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Terrestrial Planets paper

Atmospheric escape processes and subsequent isotope fractionation, with emphasis on the D/H ratio of the terrestrial planets.

Abstract

Isotope fractionation in atmospheres can provide constraints on planetary evolution. Escape processes and observed fractionations are discussed. D/H ratios can provide insight into the history of water on a planet. A scheme for calculating the D/H evolution of the Venusian atmosphere using time-varying escape fluxes is proposed. A different, two-stage model with a global resurfacing injection into the remains of the primordial atmosphere is used to predict a 200m primordial ocean and global resurfacing injection of 5 times the current atmospheric hydrogen content. This model predicts a highly elevated D/H ratio of greater than unity prior to the global resurfacing event. A simple, non-chemical model for the D/H evolution of the Martian atmosphere is discussed and rejected.

1 ≠ Introduction

Section 2 discusses the initial origin of an atmosphere on accreting planetesimals and its evolution during heavy bombardment. Section 3 discusses losses from an atmosphere after this primordial stage, summarizing thermal and non-thermal escape processes. Section 4 mentions limiting factors restricting escape fluxes. Section 5 introduces the concept of fractionation, whereby light isotopes are preferentially removed relative to heavier ones. Observed fractionations of the noble gases, C, N, O and H on the terrestrial planets are discussed. Section 6 focuses on the D/H ratio on Venus, proposing a scheme for calculating its evolution and evaluating the reliability of current relevant data. Section 7 adapts Gurwellπs (1995) model to include a contribution from a global resurfacing event and finds that a 200m primordial ocean and global resurfacing injection of ~5 times the current atmospheric hydrogen content can reproduce the observed D and H content. Section 8 discusses problems with the observed Martian D/H ratio and investigates a simple, non-chemical scheme for its evolution.

2 - Origin of an atmosphere

As the planets accreted from planetesimals they were heated by the energy of accretion and began to outgas their volatiles to form an atmosphere. This may have begun while the planets were still in the planetesimal stage or somewhat later (Donahue, 1986). Continued accretion and heavy bombardment of the proto-atmosphere will both add volatiles to and remove volatiles from the planet. Addition occurs due to the presence of volatiles in the impactor and removal occurs if sufficient energy is transferred to volatiles to remove them from the atmosphere (Lange and Ahrens, 1982; Chyba, 1987, 1990; Melosh and Vickery, 1989). Different models of condensation and accretion in the solar nebula lead to very different pictures of the early volatile inventories of the planets, particularly that of water and particularly with regard to Venus (Hunten, Donahue, Walker, and Kasting, 1989). Lewis and colleagues favour a dry primordial Venus (e.g. Lewis, 1973; Lewis and Prinn, 1984). Others conclude that all of the terrestrial planets had essentially the same initial inventory of volatiles (e.g. Walker, 1975; Wetherill, 1985, 1990; Cameron, 1988).

Further volatiles are added to this primordial atmosphere over the course of geological time. The outgassing of volatiles continues and cometary input may be important (Krasnopolsky, 1985, Grinspoon and Lewis, 1988). The importance of cometary sources is still hotly debated (Donahue and Hodges, 1992).

3 - Loss of volatiles from an atmosphere

This can be accomplished in one of two ways. Either the volatiles can react with surface species or they can escape upwards.

Could volatiles, once in an atmosphere, have been extracted into surface minerals and perhaps later removed into the planetary interior by geological cycling? Given the thermal state of Venus, the answer for that planet is likely to be no (Pepin, 1989). On the other hand, the Martian regolith is believed to be capable of carrying many times more CO2 and H2O than the observable reservoirs (atmosphere - ice caps - layered terrain) (Fanale and Jakosky, 1982).

Escape processes fall into two categories, thermal and non-thermal. In thermal escape, the loss of gas from a planet is powered by thermal energy resident in the gas or deposited there during the escape process.

3a - Thermal Escape

In the limit of low escape flux, the Jeans escape process describes the thermal escape. It breaks down at higher escape fluxes which perturb the static structure of the atmosphere. Jeans escape uses the concept of an exobase. Above this level the mean free path is long enough for a particle to be able to travel ballistically upwards and off to infinity with experiencing a collision with another atmospheric particle. This process was formulated by Jeans (1925) and has been reviewed many times since (e.g. Chamberlain, 1963; Chamberlain and Hunten, 1987).

The escape flux is

$$\varphi_j = n_c w_j = n_c B U (1+\lambda_c)\exp(-\lambda_c)/2\pi^{1/2} \qquad \boxed{(1)}$$

$$\lambda = GMm/kTr = r/H \qquad \boxed{(2)}$$

$$U = \sqrt{2kT/m} \qquad \boxed{(3)}$$

$$n_{ct} Q H_{ct} = 1 \qquad \boxed{(4)}$$

(Hunten, 1982)

More realistic treatments (e.g. spherical atmosphere model) modify this result somewhat (Chamberlain, 1963; Chamberlain and Hunten, 1987).

n_c is the density of the escaping constituent with the subscript indicating the exobase, or critical level. In (4) the "t" means total for all constituents. w_j is the effusion velocity defined by the second equality in (1). B is a fudge factor between 0.5 and 0.8. G is the gravitational constant, M is the planetary mass, m is the mass of the atom, k is Boltzmann's constant, T is the temperature of the isothermal exosphere, r is the distance form the centre of the planet, $H = kT/mg$ is the scale height, with g the gravitational acceleration, and Q is a collision cross-section, typically 10^{-14} - 10^{-15} cm^2. Equation (4) defines the exobase in terms of this cross-section; a typical terrestrial value of n_{ct} is 6 x 10^7 cm-3, found at 400-500 km.

