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1 **Response of vegetation in central Japan to precession during the last**
2 **147,000 years: A lignin record from Lake Biwa core BIW08-B**

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18
19 **ABSTRACT**

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

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

34

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

37

38 **1. Introduction**

39 Central Japan is located near the atmospheric and oceanic boundaries between the
40 subarctic and subtropical regimes. Paleoenvironmental change in this region is therefore
41 sensitive to latitudinal shifts of these boundaries in the northwestern Pacific region.
42 Marine records have demonstrated that the oceanic subarctic boundary in the
43 northwestern Pacific has been displaced in response to the Earth's precession (e.g.,
44 Aizawa et al., 2004; Koizumi et al., 2004; Yamamoto et al., 2004; Oba et al., 2006) and
45 millennial forcing (e.g., Yamamoto et al., 2005b; Isono et al., 2009) and have also
46 shown that the atmospheric boundary has shifted in response to orbital and millennial
47 forcing (e.g., Tada et al., 1999; Irino and Tada, 2000, 2002; Nagashima et al., 2007,
48 2011; Takahara et al., 2010).

49 Pollen studies have demonstrated a remarkable difference in vegetation on the
50 Japanese Islands between the Holocene and the last glacial maximum (LGM) (compiled
51 in Tsukada, 1985; Takahara et al., 2000). At the LGM, boreal coniferous forests
52 occupied the modern cool-temperate deciduous broadleaf and mid-temperate conifer
53 forest zones (NE Japan), and temperate coniferous forests occupied the modern
54 warm-temperate evergreen forest zone (SW Japan). This difference in vegetation can be
55 attributed to the lower air temperature and precipitation of the LGM (Tsukada, 1985).
56 Although continuous records of pollen are scarce, spliced records from on-land cores
57 and some long-term records have demonstrated how the vegetation of central Japan
58 changed in response to glacial–interglacial cycles (e.g., Tsukada, 1988; Miyoshi et al.,
59 1999; Igarashi and Oba, 2006; Nakagawa et al., 2008; Hayashi et al., 2010a, b; Takahara
60 et al., 2010).

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

69 Lignin is an abundant, stable, phenolic macromolecule uniquely found in the cell
70 walls of vascular land plants. Alkaline CuO oxidation of lignin yields four groups of
71 structurally related products: the p-hydroxy, vanillyl, syringyl, and cinnamyl groups
72 (Hedges and Mann, 1979) (Fig. 2). The vanillyl group is abundant in gymnosperms,

73 whereas the syringyl group is specific to angiosperms. The cinnamyl group is abundant
74 in the non-woody tissues of vascular plants and grasses (Hedges and Mann, 1979; Goñi
75 and Hedges, 1992). The relative abundance of the vanillyl, syringyl, and cinnamyl
76 groups, therefore, is often used as an index of paleovegetation.

77 Lignin has been investigated in sediment cores from Lake Biwa, Japan (Ishiwatari
78 and Uzaki, 1987; Ishiwatari et al., 2009), Lake Baikal, Siberia (Orem et al., 1997;
79 Ishiwatari et al., 2005), and also in marine cores (Yamamoto et al., 2005a; Inagaki et al.,
80 2009). These studies have shown glacial–interglacial and longer-term variations in
81 lignin abundance and composition, which are attributable to diagenesis, vegetation
82 changes, and sea level changes. Ishiwatari and Uzaki (1987) attributed the decreasing
83 trend of lignin abundance with increasing depth in a Lake Biwa sediment core to
84 degradation of lignin during diagenesis. The time resolution of lignin records has
85 generally been lower than that of other records because the time and effort required for
86 conventional lignin analysis have hindered this work.

87 Pyrolysis–gas chromatography–mass spectrometry with in situ methylation with
88 tetramethylammonium hydroxide (TMAH-pyrolysis-GC/MS) has been used recently for
89 analysis of macromolecules such as lignin (e.g., Clifford et al., 1995; Hatcher et al.,
90 1995). TMAH-pyrolysis-GC/MS yields lignin phenols that are equivalent to those
91 produced by conventional alkaline CuO oxidation (Hatcher et al., 1995; Yamamoto,
92 2000). In this method, organic matter is pyrolyzed in the presence of TMAH, and the
93 pyrolysates are transformed to a methyl ester, a methoxy benzene, and so forth. The
94 derivatized pyrolysates are then analyzed with on-line GC/MS. This method enables
95 more rapid analysis with a small amount of sample (~0.1 mg C) compared with the
96 conventional alkaline CuO oxidation method.

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

101

102 **2. Materials and methods**

103 *2.1. Study area*

104 Located in central Japan at an elevation of 84 m, Lake Biwa is surrounded by
105 mountains that are approximately 1,000 m high. Lake Biwa is the largest lake in Japan.
106 It has an area of 674 km² and a watershed area of 3,850 km² (Fig. 1). More than 118
107 rivers flow into the lake, but only one, the Seta River, discharges from it. The climate of
108 this area is strongly affected by the East Asian monsoon. The East Asian summer
109 monsoon provides warm and humid conditions, whereas the winter monsoon brings
110 snowfall to the northern part of this area and dryness to the southern part.

