Negative δ18O–δ13C relationship of pedogenic carbonate from northern China indicates a strong response of C3/C4 biomass to the seasonality of Asian monsoon precipitation

Shiling Yang⁎, Zhongli Ding, Xu Wang, Zihua Tang, Zhaoyan Gu

Key Laboratory of Cenozoic Geology and Environment, Institute of Geology and Geophysics, Chinese Academy of Sciences, Beijing 100029, China

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Evaluating how future climate changes may impact C3/C4 biomass in East Asia depends largely on the understanding of the relationship between past C3/C4 variations and Asian monsoon circulation. The glacial–interglacial variations in C3/C4 biomass have been readily ascribed to the summer monsoon. However, the internal processes governing the link of C3/C4 vegetation to the Asian monsoon have not been clearly described. Here we present isotopic results of pedogenic carbonate from northern China for the Holocene, the last and penultimate interglacial periods. Comparison of the observed and predicted δ18O values of modern soil carbonate from gravelly soils suggests that pedogenic carbonate forms mainly in warm, rainy season. Carbonate nodules from the Chinese loess demonstrate a distinct negative δ18O–δ13C relationship and a wider scatter of isotopic values in the southern Loess Plateau than in the northern part. By combining rainfall, δ18O of precipitation and the peak of C3 and C4 plant metabolism, we develop a conceptual model to explain the isotopic signatures of the carbonate nodules. Our model shows that a narrowly-focused season of monsoon precipitation at a specific site produces low δ18O values of soil water and simultaneously favors C4 over C3 plants. Our model further suggests that the scattered isotopic values of soil carbonate reflect a strong summer monsoon while the focused values indicate a weak summer monsoon. δ13C values of soil carbonate indicate a striking pattern of northward-increasing C4 vegetation for the last interglacial, while a flat spatial pattern is seen for the penultimate interglacial and the Holocene. It is inferred that the summer monsoon was stronger during the last interglacial than during the penultimate interglacial and the Holocene, leading to a northward displacement of C3 forest ecosystems into the southern Loess Plateau. In addition, an in-phase relationship between intra-nodule δ13C and δ18O values suggests a strong and possibly rapid response of C3/C4 biomass to the seasonality of Asian monsoon precipitation. In this context, if the last interglacial period (MIS 5) is taken as an analog for the projected near future, then C3 plants may be favored in the south while C4 plants may be efficient in the north.

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1. Introduction

Plants use two principal biosynthetic pathways to fix carbon, the C3 and C4 cycles. C3 plants have δ13C values ranging from −22‰ to −34‰, and C4 plants from −10‰ to −14‰. (Deines, 1980; O’Leary, 1988; Farquhar et al., 1989). Recently, many modeling studies have projected increased monsoon precipitation in East Asia under CO2-induced global warming (e.g., Kimoto, 2005; Kripalani et al., 2007; Sun and Ding, 2010). In this scenario, the regional C3/C4 biomass is expected to change, which would impact the global carbon cycle (Still et al., 2003) and agricultural production (Leakey, 2009; Liu et al., 2010) in densely populated East Asia. As such, it is important to evaluate how future monsoon changes may impact regional C3/C4 biomass.

Past C3/C4 vegetation records from the Chinese Loess Plateau may provide valuable clues on the composition of future terrestrial ecosystems. Generally, lower atmospheric pCO2, higher temperature and enhanced summer precipitation favor C4 over C3 plants (Sage et al., 1999). Recent studies have shown that C4 plants declined in glacials and increased in interglacials, with its cause being ascribed to temperature (Gu et al., 2003; Zhang et al., 2003) or both temperature and precipitation seasonality (Vidic and Montañez, 2004; An et al., 2005; Liu et al., 2005). Whichever the dominant cause, it is clear that the C3/C4 variations in East Asia are closely connected to the monsoon climate. However, the internal processes linking the C3/C4 changes to the East-Asian monsoon system have not been clearly described. This is because C3/C4 biomass and the monsoon signal are recorded in different geologic archives, the former reconstructed from the δ13C value of soil organic matter, and the latter from

⁎ Corresponding author at: Key Laboratory of Cenozoic Geology and Environment, Institute of Geology and Geophysics, Chinese Academy of Sciences, 19 Beituchengxi Road, Beijing 100029, China. Tel.: +86 10 82988526; fax: +86 10 62010846.
E-mail address: yanshi@mail.iiggcas.ac.cn (S. Yang).

