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Lipid distribution in a subtropical southern China stalagmite as a record of soil ecosystem response to paleoclimate change

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Abstract

Lipid extracts from a 61.7-cm-long subtropical stalagmite in southern China, spanning the period of *ca.* 10,000–21,000 yr ago as constrained by U–Th dating, were analyzed using gas chromatography–mass spectrometry. The higher plants and microorganisms in the overlying soils contribute a proportion of *n*-alkanes identified in the stalagmite. The occurrence of LMW (lower molecular weight) *n*-alkanols and *n*-alkan-2-ones in the stalagmite was mainly related to the soil microorganisms. We suggest that HMW (higher molecular weight) *n*-alkanols and *n*-alkan-2-ones identified in the stalagmite originate from soil organics and reflect input from contemporary vegetation. Shifts in the ratio of LMW to HMW *n*-alkanols or *n*-alkan-2-ones indicative of the variation of soil ecosystems (e.g., microbial degradation of organic matter and/or the relative abundance of soil microorganisms to higher plants) are comparable with the subtropical alkenone-SST (sea surface temperature) record of the same period. The similar trends seen in the $\delta^{13}\text{C}$ data and the lipid parameters in this stalagmite imply that the overlying soil ecosystem response to climate might be responsible for the variation of $\delta^{13}\text{C}$ values.

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Introduction

Speleothems represent an important paleoclimate record. Data have shown that the oxygen isotope ratios in stalagmites often vary in a cyclic fashion and correlate with marine oxygen isotope cycles (Dorale et al., 1992; Holmgren and Karlen, 1995; O'Neil et al., 1969; Schwarcz, 1986) and with other records of global climatic change (Genty et al., 2003; Wang et al., 2001). Indeed, the match between speleothem and ocean isotope data is so close that potentially speleothems can be used as geothermometer, the variations in oxygen isotope ratios predominantly reflecting variations in mean annual surface temperature (Harmon et al., 1978; Schwarcz, 1986). Additionally, precise dating

with mass spectrometric ^{230}Th methods (Edwards et al., 1987; Li et al., 1989; Ludwig et al., 1992) in a well-chosen stalagmite facilitates the reconstruction of high-resolution palaeoclimate record. However, not all speleothems are suitable for this type of research because a number of conditions must be satisfied before the isotope ratios can be regarded as providing reliable paleotemperature estimates. A key issue is whether calcite $\delta^{18}\text{O}$ can be interpreted solely in terms of the $\delta^{18}\text{O}$ of meteoric precipitation and equilibrium fractionation during calcite precipitation (Wang et al., 2001). This limitation makes it necessary to identify other climate proxies independent of the calcite $\delta^{18}\text{O}$ values in stalagmites.

One possibility to explore the potential climate proxy is the selection of organics present in a low abundance in speleothems (Beynen et al., 2002; Hill and Forti, 1986; Ramseyer et al., 1994, 1997; Shopov et al., 1994; White and

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Brennan, 1989). Shopov et al. (1994) demonstrated that humic substances in carbonates from speleothems have the potential to act as a record of paleoclimate, and Baker et al. (1998, 1999) have been able to demonstrate a link between stalagmite luminescence (linked to humification) and climate wetness. However, very few studies have focused upon the speleothem lipids that have been effectively employed in reconstruction of paleoclimate based on the analyses of ocean and lake sediments as well as peat deposits (Gong and Hollander, 1999; Huang et al., 1999; Street-Perrott et al., 1997; Xie et al., 2000). The next stage in this work is to investigate the distribution of common biomarkers such as *n*-alkanes and fatty alcohols in speleothems and see if they display trends in distribution and abundance, and if such trends reflect palaeoclimatic variation.

Experimental methods

Samples for lipid analyses were taken from the HS-2 stalagmite in Heshang Cave (E 110°42'29", N 30°45'18") in Qingjiang valley of the middle Yangtze River drainage area in southern China. This subtropical region is characterized by the dominance of the East Asian summer monsoon, leading to abundant rainfall. The annual average rainfall is about 1400 mm and annual temperature is between 16–17°C. The cave is located at an altitude of 205 m above sea level, developed in Cambrian limestones. The HS-2 stalagmite was located 120 m away from the cave entrance and is 61.7 cm long with a basal diameter of 24 cm.

