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The chemical nature of Europa surface material and the relation to a subsurface ocean

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Abstract

The surface composition of Europa is of special interest due to the information it might provide regarding the presence of a subsurface ocean. One source of this information is the infrared reflectance spectrum. Certain surface regions of Europa exhibit distorted H_2O vibrational overtone bands in the 1.5 and 2.0 µm region, as measured by the Galileo mission Near Infrared Mapping Spectrometer (NIMS). These bands are clearly the result of highly concentrated solvated contaminants. However, two interpretations of their identity have been presented. One emphasizes hydrated salt minerals and the other sulfuric acid, although each does not specifically rule out some of the other. It has been pointed out that accurate chemical identification of the surface composition must depend on integrating spectral data with geochemical models, and information on the tenuous atmosphere sputtered from the surface. It is also extremely important to apply detailed chemistry when interpreting the spectral data, including knowledge of mineral dissolution chemistry and the subsequent optical signatures of ion solvation in low-temperature ice. We present studies of flash frozen acid and salt mixtures as Europa surface analogs and demonstrate that solvated protons, metal cations and inorganic anions all influence the spectra and must all, collectively, be considered when assigning Europa spectral features. These laboratory data show best correlation with NIMS Europa spectra for multi-component mixtures of sodium and magnesium bearing sulfate salts mixed with sulfuric acid. The data provide a concentration upper bound of 50-mol% for $MgSO_4$ and 40-mol% for Na_2SO_4. This newly reported higher sodium and proton content is consistent with low-temperature aqueous differentiation and hydrothermal processing of carbonaceous chondrite-forming materials during the formation and early evolution of Europa.
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1. Introduction

Europa is the subject of intense scrutiny because of the possibility that its icy shell may conceal a liquid ocean capable of harboring life (Carr et al., 1998; Chyba, 2000; Chyba and Phillips, 2001). Evidence regarding crustal composition is limited, but includes sputtered atmospheric constituents (Brown, 2001; Brown and Hill, 1996; Hall et al., 1995) and near-infrared reflectance spectra of surface re-

gions from the Galileo NIMS investigation (Carlson et al., 1996). Reflectance spectra of certain Europa surface regions exhibit highly distorted H_2O vibrational overtone bands. One interpretation is that these suggest endogenic frozen salt mineral mixtures with some Na_2SO_4 converted to H_2SO_4 under irradiation at the surface (McCord, 1998a; McCord et al., 1999, 2002). The other proposes that H_2SO_4 in ice gives the best single-component match to the NIMS spectra (Carlson et al., 1999). In the former, the salts come from the ocean below. In the latter, H_2SO_4 is from radiation processing and sulfur ion implantation in water ice from the jovian plasma torus. Hopes of accurate chemical identification of the surface material, and extrapolation to a

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subsurface ocean, will depend on integrating UV, visual and IR spectral data (Fanale et al., 1999), geochemical models (Kargel et al., 2000; Spaun and Head, 2001; Zolotov and Shock, 2001), and information on the tenuous and likely sputtered atmosphere (Johnson, 2000; Johnson et al., 2002; Leblanc et al., 2002) in a holistic view. However, interpretation of the reflectance spectra requires knowledge of mineral dissolution chemistry and the subsequent optical signatures of ion-solvation in low-temperature ice. All plausible models of Europa's formation and thermo-chemical evolution indicate that the crustal ice is not pure, but rather must contain some mineral content remnant of its formation from solar nebula solids.

Europa is a differentiated Moon-sized object, with a silicate core, water-rich mantle and ice crust that is subjected to strong energy input from Jupiter-induced tidal flexing (Carr et al., 1998; Geissler et al., 1998; Greeley et al., 2004; Khurana et al., 1998; Pappalardo et al., 1998). Thus, the layers beneath the icy crust could melt forming a liquid ocean which could foster the dissolution of core minerals. Though the thickness of the ice remains controversial, it is clear that it has been disrupted extensively from below. The materials present on the surface of Europa are the products of radiation transformations, cryovolcanism, impact and gardening events that have occurred over time. In fact, chemical alteration of the ice has been shown to produce condensed hydrogen peroxide within at least some icy surface regions (Carlson et al., 1999). Also, an atmosphere composed mostly of atomic and molecular hydrogen with some atomic and molecular oxygen from radiation processing of surface ice is seen (Hall et al., 1995; Orlando and Sieger, 2003; Sieger et al., 1998; Wu et al., 1978).

