Supporting Information for "Significant enhancement in the atomic D/H ratio of the Mars atmosphere due to two distinct drivers"

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1. Supporting Tables

Table S1: Model parameters.

2. Supporting Figures

S1. Timesteps

Insolation figures

S2. The effect of insolation on the atomic D/H ratio

Supplemental exobase temperature variation figures

S3. The effect of thermospheric temperature on the D/H ratios in 6 species

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S4. The same as Figure 1, but with HDO cross sections equal to the H_2O cross sections

S5. The same as Figure 2, but also showing the percent of the total H and D column which escape.

S6. D/H ratio in escaping atoms as a function of temperature variations.

Supplemental water vapor variation figures

S7. The effect of low altitude water on the atomic D/H ratio

S8. The effect of mesospheric water on the D/H ratios in 6 species

S9. The effect of mesospheric water on the D/H fractionation factor

S10. The same as Figure 3, but with HDO cross sections equal to the H_2O cross sections

S11. The same as Figure 4, but also showing the percent of the total H and D column which escape

S12. D/H ratio in escaping atoms as a function of mesospheric water abundance.

References

Alday, J., Trokhimovskiy, A., Irwin, P. G. J., Wilson, C. F., Montmessin, F., Lefévre, F., ... Shakun, A. (2021, June). Isotopic fractionation of water and its photolytic products in the atmosphere of Mars. *Nature Astronomy*, *5*, 943-950. doi: 10.1038/s41550-021-01389-x

Fox, J. L. (2015, May). The chemistry of protonated species in the martian ionosphere. *Icarus*, *252*, 366-392. doi: 10.1016/j.icarus.2015.01.010

Included neutrals (28)	Ar, C, CO, CO_2, D, DCO, DO_2, DOCO, H, H_2, H_2O, H_2O_2, HCO, HD, HDO, HDO_2, HO_2, HOCO, N, N_2, NO, $N(^2D)$, O, $O(^1D)$, O_2, O_3, OD, OH
Included ions (35)	ArD^+, ArH^+, Ar^+, CH^+, CO_2^+, CO^+, C^+, DCO_2^+, DCO^+, DOC^+, D^+, H_2DO^+, H_2D^+, H_2O^+, H_2^+, H_3O^+, H_3^+, HCO_2^+, HCO^+, HDO^+, HD^+, HNO^+, HO_2^+, HOC^+, H^+, N_2D^+, N_2H^+, N_2^+, NH^+, NO^+, N^+, O_2^+, OD^+, OH^+, O^+
Basic output format	Number density at each altitude
Vertical extent	0-250 km; spacing 2 km
SZA	60° (dayside mean)
Chemistry	∼600 reactions including photodissociation, photoionization, bimolecular and termolecular reactions, dissociative recombination
Electron density treatment	Sum of the local ion density (Quasineutral)
Photochemical equilibrium	Not assumed
Background atmosphere	Argon at all altitudes; water below 72 km
Escape types	Thermal and non-thermal (due to ion-neutral reations)
Escaping species	H, D, H_2, HD
Boundary conditions	Surface density: CO_2, N_2
	Exobase flux: O (fixed at 1.2×10^8), H, D, H_2, HD (all non-thermal, function of atmospheric state)
	Exobase velocity: H, D, H_2, HD (thermal escape; effusion velocity)

