

Potassium in Europa's Atmosphere

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Trace element abundances in the sputtered extended atmospheres of the Galilean satellites reflect the surface abundances of these trace elements and can thus serve as signatures of surface processes on these satellites. We have measured sodium and potassium abundances in the extended atmospheres of Europa and Io, and derive sodium-to-potassium ratios of 25 ± 2 and 10 ± 3 . The large difference between the values of Na/K in these atmospheres is difficult to explain if the dominant source of sodium for Europa's surface is implantation of Io sodium, as suggested earlier. The three remaining likely sources for trace elements on the surface of Europa—metals brought in from meteoritic impact, trace elements native to the surface ices, and salts deposited in liquid water resurfacing events—are all broadly consistent with the measured sodium-to-potassium ratio at Europa. Observations of additional trace elements are required to further discriminate among these possible sources. © 2001 Academic Press

1. INTRODUCTION

Europa's atmosphere was first detected through Hubble Space Telescope observations of the 1304 and 1356 Å emission lines of neutral oxygen originating from dissociation of molecular oxygen (Hall *et al.* 1996). Initial modeling by Ip (1996) showed that the oxygen atmosphere could form from sputtering of water ice on the surface of Europa, as originally suggested by Johnson (1990), and that a tenuous extended atmosphere should also form in the process. Brown and Hill (1996) first detected this extended atmosphere through observations of sodium emission at distances of up to 20 Europa radii ($1 R_E = 1569$ km) from the satellite surface.

Detection of sodium showed that the study of Europa's atmosphere was useful not only as a tool for understanding the interaction of the magnetosphere with the surface, but also as a means for determining the non-water-ice composition of the surface. Brown and Hill (1996) suggested that sodium in the surface ices of Europa could have originated in the volcanos of Io, been injected into the Io neutral clouds, become ionized by the Io plasma torus, and finally have collided with Europa and become implanted into the surface. Brown and Hill (1996) estimated a flux of 24 g s^{-1} onto Europa from this mechanism, which was approximately the amount of sodium required to supply the atmosphere in steady state.

Several other sources of sodium in the surface ices are possible, however, including sodium intrinsic to the ices, salts deposited as evaporites in liquid water resurfacing events, and sodium brought in through meteoritic bombardment. One method of determining the source of sodium on the surface of Europa is to measure the abundance of additional trace elements in Europa's atmosphere. The ratio of sodium to these trace elements can be a signature of the processes responsible for depositing sodium and other trace species in the surface ices of Europa. We report here the detection of potassium in Europa's atmosphere and discuss implications for trace element sources. In addition, we report the first modern measurement of the sodium-to-potassium ratio in Io's atmosphere.

2. OBSERVATIONS

Simultaneous observations of potassium and sodium in Europa's extended atmosphere were made on 9 September 1998 at the W. M. Keck telescope using HIRES, the facility echelle spectrograph (Vogt *et al.* 1994). Identical observations of Io's extended atmosphere were obtained on 15 November 1998. A journal of observations is shown in Table I. Each observation consisted of a high-resolution ($\lambda/\Delta\lambda \sim 60,000$) cross-dispersed spectrum covering the range from 5570 to 7912 Å (with interorder wavelength gaps as large as 60 Å in the reddest spectral regions) in a slit 0.574 arcsec wide and 14 arcsec tall. The long dimension of the slit was aligned with the rotational pole of Jupiter, and the slit was first centered on the satellite and then offset a variety of distances from the satellite. A spectrum of the potassium spectral region from a location 16 R_E west of Europa is shown in Fig. 1. The spectrum contains copious scattered light from Europa, strong terrestrial O₂ absorption features, and 7664.90 and 7698.96 Å emission lines from potassium in Europa's atmosphere. While the 7664.90 Å line is the stronger of the two, its proximity to the terrestrial O₂ absorption makes analysis uncertain, so we concentrate instead on the weaker 7698.96 Å line. The heliocentric velocity of Europa of 12.50 km s^{-1} causes the emission line to appear blue-shifted by 0.32 Å relative to the solar potassium Fraunhofer absorption line, which is sufficient to place it into an unobstructed spectral region. To calculate the emission intensity of the potassium line, we sum the emission in three separate 3-arcsec-long regions of the slit and then

