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Radiocarbon dating organic residues at the microgram level

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Abstract

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 51.6 ka (0.162 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 60.5 ka (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 naturally mummified human skeleton from Spirit Cave, Nevada. These data indicate that the Spirit Cave human is the third oldest directly-dated human skeleton currently reported 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 previously 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 NBS [NIST] 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 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 submilligram sample studies

We have previously examined the relationship between sample size and ^{14}C activity in milligram and submilligram samples for wood sample blanks (wood recovered from what were reported as Pliocene sediments) and modern standards (ANU sucrose) [3,4]. 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 [4]. 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 our wood blanks and oxalic acid I (OX[I]) samples in the range from 1000 micrograms to 20 micrograms. Since the $^{14}C/^{12}C$ ratio for OX[I] is very close to that of the current atmosphere, these samples are insensitive to contamination by contemporary carbon and allow us to evaluate the effect of dead carbon contamination. The equivalant mass of modern and dead contaminants can then be incorporated into an algorithm similar to those of Donahue et al. [5] to calculate ^{14}C ages for microgram samples.

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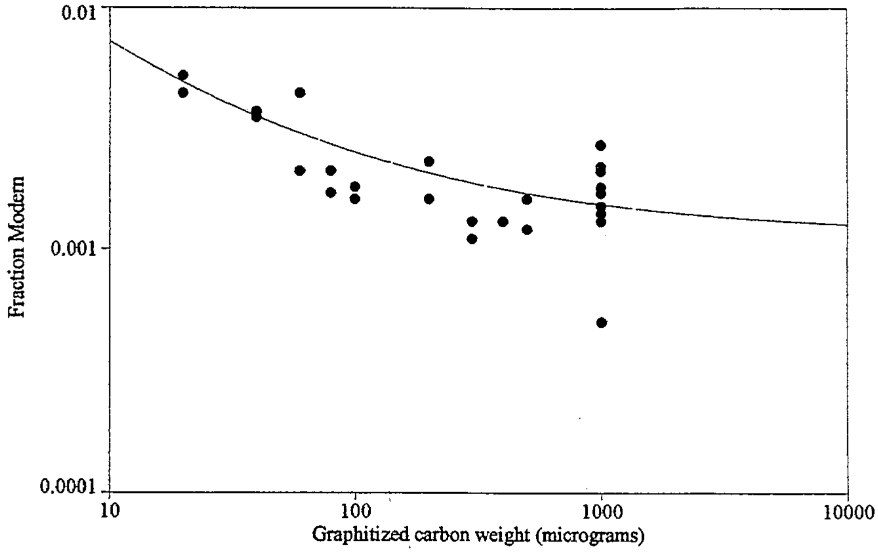

Fig. 1. Relationship of graphitized sample weight (in micrograms) to ^{14}C activity (in fraction modern carbon) for wood sample blanks: 20 to 1000 micrograms.

Our Pliocene wood blanks were pretreated with at least eight successive ABA [acid (2N HCl), base (1N carbonate-ion free NaOH) and acid (2N HCl)] treatments. At the conclusion of the ABA pretreatment, samples were treated with distilled H_2O to pH of 3 and dried in an oven maintained at 90°C. Combustion and graphitzation were carried out using procedures previously described [3] except that iron rather than cobalt was used as the catalyst.

Measurements of $^{14}C/^{13}C$ ratios were carried out at the Laboratory for Accelerator Mass Spectrometry, University of California Lawrence Livermore National Laboratory. The spectrometer, ion source and data acquisition systems have been described elsewhere [6–8]. For these experiments, ion source currents were typically 100–150 μA of $^{12}C^-$. Foil stripping at 6.5 MV yielded 2–3 μA of analyzed $^{13}C^{4+}$ beam, with ^{14}C count rates of 330–500 Hz on modern samples. Data analysis algorithms, including size-dependent corrections for contaminant carbon background, were based on those of Donahue [5].

