ADVANCES IN HANDLING SMALL RADIOCARBON SAMPLES AT THE LABORATOIRE DE MESURE DU CARBONE 14 IN SACLAY, FRANCE

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ABSTRACT. The Artemis accelerator mass spectrometry (AMS) facility, installed in 2003 in Saclay, France, is devoted to radiocarbon measurements. Samples are submitted by scientists in the fields of Quaternary geology, environmental sciences, and archaeology. The entire preparation process, originally optimized for samples with about 1 mg of carbon, has been tested in recent years for samples with a lower carbon content. In particular, we prepared and measured carbonate and organic background and reference samples ranging in mass from 0.01 to 1 mg C. These tests helped define our protocol's practical limits and determine necessary improvements. Furthermore, our experiments demonstrated that satisfactory graphitization yields (80% and higher) and low background values can be obtained with samples down to 0.2 mg of carbon. For handling smaller samples, we developed a specific process. We tested smaller reactors (5 mL in volume) and adapted the reduction parameters (H_2 pressure and temperature) accordingly. We also tested the effect of a chemical water trap on graphitization yields and ^{14}C results. This paper presents in detail the aforementioned developments and reports the ^{14}C results obtained for background and standard small samples prepared with the modified reactors.

INTRODUCTION

The LMC14 laboratory in Saclay, France, routinely measures ~4500 radiocarbon samples a year for French agency interdisciplinary research programs in fields such as environmental sciences, archaeology, and hydrology. In recent years, there has been a growing interest for measurements of samples smaller than 0.1 mg C, namely specific soil compounds and organic water fractions. Many laboratories have worked on the subject of very small samples and published papers proposing new protocols for preparations and measurements (Pearson et al. 1998; Hua et al. 2004; Santos et al. 2004, 2007; Ertunç et al. 2005; Smith et al. 2007; De Rooij et al. 2010). Our first attempt was to evaluate our capability to graphitize and to measure µg-size samples using our standard graphitization line setup and our Artemis AMS facility based on a 3MV NEC Pelletron. In a recent paper, we presented the results obtained with our 2 standard graphitization lines when preparing samples down to 0.02 mg of carbon (Delqué-Količ et al. 2013). Both lines are equipped with 12 reactors, but the reduction volume is 18 mL for the first line and 12 mL for the second.

Graphitization is performed by hydrogen reduction of CO_2 gas over an iron powder catalyst at a reaction temperature of 600 °C. To trap the water formed during reduction, cold fingers immersed in liquid nitrogen are fitted with heating coils to maintain a trapping temperature of –70 °C. Carbonate (IAEA-C1) and charcoal (wood charcoal older than 70,000 BP) background samples are measured to quantify the modern contamination (normalized ^{14}C concentration ratio $^{14}a_N = 100\%$) (Mook and van der Plicht 1999) due to chemical pretreatment, carbon extraction (by combustion or hydrolysis), and graphitization. To assess the dead carbon contamination, several small HOxI samples are prepared and measured under identical conditions. Applying the formula of Santos et al. (2007), the dead carbon contamination d varies between 0.1 and 1 µg and the modern carbon contamination m ranges from 0.3 to 2 µg. Using these background estimates, the corrected ^{14}C concentration ratios

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$^{14}a_N$ of certain standard samples prepared with our regular lines were consistent with the consensus value (Delqué-Količ et al. 2012). However, 15% of the samples containing <0.1 mg of carbon nevertheless saw a dramatic drop in graphitization yields (below 70%) with the consequence of poor $^{12}C^{3+}$ beam currents and large fractionation effects.

To improve the graphitization yields of the small samples, we reduced the volume of the reactors. Then, the pressure of gas is higher in smaller volumes, making it easier to follow the reaction process and to stop it at the right moment. A smaller-volume reactor also reduces the CO_2 sample's contact with the inner surface of the cell, leading to both a shorter reaction time and less contamination. We also decided to test a chemical ($Mg(ClO_4)_2$) water trap instead of using the technically restricting multitemperature device.

This article presents the graphitization yields obtained in these new reactors with samples down to 6 µg C. Modern and dead carbon contaminations estimated from the measurements of ^{14}C-free and HOxI samples are compared to the levels of contamination observed with the larger reactors. Finally, the ^{14}C concentration ratios of samples of IAEA-C2 are presented as a test case of the whole process of preparation and measurement developed for the very small samples.

