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Citation	Organic Geochemistry, 41(5), 491-497 https://doi.org/10.1016/j.orggeochem.2010.01.006
Issue Date	2010-05
Doc URL	http://hdl.handle.net/2115/43101
Type	article (author version)
File Information	OG41-5_491-497.pdf

Instructions for use

Paleoenvironmental significance of compound-specific $\delta^{13}C$ variations in *n*-alkanes in the Hongyuan peat sequence from southwest China over the last 13 ka

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ABSTRACT

Compound-specific $^{13}C/^{12}C$ ratios of the C_{23}, C_{25}, C_{27}, C_{29} and C_{31} *n*-alkanes in the Hongyuan peat sequence from southwest China were

measured to decipher paleoenvironmental information recorded in the $\delta^{13}C$ variations over the last 13 ka. The $\delta^{13}C$ values of the n-alkanes range between −35.4 and −30.5‰, which fall within the range of those of modern C_3 peat-forming vegetation. However, their vertical trends do not match with those in the $\delta^{13}C$ value of the C_3 peat-forming plant cellulose. Such a discrepancy between the $\delta^{13}C$ profiles implies that the n-alkane $\delta^{13}C$ values are unlikely to reflect the emersed aquatic plant signals in the bog. Because submerged/floating aquatic plants are major contributors of mid-chain (C_{23} and C_{25}) n-alkanes in the Hongyuan peat sequence, the decoupling between the C_{23} and C_{25} n-alkanes and the peat cellulose likely reflects that these mid-chain homologues primarily record the isotopic signals of submerged/floating aquatic plants. The stratigraphic profile of $\delta^{13}C$ values of submerged/floating aquatic plant n-alkanes (C_{23} and C_{25}) reveals two prominent positive excursions (0.8 to 2.4‰) during the early to middle Holocene. The excursions coincide with peat accumulation maxima and stronger Indian monsoon activity in southwest China, indicating that the $\delta^{13}C$ variations in submerged/floating aquatic plants are closely related to changes in bog primary productivity controlled by the Asian monsoon activity.

Keywords: peat, stable carbon isotopes, n-alkane, leaf wax, Holocene Climate Optimum, Asian monsoon

1. Introduction

A peat bog deposit, which is an accumulation of immature organic matter (OM) composed mainly of dead plant material, is recognized as one of

important sinks of atmospheric CO_2 because of its ability to store a large amount of carbon for many thousands of years (Borren et al., 2004). The kind and abundance of bog plants that contribute to a peat sequence can be significantly influenced by local factors such as bog surface moisture conditions, ground water level and influx of nutrient-rich groundwater and lateral variability in plant communities, while regional climate changes can affect bog vegetation and its preservation in the peat sequence through the hydrology. The records of vegetation and peat accumulation in peatlands thus hold valuable information about continental paleoenvironmental history (Blackford, 2000).

The vegetation in peat mires consists of various types of plants, including submerged, floating and emersed aquatic plants and terrestrial higher plants. Of special interest to paleoenvironmental reconstruction, the stable carbon isotopic compositions ($\delta^{13}C$) of peat-forming plants are sensitive to carbon fixation pathways and carbon sources utilized in photosynthesis, and environmental factors (e.g. temperature, humidity, productivity) that affect the $\delta^{13}C$ of carbon sources and isotopic discrimination during carbon fixation processes (Keeley and Sandquist, 1992; Hayes, 1993; Arens et al., 2000), as well as taxonomic variation within local plant communities (Arens and Jahren, 2002; Mead et al., 2005). Emersed aquatic and terrestrial higher plants generally contain long chain n-alkanes (C_{27}, C_{29} and C_{31}) in their epicuticular waxes, whereas submerged/floating aquatic plants contain a large proportion of mid-chain n-alkanes (C_{23} and C_{25}; e.g. Eglinton and Hamilton, 1967; Corrigan et al., 1973; Cranwell, 1984; Rieley et al., 1991; Ficken et al., 2000). The compound-specific $\delta^{13}C$ values of peat n-alkanes can therefore provide clues

to the paleoenvironmental information recorded in each type of plant, such as changes in continental hydrology, CO_2 availability, vegetation and productivity in a bog.

