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HIGH-PRECISION ^{14}C MEASUREMENT OF IRISH OAKS TO SHOW THE NATURAL ATMOSPHERIC ^{14}C VARIATIONS OF THE AD TIME PERIOD

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ABSTRACT. The high-precision ^{14}C measurement of bi-decade and decade samples of Irish Oak for the time period AD 50 to 1830 is presented. The samples were taken from dendrochronologically dated Irish Oak providing an absolute chronology for this period. While the natural atmospheric ^{14}C concentration shows cyclic deviations from a constant value, the amplitudes of such deviations vary considerably. Repeated measurement and interlaboratory checks justify a claim to accuracy in the data given. Comparison of a large number of data sets between Belfast and Seattle show that the different techniques of scintillation counting of $^{14}C_6H_6$ and gas counting of $^{14}CO_2$ derived from different wood species grown in different continents give no significant bias. Thus, it is justifiable to use this data set as a high-precision calibration curve for the AD period. Over most of this period bi-decade samples were measured giving a slightly reduced resolution of short-term variation when compared to the measurement of decade intervals; however, any difference is not apparent when such curves are compared. It is of much greater importance that a comparison of data sets is without bias if a combined calibration curve is to have sufficient integrity for general use. Averaging the data from Belfast and Seattle would improve the validity of such an AD ^{14}C calibration curve since it would tend to smooth out slight local variations and become internationally more acceptable.

INTRODUCTION

Since the early 1970's G W Pearson has been responsible for the ^{14}C dating laboratory and M G L Baillie for the dendrochronology of the AD era. Over the last few years improvement of technique has led to high-precision ^{14}C measurement. When this improvement is applied to the measurement of tree rings the fine detail of variation in the atmospheric ^{14}C concentration is exposed (Bruns, Munnich, and Becker, 1980; de Jong, Mook, and Becker, 1979; Pearson, Pilcher, and Baillie, 1983; Stuiver, 1982). ^{14}C measurement in the Belfast laboratory was carried out on dendrochronologically dated Irish oak divided to give decade or bi-decade samples of contiguous growth rings. The Irish oak chronology is absolute over the period presented and together with the ^{14}C measurements will provide a high-precision timescale calibration. For any calibration to have integrity it must carry appropriate error bands that are shown to be realistic. All parameters likely to give rise to errors must be investigated, corrections derived and their uncertainty included in the final error estimate (Pearson, 1979; 1980).

DENDROCHRONOLOGY

During the construction of the Belfast chronology every effort was made to ensure that the overlaps between successive ring patterns were replicated to a degree at which the chronology could stand independently (Baillie, 1973; 1977; 1982). In the final analysis it is useful to seek further and preferably independent support for the chronologies. Such support is available in Europe in a series of German chronologies, by comparison with which it is possible to demonstrate the integrity of the complex of Irish and Scottish chronologies.

The comparisons are step-wise and involve dating English chronologies against both the Irish and German chronologies. Such dating exercises were made for the later medieval, medieval, and early medieval periods and the consistency of these matches between the independent Irish and German chronologies removes any doubt about the placement of the chronologies in time (Baillie, 1982; Baillie, Pilcher, and Pearson, 1983).

^{14}C MEASUREMENT

The method used for the ^{14}C measurement of the samples presented in this paper was described in Pearson et al (1977; Pearson 1979; 1980). The system has been operative for measuring "calibration samples" since 1975. Quality controls were kept since the method was established involving the continuous monitoring of some 12 counting parameters additional to the measurement of samples, oxalic acid reference standard, and background. More than 60,000 parameter measurements were graphically displayed as a continuous quality control and used to determine instrument reliability over this whole period. Variation in overall gain during the 7 years of operation was kept within a range of $\pm$ 4½% from the balance point operating position. Pearson (1979) showed a change in gain of $\pm$ 4½% is equivalent to a change in ^{14}C

efficiency of ca 0.03% which is further decreased by a correction based on an external source channels ratio measurement. Each sample was measured for sufficient time to accumulate at least 300,000 counts, ie, better than $\pm$ 1.8^{o}/oo ($\approx \pm$ 14 years). The errors associated with the oxalic-acid reference standard and background measurement is 0.05% and 0.003 counts per minute, respectively. The additional errors associated with applied corrections are propogated in Pearson (1979; 1980) giving an overall error of approx $\pm$ 2.1^{o}/oo, ie ca $\pm$ 17 years. All samples including those previously published (Pearson *et al*, 1977; Pearson, 1980) were recalculated using the most accurate information presently available before being incorporated in this series of measurements.

