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OPTIMIZATION OF THE AMOUNT OF ZINC IN THE GRAPHITIZATION REACTION FOR RADIOCARBON AMS MEASUREMENTS AT LAC-UFF

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ABSTRACT. The Radiocarbon Laboratory of the Universidade Federal Fluminense, in Brazil, has been successfully applying the zinc reduction method for graphitization of carbon samples since the development of its early protocols in 2009. Successive methodological research aiming to improve and, ultimately, optimize the precision and accuracy of our results indicates that graphitization temperatures as low as 460°C promote erratic ^{13}C isotopic fractionation, but an approximately constant fractionation of about –5‰ is achieved at 520°C. In this work, we present isotope ratio mass spectrometry (IRMS) $\delta^{13}C$ results for ^{14}C reference materials graphitized at 550°C with variable amounts of zinc. Based on the results obtained from the addition of 20, 35, and 50 mg of zinc, we conclude that a slightly lower variation in ^{13}C isotope fractionation during graphitization is obtained with less zinc. Moreover, the average isotopic fractionation is not altered by increasing the graphitization temperature from 520°C to 550°C.

KEYWORDS: isotopic fractionation, graphitization, zinc reduction, IRMS, radiocarbon AMS.

INTRODUCTION

Seven years have passed since the establishment of the Radiocarbon Laboratory of the Universidade Federal Fluminense (LAC-UFF), the last 4 years of which include the operation of a 250kV NEC Single Stage Accelerator (SSAMS) system at the Physics Institute, in Niterói, Rio de Janeiro State, Brazil. Over this period, more than 4000 samples have been measured, including unknown age and quality control samples (Anjos et al. 2013; Macario et al. 2013, 2015; Linares et al. 2015). Currently, samples of wood, charcoal, soil, and carbonates are routinely prepared and measured in our facility. Furthermore, the laboratory has also been involved in projects with materials such as plastics, alcohol, parchment, and ceramics (Jou et al. 2015; Oliveira et al. 2015, 2016). Despite the robust results achieved so far, concerns have been raised regarding expanding the range of materials analyzed, lowering the background, and improving graphitization reaction by minimizing and controlling the isotopic fractionation that could interfere with the accuracy of results.

Concerning the graphitization reaction, we have changed from distilled zinc in quartz tubes at 700°C to Pyrex™ tubes containing zinc and titanium hydride following the procedure described in Xu et al. (2007), except that, due to technical issues, we used a temperature of 460°C (Macario et al. 2015). At that time, isotope ratio mass spectrometry (IRMS) measurements of stable isotope ratios ($\delta^{13}C$) from graphite targets produced for ^{14}C accelerator mass spectrometry (AMS) revealed a large isotopic fractionation that most likely resulted from incomplete graphitization.

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It is well known that the zinc reduction graphitization process often results in mass-dependent fractionation (Vogel 1992; Xu et al. 2007; Kim et al. 2008, 2009; Rinyu et al. 2013). Therefore, fractionation would be expected to lead to results a few parts per mil lighter than the original carbon dioxide $\delta^{13}C$ values, depending on the amount of reagents used, temperature, and time (Vogel 1992; Xu et al. 2007). However, in our case, isotopic fractionation not only reached –30‰ but also the results showed a large scattering of $\delta^{13}C$ values. The graphite targets thus obtained, with large ^{13}C fractionation when measured in the SSAMS, can potentially lead to inaccurate ^{14}C values, even if isotopic fractionation corrections based on online AMS $\delta^{13}C$ are applied. Therefore, using an independent thermocouple, we monitored the muffle furnace temperature and found a –60°C offset, which likely caused the low graphitization yields. Following these findings, the muffle furnace was replaced and the isotopic fractionation in the reaction was systematically lower (–5‰ on average) and the overall scattering was reduced by increasing the graphitization temperature to 520°C (Macario et al. 2015). Since isotopic fractionation corrections are routinely made using the online AMS system $\delta^{13}C$ values, based on the normalization by graphitized reference material, the accuracy of the ^{14}C results was maintained.

According to McNichol et al. (1992), iron seems to be a better catalyst between 575 and 650°C, but employing the Pyrex™ tubes prohibits the use of higher temperatures (Xu et al. 2007). Xu et al. (2007) and Rinyu et al. (2013) agree that by increasing the temperature to 550°C the efficiency of the iron catalyst during the graphitization reaction would be enhanced. Marzaioli et al. (2008) noticed a reduction in both the fractionation and scatter of results, from –5.3 ± 4.3‰ to –4.4 ± 3.4‰ when they increased the reaction temperatures from 530–550°C to 550–560°C.

