

# Reports

## Deuterium Content of Peat as a Paleoclimatic Recorder

**Abstract.** During the transformation of vegetable matter into peat the initial deuterium concentration decreases systematically with increasing carbon content. From this relationship the original deuterium content of the plants that formed the peat in Dutch peat bogs can be derived, and the values obtained can be correlated with past summer temperatures in the Netherlands.

The natural deuterium content of organically bound hydrogen in plants is correlated with that of precipitation (1). Furthermore, the deuterium content of precipitation mainly depends on the climate and decreases with decreasing annual mean temperature (2). This is explained by the model proposed by Epstein (3), in which precipitation is treated as a Rayleigh condensation process on a global scale. As a consequence, the deuterium content of recent plants is closely related to the climate. A similar dependence on climate may therefore be expected for the deuterium concentration in

subfossil plant material such as peat. In order to check this conclusion experimentally, the natural deuterium abundance in <sup>14</sup>C-dated peat samples (4) from different climatic periods has been analyzed.

The accurate determination of the relative D:H ratio was performed with a mass spectrometer specially equipped for the purpose (5). A commercial Varian isotope-ratio instrument, type M 86, which has an accuracy of better than 1 per mil, was used. The peat samples had to be converted to hydrogen gas for analysis, and this was done by combusting the samples to carbon

dioxide and water. Subsequently, the carbon dioxide was separated from the water, which was then reduced over hot zinc to hydrogen gas. The technique for preparing samples is described elsewhere (1). The overall accuracy in measurement is only about  $\pm 2$  per mil since the various steps in the sample preparation introduce additional errors. The results are reported in per mil deviation from standard mean ocean water (SMOW) (6). A negative  $\delta^D$  value means that the hydrogen in the sample contains less deuterium than the standard, and vice versa.

The chemical transformation of plant debris to mature peat is effected by microbial agents, chiefly bacteria and fungi. This change is accompanied by an increase in carbon content of the organic substance, which fact is used to characterize the degree of decomposition (7). Furthermore, isotope fractionation can occur during the various stages of peat development, and there also might be a correlation with age.

In order to investigate this, peat samples deposited during the last 9000 years were analyzed. In this time range climatic changes were relatively small compared to those during glacial times, so that the influence of climate would be of minor importance.

The deuterium content of Holocene peat samples is plotted against their carbon content in Fig. 1. The deuterium concentration decreases with increasing carbon content of the peat but is not directly correlated with age (the age is given in parentheses for some samples). Chemical change is thus the only factor responsible for the systematic decrease in the deuterium content of peat, the change in the deuterium being 2.8 per mil for 1 percent change in the carbon content. From 50 percent (original plant material) to 63 percent (mature peat) carbon concentration, the total deuterium depletion is thus about  $-34$  per mil. The relation is valid for different types of Dutch peat. For peat in South Africa (Pretoria) a similar relation seems to hold, with the difference that the line is now shifted to a  $\delta$  value that is 18 per mil higher as a consequence of the warmer and semiarid climate at this locality.

The deuterium-carbon dependence can be expressed generally by the empirical formula

$$\delta(\text{peat}) = -2.8 C + T \text{ (per mil)} \quad (1)$$

Table 1. Relative deuterium concentration in different types of peat and *Pinus* wood samples of various ages. The first ten samples are used to establish a relation (Eq. 1) between the carbon concentration and the deuterium content (the carbon content is given on a dry ash-free basis). The last column gives the deuterium content of the original plant material as derived from Eq. 1.

