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Upper limits to the outflow of ions at Mars: Implications for atmospheric evolution

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Abstract. Escape of ions is potentially important for the evolution of volatiles on Mars, but the mechanisms and rates of ion escape processes are not fully understood. Instruments on the Russian Phobos 2 orbiter have, however, measured fluxes of heavy ions apparently of ionospheric origin in the optical shadow of Mars. These ions are assumed to arise from escape processes induced by the interaction of the solar wind with the ionosphere. We determine here upper limits to the ion loss rates by imposing upward flux boundary conditions on models of the low and high solar activity Mars ionosphere. The maximum fluxes obtained for high solar activity are about a factor of 4 larger than the fluxes derived from the Phobos ASPERA measurements, and the major ion is predicted to be O_2^+ rather than O^+ . If ions are scavenged at or near their maximum rates, the resulting escape fluxes are significant when compared to other non-thermal escape mechanisms for heavy atoms.

Introduction

Non-thermal mechanisms by which heavy species, such as C, N, and O, may escape from the atmosphere of Mars have been identified, but not completely quantified, and the escape processes for O are probably the most uncertain. Although interactions with the crust may play a role, a quantitative understanding of the processes by which O is irreversibly lost to space is crucial to reconstructing the time-dependent Martian inventories of H_2O and CO_2 .

McElroy et al. [1977] suggested that dissociative recombination of O_2^+ was the major escape mechanism for O, producing escape fluxes of about $6 \times 10^7 \text{ cm}^{-2} \text{ s}^{-1}$. (Here and in the texts that follows, all fluxes quoted are referred to the surface.) This value is about half the more easily evaluated thermal H escape rate [e.g., *Anderson*, 1974], and *McElroy et al.* [1977] proposed that H and O are constrained on time scales of the order of 10^5 years to escape in the stoichiometric ratio of H_2O , thus preserving the oxidation state of the atmosphere. It now appears that the present O escape flux due to dissociative recombination, which is in the range $(3-6) \times 10^6 \text{ cm}^{-2} \text{ s}^{-1}$, [*Lammer and Bauer*, 1991; *Fox*, 1993a; *Zhang et al.*, 1993], is more than an order of magnitude smaller than the H escape flux. O escape due to sputtering by O^+ pick-up ions is another important loss process, with estimated O loss rates ranging from $4 \times 10^5 \text{ cm}^{-2} \text{ s}^{-1}$ [*Zhang et al.*, 1993], to $3 \times 10^6 \text{ cm}^{-2} \text{ s}^{-1}$ [*Kass and Yung*, 1996].

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Processes that lead to direct escape of ions have received less attention, partly because initial estimates for the loss rates were low, and partly because the mechanisms for loss of ions are not well understood [e.g., *Michel*, 1971; *McElroy et al.*, 1977; *Cloutier and Daniell*, 1979]. Recently, however, instruments on the Russian Phobos 2 orbiter detected significant fluxes of tailward-streaming heavy ions in the optical shadow of Mars that were attributed to escaping O^+ and O_2^+ of ionospheric origin. The ASPERA (automatic space plasma experiment with a rotating analyzer) measured the composition, energy and angular distribution of ions with energies in the 0.5–24 keV range [e.g., *Lundin et al.*, 1989]. Most of the ions were identified as O^+ , but at times heavier ions, such as O_2^+ , were found to dominate. The total escape rate of O ions was estimated as $3 \times 10^{25} \text{ s}^{-1}$, which corresponds to a global average escape flux of $2.1 \times 10^7 \text{ cm}^{-2} \text{ s}^{-1}$. The Phobos toroidal analyzer spectrometer (TAUS) detected fluxes of a single heavy ion that was assumed to be O^+ in the central region of the plasma sheet, with a global average flux of $3.5 \times 10^6 \text{ cm}^{-2} \text{ s}^{-1}$ [e.g., *Verigin et al.*, 1991].

