# Carbon-13 Variations in Sequoia Rings and the Atmosphere

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RECENTLY THE WRITER presented data on the isotopic composition of carbon in some 80 specimens of modern and fossil plants and coal (*1*). Modern land plants displayed a range of composition amounting to some 0.7 percent of the ratio $C^{13}/C^{12}$; the average depletion in $C^{13}$ with respect to atmospheric carbon dioxide was found to be about 1.8 percent. Coal samples, and specimens of fossil wood up to 25,000 years or more in age fell within the range of modern wood, though the fossil woods showed a tendency to be slightly enriched in $C^{13}$ with respect to the modern wood average. There was no correlation of isotopic composition with age, and the data and precision of analysis thus implied that the mean isotopic composition of atmospheric carbon dioxide has not varied by more than about 0.2 percent during the last 25,000 years and in fact has probably been constant to about this degree since Pennsylvanian time.

Plant specimens of the same species from different localities, and of different species from the same locality showed differences in isotopic composition; thus composition ranges as used above will include certain intrinsic variations due to species, individual, and geography. These factors can be eliminated by analyzing wood from the radial growth of a single tree; one is then concerned only with variations in the atmospheric carbon dioxide, of interest to the geochemist, and with variations in the isotopic fractionation of the plant, of possible interest to plant physiologists. These two effects may be additive or subtractive, and one will of course observe the resultant; we are interested in whether a steady trend in isotopic composition is observed, or only variations about a mean value. In the latter case the data would indicate that neither the isotopic composition of the atmospheric $CO_2$ nor the fractionation factor of the tree changed systematically with time, except in the unlikely event that the effects had just cancelled each other. It was felt that the oldest possible tree, that is, a sequoia, should be analyzed first in order to obtain the gross variation over the maximum time span available.

A complete radial of one of the oldest sequoias was obtained through the courtesy of Professor Edmund Schulman of the Laboratory of Tree-Ring Research, University of Arizona. He very kindly dated the rings of the radial specimen from the original dating of the tree by A. E. Douglass. Successive rings were cut out of the radial at approximately fifty-year intervals, and the central portions, carefully separated from the exterior parts to avoid contamination, were combusted to carbon dioxide and analyzed in the mass spectrometer in the manner previously described (*1*). In some cases where the rings were very thin, two or three rings were used for one sample. About 14 mg of wood were used for each sample, and in each case care was taken to include the full thickness of the ring or rings in the sample.

The specimen analyzed is *Sequoia gigantea* from the Enterprise millsite, Springville, California, near the southern limit of the strip in the Sierra Nevadas in which these trees grow. This particular tree is Huntington's tree number 195 (*2*) and Douglass has used the notation D-22 for the specimen (*3, 4*). The first complete ring was dated by Douglass as 1087 B.C. (*3*), and he was later able to establish that the missing central growth dated from 1115 B.C. (*4*, p. 26). Thus some 28 years are missing from the beginning of the record. The rings extend to A.D. 1883 + but beyond A.D. 1650 the wood begins to be badly decayed and analyses were not made beyond this point. The interval over which the analyses extend is thus from 1072 B.C. to A.D. 1649, a span of some 2700 years.

In Fig. 1 the results of the isotopic analyses are plotted against age as given by the annual rings, an abscission having been made on the abscissa at A.D. 500 so that the span from A.D. 500 to 1700 is continued below the earlier span with a repeated ordinate. The units on the ordinate are the δ values used previously (*1*) for the $C^{13}$ enrichment with respect to a standard working gas expressed in per mil, that is,

$$\delta\ (0/00) = \left(\frac{R_{\text{sample}} - R_{\text{std.}}}{R_{\text{std.}}}\right) 1000,$$

where $R$ is the ratio $C^{13}/C^{12}$. The standard has the isotopic composition of the average marine limestone (*1*); the values in Fig. 1 are negative and are thus "lighter" than limestone carbon (i.e., depleted in $C^{13}$) by some 2 percent. The precision of measurement is ± 0.1 per mil, or about the diameter of the dots in the diagram. Thus one sees at once that significant variations in isotopic composition are present.

