RADIOCARBON, Vol 46, Nr 2, 2004, p 949–955

^{14}C CONCENTRATIONS OF SINGLE-YEAR TREE RINGS FROM ABOUT 22,000 YEARS AGO OBTAINED USING A HIGHLY ACCURATE MEASURING METHOD

Toshiyuki Gandou[1] • Hirohisa Sakurai[1,2] • Wataru Katoh[1] • Yousuke Takahashi[1] • Syuichi Gunji[1] • Fuyuki Tokanai[1] • Hiroyuki Matsuzaki[3]

ABSTRACT. We have measured the radiocarbon concentrations in single-yr tree rings of old wood by accelerated mass spectrometry (AMS) using a multicathode. The ^{14}C concentrations of 10 single-yr tree rings were measured in 100 tree rings at intervals of 10. For each single-yr tree-ring sample, typically 80 measurements of the ^{14}C concentrations were carried out using multicathodes. The sample standard deviations indicated that there are other fluctuations of typically 1.5%, in addition to the fluctuation of the Poisson counting statistics which is typically 3% for each measurement. The average ^{14}C date of the tree rings was 22,130 ± 306 BP for all 624 data of single-yr tree-ring samples measured by the multicathodes. From the calibration data of Lake Suigetsu, the calendar dates of these 100 tree rings were located between 25,400 cal BP and 26,150 cal BP. The ^{14}C dates changed between 21,979 BP and 22,272 BP, with an error of approximately 50 BP, corresponding to a precision of approximately 0.5%. There was a step with a change of approximately 144 BP for each 10 yr in the time profile.

INTRODUCTION

Approximately 20,000 yr ago, radiocarbon concentrations in the atmosphere were about 40% higher than those of the present day (Beck et al. 2001; Kitagawa and Plicht 1998). This difference may be attributed to 2 different causes: one is a change in the production rate of ^{14}C which arose from the variation of geomagnetic fields and/or the variation of the solar modulation of cosmic rays (Beer 2000a; Beer et al. 2000b); the other is an environmental change of the earth which set off a change in the carbon cycle. However, the main cause is unknown. The response of the ^{14}C concentration to the 11-yr solar modulation is a good indicator for investigating the dominant effect (Stuiver and Braziunas 1993, 1998). If the energy spectra of the cosmic rays entering the heliosphere and the solar activities are similar to those during the Holocene, the 11-yr modulation of ^{14}C concentration should increase the amplitude of the modulation corresponding to the decrease in the geomagnetic fields. On the contrary, if the geomagnetic fields are similar to those during the Holocene and the solar activities are different from those during the Holocene, the 11-yr modulation might show a different profile from the 11-yr modulation during the Holocene. Meanwhile, if the increase in ^{14}C concentrations in the atmosphere arises from a change in the carbon cycle, the amplitude and the profile of the 11-yr modulation would be different from those during the Holocene.

^{14}C concentrations in tree rings are indicative of past terrestrial and extraterrestrial environments. Since tree rings record ^{14}C concentrations in chronological order with a time resolution of 1 yr, ^{14}C measurements in single-yr tree rings provide the ^{14}C concentration in the atmosphere for the period of 1 yr. In particular, ^{14}C measurements of the single-yr tree rings of old wood samples are essential for investigating the 11-yr periodicity of solar activity in the past. The expected amplitude in the modulation of the ^{14}C concentrations in the tree rings due to the 11-yr solar cycle is approximately 0.5% to 1%, although the variation of the production rate of ^{14}C is estimated to be approximately 30% based on the observation of the neutron flux at present. The small amplitude in the modulation results from the ^{14}C concentration being reduced to approximately 1/100 by terrestrial carbon circulation in the atmosphere and the ocean (Kocharov et al. 1995; Oeschger et al. 1975; Peristykh and

---

[1] Department of Physics, Yamagata University, 1-4-12 Kojirakawa, Yamagata 990-8560, Japan.
[2] Corresponding author. Email: sakurai@ksprite.kj.yamagata-u.ac.jp.
[3] Research Center for Nuclear Science and Technology, The University of Tokyo, Tokyo 113-0032, Japan.

Proceedings of the 18th International Radiocarbon Conference, edited by N Beavan Athfield and R J Sparks
RADIOCARBON, Vol 46, Nr 2, 2004, p 949–955

Damon 1998). Therefore, measurements of the ^{14}C concentrations for the single-yr tree rings of old wood are desired with an accuracy of 0.5%.