METHODS

The design of the smaller reactor is very similar to that of the regular apparatus; the reactor's inner diameter is narrower, however, and a smaller pressure transducer with a lower pressure range (Omega PX72-015AV, 0–350 mbar) is used for more accurate measurements. The volume of the small reactor is 5 mL, which represents a reduction of more than 50% from the volume of the regular reactors (Figure 1).

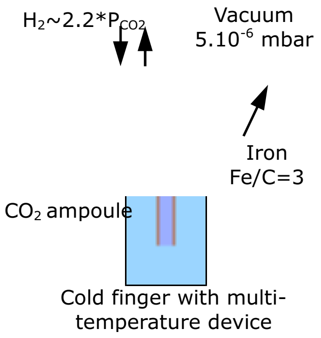

Figure 1 Schematics of the regular graphitization reactors used in the LMC14. The pressure transducer is situated just above the cold finger and the vacuum transducer is hooked up to the line immediately after the CO_2 ampoule.

The mass of iron powder used (Merck GR for Analysis, particle size 10 µm) is 3 times greater than the expected mass of carbon. However, when a sample's mass is <0.5 mg C, the 3:1 ratio produces extremely thin cathodes that are rapidly consumed under the Cs beam bombardment in the accelerator ion source. After several tests, a mass of 1.5 mg of iron is used for samples under 0.5 mg C (Delqué-Količ et al. 2012). This quantity facilitates the pressing of the C/Fe powder. Under these conditions, $^{12}C^{3+}$ beam currents between 6 and 8 µA are obtained for 20-µg C samples.

The H_2 to CO_2 ratio is around 2.2 and never higher than 2.3 to avoid the formation of CH_4 (Rinyu et al. 2007). The reduction temperature for handling "normal" size samples is 600 °C. As a lower temperature is generally advisable for preparing small samples (Turnbull et al. 2010), we first performed a few graphitizations at 450, 500, and 550 °C with 0.02-, 0.05-, and 0.1-mg C samples in order to choose the best temperature for our forthcoming experiments. Whatever the temperature, no significant differences were observed in the graphitization yields. So, it was decided to use a reduction temperature of 550 °C for our experiments.

Two reactors have been tested. The first one is equipped with a multitemperature device to trap water produced during the reaction. The volume of the reactor having been greatly reduced, the temperature gradient between the reduction area and the multitemperature device (water trap) is more difficult to maintain. Indeed, with this smaller setup, the high temperature (550 °C) of the reduction tube interferes with the "cold zone" needed to trap the water. Thus, we decided to lower the water trap temperature to –80 °C.

The second small reactor is fitted with a tube containing flakes of magnesium perchlorate anhydrous ($Mg(ClO_4)_2$ from ThermoScientific). Some 10 to 20 mg of $Mg(ClO_4)_2$ were put in the glass tube hooked up to the reactor. The flakes were changed with each new sample.

A set of 29 aliquots of CO_2 taken from a large volume of CO_2 prepared from IAEA-C6 sucrose enabled us to assess the graphitization yields and reaction times in the conditions described above. Graphitization was monitored by both pressure yield and gravimetric yield measurements. As shown by Rinyu et al. (2007), competing reactions, in particular the production of CH_4 gas, can result in a satisfactory pressure yield while masking a poor graphitization reaction.

The pressure yield data is obtained from the following equation:

$$\text{Pressure yields (\%)} = 100((P_{CO2}+P_{H2}-P_{\text{total final}})/3P_{CO2})$$

where P_{CO2} is the initial pressure of CO_2 gas in the reactor before graphitization, P_{H2} is the pressure of hydrogen introduced for the reduction, and $P_{\text{total final}}$ is the final pressure of gas remaining when the pressure stops dropping.

The gravimetric yield is the ratio of the carbon mass converted to graphite ($Mc_{(\text{graphite})}$) to the carbon mass in the CO_2 gas before the graphitization ($Mc_{(CO2\ )}$):

$$\text{Gravimetric yield (\%)} = 100(Mc_{(\text{graphite})}/Mc_{(CO2\ )})$$

In the present case, $Mc_{(\text{graphite})}$ was obtained by combusting the Fe/C mixture in an elemental analyzer (EA-IRMS analysis performed by the Service Central d'Analyse du CNRS - Solaize, France). The term $Mc_{(CO2\ )}$ was calculated from P_{CO2} based on a calibration curve established from the pressure measurements of known quantities of carbon in our reactors. EA-IRMS measurements performed on these 29 graphite samples were used to evaluate whether isotopic fractionations occur during the reduction of CO_2 gas in our new reactors.

