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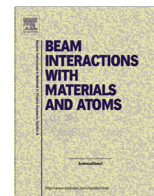
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A B S T R A C T

In this paper, we summarize the sample preparation methods currently used at the Radiocarbon Laboratory of the Universidade Federal Fluminense (LAC-UFF) in Brazil. We also report on a series of results with regards to the graphitization protocol. Tests with different temperatures and baking times were performed, and carbon stable isotope ratios of graphite were measured by an EA–IRMS (elemental analyzer coupled with an isotopic ratio mass spectrometer) to infer the completeness of the graphitization reaction. We monitored the muffle furnace temperature using an independent thermocouple and found a −60 °C offset, which may have caused the lower graphitization yields (detected from the large isotopic fractionation on several reference materials targets). At a temperature of 520 °C, the isotopic fractionation in the graphitization reaction was systematically lower (−5‰ in average) and the overall scattering was reduced. As long as isotopic fractionation corrections are made using the online stable isotopes ratios provided by the AMS system, the accuracy of the ^{14}C results should be maintained.

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1. Introduction

The Radiocarbon Laboratory of the Universidade Federal Fluminense (LAC-UFF) was established in 2009 at the Physics Institute, in Niterói, Rio de Janeiro State, Brazil, with the aim to improve existing and foster new collaborations with Brazilian archaeologists and geoscientists [1,2]. Samples used to be prepared and graphitized in Brazil and measured in foreign laboratories until 2012, when a 250 kV Single Stage Accelerator (SSAMS) system, produced by NEC, was installed and immediately put into operation. The facility at the UFF was the first ^{14}C-AMS laboratory in Latin America [1–3].

The first tests with reference materials in our SSAMS system have shown that isotopic fractionation in the graphitization step

and in the spectrometer itself could be a potential issue for our ^{14}C analysis [4]. Back then, graphitization was done using quartz tubes with distilled Zn at 700 °C during two consecutive 10 h periods, with iron as a catalyst [1]. However, in order to improve yield and quality of graphite targets, we have changed our graphitization procedure to the Zn and TiH_2 sealed-tube method following Xu et al. [5]. Currently, we use sealed Pyrex tubes with graphitization taking place at 520 °C. An inter-comparison of results between the Brazilian laboratories, LAC-UFF and the conventional low level liquid scintillation counting laboratory at CENA/USP, and the University of Georgia AMS laboratory (UGAMS) from the Center for Applied Isotopes Studies (CAIS), USA, has shown a good agreement for a limited number of unknown samples and for reference materials as well [2].

Background levels of processed graphite depend on both machine background and sample processing [6], for a certain amount of C graphitized. For monitoring laboratory backgrounds

during sample processing we use ^{14}C dead reactor graphite (donated by Purdue Rare Isotopes Measurement Laboratory) and optical calcite. Typical uncorrected background levels for processed samples are about 38 ky for inorganic (calcite) and 35 ky for organic (reactor graphite) samples respectively, while machine background is 50 ky based on "unprocessed" reactor graphite [3]. The processed backgrounds values shown here are not appropriate for smaller or older samples, but improvements are possible [5,7]. Xu et al. [5] and Rinyu et al. [7] have demonstrated that 50 ^{14}C ky or better backgrounds can be achieved for processed samples using the sealed-tube Zn and TiH_2 method with Fe as catalyst. Tests of reagents' pre-treatment and storage conditions are under way in order to improve laboratory background levels.

Up to now we have regularly prepared samples of wood, charcoal, soil and carbonates. In this work, we discuss the lower graphitization yields detected from the isotope fractionation effect observed in the graphitization reaction, and its overall effect ton accuracy and precision of ^{14}C-AMS measurements.

2. Materials and methods

After the physical and chemical pre-treatments, we combust all organic samples in sealed quartz tubes, containing baked CuO and Ag wire, at 900 °C for 3 h. For carbonate matrixes, we hydrolyze samples in H_3PO_4 to produce CO_2. For CO_2 purification we use a stainless steel line made from Swagelok tubing and ultratorr connections [1]. We now have two more vacuum systems where we can purify the CO_2-gas samples using dry ice/ethanol and liquid nitrogen traps. These new systems have reduced volume to reduce pumping time. Each of the vacuum lines consists of a single water trap, a known measured volume and 5 outputs for graphitization tubes, and is connected to a needle for carbonate septum vials and a tube breaker for organic samples combustion tubes. A scheme of the new vacuum system is shown in Fig. 1.

