Energy Distributions for Desorption of Sodium and Potassium from Ice: The Na/K Ratio at Europa

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The sputtering and decomposition of the surface of Europa by fast ions and electrons lead to the production of an atmosphere containing sodium and potassium atoms. Here time-of-flight energy distributions are measured for Na and K sputtered from a vapor-deposited ice by 200-eV electrons. These data are then used in a Monte Carlo simulation for alkalis in Europa’s atmosphere. Na/K ratios versus distance from Europa are calculated and compared to the recent observations in the range 6 to 18 Europan radii from the surface. Normalizing to the observations, the Na/K ratio for the loss rates is ∼27 and the ratio for the average surface source rates is ∼20. These ratios are very different from the Na/K ratio at Io and are larger than the Na/K ratio suggested for Europa’s putative subsurface ocean, consistent with fractionation on freezing and upwelling of ocean material. © 2002 Elsevier Science (USA)

Key Words: Europa; surface; satellite; atmosphere; composition.

1. INTRODUCTION

Sodium and potassium atoms escaping from a number of Solar System objects are seen via their resonance lines near the peak of the solar spectrum. Early observations of Na near Io (Brown and Chaffee 1974) were the first indication that a moon of Jupiter had an escaping atmosphere (Matson et al. 1974). Subsequently, Na was seen at Mercury (Potter and Morgan 1985), the Moon (Potter and Morgan 1988), and more recently, Jupiter’s moon Europa (Brown and Hill 1996). Whereas photodesorption appears to be a primary desorption process at the Moon and Mercury (Yakshinskiy and Madey 1999, Mendillo et al. 1999), Europa’s surface is exposed to an intense flux of energetic ions and electrons trapped in Jupiter’s magnetic field (Cooper et al. 2001, Paranicas et al. 2001). This causes electronically induced decomposition and sputtering of the surface (Johnston 1990, Johnson and Quickenden 1997, Madey et al. 1998). Therefore, the ultimate source of sodium and potassium for Europa’s atmosphere has been suggested to be the radiation-induced decomposition of a surface brine (Johnson 2001). This is thought to be material from Europa’s putative underground ocean which may have reached the surface at various times in the past. If this is the case, then the sputter-produced atmosphere should contain other species from this ocean which might be detected by remote sensing (Johnson et al. 1998), an exciting prospect. Alternatively, the observed Na and K atoms in Europa’s atmosphere could be material from Io implanted into Europa’s surface and subsequently sputtered (Brown and Hill 1996).

The observation of alkalis at Europa is consistent with models suggesting that Europa has frozen, hydrated salts on its surface (Fanale et al. 1974, Kargel 1991, McCord et al. 1999, 2001, Zolotov and Shock 2001). Charged particle irradiation can preferentially deplete such materials of sodium (Wiens et al. 1997, Chrisey et al. 1988, Madey et al. 1998), leaving behind, for instance, the frozen hydrated sulfuric acid (Johnson 2001) suggested by Galileo spacecraft data (Carlson et al. 1999). Most of the ejected sodium atoms return to the surface but their large excursion distances lead to redistribution across the surface of Europa. This populates the icy regions of Europa with alkalis as would implantation from the jovian plasma or micrometeorites. Therefore, measurements of the desorption of alkalis from an ice surface are needed.

Yakshinskiy and Madey (2001) measured the electronically stimulated desorption efficiency of potassium from an ice surface as well as the mean ejection energy. In this paper we present
the first laboratory measurements of the energy distributions for electronically stimulated desorption (sputtering) of sodium and potassium from ice. These data are used in a recently developed Monte Carlo simulation for a sputtered-produced atmosphere at Europa (Leblanc et al. 2001). The dependence of the sodium and potassium densities versus distance from Europa’s surface is calculated and used to obtain the Na/K ratio in Europa’s atmosphere. These are compared to the ratios obtained from Brown’s (2001) observations. In this manner the relative surface source rates for Na and K are determined and the Na/K ratios in the optical layer and at depth are estimated. It is found that the ratio of the loss rates is somewhat larger than the solar abundance ratio (e.g., Allen 1991) and is larger than the proposed concentration ratios suggested for Europa’s ocean, consistent with fractionation during upwelling (Kargel 1991, Zolotov and Shock 2001). It is also very different from the Na/K ratio at Io, in agreement with Brown’s (2001) conclusions.

