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# RECENT $^{14}C$ MEASUREMENTS WITH THE CHALK RIVER TANDEM ACCELERATOR

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ABSTRACT. The Chalk River Tandem Accelerator Mass Spectrometry System has reached a state of reliable measurement of $^{14}C$ using 2 to 5mg elemental carbon prepared by Mg reduction of $CO_2$. For two comparisons of a near-modern unknown with the NBS oxalic acid standard we obtain a total error of $\sim\pm 4.5\%$, consisting of a random system error of about $\pm 3.5\%$ combined with the statistical counting error. Measurements have been made on 70 samples in 30 days of running time during the past year. Samples included deep rock carbonates, cosmogenic $^{14}C$ in meteorites, charcoal from earthquake fault zones, collagen of bone artifacts and fossil beetle- fragments.

## INTRODUCTION

At the last Radiocarbon Conference in 1979 we detailed the evolution of a Tandem Van de Graaff $^{14}C$ dating system at Chalk River (Andrews and others, 1980). At an International Atomic Energy symposium in West Berlin in 1981 we described further development of the system and gave an appraisal of its capabilities, limitations, and prospects for improvement (Brown and others, 1981). During the past year our facilities and techniques have remained essentially unchanged. We have gained operating experience and measured a variety of sample types to demonstrate the validity and value of the technique. This paper recounts our experience and presents some illustrative results. Papers dealing with the significance of the results for specific studies will be published separately in collaboration with the submitters of the samples.

The Chalk River $^{14}C$ system is based on a MP Tandem Van de Graaff accelerator operating at 8 MV terminal voltage. $C^{4+}$ ions of 40 MeV energy emerge from the accelerator, pass through two analyzing magnets and a Wien

cross-field velocity filter and are measured by a Faraday cup in the case of $^{12}C$ or an E/ΔE counter telescope in the case of $^{14}C$. Ions of the desired isotope are switched automatically through the system by adjusting the magnetic elements. $^{14}C$ is counted for five 45-second periods followed by a 50-second integration of the $^{12}C$ current. Normally, the $^{13}C$ current is not monitored. The $^{14}C/^{12}C$ ratio obtained for a sample is normalized to that of carbon prepared from the NBS oxalic acid standard measured before and after each one or two samples.

## OPERATING EXPERIENCE

ION SOURCE PERFORMANCE. Our standard sample material for the ion source has been 2 to 5mg of elemental carbon mixed with four times its weight of reduced Fe powder. The mixture is pressed into a ring within the bore of a cylindrical aluminum sample holder through which a 6mm diameter $Cs^+$ sputtering beam passes. An attempt to achieve a higher $C^-$ emission by using a more concentrated $Cs^+$ beam of 1.3mm diameter was unsuccessful. No measurable increases in beam currents were observed and the beam was found to sputter through the carbon of the oxalic acid standards which were counted repeatedly throughout a run. In addition, Al was sputtered onto the rest of the source material, as a portion of the intense $Cs^+$ beam struck the inside of the source mount. We have tried industrial graphite, iron carbide, and graphite pyrolyzed onto a hot Ta wire from acetylene with no significant improvement in source emission. Thus, we find our original C + Fe sources to be the most satisfactory. Their output stabilizes sufficiently for measurement to start in 30 minutes, they last a long time without sputtering through, and they give as high a $C^-$ current as industrial graphite mounted in the same geometry. The carbon preparation technique, reduction of $CO_2$ by Mg in a disposable stainless steel tube at 900°C, continues to be satisfactory.

We have been able to increase our beam current 2 to 3 fold without degrading our reproducibility by using a larger beam-defining aperture at the entrance to the Tandem accelerator. We now obtain $^{12}C^{4+}$ beam currents of 1 to 3 μA corresponding to $^{14}C$ counting rates of 100 to 300 per minute for modern carbon and 0.5 to 1.5 per minute for a background sample.

BACKGROUND. Our experience with background during the past year is shown in figure 1. Our original practice had been to carry over a background sample of carbon prepared from limestone from one loading of the ion source to another within a run. The May and September runs show that the count on such a background sample tends to rise with each successive loading, perhaps because of exposure of the caesiated surface of the carbon to atmospheric $CO_2$ during load change. In the fourth load of the September run, a new background sample gave a much lower value than the sample carried through the four loadings. In subsequent runs, new background samples have been used for each load. The hatched band marked "Limestone Background" is the average level obtained for all fresh background carbon samples measured during the past year. Since all the limestone carbon samples were prepared from aliquots of a single preparation of carbon by our standard procedure, the fluctuations in the measured background level must result from contamination introduced during the preparation or loading of the sample holders. Within a given load we have found the background count to remain constant.

