

## GLASGOW UNIVERSITY RADIOCARBON MEASUREMENTS VII

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### INTRODUCTION

This list presents results obtained during 1971-1972 and is a continuation of research evaluating natural  $C^{14}$  levels for which data have been published previously (Baxter *et al.*, 1969; Baxter and Walton, 1970; Farmer *et al.*, 1972). The results of these studies are presented as  $\delta C^{14}$  and  $\Delta$  values based on age-corrected activities, although this correction is very small. Errors quoted are  $1\sigma$  counting uncertainties only. Pretreatment procedures are outlined in the text and analytical methods are essentially unchanged. Gas proportional counting of  $CH_4$  in a 0.5L detector is employed (Baxter *et al.*, 1969). Mass spectrometric analyses are performed to a precision of 0.1‰ ( $\pm 2\sigma$ ) on a V.G. Micromass 602B stable isotope mass spectrometer.

### ACKNOWLEDGMENTS

This work is supported by grants from the Natural Environment Research Council. We wish to thank the individuals and organizations who supplied sample materials. We are also grateful to T. D. B. Lyon for supervision of mass-spectrometric techniques and to A. J. A. Brown for efficient technical assistance.

### SAMPLE DESCRIPTIONS

#### I. TREE-RING SAMPLES

An integral part of the research program was the study of "bomb"  $C^{14}$  within recent tree rings to assess the value of different extraction techniques in pretreating wood for  $C^{14}$  analysis. Samples were single tree rings from a Scottish Silver Fir (*Abies nobilis*) planted in 1937 (felled 1970) in Glengarry Forrest (57° N Lat, 5° W Long), Inverness-shire. Acetone and petroleum ether extractions consisted of 24-hr Soxhlet extractions of wood shavings in acetone and 40/60 petroleum ether respectively, followed by drying at 100°C for 24 hr. Acid/base pretreatment consisted of successive 4-hr boilings in 4‰ HCl and 1‰ NaOH. Cellulose fractions were obtained by bleaching the ether-extracted wood and were charred at 500°C prior to combustion. The lignin fraction was obtained from the post-petroleum ether residue by the 72‰  $H_2SO_4$  method.

Study of 19th century atmospheric  $C^{14}$  concentrations in the N hemisphere (Farmer *et al.*, 1972) is based on further analyses of charred cellulose fractions from annual rings of an Oak (*Quercus robur*) planted in 1810 (felled in 1970) at Russell's Enclosure, Forest of Dean (51° 48'

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N Lat, 2° 37' Long), Gloucestershire, England. Rings for 1846-1848 were not readily separable.

Natural C<sup>14</sup> concentrations in the atmosphere of the S hemisphere during the 20th century were studied partly through analyses of annual rings of Radiata Pine (*Pinus radiata*) planted ca. 1930 (felled 1970) in Rotorua (38° 9' S Lat, 176° 16' E Long), New Zealand. Chemical pre-treatment was identical to that for the Forest of Dean Oak. The calendar year refers to the time of completion of the ring.

### Tree rings, Glengarry Forest series

Sample no.	Yr.	Fraction	$\delta\text{C}^{14}\%$	$\delta^{13}\text{C}\%$	$\Delta\%$
GU-452	1954	Whole wood	+0.7 ± 0.6	-28.7	+1.4 ± 0.6
GU-453	1957	Whole wood	+4.4 ± 0.6	-29.7	+5.3 ± 0.6
GU-454	1958	Whole wood	+12.3 ± 0.7	-28.8	+13.2 ± 0.7
GU-455	1958	Post-petrol residue	+13.4 ± 0.6	-28.1	+14.1 ± 0.6
GU-456	1962	Whole wood	+34.4 ± 0.8	-28.6	+35.4 ± 0.8
GU-457	1962	Post-petrol residue	+34.8 ± 0.7	-28.4	+35.7 ± 0.7
GU-458	1962	Cellulose	+37.0 ± 0.7	-27.8	+37.8 ± 0.7
GU-459	1963	Whole wood	+67.0 ± 0.7	-28.2	+68.1 ± 0.7
GU-460	1963	Post-acetone residue	+70.1 ± 0.9	-28.2	+71.2 ± 0.9
GU-461	1963	Post-petrol residue	+73.6 ± 0.9	-28.7	+74.9 ± 0.9
GU-462	1963	Cellulose	+72.9 ± 0.8	-27.3	+73.8 ± 0.8
GU-463	1963	Lignin	+74.9 ± 1.1	-29.0	+76.3 ± 1.1
GU-464	1963	Post-acid/base residue	+72.9 ± 0.9	-28.8	+74.3 ± 0.9
GU-465	1963	Post-acetone/ acid/base residue	+71.5 ± 0.9	-29.1	+72.8 ± 0.9
GU-466	1964	Whole wood	+88.0 ± 0.9	-28.7	+89.4 ± 0.9
GU-467	1964	Post-petrol residue	+83.4 ± 0.9	-28.6	+84.7 ± 0.9
GU-468	1964	Post-acetone residue	+88.7 ± 1.2	-28.3	+89.9 ± 1.2
GU-469	1964	Cellulose	+81.4 ± 0.9	-27.7	+82.2 ± 0.9
GU-470	1967	Whole wood	+63.1 ± 0.9	-28.4	+64.2 ± 0.9
GU-471	1969	Whole wood	+54.6 ± 0.8	-28.6	+55.7 ± 0.8
GU-472	1969	Post-petrol residue	+56.3 ± 0.8	-28.5	+57.4 ± 0.8
GU-473	1969	Cellulose	+54.0 ± 0.8	-27.7	+54.8 ± 0.8

