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^{14}C DATING WITH THE GIF-SUR-YVETTE TANDETRON ACCELERATOR: STATUS REPORT AND STUDY OF ISOTOPIC FRACTIONATION IN THE SPUTTER ION SOURCE

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ABSTRACT. The standard procedure for measuring ^{14}C at the Gif-sur-Yvette Tandetron AMS facility is described. A new sample manipulator and automated measurements are being used and have been operational for six months. Evidence of isotopic fractionation in the sputter ion source is provided. We take this into account by measuring the $^{13}C/^{12}C$ ratio of the sample in the accelerator.

INTRODUCTION

^{14}C dating of samples containing 0.5-2mg of carbon has been routinely performed at the Gif-sur-Yvette Tandetron accelerator since 1985. The precision and reproducibility of our routine measurements is 1% for samples younger than 5000 BP. Our age limit is mainly due to contamination during sample pretreatment as well as target preparation and is close to 45,000 BP. The performance of the methodology was described at the last AMS Symposium in Niagara-on-the-Lake (Arnold *et al,* 1987).

Since the beginning of 1988, we have acquired a new sample manipulator, designed and built at the Isotrace Laboratory of the University of Toronto (Wilson *et al,* 1984). It has two stepping motor-driven micrometers in the X and Y directions and is controlled by a microcomputer with automatic changeover from one sample to the next. The micrometers are also used to move the sample under the cesium beam for analysis of different target areas. We have developed complete automatization of measurements with this new manipulator. We currently measure 6 targets per 10 working-hour day: 2 standards and 4 unknown samples.

Since this fully automated system is in operation, we have observed a small deterioration of the current output of the prepared targets as well as phenomena of isotopic fractionation.

GENERAL PROCEDURE

Sample Preparation

Solid targets are prepared by direct CO_2 catalytic reduction on iron powder using basically the same reaction vessel as that described by Vogel *et al* (1984). The volume of the reaction vessel is 8cc. Based on pressure monitoring, the total reduction time is from 6–8 hr for CO_2 samples of 0.5–2mg of carbon using irregular-shaped iron powder of 150μm. Reaction time

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was much shorter, <1 hr, with 325 mesh powder, but the carbon generally formed apart from the iron and could not be used to prepare a homogeneous target. We presently use 4 reactors at the same time so that this relatively long reaction time is not a limiting factor.

In order to reduce memory effect in the vessel, the reactor is baked overnight at 90°C under vacuum and the iron powder is heated to 690°C, before each sample reduction. The iron is heated to 650°C for the CO_2 reduction.

Usually, 7mg of iron are used for 1mg of carbon, this ratio being kept constant for samples and standards. When the reaction is finished, the quartz tube containing the iron-carbon mixture is filled with pure argon, closed with a silicon stopper and stored until needed to prevent contamination from atmospheric CO_2.

Measurements

The system shown in Figure 1 is used for pressing the iron-carbon mixture into a flat pellet, 3mm in diameter, ready for measurement.

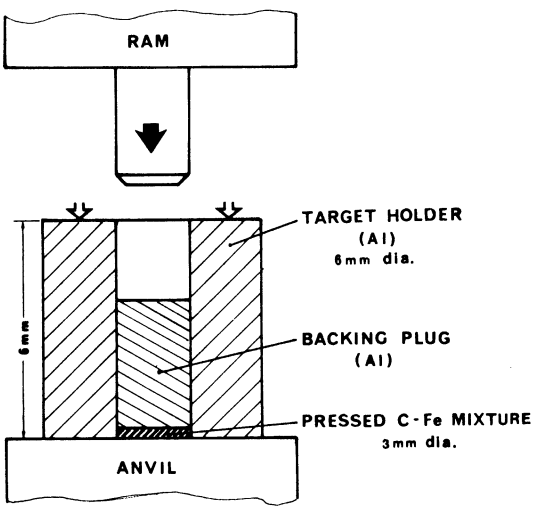


Fig 1. Target press arrangement. A force of ca 1.3 tons is exerted on the ram, corresponding to pressure of ca 18kbars.

