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Authors
Santos, G.M.
Southon, J.R.
Griffin, S.
et al.

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Ultra small-mass AMS ^{14}C sample preparation and analyses at KCCAMS/UCI Facility

G.M. Santos *, J.R. Southon, S. Griffin, S.R. Beaupre, E.R.M. Druffel

Earth System Science, University of California, Irvine, B321 Croul Hall, Irvine, CA 92697-3100, USA

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Abstract

We have developed techniques for accurately and precisely measuring samples containing less than a few hundred micrograms of carbon, using a compact AMS system (NEC 0.5 MV 1.5SDH-1). Detailed discussions of the sample preparation, measurement setup, data analysis and background corrections for a variety of standard samples ranging from 0.002 to 1 mgC are reported. Multiple aliquots of small amounts of CO_2 were reduced to graphite with H_2 over pre-baked iron powder catalyst. A reduction reaction temperature of 450 °C was adopted for graphite samples below 0.05 mgC, rather than the usual 550 °C used on samples of 0.1–1 mgC. In our regular reactors (~3.1 cm^3), this reduction in temperature improved the graphite yield from ~60 to 90–100% for samples ranging from 0.006–0.02 mgC. The combination of lower reaction temperature with a reduced reactor volume (~1.6 cm^3) gave yields as high as 100% on graphite samples <0.006 mgC. High performance measurements on ultra-small samples are possible also due to a modified NEC MC-SNIC ion-source that generates C^- currents of 1 μA per μg of carbon for samples in the 0.002 to 0.010 mgC range, combined with on-line measurement of ^{12}C and ^{13}C (AMS $\delta^{13}C$) to correct machine-induced isotopic fractionation. Source efficiencies are in excess of 10%, which enables 4–5% of the radiocarbon atoms in 0.005–0.010 mgC samples to be measured. Examination of the background samples revealed two components: (a) 0.2–1 μg of modern carbon and (b) 0.1–0.5 μg of dead carbon. The latter component can be ignored when measuring unknown samples paired to small standards of precisely identical size (matching size normalizing standard method). Otherwise, one must make corrections for both background components. Ultra-small samples from 0.002 to 0.01 mgC can be measured with accuracy and precision of a few percent, based on scatter in results for multiple aliquots of a primary standard and deviations of secondary standards from their known values.
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1. Introduction

An increasing demand to measure small samples at the Keck Carbon Cycle AMS (KCCAMS) facility motivated us to evaluate our ability to reduce sample sizes in terms of graphite sample preparation and spectrometer capabilities. We discuss the strategies adopted to maximize graphite yields, to set up the AMS system, and the approach used to better constrain the effect of extraneous carbon on the AMS ^{14}C results.

2. Experiments, results and discussions

Our first interest was to determinate the performance of our AMS system (NEC 0.5 MV 1.5SDH-1) under conditions of reduced carbon sample size and consequently ion beam current intensity. We initially produced smaller aliquots of graphite samples by reducing the carbon sample size from 1 mg to 0.002 mgC and verifying the intensity of the beam current produced and the accuracy and precision that these targets could achieve.

2.1. Beam current investigation

In March of 2004, we measured the first wheel of small samples graphitized using our regular sample preparation protocol [1]. It was composed entirely of NIST OX-I,

* Corresponding author. Fax: +1 949 8243256.
E-mail address: gdossant@uci.edu (G.M. Santos).
URL: www.ess.uci.edu/AMS (G.M. Santos).

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OX-II and Argonne Lab Premium coal POC#3 samples ranging from 0.18–0.6 mgC. The primary normalizing standards used (OX-Is) were of regular size (~1 mgC) and produced an average $^{12}C^{1+}$ beam current intensity of 40 μA, while the smallest samples delivered only 18 μA. Since the graphite samples were produced using 4–5 mg of iron catalyst independent of sample size, this decrease in beam current intensity was expected [2–5]. Eight individual measurements were obtained for each target with approximately 35,000 counts each. No dependence of $^{14}C/^{12}C$ ratios on ion beam current was observed from samples in this size range. This encouraging result led to further experiments, testing standards samples from ~0.015 to 1 mgC. However, we observed that the measured $^{13}C/^{12}C$ and $^{14}C/^{12}C$ ratios were affected directly by the decrease in ion beam current intensity generated by samples <0.1 mgC.

Previous investigations with large samples demonstrated that the intensity of the ion beam current could be increased by at least 15% by decreasing the amount of catalyst used during graphitization from 4–5 mg to 2 mg of Fe (Fig. 1). The assumption that we could generate higher ion beam current intensity for smaller samples by decreasing the Fe/C ratio, and thereby reduce the machine-induced isotopic fractionation [3,4] was subsequently tested on samples ranging from 0.004 to 0.1 mgC. For these experiments we used conventional NEC target holders, to avoid any artifacts from target surface depth. As expected, ion beam currents from targets produced with less catalyst were initially higher compared with those from cathodes where the usual amount of catalyst was used, but they did not last long and collapsed dramatically as the sample was being sputtered by the cesium beam (Fig. 2). The overall effect on $^{14}C/^{12}C$ and $^{13}C/^{12}C$ ratios was a large decrease in accuracy when compared with results produced by graphite reduced on 4–5 mg of Fe. Therefore, all test samples reported in the following sections were prepared using 4–5 mg of Fe.

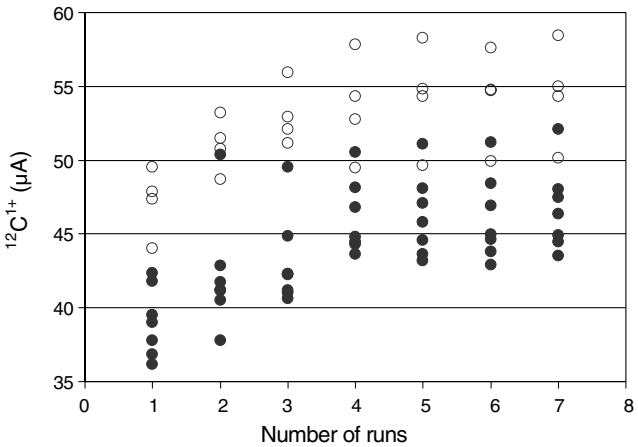

Fig. 1. Comparison of $^{12}C^{1+}$ beam currents generated by 1 mgC graphite targets of OX-I produced with 2 mg and 4–5 mg of Fe. The closed circles (●) represent the 1 mgC graphite samples catalyzed with 4–5 mg of Fe, and the open circles (○) represent 1 mgC graphite samples on 2 mg of Fe. Seven individual measurements were obtained for each target with approximately 35,000 counts each.

