

## ENCELADUS: A SOURCE OF NITROGEN AND AN EXPLANATION FOR THE WATER VAPOR PLUME OBSERVED BY CASSINI

M. J. LOEFFLER, U. RAUT, AND R. A. BARAGIOLA<sup>1</sup>

University of Virginia, Laboratory for Atomic and Surface Physics, Engineering Physics, Charlottesville, VA 22904;  
mjl8r@virginia.edu, ur5n@virginia.edu, raul@virginia.edu

Received 2006 May 31; accepted 2006 August 16; published 2006 September 19

### ABSTRACT

Recently, the *Cassini* spacecraft observed an unexpected emission of plumes of water vapor, nitrogen, and icy particles from the southern polar region of Saturn's icy moon Enceladus. While these findings support previous ideas of geological activity in this icy moon, there is no experimental evidence explaining how these plumes could be produced at the low (~130–160 K) surface temperatures. Here we show that similar behavior appears when heating water-ammonia ices that have been irradiated with protons that simulate Saturn's energetic ion environment. In our experiments, the behavior results from the eruption of high-pressure bubbles of hydrogen and nitrogen molecules that accumulate in the ice due to the radiolytic decomposition of ammonia. The thermal release of nitrogen can explain the intriguing finding of  $N^+$  in the inner magnetosphere. Thus, our laboratory simulations indicate that radiation processing of the surface of Enceladus may explain much of the extraordinary phenomena that have been observed by *Cassini*.

*Subject headings:* infrared: general — methods: laboratory —  
planets and satellites: individual (Enceladus, Saturn) — radiation mechanisms: general

*Online material:* color figures

### 1. INTRODUCTION

The measurements of *Voyager*, remote sensing, and more recently the *Cassini* spacecraft have shown unique conditions at and around Enceladus. The surface of this satellite is the brightest and most diverse among the Saturnian satellites (Porco et al. 2006; Verbiscer et al. 2005). Furthermore, the densest part of the E-ring and a neutral OH torus fall near the orbit of Enceladus, suggesting that they originate from sources in this satellite (Jurac et al. 2001a). Besides water and its dissociation products, *Cassini* detected nitrogen from an unknown source near Enceladus (Smith et al. 2005; Young et al. 2005). Recent fly-bys have shown temperatures as high as 145 K near the South Pole (Spencer et al. 2006), much higher than the subsolar temperature (~80 K; Spencer et al. 2006). In addition, *Cassini* detected a spectacular fountain of water ice particles and vapor emanating from this South Polar region (Hansen et al. 2006; Porco et al. 2006; Spahn et al. 2006; Waite et al. 2006). This is astounding since, even at 145 K, water evaporates at a rate (Sack & Baragiola 1993) that is many orders of magnitude slower than that needed to entrain particles observed in this fountain.

The origin of the thermal anomalies, water bursts, nitrogen in the inner magnetosphere, E-ring particles, and OH torus remains largely unexplained. Since the first measurements of *Voyager*, it has been thought that Enceladus is geologically active (Smith et al. 1982; Squyres et al. 1983) due to an uncertain heat source (Porco et al. 2006) that could melt a subsurface material, such as a solid solution of water and ammonia (Lewis 1971), which has an eutectic point of 173 K at the dihydrate composition ( $NH_3 \cdot 2H_2O$ ). It has been postulated that this heat source could be provided by tidal heating (Ross & Schubert 1989; Squyres et al. 1983) that could be enhanced by an orbital resonance (Wisdom 2004), since radiogenic heating may be insufficient on Enceladus (Ellsworth & Schubert 1983; Squyres et al. 1983) even though it may lead to local melting