2. LABORATORY SIMULATION

The experimental measurements were performed at Rutgers University in an ultrahigh vacuum environment. We dose the surface of an amorphous ice (formed by vapor deposition onto a metal substrate held at 100 K) with Na and K atoms from SAES Getters sources (Yakshinskiy and Madey 2001). Upon adsorption of the alkalis, electron transfer to the ice forms solvated Na$^+$ and K$^+$ in the surface and subsurface layers (Barnett and Landman 1993, Fuke et al. 1999) as indicated by X-ray photoelectron spectroscopy (Yakshinskiy and Madey 2001). In Europa’s icy equatorial regions sublimation occurs and elsewhere the bombarding plasma produces H$_2$O vapor by sputtering the ice-rich regions. As essentially all of the sublimed H$_2$O and $\sim$80% of the sputtered H$_2$O return to the surface (Johnson 1990), Europa’s surface layer is formed by vapor deposition as in the laboratory experiment. In addition, most of the Na and K atoms that are desorbed or sputtered from Europa return to the surface, and a large fraction of those adsorb in ice-rich regions (Johnson 2000). Therefore, the procedure for formation of the laboratory samples roughly reproduces the atmospheric Na or K absorbed on ice grains in Europa’s regolith. The results here may also be representative of loss of alkalis from the hydrated minerals on Europa’s surface, but the dominant source of atmospheric alkalis is sputtering (desorption) from ice-rich regions (Johnson 2000).

At temperatures on the order of 100 K, the solvated alkalis have a relatively low diffusion rate so the adsorbed alkalis would typically be surficial. However, diffusion of the adsorbed or intrinsic alkalis is enhanced under charged-particle irradiation. This irradiation-enhanced diffusion is important in maintaining a surface population of alkalis (McGrath et al. 1986) but it also makes the laboratory measurement of the absolute desorption cross section difficult.

Photodesorption is the likely dominant steady-state source of the lunar sodium atmosphere (Yakshinskiy and Madey 1999), based on the measured photodesorption cross section and energy distributions. In contrast, electronic sputtering by the fast ions and electrons is believed to be the dominant source of desorbed alkalis at Europa (Johnson 2000, Johnson et al. 1998). That is, the jovian charged particle energy flux to Europa’s surface is dominated by energetic (>10 keV) protons and electrons (Cooper et al. 2001, Paranicas et al. 2001). These incident particles primarily produce secondary electrons from a few eV to $\sim$1 keV (average energy $\sim$50 eV). Since desorption of alkalis from ice exhibits a threshold less than $\sim$4 eV, with the yield increasing with increasing electron energy (Yakshinskiy and Madey 2001), the secondary electrons act to desorb alkalis. The desorption mechanism has been described by Yakshinskiy and Madey (1999, 2001). It involves electron transfer to adsorbed ionic Na$^+$ to make neutral Na in a repulsive state, causing the neutral to desorb. Therefore, we bombard ice surfaces dosed with either Na or K atoms using 200-eV electrons, representative of the upper limit of secondary electrons produced by the incident energetic ions and electrons. We note that except near threshold, the ejecta energy distributions are very insensitive to the incident electron energy.

Using the surface ionization detector described elsewhere (Yakshinskiy and Madey 2000) and time-of-flight analysis of the ejected alkalis, the energy distributions of the desorbed sodium and potassium are obtained. Since incident electrons are also capable of removing H$_2$O (Johnson 1990, Sieger et al. 1998), the total amount of material removed in obtaining a spectrum is kept to less than a monolayer.

For the energy distributions derived from measured time-of-flight distributions shown in Fig. 1, experimental constraints...
cause uncertainties at very low energies (<0.02 eV) and very high energies (>1 eV). The spectra are shown normalized at the peak values and are seen to have a dependence roughly that seen in other electronic sputtering processes. Each exhibits a peak at low energies with a slowly decreasing but nonthermal tail which decays roughly as $E^{-2}$ (Johnson and Liu 1996). The Na distribution is broader than the K distribution. The peak occurs at ~0.04 eV for Na and at a slightly smaller energy for K. Within the uncertainties (~ ± 0.01 eV at the peaks), these are similar to that found in the sputtering of H$_2$O by keV heavy ions (~0.03 eV; Reimann et al. 1984). The electronic sputtering of ice by fast light ions also exhibits a large contribution at low ejecta energies (Johnson 1998). That these spectra all have significant low-energy contributions may be due to the fact that the surface is porous and composed of a frozen volatile. The maxima in the energy spectra measured here are lower than that observed for sputtering of Na from Na$_2$SO$_4$ by energetic heavy ions (~0.14 eV) (Wiens et al. 1997). Moreover, all of these spectra exhibit nonthermal tails at the highest ejecta energies, which for incident heavy ions have a momentum transfer component that extends to higher energies than measured here.

