Variation of Radiocarbon Concentration in Modern Wood

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It has recently been pointed out by several authors[1-7] that the atmospheric radiocarbon is increasing because of nuclear tests. The present authors have also detected a remarkable change of the atmospheric radiocarbon concentration after 1953. This recent increase of radiocarbon and the Suess effect[8-10], i.e. the dilution effect of atmospheric radiocarbon by combustion of fossil fuel play an important role in the studies on the carbon dioxide cycle in nature. The present paper presents the results of the measurements on the change of the atmospheric radiocarbon contents in recent years using the carbon in tree rings taken from Honshu Island. We used the tree rings of Japanese cedar (*Crytomeria Japonica*) of which the place of growth and the date of cut were known. The measurements of radiocarbon were made with an acetylene filled proportional counter shielded with iron plates and provided by anticoincidence counters.

Experimental Procedures

Apparatus.—A stainless steel tube proportional counter is placed in the middle of eleven anticoincidence Geiger counters inside of an iron shield of 23 cm. in thickness. The pulses from the proportional counter are delaye 10 micro second and are mixed with the pulses of the anticoincidence counters. The background of the proportional counter is 5.46±0.3 counts per minute. The proportional counter used for these experiments has the dimensions of 3.5 cm. in inner diameter and of 52 cm. in length. The center anode is stainless steel wire of 0.05 mm. in diameter. The effective volume of the counter is 420 ml.

Preparation of Acetylene from a Wood Sample.—A wood sample is heated in a metal crucible in order to remove the volatile organic substance. This procedure makes the sample charcoal. The charcoal is converted into strontium carbonate by the following procedures; combustion in a current of oxygen, absorption of carbon dioxide in 6 N ammonia water, precipitation of calcium carbonate from an ammonium carbonate solution, evolution of carbon dioxide with hydrochloric acid from the calcium carbonate, absorption of carbon dioxide into ammonia water and precipitation of strontium carbonate. The preparation of acetylene from the strontium carbonate is done in a stainless steel tube which is illustrated in Fig. 1.

The mixture of strontium carbonate (8 g.) and magnesium powder (8 g.) is heated in the stainless steel tube by an electric furnace. The tube is connected to a vacuum line and when the temperature rises to 300~400°C the pumping system is cut by the metal cock. The best way to get a good result is to heat the tube up to 800~900°C for more than 4 hr. Very often a kind of explosion was observed during the heating up to 800°C. The

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[1] W. S. Broecker and A. Walton, *Science*, **130**, 309 (1959).

[2] G. S. Bien and H. E. Suess, *Z. für Physik*, **154**, 172 (1959).

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[5] T. A. Rafter and G. J. Fergusson, *N. Z. J. Sci. Tech.*, **B38**, 871 (1957).

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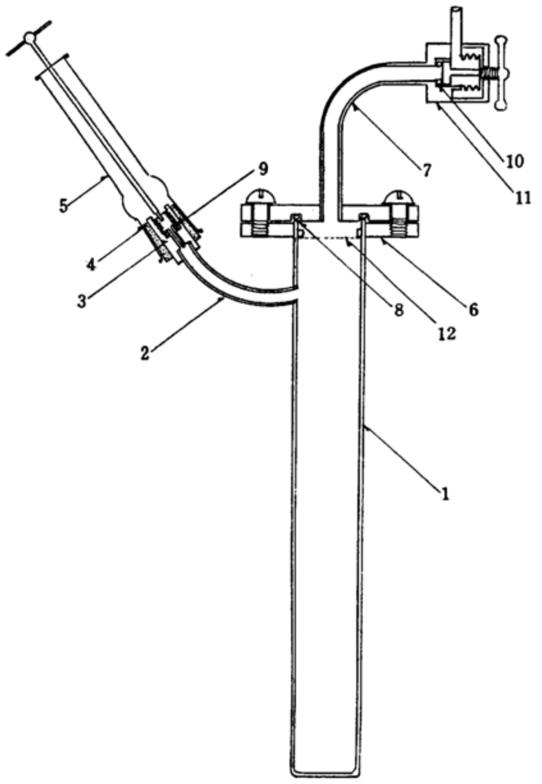

