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Research Paper

Radiocarbon age anomalies of land snail shells in the Chinese Loess Plateau

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A B S T R A C T

In the Chinese Loess Plateau, land snail shells are often the only material available for dating in paleoenvironmental and archaeological research. However, the geochronological suitability of land snail shells is limited because of poor knowledge about their deposition dynamics, particularly with regards to the incorporation of inorganic carbonate and the resulting age anomalies. To evaluate the factors controlling these age anomalies, radiocarbon and stable carbon analyses were carried out on surface soils, as well as the shells and organic bodies of different modern snail species from different ecological habitats. The results showed that all specimens were depleted in ^{14}C, indicating the influence of inorganic, radiocarbon-free carbonate on the ^{14}C-activity of the snail shells. The apparent ^{14}C-deficiencies and the resultant age anomalies of both the *Cathaica* and the *Bradybaena* snail shells were within close ranges across the Chinese Loess Plateau, indicating that the shells of these species could, after corrections for radiocarbon anomalies, provide reliable age estimates. The apparent ^{14}C-deficiencies were closely associated with the ecological habitats of the snails. The shells of the ground-dwelling *Bradybaena* had the smallest age offsets (533 ± 150 a), followed grass-dwelling *Cathaica* (1107 ± 138 a) and *Cathaica* living on trees (1550 ± 345 a). These results suggest that the availability of calcium in the respective ecological habitats is an important factor in explaining the apparent ^{14}C-deficiencies. The influence of carbonate on the stable carbon isotope composition of shells is overwhelmed by the organic diets of snails, making $\delta^{13}C$ unsuitable for identifying and correcting shell age anomalies. The radiocarbon activities of surface soils (A_{calc}) increase with weathering intensity. Thus, a significant uncertainty could be caused by assuming that A_{calc} is zero when estimating the proportions of different carbon sources in shells, as has been the case in most previous studies.

1. Introduction

Land snail shells are commonly preserved in various terrestrial sediments and are often the only material available for dating in paleoenvironmental, geological, and archaeological investigations. Nevertheless, the use of such samples as ^{14}C dating materials is restricted by the well-documented age anomalies of aragonite shells, which are thought to occur as a result of snails incorporating ^{14}C-free carbon (Goodfriend and Stipp, 1983; Goodfriend, 1987; Pigati et al., 2004, 2010; Quarta et al., 2007; Romaniello et al., 2008; Romaniello and Mastronuzzi, 2008; Xu et al., 2010). Moreover, the amplitudes of age anomalies vary among different species and regions. Early studies showed that almost all of the shell carbonate from large snail taxa had ^{14}C-deficiencies (Rubin et al., 1963; Tamers, 1970; Goodfriend and Stipp, 1983; Goodfriend and Hood, 1983; Goslar and Pazdur, 1985; Yates, 1986; Goodfriend, 1987; Zhou et al., 1999). The minute *Vallonia* from the late-Pleistocene strata in the southern Great Basin yielded ^{14}C dates consistent with the ^{14}C ages of carbonized woods (Brennan and Quade, 1997). However, a study in southern Arizona showed that the radiocarbon activity of *Vallonia cyclophorella* was obviously influenced by limestone (Pigati et al., 2004). Recently, a systematic analysis of small terrestrial gastropod shells from North America indicated that approximately 78% of sampled shell aliquots were not affected by limestone or other carbonate rocks and that the remaining samples contained only 5–10% dead carbon (Pigati et al., 2010).

China's widespread loess deposits contain a continuous record of eolian activity in central Asia. Such a record of environmental change is equaled only by deep ocean basins, where sedimentation rates typically are one to two orders of magnitude less than in the Chinese loess region (Porter, 2001). However, the lack of suitable

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dating materials in the loess region, in particular, those that can produce absolute ages, limits the use of loess deposition records in further studies on the underlying mechanisms of climate change in China and its association with global climate changes.

The advance and development of luminescence dating has helped to refine loess chronostratigraphy, but serious difficulties have often been encountered when attempting to establish accurate loess chronologies (Zhou et al., 2010). There seems to be growing evidence for the disagreement between the obtained luminescence age estimates and the expected ages from loess sections with clear stratigraphy (Buylaert et al., 2007, 2008; Qin and Zhou, 2007). Consequently, further understanding of luminescence signals, and testing and validation of the techniques are needed before luminescence dating may provide independent accurate chronologies for loess deposits (Roberts, 2008). Independent, absolute age estimates are especially important to check and test the reliability of luminescence techniques.

Land snail shells are well preserved in loess sediments and are often the only material available with the potential for providing relatively precise independent dating of loess deposits. To constrain the dead carbon problem, we performed preliminary research on live snails and found that *Cathaica* consistently incorporate dead carbon from soil carbonate, implying that snail shells have good potential as a radiocarbon material in the Chinese Loess Plateau (Xu et al., 2010). However, this previous study was limited to one genus (*Cathaica* dwelling on grass). It is far from certain whether the conclusions from this study can be extrapolated to other species.

