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Aeolian *n*-alkane isotopic evidence from North Pacific for a Late Miocene decline of C_4 plant in the arid Asian interior

Guodong Jia [a,b,*], Zhiyang Li [b], Ping'an Peng [c], Liping Zhou [d]

[a] State Key Laboratory of Isotope Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, China
[b] CAS Key Laboratory of Marginal Sea Geology, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, China
[c] State Key Laboratory of Organic Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, China
[d] Laboratory for Earth Surface Processes, Department of Geography, and Centre for Ocean Research, Peking University, Beijing 100871, China

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ABSTRACT

Aeolian deposition in the central North Pacific has been well recognized to originate from arid Asian interior. While there is no doubt about the transport of organic matters along with the mineral dust from the source region, little is known about the nature and changes of the terrestrial organic compounds preserved in the deep sea sediments. In this study, higher plant leaf wax *n*-alkanes from ODP Site 1208 and Site 886 in the North Pacific since the middle Miocene were analyzed to explore long-term changes in vegetation and climate in the source region. Accumulation rates of leaf wax *n*-alkanes show an increasing trend, consistent with the documented climatic drying of the Asian interior since the late Miocene. The records of carbon isotopic enrichment factors of C_{29} *n*-alkane relative to atmospheric CO_2 ($\varepsilon_{C29-CO2}$) show a prominent decrease from ~12 to ~8 Ma. The average $\varepsilon_{C29-CO2}$ value prior to ~8 Ma is 0.8‰ heavier than after ~8 Ma. Although almost all values of $\varepsilon_{C29-CO2}$ (−25.3 to −21.3‰) are well within the range of C_3 plants, adjustment of isotope discrimination by C_3 plants is not considered as the main cause of the observed variations. Instead, changes in relative abundance of C_3 vs. C_4 plants are invoked to interpret the $\varepsilon_{C29-CO2}$ records. Higher C_4 contribution (17.7 ± 5.3%) to the local vegetation is inferred for the period *prior to* ~8 Ma, implying a slightly warmer climate in the source region. A marked decline in C_4 plants from ~12 to ~8 Ma, interpreted as a result of regional temperature drop, coincides with the prominent growth of northern Tibetan Plateau around 8 Ma, along with the global cooling climate. Our results therefore point to apparently close links among plateau uplift, development of drying and cooling climates, and vegetation changes in the Asian interior.

1. Introduction

The late Miocene–early Pliocene C_4 plant expansion, one of the most profound ecological changes during the Cenozoic, is well documented across the tropical and subtropical continents (cf. Edwards et al., 2010; Tipple and Pagani, 2007). Declining partial pressure of atmospheric CO_2 (pCO_2) has long been considered as a key driver for this event (Cerling et al., 1997; Ehleringer et al., 1991, 1997). However, new geological evidence revealed a long period of stasis in the level of pCO_2 during the C_4 expansion (Pagani et al., 1999; Pearson and Palmer, 2000; Royer et al., 2001), hence calling for alternative interpretations. A sharp pCO_2 drop to below 500 p.p.m.v was recorded at 25–30 Ma during the Oligocene (Pagani et al., 2005; Royer, 2006). While this would be energetically favorable for C_4 photosynthesis, Christin et al. (2008) and Vicentini et al. (2008) suggested declining pCO_2 as a key selection pressure for the evolutionary origins of C_4 photosynthesis in the grasses, rather than its expansion. The C_4 plant success is therefore postulated as a result of climate change. Seasonal and/or drying climates, caused by large-scale hydrological changes, have been proposed for the Miocene replacement of C_3 woody vegetation by C_4 grasslands in south Asia (Dettman et al., 2001; Huang et al., 2007; Quade et al., 1989, 1995). Although increasing temperatures would have favored C_4 over C_3 plants (Cerling et al., 1993), there is no evidence for a global rise in temperatures during the late Miocene (Zachos et al., 2001). Nevertheless, temperature is crucial for present global distribution pattern of C_4 grasses, i.e. mostly in low latitudes and altitudes (e.g. Edwards et al., 2010). A cluster of C_4 origins occurred at the Mid-Miocene climatic optimum, coinciding with the rise in temperature (Vicentini et al., 2008). Most investigations on the evolution of C_4 plants have hitherto focused on the low-latitude tropical–subtropical vegetation, but the early history of C_4 plants remains enigmatic for the mid-latitudes due to the paucity of the geologic records.

Stable carbon isotopic composition ($\delta^{13}C$) of palaeosol carbonate and herbivore tooth enamel has been used to investigate the late Cenozoic C_4 signals in terrestrial ecosystems (Tipple and Pagani, 2007). In the recent decade, leaf wax lipids from terrestrial higher plants in

* Corresponding author at: State Key Laboratory of Isotope Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, China. Fax: +86 20 85290278.
E-mail address: jiagd@gig.ac.cn (G. Jia).

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marine sediments have proven useful for such studies, and compound-specific $\delta^{13}C$ of leaf wax *n*-alkanes has been particularly successful in the reconstruction of the late Cenozoic vegetation changes. For example, $\delta^{13}C_{alkane}$ records from the northern Indian Ocean provide a strong support to the late Miocene C_4 expansion that was revealed by the terrestrial records on the tropical continents (Freeman and Colarusso, 2001; Huang et al., 2007). Compared with terrestrial records, the $\delta^{13}C_{alkane}$ data from marine sediments have the potential of deciphering the history of C_4 plant dynamics on much wider scales, because *n*-alkanes input to the oceans mainly by aeolian transport should represent a regionally integrated signal of the terrestrial ecosystem.

Aerosol monitoring and satellite data indicate that the mid-latitude Asian interior, notably the inland basins on the north and northwest side of the Tibetan Plateau, is the most important source region for aeolian dust over the North Pacific (e.g. Wilkening et al., 2000; Fig. 1). Geochemical studies on the silicate fractions in deep-sea sediments in the central North Pacific also indicated their Asian origin (Chen et al., 2007; Pettke et al., 2000; Sun, 2005). Therefore, aeolian deposits transported to the Pacific by the westerlies are valuable geological archives of past climatic and environmental changes in Asian interior (Pye and Zhou, 1989; Rea et al., 1985). Arid climate in Asian interior has been shown to persist throughout the Neogene (Kent-Corson et al., 2009; Sun and Wang, 2005; Sun et al., 2010), and indeed the region was postulated to be a center of origin for C_4 photosynthesis (Sage, 2004). However, it remains unknown about how the vegetation photosynthetic pathways have evolved in the aeolian source region during the Neogene although C_4 plants are presently a minor component mainly due to the low growing season temperature (generally <20 °C). In this study, we hypothesize that C_4 plants might have contributed more to the regional ecosystem during warm periods such as the middle Miocene. We then test this hypothesis through a study on the $\delta^{13}C_{alkane}$ records since the middle Miocene using sediments from ODP Site 1208 and Site 886 in the North Pacific. Given the scarcity of the Neogene geological records from the mid-latitudes, it is hoped that our study reported here will contribute to a better understanding of regional and global C_4 plant dynamics during the Neogene.

