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François Leblanc, Robert E. Johnson

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Role of molecular species in pickup ion sputtering of the Martian atmosphere

F. Leblanc¹ and R. E. Johnson

Engineering Physics and Department of Astronomy, University of Virginia, Charlottesville, Virginia, USA

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[1] This paper presents a new approach for calculating the sputtering of an atmosphere by impacting particles when there are molecular species at the exobase. We couple a test particle Monte Carlo approach with a molecular dynamic model to describe the collisions between hot particles and cold molecules in the Martian atmosphere. It is shown that both the heating efficiency and sputtering by pickup ions are reduced from that in an atomic thermosphere. The yields are given for three different ratios of atoms to molecules at the exobase and are used to obtain a better estimate of the total loss of atmosphere due to the pickup ion sputtering. Using the pickup ion fluxes of *Zhang et al.* [1993], ~ 120 mbar of O and ~ 60 mbar of CO₂ are lost. The loss of O if associated with H₂O would be equivalent to ~ 4 m averaged over the Mars surface. INDEX

TERMS: 2455 Ionosphere: Particle precipitation; 5705 Planetology: Fluid Planets: Atmospheres—evolution; 6225 Planetology: Solar System Objects: Mars; KEYWORDS: Mars, sputtering, atmospheric loss

1. Introduction

[2] The evolution of the Martian atmosphere over the last 3.5 Gyr remains an interesting but unsolved problem [Carr, 1999]. Luhmann and Kozyra [1991] showed that sputtering of the atmosphere by incident O⁺ pickup ions may remove sufficient atmosphere to reduce the greenhouse effect so that the atmosphere collapses [Jakosky et al., 1994]. Pickup ion formation occurs following solar EUV and photoelectron ionization in the Martian corona. Because of the absence of a large permanent magnetic field, these newly ionized particles can be accelerated by the partially deflected fields frozen into the solar wind. They move along gyroradial trajectories in the Martian tail direction, but a fraction reimpact the atmosphere and collide with neutral particles with sufficient energy to eject atoms and molecules. Since these collisions mainly occur near the exobase, the species able to reach that altitude are the most influenced by the pickup ions. Therefore this process is also thought to play an important role in the isotopic fractionation as suggested by Jakosky and Jones [1997] and estimated by Johnson et al. [2000]. Analysis of the present isotope ratios suggests that 85–90% of Ar, C, H, and N may have been lost by sputtering consistent with this model [Jakosky and Jones, 1997].

[3] Large differences in the net loss of atmosphere due to this mechanism have been estimated in several papers [Jakosky et al., 1994; Kass and Yung, 1995; Johnson et al., 2000; Leblanc and Johnson, 2001]. In most of these models either the molecular nature of the atmosphere near the exobase was simplified or the atmosphere was treated as if it were fully dissociated to obtain an estimate of the atmospheric sputtering rate. Kass and Yung [1995, 1996] (hereinafter collectively referred to as KY) were the first to consider the collisions involving molecules. In doing this, they obtained a large increase in the sputtering rate over that determined using a fully dissociated atmosphere. Recently, they used new cross-section data to improve their model [Kass, 1999; D. M. Kass and Y. L. Yung, Evolution of the Martian atmosphere: Results of a

Monte Carlo model of sputtering, submitted to *Icarus*, 2001] (hereinafter referred to as Kass and Yung, submitted manuscript, 2001).

[4] In this paper we carry out a detailed calculation of pickup ion sputtering of an atmosphere having molecular species at the exobase. In an earlier paper we used a single species, atomic O atmosphere, to examine the three-dimensional (3-D) effects of pickup ion sputtering at Mars [Leblanc and Johnson, 2001]. Here we use a simple 1-D model, as did KY, but use a new method to describe collisions in a multispecies atmosphere having molecules at the exobase. This presents a problem because the struck molecules can dissociate or they can be vibrationally excited and carry that energy into the next collision. These processes have been suggested to considerably enhance sputtering (KY). Here we show that that is not the case.

