[RADIOCARBON, VOL 22, No. 2, 1980, P 291-298]

POSSIBILITY OF CLIMATICALLY INDUCED VARIATIONS IN THE ^{14}C AND ^{13}C ENRICHMENT PATTERNS AS RECORDED BY A 300-YEAR-OLD NORWEGIAN PINE

D D HARKNESS and B F MILLER

N E R C Radiocarbon Laboratory, Scottish Universities Research and Reactor Centre, East Kilbride, Scotland

ABSTRACT. The secular patterns of Δ and $\delta^{13}C$ measured in wood cellulose are compared with a palaeotemperature index published for the immediate growth region. ^{14}C enrichment shows an overall decrease of ca 20‰ (Δ) during the 18th and 19th centuries with shorter term (decade) variations superimposed on the general trend. Measured Δ values correlate significantly with the average mean summer temperatures and indicate a linear coefficient of ca -10.2‰ $°C^{-1}$. Short-term variations in the natural concentration of ^{14}C which are closely related to climatic change may reflect the latitudinal dependence for atmospheric mixing.

The secular trend in $\delta^{13}C$ covers a range of 2‰ but variations of this magnitude reflect influences other than those directly associated with climatic change, eg, possible assimilation of recycled biospheric CO_2 during early life and post AD 1850 anthropogenic effects. No evidence was found to suggest a significant correlation between $\delta^{13}C$ and the mean atmospheric temperature during summer growth periods.

INTRODUCTION

The sensitivity of tree growth to variations in climate, and in particular, under conditions of environmental stress, can provide a record of past regional climate (Fritts, 1976). It has been postulated (Pearman, Francey, and Fraser, 1976; Wilson and Grinsted, 1977; Grinsted, Wilson, and Ferguson, 1979) that the prevailing atmospheric temperature during growth is reflected to a measureable extent in the $^{13}C/^{12}C$ ratio of the wood produced. Although the true climatic significance and magnitude of such measured $^{13}C/^{12}C$ variations has been questioned (Yapp and Epstein, 1977; Stuiver, 1978). The apparent marked correlation between the trends for atmospheric ^{14}C concentration and global temperature since the 12th century has been evidenced by de Vries (1958; 1959), Damon (1970), and Suess (1970).

As discussed by Stuiver (1978) and Farmer (1979), investigation of the direct influence of climate on the relative isotopic abundances in wood is confounded by anthropogenic changes induced in atmospheric CO_2 during the past century, the period for which most accurate meteorologic information is available. So far, pre-19th century comparisons, for example, that of Grinsted, Wilson and Ferguson (1979), have relied on historical and inferred temperatures which, for the most part, were derived for locations remote from the area of tree growth. The construction by Matthews (1976a, b) of an annual summer temperature index representative of tree-line conditions in the southern Norwegian fjell since AD 1700 has enabled investigation of the possible influence of climate on the $^{13}C/^{12}C$ and $^{14}C/^{12}C$ ratios recorded in growth sensitive wood from the immediate region.

EXPERIMENTAL METHOD

The isotopic data reported for this investigation were measured for a single tree *(Pinus sylvestris)* which had grown in a forest at ca 850m

altitude on the NE facing valley side at Visdalen, Jotunheimen, Norway (62° N, 9° E). As for southern Norway, in general, this region is subject to a prevailing southwesterly (North Atlantic) airflow which is particularly marked during the summer months. The growth site is also remote from any major urban center and, therefore, the recorded isotopic values are unlikely to have been distorted by localized emissions of fossil CO_2.

A complete radial cross-section was cut during summer 1971 from the base of the tree which had been felled the previous winter. The growth pattern shows an appreciable variation in ring width (in the range 0.3 to 3.2mm per annum) and records a total of ca 280 years growth prior to felling.

Wood samples were taken along selected radii in contiguous increments of five or ten years' growth. Only one radius was sampled for $^{14}C/^{12}C$ measurement, but eventually sections from four radii, set at approximately 90° intervals, were recovered for $^{13}C/^{12}C$ analyses. All wood samples were finely divided and then rendered to cellulose via digestion in 5 percent NaOH (80°C, 24 hours) followed by bleaching in Na ClO_2/HCl solution (80°C, 24 to 48 hours). The recovered cellulose was washed with demineralized water until acid free and finally dried under vacuum.

