MICROSCALE AMS ^{14}C 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 that the sample combustion process is the largest contributor, adding *ca.* 1 µg of carbon with a less-than-modern ^{14}C concentration.

INTRODUCTION

The development of techniques for ^{14}C analysis by AMS has greatly reduced carbon sample size requirements compared to what is needed for beta counting. The 0.5–1.0 mg of carbon now used to make routine ^{14}C measurements has allowed many fields to take advantage of the opportunities provided by AMS, but there are still some classes of oceanographic and environmental samples that cannot meet this carbon requirement. At the National Ocean Sciences Accelerator Mass Spectrometry (NOSAMS) facility we are seeking a reliable protocol for the analysis of samples that supply less than a few hundred micrograms of carbon (µgC); this paper describes in detail our approach to analyzing samples containing no more than 150 µgC.

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

$$m_x F_x = m_s F_s + m_d F_d \tag{1}$$

and

$$m_x = m_s + m_d \ , \tag{2}$$

(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

$$F_s = r_x F_x - (r_x - 1) F_d \ , \tag{3}$$

where $r_x \equiv m_x/m_s$ is the dilution factor. Propagation of error then results in the following equation, where σ is the standard deviation and measurement precision $P \equiv \sigma_m/m$:

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

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

Term **a** dominates the result; the other two terms can be manipulated toward zero by 1) the use of a ^{14}C-"dead" diluent (σ_{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 $P = 0.01$, $F_s - F_d = 0.5$, $\sigma_{Fd} = 0.004$, $\sigma_{Fx} = 0.005$ at 500 µgC, and $\sigma_{Fx} = 0.010$ at 100 µgC, Figure 1A shows that the calculated error in the ^{14}C content of the original sample, σ_{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. Whereas 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, σ^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 σ_{Fs} for a representative 10 µgC sample diluted over a range of r_x, where the size dependence of σ_{Fx} has been approximated as $\sigma_{Fx} = 0.06e^{-0.018Mx}$ 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.

At NOSAMS, we have been working to achieve precise, accurate analysis of small carbon samples without requiring the addition of a diluent. Here we report our method for preparing graphite targets containing microgram quantities of carbon along with the results of AMS analyses of standard materials (HOxI, HOxII, Johnson Matthey Electronics (JME) graphite powder, and IAEA C-1 Carrara marble carbonate) having known-fraction modern carbon (f_m), and we discuss the complex issue of evaluating background carbon contamination during sample preparation and analysis.

METHODS

HOxI and HOxII Standards

At NOSAMS, large batches of CO_2 are prepared from NIST Oxalic Acid I (HOxI, $f_m \equiv 1/0.95$) and Oxalic Acid II (HOxII, $f_{mHOxII}/f_{mHOxI} = 1.2933 \pm 0.0004$) standard reference materials (SRM 4990B and SRM 4990C: Currie and Polach 1980; Stuiver 1983) once every two or three years. These standard gases have a minimal associated processing blank due to large batch preparation, and are used for routine preparation of AMS standards. Subsamples of the 1992 and 1995 batches of these gases were used to prepare all the HOxI and HOxII small graphite targets discussed in this paper.

