Microscale AMS 14C Measurement at NOSAMS

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ABSTRACT

Techniques for making precise and accurate radiocarbon accelerator mass spectrometry (AMS) measurements on samples containing less than a few hundred micrograms of carbon are being developed at the NOSAMS facility. A detailed examination of all aspects of the sample preparation and data analysis process shows encouraging results. Small quantities of CO_2 are reduced to graphite over cobalt catalyst at an optimal temperature of 605°C. Measured $^{14}C/^{12}C$ ratios of the resulting targets are affected by machine-induced isotopic fractionation, which appears directly related to the decrease in ion current generated by the smaller sample sizes. It is possible to compensate effectively for this fractionation by measuring samples relative to small standards of identical size. Examination of the various potential sources of background ^{14}C contamination indicates the sample combustion process is the largest contributor, adding *ca.* 1 μg of carbon with a less-than-modern radiocarbon concentration.

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Although sample size problems can potentially be resolved by adding sufficient diluent carbon of known isotopic composition, an analysis of the uncertainties associated with this approach suggests it may not yield results at a useful level of precision. The mass balance equations

$$(1) \qquad m_x F_x = m_s F_s + m_d F_d$$

and

$$(2) \qquad m_x = m_s + m_d$$

(where m designates mass, F the ^{14}C fractional abundance, and x, s, and d are the composite, the sample, and the diluent) can be rewritten as

$$(3) \qquad F_s = r_x F_x - (r_x-1)F_d$$

where $r_x{}^o m_x/m_s$ is the dilution factor. Propagation of error then results in the following equation, where s is the standard deviation and measurement precision $P{}^o s_m/m$:

$$(4) \qquad s^2_{Fs} = r^2_x s^2_{Fx} + (1-r_x)^2 s^2_{Fd} + (F_x-F_d)^2 (2P^2) r^2_x$$

$$\qquad\qquad\qquad \mathbf{a} \qquad\qquad \mathbf{b} \qquad\qquad\qquad \mathbf{c}$$

Term **a** dominates the result; the other two terms can be manipulated toward zero by 1) the use of a [14]C-"dead" diluent (s_{Fd} approaches zero in **b**), 2) choosing a diluent of isotopic composition identical to the sample (F_x-F_d goes to zero in **c**), and/or 3) optimizing measurement precision, P, in **c**. Choosing optimal realistic values of $P=0.01$, $F_s-F_d=0.5$, $s_{Fd}=0.004$, $s_{Fx}=0.005$ at 500 µgC, and $s_{Fx}=0.010$ at 100 µgC, Figure 1A shows the calculated error in the ^{14}C content of the original sample, s_{Fs}, is inversely related to sample size, rendering dilution least practical in the size range where it would be most useful.

Detailed examination of equation (4) clarifies the potential as well as limitations of dilution. While term **c** is always small due to the P^2 multiple, and term **b** can be kept artificially small, it is evident that in a precise formulation of this equation, s^2_{Fx} in term **a** is a function of the size of the composite. This creates a potential situation in which the increased uncertainty due to the dilution factor is partially offset by the better precision obtainable when measuring the larger sample. Figure 1B highlights s_{Fs} for a representative 10 µgC sample diluted over a range of r_x, where the size dependence of s_{Fx} has been approximated as $s_{Fx}=0.06e^{-0.018Mx}$ and the other variables of equation (4) are given the same values as in Figure 1A. The improved measurement precision at larger sample size makes dilution by a factor of 10 just as precise as 5-fold dilution, but uncertainties *ca.* 100‰ remain impractical for most applications. Dilution may still be the option of choice, however, for extremely small, irreplaceable samples for which the risks involved with uncertain graphitization and AMS performance are too great.

RESULTS AND DISCUSSION

Between September 1994 and September 1996 we analyzed a total of five small sample wheels at NOSAMS, one of which was composed almost entirely of standards containing [150 µgC, for the purpose of evaluating AMS performance in the analysis of microgram-sized targets. The rest of the wheels each contained 10-20 specially prepared small HOxI and HOxII standards spanning the range of sample sizes being analyzed, in place of the usual 1 mg standards. We therefore have raw data for a total of 51 small HOxI and 32 small HOxII standards with which to assess AMS performance within this size range.

