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GEOCHEMICAL DETERMINATION OF BIOSPHERIC CO₂ FLUXES TO THE ATMOSPHERE

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The objective of this research is to increase our knowledge of past biospheric carbon reservoir changes that have resulted in increases, or reductions, of atmospheric CO_2 levels. This research program started in mid-1979 and investigates various aspects of the carbon cycle through the use of $^{13}\text{C}/^{12}\text{C}$ and $^{14}\text{C}/^{12}\text{C}$ abundance ratios.

Past atmospheric carbon isotope ratio changes are recorded in trees because carbon, derived from atmospheric CO_2 through photosynthesis, is incorporated into their cells. The cell wall cellulose, formed each year during the growing season, has a $^{14}\text{C}/^{12}\text{C}$ and $^{13}\text{C}/^{12}\text{C}$ ratio that reflects the ratios of the atmospheric CO_2 of that year. These ratios are not entirely identical to the atmospheric ratios because during photosynthesis the tree discriminates systematically against the heavier ^{13}C and ^{14}C isotopes. Such discrimination depends on environmental factors, and as a result changes in humidity, precipitation, nutrients, light intensity and temperature may cause the tree to record changes in the above isotope ratios.

When studying $^{14}\text{C}/^{12}\text{C}$ isotope ratio changes in tree-rings, it is possible to account for the changes in tree isotope discrimination by normalizing on a fixed $^{13}\text{C}/^{12}\text{C}$ ratio ($\delta^{13}\text{C} = -25$ per mil). One therefore can obtain a $^{14}\text{C}/^{12}\text{C}$ record that is independent of changes in isotope discrimination of the tree. However, in order to obtain a proper $^{13}\text{C}/^{12}\text{C}$ record that is independent of these changes one has to understand the mechanisms that induce the $^{13}\text{C}/^{12}\text{C}$ variability. Studies of tree-ring $^{13}\text{C}/^{12}\text{C}$ records are therefore much more difficult than $^{14}\text{C}/^{12}\text{C}$ tree-ring studies, and they have so far been less successful.

During the current contract year we determined ^{13}C trends in trees from Kodiak Island, Alaska and from Chile. We also are very much interested in long-term ^{13}C trends in Bristlecone Pine from the White Mountains, Nevada. Dr. Ferguson of the University of Arizona has promised delivery of these samples for April 1981. Immediately upon receipt of these samples we will concentrate our work on the Bristlecone Pine ^{13}C record.

A major contribution in the understanding of the global transfer of carbon between the various earth reservoirs are made in a DOE supported paper entitled "Atmospheric ^{14}C changes resulting from fossil fuel CO_2 release and cosmic ray flux variability". This paper is in press in the Journal Earth and Planetary Sciences Letters. It contains a ^{14}C record of the 19th and first half of the 20th century of circa 110 single year ^{14}C tree-ring determinations with a precision of 2 per mil or better. This high-precision record is of critical importance in understanding the fate of fossil fuel produced carbon dioxide. The record is used to test carbon reservoir models that describe quantitatively the past and future fate of fossil fuel-produced carbon dioxide. The models take into account both fossil fuel CO_2 release and the natural modulation of the cosmic ray flux responsible for the atmospheric ^{14}C production. The best reproduction of the observed data is obtained for a box-diffusion model with an oceanic eddy diffusion coefficient of $3 \text{ cm}^2/\text{sec}$, a CO_2 atmosphere ocean gas exchange rate of $21 \text{ moles/m}^2 \text{ yr}$ and biospheric residence time of 60 years. Having established these optimal model parameters (see attached pre-print), the model is used for the calculation of ^{13}C changes caused by fossil fuel and biospheric CO_2 releases.

Tree-ring ^{13}C records show more variability than expected from atmospheric ^{13}C changes alone. Such variability can be introduced by external changes in microenvironment outside the tree (recycling of biospheric CO_2 that is labelled with less ^{13}C than atmospheric CO_2), or by internal changes in isotope fractionation ("isotope discrimination") of the tree that are related to environmental factors such as light intensity, humidity, growth rates, temperature, etc. Farquhar recently developed a theory relating the tree's isotope fractionation to the leaf's internal CO_2 pressure. His approximate equation relates the isotope ratio ($\delta^{13}\text{C}$) to the ratio of the leaf CO_2 pressure (C_i) and the atmospheric CO_2 pressure (C_a) according to

$$\delta^{13}\text{C} = 11.1 - 27.6 C_i/C_a$$

There is also the relationship

$$C_i = C_a - A/g$$

where A is the rate of assimilation and g the leaf conductance.

According to Farquhar, C_i decreases at low irradiance, which could explain the higher $\delta^{13}\text{C}$ levels often encountered in the early stages of tree-growth (so-called juvenile effect). Here one would assume improved light conditions with age. In many cases C_i also increases when CO_2 assimilation rates are drastically reduced. Thus the $\delta^{13}\text{C}$ values would generally be most negative when the conditions of growth are optimal.

When CO_2 assimilation is reduced by reducing stomatal conductance, and hence C_i , the $\delta^{13}\text{C}$ values will also increase. Thus during low humidity conditions $\delta^{13}\text{C}$ values are less negative (all according to Farquhar's model).

The above treatment of tree isotope fractionation shows the importance of monitoring changes in environmental parameters such as temperature and humidity. In the absence of measurements from nearby weather stations, one

can use oxygen isotope ratios of the tree cellulose in deriving temperature and humidity data. This method was explored by R. L. Burk in our laboratory, and is discussed in the attached Science pre-print. The oxygen isotope work shows that leaf water and cellulose oxygen isotope ratios are strongly influenced by humidity. We therefore use this method in deciphering possible causes of pronounced short-term ^{13}C changes in tree-rings.

^{13}C records were obtained for trees from Kodiak Island, Alaska and from Southern Chile.

1. Kodiak Island $\delta^{13}\text{C}$ record.

The Sitka spruce tree (*Picea sitchensis*) used for our studies was collected at Shakmanof Cove (57.91°N, 152.6°W) on Kodiak Island, Alaska in 1979. The 75-ft tall tree was surrounded by dense underbrush up to approximately 10 feet in height. The area is very sparsely forested and there was no canopy development around the sample tree. Commercial tree cutting did not take place in the surrounding region. Soils consisted primarily of weathered volcanic ash over bedrock. The tree was cut at the head of a North-South oriented bay and was somewhat protected from storm activity. Average growing season weather condition parameters are: windspeed 3.7m/sec, temperature 10.2°C, rainfall 11.4 cm/month and relative humidity (average of morning and afternoon values) 77.9%.

The $\delta^{13}\text{C}$ time-pattern in this tree was studied in detail by determining the $\delta^{13}\text{C}$ values of about 400 samples. Four radii were chosen, each 90 degrees apart. The demonstrated variability within a single tree-ring is considerable (see figure 1), and amounts to 2 per mil in extreme cases (e.g. the year 1970). However, the tree $\delta^{13}\text{C}$ record also shows systematic

differences between the radii. Once the tree produces higher $\delta^{13}\text{C}$ ratios for a certain side, it has a tendency to keep these higher ratios during the rest of its life (in this instance circa 100 years).

The systematic differences can be removed by normalizing the $\delta^{13}\text{C}$ averages of each radius on a fixed $\delta^{13}\text{C}$ value (-25 per mil). The resulting curves show less internal variability between the four radii (figure 2).

A possible "juvenile" effect is indicated by the $\delta^{13}\text{C}$ increase of about 2 per mil between 1876 and 1886 (figure 1). The duration of this effect is fairly short; for our Douglas firs in the state of Washington, the "juvenile" stage often lasts a century or longer. The difference may relate to factors causing differences in isotope discrimination during early growth. For instance, it is possible that the young Douglas firs received reduced light intensity over a much longer interval than the spruce tree. An alternative explanation would be differences in biospheric CO_2 recycling. Perhaps the Douglas firs were utilizing a mixture of air CO_2 and biospheric CO_2 over a longer interval before reaching canopy height.

Because the tree's isotope fractionation may change with changes in environmental conditions, we investigated correlations between the $\delta^{13}\text{C}$ changes and tree-ring thickness, tree-ring density and temperature. Humidity records are presently being examined.

The average ring-widths of the Kodiak spruce are plotted in figure 3. The ring-widths show the general pattern of change related to the aging of the tree, with narrower rings towards the present (from ca 5.2 mm in 1900 to ca 4.2 mm near 1970). Because the $\delta^{13}\text{C}$ values tend to be more negative towards the present, a relationship exists between ring-width r and δ value:

$$\delta = 0.217r - 25.5 \text{ per mil}$$

This relationship ($r = 0.354$) is given in figure 4. This correlation is significant at the 1 part in a thousand level.

No significant correlation is found between $\delta^{13}\text{C}$ values and May-August growing season temperatures (figure 5) and between $\delta^{13}\text{C}$ values and precipitation for the same months (figure 6).

The average $\delta^{13}\text{C}$ values for each ring of the Kodiak tree, and a ten year moving average, are given in figure 7. The ten year moving average is used to identify the main trend in the $\delta^{13}\text{C}$ record. Year to year ring thickness changes around the main trend (figure 3) may possibly relate to year-to-year changes in $\delta^{13}\text{C}$ values around the main trend of figure 7. When correlating the annual deviations around the main trends (defined as a 9 year moving average), we do find a correlation at the 2 percent significance level (figure 8). Thus the changes in environmental conditions, such as water-stress and winter severity, that influence ring-thickness also appear to somewhat influence the ^{13}C ratios. For deviations from the main trend of respectively $\Delta\delta$ and Δr , the relationship is

$$\Delta\delta = 0.096 \Delta r + 0.10 \text{ per mil}$$

For a change in average thickness of 1 mm, the corresponding change in ^{13}C value would be only 0.09% per mil. Thus, if we would assume that the long term trend in ring-widths from 5.2 to 4.2 mm is caused by long-term changes in environmental conditions comparable to the changes experienced on a shorter time scale, only 0.1 per mil of the 2 per mil long-term trend in ^{13}C could be explained in this manner.

The above analysis eliminates external environmental changes that result in ring thickness changes as a principal contributor to the long-term ^{13}C change in the Kodiak tree. It is still possible, however, that during the aging of the tree the internal ^{13}C isotope fractionation changes. For instance, it is conceivable that the radiative, and stomatal, distribution in the tree crown changes with age. Such a change in distribution would result in a change in average $\delta^{13}\text{C}$ values that is not necessarily related to variability in environmental parameters such as nutrient availability, temperature and water stress.