In analyzing his observations, Brown (2001) assumed the energy spectra for ejection of Na and K were roughly the same. Here it is seen that this is not an unreasonable assumption although there are noticeable differences, as seen in Fig. 1. Yakshinskiy and Madey (1999, 2000, and in preparation) also measured the energy distributions for desorption of Na and K from silicon dioxide by electrons. The mean energy of K ejected from a silicate is also slightly lower than that for Na, but different energetics are found for desorption of Na and K from other oxide surfaces (Madey et al. 1998). Assuming a linear dependence at low $E$ and a form $CEUx/(E + U)^{2+x}$, where $x$ and $U$ are fitting parameters and $C$ is a normalization constant, the data were fit. This form for the energy spectra of Fig. 1 was used in the atmospheric model described below.

3. ATMOSPHERIC MODEL

Leblanc et al. (2001) (hereafter, LJB) constructed a Monte Carlo model of the sputtered sodium atmosphere at Europa. This was normalized to an extensive set of observations. In this model, atoms are launched from the surface according to a spatial, energy, and angular distribution determined by sputtering of Europa’s surface. The ejected atoms are tracked through the ambient O$_2$ atmosphere (~10$^{15}$ O$_2$/cm$^2$; Hall et al. 1995) until they return to the surface, reach the boundary of our simulation volume, or are ionized by electrons and swept away by the jovian magnetosphere’s motional electric field. The simulation is carried out in Europa’s rest frame accounting for the gravitational forces of Jupiter and Europa. In the simulation the centrifugal, Coriolis, and radiation pressure forces, as well as the local ionization rate, are all accounted for as described in LJB. Because of Jupiter’s significant gravity, a “banana-shaped” cloud of Na is seen. Figure 2 is from LJB with the surface source rate

FIG. 2. Simulated Na cloud at Europa showing position of Europa relative to Jupiter at which modeling was done, near western elongation (~290°). Jupiter is represented by the circle on the axis $x = 0$. Lines are contours of equal density, and axes are indicated: positive $x$ toward the sun; $y$-axis is the E/W direction in Fig. 3 with positive $y$ away from Jupiter and N/S perpendicular to the plane shown. Scale on right is density (Na/cm$^3$) in powers of 10 (from Leblanc et al. 2001).
normalized to the sodium observations. The spatial distribution of the surface source in LJB was assumed to vary as the cosine of the angle from the apex to the hemisphere trailing Europa's motion. This is the hemisphere preferentially irradiated by the energetic ions (Pospieszalska and Johnson 1989, Cooper et al. 2001) and electrons (Paranicas et al. 2001). The LJB simulation described the observations well within \( \sim 20 \) \( R_E \) but was less successful at much larger distances due to temporal variability, Europa's changing position during the measurements, and Io's sodium. Here we focus on distances less than 20 \( R_E \) for which Brown (2001) observed the Na/K ratios.

In modeling the sodium cloud, LJB suggested an energy spectrum which appeared to reproduce the principal aspects of the cloud morphology. This spectrum is remarkably close to that reported in Fig. 1. The inset to Fig. 1 shows the agreement between the energy distribution found in LJB (dashed line) and the laboratory measurements of the sodium energy distribution described in Section 2 (stars). Therefore, the measurements presented here support the assumption that the observed sodium is mostly ejected from icy surface layers (Johnson 2000). In the simulation described above we use the fits to the measured energy spectra shown in Fig. 1. For both Na and K atoms we extend the data in Fig. 1 to higher ejecta energies by attaching an energetic tail. This roughly accounts for a contribution due to collision cascade sputtering from more reactive materials, as discussed in LJB. At the distances of interest here (<\( \sim 20 \) \( R_E \)), the densities are not very sensitive to the tail nor are they very sensitive to the spatial variation in the ionization lifetime and to radiation pressure. Therefore, for K we use an average electron impact ionization rate which is \( \sim 1.2 \) times (Brown 2001) that of the local Na ionization rate in LJB.

