

# TOTAL ATMOSPHERIC LOSS FROM UPPER-ATMOSPHERIC STRUCTURE OF $^{36}\text{Ar}/^{38}\text{Ar}$ OBSERVED BY MAVEN.

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## Introduction

The MAVEN (Mars Atmospheric and Volatile Evolution Mission) spacecraft has been in orbit for 2 years and has enabled detailed estimates of current atmospheric loss processes. Calculating the cumulative loss throughout Mars' history will require extrapolating all escape rates back in time through changing solar and atmospheric conditions. One method to estimate total loss is through the observed enrichment in heavy isotopes relative to light isotopes of a species in the atmosphere (D/H,  $^{15}\text{N}/^{14}\text{N}$ ,  $^{13}\text{C}/^{12}\text{C}$ ,  $^{38}\text{Ar}/^{36}\text{Ar}$ ), as light isotopes are preferentially removed. In this study we examine how argon isotope ratios vary from the lower atmosphere to the exobase, where they can escape to space.

$^{38}\text{Ar}$  is enriched relative to  $^{36}\text{Ar}$  in Mars' bulk atmosphere compared to Earth's bulk atmosphere. Earth's atmospheric  $^{36}\text{Ar}/^{38}\text{Ar}$  ratio is thought to be the result of efficient outgassing of juvenile gases from the interior and lack of significant loss because it is nearly equal to  $^{36}\text{Ar}/^{38}\text{Ar}$  in the solar wind, chondrites, and Jupiter's atmosphere. If Mars' atmosphere formed with the same primitive ratio, then it has since been fractionated. Ar is unlikely to react chemically with the surface in significant amounts, so the observed enrichment must be a consequence of loss to space.

Ar is primarily removed by sputtering, where some ionized oxygen atoms that are picked up in the exosphere by the interplanetary magnetic field re-impact the upper atmosphere with sufficient energy to eject other particles into space. While this process is not inherently mass-fractionating, if some atoms or molecules are more abundant at altitudes where particles are removed, they will be lost preferentially over time. The exobase, though not a sharp transition, can be thought of as the altitude at which particles can escape and is defined to be where a particle's mean free path is equal to the atmospheric scale height. Above the homopause, below which the atmosphere is well-mixed, species diffusively separate due to their different masses. Thus, at the exobase, lighter isotopes of a given species will be more abundant in the exosphere relative to their heavier counterparts than in the well-mixed lower atmosphere. Removal via sputtering from the light-isotope-enriched upper atmosphere over time causes a depletion of light isotopes from the initial ratio and this change is reflected in the lower atmosphere.

To assess how much Ar has escaped to space, we need at minimum, the initial atmospheric ratio, the present-day ratio, and the ratio at which  $^{36}\text{Ar}$  is sputtered relative to  $^{38}\text{Ar}$ . We assume the first to be equal to the ratio in primitive solar system objects and the second has been measured in situ by the SAM (Sample Analysis at Mars) instrument on the Curiosity rover. The last we take to be the relative value of  $^{36}\text{Ar}/^{38}\text{Ar}$  at the exobase to that at the homopause. These altitudes (admittedly representative of transitional regions) are typically assumed to be about 200 and 120 km, respectively. Here, we determine homopause and exobase altitudes empirically for thousands of MAVEN orbits between February 2015 and August 2016 from NGIMS (Neutral Gas and Ion Mass Spectrometer) measurements of  $\text{N}_2$  and Ar. Then, we calculate the expected fractionation of  $^{36}\text{Ar}$  and  $^{38}\text{Ar}$  between those altitudes. Finally, we use the derived ratios of exobase  $^{36}\text{Ar}/^{38}\text{Ar}$  to lower-atmospheric  $^{36}\text{Ar}/^{38}\text{Ar}$  as inputs to model of Ar isotope evolution that accounts for additional atmospheric supply and loss processes and calculates total Ar escape. Thus, we find a range of total  $^{36}\text{Ar}$  lost as a result of the variability in observed upper atmospheric densities and temperatures. The average loss value is  $66\% \pm 5\%$ . We discuss the possible causes of upper atmospheric variability, uncertainties in this technique, and what our conclusions mean with respect to Mars' early atmospheric pressure.

