Earth and Planetary Science Letters 321-322 (2012) 32–40

Contents lists available at SciVerse ScienceDirect

Earth and Planetary Science Letters

journal homepage: www.elsevier.com/locate/epsl

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

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ARTICLE INFO

Article history:
Received 19 July 2011
Received in revised form 28 December 2011
Accepted 29 December 2011
Available online 2 February 2012

Editor: P. DeMenocal

Keywords:
C_4 plant evolution
Asian interior
marine record
n-alkanes
North Pacific

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 ($17.7 \pm 5.3\%$) 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

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doi:10.1016/j.epsl.2011.12.044

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 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

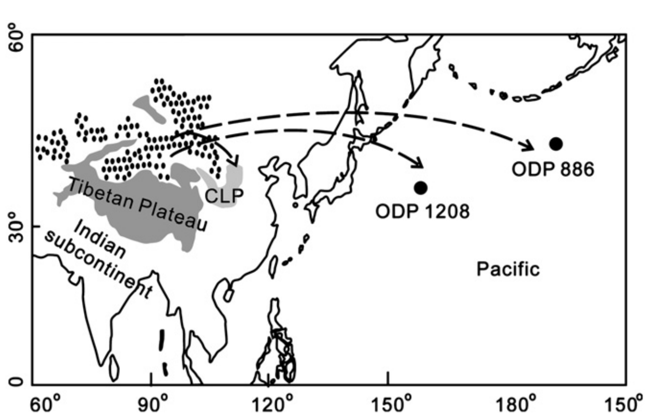

Fig. 1. Map of the North Pacific Ocean and Asian continent, showing high topography of >3000 m above sea level (dark gray area), desert distributions (dotted area), the Chinese Loess plateau (CLP, light gray area), and ODP Sites 1208 and 886. The dashed arrows visualize the track of modern dust transport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