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Loss of Atmosphere from Mars Due to Solar Wind–Induced Sputtering

D. M. Kass* and Y. L. Yung

Because Mars does not have a strong intrinsic magnetic field, the atmosphere is eroded by interactions with the solar wind. Early solar-system conditions enhanced the sputtering loss. It is calculated that ~3 bars of carbon dioxide (CO_2) have been sputtered over the last 3.5 billion years. This significant increase over the previous estimate by Luhmann *et al.* of ~0.14 bar of CO_2 is the result of the development of a more complete model. The model also predicts slightly greater loss of water—~80 meters instead of the ~50 meters predicted by Luhmann *et al.* Because estimates of CO_2 on early Mars range from 0.5 to 5 bars, the 0.14-bar estimate is insignificant but the ~3-bar estimate will have a large effect on our understanding of the planet's evolution.

Martian geomorphology, notably the channels, appears to indicate that the planet once had significant quantities of water at or near the surface and a much higher surface temperature, possibly caused by an atmospheric greenhouse effect. Although there are questions about how much a greenhouse effect could raise the temperature (*1*), most current models require an atmosphere of at least 0.5 bar of CO_2 in order that liquid water be near the surface (*2–5*). Because the current martian atmosphere has only 7 mbar of CO_2 and only a small amount of H_2O, an important question is the fate of the early water and CO_2.

There are two major possibilities: Either the early atmosphere is sequestered somewhere in the planet (*5*) or it has been lost to space. McElroy *et al.* (*6*) pointed out that the water loss might have been determined by solar wind pickup of ionized exospheric O^+, because H loss by Jeans escape is easily accomplished. However, neither Jeans escape nor solar wind pickup is capable of removing significant amounts of CO_2 or water over the lifetime of the planet's "contemporary" atmosphere. Luhmann and colleagues (*7, 8*) proposed that atmospheric sputtering by exospheric O^+ could account for the loss of a significant amount of the O in the water but could not account for the CO_2 loss. In this process, O^+ ions of exospheric origin are accelerated by the interaction of the solar wind and interplanetary magnetic field with the upper atmosphere. These ions follow helical trajectories along interplanetary magnetic field lines draped over Mars and often reimpact the atmosphere with significant amounts of energy (upwards of 1 keV). During the impact, they can, through collisions, accelerate and cause other particles to escape (*8*).

Luhmann *et al.* (*7*) used a model to calculate the sputtering loss of CO_2 and water from Mars over the last 3.5×10^9 years. They calculated the escaping flux at three epochs (3.5 Gyr ago, 2.5 Gyr ago, and the present), referred to as 6 EUV, 3 EUV, and 1 EUV, respectively (*9*), due to the enhancement of the extreme ultraviolet (EUV) over present values. At each epoch, they first calculated the flux of reimpacting O^+ ions (*10*). Then they used an analytical model (*11*) to calculate the efficiency (the number of particles ejected per incident particle) of the C and O. These values were used to calculate total fluxes integrated over the planet. By assuming that the C and O come from CO_2 and H_2O (and adding in other escape fluxes of O), they were able to calculate the loss rate of CO_2 and H_2O at each epoch. These rates were then integrated from 3.5 Gyr ago to the present. Luhmann *et al.* (*7*) found that ~0.14 bar of CO_2 and ~50 m of water have been lost. Although this is sufficient water to form the erosional features, the calculations account for only a fraction of the necessary CO_2.

Luhmann *et al.* (*7*) appear to have neglected several factors in their model. The first of these factors is a result of their treating CO_2 as atomic components when interacting with the initial ion. However, when a CO_2 molecule is involved in a collision, all components are affected and thus the C effectively has the cross section of the whole molecule. Moreover, they treated CO_2 as an indivisible particle during collisions with secondary particles. This greatly reduces the escape rate because the escape energy of a CO_2 molecule is much greater than that of its components. Both of these assumptions decrease escape efficiencies.

We used a general Monte Carlo–type atmospheric sputtering model (*12*) adapted for Mars. The initial conditions were chosen to match those of Luhmann and colleagues (*7, 8*). Apart from the polyatomic dissociation (*13*), our model uses elastic collisions with anisotropic scattering functions (*14*). Many of the cross sections used in the calculation are the hard-sphere geometric cross sections, but, where they exist, more realistic energy-dependent cross sections were used (*15*).

