^{14}C DATING OF SOIL ORGANIC CARBON (SOC) IN LOESS-PALEOSOL USING SEQUENTIAL PYROLYSIS AND ACCELERATOR MASS SPECTROMETRY (AMS)

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ABSTRACT. The chemical extraction of soil organic carbon (SOC) fractions from soils often does not produce satisfactory results for radiocarbon dating. In this study, a sequential pyrolysis technique was investigated. The soil was pyrolyzed at temperatures of 200, 400, 600, and 800 °C to partition organic carbon into pyrolytic volatile (Py-V) and pyrolytic residue (Py-R) fractions. The preliminary results show that the ^{14}C dates of both fractions become progressively older as the pyrolysis temperature is increased. In addition, the ages of the Py-V fractions are consistently younger than the corresponding Py-R fractions extracted at the same temperature. Experimental results of known-age paleosol samples indicate that the Py-V fractions obtained between 600 and 800 °C yield the most reliable ages. This technique provides a new approach to improve the accuracy of ^{14}C dating of loess-paleosol sequences.

INTRODUCTION

Loess-paleosol sequences are valuable natural archives that preserve high-resolution continental proxy records of past climate. In order to understand these records in a global context, it is critical to establish accurate age models for individual sequences. In samples from the Late Quaternary, radiocarbon has been used with some success to date loess-paleosols; however, these deposits often do not contain ideal dating materials such as wood or charcoal (Zhou et al. 1992; Wang et al. 2003). One possibility is to date soil organic carbon (SOC), which contains fulvic acids, humic acids, and humin. Any of these fractions can be dated, but all are subject to potential organic contamination, introduced through natural and anthropogenic pathways and inherited from detrital materials. These organic compounds are not removed by the usual acid-base-acid (ABA) pretreatment method (Head et al. 1989), and dates on fulvic acids, humic acids, and/or humin may produce inconsistent ^{14}C results (Perrin et al. 1964; Scharpenseel and Schiffman 1977; Gilet-Blein et al. 1980; Becker-Heidmann et al. 1988; Head et al. 1989; Martin and Johnson 1995; Abbott and Stafford 1996; Paul et al. 1997; Huang et al. 1999; Muhs et al. 1999). Hence, there is a need for further development of specialized pretreatment methods that can be used to date soil organic matter in loess-paleosols.

Several methods have been conceived to improve bulk ^{14}C dates in sediments that contain heterogeneous carbon sources (McGeehin et al. 2001; Wang et al. 2003; Rosenheim et al. 2007). Wang et al. (2003) used a pyrolysis technique at 800 °C in the Peoria Loess deposit. In that study, ^{14}C dates of the pyrolysis volatile (Py-V) and pyrolysis residue (Py-R) fractions were measured by liquid scintillation counting and it was observed that Py-V fractions were consistently younger than Py-R fractions. Wang et al. (2003) attributed this difference to the soil residence times of each fraction in the loess.

Here, we expand this technique to date a range of temperature fractions in Chinese loess. Chinese loess-paleosol sequences are characterized by low organic contents that are heterogeneous with respect to ^{14}C (Liu 1985). Using accelerator mass spectrometry (AMS), we were able to measure

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minute Py-V and Py-R carbon fractions from a number of sites. The method was validated by analyzing a series of known-age paleosol samples. The method was then applied to a loess-paleosol sequence of unknown age, in Luochuan, China.

MATERIALS AND METHODS

Sampling and Pretreatment

Two paleosol samples were collected from a loess-paleosol sequence at Licun in Qishan County, Shaanxi Province, China (34°28′N, 107°50′E) in 2005. One sample was collected in the upper ash pit of the Quanhu relics, Quanhu Village, Huan County, Shaanxi Province, China (34°30′N, 109°46′E), and comes from the Miaodigou 2nd period within the early Longshan culture, in the central Yellow River region. This site is transitional between the Yangshao and Longshan cultures, with a calibrated age of ~4100 BP (Huanxian Quanhucun 2003). Two paleosol and charcoal samples were collected at the Donglongshan ruins in southeastern Shangluo City, Shaanxi Province (33°26′N, 110°47′E). These correspond to a cultural stage of the Xia Dynasty (4070–3600 BP) (Xia-Shang-Zhou Dating Project Group 2000). Samples were collected at depths of 35 and 60 cm below the surface. Pottery fragments found in the paleosol horizons were identified as utensils common to the Xia Dynasty.