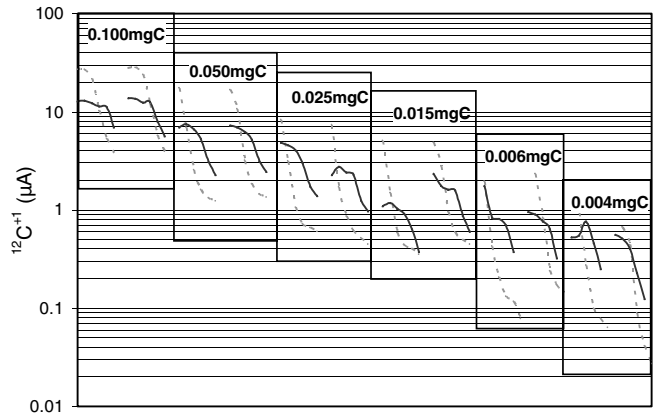

Fig. 2. Comparison of $^{12}C^{1+}$ beam currents generated by small OX-Is (range between 0.1 to 0.004 mgC) produced with 2 mg (dashed lines) and 4–5 mg (solid lines) of Fe catalyst. Six individual measurements were obtained for each target. Each measurement corresponds roughly to a maximum of 35,000 counts for the largest sample to 100 counts for the smallest. To measure small samples each measurement was time limited by 100 s maximum.

Ion source upgrading has been a major part of our in-house development program, since the purchase of the AMS system in 2002 [6]. As part of this program, in 2003 we replaced the NEC sample holders with a new design where graphite is loaded into a 1 mm hole from the front, using a hammer and a steel pin (Fig. 2 in [7]). All data presented in the paper were measured using these holders, except for the comparison with the different amounts of Fe catalyst mentioned above. In December of 2004, the replacement of the ionizer assembly [7] provided a more efficiently focused Cs beam, where source output could be maintained until essentially all of the sample material was consumed. Measurements on ultra-small samples showed that we could measure up to 4–5% of the radiocarbon atoms in 0.002 to 0.01 mgC samples for which $^{12}C^{-}$ beam currents of around 1 μA per μg of carbon were achieved (Fig. 3).

2.2. Combustion of ultra-small samples

There are two ways to produce small standards and blanks for comparison with small unknown samples: (a) weigh individual small amounts of reference material to match sample sizes or, (b) split CO_2 gas from a larger combusted sample (~1 mgC, for example). The latter method is easier because it only requires manipulation of the CO_2 gas sample in the graphitization vacuum line. However, it is only valid if it can be shown that it gives the same results as when small individually combusted aliquots are used. A previous study reported that no differences can be observed between the two methods [4]; however, we decided to carry out our own experiments to validate this observation using our own vacuum lines and combustion procedures.

For this purpose, OX-I samples were weighed out in the range of 0.029 to 0.051 mg to produce graphite standards

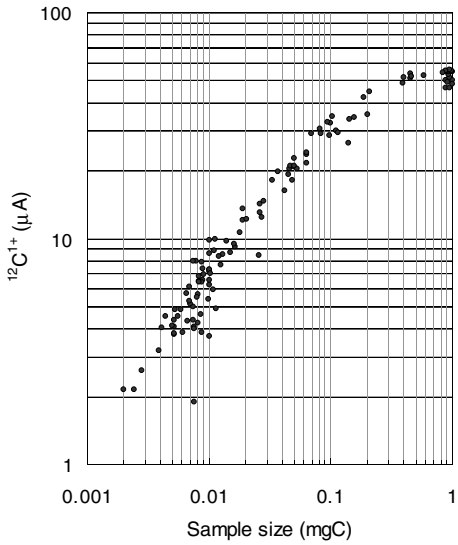

Fig. 3. Plot of the maximum $^{12}C^{1+}$ beam current verses sample size, for samples graphitized on 4–5 mg of Fe catalyst.

ranging from 0.0035 to 0.01 mgC. Aluminum foil and the tools used to weigh out the small standards were first cleaned of carbon. The Al foil was cleaned by rinsing with methanol, then de-ionized water, 10% hydrochloric (HCl) acid and then again with de-ionized water. The tools used to measure out the standards were rinsed with 10% HCl and then de-ionized water. Both the cleaned Al foil and tools were then baked in a 550 °C oven for two hours. Small standards were individually weighed out on a Sartorius M2P microbalance to ±0.001 mg. A piece of cleaned Al foil was placed on the scale tray using tweezers. A small amount of OX-I (or OX-II, IAEA-C7 or coal) was sprinkled on a cleaned watch glass. Using jeweler micro forceps and a 4X single lens magnifier a small aliquot of standard was picked up and transferred to the Al foil for weighing. Once weighed, the aliquot was picked up again and introduced into a pre-baked 6 mm Vycor tube for combustion. Silver foil or wire and cupric oxide were then added to the combustion tube according to established methods [1]. Production of a background coal sample was more problematic since the high density and high carbon content of coal made individual combustions very difficult. A 0.035 mg sample of unprocessed coal still produced many split graphite samples of 0.005 to 0.010 mgC into the graphite vacuum line and that was the smallest individual combusted coal measured out. No significant differences were observed from the AMS ^{14}C measurements of standards and blanks weighed out individually or CO_2 split from larger combustions, in agreement with the results reported previously [4]. Therefore, all test samples reported in the following sections were prepared using splits from CO_2 gas of larger combusted sample.

2.3. Optimization of graphite production

Our regular volume reactors have a volume of ~3.1 cm^3 and are based on modified 1/4″ Ultra-Torr tees, Swagelok plug valves, and 4.5 mm × 6 mm × 50 mm borosilicate culture tubes (Fig. 4a). Graphite targets are produced from CO_2 of large combusted standards, reduced by hydrogen at 550 °C to graphite over pre-baked Fe powder catalyst (Alfa-Aesar, −325 mesh). The reduction process is monitored by pressure transducers (Omega PX139, 0–30 psi) and normally takes less than 120 min to reach completion [8]. Water produced during reaction is removed chemically by absorption in magnesium perchlorate. Details of the sample preparation process for regular size samples (0.1–1 mgC) can be found in Santos et al. [1].