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paleoclimate proxies such as magnetic susceptibility (Gu et al., 2003; Zhang et al., 2003; Vidic and Montañez, 2004; Liu et al., 2005).

Warm-season precipitation is a defining feature of the summer monsoon circulation. The $\delta^{18}O$ value of precipitation ($\delta^{18}O_p$) integrates all aspects of atmospheric transport from source to sink and shows a strong seasonal variation in response to the monsoon system (Rozanski et al., 1993; Araguás-Araguás et al., 1998; Johnson and Ingram, 2004; Vuille et al., 2005). Thus $\delta^{18}O_p$ is ultimately a recorder of the summer monsoon system. Pedogenic carbonate nodules are abundant at the base of interglacial paleo-loess within Chinese loess (Liu, 1985). Their carbon ($\delta^{13}C_C$) and oxygen isotope ($\delta^{18}O_C$) composition record the proportion of C3/C4 vegetation and the $\delta^{18}O$ value of soil water (ultimately derived from meteoric water), respectively (Wang and Zheng, 1989; Han et al., 1997; Wang and Follmer, 1998; Ding and Yang, 2000). Therefore, investigation of $\delta^{18}O$–$\delta^{13}C$ relationship of carbonate nodules may have great potential to explore the monsoon-C3/C4 vegetation linkage, which is central to the prediction of C3/C4 response to the projected climate change.

In this study, we first investigate the $\delta^{18}O_p$ values in modern soils at two sites around the Loess Plateau, where the continuous $\delta^{18}O_p$ data are available from the Global Network of Isotopes in Precipitation (GNIP) (IAEA/WMO, 2006), in order to identify the season of carbonate formation. We then present the temporal and spatial isotopic results of interglacial carbonate nodules from Chinese loess, the $\delta^{18}O$–$\delta^{13}C$ relationship, and examine the causes of these patterns.

2. Setting, materials, and methods

Fifty-nine samples of modern soil carbonate were taken from gravelly soils on river terraces at Baotou and Yinchuan (Fig. 1A). Gravels in these deposits are dominated by dioritic amphibolite and some metasedimentary rocks. Carbonate clasts are rare to absent, thus insuring against detrital contamination of our secondary carbonate samples by local bedrock. No surface soil horizons (A horizons) show visible darkening from organic matter. The soil carbonate is characterized by thin, discontinuous to semi-continuous coatings on pebbles at both sites. According to the classification scheme of Gile et al. (1966), the development of carbonate is assigned to Stage I to weak Stage II and is assumed to require $10^5$ to $10^6$ years.

