

## Measurements of Time Variation of Cosmogenic $^{14}\text{C}$ from 2500-Year-Old Tree Rings

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**Abstract.** Although a few reports about the  $^{14}\text{C}$  content in tree rings have been given for the 11-year periodicity of solar activity during the 18th-19th centuries, there are no data related to the 11-year cycle for more distant times (i.e. > 1000 year ago). To address this, we have started to measure, at single year intervals, the concentrations of  $^{14}\text{C}$  in old tree rings of wood buried ca. 2500 years ago by a volcanic eruption. Our highly accurate  $^{14}\text{C}$  measuring system is composed of a benzene synthesizer capable of producing a large quantity (10g) of benzene and a Quantulus 1220<sup>TM</sup>. To estimate the calendar age of the wood, we carried out  $^{14}\text{C}$  dating for five tree rings from the wood, sequentially separated by 40 years, 60 years, 60 years, and 45 years. From the results, the most probable age of the tree rings was 430 B.C., using Stuiver's calibration data. Also, with the accuracy of 0.2% the radiocarbon ages were measured for a sequence of the 11 single-year tree rings. The standard deviation of the 11 radiocarbon ages is 24.1yr BP for the average and it was slightly greater than the error of the measurement 21 yr BP.

estimate the date when the wood samples were alive. In addition to the chronological function,  $^{14}\text{C}$  concentrations in tree rings are a proxy data of the past terrestrial and extraterrestrial environments. As  $^{14}\text{C}$ , moreover, is the cosmogenic isotope produced by galactic cosmic rays in upper atmosphere, the  $^{14}\text{C}$  concentrations in the tree rings represent them in the atmosphere at those days, and in turn they relate to the flux of cosmic rays coming to the earth at the old those days.

Since tree rings record the  $^{14}\text{C}$  concentrations in the chronological order at a time resolution of one year, the  $^{14}\text{C}$  measurements for single year tree rings provide us the  $^{14}\text{C}$  concentrations in the atmosphere for the time interval of one year. As the cosmic rays are modulated by time variations of the geomagnetic and helio-magnetic fields, the  $^{14}\text{C}$  concentrations in tree rings are affected by the modulation of cosmic rays (Fujii, 1997; Raisbeck, 1981; Perko, 1983). In particular, the  $^{14}\text{C}$  measurements of the tree rings for the single year are essential to investigate the 11-year periodicity of solar activity in the past time, because there are no observing data of sunspot numbers, which represent the 11-year periodicity, before A.D.1700.

As known by Maunder minimum, also, there are very quiet periods in long-term solar changes. In fact, using the bi-decadal  $\Delta^{14}\text{C}$  records in wood over a 9600 year period, Stuiver and Braziunas (1989) presented the modulation of cosmic ray flux due to the sun with the periodicity of 420 yr, 200 yr, and 140 yr. Moreover, Kocharov, et al. (1995) reported that the variations of  $^{14}\text{C}$  content in the tree rings over the last several hundred years are related with the 11-year periodicity of solar activity. In particular, data of 22-year periodicity during A.D.1654 to 1714 (Maunder Minimum) when sunspots were absent, if it is confirmed, is useful to study dynamo models during deep minima of solar activity (Kocharov, 1995). However, we do not have any data related to the 11-year cycle for more distant time (i.e. >

### 1 Introduction

$^{14}\text{C}$  dating is a reliable chronology in the range of 50 thousands years. Combination between the Dendrochronology and the  $^{14}\text{C}$  dating has completed a calibration data issue INTCAL98 that shows a relationship between a radiocarbon age and the calendar age at a time resolution of decade for the interval of approximately 10000 years (Stuiver, 1998). Hence, using the calibration curve we can accurately

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1000 yr ago), although the amplitude of  $\Delta^{14}\text{C}$  with the 11-year cycle during the 18th~19th centuries was reported as 0.14% and 0.48% for Pacific trees and Russian trees, respectively (Braziunas, 1993; Kocharov, 1995).

Therefore, we have started to measure at single year intervals the concentrations of  $^{14}\text{C}$  in old tree rings of wood buried ca. 2500 years ago, to investigate precisely the time variations of the  $^{14}\text{C}$  concentration in the atmosphere at the time, paying attention to the periodicity of solar activity such as 11-year cycle. The expected variation of the  $\Delta^{14}\text{C}$  content in the tree rings due to the 11-year solar cycle would be less than 0.5% as shown in the experimental results, because the variation of the production rate of  $\Delta^{14}\text{C}$  is estimated to be about 30% from the observation of neutron flux at the present time and the  $\Delta^{14}\text{C}$  is thinned out to approximately 1/100 by terrestrial carbon circulation among the atmosphere, ocean, and biosphere (Stuiver, 1989). Hence, we have constructed a  $^{14}\text{C}$  measuring system with high accuracy (0.2%) which is composed of a benzene synthesizer capable of producing a large quantity of benzene 10g and a liquid scintillation counting system Quantulus 1220<sup>TM</sup> with an ultra-low background level (Wallac).