[5] We couple a 1-D Monte Carlo (MC) simulation with a molecular dynamic (MD) model of the collisions involving molecules [Allen and Tildesley, 1987]. The MC simulation describes the motion of the hot atoms and molecules under the effect of gravity and collisions, whereas the MD model describes the individual collisions giving the probability of dissociation and vibrational excitation. This very detailed procedure is necessary to determine whether or not the energy transported by the vibrationally excited molecules leads to considerably enhanced atmospheric sputtering.

[6] In section 2 we first give the method used to describe the multispecies atmosphere, and then we describe the MD treatment of the collisions initiated by incident pickup ions. Section 3 presents the results for three different atmospheres representing different epochs of Mars history. In section 4 we give an estimate of the total direct loss of atmosphere due to this mechanism.

2. Monte Carlo Coupled With Molecular Dynamic Simulations

[7] The nature of this simulation is like that of the simulations by KY and Johnson et al. [2000]. Since the incident pickup ions are neutralized by charge exchange collisions well before reaching the exobase altitude [Luhmann and Kozyra, 1991], the resulting neutral particles are followed in an atmosphere with which they interact by collisions. The atmosphere simulated is one dimension

¹Now at Service d'Aéronomie du CNRS, Verrières-Le-Buisson, France.

sional, and the MC simulation used is a test particle approximation, which means that only hot particles are followed. That is, the atmosphere is thought of as having a background thermal population which remains fixed and a hot particle population of those struck atoms or molecules which have an energy much larger than the mean thermal energy. The dominant species at the exobase are CO_2 at present and O at early Mars. Since the CO_2 molecule can dissociate into CO, O, and C under the effect of impacting particles, we consider an atmosphere composed of CO_2 , CO, C, and O. The C species is introduced only as a product of the dissociation of the CO_2 molecules and not as a permanent element of the Martian atmosphere at the exobase. This is in agreement with predictions of *Zhang et al.* [1993] and *Bougher and Roble* [1991].

[8] In the MC model, representative collisions are selected after each time step. Each collision between an energetic atom and an atmospheric molecule or between a hot molecule and another atom or molecule is described in this paper using a classical MD model. In this model, interaction potentials between each of the atoms involved in each collision are specified. Subject to these potentials, the equations of motion of the colliding atoms or molecules are integrated using a fourth-order Gear predictor corrector model [Allen and Tildesley, 1987]. This approach is identical to that used by *Johnson and Liu* [1998] to calculate collisional dissociation cross sections for energetic O on CO_2 . We use the same interaction potentials, although recently better potentials have been obtained [Johnson et al., 2002], because the differences do not significantly change the sputter yields. Therefore the outcomes of the collisions are the same as those given by *Johnson and Liu* [1998], which were incorporated by KY in their recent model. However, here we use these interaction potentials to describe collisions involving molecules including those in which hot molecules carry vibrational excitation. Each collision calculation is stopped either when a dissociation occurs or after a time long enough to be sure that no dissociation occurs. Random numbers are used to choose the impact parameter and the orientation of the struck molecule. This method is computationally expensive but avoids using an approximate model for the critical collision cross sections.

[9] Since the method and potentials of interaction used here are the same as the ones described by *Johnson and Liu* [1998], we tested that we reproduce the collisional cross sections for $\text{CO}_2 + \text{O}$, $\text{CO}_2 + \text{CO}_2$, and $\text{CO} + \text{O}$ given in that paper. The impact parameter is chosen between zero and a maximum value larger than 3 Å for O and C, larger than 4.0 Å for CO_2 , and larger than 3.5 Å for CO. These values are obtained from the plots of *Johnson and Liu* [1998]. The collisions with higher impact parameter are neglected in our simulation. These can be important for total energy loss and, hence, heating of the atmosphere but are not important for the estimation of the atmospheric sputtering [e.g., *Johnson et al.*, 2000].

[10] The other unique aspect of these calculations is that the internal energy of the molecule, which is partitioned among vibration and rotational modes in the molecule's center of mass frame, is preserved from one collision to the next. Therefore hot particles can carry their internal energy into the next collision. Because the simulations involve many collisions, the statistics are such that we do this in a simple way. We directly carry the vibrational and translational motion at the point the previous collision ends into the next collision. That is, we do not let it evolve. This actually will give an overestimate of the effect because the weak collisions at very large impact parameters, which we neglect here, would act to cool the excited molecule. For this reason, we perform MC simulations in which we maintain all of the internal energy and ones in which we fully quench it for comparison.

