

Tritium and Deuterium Content of Atmospheric Hydrogen

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The tritium and deuterium content of 24 samples of atmospheric hydrogen collected at ground level near Buffalo, N.Y. (U.S.A.), Hamburg (Germany), and Nürnberg (Germany) during 1954 to 1956 was measured.

At the beginning of 1954 the T/H-ratio was found to have been $9.18 \cdot 10^{-14}$, i. e. about a factor of 10 higher than 1949 (FALTINGS and HARTECK) and 1951 (v. GROSSE et al.), probably due to the first explosion of a thermonuclear device in November 1952. In spite of a major test series of thermonuclear weapons in spring of 1954 (Operation CASTLE) no further increase in the tritium content was found during 1954 and 1955. It shows instead a seasonal variation with low tritium content in summer and about a threefold higher one in winter. Simultaneously, there is a good correlation between the tritium and deuterium concentrations. From 1956 on a noticeable increase in the tritium content due to more man-made HT produced or released by thermonuclear devices into the atmosphere was found, in agreement with measurements by GONSIOR. A possible explanation of the experimental results as well as a mode to test the validity of the model suggested is given.

The deuterium concentrations of the samples analysed vary between about +7 percent and -17 percent, compared to Standard Lake Michigan Water with a ratio D/H = 0.0148 ± 0.0002 mol percent. Although from these results only a correlation factor between the tritium and deuterium content of "mean atmospheric hydrogen" and not their absolute values can be derived it is obvious that atmospheric hydrogen and the water vapour of the atmosphere are not in thermodynamic equilibrium, as has been pointed out before by HARTECK and SUESS.

In the past decades much attention has been given to the composition of the terrestrial atmosphere. During the initial stages of this investigation, the main interest was necessarily restricted to the composition of the lowermost layer of the atmosphere while more recently the main emphasis has been shifted to the vertical distribution of the various constituents as well as to their isotopic composition. Although practically all of the minor constituents have been investigated more or less extensively, there is a remarkable lack of information on the abundance, distribution, and isotopic composition of the free hydrogen of the atmosphere.

Due to the inherent experimental difficulties in determining the very small hydrogen content of air, the first measurements gave results which are certainly wrong (10^{-2} mol percent). However, DEWAR¹ as early as 1902, found the hydrogen content of air to be not more than 10^{-3} mol percent, and in 1914 detected only $8 \cdot 10^{-5}$ mol percent². The most extensive as well as the most careful measurements

appear to have been performed in 1923 by P. M. SCHUFTAN, whose results apparently have never been published but are quoted by PANETH³. He found the hydrogen content to be $5 \cdot 10^{-5}$ mol percent independent of both his analytical procedure and the origin of the air samples. This value is still to be found in all modern compendia on this subject — (except in such cases where the existence of hydrogen as a constituent of the atmosphere is still considered to be doubtful⁴) — and apparently more recent data are not available.

To the best of our knowledge, the deuterium content of atmospheric hydrogen has only been determined once before. HARTECK and SUESS⁵, by employing a pycnometric method, determined the density of water samples (obtained by passing the crude He-Ne-fraction of an air liquefaction plant over hot CuO) relative to that of Hamburg tap water. Assuming the density difference to be entirely due to a difference in the deuterium content, they found the D/H-ratio of atmospheric hydrogen to be (25 ± 7)

* Publication authorized by the Director, U.S. Geological Survey.

¹ J. DEWAR, *Proc. Roy. Inst., Lond.* **17**, 223 [1902].

² J. DEWAR, *Proc. Roy. Inst., Lond.* **21**, 240 [1914].

³ F. A. PANETH, *Quart. J. R. Meteor. Soc., Lond.* **63**, No. 271, 433 [1937].

⁴ R. M. GOODY, "The Physics of the Stratosphere," Cambridge Univ. Press, Cambridge 1954.

⁵ P. HARTECK and H. SUESS, *Naturwiss.* **36**, 218 [1949].



percent higher than that of tap water. Although this assumption may not be entirely justified as the density difference may at least be partly due to a different ratio of the oxygen isotopes, their result is in rather good agreement with the results which will be presented here. (Suess later had this result qualitatively confirmed by a mass spectrometric analysis made by Urey's group at the University of Chicago⁶.)

