

**SULFURIC ACID HYDRATE ON EUROPA: EXOGENIC CONTROLS ON THE RADIOLYTIC SULFUR CYCLE.** J. B. Dalton, III<sup>1</sup>, J.H. Shirley<sup>1</sup>, C. Paranicas<sup>2</sup>, T. Cassidy<sup>1</sup>, LM. Prockter<sup>2</sup>, and L. W. Kamp<sup>1</sup>, <sup>1</sup>Jet Propulsion Laboratory, California Institute of Technology, 4800 Oak Grove Drive, Pasadena, CA 91109, <sup>2</sup> Johns Hopkins University Applied Physics Laboratory, 11100 Johns Hopkins Road, Laurel MD 20723.

**Introduction:** Its probable subsurface ocean of liquid water has marked Jupiter's moon Europa as a prime target of astrobiological interest. Surface deposits derived from that ocean remain our most direct source of information on the ocean's chemistry. While some deposits may have originated from oceanic composition, they have been subjected to exogenic processes, primarily magnetospheric charged particle bombardment, since the time of emplacement. Spectral modeling using cryogenic reference spectra has now begun to separate such exogenic effects from the interior processes responsible for the original composition.

**Background:** Observations from Galileo's Near Infrared Mapping Spectrometer (NIMS) have revealed that the surface is composed primarily of water ice, with hydrated sulfate salts and sulfuric acid hydrate, as well as volatile ices including SO<sub>2</sub> and CO<sub>2</sub> [1,2]. Jovian magnetospheric charged particles continually impinge upon Europa's surface, driving radiolytic chemistry, modifying endogenic materials deposited at the surface, and implanting a number of mainly Iogenic elements including H, O, S, K, Na, Cl and possibly Mg. While it is not clear whether the hydrated salts can be created purely from magnetospheric bombardment of implanted ions, production of H<sub>2</sub>SO<sub>4</sub> hydrate from H<sub>2</sub>O and SO<sub>2</sub> ices by radiolysis has been demonstrated in the lab [2]. Separating the exogenic effects of radiolytic, photolytic, and other processing from the endogenic subsurface processes is critical to understanding the surface and subsurface compositions at Europa.

Spectral modeling of NIMS observations using temperature-appropriate cryogenic reference spectra of candidate surface materials has been demonstrated as a

powerful technique for evaluating the composition of icy satellite surface deposits [3,4,5]. Since Jovian plasma corotates at approximately the planetary rotation rate, particles overtake Europa in its orbit so that its trailing hemisphere receives a much higher dose of radiolytic flux than the leading hemisphere [6]. Previous work [5] demonstrated a gradient in H<sub>2</sub>SO<sub>4</sub> hydrate abundance that correlates with the electron and sulfur ion fluxes [7] near the leading/trailing hemisphere boundary. Here we extend that analysis to include NIMS observations in more distant regions.

**Methodology:** This work has three main aspects: first, availability of cryogenic reference spectra; second, calibration and modeling of the NIMS observations; and third, modeling of incident electron and ion fluxes to determine total dose for a given location.

**Cryogenic reflectance spectroscopy.** Visible to near-infrared (VNIR, 0.3-2.5 μm) reflectance spectra of candidate surface materials were obtained using cryogenic environment chambers at USGS-Denver, NASA-Ames Research Center and the JPL Planetary Ice Characterization Laboratory (PICL) [1,8]. Candidates included epsomite, hexahydrate, bloedite, mirabilite, undecahydrate, and MgSO<sub>4</sub> and Na<sub>2</sub>SO<sub>4</sub> brines. Brines were flash-frozen in liquid nitrogen, and hydrated salts were ground and sieved to 100-μm size fraction before measuring their spectra at 100 or 120 K. H<sub>2</sub>SO<sub>4</sub> hydrate spectra were provided by R.W. Carlson [9] and synthetic water ice spectra were generated using a Hapke reflectance model [1,4,5].

**Calibration and modeling of NIMS observations.** In prior work we applied an updated radiation noise removal method [5,10] to the NIMS 14ENSUCOMP01

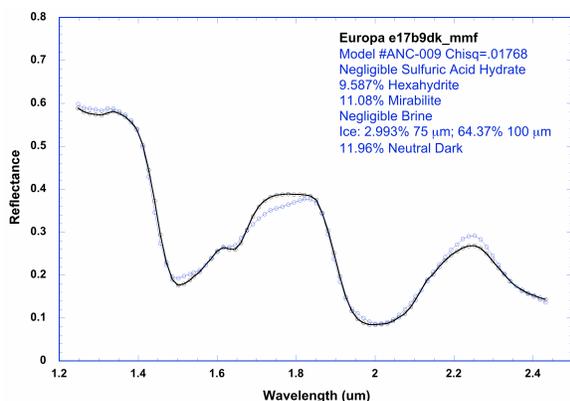


Figure 1. Spectral model (blue) of E17 encounter NIMS data (black) from an icy region on Europa's leading hemisphere. The model predicts ~20% salt hydrates but no brines or H<sub>2</sub>SO<sub>4</sub> hydrate. Ice grains of 100 μm (~65%) gave the best match.

