[RADIOCARBON, VOL 31, NO. 3, 1989, P 833–838]

IMPROVED PRECISION ^{14}C MEASUREMENTS AND NATURAL ^{14}C VARIATIONS AROUND 10,000 CAL BP

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ABSTRACT. Thirty-one samples of 5 tree rings from a single oak trunk with 300 tree rings were measured with improved precision to study natural ^{14}C variations in the period from ca 9750 – 10,050 cal BP. Negative correlation was found between $\Delta^{14}C$ values and tree-ring indices. The pattern of ^{14}C changes in the studied interval closely resembles the changes observed in several periodically spanned intervals within the limits of high-precision calibration data sets.

INTRODUCTION

First attempts at calibrating the ^{14}C time scale at the boundary of the Late Glacial and Holocene by Stuiver (1970, 1971), Tauber (1970) and Vogel (1970) were placed in a new light after 15 years with the expansion of the floating oak and pine chronologies by Becker and Kromer (1986) and publication of the Calibration Issue of *RADIOCARBON*, with tentative calibration data from the 8th–13th millennia BP (Kromer *et al*, 1986; Stuiver *et al*, 1986). Recent high-precision measurements of ^{14}C concentration in tree rings confirm the general trend of ^{14}C changes predicted by earlier dating of the Lake of Clouds varves (Stuiver, 1970, 1971). Progress in studies of ^{14}C changes in the Late Glacial and Early Holocene is essentially limited by the scarcity of well-preserved trunks of this age. We present here results of ^{14}C measurements in a sequence of 300 tree rings of a single oak found in Lublinek, central Poland.

COUNTING SYSTEM AND LABORATORY PROCEDURES

Counting system – consists of a proportional counter of 4.5L total volume filled with pure CO_2 to 2.2 atm pressure, connected with CAMAC system electronics and a small microcomputer for data collection and preliminary statistical analysis (Walanus, 1986), and a separate vacuum line for combustion of samples and purification of CO_2.

Counting procedure – each sample is counted for 5–6 days (some samples repeated); partial results are recorded in 20-min intervals and then used to calculate full-day averages. For each single-day measurement, corresponding values of background and modern standard counting rates, are calculated. These are used to determine single-day values of ^{14}C activity for the unknown sample. The series of single-day partial results is finally used to calculate relative sample activity, conventional ^{14}C age and corresponding errors.

Background – the actual value of background was evaluated, allowing for its dependence on 1) counting gas purity, 2) changes in intensity of the hard component of cosmic radiation, 3) slight temporal changes of background caused by residual contamination after the Chernobyl accident (*cf* Pazdur & Zastawny, 1987). Dependence of background on CO_2 pressure was found insignificant.

Modern ^{14}C activity standards – CO_2 obtained by direct combustion of NBS oxalic acid was used as the primary standard of modern ^{14}C activity. Secondary laboratory standards were provided by tree-ring samples selected from well-preserved oak trunks from the Odra valley, dated dendrochronologically with the South German-Swiss Master Chronology (Becker, 1981; Goslar, 1987). The actual value of the modern standard count rate was evaluated allowing for its dependence on counting gas purity and CO_2 pressure in the counter. The measured ^{14}C activity of secondary standards agreed well with activity calculated from the known absolute age.

Dendrochronological measurements – were performed on apparatus designed by Goslar (1987). Thicknesses of individual tree rings, measured with an accuracy of 0.05mm in 8 radial directions, were averaged. Samples for ^{14}C measurements were cut in the form of 5-yr segments from well-preserved parts of the trunk.

Pretreatment – identical AAA procedure (4% HCl, 80°C, 20h; 4% NaOH, 80°C, 20h; 4% HCl, 80°C, 20h) was applied to all dated samples. Loss of mass during pretreatment was ca 60%. Pretreated samples were charred in a stream of nitrogen and then combusted and purified in a separate vacuum line designed especially for this study to avoid any possibility of contamination with other samples processed in the laboratory.

