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EVOLUTIONARY IMPACT OF SPUTTERING OF THE MARTIAN ATMOSPHERE BY O^+ PICKUP IONS

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Abstract. Nonthermal processes such as dissociative recombination of ionospheric molecules are known to lead to loss of atmospheric constituents (N, O, C) at Mars where the gravitational potential is easily overcome by the energy imparted to the product atoms. Moreover, observations of escaping planetary ions on the PHOBOS-2 spacecraft showed that the solar wind is presently scavenging significant amounts of both oxygen and molecular species as it flows past the planet. Because both the sun and the atmosphere of Mars have changed over time, the evolutionary importance of these processes cannot be estimated by simply multiplying the contemporary loss rates by the solar system age. Models of these loss mechanisms must include consideration of the evolution of the solar EUV intensity and solar wind and their effects. Here we describe calculations of solar wind-induced loss rates for evolving solar and atmospheric conditions like those described by Zhang et al. [1992a], but including sputtering of the Martian atmosphere by reentering O^+ pickup ions. The inclusion of the sputter loss increases by about 30% the cumulative, estimated loss of oxygen to that in ~ 50 m of water (global surface depth) over the last ~ 3.5 billion years, when contemporary loss mechanisms are thought to have become dominant. More significant is the result that these ions also sputter CO_2 and its fragments in substantial amounts. That integrated loss is equivalent to ~ 0.14 bar atmospheric CO_2 pressure, of the order of some estimates of Mars' early atmospheric inventory.

Introduction

Mars is thought to have had both substantial amounts of surface water and a much thicker atmosphere ~ 3.5 billion years ago [e.g., see McKay and Stoker, 1989 and references therein]. Estimations of the planet's "inventory" at this time place the pressure of the early atmosphere at ~ 0.1 bar or more (compared to the present ~ 7 mb) and include a planet-wide equivalent "ocean" of liquid water of a few meters to a km depth. The evolution of the now thin atmosphere is thought to have proceeded by some combination of escape to space and surface adsorption. The amounts of water ice and carbonate that remain on Mars will be determined to some extent by Mars Observer [e.g., see Feldman and Jakosky, 1991], but the amount that has escaped to space in the past must be determined by modeling the escape processes over time. This requires that one take into account all significant escape processes adjusted for the evolving sun and atmosphere.

Several important atmospheric constituents at Mars, namely N, O, and C, are known to undergo nonthermal escape to space due to dissociative recombination of N_2^+, O_2^+ and CO^+, respectively, in the ionosphere [McElroy, 1974; McElroy et al., 1977; Fox and Dalgarno, 1983]. This photochemical process can impart sufficient energy to the product atoms that they escape the planet's gravitational field (the required escape velocity at Mars is ~ 5 km/s or ~ 0.125 eV/amu). The resulting neutral escape fluxes can be calculated from models that require knowledge of the atmospheric density and composition, and of the ionizing EUV flux of the sun.

Atomic oxygen is the major heavy constituent of the Martian exosphere according to current models [e.g. Nagy and Cravens, 1988; Nagy et al., 1990; Ip, 1990]. This oxygen "corona" is a direct consequence of the dissociative recombination process in Mars' mainly O_2^+ ionosphere [see McElroy et al., 1977]. The resulting "hot" oxygen atoms can be lost if they are moving upward and have energies in excess of ~ 2 eV. In addition, the much greater number of hot atoms that are left behind to populate the exosphere can be ionized by a variety of mechanisms including photoionization by solar EUV, charge exchange with solar wind protons, and impact ionization by solar wind electrons. The oxygen ions produced in the corona can be picked up by the solar wind electric field and removed from Mars [e.g., see Luhmann, 1990], or they can reenter the atmosphere where they can sputter neutrals from the region near the exobase [see Luhmann and Kozyra, 1991]. Note that there is a distinction between sputtering by solar wind protons and helium ions [Watson et al., 1980], which is assumed negligible here, and sputtering by the heavy reentering pickup ions. The pickup ions do not suffer from the same degree of deflection because of their large gyroradii and they are more efficient sputtering agents than protons and helium ions [Johnson, 1990]. These three loss processes are coupled by their relationship to the generation of the hot O corona and their various connections to the solar EUV flux.

