

Radiocarbon abundances in tree rings from the Spoerer minimum

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Abstract. Year-by-year measurements of the radiocarbon (¹⁴C) content of tree rings formed during the Spoerer minimum (1414-1534 AD) have been carried out with an accuracy of 0.3 %. The measurements were made using the liquid scintillation method. Liquid benzene samples of 10 ml were prepared from single-year tree ring samples of 70 g taken from a 700 year-old Yaku cedar tree. The absolute year was determined using the bomb effect, which has its peak of radiocarbon content in 1964.

Our first results of year-by-year measurements of ¹⁴C content in the tree ring samples between 1410 and 1480 AD agree well with the pioneering work of Stuiver et al., which was obtained by combining tree rings of 10 years.

1 Introduction

The production rate of cosmogenic isotopes such as ¹⁴C (radiocarbon) and ¹⁰Be are a good indication of the level of solar activity because galactic cosmic rays are modulated by solar magnetic activity. The level of solar activity has changed in many ways in the past and the time scales of the change vary widely. From the viewpoint of the effect of the sun on the earth, 11 year- to several hundreds of years periodicities are most important. Cosmic rays, modulated by the sun, enter the atmosphere of the earth and produce ¹⁴C. The ¹⁴C forms CO₂ and circulates within the global carbon cycle. Due to the large capacity of the carbon reservoirs and the long residence times in these reservoirs, the amplitude of the change of ¹⁴C content is much suppressed.

As to the 11 year periodicity the change of ¹⁴C concentration may be very small, typically less than 1 %. Stuiver and Quay (1980) precisely measured the ¹⁴C content in tree rings every 10 years for the past millenium . Their results show there are several peaks of radiocarbon content in the last millennium with about a two hundred year periodicity. These

peaks correspond to minima of solar activity if the variation was caused by the sun. The period of the peak around 1700 AD called the 'Maunder minimum' is closely related to the sunspot number, which was almost nil in this period. The radiocarbon content in this period was investigated in detail by Stuiver and Braziunas (1993) and Kocharov (1995). They have shown that the solar activity was weak but not nil and it exhibited periodicities longer than 11 year. This contrasts with the 11 year period of normal solar activity. The Maunder minimum is well known as a period in which the global climate became cold. The question whether the Schwabe cycle in the Maunder minimum was 11 years or, say, 22 years has not yet been answered clearly. On the other hand, the peak of ¹⁴C content around 1500 AD (the Spoerer minimum) has not yet been studied precisely. It is important to know the precise radiocarbon content in this minimum and the others.

Therefore we have started a project to measure the radiocarbon content in single-year tree ring samples of Japanese Yaku cedar (*Cryptomeria japonica*) for investigation of the past variability of solar activity over a 1000 year time scale. In order to carry out the study described above for the period including the Spoerer and the Wolf minima, and to answer the question as to whether or not solar activity really plays important role in climatic phenomena, we have developed a new sample preparation system (Muraki et al., 1998) and introduced a low background β -ray counting system using the liquid scintillation method for precise measurements. In this paper we describe our ¹⁴C system and report results of the first measurements of 1410-1480 AD tree rings, which includes part of the Spoerer minimum.

2 Methods

There are two methods of ¹⁴C measurement, the radioactivity measurement of β -decay of ¹⁴C and the direct counting of ¹⁴C nuclides using accelerator mass spectroscopy (AMS). Nagoya University has developed an AMS facility with a high accuracy for precise measurements of radiocarbon (Naka-

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mura, 2001). By this year, it has achieved a good accuracy of less than 0.5 % for ^{14}C measurements. Previously the AMS facility could not achieve this accuracy, and instead we adopted the method of radioactivity measurement with a liquid scintillator. Furthermore, it is also not possible to occupy the machine for only this one purpose with a large number of samples.

A well-designed system must produce a large amount of benzene (about 10 ml or more) at once. Furthermore the system must have several detectors to enable many sample measurements to be made in parallel. The benzene synthesizing system used is based on a method developed in the Geographical Research Institute of St. Petersburg University, Russia (Arslanov, 1987; Arslanov et al., 1993). Three low background β -ray counting systems (Quantulus 1220TM, Wallac Co., Finland), have been used for radioactivity measurements with the benzene-based liquid scintillator.

