

# Ion-Solid Interactions in Astrophysics

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## Abstract

This article gives an overview of the energetic ion spectra in different parts of the universe, the expected effects of ion interactions with airless celestial bodies, and some evidence for their occurrence. It is based mostly on research in a variety of topics at the author's laboratory but references are provided to the most current research elsewhere. The emphasis is on atomic collisions on molecular ices, which are both of greatest astrophysical interest and the subject of most past and current research. Many unsolved problems are stated or discussed, spanning from desorption of ices by thermal  $\text{He}^+$  ions to the possible role of atomic collisions in the origin of life in the universe.

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## 1. Energetic Ions in Space

Living in our planet, protected by an atmosphere and a magnetic field, it is not apparent that most of the universe is violent, permeated with energetic radiation. But a glimpse of this violence can be had from beautiful polar auroras, from reports of the dangers of the ozone hole or the disruption of communications by solar storms, and by stunning astrophotographs of the surroundings of young and dying stars. Figure 1 shows an image of the Menzel 3 stellar object (Ant Nebula) taken by the Hubble Space Telescope. The gas outflow from the central dying star is quite visible. It moves at very high speeds,  $\sim 500$  km/s in an intriguing, and yet unexplained, bipolar pattern. Given the high gas velocities (that can reach  $v_{\text{Bohr}} = 2188$  km/s near white dwarfs spawning other planetary nebulae), such stellar outflow can sputter surrounding objects, such as grains (typically of nm to  $\mu\text{m}$  size). In addition, there are more energetic particles, cosmic rays and ions in shock waves originating in supernovae, starburst regions and super massive black holes at active galactic centers. In our Solar system, the most common energetic particles are found in the escaping solar corona (solar wind, flares, and coronal mass ejection), ions in planetary magnetospheres, and galactic cosmic rays. Such ions impact the surface of objects that lack a protective atmosphere or magnetic field. The most affected are small unshielded bodies, such as comets,



Figure 1. Nebula Menzel 3 (Ant Nebula) STScI-PRC2001-05. Credit: NASA, Space Telescope Science Institute.

asteroids, grains, and most satellites, which also have a weak gravity needed to bind significant atmospheres.

The evidence for energetic ion impact on surfaces is indirect, with the exception of returned Moon rocks, which have been analyzed in detail, captured interplanetary and cometary grains that show ion tracks and, in the near future, samples implanted with solar wind ions returned by the Genesis mission (Burnett et al., 2003). The most common evidence of ion impacts is indirect, from spectroscopic analysis of reflected stellar light that sometimes reveals the presence of molecules synthesized by radiation and from the observation of atmospheres of non-thermal origin around Europa and Ganymede (two satellites of Jupiter), Saturn's rings, the Moon and Mercury. Such atmospheres can be explained to result from sputtering by either magnetospheric ions or the solar wind.

### 1.1. SOLAR ENERGETIC PARTICLES

The solar wind is expanding magnetized plasma emanating from the Sun, consisting of low energy electrons, energetic ions and a magnetic field. The ions are  $\sim 96\%$   $H^+$ ,  $\sim 4\%$   $He^{++}$  and trace amounts of multiply-charged O, C, Si, Fe, and other species. On average, they move with a most probable velocity  $v \sim 450$  km/s ( $\sim 1$  keV/amu) and a fast component at  $\sim 750$  km/s. The flux of the solar wind at

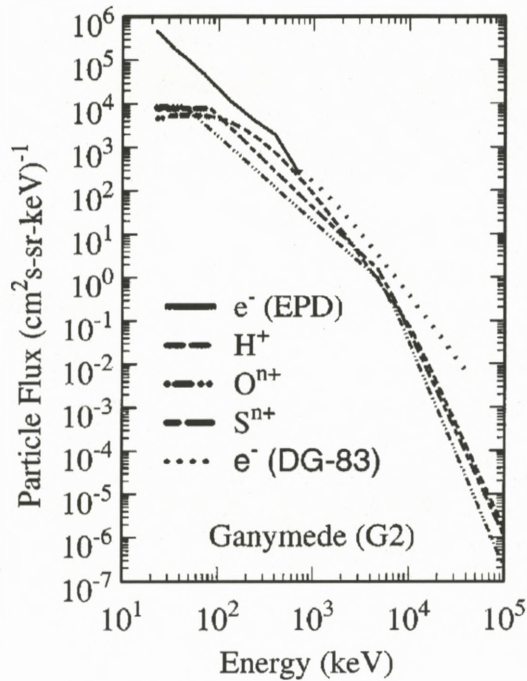


Figure 2. Flux spectra of particles near Ganymede. Compiled by Cooper et al. (2001).

the Earth ( $R = 1$  AU) is  $\sim 2 \times 10^8$  particles/cm<sup>2</sup>-s and decays as  $1/R^2$ , where  $R$  is the distance to the Sun. The solar wind is not stable, variations in solar activity change its flux and velocity distribution constantly. Sporadically the Sun emits solar flares, which are bursts of ions of higher energy than the solar wind, reaching hundreds of MeV (Mewaldt et al., 2005). The most violent eruption from the sun is when a prominence in the corona becomes detached, this is called a coronal mass ejection and can attain very large velocities, 3000 km/s. When the coronal mass ejections reach the Earth they produce great perturbations in the geomagnetic field that induce large electric fields in electric power distribution systems (e.g., the Quebec Blackout of 1989). Strong efforts to understand space weather, i.e., the changing environment around the Earth due to the interaction of solar energetic particles with the magnetosphere, are motivated by the idea that one can predict the occurrence and magnitude of coronal mass ejections. Space research is also focused on radiation effects on spacecraft (e.g., communication satellites) such as in semiconductor devices which can malfunction due to single ion impacts: single event upsets, latchup and burnout (Messenger and Ash, 1997), and electrostatic charging that can produce arcs across spacecraft components (Baker, 2002).