In the present study, we systematically analyzed live snails from different ecological habitats and surface soils collected across the Chinese Loess Plateau. The radiocarbon activities and $\delta^{13}C$ of both the bodies and shells of live snails were measured. The main purpose of this study was to evaluate the age anomalies of the snails and factors controlling these anomalies in the Chinese Loess Plateau by analyzing proportions of different source carbon in the shells.

2. Materials and methods

The study area is located in the Chinese Loess Plateau. Loess parent material originates in the desert basins that constitute the primary source of dust in northwestern China. The climate is dominated by the Asian monsoon, which is characterized by dry, cold winters and humid, warm summers. Precipitation decreases in a northwest direction with increasing distance from the tropical Pacific Ocean, the main source of water vapor in the region. In contrast, the deposit rate of loess increases to the northwest because of high intensive wind activities and short distances between dust sources and sinks. The low dust accumulation rate and increased precipitation result in relatively strong pedogenesis in the southeast part of the plateau. Across the plateau, vegetation is dominated by grass, and trees grow only occasionally in the valley bottoms or other low areas.

The live land snails used in this study were collected mainly from the Chinese Loess Plateau (Fig. 1). Three genera with four ecological habitats, representing common large species in the plateau, were collected: (1) *Cathaica* dwelling on trees; (2) *Cathaica* dwelling on grass; (3) *Bradybaena* dwelling on ground; and (4) *Plectotropis* dwelling on loess walls and cliffs. *Cathaica* are composed primarily of two species: *pulveratricul*a and *pulveratrix*, which have no obvious difference in their dwelling habitat. To reduce the effect of individual anomalies, each sample consists of at least 40 adults. At the same time, surface soils were sampled in 10 locations to determine the radiocarbon activity of soil carbonates. With the exception of samples from Jingbian and Sanmenxia, all soil samples were collected at the same sites where the snails were collected.

The living snails were drowned in boiled deionized water, and the soft parts were separated from the shells using forceps. To avoid contamination during sample preparation, the shells were crushed into pieces during pretreatment to minimize the potential for adsorption of atmospheric ^{14}C. The shell pieces were treated following the method described by Pigati et al. (2004). The shells

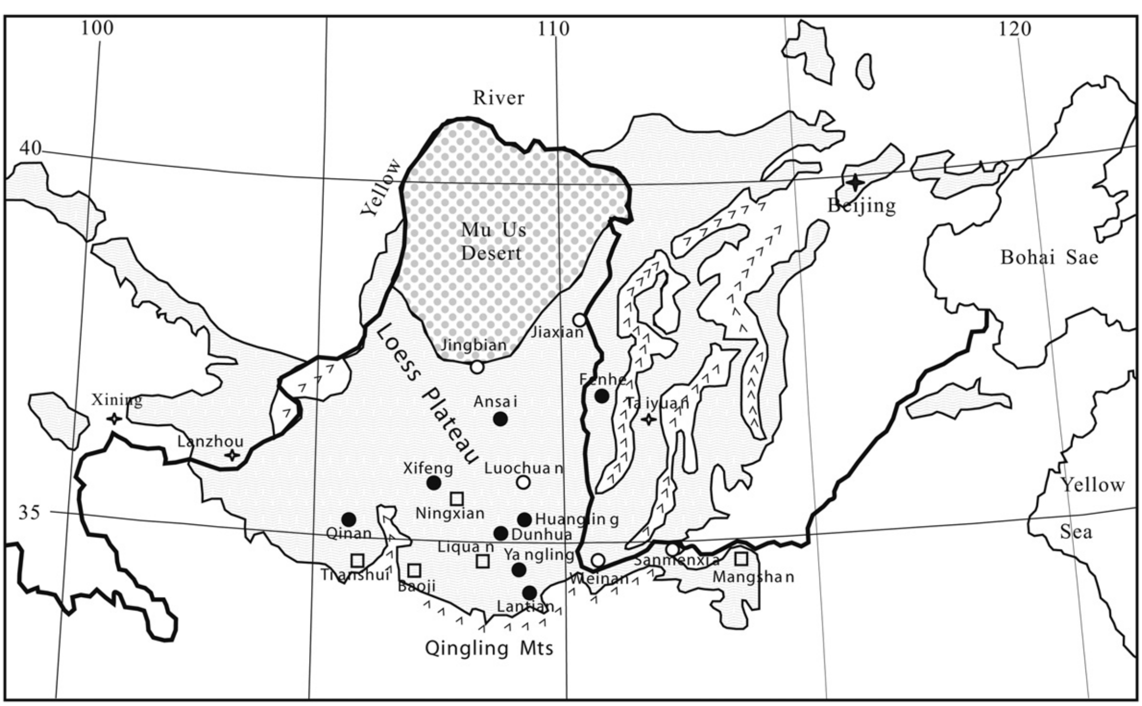

Fig. 1. Locations of the study areas and sampling sites in Chinese Loess Plateau. Open squares represent samples for both snails and surface soils, while solid and open circles indicate the sites from which only snails or surface soils were collected, respectively.

were reacted with 6% NaOCl for 48–72 h to remove organic matter, washed repeatedly, and sonicated for 5–10 min to remove adhering materials. The cleaned samples were then briefly washed with 0.01 HCl to remove adhering carbonate, rinsed with distilled water, dried using a filter vacuum, and then dried further in a vacuum oven overnight at 70 °C. The dried samples were ground into 150 μm powder for analysis. The surface soils were sieved and then reacted with 8.8 M H_2O_2 to remove organic carbon before radiocarbon analysis.

