Tellus (1979), *31*, 124–137

On the ^{13}C record in tree rings. Part I. ^{13}C Variations in northern hemispheric trees during the last 150 years

By H. D. FREYER, *Institute of Chemistry 2, Nuclear Research Center, 5170 Jülich, Federal Republic of Germany*

(Manuscript received April 24; in final form September 4, 1978)

ABSTRACT

^{13}C data from 26 trees of different northern hemispheric locations are presented covering the time interval of the last 150 years. It has been found that the mean ^{13}C data of these trees during the 1850–1920, 1920–1940 and 1960–1975 time intervals decrease with an almost linear slope, while the data in the 1940–1960 time interval are increasing. The total $\delta^{13}C$ shift since industrialization found from our trees amounts to nearly $-2‰$ which is higher than the linear $\delta^{13}C$ decrease of $-1‰/100$ years due to the biogenic and fossil CO_2 input into the atmosphere, as assumed previously in model calculations of Siegenthaler et al. (1978). The mean data within the given error-probability correspond to those of other authors with the exception of the data for the 1920–1940 time interval. The disturbances in ^{13}C data for recording of increasing atmospheric CO_2 levels have been pointed out.

1. Introduction

Atmospheric carbon dioxide comprises the stable carbon isotope species $^{12}CO_2$ and $^{13}CO_2$ and the radioactive $^{14}CO_2$ one. Due to the long-term increase of atmospheric CO_2 its carbon isotope ratio changes with time. Emitted CO_2 from combustion of fossil fuels as well as CO_2 released by man's modifications of land biota and soils (respiration CO_2) are marked with respect to atmospheric background CO_2 by a $\delta^{13}C$ deficit of about $-18‰$ (PDB scale). Both, fossil and nonfossil respiration CO_2 cannot be distinguished by their ^{13}C, but their ^{14}C values. The ^{14}C content of atmospheric CO_2 corresponds nearly to that of nonfossil CO_2; in fossil CO_2, however, the ^{14}C isotope had decayed. Therefore, a decrease in the $^{14}C/^{12}C$ ratio reflects the fossil fuel production of CO_2, whereas a decrease in the $^{13}C/^{12}C$ ratio is due to both, fossil fuel combustion and alteration of land biota.

Atmospheric CO_2 variations have been measured carefully only over the last 20 years (e.g. Keeling et al., 1976a, b and others). Measurements within the foregoing time interval back to the preindustrial period are less reliable. Atmospheric CO_2 variations of this past can possibly be recognized by carbon isotope studies of fixed atmospheric CO_2 in wood in tree rings. The dilution of the atmospheric $^{14}CO_2$ content by fossil CO_2 (so-called Suess effect) has been proposed and measured in tree rings at first by Suess (1955). Later results have been summarized by Damon et al. (1973). Measurements of $^{13}C/^{12}C$ ratios in tree rings have been reported by different groups (Farmer and Baxter, 1974a, b; Freyer and Wiesberg, 1973, 1974a, b, 1975; Galimov, 1976; Mook and Tans, 1978; Pearman et al., 1976; Rebello and Wagener, 1976; Stuiver, 1978; Wilson, 1978). Recently, Stuiver (1978) has used his own data and those of Freyer and Wiesberg (1974a, b) and Rebello and Wagener (1976) for estimation of the past biospheric CO_2 source.

In this paper additional ^{13}C data from different trees of the northern hemisphere covering the time period of the last 150 years are presented. These data have been taken for preliminary model evaluation of the past atmospheric CO_2 increase and total anthropogenic CO_2 production since industrialization (Freyer, 1978b).

0040-2826/79/020124-14$02.50/0

2. Experimental procedure and precision of analyses

Wood consists of the main components cellulose, hemicellulose and lignin. The relative fractions may not be constant over the entire age of wood (Nikitin, 1966). The carbon isotope ratios also are different. The main cellulose fraction is enriched in ^{13}C relative to total wood by about 1.4‰ (Freyer and Wiesberg, 1974b) which is consistent with recent analyses that cellulose (40–50% of total wood; Kürschner and Popik, 1962; Nikitin, 1966) differs in ^{13}C from lignin (15–30%) by $+(2.8 \pm 0.2)$‰ and from hemicellulose by $-(1.3 \pm 0.3)$‰ (measurements on 14 oak samples; Freyer and Wiesberg, unpublished).

For the isotopic record of wood, cellulose was chosen which was isolated according to Sohn and Reiff (1942) and Kürschner and Popik (1962). Wood samples were taken at time intervals of either 2 or 5 years. The samples were first treated for about 2 h with NaOH (5%) at 60 °C in order to convert the wood into a reactive form and also to resolve hemicellulose, resins and tannic acids. After washing, the samples were treated for about 2 days with a buffered sodium chlorite solution (7% $NaClO_2$, 1% KH_2PO_4) which was renewed after 1 day. During the oxidation procedure the samples were mechanically crushed in order to facilitate the conversion of lignin and accompanying matter into a soluble form. The pure bleached cellulose residue was then burned in circulating oxygen at 150 torr according to a modified procedure described by Craig (1953).

The purified CO_2 was analysed for its $^{13}C/^{12}C$ ratio on a Micromass 602C mass spectrometer. The $\delta^{13}C$ values are reported in the conventional manner as ‰ differences from the PDB standard. The absolute calibration has been checked with the Heidelberg laboratory (Esser, 1975). The reproducibility of the isotopic analysis including sample preparation for an internal homogenized wood standard from the year 1973 up to now is ± 0.11‰ (1σ).

Only one radial cut was analysed for each tree. It has been shown that natural isotopic variations of about 1‰ in a single tree ring exist (Freyer and Wiesberg, 1974b). In recent measurements (de Silva, 1978), smaller variations in different radial cuts of an oak tree were found, which amounted to only $\pm(0.09$ to $0.14)$‰ (1σ) (analyses of five successive tree rings for seven radial cuts). Besides, the reproducibility for the relative ^{13}C difference between single tree rings in different radial cuts ($1\sigma = \pm 0.135$‰) was nearly of the same value as for the measurements of the internal wood standard used. Similar results, i.e. nearly equal relative ^{13}C changes in different radial cuts in the cellulose fraction of a tree, have been found also by Mazany et al. (1977). Very high variations of about 4–5‰ around the periphery of a tree have been reported recently by Mook and Tans (1978), which have never been observed in our analyses and those of Mazany et al. (1977).

3. Origin of samples

The tree species included in the present investigation are summarized in Table 1. Locations from at least three different regions in the northern hemisphere were selected, partly because of the claim that trees in these regions are exposed to a well-mixed atmosphere. The trees from the Black Forest (Germany), the French Atlantic Coast, the Spanish Pyrenees and Azores have been analysed by Wiesberg (1974); the results (with exception of the Black Forest pine) have been published by Freyer and Wiesberg (1974a, b, 1975). The trees from North Carolina (U.S.A.) have been analysed by de Silva (1978). Detailed analyses of the Eifel (Germany) trees will be reported in a succeeding paper (Freyer, 1978c). All recorded periods given in Table 1 are coincident with the total time of growth of the trees.