## 1.2. IONS IN PLANETARY MAGNETOSPHERES

The ion fluxes and energies in planetary magnetospheres are larger than in the solar wind, particularly around Jupiter ( $R = 5.2$  AU) and Saturn ( $R = 9.54$  AU). Figure 2 (taken from Cooper et al., 2001), is a compilation of energy distributions of high-energy ions and electrons near Ganymede, a satellite of Jupiter. One can see that the ions are mostly  $H^+$ , oxygen and sulfur with an energy distribution that has a broad peak at 10–100 keV. There is in addition a low energy (thermal) plasma component (not shown) that extends to eV energies. The ion distributions are measured in space, in the vicinity of the satellite. There are no measurements of the actual flux impinging on the surface, which should be different due to electrostatic charging of the surface and to the presence of magnetic fields. For instance, all of the electrons and most of the ions are thought to be excluded from the equatorial surface regions of Ganymede, due to its intrinsic magnetic field, a rare occurrence among satellites.

## 1.3. COSMIC RAYS

The more energetic ions in space are the galactic cosmic rays, which are found over an enormous range of energies, extending up to more than  $10^{20}$  eV. Figure 3 (Simpson, 1983) shows the energy distribution of different cosmic ray ions in the solar system. It falls at low energies, compared to the expected interstellar cosmic ray flux, due to the magnetic field of the solar wind. Cosmic rays can produce a multitude of effects, such as sputtering, amorphization, the single events in semiconductor devices mentioned above, and chemical alterations, either directly or through secondary particles resulting from nuclear reactions. Measurements of the density of etchable (amorphous) tracks in minerals produced by cosmic rays, coupled with estimates of the cosmic ray flux are used for dating rocks and man-made stone artifacts or pottery.

# 2. Astronomical Surfaces

## 2.1. PLANETARY REGOLITHS

The surfaces of airless bodies in space are not only subject to energetic ion and photon irradiation but are also impacted by meteorites, particularly by micron size particles. Micrometeorite impact pulverizes mineral and icy surfaces (comminution) and the local heat produced can melt the surface and even cause the thermionic emission of electrons and ions. Most of the debris ejected from the surface falls back on the surface (except in very small bodies of negligible gravity)

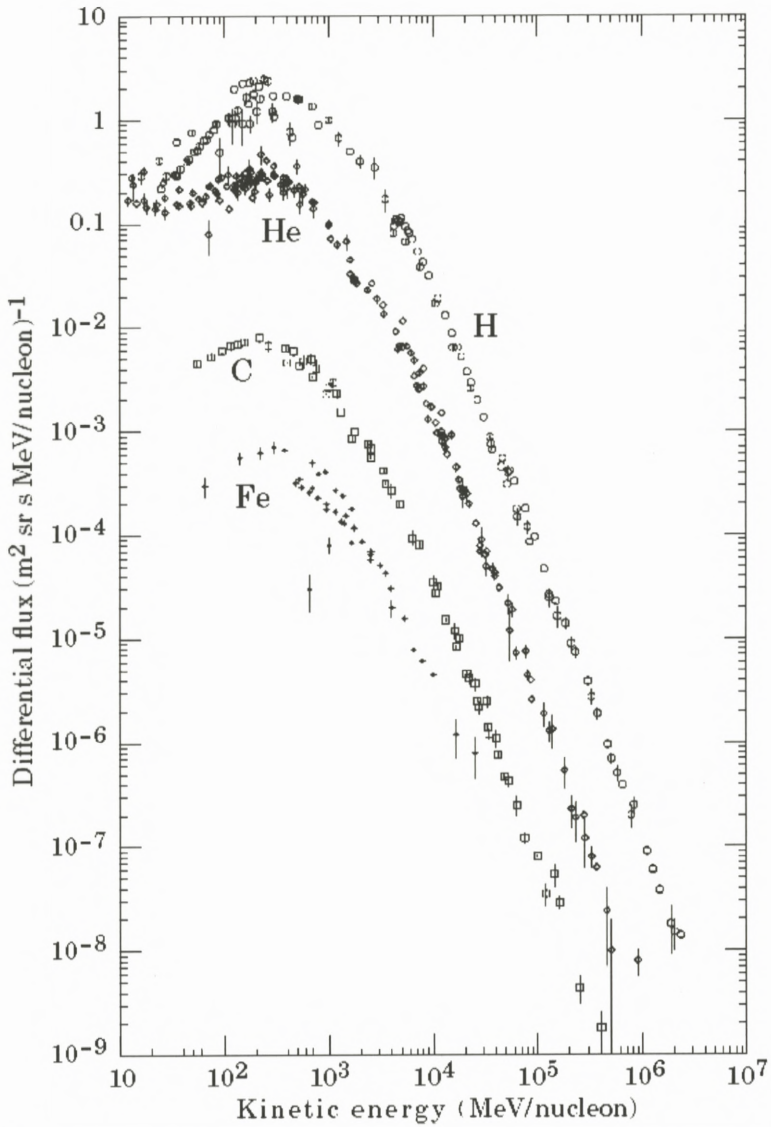


Figure 3. Flux spectra of the primary ions in cosmic rays. From Simpson (1983).

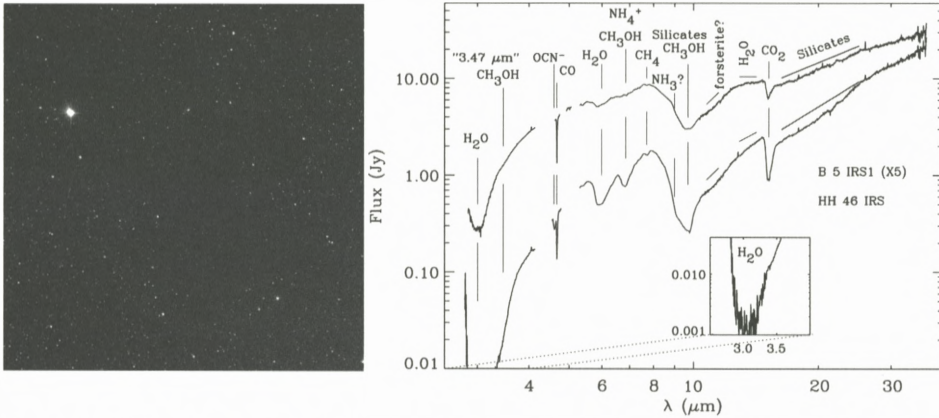


Figure 4. The Barnard 5 dark molecular cloud (left) associated with the constellation of Perseus and the infrared spectra obtained by the Spitzer telescope in the directions of embedded stars B5 IRS 1 (top, multiplied by 5) and HH 46 IRS (bottom). The labels identify absorbing molecules (Boogert et al., 2004).

and is impacted again by the continuing meteorite flux. These processes mix and redistribute the soil and bury ion irradiated material below the surface; this is called gardening or reworking. The gardening by micrometeorites, added to sputtering, re-deposition, and chemical alteration by energetic ion and photon impact is referred to as space weathering, and the highly porous and chemically altered surface layer is called the regolith (Hapke 2001; Chapman, 2004).