Accuracy – standard errors of measured values were estimated from the scatter observed in single-day results. A series of 25 determinations of background counting rate (over 14 months) indicates that the observed scatter of single-day values is 1.3 times greater than that predicted by Poisson statistics. Similar error multipliers were estimated to be equal to 1.5 (standard of modern ^{14}C activity, 51 measurements) and 1.4 (samples). Normalized average counting rate of background and modern standard are equal respectively to $B = 6.669 \pm 0.019$ cpm and $A_0 = 48.668 \pm 0.043$ cpm, thus yielding the factor of merit $F = A_0/B^{1/2} = 18.8$. The estimate of error of sample activity is calculated from the observed scatter of single-day results, errors of average values of B and A_0 (same for all samples), errors of determinations of the amount of CO_2 in the counter and $\delta^{13}C$ value, and errors of introduced corrections. Results obtained in a series of 12 repeated measurements indicate that the observed scatter of ^{14}C activity is 1.1 greater than that estimated in this way.

RESULTS AND DISCUSSION

Values of conventional ^{14}C ages of 31 samples, including results obtained in replicate mesurements *vs* tree-ring number are shown in Figure 1. The mean standard error of the individual age determination equals ca 40 yr. Besides two outlying values obtained on undersized samples, the series of results may be regarded as internally consistent. The results were tenta-

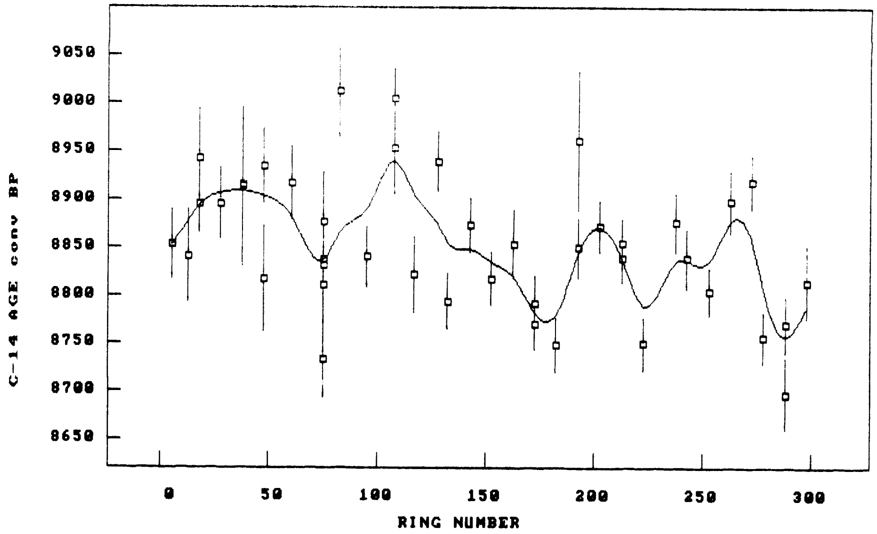

Fig 1. Results of ^{14}C measurements in 31 samples of Lublinek oak. The smoothed curve represents the spline function (Reinsch, 1967).