2. Study sites, chronology and method

ODP Site 1208, Leg 198 is located at 3346 m water depth close to the center of the Central High of Shatsky Rise in the North Pacific Ocean (36°7.6′N, 158°12.1′E; Fig. 1; Shipboard Scientific Party, 2002). A total of 392.3 m was drilled at the site in 2002, and a thick, apparently complete upper Miocene to Holocene sequence composed

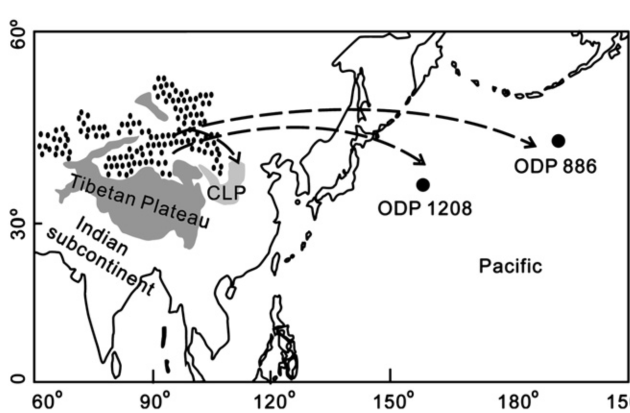

Fig. 1. Map of the North Pacific Ocean and Asian continent, showing high topography of >3000 m above sea level (dark gray area), desert distributions (dotted area), the Chinese Loess plateau (CLP, light gray area), and ODP Sites 1208 and 886. The dashed arrows visualize the track of modern dust transport to the north Pacific originating from the Asian interior.

of nanofossil ooze and nanofossil clay was recovered between 0 and 251.6 m below seafloor (mbsf), below which lied about 60 m of less expanded lower and middle Miocene section (Shipboard Scientific Party, 2002). Neogene nannofossil biostratigraphy indicates a relatively complete stratigraphy with all zones from CN5 through CN15 (middle Miocene–Holocene). In this work, a detailed age-depth model from calcareous nannofossils for the site established by Bown (2005) is applied, and the age control points are plotted in Fig. 2b. A total of 123 sediment samples from the upper 312.5 m at an average interval of 2.56 m were analyzed in this study. According to the nannofossil-based age model, our samples span from the middle Miocene (~16 Ma) to the late Quaternary with an average time resolution of 0.13 Ma.

ODP Site 886, Leg 145 (44°42′N, 168°18′W, Fig. 1) was retrieved at the depth of 5710 m in 1992. A composite section at this location was constructed for the site (Dickens et al., 1995), which consists of 24 m of clay with diatoms overlying 30 m of clay bearing diatom ooze. The basal unit from 54 m to 71 m is a hydrothermal ooze. The age model for the upper 55 m, based on magnetostratigraphy, was established by Rea et al. (1998) and is applied in this work. The age control points are plotted in Fig. 2a. A total of 40 sediment samples from the upper 55.55 m from the site were analyzed in this study, and these samples span from the middle Miocene (~11 Ma) to the late Quaternary with an average time resolution of 0.29 Ma.

The mean linear sedimentation rate is about 20 m Ma^{-1} at Site 1208, and about 5.5 m Ma^{-1} at Site 886 since the late Miocene. The much higher sedimentation rate at Site 1208 is due to the high content of marine carbonate (10–89%) in the sediments of the core; no carbonate is preserved at Site 886 (below the carbonate compensation depth).

Sediment samples were freeze-dried and ultrasonically extracted three times with dichloromethane. The hydrocarbon fraction was isolated from the total extract using silica gel column chromatography (~2 g silica) by eluting with hexane (10 ml), and then purified for *n*-alkanes using urea adduction. Purified *n*-alkanes were then identified by comparison of retention times defined by gas-chromatography (GC) analysis of a mixed *n*-alkane standards. An internal standard of C_{36} *n*-alkane was used for quantifications.

$\delta^{13}C$ of leaf wax *n*-alkanes was analyzed by gas chromatography–isotope ratio mass spectrometry (GC–IRMS), using a HP 6890 GC connected to a Delta Plus XL mass spectrometer via a GC-C III interface. Prior to the $\delta^{13}C$ analyses, CO_2 reference gas was calibrated relative to VPDB. Instrumental performance was routinely checked using an *n*-alkane standard mixture containing 9 *n*-alkane homologues (carbon numbers between 12 and 32) with known $\delta^{13}C$ values provided by Indiana University. For isotopic standardization, CO_2 reference gas was automatically introduced into the mass spectrometer in a series of pulses at the beginning and the end of each analysis. Every sample was analyzed at least twice, and the average value, with $\sigma \leq 0.25‰$, is reported here.

