

¹⁴C DATING OF ~2500-YR-OLD CHOUKAI JINDAI CEDAR TREE RINGS FROM JAPAN USING HIGHLY ACCURATE LSC MEASUREMENT

Hirohisa Sakurai¹ • Wataru Kato • Yosuke Takahashi • Kayo Suzuki • Yui Takahashi • Shuichi Gunji • Fuyuki Tokanai

Department of Physics, Yamagata University, 1-4-12 Kojirakawa, Yamagata 990-8560, Japan.

ABSTRACT. Radiocarbon ages of 8 decadal tree rings and 66 single-yr tree rings have been measured with a highly accurate liquid scintillation counting (LSC) system (0.2% error) after synthesizing 10.5 g of benzene for each α -cellulose sample produced from tree rings of Choukai Jindai cedar in Japan (39°N). The ¹⁴C ages were between 2449 and 2539 ¹⁴C yr BP for the 21 samples. From the wiggle-matching of the data set using the IntCal04 (Reimer et al. 2004) calibration data in OxCal v 3.10 (Bronk Ramsey 2005), the estimated age of the outer edge of the Choukai tree rings was 477.5 BC (± 12.5 yr) with a confidence level of 95.5%; hence, the Choukai tree rings range from 2757 to 2437 cal BP. The age indicates an improved eruption date of the Choukai Volcano. The statistical errors at 1 σ are approximately ± 10 and ± 7 ¹⁴C yr for the 5-yr data and the decadal data from the single-yr measurements, respectively. For the interval between 2580 and 2520 cal BP, it is statistically significant that the Choukai ¹⁴C ages are ~ 16 ¹⁴C yr older on average than both the IntCal04 and QL German oak ($\sim 50^\circ$ N) data sets. The $\sim 2.0\%$ offset is informative for the study of regional offset in the Far East.

INTRODUCTION

IntCal04 (Reimer et al. 2004) shows a flat range of radiocarbon ages for the 300-yr period between 2670 and 2370 cal BP. This region is wedged between 2 remarkable excess periods of atmospheric $\Delta^{14}\text{C}$, the Maunder and Spörer events, characterized by changes in the calibration curve over 10,000 yr. In fact, Stuiver and Braziunas categorized 2 types of Maunder and Spörer oscillations by the duration of periods of high atmospheric ¹⁴C and showed that there were 9 Maunder-type and 8 Spörer-type events in the 9600-yr record (Stuiver and Braziunas 1989). Moreover, for the 4 episodes of triple oscillations, each of which contains at least 2 of the Maunder- and Spörer-type events in a 700-yr period, the authors implied that the ¹⁴C oscillations are explained by solar-wind forcing. Because the Sun shows strong 11-yr cyclic activity, the episodic variability of the 11-yr modulation of ¹⁴C concentration in tree rings could reveal the dynamic behavior of changes on the Sun's surface.

As the Choukai Jindai cedar age is located in one of the episodes between 2830 and 2150 cal BP, its tree rings should be suitable for investigating the variability of ¹⁴C concentration in this period. An old wood sample buried in clay by the eruption of Mt Choukai (39°05'N, 140°03'E) in Japan ~ 2500 yr ago was dug out in the spring of 1996. As seen in Figure 1, the wood was well preserved (evident by the clear barks on the outside) and produced ~ 320 tree rings, each 0.5–3 mm wide. However, the exact calendar age of the Choukai cedar is unknown because the tree rings could not be dated by dendrochronology. Therefore, we ¹⁴C dated 21 portions of the Choukai cedar (0.2% error) and determined the calibration age of the tree rings via wiggle-matching using the IntCal04 calibration curve.

The IntCal04 calibration is important not only for the age determination of the Choukai cedar, but also for refinement of the IntCal04 calibration curve for old Japanese tree rings. Since the data sets employed in the IntCal04 calibration curve during the episode era are from Irish oak, German oak, and woods in the western USA, the results of the wiggle-matching may provide information about the regional effects of atmospheric ¹⁴C concentrations in the Northern Hemisphere and may validate the random walk model applied to IntCal04. Moreover, in Japanese archeological research, the time profile of the ¹⁴C ages for the era from which the Choukai cedar dates occupies a key position when we consider the time scale of the prehistoric Yayoi culture (Sakamoto et al. 2003).