Note that $n_c\ exp\ (-\lambda_c) = n\ exp(-\lambda)$ by the barometric equation, leaving the slowly varying $(1+\lambda_c)$ as the only remnant of conditions at the exobase in equation (1)

The concept of a sharp exobase is an approximation used in almost all computations of escape fluxes, thermal or non-thermal. For the thermal case, a detailed discussion (Chamberlain, 1963) has shown that essentially no error results; such an investigation has not been made for other mechanisms, but only small errors, at most, would be expected. The fudge factor *B* allows for the depopulation of the high-velocity tail of the Maxwell-Boltzmann distribution due to loss of escaping atoms.

Thus we have a relation between the escape flux and the critical density n_c. One might think that n_c was determined by the atmospheric structure and that the flux can thus be obtained. It is often the reverse, however. The hydrogen flux can be determined by processes acting hundreds of km below the escape level, and the Jeans equation then serves to adjust the density appropriately (Hunten, 1973a, 1973b).

At higher escape fluxes an escaping light gas can carry heavier constituents along with it, even though such gases could not escape according to the Jeans formula. Such an atmosphere is said to be in blowoff or undergoing hydrodynamic escape. If the escaping gas is moving at speeds approaching sonic, large drag forces arise with any other gases. If the flow velocity becomes supersonic above the exobase atmospheric densities are so low that gas drag can be neglected and the Jeans formulation is valid. If the flow velocity becomes supersonic below the exobase gas drag ceases to be negligible and the Jeans formulation is invalid. The drag on the heavier gases has to be calculated from a diffusion equation.

Blowoff will generally lead to small isotopic fractionation but can process large quantities of gas. Jeans escape can lead to very large fractionations due to the negative exponential dependence of the flux on λ but, as it operates in regions of low density, cannot process large quantities of gas (Hunten, Donahue, Walker, and Kasting, 1989)

<u>3b - Jeans escape</u>

Nonthermal processes are listed in table 1. This is taken from and the discussion closely follows Chamberlain and Hunten (1987). All but one (3b - photodissociation) of these processes involve ions. As ions can be accelerated by electric fields they can reach speeds significantly above the thermal speed. Collisions and reactions then imprint this excess energy on the neutral population, permitting escape. Ions generally have difficulty escaping as they can be trapped in magnetic fields; even a body that has no internal field is generally enveloped in a field of solar-wind origin. However, ions can sometimes escape directly along open field lines (7 - ion escape). Charge exchange, process 1, can get rid of the charge while retaining most of the kinetic energy of the original ion. In processes 2 - 4, excess energy of reaction, or of the bombarding photon or electron, is converted into kinetic energy of the dissociated atoms. The incident fast particle in process 5 is normally an ion; fast atoms will work almost as well, but tend to be scarce. Acceleration of the ion is shown in process 8. The term "knock-on" tends to be applied when there is a single collision; "sputtering" refers to a multiple process, very common in electrical discharges, in which several atoms or molecules can be ejected in a backward direction. In process 6, an ion is produced far enough from the planet to be in the solar wind and be swept up in the flow.

A suprathermal atom can only escape if it is aimed upwards, is faster than the escape velocity, and is above the exobase. Slower atoms may remain bound and form a non-thermal corona. Coronal atoms are particularly exposed to process 6. Processes that lead to corona formation on a large body may lead to escape on a smaller body.

Table 2 summarizes the significant escape mechanisms thought to be operating on the terrestrial bodies (Hunten, Donahue, Walker, and Kasting, 1989).

4 - Limitations on escape processes

There are three major stages in the escape process: transport through the atmosphere, conversion to the escaping form, and the actual escape. Normally one of these will be slowest and will be the "bottleneck" that controls the escape flux (Hunten, 1982). For example, terrestrial hydrogen loss is limited by upward diffusion, and blowoff is limited by the energy supply.

Transport through the atmosphere:
Both diffusion (or molecular diffusion) and eddy mixing (or eddy diffusion) contribute to a diffusion equation. For a minor atmospheric constituent it is found that the limiting (or maximum) flux is

$$b f_t / H_a \qquad (5)$$

$b = D n_a$, where D is the diffusion coefficient and n_a is the total atmospheric number density. b is constant throughout the upper atmosphere (e.g. Hunten, 1982). H_a is the scale height of the background atmosphere. f_t is the mixing ratio of all forms of the escaping gas (e.g. H, H_2, H_2O for hydrogen).

Conversion:
To use a terrestrial example, the dominant forms of hydrogen in the lower stratosphere, CH_4 and H_2O, are broken up, producing H_2. H_2 must then be broken up into H in the middle thermosphere.

Escape:
In principle ion production can be limiting for almost all processes in table 1. Energy does not seem to be a limitation for any current atmosphere. It is likely to be a major limitation in the blowoff of a primitive atmosphere.

