

CHEMICAL DYNAMICS IN EXTREME ENVIRONMENTS
 Advanced Series in Physical Chemistry-Vol.11
 Editor: Rainer A. Dressler
 (World Scientific-Singapore)
 2000

CHAPTER 8

SURFACE CHEMISTRY IN THE JOVIAN MAGNETOSPHERE RADIATION ENVIRONMENT

Robert E. Johnson

Engineering Physics, Thornton Hall B103
University of Virginia, Charlottesville, VA 22903
Tel.k: (804) 924-3244. Fax: (804) 924-1353
 E-mail: rej@virginia.edu

Contents

1. Introduction	390
2. Observations	393
3. Radiation Chemistry	400
4. Hydrated Minerals	408
5. Summary	412
Acknowledgments	414
Appendix	414
References	415

1. Introduction

One of the most exciting areas of research in Planetary Science is the study of the chemistry induced in the surfaces of the icy moons of Jupiter by the Jovian magnetospheric particle radiation. Observations by Galileo of Io, Europa, Ganymede and Callisto (Fig. 1) using the newly discovered telescope initiated enormous controversy and changed our image of the solar system over three centuries ago. Now observations of these moons using the

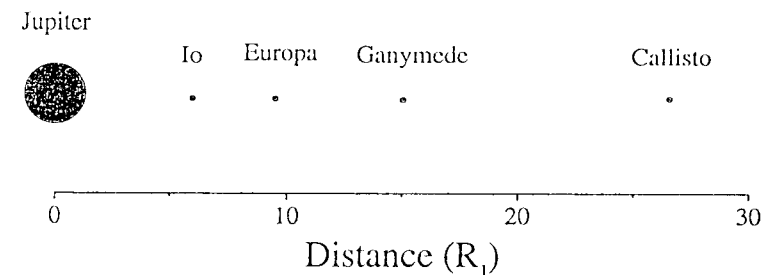


Fig. 1. A schematic diagram of the orbital positions of the moons of Jupiter discovered by Galileo. Their positions are scaled to Jupiter's radius (R_J) with properties given in Table 1. Note: these satellites, like our moon, are all phase locked to the parent planet, hence the same side faces Jupiter throughout each moon's orbit. Since the magnetic field is attached to Jupiter, it rotates faster, therefore, in addition to ions and electrons moving up and down the field lines and impacting the satellites, there is a net preferential flow onto the hemisphere trailing the satellite's motion.

Table 1. Surface properties of Galilean satellites.

	$R_{JM}(R_J)^a$	$R(\text{km})^b$	$T(K)^c$	Constituents ^d	Atmosphere ^e
Io	5.90	1820	80–150	SO ₂ , S _x , Na K, Cl	SO ₂ , Na K, Cl
Europa ^f	9.40	1570	80–130	H ₂ O, SO ₂ , Na K, H ₂ O ₂ , S _x	O ₂ , Na, K
Ganymede ^g	15.0	2630	80–150	H ₂ O, O ₂ O ₃ , CO ₂	O ₂ , Na, O
Callisto ^f	26.4	2400	80–150	H ₂ O, CO ₂	CO ₂ , H ₂ O

^aDistance from Jupiter in Jupiter radii, $R_J = 7.14 \times 10^4$ km.

^bRadius of moon in km.

^cAverage temperature range. Note: surfaces segregated into bright, cold volatile regions and dark refractory regions with different temperatures.

^dSurface constituents are at present being identified using NIMS and the UVS instruments on Galileo. Hydrated mineral bands are seen on Europa, Ganymede and Callisto. On Europa suggestive of frozen dilute sulfuric acid,⁷ but other models have been proposed.¹⁴ CII, CN, and OII bands seen. Some species inferred from atmosphere and plasma.

^eSpecies identified to date in atmosphere. Plasma is primarily H⁺, O^{+z}, S^{z+}.

^fSuggested as having an underground "ocean."

^gHas its own magnetic field.

instruments on the Galileo spacecraft and Hubble Space Telescope (HST) are again leading to radically new insights on the origins of bodies in our solar system and, possibly, to new insights into the origins of biologically active molecules. This understanding is expected to grow dramatically again when the CASSINI spacecraft examines Saturn's moons beginning in 2004.

A critical issue for interpreting the new observations is to obtain an understanding of the chemistry induced in the surfaces of the Galilean satellites by the energetic ions and electrons trapped in the giant magnetosphere of Jupiter. These energetic particles produce new molecular species in the surface and cause desorption of atoms and molecules. The desorbed species form an ambient gas around each object, which contributes to the tenuous atmospheres and ionospheres on these moons.¹ Therefore, if the interaction of the radiation with the candidate surface materials is understood, direct collection of the ionized component by mass spectrometry from an orbiting probe can be used to determine the surface composition.^{2,3}

Whereas the dominant surface material on the outer three Galilean moons is ice, the inner moon, Io, is the most active volcanic object in the solar system. Therefore, it has been totally dehydrated and has a surface coated with sulfur dioxide.⁴ This surface is exposed to significant levels of ion, electron and UV photon radiation. At the time of this writing, one of the moons, Ganymede, is the first nonplanetary body in the solar system on which an intrinsic magnetic field has been discovered.⁵ This field provides a useful tool. Since it partially deflects the incident radiation, observers can compare the surface chemistry in the highly irradiated regions with that in lightly irradiated regions.

Also remarkable is the fact that the other two icy moons, Europa and Callisto, have unusual conducting properties as indicated by the magnetometer measurements on the Galileo spacecraft. This effect has been tentatively attributed to the presence of underground, tidally heated oceans,⁶ although we recently suggested that an irradiation-produced material⁷ can act as a conducting layer. However, the ocean hypothesis is attractive as it is based on models for their formation, differentiation and tidal heating by Jupiter.⁸ Also, the magnitude of the conductivity of the object deduced from the time variability of the local fields appears to be appropriate for a "salty" ocean. As a further support of this hypothesis, the surface of Europa appears to be young and chaotic suggestive that fresh material has "recently" reached the surface.⁹⁻¹³ One model for such activity is that ice warmed by tidal heating under a few kilometers-thick frozen layer, can

be extruded onto the surface in some regions with the surface subducted causing burial of material in other regions.

Recent infrared spectra of the shifted suppressed water bands indicate that the surface of Europa contains hydrated minerals. These have been suggested to be hydrated salts and organics,¹⁴ which would also be consistent with material from an underground ocean. Because of this strong, but indirect, evidence for an ocean, Europa is now considered to be an object on which biological materials could have evolved. Such an evolution, if it occurred, could have been driven by the heat created by the tidal interaction with Jupiter, although recently this has been suggested to be too small.¹⁵ It has also been suggested that the energy of the Jovian magnetospheric particle radiation incident on to the surface could drive chemistry needed for initiating biological evolution.^{16,17}

A recent laboratory comparison of the shape of the water of hydration bands with the spectra obtained by the Galileo spacecraft indicates that the hydrated material mentioned above might in fact be frozen, hydrated H_2SO_4 .⁷ This material would be produced by the charged particle irradiation of sulfate salts, sulfur or SO_2 in an ice matrix.² Therefore, a sulfur chemical cycle is maintained by the incident radiation, a cycle similar to that occurring at higher temperatures in the atmospheres of the Earth and Venus.⁷ On Europa, this involves oxidants such as SO_4^{2-} , H_2O_2 ¹⁸ and O_2 ¹⁹ which have potential importance for the proposed prebiotic chemistry.

In this chapter, I will briefly review the observations relevant to the Jovian radiation environment and the suggested surface materials on the large moons. I will then summarize what is known about the radiation-induced surface chemistry and, finally, I will suggest laboratory studies and molecular dynamics simulations that might be carried out to contribute to an understanding of the surface chemistry relevant to this exciting planetary environment. More extensive reviews of various aspects exist and will be referred to below rather than repeating those summaries.^{1,19,20} In addition, a review of the physics of the sputtering process was presented recently²¹ and an overview was provided in the Reviews of Modern Physics.²²

2. Observations

When the Pioneer and Voyager spacecraft passed through the Jovian system in the 1970's a much more intense radiation environment was found than was expected.²³ The particle radiation consisted of energetic ions trapped in

Jupiter's giant magnetic field. These ions had as their source the icy satellites that orbit within the Jovian magnetosphere and, hence, the plasma composition was determined by the surface composition.³ Using the data from the Energetic Particle Detector on the Galileo spacecraft, the ion and electron fluxes^{16,24} are given in Fig. 2. In addition, a low energy plasma component exists.^{25,26} Since the dominant volatile on Io is SO₂ (with S_x) and with H₂O the dominant volatile on the other three moons, the composition of the plasma is predominantly H⁺, O²⁺, S²⁺. A smaller component of undissociated molecular ions (SO₂⁺, SO⁺, NaX⁺, where X is O or S) is found, primarily, close to Io, the principal source of the plasma. In addition to ionized Na, Cl¹⁺ was recently discovered, indicating Cl is present in Io's surface.²⁷ Although the flux of ions and electrons in this plasma is not large by laboratory standards, the plasma energy flux incident on