In the southwest of China, Holocene peat mires are widely distributed on the northeast edge of the Tibetan Plateau. Some have been intensively studied to reconstruct Holocene climate changes over the last 13 ka using proxies such as total organic carbon (TOC) content, grayscale (Zhou et al., 2002), humification degree (Wang et al., 2004), ash content (Yu et al., 2006), compositional changes in various lipid biomarkers (Zheng et al., 2007) and stable carbon and oxygen isotopic compositions of plant cellulose (Hong et al., 2001, 2003; Xu et al., 2006; Large et al., 2009). The peat deposits from southwest China thus provide a good opportunity to examine the paleoenvironmental significance of compound-specific $\delta^{13}C$ variations in peat n-alkanes in a bog sequence because of the existing paleoclimatic information. Records of peat n-alkanes are particularly robust because of their low susceptibility to microbial degradation relative to other types of lipid compounds (Meyers, 2003; Zheng et al., 2007). Furthermore, their preferential production in plant leaves rather than the roots (Pancost et al., 2002) makes their stratiform depositional records good paleoenvironmental archives, especially in a bog where plant macrofossils are sometimes poorly preserved.

We present stratigraphic profiles of the $\delta^{13}C$ values of n-alkanes derived from peat-forming plants in the Hongyuan peat sequence, and elucidate paleoenvironmental information recorded in the $\delta^{13}C$ variations by comparing our results with the records of published studies on the Asian Monsoon evolution in southwest China over the last 13 ka.

2. Samples and analysis

2.1. Setting and stratigraphy of Hongyuan peat deposit

The Hongyuan peat deposit covers an area of 4500 km[2] on the Qinghai-Xizang Plateau in the Sichuan Province of western China, where land elevation gradually increases to the south towards the Tibetan Plateau. The location lies in a transition zone between semi-humid sub-alpine and semi-humid temperate climates, and it is strongly influenced by the southwest monsoon from the Indian Ocean. This situation makes the site particularly sensitive to climatic change. The climate in the area is cool-humid and 80% of the precipitation occurs in June, July and August with the summer monsoon. The peat has accumulated mainly in the wet summer months, and its accumulation is best developed on the gradual slopes of the basin margins where water input is mainly controlled by precipitation (Zheng et al., 2007). However, its deposition has been terminated by recent industrial development in the area (Zhou et al., 2002).

A core of the 4.5 m thick peat sequence was recovered at a location 2 km southeast of the city of Hongyuan at an elevation of 3505 m above sea level (32º48'N, 102º32'E; Fig. 1). The core is composed of a basal 55 cm thick dark brown and grayish-green mud layer and 395 cm thick sequence of brown to dark brown acid peat with a large amount of undegraded plant residue. We developed the age-depth model on the basis of calibrated calendar ages provided by Zhou et al. (2002) that were obtained from accelerator mass spectrometry (AMS) ^{14}C age measurements. The peat accumulation rate averages 33.8 cm/ka and the basal age of the entire core sequence is 13 ka. Lack of any abrupt changes in color or composition and

the absence of disturbance of laminations show that the peat continuously accumulated since the start of the last deglaciation, except for the uppermost part of the core where it has been disturbed by industrial drainage (Fig. 2).

2.2. Lipid analysis

Our samples consist of 1 cm intervals taken every 10 cm in the 4.5 m core. Lipids were ultrasonically extracted with chloroform from ca. 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 N_2 stream (Zheng et al., 2007). Aliphatic hydrocarbons were isolated using silica gel column chromatography (230-400 mesh; 1% H_2O 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 a 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). He was used as carrier gas. The GC oven temperature was programmed from 50 to 120°C at 30°C/min, then to 310°C (held 15.5 min) at 6°C/min. GC/MS analysis was performed using a Hewlett-Packard 5973 Mass Selective Detector coupled to a Hewlett-Packard 6890 plus 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 in the GC analysis. The compounds were identified on the basis of their mass spectrum, GC retention time, and comparison with published mass spectra in the literature.

2.3. Compound-specific stable carbon isotope analysis

In order to improve the accuracy of the compound-specific stable carbon isotope ratio ($\delta^{13}C$) analysis, the *n*-alkane fractions were purified using the urea adduction technique of Yamamoto and Kawamura (2010). Briefly, a saturated solution of urea in MeOH was added to the saturated hydrocarbon fraction in *n*-hexane/acetone (2:1) and gently stirred overnight using a mechanical stirrer to complete the adduction. After the adduction, the solvent was removed from the precipitate, which was rinsed (3x) with fresh solvent (*n*-hexane/acetone, 2:1) to completely remove non-adducted material. The adduct crystals were dried under a N_2 stream, and the *n*-alkanes were recovered in *n*-hexane after dissolution of the crystals in water.