One variable that appears to be age dependent is ring density. Maximum and minimum and average ring density was measured for one radius (radius C) of the Kodiak tree. The ring widths along this radius do not change very much with the aging of the tree (the previous discussion of ring-widths was for the average of the 4 radii), and as a consequence there is no significant correlation for radius C between ring-width and ^{13}C ratios (figures 9 and 10). There is also no significant correlation between radius C $\delta^{13}\text{C}$ values and average ring density, or minimum density (figures 11 and 12). Yet we do see an excellent correlation between $\delta^{13}\text{C}$ and maximum density d_m at the better than 1 part in 10,000 significance level (figure 13):

$$\delta = 5.26d_m - 27.70 \quad (r = 0.479)$$

The data analysis given above identified two parameters, ring thickness and maximum density, that co-vary with the $\delta^{13}\text{C}$ values. A direct comparison of the 10 year moving averages of these quantities is given in figures 14 and 15.

The latewood in a tree-ring contains the wood with maximum density. The width of the latewood ring r_{lw} correlates with the $\delta^{13}C$ values of the C radius at the 5% significance level (figure 16).

A comparison of the 10 year moving averages of the latewood thickness and ^{13}C ratios of the C radius is given in figure 17.

The average latewood thicknesses of the four radii do not correlate significantly with the average $\delta^{13}C$ values (figure 18).

Although the Kodiak tree's $\delta^{13}C$ record follows the overall trend in isotope ratio change derived by other researchers from northern hemispheric trees, there is the distinct possibility that aging of the tree, with its corresponding change in latewood density and latewood thickness, causes part of the $\delta^{13}C$ change. Additional analyses of the Kodiak tree are therefore, oriented towards the latewood and earlywood ^{13}C distribution in individual rings.

2. Southern Chile $\delta^{13}C$ record.

Two Nothofagus pumillio trees were cut in 1980 in Chile at (a) the Torres del Paine National Park (51.2°S, 72.6°W) and (b) Rio Grande (53.95°S, 69.05°W) on Tierra del Fuego. The Torres del Paine Tree was growing in a very sparsely forested area without significant canopy development. Winds in this area are reported to be strong much of the year. Average growing season weather conditions for nearby Punta Arenas are: wind speed 4.8 m/sec, temperature 9.9°C, rainfall 2.6 cm/month and relative humidity 63% (average of 9.00h, 14.00h and 19.00h values).

The Tierra del Fuego tree was growing at the edge of grasslands in a transition zone towards more forested conditions. There was some minor canopy development. Winds in this area are strong year-round and penetrated

the site of the tree. The average growing season weather for nearby Punta Arenas is given above.

Four radii of the Paine tree were measured for ^{13}C content. The detailed analyses of 350 samples are given in figure 19. The internal variability within the single year rings again can be reduced by matching the average tree-ring values for each radii. The resulting internal variability, after normalization, is given in figure 20.

Average $\delta^{13}\text{C}$ values of each tree-ring, and a ten year moving average, are given in figure 21. The observed long-term trend in this tree differs significantly from that of the Kodiak tree. Instead of a reduction in ^{13}C content towards the present, the Paine tree exhibits a more or less constant level.

The observed $\delta^{13}\text{C}$ values correlate with external climatic variables to a limited extent only. October-March temperatures correlate with $\delta^{13}\text{C}$ at the 10 percent significance level over the 1919-1950 interval (figure 22a), but these parameters do not correlate significantly when the 1950-1980 interval is included (figure 22b). October-March precipitation and humidity does not correlate significantly with the $\delta^{13}\text{C}$ values (figures 23 and 24).

The Paine Nothofagus tree does not show a juvenile stage with drastically different $\delta^{13}\text{C}$ ratios. On the other hand, the Rio Grande Nothofagus shows a very large $\delta^{13}\text{C}$ change during its first 40 years of growth (figure 25). The atmospheric ^{13}C levels would have to change a full 5 per mil between ground surface level and canopy height, if responsible for this effect. It appears unlikely that such a large ^{13}C gradient exists for the present-day forest configuration and for the high average windspeeds. We are therefore currently exploring possible growth effects of the tree

through density analyses. Of course another possible explanation could be a drastic reduction in forested area (through fire) in the late part of the century. Tierra del Fuego is known to have a long history of frequent major fires.

3. Atmospheric $\delta^{13}\text{C}$ measurements.

The addition of biospheric CO_2 to atmospheric CO_2 of marine air was investigated by comparing $\delta^{13}\text{C}$ values of air collected from the coast and nearby forested areas. The collection site was near La Push, Washington (47.9°N , 124.6°W). Samples were taken in 5 liter glass bulbs both on the beach and within the nearby forest canopy.

Air samples were taken on two different mornings at one hour intervals from before sunrise until approximately 3 hours after sunrise (figures 26 and 27). Samples from beneath the forest canopy have consistently more negative values than samples taken at the beach locality.

The canopy where the samples shown in figure 26 were taken is not very dense and is approximately 75 meters from the mean higher high water line (MHHWL). Although consistently lower in $\delta^{13}\text{C}$ the inland $\delta^{13}\text{C}$ values track the beach values very closely.

Samples taken beneath the canopy and shown in figure 27 are from a very dense canopy approximately 300 meters from the MHHWL. The beach samples used for figures 26 and 27 were all taken at the same location. The long-term measurements at the beach (figure 28) show a gradual increase in $\delta^{13}\text{C}$ values towards the end of the growing season.

The latewood $\delta^{13}\text{C}$ ratios of nearby Spruce trees are usually more negative than other portions of the ring which suggest that other factors than seasonal atmospheric ^{13}C values control the wood ^{13}C composition.

The $\delta^{13}\text{C}$ values for portions of two Sitka spruce tree-rings are as shown below:

1977 ring, from start of earlywood to latewood: -24.70, -25.78,
-25.66, -25.83 and -27.48 (latewood).

Also the 1978 ring: -25.58, -26.22, -26.46, -25.94 and -27.02 (latewood).

The above observations indicate a biospheric $\delta^{13}\text{C}$ component of about 0.5 per mil in the atmospheric CO_2 of a lightly forested area 75 meters from the coast, and up to 2 per mil for the dense forest 300 meters from the coast. Any change in this contribution will influence the $\delta^{13}\text{C}$ record of a tree.

4. Carbon reservoir modeling results.

A carbon reservoir model was used to estimate the effects of the fossil fuel CO_2 release and a possible biospheric source of CO_2 on the atmosphere CO_2 and $\delta^{13}\text{C}$ levels. A box-diffusion model similar to that developed by Oeschger et al was used to predict the time history of the $\delta^{13}\text{C}$ of atmospheric CO_2 for four different scenarios of biospheric input of CO_2 . The model exchange parameters have been determined by comparing model calculations to two fundamental sets of measurements: (1) the atmospheric dilution of ^{14}C between 1860 and 1952 and (2) the atmospheric increase of CO_2 since 1959 as determined by Keeling. As discussed in the accompanying paper, we have obtained an optimal fit of both of the above observations, when a CO_2 gas exchange rate of $21 \text{ moles m}^{-2} \text{ yr}^{-1}$ and an oceanic vertical diffusion rate of $3 \text{ cm}^2 \text{ sec}^{-1}$ are used in the model.

The time history of $\delta^{13}\text{C}$ of atmospheric CO_2 was calculated using the model with the above exchange parameters, zero biospheric growth rate and ^{13}C fractionation factors during air-sea CO_2 exchange as determined by Siegenthaler and Munnich (in press). The four scenarios examined are described as follows:

A) fossil fuel CO₂ release only, B) a biospheric release always equal to 50% of the fossil fuel CO₂ release, C) a biospheric release of 120 Gigatons with a Gaussian distribution centered at 1890 and D) a biospheric release of 170 Gigatons with a Gaussian distribution centered at 1945.

The changes in the atmospheric CO₂ levels and the $\delta^{13}\text{C}$ of the atmospheric CO₂ for these scenarios are presented in figures 29 and 30, respectively.

Our modeling results indicate a possible decrease in $\delta^{13}\text{C}$ from 1860 to 1975 between 0.75 and 1.28‰. The 1.28‰ decrease calculated for Case D is forced to use a pre-industrial CO₂ level of 260 ppm, significantly lower than has been suggested by Keeling's review of the literature.

Also for Case C, the atmospheric CO₂ level between 1958 and 1975 is lower than the measurements; for the other three scenarios the model calculated CO₂ levels agree within 1 ppm of the measured concentrations.

The 1900 to 1974 $\delta^{13}\text{C}$ decrease measured for the Kodiak tree is ~2 per mil (figure 7). A change of similar magnitude is also suggested by the work of Freyer. However, a $\delta^{13}\text{C}$ change of this magnitude is difficult to obtain from the box diffusion model, without assuming extremely low pre-industrial CO₂ levels. This suggests that part of the measured $\delta^{13}\text{C}$ decrease in the Kodiak trees relates to internal variability in isotope fractionation during the life of the tree. The factors causing this variability must be determined before a reliable atmospheric $\delta^{13}\text{C}$ time history can be deciphered from the $\delta^{13}\text{C}$ record preserved in trees.

KODIAK: 4 RADII

FIG. 1

KODIAK: NORMALIZED 4 RADII

FIG. 2

KODIAK 4 RADII

FIG. 3

KODIAK 4 RADII

FIG. 4

KODIAK 4 RADII

FIG. 5

KODIAK 4 RADII

FIG. 6

KODIAK 4 RADII

FIG. 7

KODIAK 4 RADII

KODIAK 2C

FIG. 9

KODIAK 2C

FIG. 10

KODIAK 2C

FIG. 11

KODIAK 2C

FIG. 12

KODIAK 2C

KODIAK 4 RADII

FIG. 14

KODIAK 2C

FIG. 15

KODIAK 2C

FIG. 16

KODIAK 4 RADII

FIG. 17

KODIAK 4 RADII

FIG. 18

PAINE: 4 RADII

FIG. 19

PAINE: NORMALIZED 4 RADII

FIG. 20

PAINE: AVG 4 RADII & MOV AVG

FIG. 21

1919 - 1950 only

OCT - MAR T

FIG. 22a

PAINE

FIG. 22^b

PAINE

FIG. 23

TORRES DEL PAINE

FIG. 24

RIO GRANDE, TIERRA DEL FUEGO

FIG. 25

KEY

- Rialto Beach
- x Rialto Canopy

WIND SPEED

time	knots
4:00am	0
7:00am	0
10:00am	3

FIG. 26

KEY

- o Rialto Beach
- x Underneath Canopy near Mora

WIND SPEED

time	knots
4:00am	0
7:00am	6
10:00am	8

FIG. 27

FIG. 28

FIG. 30

ATMOSPHERIC ^{14}C CHANGES RESULTING FROM FOSSIL FUEL CO_2 RELEASE

and

COSMIC RAY FLUX VARIABILITY

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EARTH and PLANETARY SCIENCE LETTERS - in press

ABSTRACT

A high precision tree-ring record of the atmospheric ^{14}C levels between 1820 and 1954 is presented. Good agreement is obtained between measured and model calculated 19th and 20th century atmospheric $\Delta^{14}\text{C}$ levels when both fossil fuel CO_2 release and predicted natural variations in ^{14}C production are taken into account. The best fit is obtained by using a box-diffusion model with an oceanic eddy diffusion coefficient of $3 \text{ cm}^2/\text{sec}$, a CO_2 atmosphere-ocean gas exchange rate of $21 \text{ moles/m}^2 \text{ yr}$ and biospheric residence time of 60 yrs.

