WATER ON MARS AND VENUS

T.M. Donahue
Department of Atmospheric, Oceanic and Space Sciences
University of Michigan, Ann Arbor, MI 48109

ABSTRACT

This paper reviews evidence relating to the abundance of water on early Mars and Venus from measurements of the present abundance of hydrogen compounds, deuterium to hydrogen (D/H) ratios and escape fluxes. For Mars, recent measurements of D/H ratios in SNC hydrous minerals provide data on the ratios at earlier times to augment present atmospheric values. Interpretation of these data shows that they are consistent with the presence of scores to hundreds of meters of liquid water on early Mars, as well as less, but still abundant, water in today's crust. They also require concentrations of hydrogen compounds in the early atmosphere orders of magnitude higher than is present today to support large scale hydrogen escape. For Venus, a very large D/H enhancement (160 fold) implies at least 3 to 4 meters liquid equivalent of early water (depending on how much hydrogen is in the atmosphere today). It is consistent with much more, even the equivalent of a full terrestrial ocean. The low escape flux and high fractionation factor place severe constraints on volcanic or cometary sources. Some of the present water can have been injected by volcanism but comets as important sources appear to be excluded.

INTRODUCTION

Among the terrestrial planets only Earth now can boast of an ocean of water. Mercury and the Moon are bone-dry. So is the atmosphere of Venus, where the water vapor mixing ratio below the clouds is only 30 ppm. How much water is below its surface is unknown. On Mars too the water content of the atmosphere is variable, but low; the average value is 10 precipitable μm. Again, as on Venus, how much water is in the crust and mantle is not known but is the subject of much speculation because of evidence for vigorous fluvial activity in the recent as well as the distant past. The polar caps clearly provide a reservoir for water under present climatic conditions, water that could be mobilized under certain circumstances, such as higher obliquity or more favorable orbital characteristics.

The purpose of this paper is to examine evidence that both Venus and Mars once had much more water in their atmospheres, hydrospheres (perhaps) and crusts than they do today. Even the early equivalent of a full terrestrial ocean on Venus cannot be excluded. The evidence in question is the highly fractionated state of hydrogen and deuterium on both planets, especially Venus, compared to Earth and other solar system objects. On Mars R, the ratio of deuterium to hydrogen in atmospheric water vapor is $(8.1 \pm 0.3) \times 10^{-4}$.[1,2] Here

$$2R = [HDO]/[H_2O], \qquad (1)$$

where $[x]$ is the atmospheric columnar abundance of species x. R is greater on Mars than in terrestrial ocean water (SMOW) by a factor of 5.2 ± 0.2. (There is evidence that Martian mantle water is not more than 50% richer in deuterium than SMOW.[3]) On Venus R is huge -- 2.5×10^{-2}, 160 times that of SMOW.[4,5,6,7,8,9] If we assume -- as is reasonable -- that all three planets started with about the same value of R in their water, we can show that these results most probably mean that both Mars and Venus have lost a lot of the hydrogen associated with water, or other hydrogen compounds that resided in reservoirs containing much more hydrogen in the past than they do today. The challenge is to use the measurements of R, of the present abundance of atmospheric hydrogen compounds and of hydrogen and deuterium escape fluxes to infer what the abundances were in the past. Recent measurement of the

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D/H ratio of water in the Martian crust as it was hundreds of millions or perhaps billions of years ago[3] will also be extremely useful in this exercise.[10]

Suppose atomic hydrogen is escaping from the atmosphere of a planet with a flux ϕ_1 and deuterium with a flux ϕ_2, where the fluxes are related by the fractionation factor f,

$$f = \phi_2/R\phi_1 . \tag{2}$$

Here

$$R = [D]/[H]. \tag{3}$$

f, which also can be expressed in the form

$$f = \frac{d[D]}{[D]} \Big/ \frac{d[H]}{[H]} , \tag{4}$$

measures the relative ease with which deuterium escapes. The abundance of hydrogen and deuterium are then governed by the differential equations

$$\frac{d[H]}{dt} = P - \phi_1 = P - K[H], \tag{5}$$

$$\frac{d[D]}{dt} = R_S P - Rf\, KH, \tag{6}$$

where it is assumed that there is a source of hydrogen of strength P and of deuterium $R_S P$. K is a proportionality constant. In case P is small or absent, Eq. (4) can be integrated at once to give the ratio of the size of the reservoir at time t_2 to a later time t_1

$$r(t_1,t_2) = \frac{[H(t_2)]}{[H(t_1)]} = \left(\frac{R(t_1)}{R(t_2)}\right)^{\frac{1}{1-f}} . \tag{7}$$