Paleosol samples were also collected from Xiaheimugou, Luochuan Plateau, Shaanxi Province (35°45′N, 109°25′E). The Luochuan Plateau belongs to the Loess Plateau region, and is located north of the Wei River with an average altitude of 1072 m. Six samples were collected at this site, from depths of 70, 125, 215, 255, 408, and 455 cm.

The soil samples were soaked in deionized water overnight, then transferred to an ultrasonic bath for 30 min to completely disintegrate and homogenize the samples. The wet samples were sieved using a 180-μm mesh to separate rootlets. The samples were then treated with 1M HCl at 70 °C for 2 hr to remove carbonates, then rinsed repeatedly until neutral, and oven-dried overnight at 60 °C. Finally, the desiccated samples were transferred into glass vials and sealed, to await the pyrolysis step.

Charcoal from the Loess Plateau is derived from the incomplete combustion of terrestrial plants used by early dwellers as fuel, and is not subject to reworking. Therefore, it is an ideal material for ^{14}C dating and can provide accurate age constraints for archaeological sites. The charcoal samples were treated using a conventional acid-base-acid (ABA) method. First, the samples were rinsed with deionized water in an ultrasonic bath, and then treated with 1N HCl in a water bath at constant temperature (60 °C) for 2 hr to remove carbonates. The samples were rinsed repeatedly with deionized water until neutral, followed by 1N NaOH in a water bath for another 2 hr to ensure the complete removal of humic and fulvic acids. For some samples, this procedure was repeated several times until the supernatant was clear. The samples were rinsed repeatedly with deionized water until neutral and 1N HCl was again added to the samples to ensure that the samples would be pH neutral. Again, the samples were rinsed repeatedly with deionized water until neutral. The samples were then dried in an electric oven at 60 °C. Conventional combustion was used to oxidize the charcoal samples to CO_2.

Pyrolysis Using Sequential Combustion

The pyrolysis method reported by Wang et al. (2003) was modified in this study. The system consisted of a pyrolysis-combustion system (Figure 1a) and a gas intake control system (Figure 1b). The pyrolysis-combustion system contained inner and outer quartz tubes (Figure 1), connected only through the opening of the inner tube. The sample was inserted in the inner tube. The outer tube was constantly purged with O_2, while the inner tube was purged with either Ar gas for pyrolysis or O_2 gas for combustion, after the pyrolysis step for a given temperature was completed.