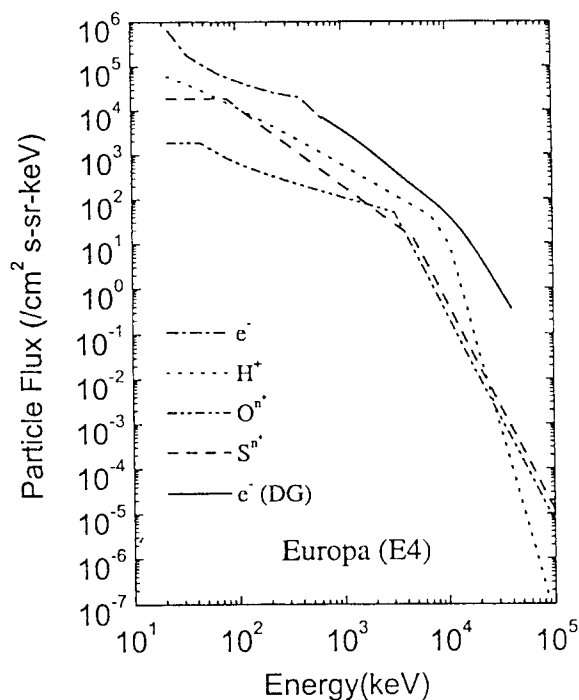


Fig. 2. The ambient, energetic plasma flux at Europa, assumed isotropic, of energetic ions (H⁺, O⁺, S⁺) and electrons: taken from Cooper *et al.*¹⁶ Measured by the Energetic Particle Detector (EPD) on Galileo. Curve labeled DG are the higher electron energies based on Voyager data.²⁸

the surfaces or atmospheres of Europa and Io is much larger than the solar UV flux.¹⁶

An important issue for irradiation chemistry is the dose versus depth into the surface. This was computed by J. Cooper *et al.*¹⁶ and the results for Europa are shown in Fig. 3. Here the vertical axis is the time to achieve a dose of 100 eV per molecule in H₂O. This is a useful form since we note below that radiation chemists typically give radiation effects as *G*-values, the number of a particular molecular species created or destroyed for each 100 eV of energy deposited. Geologists have suggested that the youngest surface ages are $\sim 10^{6-7}$ years on Europa,¹³ hence, the significant dose, as

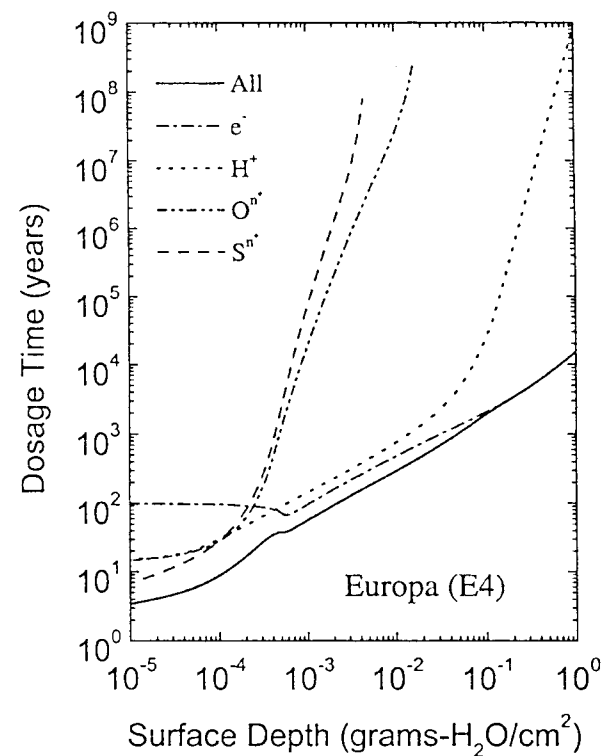


Fig. 3. Time versus depth for the ions and electrons in Fig. 2: taken from Cooper *et al.*¹⁶ The time on the vertical axis is that time it takes for each molecule to receive, on the average, a dose of 100 eV. This is a significant dose for which each molecule has likely been dissociated and it allows easy use of a *G*-value (probability of a molecular change per 100 eV deposited). The horizontal axis gives the depth scaled by density.

expressed in Fig. 3, is achieved at all depths above ~ 1 cm at unit density in geologically relevant times. Since over most of the surface the solar photon penetration depths are much smaller than this, the optical layer is totally altered by the particle irradiation in relatively short times. Proposed plans for a mission to find chemical products of prebiologic activity or, possibly, biological activity in Europa's surface will probably require sampling at depths > 10 cm based on a porosity ~ 0.8 . That is, a critical issue for planning future missions is determining the radiation dose (hence, depth) that biologically important molecules could receive and still be identified by their radiation-induced decomposition products.

The most penetrating of the detected incident particles are electrons with energies of 10's of MeV²⁸ and the dominant carrier of energy are the keV–MeV electrons.¹⁶ It is seen in an electron microscope that energetic electrons cause the growth of voids in ice.²⁹ These are formed by defect production and by inducing mobility of both intrinsic and radiation-induced defects.³⁰ The formation of such voids can produce an efficient light-scattering and, hence, optically bright surface.³¹ Therefore, I have suggested that this effect produces the bright surface in the polar regions on Ganymede, often referred to as "Ganymede's polar caps." Since the energetic electrons have long penetration depths and follow field lines, the cap boundary is found to coincide with the regions where open field lines intersect Ganymede's surface as modeled recently by K. Khurana and R. Pappalardo (private communication). At Io, on the other hand, radiation darkens the sulfur containing surface materials by producing molecular chains. At low latitudes, any radiation damage of Io's surface material is rapidly covered by SO₂ and annealed. But at the poles, this process is very slow, accounting for its "dark polar caps" or, rather, brighter equatorial region.³¹

Matson *et al.*³² first realized that the incident magnetospheric ion radiation could account for the observation of the desorbed Na seen as a "cloud" near the moon Io.³³ The discovery of the intense energetic particle environment appeared to also explain in part two of the best known features of these moons: hemispherical differences in their reflectance and the polar spectral features on Io and Ganymede.⁴ The hemispherical differences have been attributed to preferential plasma energy deposited onto the hemisphere that trails the orbital motion on these moons which are tidally locked to Jupiter.^{1,4,34,35} The Ganymede polar spectral feature appear to be due to particles flowing along the magnetic field lines to the poles,

as discussed above, and the efficient sublimation and annealing of radiation damage in the equatorial regions.³¹

The discovery of the energetic Jovian plasma by Voyager and Pioneer spacecraft led Brown, Lanzerotti and coworkers^{36,37} to study the sputtering of the principal surface constituents of the Galilean satellites, H₂O and SO₂ ices at $T < 150$ K. The sputtering yield for ice is given in Fig. 4(a). They found, surprisingly, that whole molecules dominated the ejecta (Fig. 4(b)) and that the yields (number of molecules ejected per ion incident) were much larger than expected. They also found that sputter ejection of molecules was initiated not only by momentum transfer to the atoms in the solid but also by the electronic ionization and excitation produced by the fast ions incident on these ices. They named the latter process electronic sputtering. This is a process closely related to electronically

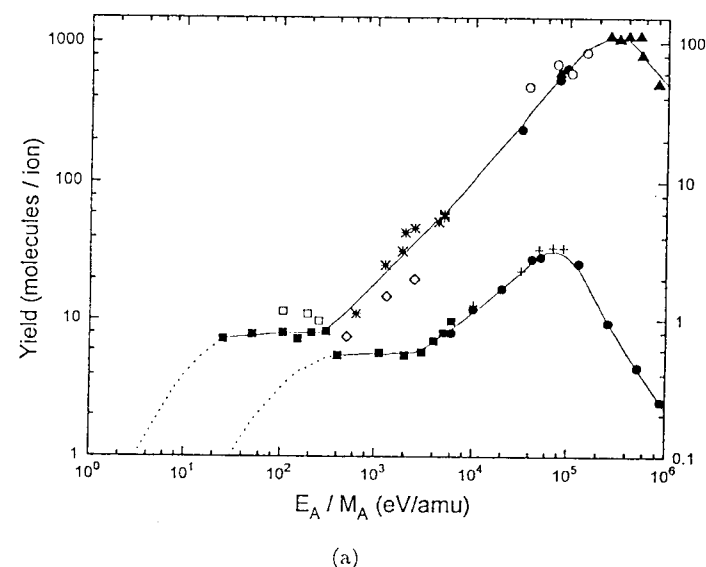


Fig. 4. (a) The ice sputtering yield (number of equivalent H₂O molecules ejected per ion incident) versus the ion energy: taken from Shi *et al.*¹⁰³ The top curve and left hand axis is for incident O⁺ and the bottom curve and right hand axis is for incident H⁺. The structure at low velocity is sputtering due to momentum transfer and that at higher velocities is due to electronic excitation and ionization, which is the dominant sputtering process in ice and closely related to electronically-stimulated desorption.^{1,19} (b) The sputtering yield of D₂O versus surface temperature for 1.5 MeV He⁺ ions (Dots: mass 20; Square: mass 4; Triangle: mass 32). There is a T independent component but the decomposition products, D₂ and O₂ are T dependent: taken from Brown *et al.*³⁸

containing hydrated minerals.¹⁴ The presence of SO₂ in a water ice surface containing H₂O₂ and subject to irradiation suggested to us that hydrated H₂SO₄ should also be present, as in cloud particles at the Earth and Venus. During the writing of this manuscript we showed that bands associated with water of hydration, seen in the IR by NIMS on Galileo, were reasonably well fit by the spectra of frozen H₂SO₄·XH₂O.⁷ This data had been used to suggest the presence on the outer three moons of organics in ice and certain hydrated salts and carbonates: Na₂CO₃·XH₂O (62%), Na₂Mg(SO₄)₂·XH₂O (30%), Na₂SO₄·XH₂O (8%).⁴⁸ The latter identifications were based on models of satellite formation and evolution that predicted the presence of such materials.⁸ In addition, Na₂SO₄ is a material suggested to be on the dehydrated moon Io⁴⁹ and was noted to be radiation modified by Nash and Fanale.³⁵ If sulfate salts are present, radiation-induced decomposition is the likely source of the SO₂ and Na seen at Europa^{2,50,51} and the observed CO₂^{2,50} may be the product of an irradiated organic, like the carbonate suggested above.

