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REDUCTION IN BACKGROUNDS OF MICROSAMPLES FOR AMS 14C DATING

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ABSTRACT. Vogel, Nelson and Southon (1987) determined that the total-system 14C background values in catalytically reduced graphitic carbon samples of 500 mg or less were inversely proportional to their weights. We have used wood reportedly of Pliocene age (i.e., 14C "dead") to further examine this relation. Our observations are consistent with the conclusions of Vogel, Nelson and Southon (1987). It appears that contamination can be characterized as if a constant level of modern carbon is being added. We also report a significant overall net reduction in total system background values ca. 45% for combusted samples from levels previously reported by Vogel, Nelson and Southon (1987).

INTRODUCTION

Over the past two decades, most of the advantages of accelerator mass spectrometry (AMS) anticipated by early researchers have been fully realized (Muller 1977, 1979; Nelson, Korteling and Scott 1977; Bennett et al. 1977). These include reduction by several orders of magnitude in sample size and counting times. An anticipated advantage--increasing the 14C time scale beyond that typically possible with decay counting--has not yet occurred (Taylor 1987, 1991). The expectation of extending the temporal range of 14C dating from the currently routine 40/50 ka to as much as 100 ka was based on several considerations. Cosmic radiation, a major source of background in conventional decay counting, is essentially eliminated in AMS technology (Beukens 1992). A 1-mg sample of carbon 100 ka old should still contain 235 14C atoms. The measurement of a 14C atom in a 150-mg sample would yield a 14C age of $103,000 \pm 8000$ BP (Mueller 1977). However, to undertake any such experiment, it would be necessary to prepare "contamination-free samples" (Purser 1978).

We report here experiments directed at reducing the level of 14C contamination exhibited in microsamples. We define microsample as any sample containing <500 mg of graphitic carbon. We focused our studies on standardizing pretreatment, combustion and graphitizing procedures using wood reported to have been collected from Pliocene-age sediments. We used 14C-"dead" terrestrial organic matter as source material for our background experiment instead of anthracite coal for two reasons. The first reason is the combustion characteristics of wood more realistically represent the majority of archaeological samples measured in the laboratory. The second reason is it has been difficult to obtain truly 14C-free anthracite coal.

SOURCES AND LEVELS OF contamination

Many approaches have been taken by AMS researchers to minimize contamination effects. Despite these efforts, routine backgrounds ranging from 0.1 to 1.0% modern (pMC) (.001 to .01 fraction modern) are typically reported for graphitized samples of 1 mg or above. The equivalent 14C ages exhibited in these background blanks synthesized from CO₂ are in the 35 to 55 ka BP range.

The sources of contamination yielding these backgrounds have been variously identified. Table 1 lists some potential sources. Tandem laboratories reporting specific experiments to quantify their background levels note a hierarchy of values beginning with machine background. Some laboratories, such as the Nuclear Physics Laboratory, University of Washington in Seattle, define these values as activity generated in the beam line

reaching the detector with the ion source closed off from the remainder of the tandem system (Schmidt, Balsley and Leach 1987). The Seattle tandem was measured at 190 ka BP (0.001 pMC), i.e., no counts detected in 30 min. An equivalent result was obtained with their ion source open to the beam transport system containing an empty aluminum target holder. The Isotrace Laboratory (Beukens 1992) reported an apparent age of an empty aluminum target holder to be 85 ka BP (0.0025 pMC).

TABLE 1. Potential Sources of Background in AMS ^{14}C Measurements Using Catalytically Condensed Graphitic Carbon Targets

A. Machine background: ^{14}C detected when graphite in the sample holder does not contain ^{14}C .

1. Detector anomaly: ^{14}C pulse registered in detector circuitry when no ^{14}C ion is present.
2. Ion identification anomaly: particle of same ^{14}C mass/energy ratio as ^{14}C --but which is not ^{14}C --reaches detector.
3. Beam-line contamination: ^{14}C internally derived from an accelerator beam line component reaches detector.