Loading of the sample holder and the prevacuum of the sample chamber (using a small 80L/sec turbomolecular pump) takes ca 1 hr. The sample holder is then introduced into the ion source, which runs continuously. Before measurement, the entire surface of each target is moved under the Cs beam for ca 25 min to obtain stable currents and to remove surface contamination.

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We analyze each sample in 6 areas of the target surface. The centers of the 6 analyzed areas are located on a circle of 1.5mm diameter. The cesium beam on the target is estimated to be 0.7mm in diameter, so that the 6 analyzed areas are generally well separated. The analysis of one target area consists in successive measurements of $^{12}C^{3+}$ and $^{13}C^{3+}$ currents in two separated Faraday cups located after the first analyzing magnet, followed by the counting of ^{14}C events over a period of 100 sec in a two-stage gas ionization detector. After the ^{14}C counting time, $^{13}C^{3+}$ and $^{12}C^{3+}$ currents are measured again and the sample is moved to the next analyzing point. For each location of the sample, we calculate the mean ^{12}C and ^{13}C currents, and the isotopic ratios r13 and r14, which are, respectively, the $^{13}C^{3+}$ / $^{12}C^{3+}$ and $^{14}C^{3+}$ / $^{12}C^{3+}$ ratios. A correction for isotopic fractionation is applied by calculating $r14N = r14/(r13)^2$ (Beukens, Gurfinkel & Lee, 1986). The precision of measurement of the $^{12}C^{3+}$ and $^{13}C^{3+}$ currents is only limited by the current instabilities in the ion source, and is generally lower than 1‰. From the comparison of the $^{13}C^{3+}$ / $^{12}C^{3+}$ ratios before and after the ^{14}C counting time, the precision of the r13 measured on each analyzed area is estimated to be better than 2–3‰.

Five cycles consisting each in the successive measurements of the first Oxalic-I acid standard, the 4 unknown samples and the second Oxalic-I acid standard, are repeated for a complete run. Thus, the total counting time of a sample is 3000 sec, and corresponds, for a recent sample, with an output current of 5μA to an integration of ca 30,000 ^{14}C events.

For each sample and standard, a weighted mean of the 30 individual measurements of the r14N ratios is calculated. The error estimated for this mean R14N ratio is taken as the greatest of either the internal error (the error calculated from the ^{14}C counting statistics) or the external error (estimated from the variance of the 30 individual r14N measurements). The activity of a sample is then obtained by the ratio of the mean R14N of the sample to the mean R14N of the two standards, times the ^{14}C activity of the Oxalic-I acid. In the same manner, provided that no fractionation occurs during target preparation or sputtering process, the $\delta^{13}C$ can be estimated from the comparison of the mean R13 ratio of the sample with that of the two standards.

RESULTS AND DISCUSSION

Target Current Output

The current obtained with our targets usually starts at a value of ca 7–8μA of $^{12}C^-$ when first exposed under the Cs beam, while 10μA would usually be obtained with pure graphite. This current decreases rapidly for ca 5–10 min and then remains about constant for several hours with a maximum drift of ca 15%/hr. The $^{12}C^-$ currents obtained from 150 targets recently measured in our system are plotted in Figure 2. The currents obtained from these targets have a wide range of variation and average 2.5μA, which is about twice as low as the average currents obtained no more than 6 months ago. We do not yet have any satisfactory explanation for this loss in performance, since no drastic experimental conditions have

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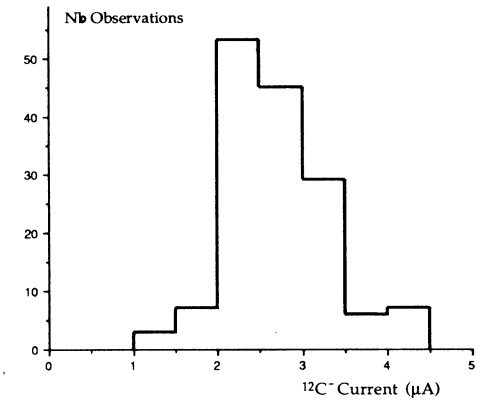


Fig 2. Histogram of the mean ^{12}C- current output observed during the measurements of the last 150 targets prepared at Gif

changed in our target preparation procedure. The only change consists of an increase of the diameter of the pellets from 2–3mm, but the force exerted on the ram of our press device has been increased accordingly to keep the working pressure to ca 18kbars.