Accelerator mass spectrometry (AMS) measurement is advantageous for both a small quantity of sample and the simultaneous measurement of a large number of samples. Although the typical measurement accuracy is 0.5% for contemporary carbon, for old samples this accuracy can also be realized by AMS measurement using a multicathode method with graphite samples produced from the same tree-ring samples.

We have measured the ^{14}C concentrations in single-yr tree rings of old wood, of which the ^{14}C date is approximately 22,000 BP using AMS with multicathodes. In order to confirm the usefulness of the multicathode measurement method, the ^{14}C concentrations in 10 single-yr tree rings were measured in 100 tree rings at intervals of 10. We describe the results of the multicathode measurement for the single-yr tree rings and the variation of ^{14}C concentrations in 100 tree rings dating as far back as 22,000 yr ago.

METHODS

The tree rings used in this study are from a sample of old wood that was dug out from the bottom of the river at Kaminoyama City (38°07′N, 140°17′E) in Japan. Many old fallen trees are buried in the geological layers of this area, and the layer from which the sample was dug out was close to, although slightly younger, than that of Aera tephra, which is marked by a volcanic eruption in the vicinity of 23,000 BP. From the appearance of the area, it is considered that many trees were rapidly felled at the same time and were immediately buried.

The number of tree rings was approximately 130 and their typical width was 1 mm. For this experiment, we measured the ^{14}C dates of 10 tree-ring samples (labeled KY10 to KY95). Each tree-ring sample was separated by hand into single-yr intervals in order to measure the concentration of ^{14}C. Because α-cellulose in the cell walls is the most reliable chemical component of wood for measuring the annual concentration of ^{14}C, its chemical extraction was carried out using acid and alkaline solutions. Approximately 1 g of α-cellulose was extracted from 5 g of wood sample for a single-yr tree ring.

For the multicathode measurement of a single-yr tree ring, approximately 10 graphite samples were produced from the α-cellulose by the same process. First, 28 mg of cellulose was burned by chemical reaction with copper oxide (CuO) to produce carbon dioxide (CO_2); sulfur was removed with a silver sheet. Graphite was then produced by hydrogen reduction of the CO_2 in the presence of iron powder (1 mg) as catalyst. The graphite was pressed into the cathode container at 60 PSI using a pressing machine. Because it is important to produce identical graphite samples, we attempted to keep the ratio of graphite to iron at 1:1 by weight. The weight ratios of graphite to 1 mg of iron were between 0.6 and 1.2, which indicates that the graphite samples were similar.

Measurements of ^{14}C in the graphite samples were carried out using the 5 MeV Tandem accelerator at the Micro-Analysis Laboratory, The University of Tokyo (MALT). ^{12}C, ^{13}C, and ^{14}C were injected into the AMS with 6000 cycles of 0.12 sec per cycle by sequential injection. Hereafter, the 6000 cycles are referred to as 1 turn. The injected current of ^{12}C was maintained between 6 and 9 μA.

The ^{14}C dates of each graphite sample were calculated from the measured value of $^{14}C/^{12}C$ for the graphite samples of cellulose and the National Institute of Standards and Technology (NIST) standard samples. In the calculation, the value of $\delta^{13}C$ for cellulose measured with a mass spectrometer was used for the isotope fractionation correction.

RESULTS AND DISCUSSION

The numbers of multicathodes and turns for the measurements are shown in Table 1 for each tree-ring sample. Because the number of ^{14}C in the samples is counted to typically 1000 for 1 turn, the relative statistical error is approximately 3% from Poisson counting statistics. Hence, by measurements using 10 multicathodes with 8 turns, we can obtain the relative statistical error of approximately 0.35% for a tree-ring sample from the total counts of ^{14}C. Strictly speaking, however, the conditions for each multicathode and each turn are not identical, although the multicathodes were produced from the same cellulose and they were measured under similar AMS conditions. Therefore, first of all, the statistical behavior was investigated using the data of the multicathode measurements.

Table 1 Numbers of multicathodes, turns, and measurements for the tree-ring samples.

