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Modifying a sealed tube zinc reduction method for preparation of AMS graphite targets: Reducing background and attaining high precision

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Abstract

The sealed tube zinc reduction method for converting CO_2 to graphite for AMS ^{14}C measurements was originally developed for rapid production of graphite in biomedical tracer experiments. The method was usually thought to have low precision and a high background. We have modified the zinc reduction method originally outlined in Vogel [J.S. Vogel, Radiocarbon 34 (3) (1992) 344] by carefully controlling the amounts of reagents (zinc, titanium hydride and Co or Fe catalyst) and now routinely obtain a precision of 2–3‰ and a relatively low background of ∼50,000 ^{14}C years when analyzing for ^{14}C at the Keck Carbon Cycle AMS facility at UC Irvine. Fractionation of carbon isotopes does occur during graphitization and depends on the graphitization yield, which can be affected by the amounts of reagents used and other conditions. The $\delta^{13}C$ of our zinc-reduced graphite is usually lighter by 2–3‰ than the CO_2 from which it is made, but this is corrected for in our system by simultaneous measurement of $^{13}C/^{12}C$ along with $^{14}C/^{12}C$ by the spectrometer. This method is suitable for ^{14}C enriched samples, as well as natural abundance ^{14}C samples, especially those with modern ^{14}C contents. With improved precision and background, we believe that many disciplines can benefit from this technique because of its low cost and rapid production of graphite.
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1. Introduction

The production of uniform and high quality graphite targets is essential for the optimal performance of any AMS system. Graphite production for AMS ^{14}C measurements is most commonly achieved by hydrogen reduction of CO_2 with iron or cobalt catalyst [2,3]. The method has proved to be precise, accurate and have a low background while being suitable for all types of natural samples. The graphitization yield can be monitored during the reaction and is often close to 100%. At yields close to 100% isotopic fractionation between the original CO_2 and the graphite produced is very small, although large fractionation can occur with low yields. Samples as small as 2 μg carbon can be successfully converted to graphite [4]. Graphite produced by hydrogen reduction is also well behaved in the cesium sputter ion source, producing high and long-lasting current. However, building a hydrogen reduction line is relatively costly because of the requirements for pressure monitoring and the need for multiple ovens for hydrogen reactors. Hence, the number of reaction vessels is usually a limiting factor for the throughput of samples using hydrogen reduction.

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Jull et al. [5] and Slota et al. [6] developed zinc reduction methods for precise AMS ^{14}C measurements. Both techniques use a Zn finger at 400–500 °C to reduce CO_2 to CO and an Fe finger at 700–750 °C to covert CO to graphite. The main difference between the two methods is that Slota et al. eliminated the use of H_2. Both methods were reported to be precise and accurate, but again, the graphite production was limited by the number of reaction units on the vacuum line. Slota and Taylor [7] experimented using a small sealed tube with Fe and Zn in the same tube to make graphite from CO_2 and claimed that the graphite was equivalent to the graphite produced in the two-fingered apparatus. However, a very long time was required for reduction.

The sealed tube zinc reduction method we modified is adapted from one described in Vogel [1]. This method was originally developed for converting CO_2 to graphite for biomedical research materials that had elevated ^{14}C from labeling experiments. To avoid sample-to-sample contamination, Vogel [1] used disposable gas manifolds for CO_2 transfer, trapped water in the combustion tube and sealed CO_2 into Pyrex tubes pre-loaded with zinc, TiH_2, and a smaller tube with Fe or Co catalyst. Graphitization was accomplished by putting the entire sealed tube into a 550 °C oven. This method allows rapid production of large numbers of graphite samples without cross-contamination (∼300 samples/week/person). Ognibene et al. [8] modified the method by replacing the Pyrex tubes (which needed to be produced as well as sealed) with septa-sealed vials and eliminating the use of TiH_2 as a source of H_2 pressure. Instead, they used H_2O directly from the combusted biochemical sample without separating it from CO_2. With the modification, the authors reported that a single technician could prepare approximately 150 samples in an 8 h day. However, this sealed tube method has too low precision (10–20‰ reported by Vogel [1] and 9.8‰ by Ognibene et al. [8]) and a background (∼1 pMC and variable, reported by Vogel [1]) too high to be used routinely for natural abundance radiocarbon samples.

Ten years ago, we adapted the original sealed tube zinc reduction method from Vogel [1] for samples that have relatively high amounts of ^{14}C (i.e. with bomb ^{14}C to a few thousand years old), and which are not smaller than 0.5 mg C [9]. We achieved a precision of 5–6‰ and a background of ∼40,000 ^{14}C years when our zinc-reduced graphite was measured for ^{14}C at LLNL CAMS facility, which measures only $^{14}C/^{13}C$ ratio and not $^{13}C/^{12}C$. In the last several years, we have modified the original method by carefully controlling the amounts of reagents (zinc, titanium hydride and Co/Fe) and most importantly, by using the simultaneously measured AMS $\delta^{13}C$ for correction of isotopic fractionation during graphite production. We now routinely obtain a precision of 2–3‰ and a relatively low background of 50,000 ^{14}C years when analyzing for ^{14}C at the Keck Carbon Cycle AMS facility at UC Irvine.

In this paper, we describe our modified Zn reduction procedure, the experiments done to investigate carbon iso-tope fractionation and report the precision and background obtained in our lab for measurements made over the last three years. With improved precision and background, we believe that many disciplines can benefit from this technique because of its low cost and rapid production of graphite.

2. Method

2.1. Procedures

Dry organic solid samples equivalent to about 1–1.5 mg of C are combusted with clean CuO in 6 mm O.D. quartz tubes at 900 °C for 2 h. CO_2 from the combustion is extracted cryogenically using the simple vacuum line shown in Fig. 1(a). The vacuum system consists of a mechanical pump and a liquid nitrogen trap between the pump and the line that prevents oil from back streaming to the line. The quartz tube with CO_2 is cracked open in the tube cracker. A dry ice and ethanol slurry is placed on the first trap in the line to freeze out water. A dewar filled with liquid nitrogen is placed on the second trap for freezing down CO_2. Any non-condensable gases, mostly N_2, are pumped away. The purified CO_2 is transferred to a known-volume reservoir and quantified by measuring the CO_2 pressure. This is used to calculate the yield of sample combustion, which we compare with an elemental analyzer (FISONS NA-1500) to check the volume of our measuring system.