B. Combustion/acidification background: ^{14}C introduced during production of CO_2 from sample.

1. Materials contamination: ^{14}C introduced from materials in combustion/acidification tube.
2. Tube contamination: ^{14}C introduced from combustion tube.

C. Graphitization background: ^{14}C introduced during the graphitization process.

1. Materials contamination: ^{14}C introduced from materials in reaction tube.
2. Tube contamination: ^{14}C introduced from reaction tube.

D. Pseudo ^{14}C - "dead" sample background: ^{14}C is present in a sample material that should not contain ^{14}C because of its geologic age.

1. Non- ^{14}C - "dead" sample: sample erroneously assumed to contain no ^{14}C .
2. Contaminated ^{14}C - "dead" sample: ^{14}C introduced into material that contains no ^{14}C .

More typically, an overall machine background in a tandem system is measured using some type of geologic graphite. As far as we are aware, the oldest reported ^{14}C value on geologic graphite is $69,030 \pm 1700$ BP (Schmidt, Balsley and Leach 1987) for a sample powdered and encapsulated under argon. A sample powdered in air showed somewhat higher values--ca. 58-60 ka BP. Typical values reported over the last decade by other AMS laboratories for the apparent ^{14}C age of geologic graphite range from 50-60 ka.

As noted above, backgrounds in samples converted from CO_2 to some type of graphitic carbon are, in most cases, significantly higher, increasing in relation to decreasing sample weights in the submilligram range. Currently, in most AMS systems, the sample conversion process involves two steps: combustion (non-

carbonates), or acidification (carbonates), for the production of CO₂ followed by the production of a catalytically reduced graphite or graphitic carbon. Researchers who have examined and published, in some detail, their studies of ¹⁴C background problems report sample conversion background values in the range of ca. 0.4 pMC (the equivalent of ca. 44 ka BP) to 0.07 pMC (ca. 58 ka) on 1-10 mg size samples (Gillespie and Hedges 1984; Vogel, Nelson and Southon 1987; Arnold et al. 1987; Schmidt, Balsley and Leach 1987; Gurfinkel 1987; Beukens 1992). These values represent the combined or "total system" (Vogel, Nelson and Southon 1987) combustion or acidification and graphitization background as defined in Table 1. Several of these studies indicated, or at least suggested, that below ca. 1 mg, ¹⁴C background concentrations in graphitic carbon samples increased as a function of decreasing sample weight.

The most detailed study of the effect of sample weight on ¹⁴C total system background for microsamples was undertaken by Vogel, Nelson and Southon (1987). Using anthracite coal as source material, their data indicated a constant level of contamination for samples >500 mg, but showed a general trend in which the measured ¹⁴C increased as a function of the decreasing sample weight below 500 mg. For samples >500 mg, the average total system background was ca. 0.5 pMC, which is equivalent to ca. 43 ka BP. Below 500 mg, the best fit of the ¹⁴C activity (% modern) to sample weight (mg graphitic carbon) relation was interpreted to indicate that a constant amount of contamination, equivalent to 2.2 ± 1.1 mg of modern carbon, was added to each microsample during combustion and/or graphitization. The inference was that, as the amount of material graphitized decreased, the continuous addition of contamination resulted in a progressive net decrease in the apparent age of the final graphitized product.

The sources of contamination that were evaluated (Vogel, Nelson and Southon 1987) for the combustion step included adsorbed CO₂ or CO gas on the walls of the Vycor tubing and residual traces of carbon in the CuO used as the source of the oxygen. In the graphitization process, the possibility of memory effects due to the exchange of adsorbed CO₂ or CO with sample CO₂ were examined, along with traces of carbon in the Fe catalyst. Finally, adsorption of CO₂ on the graphitized material and small amounts of contamination picked up during storage and handling (e.g., loading and pressing the graphitic carbon into a target holder) and placement of the target holder in the ion source were also considered. Based on their experiments, Vogel, Nelson and Southon (1987) concluded that between 60 and 70% of the contamination resulted from the release of CO₂ from the Vycor tubing at the high (900°C) temperatures used during combustion.