and structural changes in the ice by decay of radiogenic species in the interior of the moon (Priolnik & Bar-Nun 1990). The liquid melted by this heat source could surface occasionally when cracks open, producing new smooth terrain, or burst out in cryovolcanism (Kargel & Pozio 1996), which could feed the E-ring. Since Enceladus is embedded in Saturn's magnetosphere, ion irradiation may preferentially remove ammonia (or its components) by sputtering (Lanzerotti et al. 1984), which would allow a much lower  $NH_3$  concentration on the surface (Brown et al. 2006; Emery et al. 2005; Verbiscer et al. 2006) than in the bulk. The effects of magnetospheric ion irradiation are evident in the chemical alteration of the surfaces of satellites of Jupiter (Carlson et al. 1999) and other satellites of Saturn (Noll et al. 1997). Here we present laboratory studies of ion irradiation and thermal annealing of water—ammonia mixtures applicable to Enceladus and possibly to other objects in the outer solar system.

### 2. EXPERIMENTAL SETUP

The experiments were performed in vacuum at  $2 \times 10^{-10}$  torr using a mass-analyzed beam of 100 keV protons. Solid ammonia-water films were grown at 80 K on the gold mirror surface of a quartz-crystal microbalance (QCM) to a thickness of  $\sim 2 \mu m$  ( $148 \mu g cm^{-2}$ ), slightly larger than the depth of penetration of the ions (Ziegler 2003). The mixtures were grown using two separate gas dosers with the 1 : 2  $NH_3$  :  $H_2O$  ratio of the dihydrate, as this is one of the equilibrium phases for ice mixtures with <65.4 percent by weight ammonia (Hogenboom et al. 1997). The samples were then annealed to 120 K to achieve uniform mixing. Irradiations were done at 70 K while monitoring the samples with infrared reflectance (1.5–15  $\mu m$ ), a mass spectrometer (MS) aimed at the surface, and gravimetry using the microbalance. More details on the experimental setup can be found in Loeffler et al. (2006a).

<sup>1</sup> Corresponding author.

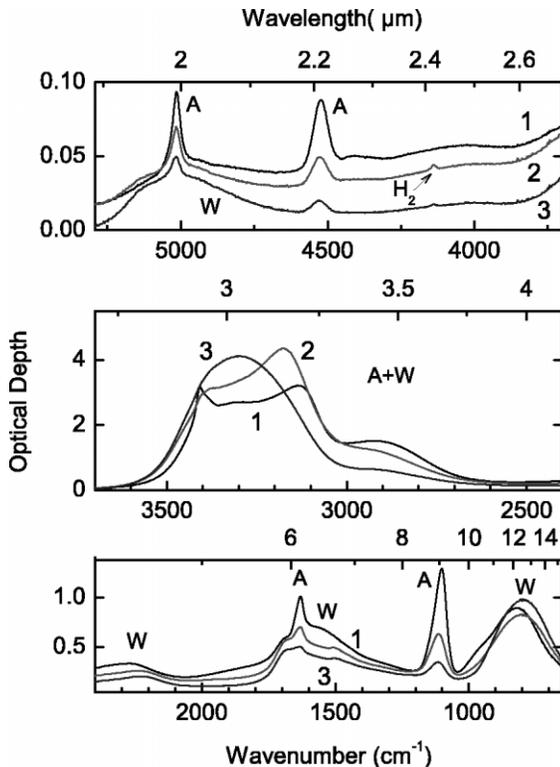


FIG. 1.—The 1 : 2 ammonia-water mixture at 70 K (1) before and (2) after irradiation with  $2.45 \times 10^{15} \text{ H}^+ \text{ cm}^{-2}$  and (3)  $9.5 \times 10^{15} \text{ H}^+ \text{ cm}^{-2}$  at 100 keV. Features are labeled as W for water and A for ammonia. [See the electronic edition of the Journal for a color version of this figure.]