Figure 1 also shows the results of measurements on industrial graphite and an empty Al sample holder in the standard geometry. These are significantly lower than all but one of the limestone measurements. We consider this to be the inherent background level in our machine at the present time, equivalent to a sample with an age of $\sim$56,000 years. Attempts to reduce the background by installation of a cold trap close to the ion source and by flushing the ion source chamber with dead $CO_2$ just prior to pump-down have not been successful.

REPRODUCTIBILITY. Statistical analysis of multiple measurements of unknown samples with respect to the standard during the past year indicate a random system error of $\sim$5% for a single measurement, in addition to counting statistics. For our usual practice of two measurements per sample this results in an error of $\sim\pm$3.5%. When this error is combined quadratically with the counting statistical error ($\pm$3%) associated with our usual counting times, the result is a total error of $\sim\pm$350 years for a modern sample.

COMPARATIVE MEASUREMENTS. We have tested our system with a series of samples prepared from a weak $^{14}CO_2$ spike diluted quantitatively with $^{14}C$-free $CO_2$. Figure 2

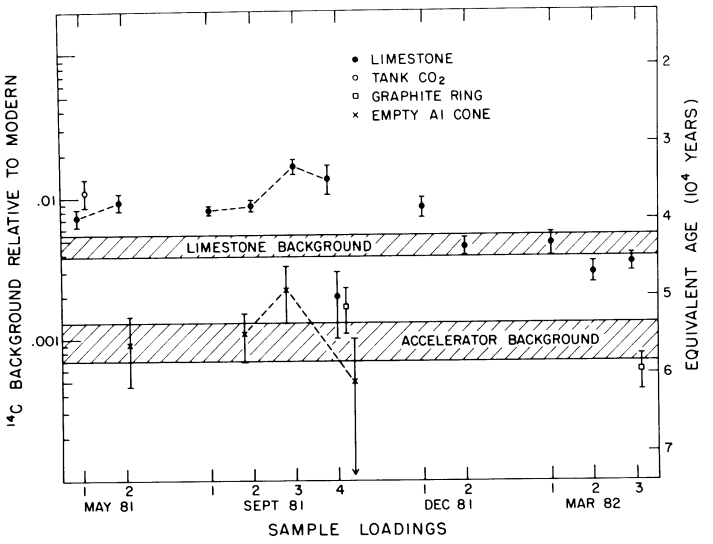



Figure 1. $^{14}C$ background in the Chalk River MP Tandem Accelerator, 1981-82

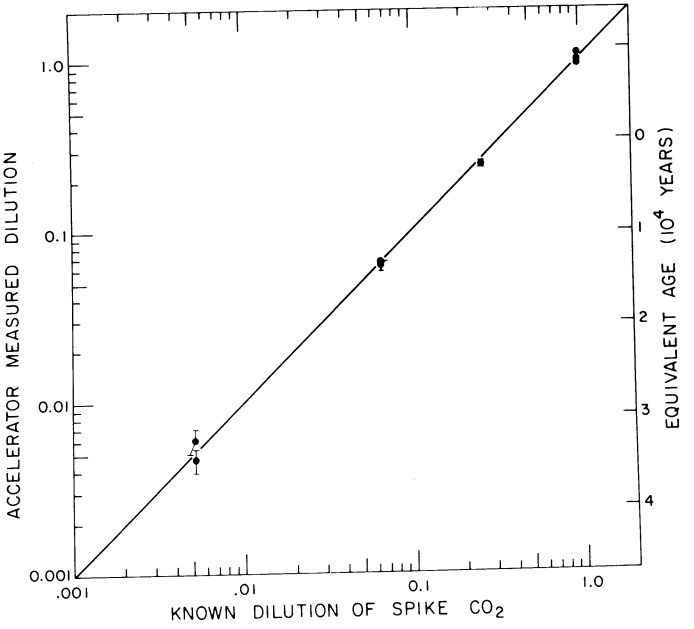



Figure 2. Accelerator measurements of quantitatively diluted spike $^{14}CO_2$

shows the linear correspondence we obtain between measured and known concentrations over a 250-fold dilution. Reasonable replication was obtained on multiple samples measured at different times over the span of more than a year. The greatest dilution corresponds to 1.2% modern or an age of ca 35,000 years.

In each group of samples we have measured, some have been measured radiometrically at a previous time. Comparative results are presented in Table 1. The errors quoted for the accelerator measurements are estimated overall measurement errors ($1\sigma$) as discussed above. Errors quoted for radiometric measurements are assumed to be simple counting statistical errors as is the usual practice.