4. Results and discussion

4.1. *^{13}C variations in twentieth-century European and North American trees*

It is apparent from former measurements (Freyer and Wiesberg, 1974b) that there is a scatter of relative isotopic values obtained from individual trees, which is by far larger than the reproducibility of measurements or the natural variations within one tree ring. Such scatter is possibly due to local and physiological factors. Some of these factors with major (environmental CO_2, pollution effect) or minor significance (temperature effect) have been discerned (Freyer, 1978c; de Silva, 1978). Therefore, a relatively large

Table 1. *Location and recorded periods for the analysed trees*

Location	Species	Recorded Periods
Black Forest (Germany)	Pinus silvestris, Pi 1	1774–1970
French Atlantic coast	Quercus robur, Qu 1	1901–1972
	Quercus robur, Qu 2	1904–1972
	Quercus robur, Qu 3	1897–1972*
	Pinus maritima, Pi 2	1897–1972
	Pinus maritima, Pi 3	1885–1972
Spanish Pyrenees	Quercus lusitanica, Qu 4	1910–1972†
	Quercus lusitanica, Qu 5	1908–1972
Azores	Platanus acerifolia, Pl 1	1947–1972
North Carolina (USA)	Quercus rubra, Qu 6	1910–1975
	Quercus alba, Qu 7	1906–1975
	Quercus rubra, Qu 8	1900–1975
	Quercus alba, Qu 9	1904–1975
	Populus alba, Po 1	1932–1975
	Pinus virginiana, Pi 4	1922–1975
	Pinus serotina, Pi 5	1884–1975
Eifel (Germany)	Quercus robur, Qu 10	1890–1975
	Quercus robur, Qu 11	1896–1975
	Quercus robur, Qu 12	1914–1975
	Fraxinus excelsior, Fr 1	1920–1975
	Quercus petraea, Qu 13	1932–1975
	Quercus robur, Qu 14	1890–1973
	Quercus robur, Qu 15	1908–1973
	Aesculus hippocastanum, Ae 1	1854–1973
	Fraxinus excelsior, Fr 2	1888–1973
	Pinus silvestris, Pi 6	1924–1973

* Analysed period: 1948–1972.
† Three different cuts analysed.

number of trees have to be analysed to get a representative record. Different tree species and even different trees of one species exhibit different $\delta^{13}C$ (PDB) values. For comparison, the ^{13}C variations over the time record of a tree have been calculated as deviations from the tree specific isotopic value. In earlier publications (Freyer and Wiesberg, 1974a, b, 1975) an average value obtained from all measurements over the whole time record (i.e. time of growth) of a tree has been used. The deviations reported in this calculation are based on the average tree specific value within the years 1930–1950 A.D. This time interval may be recognized first of all as arbitrary. But it has been found that the ^{13}C values at that interval exhibit an irregular trend (i.e. a decreasing trend for the first and an increasing trend for the second decade of this interval). Secondly, the relative ^{13}C values of two different sets of Eifel (Germany) trees correspond to each other at that time interval, while they are different at other periods due to local environmental and pollution effects (Freyer, 1978c).

In spite of disturbances the whole ^{13}C record within this century derived from our measurements on 10 French Atlantic Coast trees (including those from the Spanish Pyrenees and Azores) (Freyer and Wiesberg, 1974a) and two British trees (Farmer and Baxter, 1974b) have been found to be similar. Our results are reported in Fig. 1. Additional measurements on seven North Carolina (U.S.A.) trees (de Silva, 1978) are given in the same figure. The French Atlantic Coast trees were measured in 5-year averages, those from North Carolina in 2-year averages. The bars represent the mean reproducibility of deviations (t-distribution) from the average 1930–1950 values of the individual trees.

The general trend recognized from these

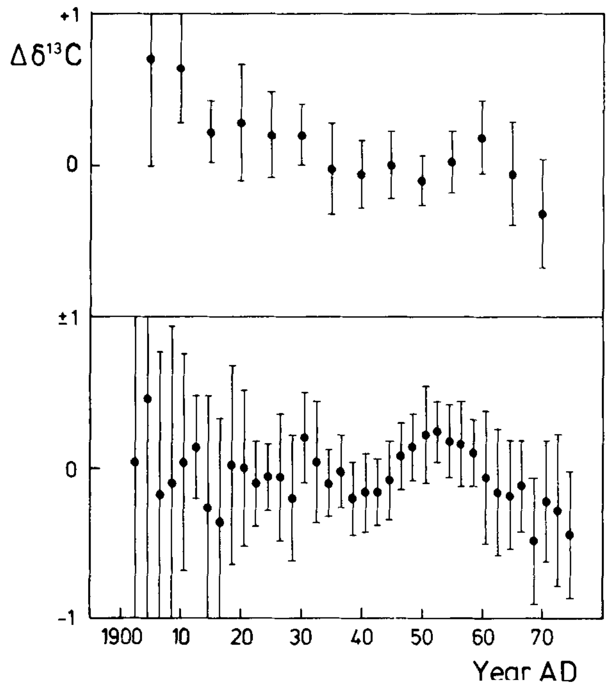

Fig. 1. $\Delta\delta^{13}C$ variations in twentieth-century European (upper data set) and North American trees (lower data set) based on the average 1930–1950 individual tree specific values. The bars represent the deviations (t-distribution), assuming an error-probability of 90%.

measurements is an overall ^{13}C decrease in this century which is interrupted for a time interval from about 1940 to 1960. Larger differences between both sets of measurements are obvious for the youth of these trees at the beginning of this century. The French Atlantic Coast trees have remained isolated over the whole time of growth, while the North Carolina trees, now isolated, have been partly situated in their youth stage in a forest canopy. A difference in $\delta^{13}C$ between forest and free atmospheric CO_2 exists which is described below.

4.2. ^{13}C *variations in nineteenth-century trees and youth trend in forest trees*

Very few measurements have been performed within nineteenth-century wood. One of our measurements on a Black Forest (Germany) pine, given in Fig. 2, is dated back to 1774 A.D. Different time periods are pointed out by the ^{13}C record. During the youth stage of this tree, which holds for about 20 years, the ^{13}C values are increasing. This stage is followed by an interval with relatively constant ^{13}C values. Since the beginning of industrialization at about 1850 the ^{13}C values are decreasing. This decrease is interrupted at about 1940. The later increase and decrease is rather high, which is possibly due to local influences, but it coincides with disturbances observed for the other northern-hemisphere trees at the same time interval.

Similar records of youth trend and decreasing ^{13}C values in the late nineteenth and early twentieth century are exhibited by two other trees. The results obtained on both trees (Fig. 3)—a Douglas fir from a forest of Olympic Peninsula, Washington, U.S.A. (Stuiver, 1978) and a chestnut tree, isolated at least since 1890, from the Eifel, Germany (Freyer, 1978c)—have been used additionally for calculations of nineteenth-century ^{13}C variations.