Preliminary examination of the reaction yield data, by monitoring the pressure decrease during graphitization, showed that the reduction of small samples (<0.025 mgC) at 550 °C was incomplete. This observation was confirmed by independent analyses of small graphitized samples of OX-I and IAEA-C6 by measuring their carbon content and isotopic composition using an elemental analyzer (EA) coupled on-line to a stable isotope ratio mass spectrometer (IRMS). Results showed a tendency toward isotopic fractionation and decreased yield, especially for samples less than 0.01 mgC. Multiple tests (described on Section 2.4) were performed to achieve the optimal reaction temperature. Lowering the temperature to 450 °C allowed us to successfully graphitize samples as small as 0.006 mgC.

To decrease this sample size limit further, we built a set of small-volume reactors (~1.6 cm^3 – Fig. 4(b)). These are direct replacements for the regular reactors on the vacuum line and can graphitize 0.002 mgC samples. EA-IRMS $\delta^{13}C$ analyses indicated that ultra-small samples (0.002–0.01 mgC) produced in these small reactors were less isotopically fractionated than those produced in the regular reactors. To better monitor the graphitization yields and to decrease the uncertainty on the graphite target masses,

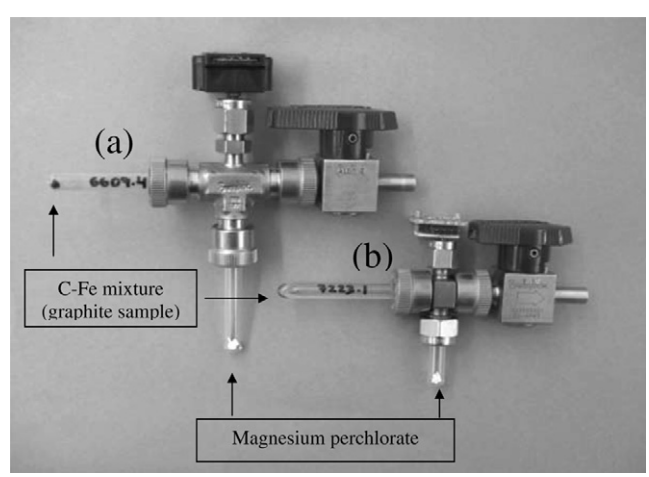

Fig. 4. (a) Regular reactor (~3.1 cm^3): modified 1/4″ Ultra-Torr tees, Swagelok plug valves, 4.5 mm × 6 mm × 50 mm borosilicate tubes and Omega PX139 pressure transducers (0–30 psi); (b) Small reactor (~1.6 cm^3): modified 1/4″ Ultra-Torr unions and Swagelok plug valves, 2.7 mm × 6 mm × 30 mm reduced-volume and 4.5 mm × 6 mm × 30 mm borosilicate tubes, and SM5812 pressure transducers (0–5 psi).

the Omega PX139 pressure transducers were replaced with more sensitive ones (Silicon Microstructures SM5812, 0–5 psi), and an additional pressure readout box calibrated for the SM5812's was installed on the line for easy switching between the two.

2.4. EA-IRMS measurements of small samples

To separate machine-induced fractionation effects from possible graphite fractionation or low yield on ultra-small graphite production, EA-IRMS measurements were performed on 0.002–0.04 mg graphite samples produced from the standards OX-I and IAEA-C6. Errors on the isotopic measurements were expected to be higher (±2‰) than the usual 0.15‰ because of the low signals provided by the samples of low carbon content. Decreased helium flow rates and the use of many size-matched aliquots of carbon reference materials, were used to aid in the accurate integration of carbon peaks from these small samples and to provide calibration corrections. Pure pre-baked Fe was selected to be measured for background corrections, since it is used as the catalyst during graphite production. The EA-IRMS measurements showed that the $\delta^{13}C$ of the pre-baked Fe (−18‰) was very close to the isotopic composition of OX-I. Eighty four graphite targets were prepared for these measurements to check the following variables that could potentially control the outcome of the CO_2 to graphite reduction process: (a) reaction temperatures: 450, 500 and 550 °C (Fig. 5), and (b) graphite reactor volume: regular (~3.1 cm^3) verses small reactor (~1.6 cm^3), for targets reduced at 450 °C (Fig. 6(a) and (b)).

The EA-IRMS measurements (Fig. 5) indicate the presence of isotopic fractionation during graphitization process (also observed by Van der Borg and collaborators [9]), possibly correlated with incomplete reduction reactions, as indicated by the nanometric measurements of yield. Note

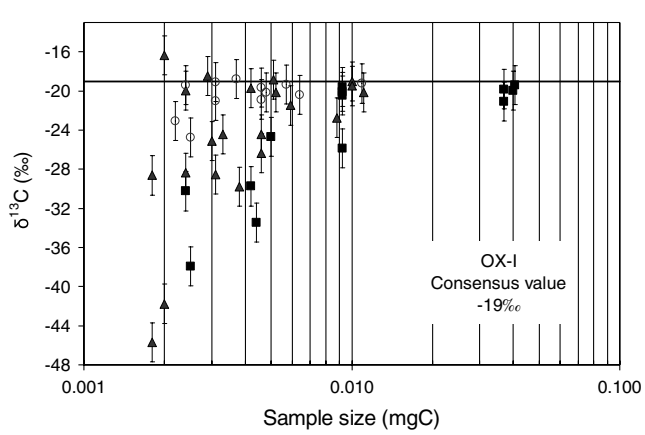

Fig. 5. EA-IRMS measurements performed on carbon–catalyst mixtures (graphite samples) from OX-Is ranging from <0.002 to 0.04 mgC to evaluate the graphite isotopic fractionation dependence on temperature reduction of 450 °C (○), 500 °C (▲) and 550 °C (■). All graphite samples were produced in our regular reactors of ~3.1 cm^3. Solid line represents consensus values [16].