Hydrolysis of Carbonates

Six aliquots of CO_2 were prepared from a single chip of IAEA C-1 carbonate ($f_m = 0.0000 \pm 0.0002$ (Rozanski *et al.* 1992)) to use in evaluation of background carbon added during the graphitization and target preparation procedures. The CO_2 was prepared by H_3PO_4 hydrolysis of a single HCl-etched C-1 chip and six subsamples were taken of between 1.7 and 4.0 µmol carbon. Because our interest was in determining the amount of background carbon added during graphitization and target preparation, a large amount of carbonate was hydrolyzed (>1 mg) relative to the subsamples of gas taken for analysis. In this way the contribution of the hydrolysis processing blank was minimized and the CO_2 generated is the "dead" analogue to our "modern" HOxI and HOxII bulk standard reference gases.
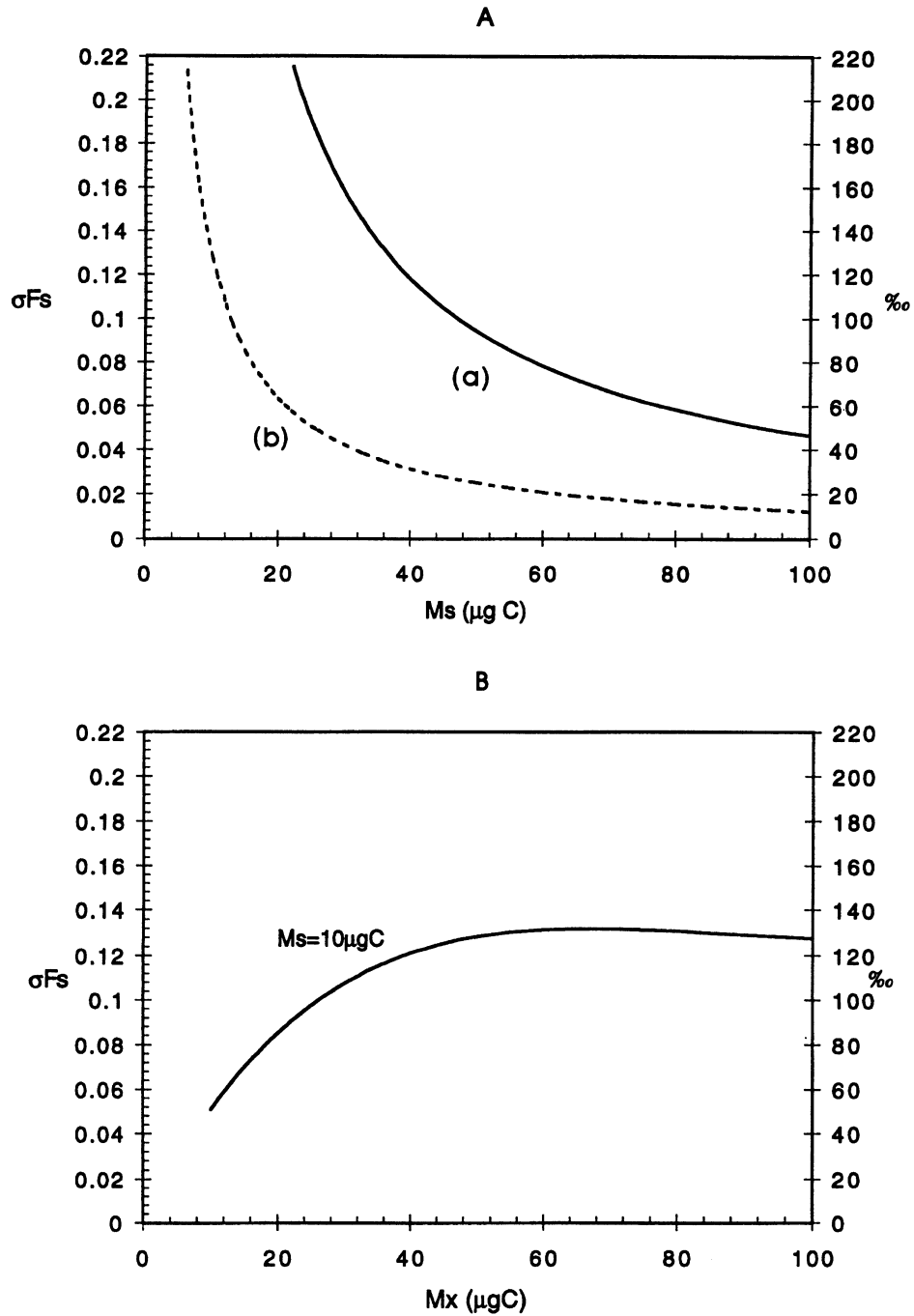
A

B

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

Combustion Blanks: JME and HOxI Powders

To determine the contribution of blank carbon added to organic samples that must be combusted to obtain CO_2, two small aliquots of HOxI powder and five of JME pure graphite (median f_m = 0.0002, >68 kY) were converted to CO_2 by standard methods. The CO_2 obtained was reduced to graphite and its f_m was compared to the standards' original values. In addition, numerous empty tube combustion blanks were prepared in an attempt to measure directly the organic carbon combustion blank size and f_m.

For combustion, 9-mm diameter Vycor® combustion tubes containing 2 g CuO and 100 mg Ag crystals were pre-baked at 850°C for 5 h. The tubes were loaded with weighed HOxI or JME powder, or left empty in the case of blanks. The tubes were evacuated, flame-sealed, and converted to CO_2 by a second, identical combustion step. The CO_2 obtained from the HOxI and JME samples was purified by passing through an isopropanol/dry ice water trap and was converted to graphite according to the methods described below.