The $^{13}C/^{12}C$ ratios of the purified *n*-alkanes were determined using a HP 6890 gas chromatograph coupled to a Finnigan MAT Delta Plus isotope ratio mass spectrometer via a Finnigan MAT combustion furnace maintained at 850 °C. The chromatograph was equipped with HP-5MS fused silica column (30 m × 0.32 mm i.d., 0.25 μm film thickness) and the oven was programmed from 50 to 120 °C at 30 °C/min, then to 310 °C (held 22 min) at 5 °C/min. One to two μl were injected via an on-column injector with an internal standard of known isotopic composition (C_{20} *n*-alkanoic acid methyl ester; $\delta^{13}C$ –26.21‰). The $\delta^{13}C$ values are expressed as per mil (‰) relative to Vienna Pee Dee Belemnite (VPDB). Most measurements were duplicated. Reported $\delta^{13}C$ data represent an averaged value of the duplicate analyses. An external standard consisting of C_{16} to C_{30} *n*-alkanes of known isotopic compositions was injected daily to check data quality and ensure the

analytical error remained below ±0.5‰ (Bendle et al., 2007).

3. Results

The Hongyuan peat core samples contain C_{21} to C_{35} n-alkane homologues with a strong odd/even predominance (CPI_{25-33} 1.7 to 15.6) as major aliphatic hydrocarbons (Zheng et al., 2007). Mid-chain n-alkanes (C_{21} to C_{25}) with an odd/even predominance and maximum at C_{23} or C_{25} are typical of submerged/floating aquatic plants, whereas long chain n-alkanes (C_{27} to C_{31}) with an odd/even predominance are predominantly found in emersed aquatic and terrestrial higher plants (e.g. Eglinton and Hamilton, 1967; Corrigan et al., 1973; Cranwell, 1984; Rieley et al., 1991; Ficken et al., 2000).

Stable carbon isotopic compositions ($\delta^{13}C$) determined for C_{23} to C_{31} odd carbon numbered n-alkanes range from −35.4 to −30.5‰ and show fluctuations that are specific for each except for the uppermost 40 cm, where every n-alkane $\delta^{13}C$ profile shows a concomitant 2.4 to 3.6‰ increase (Fig. 2). The values for C_{23} n-alkane are relatively high (−32.9 to −31.5‰) in the lower 230 cm of the sequence, and decrease to −33.7‰ toward 180 cm, which is followed by fluctuations between −34.3 and −33.1‰ at the 180 to 50 cm interval. The values for C_{25} n-alkane are relatively low (−33.5 to −32.9‰) in the basal 60 cm, increase abruptly to −32.1‰ at 370 cm before fluctuating between −33.4 to −30.8‰ in the 370 to 190 cm interval, and then drop again and remain low between −34.0 to −32.4‰ up to 40 cm. In contrast, the values for C_{27}, C_{29} and C_{31} n-alkanes show fluctuations between −35.4 and −31.3‰. The values are relatively constant (−32.8 ± 0.5‰) in the lower 300 cm, while relatively low values (−34.2‰ ± 0.7‰) are observed in the 130 to 80 cm

interval. The variations in the n-alkane $\delta^{13}C$ are positively correlated with each other (r 0.57 to 0.89). In particular, a relatively high correlation coefficient is observed in the $\delta^{13}C$ values between the C_{23} and C_{25} n-alkanes (r 0.84, $p < 0.01$), the C_{27} and C_{29} n-alkanes (r 0.83, $p < 0.01$), and the C_{29} and C_{31} n-alkanes (r 0.89, $p < 0.01$) as compared with those between the C_{23} and C_{27}, C_{29} and C_{31} n-alkanes, the C_{25} and C_{27}, C_{29} and C_{31} n-alkanes, and the C_{27} and C_{31} n-alkanes (r 0.57 to 0.70).

4. Discussion

4.1. Origin of peat n-alkanes

The stable carbon isotopic compositions ($\delta^{13}C$) of odd carbon numbered C_{23} to C_{31} n-alkanes are consistently in the range those observed for modern submerged/floating aquatic plant n-alkanes (–41.9 to –16.6‰; Mead et al., 2005) and leaf wax n-alkanes in typical Far East C_3 vegetation (–36.0 to –21.5‰; Chikaraishi and Naraoka, 2003). However, large variability in the n-alkane $\delta^{13}C$ of modern peat vegetation and range overlap with those of submerged/floating macrophytes and emersed/terrestrial land plants do not allow us to identify their specific plant source.