Due to tidal heating and radiation-induced desorption, Io has lost most of its water and other light species. Therefore, in addition to SO₂ and its radiation products (e.g. S₂O or SO₃), Na₂SO₄,⁵² Na₂S_x,⁵³ S_x and NaCl²⁷ are suggested surface constituents. Decomposition of these materials is the likely source for the well known Na “cloud” at Io, extensively studied from earth. Observations and models also suggest that there should be silicate intrusions. Recently, a silicate flow from an Io volcano was identified.⁵⁴ However, over most of the satellites’ surfaces the rocky material appears to be covered by the dominant volatile: SO₂ at Io and H₂O at Europa and Ganymede as ice or a hydrated species. Callisto was seen to have clean water ice bands but the surface is dominated by an unidentified dark contaminant, possibly micrometeorite debris collected on its surface, and its physical surface features appear to be modified by outgassing of a volatile like CO₂.^{41,55} To interpret the new spectral data, a clear understanding of the surface chemistry of the absorption bands and of the desorbed species is now required. Such an analysis can, in principle, be used to date geologically young features on these moons.¹⁶

3. Radiation Chemistry

The study of the irradiation of ice has a long history due, in part, to the considerable interest in radiation biology in the 1950’s and 1960’s. Freeze-dried samples of biomolecules were often irradiated and compared, spectrally

and by using ESR, to irradiated, degassed ice samples.⁵⁶ In spite of this history, useful quantitative information for radiolysis relevant to the planetary problems described above is scarce. Therefore, at the time of Voyager, Brown, Lanzerotti and coworkers^{36,37} initiated studies of the ices and Nash and Fanale³⁵ initiated studies of the spectral changes due to irradiation of those refractory materials thought to exist at Io. We recently reviewed the database on the radiation chemistry of ice as it relates to the icy satellites.²⁰ I also recently reviewed the database for the sputtering of ices by energetic ions.¹⁹ These papers and the exciting spacecraft and HST data have stimulated a large amount of recent work which is summarized below.

The temperature range of interest is between ~ 70–90 K near the poles and varies from ~ 90 K nightside near the equators to ~ 120–150 K dayside depending on the albedo in the equatorial region. This is a range of temperature variation over which radicals can be made mobile and react. There are a number of agreed upon radiation products which are both relevant to the planetary problem and reasonably well studied. Whereas it was thought that protons are mobile even in an amorphous ice, recently it has been suggested that they trap efficiently.⁵⁷ Following recombination, the principal products in photolysis or radiolysis of ice, H and OH, come from the primary dissociation channel: H₂O → H + OH. Whereas H is thought to diffuse effectively at most relevant temperatures, at low temperatures the OH traps in ice, as indicated by the ESR spectra and by the blue shifted OH absorption band at ~ 0.28 μm.^{56,58} On the other hand the more mobile H atoms diffuse and can react forming H₂. When the sample is in a good vacuum, as it is on the surfaces of these moons, the H₂ diffuses to the vacuum interface and escapes leaving behind a chemically altered ice. A second channel, that has ~ 10% branching ratio in the gas-phase under solar UV is H₂O → H₂ + O. Single event production of H₂ from ice, seen by Reimann,⁵⁹ was recently confirmed to occur even with low energy electrons, at least at the ice–vacuum surface.⁶⁰ The loss of H₂ leaves behind a reactive O. Recent experiments suggest the irradiation-induced formation of a species such as H₂O–O.⁶¹

Because any H₂ produced diffuses efficiently and is lost to the vacuum, the ice is permanently altered. Therefore, there is a depletion of H and formation of “trapped” O and OH, so the surface layers of the grains are oxidizing. They also should have an enhanced *D/H* ratio.¹ The O and OH radicals can react directly: OH + OH → H₂O₂ and OH + O → HO₂ or

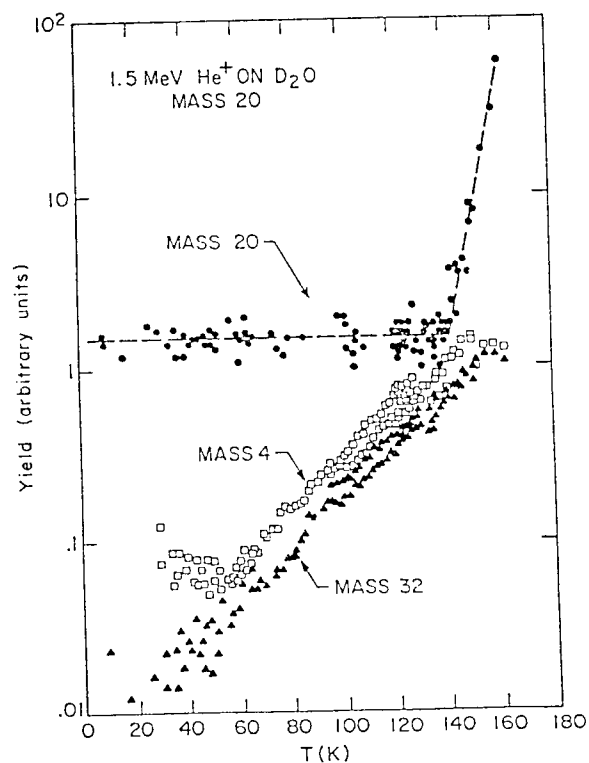


Fig. 4. (Continued).

stimulated desorption. However, unlike desorption the sputtering yield was found to vary *nonlinearly* with the energy deposited per unit path length by the incident fast ions. They noted at the time that this new electronic sputtering process was so efficient that kilometers of material could have been removed from these objects during their lifetime.³⁷ Although this was certainly an overestimate due to the extrapolations made and the incomplete knowledge of Europa's surface, sputtering is a dominant process at Europa. In addition, the electronic sputtering process is in fact closely related to the radiation chemistry produced in ice by the fast ions and electrons.²⁰

Subsequent work has shown that new more volatile molecules are also produced and desorbed by energetic ions [Fig. 4(b)], and the desorption efficiencies depended on the material temperature.³⁸ This dependence is

due to the radicals or defects becoming mobile. Since the principal products ejected from ice, in addition to H_2O , are H_2 and O_2 , we predicted that the icy satellites could have tenuous O_2 atmospheres.^{1,39} That is, the desorbed H_2 is light and escapes readily from a moon's gravitational field but the heavier O_2 produced on the Galilean satellites would not. However, unlike H_2O , once formed O_2 would not condense at the surface temperatures on these moons, $> \sim 80$ K. Remarkably an O_2 atmosphere was recently observed by HST both on Europa and Ganymede.⁴⁰ An even more tenuous CO_2 atmosphere was observed on Callisto by the Galileo spacecraft.⁴¹ Because CO_2 does not condense efficiently at the surface temperatures on Callisto, it must be trapped in the ice or be created by the radiation prior to desorption. Finally, the gravity filter that allows H_2 to escape much more efficiently than O_2 also means that the D/H ratio in the surface layer will be much larger than the solar values.^{1,2,19}

In a parallel set of discoveries, a reflectance band in the visible, similar to that for solid O_2 ,⁴² was seen at low latitudes on Ganymede. In addition, a UV feature associated with O_3 was seen on Ganymede^{43,44} and on the icy satellites of Saturn.⁴³ Coupled with these observations was the much earlier discovery of a band indicative of SO_2 in ice at Europa⁴⁵ and Callisto⁴⁶ and the recent discovery of CO_2 trapped in the icy surfaces.⁴¹ The SO_2 was initially assumed to be due to sulfur ions originating at Io implanted into the ice at Europa,^{45,47} but the SO_2 is also a radiation decomposition product like the O_2 , as discussed below.^{2,7} The CO_2 source is probably internal as carbon ions have not yet been seen in the plasma.

Although the presence of these species *suggests* that the ions actually bombard the surface, the clearest signature that radiation-induced chemistry is occurring in these icy surfaces was recently reported. That is, the radiation-induced product, H_2O_2 , has been seen in both the IR and the UV in the surface ice of Europa.¹⁸ Therefore, it is now established that the radiation-induced changes in the surface occur at a rate that significantly exceeds the geologic resurfacing rate. However, accurate radiation-induced yields (or G -values, yield/100 eV deposited) are typically *not available* to successfully determine surface dose. This is unfortunate as such information can be used to determine the age of the optical surface.

Recent data from the near IR mapping spectrometer (NIMS) of the Galileo spacecraft has also identified areas on the moons in which the water bands are shifted and suppressed, consistent with large surface areas

$O_2 + H$. In addition, lattice relaxation around a species like H_2O-O might lead to H_2O_2 and HO_2 . The latter products have been identified by ESR and by absorption features in the UV.^{56,58,62}

The source of the observed O_2 is less certain. $H_2 + \frac{1}{2}O_2$ are the decomposition products of irradiated ice.^{56,59} O_2 is formed in the gas-phase by reactions involving the products above. However, following exposure to ionizing radiation, O_2 is found to evolve from an initially degassed ice sample on warming.⁵⁶ G -values (or yields) larger than those for the gas-phase were found for ice although simple chemical rate equations predict otherwise. In studying the radiation effects on the icy satellites, Brown, Lanzerotti and coworkers showed O_2 is directly produced and ejected into the vacuum by energetic ions.^{38,63} More recently, UV photons⁶⁴ and low energy electrons⁶⁵ were shown to produce O_2 with a threshold energy ~ 10 eV.