A possible explanation could be a loss of the "catalytic properties" of the iron powder used. In support of this hypothesis, we have observed a general increase of ca 1 hr of the total reduction time of the CO_2. The reduction time is much more variable than previously and we generally observe higher current outputs for the samples showing a rapid reduction time.

Moreover, the high performances of catalytically condensed carbon described by Vogel *et al* (1984) have never been reached in our laboratory. Our material appears to have sputtering characteristics quite different from those described by Vogel, Southon and Nelson (1987). In particular, the currents rapidly decrease shortly after setting the targets under the Cs beam and tend to be lower than those obtained with pure graphite. Some targets glow when first exposed to the Cs beam and start with current output generally smaller than the other targets, but the glow disappears very rapidly, in <30 sec. Current output of glowing samples remains low, even after the disappearance of the glow, in contrast with the observations of Vogel, Southon and Nelson (1987).

Fractionation

Figure 3 is a histogram of ^{13}C fractionations measured between the pairs of Oxalic-I acid standards during the last 45 routine runs with our new sample manipulator. The histogram shows dramatically high fractionation

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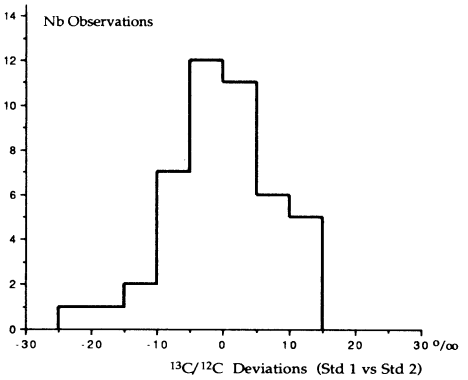


Fig 3. Histogram of the $^{13}C/^{12}C$ deviations measured between the 2 Oxalic-I acid standards during the last 45 routine runs

values, which probably cannot be explained by sample-preparation-induced fractionation. Bulk fractionation of catalytically condensed carbon generally does not exceed 1–2‰, when the reduction of CO_2 proceeds to >97% completion. We estimate that at least 95% completion is always reached, by monitoring pressure during CO_2 reduction.

We think that the major cause for these fractionations lies in the Cs sputtering process. Vogel *et al* (1987) have shown that in a Cs sputter source, thermal effects play an important role on both current output of catalytically condensed material mixed to a binder and on isotopic fractionation. However, if the current output of our targets is relatively low and variable, the thermal effects that we observe do not really correspond to the observations made by Vogel *et al* (1987). Moreover, the direction of the fractionations we observed disagrees with their observations, since targets with poor current output often have most negative fractionations.

The calculations of Nadeau *et al* (1987) show that two major processes can be responsible for large variations of isotopic ratios in a Cs sputtering source: the work function of the surface sputtered and the surface topography. We plotted (Fig 4) three examples of variations of the $^{13}C/^{12}C$ ratios observed in different targets during the standard procedure of measurement. Figure 4A shows that these ratios are more-or-less reproducible through the whole surface of the sample, while in Figure 4B, these ratios can differ from one location to another by 25‰. Figure 4C shows large variations through the surface of the sample as well as variations with time for the same analyzed area. The variations of the $^{13}C/^{12}C$ ratios in these examples are much larger than the instrumental errors of measurement and are most likely due to variations of surface conditions of the target as predicted by Nadeau *et al* (1987). However, such large variations for the same target indicate large variations of the work function across the target surface that can only be explained by inhomogeneities of the carbon-iron mixture. Such inhomogeneities are not observed at the macroscopic scale. Isotopic variations due to surface topography should be limited in the present case,