Approximately 1 mg C as CO_2 is frozen into the reaction tube using liquid nitrogen (see Fig. 1(b) and next paragraph). The remainder is expanded into a finger on the left of the vacuum line where we insert a gas-tight syringe through the septum on a three way Ultra-Torr tee to take a subsample of the CO_2 that is injected into a He-filled vial for $\delta^{13}C$ measurement by Gas Bench coupled with IRMS (Thermo Electron Delta Plus).

The reactor tube with frozen CO_2 is sealed using a torch. The total length of the sealed tube is ∼110 mm long; a shorter tube may help graphitizing small samples [10]. The tube is placed upright in a metal heating block capable of withstanding temperatures of 550 °C. The block and tubes are then placed inside a furnace for graphitization. The furnace is set to 500 °C for 3 h and 550 °C for 4 h (then cools slowly, usually overnight). Filamentous graphite forms at the surface of the catalyst.

Graphite samples are stored in the reaction tubes until immediately prior to pressing into sample holders for AMS measurement. To remove the sample from the tube without introducing glass fragments, we gently slide the inside 6 mm tube with graphite/catalyst mixture horizontally to the top end of the tube, then crack open the outside 9 mm tube near the bottom, just above the Zn/TiH_2 powders. Graphite is hammered into the central 1 mm diameter hole in the aluminum target holder [11]. The graphite targets are analyzed for ^{14}C at Keck Carbon Cycle AMS facility at UC Irvine [12,13].
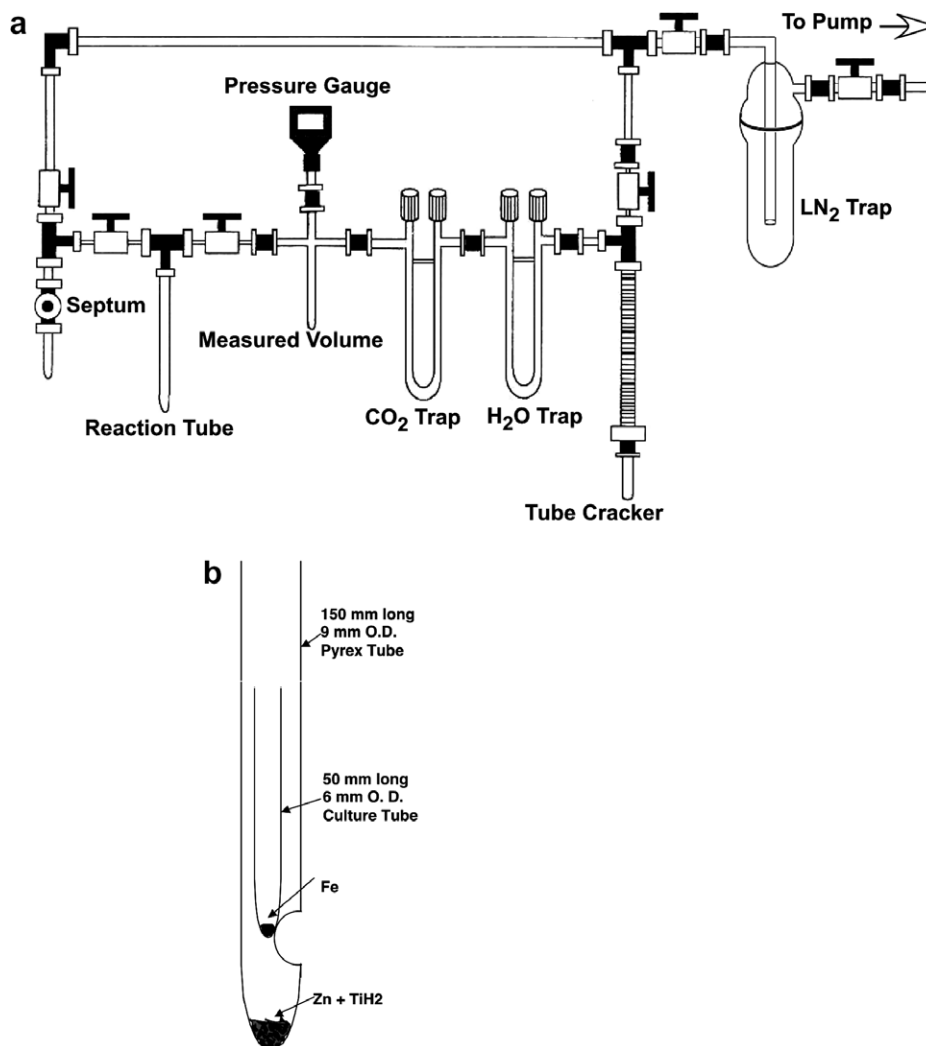
Fig. 1. (a) Vacuum line set up to extract CO_2 cryogenically from a cracked combustion tube. (b) Reaction tube. A 9 mm O.D. Pyrex reactor tube with reductants zinc (Aldrich, #324930) and titanium hydride (Alfa Aesar, #12857) in bottom and catalyst iron (Alfa Aesar, #39813) in a 6 mm O.D. Pyrex culture tube sitting on a dimple 2 cm from the base of the outside tube.

The samples we discuss here were combusted, but we also use the same vacuum lines to purify CO_2 from heated molecular sieve traps [14,15], or from larger air samples from canisters [14]. These kinds of samples are more time consuming (for example, baking out and reactivating a molecular sieve trap will take ~1.5 h per sample). Therefore, our approach is to have multiple extraction lines and to freeze the purified CO_2 directly into the reaction tube at the end of each extraction, with no need to store it in a break-seal tube first as would be the case if we transferred the sample to another line for H_2-reduction of graphite.

