**MARTIAN ATMOSPHERE**

**Mars’ atmospheric history derived from upper-atmosphere measurements of $^{38}\text{Ar}/^{36}\text{Ar}$**

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The history of Mars’ atmosphere is important for understanding the geological evolution and potential habitability of the planet. We determine the amount of gas lost to space through time using measurements of the upper-atmospheric structure made by the Mars Atmosphere and Volatile Evolution (MAVEN) spacecraft. We derive the structure of $^{38}\text{Ar}/^{36}\text{Ar}$ between the homopause and exobase altitudes. Fractionation of argon occurs as a result of loss of gas to space by pickup-ion sputtering, which preferentially removes the lighter atom. The measurements require that 66% of the atmospheric argon has been lost to space. Thus, a large fraction of Mars’ atmospheric gas has been lost to space, contributing to the transition in climate from an early, warm, wet environment to today’s cold, dry atmosphere.

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Gases are being lost from the Mars atmosphere to space today [e.g., (1, 2)], potentially in quantities sufficient to change the planet’s climate [e.g., (3)]. A goal of the Mars Atmosphere and Volatile Evolution (MAVEN) mission is to quantify the amount of gas lost to space through time using measurements of the upper-atmospheric structure made by the Mars Atmosphere and Volatile Evolution (MAVEN) spacecraft. We derive the structure of $^{38}\text{Ar}/^{36}\text{Ar}$ between the homopause and exobase altitudes. Fractionation of argon occurs as a result of loss of gas to space by pickup-ion sputtering, which preferentially removes the lighter atom. The measurements require that 66% of the atmospheric argon has been lost to space. Thus, a large fraction of Mars’ atmospheric gas has been lost to space, contributing to the transition in climate from an early, warm, wet environment to today’s cold, dry atmosphere.

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As a consistency check, we independently used number-density profiles to derive atmospheric temperatures for $^{36}\text{Ar}$, $^{40}\text{Ar}$, and CO$_2$ separately. The values are all within the observational and best-fit uncertainty of each other, confirming that diffusive separation is occurring as expected and allowing us to extrapolate to other gases.

Exobase altitude is derived from the composition of the neutral atmosphere measured by NGIMS (17). The exobase is defined as the altitude at which the atmospheric scale height equals the gas molecular mean free path or, equivalently, the altitude at which an upward-moving atom has a 1/e chance of not undergoing a collision before escaping to space. We have calculated the exobase altitude both ways as a consistency check and obtain similar results.

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**Fig. 1. Diffusive separation by mass above the homopause.** Examples of the ratio of $N_2$ to $^{40}\text{Ar}$, both measured by MAVEN NGIMS, during a single orbit. The altitude at which the ratio equals the lower-atmosphere value, shown by the vertical dashed line, is the nominal homopause altitude. (A) Well-behaved example showing the ability to extrapolate the ratio down to the surface value to derive the homopause altitude. (B) Example showing structure at lower altitudes that complicates the extrapolation.
Throughout the mission, owing to precession of the orbit in both local solar time and latitude (4), the results shown represent a complicated combination of real geophysical variations with latitude, local solar time, solar zenith angle, geographical location, and season. Because of the limited set of observations, it is not possible to separate the variations due to each of these properties. Figure 3 shows the variation of homopause and exobase altitudes plotted against solar zenith angle (SZA) (20). 

The trends of exobase and homopause altitudes follow each other closely. This is shown in Fig. 3 as a nearly constant difference between them as each one changes. This result suggests that the two are rising and falling largely in response to behavior at lower altitudes, below the homopause, that compresses or distends the lower atmosphere. We expect the lower atmosphere to be more sensitive to seasonal forcing either directly, through the changing Sun-Mars distance, or indirectly through seasonally variable atmospheric dust that can absorb sunlight and heat the lower atmosphere (18).