For modern Mars, an atmosphere from Nair *et al.* (*16*) ranging from 50 up to 240 km was extrapolated hydrostatically up to 450 km. The model includes the seven most common species on Mars at these altitudes (CO_2, CO, O, H_2, N_2, N, and H). The ancient atmospheres of 3.5 Gyr and 2.5 Gyr ago were taken from Luhmann *et al.* (*7*). They modeled only the two major species (O and CO_2) between 150 and 300 km. Both atmospheres were extrapolated to cover the range from 125 up to 450 km.

Our basic model was compared to the results in Luhmann and Kozyra (*8*) for both Venus and Mars. When the model was modified to reflect the assumptions of their two-stream model (where the particles are treated as an upward and a downward flux), the results agreed to within 30% (see Table 1). This is a reasonable difference, given the coarseness and uncertainties of both models. The analytical models of Johnson (*11, 17*) also have similar accuracies and match our model results to within 20%. Using these comparisons and considering the number of poorly constrained parameters, we believe that the calculated efficiencies of the models are probably accurate to within 50% (*18*).

Although the efficiencies are accurate to within 50%, the total escape fluxes are much less accurate. The flux of impacting ions is an important parameter in calculating the escape fluxes and integrated losses. There is a factor of 10 uncertainty in the modeling of the impacting flux, which affects the calculated escape fluxes and integrated losses and causes these values to also be uncertain to within a factor of 10. But because we used the impacting fluxes from Luhmann *et al.* (*7*), this is effectively a systematic error when we compare our results to theirs.

We used our model to calculate the escape efficiency for C and O at each epoch (Table 1). The total efficiency (the number of atoms, regardless of species) does not vary much because it is controlled primarily by the escape energy, which depends only on gravity. Although the total number of atoms is fairly constant, the relative fraction of each species is controlled by the composition of the atmosphere around the exobase (the altitude at which the integrated density above is one mean free path length). The precipitating O^+ generally has its first collision near the exobase (because of the definition of the exobase). The exponential increase in density of the atmosphere results in a rapid decrease in the collisional path length below this point and causes most of the subsequent collisions to occur within a

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relatively narrow altitude band around the exobase. Thus, the relative abundance of the atmospheric constituents in this area affects the relative escape efficiencies.

Because the relative abundance of CO_2 at the exobase increases with time (*19*), it is expected that the C:O escape efficiency ratio will increase. A C:O ratio of ~1:2 is due to the fact that CO_2 is the dominant species. The deviation is due to the presence of other species in the atmosphere, especially O and CO. Also, because it is lighter, C is preferentially lost from the CO_2. The slight excess of C (compared to the 1:2 ratio expected from CO_2) escaping at present is more than balanced by the O fluxes that are due to other escape mechanisms.

The results indicate that the effects neglected by Luhmann *et al.* (*7*) in their analytical model are important on Mars. Treating CO_2 as a polyatomic molecule that dissociates in collisions with the intial ion increases the efficiency, but this is a minor effect because these collisions account for only ~10% of the escape efficiency. The major increase in efficiency comes from secondary collisions that dissociate CO_2 and occurs for three reasons. First, the cross section of C is about one-third that of CO_2, and thus the mean free path for C is longer than for CO_2 and C can escape from deeper collisions. Second, energy is more efficiently transferred between particles with similar masses. The mass of the incident particles is closer to the mass of the individual atoms than to that of the molecules, and thus the target particle will tend to receive more energy overall. The final increase in efficiency arises from the fact that, in a collision where CO_2 does not dissociate, the energy transferred to the CO_2 is distributed equally among all three atoms. If the CO_2 dissociates, the energy does not have to be equally distributed, and thus one atom can receive sufficient energy to escape from a collision that would not transfer sufficient energy to the entire molecule. The last two effects are somewhat counterbalanced by the loss of the CO_2 binding energy in the inelastic collisions, but the three effects combined do result in an order-of-magnitude increase in escape efficiency.

We multiplied the model efficiencies for each epoch by the precipitating O^+ fluxes calculated by Luhmann and colleagues (*7*, *8*) to obtain the actual escaping fluxes (Table 2). As can be seen from Fig. 1, all fluxes have decreased with time. This is especially true for the sputtered species—even for CO_2, whose efficiency increases with time. The closer it is to the present, the weaker are the EUV and solar wind and thus the smaller is the precipitating flux. The large decrease in precipitation overwhelms any small increases in efficiency.