The simulation region in LJB is divided into cells, and the times for atoms ejected from the surface to pass through each cell are recorded and summed. From the residence times the steady-state density in each cell can be calculated using a surface flux and the number of atoms in the simulation. Using the local densities the morphology of the sodium and potassium clouds can be calculated as shown for sodium in Fig. 2. Since the atoms in each cloud can be seen by their resonance fluorescence, we calculate the line-of-sight column densities. That is, we integrate the number of atoms per unit volume lying along an observation direction. Rather than normalize the Na and K simulations separately to the observations, we calculate the ratios of the line-of-sight column densities versus distance. Therefore, this calculation has only one free parameter, the ratio of the rate of desorption of sodium and potassium. In Fig. 3a we give the ratios of the line-of-sight column densities versus distances from Europa using the fits to the energy distributions in Fig. 1. In Fig. 3a we use equal surface source rates for Na and K. This allows the actual surface source rates to be obtained by scaling to observation. These ratios are calculated for Europa near the western elongation (\( \sim 290^\circ \)), the geometry shown in Fig. 2. Ratios of the line-of-sight column densities are calculated versus distance from Europa along axes through Europa's position: east/west (E/W) scans toward Jupiter (east) and away from Jupiter (west) inside Europa's orbital plane. The differences of the ratios in Fig. 3a are primarily due to the differences in mass between K and Na and to the shifted energy spectrum for K compared to Na.

Because the Na/K ratios in Fig. 3a are larger than one for equal source rates, sodium atoms more easily reach the distances considered. It is also seen that the dependence on distance from Europa is somewhat different in the two observation directions, primarily due to the influence of Jupiter. As is the case for neutrals from Io's atmosphere, and as seen in Fig. 2, the atoms preferentially "fall" toward Jupiter. Therefore, the Na/K ratio is somewhat smaller in the jovian direction, as K can escape more readily and remain in the atmosphere longer than it does on the antijovian side of Europa.

Shown in Fig. 3b are the ratios of the sodium and potassium column densities near Europa observed by Brown (2001). These data are extracted from the line intensities for sodium and potassium. They are averages of observations on either side of Europa.

![Figure 3](image-url)
roughly along the E/W direction (Brown 2001) and are plotted versus distance from Europa. At these distances, the Na/K ratios are nearly independent of the distance from Europa. This is consistent with the average of the E/W scans from the simulations in Fig. 3a, which is also shown in Fig. 3b normalized to Brown’s (2001) data. The ratios calculated in this region using the measured velocity distribution are also nearly independent of distance from Europa.

By normalizing the average of the E/W scans in Fig. 3a to the observations in Fig. 3b, we obtain a ratio, Na/K ∼ 20 ± 4, for the average surface source rates. From these simulations we can also obtain the ratio of the net loss rates of sodium and potassium. Primarily because of the effect of Jupiter, this is not simply a ratio of that fraction of the energy spectra in Fig. 1 which is larger than Europa’s escape energy. We found that ~30% of the Na and ~25% of the K ejected from the surface are lost by either leaving the simulation region or being ionized in the simulation region. If we ignore the fraction of those ionized alkalis that are picked up and accelerated back into the surface, the globally averaged loss ratio obtained from the above numbers (Na/K) is ~1.3 times the ratio of the source rate. This is similar to the atmospheric ratios in Fig. 3a. Using the ratio of the surface source rates estimated above, the Na/K ratio for the loss rates is ∼27. Since the ionized fraction reimpacting the surface for K is likely larger than that for Na, this is a lower limit.

Although the source rate for sodium was converted into a rough estimate of sodium surface concentration in Johnson (2000) and LJB, this required estimating the average sputtering yield and the charged particle flux. To convert the ratio of source rates into a ratio for the surface concentrations requires knowledge of the relative desorption cross sections. Yakushinsky and Madey (2001) estimate roughly similar desorption cross sections for 200-eV electrons. These are ∼5 × 10⁻¹⁹ cm² (within a factor of 2) for the Na and the K. Therefore, to first order, the ratio of the average surface concentration is the same as the ratio of the source rates.

In Table I, the Na/K ratios found here are compared to the solar value and the atmospheric ratios at Io, the Moon, and Mercury. Possible sources of alkalis at Europa are Na⁺ and K⁺ which are formed at Io and eventually implanted in Europa’s surface. Since these are both minor ions in the jovian plasma, there are no accurate measurements of this ratio in the plasma near Europa. However, we showed earlier that the implantation rate is much smaller than the loss rate (Johnson 2000, Leblanc et al. 2001). It is also seen in Table I that, as pointed out by Brown (2001), the Na/K ratio at Io is very different from that found at Europa, suggesting that Io is not a primary source of the alkalis observed.

