THE PHYSICS AND CHEMISTRY OF SPUTTERING BY ENERGETIC PLASMA IONS

R.E. JOHNSON and F. LEBLANC
Engineering Physics, University of Virginia, USA; E-mail: rej@virginia.edu

Abstract. Energetic ions from the solar wind, local pick-up ions or magnetospheric plasma ions impact the atmospheres and surfaces of a number of solar system bodies. These energetic incident ions deposit energy in the gas or solid. This can lead to the ejection of atoms and molecules, a process referred to as sputtering. In this paper we first describe the physics and chemistry of atmospheric and surface sputtering. We then apply this to the production of a thin atmosphere on Europa by magnetospheric ion bombardment of Europa's surface and show that Europa loses more Na atoms than it receives from the Jupiter magnetosphere. The loss of atmosphere from Mars in earlier epochs by pick-up ion sputtering of that atmosphere is also calculated.

1. Introduction

The flow of the solar wind plasma, a plasma trapped in a planetary magnetic field or a local pick-up ion plasma onto a surface or onto the exobase of an atmosphere can cause chemistry, heating and the ejection of atoms or molecules. These processes, which can affect the evolution of a solar system object are often referred to as sputtering. In the laboratory, sputtering is a procedure in which a flux of heavy ions produces a vapor above a material that would otherwise have a low vapor pressure. This is often done for controlled vapor deposition of a thin coating on a glass or on an electronic device. Here we consider the ejection of atoms and molecules from a natural surface or atmosphere by an energetic incident plasma ion or electron (Johnson, 1990). The effect of solar wind and solar flare ion sputtering of the lunar surface has been of long term interest and may contribute to the observed lunar atmosphere (Sprague *et al.*, 1992). Similarly the observed sodium cloud at Io was suggested as being produced by the energetic ion bombardment of Io's surface (Matson *et al.*, 1974). Based on their initial laboratory experiments, Lanzerotti, Brown and co-workers first suggested that large amounts of surface are sputtered and an atmosphere is produced over the surface of Europa by ion bombardment (Lanzerotti *et al.*, 1978). Later this atmosphere was shown to be dominated by sputter-produced O_2 (Johnson *et al.*, 1982) which was recently observed (Hall *et al.*, 1995). By analogy with the ejection of material from surfaces, Haff and Watson (1979) thought that atmospheres might also be sputtered by energetic ions. This has since been shown to be an important evolutionary process at Mars (Jakosky *et al.*, 1994), Io (Smyth and Combi, 1988) and Europa (Saur *et al.*, 1998).

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In this article honoring the work of J.L. Steinberg we review the physics and chemistry of sputtering since, not only does it affect the evolution of solar system objects, but it is often the source of the local plasma. For instance, atmospheric sputtering plays an important role in forming the Io plasma torus and the sputtering of the icy Saturnian satellites and the E-ring is the likely source of the trapped plasma in Saturn's inner magnetosphere. We first outline the physics and chemistry of sputtering, relying heavily on an earlier monograph (Johnson, 1990) and previous reviews (Johnson, 1994, 1996, 1998). We then consider examples for which we have recently made progress in relating space observations to the plasma sputtering processes.

2. Physics and Chemistry of Sputtering

Sputtering is a process by which an energetic ion deposits its energy in a material initiating a cascade of events which eventually leads to the ejection of atoms or molecules from the surface. Ions lose their energy by direct knock-on (momentum transfer) collisions with an atom in the material and by electronically exciting the atoms and molecules in the material. The effects produced by the incident ion are typically described using the stopping power of the material for a given ion, dE/dx, which is the energy lost per unit path length. Therefore, dE/dx can be roughly written in terms of knock-on (n) and electronic excitation (e) contributions: $(dE/dx)_n + (dE/dx)_e$.