CO_2 from the "empty" blank tubes was quantified for each tube using a variety of methods. The majority were cracked open and their CO_2 purified and quantified on a special micro-manometer vacuum system. Using this approach, enough gas was obtained to prepare two "pooled blank" graphite targets, one containing *ca.* 25 µgC and the other containing *ca.* 20 µgC. The carbon in six additional samples was quantified on a HP 5890 Series GC system equipped with a flame ionization detector (FID). The CO_2 from these samples was released into the GC after being trapped on a Porapak® column under pure O_2. Helium was the GC carrier gas, and carbon was detected as CH_4 by the FID. Finally, the contents of eight more combustion blanks were analyzed on a Dycor Residual Gas Analyzer (RGA).

Graphite Preparation

We have adapted the standard reduction procedure as described by Vogel, Southon and Nelson (1987) for the preparation of graphite samples containing microgram quantities of carbon.

CO_2 samples are introduced into small-volume graphite reactors that have geometries similar to the NOSAMS automated systems, but that have been scaled down to accommodate 6-mm diameter tubing. Graphite is formed in a horizontal 50-mm-long Vycor® tube, while a 75-mm vertical Pyrex® cold finger is kept at *ca.* –40°C. The average total reactor volume is *ca.* 3.5 mL. An excess of H_2 (2.5–3.5 H_2:CO_2) is added to the reactors, and the CO_2 is reduced to graphite on twice-cleaned (400°C for 0.5 h under 0.7 atm. H_2, twice), 325 mesh, spherical cobalt catalyst. Co, rather than dendritic Fe, was chosen because it provides a minimum catalyst surface area to volume ratio. This increases the physical size of the small samples by allowing a Co:C mass ratio of 20–100, the larger ratios corresponding to the smallest samples. Reaction temperature for reduction varied between 595 and 645°C, until 605°C was chosen as the optimal reaction temperature (see discussion below); individual temperature controllers regulate each reactor. Reactions are allowed to continue for a maximum of 6 h, and gas pressure is monitored throughout. Conversion to graphite is calculated as a percent yield based on the original and final gas pressures within the reactor.

The mixture of graphite and Co is pressed into aluminum AMS targets that have been drilled with 1.0-mm diameter holes. The holes are top-loaded with a compression pin, a layer of silver powder, and then the graphite mixture.

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.

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, we added the effect of size on reaction yield, creating a 2^4 factorial.

The 2^3 matrix [T × R × H] and the 2^4 matrix [T × R × Q × 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 sur-

TABLE 1. Factorial Analysis Parameters

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

face 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.
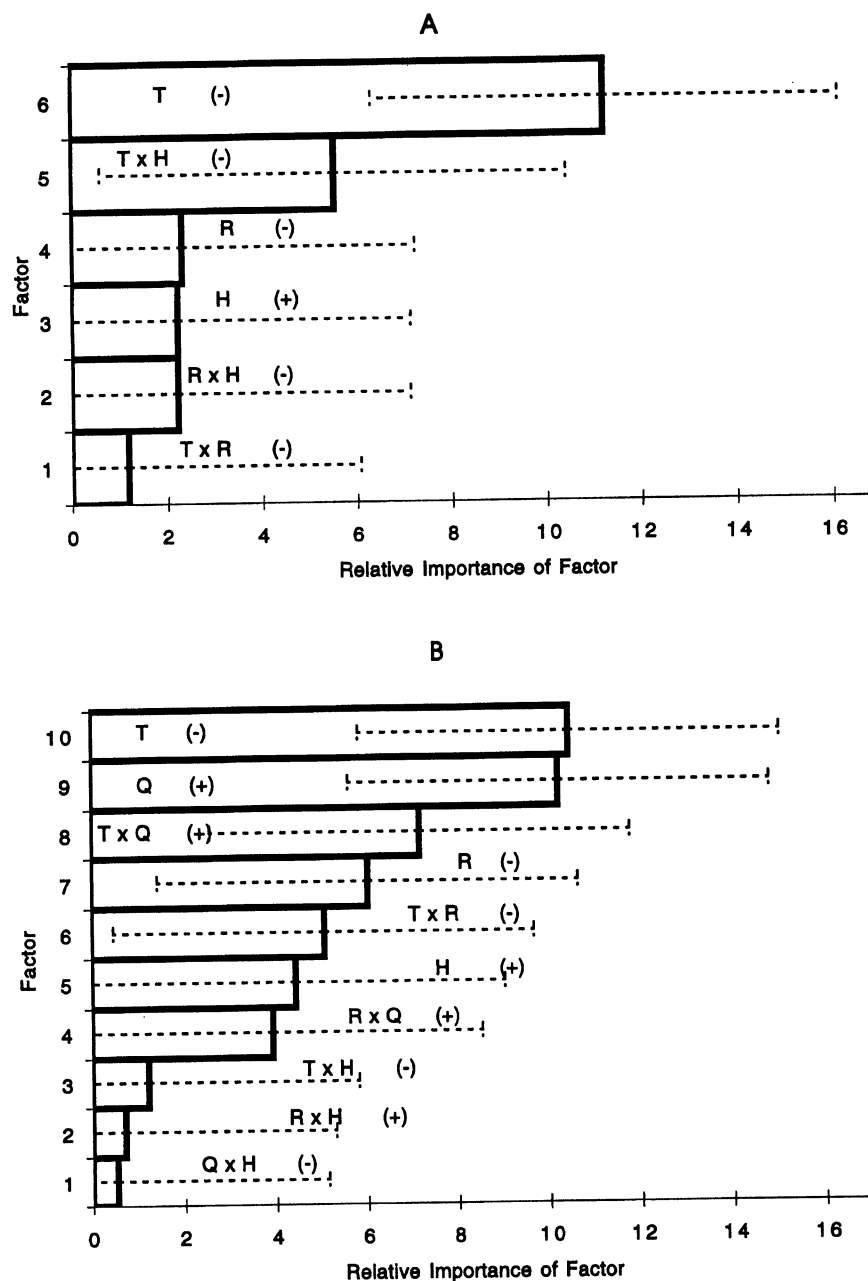
A

