

DEUTERIUM CONTENT OF ORGANIC MATTER

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The natural deuterium content of organically bound hydrogen shows systematic variations that depend on the origin of the samples. The hydrogen of both marine and land plants contains several percent less deuterium than the water on which the plants grew. Coal and oil is further depleted in deuterium with respect to plants, and natural gas is still more depleted in deuterium with respect to the coal or oil from which it is derived.

1. Introduction

Since the first precise deuterium measurements were carried out by Friedman in the early fifties [1], a large body of deuterium data has been published. This has contributed greatly to a better understanding of the physical processes responsible for isotope fractionation in the water cycle.

Little attention has been paid, however, to the natural abundance of deuterium in organic matter. In 1955 Bokhoven and Theeuwes [2] determined the deuterium content of hydrogen in a few samples of organic material, but their measuring accuracy was too poor to detect more than that the heavy isotope is depleted in wood, coal and oil with respect to water (precipitation in the Netherlands). Furthermore, the deuterium contents of two natural gases have been reported [3, 4].

We have determined the relative ratio D/H in about 100 samples of organic material and find systematic variations which depend on the origin and history of the samples. Since the techniques employed for preparing the samples for mass-spectrometric analysis are novel, they will be described briefly before a survey of the results is given.

The accurate determination of the relative ratio D/H is performed in a mass spectrometer especially equipped for the purpose [1]. We use a commercial Varian MAT isotope ratio instrument, type M86, which has an accuracy of better than 1‰. The sam-

ple has to be converted to hydrogen gas for analysis, and this is done by combusting it to carbon dioxide and water and subsequently reducing the water with heated zinc. It is important that all steps be quantitative, since incomplete yields inevitably produce isotope fractionation which change the isotope ratio in an uncontrolled manner. The results are reported in permille deviation from standard mean ocean water (SMOW) [5]. A negative δD value means that the hydrogen in the sample contains less deuterium than the standard and vice versa.

2. Combustion technique

The combustion is performed in a closed system (fig. 1) in which oxygen is circulated by thermal convection over the heated sample, A, and through a vertical copper oxide oven, B. The latter, which is kept at about 700°C, maintains circulation at a rate of ca. 300 ml/min. The combustion tube, C, is of quartz glass which is glued to a metal stopper, D, sealed with a rubber O-ring. In front of the sample boat a quartz wool plug, E, is inserted to entrain products of pyrolysis. In the copper oxide oven incompletely oxidized products are converted quantitatively to carbon dioxide and water. The oven is connected to a cooling trap, F, in which the water and carbon dioxide are frozen out with liquid nitrogen. The trap is connected to the combustion

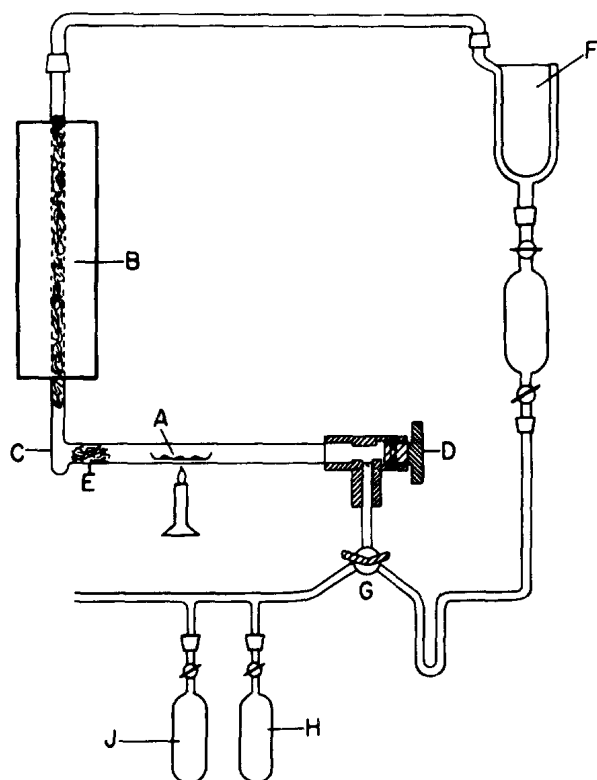


Fig. 1. Combustion system for organic material. The system is filled with pure, dry oxygen which circulates over the heated sample by thermal convection at a rate of 300 ml/min. A, sample; E, quartz wool plug; C, quartz glass tube; B, oven; F, trap filled with liquid nitrogen to collect the carbon dioxide and water; D, metal cap sealed with O-ring; G, three-way stopcock; H, collection vessel for water; I, collection vessel for carbon dioxide. The burette below F is used to insert alkane gases into the system.

tube by means of a three-way stopcock, G, to close the circuit.