VALIDITY AND ACCEPTABILITY OF CALIBRATION CURVES

Many factors should be considered before a calibration curve is universally acceptable; some of these are discussed by Stuiver (1982) and Pearson, Pilcher, and Baillie (1983). The accuracy of ^{14}C measurement is perhaps the most important single factor that is entirely dependent upon laboratory technique and method of operation. Comparing Belfast and Seattle data provides an opportunity to examine all these factors in detail - the technique, methods, species measured, and origin of sample material, all being completely different. Seattle measurements (Stuiver, 1982) were made on Pacific Northwest Douglas Fir and California Sequoia using a gas proportional counting system to measure CO_2 from sample cellulose. The Belfast data was obtained from the liquid scintillation counting of benzene synthesized from Irish oak sample carbon. The Belfast laboratory is at ground level and the Seattle laboratory underground.

Similar dendro-age decades were measured from the different species by the Belfast and Seattle laboratories for the time period AD 950 to 1270 (only three decades centered on 1185, 1205, and 1245 were omitted by Belfast due to insufficient material). The results are given in figure 1 (Seattle results were taken from Stuiver, 1982 from fig 2 and can only be calculated to the nearest five years). The agreement between these data sets indicates that continental differences and species variability is negligible. If it is accepted that variations outside of laboratory-induced errors are negligible, as our operation illustrates, then an averaging of such data will provide an international calibration curve, at least for the temperate parts of the northern hemisphere.

Comparison of the Seattle measurement with other calibration curves, namely La Jolla Bristlecone Pine (Suess, 1978) and Heidleberg German Oak (Bruns, Munnich, and Becker, 1980) were adequately discussed in Stuiver,(1982) and because the agreement between the Belfast and Seattle measurements is very close, a further analysis of the Belfast data against these calibration curves would contribute little additional information. The calibration proposed by Klein *et al* (1982) is illustrated with the combined averaged data of Pearson and Stuiver over bi-decade intervals in figure 2. Very little similarity exists between the two curves and even with the very wide band width of the Klein *et al* curve, the two band widths are completely separate over significant periods. Furthermore, a distinct bias over extensive periods exists where the two overlap, and would result in the converted dates giving quite a different range of calendar years depending on the particular curve used.

INTER-LABORATORY COMPARISON

The Belfast laboratory has participated in a number of inter-laboratory comparisons during the last 3-4 years. The Harwell/British Museum benzene measurement UK study (Otlet *et al*, 1980) showed the Belfast results (Pearson, 1980) to be within the errors quoted from the weighted mean value of all the participating laboratories. In 1979 the Belfast laboratory measured four samples of the new oxalic acid reference standard on behalf of the National Bureau of Standards, USA. Each sample was measured to a precision of better than $\pm$ 2‰ ($\pm$ 16 years) and all were found to be within $\pm$ 5 years of the mean value obtained from the 9 participating laboratories (W D Mann, pers commun) showing a bias of less than 0.16‰, ie < 2 years.