[11] Molecular dynamics approaches are used to describe the collisions between a CO_2 molecule and any other type of particle and between CO and any other type of molecule except CO. These collisions are described with a hard sphere approximation because there are very few collisions of this type involving relatively low

energy particles which do not dissociate efficiently. For the same reason we use a hard sphere approximation to describe the collisions with molecules when both interacting particles have energy lower than 20 eV. Collisions between two atoms are described as done by *Johnson et al.* [2000] and *Leblanc and Johnson* [2001] with a universal potential [Ziegler et al., 1985]. The electronic energy loss [Eckstein, 1991] is deducted after each collision following the formulation of *Oen and Robinson* [1976]. Although this loss represents only few percent, *Johnson et al.* [2000] showed that it affected the atmosphere loss.

3. The 1 EUV, 3 EUV, and 6 EUV Epochs

[12] *Zhang et al.* [1993] have defined three different periods in Martian history. Although their results are controversial, they have been used by KY and in our previous work. Here these epochs are interesting as the relative amounts of O and CO_2 at the exobase differ considerably, from predominantly CO_2 in the present epoch to predominantly O in the earliest epoch considered. For each period the flux of solar EUV radiation is given relative to the present EUV flux at solar minimum (1 EUV). The 6 EUV period was assumed to correspond to a very early epoch of the solar system with an EUV flux 6 times greater than the present EUV flux. This period is now thought to correspond to a time when Mars still had an active magnetic field, which would, at least partially, protect its atmosphere from the solar wind and, therefore, from the sputtering by pickup ions [Acuña, 1998]. However, we will consider this case to estimate the yield at the beginning of the decay of the magnetic field 3.5 Gyr ago. The 3 EUV flux is assumed to correspond roughly to the period around 2.5 Gyr ago. During this period the magnetic field is thought to have fully decayed, leaving a remanent field not strong enough to protect the Martian atmosphere from the incident pickup ions.

[13] Whereas an average energy and incident angle have been used in many calculations, here we also follow a large number (10,000) of incident particles to represent the incident energy and angle dependence of the neutralized particle reaching the exobase. In the 1 EUV epoch the range of energies is typically between 100 eV and 13 keV, in the 3 EUV epoch it is between 100 eV and 25 keV, and in the 6 EUV epoch it is between 100 eV and 55 keV. We neglect the particles with energy lower than 100 eV because of their small contribution to the total escape.

[14] Each incident particle is followed from 400 to 115 km, from 500 to 115 km, and from 600 to 122 km from the surface in the 1 EUV, 3 EUV, and 6 EUV epochs, respectively. These particles collide with species in an atmosphere for which density and temperature are shown in Figures 1 and 2, respectively. These profiles are also deduced from *Zhang et al.* [1993] and, again, are used for convenience to compare to earlier work. We added CO because this species has been shown to be nonnegligible in the present atmosphere [Bougher and Roble, 1991; McElroy et al., 1977]. The profiles for CO for the 3 EUV and 6 EUV epochs are extrapolated from the 1 EUV epoch. The C species produced by dissociation of CO_2 or CO is not represented in these figures since it remains a minor component of the Martian atmosphere. The temperature profile (Figure 2) for these atmospheres is also deduced from *Zhang et al.* [1993] assuming that the neutral species all have the same temperature.

[15] Each incident particle is tracked through the atmosphere and is eventually eliminated for the following reasons.

1. The few percent of the incident O that reach the bottom limit are considered to be thermalized since at this altitude the atmospheric density is high. Figure 3 provides the total energy loss by an incident particle with respect to the altitude for the three epochs. It shows that from 70 to 90% of the initial energy is lost by the particle before reaching ~ 115 km in the 1 EUV and 3 EUV epochs and ~ 122 km in the 6 EUV epoch.

