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**Environmental influences over the last 16 ka on compound-specific $\delta^{13}\text{C}$ variations
of leaf wax *n*-alkanes in the Hani peat deposit from northeast China**

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22 **Abstract**

23 Compound-specific carbon isotope ratios ($\delta^{13}\text{C}$) of leaf wax *n*-alkanes (C_{21} - C_{33} odd
24 carbon numbered *n*-alkanes) were measured in the Hani peat sequence from northeast
25 China. These data were compared with lipid biomarker compositions to assess changes
26 in local vegetation and paleoclimate for the last 16 ka. The $\delta^{13}\text{C}$ values of *n*-alkanes
27 range between -36.6 to -30.7‰ , showing that the compounds originate from C_3 plants.
28 Much larger variations ($\sim 5.4\text{‰}$) in the *n*-alkane $\delta^{13}\text{C}$ values than those of atmospheric
29 CO_2 during the last 16 ka ($< 0.5\text{‰}$) indicate that the isotopic values were affected by
30 environmental factors in addition to the postglacial $\delta^{13}\text{C}$ variations in the atmospheric
31 reservoir. The stratigraphic records of $\delta^{13}\text{C}$ reveal decoupled fluctuations among the
32 individual *n*-alkanes, particularly between 15.5 to 11.4 ka. Synchronous excursions in
33 the $\delta^{13}\text{C}$ offsets among individual *n*-alkanes ($\Delta\delta^{13}\text{C}$) and lipid biomarker paleoplant
34 proxies (*Paq*, and $\text{C}_{23}/\text{C}_{31}$ and $\text{C}_{27}/\text{C}_{31}$) from 14.9 to 13.2 ka and 12.7 to 11.6 ka suggest
35 that vegetational changes are the most likely causes for the decoupled $\delta^{13}\text{C}$ variations.
36 Parallel fluctuations of the $\delta^{13}\text{C}$ values of terrestrial higher plant-derived C_{29} and C_{31}
37 *n*-alkanes and the *n*-alkane average chain-length (ACL) from 11 to 6 ka indicate that the
38 $\delta^{13}\text{C}$ variations responded to net evaporation changes. Negative shifts in the *n*-alkane
39 $\delta^{13}\text{C}$ values coinciding with the ACL decreases at 10.5-9.3 ka and 8.1 ka indicate the
40 short-term onset and fluctuations of the summer monsoon strength in eastern China
41 during the early Holocene.

42

43 **Keywords:** peat; stable carbon isotopes; *n*-alkane; leaf wax; Holocene; Asian monsoon

44

45 **1. Introduction**

46 A peat deposit, which is an accumulation of partially decomposed and
47 thermally immature organic matter that is mainly composed of autochthonous vascular
48 plant debris, holds valuable information about continental paleoenvironmental histories

49 (Blackford, 2000). The kind and abundance of bog vegetation that contributes to a peat
50 sequence can be significantly influenced by local factors such as bog surface moisture
51 conditions, ground water level, influx of nutrient-rich groundwater, and lateral variety in
52 plant communities, while regional climate changes can affect bog vegetation and its
53 preservation in the peat sequence through the hydrology. Plant fossil records in the peat
54 can therefore serve as a proxy for past climate changes (Barber, 1985). Indeed, various
55 studies have reconstructed paleoenvironmental histories of peat bogs using pollen, plant
56 macrofossils and the stable carbon and oxygen isotopic compositions of plant cellulose
57 (Pendall et al., 2001; Hong et al., 2001; Xu et al., 2006; Schröder et al., 2007), as well
58 as other proxies like humification indices (Blackford and Chambers, 1993; Baker et al.,
59 1999; Wang et al., 2004) and testate amoebae (Charman, 2001).

60 Molecular compositions of lipid biomarkers derived from peat-forming plants
61 have also been shown to be important proxies to reconstruct past changes in bog
62 environments (Ficken et al., 1998; Nott et al., 2000; Pancost et al., 2002; Xie et al.,
63 2004; Zhou et al., 2005; Zheng et al., 2007; López-Díaz et al., 2010). Records of peat
64 *n*-alkanes are particularly robust because of their low susceptibility to microbial
65 degradation relative to other types of lipid compound classes (Meyers, 2003; Zheng et
66 al., 2007; Zhou et al., 2010), and their preferential production in the plant leaves rather
67 than the roots (Pancost et al., 2002) make their stratiform depositional records
68 preferable for paleoenvironmental archives, especially in a bog where plant
69 macrofossils are sometimes poorly preserved.

70 Several studies have also employed compound-specific carbon isotopic
71 analyses of *n*-alkanes to obtain additional paleoenvironmental information (Ficken et al.,
72 1998; Xie et al., 2004). Because the individual leaf wax *n*-alkanes in a peat bog
73 originate from a mixture of various types of vegetation with specific *n*-alkane
74 distributions and carbon isotopic compositions ($\delta^{13}\text{C}$) (e.g. Corrigan et al., 1973; Ficken
75 et al., 1998; Yudina and Savel'eva, 2008), a combination of *n*-alkane distributions and

76 their $\delta^{13}\text{C}$ values can make it possible to identify changes in the contributing plant
77 species. Furthermore, the $\delta^{13}\text{C}$ of terrestrial and peat-forming C_3 plants is partially
78 controlled by isotopic fractionations that reflect physiological responses to conditions in
79 their growing environment, such as humidity, temperature, and light level (Arens et al.,
80 2000; Hong et al., 2001). Thus, the leaf wax $\delta^{13}\text{C}$ values may also provide information
81 about the local paleoenvironment.

82 In the northeastern part of China, Holocene peat mires and lakes are widely
83 distributed, some of which have been intensively studied to reconstruct the Holocene
84 climate changes that were induced by variations in the Asian monsoon activity. For
85 example, paleoenvironmental proxies such as paleo-lake levels, pollen and
86 loess/paleosol records have revealed an increase in summer monsoon precipitation
87 during the last deglaciation and the early Holocene (An et al., 2000 and references
88 therein). Recently, the stable carbon and oxygen isotopic compositions of plant cellulose
89 (Hong et al., 2005, 2009a) and the molecular and hydrogen isotopic compositions of
90 lipid biomarkers (Seki et al., 2009; Zhou et al., 2010) have been examined in the Hani
91 peat deposit from northeastern China to reconstruct paleoclimatic history for the last 16
92 ka.

93 In this study, we present the $\delta^{13}\text{C}$ profiles of leaf wax *n*-alkanes in the Hani
94 peat sequence, and we use these profiles to reconstruct paleoenvironmental changes that
95 are recorded in the $\delta^{13}\text{C}$ of terrestrial higher plants. The combination of the $\delta^{13}\text{C}$ and
96 molecular distribution of *n*-alkanes allows us to estimate changes in source vegetation
97 and paleoclimatic history in northeastern China over the last 16 ka.