TABLE I
Journal of Europa and Io Sodium and Potassium Observations

Date	Time (UT)	Object	Slit position	exp (s)	Airmass	Notes
9 Sep 1998	08:01	Europa	6.5 R_E east	1800	1.48	Offsets are in RA only
9 Sep 1998	08:37	Europa	9.3 R_E east	1800	1.30	$\dot{r} = 12.5$, $\dot{\Delta} = 9.4 \text{ km s}^{-1}$
9 Sep 1998	09:12	Jupiter	centered	10	1.20	Calibration source
9 Sep 1998	09:14	Europa	13.0 R_E east	1800	1.19	
15 Nov 1998	09:08	Jupiter	centered	10	1.63	Calibration source
15 Nov 1998	09:20	Io	9.7 R_{Io} east	600	1.75	Offsets in Io orbital plane
15 Nov 1998	09:33	Io	13.6 R_{Io} east	600	1.75	$\dot{r} = -10.8$, $\dot{\Delta} = 12.5 \text{ km s}^{-1}$
15 Nov 1998	09:47	Io	19.4 R_{Io} east	600	1.87	
15 Nov 1998	10:01	Jupiter	centered	20	2.04	Calibration source

Note. \dot{r} is the heliocentric velocity and $\dot{\Delta}$ the geocentric velocity of the observed object.

subtract a best-fit solar continuum (determined from the spectrum of Europa itself) to the region within $\pm 1.7 \text{ \AA}$ of spectrum (avoiding the Fraunhofer line) and integrate the emission line over 0.50 \AA . Absolute intensity calibration is performed by comparison to the spectrum of the equator of Jupiter, which is assumed to have a brightness of 7.4 MR \AA^{-1} ($1 \text{ Rayleigh} = \frac{1}{4\pi} \times 10^6 \text{ photons cm}^{-2} \text{ s}^{-1} \text{ SR}^{-1}$) at this wavelength (Woodman *et al.* 1979). The column density of potassium is then calculated from the g -values given by Chamberlain and Hunten (1987) scaled to Jupiter's heliocentric distance of 4.99 AU and corrected for the increased solar flux outside of the Fraunhofer line. Using $g = 0.345 \text{ photons s}^{-1} \text{ atom}^{-1}$ we calculate the column densities shown in Fig. 2.

The sodium emission intensities and column densities are determined identically except that the sodium emission is not sufficiently doppler-shifted out of the strong sodium Fraunhofer absorption feature, so we first subtract a scaled spectrum of the center of Europa to remove the continuum emission. Absolute intensity calibration is obtained by assuming a brightness of

5.4 MR \AA^{-1} for the equator of Jupiter (Woodman *et al.* 1979), and measured values are shown in Fig. 2. The brightness of the equator of Jupiter changes on time scales of years to decades (Beebe *et al.* 1989), so the absolute calibration is likely only accurate to $\pm 20\%$, but the relative calibration from sodium to potassium—and thus the ratio—should be much more accurate. Sodium g -values are taken from Brown and Yung (1976) and corrected for the reduced flux that the sodium atoms see in the wings of the absorption feature. The measured sodium is optically thin at all points as measured from the line ratio of 1.70 ± 0.05 , consistent with 1.66 expected for optically thin emission. Using a value of $g = 0.22 \text{ photons s}^{-1} \text{ atoms}^{-1}$ for the D_2 line at 5889.95 \AA , we obtain the column densities shown in Fig. 2. These column densities agree well with those measured by Brown and Hill (1996) after taking into account the factor-of-two calibration error in the Brown and Hill data discussed by Brown (in preparation).

The Io sodium and potassium spectra are analyzed in the same manner as those for Europa, correcting the g -values for Io's

