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Radiation effects in astrophysical ices

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Abstract. The interaction of heavy ions with astrophysical ices was studied at different beamlines of GANIL by infrared absorption spectroscopy. This allowed simulating in the laboratory the physico-chemical modifications induced in icy objects in space, exposed to radiation fields such as the solar wind, magnetospheric particles and interstellar cosmic rays. We briefly discuss sputtering, destruction and formation of molecules, amorphization and compaction, implantation, and finally the formation of organic molecules. This latter topic is related to the question of the initial conditions for the emergence of life.

1. Introduction

Ices are ubiquitous in space: in the dense phases of the interstellar medium (dense molecular clouds and proto-stellar cores, shown in figure 1) and in the solar system. The molecules can be formed or freeze onto surfaces of dust grains and form thin icy mantles. In the Oort cloud and the Kuiper belt of the solar system, together with dust (carbon based materials, silicates), they can form icy bodies, some of them being the progenitors of comets. They can cover the surfaces of the giant planets' satellites. Simple molecules such as H_2O, CO, CO_2, NH_3, CH_4 etc. are the dominant species, but more complex, organic molecules (alcohols etc.) have been detected. The ices are continuously exposed to ionizing irradiation (UV photons, electrons, ions); this may induce several physico-chemical processes. Among them are fragmentation/radiolysis, followed by chemical reactions and formation of new molecules; structural/phase changes; and desorption/sputtering of molecules from the surface [1]. In astrophysical studies on interaction of radiation with ices, effects induced by weakly ionizing radiation such as UV photons and keV-MeV light ions (H, He) was extensively studied in the laboratory. This was driven by the use of keV to MeV proton accelerators, that are relatively small and more common than heavy ion accelerators such as GANIL, which are indeed large scale installations of which only a few exist in the world. Here, we therefore focus on the contribution of heavier ions (C, O, S, Fe), which are also present in space.

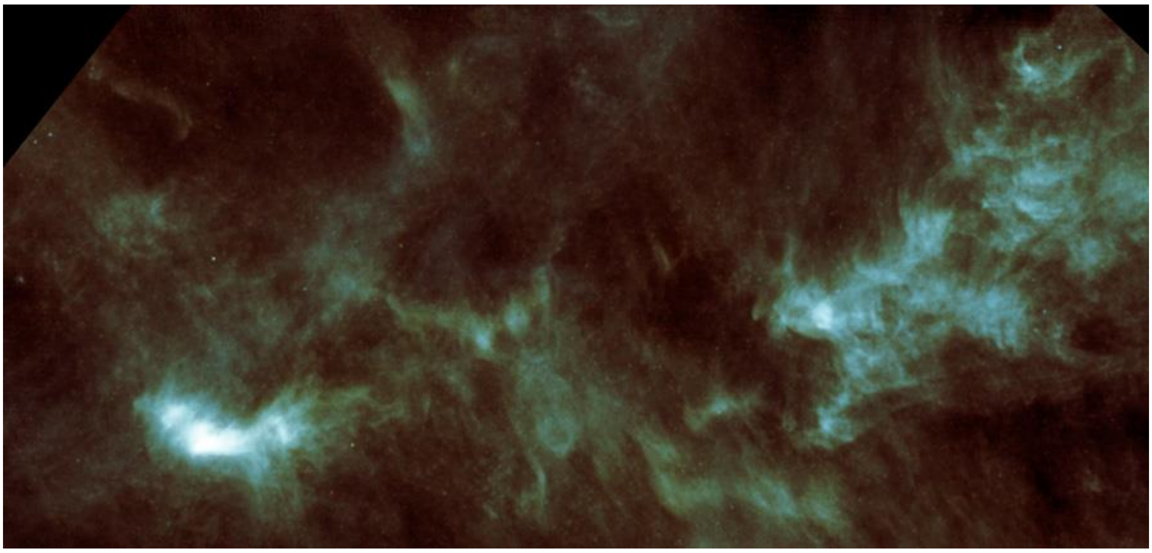

Figure 1. Herschel's infrared view of part of the Taurus Molecular Cloud, which is about 450 light-years from Earth and is the nearest large region of star formation. Image credits: ESA/Herschel/SPIRE (reproduced with permission).