98

99 **2. Experimental**

100 **2.1. Setting and stratigraphy of the Hani peat deposit**

101 The Hani peat bog (42°13'N, 126°31'E) is located near Liangshui in Jilin
102 Province (Fig. 1) at an elevation of 900 m and is surrounded by the numerous volcano

103 cones and crater lakes that form the Long Gang volcanic field. The peat covers an area
104 of 16.8 km² in a percolation mire where the Hani River has its source, and the stable
105 swampy environment has allowed development of a peat layer more than 9 m thick
106 since the end of the Last Glacial Maximum.

107 A core of the 963 cm thick peat sequence was recovered from near the center of
108 the Hani bog. It is mainly composed of peat of various colors with occasional
109 intercalations of mud and sand layers. The basal 33 cm of the core is marked with a
110 dark gray mud layer, which is followed by a 204 cm-thick black-brown peat layer. The
111 interval between 726 and 126 cm below the bog surface consists mainly of dark-brown
112 peat. A mixed layer of light-brown peat with coarse sand and a layer of light-brown peat
113 with abundant plant debris are intercalated at 640-606 and 316-246 cm depth intervals,
114 respectively. The uppermost 126 cm interval near the surface is composed of 60
115 cm-thick brown peat and 40 cm-thick light-brown peat layers, in ascending order, which
116 is capped with 26 cm of undegraded grass fragments (Fig. 2).

117 We developed an age-depth model based on calibrated calendar ages that were
118 obtained from accelerator mass spectrometry (AMS) ¹⁴C ages provided by Zhou et al.
119 (2010) using CALIB 4.3 software (Stuiver and Reimer, 1993; Stuiver et al., 1998; Fig.
120 2). The peat accumulation rate averages 62 cm/ka, and the basal age of the entire 960
121 cm core sequence is 15.5 ka.

122

123 **2.2. Lipid analyses**

124 The samples consist of 1 cm sediment slices taken every 10 cm in the core.
125 Lipids were ultrasonically extracted with CHCl₃ from ca. 1-2 g of freeze dried sample at
126 the State Key Laboratory of Loess and Quaternary Geology in Xi'an, China. The
127 extracts were concentrated on a rotary evaporator under vacuum and taken to dryness
128 with a N₂ stream (Seki et al., 2009; Zhou et al., 2010). Aliphatic hydrocarbons were
129 isolated using silica gel column chromatography (230-400 mesh; 1% H₂O deactivated)

130 by elution with 1.5 ml *n*-hexane at the Institute of Low Temperature Science, Hokkaido
131 University.

132 Analysis of aliphatic hydrocarbon fractions was performed using gas
133 chromatography (GC) and GC/mass spectrometry (MS). GC analysis was performed
134 using a Hewlett-Packard 6890 gas chromatograph equipped with an on-column injector,
135 CP-Sil 5 CB fused silica column (60 m × 0.32 mm i.d., 0.25 μm film thickness) and a
136 flame ionization detector (FID). Helium was used as carrier gas. The GC oven
137 temperature was programmed from 50 to 120°C at 30°C/min, from 120 to 310 °C at
138 6 °C/min, and then held isothermally for 15.5 min. GC/MS analysis was performed
139 using a Hewlett-Packard 5973 Mass Selective Detector coupled to a Hewlett-Packard
140 6890 gas chromatograph equipped with a HP-5MS fused silica column (30 m × 0.25
141 mm i.d., 0.25 μm film thickness). The temperature program was the same as for the GC
142 analysis. The compounds were identified on the basis of their mass spectra, GC
143 retention times, and comparison with literature mass spectra.

144

145 **2.3. Compound-specific stable carbon isotope analysis**

146 In order to improve the accuracy of the compound-specific stable carbon isotope
147 ratio ($\delta^{13}\text{C}$) analyses, the *n*-alkane fractions were purified using the urea adduct
148 technique of Yamamoto and Kawamura (2010). Briefly, a saturated solution of urea in
149 methanol was added to the hydrocarbon fraction dissolved in *n*-hexane/acetone (2:1)
150 and gently stirred overnight using a mechanical stirrer to complete the adduction. After
151 adduction, the solvent was removed from the urea precipitate, which was rinsed with
152 fresh solvent (*n*-hexane/acetone, 2:1) three times to remove non-adducted materials.
153 The urea crystals were dried under a N₂ stream and the *n*-alkanes were recovered in
154 *n*-hexane after dissolution of the crystals in water.

155 $^{13}\text{C}/^{12}\text{C}$ ratios of the purified *n*-alkanes were determined using a HP 6890 GC
156 coupled to a Finnigan MAT Delta Plus isotope ratio mass spectrometer via a Finnigan

157 MAT combustion furnace maintained at a temperature of 850 °C. The GC was equipped
158 with HP-5MS fused silica column (30 m × 0.32 mm i.d., 0.25 μm film thickness). The
159 GC oven was programmed from 50 to 120 °C at 30 °C/min, from 120 to 310 °C at
160 5 °C/min, and then held isothermally for 22 min. One to 2 μl of sample solution were
161 injected into the GC via an on-column injector with an internal standard of known
162 isotopic composition (C₂₀ *n*-alkanoic acid methyl ester; δ¹³C = -26.21‰). The δ¹³C
163 values are expressed as per mil (‰) relative to the Vienna Pee Dee Belemnite (VPDB).
164 Most measurements were duplicated. Reported δ¹³C data represent an averaged value of
165 the duplicate analyses. An external standard consisting of C₁₆ to C₃₀ *n*-alkanes of known
166 isotopic compositions was daily injected into the GC/IRMS system to check the data
167 quality and to ensure that the analytical error of the *n*-alkanes remained below ±0.5‰
168 during the analyses (Bendle et al., 2007).

169

170 **3. Results and Discussion**

171 **3.1. δ¹³C values of leaf wax *n*-alkanes in the Hani peat core**

172 The Hani peat core samples contain C₂₁ to C₃₅ *n*-alkanes with a strong
173 odd-over-even carbon number predominance (CPI = 3.1 to 7.5) as major aliphatic
174 hydrocarbons (Fig. 2). Generally, submerged and floating macrophytes contain a large
175 proportion of *n*-alkanes that maximizes at C₂₁, C₂₃, or C₂₅, whereas vascular land plants
176 and emersed macrophytes contain C₂₇, C₂₉ and C₃₁ *n*-alkanes as constituents of their
177 epicuticular waxes (e.g. Eglinton and Hamilton, 1967; Corrigan et al., 1973; Cranwell,
178 1984; Rieley et al., 1991; Ficken et al., 2000). Distribution patterns of these *n*-alkanes
179 show significant variations throughout the core (Fig. 2), suggesting variable
180 contributions from both types of plants.