For trees in the state of Washington the measured 1949 -1951 atmospheric $\Delta^{14}\text{C}$ level was 20.0 ± 1.2 per mil below the 1855 - 1864 level. Model calculations indicate that in 1950 industrial CO_2 emissions are responsible for at least 85% of the $\Delta^{14}\text{C}$ decline, whereas natural variability accounts for the remaining 15%.

1. INTRODUCTION.

In recent years, carbon reservoir models have been used to describe quantitatively the past and future fate of fossil fuel-produced carbon dioxide. The ultimate test of models of the global carbon cycle is the reproduction of observed data. One critical set of observations is derived from the atmospheric ^{14}C change related to the release of ^{14}C -free fossil fuel CO_2 . We measured, with high precision, tree ring ^{14}C levels that record the ^{14}C content of Pacific marine air CO_2 between AD 1820 and 1954. We tried to reproduce the time change in $\Delta^{14}\text{C}$ observed in these data using a carbon exchange box-diffusion model that attempts to take the natural atmospheric ^{14}C production rate variability into account.

The first measurements of 19th and 20th century anthropogenic atmospheric ^{14}C dilution were made by Suess (1), who compared the ^{14}C levels of mid-nineteenth century wood with those of the mid-twentieth century. After correction for ^{14}C decay in the older wood he concluded that the mid-twentieth century reduction in atmospheric ^{14}C level was probably less than 1 percent. Later measurements have increased this estimate to the 2.3 to 3.0 percent range (2-6). The reduction in atmospheric ^{14}C level can only be followed to 1952 because nuclear bomb produced ^{14}C was added subsequently. The reduction of ^{14}C levels between the mid-nineteenth and twentieth century has been named the Suess effect, and has been attributed to the atmospheric release of anthropogenic-produced CO_2 lacking ^{14}C . However, during this time interval the atmospheric levels of ^{14}C would have varied even without the influence of man. Atmospheric levels of ^{14}C measured over the last millennium vary several percent (7).

The cosmic ray induced ^{14}C production rates (Q) are influenced by the sun's modulation of magnetic properties of the solar wind, and by changes in earth geomagnetic field intensity. In the following discussion, we attempt to quantify the natural variation of Q during the 1850-1950 interval and calculate the relative effect that fossil fuel and natural variation in Q have on the atmospheric ^{14}C records. Previous calculations (8, 9) also attempted to account for the natural variability in Q when discussing fossil fuel dilution of the atmospheric ^{14}C levels. The present calculations use a new interpretation of cosmic ray flux modulation that yields a larger natural Q variability (7). The high precision ^{14}C data also allow a search for ^{14}C change in the per mil range.

The incorporation of natural ^{14}C variability in carbon reservoir modeling is required to obtain a more accurate understanding of the atmospheric ^{14}C dilution due to fossil fuel produced CO_2 .

2. SITE AND CHEMICAL TREATMENT.

Important for the determination of a global 1860-1950 atmospheric $\Delta^{14}\text{C}$ change is the selection of the trees and the chemical treatment of the wood. Regional ^{14}C depression exceeding the global average in industrial areas is a possible complication. Also the "feedback" of nuclear bomb ^{14}C in mobile compounds to earlier formed rings may interfere with the assumption that each ring accurately records the atmospheric ^{14}C level of the year of its formation.

Wood of two Douglas Firs from the Olympic Peninsula ($47^\circ 46'\text{N}$, $124^\circ 06'\text{W}$) was used for this study. The site is 15 miles from the ocean, and predominant onshore winds bring in air that has been transported over the Pacific

Ocean. Tree A grew from 1815 to 1972, whereas tree C grew from 1914 to 1975. The heartwood-sapwood boundaries of trees A and C were, respectively near the 1930 and 1957 rings. At the start of nuclear bomb testing, the heartwood-sapwood boundaries are estimated to have been near 1895 for the A tree, and near 1939 for the C tree. In both cases we assume a constant sapwood thickness when estimating this earlier heartwood-sapwood boundary.

Alpha cellulose was extracted from the wood of the C tree. Wood samples of the A tree were all treated at 60°C with 2 percent NaOH and HCl solutions to remove resins, sugars, and a portion of the lignin (the so-called De Vries method). This treatment may not remove all components that were added after the year of growth (10). The influence of incomplete removal of these late additions on the ^{14}C ratio was studied by comparing the ^{14}C activities of wood treated by the De Vries method with the ^{14}C activities of alpha cellulose derived from the same wood. The largest differences in ^{14}C activity of sample pairs were found in rings that were transformed into heartwood after 1952 when nuclear bomb ^{14}C was added to the atmosphere. Here the "De Vries" wood of four sample pairs of the C tree (1942, 1945, 1948 and 1951) was an average of 3.8 ± 1.4 % higher in ^{14}C activity. Similarly, De Vries wood of the A tree of the years 1918 to 1930 was an average of 6.3 ± 0.8 % higher in ^{14}C activity than alpha cellulose from the C tree. Clearly the De Vries method does not remove all material incorporated during the later stage of heartwood formation. However, an increase of about 50 percent in atmospheric ^{14}C level due to bomb testing during heartwood formation resulted in a hundred times smaller ^{14}C contamination of De Vries treated wood. Pre-bomb variations in ^{14}C level are

in the percent range only, and the calculated contamination is a few tenths of a per mil. This agrees with the measurements of 8 sample pairs of the C tree (1918, 1921, 1924, 1927, 1930, 1933, 1936, and 1939), for which De Vries treated wood on average differs only 0.7 ± 0.8 per mil in ^{14}C activity from alpha cellulose. The ^{14}C level of De Vries treated wood of the A tree formed prior to 1895 should therefore represent the actual atmospheric ^{14}C level.

As part of our alpha cellulose preparation, we remove extractives in petroleum ether. The extractives and the cellulose of pre-1939 rings of the C tree have about identical ^{14}C activities. Much higher ^{14}C levels are encountered in the extractives of the rings that were transformed to heartwood in our nuclear age (figure 1). For instance, the cellulose of the 1948 ring of the C tree has a $\Delta^{14}\text{C}$ activity of about -2 percent, but mobile compounds that were incorporated later in the heartwood of the rings have a $\Delta^{14}\text{C}$ activity of +44 percent. The amount of carbon derived from the extractives was about 1/10th of the cellulose carbon, and thus the 4‰ higher ^{14}C level of 1948 De Vries treated wood can be attributed to a removal of extractives that is only about 90 percent complete.

3. MEASUREMENTS.

Tree ring $\Delta^{14}\text{C}$ levels (the relative deviation in ^{14}C activity from the NBS oxalic acid standard after correction for decay and isotope fractionation (11)) are given in table 1 and figure 2 for the 1820-1954 interval. The lack of sufficient wood of the A tree required a combination of some rings for the 1890 to 1915 interval. The $\Delta^{14}\text{C}$ values of De Vries

treated wood of the A tree reported between 1895 and 1915 may also be a few per mil too high due to the previously discussed "feedback" of nuclear bomb ^{14}C . These years will be remeasured.

The twentieth century reduction in atmospheric ^{14}C level reported here is less than the change reported by Tans et al. (6) for trees from the Netherlands. The difference between those measurements and our three-year moving average is plotted in figure 3. Tans et al., used wood from three trees, of which only one yields a couple of 20th century $\Delta^{14}\text{C}$ values that agree with our data. The other two trees (triangle and plus signs in figure 3) have an increasing divergence with the Pacific Northwest data towards the present. This trend could be explained by a regional fossil fuel CO_2 contamination of the Dutch trees, resulting in more depleted values.

4. NATURAL ATMOSPHERIC ^{14}C VARIABILITY

Our measurements of the atmospheric ^{14}C levels during the last 1000 years indicate that the carbon reservoirs are not in steady state equilibrium with respect to atmospheric ^{14}C levels. The response of such a dynamic system to a fossil fuel CO_2 pulse depends on the point in time when such a perturbation is imposed. The 19th and 20th century atmospheric ^{14}C dilution is therefore uniquely tied to the natural ^{14}C levels of these centuries. Furthermore, the calculated ^{14}C dilution in a dynamic model would not be identical in size to the dilution calculated from models where the fossil fuel CO_2 pulse is superimposed on steady state conditions.

The ^{14}C record of the current millennium clearly shows that the $\Delta^{14}\text{C}$ values observed in the mid-twentieth century are not exceptionally low

(lower curve in fig. 4) when compared to the ^{14}C activities encountered in the 12th and 13th centuries. This similarity in $\Delta^{14}\text{C}$ levels is most likely the result of a long-term increase in ^{14}C production rates that relates to the decrease in the earth's geomagnetic field intensity (12).

If we approximate the long-term $\Delta^{14}\text{C}$ trend (attributed to geomagnetic field intensity changes over the past several thousand years) by a sinusoidal curve (13), and remove this trend from the observed record, the twentieth century "geomagnetically" corrected $\Delta^{14}\text{C}$ levels now fall below the pre-1900 natural levels (upper curve in figure 4). This at least agrees with the concept of an anthropogenic dilution of the atmospheric ^{14}C reservoir.

On a shorter time scale the fine structure in the annual ^{14}C levels may be related to 11 and 22 year solar cycle modulation of the cosmic ray flux. However, our annual record (figure 2) indicates a magnitude of such ^{14}C variability not much beyond the uncertainty of the measurements (circa 1.5 ‰). This contrasts with the earlier work by Baxter and Farmer on English oak (14), who suggested large year to year changes. As shown in figure 5, our high precision ^{14}C determinations of three wood samples (each containing three rings) from an oak tree of the same English forest do not indicate a large annual ^{14}C variability in England. A further discussion of these short time scale ^{14}C variations is given in section 7.