Fig. 1. Tube for preparation of acetylene.
1. Stainless steel tube of 30 mm. in diameter, 780 mm. length
2, 7. Copper tube of 8 mm. in diameter
3. Metal cock for the injection of water
4. Rubber stopper
5. Glass cylinder of 20 mm. in diameter, 150 mm. in length
6. Steel frange
8, 9, 10. O-ring
11. Metal cock
12. Glass filter

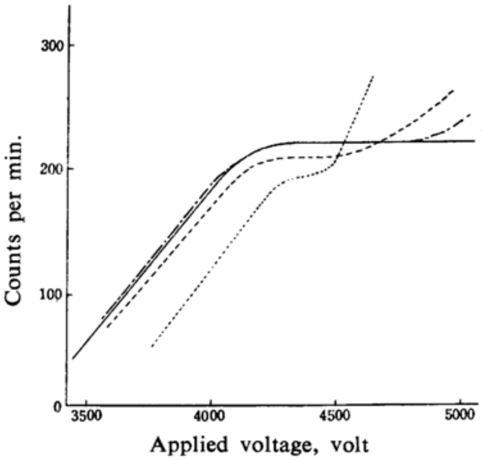

Fig. 2. Characteristic curves of acetylene filled (1 atm.) proportional counter.
——— Pure acetylene
---- Acetylene with 0.1% air
--- 〃 0.2% air
------ 〃 0.9% air

explosion can be detected by a sudden temperature rise. The explosion takes place around 450~600°C and if the reaction were stopped just after the explosion, one would get around 60% of acetylene of the calculated value*. Heating up to 800°C after the explosion gives good acetylene yield of 85~95% of the calculated value.

After the preparation of carbide in the stainless steel tube, this is connected to another vacumm line with several cold traps for the purification of acetylene. Acetylene and hydrogen which are evolved by adding water through the side tube to carbide are dried with dry ice in the cold trap. The acetylene is separated from the hydrogen by a trap cooled with liquid nitrogen. The charcoal trap cooled with dry ice removes effectively the contaminated radon from the acetylene. However, since contamination of radon, though it is trace amount (less than one count per minute), was observed even with these purifications, the acetylene had to be stored in a flask more than three weeks before the activity measurement was made.

Characteristics of the Acetylene Filled Counter.—A solid curve in Fig. 2 shows a typical characteristic curve of an acetylene filled proportional counter. The slope of the plateau is constant over the wide range of acetylene pressure within 2% increase per 100 volts. The starting voltage of the plateau is

$$V = (2100 + 2.98 \times P) \text{ volts}, \quad 200 < P < 800$$

where P is the pressure of acetylene in mmHg.

The counter was used with a voltage higher than the starting voltage by 250 volts.

The characteristic curve of the proportional counter changes with the content of impurity of acetylene as is shown in Fig. 2. The allowable maximun amount of impurities such as moisture or air which gives a serious effect on the characteristic curve is abous 0.2% of the total gas. This amount is large enough to operate the counter in a good condition without any special care such as is necessary for the carbon dioxide filled counter that is seriously affected by contaminated air of 0.001% of filling gas[11].

Effect of the Tritium Activity.—Fig. 3 shows counts per minute for the different amounts of acetylene gases of modern and dead carbon. There is no change in counts per minute in the case of dead carbon. This indicates that the acetylene produced from dead carbon (from coal or lime) has no activity. The extrapolated values of counts per minute at pressure zero for modern and dead carbon agree with each other within the experimental error of 0.06 count per minute. This shows that the observed activity of the acetyene produced from modern carbon is attributed to the carbon and not to the tritium in acetylene.

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* When the amount of reaction mixture is large, the temperature rise at the explosion is high enough to produce carbide in fairly good yield.

[11] Hl. de Vries and W. Barendsen, *Physica*, **19**, 987 (1953).