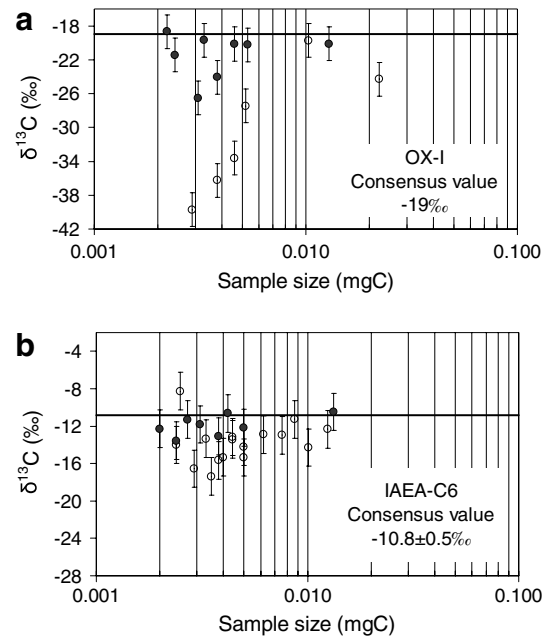

Fig. 6. EA-IRMS measurements performed on carbon–catalyst mixtures (graphite samples) from (a) OX-Is and (b) IAEA-C6 ranging from 0.002 to >0.02 mgC to compare isotopic fractionation between graphitization within small-volume (~1.6 cm^3 (●)) and regular volume (~3.1 cm^3 (○)) reactors for targets reduced at 450 °C. Solid lines represent consensus values [16,17].

that graphite fractionation is small (~4‰) even for samples with <0.005 mgC, that are graphitized in small-volume reactors at 450 °C (Fig. 6(a) and (b)).

We do not understand why OX-I graphite samples produced in our regular reactors (~3.1 cm^3) appear to fractionate more than IAEA-C6s. Most of the IAEA-C6 and OX-I EA-IRMS results were obtained in separate runs. Although we attempted to calibrate the EA-IRMS with numerous aliquots of small and ultra-small standards as described earlier, conditions were not ideal and there may have been run to run variations. Also, peak areas were not linear with nanometrically measured graphite sample sizes, probably due to sample losses during transfer to the pre-baked (180 °C) tin capsules used for EA combustion. Final results were corrected and calibrated according to the IRMS peak areas, not the nanometrically determined sizes of the graphite samples.

Despite large errors in the isotopic composition of the targets evaluated here, graphite fractionation for ultra-small samples (EA-IRMS $\delta^{13}C$) can be clearly separated from possible machine-induced fractionation effects (AMS $\delta^{13}C$), because the machine effects are normally larger (~20‰ – Section 2.7) compared with the 1–4‰ shifts from graphitization effects.

2.5. Scanning electron microscopic (SEM) pictures: regular verses ultra-small samples

SEM pictures of catalyst powder, graphite sample of 1 mgC and small graphite samples of <0.06 mgC

(Fig. 7(a)–(f)) were taken at the Materials Characterization Facility, UCI, using a Schottky thermal field emission FEI/Philips XL-30 SEM with back scattered electron detector. The SEM picture (Fig. 7(b)) shows the filamentous graphite growth on pre-baked iron Alfa-Aesar −325 mesh (Fig. 7(a)).

It is known that after iron carbide (Fe_3C) layers form on the surface, they break up into sub-micron particles. Carbon is deposited on the rear face of these particles, which remain at the tips of the filaments as they grow (Fig. 7(b)) [10]. For small and ultra-small samples that same process takes place, however, the amount of carbon may be not enough to produce filaments, and only small patches of iron carbide (Fe_3C) are formed. The effect can be observed on the SEM pictures of graphite samples with 0.057 mgC (Fig. 7(c) and (d)) and 0.011mgC (Fig. 7(e) and (f)) on 4–5 mg of Fe catalyst.

2.6. AMS ^{14}C measurement setup and data analysis

Two alternative measurement setups (Fig. 8) can be adopted depending on the size range of the unknown samples being analyzed. Each possibility requires a different background correction procedure. For example, the selection of a matching-size measurement, where all normalizing standards and secondary standards are matched to the size of unknown samples (matching size method), seems very attractive since it eliminates any extra correction as is shown in diagram (Fig. 8). Realistically, it is very uncommon that all unknown samples to be measured have exactly the same sizes. Either numerous standards and blanks must be provided, or another approach must be used (the non-matching size method of diagram – Fig. 8).

We found that the measurement of ultra-small samples can be also compromised by limited dynamic range of the current measurement system if 1 mgC OX-I standards are used to normalize unknown samples $\leqslant$0.01 mgC. To overcome this effect, we set up and tune the AMS system using ~1 mgC graphite samples. When precision and accuracy on these targets are satisfied we switch to more sensitive current integrator ranges and perform the measurement using a smaller size of normalizing OX-I standards. To measure ultra-small samples, normalizing standards should be preferably larger than 0.01 mgC to