METHODS AND RESULTS

For our study we used wood collected in the early 1930s by staff members of the Department of Geology, University of California, Los Angeles, from what were reported to be Pliocene sediments in the Lake Manix basin, Mohave Desert, southern California (R. Berger, personal communication). We assumed that this wood sample would be ¹⁴C-free. Other than some erosion of the surface, presumably caused by sand blasting, the purported Pliocene-age wood is in very good physical condition. To examine its degree of contamination, a 5-g piece was subjected to successive acid (2N HCl), base (1N carbonate-ion free NaOH) and acid (2N HCl) (ABA), chemical pretreatment. During each step, the sample was heated to 90°C and that temperature was maintained for the times indicated below. Figure 1 shows the results of these measurements. In Figure 1, the data associated with "0" pretreatment indicates that the wood sample was not pretreated. Each succeeding pretreatment step consisted of subjecting the sample to 15-min acid, and then successive 45-min (pretreatment 1), 1-h (pretreatment 2), 2-h (pretreatment 3) and 3-h (pretreatment 4) base treatments--followed in each case by 15-min acid treatments--so that the pretreatment 4 sample underwent a total of 6 h, 45 min of base pretreatment. At the conclusion of each pretreatment regime, samples were treated with distilled H₂O to pH of 3 and dried in an oven maintained at 90°C. At least two replicate wood segments of 1.6 mg were taken for combustion and graphitization at each pretreatment step; data on replicate analysis are presented in Figure 1. We interpret the data in Figure 1 to indicate that, by the second repeat of the pretreatment regime (pretreatment

2), no additional measurable ^{14}C contamination was being removed by further ABA pretreatment in our wood sample.

Fig. 1. Influence of pretreatment on purported Pliocene-age wood sample on ^{14}C activity (pMC) and equivalent age (ka) for 1 mg weight graphitic carbon samples. In the x axis, 0 indicates no pretreatment.

Using the Pliocene-age wood that underwent at least eight successive ABA pretreatments, we examined the ^{14}C activity in graphitic carbon samples ranging from 10 to 1000 mg. Samples were combusted in 9-mm Vycor tubes in which CuO in wire form and Ag powder (99.999% pure) were placed. Prior to use, the tubes were heated in air to 900°C for at least 1 h and the copper oxide was heated in air at 800°C for at least 3 h. After evacuating to at least 10^{-4} Torr, the tubes containing the sample were sealed, placed in a muffle oven and slowly (not exceeding 5°C per min) brought up to 900°C and held at that temperature for 3 h. At temperatures above 500°C , the CuO undergoes pyrolytic decomposition, providing O_2 for oxidation. After 3 h, the furnace is slowly cooled to 650°C , where the temperature is maintained for 2 h before cooling to room temperature at a rate not exceeding 10°C per min. During the 650°C dwell period, the reduced copper combines with the halogens and catalyzes the conversion of any CO to CO_2 , NO_x to N_2 and SO_x to CuSO_4 . The prolonged cool-down period also promotes re-oxidation of the Cu, thereby eliminating excess oxygen (Boutton 1991).

The Pliocene-age wood yielded ca. 1 mg of C for each 1.6 mg combusted. Using this number as a guideline, appropriate weights of wood were combusted to yield a sufficient amount of CO_2 . Appropriate aliquots of CO_2 from these combustions were used in the graphitization experiments described below.

Graphitization was carried out at the University of California, Riverside Radiocarbon Laboratory (UCR) on an apparatus shown in Figure 2 using a method based on that described by Vogel, Nelson and Southon (1987). Combustion tubes were broken under vacuum, the CO_2 collected at liquid nitrogen temperatures and then passed through an ethanol-dry ice bath and a cuprin/cuprox furnace maintained at 600°C . The CO_2 was transferred into a 1-cc-volume reactor tube (6×50 mm) containing 2.5-3 mg of cobalt that had been reduced under hydrogen at 400°C for 1 h. After the CO_2 was transferred at liquid nitrogen temperatures and a vacuum of at least 10^{-4} Torr reached, hydrogen was added to each reactor tube in an amount twice plus 10% of the stoichiometric amounts needed for a complete reduction of the CO_2 . Liquid nitrogen was removed, and after the CO_2 reached room temperature, a heater was placed around the catalyst portion of each reactor and the temperature raised to and maintained at $620 \pm 4^{\circ}\text{C}$. A cold trap of ethanol and dry ice was used to trap out water produced during the reaction. Pressure inside the reactor tube, which began at ca. 900 Torr for a 1000- μg sample and ca. 12 Torr for a 10-mg sample, was recorded every 10 min. A plot of pressure versus time documented the completeness of the graphitization reaction by recording the pressure for each sample inside the reactor tube. The typical residual pressure at the completion of the reaction was ca. 100 Torr for a 1000- μg sample and ca. 5 Torr for a 10- μg sample. The graphite-coated cobalt was stored in glass vials until it was loaded into aluminum sample holders for AMS ^{14}C measurement.