The Belfast laboratory recently participated in the Glasgow inter-laboratory calibration project involving 20 ^{14}C laboratories (Scott, Baxter, and Aitchison, 1981). The measurement of eight identical wood samples supplied by A Hayworth Aberystwyth, was made by each of the participating laboratories and the results presented by Stenhouse and Baxter (ms, Proc: ^{14}C and Archaeology, Groningen 1981). All eight samples were measured by Belfast to a precision of $\pm$ 18-20 years and showed a mean bias of four years from the weighted average of all the results. However, the study suggested that the Belfast quoted error should be multiplied by 1.27 which would change our average quoted error $\pm$ 17 years to that of $\pm$ 21 years, but did not rule out the possibility that unity is still valid since the number of samples measured was small. The reproducibility of measurements in the Belfast laboratory indicates that 1.27 would be a maximum error multiplication factor. Internal duplication of analysis would be consistent with an error multiplier of unity.

In addition to the above inter-laboratory comparisons, especially with Seattle, the Belfast laboratory also measured 18 samples of Irish oak covering > 360 years over the period previously measured by de Jong and Mook (de Jong, Mook, and Becker 1979). These results agree with de Jong's measurements (Pearson, Pilcher, and Baillie, 1983) and show a bias of < 20 years. From the above comparisons and interlaboratory checks it seems reasonable that any bias on the results presented here is small in relation to the mean error quoted of ± 17 years.

DECADE OR BI-DECADE CALIBRATION

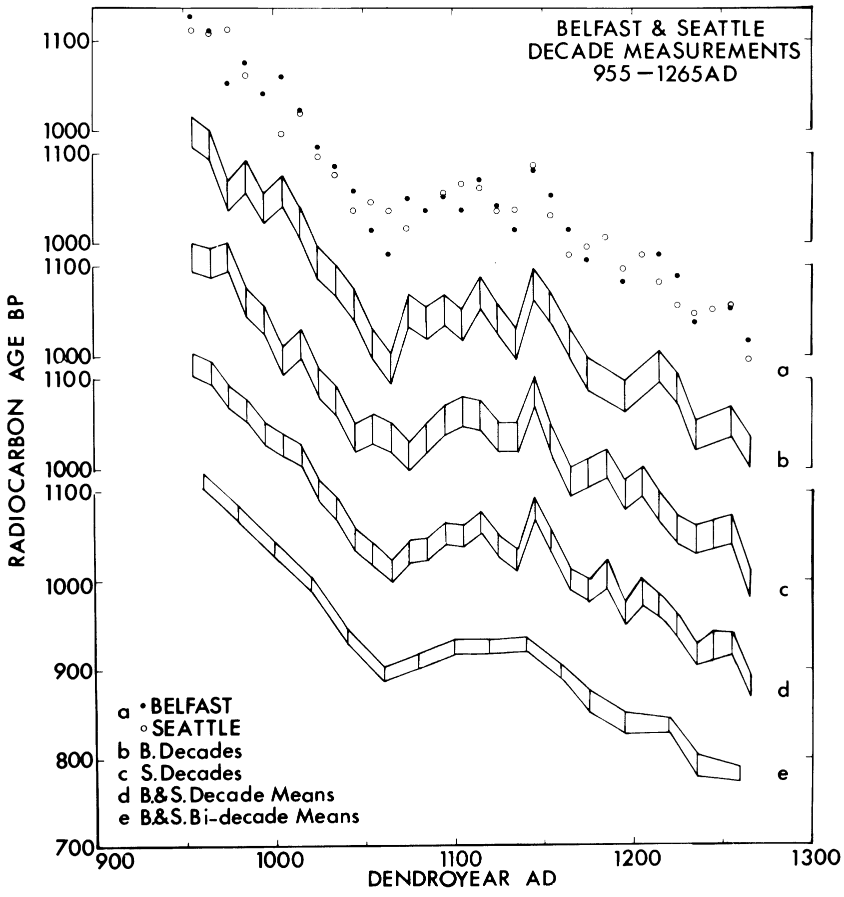

Fig 1 Comparison of data between Belfast and Seattle

Stuiver, 1982 concluded from his measurement of single-year samples over time periods AD 1510-1625 and AD 1820-1952 that the scatter of single-year data around the decade average trend is entirely compatible with the scatter expected solely from the quoted errors in the single-year measurements. He also concludes that any calibration made from decade measurements could be used by both single-year samples and decade samples to give equally accurate dendro-ages.