Table S1. High-level summary of model characteristics

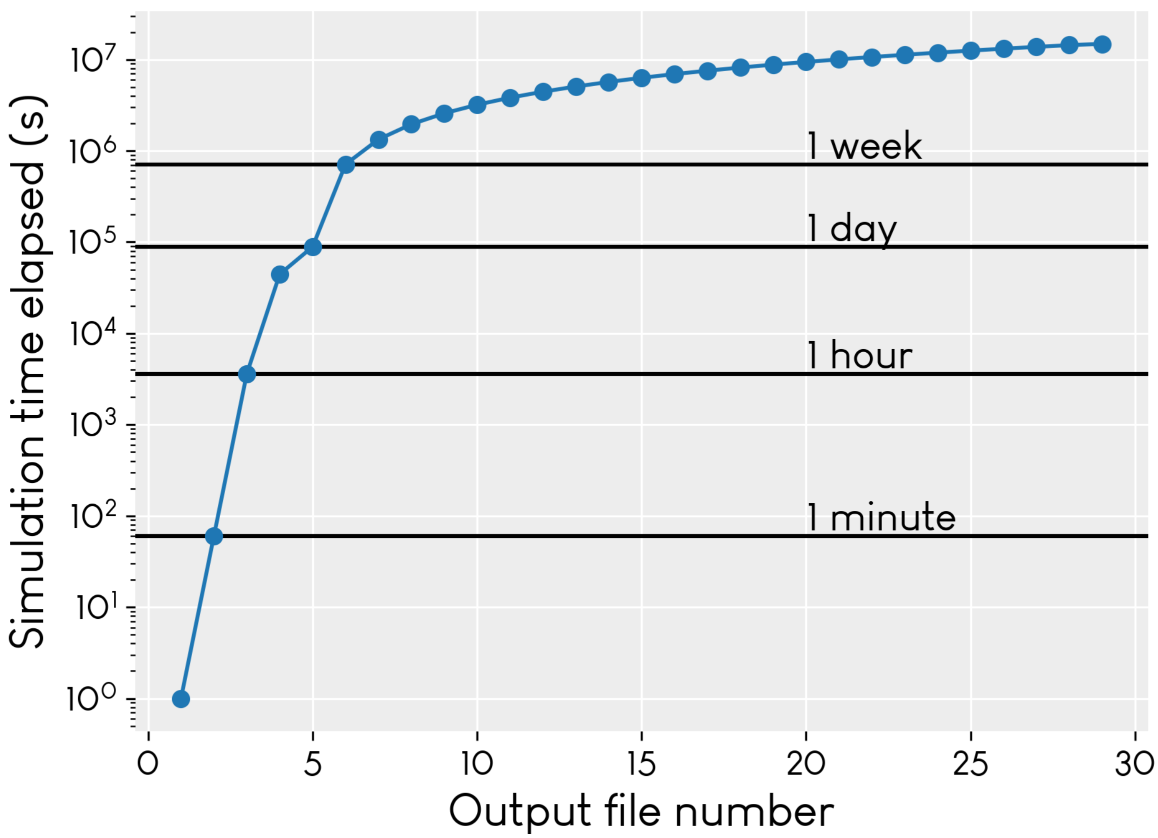

Figure S1. Times at which we save the model state for the seasonal cycle simulations. Note the small non-linearity caused by changing from logarithmically spaced steps between 1 second–1 day to linearly spaced steps (every week). This appears as an artifact in Figure 2.

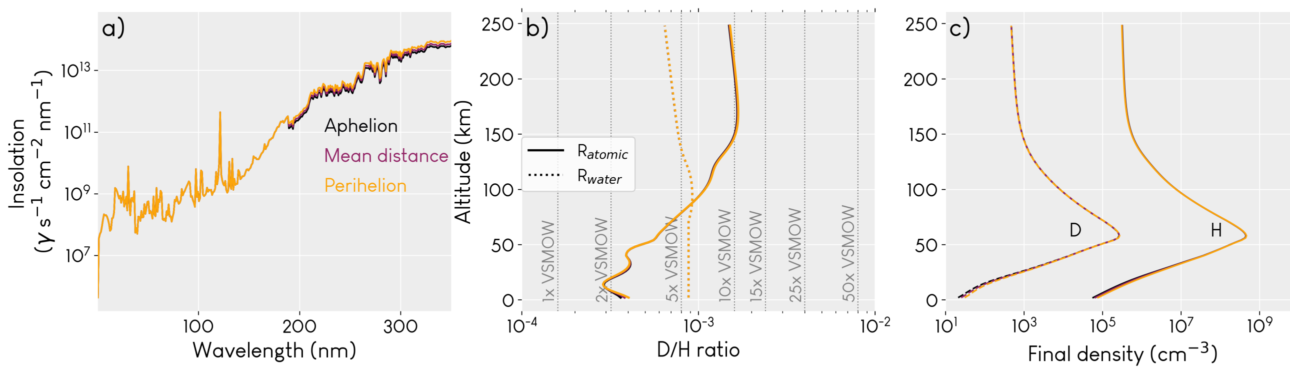

Figure S2. The effect of insolation on the atomic D/H ratio. a) Insolation profiles adopted for three different model runs. The profiles extend out to 2400 nm, but here we only show out to 350 nm for legibility. b) Resulting D/H profiles in atomic hydrogen and water. Insolation has very little effect. c) The associated density profiles for D and H, demonstrating very little variation.