In the sputtering of refractory solids for vapor deposition, it is knock-on collisions that cause the ejection of atoms from the surface. Each atom set in motion (a recoil) by the incident ion in turn collides and produces additional recoils, so there is a cascade of collisions. It is straight forward to show that, if the cascade of collisions evolves fully, the spectra of recoil energies, E, produced has the form $\beta E_i/E^2$, where E_i is the incident ion energy. Sputtering then occurs when an atom or molecule in the material reaches the surface (exobase for an atmosphere) with sufficient energy to overcome the energy barrier (gravity for an atmosphere). If the cascade of collisions evolves sufficiently to become nearly isotropic, then the energy spectrum above can be used to estimate the number of recoils which are sputtered per ion incident, the yield, Y (Johnson, 1990; 1994): $Y \approx \alpha\beta\,[S_n\,/\,U\,\sigma_d]$. Here S_n is the stopping cross section $[(dE/dx)_n = n\,S_n$, where n is the material number density] giving the knock-on contribution to the energy loss. The quantity U is the barrier to escape from the material [a chemical barrier for a solid and the gravitational escape energy for an atmosphere], and σ_d is the collision cross section between the surface (exobase) species and the exiting atoms or molecules. Finally, α contains the angular factors and corrects for the fact that the cascades are not isotropic. The remarkable aspect of this expression, noted by Haff and Watson (1979), is that it is independent of density! This allows it to be applied to both atmospheres and solids. Monte Carlo simulations of atmospheric sputtering confirm the above form for Y (Johnson *et al.*, 2000). However, the parameters α and σ_d have been estimated incorrectly in many applications. The form for Y has been confirmed empirically for surface sputtering (e.g., Andersen and Bay, 1981). The recoil energy distribution, if applicable at the surface leads to a spectrum of ejected atom energies $f(E) \approx 2EU/(E+U)^3$. This expression has also been established experimentally for surface sputtering. Because of the importance of 'edge' effects it decreases more slowly with increasing E in atmospheric sputtering (Smyth and Combi, 1988; Johnson *et al.*, 2000).

Since the Jovian plasma ions do not bombard a refractory, lunar-like surface, but rather the Gallilean satellite surfaces which are composed of low-temperature condensed gas solids and salts, a new experimental effort was launched (Nash and Fanale, 1977; Brown *et al.*, 1978). These materials typically have much smaller surface binding energies. As they are also electric insulators, they can retain the electronic excitations produced by the incident ions long enough to produce luminescence and non-radiative energy release events. The energy release events can cause bond breaking and, often, the direct desorption of a species like Na (Yashinsky and Madey, 1999). In addition, when the excitation density is high, sufficient energy may be released to cause large amounts of material loss. This is the case for water ice as shown in Figure 1 for bombardment by energetic H^+ and O^+. The hump at low velocities is due to knock-on collisions but the much larger peak in the yield at high velocities is due to the electronic excitations and ionizations. Brown, Lanzerotti and co-workers (e.g., Brown *et al.*, 1978) referred to this as electronic sputtering. Because the energy flux for the Jovian plasma ions peaks in the 10 keV-1 MeV region (Cooper *et al.*, 2000), the sputtering of the icy Galilean satellites is predominantly electronic.

For the ions and ices of interest in the Jovian plasma the dependence on $(dE/dx)_e$ was shown to be $Y \approx c\,[(l/U)\ (dE/dx)_e]^2$ where $l = n^{-1/3}$ (Johnson 1990; 1998). This expression for Y is clearly dependent on the density and, therefore, is not applicable to atmospheres. The equivalent atmospheric process is ionization followed by dissociative recombination near the exobase leading to loss. This is similar to an individual surface desorption event (Johnson, 1990; 1994). The quadratic dependence in Y indicates it is the combined effect of many ionizations and excitations that produce the large yields seen in Figure 1. In both knock-on and electronic sputtering the yield depends inversely on the binding energy U. Because bond breaking occurs, new molecules can be formed and ejected. Therefore, for an atmosphere, fragments (low U) are preferentially ejected, but for a solid the most volatile species formed (low U) will be sputtered preferentially. This is seen to be the case in Figure 2 for deuterated ice. Whereas bond breaking initially forms OD + D or D_2 + O, the O, D and OD have strong binding energies to the solid. Therefore the principal ejecta are D_2, D_2O and O_2. That is, even though decomposition of ice is inefficient, D_2 when formed is readily lost leaving an oxidizing surface so that O_2 gradually forms (Reimann *et al.*,1984). For ice the principal ejecta are H_2O, H_2, and O_2. At Europa, H_2 which is light, directly escapes whereas the H_2O and O_2 do