¹Corresponding author. Email: sakurai@sci.kj.yamagata-u.ac.jp.



Figure 1 A photograph of the Choukai Jindai cedar tree-ring sample and the location in Japan

¹⁴C Measurements

The tree rings are numbered from Y0 to Y225 from the center portion to the outer edge of the Choukai cedar. There were 10 tree rings from Y225 to the outer edge. We assigned Y0 to a tree ring that is beyond ~85 tree rings from the center core. We then measured the ¹⁴C ages of 8 decadal samples (D5, D20, D30, D40, D50, D60, D180, D225) and 66 single-yr samples from Y80 to Y145. For instance, D5 is a 10-yr wood section from Y1 to Y10. Moreover, the single-yr data were averaged into twelve 5-yr data points: H82, H87, H92, H97, H102, H107, H112, H117, H122, H127, H132, H137. For example, H82 is a 5-yr wood section from Y80 to Y84, and D143 is averaged with 6-yr data from Y140 to 145. Thus, 21 ¹⁴C dates are used for the wiggle-matching. The ¹⁴C age of the decadal sample D140 was measured in order to compare it with the average ¹⁴C ages of the single-yr samples from Y136 to Y145.

The single-yr tree rings and 10-yr wood sections were taken from a block of boiled wood using tweezers. The sample was milled prior to chemical treatment. As α -cellulose in the cell walls is the most reliable chemical component of wood used for measuring the annual concentration of ¹⁴C, it was chemically extracted. The α -cellulose extraction involves 3 steps: 1) removing oils, saps, and resins with hexane and ethanol; 2) lignin removal with NaOCl solution; and 3) α -cellulose separation with NaOH and HCl solutions. The yield of the α -cellulose from the wood was ~33% by weight. Approximately 38 g of α -cellulose was extracted from 130-g wood samples.

Benzene was synthesized from the extracted α -cellulose because benzene has 6 carbon atoms in a molecule and works well as a solvent for liquid scintillations. The cellulose was first burned in oxygen at a pressure of 100 psi to produce carbon dioxide (CO₂). Acetylene gas (C₂H₂) was produced from the reaction of CO₂ with lithium carbide (Li₂C₂), and the benzene was polymerized from the acetylene gas. The amount of synthesized benzene was typically 10.5 g, while the benzene used for

¹⁴C dating is usually 3 g at most. The yield from the CO₂ to C₆H₆ reaction was ~80% in number of carbon atoms. Since the ¹⁴C age of a sample is calculated with a ratio of the concentrations of ¹⁴C between the sample and a standard sample (Stuiver and Polach 1977), using the same chemical process the standard benzene sample is synthesized from oxalic acid (SRM 4990-C) with a known concentration of ¹⁴C certified by the National Institute of Standards and Technology (NIST).

¹⁴C in the synthesized benzene was measured using the liquid scintillation counting (LSC) system Quantulus 1220™ with an ultra-low background level. The benzene was poured into a high-purity Teflon®/copper counting vial (20 mL), and butyl-PBD was added as the scintillator at the proportion of 15 mg/mL of benzene. Moreover, we chose similar quality vials for light yields and background rates for the samples (Sakurai et al. 2003; Kato et al., forthcoming). The pulse height distribution of output signals is useful for the elimination of signals apart from the ¹⁴C-ray spectrum. Typically, the background rate is 0.087 ± 0.004 cpm per 1 g benzene for 10.5 g of benzene produced from a marble sample. Since the counting rate of the tree-ring sample is ~84 cpm for 10.5 g benzene, a measuring time of 2 days is needed to achieve a statistical accuracy of 0.2%. Although the Quantulus can operate at high stability for long-term measurements (Suzuki et al. 1999; Endo et al. 2000), to ensure the reliability of the measurements we employed cyclic measurements of the tree-ring sample, the background sample, and the standard sample. We also confirmed that the total systematic error is <0.1%, accounting for factors such as a slight difference in the quantity of benzene and scintillator poured in a vial, the volatilization of benzene in the measurement, and differences in the quality of the vials.