5 - Fractionation

It is obvious that a light isotope, undergoing any kind of accelerating process, will receive a greater increase in velocity than a heavy isotope due to conservation of energy and momentum. This gives lighter isotopes a greater chance of reaching escape velocity and leaving the atmosphere. Preferential escape of a light isotope (fractionation) can change the isotopic composition of an element. Observation of such changes gives valuable clues to the history of an atmosphere. Note that fractionation requires loss of a portion of the atmosphere.

Suppose that the escape of two isotopes satisfies the following equation:

$$f \, dn_1/n_1 = dn_2/n_2 \qquad (6)$$

f is called the fractionation factor, usually less than unity if n_1 is the lighter isotope. If *f* remains constant then the process is said to be Raleigh fractionation and it can be integrated to give

$$n_2/n_1(t) = n_2/n_1(0)\left(\frac{n_1(0)}{n_1(t)}\right)^{1-f} \qquad (7)$$

If *f* is zero (none of the heavier isotope escapes) then the isotope ratio evolves as efficiently as possible, with the ratio being inversely proportional to the amount of the escaping gas present. To change the ratio by a factor of two requires the escape of half the lighter isotope. It can be seen that significant fractionation requires the loss of a significant amount of gas.

If *f* is greater than zero, then fractionation is less efficient and even more of the lighter isotope (along with some of the heavier isotope) must escape to give the same fractionation.

Isotopes of interest for fractionation studies include H, C, N, O and the noble gases. We tend to study fractionation of the different noble gas elements as one system as their chemistry is the same - they don't have any. Their huge range of masses, many isotopes, and the fact that we can be reasonably sure that the entire planetary inventory resides in the atmosphere makes them very useful.

5a - Noble gases

Figure 1 shows that the noble gases are very underabundant (relative to solar composition) in all terrestrial planets. Figure 1 refers to the atmospheric inventories of the bodies but we can be reasonably sure that the entire inventory of noble gases resides in the atmosphere. The lighter noble gases are more underabundant than the heavier ones. This is reassuring, as it is difficult to conceive of a process leading to the opposite result. The Ne:Ar:Kr ratios for all three planets and the CI chondrites are very similar, if the high end of the Venusian Kr and Xe error bars are used (Pepin, 1989; Pepin, 1991). The lower end of the error bars suggests a Venusian Ar:Kr:Xe ratio that is close to solar. Does the similarity of the Ne:Ar:Kr ratios suggest a single parent reservoir or is the coincidental result of derivation from compositionally different sources by fractionation, mixing, or both? The isotope data for the four elements are significantly different, ruling out the single parent notion (Pepin, 1989; Pepin, 1991). Data for Kr and Xe are shown in figures 2 and 3. It can be seen that a scheme for generating the observed similar elemental ratios but strikingly different isotopic ratios will not be simple. Xe is a complication in that any simple extrapolation of elemental abundances would predict higher Xe abundances than are observed. The complexity of the noble gas isotope ratios on the terrestrial planets can be appreciated by noting that the largest paper ever published in Icarus was written on this subject (Hunten, 1998, personal communication, referring to Pepin, 1991)

5b - Carbon and Nitrogen

Figure 1 shows that the relative depletions of C and N in CI chondrites and planetary atmospheres are much less than those for the noble gases. Reservoirs of C and N in planetary interiors will decrease the total planetary depletion still further. Two general conclusions follow: contemporary C and N could not have derived directly from a primordial source of solar composition, and they were probably not in the gas phase during most or all of the episodes of fractionating loss experienced by the noble gases. The first implies solid source materials, chemically fractionated from solar compostion, and the second a sequestering of these elements in nonvolatile form in whatever planetary or preplanetary enviroments the major losses of noble gases occurred (Pepin, 1989). As noble gases were merely adsorbed onto dust grains in the solar nebula and not chemically bound like other, more reactive species, they would have formed an atmosphere before the chemically bound species were released, giving the noble gases the chance to undergo fractionation without fractionation of other species (Donahue, 1986).

Table 3 gives isotope ratios for C and N. $^{13}C/^{12}C$ ratios overlap where they have been measured. Carbon studies are complicated by the existence of large surface reservoirs of carbonate rocks - this accounts for the non-zero terrestrial measurement which refers to atmospheric carbon. $^{15}N/^{14}N$ ratios differ significantly between the chondrites and Earth with a huge difference between these and the Martian value. Venus data is uncertain, with less enrichment than Mars, but no comparison with it and the terrestrial/chondrites results. The large ^{15}N enrichment on Mars has been explained in terms of non-thermal N loss (McElroy, Yung and Nier, 1976; Nier and McElroy, 1977; McElroy, Kong and Yung, 1977).

5c - Oxygen and Hydrogen

The Martian, Venusian, terrestrial and solar $^{18}O/^{16}O$ ratios are similar, 0.0019 +/- 0.0002, 0.0020 +/- 0.0003, 0.00204, and 0.0021 +/- 0.0007 respectively (Biemann, Owen, Rushneck, LaFleur and Howarth, 1976; Bezard, Balateau, Marten and Coron, 1987). This similarity suggests that little fractionation of O has occurred. Given current Martian atmospheric loss rates that suggests that there is a large reservoir (e.g. surface minerals, ice) of O available to the atmosphere.

