Tritium Loss from Iron Meteorites by Solar Wind Hydrogen

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An estimate of the diffusion loss of tritium from iron meteorites in space cannot be based, in a direct manner, on the results of diffusion measurements in the laboratory, because the hydrogen content of the samples in the laboratory is always higher by many orders of magnitude than is the tritium content of iron meteorites in space, which results from bombardement by cosmic rays. This is true because the kinetics of gas loss from a metal change with concentration and temperature, especially the kinetics of hydrogen loss from meteoritic iron, where the amounts of cosmic ray-produced tritium are sufficiently small to be trapped completely by chemisorption of nickel. Estimates based on diffusion data for hydrogen in the laboratory lead to much higher rates of hydrogen loss than can be expected for cosmic ray-produced tritium in meteorites.

In this connection, however, the fact has to be considered that meteoritic iron in space may not only contain hydrogen isotopes derived from cosmic ray-induced spallation processes, but also derived from solar wind bombardement. The steady-state hydrogen content of an iron meteorite, resulting from such bombardement in outer space, depends, of course, on the size and the structure of the meteoritic body. In general, the body will have to be assumed to possess a grain structure and this complicates the situation considerably. In any case, it can be shown that the steady-state hydrogen content is much higher than the tritium content and this makes it possible to use laboratory diffusion data in a calculation of the diffusion losses of tritium. By using the laboratory data of FESTAG, FECHTIG and SCHULTES, it can be shown that cosmogenic tritium will be lost almost completely whenever the temperature is close to 0 °C, or higher. Only meteorites consisting of grains of a size exceeding several millimeters retain tritium at such temperatures.

As is well known, there is often found much less tritium in iron meteorites than is to be expected from cosmic ray intensity. In order to explain this a diffusion loss of tritium after the fall of the meteorites has been discussed [1-3]. Indeed, the diffusion of hydrogen in meteoritic iron at room temperature was found to be fast enough [1,4] to may account for this loss.

But since, at the same time, in iron meteorites often a deficiency of ^{3}He is observed [5], it is very likely that the tritium loss already exists in space (at first discussed by HINTENBERGER and WÄNKE [5]; cf. also [6]). Obviously, in such cases the escape process of the cosmic ray produced tritium must be so fast that the mean residence time of a tritium atom in the meteorite is smaller than its mean life time (before decaying to ^{3}He; 17,8 years). This presumption is not new; but to prove it, it seems not to be sufficient to demonstrate experimentally that the hydrogen diffusion in meteoritic material is large enough at the temperatures in question.

As is known from permeation measurements, there are deviations from the linear relation between permeation rate and the square root of the pressure of the (diatomic) gas, and that is the more marked the lower the temperature and the gas pressure (cf. the references given by JOST [7]). The reasons for this are found in volume effects as well as slow steps in the surface reaction. Therefore, at such extremely small hydrogen concentrations, as the stationary tritium content in iron meteorites (at most of the order of $10^7/cm^3$), it seems to be impossible to make any reliable prediction of the diffusion loss in space on the basis of measurements performed under laboratory conditions. This results from the fact that in all laboratory systems the hydrogen concentration in the solid samples and (especially) the hydrogen partial pressure outside the samples have been higher by several orders of magnitude than under space conditions.

Furthermore, in the case of nickel containing meteoritic iron a strong chemisorption of hydrogen

[1] H. FECHTIG, J. G. FESTAG, and H. SCHULTES, Preprint 1966, Z. Naturforschg. 22 a, 765 [1967].

[2] A. E. BAINBRIDGE, H. E. SUESS, and H. WÄNKE, Geochim. Cosmochim. Acta 26, 471 [1962].

[3] E. L. FIREMAN and J. DE FELICE, Geochim. Cosmochim. Acta 18, 183 [1960]; J. Geophys. Res. 65, 3035 [1960].

[4] D. E. FISHER, Preprint 1966; to be published in J. Geophys. Res.

[5] H. HINTENBERGER and H. WÄNKE, Z. Naturforschg. 19 a, 210 [1964].

[6] H. HINTENBERGER, L. SCHULTZ, H. WÄNKE, and H. WEBER, Preprint 1967 (Berichte aus der Meteoritenforschung, No. 83, Mainz).

[7] W. JOST, Diffusion in Solids, Liquids, Gases, Academic Press, New York 1960, p. 306.

is to be expected at the low temperatures, so that as small amounts of hydrogen as the cosmic ray produced tritium would be completely trapped. Under these conditions calculated rates of the tritium loss based on diffusion data would lead to much higher rates than can be expected.