Moreover, to check for a laboratory offset of the measured ¹⁴C ages, 2 samples of the decadal sample D50 and single-yr sample Y109 were measured by accelerator mass spectrometry (AMS) (MALT, University of Tokyo) using the same α-cellulose samples measured by LSC. The age differences between AMS and LSC measurements were 19 ± 23 and -18 ± 33 ¹⁴C yr for the decadal and the single-yr samples, respectively, proving the consistency of both measurement methods (Sakurai et al. 2004).

RESULTS AND DISCUSSION

All measurements of ¹⁴C concentration were carried out with a statistical accuracy of <0.2% for the 21 samples from D5 to D225. The ¹⁴C ages were between 2449 and 2539 ¹⁴C yr BP for 21 samples. The errors of the decadal samples are between ~16 and 22 ¹⁴C yr as a standard deviation, while errors for the 5-yr samples are between ~8 and 13 ¹⁴C yr from the average of the single-yr data. Using OxCal v 3.10 (Bronk Ramsey 2001, 2005) the wiggle-matching for the IntCal04 (Reimer et al. 2004) calibration data showed that the calendar age of D225 is 500–475 BC with a 95.4% confidence level (Figure 2). Moreover, we investigated the effect of the difference between the sample data set and the IntCal04 data set to the estimated calendar age of the D225 using the following equation:

$$\Delta Z = \frac{T_s - T_{int}}{\sqrt{\sigma_s^2 + \sigma_{int}^2}}$$

where T_s and T_{int} are the ¹⁴C ages of the sample and the IntCal04 data, respectively, and σ_s and σ_{int} are the errors of the sample and the IntCal04 data, respectively. Figure 3 shows the average values (ΔZ^2) of 21 samples as a function of the estimated calendar age of sample D225. If the difference between the ¹⁴C ages of the sample and the IntCal04 data is under a Gaussian distribution with the variance of $\sigma^2 = \sigma_s^2 + \sigma_{int}^2$, the sum of ΔZ^2 for 21 samples relates to the product of Gaussian proba-

bilities for each sample. Hence, the calendar ages of the sample for the small values of (ΔZ^2) imply good estimated ages. In Figure 3, as the ΔZ^2 value at 487.5 BC is smallest, we define D225 (Y225) as 487.5 BC (± 12.5 yr). Mitsutani (2001), a Japanese dendrologist, dated the Mt Choukai eruption at 466 BC from the chronology of a Choukai Jindai cedar, using different samples than ours. Since the outer edge of our tree rings is Y235, the estimated date of the outer edge is 477.5 BC (± 12.5 yr) from the wiggle-matching. Our Choukai sample dates compare well with the wood employed in the dendrochronology within the 95.4% confidence level. Therefore, the Choukai tree rings ages range from 2757 to 2437 cal BP.