The $\delta^{13}C$ of C_3 plants are generally controlled by various ecological and physiological factors in addition to the $\delta^{13}C$ of atmospheric CO_2 (Farquhar et al., 1982; Arens et al., 2000). Specifically, because the $\delta^{13}C$ values of C_3 plants are closely related to changes in the relative humidity and temperature of air (Edwards et al., 2000), the $\delta^{13}C$ of C_3 emersed peat-forming plants are recognized as a proxy indicator for the summer monsoon activity in southwest China (Hong et al., 2001, 2003, 2005). This isotopic proxy is based on the observation that the surface moisture in the

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Hongyuan region depends mainly on rainfall caused by the monsoon in summer months. Hence, if the peat n-alkanes originate from emersed aquatic plants in the bog, both the $\delta^{13}C$ values should exhibit parallel fluctuation patterns.

Fig. 3a shows the stratigraphic fluctuations in the $\delta^{13}C$ values in C_3 emersed peat-forming plant (*Carex*) cellulose from the Hongyuan site (Hong et al., 2003). The values are relatively high around 12.0 to 11.8 ka, decrease at 11.2 ka and remain relatively low between 10.8 and 5.3 ka, suggesting a relatively warm-wet climate associated with the intensification of the Indian Monsoon activity in the early to middle Holocene. Such a climate condition is consistent with the results of various paleoenvironmental proxies from south China (Gasse et al., 1991; Lister et al., 1991; Zhou et al., 2002; Hong et al., 2003; Wang et al., 2004; Dykoski et al., 2005; Yu et al., 2006; Zheng et al., 2007), although lake level records and climate model simulations indicate that a peak in precipitation occurred at 12.0 ka in southwestern China (An et al., 2000; He et al., 2004). In contrast, the $\delta^{13}C$ profiles of the peat n-alkanes (weighted mean of the $\delta^{13}C$ of the C_{23} and C_{25} n-alkanes, the C_{27} and C_{29} n-alkanes and the C_{29} and C_{31} n-alkanes; Fig. 3b) exhibit relatively high values from 10.9 to 5.9 ka, showing variations that are opposite to the $\delta^{13}C$ value of peat cellulose (Figs. 3a, 3b). Because Hong et al. (2003) reported a parallel fluctuation in the $\delta^{13}C$ values between mixed plant cellulose and *Carex* cellulose, the decoupled fluctuation patterns between the $\delta^{13}C$ profiles imply that the n-alkane $\delta^{13}C$ variations are unlikely to reflect the emersed aquatic plant signals.

One possible explanation for the decoupling could be that the n-alkane $\delta^{13}C$ values have been affected by diagenetic change (Huang et al.,

1996; Ficken et al., 1998; Nguyen Tu et al., 2004; Chikaraishi and Naraoka, 2006; Seki et al., 2010). However, Huang et al. (1997) reported that higher molecular weight n-alkanes in surface soil are isotopically unchanged during biodegradation. In addition, the higher resistance of n-alkyl compounds to microbial degradation relative to other types of OM such as cellulose (Briggs et al., 2000) and relatively good preservation of the herbaceous organic matter in the Hongyuan peat deposit (Zheng et al., 2007) exclude such a possibility.

Generally, lipid biomolecules such as n-alkanes are depleted in ^{13}C relative to bulk tissue, and the magnitude of the carbon isotopic fractionations during lipid biosynthesis significantly varies not only in a single plant species but also among various plant classes (Collister et al., 1994; Lockheart et al., 1997; Chikaraishi and Naraoka, 2003, 2004a, b). For example, ^{13}C depletion in n-alkyl lipids relative to bulk tissue in certain C_3 gymnosperm cedars varied from 2.4 to 9.9‰ and those in C_3 angiosperm species from 2.3 to 6.3‰ (Chikaraishi and Naraoka, 2004a, b). Because the variation in the cellulose $\delta^{13}C$ values at the Hongyuan site is ca. 5‰ (Hong et al., 2003), the decoupling between the cellulose and n-alkane $\delta^{13}C$ variations could be explained by variation in the isotopic fractionation during lipid biosynthesis. Nevertheless, most $\delta^{13}C$ records of raw leaf lipids and sedimentary n-alkanes in the literature reveal quite similar seasonal and stratigraphic variations with those in bulk tissue, despite such large variability in the isotopic fractionations (Lockheart et al., 1997; Huang et al., 1999).