2.1 Tree ring sample

A block from the trunk of a cedar tree grown in Yaku Island (30°18' N, 130°30' E), southern Japan, is used in this study. This tree was cut in 1994. This block is a sector of the trunk section with a radius of 1.5 m, an opening angle of 30° and a thickness of 20 cm. Annual tree rings were counted from the outside to the center. The total number of rings is 714. Each ring corresponding to the period of the Spoerer minimum, was cut from the block into small pieces.

2.2 Sample preparation

Wood samples were pretreated using essentially the method of Stenhouse (1976). Each annual sample of tree ring was milled into pieces with a size less than 0.5 mm and extracted at 230 °C for 6 h with a benzene-ethyl alcohol mixture (in proportion 1 : 1) in a Soxhlet apparatus to remove resin, and subsequently dried in a vacuum oven under 105°C for 90 minutes. Then the sample was bleached using a $\text{NaClO}_2/\text{HCl}$ solution at 80 °C to remove lignin and extract cellulose. The resultant cellulose was then immersed in boiling distilled-water for 30 min. and washed with distilled water at room temperature and dried overnight at 105°C.

The samples of the cellulose were combusted to CO_2 in high pressure oxygen within a stainless steel vessel. The CO_2 reacts with lithium metal in an evacuated vessel at 800 °C to produce Li_2C_2 . Distilled water is dripped onto the Li_2C_2 producing acetylene, which was purified with a solution of $\text{CuCl}_2 + \text{FeCl}_3 + \text{H}_2\text{SO}_4$, dried with KOH pellets, and then trimerized to benzene in a vessel using the catalyst $\text{V}_2\text{O}_5\text{-Al}_2\text{O}_3\text{-SiO}_2$ (Arslanov et al., 1993). This method allows production of high-purity benzene at room temperature with a yield of more than 90 %.

The butyl-PBD was added in the benzene in concentration of 15 g liter⁻¹ to produce the liquid scintillator. The liquid scintillator was then poured into a cylindrical Teflon/copper vial.

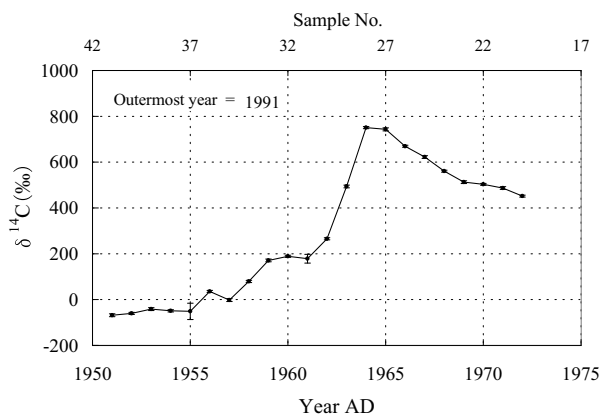


Fig. 1. Bomb effect of ^{14}C in Yaku cedar

2.3 ^{14}C counting

The activity of ^{14}C in the liquid scintillator was measured with the scintillation counting system Quantulus 1220TM. In order to measure radiocarbon content with good accuracy, one needs a large volume of benzene samples and a long measuring time. We use three Quantulus systems to achieve good efficiency in our measurement routine; these are at the Solar-Terrestrial Environment Laboratory of Nagoya University (STEL), the Institute for Hydrospheric-Atmospheric Sciences of Nagoya University (IHAS) and the International Research Center for Japanese Studies (RCJS). As a tradeoff, intercomparison of calibration between the three apparatuses is necessary. We usually measure several benzene samples in a measuring run; a benzene sample synthesized from NIST oxalic acid as NBS standard, a secondary standard benzene produced in Russia, which has about 5 times larger activity than the modern standard, reagent benzene as dead carbon sample for background, and some benzene samples synthesized from tree rings of Yaku cedar. Our basic counting scheme is as follows. All samples are counted for 20 minutes each and repeated 150 to 200 cycles, requiring a total counting time of 2 to 3 days for each sample. In each 10 cycles, an external γ -ray source is introduced near the sample to measure the γ -ray Compton spectrum and calibrate the gain of the system, also the quenching effect in benzene and vial efficiency with an index called "SQP channel", which is the ADC channel corresponding to 99 % of total counting in the spectrum.

