



Graphitization reaction via zinc reduction: How low can you go?



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ABSTRACT

In a previous work, isotopic fractionation in the graphitization reaction for Radiocarbon Accelerator Mass Spectrometry (¹⁴C-AMS) was evaluated for amounts of Zn ranging from 20 to 50 mg. The results have shown that a slightly lower variation in $\delta^{13}\text{C}$ during graphitization was achieved with less Zn. In the present paper, assuming that low amounts of Zn would provide the best results, we go further and test isotopic fractionation for 0, 10 and 20 mg of Zn in the graphitization reaction. The results show that the use of 10 mg of Zn yields similar fractionation to that using 20 mg, while using only TiH₂ and no Zn produces the same scattering for amounts from 30 to 50 mg. The absence of Zn, on the other hand, plays a major role on the reaction yield for the tested conditions, limiting it to 50%.

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1. Introduction

Isotopic fractionation is a result of physical, chemical or biological processes and, given one specific pathway, it can be a proxy for the completeness of the reaction. Sample preparation protocols for ¹⁴C Accelerator Mass Spectrometry (¹⁴C-AMS) generally involve the conversion of CO₂ to graphite for the extraction of an ion beam within a cesium sputtering ion source [31] and such reaction is likely to give origin to isotopic fractionation. Different procedures based on the reduction of CO₂ to CO, followed by the reduction of CO to solid carbon in the presence of a metal catalyst, such as Fe or Co, have been used to produce graphite [29,7,25,30,28]. The catalyst not only increases the reaction speed but also acts as a binder and a thermal conductor, benefiting the current extraction within the ion source [29]. Vogel et al. [29] used H₂ as a reducing agent whereas Jull et al. [7] and Slota et al. [25] employed Zn reduction. McNichol et al. [16] compared the two methods and observed that although H₂ speeds up the reaction, yields can be variable. Vogel [30] used TiH₂, as a source of H₂, and Zn in order to recycle the

hydrogen from water. The amount of H₂ in the reaction needs to be controlled because an excess of hydrogen increases methane formation during graphitization [28,17,20]. Such method had the drawback of increasing background values due to the larger surface when compared to the hydrogen reactors and, therefore, it was developed only for biomedical samples as it could lower the age limit for archaeological applications. Xu et al. [28] modified this method and achieved background values as low as 50 ka and precision of approximately 2–3‰ at the Keck Carbon Cycle AMS facility at UC Irvine [26]. However, mass-dependent fractionation was still present, leading to results a few parts per mil lighter than the original CO₂ $\delta^{13}\text{C}$ values, depending on the amount of reagents used, temperature and time [30,28]. Indeed, temperature plays a major role considering that discrepancies as large as –30‰ and great scattering of results were reported for graphitization temperatures as low as 460 °C [12]. Since the ¹⁴C ratios of the produced graphite targets are meant to be measured in the accelerator mass spectrometer, such large isotopic fractionation can lead to inaccurate values, especially if isotopic fractionation corrections based on online AMS $\delta^{13}\text{C}$ are not applied. On the other hand, if isotopic fractionation corrections are routinely obtained using the online AMS system $\delta^{13}\text{C}$ values, based on the normalization by graphitized reference mate-

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rial, subject to the same isotopic fractionation, the accuracy of the ^{14}C results can be maintained as long as fractionation is constant.

Apart from reaction temperature, one of the factors that can interfere with the degree of isotopic fractionation is the amount of reagents used. Xu et al. [28] proposed using amounts of zinc from 30 to 35 mg and 10 to 15 mg of TiH_2 to produce 1 mg C graphite targets. Moreover, the authors argue that the degree of fractionation is inversely related to the Zn/ TiH_2 ratio, noting that too much Zn (>50 mg/mg C), on the other hand, may increase fractionation. Rinyu et al. [21], in turn, recommended the use of larger amounts of zinc (~50 mg) as a way to reduce the degree of isotopic fractionation.

Reducing the amount of reagents is not only desirable for economical reasons but it also has the potential of lowering the background as they are a potential source of modern carbon. Khosh et al. [10] claims that most of the modern carbon contamination in graphitization is due to adsorbed ambient CO_2 on the surface of reaction tubes and added reagents. Orsovszki and Rinyu [20] reported increased blank ^{14}C levels for larger amounts of Zn. These authors compared the reactions using 60 mg Zn/10 mg TiH_2 and 15 mg Zn/no TiH_2 and observed higher intensity currents within the accelerator for the latter. Concerning isotopic fractionation, they have reported results for stable isotopes IRMS measurements in CO_2 and for accelerator measurements in graphite. Therefore, despite most of the results for high purity samples are in good agreement, it was not possible to evaluate the degree of isotopic fractionation related specifically to the graphitization reaction.

Tschekalinskij et al. [27], in their study on new catalyst mixtures aiming to achieve optimal reduction parameters, have also tested isotopic fractionation in the reaction with Zn and TiH_2 at 600 °C and concluded that the best amounts of reagents for their system were 20 mg of zinc and 8 mg of titanium hydride, reaching -0.2% from expected values.

