

## Sputtering of sodium on the planet Mercury

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The discovery of a column density of neutral sodium vapour ( $\sim 10^{11}$ – $10^{12}$  atoms Na cm<sup>-2</sup>) associated with the solar-facing side of the planet Mercury<sup>1</sup> has rekindled interest in the possible presence of atmospheric gases on that planet. Recent observations<sup>2</sup> confirm the presence of Na emission, with its centroid shifted to the sunward limb. The sodium fluorescence is observed in the visible range. Previous ultraviolet observations by Mariner 10 provided evidence for the presence of H and He in the atmosphere ( $\sim 10^{11}$  and  $10^{12}$  atoms cm<sup>-2</sup> respectively<sup>3</sup>) and gave upper limits on other possible species (such as O, Ne, Ar and C). Whereas the H and He can be explained primarily by capture from the solar wind<sup>4</sup>, we show here that this is not so for Na by evaluating the depletion rates. Photon and ion bombardment can release Na from its normal bonding state, producing adsorbed and ejected Na in ballistic trajectories. We show that ion sputtering cannot account for the observed column density but is an important loss mechanism for Na. Photons are likely to be the dominant stimulus, both directly through photodesorption and indirectly through thermal desorption of adsorbed Na. We therefore conclude that the atmosphere produced is characterized by the planet's surface temperature, with the ion-sputtered Na contributing to a lesser, but more extended, component of the atmosphere.

We take the exospheric column density of the observed Na to be  $N \approx \Phi_s \tau$  where  $\Phi_s$  is the supply flux of Na to the 'atmosphere' and  $\tau$  is the lifetime of a Na atom in this atmosphere. If the source is a sputter (desorption) source we can write  $\Phi_s = \Phi_i f \bar{Y}_i$  where  $\Phi_i$  is the stimulating radiation flux of type  $i$ ,  $\bar{Y}_i$  is the surface-averaged yield and  $f$  is the fractional atomic concentration of Na in the surface layer. Table 1 contains our estimates for  $f$ ,  $\Phi_i$ ,  $\bar{Y}_i$  and  $\tau$ , and the resulting column densities for ion and photon sputtering of Na. The calculated column densities are in general smaller than required by the observations, with photon sputtering providing the largest atmosphere. **Surface composition ( $f$ ).** Although the surface composition of Mercury is not well known, analogies are most often made with lunar materials. Based on a typical composition for lunar rocks<sup>5</sup> we estimate the atomic fraction of Na on the surface to be  $f \approx 0.002$ , which implies a surface significantly depleted in alkalis. Sodium is likely to be bound to oxygen (for example, in NaAl<sub>2</sub>Si<sub>3</sub>O<sub>8</sub> feldspar) with a binding energy  $U \approx 2$  eV. If Mercury remained active after formation, this would tend to enhance the concentration of Na-containing minerals in the crust. In addition, meteorite action in the upper metres of the surface can refresh the surface through overturning of the regolith. In the upper centimetres irradiation by energetic particles can enhance the diffusion of Na in and through the surface layer down to the penetration depths of the most energetic ions<sup>6</sup>. For example, under high electron fluxes diffusion of Na is observed in glasses, a likely component of the surface<sup>7</sup>.

Under low-flux, but long-term, ion bombardment the more volatile species would tend to diffuse preferentially to the surface, enhancing the Na concentration, some of which may exist as adsorbed Na. Finally, exogenic sources such as the solar wind and meteoritic material can contribute Na.

Ejected Na atoms recondensing on the surface would generally be adsorbed with reduced bonding to the surface because the initially attached O would make new and/or tighter bonds with the other surface species. On a rough surface of rocky material containing Na the ejection and reabsorption of the species is enhanced twofold over other, less volatile, species<sup>8</sup>. In the presence of a small O atmosphere, on the other hand, the adsorbed Na and O atoms could combine chemically at the surface. There are therefore a number of processes that affect the state of the Na. In the absence of more detailed knowledge of the surface, we used  $f = 0.002$  and  $U = 2$  eV to describe the ejection of Na.

