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Diurnal variation of sodium and potassium at Mercury

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Abstract–A summary is given of our published observations showing a large (3 to 4) morning/afternoon ratio of the abundances of sodium and potassium. The proposed mechanism is deposition of ions and atoms on the cold night side, followed by their outward diffusion and evaporation as the Sun rises. Published criticisms of this mechanism are discussed and answered. The rate at which Na atoms can evaporate from the surfaces of the Moon and Mercury is uncertain, but, after a review of laboratory measurements, we propose that it is substantial at temperatures of 400 K and higher. Possible reasons are discussed why another group does not find the diurnal variation. There are differences in observing geometry, but the matter remains unclear.

INTRODUCTION

The atmospheres of the Earth, Mercury, and the Moon contain sodium and potassium ablated from meteoritic material that is heated on passage through the atmosphere (in the case of the Earth) or volatilized from meteoritic and regolith material upon impact (in the case of Mercury and the Moon). At the Earth the Na and K are largely confined to a layer at ~90 km in altitude where the major effect of ablation occurs. Subsequent chemistry then maintains a thin region of atoms, and at lower altitudes processes the atoms into more complex molecules which eventually fall to the ground in rain or are adsorbed on to dust. At the Moon and Mercury, where the atmosphere is less than a picobar, atoms are liberated at the surface and then migrate about in ballistic hops until they are ionized and swept away in electric fields in the solar wind or adsorbed on to cool surface materials. Ground-based telescopic spectroscopy is used to determine the abundance, distribution, and character of the Na and K atmospheres in an effort to determine their sources, behavior and sinks.

The presence of large morning maxima in the abundances of both sodium and potassium was seen by Sprague *et al.* (1997). In an earlier publication (Sprague, 1992) of the potassium data, the suggested mechanism was implantation of ions on the night side, followed by release after dawn as the surface was warmed by the Sun. Migration of atoms across the terminators and deposition on the night side is also likely.

Killen and Morgan (1993a,b) published two papers criticizing this model and presenting an analysis whose result was that it could not produce a morning/afternoon ratio greater than a factor of 3. The first paper also suggests that the rate of evaporation of Na atoms after sunrise is unacceptably fast, so that the morning maximum would be confined to a very narrow region just on the sunlit side of the dawn terminator. The second presents an analysis claiming that the rate of thermal evaporation back into the atmosphere (an integral part of the mechanism proposed by Sprague, 1992) is too slow to be important and implying that ion sputtering is required. An examination of their published sodium data for Mercury showed no morning enhancement, but a small afternoon one. In this paper we reconsider these matters. The claimed upper limit does not exist. Laboratory measurements obtained more recently do indicate a substantial evaporation rate of Na from a surface of SiO_2 at 400 K. As for the discrepancy in the measured morning/afternoon ratio, we surmise that it may be related to differing techniques of observation and data analysis, but it is still puzzling.

The following paragraph summarizes the discussion by Hunten *et al.* (1988) of the source and behavior of atoms in Mercury's atmosphere. The source may be meteoroid bombardment, releasing atoms from the impactor and the surface materials, or diffusion from deeper levels, followed by release by thermal evaporation, charged-particle sputtering, or photon-stimulated desorption (PSD), sometimes called "photosputtering". Once released into the atmosphere, an atom executes a ballistic orbit to some nearby point on the surface, from which it may be reflected or adsorbed and re-emitted. The duration and length of each hop are ~250 s and 120 km for Na at a temperature typical of the day side, somewhat larger for suprathermal atoms and smaller for thermal K atoms. While in the atmosphere an atom may be photo-ionized and either recycled to the surface or lost to the solar wind. The efficiency of recycling may be 0.5 or somewhat greater. The number of hops before ionization is ~40.