The less negative $\delta^{13}C$ values might be partly related to a bacterial contribution of n-alkanes because various nonphotosynthetic bacteria in soil

have been found to contain C_{26} to C_{30} hydrocarbons (Albro, 1976) with 2.5 to 3.5‰ less negative $\delta^{13}C$ values than higher plants (Huang et al., 1996). In support for this idea, Zheng et al. (2007) estimated stronger microbial activity between 10.4 and 4 ka based on the compositional changes in lipid biomarkers in the Hongyuan site. Alternatively, changes in species composition within the peat plant community could have affected the n-alkane $\delta^{13}C$ variations, because peat n-alkanes are commonly derived from an assemblage of different plants, each with specific n-alkane distributions and $\delta^{13}C$ values (Ficken et al., 1998). However, CPI values in our samples are much higher (CPI_{25-33} 1.7 to 15.6) than those in bacteria (Albro, 1976), and the lack of a relation between the molecular distribution (e.g. ACL: average chain length of n-alkanes) and the $\delta^{13}C$ values of n-alkanes (Fig. 5) suggests that changes in species composition of peat vegetation are unlikely factors altering the n-alkane $\delta^{13}C$ values.

Previous lipid biomarker results on the Paq paleoplant proxy that approximates the proportion of aquatic (submerged and floating) macrophytes to total peat-forming plant taxa in the Hongyuan peat sequence showed that submerged/floating aquatic plants are major contributors of mid-chain (C_{23} and C_{25}) n-alkanes in the bog since 11.7 ka (Zheng et al., 2007). Thus, the decoupling between the C_{23} and C_{25} n-alkanes and the peat cellulose likely reflects that these mid-chain homologues primarily record the isotopic signals of submerged/floating aquatic plants. The common origin of the C_{23} and C_{25} n-alkanes are also supported by a good positive correlation in their $\delta^{13}C$ values.

Stratigraphic variations in the weighted-mean $\delta^{13}C$ values of the C_{27} and C_{29} n-alkanes, and the C_{29} and C_{31} n-alkanes show overall similarities

with those of C_{23} and C_{25} n-alkanes and are positively correlated with each other (r 0.70 to 0.90, $p < 0.01$), although the latter exhibit much greater fluctuation between 10.2 and 6.6 ka (Fig. 3b). Because submerged aquatic plants are known to produce C_{27}, C_{29} and C_{31} n-alkanes in addition to their mid-chain homologues (Ficken et al., 2000), the $\delta^{13}C$ increases in the C_{27}, C_{29} and C_{31} n-alkanes from 10.9 to 5.9 ka might be attributed to an increased input of ^{13}C-enriched long chain n-alkanes from submerged/floating aquatic plants. Although previous biomarker study in the Hongyuan peat sequence revealed relatively low Paq values during the early to middle Holocene as compared with the late Holocene (Zheng et al., 2007), suggesting a relatively smaller n-alkane contribution from submerged/floating aquatic plants, it should be noted that the Paq may not be so representative of the peat vegetation as it is a proxy developed in lacustrine environments. In fact, several *Sphagnum* species are reported to have C_{31} n-alkanes as a dominant component (Ficken et al., 1998; Nott et al., 2000; Xie et al., 2004; Nichols et al., 2006; Bingham et al., 2010), whereas C_{31} n-alkane is generally a minor component in submerged/floating aquatic plants as compared with the others (Ficken et al., 2000). The $\delta^{13}C$ values of the long chain n-alkanes thus probably represent mixed isotopic signals from the submerged/floating aquatic plants and emersed aquatic/terrestrial higher plant species.

4.2. Factors controlling aquatic plant n-alkane $\delta^{13}C$ variation

The $\delta^{13}C$ profile of submerged/floating aquatic plant n-alkanes (weighted mean of $\delta^{13}C$ values of C_{23} and C_{25} n-alkanes) shows two prominent positive excursions (0.8 to 2.4‰) during the early to middle Holocene (shaded bands in Fig. 3). The much larger magnitude of the

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excursions than those of atmospheric CO_2 during the last 13 ka (~0.5‰; Leuenberger et al., 1992) indicates that the $\delta^{13}C$ variation was influenced by several factors in addition to the postglacial $\delta^{13}C$ variation in the atmospheric reservoir. Likely candidates for the variation include changes in vegetation and environmental factors such as temperature, pH, salinity and aeration, that affect the concentration of dissolved CO_2 and aquatic primary productivity (Keeley and Sandquist, 1992; Fontes et al., 1996).