## 2.2. REMOTE SENSING OF SURFACES IN SPACE BY OPTICAL REFLECTANCE SPECTROSCOPY

Our knowledge of regolith processing comes from analysis of lunar rocks and simulations in the laboratory, inferences obtained from comparing scattering models to measurements of light reflected from the sun and of radar reflectance from ground based transmitters. The spectral analysis of reflected light in the infrared region can give information on surface composition from the absorption resulting from excitation of characteristic molecular vibrations and, in some cases, the temperature of the surface. However, infrared reflectance spectra may be distorted by scattering effects, by the fact that transitions in symmetric molecules are very weak (“forbidden”), and by the broadness and overlap of the absorption bands in solids. This last factor is particularly severe in large molecules (e.g., organics), making it difficult to identify them with confidence.

While radio astronomy gives abundances of gas-phase interstellar molecules, infrared spectroscopy gives most of the composition information of grains in-

terstellar clouds. These grains, typically  $\sim 100$  nm in size, are coated by a mantle of condensed gas (ice) in cold environments. Diffuse interstellar clouds having gas densities of the order of  $100$  atoms/cm<sup>3</sup> are at about  $100$  K, while in molecular clouds with gas densities of  $\sim 10^4$  atoms/cm<sup>3</sup> temperatures are much lower,  $\sim 10$  K. The composition of the grains and their mantles can be determined by aiming a telescope at a star embedded in or behind the cloud, such that the light is partially absorbed. An example is Figure 4 that shows absorption bands in the light from two young stars embedded in a dark molecular cloud (Barnard 5) associated with the constellation of Perseus (Boogert et al., 2004). The vibrational frequencies responsible for infrared absorption are specific to the molecules present and to their local (near-neighbor) environment, and are identified by comparison with laboratory spectra of pure and mixed ices grown by vapor deposition in vacuum and irradiated with UV photons or energetic particles (d'Hendecourt and Dartois, 2001; Strazzulla et al., 2001; Moore et al., 2001).

### 3. Atomic Collision Topics and Questions

We now turn into specific topics in atomic collisions in solids that have astrophysical applications: sputtering, amorphization, electron emission and electrostatic charging, and radiation chemistry.

#### 3.1. SPUTTERING

Both elastic (knock-on) and electronic sputtering are important in astronomical environments. Elastic sputtering usually dominates at low projectile velocities, and is the primary mechanism for erosion of minerals and ices by the solar wind and low energy plasmas. The success of sputtering theories and computer simulations in describing elastic sputtering of elemental solids does not translate into the more complex natural solids such as molecular ices and silicates. In spite of their popularity with modelers, Monte Carlo codes like TRIM are not appropriate to simulate sputtering of minerals by low energy ions for two main reasons. First, simplified models of surface binding energies and the neglect of attractive potentials fail in multicomponent insulators, and second, radiation assisted diffusion and chemical reactions in the collision cascade cause compositional changes that currently cannot be predicted. Both these challenges are ripe for exploration with detailed quantum-mechanical molecular dynamics that can help identify the important physics and ways to improve Monte Carlo codes.



### 3.1.1. *Atomic Collisions on the Moon Surface*

The realization that energetic solar wind ions can sputter the Moon surface was realized from the beginning of the Apollo project. Lunar samples returned since 1969, and still being analyzed, showed evidence of erosion by sputtering, redeposition of sputtered ejecta in porous surfaces, preferential sputtering such as that leading to the formation of Fe nanoparticles by reduction of iron oxides (Dukes et al., 1999), ion implantation, and cosmic ray tracks. Many of these effects were anticipated by Wehner (1964) years before the first Apollo landing. Reviews of sputtering and chemical alteration processes on the Moon, asteroids, and Mercury, from different perspectives, can be found in Johnson and Baragiola (1991), Hapke (2001) and Chapman (2004).

### 3.1.2. *Sputtering of Regoliths – Effect of Porosity, Redeposition*

Even if laboratory data for sputtering of a mineral is known, its application to a porous regolith, such as the Moon's, is not straightforward. In a very rough or porous surface, an important part of the flux of sputtered species is intercepted by nearby surfaces. The effect is observed as a reduction of the sputtering yield over that of flat surfaces and in the appearance of surface coatings due to re-deposition of material (Hapke and Cassidy, 1978) and is a current topic for computer simulations (Cassidy and Johnson, 2005). The magnitude of the effect depends on several factors, such as the angular and energy distribution of sputtered particles, the topography of the surface, the sticking of ejected particles when they hit an adjacent surface, temperature, and the type of material. The sticking of sputtered particles depends in turn on their identity (and surface binding energy), kinetic energy, angle of impact and type of surface. One of the most important unknown in the calculations is the probability of sticking for ejected atoms or molecules with energies between a few tenths of eV and a few eV, which is a range where molecular dynamics simulations can be applied, once the non-trivial task of finding adequate interatomic potentials in silicates is done.

### 3.1.3. *Grain Destruction*

Cosmic rays impacting interstellar grains can sputter the grain and any existing ice mantle. The process can occur by atomic ejection at both ends of the ion track (Schutte, 1996). In addition, it has been proposed that grain destruction can occur by evaporation, if the energy absorbed by the grain is sufficient to cause a sufficient temperature increase. Modern molecular dynamics simulations have shown that the thermal sputtering yields are much smaller than anticipated (Bringa and Johnson, 2004).