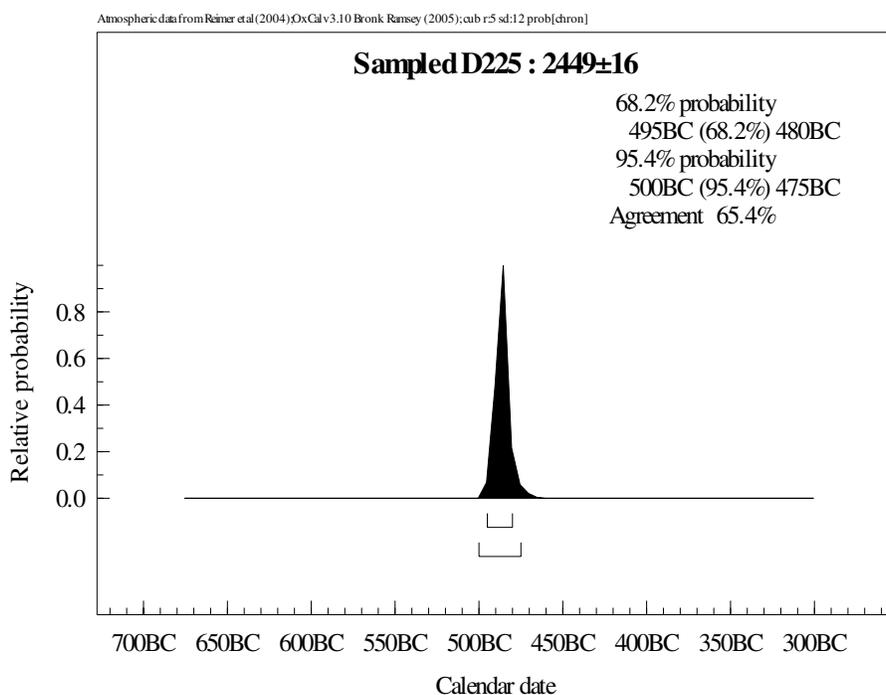


Figure 2 Most probable calendar date of the Choukai sample calculated by OxCal (v 3.10) for the IntCal04 calibration curve. At the 95.4% confidence level, sample D225 is between 500 and 475 BC.

The ^{14}C ages of the 21 samples compared with the IntCal04 calibration curve, positioned so that D225 is at 2437.5 cal BP (see Figure 4). For the 8 decadal samples, the difference of ^{14}C ages between the sample and the IntCal04 data is between -33 and 42 ^{14}C yr, and the difference in ΔZ values is between -1.6 and 1.6 . For the thirteen 5-yr samples, including D143, the difference in ^{14}C ages is between -17 and 34 ^{14}C yr, and ΔZ values are between -1.0 and 1.9 . As shown in Figure 5, the distribution of each ΔZ for 21 samples ranges between -1.75 and 2.25 , with the averages of ΔZ greater than zero: ~ 0.29 and ~ 0.87 for the decadal samples and the 5-yr samples, respectively.

The average offsets for the IntCal04 curve are 15.3 ± 4.6 and 6.0 ± 7.9 ^{14}C yr for the 5-yr and decadal samples, respectively. Although the offset of the 5-yr samples from single-yr measurements is greater than that of the decadal samples, it is not caused by the cutting of the wood sections because the ^{14}C age of the decadal sample D140 and the average from single-yr samples at the same wood section are 2476.4 ± 22.1 and 2480.6 ± 6.2 ^{14}C yr BP and are therefore consistent with each other.

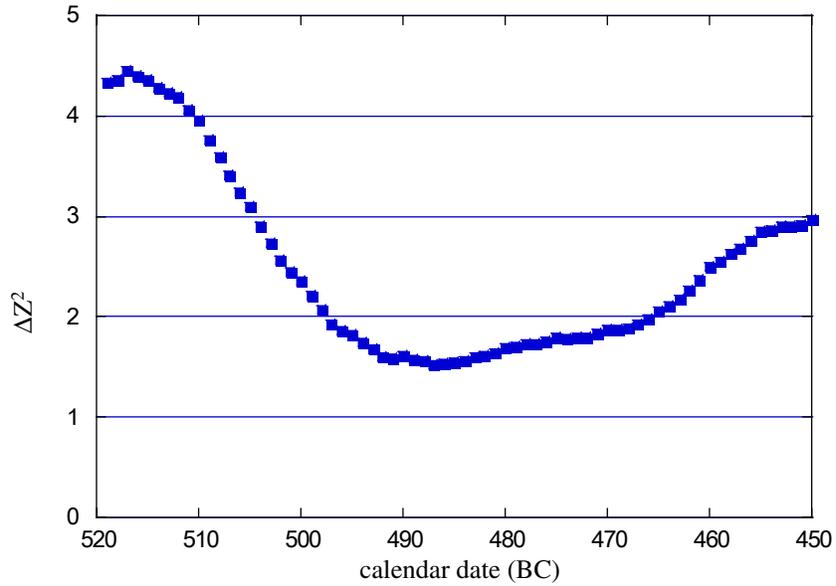


Figure 3 Most probable calendar date of the Choukai sample calculated by ΔZ^2 (see text). The calendar date of the minimum value is 487.5 BC for sample D225.