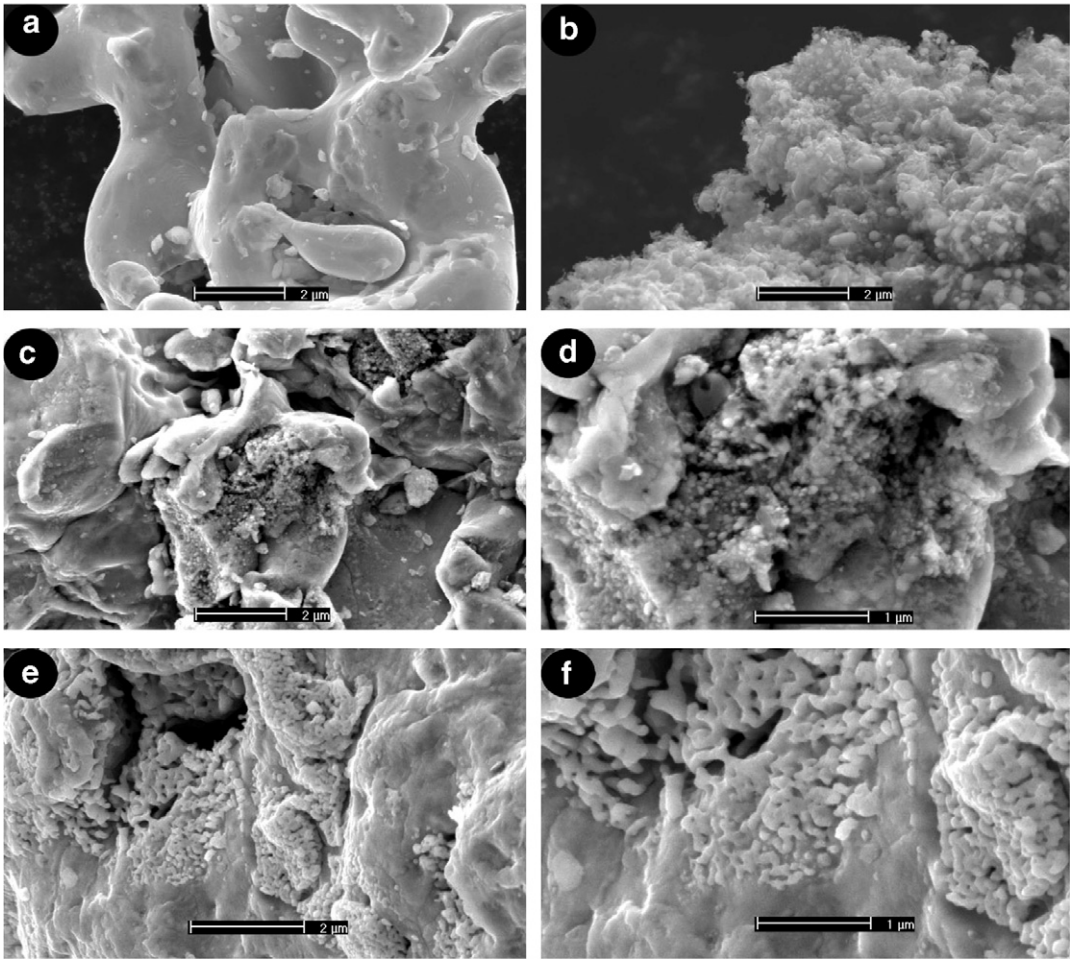

Fig. 7. SEM pictures: (a) Fe powder from Alfa-Aesar, −325 mesh, pre-baked at 400 °C under 1 atmosphere of H2; (b) 1 mgC graphite sample; (c) 0.057 mgC graphite sample (2 µm magnification) and (d) (1 µm magnification), and (e) 0.011 mgC graphite sample (2 µm magnification) and (f) (1 µm magnification).

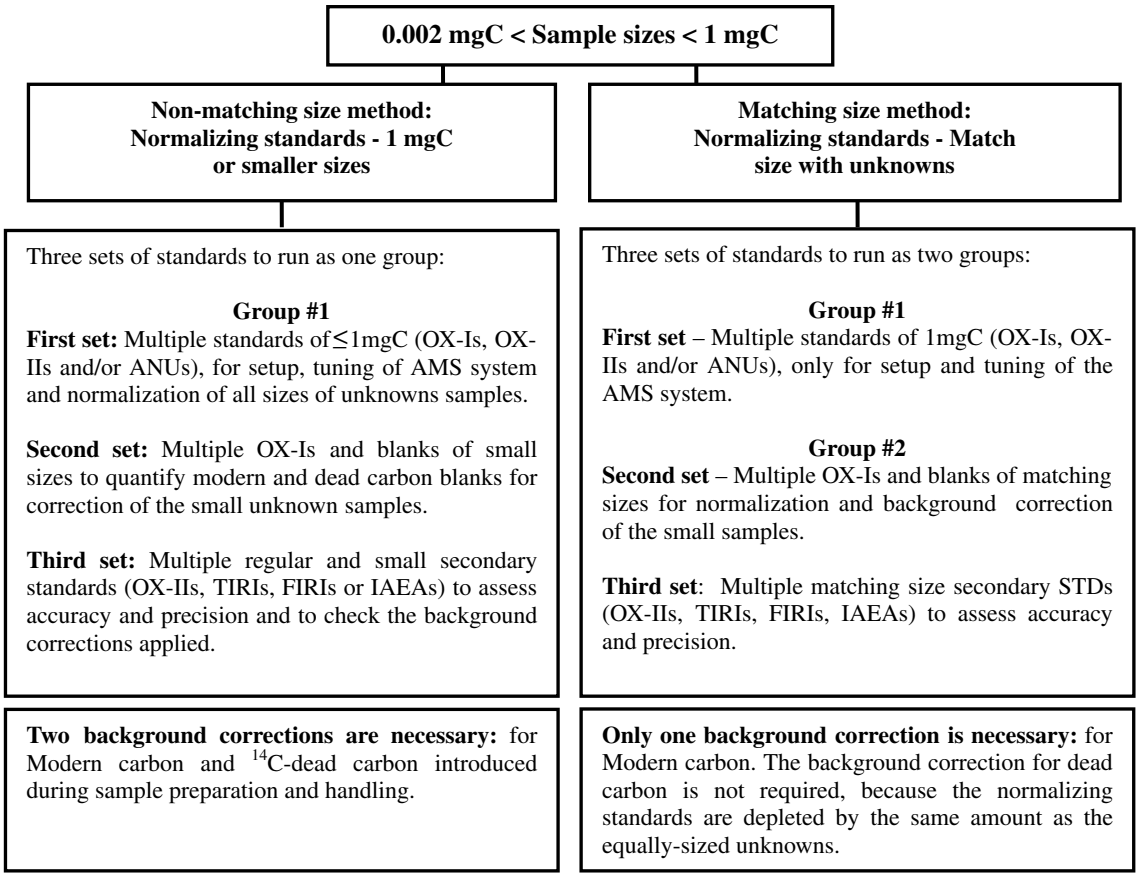

Fig. 8. An outline of the two possibilities for a AMS ^{14}C measurement setup depending on the span of unknown sample sizes being analyzed.

ensure high, long-lasting beam currents. However, appropriate background correction must be applied. These issues will be addressed in Section 2.8 and Appendix A.

For data analysis, we use the stripchart module in NEC's "abc" analysis code for detailed scanning of data from individual measurement runs, and the Lawrence Livermore "Fudger" AMS analysis software for the actual analysis [11]. These tools help to determine the causes of anomalous measurements, such as accelerator or ion source sparks or other problems, and to remove them. After anomalous readings are removed, the "clean" results are normalized to a set of six or more aliquots of the OX-I standard and then corrected for isotopic fractionation using AMS $\delta^{13}C$ measurement results. The normalized results are then pasted into an Excel spreadsheet where the appropriate background corrections, based on measurements of multiple small graphite samples of ^{14}C-free material (coal) and an extra set of small modern standards (OX-Is), are performed (Section 2.8) to produce the final data. To verify the robustness and reliability of the corrections, an independent set of multiple secondary standards (such as IAEA C6, C7, C8 and OX-Is and II-s, TIRIs, FIRIs, etc) must be measured on the same wheel (Section 2.9).