These large escape fluxes have been attributed to the direct interaction of the solar wind with the ionosphere of Mars, in which ions above the ionopause are “picked up” by the convection electric field of the flowing solar wind plasma [e.g., *Luhmann*, 1990]. Ions in the topside of the ionosphere may also be convected horizontally toward the tail due to electrodynamic processes induced by the solar wind [e.g., *Cloutier and Daniell*, 1979]. Such interactions are characteristic of bodies without an intrinsic magnetic field. *Luhmann et al.* [1995] suggested that the heavy ions observed by instruments on the Pioneer Venus spacecraft in the tail rays of Venus were pickup ions resulting from the penetration of the solar wind convection electric field into the terminator ionosphere.

The discovery of these escaping ions was not totally unexpected. Early attempts to reproduce the ion density profiles measured by the retarding potential analyzer on Viking [*Hanson et al.*, 1977] as photochemical or diffusive equilibrium profiles predicted topside densities that were too large and that had to be reduced by assuming some physical or chemical loss process. For example, in their photochemical equilibrium (PCE) model, *Fox and Dalgarno*, [1979] found it necessary to increase the loss rate of O_2^+ by assuming that the Martian electron temperatures (T_e) were unrealistically small [*Chen et al.*, 1978; *Rohrbaugh et al.*, 1979; *Hanson and Mantas*, 1988]. *Chen et al.* [1978] found that the measured O_2^+ density profile could be reproduced only if an upward velocity of about $1 \times 10^5 \text{ cm s}^{-1}$, corresponding to an upward flux of $5 \times 10^7 \text{ O}_2^+ \text{ cm}^{-2} \text{ s}^{-1}$, were imposed at the top boundary. More recently, *Shinagawa and Cravens* [1989] suggested that the loss of ions was due to the divergence of the horizontal ion fluxes, by analogy to Venus. In the Venus ionosphere, sig-

nificant day-to-night fluxes of ions have been observed, most of which converge and flow downward on the nightside, forming a nightside ionosphere. A fraction of these antisunward flowing ions apparently escape from the gravitational field of the planet as well [e.g., *Knudsen, 1992*].

Using a 1-D model that included photochemistry and transport, *Fox [1993]* reproduced the Viking O_2^+ profile with an upward flux at the top boundary that was approximately equal to the maximum flux that could be imposed, about $4.75 \times 10^7 \text{ cm}^{-2} \text{ s}^{-1}$, equivalent to a global average flux of $2.4 \times 10^7 \text{ cm}^{-2} \text{ s}^{-1}$, in good agreement with the value determined by *Chen et al. [1978]*.

Recently, *Kar et al. [1996]* constructed a simple model of the Mars ionosphere, and identified the upper boundary of the PCE region for O_2^+ as 160 km. By comparing their model to the Viking measurements, they derived a total loss rate for O_2^+ of $(3 - 4) \times 10^{26} \text{ s}^{-1}$, or global average fluxes of $(2.0 - 2.8) \times 10^8 \text{ cm}^{-2} \text{ s}^{-1}$. These values are much larger than those derived by *Chen et al. [1978]* or by *Fox [1993]*. Furthermore, they are larger than one estimate of the maximum capacity of the solar wind, $1.4 \times 10^8 \text{ O}_2^+ \text{ cm}^{-2} \text{ s}^{-1}$ [*Lundin et al., 1991*]. *Kar et al.* did not address the order of magnitude difference between their computed escape fluxes and those determined by *Chen et al. [1978]* and *Fox [1993]*.

We revisit this question here by using numerical models of the Martian ionosphere to determine upper limits to the escape fluxes for each of 11 ions due to the limits on ionospheric production. We find that ion loss should be dominated by O_2^+ rather than by O^+ . We also show that, if ions are being swept away at near their maximum rates, the loss rates inferred are of the same order as or larger than many other non-thermal mechanisms, and should be accounted for in models of the history of Martian volatiles.