Increasing ^{13}C values during the youth stage are a common feature observed even for other forest trees included in our measurements. This phenomenon is related to ^{13}C variations of the environmental CO_2 in a forest stand. It is well known that large diurnal CO_2 fluctuations occur in a forest canopy which become progressively

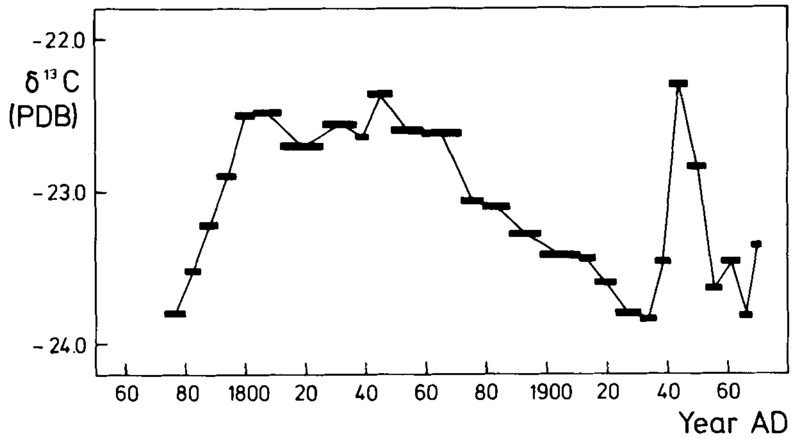

Fig. 2. $\delta^{13}C$ variations in *Pinus silvestris* (Pine; Black Forest, Germany) from 1774–1970 A.D.

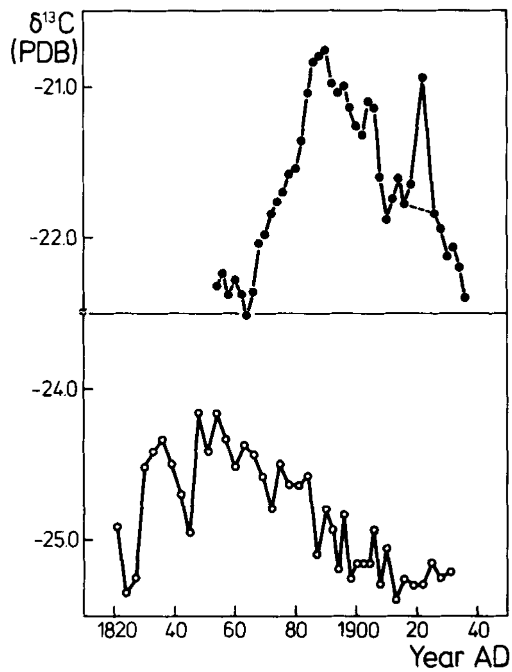

Fig. 3. $\delta^{13}C$ variations in *Pseudotsuga menziesii* (Douglas fir; Olympic Peninsula, Washington, U.S.A.) [lower measurements] and in *Aesculus hippocastanum* (chestnut tree; Eifel, Germany) [upper measurements] at quoted time intervals. The Douglas fir has been analysed by Stuiver (1978); the data were obtained from a figure in Stuiver's paper.

smaller with the height of sampling (Lieth, 1963; Baumgartner, 1969; Bischof and Odh, 1976). During the night the CO_2 concentrations at ground level increase in accordance with depletions in ^{13}C (with respect to free atmospheric CO_2) due to addition of soil and plant respiration CO_2 (Keeling, 1958). For peak minima CO_2 concentrations at midday the ^{13}C values correspond to those in free atmospheric CO_2 because of turbulent atmospheric mixing. As the net effect a slight depletion in ^{13}C of ground-level CO_2 remains at daytime which is recorded by a young forest tree. This daytime depletion will disappear at a certain height within or above the canopy, which means that the ^{13}C record of an older forest tree reflects free atmospheric CO_2 more (see e.g. summary given by Freyer, 1978a).

4.3. *Mean ^{13}C record in trees since beginning of industrialization*

From the different sets of measurements the mean ^{13}C record since the beginning of industrialization has been calculated. Without any distinction the first 20 years of each tree were omitted to avoid the possible youth trend. The mean data for the 1920–1975 time interval from measurements of the European and North American trees are illustrated in Fig. 4. Further measurements on Eifel (Germany) trees—characterized as polluted and unpolluted trees (Freyer, 1978c)—were included at time intervals, at which both sets of trees had been exposed to normal free atmospheric CO_2.

Similar calculations have been performed for the 1798–1937 time interval from measurements of the nineteenth-century trees given in Figs. 2 and 3. The ^{13}C values for the youth trend of these trees (which

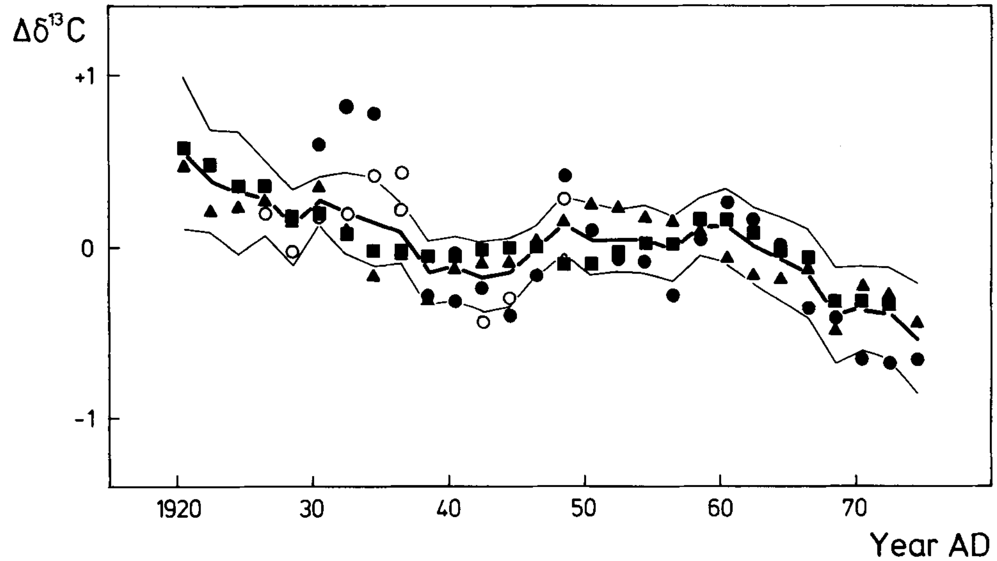

Fig. 4. Mean $\Delta\delta^{13}C$ variations from different sets of tree-ring measurements based on the average 1930–1950 values of individual trees for the 1920–1975 time interval. The different symbols stand for measurements on European trees (full squares), North Carolina trees (full triangles), unpolluted Eifel trees (full circles) and polluted Eifel trees (open circles). The upper and lower line represent the deviations (t-distribution), assuming an error-probability of 95%.

