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RADIOCARBON DATING ORGANIC RESIDUES AT THE MICROGRAM LEVEL

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The relationship between submilligram sample size and ^{14}C activity for sample blanks (wood from Pliocene sediments) and a contemporary standard (oxalic acid [I]) for catalytically-reduced graphitic carbon have been examined down to 20 micrograms. The mean age of our 1 milligram wood sample blanks is now about 51.3 ka (0.168 pMC) while the mean for 20 microgram sample blanks is about 42.9 ka. So far, our lowest value for a 1 milligram wood sample blank is about 60.5ka (0.056 pMC). We have determined a mean ^{14}C age of about 9.4 ka from a suite of seven organic extracts from hair, bone and matting from a mummified human skeleton from Spirit Cave, Nevada. These data indicate that the Spirit Cave human is the third, oldest directly-dated, human skeleton currently known from North America.

1. Introduction

Previous studies of sample blanks in AMS systems employing catalytically-reduced graphitic carbon noted the significant increase in backgrounds levels with reductions in submilligram sample weights of graphitized carbon. Vogel *et al.* [1] proposed that background mass dependence resulted from the introduction of a constant amount of modern carbon during the preparation of the graphitic carbon from CO_2. Their suggested model was that, as a constant amount of younger contamination is added, there is a corresponding progressive net increase in ^{14}C activity which translates into an increasing younger net apparent ^{14}C age of sample blanks as a function of decreasing sample weight.

At least one other laboratory has reported the same type of mass dependence in sample blanks in addition to increasing variability as a function of sample size [2].

Using anthracite coal, Vogel *et al.* [1] determined that for samples below about 500 micrograms, the best fit of ^{14}C activity to sample weight indicated that the equivalent of 2.2 ± 1.1 micrograms of modern carbon was being added. In their study, the activity of the "modern" ^{14}C contamination was assumed to be equivalent to the defined contemporary activity of a modern ^{14}C standard such as 0.95 oxalic acid [I] or 0.74 oxalic acid [II]. The sources of contamination which they evaluated for their combustion step was adsorbed CO or CO_2 on the walls of the Vycor tubing and residual traces of carbon in CuO used as the oxygen source. They also noted memory effects in the vacuum system and residual traces of carbon in the Fe used as the catalyst during the graphitization step. They concluded ty ,that 60% to 70% of the contamination occurred as a result of the release of adsorbed CO_2 from the Vycor tubes used in the combustion step.

2. UCR/LLNL

We have previously examined the relationship between sample size and ^{14}C activity in milligram and submilligram samples for both sample blanks and modern standards [3,4]. For sample blanks, we utilized wood recovered from Pliocene sediments and for modern standards ANU sucrose and oxalic acid [I] (OX[I]). In our initial study, our results supported the observations of Vogel *et al.* [1], i.e., that for samples below 500 micrograms, the ^{14}C background values increased as a function of sample weight. However, the best fit of our data characterized the constant addition of the equivalent of 1.03 ± 0.4 micrograms of modern carbon, approximately half of that reported by Vogel *et al.* [1]. The mean (N=19) ^{14}C age of our 1 milligram sample was about 52.1 ka and our lowest ^{14}C value was 56.1 ka (0.09 pMC). The mean (N=2) ^{14}C value for our smallest samples (10 micrograms) was about 20.3 ka (9 pMC). For the ANU samples greater than 100 micrograms, our measured ^{14}C values were within $\pm 1.0\%$ of the expected activity [5]. However, for ANU samples below 100 micrograms, the ^{14}C activity was below the expected value by as much as 2% on a 40 microgram sample.

In an attempt to further reduce potential contamination for submilligram size samples, a new vacuum apparatus was constructed which included the use of a turbo molecular pump with a dry diaphragm backing pump and stainless steel pressure recording transducers. Before initial use, the glass line was washed with isopropyl alcohol and HPLC grade water. We also have employed exclusively trace metal grade reagents in the preparation of samples. Using this apparatus and reagents, we measured ^{14}C activity in wood blanks and OX[II] samples in the range from 1000 micrograms to 20 micrograms.