In order to calculate the total fluxes, we assumed that each C atom comes from a CO_2 molecule whose O atoms escape separately. The escaping O that cannot be part of a CO_2 molecule (constrained by the C flux) is reported as the H_2O flux. It contains not only the O lost through sputtering but also the O lost by the other major mechanisms such as dissociative recombination. Photochemistry of the martian atmosphere indicates that this O effectively

Table 1. Sputtering efficiency per incident O^+ calculated by the model for three epochs. The values for the current work are the complete model with dissociation and full accounting of all secondary particles. The simplified model is a modification of the full model that implements the assumptions of Luhmann and Kozyra and the 1 EUV epoch should be compared to their calculated efficiency of 0.87. These are also the assumptions that Johnson (*17*) used when he calculated an efficiency of 0.57 for the present (1 EUV) (*8*). The assumptions of the simplified model ensure that no C will be sputtered. All of the efficiencies are in atoms per impacting 1-keV O^+. All ages are since the formation of the solar system.

Model	Epoch		
	6 EUV (1 Gyr)	3 EUV (2 Gyr)	1 EUV (4.5 Gyr)
Current work			
O	16.8	15.4	13.5
C	4.13	5.50	7.00
Simplified model			
O	1.70	1.25	0.65
C	0.00	0.00	0.00

Table 2. Net escape fluxes from Mars for three epochs. Each flux (in particles per second) is integrated over the disk of Mars and over the range of energies for the initial particles (*10*). The first line, sputtered O, is the loss of O from Mars due to sputtering calculated in the current work. The next two lines, exospheric O and pickup O^+, are the two other major O loss processes. These values are taken from Luhmann *et al.* (*7*). The sputtered CO_2 flux is the integrated value calculated in the current model. Because the model assumes that each C lost comes from a CO_2 molecule (assuming that the O escapes on its own), this is just the carbon flux from Table 1. The escaped H_2O flux is the flux of water from the other two listed O escape mechanisms as well as sputtering. Here also it is assumed that the necessary H atoms escape for each O. The O escaping as part of the CO_2 is not counted for the water. All ages are since the formation of the solar system.

Parameter	Epoch		
	6 EUV (1 Gyr)	3 EUV (2 Gyr)	1 EUV (4.5 Gyr)
Sputtered O	3.1×10^{28}	1.8×10^{27}	4.7×10^{24}
Exospheric O	1×10^{27}	5×10^{26}	8×10^{24}
Pickup O^+	3×10^{27}	4×10^{26}	6×10^{24}
Sputtered CO_2	7.8×10^{27}	6.4×10^{26}	2.4×10^{24}
Escaped H_2O	1.9×10^{23}	1.4×10^{27}	8.6×10^{25}

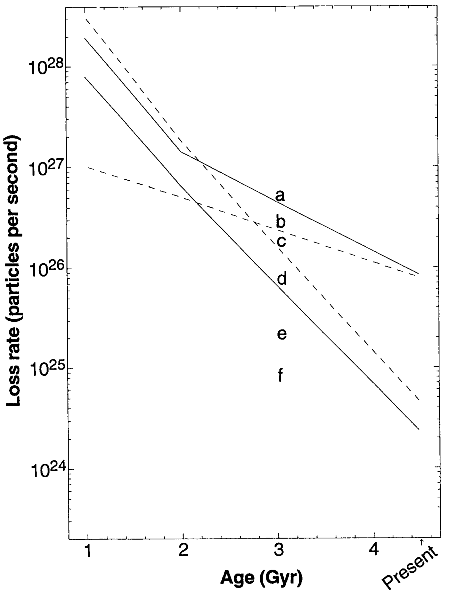

Fig. 1. The sputtering loss rates over the history of the martian atmosphere. The loss rates have been integrated over the planet and (for sputtering) over all incident energies. The actual fluxes were calculated only at 1 Gyr, 2 Gyr, and 4.5 Gyr ago (present). The actual values are listed in Table 2. The sputtered flux for CO_2 (curve d) is based on the escape rate of C and assumes that sufficient O will escape to compensate. The total H_2O (curve a) represents all the rest of the O because the H is easily lost (*16*). The O comes primarily from sputtering (curve c) and exospheric loss (curve b). The exospheric O is from O_2^+ dissociative recombination. For comparison to the sputtered fluxes calculated in the current work (curves c and d for the O and CO_2, respectively) curves e and f, the sputtered fluxes for O and CO_2 from Luhmann *et al.* (*7*), are also included. Age is since the formation of the solar system.

comes from H_2O (*16*).