111 The borehole core BIW08-B (100.3 m long) was collected in 2008 by drilling
112 offshore of Okishima in Lake Biwa (35°13'41.15"N, 136°03'21.19"E) at a water depth
113 of 53 m (Fig. 1; Takemura et al., 2010). The sediments consist of dark-gray massive
114 silty clay from 0 to 89 m, sandy silt containing abundant sand and plant debris from 89
115 to 99 m, and dark-gray massive silty clay from 99 to 100.3 m (Fig. 3; Sato et al.,
116 submitted). The results of analysis for top 44 m are reported in this paper. An age–depth
117 model of top 44 m was created using radiometric ages of 14 volcanic ash layers (Fig. 4;
118 Takemura et al., 2010; Takemura et al., in preparation). The average sedimentation rate
119 was 0.3 m/ky. The sediment was stored at 4°C for one-half year. A total of 80 samples
120 (2.5 cm thick) were collected from the upper 44 m (0–147 ka) of the core, and the

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

122

123 2.2. *Organic carbon analysis*

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

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

134

135 2.3. *Lignin analysis*

136 Pyrolysis gas chromatography-mass spectrometry with in situ methylation with
137 tetramethylammonium hydroxide (TMAH-pyrolysis-GC/MS) was carried out using a
138 Japan Analytical Industry JHP-5 Curie point pyrolyzer that was directly connected to
139 the injection port of a Hewlett Packard 5973 gas chromatograph-mass selective detector.
140 The column used was a Chrompack CP-Sil5CB (length, 30 m; i.d., 0.25 mm; thickness,
141 0.25 µm). The sediment sample (ca. 20 mg) was placed on a Ni-Co pyrofoil plate with
142 30 µl of 5% TMAH in methanol and 20 µl of internal standard solution (0.1 g/L
143 n-nonadecanoic acid in hexane). After drying, the sample was wrapped in pyrofoil. The
144 sample was heated at 590°C for 20 sec in the pyrolyzer, and the generated compounds

145 were transferred to the GC splitless injection system at 300°C with a helium carrier gas.
146 The oven temperature was programmed from 70°C to 310°C at 4°C/min after the initial
147 hold time of 1 min, and then it was held isothermally at 310°C for 30 minutes. The mass
148 spectrometer was run in the full scan ion-monitoring mode (m/z 50-650). Electron
149 impact spectra were obtained at 70 eV. Identification of lignin phenols was achieved by
150 comparison of their mass spectra and retention times with those of authentic standards.
151 Concentrations of lignin phenols were obtained according to the following equation:

152

$$153 \quad \text{Conc}_A = W_{IS} (\text{Area}_A/\text{RF}_A)/(\text{Area}_{IS}/\text{RF}_{IS})/W_{SD}$$

154

155 where Conc_A is the concentration of compound A ($\mu\text{g/g}$), W_{IS} is the weight of internal
156 standard (μg), Area_A is the peak area of compound A on the ion chromatogram of its
157 molecular ion, Area_{IS} is the peak area of internal standard (n-nonadecanoic acid) on the
158 ion chromatogram of m/z 74, RF_A and RF_{IS} are the response factors of compound A and
159 internal standard, and W_{SD} is the sample weight (μg). W_{IS} was 2 μg in this study. The
160 response factors of lignin phenols (RF_{LG}) and internal standard (RF_{IS}) were determined
161 by the analysis of the authentic standards (lignin phenols and n-nonadecanoic acid)
162 according the following formula:

163

$$164 \quad \text{RF}_{LG} = \text{Int}_M/\text{Int}_{50-650}$$

$$165 \quad \text{RF}_{IS} = \text{Int}_{74}/\text{Int}_{50-650}$$

166

167 where Int_M is the intensity of molecular ion in the mass spectrum of ligninphenol, Int_{74}
168 is the intensity of m/z 74 fragment ion in the mass spectrum of n-nonadecanoic acid,

169 and Int₅₀₋₆₅₀ is the sum of ion intensities from m/z 50 to m/z 650. The response factors
170 of lignin phenols and n-nonadecanoic acid obtained by this way were listed in Table 1.
171 The standard deviations in replicate analysis (five times) were 10, 7, 15 and 8 % of the
172 concentration for total syringyl phenol (S), total vanillyl phenols (V), total cinnamyl
173 phenol (C) and total eight lignin ($\Sigma 8$; S+V+C), respectively, and they were 0.01, 0.03
174 and 0.06 for S/V and C/V ratios and the ratio of acid to aldehyde of vanillyl phenol
175 [(Ad/Al)_v ratio], respectively.

176

177 **3. Results**

178 *3.1. Total organic carbon (TOC) content*

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

182

183 *3.2. Lignin abundance*

184 $\Sigma 8$ (mg/10g sediment), which is the total amount of eight lignin phenols belonging
185 to the vanillyl, syringyl, and cinnamyl groups (Fig. 2), varied between 0.02 and 2.71,
186 with an average of 0.19 (Fig. 5). Λ (mg/100mg TOC), which is the total amount of the
187 eight lignin phenols in 100 mg of TOC, varied between 0.02 and 0.66, with an average
188 of 0.14 (Fig. 5). Lignin concentration ($\Sigma 8$) tended to decrease downward in the study
189 core and reached levels beneath the detection limit below 44 m (~147 ka). This
190 tendency is consistent with that found in a previous lignin study of a sediment core from
191 Lake Biwa (Ishiwatari and Uzaki, 1987), which attributed the trend to degradation of
192 lignin during diagenesis.