Regional differences in natural ^{14}C levels should be considered also. We have not been able to detect any differences beyond our measuring precision of 1.5 per mil in natural ^{14}C levels of contemporaneous wood of northern hemispheric origin between 32°N and 52°N latitude. $\Delta^{14}\text{C}$ levels also appear independent of altitude because high altitude Bristlecone pine has the same

^{14}C levels as low altitude Douglas fir of the Pacific Northwest. The ^{14}C levels of contemporaneously grown wood pairs are given in table 2. The work of Lerman et al. (4) suggests a $\Delta^{14}\text{C}$ level about four per mil lower for part of the Southern Hemisphere. However, our preliminary work on cellulose samples from the southern hemisphere yields $\Delta^{14}\text{C}$ levels comparable to the Washington state $\Delta^{14}\text{C}$ record. Three samples (1920-22, 1922-1925 and 1932-1934) of a *Nothofagus* tree ($51^{\circ}6'S$, $72^{\circ}54'W$) averaged only $0.6 \pm 1.3\text{‰}$ below the values reported for the C tree.

5. MODEL CALCULATIONS.

A box-diffusion model as described by Oeschger et al. (15) was constructed to parameterize global carbon exchange. Important exchange parameters in this model are the CO_2 gas transfer rate (F , in moles $\text{m}^{-2}\text{yr}^{-1}$), the vertical diffusion rate in the ocean (K_z , $\text{cm}^2 \text{sec}^{-1}$) and the biospheric residence time (τ , yrs). Many uncertainties surround the biological growth factor. We therefore assumed a constant biomass for all the calculations discussed in this section.

The natural variability of the measured atmospheric ^{14}C levels during the current millennium (fig. 4) indicate that the atmospheric ^{14}C content would not have been constant after 1860 even if fossil fuel CO_2 had not been released. This natural variability is related by us to the solar modulation of the cosmic ray flux and associated ^{14}C production in the upper atmosphere (7). To evaluate the solar modulation for our present investigation we first calculated, using a box-diffusion model, the ^{14}C production rate (Q_M , in atoms $\text{sec}^{-1}\text{cm}^{-2}$ earth surface) during the 1600-year interval prior to fossil fuel addition. Average Q_M values over the time interval

of the recorded AD 1723-1855 sunspot cycles (each lasting on average of about 11 years) were calculated as were average sunspot numbers ($\bar{S}$) over these cycles (16). A regression procedure was used to calculate the dependence of $\bar{Q}_M$ and $\bar{S}$, as described previously (7). With this information, we then used the sunspot record between 1855 and 1953 to estimate $\bar{Q}_M$ over this time interval and calculate the atmospheric $\Delta^{14}\text{C}$ level that would occur with and without the fossil fuel perturbations.

Three versions of the box diffusion models were used to calculate atmospheric ^{14}C levels and to examine the sensitivity of our analysis to the magnitude of the exchange parameters. The description of the three model versions is found in table 3. Model A is the version described by Siegenthaler and Oeschger (17), model B differs from A by having a $K_z = 3 \text{ cm}^2 \text{ sec}^{-1}$ and $F = 21 \text{ moles m}^{-2} \text{ yr}^{-1}$ whereas model C is the same as B with $\tau = 30 \text{ years}$ (18, 19).

The higher F and K_z values in model B and C are derived from the oceanic distribution of bomb produced ^{14}C (20-22). However, this higher value of K_z implies a steady state ^{14}C activity in the deep ocean ($>2000 \text{ m}$) that is significantly higher (-100‰) than that measured between 50°N and 50°S during GEOSECS (-190‰) (21). We chose to use a K_z value reflecting ocean transport processes that apply over a time scale closer to that of the fossil fuel addition, even though it violates steady state equilibrium.

9 For each model version $\bar{Q}_M$ values were calculated, and the dependence of $\bar{Q}_M$ and $\bar{S}$ were determined (table 3). The next step is to use the sunspot record and an appropriate relationship between Q_M and S to calculate the ^{14}C production rates and atmospheric ^{14}C levels during the time interval of fossil fuel addition. The uncertainty of these model calculations depends

in part on the uncertainty of the $\bar{Q}_M$ and $\bar{S}$ relationship. As mentioned previously (7), variations in the atmospheric ^{14}C levels may be caused by variables other than production rate changes (i.e. climate, biospheric reservoir size, ocean mixing and chemistry, etc.). However, the strong correlation between calculated changes in $\bar{Q}_M$ and solar activity (7, 23, 24, 25) suggest this is a first order effect, and only this effect has been incorporated into the calculations.

By extrapolating the $\bar{Q}_M$ - $\bar{S}$ relationship calculated from the ^{14}C record prior to 1855 to the following 100 years, we assume that whatever processes cause the $\bar{Q}_M$ changes continue to do so in a similar manner. The uncertainty in this assumption is debatable, but using a $\bar{Q}_M$ - $\bar{S}$ relationship is preferable to assuming the anthropogenically unperturbed atmospheric $\Delta^{14}\text{C}$ levels would have remained constant up to 1955. Another complication in the modeling procedure is less obvious and involves the choice of the time at which to start the model calculations. At this starting time, the model's reservoirs are assumed to be in chemical and isotopic equilibrium, and then are perturbed from this condition. However, as seen in figure 4, the long-term atmospheric ^{14}C record indicates that the atmospheric carbon reservoir oscillates about an equilibrium condition. Thus, the imposition of an equilibrium state at a particular time is arbitrary. Generally, the further back in time the models' initial conditions are set, the less sensitive the model calculations at a succeeding time are to these conditions. Thus starting the model calculations in 1855 was not considered to be the best approach. Instead we imposed steady state initial conditions in either 1735 or 1815, for which $\bar{Q}_M$ - $\bar{S}$ relationships determined over the 1723-1855 and 1798-1855 time intervals were used respectively to calculate atmospheric

^{14}C levels. This procedure allows the model to feed back into the post-1860 atmospheric ^{14}C calculations, ^{14}C changes that are close to observed atmospheric values.

6. THE RELATIONSHIP BETWEEN ^{14}C PRODUCTION RATES AND SOLAR ACTIVITY.

The calculated production rate changes $\Delta\bar{Q}_M$ (the percent difference from AD 300-1860 average production rate) have been attributed to changes in solar modulation of the cosmic ray flux (7, 23-25). The model calculated relationship between $\bar{Q}_M$ and $\bar{S}$ (table 3) can be compared with the relationship derived from observed post-1937 atmospheric neutron fluxes, which yield a $d\bar{Q}/d\bar{S}$ value of -0.0041 ± 0.0010 (7, 23). Previously we calculated a $d\bar{Q}_M/d\bar{S} = -0.0048$ for the 1800-1860 interval from atmospheric ^{14}C variations, using reservoir model A (7, 23). The data base for our present calculations is more extensive, and we now obtain a $d\bar{Q}_M/d\bar{S}$ value of -0.0029 ± 0.0010 for the 1793-1855 interval (table 3). Between 1723 and 1855, $d\bar{Q}_M/d\bar{S}$ is -0.0060 ± 0.0026 , which suggests an increase in solar modulation when approaching the Maunder minimum in the late 17th century. For model version C the calculated $d\bar{Q}_M/d\bar{S}$ values for these time intervals are the same, within the error of the calculations (table 3). Thus the model with the shorter biosphere residence time indicates a similar degree of cosmic ray flux modulation when approaching the Maunder minimum.

All calculations suggest, for the 1723-1855 interval, a ^{14}C production rate—sunspot dependency slightly stronger than indicated by the $d\bar{Q}/d\bar{S} = -0.0051$ upper limit obtained from post-1937 neutron flux observations (7). However, within the error of the $d\bar{Q}_M/d\bar{S}$ calculations (table 3) the values agree with the independently determined $\bar{Q}$ - $\bar{S}$ relationship derived from 20th century neutron flux measurements.

The model calculated values of $d\bar{Q}_M/d\bar{S}$ are derived from a geomagnetically corrected ^{14}C record. It should be noted that differences between $d\bar{Q}_M/d\bar{S}$ values derived from the observed atmospheric $\Delta^{14}\text{C}$ record, and the geomagnetically corrected record, are very small. For example using model B and the geomagnetically corrected ^{14}C record results in $d\bar{Q}_M/d\bar{S} = -0.00517$ whereas $d\bar{Q}_M/d\bar{S} = -0.00522$ using the uncorrected record. Although the differences are small, we removed the geomagnetic long-term trend because otherwise the derived $\bar{Q}_M$ - $\bar{S}$ relationship is influenced by geomagnetically induced change in atmospheric $\Delta^{14}\text{C}$ level.

7. RESULTS OF MODEL CALCULATIONS.

Atmospheric ^{14}C levels were calculated from models A, B, and C for both the anthropogenically perturbed and unperturbed conditions. For each model, two solar modulation (1723-1855 and 1793-1855) dependencies between $\bar{Q}_M$ and $\bar{S}$ were used. A comparison between the measured atmospheric ^{14}C levels and model calculated ^{14}C time change is presented in figure 6. The shaded area represents the ^{14}C depletion due to fossil fuel CO_2 addition. Annual CO_2 production rates were taken from Keeling (26). The atmospheric CO_2 concentrations calculated by each of the three models agreed to within 1 ppm with the observed CO_2 increase between 1950 and 1974 (8).

All the model calculations of ^{14}C activity in the post-1860 interval agree within a few per mil with the measured values. As mentioned above, the date for the start of the model calculations (i.e. either 1735 or 1815) was chosen to obtain a good fit to the observed ^{14}C record between 1815 and 1855. Interestingly, with the $\bar{Q}_M$ - $\bar{S}$ dependencies presently used, none of the models can completely account for the dip in ^{14}C activity measured between 1780 and 1800. However, under-reporting of sunspot numbers is possible for

the record prior to 1800 (J.A. Eddy, personal communication).

The pattern of atmospheric ^{14}C change from 1860 to 1955 is presented in closer detail in figure 7, where the per mil differences from 1860 ^{14}C activity level is examined. The similarity of the model calculations suggests that the ^{14}C record alone cannot be used to choose one model over another, especially when one considers the uncertainty of the $\bar{Q}_M$ - $\bar{S}$ relationship and the error in the cumulative CO_2 release (ca. 10 percent (26)), and to a lesser degree the error in the ^{14}C measurements (± 0.6 per mil) for the decade averages. We prefer to examine further the results for model B because this version uses F and K_z values which are more representative of the oceanic bomb ^{14}C distributions, as discussed above. We also prefer to use the $\bar{Q}_M$ - $\bar{S}$ relationship that represents the 1723-1855 interval (i.e. $d\bar{Q}_M/d\bar{S} = -0.00617$) as this longer time interval provides a better representation of solar modulation and sets the initial steady state conditions in the model further back in time, as discussed above.

The results of calculations using model B indicate a change in $\Delta^{14}\text{C}$ between 1860 and 1950 of -18.4‰ when both the predicted natural variability and the fossil fuel CO_2 release are included. The measured ^{14}C change between the 1855-1864 decade and the years 1949-1951 is $-20.0 \pm 1.2\text{‰}$ (table 1).