*Comment:* comparison of these results with atmospheric C<sup>14</sup> levels confirms that single tree rings are valid indicators of atmospheric C<sup>14</sup> concentrations during wood growth period. Although not conclusive from the above data, physiology and chemistry of growing wood suggests that cellulose or lignin fractions may be more valid than whole wood for some trees in studying past annual C<sup>14</sup> levels. The lengthy laboratory procedure for chemical isolation is probably justified by resultant minimal contamination by non-contemporaneous carbonaceous material, e.g., resins (Jansen, 1970; Fairhall and Young, 1970; Olsson *et al.*, 1972).

**Tree rings, Forest of Dean series**

Sample no.	Yr.	$\delta C^{14}\%$	$\delta C^{13}\%$	$\Delta\%$
GU-474	1835	+0.6 $\pm$ 0.6	-24.6	+0.5 $\pm$ 0.6
GU-475	1877	+1.8 $\pm$ 0.6	-24.1	+1.6 $\pm$ 0.5
GU-476	1845	-0.4 $\pm$ 0.5	-24.9	-0.4 $\pm$ 0.5
GU-477	1846-48	-0.1 $\pm$ 0.5	-24.4	-0.2 $\pm$ 0.5

*Comment:* these results complete measurements of annual  $C^{14}$  levels for 1829-1865 (Farmer *et al.*, 1972). The  $C^{14}$  data are highly correlated with solar activity via the expression  $\Delta_T = 127.88 - 0.0141 R_{T-5} - 0.0689 T$  where  $\Delta_T$  = deviation from  $0.95 \times$  NBS oxalic acid  $C^{14}$  level at time T (in calendar yr),  $R_T$  = mean sunspot no. at time T.

The above expression corresponds to an F value of 38.23, significant at the 5% level, indicating dependence of  $C^{14}$  levels on solar activity and the inconstancy of annual  $C^{14}$  concentrations at these lats of N hemisphere. Further implications of the results are discussed elsewhere (Farmer and Baxter, 1972).

**Tree rings, Rotorua Forest series**

Sample no.	Yr.	$\delta C^{14}\%$	$\delta C^{13}\%$	$\Delta\%$
GU-478	1934	-2.2 $\pm$ 0.8	-25.7	-2.0 $\pm$ 0.8
GU-479	1936	-1.4 $\pm$ 0.6	-25.9	-1.2 $\pm$ 0.6
GU-480	1938	-0.9 $\pm$ 0.6	-24.8	-1.0 $\pm$ 0.6
GU-481	1939	-1.2 $\pm$ 0.6	-25.3	-1.1 $\pm$ 0.6
GU-482	1940	-0.6 $\pm$ 0.6	-25.3	-0.6 $\pm$ 0.6
GU-483	1941	-0.9 $\pm$ 0.6	-24.6	-0.9 $\pm$ 0.6
GU-484	1942	-2.3 $\pm$ 0.6	-25.3	-2.2 $\pm$ 0.6
GU-485	1943	-1.7 $\pm$ 0.6	-25.6	-1.6 $\pm$ 0.6
GU-486	1944	-2.0 $\pm$ 0.6	-24.9	-2.1 $\pm$ 0.6
GU-487	1945	-1.6 $\pm$ 0.6	-25.4	-1.5 $\pm$ 0.6
GU-488	1949	-1.7 $\pm$ 0.6	-24.3	-1.8 $\pm$ 0.6
GU-489	1950	-2.4 $\pm$ 0.6	-24.1	-2.6 $\pm$ 0.6
GU-490	1951	-2.7 $\pm$ 0.6	-24.1	-2.9 $\pm$ 0.6
GU-491	1952	-3.5 $\pm$ 0.8	-25.0	-3.5 $\pm$ 0.8

*Comment:* implications of these and other S hemisphere data are discussed in Section IV.

