

ON THE CLIMATIC INTERPRETATION OF THE HYDROGEN ISOTOPE RATIOS IN RECENT AND FOSSIL WOOD

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SUMMARY. - The deuterium/hydrogen ratio of carbon-bound hydrogen in tree cellulose is principally determined by the deuterium content of the precipitation, the isotopic enrichment in the leaves and the biochemical fractionation involved in the synthesis of cellulose.

Measurements of δD values on recent and fossil wood of *Pinus sylvestris* L. from the Cairngorm mountains (Scotland) suggest a predominant influence of relative humidity on the overall fractionation. If this conclusion is confirmed, it will prove possible to use the deuterium content in fossils to detect pluvial periods.

INTRODUCTION.

The measurement of stable isotopes, more particularly oxygen - 18, in polar ice sheets and in carbonates deposited on the ocean bed, have for some time been providing information on the complex problem of climatic change.

However, isotopic studies on organic matter of continental origin are rare. This paper deals with the possible relationship between the deuterium content of tree cellulose and climatic factors. Present research shows that this relationship is not as simple as was once thought.

PRINCIPLES OF ISOTOPIIC FRACTIONATION.

Most elements occur in nature as a mixture of stable isotopes. Water, for example, consists approximately of the following mixture (DANSGAARD, 1964) :

+	997680 ppm H ₂ O	mass 18
+	320 ppm HDO	mass 19
+	2000 ppm H ₂ ¹⁸ O	mass 20

The heavier HDO molecules have a greater bond energy than the lighter H₂O molecules. As a result HDO is found preferentially in the condensed phase. The ratio of D/H in both phases (liquid and vapour) depends solely on temperature, whereby isotope fractionation increases with decreasing temperature. This process is called equilibrium fractionation.

The heavier HDO molecules are also less mobile, which means that their diffusion rate within a medium is smaller, compared to H₂O. This results in a kinetic fractionation effect, depending on the turbulence of the medium.

In most situations both fractionation processes occur simultaneously.

The isotopic fractionation factor a , between phases or substances A and B, is given by

$$a_{A-B} = \frac{[D/H]_A}{[D/H]_B}$$

when $a > 1$ enrichment occurs
 $a < 1$ depletion occurs

Because isotopic effects are small, and a close to unity, the notion fractionation, symbol ϵ , is often used.

$$\epsilon = (a - 1) \times 10^3 \text{ (‰)}$$

The measured isotopic ratio is expressed relative to an international standard, i.e. the V-SMOW waterstandard, as defined by CRAIG (1961).

$$\delta D \text{ (in per mil)} = \frac{R_{\text{sample}} - R_{\text{standard}}}{R_{\text{standard}}} \times 1000$$

where $R = \frac{[D]}{[H]}$

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EXPERIMENTAL METHOD :
TREE CELLULOSE AS D/H INDICATOR.

In comparison with peat, which consists of a mixture of many plant species, recent and fossil wood has the advantage that one can make measurements on a single plant species. Although both can be dated by the ^{14}C method, wood from temperate regions can be easily analysed for individual years, due to the presence of annual tree rings. If necessary, early wood and late wood (formed in spring and summer respectively) can be analysed.

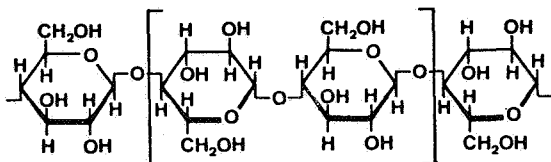


Fig. 1. Chemical structure of cellulose.

One single chemical component of the wood is measured, more particularly cellulose (fig. 1). This is done because the different chemical constituents of wood, varying in relative proportions, have been shown to be isotopically different (EPSTEIN *et al.*, 1976). Cellulose has moreover the advantage that it is also common to non-lignified plants and thus constitutes an universal measurable component.

The isolation of α -cellulose from the raw wood sample (+ 200 mg) is accomplished by extraction of the resins and lipids in an azeotrope toluene-ethanol mixture, oxidation of the lignin by means of NaClO_2 and removal of the hemicellulose by NaOH . As the hydroxyl groups in cellulose are exchangeable with water in time, the α -cellulose is nitrated to obtain only the non exchangeable carbon-bound hydrogens. After a total combustion of the cellulose to H_2O , CO_2 and nitrogen oxides, the water is reduced to hydrogen gas over zinc at ca. 380°C . The D/H ratio of the hydrogen gas is finally measured in a stable isotope mass spectrometer.

FACTORS INFLUENCING THE D/H RATIO IN TREE CELLULOSE.

Deuterium fractionation takes place at different levels before its final incorporation into the cellulose (fig. 2).

1. Fractionation in Precipitation.

Precipitation water is taken up by plants by means of their roots. The deuterium content of precipitation decreases from the equator towards the poles. Both air temperature and trajectory of the air masses are factors controlling the δD content of precipitation. A temperature gradient for temperate regions of $\pm 5\%$ per $^\circ\text{C}$ is found (VAN DER STRAATEN, 1981; YAPP and EPSTEIN, 1982a). SCHOCH *et al.* (1983) noted that precipitation from northern air masses is more depleted in D than those from southern air masses.