The calculated $\Delta^{14}\text{C}$ values include estimated geomagnetic induced changes of the atmospheric $\Delta^{14}\text{C}$ levels, as described above. This correction amounts to a $+2.1\text{‰}$ increase in ^{14}C level between 1860 and 1950. The change in atmospheric ^{14}C levels that would have resulted from the solar induced variability in ^{14}C production rates during the 1860 and 1950 interval was calculated to be -4.8‰ . When fossil fuel is added in the model calculations, the ^{14}C level in 1950 changes an additional -15.7‰ .

Our estimated natural depletion in atmospheric ^{14}C levels is greater in the more recent part of the 1860-1950 interval, as seen in fig. 6. Before 1930 almost all (i.e. >95%) of the model calculated ^{14}C depletion is due to fossil fuel addition. In 1950, natural variability accounted for 15% of the measured Suess effect.

The previous discussion of model calculations of atmospheric ^{14}C levels uses ^{14}C production rates and sunspot numbers averaged over approximately 11 year cycles. So far we have not taken into account annual variations in production rate within a single solar cycle. Whereas the long-term trend in 20th century neutron flux observations gives a $d\bar{Q}/d\bar{S}$ of -0.0041 , the modulation within a solar cycle yields $dQ/dS = -0.00242$ (7, 27). To determine the effect of yearly variations in ^{14}C production rates, we incorporated the following solar modulation relationship in Model B to calculate annual changes in atmospheric $\Delta^{14}\text{C}$ level:

$$Q_M = 1.735 - 0.00617 \bar{S} - 0.00242 (S - \bar{S}).$$

A comparison between the calculated atmospheric $\Delta^{14}\text{C}$ curve and the measured tree-ring $\Delta^{14}\text{C}$ levels is made in figure 8. To facilitate such a comparison, we matched the calculated and measured decade (1855-1864) averaged $\Delta^{14}\text{C}$ values, and as a result lowered all calculated $\Delta^{14}\text{C}$ values by 1.4 ‰.

Because the use of $\bar{S}$ over the 11 year cycle creates discontinuities in the production rates at the end of each solar cycle, we calculated five year moving averages of $\bar{Q}_M$ to which we added the calculated yearly change in Q (i.e., $-0.00242 (S - \bar{S})$), so that a continuous production curve could be obtained. The 11 year ^{14}C production cycle causes rather small

perturbations in the calculated atmospheric ^{14}C levels. The model calculated amplitude of the "cycle" is about 1‰, and cannot be observed in the actual record because the measuring precision of each point is only about 1.5‰. The comparison of a three year moving average of the yearly data in figure 1, (with the omission of the 1895-1915 interval because the ^{14}C levels of these samples are suspect, as discussed previously), indicates that the calculated long term (1860-1950) change agrees with the measurements. However, the agreement between the fine structure of both curves is less good. To prove the existence of the 11 year $\Delta^{14}\text{C}$ oscillation one would need improved measuring precision to the 0.5 per mil range. An independent confirmation of the measured $\Delta^{14}\text{C}$ perturbations of a few per mil (such as the one near 1933) is also needed before such oscillations can be considered proven.

8. THE GLOBAL CARBON CYCLE.

The increase in atmospheric CO_2 level, calculated for model B, is from 297 ppm in 1860 to 311.8 ppm in 1950, or 5.0 percent. The corresponding 1.6 percent atmospheric $\Delta^{14}\text{C}$ change attributed to fossil fuel addition is smaller because part of the radiocarbon deficit is stored in the oceans and biosphere. By 1950 the atmospheric $^{14}\text{CO}_2/\text{CO}_2$ attenuation factor is 0.32 for the industrial CO_2 release. In addition, the model calculations indicate a reduction in radiocarbon between 1860 and 1950 for the model biosphere from 97.8 percent to 96.5 percent, and for the oceanic mixed layer from 94.5 percent ($\Delta^{14}\text{C} = -55\%$) to 93.7 percent ($\Delta^{14}\text{C} = -63\%$). The $\Delta^{14}\text{C}$ level measurements on annual coral rings provide a check on some of the calculated mixed layer $\Delta^{14}\text{C}$ values. Druffel and Linick (28) determined from a Florida Keys coral analogous mixed layer $\Delta^{14}\text{C}$ levels of -51

$\pm 2\%$ for the pre-industrial 19th century and of -61% for the year 1955. However, Nozaki et al. (29) measured between 1900 and 1950 a $\Delta^{14}\text{C}$ reduction of about 22 per mil for a Bermuda coral. This large change, as discussed by Nozaki and co-workers, may be caused by a local exchange rate of ^{14}C with the deep water that is smaller than the global world ocean average. The 10 per mil change of the Florida coral agrees well with our model B calculated change of 8 per mil.

Recently Druffel (30) has estimated a 6% decrease in mixed layer $\Delta^{14}\text{C}$ levels between 1930 and 1954 in the eastern Pacific using corals collected in the Galapagos. This compares to our Model B calculated decrease of 4% over this same time interval. However, the inferred mixed layer $\Delta^{14}\text{C}$ record at this location is complicated by the variability of upwelling of deeper $\Delta^{14}\text{C}$ depleted water, and thus may not reflect only atmospheric $\Delta^{14}\text{C}$ changes.

A recent point of debate has been the amount of carbon taken up, or released, by the biosphere during the current episode of anthropogenic disturbance. The biospheric reservoir size was kept constant for our calculations as discussed above. Thus, all industrial CO_2 not present in the atmosphere by 1950 is in the model ocean. We investigated the influence of biospheric CO_2 releases on atmospheric $\Delta^{14}\text{C}$ levels by reducing the biospheric reservoir size between 1860 and 1950 according to a biospheric pattern suggested previously (31, 32) (i.e. Gaussian distribution centered at 1860 with a $\sigma = 20$ years, and CO_2 release totalling 120×10^9 tons). The differences with the model $\Delta^{14}\text{C}$ calculations made above are small because the released biological CO_2 has nearly the same ^{14}C content as atmospheric CO_2 . For this biospheric release pattern the 1860-1950 change

in model B calculated atmospheric $\Delta^{14}\text{C}$ level differs less than 0.5 per mil from the -18.4‰ calculated earlier. However, to accommodate the large biospheric CO_2 flux the model calculations have to start with a lower atmospheric CO_2 content of 280 ppm.

9. CONCLUSIONS.

Evidently, global carbon box-diffusion models can adequately account for the 1860-1950 change in atmospheric $\Delta^{14}\text{C}$ level when estimated fossil fuel CO_2 releases and predicted cosmic ray flux changes are incorporated in the model. For instance, Model B, with a vertical eddy diffusion rate of $3.0 \text{ cm}^2 \text{ sec}^{-1}$ in the oceans, correctly predicts the change in trend around 1937 when the gradient changes from -2.8‰ per decade to -6.8‰ per decade. Because the calculated results are not very sensitive to the choice of model parameters the Suess effect cannot be used for the fine tuning of models, especially since the fossil fuel CO_2 releases, cosmic ray flux modulation, and measured $\Delta^{14}\text{C}$ levels each have their inherent inaccuracies. The model calculations also show minimal changes in $\Delta^{14}\text{C}$ level when an anthropogenic reduction in biospheric reservoir size is simulated.

Model calculations indicate 11 year $\Delta^{14}\text{C}$ perturbations with an amplitude of about 1 per mil. The measured $\Delta^{14}\text{C}$ record is not yet sufficiently precise to confirm these oscillations.

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REFERENCES.

1. H.E. Suess, Radiocarbon concentration in modern wood, *Science* 122 (1955) 415.
2. J. Houtermans, H.E. Suess, and W. Munk, Effect of industrial fuel combustion on the carbon-14 level of atmospheric CO₂, in: *Radioactive Dating and Methods of Low-level Counting*, Int. At. Energy Agency, STI/PUB/152, (1967) 57.
3. G.J. Fergusson, Reduction of atmospheric radiocarbon concentration by fossil fuel carbon dioxide and the mean life of carbon dioxide in the atmosphere, *Proc. Roy. Soc. (London) Ser. A*, 243 (1958) 561.
4. J.C. Lerman, W.G. Mook, and J.C. Vogel, C-14 in tree rings from different localities, in *Radiocarbon variations and absolute chronology*, Proceedings of the Twelfth Nobel Symposium, Uppsala University, Wiley Interscience, I.U. Olsson, ed. (1970), 275.
5. P.E. Damon, A. Long, and E.I. Wallick, On the magnitude of the 11-year radiocarbon cycle, *Earth and Plan. Sci. Letters* 20 (1973) 300.
6. P.P. Tans, A.F.M. de Jong, and W.G. Mook, Natural Atmospheric ¹⁴C variation and the Suess effect, *Nature* 280, (1979) 826.
7. M. Stuiver and P.D. Quay, Changes in atmospheric carbon-14 attributed to a variable sun, *Science* 207 (1980) 11.
8. C.A. Ekdahl and C.D. Keeling, Atmospheric carbon dioxide and radiocarbon in the natural carbon cycle: 1. Quantitative deductions from records at Mauna Loa observatory and at the South Pole.
R. Bacastow and C.D. Keeling. 2. Changes from A.D. 1700 to 2070 as deduced from a geochemical model. *In: Carbon and the Biosphere*, G.M. Woodwell and E.V. Pecan, eds.; Conf. 720510 U.S. A.E.C. Techn. Inf. Center (1973) 51-85; 86-135.

9. D.C. Grey and P.E. Damon: Sunspots and radiocarbon dating in the Middle Ages, Ch. 6, in: Scientific Methods in Medieval Archaeology, R. Berger (ed.), Univ. of Cal. Press, Berkeley (1970), 167.
10. W.F. Cain, and H.E. Suess, Carbon-14 in tree rings, J. Geophys. Res. 81 (1976) 3688.
11. M. Stuiver and H.A. Polach, Discussion-Reporting of ^{14}C data, Radiocarbon 19 (1977) 355.
12. C.E. Barton, R.T. Merrill and M. Barbetti, Intensity of the earth's magnetic field during the past 9000 years, Phys. Earth Planet. Inter. 20 (1979) 96.
13. J.C. Houtermans, Geophysical Interpretations of bristlecone pine radiocarbon measurements using a method of fourier analysis of unequally spaced data. Thesis, Univ. of Bern Switzerland (1971).
14. M.S. Baxter and J.G. Farmer, Radiocarbon: short-term variations, Earth and Plan. Sci. Letters 20 (1973) 295.
15. H. Oeschger, U. Siegenthaler, U. Schotterer and A. Gugelmann, A box diffusion model to study the carbon dioxide exchange in nature, Tellus 27 (1975) 168.
16. J.A. Eddy, The Maunder Minimum, Science 192 (1976) 1189.
17. U. Siegenthaler and H. Oeschger, Predicting future atmospheric carbon dioxide levels, Science 199 (1978) 388.
18. A. Björkström, A model of CO_2 interaction between atmosphere, oceans, and land biota, in SCOPE Report 13: The global Carbon Cycle, edtrs. B. Bolin, E.T. Degens, S. Kempe and P. Kettner, Wiley, Chicester (1979) 403.
19. W.H. Schlesinger, Carbon Balance in Terrestrial Detritus, Ann. Rev. Ecol. Syst. 8 (1977) 51.