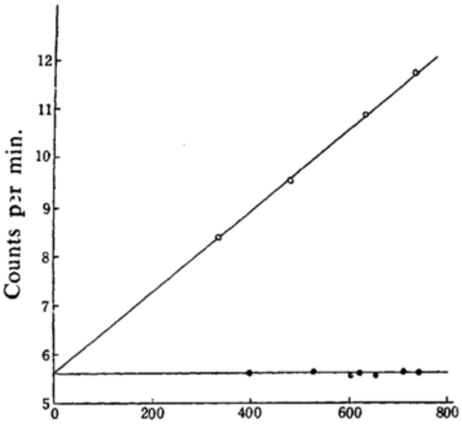

Fig. 3. Relation between counts per minute and pressure of acetylene.
○ Modern carbon, ● Dead carbon

Counting Procedure.—Acetylene gas stored more than three weeks is filled in the proportional counter and its characteristic curve is measured. According to the characteristic curve and the pressure in the counter one sets high voltage to be applied. The counting time is usually 48 hr. and the counts are checked every 5 or 10 hr. Background measurements are made for 24 hr. in every two or four days.

Experimental Results

Table I summarizes the data of the measurements of radiocarbon concentrations in the tree ring samples which were obtained from tree No. 1. Tree No. 1 grew in Akita Prefecture in Honshu Island. This tree has an age of 177 years and was cut in December, 1958. Each tree ring has more than 2 mm. thickness and shows clear boundaries.

The first column of Table I indicates the intervals in which the tree rings grew. The second column shows observed counts per

TABLE I. VARIATION OF C-14 CONCENTRATION IN TREE RINGS GROWN BETWEEN 1789 AND 1950 (Sample tree No. 1)[a]

Intervals of growth of tree ring	Counts per min. / g. carbon	C-14 concentration[b]
Aug.1782~Sept.1798	11.69±0.18	0.960±0.015
Aug.1799~Sept.1808	12.02±0.18	0.986±0.015
Aug.1809~Sept.1818	12.19±0.18	1.000±0.015
Aug.1819~Sept.1828	11.90±0.18	0.976±0.015
Aug.1829~Sept.1838	12.10±0.18	0.988±0.015
Aug.1839~Sept.1848	12.19±0.18	0.998±0.015
Aug.1849~Sept.1858	12.14±0.18	0.990±0.015
Aug.1859~Sept.1863	12.24±0.18	1.000±0.015
Aug.1864~Sept.1868	12.24±0.18	1.000±0.015
Aug.1869~Sept.1873	12.39±0.18	1.010±0.015
Aug.1874~Sept.1878	12.47±0.14	1.015±0.011
Aug.1879~Sept.1883	12.49±0.18	1.015±0.015
Aug.1884~Sept.1888	12.18±0.14	0.986±0.011
Aug.1889~Sept.1893	12.63±0.18	1.028±0.015
Aug.1894~Sept.1998	12.40±0.18	1.008±0.015
Aug.1899~Sept.1903	12.47±0.14	1.011±0.011
Aug.1904~Sept.1908	12.47±0.18	1.011±0.015
Aug.1909~Sept.1913	12.52±0.18	1.013±0.015
Aug.1914~Sept.1918	12.47±0.18	1.010±0.015
Aug.1919~Sept.1923	12.02±0.18	0.974±0.015
Aug.1924~Sept.1928	12.20±0.18	0.982±0.015
Aug.1929~Sept.1933	12.39±0.14	1.000±0.011
Aug.1934~Sept.1938	12.60±0.18	1.017±0.015
Aug.1939~Sept.1943	12.02±0.18	0.968±0.015
Aug.1944~Sept.1945	12.42±0.18	1.000±0.015
Aug.1945~Sept.1946	12.52±0.14	1.011±0.011
Aug.1946~Sept.1947	12.10±0.18	0.974±0.015
Aug.1947~Sept.1948	12.04±0.18	0.970±0.015
Aug.1948~Sept.1949	12.38±0.18	0.997±0.015
Aug.1949~Sept.1950	11.78±0.18	0.949±0.015

a) The data are normalized to the concentration of C-14 of the hypothetical modern wood which would not have been affected by industrial effect and nuclear tests.
b) Grown in Akita Prefecture in Honshu Island.

