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PHOTOCHEMICAL ESCAPE FROM MARS AS A CLIMATE DRIVER: HOW IMPORTANT? R. J. Lillis¹, D. Y. Lo², A. Rahmati¹, J. I. Deighan³, J. L. Fox⁴, R. Yelle², Y. Lee⁵, F. Leblanc⁶, J.-Y. Chaufray⁶, T. Cravens⁷, M. Gacesa⁸, M. Chaffin³, B. M. Jakosky³

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Introduction: Atmospheric escape has been a primary driver of climate evolution over Martian history [1] and continues to this day. Geomorphologic evidence shows that the Martian climate supported significant fluvial activity and aqueous alteration prior to ~3.7 Ga [2,3], indicating that a thick atmosphere most have existed, at least episodically, in this epoch. However, to understand a) the atmospheric pressure on early Mars and b) the time history of its decline, we need to understand the physical processes by which atmosphere escapes. A primary goal of the MAVEN mission [4] is to elucidate these processes and understand their relationship to solar drivers such as extreme ultraviolet and solar wind pressure. One such process is known as *photochemical escape*, whereby dissociative reactions in the Martian upper ionosphere provide sufficient energy for the atomic products of the reaction to escape Mars' gravity. O, N, C, and H have been escaping from Mars in this manner over Martian history, their escape rates depending on solar extreme ultraviolet irradiance (which was much higher in the past) and the composition of the atmosphere near the exobase (the approximate boundary, at ~200 km altitude, between the collisional atmosphere in the exosphere) [5]. MAVEN measurements can be used to derive escape rates for these species. Here we review the current state of knowledge of this process, likely cumulative loss of atmosphere over Mars history, as well as needed work and future challenges.

Oxygen escape today: when CO₂ and O are ionized by solar EUV radiation in Mars' upper atmosphere, the resulting CO₂⁺ and O⁺ ions quickly react with neutral O and CO₂ respectively to form CO and O₂⁺, which is long-lived and hence the dominant ion. When O₂⁺ recombines with thermal electrons, it dissociates, and the now-free O atoms can escape Mars' gravity if they do not lose energy through too many collisions with neutrals. This is called dissociative recombination (DR). MAVEN data can be used to calculate the volume rate of DR and the energy distribution of the resulting hot O atoms. A Monte Carlo code that simulates hot O collisions and trajectories, then calculates the probability, as a function of altitude, that these hot atoms can escape. Integrating the product of production rate and escape probability gives escape flux, which shows a

super-linear relationship with solar EUV photoionization frequency (figure 1) [6].

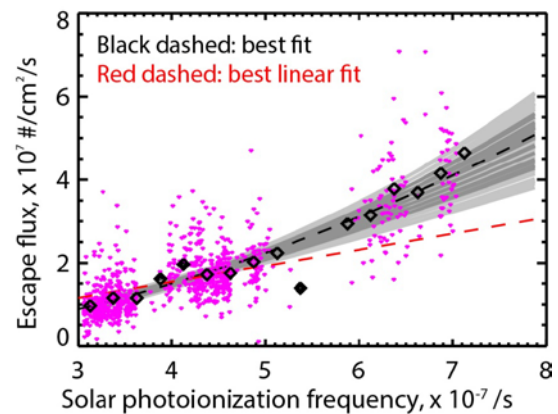


Figure 1: oxygen escape fluxes (individual orbits in pink, binned averages as black diamonds) from O₂⁺ dissociative recombination, derived from MAVEN data [6], as a function of CO₂ photoionization frequency.

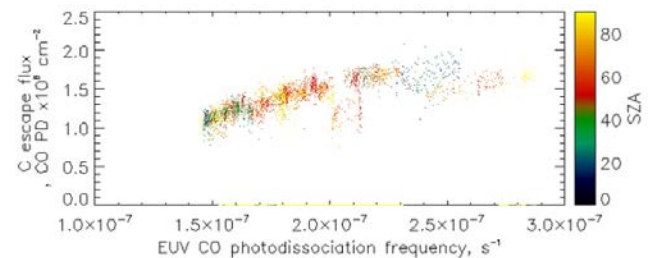


Figure 2: carbon escape fluxes from CO photodissociation, derived from MAVEN data (unpublished).

Carbon escape today. The primary source of hot and escaping carbon in the Martian atmosphere is the photodissociation of carbon monoxide (CO) [7]. For each profile of in situ measurements from MAVEN, we calculate rates of CO photodissociation, and hence production of hot carbon atoms. We then use measured irradiance and known energy thresholds for CO photodissociation, plus conservation of energy and momentum, to calculate the probability distribution for the initial energies of the resulting hot carbon atoms. The same Monte Carlo model then calculates escape probabilities, enabling escape fluxes to be estimated. Derived carbon fluxes are a factor of ~20 lower than oxygen and show a linear relationship with solar EUV at low solar activity but appear to be independent at mod-

erate solar activity (figure 2). *This factor of ~20 is a major puzzle since it implies that oxygen escape has not primarily been from CO₂ but from water, so where did the CO₂ go?*

Nitrogen escape today: Similar to carbon, photodissociation of N₂ leads to hot and escaping N atoms. Cui et al. [8] used a similar approach as for oxygen to calculate escape fluxes, but interestingly, these do not show a clear dependence on solar activity (figure 3).