Figure 1 presents the results for our wood blanks. The mean (N=26) ^{14}C value for 1 milligram samples is 51.3 ka (0.168 pMC); the lowest ^{14}C value so far achieved is 60.5 ka (0.056 pMC). The mean (N=2) apparent ^{14}C age for the 20 microgram wood samples is 42.9 ka. The solid line in Figure 1 shows the relationship between sample weight and ^{14}C activity to fit the trend of the data points. In this representation, we estimate a constant addition of modern carbon contamination as approximately equivalent to 0.1 ± 0.05 micrograms of modern carbon. However, our current data makes it difficult to find a best fit of our current data using the model of an inverse relationship between ^{14}C activity and sample weight below about 100 micrograms unless we also include a constant term of 0.15 ± 0.05 pMC.

Figure 2 represents the relationship of sample weight and ^{14}C activity for OX[II]. Above 300 micrograms, all OX[II] samples fell within the $\pm1\%$ range (dashed line) of 103.98 pMC, the expected OX[II] value [6]. Below about 300 micrograms, the results show decreasing ^{14}C activity, though the magnitude of this decrease varies from run to run. There are several possible explanations for these results, including contamination from dead carbon, size-dependent isotopic fractionation in the graphitization step, or fractionation in the ion source itself. We plan future studies to identify the source(s) of these effects.

3. Dating Organic Residues: Spirit Cave Human

Applying our microgram AMS ^{14}C capabilities, we have undertaken ^{14}C measurements on a suite of hair, bone, and woven plant samples from a human burial recovered from Spirit Cave, Churchill County, Nevada [7, 8]. From the time of its excavation in 1940, it has been regarded as being of late Holocene age--somewhere in the range of 1500 to 2000 BP [9]. Table 1 presents the results of the seven ^{14}C values obtained on this burial measured over a period of two years using two different graphite lines. Good agreement between the two sets of measurements suggests that our size dependent backgrounds have been correctly calculated and applied. Three of these values were obtained on total amino acid fractions extracted from plant materials. We are not aware of any previous published ^{14}C values on amino acids extracted from plants.

Based on these data, the Spirit Cave human has been assigned an early Holocene age of about 9.4 ka and is at present the third oldest directly dated human skeleton in North America. Only the Midland [10], Anzick [11], and Mostin [12] human skeletons have older dates assigned to them which are currently considered by most investigators to be valid. Other North American human bone samples previously assigned older ages have been reevaluated and shown to be of middle to late Holocene age [13]. For Anzick and Mostin, the age assignment is based on ^{14}C data; for Midland, uranium series data have been employed.

4. Conclusion

The continuing examination of laboratory procedures has reduced levels of contamination in catalytically-reduced graphitic carbon samples to the equivalent of 0.1 ± 0.05 micrograms of modern carbon. In one case, we have achieved an equivalent age of approximately 60.5 ka on a 1 milligram sample of wood recovered from Pliocene sediments. We also have developed techniques to obtain AMS ^{14}C measurements on as little as 20 micrograms of carbon. Using these techniques, we have obtained a suite of ^{14}C values which documents an early Holocene age for the Spirit Cave human.

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Table 1

Radiocarbon determinations on organic extracts from human bone and hair: Spirit Cave, Nevada

sample type	fraction	sample number	^{14}C age (BP)	$\delta^{13}C$ (‰ PDB)
hair[a)]	total organics	UCR-3261-2/CAMS-12354	9360±60[c)]	-18.6
		UCR-3261-2/CAMS-14224	9450±60[c)]	-18.6
	total amino acids	UCR-3261-4/CAMS-12353	9350±70[c)]	-18.0
bone[a)]	total amino acids	UCR-3260/CAMS-12352	9430±60[c)]	-15.7
mat[b)]	total amino acids	UCR-3323/CAMS-24199	9430±70	-22.6
tule[b)]	total amino acids	UCR-3324-1/CAMS-24194	9410±60	-20.2
		UCR-3324-2/CAMS-24197	9460±60	-21.9

a) Old graphite line.
b) New graphite line.
c) Reference [7].

FIGURE CAPTIONS

Figure 1. Relationship of graphitized sample weight (in micrograms) to ^{14}C activity (in percent modern carbon [pMC]) for Pliocene wood sample: 20 to 1000 micrograms. Above about 100 micrograms, the best fit of the data indicates a constant addition of 0.1±0.05 micrograms of modern carbon. Below 100 micrograms, there appears to be a constant term which is equal to 0.15±0.05 pMC.