Until a few months ago measurements of the T/H-ratio of atmospheric hydrogen were about as scarce as the deuterium measurements. This is the more surprising as the natural occurrence of tritium was first discovered by FALTINGS and HARTECK in atmospheric hydrogen⁷. They found in their samples, collected near Hamburg, Germany, at the beginning of 1949, a T/H-ratio of $(0.38 \pm 0.12) \cdot 10^4$ T.U. (1 T.U. corresponds to a T/H-ratio of 10^{-18}). With the exception of some preliminary measurements by BEGEMANN and LIBBY⁸, this ratio appears to have been measured only once again by GROSSE, KIRSHENBAUM, KULP and BROECKER⁹. The latter authors found in air samples collected near Buffalo, N.Y., U.S.A., during 1951 a T/H-ratio of $(1.66 \pm 0.1) \cdot 10^4$ T.U.

Several months ago, GONSIOR¹⁰ reported on the T/H-ratios determined on about 20 samples of atmospheric hydrogen collected near Hamburg and Nürnberg (Germany) during 1956–58. He found an approximately linear increase in the T/H-ratio of $5 \cdot 10^4$ T.U. per year from about $10 \cdot 10^4$ T.U. at the beginning of 1956 to about $25 \cdot 10^4$ T.U. at the end of 1958. Superimposed on this linear increase are irregular short-term variations. The increase is ascribed to the production of HT by thermonuclear devices, which are known to release or produce substantial quantities of tritium. By extrapolating back to the beginning of 1954, GONSIOR arrives at an extrapolated T/H-ratio which is in agreement with the previous results by FALTINGS and HARTECK⁷ and GROSSE et al.⁹. He considers the assumption of a linear increase since 1954 to be justified as the first major test series of thermonuclear devices began in March 1954 in the Pacific (Operation CASTLE).

The tritium results presented here are of special

interest as they were obtained on samples collected during 1954–56 and hence should allow us to prove or to disprove the validity of the extrapolation made by GONSIOR. In addition, it is the first time that deuterium and tritium determinations have been performed on the same samples, a fact which proves to be extremely helpful in interpreting the data.

Experimental Techniques

All samples analysed were kindly supplied by the Linde Air Products Company and the Linde's Gesellschaft für Eismaschinen, Abtlg. Gasverflüssigung, respectively. They were obtained by passing the crude He-Ne-fraction in the air liquefaction plants at Buffalo, N.Y., U.S.A., and Hamburg and Nürnberg (Germany) over hot CuO and freezing out the water. The water samples were carefully sealed until the time of analysis in order to avoid contamination with atmospheric moisture. Aliquots of the samples were analysed for deuterium and tritium separately.

A. Deuterium

Ten milligram aliquots of the water samples were converted to hydrogen by passing the water vapor over hot uranium metal. Total reaction was assured by recycling any unreacted water over the uranium. The hydrogen gas sample was then analysed for its D/H ratio in a $6''-60^\circ$ NIER type mass spectrometer especially designed to collect masses 2 and 3 (H_2^+ and HD^+) simultaneously¹¹. A precision of $\pm 0.1\%$ of the ratio was obtained. The results are given relative to Standard Lake Michigan Water.

A result of $+5\%$ indicates that the sample contains 5% more deuterium than Standard Lake Michigan Water. Although our Standard Lake Michigan Water contains $0.0148 \pm .0002$ mol percent D, the uncertainty in this value is greater than the precision of our isotope difference measurements.

B. Tritium

Fourty milligram aliquots of the carefully degassed water samples were converted quantitatively to hydrogen by means of hot Zn at 400°C . The hydrogen liberated was purified by passing it through a trap cooled with liquid nitrogen, and then pumped with a TOEPLER pump into a counter (360 cc, 30 cm long), which had previously been filled with 0.5–1.0 cm of toluene vapor. About 4 cm of argon were added. The counter was then placed in a ring of anti-coincidence counters (60 cm long), surrounded by an iron shield (30 cm). The amount of tritium was determined by counting its activity in the GEIGER region. The background of the counter was (3.6 ± 0.1) cpm, the net counting rate with 10 cm of hydrogen gas 10–30 cpm. The counter was calibrated by using a tritium standard (no. PS 42 975) obtained from the National Bureau of Standards, Washington, D.C. Each sample was counted at least twice, the relative accuracy of the results is about 2% (reproducibility and statistical error), the absolute accuracy 3–4%.

⁶ H. E. SUSS, Trans. Amer. Geophys. Un., **34**, 343 [1953].

⁷ V. FALTINGS and P. HARTECK, Z. Naturforschg. **5a**, 439 [1950]; Nature, Lond. **166**, 1109 [1950].

⁸ F. BEGEMANN and W. F. LIBBY, Geochim. Cosmochim. Acta **12**, 277 [1957].

⁹ A. V. GROSSE, A. D. KIRSHENBAUM, J. L. KULP and W. S. BROECKER, Phys. Rev. **93**, 250 [1954].

¹⁰ B. GONSIOR, Naturwiss. **46**, 201 [1959].

