## Seasonal enhancement in upper atmospheric D/H at Mars driven by both thermospheric temperature and mesospheric water

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#### Abstract

The D/H ratio in water on Mars, Rwater, is  $4-6\times$  the Earth ratio, signifying past water loss to space. Recently, measurements have revealed high values of the D/H ratio in hydrogen, Ratomic, in the thermosphere during southern summer. Here, we use a photochemical model to explore the potential drivers of Ratomic, testing three: thermospheric temperatures, excess mesospheric water, and changing insolation. We find that Ratomic can achieve values between  $15\times$  the Earth ratio (due to water) and  $25\times$ the Earth ratio (due to temperature). The effects arise because H escape is diffusion-limited, while D escape is energy-limited. Our results underscore how Ratomic reflects mesospheric dynamics, and the need for concurrent measurements of mesospheric water, thermospheric temperatures, and Ratomic to understand seasonal changes in the martian water cycle and atmospheric loss.







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#### Key Points:

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8	• Seasonal increases in exobase temperature or mesospheric water can enhance the
9	upper atmospheric atomic D/H ratio up to 25 times VSMOW.
10	• The enhancement occurs due to dynamical differences, leading to similarities in
11	D/H ratio but differences in abundance and escape.
12	- Concurrent measurements of temperatures, water vapor, and the $\mathrm{D}/\mathrm{H}$ ratio will
13	enhance our understanding of atmospheric escape from Mars.

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#### 14 Abstract

The D/H ratio in water on Mars,  $R_{water}$ , is 4–6× the Earth ratio, signifying past water 15 loss to space. Recently, measurements have revealed high values of the D/H ratio in hy-16 drogen, R<sub>atomic</sub>, in the thermosphere during southern summer. Here, we use a photo-17 chemical model to explore the potential drivers of R<sub>atomic</sub>, testing three: thermospheric 18 temperatures, excess mesospheric water, and changing insolation. We find that  $R_{atomic}$ 19 can achieve values between  $15 \times$  the Earth ratio (due to water) and  $25 \times$  the Earth ra-20 tio (due to temperature). The effects arise because H escape is diffusion-limited, while 21 D escape is energy-limited. Our results underscore how R<sub>atomic</sub> reflects mesospheric dy-22 namics, and the need for concurrent measurements of mesospheric water, thermospheric 23 temperatures, and R<sub>atomic</sub> to understand seasonal changes in the martian water cycle 24 and atmospheric loss. 25

#### <sup>26</sup> Plain Language Summary

The high ratio of deuterium (D) to hydrogen (H) measured in water molecules on 27 Mars indicates that much of Mars' past water has escaped to space. Recent measure-28 ments of the D/H ratio in the atoms themselves using data from the MAVEN spacecraft 29 have revealed a ratio as high as 100 times the Earth value. In this work, we use a com-30 putational model of the Mars atmosphere to explore whether the large values could be 31 caused by seasonal changes in three atmospheric parameters: the upper atmospheric tem-32 perature, the presence of extra water vapor in the middle atmosphere, and the incom-33 ing solar radiation. We find that temperature and water vapor have comparable effects, 34 with each leading to an atomic D/H ratio similar to those found by MAVEN observa-35 tions. We also explain how temperature and water affect the dynamics of H and D in 36 the atmosphere to cause the change in the ratio. 37

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#### 1 Background and Motivation

Isotope ratios in planetary atmospheres encode a history of atmospheric escape.
On Mars, the argon isotope system reveals how sputtering has affected atmospheric loss
(Jakosky et al., 2017; Slipski & Jakosky, 2016); nitrogen is used to reconstruct potential past atmospheric compositions (e.g. Pieris & Jakosky, 2022; Hu & Thomas, 2022);
and hydrogen probes long-term water loss (Owen et al., 1988; Yung et al., 1988; Carr,

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- <sup>44</sup> 1990, and many others). Because of the interest in water loss from Mars, the isotopic
- ratio of deuterium (D) and hydrogen (H) is typically measured in water as:

$$R_{water} = \frac{[HDO]}{2[H_2O]},$$
(1)

where square brackets represents a number density (abundance).  $R_{water}$  is 4–6 × VS-MOW (Vienna Standard Mean Ocean Water, the ratio measured in Earth's oceans) (Owen et al., 1988; Bjoraker et al., 1989; Krasnopolsky et al., 1997; Encrenaz et al., 2018), with local variations between 1–10× VSMOW (Villanueva et al., 2015, 2021, 2022). This enhancement relative to Earth is thought to be driven by escape to space of H and D, which on Mars are primarily sourced from the water molecules H<sub>2</sub>O and its isotope HDO.

