EXPERIMENTAL CONDITIONS FOR ^{14}C GRAPHITE PREPARATION AT THE GXNU LAB, CHINA

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ABSTRACT. As a required sample preparation method for ^{14}C graphite, the Zn-Fe reduction method has been widely used in various laboratories. However, there is still insufficient research to improve the efficiency of graphite synthesis, reduce modern carbon contamination, and test other condition methodologies at Guangxi Normal University (GXNU). In this work, the experimental parameters, such as the reduction temperature, reaction time, reagent dose, Fe powder pretreatment, and other factors, in the Zn-Fe flame sealing reduction method for ^{14}C graphite samples were explored and determined. The background induced by the sample preparation process was $(2.06 \pm 0.55) \times 10^{-15}$, while the $^{12}C^-$ beam current were better than 40μA. The results provide essential instructions for preparing ^{14}C graphite of ~1 mg at the GXNU lab and technical support for the development of ^{14}C dating and tracing, contributing to biology and environmental science.

KEYWORDS: AMS, ^{14}C, graphitization conditions, Zn-Fe reduction.

INTRODUCTION

Accelerator mass spectrometry (AMS) is a detection technology with the advantages of less sample usage, short measurement time, and high sensitivity (Bennett et al. 1977; Nelson et al. 1977), making it relevant to various general cases. As the method with the highest sensitivity to measure ^{14}C, it is widely used in archaeology, geology, oceanography, biomedicine, and environment science (Nielsen 1952; Lubritto et al. 2004; Marzaioli et al. 2005; Salehpour et al. 2015; Shen et al. 2015, 2019, 2022a, 2022b; Cheng et al. 2020). The high-precision and low-background ^{14}C measurements rely on the appropriate graphite preparation conditions and reliable graphite preparation system. Therefore, establishing a high-quality ^{14}C graphite preparation process and improving ^{14}C graphite experimental conditions are significant work for every radiocarbon laboratory worldwide (Kitagawa et al. 1993; Meng et al. 2002; Santos et al. 2007a; Khosh et al. 2010; Hua et al. 2016; Barile et al. 2019; Shen et al. 2022c).

As a vital method to synthesize ^{14}C graphite, the Zn-Fe reduction method was first proposed by Jull et al. (1986) and Slota et al. (1987). Xu et al. (2007) and Walker et al. (2019) introduced a method for the synthesis of carbon samples by the Zn-Fe flame sealing reduction method, which not only overcomes the problem of atmospheric leakage in the reduction unit caused by the traditional online Zn-Fe reduction method (Bronic et al. 2010) but also avoids the problems of water vapor and CH_4 production during the reaction, effectively reducing the background and improving the accuracy of the results. In addition, further studies by Macario et al. (2016) and Dee et al. (2000) showed that the ratios of the reducing agent and catalyst to sample, and their treatment method were significantly related to the quality and performance of the graphite target.

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In this study, ^{14}C graphite samples (≈1 mg C) were synthesized by the Zn-Fe flame sealing reduction method, and the experimental conditions were optimized based on a series of experiments, such as the selection of a reduction furnace, reaction temperature, time, reagent dose, and pretreatment of Fe. By analyzing the recovery rate, $^{12}C^-$ beam current, measurement sensitivity, and modern carbon contamination, the optimized experimental conditions for synthesizing trace ^{14}C graphite samples by the Zn-Fe flame sealing reduction method were obtained. The background value of the experiment was evaluated using processed commercial graphite, and international standard samples (OXII, CSC, IAEA-C8) were used to evaluate the stability and reliability of the method, aiming to obtain higher performance ^{14}C graphite for GXNU-AMS measurement.

MATERIAL AND METHODS

Reagents and Materials

Zn powder (Sigma-Aldrich #324930, <150 μm, 99.995%) was used for the reduction of CO_2 to CO, Fe powder (Sigma-Aldrich #209309, 325 mesh, 97%) was used as a catalyst for reducing CO to C, and CuO powder (Sinopharm Chemical Reagent Co., Ltd, analytical grade, 99.7%) was used for combustion. The reference material OXII (SRM 4990C) was from the National Institute of Standards and Technology (NIST). C1 and C8 were from the International Atomic Energy Agency (IAEA). Chinese sugar carbon (CSC) was obtained from Xi'an AMS Center. The carbon powder samples were commercial graphite (CAS#1333-86-4) obtained from Alfa Aesar Co., Ltd.