Optimization of Graphite Production Reaction

There are many variables that could potentially control the outcome of the $CO_2 \rightarrow C(gr)$ reduction; our goal was to identify and optimize reaction conditions for the most critical of these factors. The percent conversion of CO_2 to graphite was used as a direct index of reaction performance. Preliminary examination of the reaction yield data showed that production of high-quality small samples is highly sensitive to minor variations in reaction conditions, but the scatter exhibited in the results and the large number of variables precluded the use of standard regression analysis methods.
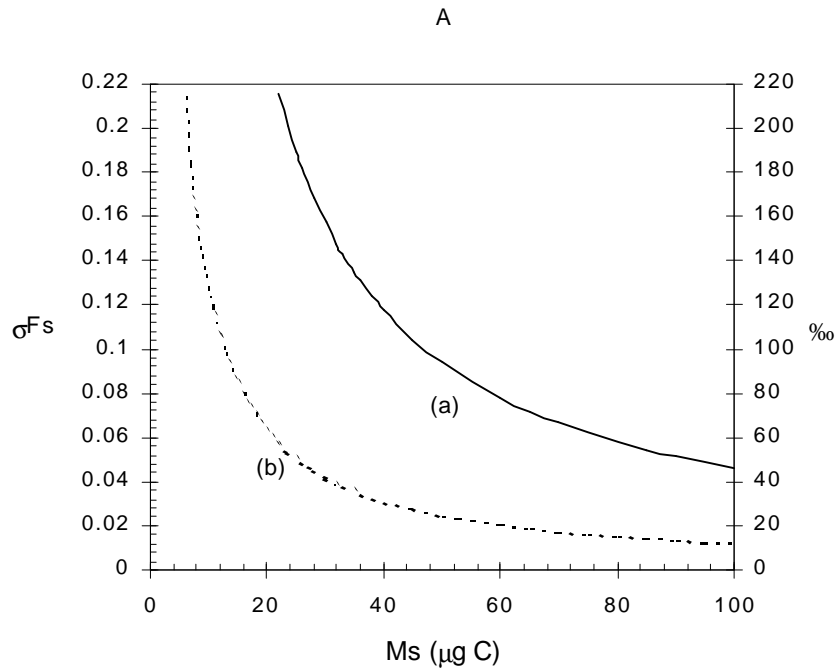
A

Fig. 1. A. Calculated error s_{Fs} for dilution to a conventional sample size of 500 μgC (a) and for dilution to 100 μgC only (b). B. Calculated error s_{Fs} for dilution of a 10μgC sample up to $r_x=10$ using a variable $s_{Fx}=0.06e^{-0.018Mx}$. Increased precision in s_{Fx} partially offsets the dilution error.
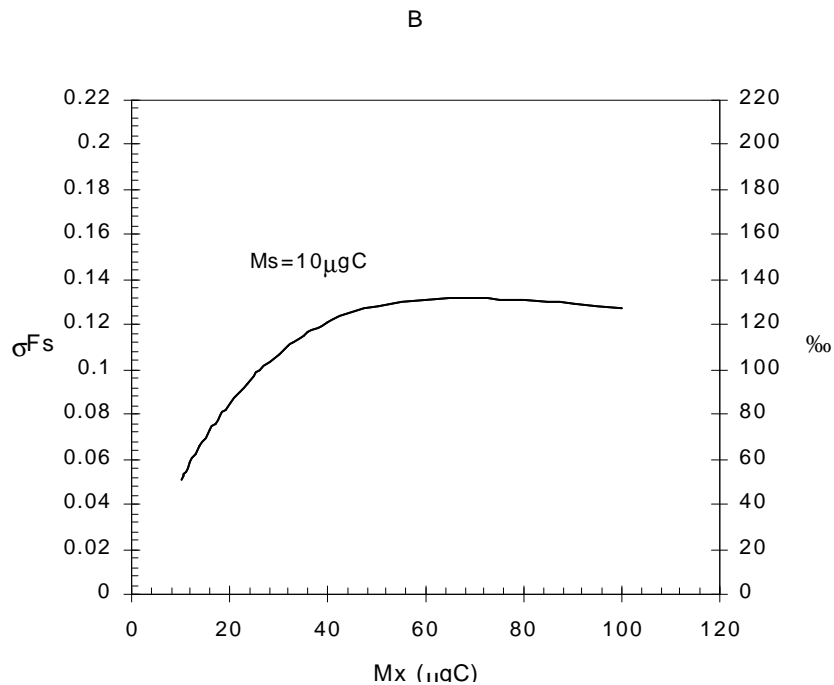
B