Graphitization takes place separately in sealed Pyrex tubes in a muffle furnace at 520 °C (460 °C until the present work). We use the Zn and TiH_2 method with iron as catalyst following Xu et al. [5]. The produced graphite targets yield intense and stable currents in the SSAMS [3]. On the other hand, the large scattering of the stable isotopes ratios measured in the SSAMS calls the attention to the isotopic fractionation issue, which is likely to be the result of incomplete graphitization reaction [1] in addition to machine induced fractionation [3]. Although isotopic fractionation effects can be corrected by stable isotopes ratios provided by the AMS system [8], the concern about fractionation in graphitization reaction resides in reduced currents (and consequently smaller graphite targets), and the possibility of non-mass dependence of ^{12}C and ^{13}C currents within the AMS [3].

3. Graphitization tests

With the aim to understand the isotopic fractionation in our sealed-tube Zn and TiH_2 graphitization reaction we evaluated $\delta^{13}C$ values of a set of graphites prepared from reference materials by an Elemental Analyzer (NA1500, Carlo Erba) coupled with an IRMS (Delta Plus XP, Thermo Fisher) at the Keck-CCAMS Facility at University of California, Irvine, USA (KCCAMS/UCI). The $\delta^{13}C$ EA–IRMS results (Fig. 2) confirm the poor yield in the graphitization reaction, indicated by large isotopic fractionation effects of very negative $\delta^{13}C$ values of the graphite, compared to the known $\delta^{13}C$ of the reference materials. It is known that the zinc reduction graphitization process often results in mass-dependent fractionation [5,7,9]. Depending on the amount of reagents used and graphitization conditions, such as temperature and time, the fractionation would lead to 1–8‰ lighter in graphite than the original CO_2 $\delta^{13}C$ values [5,9]. However, in our case, isotopic fractionation not only reaches -30‰ but also shows a large scattering of $\delta^{13}C$ values. Those graphite targets, once 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.

Concerning the ^{14}C measurements, a set of reference materials was prepared at LAC-UFF and measured at the compact AMS system (NEC 0.5 MV 1.5SDH-1) of the KCCAMS/UCI facility [8].
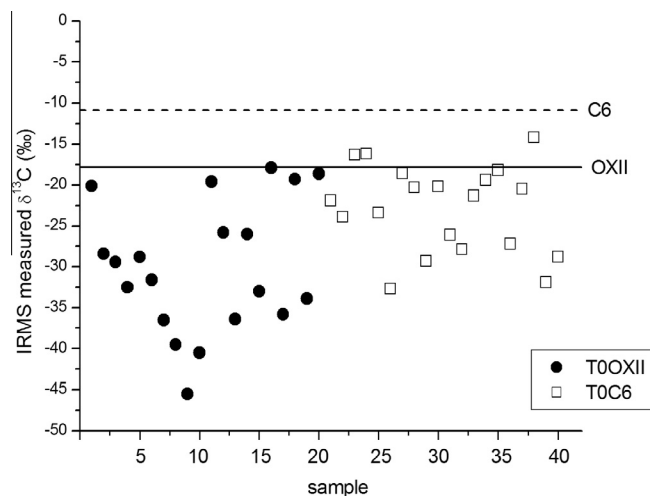