2.2. Reaction tube preparation

The reaction tube preparation is as described in Vogel [1]; the major difference is that we have modified the amounts of Zn and TiH_2 reagents. The reaction tube is a 152 mm long, 9 mm O.D. Pyrex tube that is sealed at one end, with a small indentation ~2 cm above the bottom (see Fig. 1(b)). Tubes are pre-baked at 500–550 °C for 7 h. We use 30–35 mg zinc (Aldrich, #324930) and 10–15 mg titanium hydride (Alfa Aesar, #12857) that are placed in the bottom of the 9 mm tube. The catalyst – we now use Fe (Alfa Aesar, 350 mesh, #39813) [16], in a ratio of 3–5 mg catalyst per gram of C – is weighed separately into in a pre-baked, 50 mm long, 6 mm O.D. Kimble culture tube which is handled with gloves. The 6 mm tube is then inserted into the 9 mm tube so that it is suspended above the Zn and TiH_2 powders by the indentation (see Fig. 1(b)). The presence of zinc in graphite decreases sputtering yield in the ion source [8].

We use three different sizes of Chalazion curettes to measure the amount of reagents quickly and relatively accurately without weighing them out individually. With practice, a precision of ±1–2 mg can be achieved. The amounts of agents given above here are optimal for $1 ± 0.2$ mg C even though samples as small as 0.1 mg C

have been graphitized successfully under the same conditions.

Although we used Co as a catalyst for many years, we recently switched to Fe. Both catalysts make good graphite, but graphite formed with Fe performs better in the ion source of our AMS system. The Zn/Fe graphite is less fluffy than the Zn/Co graphite and thus easier to get inside the target holder. At the moment, we are not pre-cleaning any of the reagents, but are still able to obtain satisfactory background ($\sim$50,000 ^{14}C years). In addition, we store prepared tubes – loosely covered with Al foil – in ambient lab air for up to a week or two without apparent adverse effects on background or precision.

2.3. Experiments

As pointed out by Vogel et al. [1], mass-dependent fractionation of carbon isotopes does occur during the zinc reduction graphitization process. The authors reported an average of 2.2‰ lighter in δ^{13}C for the finished graphite with 80% conversion yield than the initial CO_2 at reaction temperature of 435 °C. For graphite with lower yields, the fractionation is larger, but still usually less than 5‰. In order to investigate the degree and conditions of isotopic fractionations involved in this zinc reduction graphitization method and to search for the optimum graphitization conditions, we graphitized a set of OX1 and ANU standards using different amount of reagents (Zn from 8 to 51 mg, TiH$_2$ from 4 to 29 mg and Co from 2 to 8 mg). The amount

of sample graphitized is either 1 mg C or 0.5 mg C. Most of the graphite was used for ^{14}C measurement and a small portion of the graphite was also measured for δ ^{13}C and C% by EA-IRMS on a Thermo Electron Delta Plus. The graphitization yield is calculated as follows:

Graphitization yield(%)
$$= [C\% \cdot \text{Graphite–catalyst mixture(mg)}]/C_{added} \text{ (mg)},$$

where C% is the percentage of C in the graphite–catalyst mixture as determined by elemental analyzer, the graphite/catalyst mixture mass (mg) is determined by weighing before pressing the sample and C_{added}, the amount of C (reported as mg C) in CO_2 originally sealed in the reduction tube, was determined using the pressure of CO_2 in a known volume on the vacuum line.

Errors involved in the graphitization yield calculation come from three sources: the calibration of the measured volume for CO_2, possible physical loss during transfer of the graphite–catalyst mixture for weighing and the C% measurement by EA. The relative errors for these three sources are estimated at 2.0%, 1.3% and 1.0%, respectively, yielding a total estimated error for an average graphitization yield of 86% (Table 1) of about ±2% (1σ). Another method for determining gravimetric yield, based on comparing the weight of the 6 mm inner tube before and after graphitization consistently yielded mass increases in excess of what was expected from 100% conversion of CO_2 to C