When interpreting fossil $\delta^{13}C$ record, there is a source of uncertainty in the $\delta^{13}C$ value of ancient atmospheric carbon dioxide ($\delta^{13}C_{CO2}$), whose high-resolution record for the Neogene only became available recently (Fig. 3c; Tipple et al., 2010). Using this $\delta^{13}C_{CO2}$ record, we calculated the isotopic enrichment factors for C_{29} *n*-alkanes relative to the atmospheric CO_2 ($\varepsilon_{C29-CO2}$) as follows:

$$\varepsilon_{C29-CO2-} = \left(\delta^{13}C_{C29} - \delta^{13}C_{CO2}\right) / \left(\delta^{13}C_{CO2} + 1\right)^{*} 1000 \quad (1)$$

Here, the sign of $\varepsilon_{C29-CO2}$ is opposite to the conventionally used carbon isotope discrimination (Δ) (Farquhar et al., 1989) which is a measure of the atmosphere relative to the plant. Before the calculation, the 0.5-Ma $\delta^{13}C_{CO2}$ record of Tipple et al. (2010) was interpolated to derive data points with ages corresponding to our $\delta^{13}C_{C29}$ record. The mean standard errors for the dataset of 0.5-Ma $\delta^{13}C_{CO2}$ and our

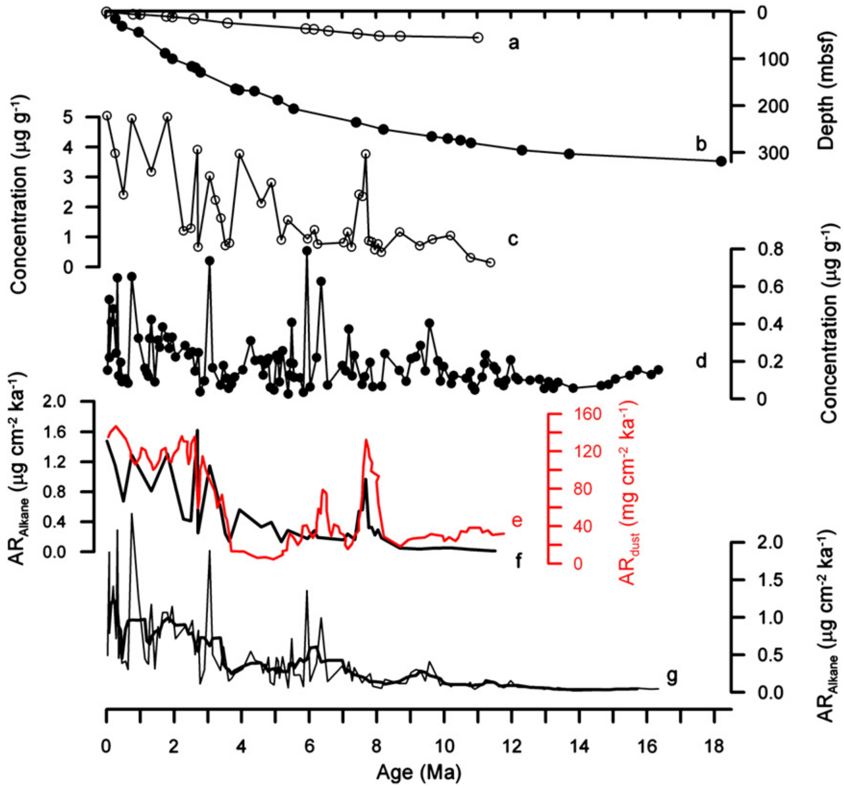

Fig. 2. Depth-age profile of (a) ODP Site 886 and (b) ODP Site 1208, concentration of $C_{27+29+31}$ *n*-alkanes at (c) Site 886 and (d) Site 1208, and the accumulation rate of $C_{27+29+31}$ *n*-alkanes at (f) Site 886 and (g) Site 1208. (e) Dust accumulation rate at Site 886 from Rea et al. (1998).

$\delta^{13}C_{C29}$ measurements are ~0.22‰ and 0.25‰, respectively. So the propagated error for the $\varepsilon_{C29-CO2}$ calculations is ~0.33‰. The use of $\varepsilon_{C29-CO2}$ values here skips a step of converting *n*-alkane values to bulk values conventionally used in literature (e.g., Hughen et al., 2004), because the apparent fractionation between *n*-alkanes and bulk organic matter for C_3 plant is ~3‰ larger than C_4 plants (Chikaraishi and Naraoka, 2003; Collister et al., 1994), and even within C_3 plants the fractionation can vary as much as 10% (Diefendorf et al., 2011).

3. Results

High-molecular weight *n*-alkanes from the two study sites range from C_{23} to C_{33}, with C_{27}, C_{29}, and C_{31} being the most abundant. The C_{27} to C_{31} *n*-alkanes show strong odd-over-even chain length predominance. The carbon preference index (CPI) values vary from 1.7 to 9.5 with a mean of 4.7 ± 1.2 for Site 1208 and of 5.0 ± 1.4 for Site 886. Concentrations of $C_{27+29+31}$ *n*-alkanes at Site 886 are much higher than at Site 1208 (Fig. 2c and d), likely caused by the lower sedimentation rates at Site 886. However, the mass accumulation rates of $C_{27+29+31}$ *n*-alkanes (AR_{alkane}) at both sites are comparable. The AR_{alkane} values are at the lowest for the interval prior to ~8 Ma, gradually increase from 8.0 to 3.6 Ma, and then show a prominent rise after 3.6 Ma (Fig. 2f and g).

The abundance of C_{27} *n*-alkane is the lowest one among the three odd-number alkanes, which makes the $\delta^{13}C_{nC27}$ values unavailable for some samples. $\delta^{13}C_{29}$ and $\delta^{13}C_{31}$ are strongly correlated to each other ($r = 0.80$ for Site 1208, and 0.83 for Site 886). Therefore, in the subsequent discussions, we shall focus on $\delta^{13}C_{29}$ (Fig. 3a). The $\delta^{13}C_{29}$ values from the two sites are comparable and show consistent variations with a long-term decreasing trend by an average of ~2.5‰ since the middle Miocene. During the middle Miocene (prior to ~12 Ma), the $\delta^{13}C_{29}$ display a slightly decreasing trend from −28.5 to −30.0‰ between 16.3 and 12.5 Ma, followed by an abrupt increase around 12 Ma. The late Miocene is characterized by a long-term decrease of $\delta^{13}C_{29}$ by ~2.0‰ from 12 to 6 Ma. The $\delta^{13}C_{29}$ remains relatively constant (-30.2 ± 0.4‰) during the latest Miocene and early Pliocene from ~6 to 3.6 Ma. From ~3.6 Ma onwards, there occurs a second long-term decrease of $\delta^{13}C_{29}$ by ~1.5‰.

The $\varepsilon_{C29-CO2}$ values vary from −21.3 to −25.0‰ at Site 1208 and −22.6 to −25.3‰ at Site 886. There is an extreme of −21.3‰ at ca. 12 Ma at Site 1208 (Fig. 3d). The $\varepsilon_{C29-CO2}$ is ~0.8‰ heavier when the average pre-8 Ma record is compared with the average post-8 Ma record. This difference is larger than the standard error of $\varepsilon_{C29-CO2}$ estimates. There appears no trend of change for the last 8 Ma, and therefore, the decline of $\varepsilon_{C29-CO2}$ from ~12 Ma to ~8 Ma represents a most marked change in the secular $\varepsilon_{C29-CO2}$ history.

