$\delta^{13}\text{C}$ records of Japanese cedars from Yakushima Island and past atmospheric CO_2

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$\delta^{13}\text{C}$ records of annual growth rings of two Japanese cedars (*Cryptomeria japonica*) from Yakushima Island, southern Japan are presented for the past 200 years. Some portions of the short-term fluctuations in the $\delta^{13}\text{C}$ records from the Japanese cedars are correlated with the variabilities of the ring-thickness index. Regressions between the ring-thickness indices and $\delta^{13}\text{C}$ values were used to "correct" the $\delta^{13}\text{C}$ records for local climate and environmental effects. These corrected $\delta^{13}\text{C}$ records from the two Japanese cedars show a steady downward trend with time, but with pronounced short-term fluctuations superimposed on the trend. The overall $\delta^{13}\text{C}$ fall from 1870 to the present is between 1.2–1.4‰, consistent with the $\delta^{13}\text{C}$ records of atmospheric CO_2 estimated from ice-core bubbles, which show a fall of 1.14 ± 0.15 ‰ from 1740 to the present (Friedli *et al.*, 1986). The $\delta^{13}\text{C}$ fall seems to be related to the increase in the concentration of atmospheric CO_2 as a result of fossil fuel burning and deforestation. The corrected $\delta^{13}\text{C}$ records show small increases at 1900 and 1950, which can not be explained satisfactorily at present.

INTRODUCTION

In order to better understand the carbon cycle and how human activities may be influencing it, it is important to reconstruct atmospheric CO_2 concentration and $\delta^{13}\text{C}$ values of CO_2 . The $\delta^{13}\text{C}$ values in a tree can reflect variations of the atmospheric CO_2 incorporated by the tree; however, they are also influenced by changes in the photosynthetic fractionation of the tree itself. Numerous investigations of $\delta^{13}\text{C}$ records in trees, but from limited areas such as Europe, America etc., have already been reported (i.e., Freyer, 1979a, 1986; Tans and Mook, 1980; Stuiver *et al.*, 1984; Leavitt and Long, 1988, 1989). These published records, however, have not been consistent because $\delta^{13}\text{C}$ values in trees reflect the effects of various climatic and environmental factors. For example, recycled biospheric CO_2 may change the $\delta^{13}\text{C}$ values in some local environments (Keeling, 1958). In addition, the tree may have a variable fractionation

of carbon isotopes during the photosynthetic reaction influenced by local climatic and environmental changes (Francey and Farquhar, 1982). If these effects can be quantified, much information can be extracted from trees concerning climatic history and atmospheric CO_2 change for periods and localities for which recorded data are not available.

Secular $\delta^{13}\text{C}$ changes in annual growth ring of two Japanese cedars from Yakushima Island, southern Japan are presented in this paper. We corrected a part of the *in-situ* variability of isotopic fractionation by normalizing the $\delta^{13}\text{C}$ values to constant ring-thickness, taking a similar approach to Stuiver *et al.* (1984), and reconstructed the past atmospheric CO_2 change.

SAMPLES AND EXPERIMENTAL METHODS

Tree samples

Two Japanese cedars were collected from Yakushima Island, which is located in the

southern extremity of Kyusyu, Japan. The mean annual temperature there is 18°C while the mean monthly temperature is 10°C in January and 27°C in August. Mean annual precipitation during the last 30 years was 1800 mm, and occasionally the annual precipitation exceeds 10,000 mm (Miyawaki, 1980).

The two Japanese cedars, Lab. Nos. YKR-1 and YKR-2, were cut down in late summer of 1990. YKR-1 from a northern area in Yakushima Island has 251 annual growth rings (AD. 1740–1990), and YKR-2 from a south-east area has 200 annual growth rings (AD. 1791–1990).

Preparation of wood sample and isotopic analysis

Wood consists of various components; cellulose, hemicellulose, lignin, and other sub-components. It is important to isolate a single component from wood and to measure the isotopic composition because the $\delta^{13}\text{C}$ value and abundance of various component are not uniform (Freyer, 1986). Therefore, we isolated cellulose component (alpha-cellulose) for carbon isotopic analysis.

The wood chips with 5-year successive tree-rings were ground in a Wiley mill to 64-mesh size. Cellulose was prepared from the wood powder (100–200 mg) using a method modified from Wise *et al.* (1946). Firstly, the sub-components; resin, lipid, pectin etc., were extracted using a Soxhlet extractor with benzene-ethanol mixture (1:2, v/v) and acetone. Secondly, lignin was removed by acidified solution of sodium chlorite at 70°C on five repeated runs. Finally, hemicellulose was dissolved by sodium hydroxide solution (17.5%) at room temperature. The sample was neutralized, washed several times with hot distilled water and dried slowly at 60°C in vacuo.