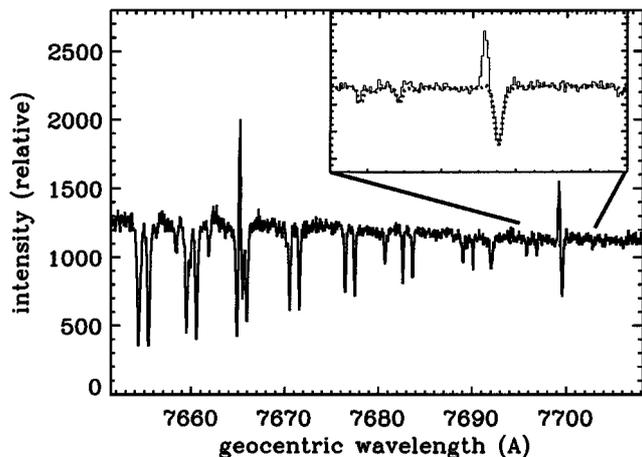


FIG. 1. A spectrum of Europa's extended atmosphere at a point $16.06 R_E$ from Europa. The spectrum shows copious scattered light from Europa, O_2 absorption bands from the terrestrial atmosphere, and the 7664.90 and 7698.96 \AA emission lines of potassium.

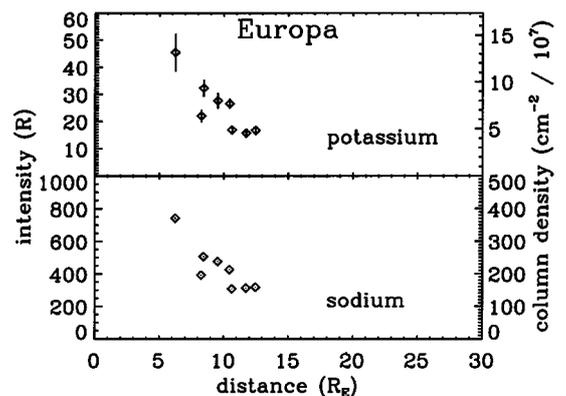


FIG. 2. Measured intensities and derived column densities of potassium and sodium as a function of distance from Europa, in units of radii of Europa ($R_E = 1569 \text{ km}$). The apparent scatter in the measurements is caused by nonradial spatial structure in Europa's atmosphere.

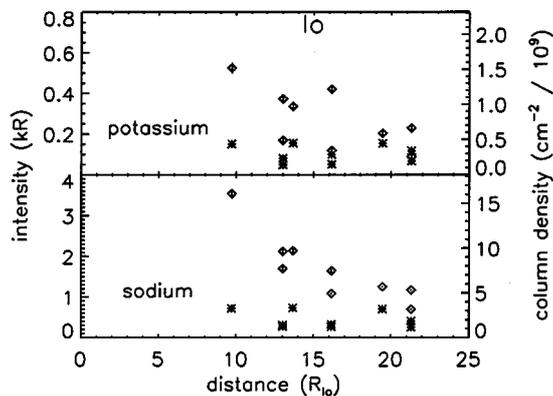


FIG. 3. Measured intensities and derived column densities of potassium and sodium as a function of distance from Io, in units of radii of Io ($R_{Io} = 1815$ km). Measurements of slow potassium and sodium are shown as diamonds, while measurements of the fast potassium and sodium jet ($15\text{--}60$ km s^{-1}) are shown as asterisks. The apparent scatter in the data is caused by well-known spatial structure in the Io neutral cloud.

heliocentric velocity of -10.8 km s^{-1} . Measured brightnesses and calculated column densities are shown in Fig. 3. In the Io observations we also detected a high-speed jet of sodium and potassium (with line-of-sight velocities of 15 to 60 km s^{-1}) south of the satellite orbital plane. Separate column density measurements are made for this jet.

The measured sodium-to-potassium ratio (Na/K) is determined at each position and shown as a function of distance for both satellites in Fig. 4. The measurements are consistent with a constant value of $Na/K = 25 \pm 3$ in the extended atmosphere of Europa and a value of 10 ± 3 in the extended atmosphere of Io, with a lower value of 6 ± 1 in Io's high-speed jet. This average value of Na/K for Io is a factor of 3 smaller than the measured $Na/K \approx 30$ reported by Trafton (1981) in the only other published measurement of this ratio. The disagreement with this previous measurement is not surprising. Trafton used the

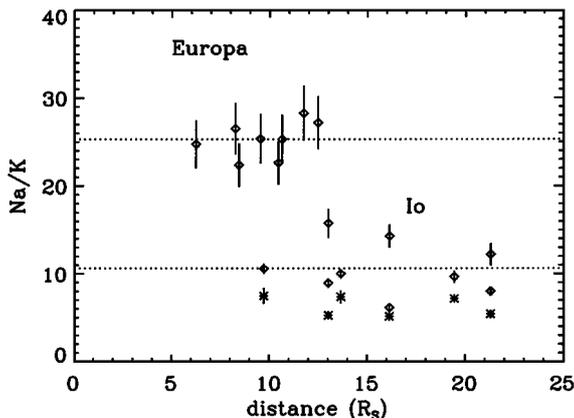


FIG. 4. The sodium-to-potassium ratio as a function of distance from Europa and from Io, in units of satellite radii. For Io we plot the ratio measured in the fast jet as asterisks.