To test the entire sample preparation process, small quantities of IAEA-C1 and IAEA-C2 carbonates (between 0.5 and 1 mg) were hydrolyzed in our regular preparation line (Cottereau et al. 2007), graphitized with our new reactors and then measured for ^{14}C content. A large volume of CO_2 prepared from HOxI oxalic acid standard supplied several aliquots of CO_2 for our experimental graphitizations. The IAEA-C1 and HOxI graphite samples allowed us to control the new graphitization cells' background levels (respectively, modern and dead carbon contaminations).

RESULTS

Graphitization Yield

As observed by Rinyu et al. (2007), the gravimetric yield gives smaller values than the pressure yield for a large majority of samples (Table 1). This behavior is caused by competing reactions that lead to the formation of CH_4 and/or CO. In the present case, it can also be explained by the gravimetric yield calculation method. When the Fe/C powder is removed from the tube and placed in the elemental analyzer, residues on the inside of the tube may minimize the quantity of carbon measured. Furthermore, the differences between both yields are probably increased by the high uncertainty of the $Mc_{(graphite)}$ term. At any rate, the gravimetric and pressure yields are higher for samples graphitized in the small reactors with the $Mg(ClO_4)_2$ trap (Figure 2). This trend is confirmed by the $\delta^{13}C$ values, which are closer to the IAEA-C6 consensus value ($\delta^{13}C = -10.8‰$) for samples graphitized in the small-volume reactor equipped with the alternative water trap.

Table 1 Experimental results for IAEA-C6 samples.

Type of graphitization reactor	Mass of carbon (µg)	Reaction time (min)	Gravimetric yield (%)	Pressure yield (%)	$\delta^{13}C$ (‰) ±0.3‰
Large-volume reactor + cryogenic trap at –80 °C	353	240	89	72	–8.5
	61	180	66	80	–10.3
	45	195	66	83	–11.2
	40	—	32	86	–14.7
	29	180	62	101	–10.5
	17	110	48	65	–17.5
	13	150	41	80	–12.4
Small-volume reactor + cryogenic trap at –80 °C except* at –100 °C	239	150	105	67	–11.8
	177	190	118	66	–14.1
	56	140	65	77	–10.3
	53	90	47	99	–13.0
	47	150	64	73	–11.0
	40	120	67	116	–15.5
	30	90	75	75	–11.2
	16*	100	31	72	–14.7
	13*	45	56	77	–15.6
	12	60	47	57	–10.0
	12	90	44	21	–10.5
	11	50	62	71	–15.1
	11	60	60	24	–16.4
	11*	60	66	85	–13.1
Small-volume reactor + $Mg(ClO_4)_2$ trap	36	40	70	106	–10.8
	32	60	92	71	–10.7
	29	85	85	91	–10.6
	14	90	81	87	–11.1
	13	30	46	50	–12.5
	10	90	110	87	–11.2
	8	80	102	90	–9.5
	6	60	76	93	–17.0

Reaction Time and Reduction Temperature

We usually define the reaction time as the time needed to obtain a plateau in the pressure curve. The reaction times of very small samples are generally shorter than those of regular-size samples. In Table 1, we observe that samples between 0.01 and 0.06 mg C graphitized in our large-volume cells have reaction times of 2 to 3 hr, whereas regular-size samples have reaction times of 4 to 5 hr

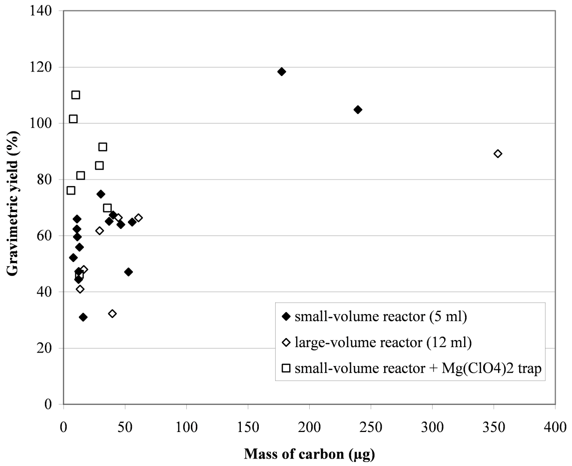

Figure 2 Gravimetric yield data for different carbon masses graphitized in 3 different types of reactors.