Despite the key role of the atomic species in the parching of the planet, few measurements exist of the atomic D/H ratio,

$$R_{\text{atomic}} = \frac{[D]}{[H]}.$$
(2)

This is mainly due to measurement difficulties: a high resolution is required to resolve 54 the H and D Lyman  $\alpha$  emissions. Some measurements have been made using the Hub-55 ble Space Telescope's Goddard High Resolution Spectrograph and Space Telescope Imag-56 ing Spectrograph (Bertaux et al., 1992; Krasnopolsky et al., 1998; Clarke et al., 2006) 57 during Mars aphelion. Combined with these, new results obtained with the MAVEN (Mars 58 Atmosphere and Volatile EvolutioN) IUVS (Imaging UltraViolet Spectrograph) through-59 out the Mars year suggest a strong seasonal variation in H and D brightness and the de-60 rived R<sub>atomic</sub> (Clarke et al., 2022; Chaufray et al., 2021), distinct from effects of individ-61 ual dust storms, suggesting a repeatable, seasonal driver. Because the emission bright-62 ness of Lyman  $\alpha$  directly probes the escaping atomic species, these measurements en-63 able additional insight into atmospheric escape. 64

In this work, we study the sub-annual response of  $R_{atomic}$  due to seasonal perturbations and the driving dynamical or chemical processes. We use a 1D photochemical model (E. M. Cangi et al., 2023) to explore three options for the driver of  $R_{atomic}$  enhancements: greater thermospheric temperatures, which have a significant effect on the D/H fractionation factor (E. M. Cangi et al., 2020); changing insolation, which affects photodissociation and ionization and atmospheric chemistry; or increased mesospheric
water, demonstrated to enhance H escape (e.g. Chaffin et al., 2021; Stone et al., 2020;
Chaffin et al., 2017). To simulate an annual cycle and examine the time-dependent photochemistry of the atmosphere, we simulate one Mars season per model run, using the
output of one run as input for the next. We find that the thermospheric temperature
and mesospheric water can both cause significant variations in R<sub>atomic</sub>, while insolation
changes are negligible.

Our present work demonstrates how subtle differences in the underlying dynamics of H and D lead to similarities in their thermospheric ratio, but differences in their abundances in the upper atmosphere and escape to space. This suggests the possibility of using measurements of D/H in atoms in the thermosphere as a probe for mesospheric dynamics. We thus highlight a need for concurrent observations of D/H, thermal structure, and atmospheric water abundances from surface to space to enable new insights into atmospheric escape and water loss from Mars.

#### <sup>84</sup> 2 Modeling methods

We use the same modeling approach as E. M. Cangi et al. (2023). Full details of the model, bluejay, are available in that paper and the archived code (E. Cangi & Chaffin, 2023), and the model parameters are summarized in Table S1. The three variable atmospheric parameters of thermospheric temperature, mesospheric water, and solar input are handled by the model in the following ways:

 $_{90}$ 1. Thermospheric temperature: Past work has shown that the thermospheric tem-<br/>perature strongly affects D/H fractionation (E. M. Cangi et al., 2020) and Jeans<br/>escape. Our model prescribes temperature as a function of altitude, controlling<br/>it by modifying  $T_{exo}$ , the temperature at top of the model (250 km).  $T_{exo}$  can take<br/>on the values 175 K ("winter"-like conditions), 225 K ("spring"/"fall"), or 275 K<br/>("summer").

Mesospheric water abundance: Water can enter the mesosphere due to dust
 activity (Villanueva et al., 2021; Chaffin et al., 2021; Holmes et al., 2021; Stone
 et al., 2020; A. A. Fedorova et al., 2020; Vandaele et al., 2019; Aoki et al., 2019;
 Heavens et al., 2018; Chaffin et al., 2021) or other seasonal effects (Shaposhnikov
 et al., 2019; Neary et al., 2020), driving H escape (Chaffin et al., 2021; Stone et

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al., 2020). In our model, we prescribe water abundance below 72 km, allowing the 101 model to solve or the abundance above that level. We define three scenarios: a 102 dry mesosphere ("aphelion" conditions), a mesosphere with average moisture, and 103 a wet mesosphere ("perihelion"). 104

