Temperature Dependence of Isotope Ratios in Tree Rings

(oak tree/weather records/climate)

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ABSTRACT The stable isotope ratios of carbon, oxygen, and hydrogen have been measured for a German oak in wood samples of roughly three years each, for the years 1712–1954 A.D., and correlated with the existing weather records from England, Basel, and Geneva to evaluate the empirical temperature coefficients. Isotope ratios in a second official oak, measured for the years 1530–1800 A.D., show the cold temperatures of the Little Ice Age interspersed with warm intervals.

Information on climate may be stored in bio-organic deposits. In particular, tree rings may provide a record of climate for the last few thousand years. Variations in air temperature cause variations in the stable isotope ratios in the new wood as it grows. An additional variable is the temperature of formation of precipitation that nourishes the tree.

Stable isotope ratios in land plants depend on several temperature-dependent functions. To evaluate their temperature coefficients, we need to know the isotope ratios in atmospheric CO_2 and in rainwater that nourishes the plants. There is good reason to believe that atmospheric CO_2 has remained unchanged for a long time, say millions of years, so this is not an unknown. Also, the isotope ratios in precipitation have been studied over the world's surface for the last 15 years and have been reported in the data compilations of the International Atomic Energy Agency. So we know the percent of $^{18}O/^{16}O$ and D/H in rainwater as a function of altitude and latitude and longitude of the surface of the earth. These ratios may have undergone variations in the past caused by changes in the global temperature (1).

The equilibrium temperature coefficients of the stable isotopes of H, C, and O in cellulose (trees being 69% cellulose, the remainder being mainly lignin) have been found by calculation to be large enough so that variations of a few degrees in air temperature should cause measurable effects (2). In general, however, the observed effects may be expected to be larger than the equilibrium effect, the latter depending on the difference of the rates for the forward and back reactions. It is known that, at least for $^{13}C/^{12}C$ in marine plankton (3, 4) and for D/H in peat (5), the measured coefficients are approximately equal to the computed values. Until now, the temperature coefficients in trees have not been measured.

Anyhow, because of variations in $^{18}O/^{16}O$ and D/H ratios in precipitation, the stable isotope thermometers in trees must be calibrated; namely, the observed variations in rings formed in the last few hundred years must be compared with the official weather records of variations in air temperature in the neighborhood of the tree, to yield empirical values for the

Abbreviation: ppt, parts per thousand.

changes in isotope ratios per degree Centigrade change in temperature. Numerical air temperatures have been recorded at best for no more than about 300 years in Europe, and for only about 100 years in America. Of course, the temperature records and the recently formed tree rings may be perturbed by local climate changes caused by increasing heat and air pollution of the cities growing up around the existing weather stations and around the trees. Also, the introduction of fossil fuel CO_2 (Suess effect) is expected to perturb the $^{13}C/^{12}C$ ratios in rings grown after 1890.

In the present paper are reported measurements of $^{13}C/^{12}C$, $^{18}O/^{16}O$, and D/H in the rings of an oak that grew in Aalen, Germany, 10° 11′ east, 48° 50′ north, about halfway between Mannheim and Munich, from 1700 to 1965 A.D. Its rings were dated at the Forest Botanical Institute, University of Munich, by comparison with the official oak-tree chronology developed at Stuttgart (6). Air temperature records (7) exist for nearby Basel since 1755, for Geneva since 1768, and for England (8) from 1698. The measured isotope ratios as a function of tree-ring data have been compared with these official temperature records for 1712–1954 A.D. using the dated tree-ring sequence to determine the corresponding age of the tree rings in years. In this way, temperature coefficients of the stable isotope ratios have been evaluated, as a phenomenological effect. The stable isotope ratios have also been measured in a second official oak dated by the Munich laboratory for the years 1530–1800 A.D., for most of which period no records of air temperatures exist from mercury thermometers.