Fig. 2. Measured EA–IRMS $\delta^{13}C$ values of graphite from OXII and IAEA C6 reference materials prepared at 460 °C for 7 h, with reaction tubes lying down on aluminum silicate ceramic plates during graphitization. Lines represent the consensus $\delta^{13}C$ values of the reference materials.
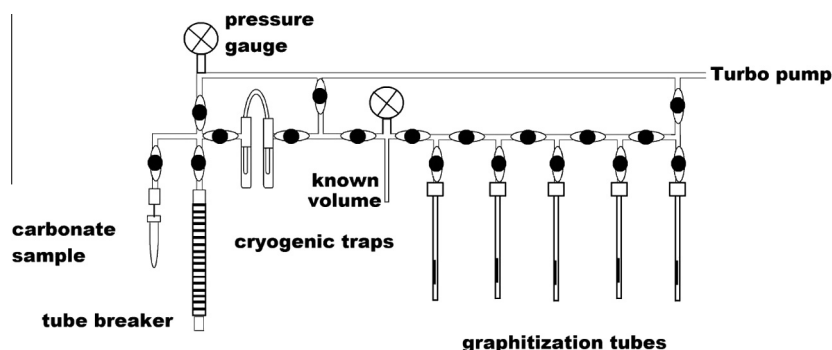

Fig. 1. New vacuum system for graphitization at LAC-UFF.

Results for IAEA C2 and C6 as well as OXII are shown in Fig. 3. Background samples were also measured, optical calcite (CA) and reactor graphite (GR).

In order to investigate the source of the large isotopic fractionation, we performed a few tests structured as follows. We have prepared 3 batches of graphite from OXII, IAEA C6 and IAEA C2 reference materials. The first batch (T1) was graphitized at the muffle furnace for 7 h at 460 °C (this temperature value was assigned once the temperature offset of about −60 °C was determined by independent thermocouple measurements). For the second batch (T2) we used the same temperature (460 °C) and baked the tubes for 10 h. For the third batch (T3) we used a different muffle furnace at 520 °C for 7 h with air circulation to provide homogeneous distribution of heat inside the furnace. For the three tests we used a metal block and placed the tubes in upright position, following established protocols [5,7], instead of placing the tubes down in lying position inside aluminum silicate ceramic plates (our standard protocol). The mixture of iron and graphite from the three batches were sent to the Stable Isotope Facility (SIF) of the University of California, Davis (UCD), USA for EA–IRMS analyses (PDZ Europa ANCA-GSL elemental analyzer interfaced to a PDZ Europa 20-20 isotope ratio mass spectrometer from Sercon Ltd.,

Cheshire, UK) and the results are presented in Fig. 4. From the results we can observe that the position of the tubes made no difference and the scattering is the same as the observed before in Fig. 2. Increasing the time of baking made no relevant difference either. For test 3 it can be observed that despite fractionation is still present, the difference between consensus values of each reference material and the measured values are approximately constant and less scattering is observed. Fig. 4 shows the plot of EA–IRMS measured $\delta^{13}C$ values for the reference materials versus the known $\delta^{13}C$ values. The correlation is linear and the average difference is −5‰ (see Fig. 5). Nevertheless, these small deviations should not be an issue for the ^{14}C data if the isotopic fractionation correction is made using AMS online-$\delta^{13}C$ [6], measured on prepared graphite. Therefore, the reduced scattering is expected to lead to improvements in precision and accuracy of our SSAMS ^{14}C analysis. Fraction Modern values for IAEA C2 reference material graphitized at 520 °C for 7 h and measured at LAC-UFF are shown in Fig. 6.