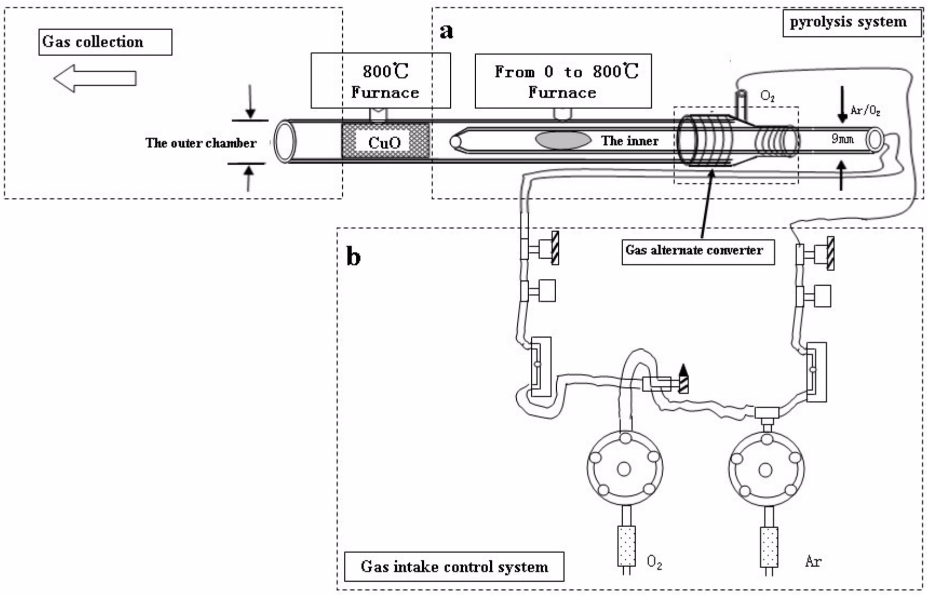

Figure 1 Schematic diagram of stepped-pyrolysis-combustion system

The flow rate of the purging gases was adjusted and controlled by a valve with a flow meter. A cartridge impregnated with CuO was inserted into the outlet of the outer tube to improve the combustion yield and conversion of CO to CO_2. Two tube furnaces were employed, one installed on the outer section surrounding the CuO catalyst and set to a fixed temperature of 800 °C. The other furnace was installed near the section of tube containing the sample, and its temperature could be programmed. Pyrolysis was implemented sequentially at 200, 400, 600, and 800 °C. The samples were heated from room temperature to 200 °C for 0.5 hr, then increased to 400 °C for 0.5 hr, then increased to 600 °C and held for 0.5 hr, then heated to 800 °C for 0.5 hr. Volatile organic compounds were released from the sample at different temperatures and carried by Ar gas into the outer chamber. There, they were combusted at 800 °C under a flow of O_2 and catalyzed by CuO. The CO_2 from the combustion system was collected after passing several cold traps for further purification. After the completion of each step of the pyrolysis process, the inner chamber was flooded with O_2 to combust the remaining charred organic residues at 800 °C to extract the Py-R fractions (Figure 2).

Graphitization of CO_2 and Measurement of ^{14}C Using AMS

Carbon dioxide samples collected during the sequential combustion process were converted to graphite using the zinc reduction method. In this technique, CO_2 is reduced using Zn powder in the presence of an Fe catalyst (Slota et al. 1987; Jull 2007). The ^{14}C content of the graphite was measured in the Xi'an AMS facility with a measurement uncertainty of $^{14}C/^{12}C$ for a modern sample of better than 0.2% in routine operation. The minimum measurable ratio of $^{14}C/^{12}C$ in this machine is 3.1×10^{-16} (Zhou et al. 2006, 2007).

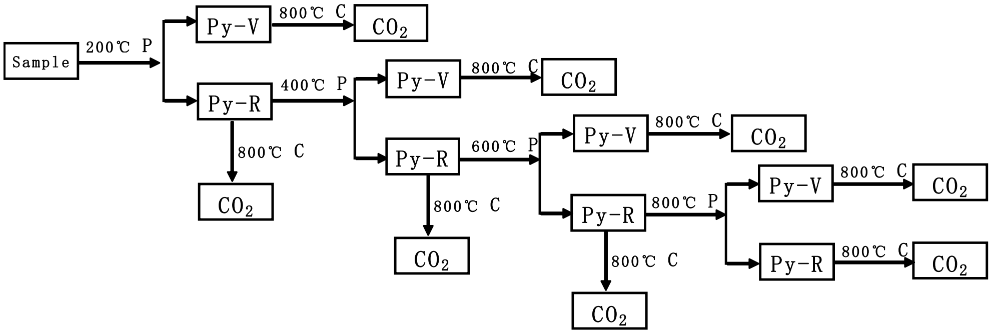

Figure 2 Temperature-stepped pyrolysis flowchart (P = pyrolysis; C = combustion).

RESULTS AND DISCUSSION

Four loess-paleosol samples (1 unknown-age sample from Lichun, 1 known-age sample from the Quanhu relics, and 2 known- age samples from the Donglongshan relics) were analyzed for ^{14}C in different fractions obtained by sequential pyrolysis at temperatures ranging from 200 to 800 °C. These measurements were used to determine the ages of the Py-V and Py-R fractions, and to find an optimal pyrolysis temperature to date loess-paleosol samples. The method was also applied to loess-paleosol samples of uncertain age, from Luochuan.

Results of ^{14}C in Fractions of SOC in a Paleosol Sample from Lichun

Table 1 gives the ^{14}C ages of the Py-V and Py-R fractions, combusted at 400 and 800 °C, and SOC ages, combusted at 800 °C. The ^{14}C ages of the Py-R fractions are older than that of the SOC, and the Py-V fractions are younger. It has been reported that younger soluble organics can be introduced into loess-paleosol through agricultural activity or from other modern sources, and thus soil organic matter may yield a younger age than expected (Head et al. 1989; Zhou et al. 1990). The results in Table 1 indicate that pyrolysis effectively removes younger carbon in the Py-V fraction at 400 °C, and suggests that this method can be used to isolate a more reliable organic carbon fraction for ^{14}C dating loess-paleosols.

Table 1 ^{14}C ages of 400 °C pyrolysis volatile (Py-V) and pyrolysis residue (Py-R) fractions and total organic content (TOC).