In this paper we consider the role of the hydrogen injected into the meteorites by the solar wind. Its behaviour (and that of the tritium, too) depends mainly on its concentration. Therefore, our first aim is to get an estimate of the steady state hydrogen content of iron meteorites under the influence of the solar wind. Then we shall discuss in general the behaviour of the tritium in iron meteorites under the aspect of diffusion kinetics. For larger meteorites solar wind injected hydrogen may be supposed to be only of importance for a thin surface layer. But, as turns out in this paper, this seems not to be true.

1. An Estimate of the Steady State Hydrogen Content of Iron Meteorites under the Influence of the Solar Wind

For the solar wind we assume a mean proton flux of $j = 10^8/cm^2$ sec, and a mean proton energy of $3 - 5$ keV. Then we have the following situation:

The range of these protons in iron is approximately 10^{-4} cm. The statistical process of the energy loss to the lattice atoms leads to a range distribution, even for monoenergetic particles, which is in this case of the order of 10^{-5} cm [8]. The distribution in direction and energy of the incoming protons broadens the range distribution, but for our rough estimate we neglect this. Hence, under the outer surface of a meteorite at a depth of 10^{-4} cm, there is a source layer of hydrogen with a productivity of 10^8 particles/cm² sec. This hydrogen flows outwards as well as to the inside of the meteorits, in the course of which a stationary hydrogen concentration is set up in the source layer which depends on the productivity, and the hydrogen mobility in the lattice.

For larger meteorites the conditions in a thin surface layer of 10^{-4} cm thickness are only of minor interest compared with the behaviour of the hydrogen which diffuses into the meteorite. But in polycrystalline or grained (heterogeneous) material the situation is rather complicated. Therefore we treat the problem by means of a simplified model.

[8] See e. g. J. BIERSACK, HMI-B 37 [1964].

As a preparation for this let us consider a plain-parallel iron sheet of infinite dimension, one side of which receives the proton flux. Fig. 1 shows a section of this sheet. The source layer is at the depth Δx under the surface facing the sun. Under steady
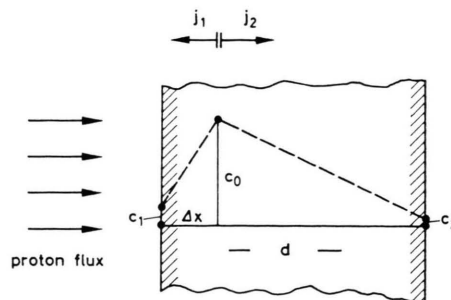

Fig. 1. Section of an infinite iron sheet, one side of which receives the proton flux. Hydrogen source layer at depth Δx. c_1, c_2 are the steady state hydrogen concentrations on the surface, c_0 that at the source layer.

state conditions the hydrogen flows off to both sides, and the ratio of the diffusion fluxes is approximately

$$j_1/j_2 \approx (d - \Delta x)/\Delta x .$$

This holds under the supposition that the phase boundary reaction are not rate determining, and it is neglected that (due to the different desorption rates) the stationary surface concentrations of hydrogen are different at the two sides of the sheet. Both surface concentrations are neglected with respect ot the concentration in the source layer. Fig. 1 shows qualitatively the real situation.

Let us now consider the situation in a larger meteorite which consists of grains. At first we have to transform the rather complicated real conditions into a proper model. For this purpose we have to introduce some idealizations and simplifications. The consequences of the more serious of these are discussed later in section 3.

(a) We assume a uniform grain size of the surface grains (of diameter d) and a regular shape. Then the structure of the body, reduced to a very undifferentiated norm, may be represented by Fig. 2.

(b) We consider the problem as one-dimensional. Only those fluxes, which are perpendicular to the surface of the meteorite are taken into account; those parallel to it (i. e. especially the escape of the injected gas from the lateral parts of the surface grains) are neglected within the scope of our rough estimate.
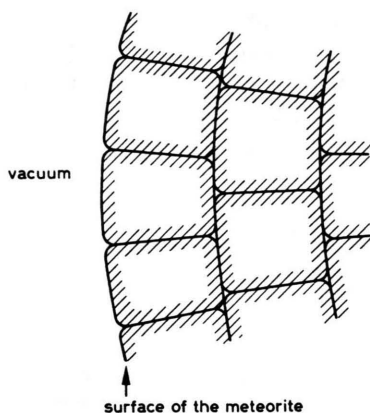
Fig. 2. Schematic structure of a grained meteorite. Undifferentiated norm for the purpose of calculations.

vacuum

surface of the meteorite

(c) The rate determining steps for the escape of hydrogen are the transport processes, not the surface reactions.