It is still an open question whether past changes in climate and air masses had

the same impact on the δD content of precipitation as in recent times. A study by RUDOLPH *et al.* (1983) on the relationship between δD and noble gases in fossil waters older than 15000 B.P. suggests a more gradual temperature gradient than at present.

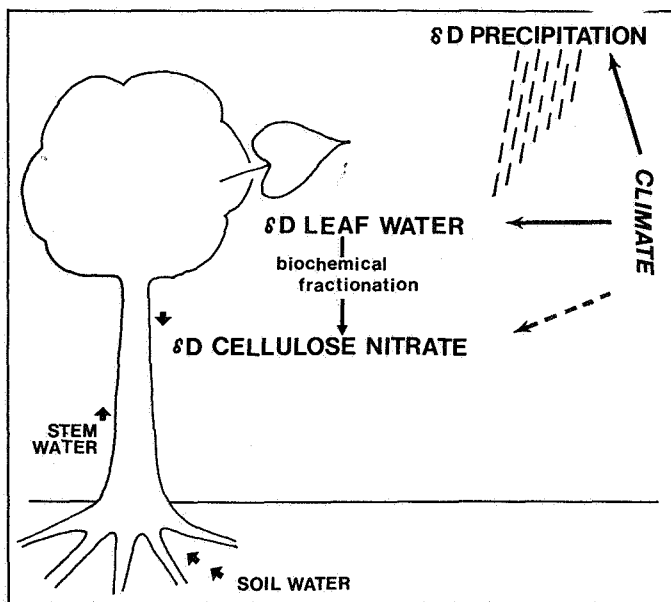


Fig. 2 - Schematic representation of the impact of climate on the deuterium fractionation (δD) involved in the formation of tree cellulose.

2. Fractionation in Leaves.

Because no significant fractionation occurs during the uptake of water by the roots and its transport through the xylem (WERSHAW *et al.* 1970; FORSTEL *et al.* 1974), the water arriving at the leaves has still the same δD content as the precipitation water. Complications may arise when a significant fractionation of the rain-water occurs before uptake by the plants, due to evaporation, or mixing of the precipitation water with soil water of different isotopic composition.

However it is in the leaves that the water becomes strongly enriched relative to the precipitation water, i. e. up to 45 ‰ (BRENNINKMEIJER, 1983).

If one considers a tree leaf as an evaporating water-reservoir with an input of liquid water and an output of water vapour, in a steady-state condition, the following model is obtained (CRAIG and GORDON, 1965; YAPP and EPSTEIN, 1982).

$$\delta D_L = a_e a_k (1-h) (1000 + \delta D_r) + a_e h (1000 + \delta D_a) - 1000 \quad (1)$$

where δD_L = δD of leaf water

a_e = equilibrium fractionation factor

a_k = kinetic fractionation factor

h = relative humidity, ranging from 0 to 1

δD_r = δD of water taken up by the roots

δD_a = δD of atmospheric water vapour.

As mentioned before, a_e depends solely on the temperature with reported values at 20°C and 25°C of 1.0852 and 1.0793 respectively (MAJOUBE, 1971).

The kinetic fractionation factor a_k depends on the degree of turbulence of the air layer through which the diffusion takes place, and hence explaining its dependence on wind rates. Measured values for static conditions are 1.025 (MERLIVAT, 1978) or 1.021 (MAGENDANS, 1981) and for turbulent conditions 1.015 (VAN DER STRAATEN, 1981).

Equation (1) shows the importance of the relative humidity on δD of the leaves. Increasing relative water content of the air results in lower deuterium values of the leaf water.

3. Biochemical Fractionation.

Little is known about this kind of fractionation. Sugars synthesized in the leaves are translocated through the phloem to the cambium meristem of the stem, where they are linked together forming cellulose as a constituent of the cell wall. These transport processes and biochemical reactions lead to a depletion of cellulose up to -50 ‰ relative to the leafwater (BRENNINKMEIJER, 1983). The biochemical fractionation appears to be more or less constant, although a small temperature affect cannot be ruled out.

A CASE STUDY : D/H RATIOS IN RECENT AND FOSSIL PINE TREES ON A SLOPE IN THE CAIRNGORM MOUNTAINS, N.E. SCOTLAND.

To interpret δD values in fossil wood it is necessary to compare these data with δD data of recent wood from the same area. Moreover, knowledge of the factors influencing the δD content in a particular area is of great importance. Indeed it is quite possible that in one area temperature is the overriding factor, whereas at another site other factors are predominant.

As a study-area we chose a north-facing slope of the Cairngorm mountains (max. 1300 m) in the Northeast of the Scottish Highlands. The area is particularly prone to strong winds and the relative humidity increases rapidly with altitude (DYBECK and GREEN, 1955; PEARS, 1966). Nowadays adult pine trees (*Pinus sylvestris* L.) are found up to + 500 m. At higher altitudes, only seedlings occur. Fossil pine stumps however are found to an altitude of 730 m (fig. 3). As the sequence of fossil wood extends back to about 7000 BP (VANHOORNE *et al.*, 1976, 1977, 1978) a δD record for this time-interval can be established.