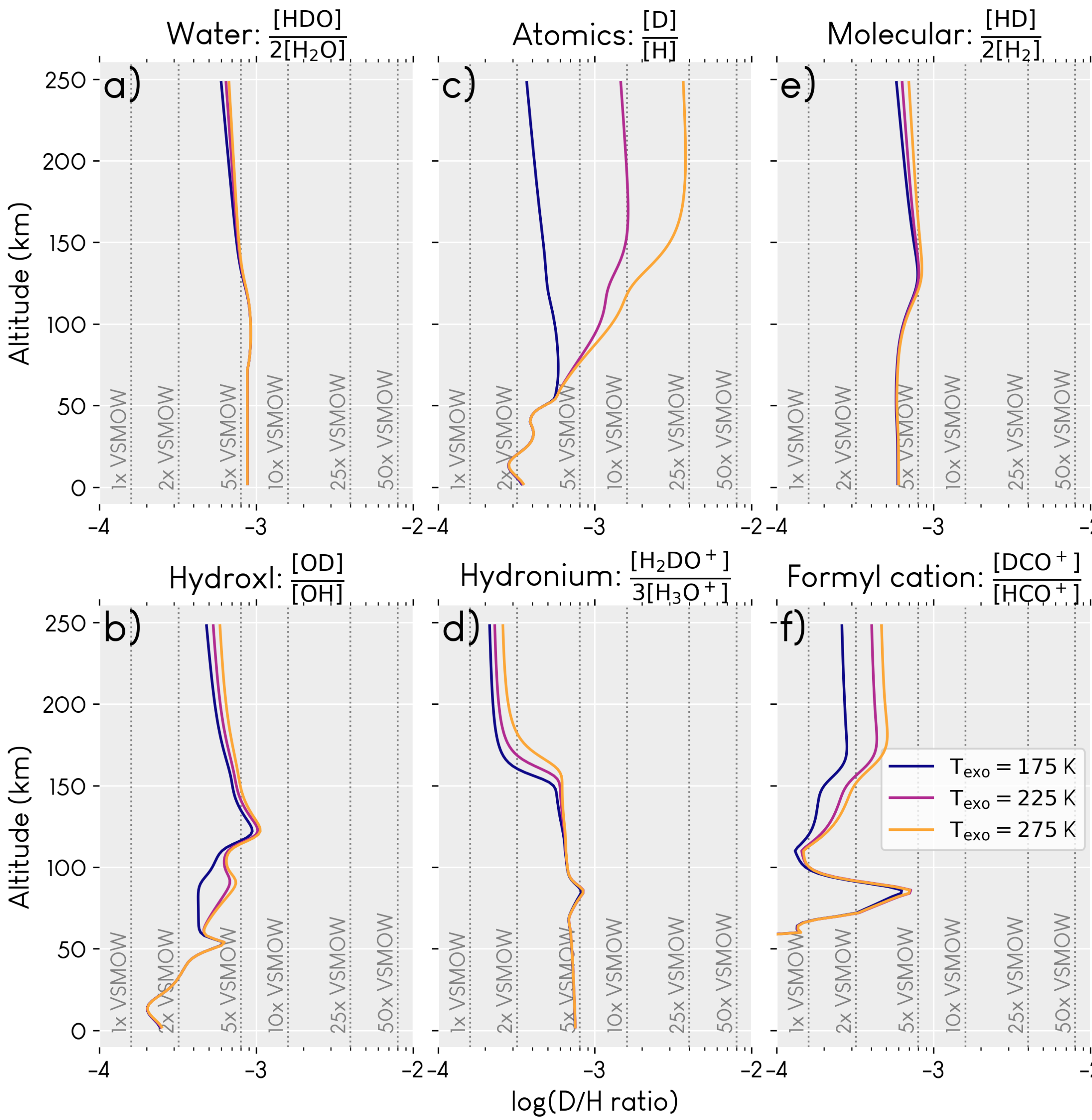

Figure S3. The D/H ratio in 6 different species containing H and D, with exobase temperature as the variable. No species shows as much variation in the D/H ratio as the atoms. Hydronium and the formyl cation show moderate variation, likely because these are terminal ions: the base species (CO and H_2O) have the highest proton affinities in the atmosphere (Fox, 2015).