As an independent evaluation of overall analytic precision, wood samples from a bulk 'pre-1950' standard *(Pinus)* were interposed at regular (five sample) intervals in both the $^{14}C/^{12}C$ and $^{13}C/^{12}C$ analysis programs.

$^{14}C/^{12}C$ measurement. ^{14}C enrichments were measured for cellulose samples, each corresponding to ten years' growth, using the liquid scintillation method (Harkness and Wilson, 1972). To allow radiometric normalization, $\delta^{13}C$ values were measured using CO_2 produced as the first stage in each synthesis. The alternative approach of 'burning back' a small aliquot of the product benzene for $\delta^{13}C$ determination was not required since, in all instances, carbon recovery in the conversion of cellulose to benzene was better than 92 percent. Two sets of enrichment data were calculated for all samples and replicate standards. Different scintillation spectrometers were used for the individual counting runs and these, in turn, were separated by six month storage of the prepared scintillation cocktails at −10°C.

Replicate analyses from the 'pre-1950' wood standard (table 1) show no evidence for unquantified experimental error in the $D^{14}C$ measurement program. Sample enrichment values ($D^{14}C$) as calculated from each counting run also duplicated with the calculated $\pm 2\sigma$ analytic confidence limits. The weighted mean $D^{14}C$ value was, therefore, taken as representative for each sample. These data, age corrected via the relationship

$$\Delta‰ = D^{14}C‰ + \frac{(1950 - \text{'midgrowth' date})}{8.033}$$

are presented in figure 1a for pre-1950 growth. Additional Δ values mea-

https://doi.org/10.1017/S0033822200009589 Published online by Cambridge University Press

sured for the growth periods AD 1952 to 1961 and AD 1962 to 1970 are, respectively, 140.2 ± 5.0‰ and 647.4 ± 6.5‰.

$^{13}C/^{12}C$ measurement. Stable isotope ratios, other than those required for radiometric normalization, were measured using CO_2 produced by quantitative oxidation of mg-sized samples of cellulose, each corresponding to five years' growth. The semi-micro-scaled combustion system is constructed in flame-sealed quartz. Combustion involved external heating of the sample held in a static atmosphere of pure O_2 (~760mm Hg pressure) followed by slow pumping of the product gases through a CuO packed furnace held at 850 ± 20°C. CO_2 was dried and retained in a series of cryogenic traps and then purified by double distillation (pumped to a residual pressure of less than 10^{-4} Torr at −195°C). The volume of CO_2 recovered was monitored in a calibrated volume from which aliquots of gas were transferred to a Micromass 602B mass spectrometer. $\delta^{13}C$ PDB was calculated from the sample $^{13}C/^{12}C$ enrichment as measured against a bulk CO_2 working standard ($\delta^{13}C$ PDB = −27.6‰) which is routinely calibrated against CO_2 prepared from the international standards NBS21 (graphite) and NBS20 (Solenhofen limestone).

Replicate analyses from the bulk wood standard (18 samples) showed an overall variation of ± 0.15‰ for the complete analytic procedure, *ie*, cellulose extraction, CO_2 production, and instrumental measurement.

TABLE 1

Replicate ^{14}C analyses from 'pre'-1950' wood standard

$D^{14}C‰ \pm 1\sigma$				$‰ \pm 1\sigma$
1st counting run (A)	(a)	2nd counting run (B)	(b)	Mean	
-24.1 ± 7.4		-36.4 ± 6.1		-31.4 ± 4.7	-28.9 ± 4.7
-14.6 ± 7.8		-34.0 ± 6.1		-26.6 ± 4.8	-24.2 ± 4.8
-22.8 ± 7.4		-14.2 ± 6.1		-17.7 ± 4.7	-15.2 ± 4.7
- 6.2 ± 7.7		- 9.6 ± 6.4		- 8.2 ± 4.9	- 5.7 ± 4.9
-17.4 ± 7.4		-20.3 ± 6.1		-19.1 ± 4.7	-16.6 ± 4.7
-16.9 ± 7.9		-17.1 ± 5.8		-17.0 ± 4.7	-14.5 ± 4.7
				(Mean)=	-17.5 ± 2.2.