The soft snail bodies were treated with 10% HCl for 6 h at 25 °C to remove the inorganic carbon and then rinsed 3–5 times in deionized water. Next, the bodies were dried using a filter vacuum, and further dried in a vacuum oven at 70 °C overnight. Finally, the dried soft bodies were crushed and ground into powder.

The radiocarbon activities of the snail shells and soft bodies were measured using liquid scintillation spectrometry with benzene as the scintillation solvent. The shells and the carbonate in the soils were converted into CO_2 by acid hydrolysis using HCl under a vacuum, and the organic matter powder was combusted in an oxygen stream at 900 °C. The CO_2 produced in this process was purified and collected with liquid nitrogen and then converted to Li_2C_2 by reacting with lithium at 800 °C. After cooling, C_2H_2 was obtained through hydrolysis of the Li_2C_2 and then catalyzed into benzene. Next, the benzene was mixed with the scintillator, a mixture of MSB + Butyl PDB. Radiocarbon activity was then measured using liquid scintillation spectrometry (Quantulus™1220).

For stable carbon isotope analysis, the powders of aragonite shells and soft snail bodies were reacted with 100% phosphoric acid or combusted offline, respectively. The CO_2 produced was collected with liquid nitrogen, and isotopic ratios of $^{13}C/^{12}C$ were measured by MAT 252 mass spectrometer. The isotopic data are reported in the conventional notation as per mil (‰) deviations relative to the PDB standard with uncertainties (1σ) of ±0.1‰.

3. Results

The radiocarbon activities of the land snails sampled in this study are shown in Table 1. The radiocarbon activities of soft bodies range from 105.43 to 109.94 pMC with an average of 107.4 ± 1.57 pMC for all snails, which is indistinguishable from those measured in tree leaves (108.08 ± 1.87 pMC) (Xu et al., 2010). This finding suggests that the carbon isotope compositions of organic bodies are derived mainly from organic diets. In contrast, the aragonite shells display obvious ^{14}C-depletions in comparison to atmospheric CO_2, indicating an influence from ingested inorganic carbon. The ^{14}C-deficiencies vary between snails from different ecological habitats. The shells of *Bradybaena* have higher radiocarbon activities, ranging from 99.45 pMC to 105.69 pMC (Table 1). The radiocarbon activity of *Plectotropis* is the lowest, with a value of 82.85 ± 0.68 pMC (Table 1). For *Cathaica*, the shell activities of the snails dwelling on trees display relatively larger variations (85.32–96.50 pMC) when compared with those found dwelling on grass (93.8–99.57 pMC), and the former also have larger ^{14}C-deficiencies than the latter at the same sampling sites (Table 1).

The radiocarbon activities of carbonate in the surface soil samples show a pattern of increasing with increases in the weathering intensity of surface soils in the studied areas. The susceptibility signal is generally regarded as originating primarily from *in situ* pedogenic production of fine grained magnetic minerals, with production rates increasing under mild, moist conditions (Zhou et al., 1990; Hao and Guo, 2005). During the early period of pedogenic processes, the proportion of pedogenic carbonate increases. The pedogenic carbonate incorporates new carbon derived from the atmosphere, plant respiration and decay of organic matter, all of which are enriched in ^{14}C. As a result, highly weathered soils, such as those from Baoji and Tianshui, have higher radiocarbon activities (>40 pMC) and magnetic susceptibility (>150 × 10^{-8} m^{-3} kg^{-1}) than those with low weathering intensity

Table 1
Summary of measurements and calculated results for snails collected from the Chinese Loess Plateau. The carbon isotope compositions of *Cathaica* dwelling on grass are from Xu et al. (2010).