This is independent of ϕ_1 and depends only on the change in the D to H ratio and the fractionation factor. Otherwise the solution of Eqs. (5) and (6) for R[11,12,13] is the time dependent expression

$$R = R_S/f - (R_S/f - R_o)\exp(-\int \phi_1\, fdt'/[H_{SS}]), \tag{8}$$

where R_o is the initial D/H ratio and $[H_{SS}]$ is the steady state hydrogen abundance that prevails when escape balances production. The steady state D to H ratio is given by

$$R_{SS} = R_S/f \tag{9}$$

(In integrating Eqs. (4), (5) and (6), we assume that f is time independent. This is a very shaky assumption. Both f and ϕ_1 have surely varied considerably during the lifetime of Mars and Venus. There has been only one attempt to model this variation.[14] It needs to be repeated for Venus and extended to Mars in the light of today's knowledge.) For Jeans escape ϕ_2/ϕ_1 and R covary unless the exospheric temperature changes. In terms of the characteristic hydrogen lifetime,

$$\tau_1 = [H_{SS}]/\phi_1 , \tag{10}$$

the approach to a steady state in Eq. (8) is described by a lifetime

$$\tau_{SS} = \tau_1/f. \tag{11}$$

WATER ON MARS

In the case of Mars, the present rate of loss of hydrogen in the form of H and H_2 by thermal or so-called "Jeans" escape can be measured and modeled. A recent calculation of ϕ_1 averaged over the solar cycle, based on observed atomic hydrogen densities in the upper atmosphere, gives[15]

$$\phi_1 = 2.4 \times 10^8 \, cm^{-2}s^{-1}, \tag{12}$$

where

$$\phi_1 = \phi(H) + 2\phi(H_2) + \phi(HD), \tag{13}$$

$$\phi_2 = \phi(D) + \phi(HD). \tag{14}$$

The fractionation factor for Jeans escape of D and HD from Mars under present conditions has been calculated to be 0.32.[16]   Other escape mechanisms are known to be important for Earth[17] and Venus[18,19] and may also be so for Mars. To allow for this eventuality, f will be treated as a parameter in this paper. It should be kept in mind also that ϕ_1 for Mars may be larger than Eq. (12) today, and that it may have varied even during the recent few hundred million years and, thus, that the contents of Martian water reservoirs may in fact have been considerably different (probably higher) than those determined in this paper.   On the other hand, because Jeans escape flux from Mars is so large compared to the Jeans flux from either of the other planets, it probably dominates other escape modes on that planet. Measurements that enable an evaluation of all escape processes certainly should be included in any future mission to Mars, so crucial it is to understand the evolution of water. Relationship (9) shows that Martian water can be in a steady state with a source and escape if R_S is about twice that of SMOW and the strength of the source at least $2.5 \times 10^8 \, cm^{-2}s^{-1}$.   The first is possible, the second unlikely, as we shall eventually discuss in greater detail.

We shall assume that water in the crust exchanges freely with atmospheric water vapor at present and in the past, as indicated by the evidence for interaction of highly deuterated crustal water with minerals found in SNC meteorites. Thus, the D to H ratio, R, will covary in the atmosphere and in crustal water. If some of the crustal water is stored as ice in equilibrium with liquid water, the D to H ratio in the ice will be about 1.27 times the value in the vapor and liquid phase.[16] To the extent that there is exchangeable water in the solid phase, the estimates of reservoir sizes in this paper are lower limits. Following a treatment by Yung et al,[16] we assume that there is very much more water in the crust than in the atmosphere. The total amount of hydrogen present in the two reservoirs is

$$h(t) = c(t) + a(t). \tag{15}$$

Integration of Eq. (4), where

$$\phi_i = -\frac{dh_i}{dt}, \tag{16}$$

gives Eq. (7) for the ratio of the water reservoir at t_2 to the reservoir at a later time t_1 in the form

$$r(t_1, t_2) = \frac{a(t_2) + c(t_2)}{a(t_1) + c(t_1)} = \left(\frac{R(t_1)}{R(t_2)}\right)^{\frac{1}{1-f}}, \tag{17}$$

which, as we have already seen, is independent of ϕ_1. The actual size of the present reservoir does depend on the escape rate, however. The smaller the change in R over a given period of time the larger the reservoir must be compared to the amount of hydrogen (and deuterium) lost. In fact, since

$$c(t_1) = c(t_2) - \int_{t_1}^{t_2} \phi_1 \, dt, \tag{18}$$

and

$$c(t) \gg a(t), \tag{19}$$

$$c(t_1) \cong \int_{t_1}^{t_2} \phi_1 \, dt/(r-1). \tag{20}$$

$c(t_1)$ increases rapidly as r approaches unity.