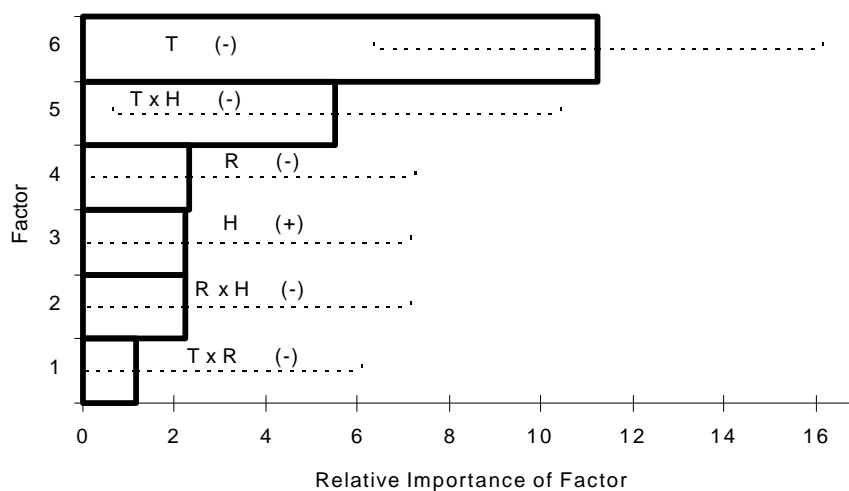| Variable	Median	(-)	(+)
Temperature (T)	608°C	[606	μ 610°C
Carbon:Cobalt (R)	59.2 μgC/mg Co	[58.8	μ 59.6
H_2:CO_2 (H)	3.20 (mol:mol)	[3.16	μ 3.24
Quantity (Q)	40 μg C	[39.6	μ 40.4

A

B

Fig. 2. A. 2^3 factorial analysis of T, R, and H effects on reaction yield. B. 2^4 factorial analysis of T, R, H, and Q effects on reaction yield. A (+) indicates the upper range of the factor improves % yield, while a (-) indicates the lower range improves % yield. The variables are described in the text.
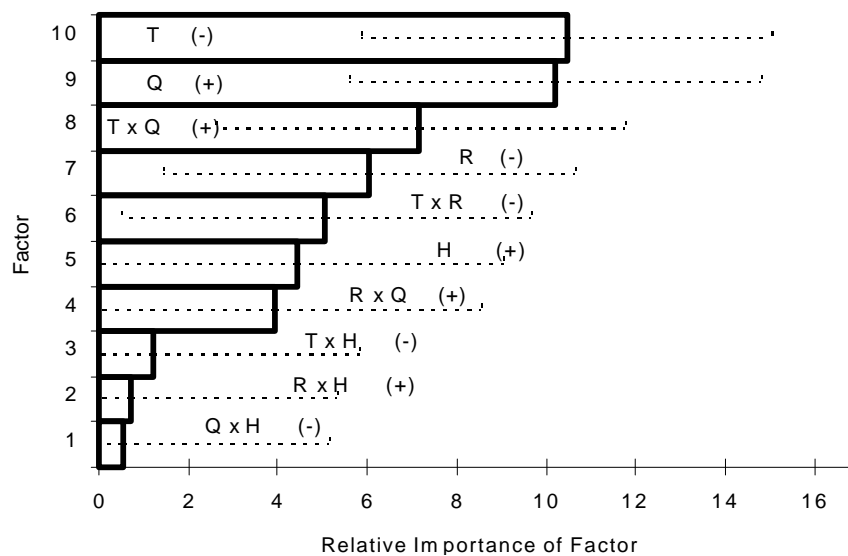
Verkouteren and Klouda (*1992*) have previously demonstrated the utility of bi-level factorial design analysis in unraveling the complexities associated with graphite preparation. A preliminary inspection of our data suggested which variables were likely to be the most significant controls on the graphite reaction. A two-level, 2^3 factorial design was applied to determine the relative dependence of reaction yield on temperature (T), carbon:cobalt ratio (R), and $H_2:CO_2$ ratio (H). The assumption had been made that a fourth variable, the sample quantity (Q), has a positive correlation with reaction success - large samples are easier to reduce. To test this assumption, the effect of size on reaction yield was added, creating a 2^4 factorial.

