

**RADIOCARBON VARIATIONS IN CONSECUTIVE SINGLE  
RINGS OF A 4000-YEAR-OLD PINE FROM THE BRITISH ISLES**

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**ABSTRACT.** At the Ninth International Radiocarbon Conference a paper was presented concerning possible short-term  $^{14}\text{C}$  variations in 4000-year-old red deer antlers (*Cervus elaphus*) found in Neolithic flint mines in Norfolk, England (Burleigh and Hewson, 1980). It was argued, on archaeological grounds, that the true age of the samples varied by a few years at most. Their radiocarbon ages, however, varied by a considerably greater amount than could be explained by the errors in the measurements. Duplication of the measurements confirmed this unexpected variation.

Farmer and Baxter (1972) claimed a significant correlation of atmospheric  $^{14}\text{C}$  levels in the northern hemisphere with sunspot number based on radiocarbon assay of single tree rings for the period 1829 to 1865. In contrast, Stuiver (1978) stated that a series of single-year Douglas Fir measurements did not show a statistically significant periodicity.

This paper reports measurements made on a series of single-year dendrochronologic samples of approximately the same age as the red deer antlers, which have been carried out at the British Museum Research Laboratory. The results show that the variation in  $^{14}\text{C}$  between rings is not statistically significant; some other explanation must be sought for the anomalous antler measurements.

*The dendrochronological sample, its preparation and pretreatment*

A suitable sample of wood for the measurements was supplied by the Palaeoecology Laboratory of the University of Belfast. It consisted of a transverse segment approximately 5cm thick of the trunk of a pine on which about 220 growth rings were visible. It had been recovered from Sharvogues Bog, County Antrim, and a sample from rings 11 to 20 had been dated by the Belfast Radiocarbon Laboratory to  $4015 \pm 45$  BP (UB-624, Smith, Pearson, and Pilcher, 1973). The mean width of the rings was about 1mm and rings 21 to 61 inclusive only were considered large enough to be accurately separated.

It was established by sanding both horizontal faces of the segment and by counting the rings on seven separate radii, that all the rings of interest were intact and continuous. By working carefully with a chisel from the outer rings towards the center, it was possible to separate the rings at the boundary between the spring wood and the denser late wood growth of the preceding year. The material removed at the interface between rings was discarded to minimize cross-contamination. In this manner, samples of each year's growth were obtained, which weighed between 6gm and 60gm with an estimated cross-contamination between adjacent rings of at most 3 percent.

The wood was in very good condition and showed no sign of decay. Thus, it was possible to grind the material from each ring to a fine powder (less than 1.2mm). Sufficient material was available from rings 49 to 60 for two independent measurements to be made and so the wood from these rings was divided into two samples at this stage.

It is generally recognized that the best pretreatment method for wood samples is to oxidize and dissolve all but the cellulose component, thus ensuring the destruction and removal of all contamination (Long and others, 1979; Cain and Suess, 1976; Tans, de Jong, and Mook, 1978). However, most of the sample material is destroyed with the contaminants in this method. In view of the limited quantity of material available, it was decided that a less drastic technique should be used. Experience at this laboratory, which coincides with the recommendations of other workers (Long and others, 1979; Jansen, 1972), suggests that a Soxhlet extraction is highly effective in removing contamination and, in particular, in removing the resin component from pine wood without destroying valuable sample material. For this reason, the technique was used in this project.

Acetone was selected as the solvent because it can be readily driven off after pretreatment. Preliminary experiments demonstrated that the material extracted from the samples had a noticeable absorbance relative to acetone in the 350 to 400nm region of the spectrum. Thus, this phenomenon was used to monitor the progress of the extraction procedure. It was determined in this manner that a minimum of 24 hours extraction was sufficient to remove the resin component.

The samples were dried in groups for an initial period of a minimum of 24 hours in a hot oven. They were then dried individually for 24 hours at 80°C in a vacuum oven to ensure that acetone driven off from one sample was not reabsorbed by another. They were then stored individually in air-tight boxes pending chemical synthesis.

#### *Chemical synthesis and counting procedure*

At this radiocarbon laboratory, as at many others, samples are converted to benzene and their <sup>14</sup>C activity is estimated by liquid scintillation counting. The methods used follow those first described in the 1960's (Tamers, 1960; 1965; Noakes, Kim, and Stipp, 1965) with minor modifications and innovations (Burleigh, 1972; 1974). Yields from the chemical conversion are about 95 percent and the purity of the benzene produced is comparable with that prepared by other laboratories (Fraser and others, 1974). The samples for this experiment were synthesized following routine procedures; the carbon dioxide initially produced was sub-sampled for measurement of stable carbon isotopes.