The major characteristic of the observed isotopic

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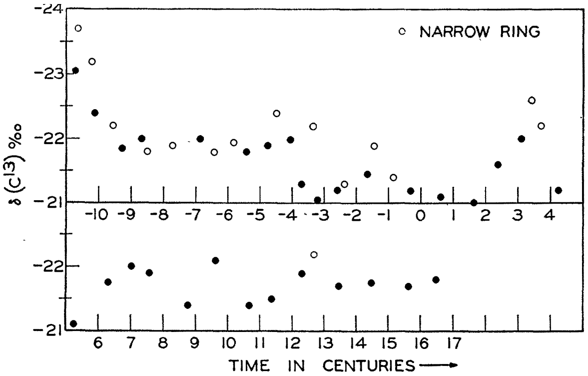

FIG. 1. Variation of carbon-13 concentration in annual rings of *Sequoia gigantea* from 1072 B.C. to A.D. 1649. Ordinal values represent $C^{13}$ enrichment in per mil with respect to an arbitrary standard which has the isotopic composition of average marine limestone.

variations is the fact that the variations are extremely small and show no systematic trend with time. This observation does not hold for the first 150 years of growth where a steady increase in $C^{13}$ concentration is observed; this is the period of most rapid growth, and it is an interesting question whether a growth effect or a real atmospheric effect operated at this point. The problem is particularly tantalizing since apparently there are no available older sequoias to extend the record substantially back in time; however, some insight may be gained by a study of contemporaneous and younger trees. For the rest of the time span the variations show a rather steady rise and fall over periods of several hundred years; the period from 928 to 477 B.C. shows a constant isotopic composition within the precision of analysis ($\delta = -21.9$ per mil), and the last 300 years of the curve, A.D. 1344 to 1649, is also constant at $-21.7$ per mil. Thus there is no steady trend with time and the probability appears strong that the mean isotopic composition of the atmospheric carbon was essentially constant over this 2500-year span, and further, that the fractionation factor does not change systematically with the age of the tree.

Interpretation of the fine structure of the curve is limited by our lack of knowledge of the exact mechanism by which plants fractionate the isotopes. The data indicate that very small radial inhomogeneities in isotopic composition are well preserved, though a certain amount of "smoothing" during the years immediately subsequent to the growth of each ring cannot be definitely excluded. The overall preservation of the isotopic record in sequoia has been definitely established by radiocarbon dating (*5*). There appears to be no correlation of isotopic composition with the width of the rings; the ring widths were measured prior to the analyses and a plot of these widths against age shows no general similarity to Fig. 1. The unfilled circles in Fig. 1 represent rings which were of excessively narrow width compared with the general average of rings in the vicinity; there appears to be some tendency for these narrow rings to be relatively depleted in $C^{13}$ when the slope is changing, but in the period from 900 to 500 B.C. there are large variations in the width of the analyzed rings while the isotopic composition is constant. Figure 1 also shows no overall similarities to the graphs of average sequoia ring widths against time given by the various workers in this field (*2–4, 6–9*).

Variations in the thickness of tree rings are generally interpreted as reflections of the total precipitation during the year or years preceding the growth of each ring (*4, 7, 9*), though temperature and solar radiation have also been stated to be important (*8*), especially in high latitudes (*10*). However, a relationship of isotopic composition with precipitation cannot be definitely excluded on these grounds, since it has been recognized that sequoia annual growth in many individual trees shows a relatively poor relationship with rainfall compared to certain other conifers of drier regions. Douglass has shown that sequoias growing on ridges or steep slopes may show a significant relationship to rainfall, but that the ring records of sequoias in basin sites are individually quite unreliable as rain gages, especially in the early centuries of growth; the specimen D-22 here analyzed is of this basin type (*3*). Accordingly, Dr. Schulman undertook an analysis of the data in terms of other and better growth indices of the climatic nature of the intervals near the analyzed rings, and reported as follows: "The data on $C^{13}$ composition seem to have no apparent relation to the inferred rainfall for corresponding dates, as judged by the rain-sensitive growth indices of nearby regions for the last five centuries and more distant regions for fifteen earlier centuries. I examined your $C^{13}$ dates not only for the corresponding estimated rainfall departures but also with reference to the inferred general maxima, minima, and trends in rainfall near these dates. However, my analysis was necessarily quite approximate."

The isotopic composition of atmospheric carbon dioxide is regulated by the exchange reaction with the 60 times greater reservoir of carbon in the sea; the temperature coefficient of the exchange equilibrium constant is 6° C for a 1 per mil variation in the enrichment factor using Urey's calculation based on empirical data, and must be greater, probably about 8° C for 1 per mil because of the newer corrected values for the isotopic composition of atmospheric carbon dioxide (*1*). This change must be reflected almost entirely in the atmosphere because of the proportions of the phases. Thus, to account for the fluctuations in Fig. 1, of the order of 1 per mil, by changes in mean temperature, variations in temperature of the order of magnitude of those estimated to have been the maximum variations between glacial and inter-glacial periods are required (*11*).