193 $\Sigma 8$ and Λ were intermittently elevated (Fig. 5). Between 17.5 and 11.3 ka (five
194 samples; peak at 13.7 ka), both $\Sigma 8$ and Λ were significantly high. Smaller peaks in $\Sigma 8$
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

217 0.07 and 0.07, respectively; Shuichi Yamamoto, unpublished data). The S/V ratio
218 showed maximal peaks at early MIS-5e, early MIS-5c, late MIS-5b to early MIS-5a, the
219 MIS-4/3 boundary, middle MIS-3, and early MIS-1 (Fig. 5).

220 The ratio of cinnamyl (C) to vanillyl (V) phenols (C/V ratio), which indicates the
221 contribution of non-woody tissues and herbaceous plants (Hedges and Mann, 1979),
222 ranged from 0.04 to 1.44, with an average of 0.36. The C/V ratio showed maximal
223 peaks at late MIS-6, early MIS-5b, mid MIS-3 (~38 ka), and at the MIS-2/1 boundary
224 (Fig. 5).

225

226 **4. Discussion**

227 *4.1. Terrestrial versus aquatic organic matter*

228 A linear relationship exists between TOC and $\Sigma 8$ in sediments from core BIW08-B
229 ($r = 0.90$; Fig. 6). The intercept and slope of the regression line are 0.85 and 1.31,
230 respectively. There are two potential sources of organic carbon, i.e., terrestrial organic
231 carbon derived from land and aquatic organic carbon produced in the lake. We thus
232 assumed that the intercept represents the average organic carbon content produced in the
233 lake and that the slope represents the relative abundance of lignin to terrestrial organic
234 carbon. According to this assumption, terrestrial organic carbon (TROC) and aquatic
235 organic carbon (AQOC) are computed by the following formulae, respectively.

236

$$237 \quad \text{TROC (\%)} = 1.31 \times \Sigma 8 \text{ (mg/10g)}$$

$$238 \quad \text{AQOC (\%)} = \text{TOC (\%)} - \text{TROC (\%)}.$$

239

240 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 Lake 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, $\Sigma 8$, 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, $\Sigma 8$, 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 $\Sigma 8$ 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

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

271

272 4.2. Changes in the contributions of gymnosperms and angiosperms

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

286 The correspondence to pollen assemblages indicates that a higher S/V ratio reflects
287 a warmer climate with cool-temperate deciduous broadleaf forests (angiosperms) and
288 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 $\delta^{18}\text{O}$ record (Wang et al., 2001, 2008). This

313 correspondence is consistent with the viewpoint that variation in summer air
314 temperature (variation in the abundance of the angiosperm *Quercus*) in central Japan
315 was linked to intensification of the East Asian summer monsoon and that maxima of
316 gymnosperm *Cryptomeria* pollen lagged the July 21 insolation at 65°N and the
317 Hulu-Sanbao monsoon maxima by ~8 kyr (Fig. 9; Igarashi and Oba, 2006; Yamamoto,
318 2009).

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

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

333 The out-of-phase variation in air temperature and precipitation caused the repetition
334 of warmer, dry and cooler, wet climates in central Japan on a precessional cycle,
335 inducing replacement among cool-temperate deciduous broadleaf forests, subalpine
336 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

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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

497 Figure captions

498

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

503

504 **Fig. 2.** The degradation products of lignin by alkaline CuO oxidation (Hedges and
505 Parker, 1976; Hedges and Mann, 1979). The hydroxy groups are converted to methoxy
506 groups in TMAH pyrolysate.

507

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

509

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

511

512 **Fig. 5.** Changes in total organic carbon (TOC) content, $\Sigma 8$, Λ , S/V, C/V, (Ad/Al)_v, and
513 terrestrial and aquatic organic matter contents (TROC and AQOC, respectively) in core
514 BIW08-B during the last 147,000 years.

515

516 **Fig. 6.** Plot of total organic carbon content (TOC) against total lignin concentration ($\Sigma 8$)
517 in BIW08-B samples.

518

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

521

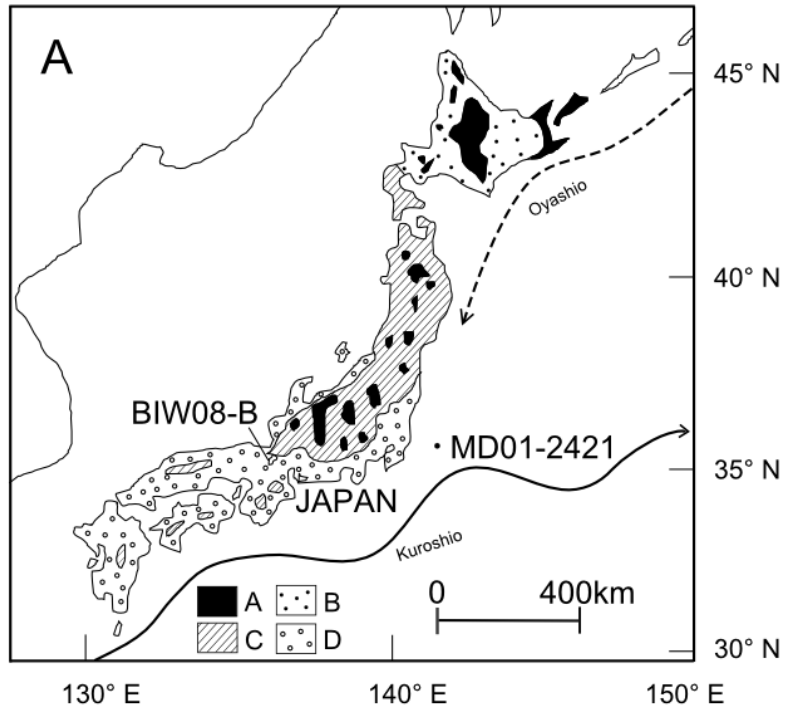
522 **Fig. 8.** Changes in (A) the relative abundances of deciduous broadleaf tree, Japanese