EXPERIMENTAL

In a 2 inch (5.1 cm) thick slice cut across the tree, a groove $^1/_3$ inch (0.84 cm) wide and $^1/_3$ inch deep was milled perpendicular to the tree rings, that is, along a radius of the tree, from the innermost (oldest) part of the tree out to the bark. Each time that the milling tool had moved $^1/_3$ inch, the sawdust produced was collected into an individual vial with the aid of a camel's hair brush. Each sample consisted of sawdust from 3 or 4 rings, depending on the variations in ring widths, the total number of samples being 68 for the time span 1712–1954 A.D.

The stable isotope ratios were measured in the sawdust samples by mass spectrometry. The spectrometer has a very small quartz manifold, by volume about 100 cm³. About 5 mg of sawdust were used for each measurement. The chemical reactions used were as follows:

(a) For measurement of $^{13}C/^{12}C$, the sawdust was burned to completion in oxygen gas, yielding CO_2.

(b) For measurement of $^{18}O/^{16}O$, $HgCl_2$ + sawdust yields CO_2

gas (9) when heated; HCl is removed with a quinoline trap.

(c) For measurement of D/H, sawdust is heated with powdered uranium, to yield H_2.

For each measurement, the amount of reagent used was much larger than needed for 5 mg of sawdust, to insure that the reaction was complete so that there would be no fractionation. The residue was inspected, after cooling, for the same reason. The measured variations are expressed in the form:

$$\delta_{13} = \left\{ \frac{(^{13}C/^{12}C) \text{ sample}}{(^{13}C/^{12}C)_0} - 1 \right\} \times 1000$$

$$\delta_{18} = \left\{ \frac{(^{18}O/^{16}O) \text{ sample}}{(^{18}O/^{16}O)_0} - 1 \right\} \times 1000 \quad [1]$$

$$\delta_D = \left\{ \frac{(D/H) \text{ sample}}{(D/H)_0} - 1 \right\} \times 1000$$

The normalizing ratios $(^{13}C/^{12}C)_0$, $(^{18}O/^{16}O)_0$, and $(D/H)_0$ have been chosen arbitrarily as the measured ratios for the years 1712–1714 A.D. The sapwood of the oak extended over about 30 tree rings. Thus, for about 30 years each tree ring was bathed in flowing sap from ground water. Consequently, it is to be expected that oxygen in the alcohol groups of cellulose, its modular formula being $(HCOH)_n$, is exchanging with sap water, and thus that the stable isotope ratio of oxygen in each ring is averaged over about 30 years (10). There is less reason to believe that carbon in the wood is exchanging with carbon dioxide dissolved in sap, but it has not been proven that there is no exchange (11). On this account, the measured isotope ratios are reported in the form of a running average over nine samples at a time, namely, as an average over the time that a given ring is sapwood. Winter air temperatures, from official weather records, were averaged in the same way because of the large fluctuations from year to year in air temperature. Temperatures for January, February, and March show the major increase since the Little Ice Age (1440–1850 A.D.), whereas the summer temperatures then were not much different from now (12). So the average yearly temperatures vary in the same way as the average temperatures of January, February, and March, but with a somewhat smaller amplitude. Oak trees make the greatest growth of the year in early spring when the ground thaws and the winter's accumulation of precipitation melts, so it seems reasonable that they will be sensitive to late winter temperatures, especially for isotopes of oxygen and hydrogen, which come from the melt water and depend on the temperature at which precipitation formed.