A muffle furnace (SX2-2.5-12N, Shanghai Yiheng Scientific Instrument Co., Ltd., China) and a customized graphite reduction furnace (GXU-1, Chery Glass Products Co., Ltd., China) were used in the reduction and oxidation reactions. A high-temperature oven (GW-150B, Bangsi Instrument Technology (Shanghai) Co., Ltd.) was used in material baking. Two analytical balances (Mettler Toledo XP2 and ME155D, United States) with reading precisions of 1 μg and 10 μg, respectively, were used for sample weighing.

^{14}C Sample Preparation Vacuum Line

The layout of the ^{14}C sample vacuum line is shown in Figure 1. The main components include a vacuum pump, CO_2 trap, quartz tube, water trap, valve, and vacuum gauge (Shen et al. 2022c). According to its functions, the device is divided into a vacuum maintenance unit, a CO_2 purification unit, and a CO_2 reduction unit. The entire device adopts quartz glass as the main structural material, which has good vacuum performance and allows the entire experimental process to be observed.

Before sample preparation, the quartz glass tubes were placed in a high-temperature furnace at 500°C for 5 hr to remove carbon contamination. The samples and CuO were mixed in the oxidation tube under vacuum conditions and then subjected to flame seal treatment. After combustion in a muffle furnace, the carbon in the sample was oxidized into CO_2 and then introduced to the vacuum system. The CO_2 gas first passed through alcohol liquid nitrogen cold trap 5 at –90°C to thoroughly remove the water vapor and then entered liquid nitrogen cold trap 6 at –196°C, where it was frozen. Next, any noncondensable gases, such as N_2 and O_2 were pumped away. The purified CO_2 was heated and transferred to a gasreservoir 7 (with a fixed volume of approximately 23 mL), quantified by measuring the CO_2 pressure (1 mg carbon corresponds to approximately 80 mbar), transferred to a reduction tube containing a
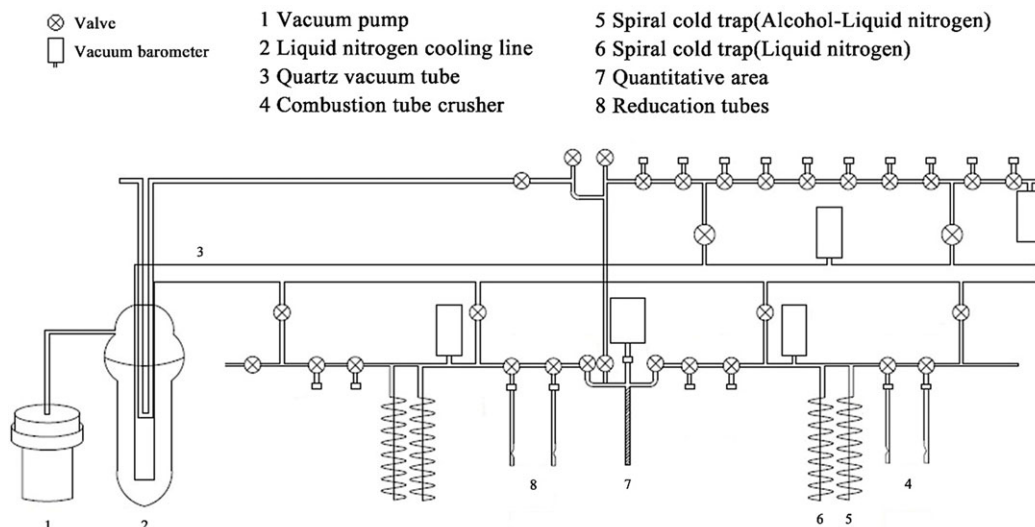
Valve
Vacuum barometer