Tree-ring sample	Nr of multicathodes	Nr of turns	Nr of measurements
KY10	10	8	80
KY20	8	4	32
KY30	8	9	72
KY40	8	9	72
KY50	10	8	80
KY60	8	4	32
KY70	8	9	72
KY80	8	4	32
KY90	10	8	80
KY95	8	9	72

For the measurement of a multicathode, the distribution of counts per turn was statistically investigated. The statistical indicators are as follows:

1. $1/\sqrt{N}$, where N is average count of ^{14}C per turn;
2. The relative sample standard deviation (RSD1) calculated from the concentrations of ^{14}C/^{12}C per turn;
3. The relative standard deviation (RSD2), which is the ratio of the σ value to the mean of the Gaussian distribution obtained from the distribution of the concentrations of ^{14}C/^{12}C per turn, as shown in Figure 1. (The figure, for instance, shows the distributions of the concentrations of ^{14}C/^{12}C per turn measured for the multicathodes for samples KY10 and KY70, respectively. The curves represent the best-fitted Gaussian distribution using a least-squares method.);
4. The reduced χ^2 values for the least-squares fitting of the Gaussian distribution.

These values are listed for each tree-ring sample in Table 2.

The values of $1/\sqrt{N}$ are approximately between 2.7% and 3.1%, and indicate the relative standard deviations (PSD), assuming Poisson counting statistics for the ^{14}C counts. The RSD1s were between 3.2% and 3.5% for each tree-ring sample, except samples KY50 and KY80. By removing 2 data from KY50 and 3 data from KY80, respectively, by the χ^2 test, the RSD1s were determined to be 3.6%. Since the significance levels before and after the removal are from 10^{-11}% to 1.3% for KY50 and from 10^{-3}% to 5% for KY80 in the χ^2 distributions, their data were removed. The RSDs are the same as or greater than the PSDs. This indicates that the RSD1s include other fluctuations of typically 1.5%, in addition to the fluctuation of the Poisson counting statistics. Moreover, we attempted to apply Gaussian fitting to the distributions of the concentrations of ^{14}C/^{12}C per turn, although the

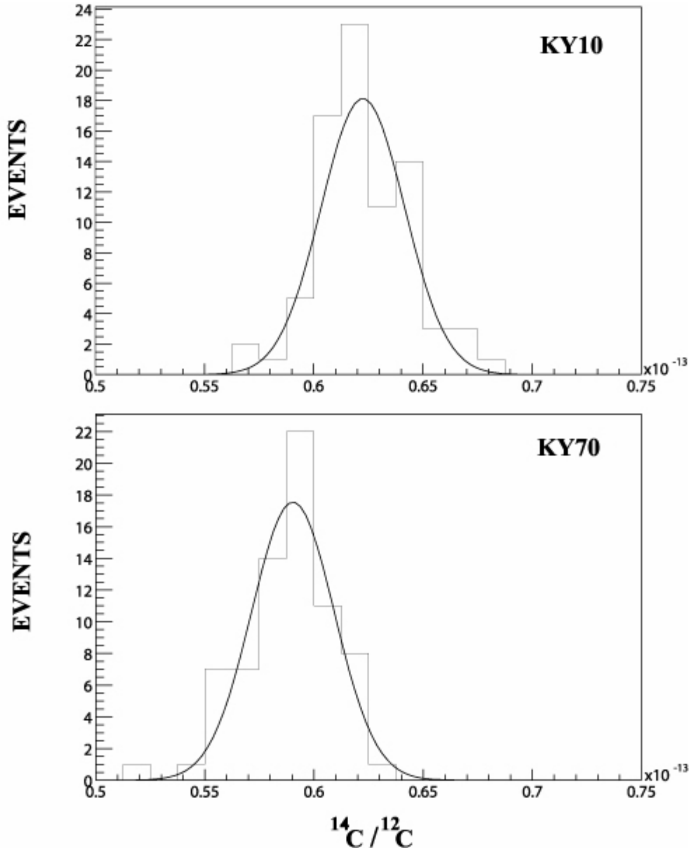

Figure 1 Distributions of the concentrations of $^{14}C/^{12}C$ per turn measured for the multicathodes of single-year tree rings KY10 and KY70. The curves represent the best-fitted Gaussian distribution using a least-squares method.

Table 2 Statistical values obtained from the multicathode measurements of the concentrations of $^{14}C/^{12}C$ for the tree-ring samples (see text).