Aiming to achieve lower isotopic fractionation and scattering of results, Macario et al. [13], following Xu et al. [28] and Rinyu et al. [21], evaluated the effects of the amount of zinc in ^{13}C isotopic fractionation at 550 °C. Using Isotope Ratio Mass Spectrometry (IRMS) to measure $\delta^{13}\text{C}$ values of reference materials graphitized with amounts of zinc ranging from 20 to 50 mg, Macario et al. [13] observed an approximately constant fractionation of about -5% , similar to what had been observed at 520 °C for 30–35 mg of zinc in a previous work [12]. Moreover, it was noticed a slightly lower dispersion in the isotopic fractionation using less zinc.

In the present study we aim to evaluate the impact of even lower amounts of zinc on isotopic fractionation, scattering of results and reaction yield. For this purpose, we tested different reference materials graphitized with TiH_2 over Fe catalyst. Isotopic fractionation is inferred from the comparison of IRMS $\delta^{13}\text{C}$ measurements with consensus values.

2. Methods

Isotopic fractionation in the graphitization reaction was evaluated through the measurement of carbon stable isotope ratios in reference materials using an IRMS system. Samples of IAEA reference materials C2 carbonate (consensus $\delta^{13}\text{C} = -8.25 \pm 0.31\%$) and C6 sucrose (consensus $\delta^{13}\text{C} = -10.80 \pm 0.47\%$) [22,23] as well as NBS oxalic acid (OXII) standard 4990c (certified $\delta^{13}\text{C} = -17.8 \pm 0.1\%$) [14] were prepared for this investigation. The recommended values of the IAEA quality control materials are the result of the statistical evaluation of an interlaboratory comparison [22,23]. Organic samples were combusted to CO_2 in sealed quartz tubes containing previously cleaned CuO (Fisher Scientific, carbon compounds 0.0004%) and Ag wire (Aldrich $\geq 99.99\%$ 0.5 mm diameter), at 900 °C for 3 h whereas carbonate samples were hydrolyzed

by the addition of 1 mL 85% H_3PO_4 into evacuated vials left to rest from 12 to 24 h. A stainless steel line connected to a turbomolecular pump was used for pumping out tubes and carbonate vials while two similar lines were used to purify the CO_2 from the samples [12]. Essentially, the methods used in this test follow the laboratory protocols and are not different from the ones routinely employed for unknown samples [12].

Borosilicate glass graphitization tubes with 9 mm OD, 15 cm long and containing 10–15 mg of TiH_2 (Alfa Aesar 99%) were used. Inside this graphitization tube sits a 6 mm OD Durham tube containing approximately 5 mg of Fe powder (Alfa Aesar –325 mesh, reduced, 98%). Each CO_2 sample was split within the vacuum line into 3 graphitization tubes containing different amounts of Zn (Aldrich 99.995% powder < 150 μm): 20 mg, 10 mg and no Zn. Sample mass in each tube varied between 0.7 and 1.5 mg C. Torch sealed tubes with reagents and the CO_2 from the samples were taken to a muffle furnace at 550 °C for 7 h. The obtained mixture of Fe and graphite was placed in double tin capsules for measurement in the IRMS.

The samples underwent EA-IRMS analysis in the Stable Isotope Facility (SIF) of the University of California, Davis (UCD), USA. The equipment employed was an Elementar 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). After sample combustion at 1080 °C in a reactor with CuO and Tungsten (VI) Oxide, oxides were removed in a reduction reactor (reduced Cu at 650 °C) whereas water was extracted by means of a magnesium perchlorate trap using helium carrier. A molecular sieve adsorption trap separated the CO_2 before its insertion into the IRMS.

The analysis was carried out alternating the samples with several replicates of at least two different laboratory standards, calibrated against NIST Standard Reference Materials (IAEA-N1, IAEA-N2, IAEA-N3, USGS-40, and USGS-41). A preliminary isotope ratio was measured for each sample relative to reference gases analyzed and then a correction for the entire batch was applied based on the known values of the included laboratory standards. As usual, $\delta^{13}\text{C}$ results were expressed relative to the international standard V-PDB (Vienna PeeDee Belemnite) [4,24] and the typical standard deviations for both long term reference measurement and for this batch of samples were equal to 0.2‰.

3. Results and discussion

Results of IRMS $\delta^{13}\text{C}$ for the whole batch of samples ($n = 86$) plus those ($n = 80$) from the previous test [13] are presented in Fig. 1 as the discrepancy from consensus values against the yield, which was calculated as the ratio of carbon amount measured in the IRMS for the combusted graphite samples over that measured before graphitization. Transferring the samples from graphitization tubes to tins can lead to mass losses and therefore inaccuracies in yield estimate. Such losses mean that casual errors may happen, eventually leading to a few outliers. Even so, the yield estimate discloses important patterns in the comparison of amounts of reagents.

From the data distribution, a correlation between the yield and the degree of isotopic fractionation can be inferred if we take into account all the results. The linear fit corresponds to $y = 3.2(0.5)x - 7.7(0.3)$ with $\chi^2 = 0.88$ (dotted line in Fig. 1). However, if we look separately at the results of the groups with and without zinc, two different patterns arise. Although for the reaction with Zn we still see an anti-correlation between the yield and the isotopic fractionation (corresponding to a linear fit of $y = 6.5(0.7)x - 9.9(0.5)$ with $\chi^2 = 0.65$ solid line in Fig. 1), in agreement to what had been observed by other authors [28,5] for the

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