On the opposite end of the energy scale, sputtering of ice mantles can occur by thermal ions if they carry high potential energy, e.g.  $\text{He}^+$ ,  $\text{He}^{++}$  or other mul-

tively charged ions. The mechanism, Auger desorption (Baragiola, 2005) is one in which the ion captures a valence electron from a condensed molecule, with the energy released exciting simultaneously another valence electron. Energetically, it is favored that the two final holes remain in different molecules. Their Coulomb repulsion energy, acting before the holes can drift away, can transform into kinetic energy and result in desorption. For this process to occur, the recombination energy of the incoming ion must exceed the energy of the two holes in the lattice. Such a condition will exist for  $\text{He}^+$  impacting most condensed gases, and for  $\text{H}^+$  on some ices with sufficiently small band gap. Less abundant multiply charged ions can be expected to produce Auger desorption with a higher probability per ion impact. There is a need for measurements and theory of Auger desorption from ices that will allow predictions of desorption yields.

#### 3.1.4. *Sputtering of Ices (Satellites, Rings, Comets, Outer Planets, Interstellar Grains)*

This topic has been reviewed from the point of collision physics by Johnson and Schou (1993) in general, and by Baragiola et al. (2003) for water ice, the most prevalent condensed gas in astrophysics. The reader is referred to those papers for details. Basically, the physical principles of electronic sputtering of ices are known, but the details are not and therefore predictions are not possible in general. What is known is that the electronic excitations produced by fast ions in insulators can result in the formation of repulsive states through several different pathways spanning times from roughly  $10^{-16}$  to  $10^{-11}$  s, depending on whether the states are formed promptly or through electron-ion recombination. What is not known, except for a handful of cases (i.e., the condensed rare gases), is the nature of the repulsive states and how they relax. Competing with the intermolecular repulsion is relaxation by decay through multiphonon, autoionization and radiative processes. As a result of the unknowns, most reliable quantities, such as sputter yields and distributions, come from experiments.

#### 3.1.5. *Generation of Atmospheres by Sputtering*

Sputtering and desorption by solar ultraviolet photons and energetic charged particles from the solar wind and planetary magnetospheres can eject material from the surface of an astronomical body with a faint atmosphere. Depending on its velocity, the ejected material may escape the gravitational pull or may contribute to the formation of an atmosphere, adding to any existing contribution of sublimation (Shi et al., 1995; Cooper et al., 2001), volcanism or meteorite impact ejection. The effect of the incoming ions is more extensive, since they interact with the atmosphere dissociating molecules, adding to photodissociation by solar radiation (limited to daytime). The dissociation fragments can in turn scatter, react, and/or

be trapped in collisions with the surface. The generation of atmospheres by sputtering of ices is thought to be important in the icy satellites Ganymede and Europa of Jupiter, in most satellites of Saturn, Uranus, Neptune and trans-Neptunian objects. In addition, sputtering of Na from plagioclase feldspar minerals on Mercury and the Moon is thought to be an important source of the sodium exospheres that have been observed around those rocky bodies (Killen et al., 2004).

### 3.2. AMORPHIZATION OF CRYSTALLINE MINERALS AND ICES

Crystalline silicates and ices are amorphized at relatively low doses by ion impact, not only at low energies as a result of elastic collisions (Brucato et al., 2004; Demyk et al., 2004) but also in ionization tracks produced by swift heavy ions (Meftah et al., 1994). In the latter case, if the energy deposition in the track is sufficiently dense, local melting occurs followed by an extremely fast re-solidification which leads to amorphization. Amorphous tracks are etched preferentially by chemical means and this enables easy visualization for measurements of ion fluxes or for dating. We note that amorphization of minerals by radiation damage is of great importance also in the encapsulation of radioactive waste in the nuclear energy. Most models of amorphization are empirical and the current view is that the problem is unsolved (Trachenko, 2004).

For water ice on icy satellites, the efficient amorphization by ions competes with thermal crystallization of amorphous ice. This gives the ratio of amorphous to crystalline ice obtained by infrared reflectance spectroscopy a valuable diagnostic value (Hansen and McCord, 2004). Figure 5 shows the drastic changes in the OH stretch vibration band of water during amorphization by ions (Baragiola et al., 2005) that demonstrate that the band shape is a sensitive indicator of the crystallinity of the ice. It is noteworthy and not yet understood that, while the shape of the infrared band evolves towards that of amorphous ice upon irradiation, significant differences remain. The temperature used in these experiments was 70 K to simulate amorphization of crystalline ice on Europa, a phase that may be produced by melting ice in tectonic processes or in meteorite impacts. The  $\text{Ar}^+$  ions were used to simulate the  $\text{S}^+$  ions that abound in the Jovian magnetosphere without the complication of chemical effects.

### 3.3. ELECTROSTATIC CHARGING OF SURFACES

Astronomical surface materials (minerals or ices) are electrical insulators and, therefore, charge electrostatically when exposed to charged particles and ionizing photons. Surfaces charge positively by capturing a slow positive ion or by electron emission when hit by a sufficiently energetic ultraviolet photon or a fast ion. They