The stalagmite was cut along its growth axes and sub-samples were obtained from the cut surfaces for ^{230}Th dating and $\delta^{18}\text{O}$, $\delta^{13}\text{C}$, and lipid analyses. The $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ data from the stalagmite have been reported elsewhere (Huang et al., 2001). The location of U–Th analyses is presented in Fig. 1.

After grinding to 100 mesh (0.154 mm), the samples (70–100 g each) for lipid analysis were Soxhlet-extracted with chloroform. The total lipid extracts were fractionated by flash column chromatography into saturated hydrocarbons, aromatics, and nonhydrocarbons by successively eluting with *n*-hexane, benzene, and methanol. The nonhydrocarbons containing acids, alcohols, ketones, and wax esters were heated with *N,O*-bis(trimethylsilyl)trifluoroacetamide before GC/MS analysis. Blanks were also analyzed for control of possible laboratory contamination. External standards were used for compound quantification.

A Hewlett–Packard 5973A mass spectrometer, interfaced directly with a 6890 gas chromatograph equipped with a HP-5MS fused silica capillary column (30 m \times 0.25 mm i.d.; film thickness 0.25 μm) was used for molecular analyses. The operating conditions were as follows: temperature ramped from 70 to 280°C at 3°C/min, held at 280°C for 20 min, carrier gas He; ionization energy of the mass spectrometer set at 70 eV; scan range from 50 to 550 u.