Table 1
Experimental data

| UCIT#	Standard	Condition	CO$_2$ added (mg)	Zn (mg)	TiH$_2$ (mg)	Co (mg)	δ^{13}C	Δ^{14}C	% Graphitized
10537_5	ANU	Regular	0.5	30.3	16.8	5.1	−16.4	484.8	82
10536_3	ANU	Double time	1.0	29.8	17.5	5.1	−15.3	487.9	79
10537_2	ANU	Regular	1.0	30.8	17.0	2.1	−14.8	492.8	82
10537_1	ANU	Regular	1.1	30.4	16.9	8.2	−14.6	491.7	89
10536_2	ANU	Regular	1.0	30.0	16.9	5.1	−14.1	487.3	86
10537_3	ANU	Regular	1.0	29.4	10.0	5.2	−13.3	486.0	93
10537_4	ANU	Regular	1.0	30.6	20.0	4.8	−14.6	487.3	
10536_1	ANU	Regular	1.0	50.9	17.2	5.2	−14.4	488.2	86
10602_1	ANU	Regular	1.0	48.2	28.7	5.1	−16.7	497.7	73
10602_2	ANU	Regular	1.0	21.5	10.9	4.7	−15.0	489.7	85
10602_3	ANU	Regular	1.0	8.0	4.6	4.7		490.0	
10603_1	ANU	Regular	1.0	50.0	4.7	5.1	−11.5	493.3	91
10603_2	ANU	Regular	1.0	33.8	16.4	5.2	−14.0	498.6	82
10534_4	OX1	Regular	0.5	29.8	16.6	5.1	−25.4	31.8	
10534_3	OX1	Double time	1.0	30.4	17.5	5.2	−22.4	28.7	88
10535_4	OX1	Regular	1.0	30.3	17.2	2.2	−24.7	32.1	84
10535_3	OX1	Regular	1.0	30.2	16.6	8.0	−22.5	29.3	99
10535_1	OX1	Regular	1.0	30.7	17.6	4.9	−23.6	31.8	87
10534_2	OX1	Regular	1.0	30.0	10.0	5.2	−21.8	30.2	96
10535_2	OX1	Regular	1.0	30.4	20.2	4.8	−23.7	30.9	83
10534_1	OX1	Regular	1.0	50.7	17.2	5.2	−22.7	29.2	91
10600_1	OX1	Regular	1.0	47.8	28.0	4.8	−25.3	37.3	69
10600_2	OX1	Regular	1.0	18.5	10.6	4.8	−25.4	30.3	84
10600_3	OX1	Regular	0.9	13.3	4.1	4.8	−23.2	30.8	79
10600_4	OX1	Regular	1.0	9.3	13.8	5.5	−27.4	31.2	72
10601_1	OX1	Regular	1.0	47.6	5.0	4.8	−20.2	33.7	95
10601_2	OX1	Regular	1.0	30.5	14.7	4.7	−23.2	33.9	84
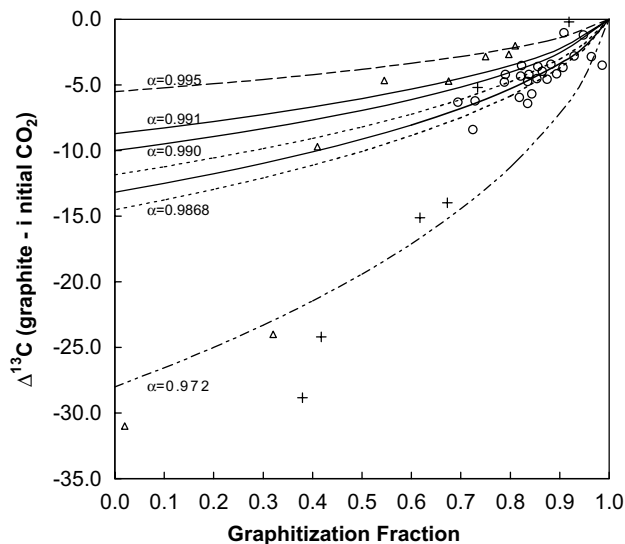
Fig. 2. Measured and modeled ^{13}C isotope fractionation as a function of graphitization yield (for four sealed tube methods). Lines are calculated fractionations based on a closed system Rayleigh model. Lines 0.990 and 0.991 are based on theoretical $\alpha_{graphite–CO_2}$ [22,23] at 500 °C and 550 °C respectively. The curve of 0.995 is the best fit of data from Kitagawa et al. [10] on their sealed tube H_2/Fe system. Other data points are from Vogel [1] (sealed tube Zn/TiH$_2$ system, shown as "$\triangle$") and Verkoueren et al. [17] (sealed tube H_2/Fe + Mn system, shown as "+"). The dashed line calculated using $\alpha_{graphite–CO_2}$ of 0.972 is the best fit for data of Verkoueren et al. [17]. The open circles (○) are data from this work. The best-fit $\alpha_{graphite–CO_2}$ for our data set is 0.9868 ± 0.0013, shown as solid line with dashed lines for the 95% confidence bands. The smaller $\alpha_{graphite–CO_2}$ indicates that the actual graphitization reactions are influenced by kinetic fractionation.

on the graphite. We attribute the extra weight to the deposition of ZnO on the glass wall.

Results are shown in Table 1 and Figs. 2 and 3. Both OXI and ANU behave similarly in our tests. As expected, overall fractionation ($\delta^{13}C$ difference between graphite and initial CO_2) is minimized when graphitization yield is higher (Fig. 2). The minimum fractionation observed was 1‰. Fractionation decreases when the Zn/TiH$_2$ ratio increases (Fig. 3(a)). Too much TiH$_2$ will increase fractionation (Fig. 3(b)), likely because CH$_4$ may form when excess H$_2$ is present. Also shown in Fig. 3(b), too much Zn (>50 mg/mg C) may increase the fractionation. The effect of catalyst amount on ^{13}C fractionation is not significant in the range we investigated. Based on the experiments described above, we set the amount of reagents and catalysts we currently use for a 1 mg C sample to be: 30–35 mg Zn, 10–15 mg TiH$_2$ and 3–5 mg Fe. Using these amounts, we typically obtain 85–90% yield, with an average fractionation of 2–3‰ in $\delta^{13}C$.

Increasing graphitization time from 4 h at 550 °C to 8 h had no effect on yield or isotopic fractionation. We did not attempt to stop the reaction early to study the effect of incomplete graphitization, or to test whether we could shorten the graphitization time, because it is convenient to leave the reaction overnight.
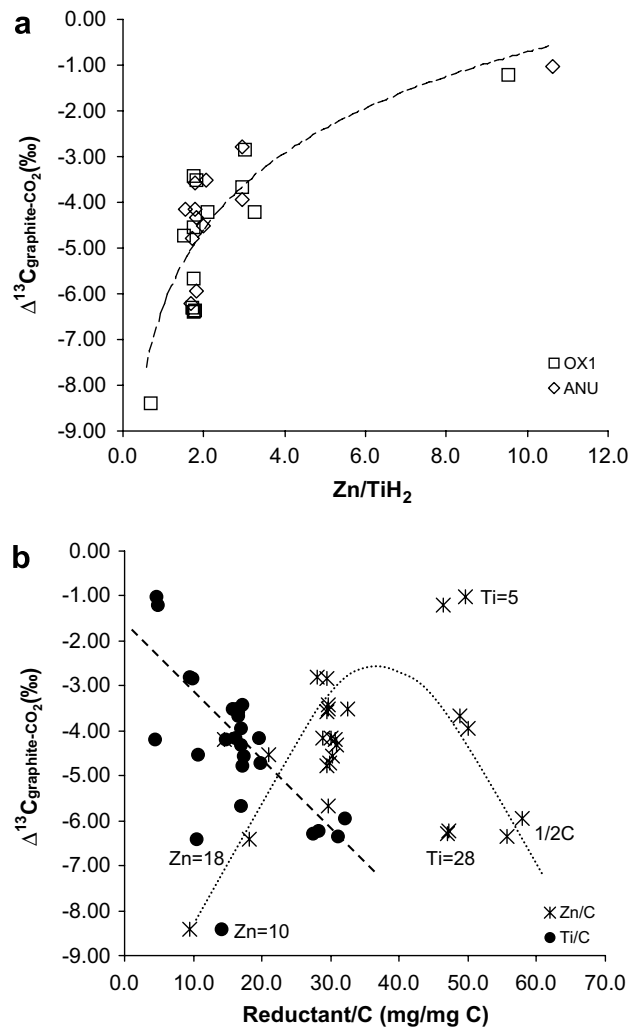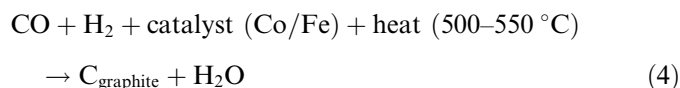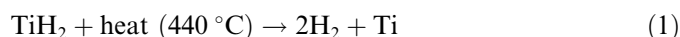