In order to interpretate the fossil data, cellulose of recent trees and seedlings was analysed for its deuterium content (δD_C).

The δD_C values for the trees are plotted against altitude in fig. 4. The dots represent adult trees (mean of four directions) while all other symbols represent seedlings above the tree-limit. If the \blacklozenge and \blacktriangle data are eliminated a linear regression of $\delta D_C = -0.14 m + 0.02$ is

obtained. The linear correlation coefficient $r = -0.96$. The aberrant data coincide with extremely windy sites (\blacktriangle) or more sheltered sites (\blacklozenge).

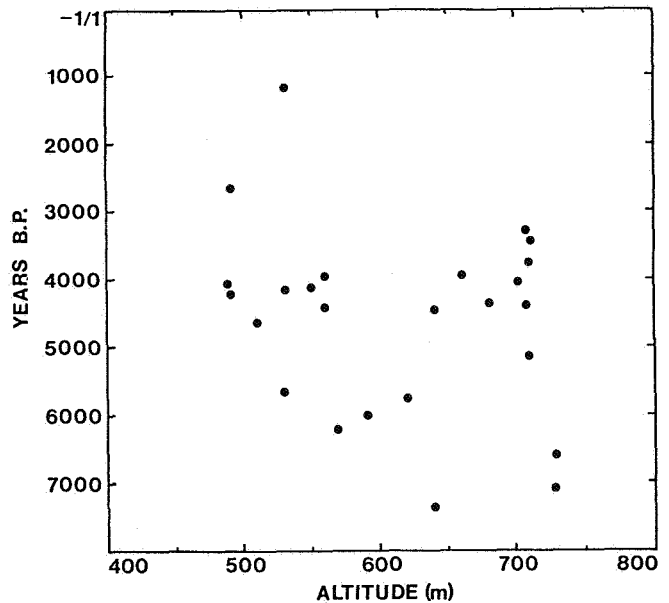


Fig. 3 - Radiocarbon datings (dated by ANTW and IRPA) of fossil pine stumps from the Cairngorms plotted against altitude.

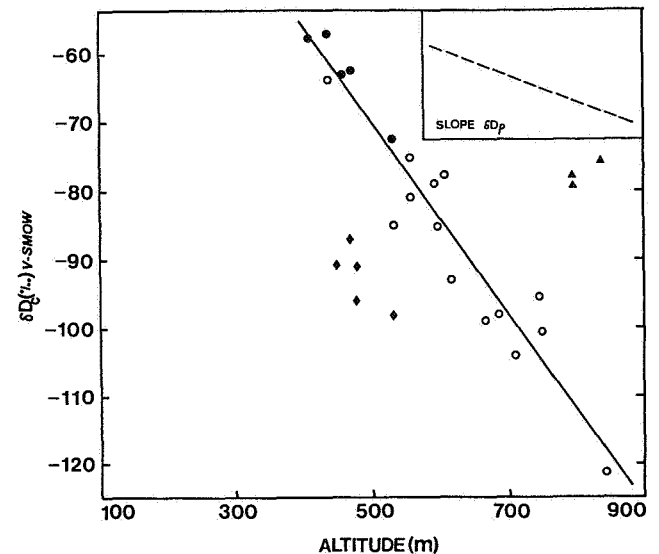


Fig. 4 - A plot of the δD_C values of the nitrated tree cellulose against altitude. Dots represent adult trees, all other symbols represent seedlings (see text). The line is a least squares fit for the data indicated by dots and circles. The correlation coefficient is -0.96 . In addition the slope of δD_P (precipitation) is plotted, assuming a decrease of δD_P with altitude of -4‰ per 100 m.

The small number of measurements of D/H on environmental water carried out so far are insufficient to determine the absolute fractionation between deuterium in precipitation and cellulose (DUBOIS, 1984).

However it is possible to estimate its relative relationship. Taking into account the maximum reported value of decrease of δD_p (precipitation) with altitude, i.e. $-4\text{‰}/100\text{ m}$ (SIEGENTHALER and OESCHGER, 1980) and our value of δD_c (cellulose nitrate) of $-14\text{‰}/100\text{ m}$, we obtain a slope of $3.50\text{‰}/\delta D_c/\delta D_p$ instead of the 0.91‰ of EPSTEIN's linear regression (YAPP and EPSTEIN, 1982b) obtained from trees growing throughout the North American continent.

These results indicate that in this mountainous area the isotopic composition of the precipitation water is not the primary factor controlling the D/H ratio in tree cellulose. The high slope in Fig. 4 can be explained by the increase of the relative humidity with altitude in this area, effecting a decrease in deuterium content of the leaf water and thus of δD_c . Aberrant results can be attributed to a wind affect, modifying the local relative humidity.

Therefore we feel that in this area temperature is not the factor with which to correlate fossil δD values, but rather the relative humidity, which in turn is related to rainfall. This seems to be confirmed by the first fossil results, which will be published elsewhere. Obviously further study should be aimed at resolving the interpretation of stable isotope measurements in order to gain a better understanding of palaeoclimatic change.

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