20. M. Stuiver, ^{14}C distribution in the Atlantic Ocean, *J. Geophys. Res.* 85 (1980) 2711.
21. M. Stuiver, H.G. Ostlund and T.A. McConnaughey, GEOSECS Atlantic and Pacific ^{14}C distribution in SCOPE Report 16: Global Carbon Modeling, Wiley and Sons, in press.
22. W.S. Broecker, T.H. Peng and R. Engh, Modeling the carbon system, in Proc. Tenth Int. Radiocarbon Conference, Bern/Heidelberg, eds. M. Stuiver and R. Kra, *Radiocarbon* 22 (1980) 565.
23. M. Stuiver and P.D. Quay, Patterns of Atmospheric ^{14}C changes, *Radiocarbon* 22 (1980) 166.
24. M. Stuiver, Solar variability and climatic change during the current millennium, *Nature* 286, (1980) 868.
25. M. Stuiver and P.M. Grootes, Trees and the ancient record of heliomagnetic cosmic ray flux modulation, in: NASA Proceedings of the Conference on the Ancient Sun: Fossil record in the Earth, Moon, and Meteorites, Pergamon Press (1980) 165.
26. C.D. Keeling, Industrial Production of carbon dioxide from fossil fuels and limestone, *Tellus*, XXV (1973) 174.
27. K. O'Brien, Secular variations in the production of cosmogenic isotopes in the Earth's atmosphere, *J. Geophys. Res.* 84 (1979) 423.
28. E.M. Druffel and T.W. Linick, Radiocarbon in annual coral rings of Florida, *Geophys. Res. Letters* 5, no. 11 (1978) 913.
29. Y. Nozaki, D.M. Rye, K.K. Turekian, and R.E. Dodge, A 200-year record of carbon-13 and carbon-14 variations in a Bermuda coral, *Geophys. Res. Letters* 5, No. 10 (1978) 825.
30. E. M. Druffel, Radiocarbon in annual coral rings from the eastern tropical Pacific Ocean, *EOS* 61 (53) (1980) 1248.

31. M. Stuiver. Atmospheric carbon dioxide and carbon reservoir changes
Science 199 (1978) 253.
32. U. Siegenthaler, M. Heimann and H. Oeschger, Model responses of
the atmospheric CO₂ level and ¹³C/¹²C ratio to Biogenic CO₂ input
in Carbon Dioxide, Climate and Society, Proceedings of a IIASA work-
shop, J. Williams, ed. (1978) 79.

TABLE 1

Tree-ring derived atmospheric $\Delta^{14}\text{C}$ values. The $\Delta^{14}\text{C}$ values are the relative deviations of the measured ^{14}C activity from 95 percent of the activity of the NBS oxalic acid standard, after normalization to a $\delta^{13}\text{C}_{\text{PDB}} = -25$ per mil and after correction for ^{14}C decay (11) ($T_{1/2} = 5730$ yrs). Two different Douglas Firs, A and C, were used. Tree A covers the 1820-1914 interval; tree C, the years 1916-1954. $\Delta^{14}\text{C}^*$ values for the 1895-1914 period may be a few per mil too high due to the incorporation of nuclear bomb ^{14}C (see text). Alpha cellulose was used for tree C, and de Vries treated wood for tree A (see text). The 1915 ring was too small for ^{14}C analysis.

Yrs. of growth	$\Delta^{14}\text{C}$ (‰)	Yrs. of growth	$\Delta^{14}\text{C}$ (‰)	Yrs. of growth	$\Delta^{14}\text{C}$ (‰)
1820	2.9 ± 1.2	1861	-2.6 ± 1.7	1916	-12.5 ± 1.8
1821	2.9 ± 1.3	1862	-8.0 ± 2.0	1917	-9.6 ± 1.3
1822	-1.3 ± 1.7	1863	-6.8 ± 1.7	1918	-10.9 ± 1.0
1823	2.5 ± 1.7	1864	-5.5 ± 1.6	1919	-11.7 ± 1.7
1824	0.7 ± 1.2	1865	-3.9 ± 1.5	1920	-12.3 ± 1.8
1825	1.0 ± 1.6	1866	-5.5 ± 1.8	1921	-10.6 ± 1.8
1826	1.3 ± 1.6	1867	-3.4 ± 1.1	1922	-11.2 ± 1.9
1827	3.8 ± 1.2	1868	-3.9 ± 1.3	1923	-15.0 ± 1.6
1828	2.1 ± 1.0	1869	-4.2 ± 1.3	1924	-10.6 ± 1.8
1829	4.3 ± 1.7	1870	-4.7 ± 1.4	1925	-10.6 ± 1.6
1830	3.1 ± 1.6	1871	-5.4 ± 1.4	1926	-15.9 ± 1.6
1831	0.6 ± 1.2	1872	-4.7 ± 1.2	1927	-14.3 ± 2.1
1832	1.6 ± 1.4	1873	-4.5 ± 1.7	1928	-16.0 ± 1.8
1833	-0.2 ± 1.4	1874	-5.6 ± 1.7	1929	-17.6 ± 1.2
1834	-0.9 ± 1.9	1875	-4.3 ± 1.2	1930	-14.2 ± 1.7
1835	-0.7 ± 1.7	1876	-6.7 ± 1.7	1931	-16.6 ± 1.8
1836	-0.5 ± 1.2	1877	-5.5 ± 1.5	1932	-20.2 ± 1.3
1837	-2.6 ± 1.6	1878	-5.8 ± 1.1	1933	-18.5 ± 1.8
1838	-2.0 ± 1.0	1879	-4.4 ± 1.5	1934	-15.5 ± 1.8
1839	-1.4 ± 1.4	1880	-3.7 ± 1.6	1935	-16.6 ± 1.9
1840	-1.2 ± 1.4	1881	-4.1 ± 1.6	1936	-16.4 ± 1.7
1841	-3.9 ± 1.7	1882	-2.7 ± 1.7	1937	-16.5 ± 1.7
1842	-1.6 ± 1.4	1883	-2.3 ± 1.2	1938	-15.6 ± 1.2
1843	-2.0 ± 1.1	1884	-2.6 ± 1.7	1939	-18.1 ± 1.9
1844	-1.2 ± 1.2	1885	-4.0 ± 1.4	1940	-21.0 ± 2.0
1845	-1.8 ± 2.4	1886	-6.3 ± 1.1	1941	-19.2 ± 1.9
1846	-0.7 ± 1.3	1887	-6.7 ± 1.2	1942	-19.1 ± 1.3
1847	-0.9 ± 1.3	1888	-6.5 ± 2.1	1943	-23.3 ± 1.2
1848	-1.9 ± 1.4	1889	-6.1 ± 1.4	1944	-21.3 ± 1.4
1849	-0.7 ± 1.4	1890-1891	-4.1 ± 1.6	1945	-22.3 ± 1.8
1850	-0.5 ± 2.4	1892-1893	-3.7 ± 1.4	1946	-----
1851	-2.1 ± 2.4	1894-1895	-3.9 ± 1.2	1947	-20.9 ± 1.6
1852	0.7 ± 2.3	1896-1897	$-2.7 \pm 1.7^*$	1948	-22.1 ± 1.7
1853	-3.9 ± 1.3	1898-1899	$-4.2 \pm 1.9^*$	1949	-25.0 ± 1.7
1854	-3.5 ± 2.4	1900-1901	$-1.9 \pm 2.0^*$	1950	-24.8 ± 1.7
1855	-4.6 ± 1.6	1902-1903	$-3.5 \pm 1.4^*$	1951	-24.8 ± 1.7
1856	-4.8 ± 1.3	1904-1905	$-4.1 \pm 1.6^*$	1952	-25.1 ± 1.7
1857	-5.8 ± 1.6	1906-1907	$-3.6 \pm 1.2^*$	1953	-24.0 ± 1.6
1858	-2.8 ± 1.9	1908-1909	$-6.9 \pm 1.7^*$	1954	-22.2 ± 2.5
1859	-3.6 ± 1.8	1910-1911	$-7.2 \pm 1.1^*$		
1860	-5.0 ± 1.7	1912-1914	$-8.3 \pm 0.9^*$		

TABLE II

A comparison of $\Delta^{14}\text{C}$ levels of pairs of contemporaneous wood grown in different regions. The alphabetical listing of the trees follows our laboratory code.

Years AD	$\Delta^{14}\text{C} \text{ ‰}$	Tree	Latitude	Species
1846-1855	-1.8 ± 0.6	A	47°46'N, 124°06'W	Douglas Fir
1846-1855	-2.7 ± 1.7	AR	32°23'N, 110°41'W	Douglas Fir
1842-1844	0.7 ± 1.7	FD	51°48'N, 2°37'W	Oak
1842-1844	-1.6 ± 0.7	A	47°46'N, 124°06'W	Douglas Fir
1836-1838	0.7 ± 1.8	FD		
1836-1838	-1.6 ± 0.7	A		
1829-1831	3.9 ± 1.8	FD		
1829-1831	2.6 ± 1.0	A		
1810-1819	2.3 ± 1.7	F	43°7'N, 123°40'W	Douglas Fir
1810-1819	3.0 ± 0.6	B	46°45'N, 121°45'W	Douglas Fir
1790-1799	-9.1 ± 1.7	F		
1790-1799	-6.2 ± 0.6	B		
1480-1489	9.7 ± 1.6	R	~47°N, ~122°W	Douglas Fir
1480-1490	8.6 ± 1.8	BP	~36°N, ~118°N	Bristlecone Pine
1080-1089	-8.5 ± 1.1	S	48°40'N, 123°40'W	Douglas Fir
1080-1090	-7.2 ± 2.7	BP	~36°W, ~118°N	Bristlecone Pine
1310-1319	-3.5 ± 1.8	S	48°40'N, 123°40'W	Douglas Fir
1310-1319	-0.7 ± 1.6	R	~47°N, ~122°W	Douglas Fir
1300-1309	2.3 ± 1.2	S		
1300-1309	-1.8 ± 1.8	R		
880-899	-15.1 ± 1.8	S	48°40'N, 123°40'W	Douglas Fir
880-899	-14.5 ± 1.4	RC	~36.5°N, 118.5°W	Sequoia
240-249	-12.7 ± 1.4	RC	~36.5°N, 118.5°W	Sequoia
240-249	-15.4 ± 1.5	SR	~36.5°N, 118.5°W	Sequoia

TABLE III.