1) Standard comprises homogeneous bulk wood sample *(Pinus)* corresponding to 8-years' growth during AD 1920 to 1940.

2) Enrichment data calculated using 5568-year half-life for ^{14}C.

3) Mean $D^{14}C = \frac{Ab^2 + Ba^2}{a^2 + b^2} \pm \left[\frac{a^2b^2}{a^2 + b^2}\right]^{0.5}$

https://doi.org/10.1017/S0033822200009589 Published online by Cambridge University Press

The secular pattern of $\delta^{13}C$ obtained from a single complete radius is presented in figure 2a. However, variations in $\delta^{13}C$ significantly greater than the accepted limits for analytic precision were also recorded among wood samples of contemporaneous growth taken at different radial positions in the cross-section of the tree.

DISCUSSION

$^{14}C/^{12}C$ pattern. The validity of the measured enrichment values as a record of past atmospheric ^{14}C concentrations in the Visdalen region is supported by the gradual 20‰ decrease in Δ as recorded over the first half of this century (Suess effect), the lack of a measurable amount of 'bomb ^{14}C' in wood of pre-1950 growth, the good agreement obtained between the post-1960 wood, and the rapidly changing atmospheric values

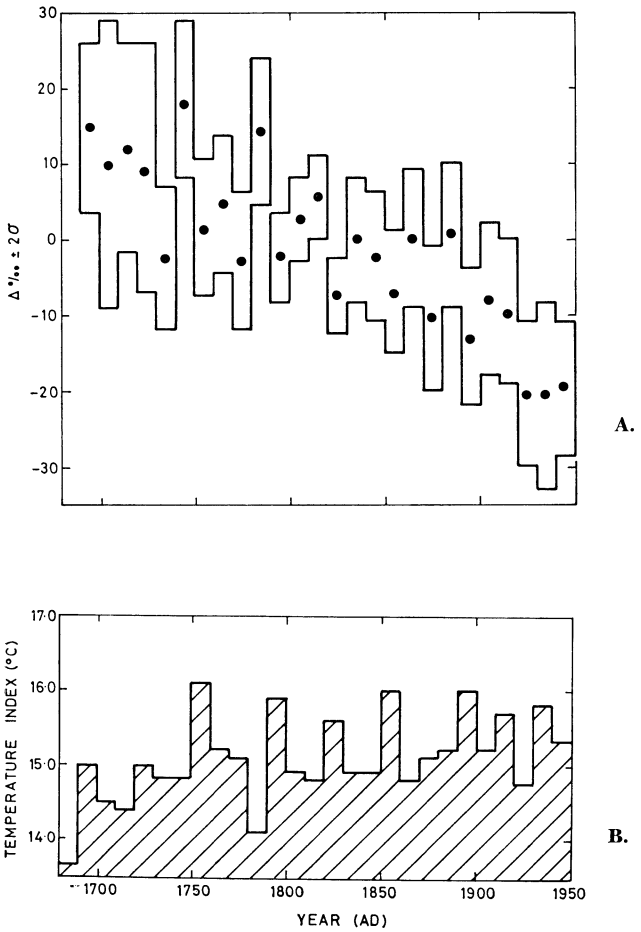

Fig 1A. Secular pattern of (10-year averaged) ^{14}C enrichment AD 1690 to 1950.
B. 10-year averaged temperature index AD 1680 to 1950.

https://doi.org/10.1017/S0033822200009589 Published online by Cambridge University Press

monitored directly and at comparable latitude (Nydal, 1968; Ergin, Harkness, and Walton, 1970; 1972).

The magnitude and secular trend of the decadal averaged variations in ^{14}C concentration (fig 1A) are in general agreement with corresponding data obtained from northern hemisphere trees (see, eg, Damon, Lerman, and Long, 1978, fig 2). Significant features in the Visdalen record are an overall decrease of ca 20‰ (Δ) during the two centuries prior to AD 1890, the resolution of short-term variations superimposed on the general trend, and an apparent inverse relationship between atmospheric ^{14}C concentration and the coincident summer temperature index for this region (fig 1B).