### 3. RESULTS

#### 3.1. Effects Seen During Irradiation

Figure 1 shows the evolution of the infrared spectra of an ice mixture during irradiation. The spectra are dominated by water and ammonia features but also contain a weak band at  $4139 \text{ cm}^{-1}$  from  $\text{H}_2$  and a  $\sim 20$  times weaker band at  $2325 \text{ cm}^{-1}$  from  $\text{N}_2$ . These dipole transitions in  $\text{H}_2$  and  $\text{N}_2$  are forbidden for the free molecules; their appearance is likely due to symmetry breaking perturbations at defect sites (e.g., molecules trapped at vacancies). The fluence dependence of the band areas of infrared transitions for  $\text{NH}_3$  ( $4523 \text{ cm}^{-1}$ ),  $\text{H}_2$ , and  $\text{N}_2$  are shown in Figure 2 (top); the initial drop in  $\text{NH}_3$  agrees with the low-fluence measurements of Strazzulla & Palumbo (1998). The mass loss measured by the microbalance during the course of this experiment shows that  $<30\%$  of the ammonia is removed by ion impact (sputtering). Thus, the 81% drop in the  $\text{NH}_3$  band area is not only due to sputtering but mainly due to the decomposition of the molecule and formation of radiation products trapped in the ice, which include  $\text{H}_2$  and  $\text{N}_2$  (Fig. 2, top). The two lower panels in Figure 2 show the fluxes of ejected  $\text{H}_2$  and  $\text{N}_2$  measured by the MS, and the total sputtering yield, defined as the number of molecules ejected per incident ion. These quantities increase with fluence peaking at  $\sim(2-3) \times 10^{15} \text{ ions cm}^{-2}$ , suggesting that they are related to the accumulation of trapped species, such as H,  $\text{H}_2$ , N,  $\text{NH}_x$ , and  $\text{N}_2$ . Although the MS signal due to the  $\text{NH}_3$  is masked by OH from the water background, we were able to monitor the NH cracking product with the MS and found it to be below the noise level during irradiation, indicating that ejection of intact  $\text{NH}_3$  molecules or  $\text{NH}_x$  fragments is a minor contributor to sputtering. The drop in the sputtering yield and the MS signals at high

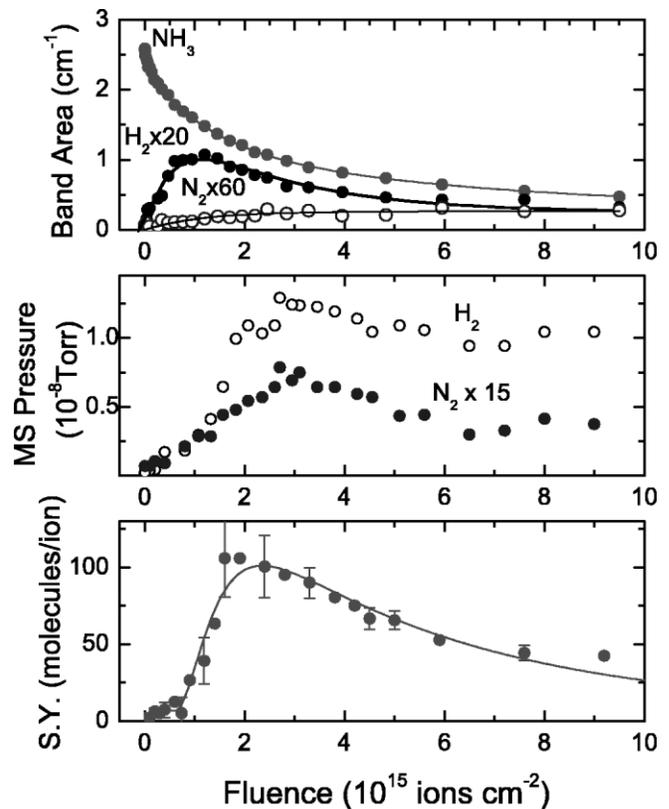


FIG. 2.—Evolution of a 1 : 2 ammonia-water mixture during irradiation with 100 keV protons at 70 K. *Top*: Fluence dependence of the infrared band area of  $\text{NH}_3$ ,  $\text{H}_2$ , and  $\text{N}_2$ . *Middle*: Raw data of gas ejection measured by the mass spectrometer. *Bottom*: Sputtering yield averaged over different experiments. The sputtering yield was calculated by dividing the mass loss by 17 amu. The lines shown are to guide the eye. [See the electronic edition of the Journal for a color version of this figure.]

fluences is correlated with the depletion of the radiolytic products (and ammonia) inside the film. We note that these processes do not have a thermal origin, since interruption of irradiation stopped changes in the infrared spectra, the outgassing flux, and the mass loss.