Energetic ion observations recently obtained on the PHOBOS-2 spacecraft [e.g. Lundin et al., 1990; Verigin et al., 1991] have inspired quantitative estimates of the net loss of atmospheric constituents by solar wind scavenging. Some of these calculations invoke momentum conservation arguments [e.g. Perez-de-Tejada, 1989; Lundin et al., 1991] which are based on the assumption that the planetary obstacle has a particular cross section to the incident solar wind within which it extracts the incident momentum. One of the difficulties with such approaches is the lack of constraints concerning both the efficiency of the momentum transfer and the size of the region of transfer. Another is the lack of specificity regarding the physics involved, which makes it difficult to evaluate the effects of the process through the history of the solar system. Our current understanding of solar wind interactions with the atmospheres of the weakly magnetized planets [e.g., see the review by Luhmann and Bauer, 1992] allows us to model some of the details of the scavenging process over time. Of course, this presumes that the contemporary loss processes have been dominant since a solar system age of ~ 1 billion years (~ 3.5 byr ago), and implies that the magnetic field of Mars was not a consideration after that time as suggested by the dynamo models of Schubert and Spohn [1990].

Of the aforementioned processes (nonthermal escape of neutrals due to photochemistry, ion pickup by the solar wind, and sputtering of neutrals by reentrant pickup ions) Zhang et al. [1992a] calculated the oxygen loss rates of the first two for three epochs in the history of the solar system corresponding to solar EUV intensities of 6, 3, and 1 times the present value. According to the solar evolution model of Zahnle and Walker [1982], these values represent solar system ages of ~ 1.0, 2.0, and 4.5 billion years, respectively. In this note we present the corresponding results for the sputtering process. We show that oxygen sputtering losses are comparable to those from the other mechanisms. However, the accompanying CO_2 losses,

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which have not been considered previously, are a significant fraction of some estimates of the content of the early Martian atmosphere.

Description of the Model

Zhang et al. [1992a] calculated the expected properties of the thermal upper atmosphere as well as the oxygen exosphere densities for the 1, 3 and 6 EUV epochs. These are reproduced in Figures 1a and 1b to show the "target" gas used in the sputtering calculation. The exobase altitudes are also indicated. These models were calculated under the assumption that the current lower atmosphere properties prevailed during these epochs, whereas the actual lower atmosphere may have been considerably thicker and more water and/or ammonia or methane-rich [e.g., Kasting, 1991]. Nevertheless, the "greenhouse" phase may have been over by ~ 3.5 billion years ago [see McKay and Stoker, 1989], so that this presumption is not regarded as a serious shortcoming in the calculations.

To calculate the escape rates due to the pickup ion sputtering process, it is necessary to have descriptions of not only the atmosphere target gas and the exospheric source of the precipitating pickup ions, but also of the solar wind properties that determine the precipitating pickup ion fluxes and energies, namely solar wind velocity and magnetic field. For this purpose we invoke the model used by Zhang et al. [1992a] to obtain their evolutionary solar wind charge exchange and electron impact-ionization rates. The solar wind velocity and magnetic field history for this model, which is due to Newkirk [1980], is reproduced in Figure 2. We then applied the method of Luhmann and Kozyra [1991] to calculate the precipitating atomic oxygen ion fluxes for the three epochs. Briefly, this method utilizes the "upstream" solar wind parameters at the solar system ages of 1.0, 2.0 and 4.5 billion years (from Figure 2) in a gas-dynamic solar wind interaction model [Spreiter and Stahara, 1980] to determine the magnetic field (B) and electric field (E = -V x B) in the space around Mars. For the purpose of these estimates it is presumed that the solar wind magnetic field is perpendicular to its velocity. Several thousands of test particle O^+ ions are then launched on a grid over the dayside hemisphere and the ion trajectories are numerically integrated (using the standard charged particle equation of motion with the Lorentz force determined from the gas dynamic model) until they either cross the terminator plane or intersect the "ionopause" boundary of the interaction model which is close to the exobase altitude on the dayside. Those ions that cross the dayside inner boundary are weighted by the ion production rate at their launch site, and the resulting flux is binned as a function of the ion's energy at the boundary crossing. In the present case, the flux is also binned as a function of zenith angle (with respect to the vertical). We note that the ion production rates used here include photoionization (6, 3 and 1 times the present values, as appropriate), charge exchange, and impact ionization determined as described in Zhang et al. [1992b]. Finally, the resulting sputtering yields due to this pickup O^+ ion impact are determined from these results.