¹¹ I. FRIEDMAN, Geochim. Cosmochim. Acta **4**, 89 [1953].

Sample no.	Place of collection	Date of collection	T/H [10 ⁴ T.U.]	δ D/H [%]
1	Buffalo, N.Y.	Jan. 2–9, 1954	9.18	– 8.95
2	Buffalo, N.Y.	May 25–28, 1954	7.38	– 6.52
3	Buffalo, N.Y.	Nov. 22–26, 1954	6.39	– 8.87
4	Buffalo, N.Y.	Nov. 26–Dec. 3, 1954	7.75	– 12.10
5	Buffalo, N.Y.	Dec. 3–13, 1954	9.00	– 7.28
6	Buffalo, N.Y.	Mar. 25–Apr. 3, 1955	11.5	– 4.01
7	Buffalo, N.Y.	May 21–30, 1955	5.99	– 13.65
8	Buffalo, N.Y.	June 10–18, 1955	7.75	– 6.60
9	Buffalo, N.Y.	Aug. 12–20, 1955	5.66	– 13.45
10	Buffalo, N.Y.	Sept. 17–29, 1955	4.17	– 16.45
11	Buffalo, N.Y.	Oct. 8–16, 1955	4.99	– 13.10
12	Buffalo, N.Y.	Nov. 6–13, 1955	7.16	– 6.10
13	Buffalo, N.Y.	Dec. 17–25, 1955	5.99	– 10.20
14	Hamburg, Germany	Dec. 18, 55–Jan. 21, 56	12.6	+ 5.89
15	Buffalo, N.Y.	Jan. 19–23, 1956	6.03	– 7.53
16	Hamburg, Germany	Mar. 22–25, 1956	12.6	+ 6.85
17	Buffalo, N.Y.	Apr. 15–21, 1956	9.09	– 6.29
18	Buffalo, N.Y.	May 8–15, 1956	9.72	– 9.05
19	Hamburg, Germany	May 12–15, 1956	11.8	+ 5.62
20	Nürnberg, Germany	May 29–June 2, 1956	3.50	– 0.60
21	Nürnberg, Germany	June 13–23, 1956	3.37	+ 0.20
22	Nürnberg, Germany	Aug. 27–Sept. 1, 1956	13.4	– 2.42
23	Nürnberg, Germany	Sept. 20–Oct. 5, 1956	11.8	– 3.85
24	Buffalo, N.Y.	Oct. 21–28, 1956	11.3	– 6.28

Table 1. The tritium and deuterium content of atmospheric hydrogen. The tritium content is given in 10⁴ T.U. (1 T.U. \rightarrow T/H = 10⁻¹⁸), the accuracy of the results is 3–4%. The deuterium content is expressed by the difference δ of the D/H-ratio in the sample and that of Lake Michigan water [(D/H)_{Sample} = (D/H)_{L.M.}(1 + δ)]. The error of the D/H-ratios is 0.1%. The deuterium content of the 5 first samples had been measured previously by CRAIG¹². His results are in good agreement with those presented here.

Experimental Results and Discussion

The results of both the deuterium and the tritium measurements are presented in Table 1.

Fig. 1 shows our tritium results as well as all others which have been published previously (left ordinate scale), together with the tritium content of Chicago precipitation^{8, 13–15} covering the same period of time (right ordinate scale). It is obvious that there was no linear increase in the tritium content of atmospheric hydrogen starting in 1954, i. e. following the CASTLE test series of thermonuclear weapons. At this time the tritium content was already about ten times higher than 1949 and 1951. During 1954 and 1955 the tritium content appears to show some seasonal variations with high concentrations in winter and about threefold lower ones in summer. A definite increase is only noticeable from 1956 on. According to these results there is no indication that there was any significant amount of HT produced during Operation CASTLE.

The increase in the tritium content between 1951 and 1954 is believed to be due to Operation Ivy (November 1952); the increase from 1956 on to be due to the U.S.S.R. test series of thermonuclear weapons during the latter part of 1955, and the following tests conducted by the U.S.S.R., U.S., and U.K. (see Fig. 1). On first sight this explanation may appear rather strange as it implies that all test series except CASTLE produced substantial quantities of HT. This is even stranger when considering the fact that the increase in the tritium content of precipitation following CASTLE was very much larger than that following IVY (Fig. 1). Actually, the latter, has frequently been overlooked entirely. However, it must be kept in mind that the first thermonuclear device, detonated in November 1952 is said to have been unique in its design. It is supposed to have been a refrigerated device, containing a liquid deuterium-tritium mixture, whereas in the subsequent fusion explosions this D-T-mixture has been replaced by a ⁶Li-D mixture (or compound)¹⁶. Dur-

¹² H. CRAIG, Private communication.