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 that the upper range of the factor improves % yield, while a (−) indicates that the lower range improves % yield. The variables are described in the text.

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}.
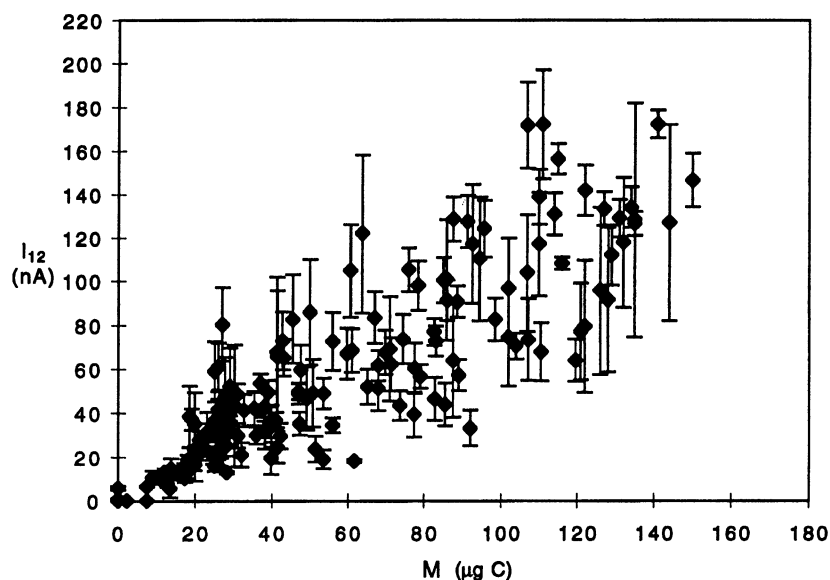

Fig. 3. Observations showing that the ^{12}C current measured for small samples varies with size, according to the approximate relationship $I_{12} = 0.9M$. M = mass of carbon in micrograms; I_{12} = ^{12}C current in nanoamperes.

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.

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 $\delta^{13}C$ for small HOxI and HOxII standards and the pre-

graphite $\delta^{13}C$ 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 $\delta^{13}C$ values for HOxI are −19.0 to −19.3‰ and for HOxII, −17.6 to −17.7‰.