523 cedar *Cryptomeria*, and pinaceous tree pollen to total tree pollen in the BIW95-4 and

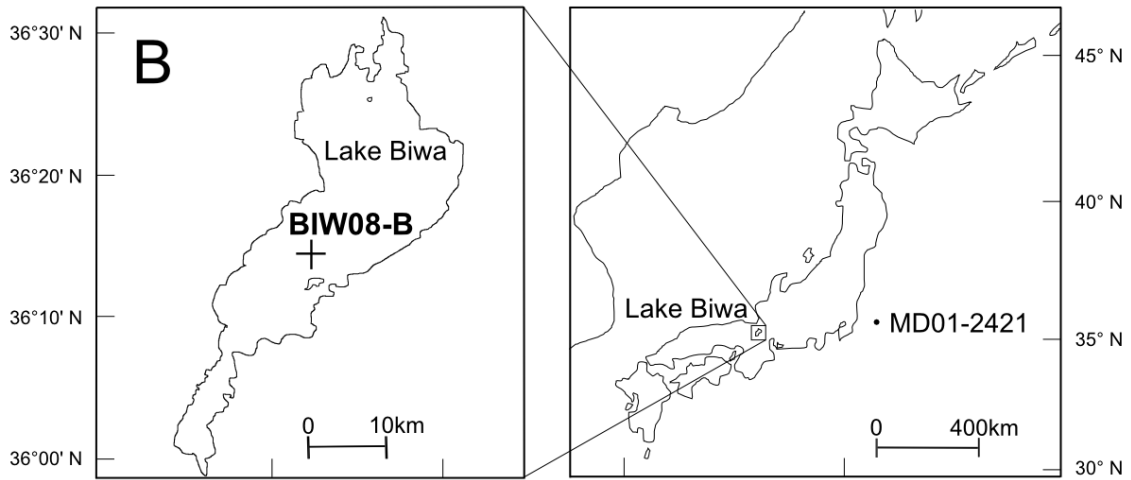
524 Takashima-oki cores and (B) S/V ratio in the BIW08-B and MD01-2421 cores.

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).