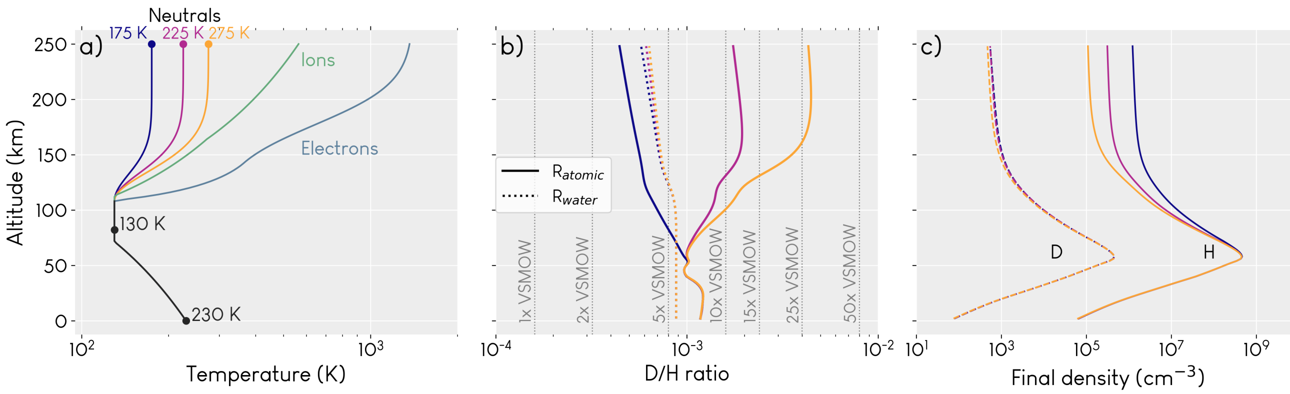

Figure S4. The same as Figure 1, but with both HDO and H_2O set to use the H_2O photochemical cross sections. Using the same cross sections for HDO and H_2O can artificially increase the calculated atomic D/H ratio by a factor of ∼2–4 in the lower atmosphere, even with a coarse wavelength resolution of 1 nm (the scale at which we bin our cross sections). This effect is expected according to work by Alday et al. (2021), which showed that photochemical cross sections are more important than condensation effects in the lower atmosphere. While we do not include condensation effects in our model, the importance of photolysis cross sections remains.

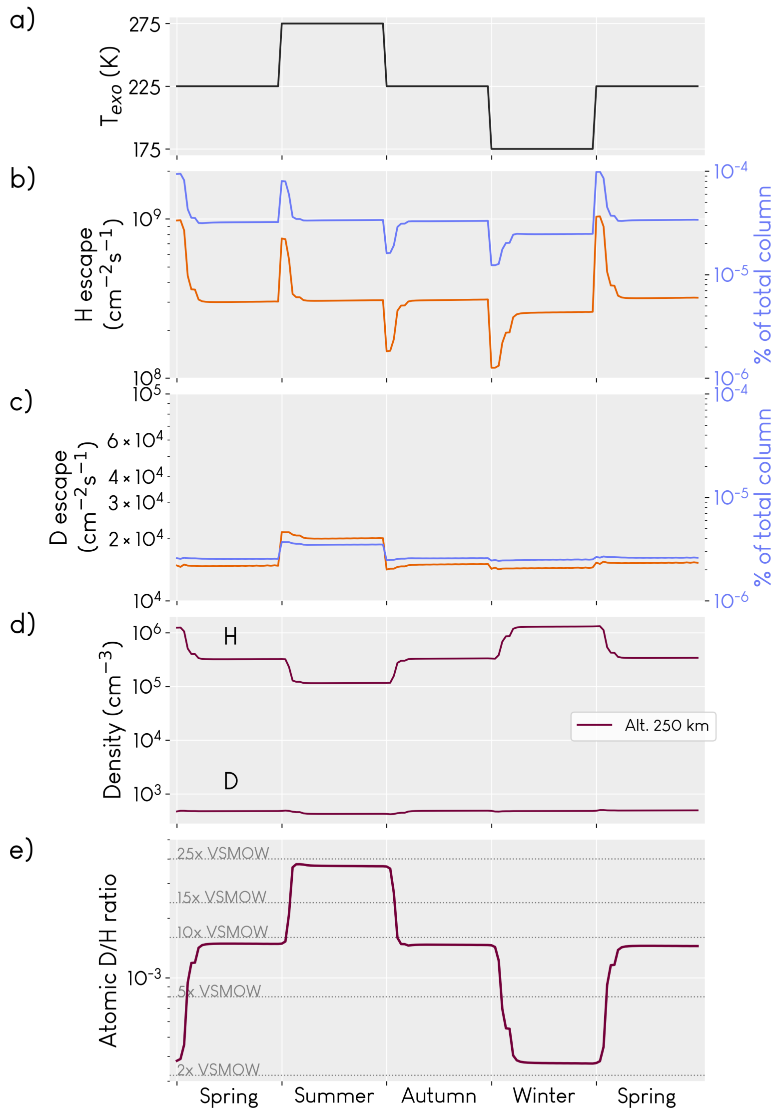

Figure S5. The same as Figure 2, but also showing the amount of escaping H or D atoms as a percent of the total column. The percent escaping D atoms is lower than the percent escaping H, as expected since D atoms are more easily retained due to a higher mass.