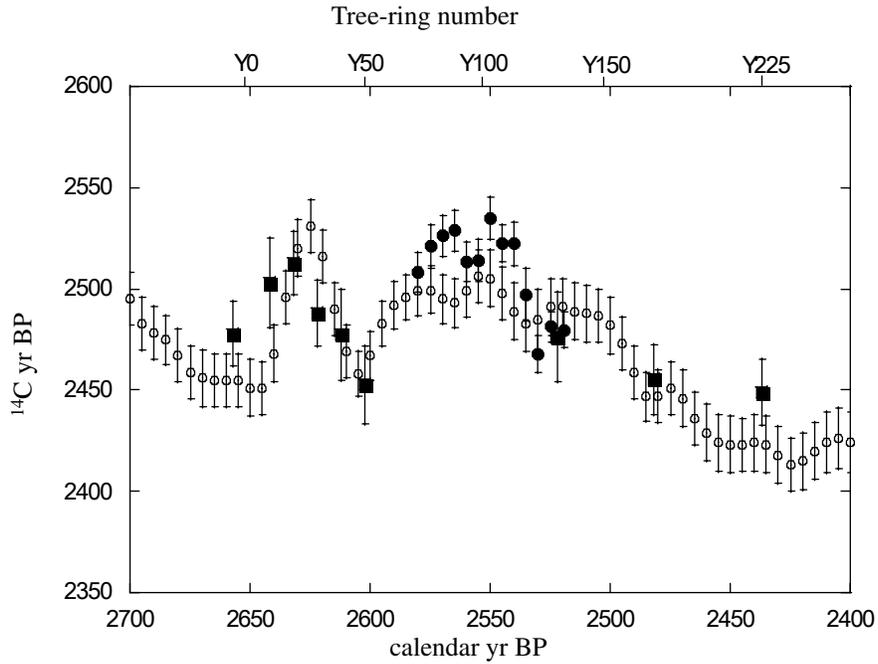


Figure 4 Time profile of ¹⁴C ages of the Choukai samples when sample D225 is defined at 2437.5 cal BP (487.5 BC) relative to the IntCal04 data (open circles). The solid circles and the solid squares represent the 5-yr and the decadal sample groupings, respectively. The error bars at 1- σ are from ± 9 to ± 12 ¹⁴C yr and from ± 16 to ± 22 ¹⁴C yr for the solid circles and the solid squares, respectively. The error bars of the IntCal04 data are from ± 12 to ± 14.5 ¹⁴C yr.