Figure 1b and c, show the decade measurements with 1σ band widths of Belfast and Seattle data, respectively. The decade measurement variations are also compatible to the normal statistical variations expected around a smooth trend curve. Many decade variations on one curve are canceled when averaged with the other laboratory's data, supporting the hypothesis of a smooth curve (fig 1, e). The decade at 1140 and 1150 dendro-age do show agreement on significant variations in the decade calibrations of each laboratory and are completely canceled out when averaged as bi-decade samples (fig 1, e). While these decade variations may be due to a random statistical coincidence like the decade variations that cancel each other out, this cannot be assumed. Some smoothing is bound to occur with any calibration that exceeds one year interval measurement; thus, for samples that have growth periods of less than the calibration interval, a corresponding increase in the calibration error will have to be made to allow for this smoothing factor. Although smoothing errors are significant for short-lived samples, unless the sample is measured to a high-precision, ie ca $\pm$ 20 years, the effect of such additional error is small.

The above arguments for a bi-decade calibration and additional error requirement for short-lived samples is supported by the successive averaging of 20 single-year measurements from the single-year series (Stuiver, 1982) and 4 of the 5-year separated annual growth rings given by de Jong (1982, pers commun).

TIME-SCALE CALIBRATION

The ^{14}C time-scale calibration curve AD 50-1840 is presented in figure 3, drawn from the high-precision measurement (σ = $\pm$ 17 years which includes all correction errors) of some 74 bi-decade and 33 decade samples of Irish oak. Duplicate measurements are represented as mean values with appropriate reduction of precision. All ^{14}C ages were calculated using a 5568-year half-life and are measured directly against NBS oxalic acid reference standard in which zero in ^{14}C years BP is equal to the calendar year of AD 1950. If it is assumed that the dendro-age is without error, then the ^{14}C

measurement will provide an accurate calendrical age conversion. Figure 2 shows the variation in calendar age band width and growth period > 20 years, when a comparison is made between the averaged Belfast and Seattle curve and the ± 20 year limits proposed by Klein et al (1982).

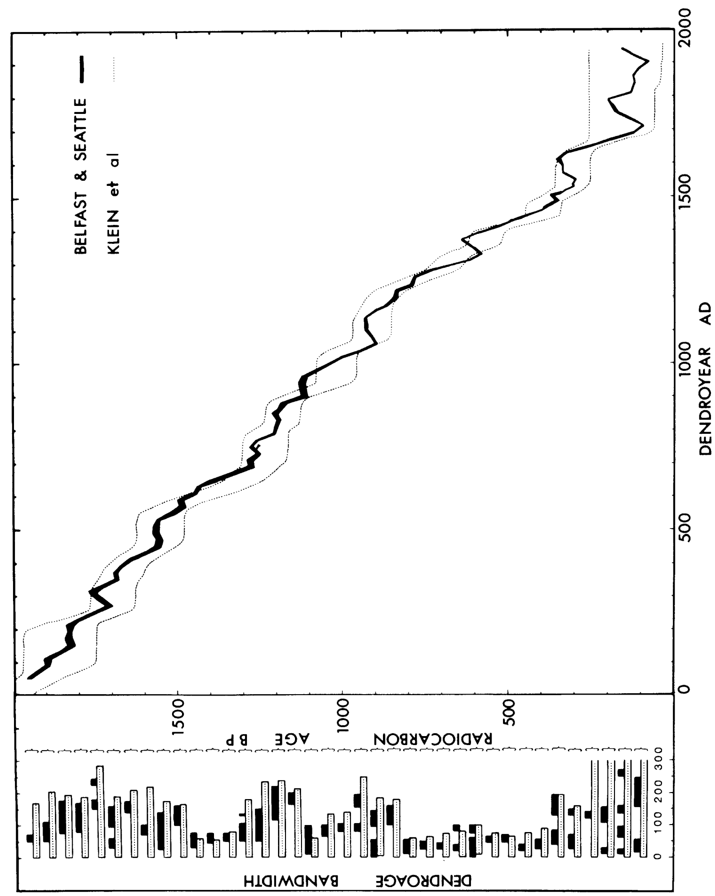

Fig 2 Comparison of combined Belfast and Seattle data (bi-decade intervals) with proposed curve of Klein et al (1982)