1 Vacuum pump
2 Liquid nitrogen cooling line
3 Quartz vacuum tube
4 Combustion tube crusher

5 Spiral cold trap(Alcohol-Liquid nitrogen)
6 Spiral cold trap(Liquid nitrogen)
7 Quantitative area
8 Reduction tubes

Figure 1   Layout of the ^{14}C sample vacuum line.

catalyst Fe and reducing agent Zn using a liquid nitrogen cold trap, and sealed with a torch. Then, the reduction tube was placed inside a muffle furnace or a customized graphite reduction furnace, whereby graphite formed at the surface of the iron powder in the reduction tube. Finally, the graphite and iron powder were pressed into the AMS cathodes for measurement.

Type of Reduction Furnace

Most ^{14}C laboratories use a muffle furnace for oxidation combustion and CO_2 reduction treatment (i.e., the entire sealed Zn tubes are held at a constant temperature). To explore better synthesis conditions of graphite for the Zn-Fe method, in addition to the conventional muffle furnace method, we also adopted a 10-hole Condensing Graphite Reduction Furnace (CGRF) (Shen et al. 2022c) for CO_2 reduction, which was initially designed for the H_2-Fe method and could apply a thermal gradient to Zn tube reactors during graphitization. With the 10-hole condensing graphite reduction furnace, the Fe and Zn catalysts are held at high reaction temperatures ($\sim$600°C), whereas the tops of the Zn tube reactors are held at ambient temperatures (20–25°C). The principle of the method is very similar to that described by Xu et al. (2007) and Orsovszki et al. (2015) for the graphitization of 1–100 µg C samples. However, our study focuses primarily on improving Zn graphitization efficiency for 1 mg C samples.

Pictures of our reduction furnace and two Zn reactor tubes after different furnace graphitization processes are shown in Figure 2. At 600°C, zinc evaporates from the bottom of the outer tube, and the zinc oxide resulting from the reduction of CO_2 forms a white band on the cooler part of the inside of the outer tube close to the heat source. In addition, excess zinc forms another fluffy band close to the cooler part of the reaction cell (Figure 2b), increasing the efficiency of filamentous graphite and/or Fe-carbide formation (Orsovszki et al. 2015).

The performance of the graphite, such as ^{12}C$^-$ beam current, ^{14}C background, and recovery, synthesized by a condensate graphite reduction furnace and a muffle furnace, were compared, as shown in Table 1. There was no significant difference in ^{12}C$^-$ beam current and ^{14}C blank
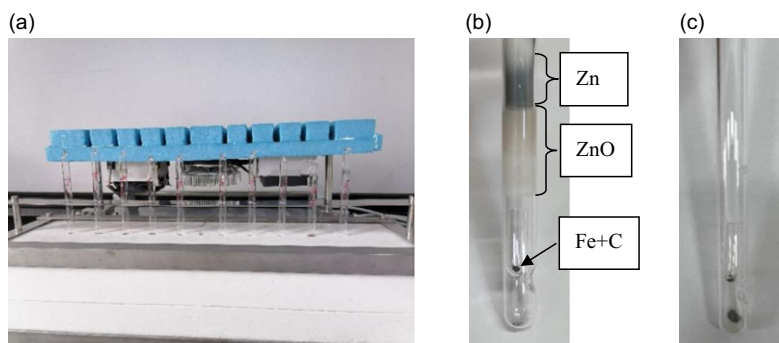
Figure 2   A customized 10-hole graphite reduction furnace (a) and the reduction tube after graphitization using the customized furnace (b) and muffle furnace (c).

values between the two types of furnaces. However, the recovery of graphite synthesized by a condensate graphite reduction furnace is much higher than that of a muffle furnace, which further supports the experimental views of Orsovszki et al. (2015) and Santos et al. (2007b).

Pretreatment and Dose of CuO

Pretreatment of CuO
The pretreatment was meant to clean up the potentially absorbed atmospheric CO_2 on the surface of CuO at high temperatures. In our study, ~1 mg of commercial graphite was used as the blank, and ~20 mg of CuO was precleaned in three groups: 900°C for 3 hr, 600°C for 3 hr, and an untreated group. The AMS measurement results are shown in Table 2.