Lab No.	Locality	Genera	Dwelling	$\delta^{13}C_{body}$	$\delta^{13}C_{shell}$	A_{shell}[a] ± SD[b]	A_{body}[a] ± SD[b]	f_{met} (%)	f_{calc} (%)	f_{atmt} (%)	P	Age anomaly (yr)
CNR-421	Mangshan	*Cathaica*	Tree	−24.61	−10.44	87.78 ± 0.9	107.62 ± 1.04	58	28	14	0.67	1906 ± 112
CNR-278	Mangshan	*Cathaica*	Grass	−22.89	−9.64	96.05 ± 0.81	108.25 ± 1.27	69	19	12	0.76	1184 ± 116
CNR-422	Fenhe	*Cathaica*	Tree	−26.53	−11.66	85.32 ± 0.89	106.22 ± 1.29	57	30	13	0.68	2120 ± 114
CNR-269	Fenhe	*Cathaica*	Grass	−25.36	−11.98	93.75 ± 0.89	107.66 ± 1.07	70	21	8	0.78	1349 ± 110
CNR-423	Ansai	*Cathaica*	Tree	−24.65	−10.46	90.99 ± 0.97	109.46 ± 1.22	60	26	14	0.70	1617 ± 116
CNR-275	Ansai	*Cathaica*	Grass	−26.25	−11.30	96.68 ± 0.96	107.12 ± 1.13	66	18	16	0.81	1110 ± 116
CNR-424	Ningxian	*Cathaica*	Tree	−23.50	−8.37	95.92 ± 1.13	108.79 ± 1.18	57	19	23	0.71	1218 ± 130
CNR-272	Ningxian	*Cathaica*	Grass	−20.33	−6.46	96.97 ± 1.03	108.88 ± 0.93	59	18	23	0.66	1149 ± 109
CNR-425	Qinan	*Cathaica*	Tree	−23.30	−8.85	93.98 ± 0.97	105.43 ± 1.02	62	19	19	0.73	1377 ± 113
CNR-289	Qinan	*Cathaica*	Grass	−25.45	−12.24	97.78 ± 0.88	108.20 ± 0.97	75	17	8	0.83	1008 ± 103
CNR-426	Liquan	*Cathaica*	Tree	−24.37	−9.03	95.46 ± 0.64	107.17 ± 1.07	59	19	22	0.74	1249 ± 108
CNR-292	Liquan	*Cathaica*	Grass	−24.63	−11.51	97.42 ± 0.83	107.89 ± 0.94	74	17	8	0.82	1047 ± 98
CNR-427	Xifeng	*Cathaica*	Tree	−26.32	−12.16	93.70 ± 0.71	107.10 ± 1.28	68	21	11	0.79	1361 ± 104
CNR-273	Xifeng	*Cathaica*	Grass	−22.42	−7.03	97.83 ± 0.91	108.31 ± 0.96	55	17	28	0.70	1070 ± 103
CNR-428	Huangling	*Bradybaena*	Ground	−24.70	−10.73	102.22 ± 1.05	106.23 ± 1.04	76	11	14	0.88	654 ± 113
CNR-270	Huangling	*Cathaica*	Grass	−23.86	−8.49	98.35 ± 0.88	108.20 ± 0.96	60	16	24	0.76	1009 ± 101
CNR-429	Tianshui	*Bradybaena*	Ground	−23.50	−9.37	101.45 ± 0.98	106.00 ± 1.02	69	15	17	0.81	703 ± 106
CNR-276	Tianshui	*Cathaica*	Grass	−25.87	−11.99	98.86 ± 0.81	108.00 ± 1.04	73	16	11	0.84	922 ± 102
CNR-430	Baoji	*Bradybaena*	Ground	−24.50	−10.73	105.81 ± 1.36	108.26 ± 1.28	76	11	13	0.87	377 ± 141
CNR-279	Baoji	*Cathaica*	Grass	−22.51	−8.04	95.45 ± 1.03	107.93 ± 1.03	59	19	21	0.70	1255 ± 116
CNR-431	Yangling	*Bradybaena*	Ground	−25.25	−10.93	105.69 ± 1.04	109.92 ± 1.06	75	10	15	0.89	383 ± 107
CNR-280	Yangling	*Cathaica*	Grass	−24.37	−10.89	96.06 ± 0.84	107.70 ± 0.81	71	19	11	0.79	1167 ± 93
CNR-432	Lantian	*Bradybaena*	Ground	−22.25	−10.13	1.037 ± 1.36	107.84 ± 1.04	77	14	9	0.85	550 ± 110
CNR-278	Lantian	*Cathaica*	Grass	−25.25	−11.92	99.57 ± 0.82	107.32 ± 1.05	86	10	5	0.88	865 ± 103
CNR-433	Dunhua	*Plectotropi*	Cliff	−21.10	−8.08	82.85 ± 0.86	109.94 ± 1.26	48	34	18	0.48	2432 ± 113
CNR-277	Dunhua	Cathaica	Grass	−24.10	−8.80	95.39 ± 0.88	108.20 ± 0.96	58	20	22	0.72	1250 ± 103

[a] A uncorrected for isotopic fractionation.
[b] PMC = % modern carbon (1950).

Table 2
Radiocarbon activities and magnetic susceptibility (MS) of the surface soils across the Chinese Loess Plateau.

Lab No.	Location	Acalc[a] ± SD[b]	Ms($10^{-8}/m^3$ kg)
CNR-486	Jiaxian	12.89 ± 0.53	69
CNR-493	Jingbian	8.89 ± 0.32	41
CNR-488	Samenxia	13.36 ± 0.45	76
CNR-495	Mangshan	20.57 ± 01.05	83
CNR-489	Liquan	25.22 ± 0.72	119
CNR-490	Luochuan	18.20 ± 0.45	84
CNR-491	Ningxian	20.71 ± 0.57	96
CNR-492	Weinan	23.90 ± 0.82	102
CNR-487	Tianshui	41.95 ± 1.22	158
CNR-494	Baoji	55.07 ± 0.99	165

[a] A uncorrected for isotopic fractionation.
[b] PMC = % modern carbon (1950).