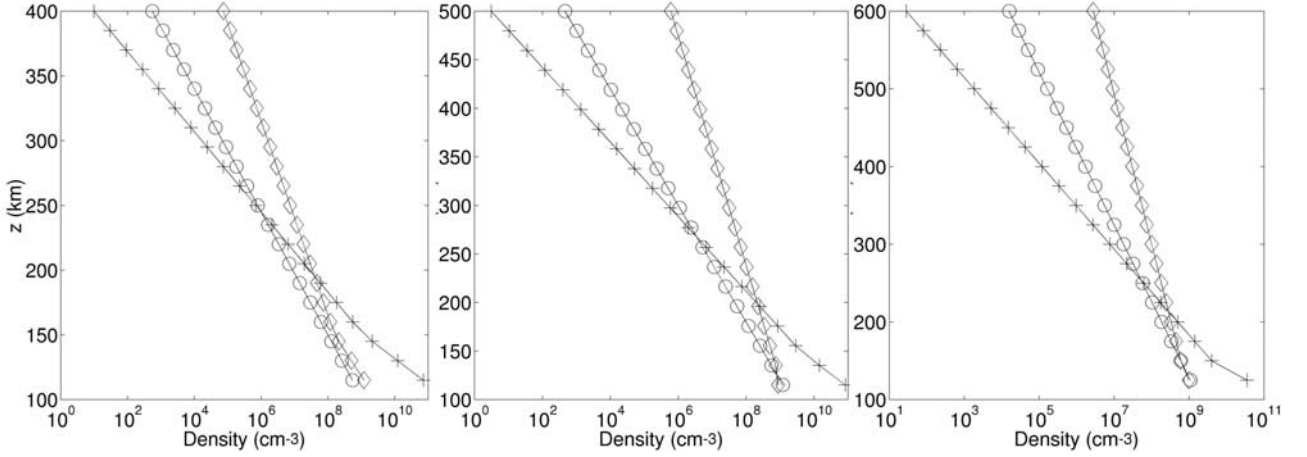


Figure 1. Density profiles of the main species composing the Martian atmosphere between 400, 500, and 600 km and 115 km in altitude for the (left) 1 EUV case, (middle) 3 EUV case, and (right) 6 EUV case, respectively. Diamonds, O atom; circles, CO molecule; and crosses, CO₂ molecule.

2. The incident O may be backscattered (between 7 and 14%) and cross the top limit of the domain, where it either is suppressed if it has an energy higher than the escape energy or is followed on a ballistic trajectory until it again crosses the top limit.

3. The incident O may become thermalized by colliding with neutral particles. Each time that this particle collides with a cold atmospheric particle, a test is made of the energy of the particles after the collision. Each particle that has an energy higher than the escape energy at the altitude of the collision is followed in the same way as the incident particle is followed. Particles with energy lower than the corresponding escape energy are suppressed since they cannot contribute to the loss of atmosphere.

[16] The last simplification is consistent with our frozen atmosphere, in which we do not change the thermal or vertical structure due to heating or hot particle transport. *Leblanc and Johnson* [2001] showed that in fact, this flux could significantly heat the atmosphere in earlier epochs when atoms dominate the exobase. However, the presence of molecules in a large proportion at the exobase significantly affects the local heating. In order to determine this, we also have constructed a full direct simulation Monte Carlo where all the particles of the atmosphere are followed. As done by *Leblanc and Johnson* [2001], the effect of several hundred incident particles is simulated, and the derived heating is calculated and compared with the EUV heating. We find that a large proportion of the initial energy of the incident particles is used to dissociate and vibrationally excite the molecules, reducing significantly the amount of translational energy available immediately as heat. As shown in Figure 3, the incident O⁺ ions mainly lose energy by collisions with the CO₂ molecules. Around 10% of these collisions lead to dissociation of the CO₂ molecule: either $\text{CO}_2 \rightarrow \text{CO} + \text{O}$ or $\text{CO}_2 \rightarrow \text{C} + \text{O} + \text{O}$ in a ratio of about 3 to 1. Because of the reduced heating rate, using a test particle approach, in which only the particles with enough energy to escape are followed, is appropriate.