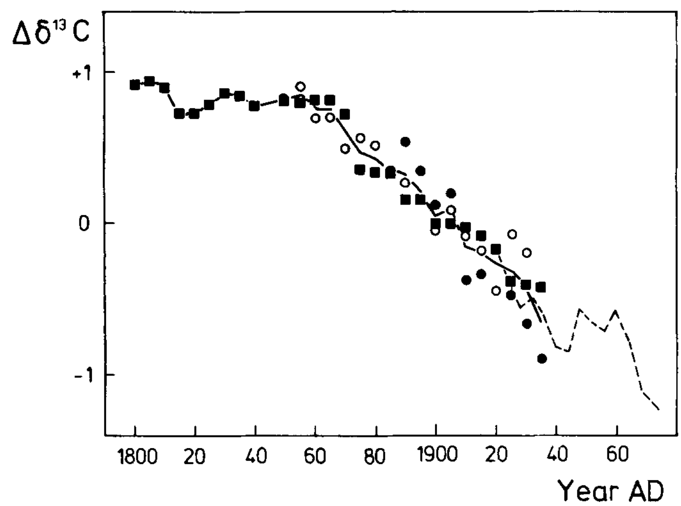

Fig. 5. $\Delta\delta^{13}C$ variations from tree ring measurements in *Pinus silvestris*, Pi 1 (full squares), *Pseudotsuga menziesii*, Ps 1 (open circles) and *Aesculus hippocastanum*, Ae 1 (full circles) based on the average 1890–1920 value of each tree. The ^{13}C record of these trees is connected with the record for the 1920–1975 time interval (broken line) from Fig. 4. The relative ^{13}C data for the average 1890–1920 and 1930–1950 values differ by −0.7‰ at the mean based on the individual $\Delta\delta^{13}C$ values for both sets in the overlapping 1920–1937 time interval.

lasts for the Douglas fir and chestnut tree for about 30 years) as well as peak ^{13}C values for the chestnut tree in the 1918–1927 time interval were omitted. The disturbances in the Eifel chestnut tree will be discussed in terms of a modified tree physiology as a consequence of an air pollution effect (Freyer, 1978c). The ^{13}C record is illustrated in Fig. 5. The mean record for the 1920–1975 time

Table 2. *Mean $\Delta\delta^{13}C$ data for different trees for the 1798–1975 time interval, calculated as deviations from the average $\delta^{13}C$ values of the periods 1890–1920 (1798–1937 time interval) and 1930–1950 (1920–1975 time interval) for each tree*

$\Delta\delta^{13}C$			
Years A.D.	Mean $\pm t\cdot\frac{\sigma}{\sqrt{n}}$	Years A.D.	Mean $\pm t\cdot\frac{\sigma}{\sqrt{n}}$
1798/1802*	+0.91 (1)†	1920/21*	+0.55 ± 0.44 (6)†
03/07	+0.94 (1)	22/23	+0.39 ± 0.30 (6)
08/12	+0.90 (1)	24/25	+0.32 ± 0.36 (6)
13/17	+0.72 (1)	26/27	+0.29 ± 0.22 (10)
18/22	+0.72 (1)	28/29	+0.12 ± 0.22 (12)
23/27	+0.78 (1)	30/31	+0.27 ± 0.14 (18)
28/32	+0.86 (1)	32/33	+0.20 ± 0.24 (18)
33/37	+0.84 (1)	34/35	+0.15 ± 0.26 (20)
38/42	+0.77 (1)	36/37	+0.09 ± 0.18 (20)
43/47	—	38/39	−0.15 ± 0.19 (20)
48/52	+0.81 ± 0.13 (2)	40/41	−0.12 ± 0.19 (22)
53/57	+0.85 ± 0.64 (2)	42/43	−0.18 ± 0.20 (22)
58/62	+0.75 ± 0.76 (2)	44/45	−0.15 ± 0.20 (23)
63/67	+0.75 ± 0.70 (2)	46/47	−0.01 ± 0.14 (23)
68/72	+0.61 ± 1.46 (2)	48/49	+0.13 ± 0.17 (24)
73/77	+0.46 ± 1.33 (2)	50/51	+0.05 ± 0.21 (19)
78/82	+0.42 ± 1.14 (2)	52/53	+0.04 ± 0.18 (21)
83/87	+0.34 ± 0.19 (2)	54/55	+0.05 ± 0.20 (21)
88/92	+0.31 ± 0.49 (3)	56/57	−0.01 ± 0.19 (21)
93/97	+0.21 ± 0.27 (3)	58/59	+0.12 ± 0.17 (21)
98/1902	+0.02 ± 0.23 (3)	60/61	+0.12 ± 0.22 (21)
03/07	+0.09 ± 0.25 (3)	62/63	+0.01 ± 0.22 (21)
08/12	−0.16 ± 0.47 (3)	64/65	−0.07 ± 0.25 (21)
13/17	−0.20 ± 0.31 (3)	66/67	−0.15 ± 0.26 (22)
18/22	−0.27 ± 0.39 (3)	68/69	−0.40 ± 0.28 (22)
23/27	−0.32 ± 0.52 (3)	70/71	−0.36 ± 0.25 (22)
28/32	−0.43 ± 0.58 (3)	72/73	−0.39 ± 0.27 (22)
33/37	−0.66 ± 2.98 (2)	74/(75)	−0.53 ± 0.32 (12)

* The measurements have been performed at different time intervals (Figs. 1–3). The values have been calculated for the given five (1798–1937) and two (1920–1975) year intervals. The 1975 tree ring is included only partly.

† The deviations $t(\sigma\sqrt{n})$ follow from the t-distribution, assuming an error probability of 95%. The number of analysed trees is given in parentheses.

interval is connected with the former one. All mean numerical data are given in Table 2.

The total ^{13}C decrease since the beginning of industrialization amounts to about 2‰ maximally. A decrease in ^{13}C values has to be expected because of increasing atmospheric CO_2 levels, but other effects become evident which then disagree with the present model conception (e.g. Machta, 1973) of exponentially increasing CO_2 levels of the past. During the first time interval between 1860 and 1920 the ^{13}C values decrease at a rate which could not have been caused even by complete retention of all fossil CO_2 introduced into the atmosphere. The total $\delta^{13}C$ shift obtained from tree ring data during that time interval amounts to about −1.2‰. Assuming $617\cdot10^{15}$ g C = 290 ppm CO_2 as pre-industrial atmospheric CO_2 concentration (Bray, 1959), a complete retention of the cumulative fossil CO_2 input of $26\cdot10^{15}$ g C in the 1860–1920 period (Freyer, 1978a) would have resulted in a $\delta^{13}C$ shift of only −0.7‰. For the time interval between 1940 and 1960, the input of fossil CO_2 into the atmosphere has been increasing; however, this effect cannot be recognized in the observed ^{13}C fluctuations for this period, even when disturbances of the record are supposed. Only the decreasing ^{13}C values within the 1960–1975 time interval agree qualitatively with direct measurements of atmospheric CO_2 levels.

4.4. *Comparison with ^{13}C tree ring data measured by other authors*

It is obvious from Figs. 4 and 5 that the mean ^{13}C data during the 1850–1920, 1920–1940 and 1960–1975 time intervals decrease almost linearly with time. During the 1940–1960 interval an increase is observed with lower linear correlation (see correlation coefficients for linear regression of mean "c" values with time, Tables 3 and 4). Tables 3 and 4 summarize the mean linear regression slope in these time intervals calculated for all our analysed trees, even if low or no correlation exists for individual sets of measurements. From the slope the total ^{13}C shift during the 1850–1920 and 1920–1975 time intervals has been obtained, partly by extrapolation, when the measurements do not cover the whole time interval.