Prior to combustion the sample is dried by heating it for 1 hr in a drying oven at 105°C, then it is weighed into a porcelain boat (ca 120 mg) and placed into the quartz tube through the stopper, D. After insertion of the sample the system is evacuated and filled with previously dried cylinder oxygen. The sample is then heated cautiously with a bunsen burner in the circulating stream of oxygen until all the material has burnt away. Thereafter the quartz wool plug, E, is heated thoroughly. When the combustion is completed, the system is evacuated and the water and carbon dioxide frozen over into vessels attached

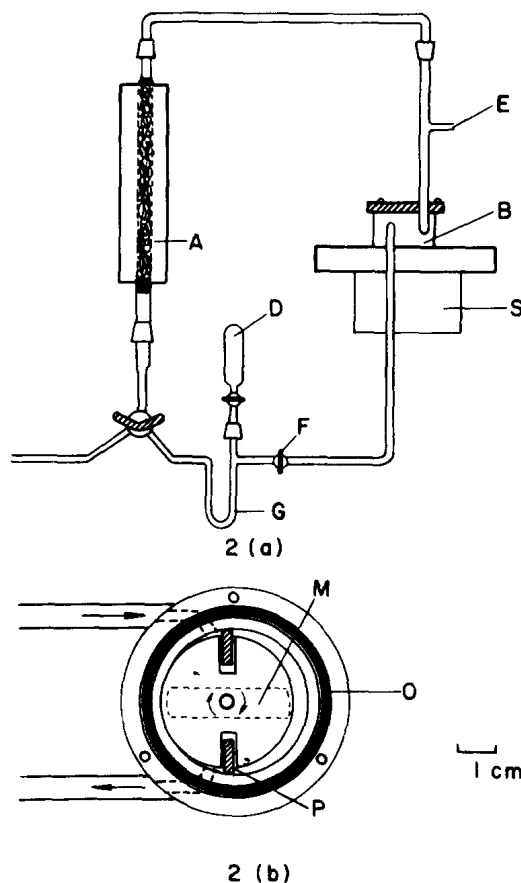


Fig. 2. Reduction system. The water sample (70 mg) evaporates from the U-tube E into the reduction tube filled with heated zinc wool. Circulation is maintained by the circulation pump B. Fig. 2b gives details of the circulation pump as seen from above. A, oven; E, to manometer; B, circulation pump; S, magnetic stirrer; F, stopcock; D, collection vessel for hydrogen gas; G, U-tube for water sample; P, paddle O, rubber O-ring; M, magnet.

to the pumping line. The apparatus is also used to combust alkane gases, in which case no oxygen is added and the combustion is effected solely in the copper oxide oven.

3. Reduction of water to hydrogen

In previously reported reduction systems the water sample is allowed to evaporate into a reducing oven (Zn, Mg or U) and the produced hydrogen pumped into a sample container by means of an automatic

Toepler pump [1, 6]. We have developed a technique which does away with the Toepler pump. The hydrogen remains in the system and is circulated over the water sample, thus transporting the vapour into the oven A (fig. 2). About six samples can be prepared per hour in the apparatus.

The circulation is effected by a small magnetically operated rotor pump, B (fig. 2b). It consists of an aluminium rotor excentrically mounted in a brass casing closed with an O-ring and a glass top. The rotor has two sliding paddles, P, which are pressed against the casing by centrifugal force and in which a small magnet, M, is imbedded. It is turned by means of a magnetic stirrer, S. The pump pumps about 1.2 l per min, independent of pressure.

The water to be reduced (about 70 mg) is frozen in the U-tube C (fig. 2) and the system closed by fitting a gas container, D, into place. After the system is evacuated completely and all stopcocks have been closed, the water is allowed to evaporate into the reduction oven A. When the pressure indicated on the manometer attached at E reaches 20 Torr, the pump is started and stopcock F opened. When the pressure ceases to rise (at about 300 Torr), the reduction is completed. A sample of the hydrogen gas is then collected in container D for measurement.

The reduction oven contains a 30 mm diameter glass tube filled with about 40 g of zinc wool, enclosed in stainless steel gauze, and is heated to 390°C, i.e., somewhat below the melting point of zinc. Usually about 40 samples can be reduced with one filling. At this stage the remaining zinc has sublimated to cooler regions of the oven and is not effective any more.