The data show that the trace amount of modern carbon in CuO will slightly affect the experimental background. The treatment of CuO at 900°C for 3 hr and 600°C for 3 hr is better. Considering the possible decomposition reaction of CuO at high temperatures and the pollution caused by reoxidation after cooling, we adopted 600°C for CuO pretreatment.

Dose of CuO
Considering that excess CuO may introduce modern carbon (Zhou et al. 2001), we checked the relationship between the CO_2 recovery rate in the combustion reaction and the amount of CuO used. Commercial graphite (~1 mg) mixed with CuO sample sizes from 20 mg to 140 mg was placed in a muffle furnace at 900°C for 2 hr to fully react and generate CO_2, quantified by measuring the CO_2 pressure in our vacuum line. The results are shown in Table 3. As seen from the table, the CO_2 recovery rate is stable at approximately 98%, indicating that the 20–30 mg CuO dose is sufficient for ~1 mg of graphite to be fully oxidized to CO_2 in our experimental conditions.

Pretreatment and Dose of Fe powder

Pretreatment of Fe powder
Pretreatment of Fe powder is a key step in the ^{14}C graphite synthesis process to clean up the potentially absorbed atmospheric CO_2. Therefore, the sample contaminations from different Fe treatment processes were investigated. Approximately 3 mg of Fe powder was pretreated in five groups, i.e., heated under vacuum at 600°C for 0.5 hr, 1 hr, and 2 hr, heated at 400°C in open air for 3 hr, and an untreated group. The AMS measurement results are shown in Table 4.

Table 1   Experimental results of reduction furnaces.

Reduction furnace	Fe pretreatment	$^{12}C^-$ beam current/μA	$^{14}C/^{12}C$ background/ $\times 10^{-15}$	pMC	Graphite recovery/%
Muffle furnace	Air 400°C 3 hr	41 ± 1	5.65 ± 0.42	0.48 ± 0.04	65.6 ± 0.7
Muffle furnace	Air 400°C 3 hr	38 ± 1	6.04 ± 0.45	0.51 ± 0.04	77.6 ± 0.8
Muffle furnace	Air 400°C 3 hr	44 ± 1	5.82 ± 0.44	0.49 ± 0.04	75.5 ± 0.8
CGRF	Air 400°C 3 hr	42 ± 1	6.40 ± 0.48	0.54 ± 0.04	88.7 ± 0.9
CGRF	Air 400°C 3 hr	43 ± 1	5.33 ± 0.40	0.45 ± 0.03	89.1 ± 0.9
CGRF	Air 400°C 3 hr	40 ± 1	6.13 ± 0.46	0.52 ± 0.04	85.8 ± 0.6

Table 2   AMS results of different CuO treatments.

CuO treatment method	$^{12}C^-$ beam current/μA	$^{14}C/^{12}C$ Background/$\times 10^{-15}$	pMC
900°C 3 hr	37 ± 1	5.86 ± 0.44	0.50 ± 0.04
900°C 3 hr	36 ± 1	6.38 ± 0.48	0.54 ± 0.04
600°C 3 hr	36 ± 1	6.17 ± 0.46	0.52 ± 0.04
600°C 3 hr	38 ± 1	6.13 ± 0.46	0.52 ± 0.04
Untreatment	35 ± 1	6.59 ± 0.49	0.56 ± 0.04
Untreatment	43 ± 1	6.48 ± 0.49	0.55 ± 0.04

Table 3   Experimental results of CuO dose and CO_2 recovery rate in the combustion.