We have precisely determined the calendar age of the wood sample to estimate the phase of the long-term solar changes that the wood sample was. For the 11 tree rings, also, we have measured the radiocarbon ages for each single-year tree ring. In this paper, we describe about the age of the wood sample and the variability of the  $^{14}\text{C}$  concentrations in the 11 tree rings.

## 2 Experimental methods

### 2.1 Wood Sample and Sample Treatment



**Fig. 1** Photograph of a trunk of the Choukai-Jindaisugi. This is a cedar wood buried about 2500 years before, and the diameter and the length were about 1.2 m and 1.1 m, respectively. It has about 300-tree rings and the width of the single tree ring is 0.5mm~0.3mm. We named the 60 th tree ring from the core Y0 and named the outside tree rings Y1,Y2,Y3~Y250 toward to the outside from it one by one.

As shown in Fig.1, the old wood sample of a cedar tree, which was buried in clay by a volcanic eruption of Mt. Choukai (140° 03'E, 39° 05'N) ca. 2500 years ago, was dug out in spring 1996 and was well preserved as seen by the

clear barks on the outside. It had about 300 tree-rings, at each 0.5~3.0 mm wide. The tree rings were separated with a single year intervals to measure the concentration of  $^{14}\text{C}$ . The separation was carried out by stripping the tree rings with tweezers from a block of boiled wood. The stripped wood was milled for chemical treatment.

The cell walls of the tree ring are composed of  $\alpha$ -cellulose and they are fixed in each tree ring when they are produced, while hemi-cellulose and lignin can move among tree rings. Hence  $\alpha$ -cellulose is the most reliable chemical component of the wood for measuring the annual content of  $^{14}\text{C}$ . The  $\alpha$ -cellulose extraction is carried out in three steps as follows; 1) removing oils, saps, and resins with hexane and ethanol, 2) lignin removal with NaOCl solution, 3)  $\alpha$ -cellulose separation with NaOH and HCl solutions. The yield of the  $\alpha$ -cellulose from the wood was approximately 33% by weight. Approximately 38 g alpha cellulose was extracted from 130 g wood sample for single-year tree ring.

From the extracted  $\alpha$ -cellulose benzene was synthesized, because benzene has many carbon atoms in a molecule and works well as a solvent for liquid scintillations. At first, the cellulose was burned in oxygen at a pressure of 7 atom to produce carbon dioxide  $\text{CO}_2$ . Using the carbon dioxide, acetylene gas  $\text{C}_2\text{H}_2$  was produced via lithium carbide  $\text{Li}_2\text{C}_2$  and then the benzene was polymerized from the acetylene gas. The amount of synthesized benzene was typically 10 g, while the benzene used for the  $^{14}\text{C}$  dating is usually 3 g at most. The yield from the  $\text{CO}_2$  to  $\text{C}_6\text{H}_6$  was approximately 80% in number of carbon atoms.

The concentration of  $^{14}\text{C}$  in the sample is always shown, compared with a standard concentration of  $^{14}\text{C}$  at A.D.1950. Using the same chemical process the standard benzene sample is synthesized from Oxalic Acid (SRM 4990-C) having the standard concentration of  $^{14}\text{C}$  in A.D.1950 certified by NIST (National Institute of Standards and Technology).

### 2.2 $^{14}\text{C}$ Measurement

The measurements of  $^{14}\text{C}$  in the synthesized benzene were carried out using the liquid scintillation counting system Quantulus. The benzene was put in a high purity teflon/copper counting vial (20 ml) and butyl-PBD was added as the scintillator in the proportion of 15mg per 1mL of benzene. The system is surrounded by active and passive shieldings that consist of an oil scintillator cylinder and a layers of low activity lead (630 kg), copper and cadmium. The vial is mounted inside the counter with a lift machine controlled by an outside computer system. The  $\beta$  rays from the  $^{14}\text{C}$  in the vial are acquired as a pulse height distribution after a various electronic noise reduction such as anti-coincidence. The pulse height distribution is useful for the elimination of signals apart from  $^{14}\text{C}$   $\beta$ -ray spectrum. Typically the background rate is 1 cpm for 10.5 g dead benzene sample (DBS) without  $^{14}\text{C}$  and the counting rate for standard benzene (SBS) is 140 cpm for 10.5 g.

As the counting rate of the old tree ring sample(TBS) is approximately 80 cpm for 10.5 g benzene, a measuring time of 2 days is demanded to achieve a statistical accuracy of 0.2%. Although the Quantulus has high stability for long

term measurements, to ensure the reliability of the measurements we have been employing the cyclic measurements by the order of TBS, DBS, and SBS. We, also, have confirmed that the systematic error is totally less than 0.1 % for the factors such as the quantity of benzene and scintillator, volatilization of benzene, and the uniformity of the vial.