The 2^3 matrix [T x R x H] and the 2^4 matrix [T x R x Q x H] were calculated using a table of contrast coefficients (equivalent to Yates' algorithm) (Box, Hunter, and Hunter *1978*). Data from our first batches of small HOxI and HOxII standards were divided into two levels, (-) and (+), around the median of the range of each variable (Table 1); data whose analytical error crossed the median were eliminated. The 46 acceptable samples were distributed fairly uniformly among the 8 categories of the 2^3 matrix (*min*{n_i}=3). The result of the 2^4 matrix is less robust due to a lack of replicate data points for many of the 16 run categories. In both cases error bars are calculated from a pooled estimate of run variance. Results of the factorial analyses (Fig. 2) confirmed qualitative trends that had been observed in the data: reaction yield improves at lower temperatures and larger samples favor better yields. Cobalt-catalyzed reduction appears to be more successful at temperatures below 608°C, lower than the 625°C normally employed when using dendritic Fe. Since this discovery, we have adopted 605°C as our reaction temperature when preparing small samples on cobalt. Yields are routinely > 90% under these conditions. We have no direct evidence of the mechanistic effect the low temperature has on the system, but one possibility includes partial inactivation of the catalyst surface at higher temperatures. Variation in H is not significant over the small range of values studied, and the slight negative dependence on R is probably unimportant as well.

AMS Performance of Small Samples

Since we are interested in determining AMS performance under conditions of reduced carbon ion beam intensity, all the isotope ratio data reported here have been compared to measured ^{12}C ion current (I_{12}) rather than sample size. The I_{12} beam is measured in a Faraday cup after the 110° spectrometer magnet, after being chopped by a factor of *ca.* 95. The currents shown are electrical currents of the $^{12}C^{3+}$ ions; particle currents would be 1/3 of these values. Figure 3 shows that I_{12} is a reasonable proxy for sample size, and we believe that the precision of the measured isotope ratios is likely to be related more directly to I_{12} than to the overall sample size. Both I_{12} and measured isotope ratios are also found to be time-variant within the accelerator as discussed below, a further indication that bulk sample size is not as informative a performance index as is the measured I_{12}.

Figure 4 shows the dependence on current of the $^{14}C/^{12}C$ ratios obtained for small standards. Individual time-point measurements obtained for each target are compared to the average isotope ratios of HOxI and HOxII standards of regular (1 mg) size that were included in the small-sample wheels. These data represent an average of 4 min per point (roughly 10^3 counts), with 3-6 points recorded per standard. Three samples that failed to generate any stable, measurable current have been excluded. These contained < 10 µgC, and are defined as "AMS failures". Both HOxI and HOxII small standards show a characteristic decrease in $^{14}C/^{12}C$ below 100 µgC; a relationship that has been observed previously by Klinedinst *et al.* (*1994*), Brown and Southon (*1997*), and other groups.
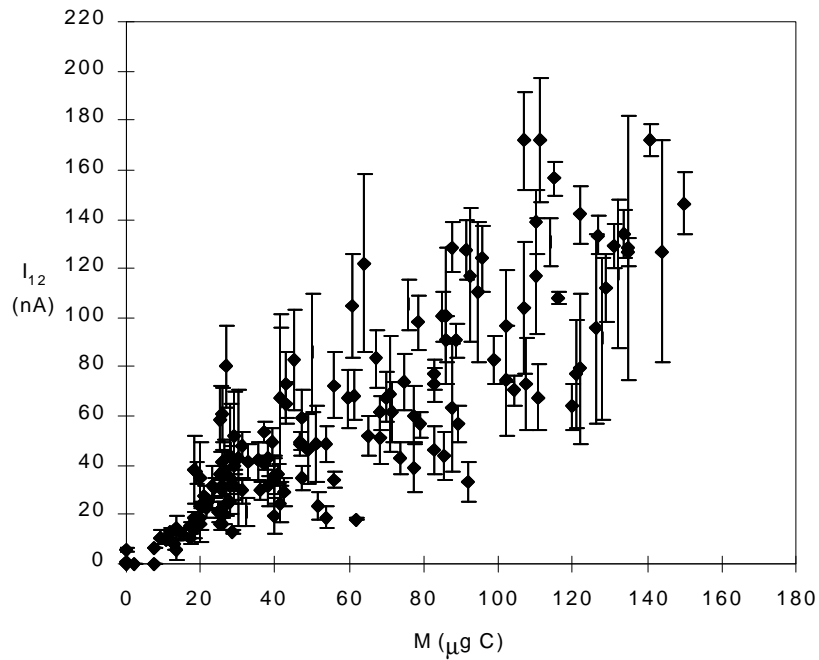
Fig. 3. Observations showing that the ^{12}C current measured for small samples varies with size, according to the approximate relationship $I_{12}=0.9M$. M=mass of carbon in micrograms; $I_{12} = {}^{12}$C current in nanoamperes.