Sample size/mg	CuO/mg	CO_2/mbar	Carbon mass in calibrated volume/mg	CO_2 recovery rate/%
1.019	23.6	74.9	0.994	97.6 ± 1.0
1.024	40.1	75.8	1.006	98.3 ± 1.0
1.111	62	81.7	1.084	97.6 ± 1.0
1.139	81.9	84.9	1.127	98.9 ± 1.0
1.068	101.6	78.3	1.039	97.3 ± 1.0
1.158	121.4	86.1	1.143	98.7 ± 1.0
0.966	140	72.2	0.958	99.2 ± 1.0

The data show that the ^{14}C backgrounds before and after the treatment of Fe powder are significantly different. The average background value heating at 400°C in open air is 0.54± 0.02 pMC, and the fluctuation is lower than in other conditions. Under vacuum conditions, the average background values of heating at 600°C for 0.5 hr, 1 hr, and 2 hr are 0.58± 0.17 pMC, 0.57 ± 0.05pMC, and 0.59± 0.07 pMC, respectively. There were no significant differences in the ^{14}C background between the treatment groups under open air and under vacuum for different times. The average $^{12}C^-$ current is greater than 30 μA for the Fe powder heated under vacuum at 600°C for 0.5 hr, 1 hr, and 2 hr, and the average $^{12}C^-$ current is greater than 40 μA for the Fe powder heated at 400°C in open air for 3 hr, which is higher than that under other treatment conditions. The graphite recovery rates are all above 80% for Fe powder heating at 400°C in open air and heating at 600°C under vacuum for 0.5 hr and 1 hr, and the fluctuation is low. Additionally, we did not find significant differences in the graphite recovery rates between the treatment groups under open air and under vacuum for different times. Therefore, air heating at 400°C for 3 hr is an ideal pretreatment method for us considering the $^{12}C^-$ current, background, recovery rate, and convenience factor.

Ratio of Fe/C

The Fe/C ratio affects the values of the $^{12}C^-$ beam current and background of ^{14}C. With increasing Fe powder dose, sample carbon contamination will increase by 0.35 μgC per mg Fe (Dee et al. 2000). However, a low Fe/C ratio will cause beam current instability (Jull et al. 1986). Therefore, we investigated the relationship between the background level and the Fe/C ratio. For the commercial graphite of ~1 mg, the sample sizes of catalyst Fe powder ranged from 0.1 mg to 5 mg (after heating in open air at 400°C for 3 hr), as shown in Figure 3. With the decrease in the Fe/C ratio, the background of $^{14}C/^{12}C$ decreases slowly before finally reaching a

Table 4 Results of the Fe powder pretreatment experiment.

Sample ID	Sample size/mg	Carbon mass in calibrated volume/mg	Amount of graphite/mg	Graphite recovery/%		Fe pretreatment	Dose of Fe/mg	$^{12}C^-$ beam current/μA	$^{14}C/^{12}C$ background		pMC (error)
1	1.008	0.969	0.596	61.50	75 ± 21	Vacuum 600°C 2 hr	2.870	23	5.19×10^{-15}	0.42	0.58 ± 0.17
2	1.097	1.074	0.71	66.10		Vacuum 600°C 2 hr	2.863	28	8.94×10^{-15}	0.76	
3	1.112	0.985	1.022	100.00		Vacuum 600°C 2 hr	3.108	30	6.71×10^{-15}	0.57	
4	0.968	0.930	0.798	85.76	83 ± 5	Vacuum 600°C 1 hr	2.789	37	5.62×10^{-15}	0.48	0.57 ± 0.05
5	1.041	0.877	0.693	78.98		Vacuum 600°C 1 hr	3.505	28	6.95×10^{-15}	0.59	
6	1.096	1.023	0.924	90.29		Vacuum 600°C 1 hr	2.796	38	6.69×10^{-15}	0.57	
7	1.078	0.848	0.683	80.53		Vacuum 600°C 1 hr	2.899	31	6.99×10^{-15}	0.59	
8	1.322	1.260	1.030	81.77		Vacuum 600°C 1 hr	2.884	28	7.26×10^{-15}	0.62	
9	1.142	1.120	1.094	97.66	92 ± 6	Vacuum 600°C 0.5 hr	2.969	37	8.35×10^{-15}	0.71	0.59 ± 0.07
10	1.120	1.068	0.869	81.33		Vacuum 600°C 0.5 hr	2.780	34	6.82×10^{-15}	0.58	
11	1.044	0.972	0.911	93.76		Vacuum 600°C 0.5 hr	2.878	35	6.23×10^{-15}	0.53	
12	1.238	1.163	1.079	92.80		Vacuum 600°C 0.5 hr	3.502	34	6.78×10^{-15}	0.58	
13	1.123	1.075	1.012	94.13		Vacuum 600°C 0.5 hr	3.139	34	6.42×10^{-15}	0.55	