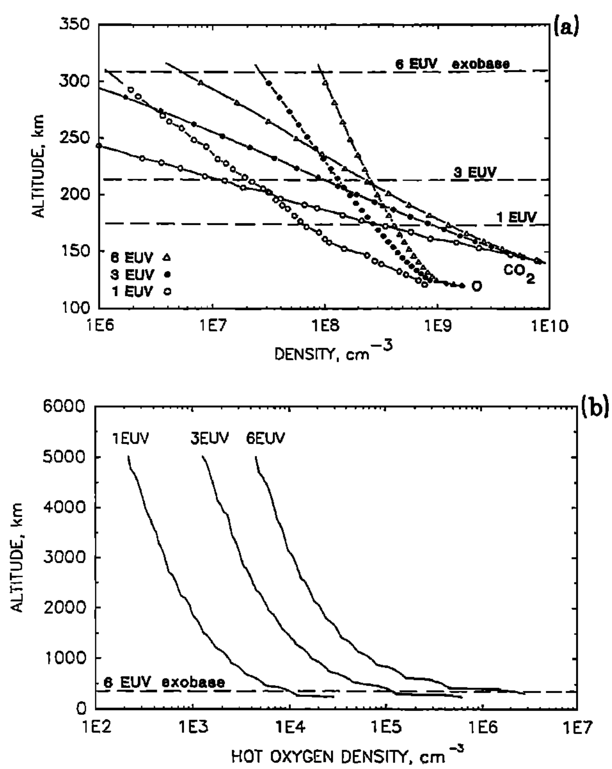

Fig. 1. Model upper atmospheres (a) and exospheres (b) used here for both the "target" gas for sputtering, and as the source of the causative precipitating pickup ion fluxes [from Zhang et al., 1992a]. These were calculated for the present Mars atmosphere exposed to 1, 3, and 6 times the present solar EUV flux, corresponding approximately to solar system ages of 1.0, 2.0 and 4.5 billion years.

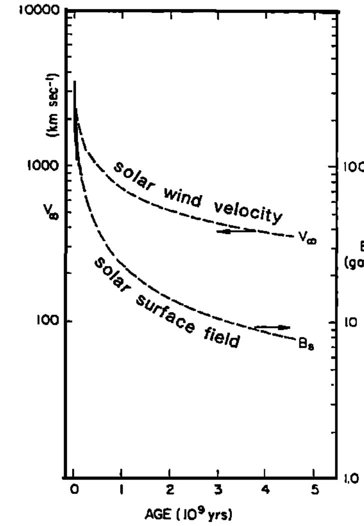

Fig. 2. Model for the evolving solar wind velocity and the solar magnetic field (at the solar source surface) [from Newkirk, 1980]. The magnetic field used here was reduced in magnitude at the distance of Mars by an amount consistent with the radial divergence of the solar wind. The velocity model was also used by Zhang et al. [1992a] to calculate ionization rates.

The sputtering yield, Y_i, is defined as the number of species i ejected per ion incident on an exobase of a gravitationally bound gas. Y_i includes particles ejected directly in a collision with the ion and those ejected due to a cascade of collisions initiated by the ion [Sieveka and Johnson, 1984; McGrath and Johnson, 1987; Johnson, 1990]. Each contribution is calculated as a ratio of the mean-free-path for energizing the particle divided by a mean-free-path for escape [Johnson, 1990, 1992]. This becomes

$$Y_i = c_i \left[\frac{0.5}{\cos\theta} \frac{\sigma(T>U_i)}{\sigma_d} + \frac{3}{\pi^2} \frac{\alpha}{\cos\theta^{1.6}} \frac{S_n}{U_i \sigma_d} \right]$$

where c_i is the concentration of species i. Here θ is the angle relative to normal incidence (π minus the zenith angle), σ is the collision cross section for a particle receiving an energy transfer $T > U_i$, where U_i is the gravitational potential energy at the exobase, and σ_d is the cross section for escape of the struck particle. The constants $(3/\pi^2)$ and α are obtained from the transport equation and S_n is the energy transfer cross section [Johnson, 1990].