3 Results and discussion

The absolute date of the tree rings was determined by measuring the ^{14}C content in the outer annual rings using the fact that the 'bomb effect' made a peak of ^{14}C content in 1964 (Muraki et al., 1998). The 'bomb effect' results from nuclear weapon tests in the 1950s and early 1960s which produced anomalous artificial ^{14}C and increased the concentration of atmospheric ^{14}C . This measurement was performed by using AMS at Nagoya University with graphite targets obtained

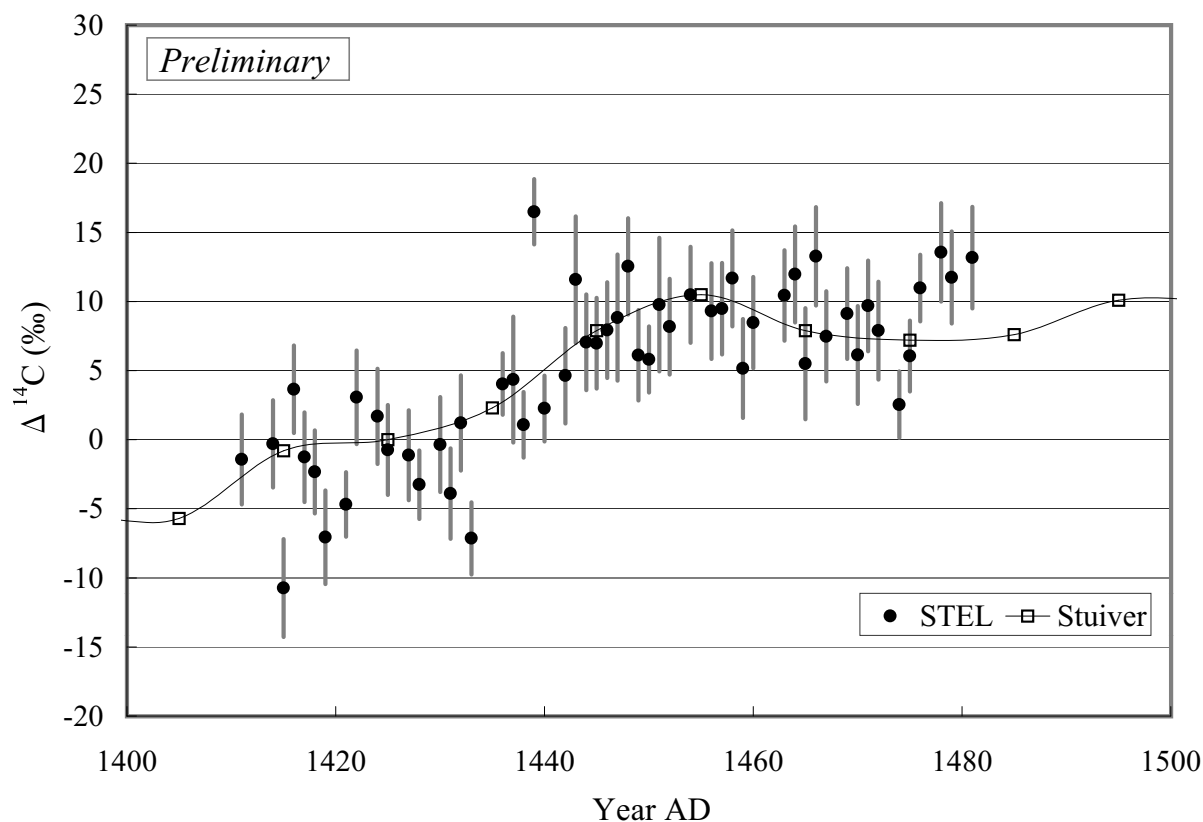


Fig. 2. Radiocarbon content in tree rings from the Spoerer minimum.

by converting cellulose extracted from the tree ring samples (Kitagawa, 1993). Figure 1 shows the bomb effect; the peak of ^{14}C content is seen at sample number 28 (upper scale of fig.1), which should correspond to the year 1964. Thus it is shown that the outermost ring, No.1, was grown in 1991.