527

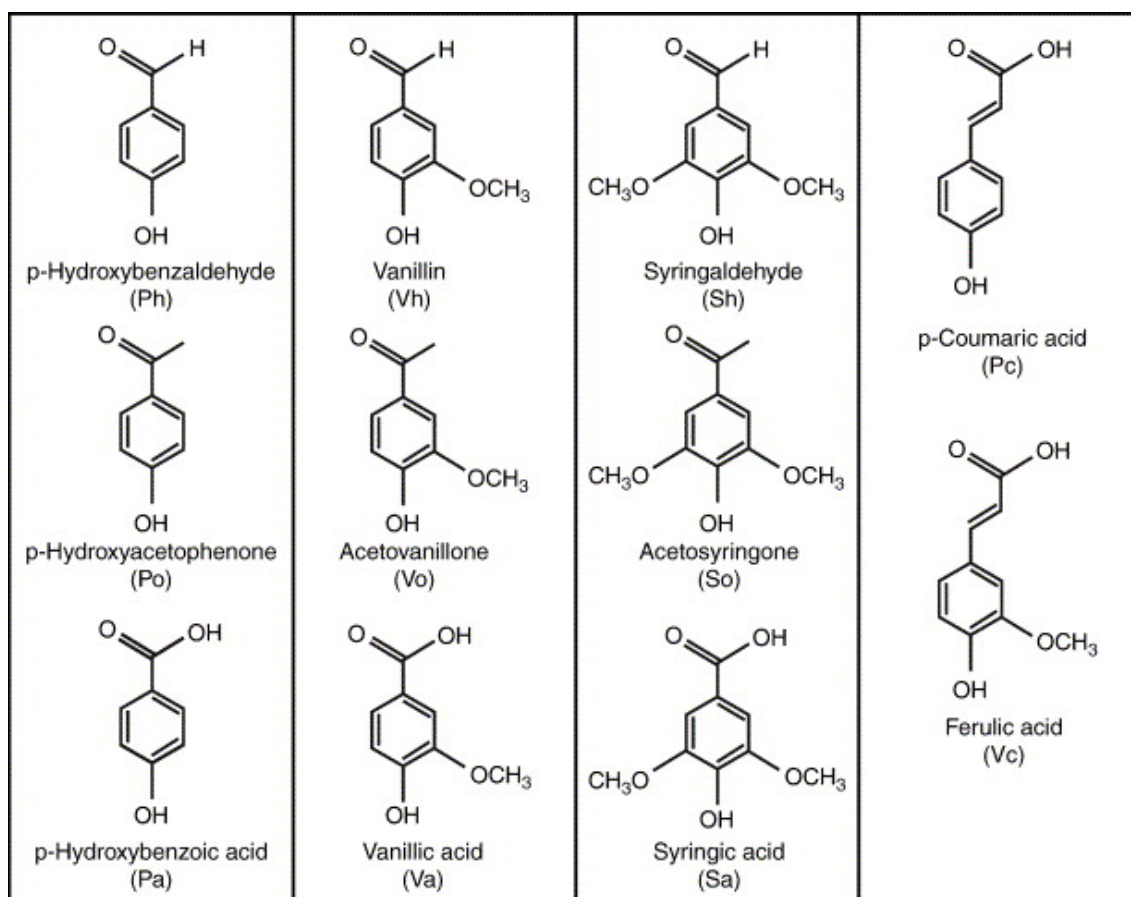


528

529

530 Fig. 1

531



532 p-Hydroxy phenols

Vanillyl phenols

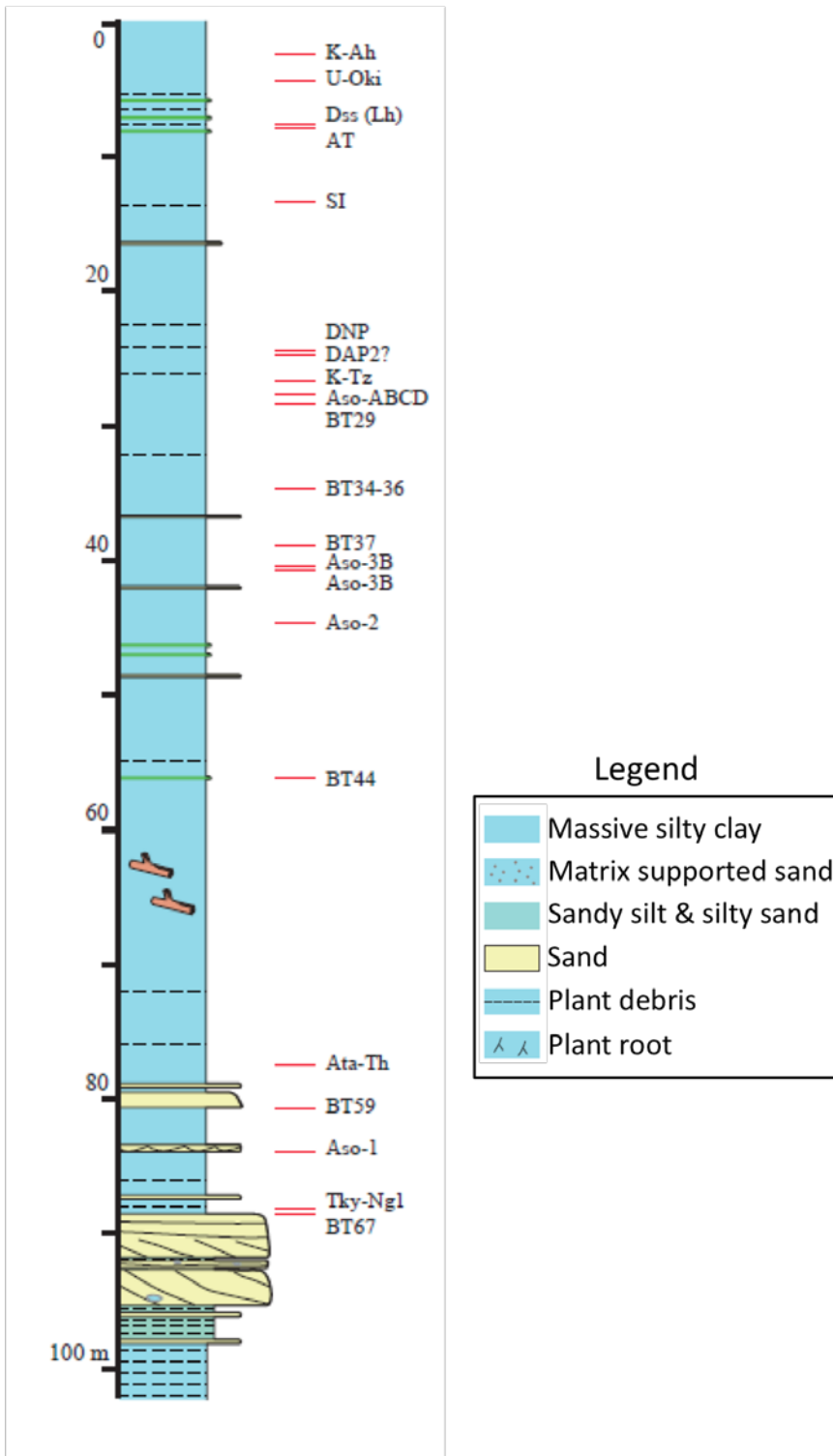