The chemical identity of the surface, when analyzed in conjunction with other mission data, can be considered as fingerprints of the past geochemical and geophysical activity. The association of the material with the disrupted regions on the surface strongly suggests an endogenic origin (McCord et al., 1998a, 1998b). Geochemical models suggest that salts such as $MgSO_4$ with Na_2SO_4 can be produced by low-temperature aqueous alteration of solar nebula material, as seen in carbonaceous chondrites (Kargel et al., 2000). This is expected to lead to the formation of Mg–Na–Ca-sulfate rich material, which, due to the presence of sulfidic base material, could also form some sulfuric acid (Kargel et al., 2000). Typically, salts in natural environments occur as mixtures, controlled by their source material, solubilities and formation temperatures. The relative abundances of these compounds depend upon the planetary condensation and internal Europa evolution temperatures, with lower temperatures favoring a relatively high sodium concentration. Some modeling has also been carried out which addresses the role of basic (Marion, 2001) and acidic conditions (Marion, 2002) on the freezing of aqueous solutions containing sodium and magnesium bearing sulfate salts.

The Galileo mission's Near Infrared Mapping Spectrometer (NIMS) returned infrared (IR) reflectance spectra (Carlson et al., 1996) exhibiting asymmetric absorption bands in the 1–3 μm spectral region (McCord et al., 1998a, 1998b). The primary features in this region are attributed to water ice overtones that shift in frequency and become asymmetric when ice contains certain types of impurities or when water molecules are in confined geometries. The asymmetric spectral signatures in the 1–3 μm region are concentrated on Europa in lineaments and chaotic terrain (McCord et al., 1998a, 1998b). We previously demonstrated that rapidly frozen brines give better spectral matches to the NIMS non-ice endmember spectrum than hydrous crystalline minerals (McCord et al., 2002). This rapid quenching/glass forming process preserves the water structures associated with the solvated ions in brine solutions. The complex cation, anion and proton solvation structures formed during flash freezing of aqueous solutions are possible sources of the perturbed optical signatures observed in the NIMS spectra. Thus, we undertook studies of flash frozen acid and salt mixtures as Europa surface analogs to examine the relative contribution of endogenic vs exogenic surface contamination.

2. Experimental

Infrared reflectance and temperature programmed dehydration were performed under low vacuum in a custom built chamber. The sample holder was a polished copper plate mounted to a rotatable flange which allows measurements to be taken both in diffuse and specular reflection. The sample mount was cooled with liquid nitrogen and resistively heated to achieve a temperature range of 77–400 K. Spectra were obtained using a Bruker Equinox 55 FTIR Spectrometer with an externally mounted detector (MCT, Infrared Associates Inc.). Infrared measurements were taken in diffuse reflection to more accurately base a comparison to the observational spectra from the Near Infrared Mapping Spectrometer aboard the Galileo spacecraft (McCord et al., 1998a, 1998b).

Salt solutions and acids were mixed in 1:8 mole ratio, with varying proportions of H^+, Na^+, and Mg^{2+} but constant SO_4^{2-} concentration. The samples were prepared by injecting saturated or highly concentrated acid or salt solution doses in multiple aliquots of small volume (10–25 μL) onto the cold sample surface through a septum port in the chamber. Previous experiments have made use of mixing a spectrally inert microcrystalline nucleus (diamond or SiO_2) to control grain size and limit optical penetration depth to obtain spectra comparable to those of NIMS (Carlson et al., 1999; Dalton, 2003). The spray technique utilized here produces a frosty texture that achieves equally acceptable spectral characteristics. The salts and acids used in this experiment were obtained from Aldrich and include $MgSO_4$, $MgCl_2$, Na_2SO_4, H_2SO_4, HNO_3, and HCl. Salt solutions were prepared at saturation at room temperature, while acids were mixed in 1:8 mole ratio with water. The solutions froze instantaneously on contact with the cold copper surface. De-

hydration was achieved by annealing the samples from the dosing point at 100 K up to a temperature adequate for water sublimation (~220 K) but below the crystallization point (>250 K) of the solutions. This is to simulate the long term erosion and thermal cycling of the surface of Europa in the vacuum of space. As a result of this dehydration step, the absolute concentrations of the salts in the ice are not known. All percentages reported here are in terms of mole fractions of the salts relative to each other.