181 Fig. 3 presents the profiles of the stable carbon isotopic compositions (δ¹³C)
182 of C₂₁ to C₃₃ odd carbon number *n*-alkanes in the Hani peat core. The δ¹³C values of leaf
183 wax *n*-alkanes in the peat samples range from -36.6 to -30.7‰ (Fig. 3), which is in the

184 range of the $\delta^{13}\text{C}$ values reported for leaf wax *n*-alkanes in various Far East C_3 plants
185 (Chikaraishi and Naraoka, 2003) and in surface soil samples from eastern China
186 dominated by C_3 broad leaved forests (Rao et al., 2009). Inasmuch as cellulose $\delta^{13}\text{C}$
187 values have revealed that the contemporary vegetation in the Hani peat bog is
188 dominated by C_3 plant species (Hong et al., 2005), the leaf waxes likely originate from
189 the C_3 vegetation that flourished in the Hani peat bog. The $\delta^{13}\text{C}$ values of the leaf wax
190 *n*-alkanes are, however, ca. 8‰ isotopically depleted in ^{13}C compared with those in the
191 plant cellulose (Hong et al., 2005). Such depletion in leaf wax *n*-alkanes relative to peat
192 cellulose reflects increased carbon isotopic fractionation between lipids and plant
193 tissues in the acetate-malonate biosynthetic pathway (Collister et al., 1994).

194 The $\delta^{13}\text{C}$ of C_3 plants is partially controlled by the isotopic fractionations that
195 are affected by various ecological and physiological factors and the species composition
196 of their source vegetation (Arens et al., 2000), in addition to the isotopic composition of
197 atmospheric CO_2 . Much larger variations ($\sim 5.4\%$) in leaf wax *n*-alkanes (Fig. 3) than
198 those of atmospheric CO_2 during the last 16 ka ($\sim 0.5\%$; Leuenberger et al., 1992)
199 indicate that the $\delta^{13}\text{C}$ variations were mainly controlled by factors other than the
200 postglacial $\delta^{13}\text{C}$ variations in the atmospheric reservoir.

201

202 **3.2. Impact of vegetational changes on the $\delta^{13}\text{C}$ of leaf wax *n*-alkanes**

203 Our records of the compound-specific $\delta^{13}\text{C}$ values show decoupled
204 fluctuations among the individual *n*-alkanes (Fig. 3). In particular, the decoupling is
205 prominent in the 960 to 650 cm interval where the $\delta^{13}\text{C}$ values of the C_{25} and C_{27}
206 *n*-alkanes decrease to as low as -36.6% in contrast to the smaller fluctuations from
207 -34.8 to -30.7% in the $\delta^{13}\text{C}$ values of the other *n*-alkanes (C_{21} , C_{23} , C_{29} , C_{31} and C_{33})
208 (Fig. 3). In the lower half of this interval (960 to 739 cm), the $\delta^{13}\text{C}$ profiles of the C_{23}
209 and C_{25} *n*-alkanes exhibit a 2.0 to 2.5‰ negative shift, but equivalent shifts are not
210 observed in the other *n*-alkane records. In the upper half of the interval (739 to 650 cm),

211 although C₂₁ to C₂₉ *n*-alkane profiles show concurrent δ¹³C negative shifts, the
212 magnitudes of the shifts are significantly different among the compounds: those for C₂₅
213 and C₂₇ are ca. 3.8‰, whereas those for the other *n*-alkanes are only 1.5 to 2.0‰ (Fig.
214 3).

215 The leaf wax *n*-alkanes in a peat bog are commonly derived from an
216 assemblage of different plants, each with specific *n*-alkane distributions and δ¹³C values
217 (Ficken et al., 1998). Hence, the decoupling in the δ¹³C variations of *n*-alkanes with
218 different chain-lengths may indicate that the δ¹³C values of individual *n*-alkanes reflect
219 changes in plant community compositions that contribute to the peat *n*-alkanes. In
220 support of this idea, pollen records from Lake Sihailongwan, northeast China, have
221 revealed a gradual transition from steppe and open taiga-like woodland communities
222 during the late glacial to the earliest Holocene toward the dense deciduous forests that
223 are similar to modern flora (Schettler et al., 2006; Stebich et al., 2009). Similarly, the
224 ecophysiological responses to environment stresses may have been different among the
225 assemblage of peat-forming plants, which would further emphasize the δ¹³C offsets
226 among individual compounds.

227 In this study, we assessed the possible impact of changes in the plant
228 communities on the δ¹³C variations by comparison with the *Paq* and the concentration
229 ratios of the C₂₁ to C₃₃ odd carbon number *n*-alkanes against the C₃₁ *n*-alkane. The *Paq*
230 (Ficken et al., 2000) is a paleoplant proxy expressed by the following equation:

$$231 \quad Paq = (C_{23}+C_{25})/(C_{23}+C_{25}+C_{29}+C_{31})$$

232 that can reveal the proportion of aquatic (submerged and floating) macrophytes to total
233 peat forming plant taxa and has already been shown to be informative in the Hani peat
234 deposit (Seki et al., 2009; Zhou et al., 2010). The *n*-alkane ratios, especially the C₂₇/C₃₁
235 and C₂₃/C₃₁ ratios are also known as paleoplant proxies. The C₂₇/C₃₁ concentration ratio,
236 which was originally described as C₃₁/C₂₇ ratio in Schwark et al. (2002), is generally
237 considered to express the relative contribution of C₃ grasses whose leaf wax *n*-alkanes

238 are dominated by the C₃₁ homologue. However, the dominant *n*-alkane chain-lengths in
239 contemporary vegetation at the Hani peatland (Table 1) and the surrounding mountains
240 (Schröder et al., 2007; Makohonienko et al., 2008) from the literature suggest that the
241 C₃₁ *n*-alkane may also be supplied to the peat deposit by some mosses and trees (e.g.
242 *Juglans*, *Betula*, *Abies*, *Taxus*, *Tilia*, *Fraxinus* and *Larix*) besides C₃ grasses. In contrast,
243 the C₂₃/C₃₁ concentration ratio can represent the contribution of *Sphagnum* species
244 (Pancost et al., 2002). It is based on the observation that *Sphagnum* yields preferentially
245 C₂₃ and C₂₅ *n*-alkanes compared to other homologues (Ficken et al., 1998; Nott et al.,
246 2000; Pancost et al., 2002; Table 1).

247 In Fig. 4, we compare the profiles of the *Paq* and the *n*-alkane biomarker
248 ratios with those of the δ¹³C offsets between the C₃₁ *n*-alkane and the C₂₁, C₂₃, C₂₅, C₂₇,
249 C₂₉ and C₃₃ *n*-alkanes; hereafter expressed as Δδ¹³C (C₃₁ – C₂₁), Δδ¹³C (C₃₁ – C₂₃), Δδ¹³C
250 (C₃₁ – C₂₅), Δδ¹³C (C₃₁ – C₂₇), Δδ¹³C (C₃₁ – C₂₉) and Δδ¹³C (C₃₁ – C₃₃), respectively. The
251 Δδ¹³C records reveal significant positive excursions from 14.9 to 13.2 ka and 12.7 to
252 11.6 ka, although the magnitudes of the excursions of Δδ¹³C (C₃₁ – C₂₁), Δδ¹³C (C₃₁ –
253 C₂₉) and Δδ¹³C (C₃₁ – C₃₃) are much smaller than those of Δδ¹³C (C₃₁ – C₂₃), Δδ¹³C (C₃₁
254 – C₂₅) and Δδ¹³C (C₃₁ – C₂₇) (Figs. 4a, b). The simultaneous changes in paleoplant
255 proxies with the excursions strongly suggest that vegetational changes are the most
256 likely causes for the decoupled variations among the *n*-alkane homologues. Changes in
257 the sedimentary environment may also have potentially affected the δ¹³C values through
258 the enhancement of allochthonous plant input from the surrounding forests. However, a
259 lack of any clear relation between the δ¹³C variations and the peat lithology suggests
260 that such an increase is unlikely.