We use the structure derived from CO2, N2, and 40Ar, combined with the behavior expected for diffusive separation, to determine the degree of fractionation of 38Ar/36Ar between the homopause and exobase. We have not used 38Ar and 36Ar measurements for each orbit to derive this fractionation because of the larger uncertainty in the measurements of these low-abundance gases. However, we have examined measured 38Ar and 36Ar abundances during the MAVEN deep-dip campaigns that take the spacecraft to lower altitudes, nearer to the homopause. The results confirm both the diffusive separation and the fractionation between the homopause and exobase (20).

We combine the fractionation through the upper atmosphere with the observed enrichment of 36Ar/38Ar in the lower atmosphere and an assumed initial ratio to derive the total amount of argon that has been removed from the system. For the lower atmosphere, we use the MSL measurements of 36Ar/38Ar (9). We use the terrestrial value of 5.3 for the initial value; solar, meteorite, and derived martian mantle values are all close to this (8) and would all give similar results.

Rayleigh fractionation [e.g., (24)] can be used with these values to derive the fraction of gas that has been lost from the system. Rayleigh fractionation calculates the isotopic ratio of the remaining gas as a function of the fraction of gas that has been lost. However, argon has been added into the atmosphere through time by outgassing from the interior, impact of asteroids and comets, and weathering of crustal materials. Each of these processes adds gas that has the same isotope ratio as the initial value, partially resetting the atmospheric isotope ratio. We use a time-marching model of these additional processes (25), integrated from 4 billion years ago to the present, to calculate the resulting loss. In each time step in the model, gas is added by these processes or removed by loss to space, and the fractionation at each time step is adjusted appropriately by Rayleigh fractionation (for sputtering loss) or dilution (for addition of gas to the atmosphere). Details are given in (20), and the results are shown in Fig. 4. Taking the average value of all of the measurements, 66% of the 36Ar that was ever in the atmosphere has been removed to space. Eliminating the unrealistically low homopause values, which affect the points only at the far right side of Fig. 4, does not change this result substantially.

There are two easily quantifiable sources of uncertainty in this result. First, the result depends on the ratio of N2/38Ar measured in the lower atmosphere by MSL. Their current best estimate has an uncertainty of ~10% (22). When carried through the analysis, this gives an uncertainty of ~1.5% in the amount of 38Ar lost. Second, the model itself balances multiple processes, including the amount of volcanic outgassing, crustal degassing from weathering, and sputtering loss (25). Different combinations of model parameters can be used to fit the observations; in each model, the evolution through time will vary slightly, resulting in loss of a slightly different fraction of Ar. Each dashed line in Fig. 4 is labeled with the average 38Ar loss for the full range of models that fit the data, but the fraction of 38Ar lost can vary from the amount indicated by ~4.5% (20). These two sources of error can be combined in quadrature, assuming that they are independent; doing this, we estimate that the 38Ar loss is 66% ± 5% (26). Possible systematic uncertainties resulting from changes in atmospheric structure or composition through time are more difficult to quantify. We have assumed that the fractionation in 38Ar/36Ar between the homopause and exobase has stayed constant through time; variations in lower-atmosphere properties or in upper-atmosphere heating through time, by themselves, would not affect this fractionation.

We can use the results on argon loss to determine the amount of other gases that would have been lost by the same sputtering mechanism, based on the relative collision cross sections and the relative abundances of the gases at the exobase target for sputtering. This is done with the model of (25) and calculating the absolute number of atoms of Ar, O, and the atomic components of CO2 that are lost. O can come from either CO2 or H2O, as both are photodissociated by sunlight. In the model results, loss of CO2 typically can remove ~10 to 20% of the CO2 in the atmosphere. Loss of O would have removed ~30 times the number of atoms relative to CO2 (11); if the O that is lost comes primarily from CO2, then sputtering loss of CO2 can approach a bar or more (20). If the O lost comes from H2O, then loss of CO2 would have been smaller but loss of water would have been substantial (20). We can compare these results with those inferred from the direct loss of O today. Leblanc et al. (27) made an independent estimate of loss rate at the present as observed by MAVEN. Again, if all of the O comes from CO2, then as much as half a bar or more of CO2 could have been removed by sputtering through time (20).