3. Results and discussion

3.1. The relation of salt hydrolysis to acidity

Salt solutions, such as Earth's ocean, are generally considered to be of moderate pH since they are the result of acid–base neutralization reactions. For example, Na^+ is not capable of undergoing hydrolysis since it is the conjugate acid of a very strong base, thereby rendering it an extremely weak acid. However, cations such as Fe^{2+} and Mg^{2+} have large Z^2/r ratios (where Z is charge and r is the ionic radius) and therefore may react with water. Hydrolysis releases protons: i.e. $Mg^{2+} + H_2O \rightarrow MgOH^+ + H^+$. The proton is highly reactive and quickly forms a hydronium (H_3O^+) or Zundel cation ($H_5O_2^+$). The proton is also the primary product of the radiolysis of water ice. Although under terrestrial conditions, the hydrolysis of Mg^{2+}, released from the dissolution of $MgSO_4$, is counterbalanced by the weak nature of the second proton of sulfate, efficient ionization of HSO_4^- has been observed in low-temperature ice (Tomikawa and Hitoshi, 1998). The ionization probability was seen to increase exponentially with decreasing temperature, which should result in net release of solvated protons from magnesium hydrolysis over the temperature range typical of the Galilean satellite surfaces. This factor could provide a source term for a spectral signature of acids on an icy surface even if the contaminant material is endogenic in origin.

3.2. Infrared spectra of flash frozen salt and acid solutions

Fig. 1 shows a series of infrared spectra of flash frozen acids and salt brine solutions in the 1.4–2.6 μm region. For comparison, a NIMS non-ice endmember spectrum (McCord et al., 1999, 2002) is also shown. The spectra shown in Fig. 1 share a number of common features. Specifically, all spectra exhibit strong asymmetric peaks at 1.5 and 1.95 μm and most of the spectra have weak shoulder features at 1.58, 1.65, 1.80, and 2.2 μm. The feature at 1.65 mm is a distinct indicator of crystalline ice. The first three spectra are for flash frozen HNO_3, $MgCl_2$, and $MgSO_4$ and the following three are for flash frozen H_2SO_4, Na_2SO_4 and the NIMS spectrum. The position and width of the 1.95-μm feature of the NIMS spectra are reproduced well by all species containing sulfate anions. This feature can be associated with
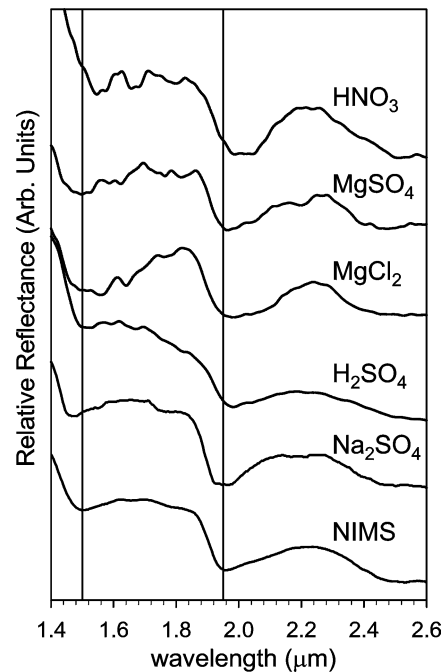

Fig. 1. Diffuse infrared reflectance spectra of selected flash frozen acids and salts. The bottom spectrum is the NIMS Europa non-ice endmember spectrum (McCord, 1998a, 1998b; McCord et al., 1999, 2002). Variations in the asymmetry of the 1.9–2.4 μm band are largely influenced by the nature of the anion–ice interaction, whereas bands in the 1.5–1.8 μm region are predominantly controlled by the cation and/or the presence of protons. Examining the role of both the cation and anion is critical in understanding these spectral signatures.

the $\nu_2 + \nu_3$ combination band of water, which is known to be perturbed by anions with diffuse charge distributions, such as SO_4^{2-} (Cannon et al., 1994). The perturbations on the hydrogen bonded network surrounding the anion are strong, resulting in a red-shift in stretch and a blue-shift in bend frequencies relative to bulk ice. Indeed, molecular dynamics simulations of the liquid phase indicate that the hydrogen atoms associated with the first solvation sphere are oriented toward the anion (Cannon et al., 1994). These average molecular arrangements are expected to be preserved during the flash freezing process. Singly charged anions, such as NO_3^- and Cl^-, show features close to that of the NIMS but careful inspection shows discernable and reproducible differences, particularly in the 2.2 and 2.09 μm shoulder features.