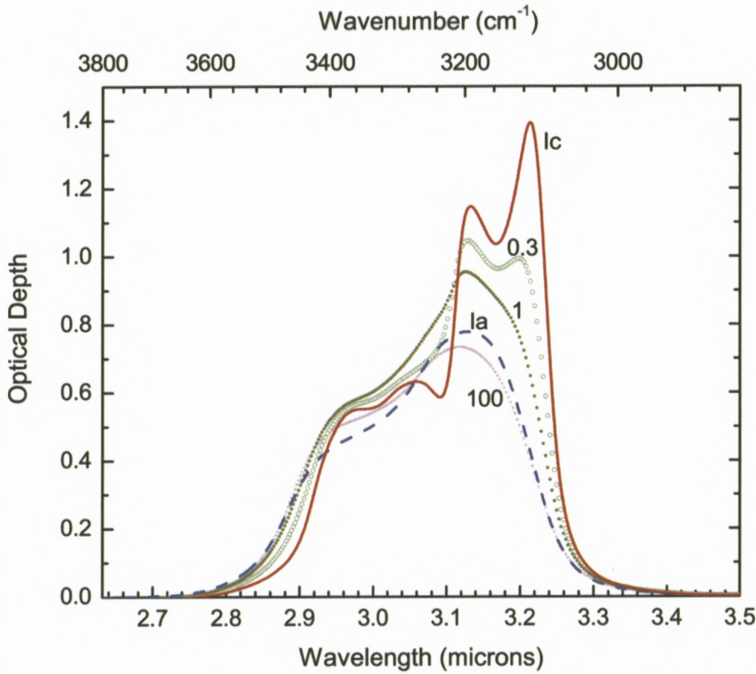


Figure 5. Optical depth of the infrared vibrational band due to the OH stretch in ice, measured at 70 K for a  $\sim 10^{18}$   $\text{H}_2\text{O}/\text{cm}^2$  crystalline ice film grown at 150 K and irradiated at 70 K by 100 keV  $\text{Ar}^+$  ions at normal incidence. Ic-unirradiated crystalline (cubic) ice. The spectra with symbols show Ic irradiated to different fluences indicated by the numbers adjacent to the curves, in units of  $10^{13}$  ions/ $\text{cm}^2$ . The dashed curve labeled Ia is the spectrum of amorphous ice grown at 20 K and taken to 75 K. From Baragiola et al. (2005).

can charge negatively when impacted by either slow or high energy electrons with a secondary electron emission coefficient less than unity. It is difficult to predict the amount of charge accumulated on a surface because it depends on material properties, the balance between fluxes of incoming and ejected charges, their energy distribution, and the surface electrical potential. When the surface is inhomogeneous or when the particle flux and/or electromagnetic field is not uniform (for example part of the surface being in the shadow) the resulting differential charging will induce electric fields that can affect electron emission and may induce electrical breakdown. These conditions are relevant for electrically insulating surfaces in spacecraft, where the breakdown can produce malfunction by spurious electrical noise, and also permanent damage (Garrett and Whittlesey, 2000). Electrostatic charging can affect the dynamical behavior of small grains in regions of significant electromagnetic fields, such as planetary magnetospheres. A

most striking example is the presence of the spokes in Saturn's rings, thought to be caused by a competition of gravitational and electromagnetic forces (Mitchell et al., 2006). Analysis of the complex problem of electrostatic charging in dusty plasmas (e.g., Jurac et al., 1995; Weingartner and Draine, 2001) is still in its infancy and is hindered by the scarcity of data on electron emission from insulators by ions and electrons at energies below 100 eV and on surface charging with ion beams.

### 3.4. RADIATION CHEMISTRY

The similarity in the composition of volatiles in comets and the ice mantles of interstellar grains led early to the idea that interstellar ices are integrated into comets. However, the degree to which this occurs is still an unsolved problem. Icy grains can evaporate in the protoplanetary nebula and later condense into comets while being concurrently processed by the strong radiation environment. Alternatively, grains that have been exposed to energetic radiation in the interstellar medium may be incorporated with little alteration into comets in the outer regions of the protoplanetary disk. In both cases, energetic radiation will synthesize molecules and store radicals in the ice, but to a degree which is not fully understood. Figure 6 shows the results of radiation chemistry in a hydrogen peroxide film irradiated at 17 K with 50 keV protons that deposit their energy mainly by electronic processes. One can notice that irradiation produces new molecules: water, diatomic oxygen and ozone, which remain trapped in the sample at these low temperatures. Analysis of the infrared spectra, taking into account interference effects in the thin ice films, can be used to obtain quantitative fluence dependences, shown in Figure 7. A linear dependence of column density with fluence indicates that the product is formed in single collisions (case of water), in contrast with the case of di- and tri-atomic oxygen molecules. Other atoms and molecules are thought to be trapped as well but are very weakly sensitive to infrared light or, as in the case of OH radicals and HO<sub>2</sub> molecules, their absorption bands are hidden by the much stronger bands due to water and hydrogen peroxide.

We have used this type of radiolyzed material, obtained after high fluence irradiation, to study the evolution during heating using TDS (thermal desorption spectroscopy, also known as TPD: temperature programmed desorption). The material is thought to be a model system for cometary grains containing radiation processed ice and their behavior as the comet warms up on approach to the Sun and loses mass through sublimation of volatile gases. One needs to take into account in any thermal processing that the molecules desorbing may not be just the original trapped gas. Warming may allow chemical reactions involving frozen

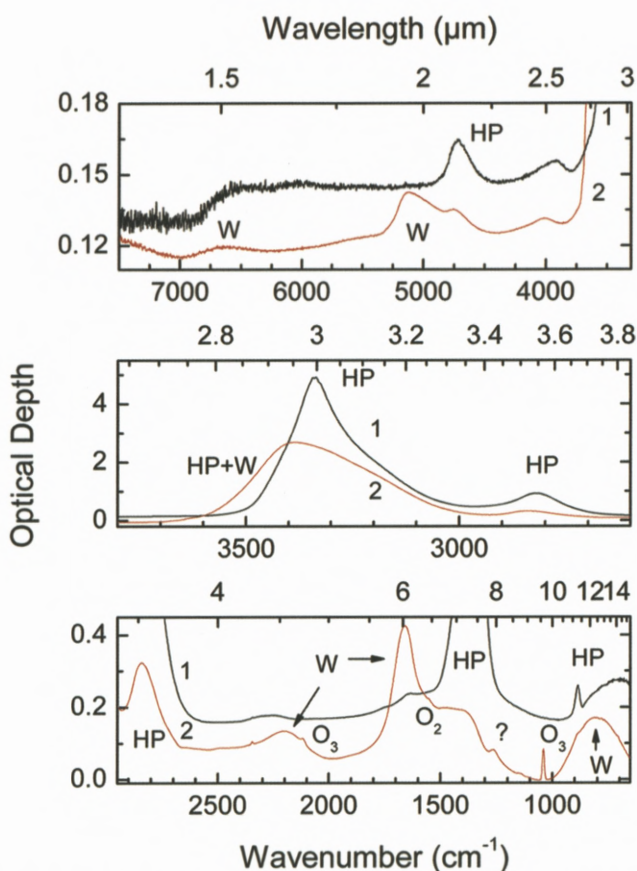


Figure 6. Infrared spectra of a solid  $\text{H}_2\text{O}_2$  sample before (1) and after (2) irradiation at 17 K to a fluence of  $1.8 \times 10^{15} \text{ H}^+$  ions  $\text{cm}^{-2}$  at 50 keV.  $\text{H}_2\text{O}_2$  is labeled as HP,  $\text{H}_2\text{O}$  as W. From Loeffler et al. (2006a).

radicals to overcome energy barriers and to alter the original composition of the ice by forming or destroying molecular species.

