551. 57 : 535. 217(203)

Amount of Water Photochemically Decomposed in the Upper Atmosphere

by
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Abstract

Water molecules are photochemically decomposed to oxygen and hydrogen ions in the upper atmosphere. These hydrogen and oxygen ions diffuse into the intersteller space with the specific escaping rates respectively. Both from the abundance ratio of protium and deuterium in the earth's crust and oceanic water and from their escaping ratios, the amount of water decomposed since the born of the earth can be calculated. This amount is in the functional relation with the content of deuterium in the primordial earth. The oxygen thus formed has played an important role in oxidation of primordial atmosphere and the earth's crust. It is also suggested that existence of ferric iron in the Pre-Cambrian rocks is probably due to such oxygen atoms.

Introduction

The amount of water decomposed by photo-dissociation in the upper atmosphere[1] can be calculated. Some dissociated hydrogen atoms diffuse into the interplanetary space from the earth's gravitational field. Protium atoms diffuse at a higher rate than deuterium atoms. It is assumed that almost all oxygen atoms have remained in the earth's atmosphere. The present calculation shows that 10^{23} grams of water, corresponding to 10 % of the mass of the oceanic water, have been decomposed and the oxygen atoms thus released are equal to that of the present atmosphere. These oxygen atoms must have played important roles in the development of the atmosphere and earth's crust.

The writer wishes to express his gratitude to Prof. Y. Miyake, Tokyo Educational Univ. and Prof. H. C. Uray, California Univ. for their guidances.

Calculation

The present calculation depends on the assumption that the concentration of deuterium in the oceanic water[2)~4)] which constitutes almost all the entire hydrosphere has resulted from the slower rate of deuterium than protium in the above-mentioned diffusion.

The diffusion velocity of each isotope, is expressed by the next equation (1)[5)~7)].

$$V=\frac{n}{2\sqrt{\frac{\pi m}{2KT}}}e^{\frac{-mgR^2}{KTR_c}}\left(\frac{mgR^2}{KTR_c}+1\right) \qquad (1)$$

Here, m is the mass number of each isotope. m is 1 in protium and 2 in deuterium.

n is the number of each isotope which presents in the atmosphere above the unite square of the earth's surface.

R is the radius of the earth.

R_c is the distance between the earth centre and the place from which each atom diffuses into the interplanetary space.

Then, the ratio of both diffusion rates is given by the next equation (2).

$$\frac{V_{(\text{protium})}}{V_{(\text{deuterium})}}=\frac{\dfrac{n_{(\text{protium})}}{2\sqrt{\dfrac{\pi}{2KT}}}e^{\frac{-gR^2}{KTR_c}}\left(\dfrac{gR^2}{KTR_c}+1\right)}{\dfrac{n_{(\text{deuterium})}}{2\sqrt{\dfrac{\pi}{KT}}}e^{\frac{-2gR^2}{KTR_c}}\left(\dfrac{2gR^2}{KTR_c}+1\right)}\doteqdot 10^5 \qquad (2)$$

Furthermore, dP and dD, the values of protium and deuterium atoms respectively, which have diffused from the earth's gravitational field into the interplanetary space, are expressed as follows.

$$dP=4\pi R_c{}^2{}_{(\text{protium})}\times V_{(\text{protium})}\times(\text{Geological ages})$$

$$dD=4\pi R_c{}^2{}_{(\text{deuterium})}\times V_{(\text{deuterium})}\times(\text{Geological ages}) \qquad (3)$$

From equations (2) and (3),

$$dP/dD=\frac{R_c{}^2{}_{(\text{protium})}}{R_c{}^2{}_{(\text{deuterium})}}\times\frac{V_{(\text{protium})}}{V_{(\text{deuterium})}}=10^5 \qquad (4)$$

The following assumptions are made in the above calculations.

(1) The diffusion rate of each isotope has remained constant, because the increase of the earth's gravity by the fall of meteorites is negligible through the geological ages, at least after the appearance of the "proto-ocean" which could supply enough water to the upper atmosphere.

(2) Temperature is assumed conveniently to be 1000°K for both hydrogen isotopes, although closer attention should be paid to this.

(3) $R_c{}^2{}_{(\text{protium})}=R_c{}^2{}_{(\text{deuterium})}$

This assumption is not serious, as understood in equation (4).

(4) n(protium) /n(deuterium) in equation (2) is assumed to be equal to the isotopic composition of the present atmospheric moisture.[8)~14)]

The gains and losses of hydrogen isotopes on the earth's surface expressed by the term dP/dD can be also obtained from an independent calculation, i. e., from the concentration of deuterium in the oceanic water. The present deuterium molar content in the entire oceanic water, $D_{(\text{present})}$ is obtained from equation (5).

$$D_{(\text{present})}=1.4\times10^{24}\times\frac{2}{18}\times D_{(\text{P})}\times10^{-2} \qquad (5)$$

Here, 1.4×10^{24} is the present amount of the oceanic water, expressed in gram.