Depth (cm)	Lab code	Material dated	^{14}C age (BP)
120	XA1984	Py-V	2641 ± 20
	XLLQ1501	TOC	3400 ± 105
	XLLQ1500	Py-R	4270 ± 120
220	XA1970	Py-V	5435 ± 40
	XA1729	TOC	6791 ± 28
	XLLQ1494	Py-R	8560 ± 145

^{14}C Dating of SOC in Paleosol from Quanhu Relics

The ^{14}C dating of SOC in paleosol from the Quanhu relics produced an age of 3680 ± 30 BP, which was younger than the expected archaeological age (~4100 BP). Table 2 presents the results of ^{14}C dating on pyrolytic fractions of SOC of this paleosol. When the pyrolysis temperature was <600 °C, the Py-V fractions were younger than the SOC ages. The relatively young Py-V fractions, collected below 600 °C, could include fats, carbohydrates, proteins, and low-carbon saturated alkanes originating from the decomposition of rootlets and/or translocation/percolation of soluble organic substances (Wang et al. 2003). When the pyrolysis temperature was raised to temperatures >600 °C, the Py-V fractions produced ages that were older than the SOC ages. This is consistent with polymerized organic matter contained in clay minerals (McGeehin et al. 2001). Ages of the Py-R fractions obtained at 600 and 800 °C were the oldest, which could result from the oxidation of inherited carbon in detrital material. These fractions could include lignin and lipids that are insoluble in water and relatively resistant to biodegradation processes (Huang et al. 1999; Lu et al. 2000). The Py-V fraction obtained at 600–800 °C gave an age of 4170 ± 30 BP (Table 2), which is consistent with the archaeological age. This suggests that the Py-V fraction obtained at 600–800 °C should yield the most reliable age for the paleosol. With an increase in pyrolysis temperature from 200 to 800 °C, the age of the volatilized fraction increased proportionally. Ages of Py-V fractions were much younger than those of Py-R fractions (Figure 3), and the ^{14}C ages of the Py-R fractions were as much as 5000 yr older than those of the Py-V fractions (Table 2).

Table 2 ^{14}C dating of pyrolytic fractions of SOC in paleosol from Quanhu relics.

Lab code	Py-V temperature	^{14}C age (BP)	Lab code	Py-R temperature	^{14}C age (BP)
XA1996	Room temp. to 200 °C	1890 ± 30	XA471	Room temp. to 200 °C	4510 ± 20
XA1164	200–400 °C	2110 ± 20	XA472	200–400 °C	5900 ± 30
XA1165	400–600 °C	3130 ± 30	XA473	400–600 °C	7250 ± 40
XA1166	600–800 °C	4179 ± 30	XA474	600–800 °C	8989 ± 30

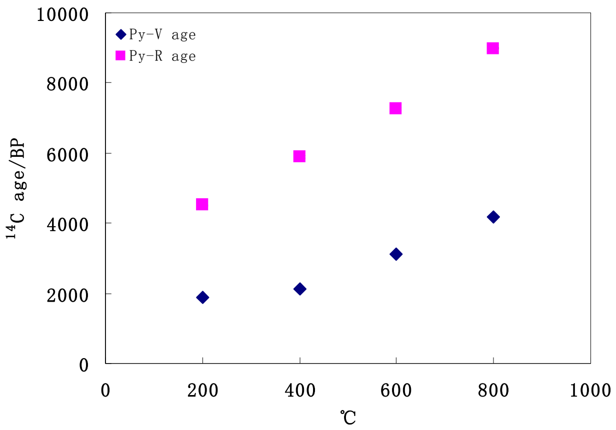

Figure 3 Relationship between ^{14}C ages of Py-V and Py-R fractions and pyrolysis temperatures. The error bars are too small to be visible.

^{14}C Dating of SOC in Paleosol from the Donglongshan Relics Site

Tables 3 and 4 list the ^{14}C dating results of the pyrolysis fractions of SOC in paleosol samples collected at depths of 35 and 60 cm at the Donglongshan relics site. A similar trend to that discussed above was observed in these 2 sample sets, i.e. the age of both the volatile and residue fractions obtained by pyrolysis increased with increasing pyrolysis temperatures, but this trend is not significant. The age of the pyrolysis residues at 400 and 600 °C are similar. The ^{14}C ages of the charcoal extracted at 35 and 60 cm depths at the Donglongshan relics site were 3410 ± 50 and 3870 ± 40 BP, respectively, which fall within the late Xia Dynasty. The measured ^{14}C ages in the Py-V fractions pyrolyzed at 600–800 °C (3419 ± 30 and 3898 ± 30 BP) agree well with the age of extracted charcoal from the corresponding depth. This result confirms that the Py-V fraction obtained by pyrolysis at 600–800 °C is the best fraction for ^{14}C dating this paleosol. The Py-R fractions generated at 200, 400, 600, and 800 °C are likely a mixture of organics formed from different processes and at different times, and these fractions can significantly interfere with the accuracy of a bulk SOC ^{14}C date.