Some hydrogen is dissolved in the hot zinc, causing a measurable fractionation effect with the dissolved hydrogen depleted in deuterium. The size of the effect depends on the amount of zinc and the temperature, with the result that the isotopic ratio of consecutive samples steadily decreases at a rate of 1.5‰ per g of water reduced. A correction for this effect is applied by interpolating between the results for standard water samples which are run at regular intervals (every 10th sample). The hydrogen dissolved in the zinc is effectively pumped away between samples so that the memory effect is small.

4. Results

4.1. *Living plants*

It is to be expected that the deuterium content of the organically bound hydrogen in plants be in some way related to the deuterium content of the moisture absorbed from the soil during growth. Land plants should thus reflect the isotopic composition of the precipitation which varies from approximately that of ocean water in temperate coastal areas (relative D content, $\delta D = 0\text{‰}$) to considerably lower values for cold inland sites ($\delta D \approx -100\text{‰}$) [7]. Systematic differences of about this order of magnitude should therefore occur between plants from different localities.

On the other hand it is known that the moisture in leaves is considerably enriched in the heavy isotopes with respect to the local precipitation [8]. This enrichment is due to isotopic fractionation during evapo-transpiration and can vary for different plant species.

Table 1
Deuterium content of organically bound hydrogen in various plants from different localities and in different parts of the same plant (poplar) from Pretoria. δD is the relative deuterium concentration in permille with respect to standard mean ocean water (SMOW).

Locality	Plant	Part	$\delta D(\text{‰})$
Pretoria (South Africa)	Poplar	Stem	- 61
		Branch	- 59
		Bark	- 74
		Leaf	- 63
		Leaf sap (0900 a.m.)	+ 60
	Acacia	Branch	- 37
	Eucalyptus		- 39
	Cedar		- 34
	Pine		- 35
	Oak		- 50
	Peach		- 62
	Willow		- 73
Groningen (Nether- lands)	Willow	Branch	- 72
	Oak		- 75
	Pine		- 72
Nussdorf (South Germany)	Willow	Branch	-112
	Pine		-112
	Reed		-103

Table 2

Comparison between the deuterium content of wood from different localities and the average deuterium content in summer precipitation. ΔD , difference in deuterium content between precipitation and wood.

Locality	Deuterium content, δD (‰)		ΔD (‰)
	Wood	Precipitation	
Pretoria (South Africa)	- 49	-10 [10-12]	39
Groningen (Nether- lands)	- 73	-40 [4]	33
Nussdorf (South Germany)	-109	-80 [13]	29

For these reasons similar plants from three selected areas were analysed in this preliminary investigation. To establish whether and in what measure a sample is representative of the plant as a whole, different parts of the same plant were also measured. Some typical results are given in table 1. The organically bound hydrogen is in all cases considerably depleted in deuterium with respect to the water on which the plants grew. No significant difference exists between wood from a branch of a poplar tree and the trunk, while the leaves contain slightly less deuterium and the bark still less. The differences may be due to differing chemical composition [9] but on the whole the variations appear to be small when compared with the spread observed between individual plants. In view of these results branch wood was considered suitable for comparative purposes.

In all three areas the organic matter is depleted in deuterium by about 30‰ with respect to the average summer rainfall and the groundwater (see table 2 and fig. 3). The actual isotope fractionation during assimilation is larger because, as mentioned above, the plant sap is enriched in deuterium by evapo-transpiration. Since the degree of enrichment varies with the time of day, the fractionation during photosynthesis cannot be estimated at this stage.

While there appears to be little variation in the deuterium content of plants from Groningen and Bavaria respectively, the plants that grew in Pretoria

Table 3

Relative deuterium content of marine organisms collected at Port St. Johns, Transkei, South Africa.

Organism	δD (‰)
Green seaweed	- 57
Brown seaweed	- 95
Green seaweed	-103
Mosslike alga	-166
Codfish	- 13
Sea urchin	- 82
Mussel	- 99

show a considerable scatter. This is probably due to variations in the rate of transpiration between different species which, in the drier climate of South Africa, has a more marked effect on the isotope enrichment of the plant sap. Plant sap collected at the same time of day from living leaves of different plants does indeed show a correlation between the degree of isotope enrichment in the sap and the deuterium content of the wood.