(d) We assume that the diffusion of hydrogen along the grain boundaries is a fast process compared to the volume diffusion through the grains.

(e) The formation of molecular hydrogen within the meteorite (e. g. in cracks or at grain boundaries) cannot be excluded. But we neglect this possibility with the exception of one single case which is discussed in section 3.

(f) For the mobile hydrogen we assume a distribution equilibrium between the grain boundary and the bordering volume of the grains of the form $c_{\text{boundary}} = \gamma (c_{\text{volume}})^{2/3}$. But due to the lack in a more precise information we must accept γ to unity.

A hydrogen source layer is found only in the surface grains. The difference from the situation in Fig. 1 is that the hydrogen atoms leaving the inner surfaces of the source grains (j_2) cannot flow away unhindered. According to assumption (d) the hydrogen coming out of the inner surfaces will mainly proceed along the grain boundaries; and, in the steady state, all inner grains will have a hydrogen content which corresponds to the stationary hydrogen concentration at the inner grain boundaries of these surface grains. Therefore it is our aim to get an estimate of the steady state hydrogen concentration at the inner grain boundaries of the surface grains.

At first we have the following balance:

$$S = |j_1| + |j_2| \quad [\text{cm}^{-2} \text{sec}^{-1}] \qquad (1)$$

where S is the productivity of the source layer and is identical to the injection rate, j. For the fluxes j_1 and j_2 we find (notations as in Fig. 1) :

$$|j_1| = D \cdot (c_0 - c_1)/\Delta x, \qquad (2)$$

$$|j_2| = D \cdot (c_0 - c_2)/(d - \Delta x) \qquad (3)$$

where $D [\text{cm}^2/\text{sec}]$ is the coefficient of volume diffusion of hydrogen in the grain material.

To calculate the diffusion along the grain boundaries and the hydrogen flux leaving the meteorite in this way, we may imagine an area parallel to the meteorite surface and intersecting the surface grains (e. g. at the depth $d/2$, taken from the surface). This area is intersected by all grain boundaries which are perpendicular to the meteorite surface (cf. Fig. 2). Then, according to assumption (f), the diffusion flux per cm of section line is given by

$$|j'_3| = D_s \cdot (c_2^{2/3} - c_1^{2/3})/d \quad [\text{cm}^{-1} \text{sec}^{-1}]$$

with $D_s [\text{cm}^2/\text{sec}]$, the coefficient of grain boundary diffusion. The mean total length of all section lines per cm^2 of the area may be $\lambda [\text{cm}/\text{cm}^2 = \text{cm}^{-1}]$, the order of which we may estimate (for grains considered as cubic) by $2/d$. Thus we obtain for the mean grain boundary diffusion flux per cm^2 of meteorite surface in the steady state

$$|j_3| \equiv |j_2| = D_s \, 2 \, (c_2^{2/3} - c_1^{2/3})/d^2 \quad [\text{cm}^{-2} \text{sec}^{-1}]. \qquad (4)$$

The Eqs. (1) – (4) contain five unknown quantities, if the diffusion coefficients are known: c_0, c_1, c_2, j_1, j_2. An additional equation to determine c_1 would have to be related to the rate of the surface reactions. But since [assumption (c)] these are not rate determining for the hydrogen escape, we consequently neglect c_1 as small compared to c_0 and c_2. Then, for the interesting quantity c_2, we obtain

$$c_2 + \alpha \, c_2^{2/3} - \beta = 0 \qquad (5)$$

where $\alpha = (2 \, D_s)/(D \, d)$, and $\beta = (\Delta x \cdot S)/D$.

Under steady state conditions, as mentioned above, all inner grains have the hydrogen concentration c_2. But the question is after what time they reach this amount. When the gas transport along the grain boundaries is not the rate determining step [assumption (d)] then, the "fill up time" of a grain, is

$$\tau \approx d^2/(4 \, \pi^2 \, D) \quad [\text{sec}] \qquad (6)$$

(this holds for spheres of diameter d). The same time would be required for the outflow of the gas if

the outer gas pressure would suddenly disappear. Of the same order as this is the mean residence time of a tritium atom in the grain after its formation by the cosmic radiation. Of special interest, with respect to the tritium balance of the meteorite, is the comparison of this mean residence time with the mean life time of the tritium nucleus (17.8 years).

2. Results

For the numerical calculations we have to consider that the data on diffusion coefficients available up to now are probably correct only within the order of magnitude. Therefore, for all other quantities, we shall also use only the orders of magnitude.