Carbonate nodules, a common form of pedogenic carbonate in the Chinese loess, were collected from 22 loess sections (Fig. 1A). These sites lie along two approximately north–south loess transects, stretching from Hongde to Yangling and Hengshan to Lantian. At present, the mean annual precipitation and temperature are ~400 mm and ~8.5 °C in the north, the values in the south being ~600 mm and ~13.5 °C. Most sections consist of the loess (L)–soil (S) sequence S0, L1, S1, L2, and S2 (Fig. 2), although over 30 loess–soil couplets have been identified in complete Chinese loess sequences (Rutter et al., 1991; Ding et al., 1993, 1999b; Yang and Ding, 2010). The loess units L1 and L2 were deposited during the last and penultimate glacial periods, respectively. Both L1 and L2 are yellowish in color and massive in structure. Previous studies (Kukla, 1987; Ding et al., 2002; Lu et al., 2007) have shown that L1 is correlated with marine isotope stages (MIS) 2 to 4, and the L2 loess unit with MIS 6. The Holocene soil, S0, is dark in color because of its relatively high organic matter content, and has been partly or totally eroded, or disturbed by agricultural activities at most sites. The soil units S1 and S2 developed in the last and penultimate interglacial periods and correlate with MIS 5 and 7, respectively (Kukla, 1987; Ding et al., 2002; Lu et al., 2007). Both of the soils are brownish or reddish in color, and have an A–B–C horizon sequence. Soil unit S2 is composed of two soils (S2-1 and S2-2) and a thin intervening loess horizon. Based on a stacked orbital timescale of Chinese loess (Ding et al., 2002), the soil units S0, S1, S2-1 and S2-2 formed in the periods 11–0 ka, 128–73 ka, 219–190 ka, and 245–234 ka, respectively. Details of site locations and lithostratigraphy are given in Yang and Ding (2008).
Fig. 2. Stratigraphic column and median grain size (Md) for the Hongde–Yangling and Hengshan–Lantian transects, and correlation with a stacked benthic δ¹⁸O record (Lisiecki and Raymo, 2005) and a stacked Chinese loess particle size record (Chiloparts) (Ding et al., 2002). Interglacial paleosols (shaded zones) are characterized consistently by finer particle sizes, compared to the loess horizons above and below them. Grain size was measured with a SALD-3001 laser diffraction particle analyzer. The particle analytical procedures were as detailed by Ding et al. (1999a).
We used mean weighted $\delta^{18}$O and local mean temperatures to predict the mean $\delta^{18}$O values of pedogenic carbonate ($\delta^{18}$Ocarb) for different periods. Monthly mean data for weighted $\delta^{18}$O, temperature, and precipitation are shown in Fig. 1B. The fractionation factor ($\alpha$) between calcite and water was calculated using the equation of Kim and O’Neil (1997): $1000\ln(\text{Calcite–H}_2\text{O}) = 18.03 \cdot (10^3 T^{-1}) - 32.42$, where $T$ is in Kelvin (Kim and O’Neil, 1997). Considering significant seasonal fluctuations in temperature and precipitation (Fig. 1B), the predicted $\delta^{18}$Ocarb values are calculated for warm, rainy season (June to September), cold, dry season (October to May), and annual period (Table 1). Results show that the observed $\delta^{18}$Ocarb values below depth of 50 cm for both profiles fall closer to the predicted values for warm, rainy season than those for annual or cold, dry period (Fig. 3), indicating that pedogenic carbonate in northern China forms mainly in warm, rainy season.

The modern climate of East Asia is characterized by seasonal alternations of wet, warm summer monsoon and dry, cold winter monsoon (Fig. 1). The precipitation of pedogenic carbonate results from supersaturation of the soil solution with respect to calcite, mainly associated with dewetting of soil by evapotranspiration (Quade et al., 1989) and/or decrease in soil pCO$_2$ (Breecker et al., 2009). Therefore, wet–dry cycles are required for pedogenic carbonate formation (Breecker et al., 2009). Chinese loess is composed mainly of loosely cemented silt (Liu, 1985; Liu and Ding, 1998), which allows rainwater to infiltrate quickly (Chen et al., 2008). The infiltrated rainwater mainly affects the moisture content in the near-surface soil (0 to 3 m depth) (Chen et al., 2008). Recent studies have shown that the temporal changes in soil moisture are closely related to the seasonal precipitation (Fu et al., 2003; Chen et al., 2008; Guan et al., 2009; Hu et al., 2010), and the soil moisture content decreases considerably during dry intervals between rain events (Chen et al., 2008). All these conditions favor the formation of soil carbonate in the season when the East–Asian summer monsoon prevails.

4. $\delta^{18}$O–$\delta^{13}$C relationship for carbonate nodules from the Chinese loess

4.1. Intra-nodule (temporal) changes in $\delta^{13}$C and $\delta^{18}$O values

Microscopic examination of thin sections reveals a brown micritic ground mass for the large nodule, throughout which are dispersed detrital grains mainly of quartz and feldspar. These detrital grains, coarse silt in size, comprise ~10% of the nodule volume. The isotopic results (Fig. 4A, B) show significant intra-nodule (temporal) variations, with $\delta^{13}$C values (VPDB) ranging from −4.2% to −6.8% and $\delta^{18}$O values from −8.6% to −10.2%. A striking feature is that $\delta^{18}$O values vary inversely (R = 0.85) with $\delta^{13}$C values (Fig. 4B, C). The growth center of the nodule is hard to find, as it displays neither growth layers (Fig. 4A) nor unambiguous symmetry of isotopic curves (Fig. 4B).