A suitable quantity of PPO was dissolved in scintillation grade toluene to give a final concentration of 4gm per liter when 0.5ml of the solution was added to 5.5ml of benzene. It was intended to measure the specific activity of the samples in large groups to facilitate direct comparison of their counting rates. As it was not possible to devote more than a part of the laboratory's output to the project, this made it necessary to store most of the samples, in the form of benzene, for some time whilst work on the remainder of the group was completed. In such a situation, there is a risk of losing some benzene by evaporation. Therefore, it was decided to flame-seal the sample cocktails immediately

after synthesis of the benzene in low potassium glass ampules and to count them in this form. Previous experiments had shown that the variation of the background count rate of the ampules was comparable with that of the glass vials normally used for low level work whilst the stability of the counting rate of such sealed samples had been demonstrated over a number of years. In four cases, the flame seals proved to be inadequate and the samples had to be discarded.

A number of oxalic acid modern and background reference samples were synthesized for the project and made up in a similar manner to the samples. In addition, ten quenched reference samples were made by diluting  $^{14}\text{C}$  labelled toluene to produce a PPO/toluene/benzene cocktail and adding appropriate quantities of acetone.

#### RESULTS

The results in this paper have been subjected to a statistical analysis of variance. In this technique, the squares of the (1 sigma) measurement errors for related measurements are added together to form the total sum of squares (corrected to the mean of the measurements). A single  $^{14}\text{C}$  measurement is taken to be the age calculated from the result of one 100-minute count of a benzene sample relative to background and modern standards, after correction for fractionation effects and for the age effect for the ring from which the sample was drawn relative to the first year of growth of the tree.

The contribution to the sum of squares of the various factors in the experiment (such as ring to ring variation or variation between duplicates) is calculated. For example, the contribution of nine pairs of duplicate measurements is found by adding together nine terms which are each the square of the difference of one result of each pair from the mean of each pair. The factor sums of squares are subtracted from the total to give the residual sum of squares.

The mean square for each factor and for the residual is calculated by dividing the sum of squares by the appropriate number of degrees of freedom. The standard deviation of the residual is the square root of the mean square and is the best estimate of the underlying precision of the measurements. If the *f* ratio for a factor, *ie*, the ratio of the factor mean square to the residual mean square, is significantly larger than one, then that factor has had a detectable effect on the variation between the measurements. The significance point is determined by reference to tables of the F distribution. Tables of the F distribution and a full explanation of the analysis of variance technique can be found in most statistical textbooks on the design and analysis of experiments (see eg, Snedecor and Cochran, 1967).

The  $\delta^{13}\text{C}$  values of the carbon dioxide produced in the synthesis process lay in the range  $-24\%$  to  $-25.5\%$ , which is in good agreement with the value of  $-25.1\%$  obtained by the Belfast laboratory. An analysis of variance of the measurements made on the rings from which two samples were available is given in table 1. The standard deviation of the

TABLE I  
 An analysis of variance of  $\delta^{13}\text{C}$  measurements made on the duplicate samples from rings 49 to 60 inclusive  $F_{11,12,5 \text{ percent}} = 2.72$

| Source        | Degrees of freedom | Sums of squares | Mean square | Standard deviation | f ratio |
|---------------|--------------------|-----------------|-------------|--------------------|---------|
| Between rings | 11                 | 1.61            | .15         | .38                | 2.0     |
| Residual      | 12                 | 0.88            | .07         | .27                |         |
| Total         | 23                 | 2.49            |             |                    |         |

residual within ring variation agrees with the precision of measurement of the mass spectrometer of  $\pm 0.25\%$ . The f ratio is not large enough to be considered statistically significant but, nonetheless, suggests that there is a ring to ring variation of about  $\pm 0.25\%$ . Such a variation is equivalent to a  $\pm 4$  year error in the radiocarbon age estimate which is negligible in comparison with other measurement errors. Hence, whilst the  $\delta^{13}\text{C}$  value of sample was monitored for gross deviations from the expected value, the overall mean value of  $-24.7\%$  was used as the correction factor in subsequent age calculations.