These comparisons encompass the complete determinations involving independent sample selection and preparation in different laboratories not necessarily using exactly the same purification procedures. The accelerator samples were small discrete portions of material rather than representative fractions of the large portions used for the radiometric measurements at an earlier time. In view of the opportunities for occurrence of differences in material actually measured, the correlation of results is encouragingly good. Of the two instances where the difference in results exceeds twice the quadratically combined standard deviations of the measurements, one (the Indian campsite charcoal) is probably attributable to different sample materials and the other (the mammoth bone) to the difficulty of obtaining reproducibly-dateable material from bone. Unfortunately the radiometric value for Farmington $CO_2$ (from which carbon was prepared for the accelerator measurement after 20 years storage) is of low accuracy due to the small sample size. Obviously it is desirable to obtain direct intercomparisons using homogeneous $CO_2$ samples that have been measured radiometrically with high accuracy.

## DATING RESULTS

Rather than making a Herculean effort to achieve the 1% or better accuracy attained by radiometric measurement and expected for the dedicated machines, we have accepted the 4 to 5% accuracy consistently obtainable with our system and proceeded to measure a number of samples for which this is perfectly acceptable. This is the case for most samples more than a few thousand years old.

TABLE 1. COMPARATIVE RADIOMETRIC AND ACCELERATOR MEASUREMENTS

| Sample | RADIOCARBON AGE (Years bp)# Radiometric | Accelerator | Difference |
|---|---|---|---|
| Charcoal-Indian campsite | 1870 ± 175 "From same site"(S-501) * | 270 ± 360<br>0 ± 320 | 4.σ |
| Bone collagen-human | 2610 ± 65 (S-1285) * | 2470 ± 340 | 0.4σ |
| Bone collagen-mammoth | 15500 ± 130 (GSC-3053) ** | 17900 ± 500<br>17860 ± 440 | 4.7σ |
| Charcoal-Wasatch Fault | "With modern nails" | 220 ± 340 | 0.7σ |
| Charcoal-Wasatch Fault | 130 ± 95 † | 390 ± 330 | 0.7σ |
| Charcoal-Wasatch Fault | 1350 ± 70† | 1560 ± 340 | 0.6σ |
| Charcoal-Wasatch Fault | 4580 ± ? † | 4030 ± 280 | <1.5σ |
| $CO_2$ from Farmington meteorite. Same $CO_2$ for both measurements. | (dpm/kg meteorite) 47 ± 10 ‡ | 48.2 ± 3.2 | 0.1σ |
| $CO_2$ from Bruderheim meteorite. Independent portions of meteorite. | (dpm/kg meteorite) 57 ± 3 ‡ | 49.8 ± 1.8 | 2.0σ |

\# $^{14}C$ half-life = 5568 years

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† Dicarb Radioisotopes Co , Gainesville, Florida 32601, U S A

‡ de Felice and others (1963); Fireman (1978)

During the past year we have had four runs in which we have measured 70 samples in 30 days of running time. Detailed date lists will be published elsewhere. Here we present our dates in graphical form to demonstrate the reproducibility attained in routine analysis and the range of sample types and ages that have been measured.

METEORITE SAMPLES. Measurement of the $^{14}C$ content of meteorites is an excellent application of the accelerator technique since only very small samples are available. Our samples have been a few mL $CO_2$ extracted by E L Fireman of the Smithsonian Astrophysical Observatory from North American and Antarctic meteorites. Many of these have been counted in small volume proportional counters in past years. We have obtained about 5-fold higher precision and extended the terrestrial age limit to 50,000 years from the 25,000 years limit of radiometric measurements on the small amounts of sample available. Figure 3 shows our experience with reproducibility on multiple measurements of these samples. The error bars are counting statistics only; in many cases, the spread in the repeat data exceed these estimates reflecting the presence of the ~5% system fluctuation discussed previously. In two cases (137,167) one measurement is far out and obviously should be discarded. Usually, such results can be associated with some operational aberration during the measurement. Fireman and others (1982) and Andrews and others (1982) have reported aspects of these meteorite measurements.

ARCHAEOLOGIC SAMPLES. The Archaeological Survey of Canada provided 17 bone samples which have been analyzed, some several times. Most of these were animal bones from the Yukon which showed evidence of use as tools by man when fresh. Dating was done on collagen recovered from these bones by mild HCl and NaOH extractions. Two samples had been measured radiometrically and are reported in Table 1. Significant new dates were obtained for the other samples which were too small for radiometric measurement.

Figure 4 shows the reproducibility and age range of these samples. The brackets embrace different carbon samples prepared from the same bone measured in accelerator runs separated by several months. Samples 3 and 4 were from a common preparation of carbon, as were 15 and 16, but the other pairs were processed independently from common bone samples.