3. Insolation: Mars' orbit is eccentric, which affects the amount of UV insolation 105 available to drive photodissociation and ionization of atmospheric molecules. We 106 use the solar spectra for at 1.67 AU, 1.524 AU, and 1.38 AU. 107

As mentioned, the effect of the insolation variation was negligible (see Figure S2), 108 and will not be discussed. We also explored a set with extra water added in the lower 109 atmosphere (see Figure S7), but this also had a negligible effect on R<sub>atomic</sub>. 110

Timesteps in the model are logarithmic; they start small (dt  $\approx 10^{-3}$  seconds) and 111 become larger near the end (dt $\approx 10^7$  seconds). The model state is saved in quasi-logarithmically 112 spaced points from 1 second to 1 day, then once per week after. This scheme is shown 113 in Figure S1. 114

We use the best available photodissociation cross sections for HDO (Cheng et al., 115 1999, 2004; Chung et al., 2001). We also ran several simulations in which both  $H_2O$  and 116 HDO use the  $H_2O$  cross sections, resulting in a 2.5× larger ratio around 60 km, consis-117 tent with Alday et al. (2021), but a negligible change to the D/H ratio above 80 km (see 118 Figures S4 and S10). 119

We run three sets of simulations: "Temperature", "Water", and "Insolation". For 120 each set, we model an annual cycle by imposing the appropriate seasonal input param-121 eters on the model, running it for one "season" (1/4 of a Mars year,  $\sim 1.48 \times 10^7$  sec-122 onds), and then using the atmospheric state at the end of each simulation as the initial 123 conditions for the next season in the cycle. In all simulations, there are no sub-seasonal 124 changes in the temperature profile, the water profile below 72 km, or the insolation pro-125 file, in order to clearly separate the atmospheric response to a forcing impulse. 126

#### 3 Two controls on escape to space: energy and supply 127

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Two major variables affect the escape of light atoms like H and D to space: the amount of energy available to these atoms, and their total abundance in the upper atmosphere. 129

In order to escape from the atmosphere, atoms must do two things: reach the escape region (exobase), and gain enough energy to exceed escape velocity.

The importance of energy is fairly straightforward. Atoms with velocities in the high-energy tail of the Maxwell-Boltzmann distribution have enough energy to escape in the thermal Jeans escape regime; other atoms do not, but may gain excess energy through non-thermal processes, mostly involving ions or the solar wind in some way (Hunten, 1982). Previous work has shown that the mass difference of H and D leads to H escape being mostly thermal, while D escape is mostly non-thermal (E. M. Cangi et al., 2023; Krasnopolsky, 2002).

Supply is slightly more complex, and requires us to consider the atmosphere as an integrated whole. Water is the main reservoir of H and D at Mars, and is primarily present in the lower atmosphere. This means that the lower atmosphere is a source region for H and D, which are freed when water dissociates and then transport up toward the exobase. As temperatures rise and the atmosphere expands, the density of heavier species at a given altitude near the homopause increases, making it more difficult for H and D to diffuse upward due to more frequent collisions (Mayyasi et al., 2018), thus limiting the supply of atoms to the thermosphere. There is thus some maximum vertical flux of light gases. The limiting flux (Hunten, 1973) has been used to describe the maximum upward flux of a species possible in an isothermal atmosphere, defined as follows (Hunten, 1973):

$$\phi_{\ell} \cong \frac{D_i n_i}{H_a} \left( 1 - \frac{m_i}{m_a} \right) \tag{3}$$

$$\cong \frac{bf_i}{H_a} \quad \text{(for minor species)},$$
(4)

where  $D_i$ ,  $n_i$  and  $m_i$  are the diffusion coefficient, density, and mass of species *i*, and  $H_a$ and  $m_a$  are the mean scale height and molecular mass of the background atmosphere. Equation 4 is valid for minor species like H and D; here *b* is the binary diffusion parameter, and  $f_i$  is the mixing ratio of species *i*. When the actual vertical flux of a species equals the limiting flux,  $\phi_{esc} = \phi_{\ell}$ , the mixing ratio of that species is constant with height and its escape to space is described as diffusion-limited (Hunten, 1973).