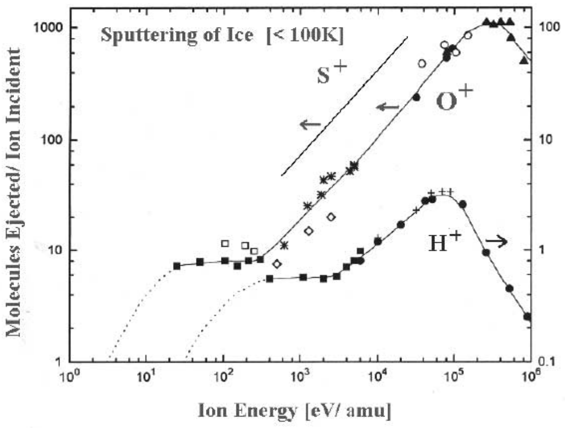

Figure 1. The sputtering yield (equivalent H_2O molecules ejected per ion incident) for water ice at ~77K for incident O^+, S^+ (left hand axis) and H^+ ions (right hand axis). Lines are model fits of data indicated by points.

not. Because the H_2O sticks when it returns to the surface but O_2 does not stick at the temperatures at Europa, a very thin O_2 atmosphere was predicted (Johnson *et al.*, 1982) and recently detected (Hall *et al.*, 1995). Of course, bond breaking, decomposition and chemistry occur in all of the materials suggested for the icy Galilean and Saturnian satellites (Johnson, 2001). Therefore, other decomposition products are also present in Europa's atmosphere (Johnson *et al.*, 1998).

3. Surface Sputtering

3.1. EUROPA

Although sputtering is the likely source of the Na atoms observed in the atmosphere of Europa, the ultimate origin of the sodium is not fully understood. Based on their first observations, Brown and Hill (1996) suggested that source of the Na was ions from Io implanted into Europa's surface. Johnson (2001) used a model for sputtering and implantation to show that decomposition of Europa's subsurface materials by the incident plasma more likely to be the principal source of the sodium. This conclusion was also drawn by comparing the Na to K ratios at Europa and Io (Brown, 2001) and it bears on whether material from the putative underground ocean has reached Europa's surface in geologically recent times.

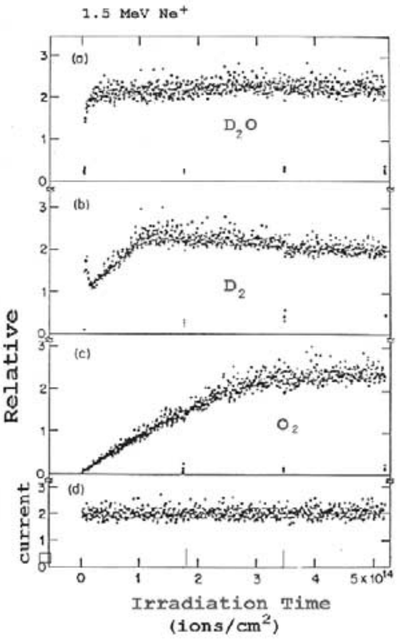

Figure 2. The sputtering rate vs. irradiation time for sputtering of low temperature D_2O ice by 1.5 MeV Ne^+ ions (Reimann *et al.*, 1984). These ions have a $(dE/dx)_e$ equivalent to energetic ions in the Jovian magnetosphere (Cooper *et al.*, 2001).