The asymmetric feature at 1.5 μm can be associated with the $\nu_1 + \nu_3$ combination band overtone of water and appears highly correlated with the presence of localized positive charge density. The spectra for material containing magnesium shows a very weak absorption at 1.80 μm, a feature clearly present in NIMS and the spectra for HNO_3, H_2SO_4, and Na_2SO_4. Thus, we associate the strong 1.80 μm feature as well as the induced asymmetry of the envelope between 1.5 and 1.8 μm primarily with the presence of protons and small cations such as Na^+. Although the hydrated proton is very mobile and ill defined in the liquid phase, it is immobilized in low-temperature ice (Cowin et al., 1999). The H^+

and Na$^+$ interact strongly with the surrounding water leading to polarization of the molecules and an elongation of the O–H bonds and the hydrogen bonding interactions between the first and second shells is increased. Calculations indicate (Lee et al., 2004) that the ion–oxygen distances are 2.3–2.4 Å for H$^+$ (H$_2$O)$_{n=1-6}$ and 2.4–2.5 Å for Na$^+$ (H$_2$O)$_{n=1-6}$. Thus, the overall structures and fundamental vibrational frequencies associated with these solvated cations are very similar (Bauschlicher et al., 1991). This is essential information that has not been taken into account when analyzing NIMS data on the distorted H$_2$O bands on Europa.

Fig. 1 also shows that the best *single-component* match to NIMS spectra is for H$_2$SO$_4$. Our spectrum is identical to that obtained by Carlson et al. (1999), using a diamond paste seeding method. The acids studied here are strong acids and are well-known sources of protons in aqueous solution and ice. Though it is tempting to suggest that acid mixtures are good surrogates for radiation-induced defects in ice, there are several significant discrepancies. Substitution of a water molecule by an acid molecule results in the increase of L-type orientational defects and hydronium ions, as well as concomitant reductions of D-type defects and hydroxyl ions (Takei and Maeno, 1987). The acid molecule also contributes its own fully solvated counter-anion, while radiation processed ice does not necessarily maintain charge neutrality. Thus, local defect configurations and equilibrium concentrations are not the same as those produced by incident radiation. Though H$_2$SO$_4$ produces a good, but not perfect, single component spectral match, we must consider multicomponent mixtures that might be better matches and that are more consistent with the inhomogeneous spatial distribution of the non-ice material and geochemical models.

3.3. Infrared spectra of flash frozen salt and acid mixtures

The compositions of several of the mixtures studied are presented in Table 1 and are relevant to those derived from models based on simple low-temperature aqueous dissolution of a primitive chondrite (Fanale et al., 2001; Kargel et al., 2000). Attempts to match the observed spectra by numerical weighted summing of lab spectra of pristine mineral samples (McCord et al., 1999) does not take into account nonlinear solute interactions with ionic strength, pH or limiting solvation volume, especially considering the degree of dehydration involved in these experiments. It is therefore necessary to actually mix these components together to make a valid assignment.
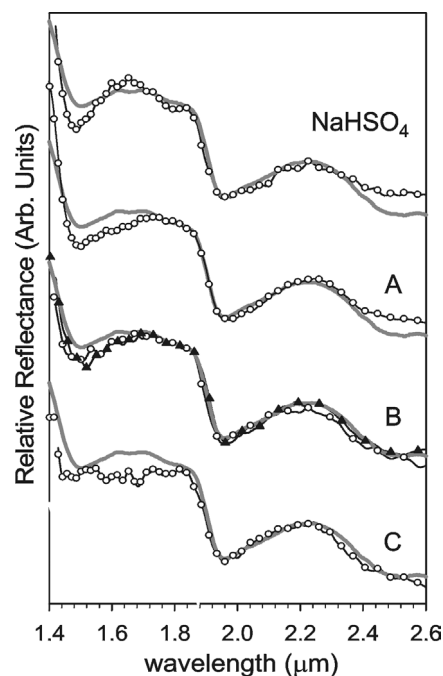

Fig. 2. Direct comparison of the diffuse reflectance spectra of selected flash frozen sulfate salt/acid mixtures to the NIMS data (gray line). The top spectrum is that of NaHSO$_4$. Spectrum A is a three component mixture containing 0.5:0.1:0.4 MgSO$_4$:Na$_2$SO$_4$:H$_2$SO$_4$, respectively. Spectrum B is of a solution with ratios 0.5:0.25:0.25 (open circles). Superimposed on spectrum B is the equivalent solution starting from NaHSO$_4$ rather than equal amounts Na$_2$SO$_4$ and H$_2$SO$_4$ (dark triangles). Frozen samples of the three component solutions give near perfect matches to NIMS data and clearly emphasize the role composites play in the surface composition of Europa. Each spectrum shows excellent agreement with the NIMS data in the 1.9–2.4 μm region as a result of the common sulfate anion. The spectrum labeled C containing 70 mole-percent MgSO$_4$ does not fit the NIMS data well. Solutions B and C also show good agreement with NIMS in the 2.5 μm region.