Locality	Sample	Age (years)	Carbon (%)	$\delta^D_{\text{SMOW}}$ (per mil)	$\delta^D_{\text{corr}}$ (per mil)
<i>Netherlands</i>					
Groningen	Tree branches (average)	Recent	50.0	-63	-63
Lathem	Peat	2,000	51.3	-72	-68
Schoorl	Peat	2,500	60.2	-93	-64
Emmen	Peat (moss)	2,500	52.8	-80	-72
Schippluiden	Peat	3,400	56.1	-76	-59
Emmen	Peat (Hypnaceae)	5,100	62.4	-98	-64
	Peat (moss)	5,100	60.3	-95	-66
	Peat (Hypnaceae)	6,000	59.7	-87	-60
	Peat (Hypnaceae)	6,800	63.4	-102	-65
	Peat	8,500	61.0	-90	-59
	Peat (forest)	10,000	61.0	-101	-70
	Peat (moss)	11,200	54.2	-87	-75
Denekamp	Peat	11,600	56.3	-99	-81
Peelo	Peat	33,500	52.5	-103	-96
Amersfoort	Peat	>52,000	49.5	-64	-64
Groningen	Branch ( <i>Pinus</i> )	Recent	50.0	-51	-51
Emmen	Stem ( <i>Pinus</i> ) A2*	5,000	50.2	-47	-47
	Stem ( <i>Pinus</i> ) C4	5,000	51.0	-57	-54
	Stem ( <i>Pinus</i> ) B2	6,000	53.8	-37	-26
	Stem ( <i>Pinus</i> ) D2	6,200	55.0	-68	-54
	Stem ( <i>Pinus</i> ) D°1	7,000	56.1	-56	-39
<i>Belgium</i>					
Zelzate	Peat	12,300	55.2	-97	-82
<i>South Africa</i>					
Pretoria	Tree branches (average)	Recent	50.0	-46	-46
	Peat	440	58.2	-72	-45
	Peat	5,200	61.5	-81	-45

\* The numbers refer to the stumps as described in (9).

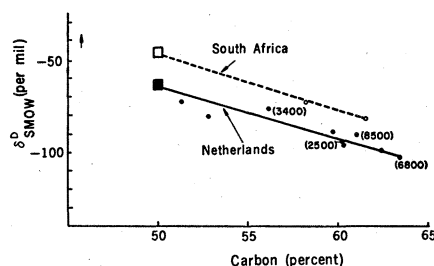


Fig. 1. Decrease of the deuterium content of peat with increasing carbon content. The age of a peat sample (indicated for some samples in parentheses) has no bearing on the deuterium-carbon relation. Two peat samples from Pretoria fall on a line with a slope similar to that for the Dutch peat samples. The filled and open squares represent the average  $\delta$  values for wood from the Netherlands and Pretoria, South Africa, respectively.

where the factor  $-2.8$  is the characteristic constant for the chemical change and does not seem to depend on the type of peat, the climatic conditions, or the age;  $C$  denotes the carbon concentration and varies between 50 and 63 percent. The additive constant  $T$  depends on the climate and the orographic situation of the sampling area. For Dutch peat  $T = +77$ , and for South African peat  $T = +95$ .

Equation 1 implies that the measured  $\delta$  value of peat can be used to determine the original isotopic composition of the plant material by means of the carbon concentration. In this manner a direct comparison of the isotopic composition of recent and ancient plants becomes possible.

There is, however, one problem. The average carbon content of recent biogenic material normally varies between 49 percent and 51 percent in well mixed samples. In extreme cases, such as the selective accumulation of spores or leaves, the carbon concentration can deviate even more. Such samples, which can be identified by inspection of the material, should be excluded for this purpose, unless all the relevant parameters can be determined on the same recent material. In the case of wood, the recent carbon content of a certain species can be determined more accurately, and the result can be used as the basis for a correction for fossil wood of the same species. Nevertheless, an uncertainty of  $\pm 1$  percent in the initial carbon concentration of the fossil material remains possible and confines the accuracy of the correction to about  $\pm 3$  per mil, as deduced from Eq. 1. The initial values deduced by means of Eq. 1 are listed in Table 1, last column.

The mean deuterium composition of the first nine peat samples in Table 1, reduced to the original  $\delta$ -value ( $-64$  per mil), is approximately the same as the average for recent wood in the area. Deviations from this average were probably caused by climatic fluctuations, since a similar isotopic pattern was observed by Dansgaard *et al.* (8) on an ice core from Greenland. Samples older than 10,000 years were formed during the interstadials of the Last Ice Age, when it was considerably cooler than at present. These samples show a lower initial deuterium content. The maximum depletion effect observed is  $-33$  per mil in a Dutch peat sample formed just when the Denekamp interstadial set in.