From a collaboration between PUC-Rio and CIMAP-CIRIL with the goal to study sputtering of LiF by MeV ion beams, a subject under intense research in both laboratories (see [3] and references therein), emerged a new research topic at GANIL: heavy ion induced radiation effects in astrophysical ices. Indeed, at PUC, the investigation of sputtering of secondary ions from ices by MeV heavy ions started a decade ago [4, 5]. It was observed that the dependence of the ion desorption yield on the projectile stopping power was strong enough that it can compensate for the low abundance of heavy ion constituents of cosmic rays and, therefore, produce effects in solids comparable to those induced by protons and alpha particles. The sputtering occurs basically through neutrals, whose yields are orders of magnitude higher than that of secondary ions.

It was then realized that a new method could be coupled for sputtering yield measurement of ices: Fourier Transform Infrared Spectroscopy (FTIR) was able not only to identify formed molecules in the target and measure their formation and destruction cross sections, but also to measure total sputtering yields. Indeed, following the decrease of peak areas of infrared bands during ion beam bombardment and compensating for the newly created species, the removal rate of material could be determined. Consequently, in close collaboration between CIMAP/Caen, IAS/Orsay and PUC/Rio de Janeiro, the radiolysis and sputtering of ices such as CO and CO_2 by swift heavy ions (cosmic ray analogs) at about 15K was studied. The research was strongly supported by the French-Brazilian CAPES-COFECUB exchange program. Since 2010, INAF/Catania joined, and, supported by the COST Action "The Chemical Cosmos", the studies were extended to effects induced by slow heavy ions (solar wind and giant planet's magnetospheres).

2. Cosmic rays

The first laboratory simulations of the interaction of heavy cosmic ray ions with ices were performed within a joint-doctorate program between the PUC-Rio de Janeiro and the University of “Caen-Basse Normandie”. E. Seperuelo Duarte, graduate from Astronomy, was able to apply the new approach in the study of CO_2 ice sputtering by 46 MeV Ni at the IRRSUD beam line of GANIL [6]. The experiment was repeated for CO ice sputtering induced by 50 MeV Ni (again at IRRSUD) and by 537 MeV Ni (at the SME beamline) [7]. A strong non-linear increase of sputtering yields Y with deposited energy in CO ice due to electronic sputtering was observed as shown in figure 2. The quadratic dependence with the electronic stopping power, $Y \sim S_e^2$, is in excellent agreement with previous results obtained with light ions, at lower energies, by Brown et al. [8]. The stopping power $S_e = -dE/dx$ of a material is equal to the energy E deposited per unit path length x by the projectile.

Therefore, even taking into account the low abundance, the total number of heavy ion desorbed/sputtered molecules is higher than that desorbed by protons. This observation now needs to be taken into account for understanding the evolution of astronomical objects such as dense molecular clouds (figure 1). The heavy ion induced desorption contribute to explain for the observed presence of gas phase molecules in such clouds. In the absence of these processes, it is expected that all CO molecules should condense on small grains in cold (10 K) dense clouds within timescales shorter than these clouds ages, and form an icy mantle. Processes discussed to explain the gas phase molecules include photodesorption of ices by secondary UV photons from cosmic ray interaction with hydrogen or “spot heating” of grains, not to be confused with our observation related to electronic sputtering [7]. Deep inside dense clouds, each of the three processes (electronic desorption by the heavy ion fraction of cosmic rays, and “spot heating” of grains by cosmic rays, photodesorption) yield comparable contributions to the total desorption yields [7].