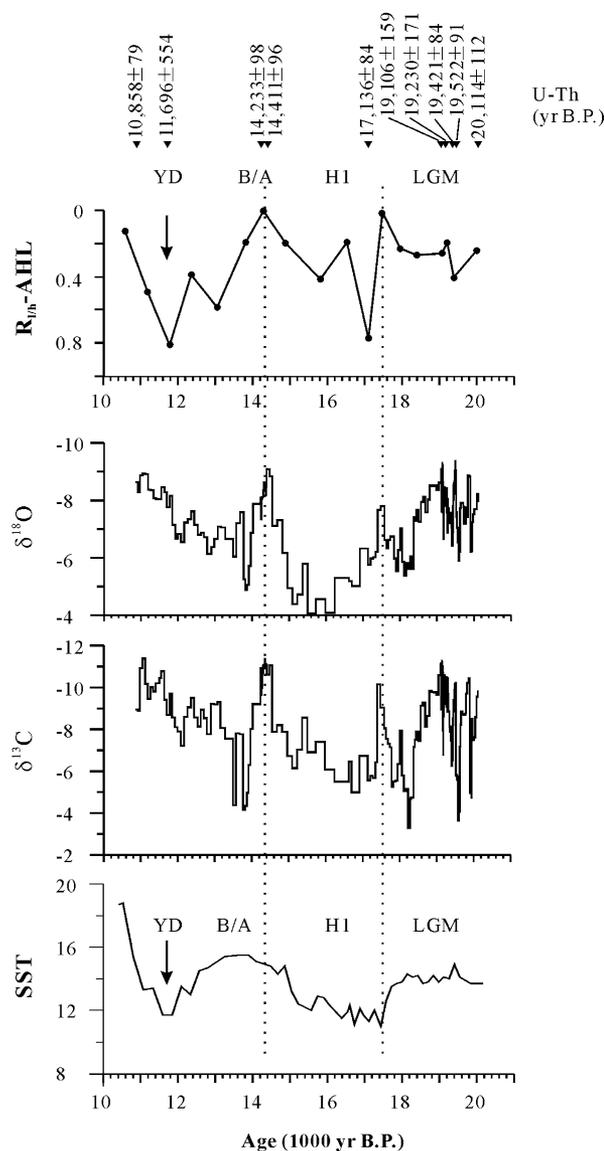


Fig. 1. Profiles of the ratio of LMW to HMW *n*-alkanols ($R_{1h}\text{-AHL}$), $\delta^{18}\text{O}$ (‰, VPDB), and $\delta^{13}\text{C}$ (‰, VPDB) of the stalagmite, together with the SST record in subtropical Northeast Atlantic (Reprinted with permission from Bard et al., 2000. Copyright 2000 American Association for the Advancement of Science.), YD, the Younger Dryas; H1, Heinrich event 1; B/A, Allerød–Bølling; LGM, last glacial maximum. The temporal constraint was provided by U–Th analysis. Two dashed lines show the samples most notable in lipid carbon distribution (refer to Figure 2, 9.25–13.8 cm and 21.50–23.80 cm) and characterized by the apparently decreased $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values.

Results and discussion

Lipid origins

The content of total extractable organic matter in the stalagmite ranges from 24.4 to 102.7 $\mu\text{g/g}$. Normal alkanes in the extracts range from C_{15} to C_{33} (Fig. 2a) with maxima at C_{18} and C_{29} or C_{31} in a bimodal distribution. A distinct odd-over-even carbon predominance (CPI_n 1.15–1.70; refer