Fig. 3. (a) Relationship between ^{13}C fractionation and Zn/TiH$_2$ ratio. Fractionation decreases when the Zn/TiH$_2$ ratio increases. The dashed line is the best logarithmic fit of the data ($R^2 = 0.640$). (b) Relationship between ^{13}C fractionation and reductant/C ratios. It shows that too much TiH$_2$ and too much Zn (>50 mg/mg C) may increase ^{13}C fractionation. The dashed straight line is the best linear fit for the Ti/C data, excluding two points of Zn = 10 mg and Zn = 18 mg ($R^2 = 0.688$). The dashed curve line is the approximate trend for the Zn/C data (except for the points of either very high or low Ti H$_2$).

3. Results and discussion

3.1. Graphitization reactions and conditions

The following are reactions responsible for graphite formation within the sealed reaction tube [5,17–19]:

$$TiH_2 + heat\ (440\ °C) \rightarrow 2H_2 + Ti \tag{1}$$

$$CO_2 + H_2 \rightarrow CO + H_2O \tag{2}$$

$$CO_2 + Zn \rightarrow CO + ZnO \tag{3}$$

$$CO + H_2 + catalyst\ (Co/Fe) + heat\ (500–550\ °C)$$
$$\rightarrow C_{graphite} + H_2O \tag{4}$$

$$2CO \rightarrow C_{graphite} + CO_2 \qquad (5)$$

$$Zn + H_2O \rightarrow ZnO + H_2 \qquad (6)$$

Previous studies show that the presence of H_2 helps increase the rate of graphite formation [1]. McNichol et al. [18] observed that the reaction rate of CO to graphite is more rapid in the presence of H_2 (compared to Zn reduction alone with Fe as catalyst). As shown in reaction (1), TiH_2 provides the source of H_2. Strictly speaking, our method is a combination of both H_2 and Zn reduction and the function of Zn here is not only for reducing CO_2 to CO, but most importantly, recycling the H_2O back to H_2 (Reaction 6). Ognibene et al. [8] reported using H_2O from combustion of biochemical samples (without separating it from CO_2) as the H_2 source, which simplified the CO_2 extraction greatly. However, the amount of water is highly variable in different types of natural samples and would be difficult to control in our application. Some samples may not have enough water to provide the source of H_2 while others may overwhelm the capacity of the Zn.

Other possible reactions within the sealed reaction tube [5,17–19] are:

$$2CO + 2H_2 \rightarrow CO_2 + CH_4 \qquad (7)$$

$$CO + 3H_2 \rightarrow H_2O + CH_4 \qquad (8)$$

$$C + 2H_2 \rightarrow CH_4 \qquad (9)$$

As we can see, CH_4 could form in the reaction tube, especially in the presence of excess H_2. McNichol et al. [18] show that in their H_2/Co system, CH_4 rose to a low pressure of 0.03–0.08 atm when CO started to form and remained for the rest of the reaction (8 h). CH_4 was also present in the Zn/Fe method. Verkouteren et al. [18] and Verkouteren and Klouda [19] also demonstrated the correlation of CH_4 production and the presence of H_2. For our Zn reduction method, the formation of CH_4 may be one of the causes for low graphitization yield and isotope fractionation, especially with high amounts of TiH_2.

Graphitization condition is set at 500 °C for 3 h and 550 °C for 4 h in a Muffle furnace in our method. The temperature settings were adapted from Vogel [1]. The only change we made is prolonging the time at 550 °C from 2 to 4 h, which helps small samples to graphitize. In the Zn reduction method with Fe as catalyst (no H_2 added) by Slota et al. [6], the temperature was set to 500 °C for the Zn finger and 750 °C for the Fe finger. The Arizona AMS facility's current setting for the Fe finger is 600 °C. The temperature settings for the Zn reduction method (with small amounts of H_2 present) at the ANTARES AMS Center are 400 °C for Zn and 600 °C for Fe, respectively [20]. The lower temperature of 500 °C in the first step may favor the CO formation and 550 °C in the second step may favor the graphite formation over Fe. McNichol et al. [18] studied the effect of temperature, different catalysts and reducing agent on graphitization by studying the gas composition changes of CO_2, CO and CH_4 during the formation of graphite. Their studies show that conversion of CO$_2$ to CO with H_2 is most rapid at 750 °C, but conversion of CO to graphite is impossible at that temperature due to possible sintering of the catalyst. Also Fe appears to be a better catalyst (faster than Co) at temperatures between 575 and 650 °C. We keep the reaction temperature between 500 and 550 °C because we use Pyrex tubing, which is much cheaper and much easier to torch seal than quartz tubing.