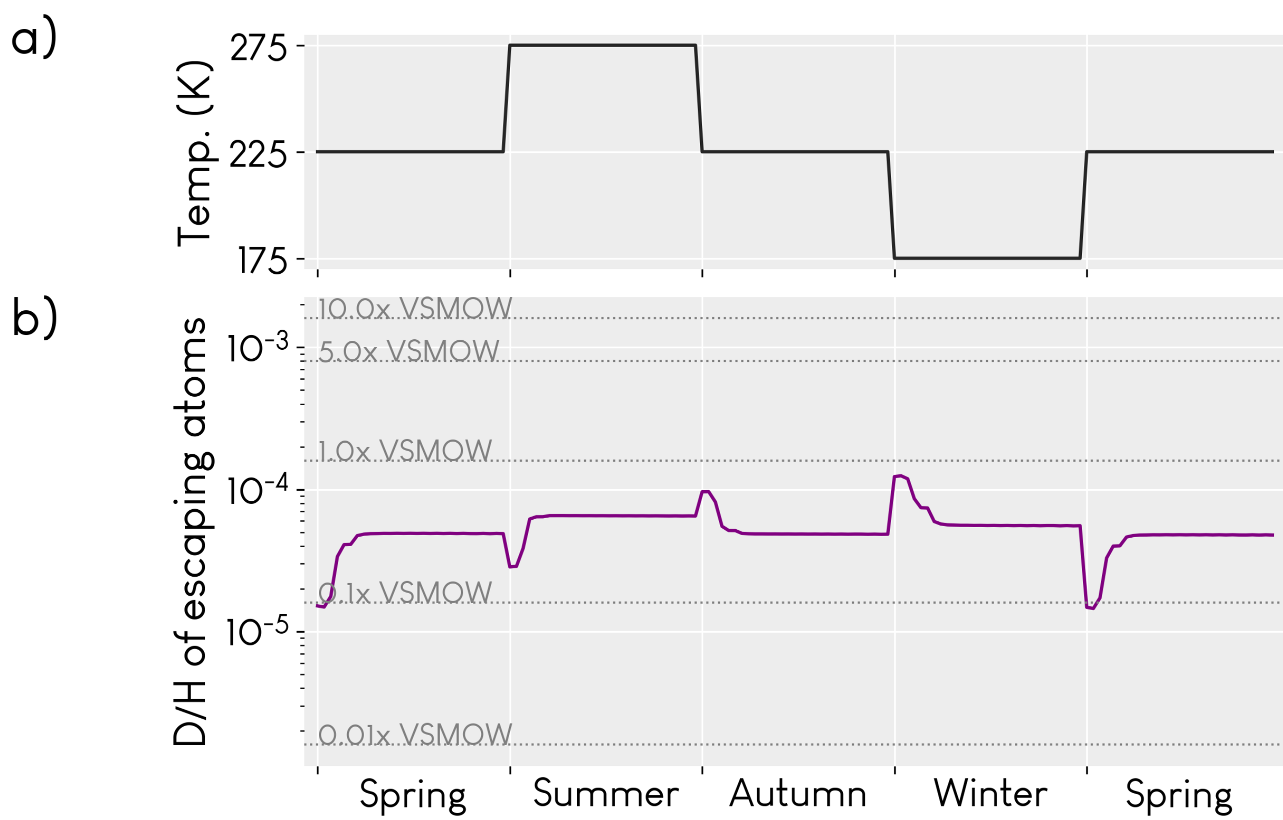

Figure S6. The D/H ratio of escaping atoms as a function of exobase temperature variations.

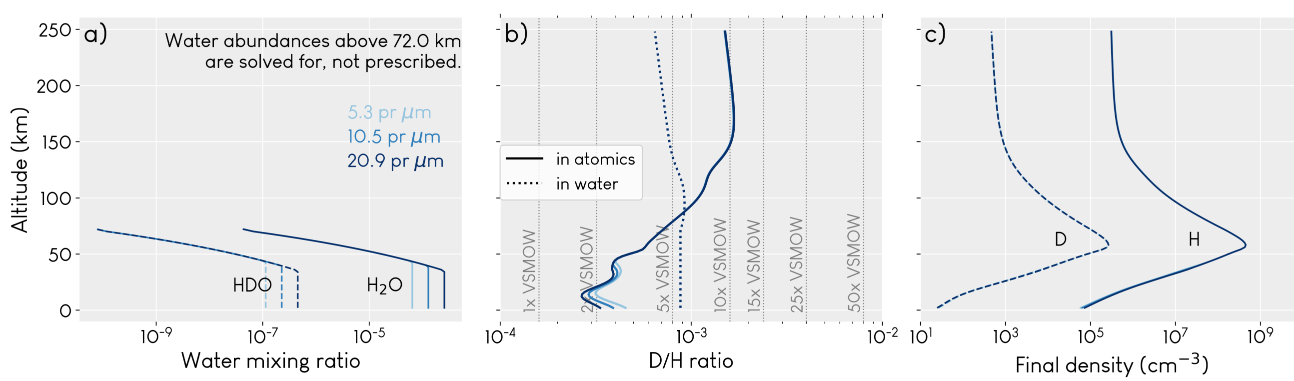

Figure S7. The same as Figures 1 and 3, but here showing how variation of lower atmospheric water content has a negligible effect on atomic D/H.