When these planetary loss rates are integrated over the past 3.5 Gyr, the total CO_2 and H_2O lost since the current atmosphere formed can be calculated: 1.6×10^{44} molecules of CO_2 and 4×10^{44} molecules of H_2O. The sputtered CO_2 represents ~3 bars, and the H_2O is equivalent to ~80 m of water (*20*).

The integrated fluxes are important for our understanding of the history of the martian atmosphere and surface. Certain features, notably channels, seen on Mars have been interpreted as erosional features caused by liquid water on or near the surface. There has been a lot of modeling of possible early atmospheres and surface conditions on Mars in order to consider how these features could have formed. There are two important parameters: mean surface temperature and volume of water. The problem is that the models indicate that at least 50 m of water (*21*) and 0.5 bar of CO_2 (*3*) are needed to create the features. Although CO_2 cannot itself raise the surface temperature to 273 K (*1*), sufficient heating could be achieved with as little as 0.5 bar of CO_2 [for ice-covered lakes (*3*)], and ~1 bar meets the requirements of most models. Until now, the problem has been determining where this water and CO_2 went. With our current modeling results, this is no longer a problem: All of the water and CO_2 could have been lost to space by sputtering (and other escape mechanisms) over the age of the planet.

Because most of the major sputtering occurred early in the history of Mars, it is difficult to test the model results. Actual measurements of the modern escape fluxes of heavier species from Mars would help to constrain at least the value for the present epoch and verify the validity of the sputtering model itself. This is especially the case for C, because sputtering appears to be its dominant escape mechanism (for O, the other escape mechanisms will overwhelm the contribution from sputtering). Atmospheric stable isotope data may also help to constrain the total amount of each species lost from the atmospheric reservoir, but there appear to be large uncertainties in the interpretation of the data (*22*). The best method of constraining the model of the early atmosphere is probably to make in situ geochemical and geological measurements on Mars.