The deuterium depletion in peat during colder periods (corrected for chemical change) should reflect the decrease in temperature, as is the case for precipitation (2). The temperature variation (mean July temperature) during the last glacial stage in the Netherlands could be established by pollen analyses on peat samples (9) so that a comparison between the isotopic composition of peat and the temperature is possible. Figure 2 shows a good relationship between the original deuterium content of peat and the temperature. It can be described mathematically by

$$\delta_{\text{corr}}(\text{peat}) = 3.2 t - 116 \text{ (per mil)} \quad (2)$$

where  $t$  is the mean July temperature in the Netherlands in centigrade degrees.

The filled square in Fig. 2 represents the present average deuterium value for wood in the Netherlands. The open circle is the present mean deuterium value for wood in Pretoria (mean January temperature). This value cannot be interpreted in terms of Epstein's model since Pretoria is situated in the zone where the bulk of moisture evaporates from the oceans. The point at  $17.8^\circ\text{C}$  represents the period from 2000 to 8500 years ago, when the average temperature was a little higher than at present. The value at  $18.7^\circ\text{C}$  was derived from five *Pinus* wood samples (5000 to 7000 years ago) (10), corrected for the systematically higher deuterium values ( $+12$  per mil) of the genus *Pinus* with respect to the average for wood (see Table 1).

A uniform drop in temperature over the whole globe should not basically change the distribution of deuterium in precipitation, apart from a possible

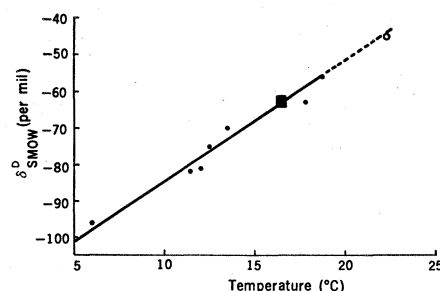


Fig. 2. Deuterium concentration in Dutch peat, corrected for chemical change, as a function of the mean July temperature in the Netherlands. The filled square is the average for recent wood, and the open circle represents recent wood from Pretoria at mean January temperature.

shift of the climatic belts. The general deuterium depletion with decreasing temperature therefore indicates that the temperature difference between low and high latitudes did not remain constant but increased during the Last Ice Age.

On the basis of the measurements presented here it appears possible to derive paleoclimatic information from the deuterium content of peat. The original deuterium content of the peat can be deduced by means of the carbon content of the sample, and this can be compared with the value obtained for recent plant material in the area. A lower deuterium content in the sample then points to an increase in the temperature gradient between the tropical oceans and the site, that is, to cooler (Ice Age) conditions. With the aid of Fig. 2, actual temperatures can be deduced under certain conditions.

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#### References and Notes

1. W. E. Schiegl and J. C. Vogel, *Earth Planet. Sci. Lett.* **7**, 307 (1970).
2. W. Dansgaard, *Tellus* **16**, 436 (1964).
3. S. Epstein, in *Proc. Conf. Nucl. Processes Geol. Settings*, 2nd (1956).
4. Dr. J. C. Vogel collected the samples from Groningen, Emmen, and Pretoria and made the rest available from the Groningen  $^{14}\text{C}$  Laboratory.
5. J. Friedman, *Geochim. Cosmochim. Acta* **4**, 89 (1953).
6. H. Craig, *Science* **133**, 3467 (1961).
7. W. Francis, *Coal, Its Formation and Composition* (Arnold, London, ed. 2, 1961).
8. W. Dansgaard, S. I. Johnsen, J. Möller, C. C. Langway, Jr., *Science* **166**, 377 (1969).
9. J. C. Vogel and W. H. Zagwijn, *Radiocarbon* **9**, 63 (1967).
10. J. C. Vogel, W. A. Casparie, A. V. Munaut, *Science* **166**, 1143 (1969).
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