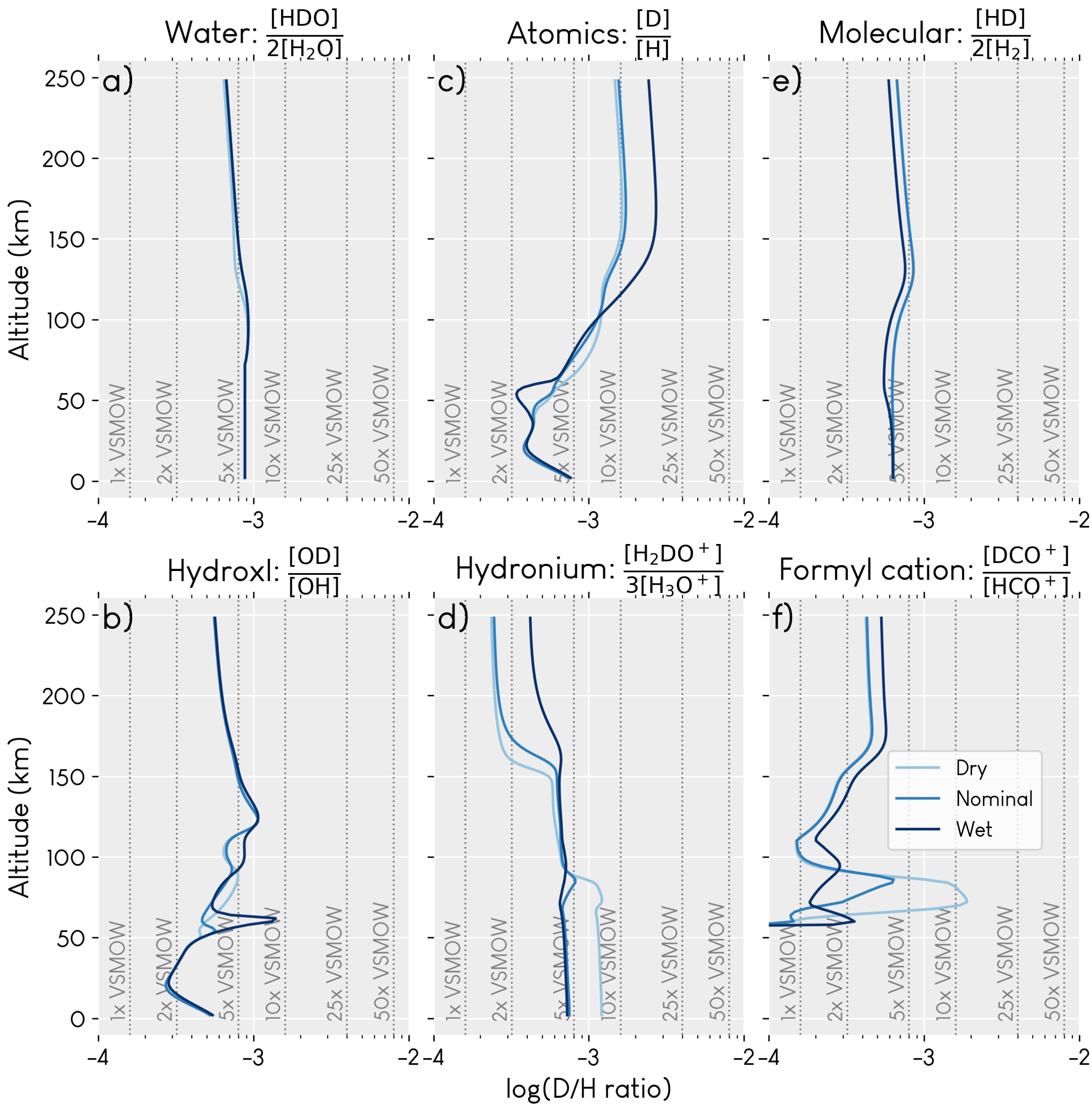

Figure S8. The same as Figure S3, but with mesospheric water abundance as the variable.

