REPORT

MARTIAN ATMOSPHERE

Mars' atmospheric history derived from upper-atmosphere measurements of $^{38}Ar/^{36}Ar$

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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 $^{38}Ar/^{36}Ar$ 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.

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 (*4*, *5*). Processes that strip gas to space preferentially remove the lighter of pairs of isotopes, leaving the remaining atmosphere enriched in the heavier isotope [e.g., (*6*)]. An observed heavy-isotope enrichment is a strong indicator that loss to space has occurred (*3*, *7*). We examine the ratio of $^{38}Ar/^{36}Ar$. Previous measurements have indicated an enrichment of ^{38}Ar in the present-day atmosphere (*8*, *9*). Measurements from MAVEN now provide the detailed upper-atmosphere structure that allows us to calculate quantitatively the amount of gas lost to space. Although $^{13}C/^{12}C$, $^{15}N/^{14}N$, and D/H (D, deuterium) also show heavy-isotope enrichment (*3*), Ar does not react chemically and is a simpler quantitative indicator of how much gas has been lost.

Argon is readily removed to space by a single process, sputtering by pickup ions (*10*). Ions are accelerated by the solar wind into the upper atmosphere at high velocity, where they collide with and eject atoms to space (*11*). The sputtering process itself does not distinguish significantly between ^{38}Ar and ^{36}Ar [e.g., (*12*)]. However, higher abundances of ^{36}Ar relative to ^{38}Ar are present in the vicinity of the exobase, the altitude from which most loss occurs, because of their differing atmospheric scale heights (*13*). Atmospheric gas is generally well mixed up to ~120-km altitude [the homopause (*14*)]; diffusion becomes more rapid than large-scale mixing at higher altitudes, and each gas will have an atmospheric scale height corresponding to its atomic or molecular mass. Above the homopause, ^{36}Ar has a larger scale height than ^{38}Ar, and the ratio of $^{38}Ar/^{36}Ar$ is expected to decrease with altitude. Removal of atoms from the vicinity of the exobase, around 200-km altitude [e.g., (*15*)], therefore will preferentially remove ^{36}Ar because it is relatively more abundant at that altitude. As a result, the gas remaining behind becomes enriched in the heavier ^{38}Ar. We can use the fractionation between the homopause and the exobase, along with a measurement of the enrichment observed in the bulk atmosphere, to determine quantitatively the fraction of the total argon that has been removed from the system.

We use measurements from the MAVEN Neutral Gas and Ion Mass Spectrometer [NGIMS (*16*)] instrument to determine the altitude of both the homopause and the exobase for each orbit. Homopause altitude is derived from the observed ratio of $N_2/^{40}Ar$ by using the method of (*17*). These gases do not condense under martian conditions, so their abundance is not expected to vary with season. Taking their ratio removes variations in their individual mixing ratios stemming from seasonal variations in the atmospheric CO_2 abundance (*18*, *19*). The altitude at which the ratio of these gases equals their ratio in the bulk atmosphere is the nominal homopause; at lower altitudes, the ratio should be constant because of rapid mixing (*15*). MAVEN does not make measurements to as low as the homopause, so we extrapolate the measured ratio downward to determine the homopause altitude (*20*).

We use the bulk-atmosphere ratio of $N_2/^{40}Ar$ derived from in situ Mars Science Laboratory (MSL) measurements at the surface (*21*). We take this ratio to be 1.25, based on the most-recent analyses (*22*). Figure 1 shows an example of the ratio $N_2/^{40}Ar$ as a function of altitude, showing the enrichment of the lighter isotope above the homopause and the extrapolation to determine the homopause altitude. The homopause altitude was derived by this method separately for each orbit (Fig. 2).

As a consistency check, we independently used number-density profiles to derive atmospheric temperatures for N_2, ^{40}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 (*20*).

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 (*20*). Figure 2 shows the exobase altitude determined throughout the MAVEN mission.

The inferred homopause and exobase altitudes shown in Fig. 2 show substantial variation throughout the mission. The location of periapsis evolves