TABLE II. VARIATION OF C-14 CONCENTRATION IN TREE RINGS GROWN AFTER 1950

Intervals of growth of tree rings	C-14 concentration in tree rings		
	Sample No. 1	Sample No. 2[a]	Sample No. 3[b]
Aug. 1950~Sept. 1951	1.010±0.015		
Aug. 1951~Sept. 1952	1.000±0.015		
Aug. 1952~Sept. 1953	0.994±0.014		
Aug. 1953~Sept. 1954	1.012±0.014		
Aug. 1954~Sept. 1955	1.034±0.014		
Aug. 1955~Sept. 1956	1.050±0.011	1.037±0.011	
Aug. 1956~Sept. 1957	1.092±0.015	1.081±0.011	1.084±0.011
Aug. 1957~Sept. 1958	1.122±0.014[c]	1.083±0.011	1.086±0.011
Aug. 1958~Sept. 1959		1.238±0.011	1.240±0.011

a) Grown on the campus of Gakushuin University in Tokyo.
b) Grown in Mie Prefecture in Honshu Island.
c) This sample includes the tree rings up to December, 1958.

minute for one gram carbon of each sample. The third column gives the concentrations of C-14 in tree rings at the year indicated in the first column. The concentrations are normalized to the mean value of 18 measured concentrations between 1782 and 1913 (Table I). This mean value will be referred to as a concentration of C-14 in hypothetical modern wood which would not have been affected by industrial effect and nuclear tests.

Table II gives a summary of our data on the tree ring samples after 1950. The second column shows the concentrations of C-14 in the samples which were obtained from tree No. 1. The third and the fourth columns give the results on the trees which grew in Tokyo and Mie Prefecture. Tree No. 2 (the third column) was cut in September, 1959, and No. 3 (the fourth column) in August, 1959. These three series of measurements agree well, and indicate a remarkable increase after the autumn of 1958. The errors indicated in Tables I and II include only statistical counting errors (standard deviations).

Discussion

The tree ring is a sample formed by constant accumulation of carbon from the atmosphere and is dated by clear boundaries. The examination of the data on the concentration of C-14 in the tree rings gives information on the annual average concentration of C-14 in the atmosphere. Moreover, if samples from the same species of tree were used, the differences of the possible isotopic fractionation among the samples might be negligibly small*. These make the tree ring samples adequate for the studies on the annual variation of C-14 concentration in the atmospheric carbon. However there are some questions about the nature of the sample. First, there is a possibility that the carbon which is taken up through the root could be used for assimilation. Second, the carbon dioxide from the pedosphere might be utilized for assimilation by aerial transport to leaf level. Finally there is a question when the organic substance in a certain part of tree ring was synthesized from the carbon dioxide.

The first and the second question had been discussed by W. Whitaker et al.[12] They suggested a possible influence of the uptake of older carbon by the root system as the most likely explanation of differences in radiocarbon contents of trees from different enviroments. If such an influence plays an important role for a tall tree, the increase in radiocarbon contents in tree rings after 1953 would be less than the increases in atmospheric radiocarbon contents. The authors favor the assumption that this influence is negligibly small because the direct experimental evidences on young pea and barley plants show a small amount of uptake of carbon dioxide through the root system[13]. The experimental results of Whitaker et al. on the effect of the aerial transport for carbon dioxide from pedosphere to leaf level show the absence of any significant amount of old carbon cycling from pedosphere to the leaves of trees.

On the circulation of synthesized organic substances in the tree we have some knowledge which will serve to show when the organic substances in a certain part of the tree ring was synthesized from the atmospheric carbon dioxide. The large cells which are adjacent to the boundary of a tree ring are formed in the spring of the year from the carbon dioxide existing in the atmosphere and from the organic substances, which were synthesized after the summer of the preceding year and have been stored in the older tree rings. The cells which are formed after the middle of the summer of the year become smaller. Finally the smallest cells are formed in September forming the boundary of the tree ring. A large part of the organic substances synthesized during the middle of summer and autumn is stored in a newly formed tree ring[14]. The stored organic substances will be used for the formation of new cells in the next spring. It is therefore desirable to cut down the tree in summer for the measurement.

In general it can be said that the tree ring is made by the atmospheric carbon dioxide during August of the preceding year and September of this year. Although formation of boundaries can be influenced easily by the climate of the place where the sample tree grew, the expected error of the indicated intervals of growth of tree rings in Table I and II may be within one month.