Model versions and parameters used for the calculations. K_z is the vertical diffusion coefficient, F the ocean-atmosphere gas exchange rate, τ the biosphere residence time, N_B/N_A the ratio of the biospheric and atmospheric carbon reservoirs, and Q_∞ the steady state ^{14}C production rate of the model. The model calculated ^{14}C production rates (in atoms/sec cm^2 of earth surface), and average sunspot number $\bar{S}$ per 11 yr solar cycle, yield the listed $d\bar{Q}_M/d\bar{S}$ values and the production rate Q_0 for $\bar{S} = 0$. The geomagnetically corrected ^{14}C record was used for these calculations. The initial assumed CO_2 level, prior to anthropogenic releases, is labelled CO_2^* .

		A	B	C
K_z $\text{cm}^2 \text{ sec}^{-1}$		1.25	3	3
F $\text{moles m}^{-2} \text{ yr}^{-1}$		19	21	21
τ yr		60	60	30
N_B/N_A		2.4	2.5	2.5
Q_∞ $\text{at sec}^{-1} \text{ cm}^{-2}$		1.57	1.71	1.71
CO_2^* ppm		292	297	297
AD 1723-1855	$d\bar{Q}_M/d\bar{S}$	$-(60 \pm 26)10^{-4}$	$-(62 \pm 29)10^{-4}$	$-(78 \pm 31)10^{-4}$
	Q_0	1.61 ± 0.13	1.73 ± 0.15	1.80 ± 0.16
AD 1798-1855	$d\bar{Q}_M/d\bar{S}$	$-(29 \pm 10)10^{-4}$	$-(29 \pm 12)10^{-4}$	$-(65 \pm 30)10^{-4}$
	Q_0	1.58 ± 0.04	1.69 ± 0.06	1.86 ± 0.13

Figure Legends

- Fig. 1. $\Delta^{14}\text{C}$ values of organic materials extracted from tree-rings with petroleum ether. The extractives from 1940 and following years contain nuclear bomb ^{14}C from the post 1952-era. The dashed line represents cellulose $\Delta^{14}\text{C}$ values.
- Fig. 2. Atmospheric $\Delta^{14}\text{C}$ levels, derived from tree-rings, between 1820 and 1954. Single year determinations are given, except for the 1890-1915 interval (table 1). The vertical bar denotes one standard deviation. $\Delta^{14}\text{C}$ levels of the 1895-1915 interval probably give an upper limit only (see text).
- Fig. 3. The difference in $\Delta^{14}\text{C}$ levels of wood from trees of the Netherlands and the state of Washington. The graph indicates by how much the $\Delta^{14}\text{C}$ values of two Dutch trees (triangles and plusses) are below the three year moving average $\Delta^{14}\text{C}$ values of the Washington tree.
- Fig. 4. Atmospheric $\Delta^{14}\text{C}$ levels of the current millennium, uncorrected (lower curve) and corrected for long-term geomagnetic induced changes (upper curve).
- Fig. 5. A comparison of annual $\Delta^{14}\text{C}$ variability of wood from the state of Washington and England. The measurements of English wood in our laboratory (diamonds) do not confirm the large variability reported previously (14).
- Fig. 6. Carbon reservoir model calculated $\Delta^{14}\text{C}$ levels of the 19th and 20th century. In each section the upper curve represents the calculated natural atmospheric $\Delta^{14}\text{C}$ level, whereas the lower curve gives the calculated level when the release of fossil fuel CO_2 is taken into account. Plus points are the decade averaged measured $\Delta^{14}\text{C}$ levels, except for the 1952 endpoint. Calculations start either in 1735 (top) or

1815 (bottom). Model A, B, and C parameters are given in table 3.

The shaded area represents the influence of fossil CO₂ release.

Fig. 7. A comparison of measured decade averaged $\Delta^{14}\text{C}$ values (squares), and model calculated $\Delta^{14}\text{C}$ levels, all relative to the year 1860 (see text).

Fig. 8. Model calculated $\Delta^{14}\text{C}$ levels (dashed line) that take into account the year to year solar modulation. The calculated amplitude of the 11 year cycle is about 1 per mil. The heavy solid line is the three year moving average of single year tree-ring measurements, with standard deviation (shaded area). Suitable single year measurements are not yet available for the 1895-1915 interval (see text).

fig 1

fig 2

fig 3

fig 4

fig 5

fig 6

fig 7

OXYGEN ISOTOPE RATIOS IN TREES
REFLECT MEAN ANNUAL TEMPERATURE AND HUMIDITY

in press SCIENCE

ABSTRACT

$\delta^{18}\text{O}$ values in tree ring cellulose closely reflect $\delta^{18}\text{O}$ values in atmospheric precipitation and hence mean annual temperature. The change in $\delta^{18}\text{O}$ in cellulose is 0.41‰ per $^{\circ}\text{C}$ for selected near-coastal stations. $\delta^{18}\text{O}$ in precipitation and cellulose also change with altitude as demonstrated for Mt. Rainier, Washington. A lapse rate of $5.2 \pm 0.5^{\circ}$ per 1000 meters calculated from cellulose $\delta^{18}\text{O}$ values fits with the accepted mean annual lapse rate of 5°C per 1000 meters for this region. Cellulose $\delta^{18}\text{O}$ and $\delta^{18}\text{O}$ values of CO_2 equilibrated with leaf water differ by a fixed .16 per mil.

Oxygen isotope ratios (1) have been used extensively as indicators of past climate through measurements on water and carbonate derived from glacial ice, foraminifera, molluscs, and sedimentary carbonates (2). Important climatic information can be derived because the variation in the ratio of ^{18}O to ^{16}O in chemical compounds is dependent on equilibrium and kinetic effects which are related to temperature. Recently the ^{18}O content of tree ring cellulose and wood have been used as an indicator of past climate (3).

It has been demonstrated that the ^{18}O composition of plant cellulose is related to environmental water and may relate to humidity as well (4). It is also known that precipitation $\delta^{18}\text{O}$ values get more negative with increases in altitude and latitude. $\delta^{18}\text{O}$ values for precipitation from coastal stations closely follow mean annual temperatures (5). To investigate the possibility that the temperature dependence for $\delta^{18}\text{O}$ in precipitation is also reflected in the $\delta^{18}\text{O}$ values of tree rings, we measured the $\delta^{18}\text{O}$ composition of cellulose (6) from trees collected at various latitudes along the west coast of the United States, and from various altitudes on Mt. Rainier (Washington).

International Atomic Energy Agency (IAEA) yearly weighted average precipitation $\delta^{18}\text{O}$ data (7) and cellulose $\delta^{18}\text{O}$ in Figure 1A show a parallel change with respect to latitude ($r^2 = .98$). In view of this agreement and the relationship between $\delta^{18}\text{O}$ in precipitation and mean annual temperature shown in Figure 1B a direct correlation can be made between $\delta^{18}\text{O}$ in cellulose and mean annual temperature (Figure 1C). Soil water collected during the growing season in part reflects earlier precipitation events and hence a comparison is made with mean annual temperature rather than mean growing

season temperature. Coastal trees were emphasized in this study because of the linear relationships between $\delta^{18}\text{O}$ in precipitation and temperature for coastal regions (5), the fact that humidity is relatively constant ($67 \pm 6\%$), and because greater variation in the oxygen isotope ratio of cellulose has been demonstrated for trees grown in more continental regions (8).

Figure 1C demonstrates the value of this method for paleoclimatic work. The maximum error in the mean of the cellulose $\delta^{18}\text{O}$ data is $\pm 0.2\text{‰}$ and thus it should be possible to detect long-term climatic changes in north Pacific coastal areas of approximately 0.5°C . Because individual sites may be subject to local conditions which may affect the $\delta^{18}\text{O}$ ratios, samples from a range of latitudes are preferred for paleoclimatic work. Comparisons with meteorological data and $\delta^{18}\text{O}$ data for precipitation or soil water are essential to demonstrate that this method can be used for a given area.

Figure 2A demonstrates an altitude effect for the $\delta^{18}\text{O}$ composition of precipitation at Mt. Rainier, Washington. Precipitation samples were collected approximately every two weeks during the 1976-1978 growing season (May - September). A similar effect for $\delta^{18}\text{O}$ values in cellulose averaged from 1976-1978 tree rings is shown in Figure 2B(9).

This altitude effect on Mt. Rainier can be used to evaluate the general reliability of the change in $\delta^{18}\text{O}$ values per degree Celsius developed from data collected on trees from different latitudes (Figure 1A). Using the calculated change in the $\delta^{18}\text{O}$ composition of cellulose of $0.41 \pm 0.06\text{‰}$ per degree Celsius from Figure 1C, the temperature lapse rate on Mt. Rainier is $5.2 \pm 0.5^\circ\text{C}$ per 1000 meters. This value compares favorably with the

value of 5°C per 1000 meters from meteorological data (10).

It should be emphasized that the temperature relationships for the latitude and the altitude data are only first approximations. More extensive work is needed for refinement. However, the initial results are encouraging for use of this method as a temperature indicator.

It is clear from Figure 1A that by adding 35.1‰ to the $\delta^{18}\text{O}$ precipitation values, cellulose $\delta^{18}\text{O}$ values can be calculated. This systematic increase in $\delta^{18}\text{O}$ could be attributed to a biological fractionation factor. Such a simple model however does not explain $\delta^{18}\text{O}$ data obtained from trees grown east of the Cascade Mountain range. A tree grown at Manashtash Ridge near Ellensburg, Washington derived its water from a year-around spring with an average $\delta^{18}\text{O}$ value of $-16.3 \pm 0.6\text{‰}$ ($n = 17$, intermittent samples over three years). According to the above model the $\delta^{18}\text{O}$ values for cellulose should equal approximately 18.8‰. Actual values average 27.3‰, suggesting that there are other important factors involved. Current knowledge regarding the oxygen isotope uptake into cellulose suggests that humidity (11) and $\text{CO}_2 - \text{H}_2\text{O}$ equilibrium are factors which must also be considered (4).

It is well established that the oxygen in cellulose comes principally from carbon dioxide (12). DeNiro and Epstein (13) demonstrate that CO_2 completely equilibrates with plant water prior to cellulose synthesis. If we assume that CO_2 isotopically equilibrates with average leaf water then values for cellulose can be calculated using equations for calculating leaf water $\delta^{18}\text{O}$ combined with the standard equation for equilibrating CO_2 and water. For steady-state equilibrium conditions the leaf water equation (14) can be written as follows:

$$\delta_{LW} = \delta_I (1-h) + h\delta_{AV} + \epsilon^* + \epsilon_K (1-h) \quad (1)$$

where δ_{LW} = $\delta^{18}O$ composition of leaf water, δ_I = $\delta^{18}O$ composition of water supplied to the leaf by the stem, δ_{AV} = $\delta^{18}O$ composition of atmospheric water vapor, ϵ^* = equilibrium fractionation factor, ϵ_K = kinetic fractionation factor and h = relative humidity (15). Equation (1) has also been used to model experimental results on the ^{18}O composition of bean plants, however it was derived without assuming complete equilibration of CO_2 with plant water (16).