Calculations

We have constructed models of the dayside ionosphere from 100 to 400 km for low solar activity [*Fox, 1993*] and for high solar activity [*Fox et al., 1995*]. The high solar activity model is more realistic than that of *Fox [1993]*, where the low solar activity neutral thermosphere was merely subjected to the high solar activity solar fluxes. In addition, *Fox [1993]* computed the upward fluxes for only five ions, compared to 11 here. Production rate profiles of some of the ions are shown in Figures 1a and 1b, and the resulting steady-state density profiles in Figures 2a and 2b.

A crude way to estimate the maximum upward flux of an ion is to integrate its production rate above the PCE region. The upper boundary for PCE is located where the chemical lifetime of an ion, $\tau_c = n/L$, where L is the total chemical loss rate of the ion and n is its number density, is equal to the diffusion time. The diffusion time is usually estimated as $\tau_D = H^2/D$, where H is the scale height of the neutral atmosphere and D is the ion diffusion coefficient. For O_2^+ at low solar activity, this boundary is at about 188 km, and is lower than those of $O^+(^4S)$ and $O^+(^2D)$, which are at about 219 and 226 km, respectively. At high solar activity, the PCE boundaries are near 214 km for O_2^+ , and 229 and 235 km for $O^+(^4S)$ and $O^+(^2D)$, respectively.

O_2^+ is produced in the ionosphere of Mars mostly in reactions of CO_2^+ with O and O^+ with CO_2 . The total integrated production rate of O^+ and CO_2^+ is $(6.0 - 17.4) \times 10^7 \text{ cm}^{-2} \text{ s}^{-1}$, where the smaller value of the range given here and in the

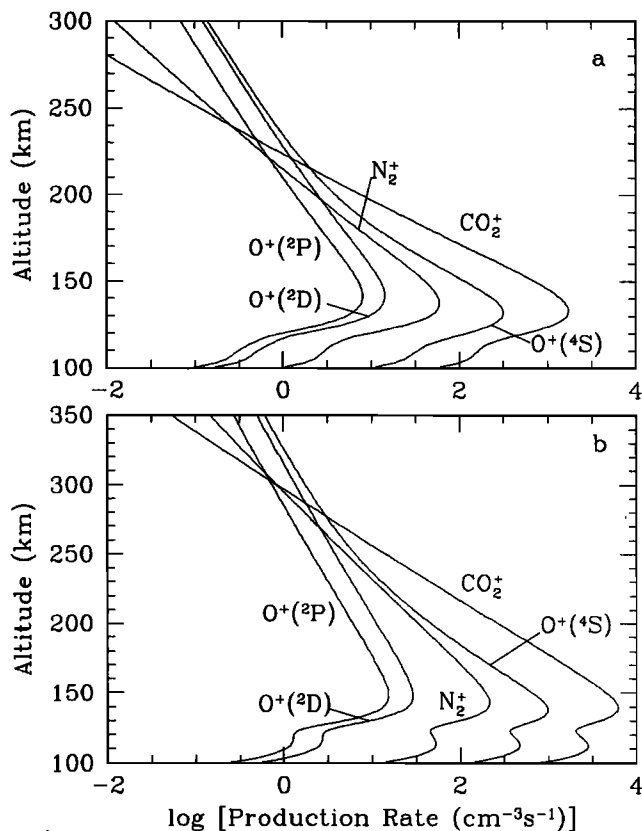


Figure 1. Production rates of the most important ions at (a) low solar activity, (b) high solar activity

text that follows is for low solar activity and the larger value is for high solar activity. For $O^+(^4S)$ and $O^+(^2D)$, the integrated production rates above their PCE boundaries are $(5.3 - 29) \times 10^6 \text{ cm}^{-2} \text{ s}^{-1}$ and $(3.6 - 17) \times 10^6 \text{ cm}^{-2} \text{ s}^{-1}$, respectively.