Table I. Early and late crustal water reservoirs (constant escape flux)

f	0	0.1	0.32	0.6
r	5.2	6.2	11.3	62
	$c(t_1)$ meters			
t_1				
Present	1.3	0.98	0.5	0.084
	$c(t_2)$ meters			
t_2				
4.5 Ga	6.7	6.1	5.7	5.2

Here time is measured backward from the present so that $t_1 < t_2$. Table I gives r and the depth of the water reservoir expressed as meters of liquid water at $t_1 = 0$ and $t_2 = 4.5$ Ga if ϕ_1 has a constant value given by Eq. (12). To allow for the possibility of an important contribution to the escape flux by mechanisms in which escape of deuterium is inefficient compared to Jeans escape, r and $c(o)$ and $c(t_2)$ are shown for several values of f. No matter how effectively deuterium was retained, these crustal reservoirs are small. As others have pointed out,[16,20] increasing ϕ_1 causes $c(t_2)$ and $c(o)$ to increase correspondingly. And if Mars was much warmer and wetter during part of its life than it is today, escape rates then could have been much higher than today.

In all cases, the early reservoirs $c(t_2)$ are very small compared with the amount of water that was almost surely mobilized when valley networks and catastrophic flood channels were produced on the Martian surface. Production of the flood channels apparently requires that there exist a planet-wide reservoir of crustal water hundreds of meters deep.[21] In early times, after the late heavy bombardment, the climate may have been warm enough for precipitation to produce such fluvial features as the valley networks.[22-24] Erosion of early surface features, possibly by fluvial activity, was extensive.[25,26] Some have argued that there is geological evidence that the planet has undergone frequent episodes of moderate climate with abundant surface water. These may have been triggered by release of water and CO_2 during periods of volcanism as recently as 500 million years ago.[27] Furthermore, the inclination

of the Martian spin axis varies secularly. During periods of high obliquity, water now in polar deposits could have been mobilized.[21] Thus, ϕ_1 was almost surely much larger at times in the past than it is today. But, until recently, there has been no guidepost to determine how much.

Recent measurements of the D to H ratio in hydrous minerals contained in three of the ten SNC meteorites[3] may give R in crustal water and thus in the atmosphere at one time in the past for comparison with the present and original values. In the case of Zagami, one of the Shergottites examined, the time of crystallization is controversial. Early whole rock chronometry set the time at 1.3 Ga,[28] whereas some favor a date as late as 180 Ma.[29] Very surprisingly, the SNC D to H ratio measurements showed that the ratio for some apatites in Zagami was as large as today's atmospheric value. These elevated values apparently require that crustal water, which interacted with the igneous SNC rocks shortly after they crystallized and exchanged with deuterium-poor mantle water, had a D to H ratio, R, 180 Ma to 1.3 Ga, indistinguishable from R today. There must have been an active hydrothermal system exchanging atmospheric and crustal water as recently as the time at which Zagami crystallized. The authors of the paper reporting these measurements[3] suggest that the lower values of R found for most hydrogen samples of hydrous minerals resulted from incomplete exchange of crustal water with pristine, low R mantle water. Presumably magmatic water would have intruded into the crust along with the rest of the magma. They also argued[3] that hydrothermal alteration would not have significantly post-dated primary crystallization of the magmas. Donahue[10] has examined the possibility that some of the water forming the hydrous phase was crustal water with the same R as atmospheric water vapor, at the time, t_z, when Zagami apatites crystallized. The largest apatite D to H ratio would then be the value of R for atmospheric and crustal water at that time or at the time the water was last exposed to the atmosphere. Hence, R was about as high then as it is today. From the published data and the precision claimed for the measurements, it is difficult to see how R could have been more than five percent lower than the present R. In fact, any value of $R(t_z)$ up to $R(o)$ seems to be possible. At a constant loss rate equal to today's value of ϕ_1, R would have fallen to 80% of today's 180 Ma ago and 40% 1.3 Ga ago. Such low values are certainly excluded. If, indeed, $R(t_z)$ was, say, five percent lower than its present value when these minerals crystallized, the amount of hydrogen and deuterium that have since escaped must be small compared to the amount in the reservoir 0.18 or 1.3 billion years ago. But in 0.18 Gyr hydrogen associated with 0.2m of water in liquid form and in 1.3 Gyr that associated with 1.4m of water would have escaped at present escape rates. These amounts of water are much larger or comparable to all values of $c(t)$ in Table I.

Table II. Crustal water (meters), escape fluxes ($cm^{-2}s^{-1}$), Zagami 0.18 Gyr old, $R(o) = 1.04R(t_z)$

f	0	0.32	0.6	0.8
$c(t_1)$ (present)	5.5	3.7	2.1	1.0
$c(t_z)$ (180 Ma)	5.7	3.9	2.3	1.2
$c(t_2)$ (4.5 Ga)	28	42	132	3800
$\phi_1(t_z, t_2)$	1.1 (9)	1.8 (9)	6.3(9)	1.9 (10)
ϕ_1 (3.5−4.5 Ga)	4.8 (9)	8 (9)	2.7 (10)	8 (11)

In fact, examination of the published SNC data[3] indicates that an extremely conservative estimate of the lower limit to the ratio of $R(o)$ to $R(t_z)$ is 1.04. r in this case would be given by

$$r = (1.04)^{\frac{1}{1-f}}, \tag{21}$$

and

$$c(o) = \frac{\phi_1 t_z}{r-1}. \tag{22}$$

$c(o)$ is given in Table II for several values of f. Finally, the crustal water content when fractionation began, $c(t_2)$, is calculated, where

$$c(t) = r_o \, c(o) \tag{23}$$

with

$$r_o = r(o, t_z) = 5.2^{\frac{1}{1-f}}. \tag{24}$$

$c(t_2)$ is also tabulated in Table II. All of these quantities are, of course, considerably larger than the corresponding entries in Table I. They are lower limits for the crustal inventories.