To examine the effect of sodium content, we flash froze NaHSO$_4$ and Na$_2$SO$_4$ solutions containing H$_2$SO$_4$. These mixtures may produce a similar chemical composition expected for radiation processed hydrated Na$_2$SO$_4$ (Carlson et al., 2002; Johnson et al., 2002; McCord et al., 2002). Plotted at the top of Fig. 2 is the spectrum of NaHSO$_4$ in direct comparison to the NIMS non-ice endmember spectrum (gray line). Also shown in Fig. 2 are spectra of NaHSO$_4$ and Na$_2$SO$_4$:H$_2$SO$_4$ solutions that contain various amounts of MgSO$_4$. The spectrum marked A (open circles) corresponds to a solution of 50% MgSO$_4$, 10% Na$_2$SO$_4$, and 40% H$_2$SO$_4$. This magnesium-rich solution has a noticeably increased absorption at 1.6 μm relative to that for the NaHSO$_4$ spectrum above, however the absorption at 1.5 μm is still too strong compared to NIMS. There are two spectra labeled B; one created from a mixture of MgSO$_4$ and NaHSO$_4$ (open circles), the other an equivalent mixture of MgSO$_4$ with equal amounts Na$_2$SO$_4$ and H$_2$SO$_4$ (filled triangles). The spectra are in excellent agreement with each
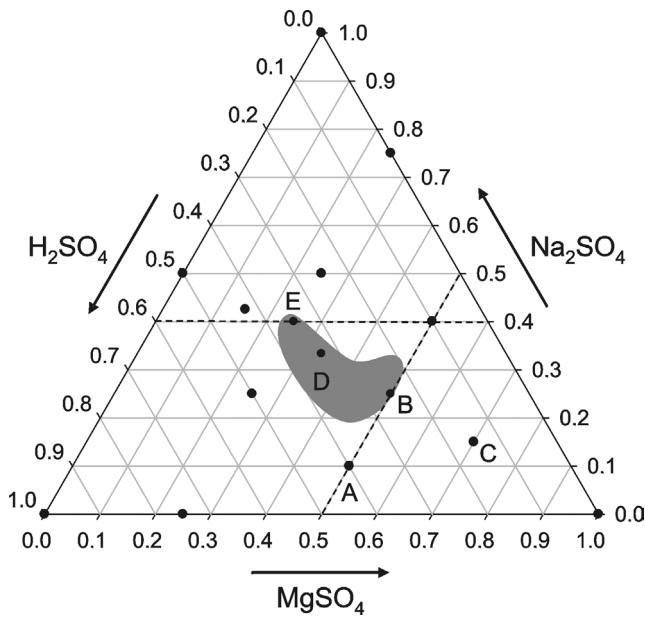
Table 1
Relative concentrations in mole-percent of constituents of flash frozen brine solutions that are models for the surface of Europa. Solution B can be equivalently made from NaHSO$_4$ rather than equal amounts of Na$_2$SO$_4$ and H$_2$SO$_4$

	MgSO$_4$	Na$_2$SO$_4$	H$_2$SO$_4$
A	0.50	0.10	0.40
B	0.50	0.25	0.25
C	0.70	0.15	0.15
D	0.33	0.33	0.33
E	0.24	0.40	0.35

Fig. 3. Three-component diagram that brackets the relative concentrations of H_2SO_4, Na_2SO_4, and $MgSO_4$ that is likely present on the surface of Europa. The relative positions are determined from the laboratory concentrations and the gray zone delineates the best fits to the NIMS data. The best spectral matches occur for points B, D, and E. In general, a reasonable match is achieved when the amount of $NaSO_4$ is as high as 40 mol%, whereas the $MgSO_4$ cannot exceed 50 mol% (as indicated by dashed lines). Assuming this material is from an endogenous source, this information can be used to bracket the geochemical models on the evolution of the planet interior.

other, indicating that the flash freezing process traps the system in its fully dissolved state. Spectrum C is rich in $MgSO_4$ and matches poorly, whereas there is a near perfect spectral match for mixtures B, D, and E to the NIMS data.