Concurrent AMS measurement of the ^{13}C/^{12}C ratio for small standards also shows apparent fractionation at lower sample currents, although the relationship is somewhat less pronounced for ^{13}C than for ^{14}C. It is possible that instrument tuning affects ^{13}C detection differently than it affects ^{14}C, and therefore generates a slightly less uniform relationship between ^{13}C and I_{12}. Figure 5A shows the difference between the AMS measured δ^{13}C for small HOxI and HOxII standards and the pre-graphite δ^{13}C values of the CO_2 from which they were prepared (measured on a VG Prism stable isotope mass spectrometer). The difference is expressed as $\Delta\delta^{13}C = \delta^{13}C_{AMS}- \delta^{13}C_{VG}$. The VG Prism δ^{13}C values for HOxI are -19.0 to -19.3‰ and for HOxII are -17.6 to -17.7‰.

Fig. 4. Dependence of the measured ^{14}C/^{12}C isotope ratios for HOxI (A) and HOxII (B) small
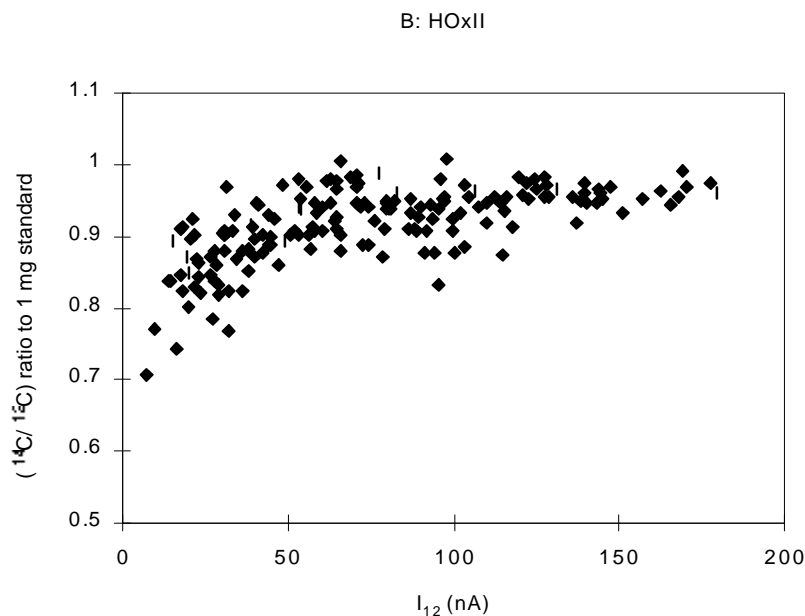
B: HOxII