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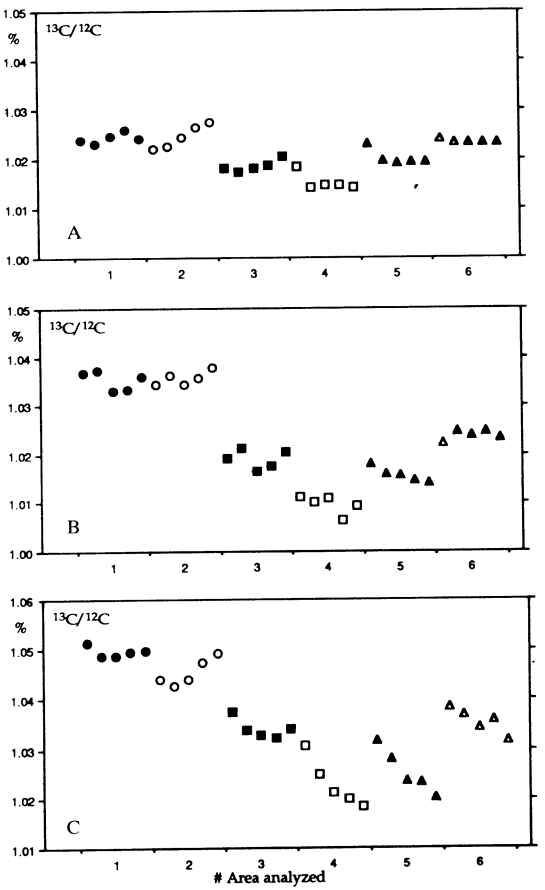


Fig 4. Examples of $^{13}C^{3+}/^{12}C^{3+}$ ratios measured in the 6 analyzed areas of 3 targets during a run. The time between the measurements of 2 successive areas is close to 2 min; the time between 2 measurements in the same area is ca 1 hr.

as an angle-limiting aperture was placed before the first mass analyzer, as recommended by Beukens, Gurfinkel and Lee (1986).

We made a statistical analysis on the measurements performed on 90 Oxalic-I acid (45 pairs), in order to determine whether the $^{13}C/^{12}C$ ratio could be used to correct the $^{14}C/^{12}C$ ratio for sputtering fractionation. Unfortunately, the poor precision of the $^{14}C/^{12}C$ ratio obtained after a 100-sec counting time does not permit adequate modeling of the relationship between the r14 and r13 ratios out of the 30 measurements made on the same target. The standard deviation is usually smaller for r14N ($^{14}C/^{12}C$ ratio corrected for isotopic fractionation as described above) than for r14 measurements ($^{14}C/^{12}C$ ratio without correction) on the same target. This is the only clue for a correlation.

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A correlation may also exist between the relative variations of the mean R13 and R14 ratios measured in the two standards during the same run. The precision of the ratio of R14 of Standard 1 *vs* Standard 2 is calculated from the counting statistics and is close to 1%. The confidence interval for the mean R13 ratio depends mainly on the reproducibility of the $^{13}C/^{12}C$ measurements during a run. This confidence interval may differ from one target to another as shown in Figure 4. The confidence interval was calculated from the variance of the 30 r13 measurements from the same target. In this case, the errors of the relative R13 ratio of Standard 1 *vs* Standard 2 vary from 2–5‰. We plotted, in Figure 5, the relative variations of the