## Homopause and Exobase Calculations

The atmosphere is well-mixed below the homopause and governed by diffusion above it. MAVEN's periapse altitudes are typically  $\sim 150$  km and as low as 120 km during deep-dip campaigns. So the spacecraft only reaches the vicinity of the homopause, but we observe the separation of different atmospheric species every orbit (Fig. 1). Taking the lower atmospheric  $\text{N}_2$  to Ar mixing ratio measured by SAM (Franz, personal communication) as the defining homopause value, we extrapolate  $\text{N}_2/\text{Ar}$  profiles downward to determine the altitude of the homopause. Though  $\text{N}_2/\text{CO}_2$  and  $\text{Ar}/\text{CO}_2$  will vary below the homopause as the pressure changes seasonally, the  $\text{N}_2/\text{Ar}$  should remain constant as neither condenses out of the atmosphere. We have verified that these species are diffusively separating by calculating scale heights from  $\text{N}_2$  and Ar densities at these altitudes and comparing the

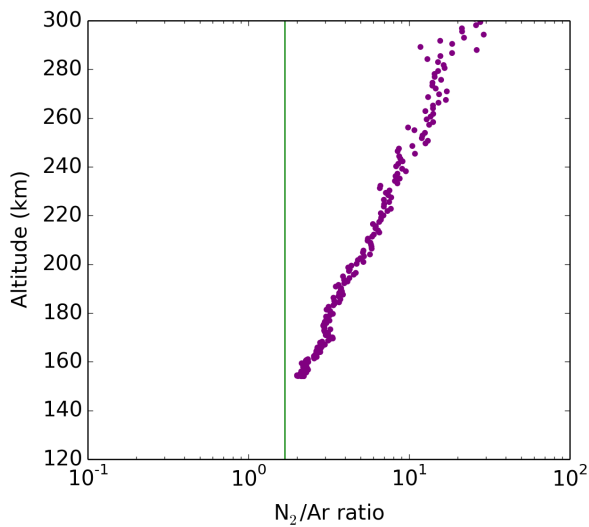


Figure 1: Profile of  $N_2/Ar$  as measured by NGIMS for a single inbound orbit. The green line is the lower atmospheric value of  $N_2$  to Ar measured by SAM.

temperatures. This process was repeated for all possible inbound NGIMS density measurements (Mahaffy et al., 2015b,a) below 200 km over 18 months worth of orbits. The homopause and exobase altitudes for each orbit are shown in Fig. 2.

We used two independent methods to find exobase altitudes for every orbit (Fig. 2). For the first, we integrate  $n\sigma$ , where  $n$  is the number density of  $CO_2$  and  $\sigma$  is the collisional cross section, from a point well above the exobase to where  $N\sigma$  (column density,  $N$ ) is 1. Since the exobase is defined as the altitude at which the scale height equals the mean free path, we also determine the Ar scale height,  $H$ , at each altitude and find where  $H = n\sigma$ . These two methods give similar values for the exobase for each orbit.

MAVEN's orbit precesses so the periape points where these measurements are made sample a range of latitudes and local times and cover nearly a full cycle of  $L_s$  values. The observed changes in both altitudes with time are not straightforward to interpret. The separation between the homopause and exobase is roughly constant as they respond to varying conditions in the lower atmosphere. Seasonal variations of the homopause are observed on Earth as circulation changes (Offermann et al., 2007), so a similar effect may be expected. Gravity waves have been seen with MAVEN (Yigit et al., 2015) and the vertical mixing they induce should cause changes in the homopause (Imamura et al., 2016). A more detailed study of the changing environment at these altitudes will enable a better understanding of the orbit-orbit variation we see as well as the long term trends. Additionally, this technique gives some extremely low