(soils from Jingbian and Jiaxian) (Table 2). The ^{14}C activities of surface soils with medium weathering intensity in the central Chinese Loess Plateau are approximately 20 pMC.

4. Discussion

4.1. Estimating the fractions of different carbon sources in the shells

Precise estimation of the proportions of carbon from different sources incorporated into land snail shells is a key to understanding the factors controlling both isotopic composition and age anomalies of snail shells. Possible sources of shell carbon include atmospheric CO_2, inorganic carbonate, and organic dietary sources. Dietary sources include live vegetation and organic detritus. Since the 1960s, organic detritus derived from plants often has higher ^{14}C-activity than live vegetations because of nuclear bomb testing (Hua, 2004). The modeling results of Pigati et al. (2010) also showed that the ^{14}C-activity of snail diets for a given year would be higher than that of atmospheric CO_2 for the same year if the snails consumed organic detritus. As a result, a high proportion of organic detritus in the organic food would result in a high ^{14}C value in the organic body because the carbon present in soft bodies is derived mainly from organic foods (Deniro and Epstein, 1978). In present study, there is no significant difference between the soft body samples and plant leaves from the same year, indicating that the ingested detritus has little influence on the ^{14}C concentration in the soft body. This conclusion is supported by the ecological habitats of the snails included in this study. Both *Cathaica* and *Bradybaena* are well-known harmful animals in agriculture and gardening because they favor eating juicy plants, particularly tiny leaves and sprouts (Yang et al., 2010). Thus, the organic diets of the studied snails are likely dominated by live plants rather than organic detritus, and the carbon isotope compositions of soft bodies mainly reflect the composition of these plants.

The proportions of the shell carbon from various sources are calculated using the following equations, which involve both mass balance and isotope fractionations between different carbon phases during the formation of the snail shells (Xu et al., 2010):

$$f_{met} + f_{calc} + f_{atm} = 1 \quad (1)$$

$$\delta^{13}C_{HCO_3^-} + 1000 = \alpha_{13}\frac{f_{met}\delta^{13}C_{met} + f_{calc}\delta^{13}C_{calc} + f_{atm}\delta^{13}C_{atm} + 1000}{1 + 2f_{calc}(\alpha_{13} - 1)} \quad (2)$$

$$A_{HCO_3^-} = \alpha_{14}\frac{f_{met}A_{met} + f_{calc}A_{calc} + f_{atm}A_{atm}}{1 + 2f_{calc}(\alpha_{14} - 1)} \quad (3)$$

where f is the carbon fraction, and the subscripts met, calc, and atm represent, respectively, the metabolic, soil carbonate, and atmospheric carbon sources for the CO_2–H_2O–$CaCO_3$ system in the snail body fluid from which the shell is deposited. α_{13} and α_{14} indicate the ^{13}C–^{12}C and ^{14}C–^{12}C fractionation factors, respectively, and $\alpha_{14} = \alpha_{13}^2$ (Wigley and Muller, 1981). At 20 °C, $\alpha_{13} = 1.0091$ (Mook et al., 1974; Vogel, 1959). $A_{HCO_3^-}$, A_{met}, A_{atm}, and A_{calc} are radiocarbon activities of the HCO_3^- pool, metabolic CO_2, atmospheric CO_2, and soil carbonate, respectively.

Previous studies (Mook and Vogel, 1968; Rubinson and Clayton, 1969; Mook et al., 1974) have found a 2.7‰ offset between bicarbonate and aragonite precipitated in isotopic equilibrium. Thus, $\delta^{13}C^-_{HCO3} = \delta^{13}C_{shell} - 2.7$, where $\delta^{13}C_{shell}$ is the measured isotope composition of the snail shell.

The $\delta^{13}C_{atm}$ is assumed to be −8‰ (Wahlen, 1994). $\delta^{13}C_{calc}$ is the value of carbonates in the surface soils. According to a previous study (Gu, 1991), $^{13}\delta_{calc}$ of the surface soil in the Chinese Loess Plateau ranges from −3‰ to −9‰, with an average of −6‰. In this study, the average value of −6‰ is taken as $\delta^{13}C_{calc}$. Our previous study showed that the uncertainty caused by this simplification was not significant (Xu et al., 2010) (1–2% for f_{atm} and f_{met}, but no obvious influence on f_{calc}).

In Eq. (3), $A_{HCO_3^-} = (1 + 0.0027)^{-2}A_{shell}$, A_{shell} and A_{met} are the measured ^{14}C activities of shells and bodies (A_{body}) of live snails. A_{calc} is the measured radiocarbon activity of carbonate in surface soils.