¹³ S. KAUFMAN and W. F. LIBBY, Phys. Rev. **93**, 1337 [1954].

¹⁴ H. v. BUTTLAR and W. F. LIBBY, J. Inorg. Nucl. Chem. **1**, 75 [1955].

¹⁵ F. BEGEMANN, Final Report, Contract No. AF 18(600)-564 [1957].

¹⁶ A. G. W. CAMERON, Can. J. Phys. **37**, 322 [1959].

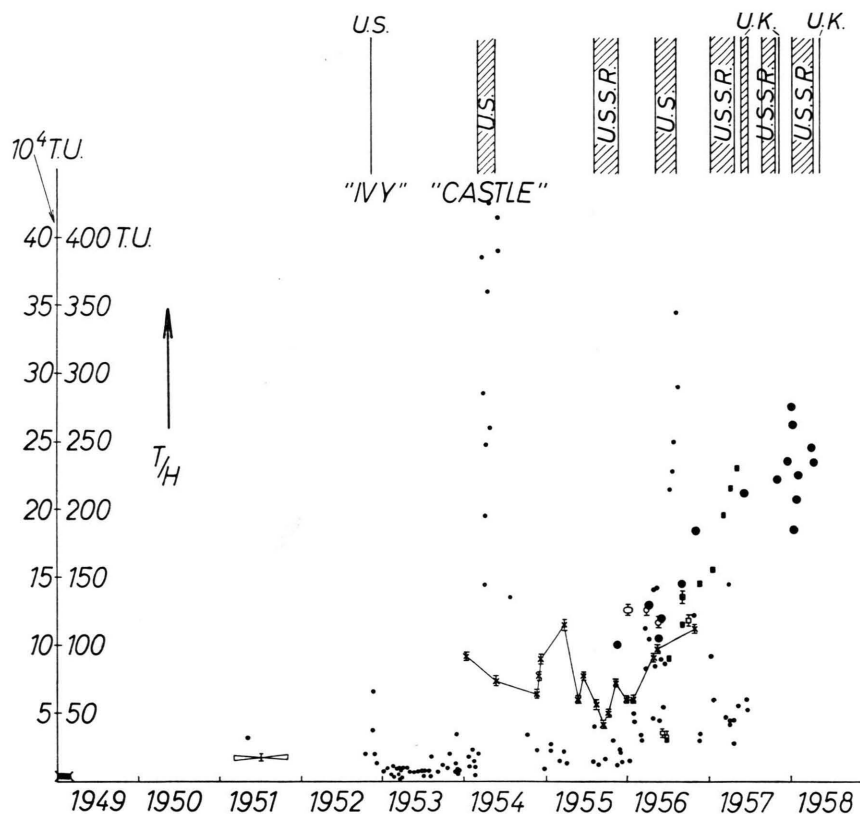


Fig. 1. Tritium content of atmospheric hydrogen (left ordinate scale) and of Chicago precipitation (right ordinate scale).

crossed dot Hamburg, Germany
(FALTINGS and HARTECK⁷)

⊗ Buffalo, N. Y., U.S.A.
(v. GROSSE et al.⁹)

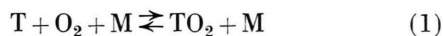
● Hamburg, Germany } (GONSIOR¹⁰)
■ Nürnberg, Germany

× Buffalo, N.Y., U.S.A. } This paper
○ Hamburg, Germany
□ Nürnberg, Germany

The times of the major test series of thermonuclear devices are indicated. The Chicago precipitation data (•) are taken from ref. 8, 13–15.

ing the U.S.S.R. test series at the end of 1955 and some or all of the following test series, on the other hand, according to confirmed reports, some of the H-bombs were detonated at great altitudes. This, then, may be assumed to be the reason why during these test series substantial quantities of HT were produced while this was not the case during the low-altitude Operation CASTLE.

Fig. 1 shows one more interesting feature which might be worth mentioning: Under natural conditions, i. e. before the first man-made tritium was released into the atmosphere the tritium concentration in atmospheric hydrogen was about 10^3 times that found in atmospheric moisture. According to HARTECK¹⁷ this fact can be explained in the following way: The cosmic ray produced atomic tritium has essentially two possibilities to react:



Reaction (1) is the most probable one, the formation of the free radical TO_2 in a three body collision. The TO_2 will undergo further reactions and finally end up as HTO. However, when inserting the known

reaction constants, and the concentrations of the reactants involved, the HT/HTO-ratio arrived at is lower by several orders of magnitude than what has been found experimentally. Hence the TO_2 -radical must be decomposed photochemically before it undergoes further reactions and thus enable the tritium again to form more HT according to reaction (2).