In Fig. 3b, the $\delta^{13}C$ values of the submerged/floating aquatic plant n-alkanes (C_{23} + C_{25}) exhibit variations concomitant with the peat accumulation rate. The accumulation rate increases to >50 cm/ka at 10.2-9.3 and 7.3-6.6 ka where the $\delta^{13}C$ values of the n-alkanes are maximized (Fig. 3b, c). Increase in the accumulation rate is also observed at 5.4-5.2 ka, however, the corresponding $\delta^{13}C$ excursion is small and indistinct due to relatively large background variations. In the Qinghai-Xizang Plateau, low annual temperature promotes accumulation of OM and formation of peat by making evaporation and transpiration processes slower and decreasing microbial reworking and hydrolysis of OM (Wang et al., 2004). Thus, relatively high TOC values between 10.4 and 5.0 ka in the Hongyuan peat sequence (Zheng et al., 2007) imply yearly cool paleoclimate conditions that are suitable for peat accumulation. Because peat accumulation generally occurs when annual primary productivity in peat-forming systems exceeds the rate of remineralization (Aucour et al., 1999), the increases in peat accumulation and the $\delta^{13}C$ excursions in the submerged/floating aquatic plant n-alkanes likely resulted from changes in bog primary productivity.

Coincidence is also found between the n-alkane and the peat cellulose $\delta^{13}C$ values: the relatively low $\delta^{13}C$ values of peat cellulose occur

with the n-alkane $\delta^{13}C$ maxima at 10.2-9.3 and 7.3-6.6 ka (Fig. 3a, b). Although one to one correlation is difficult because of the lower resolution of our stratigraphic data, the relation suggests that the bog productivity changes that caused the n-alkane $\delta^{13}C$ excursions are the likely consequence of the monsoonal climate variation. Such a relation is consistent with the previous confirmation that the Indian summer monsoon that brings essential water for vegetation growth is one of the most important factors influencing peat formation in the Qinghai-Xizang Plateau (Wang et al., 2004; Zheng et al., 2007).

The $\delta^{13}C$ value of aquatic plants is especially sensitive to their carbon source (Keeley and Sandquist, 1992). The $\delta^{13}C$ increases at 10.2-9.3 and 7.3-6.6 ka may therefore reflect changes in availability of dissolved CO_2 and HCO_3^- to the submerged leaves of aquatic macrophytes. As bog primary productivity increased, the pH of freshwater would have risen (Talling, 1976), which in turn would have lowered the concentration of dissolved CO_2 in the bog water. In such a depleted condition of dissolved CO_2, the carbon source around the submerged leaves is more likely to be finite as a result of the much smaller diffusion coefficient of CO_2 in water than in air, and this change would have reduced discrimination by Rubisco, making the $\delta^{13}C$ value of submerged aquatic plants more ^{12}C-depleted (Keeley and Sandkist, 1992). Alternatively, submerged aquatic plants might have biosynthesized more ^{13}C-enriched n-alkanes by using HCO_3^- as carbon source (Chikaraishi and Naraoka, 2003; Aichner et al., 2008) because HCO_3^- is known to be more ^{13}C-enriched by ca. 7 to 11‰ than dissolved CO_2 (Mook et al., 1974). Furthermore, selective removal of $^{12}CO_2$ from the bog surface waters as a result of intensive peat deposition and changes in the species composition of

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the source vegetation can also affect the $\delta^{13}C$ excursions (Ficken et al., 1998; Mead et al., 2005).

Although these relations should be confirmed by studies of more widespread regions, our results indicate that the $\delta^{13}C$ values of submerged aquatic plant n-alkanes can serve as a new proxy for climate-influenced bog primary productivity in southwest China. Ombrotrophic conditions and the relatively smaller size of the bog carbon reservoir vs. the ocean and the atmosphere probably make the $\delta^{13}C$ values of submerged/floating aquatic plant n-alkanes sensitive to the climate variations associated with monsoon activity.

5. Conclusions

Compound-specific stable carbon isotope compositions ($\delta^{13}C$) of n-alkanes derived from peat-forming aquatic and terrestrial higher plants (C_{23}, C_{25}, C_{27}, C_{29} and C_{31}) were measured in the Hongyuan peat sequence to elucidate paleoenviromental information that can be recorded in the $\delta^{13}C$ variations over the last 13 ka. The $\delta^{13}C$ values of peat n-alkanes fall within the range of the n-alkanes in modern C_3 peat-forming vegetation. However, their stratigraphic fluctuations are opposite to the $\delta^{13}C$ of peat cellulose, suggesting that the n-alkane $\delta^{13}C$ values are unlikely to reflect the emersed aquatic plant signals. Instead, the $\delta^{13}C$ profile of submerged/floating aquatic plant n-alkanes (weighted mean of the $\delta^{13}C$ values of C_{23} and C_{25} n-alkanes) exhibits two prominent positive excursions (0.8 to 2.4‰) that coincide with peat accumulation maxima and stronger Indian monsoon activity at 10.2-9.3 and 7.3-6.6 ka in southwest China, indicating that the $\delta^{13}C$ variations of submerged/floating aquatic plants are closely related with changes in bog

primary productivity in association with the monsoon activity.