The limiting flux does not apply perfectly throughout real atmospheres, which are typically not isothermal and have complex chemistry and transport. In studies of Mars, the limiting flux is typically evaluated at the homopause, near the top of the mesosphere,



**Figure 1.** a) Model input: Temperature profiles adopted to simulate seasonal variation. b) Model output: Response of the D/H atmospheric profile (at the end of the associated simulation)/season. c) Associated D & H density profiles. Note that in panels b and c, the colors of the lines map to the neutral temperatures in panel a.

which separates the lower atmospheric source of H and D and the escape region (e.g. Zahnle 148 et al., 2008). The mesosphere is also the only part of the atmosphere that is at all close 149 to isothermal. Using our model, we can calculate representative limiting fluxes using equa-150 tion 4 and compare to typical escape values. For H,  $\phi_{\rm esc,H} = 1-1.1 \times 10^8 \text{ cm}^{-2} \text{s}^{-1}$  (Jakosky 151 et al., 2018), but the representative limiting flux is  $\phi_{\ell,H} = 4-6 \times 10^8 \text{ cm}^{-2} \text{s}^{-1}$ . The 152 similarity in  $\phi_{\ell,H}$  and  $\phi_{\text{esc},H}$  means that supply to the upper atmosphere is the most sig-153 nificant barrier to H escape. On the other hand, for D, the typical escape rate is  $\phi_{esc,D} =$ 154  $5-14 \times 10^3$  cm<sup>-2</sup>s<sup>-1</sup>(E. M. Cangi et al., 2023), and the representative limiting flux is 155  $\phi_{\ell,D} = 4-5 \times 10^5 \text{ cm}^{-2} \text{s}^{-1}$ . The limiting flux being larger than the escape flux means 156 that upper atmospheric supply is not a barrier to escape for D; rather, due to D's higher 157 mass, its energy is the more important controlling factor of its escape. Essentially, on 158 Mars, H escape is diffusion-limited (or supply-limited), while D escape is energy-limited 159 (sometimes also called kinetically limited). 160

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For the remainder of this paper, we will discuss energy-limited escape mostly in reference to D, and diffusion-limited escape in reference to H. 162

#### Warmer exospheric temperatures increase R<sub>atomic</sub> by driving H es-4 163 cape and throttling resupply from below 164

Figures 1 and 2 show the model results from variation of the exobase temperature 165 (which also changes the overall thermospheric temperature, due to the functional form 166 we use for temperature), with altitude profiles of  $R_{\text{atomic}}$  and H and D densities shown 167

in Figure 1 and time evolution of R<sub>atomic</sub>, the densities, and their escape fluxes shown
 in Figure 2.

Figure 1a shows the temperature profiles adopted. Ion and electron profiles are held 170 fixed due to limited new data available to constrain them (E. M. Cangi et al., 2023; Han-171 ley et al., 2022) and the fact that due to observing geometries and instrument pointing 172 requirements, it is difficult to obtain simultaneous temperature measurements of differ-173 ent populations such as neutrals and ions (Gupta et al., 2022). Panel 1b shows how R<sub>atomic</sub> 174 and R<sub>water</sub> respond; R<sub>water</sub> is mostly unaffected, while R<sub>atomic</sub> ranges from 2 to nearly 175  $25 \times$  VSMOW in the upper atmosphere. This response is largest in the atoms; D/H ra-176 tios in other species are less pronounced (see Figure S3). Figure 1c shows a minimal change 177 to upper atmospheric D, whereas a higher temperature leads to a  $10 \times$  rarefaction of H, 178 the same amount by which the D/H ratio increases. 179

Figure 2 shows the same information over the full annual cycle by placing time on the horizontal axis. Panel 2c shows even more clearly that the primary driver of the increase in  $R_{\text{atomic}}$  is the large decrease of the H density.

The responses of D and H escape to temperature perturbations are dissimilar, as 183 shown in panels 2d and e. As explained previously, H escape is diffusion-limited, and es-184 cape depends on both energy available to the escaping atoms and supply of said atoms. 185 Thus, when the temperature rises, a larger fraction of upper atmospheric H suddenly has 186 enough energy to escape, creating the spikes in flux in panel 2d. However, the resupply 187 of H from below is mostly unchanged, so after a short time, the thermospheric H den-188 sity decreases and H escape returns to its prior value, but the density of H at the exobase 189 is depleted (as discussed by Mayyasi et al., 2018). A similar effect occurs when the tem-190 perature drops: less energy available means the escape rate suddenly drops, allowing the 191 H abundance near the exobase to rebound, later returning the escape rate to its prior 192 value. The net effect to the seasonally-integrated escape rate is negligible. 193

On the other hand, as long as the temperature is enhanced, so too is D escape, which is energy-limited. There was already plenty of D in the escape region that only needed some extra energy (which is made available by the temperature increase) to escape.