samples on the generated ^{12}C ion current. Ratios have been normalized to average values obtained for HOxI and HOxII standards of conventional size.
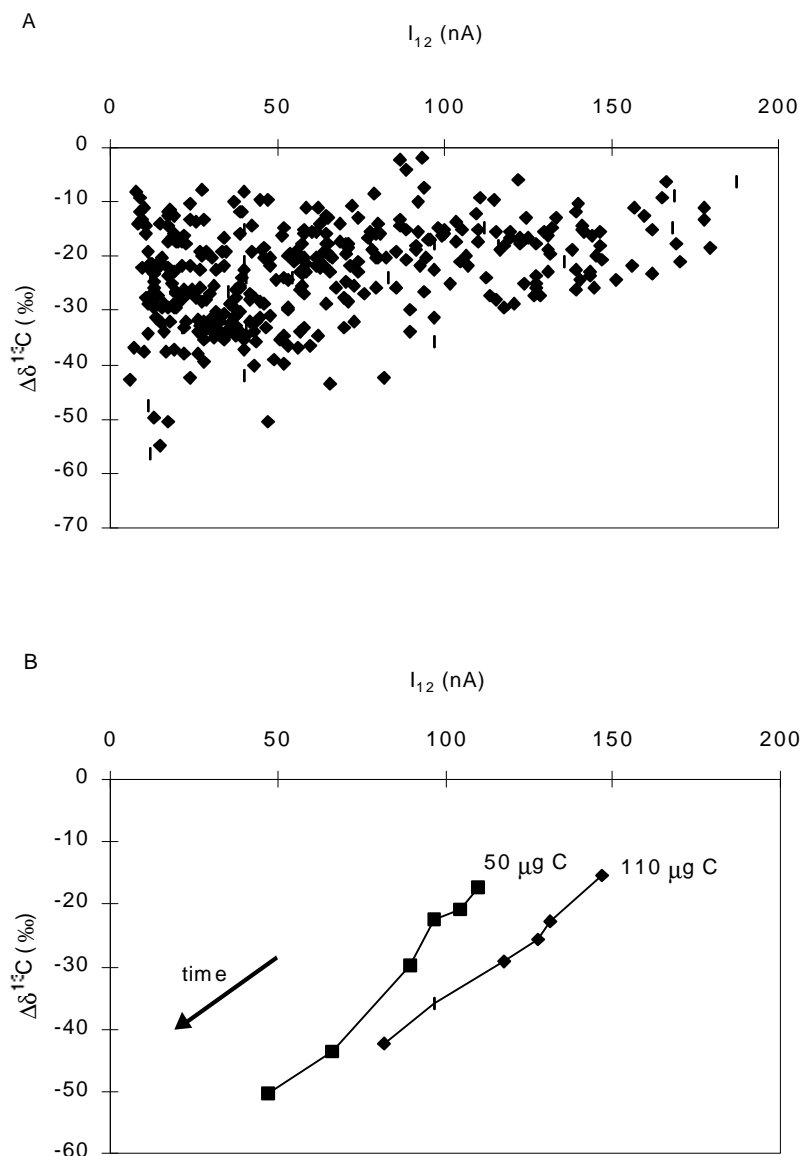
A

I_{12} (nA)

B

I_{12} (nA)

Fig. 5. A. ^{13}C fractionation of HOxI and HOxII small samples as a function of the generated ^{12}C ion current for all discrete time points. B. $\Delta\delta^{13}C$ and I_{12} variation within samples as a function of elapsed measurement time.

There are several potential reasons for the observed isotope ratio dependence on sample size. Explanations that invoke fractionation or contamination during the graphite production step are among the more popular candidates. Van der Borg *et al.* (*1997*) showed that fractionation can occur during the graphitization process: reactions that failed to reach completion produced graphite that was depleted in ^{14}C and ^{13}C, and left residual CO_2 that was isotopically enriched. However, examination of our yield data indicates there is no apparent correlation between percent conversion of CO_2 to graphite and the isotope ratios subsequently measured during

AMS analysis. This argues against a fractionation effect induced during any phase of the sample preparation. Similar results have also been obtained by McNichol *et al.* (*1992*).