The D/H ratios that have been observed in the solar system are significantly different. The Martian, Venusian, terrestrial and predicted primordial solar D/H ratios are $(9+/-4)x10^{-4}$, $(2.2+/-0.6) \times 10^{-2}$, 1.56×10^{-4}, and 2×10^{-5} respectively (Owen, Maillard, de Bergh, Lutz, 1988; Hartle and Taylor, 1983; Hagemann, Nief and Roth, 1970, Geiss and Reeves, 1981). The terrestrial ratio is strikingly close to that in carbonaceous chondrites and the only cometary datum, that of Halley (Geiss and Reeves, 1981; Eberhardt et al, 1987). Models for the formation of the Jovian planets predict that Jupiter's current D/H ratio should be close to the primordial solar ratio and this is roughly confirmed by observations (Hubbard and MacFarlane, 1980; Encrenaz and Combes, 1982). The best working hypothesis is that whatever enrichment process changed the solar nebula ratio to the terrestrial, chondritic, and cometary ratio had the same effect on the other terrestrial planets as well. Venus and Mars were then enriched further.

To track the evolution of water on a body we could track either the hydrogen or the oxygen. As oxygen is present as many species, and has many surface reservoirs, and hydrogen is present primarily as H_2 and H_2O, both usually gaseous, hydrogen is more useful in this role. As water is probably the most important species in determining how a planet evolves, knowledge of the evolution of the D/H ratio of a planetary atmosphere can be very useful.

6 - D/H ratio on Venus

The current D/H ratio is approximately 140 times that of the Earth. Two models for evolution to this have been advanced: the primordial ocean model which, noting the similarities in the g/g endowment of C and N in Venus and the Earth, proposes that Venus, currently very dry (1.5 cm of liquid water averaged over the planet's surface area compared to the Earth's 3 km - Hartle, Donahue, Grebowsky, and Mayr, 1996), had a large early endowment of H_2O which has been lost over the age of the solar system (Kumar, Hunten and Pollack, 1983), and the steady state model which notes that Venus's atmospheric H_2O budget will be lost in a very short time at current escape rates, suggesting that the observed atmospheric losses are in steady state with sources (Grinspoon and Lewis, 1988). A major complication is the "Global Resurfacing Event" revealed by Magellen images which wiped clean the geological record 0.5 Bya (Schaber et al, 1992). Without the geological record we have essentially no constraints on the state of the planet before this time.

Current escape rates and the D/H fractionation factor are found by a mixture of observation and theory. Observation gives constraints on the total escape rate and, via species number densities, constraints on the various escape mechanisms. Theory provides D and H escape fluxes for the various escape mechanisms, subject to the constraints. As most observations do not distinguish between D and H, the fractionation factors of the various processes are calculated theoretically and changed according to the latest ideas quite frequently. When an average fractionation factor is found for the current atmosphere, most primordial ocean models extrapolate backwards assuming Rayleigh fractionation and current loss rates or escape timescales. This is somewhat unsatisfactory. The major work on how the escape fluxes from each mechanism will change with water content is Kumar, Hunten, and Pollack (1983), hereafter KHP. Many papers have tweaked current loss rates or fractionation factors but, to my knowledge, none have attempted to describe their variation with water content. KHP investigated D/H ratio evolution using the Rayleigh fractionation model. My intention in this paper was to investigate the evolution of the D/H ratio using the KHP escape fluxes without assuming Rayleigh fractionation. Unfortunately, only a few days before the deadline, I discovered a major error in my work. The KHP escape fluxes are given in terms of H vapour mixing ratios at the homopause. For any non-condensable gas this is the same as the vapour mixing ratio in the bulk atmosphere, allowing one to calculate how the escape fluxes and bulk atmosphere vapour mixing ratio change with time and to integrate backwards from the current state of the Venusian atmosphere. Alas, I did not realise that a cold trap in the Venusian atmosphere leading to the condensation of H_2O would render this approach erroneous. Instead of presenting useful results on this subject I am reduced to outlining a scheme for calculating the evolution of the D/H ratio and water content of the Venusian atmosphere.

6a - Proposed scheme for modeling the evolution of water on Venus

Figure 4, taken from KHP, shows how the escape flux of hydrogen varies with H vapour mixing ratio at the homopause. Fractionation factors (e.g. Donahue and Hartle, 1992) for the various escape mechanisms lead to the escape fluxes of D and H. To calculate changes in the amount of D and H in the Venusian atmosphere one needs to relate them to the H vapour mixing ratio at the homopause. The H vapour mixing ratio at the homopause is twice the H_2O vapour mixing ratio at the cold trap. Equations 45 and 46 of Kasting and Pollack (1983) can be integrated to give the H2O mass mixing ratio and temperature as a function of pressure. This information can be converted into the H_2O vapour mixing ratio as a function of pressure and the hydrostatic equation can then convert this into a function of altitude. Integrating this in altitude allows one to relate the total amount of H_2O in the Venusian atmosphere to the H vapour pressure at the homopause as required. It is necessary to make assumptions regarding the temperature of the cold trap, composition of the non-condensable part of the atmosphere and surface pressure. It is usual to assume a cold trap temperature of 170K, present-day composition of the non-condensable part of the atmosphere, and I'm not sure what the surface pressure assumption is (Kasting and Pollack, 1983). It is also assumed that the local D/H ratio is constant up to the homopause. This is not necessarily true. Yung, Wen, Pinto, Allen, Peirce, and Paulson (1988) showed that it is not true for Mars. This work could have been done in this project had I realized my mistake earlier.