7665 Å line, which is brighter but is affected by terrestrial O_2 absorption and is therefore more difficult to calibrate. Trafton (1981) measured sodium and potassium abundances separately over the course of a year and reported Na/K as the ratio of the maxima of these measurements. We now know that sodium abundance varies by a factor of at least 6 on time scales of days to months (Brown and Bouchez 1997), so the ratio of measured maxima is only a crude approximation to the true value of Na/K. Our simultaneous and well-calibrated measurements should provide a much more robust value for Io's Na/K.

3. TRANSPORT FROM IO TO EUROPA?

The measured Europa atmosphere sodium-to-potassium ratio of 25 ± 2 is at least a factor of 2.5 higher than that measured around Io, suggesting that the Brown and Hill (1996) hypothesis that Io is the source of Europa's sodium might be incorrect. While time-variability might be able to account for these differences, no evidence or postulated mechanism for such variability exists, so we will not consider this possibility. To determine if the large difference between Europa and Io Na/K values rules out Io as a source for Europa's sodium and potassium atmospheres, we first need to determine the extent to which Na/K could be fractionated on the trip from Io to Europa. As detailed below and shown schematically in Fig. 5, we find that all processes which occur between loss of material from Io's surface and implantation on Europa decrease Na/K, showing that Europa's large Na/K cannot be explained by the low Na/K Io source.

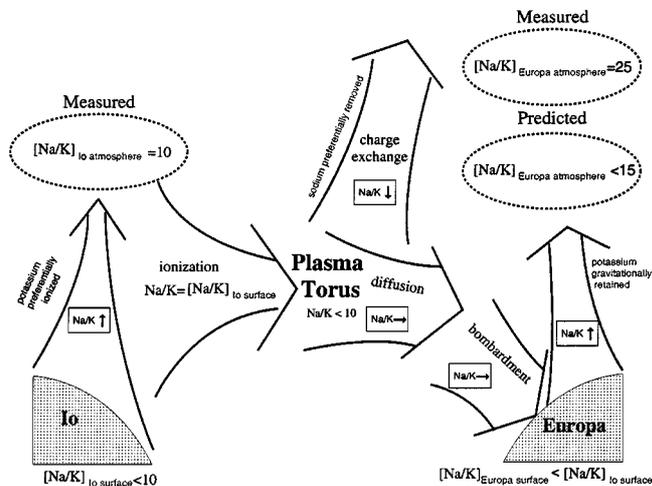


FIG. 5. Transport of sodium and potassium from Io's surface to Europa's atmosphere. Io's atmospheric value of $Na/K = 10$ constrains the surface of Io—and thus the input to the plasma torus—to $Na/K < 10$. As plasma diffuses outward to Europa, charge-exchange will preferentially remove sodium, resulting in an even lower value of Na/K for the plasma bombarding Europa's surface. The input into Europa's sputtered atmosphere should thus have $Na/K < 10$, but potassium is heavier and thus preferentially retained by the satellite, so Na/K will increase by $\sim 50\%$, resulting in a value for Na/K in Europa's atmosphere of less than 15. The measured value of $Na/K = 25$ in Europa's atmosphere shows that Io cannot be the primary source of these trace elements on the surface of Europa.