Also entered in Table II, as are the average fluxes

$$\phi_1(t_z, t_2) = \frac{c(t_2) - c(t_z)}{t_2 - t_z}, \tag{25}$$

where t_z is 180 Ma, t_2 is 4.5 Ga and c is expressed in terms of hydrogen atoms per cm^2 column. Shown also as fluxes 4.32 times as large as these, such as would have been required if the hydrogen was lost mainly during the first billion years as would have been the case if the warm, wet[26] time on Mars was as early as geological evidence indicates. In fact, this period may have lasted only for the first 500 Myr. In this case the fluxes listed must be doubled.

Table III. Crustal water (meters) and escape fluxes ($cm^{-2}s^{-1}$), Zagami 1.3 Ga, $R_1(o) = 1.04 \, R(t_z)$

f	0	0.32	0.6	0.8
$r(t_z)$	1.038	1.057	1.1	1.21
$c(t_1)$ (present)	37	25	14	6.7
$c(t_z)$ (1.3 Ga)	38.4	26.4	15.4	8.1
$c(t_2)$ (4.5 Ga)	191	278	880	2.5 (4)
$\phi_1(t_z, t_2)$	7.5(9)	1.2 (9)	4.2 (10)	1.2 (12)
ϕ_1 (3.5-4.5 Ga)	3.2 (10)	5.3 (10)	1.8 (11)	5.3 (12)

$c(t_2)$ still falls very much short of the 400 to 500 meters of water called for in some channel and basin creating scenarios, if f is fixed at 0.32. Another scenario is provided if Zagami apatites are assumed to be 1.3 Gyr old. During those 1.3 Gyr, 1.4m of water would have escaped at the present loss rate. All reservoirs and fluxes in Table II would be multiplied by a factor of 1.4/0.2. The various

values of c and ϕ_1 are listed in Table III. Here much more respectable early water inventories are called for, particularly if ϕ_1 was larger than $2.4 \times 10^8 \, cm^{-2}s^{-1}$ for much of the past 1.3 Gyr. Early escape fluxes orders of magnitude larger than today's would be called for.

But the Zagami results do not constrain the D to H ratio in crustal water at t_z to be as small as 96% of the present R. They allow an arbitrarily close match, so that $r-1$, in principle, can be as small as we choose. It is legitimate, for example, to ask how large R must have been when the apatites crystallized, if the original water reservoir was arbitrarily large, say 500m. To accommodate any desired reservoir depth $c(t)$, 4.5 Gyr ago, the ratio of R at t_z to $R(o)$ must be

$$R(t_z)/R(o) = \left[(c(t)/11.3)/(\phi_1 t_z + c(t)/11.3) \right]^{0.68}. \tag{26}$$

for Jeans escape. For $c(t_2)$ 500 km, $c(o)$ would be 44 meters and $R(t_z)$ 0.997 today's R if t_z is 1.3 Ga. The average escape fluxes would then have been about 400 times those of today if enhanced escape was restricted to the first billion years. Table IV shows the ratios of $R(t_z)$ to $R(o)$ for a range of fractionation factors and for $t_z = 180$ Ma and 1.3 Ga if $c(t_2)$ was 500 meters 4.5 Ga ago.

Table IV. Crustal reservoirs in meters now and at t_z if the original Reservoir $c(t)$ was 500m Deep. Ratio of $R(t_z)$ to $R(o)$ required if $c(t_2)$ was 500m.

f	0		0.32		0.6	
r_o	5.2		11.3		62	
time	c	$R(t_z)/R(t_1)$	c	$R(t_z)/R(t_1)$	c	$R(t_z)/R(t_1)$
present	96.1		44.3		8.1	
$t_z = 180$ Ma	96.3	0.998	44.5	0.997	8.3	0.990
$t_z = 1.3$ Ga	97.4	0.987	45.5	0.980	9.5	0.940
$t_2 = 4.5$ Ga	500		500		500	