4.2. Spatial changes in $\delta^{13}$C and $\delta^{18}$O values

The isotopic values for the nodules from the transect sites show much larger variations than the intra-nodule changes (Fig. 4B, D, E), $\delta^{18}$O (Fig. 1B) and modern surface temperature (Fig. 1B) to predict the mean $\delta^{18}$O values for pedogenic carbonate at Baotou and Yinchuan, assuming the fractionation factor ($\alpha$) between calcite and water of 1000ln(calcite–H$_2$O) = 18.03 (10$^3$ T$^{-1}$) − 32.42, where $T$ is in kelvins (Kim and O’Neil, 1997). Considering significant seasonal fluctuations in temperature and precipitation (Fig. 1B), the predicted $\delta^{18}$O values are calculated for warm, rainy season (June to September), cold, dry season (October to May), and annual period (Table 1). Results show that the observed $\delta^{18}$O values below depth of 50 cm for both profiles fall closer to the predicted values for warm, rainy season than those for annual or cold, dry period (Fig. 3), indicating that pedogenic carbonate in northern China forms mainly in warm, rainy season.

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Table 1

<table>
<thead>
<tr>
<th>Site</th>
<th>Period</th>
<th>Mean precipitation (mm)</th>
<th>Mean temperature (°C)</th>
<th>Mean weighted $\delta^{18}$O$_{pb}$ (‰, VSMOW)</th>
<th>1000ln($\alpha$)</th>
<th>$\alpha$</th>
<th>Predicted $\delta^{18}$O$_{carb}$ (‰, VSMOW)</th>
<th>Predicted $\delta^{18}$O$_{carb}$ (‰, VPDB)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Baotou (40.72°N, 109.81°E)</td>
<td>Annual</td>
<td>307</td>
<td>6.9</td>
<td>7.66</td>
<td>31.9614</td>
<td>0.0325</td>
<td>24.57</td>
<td>−6.14</td>
</tr>
<tr>
<td>1101 m a.s.l.</td>
<td>June to September</td>
<td>237</td>
<td>20.0</td>
<td>7.41</td>
<td>29.0843</td>
<td>0.0295</td>
<td>21.89</td>
<td>−8.75</td>
</tr>
<tr>
<td>October to May</td>
<td>70</td>
<td>0.3</td>
<td>8.50</td>
<td>33.5153</td>
<td>0.0341</td>
<td>25.30</td>
<td>−5.44</td>
<td></td>
</tr>
<tr>
<td>Yinchuan (38.52°N, 106.03°E)</td>
<td>Annual</td>
<td>193</td>
<td>8.8</td>
<td>6.94</td>
<td>31.5725</td>
<td>0.0320</td>
<td>24.87</td>
<td>−5.86</td>
</tr>
<tr>
<td>1151 m a.s.l.</td>
<td>June to September</td>
<td>138</td>
<td>20.6</td>
<td>6.87</td>
<td>28.9587</td>
<td>0.0294</td>
<td>22.31</td>
<td>−8.34</td>
</tr>
<tr>
<td>October to May</td>
<td>55</td>
<td>2.8</td>
<td>7.08</td>
<td>32.9179</td>
<td>0.0335</td>
<td>26.15</td>
<td>−4.62</td>
<td></td>
</tr>
</tbody>
</table>

We used mean weighted $\delta^{18}$O values of local precipitation ($\delta^{18}$O$_{pb}$) and local mean temperatures to predict the mean $\delta^{18}$O values of pedogenic carbonate ($\delta^{18}$O$_{carb}$) for different periods. Monthly mean data for weighted $\delta^{18}$O, temperature, and precipitation are shown in Fig. 1B. The fractionation factor ($\alpha$) between calcite and water was calculated using the equation of Kim and O’Neil (1997): $1000\ln(\text{Calcite–H}_2\text{O}) = 18.03 \cdot (10^3 T^{-1}) - 32.42$, where $T$ is in kelvins (K) = °C + 273.15. The predicted $\delta^{18}$O$_{carb}$ values were then obtained using the formula $\alpha = (1000 + \delta^{18}$O$_{carb})/(1000 + \delta^{18}$O$_{pb}$). The $\delta^{18}$O$_{carb}$ values expressed in VSMOW were converted to the VPDB scale using the relationship $\delta^{18}$O$_{VPDB} = 0.97002 \cdot \delta^{18}$O$_{VSMOW} - 29.985$. (Coplen et al., 1983).
with the δ$^{13}$Ccc (VPDB) values ranging from −1.5‰ to −9.1‰ and the δ$^{18}$Ocp (VPDB) values from −7.0‰ to −11.1‰. During the last interglacial (S1), lower δ$^{13}$Ccc values occurred in the south (34°–36°N) than in the north (36°–38°N), showing a clear north–south gradient, while a flat spatial pattern is seen for the penultimate interglacial (S2-1 and S2-2) (Fig. 4D). For the Holocene (S0), the southern sites show slightly higher δ$^{13}$Ccc values than the central sites (Fig. 4D). The δ$^{18}$Ocp values are generally higher in the south (34°–36°N) than in the north (36°–38°N) for S1 and S2 times, while slightly lower δ$^{18}$Ocp values occur in the south than in the central part for S0 period (Fig. 4E). Both δ$^{13}$Ccc and δ$^{18}$Ocp values are more scattered in the south (34°–36°N) than in the north (36°–38°N). Again, a good inverse correlation (R = 0.56) between δ$^{13}$Ccc and δ$^{18}$Ocp values is observed (Fig. 4F).