A: HOxI

B: HOxII
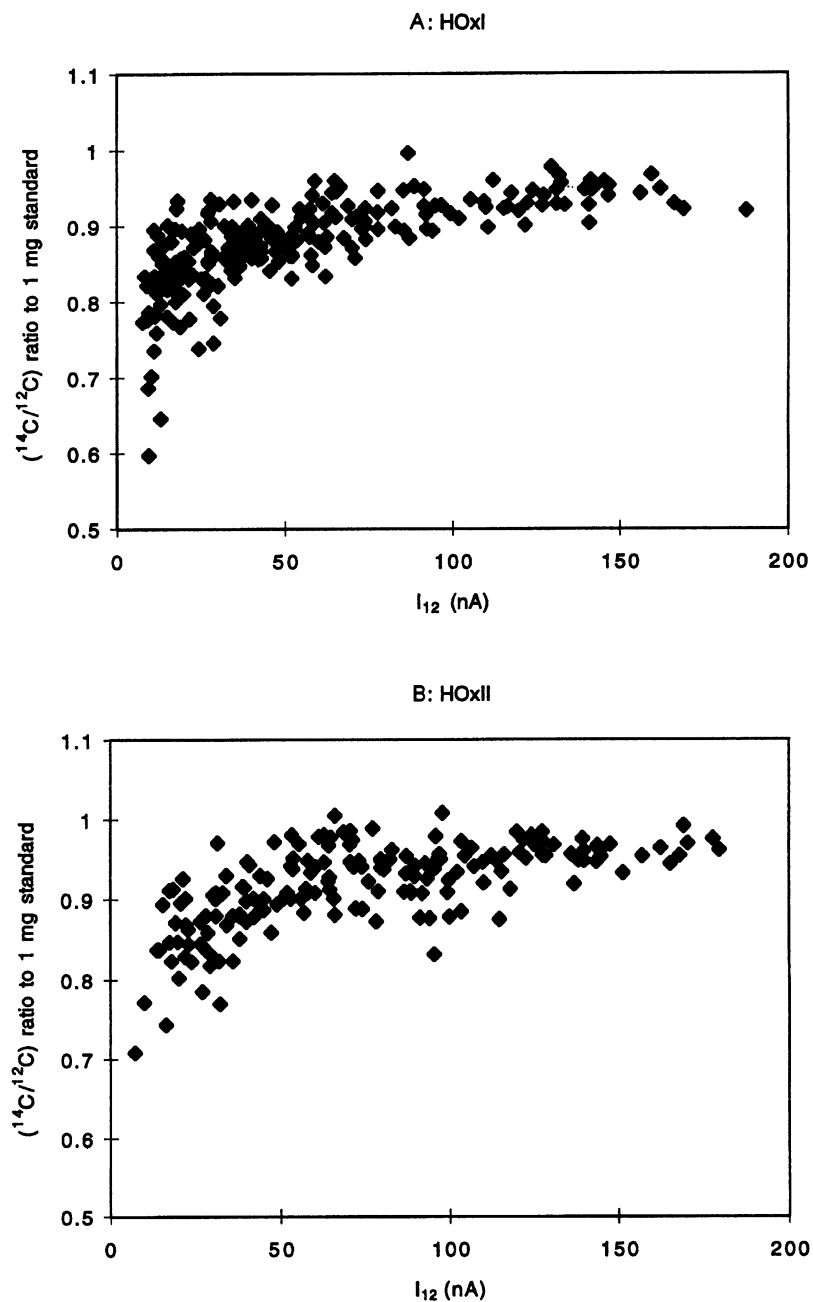

Fig. 4. Dependence of the measured $^{14}C/^{12}C$ isotope ratios for HOxI (a) and HOxII (b) small samples on the generated ^{12}C ion current. Ratios have been normalized to average values obtained for HOxI and HOxII standards of conventional size.
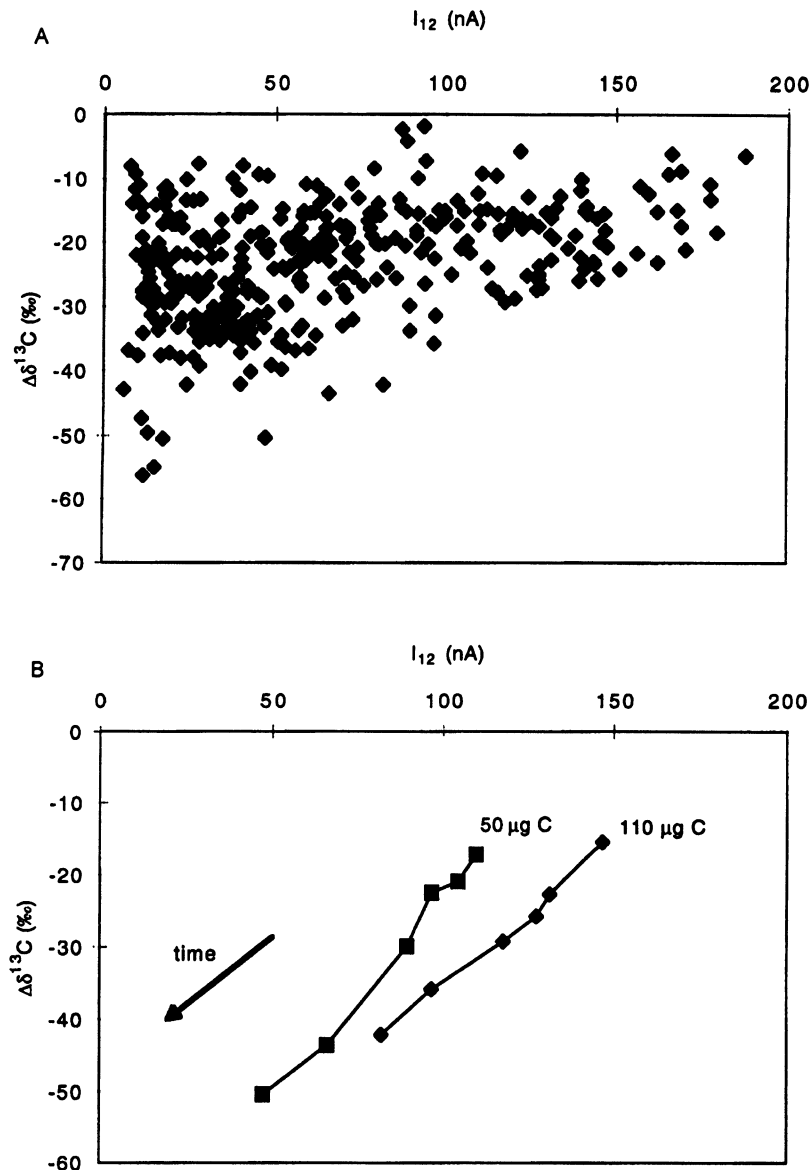
A

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 fraction-

ation 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 crosstalk 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.

Compensation for Machine-Induced Fractionation: Accuracy of HOxI and HOxII f_m Results

It is apparent from the preceding discussion that machine-induced fractionation effects are an important constraint on the accuracy of small-sample measurements. The significant correlations between I_{12}, ^{14}C/^{12}C and $\Delta\delta^{13}$C might allow a ^{14}C correction factor model based on I_{12} and/or $\Delta\delta^{13}$C. For example, ^{14}C/^{12}C could be corrected using the assumed exponential relationship to I_{12}, but the true relation is clearly more complex and remains unknown. Instead we have attempted to assess the level of precision and accuracy that can be achieved by matching samples with identically prepared, size-matched small standards to provide machine-based compensation for isotopic effects. The standards and adjacent samples are expected to behave similarly with regard to time-variant machine conditions and tuning. The f_m values calculated relative to these standards no longer show a size-dependent fractionation.

To confirm that this approach is effective, 28 HOxI and HOxII standards ranging from 2 to 71 µgC were analyzed in descending order of size on a single AMS wheel devoted to assessing small standard performance. Their $^{14}C/^{12}C$ ratios relative to 1-mg standards are part of Figure 4, where isotopic fractionation is apparent.