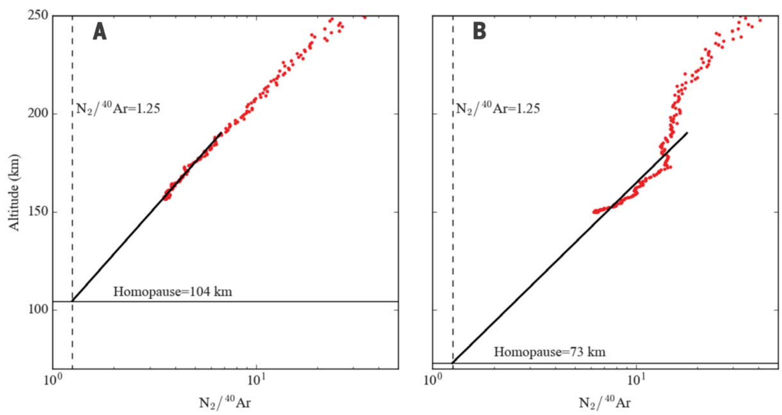

Fig. 1. Diffusive separation by mass above the homopause. Examples of the ratio of N_2 to ^{40}Ar, both measured by MAVEN NGIMS, during a single orbit. The altitude at which the ratio equals the lower-atmosphere value, shown by the vertical dashed line, is the nominal homopause altitude. (**A**) Well-behaved 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.

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throughout the mission, owing to precession of the orbit in both local solar time and latitude (*4*). Thus, 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) (*23*).

The trends of exobase and homopause altitudes follow each other closely. This is shown in Fig. 3 as a nearly constant difference between them even as each one by itself 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 CO_2, N_2, and ^{40}Ar, combined with the behavior expected for diffusive separation, to determine the degree of fractionation of $^{38}Ar/^{36}Ar$ between the homopause and exobase. We have not used ^{38}Ar and ^{36}Ar 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 ^{38}Ar and ^{36}Ar 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 $^{38}Ar/^{36}Ar$ 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 $^{38}Ar/^{36}Ar$ (*9*). We use the terrestrial value of 5.3 for the initial value; solar, meteorite, and derived martian mantle values all are 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 ^{36}Ar 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.

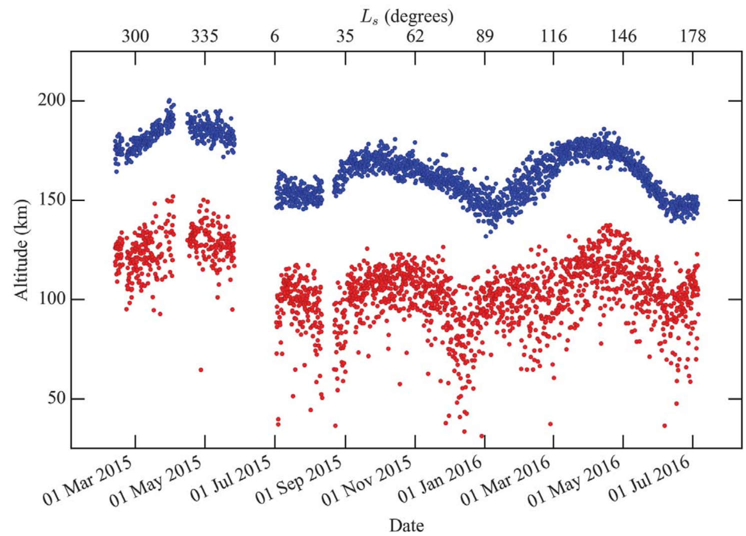

Fig. 2. Derived values of exobase and homopause altitudes from MAVEN data. Measurements run from February 2015 through June 2016. Earth calendar dates are shown along the bottom, and Mars season (L_s, areocentric longitude of the Sun) along the top. Exobase altitude is shown in blue, homopause in red.

There are two easily quantifiable sources of uncertainty in this result. First, the result depends on the ratio of $N_2/^{40}Ar$ 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 ^{36}Ar 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 ^{36}Ar loss for the full range of models that fit the data, but the fraction of ^{36}Ar 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 ^{36}Ar 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 $^{38}Ar/^{36}Ar$ 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 CO_2 that are lost. O can come from either CO_2 or H_2O, as both are photodissociated by sunlight. In the model results, loss of CO_2 typically can remove ~10 to 20% of the CO_2 in the atmosphere. Loss of O would have removed ~30 times the number of atoms relative to CO_2 (*11*); if the O that is lost comes primarily from CO_2, then sputtering loss of CO_2 can approach a bar or more (*20*). If the O lost comes from H_2O, then loss of CO_2 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 CO_2, then as much as half a bar or more of CO_2 could have been removed by sputtering through time (*20*).

The early Mars atmosphere may have had a CO_2 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., (*28*)]. 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 CO_2 lost to space could have been this large. CO_2 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.