The carbon ratios (δ_{13}) for the years 1890–1950 A.D. have been corrected for fossil carbon production (Suess effect); the maximum correction, that for the year 1950 A.D., was taken as $+8.4\%$ or a maximum increase of $+2.1$ parts per thousand (ppt) in δ_{13}. This correction was estimated as follows. In wood from rings of 1920 A.D. two radiocarbon dates were measured by Dr. Rainer Berger, U.C.L.A., as 375 ± 35 years old with respect to 1950 A.D., whereas the actual age is 1950–1920 = 30 years, corresponding to 4.2% dilution of atmospheric ^{14}C O_2 by inert CO_2 produced by man's burning of coal and oil up to 1920. In 1950 the correction for ^{14}C at this particular place should be 8.4% and the correction for ^{13}C dilution in atmospheric CO_2 therefore should be 8.4% of 25 ppt or 2.1 ppt. (See further discussions in ref. 13.) The ratios and temperatures were correlated by least squares analysis, expressing

TABLE 1. *Temperature coefficients computed from measured isotope ratios and weather records*

Isotope ratio	Temperature coefficient	No. of samples
$^{18}O/^{16}O$	$+ [(5.29 \pm 0.68)T_{England}]$ppt/°C	68
	$+ [(2.91 \pm 0.41)T_{Basel}]$ppt°/C	56
	$+ [(2.86 \pm 0.52)T_{Geneva}]$ppt/°C	56
$^{13}C/^{12}C$	$+ [(2.73 \pm 0.67)T_{England}]$ppt/°C	68
	$+ [(2.01 \pm 0.37)T_{Basel}]$ppt/°C	56
	$+ [(2.37 \pm 0.41)T_{Geneva}]$ppt/°C	56
D/H	$+ [(89.5 \pm 16.0)T_{England}]$ppt/°C	68
	$+ [(67.4 \pm 6.4)T_{Basel}]$ppt/°C	56
	$+ [(71.4 \pm 8.2)T_{Geneva}]$ppt/°C	56

Experimental temperature coefficients were computed by correlating the isotope ratios with official average winter temperatures (averaged over January, February, and March).

the ratios in the form,

$$\delta = a + bT \quad [2]$$

and evaluating the coefficients a and b, (a is the value of δ at $T = 0$, b is the temperature coefficient). The numerical value of b is shown in Table 1. Measured ratios are plotted in Fig. 1a and b. In a manner of speaking, trees store old rainwater. To the isotope fractionation caused by evaporation of water vapor from the oceans and precipitation as rain, the tree adds a further fractionation caused by absorption of ground water into the salt and sugar solutions in the root system, and by manufacture into cellulose and lignin. The combination of these processes appears to have produced large effects in this first tree.

In the second tree, the isotope ratios all indicate (Fig. 2) that the Little Ice Age was colder than now and that there were warm periods in 1650, 1570, 1730, and 1790. Judging from the warm period at 1730, the temperature coefficient for carbon appears to be the same as in the first oak but those for oxygen and hydrogen are half as large. This could be accounted for if for the second oak the water supply was half from new precipitation and half from long-stored ground water. Actually, nothing is known of the water supply of the second oak, whereas the water supply of the first oak was completely from new precipitation. Judicious selection of old trees for further climate study with regard to the source of their water supply seems indicated.

YEARLY FLUCTUATIONS, SIGNAL "NOISE"

Yearly variations of $^{13}C/^{12}C$ in atmospheric CO_2 resemble a sine function with a few parts per thousand peak-to-peak amplitude; the amplitude may be geographically dependent (14). All available data on this seasonal variation appear to show depletion of ^{13}C in the winter, enhancement in summer, and the greatest rate of change in spring and fall. Thus, if spring comes early or late, namely, if the tree begins its major growth of a new ring early or late with respect to the inflection point of the sine curve, the $^{13}C/^{12}C$ ratio in the new wood may be depleted or enhanced with respect to the average ratio.

One expects that similar yearly variations occur for $^{18}O/^{16}O$ in atmospheric CO_2. For comparison it is known that there is a similar seasonal variation (15) both for $^{18}CO/^{16}CO$ and for $^{13}CO/^{12}CO$ in the atmosphere of a few parts per thousand.