(Continued)

Table 4 (*Continued*)

| Sample ID	Sample size/mg	Carbon mass in calibrated volume/mg	Amount of graphite/mg	Graphite recovery/%		Fe pretreatment	Dose of Fe/mg	$^{12}C^-$ beam current/μA	$^{14}C/^{12}C$ background		pMC (error)
14	0.937	0.730	0.665	91.12	92 ± 5	Air 400°C 3 hr	2.626	47	5.96×10^{-15}	0.51	0.54 ± 0.02
15	0.938	0.844	0.749	88.73		Air 400°C 3 hr	3.106	39	6.37×10^{-15}	0.54	
16	1.002	0.899	0.801	89.13		Air 400°C 3 hr	2.640	43	6.46×10^{-15}	0.55	
17	1.010	0.838	0.759	90.60		Air 400°C 3 hr	2.889	41	6.22×10^{-15}	0.53	
18	1.015	0.813	0.819	100.0		Air 400°C 3 hr	2.726	36	6.68×10^{-15}	0.57	
19	1.181	1.164	0.938	80.55	90 ± 13	Untreatment	2.554	19	1.89×10^{-14}	1.58	1.49 ± 0.13
20	1.078	0.816	0.848	100.0		Untreatment	2.889	17	1.66×10^{-14}	1.39	
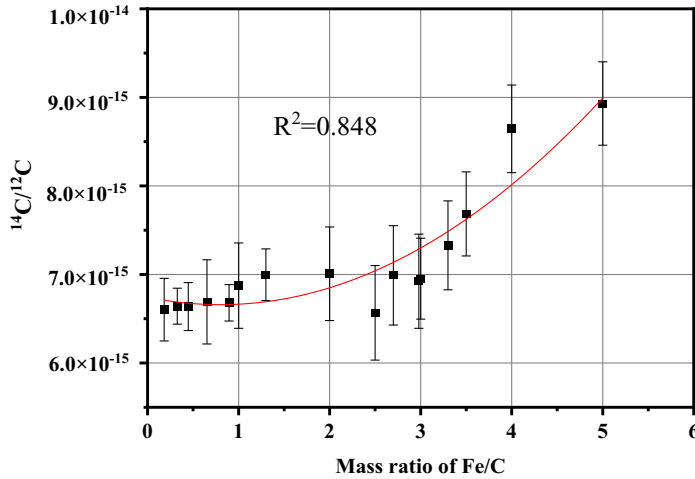
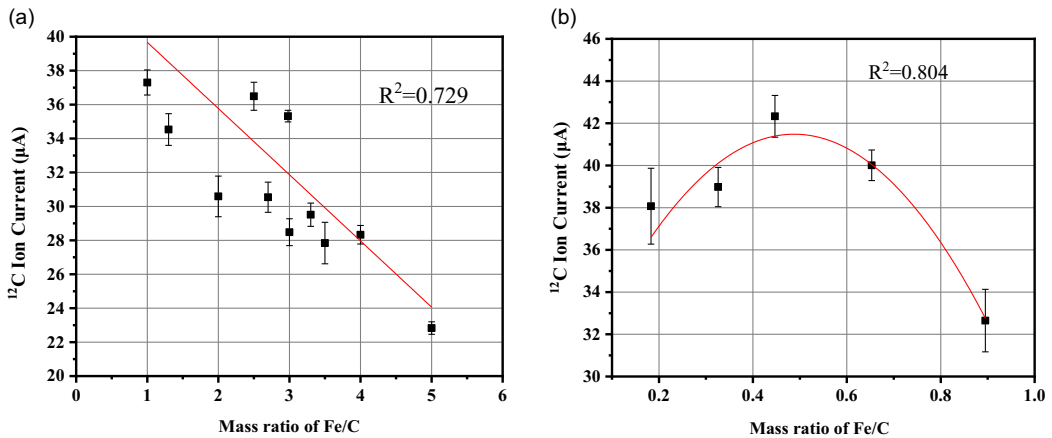Figure 3   Relationship between Fe/C and ^{14}C/^{12}C.