Syringyl phenols

Cinnamyl phenols

533

534 Fig. 2.

535

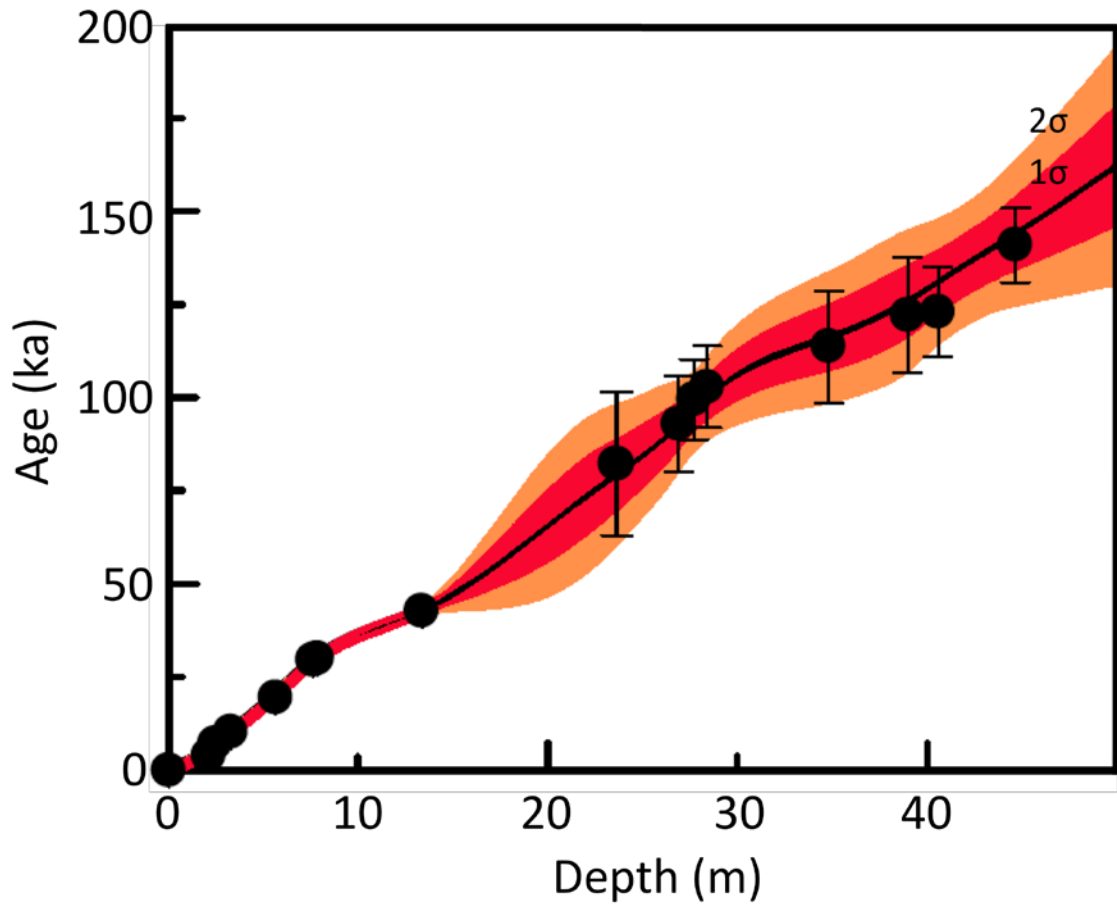


536

537 Fig. 3