Figure 2. Relationship of graphitized sample weight (in micrograms) to ^{14}C activity (pMC) for OX[II] contemporary standard: 20 to 1000 micrograms. The dashed line represents ±1% of 103.98 pMC. The typical counting error for these measurements have been noted for a 100 milligram size sample.

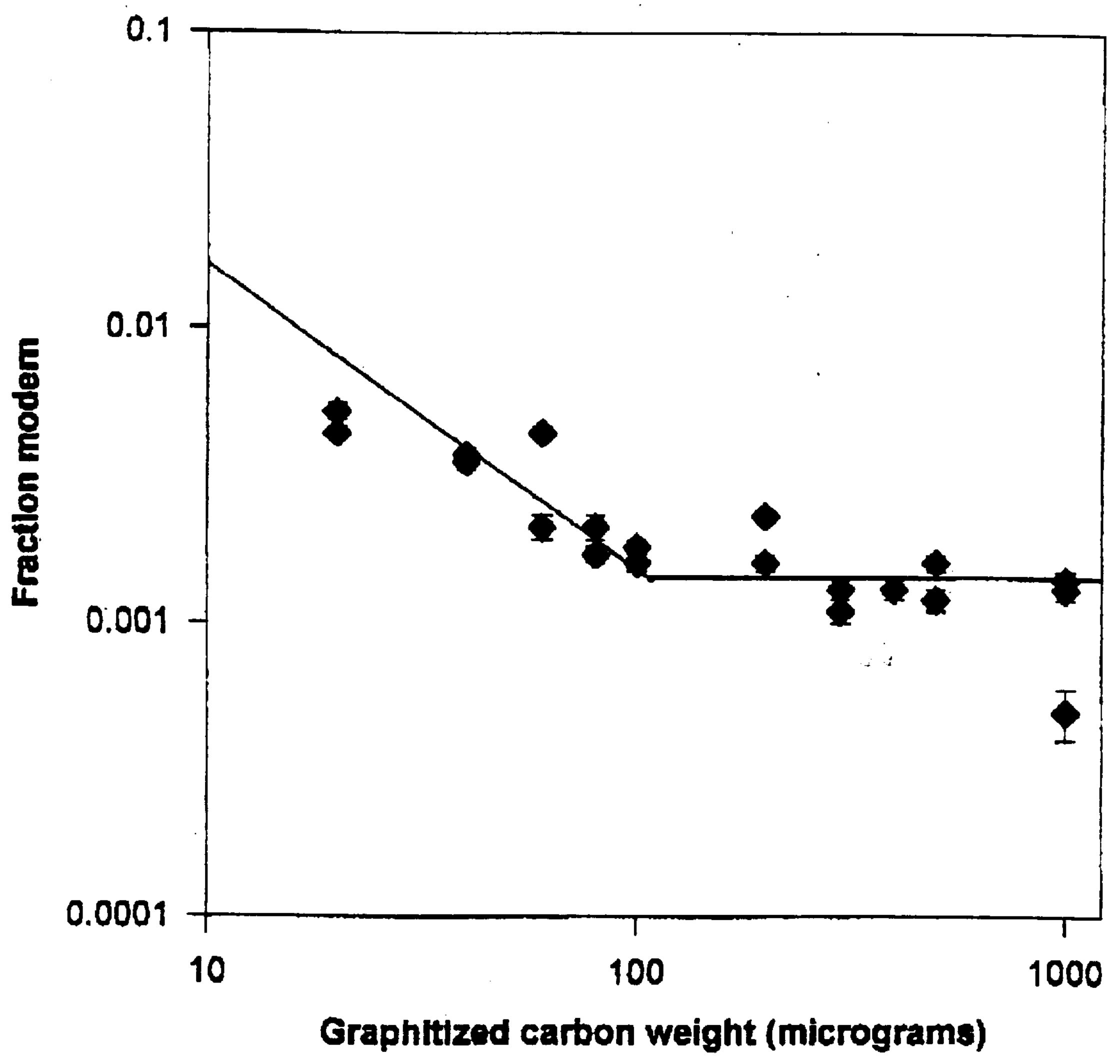
0.1
0.01
0.001
0.0001
Fraction modern
10
100
1000
Graphitized carbon weight (micrograms)