The uniqueness of H as a diffusion-limited species on Mars is important in understanding D/H variations and escape; the D/H ratio of other isotopologue pairs (see Fig-

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Figure 2. Atmospheric behavior over one Mars year. a) Model input: Exobase temperature.
b) H and c) D escape to space (total, thermal, and non-thermal) in response to the temperature changes of panel a). d) Changes to H and D densities as a result of escape and vertical transport.
e) The resulting effects on R<sub>atomic</sub>.



Figure 3. The same as Figure 1, but for different initial mesospheric water abundances (panel a). In panel a, which shows the initial state, we do not include the upper atmosphere (which is solved for in the model). The profile with the most water has a peak mixing ratio of nearly 300 ppm of water at its peak, which is comparable to what has been observed during dust storms (e.g. Vandaele et al., 2019).

ure S3) do not show such dramatic temperature dependence, as heavier molecules in these
other isotopologue pairs are less abundant and do not escape as readily as H or D.

#### 5 Extra mesospheric water increases R<sub>atomic</sub> by supplying more H above the mesosphere

Figure 3 shows the altitude profiles of  $R_{atomic}$  and D and H densities that result from varying the mesospheric water abundance. Changing the water abundance in the mesosphere makes only a small difference in the total amount of water in the atmosphere (in precipitable micrometers, it is 10.4, 10.5, and 10.9 pr  $\mu$ m for the low, mean, and high water cases respectively).

Our "perihelion" water profile has nearly 300 ppm at its peak in the mesosphere, which is similar to observations during dust storms, (e.g. Vandaele et al., 2019) and was chosen to demonstrate an edge case of high water conditions. Perturbations of this magnitude to the water profile can also spur an enhancement of  $R_{atomic}$  (Figure 3b), but with a smaller magnitude (to 10-15× VSMOW, compared with 2-25× VSMOW in Figure 2c). Figure S8 also shows the D/H ratio in other species.

When water is introduced into the mesosphere, D and H respond differently. The abundances of both species peak at a higher altitude as mesospheric water increases, which is logical given the greater abundance of source water molecules at higher altitudes. The



Figure 4. The same as Figure 2, but in response to changing water abundance in the mesosphere, which also propagates upwards. Because the water is supplied above the cold trap, both H and D escape in this scenario are sustained throughout the perihelion season, and the D/H ratio also increases because H escape increases relatively more than D escape.

increase in upper atmospheric D density also exhibits a stronger response to the perturbation than H. This is because no additional energy has come into the system, only supply; thus, D escape does increase somewhat, but not as much as H escape.

The relative changes in escape and density of H and D as a result of mesospheric water are shown in Figure 4. Adding water into the mesosphere has two main effects. First, the dissociated water supplies both D and H to the upper atmosphere. This additional supply enables a greater enhancement of H escape (150% increase) than D es-

cape (85% increase). This is because diffusion-limited H escape is most strongly controlled by the supply of escape-capable atoms, while the main control on D escape is the energy available. We have not changed the temperature (and therefore the energy) in this scenario, so the overall change to D escape is smaller than for H escape. Second, this preferential enhancement of H escape means that the increase of H (a 145% increase) in the upper atmosphere is less pronounced than for D (a 282% increase).

Because of the greater relative enhancement of H escape, we should also expect to see a decreased fractionation factor of escape (E. M. Cangi et al., 2020) when the mesosphere has extra water; this expectation is confirmed in Figure S9.

#### 233 6 Discussion

The key takeaway is: both thermospheric temperature variations and mesospheric water abundance variations can affect the value of  $R_{atomic}$  in the upper atmosphere with similar efficacy, but differ in the effects on escape and raw abundance.