Relatively high G -values ($\sim 0.15/100$ eV) are obtained if ice is irradiated at low temperatures in a closed system and then warmed.⁵⁶ However, recent laboratory data suggest lower G -values, so that the early experiments may have been affected by small amounts of contaminants such as CO_2 . For instance, Baragiola and coworkers suggest very small G -value ($\sim 0.003O_2/100$ eV) for a thin ice layer irradiated by keV protons.⁶⁶ Assuming that the low energy electron desorption data of Seiger *et al.*⁶⁵ are applicable to the secondary electrons produced by a fast ion, and using a W -value (average energy per ion-electron pair produced) for light ions of ~ 26 eV, a somewhat larger G -value ($\sim 0.01O_2/100$ eV) is obtained. But this is still smaller than in the early experiments. Since production and loss of hydrogen occurs with higher G -values, implying O must eventually be produced, there are some inconsistencies to be resolved. Therefore, additional measurements are needed for the amount of O_2 produced per incident fast ion, both that directly desorbed (sputtered) and that produced and trapped in the solid. This is needed as a function of temperature in order to determine the amount of ambient gas and the potential for chemical synthesis. Since there is a dE/dx dependence in the production of O_2 , experiments are needed to determine the efficiency of the production of O_2 for a broad range of ion types and velocities or a clear model for O_2 formation is needed. In addition, since radiation followed by annealing occurs in the equatorial regions of these moons, the earlier experiments, on gas evolving from warmed ice or from a hydrated salt irradiated at low temperature, need to be repeated.

Reimann *et al.*⁵⁹ measured the fluence and temperature dependence for the production of O_2 from a thin ice sample in a vacuum exposed to energetic Ne^+ [Fig. 5(a)]. These ions were used to represent the energetic O^+ ions in the Jovian plasma. They found a correlation between the loss of

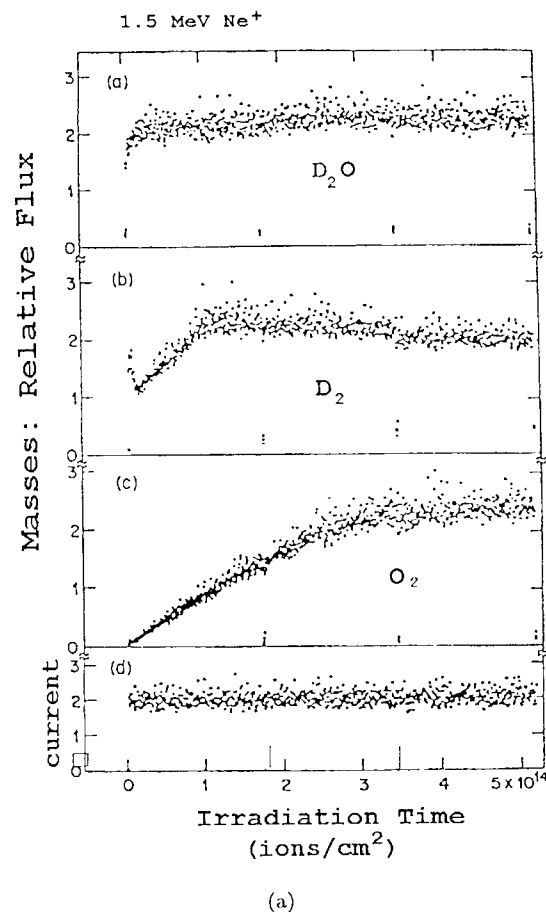


Fig. 5. (a) The production of D_2 , O_2 and D_2O from a D_2O ice sample by energetic Ne^+ (used to model the effect of the O^+ flux in Fig. 2) as a function of irradiation time given as number of impinging ions per square centimeter. If beam is turned off at any point, each signal immediately restores when beam is turned on, indicating the ice is altered: taken from Reimann *et al.*⁵⁹ (b) The production of O_2 by low energy electron irradiation of ice: taken from Seiger *et al.*⁶⁵ Curves are for 100 eV and 50 eV electrons, as indicated, and the symbols are for different temperatures showing the scaling of the yields.

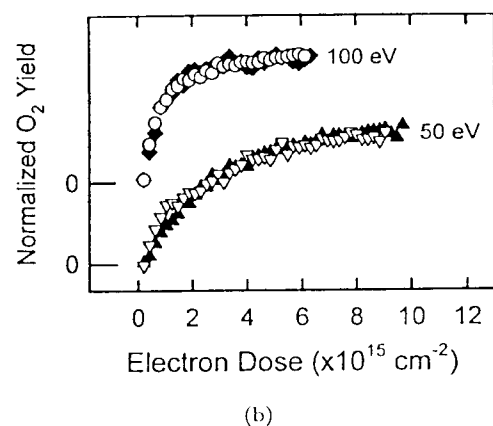


Fig. 5. (Continued).

H₂ and the production and loss of O₂. It is seen in Fig. 5(a) that H₂ exhibits a prompt component followed by a gradually increasing component. The former is due to a single event near the surface and the latter depends on the film thickness for ions penetrating to the substrate. The O₂ signal was initially zero but grew linearly with the irradiation dose. This indicates that O₂ is not a direct radiation product (as discussed above), but requires that the ice is first altered: e.g. the formation of trapped radicals or other precursors. This was confirmed by shutting the beam off and letting the sample sit.⁵⁹ On turning the beam back on, the O₂ signal immediately restored indicating that a “permanent” change occurred. The initial linear increase in O₂ was followed by a second region of growth. Finally, both the H₂ and O₂ signals decreased as the film thinned. For low energy electron impact on a very thin ice surface, Seiger *et al.*⁶⁵ found results surprisingly similar to those for MeV Ne⁺ on ice as seen in Fig. 5(b).

Reimann *et al.*⁵⁹ noted an activation barrier of 0.05–0.07 eV and considered diffusion of the radicals produced. Seiger *et al.*⁶⁵ concluded that a nondiffusing precursor is first formed (cross section $\sim 10^{-18}$ cm² in the surface layer) in a manner that is temperature dependent, accounting for the scaling of the results at different *T* in Fig. 5(b), and a subsequent impacting electron directly produces O₂ (cross section $\sim 10^{-16}$ cm²). [A candidate precursor may be the H₂O–O mentioned earlier⁶¹]. They pointed out that the low fluence dependence seen in Figs. 5(a) and 5(b) is inconsistent with

the diffusion model. This is the case unless “diffusion” is fast and temperature independent over the region studied. Therefore, a “hot O” atom reacting with trapped OH, O(hot) + OH → H + O₂, is a candidate.

In these studies the role of the surface, the sample temperature and the sample structure (defects, voids and crystallinity) appear to be important but require further study. As mentioned earlier, void formation has been imaged when ice is placed in an electron microscope.²⁹ However, the relationship between the formation of interior surfaces and O₂ production has not been studied, although it appears that O₂ may be formed more efficiently at a surface.

The radiation product H₂O₂ is seen in the photolysis and radiolysis of ice,^{56,67} and the role of electron scavengers has been studied.⁶⁸ H₂O₂ has now been identified in UV and IR spectra of Europa’s surface where it appears to be ubiquitous.¹⁸ As stated earlier, this confirms that energetic ions are reaching the surface and that the radiolysis of ice is occurring. It is now generally accepted that the very thin O₂ atmosphere at Europa⁴⁰ is produced by the radiolysis of ice, as suggested earlier.^{1,39} At Ganymede, sublimation may be more vigorous due to higher average surface temperature, although the temperatures in the icy patches may be similar to those on Europa. In any case, the production of O₂ at Ganymede could involve gas-phase chemistry⁶⁹ at low temperatures, which would also require new rate coefficients. In addition, a pair of weak bands in the visible have been associated with the presence of O₂ inclusions in the surface of Ganymede.^{30,42} Because of the surface temperatures (> 80 K), it has been suggested that the codeposited O₂ may be trapped by water molecules, or it may be formed and trapped in voids in an ice³⁰ or in a hydrated mineral surface.⁷⁰ In Fig. 6, the data for O₂ codeposited with ice and deposited as solid O₂ are compared to the reflectance spectrum. The former appear to this author to show reasonable agreement with the space observations. However, in a series of papers,⁶⁶ Baragiola and coworkers suggested that using the peak positions was most important in the comparison and concluded that solid O₂ exists on the surface in cracks or crevices which are only temporarily exposed to sun light. If correct, this would require very low (< 40 K) surface temperatures.⁷⁰ If trapping O₂ in ice is problematic, as they suggest, it is possible that the O₂ may be formed and trapped in a hydrated mineral.^{2,70} In any case, the physical-chemical explanation of this band is not available. It may be associated with a specific terrain type.

