

## Water on Mars: Isotopic constraints on exchange between the atmosphere and surface

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### Abstract.

Using a new measurement of the D/H fractionation efficiency and new estimates of the water loss, we calculate that Mars has the equivalent of a  $\sim 9$  m global water layer in a reservoir that exchanges with the atmosphere. The measured D/H enrichment is about 5 times the terrestrial value, but without exchange, the atmosphere converges on an enrichment of 50 in about 0.5 Ma. Due to the large buffering reservoir and the rapid loss rate ( $10^{-3}$  pr- $\mu\text{m}$  yr $^{-1}$ ), the small atmospheric reservoir, averaging 10 pr- $\mu\text{m}$ , is unlikely to be in continuous isotopic equilibrium with the full 9 m exchangeable reservoir. Instead, it presumably equilibrates during periods of high obliquity; the atmospheric D/H ratio is expected to be enriched in between such periods. If isotopic exchange with a small (4 mm global layer) reservoir occurs under current conditions, it possible for the atmospheric D/H ratio to be within 10% of its long term equilibrium.

Mars currently has little detectable water. The atmosphere is very dry, with an average of 10 pr- $\mu\text{m}$  [Jakosky and Farmer, 1982; Carr, 1996; Kieffer *et al.*, 1992]; where 1 precipitable micron (pr- $\mu\text{m}$ ) of water is equivalent to a 1  $\mu\text{m}$  deep layer over the entire surface when all the water is precipitated out. The only observed long-term water reservoir is the northern polar cap. Yet there are several lines of evidence suggesting that Mars had a larger reservoir in the past. One line of evidence is the large deuterium enrichment in atmospheric water [Owen *et al.*, 1988; Krasnopolsky *et al.*, 1997]. This implies that significant amounts of water have been lost from the surface by a fractionating mechanism [Yung *et al.*, 1988]. A second line of evidence for large amounts of water in the past is the channels and other geomorphic evidence that appear to have been created by flowing water [Carr, 1996; Kieffer *et al.*, 1992]. Quantitative estimates of the amount of water on Mars based on these two observations are very different.

Modeling by Yung *et al.* [1988] of the atmospheric D/H ratio using estimates for the fractionation due to H escape to space indicated that the planet currently has the equivalent of a global layer of water  $\sim 0.2$  m thick.

This is the residual from an initial reservoir equivalent to a  $\sim 3.6$  m global layer of water. In contrast, the geological estimates range from a global thickness of 100 m to 1 km [Carr, 1996; Kieffer *et al.*, 1992]. Estimates of the size of the northern polar cap imply it contains the equivalent of 8 m to 12 m of water [Zuber *et al.*, 1998]. In this work we attempt to bring some of these estimates into agreement.

We start with a revision of Yung *et al.*'s [1988] model for the atmospheric D/H ratio. We assume, based on the results of Yung *et al.* [1988], that the loss process is a simple Rayleigh distillation, following the relationship:

$$R(t) = R(0) \left( \frac{c+l}{c} \right)^{1-F} \quad (1)$$

where  $R(t)$  is the D/H ratio at a time  $t$ ,  $c$  is the size of the residual mixed reservoir at time  $t$ ,  $l$  is the total amount lost, and  $F$  is the fractionation factor, the ratio of D/H of the escaping molecules to that of the bulk atmosphere.  $F = 0$  indicates that no deuterium escapes while  $F = 1$  indicates that it escapes as easily as hydrogen.

Measurements of the D/H ratio in atmospheric water vapor indicate that  $R(\text{present}) \sim 5.5$  times the terrestrial value [Owen *et al.*, 1988; Krasnopolsky *et al.*, 1997]. Given that most of the water on Mars is probably ice (in the northern polar cap), this is modified by the fractionation of  $\sim 0.79$  between water vapor and ice at Martian temperatures (230K) [Matsuo *et al.*, 1964] to yield an effective  $R(\text{present}) \sim 7$ . Recent measurements indicate that  $F = 0.02$  [Krasnopolsky *et al.*, 1998], significantly smaller than 0.32, the value from modeling [Yung *et al.*, 1988]. Recent modifications allow the model to better agree with the observations [Cheng *et al.*, 1999]. Yung *et al.* [1988] assumed a constant water loss over the age of Mars at the current rate ( $10^{-3}$  pr- $\mu\text{m}$  yr $^{-1}$  — based on the H loss rate [McElroy, 1972]), we instead assumed that  $\sim 50$  m lost ([Kass and Yung, 1995], revised by Kass [1999]). Those results are based on O loss rates since the end of late heavy bombardment (or  $\sim 3.5$  Gyr ago) and take into account changes in the loss rate over time. By assuming that water on Mars started with terrestrial composition (based on water in carbonaceous chondritic meteorites assumed to be the source of Martian water [Yang and Epstein 1983; Carr, 1996]), we can solve equation (1) for the current amount of water on Mars.