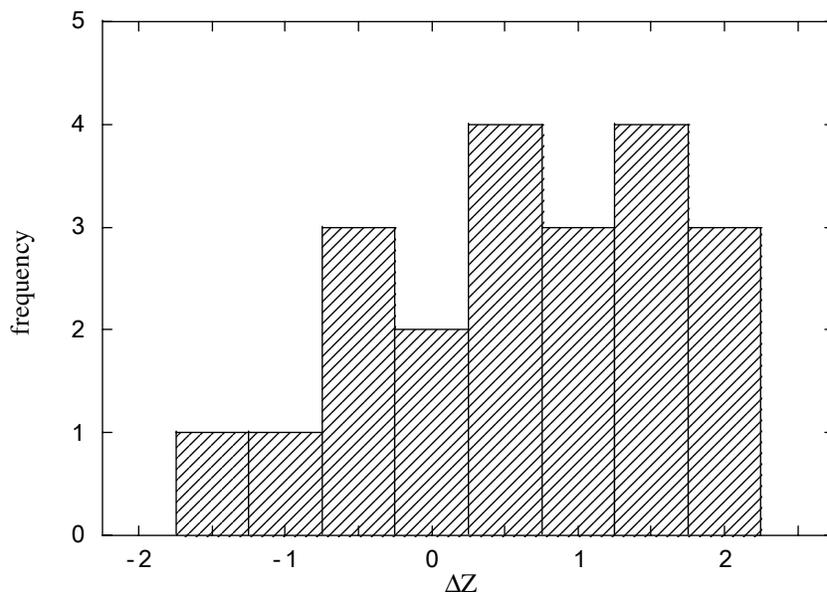


Figure 5 Distribution of the relative difference (ΔZ) of ^{14}C ages between the Choukai samples and IntCal04 data. All of the differences are within $\pm 2\sigma$.

We compared our data set with the IntCal04 Seattle data set (QL) between 2700 and 2400 cal BP. In the Seattle data set (QL), only 1 bidecadal data point was excluded because of the discrepancy in the decadal data sets, and a few data with the same year and 1-yr difference in cal BP were averaged with a weighted error. In Figure 6, the decadal data set of 14 Choukai samples is compared to the QL data set. For the single-yr ^{14}C ages from Y80 to Y145 in the Choukai samples, the 6 decadal data were calculated in 10-yr averages. The remaining Choukai data are used for the decadal samples. Although the differences of each ^{14}C age between the Choukai and the Seattle data sets range from -26 to 28 ^{14}C yr, the offsets for the Seattle data set are 18.5 ± 8.0 and 5.2 ± 14.2 ^{14}C yr on average for the data from the single-yr and the decadal samples, respectively.

In Figures 4 and 6, between 2580 and 2520 cal BP the Choukai data are plotted with $1\text{-}\sigma$ statistical errors of approximately ± 10 and ± 7 ^{14}C yr for the 5-yr and decadal data from single-yr measurements, respectively. For the average offsets ($1\text{-}\sigma$ error), the duration is statistically significant and shows that the Choukai ^{14}C ages are older for both the IntCal04 and QL data sets. Using this older ^{14}C age of ~ 16 ^{14}C yr on average at the Choukai location, we might be able to better define the regional distribution of volcanic CO_2 emissions, CO_2 circulation on the coast of Japanese islands, and atmospheric processes of air-mass motions at the constant production rate of ^{14}C , etc.

Due to the dilution of atmospheric ^{14}C concentrations, it is difficult to estimate the actual flux of the ongoing volcanic CO_2 emissions at the Choukai location. In the Choukai region, which is in the Sea of Japan, the indication is that the bottom water turns over within a short time of ~ 100 yr and is influenced by the low- $\Delta^{14}\text{C}$ surface water ($\sim 90\%$ in northern Sea of Japan) (Kumamoto et al. 1998). This pattern might locally affect the circulation of atmospheric CO_2 in the ocean.

It is also worth noting that the ^{14}C data of Anatolian wood ($\sim 40^\circ\text{N}$) in the early 8th century BC is offset by ~ 30 ^{14}C yr from the Seattle data set of the German oak ($\sim 50^\circ\text{N}$); the Choukai cedar from the 7th century BC is located at a similar latitude of 39°N (Kromer et al. 2001; Manning et al. 2001).