A better method to determine the maximum escape fluxes for a steady-state model is to impose a small upward velocity boundary condition at the top of the model, and increase the velocity until a solution can no longer be obtained. As the flux approaches the limiting value, the density at the top decreases and the resulting upward flux levels off. Eventually a point is reached where convergence cannot be obtained for even very small (0.5%) increases in the velocity. Although there are certainly other effects, including numerical problems, that can affect the convergence of the density profiles, it is clear that in a steady-state model, a solution cannot be achieved if the loss rates at the top exceed that which can be supported by the net production rate of ions. The limiting dayside fluxes obtained for all the ions are given in Table 1. The limiting upward fluxes of O^+ ions are about $(6.7 - 18) \times 10^6 \text{ cm}^{-2} \text{ s}^{-1}$. The density profiles for the maximum flux boundary conditions are shown in Figures 2a and 2b. A comparison of the low solar activity densities with the Viking measured values shows good agreement.

The maximum upward flux for O_2^+ is a factor of about 7 larger than that of O^+ : about $(4.7 - 13.5) \times 10^7 \text{ cm}^{-2} \text{ s}^{-1}$. The upper limit to the total dayside escape flux for all ions is $(6.1 - 19.7) \times 10^7 \text{ cm}^{-2} \text{ s}^{-1}$, which corresponds to total ion escape rates of $(4.4 - 14.2) \times 10^{25} \text{ s}^{-1}$. The total ion escape fluxes derived from the ASPERA data at high solar activity

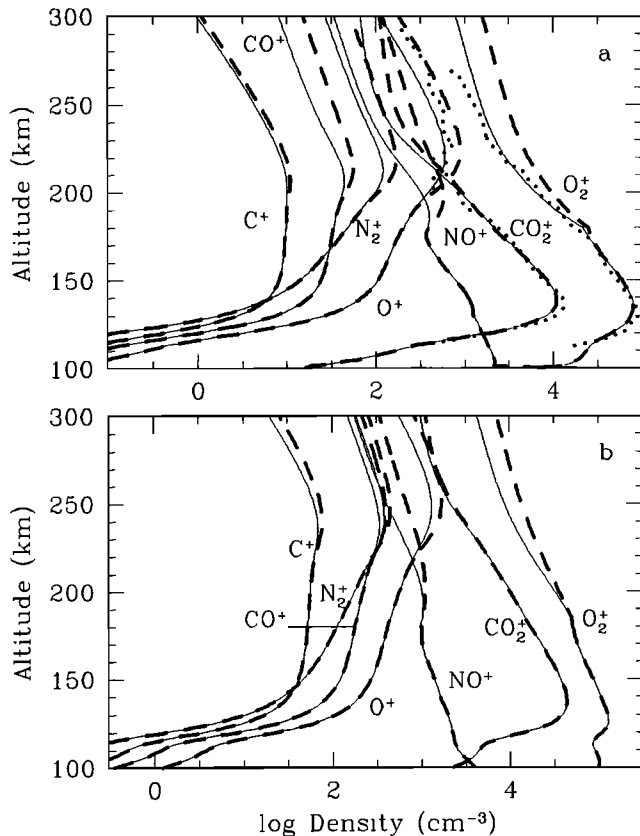


Figure 2. Computed density profiles of the most important ions for no-flux (dashed curves) and maximum upward flux (solid curves) boundary conditions. (a) Low solar activity. The dotted curves are the Viking measured values [Hanson *et al.*, 1977]. (b) High solar activity.

Table 1. Maximum Upward Fluxes of Ions on the Day-side for Low and High Solar Activities

Ion	Flux $10^6 \text{ cm}^{-2} \text{ s}^{-1}$	
	Low SA ^a	High SA ^a
O ₂ ⁺	47	135
CO ₂ ⁺	3.7	27
NO ⁺	2.0	5.3
N ₂ ⁺	1.6	5.5
CO ⁺	0.47	4.5
O ⁺ (⁴ S)	4.5	13.1
O ⁺ (² D)	2.2	4.8
O ⁺ (² P)	.0096	0.035
C ⁺	0.059	0.63
N ⁺	0.25	0.85
Ar ⁺	0.078	0.026

Global average fluxes are approximately half the values shown.