## II. VINTAGE WINE SAMPLES

Additional measurements of atmospheric  $C^{14}$  concentrations in S hemisphere in the 20th century were made through continuing wine analyses previously reported (Farmer *et al.*, 1972). Grapes were picked in March of the year of production of each wine sample after ca. 4 to 5 mos. on the vine. All wines were produced from grapes picked at vineyards in the Eden Valley (34° 34' S Lat, 139° E Long), New South

Wales, Australia with the exception of the 1929 and 1941a samples derived from grapes grown in the Murray Region (33° 20' S Lat, 142° 30' E Long), South Australia.

#### Vintage wine, Australia series

Sample no.	Yr.	$\delta C^{14}\%$	$\delta C^{13}\%$	$\Delta\%$
GU-492	1929	$-1.5 \pm 0.6$	-30.7	$-0.4 \pm 0.6$
GU-493	1934	$-3.3 \pm 0.6$	-28.0	$-2.7 \pm 0.6$
GU-494	1938	$-3.7 \pm 0.6$	-30.1	$-2.7 \pm 0.6$
GU-495	1939	$-1.8 \pm 0.6$	-25.8	$-1.6 \pm 0.6$
GU-496	1940	$-1.5 \pm 0.6$	-26.9	$-1.1 \pm 0.6$
GU-497	1941	$-2.1 \pm 0.6$	-28.6	$-1.4 \pm 0.6$
GU-498	1941a	$-1.0 \pm 0.6$	-25.3	$-1.0 \pm 0.6$
GU-499	1942	$-2.2 \pm 0.6$	-27.0	$-1.9 \pm 0.6$

#### III. WHEAT SEED SAMPLES

The survey of 20th century annual  $C^{14}$  levels in S hemisphere was supplemented by the analyses of Australian wheat seed samples grown in New South Wales (exact location undefined), the 1920, 1921, 1932a, and 1936 samples at the State Research Farm, Werribee (37° 52' S Lat, 145° 8' E Long), Victoria and the remaining 1932 sample at the Crop Research Division, DSIR, Lincoln (43° 38' S Lat, 172° 30' E Long), New Zealand. Calendar year refers to time of harvest.

#### Wheat seeds, Australasian series

Sample no.	Yr.	$\delta C^{14}\%$	$\delta C^{13}\%$	$\Delta\%$
GU-500	1910	$+1.1 \pm 0.8$	-24.1	$+1.0 \pm 0.8$
GU-501	1915	$+1.3 \pm 0.5$	-22.1	$+0.7 \pm 0.5$
GU-502	1919	$-1.0 \pm 0.6$	-22.9	$-1.4 \pm 0.6$
GU-503	1920	$-1.5 \pm 0.8$	-22.7	$-2.0 \pm 0.8$
GU-504	1921	$-1.7 \pm 0.8$	-23.2	$-2.0 \pm 0.8$
GU-505	1925	$-1.6 \pm 0.6$	-23.0	$-2.0 \pm 0.6$
GU-506	1932	$-0.7 \pm 0.6$	-21.9	$-1.4 \pm 0.6$
GU-507	1932a	$-0.2 \pm 0.6$	-22.9	$-0.6 \pm 0.6$
GU-508	1936	$-0.9 \pm 0.8$	-23.0	$-1.3 \pm 0.8$

#### IV. WOOL SAMPLES

Several sheep's wool samples from Australia were analyzed. The 1922 sample was grown at Harrogate (35° S Lat, 139° E Long), South Australia, the 1923 and 1924 samples at Native Valley, Nairn (35° S Lat, 138° 55' E Long), South Australia and the 1946 and 1947 samples at Robe (37° 10' S Lat, 139° 45' E Long), South Australia. Calendar year refers to time of shearing, each wool sample representing ca. 1 yr growth prior to shearing in the early months of the year. Samples were charred at 500°C prior to combustion in the gas preparation system.

**Wool, Australia series**

Sample no.	Yr.	$\delta C^{14}\%$	$\delta C^{13}\%$	$\Delta\%$
GU-509	1922	$-0.7 \pm 0.6$	-23.4	$-1.0 \pm 0.6$
GU-510	1923	$-1.5 \pm 0.6$	-23.8	$-1.8 \pm 0.6$
GU-511	1924	$-1.4 \pm 0.7$	-27.6	$-0.9 \pm 0.7$
GU-512	1946	$-1.9 \pm 0.6$	-21.0	$-2.7 \pm 0.6$
GU-513	1947	$-2.2 \pm 0.7$	-21.5	$-2.9 \pm 0.7$

*Comment:* collective results of  $C^{14}$  analyses of tree rings, wines, wheat seeds, and wool from S hemisphere constitute a detailed series of measurements of annual  $C^{14}$  levels during 20th century. The data indicate a general decrease of ca. 0.05% ( $\Delta$ ) per yr to a value of  $-2.45\%$  in 1951-52. No correlation between  $C^{14}$  and sunspot no. is evident and, within statistical error, the decrease is linear. Thus annual fluctuations previously noted in N hemisphere for this interval (Baxter and Walton, 1971) are probably dampened below detectable levels in S hemisphere.

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