When equilibrating CO_2 with leaf water, the CO_2 gas will obtain a $\delta^{18}O$ value according to:

$$\delta_{CO_2} = \delta_{LW} + 10^3(\alpha - 1) + (\alpha - 1) \delta_{LW} \quad (2)$$

where α is the $CO_2 - H_2O$ fractionation factor (17).

The final equation for calculating $\delta^{18}O$ values in cellulose then becomes:

$$\delta^{18}O_{\text{cellulose}} = \alpha(10^3 + \delta_I(1 - h) + \epsilon^* + \epsilon_K + (\delta_{AV} - \epsilon_K)h) - 10^3 + K \quad (3)$$

A major unknown in the above equation is the value of ϵ_K . ϵ_K is known to vary with wind speed (18) and has been calculated from kinetic theory at 16‰, 21‰, and 32‰ for turbulent, laminar and static boundary layer conditions (19). Detailed work in controlled environment chambers is needed to define ϵ_K for the trees under discussion. We have assumed a value of +16‰, representing turbulent leaf boundary layer conditions, for the calculations shown in Table 1. If the value for ϵ_K is incorrect a change will need to be made in the value of K . If, for example, ϵ_K = 21‰, then K would have to equal approximately -18‰ to achieve the same cellulose $\delta^{18}O$ values as obtained with an ϵ_K = 16‰.

The constant K is added to equation 3 because investigations of deuterium and carbon-13 in cellulose have suggested biological fractionation factors for those isotopes (20). Assuming that biochemical reactions involved in cellulose production also fractionate oxygen, a constant K has to be added to the basic equation. K equals -16‰ when fitting actual cellulose values measured over a range of latitudes to the basic equation.

It is important to note that correlations with temperature given earlier are relationships which depend on the influence of temperature on the isotopic composition of precipitation rather than any direct temperature effect. Our model relates only to those changes in oxygen isotope composition which occur in and immediately around the tree leaf.

The $\delta^{18}\text{O}$ values calculated using Equation (3) agree rather closely with measured values (Table I, $r^2 = 0.96$). Note that the model calculated $\delta^{18}\text{O}$ value for the tree from Manashtash Ridge is much closer to the measured value than the value from the simple model mentioned above. This difference is thought to be related to the large (~30%) difference in humidity between coastal sites and Manashtash Ridge.

If, instead of substituting temperature (t) and h, we use t and the measured cellulose values, equation 3 can then be used to calculate relative humidity (21). The calculated values (Table I) are all within one standard deviation of the average measured daytime relative humidity values for the growing season (22).

Valuable information on past changes in humidity can be obtained using measured cellulose $\delta^{18}\text{O}$ values and our model, if D/H or other isotope ratios can provide source water (δ_{I}) $\delta^{18}\text{O}$ values. A 1‰ change in δ_{I} represents approximately a 1‰ shift in cellulose $\delta^{18}\text{O}$ values.

We have used equation (3) to calculate humidity values and could make a similar calculation for temperature since α and ϵ^* in the model are a function of temperature. The change with respect to temperature, however, is approximately 0.2‰ per °C which is a small effect compared to changes in relative humidity (1% change in relative humidity $\approx$ 0.3‰ change in cellulose $\delta^{18}\text{O}$).

Epstein et al. (4) have shown that the fractionation factor (23) between aquatic plants and their surrounding water is 1.027. The calculated fractionation factor for the samples in Table I, using 100% relative humidity to approximate conditions under which aquatic plants grow, is either 1.027 or 1.026. This suggests that the model can be used for aquatic plants as well as terrestrial plants. However, it should be noted that ϵ^* no longer maintains its physical significance and must be treated as a constant.

We have shown that the oxygen isotope content of cellulose from trees can be used as a temperature indicator in specific west coast areas where humidity values are fairly constant. An empirical model is derived which incorporates the currently known factors which determine $\delta^{18}\text{O}$ values in cellulose. Model results suggest that $\delta^{18}\text{O}$ of source water, humidity, leaf boundary layer dynamics, and the $\delta^{18}\text{O}$ composition of atmospheric water vapor are factors which must be considered when evaluating oxygen isotope data in tree rings (24).

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- (9) For a complete discussion of the portion of the trees sampled see reference (8).
- (10) S.C. Porter, J. Glaciology 18, 101 (1977).
- (11) A. Long, J.C. Lerman, and A. Ferhi, in Short Papers, 4th Int'l. Conf. Geochronol., Cosmochronol., Isotope Geology, Snowmass-at-Aspen, 20-25 August 1978; R.E. Zartman (ed.), (U.S. Geol. Surv. Open-file Report 78-701), 253, (1978).
- (12) A. Stemler and R. Radmer, Science 190, 457, (1975).
- (13) M. DeNiro and S. Epstein, Science 204, 51 (1979).
- (14) The original equation is from H. Craig and L. Gordon, Stable Isotopes in Oceanographic Studies and Paleotemperatures Conference, Spoleto; (July 26-30, 1965). It was first applied to leaf water in a dissertation by W. Schiegl and reported in W. Schiegl, Nature 251, 582 (1974).
- (15) δ_{AV} is assumed to be in equilibrium with average $\delta^{18}O$ of precipitation $\epsilon^* = 2.644 - 3.206 (10^3/T) + 1.534 (10^6/T^2)$ where T is in degrees Kelvin - Y. Bottinga, H. Craig; Earth Planet. Sci. Lett. 5, 285 (1969); only daytime humidity values are used. Temperatures used are daily averages since daytime-only values were not usually available.
- (16) A. Ferhi and R. Letolle, Physiol. Vég. 17, 107, (1979).
- (17) Y. Bottinga, H. Craig; Earth Planet. Sci. Lett. 5, 285 (1969);

$$\alpha = \frac{(5.112 - 0.214t + 0.00041t^2 + 1000)}{1000}$$
where t is in degrees centigrade.

- (18) H. Forstel, A. Putral, G. Schleser, H. Leith in Isotope Ratios as Pollutant Source and Behavior Indicators, (Proceedings of a Symposium, International Atomic Energy Agency, 18-22 November, 1974,
- (19) F. Farris and B. Strain, Rad. and Environm. Biophys. 15, 167 (1978); G. Dongmann, H. Nurnberg, H. Forstel, K. Wagener, Rad. and Environm. Biophys. 11, 41 (1974).
- (20) H. Ziegler, C. Osmond, W. Stichler, P. Trimborn, Planta 128, 85 (1976); C. Bennedict, Ann. Rev. Plant Physiol. 29, 67 (1978), R. Park, S. Epstein, Plant Physiology 36, 133, (1961).
- (21)
$$h = \frac{\delta^{18}O \text{ cellulose} + 1016 + \alpha(-10^3 - \delta_I - \epsilon^* - \epsilon_K)}{\alpha(\delta_{AV} - \epsilon_K - \delta_I)}$$

 $K = -16$ (see text).
- (22) Growing season used for Fairbanks was June, July, August; for Ketchikan, May through August; and for the sites in Washington and California, May through September. Water $\delta^{18}O$ values (δ_I) used in the model are from an interpolation of IAEA values (see (Figure 1C) or from our direct measurements on lakewater (Fairbanks) or precipitation (Tyee).
- (22)
$$\alpha^* = \frac{1 + \delta^{18}O \text{ cellulose}/1000}{1 + \delta^{18}O \text{ precipitation}/1000}$$
- (23) This research was supported by Department of Energy Contract DE-AT06-79 EV10206 and NSF grant EAR-7904523, Geochemistry Program.

Table I

Model Test Data

Location name	Latitude °N	Growing Season Daytime h %	Average Growing Season °C	Source Water δ^1_1 ‰	Measured Cellulose $\delta^{18}_{0\%}$	Model calcu- lated $\delta^{18}_{0\%}$	Model calc- ulated Humidity h %	Model calc- ulated $\delta^{18}_{0\%}$ h=100%	α
Fairbanks	64.8	59.3 $\pm$ 11.7	14.6	-16.6	21.8	20.6	55.0	9.6	1.027
Thorne Bay	55.2	72.3 $\pm$ 6.3	13.8	-11.3	23.9	22.8	68.4	15.3	1.027
Tyee	48.1	70.5 $\pm$ 4.9	13.4	- 7.7	26.9	27.2	71.5	19.1	1.027
Manashtash	46.9	35.3 $\pm$ 5.8	18.1	-16.3	27.3	26.5	32.4	9.2	1.026
Arcata	41.0	(70)—	13.1	- 6.9	27.6	28.2	72.3	20.0	1.027
La Jolla	32.7	66.8 $\pm$ 4.4	20.0	- 4.4	30.8	30.0	64.0	21.2	1.026

Figure Captions

Figure 1A ($\square$) $\delta^{18}\text{O}$ IAEA precipitation values, latitude 34.9°N Santa Maria, California; 47.7°N Destruction Island, Washington; 60.8°N Bethel, Alaska; 71.3°N Point Barrow, Alaska.

(+) $\delta^{18}\text{O}$ cellulose values latitude 32.7°N La Jolla, California, Pinus torreyana, (1 sample representing 3 growing seasons); 41.0°N Arcata, California, Picea sitchensis, (3 individually sampled rings); 48.1°N Tyee, Washington, Pseudotsuga menziesii (59 individually sampled rings); 55°N Thorne Bay, Alaska, Picea sitchensis (5 individually sampled rings); 64.8°N Fairbanks, Alaska, Picea glauca (21 individually sampled rings).

Figure 1B Correlation between $\delta^{18}\text{O}$ in precipitation (IAEA data) and mean annual temperature.

Figure 1C Cellulose $\delta^{18}\text{O}$ values (from Figure 1A) plotted versus mean annual temperature. The point with the greatest deviation from the least squares line is also the point with the greatest distance to a weather station (45 km for temperature data).

Figure 2A $\delta^{18}\text{O}$ in precipitation during the 1976-1978 growing seasons (May-September, collected every two weeks) at different elevations on Mount Rainier, Washington. The independent variable was plotted on the ordinate to emphasize the effect of altitude.

Figure 2B $\delta^{18}\text{O}$ in cellulose from Pseudotsuga menziesii (3 individually sampled rings, 1976-1978) at five different elevations on Mount Rainier, Washington (latitude 46.8°N).

Figure 1A

Figure 1B

Figure 1C

Figure 2A

Figure 2B