Sodium atoms are sputtered from Europa's surface by incident ions according to an energy distribution like $f(E)$ given earlier (Weins *et al.*, 1997). The ejected Na cross a thin atmosphere consisting mainly of O_2 and move along bound or escape ballistic trajectories determined by the gravity of Europa and Jupiter. Although a simple spherically-symmetric, analytic model of a sputtered atmosphere was shown to roughly reproduce the averaged observations (Johnson, 2000), N-S and E-W asymmetries observed more recently by Brown require a more accurate three dimensional simulation of the motion of the Na atoms. Such a calculation also allows one to extract more detail on the spatial and energy distribution of the sputter source. Each particle ejected from the surface is followed along its trajectory until either it reaches a maximum distance from Europa, is ionized by energetic electrons trapped in Jupiter's magnetosphere, or reimpacts Europa's surface. We typically follow several hundred thousand particles and compute the density of the generated sodium cloud. The flux ejected from the Europa surface is chosen to be distributed from trailing to leading hemispheres following a cosine law with a maximum on the trailing hemisphere and a null flux at the leading hemisphere (Popieszalska and Johnson, 1989). The probability of ionization is integrated over the trajectory following Smyth and Combi (1988). Figure 3 reproduces the shape of the Na cloud around Europa obtained for this set of parameters. The emission of the Na atoms along a line of sight as seen from the Earth is then calculated and

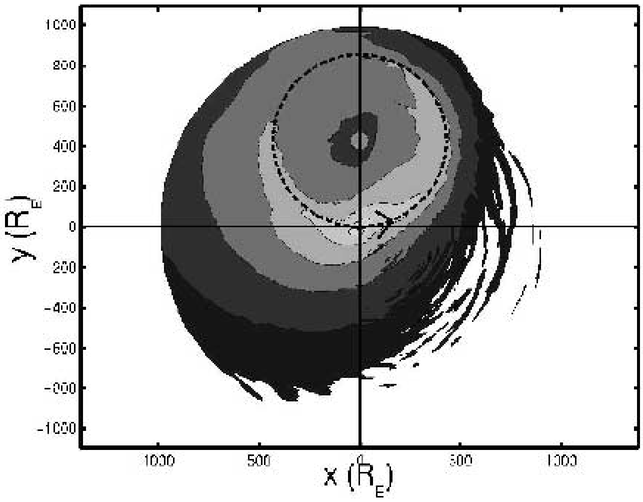

Figure 3. Cut along the Europa's orbit plane of the sodium cloud. The figure is centered on Europa and Jupiter is represented by the circle on the axis x=0. The different grays correspond to density from 10^{-2} Na/cm^{-3} close to Europa to values of 10^{-3}, 10^{-4}, 10^{-5} and 10^{-6} Na/cm^{-3} for the darker ones. We followed 500,000 particles until 1000 R_E.

compared with recent observations made by Brown. The best agreement found has been obtained for a flux of ~6x10^7 Na/cm^2/s with a binding energy U equal to 0.055 eV. This implies a loss of ~6 10^6 Na/cm^2/s for Europa which is 7 to 30 times higher than the estimate flux of Na impacting Europa from the magnetosphere. Therefore, the source of ejected Na atoms from the Europa surface is likely to be endogenic. In addition, we show that direct ejection of atoms from the surface, although dominant, is not the only source of the observed Na, and that the effective binding to the surface is lower than that measured by Weins *et al.* (1997) because the surface is porous and the Na is ejected from icy as well as refractory regions.

3.2. SATURN'S ICY SATELLITES AND E-RING

A model for the extensive laboratory data for the sputtering of low temperature water ice was recently constructed and used to calculate the sputtering of the icy satellites and E-ring grains by Saturn's magnetospheric plasma ions (Jurac *et al.*, 2001). At the temperatures of interest, the principal ejecta is H_2O. H_2O is dissociated in Saturn's plasma more rapidly than it is ionized producing an OH cloud, originally observed by Shemansky *et al.* (1993). Since, unlike Europa, the icy satellites are small the escape fraction is large, so the sputter contribution from the icy satellites and E-ring grains can be modeled using the initial sputtered-molecule energy distribution $[f(E)$ with $U \approx 0.055 eV]$ and the lifetime for dissociation and ionization. Although sputtering is likely to be the ultimate source of the observed OH as well as the magnetospheric plasma, Jurac *et al.* (2001) found that a detailed calculation, including all enhancements, could not account for the observations.