It is to be expected that the isotope fractionation of hydrogen during photosynthesis can be studied more conveniently in water plants, since here the additional complication caused by evaporation is not present. In the samples of submerged marine plants and animals we have measured (table 3 and fig. 3), a depletion of about 76‰ in deuterium with respect to sea-water was observed. The scatter in the deuterium concentration, however, is larger than that found in the terrestrial plants measured thus far. One sample of marine algae shows an extremely low relative deuterium concentration of -166‰. This sample also had an unusually high carbon content of 65% compared to about 50% in other plants, which suggests that the deuterium content may depend on the chemical composition of the organic matter.

Of the three marine animals we analysed, the mussel and urchin had a relative deuterium content similar to that of the plants, while the flesh of a codfish contained considerably more deuterium (-13‰).

4.2. Fossil organic material

The hydrogen bound in coal contains less deuterium than that in living plants (table 4). Nineteen samples from five different seams in the Ecca series of the Transvaal and Natal (South Africa) show a

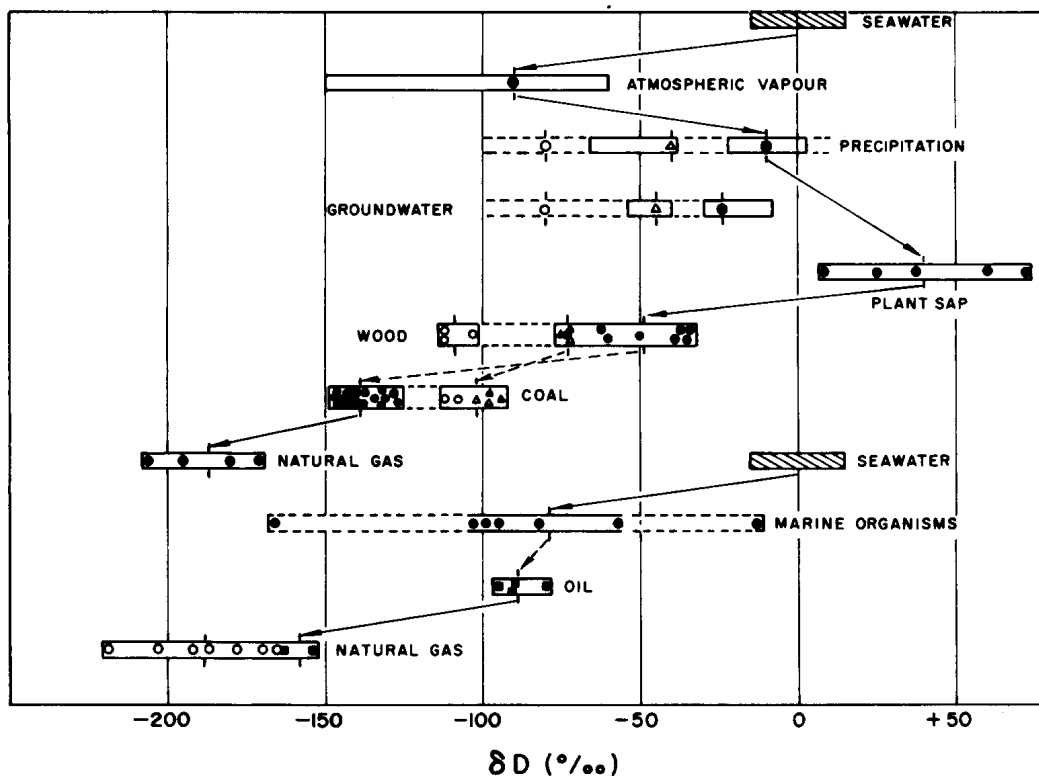


Fig. 3. Deuterium concentration in organically bound hydrogen. ●, South Africa; △, Netherlands; ○, Germany; ■, Middle East. Only mean values are given for atmospheric vapour, precipitation and groundwater. Wood is depleted in deuterium by approximately 30‰ with respect to the precipitation in the area. A general tendency to lower deuterium concentrations in coal with respect to wood is observed. A further depletion in the deuterium occurs in natural gases derived from coal. Marine plants and animals show a large spread in their deuterium concentration, while oil from the Middle East only shows a small scatter. Natural gases derived from oil contain less deuterium than the oil.

remarkably small spread around an average value of $\delta D = -140\text{‰}$, the extreme values being -127‰ and -147‰ . Six samples from the Middle Carboniferous in the Netherlands and Germany have a relative deuterium content, δD , of $-(102 \pm 10)\text{‰}$ which shows that, in the case of coal, the isotopic composition also depends on the locality. The low values for coal may mean that the deuterium content is decreased during the coalification process, but it also may be a result of the climatic conditions at the time of deposition. In this respect it is interesting to note that the climate during the Ecca is considered to have been cool and moist, while the Carboniferous was warm and moist [9, 14].