So far, we do not have evidence that the matching size method is better than the non-matching size one or vice-versa. Our main driver for selecting a specific measurement setup has been the range of sample sizes to be measured in a given run. Note that many positions within the sample wheel are sacrificed to load standards that will help tuning and normalization, address background levels and verify the corrections applied (Fig. 8).

2.7. AMS $\delta^{13}C$ correction

Since our AMS system measures all carbon isotopes, we have the capability to address and correct the machine-induced fractionation when it happens. For our regular size samples, the on-line $\delta^{13}C$ correction clearly reduces the scatter on the final AMS ^{14}C results. For small and ultra-small samples, the AMS $\delta^{13}C$ results differed as much as 20‰ from those of the original material with an overall trend (average over many runs – Section 2.9) to lighter values. However, such a trend or the larger scatter itself did not occur in every single run. So far, we do not have enough data to say definitively that the on-line $\delta^{13}C$ correction is always necessary for small samples, but the use of that correction certainly helped to reduce the scatter and improve the accuracy of most of AMS ^{14}C results shown here. For consistency, we always correct the AMS ^{14}C results using the AMS $\delta^{13}C$ values as described in Section 2.6, for any sample size.

2.8. Background corrections

The systematic trends in the normalized results from known standards and backgrounds with decreasing sample size are associated with two constant background components: (a) modern carbon – mostly introduced during sample preparation and handling, and (b) dead carbon – probably due mostly to the presence of ^{14}C-free carbon in the graphitizing catalyst. The latter component can be ignored when measuring unknown samples paired to small standards of identical size (matching size method), because the values for unknown sample and standard are diluted identically. Otherwise, one must make corrections for both "modern" and "dead" background components.

The modern carbon blank (m) can be quantified from the measured isotope ratios of small coal samples or any other ^{14}C-free material processed in the same fashion as the other samples. Isotope ratios for small coal samples, expressed as fractions of the modern radiocarbon standard (F) are shown in Fig. 9. The corrections are validated by applying them to aliquots of multiple secondary standards measured on the same wheel, with standards that are at least a half-life old providing the most sensitive tests.

The dead carbon blank (d) is quantified from ΔF, which are the deviations of the measured fraction modern carbon for small OX-I samples from those of large normalizing OX-I standards (Fig. 10). These are also validated when applied to multiple modern or near-modern secondary standards (such as IAEA C6, OX-II, additional OX-Is not used for normalization) measured on the same wheel.

The examination of the blank (Figs. 9 and 10) revealed that m typically varies from 0.2–1 μg, while d varies from 0.1–0.5 μg. These figures show data collected over a long period, and scatter within an individual wheel is usually

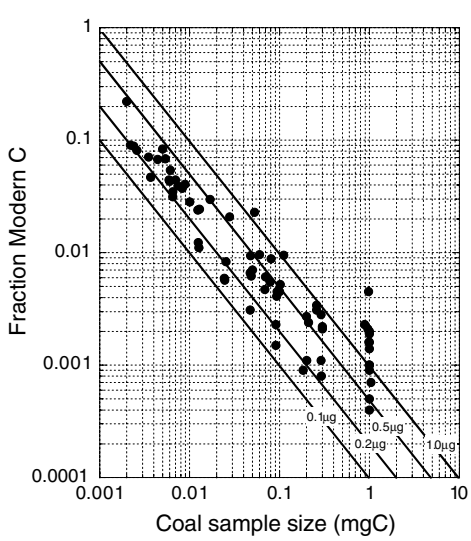

Fig. 9. Fraction modern C values for coal samples from 0.002 to 1 mgC sample size. The solid lines represent the effects of fixed amounts (0.1, 0.2, 0.5 and 1.0 μgC) of modern carbon contamination (m in Section 2.8 and Appendix A).

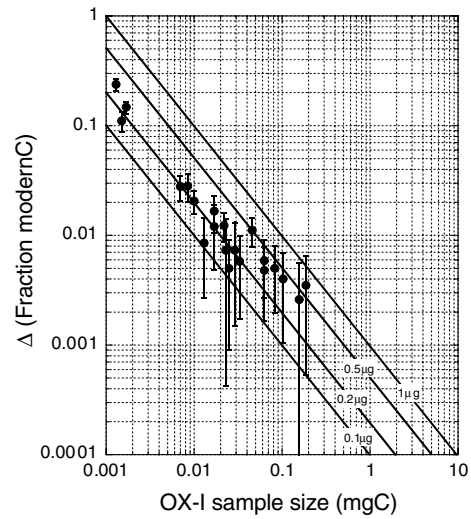

Fig. 10. Δ Fraction modern C for small and ultra-small OX-I samples of ~0.0015 to 0.2 mgC measured against 1 mgC normalizing OX-I standards. The solid lines represent the effects of fixed amounts (0.1, 0.2, 0.5 and 1.0 μgC) of dead carbon contamination (d) introduced during sample processing. Error bars represent propagated errors.

significantly less. Some of these variations may be associated with graphitizer memory effects [12], and variations in the amount and cleanliness of the catalyst in our graphitization reactors, and some may be due to variations in the blank material itself.

The extraneous carbon incorporated in any sample of mass M can be corrected by the following equations:

$$\text{Modern carbon correction}: \mathrm{MCC}(M) = m/M, \tag{1}$$

where m is the constant amount of modern C introduced during sample processing, and M is the sample size;

$$\text{Dead carbon correction}: \mathrm{DCC}(M) = d/M, \tag{2}$$

where d is the constant amount of dead C introduced during graphitization, M is the sample size.

The errors associated with the parameters m and d can be easily estimated from plots like these in Figs. 9 and 10. Typically they are in the range of 50% of the parameters themselves, i.e. $\sigma_m = m/2$ and $\sigma_d = d/2$. To calculate the appropriate error for the "Modern" and "Dead" corrections, Eqs. 1 and 2, respectively, we use the following equations:

$$\sigma_{\mathrm{MCC}}(M) = \mathrm{MCC}(M) \cdot \sigma_m/m, \text{and} \tag{3}$$

$$\sigma_{\mathrm{DCC}}(M) = \mathrm{DCC}(M) \cdot \sigma_d/d \tag{4}$$

Finally, the relationship between the corrected fraction modern carbon for the incorporation of extraneous carbon and, the measured fraction modern carbon can be expressed as:

$$F' = [\mathrm{F\text{-}MCC}(M)]/[1 - \mathrm{DCC}(M) - \mathrm{MCC}(M)]. \tag{5}$$

where F and F' are the measured and corrected fraction modern values for the sample. This formula closely approximates Eq. (A.3) of Donahue and collaborators

[13], where the combined blank correction MCC(M) + DCC(M) and the overall fraction Modern value for the blank MCC(M)/[MCC(M) + DCC(M)] are the equivalent of "f" and "g" in the Donahue formulation, respectively. Details of these formulae can be found in Appendix A.