### 3 Results and Discussion

#### 3.1 Age of the Wood

Radiocarbon age (yr BP) of a sample is calculated from the  $^{14}\text{C}$  concentration, referring the  $^{14}\text{C}$  concentration at A.D.1950 that is evaluated for the oxalic acid from NIST and hence A.D.1950 is the origin of yr BP and 0 yr BP. The equation is as follows;

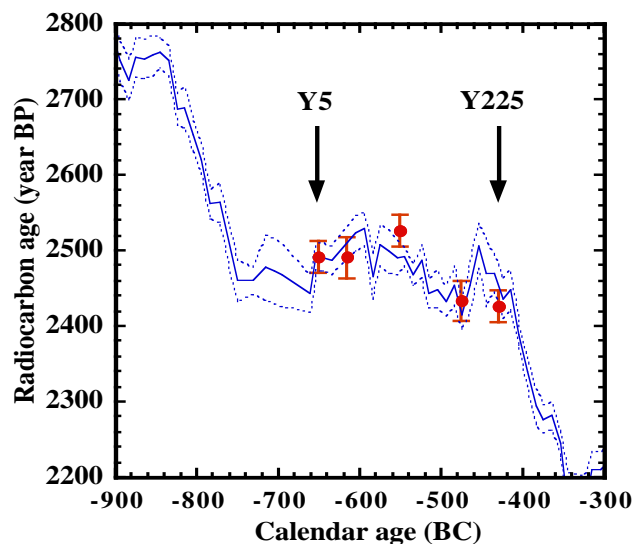
$$t = \frac{1}{\lambda} \cdot \ln \frac{A_{sn}}{A_{on}}$$

where,  $\lambda = 1.21 \times 10^4$  (1/year).  $A_{sn}$  and  $A_{on}$  are the  $^{14}\text{C}$  concentrations of the measured sample and the standard sample, respectively. With  $\delta^{13}\text{C}$   $A_{sn}$  and  $A_{on}$ , also, are made a correction for the fractionation of photosynthesis. Since the calibration curve, that shows a relation between radiocarbon ages and calendar ages, is not a linear function, a radiocarbon age corresponds to some calendar ages and hence the estimated calendar age has ambiguity of a width of the age. For the wood sample with many tree rings, however, it is possible to reduce the ambiguity of the age estimation. When tree ring samples are taken for several intervals, they are sequential order and the age gaps between each sample are known from the number of tree rings. Hence we can determine a most probable calendar age with a smaller estimation error from the condition that the radiocarbon ages are satisfied with the calendar ages with the fixed age gaps

We have carried out  $^{14}\text{C}$  dating for five tree rings from the wood, sequentially separated by 35 years, 66 years, 76 years, and 45 years. Y5, Y40, Y104, Y180, and Y225, respectively, toward the outside from the center we call the tree rings. Each sample consists of decadal tree rings and Y5 is approximately 35 years distant from the core of the trunk. Their radiocarbon ages were  $2491 \pm 23$  yr BP,  $2523 \pm 28$  yr BP,  $2527 \pm 21$  yr BP,  $2421 \pm 29$  yr BP, and  $2427 \pm 23$  yr BP, respectively. For the analysis we have employed Oxcal program developed by Ramsey (2000). It is a fitting method to the calibration curve taking account of the both statistical distributions of the measurement and the calibration data.

The analysis indicated that the most probable age is 445 B.C.  $\sim$ 415 B.C. at Y225 with 63.6% probability and 520 B.C.  $\sim$ 400 B.C. with 95.4% probability. For Y5, Y40, Y104, Y180, and Y225 we show in Fig. 2 the estimated calendar ages on the histogram of the decade calibration data by (Stuiver, 1998). The wood sample is in the range between B.C. 700 and B.C. 400. The age region is flat in the calibration data and hence it indicates that the  $^{14}\text{C}$  concentration was decreasing at the duration. This region is

very interested because the time variation of the  $^{14}\text{C}$  concentration is Sporer like. When we measure the single-year  $^{14}\text{C}$  concentration for the region, we can investigate the 11-year periodicity of solar activity for the very quiet sun compared with Maunder minimum.