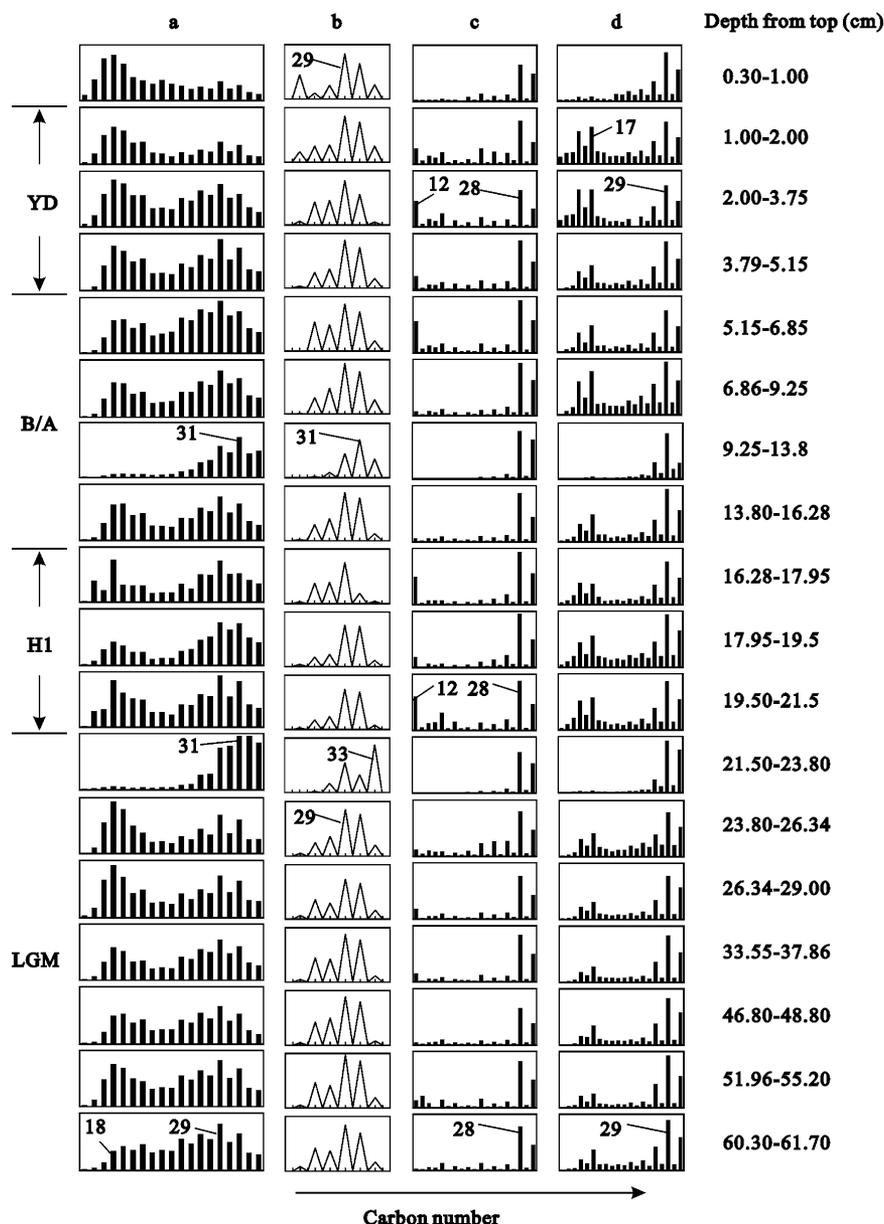


Fig. 2. Relative abundance (vertical) versus carbon distribution (horizontal) of (a) total *n*-alkanes, (b) HMW *n*-alkanes related to higher plant input only ($A_{21} + 2i$ values, refer to the text), (c) *n*-alkanols, and (d) *n*-alkan-2-ones at different horizons. YD, the Younger Dryas; H1, Heinrich event 1; B/A, Allerød-Bølling; LGM, last glacial maximum. The carbon number distribution is from C_{15} to C_{33} for total *n*-alkanes, C_{23} to C_{33} for plant wax *n*-alkanes, C_{12} to C_{30} for *n*-alkanols, and C_{12} to C_{31} for *n*-alkan-2-ones.

to Fig. 3 for the definition) was observed above C_{22} throughout the profile (Fig. 2a). LMW *n*-alkanes have no odd- or even-carbon-numbered preference (Fig. 2a), a distribution pattern found in bacteria (Albro, 1976; Freeman and Colarusso, 2001; Huang et al., 1995), fungi (Jones, 1969) and algae (Gelpi et al., 1970; Weete, 1976). It therefore is probable that *in situ* microorganisms growing on carbonate minerals of the stalagmite directly contribute the LMW *n*-alkanes; caves have been shown to have greater microbial activity than previously thought (Northup and Lavoie, 2001). Freeman and Colarusso (2001) have reported on the presence of microbially derived LMW *n*-alkanes in

soils, and some of the contribution of these components in the speleothem may be directly from soil microorganisms (algae, cyanobacteria, fungi, and other bacteria).

HMW *n*-alkanes are present in the stalagmite. Odd numbered HMW *n*-alkanes are important components of epicuticular waxes from the leaves of vascular plants. *n*-Alkanes extracted from fossil leaves (Logan et al., 1995), modern soils (Huang et al., 1996), recent and aged sediments (Otto et al., 1994) with inferred input from terrestrial vegetation (Huang et al., 1995), all have large relative abundances of these HMW *n*-alkanes (Freeman and Colarusso, 2001). It is therefore possible that vascular plants contribute part of the