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TABLE 1. Variations of Na and K through the day.*

Element	Early morning	Morning	Midday	Afternoon	Late afternoon
Na	17 (19)	17 (16)	13 (11)	7 (3)	5 (3)
Na*	13 (6)	14 (10)	13 (11)	7 (3)	5 (3)
K	–	118 (97)	–	27 (10)	–

Sodium abundances in units of 10^{10} atoms cm^{-2}; potassium in 10^7 atoms cm^{-2}. For the Na line, the data from May 1988, frame 251, were omitted.

DIURNAL VARIATIONS OF SODIUM AND POTASSIUM

The observed data for the diurnal variations were presented and discussed by Sprague *et al.* (1997). Their Figs. 4 and 5 show the individual points and the averages. For the reader's convenience these averages are repeated here in Table 1, to which we have added in parentheses the standard deviations, which are rather large. A second line repeats for Na these quantities with four data points omitted. These points show the largest Na abundances ever observed and must represent some unusual circumstance. Figure 3 of Sprague *et al.* (1997) shows how the planetary image fell on the spectrograph slit in such a way that one-dimensional spatial resolution was obtained, though blurred by astronomical "seeing". The amount of the blur could be obtained by analysis of parts of the spectrum other than those containing the emission lines. The sodium data were then corrected for the blur. This could not be done for the potassium data, which had been obtained and analyzed several years earlier. The sodium data shown in the table were selected to represent equatorial and low latitudes in five zones of local time; the smaller set for potassium is shown in two zones. It can be seen that the morning/afternoon ratios are large: >3 for sodium and 4 for potassium. Not shown is the fact that for potassium there is no overlap between the individual morning and afternoon results.

A similar effect has been seen for Ar on the Moon (Hodges *et al.*, 1974). There the landed mass spectrometer was unable to make measurements during the day because of gases released from other hardware in the vicinity, but a dawn maximum could still be seen. The measurements were quantitatively explained by condensation on the cold night side and evaporation as the Sun rose.

As mentioned above, Sprague (1992) suggested that the potassium results could be explained by implantation and neutralization of ions from the magnetotail on the night side, with release back to the atmosphere as the ground warmed up after sunrise. We note that this mechanism is likely to be supplemented by a mechanism similar to that for lunar argon, transport of atmospheric atoms across the morning and evening terminators and deposition on the cold night side.

Killen and Morgan (1993a) presented a model whose result was that the morning/afternoon ratio from Sprague's mechanism could not exceed 3. Our version of this model does not give this limit; we shall first present it and then comment on the difference. The total contents of K or Na atoms in the morning (A.M.) and afternoon (P.M.) sectors are represented by a and p. These atoms are photo-ionized with a lifetime τ, so that the loss rates (s^{-1}) of atoms from the two sectors are a/τ and p/τ. If f is the fraction of ions recycled to the night side, the deposition rate there is

$$f(a+p)/\tau \qquad (1)$$

Even in the absence of recycling, there is a source of atoms to the day side atmosphere, which would be the same for each sector and equal to p/τ, the loss rate from the afternoon sector. The algebraic sum of the gains and losses to the morning sector should be equal to zero; thus,

$$-\frac{a}{\tau}+\frac{p}{\tau}+\frac{f(a+p)}{\tau}=0 \qquad (2)$$

$$\frac{a}{p}=\frac{1+f}{1-f} \qquad (3)$$

As f approaches 1, this ratio approaches infinity, which is reasonable because all the atoms produced in both sectors are fed back to the morning one.

The derivation by Killen and Morgan (1993a) differs in Eq. (1), where they use the average of a and p instead of the sum. Mathematically this assumption is equivalent to limiting the recycling fraction f to 0.5, which does give 3 as the largest value of a/p in Eq. (3).

Another important factor influencing the source and release of both Na and K from the surface is the strong variations of insolation caused by Mercury's spin-orbit resonance (Soter and Ulrichs, 1967). The influence is particularly large near Mercurian longitude 265°, where the height of the Sun above the horizon does not exceed 10° until just after 9.4 h local time on Mercury (24.9 Earth days after sunrise). This effect has not been taken into account in any published studies of the distribution of Na or K near the dawn terminator.