#### 3.2. Effects Seen During Post-Irradiation Warming

To explore the effects of temperature changes on the irradiated ices, we warmed the samples at  $0.2 \text{ K minute}^{-1}$  after irradiation, while measuring the infrared spectra, the mass loss, and the flux of the desorbed gas (Fig. 3). The  $\text{H}_2$  and  $\text{N}_2$  band areas decrease steadily during warming, even though there are no corresponding changes in the QCM and MS between 70 and 115 K. Since this decrease in the band area is not due to a loss of molecules, it is likely related to the annealing of defects that enabled these dipole forbidden transitions, as has been seen for  $\text{O}_2$  in condensed gases (Loeffler et al. 2006b).

During warming we observed two types of gas ejection: the usual thermal outgassing and strikingly fast ( $\leq 100 \text{ ms}$ ) bursts occurring at a frequency that peaks at  $\sim 125 \text{ K}$  and ceases by  $\sim 130 \text{ K}$ . The mass loss from the sample during each burst was below our level of detection ( $\sim 3 \text{ ng}$ ), but there was a cumulative loss of  $14.2 \mu\text{g cm}^{-2}$  due to these bursts and the underlying broad desorption peak. The bursts observed in the total flux, as is seen in the flickering of the ionization gauge, and in MS signals are due to hydrogen, nitrogen, and water. The broad desorption peak contains mainly water and  $\text{H}_2$  with little nitrogen; we note that this desorption peak corresponds to an 8% drop in the area of

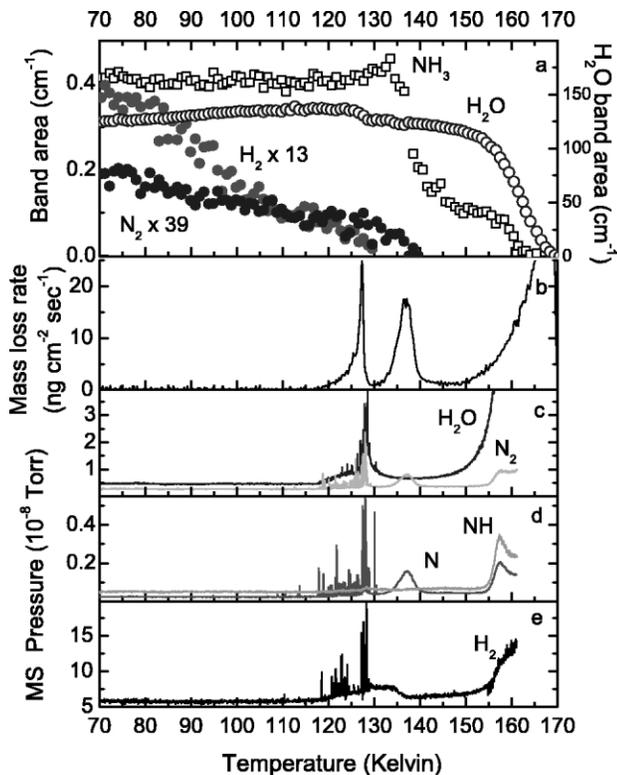


FIG. 3.—Evolution of a 1:2 ammonia-water sample irradiated with  $7.5 \times 10^{15} \text{ H}^+ \text{ cm}^{-2}$  at 70 K during warming at  $0.2 \text{ K minute}^{-1}$ . (a) Band areas calculated from the infrared spectra, (b) mass-loss rate from microbalance ( $\text{ng cm}^{-2} \text{ s}^{-1}$ ), and (c–e) pressure reading in the MS uncorrected for relative efficiencies. The MS data are not plotted beyond 161 K because it includes molecules coming from surfaces outside the irradiated area. [See the electronic edition of the Journal for a color version of this figure.]