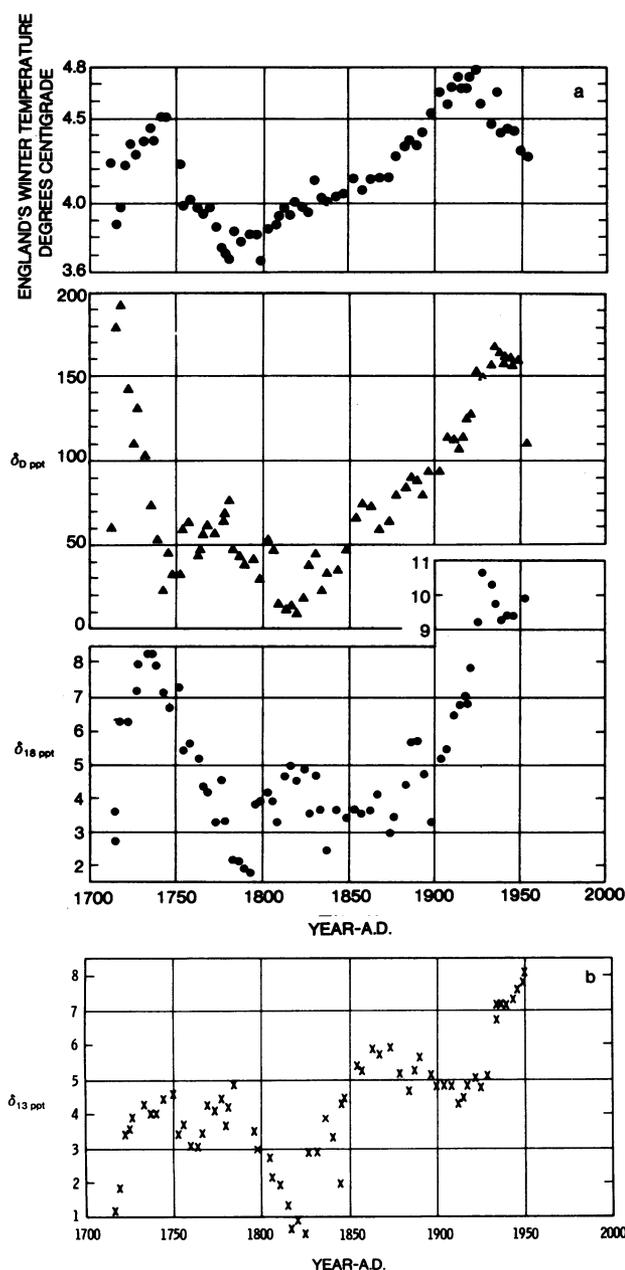FIG. 1. (a and b) Plots of δ_{18}, δ_{13}, δ_D, and winter temperatures against date for first oak.

related to average air temperatures at ground level. At higher latitudes where trees make a rapid spring growth consuming the melt water from accumulated winter snow, both that on the surface of the ground and that stored in the soil as winter frost, the new tree ring contains oxygen whose isotope ratio represents an average over the winter-time precipitation. If the winter has been colder than average, the melt water is depleted in ^{18}O, and if warmer than average, then it is enriched, to the degree of several parts per thousand. Study of the IAEA data shows that δ_{18} is independent of total rainfall.

Comparison of a plot of δ_{18} against δ_D in tree rings with that in precipitation shows that the slope of 8 for precipitation no longer obtains, probably because the rates of exchange of D and ^{18}O between cellulose and sap are quite different from each other. (Thus, it may be now possible to study dynamic physiology of trees, as a research independent of the study of climate.)