(Delqué-Količ et al. 2012). In the 5-mL reactors, reaction times vary between 45 min and 2.5 hr for samples between 0.01 and 0.06 mg C. The smaller volume of the reaction cell has clearly minimized the reaction time. The system for trapping water, we further note, does not seem to affect the reaction time.

We also observe that the pressure of 4 samples with carbon masses below or close to 10 µg flattens out after 10 min (Figure 3). Three of these samples were graphitized in the reactor with the water chemical trap. Reducing the reaction temperature from 550 to 500 °C enables graphitization to start up again. Even if we cannot explain this effect, it corroborates the observation made by others (Santos et al. 2007; Turnbull et al. 2010), that low reaction temperatures produce the best graphitization yields for samples under 10 µg C. It appears necessary to perform some more experiments at 500 and 450 °C for samples close to and below 10 µg C to check if lower temperatures improve significantly the reaction time and/or the graphitization yield.

AMS ^{14}C Measurements

With routine measurements (graphite targets of 0.2–1 mg C), the ^{12}C current out of the source is in the range 20–50 µA. The cathodes are generally submitted to 10 runs of 3 min each. For smaller samples (<0.2 mg C), the Cs ion flow that generates the ^{12}C beam current in the MC-SNICS cesium sputter ion source of the AMS facility is reduced to avoid quick deterioration of the samples under the beam. In this way, graphite targets last longer and 7 to 10 runs can be used for calculations. The ^{12}C beam currents measured for samples ranging from 0.01 to 0.2 mg C are between 1.5 and 20 µA. The ^{14}C/^{12}C ratios are corrected for fractionation with the AMS-measured δ^{13}C values and normalized to an averaged value of 3 to four 1-mg C HOxI samples measured in the same batch. We observed, as others did (von Reden et al. 1998; Santos et al. 2007), a mass-dependent fractionation effect for samples under 0.1 mg C. The AMS-measured δ^{13}C results are lighter and can differ as much as 10 to 20‰ from the expected values. The data are not corrected for machine background. In fact, the machine blank, regularly measured with targets made of natural geological graphite, has an average ^{14}C concentration ratio of 0.015% which is considered negligible.

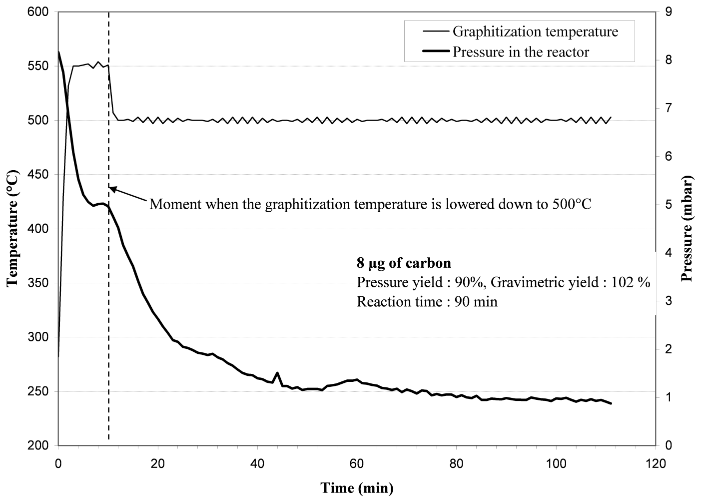

Figure 3 Graphitization curves for a sample containing 8 µg of carbon in the small-volume reactor with the $Mg(ClO_4)_2$ trap. When the reduction temperature is changed from 550 to 500 °C, the pressure drops again. The reaction time is the time needed to obtain a plateau in the pressure curve.

Background Levels

The ^{14}C activities of ^{14}C-free samples (IAEA-C1 carbonate and ^{14}C-free wood charcoal) assessed with our different graphitization line setups are plotted in Figure 3a. Figure 3b presents the deviations of normalized ^{14}C concentration ratios from the recommended value ($^{14}a_N$ = 105.26%) for HOxI standard samples.