This technique for background correction is very simple, since the mathematical formulae are simpler compared with those of other approaches [2,5,13], and the two components (m and d) can be determined and verified separately. However, for reliable results they must be measured for every wheel of small and ultra-small samples, and validated on independent sets of secondary standards of appropriate sizes and radiocarbon activity values (Fig. 11).

2.9. AMS performance of small and ultra-small samples

In order to evaluate the accuracy of these protocols, multiple small aliquots of several standards were measured on several independent wheels each containing 10–20 specially prepared small OX-Is, OX-IIs and coals spanning the size range of the "unknown" samples being analyzed. Here the "unknowns" were multiple independent standards spanning a range of fraction modern C values: extra small OX-Is plus IAEA C6, C7 and C8. To minimize graphite fractionation, a reduction reaction temperature of 450 °C was used for all samples <0.1 mgC, and reductions for samples <0.08 mgC were performed in the small-volume reactors (Section 2.3). Standards were generated from splits of CO_2 gas made with ~1 mgC of material. All results plotted on Fig. 11 were obtained by the non-matching method (Fig. 8). Fig. 11 contains dates from runs using large (1 mgC) or small (0.008–0.015 mgC) normalizing OX-Is and these are not distinguished in the figure. Data analyses and background correction procedures were applied as described on Sections 2.6, 2.8 and Appendix A.

3. Summary

Consistent with other studies [3–5] we observed that $^{14}C/C$ ratios for small near-modern samples decrease systematically with sample size. There has been debate whether this effect is due to real isotopic fractionation, primarily a func-

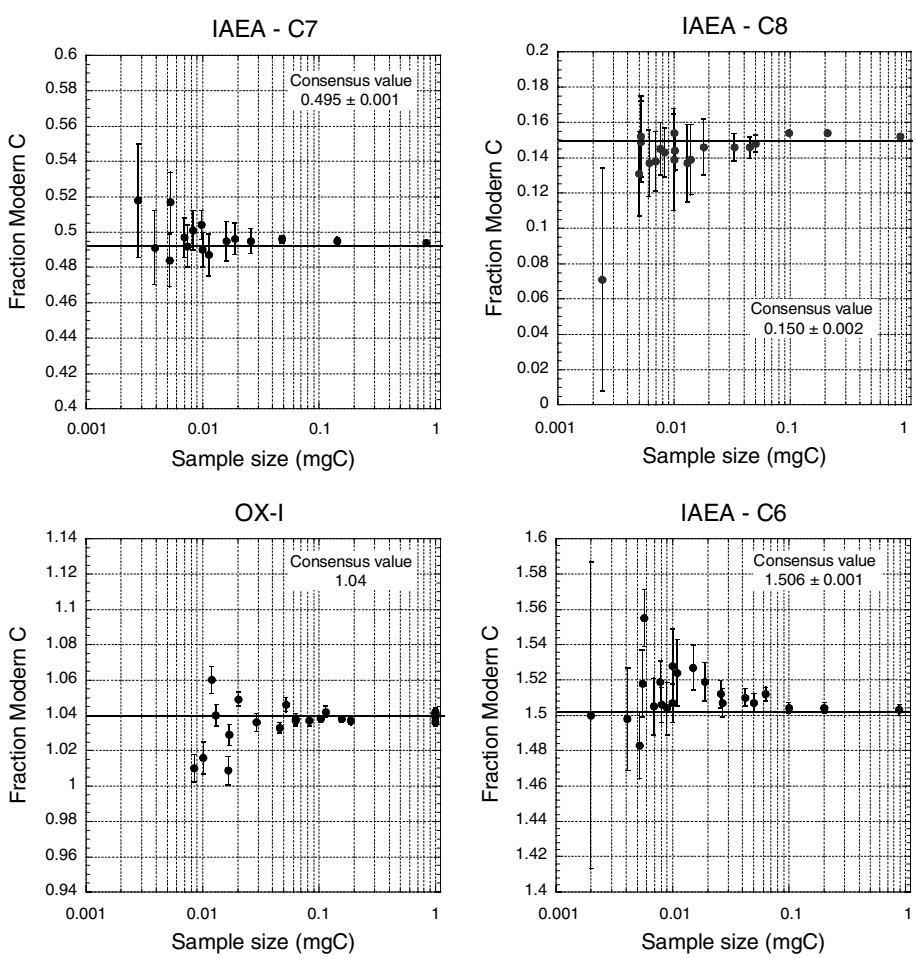

Fig. 11. Fraction modern C results for the IAEA C6, C7, C8 and OX-I samples between 0.002 and ~1mgC from multiple AMS ^{14}C measurements. These results were normalized to independent sets of six normalizing OX-I standards. For samples in the tens of microgram range, this independent set was composed of regular graphite targets (1mgC). For ultra-small samples (<0.010 mgC), the normalizing standards ranged from 0.008 to 0.015 mgC. All results have been corrected for fractionation using AMS $\delta^{13}C$ measurements. Blank corrections have been applied using the formulae presented (Section 2.8 and Appendix A), with uncertainties derived from the scatter in the blank data. Solid lines represent consensus values [17].

tion of machine conditions [3,4] or to dead carbon incorporated within the sample during preparation [5,14].

In our case, we observed the incorporation of contamination from "dead" as well as "modern" sources that when properly addressed and corrected (Section 2.8) and, validated by measuring secondary standards on a range of sizes and radiocarbon activities (Section 2.9) can provide reliable AMS ^{14}C results for samples as small as 0.002 mgC.