Considering that, in this experiment, the degree of isotopic fractionation was only affected by temperature, we can conclude that the temperature of 460 °C was not enough to guarantee the completeness of the reaction, so incomplete graphitization was the cause of fractionation. In order to improve the graphitization even
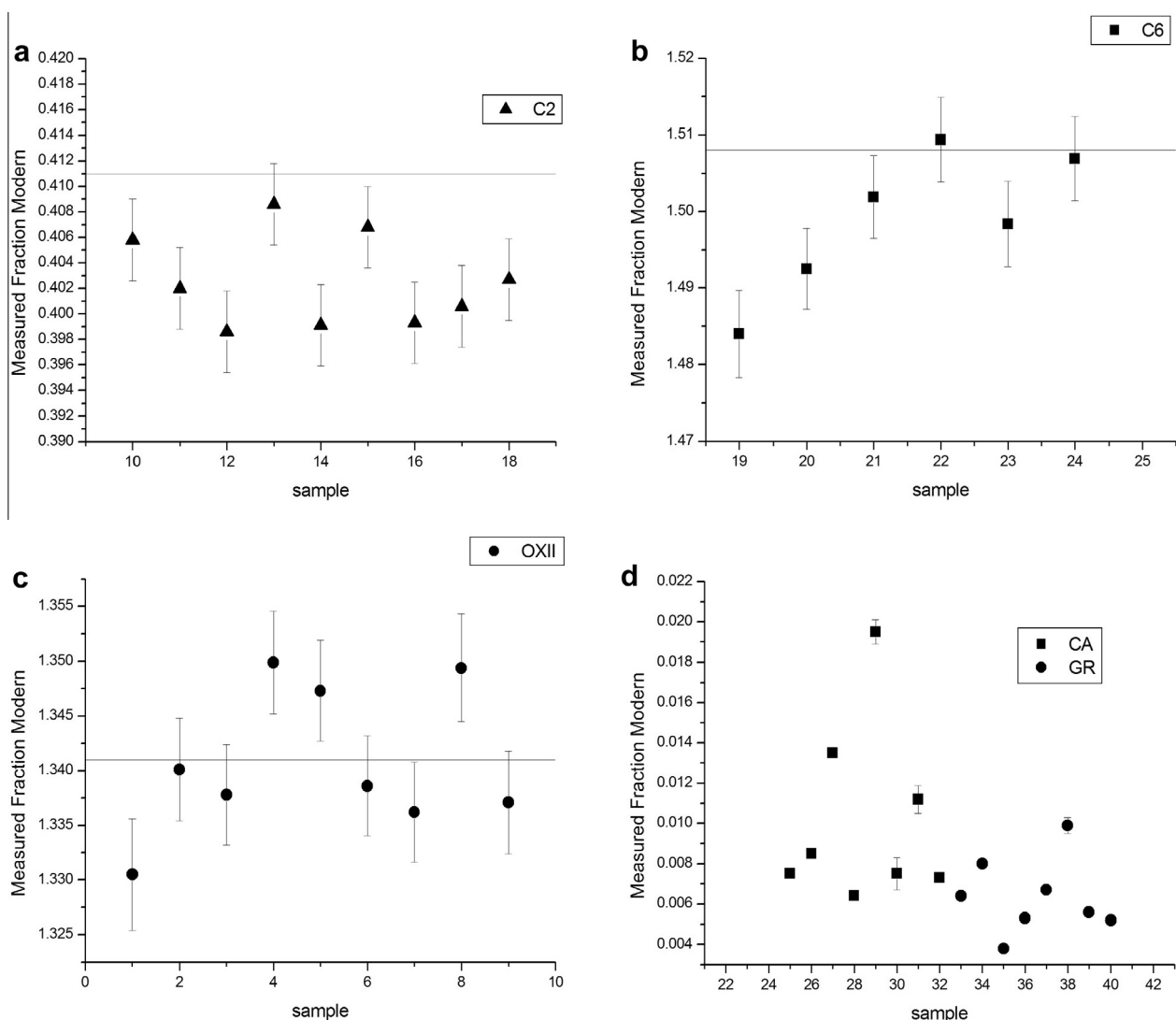