Since we started applying the zinc and titanium hydride method, we have used amounts of zinc from 30 to 35 mg and 10 to 15 mg of TiH_2 to produce 1-mg-C graphite targets following Xu et al. (2007). However, Rinyu et al. (2013) suggest that the use of larger amounts of zinc, such as 50 mg, could reduce isotopic fractionation. Xu et al. (2007), in turn, observe that fractionation decreases when the Zn/TiH_2 ratio increases, but, on the other hand, too much zinc (>50 mg/mg C) may increase fractionation. Therefore, aiming to improve our graphitization protocol even further, in the present work we test the effects of the amount of zinc and a reaction temperature of 550°C for ^{13}C isotopic fractionation.

METHODS

In order to evaluate the isotopic fractionation in the graphitization reaction, we have measured the carbon stable isotope ratios for different reference materials using an IRMS system. The test was performed using NBS oxalic acid (OXII) standard 4990c ($\delta^{13}C = -17.8 \pm 0.1$‰) (Mann 1983) and IAEA reference materials C2 carbonate ($\delta^{13}C = -8.25 \pm 0.31$‰) and C6 sucrose ($\delta^{13}C = -10.80 \pm 0.47$‰) (Rozanski 1991; Rozanski et al. 1992). For CO_2 conversion, we combusted all organic samples in sealed quartz tubes, containing previously heated cupric oxide (Fisher Scientific, carbon compounds 0.0004%) and silver wire (Aldrich ≥99.99% 0.5 mm diameter), at 900°C for 3 hr and hydrolyzed the carbonate samples by inserting 1 mL of 85% phosphoric acid into evacuated vials and leaving them to rest for 12 to 24 hr. A vacuum stainless steel line was used for pumping out tubes and carbonate vials, while two dedicated lines were used for CO_2 purification (Macario et al. 2015).

The graphitization tubes are made from borosilicate glass, have a 9 mm outer diameter (OD), are 15 cm long and contain 10–15 mg of titanium hydride (Alfa Aesar 99%). A 6-mm-OD

Durham tube, which sits inside the larger reaction tube, contains approximately 5 mg of iron powder (Alfa Aesar -325 mesh, reduced, 98%). After conversion to CO_2, each sample was split within the vacuum line in three graphitization tubes containing different amounts of zinc (Aldrich 99.995% powder <150 mμ): 20, 35, and 50 mg. The amount of sample in each tube varied between 0.7 and 1 mg C. The tubes containing reagents and gas samples were heated at 550°C for 7 hr, and the obtained mixture of iron and graphite was placed into 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. The equipment used 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). Samples were combusted at 1080°C in a reactor with copper oxide and tungsten (VI) oxide. After combustion, oxides were removed in a reduction reactor (reduced copper at 650°C) and water was removed by means of a magnesium perchlorate trap using a helium carrier. The CO_2 was separated using a molecular sieve adsorption trap before entering the IRMS.

During analysis, samples were alternated with several replicates of at least two different laboratory standards, previously calibrated against NIST standard reference materials (IAEA-N1, IAEA-N2, IAEA-N3, USGS-40, and USGS-41). For each sample, a preliminary isotope ratio was measured relative to the reference gases analyzed, then corrected for the entire batch based on the known values of the included laboratory standards. The δ^{13}C results were expressed relative to international standard V-PDB (Vienna PeeDee Belemnite), and the typical standard deviation for both the long-term reference measurement and for this batch of samples was 0.2‰.

RESULTS AND DISCUSSION

IRMS δ^{13}C results for the whole batch of samples are presented in Figure 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. From the data distribution, it is possible to see that, as expected, all samples present sensitive ^{13}C isotopic fractionation. However, the degree of fractionation and the dispersion of data warrant discussion. The correlation between the yield and the degree of isotopic fractionation can be inferred from the results. Ideally, it is important to ensure the

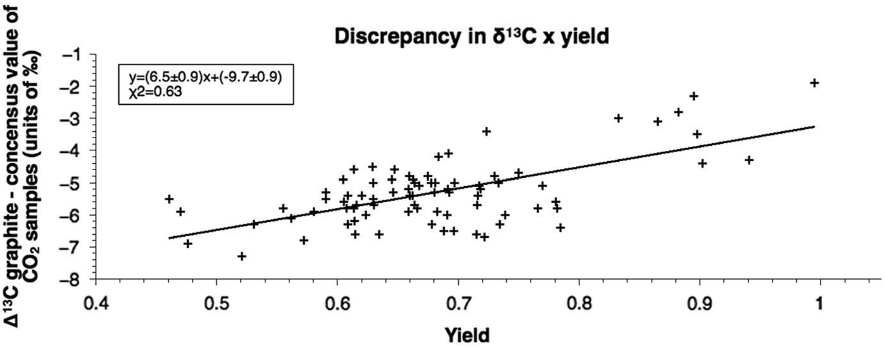

Figure 1 Discrepancy in IRMS δ^{13}C results versus yield of carbon in graphitization reaction. The solid line represents the linear fit of the results.