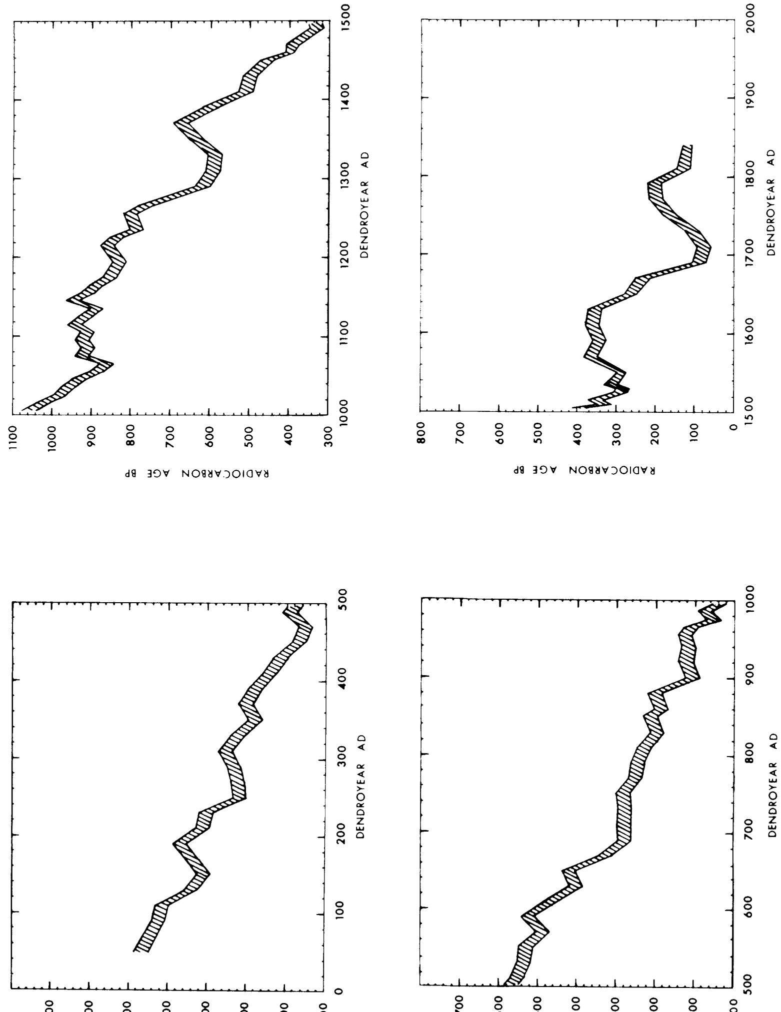

Fig 3 Bi-decade/decade interval measurements of Irish oak. Shaded area is $\pm$ 1σ error band.

CONVERSION OF ^{14}C AGE TO DENDRO-AGE

Details for conversion of ^{14}C age to dendro-age are given in Stuiver (1982) and Pearson, Pilcher, and Baillie (1983) and suffice for the calibration data presented here. For samples of short growth, an additional error should be added into the date error equation to compensate for the smoothing factor of bi-decade measurement. This value (σ_3) would be ca 15 years for a single-year growth, to zero for 20-years growth sample

$$\sigma_0 = \sqrt{\sigma_1^2 + \sigma_2^2 + \sigma_3^2}$$

where σ_0 = final error estimate, σ_1 = error on date, σ_2 = error on calibration.

CONCLUSION

It has been shown that good agreement is possible between laboratories and that error estimates can be close to those quoted. A claim to accuracy can be made for the measurements presented in this paper. It is important for the acceptance of ^{14}C dating that the accuracy of routine dating is continuously assessed and improved.

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