Assume that sodium and potassium exist on the surface of Io with an abundance ratio of $[\text{Na/K}]_{\text{Io surface}}$. In steady state, the ratio of sodium to potassium that is sputtered from the surface will be identical to $[\text{Na/K}]_{\text{Io surface}}$ (Johnson 1990). Upon leaving the surface, sodium and potassium will be ionized at different rates. At the location of Io during the observations, the lifetime of sodium against electron impact ionization is approximately 4.5 hours (Smyth and Combi 1988), while that for potassium is 20% shorter, or about 3.8 hours. Photoionization lifetimes for sodium and potassium are 400 and 270 hours, respectively (Smyth and Marconi 1995). Potassium will thus be ionized more quickly than sodium, and Na/K measured in Io's extended atmosphere will be larger than $[\text{Na/K}]_{\text{Io surface}}$. This ratio will continue to increase with length of time since the materials left the surface of Io. This effect is seen in the high-speed jet at Io, which presumably consists of material more recently on the surface of Io and which has a lower value of Na/K than the slower material. Many unknown processes could occur between the time the materials leave the surface of Io and when we observe them, including atmospheric entrainment and molecular processes, but in all cases these processes simply increase the amount of time that sodium and potassium are exposed to ionizing electrons, so potassium is selectively removed and Na/K increases. The value of Na/K in Io's extended atmosphere, which we measure to be $[\text{Na/K}]_{\text{Io atmospheres}} = 10$, thus represents an upper limit to $[\text{Na/K}]_{\text{Io surface}}$, so we conclude that $[\text{Na/K}]_{\text{Io surface}} < 10$.

Eventually, all of the sodium and potassium removed from Io's surface will be ionized and incorporated into the Io plasma torus. In steady state, the input into the Io plasma torus will therefore have a Na/K of $[\text{Na/K}]_{\text{Io surface}}$. Once entering the plasma torus, the two main sinks for plasma are outward diffusion, which will not change Na/K, and charge-exchange of ions with neutrals, which will remove the ions from the system (as fast neutrals) and modify Na/K. The dominant charge-exchange reaction which removes sodium is the resonant reaction with neutral sodium atoms (McGrath and Johnson 1989). Assuming that the same holds for potassium and that the cross sections are approximately similar, we estimate that the loss rate of sodium due to charge-exchange is higher than that of potassium by a factor of approximately Na/K, because the charge-exchange reaction rate goes as a product of the ion and neutral density of each species. Sodium is therefore preferentially lost as the plasma diffuses outward from Io to Europa, so the value of Na/K for the plasma bombarding Europa must be lower than $[\text{Na/K}]_{\text{Io surface}}$, which in turn must be lower than $[\text{Na/K}]_{\text{Io atmosphere}}$.

The plasma torus bombards Europa and implants ions at a rate proportional to their plasma density, which must be less than $[\text{Na/K}]_{\text{Io atmosphere}}$. Sputtering will, as on Io, remove sodium and potassium proportional to their abundance in the surface ices. At Europa, the electron density is much lower than at Io, so the lifetime against electron impact ionization is much longer: up to 100 hours for sodium and 80 hours for potassium (Brown and Hill 1996). No significant ionization will occur in the time between the time when these atoms are ejected from the surface

and when we observe them, so unlike at Io, Na/K will remain unchanged from this process.

The final process which could change Na/K occurs because of the mass difference between the two atoms. If they both leave the surface of Europa with the same energy, the velocity of sodium will be 30% higher than that of potassium, thus more sodium than potassium will escape into the extended atmosphere. We estimate the magnitude of this effect in two manners. First, if assume that sodium and potassium are sputtered from the surface with a Sigmund–Thompson velocity distribution (an analytic approximation which fits experimental sputtering velocity distributions) appropriate for the ejection of water ice products (Reimann *et al.* 1984), we find (ignoring the gravitational effect of Jupiter) that $\sim 22\%$ of the sodium achieves escape velocity, while only $\sim 12\%$ of the potassium does; thus Na/K measured in the extended atmosphere will be $\sim 80\%$ higher than the value leaving the surface. In fact, the real effect will not be this large, as the atoms that do not escape will reimpact the surface of Europa and increase the relative potassium abundance on Europa's surface. In the absence of ionization, this process would continue until in steady state Na/K in the extended atmosphere was the same as the impacting value. Because atoms will eventually be ionized instead of cycling forever, the true value will be somewhere in between.