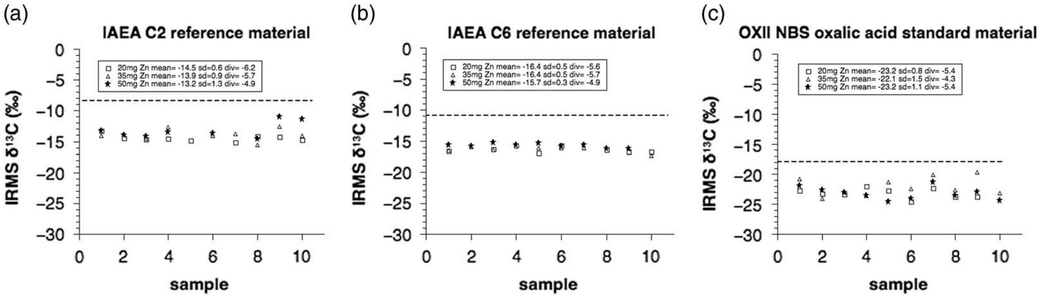

Figure 2 Measured IRMS $\delta^{13}C$ for analyzed reference material graphitized with different amounts of zinc, represented by different symbols in all graphs: squares for 20 mg, triangles for 35 mg, and stars for 50 mg. The dashed lines mark the $\delta^{13}C$ consensus values for (a) C2, (b) C6, and (c) OXII samples.

completeness of the graphitization reaction, keeping isotopic fractionation to a minimum. However, as long as the degree of fractionation is approximately constant, online measurement of stable isotope ratios in the accelerator for both unknowns and standards allows effective corrections to be made.

In order to evaluate a possible bias that would result from fractionation during sample conversion to CO_2, either in carbonate hydrolysis of C2 samples or combustion of OXII and C6 samples, we present the results for each CO_2 sample split and graphitized in three different graphitization tubes (Figures 2a–c).

If isotopic fractionation was affecting the conversion to CO_2, a pattern of discrepancy from the consensus value would be observed in separate groups; however, the mean values for each sample seem to be fairly constant. Therefore, the whole batch of samples can be treated as a group, and differences in the amounts of TiH_2 and Zn and the ratios between these quantities can be evaluated. Considering the discrepancy from consensus values of samples plotted against the amount of TiH_2 used (Figure 3), no pattern can be observed in the studied range.

According to Xu et al. (2007), the degree of isotopic fractionation can also be related to the Zn/TiH_2 ratio since they observed that fractionation decreases when the Zn/TiH_2 ratio increases in the range of 1:2 to 12:1. In Figure 4, we present the results for the discrepancy from the consensus value against the Zn/TiH_2 ratios. From the results, we see that the lowest degree of fractionation is achieved for ratios around 3:1. On the other hand, the least scattering is observed for the lower ratios. In the studied range, from 3:2 to 5:1, there does not seem to be any pattern.

No significant difference is observed between the results obtained from different amounts of zinc in the studied range (Figure 5). It is possible to infer, however, that the lowest discrepancy is achieved by the 35-mg zinc group. On the other hand, this group is also responsible for the largest scattering, while the least scattering is observed for the 20-mg zinc group. As discussed above, although minimizing the degree of isotopic fractionation is desirable, guaranteeing its linearity is crucial to allow isotopic fractionation corrections for ^{14}C measurements in the accelerator. As observed by Marzaioli et al. (2008), the normalization with graphitization standards cancels out fractionation both due to sample preparation and to the machine. The pattern of the isotopic fractionation degree within a wider range of zinc amounts is yet to be understood.