Tree-ring sample	$\frac{1}{\sqrt{N}}$ (%)	$\frac{SD}{^{14}C/^{12}C}$ (%)	$\frac{\sigma}{mean} GaussFit$ (%)	$\frac{\chi^2}{\nu}$
KY10	3.1	3.5	3.1	1.5
KY20	2.8	2.8	3.4	0.6
KY30	2.8	3.3	3.5	1.5
KY40	2.8	3.2	3.8	1.3
KY50	3.1	5.0 (3.6)	3.2 (3.2)	0.9 (0.9)
KY60	2.8	3.2	3.6	0.1
KY70	2.8	3.4	3.2	1.0
KY80	2.8	4.2 (3.6)	5.5 (4.5)	2.0 (2.0)
Y90	3.1	3.2	3.0	0.7
KY95	2.7	3.3	3.1	0.3

number of events is not large. The RSD2s from the best-fitted Gaussian curves were similar to the RSD1s, indicating that the distributions of the concentrations of ^{14}C/^{12}C per turn are not significantly different from the Gaussian distribution, although the reduced χ^2 values scatter from 0.1 to 2.0. On the basis of these results, to determine the estimated error in the average concentration of ^{14}C/^{12}C of the multicathode measurement for each tree-ring sample, we used the value of the sample standard deviation divided by the square root of the number of data, which is the mean error of the mean.

Figure 2 shows the ^{14}C dates for all of the turn data of each tree-ring sample. The average ^{14}C date of the tree-ring samples from KY10 to KY95 was 22,130 BP, with the standard deviation of 306 BP from the 624 data obtained from the measurements of multicathodes for the single-yr tree-ring samples. Except for 2 ^{14}C dates of KY50, the ^{14}C dates of 622 data for the tree-ring samples were within 3 standard deviations. The ^{14}C date of an outer portion of the tree ring KY95 was 22,198 ± 31 BP. Moreover, the ^{14}C date of the same tree-ring sample was 22,169 ± 86 BP according to the measurement using the highly accurate liquid scintillation counting system (LSC) at Yamagata University (Suzuki et al. 199; Endo et al. 2000; Sakurai et al. 2003). Results obtained using AMS and those obtained using LSC were consistent with each other, confirming the accuracy of the AMS measurements. From the calibration data of Lake Suigetsu (Kitagawa and Plicht 1998), the calendar dates of these 100 tree rings were located between 25,400 cal BP and 26,150 cal BP. The calibration data showed that the ^{14}C dates varied considerably between the calendar dates.

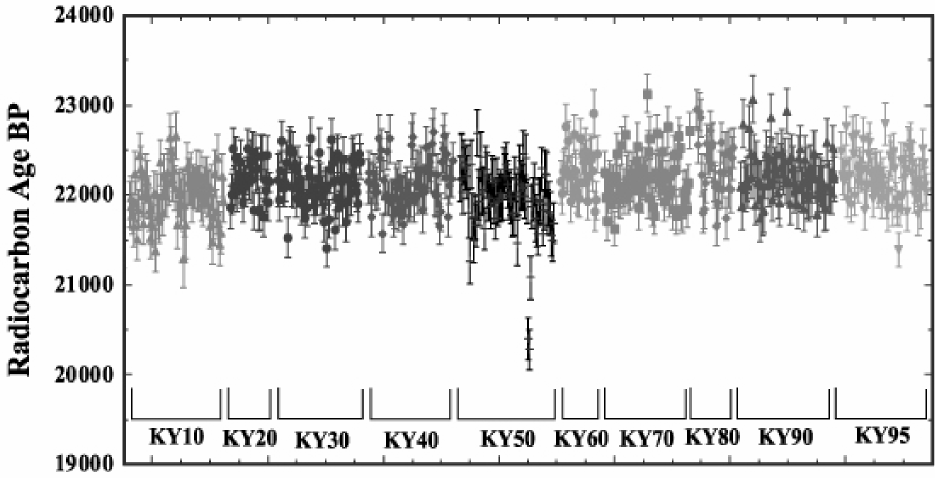

Figure 2 ^{14}C dates for all turn data of each tree-ring sample. The average ^{14}C date of the tree rings from KY10 to KY95 was 22,130 BP, with the standard deviation of 306 BP from the 624 data. Except for 2 ^{14}C dates of KY50, the ^{14}C dates were within the 3 standard deviations.