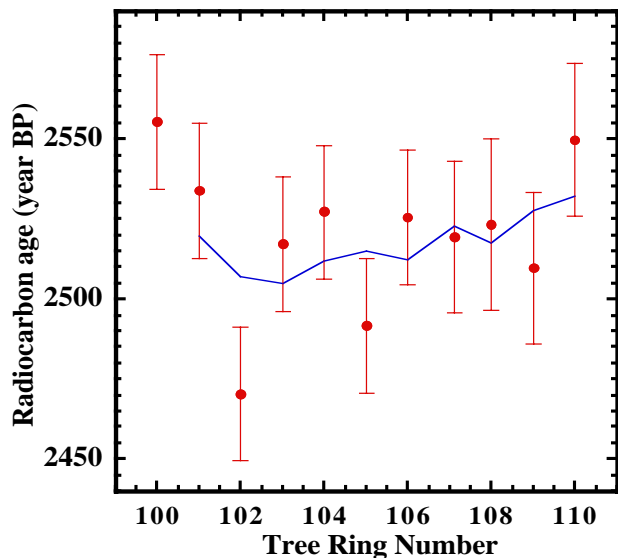


**Fig. 2**  $^{14}\text{C}$  dating of the Choukai-Jindaisugi sample with the calibration data. The blue solid line shows Stuiver's calibration curve which is a relation between radiocarbon age and calendar age. The dotted lines represent  $1\sigma$  error of the calibration data. The calibration curve is constructed from the  $^{14}\text{C}$  concentrations of decade tree rings. The solid circles with  $1\sigma$  error bars are plotted at the most probable calendar ages for the tree rings of Y5, Y40, Y104, Y180, and Y225. The calculation with Oxcal resulted in 445 B.C.  $\sim$ 415 B.C. at Y225 with 63.6% probability.

#### 3.2 $^{14}\text{C}$ Concentrations of 11 Tree rings

We have measured the  $^{14}\text{C}$  concentrations of 11 single-year tree rings from Y100 to Y111 with the accuracy of 0.2%. In Fig. 3, their radiocarbon ages are plotted as a function of the tree ring number. The standard deviation of the 11 radiocarbon ages is 24.1 yr BP for the average and it was slightly greater than the error of the measurement 21 yr BP.

In the figure the light curve is a three point moving average of the radiocarbon ages that has a standard deviation of approximately 12 yr BP. The difference between the maximum and the minimum was approximately 27 yr BP in the moving averaged points. Although with only 11 data we can not clarify the amplitude of 11-year periodicity even our high accurate  $^{14}\text{C}$  measurements, the half of difference is corresponding to 2.7‰ with  $\Delta^{14}\text{C}$ , if we compare the amplitude of  $\Delta^{14}\text{C}$  with the 11-year cycle during the 18th  $\sim$  19th centuries 1.4‰ and 4.8‰ for Pacific trees and Russian trees, respectively (Braziunas, 1993; Kocharov, 1995).



**Fig. 3** The radiocarbon ages (yr BP) of the sequence 11 single-year tree rings. The error bars are the counting statistical errors of  $1\sigma$ . The light curve shows a three points moving average with a standard deviation of 12 yr BP and the difference between the maximum and the minimum is 27 yr BP in the curve.

#### 4 Conclusion

To investigate the time variation of cosmic rays at an ancient time, we have started the measurements of the  $^{14}\text{C}$  concentrations of the single-year tree rings in the past of 2500 year. A measuring system with the high accuracy of 0.2% has been constructed employing a benzene synthesizer capable of producing a large quantity 10 g of benzene and a liquid scintillation counting system Quantulus 1220 <sup>TM</sup> with an ultra-low background level.

We have precisely determined the calendar age of the wood sample Choukai-Jindaisugi cedar to estimate the phase of the long-term solar changes that the cedar was in. Radiocarbon age (yr BP) of a sample is calculated from the  $^{14}\text{C}$  concentration, referring the  $^{14}\text{C}$  concentration at A.D.1950 that is evaluated for the Oxalic acid from NIST. For the  $^{14}\text{C}$  the wood sample with tree rings is advantageous because they are sequential order and the age gaps between each sample are known. Hence we can determine a most probable calendar age with a smaller estimation error using the characteristics. For the five portions of Y5, Y40, Y104, Y180, and Y225, the radiocarbon ages were  $2491 \pm 23$  yr BP,  $2523 \pm 28$  yr BP,  $2527 \pm 21$  yr BP,  $2421 \pm 29$  yr BP, and  $2427 \pm 23$  yr BP, respectively. The Oxcal analysis indicated that the most probable age is 445 B.C.  $\sim$  415 B.C. at Y225 with 63.6% probability and 520 B.C.  $\sim$  400 B.C. with 95.4% probability.

With the accuracy of 0.2% the  $^{14}\text{C}$  concentrations were measured for the 11 single-year tree rings from Y100 to Y111. The standard deviation of the 11 radiocarbon ages is 24.1 yr BP for the average and it was slightly greater than the error of the measurement 21 yr BP. The measurement of  $^{14}\text{C}$  concentrations is in process for the successive single-year tree rings and the 11-year periodicity of solar activity in the past of 2500 year will be found out from those data.

#### 5 References

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