With regard to the uncertainty in D and D_s, c_2 is computed for ranges of the variables, D, D_s, and d larger than might be expected. The value of D_s can only be estimated on the basis of other systems, since there are no data for meteoritic material. However, it is obvious from Table 1 that in spite of this uncertainty one can still obtain some evident results.

In Table 1, $\log c_2$ is tabulated as a function (Eq. 5) of D, D_s, d. The D-values of hydrogen in

α-iron (20 °C)[9] and in meteorite iron (20 °C and 100 °C)[1] are indicated. In Fig. 3 $\log \tau$ is plotted against $\log D$ with the grain diameter, d, as parameter (Eq. 6). For comparison some characteristic diffusion coefficients are indicated, as well as the mean life-time of ^{3}H.
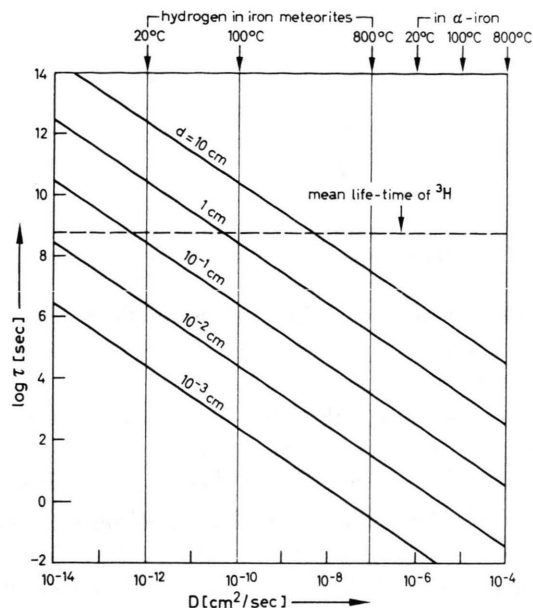

Fig. 3. $\log \tau$ as function of D and d (cf. Eq. 6). Some characteristic diffusion coefficients of hydrogen are indicated.

3. Discussion of the Method

The model used to estimate the steady state hydrogen content of iron meteorites in space under the influence of the solar proton flux reduces the real conditions to a rather simple norm. With respect to the uncertainty of all the data involved it seems reasonable, in principal, to use a rough approximation. But the question is to what extent is the approximation valid. Therefore we will discuss some of the assumptions mentioned in section 1 in more detail.

Assumption (c): Since meteorite iron usually contains $5-10\%$ of nickel, all surfaces which are in contact with hydrogen will keep hydrogen chemisorbed. Its concentration may be smaller on the outer surface of the meteorite, due to the UV radiation, but at the inner surfaces and the grain boundaries the concentration will be very large as compared to $(c_2)^{2/3}$. For, at the low temperatures in question, chemisorbed hydrogen will be bound

| D_s[cm²/sec] | d cm | Coefficient of volume diffusion D[cm²/sec] |
| | | α-iron | | Meteorite iron | | |
		20°C 10^{-6}	10^{-8}	100°C 10^{-10}	20°C 10^{-12}	10^{-14}
10^{-4}	10^{-3}	7,5	7,5	7,5	7,5	7,5
	10^{-2}	9	9	9	9	9
	10^{-1}	10	10,5	10,5	10,5	10,5
	1	10	12	12	12	12
10^{-5}	10^{-3}	9	9	9	9	9
	10^{-2}	10	10,5	10,5	10,5	10,5
	10^{-1}	10	12	12	12	12
	1	10	12	13,5	13,5	13,5
10^{-6}	10^{-3}	10	10,5	10,5	10,5	10,5
	10^{-2}	10	12	12	12	12
	10^{-1}	10	12	13,5	13,5	13,5
	1	10	12	14	15	15
$\log \beta$		10	12	14	16	18

Table 1. Steady state hydrogen content in iron meteorites. Listed is $\log c_2$ as a function of D, d, and D_s (cf. Eq. 5). Some characteristic D values are indicated. For $\log \beta$ cf. the discussion of assumption (d).

[9] R. C. FRANK, D. E. SWETS, and D. L. FRY, J. Appl. Phys. **29**, 892 [1958].

nearly irreversibly. Then, of course, it will not be involved in the hydrogen equilibrium between the grain surface and its volume, but it should be important for fast phase boundary reactions.

Assumption (d): If the grain boundary diffusion is not as important as is supposed here (with respect to the normal situation where, at low temperatures, grain boundary diffusion is predominant over volume diffusion), then there is only one alternative, and it is already included in this model: with increasing grain diameter d the quantity c_2 approaches more and more closely the hydrogen concentration in the source layer, c_0. In the extreme case of one single grain which is struck all around by the solar wind, its volume gets the steady state hydrogen concentration c_0. As one may see from Table 1, this maximum value (listed as $\log \beta$ in Table 1) may also be reached in grained bodies.