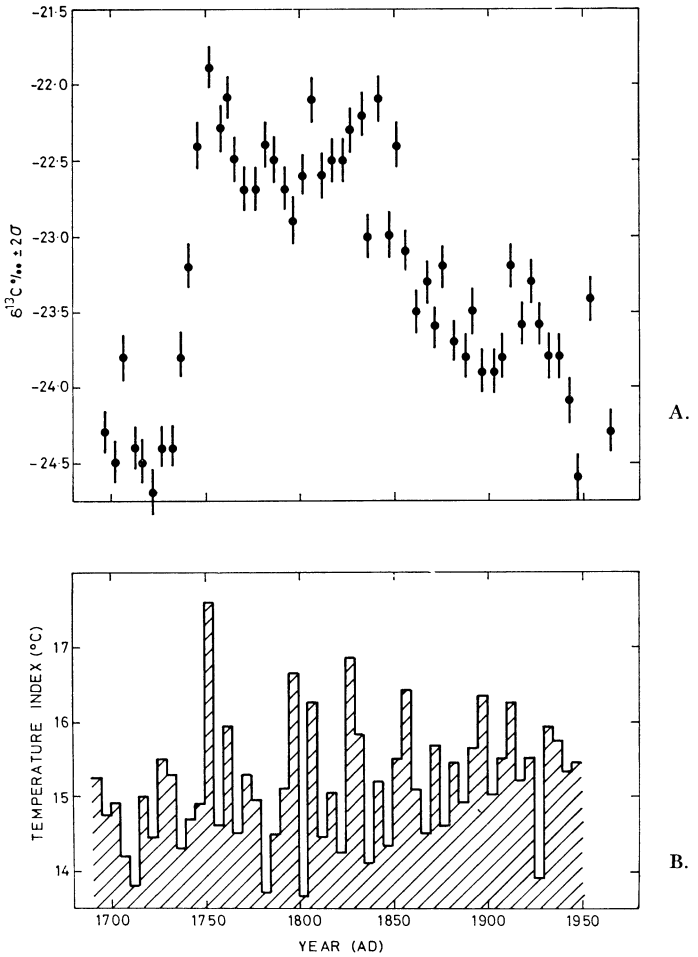

Fig 2A. Secular trend in ^{13}C enrichment AD 1695 to 1970. Values are for 5-year growth increments from a single radius.

B. 5-year averaged temperature index AD 1690 to 1950.

https://doi.org/10.1017/S0033822200009589 Published online by Cambridge University Press

Only the ^{14}C enrichment values measured from pre-AD 1890 wood are considered for direct climatic comparison, thus avoiding the well recognized industrial impact on the 20th century atmosphere. Linear regression analyses of 20 data pairs covering the period AD 1690 to 1890 (fig 3) gave a correlation coefficient of −0.638 and the mean relationship $\Delta‰ = -10.18T + 155.9$.

The Visdalen data, therefore, support the general consensus that variations in solar activity are the primary cause of concurrent short-term fluctuations in both atmospheric ^{14}C concentration and climate. However, the geophysical factors that relate solar activity with natural ^{14}C variations of the magnitude and apparent temperature sensitivity as monitored for Visdalen are less readily accepted. In particular, attention has been drawn to the fact that mathematical models designed to quantify the dynamics of inter-reservoir exchange for carbon fail to predict such short-term variations in atmospheric ^{14}C concentration (Ekdahl and Keeling, 1973). We suggest that, in relation to short-term changes, these models take an oversimplified view of the earth's atmosphere. In most models, the total atmosphere is represented as a single homogeneous carbon reservoir that exhibits first-order kinetic exchange with the oceans and terrestrial biosphere. Consequently, an inherent tendency to ignore atmospheric mixing patterns exists. Our contention that the atmospheric structure may require a more realistic interpretation is based on the marked seasonal and latitudinal dependence recorded for the transfer of 'bomb ^{14}C' (Nydal, 1968) and by the fact that approximately ten years were required for the uniform distribution of this artificial input throughout the stratosphere/troposphere system (Harkness, 1970). There can be no question that exchange of carbon between the atmosphere and oceans will have a marked damping effect on secular variations in ^{14}C concentration induced by changes in the natural production rate — an attenuation factor of 100 has been suggested by Damon, Lerman, and Long, (1978). However, the