the water absorption band at  $\sim 800 \text{ cm}^{-1}$  (Fig. 3, top). The next peak in the mass-loss rate, at 137 K, is correlated with the emission of nitrogen, and contains  $22.1 \mu\text{g cm}^{-2}$  or 51% of the mass of nitrogen (in  $\text{NH}_3$ ) in the film before irradiation. This loss of nitrogen at this temperature is nearly 5 times larger than that due to the decrease of ammonia, inferred from the drop of the infrared absorption band at the top of Figure 3. As seen for other gases (see, e.g., Vidal et al. 1997) this broad  $\text{N}_2$  peak occurs during crystallization of the water ice that remains in the sample, possibly as a result of the enhanced diffusion paths along the newly formed grain boundaries. At higher temperatures, the small drop of the  $\text{NH}_3$  absorption band and the increase of the  $\text{NH}$  signal in the MS due to  $\text{NH}_3$  cracking indicate desorption of the ammonia that remained trapped in the ice after crystallization. We note that there is no emission of intact ammonia molecules below 140 K.

The peak in the desorption of water, seen between 115 and 130 K, was unexpected, because in both pure water ice (Sack & Baragiola 1993) and in an unirradiated mixture, this degree of sublimation is only seen at much high temperatures. This desorption peak is not directly related to  $\text{H}_2$  accumulation in the ice, since the fluence ( $1.2 \times 10^{15} \text{ ions cm}^{-2}$ ) that maximizes trapped  $\text{H}_2$  (Fig. 2) is significantly smaller than that for maximum water desorption ( $7.5 \times 10^{15} \text{ ions cm}^{-2}$ ). Since the water desorption peak is always accompanied by outbursts of  $\text{H}_2$  and  $\text{N}_2$ , we propose that these gases aggregate as gas bubbles of increasingly higher pressure inside radiation-induced voids in the ice (Loeffler et al. 2006b). We note that trapped gas is expected to accumulate to nearly solid-state densities, implying

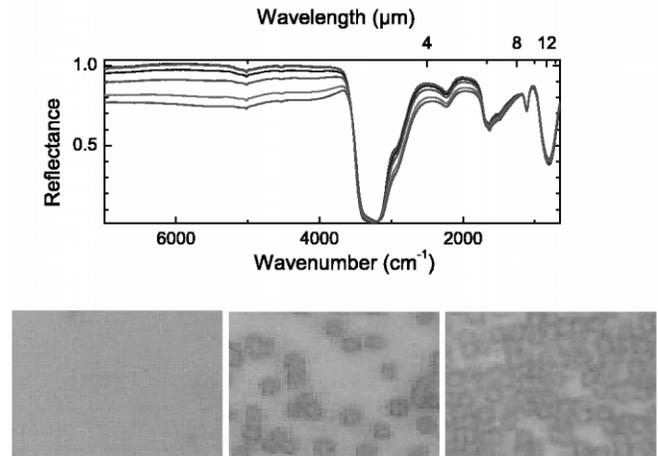


FIG. 4.—Top: Evolution of the infrared reflectance of a 1:2 ammonia-water sample deposited on a gold substrate and irradiated by  $7.5 \times 10^{15} \text{ H}^+ \text{ cm}^{-2}$  at 70 K during warming at  $0.2 \text{ K minute}^{-1}$ . The decrease in reflectance above  $4000 \text{ cm}^{-1}$  is seen at increasing temperatures (from top to bottom) of 108, 118, 122, 125, 127, and 129 K. Bottom: Micrographs of the sample after irradiation before warming (left), in the beginning of the bursts (middle), and near the end of the bursts (right). The scale of the micrographs is  $50 \times 36 \mu\text{m}$ . [See the electronic edition of the Journal for a color version of this figure.]