261

262 3.2.1. Vegetational change from 14.9 to 13.2 ka

263 Parallel increases in the C₂₃/C₃₁ ratios and the Δδ¹³C (C₃₁ – C₂₃), Δδ¹³C (C₃₁ –
264 C₂₅), Δδ¹³C (C₃₁ – C₂₇) and Δδ¹³C (C₃₁ – C₂₉) values from 14.9 to 13.2 ka (Figs. 4a-4c)

265 indicate that a relative increase in the contribution of *Sphagnum* species to the peat
266 *n*-alkanes is the most likely cause for the $\Delta\delta^{13}\text{C}$ increases in this period. This notion is
267 supported by the significant increases in the relative abundance of C_{21} and C_{25} *n*-alkanes
268 against the C_{31} *n*-alkane (Fig. 4c), because these homologues are predominantly found
269 in *Sphagnum* species (Ficken et al., 1998; Nott et al., 2000). Furthermore, the
270 magnitudes of the $\delta^{13}\text{C}$ offsets from the C_{31} *n*-alkane are $\sim 3.4\text{‰}$ for the C_{25} *n*-alkane
271 and $\sim 3.8\text{‰}$ for the C_{27} *n*-alkane, which match well with those observed in modern
272 *Sphagnum* species in which the $\delta^{13}\text{C}$ of the C_{25} and C_{27} *n*-alkanes are $\sim 3.4\text{‰}$ more
273 ^{13}C -depleted than the C_{31} *n*-alkane (Ficken et al., 1998). The potential contribution from
274 submerged/floating aquatic plants other than *Sphagnum* could have increased because
275 the C_{23} *n*-alkane is also abundant in these aquatic macrophytes (Ficken et al., 2000; Nott
276 et al., 2000). However, such vegetational changes are not supported by macrofossil
277 evidence from the Hani peat sequence (Schröder et al., 2007).

278 On the other hand, the pollen proxy record in nearby Lake Sihailongwan
279 revealed an increased influx from *Betula* between 14.3 to 14.0 ka (Stebich et al., 2009).
280 Because the C_{27} *n*-alkane is commonly found in *Betula* and *Fagus* trees (Table 1; Ali et
281 al., 2005; Sachse et al., 2006), parallel increases in the $\text{C}_{27}/\text{C}_{31}$ and the $\Delta\delta^{13}\text{C}$ ($\text{C}_{31} - \text{C}_{27}$)
282 from 14.4 to 14.1 ka (Fig. 4) might correspond to climate amelioration at the beginning
283 of the Late Glacial.

284 Relatively high Paq values and D-depleted hydrogen isotopic compositions of
285 the *n*-alkanes during 14 to 11 ka (Seki et al., 2009; Fig. 4) indicate that the increases in
286 aquatic plants likely are the consequence of enhanced water availability for the
287 peat-forming plants. In percolation mires like the Hani sequence, rainwater generally
288 flows over the peat surface and infiltrates the peat body during the wet growing season
289 due to the slope of the peat surface and the large amount of precipitation in the summer.
290 However, macrofossil records from the Hani mire suggest that the establishment of the
291 initial stage of percolation conditions did not occur until at least 12.6 ka (Schröder et al.,

292 2007). Hence, the water availability is likely to have been controlled by groundwater
293 level during this period although a marked rise in the total pollen concentrations and
294 increases in frequencies of moss and fern spores and the accumulation rate of biogenic
295 silica in nearby lake Sihailongwan suggest an increased precipitation during 14.5 to
296 13.6 ka (Stebich et al., 2007, 2009).

297

298 3.2.2. Vegetational change from 12.7 to 11.6 ka

299 Simultaneous increases in $\Delta\delta^{13}\text{C}$ ($\text{C}_{31} - \text{C}_{27}$) values and $\text{C}_{27}/\text{C}_{31}$ ratios from
300 12.7 to 11.6 ka (Figs. 4b, d) indicate a relative increase of ^{13}C -depleted C_{27} *n*-alkanes
301 and/or a relative decrease of ^{13}C -depleted C_{31} *n*-alkanes during this time interval.
302 Because a certain *Sphagnum* species, *Sphagnum fuscum*, is known to have a large
303 abundance of the C_{27} *n*-alkane (Corrigan et al., 1973; Sachse et al., 2006; Yudina and
304 Savel'eva, 2008) and to contain C_{23} , C_{25} and C_{27} *n*-alkanes whose $\delta^{13}\text{C}$ are 1.3 to 2.0‰
305 lower than those of the C_{29} and C_{31} *n*-alkanes (Ficken et al., 1998; Xie et al., 2004), the
306 increased contribution of this species can consistently explain the high $\text{C}_{27}/\text{C}_{31}$ ratios and
307 the increase in the $\Delta\delta^{13}\text{C}$ ($\text{C}_{31} - \text{C}_{23}$), $\Delta\delta^{13}\text{C}$ ($\text{C}_{31} - \text{C}_{25}$) and $\Delta\delta^{13}\text{C}$ ($\text{C}_{31} - \text{C}_{27}$) values
308 during the 12.7 to 11.6 ka period (Figs. 4a, b). The lack of change in the $\text{C}_{23}/\text{C}_{31}$ ratios
309 suggests that the contribution of *Sphagnum* mosses did not increase, unlike the period
310 from 14.9 to 13.2 ka; however, it should be noted that the $\text{C}_{23}/\text{C}_{31}$ ratio does not always
311 indicate an abundant *Sphagnum* contribution to peat deposits when the predominant
312 *Sphagnum* species possesses both the C_{27} and C_{31} *n*-alkanes as its major components
313 (Nott et al., 2000).

314 On the other hand, pollen records in nearby Lake Shihailongwan show
315 increases in the relative abundance of certain conifers (*Larix*, *Picea*) during the period
316 of Younger Dryas-like climate deterioration (12.4-11.7 ka; Stebich et al., 2007, 2009).
317 Because the leaf wax of these conifer trees contains the C_{31} *n*-alkane with a more
318 ^{13}C -enriched $\delta^{13}\text{C}$ value than the C_3 angiosperms (Chikaraishi and Naraoka, 2003;

319 Maffei et al., 2004; Pedentchouk et al., 2008), the high C_{27}/C_{31} and $\Delta\delta^{13}C$ values (Fig.
320 4) could be consequences of a relative decrease in the proportions of ^{13}C -depleted C_{31}
321 *n*-alkanes due to increases in conifer contributions.