Escape fluxes orders of magnitude larger than those of today are possible if the hydrogen concentration in the atmosphere was correspondingly larger. A fundamental limitation to the escape flux is the so-called limiting flux determined by the mixing ratio of hydrogen in all of its forms in the lower atmosphere below the homopause.[30] In the case of the Martian atmosphere, the dominant hydrogen species there (at least under today's conditions) is H_2,[14,31] so

$$\phi_l = 2 \; b f_{H_2}/H_a = 2.25 \times 10^{13} f_{H_2} \, cm^{-2}s^{-1}, \tag{27}$$

where f_{H_2} is the mixing ratio of H_2 near the homopause, H_a is the mean atmospheric scale height there, and

$$b = D_{H_2}/n_a. \tag{28}$$

Here D_{H_2} is the H_2 molecular diffusion coefficient and n_a the atmospheric density. In today's atmosphere, with $f_{H_2} = 2 \times 10^{-5}$, ϕ_l is larger than the escape flux by a factor of about 2. This is because much of the escaping hydrogen is in the form of H_2, which escapes slowly compared to H. To attain an escape flux of $10^{11} \, cm^{-2}s^{-1}$, f_{H_2} would need to be equal to or larger than 0.40%. If it is

warranted, scaling from today's atmosphere, where a homopause mixing ratio f_{H_2} of 2×10^{-5} corresponds to a water vapor abundance of 10 precipitable μm in the lower Martian atmosphere, would require that the average Martian atmosphere for the first 3.2 billion years contain an average of 2 precipitable centimeters of water vapor. However, the whole issue of how the hydrogen mixing ratio in the upper atmosphere relates to the amount of water vapor in the troposphere on an early warmer, wetter Mars given the likely presence of a cold trap,[32] is one of the major uncertainties besetting this entire problem.

Enhanced escape of hydrogen can be effected by increasing the exospheric temperature of the upper atmosphere until the flow bottleneck is transferred from the exosphere to the region near the homopause and the flux becomes diffusion limited. This is something that almost surely would have happened during the period of high euv solar luminosity when the solar system was young. The fractionation factor for Jeans escape would increase by a significant amount if the exospheric temperature were to increase appreciably. This is because the escape flux of the more massive species D, HD and H_2 increase much more rapidly with temperature than that of H does. Taking account of the change in densities at the exobase n_{ci} as well as the change in effusion velocity w_{ci} where

$$\phi_i = n_{ci} w_{ci},$$

$\phi(H)$ would change by a factor of 4.4, $\phi(H_2)$ and $\phi(HD)$ by a factor of 10.5 and $\phi(HD)$ by a factor of 34 if the exospheric temperature should change from 365K to 500K.[16] The ratio ϕ_2/ϕ_1, and consequently the fractionation factor, would increase by a factor of 1.53 making $r_o(o,t_2)$ grow from 11.3 to 27. Secondly, the escape rate would increase if the supply of hydrogen compounds (H_2 in today's atmosphere) below the diffusion barrier should be increased. In fact, when limiting flux applies, the escape flux depends only on the total hydrogen mixing ratio in this region, as we have seen. Ultimately, however, increasing the mixing ratio of the dominant hydrogen constituent in the upper atmosphere and the escape rate by orders of magnitude, as this discussion demands, would appear somehow to require a corresponding increase in the dominant hydrogen constituent in the lower atmosphere, water vapor.

Something has to be done to dispose of the oxygen counterpart of the escaping hydrogen. McElroy and Donahue[33] in fact argued that energetic oxygen atoms resulting from dissociative recombination of O_2^+, escape from the upper atmosphere at a rate half the hydrogen escape rate, and control hydrogen escape as the result of a feedback process that maintains the stability of the CO_2 atmosphere. However, it now appears that neither dissociative recombination of O_2^+[34] nor sputtering of oxygen atoms[35] can remove oxygen nearly fast enough to prevent a significant change in the redox state of the atmosphere in a time of the order of 10^5 years. If this is true, it is difficult to see how the redox state of the atmosphere can be maintained without another oxygen sink -- such as surface oxidation.[36] Presumably, this would be true even in the very different circumstances of the early atmosphere. However, the necessary investigation of the aeronomy of that atmosphere remains to be carried out. There are essential elements missing in our understanding of an early Mars atmosphere which must be warm, wet and support a hydrogen escape flux hundreds of times as large as the one today. As Kasting[32] has pointed out, a simple $CO_2 - H_2O$ greenhouse cannot be invoked to provide us with a warm wet Mars because of the effects of condensation and cloud formation. Alternative processes capable of producing early valley networks without precipitation[26] and thus without requiring a very humid atmosphere will *not* result in the loss of massive amounts of hydrogen which the D to H measurements seem to require.

Another limit on the maximum possible escape flux, no matter how wet the atmosphere, is set by the solar insolation available below 185nm to photolyze H_2O at 1.5 AU. After allowance for enhanced uv from the young sun,[37] solar cycle effects, absorption by other atmospheric species and solar cycle variation, a generous estimate of this limit is $5 \times 10^{11} cm^{-2} s^{-1}$. If escape occurred mainly during the first billion years this means that $c(t_2)$ could not have exceeded 2200m and $c(o)$ consequently, 190m. Thus it is difficult to allow more than 190m of water in the modern crust to drive hydrothermal systems or account for catastrophic outflow channels if the early warm wet period of

enhanced escape lasted only 1 Gyr. Extending the period buys only a little relief because the ultraviolet luminosity of the sun should have been reduced to its present level 3.5 Ga. This would reduce the maximum photolysis rate significantly, by a factor of about 2.