[17] In Table 1 we give yields for the four species composing our model Martian atmosphere in each of the three epochs considered in this simulation. The yield is defined as the number of ejected particles of each species divided by the total number of incident particles.

[18] We first compare these results with a 1-D, single-species model in which the atmosphere consists only of O atoms (“equivalent O atmosphere”). That is, a CO₂ molecule is replaced by three O atoms, and a CO molecule is replaced by two O atoms, with the net density of O deduced from Figure 1. The results in Table 1 are close to those given by *Johnson et al.* [2000] even though we use a more accurate description of the flux [*Luhmann et al.*, 1992] and

include the atmospheric structure. In Table 1 we also give the total number of escaping atoms (“total atomic yields”) deduced from the multispecies calculation. These yields are seen to be more than 35% smaller when CO₂ is included and collides as a molecule rather than being approximated as a dissociated species. This means that the presence of CO₂ at the exobase not only affects the plasma heating but also reduces the total loss due to the incident pickup ions, in contrast to the result of KY. That this should be the case is shown below.

[19] For comparison we first ignore dissociation and calculate the loss of atmosphere for the case where the molecules are assumed to be atom-like with masses equivalent to the molecular masses (CO and CO₂). These calculations are like those carried out earlier for considering noble gases in the atmosphere [*Johnson et al.*, 2000]. The yields obtained here are also given in Table 1 (“Atmosphere of Multispecies Atom-like Molecules”) and are seen to be ~20% smaller for the three epochs than in the equivalent O atmosphere.

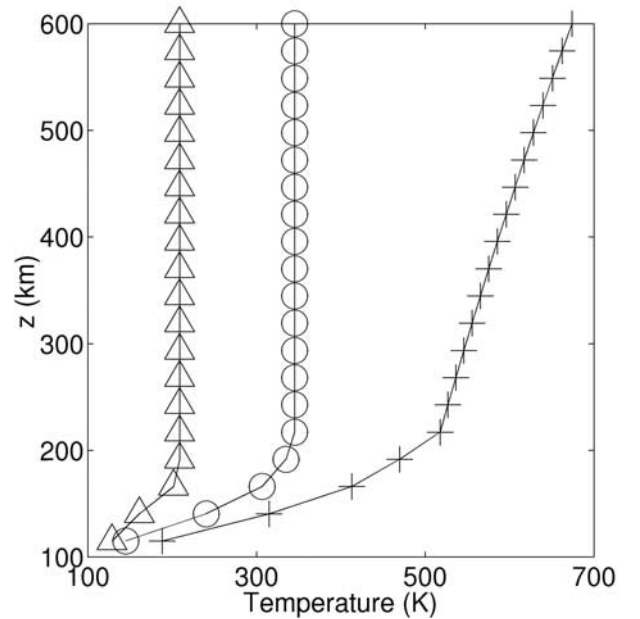


Figure 2. Temperature profiles of the neutral atmosphere for the three epochs. Triangles, 1 EUV epoch; circles, 3 EUV epoch; and crosses, 6 EUV epoch.

This is not surprising as the atmosphere at the exobase now contains heavier particles with larger escape energies than that for O. The number of collisions which transfer more than 6 eV (the CO₂ escape energy) from an incident O atom to a CO₂ molecule is much smaller than the number of collisions which transfer 2 eV to an O atom. In fact, it is more difficult to sputter a heavy CO₂-like atom than to sputter three atoms of oxygen since “hard” collisions with high energy exchange and small impact parameter occur much less often than “soft” collisions. If dissociation is allowed to occur, this reduces the escape energy of the possible ejecta but additional energy is required. That is, an incident particle colliding with a molecule needs to transfer ~ 10 eV in order to dissociate a CO₂ molecule. In fact, the cross-section calculations indicate that about 3 times this amount is required for dissociation to become likely [Johnson and Liu, 1998]. Therefore, although the cross sections used in the “Atmosphere of Multispecies Atom-like Molecules” case differ from those in the full calculation allowing dissociation, the yield is also seen to be reduced.