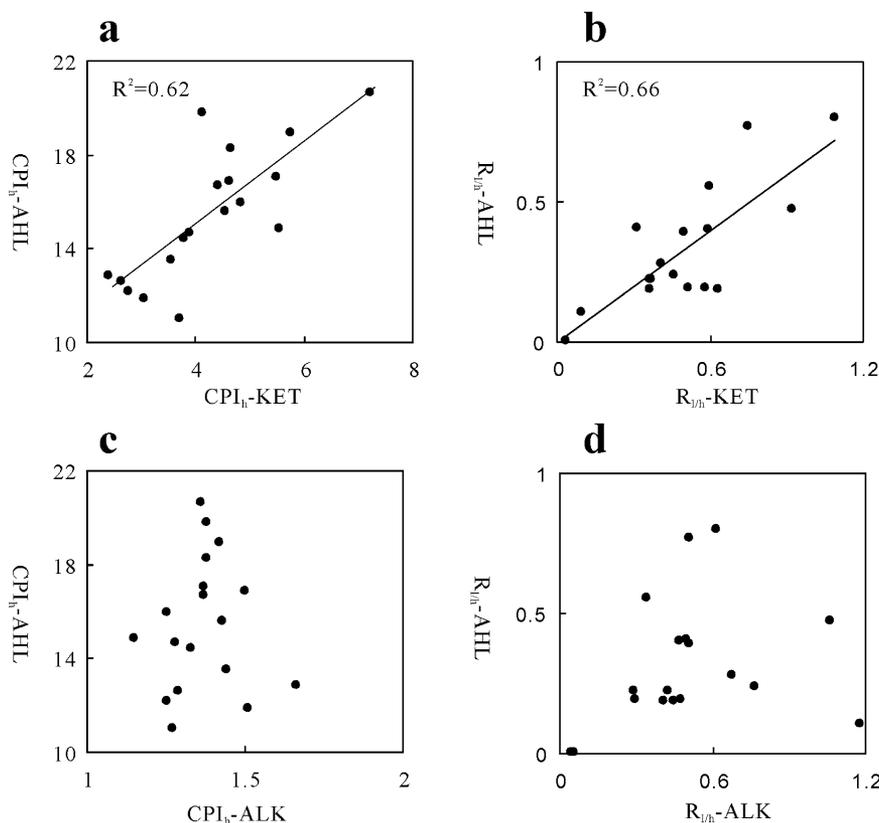


Fig. 3. Plots showing the correlations of *n*-alkanols (AHL) with *n*-alkan-2-ones (KET) and *n*-alkanes (ALK) in CPI_h (a, c) and $R_{1/h}$ (b, d). CPI_h -ALK (*n*-alkanes) = $[\sum C_{21-31}(\text{odd}) + \sum C_{23-33}(\text{odd})]/2 \sum C_{22-32}(\text{even})$, CPI_h -AHL (*n*-alkanols) = $[\sum C_{20-28}(\text{even}) + \sum C_{22-30}(\text{even})]/2 \sum C_{21-29}(\text{odd})$, CPI_h -KET (*n*-alkan-2-ones) = $[\sum C_{21-29}(\text{odd}) + \sum C_{23-31}(\text{odd})]/2 \sum C_{22-30}(\text{even})$. $R_{1/h}$ the ratio of lower ($<C_{20}$) to higher molecular weight ($>C_{20}$) homologues.

HMW *n*-alkanes preserved in soils which were finally transported to the stalagmite. The low CPI_h values seen in HMW *n*-alkanes (CPI_h 1.15–1.70) indicate the occurrence of other origins. Contributions from soil parent material to HMW *n*-alkanes were observed in some paleosol samples (Freeman and Colarusso, 2001), which may also complicate the HMW *n*-alkane distribution in the stalagmite. Besides, fungi, algae, and nonphotosynthetic bacteria capable of producing HMW *n*-alkanes may also contribute the autochthonous homologues in the stalagmite. In order to differentiate the odd numbered higher plant *n*-alkanes from those of the other two origins (soil parent materials and stalagmite microorganisms) characterized by a CPI value of unity, the following expression has been used,

$$A_{21+2i} = C_{21+2i} - 0.5(C_{22+2i} + C_{20+2i}) \quad (i = 1-6),$$

where C_{21+2i} is the measured concentration of each odd numbered *n*-alkane and A_{21+2i} the amount of each odd numbered *n*-alkane originally related to higher plant input. This has been used by Schneider et al. (1983), Sicre et al. (1987), Simoneit et al. (1991), and Villanueva et al. (1997) to distinguish odd-numbered plant *n*-alkanes from those with a CPI value of unity in aerosols and sediments. The distribution of HMW *n*-alkanes related to the higher plant input in the stalagmite was shown in Fig. 2b. Most samples

were dominated by the C_{29} homologue, while two samples were dominated by C_{31} (9.25–13.8 cm) or C_{33} (21.50–23.80 cm) homologue. This indicates the change of soil ecosystems as discussed below.

n-Alkanols extracted from the stalagmite are mainly C_{12} to C_{30} homologues, maximizing at C_{28} (Fig. 2c). An obvious even-over-odd carbon number predominance was seen above C_{22} throughout all samples (CPI_h 11.1–20.6). A series of *n*-alkan-2-ones, ranging in carbon number from C_{12} to C_{31} , were detected in the profile (Fig. 2d). These *n*-alkan-2-ones have a maximum at C_{29} and a strong odd-over-even carbon number predominance (CPI_h 2.4–7.2).