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**Table 1.** Estimates of Exchangeable Water Reservoir Sizes.

|            | 3 m lost |           | 50 m lost |           |
|------------|----------|-----------|-----------|-----------|
|            | globally | polar cap | globally  | polar cap |
| $F = 0.02$ | 0.5 m    | 300 km    | 8 m       | 1100 km   |
| $F = 0.32$ | 0.2 m    | 200 km    | 3 m       | 700 km    |

Amount of water remaining for different amounts lost, depending on the  $F$  factor used. The loss of 3 m is from *McElroy* [1972], 50 m loss from *Kass* [1999],  $F = 0.02$  is from *Krasnopolsky et al.* [1998], and  $F = 0.32$  from *Yung et al.* [1988]. The amounts are expressed as a global layer of water. For comparison, each amount is also expressed as a polar cap of a given diameter (calculated according to *Patterson* [1981]; for comparison Antarctica is about 4000 km in diameter, and the Martian Northern permanent cap is about 1200 km in diameter). All values are calculated using Rayleigh distillation [*Yung et al.*, 1988].

Using the above measurements and assumptions ( $l = 50$  m,  $R_t = R(\text{present}) = 7$ ,  $R_0 = 1$ , and  $F = 0.02$ ), we calculate that Mars currently has a reservoir equivalent to a global layer of water 8 m thick. This is equivalent to a volume of  $1.2 \times 10^6$  km<sup>3</sup> of water. It is a lower limit for the total amount of water on Mars since there may be reservoirs that do not exchange with the atmosphere or near surface reservoirs. Table 1 illustrates the relative importance of our revised values of  $F$  and  $l$ . The majority of the change from the *Yung et al.* [1988] result of 0.2 m remaining is caused by the revised  $l$  value, but the new value for  $F$  is also significant.

The volume of water we estimate to exist on Mars can be converted into an equivalent polar cap with an empirical glaciological relationship [*Patterson*, 1981]:

$$\log S = \frac{\log V}{1.23} + 1 \quad (2)$$

where  $S$  is the area of the cap in km<sup>2</sup> and  $V$  is its volume, in km<sup>3</sup>. While derived based on terrestrial ice caps, it appears to be a reasonable fit for Mars [*Zuber et al.*, 1998]. Our estimated volume is equivalent to a polar cap  $\sim 1100$  km in diameter. The Martian northern permanent cap is  $\sim 1200$  km in diameter and has an estimated volume between  $1.2 \times 10^6$  km<sup>3</sup> and  $1.7 \times 10^6$  km<sup>3</sup> [*Zuber et al.*, 1998] (for comparison, Antarctica is about 4000 km in diameter and contains  $\sim 30 \times 10^6$  km<sup>3</sup> of ice). If the Martian Northern polar cap is water dominated, it could account for the entire exchangeable reservoir. There are several other reservoirs that may contain additional water, but whose sizes have not been measured. This includes near surface ground ice (possibly in the layered terrains) and adsorbed regolith water [*Carr*, 1996; *Kieffer et al.*, 1992].

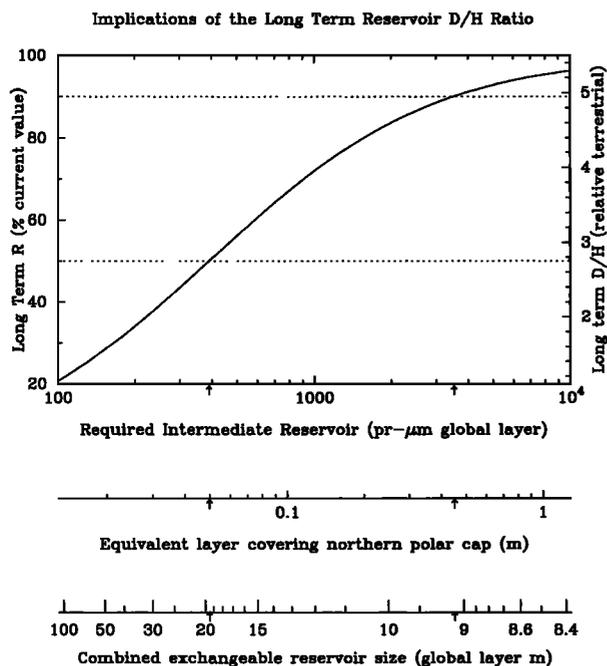
The fact that the entire northern polar cap needs to be in isotopic equilibrium with the atmosphere to explain the measured D/H enrichment is problematic. Under current Martian conditions it is difficult to see