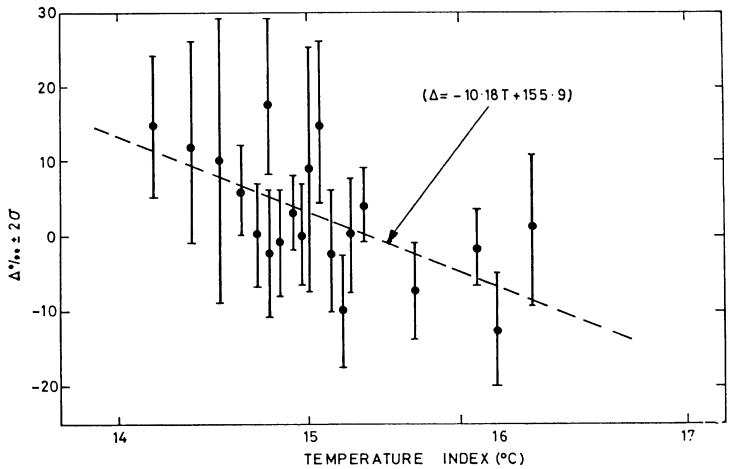

Fig 3. Regression of measured ^{14}C enrichment on temperature.

https://doi.org/10.1017/S0033822200009589 Published online by Cambridge University Press

counter-influence of a seasonal and latitudinal dependence for the net stratosphere to troposphere transfer of naturally produced ^{14}C allied with the finite time for tropospheric mixing might well contribute to measureable short-term variations in ^{14}C concentration that are also geographically dependent. The current application of high precision ^{14}C analysis in dendrochronologic studies, and, in particular, the direct comparison of known-age wood of European and North American origin, should resolve this issue.

$^{13}C/^{12}C$ pattern. The lack of a clear climatic (temperature) signal in the $^{13}C/^{12}C$ record of the Visdalen pine is immediately evident from comparison of figures 2a and 2b. Samples extracted from alternative radii showed that while the secular trend in $\delta^{13}C$, as in figure 2a, holds for the complete cross-section of the tree, a noise pattern of up to $\pm$ 0.4‰ amplitude must be accepted for contemporaneous growth. Comparable variations in time-equivalent wood have been noted by Freyer and Wiesberg (1975) and Grinsted, Wilson, and Ferguson (1979).

The marked depletion in $\delta^{13}C$ in wood laid down prior to AD 1745 is considered to reflect a 'juvenile' effect as postulated by Wilson and Grinsted (1977), *viz,* the direct assimilation during photosynthesis of biologically transpired CO_2 entrained by the vegetational canopy. After approximately 50 years of growth, the $\delta^{13}C$ record of the Visdalen pine appears to stabilize, presumably due to foliage with clear access to the free atmosphere. The decline in ^{13}C enrichment after AD 1850 is in accordance with the onset of anthropogenically induced changes in the isotopic composition of atmospheric CO_2 (Stuiver, 1978).

The attempt to resolve a climatically induced component in the $\delta^{13}C$ record was restricted to wood from the growth period AD 1745 to 1855. $\delta^{13}C$ values measured from other radii were combined with those reported in figure 2a. Linear regression of this sample set against the coincident temperature index values (fig 2b) gave a correlation coefficient of +0.292 (45 data pairs).

The lack of a clear response by the $^{13}C/^{12}C$ ratios to climatic change seems ominous for a tree whose physical growth rate was, doubtless, largely dependent on summer temperature. The lack of concordance and, in particular, the marked circumferential variations in ^{13}C enrichment may, however, reflect on the sampling approach. No attempt was made to separate early and late wood for independent analyses. On reflection, it seems likely that significant variations in $\delta^{13}C$ can occur between these seasonal components. If so, then this phenomenon together with positional variations in the relative proportions of early to late wood for a given growth period could explain the observed noise pattern for $\delta^{13}C$. Further investigation of this and other factors relating to wood production is underway.

ACKNOWLEDGMENTS

We are indebted to J A Matthews, University of Cardiff, who provided the tree section and assisted in compiling the annual tempera-

ture index values used in this investigation. The continued support from the Natural Environment Research Council for research at the Radiocarbon Laboratory is gratefully acknowledged.