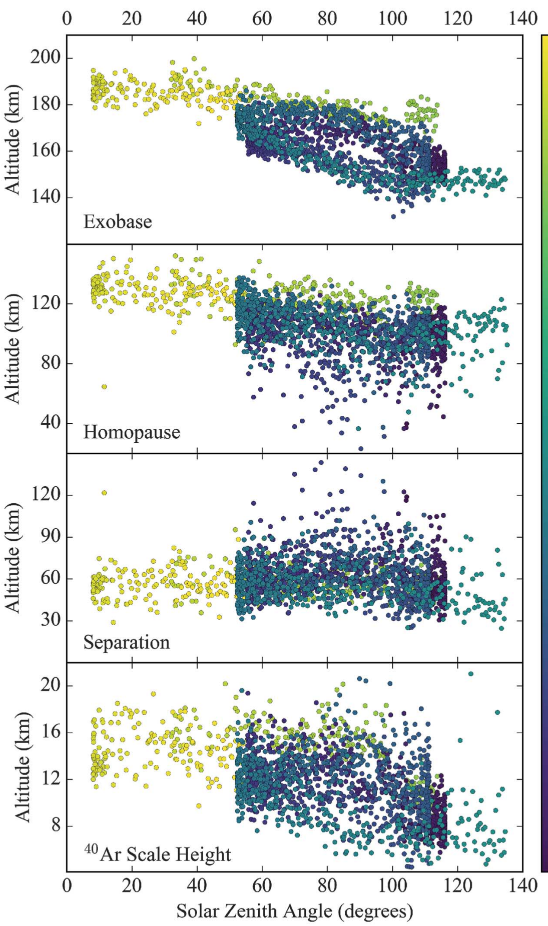

Fig. 3. Solar-zenith–angle dependence of upper-atmosphere structure. Panels show the argon exobase altitude, homopause altitude, separation between the homopause and exobase, and atmospheric scale height derived from ^{40}Ar measurements, as a function of the solar zenith angle throughout the mission.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

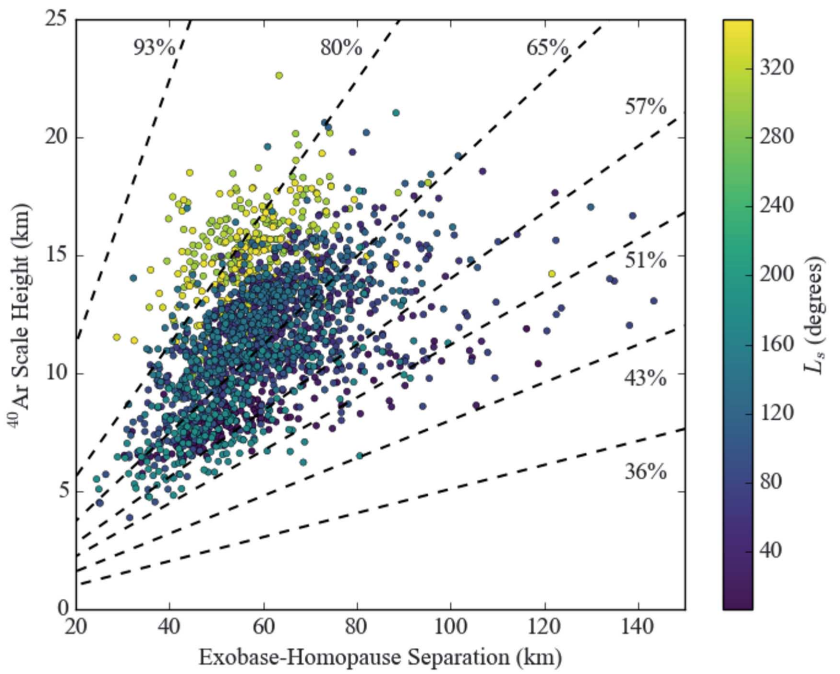

Fig. 4. Derived fraction of atmospheric Ar lost to space. Data points represent values derived for ^{40}Ar scale height and separation between the homopause. Each point represents a single orbit and is color coded by SZA. Dashed lines represent the fraction of ^{36}Ar lost to space, integrated through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

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*).

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22. Mahaffy *et al*. (*21*) derived a ratio of 1.0. Subsequent measurements have refined this to 1.25, with an uncertainty of ~10% (*35*). 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°.
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ACKNOWLEDGMENTS

The MAVEN mission is supported by NASA. We are grateful for support from all components of the project, including the spacecraft, operations, instrument, science, and project teams. N.A. was supported by the Mohammed Bin Rashid Space Center in the United Arab Emirates. Data from the MAVEN mission have been made available via the Planetary Data System and are accessible at http://atmos.nmsu.edu/data_and_services/atmospheres_data/MAVEN/maven_main.html.

SUPPLEMENTARY MATERIALS

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

9 August 2016; accepted 6 March 2017
10.1126/science.aai7721

Science

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Science **355** (6332), 1408-1410.
DOI: 10.1126/science.aai7721

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.

Science, this issue p. 1408