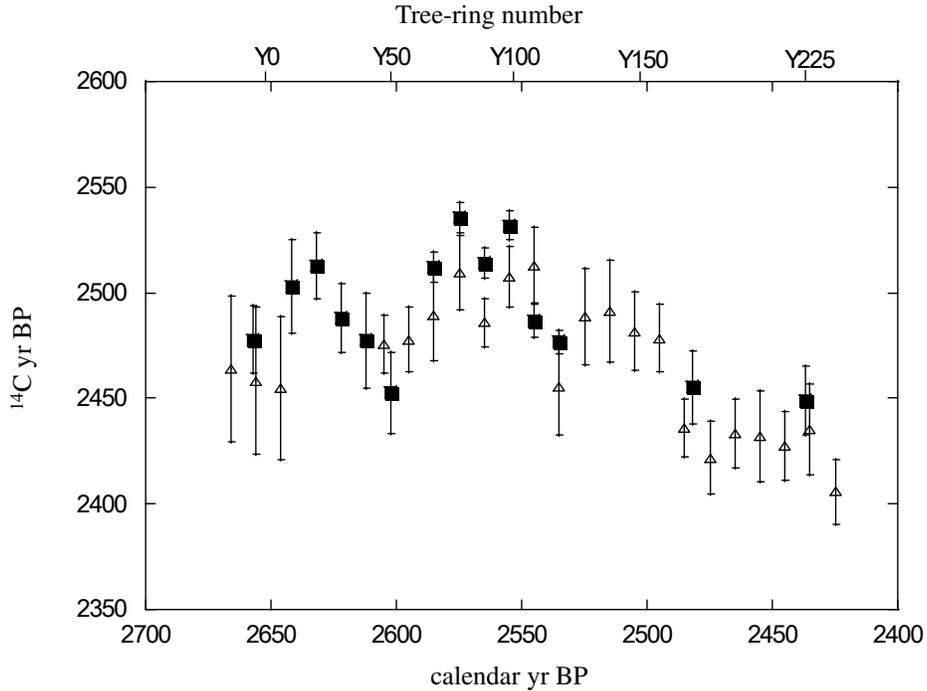


Figure 6 Time profile of the ¹⁴C ages of the Choukai samples (solid squares) compared with the Seattle data (open triangles). For the interval between 2580 and 2520 cal BP, the error bars at 1 σ for the Choukai data are from ± 6 to ± 8 ¹⁴C yr. The error bars of the rest of the Choukai data are from ± 16 to ± 22 ¹⁴C yr. The error bars of the QL data are from ± 12 to ± 34.5 ¹⁴C yr.

However, as the Choukai samples lie in a flat region of the ¹⁴C data between 2 $\Delta^{14}\text{C}$ excesses in the 8th and 4th centuries considered as 2 “deep” solar minima, this period might not be similar to the enhanced seasonal ¹⁴CO₂ during periods of low solar magnetic activity, even if the Choukai data set is affected by a regional offset (Kromer et al. 2001).

Since the intensity of cosmic rays in the atmosphere is greater at higher latitude, the geomagnetic latitudes of the German oak (~50°N), Anatolian wood (~37°N), and Choukai cedar (~30°N) are naturally conducive to the production rate of ¹⁴C. For a study of the relationship between solar activity effect and regional effect, however, it is necessary to accumulate data sets in a variety of areas in this time period because the atmospheric concentration of ¹⁴C has to take into account the time scales of air mixing between the stratosphere and the troposphere and carbon flux with the ocean for each area in the hemisphere (Braziunas et al. 1995). This Choukai data set can be useful for such investigations.

CONCLUSIONS

We measured the concentration of ¹⁴C in Choukai Jindai cedar in Japan to investigate the variability of solar activity in the past associated with the 11-yr periodic cycle. The ¹⁴C ages of 8 decadal tree rings and 66 single-yr tree rings were measured with a highly accurate LSC system (0.2% accuracy) after synthesizing a large quantity (10.5 g) of benzene for each α -cellulose sample produced from the tree-ring samples. Using the IntCal04 calibration curve with a 5-yr span as a calibration curve of the wiggle-matching by OxCal (v 3.10), thirteen 5-yr data sets were formed by averaging 66 single-yr dates. The ¹⁴C ages were between 2449 and 2539 ¹⁴C yr BP for 21 samples. After wiggle-match-

ing, the estimated age of the outer edge of the Choukai tree rings was 477.5 BC (± 12.5 yr) with a confidence level of 95.5%. Therefore, the Choukai tree rings range from 2757 to 2437 cal BP.

Since this Choukai cedar is believed to be a tree that fell during an eruption of Choukai Volcano, the 477.5 BC (± 12.5 yr) age indicates the time of the eruption. This improved date range for the eruption is an important contribution for the study of Choukai Volcano (Iguchi 1988).