Finally, Figure 3 shows a time profile of the ^{14}C dates for the tree-ring number. The ^{14}C date for a tree-ring number is derived from the average value of the concentrations of ^{14}C/^{12}C per turn obtained by the measurements for the multicathodes of the single-yr tree ring, and the error bar from the mean error of the mean for the concentrations. Two and 3 ^{14}C dates from the KY50 and KY80 samples, respectively, are removed by a χ^2 test with the significance level of 1%. The ^{14}C dates changed between 21,979 BP and 22,272 BP, with an error of approximately 50 BP, corresponding to a precision of approximately 0.5%. As shown in the figure, the average ^{14}C ages between KY10 and KY50 and between KY60 and KY95 were 22,080 BP and 22,224 BP, respectively, indicating a step with a change of 144 BP in the ^{14}C date for a 10-yr period in the vicinity of KY50. Both sample processing and AMS measurements were carried out in the following order with 4 AMS machine times: KY10, KY50, and KY90 for the 1st; KY20, KY60, and KY80 for the 2nd; KY30, KY40, KY70, and KY95 for the 3rd; and KY50 again for the 4th, respectively. Since the analyzing order is approximately random and the difference between 2 measurements for KY50 was about 40 BP, the possibility of a systematic effect causing the shift of 144 BP is very small. By taking into account the Lake Suigetsu data, which shows a change of 940 BP in ^{14}C date for 7 yr during the calendar dates, the rapid change in the ^{14}C dates for this tree-ring sample implies that the concentrations of ^{14}C/^{12}C in that period were highly variable.

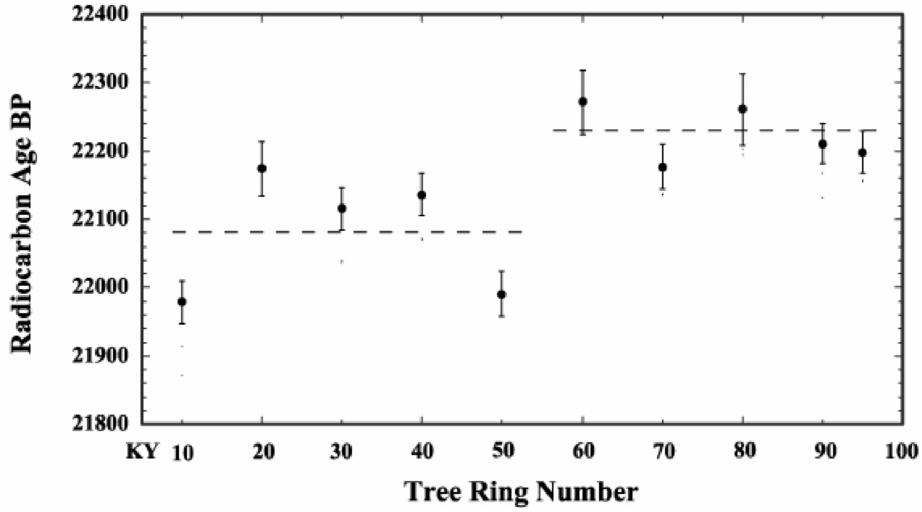

Figure 3 Time profile of ^{14}C dates for the tree-ring number using the mean error mean as the estimated error on average. Dotted lines represent the average ^{14}C dates between KY10 and KY50 and between KY60 and KY95. The ^{14}C dates underwent a change between 21,979 BP and 22,272 BP with the error of approximately 50 BP, corresponding to the precision of approximately 0.5%. As shown in the figure, the average ^{14}C ages between KY10 and KY50 and between KY60 and KY95 were 22,080 BP and 22,224 BP, respectively, indicating a step with a change of 144 BP in the ^{14}C date for a 10-yr period in the vicinity of KY50.

CONCLUSION

We have measured the ^{14}C concentrations in single-yr tree rings of old wood by AMS using a multicathode. The measurement of ^{14}C using a multicathode has 2 advantages. One is an enhancement of the statistical accuracy and, hence, it is expected that the ^{14}C concentrations are measured with high precision. The other advantage is that using a multicathode enables the testing of systematic errors caused by the process of graphite production, and, in turn, this improves the accuracy of the AMS measurement (Sakurai et al. 2004; Guo et al. 2000; Tuniz et al. 1998).

In order to confirm the applicability of the multicathode measurement method, the ^{14}C concentrations in 10 single-yr tree rings were measured in 100 tree rings at intervals of 10. For the multicathode measurement of a single-yr tree ring, approximately 10 graphite samples were produced from its α-cellulose by the same process. For the outer sample of the tree ring, the ^{14}C dates were 22,198 ± 31 BP by AMS and 22,169 ± 86 BP by LSC, respectively, confirming the accuracy of the AMS measurements with the multicathode.