3.2. Carbon isotope fractionation

Mass-dependent fractionation of carbon isotopes does occur during this sealed tube zinc reduction graphitization, depending on the amount of reagents used and other conditions. $\delta^{13}C$ of graphite can be lighter by 1–8 ‰ than the initial CO_2 under the conditions we investigated.

Fig. 2 illustrates the measured and modeled ^{13}C isotopic fractionation as a function of graphitization yield. The calculated fractionation shown as solid lines is from a simple closed system Rayleigh model [21]:

$$\Delta_{graphite–CO_2} = -(1 - F)/F \cdot (\alpha_{graphite–CO_2} - 1) \cdot 1000 \ln(1 - F),$$

where $\Delta_{graphite–CO_2}$ is the difference of $\delta^{13}C$ between graphite (product) and CO_2 (reactant) as ‰, F is the fraction of graphite formation and $\alpha_{graphite–CO_2}$ is the isotopic fractionation factor between graphite and CO_2 at the reaction temperature. The theoretical $\alpha_{graphite–CO_2}$ [22,23] is 0.9900 and 0.9913 at 500 °C and 550 °C respectively. A value of $\alpha_{graphite–CO_2}$ less than 1 indicates that the product graphite is depleted in ^{13}C relative to CO_2 at equilibration. If the reaction is 100% complete, i.e. all CO_2 is converted to graphite, then there should be no isotopic fractionation ($\Delta_{graphite–CO_2} = 0$). Our experimental data shows that isotope fractionation exists when the graphitization yield is low. The best-fit $\alpha_{graphite–CO_2}$ is only 0.9868 ± 0.0013 (with 95% confidence and a chisq of 29.8), significantly less than the theoretical fractionation factor. In reactions governed by kinetics, the light isotopes are more concentrated in the products. Thus the deviation of the experimental data from the theoretical prediction suggests some influence of kinetically controlled fractionation. The curve of 0.995 is the best fit of data from Kitagawa et al. [10] on their sealed tube H_2/Fe system. Other data points are from Vogel [1] and Verkoueren et al. ([17], sealed tube H_2/Fe + Mn system). The solid line calculated using $\alpha_{graphite–CO_2}$ of 0.972 is the best fit for data of Verkoueren et al. [17]. The much smaller $\alpha_{graphite–CO_2}$ is due to the fact that some of those highly fractionated reactions were stopped early to intentionally obtain the incomplete graphitization fractionation. Also, the actual graphitization process consists of complicated multi-step reactions, which may not be represented by the simple Rayleigh model. Isotopic fractionation can become much higher for small samples when graphitization cannot be completed [4,17,20,24,25]. The kinetic effect is much more significant for these reactions.
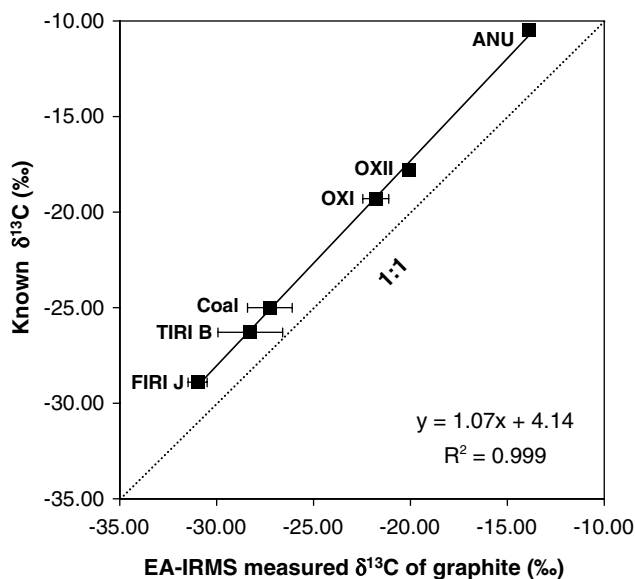
Fig. 4. Plot of $\delta^{13}C$ of graphite (Zn/Fe) versus known $\delta^{13}C$ of the initial CO_2. This figure shows that fractionation is relatively constant ($\sim$2–3‰) over the range of natural $\delta^{13}C$ level under our regular graphitization conditions, which gives us confidence that this fractionation can be corrected using simultaneously measured AMS $\delta^{13}C$.

The amount of Zn is a major control of the quality of the graphite produced by our sealed-tube method. The fractionation of C isotopes increases with amounts of Zn smaller than 10 mg (Fig. 3(b)), while too much Zn (>50 mg/mg C) may increase the fractionation with no clear explanation (Fig. 3(b)). Fig. 3(b) also clearly demonstrates that excess TiH_2 will increase fractionation, which supports the theory of formation of CH_4 when excess H_2 is present. The least fractionation was observed when 5 mg of TiH_2 was used. For the H_2 reduction method, a H_2/C ratio of 2:1–3:1 is often used [26]. If we adopt the same approach, then the amount of TiH_2 should be between 8.3 and 12.5 mg.

Fig. 4 (using Fe as catalyst) shows that fractionation is relatively constant over the range of natural $\delta^{13}C$ level under our regular graphitization conditions, which gives us confidence that this fractionation can be corrected using simultaneously measured AMS $\delta^{13}C$ as long as all the samples and standards are prepared in the same way.

3.3. Graphite performance in ion source

The graphite targets prepared using this method generally perform well in our AMS ion source. The graphite made with Co as catalyst normally yields $\sim$40 µA $^{12}C^+$ current at the high energy Faraday cup in our AMS system. Switching catalyst from Co to Fe has significantly improved the current to $\sim$50–60 µA, compatible to that of H_2/Fe graphite run in the same system. Graphite made from small samples of 0.1–0.2 mg C also produces stable long lasting current, but usually only about 70–80% of the output from a large sample. The "burn-in time" (time for current to come up to a stable level) is usually longer

for Zn reduced graphite than H_2 reduced graphite. Using Fe as catalyst has shortened this burn-in time. Currents from Zn/Fe graphite come up about 50% faster than Zn/Co graphite. An advantage in using the low energy AMS at UCI is the lack of problems from di-lithium ($7Li_2$), which was sometimes a problem when our Zn reduced targets were measured at CAMS-LLNL; these problems were usually traced to impurities in specific batches of the small inner Pyrex tubes.