pressures as high as 1000 atmospheres. Similarly to what occurs in the trapping of gases in nuclear fusion reactors (Das & Kaminsky 1976; Gittus 1978), when the gas pressure exceeds the fracture strength of the ice, gas in surface blisters bursts out exfoliating the blister top, resulting in the ejection of vapor and small ice particles. Although of a different origin, this mechanism is similar to the ejection of icy particles from gas-loaded ice during warming (Laufer et al. 1987). When the blisters rupture, they scatter light causing a decrease in the reflectance of the sample, as shown in Figure 4 (top). The resulting surface topography has been photographed in situ with a long distance microscope, Figure 4 (bottom), showing the appearance of features on the order of  $5 \mu\text{m}$  across. The ejected particles could be smaller since the blister top could break into smaller pieces when the ice ruptures, of the order of the micron size E-ring particles deduced by Showalter et al. (1991) through the modeling of *Voyager* photometric data.

#### 4. ASTROPHYSICAL IMPLICATIONS

At Enceladus, a layer of ammonia dihydrate that resurfaces by some endogenic process will be irradiated by magnetospheric protons to an energy fluence of  $1 \times 10^{18} \text{ keV cm}^{-2}$  (corresponding to  $1 \times 10^{16} \text{ 100 keV ions cm}^{-2}$ ) in  $\sim 25 \text{ yr}$ , using data from Jurac et al. (2001b). This time is probably a lower limit since the flux may be an overestimate (Paranicas et al. 2004). Magnetospheric ion irradiation will deplete the surface of ammonia, making improbable its detection by infrared reflectance (Brown et al. 2006; Emery et al. 2005; Verbiscer et al. 2006) until the next resurfacing event occurs. Irradiation also causes ejection of hydrogen and nitrogen from the surface. In particular, the nitrogen emission explains the observation of  $\text{N}^+$  near Enceladus by the *Cassini* Plasma Spectrometer (CAPS; Smith et al. 2005; Young et al. 2005) and of the neutral  $\text{N}_2$  observed by the *Cassini* Ion and Neutral Mass Spectrometer (INMS; Waite et al. 2006).

The desorption of water vapor and ejection of icy particles at temperatures as low as 115 K can explain the plume of gas

and particles emitted from the South Polar region of Enceladus observed by the *Cassini* Ultraviolet Imaging Spectrograph (UVIS; Hansen et al. 2006). Scaling our results for desorbed gas between 100 and 130 K to the size of the region responsible for the plume, estimated from the images (Porco et al. 2006) to be  $2.4 \times 10^4 \text{ km}^2$ , leads to  $\sim 3.4 \times 10^8 \text{ kg}$  of ejected material where we have taken into account that higher energy ions and electrons will alter the surface material to depths  $\sim 100$  times larger than 100 keV ions (Cooper et al. 2001). This number gives our plume a lifetime of  $\sim 25$  days using the escape rate of  $150 \text{ kg s}^{-1}$  estimated by Hansen et al. (2006). This number of days, although possibly sufficient to explain a sporadic plume compatible with the variability of the Saturnian environment (Esposito et al. 2005; Porco et al. 2006), is certainly a lower limit for the lifetime of the plume. Gardening of the

regolith, as has been observed in the Moon, will occur by impacts of micrometeorites, including ice grains from the rings, burying and mixing the radiolytic products to depths much larger than the penetration range of the energetic particles. The effect of this turnover will be to substantially increase the thickness of the ammonia depletion region and the lifetime of the plumes. In addition, if the decay of radioactive elements turns out to be a significant source of heat, it will also enhance the decomposition of ammonia and the formation of radiolytic products, possibly throughout the ice mantle.

This research was supported by NASA Planetary Atmospheres and *Cassini* program and by NSF Astronomy. M. J. L. thanks the Virginia Space Grant Consortium for a fellowship.