The HMW *n*-alkanols and *n*-alkan-2-ones display good correlations not only in concentration (Table 1) but also in CPI values (Fig. 3a), clearly hinting at a common origin for the two series. High-maturity sedimentary rocks lack *n*-alkanols, although some contain *n*-alkan-2-ones (George and Jardine, 1994). Long-chained ($>C_{21}$) fatty alcohols with a strong even-over-odd preference can be crudely assigned to the contribution of vascular plant tissues (Lockheart et al., 2000; Logan et al., 1995). The CPI values (11.1–20.6) of the stalagmite *n*-alkanols are in the range observed in higher plants (Huang et al., 1995), modern soils (Bull et al., 2000) and paleosols (Freeman and Colarusso, 2001). The probable origin of the HMW *n*-alkanols in the

Table 1
Correlation coefficients (r^2) of organic compounds in the stalagmite based on the analysis of abundance

	L-ALK	H-ALK	L-AHL	H-AHL	L-KET	H-KET
L-ALK	1	0.39	0.37	0.09	<u>0.56</u>	0.19
H-ALK		1	0.19	0.01	<u>0.54</u>	0.05
L-AHL			1	0.19	<u>0.50</u>	0.10
H-AHL				1	0.01	<u>0.60</u>
L-KET					1	0.11
H-KET						1

Notes. L-ALK: C₁₅–C₂₀ *n*-alkanes, H-ALK: C₂₁–C₃₃ *n*-alkanes, L-AHL: C₁₂–C₂₁ *n*-alkanols, H-AHL: C₂₂–C₃₀ *n*-alkanols, L-KET: C₁₃–C₂₀ *n*-alkan-2-ones, H-KET: C₂₁–C₃₁ *n*-alkan-2-ones. The underlined values are those significant at a 99.9% level.

stalagmite is vascular-plant-derived organic matter in the overlying soil.

n-Alkan-2-ones are lipids commonly found in sediments and soils, usually occurring in the form of a homologous series with a high predominance of odd-numbered carbon. Recently, this group of compounds has been reported in biomass (Hernandez et al., 2001; Jaffe et al., 2001; Qu et al., 1999; Rieley et al., 1991), suggesting direct biological inputs to soils. Additionally, both microbial oxidation of *n*-alkanes and β -oxidation and subsequent decarboxylation of fatty acids have been suggested as possible sources of soil *n*-alkan-2-ones (Cranwell et al., 1987; Jaffe et al., 1993; Lehtonen and Ketola, 1990). All the evidence suggests that the most probable origin of the HMW *n*-alkan-2-ones found in the speleothem is the soil, a conclusion supported by the strong correlation with HMW *n*-alkanes. The low correlation coefficients between HMW *n*-alkanes and HMW alkanols/alkan-2-ones (Fig. 3c) might be caused by either the biodegradation on *n*-alkanols/alkan-2-ones or the existence of additional origins (e.g., parent soil materials, stalagmite fungi, etc.) for the former as mentioned above.

LMW *n*-alkanols and *n*-alkan-2-ones show no correlation with the HMW homologues (Table 1), indicating the additional origins for the LMW homologues. The LMW *n*-alkanols were identified in soils from humic horizon and mineral horizon (Bull et al., 2000), and assigned to microbial reduction of *n*-alkanoic acids (Jambu et al., 1993). Microbial lipids and/or microbial transformation of other lipids may contribute the LMW *n*-alkanols and *n*-alkan-2-ones in the stalagmite.