To further explore this mass fractionation, we determined the expected effect on Na/K by using a Monte–Carlo model for the full three-body gravitational interaction with atoms ejected from Europa's surface (Brown 1997). Again, assuming that the sodium and potassium leave the surface of Europa with the velocity distributions described above, we find that the expected measured value of Na/K at the location of our measurements should be $\sim 50\%$ higher than the incoming value. This value is slightly smaller than the value we calculated above because the additional gravitational force of Jupiter allows lower velocity atoms to escape and slightly lessens the mass fractionation. Again, because of surface recycling this value should be lower, but we will keep this value as an upper limit.

We thus find that our measured Na/K for Europa's extended atmosphere of 25 ± 2 corresponds to a lower limit for Na/K of Europa's surface of ~ 17 . As discussed above, we found that the strong upper limit to Na/K expected from Io ion implantation is ~ 10 . We can find no way to reconcile these two numbers if the source of sodium and potassium on Europa is sodium and potassium originally derived from Io. We thus conclude that the trace elements sputtered into Europa's extended atmosphere are intrinsic to the surface of Europa, contrary to the initial suggestion of Brown and Hill (1996).

4. IMPLICATIONS OF EUROPA'S Na/K

The measured Na/K in Europa's extended atmosphere is intermediate between values measured elsewhere in the Solar System, which range from a low of 2 in the earth's crust to a high of 190 in Mercury's atmosphere (Table II). The large difference

TABLE II
Sodium to Potassium Ratios in the Solar System

Object	Na/K	Ref
Mercury	80–190	Potter and Morgan (1997)
Moon	6	Potter and Morgan (1988)
Earth atmosphere	20–150	Gault and Rundle (1969)
Io	10	this work
Europa	25	this work
Cosmic abundance	20	Allen (1991)
Meteorites	13	Allen (1991)
Lunar rocks	2–7	Allen (1991)
Earth crust	2	Lide (1996)
Earth seawater	45	Lide (1996)

between Na/K at Io and at Europa rules out Io as the source for Europa trace species. The other possibilities which seem likely are that potassium and sodium are brought in through meteorite bombardment, that they are intrinsic to the surface ices of Europa, or that they are deposited from an internal liquid water in resurfacing events.

Meteorite bombardment should bring sodium and potassium to the surface of Europa with a Na/K presumably equal to that of terrestrial meteorites, or about 13, on average. Such a value is approximately consistent with the measured value at Europa, taking into account the mass fractionation. The nondetection of a sodium atmosphere around Ganymede (Brown 1997) might rule this source out, but the uncertainties as to how sputtering is affected by Ganymede's magnetic field prevent a strong conclusion.

We also briefly discuss the value of Na/K expected for trace elements intrinsic to the ices and for trace elements deposited in liquid water resurfacing events. Aqueous alteration in Europa's past could have selectively removed certain salts from the surface ices and preferentially enriched them in the water component. Assuming for concreteness that the dominant sodium- and potassium-containing compounds are the sulfates, Na₂SO₄ and K₂SO₄ (Kargel 1991), the sodium solubility is more than four times that of potassium (Lide 1996), thus sodium would be depleted relative to potassium in the remaining solid material and would be enriched in the liquid. We note a similar occurrence at the Earth, where the crust has Na/K ~ 2 while the oceans have Na/K ~ 45 (though potassium is selectively depleted in the Earth's oceans also because of its use by biological organisms). We therefore generally expect that intrinsic surface materials will have a lower value of Na/K than will resurfacing deposits that originate from internal liquid water.

Unfortunately, we do not know the prealteration value of Na/K for Europa, so we cannot predict the likely present surface or ocean value. If we take the cosmic Na/K of 20 as a starting point we might suggest that Europa's Na/K of 25 implies oceanic enrichment, however the uncertainties in the velocity fractionation mean that the true Na/K at Europa's surface could be as low as 17, implying crustal depletion of sodium. With the current data,

discrimination between any of these potential sources for trace elements on the surface of Europa is clearly impossible.

Final resolution of the source of trace elements on the surface of Europa will not be possible until additional elements are measured. The two next-most-easily detected trace elements will be calcium and magnesium. These elements both have cosmic abundances even higher than sodium, so a meteorite source should have high abundances of both elements. In contrast, magnesium and calcium compounds differ greatly in solubility, so the ratio of these two compounds should serve to discriminate between solid and liquid sources. Such measurements of trace elements will help determine the sources of composition of non-water-ice materials on the surface of Europa.

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