To show that I have been doing something for the past few months, I append plots showing how the D/H ratio, H content, D content, total escape flux and hydrogen vapour mixing ratio evolve under my erroneous assumption and the commented code (figures 5 ≠ 9, Appendix 1). The code contains the initial conditions. Had this work been of any use I would have discussed the implications of evolving back to about a full terrestrial ocean of water with a D/H ratio of about 1×10^{-5}.

<u>6b - Current data relevant to the evolution of water on Venus</u>

D/H ratio:
(1.6+/-0.2) x 10^{-2}, later revised to *(2.5+/-0.6) x 10^{-2}*
(Donahue, Hoffman, Hodges, and Watson 1982)
(Donahue and Hodges, 1993)
(Pioneer Venus Large Probe Neutral Mass Spectrometer)
(from HDO/H_2O ratio between 25 and 50 km)

(2.2+/-0.6) x 10^{-2}
(Hartle and Taylor, 1983)
(Pioneer Venus Orbiter Neutral Mass Spectrometer)
(from [mass 2]$^+$/H^+ ratio in heterosphere)

(1.9+/-0.6) x 10^{-2}
(de Bergh, Bezard, Owen, Crisp, Maillard, and Lutz, 1991)
(Ground-based)
(from HDO/H_2O between 32 and 42 km)

< (2 - 5) x 10^{-3}
(Bertaux and Clarke, 1989, vigourously critized by Donahue, 1989)

(International Ultraviolet Explorer)

The accepted data are in good agreement. The agreement between the lower atmosphere water D/H ratio and the upper atmosphere monatomic hydrogen D/H ratio is reassuring, suggesting that the D/H ratio is similar in the major hydrogenic components of both the lower and the upper atmosphere. It is unlikely that there are significant spatial or temporal variations in the D/H ratio.

H_2O measurements:
Figure 10 shows the wide variety of results for the water vapour mixing ratio on Venus (Donahue and Hodges, 1992). Re-analysis of the Pioneer Venus Large Probe Neutral Mass Spectrometer (PV LNMS) data invoking a terrestrial contaminant yields 28ppm as the water vapour mixing ratio, constant with altitude below 50km (Donahue and Hodges, 1993). The four Pioneer Venus probes found an order of magnitude variation in water vapour mixing ratio with latitude from 60' to the equator (Revercomb, 1985). The original PV LNMS analysis yielded a steep increase of water vapour mixing ratio with increasing altitude until 10km, requiring a surface sink or another major atmospheric hydrogenic compound. This is difficult to explain. The gradient is not present in the re-analysis, however the re-analysis did not tie together all the loose ends and may not be correct. Venera probes observed a more gradual increase in water vapour mixing ratio with increasing altitude until 50 km. All this uncertainty leads to a wide range in H_2O content for the Venusian atmosphere. Water vapour on Venus is hugely variable on temporal, latitudinal and altitudinal scales, making it difficult to obtain a global average of the H_2O content or of the escape fluxes for H.

Escape fluxes and Fractionation factors:
Recent estimates for the current hydrogen escape flux and fractionation factor on Venus include:

Hydrogen escape flux, averaged over a solar cycle, $0.6 - 1.4 \times 10^7$ cm^{-2} s^{-1}
$f = 0.1 - 0.14$
(Donahue and Hartle, 1992)

H escape flux, 1.6×10^7 cm^{-2} s^{-1}
D escape flux, 3.6×10^4 cm^{-2} s^{-1} (dominated by collisional ejection)
$f = 0.125$
(Gurwell and Yung, 1993)

Collisional ejection is a negligible escape process.
(Hodges, 1993, improving on the model of Gurwell and Yung, 1993)

H escape flux, averaged over a solar cycle, 3.6×10^7 cm^{-2} s^{-1}
D escape flux, averaged over a solar cycle, 4×10^5 cm^{-2} s^{-1}
$f = 0.44$
(Hartle, Donahue, Grebowsky, and Mayr, 1996)

Hydrogen escape flux, 2×10^7 cm^{-2} s^{-1}

$f = 0.022$
(Kumar, Hunten, and Pollack, 1983, and correction by Krasnopolsky, 1985)

The fluxes are highly uncertain as they depend on relatively unknown properties of the Venusian atmosphere like the temperature structure of the nightside ionosphere. The fractionation factors are highly uncertain because they are purely theoretical and change with every publication.

6c - The evolution of water on Venus

With all this data, what can we say about the evolution of D/H on Venus? A major problem is the erased geological record. A Global Resurfacing Event about 1/2 Bya erased the geological record, leaving us with practically no constraints on the first 4 By of Venusian history. The effect of the Global Resurfacing Event on the H_2O content of the atmosphere is an unknown. It could have injected large amounts of H_2O into the atmosphere from a reservoir of unknown D/H enrichment.