When atmospheric ^{14}C is taken up by trees through photosynthesis and the wood samples are treated chemically or physically, there can be a difference in the yields of reactions between nucleids with different masses (that is, isotopic fractionation). In order to correct for isotopic fractionation, we measure $\delta^{13}\text{C}$ (the deviation in permil of ^{13}C concentration from the PDB standard) and then apply the resulting correction to ^{14}C (Stuiver and Polach, 1977):

$$A_{\text{corr}} = A(1 - 2(25 + \delta^{13}\text{C})/1000), \quad (1)$$

where A_{corr} and A are the radioactivity of ^{14}C , corrected and uncorrected respectively, for $\delta^{13}\text{C}$. In this study $\delta^{13}\text{C}$ of the sample benzene was measured using a mass spectrometer (Finnigan MAT-251TM). The average value $\delta^{13}\text{C}$ and its standard deviation are -22.87 ± 0.32 permil. The measured $\delta^{13}\text{C}$ values were used for the correction of the ^{14}C content.

The content of ^{14}C is expressed by the deviation $\Delta^{14}\text{C}$ of massic radioactivity of a sample from that of the mod-

ern standard, which is 0.7459 times the massic radioactivity of the new oxalic acid (SRM 4990C) supplied by National Institute of Standards and Technology as the NBS standard (Stuiver and Polach, 1977; Stuiver, 1983).

A Figure of Merit (FOM) was calculated to select the best counting region of the scintillation intensity spectrum. The FOM is defined as $FOM = E^2/B$, where E in % is the counting efficiency as a ratio of the massic count rate of the NBS standard in the selected region to its massic radioactivity, and B is the background count rate in cpm of the dead benzene sample in the same spectrum region. A typical value of FOM is 9700 with values of E of 81% and B of 0.68 cpm for 10 ml benzene samples in a Teflon vial.

The typical count of the NBS standard in the selected region is 450,000 counts in the present conditions of measurement. The value of $\Delta^{14}\text{C}$ was calculated from the ratio of the net massic count rate of the sample in the selected region to that of the NBS standard, corrected for the isotopic fractionation and the age of the growth year of the tree ring. The count rate of NBS was corrected for the year 1950. The three Quantulus systems were calibrated to each other using the NBS standards.

We have checked our benzene synthesis system and ^{14}C

counting system using a cellulose sample whose radioactivity is known. A C-3 sample distributed by IAEA was used for this purpose. The measured activity for C-3 sample was 292.7 ± 2.9 permil, which is in good agreement with the value 294.1 ± 0.6 permil as the consensus value of the C-3 (Rozanski et al., 1992). Occasionally we checked C-3 sample and the $\Delta^{14}\text{C}$ was found to be within 2σ of the statistical error.

Figure 2 shows $\Delta^{14}\text{C}$ values measured for the single-year tree ring samples versus the year of tree ring growth for the period 1410-1480 AD corresponding to the first half of the Spoerer minimum. Vertical bars with the plots indicate statistical errors. The curve shown guides the eye through the results of the decadal measurements of Stuiver (1998). The trend of our results agree with those of Stuiver, but with somewhat larger variation. According to our preliminary analysis, there can be periodicities larger than 11 year. If this is true, our results can be compared with those for the Maunder minimum. In order to confirm this result, more precise analysis is needed and the measurements should be extended to the full period of the Spoerer minimum.

4 Conclusions

We have measured the ^{14}C content in annual tree rings from a Japanese Yaku cedar between the years 1410 and 1480 AD (a part of the Spoerer minimum) with a high-precision liquid scintillation method. The trend of the $\Delta^{14}\text{C}$ values obtained is in agreement with previous work for decadal tree rings carried out by Stuiver et al. However, the amplitude of the variation may be larger than suggested in the previous work. Also some periodicity seems to be present but this cannot be confirmed at present. Further efforts will be necessary to extend the period to the entire Spoerer minimum and to find a clear periodicity in amplitude of the $\Delta^{14}\text{C}$.

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