3.4. Precision and accuracy

Our primary standard for ^{14}C measurement is OXI. We normally use seven OXI standards in a 40-position wheel. All unknown samples and secondary standards are normalized to OXI. We also use at least three secondary standards in each wheel for quality control. Usually we use two OXII, one ANU, one TIRI wood B or one FIRI J (Barley) as secondary standard in one wheel. Simultaneously measured AMS $\delta^{13}C$ is used for isotope fractionation correction in ^{14}C result calculation. The use of AMS $\delta^{13}C$ corrects isotope fractionation that occurred in natural processes, as well as the fractionation that happens inside the AMS system and during graphite formation. This has significantly improved the precision of our Zn reduced graphite. Even though the analysis of CO_2 $\delta^{13}C$ by stable isotope mass spectrometry is a more precise measurement it will not take into account any fractionation that occurred during graphitization and AMS measurement. Also, it should be noted that many AMS systems lack the capability to measure ^{12}C and ^{13}C on the high-energy side and some systems do not make as precise measurement even if they have the capability. For those systems, this method will give slightly less precise results ($\sim$5–6‰) if only IRMS measured $\delta^{13}C$ is used for fractionation correction.

Fig. 5 is an example of measurements of our secondary standard OXII in the last three years. Table 2 is the summary of all measured secondary standards compared to the consensus values. Our measured values overlap the consensus values within the analytical error. Our accuracy is good and our precision has been improving over time, we now routinely achieve a precision of 2–3‰.

3.5. Background

Background for ^{14}C measurement can come from contamination of sample, combustion, graphitization and AMS machine background. As shown in Fig. 6, the background of our measurements has improved over the three years. We now routinely obtain a satisfactory background of about $\sim$50,000 ^{14}C years for 1 mg C sample, without pre-distillation of Zn or pretreatment of other reagents. We have found that pre-distillation of Zn can further improve background (Shuhui Zheng, unpublished data), as well as reducing the amount of Zn used. Machine background improvement [12], use of an ABA (acid–base–acid) pre-cleaned USGS coal (a bituminous coal from the
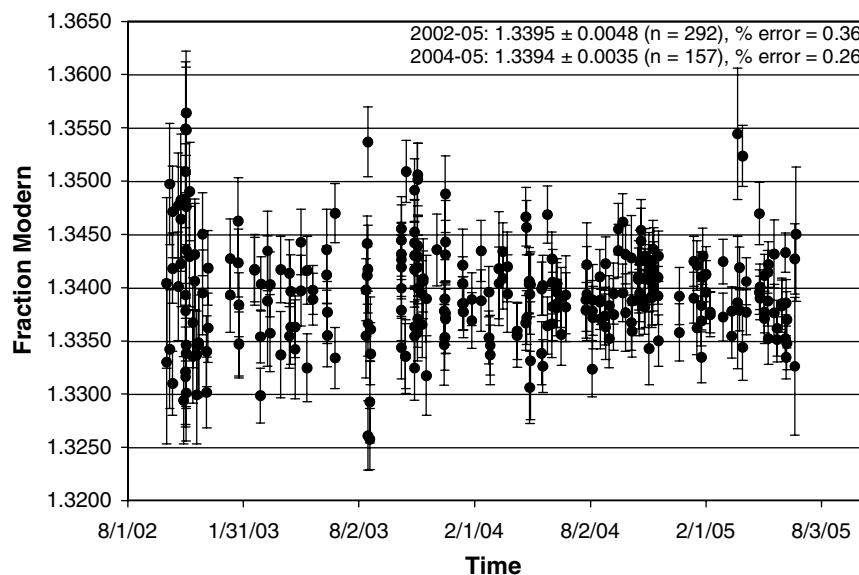
Fig. 5. ^{14}C analyses of OXII over time – indicating high precision of the measurements.

Table 2
Summary of all measured secondary standards compared to the consensus values

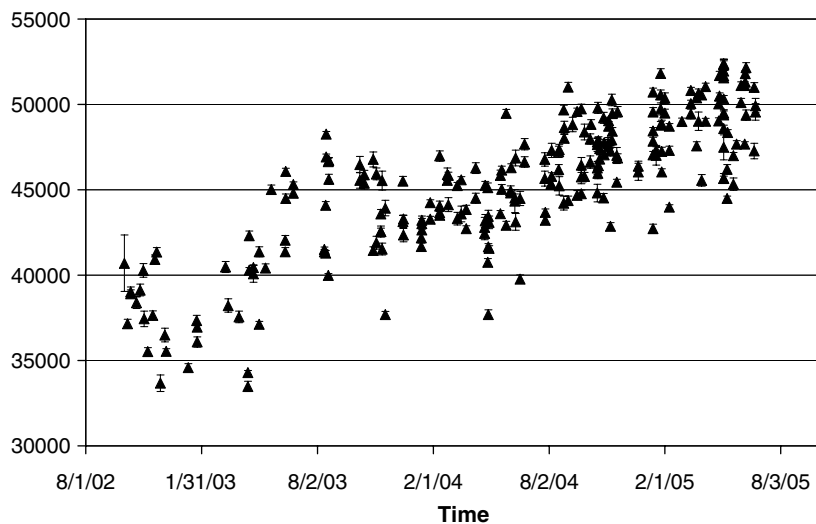| Reference materials	Consensus values	UCI (2002-05)		UCI (2004-05)	
		(FM/age)	% Error (n)	(FM/age)	% Error (n)
ANU	1.5061 ± 0.0011	1.5011 ± 0.0056	0.37 (155)	1.5018 ± 0.0048	0.32 (97)
OXII	1.3417 ± 0.0019	1.3395 ± 0.0048	0.36 (293)	1.3394 ± 0.0035	0.26 (157)
FIRI J	1.1052 ± 0.0005			1.1062 ± 0.0018	0.16 (13)
TIRI wood B	4519 ± 19 (age)	4525 ± 27	0.34 (112)	4525 ± 22	0.28 (70)

Fig. 6. Improvement of background (coal) over time.