3.4. Comparison of results to astronomical observation

In Fig. 3 is plotted a three-component diagram for the relative mole fraction of ternary mixtures of $MgSO_4$, Na_2SO_4, and H_2SO_4, assuming the presence of the minimum number of solvation waters. This diagram contains a summary of the lab spectra obtained and, with the exception of pure H_2SO_4, no single component spectrum is a reasonable match. The quality of fit was determined by the match of the band intensities and widths for each of eight spectral features located at 1.5, 1.58, 1.65, 1.80, 1.96, 2.09, 2.1, and 2.2 μm. The best fits to the NIMS non-ice material spectrum, which are contained within the gray region in Fig. 3, should be indicative of the relative concentrations of $MgSO_4$, $NaSO_4$, and H_2SO_4 in the Europa non-ice material. It should be noted that the relative amount of water is very small due to the annealing process and should be appropriate for comparing the NIMS non-ice endmember spectra. The correlation between the spectral features and the cation concentration from our data places upper limit concentrations of 50 mol% $MgSO_4$ and 40 mol% Na_2SO_4 for Europa non-ice material. This high Na_2SO_4 content is predicted in models of Europa with a rel-

atively warm ocean and thin crust (Kargel et al., 2000). It is also consistent with the notion that sputtering of sodium-bearing salts is the source term for at least some of the Na observed in the tenuous atmosphere (Johnson et al., 2002; McCord et al., 2002). It is clear from these data that the presence of solvated protons is a necessary but not sufficient condition for interpreting the NIMS data.

The persistent presence of these sulfate minerals depends upon their thermal and radiation stability as well as the flux into or away from the surface. Dehydration of $MgSO_4$ and Na_2SO_4 minerals does not occur on a time frame less than several million years at average Europa surface temperatures and pressures (McCord et al., 2001). The sulfate ions and the associated waters of hydration are also quite stable to ionizing radiation (McCord et al., 2001). Radiation processing of frozen brines involves charge-transfer electronic transitions, which can neutralize a nearby Na^+, leading to the desorption of neutral atomic sodium with a non-thermal velocity distribution (Yakshinskiy and Madey, 1999), as observed by emission spectroscopy of the Europa atmosphere (Brown and Hill, 1996). Sputtering or electronic removal of neutral Mg from frozen $MgSO_4$ solutions is inefficient, since it is present as a solvated Mg^{2+} or $MgOH^+$ entity.

4. Conclusions

In summary, the NIMS reflectance spectral data of the Europa non-ice regions can be interpreted well in terms of the simultaneous existence of trapped protons and solvated Na^+, Mg^{2+}, and SO_4^{2-} ions. The source of the 1–3 μm spectral perturbations in ice are due to the geometric and electrostatic reorganization of the local hydrogen bonding networks associated with ion-solvation. Our results show that H^+, Na^+, and Mg^{2+} have characteristic effects on the spectral profile in the 1.5 μm band that can be used to estimate relative proportions thereof. Surface acidity is indicated by these results, and its presence is in addition to, not exclusive of, the presence of other salt cations from an endogenic source. Thus, although radiolysis of the europan surface must generate trapped protons, low-temperature ion hydrolysis will also contribute significantly to the acidity. The relative concentration of Na^+ suggested by our observations is higher than previous studies indicated. Comparing this to geochemical models of Europa formation implies a relatively cold condensation from primitive remnant chondrites (Kargel et al., 2000).

A europan surface composed of frozen mixed salt brines is the most consistent explanation of all available data. This includes (i) existing geochemical models, (ii) the distribution of non-ice spectra in the disrupted regions and along linea, (iii) the observed radiation-induced sputtering of neutral Na, and (iv) the observed ultraviolet absorption bands consistent with the presence of an oxide of sulfur. This interpretation bridges previous conflicting interpretations, as pointed out earlier on less evidence (McCord et al., 2002),

and helps provide a generally useful paradigm for assigning future spectra.

Since solvated ions can have very large effects on the dielectric properties of the hydration water molecules, techniques that are sensitive to variations in the dielectric properties, such as terahertz spectroscopy or radar, should be developed for future missions to Europa. The chemical and physical effects of high ion content on ice also suggests that studies of the electron, ion and photon radiolysis of ice will also be strongly influenced by salt contamination.

Acknowledgments

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