The data from the wheel were then reanalyzed by the NOSAMS automatic data analysis program (Seguin *et al.* 1994) by carefully rotating the 28 targets through 4 permutations of the classifications "sample" and "standard". Analysis #1 computed f_m values for 17 "samples" relative to 11 designated HOxI and HOxII "standards" chosen randomly throughout the wheel. Analysis #2 computed f_m values for "samples" relative to a different subset of randomly selected HOxI and HOxII "standards". Analysis #3 designated all 8 HOxII targets as "standards", while analysis #4 designated 8 similar HOxI targets as the "standards". This scheme was implemented to remove as much bias as possible from the analysis procedure, while generating at least two, and usually three, f_m values for each target. The NOSAMS data analysis program made this possible through built-in flexibility that allows any AMS target to be designated a "standard" if desired.

The f_m results from this approach were averaged for each sample (Fig. 6). The error bars shown are the standard deviations of the multiple results for each sample, unless this value is smaller than the Poisson error calculated based on the number of ^{14}C counts, in which case the Poisson error is shown. The HOxI targets yielded an average $f_m = 1.048 \pm 0.018$; the HOxII targets averaged $f_m = 1.363 \pm 0.018$. Neither set of standards, when analyzed in this way, shows any apparent size dependent fractionation effect. Based on this outcome, the NOSAMS facility has begun routinely analyzing microgram samples relative to size-matched small standards to minimize size-related fractionation effects.