There may be the planet-wide equivalent of 30m of water stored today in the polar caps.[38] This water may be mobilized at intervals of 10^5 to 10^6 years because of changes in obliquity and eccentricity. Because these interludes are short on planetary time scales or the crystallization age of Zagami, this polar cap water can be taken to exchange effectively with atmospheric and crustal water. The treatment presented here would still be valid except that $c(o)$ would have to be at least as large as the polar cap reservoir. If the polar caps sequester a large amount of water which has only infrequently been mobilized, the planet's exchangeable water would have been occasionally diluted with water having a low D to H ratio. The present R would be lower than it would have been if straightforward fractionation had occurred and the enhancement factor 11.3 would be an *underestimate*. Numerical modelling would be required to explore this contingency further, but the basic conclusions reached here, that an early large crustal reservoir is allowed by deuterium to hydrogen ratio measurements, would not change. This is true also, of course, for any sizable reservoir that might ordinarily be sequestered but is mobilized occasionally. Whenever that might occur, large amounts of deuterium-poor water would mingle with the rest of the water in the planet's interchangeable reservoirs.

This analysis assumes that there is no important exogenous source of hydrogen and deuterium, such as would result from deposition of water on Mars by incoming comets. If the D to H ratio in the source is low and the rate of hydrogen input is comparable to the escape flux, the effect of such a source would be to produce a low net escape rate with a large fractionation factor. Consequently, R would change more slowly with time than if the source were absent, and smaller crustal reservoirs would be implied by any given ratio of $R(t_z)$ to $R(o)$. If, for example, the production term in Eq. (6) is assumed to be $\alpha\phi_1$ and the D to H ratio in the source assumed to be βR, the differential equations (5) and (6) that control the evolution of $[H]$ and $[D]$ during the time from 0 to t_z, when ϕ_1 is constant, become

$$\frac{d[H]}{dt} = (\alpha - 1)\phi_1 \tag{29}$$

$$\frac{d[D]}{dt} = (\beta\alpha - f)R\phi_1. \tag{30}$$

Thus the effective fractionation factor f' defined in (4) becomes

$$f' = (0.32 - \beta\alpha)/(1 - \alpha). \tag{31}$$

If $\beta < 0.32$, that is if the D to H ratio in cometary water is less than 2.6×10^{-4}, f' increases slowly with α until α approaches 1. At $\alpha = 1$, where the net hydrogen flux vanishes, f' is singular. Above $\alpha = 1$, f' increases from large negative values to a node at $\alpha = 0.32/\beta$ after which f' approaches β as α goes to infinity. On the other hand, if the D to H cometary ratio is greater than 2.6×10^{-4}, so that $\beta > 0.32$, f' goes to 0 at $\alpha = 0.32/\beta$. Beyond the singularity at $\alpha = 1$, f' decreases rapidly at first and then slowly approaches β as α gets large. The interesting D to H ratios for water in comets bracket 2.6×10^{-4}. One case is that of SMOW, 1.56×10^{-4}, the other is that of comet Halley, which has recently been set[39] at $3.08(+0.38,-0.68)\times10^{-4}$. In either case the effect of injection of water from comets on the estimated size of the crustal reservoir is small until α is about 0.8. There, if $\beta = 0.37$, f' becomes 0.024, r becomes 1.039 and $c(o)$ 36m instead of 25m, as it was without comets. If $\beta = 0.19$ these quantities change to $f' = 0.83$, $r = 1.245$ and $c(o) = 5.7$m (t_z is 1.3 Ga). A flux of 1.9×10^8 hydrogen atoms cm s^{-1} would be effected by one 10^{18} gm comet impacting on average every 3.4 million years if 5% of the comets mass is assumed to be hydrogen. This impact rate is higher by orders of magnitude than the generally accepted rate for Mars.[40]