Our results also showed that graphite targets containing <0.025 mgC are indeed prone to machine-induced isotopic fractionation. Some of the AMS $\delta^{13}C$ results for small samples (several independent wheels containing only standards – Section 2.9), showed systematic trends to lighter values sometimes as much as 20‰ from those of the original material, and/or increased the scatter. However, such trends were not consistent for every single run, suggesting that conditions had changed from run to run. Overall, the use of on-line $\delta^{13}C$ corrections has improved the quality of our measurements on small and ultra-small samples, but the issue of machine-induced isotopic fractionation is complex, and only a long term evaluation can definitively clarify this issue.

As discussed in Section 2.2, we obtained comparable results from ultra-small aliquots of standards and blanks that were combusted individually and those split from relatively large CO_2 aliquots, indicating that our combustion blank is small. This use of CO_2 splits significantly reduces the difficulty of characterizing graphitization blanks and machine fractionation, as in the present experiments. However for samples which must be chemically pre-treated before combustion, the use of true procedural blanks with sizes similar to the unknowns is essential. This requirement significantly increases the uncertainties associated with the results obtained from such samples [15].

This study has shown that small quantities of CO_2 can be converted reliably into high-quality graphite targets. For samples ranging from 0.05 to 1 mgC, graphite reduction is carried out over iron powder catalyst (Alfa-Aesar −325 mesh) at 550 °C into our regular reactors (volume of ~3.1 cm^3). For samples <0.05 mgC the optimal temperature is reduced to 450 °C, and for samples <0.02 mgC we also use the small reactors (volume of ~1.6 cm^3) to avoid any decrease in reaction yield and to minimize fractionation. AMS ^{14}C analysis of samples containing as little as 0.01 mgC has become routine in our laboratory, accuracy and precision sometimes approaching ±10‰ for 0.01 mgC samples. Depending on sample sizes and number of unknown samples to be measured either the size matching or non-size matching methods can be used. Ultra-small samples from 0.002 to 0.01 mgC can be measured with accuracy and precision of a few percent.

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Appendix A

Assume that samples to be measured by AMS ^{14}C are contaminated with a constant mass (m) of modern carbon with isotope ratio R_s equal to that of primary OX-I standard and mass (d) of ^{14}C-free or dead carbon.

The measured isotope ratio $R(M)$ for a sample of mass M and isotope ratio R can be expressed as

$$R(M) = (M \cdot R + m \cdot R_s)/(M + m + d). \tag{A.1}$$

The measured ratio for a blank (^{14}C-free sample) of mass M is

$$B(M) = (m \cdot R_s)/(M + m + d), \tag{A.2}$$

And the measured ratio for a standard of mass M (i.e. the same size as the unknowns) is

$$R_s(M) = (M \cdot R_s + m \cdot R_s)/(M + m + d). \tag{A.3}$$

Them from (A.1)–(A.3),

$$R(M) - B(M) = (M \cdot R)/(M + m + d), \text{and} \tag{A.4}$$

$$R_s(M) - B(M) = (M \cdot R_s)/(M + m + d), \tag{A.5}$$

Dividing (A.4) by (A.5) then gives

$$R/R_s = [R(M) - B(M)]/[[R_s(M) - B(M)]. \tag{A.6}$$

To correct for the extraneous carbon incorporated in the sample, we defined a modern carbon correction as

$$\mathrm{MCC}(M) = B(M)/R_s, \tag{A.7}$$

i.e. the measured isotope ratio of a blank of mass M as a fraction of the ratio for a large standard ($M_s \gg m, d$). Similarly, we defined a dead carbon correction of

$$\mathrm{DCC}(M) = [1 - R_s(M)]/R_s \tag{A.8}$$

i.e. the fractional deviation of the isotopic ratio for a standard of mass M from that of a large standard where $M_s \gg m, d$.

Then from (A.6)–(A.8), we obtained:

$$R/R_s = \{[R(M)/R_s] - \mathrm{MCC}(M)\} \\ /[1 - \mathrm{DCC}(M) - \mathrm{MCC}(M)], or \tag{A.9}$$

$$F\prime = [F - \mathrm{MCC}(M)]/[1 - \mathrm{DCC}(M) - \mathrm{MCC}(M)], \tag{5}$$

where F and $F'$are the uncorrected and corrected isotopic ratios of the unknown sample, expressed as fractions of the corresponding ratios for large standards.

From (A.2) and (A.7), we derived the MCC correction (Eq. (1) – Section 2.8) as:

$$\mathrm{MCC}(M) = m/(M + m + d) \approx m/M, \text{and} \tag{A.10}$$

From (A.3) and (A.8), we derived the DCC correction (Eq. (2) – Section 2.8) as:

$$\mathrm{DCC}(M) = d/(M + m + d) \approx d/M \tag{A.11}$$

For typical values $m \sim 0.5$ μg, $d \sim 0.2$ μg, these approximations are correct to within 30% down to sample masses $M = 2$ μg, within the scatter of the results for small standards and blanks in this size range.

When the standards used for normalization are relatively small (<0.025mgC – Section 2.6), they too are significantly affected by the dead carbon contamination. In this case, we have to re-write from (A.8):

$R_s(M_s) = R_s$ [1-DCC(M_s)], where $R_s(M_s)$ is the measured isotopic ratio for a normalizing of mass M_s. Therefore,

$$R_s = R_s(M_s)/[1 - \mathrm{DCC}(M_s)]. \tag{A.12}$$

Substituting this expression into the right hand side of Eq. (A.9) and eliminating quadratic terms in the small quantities DCC(M), DCC(M_s) and MCC(M) gives:

$$\begin{aligned} R/R_s &= \{[R(M)/R_s(M_s)] - \mathrm{MCC}(M)\} \\ &\quad /[1 + \mathrm{DCC}(M_s) - \mathrm{DCC}(M) - \mathrm{MCC}(M)], \textit{or} \\ F' &= [F - \mathrm{MCC}(M)]/[1 - \mathrm{DCC}(M_s) \\ &\quad - \mathrm{DCC}(M) - \mathrm{MCC}(M)], \end{aligned} \tag{A.13}$$

where the F is the measured isotopic ratio for the unknown sample expressed as a fraction of the (possibly small) normalizing standard.

The Eq. (A.13) contains two opposing dead carbon corrections, one for the unknown sample and other for the normalizing standards. This allows the use of any sample size for the normalizing standard set: when the mass of the normalizing OX-I standards is small the DCC(M_s) term compensates the effect of d on the standards themselves. When 1mgC OX-I standards are used the term can be disregarded. When exact size matching is used DCC(M_s) and DCC(M) terms cancel.

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