Examination of the results listed in Table I shows a constant concentration of C-14 in the atmosphere between 1782 and 1950 within an error of 2%. Fergusson[10] reported 2% depletion of C-14 concentration in the atmospheric carbon dioxide between 1860 and 1954. Although the limits of statistical counting error of the data are rather broad, the present data seem to support the opinion that the depletion is less than 2% between 1782 and 1950.

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* The measurements on the isotopic ratio of $^{13}C/^{12}C$ in tree ring carbon by Fergusson[10] and Broecker et al.[1] show a constant value on the samples from a tree or the trees of same species.

12) W. W. Whitaker, S. Valastro, Jr. and M. Williams, *J. Geophys. Res.*, **64** 1023 (1959).

13) J. A. J. Stolwijk and K. V. Thimann, *Plant Physiol.*, **32**, 513 (1957).

14) J. H. Priestley, *New Phytologist*, **24**, 316 (1930).

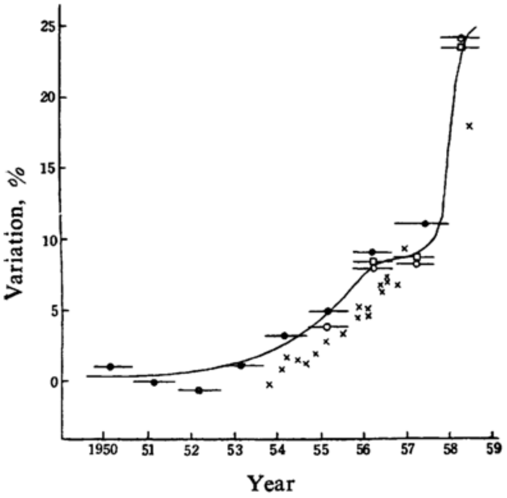

Fig. 4. Variation of C-14 concentration in the atmosphere.

Data of this paper
- ● Akita
- ○ Tokyo
- □ Mie
- —— Interval of growth of tree ring.
- Standard deviation; 1.1~1.5%

Data by Rafter and Fergusson, ×

All the data in Table II as are plotted in Fig. 4 show no essential difference among the three samples except the value of sample No. 1, 1957—1958. Since sample No. 1 was cut in December, 1958 and its last tree ring (1957—1958) was very likely to have incorporated the atmospheric carbon in December, 1958, the higher value corresponds to a sudden increase of atmospheric radiocarbon in the autumn of 1958. It could be concluded that there was no local variation along the south east shore line of Honshu Island from the fact that there is no meaningful difference among the values of the three samples. Bien and Suess[2)] reported the variation of C-14 concentration in the tree ring samples up to 1957. These values agree with the present data within the experimental errors. It seems very likely that the local variation of the atmospheric radiocarbon contents is very small, at least in the temperate zone of the northern hemisphere.

In Fig. 4 the plot of the variation of C-14 concentration in the southern atmosphere reported by Rafter and Fergusson[5,6)] indicates a systematic delay of the variation to that of the present data. Although the limits of error on the time scale of the present data are rather broad, the delay of the variation of the atmospheric C-14 concentration in the southern hemisphere seems to be several months in length. Broecker and Walton[1)] discussed the difference of the atmospheric C-14 concentration between the northern and southern hemispheres. The present result seems to agree with that of Broecker and Walton.

Summary

1) Using the tree ring samples, the variation of C-14 concentration in the atmosphere since 1782 has been measured by the use of trees growing in Japan. The results show a constant concentration of C-14 in the atmosphere during 1782 and 1950 within the error of 2%.

2) The depletion of C-14 concentration in the atmospheric carbon dioxide between 1782 and 1950 seems to be less than 2%.

3) The observed annual variations on the samples from Tokyo, Akita and Mie Prefectures show almost the same amount of increase after 1953. There is a good agreement between our data and those on the tree ring samples taken in California by Bien and Suess. The concentration of C-14 in the atmosphere averaged over a year seems to have little difference in the temperate zone of the northern hemisphere.

4) The variation of C-14 concentration in the atmosphere of the southern hemisphere seems to follow that of the northern hemisphere with a time lag of several months.

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