Pocahontas #3 coal bed, collected in Buchanan County, Virginia in 1986), pre-combustion of sieved CuO and switching to Fe as catalyst all helped to reduce the background. We have also found that maintaining low backgrounds depends on the 'freshness' of the Zn powder. We put small aliquots of the Zn and TiH$_2$ powders into small vials for day-to-day use to decrease exposure to air.

Backgrounds for 0.5 mg C samples are about 43,000 ^{14}C years and one measurement of 0.25 mg coal gave a background of 41,000 ^{14}C years. Blank levels could become problematic for very small (<0.1 mg) and old samples. We plan to further investigate if pre-distillation of Zn powder will improve the background for small samples and thus expand the application of this method to small samples.
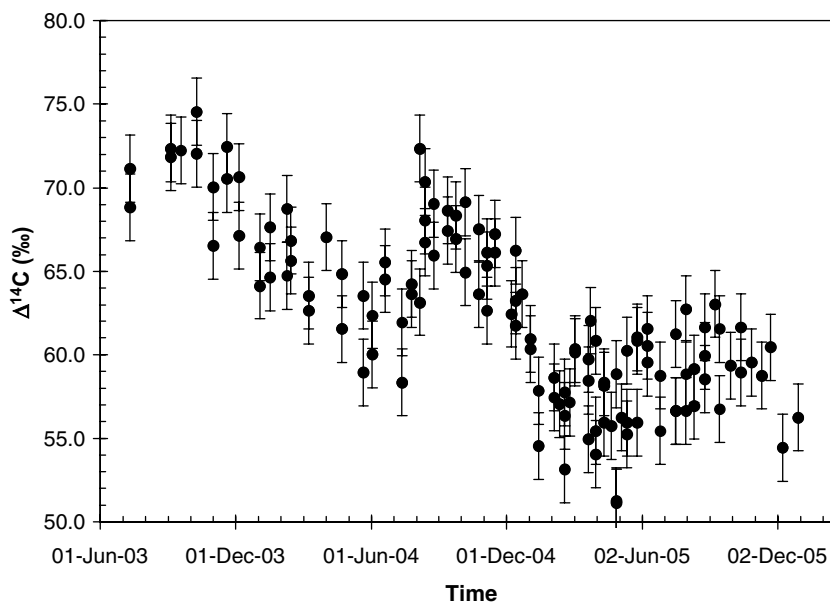
Fig. 7. Point Barrow $\Delta^{14}C$ – a good example of our high precision measurements.

3.6. An example of high precision ^{14}C measurements

We present here the time series of atmospheric $^{14}CO_2$ at a coastal site at Point Barrow, Alaska (71 °N, 157 °W) from July, 2003 to August, 2005 (Fig. 7). Air samples were collected into evacuated 6 L canisters and pressurized to about 2 atm. Upon returning to the lab, CO_2 was extracted cryogenically on a vacuum line and graphitized using the method described above and then analyzed for ^{14}C at our at AMS facility at UC Irvine. The high precision measurements ($\sim$2‰) allow us to clearly see seasonal cycles in the distribution of ^{14}C with time: a broad minimum around February and a maximum in September with an amplitude of 7‰. In this period, $\Delta^{14}C$ decreased by 5.5‰/year, to $\sim$57‰ in mid-2005. The peaks may be due to the joint effects of stronger stratosphere injection in April and May, and higher soil respiration with enriched $^{14}CO_2$ between May and August; and the valleys may be due to less soil respiration and more fossil fuel burning in the winter months. This seasonality was also observed at Jungfraujoch by Levin and Kromer [27]. Simulations with the model of atmospheric transport and chemistry (MATCH) will be presented and discussed in another paper elsewhere [28]. This work has proved that ^{14}C is a unique tracer for discriminating sources between fossil and biosphere carbon emissions, and the sealed tube Zn reduction method for graphite preparation is suitable for high precision ^{14}C measurements for carbon cycle studies.

4. Conclusions

The modified sealed tube Zn reduction method has been shown to produce high quality graphite for high precision (2–3‰) and high accuracy ^{14}C measurements by AMS, with a relatively low background of $\sim$50,000 ^{14}C years on 1 mg C. The precision is as good as that achieved with the more widely used H_2 reduction method for 1 mg C samples if reagents are measured carefully and most importantly, if simultaneously measured AMS $\delta^{13}C$ is used for isotopic fractionation correction.

The major advantage of the Zn reduction method is that the system is relatively inexpensive and easy to set up (Table 3). A single technician can process 40 graphite samples from purified CO_2 or 20 from combusted samples in an 8 h day. However, the method may not work well with very small (<0.1 mg) and old samples. Distilling zinc should improve our background level and we will investigate this possibility so that we may expand the application of this method to smaller samples in the future. We believe that many disciplines can benefit from this technique because of its low cost and rapid production of graphite.

Table 3
Advantages and disadvantages of zinc sealed tube reduction method

Advantages
- Low cost – just a simple vacuum line and an oven
- Rapid – a large number of samples can be prepared in the same day
- Convenient – graphite can be saved for a long time in sealed tubes
- High precision (2–3‰) – if AMS $\delta^{13}C$ is used for fractionation correction
- Acceptable background – 50,000 years without pre-cleaning any metal powders

Disadvantages
- No way to monitor the reaction
- Reaction can be strongly fractionating – precision will not be as good (5–6‰) if simultaneously measured AMS $\delta^{13}C$ is not available
- Background still higher than H_2 reduction method – not appropriate for very small or very old samples

Acknowledgements

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