The absolute concentrations of the  $\text{H}_2\text{O}$ ,  $\text{O}_2$ ,  $\text{H}_2\text{O}_2$  and  $\text{O}_3$  molecules and their dependence on irradiation fluence was obtained by TDS using a combination of experimental techniques: UV-visible and infrared reflectance spectroscopy, quartz crystal microbalance microgravimetry and mass spectrometry (Loeffler et al., 2006b). The results of the last two techniques are shown in Figure 8 which suggest fractionation in the gas release from comets. The very high radiation yields for the decomposition of hydrogen peroxide can be explained by the occurrence of a chemical chain reaction.

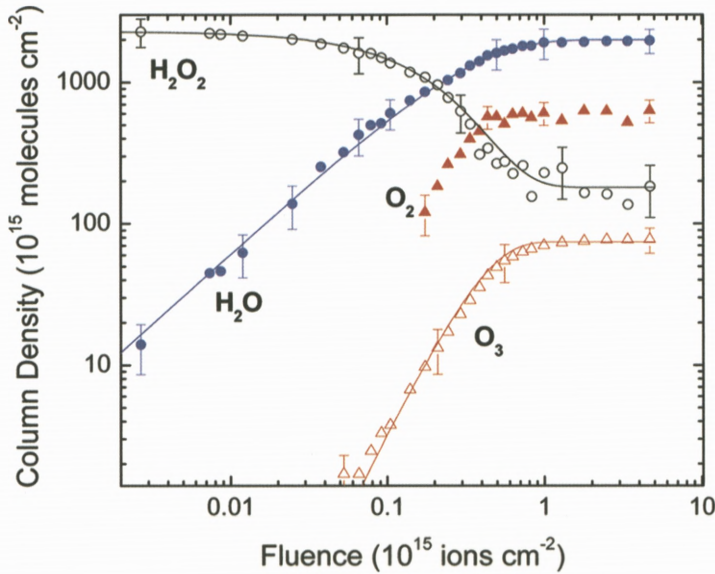
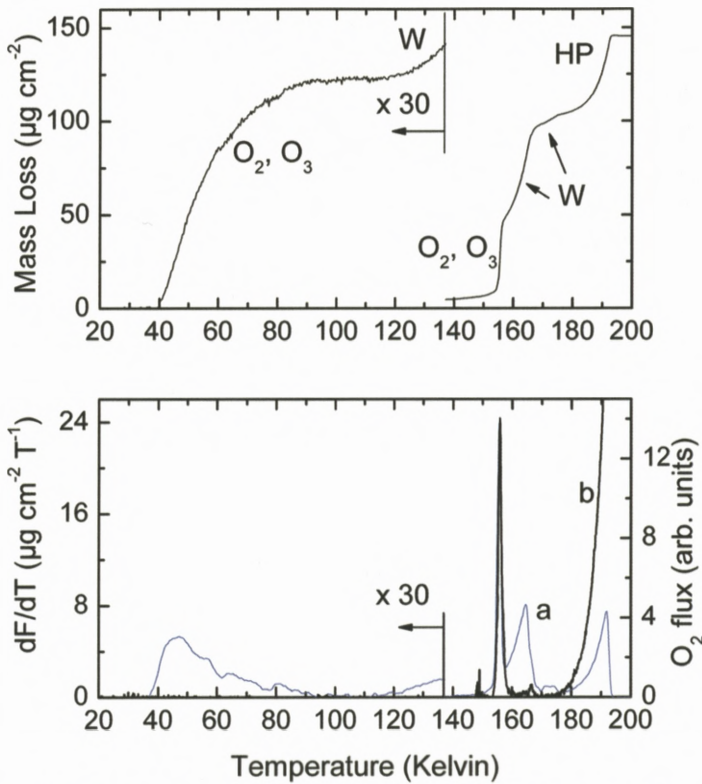


Figure 7. The production of water,  $\text{O}_2$ , and ozone in a film of  $2.6 \times 10^{18} \text{ H}_2\text{O}_2 \text{ cm}^{-2}$  irradiated with  $50 \text{ keV H}^+$ . From Loeffler et al. (2006a).

Another scenario for the thermal evolution of radiation processed ice is the diurnal cycle of the surface of icy satellites immersed in the magnetosphere of giant planets. This is one aspect of more general phenomena. The state of the surface of these bodies is determined by a competition of radiation damage and erosion due to energetic particles, photons, meteorite impact, and sublimation, by thermal diffusion, by interactions with the atmosphere, and radiation enhanced chemical processes, such as synthesis of radicals and new molecules, creation of optically active centers, phase transitions, release of trapped gases, and surface roughening. While one can study each aspect individually, it is important to consider the different ways in which synergism can occur and plan experiments to test them.