The uncertainty in H_2O content and H escape flux cause large uncertainty in the hydrogen escape timescale, 125 to 800 My (Gurwell, 1995). A pure steady state model with cometary H_2O input is now thought to be unlikely (Grinspoon, 1993, basing this on Gurwell and Yung, 1993, before Hodges, 1993, invalidated their conclusions). However, with the regular changes in H_2O escape flux and content, and fractionation factor, it is impossible to write it off. It is a shame that Grinspoon and Lewis (1988) did not apply their model of cometary volatile input (the only alternative to the primordial ocean model) to the other terrestrial planets as well; this would most likely have given useful constraints on their input flux and other parameters.

Current and past outgassing rates are not really constrained at all as we do not know the water content of Venusian lavas.

Most workers in the field, barring the Devil's advocates of the steady state theory, believe that Venus began with a similar H_2O content to that of Earth. Past escape fluxes are even more uncertain than current ones, and it is perfectly feasible that Venus could have lost such a large amount of hydrogen over geological time. If a large amount was lost by these different methods, then large D/H enrichments are possible.

One problem with this approach is the 300 kg cm^{-2} oxygen left over after the hydrogen escapes. (Donahue and Hodges, 92). To store it in the body of the planet may have required the oxidation of 200 km of crust. This is a daunting requirement for a planet which currently lacks subduction. However, it may have been processed long ago, in a more geologically active epoch.

In conclusion, Venus is currently very dry by comparison to the Earth. Its elevated D/H ratio suggests loss of a significant amount of H. The current H_2O content, H and D escape fluxes are not well understood, and past ones are even less well understood. Current and past H_2O input rates are not well understood either. A Global Resurfacing Event 1/2 Bya could have had a major effect on D and H content.

Using current escape fluxes and fractionation factors to evolve back to an early full terrestrial ocean is not convincing in the slightest. The current uncertainties are too large and there is no evidence that they applied to earlier atmospheres. Venus may well have had an early full terrestrial ocean but evidence for it comes from models of planetary accretion not atmospheric evolution.

7 - Primordial Ocean / Global Resurfacing Event model for the evolution of water on Venus

Gurwell (1995) has proposed a combined primordial ocean/steady-state model to explain the D/H ratio. I have adapted this to investigate a combined primordial ocean/global resurfacing injection model.

Following the approach of Gurwell (1995), I have hydrogen escaping on a timescale τ with fractionation factor f. There are two sources of hydrogen, one a primordial injection of H and D 4.5 Bya, the other a global resurfacing injection of H and D 0.5 Bya. This must evolve to the current H content and D content of the Venusian atmosphere.

The D content is given by

$$P_D e^{-ft/\tau} \qquad (4.5 - 0.5 \text{ Bya}) \qquad (8)$$

$$P_D e^{-ft/\tau} + G_D e^{f(T \neq t)/\tau} \qquad (0.5 \text{ Bya} \neq \text{present}) \qquad (9)$$

and the H content is given by

$$P_H e^{-t\pi/\tau} \qquad (4.5 - 0.5 \text{ Bya}) \qquad (10)$$

$$P_H e^{-t/\tau} + G_H e^{(T \neq t)/\tau} \qquad (0.5 \text{ Bya} \neq \text{present}) \qquad (11)$$

where P_D is the size of the primordial injection of D and G_D is the size of the global resurfacing injection of D, and P_H and G_H are defined similarly for H. t is time measured from 4.5 Bya and T is the time between the primordial injection at $t = 0$ and the global resurfacing injection 4 By later.

Requiring the D/H ratios of the two sources to have the terrestrial value reduces the number of variables to two, equal to the number of constraints. The system can hence be solved. Table 4 shows the size of the primordial and global resurfacing injections for a variety of τ and f consistent with section 5b. Bearing in mind the cautionary words of Lewis (1998, personal communication, "Give me five free parameters and I'll fit an elephant!"), it can be seen that a range of τ and f can give a similar primordial H abundance to the terrestrial value (1.6×10^{32}) and an global resurfacing injection smaller than Grinspoon's (1993) upper limit on the H added to the atmosphere (1.2×10^{29}). This is very interesting, as this simple model has reproduced the current H and D content of the Venusian atmosphere with a primordial H content predicted by accretion models and a small global resurfacing injection. Major limitations of the model are the assumption of constant τ and f. The evolution of the early atmosphere is unlikely to be like that of the present atmosphere, with hydrodynamic escape possibly playing a major role.

Let us consider in more detail one of these cases; τ = 300 My and f = 0.3. These values are chosen because they are not extremal, so new data or theory may not invalidate them quickly, and because they predict interesting values of the two H injections; a primordial ocean of 200 m depth and a global resurfacing injection of 8 cm, or ~5 times the current inventory.

Figures 11 ≠ 13 show the evolution of the D/H ratio, the D content, and the H content in the atmosphere. The main point of interest is the huge D/H ratio just prior to global resurfacing. A D/H ratio greater than unity has, to my knowledge, not been predicted before in any evolutionary model. Prior to the global resurfacing, the D/H ratio evolves exponentially as it must by equations (8) and (10). At the global resurfacing, the D content of the atmosphere is increased by ~15%, and the H content of the atmosphere is increased by ~2.5 orders of magnitude. Equations (9) and (11) then tells us that the D/H ratio after this discontinuity evolves exponentially with the same time constant as before, $\tau/(1-f)$ or 430 My since the H is essentially all new and the D essentially all old, rendering one of the two terms in each equation negligible.