[20] Finally, KY suggest that it is the internal energy carried by struck molecules or their molecular fragments that plays an important role. This effect does not appear to be significant in our simulation, in which these collisions are directly calculated and not modeled. That is, we found a small decrease of the yield of 4–8% when the internal energy of the molecules is not conserved from one collision to the other. The internal energy of the molecule is, of course, never greater than ~ 10 eV. Indeed, the triatomic molecule typically requires more internal energy because it is rarely equally distributed among the different components of the molecule. We find that a collision made between an excited molecule and a cold background molecule more often quenches than it gives significantly enhanced dissociation. That is, the assumption of randomizing the total center of mass energy given by KY is only appropriate for very low energy collisions in which the long-range attractive potential allows the collision complex to form a quasi-bound long-lived species in which randomization can occur. Johnson and Liu [1998] showed that the fragments from collisions involving even ground state molecules do exit nearly isotropically, as assumed by KY, but we did not test the fate of the net center of mass energy, nor did we carry out calculations for internally hot molecules as done here.

[21] Table 1 gives yields for the three epochs, for which the composition of the atmosphere at the exobase altitude changes significantly. This composition is dependent on the temperature of the atmosphere (Figure 2) since the thermal diffusion dominates the atmosphere above 150 km in altitude [Bougher and Roble, 1991; Zhang et al., 1993]. Figure 4 provides the ratio between O and CO₂ density as a function of altitude for the three epochs. This

Table 1. Efficiency of Incident O⁺ Pickup Ions in Ejecting Atmospheric Particles

	Epochs of Martian History		
	1 EUV	3 EUV	6 EUV
<i>Multispecies Molecular Atmosphere</i>			
Yield of O	0.86	1.66	1.99
Yield of CO ₂	0.12	0.05	0.02
Yield of CO	0.09	0.06	0.06
Yield of C	0.22	0.24	0.33
Total atomic yields	1.6	2.2	2.5
<i>Atmosphere of Multispecies Atom-like Molecules</i>			
Yield of O	0.41	1.12	1.58
Yield of CO ₂	0.46	0.40	0.26
Yield of CO	0.12	0.16	0.38
Total atomic yields	2.0	2.6	3.1
<i>Equivalent O Atmosphere</i>			
Total atomic yields	2.6	3.0	3.9

ratio is equal at the exobase to 0.3 for the 1 EUV epoch (0.1 in atomic concentration), 2.0 for the 3 EUV epoch (0.6 in atomic concentration), and 12 for the 6 EUV epoch (4 in atomic concentration) consistent with Johnson and Luhmann [1998]. Therefore it is not surprising to find that the ratio between the sputter yield of the oxygen and that of the CO₂ follows a similar trend.

[22] Because these yields are independent of the flux, the results in Table 1 can be applied for appropriate exobase conditions. To deduce the total loss of Martian atmosphere from these yields, we will again use the estimate of the incident flux of pickup ions used by Johnson and Luhmann [1998] since better estimates are not available: a flux of 5×10^5 part/cm²/s for the 1 EUV epoch, 9×10^7 part/cm²/s for the 3 EUV epoch, and 1×10^9 part/cm²/s for the 6 EUV epoch. Since only one hemisphere is bombarded, 4.0×10^{23} , 7.5×10^{25} , and 8.6×10^{26} incident pickup ions reached the Martian atmosphere per second in the 1 EUV, 3 EUV, and 6 EUV epochs, respectively. From Table 1 and this flux we can deduce that the total loss of atmosphere due to the pickup ions between 1 Gyr and the present epoch (4.5 Gyr) is equal to 3.5×10^{41} CO₂ molecules (6 mbar of CO₂), 6.5×10^{41} CO molecules (7 mbar of CO), and 3×10^{42} atoms of carbon (15 mbar of C). This gives a total carbon loss, which means total CO₂ loss, of 3×10^{42} , or ~ 60 mbar. The total loss of O is 2×10^{43} O (120 mbar of oxygen), with only $\sim 10\%$ connected with CO₂ loss. If the remainder is connected with water loss, as has been assumed by some authors, then this is ~ 4 m of H₂O. This study is a