4. Discussion

4.1. Drying of the dust source region

Deposition of mineral aerosols accounts for a substantial fraction of the non-biogenic portion of deep-sea sediments in the central North Pacific, where previous studies estimated that 75–95% of the surface sediment is derived from atmospheric dust fallout (Leinen and Heath, 1981). Satellite imagery of the tracks of dust transport and studies of dust tracers unambiguously showed that dust from central Asia dominates the central North Pacific today (e.g., Rea, 1994; Wilkening et al., 2000). Nd isotopic composition of modern detrital silicate samples in the central North Pacific is shown to be comparable to those of Chinese Loess Plateau (CLP) (John et al., 2001; Jones et al., 1994; Nakai et al., 1993; Pettke et al., 2000), suggesting that aeolian dust in the central North Pacific and the CLP derives from the same source (Sun, 2005). In addition, the uniform Nd isotopic composition since 12 Ma (Pettke et al., 2000), possibly even since the late Eocene (Pettke et al., 2002), precludes a major change in the provenance of the dominant dust component. More recently, Nd–Sr isotopic studies suggest that the dust source region for both the

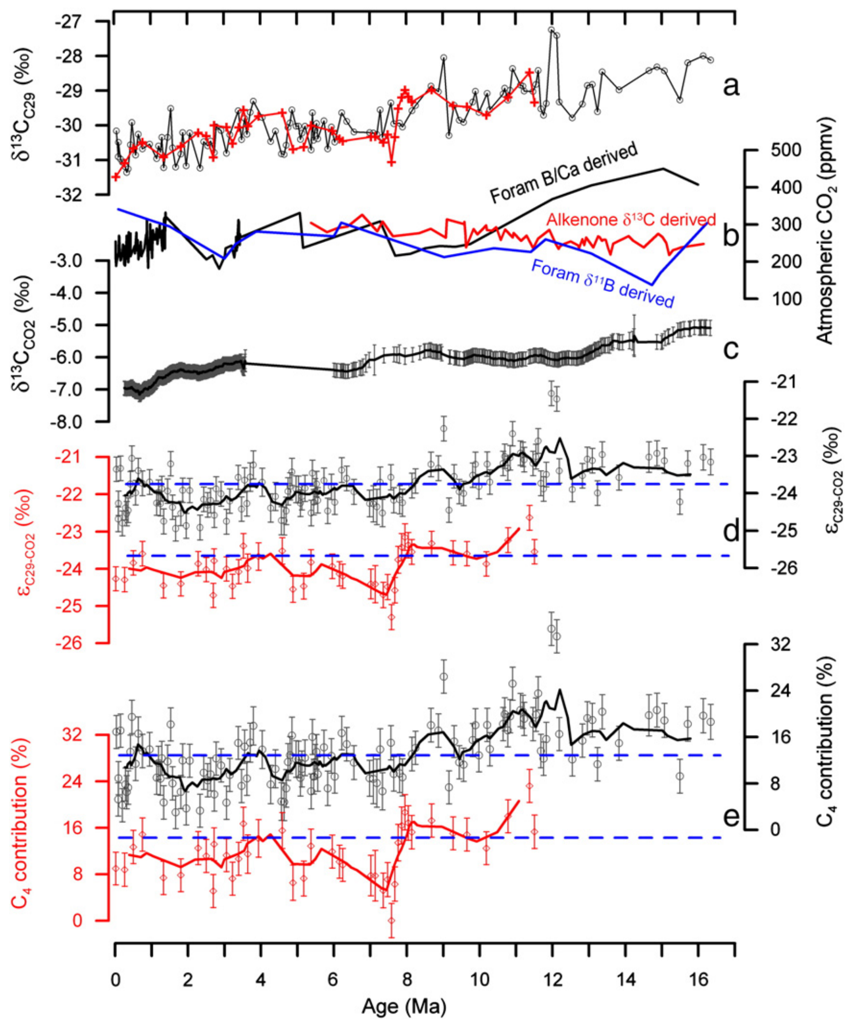

Fig. 3. (a) Downcore records of C_{29} *n*-alkane $\delta^{13}C$ at Sites 1208 and 886; (b) Published pCO_2 records since the mid-Miocene using different methods. Alkenone $\delta^{13}C$-derived pCO_2 is from Pagani et al. (2005); Foram $\delta^{11}B$-derived pCO_2 is from Pearson and Palmer (2000), and B/Ca ratio-derived pCO_2 is from Tripati et al. (2009). (c) Record of $\delta^{13}C$ of atmospheric CO_2 from Tipple et al. (2010). The data hiatus between 6 and 3.6 Ma is simply linearly interpolated; (d) Downcore variations of C_{29} *n*-alkane carbon isotopic enrichment factors ($\varepsilon_{C29-CO2}$) calculated from data of (a) and (c); (e) C_4 plant contributions by the assumption that $\varepsilon_{C29-CO2}$ reflected the relative abundances of C_3 vs. C_4 plants. Curves in the (b), (c), (d), and (e) are the 0.5-Ma running mean. Red symbols and curves in (a), (d), and (e) are for Site 886 and black and gray ones for Site 1208. The errors are 1σ.

proximal CLP (via near-surface northwest winter monsoon) and the distal North Pacific (via high-altitude westerlies) is the deserts on the northern margin of the Tibetan Plateau, i.e., Taklimakan, Qaidam, Badain Jaran, and Tengger deserts (Chen et al., 2007; Rao et al., 2009). In this paper we refer to this source region as Asian interior. Fine particles from these deserts are mainly derived from the widely distributed proluvial deposits associated with intensive Tibetan uplift (Derbyshire et al., 1998; Ji et al., 1999; Li et al., 2009a). The dominance of dust from the northern margin of the Tibetan Plateau, therefore, suggests a close link between aeolian deposition in the CLP and the North Pacific and the evolution of the Tibetan Plateau, i.e., the uplift and growth of the Tibetan Plateau not only gives rise to the increasingly drier climate conditions, but also generates the detrital materials favoring dust production (Chen et al., 2007).