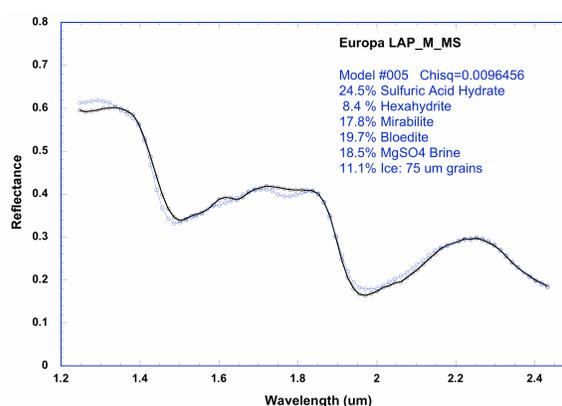


Figure 2. Spectral model (blue) of NIMS data (black) from dark plains unit near the leading-trailing side boundary. The model predicts ~25% H<sub>2</sub>SO<sub>4</sub> hydrate and ~46% hydrated salts, with ~20% MgSO<sub>4</sub> brine. 75-μm-diameter ice makes up ~10% of the mixture.

observation, greatly reducing the influence of noise spikes caused by radiation hits on the detectors. Here we augment that dataset with two additional NIMS observations: 17ENSUCOMP02, from a high latitude location on the leading hemisphere at 63° S, 120° W, and 15ENSUCOMP01, from an equatorial location, also on the leading hemisphere, at 7.8° N, 114° W.

We applied a standard linear mixture model to match the NIMS spectra using linear combinations of the candidate material spectra. A neutral dark component was included to account for shadowing and phase angle effects. The model used the  $\chi^2$  least-squares goodness-of-fit estimator and a simplex algorithm [4,5] to determine the best match. Several tens of thousands of combinations were examined for each observation.

*Electron and ion flux estimates.* The trailing hemisphere apex is expected to receive the highest concentration of Jovian magnetospheric ions and electrons, with bombarding fluxes falling off from that point to the leading hemisphere apex. Modeling, even in the case of an inert Europa, reveals a more complicated picture showing that the pattern depends on particle species and energy. One striking asymmetry is due to energetic electrons and sulfur ions preferentially bombarding the trailing hemisphere [6]. The energetic electrons provide ionizing energy, which can alter the surface composition by both creating and destroying surface compounds. Implanted sulfur ions provide a raw source of elemental sulfur, complementary to possible geologic/oceanic sources.

**Results:** Our linear spectral model can now distinguish material abundances within individual geologic units to within  $\pm 3\%$  in Galileo NIMS Europa observations [5]. Figure 1 shows a NIMS spectrum (heavy black line) from an icy region on the leading hemisphere, where the charged particle flux is lowest. The spectrum is dominated (65%) by water ice of  $\sim 100\text{-}\mu\text{m}$  grain size, with a small ( $\sim 20\%$ ) complement of hydrated sulfate salts, but no noticeable brine or sulfuric acid component. In contrast, the NIMS spectrum in Figure 2 was derived from dark plains materials located near the leading/trailing side boundary [5]. The strong asymmetry in the 1.5- and 2.0- $\mu\text{m}$  features is diagnostic of hydrated material. The best fit model invokes  $\sim 25\%$  sulfuric acid hydrate in this case, with  $\sim 46\%$  hydrated salts and 20%  $\text{MgSO}_4$  brine. The remaining  $\sim 10\%$  is water ice of mainly 75- $\mu\text{m}$  grain size.

Modeling of the E15 and E17 observations yielded compositions invoking almost no sulfuric acid hydrate, except in the vicinity of dark linear features (linea). Even the iciest regions required 8-20% salt hydrates to provide an optimum fit. Water ice grain sizes obtained (50-100  $\mu\text{m}$ ) are consistent with earlier work [11].

Figure 3 contains estimates of  $\text{H}_2\text{SO}_4$  abundance derived from individual geologic units at various longitudes. The cluster of values near the 180° meridian separating leading and trailing hemispheres (left) were determined from ancient ridged plains units in NIMS observation E14ENSUCOMP01 [5]. New values for the leading hemisphere (E15, E17, right) are consistent with independent predictions of other investigators [3,6] that the  $\text{H}_2\text{SO}_4$  abundance approaches zero near the apex of the leading hemisphere, where the combined electron and sulfur ion fluxes are lowest.

**Conclusion:** Sulfuric acid hydrate abundance ultimately must be controlled by total cumulative energy dose, available sulfur, or a combination of both. The depth into the surface at which we observe this material may also be relevant because charged particles have much different penetration depths. But separating the influence of energy and available sulfur may make it possible to utilize sulfuric acid hydrate abundance as a proxy for exposure age. This could prove highly valuable on sparsely cratered bodies like Europa.

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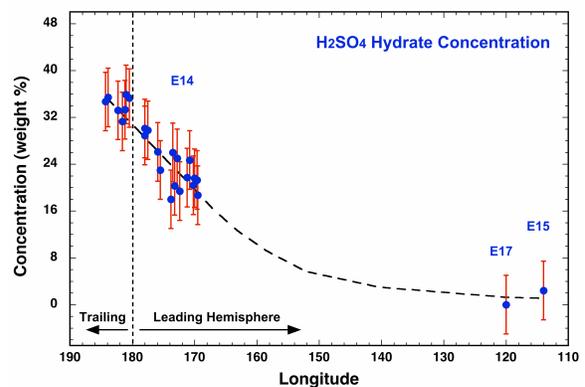


Figure 1.  $\text{H}_2\text{SO}_4$  hydrate concentration with longitude, from Galileo NIMS observations. Observations taken toward the leading hemisphere apex (E15 and E17, right) continue the trend of decreasing  $\text{H}_2\text{SO}_4$  with decreasing total deposited particle energy flux.