TIME DEPENDENCE; SLOPE DISTRIBUTION

Another comment by Killen and Morgan (1993a) is that the implanted atoms should diffuse out of the surface layer so rapidly after local sunrise that any morning enhancement would be confined to a very narrow region bordering the terminator. They do not explain why this should be a problem for the mechanism; perhaps such confinement was assumed to make the phenomenon hard to observe. Although we agree that the release would be very rapid as soon as the Sun illuminates a given area, other effects will spread the morning enhancement over a much wider range of local time after sunrise:

(1) Mercury's surface is not a perfectly smooth sphere, rotating uniformly with respect to the Sun, as was assumed by Killen and Morgan; areas sloping away from the Sun are not illuminated until the Sun is well above the local horizon;

(2) After atoms are released, they hop around, executing a considerable number of hops (the estimate of 40 mentioned above is by by Hunten and Sprague, 1997) and therefore spread well away from their source before they are ionized and lost.

The slope distribution may be estimated by use of an equation given by Hapke (1984). His theory contains several parameters that can be selected to fit photometric observations of a planet, obtained over a wide range of angles of illumination and observation. Among these parameters is the mean slope $\bar{\theta}$, found to be 21° by Veverka *et al.* (1988). This mean slope appears in Hapke's Eq. (44) which gives the slope distribution, shown here in Fig. 1. The maximum area per increment of solar elevation, and therefore the maximum rate of release of atoms, occurs at a solar elevation angle of nearly 30°, and the release continues to 60°, one-third of the Mercury day at the equator. At higher latitudes the delay is even greater. This result has several limitations, but still shows that the effect of the slope distribution is large. Half the sloping regions face towards the Sun rather than away from it, and these areas presumably release their implanted atoms within a few Earth days of sunrise for a level surface.

The second effect, spreading away from the source, may be treated as a random walk. The hop distance is approximately twice the scale height; the latter is 30–100 km for Na at temperatures of 300–1000 K. For 40 hops the mean spreading distance is $2\sqrt{40}$ scale heights, or 400–600 km. The larger distance is almost half of the planetary radius. The same estimate describes migration of the atoms from the day to the night sides, except that on the cold night side they may stick after only a few hops.

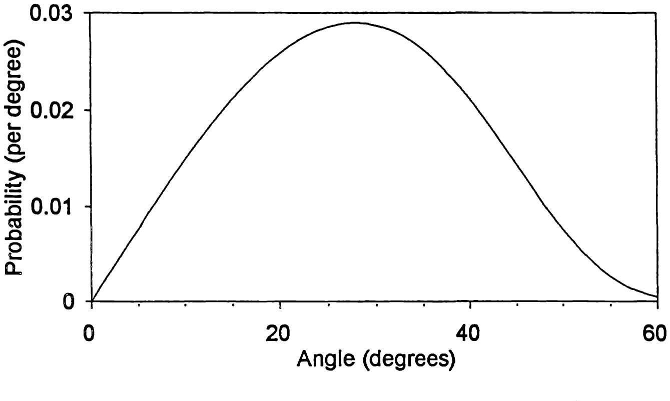

FIG. 1. One-dimensional slope distribution obtained by fitting the model of Hapke (1984) to observed photometric data. For example, the probability of a slope between 28 and 29° is ~0.029.

DIFFUSION; EVAPORATION RATE

The mechanism of Sprague (1992) assumes two populations of K (and Na) atoms in the soil: the diurnally varying component that is implanted on the night side and the unspecified source that is present everywhere and is responsible for the mean atmosphere. Killen and Morgan (1993a) suggest that half or more of the implanted atoms will diffuse away into a grain and away from its surface, and not enter the atmosphere. This idea depends, as they note, on the boundary condition at the surface, which we discuss below. But in any case, it is not appropriate to consider the effect of only a single diurnal cycle. After the first cycle half the atoms should indeed diffuse inward. In the second morning they will still be there, and will be joined by more atoms; after many cycles the density below the implanted layer will approach that of the layer itself. From then on, to a good approximation all the atoms implanted during the night will be released to the atmosphere. In truth, half of them still move downwards, but they are replaced by atoms from below that have survived from previous cycles.