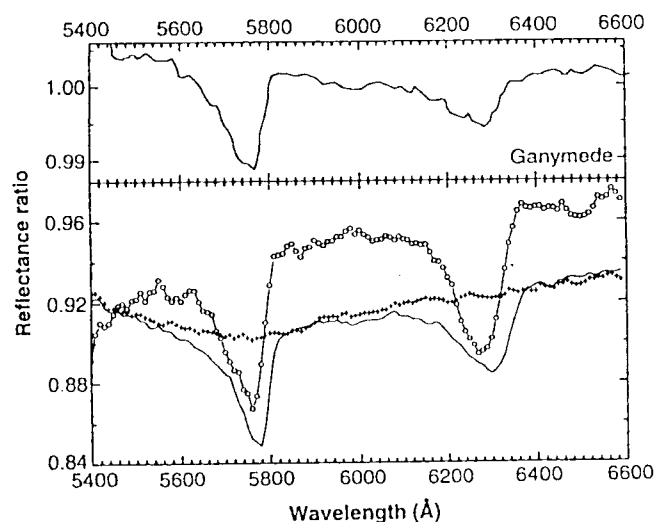


Fig. 6. Upper panel: absorption bands of Ganymede which are attributed to "solid O₂"⁴² (obtained as a ratio of Ganymede's trailing hemisphere reflectance to that of Callisto's). Lower panel: pure O₂ at 26 K (line with circles), codeposited O₂ + H₂O ice film at 26 K (solid curve). Same after warming to 100 K, (pluses): taken from Vidal *et al.*⁶⁶

HST observations in the UV of a broad band roughly consistent with the Hartley band, suggest the presence of O₃ in the surface of Ganymede.⁴³ The possible presence of O₃ is important, since O₃ is not a direct radiation product of ice,^{56,71} but forms readily in O₂.⁷¹⁻⁷³ Therefore, its presence reinforces the concept that a condensed form of O₂ exists: e.g. trapped in voids in the ice³⁰ or other irradiated surface material.⁷⁰ Initially, a broadened O₃ band was used to roughly fit the data, but evidence for another band at longer wavelengths is clear.⁴³ In Fig. 7, the solid O₃ band, which differs little from O₃ trapped in O₂, is shown. The second band may be associated with trapped OH but here I show a-CH₂O band in an organic compound. The presence of such a band would not be surprising as CO₂ and H₂O both exist in the irradiated surface.

A number of studies have been carried out on the sputtering of CO₂, SO₂, and S₈, all proposed or observed volatiles on these moons.^{19,74} The ejecta, as in the sputtering of water ice, are the parent molecules plus those decomposition products having high volatility¹⁹ allowing them to be easily driven into the gas-phase (e.g. CO and O₂ from CO₂; and SO and O₂ from

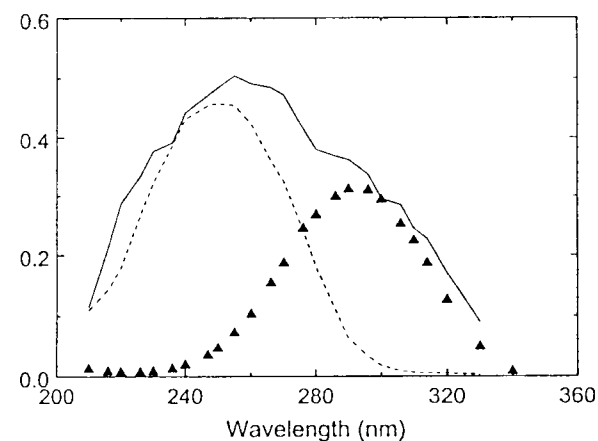


Fig. 7. Hubble Space Telescope UV spectrum (solid line), ratio of trailing hemisphere reflectance converted to an absorbance.⁴³ Broken line: condensed form of O₃⁷²; triangles: -CH₂O in isobutyraldehyde.¹⁰⁵

SO₂; S₂ from S₈). Equally interesting are the potential refractory products such as polymerized carbon and sulfur, and the sulfur and carbon suboxides.⁷⁵ However, there is very little data on the physical, chemical or spectral properties of the refractory materials formed in an ice that contains CO₂, SO₂ or sulfur.⁷⁴ Complex irradiation produced, carbon based materials, named Tholins (muddy) by C. Sagan, have been suggested as being present on the surfaces by the Galileo NIMS spectra.¹⁴ Earlier Nash and Fanale³⁵ studied irradiation alteration of reflectance of potential satellite minerals to fit Io's spectrum. The general reddening of the visible-near-UV reflectance at Europa has been attributed to irradiation-induced changes in grain size⁴⁷ and to radiation-induced chemistry forming a polymerized sulfur.^{34,76,77} Agreement with the optical reflectance data requires < 1% of the refractory component of a photolyzed, frozen H₂S + H₂O mixture.^{7,78} However, definitive identifications and quantitative evaluations under known radiation environments have not been made and competing evaporative processes have also been suggested to account for the reddening of the optical spectra.⁷⁹

There are fewer studies giving absolute yields for mixed ices subjected to charged particle radiation. Two relevant mixtures for Europa, Ganymede and Callisto are H₂O + SO₂ and H₂O + CO₂. The latter may also be important for the Uranian moons.⁸⁰ Chemical pathways have been studied but

not the absolute yields for producing new species. Clearly, complex hydrocarbons of the type seen in cometary comas can be formed in Europa's surface and then subducted into the putative underground ocean. Moore and coworkers⁸¹⁻⁸³ and Strazzulla and coworkers⁸⁴⁻⁸⁶ have studied mixtures of H₂O with CO and CO₂ as well as other carbon containing molecules and complex mixtures relevant to comets at low temperatures (< 20 K). They have shown that among other species, carbonic acid, H₂CO₃, is formed. This is a species not yet identified on the icy satellites but should also be a product of radiation-induced desorption of Na from Na₂CO₃ · XH₂O (see Appendix). They have obtained relative yields but data at those temperatures relevant to the icy satellites are needed. In a recent paper⁸³ absolute yields for mixtures of H₂O + CO have been obtained.

Delitsky and Lane⁸⁷ used such studies to outline the chemical pathways that might be relevant on these moons. However, detailed quantitative information for the separate pathways is needed. Earlier, Haring and coworkers,⁸⁸ among others, measured ejected molecule mass spectra and ejecta energy spectra for a number of mixtures. These studies indicate that a variety of products are formed and ejected into the gas-phase. However, absolute yields for desorbed species from mixed ices were not given but are needed to understand the ambient gas at each of the icy satellites.^{1,2,19}

The plasma ion bombardment also leads to implantation of reactive atoms into the surface. Therefore, quantitative data is also needed on the chemistry induced by reactive atoms Na and S. These atoms are introduced as energetic ions from Io and are implanted into Europa's low temperature water/ice or into its hydrated mineral surface. On implantation into and annealing of an ice depleted in H, S is likely to form SO⁴⁷ and then annealing or further bombardment produces SO₂ giving the 0.28 μm band,⁴⁶ although recent Galileo data⁸⁹ suggests the SO₂ is associated with the non-ice regions as in the model in Ref. 7. Incident Na is likely to form NaOH. This latter molecule has not yet been seen by NIMS on Europa and, therefore, would have to be present at less than a few percent if it exists in the surface material.

4. Hydrated Minerals

The hydrated minerals, suggested as being present on Europa by the Galileo NIMS data and by the possible presence of an underground ocean, were described earlier. One model has them being hydrated versions of the

minerals expected on Io. The principal chemical issue learned from the above is that plasma bombardment causes changes in the spectra³⁵ and the preferential loss of H (as H₂) which leads to a surface layer which is oxidizing.²⁰ Therefore, the favored chemical pathways are fairly clear¹⁹ and are considered in the Appendix. The presence of both SO₂ and H₂O₂ led us to look at the sulfur chemistry in Europa's radiation environment.⁷ A principal product is a sulfate, which is a good oxidant, probably in the form of hydrated H₂SO₄ as mentioned earlier. The comparison of this species to the water of hydration bands in the NIMS spectra is shown in Fig. 8. Although the agreement is far from perfect, small shifts are expected due to ion radiation³⁵ and agreement with other radiation products reinforces the presence of H₂SO₄ · XH₂O⁷ as discussed below. Radiation yields for producing hydrated H₂SO₄ at the temperatures and for the relevant incident particle energies are not available. Moore⁹⁰ irradiated an H₂O/SO₂ mixture and observed a refractory product that was consistent with the presence of H₂SO₄, but did not identify the product. Also, in pure SO₂, SO₃ is produced efficiently ($G \sim 5/100$ eV).⁹⁰ In the presence of H₂O this exothermically yields H₂SO₄. Similarly, sulfur particles in water produce H₂SO₄ under irradiation with quite high G -values.⁹¹

Therefore, sulfur may be introduced into Europa's system as implanted sulfur, as a sulfate or sulfide from an underground ocean or as SO₂ and S_x gas as at Io, as shown schematically in Fig. 9. The sulfate, either delivered to the surface or formed by irradiation as discussed above is very stable

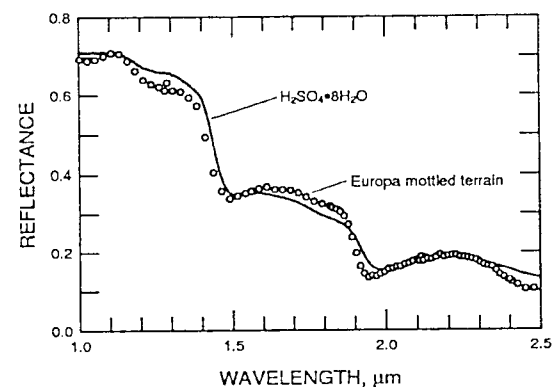


Fig. 8. Diffuse reflectance versus wavelength in microns. A comparison of a dilute (1/8) frozen sulfuric acid spectrum (line) with the spectrum from the NIMS instrument on Galileo (dots): taken from Carlson *et al.*⁷