Another possible explanation for the decrease in isotope ratios is the addition of a background carbon contaminant during graphite production or during analysis of the AMS targets. Data published by Brown and Southon (*1997*) for a very similarly behaving suite of small standards indicate that our source of contamination, if any, may be independent of sample size. They suggest carbon contained within the catalyst matrix or residual carbon in the AMS ion source. At NOSAMS, [14]C-"dead" graphite measured immediately following modern samples fails to show significant sample cross-talk or other problems inherent to the source. We believe it is also unlikely that the isotope ratios are being altered by the presence of large amounts of background carbon within the Co catalyst. This is based on observation of instances when isotope ratios and ^{12}C currents co-vary within individual samples (Fig. 5B). If background carbon were incorporated within the sample during processing or were contained in the Co matrix, a time-series plot would be expected to show a constant or randomly varying isotope ratio over the course of analysis, not the systematic decrease in isotope ratio we have observed for these and many additional samples. The $\Delta\delta^{13}$C and I_{12} changes in Figure 5B appear to be a function of elapsed measurement time. These data suggest that the effective fractionation we have observed is primarily a function of machine conditions, not the result of isotopically light carbon incorporated uniformly within the sample during preparation.

Support for this hypothesis comes from consideration of the differing beam dynamics at high and low current levels. Instrument tuning is always carried out using 1-mg standards. The current beams generated by these large targets have a correspondingly higher beam divergence than do beams generated by small samples, due to increased Coulomb repulsion in the presence of higher space charge density. The instrument is tuned to compensate for the fractionation induced within the large sample. Because Coulomb repulsion affects lighter isotopes more strongly, it is possible that ^{12}C detection is less efficient relative to ^{14}C detection for large samples, but that the detection difference may be less pronounced for low-density small samples. The net effect would be an apparently lower ^{14}C/^{12}C ratio for small samples. While this argument is qualitative, it provides a physically plausible mechanism for the observed effects. Details of the beam dynamics model can be found in von Reden *et al.* (*1998*).

At NOSAMS, we have found different explanations for the sources of background contamination and fractionation than have previously been identified by some of the AMS groups mentioned in the above discussion. This points to the need for individual AMS facilities to conduct independent and thorough evaluations of their analytical procedure, because it is likely that the results will display characteristics unique to each facility.

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CONCLUSIONS

At NOSAMS, preparation and AMS analysis of samples containing 10-150 μgC has exhibited an encouraging level of success. These results have promising implications for several oceanographic and environmental research areas, including the pore water carbon cycle, oceanic dissolved organic carbon studies, and molecular-level ^{14}C analysis. All are areas in which available sample size has been the main limitation on the use of ^{14}C AMS.

1. Small quantities of CO_2 can be converted reliably into high-quality graphite for AMS. Reduction is carried out over cobalt catalyst at 605°C in small-volume reactors. The reaction appears especially sensitive to temperature, showing a decrease in reaction yield at high temperature.
2. AMS targets containing [150 μgC are prone to machine-induced isotopic fractionation, which appears directly related to the lower levels of carbon ion

current generated by these samples. This may be caused by inherent limitations in the instrument design and tuning capabilities of the NOSAMS accelerator.

3. Carbon contamination within the NOSAMS source does not appear to be significant enough to affect the outcome of small target analyses; neither does addition of modern-equivalent carbon during the graphitization process. Time-variant data for HOxI and HOxII targets is evidence against the addition of a large amount of "dead" carbon during graphitization, although amounts equivalent to less than the machine fractionation effect may be present. Carbon added during the combustion of small organic samples is still under investigation, but preliminary work indicates this blank is *ca.* 1 μg and has significantly less than modern ^{14}C concentration.

4. It is possible to compensate effectively for machine fractionation and blank carbon contributions by measuring small samples relative to size-matched small standards. There are two possible options for preparation of the small standards: reduction of small splits of a large, homogeneous gas standard, or combustion and subsequent reduction of individual small aliquots of the original standards. When analyzing small, combusted organic samples relative to small HOxI and HOxII standards, choosing the first option requires a subsequent blank correction to the sample f_m, while the second option would eliminate this correction. Because it is more difficult and less time-efficient to prepare individually combusted standards of precise mass, we continue to perform our routine analyses with small splits of a large standard and then apply a separate combustion blank correction. Small HOxI and HOxII standards measured relative to each other using this approach no longer show a size-dependent isotopic fractionation.