The same procedure has been performed on tree ring data published by other authors (Table 5), which had been available not as numerical values, but in graphical form (with exception of the data of Rebello, 1974). These data are from the measurements of Farmer and Baxter (1974a) on two British forest trees (oak and European larch), Mook and Tans (1978) on four Dutch trees (oaks), Wilson (1978) on one Californian mountain tree (bristlecone pine), Rebello (1974) and Rebello and Wagener (1976) on one Brazilian mountain tree (araucaria, two cross-sections), Pearman et al. (1976) on two Tasmanian forest trees (King Billy pines) and Fraser et al. (1976) on additional three Tasmanian forest trees (King Billy pines; mean curve).

Information on the coincidence of the analysed periods and the time of growth of the measured trees is very scarce. Therefore a possible youth trend may be included in these measurements. In the case of the Farmer and Baxter (1974a) data, the trees had been planted some decades before the beginning of the analysed period, while in the case of the Rebello (1974) tree all rings had been analysed. The measurements of Fraser et al. (1976) start in 1850. An irregular trend of $\delta^{13}C$ values observed within the 1850–1895 time interval have been omitted for calculation of mean values. The measurements of Wilson (1978) are dated back to about 1750, which tally extremely well with our measurements on the pine from the Black Forest until 1920, i.e. constant ^{13}C values for the late-eighteenth century and the first half of the nineteenth century followed by a sharp decrease in $\delta^{13}C$ since 1850.

Our final mean "a" data of slope and shift and those found from measurements of other authors are summarized in Table 6. The excellent agreement of data for the 1850–1920 time interval is evident, neglecting the measurements of Fraser et al. (1976) for the 1850–1895 time interval. Even the data of the positive and negative slopes for the 1940–1960 and 1960–1975 time intervals, respectively, correspond to each other within the given error probability. A main, perhaps random, discrepancy between our observations and those of other authors exists for the mean data of the 1920–1940 slope and, consequently, for the shift during the 1920–1975 time interval. Only three of our slopes at the 1920–1940 time interval from a total of 20 have a positive sign, which are all from measurements that do not cover the whole time interval. If our slopes for trees of regions C and D (Table 4), which were not standing for the whole

Table 3. *Mean $\delta^{13}C$ slope and extrapolated $\delta^{13}C$ shift for the 1850–1920 time interval obtained from the nineteenth-century trees (Fig. 5)*

Tree species	Slope (‰ · yr^{-1}) (1850–1935)	Shift (‰) (1850–1920)
Pi 1	−0.016 (0.98)**	−1.13**
Ps 1	−0.015 (0.97)**	−1.02**
Ae 1	−0.030 (0.97)*	−2.11*
Mean "a"	-0.018 ± 0.008	-1.28 ± 0.58
Mean "b"	-0.020 ± 0.020	-1.42 ± 1.49
Mean "c"	−0.017 (0.99)	−1.21

Note: Mean "a" has been calculated considering individual values as twofold (which are marked by two asterisks) obtained from data covering the whole time interval and as single (which are marked by one asterisk) obtained from data covering only a part of the time interval. The deviations $t \cdot (\sigma/\sqrt{n})$ follow from the t-distribution, assuming an error-probability of 95%. Mean "b" has been calculated considering individual values as single. Mean "c" has been calculated from the mean data in Table 2. Values in parentheses are the correlation coefficients r.

Table 4. *Mean $\delta^{13}C$ slope and extrapolated $\delta^{13}C$ shift for the 1920–1975 time interval obtained from the individual trees summarized in Table 1. Tree species A: European trees (from the French Atlantic coast, Spanish Pyrenees, Azores). B: North Carolina trees. C: Unpolluted Eifel (Germany) trees. D: Polluted Eifel (Germany) trees*

Tree species by regions	Slope (‰ · yr⁻¹) (1920–1940)	(1940–1960)	(1960–1975)	Shift (‰) (1920–1975)
A, Qu 1	−0.033 (0.40)**	+0.005 (0.16)**	−0.026 (0.33)**	−0.06**
Qu 2	−0.020 (0.46)**	+0.020 (0.32)**	−0.013 (0.20)**	+0.07**
Pi 2	−0.045 (0.78)**	+0.019 (0.68)**	−0.094 (0.94)**	−2.02**
Pi 3	−0.054 (0.80)**	+0.026 (0.56)**	−0.055 (0.94)**	−0.87**
Qu 4.1	−0.057 (0.76)*	+0.031 (0.71)**	−0.031 (0.90)**	−1.39*
Qu 4.2	−0.073 (0.72)*	+0.012 (0.34)**	−0.024 (0.63)**	−1.84*
Qu 4.3	−0.059 (0.97)*	−0.010 (0.31)**	−0.007 (0.42)**	−1.76*
Qu 5	+0.029 (0.64)*	−0.032 (0.76)**	−0.117 (0.95)**	−1.64*
Qu 3	—	+0.096 (0.86)*	−0.054 (0.92)**	—
Pl 1	—	—	−0.004 (0.13)*	—
B, Qu 6	−0.019 (0.34)*	+0.024 (0.58)**	−0.022 (0.62)**	−0.12*
Qu 7	−0.018 (0.28)*	−0.007 (0.33)**	−0.066 (0.83)**	−1.37*
Qu 8	−0.072 (0.74)**	+0.022 (0.30)**	−0.010 (0.20)**	−0.81**
Qu 9	−0.014 (0.16)**	−0.029 (0.72)**	+0.003 (0.12)**	−0.89**
Po 1	—	−0.186 (0.90)*	−0.040 (0.50)**	—
Pi 4	—	+0.050 (0.63)**	−0.049 (0.56)**	—
Pi 5	−0.025 (0.58)**	+0.034 (0.60)**	+0.025 (0.39)**	−0.48**
C, Qu 10	−0.147 (0.84)*	+0.056 (0.69)**	−0.108 (0.70)**	−4.26*
Qu 11	−0.103 (0.76)*	0.000 (0.01)**	−0.005 (0.20)**	−2.41*
Qu 12	−0.154 (0.79)*	−0.043 (0.52)**	−0.112 (0.81)**	−3.72*
Fr 1	—	+0.025 (0.33)**	−0.075 (0.85)**	—
Qu 13	—	−0.017 (0.44)*	−0.079 (0.86)**	—
D, Qu 14	+0.014 (0.28)*	−0.003 (0.02)*	—	
Qu 15	+0.048 (0.49)*	+0.010 (0.07)*	—	
Ae 1	−0.005 (0.12)*	+0.014 (0.10)*	—	
Fr 2	−0.124 (0.74)*	+0.213 (0.99)*	—	
Pi 6	—	+0.042 (0.96)*	—	
Total, Mean "a"	−0.044 ± 0.019	+0.013 ± 0.016	−0.045 ± 0.012	−1.24 ± 0.49
Total, Mean "b"	−0.047 ± 0.026	+0.014 ± 0.026	−0.044 ± 0.018	−1.47 ± 0.65
Total, Mean "c"	−0.029 (0.93)	+0.013 (0.78)	−0.046 (0.97)	−1.09

Note: For calculations of mean values, see note to Table 3.

time interval as well as the generally unusual positive slopes of trees analysed by Mook and Tans (1978) are omitted, the discrepancy will be lowered. It should be further noted that the slope obtained from our mean curve (mean "c", Table 4) is lower than the mean "a" value.