Previous studies have often simplified the radiocarbon activity of inorganic carbonate as zero when evaluating the influence of inorganic carbonate (Goodfriend and Stipp, 1983; Goodfriend, 1987; Romaniello et al., 2008; Xu et al., 2010). However, our results show that the ^{14}C-activity of the surface soils from Chinese Loess Plateau changes with weathering intensity, ranging from 8 pMC to approximately 55 pMC (Table 2). To evaluate the influence of carbonate ^{14}C activities in surface soils, we modeled the variations of f_{atm}, f_{met}, and f_{calc}, with A_{calc} changing from 0 pMC to 0.55 pMC for *Bradybaena* from Baoji (the least ^{14}C deficient) and *Plectotropis* from Dunhua (the most ^{14}C deficient). Our results show that the influence of A_{calc} on the f_{met} and f_{calc} varies between samples (Fig. 2). The *Plectotropis* sample shows a large amplitude variation in f_{calc} and f_{met} with changing A_{calc}. f_{calc} increases from 25% to 49% when A_{soil} increases from 0 pMC to 0.55 pMC, while f_{met} decreases from 59% to 30% (Fig. 2). In contrast, the amplitudes of f_{met} and f_{calc} variations are low for the *Bradybaena* sample from Baoji (Fig. 2). f_{atm} shows little change with variations in A_{calc} for both the *Bradybaena* and the *Plectotropis* samples, indicating that the changes in ^{14}C activities observed in surface soils have little influence on the proportions of atmospheric carbon incorporated into their shells (Fig. 2). In summary, the A_{calc} changes may have a large effect on the estimated values of f_{met} and f_{calc} but only slight effect on those of f_{atm}, suggesting that the simplification of taking A_{calc} as zero underestimates the contribution of inorganic carbonate to shell carbon and amplifies the influence of dietary organic material, particularly for snails with large ^{14}C-deficiencies and those living in areas with intensively weathered soils. In this study, the surface soils of the sampling sites have median

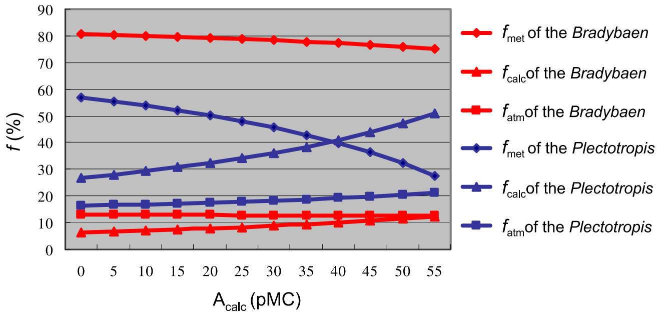

Fig. 2. Variations of f_{met}, f_{calc}, and f_{atm} with A_{calc} modeled by analysis of *Bradybaena* and *Plectotropis* from Baoji (red) and Dunhua (blue). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

weathering intensities except for those of Baoji and Tianshui. A_{calc} is therefore taken as 48.50 pMC (the average values of A_{calc} in Baoji and Tianshui) for the snails from Baoji and Tianshui and 25.33 pMC (the mean values of A_{calc} in the central Chinese Loess Plateau) for the remaining samples. The calculated proportions of different carbon sources incorporated into the shells are presented in Table 1.

4.2. Age anomaly and its association with ecological habitats

To estimate the age anomalies of land snail shells, isotopic fractionation correction is necessary. The fractionation-corrected $A_{corrected}$ term can be calculated from the measured term $A_{measured}$ using a standard formula (Stuiver and Polach, 1977):

$$A_{corrected} = A_{measured}\left(1 - \frac{2\left(\delta^{13}C + 25\right)}{1000}\right) \quad (4)$$

This equation is valid only for the component of shell carbon derived directly or indirectly from atmospheric CO_2 (Pigati, 2002), otherwise Eq. (4) should be;

$$A_{corrected} = A_{measured}\left(1 - \frac{2\left(\delta^{13}C_{nlc} + 25\right)}{1000}\right) \quad (5)$$

$\delta^{13}C_{nlc}$ is the carbon isotope of the shell carbonate derived from non-carbonate sources. Substituting $\delta^{13}C_{HCO3}^{-} = \delta^{13}C_{shell} - 2.7$ and $\alpha_{13} = 1.0091$ into Eq. (2), the following equation is obtained;

$$\delta^{13}C_{shell} = \frac{f_{met}(1.0091\delta^{13}C_{met}+11.8)+f_{atm}(1.0091\delta^{13}C_{atm}+11.8)+f_{calc}(1.0091\delta^{13}C_{calc}-6.35)}{1+2f_{calc}(1.0091-1)} \quad (6)$$

and the proportion of non-carbonate sources (P) is:

$$P = \frac{f_{met}(1.0091\delta^{13}C_{met}+11.8)+f_{atm}(1.0091\delta^{13}C_{atm}+11.8)}{f_{met}(1.0091\delta^{13}C_{met}+11.8)+f_{atm}(1.0091\delta^{13}C_{atm}+11.8)+f_{calc}(1.0091\delta^{13}C_{calc}-6.35)} \quad (7)$$

Thus, Eq. (5) becomes;

$$A_{corrected} = A_{shell}\left(1 - \frac{2\left(p\delta^{13}C_{shell} + 25\right)}{1000}\right) \quad (8)$$

and the age anomaly (Δ) can be calculated by;

$$\Delta = -8033\ln\left(\frac{A_{shell}\left[1 - \frac{2\left(P\delta^{13}C_{shell}+25\right)}{1000}\right]}{A_{atm}}\right) \quad (9)$$