^aSolar Activity

are smaller than our values, but only by a factor of about 4. This difference may arise from uncertainties in the numbers themselves, or from a number of other sources. First, our computed flux is an upper limit, and we have no evidence

that the loss rates at high solar activity are comparable to the upper limit. By contrast, the agreement between the solar minimum (Viking) measured O₂⁺ densities and those of the maximum upward flux model suggests that the ions are being lost at near their maximum rate. Even at low solar activity, however, the “loss” may not represent removal from the gravitational field of the planet. On Venus, most of the nightward ion flow converges and flows downward on the nightside, and thus does not lead to escape [cf. Knudsen, 1992]. This may be true also for Mars.

Discussion and Conclusions

The loss rate of ions due to solar wind pickup has been estimated as the integrated photoionization rate above the ionopause [Michel, 1971; McElroy *et al.*, 1977]. Luhmann *et al.* [1992] added charge exchange with solar wind protons and electron-impact ionization as sources of O⁺ ions in the pickup region, and estimated the integrated loss rate as $5 \times 10^6 \text{ cm}^{-2} \text{ s}^{-1}$. Nightward convection of ions near the ionopause induced by electrodynamic interactions with the solar wind may also occur. In any case, if the ionopause is above the PCE region, as the ions are swept away, an upward flow will be set up to replace the ions that are removed, and the maximum loss rate may be larger.

The O₂⁺ escape rate derived by Kar *et al.* [1996], $4 \times 10^{26} \text{ s}^{-1}$ ($2.7 \times 10^6 \text{ cm}^{-2} \text{ s}^{-1}$) for Viking conditions is an order of magnitude larger than ours. A number of differences in defining the diffusion time are apparent, which affect only the estimate of the production rate above the PCE boundary slightly. The largest difference is that Kar *et al.* [1996] adopted the T_e profile of Chen *et al.* [1978], which is significantly higher in the 160–200 km region than that of Rohrbaugh *et al.* [1979], which we used. It should be noted, however, that the O₂⁺ flux that Chen *et al.* inferred is in good agreement with ours.

Our model also predicts that O₂⁺ should be the major escaping ion, whereas Lundin *et al.* [1989] have identified the major ion as O⁺. We have neglected charge exchange of neutral O with solar wind protons, and solar wind electron-impact [Luhmann *et al.*, 1992], and both effects will increase the O⁺ escape flux slightly. Solar-wind-induced convection will cause the lighter ions to escape preferentially [R. Hartle, private communication, 1997]. It might be argued that this composition difference in the escape flux is evidence that ions are not escaping at the maximum rates.

The maximum escape rates due to the solar wind interaction are significant from an evolutionary perspective. The maximum global average escape flux of O in all ions is about $(5.5 - 18) \times 10^7 \text{ cm}^{-2} \text{ s}^{-1}$. Thus solar-wind-induced escape could bring the total escape flux of O up to half the H escape flux (or more!), if the ions are lost at close to their maximum rates.

Clearly, loss of ions in the direct interaction of the solar wind with the ionosphere has the potential to dominate the loss of volatiles from Mars at present and in the past. Important measurements that could be made to determine the ion loss rate include in situ measurements of the day-to-night ion fluxes in the terminator region, and of the dayside and nightside ion densities. These data should indicate what fraction of the ions leaving the dayside converge and flow downward on the nightside, and thus do not escape. Further measurements of ion fluxes accelerated down the tail of the planet

would also be of value. In addition, it is hoped that more detailed theoretical studies of the solar-wind-induced escape processes will be undertaken to further constrain these loss rates.

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