The statistical errors (1σ) are about ± 10 and ± 7 ^{14}C yr for the 5-yr data and the decadal data from single-yr measurements, respectively. Between 2580 and 2520 cal BP, the offsets of the Choukai data for the IntCal04 data and the Seattle data of German oak ($\sim 50^\circ\text{N}$) were on average 15.3 ± 4.6 and 18.5 ± 8.0 ^{14}C yr. For the entire time frame, it is statistically significant that the Choukai ^{14}C ages are ~ 16 ^{14}C yr older on average for both the data sets of IntCal04 and QL. The $\sim 2.0\%$ offset is informative for the study of regional offset because the Choukai cedar was located in Japan (39°N), and the data is from an episode of the triple oscillation between 2830 and 2150 cal BP.

REFERENCES

- Braziunas TF, Fung IY, Stuiver M. 1995. The preindustrial atmospheric $^{14}\text{CO}_2$ latitudinal gradient as related to exchanges among atmospheric, oceanic, and terrestrial reservoirs. *Global Biogeochemical Cycles* 9:565–84.
- Bronk Ramsey C. 2001. Development of the radiocarbon program OxCal. *Radiocarbon* 43(2A):355–63.
- Bronk Ramsey C. 2005. OxCal program v3.10 [software and online manual]. URL: <http://www.rlaha.ox.ac.uk/oxcal/oxcal.htm>.
- 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):1933–7.
- Iguchi T. 1988. The collapse of volcanic edifice and debris flow in Japan. *Report of the National Research Center for Earth Science and Disaster Prevention* 41: 198–232.
- Kato W, Sakurai H, Suzuki K, Takahashi Y, Gandou T, Agatsuma N, Gunji S, Tokanai F. Forthcoming. Light yield and pulse-height spectra of high-purity Teflon vials for accurate ^{14}C measurement in old tree rings. In: Chalupnik S, Schönhofer F, Noakes JE. *LSC 2005, Advances in Liquid Scintillation Spectrometry*. Tucson: Radiocarbon.
- Kromer B, Manning S, Kuniholm P, Newton M, Spurk M, Levin I. 2001. Regional $^{14}\text{CO}_2$ offsets in the troposphere: magnitude, mechanisms, and consequences. *Science* 294:2529–32.
- Kumamoto Y, Yoneda M, Shibata Y, Kume H, Tanaka A, Uehiro T, Morita M. 1998. Direct observation of the rapid turnover of the Japan Sea bottom water by means of AMS radiocarbon measurement. *Geophysical Research Letters* 25:651–4.
- Manning S, Kromer B, Kuniholm P, Newton M. 2001. Anatolian tree rings and a new chronology for the East Mediterranean Bronze–Iron ages. *Science* 294:2532–5.
- Mitsutani T. 2001. Dendrochronology and cultural asets. *Art of Japan* 421:92–3. In Japanese.
- Reimer PJ, Baillie MGL, Bard E, Bayliss A, Beck JW, Bertrand CJH, Blackwell PG, Buck CE, Burr GS, Cutler KB, Damon PE, Edwards RL, Fairbanks RG, Friedrich M, Guilderson TP, Hogg AG, Hughen KA, Kromer B, McCormac G, Manning S, Bronk Ramsey C, Reimer RW, Remmele S, Southon JR, Stuiver M, Talamo S, Taylor FW, van der Plicht J, Weyhenmeyer CE. 2004. IntCal04, terrestrial radiocarbon age calibration, 0–26 cal kyr BP. *Radiocarbon* 46(3):1029–58.
- Sakamoto M, Imamura M, van der Plicht J, Mitsutani T, Sahara M. 2003. Radiocarbon calibration for Japanese wood samples. *Radiocarbon* 45(1):81–9.
- 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. 2004. 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* 223–224:371–5.
- Stuiver M, Polach H. 1977. Discussion: reporting of ^{14}C data. *Radiocarbon* 19(3):355–63.
- Stuiver M, Braziunas F. 1993. Atmospheric ^{14}C and century-scale solar oscillations. *Nature* 338:405–7.
- 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.