The calculated results of P are shown in Table 1. P is greater than 0.66 for all samples except for *Plectotropi*, which has a value of 0.48. The values of P for *Bradybaena* are the highest of all the species, with an average value of 0.86 ± 0.03. There is no significant difference in P between *Cathaica* inhabiting trees (0.72 ± 0.04) and grass (0.77 ± 0.06). P is taken as the average values of the species in each habitat for isotopic fractionation correction: 0.72 for *Cathaica* dwelling on trees, 0.77 for *Cathaica* on grass, 0.86 for *Bradybaena* on the ground, and 0.48 for *Plectotropi* on loess cliffs.

The age anomalies are shown in Table 1. The results show that the age anomalies of both *Cathaica* and *Bradybaena* shells are relatively concentrated across the Chinese Loess Plateau. *Cathaica* dwelling on grass has the lowest disparity across the Chinese Loess Plateau with a standard derivation (STD) of 137 a, and the STDs are 151 a and 346 a for *Bradybaena* dwelling on the ground and *Cathaica* on trees, respectively. The low disparity errors are much smaller than the measurement errors for the samples with relatively old ages, demonstrating that the radiocarbon activities of the *Cathaica* and *Bradybaena* shells could provide a relatively reliable age after age anomaly correction. The *Plectotropi* shells have incorporated a large amount of inorganic carbon ($f_{calc} = 32\%$) and have the largest age anomaly (2151 a) (Table 1). To the best of our knowledge, this age anomaly is the largest one that has been measured in the Chinese Loess Plateau.

Although the age anomalies of both *Cathaica* and *Bradybaena* shells are concentrated across the Chinese Loess Plateau, the proportion of carbonate carbon (f_{calc}) and age anomalies vary among the different snail habitats. In all of the sampling sites, the shell ^{14}C activities of *Cathaica* dwelling on grass are larger than the values of *Cathaica* on trees but lower than those of *Bradybaena* found on the ground (Table 1). As a result, *Cathaica* dwelling on the grass has a smaller shell age anomaly (1107 a) than *Cathaica* on the trees (1550 a) but a larger anomaly than the *Bradybaena* inhabiting the ground (494 a) (Table 1). These characteristics suggest that the availability of calcium might have some influence on the age anomalies of snail shells (Goodfriend and Stipp, 1983; Pigati et al., 2010). The snails that have difficulty obtaining calcium would ingest a large amount of inorganic carbonate at one time for their later growth and thus have a large ^{14}C-depletion and age anomaly (Goodfriend and Stipp, 1983). The limitation of calcium availability is associated not only with the mineral composition of the underlying land surface but also with the snail's habitat. In this study, the ecological habitat might be the major factor affecting the availability of calcium because the surface soils are enriched in carbonate across the study sites. Calcium is more readily available

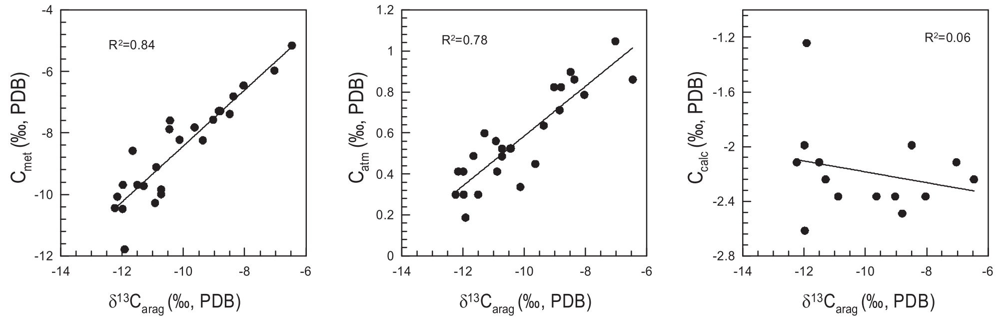

Fig. 3. Correlations between C_{met}, C_{atm}, C_{calc} and $\delta^{13}C_{arag}$.

to *Cathaica* found on the grass than to those found on trees as the latter must crawl down to the ground in order to obtain calcium from the soil. Neither of these species can obtain calcium as easily as ground-dwelling *Bradybaena*, for which calcium is continuously available. Finally, *Plectotropi* dwell on the loess walls and cliffs where moss and lichen grow. The snails might scratch the moss and lichen to obtain food. During the scratching process, the snails could ingest a large amount of inorganic carbonate and thus have a large age anomaly.

In summary, the ^{14}C-deficiency and resultant age anomalies of both *Cathaica* and *Bradybaena* shells show a good concentrated distribution across the Chinese Loess Plateau, indicating that the shells of these species could provide relatively reliable age estimates after correction for anomalies. The calcium availability associated with their ecological habitats might be an important factor in determining the shell age anomalies of both *Cathaica* and *Bradybaena*. The large age anomaly of *Plectotropi* shells could be related to the large amount of inorganic carbonate ingested during the process of scratching food.