Several laboratory studies have shown the presence of trapped radicals in radiolyzed or photolyzed condensed gases. Here I summarize the results for water ice, by far the most abundant of those substances. Dissociation of water in the solid state often leads to immediate reformation of the molecule, since the dissociation fragments suffer collisions with surrounding molecules and cannot escape. The consequence of this phenomenon, called the *cage effect*, is a substantially smaller yield of radiation products in solids as compared to the gas phase. For radiation of slow linear energy transfer (LET, deposited  $dE/dx$ ) isolated H, O and OH radicals



*Figure 8.* Thermal desorption for an initially solid hydrogen peroxide film irradiated with 50 keV protons at 17 K to a final composition of 69.2% H<sub>2</sub>O, 22% O<sub>2</sub>, <6.2% H<sub>2</sub>O<sub>2</sub> and 2.6% O<sub>3</sub>. The amounts of water and hydrogen peroxide include a few percent of the radical OH. Top: Mass loss due to sublimation, measured with a quartz-crystal microbalance. W: water, HP: hydrogen peroxide. Bottom: Mass loss rate *versus* temperature while heating at a constant rate and mass spectrometer reading at mass 32. The large rise in (b) beginning at 180 K is O<sub>2</sub> from H<sub>2</sub>O<sub>2</sub> decomposition off the vacuum chamber walls. From Loeffler et al. (2006b).

produced at low temperatures become mobile at  $\sim 100\text{--}120$  K, and react to form stable molecular products such as H<sub>2</sub>O<sub>2</sub>, O<sub>2</sub>, and HO<sub>2</sub>. Energetic ions, on the other hand, can produce a high density of radicals in their track, which can recombine immediately. This causes a higher yield of new molecular products as compared with the case of gamma rays or fast electrons. It is very important to stress this differences since one often finds in the literature the erroneous claim that, since fast ions produce many low energy secondary electrons in the solid, fast ion solid interactions can be reproduced using incident 5–100 eV electrons.



#### 3.4.1. *O<sub>2</sub> Synthesis from Water Ice*

Of the molecular products of water ice, oxygen is particularly important because it was detected in its solid form on Ganymede, a satellite of Jupiter. This detection is very perplexing because, at the reported high diurnal temperatures in Ganymede, the vapor pressure of O<sub>2</sub> exceeds the atmospheric pressure by several orders of magnitude. Although it was clear that the oxygen must come from radiolysis of water it is not clear if the pathway occurs in the atmosphere or within the surface ice. The first prediction was that enough O<sub>2</sub> could be generated by ice radiolysis and trapped in the surface ice.

Although O<sub>2</sub> ejection from ice had been demonstrated in sputtering experiments (reviewed by Baragiola et al., 2003), O<sub>2</sub> trapping was found to be orders of magnitude too small to explain the Ganymede observations (Vidal et al., 1997; Bahr et al., 2001). Recent, more elaborate experiments by Teolis et al. (2005) using 100 keV argon ions confirmed the low concentrations of trapped oxygen and shed light on the production mechanism. The authors found a complex dependence of O<sub>2</sub> sputtering on irradiation fluence that is correlated with that of the total sputtering yield. The results suggest that O<sub>2</sub>, formed in the projectile track by recombination of radicals, diffuses to the surface where it is trapped and then ejected via sputtering or thermal desorption. Depth profiling by sputtering shows that a high concentration of O<sub>2</sub> can trap in a sub-surface layer during bombardment at 130 K due to the formation of hydrogen and its escape from that region. Although the details of the microscopic processes have not yet been worked out, it is apparent that radiation induced diffusion is important and that hydrogen peroxide, often cited as a precursor for molecular oxygen, is of minor significance (Teolis et al., 2005).

#### 3.4.2. *Ozone Synthesis*

Whenever O<sub>2</sub> is present in a radiation experiment, the synthesis of ozone is expected, but at a very low level. In the case of pure water ice, no ozone was found in decades of experimentation. This presents a problem for the interpretation of the presence of ozone on Saturn's satellites Rhea and Dione (Noll et al., 1997). One could argue for the presence of condensed oxygen from which ions readily synthesize ozone (Baragiola et al., 1999; Famá et al., 2002). However, this would not explain why there is no ozone at Tethys, a satellite of similar size which is in an environment with more oxygen.

A recent development may help to solve the puzzle, the discovery that the amount of radiolytic O<sub>2</sub> trapped can be increased dramatically by co-deposition of water during ion irradiation. The co-deposition simulates the return of sputtered water molecules to the surface of an icy satellite due to gravity or by the effect

of regolith porosity/topography and causes the burial of a high concentration of radiolytic  $O_2$ . Teolis et al. (2006) showed that ozone, which cannot be formed from ice under vacuum, can readily be synthesized from the high concentration of buried  $O_2$ . The amount of  $O_3$  (and  $O_2$ ) trapped depends sensitively on the ratio of re-deposition to sputtering fluxes, that should vary with the type of terrain and the flux of magnetospheric ions.

#### 3.4.3. *Synthesis of Hydrogen Peroxide*

The hydrogen peroxide molecule is important because it was identified in the Galilean satellite Europa through the absorption of solar infrared and ultraviolet light. This observation attracted significant attention and led to laboratory studies of  $H_2O_2$  synthesis in ice by energetic protons and heavy ions, using infrared spectroscopy (Moore and Hudson, 2000; Gomis et al., 2004; Loeffler et al., 2006a, 2006c). In addition, Bahr et al. (2001) observed that thermal desorption of ice radiolyzed by 100 keV protons released not only water, as expected, but also  $HO_2$  and  $H_2O_2$  molecules. All these results not only explain the levels of  $H_2O_2$  detected on Europa but the detailed analysis of infrared reflectance also serve to identify the state of the peroxide at the molecular level.

#### 3.4.4. *Other Ices*

The cases described above are relatively simple and, in principle, could be modeled by using what we know of collision physics to obtain the spatial and temporal distribution of species that will then be used as input in chemical kinetics programs. More complicated pathways result from organic ices, and from ice mixtures (Delitsky and Lane, 1998). Significant recent research of ion interactions with ices containing carbon-bearing species includes the papers of Gerakines et al. (2000), Strazzulla and Palumbo (2001), Baratta et al. (2002), Moroz et al. (2004), Hudson et al. (2005), Ruitkamp et al. (2005) and Brunetto et al. (2006).

### **4. Was Ion Irradiation Needed for Primordial Life?**

Since Louis Pasteur falsified the Aristotelian dictum that life can arise spontaneously from non-living matter, one of the grandest unsolved scientific problems of all times has been: what is the origin of life? (Outside science there are answers to this question that are simple but lack predictive power.)