The isolated alpha-cellulose was heated together with cupric oxide as an oxidizing agent in a sealed Vycor tube at 850°C and converted to CO_2 and H_2O . The CO_2 was dried cryogenically using pentane slush trap at -130°C and then analyzed on a Finnigan MAT 250 and 251 mass

spectrometers. The $\delta^{13}\text{C}$ values were calculated with respect to the PDB standard calibrated on the NBS 20 and NBS 21 standards. Repeated measurements of the laboratory cellulose standard indicate a reproducibility of 0.10‰ at 1 σ level for combustion and mass spectrometric analysis (Kitagawa, 1987). When cellulose preparation and sample combustion are included, the standard deviation in the $\delta^{13}\text{C}$ measurements slightly increases to 0.12‰.

Tree-ring thickness measurements

An annual growth ring of Japanese cedar consists of an early and a late wood. The transition from the late wood to the early wood of next year is clear, while the transition from early wood to late wood is more gradual. The tree-ring thickness of the two tree-sections, YKR-1 and YKR-2, were measured. After this, the ring-thickness indices (RI) were calculated by following the method described by Fritts (1976) and using the formulas:

$$\text{RI} = W(\text{measured}) / W(\text{expected}) \quad (1)$$

and

$$W(\text{expected}) = A \cdot \exp(-BT), \quad (2)$$

where $W(\text{measured})$ represents tree-ring thickness measured for each tree. $W(\text{expected})$ is calculated by eq. (2) and $W(\text{measured})$, using the least-squares method for age, T . A and B are constants. Subsequently, we calculated 5-year mean ring-thickness indices.

RESULTS AND DISCUSSION

$\delta^{13}\text{C}$ variations in annual growth rings of Japanese cedar

Figure 1 show the variations of $\delta^{13}\text{C}$ and 5-year mean RI values of the two Japanese cedars. The two records show constant $\delta^{13}\text{C}$ values until about 1870 and a steady downward trend thereafter, with pronounced short-term fluctuations superimposed on the trend.

The overall $\delta^{13}\text{C}$ fall for the two Japanese cedars from 1870 to the present are consistent, amounting to 1.2–1.4‰. One of the remarkable

Fig. 1. $\delta^{13}\text{C}$ values and ring-thickness indices in annual growth rings of two Japanese cedars from Yakushima Island, southern Japan. Open and solid squares indicate data from YKR-1 and YKR-2, respectively.

features of the short-term fluctuations superimposed on the trend is that RI fluctuations frequently appear synchronously (Fig. 1). Such consistent behavior between $\delta^{13}\text{C}$ and RI values has also been reported by Leavitt and Long (1986) and Stuiver *et al.* (1986).

RI values are influenced by climatic changes (temperature, humidity, light intensity and etc.), as described by Fritts (1976), and it is likely that fractionation of carbon isotopes between atmosphere and tree cellulose fluctuates are influenced by climatic changes.

The relationship between $\delta^{13}\text{C}$ and RI values

may be seen in the C_3 -plant carbon isotope fractionation model of Francey and Farquhar (1982):

$$\delta^{13}\text{C} = \delta^{13}\text{C}_a - a - (b - a) \cdot C_i / C_a \quad (3)$$

and

$$C_i = C_a - A / g. \quad (4)$$

The $\delta^{13}\text{C}_a$ refers to atmospheric CO_2 and a and b are constants. The CO_2 concentration of the atmosphere and the plant interior, C_a and C_i , respectively, are related by the rate of assimilation, A , and the CO_2 conductance of the boundary layer and stomata pores to the diffusion of

Fig. 2. Relationships between $\delta^{13}\text{C}$ and ring-thickness indices of Japanese cedars from Yakushima Island (a: YKR-1, b: YKR-2). Open and solid squares indicate pre-1870 yr. and post-1870 yr., respectively. Solid lines show the regression lines for the data of pre-1870 yr.

CO_2 , g.

With this model, the positive $\delta^{13}\text{C}$ deviations above the long-term trend imply that the assimilation (A) is high and/or conductance (g) is low. This positive $\delta^{13}\text{C}$ deviations occur in those years when the RI values are relatively large. Therefore, the high assimilation may be more important than the stomata conductance. In Yakushima Island, with high precipitation in the area, stomata may not close frequently as would happen if there were water stress.

Figure 2 shows the relationships between $\delta^{13}\text{C}$ and RI values of each tree. Correlations between $\delta^{13}\text{C}$ and RI values are found for the two trees prior to 1870 (YKR-1, $r=0.45$ and $p<0.05$; YKR-2, $r=0.62$ and $p<0.1$). Short-term fluctuations in the $\delta^{13}\text{C}$ records of trees appear to be related to the RI change.

$\delta^{13}\text{C}$ variation in atmospheric CO_2

The correlations between $\delta^{13}\text{C}$ and RI were used to "correct" each $\delta^{13}\text{C}$ record for environmental influences responsible for high-frequency fluctuation because long-term meteorological records are not available in Yakushima Island. The records for Japanese cedars, corrected by the $\delta^{13}\text{C}$ -RI relation before 1870 and normalized as differences from the respective 1810–1870 means, are shown in Fig. 3a. The

$\delta^{13}\text{C}$ records are flat prior to about 1870 and decrease thereafter. The overall drop of $\delta^{13}\text{C}$ records from 1870 to 1990 is about 1.2–1.4‰, which is consistent with the uncorrected records.