The three samples that "failed AMS" as defined above are not included in Figure 6, as they gave no measurable ion current. At NOSAMS, very few conventional filamentous graphite targets contain-
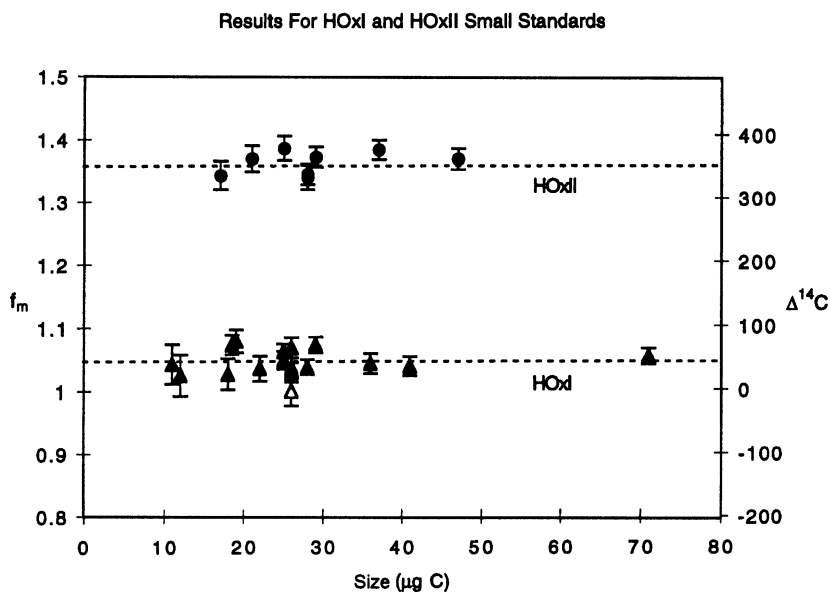

Fig. 6. Results obtained for HOxI and HOxII small standards when f_m values are calculated relative to adjacent small standards of similar size. Δ = sample for which Poisson error was used.

ing <10 μgC have generated a sustained ion current, and when current is produced the isotope measurements are greatly affected by the internal fractionation effects mentioned above. For this reason we try to maintain a minimum sample size of 15–20 μgC to increase the probability of a successful measurement.

Contribution of Background Carbon in the Analysis of Small Samples

To evaluate further the contributions of background carbon, and to increase our confidence that the machine effects discussed above were not due to carbon contamination, we performed several additional analyses.

Machine or Source Blank

Measurement of pure JME powder is routine at NOSAMS for assessing and correcting for machine background on every wheel that is run. The JME data on average indicate a machine background ^{14}C level of 0.0002 f_m. This value represents the total number of scattered particles such as ^{13}C^{2+}, ^{7}Li$_2$ dimers, and true ^{14}C^{3+} ions from internal contamination, all normalized to I_{12} output. A "memory" effect between samples has never been seen. ^{14}C "dead" standards measured between modern samples show no contamination, nor was any effect observed when samples containing five times modern ^{14}C concentration were inadvertently run on the machine.

Graphitization Blank

Background carbon added during graphite production can be ascertained by preparing small graphite samples from large batches of CO_2 (Vogel, Nelson and Southon 1987). In this way, sample processing blanks are minimized and the CO_2 used in graphite preparation is assumed to reflect the true composition of the standard reference material. This principle was applied for preparation and analysis of the HOxI and HOxII standards discussed above. The observation of *intra*-sample isotopic variability in the HOxI and HOxII targets argues against a large ^{14}C dead blank being uniformly incorporated during sample processing. Because it is also possible that a substantial modern carbon equivalent bank is incorporated during graphite preparation, six IAEA C-1 samples were included on the wheel devoted to analysis of small standards. These targets were the "dead" carbon analogues to our "modern" HOxI and HOxII small targets. Within the precision of the determination, the cumulative blank associated with cobalt-catalyzed reduction and AMS target preparation is *ca.* 0.12 μgC equivalent modern carbon (Fig. 7). This is nearly indistinguishable from one of our two JME graphite powder reference materials (JME D24B28).

Combustion Blank

Most small samples that we anticipate analyzing are from organic carbon sources and require combustion to CO_2 prior to graphite preparation. This represents an additional processing step that could contribute significant amounts of background carbon to the samples. We have taken several approaches to assessing both the quantity and f_m of the carbon introduced during the combustion process.