4.5. *Disturbances in ^{13}C data for recording of increasing atmospheric CO_2 levels*

The total ^{13}C shift in tree rings since industrialization obtained from the mean data of Table 6 amounts to about −2‰. This large total effect has to be attributed mainly to increasing atmospheric CO_2 levels, although it may be superimposed by other environmental factors. The decreasing ^{13}C data during the late nineteenth and early twentieth century found among all analysed trees of different geographical locations in the northern and southern hemisphere are nearly identical. In twentieth-century trees larger variations of data exist. It is by

Table 5. *Mean $\delta^{13}C$ slope and extrapolated $\delta^{13}C$ shift for the 1850–1920 and 1920–1975 time intervals obtained from tree ring data of other authors*

Authors	Analysed periods	Slope (‰ · yr^{-1}) (before 1920)	(1920–1940)	(1940–1960)	(after 1960)	Shift (‰) (1850–1920)	(1920–1975)
Farmer and	1900–1964	neg.	ca. +0.01**	ca. 0.00**	neg.	—	—
Baxter (1974a)	1905–1968	neg.	ca. −0.05**	ca. +0.06**	ca. −0.06*	—	ca. −0.70*
Mook and	1851–1968	−0.012 (0.48; 22)**	−0.001 (0.01; 7)**	+0.009 (0.18; 8)**	−0.040 (0.28; 4)*	−0.82**	−0.46*
Tans (1978)		−0.010 (0.43; 22)	−0.015 (0.38; 7)	+0.009 (0.15; 8)	−0.028 (0.29; 4)	−0.69	−0.16
	1859–1972	−0.010 (0.32; 21)**	−0.005 (0.12; 7)**	+0.010 (0.23; 8)**	+0.001 (0.02; 9)*	−0.67**	+0.20*
		−0.006 (0.26; 21)	−0.016 (0.41; 7)	+0.005 (0.16; 8)	−0.026 (0.34; 9)	−0.42	−0.03
	1899–1971	−0.032 (0.29; 9)*	+0.042 (0.82; 8)**	+0.062 (0.51; 13)**	+0.032 (0.30; 12)*	−2.21*	+1.88*
		−0.021 (0.27; 9)	+0.027 (0.60; 8)	+0.068 (0.72; 13)	+0.016 (0.21; 12)	−1.46	+1.91
	1923–1967	—	+0.031 (0.65; 6)**	+0.084 (0.79; 6)**	neg.	—	—
		—	+0.028 (0.75; 6)	+0.039 (0.80; 6)	pos.	—	—
Wilson (1978)	1750–1960	const. (before 1850) −0.018 (0.91; 7)**	pos.	neg.	—	−1.23**	—
Rebello (1974),	1888–1972	−0.038 (0.91; 7)*	−0.001 (0.01; 5)**	−0.029 (0.95; 5)**	neg.	−2.67*	—
Rebello and Wagener (1976)	1920–1972	—	+0.007 (0.35; 5)**	−0.014 (0.58; 5)**	−0.034 (0.53; 3)*	—	−0.73*
Pearman et al.	1895–1970	−0.006 (0.67; 6)*	−0.015 (0.94; 5)**	+0.023 (0.84; 5)**	neg.	−0.42*	—
(1976)	1895–1970	−0.012 (0.92; 6)*	−0.014 (0.86; 5)**	+0.033 (0.87; 5)**	pos.	−0.84*	—
Fraser et al. (1976)	1850–1975	−0.015 (0.89; 6)[3]*	−0.011 (0.65; 5)[3]**	+0.026 (0.71; 5)[3]**	−0.036 (0.89; 3)[3]**	−1.08[3]*	−0.16[3]**
	Total Mean "a"	−0.016 ± 0.005	−0.002 ± 0.009	+0.024 ± 0.012	−0.029 ± 0.017	−1.14 ± 0.38	−0.07 ± 0.47

Note: For calculation of mean values, see note to Table 3. Values in parentheses are the correlation coefficients r and the number of analysed samples within the time interval. Slopes based on less than three analysed samples within the time interval have been omitted; they are marked only as positive (pos.) or negative (neg.) slopes. First data given for Mook and Tans (1978) are from $\delta^{13}C$ values without corrections; second data, which have not been considered for calculation of mean values, are from $\delta^{13}C$ values with individual (temperature) corrections.

Table 6. *Summary of final mean "a" data from Tables 3–5*

	Slope (‰ · yr^{-1})				Shift (‰)	
	(1850–1920)	(1920–1940)	(1940–1960)	(1960–1975)	(1850–1920)	(1920–1975)
Mean "a" (Table 3 + 4)	−0.018 ± 0.008 (5)	−0.044 ± 0.019 (27)	+0.013 ± 0.016 (44)	−0.045 ± 0.012 (43)	−1.28 ± 0.58 (5)	−1.24 ± 0.49 (23)
Mean "a" (Table 5)	−0.016 ± 0.005 (13)	−0.002 ± 0.009 (26)	+0.024 ± 0.012 (26)	−0.029 ± 0.017 (11)	−1.14 ± 0.38 (13)	−0.07 ± 0.47 (11)
Total, Mean "a"	−0.017 ± 0.004	−0.023 ± 0.012	+0.017 ± 0.011	−0.042 ± 0.010	−1.18 ± 0.29	−0.86 ± 0.40

Note: Values in parentheses are the number of data considered for calculation of mean "a", which are not identical with the number of analysed trees; see note to Table 3.

all means possible that nineteenth-century trees are a better ^{13}C recorder of atmospheric CO_2 variations than twentieth-century trees, even if the trees had been selected carefully. It will be shown in a succeeding paper (Freyer, 1978c) that human activities other than those to increase atmospheric CO_2 levels could affect the ^{13}C record to a considerable extent.

Temperature fluctuations may be another disturbing factor of the ^{13}C record, but the direct temperature effect is at the most of the order of 0.1–0.3‰ variation in $\delta^{13}C$ per °C; moreover, the sign of this effect is not well established. Pearman et al. (1976) have found increasing $\delta^{13}C$ data in tree rings with increasing summer temperatures; somewhat modified data will be given by de Silva (1978). Nevertheless, a direct ^{13}C response may have some consequences, especially for the 1920–1960 time interval. A maximum of mean annual temperatures in the northern hemisphere existed in 1940 with about 0.5 °C above the 1920 temperature levels (*Inadvertent Climate Modification*, 1971).