Figure 4   Relationship between ^{12}C$^-$ beam current and Fe/C ratio. (a) Fe/C >1, and (b) Fe/C <1.

balance value of approximately 6.5×10^{-15}, which is a considerably better value when the mass ratio of Fe/C is lower than 3.

To explore the lower limit ratio of Fe/C, we also checked the relationship between the ^{12}C$^-$ beam current value and the Fe/C ratio, as shown in Figure 4(a). With increasing Fe/C, the ^{12}C$^-$ beam current decreases gradually because the decrease in the amount of carbon attached to the unit Fe powder affects the ^{12}C$^-$ beam current. Meanwhile, we explored the ^{12}C$^-$ beam current when Fe/C<1, as shown in Figure 4(b). With the decrease in Fe/C, the ^{12}C$^-$ beam current first increased and then decreased. The maximum value ($\approx$43 μA) is obtained when Fe/C is approximately 0.5.

However, the average graphite recovery rate under this condition is only approximately 50%, and the durability and stability of the ^{12}C$^-$ beam current with an Fe/C ratio of 2.5 were better
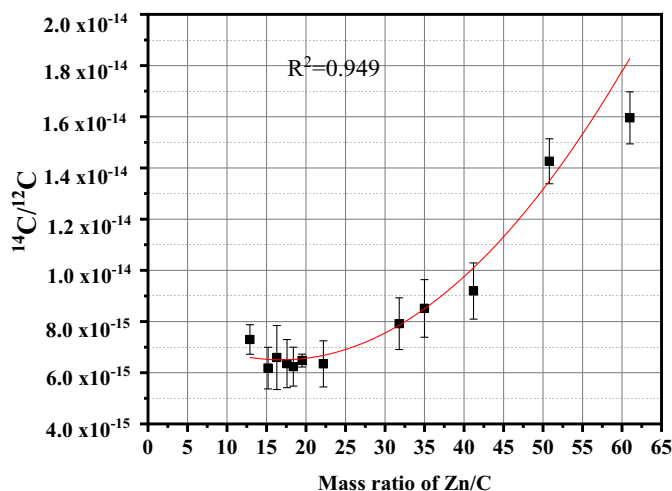
Figure 5   Relationship between Zn/C and $^{14}C/^{12}C$ of blank samples.

than those with an Fe/C ratio of 1.5, which is consistent with the conclusion of Orsovszki et al. (2015). Therefore, the ratio of Fe/C is determined to be 2.5–3.0 in our laboratory, considering both the background value and the beam current durability.

Ratio of Zn/C

According to the chemical reaction formula, the mass ratio Zn/C required for the complete reaction of the equation is 10.88, and with the increase in Zn/C, the graphite yield and $^{12}C^-$ beam current increase rapidly (Macario 2016). However, excess Zn powder may also introduce modern carbon contamination. Therefore, we checked the relationship between the $^{14}C/^{12}C$ backgrounds and the amount of Zn powder used. For the CO_2 containing ~1 mg carbon, the reducant Zn powder sample sizes ranged from 10 mg to 60 mg, as shown in Figure 5. With the increase in the Zn/C ratio, the background of $^{14}C/^{12}C$ decreases slightly and then gradually increases, indicating that the Zn powder contains a small amount of modern carbon, which considerably influences the ^{14}C background.