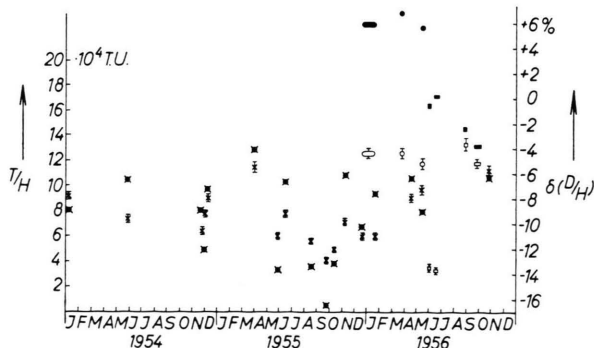


Fig. 2. Tritium content and relative deuterium concentration of atmospheric hydrogen [$\delta(D/H)$ Lake Michigan = 0].

× T-content; crossed dot $\delta(D/H)$ Buffalo, N.Y., U.S.A.
○ T-content; ● $\delta(D/H)$ Hamburg, Germany
□ T-content; ■ $\delta(D/H)$ Nürnberg, Germany

¹⁷ P. HARTECK, J. Chem. Phys. **22**, 1746 [1954].

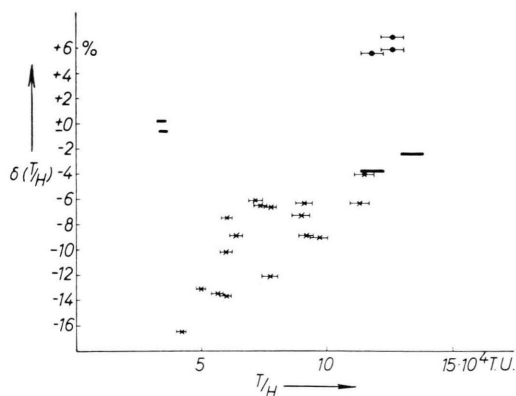


Fig. 3. Correlation between tritium and deuterium content of atmospheric hydrogen. X Buffalo, N.Y., U.S.A.; ● Hamburg, Germany; ■ Nürnberg, Germany.

Another possibility for the tritium to form HT has been pointed out by ROWLAND¹⁸. He suggests that the hot atom reaction



may be partly responsible for the formation of HT. However, this reaction has not yet been detected.

In Fig. 2 and 3 the results of the tritium and deuterium analyses are plotted together. The data show a definite correlation, which is especially good for the Buffalo samples from December 1954 to December 1955 (Fig. 2). Whenever the tritium content is high the deuterium concentration is also high, and vice versa. The conclusions to be drawn from this correlation are:

1. The variations in the tritium content are not caused by locally adding noticeable quantities of HT to the natural reservoir, a possibility which otherwise cannot be excluded altogether in view of the widespread use of tritium in solving technological as well as scientific problems.

2. At least from the end of 1954 to the end of 1955 the excess HT must have been distributed rather homogeneously in the atmosphere. The energy released by even the largest test series is by far not sufficient to cause any noticeable change in the amount of HD present in the atmosphere. Hence, as far as the HD is concerned, one is still dealing with the natural inventory. If the excess HT, then, would not have been distributed homogeneously throughout the atmosphere, one should find varia-

tions in the tritium content of the samples, due to general meteorological conditions, without having corresponding changes in the deuterium concentration. This, for example, appears to be the case for the Nürnberg samples which were collected during the latter part of 1956 at which time there was already some more man-made HT released into the atmosphere.

The question, then, is how to explain the variations. First, there is the trivial explanation that the water available for isotopic analysis was a mixture of water obtained by the oxydation of atmospheric hydrogen and of atmospheric moisture or tap water. In this case the variations might be caused by a change in the relative amounts of the two components. Fortunately, the tritium content of atmospheric moisture as well as that of tap water is negligible compared to that of atmospheric hydrogen (see above). Hence, this explanation would require the samples with low tritium content to contain at least 70% ordinary water. According to Linde, however, all samples contain no more than 2% of water foreign to water obtained by the oxydation of atmospheric hydrogen, thus excluding this possibility.