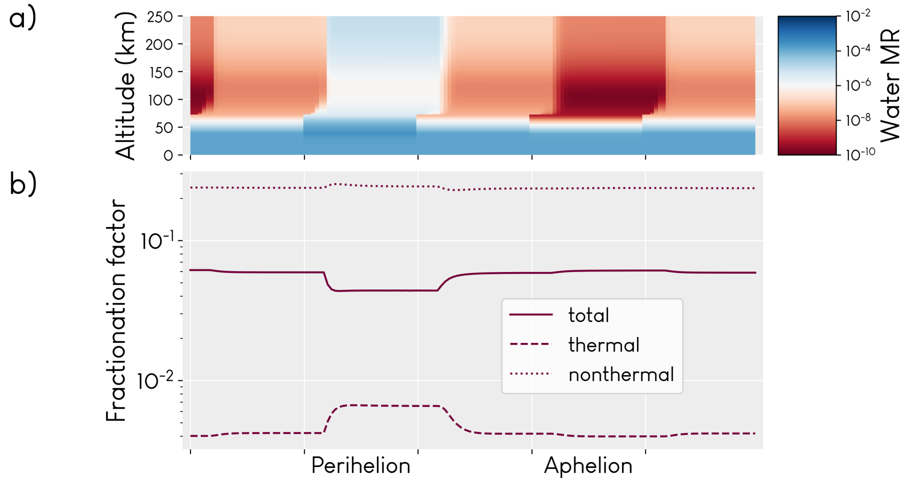

Figure S9. The D/H fractionation factor as a function of the atmospheric water content over time. The smaller value during high water conditions ("summer") occurs because the extra water in the mesosphere overcomes the diffusion limit bottleneck, enabling much higher H escape, but with little effect to the D escape, which is energy-limited.

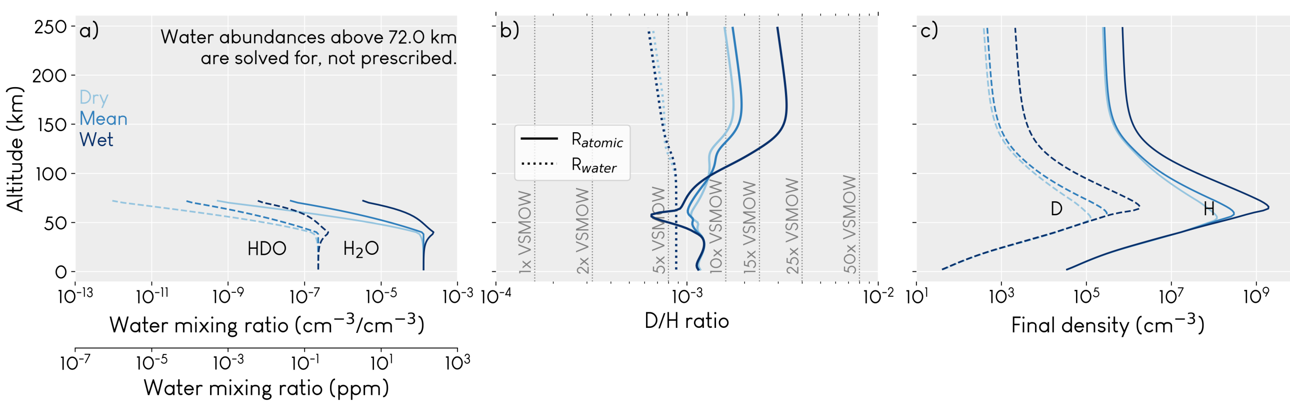

Figure S10. The same as Figure 3, but with both HDO and H_2O set to use the H_2O photochemical cross sections. Similar to Figure S4, using the same cross sections for HDO and H_2O increases the calculated atomic D/H ratio by a factor of ∼2–4 in the lower atmosphere.