WATER ON VENUS

Space missions have provided a wealth of information about hydrogen compounds and hydrogen escape for Venus. Particularly productive were the Pioneer Venus Multiprobe and Orbiter (PVMP and PVO) missions and remote spectrographic observations from Earth and Galileo. Direct measurement of the ratio of HDO to H_2O densities by the Pioneer Venus Large Probe Neutral Mass Spectrometer (LNMS),[5] inferences from ionospheric observations of 3 amu and 2 amu ions,[4,6,7] two near infrared spectral measurements of HDO and H_2O[8,9] mixing ratios all agree that R on Venus is 120 to 160 times that of SMOW. PV ion and neutral density measurements revealed that there are only two significant channels of hydrogen and deuterium escape. Almost all of the escaping hydrogen originates from the post-midnight hydrogen bulge in the upper atmosphere of the planet. Calculations indicate that charge exchange of hot H^+ ions with thermal H atoms causes a planet-wide average hydrogen escape flux of $9 \times 10^6 \, cm^{-2}s^{-1}$ during solar maximum.[19] The fractionation factor is 0.02. Ion density profiles[18] show that H^+ and D^+ ions are accelerated out of this region by a charge separation electric field. The planet-wide average flux of H^+ produced by this mechanism is $1.4 \times 10^7 \, cm^{-2}s^{-1}$ during solar maximum. f is 0.17. No other escape mechanism is important. Ejection of hydrogen atoms after collisions with fast oxygen atoms, once thought to be important,[41] has been shown by Hodges[42] to make only a meager contribution to the total escape rate. Most energetic oxygen atoms are created so deep in the atmosphere that they lose most of their energy in collisions with other oxygen atoms well below the base of the exosphere. Thus, during solar maximum in 1978 and 1979, the planet-wide escape flux was $2.3 \times 10^7 \, cm^{-2}s^{-1}$ with an average fractionation factor of 0.11. During the PVO reentry in the latter half of 1992, the solar 10.7cm radio flux was at a level of $125 \times 10^{22} \, Wm^{-2}Hz^{-1}$ compared to $200 - 250 \times 10^{22} \, Wm^{-2}Hz^{-1}$ in 1978-1979. The H^+ densities in the bulge region were only 0.125 times those measured during solar maximum,[19] so the electric field driven hydrogen escape flux was reduced to $1.7 \times 10^6 \, cm^{-2}s^{-1}$. On the other hand, the atomic hydrogen density increased in the bulge as solar activity decreased, because the outflow due to escape was much reduced while the trans-terminator flow into the bulge continued.[43] The charge transfer escape flux, being proportional to the product of the H and H^+ densities, was only slightly reduced to $0.7 \times 10^7 \, cm^{-2}s^{-1}$. This made the escape flux in 1992 only $0.87 \times 10^7 \, cm^{-2}s^{-1}$ and the fractionation factor 0.05. Thus, the solar cycle average escape fluxes are $0.8 \times 10^7 \, cm^{-2}$ for the electric field driven flow and $0.8 \times 10^7 \, cm^{-2}$ for charge transfer, making a total average flux of $1.6 \times 10^7 \, cm^{-2}s^{-1}$ with a fractionation factor of 0.1.

It is, however, questionable that the charge transfer escape flux should be added to the electric field driven flow. Instead, it appears more likely that included in the latter flow are the ions which will undergo charge transfer collision at higher altitude. In this case, the escape flux varies from $1.4 \times 10^7 \, cm^{-2}s^{-1}$ to $0.17 \times 10^7 \, cm^{-2}s^{-1}$ with solar activity. The average flux is $0.8 \times 10^7 \, cm^{-2}s^{-1}$ and the fractionation factor 0.17. This interpretation is strongly reinforced by an analysis of the rate at which the hydrogen density in the bulge increased as loss of hydrogen from the bulge decreased with reduced solar activity.[43] The rate at which the column density grows should equal the rate at which it decreases when solar activity is turned on again, which is the escape flux. This rate was $8 \times 10^7 \, cm^{-2}s^{-1}$ for hydrogen and $2.3 \times 10^5 \, cm^{-2}s^{-1}$ for deuterium from the bulge, resulting in a fractionation factor of 0.12. The planet-wide average hydrogen flux would thus be $1.6 \times 10^7 \, cm^{-2}s^{-1}$, which is very close to the measured electric field driven flow during solar maximum without contribution from charge exchange.

Both the PV LNMS and infra-red studies agree that the water vapor mixing ratio below the clouds is 30 ppm.[44,45] The LNMS also detected 2 amu and 3 amu species. Analysis of these data indicate that, whereas most of the 2 amu species are terrestrial H_2 molecules emanating from mass spectrometer surfaces and some of the 3 amu species are H_3^+ produced by dissociative ionization of internally generated methane, there is a possibility that some of these species are H_2 and HD from the Venus atmosphere. Mixing ratios as small as 0 and as large as 10 ppm below 25 km are possible.[45] We consider two possibilities: the hydrogen budget amounts to 30 ppm of H_2O and that it amounts to 40 ppm of H_2O and H_2. In either case, from Eq. (7), with $f = 0.11$, we have an r of 260. This means that, when fractionation began, Venus had 260 times as much hydrogen as it has now, if there

are no important endogenous or exogenous sources of hydrogen. If the hydrogen was all in the form of H_2O, there would have been 320 or 430 g/cm^2 of water, which is equivalent to 3.2 or 4.3m of liquid water, 0.10% or 0.13% of a full terrestrial ocean. τ_H would be 230 or 300 Myr. If, however, the escape flux is only $0.8 \times 10^7 cm^{-2}s^{-1}$ and the fractionation factor 0.17, these quantities would charge to 5.1 and 6.9m of water and 460 to 600 Myr.