Because the incident O^+ (or neutralized O) makes hard energy transfer collisions only with the atomic constituents in CO_2 (i.e. with either C or O) the molecule often dissociates [Sieveka and Johnson, 1984]. Therefore we have shown that it is a good approximation to use atomic quantities [Johnson, 1990, 1992], treating the CO_2 as a sum of a C and 2 O's. Further, the cross sections σ ($T > U_i$) and S_n vary much more slowly with incident ion energy [Johnson, 1990] than does the incident ion flux. Since the angular dependence is also found to be steep, we estimate the escape using the integrated flux and evaluate the effective yield at 1 keV O^+ with the average $\cos\theta \approx 0.577$ [Luhmann and Kozyra, 1991]. Using this, the expression above has been applied recently to calculate the ejection of O from the exobase of Mars [Johnson, 1992] giving $Y_o \approx c_o^*$ (6.3). Here c_o^* is the atomic concentration of atomic O at the exobase. We have also estimated the yield of C, as either C, CO, or CO_2, for an incident 1 keV O^+ at $\cos\theta = 0.577$ to be $Y_o \approx c_{co2}^*$ (0.67). These values are rough lower limits as we have ignored any heating at the exobase, have only included in the single collision contribution the cross section for directly striking C, and have not included O loss from O originating in CO_2. The collision cross sections and energy loss cross sections used were obtained from the so-called universal cross section [Ziegler et al., 1985]. These assumptions allow us to estimate the contribution of sputtering to the loss of material from Mars.

Results

Figure 3 shows the calculated precipitating pickup ion fluxes as a function of both energy and zenith angle for the 6, 3 and 1 times present EUV cases. Application of the sputter yields described above using these distributions, together with the "target" atmospheres shown in Figure 1, gives the escape fluxes in Table 1. These include both O and CO_2 since they are the major constituents of the target gas at the exobase. The nonthermal loss rates and O^+ pickup results of Zhang et al. [1992b] are also given for comparison. Using the Zahnle and Walker [1982] solar evolution model, we can convert these to the time series in Figure 4 which can be integrated to estimate the total amounts of O and CO_2 (or its fragments) lost to space in the last ~ 3.5 billion years. We obtain values of ~ 2 x 10^{44} atoms for oxygen and ~ 6 x 10^{42} molecules for CO_2. This oxygen loss is equivalent to that in ~ 50 m of water (about 30% greater than the estimate of Zhang et al. [1992a] without sputtering), while the sputtered CO_2 would have supplied an atmosphere of ~ 0.14 bar.

The relative importance of the history of the solar EUV flux, as opposed to the solar wind, on this result can be roughly assessed in the following way. The neutral exosphere escape rate evolution (except for the sputtered component) is, of course, completely determined by the EUV change. On the other hand, while the EUV controls the density of the exospheric seed population for pickup ion scavenging, either the EUV or the solar wind parameters can dominate the pickup ion production rate and thus also the flux of the sputtering agents. (Impact ionization by solar wind electrons is found to be more important than photoionization at Mars in the current epoch [Zhang et al., 1992a]). At the same time, the relative amount of sputtering of O, as opposed to CO_2, depends on the EUV-determined composition at the exobase (see Figure 1a). The relationship between the loss rates and parameters such as solar EUV flux is thus highly nonlinear even in the absense of solar wind changes. Nevertheless, it is useful to think of the present model for escape as being most dependent on the EUV flux except in the area of pickup ion production rates. Because this complex interplay of parameters and processes is combined with the uncertainty in the historical solar luminosity and solar wind, one can appreciate that orders of magnitude changes in the calculated escape rates could result from the use of different EUV flux and solar wind histories. Thus the present results should be regarded mainly as an illustration of the potential importance of the included processes given our present understanding of the sun's history.