As seen in Figure 5, the $^{14}C/^{12}C$ background value is stable at approximately 6.5×10^{-15} when the sample size of Zn is 15–25 mg, which is the most suitable range for the reduction of 1 mg of graphite. When the amount of Zn powder is more than 30 mg, the background increases with the increased sample size of Zn. Another possible reason is that when the amount of Zn is excessive, the carbides formed by Zn and C exist in the mixture of Fe powder and graphite, which affects the synthesis of graphite and increases the experimental background (Santos et al. 2007b). Therefore, the ratio of Zn/C was determined to be 18–22 mg Zn/mg C in our laboratory.

Temperature and Time of Reduction

The recovery rate of graphite is important and sensitive to the temperature and time of reduction. Therefore, we investigated the relationship between temperature or time of reduction and recovery rate when the other conditions were the same. The influence of the reduction temperature on the recovery rate is shown in Figure S1(a). The recovery rate

increases with the reduction temperature and eventually reaches a balance value of approximately 90% at temperatures ranging from 650°C to 700°C. Figure S1(b) shows the influence of reduction time on the recovery rate, which increases with the reduction time and reaches an equilibrium value of 8–9 hr, with a recovery rate of over 98%. For these reasons, our lab's reduction temperature and time are set to 650°C–700°C and 8–9 hr, respectively.

AMS MEASUREMENTS

According to the established experimental conditions for preparing ^{14}C graphite using the Zn-Fe method, the samples were oxidized, purified, graphitized, and finally measured with AMS. Commercial blank graphite was directly measured to check the machine background, and the results are shown in Figure S2(a). The background value of unprocessed commercial graphite was 0.27 ± 0.02 pMC, and the ^{14}C/^{12}C value was 3.14 ± 0.27 × 10^{-15}, equivalent to a ^{14}C age of approximately 47,000 years. The experimental results for the process blank of the Zn-Fe method are shown in Figure S2(b). The background value ranged between 0.49 pMC and 0.62 pMC, the mean value was 0.55 ± 0.04 pMC, and the ^{14}C/^{12}C ratio was 6.47 ± 0.48 × 10^{-15}, equivalent to a ^{14}C age of approximately 40,500 years. In addition, three international standard samples, OXII, Chinese sugar carbon (CSC), and IAEA-C8, were prepared and measured using AMS. The experimental results for the oxalic acid standard are shown in Figure S2(c). The average pMC of oxalic acid was 134.11 ± 0.41 pMC, which is consistent with the recognized standard value of 134.07 pMC within the allowable error (the precision of the system ~ 0.6%). The pMC value of CSC was 136.32 ± 0.48 pMC, which was consistent with the recognized standard value of 136.2 pMC. Moreover, the pMC value of IAEA-C8 was 15.17 ± 0.22 pMC, as shown in Figure S2(d), which was also consistent with the recognized standard value of 15.03 pMC.

CONCLUSION AND DISCUSSION

In this study, ^{14}C samples of 1 mg of carbon were prepared by the Zn-Fe reduction method and verified with AMS under the following optimal conditions: 20–30 mg CuO powder was pretreated at 600°C for 3 hr, 2.5–3.0 mg Fe powder and 18–22 mg Zn powder were pretreated at 400°C in open air for 3 hr, and reduction treatments were performed in a condensed graphite reduction furnace at 650°C for 8 hr. The AMS measurement results show that the average value of OX-II is 134.11 ± 0.41 pMC, the CSC average value is 136.32 ± 0.48 pMC, and the IAEA-C8 average value is 15.17 ± 0.22 pMC, all of which are consistent with the recognized standard value. The ^{14}C/^{12}C ratio of the process blank was (6.47 ± 0.48) × 10^{-15}, equivalent to a ^{14}C age of approximately 40,500 years. After deducting the machine background of (3.14 ± 0.27) × 10^{-15}, the background induced by the sample preparation process with the above method was (2.06 ± 0.55) × 10^{-15}. The preliminary results show that this sample preparation method is reliable, can provide technical support for the development of ^{14}C dating and tracing at GXNU, and contributes to biology and environmental science.

SUPPLEMENTARY MATERIAL

To view supplementary material for this article, please visit https://doi.org/10.1017/RDC.2024.73

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