8 - D/H ratio on Mars

The current Martian D/H ratio is uncertain. Measurements of HDO/H_2O suggest that it is approximately (6+/-3) times that of the Earth if the ratio in water is representative of the D/H ratio (Owen, Maillard, de Bergh, and Lutz, 1988; Krasnopolosky, Bjoraker, Mumma, and Jennings, 1997). Recent measurements of HD/H_2 suggest that it is depleted by a factor of 2 relative to the terrestrial value if the ratio in molecular hydrogen is representative of the D/H ratio (Krasnopolosky, Mumma, and Gladstone, 1998). Krasnopolosky et al do not propose this. Rather, they suggest that the photochemical scheme of Yung, Wen, Pinto, Allen, Peirce, and Paulson (1988), introduced in response to the Owen et al observations, be modified so that the reaction

$$HD + H_2O = HDO + H_2 \quad \text{(R1)}$$

be thermodynamically rather than kinetically controlled. This brings the observed (HD/H_2)/(HDO/H_2O) ratio into reasonable agreement with its predicted value. It also changes the Yung et al fractionation factor of 0.32 to 0.02. Krasnopolosky et al do not make any statement on value of the D/H ratio for Mars, only noting the previously mentioned results for water. Their modification of the control of reaction R1 requires that the rate constant be ten orders of magnitude greater than the laboratory value. A paradox exists between observation and theory and the D/H ratio is uncertain. I will use the D/H ratio found by Owen, Maillard, de Bergh, and Lutz (1988) as no one has made any other predictions.

On Mars, surface sinks and sources of D/H are potentially important. The current escape rate of H corresponds to the loss of 2.5m of H_2O over geological time. Yung, Wen, Pinto, Allen, Peirce, and Paulson (1988) found that 3.4m has been lost over geological time, with 0.2m remaining. This is significantly less than the 500m Carr (1986) predicts from geological evidence, the 50m Greeley (1987) predicts from volcanism alone and the 60m Jakosky (1990) predicts from adding the effects of obliquity cycles into Yung's model.

Carr (1990) argued that the atmospheric D/H is not necessarily representative of the bulk planet D/H, noting that it is only the same as the exchangeable near-surface D/H. Floods, volcanism and cometary impacts will all reset the atmospheric D/H. Jakosky (1991) criticized Carr's conclusions, noting that these events happened early in geological time and will have a small effect on the current atmosphere, negligible by comparison with cycling between the polar caps due to obliquity variations.

<u>8a - Investigation of the evolution of the Martian D/H ratio</u>

Using the current loss rate and a non-chemical derivation of the fractionation factor I now investigate the evolution of the D/H ratio.

Model: The current loss rate of D+H = R = 1.2 x 10^{12} m^{-2} s^{-1} (McElroy, Kong, and Yung, 1977). This takes place by Jeans escape. The escape flux of (H+D) is regulated by non-thermal escape of O such that H_2O is escaping from Mars (McElroy, 1972; McElroy and Donahue, 1972). Two factors make D escape less efficient than H escape: (1) diffusive separation above the homopause, and (2) different fractions of the Maxwell-Boltzmann speed distribution at the exobase lying above the escape velocity.

In an isothermal region above the homopause each component satisfies the following equation:

$$N(r) = N(r_0)\exp\left(-\frac{GmM}{kT}\left(\frac{1}{r_0}-\frac{1}{r}\right)\right) \qquad (12)$$

where N is the number density, G is the gravitational constant, m is the molecular mass, M is the planetary mass, k is Boltzmannπs constant, T is the temperature, and r and r_0 are distances from the centre of the planet.

Thus

$$N_H(r) = N_H(r_0)\exp\left(-\frac{G(amu)M}{kT}\left(\frac{1}{r_0}-\frac{1}{r}\right)\right) \qquad (13)$$

$$N_D(r) = N_D(r_0)\exp\left(-2\frac{G(amu)M}{kT}\left(\frac{1}{r_0}-\frac{1}{r}\right)\right) \qquad (14)$$

where *amu* is one atomic mass unit.

Let r_0 correspond to the homopause and r to the exobase. Then, by equations (1) ≠ (3) and assuming B to be the same for both species the Jeans escape flux is proportional to:

$$\frac{1}{\sqrt{m}}N(r)\exp\left(-\frac{GmM}{kTr}\right)\left(1+\frac{GmM}{kTr}\right) \qquad (15)$$

Thus the H escape flux is proportional to

$$N_H(r_0)\left(1+\frac{G(amu)M}{kTr}\right)\exp\left(-\frac{G(amu)M}{kTr}\right)\frac{1}{\sqrt{(amu)}} \qquad (16)$$

and the D escape flux is proportional to

$$N_D(r_0)\left(1+2\frac{G(amu)M}{kTr}\right)\exp\left(-2\frac{G(amu)M}{kTr}\right)\frac{1}{\sqrt{2(amu)}} \qquad (17)$$