Terrigenous organic matter, e.g., the leaf wax lipids from vascular plants, has been found to be a significant fraction of aerosols over the North Pacific and in the surface sediments of the ocean (Kawamura, 1995; Kawamura et al., 2003; Ohkouchi et al., 1997; Simoneit et al., 2004). Therefore, the deposited terrigenous organic matter therein could provide valuable information on the evolution of terrestrial climate and vegetation in the Asian interior. The high CPI_{27-31} values of *n*-alkanes since the middle Miocene from our results clearly indicate their higher plant origin and negligible diagenetic alterations (Eglinton and Hamilton, 1967). Accordingly, our AR_{alkane} record can be used as the first order approximation of aeolian dust accumulation in the study sites. Variations in dust mass accumulation rate from terrestrial and marine sediments have been used to infer the atmospheric dust budget and associated inland aridity (Kohfeld and Harrison, 2001; Rea et al., 1998; Sun and An, 2005). AR_{alkane} variations in this study are similar to the previously reported dust deposition records in the central North Pacific (Fig. 2e; Rea et al., 1998). There is an abrupt increase in dust flux since ~3.6 Ma, implying the intensified drying in the source area. The late Miocene peaks of AR_{alkane}, especially the one centered at 7.7 Ma from Site 886 (Fig. 2f), are consistent with dust flux peaks identified by Rea et al. (1998), which was interpreted to reflect a period of climatic (or vegetational) instability between two more stable periods.

4.2. Changes of $\varepsilon_{C29-CO2}$ values since the middle Miocene

Changes in modern vegetation $\delta^{13}C$ can be attributed to either the relative contributions of C_4 (with $\delta^{13}C$ between −10 and −14‰) and C_3 plants (with $\delta^{13}C$ between −23 and −35‰) or the adjustment of isotopic discrimination by C_3 plants due to environmental factors such as water stress, both of which are associated with climate conditions. These modern values have been usually applied to discuss the

$\delta^{13}C$ related to past vegetation. However, the effect of $\delta^{13}C$ change in ancient atmospheric CO_2 on the plant $\delta^{13}C$ values needs to be considered in the reconstruction of vegetation change (e.g. Tipple et al., 2010). As can be seen in Fig. 3a and c, our $\delta^{13}C_{alkane}$ records since the middle Miocene display a largely similar trend as the $\delta^{13}C_{CO2}$ record. As the changes in $\delta^{13}C$ of atmospheric CO_2 have been incorporated in plant $\delta^{13}C$, we removed the $\delta^{13}C_{CO2}$ as background from our $\delta^{13}C_{alkane}$ records in order to obtain a net vegetation $\delta^{13}C$ signal, i.e. the $\varepsilon_{C29-CO2}$ curves in Fig. 3d. We then use thus derived $\varepsilon_{C29-CO2}$ records to discuss vegetation changes in the following sections.

Before interpreting our $\varepsilon_{C29-CO2}$ records, we examined the data for modern plants from eight publications that involved analysis of plant $\delta^{13}C_{alkane}$. These reported data include 201 $\delta^{13}C_{C29}$ measurements of individual plants belonging to 190 species growing under various geographic conditions across five continents, e.g. grasslands, woodlands, savannas, rain forest, semi-deserts, and gardens and university campus. As shown in Fig. 4, the mean $\varepsilon_{C29-CO2}$ value is -26.5 ± 3.0‰ (n = 149) for C_3 plants and -13.8 ± 2.4‰ (n = 52) for C_4 plants. The $\varepsilon_{C29-CO2}$ values for C_3 plants display a wide range from -37.4‰ to -20.1‰.

In our records (Fig. 3d), all values of $\varepsilon_{C29-CO2}$ are well within the range for C_3 plants, but significantly higher than the mean value of C_3 plants. Although the ~0.8‰ difference between the average pre-8 Ma record and the average post-8 Ma record seems not particularly large, we consider it as representing an important event. This is because sedimentary leaf wax *n*-alkane $\delta^{13}C$ can document community, or even landscape-level $\delta^{13}C$ by naturally integrating plant species-level $\delta^{13}C$ in space and time, smoothing down the great variability among species, and preserving signals of common factors that control the average plant $\delta^{13}C$ (e.g. Li et al., 2009b; Wei and Jia, 2009). In the following sections, we discuss three scenarios as possible causes for the $\varepsilon_{C29-CO2}$ variations: (1) contributions of aeolian *n*-alkane from other source areas in addition to the Asian interior, (2) the isotopic fluctuations of pure C_3 vegetation due to environmental change, and (3) varying contributions of C_4 plants.

In the first scenario, the presence of significant additional source areas of aeolian *n*-alkanes to the study sites would confound the interpretation of our $\varepsilon_{C29-CO2}$ records as the signals of vegetation change in the Asian interior. A recent investigation on *n*-alkane $\delta^{13}C$ in marine aerosols in the subtropical western North Pacific (27°04′ N, 142°13′E) indeed suggests that the southerly monsoon wind in summer can bring aerosol *n*-alkanes, characterized by heavier $\delta^{13}C$ values, from the Southeast Asia and Australia, where C_4 plants are abundant; and the winter aerosol *n*-alkanes are lighter in $\delta^{13}C$ values without C_4 signal, suggestive of North Asian input (Bendle et al., 2006). However, we consider that the southerly input of aeolian *n*-alkanes is insignificant at our study sites, because (1) the signal of C_4 plants is weak for the late Quaternary and even for the last 8 Ma, if any, in our $\varepsilon_{C29-CO2}$ records, and (2) the established vegetation $\delta^{13}C$ records in the South and East Asia from tropical to temperate zones exhibit an increasing trend or an abrupt increase, suggestive of C_4 expansion, during the period from late Miocene to the Pliocene (e.g., Ding and Yang, 2000; Jia et al., 2003; Quade et al., 1989), which is opposite to the pattern observed here. To reconcile the observations of Bendle et al. (2006) with our argument, we hypothesize that the Pacific subtropical high, with its northernmost position at ~30°N in summer, would have acted as a barrier for the southerly monsoon wind carrying the terrestrial lipids from the Southeast Asia and Australia to our study sites.