$D_{(\text{P})}\times10^{-2}$ is the molar concentration of deuterium in the present oceanic water.

If the water volume that has undergone photo-dissociation is assigned to $A\times10^{24}$ grams, $(1.4+A)\times10^{24}$ grams is the total mass of the original or juvenile water which has appeared on the earth's surface and the average deuterium content of which is assumed as $D_{(\text{o})}\times10^{-2}$. Then, deuterium contained in the original water, $D_{(\text{original})}$ is

$$D_{(\text{original})}=(1.4+A)\times10^{24}\times\frac{2}{18}\times D_{(\text{o})}\times10^{-2} \qquad (6)$$

From equations (5) and (6), gain or loss of deuterium is expressed as follows.

$$dD=\frac{1}{9}\times10^{22}\{(1.4+A)\times D_{(\text{o})}-1.4\times D_{(\text{P})}\} \qquad (7)$$

From the same calculations, dP is

$$dP=\frac{1}{9}\times 10^{22}\{(1.4+A)\times(100-D_{(o)})-1.4\times(100-D_{(p)})\} \qquad (8)$$

From equations (7) and (8), dP/dD is given.

$$dP/dD=\frac{100A+1.4\times(D_{(p)}-D_{(o)})-AD_{(o)}}{AD_{(o)}-1.4\times(D_{(p)}-D_{(o)})} \qquad (9)$$

Finally the value of A is expressed by combining equation (9) with equation (4).

$$A=\frac{1.4\times 10^{3}\times(D_{(p)}-D_{(o)})}{10^{3}\times D_{(o)}-1} \qquad (10)$$

Equation (10) means that the value of A is solely a function of $D_{(o)}$, because $D_{(p)}$ is a constant value. That is, if the accurate $D_{(o)}$ value is known, the volume of water that has undergone photo-dissociation and the number of generated oxygen atoms can be calculated. Numerical relations between the deuterium concentration of the original water and the photo-dissociated water volume are presented in Table 1. The smaller the molar concentration of deuterium in the original water is, the larger the amount of water requires to have undergone photo-dissociation. Negative values in Table 1 mean that the earth has obtained much exogenous hydrogen enriched by deuterium.

Table 1 Relation between the deuterium concentration of the original water and the amount of the photo-dissociated water

$D_{(o)}$ (%)	A (10^{24}gr.)
0.0255	−0.56
0.0200	−0.33
0.0155	±0.00
0.0150	+0.05
0.0145	+0.10
0.0100	+0.85
0.0055	+3.3

$D_{(o)}$ in question may be made clear by the statistical investigation of P/D values in rocks, magmatic waters and especially meteorites[15)~41)], even though the data available at present are not sufficient. P/D values in thermal waters have been investigated by many authors. Thermal waters, except for oil field brines[42)~45)], have usually smaller values in P/D than the oceanic water. Typical post-volcanic activity at Noboribetsu in Hokkaido[46)~49)], Japan discharges more than 10^4 tons of water daily and the temperature of which is as much as 200∼230°C. P/D value in this hydrothermal water, which is considered to have a close relation to the volcanic activity, is smaller than that of the oceanic water and even of the fresh water when the activity is strong[49)]. Furthermore, T. Chitani and his co-workers have found that more than 70 % of hot spring waters have lower P/D values than the fresh waters[50)]. These facts seem to show that thermal waters from volcanic sources have lower values in P/D. But the writer can not get any information of the true $D_{(o)}$ value from these data. It is considered to be most essential that P/D values in meteorites are determined. If an intermediate P/D value among those reported is applied in the present calculation, it is estimated that 10^{23} grams of water have undergone photo-dissociation, although this estimate necessitates more data of meteorites.

In the present calculation, P/D values of materials in the biosphere and in glaciers[51)~55)] are neglected, together with those introduced to the earth's surface by cosmic rays[56]. But these could not change effectively the average of the present P/D values on the earth, i.e., P/D value of the oceanic water.

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高層大気圏において光分解された水量

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要 旨

地球高層大気圏（およそ300 km，1,000°K）において水分子は紫外線によつて水素イオンと酸素イオンとに解離される。この水素イオン（protium および deuterium）と酸素イオンは固有の速度をもつて惑星空間に拡散する。

地球地殻上における protium と deuterium の収支と惑星空間への拡散速度比から，地質年代間に光分解された水量を計算することができる。この量は第10式，第1表で示されるように，隕石中の deuterium の量と函数関係にあり，10^{23} g以上と考えられる。この光分解によつて生成した酸素イオンは，原始大気および地殻の酸化に重要な寄与を果したと考えられる。

この結果は，原生代の岩石中に三価鉄の存在する事実に対し一解釈を与える。