Seasonal periods of high thermospheric temperatures increase R<sub>atomic</sub> by deplet-237 ing the upper atmosphere of H. This depletion occurs due to a brief enhancement of H 238 escape (Figure 2d) and reduced, diffusion-limited re-supply from below. At the same time, 239 D escape is enhanced slightly, but not enough to meaningfully deplete the upper atmo-240 sphere of D (Figures 1 and 2), and the elevated, energy-limited escape can be sustained 241 as long as the temperature perturbation lasts (Figure 2e). A similar effect on H has been 242 observed during space weather events with MAVEN. In September 2017, heightened so-243 lar activity briefly enhanced thermospheric heating caused a 25% decrease in H density 244 and a temporary  $5 \times$  increase in H escape (Mayyasi et al., 2018), comparable to seasonal 245 variations in H escape. 246

Seasonal mesospheric water releases extra H and D atoms, increasing the supply of atoms that can more easily reach the escape region. This means that escape of both H and D is sustained while the water perturbation is present. Because of the diffusionlimited nature of H escape, a relatively greater proportion of the H supplied to the upper atmosphere will escape compared to the supplied D. This leads to a build-up of D in the upper atmosphere and an enhanced R<sub>atomic</sub>.

Close examination of Figure 4 will reveal that while thermal H escape increases by a factor of  $\sim 2.5 \times$  after the introduction of mesospheric water, non-thermal escape only

increases by a factor of  $\sim 2$ . This is likely because the dissociation of water leads directly 255 to the creation of neutral H (D), which can then escape thermally. On the other hand, 256 non-thermal escape occurs when hot H (D) is created in ionospheric reactions, most im-257 portantly HCO<sup>+</sup> (DCO<sup>+</sup>) dissociative recombination (E. M. Cangi et al., 2023; Gregory 258 et al., 2023). HCO<sup>+</sup> (DCO<sup>+</sup>) is a terminal ion (Fox, 2015), so neutral H (D) in the up-259 per atmosphere must first be incorporated into  $HCO^+$  ( $DCO^+$ ) and then later be freed 260 through dissociative recombination before it can escape non-thermally; evidently, these 261 chemical pathways are already saturated. Along the way, neutral H (D) may also find 262 its way into a number of other species; in essence, the path for H (D) to non-thermal es-263 cape is less direct than to thermal escape. 264

Not all atoms escape. Some H and D may also mix downwards, which is required 265 for the exchangeable reservoir of water to attain its present D/H ratio. It is difficult to 266 quantify the exact amounts which mix down, as we do not track individual atoms, but 267 we can estimate the amount of escape relative to the total H and D columns. Figures 268 S5 and S11 show the same information as Figures 2 and 4, but with an additional plot-269 ted line showing the fraction of the total H or D column which escapes; for H, this is  $\sim$ 270  $4 \times 10^{-5}\%$  (0.4 ppm) on average, and for D,  $\sim 3 \times 10^{-6}\%$  (0.03 ppm, 30 ppb). The 271 D/H ratio of escaping atoms is also rarely higher than  $1 \times VSMOW$  (see Figures S6 and 272 S12), consistent with the notion that even in periods of elevated D escape, most D is re-273 tained on the planet. 274

Apart from the drivers of  $R_{atomic}$  discussed here, other fractionating processes may 275 add nuance to the mobilization or retention of D. One is the preferential condensation 276 of HDO over H<sub>2</sub>O (Bertaux & Montmessin, 2001; Lamb et al., 2017), which may tem-277 porarily reduce D escape by sequestering it in the seasonal water ice polar caps (Fisher, 278 2007; Vos et al., 2022) and clouds (Moores, Osinski, et al., 2011). On the other hand, 279 adsorption fractionation of water on dust grains has a fractionation factor of  $1.97 \pm 0.74$ , 280 leading to a D/H ratio up to  $21 \times$  VSMOW in adsorbed water (Moores, Smith, & Boyn-281 ton, 2011). Little dust has been observed above 60 km, so dust adsorption/desorption 282 is not thought to be a direct delivery method for water above that altitude (Neary et 283 al., 2020; Vandaele et al., 2019; A. Fedorova et al., 2018), but the process may enable 284 D to reach the bottom of the mesosphere; at present, dedicated studies in this area are 285 not available in the literature. 286

287	Similarly large values of $\mathbf{R}_{\mathrm{atomic}}$ have been observed at Mars with the MAVEN IUVS
288	instrument. Using the low resolution mode, Chaufray et al. (2021) calculated $R_{\rm atomic}$ at
289	200 km and T= 220 K up to $1.7 \pm 0.4 \times 10^{-2}$ , or $106 \times$ VSMOW; other values range
290	as low as 1× VSMOW, but frequently fall between 20–40× VSMOW. Through obser-
291	vations of the H corona, Chaffin et al. (2018) calculated $\rm R_{atomic}{=}20{-}91{\times}VSMOW.$ Mea-
292	surements of $R_{atomic}$ using the echelle channel (higher resolution) are also currently un-
293	derway, with initial results hinting at a strong seasonal response in both D and H bright-
294	ness and $\mathrm{R}_\mathrm{atomic}$ (Clarke et al., 2022). Past work by the same team has also revealed sea-
295	sonal enhancement of atomic D brightness without a concurrent atomic D/H ratio cal-
296	culation (Mayyasi et al., 2019). Our results generally agree with these measurements while
297	also adding the important context of the two distinct drivers of $R_{atomic}$ .