For a single-yr tree-ring sample, typically the ^{14}C concentrations of 80 measurements were obtained using the multicathodes and, hence, we have obtained 624 data in total for the 10 tree-ring samples. The statistical behavior was investigated and compared using Poisson counting statistics for the data set of each tree-ring sample. The sample standard deviations indicated that they include other fluctuations of up to 2%, in addition to the fluctuation of the Poisson counting statistics (Tuniz et al. 1998). From the best-fitted Gaussian curves, the distributions of the concentrations of ^{14}C/^{12}C were not significantly different from the Gaussian distribution.

The average ^{14}C date of the tree rings was 22,130 ± 306 BP for all 624 data. From the calibration data of Lake Suigetsu, the calendar dates of these 100 tree rings were located between 25,400 cal BP and 26,150 cal BP.

The time profile of the ^{14}C dates changed between 21,979 BP and 22,272 BP, with an error of approximately 50 BP, corresponding to a precision of approximately 0.5% using the mean error of the mean as the estimated error on average. From these refined measurements using the multicathode, we identified a step with a change of approximately 144 BP in ^{14}C date for a 10-yr period in the vicinity of KY50 in the time profile. Since both sample processing and AMS measurements were carried out by approximately random order with 4 AMS machine times, it is highly possible that the discrete step is regarded as a real shift. By taking into account Lake Suigetsu data between the calendar dates, the rapid change in the ^{14}C dates in the tree rings implies that the concentrations of ^{14}C/^{12}C in that period were highly variable.

REFERENCES

Beck JW, Richards DA, Edwards RL, Silverman BW, Smart PL, Donahue DL, Hererra-Osterheld S, Burr GS, Calsoyas L, Jull AJT, Biddulph D. 2001. Extremely large variations of atmospheric ^{14}C concentration during the Last Glacial Period. *Science* 292: 2453–58.

Beer J. 2000a. Long-term indirect indices of solar variability. *Space Science Reviews* 100:1–15.

Beer J, Mende W, Stellmacher R. 2000b. The role of the sun in climate forcing. *Quaternary Science Reviews* 19:403–15.

Endo K, Sakurai H, Sekiguchi H, Gunji S, Kato A, Furusawa S, Inui E, Suzuki A, Hamano M. 2000. ^{14}C measurement of synthesized benzene from old tree rings. *IEEE Transactions on Nuclear Science* 47(6):302–5.

Guo Z, Liu K, Lu X, Ma H, Li K, Yuan S, Wu X. 2000. The use of AMS radiocarbon dating for Xia-Shang-Zhou chronology. *Nuclear Instruments and Methods in Physics Research B* 172:724–31.

Kitagawa H, van der Plicht J. 1998. Atmospheric radiocarbon calibration to 45,000 yr BP. *Science* 279:1187–90.

Kocharov GE, Ostryakov VM, Peristykh AN, Vasil'ev VA. 1995. Radiocarbon content variations and Maunder Minimum of solar activity. *Solar Physics* 159: 381–91.

Oeschger H, Siegenthaler U, Gugelmann A, Schotterer U. 1975. A box diffusion model to study the carbon dioxide exchange in nature. *Tellus* 27:168–92

Peristykh A, Damon PE. 1998. Modulation of atmospheric ^{14}C concentration by the solar wind and irradiance components of the Hale and Schwabe solar cycles. *Solar Physics* 177:343–55.

Sakurai H, Sawaki Y, Matsumoto T, Aoki T, Kato W, Gandou T, Gunji S, Tokanai F. 2003. Characteristics of high-purity Teflon vial for ^{14}C measurement in old tree rings. *Nuclear Instruments and Methods in Physics Research A* 505:454–7.

Sakurai H, Gandou T, Kato W, Sawaki Y, Matsumoto T, Aoki T, Matsuzaki H, Gunji S, Tokanai F. Forthcoming. AMS measurement of C-14 concentration in a single-year ring of a 2500-year-old tree. *Nuclear Instruments and Methods in Physics Research B*.

Stuiver M, Braziunas F. 1993. Sun, ocean, climate and atmospheric $^{14}CO_2$. *The Holocene* 3:289–305

Stuiver M, Braziunas F. 1998. Anthropogenic and solar components of hemispheric ^{14}C. *Geophysical Research Letters* 25(3):329–32.

Suzuki A, Sakurai H, Endo K, Noma M, Gunji S, Inui E, Hamano M. 1999. Pulse-height distribution of β rays in ^{14}C Measurement with liquid scintillation counting system Quantulus. IEEE *Transactions on Nuclear Science* 46(3):302–5

Tuniz C, Bird JR, Fink D, Herzog GF. 1998. *Accelerator Mass Spectrometry*. Boca Raton: CRC Press. 300 p.