Lipid correlations with temperature records

The climate in China is characterized by seasonal alternations of the East Asian winter monsoon, historically associated with cold intervals, and the summer monsoon, historically associated with warm periods. In north central China, loess records show clear evidence for monsoon changes that are possibly linked to global climate (Kukla and An, 1989; Porter and An, 1995). Recently, in southern China high-resolution oxygen isotope records of stalagmites

were demonstrated to bear a remarkable resemblance to oxygen isotope records from Greenland ice cores, suggesting that East Asian monsoon intensity changed in tune with Greenland temperature (Wang et al., 2001) and supporting the idea that millennial-scale events first identified in Greenland are hemispheric (Broecker, 1994; Kienast et al., 2001; Schulz et al., 1998). The stalagmite studied herein spans, as dated by U–Th analyses, a part of the last glaciation, within which two cold paleoclimate events (the Younger Dryas and Heinrich event 1) and the intervening Allerød–Bølling warm event have been recorded by the oxygen isotope data (Fig. 1). This is in line with the loess records in north central China and other stalagmite data from Southern China (Wang et al., 2001).

Apparently, the climate events left an imprint on the carbon distributions of the lipids; the YD and H1 events are marked by an increase of LMW *n*-alkanols (C₁₂ *n*-alkanol in particular) and LMW *n*-alkan-2-ones (Fig. 2c, 2d). The ratio of LMW to HMW ($R_{1/h}$) *n*-alkanols indicative of the relative variation of microorganisms to higher plants and/or the contribution of microbial degradation displays a certain degree of similarity with the trends of the stalagmite $\delta^{18}\text{O}$ and the recently reported subtropical sea surface temperature (SST) based on C₃₇ alkenone unsaturation data (Bard et al., 2000) (Fig. 1). Higher $R_{1/h}$ values correspond to the enhanced $\delta^{18}\text{O}$ and lower alkenone-based SST values, implying the relatively increased contribution of microorganisms to soil ecosystems during the cold periods. Since soil microbes might be more tolerant to cold climate than higher plants, it is reasonable that greater $R_{1/h}$ values were seen in samples corresponding to cold climates. These functionalized molecules are expected to be at least as bioavailable as the *n*-alkanes, so they can carry a record related to climate. However, the *n*-alkanols $R_{1/h}$ correlative with *n*-alkan-2-ones $R_{1/h}$ (Fig. 3b) have no correlation with *n*-alkanes $R_{1/h}$ (Fig. 3d). The possibility of parent soil materials releasing HMW *n*-alkanes and the stalagmite microbes contributing to *n*-alkanes mainly has complicated the *n*-alkane distributions. As LMW *n*-alkanols are related to the soil microbes (e.g., microbial lipids and/or microbial degradation on other lipids), and HMW *n*-alkanols to the soil organics from contemporary higher plants, the similarity between *n*-alkanol and the climate records is a consequence of the variation of soil ecosystems (e.g., the variation of soil microbes relative to the vegetation and/or the contribution of microbial degradation) related to the climate. However, the selective degradation and diagenesis in the stalagmite might also influence the *n*-alkanol ratio of the top few samples.

Bard et al. (2000) reported that the H1 event was characterized by two depositional phases centered at 16,000 (H1a) and 17,500 yr ago (H1b). Similar peaks were also found during H2 events. They were proposed to be the pervasive millennial-scale cycles that consistently punctuate the intervals between Heinrich events. The low resolution in this lipid study prevents us from the detailed evaluation of these cycles, although variation of molecular parameters

does exist during the H1 event. In addition, the LGM in subtropical Northeast Atlantic was recently believed to be a rather mild period (Bard et al., 2000), fitting well with *n*-alkanol record in the subtropical southern China (Fig. 1).