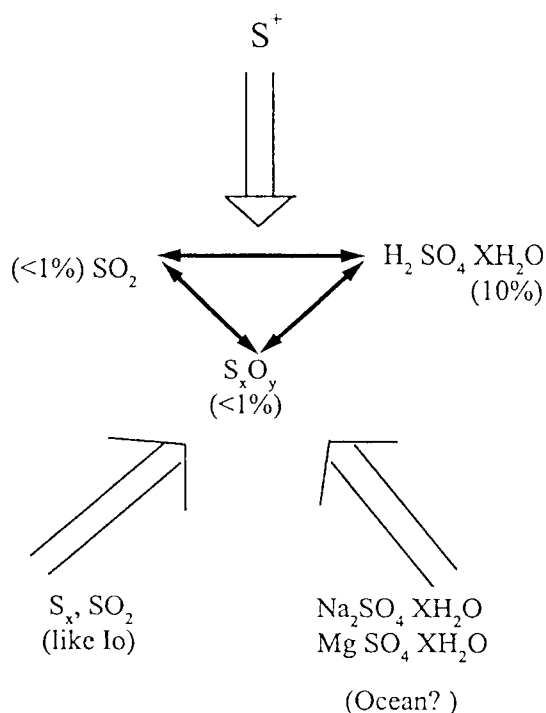


Fig. 9. The sulfur cycle as deduced from approximate radiolysis yields. Sulfur can enter the system by implantation from Io, possibly gases from beneath the surface as at Io, or as an ocean salt exposed to the surface. Radiation chemistry is fast, so the species are cycled through the various sulfur forms shown here. The relative amounts agree with the fits in Ref. 7.

under irradiation.⁹²⁻⁹⁵ G -values for decomposition are $\sim 10^{-3}$ to 10^{-4} /100 eV for X-rays and gamma-rays incident on Li_2SO_4 .⁹⁶ Ions would produce decomposition more efficiently but still with relatively low G values. Therefore, we suggest that hydrated H_2SO_4 is the dominant species in the dark/chaos areas on Europa. This decomposes into SO_2 ($< 1\%$) and polymerized sulfur ($< 1\%$). Spectral comparisons are given in Ref. 7 and rough quantitative agreement is achieved for all three species. Since Europa appears to have a single principal darkening agent, this scenario would suggest it is polymerized sulfur. If this analysis is correct, the dark and young areas would appear to be regions in which a sulfur containing material is brought to the surface⁷ either by venting or by break through of a melt.¹¹ Therefore, as illustrated in Fig. 9, the sulfur species in the chaos areas^{9,10} mentioned

above could be brought to the surface as hydrated salts, as SO_2 trapped in ice, or as polymerized sulfur all leading to the *same mix* of SO_2 , frozen dilute sulfuric acid and polymerized sulfur. Because the radiation doses in the optical layer (Fig. 3) are large for the suggested geologic ages,¹⁶ radiation-induced equilibrium is established among these sulfur forms.

Thermal processing has also been proposed⁷⁹ and a recent model suggests organic species are dominant in the ocean. Since similarly reddened spectra can be obtained for carbon containing species,⁹⁷ radiation cycling of a carbonate producing frozen dilute carbonic acid, CO_2 , and carbon suboxides is also possible (Appendix).

Hydrated sulfates and carbonates in the form of salts had been suggested as the dominant materials in the geologically young regions of Europa as mentioned earlier.¹⁴ On an oxidizing surface, irradiation of hydrated Na_2CO_3 should produce Na_2O , Na_2O_2 and CO_2 in ice (Appendix) in addition to free Na. Although the hydrated sulfates are much more stable, as discussed above for frozen dilute (hydrated) H_2SO_4 , a hydrated Na_2SO_4 will also readily lose Na.^{51,52,98} In fact, an atomic Na component is seen in the very tenuous ambient gas over Europa's surface.⁹⁹ Having lost Na, the hydrated sulfate can form hydrated $HNaSO_4$ first and then hydrated H_2SO_4 , although this needs to be confirmed in the laboratory. In competition with this is implantation of Na from the neighboring satellite Io as shown in Fig. 10. Recent analysis indicates Europa is a net source of Na^{51,99} (i.e. the loss rate is larger than the implantation rate) suggesting an internal source of Na.

Models of the icy satellites also suggest that hydrated $MgSO_4$ should also be present.^{8,14,35} Decomposition¹⁰⁰ of this species could again lead to hydrated H_2SO_4 , in which case MgO or $Mg(OH)_2$ should be present in the surface (Appendix) since Mg is desorbed much less efficiently. However, Mg has not yet been seen spectrally in the surface, ambient gas or plasma.

Finally, interesting "aging" effects have been noted by a number of authors.⁹⁷ That is, the geologically youngest material appears to have more of the "dark/red" contaminant. With geological aging these terrains appear to have brightened in time.^{11,12} This can occur by a "volcanic" emplacement of dark particulates that are gradually mixed with the underlying icy material by micrometeorites or buried by vapor deposition. Transport of sputtered and thermally desorbed H_2O can slowly coat a surface^{13,31,101} or the radiation bombardment of a clear transparent (hence, dark) ice formed

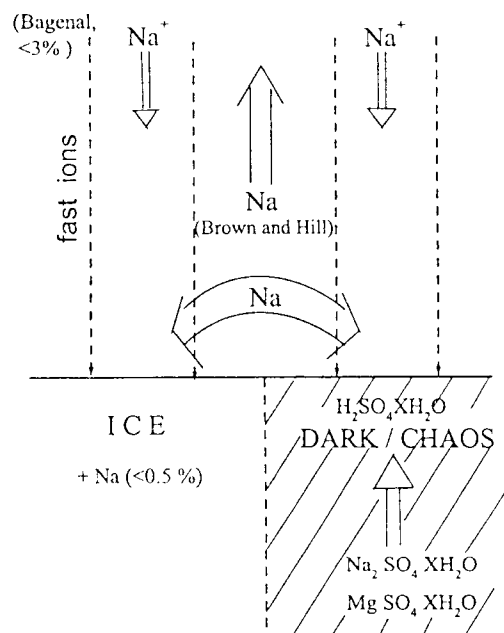


Fig. 10. The redistribution of Na on Europa's surface. Na is implanted from Io either into ice or into the dark terrain, or it is brought to the surface as a hydrated mineral. Sputtering and photodesorption¹⁰⁶ release the Na into the gas phase so it is redistributed⁵¹ and seen in the gas phase as escaping Na.⁹⁹ If Na comes from a sulfate, the processing of the sulfate is described in Fig. 9.

from a melt could lead to brightening, as discussed above.³¹ In addition, on changing the amount of hydration, minerals can change color. For instance, P. Williams and coworkers (private communication) showed that hydrated copper sulfate lost its blue color under irradiation and became clear. Then on exposure to H_2O , its color was restored. Therefore, in radiation equilibrium, the level of hydration in a refractory region depends on transport of water from the icy regions. Finally, if the red material in the fresh surface is a sulfur contaminant, the radiation-induced conversion of sulfur imbedded in water ice into hydrated sulfuric acid and SO_2 would appear to brighten the surface.⁷ These are all potential radiation-induced aging processes.

5. Summary

There is recent spectral data on the icy moons of Jupiter that is not yet understood and the spectral data base will continue to increase with new data

from Galileo, HST, CASSINI and the proposed Europa probe. Therefore, understanding the formation and evolution of the surface composition, the ambient gases and the local plasmas for the Jovian satellites is now becoming possible.^{2,87} Such an understanding is critical for determining the origins and evolutions of these moons. Of particular interest to NASA and the public is the possibility of prebiological or biologic activity in the solar system.^{16,17} In this respect, the moon Europa is a prime target and there are intriguing spectral signatures as discussed.

Since the surfaces of these objects are bombarded by UV photons and energetic ions and electrons, interesting low temperature, surface chemistry occurs which can both obscure the understanding of the intrinsic processes and can play an important role in the chemical evolution of the satellite. Compared to geologic time scales, the surface of Europa is rapidly processed by radiolysis and photolysis, so that even geologically young surfaces are in radiation-induced chemical equilibrium. Io's surface is a possible exception as it is continuously replenished by volcanism. At Ganymede, the fact that poles and equators experience very different radiation dose rates will be useful as the new spectral reflectance data is analyzed. Recently, Denk and coworkers identified a color change across the magnetic boundary in a *single* geologic unit.¹⁰²

At Europa, the intense radiation bombardment also produces an ambient gas of sputtered molecules^{1,19,103} and volatile decomposition products.² Only a couple of species in this atmosphere have been identified: O_2 from water/ice and Na and K from decomposition of hydrated minerals and, likely, H_2O , SO_2 and CO_2 . However, this atmosphere must contain many other molecular species, either intrinsic or formed locally, and these will be observable either telescopically or by *in situ* sampling on a future probe.² This presents the exciting possibility of identifying surface constituents by detecting the gas-phase products. Because the sputtering yields by heavy energetic ions (O^+ , S^+) are very large (Fig. 4), even massive organic molecules imbedded in the ice can be ejected into the gas-phase¹⁰⁴ and be detected.²

What is surprising is that the database for absolute product yields from energetic charged-particle-induced solid state chemistry is very poor in spite of the years of work on radiolysis and photolysis. Even the yields of H_2O_2 and O_2 from ice by radiolysis are not agreed upon. This lack may simply be a matter of focusing the attention of the chemistry community on the

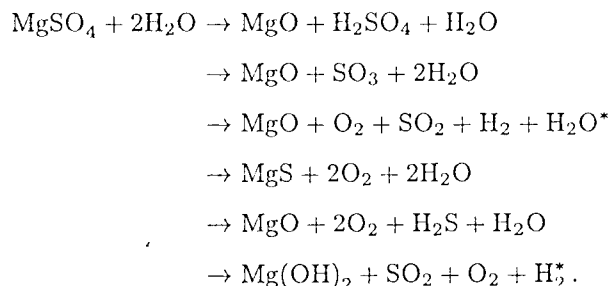
relevant materials and relevant incident radiation. Since definitive space data is now becoming available, and since the questions, such as the origins of these moons, the possibility of underground oceans, and the potential of Europa for prebiotic chemistry, are fundamental, this is an opportune time for new work on radiation-induced solid state chemistry.