Presenting background results as such distinctly emphasizes the mass ranges of modern and dead carbon introduced in our samples over the course the entire preparation process. The data obtained with the small-volume reactors for IAEA-C1 samples fit the modern contamination range of 0.1 to 1 µg defined with previous values of ^{14}C-free samples graphitized in the large-volume reactors. Nevertheless, 8 values are above the 0.3-µg solid line that represents the higher level of modern contamination for IAEA-C1 samples reduced in the 12-mL reactors. As the vacuum level is the same in both the new cells and the standard reactors (5×10^{-6} mbar), we suspect that the higher levels were caused by the hydrolysis step of the carbonate samples. In fact, in the large reactors, we graphitized small aliquots of CO_2 sampled from a large batch of gas prepared from a large amount of IAEA-C1 carbonate (20g). In this case, the amount of modern contamination present in each of the aliquots is only a fraction of the total contamination added when preparing the large IAEA-C1 sample. It can be considered that this fraction of modern contamination is smaller than the amount of contamination added when preparing separately small samples as was done for CO_2 graphitized in the small reactors.

The water removal method (cryogenic or chemical) does not seem to have any effect on the level of modern contamination. The HOxI samples fall into the higher part of the dead carbon range previously defined with the large reactors; 2 values are even above 1 µg of dead carbon. The iron powder may be responsible for these higher values. The catalyst used for these experiments and the one used for the graphitizations in the large reactors are from different batches. Nevertheless, as all of the samples processed in the small-volume reactors were measured in the same batch, a machine effect could also explain these higher ^{14}C concentration ratios. The water chemical trap does have any effect of the level of ^{14}C-free contamination, compared to the cryogenic water trap.

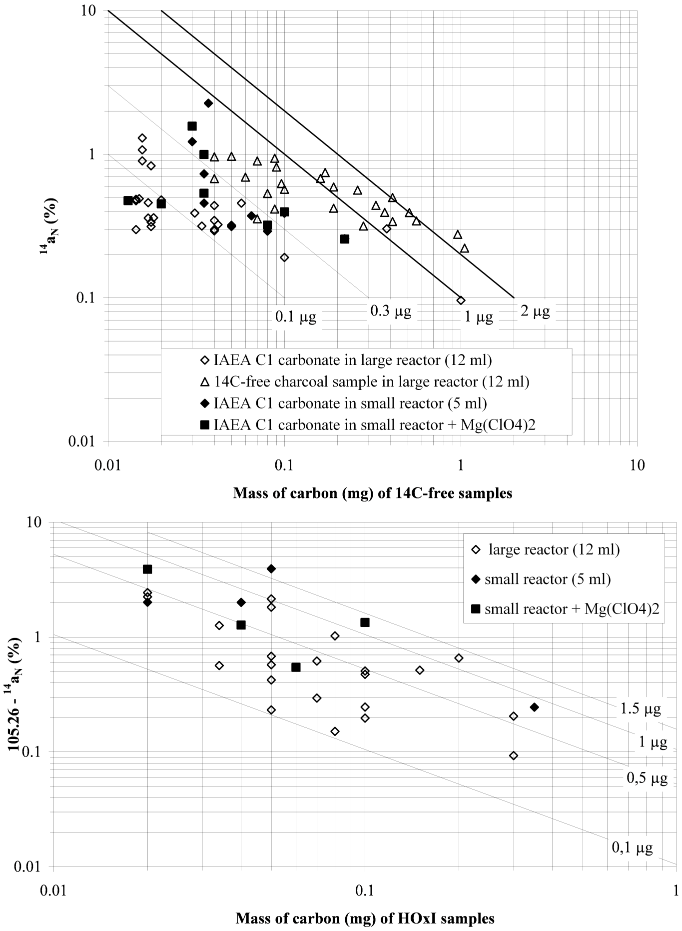

Figure 4 The normalized ^{14}C concentration ratio of the background as a function of the sample size. (A, top) IAEA-C1 samples and ^{14}C-free wood charcoal samples. The solid lines represent fixed amounts of modern carbon. (B, bottom) Deviation of the normalized ^{14}C concentration ratio from the standard value (105.26–$^{14}a_N$) of the HOxI standard as a function of the sample size. The solid lines represent fixed amounts of dead carbon.

Results for IAEA-C2 Samples

Four samples of IAEA-C2 were prepared with the small reactors and measured in the same batch of IAEA-C1 and HOxI samples (Figure 5). The $^{14}C/^{12}C$ ratios were corrected for fractionation and normalized as explained in the previous paragraph. The raw results were corrected using the approach described by Santos et al. (2007). Background corrections of $m = 0.5 \pm 0.5$ µg and $d = 0.5 \pm 0.5$ µg were applied, consistent with the values calculated in this specific batch of measurement. The error bars represent the error for background correction and the standard deviation σ. All the results are consistent with the consensus value.