**Sputtering (desorption) yield ( $Y$ ).** When either electronic or collisional energy is deposited by incident radiation, atoms or molecules can be ejected from the surface. We divide the processes in Table 1 into two categories according to the type of energy deposition. The yield depends on the environment of the species of interest (that is, surface composition, roughness (or porosity)<sup>9</sup> and temperature), the energy density deposited near the surface, and the nature of the binding of the species to the surface. At low temperatures and low excitation densities,  $Y$  becomes independent of temperature and linear in the deposited energy density. The yield increases with increasing angle of incidence to the normal, which we ignore to approximately account for roughness. For this minimum-yield case  $\bar{Y}_i = \bar{\Delta z}_i / \lambda_i$ , where  $\bar{\Delta z}_i$  is a weighted sputter depth and  $\lambda_i$  is the mean path between energizing events<sup>10</sup>.

For collisional sputtering by ions,  $\bar{\Delta z}_i$  is proportional to  $U^{-1}$  and  $\lambda_i^{-1}$  is proportional to  $S_n$ , the nuclear stopping (energy loss) cross-section. For a material consisting of atoms of similar masses,  $Y = c \alpha S_n / U$ , where  $c = 4.2 \times 10^{14}$  cm<sup>-2</sup> and  $\alpha$  is a factor depending primarily on the mass of the incident particle<sup>11</sup>. We use  $\alpha = 1$  and  $S_n = 5 \times 10^{-16}$  and  $3 \times 10^{-15}$  eV cm<sup>2</sup> for H and He respectively. This sputtering process is characterized by an energy spectrum of the ejected Na of the form  $E/(E+U)^3$ , which determines the ballistic flight times and the gravitational escape fraction.

Sputtering due to the electronic energy deposited by ions, electrons and photons occurs when this energy produces, directly or indirectly, repulsive states between a surface atom and a neighbour. Here  $\lambda_i^{-1} = n \sigma_i$ , the atomic number density times the excitation cross-section. As ejection occurs from the first monolayer,  $\bar{\Delta z}_i \approx P_e n^{-1/3}$ . Because electronic recombination of a localized ionization in insulators occurs repulsively,  $\sigma_i$  is roughly the 'ionization' cross-section for the binding electrons and  $P_e \approx 0.1$  (refs 10, 12-15). For electron-stimulated desorption ( $\sim 50$ -eV electrons,  $\sigma_i \approx 10^{-16}$  cm<sup>2</sup>), using  $n^{2/3} \approx 2 \times 10^{15}$  atoms cm<sup>-2</sup> gives  $Y \approx 0.02$ , consistent with the results for desorption of Na from alkali halides<sup>13</sup>. For energetic ions  $\sigma_i \approx S_e / W$ , where  $S_e$  is the electronic stopping cross-section ( $S_e = 3 \times 10^{-15}$  and  $2 \times 10^{-14}$  eV cm<sup>2</sup> for H and He, respectively) and  $W$  ( $\sim 20$ – $30$  eV) is the mean energy required to produce an electron-hole pair at an oxygen site. For solar photon-stimulated desorption we can use the photodissociation rate ( $J$ ) of, for instance, NaO<sub>2</sub>

Table 1 Sputtered atmospheric column densities

	Collisional sputtering			Electronic sputtering		$h\nu$
	H <sup>+</sup>	He <sup>2+</sup>	H <sup>+</sup>	He <sup>2+</sup>		
$\bar{Y}_i^*$	$\sim 0.1$	$\sim 1$	$\leq 0.04$	$\leq 0.02$	} $\leq 10^{10}$ – $10^{11}$	
$\Phi$ (cm <sup>-2</sup> s <sup>-1</sup> )	$\sim 10^8$ – $10^9$	$\sim 10^7$ – $10^8$	$\sim 10^8$ – $10^9$	$\sim 10^7$ – $10^8$		
$N$ (atoms Na cm <sup>-2</sup> )†	$2 \times 10^7$ – $2 \times 10^8$	$2 \times 10^7$ – $2 \times 10^8$	$\leq 10^7$ – $10^8$	$\leq 10^6$ – $10^7$		$\leq 2 \times 10^{10}$ – $2 \times 10^{11}$

\*  $U = 2$  eV was used as a rough estimate of the chemical binding energy. The estimates ignore the possibility of adsorbed Na and enhancements due to higher surface temperatures.