The early Mars atmosphere may have had a CO2 partial pressure of a bar or more, in order to produce sufficient greenhouse warming to have allowed liquid water to be stable at the surface [e.g., (29)]. If that were the case, our results suggest that a large fraction of that early, thick atmosphere could have been removed to space by pickup-ion sputtering. The evidence for ongoing escape [e.g., (1, 5)] and the likelihood that the loss rate was much greater early in Mars’ history (11) because of the greater intensity of the solar extreme ultraviolet radiation and of the solar wind drivers [e.g., (29)] means that the amount of CO2 lost to space could have been this large. CO2 also can be removed by other processes that do not affect argon, including pickup by the solar wind and photochemically driven escape [e.g., (30, 31)], so this loss represents a lower limit on the total amount that would have been lost.

Fig. 2. Derived values of exobase and homopause altitudes from MAVEN data. Measurements run from February 2015 through June 2016. Earth calendar dates are shown along the bottom, and Mars season (Ls, aereocentric longitude of the Sun) along the top. Exobase altitude is shown in blue, homopause in red.
The evidence from the MAVEN observations suggests that a large fraction of the martian volatile inventory has been removed to space and that loss to space has been an important process in the evolution of the martian atmosphere through time. CO$_2$ loss from the atmosphere likely resulted from a combination of loss of a majority of gas to space, removal of a smaller fraction to the shallow subsurface as carbonate minerals or as adsorbed gas (32), and removal of an even smaller portion to the polar caps, where it resides today as ice (33). These changes appear to be large enough to account for the change in martian climate inferred from the planet’s geomorphology (34).

REFERENCES AND NOTES
13. Although described as a single altitude, the exobase reflects processes driving or inhibiting escape that act over a wide range of altitudes; the distinction does not affect our quantitative results.
20. See supplementary materials.
22. Mahaffy et al. (22) derived a ratio of 1.0. Subsequent measurements have refined this to 1.2, with an uncertainty of ~10% (25). The value determined from the Viking lander of 1.7 (36) has a larger uncertainty and is consistent with the MSL Sample Analysis at Mars value.
23. Solar zenith angle (SZA) is the angle between the vector toward the zenith at a location and the vector toward the Sun; it is 0° when the Sun is directly overhead. Because the homopause can be up to 130 km above the surface, the Sun is still above the horizon at SZA values as high as 106°.
26. Argon also can be sputtered and removed by solar-wind pickup. However, 40Ar ion abundances measured by MAVEN are roughly three orders of magnitude lower than O or O$_2$ ion abundances, and 36Ar will be down from that by another two to three orders of magnitude (37). Loss being in proportion to number density means that 36Ar ion pickup loss has been negligible.

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**Fig. 3.** Solar-zenith-angle dependence of upper-atmosphere structure. Panels show the argon exobase altitude, homopause altitude, separation between the homopause and exobase, and atmospheric scale height derived from $^{40}$Ar measurements, as a function of the solar zenith angle throughout the mission. Points are color coded by Martian season ($L_s$) and show the effects of changing seasons.

**Fig. 4.** Derived fraction of atmospheric Ar lost to space. Data points represent values derived for $^{40}$Ar scale height and separation between the homopause. Each point represents a single orbit and is color coded by SZA. Dashed lines represent the fraction of $^{36}$Ar lost to space, integrated through time, including the effects of outgassing of juvenile gas, release of gas from impacting asteroids, and weathering of crustal materials.
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SUPPLEMENTARY MATERIALS

www.sciencemag.org/content/355/6332/1408/suppl/DC1
Materials and Methods
Supplementary Text
Figs. S1 to S3
References (38–41)

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**Most of Mars' atmosphere has been lost**

Mars has a thin atmosphere composed mainly of carbon dioxide. Evidence on the planet's surface indicates that Mars was once warmer and wetter, suggesting a thicker atmosphere in the past. Jakosky *et al.* measured the abundances of argon isotopes at different heights in the atmosphere. Because lighter isotopes are more easily ejected than heavier ones, about 66% of Mars' atmosphere has been lost into space since it formed. Understanding the history of Mars' atmosphere will help explain how and why its climate changed, informing the study of similar processes on Earth.

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