

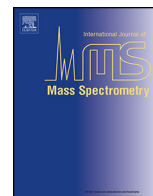


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Full Length Article

Fractionation in the graphitization reaction for ^{14}C -AMS analysis: The role of Zn \times the role of TiH_2

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ABSTRACT

Isotopic fractionation in the graphitization reaction for Radiocarbon Accelerator Mass Spectrometry measurements was evaluated. At LAC-UFF we use the TiH_2/Zn reduction method, where H_2 and Zn enable the reduction of CO_2 into graphite. In previous works, we analyzed C stable isotopes ratio for different amounts of Zn in the range of 0–50 mg and the results indicated that the amount of Zn is strongly linked to both the degree and variability of isotopic fractionation during the reaction when the quantity of TiH_2 ranges from 10 to 15 mg for samples containing between 0.7 and 1.0 mg of C. For no changes in fractionation have occurred by increasing the graphitization temperature from 520 °C to 550 °C, in the present paper we evaluate the effects of different temperatures for the H_2 release step. Previous works have also led us to question the role of Zn in the TiH_2 -based process and how it affects fractionation. Therefore, graphitization reactions without TiH_2 or without Zn, using different amounts of TiH_2 , were tested. The former reaction has required values of $\text{Zn:C} > 50$ while the latter is not recommended. When $\text{Zn:C} = 30$, minimum amounts of TiH_2 ($\text{TiH}_2:\text{C} < 20$) have led to reasonable results of isotopic fractionation (<2%).

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1. Introduction

Sample preparation for Radiocarbon Accelerator Mass Spectrometry (^{14}C -AMS) requires specific physical and chemical pre-treatments followed by conversion to a suitable matrix, allowing the extraction of intense and stable ion beams. ^{14}C AMS targets can be either CO_2 or graphite, with both advantages and drawbacks for the two types [1–4]. Sample graphitization is usually performed by reduction of CO_2 to solid carbon on a metal catalyst, using Zn [5,6], H_2 [7] or TiH_2/Zn [8,9]. The latter has been successfully applied to both regular [9] and ultra-small samples, i.e. <0.1 mg [10,11], providing a less expensive alternative to H_2 reduction method. Moreover, the TiH_2/Zn reduction method may have higher throughput, allowing more samples to be prepared in a work day. Recently, Xu et al. (presented in the 14th Accelerator Mass Spectrometry conference in Ottawa, Canada) have demonstrated another great advantage of this method, which is that the samples can be stored under vacuum in the sealed tubes since graphitization and for over a decade with no implications to the isotopic ratios.

However, mass-dependent fractionation in such reaction can lead to results a few parts per mil lighter [8,9] than the original CO_2 $\delta^{13}\text{C}$ values or even discrepancies as large as –30% and great scattering of results, what can lead to inaccurate results in the AMS system [12].

The degree of fractionation depends on the sample size, the amounts of reagents used, temperature and time of the process. Indeed, temperature plays a major role considering that discrepancies can be largely reduced when temperature is increased from 460 °C to 520 °C [12]. McNichol et al. [13] claim that Fe seems to be a better catalyst between 575 °C and 650 °C, and Tschekalinskij et al. [14] achieved very good results in the reaction with Zn and TiH_2 at 600 °C. However, such high temperatures prevent the use of Pyrex[®] tubes [9]. Xu et al. [9] proposed a two-steps reaction in which a first period at a lower temperature (3 h at 500 °C) would favor the reduction of CO_2 to CO while in the second period (4 h at 550 °C), CO would be reduced to graphite. For ultra-small samples, Xu et al. [11] lowered the reaction temperature to 450 °C for 7 h for the Zn reduction without TiH_2 after Santos et al. [15] (based on the H_2 reduction method), who had shown that lower temperatures help to increase graphitization yields. Marzaioli et al. [16], using a two-steps temperature protocol for regular-sized samples, reported a reduction in both the offset and the scattering in

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Table 1
Amounts of reagents, temperatures and periods of time for each of the tests performed.

Test	C (mg)	Zn (mg)	Zn:C	TiH ₂ (mg)	TiH ₂ :C	Temperature + time	n
A1	0.8–1.0	19–24	19–25	10–15	10–15	450 °C (3 h)+ 550 °C (4 h)	5
						500 °C (3 h)+ 550 °C (4 h)	5
						550 °C (7 h)	5
A2		–	–	10–15	10–15	450 °C (3 h)+ 550 °C (4 h)	5
						500 °C (3 h)+ 550 °C (4 h)	5
						550 °C (7 h)	4
B	0.4–1.0	–	–	3.7–18.1	6–39	550 °C (7 h)	44
C1	0.5–0.6	15–18	29–35	15–18	29–34	550 °C (7 h)	9
C2		–	–			550 °C (7 h)	9
D1	0.5–0.6	18–41	15–80	–	–	550 °C (7 h)	20
D2						550 °C (10 h)	12
E	0.5–0.6	16–18	27–33	8–41	15–79	550 °C (7 h)	23

$\delta^{13}\text{C}$ values when the reaction temperatures were increased from 530–550 °C to 550–560 °C. Macario et al. [17,18] observed similar results with temperatures of 520 °C and 550 °C [12], in which $\delta^{13}\text{C}$ mean values were depleted by approximately 5%.

Orsovszki and Rinyu [19] reported results for the reactions using 60 mg Zn/10 mg TiH₂ and 15 mg Zn/no TiH₂. They concluded that eliminating TiH₂ suppresses the formation of CH₄ during graphitization. For the process without TiH₂ there was an improvement in yield and from measurements within the accelerator they observed an increase in current intensity, while background levels remained similar for both methods.