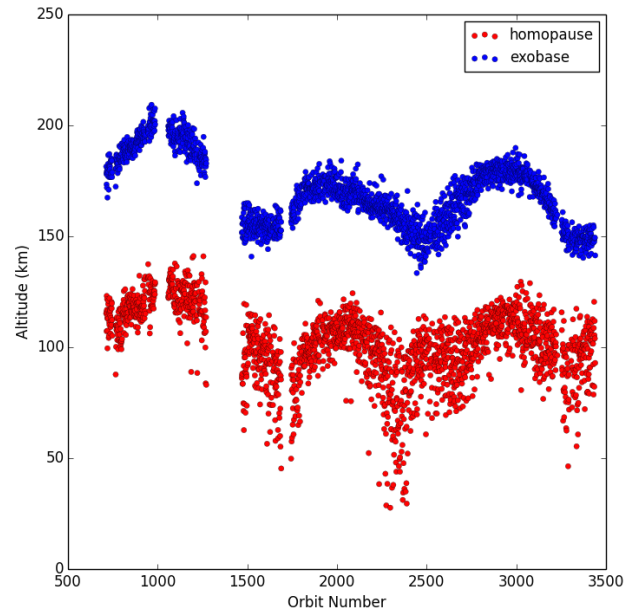


Figure 2: Homopause (red) and exobase (blue) altitudes calculated from Feb 2015 through July 2016. Values below 80 km are not realistic.

homopause altitudes resulting from wave structure and large horizontal changes even between 300 and 150 km. We think any homopause values below  $\sim 80$  km are realistic, but we do not reject any for the remainder of our analysis.

### Derived Ar loss

Once introduced into the atmosphere, Ar can be ejected into space by sputtering via collisions generated by pickup ions that have been accelerated by the solar wind. This is the dominant process for Ar loss as it does not interact with the surface. Sputtering is not a mass-dependent process, but isotope ratios are altered because light isotopes are more abundant relative to heavy isotopes in the exobase region than in the lower atmosphere (due to differences in their individual scale heights above the homopause) and therefore, more susceptible to removal. Consequently, the bulk atmosphere becomes enriched in heavy isotopes.

Here, we use the homopause-exobase separation and the measurement of  $^{36}Ar/^{38}Ar$  in the lower atmosphere from SAM to determine  $^{36}Ar/^{38}Ar$  at the exobase for each orbit. We do not attempt to use the measured  $^{36}Ar/^{38}Ar$  values at the exobase for each orbit due to the large uncertainties associated with these trace species. Thus, for each orbit we assume  $^{36}Ar/^{38}Ar = 4.2$  (Atreya et al., 2013) at the homopause and calculate the ratio at the exobase using a temperature from the  $^{40}Ar$  scale height of the same orbit.

## REFERENCES

The total fraction of  $^{36}\text{Ar}$  and  $^{38}\text{Ar}$  lost through time can be calculated using Rayleigh distillation knowing only the current bulk ratio, the past bulk ratio, and the fractionation factor of the loss process (here, the ratio of  $^{36}\text{Ar}/^{38}\text{Ar}$  at the exobase to the homopause), if one assumes a closed system (Faure, 1986). This method fails to account for other supply and loss processes that alter the atmospheric abundances of  $^{36}\text{Ar}$  and  $^{38}\text{Ar}$ , such as outgassing of the interior, delivery and removal of gas through impacts of asteroids and comets, and release of gas to the atmosphere through crustal weathering. Slipski and Jakosky (2016) modeled these effects in combination with sputtering for a wide range of parameters, but only considered a single value of the  $^{36}\text{Ar}/^{38}\text{Ar}$  sputtering fractionation factor. Because the fractionation factor depends on  $\Delta z/H$ , where  $\Delta z$  is the homopause-exobase separation and  $H$  is the scale height, each orbit corresponds to a different value of this factor. We have run simulations of the Slipski and Jakosky (2016) model for several values of  $\Delta z/H$  (dashed lines in Fig. 3) to determine what the expected total  $^{36}\text{Ar}$  loss would be if that  $\Delta z/H$  represented the true value in the Martian atmosphere over the past 4 Gyr. For each  $\Delta z/H$  we allow other parameter to vary as well (see Slipski and Jakosky (2016) for more details) resulting in a range of total loss, so the percentages of total  $^{36}\text{Ar}$  lost over Mars' history shown in Fig. 3 correspond to the average values.