A second explanation might appear to be following: The samples collected are representative of the atmosphere as a whole rather than only of its lowermost layer. The atmospheric hydrogen is continuously used up by chemical reactions, the reaction rate varying rapidly and /or the concentration(s) of the reactant(s) in question changing rapidly. Simultaneously, the hydrogen production rate varies in such a way that the total amount of atmospheric hydrogen remains constant. As the hydrogen produced will have a D/H- and T/H-ratio different from that of atmospheric hydrogen this mechanism might explain the variations found. However, the changes in the tritium and deuterium content are rather rapid, indicating a mean life time of the hydrogen of only about 2 months. This, then, poses the difficulty that all reactions which are known to produce hydrogen in significant quantities (photodissociation of water vapor, production from organic matter, decomposition of methane, production by volcanoes) when added together are by far not sufficient to produce this much hydrogen. Although it is known from aurora borealis data¹⁹ that appreciable quantities of hydrogen are bombarding the earth's atmosphere, this cannot play a major role in the hydrogen

¹⁸ F. S. ROWLAND, J. Chem. Phys. **30**, 1098 [1959].

¹⁹ See e. g. J. W. CHAMBERLAIN and A. B. MEINEL in "The Earth as a Planet," Editor G. P. KUIPER, Univ. of Chicago Press, Chicago 1954.

balance of the earth as the presence of oxygen in the terrestrial atmosphere is regarded as an indication that hydrogen is leaving the earth into space (see e. g. HARTECK and JENSEN²⁰) and is not being accreted.

At first sight the exchange between hydrogen and water vapor according to



appears to offer an explanation for the variations in the deuterium and tritium content of atmospheric hydrogen. In this case there would be no difficulty with the production rate, as these exchange reactions will leave the total amount of hydrogen unchanged. Furthermore, the atmospheric moisture content shows a rather good anticorrelation with the tritium concentration of atmospheric hydrogen, i. e. high moisture content when the tritium concentration is low and vice versa. But again there are two main objections. Firstly, according to FARKAS²¹, the exchange probability for reaction (4) at room temperature is about 10^{-45} per collision. This would mean that about 10^{29} years are required for half of the hydrogen in the atmosphere to exchange with atmospheric moisture, compared to about 2 months as required by the experimental results. Secondly, even if there would be a catalyst present in the atmosphere to speed up this reaction by 30 orders of magnitude, the deuterium results show that atmospheric hydrogen and atmospheric moisture are definitely not in thermodynamic equilibrium, as has been pointed out already by HARTECK and SUESS⁵.

A model which does explain the experimental results very nicely will be presented below. The basic assumptions are:

1) The samples analyzed are not representative of the atmosphere as a whole but only of its lowermost layer near the surface of the earth.

2) The hydrogen consists of a relative fraction x_i of "mean atmospheric hydrogen" and a relative fraction $1 - x_i$ of locally produced hydrogen, the amounts of each being different for the different samples as is indicated by the running index i .

The D/H- and T/H-ratios of the two fractions are $(\text{D}/\text{H})_0$, $(\text{T}/\text{H})_0$, $(\text{D}/\text{H})_{\text{pr}}$, and $(\text{T}/\text{H})_{\text{pr}}$, respectively, where $(\text{D}/\text{H})_0$ and $(\text{T}/\text{H})_0$ are constant by

definition, $(\text{D}/\text{H})_{\text{pr}}$ and $(\text{T}/\text{H})_{\text{pr}}$ only constant at any given location.

The variations in the isotopic ratios of the samples are then caused by a change of the relative amounts of the two components. This would, for example, be the case if the locally produced hydrogen had its origin in the decomposition of organic matter, which for various reasons certainly would depend on the season¹⁰, or if it would be produced by industrial plants near the sampling site and be dependent on wind speed and wind direction. (Although these assumptions might appear to be very complicating factors as far as any statements with regard to the isotopic composition of the "mean atmospheric hydrogen" are concerned these apparent complications will be shown below to be advantageous.) According to this model the isotopic ratios of sample number i will then be

$$(\text{T}/\text{H})_i = (\text{T}/\text{H})_0 x_i + (\text{T}/\text{H})_{\text{pr}} (1 - x_i) \quad (6)$$

and
$$(\text{D}/\text{H})_i = (\text{D}/\text{H})_0 x_i + (\text{D}/\text{H})_{\text{pr}} (1 - x_i). \quad (7)$$

Expressing the D/H-ratios by their difference from that of a standard with $(\text{D}/\text{H})_{\text{L.M.}}$, i. e.

$$(\text{D}/\text{H})_0 = (\text{D}/\text{H})_{\text{L.M.}} (1 + \delta_0),$$

$$(\text{D}/\text{H})_{\text{pr}} = (\text{D}/\text{H})_{\text{L.M.}} (1 + \delta_{\text{pr}}),$$

and
$$(\text{D}/\text{H})_i = (\text{D}/\text{H})_{\text{L.M.}} (1 + \delta_i) \text{ yields}$$

$$x_i (\delta_{\text{pr}} - \delta_0) = \delta_{\text{pr}} - \delta_i. \quad (7a)$$