Macario et al. [17,18] have reported results showing that lowering the amount of Zn reduces scattering without increasing the degree of isotopic fractionation. Moreover, Macario et al. [18] call attention to the possibility of eliminating Zn from the process. However, the degree of isotopic fractionation in such process was still too high, with a mean value of $(-6.1 \pm 1.1) \text{‰}$. Furthermore, if on the one hand Macario et al. [18] observed that the amount of TiH₂ plays no major role in the TiH₂/Zn reduction, on the other hand, they suggest that in the absence of Zn, the availability of TiH₂ should be increased to allow the completeness of graphitization reaction. Considering stoichiometry, in order to reduce CO₂ to C, at least two moles of TiH₂ should be added for each mol of CO₂. This means that for each 1 mg of C at least 8 mg of TiH₂ should be available. In fact, Tschekalinskij et al. [14] concluded that the best amounts of reagents for 1 mg samples and the reaction at 600 °C were 20 mg Zn and 8 mg TiH₂, reaching -0.2‰ from the expected values.

In the present paper, we report several tests performed to evaluate the processes without Zn and without TiH₂ (for 7 h and 10 h long processes), plus the TiH₂/Zn reduction with variable amounts of TiH₂. Moreover, we compare the results for two temperature steps with our regular 550 °C for 7 h process.

2. Methods

Using an IRMS system we have measured the C stable isotope ratios for graphitized NBS oxalic acid (OXII) standard 4990c ($\delta^{13}\text{C} = -17.8 \pm 0.1\text{‰}$) [20]. Sample combustion took place in sealed quartz tubes, containing previously heated CuO (Fisher Scientific, carbon compounds 0.0004%) and Ag wire (Aldrich $\geq 99.99\%$ 0.5 mm diameter), at 900 °C for 3 h. The gas was then purified in a stainless steel vacuum line [12] using cryogenic traps and transferred into graphitization tubes: borosilicate glass tubes with 9 mm OD and 15 cm long, containing variable amounts of TiH₂ (Alfa Aesar 99%) and Zn (Aldrich 99.995% powder <150 μm), plus a 6 mm OD Durham tube, which sits inside the larger reaction tube, containing approximately 5 mg of Fe powder (Alfa Aesar –325 mesh, reduced, 98%).

In order to evaluate the effects of graphitization reaction on isotopic ratios under different conditions, we performed a sequence of five tests.

Test **A** aimed to evaluate the possible influence of two steps of temperature in the graphitization reaction. Since the breakup of TiH₂ is expected to occur at 440 °C [9] we tried a H₂ release step as suggested by Xu et al. [9]. Samples were divided in two sets: **A1**, with 19–25 mg of Zn per 1 mg C and **A2**, with no Zn. Fifteen tubes were prepared for each set of samples. After conversion to CO₂, each sample was split within the vacuum line in 3 graphitization tubes. TiH₂ amounts were our regular 10–15 mg and the amount of sample in each tube varied between 0.8 and 1 mg C, with ratios of TiH₂:C ranging from 10 to 15. Each group of tubes containing CO₂ and reagents went through different temperature processes: 450 °C for 3 h followed by 550 °C for 4 h; 500 °C for 3 h followed by 550 °C for 4 h; and 550 °C for 7 h.

The second test (**B**) aimed to evaluate the influence of TiH₂ amounts when Zn is not used in the process. Forty-four tubes were prepared with no Zn and varied amounts of TiH₂ ranging from 3.7 to 18.1 mg and samples between 0.4 and 1.0 mg C, resulting in ratios of TiH₂:C from 6 to 39.

In the third test (**C**) we compared the results with (Zn between 15 and 18 mg or Zn:C = 29–35) and without Zn, this time using an increased amount of TiH₂ (from 15 to 18 mg) with ratios of TiH₂:C from 29 to 34.

In the fourth test (**D**), we tested different amounts of Zn covering a wide range (from 8 to 41 mg or Zn:C from 15 to 80) in the reaction without TiH₂ for 7 h and 10 h graphitization times at 550 °C.

The fifth test (**E**) aimed to verify the optimum amounts of TiH₂ (from 8 to 41 mg or TiH₂:C from 15 to 79) for approximately constant amounts of Zn (between 16 and 18 mg or Zn:C from 27 to 33).

The sample sizes in test **C**, and the following tests **D** and **E** were between 0.5 and 0.6 mg C. The regular process with a temperature of 550 °C for 7 h was used for tests **B**, **C** and **E**.

Table 1 summarizes the amounts of reagents, temperatures and periods of time for each of the tests performed. For each sample, the obtained mixture of Fe and graphite was placed in double tin capsules to prevent spilling within the mass spectrometer. The samples were sent to the Stable Isotope Facility (SIF) of the University of California, Davis (UCD), USA for EA-IRMS analysis using an Elemental Vario Micro Cube elemental analyzer (Elementar Analysensysteme GmbH, Hanau, Germany) interfaced to a PDZ Europa 20-20 isotope ratio mass spectrometer (Sercon Ltd., Cheshire, UK). Combustion took place at 1080 °C in a reactor with copper oxide (I) and tungsten (VI) oxide. Oxides were removed in a reduction reactor (reduced copper at 650 °C) and water was removed by means of a magnesium perchlorate trap using helium carrier. The CO₂ was collected using a molecular sieve adsorption trap before the IRMS. NIST Standard Reference Materials used were IAEA-N1, IAEA-N2, IAEA-N3, USGS-40, and USGS-41. The $\delta^{13}\text{C}$ values are given in relation to international standard VPDB (Vienna Pee Dee Belemnite) and the typical standard deviations were 0.2‰.

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