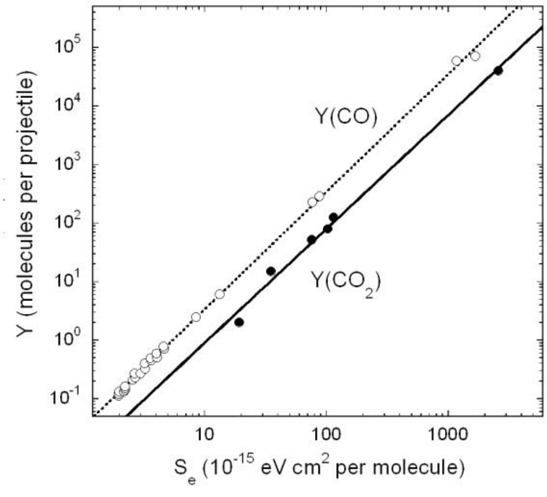

Figure 2. Sputtering yield Y of CO and CO_2 as a function of electronic stopping power S_e. A quadratic dependence $Y \sim S_e^2$ is observed [6-9].

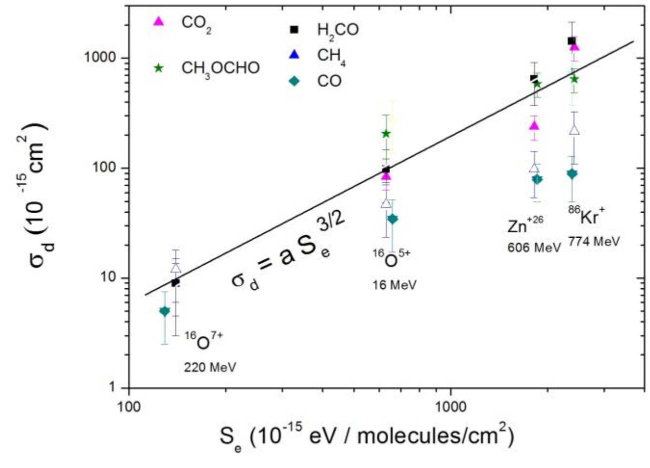

Figure 3. Destruction cross sections σ_d of ice molecules (as indicated) as a function of electronic stopping power (see text); they essentially follow a power law $\sigma_d \sim S_e^n$ with $n \approx 1.5 \pm 0.3$ [14, 17, 21].

Furthermore, heavy ions are an order of magnitude more efficient in destroying the initial molecules and corresponding radiochemical yields than protons. A quadratic dependence of the sputtering yield on stopping power is not only observed for CO ices [7, 8], but also for CO_2 ices [7, 9] (figure 2) and for high electronic stopping also for O_2, N_2 and H_2O [9] thus supporting the conclusions concerning the importance of heavy ions in modification of interstellar ices.

Since then, cosmic ray effects in many other ices have been analyzed at CIMAP-GANIL: H_2O [10-12], NH_3 [13, 14], CH_4 [15, 16], CH_3OH [17, 18], HCOOH [19-20], H_2CO [21], C_6H_{12} [22] and acetone [23]. Chemical reactions follow the fragmentation of initial molecules. This leads to formation of new species, a finding particularly interesting with ice mixtures containing the ingredients of organic molecules (H,C,N,O) [13, 22, 24, 25]. The determination of destruction and formation cross sections is one of the most important goals of this research. Considering the obtained results with low energy data, we proposed that – at least for ice targets – such cross sections depend basically only on a power ($\approx 1.5 \pm 0.3$) of the electronic stopping [14, 17, 18, 21]. As a consequence, it is possible to estimate molecular destruction rates for all cosmic ray constituents over a very large energy range. Figure 3 illustrates this “law” for methanol ice. Moreover, it turns out from these calculations that - in interstellar medium – chemical evolution induced by iron ions of cosmic rays is surprisingly faster than that induced by protons and alpha particles: for instance, the methanol half live due to iron bombardment is 3×10^{14} s (approx. 10^7 years), 700 times shorter than that induced by protons.

Often neglected compared to radiolysis induced chemical modification, the physical state of the ice (amorphous, crystalline, metastable) is also extremely important in many aspects for astrophysicists. At low temperature (about 10 K), a porous amorphous ice phase is obtained by accretion of water molecules, which is getting compacted under ion irradiation. Finally, it evolves towards a compact non-porous, but disordered amorphous phase [26]. Irradiation of crystalline water ice annealed at “high” temperature (140 K) and cooled down to approximately 10 K leads to amorphization towards this same intermediate amorphous phase [27].