Taking into account that, whatever the source of the locally produced hydrogen might be its T/H-ratio certainly will be negligible compared to that of atmospheric hydrogen (if the hydrogen is produced in thermodynamic equilibrium with water vapor the situation becomes even more favorable), equation (6) can be written as

$$(\text{T}/\text{H})_i = (\text{T}/\text{H})_0 x_i. \quad (6a)$$

Combining (6a) and (7a) results in

$$(\text{T}/\text{H})_i = \frac{(\text{T}/\text{H})_0}{\delta_{\text{pr}} - \delta_0} (\delta_{\text{pr}} - \delta_i). \quad (8)$$

Hence, if this model is correct a plot of the measured (T/H)-ratios vs. the δ_i -values will have to yield a straight line, intercepting the ordinate at δ_{pr} (Fig. 4). If all the samples from Buffalo are taken into consideration the result is

$$\delta_{\text{pr}} = - (19.3 \pm 5) \text{‰},$$

if only those are considered where the correlation between the deuterium and tritium results appears

²⁰ P. HARTECK and J. H. D. JENSEN, Z. Naturforsch. **3a**, 591 [1948].

²¹ A. FARKAS and L. FARKAS, quoted by E. K. Rideal, Proc. Roy. Soc., Lond. A **144**, 1 [1934].

to be most obvious (Dec. 54 to Dec. 55, see Fig. 2)

$$\delta_{pr} = -(28.9 \pm 2) \%$$

This result means, that the locally produced hydrogen is depleted in its deuterium content by 20–30% compared to that of Lake Michigan water. As the deuterium concentration of the hydrogen compounds which are the potential sources of the hydrogen will, on the average, have a D/H ratio by several percent smaller than that of Lake Michigan water^{11, 12} (see Fig. 4), the hydrogen produced is about 15–20% depleted in its deuterium content compared to that of the compounds which are the source of this hydrogen.

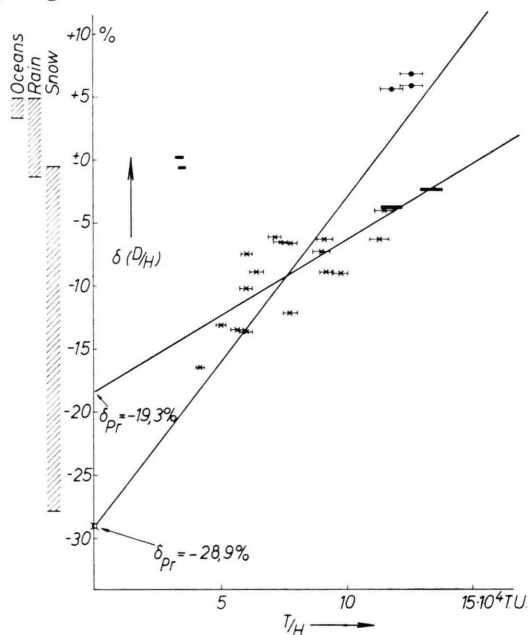


Fig. 4. Correlation between tritium and deuterium content of atmospheric hydrogen. \times Buffalo, N.Y., U.S.A.; \bullet Hamburg, Germany; \blacksquare Nürnberg, Germany. The two straight lines (equation 8) give the best fit for the data if a.) all samples from Buffalo are considered [$\delta_{pr} = -(19.3 \pm 5) \%$]; b.) only the samples collected at Buffalo between December 1954 and December 1955 are used [$\delta_{pr} = -(28.9 \pm 2) \%$]. On the left side the deuterium content of some of the potential sources of atmospheric hydrogen is indicated for comparison (ref. ^{11, 12}).

There are essentially two possibilities to explain this result:

1. The hydrogen is produced in thermodynamic equilibrium with its mother compound. The temperature at which the production takes place must then be 400–700 °C, depending on the D/H-ratio of the mother compound. (The equilibrium constants used for this calculation are those of water as given by LIBBY²² and BLACK and TAYLOR²³.)

2. The hydrogen is produced at ordinary temperatures, but not in equilibrium with its mother compound.

In both cases the possibility that the hydrogen is produced by bacteria seems to be ruled out as all hydrogen producing bacteria which have been investigated so far do produce the hydrogen in thermodynamic equilibrium or deplete the hydrogen even more in deuterium^{24, 25}.