The samples were counted in four batches. Those samples in the first two batches, consisting of duplicated measurements of rings 49 to 60, were counted for  $20 \times 100$  minute periods each, whilst those for the third and fourth batches consisting of rings 32 to 48 and 61 and 21 to 30 were counted for  $15 \times 100$  minutes each. The results of the age measurements are listed in table 2 and plotted in figure 1 and have been age corrected to the first year of growth of the tree. The means

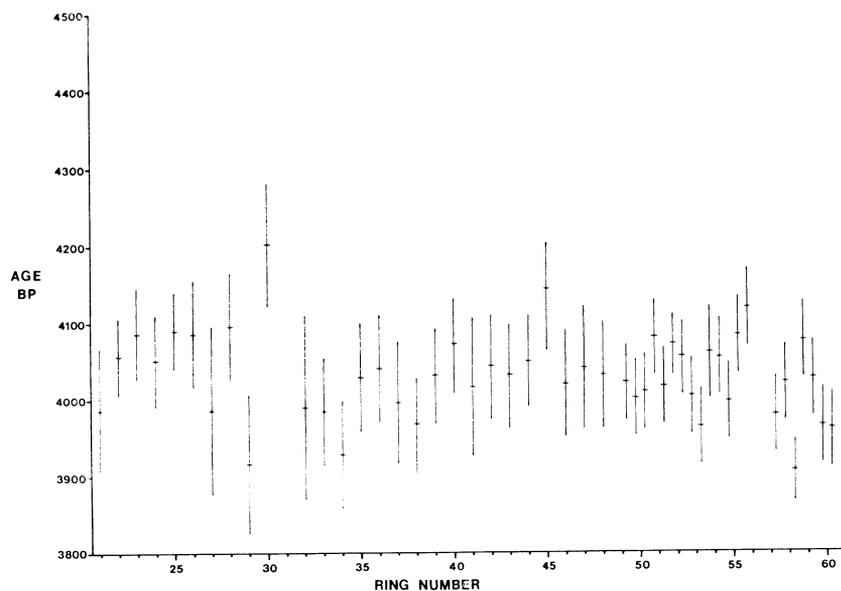


Fig 1. Age measurements and one sigma error bars plotted against ring number.

TABLE 2  
 Age measurements corrected to the first year of growth of the tree.  
 Samples from rings 31, 49a, 56b, and 57a could not be measured (see text)

| BM no. | Ring no. | Age BP | Age PC | Error |
|--------|----------|--------|--------|-------|
| 1574   | 21       | 3985   | 2035   | 80    |
| 1573   | 22       | 4056   | 2106   | 50    |
| 1572   | 23       | 4086   | 2136   | 60    |
| 1571   | 24       | 4051   | 2101   | 60    |
| 1570   | 25       | 4090   | 2140   | 50    |
| 1569   | 26       | 3985   | 2035   | 70    |
| 1568   | 27       | 3972   | 2022   | 110   |
| 1567   | 28       | 4096   | 2146   | 70    |
| 1566   | 29       | 3916   | 1966   | 90    |
| 1565   | 30       | 4203   | 2253   | 80    |
|        | 31       |        |        |       |
| 1563   | 32       | 3990   | 2040   | 120   |
| 1562   | 33       | 3989   | 2039   | 70    |
| 1561   | 34       | 3835   | 1885   | 70    |
| 1560   | 35       | 4029   | 2079   | 70    |
| 1559   | 36       | 4040   | 2090   | 70    |
| 1558   | 37       | 3996   | 2046   | 80    |
| 1557   | 38       | 3968   | 2018   | 60    |
| 1319   | 39       | 4032   | 2082   | 60    |
| 1318   | 40       | 4074   | 2124   | 60    |
| 1317   | 41       | 4016   | 2066   | 90    |
| 1316   | 42       | 4044   | 2094   | 70    |
| 1315   | 43       | 4034   | 2084   | 70    |
| 1314   | 44       | 4050   | 2100   | 60    |
| 1313   | 45       | 4145   | 2195   | 60    |
| 1312   | 46       | 4020   | 2070   | 70    |
| 1311   | 47       | 4041   | 2091   | 80    |
| 1310   | 48       | 4032   | 2082   | 70    |
|        | 49a      |        |        |       |
| 1297   | 49b      | 4023   | 2073   | 50    |
| 1286   | 50a      | 4001   | 2051   | 50    |
| 1298   | 50b      | 4011   | 2061   | 50    |
| 1287   | 51a      | 4042   | 2092   | 50    |
| 1299   | 51b      | 4017   | 2067   | 50    |
| 1288   | 52a      | 4073   | 2123   | 40    |
| 1300   | 52b      | 4056   | 2106   | 50    |
| 1289   | 53a      | 4005   | 2055   | 50    |
| 1301   | 53b      | 3964   | 2014   | 50    |
| 1290   | 54a      | 4062   | 2112   | 60    |
| 1302   | 54b      | 4055   | 2105   | 50    |
| 1291   | 55a      | 3994   | 2044   | 50    |
| 1303   | 55b      | 4084   | 2134   | 50    |
| 1292   | 56a      | 4120   | 2170   | 50    |
|        | 56b      |        |        |       |
|        | 57a      |        |        |       |
| 1305   | 57b      | 3980   | 2030   | 50    |
| 1294   | 58a      | 4023   | 2073   | 50    |
| 1306   | 58b      | 3909   | 1959   | 40    |
| 1295   | 59a      | 4077   | 2127   | 50    |
| 1307   | 59b      | 4028   | 2078   | 50    |
| 1296   | 60a      | 3965   | 2015   | 50    |
| 1308   | 60b      | 3961   | 2011   | 50    |
| 1309   | 61       | 4030   | 2080   | 90    |