The first approach involved preparation of a bulk combustion blank for direct analysis by AMS. The CO_2 obtained from combustion of multiple "empty" Vycor® tubes was quantified using a small-volume vacuum line and manometer. The tubes yielded 0.16 ± 0.09 μmol gas on average (range 0.08–0.33) for batch #1, prepared in 1995; and 0.08 ± 0.02 μmol gas on average (range 0.05–0.14) for batch #2, prepared in 1996. The gas in batch #1 likely contains a large fraction water vapor, as the vacuum line was flushed with H_2O-saturated N_2 between cracking three of the individual tubes.
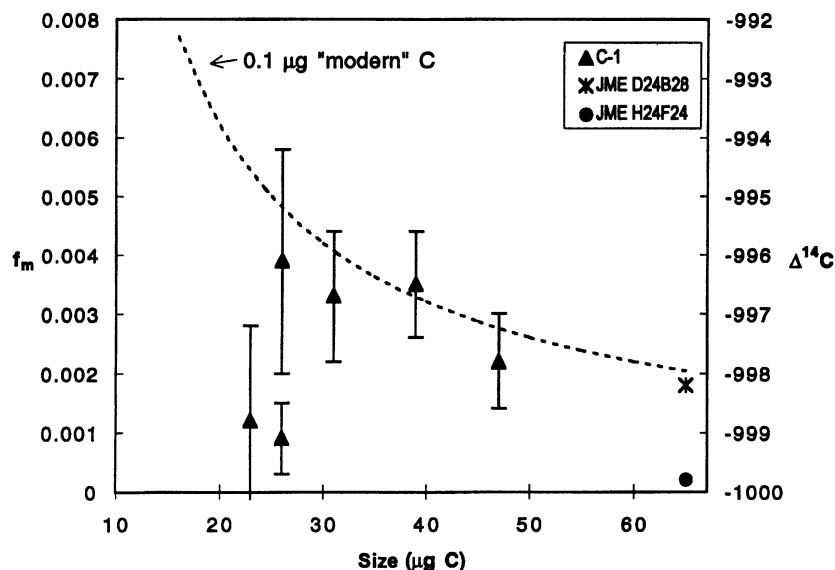
Fig. 7. Graphitization blank as measured for IAEA C-1 carbonate.

Those three tubes subsequently yielded an average of 0.23 µmol gas each. Multiple water traps were used for purifying the samples in the second batch, and the vacuum line was allowed to pump down at room temperature for 45 min between cracking each sample. The largest difference between the gas collected in the two batches is probably the average amount of water vapor contained in each.

For each batch, the CO_2 was then combined to form a bulk combustion blank sample containing *ca.* 20 µgC for batch #1 and 25 µgC for batch #2. While this method of measuring the ^{14}C content of the combustion blank obscures variability between samples, its advantage is that it allows a direct, rather than modeled, estimate of the blank's f_m. AMS analysis of the graphite prepared from these samples in both cases indicated that the combustion blank is not primarily composed of modern carbon. Batch #1 had a composite $f_m = 0.379 \pm 0.012$ and batch #2 had $f_m = 0.250 \pm 0.013$.

Because manometric determination of the gas obtained from the individual combustion blank tubes was considered uncertain, especially on the first set of attempts (batch #1), two additional approaches were taken to assess the size and chemical composition of the combustion blank. The CO_2 from six tubes was measured by gas chromatography as an alternative, carbon-specific method of determining the combustion background. Quantification was based on the ratio of peak area to that of a standard volume CO_2 injection. The six samples yielded 0.08 ± 0.02 µmol C, in good agreement with the more precisely prepared manometric batch #2 samples. The total gas composition of eight combustion tubes was also examined using a Dycor RGA, since it is reasonable to assume CO_2 and H_2O are not the only products of the combustion process. The results indicated that in addition to CO_2 and H_2O, minor amounts of CO and N_2 may contribute to the total gas generated in an empty combustion tube.

A completely independent approach to assessing the organic carbon blank is possible through combustion of small quantities of standard materials of known isotopic composition. Toward this goal, we have combusted a few small HOxI powder and JME graphite samples and converted the CO_2 into graphite for AMS small-sample analysis. The graphite prepared from these small-batch com-

bustion standards appears to confirm that the combustion blank is not primarily composed of modern carbon. The f_m measurements of these targets are not significantly different from values predicted by a simple mass balance model that incorporates the 0.08 μmolC, 0.25 f_m blank carbon contribution. Model curves can also be fit to the data to provide an independent estimate of the blank contribution. However, accurate determination of the appropriate f_m may be difficult using this approach, as the measurement error increases greatly for samples smaller than 20 μgC.

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 μg C 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.

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