322

323 **3.3. Climate changes in northeastern China recorded in the $\delta^{13}C$ of plant leaf** 324 **waxes**

325 Paleoclimate changes in northeast China for the last 16 ka are characterized
326 by a sequence of moisture changes. Various proxies document a general humidity
327 increase during the Late-glacial period with three short-term climate reversals to cool
328 and dry conditions at 13.9, 13.0 and 12.7 to 11.7 ka. In contrast, climate conditions in
329 the Holocene were relatively dry as compared to the deglacial period, however, the
330 summer monsoon rainfall record exhibits century-scale variability with maxima around
331 9.8 and 7.8 ka (An et al., 2000; Schettler et al., 2006; Stebich et al., 2007; Seki et al.,
332 2009; Zhou et al., 2010).

333 In Fig. 5, we compare the fluctuations of the $\delta^{13}C$ of terrestrial higher plant
334 *n*-alkanes (C_{29} and C_{31} *n*-alkanes) with those of the *n*-alkane averaged chain-length
335 (ACL) and the oxygen isotope compositions ($\delta^{18}O$) of Hani peat cellulose (Hong et al.,
336 2009a) in order to evaluate the influence of the paleoclimate changes on the $\delta^{13}C$
337 variations. The ACL value is the concentration-weighted mean chain-length of the C_{27} ,
338 C_{29} and C_{31} *n*-alkanes (Poynter et al., 1989), and its variations are commonly related to
339 changes in the temperature and aridity of the growing environment of alkane source
340 vegetation (Poynter et al., 1989; Kawamura et al., 2003; Schefuß et al., 2003;
341 Rommerskirchen et al., 2003). More recently, Sachse et al. (2006) reported a correlation
342 between the ACL and the hydrogen isotopic fractionation of leaf wax *n*-alkanes that
343 suggests that plants can alter the chain-lengths of their leaf waxes to minimize
344 evaporation of water vapor from their leaves. On the other hand, the cellulose $\delta^{18}O$ are
345 considered to reflect changes in surface air temperature (Hong et al., 2009a, b).

346 The ACL shows concomitant variations with the cellulose $\delta^{18}\text{O}$ (Fig. 5),
347 suggesting that the variations, in part, likely reflect plant physiological responses to
348 changes in temperature-driven evaporation. In contrast, the $\delta^{13}\text{C}$ of terrestrial higher
349 plant *n*-alkanes (C_{29} and C_{31} *n*-alkanes) exhibit fluctuations that are concurrent with the
350 ACL and $\delta^{18}\text{O}$ variations from 11.2 to 6.5 ka (light gray band in Fig. 5).

351 Stable carbon-isotopic fractionation (ϵ_p) of terrestrial higher plants is often
352 expressed as the following equation (Farquhar et al., 1982):

$$353 \quad \epsilon_p = a + (b - a) C_i / C_a$$

354 where C_i/C_a is the ratio of CO_2 concentration in the intercellular space of leaves (C_i) to
355 that in the atmosphere (C_a); a is the fractionation associated with diffusion of CO_2 from
356 the atmosphere into the intercellular space of leaves (4.4‰) and b is the fractionation of
357 CO_2 during carboxylation mediated by Rubisco (ca. 30‰). With higher evaporation
358 rates, plants would have reduced stomatal conductance to minimize the evaporative loss
359 of water from their leaves and thereby lowering C_i/C_a , which results in the $\delta^{13}\text{C}$ of the
360 plants becoming more ^{13}C enriched, and vice versa. Hence, the concurrent fluctuations
361 between the $\delta^{13}\text{C}$ and the ACL values during the early Holocene indicate that the $\delta^{13}\text{C}$
362 variations reflect plant physiological responses to changes in net evaporation in Hani
363 region during the early Holocene.

364 Nevertheless, it should be noted that the $\delta^{13}\text{C}$ variations of terrestrial higher
365 plant *n*-alkanes (C_{29} and C_{31} *n*-alkanes) do not match with the ACL variations in the 15.5
366 to 11.4 ka and 6.5 to 0.1 ka intervals (Fig. 5). This absence of agreement could be partly
367 related to the origin of the *n*-alkanes, because the C_{29} and C_{31} *n*-alkanes can also be
368 produced by several mosses found in the Hani peatland (Table 1) besides terrestrial
369 higher plant leaf waxes. Isotopic fractionation during carbon fixation in mosses is
370 generally smaller than in other peat-forming plants due to the lack of functional stomata
371 and a waxy cuticle on the leaf epidermis (Xie et al., 2004), and thus potential increases
372 in *n*-alkane inputs from mosses during wetter periods in the Late Glacial and in late

373 Holocene may conceal the $\delta^{13}\text{C}$ signals recorded in the *n*-alkanes derived from
374 evaporation-sensitive terrestrial higher plant.

375 Several lines of evidence indicate short-term enhancement of summer
376 monsoon rainfall in eastern China during the early Holocene. Wang et al. (1999)
377 examined the $\delta^{18}\text{O}$ of planktonic foraminifera in South China Sea sediments and
378 concluded that monsoon runoff and precipitation increased at ca. 9.4 and 8–8.1 ka in
379 southeast China. Nearly simultaneously, the net accumulation rate of biogenic silica
380 decreased (Schettler et al., 2006) and the $\delta^{13}\text{C}$ values of peat cellulose (Hong et al.,
381 2005) increased at 9.5 and 8.0 ka in northeast China (Fig. 5d), indicating an enhanced
382 summer monsoon rainfall at that time. Our *n*-alkane $\delta^{13}\text{C}$ records of terrestrial higher
383 plant *n*-alkanes (C_{29} and C_{31} *n*-alkanes) exhibit 1.4 to 1.8‰ negative shifts with the ACL
384 increases at 10.5–9.3 ka and 8.1 ka (dark gray bands in Fig. 5), which is likely to
385 represent the $\delta^{13}\text{C}$ responses of peat-forming terrestrial higher plant to the increases in
386 summer monsoonal precipitation in eastern China.

387 In northeast China, seasonal and inter-annual changes in temperature and
388 precipitation are connected with activity of the summer and winter monsoon. Most of
389 the annual precipitation is derived from the summer monsoon, and the distribution of
390 annual precipitation shows a gradual decrease toward the north-west. These
391 spatiotemporal patterns in monsoonal precipitation indicate that the short-term onset
392 and fluctuations of the summer monsoon strength may have significantly influenced the
393 early Holocene variations in effective precipitation in the Hani region.