## REFERENCES

- Brown, R. H., et al. 2006, *Science*, 311, 1425  
 Carlson, R. W., et al. 1999, *Science*, 283, 2062  
 Cooper, J. F., Johnson, R. E., Mauk, B. H., Garrett, H. B., & Gehrels, N. 2001, *Icarus*, 149, 133  
 Das, S. K., & Kaminsky, M. 1976, *Adv. Chem. Ser.*, 158, 112  
 Ellsworth, K., & Schubert, G. 1983, *Icarus*, 54, 490  
 Emery, J. P., Burr, D. M., Cruikshank, D. P., Brown, R. H., & Dalton, J. B. 2005, *A&A*, 435, 353  
 Esposito, L. W., et al. 2005, *Science*, 307, 1251  
 Gittus, J. 1978, *Irradiation Effects in Crystalline Solids* (London: Appl. Sci.)  
 Hansen, C. J., et al. 2006, *Science*, 311, 1422  
 Hogenboom, D. L., Kargel, J. S., Consolmagno, G. J., Holden, T. C., Lee, L., & Buyyounouski, M. 1997, *Icarus*, 128, 171  
 Jurac, S., Johnson, R. E., & Richardson, J. D. 2001a, *Icarus*, 149, 384  
 Jurac, S., Johnson, R. E., Richardson, J. D., & Paranicas, C. 2001b, *Planet. Space Sci.*, 49, 319  
 Kargel, J. S., & Pozio, S. 1996, *Icarus*, 119, 385  
 Lanzerotti, L. J., Brown, W. L., Marcantonio, K. J., & Johnson, R. E. 1984, *Nature*, 312, 139  
 Laufer, D., Kochavi, E., & Bar-Nun, A. 1987, *Phys. Rev. B*, 36, 9219  
 Lewis, J. S. 1971, *Icarus*, 15, 174  
 Loeffler, M. J., Teolis, B. D., & Baragiola, R. A. 2006a, *J. Chem. Phys.*, 124, 104702  
 Loeffler, M. J., Teolis, B. D., & Baragiola, R. A. 2006b, *ApJ*, 639, L103  
 Noll, K. S., Roush, T. L., Cruikshank, D. P., Johnson, R. E., & Pendleton, Y. J. 1997, *Nature*, 388, 45  
 Paranicas, C., Decker, R. B., Mauk, B. H., Krimigis, S. M., Armstrong, T. P., & Jurac, S. 2004, *Geophys. Res. Lett.*, 31, L04810  
 Porco, C. C., et al. 2006, *Science*, 311, 1393  
 Prialnik, D., & Bar-Nun, A. 1990, *ApJ*, 355, 281  
 Ross, M. N., & Schubert, G. 1989, *Icarus*, 78, 90  
 Sack, N. J., & Baragiola, R. A. 1993, *Phys. Rev. B*, 48, 9973  
 Showalter, M. R., Cuzzi, J. N., & Larson, S. M. 1991, *Icarus*, 94, 451  
 Smith, B. A., et al. 1982, *Science*, 215, 505  
 Smith, H. T., et al. 2005, *Geophys. Res. Lett.*, 32, L14S03  
 Spahn, F., et al. 2006, *Science*, 311, 1416  
 Spencer, J. R., et al. 2006, *Science*, 311, 1401  
 Squyres, S. W., Reynolds, R. T., Cassen, P. M., & Peale, S. J. 1983, *Icarus*, 53, 319  
 Strazzulla, G., & Palumbo, M. E. 1998, *Planet. Space Sci.*, 46, 1339  
 Verbiscer, A. J., French, R. G., & McGhee, C. A. 2005, *Icarus*, 173, 66  
 Verbiscer, A. J., et al. 2006, *Icarus*, 182, 211  
 Vidal, R. A., Bahr, D., Baragiola, R. A., & Peters, M. 1997, *Science*, 276, 1839  
 Waite, J. H., et al. 2006, *Science*, 311, 1419  
 Wisdom, J. 2004, *AJ*, 128, 484  
 Young, D. T., et al. 2005, *Science*, 307, 1262  
 Ziegler, J. F. 2003, *Stopping and Range of Ions in Matter: SRIM-2003*, <http://www.srim.org>