Fig. 3. Fraction modern carbon measured at KCCAMS/UCI for reference material prepared at LAC-UFF at 460 °C for 7 h. (a) IAEA C2; (b) IAEA C6; (c) OXII; (d) graphite (GR) and calcite (CA) blanks.
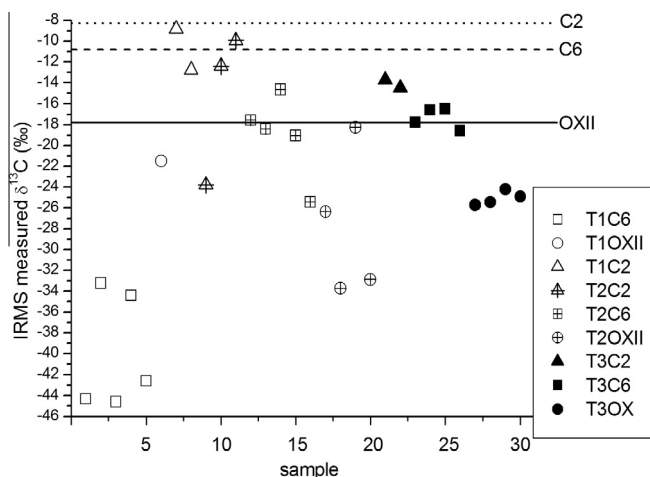
Fig. 4. Measured EA–IRMS δ^{13}C values of graphite from OXII and IAEA C6 and C2 reference materials prepared at 460 °C for 7 h (T1), at 460 °C for 10 h (T2) and for 520 °C for 7 h (T3). All reaction tubes were placed in metal blocks in upright position during graphitization. Lines represent the consensus δ^{13}C values of the reference materials.
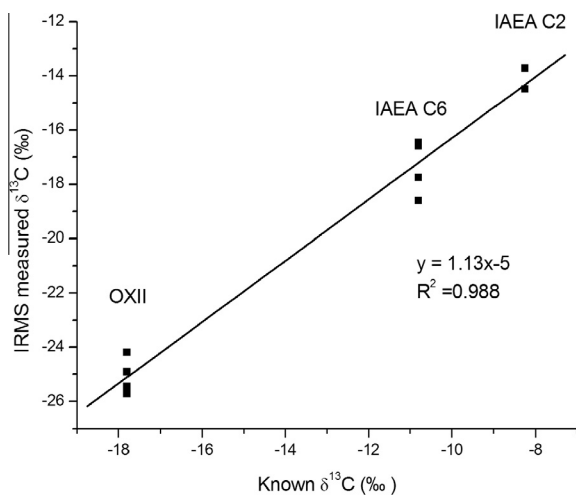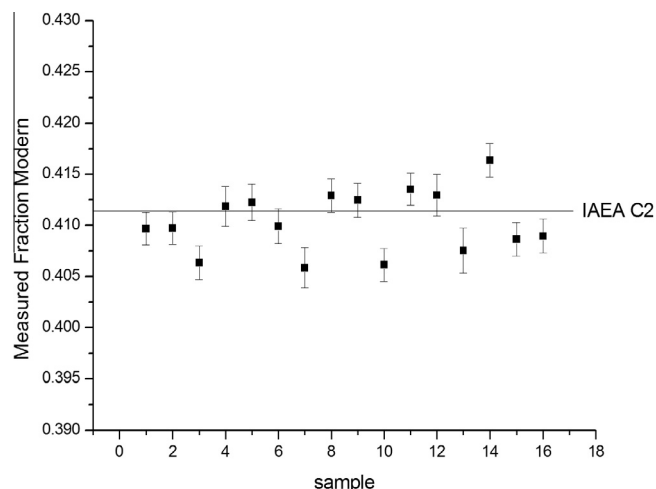

Fig. 6. Fraction modern carbon for IAEA C2 reference material prepared at 520 °C for 7 h and measured at LAC-UFF. Line represents the consensus value.

Fig. 5. Linear fit for measured IRMS δ^{13}C values of graphite vs. known values of reference materials for test 3 (T3) at 520 °C for 7 h.

further, our next steps will be to test the amount of zinc used and to increase the baking temperature to 550 °C [5,7]. Nowadays we use from 30 to 35 mg Zn to produce 1 mg C graphite targets, but Rinyu et al. [7] suggest that the use of 60 mg Zn could reduce isotopic fractionation. According to Xu et al. [5] and Rinyu et al. [7], a two-step graphitization temperature would contribute to the release of hydrogen from TiH$_2$ at 500 °C while it would increase the efficiency of the iron catalyst during graphitization reaction at 550 °C [5,7].

4. Conclusions

Monitoring of stable isotopes ratios (δ^{13}C) directly from produced graphite targets for ^{14}C-AMS measurements has disclosed large isotopic fractionation issues that most likely resulted from incomplete graphitization. Problems with the muffle furnace temperatures were identified, and the isotopic fractionation was reduced with increased graphitization temperature. Considering that isotopic fractionation corrections can be made with stable isotopes ratios measured directly in the AMS system, the accuracy of the results is preserved. Improvements in the laboratory's background levels are under way.

Acknowledgements

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