Concerning the reaction temperature, the observed results are similar to those previously obtained with a temperature of 520°C (Macario et al. 2015), in which $\delta^{13}C$ mean values were

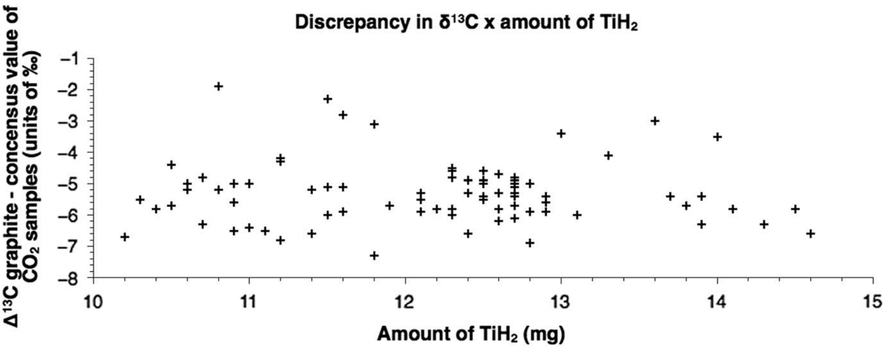

Figure 3 Discrepancy in IRMS δ^{13}C results versus amount of TiH_2 used in graphitization reaction

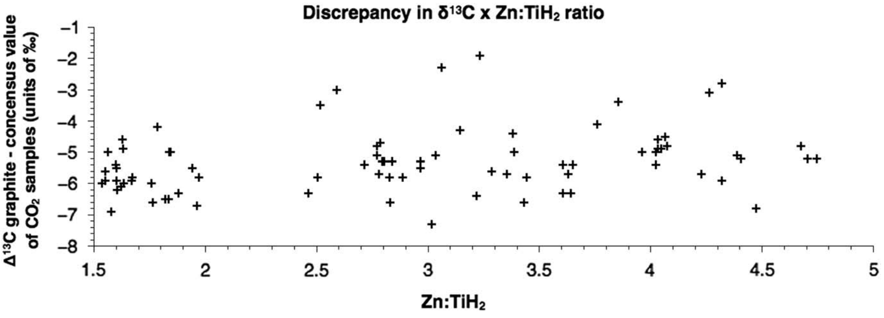

Figure 4 Discrepancy in IRMS δ^{13}C results versus the ratio Zn:TiH_2 used in graphitization reaction.

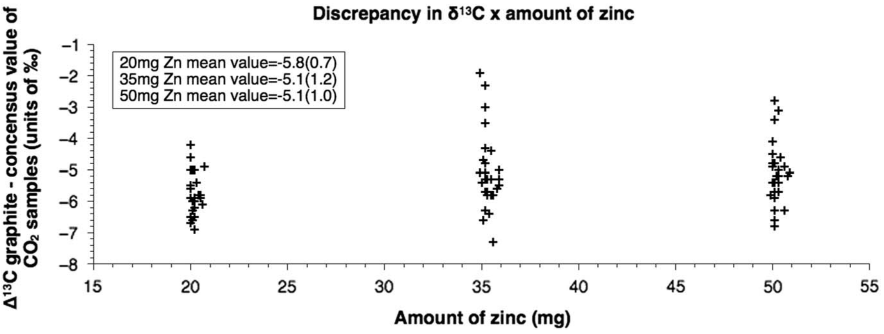

Figure 5 Discrepancy in IRMS δ^{13}C results versus amount of Zn used in graphitization reaction

approximately depleted in 5‰. Another relevant experiment would be to test graphitization in two steps of temperature, as proposed by Xu et al. (2007). The first period at a lower temperature (500°C) would favor the reduction of CO_2 to CO, while in the second period (at 550°C), CO would be reduced to graphite. On the other hand, as previously discussed, Marzaioli et al. (2008), who also use a two-step temperature protocol, show that both the offset in δ^{13}C and the scattering were reduced when the reaction temperatures were increased from 530–550°C to 550–560°C. Therefore, more tests are needed to understand the influence of the hydrogen release step in the isotopic fractionation of graphite. Based on the results of the present work and aiming to lower costs and background values, we decided to reduce to 20 mg the amount of zinc in our graphitization protocol and, until further tests are performed, to increase the temperature to 550°C.

CONCLUSIONS

Using IRMS to measure $\delta^{13}C$ values of reference materials graphitized at 550°C with different amounts of zinc, we have 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. Moreover, we have noticed a slightly lower dispersion in the isotopic fractionation using less zinc. Therefore, following this study we have changed our graphitization protocol at LAC-UFF to use 20 mg of zinc and a graphitization temperature of 550°C. Reducing the amount of reagents is not only desirable for economic reasons, but it also has the potential of lowering the background as zinc is a potential source of modern carbon. Ongoing tests on ^{14}C concentration of ^{14}C-free samples using less zinc will provide additional insights on this matter. Future plans include testing different temperatures and the influence of a two-step reaction to the isotopic fractionation.

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