Lipid profile compared with the $\delta^{13}\text{C}$ record

The *n*-alkanol $R_{1/h}$ profile is also comparable with the carbonate $\delta^{13}\text{C}$. High $R_{1/h}$ is found in samples of enhanced $\delta^{13}\text{C}$ values (Fig. 1). A number of mechanisms including soil respiration rates, pH of drip water, limestone bedrock carbon, atmospheric CO_2 , and the degassing rates of drip water may all be responsible for the variation of stalagmite $\delta^{13}\text{C}$ values (Coplen et al., 1994; Dorale et al., 1992; Dorale et al., 1998; Frappier et al., 2002; Genty et al., 2001). The similar trends seen in the $\delta^{13}\text{C}$ data and the *n*-alkanol ratio in this stalagmite imply the overlying soil ecosystems related to climate might cause the variation of $\delta^{13}\text{C}$ values. Stalagmite $\delta^{13}\text{C}$ has been proposed to have the potential to reflect changes in the overlying ecosystem's carbon budget, which might be sensitive to subtle modifications of climate and weather (Frappier et al., 2002). Ecosystem sensitivity even to weak climate signals has been modelled for marine ecosystems in the North Atlantic (Taylor et al., 2002). Thus the stalagmite lipid distribution provides a significant record in the carbon cycle related to overlying soil systems that merits further investigation.

Two samples (9.25–13.8 cm, 21.50–23.80 cm, Fig. 2) as indicated by the dash lines in Fig. 1 have the most distinctive lipid distributions throughout the stalagmite; both of them have the lowest (near to nil) LMW lipids (Figs. 2a, 2c, 2d), coinciding with the abrupt shifts in $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values (Fig. 1). Moreover, the odd-numbered plant HMW *n*-alkanes of the two samples are characterized by the dominance of C_{31} or C_{33} homologue (Fig. 2b), in striking contrast with other samples dominated by C_{29} homologue. The dominant C_{29} homologue in *n*-alkane distribution was reportedly contributed by deciduous trees (Cranwell, 1973) whilst the dominance of C_{31} or C_{33} *n*-alkane was proposed to relate to grass vegetation (Brincat et al., 2000; Cranwell et al., 1987; Meyers and Ishiwatari, 1993). The expansion of grass vegetation may prevent soil organic matter leaching from the soil to the drip water, which, in turn, impedes the growth of stalagmite microorganisms supported by soil organic matter. This may account for the decreased LMW lipids seen in the two samples. However, we are unable to assign the grass vegetation as C4 species, even though most subtropical grasslands mainly consist of C4 plants (Boutton et al., 1993). The expansion of C4 plants during the two periods would lead to enhanced $\delta^{13}\text{C}$ values, yet the stalagmite $\delta^{13}\text{C}$ record does not show this (in fact, it shows the exact opposite). Although the plant replacement cannot explain the $\delta^{13}\text{C}$ record, the coincidence of the abrupt and large shifts among lipid distributions, $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ data strongly supports a variation of soil ecosystems related to climate. Since microorganisms may have ^{13}C -enriched lip-

ids (Huang et al., 1996) comparing to higher plant lipids, and they also influence the decomposition of soil organic matter, the abrupt shift in stalagmite $\delta^{13}\text{C}$ record may relate to the shift of the relative abundance of microorganisms to higher plants and therefore the biodegradation. In addition, other complicated mechanisms such as root respiration (Frumkin et al., 2000) may contribute to the stalagmite $\delta^{13}\text{C}$ data. Notably, one of the samples is just located at the LGM and near to the transitional period from LGM to H1 event (Fig. 1 and 2), and the other is at B/A interstadial and close to the transitional from H1 to B/A. More data including the compound-specific isotopes are needed to elucidate the detailed relationship among the lipid distributions, soil ecosystems, and the shift of climate events.

Conclusions

This work demonstrates that organic materials extracted from a subtropical stalagmite in southern China record molecular signals capable of reflecting their origin and climatic change. HMW *n*-alkanols and *n*-alkan-2-ones are proposed to originate from soil organics related to vegetation inputs. LMW *n*-alkanols and *n*-alkan-2-ones are mainly contributed by soil microorganisms. The ratios of LMW to HMW *n*-alkanols or *n*-alkan-2-ones, related to the overlying soil ecosystems, are capable of recording the changing climate in the past. This biomarker approach expands the opportunities for gaining proxy records of paleoclimatic variation independent of the widely employed oxygen isotope record, and for constraining the stalagmite $\delta^{13}\text{C}$ data.

Acknowledgments

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