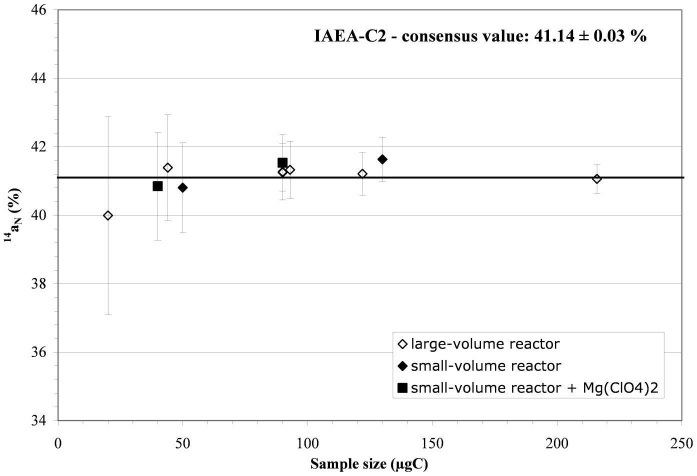

Figure 5 The normalized ^{14}C concentration ratio of IAEA-C2 as a function of sample size.

CONCLUSION

Increasing demands for ^{14}C measurements of very small samples gave us the opportunity to test the limits of our standard graphitization lines. It was clear that new reactors needed to be designed for samples below 0.1 mg C. As demonstrated in the present paper, for samples below 0.1 mg C, the 5-mL volume reactor equipped with a $Mg(ClO_4)_2$ water trap gives higher graphitization yields than the same volume reactor equipped with a cryogenic water trap at –80 or –100 °C. The reaction time does not seem to be modified by the type of water trapping. The graphitization temperature was lowered from 600 °C for 1-mg samples in large reactors to 550 °C for samples under 0.1 mg C in small reactors. At this temperature, graphitization yields are satisfactory for samples down to 10 µg C. Below or close to 10 µg C, we observe that the reaction flattens and starts up again by reducing the temperature to 500 °C. Further experiments at 500 °C and below are necessary to conclude definitely on the interest of lowering the graphitization temperature for samples close to and smaller than 10 µg C.

With our small reactors, the modern carbon contamination is between 0.1 and 1 µg. These values are satisfactory but more dispersed and slightly higher than with the large reactors. This behavior, which can be explained by our preparation protocol of the IAEA-C1 samples, shows that the first steps of preparation (cleaning and hydrolysis step) could be improved for small samples.

The dead carbon contamination is between 0.5 and 1 µg when samples are graphitized in our small reactors. These values are in the higher part of the range defined with the large reactors. This may be due to the iron catalyst, but, as all the samples have been measured in the same batch, a machine effect is suspected. The ^{14}C-free and HOxI samples graphitized in the 5-mL reactor equipped with the chemical water trap do not show higher modern and dead contamination levels than the same samples processed in the reactor equipped with the cryogenic trap. Furthermore, the use of a chemical water trap avoids the fastidious supplying of liquid nitrogen throughout the entire reaction process and could be an efficient solution to trap water during the graphitization of samples close to and below 0.1 mg C.

The 4 samples of IAEA-C2 ranging from 0.04 to 0.13 mg C graphitized in the small reactors have been successfully prepared and measured. The normalization to 1-mg C HOxI standards, the AMS

δ^{13}C corrections, and the background corrections applied for dead and modern contamination lead to results in good agreement with the consensus value. Nevertheless, very small samples (<0.04 mg C) still need to be tested in the small reactors.

In conclusion, we plan to use the 5-mL volume reactor equipped with the water chemical trap to graphitize samples from 0.04 to 0.1 mg C. To evaluate as precisely as possible the modern and dead carbon contaminations associated to the unknown samples, background samples of matched size will also be prepared, graphitized, and measured in the same way. As shown in our study with the IAEA-C2 samples, good results are obtained when the ^{14}C ratios are corrected for fractionation with the AMS-measured δ^{13}C values and normalized to an averaged value of several 1 mg C HOxI. We will use this protocol to calculate ^{14}C results for the small samples.

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