any mechanism for equilibrating the atmosphere with 8 m equivalent reservoir (at least over relatively short timescales). On the other hand, it is believed that the Martian climate changes dramatically due to changes in its obliquity [*Ward*, 1992]. The current obliquity of 25.2° is intermediate. It is believed that at higher obliquities (where the polar regions receive more isolation), there will be a higher CO<sub>2</sub> pressure and possibly more atmosphere–water interactions [*Carr*, 1996]. In such an environment, it should be easier to mobilize H<sub>2</sub>O and isotopically equilibrate the various reservoirs.

While isotopically equilibrating the full 8 m global H<sub>2</sub>O reservoir during high obliquity periods is a reasonable mechanism, it is not sufficient. Over at least the last 2 million years, the obliquity has had a period of about 10<sup>5</sup> years, with a  $\sim 10^6$  year modulation of the amplitude. The combined result is that the last time the obliquity was high (high being  $\gtrsim 30^\circ$ ) was  $4 \times 10^5$  year ago, but that high values are usually reached every  $\sim 10^5$  years [*Ward*, 1992]. The current loss rate ( $10^{-3}$  pr- $\mu\text{m yr}^{-1}$ ) is capable of removing *all* of the atmospheric water in 10<sup>4</sup> years, and has removed  $\sim 400$  pr- $\mu\text{m}$  since the last period of high obliquity. If there is no isotopic mixing, then some reservoir must supply water to the atmosphere to replace the lost water. In such a system, the isotopic value of the atmosphere rapidly reaches a steady state value based on the isotopic value of the supply reservoir and the fractionation factor. In the case of Mars, the atmosphere will reach a steady state in  $\sim 5 \times 10^5$  years at an enrichment  $> 50 (= R(0)/F)$  times the terrestrial value [*Yung et al.*, 1988; *Pathare and Paige*, 1997]. This is well beyond the measured value and implies that there is a third reservoir of intermediate size on Mars. It is in equilibrium with the atmosphere on short (annual to centenary) timescales. Neither the atmosphere nor the intermediate reservoir are in equilibrium with the full, 8 m exchangeable reservoir.

This leads to a model where there are three exchangeable water reservoirs. The first is the atmospheric (and seasonal) water and is small and rapidly fractionated by escape processes. The second is a short term reservoir that is actively interacting with the atmosphere at the present. It keeps the atmospheric water from becoming overly fractionated. While large compared to the atmospheric reservoir, it does not contain all of the exchangeable water. For convenience, we will label it the intermediate reservoir. The final reservoir is the large reservoir (primarily the northern polar cap) that holds the bulk of the exchangeable water, but it only exchanges with the other two at infrequent intervals. This does not rule out other reservoirs that do not isotopically interact with the atmosphere (such as a frozen cryosphere [*Carr*, 1996]).

For simplicity, we consider the D/H value of an atmosphere in equilibrium with the large reservoir (instead of the D/H of the reservoir itself). This equivalent atmospheric value is then expressed as a fraction of the



**Figure 1.** For a given long term atmospheric D/H value (expressed either as a percentage of the measured value or relative to the terrestrial D/H), this figure plots the required intermediate reservoir (in pr- $\mu$ m of a global layer). It also expresses the reservoir as a layer over the Northern polar cap (in m). For each assumed long term D/H value, it also shows the combined exchangeable reservoir size (expressed in m of a global layer, on a non-linear scale). The arrows indicate the cases where the equivalent equilibrium atmospheric D/H is 90% (or 50%) of the current value (see the text for further discussion).

current atmospheric enrichment (it cannot be more enriched since the atmosphere is the reservoir actually being fractionated). For any given fraction, it is possible to determine the size of both exchangeable reservoirs (Figure 1). If we assume that the equivalent equilibrium value is  $\sim 5$ , or 90% of the current atmospheric value (implying that over the last  $4 \times 10^5$  years, the atmospheric enrichment has increased from 5 to 5.5), we find that the intermediate reservoir needs to be  $\sim 4000$  pr- $\mu$ m. If, instead, the equivalent equilibrium value were half the current value, the intermediate reservoir would be  $\sim 400$  pr- $\mu$ m.