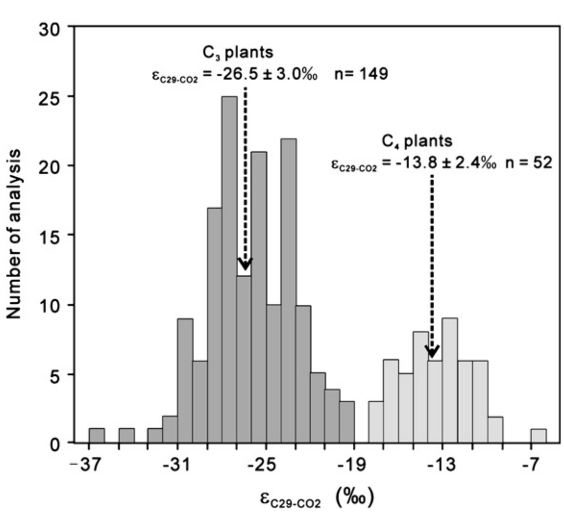

Fig. 4. Histogram of C_{29} *n*-alkane isotopic enrichment factors of modern C_3 and C_4 plants. Data of C_{29} *n*-alkane $\delta^{13}C$ compiled in this study are collected from following contributions: Collister et al. (1994), Chikaraishi and Naraoka (2003), Bi et al. (2005); Krull et al. (2006), Rommerskirchen et al. (2006), Pedentchouk et al. (2008), Vogts et al. (2009), Diefendorf et al. (2011). $\delta^{13}C_{CO2}$ values were estimated for the year of sampling based on modern secular trends (0.023‰ yr^{-1}; Keeling et al., 2001).

In the second scenario, the variations of $\varepsilon_{C29-CO2}$ are attributed to the adjustment of isotopic discrimination by pure C_3 vegetation. Recently, comprehensive studies reveal a strong positive correlation between Δ of C_3 plants and mean annual precipitation (MAP) and minor effects of temperature and latitude on Δ (Diefendorf et al., 2010; Kohn, 2010). According to these observations, our $\varepsilon_{C29-CO2}$ records would suggest a generally drier climate prior to ~8 Ma, with the driest period at ~12 Ma, than after ~8 Ma. However, this scenario is in contrast with a large body of evidence for the climate history in the Asian interior deduced from fossil tooth height, pollen and aeolian records (Fortelius et al., 2002; Guo et al., 2008; Miao et al., 2011; Sun and Wang, 2005; Sun et al., 2009), which is characterized by warmer and wetter climate during the Miocene with a persistent and progressive drying and cooling trend through the Neogene, especially since the late Miocene. For example, fossil tooth height showed little sign of increase before 11 Ma, but started to increase since 11–8 Ma in central Asia. This was interpreted as indicative of an adaptive response to increasing demands for wear tolerance and functional durability brought about by the development of more fibrous or abrasive plants in a progressively more open and arid-adapted vegetation (Fortelius et al., 2002). Pollen records from the Qaidam Basin at the northern edge of the Tibetan Plateau also suggest a stepwise decrease of thermophilic plants (like *Cedrus* and *Podocarpus*) and increase of xerophytic plants (like Chenopodiaceae and Asteraceae) since 18 Ma (Miao et al., 2011). It was not until ca. 7 Ma that aeolian sand dunes began to form in the Tarim Basin at the northwestern edge of the Tibetan Plateau (Sun et al., 2009). Palaeoclimate modeling also suggests that the Neogene uplift of Tibetan Plateau and/or the retreat of Paratethys Sea since the Miocene have led to and enhanced the arid and cool climate in the Asian interior (An et al., 2001; Kutzbach et al., 1993; Manabe and Broccoli, 1990; Zhang et al., 2007). A more recent modeling study using Earth System Model by Tang et al. (2011a) also shows that climate of the Asian interior was relatively humid during the 11–7 Ma. Therefore, it seems hard to reconcile the hypothesized adjustment of C_3 isotopic discrimination with the MAP history in the Asian interior since the middle Miocene.

Besides MAP, plant functional types (PFTs) can also explain some variability of the Δ, with lower Δ of evergreen gymnosperms than for other woody PFTs (Diefendorf et al., 2010). This is consistent with our previous dataset for $\varepsilon_{C29-CO2}$ estimates, where 16 C_3 plants have $\varepsilon_{C29-CO2}$ values > -23‰, and 8 of them are gymnosperms. Accordingly, where there a significant PFT shift toward less abundance of gymnosperms at ca. 8 Ma in the Asian interior, a decrease in $\varepsilon_{C29-CO2}$ would have occurred hence being consistent with our observed record. However, palynological studies in the Junggar Basin, the Qaidam basin and the Jiuxi Basin point to a transition from forest to steppe with an abrupt humid conifer decline and the establishment of modern-like xerophilous herbs-dominated desert vegetation occurred at least before 13 Ma (Ma et al., 2005; Miao et al., 2011; Tang et al., 2011b), much earlier than the negative excursion of $\varepsilon_{C29-CO2}$ in our record. We therefore argue that PTF shift is unlikely to be the main cause for our observed variations. Nevertheless, given the scarcity of the vegetation records in the source region, the $\varepsilon_{C29-CO2}$ changes attributable to PTF shifts remain elusive and may be clarified by more detailed reconstruction of regional vegetation history in the future.

Carbon isotopic discrimination of C_3 plants is also sensitive to the atmospheric pCO_2 (e.g. Feng and Epstein, 1995). Studies of the effects of pCO_2 on plants and ecosystems reveal that the specific leaf area and stomatal conductance decrease in response to elevated pCO_2 (Ainsworth and Long, 2005; Beerling and Woodward, 1995), potentially leading to less intercellular CO_2 concentration (C_i). As C_i falls, the $\delta^{13}C$ of the CO_2 inside the leaf is progressively enriched and the photosynthate produced is likewise enriched (Marshall et al., 2008), thus reducing the fractionation factor between leaf lipids and the atmospheric CO_2 (or higher $\varepsilon_{C29-CO2}$). For C_4 plants, moderate pCO_2 change has little influence on stomatal pore area (Raven and Ramsden, 1988). If pCO_2 change were responsible to C_3 plants $\varepsilon_{C29-CO2}$ difference between pre- and post-8 Ma in our results, a relatively low pCO_2 would have occurred after ~8 Ma. However, stringent test of such a possibility remains difficult at the moment due to the paucity of the estimates of pCO_2 change during the Neogene. In fact, the published proxy reconstructions have yielded conflicting results (Fig. 2b). For example, reconstructed pCO_2 using $\delta^{13}C$ of alkenones and $\delta^{11}B$ of foraminifera showed a general increasing trend from the mid-Miocene to the Late Miocene (Pagani et al., 1999; Pagani et al., 2005; Pearson and Palmer, 2000); whereas pCO_2 from B/Ca ratios of surface-dwelling foraminifera displayed an obviously opposite changing direction (Tripati et al., 2009) (Fig. 2b).