The characteristic time for establishing a steady state τ_{SS} would range from 2.3 to 3.5 Gyr. But R_{SS} would only be 9 times R_S (or 5.9 times R_S if f is 0.17), the D/H ratio in the putative source. Thus, the source of H_2O and HDO would need to have had a D/H ratio 17 (or 25) times terrestrial. This seems to rule out exogenous sources such as comets for the small bit of water in the atmosphere. This is quite surprising in that the escape fluxes are so small. A hydrogen flux $0.8 \times 10^7 cm^{-2}s^{-1}$ would be matched by the input of one 10^{18} gm comet every 375 million years. It may be possible to develop a scenario for water on Venus that is somewhat like that suggested for Mars, in which fractionated water is cycled from the atmosphere into the interior and back again during periods of widespread vulcanism.[47] If so, the sequestration of fractionated water, with a D/H ratio about 20 times that of SMOW, would have occurred long ago. This mechanism, however, differs only in detail from a simple Rayleigh fractionation of the sort we described for Mars.

There may have been a time when Venus had on its surface or in its atmosphere much more water than that equivalent to a few tenths of a full terrestrial ocean. If so, the hydrogen and deuterium must have blown off, driven by solar euv or impact erosion. Attempts have been made to model the effect of the increasing luminosity of the faint early sun on an early "wet" Venus, and they make a plausible case. Disposal of the oxygen left behind would not be a problem, given the probable presence of much CO, and eons of volcanic production of fresh surface magmas to be oxidized.

DISCUSSION

The most direct and plausible interpretation of measurements of the deuterium-hydrogen ratio in atmospheric and crustal species on Mars and Venus is that each planet had abundant water in both of these regions long ago but that most of it has since been photolyzed and disappeared. The similarity in the deuterium-hydrogen ratio in the present Martian atmosphere and in some hydrous minerals of igneous rocks formed between 180 million and 1.3 billion years ago means that recently there has been some kind of hydrothermal activity that cycles water between the crust and the atmosphere. This exchange may still be occurring and almost surely has occurred frequently or continuously in the past if the D to H ratio of the water in the crust is determined by escape of hydrogen from the atmosphere by Jeans escape during the past 3.5 to 4.5 billion years. The measurements also place a fairly large lower limit on the amount of water in the present and ancient crustal reservoirs which is comparable to the amount inferred from study of outflow channels, especially if the crystallization age of Zagami apatites is large.[10] But they also allow for the (likely) possibility of much more crustal water, since the D to H ratio in some samples was measured to be as large as in the present atmosphere. The atmospheric and Zagami observations alone cannot determine when the bulk of the original crustal water was lost, but allow it to be very early, provided the period of loss was not so short as to cause a violation of maximum escape flux constraints. Clearly needed to resolve issues raised by these observations and this interpretation is a better understanding of the hydrothermal regime on Mars and the physical and chemical processes accompanying massive loss of hydrogen from the ancient atmosphere.

How escape of hydrogen and deuterium evolved over the lifetime of each planet, needs to be modeled. Only when this has been done can we decide if the fractionation observed can be understood in terms of the evolution of the hydrogen isotopes during the past 4.5 Gyr. An effort was made to do this once for Venus,[14] but the calculation needs to be repeated in the light of present day understanding of escape mechanisms. Even the calculation of charge exchange loss from Venus needs to be redone, using neutral, ionic and temperature data provided by the PV Orbiter, and taking into account the effect of the solar cycle on these densities.

Thus the D to H ratio measurements in atmospheric water vapor and Zagami apatites are compatible with the presence of larger crustal water reservoirs freely exchanging with the atmosphere, now and long ago, with fractionation a consequence of loss of H and D to space since planetary accretion was completed. The problem of incompatibility of D/H measurements and geological requirements discussed by Carr[38] is thereby removed and an alternative provided to the scenarios discussed in his paper. If D enriched crustal water interacts with the atmosphere, now and in the past, in amounts as large as proposed here, most of Carr's strictures should not apply. There are problems posed by such an evolutionary history, particularly in coupling large changes in tropospheric water to corresponding changes in hydrogen mixing ratios in the upper atmosphere, in order to account for the large loss of hydrogen required early on and in disposing of the oxygen counterpart of the escaping hydrogen. Other explanations of the D to H ratio measurements exist. These measurements are, for example, clearly consistent with the presence of a crustal reservoir in contact with the atmospheric water vapor that is extensive compared to the 5m or so of water that would have been lost if the present rate of hydrogen escape had been essentially maintained throughout the lifetime of Mars. In that case another explanation of the D to H ratio would need to be found. One unlikely possibility is that Mars accreted crustal (but not mantle) volatiles rich in deuterium compared to Earth or Halley. Another possibility is that fractionation occurred during the dying phase of hydrogen blowoff driven by enhanced solar euv or impact erosion. This mechanism would need to be tested for consistency in accounting as well for the myriad other elemental and isotopic fractionation patterns in Martian volatiles[48,49] that also must be explained.

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