The combined size of all the exchangeable reservoirs depends on the assumed D/H ratio of the long term reservoir (Figure 1). By using equation (1) and the assumed long term  $R(t) \sim 6.3$  (taking into account the ice/vapor fractionation in the 90% case), the combined exchangeable reservoir contains the equivalent of 9 m global layer of water. In the case where the equilibrium value is half the current value, the combined exchangeable reservoir contains  $\sim 20$  m.

Three possible locations for the intermediate reservoir are adsorbed regolith water, a surface layer of the polar caps, or ground ice/permafrost at high latitudes.

The question is then whether or not these sources can exchange sufficiently rapidly to keep the intermediate reservoir in equilibrium with the atmosphere. In the first case, there is  $10^4$  pr- $\mu$ m of adsorbed H<sub>2</sub>O per meter of regolith depth [Fanale and Jakosky, 1982]. Using the diffusion rates from Fanale and Jakosky [1982], water can diffuse  $\sim 2$  cm to 11 cm in a year and, due to the non-linearity of diffusion,  $\sim 10$  m to 70 m in  $4 \times 10^5$  years. This means that there is  $\sim 200$  pr- $\mu$ m to 1100 pr- $\mu$ m of water exchanged yearly and  $\sim 10^5$  pr- $\mu$ m to  $\sim 7 \times 10^5$  pr- $\mu$ m over the entire interval. This implies there is sufficient exchange with the regolith to accommodate the 4000 pr- $\mu$ m needed to keep the atmospheric D/H from changing extensively.

In the case of the polar cap, the limit is the amount of water that leaves the cap and mixes with the atmosphere. In the first case, while the intermediate exchangeable reservoir is much smaller than the total reservoir, it is not small. The 4000 pr- $\mu$ m correspond to a  $\sim 0.5$  m layer of the northern polar cap. A conservative estimate of the amount of water from the polar cap that mixes is the amount of the inter-hemispherical exchange (as much as  $10^{16}$  g yr<sup>-1</sup> may mix within the northern hemisphere). Models estimate the loss from the northern hemisphere during the summer to be of the order  $\gtrsim 2 \times 10^{13}$  g yr<sup>-1</sup> [Richardson, 1999; Houben et al., 1997] which is equivalent to a  $\sim 20$   $\mu$ m layer covering the northern polar cap. So, in  $4 \times 10^5$  years, up to a 7 m layer of the cap could be cycled through the atmosphere. Furthermore, given the large amount that may mix within the northern hemisphere, the 4000 pr- $\mu$ m necessary is easily accommodated.

In the case of ground ice or permafrost, the limiting factor will be either the atmospheric transport or the diffusion through the ground, depending on the depth of the ice. Since both of those processes, as estimated above, are fast enough to allow sufficient water to exchange, a ground ice or permafrost source would also work.

Since all three possible intermediate reservoirs are easily capable of equilibrating sufficient water with the atmosphere to buffer it against moderate changes, we feel that the long term atmospheric value is close (but not equal to) the current measured value. Based on assuming a long term equivalent equilibrium value at 90% of the current value, we estimate an exchangeable reservoir of  $\sim 9$  m (a volume of  $1.3 \times 10^6$  km<sup>3</sup>, or a cap 1100 km in diameter). There is a large uncertainty in this estimate due to the uncertainty in the parameters used in the model. There should be measurable isotopic differences between the current atmosphere and the long term reservoir that coring into the northern polar cap might reveal.

Given the rapid loss of water (relative to the atmospheric column density), and the large exchangeable reservoir implied by the fractionation factor, it appears that Mars probably has multiple water reservoirs that interact on varying timescales. The current climate im-

plies that the largest exchangeable reservoirs are not in equilibrium with the atmosphere. But the atmospheric D/H values imply that an intermediate sized exchangeable reservoir is buffering the atmosphere, even at present. This leads us to postulate a three reservoir model, which implies that the current atmospheric isotopic D/H enrichment differs from the enrichment of the bulk reservoir (although it is an upper bound). Using this model, we estimate that there is the equivalent of a  $\sim 9$  m global layer of exchangeable water on Mars.

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