The mean separation distance and  $^{40}\text{Ar}$  scale height represents a total  $^{36}\text{Ar}$  loss of about 66%. Uncertainty in this result stems from the lower atmospheric  $\text{N}_2/\text{Ar}$  measurement and from the model. The uncertainty from SAM is about 10% (Franz, personal communication) which we find causes about 1.5% uncertainty in total  $^{36}\text{Ar}$  loss when going through the same analysis for lower and higher values of lower atmospheric  $\text{N}_2/\text{Ar}$ . As described above, various parameters for a given fractionation factor can reproduce the present-day  $^{36}\text{Ar}$  and  $^{38}\text{Ar}$  abundances leading to slightly different loss values. Each set of simulations for a given fractionation factor results in a range total loss of roughly 4.5% around an average value. We add these two uncertainties in quadrature and find that the total  $^{36}\text{Ar}$  loss to be  $66 \pm 5\%$ . However, the same discussion of model assumptions in Slipski and Jakosky (2016) applies here as well. In addition, we have not considered that  $\Delta z/H$  has likely changed over time or that sputtering may not be spatially uniform.

### Summary

Homopause and exobase altitudes have been found to vary together over the course of observations that total nearly a full Martian year. These trends may be seasonal, though changes in latitude and local time of the measurements make an interpretation difficult.

Using the separation distance between the well mixed

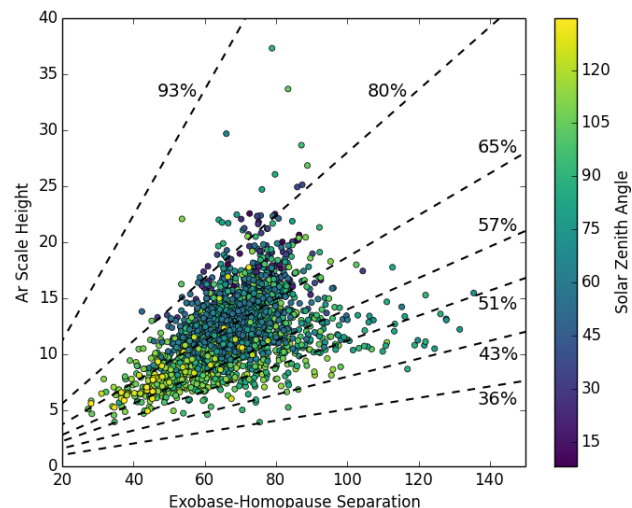


Figure 3: Values of the  $^{40}\text{Ar}$  scale height plotted against the distance between the homopause and exobase for each orbit. Colors correspond to the solar zenith angle of periapsis of each measurement. Several ratios of the separation distance to scale height were used as inputs to a model of Ar isotopic evolution and the resulting loss fractions of  $^{36}\text{Ar}$  are shown by the dashed-lines.

atmosphere and the exobase, we calculate the fractionation of  $^{36}\text{Ar}$  and  $^{38}\text{Ar}$ . Through a model of supply and loss processes of atmospheric Ar, we find that approximately  $66\% \pm 5\%$  of  $^{36}\text{Ar}$  and  $^{38}\text{Ar}$  has been lost to space. Ar is lost through sputtering by pickup ions, so this process alone could have removed about two-thirds of the early Martian atmosphere.

From estimates of present-day sputtering loss via measurements of precipitating ions (Leblanc et al., 2015) and accounting for the change in that rate through time (e.g., Luhmann et al. (1992); Chassefière et al. (2007)),  $\sim 500$  mbar total of  $\text{CO}_2$  could have been lost through sputtering. Taken together with our results from Ar isotopes, these values are consistent with an early Martian atmosphere of  $\sim 1$  bar.  $\text{CO}_2$  can be removed to space by several other mechanisms as well as sequestered in the surface as carbonates.

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