The rate of evaporation of sodium and potassium atoms is a key factor in any explanation of the morning maximum. The vapor pressure of Na metal can be expressed in terms of number density as:

$$n = Ae^{-B/T} \tag{4}$$

with $A = 8.4 \times 10^{23}$ atoms cm^{-3} and $B = 12\,163$ K. The corresponding evaporation rate is $n\bar{c}/4$, where $\bar{c}$ is the mean thermal velocity. In a study of lunar Na, we had suggested (Sprague *et al.*, 1992) that atoms are bound to the surface with an adsorption energy of ~1.1 eV, which corresponds to $B = 12\,800$ K. This value was chosen, quite independently of the vapor pressure of the metal, to fit our observations of a small thermal component in the vertical distribution, confined to the warmest region in the vicinity of the subsolar point. Elsewhere the atoms have a considerably faster velocity distribution and are observed to reach much higher altitudes. Release of these atoms was attributed to PSD. Similar results have been obtained in more recent observations (Sprague *et al.*, 1998). The model of Sprague *et al.* (1992) yields amounts of adsorbed Na atoms, at five latitudes, equal to (5 to 38) × 10^{-6} atoms cm^{-2}. The average if these values is ~2×10^{-8} of a monolayer, which is ~10^{-15} atoms cm^{-2}. Other matters discussed include the hopping of atoms around on the surface and their partitioning between the atmosphere and the surface layer; these processes, which had been discussed in earlier papers such as Hodges *et al.* (1974) and references therein, are as relevant to Mercury as to the Moon. The ideas just summarized seem reasonable to us, because they explain the component with a low scale height in the atmosphere near the subsolar point of the Moon. However, as discussed below, the observations can be satisfied just as well by a slower evaporation rate combined with a greater coverage of the surface layer.

These concepts have been generally confirmed by laboratory studies, although both evaporation and PSD were found to be slower. Desorption of alkali atoms from planetary surfaces is discussed by Madey *et al.* (1998), and evaporation of sodium atoms from a surface of SiO_2 has been measured by Yakshinskiy *et al.* (2000). A layer of Na atoms was deposited on the surface; different thicknesses were used for different experiments. Here we refer to the results for 0.4 of a monolayer, shown in their Fig. 9. One important conclusion was that the Na atoms diffuse into and out of the silica layer and do not remain as a separate deposit on the surface. At a heating rate of 7 K s^{-1}, desorption begins to be detectable at 400 K; the rate rises as the temperature increases further, and peaks at 700 K. They also find that most of the atoms do not simply reside on the surface, but are bound with an energy corresponding to the temperature for the maximum rate. They present a simple model of the desorption, which gives a result for the evaporation rate of the same form as Eq. (4) with $A = 10^{-13}$ s^{-1} and $B = 1.85$ eV or 21 500 K. The position of the observed peak is matched, but the width in the model is too narrow. (Presumably the reason for the fall-off of the rate above the peak is that the thin layer is becoming depleted.) In discussion, Yakshinskiy *et al.* are unable to account quantitatively for the discrepancy, but "conclude tentatively that diffusion into and out of the SiO_2 film influences the rate of desorption of Na in these experiments, but it may not be the dominant factor reflecting the peak width and shifts".

The rate of PSD has also been measured by Yakshinskiy and Madey (1999, 2000). For the value of the solar flux at the Moon they find the release rate per Na atom to be 6×10^{-6} s^{-1}, varying as the cosine of the solar zenith angle.