Either a large amount of additional surface is required, particularly near Enceladus, or the surfaces are not simply pure water ice but some more volatile mix. This issue will be resolved by the plasma ion measurements in the Saturnian magnetosphere by CASSINI.

4. Atmospheric Sputtering: Mars

The mechanism of sputtering of the Martian atmosphere by pick-up ions is described in Figure 4. On the dayside (left side on Figure 4), a part of the neutral atmosphere is ionized by the solar EUV and the photo-electrons from the sun. These newly ionized particles are ‘picked-up’ by the magnetic field lines initially frozen in the solar wind but distorted near Mars, and they are accelerated along gyroradial trajectories in the Martian tail direction. The gyroradius around the magnetic field lines of these pick-up ions has been estimated to be of the order of Mars radius (Luhmann and Kozyra, 1991). Some of these particles reimpact the neutral atmosphere with sufficient energy to generate new ejecta and ballistic particles. The net loss of atmosphere has been estimated in several papers (Jakosky *et al.*, 1994; Kass and Yung, 1995; Johnson *et al.*, 2000) and has been identified as one of the mechanism for loss of Martian water and CO_2. It should be particularly efficient (Johnson and Luhmann, 1998) during the period following the disappearance of the Mars magnetic field which has been estimated to occur before a period of solar intensity 3 times higher than the present intensity (3EUV) defined by Zhang *et al.* (1993). The method for calculating this loss is complex. First, the trajectories of impacting particles need to be calculated between the time of their ionization and the time they are neutralized by charge exchange collisions, which typically occurs above the atmospheric exobase (Luhmann and Kozyra, 1991). This involves describing the draping of the magnetic field around Mars’ ionopause, and the motions of electrons and ions in the vicinity of Mars. The hybrid code developed by Brecht (1997) describes this phase self-consistently.

Second, the trajectories of newly neutralized pick-up ions close to the exobase are tracked in the neutral atmosphere accounting for collisions and gravity. Although the Mars atmosphere near the exobase is primarily O and CO_2 (Bougher *et al.*, 1999), we describe it as purely atomic composed only of O at the correct total atomic density, which is realistic above the exobase. We developed a 3-D Monte Carlo model. Each incident particle ($\sim$keV) is followed in the atmosphere ($\ll$1eV), describing all the collisions until either it reaches a region where the density is so high that it has no effect (around 120 km for Mars) or it again crosses the exobase.

We calculated the loss of atmosphere and the increase in the coronal density due to the bombardment by the flux of pick-up ions suggested by Zhang *et al.* (1993) for the 3EUV epoch. The initial neutral population is described using the results of Bougher *et al.* (1999). We first calculated the heating produced by the O^+ pick-up ions using a 2D Direct Simulation Monte Carlo. This new atmosphere was then

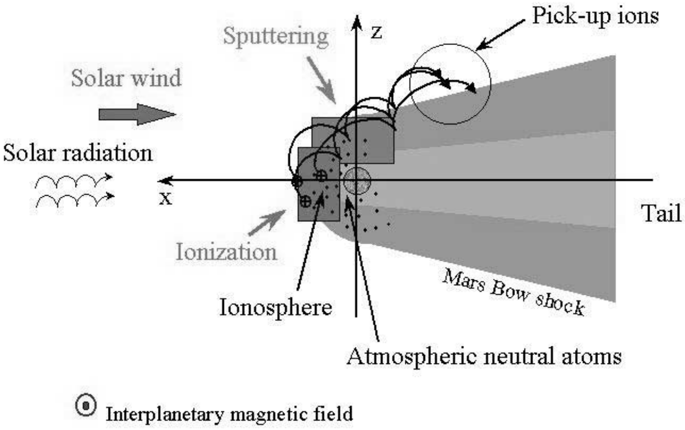

Figure 4. Sputtering of the Mars neutral atmosphere by pick-up ions dragged by the solar wind.