†  $N$  obtained from Eqs (1) and (2) with  $f = 0.002$  and  $\tau = 10^3$ .

to estimate  $\bar{Y}\Phi_i$ . At Mercury,  $\Phi_i\sigma_i = J = 10^{-3}$ - $10^{-4}$  s $^{-1}$  (ref. 16), which is used with  $P_e$  above. We also combine the appropriate solar photon flux with the extrapolated photodesorption yields from the work by Tolk and Larchuk<sup>13</sup> on NaCl, to find an estimate of  $\bar{Y}\Phi_i$  consistent with the lower value of  $J$  above.

A warm surface, such as the sunlit hemisphere of Mercury, can increase the electronic desorption yield beyond the values given here<sup>17</sup>. For temperature  $T$ , the yield can be written as  $Y[1 + A \exp(\Delta E/kT)]$ , where  $\Delta E$  is an activation energy ( $\sim 0.2$ - $0.4$  eV for liberated Na from alkali halides<sup>13,14</sup>). In effect, the penetrating ions and photons dissociate species within the solid and cause the segregation of the more volatile species at the surface. This is known to occur for many alkali-containing species<sup>13,14,17,18</sup>. For the case we are considering, the Na and O (it would be N in an azide, halide in an alkali halide) would be energetically separated by the process described above and the Na would be desorbed later. That is, subsequent bombardment enhances the transport of Na to the surface and the ejected atoms would have an energy distribution which is primarily characterized by the surface temperature with a small energetic contribution determined by direct repulsive ejection. This is also consistent with the observations for a porous surface<sup>8,9</sup>.

**Lifetime ( $\tau$ ).** In a ballistic atmosphere ( $\approx 3 \times 10^{15}$  atoms cm $^{-2}$ ) above a surface, the lifetime of an ejected neutral species is determined by its average time of flight or the ionization rate. The average solar photoionization lifetime at Mercury is  $\tau_i = 8,000$  s (refs 19, 20). We assume 2 kT as an average desorption energy for electronic sputtering, giving  $\tau_e = 500$  s. For collisionally ejected atoms of mass 23, use of the average energy  $\frac{1}{2}U$  gives  $\tau_c = 1,000$ - $2,000$  s. Solar radiation pressure on the Na can reduce these times considerably, depending on the distance from the Sun<sup>20,22</sup>. On the other hand, the sputtered species will probably not fully accommodate to the warm surface on their return<sup>23</sup>. Studies by Hapke and co-workers<sup>8,9</sup> indicate that the relative sticking coefficient for Na onto silicate (the major constituent of the lunar regolith) is very small ( $\sim 0.05$ - $0.24$ ). The lifetime of a particle may therefore be an order of magnitude larger than the ballistic lifetime, in which case ionization limits the lifetime of Na. In the following, we use a conservative average  $\tau$  of order  $10^3$  s.

**Particle radiation ( $\Phi$ ).** Ions and electrons can potentially impact the surface of Mercury in several ways. We discuss the two most important processes here.

(i) Nominal solar-wind particles ( $n = 50$  cm $^{-3}$ , 95% 1 keV H $^+$  and 5% 7 keV He $^{2+}$ ) can be expected to impact directly on the surface approximately 6% of the time<sup>4</sup>. The largest contribution hitting the planet, however, comes from the precipitation of solar-wind particles through the expected cusps in the magnetosphere and along 'closed' field lines, to which the particles have access by diffusion and/or by reconnection processes at the magnetopause. Based on estimates given by Goldstein *et al.*<sup>4</sup> we take the total particle flux incident on the surface from these processes as  $\approx 1.5 \times 10^8$  cm $^{-2}$  s $^{-1}$ .

(ii) Energetic particles produced in substorm-like processes in the magnetosphere, primarily in the planet's magnetotail, can be directed inward and guided along magnetic field lines toward the polar regions. These particles can also be diffused radially across night-side field lines rather easily by the existing plasma-wave turbulence until they reach the point where their finite gyroradii cause a direct impact on the planet. This process is more difficult to estimate because relatively little is known about Hermean substorm processes other than the measurements of energetic electrons (and possibly ions) made by Mariner 10 (ref. 24). The Helios-2 spacecraft reportedly made measurements of energetic protons ( $\sim 87$ - $176$  keV) that escape from the Hermean magnetosphere<sup>25</sup>. These particles were attributed to substorm activity and/or escape from the 'radiation belt'. Extrapolated to the planet's bow shock, the flux of these particles was  $\sim 3 \times 10^4$  cm $^{-2}$  s $^{-1}$  ster $^{-1}$  or  $3 \times 10^5$  cm $^{-2}$  s $^{-1}$  omnidirectional. If we assume the front-side bow shock to be the surface of a sphere with radius  $\sim 3R_M$  (the dawn- and dusk-side distances are larger