5. Mechanism for the negative δ$^{18}$O–δ$^{13}$C relationship

Isotopic results of pedogenic nodules from the Chinese loess show a negative relationship between δ$^{13}$Ccc and δ$^{18}$Ocp values, i.e. the lower δ$^{18}$Ocp values the higher C3 component. The three factors controlling the δ$^{18}$Ocp variations, namely the δ$^{18}$Ocp, soil temperature, and evaporation conditions, are discussed in detail as below.

If soil temperature were the major factor, then the 1.5‰ intranodule variations of δ$^{18}$Ocp (Fig. 4B) would have resulted from a −7 °C temperature change (Kim and O’Neil, 1997). Assuming a maximum length of growth period (55 ka) for the large nodule from Ganquan (Fig. 4A), its isotopic data may have a time resolution of less than 1000–1500 years. Such an amplitude change in summer temperature at millennial to centennial scales is unlikely within relatively stable interglacial periods (Ding et al., 1999a). In addition, given the small spatial changes in both mean annual and summer δ$^{18}$Ocp values over the Loess Plateau (Liu et al., 2008; Figs. 1B and 5B, C), the lower δ$^{18}$Ocp values in the north (36°–38°N) for S2 and S1 times would indicate a higher temperature in the north than in the south (Kim and O’Neil, 1997), which is inconsistent with both the modern and past trends of increasing temperature southward (Yang and Ding, 2003). These lines of evidence show a minor role of temperature in the large variations of δ$^{18}$Ocp values (Fig. 4B, E).

Increased evaporation due to enhanced aridity would produce high δ$^{18}$Ocp values and low plant density, and vice versa. Thus a positive δ$^{18}$Ocp–δ$^{13}$Ccc relationship is expected due to the significant contribution of 13C-enriched atmospheric CO2 to δ$^{13}$Ccc values, like the cases of soil carbonate from many of the world’s deserts (Quade et al., 2007), rather than the observed negative one. Furthermore, a northward increase in aridity has been found for both glacials and interglacials (Yang and Ding, 2003). Thus the δ$^{18}$Ocp values are expected to be higher in the north than in the south. On the contrary, high δ$^{18}$Ocp values are observed in the south for S2 and S1 times (Fig. 4E). Thus evaporation may also play a minor role in the large variations of δ$^{18}$Ocp values (Fig. 4B, E).

Modern δ$^{18}$Ocp values exhibit a large seasonal variation (Fig. 5) that is crucial for the understanding of the δ$^{18}$Ocp–δ$^{13}$Ccc relationship. The δ$^{18}$Ocp data show two features clearly (Fig. 5). (1) In the summer monsoon domain (Fig. 5C, D), low δ$^{18}$Ocp values occur in summer due to amount effect, overshadowing the dependence of δ$^{18}$Ocp on temperature (Araguás-Araguás et al., 1998; Johnson and Ingram, 2004; Vuille et al., 2005). This effect is visible as a distinct dip in δ$^{18}$Ocp values during July to September in the monsoon-influenced southern sites (Fig. 5C, D). (2) The summertime “dip” decreases with distance inland, in the same direction that summer monsoon penetration diminishes (Figs. 1
and 5). In this context, the summertime dip in δ18O values is a distinctive characteristic of summer monsoon precipitation.