394

395 **4. Summary and conclusions**

396 Compound-specific $\delta^{13}\text{C}$ values of C_{21} to C_{33} odd carbon number *n*-alkanes
397 (–36.6 to –30.7‰) were measured in the Hani peat deposit from northeast China to
398 assess possible changes in source vegetation and to reconstruct the regional
399 paleoclimatic history over the last 16 ka. Major changes were found in the isotopic and

400 molecular compositions of *n*-alkanes and are interpreted as follows.

401 1. The $\delta^{13}\text{C}$ profiles of individual *n*-alkanes show decoupled fluctuation
402 patterns particularly in the 960 to 650 cm interval (15.5 to 11.4 ka). A comparison
403 between the $\delta^{13}\text{C}$ offsets among individual *n*-alkane records ($\Delta\delta^{13}\text{C}$) and biomarker
404 paleoplant proxies (*Paq*, $\text{C}_{23}/\text{C}_{31}$, and $\text{C}_{27}/\text{C}_{31}$) reveal concurrent increases in $\text{C}_{23}/\text{C}_{31}$
405 ratios and $\Delta\delta^{13}\text{C}$ values from 14.9 to 13.2 ka that were most likely a result of enhanced
406 flourishing of *Sphagnum* plants (moss) during this time interval.

407 2. Larger $\text{C}_{27}/\text{C}_{31}$ ratios and increases in $\Delta\delta^{13}\text{C}$ ($\text{C}_{31} - \text{C}_{27}$) and $\Delta\delta^{13}\text{C}$ ($\text{C}_{31} -$
408 C_{25}) occur in peat deposited from 12.7–11.6 ka. These changes are likely a consequence
409 of an increased relative contribution of ^{13}C -depleted C_{27} -dominated *Sphagnum* species
410 and/or a decreased contribution of ^{13}C -depleted C_{31} *n*-alkane due to the expansion of
411 conifers.

412 3. Parallel fluctuations between the $\delta^{13}\text{C}$ values of terrestrial higher
413 plant-derived *n*-alkanes (C_{29} and C_{31}) and the *n*-alkane average chain-length (ACL)
414 values during the early Holocene suggest that the $\delta^{13}\text{C}$ variation most likely reflect plant
415 physiological responses to changes in effective precipitation (i.e., precipitation minus
416 evaporation).

417 4. The $\delta^{13}\text{C}$ variations exhibit 1.4 to 1.8‰ negative shifts at 10.5–9.3 ka and
418 8.1 ka along with decreased ACL values, indicating that the effective precipitation in
419 northeastern China was variable during the early Holocene, probably due to short-term
420 enhancement of summer monsoon rainfall at that time.

421

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429

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607

Table 1Summary of dominant *n*-alkane homologues in modern plant taxa found at Hani peatland

Plant species (Hong et al., 2005)		Dominant <i>n</i> -alkane homologues	References
<i>Sphagnum</i>	<i>palustre</i>	C23>C25	Nott et al. (2000), Baas et al. (2000)
<i>S.</i>	<i>magellanicum</i>	C31>C25>C29, C25	Nott et al. (2000), Baas et al. (2000)
<i>S.</i>	<i>acutifolium</i>		
<i>Polytrichum</i>	<i>commune</i>	C31>C29>C33 ^a	Nott et al. (2000)
<i>Calliergonella</i>	<i>cuspidata</i>		
<i>Eriphorum</i>	<i>vaginatum</i>	C31>C33>C29	Nott et al. (2000)
<i>Carex</i>	<i>schmidtii</i>		
<i>C.</i>	<i>tenuiflora</i>	C31>C33>C29 ^a	Nichols et al. (2006)
<i>Phragmitex</i>	<i>communis</i>		
<i>Typha</i>	<i>latifolia</i>	C29>C27	Cranwell (1984)
<i>Equisetum</i>	<i>heleocharis</i>		
<i>Comarum</i>	<i>palustre</i>		
<i>Larix</i>	<i>olgensis</i>	C31 ^a	Maffei et al. (2004)
<i>Betula</i>	<i>ovalifolia</i>	C27, C31 ^a	Sachse et al. (2006)
<i>Vaccinium</i>	<i>uliginosum</i>	C29>C31>C27 ^a	Nott et al. (2000)
<i>Ledum</i>	<i>palustre</i> var. <i>dilatatum</i>		
<i>L.</i>	<i>palustre</i> var. <i>angustum</i>		
<i>Chamaedaphne</i>	<i>calyculata</i>	C29>C31	Nichols et al. (2006)

^a Data adapted from different or unspecified species within the same genera.

607

608

609

609 **Figure captions**

610

611 **Fig. 1.** Map showing the location of the Hani peat bog, northeast China.

612

613 **Fig. 2.** Stratigraphic section of the Hani peat sequence with chronology and histograms
614 of distributions of *n*-alkanes. Note that *n*-alkane distribution in the lower part of the
615 column exhibits important contributions of mid-chain components from mosses. Cal
616 ages are obtained from accelerator mass spectrometry (AMS) ¹⁴C ages that were
617 provided by Zhou et al. (2010).

618

619 **Fig. 3.** Depth profiles of carbon isotope ratios ($\delta^{13}\text{C}$) of C_{21} to C_{33} odd carbon number
620 *n*-alkanes.

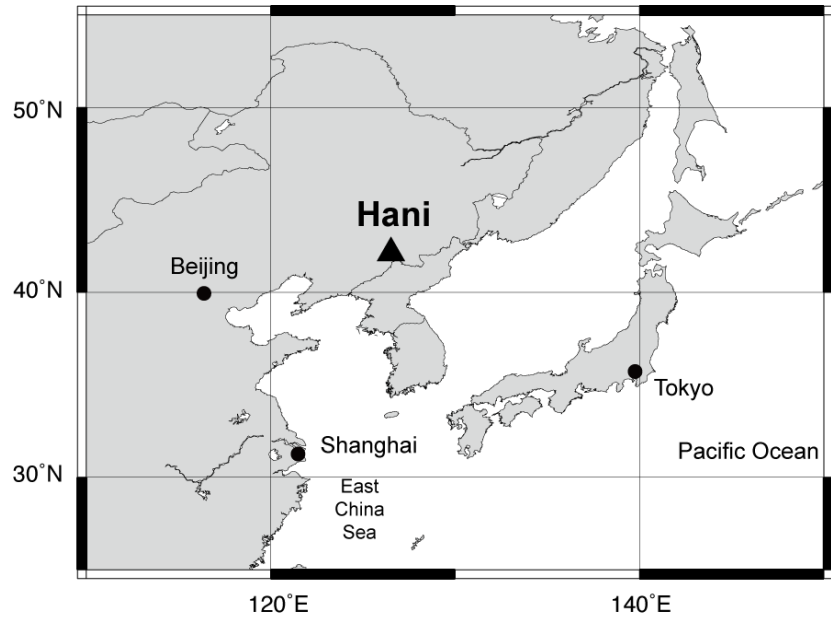
621

622 **Fig. 4.** Profiles of (a), (b) the $\delta^{13}\text{C}$ offsets ($\Delta\delta^{13}\text{C}$) between the C_{31} *n*-alkane and the C_{21} ,
623 C_{23} , C_{25} , C_{27} , C_{29} and C_{33} *n*-alkanes, (c), (d) the concentration ratios of the C_{21} to C_{29} odd
624 carbon number *n*-alkanes and the C_{33} *n*-alkane against the C_{31} *n*-alkane, and (e), (f) the
625 *Paq* and the δD of the C_{27} *n*-alkane (Seki et al., 2009) over the last 16 ka. Shaded bands
626 indicate the intervals where the $\Delta\delta^{13}\text{C}$ offsets show concomitant variations with the
627 *n*-alkane ratios.