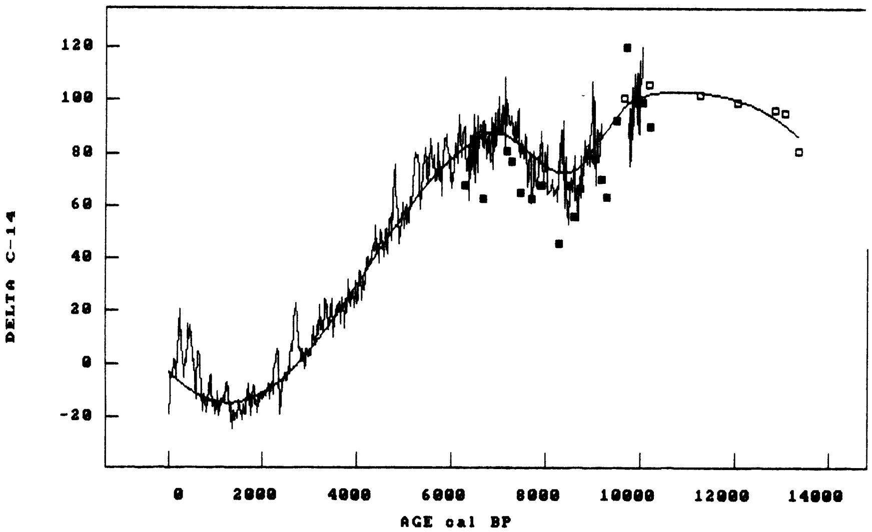

Fig 2. Approximate matching of the ^{14}C sequence from Lublinek oak (ca 9750–10,050 cal BP) to a smoothed trend of $\Delta^{14}C$ changes. Calibration data are taken from Pearson *et al* (1986), Kromer *et al* (1986) and Linick *et al* (1986); ■ – Lake of the Clouds, □ – Swedish varves (after Stuiver *et al* (1986)). Long-term trend: 0–6500 cal BP – sinusoid (Neftel, Oeschger & Suess, 1981); for the periods 6500–9200 cal BP and 9200–13,300 cal BP. 3rd order polynomial and spline function were fitted, respectively, to obtain the smoothed trend.

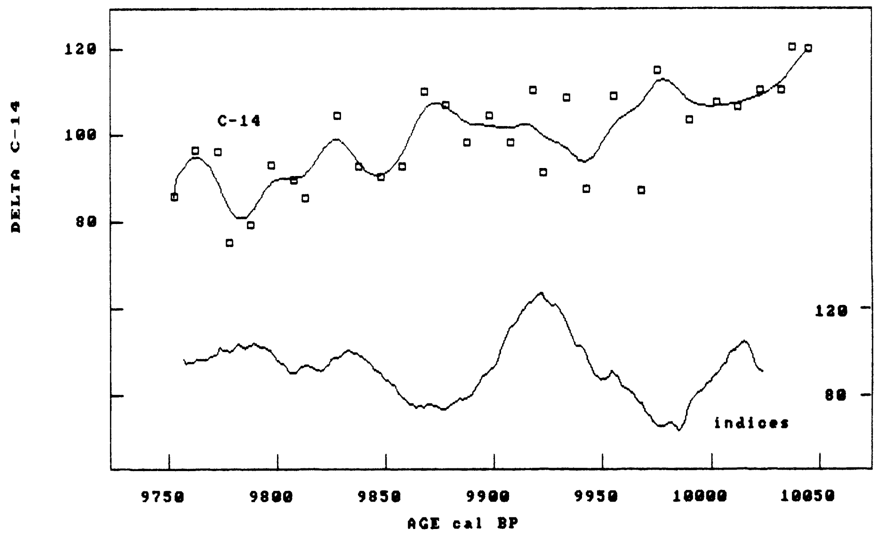

Fig 3. Upper part – $\Delta^{14}C$ values of 31 samples from Lublinek oak resulting from tentative estimates of absolute age (see text). Lower part – smoothed sequence of tree-ring indices.