Although most of the annual precipitation occurs in summer on the Chinese Loess Plateau, the significant rainy period is shorter and more concentrated in the north than in the south (Fig. 1B). Two examples are shown (Fig. 1B): (1) the ratio of summer (June to September) to annual rainfall decreases from 70% at Huanxian to 59% at Yangling, and (2) at Huanxian, there are only three months (July to September) with over 50 mm rainfall, whereas at Yangling there are six months (May to October) with over 50 mm. Under these climate conditions, the duration of carbonate formation and plant growing season is longer in the south than in the north, as shown in a conceptual model (Fig. 6).

For a specific site, the peak of C3 and C4 plant metabolism differs seasonally (Ode et al., 1980), thus the pedogenic carbonate formed in summer may record the signals of relatively low δ18O and high C4 component (high δ13C values) (Fig. 6), while that formed in spring and fall may document the signals of relatively high δ18O and high C3 component (low δ13C values) (Fig. 6). These cases result in the negative δ18Occ–δ13Cc relationship. For a spatial view of the Loess Plateau, the pedogenic carbonate in the south (Fig. 6B) may record the isotopic signatures of vegetation and precipitation for a longer period than that in the north (Fig. 6A), leading to a wide scatter of isotopic values in the south. It should be noted that the lowest δ18O values on the Loess Plateau occur in winter (Fig. 5B, C), however, the extremely low rainfall (<10 mm/month) can hardly cause the dissolution of carbonate minerals, much less the carbonate reprecipitation (Royer, 1999).

A negative δ18O–δ13C relationship has also been found in horse tooth enamel from northwestern China for the Pleistocene, and was attributed to the summer monsoon activity (Biasatti et al., 2010). These observations strongly support our findings. As pedogenic carbonate forms mainly in summer, a period of C4 plant growth (Fig. 6), its δ13C value is biased toward a C4 signal. Therefore the C4 biomass estimated from δ13Cc values should be regarded as upper limits. The negative δ18Occ–δ13Cc relationship suggests that a narrowly-focused season of monsoon precipitation at a specific site produces low δ18O values and simultaneously favors C4 over C3 plants and vice versa. Today, the summer monsoon simultaneously becomes weaker and more focused from southeast to northwest (Fig. 1B). It follows from this that, within the marginal zone of the summer monsoon, the scattered isotopic values of soil carbonate reflect a relatively strong summer monsoon (Fig. 6B) while the focused values indicate a weak summer monsoon (Fig. 6A). In contrast to the soil organic matter that records long-term annual average of the floral biomass (Wang and Follmer, 1998), the pedogenic carbonate is therefore a robust tool to reconstruct the seasonality of Asian monsoon precipitation.

6. Latitudinal patterns of C3/C4 vegetation and summer monsoon strength for different interglacial periods

The modern distribution of C3/C4 plants in East Asia is closely related to summer monsoon intensity. From southeast to northwest of China, the vegetation changes from broadleaf deciduous forest in a strong monsoon area to steppe in an intermediate monsoon region, and then to desert steppe in a weak monsoon area (Hou, 1983; Passey et al., 2009). Carbon isotope composition of soil organic matter (Rao et al., 2008) and phytoliths (Lü et al., 2000) from surface soils reveal a C3 maximum zone between 31°N and 40°N in east China. At present, the Chinese Loess Plateau is characterized by mixed C3–C4 steppe, with C3 forest dominant to the south of the Plateau, and C4
Two lines of evidence support the strengthened summer monsoon during the last interglacial. First, the soil unit S1 has stronger pedogenic characteristics than S2 and S0, as indicated by its better developed soil structure (Rutter et al., 1991; Ding et al., 1999b). Second, pollen studies have shown that forest (C3 ecosystems) occurred in the southernmost Loess Plateau during a short interval of the last interglacial (S1) (Sun et al., 1997), which well explains the northward increase in the $\delta^{13}C_{cc}$ values. The strengthened summer monsoon during the last interglacial (MIS 5) may be causally related to a decrease in global ice volume, as indicated by the sea level records (Siddall et al., 2007). The enhanced summer monsoon resulted in high precipitation and long rainy season during the last interglacial, which favored C3 forest ecosystems at least on the southernmost Loess Plateau. In this context, if the last interglacial stage (MIS 5) is referenced as an analog for near-future warming (Kopp et al., 2009), the C3 crops (e.g., wheat and soybeans) may be favored in the south while the C4 crops (e.g., maize, millet, and sorghum) may be efficient in the north.