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9. Sputtering fluxes are affected by three main parameters: the atmosphere, the solar wind, and the EUV solar emission. All three parameters have changed over the history of the solar system. The earlier atmosphere was much denser, but the major effect on sputtering is the result of the changing ratio of CO_2 to O at the exobase (*19*). The early solar wind was much stronger (both the velocity and the interplanetary magnetic field) and thus increased the amount of energy an ion gained before impacting. Although the young sun is thought to have been faint in the visible spectrum, it was much more active in the EUV. The enhanced EUV would create more ions and thus enhance the impacting flux. At 2.5 Gyr ago, the EUV flux was three times the current value, and at 3.5 Gyr ago it was six times the current value (this is for the entire EUV; the amount of ionizing radiation may have been as much as 100 times that of the current flux). Thus, the terms 6 EUV, 3 EUV, and 1 EUV are used to designate the three epochs. The solar EUV model is originally from K. J. Zahnle and J. C. G. Walker, *Rev. Geophys.* **20**, 280 (1982).
10. The impact flux was calculated by Luhmann and colleagues (*7, 8*), who used a gas-dynamic solar wind interaction model and the upstream parameters for the sun at the appropriate age to calculate the magnetic and electric fields around Mars. Then test particles were launched from a grid over the planet, and the trajectory of each one was calculated by numerical integration. If the particle impacted the planet, it was counted and weighted by the ion density of its source region. These values were then summed to give effective impacting fluxes of 4.8×10^5 (1 EUV), 1.6×10^8 (3 EUV), and 2.6×10^9 (6 EUV) particles per second per square centimeter, normalized to 1-keV particles.
11. R. E. Johnson, *Energetic Charged-Particle Interactions with Atmospheres and Surfaces* (Springer-Verlag, New York, 1990). The model calculates the number densities at the exobase and then treats the exobase as a solid surface, and the analytical sputtering formulas for solid surfaces are applied after being modified for the given situation. For the incident particle, the atmosphere is treated as having only atomic constituents (based on the number densities of the actual species). For all other collisions, all species are treated as indivisible.
12. In the Monte Carlo model, the effects of individual impacting particles are calculated. These are then averaged over a large number of impactors (5000 in most cases) to determine the average effect. For a particle, the code determines randomly (using an exponential functional form) where the next collision happens. It uses the cross sections to determine randomly what the particle collides with. The result of the collision is then determined, with the scattering angle randomly determined with the appropriate functional form. In calculation of the collision, the target particle is assumed to be stationary. This is reasonable because the mean thermal energy is ~1% of the escape energy for the species of interest. Each particle resulting from the collision is tracked. Particles continue to collide until they thermalize, escape, or go ballistic. Ballistic particles are particles that leave the atmosphere with insufficient energy to escape. They are ignored when they reimpact because they have so little energy. Once all the products of one incident particle have been tracked, the next one is calculated. We tested the model implementation by setting the parameters to create simple cases that could be analyzed analytically and by comparison to simpler models. The numerical error in a Monte Carlo model is generally proportional to $1/\sqrt{N}$ (where N is the number of trials), and testing with 50,000 particles indicates that, given the other uncertainties, 5000 particles are sufficient.
13. Because of the high energy of the impacting particles (initially ~1 keV), whenever a polyatomic particle is involved in a collision, it will dissociate completely (and thus "absorb" the binding energy). For later collisions with less energy, dissociation occurs only if the energy of the incident particle is sufficient to dissociate the target in the center of mass frame of reference.
14. Because of the lack of data on the scattering function, we modeled most of these functions using a Henyey-Greenstein function with a g (parameter) value of 0.5 for neutral collisions and a $g = 0.9$ for ions (reflecting the tendency to only charge exchange in the ion collisions). For a couple of cases for which there are some data, double Henyey-Greenstein functions were used. The model is fairly insensitive to the actual shape of the functions over a range of reasonable g values.
15. The O–O, O–N_2, and N_2–N_2 cross sections are from M. Ishimoto, M. R. Torr, P. G. Richards, and D. G. Torr [*J. Geophys. Res.* **91**, 5793 (1986)]. The O–H cross section at low energies [from R. R. Hodges Jr., *J. Geophys. Res.* **98**, 10833 (1993)] was extrapolated out to 1 keV. The remainder of the neutral-neutral cross sections are the hard-sphere geometric ones. For the ion-neutral collisions O–O^+ and O–H^+, cross sections are from R. F. Stebbings, A. C. H. Smith, and H. Ehrhardt [*J. Geophys. Res.* **69**, 2349 (1964)]. The cross section for H–H^+ came from an extrapolation of the literature survey of P. H. Smith and N. K. Bewtra [*Space Sci. Rev.* **22**, 301 (1978)]. We obtained the remainder of the cross sections by doubling the corresponding neutral cross section to account for the coulomb force. The ion-neutral cross sections are not important because they are used in less than 0.1% of the collisions.
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18. This is the error for the Monte Carlo model only and ignores any uncertainty in the calculation of the precipitating O^+ flux (which is estimated to have an uncertainty of a factor of 10, most of it due to uncertainties in the state of the young sun). There are three main sources of uncertainty in the model. The first one has to do with the cross sections and scattering functions. Very few of these have been measured or calculated quantum mechanically. Although the model is fairly insensitive to the individual values, there are so many that are poorly constrained that the overall effect is considerable. The second source of error is the atmosphere models. This is especially the case for the ancient atmospheres. The third major uncertainty is in normalizing the impacting flux. There is also some uncertainty introduced by the numerical modeling, but it is minor compared to the other three sources.
19. The relative CO_2 abundance increases because the exobase approaches the homopause (top of the well-mixed atmosphere) as the age increases. As it comes closer, diffusive separation is less effective at decreasing the relative CO_2 abundance. The exobase drops because the upper atmospheric temperature decreases, and thus the total atmospheric density decreases faster in the 3-EUV atmosphere and especially in the 1-EUV atmosphere.
20. These integrated fluxes ignore the possibility that Mars may have had a significant intrinsic magnetic field during its early history. During such periods, no sputtering would occur because there would be no flux of impacting ions.
21. V. R. Baker, M. H. Carr, V. C. Gulick, C. R. Williams, M. S. Marley, in *Mars*, H. H. Kieffer, B. M. Jakosky, C. W. Snyder, M. S. Matthews, Eds. (Univ. of Arizona Press, Tuscon, 1992), chap. 15.
22. Jakosky indicated (*4*) that, for loss from the exobase, there would need to be an equal amount of atmosphere buried in the planet. Preliminary calculations for ^{13}C indicate that between 0.5 and 5 bars of CO_2 need to be buried to match the $\delta^{13}C$ atmospheric measurements.

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