than the subsolar distance) and that these particles cover a hemisphere, the fluxes can be extrapolated to the planet's dimension. We can reasonably assume that an equal number of substorm, magnetotail-produced particles can impact the night side of the planet; the fluxes would then be  $\sim 3 \times 10^6$  cm $^{-2}$  s $^{-1}$ . If the spectrum of accelerated ions varies as  $E^{-2}$  to  $E^{-3}$ , then the flux of  $E \approx 10$  keV protons available to impact the surface would be of order  $3 \times 10^8$  cm $^{-2}$  s $^{-1}$ , or possibly as high as  $10^9$  cm $^{-2}$  s $^{-1}$ . The total proton flux used is then approximately  $10^8$ - $10^9$  cm $^{-2}$  s $^{-1}$ . More energetic particles from an active Sun can penetrate the magnetic barrier efficiently. However, we estimate their net effect to be insignificant.

As can be seen from Table 1, unless the quantities estimated above are changed drastically, ion sputtering, originally suggested by Potter and Morgan, cannot account for the observed column density. The UV photo-desorption process, which is the least reliable estimate at present, gives the largest column density. Longer-wavelength photons can also contribute to this column density by thermal stimulation of Na. This is equivalent to assuming that the accommodation to the surface is not unity. If the Na is indeed chemisorbed to the surface (rather than chemically bonded to O) then thermal desorption is likely to be an efficient means of producing the observed column density. Therefore photons, via photo desorption and thermal desorption, are likely to account for the observed column density. However, the impacting ions also play an important role because they enhance the diffusion of Na to the surface and separate Na from O. We note that in this process a related amount of O will also be released. As returning O atoms will more efficiently accommodate to the surface, a column density of O  $\leq 10^{11}$  cm $^{-2}$  is expected, within the limits set by Mariner 10 (ref. 26). We therefore suggest that the Na atmosphere is characterized by the surface temperature of Mercury, with a smaller and much more extended component produced by ion sputtering.

We can now estimate the loss of Na from Mercury. The escape fraction from the atmosphere due to electronic sputtering is negligible. Based on the energy distribution given above, this fraction is  $\sim 0.7$  for collisional sputtering. This produces a loss rate  $\sim 10^5$ - $10^6$  Na cm $^{-2}$  s $^{-1}$ , which is fairly independent of the binding assumed. Atmospheric Na is also lost by ionization. That is, the Na $^+$  can reach open magnetic field lines and be lost from the atmosphere and magnetosphere<sup>4</sup>. Here we write the escape flux as  $\beta N/\tau_i$  where  $\beta$  is the fraction of Na $^+$  that can access open field lines and  $\tau_i$  is the lifetime of the Na against ionization as given above. For He,  $\beta = 0.5^4$ . The larger mass and the solar radiation pressure imply lower ballistic trajectories for Na. We therefore use  $\beta \leq 0.1$ . From the observed column density, the depletion due to ionization processes ( $\sim 10^6$  Na cm $^{-2}$  s $^{-1}$ ) and collisional sputtering (above) are roughly comparable. Consequently, both the character of the magnetic field at Mercury and the ballistic transport of Na are important for the Na loss.

Sodium has not been specifically identified in the solar wind. If its abundance is similar to the identified elements such as Mg, Ne or Si<sup>27-29</sup>, then its total fractional content of the solar wind would be  $\sim 10^{-4}$ . This supply rate ( $< 10^5$  Na cm $^{-2}$  s $^{-1}$ ) is much less than the total loss rate of Na from Mercury. Therefore, unlike the He atmosphere, the presence of a Na atmosphere implies that Mercury is being depleted in Na at a rate equivalent to a loss in  $10^9$  yr of all of the Na in the top 1-10 m, based on  $f = 0.002$ . This would suggest a transport mechanism in the upper layers of the planet, such as recycling by micrometeorites, to maintain a Na concentration at the surface, and/or an exogenic source such as micrometeoritic material. Although ion bombardment does not produce the observed atmosphere it is likely to be important in determining the depletion rate of Na and hence in helping to constrain models for Mercury's surface.

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