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Figure captions

Fig. 1. Location of Hongyuan peat bog, southwest China.

Fig. 2. Stratigraphic section of Hongyuan peat sequence with ages and depth profiles of carbon isotope ratio values ($\delta^{13}C$) of C_{23} to C_{31} odd carbon numbered n-alkanes.

Fig. 3. Stratigraphic fluctuations in (a) $\delta^{13}C$ value of peat cellulose (Hong et al., 2003), (b) weighted-mean $\delta^{13}C$ value of C_{23} and C_{25}, C_{27}, and of C_{29}, C_{29} and C_{31} n-alkanes, (c) ACL, (d) peat accumulation rate. ACL = average chain length of C_{27} to C_{33} n-alkanes defined: ACL = $(\sum[C_i] \times i)$ $/\sum[C_i]$, $i = 27$ to 33, where $[C_i]$ is the concentration of the n-alkane of i carbon atoms. Calibrated calendar ages are shown in the right hand side of the column with a 1σ standard deviation.
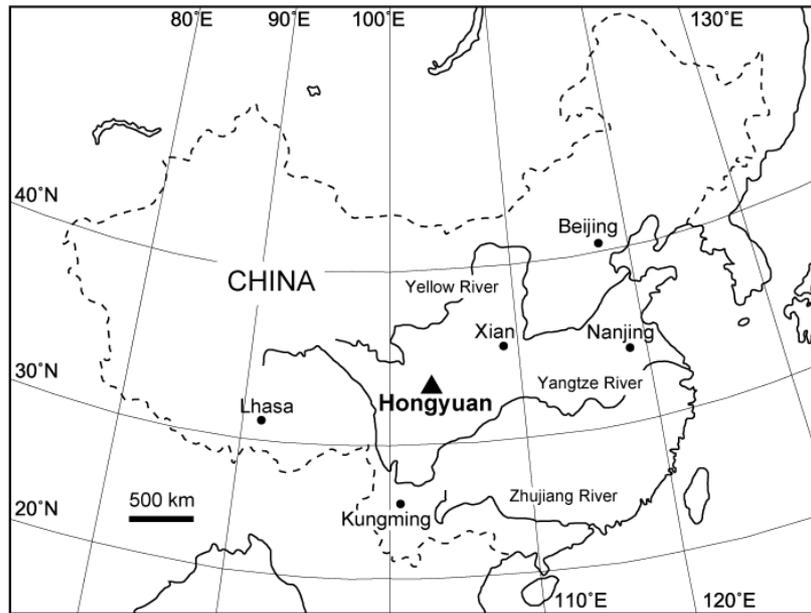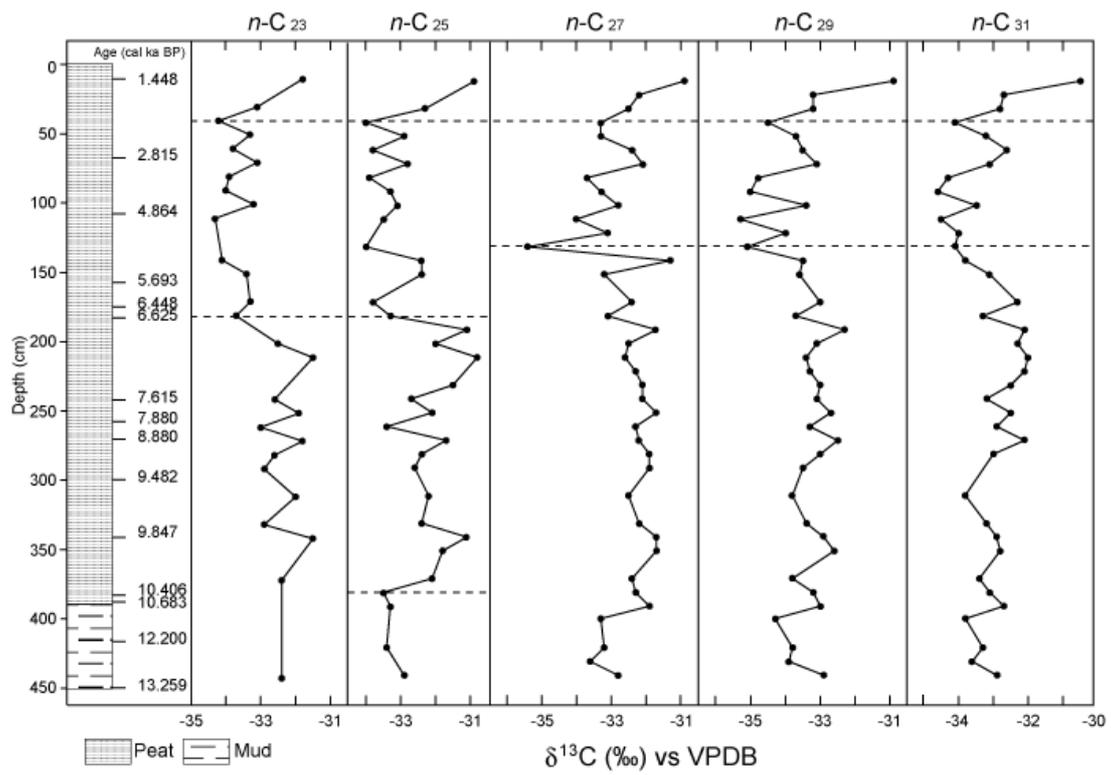
Figure 1