CONCLUSION

Every kind of thermometer has to be calibrated. The stable isotope ratios in wood depend partly directly, partly indirectly on the temperature at which it was manufactured. The present paper reports the phenomenological calibration of the oxygen, carbon, and hydrogen isotope ratios in a European oak. The long-term increase in air temperatures from the Little Ice Age to the present offered the opportunity to make this calibration. In each case the measured temperature coefficients are larger than those computed, assuming the wood to have been manufactured in equilibrium with CO_2 and H_2O, as is to be expected because kinetic effects, no doubt, play a role, and because in formation of precipitation used in the manufacture of cellulose the temperature coefficients of ^{18}O and D are large and positive. In this first attempt to study isotope thermometers in tree rings, we have lumped the temperature coefficients for cellulose manufacture with the temperature coefficients for precipitate formation for an evaluation of the overall phenomenological coefficient. We realize that many problems must be solved for a better understanding of these effects, that woody material must be grown under controlled conditions for evaluation of the temperature coefficient of cellulose manufacture, that other oaks must be compared with these oaks, and that oaks should be compared with other kinds of trees. By use of the measured temperature coefficients of these thermometers and by use of measured isotope ratios in chronologic sequences of tree rings manufactured before 1712, it now may be possible to evaluate the European climate from the centuries before the advent of mechanical thermometers (17). Use of more than one thermometer increases the likelihood that temperature effects are being observed. Other isotope thermometers in tree rings, namely nitrogen and sulfur, should also have measurable temperature coefficients.

However, the year to year variations in the oxygen isotope ratio in atmospheric CO_2 are probably less than the variations in rain and snow. Namely, at any given geographical place, the $^{18}O/^{16}O$ ratio in rain water varies by some 10 ppt during the year (16), even fluctuating by several parts per thousand month by month and day by day, depending on the temperatures at which sea water evaporated and at which the precipitation formed and, therefore, on the altitude of the clouds. In Fig. 3 are plotted (from ref. 16) the oxygen and hydrogen isotope ratios observed in precipitation at a world-wide network of stations and in Antarctic ice. The linear relation between δ_{18} and δ_D is an exact function of temperature in the troposphere, but its dependence on air temperature at ground level is valid only on the average, indicating that the average air temperatures aloft where precipitation is formed are cor-

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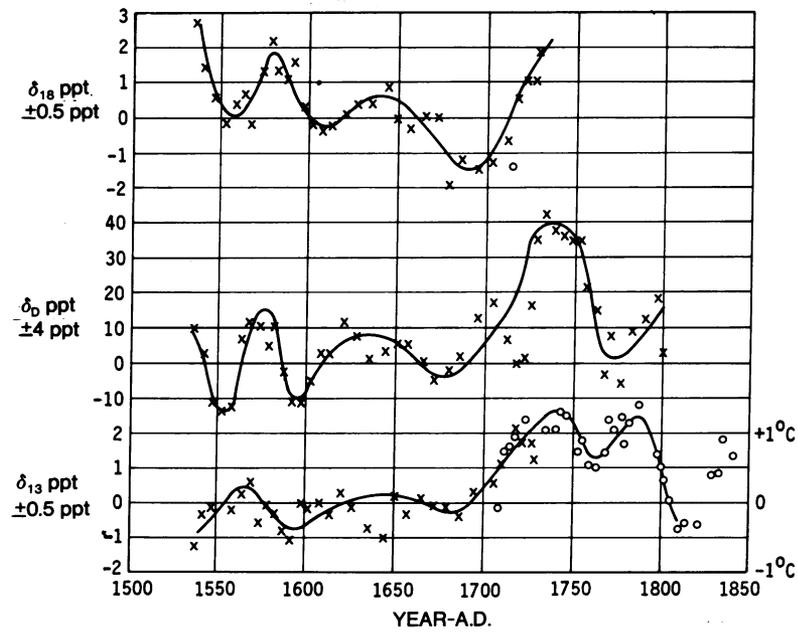
FIG. 2.   Plots of δ_{18}, δ_{13}, and δ_D against date for second oak.