Acknowledgments

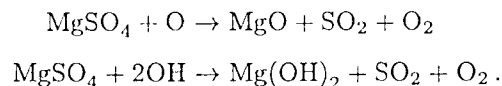
I would like to acknowledge the support of the NSF Chemistry and Astronomy Division and the Planetary Geology Division of NASA.

Appendix

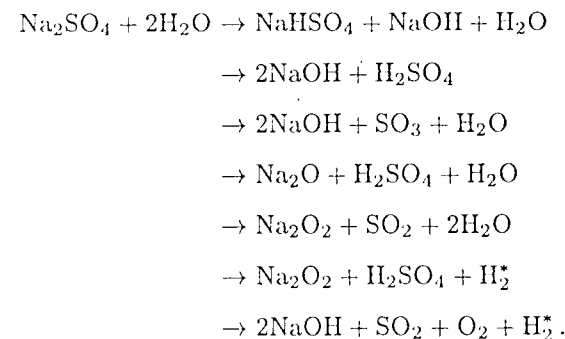
Low temperature (< 130 K) hydrated salts^{8,48} form surface brines from material that may have been extruded onto Europa's surface by volcanism or due to the huge tidal flexing (10's of meters/day). The exposure of these hydrated minerals to radiation in an environment in which H₂ is lost to space produces preferred radiation chemical pathways. Three types of materials were recently suggested¹⁴: Na₂SO₄ · XH₂O, MgSO₄ · XH₂O and Na₂CO₃ · XH₂O with X ~ 6-8. Ion bombardment can remove the water of hydration by sputtering and can dissociate molecules producing chemistry in an oxidizing surface. Some pathways, ordered according to increasing endothermicity, are listed below.²



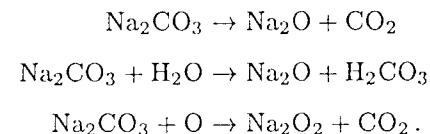
Because H₂ is lost permanently during irradiation, the processes with the asterisks are favored, although often they do not have the smallest endothermicity. More simply, an oxidizing surface can give



Therefore, if the magnesium sulfate reaches the surface and is exposed to irradiation, Mg(OH)₂, MgO and, possibly, MgS should be present on the surface of Europa. For the sodium containing salt



Na plasma ions implanted from the Io torus into an ice rich region can also give NaOH or NaO₂.² Again, the asterisks indicate favored chemical pathways due to permanent loss of H₂. Also SO₃ in the presence of H₂O immediately forms H₂SO₄.⁷ Therefore, the sulfates are driven to dilute frozen H₂SO₄, SO₂, and polymerized sulfur suboxides. Finally for the proposed carbonate Na₂CO₃ · XH₂O¹⁴ X > 6 exposed to the radiation in the presence of water and with the loss of hydrogen gives



Removal of Na from the Na containing species by electronic excitations appears to occur readily on surfaces.¹⁰⁶ Therefore, Na is desorbed principally as Na atoms⁵² by either charged particles or photons¹⁰⁶ contributing to the Na "clouds" seen at Io³³ and Europa.⁹⁹ Similarly, K is also seen.⁹⁹ This can be assisted by replacement by O or H from dissociated H₂O: e.g. Na₂O + O → NaO₂ + Na and Na₂O + H → NaOH + Na.

References

1. R. E. Johnson, *Energetic Charge-Particle Interaction with Atmosphere Surface* (Springer-Verlag, Berlin, 1990).
2. R. E. Johnson, R. M. Killen, J. H. Waite and W. S. Lewis, *Geophys. Res. Lett.* **25**, 3257 (1998).

3. R. E. Johnson and E. C. Sittler, *Geophys. Res. Lett.* **17**, 1629 (1990).
4. J. A. Burns, *Satellites* (University of Arizona Press, Tucson, 1986), pp. 1-39.
5. M. G. Kivelson, K. K. Khurana, F. V. Coroniti, S. Joy, C. T. Russell, R. J. Walker, J. Warnecke, L. Bennett and C. Polanskey, *Geophys. Res. Lett.* **24**, 2155 (1997).
6. M. G. Kivelson, K. K. Khurana, D. J. Stevenson, L. Bennett, S. Joy, C. T. Russell, R. J. Walker and C. Polanskey, *Geophys. Res. Lett.* **104** (A3), 4609 (1999).
7. R. W. Carlson *et al.*, *Science* **286**, 97 (1999).
8. J. S. Kargel, *Icarus* **94**, 368 (1991); F. P. Fanale *et al.*; D. Morrison Ed., *Satellites of Jupiter* (University of Arizona Press, Tucson, 1982), pp. 756-781.
9. P. E. Geissler *et al.*, *J. Geophys. Res.* **135**, 107 (1998).
10. R. T. Pappalardo *et al.*, *Nature* **391**, 365 (1998).
11. P. Helfenstein *et al.*, *Icarus* **135**, 41 (1998).
12. B. E. Clark *et al.* and the Galileo SSI Team, *Icarus* **135**, 95 (1998).
13. R. T. Pappalardo *et al.*, *J. Geophys. Res.* **104** (E4), 10524 (1999).
14. T. B. McCord *et al.*, *J. Geophys. Res.* **104**, 11827 (1999).
15. E. J. Gaidos, K. H. Nealson and J. L. Kirschvink, *Science* **284**, 1631 (1999).
16. J. H. Cooper, R. E. Johnson, B. H. Mauk and N. Gehrels, *Icarus*, in press (2000).
17. C. Chyba, *Nature* **403**, 381 (2000).
18. R. W. Carlson *et al.*, *Science* **283**, 2062 (1999).
19. R. E. Johnson, *Solar System Ices*, Eds. B. Schmitt, C. deBergh and M. Festou (Kluwer Acad. Pub., Netherlands, 1998), pp. 303-334.
20. R. E. Johnson and T. I. Quickenden, *J. Geophys. Res.* **102**, 10985 (1997).
21. R. E. Johnson and J. Schou, Sputtering of Inorganic Insulators, in *Fundamental Processes in the Sputtering of Atoms and Molecules* (SPUT 92). Ed. P. Sigmund (Royal Danish of Academic Sciences, Copenhagen) [Mat. -fys. Medd 43, (1993)] pp. 403-494.
22. R. E. Johnson, *Rev. Mod. Phys.* **68**, 305 (1996).
23. A. J. Dessler, *Physics of The Jovian Magnetosphere* (Cambridge University Press, Cambridge, 1983).
24. W.-H. Ip, D. J. Williams, R. W. McEntire and B. H. Mauk, *Geophys. Res. Lett.* **25**, 829 (1998).
25. F. Bagenal, *J. Geophys. Res.* **99**, 11043 (1994).
26. C. Paranicas, W. R. Paterson, A. F. Cheng, B. H. Mauk, R. W. McEntire, L. A. Frank and D. J. Williams, *J. Geophys. Res.* **104**, 17459 (1999).
27. M. Kueppers and N. M. Schneider, AGU Abstract, Eos Supp. (1999).
28. N. Devine and H. B. Garrett, *J. Geophys. Res.* **88** (A9), 6889 (1983).
29. H.G. Heide and E. Zeitler, *Ultramicroscopy* **16**, 151 (1985).
30. R. E. Johnson and W. A. Jesser, *Astrophys. J. Lett.* **480**, L79 (1997).
31. R. E. Johnson, *Icarus* **62**, 344 (1985); R. E. Johnson, *Icarus* **128**, 469 (1997); M. Wong and R. E. Johnson, *J. Geophys. Res.* **102**, 23, 25523 (1997).