### 4. DISCUSSION

The chemical composition of the optical surface of Europa (∼1 mm) is altered by the incident radiation (Carlson et al. 1999, Cooper et al. 2001). In this layer implantation and sputtering of alkalis compete with alkalis brought to the topmost atomic layers by mixing or by irradiation-enhanced diffusion. Due to sputter redistribution across Europa’s surface, the source of alkalis for the atmosphere is likely dominated by electronic sputtering (desorption) from the icy regions (Johnson 2000). Such regions are also the source of the dominant atmospheric component, O₂ (Johnson 1990). Comparing the estimated loss rate to the implantation rate, shows Europa to be a net source of sodium (Johnson 2000, Leblanc et al. 2001). Brown (2001) also concluded this by comparing the observed atmospheric ratios of Na/K at Europa and Io. In this he assumed that the energy spectra for ejected Na and K were identical and estimated the sputter contribution to the observed alkali atmosphere.

Here we present measurements of the energy spectra (Fig. 1) for electronic sputtering of Na and K from ice. The energy spectrum for desorbed sodium atoms is close to that extracted by Leblanc et al. (2001) from observations (see inset to Fig. 1). This supports the assumption in our previous work that electronic sputtering from an icy surface is the dominant ejection process for sodium. It can be seen in Fig. 1 that the ejected sodium and potassium energy spectra are similar, the potassium ejecta being on average somewhat less energetic. These newly measured energy distributions were used in a recent model to simulate the Na and K atmospheres at Europa. The calculated Na/K ratios of the line-of-sight column densities from the simulations were then normalized to the ratios of the line-of-sight column densities observed by Brown (2001). This allowed us to obtain relative surface source rates and relative loss rates.

In Fig. 3a we give the ratios of line-of-sight column densities for Na and K calculated from the alkali cloud simulations in which the newly measured energy distributions were used. These ratios can be scaled either to known surface source rates or to new observations as they become available. The averages of the E/W scans in Fig. 3a were normalized here to the observations in Fig. 3b and are seen to have roughly the same dependence on
distance from Europa as the observations. On normalizing the Na/K ratios to the observations of Brown (2001), the ratio of the average surface source rates is \( \sim 20 \pm 4 \).

Because the desorption efficiencies are similar for Na and K, the ratio of the concentrations in the optical layer is also \( \sim 20 \). The globally averaged Na atomic concentration in the surface layer is \( \sim 0.01-0.005 \) (Johnson 2000, Leblanc et al. 2001), implying a potassium concentration of \( \sim 0.0005-0.0003 \) in the optical layer. Since the surface can be depleted in the alkalis, and the incident fast ions and electrons cause diffusion of alkalis in the irradiated layer, the ratio of surface concentrations is not the best indicator of the concentration below the layer penetrated by the radiation. In steady state, the ratio below the charged-particle penetration depth is roughly equal to the ratio of the total loss rates (Johnson and Sittler 1990). Using the fractions of the sputtered sodium and potassium determined from the simulations, the concentration ratio, Na/K, below the radiation penetration depth is \( \sim 27 \).

The Na/K ratios obtained here are compared in Table I to the cosmic ratio, the ratios for other objects, and the ratio expected in Europa’s putative ocean. In agreement with Brown (2001), the Na/K ratio at Europa differs significantly from that at Io. Therefore, Io is not likely to be the source of the observed alkalis. The fact that Europa has endogenic sources of alkalis lends support to the hypothesis of a geologically active surface, possibly associated with an underground ocean. This could be the “salty” Europa proposed by a number of authors (Fanale et al. 1974, Kargel 1991, Zolotov and Shock 2001). Preferential loss of alkalis from such salts would be consistent with atmospheric alkalis and with the observation of hydrated sulfuric acid in the dark chaos regions (Carlson et al. 1999, Johnson 2001).

The Na/K ratio, \( \sim 27 \), obtained here for a depth under the surface below that for radiation penetration is somewhat larger than the ratio for the cosmic abundance. This ratio is also larger than that predicted by models of Europa’s ocean based on formation of Europa from carbonaceous chondrites (\( \sim 14-19 \); Zolotov and Shock 2001). Increased fractionation occurs during freezing and dehydration of the material as it reaches Europa’s surface, enhancing the Na/K ratio (Zolotov and Shock 2001). Therefore, the relative loss rates determined here and the relative concentrations in the model ocean are not inconsistent. Since sodium atoms are lost only \( \sim 1.3 \) times faster than potassium atoms and the surfaces are relatively young, the globally averaged ratio (\( \sim 27 \)) can be used to constrain models for fractionation on transport of warm ice to Europa’s frozen surface.

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