The compaction, i.e. the loss of open porosity of amorphous ice films was studied at the high energy beam line LISE of GANIL as well as at SME and IRRSUD in the MeV to GeV range [10]. FTIR allows to study the number of “OH dangling bonds” (i.e. pending water molecule OH bonds not engaged in a hydrogen bond in the initially porous ice structure). Combined with previous experiments using lower energy light ions from other facilities, we evaluated a cross section for the disappearance of porosity as a function of electronic stopping power over three orders of magnitude. The relevant phase structuring time scale for the ice network on icy mantles covering interstellar dust grains are present in the molecular clouds of our galaxy was compared to interstellar chemical time scales using an astrophysical model including the expected galactic cosmic ray distribution of abundances. The galactic cosmic ray distribution of ion abundances reproduces the ionization rate observed and provides ice compaction time scales in the range from 1.4×10^5 to 2×10^6 years. Ice mantle porosity or pending bonds as monitored by the OH dangling bonds, are removed efficiently by cosmic rays. Studies on the compaction and amorphization of water ice are ongoing. Similar observations have also been made for e.g. H_2O-NH_3 and other ices made of mixtures of molecules [13, 14].

3. Ion Implantation

When the penetration depth of an energetic ion that travels through a material is shorter than the thickness of the target, the ion finally is stopped and remains implanted. Implantation experiments are particularly relevant to understand the effects of different ion populations such as solar wind ions and magnetospheric particles, interacting with icy objects in the Solar System (for a review see [28]). Experiments with reactive ions (e.g., H^+, C^+, N^+, O^+, S^+) are particularly relevant because they induce all of the effects of any other ion, but in addition have a chance, by implantation in the target, to form new species containing the projectile. In recent years several implantation experiments have been conducted at the low energy facility ARIBE of GANIL. The experiments were performed with carbon and sulfur ions of energies between 10 keV and 180 keV. They are able to break 10^3-10^4 bonds per ion and thus a large number of new molecules can be formed by recombination of fragments of the irradiated species. In addition, implanted carbon and sulfur, being reactive, have a chance to form species that include the projectile with a maximum yield of one molecule per incoming ion. Recently, several experiments ([29-31], listed in table 1) have been conducted at ARIBE.

Table 1. Summary of the implantation experiments conducted so far at ARIBE.

ION (E in keV)	**TARGET T= 15-150 K**	**MAJOR PRODUCED SPECIES (in bold those containing the projectile)**	**REF**
C^{q+} (10, 30) q=2-3	H_2O	H_2O_2, $\mathbf{CO_2}$	[29]
S^{q+} (35-180) q= 7, 9, 11	H_2O	H_2O_2 $\mathbf{H_2SO_4}$ dissolved in H_2O	[30]
	CO	$\mathbf{SO_2}$	[31]
	CO_2	$\mathbf{SO_2}$	[31]

Figure 4. Artist's impression of JUICE, the JUpiter ICy moons Explorer mission, in the Jovian system. Image credits: ESA/AOES (reproduced with permission).

The results have mostly been applied to the icy moons of the giant planets in the outer Solar System, where in fact water ice is by far the dominant species. Prominent examples are the Jovian moons Europa, Callisto and Ganymede, which have been visited by the Galileo spacecraft and which are the focus of Europe's ESA next large science mission, the Jupiter Icy moons Explorer JUICE (figure 4). On these objects, several absorption features have been observed and have been attributed to C-H, H_2O_2, S-H (and/or H_2CO_3), SO_2, CO_2, and CN [32, 33].

In addition abundant surface constituents of the Galilean moons are darker, non-ice materials [34], and in the case of Europa, hydrated sulfuric acid [35]. The dark materials are thought to be carbonaceous compounds present at the time of the satellite formation or later delivered by cometary and meteoritic bombardment [36]. Results based on space observations have shown that most of the CO_2 detected on the surfaces of Callisto and Ganymede is contained in the non-ice materials [33, 34]. SO_2 is believed to be present on the surface of the icy moons as a molecule trapped in the dark material and/or the water ice [32]. Many of the icy moons orbit within their planet's magnetosphere and their surfaces are subjected to intense bombardment. The major components of the Jovian magnetosphere are protons and ions such as S^{q+} and O^{q+}, and also energetic electrons [39].