4.3. Implications of using stable carbon isotopes for ^{14}C age anomalies correction

It has been suggested that the carbon derived from carbonate, which has an isotopic composition distinct from dietary organic material and atmospheric CO_2, should have some effect on the stable isotope composition of shell aragonite. Theoretically, there is potential to use stable isotopes for ^{14}C age correction or for identifying the influence of inorganic carbonate on the age anomalies of snail shells. To evaluate this potential and the controlling factors on the $\delta^{13}C$ of shell carbon, the contributions of carbon from different sources to the stable carbon isotopic composition of the shell aragonite are calculated. The equations used in this calculation are derived from Eq. (6):

$$C_{met} = \frac{f_{met}(1.0091\delta^{13}C_{met} + 11.8)}{1 + 2f_{calc}(1.0091 - 1)} \quad (10)$$

$$C_{atm} = \frac{f_{atm}(1.0091\delta^{13}C_{atm} + 11.8)}{1 + 2f_{calc}(1.0091 - 1)} \quad (11)$$

$$C_{calc} = \frac{f_{calc}(1.0091\delta^{13}C_{calc} - 6.35)}{1 + 2f_{calc}(1.0091 - 1)} \quad (12)$$

where C_{met}, C_{atm}, and C_{calc} represent the respective contributions of carbon from dietary organic sources, atmospheric CO_2, and carbonate to the stable carbon compositions of snail shells.

Fig. 3 shows the relationship between the contributions of various carbon sources and the $\delta^{13}C$ of aragonite shells. There is no obvious correlation between C_{calc} and $\delta^{13}C_{arag}$ (Fig. 3), suggesting that using the $\delta^{13}C$ value for correcting or identifying shell ^{14}C age anomalies is not a valid approach. Related studies have also shown that the ingested carbonate has no systematic effect on carbon isotope compositions of snail shells (Tamers, 1970; Evin et al., 1980). Yates et al. (2002) likewise did not find a significant correlation between age error and $\delta^{13}C$, though age errors show a pattern of increasing with an enrichment of ^{13}C.

Both C_{met} and C_{atm} show a good correlation with $\delta^{13}C_{arag}$ (Fig. 3), indicating that the carbon isotope composition of snail shells is dominated by carbon derived from organic dietary sources and atmospheric CO_2. In contrast, the values of C_{atm} are far smaller than those of C_{met} (Fig. 3), suggesting that carbon derived from atmospheric CO_2 does not have a significant effect on the carbon isotope composition of snail shells. In addition, the values of C_{atm} are positive, while those of C_{calc} are negative (Fig. 3). These characteristics show that the contributions derived from carbonate and atmospheric CO_2 are attenuated by each other, amplifying the effect of dietary organic matter on the stable isotope compositions of shells. For example, in the snails from Lantian, C_{met} accounts for more than 98% of shell carbon isotope composition even if f_{calc} is 10%, indicating that the isotopic signals of inorganic carbonate are overwhelmed by dietary organic sources. The high proportion of C_{met} might explain the good correlation in $\delta^{13}C$ between shells and organic diet and the lack of an obvious effect of limestone on the shell stable carbon isotope compositions measured in previous studies (Deniro and Epstein, 1978; Stott, 2002; Metref et al., 2003).

5. Conclusions

This study systematically analyzed the radiocarbon and stable carbon compositions of the surface soils, aragonite shells and soft bodies of land snails with different ecological habitats across the Chinese Loess Plateau. The results show that the radiocarbon activity of surface soils increases with the weathering intensity and that the simplification of A_{calc} to zero, as has been done in previous studies, might underestimate the influence of organic carbonate on the carbon isotope compositions of snail shells, particularly for species with high shell ^{14}C-depletion living in areas with intensively weathered surface soils. ^{14}C-deficiencies and resultant age anomalies of both *Cathaica* and *Bradybaena* shells, particularly for shells of the species dwelling on grass or ground, show a good concentration across the Chinese Loess Plateau, indicating that the shells of these species could provide relatively reliable age estimates after correction of age anomalies. The age anomaly of *Cathaica* dwelling on grass (967 ± 137 a) is smaller than that of *Cathaica* on trees (1393 ± 398 a) but is larger than that of *Bradybaena* inhabiting on ground (494 ± 208 a). These findings indicate that the availability of calcium associated with ecological habitat might be a controlling factor for the ^{14}C-deficiencies of snail shells in the Chinese Loess Plateau. The shells of the *Plectotropi* have the largest age anomaly (2151 a); this large ^{14}C-deficiency of the

Plectotropi shells might be associated with the large amount of inorganic carbonate ingested during the process of scratching for food. Though the radiocarbon activities of snail shells indicate a significant incorporation of inorganic carbonate into the shells, the influence of carbonate on the stable carbon isotope compositions of shells is overwhelmed by dietary organic matter, suggesting that the use of $\delta^{13}C_{arag}$ as a base for identifying and correcting age anomalies is not a valid approach.

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