Table 3 ^{14}C dating results of pyrolytic fractions in paleosol collected from 35 cm depth at the Donglongshan site.

Lab code	Py-V temperature	^{14}C age (BP)	Lab code	Py-R temperature	^{14}C age (BP)
	Room temp. to 200 °C		XA1727	Room temp. to 200 °C	3796 ± 30
	200–400 °C		XA1725	200–400 °C	3964 ± 25
XA1733	400–600 °C	3245 ± 40	XA1738	400–600 °C	3970 ± 30
XA1734	600–800 °C	3419 ± 30	XA1723	600–800 °C	4200 ± 30

Table 4 ^{14}C dating results of pyrolytic fractions in paleosol collected from 60 cm at the Donglongshan site.

Lab code	Py-V temperature	^{14}C age (BP)	Lab code	Py-R temperature	^{14}C age (BP)
	Room temp. to 200 °C			Room temp. to 200 °C	
XA1736	200–400 °C	3389 ± 25	XA1967	200–400 °C	4133 ± 20
XA1739	400–600 °C	3402 ± 30	XA1731	400–600 °C	4144 ± 25
XA1740	600–800 °C	3898 ± 30	XA1982	600–800 °C	4380 ± 30

^{14}C Dating of Paleosol from the Xiaheimugou Profile in Luochuan

Table 5 shows the ^{14}C dating results of the 600–800 °C pyrolysis fractions of paleosol samples collected from 6 depths in Luochuan, as well as the ^{14}C dating of SOC in these samples. The ^{14}C dates of the Py-R and Py-V fractions and SOC increased with increased sampling depths. The age of the Py-R fractions were much older than their counterpart Py-V fractions, and both fractions were older than that of the SOC measurement in the same sample (Figure 4). This result again suggests that the 600–800 °C pyrolysis fraction provides the best fraction for ^{14}C dating, in the absence of wood or charcoal.

Table 5 ^{14}C dating results of SOC fractions in loess from Luochuan.

Depth (cm)	Lab code	600–800 °C Py-V (BP)	Lab code	600–800 °C Py-R (BP)	Lab code	SOC (BP)
70	XA2014	2660 ± 30	XA2028	4660 ± 30	XA2023	1710 ± 30
125	XA2010	5240 ± 40	XA2005	5750 ± 40	XA2004	4650 ± 30
215	XA2011	9950 ± 40	XA2024	11,550 ± 45	XA2020	8430 ± 40
255	XA1975	11,910 ± 30	XA1976	20,245 ± 60		
404	XA2012	21,420 ± 90	XA2029	25,050 ± 100	XA2018	20,240 ± 70
455	XA1973	24,020 ± 70	XA1972	26,780 ± 90		

CONCLUSIONS

The sequential pyrolysis experimental results of known-age paleosol samples indicate that the Py-V fraction obtained at 600–800 °C and held at 800 °C for 0.5 hr is the most suitable fraction for paleosol dating at the sites studied. This sequential pyrolysis approach may therefore improve chronologies based on bulk TOC ages. The pyrolysis-combustion technique apparently removes both younger and older contaminating carbon from SOC in the loess-paleosol samples studied here.

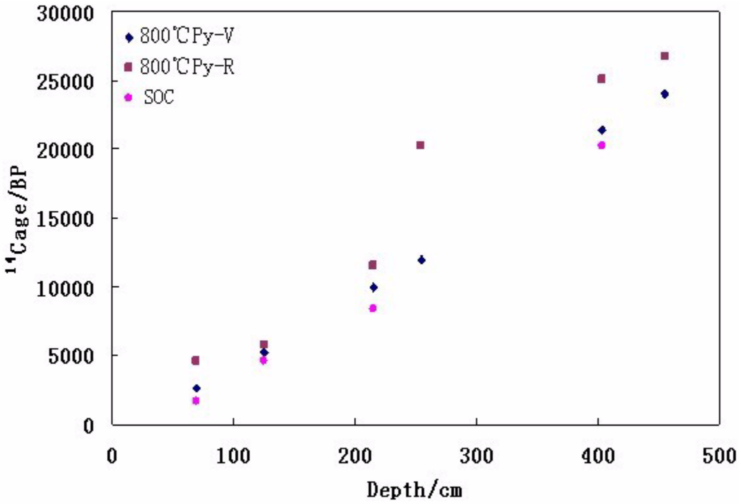

Figure 4 Relationship of ^{14}C ages of Py-V and Py-R fractions and SOC with sampling depth of loess-paleosol sequences in Luochuan. The error bars are contained within the symbols at this scale.

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