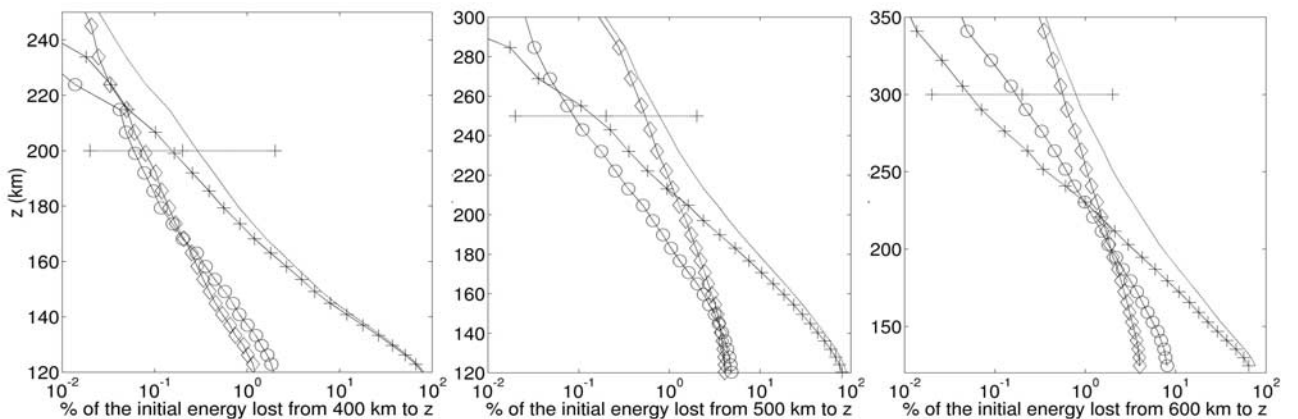


Figure 3. Total energy loss of the incident particles integrated from the top limit of the domain to the bottom limit: (left) 1 EUV case, (middle) 3 EUV case, and (right) 6 EUV case. Diamonds, by collision with the atmospheric O atoms; circles, by collision with the atmospheric CO molecules; crosses, by collision with the atmospheric CO₂ molecules; nonhorizontal solid lines, total; and horizontal solid lines, exobase altitude.

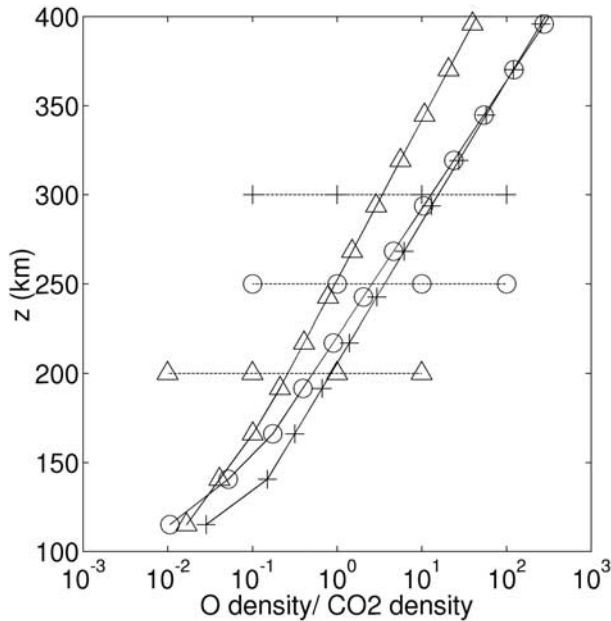


Figure 4. O/CO₂ density ratio for the three epochs of Martian history. Horizontal dashed lines, exobase altitude for the three epochs; triangles, 1 EUV epoch; circles, 3 EUV epoch; and crosses, 6 EUV epoch.

1-D model and does not include the effect due to grazing incidence particles, which are very efficient at sputtering. *Leblanc and Johnson* [2001] showed that treating these ions correctly increases the total yield of a 1-D model by roughly 20%.