Fig. 1 presents the results for our Pliocene wood blanks. The mean ($N = 15$) ^{14}C value for 1 milligram samples is 51.6 ka (0.162 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 Fig. 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 0.08 ± 0.02 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 0.12 ± 0.02 pMC. The source of this constant term is not clear but it could arise if our wood blank was not truly ^{14}C "dead" either due to a finite age or the result of the presence of residual contamination not removed by chemical pretreatment. Alternatively, it may be due to a ^{14}C count rate from residual ion source contamination.

Fig. 2 represents the relationship of sample weight and ^{14}C activity expressed as pMC for OX[I] aliquots of varying sizes, normalized to 1 mg OX[I] standards. Above 300 micrograms, all but one OX[I] samples fell within the

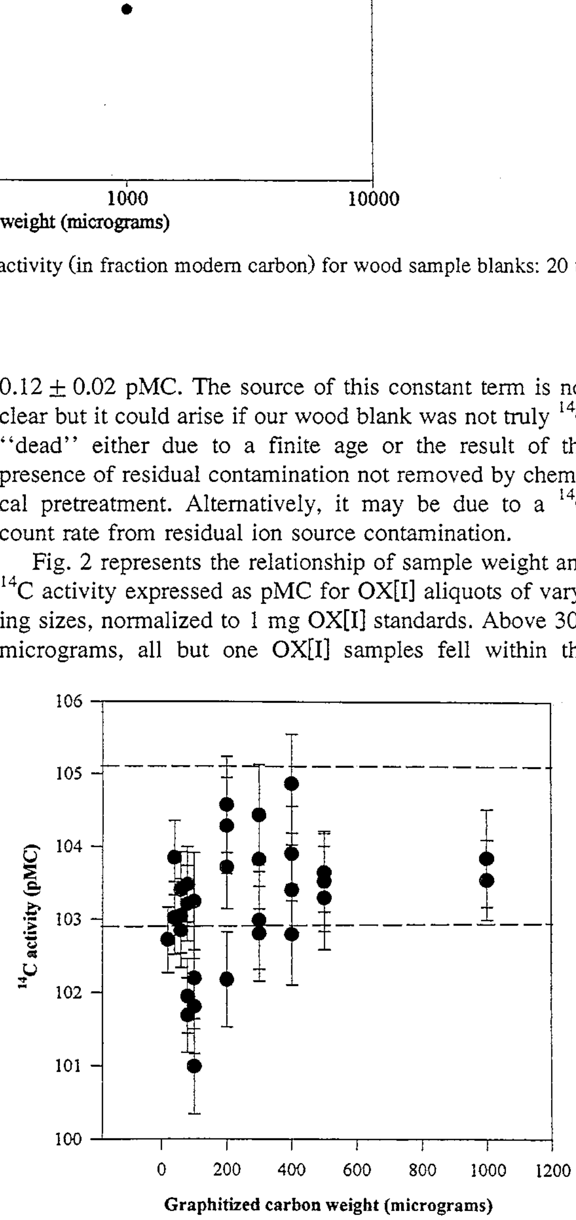

Fig. 2. Relationship of graphitized sample weight (in micrograms) to ^{14}C activity (pMC) for OX[I] contemporary standard: 20 to 1000 micrograms. The dashed line represents ±1% of 103.98 pMC.

$\pm 1\%$ range (dashed line) of 103.98 pMC, the expected OX[I] value [9]. 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 current AMS ^{14}C procedures, we have undertaken ^{14}C measurements on a suite of hair, bone, and woven plant samples (mat and tule) from a human burial recovered from Spirit Cave, Churchill County, Nevada [10,11]. 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 [12]. 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. Samples processed on the "old" and "new" graphite lines are identified in footnotes a) and b) in Table 1. The "new" graphite line refers to that which has incorporated the modifications previously described. In addition, all samples processed on the "new" graphite employed iron as the catalyst. 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 and further details will be published elsewhere.

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 ^{14}C-dated human skeleton in North America so far reported. Only the Anzick (Montana) [13], Buhl (Idaho) [14] and Mostin (California) [15] 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 are widely accepted as middle to late Holocene in age [16].

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, hair and plant fiber from 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 using cobalt catalyst.
[b] New graphite line using iron catalyst.
[c] Ref. [10].

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