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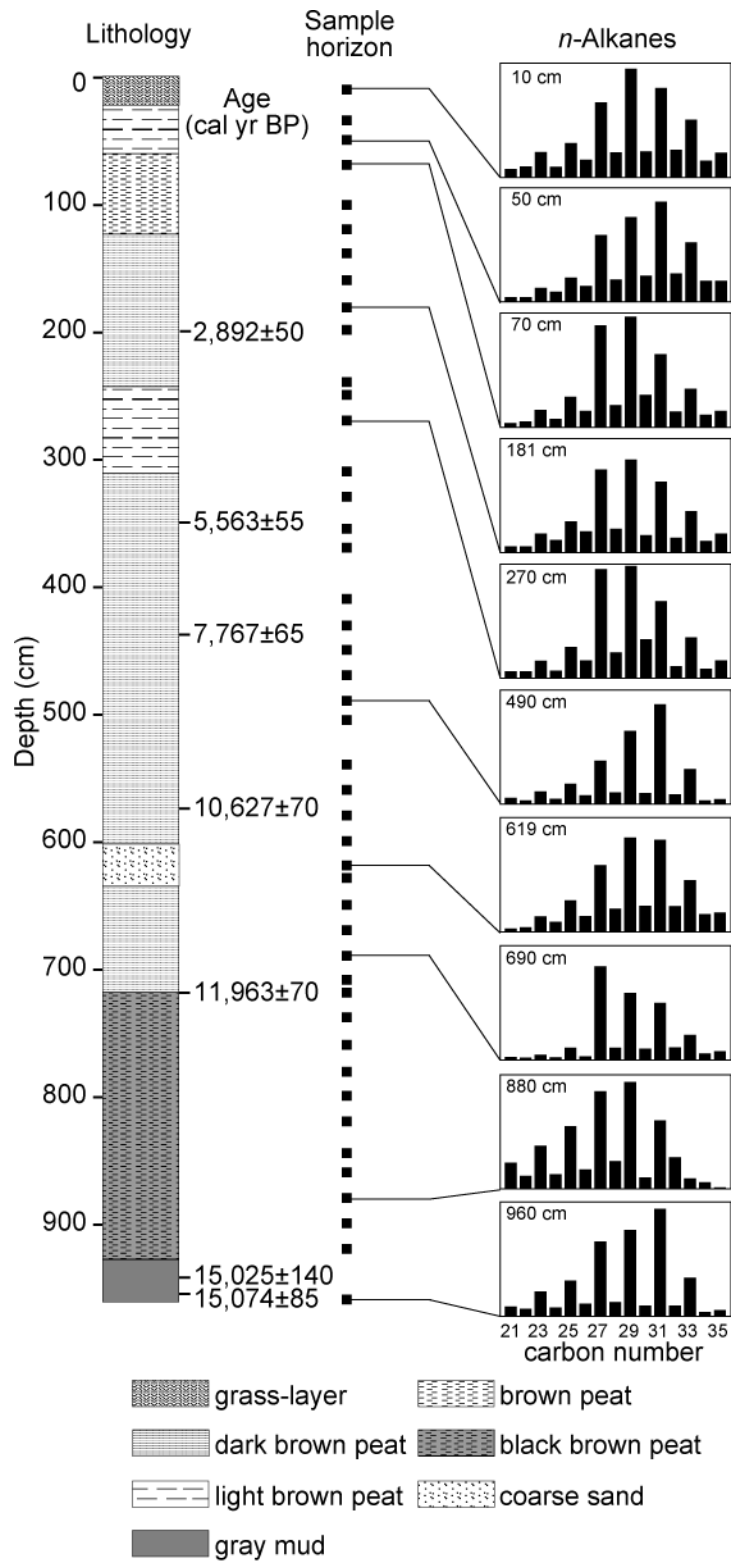
629 **Fig. 5.** Variations of (a) the $\delta^{13}\text{C}$ of terrestrial higher plant-derived *n*-alkanes (C_{29} and
630 C_{31} *n*-alkanes), (b) the ACL, and (c) the $\delta^{18}\text{O}$ (Hong et al., 2009a) and (d) $\delta^{13}\text{C}$ of peat
631 cellulose (Hong et al., 2005) in the Hani peat bog. The $\delta^{13}\text{C}$ of C_{29} and C_{31} *n*-alkanes and
632 the ACL show parallel fluctuations in a light gray shaded sequence with minimal values
633 at 10.5–9.3 ka and 8.1 ka (dark gray bands).

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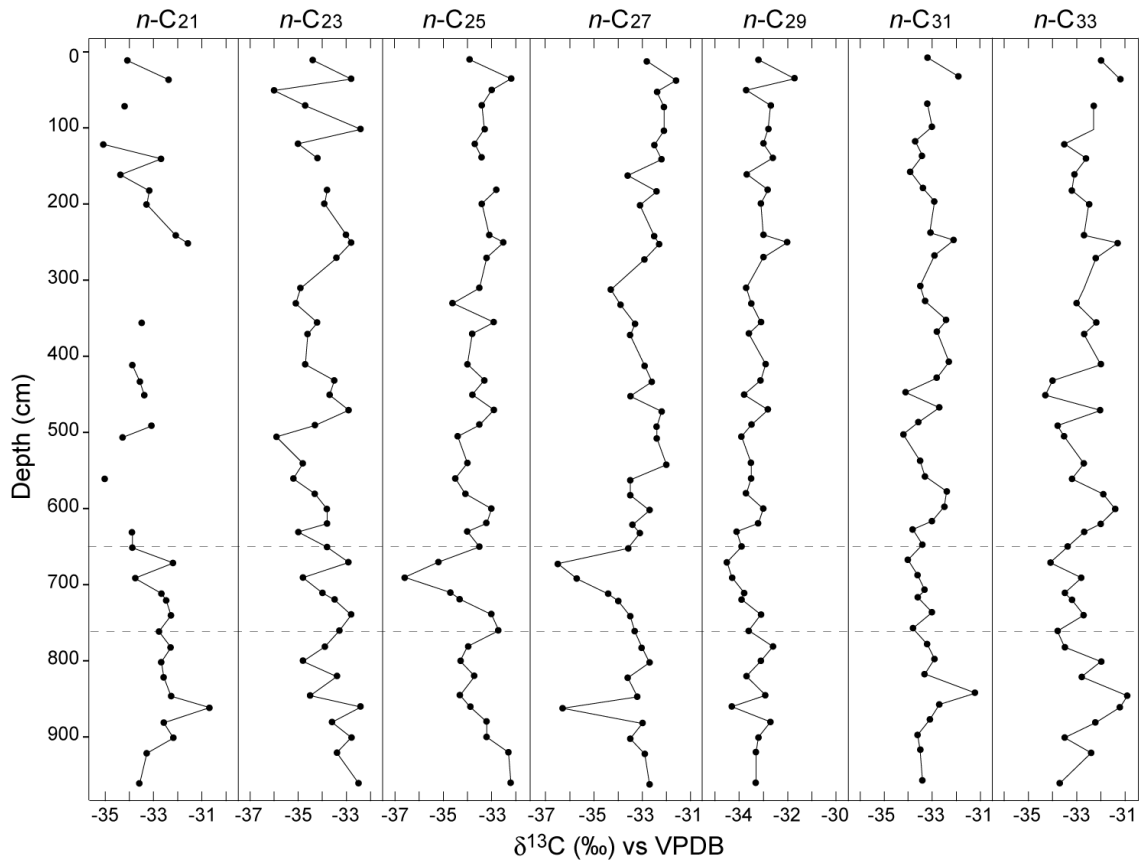
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Fig. 1