The high fluxes of those ions justify the need of implantation experiments that are conducted to contribute to the debate on the origin of the observed minor molecular species: are they native of the given satellite (endogenic source) or are they due to external effects such as ion implantation (exogenic source)? The experiments conducted at ARIBE [29-31] have given an important contribution to the discussion. As an example, in figure 5 we show the IR spectra of water ice before and after implantation of 3×10^{15} 30 keV $^{13}C^{3+}/cm^2$ (left panel) and 4.8×10^{16} 105 keV S^{7+}/cm^2 (right panel). A band appearing at about 2275 cm^{-1} upon implantation can easily be attributed to $^{13}CO_2$ (left panel of figure 5). The corresponding measured yields for ions with energies from 10 keV to 30 keV do neither depend on the charge state (q = 1-3) nor on the temperature (15 K and 80 K). They range between 0.32 and 0.57 molecules/ion, i.e. they are constant within the experimental error. The time scale necessary to accumulate the observed quantity of carbon dioxide on the surface of Europa by implantation of magnetospheric carbon ions has been evaluated to be on the order of (1.0-1.3) × 10^4 years. This time is higher than that evaluated for the production of carbon dioxide by other relevant processes, in particular by the ion bombardment stimulated formation of CO_2 at the interface between solid carbon and water ice [40]. We therefore conclude that although a relevant quantity of CO_2 can be formed by carbon ion implantation, this is not the dominant formation mechanism on the surfaces of icy satellites [29].

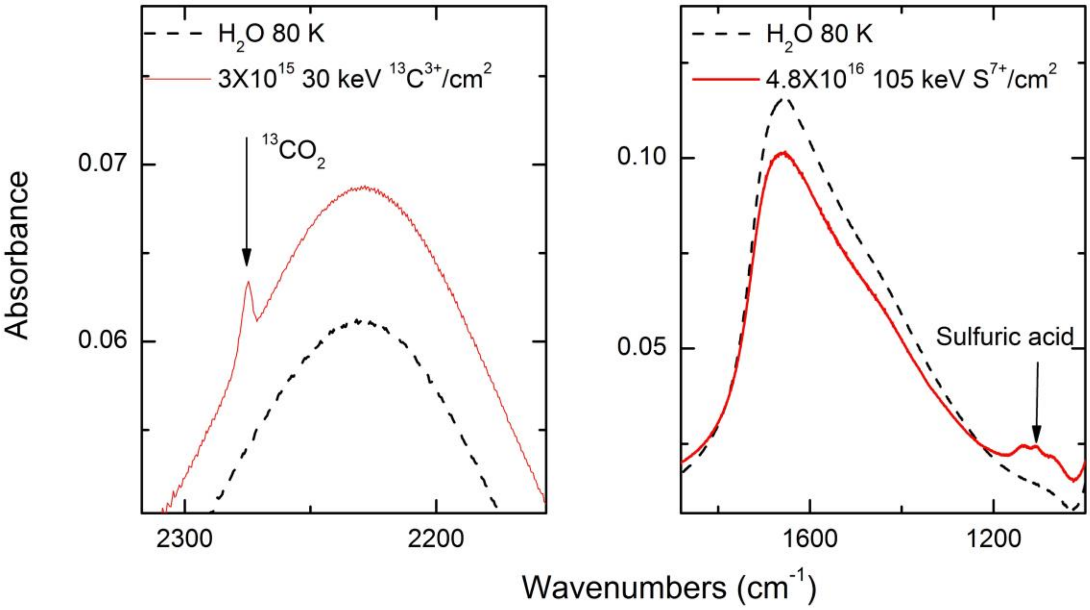

Figure 5. IR spectra of water ice before and after implantation of carbon ions (left panel) and sulfur (right panel) ions.