References

Damon, P E, 1970, Climatic versus magnetic perturbation of the atmospheric C-14 reservoir, *in* Olsson, I U, ed, Radiocarbon variations and absolute chronology, Nobel symposium, 12th, Proc: New York, John Wiley and Sons, p 571-593.

Damon, P E, Lerman, J C, and Long, Austin, 1978, Temporal fluctuations of atmospheric ^{14}C; causal factors and implications: Ann Rev Earth Planetary Sci, v 6, p 457-494.

Ekdahl, C A and Keeling, C D, 1973, Atmospheric CO_2 in the natural carbon cycle; 1. Quantitative deductions from records at Mauna Loa Observatory and at the South Pole, *in* Carbon and the biosphere, Brookhaven symposium biology, 24th, Springfield, Va: Natl Tech Inf Service, p 51-85.

Ergin, M, Harkness, D D, and Walton, A, 1970, Glasgow University radiocarbon measurements II: Radiocarbon, v 12, p 486-495.

———— 1972, Glasgow University radiocarbon measurements V: Radiocarbon, v 14, p 321-325.

Farmer, J G, 1979, Problems in interpreting tree-ring $\delta^{13}C$ records: Nature, v 279, p 229-231.

Freyer, H D and Wiesberg, L, 1975, Anthropogenic carbon-13 decrease in atmospheric carbon dioxide as recorded in modern wood, *in* Symposium on isotope ratios as pollutant source and behaviour indicators, Proc: Vienna, IAEA, p 49-62.

Fritts, H C, 1976, Tree rings and climate: London, Academic Press, p 1-54.

Grinsted, M J, Wilson, A T, and Ferguson, C W, 1979, $^{13}C/^{12}C$ ratio variations in *Pinus Longaeva* (Bristlecone Pine) cellulose during the last millennium: Earth Planetary Sci Letters, v 42, p 251-253.

Harkness, D D, 1970, Artificial carbon 14; a tracer for carbon in the atmosphere and biosphere: PhD thesis, Univ Glasgow.

Harkness, D D and Wilson, H W, 1972, Some applications in radiocarbon measurement at the Scottish Research Reactor Centre, *in* Rafter, T A and Grant-Taylor, T, eds, Internatl conf on radiocarbon dating, 8th, Proc: Wellington, Royal Soc New Zealand, B102.

Matthews, J A, 1976a, Reconstruction of 'Little Ice Age' glacier oscillations and temperature fluctuations from variations in the growth of Scot's Pine at the tree-line, central South Norway: Research discussion paper no. 9, Univ Edinburgh.

———— 1976b, 'Little Ice Age' palaeotemperatures from high altitude tree growth in South Norway: Nature, v 264, p 243-245.

Nydal, Reidar, 1968, Further investigation of the transfer of radiocarbon in nature: Jour Geophys Research, v 73, p 3617-3635.

Pearman, G I, Francey, R J, and Fraser, P J B, 1976, Climatic implications of stable carbon isotopes in tree rings: Nature, v 260, p 771-772.

Stuiver, Minze, 1978, Atmospheric carbon dioxide and carbon reservoir changes: Science, v 199, p 253-258.

Suess, H E, 1970, The three causes of the secular C-14 fluctuations, their amplitudes and time constants, *in* Olsson, I U, ed, Radiocarbon variations and absolute chronology, Nobel symposium, 12th, Proc: New York, John Wiley and Sons, p 595-606.

de Vries, Hessel, 1958, Variation in concentration of radiocarbon with time and location on earth: Koninkl Nederlandse Akad Wetensch Proc, ser B61, p 94-102.

———— 1959, Measurement and use of natural radiocarbon, *in* Abelson, P H, ed, Researches in geochemisty: New York, John Wiley and Sons, p 169-189.

Wilson, A T and Grinsted, M J, 1977, $^{12}C/^{13}C$ in cellulose and lignin as palaeothermometers: Nature, v 265, p 133-135.

Yapp, C J and Epstein, S, 1977, Climatic implications of D/H ratios of meteoric water over North America (9500-22,000 BP) as inferred from ancient wood cellulose C-H hydrogen: Earth Planetary Sci Letters, v 34, p 333-350.