The southern hemisphere tree stations quoted by Pearman et al. (1976) and Fraser et al. (1976) exhibit for that time interval, on the contrary, temperature minima during summer, while the mean annual surface temperatures of the globe as well as of the southern hemisphere show the reverse trend (*Inadvertent Climate Modification*, 1971; Lamb, 1973). In addition to the direct response, temperature fluctuations will influence the mass exchange of CO_2 between atmosphere and ocean (Eriksson, 1963) and, consequently, the isotopic exchange.

Stuiver (1978) has found a ^{13}C effect in the early 1930s at the heartwood–sapwood boundary of his tree and has interrupted, therefore, his measurements. This effect is known even from ^{14}C measurements, but only when the boundary line is visible (Cain and Suess, 1976). The observed effect of Stuiver (1978), however, falls in a time interval, at which other trees, with a heartwood–sapwood boundary at different times or having no boundary at all, exhibit similar disturbances (i.e. increasing $\delta^{13}C$ data). In the trees of Pearman et al. (1976), Mook and Tans (1978) and in our trees no heartwood–sapwood effect has been detected.

5. Conclusions

^{13}C measurements in tree rings during the first half of the nineteenth century have been performed on a bristlecone pine (Wilson, 1978) and a European pine (this work), neglecting the ^{13}C record of the Douglas fir (Stuiver, 1978) which, possibly, is attributed to a youth trend of a forest tree. It has been found that the ^{13}C values during that time interval remain relatively constant. However, many more studies have to be carried out immediately to know the variability during the pre-industrial period. A decrease of ^{13}C values since industrialization seems, however, to be well established. The effect from 1850 up tc now, obtained from our measurements, is larger than the $\delta^{13}C$ decrease of -1‰/100 years, as previously assumed in the calculations of Oeschger and Siegenthaler (1978) and Siegenthaler et al. (1978). The total effect of about -2‰ could not have been caused by temperature fluctuations; perhaps it will be somewhat altered (possibly lowered) if reliable data on the temperature effect of the photosynthetic ^{13}C discrimination in trees are known. No answer to this problem follows from the temperature-corrected data of Mook and Tans (see second data of these authors in Table 5).

Neglecting temperature corrections, the large ^{13}C shift in the late nineteenth and early twentieth centuries could not have been caused by introducing only fossil CO_2 into the atmosphere. Therefore, an additional CO_2 input into the atmosphere from destroying of land biota has to be assumed as discussed previously in statistical analyses of several authors (Adams et al., 1977; Bolin, 1977; Hampicke, 1978; Woodwell et al., 1978). Stuiver (1978) has used, partly, some of our earlier results (Freyer and Wiesberg, 1974a, b, 1975) for calculations of the past biospheric CO_2 source strength. Recently, Wilson (1978) has estimated from his ^{13}C tree ring measurements that during the late nineteenth century biospheric CO_2 had been injected into the atmosphere in amounts larger than the amount of CO_2 produced by fossil fuels up to 1950. Our uncorrected ^{13}C data of this compilation have been used for preliminary evaluation of the past atmospheric CO_2 increase and total anthropogenic CO_2 production since industrialization (Freyer, 1978b). Our calculation has been based on the empirical coincidence of the ^{13}C shift in tree rings during the 1960–1975 time interval with direct atmospheric CO_2 concentrations at Mauna Loa (Keeling et al., 1976a) converted into ^{13}C data by a $\delta^{13}C/CO_2$ short-term relationship of atmospheric CO_2 levels (Freyer, 1978a). The question, however, emerges, whether this short-term $\delta^{13}C/CO_2$ relationship is applicable to long-term increasing atmospheric CO_2 levels.

6. Acknowledgements

The co-operation of L. Wiesberg and M. P. de Silva, who have both studied ^{13}C tree ring data in their theses, is especially acknowledged. Further thanks are due to K. Kobel and H. Musall for help in sample preparation and mass-spectrometric analyses.

REFERENCES

Adams, J. A. S., Mantovani, M. S. M. and Lundell, L. L. 1977. Wood versus fossil fuel as a source of excess carbon dioxide in the atmosphere: A preliminary report. *Science 196*, 54–56.

Baumgartner, A. 1969. Meteorological approach to the exchange of CO_2 between the atmosphere and vegetation, particularly forest stands. *Photosynthetica 3*, 127–149.

Bischof, W. and Odh, S.-Å. 1976. CO_2-measurements within and above a scots pine stand. Internal Report 45. Swedish Coniferous Forest Project, 18 pp. (in Swedish).

Bolin, B. 1977. Changes of land biota and their importance for the carbon cycle. *Science 196*, 613–615.

Bray, J. R. 1959. An analysis of the possible recent change in atmospheric carbon dioxide concentration. *Tellus 11*, 220–230.

Cain, W. F. and Suess, H. E. 1976. Carbon 14 in tree rings. *J. Geophys. Res. 81*, 3688–3694.

Craig, H. 1953. The geochemistry of the stable carbon isotopes. *Geochim. Cosmochim. Acta 3*, 53–93.

Damon, P. E., Long, A. and Wallick, E. I. 1973. On the magnitude of the 11-year radiocarbon cycle. *Earth Planet. Sci. Lett 20*, 300–306.

Eriksson, E. 1963. Possible fluctuations in the atmospheric carbon dioxide due to changes in the properties of the sea. *J. Geophys. Res. 68*, 3871–3876.

Esser, N. 1975. Messung der absoluten Konzentration und des ^{13}C-Gehaltes von atmosphärischem CO_2. Diplomarbeit, Inst. für Umweltphysik, Univ. Heidelberg, 48 pp.

Farmer, J. G. and Baxter, M. S. 1974a. Atmospheric carbon dioxide levels as indicated by the stable isotope record in wood. *Nature 247*, 273–275.

Farmer, J. G. and Baxter, M. S. 1974b. Dendrochronology and ^{13}C content in atmospheric CO_2. *Nature 252*, 757.

Fraser, P. J. B., Francey, R. J. and Pearman, G. J. 1976. Stable carbon isotopes in tree rings as climatic indicators. Paper, presented at the Int. Conf. on Stable Isotopes, Lower Hutt, Wellington, New Zealand, Aug. 4–6.

Freyer, H. D. 1978a. Variations of the atmospheric CO_2 content. In *The global carbon cycle* (eds. B. Bolin, E. T. Degens, S. Kempe and P. Ketner), Chap. 3. John Wiley and Sons (in press).

Freyer, H. D. 1978b. Preliminary evaluation of past CO_2 increase, as derived from ^{13}C measurements in tree rings. In *Carbon dioxide, climate and society.* Proc. IIASA Workshop (ed. J. Williams), pp. 69–77. Oxford: Pergamon Press.

Freyer, H. D. 1978c. On the ^{13}C record in tree rings. II. Registration of microenvironmental CO_2 and anomalous pollution effect. Unpublished manuscript.

Freyer, H. D. and Wiesberg, L. 1973. ^{13}C decrease in modern wood due to the large scale combustion of fossil fuels. *Naturwissenschaften 60*, 517–518.

Freyer, H. D. and Wiesberg, L. 1974a. Dendrochronology and ^{13}C content in atmospheric CO_2. *Nature 252*, 757.