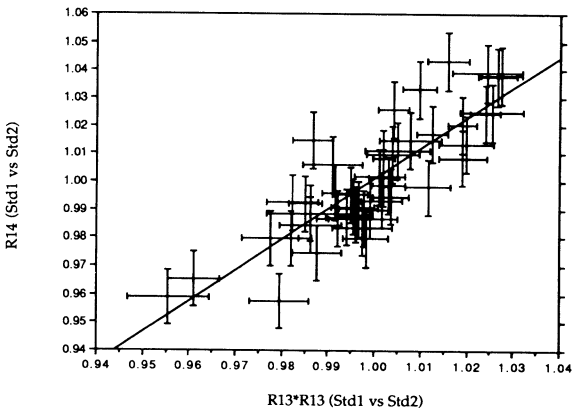


Fig 5. Variations of R14 (Standard 1 *vs* Standard 2) *vs* ratios of squared R13 (Standard 1 *vs* Standard 2) measured between the Oxalic-I acid standards during the last 45 routine runs

mean R14 ratios *vs* the square of the relative variations of the mean R13 ratios measured between the two standards during the last 45 routine runs. Figure 5 shows a strong dependence between these two parameters (coefficient of correlation = 0.84). The slope of the regression line (= 1.09, with $\sigma = 0.11$), is very close to 1. This shows that within the range of precision of the experiment, the $^{13}C/^{12}C$ ratio can be used to correct the $^{14}C/^{12}C$ ratio for all fractionations, including the sputter fractionations, as suggested by Nadeau *et al* (1987). For these 45 pairs of standards, the standard deviation of the relative R14N ($^{14}C/^{12}C$ ratios corrected for fractionation) is equal to 1.1%, in perfect agreement with the uncertainties based on the ^{14}C counting statistics, whereas the standard deviation of the relative R14 (not corrected for fractionation) is equal to 2.1%. The comparison of the ^{14}C activities of these standards based on the calculation of the $^{14}C/^{13}C$ measurements, as it is made on some AMS facilities, gives a standard deviation of 1.5% that is a bit greater than the precision expected from the counting statistics.

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CONCLUSION

$^{14}C/^{13}C$ and $^{13}C/^{12}C$ ratios can be measured simultaneously by AMS in order to correct a ^{14}C determination for natural and preparation-induced fractionations. Our data demonstrate that sputter fractionation should not be neglected. Therefore, the abundance of the three carbon isotopes should always be measured in order to reach 1% accuracy.

Target preparation should be improved in order to reach the 0.5% precision level required for oceanographic studies and archaeological dating. Despite these difficulties, catalytic reduction of CO_2 is an efficient technique, as it may provide a target with high current output and limited sputter fractionations (Bonani *et al,* 1987).

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REFERENCES

Arnold, M, Bard, E, Maurice, P and Duplessy, JC, 1987, Status report on ^{14}C dating at the Gif-sur-Yvette Tandetron: Nuclear Instruments & Methods, v B29, p 120–123.

Beukens, RP, Gurfinkel, DM and Lee, HV, 1986, Progress at the Isotrace radiocarbon facility, *in* Stuiver, M and Kra, RS, eds, Internatl ^{14}C conf, 12th, Proc: Radiocarbon, v 28, no. 2A, p 229–236.

Bonani, G, Beer, J, Hofmann, H, Synal, HA, Suter, M, Wölfi, W, Pfleiderer, C, Kromer, B, Junghans, C, and Münnich, KO, 1987, Fractionation, precision and accuracy in ^{14}C and ^{13}C measurements: Nuclear Instruments & Methods, v B29, p 87–90.

Nadeau, MJ, Kieser, WE, Beukens, RP and Litherland, AE, 1987, Quantum mechanical effects on sputter source isotope fractionation: Nuclear Instruments & Methods, v B29, p 83–86.

Vogel, JS, Southon, JR and Nelson, DE, 1987, Catalyst and binder effects in the use of filamentous graphite for AMS: Nuclear Instruments & Methods, v B29, p 50–56.

Vogel, JS, Southon, JR, Nelson, DE and Brown, TA, 1984, Performance of catalytically condensed carbon for use in accelerator mass spectrometry: Nuclear Instruments & Methods, v B5, p 289–293.

Wilson, GC, Rucklidge, JC, Kieser, WE and Beukens, RP, 1984, Development of an ion microprobe stage for accelerator mass spectrometry: Nuclear Instruments & Methods, v B5, p 200–203.

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