The few crude oil samples that have been analysed (all from the Middle East) have an average deuterium

content of $\delta D = -89\text{‰}$ (table 4). Since oil is presumably derived from marine organisms, which appear to contain slightly more deuterium (fig. 3), a small depletion in deuterium during the conversion to oil is suggested here, too. Furthermore, the deuterium concentration is greater for the sample with a lower degree of saturation, which may indicate that the isotope ratio is changed during the removal of short side chains from the hydrocarbon molecules. This implies that the derived gases be depleted in deuterium.

Finally a series of natural gases has been investigated. Hydrocarbon gases derived from oil show a relative deuterium content of $\delta D = -159\text{‰}$, a depletion of about 70‰ with respect to the crude oil itself. Gas from oil fields in Germany shows a similar

Table 4
Relative deuterium content of fossil organic material.

Material		δD (‰)
Coal		
<i>Ecca Series, Transvaal</i>		
Waterberg	seam A	-127
Waterberg	seam Z1	-132
Delmas	seam 2	-134
Blinkpan	seam 2	-137
Tavistock	seam 2	-138
Koornfontein	seam 2	-140
Eikeboom	seam 2	-141
Coronation	seam 2	-141
Landau	seam 2	-143
New Clydesdale	seam 2	-146
Blinkpan	seam 4	-128
South Witbank	seam 4	-140
Witbank Cons.	seam 4	-142
New Largo	seam 4	-145
Blesbok	seam 5	-131
Springbok	seam 5	-132
Springbok Hope Sec.	seam 5	-144
New Wakefield	seam 5	-146
Camden	B seam	-141
<i>Ecca Series, Natal</i>		
Northfield	bottom seam	-147
<i>Mid. Carboniferous, Europe</i>		
Staatsmijnen, Limburg 1		- 94
Staatsmijnen, Limburg 2		- 98
Staatsmijnen, Limburg 3		- 98
Staatsmijnen, Limburg 4		-102
Luisental, Saar		-108
Tremonia, Westphalia		-112
Oil		
<i>Middle East</i>		
Yak 1		- 90
Yak 2		- 95
Qatar		- 80
Aghajari - Qatar blend		- 91

Material	δD (‰)
Natural gas from oil	
<i>Middle East</i> (refinery gas)	
Qatar	-154
Aghajari - Qatar	-163
<i>Germany</i> (methane)	
Leopoldshafen 1	-178
Leopoldshafen 2	-187
Knielingen 1	-165
Knielingen 2	-170
Eldingen	-192
Stockstad 1	-203
Stockstad 1	-219
Methane from coal measures	
Camden, Transvaal	-171
Blinkpan, Transvaal	-180
Dannhauser, Natal	-195
Northfield, Natal	-206

depletion, that methane containing less deuterium than the higher hydrocarbons (table 4). The depletion of the heavy isotopic species in the gas with respect to the oil from which it is derived is thus borne out for the hydrogen in a similar manner as it is for the carbon isotopes ^{12}C and ^{13}C . Methane derived from coal measures in South Africa is depleted in deuterium by about 50‰ with respect to the hydrogen in the coal (table 4) so that isotope fractionation of the same order or magnitude as in the case of oil occurs here too.

5. Conclusion

The results obtained for different types of material are summarized in fig. 3. The arrows indicate the magnitude of isotope fractionation during the conversion of hydrogen from one form to another.

In this preliminary survey of the isotopic composition of organically bound hydrogen three different fractionation effects have been observed:

- (i) A depletion in the ratio D/H of several percent

during the conversion of water to organic matter in living plants,

(ii) a decrease in the deuterium content between living plants and fossil coal, and

(iii) a further depletion of deuterium during the natural production of methane from coal and oil.

These processes are somewhat complicated by the relatively large variations in the isotopic composition of the water from which all organisms ultimately derive their hydrogen, but since these variations are relatively well-known to-day, their effect can be accounted for and they need not unduly hamper the investigation of the isotope fractionation effects involved.

A better understanding of the nature and magnitude of these isotopic processes may conceivably also lead to useful applications such as the determination of the origin and history of natural gases or the climatic and meteorological conditions in the original coal swamps.

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