#### <sup>298</sup> 7 Conclusion

Our results demonstrate that thermospheric  $R_{atomic}$ , rather than  $R_{water}$ , is more sensitive to short-term perturbations in the atmospheric system due to its sensitive dependence on both thermospheric temperature and mesospheric water. Seasonal changes to these two parameters lead to similar effects on  $R_{atomic}$ , but affect the thermospheric abundances of D and H and their escape rates differently. The cause of these variations in the thermosphere is differences in the dynamics of H and D in the mesosphere; H escape is diffusion-limited, while D escape is energy-limited.

Mars is unique in the fact that its gravity, atmospheric pressure and thickness, and presence of water vapor combine to create a situation where the diffusion and escape behaviors of H and D are so different. Since other planets in the solar system have either much higher gravity, thicker atmospheres, or much less water, the same situation may not arise for H and D on other bodies. However, the lessons learned here may be potentially applied to other isotope systems on other terrestrial planets with atmospheres.

Cross-correlation of martian datasets containing upper atmospheric R<sub>atomic</sub>, thermospheric temperatures, and mesospheric water would enhance our understanding of the martian climate and water cycle. Concurrent measurements could be ingested into photochemical and climate models, providing realistic constraints, refining estimates of atmospheric escape, and helping to identify knowledge gaps. Such an approach could also

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provide insight into the dynamics of water, H, and D in the relatively difficult-to-observe upper mesosphere and lower thermosphere ( $\sim 80-110$  km).

In our quest to understand the long-term evolution of the stability of water on terrestrial planets, we must continue working both to understand the specific effects of individual processes and to develop synoptic-scale understanding of the complex ways that surfaces and atmospheres interact and alter one another.

323 8 Open Research

Our model, bluejay, is available on Zenodo (E. Cangi & Chaffin, 2023); the working copy is available in the linked Github repository. bluejay is written for Julia 1.8.5 (Bezanson et al., 2017).

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Figure 2.





Figure 4.



Figure 3.



Figure 1.



# 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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- X 2 CANGI, CHAFFIN, YELLE, GREGORY, AND DEIGHAN: ATOMIC D/H OF MARS
- 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.

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Included neutrals (28)	Ar, C, CO, CO <sub>2</sub> , D, DCO, DO <sub>2</sub> , DOCO, H, $H_2$ , $H_2O$ , $H_2O_2$ , HCO, HD, HDO, HDO <sub>2</sub> , HO <sub>2</sub> , HOCO, N, N <sub>2</sub> , NO, N( <sup>2</sup> D), O, O( <sup>1</sup> D), O <sub>2</sub> , O <sub>3</sub> , OD, OH
Included ions (35)	$\begin{array}{l} ArD^{+},ArH^{+},Ar^{+},CH^{+},CO_{2}^{+},CO^{+},C^{+},DCO_{2}^{+},\\ DCO^{+},DOC^{+},D^{+},H_{2}DO^{+},H_{2}D^{+},H_{2}O^{+},H_{2}^{+},\\ H_{3}O^{+},H_{3}^{+},HCO_{2}^{+},HCO^{+},HDO^{+},HD^{+},HDO^{+},\\ HO_{2}^{+},HOC^{+},H^{+},N_{2}D^{+},N_{2}H^{+},N_{2}^{+},NH^{+},NO^{+},\\ N^{+},O_{2}^{+},OD^{+},OH^{+},O^{+} \end{array}$
Basic output format	Number density at each altitude
Vertical extent	0-250  km;  spacing  2  km
SZA	60° (dayside mean)
Chemistry	${\sim}600$ 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 $72 \text{ km}$
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 $1.2 \times 10^8$ ), H, D, H <sub>2</sub> , 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  $\sim 2-4$  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  $\sim 2-4$  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.