of each batch are 4036, 4008, 4020, and 4044 BP, respectively, and are in good agreement with the result obtained by the Belfast Laboratory of 4030 BP when it is corrected in a similar manner.

The error estimates are calculated from the observed reproducibility of the sample, background, and modern count rates (Hewson and Hall, 1980) with an additional allowance to cover any small errors in the preparation of the samples. All the samples were counted against the same set of reference standards and, therefore, the age estimates are correlated. The following analysis takes advantage of this correlation and compares only the precision and not the absolute accuracy of the results.

Table 3 is analysis of variance of the duplicated results from the first and second batches. The figures in the column headed, standard deviation, can be interpreted as the real radiocarbon age error. Thus, for example, the underlying precision of the measurements is estimated to be  $\pm 46$  years. It is clear that the variation between duplicates, equivalent to an age error of  $\pm 38$  years, is rather less than would be expected. The difference is not significant. Thus, there is no evidence to suggest that the residual error has been overestimated, but rather, the results reinforce the belief that radiocarbon measurements made at this laboratory can be precisely reproduced.

Table 4 is an analysis of variance of all the batches. It has been constructed by scaling the residual variation for the third and fourth batches to take account of the shorter counting time and generally smaller sample sizes and pooling the result with the residual and between duplicates variation from table 3. The variation between rings has been pooled in a like manner and, therefore, this table provides the

TABLE 3  
An analysis of variance of the duplicate measurements made  
in the first and second batches

| Source             | Degrees of freedom | Sums of squares | Mean square | Standard deviation | f ratio |
|--------------------|--------------------|-----------------|-------------|--------------------|---------|
| Between rings      | 8                  | 25100           | 3140        | 58                 | 1.5     |
| Between duplicates | 9                  | 13100           | 1460        | 38                 | 0.7     |
| Residual           | 342                | 712400          | 2080        | 46                 |         |
| Total              | 359                | 750600          |             |                    |         |

TABLE 4  
An analysis of variance of all the measurements after suitable scaling  
to take account of differences in counting time and sample size

$F_{35,742,5}$  percent = 1.44

| Source        | Degrees of freedom | Sums of squares | Mean square | Standard deviation | f ratio |
|---------------|--------------------|-----------------|-------------|--------------------|---------|
| Between rings | 35                 | 90900           | 2600        | 51                 | 1.26    |
| Residual      | 742                | 1533600         | 2070        | 45                 |         |
| Total         | 777                | 1624500         |             |                    |         |

best summary of the results of the experiment. As can be seen, there is a small excess variation between rings but not sufficient as to be judged statistically significant. The excess variation, 2600-2070, is equivalent to an additional error in a radiocarbon age measurement of  $\pm 23$  years which is small compared to the usual measurement error of about  $\pm 50$  to  $\pm 70$  years. The excess variation in the antler measurements was equivalent to an additional error of  $\pm 63$  years.

#### CONCLUSION

This study has demonstrated the absence of substantial short-term  $^{14}\text{C}$  variations in a 4000-year-old pine. The sensitivity of the experiment could detect any variation large enough to cause serious errors in radiocarbon age determinations of short-lived material. Other explanations must be sought for the incompatibility of the original measurements made on red deer antlers excavated in Norfolk.

The study has also shown that the precision of low-level measurements using the liquid scintillation counting method under the conditions described for the first and second batches is about  $\pm 46$  years. However, careful analysis of a group of results can reveal additional variation between samples equivalent to an age error of as little as  $\pm 30$  years.

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