32. D. L. Matson, T. V. Johnson and F. P. Fanale, *Astrophys J.* **192**, L43 (1974).
33. R. A. Brown and F. H. Chaffee Jr., *Astrophys J.* **187**, L125 (1974).
34. R. E. Johnson, M. Nelson, T. B. McCord and J. Gradie, *Icarus* **75**, 423 (1988).
35. D. Nash and F. P. Fanale, *Icarus* **31**, 763 (1977).
36. W. L. Brown, L. J. Lanzerotti, J. M. Poate and W. M. Augustyniak, *Phys. Rev. Lett.* **49**, 1027 (1978).
37. L. J. Lanzerotti, W. L. Brown, J. M. Poate and W. M. Augustyniak, *Geophys. Res. Lett.* **5**, 155 (1978).
38. W. L. Brown *et al.*, *Nucl. Instrum. Meth.* **B1**, 307 (1982).
39. R. E. Johnson, L. J. Lanzerotti and W. L. Brown, *Nucl. Instrum. Meth.* **198**, 147 (1982).
40. D. T. Hall *et al.*, *Science* **273**, 677 (1995).
41. R. W. Carlson, *Science* **283**, 820 (1999).
42. W. M. Calvin, R. E. Johnson and J. A. Spencer, *Geophys. Res. Lett.* **23**, 673 (1996); J. Spencer, W. Calvin and J. Person, *J. Geophys. Res.* **100**, 19049 (1995).
43. K. S. Noll, R. E. Johnson, A. L. Lane, D. L. Dominigue and H. A. Weaver, *Science* **273**, 341 (1996); K. S. Noll, T. L. Rousch, D. P. Cruikshank, R. E. Johnson and Y. J. Pendleton, *Nature* **388**, 45 (1997).
44. A. R. Hendrix, C. A. Barth and C. W. Hord, *Geophys. Res.* **104** (E6), 14169 (1999).
45. A. L. Lane, R. M. Nelson and D. L. Matson, *Nature* **292**, 38 (1981).
46. K. S. Noll, H. A. Weaver and A. M. Gonella, *J. Geophys. Res.* **100**, 19057 (1995).
47. N. J. Sack, R. E. Johnson, J. W. Boring and R. A. Baragiola, *Icarus* **100**, 534 (1992).
48. T. B. McCord *et al.*, *Science* **280**, 1242 (1998).
49. F. P. Fanale, T. V. Johnson and D. L. Matson, *Science* **186**, 922 (1974).
50. R. E. Johnson, *Brazilian J. Phys.* **29**, 444 (1999).
51. R. E. Johnson, *Icarus*, in press (2000).
52. R. C. Weins, D. S. Burnett, W. F. Calaway, C. S. Hansen, K. R. Lykke and M. L. Pellin, *Icarus* **128**, 386 (1997).
53. D. B. Chrisney, R. E. Johnson, J. W. Boring and J. H. Phipps, *Icarus* **75**, 233 (1988).
54. A. S. McEwen *et al.*, *Geophys. Res. Letts.* **24**, 2443 (1997).
55. J. M. Moore *et al.*, *Icarus* **140**, 294 (1999).
56. E. J. Hart and R. L. Platzman, *Physical Mechanisms in Radiation Biology*, Eds. M. Errera and A. Forsberg (Academic, San Diego, California, 1961), pp. 93-120; B. G. Ershov and A. K. Pikaev, *Radiation Research Review* (Elsevier, Amsterdam, 1969).
57. J. P. Cowin, A. A. Tsekouras, M. J. Iedema, K. Wu and G. B. Ellison, *Nature* **398**, 405 (1999).
58. I. A. Taub and K. Eiben, *J. Chem. Phys.* **49**, 2499 (1968).

59. C. T. Reimann, J. W. Boring, R. E. Johnson, J. W. Garrett and K. R. Farmer, *Surf. Sci.* **147**, 227 (1984).
60. G. A. Kimmel and T. A. Orlando, *Phys. Rev. Lett.* **75**, 2606 (1995).
61. L. Khriachtchev, personal communication (1999); T. Orlando, personal communication (1999).
62. J. A. Ghormley and C. J. Hochanadel, *J. Phys. Chem.* **75**, 40 (1971).
63. W. L. Brown, W. M. Augustyniak, E. Simmons, K. J. Marcantonio, L. J. Lanzerotti, R. E. Johnson, J. W. Boring, C. T. Reimann, G. Foti and V. Pirronello, *Nucl. Instrum. Meth.* **198**, 1 (1982).
64. M. S. Westley, R. A. Baragiola, R. E. Johnson and G. A. Baratta, *Planet. Space Sci.* **43**, 1311 (1995).
65. M. T. Sieger, W. C. Simpson and T. M. Orlando, *Nature* **394**, 554 (1998).
66. R. A. Baragiola, C. L. Atteberry, D. A. Bahr and M. Peters, *J. Geophys. Res.* **104** (E6), 14183 (1999); R. A. Baragiola and D. A. Bahr, *J. Geophys. Res.* **103**, 25865 (1998); R. A. Vidal, D. B. Bahr, R. A. Baragiola and M. Peters, *Science* **276**, 1839 (1997).
67. A. J. Matich, M. G. Bakker, D. Lennon, T. I. Quickenden and C. G. Freeman, *J. Phys. Chem.* **97**, 10539 (1993).
68. M. H. Moore and R. L. Hudson, *Icarus* **145**, 282 (2000).
69. M. B. McElroy and Y. L. Yung, *J. Astrophys.* **196**, 227 (1975).
70. R. E. Johnson, *J. Geophys. Res.* **104** (E6), 14179 (1999).
71. P. A. Gerakines, W. A. Schutte and P. Ehrenfreund, *Astron. Astrophys.* **312**, 289 (1996).
72. V. Vaida, D. J. Donaldson, S. J. Strickland, S. L. Stephens and J. W. Birks, *J. Phys. Chem.* **93**, 506 (1989).
73. R. A. Bargiola, C. L. Atteberry, D. A. Bahr and M. Jakas, *Nucl. Instrum. Meth.* **B157**, 233 (1999).
74. G. Strazzulla, *Solar System Iccs*, Eds. B. Schmitt *et al.* (Kluwer, Netherlands, 1998), pp. 281–302.
75. D. B. Chrissey, W. L. Brown, J. W. Boring, *Surf. Sci.* **225**, 130 (1990).
76. D. J. O'Shaughnessy, J. W. Boring and R. E. Johnson, *Nature* **333**, 240 (1988).
77. W. M. Calvin, R. N. Clark, R. H. Brown and J. A. Spencer, *J. Geophys. Res.* **100**, 19041 (1995).
78. L. A. Lebofsky and N. B. J. Fegley, *Icarus* **28**, 379 (1976).
79. F. P. Fanale *et al.*, *Lunar Planet. Sci. Conf.* [CD-ROM] XXIX abstract. p. 1248 (1998).
80. L. J. Lanzerotti, W. L. Brown, C. G. Macclennan, A. F. Cheng, S. M. Krimigis and R. E. Johnson, *J. Geophys. Res.* **92**, 14949 (1987).
81. M. H. Moore, R. K. Khanna and B. Donn *J. Geophys. Res.* **96**, 17541 (1991); M. H. Moore and R. K. Khanna, *Spectrochimica Acta* **A47**, 255 (1991).
82. M. H. Moore and R. L. Hudson, *Icarus* **135**, 518 (1998).
83. R. L. Hudson and M. H. Moore, *Icarus* **140**, 451 (1999).

84. J. R. Brucato, A. C. Castorina, M. E. Palumbo, M. A. Satorre and G. Strazzulla, *Planet Space Sci.* **45**, 835 (1997).
85. G. Strazzulla and M. E. Palumbo, *Planet Space Sci.* **46**, 1339 (1998).
86. J. R. Brucato, M. E. Palumbo, G. Strazzulla, *Icarus* **125**, 135 (1997).
87. M. L. Delitsky and A. L. Lane, *J. Geophys. Res.* **103**, 31391 (1998); M. L. Delitsky and A. L. Lane, *J. Geophys. Res.* **102**, 16385 (1997).
88. R. A. Haring, R. Pedrys, D. J. Oostra, A. Haring and A. E. deVries, *Nucl. Instrum. Meth. Res. Phys. Sect.* **B5**, 476 (1984).
89. A. R. Hendrix, *EOS Trans. AGU 79* (fall meeting supp.) F335 (1998).
90. M. H. Moore, *Icarus* **59**, 114 (1984).
91. G. W. Donaldson and F. J. Johnson, *J. Phys. Chem.* **72**, 3552 (1968).
92. J. Ganjei, R. Colton and J. Murray, *SIMS*, (1978), pp. 221–229.
93. C. J. Hochancel, J. A. Ghormley and T. J. Sworski, *J. Am. Chem. Soc.* **77**, 3215 (1955).
94. E. R. Johnson and A. O. Allen, *J. Am. Chem. Soc.* **74**, 4147 (1952).
95. R. A. Haring, A. Haring, F. S. Klein, A. C. Kummel and A. E. deVries, *Nucl. Instrum. Meth.* **211**, 529 (1983).
96. T. Sasaki, R. S. Williams, J. S. Wing and D. A. Shirley, *J. Chem. Phys.* **68**, 2178 (1978).
97. D. A. Geissler, W. A. Schutte and P. Ehrenfreund, *Astron. Astrophys.* **312**, 289 (1996).
98. A. Z. Benninghoven, *Z. für Naturforsch* **A21**, 859 (1969).
99. M. E. Brown and R. E. Hill, *Nature* **380**, 229 (1996); M. E. Brown, *Icarus*, in press (2000).
100. A. Z. Benninghoven, F. G. Rudenauer and H. W. Werner, *Secondary Ion Mas. Spectrom.* (John Wiley, New York, 1987), p. 721.
101. E. M. Sieveka and R. E. Johnson, *J. Geophys. Res.* **90**, 5327 (1985).
102. T. Denk, G. Neaken, J. W. Head and R. Pappalardo, *Bull. AAS* **31** (4), 1182 (1999).
103. M. Shi, R. A. Baragiola, D. E. Grosjean, R. E. Johnson, S. Jurac and J. Schou, *J. Geophys. Res.* **100**, 26387 (1995).
104. R. E. Johnson, B. U. R. Sundqvist, A. Hedin and D. Fenyó, *Phys. Rev.* **B40**, 49 (1989); R. E. Johnson and B. U. R. Sundqvist, *Physics Today*, March 1992, p. 28.
105. J. G. Calvert and J. N. Pitts, *Photochemistry* (John Wiley and Sons, New York, 1996), pp. 368–380.
106. T. E. Madey, B. V. Yakshinsky, V. N. Ageev and R. E. Johnson, *J. Geophys. Res.* **103**, 5873 (1998); B. V. Yakshinsky and T. E. Madey, *Nature* **400**, 642 (1999).