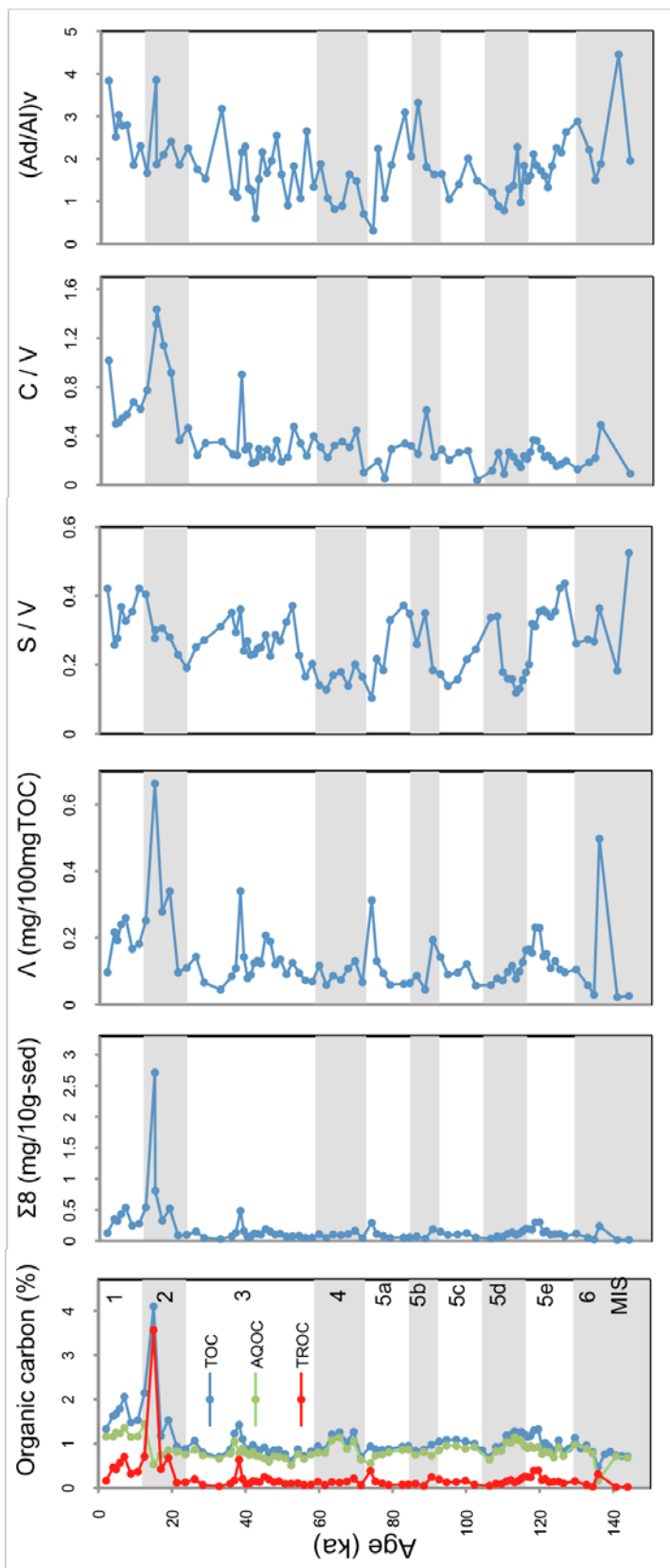
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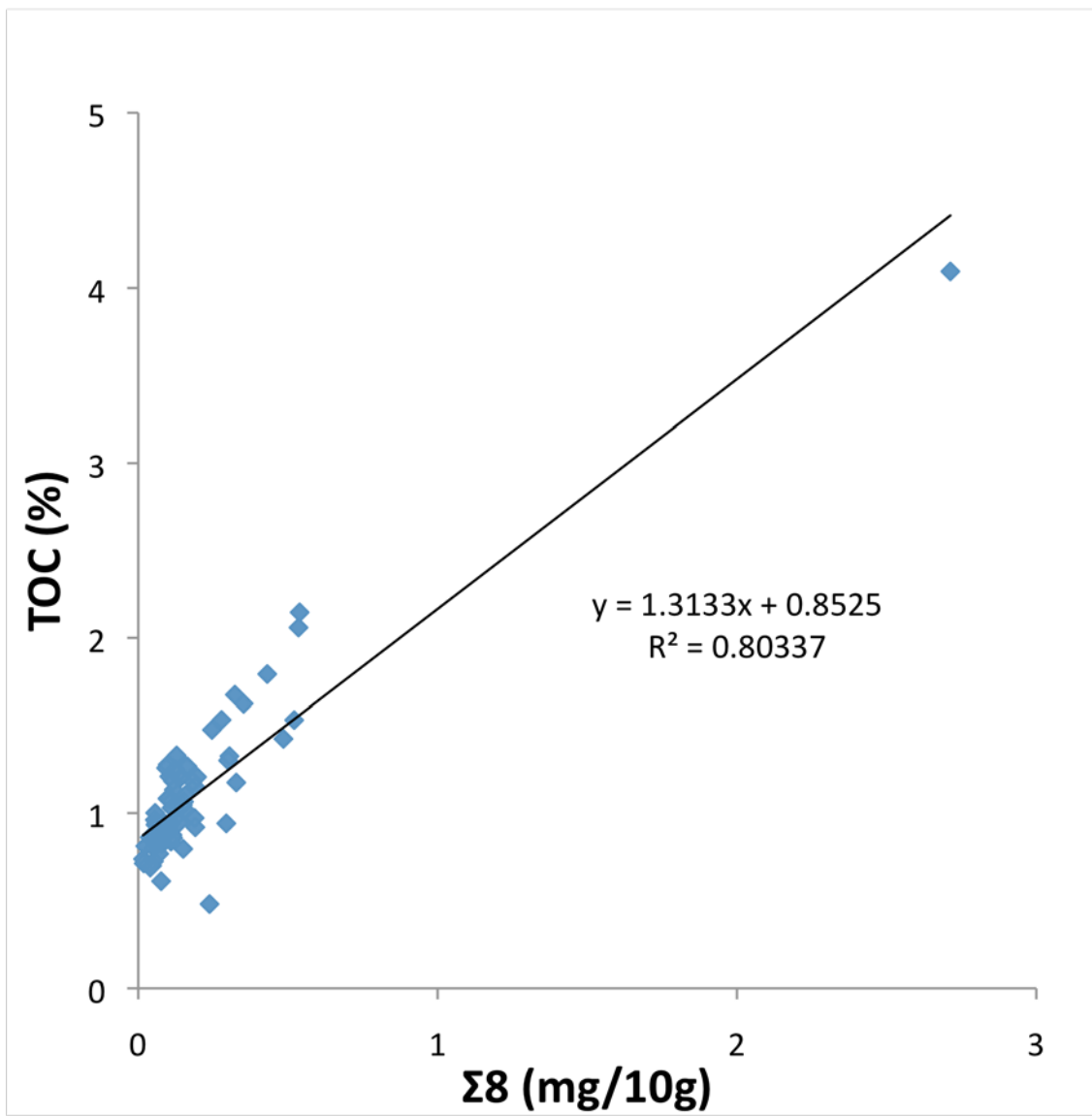
540 Fig. 4
541

