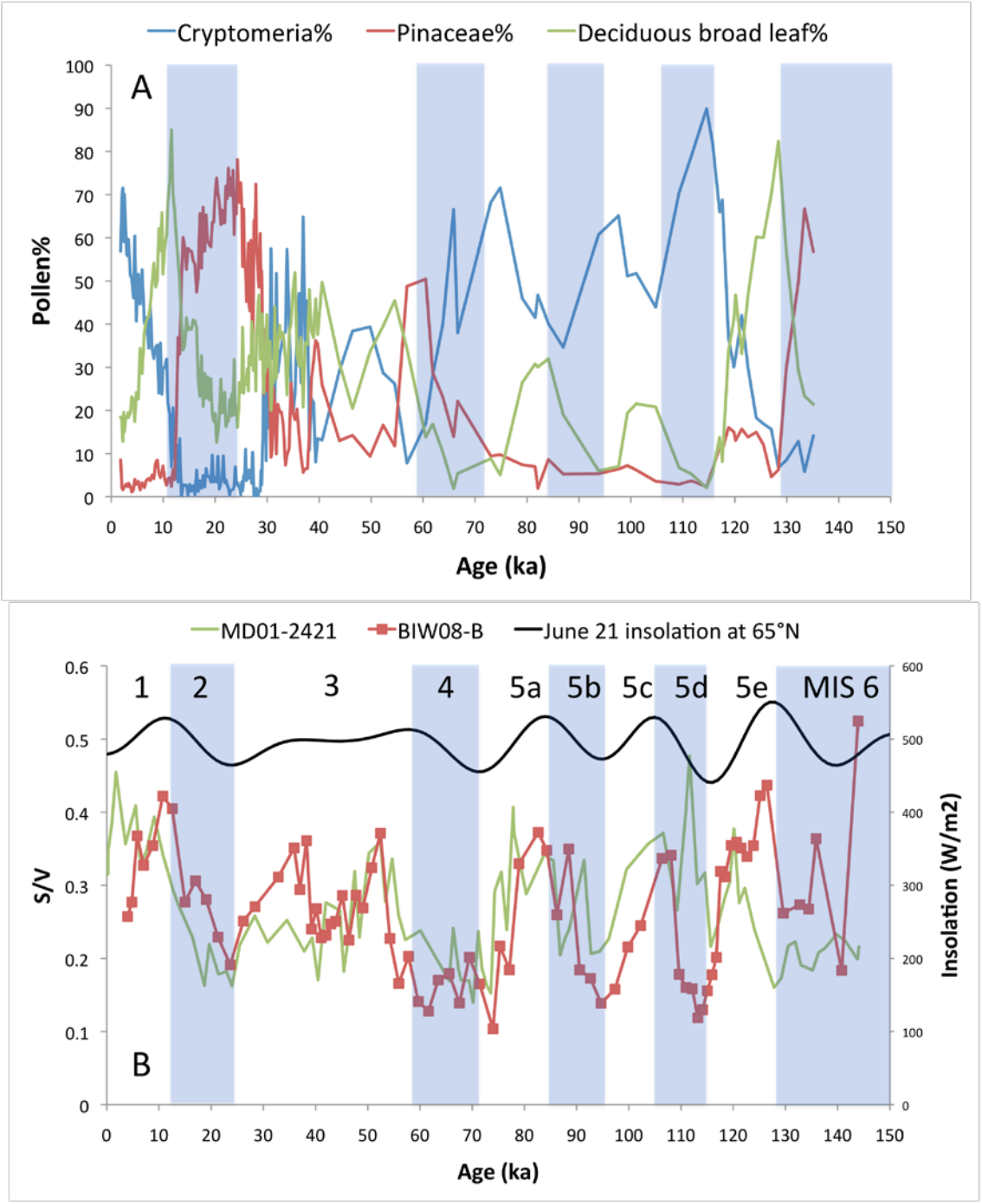
Fig. 6



548

549 Fig. 7

550


Cryptomeria%
Pinaceae%
Deciduous broad leaf%
A
Pollen%
Age (ka)
MD01-2421
BIW08-B
June 21 insolation at 65°N
1
2
3
4
5a
5b
5c
5d
5e
MIS 6
B
S/V
Insolation (W/m2)
Age (ka)

551

552 Fig. 8