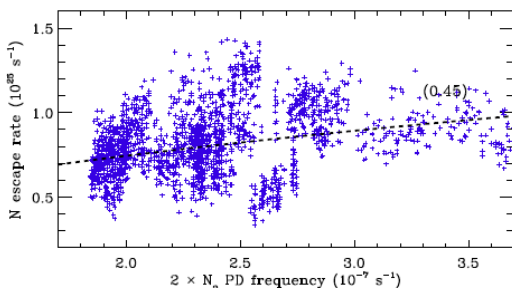


Figure 3: nitrogen escape rates from photodissociation of N₂ from Cui et al. [2018].

Hydrogen escape today: Early work [Nagy and Cravens, 1990] contended that Hot H was not a significant source of escape compared with thermal (i.e. Jeans) escape, but the recent discovery of a significant hot H corona at Mars [10] implies that photochemical reactions may be a significant source of hydrogen escape.

Does escape even rise with EUV brightness? Yes, over the range of solar EUV irradiance seen by MAVEN. But, solar UV does not just ionize upper atmospheres, it also heats them. In particular, the scale height of neutral atomic oxygen is 2.75 times greater than the CO₂ from which most hot O comes and 1.75 times greater than the N₂ and CO from which most hot C and N come from. As UV rises, more neutral oxygen floats above where these hot atoms are created, blocking their escape. With the naïve assumption that relative composition doesn't change with time, models have shown [11] that photochemical escape rates of O, C, may actually decrease if EUV rises above 10x its current value (figure 4), equivalent to ~4-4.1 Gyr ago.

How bright was the early sun? From spectral studies of G2-type (i.e. sun-like) stars in globular clusters, the EUV history of the sun can be constrained, although the uncertainty is almost an order of magnitude at 4 billion years ago, leading to significant uncertainty in estimates of cumulative photochemical escape.

Total Loss estimates: Photochemical escape was likely responsible for the loss of ~50-200 mbars of oxygen over the last 4 billion years (figure 5). Other total photochemical loss estimates await future work.

Next steps: this is a very active research topic with several MAVEN team members working on various aspects. The following developments will significantly improve our knowledge photochemical escape:

- New ab initio cross-sections for O and C collisions with CO₂.
- Lab measurements of emergent C velocities from CO₂ photodissociation.
- Updated NGIMS calibration for CO densities in the Mars atmosphere.
- Derive past compositions from present escape rates and model photochemical escape with those past compositions.

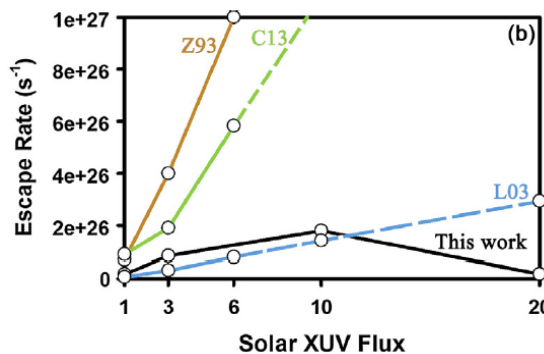


Figure 4: simulated photochemical escape rates of oxygen as a function of the ratio of solar extreme ultraviolet irradiance to current conditions[11].

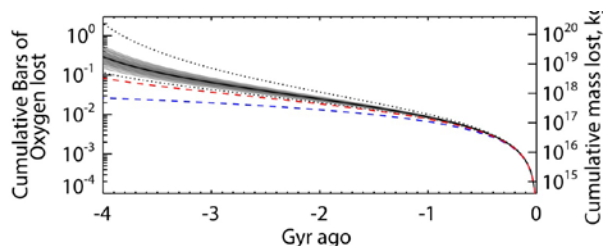


Figure 5: Cumulative oxygen loss extrapolated to 4 Ga. Back and grey lines show the best fit to MAVEN data. Dotted lines show EUV uncertainty. Dashed red and blue lines assume linear and no solar EUV dependence [6].

Conclusion: Photochemical escape was undoubtedly an important driver of Mars climate evolution. However, quantitative uncertainties remain large. To achieve accuracy in escape estimates of O, C, N, H to even a factor of two will require significant advancements in understanding the processes as well as in the history of solar extreme ultraviolet irradiance.

References: [1] Jakosky et al., *Icarus*, 2018, [2] Mangold et al., *JGR*, 2012, [3] Fassett and Head, *Icarus*, 2011, [4] Jakosky et al., *SSR*, 2015, [5] Lillis et al., *SSR*, 2015 [6] Lillis et al., *JGR*, 2017, [7] Groller et al., *PSS*, 2014, [8] Cui et al., *A&A*, 2018, [9] Nagy and Cravens, *Annales Geophys*, 1990, [10] Chaffin et al., *JGR*, 2018, [11] Zhao and Tian, 2015.