7. A rapid response of C3/C4 vegetation to the summer monsoon variations?

In arid and semi-arid ecosystems, plant productivity responds instantaneously or quasi-instantaneously to pulses of precipitation, which is known as the ‘Pulse-Reserve’ paradigm (Noy-Meir, 1973; Reynolds et al., 2004). According to this paradigm, pulses of precipitation trigger primary production and result in reserves of carbon and energy that accumulate in seeds, storage organs, etc., and these reserves are able to persist through dry interpulse periods.

To date, there are no precise age constraints for carbonate nodules owing to the lack of reliable dating methods. As mentioned earlier, the isotopic data of the large nodule (Fig. 4A, B) may have a time resolution of less than 1000–1500 years. Since the processes of soil carbonate formation are similar to those of stalagmite formation, the in-phase relationship between intra-nodule $\delta^{18}O$ and $\delta^{13}C$ values (Fig. 4B) suggests a strong and possibly rapid response of C3/C4 biomass to the seasonality of Asian monsoon precipitation on the Loess Plateau. This contention is supported by the finding of Warne et al. (2010) that the summer monsoonal rains in the Chihuahuan desert trigger a pulse of C4 plant production.

8. Conclusions

Isotopic study of modern soil carbonate shows that pedogenic carbonate in northern China forms mainly in warm, rainy season, when the East-Asian summer monsoon prevails. Carbonate nodules from the Chinese loess show a distinct negative $\delta^{18}O$–$\delta^{13}C$ relationship and a wider scatter of isotopic values in the southern Loess Plateau than in the northern part. In East Asia, $\delta^{18}O$ values of modern meteoric water decrease during summer monsoon rainy season and this summertime dip is a distinctive characteristic of summer monsoon precipitation. By combining rainfall, $\delta^{18}O$ of precipitation and seasonal difference in the peak of C3 and C4 plant metabolism, we develop a model to explain the isotopic signatures of the carbonate nodules. Our model suggests that a narrowly-focused season of monsoon precipitation at a specific site produces low $\delta^{18}O$ values and simultaneously favors C3 over C4 plants, leading to a negative $\delta^{18}O_{cc}$–$\delta^{13}C_{cc}$ relationship. Our model further indicates that, within the marginal zone of the summer monsoon, the scattered isotopic values of soil carbonate reflect a relatively strong summer monsoon while the focused values indicate a weak summer monsoon. The pedogenic carbonate is therefore a robust tool to reconstruct the seasonality of Asian monsoon precipitation.

The $\delta^{13}C_{cc}$ records show a striking pattern of northward-increasing C4 vegetation for the last interglacial (S1), while a relatively flat spatial gradient of C3/C4 biomass is seen for the penultimate

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Fig. 6. Conceptual model for seasonal-bias in the formation of pedogenic carbonate on the Chinese Loess Plateau. A) Pedogenic carbonate formation on the northern Loess Plateau (a region of weak summer monsoon). B) Pedogenic carbonate formation on the southern Loess Plateau (a region of relatively strong summer monsoon). The solid and dashed lines indicate monthly mean $\delta^{18}O$ of precipitation ($\delta^{18}O_p$) and rainfall, respectively. The shaded and dotted areas indicate C3 and C4 growing seasons, respectively. Note the higher rainfall, longer rainy season, and longer growing seasons in the south (B) than in the north (A).
interglacial (S2-1 and S2-2) and the Holocene (SO). We infer a stronger summer monsoon (higher precipitation and longer rainy season) during S1 time than during S2 and S0 times, which caused a northward displacement of C3 forest ecosystems into the southern Loess Plateau during the last interglacial. In addition, the intra-nodule isotopic data show an in-phase relationship of δ18O and δ13C values, suggesting a strong and possibly rapid response of C3/C4 biomass to the seasonality of the last interglacial. During the last interglacial, C3 plants may be favored in the south while C4 plants may be efficient in the north.

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