Figure 2

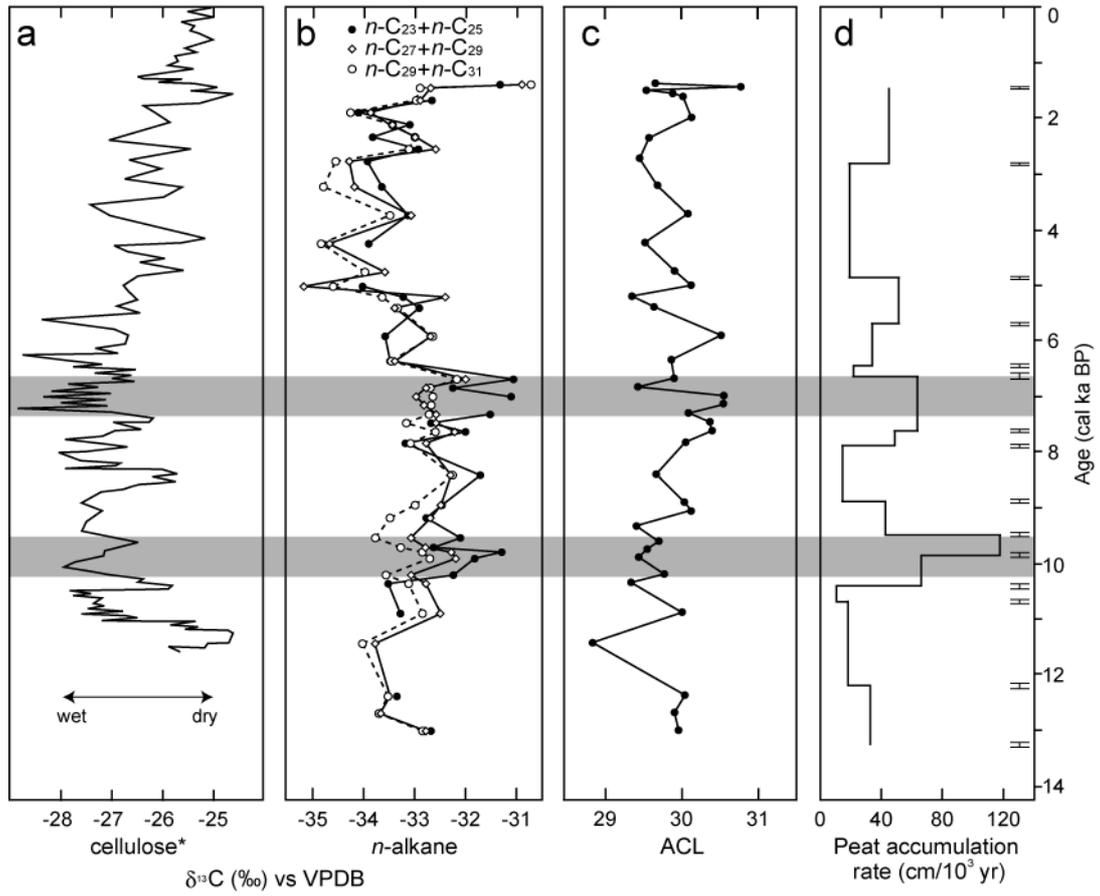Figure 3