There are four main connections between ion impacts and life: (1) the possible synthesis of the first complex organic molecules (prebiotic molecules) that were used in the first microorganisms, (2) triggering life (biogenesis), (3) the well known effect of radiation in producing mutations and cell death, (4) the production of molecules that can be the energy source to sustain life.

The famous experiment of Stanley Miller and Harold Urey of half a century ago was aimed at recreating some of the organic compounds that make up life on Earth. They passed a spark discharge through a mixture of hydrogen, methane and ammonia simulated the primordial Earth's atmosphere. After a week of operation of the apparatus they found they produced amino acids: glycine,  $\alpha$ -alanine and  $\beta$ -alanine. Subsequent research has shown that amino acids can be synthesized when replacing the spark discharge with well defined ion or photon beams and when using condensed gases.

However, the relevance of the Urey and Miller experiment on life synthesis on Earth is questioned today because these researchers used a strongly reducing mixture of gases for the atmosphere whereas the current understanding is that the early atmosphere was mildly reducing. In addition, the chirality of the artificially produced amino acids is wrong. Life favors left-handed amino acids (they cause polarized light to rotate left), whereas the experiments show that the molecules are racemic: in equal proportion of left- and right-handed polarities.

Alternatively, one can think that the molecules came from outer space in comets or meteorites. This is the theory of exogenesis, supported by circumstantial evidence such as the Murchison meteorite. This object, which fell in Australia in 1969, contained amino acids glycine, alanine and glutamic acid and other unusual types. The chirality was slightly non-racemic, at a few percent level (Pizzarello and Cronin, 2000), a very weak support for the idea that they may be related to extraterrestrial life. Still, how those amino acids were formed is an open question.

More radical is the panspermia conjecture that life is everywhere and comes into Earth from space and is distributed to other worlds from Earth. The support for this idea does not come from evidence but from respect to authority – it has been endorsed by many eminent personalities: Anaxagoras, Alexander von Humboldt, Sven Arrhenius, Fred Hoyle, and Francis Crick. The weakest point of this idea is the frailty of life against atomic collisions. It is extremely unlikely that a microbe can survive the cosmic ray background in the very long travel through interstellar space.

I end this section with reference to an old topic in ion beam science that bears on the question of this section: ion beam polymerization. It can come to the aid of overcoming an obstacle: the huge distance between the amino acids synthesized till today and the complexity of life (not to mention the functionality). The largest synthesized molecules that have been identified contain 12 atoms. In contrast, a small protein contains 100 atoms, and a small cell  $10^{10}$  atoms. Open questions are therefore: What are the conditions for formation of large molecules by ion impact? What is the largest molecule that can be synthesized? The last question arises because ions can on one hand polymerize and on the other hand break up

intra- and intermolecular bonds, as demonstrated in the previous section and in the use of radiation therapy, a topic discussed elsewhere in this volume.

#### 4.1. ENERGETIC IONS AS A SOURCE OF BIOTIC ENERGY

There has been great interest in determining if there is life elsewhere in the solar system. High hopes were placed on Mars, but the Viking spacecraft and further missions produced no evidence of life. Reports on fossilized life forms in Martian meteorites, that made headlines ten years ago, have been largely discredited. New explorations to Mars will, nevertheless, continue. Now the quest is to find evidence below the surface since energetic radiation and an oxidizing environment makes it extremely unlikely that life or remnant molecules would have survived on the surface.

The focus of astrobiologists has shifted in part to the outer solar system. Clues for the existence of an ocean on Europa, a satellite of Jupiter, tens or hundreds of kilometers below the icy crust, stimulated speculation that life might exist there. This brings up the question of the source of energy required for life, at the depths below the surface where photosynthesis is not possible. Chyba (2000) proposed that this energy may be provided by magnetospheric ions striking Europa's surface through radiolytic oxidants such as oxygen, hydrogen peroxide or ozone, would in turn release energy in reactions with hydrocarbon compounds. There has been a surge of laboratory studies in this area, which have served to quantify the radiation chemical products, as discussed above. The next question is the transport of the oxidants kilometers deep to reach the ocean, where they could fuel bacterial life, since the penetration of radiation is limited to depths of typically microns and at most a few centimeters. Such transport mechanism could be sporadic surface cracking and melting of the surface ice, created by tidal stresses, tectonic activity or meteorite impact. However, on Earth, bacteria are found in deep-sea hydrothermal vents, and in rocks kilometers below the surface, possibly fed by hydrogen and oxygen released from water by energetic ions from natural radioactivity. There is recent evidence that bacteria may subsist on an energy input of  $2.8 \times 10^{-13}$  Joules/year (1.8 MeV/year) (Kerr, 2006). Such a situation may exist in underground oceans of Europa, Ganymede, Enceladus, Charon and possible other satellites in the outer solar system. Further progress beyond the speculative stage requires an *in situ* exploration of the surfaces; currently there are exploration missions being planned to Europa and Enceladus.

## 5. Summary and Outlook

Multiple topics in ion-solid interactions are of relevance to astrophysics. The list includes: Energy deposition, knock-on sputtering (including preferential sputtering and ion emission), electronic sputtering, radiation synthesis of molecules, decomposition of molecules, formation of bubbles and blisters by ion implantation and decomposition of H-bearing compounds, ion implantation and trapping, radiation enhanced diffusion, phase changes (amorphization, crystallization), electron emission and charging. The solids of interest are mostly minerals and condensed gases and the extant knowledge of atomic collisions – mostly on elemental solids – is usually not transferable.

The most promising lines of enquiry to make an impact on astrophysics are: (1) the study of the effect of fast heavy ions, (2) the dependence of sputtering yields of ices on deposited energy, (3) the magnitude of the sputtering yield of small grains, (4) the degree to which large molecules (e.g., organic molecules) can be synthesized and/or destroyed in condensed mixed gases, (5) the conditions necessary for a particular microorganism to survive space travel, (6) synergistic effects, (7) sputtering, amorphization and compositional changes of multi-component solids for light ions; measurements and predictive theories (not just computer simulations), (8) Auger desorption of condensed gases.

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