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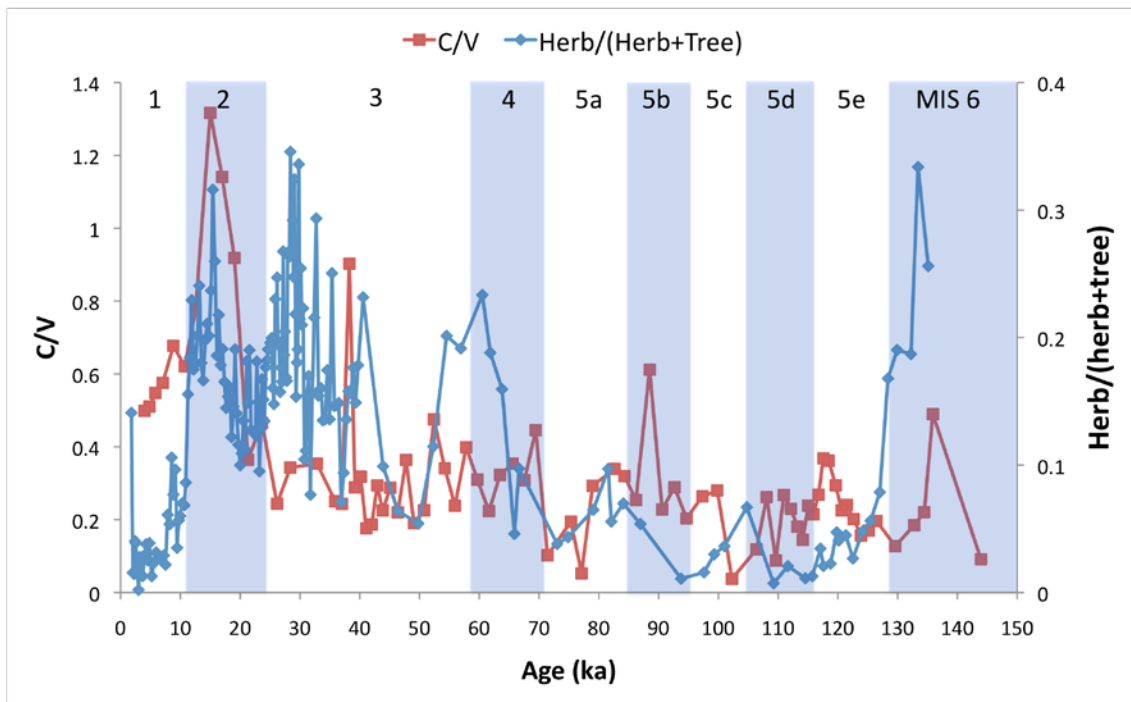
544 Fig. 5



545

546 Fig. 6

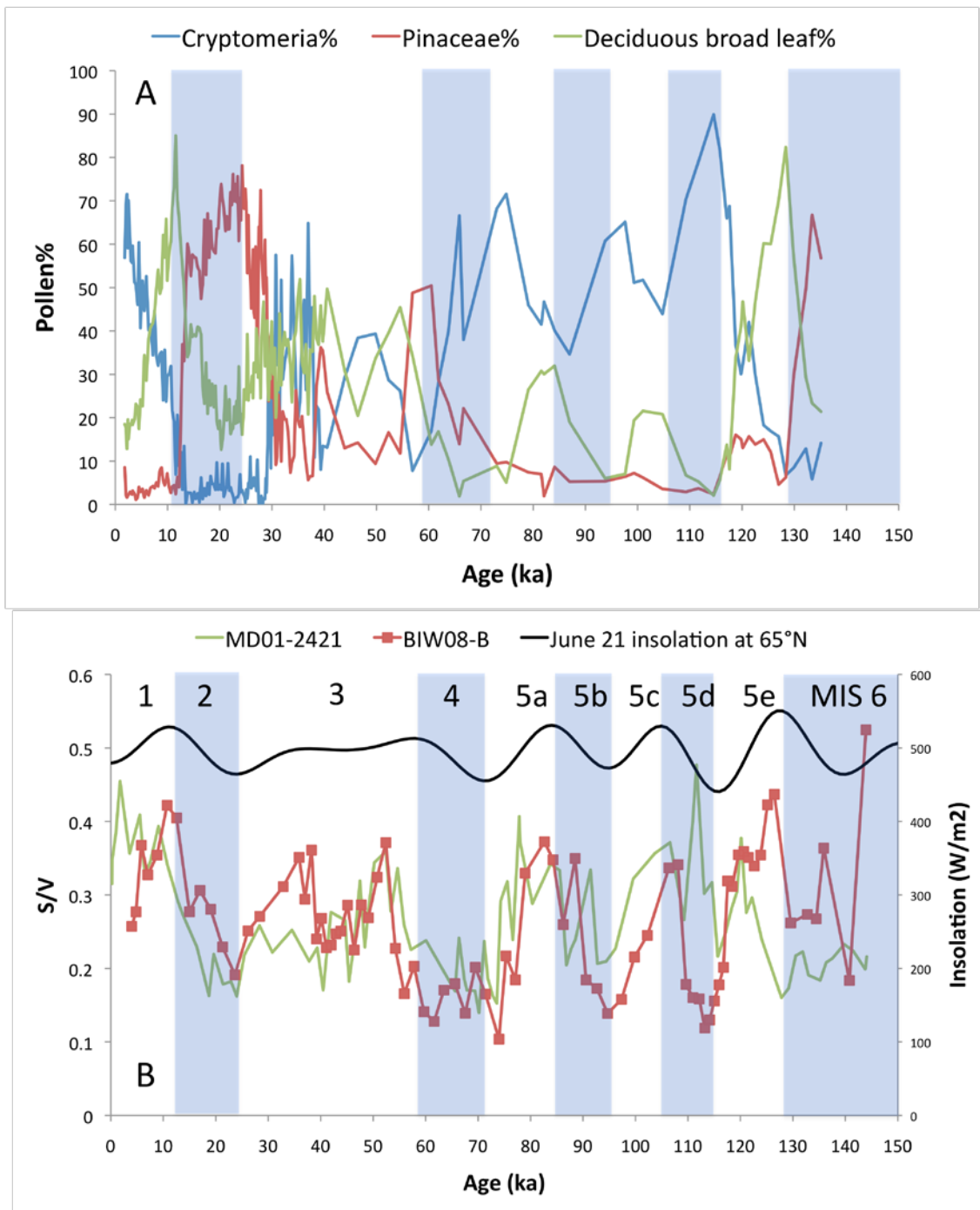
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549 Fig. 7

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551

552 Fig. 8