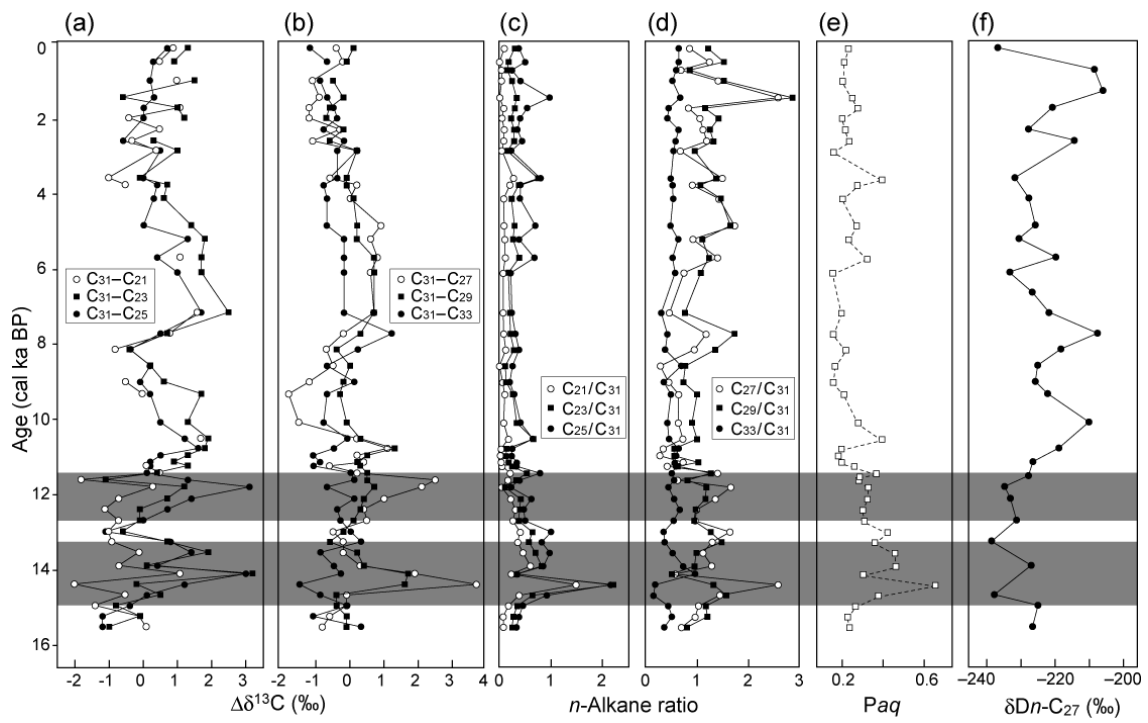
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Fig. 2



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Fig. 3



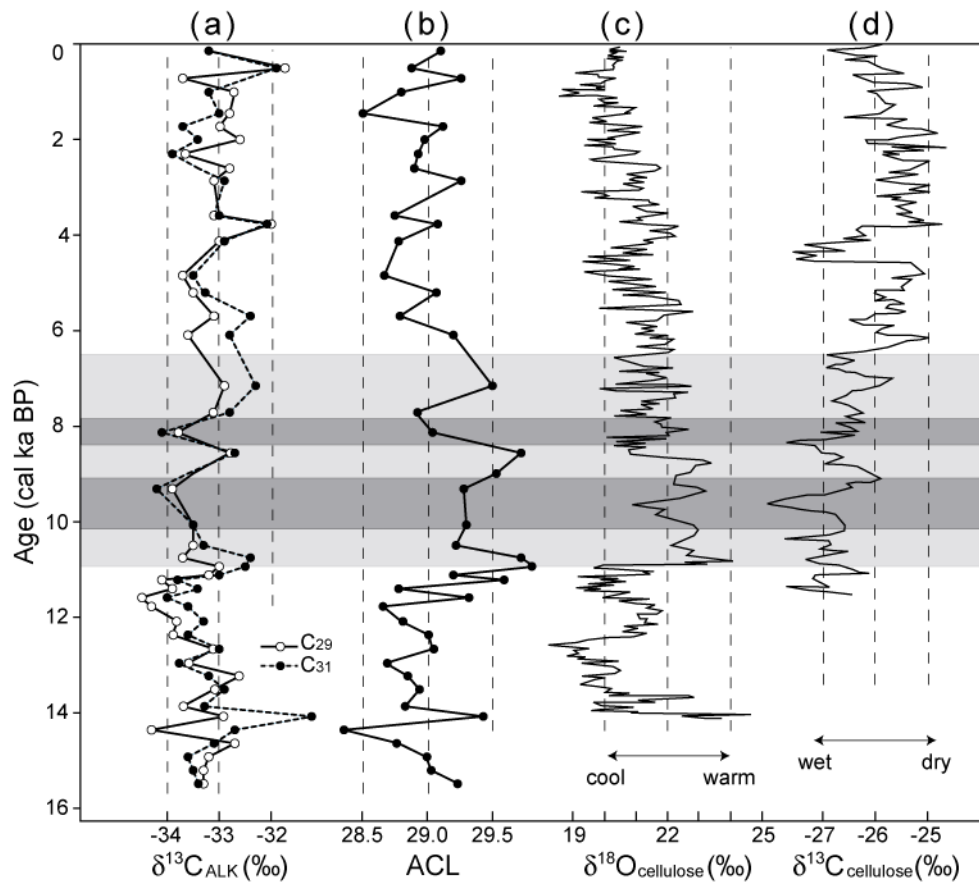
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Fig. 4



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Fig. 5