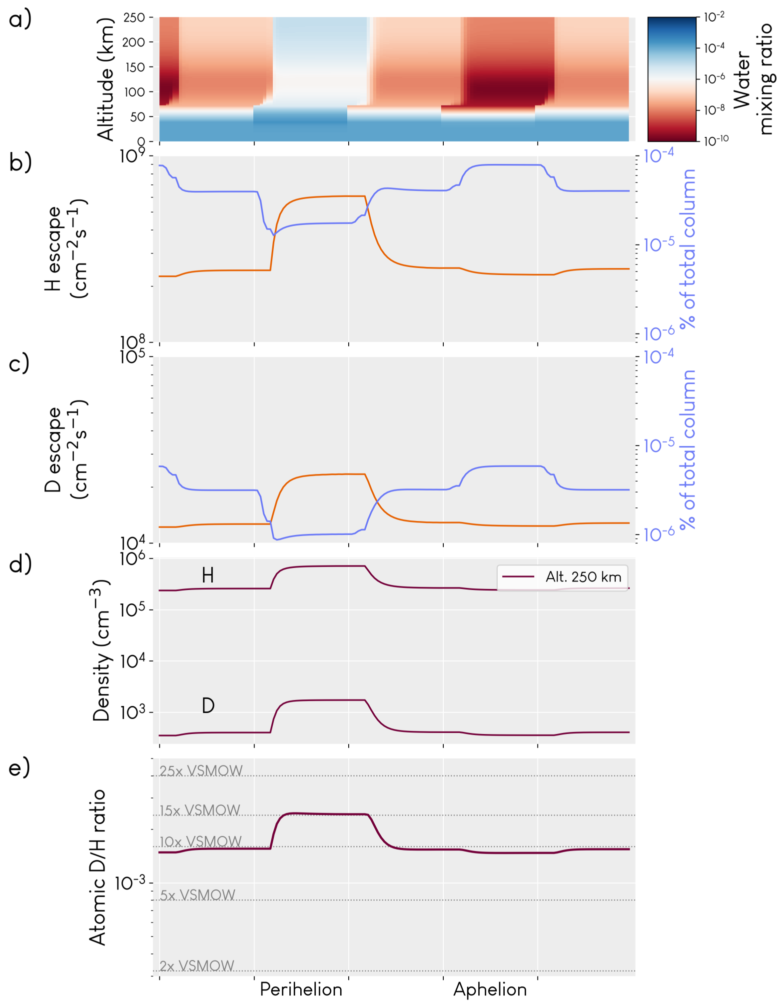

Figure S11. The same as Figure 4, but also showing the percent of the total H and D column which escape.

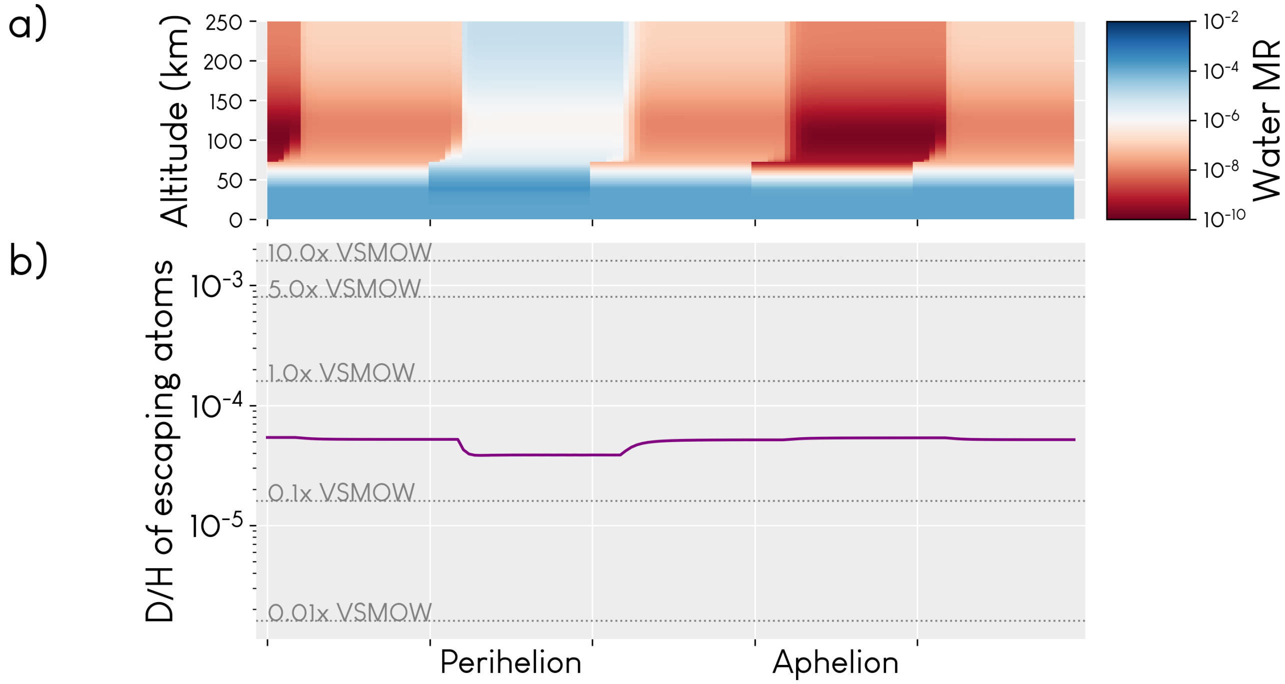

Figure S12. The D/H ratio of escaping atoms as a function of variations in water in the mesosphere.