Freyer, H. D. and Wiesberg, L. 1974b. Anthropogenic carbon-13 decrease in atmospheric carbon dioxide as recorded in modern wood. In Proc. FAO/IAEA—Symp. Isotope ratios as pollutant source and behaviour indicators, pp. 49–62. Vienna: IAEA.

Freyer, H. D. and Wiesberg, L. 1975. Review on different attempts of tracing back the increasing atmospheric CO_2 level to pre-industrial times. In Proc. 2nd Internat. Conf. Stable Isotopes (eds. E. R. Klein and P. D. Klein). USERDA CONF-751027, pp. 611–620. Oak Brook, Ill.

Galimov, E. M. 1976. Variations of the carbon cycle at present and in the geological past. In *Environmental biogeochemistry, Vol. 1. Carbon, nitrogen, phosphorus, sulfur and selenium* (ed. J. O. Nriagu), pp. 3–11. Ann Arbor, Mich.: Ann Arbor Science Publishers, Inc.

Hampicke, U. 1978. Exchanges of carbon between land biota and atmosphere, induced by man. In *The global carbon cycle* (eds. B. Bolin, E. T. Degens, S. Kempe and P. Ketner), Chap. 7. John Wiley and Sons (in press).

Inadvertent Climate Modification (SMIC). 1971. (eds. C. L. Wilson and W. H. Matthews), Cambridge, Mass.: MIT Press.

Keeling, C. D. 1958. The concentration and isotopic abundances of atmospheric carbon dioxide in rural areas. *Geochim. Cosmochim. Acta 13*, 322–334.

Keeling, C. D., Bacastow, R. B., Bainbridge, A. E., Ekdahl, C. A., Guenther, P. R., Waterman, L. S. and Chin, J. F. S. 1976a. Atmospheric carbon dioxide variations at Mauna Loa Observatory, Hawaii. *Tellus 28*, 538–551.

Keeling, C. D., Adams, J. A., Ekdahl, C. A. and Guenther, P. R. 1976b. Atmospheric carbon dioxide variations at the South Pole. *Tellus 28*, 552–564.

Kürschner, K. and Popik, M. G. 1962. Zur Analyse von Hölzern. *Holzforschung 16*, 1–11.

Lamb, H. H. 1973. Whither climate now? *Nature 244*, 395–397.

Lieth, H. 1963. The role of vegetation in the carbon dioxide content of the atmosphere. *J. Geophys. Res. 68*, 3887–3898.

Machta, L. 1973. Prediction of CO_2 in the atmosphere. In *Carbon in the biosphere* (eds. G. M. Woodwell and E. V. Pecan), AEC Symposium Series 30, 21–31. Springfield, Virginia: NTIS US Dept. Commerce.

Mazany, T., Lerman, J. C. and Long, A. 1977. Isotope dendroclimatology. Natural stable carbon isotope analysis of tree rings from an archaeological site. Paper, presented at the AAAS Poster Session, Washington, D.C., Febr. 16.

Mook, W. G. and Tans, P. 1978. Communication, presented at the IIASA Workshop on Carbon Dioxide, Climate and Society, Laxenburg, Austria, Febr. 21–24.

Nikitin, N. I. 1966. *The chemistry of cellulose and wood.* Jerusalem: Monson.

Oeschger, H. and Siegenthaler, U. 1978. The dynamics of the carbon cycle as revealed by isotope studies. In *Carbon dioxide, climate and society.* Proc. IIASA Workshop (ed. J. Williams), pp. 45–61. Oxford: Pergamon Press.

Pearman, G. I., Francey, R. J. and Fraser, P. J. B. 1976. Climatic implications of stable carbon isotopes in tree rings. *Nature 260*, 771–773.

Rebello, A. 1974. O registro de ^{13}C em aneis de crescimento de arvores e sua correlacao com o acrescimo no CO_2 atmosferico devido a queima de combustivel fossil. Thesis, Pontificia Universidade Catolica, Rio de Janeiro, 98 pp.

Rebello, A. and Wagener, K. 1976. Evaluation of ^{12}C and ^{13}C data on atmospheric CO_2 on the basis of a diffusion model for oceanic mixing. In *Environmental biogeochemistry, Vol. 1. Carbon, nitrogen, phosphorus, sulfur and selenium* (ed. J. O. Nriagu), pp. 13–23. Ann Arbor, Mich.: Ann Arbor Science Publishers, Inc.

Siegenthaler, U., Heimann, M. and Oeschger, H. 1978. Model responses of the atmospheric CO_2 level and $^{13}C/^{12}C$ ratio to biogenic CO_2 input. In *Carbon dioxide, climate and society.* Proc. IIASA Workshop (ed. J. Williams), pp. 79–87. Oxford: Pergamon Press.

de Silva, M. P. 1978. ^{13}C-Variationen in Baumjahresringen als Folge des anthropogenen CO_2-Anstiegs der Atmosphäre: Untersuchung des Einflusses von Klimaparametern. Thesis, Rheinisch-Westfälische Hochschule Aachen, 107 pp.

Sohn, A. W. and Reiff, F. 1942. Natriumchlorit als Aufschlußmittel. *Papierfabrikant 40*, 1–7.

Stuiver, M. 1978. Atmospheric carbon dioxide and carbon reservoir changes. *Science 199*, 253–258.

Suess, H. E. 1955. Radiocarbon concentration in modern wood. *Science 122*, 415–417.

Wiesberg, L. 1974. Die ^{13}C-Abnahme in Holz von Baumjahresringen, eine Untersuchung zur anthropogenen Beeinflussung des CO_2-Haushaltes der Atmosphäre. Thesis, Rheinisch-Westfälische Hochschule Aachen, 121 pp.

Wilson, A. T. 1978. Pioneer agriculture explosion and CO_2 levels in the atmosphere. *Nature 273*, 40–41.

Woodwell, G. M., Whittaker, R. H., Reiners, W. A., Likens, G. E., Delwiche, C. C. and Botkin, D. B. 1978. The biota and the world carbon budget. *Science 199*, 141–146.

ВАРИАЦИИ ^{13}C В ДЕРЕВЬЯХ СЕВЕРНОГО ПОЛУШАРИЯ ЗА ПОСЛЕДНИЕ 150 ЛЕТ

Представлены данные за последние 150 лет по содержанию ^{13}C в 26 деревьях из различных мест северного полушария. Найдено, что данные по среднему содержанию ^{13}C в этих деревьях за периоды 1850–1920, 1920–1940 и 1960–1975 г.г. убывают почти линейно, в то время как в 1940–1960 г.г. содержание ^{13}C растет. Полное изменение $\delta^{13}C$ с начала индустриализации, найденное в наших деревьях, достигает почти -2%, что выше линейного уменьшения $\delta^{13}C$ в -1% за 100 лет благодаря биогенному и от ископаемых топлив вводу CO_2 в атмосферу, как это было предположено в модельных расчетах Зигенталера и др. (1978). Средние данные в пределах вероятных ошибок соответствуют таковым у других авторов за исключением периода 1920–1940 г.г. Найде ны возмущения в данных по ^{13}C, указывающих на увеличение уровня CO_2 в атмосфере.