Freyer (1986) and Freyer and Balacey (1983) have compiled $\delta^{13}\text{C}$ data for about 60 trees, collected mainly in Europe and the eastern United States. These trees show a $\delta^{13}\text{C}$ fall of 1.5–2.0‰ from 1850 to 1980, which is larger than that in this study, and also slightly elevated values occurred at about 1950. Unfortunately, 70% of their trees are from regions having large contributions from acid rain and air pollution. Increased soil acidity by acid rain (Van Breemen *et al.*, 1982) and gaseous pollutants (Freyer, 1979b) can potentially cause a lowering of $\delta^{13}\text{C}$ of tree. Stuiver *et al.* (1984) have presented $\delta^{13}\text{C}$ records from the Pacific coast of the U.S.A. which have been normalized to ring-area variability, with a $\delta^{13}\text{C}$ drop from pre-1850 to 1980 of about 1‰. This is somewhat smaller than that of the trees presented in this study. Their records show slightly elevated $\delta^{13}\text{C}$ values at 1950, 1900, and 1600. Leavitt and Long (1989) have presented an overall fall of $\delta^{13}\text{C}$ by 1.2–1.4‰ from 1600 to the present for southwestern U.S.A. trees. This is consistent with the data presented here. There are the slightly elevated $\delta^{13}\text{C}$ values at 1950 and 1900 in their record. Finally, the $\delta^{13}\text{C}$ records

Fig. 3. $\delta^{13}\text{C}$ records of atmospheric CO_2 during the past ca., 200 years estimated, from (a) $\delta^{13}\text{C}$ change of two Japanese cedars from Yakushima Island (YKR-1, open squares; YKR-2, solid square; average value, solid line) and (b) $\delta^{13}\text{C}$ change of CO_2 from ice-core bubbles (open square) by Friedli *et al.*, (1984) and the direct measurements of atmospheric CO_2 (cross) by Keeling *et al.*, (1979, 1980).

presented here can be compared directly to the results of Friedli *et al.* (1986) who estimate an overall decrease of $1.14 \pm 0.15\text{‰}$ for the period of 1800 to 1980 based on measurements on CO_2 from ice-core bubbles, and also to the direct measurements on atmospheric CO_2 (Keeling *et al.*, 1979, 1980). Their trend is quite similar to the $\delta^{13}\text{C}$ records of our trees. Both records show a decreasing $\delta^{13}\text{C}$ trend of atmospheric CO_2 from the nineteenth century with the greatest portion of the drop from the late twentieth century onward.

It is interesting that slightly elevated values of $\delta^{13}\text{C}$ in trees are observed in Yakushima Island, Europe, and in the U.S.A. in the same periods 1900–1910 and 1950–1960. The CO_2 from ice-core bubbles may show changes with a time resolution of perhaps decade or so because the circulation of air takes place through firn until the bubble is isolated (Friedli *et al.*, 1986). Therefore, short-term fluctuations of atmospheric CO_2 are averaged and cannot be detected in ice-core records. If the maxima at 1900–1910 and 1950–1960 are due to real atmospheric changes, then these were sufficiently

pronounced to influence the biospheric carbon reservoir. Oeschger and Stauffer (1986) and Pearman *et al.* (1986) have suggested that short-time fluctuations on decadal time scales may exist as related to 'El Niño' or other environmental influences. The carbon cycle model by Stuiver *et al.* (1984) suggested that a fluctuation of 1‰ in the $\delta^{13}\text{C}$ values translates to a change in atmospheric concentration of ca., 40–50 ppm. The large positive shifts of about 0.5‰ found in our tree records (Fig. 3) may be unrealistic for global atmospheric change on short-time scale. It is, at the moment, not clear whether the short-term fluctuations are caused by some environmental effects which can not be explained by our $\delta^{13}\text{C}$ -RI relation, or local changes of atmospheric CO_2 and $\delta^{13}\text{C}$ of CO_2 related to some recycling of biospheric CO_2 in surrounding environments.

SUMMARY AND CONCLUSIONS

The $\delta^{13}\text{C}$ records of two Japanese cedars from Yakushima Island have been presented. The $\delta^{13}\text{C}$ records have been corrected for possible climate changes based on the RI variability. The

corrected records show a flat trend until 1870 and thereafter a steady downward trend. There are pronounced short-term fluctuations superimposed upon the general trends. The overall $\delta^{13}\text{C}$ fall in the Japanese cedars from the preindustrial time, 1850, to the present is about 1.2–1.4‰, consistent with the measurements of CO_2 from ice-core bubbles (Friedli *et al.*, 1986) and the direct measurements atmospheric CO_2 (Keeling *et al.*, 1979, 1980). This indicates the $\delta^{13}\text{C}$ decrease of global atmospheric CO_2 due to the increasing atmospheric CO_2 concentration in response to the input of fossil-fuel and biospheric carbon. A definite but small elevation of $\delta^{13}\text{C}$ values is noted at ca. 1950 in a wide area of the world including eastern Asia, Europe, and the U.S.A. However, it is not clear at present whether the short-term fluctuations are caused by some large climate effects or by local changes of atmospheric CO_2 and $\delta^{13}\text{C}$ of CO_2 .

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