For application to the Moon and Mercury we are interested in thermal evaporation in the 400–500 K region. In private discussion Madey has suggested that the small signal found there may be affected by desorption from the (warmer) sample support leads. He prefers to assume $B = 1.4$ eV or 16 200 K; the desorption rate at 400 K is 2.5×10^{-5} s^{-1} and the lifetime is half an Earth day. To explain the two components in the lunar atmosphere the coverage would have to be 2×10^9 cm^{-2}, greater by a factor of 100 than was obtained by Sprague *et al.* (1992). At Mercury, Na (and presumably K) atoms should leave the surface of a grain within hours or a few Earth days of sunrise at the local surface, with account taken of the distribution of slopes and the effect of latitude. If the atoms were implanted on the night side, and not just condensed, their outward diffusion is similarly rapid. With such large evaporation rates, there will be a very small surface coverage of atoms that can be released by PSD or charged-particle sputtering. A significant coverage only remains in locally shaded regions such as parts of deep craters tilted away from the Sun, especially at high latitudes.

In contrast to the coverage obtained above for the Moon, Killen and Morgan (1993b) chose to assume the much larger value of 3.4×10^{13} atoms cm^{-2}, or 3.4% of a monolayer, corresponding to a bulk number density of 2×10^{20} atoms cm^{-3}. This assumption can be true only if the loss of sodium atoms to the atmosphere has not depleted the exposed surface of the grains. Adopting an upper limit to the loss rate of 10^6 cm^{-2} s^{-1}, Killen and Morgan found that the probability to evaporate per unit time and per sodium atom was $<10^{-7}$ s^{-1}, for a temperature of 400 K. The same limit would apply to the rate of PSD. These authors prefer charged-particle sputtering as the source, and their large coverage is required to make this process viable. We prefer the smaller coverage derived above from the arguments of Sprague *et al.* (1992), which is consistent with the rates of evaporation and PSD obtained in the laboratory. The observations of Mendillo *et al.* (1999) argue strongly against charged-particle sputtering as the principal source, because they see an undiminished sodium atmosphere during total lunar eclipses when the Earth's magnetosphere shields the Moon from the solar wind.

DISCUSSION

Why do other observers not find the diurnal effect? It is large in our data, in spite of the fluctuations that are typical for Mercury. Killen and Morgan (1993a) discuss a small data set that shows very little diurnal variation and in fact has a small afternoon maximum. More recent observations by the same group (Potter *et al.*, 1999, and references therein) emphasize imaging of the sodium brightness over most of the disk, and tend to be taken when the planet is near superior conjunction when the regions near the morning and evening limbs are greatly foreshortened. The images are highly processed to sharpen the detail, and this processing is not aimed at producing good photometry near the limbs. The use of a solar telescope makes these observations possible when Mercury is close to the Sun in the sky. Our observations have been made with an astronomical telescope when Mercury was near greatest elongation from the Sun, and one or the other terminator was near the center of the disk. There is no obvious reason why these differences should be responsible for the discrepancy, but we are unable to find any other.

We have shown that the class of mechanism proposed by Sprague (1992) can in principle generate an arbitrarily large morning/evening abundance ratio. This process, deposition of ions on the night side from the magnetospheric tail, is probably supplemented by the hopping of atoms from the day side and condensation on the cold night side, like Ar atoms on the Moon. Radiation pressure, though small compared to gravity, will cause atoms to be driven across both evening and morning terminators to the night side. Atoms deposited on the surface or implanted just below it diffuse both outward and inward, as pointed out by Killen and Morgan (1993a), but it is necessary to take account of the ones that remain from previous diurnal cycles. The extremely small evaporation rate derived by Killen and Morgan (1993b) depends on the assumption that the coverage of sodium atoms on the lunar surface is large, corresponding to a bulk mass mixing ratio of several percent. If, as we believe, the coverage is orders of magnitude smaller, the derived evaporation rate rises by the same factor. The laboratory experiments of Yakshinsky *et al.* (2000) do indicate a substantial rate in the 400 K region, but temperatures this low were not the emphasis of their experiments.

It should always be kept in mind that there are at least two distinct populations of Na and K atoms on the surfaces of Mercury and the Moon: adsorbed ones that can thermally evaporate on short timescales except for temperatures colder than 300 K; and chemically-bound ones whose release requires a process such as impact of a charged particle, a micrometeorite, or a sufficiently energetic photon.

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