As was mentioned above there is the possibility that the locally produced hydrogen has its origin in hydrogen producing industrial plants in the vicinity of the sampling site. The different amounts of this hydrogen present in the samples analyzed will then be dependent on the wind speed and wind direction at the time the samples were collected. As there is no evidence that any of the samples consisted only of "mean atmospheric hydrogen" and hence did not contain any of the locally produced hydrogen, from these data, nothing can be said about the isotopic ratios $(D/H)_0$ and $(T/H)_0$ of the "mean atmospheric hydrogen," except that they have to be correlated in such a way as to fulfill equation (8). In order to find out what these ratios $(D/H)_0$ and $(T/H)_0$ are, the following approach appears to be promising: Samples from at least two different sampling sites have to be analyzed for their deuterium and tritium content. As the locally added hydrogen for the different sampling sites will probably have different ratios $(D/H)_{pr}$ and $(T/H)_{pr}$, the resulting straight lines of the plots $(T/H)_i$ vs. δ_i will not coincide, but will have to intercept one another at $(T/H)_0$, $(D/H)_0$, thus giving the desired information.

If it would be possible to collect samples of atmospheric hydrogen at any location where the contamination by locally produced hydrogen can be excluded with certainty, the isotopic ratios of this hydrogen should be the same as those arrived at by the approach suggested here. At the same time such measurements might prove or disprove the validity of the model suggested here to account for the variations of the isotopic ratios. It must be pointed out, however, that at the present time such measurements must be expected to be very difficult due to the

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large amounts of man-made HT recently released into the atmosphere (Fig. 1). Only when this man-made HT is distributed homogeneously in the atmosphere will such measurements become feasible again. As this, obviously, was not the case during 1956 (see Fig. 1 and Fig. 2) we do not consider it to be appropriate to use the results obtained on the samples collected at Hamburg and Nürnberg (Germany) for the calculation suggested above.

The results as presented in Fig. 4 clearly demonstrate that whatever the exact value of the ratio $(D/H)_0$ is, the deuterium content of "mean atmospheric hydrogen" is at least as high as, if not higher than that of water from all major sources. However, all processes which are known to produce substantial quantities of hydrogen (see above) tend to deplete the hydrogen in deuterium rather than enrich it, the degree of depletion depending on the temperature at which the production takes place. Hence, the conclusion seems to be inevitable that some kinetic effect must be responsible for the

high deuterium concentration of "mean atmospheric hydrogen." It has been suggested before⁵ that the preferential escape of protium from the exosphere into space will cause such an enrichment of deuterium. Whether or not this is sufficient to explain the experimental result will depend on the relative contributions of the various hydrogen producing processes to the total production rate, about which apparently very little is known. Certainly, more experimental work on this subject is required.

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Über die Diffusion in Germaniumkristallen, die eine Korngrenze enthalten

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Die Diffusion von Donatoren und Akzeptoren längs Kleinwinkelkorngrenzen in Germanium wurde untersucht, indem die Wanderung eines p-n-Überganges, der eine Linie gleicher Konzentration markiert, verfolgt wurde.

Eine schnellere Diffusion in der Korngrenze gegenüber derjenigen im Volumen wurde gefunden, falls die Dislokationsröhren (Dislocation-pipes), die die Korngrenze aufbauen, in Richtung der Diffusion liegen. Liegen die Röhren senkrecht zur Diffusionsrichtung, so findet keine bevorzugte Diffusion statt.

In Korngrenzen mit Dislokationsröhren in Richtung der Diffusion wurde die Diffusion von As und Sb für verschiedene Zeiten und Temperaturen untersucht. Es zeigte sich, daß sich der Vorgang nicht mit einem konstanten Diffusionskoeffizienten der Korngrenze beschreiben läßt.

Eine grobe Auswertung der Messungen nach den Formeln von WHIPPLE ergibt, daß der Diffusionskoeffizient in der Korngrenze 10^5 – 10^6 -mal größer ist als im Volumen, wobei die Annahme gemacht wird, daß der Durchmesser der Dislokationsröhren etwa sechs Gitterkonstanten ist.

Über die Diffusion in Korngrenzen sind in den letzten Jahren eine Reihe von Veröffentlichungen erschienen^{1–5}. Bei diesen Untersuchungen wurde im allgemeinen für den diffundierenden Stoff ein radioaktives Material verwendet, dessen Vorrücken gemessen wurde. Man findet, daß die Diffusion längs der Korngrenze schneller verläuft als im ungestörten Material, und zwar um so schneller, je größer der Winkel zwischen den Orientierungen der beiden Kristallite ist, die die Korngrenze bilden.

Die vorliegende Arbeit befaßt sich mit der Diffu-

sion von As, Sb, P, In und Ga in Germanium längs Korngrenzen, wobei das Vorrücken des diffundierenden Stoffes durch die Wanderung eines p-n-Überganges verfolgt wird.

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