used in the 3D code to calculate the increase of the corona density, considering those recoil particles which have sufficient energy to escape or to populate the upper corona where pick-up ions are formed. In Figure 5, density is seen to be equivalent to that estimated for dissociative recombination of the O_2 molecules for this epoch (Zhang *et al.*, 1992) except in the polar regions. Therefore, feedback will be important because the additional O atoms reaching high altitudes can be ionized by the EUV flux and become pick-up ions reimpacting the neutral atmosphere (Johnson and Luhmann, 1998). Ignoring feedback, the sputtering yield is equal to 3.6 atoms/ion, slightly lower than the 4.2 obtained in a 1D model (Johnson *et al.*, 2000) because of our more accurate description of the collisions above the exobase. We carried out a similar study for the present epoch and then extrapolated to obtain the total loss due to sputtered O atoms over the history of Mars using data in Luhmann *et al.* (1992). We find a loss of the equivalent of 4 m of water, to which should be added the larger loss by ionization in the corona estimated earlier (Luhmann *et al.*, 1992). These calculations show that sputtering is effective primarily because it changes the density in the corona where atoms are ionized and swept away.

5. Conclusions

In many solar system environments space plasmas have been shown to effect the evolution of objects. The bombarding plasma sputters either the surface material or the gravitationally bound gases. This bombardment not only leads to the ejection of

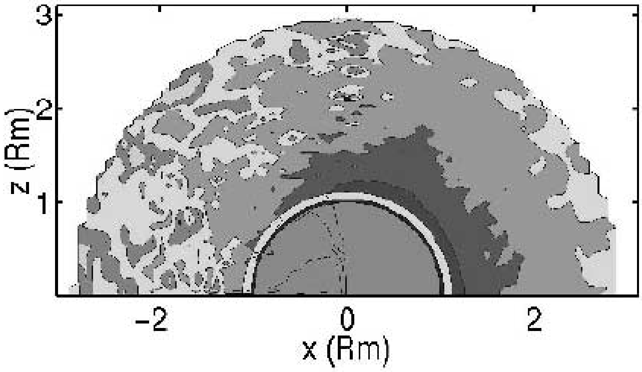

Figure 5. Corona density due to a flux of pick-up ions as defined by Zhang *et al.* (1993) for the 3EUV epoch. The different grays from darker to lighter correspond to 10^4, 10^3, 10^2 and 10^1 particles / cm^3. The sun is at the right of the figure. Mars is the gray half-circle in the center of the figure, the dark half-ring is the atmosphere below 120 km, the clear half-ring the atmosphere where the incident pick-up ions collide with the neutral atmosphere and above this circle the domain is supposed to be collisionless.

atoms and molecules but also to chemistry. Solar wind and solar flare ions sputter grains ejected from comets and the surfaces of the moon and Mercury. Pick-up ions erode the Martian atmosphere and magnetospheric plasma ions erode the atmospheres of Io, Titan and Triton, the surfaces of the other moons and the grains in planetary rings. In this article we briefly described sputtering and how Monte Carlo models can be used to describe observations for a few caes: the surface of Europa is a net source of Na; there is likely missing material in Saturn's magnetosphere; and atmospheric sputtering effects the morphology of Mars' corona and, hence, atmospheric loss by pick-up ion formation. With the recent improvements in space borne ion mass spectrometers, there will be a wealth of new data from CASSINI and from the planned missions to Mars, comets and Pluto. The critical need for interpreting this data will be the availability of good models for the flow of plasma onto an object. In addition, a new laboratory and calculational effort is needed to produce the sputtering and decomposition yields for plasma bombardment of realistic surface materials and for determining collision cross sections in the critical energy regime ($\sim$100eV - 10keV) for ions and neutrals impacting molecules.

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