

# Constraining Mars D/H Fractionation and Water Loss in Photochemical Modeling

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## Abstract

Water once flowed on Mars, but most of it has escaped to space as atomic H. To accurately quantify lost water, we must understand the ratio of deuterium (D) to H (D/H) and the fractionation factor  $f$ , a measure of efficiency of D escape vs H. Past studies have calculated  $f$ , but its range has not been fully explored. Here, we quantify the range of  $f$  as a function of atmospheric water vapor and temperature profiles and calculate the associated integrated water loss. We find that  $f$  can be 2-4 orders of magnitude lower than past studies, and that water loss ranges from 30-550 m global equivalent layer (GEL) lost, depending on  $f$  and D/H.

## 1. Introduction

Though we now know that most of Mars' ancient water was lost to space (in the form of H produced when water is photodissociated [4, 5]), atmospheric modeling studies [9, 6] typically underestimate water loss compared to geological estimates [7]. Critical to accurate modeling estimates is an understanding of the time-evolution of H escape. When H becomes hot enough to exceed the escape velocity of Mars, it escapes to space in a process known as Jeans escape. Information about H escape is encoded in the D/H ratio, since the more massive D is less likely to escape than H. The efficiency of H vs. D escape is measured with the fractionation factor,  $f$ :

$$f = \frac{\Phi_D/\Phi_H}{[HDO]/[2H_2O]} \quad (1)$$

Here, square brackets represent the population at the surface.  $f = 1$  implies non-fractionating escape of D and H, while  $f = 0$  means that D does not escape at all. In order to estimate martian water loss, it is crucial to know the time evolution of  $f$ , the H and D escape rates, and the D/H ratio. Previous studies [9, 6] have calculated some values for  $f$ , but the full range of  $f$

as a function of atmospheric properties has not been previously explored. Here, we update an existing 1D photochemical model of the martian atmosphere [1] to include D chemistry, use it to quantify the range of the D/H fractionation factor on Mars, and explore the relationship between  $f$  and integrated water loss.

## 2. Photochemical modeling with D

We expand the 1D photochemical model used by Chaffin et al. [4] to include D-bearing species (D, HD, OD, HDO, DO<sub>2</sub>, HDO<sub>2</sub>) and chemistry. While spatially limited, 1D photochemical models are the best option to study long-term atmospheric evolution, the results of which can be used to constrain more computationally expensive 3D models. We use our model to study the global mean  $f$  in an atmosphere equilibrated over 10 million years of simulation time.

The D/H ratio and the temperature and water vapor profiles are the main inputs to our model. Each remains static during simulation, but can be set initially to test sensitivity to assumptions.

The temperature profile is controlled by the temperatures at the surface, tropopause, and exobase. We define a mean profile with values drawn from the Mars Climate Database:  $T_{surface} = 192K$ ,  $T_{tropopause} = 110K$ , and  $T_{exo} = 199K$ . We then construct variations by changing one of the three temperatures by  $\pm 25\%$ , in agreement with MCD output. For instance, we call the  $T_{surface} = 240K$  experiment "High surface."

The water vapor mixing ratio is constant (well-mixed) up to the hygropause, where it follows the saturation vapor pressure (SVP) curve, and is negligible in the upper atmosphere. The main control parameter here is the lower atmospheric mixing ratio (mean:  $10^{-4}$ ). Water vapor does not transport in the model, but does interact chemically. This makes it more simpler to test sensitivity to variations.

We use the Mars global mean D/H ratio,  $5.5 \times (D/H)_{\oplus}$ . This value agrees with previous studies [9, 6]. We also tested D/H multipliers from 1-10 [8] and

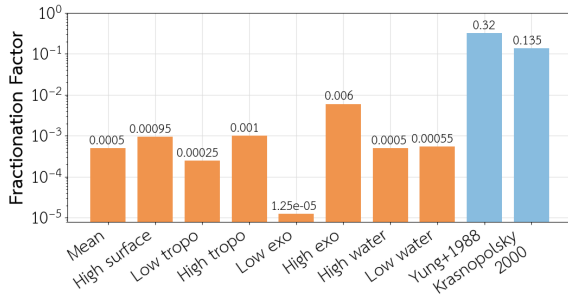


Figure 1: Our results (orange) for  $f$  vs. two earlier studies (blue). “Low exo” means in that experiment, the exobase temperature was decreased by 25%.

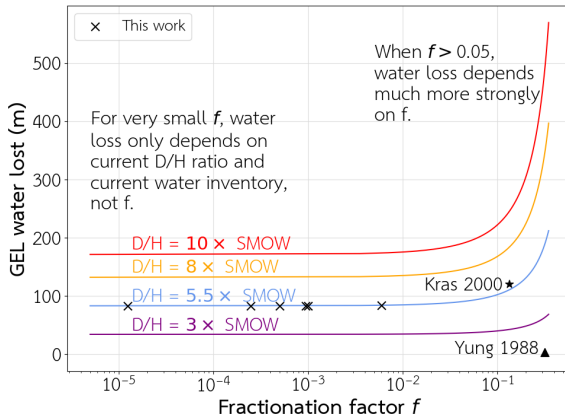


Figure 2: Martian water loss calculated with Rayleigh fractionation. GEL = global equivalent layer.

found that D/H variations do not affect  $f$ , but do affect integrated water loss (see Figure 2).

### 3. Results and discussion

Our results for  $f$  are shown in Figure 1. Our results are 2-4 orders of magnitude lower than past studies.  $f$  is most sensitive to exobase temperature changes, which is reasonable considering the exobase temperature directly affects the velocity of H atoms. Changes to the lower atmospheric water vapor mixing ratio have the smallest effect, likely because temperatures are constant for water experiments (thus, the SVP doesn't change), and water does not transport in the model.

Using Rayleigh fractionation, we estimate water lost over martian history. This method relates the current water inventory,  $f$ , the current and ancient D/H ratios, and the ancient water inventory. We find that water lost varies from 30-550 m GEL (see Figure 2).

For  $f$  as low as our results, D is almost totally retained compared to H, making it more straightforward to estimate water loss. For  $f < 0.05$ , total water loss is only sensitive to the current D/H ratio and water inventory, which we take to be 25 m GEL [8, 3]. Our results for water loss are in agreement with previous atmospheric modeling studies [6, 8] and conservative geological estimates of 100-500 m GEL [3, 2].

We are unable to reproduce larger geological estimates [7]. Accurate estimations of the ancient water budget are challenging because Rayleigh fractionation depends critically on the current water inventory. To reproduce estimates  $> 500$  m GEL, a large current water inventory can be paired with a smaller  $f$  ( $< 0.1$ ), while smaller current inventories require a larger  $f$  ( $> 0.1$ ). Alsaeed et al. [1] have concurrently verified this by considering the effects of outgassing on escape.

More work is needed to determine if the larger geological estimates can be reproduced. It should be noted that  $f$  discussed here is an atmospheric global mean; it does not consider fractionation between different water reservoirs on Mars and has likely changed over time. We will continue to study temporal variations of  $f$  to form a more holistic picture of D/H fractionation and its effect on atmospheric escape. Upcoming work will include updating the code to allow transport of water vapor and live temperature variations, and constraining the model with D densities, temperatures, and D/H ratio data from MAVEN and ExoMars TGO.

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