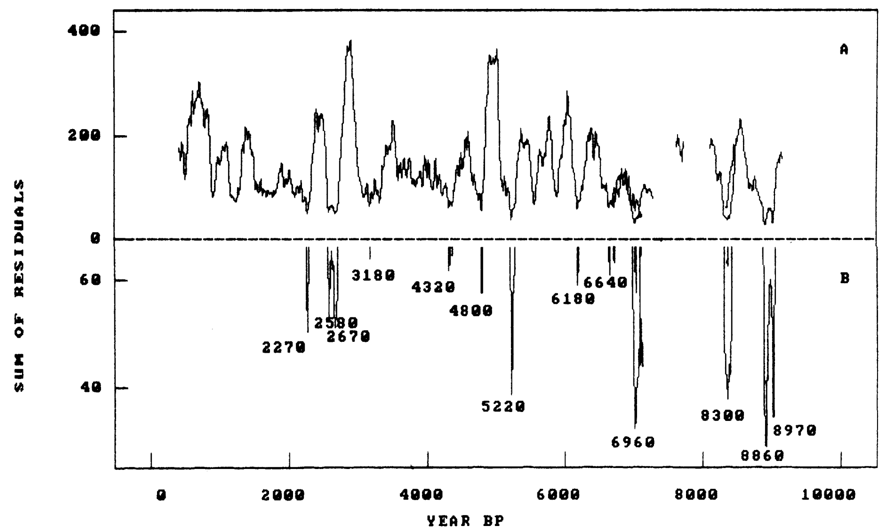

Fig 4. A. Sum of residuals obtained in wiggle-matching of the $\Delta^{14}C$ seguence of Lublinek oak to the ^{14}C calibration data, plotted *vs* matching position. B. Expanded fragment of Fig 4A showing the lowest values of S. Positions of the best fit are noted.

https://doi.org/10.1017/S0033822200012455 Published online by Cambridge University Press

tively matched to a smoothed trend of ^{14}C variations estimated from the Lake of the Clouds and Swedish varves, according to data from Stuiver *et al* (1986, Fig 6, p 977). Matched results are shown in Figure 2 with the smoothed trend of ^{14}C changes, compiled from data of Pearson *et al* (1986), Kromer *et al* (1986) and Linick *et al* (1986), including data of Tauber (1970) and Stuiver (1970, 1971) as quoted by Stuiver *et al* (1986). The absolute age range of the dated sequence is estimated at 9750–10,050 cal BP. These tentative results enable us to plot the values of $\Delta^{14}C$ in an astronomic time scale (Fig 3). There is a negative correlation of $\Delta^{14}C$ values with the smoothed sequence of tree-ring indices (calculated after fitting the negative exponential function to the tree-ring width sequence, *cf* Fritts, 1976; Schweingruber, 1983).

In order to check if the $\Delta^{14}C$ variations revealed in oak from Lublinek are similar to any patterns observed in later periods, the wiggle-matching procedure was performed over the whole range of time actually available from calibration data. Figure 4 shows the value of the sum of residuals

$$S = \sum_{i=1}^{31} \frac{(l_i - c_i - a)^2}{(\Delta l_i)^2 + (\Delta c_i)^2}$$

where: l_i and c_i denote the medium-term elements of $\Delta^{14}C$ for points of matched sequence and corresponding ones derived from calibration data, calculated for any position of matching. To separate the medium-term changes, the long-term trend in the $\Delta^{14}C$ record (see Fig 2) was subtracted from all $\Delta^{14}C$ data. On the x-axis, the actual position of the older end of the matched sequence is plotted. The value of 'a' was estimated to minimize the sum of residuals for each position of matching, so, in fact, only the shapes of curves were compared. In Figure 4B a section of Figure 4A with the lowest values of S is plotted on an expanded vertical scale. The low values of S show much similarity between the shapes of this sequence and the appropriate part of the calibration curve; for $S \leq 30$, we can regard the shapes as undistinguishable. An interesting feature is the occurrence of 3 groups of 3 peaks at 2270, 2580/2670 and 3180; 4320, 4800 and 5220; 6180, 6640 and 6960, with approximately the same distances between groups and approximately same distances of individual peaks within each group. The last group, represented by peaks at 8300 and 8860/8970, may be regarded as incomplete because of the lack of calibration data in the earlier interval. Such a presentation is another way of showing the cyclicities in the ^{14}C calibration curve. Also interesting is a decrease in the observed similarity in the obtained sequence and the compared fragment of the calibration curve going forward to the present day or, as marked by increasing values of S. The distance between the first peak of the last group (8300) and the predicted position of the obtained curve is comparable with the distances among other groups of peaks. This seems to show that changes of ^{14}C content based on Lublinek oak are consistent with those observed in later periods.

ACKNOWLEDGMENTS

This study was supported by a grant from the Central Research Project CPBP 01. 06. Thanks are due Romuald Awsiuk who performed $\delta^{13}C$ measurements.

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