For the third scenario, we hypothesize that the contribution of C_4 grasses to the regional ecosystem was larger during the warm periods such as the middle Miocene. C_4 grasses can achieve higher photosynthetic rates at lower stomatal conductance than C_3 species, thereby conserving water in hot conditions when evaporative demand is high and offering a major selective advantage over C_3 species under hot and dry climate (Osborne and Beerling, 2006). The crossover for the pre-industrial atmospheric CO_2 (280 p.p.m.v) is between 16 °C and 20 °C, with C_4 grasses being favored in warmer temperatures (Cerling et al., 1997). Several records from mid latitude North China indeed revealed C_4 increase during the interglacial times, which was thought to be caused by the concurrent temperature rise (Gu et al., 2003; Liu et al., 2005; Zhang et al., 2003). Recent phylogenetic reconstructions indicate that C_4 photosynthesis has evolved multiple times in grasses since the Oligocene (Christin et al., 2008; Vicentini et al., 2008), showing a cluster of C_4 to C_3 reversals in the early Miocene coinciding with a drop in global temperatures, and a subsequent cluster of C_4 origins in the mid-Miocene, correlating with the rise in temperature at the mid-Miocene climatic optimum (Vicentini et al., 2008). Present summer season temperatures in the dry Asian interior are generally lower than 20 °C (Pu and Zhang, 2011), which constrains C_4 grasses to be the minor component of the modern vegetation. However, considering the little changes in atmospheric pCO_2 during the late Cenozoic, were regional temperature warmer before the late Miocene, C_4 abundance would have been higher than thereafter. By using the lowest $\varepsilon_{C29-CO2}$ value of −25.3‰ in our records as the end member for regional C_3 plants (this value is higher than the global average value of −26.5‰ for C_3 plants, but is reasonable for the dry Asian interior) and the global average C_4 value of −13.8‰ as the end member for regional C_4 plants, we estimate the percentage of C_4 plants from Site 1208 dataset to be between 17.7 ± 5.3% before ~8 Ma and 10.6 ± 3.9% after ~8 Ma in our records (Fig. 3e). This estimate therefore implies the presence of moderate C_4 grasses in the Asian interior prior to ~8 Ma, and a marked decline occurred from ~12 to ~8 Ma. Our results thus suggest that the vegetation feature similar to modern situation became established after the decline of C_4 grasses around 8 Ma. Under the background of overall drying climate in the Asian interior that potentially favorable for C_4 plants, the inferred vegetation shifts from moderate toward minor C_4 plant since the late Miocene would imply a cooling trend. This cooling trend is in agreement with global and regional climate change during the late Cenozoic (e.g., Miao et al., 2011; Zachos et al., 2001). This is also consistent with the recent finding of greater proportions of C_4 grasses during the Oligocene–Middle Miocene than at present in southwestern Europe, which is attributed to the subtropical to warm-temperate conditions favorable for C_4 plants during that time (Urban et al., 2010). The above analysis therefore allows us to interpret our $\varepsilon_{C29-CO2}$ record as resulting from changes in C_4 contribution to the vegetation in Asian interior.

Palaeobotanic studies indicate that Chenopodiaceae originated from continental Eurasia in the late Cretaceous (Muller, 1981; Zhu, 1995), and C_4 photosynthesis in Chenopodiaceae has been postulated to arise in the Asian interior (Sage, 2004). Pollen data show that the modern-like Chenopodiaceae-dominated steppe in the region was established at least 13 Ma (Ma et al., 2005; Miao et al., 2011; Tang et al., 2011b). Our results provide additional information that C_4 contributions after the establishment of regional steppe landscapes approached a transient maximum at ca. 12 Ma, then became progressively decreased from ~12 to ~8 Ma, and finally stayed at a constantly low level after ~8 Ma, although community structure during the period remained stable as suggested by the unchanged pollen assemblages (Tang et al., 2011b).

4.3. Different vegetation isotopic patterns in Asian interior from monsoon influenced Asian areas

It is interesting to note that the most pronounced decrease of C_4 plants from ~12 to ~8 Ma inferred from our results (Fig. 3e) is at variance with what have been reported in the monsoon influenced Asian areas such as the Indian subcontinent and East Asia (An et al., 2005; Cerling et al., 1993; Cerling et al., 1997; Ding and Yang, 2000; Huang et al., 2007; Jia et al., 2003; Jiang et al., 2002; Morgan et al., 1994; Passey et al., 2009; Quade et al., 1989; Wang and Deng, 2005; Zhang et al., 2009). On the Indian subcontinent, $\delta^{13}C$ of ungulate teeth and fossil soil carbonates and organic matter from the Neogene Siwalik formation stretching through Pakistan, northwest India and Nepal shifts dramatically starting ca. 8–7 Ma, marking the displacement of largely C_3 vegetation, probably semi-deciduous forest, by C_4 grasslands (Cerling et al., 1993; Morgan et al., 1994; Quade et al., 1989; Quade et al., 1995). More recently, Huang et al. (2007) analyzed *n*-alkane in dust records which integrate plant leaf waxes from wide continental regions around west and southeast Asia and, to a lesser extent, East Africa. Their results revealed a significant C_4 contribution (~20%) at least at 11 Ma and a subsequent increase in C_4 contribution. In East Asia, the late Miocene C_4 plant expansion was also inferred from the $\delta^{13}C$ records of black carbon derived from terrestrial biomass burning deposited in the tropical South China Sea (Jia et al., 2003) and mammalian tooth enamel and carbonate in the north CLP or northeast to the CLP (Passey et al., 2009; Zhang et al., 2009). However, delayed expansions during the Plio-Pleistocene have also been suggested for some sites in the southern or western CLP (An et al., 2005; Ding and Yang, 2000; Jiang et al., 2002; Wang and Deng, 2005).