The variations shown in Fig. 1 show a rough periodicity of the order of 400 years, thus precluding any direct relationship with the mixing rate of the atmosphere. One may ask if they can be assigned to the rate of isotopic exchange between ocean and atmosphere; that is, the variations might be postulated to reflect the addition to the atmosphere of carbon dioxide of different isotopic composition produced from volcanic and hot spring sources. This added carbon dioxide will generally be a mixture in varying proportions of carbon dioxide from limestone and juvenile carbon dioxide. The composition of juvenile carbon dioxide is not exactly known but consideration of the observed distribution of the carbon isotopes (*1*) and recent work on the isotopic composition of carbon from various thermal areas (unpublished) indicate that its composition lies somewhere between that of limestone (0 per mil) and igneous rock carbon (– 25 per mil). Moreover, the observed variations in *Sequoia* appear to be generally in the direction of becoming enriched in $C^{13}$ with respect to the two intervals of constant isotopic composition; thus we obtain the minimum amount of carbon dioxide that must be added to the atmosphere by assuming that it is purely derived from limestone with a $\delta$ value of 0 per mil. The atmospheric carbon dioxide is about – 7 per mil (*1*), and thus one must add an amount of carbon dioxide equal to at least 15 percent of the amount in the atmosphere to enrich the atmosphere in $C^{13}$ by 1 per mil; this amount corresponds to $10^{12}$ metric tons of limestone or a layer 20 km square and 1 km thick which must be decomposed in a time of the order of 200 years. Mixing dead carbon dioxide into the atmosphere should of course dilute the radiocarbon concentration and thus decrease the specific activity of material living at this time. Consideration of the radiocarbon dates obtained from samples of known age, as compiled by W. F. Libby from his work and that of others, shows that samples which grew at various intervals within the span from 1000 to 100 B.C., where the sequoia curve indicates a change in $C^{13}$ concentration of 1 per mil, fit the calculated curve of specific activity against time as well as other known samples with no indications of deviations of the order of 15 percent.

From the above considerations of the temperature coefficient of the isotopic exchange reaction and the necessary amount of material which must be mixed into the atmosphere, it would seem to be improbable that the sequoia variations can represent world-wide changes in the mean isotopic composition of the atmosphere; rather, they may merely reflect irregular variation of the isotopic fractionation factor of the tree. The natural fractionation of the carbon isotopes by plants has been discussed in detail elsewhere (*12*); it was shown in this discussion that the environmental "cyclic enrichment process" postulated by Wickman (*13*) cannot be operative in nature and that the depletion in $C^{13}$ of terrestrial plants is most probably a result of the compounding of several fractionation stages within the plant itself. Consideration of the isotopic data indicated that gaseous diffusion of carbon dioxide is probably not a rate controlling step in the assimilation sequence and that the fractionation is thus produced in one or more equilibrium stages, depending on the reversibility of the carboxylation reaction, and in the first kinetic stage after the last equilibrium reservoir of assimilated carbon, plus any other stages in which dismutation of a carbon carrier and fractional feedback occur. Isotopic selection in the respiratory process can superimpose another fractionation factor on that attained in the assimilation process, and thus the total enrichment factor may be expected to vary considerably in different plants, not only intrinsically but also because of variations in the ratio of photosynthesis to respiration which determines the net fraction of carbon retained by the plant. It is therefore not unreasonable to expect that isotopic variations of the order of magnitude of those found in *Sequoia* can result from changes in external conditions which may affect the fractionation factor attained in the assimilation process, for example by the temperature coefficient of equilibrium stage fractionation or by causing different steps to become fractionation controlling, and which may affect the overall enrichment by producing variations in the ratio of photosynthesis to respiration. Such effects could be caused by changes in light intensity, temperature, precipitation, etc., and it is not, a priori, necessary that the isotopic effects should be correlated with variations in the width of the annual rings since the individual effects of changing external factors may be weighted quite differently in the two cases.

It is clear that many more trees and more closely spaced rings from individual trees must be analyzed before any definite conclusions concerning the fine structure of such variations can be reached. The data indicate, however, that the isotopic composition of the atmospheric carbon was constant to at least 1 per mil during the 2500-year interval from 900 B.C. to A.D. 1600 with a change in mean composition probably less than 0.2 per mil. The considerations discussed above indicate that even the 1 per mil irregular variations in *Sequoia* are more probably due to the effects of varying external conditions on the assimilation and respiratory processes of the tree rather than to atmospheric changes. Future work on the cause of such variations should be worthwhile; nevertheless it should be stressed that such variations, while real enough, are of extremely small magnitude compared to the 4.5 percent variation encountered in nature. It is this aspect which is of considerable interest with respect to the application of what may be called "natural" isotopic tracer and dilution techniques to geochemical problems, and which will be discussed in this respect elsewhere.

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