Fig. 2. Diagram of reactor apparatus used for the graphitization of CO_2 on a cobalt powder catalyst

AMS ^{14}C measurements were done at the Center for Accelerator Mass Spectrometry (CAMS), University of California Lawrence Livermore National Laboratory (LLNL) (Davis et al. 1990; Southon et al. 1990; 1992). Experiments carried out with the CAMS FN tandem accelerator using a modified GIC Model 846 ion source determined that the machine background as defined by Schmidt, Balsley and Leach (1987), i.e., with the ion source closed off from the remainder of the beam line, is 1104 ka (0 counts in 20.5 min of counting). With the ion source containing an empty aluminum target holder open to the beam transport system, a ^{14}C count rate equivalent to .009 pMC (74 ka) was measured. The average ($N=2$) ^{14}C value obtained at LLNL on natural graphite used by the UCR radiocarbon laboratory to monitor contamination from loading graphite into their target holders is $64,460 \pm 3200$ BP (CAMS-12338; $64,500 \pm 1800$ BP and CAMS-12339; $58,800 \pm 1000$ BP). The average ($N=7$) ^{14}C value obtained on graphite powder used by the LLNL laboratory is $57,900 \pm 1500$ BP ($.074 \pm .014$ pMC).

Figure 3 presents the results of the ^{14}C analysis of Pliocene-age wood pretreated in the manner described above with sample weights of the resulting graphitic carbon ranging from 10 to 1000 mg. This data is compatible with the results reported previously by Vogel, Nelson and Southon (1987; Fig. 2) except that there is about a 45% downward offset in our background values. Our 1- μg Pliocene wood mean ($N=19$) is $52,140 \pm 440$ BP; the lowest ^{14}C value obtained on a 1-mg sample was $56,150 \pm 540$ BP (0.09 pMC) whereas the average value for two 10 μg samples was ca. 20 ka (ca. 8 pMC). Accepting the Vogel, Nelson, and Southon (1987) view that the most probable interpretation of the data is a constant addition of modern carbon contamination, the best fit of our ^{14}C activity/sample weight data indicates the constant addition of the equivalent of $1.0 \pm 0.4 \mu\text{g}$ of modern carbon.

Fig. 3. Relation of sample weight on ^{14}C activity (pMC) and equivalent age (ka) from 10-1000 μg . = linear regression using least squares method to fit trend of data points. - - - = 95% confidence intervals around regression line.

CONCLUSION

The total background level present in a catalytically reduced graphitic carbon AMS ^{14}C measurement is a sum of three elements: 1) residual in-situ sample contamination--the degree of contamination remaining in a sample not removed by physical and chemical pretreatment; 2) sample conversion contamination--contamination introduced during combustion or acidification and graphitization; and 3) machine background--beam-line contamination, ion identification or detector anomalies.

This study addresses part of the second component of ^{14}C backgrounds in AMS systems, that which is contributed during the sample conversion process. Our data are consistent with the observations of Vogel, Nelson and Southon (1987) in that this contamination is consistent with a constant level of modern contamination being added. At the same time, we have demonstrated a significant overall net reduction in background values from levels previously reported by Vogel, Nelson and Southon for samples in the 10 to 1000 μg range. The next step in our program will be to examine the relationship between sample weight and ^{14}C activity in contemporary standards.

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