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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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Abstract

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

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

1. Introduction

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

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

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

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

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

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

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

2. Experimental

2.1. Setting and stratigraphy of the Hani peat deposit

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

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

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

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

2.2. Lipid analyses

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

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

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

2.3. Compound-specific stable carbon isotope analysis

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

¹³C/¹²C ratios of the purified *n*-alkanes were determined using a HP 6890 GC coupled to a Finnigan MAT Delta Plus isotope ratio mass spectrometer via a Finnigan

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

3. Results and Discussion

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

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

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

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

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

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

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

although C₂₁ to C₂₉ *n*-alkane profiles show concurrent $\delta^{13}\text{C}$ negative shifts, the magnitudes of the shifts are significantly different among the compounds: those for C₂₅ and C₂₇ are ca. 3.8‰, whereas those for the other *n*-alkanes are only 1.5 to 2.0‰ (Fig. 3).

The leaf wax *n*-alkanes in a peat bog are commonly derived from an assemblage of different plants, each with specific *n*-alkane distributions and $\delta^{13}\text{C}$ values (Ficken et al., 1998). Hence, the decoupling in the $\delta^{13}\text{C}$ variations of *n*-alkanes with different chain-lengths may indicate that the $\delta^{13}\text{C}$ values of individual *n*-alkanes reflect changes in plant community compositions that contribute to the peat *n*-alkanes. In support of this idea, pollen records from Lake Sihailongwan, northeast China, have revealed a gradual transition from steppe and open taiga-like woodland communities during the late glacial to the earliest Holocene toward the dense deciduous forests that are similar to modern flora (Schettler et al., 2006; Stebich et al., 2009). Similarly, the ecophysiological responses to environment stresses may have been different among the assemblage of peat-forming plants, which would further emphasize the $\delta^{13}\text{C}$ offsets among individual compounds.

In this study, we assessed the possible impact of changes in the plant communities on the $\delta^{13}\text{C}$ variations by comparison with the *Paq* and the concentration ratios of the C₂₁ to C₃₃ odd carbon number *n*-alkanes against the C₃₁ *n*-alkane. The *Paq* (Ficken et al., 2000) is a paleoplant proxy expressed by the following equation:

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

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

are dominated by the C_{31} homologue. However, the dominant n -alkane chain-lengths in contemporary vegetation at the Hani peatland (Table 1) and the surrounding mountains (Schröder et al., 2007; Makohonienko et al., 2008) from the literature suggest that the C_{31} n -alkane may also be supplied to the peat deposit by some mosses and trees (e.g. *Juglans*, *Betula*, *Abies*, *Taxus*, *Tilia*, *Fraxinus* and *Larix*) besides C_3 grasses. In contrast, the C_{23}/C_{31} concentration ratio can represent the contribution of *Sphagnum* species (Pancost et al., 2002). It is based on the observation that *Sphagnum* yields preferentially C_{23} and C_{25} n -alkanes compared to other homologues (Ficken et al., 1998; Nott et al., 2000; Pancost et al., 2002; Table 1).

In Fig. 4, we compare the profiles of the *Paq* and the n -alkane biomarker ratios with those of the $\delta^{13}C$ offsets between the C_{31} n -alkane and the C_{21} , C_{23} , C_{25} , C_{27} , C_{29} and C_{33} n -alkanes; hereafter expressed as $\Delta\delta^{13}C (C_{31} - C_{21})$, $\Delta\delta^{13}C (C_{31} - C_{23})$, $\Delta\delta^{13}C (C_{31} - C_{25})$, $\Delta\delta^{13}C (C_{31} - C_{27})$, $\Delta\delta^{13}C (C_{31} - C_{29})$ and $\Delta\delta^{13}C (C_{31} - C_{33})$, respectively. The $\Delta\delta^{13}C$ records reveal significant positive excursions from 14.9 to 13.2 ka and 12.7 to 11.6 ka, although the magnitudes of the excursions of $\Delta\delta^{13}C (C_{31} - C_{21})$, $\Delta\delta^{13}C (C_{31} - C_{29})$ and $\Delta\delta^{13}C (C_{31} - C_{33})$ are much smaller than those of $\Delta\delta^{13}C (C_{31} - C_{23})$, $\Delta\delta^{13}C (C_{31} - C_{25})$ and $\Delta\delta^{13}C (C_{31} - C_{27})$ (Figs. 4a, b). The simultaneous changes in paleoplant proxies with the excursions strongly suggest that vegetational changes are the most likely causes for the decoupled variations among the n -alkane homologues. Changes in the sedimentary environment may also have potentially affected the $\delta^{13}C$ values through the enhancement of allochthonous plant input from the surrounding forests. However, a lack of any clear relation between the $\delta^{13}C$ variations and the peat lithology suggests that such an increase is unlikely.

3.2.1. Vegetational change from 14.9 to 13.2 ka

Parallel increases in the C_{23}/C_{31} ratios and the $\Delta\delta^{13}C (C_{31} - C_{23})$, $\Delta\delta^{13}C (C_{31} - C_{25})$, $\Delta\delta^{13}C (C_{31} - C_{27})$ and $\Delta\delta^{13}C (C_{31} - C_{29})$ values from 14.9 to 13.2 ka (Figs. 4a-4c)

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

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

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

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

3.2.2. Vegetational change from 12.7 to 11.6 ka

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

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

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

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

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

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

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

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

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

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

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

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

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

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

4. Summary and conclusions

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

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

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

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

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

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

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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>Eriophorum</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>Phragmites</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.

Figure captions

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

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

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

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} , 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 carbon number *n*-alkanes and the C_{33} *n*-alkane against the C_{31} *n*-alkane, and (e), (f) the *Paq* and the δD of the C_{27} *n*-alkane (Seki et al., 2009) over the last 16 ka. Shaded bands indicate the intervals where the $\Delta\delta^{13}\text{C}$ offsets show concomitant variations with the *n*-alkane ratios.

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

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5