Defining λ and *x* appropriately, the H escape flux is proportional to

$$N_H(r_0)\ \ (1+\lambda)\ \ exp(-x) \qquad (18)$$

and the D escape flux is proportional to

$$N_D(r_0)\ \ (1+2\lambda)\ \ exp(-2x)\,/\,2^{1/2} \qquad (19)$$

Using the fact that the total escape flux of D and H must be equal to *R* we have

H escape flux =

$$= R\frac{\{N_H(r_0)(1+\lambda)\exp - x\}}{\{N_H(r_0)(1+\lambda)\exp - x + N_D(r_0)(1+2\lambda)\exp(-2x)/\sqrt{2}\}} \qquad (20)$$

$$= \frac{R}{1+\frac{N_D}{N_H}(r_0)\exp - x\left(\frac{1+2\lambda}{(1+\lambda)\sqrt{2}}\right)} \qquad (21)$$

D escape flux =

$$= \frac{R}{1+\frac{N_H}{N_D}(r_0)\exp x\left(\frac{(1+\lambda)\sqrt{2}}{1+2\lambda}\right)} \qquad (22)$$

I assume that $N_D/N_H(r_0)$ is the same as the bulk atmosphere. This is not supported by Yung et alπs (1988) chemistry, however it will suffice in this simple model. I also need to assume that *R*, *r* and *T* are constant. I assume a near-surface reservoir of D and H that replaces any lost (D+H) with the same amount of (D+H) ≠ but with the reservoirπs isotopic composition (Yung et al, 1988).

Model can be solved more or less analytically (Appendix 2) to yield a steady state solution (reached in ~10^8 years) of D/H of 100 times that of the reservoir. Figure 14 shows how a 300 µm atmosphere with an initially terrestrial D/H ratio evolves in the presence of a reservoir with a terrestrial D/H ratio. This uses the analytical result of Appendix 2. It agrees almost exactly with a numerical integration in Figure 15. So if reservoir D/H is lower than terrestrial, this model could reproduce the observed martian D/H. It is hard to imagine a process by which this could happen and one is forced to conclude that the model is unrealistic. That is not really surprising. The constant outgassing rate over periods of My is hard to accept with the variations in obliquity. Tempting as it is to neglect chemistry, it is unrealistic. Yung et alπs (1988) chemical model finds that each of the four steps involved in the escape of hydrogen from Mars (photochemical production of H_2, transport of H_2 to the upper atmosphere, dissociation of H_2 into H, and thermal escape of H and H_2) result in a preferential loss of H. Therefore chemistry is important.

Geological evidence strongly suggests that the Martian atmosphere was once wetter than today. Current escape rates are inadequate to remove a large enough atmosphere. Jakosky's (1990) estimate of hydrogen loss (60m of H2O) is encouraging, combining chemistry of the current atmosphere with orbital evolution to obtain an estimate in the region of that required by the geological evidence. One potential problem with this estimate is that it may cause a cold trap for H2O, drastically decreasing its escape rate.

Conclusion

A scheme for calculating the D/H evolution of the Venusian atmosphere using time-varying escape fluxes has been proposed. Implementation should be relatively straight-forward. A simple two-stage model for the D/H evolution has also been discussed. Using a global resurfacing injection into the remains of the primordial atmosphere, a 200m primordial ocean and global resurfacing injection of 5 times the current atmospheric hydrogen content have been predicted from current atmospheric properties. This model predicts a highly elevated D/H ratio of greater than unity prior to the global resurfacing event.

A simple, non-chemical model for the D/H evolution of the Martian atmosphere has been discussed and rejected.

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Appendix 2

Taking the homopause at 120 km, the exobase at 220km, and T = 300 K,

$$\exp-x\left(\frac{1+2\lambda}{(1+\lambda)\sqrt{2}}\right)$$

is approximately 0.01. Thus the H escape flux is

$$\frac{R}{1+\frac{N_D}{N_H}0.01}\approx R$$

and the D escape flux is

$$\frac{R\frac{N_D}{N_H}0.01}{1+\frac{N_D}{N_H}0.01}\approx R\frac{N_D}{N_H}0.01$$

Thus the total (D+H) input flux that must be supplied by the reservoir is

$$R\left(1+\frac{N_D}{N_H}0.01\right)$$

If this is supplied with D/H ratio of γ, where γ is small, then the H input flux is

$$R\left(1+\frac{N_D}{N_H}0.01\right)\frac{1}{1+\gamma}$$

And the D input flux is

$$R\left(1+\frac{N_D}{N_H}0.01\right)\frac{\gamma}{1+\gamma}$$

Thus

$$\frac{dN_H}{dt}\approx R\left(\left(1+\frac{N_D}{N_H}0.01\right)\frac{1}{1+\gamma}-1\right)\approx 0$$

$$\frac{dN_D}{dt}\approx R\left(\left(1+\frac{N_D}{N_H}0.01\right)\frac{\gamma}{1+\gamma}-\frac{N_D}{N_H}0.01\right)$$

This can be solved to find

$$N_H(t) = N_H(0)$$

$$N_D(t) = \left(N_D(0) - \frac{\gamma N_H}{0.01}\right)\exp\left(-\frac{0.01Rt}{(1+\gamma)N_H}\right) + \frac{\gamma N_H}{0.01}$$

The timescale for approach to the steady state is approximately 10^8 years. The steady state value of D/H is that of the reservoir D/H divided by 0.01.