[23] Again, the pickup ion fluxes have been questioned, so the above values are for the purpose of comparison with previous studies [*Luhmann et al.*, 1992; Kass and Yung, submitted manuscript, 2001; *Johnson et al.*, 2000]. These results are highly dependent on the incident flux, energy, angle, and mass distributions of the ions reaching the exobase. On the other hand, the yields presented in Table 1 are dependent primarily on the ions being O⁺ and the atmospheric composition around the exobase. They therefore can be used as new models if the pickup ion flux becomes available. Our estimate of the total loss of ~120 mbar (with ~60 mbar of CO₂) is smaller than the 450 mbar (within 15 mbar of CO₂) loss calculated by *Johnson et al.* [2000] and smaller than the original estimate given by *Luhmann et al.* [1992]. It is also much smaller than the 800 mbar of CO₂ and 50 m of H₂O loss recently calculated [*Kass*, 1999; Kass and Yung, submitted manuscript, 2001]. In fact, this smaller estimate of atmospheric loss is in better agreement with some models of the evolution of the Martian atmosphere [*Pepin*, 1994; *Jakosky et al.*, 1994; *Krasnopolsky et al.*, 1996], which suggest that the previous sputtering loss estimations were too big to explain the isotopic ratio measurements. However, it must also be kept in mind that this does not include feedback [*Johnson and Luhmann*, 1998] or the effect of direct pickup ion loss [*Luhmann et al.*, 1992]. Therefore, although more work is required to fully determine the role of the solar-wind-induced pickup ions, it is seen that the fully dissociated atmosphere does indeed give a convenient upper bound to loss, as suggested [*Johnson et al.*, 2000], and the corrections to such a model in the original papers [*Luhmann et al.*, 1992; *Jakosky et al.*, 1994] are of the right order of magnitude.

4. Concluding Remarks

[24] We present a Monte Carlo test particle approach coupled to molecular dynamic models of the Martian atmosphere bombarded

by incident O⁺ pickup ions. This paper is the first multispecies MC model in which the critical cross sections are directly calculated and not modeled. It allows us to accurately treat the dissociation of the molecules at the Martian exobase and the fate of their internal excitation energy. Using this, we give useful average yields for a number of very different mixes of species at the exobase. We have shown that assuming a fully dissociated atmosphere does give an upper bound to the loss rate, which can be useful as new models of the atmosphere and pickup ion flux become available. We have also shown that the carbon ejected primarily leaves in the fully dissociated form, with C being the dominant carbon ejecta, but that this does not lead to a large increase in the net yield as has been suggested. In fact, having molecules at the exobase is seen to reduce the effect of heating and reduces the sputtering rate as discussed above.

[25] For comparison to previous work we have also estimated the loss of atmosphere due to the sputtering by pickup ions using the fluxes tabulated by *Johnson and Luhmann* [1998] from the work of *Zhang et al.* [1993], which are smaller than those assumed by KY. The presence of molecules at the exobase significantly decreases the quantity of atmosphere lost but appears to give a total loss of atmosphere in better agreement with some models of the evolution of Mars' atmosphere and isotopic ratios [*Pepin*, 1994; *Jakosky et al.*, 1994; *Krasnopolsky et al.*, 1996]. This work also needs to be adapted to a 3-D model of the interaction between the solar wind and the Martian ionosphere [*Brecht*, 1997a, 1997b], which includes an accurate calculation of the ionization rates and pickup ion formation in the corona. Such a calculation is needed to better estimate the fraction of the coronal neutral particles directly lost following ionization and the fraction which reimpact Mars' atmosphere. The latter then would be included in a 3-D model of sputter loss to account for grazing incidence [e.g., *Leblanc and Johnson*, 2001]. In the meantime the results in Table 1 can be used to estimate the loss as new models of the history of the Martian atmosphere and the solar wind become available.

[26] **Acknowledgments.** This work was supported by NASA's Planetary Atmosphere Program.

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R. E. Johnson, Engineering Physics and Department of Astronomy, University of Virginia, Charlottesville, VA 22903, USA. (rej@virginia.edu)

F. Leblanc, Service d'Aéronomie du CNRS, Réduit de Verrières-Le-Buisson BP 3, 91371 Verrières-Le-Buisson, France. (francois.leblanc@aerov.jussieu.fr)