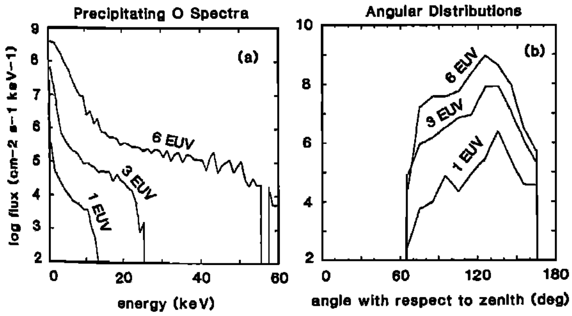

Fig. 3. (a) Calculated "precipitating" or impacting O^+ pickup ion fluxes (averaged over the dayside) for the 1, 3 and 6 EUV cases. (b) Corresponding zenith angle distributions (0 deg is vertical, upward).

Table 1

Epoch (in terms of present EUV flux)	Exospheric O escape (atoms/s)	Pickup O^+ ion (ions/s)	Sputtered O escape (atoms/s)	Sputtered CO_2 (molecules/s)
1 EUV	8 x 10^{25}	6 x 10^{24}	3 x 10^{23}	3 x 10^{23}
3 EUV	5 x 10^{26}	4 x 10^{26}	3 x 10^{26}	6 x 10^{25}
6 EUV	1 x 10^{27}	3 x 10^{27}	3 x 10^{27}	3 x 10^{26}

Discussion and Conclusion

The earliest evolutionary period for planetary atmospheres, in the first billion years of the solar system's "life", was probably catastrophic in nature. During this period, post-accretionary outgassing, delivery and removal of volatiles by impactors, and perhaps hydrodynamic outflow of a hydrogen-rich original atmosphere probably dominated the sources and sinks [see references in McKay and Stoker, 1989, for details]. It may be that we can never fully understand what occurred during this primary epoch.

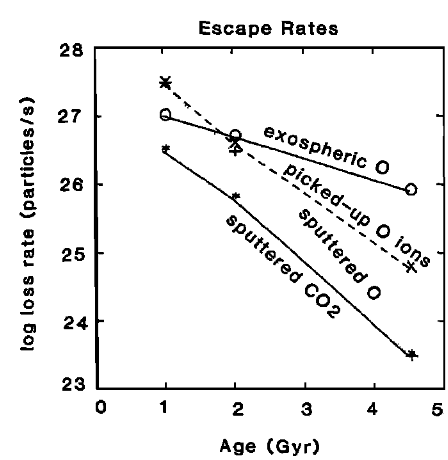

Fig. 4. Summary of the loss rates in Table 1 plotted versus solar system age, using the Zahnle and Walker [1982] model of solar EUV flux evolution to make the transformation.

However, if contemporary escape mechanisms have dominated since these more violent processes ceased, we can arguably extrapolate backward from the present using models such as that described here.

Our calculations indicate that when the evolution of the solar EUV flux and solar wind are taken into account, escape to space of major atmospheric constituents is significant compared to current estimates of early inventories for Mars water and CO_2 pressure. The CO_2 loss determined here is due solely to sputtering by reentering O^+ pickup ions. We consider the present estimates to be conservative because we did not include potential enhancements to the loss by effects such as the expansion of the exosphere by the ion impact (not all energized atoms or molecules will directly escape) [Johnson, 1990; McGrath and Johnson, 1987]. We also did not consider extreme situations that might have occurred if the sun had been much more active in the past, or other possible ion scavenging mechanisms suggested by observations at Venus [e.g., see Luhmann and Bauer, 1992].

In the post-hydrodynamic outflow eras, the only other potentially important escape mechanism for carbon is likely to be the dissociative recombination of CO^+ which is not considered here. Since McElroy [1972] estimated a current loss rate due to this process that is about equal to the 1 EUV CO_2 sputtering rate found here [Table 1], the "ancient" loss rates need to be evaluated at some point. (This evaluation would require calculations of the evolving ionospheres which allowed for the minor species CO^+.) Since the addition of another escape process can only make the present estimates of escape to space larger, we conclude that escape to space is likely to have been a major factor in atmosphere evolution at Mars, and that the solar wind interaction has played a significant role in CO_2 removal through sputtering by pickup ions.

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