The C_4 expansion in the late Miocene both on the Indian subcontinent and in East Asia has been attributed to the monsoon intensification caused by the uplift of Tibetan Plateau which attained a critical elevation by that time (e.g., Passey et al., 2009; Quade et al., 1995). The asynchronous expansion among different sites in or around the CLP was recently interpreted as evidence for a north–south shift of the "steppe C_4 maximum" or a change in monsoon regime with the local wax and wane of the East Asian summer monsoon associated with the Plio-Pleistocene growth of the Tibetan Plateau (Passey et al., 2009; Zhang et al., 2009). In contrast to these monsoon regions, the Asian interior today is located to the north and northwest of the

Tibetan Plateau and in the center of Eurasian continent, where presently monsoon circulations cannot reach and the vegetation type is desert-steppe with minimal C_4 plants. However, fossil tooth height record and modeling experiments showed the relatively humid conditions of the Asian interior before 8–7 Ma (Fortelius et al., 2002; Tang et al., 2011a). Moreover, palynological and palaeobotanical studies of more than 60 cores and sections of the Tibetan Plateau revealed three meridional vegetation zones during the late Miocene: the subtropical broad-leaved forests in the south, the warm-temperate forests and shrub in the middle, and forest-steppe in the northern edge of the plateau (Tang and Shen, 1996), indicating the reach of the southerly marine moistures, perhaps analogous to today's monsoon moisture, to the northern Plateau, and very likely, to the Asian interior. After the late Miocene the scrub-steppe and desert-steppe gradually developed in the middle and northern Plateau (Tang and Shen, 1996), implying dying away of the marine moistures. Therefore, in spite of the different C_4 dynamics between the Asian interior and the monsoon regions, the uplift and growth of the Tibetan Plateau must have played an important role in shaping the different climate patterns for regions around the Plateau.

The marked C_4 decline from our results occurs from ~12 to ~8 Ma, which would suggest a distinct cooling period along with the drying trend according to the above discussion. This cooling period coincides with the global cooling trend that would reduce the amount of water vapor held in the atmosphere since the expansion of polar ice-sheets at ca. 14 Ma (e.g. Zachos et al., 2001). Regionally, the uplift and growth of the Tibetan Plateau during the Neogene would progressively block the southerly warm marine moistures to the Asian interior (Kent-Corson et al., 2009), hence enhancing the regional drying and cooling climate. Experiments with climate models also showed that the uplift reduced the land-average temperature by about 5 °C, with the maximum drop at the mid latitude (Kutzbach et al., 1993). The observed late Miocene decline of C_4 is consistent with the timing of a prominent tectonic uplift of the Tibetan Plateau indicated by, e.g., rapid accumulation of the molasse deposits along the northern edge of Tibetan Plateau (from 13.7 or 12 Ma to 9 Ma; Sun et al., 2005; Wang et al., 2003), increase in fossil tooth height suggestive of increasing aridity in Asian interior since 11–8 Ma (Fortelius et al., 2002), onset or intensification of Indian and East Asian monsoons at 9–8 Ma (An et al., 2001, and references therein), and a major reorganization of atmospheric circulation patterns at the NE margin of the Plateau with the post-12 Ma system similar to that of today (Dettman et al., 2003). The major transition of C_4 plant abundance at ~8 Ma also supports the assumption of Rea et al. (1998) that there would be a period of climatic (or vegetation) instability at around 7.7 Ma between two more stable periods in the dust source region. Therefore, the combined effects of the global cooling and regional mountain building during the late Miocene by reducing the strength of hydrologic cycle and increasing cold air masses from higher latitudes in the Asian interior (Tang et al., 2011b) would have caused a critical drying and cooling climate that reduce the regional C_4 abundances observed in this study. Our finding thus demonstrates a close association of regional C_4 evolution with the global climate change and the uplift and growth of the Tibetan Plateau in late Miocene in the Asian interior.

After the transition discussed above, the C_4 contribution has remained around 10% without major change. This suggests that the photosynthesis of local vegetation has not been responsive to the abrupt increase in dust flux since the Pliocene as indicated by our AR_{alkane} record as well as other works (Rea et al., 1998; Sun and An, 2005). This abrupt dust increase is more likely related to the enhanced uplift and growth along the northern and eastern margins of the plateau after 3.6 Ma (An et al., 2001; Zheng et al., 2000), which could further intensify the Plio-Pleistocene drying and cooling trend in combination with the Northern Hemisphere glaciation (An et al., 2001). The fact that vegetation photosynthesis is mute toward this marked Pliocene climate change may suggest that the previous cooling event during the late Miocene has resulted in a climatic threshold that depresses C_4 plant to a minimum, i.e., the temperatures were already too low to allow for drying to enhance the abundance of C_4, in the northern Tibetan Plateau. Hence we consider that the uplift and growth of the northern Tibetan Plateau during the late Miocene was a crucial event to the regional climate and vegetation; the associated distinct temperature drop shifted the central Asian vegetation to the type with steadily low abundance of C_4 plants.

5. Conclusions

Higher plant wax *n*-alkanes are successfully extracted from two North Pacific sediment cores at the ODP Site 1208 and Site 886, and are used to explore vegetation and climate changes in the source region of the Asian interior since the middle Miocene. Accumulation rates of leaf wax $C_{27+29+31}$ *n*-alkanes from the two sites show a general increasing trend, which coincides with the well documented climatic drying in the Asian interior. The records of isotopic enrichment factors of C_{29} *n*-alkane against atmospheric CO_2 ($\varepsilon_{C29-CO2}$) display coherent variation patterns, characterized by a prominent decreasing trend from ~12 to ~8 Ma and subsequently lower values since ~8 Ma. We interpret the higher $\varepsilon_{C29-CO2}$ values prior to ~8 Ma than those thereafter as evidence for higher abundance of C_4 plants (17.7 ± 5.3%) in the source region during the middle and early late Miocene. This scenario is opposite to what have been recorded in the monsoon influenced Asian areas where the late Miocene C_4 expansion occurred. The marked C_4 decline from ~12 to ~8 Ma inferred for the Asian interior coincides with the global cooling trend and is also concurrent with a prominent uplift and growth of the northern Tibetan Plateau. We consider that the significant temperature drop induced by the combined effects of global cooling and regional mountain building under the drying background in the Asian interior is responsible for the reduction of C_4 plants to a minimum (10.6 ± 3.9%) after ~8 Ma. Our results therefore highlight the need of future studies on different climatic and vegetational responses to the uplift of Tibetan Plateau in different parts of the East Asia.

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