FIGURE 1

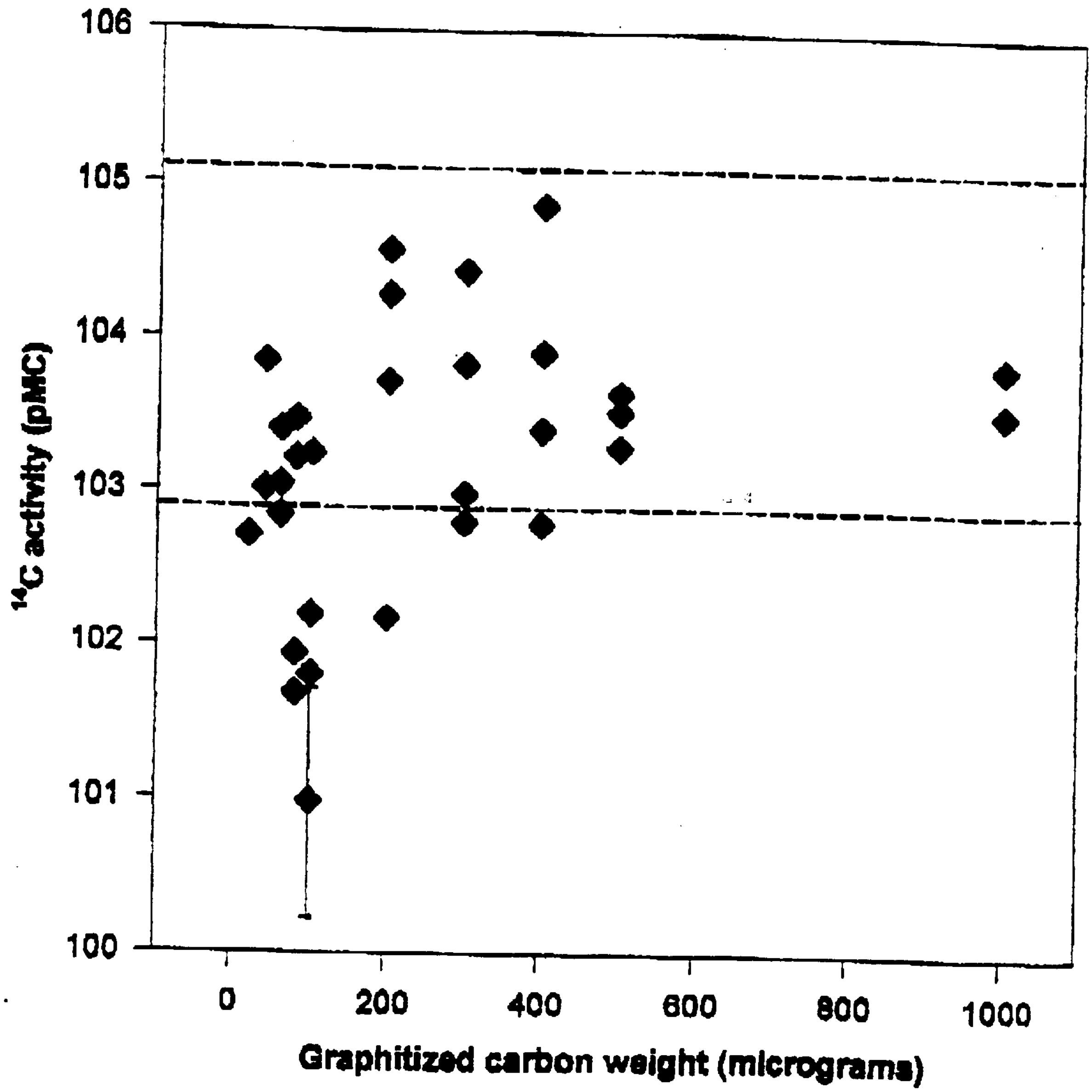
106
105
104
103
102
101
100
^{14}C activity (pMC)
0
200
400
600
800
1000
Graphitized carbon weight (micrograms)

FIGURE 2

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