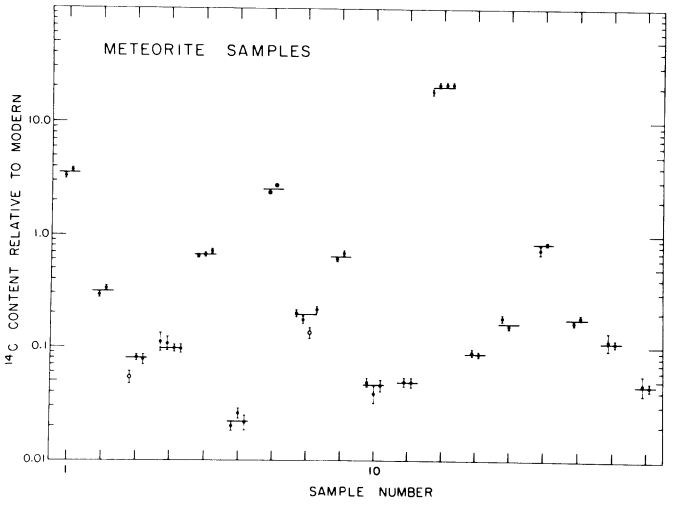



Figure 3. $^{14}$C content of meteorite samples. Error bars are counting statistics only. Open points not included in mean values shown by horizontal bars.

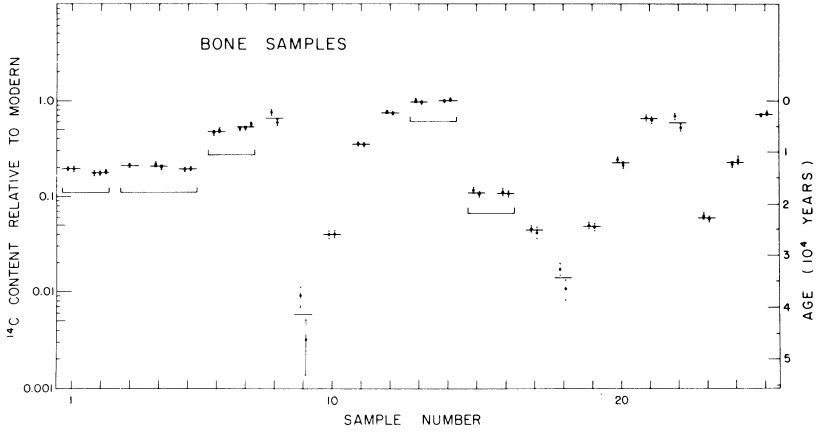



Figure 4. $^{14}$C content of bone samples. Error bars are counting statistics only. Horizontal bars are the mean values of the multiple measurements on each sample. Brackets embrace different samples prepared from the same bone and measured several months apart.

Two of the bone samples we analyzed early in our program gave impossibly young ages. We have related these discrepancies to sample processing. These samples, and one done intentionally at a later time, were extracted with hot 6-molar HCl resulting in loss of most of the protein. The small acid-insoluble organic residue remaining had an age of a few thousand years. It is estimated that such a contaminant would reduce the age of a sample prepared by our usual procedure from a true age of 15,000 to 13,000 years. Since the amount and age of such contaminants are probably variable from sample to sample, they should be removed, perhaps by solubilizing the collagen in hot water and discarding insoluble material as described by Longin (1971). We have not used such treatment as yet.

EARTHQUAKE DATING. A set of charcoal samples provided by Allen Tucker, San Jose State University, have been measured for earthquake dating purposes. The samples comprise small flecks of charcoal recovered from soil at the site of the earthquake-produced Wasatch fault near Salt Lake City, Utah. The dates of such charcoal found on the two sides of faulted strata give a maximum age for the time of faulting. Hand-picking of the small samples required for accelerator measurement is the only practical means of ensuring freedom from contamination by more recent organic material such as rootlets. These samples were combusted to $CO_2$ and reduced to carbon in our standard procedure to ensure that sample and standard were in the same form.

PALEO-ENTOMOLOGIC SAMPLES. Information on the paleo climate at a site can be obtained from the identity and age of insect remains found. In the past, dating of the insects had to rely on stratigraphy or $^{14}C$ measurements on co-existing organic matter. We have directly dated insect remains provided by Allan Morgan, University of Waterloo, finding ages of 28,000 and 32,000 years for beetle parts from two related strata in the Yukon, and ca 8000 years for fossil beetles from more southerly sites.

## CONCLUSION

These measurements have shown that we can obtain much valuable information at the present level of precision of accelerator $^{14}C$ dating. We are now shut down for the installation of a superconducting cyclotron as a post-

accelerator for the MP Tandem. The Tandem will be in operation again by 1984 and we shall then continue measurements of $^{14}C$ and other isotopes of radiochronologic interest.

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