Assumption (e): The formation of molecular hydrogen within the meteorite would alter our conclusions only if there existed a system of capillary spaces connected with each other throughout the entire volume of the meteorite (e. g. cracks and clefts). Then the gas coming out of the surface grains could disappear through these channels so fast that the gas pressure in the capillary system would be practically zero. In this case all inner particles — and for larger bodies this means the whole meteorite — would get almost no hydrogen with the exception of spallogenic tritium. But such structural conditions should be either evident or detectable by experimental tests of the sorption properties.

In summary we may observe that all the simplifications and suspected incongruities of the model would result in underestimating the steady state hydrogen content, c_2, and therefore we might expect the true values of c_2 to be even higher. But this would justify even more the applicability of laboratory data to the hydrogen release from iron meteorites under space conditions.

4. Discussion of the Results

Let us now consider the consequences of the results shown in Table 1 and Fig. 3. In reference to Table 1 one should keep in mind that the tritium concentration in meteorites is at most of the order of $10^7/cm^3$, while the concentration obtained by irradiation of samples in the laboratory experiments to which we refer [1], are in the range from $10^{12}/cm^3$ to $10^{13}/cm^3$. Pure iron at 100 °C and under atmospheric conditions (10^{-4} Torr H_2) dissolves about 10^{13} atoms of hydrogen per cubic centimeter.

Then one can see from Table 1 that at a grain size of the order of 1 mm, the steady state hydrogen concentration in the grains is higher than the tritium concentration by at least 3.5 orders of magnitude, even if we assume for the grain boundary diffusion coefficient, D_s, as high a value as 10^{-4} cm²/ sec. For lower values of D_s the hydrogen concentration increases (cf. Table 1). At a grain size of 1 cm the hydrogen concentration in the inner particles can reach that in the source layer of the surface grains, c_0. The conditions then correspond to those of experiments performed in the laboratory.

Figure 3 may be interpreted in various ways: τ may be the "fill up" time, as well as the "flow out" time, or the mean residence time of a tritium atom in the grain, respectively. We see, that for grains up to about 1 mm diameter the mean life-time of tritium is larger than its mean residence time in the grain whenever the temperature is above 0 °C. That is, the tritium will almost be released by the grain before it undergoes decay to ^{3}He. (^{3}He in iron is practically immobile as compared to hydrogen.) Only in large particles without grain boundary diffusion is a retention of tritium to be expected. The fill-up time of large single particles with diameters of 10 cm (or of non-grained surface layers of 10 cm thickness of large meteoritic bodies, respectively) is of the order of 10^3 to 10^5 years, dependent on the temperature. The fill-up time for the same volumina, but with a grained structure, is much smaller, dependent on the grain diameter.

Finally, the situation during (and also after) the fall of the meteorite is of interest. The temperature treatment which the meteorite undergoes during the fall we consider as equivalent to an annealing to 800 °C for 100 seconds. These figures are indicated in Fig. 3 for pure and meteoritic iron. We see that only rather small grains, up to some 10^{-2} cm in size, will release their hydrogen in this way. This does not even take into account the necessary removal of the gas in larger bodies along the grain boundaries, the rate of which will be increased by the temperature rise much less than the rate of the volume diffusion. Therefore it seems to be evident that the short annealing during the meteorite's fall has no importance for the tritium loss.

The time required for total release after the fall (at about room temperature) ranges from months to years, depending on the grain size of the meteorite.

5. Conclusions

Summarizing, it follows (according to our rough estimate and using preliminary data on the hydrogen diffusion coefficients) that the result of the solar proton flux in iron meteorites is a comparatively high steady state hydrogen content, which may reach that of samples under laboratory conditions. Therefore it seems to be justified to calculate the diffusion loss of tritium from iron meteorites in space by means of laboratory diffusion data. Then general-ly a continuous and rather complete release of the cosmogenic tritium is to be expected, whenever the temperature is near 0 °C, or more. A tritium retention in the meteorite is then to be expected only at grain diameters of at least several millimeters. If it is possible to obtain more precise data on the hydrogen diffusion, then it seems to be possible to get a better information about the "thermal history in space" of an iron meteorite, and that by comparing the tritium loss with that of ^{3}He (cf. the discussion of SCHULTZ [10]).

[10] L. SCHULTZ, Preprint 1967 (Berichte aus der Meteoritenforschung, No. 80, Mainz).