(1953 – 1963)
INTERNATIONAL ATOMIC ENERGY AGENCY, VIENNA, 1969
ENVIRONMENTAL ISOTOPE DATA NO 1; WORLD SURVEY
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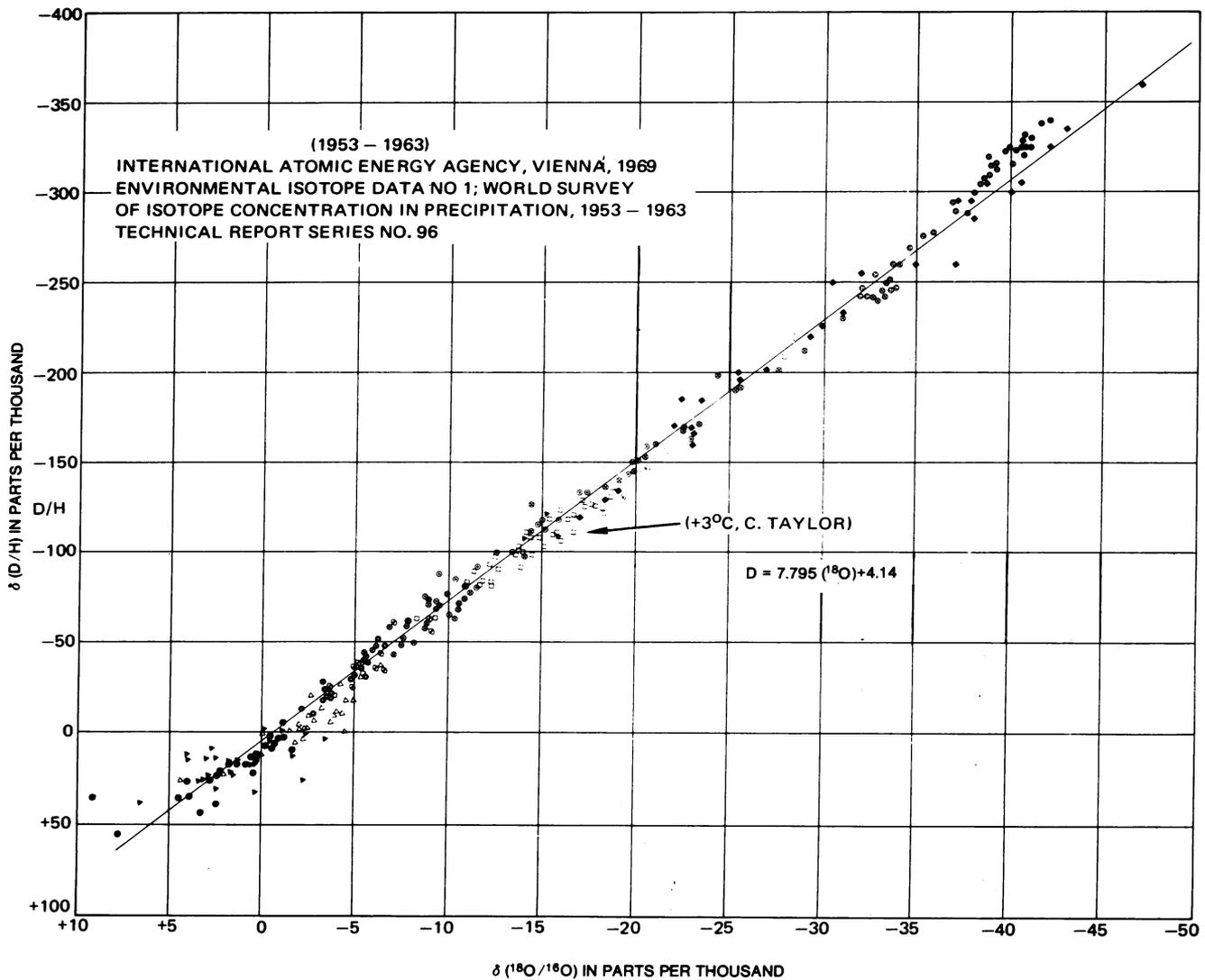(+3°C, C. TAYLOR)

$D = 7.795 \, (^{18}O) + 4.14$

FIG. 3.   Plot of δ_D against δ_{18} in world-wide precipitation using data from ref. 16.

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