The right panel of figure 5 shows that a new, multi-peaked band is formed around 1150 cm^{-1}, indicating the formation of hydrated sulfuric acid upon sulfur implantation. We have performed experiments with sulfur ions having different charges (q = 7, 9, 11) and energies (35 keV - 176 keV), implanted in water ice at 80 K. The results of our experiments indicate that the formation yields increase with ion energy, from 0.12 molecules/ion for 35 keV ions to 0.64 molecules/ion for 200 keV ions (this latter value is from [41]). From the high sulfur ion fluxes of (2×10^6-$1x10^8$) ions cm^{-2} s^{-1}) evaluated in different regions of the surface of Europa [42], Ding et al. [30] conclude that sulfur ion implantation is the dominant formation mechanism of hydrated sulfuric acid. The suggestion that the observed distribution of sulfuric acid on the surface is well correlated with the local flux of sulfur ions [42] finds a full explanation by our experimental data.

Nevertheless, the question about the origin of SO_2 remains open. We were not able to find any evidence of synthesis upon sulfur ion implantation into water ice. In fact, SO_2 has been observed on some of the icy moons by ultraviolet observations, via its band peaked at 280 nm. To explain its origin several mechanisms have been proposed, among which S implantation in water ice [43, 44], which is not supported by our experimental results. Further experimental efforts are thus necessary to clarify the question.

4. Outlook: formation of organic pre-biotic molecules

The matter in our galaxy evolves within a life cycle of stars, which depends on numerous astrophysical processes including processing by radiation fields and astrochemical processes: radiation effects, reactions at gas-grain surfaces, ice photochemistry and so on. Interstellar dust grains, after the collapse of dense molecular clouds are incorporated in protoplanetary systems. Thus, interstellar matter can contribute to the so-called primitive matter. Later on, comets (orbiting in the Oort cloud, the Kuiper belt or Jupiter family ones, made out of ices and dust) and asteroids, can feed this matter to planets such as the early Earth. Laboratory astrochemistry has shown that complex molecules (including amino acids and nucleobases) can be formed under interstellar/circumstellar conditions by vacuum UV irradiation, electron and ion bombardment of interstellar ice analogs containing small molecules (H_2O, CO, CO_2, CH_3OH, NH_3, HCOOH), that is, the basic building blocks of organic matter (H, C, N, O, and others). Therefore, irradiation processing of ice mixtures [13, 22, 24, 25, 45] may be related to the question of the origin of organic matter on Earth, bringing potential building blocks for the emergence of life on earth, and possibly on other bodies in the solar system.

At IRRSUD, ammonia-containing ices made of mixtures of small molecules such as $H_2O:NH_3$ and $H_2O:NH_3:CO$ were irradiated by 46 MeV Ni ions in an attempt to simulate the physical chemistry induced by heavy-ion cosmic rays inside dense astrophysical environments. The infrared spectra of the irradiated ice samples exhibit lines of several new species including HNCO, N_2O, OCN^-, and NH_4^+. After FTIR measurements as a function of the projectile fluence in order to determine destruction- and formation cross sections, the irradiated samples were slowly warmed up to room temperature. In the case of the irradiated $H_2O:NH_3:CO$ ice, the infrared spectrum at room temperature contains five bands that can be tentatively assigned to vibration modes of zwitterionic glycine, an amino acid, and possibly, another can be attributed to hexamethylenetetramine (HMT) [13]. If such organic molecules exist in space, it is also pertinent to study their stability when exposed to radiation [46].

Furthermore, ices containing methanol and ammonia $CH_3OH:NH_3$ were irradiated at IRRSUD. The main goal here was to make the first proper comparison between the formation of products in an ice mixture of interstellar type both by irradiation of the ice using swift heavy ions and by vacuum UV photons using a similar energy dose (in eV/molecule). It was shown that both UV photon and swift heavy ion irradiation yield similar residues formed after warm-up to room temperature of the irradiated ices [45]. In order to confirm and quantify the possible formation of even more complex organic molecules, in the near future, new irradiation experiments with ex-situ chromatographic analysis of thick residues from swift ion processing are in preparation. This could lead to the detection of new molecular components in the organic residues. These species could thus be present in circumstellar regions and comets, and were likely delivered to the primitive Earth.

Studies on radiation effects in astrophysical ices will benefit in the near future from a new ultrahigh vacuum setup IGLIAS financed by ANR (partners: CIMAP and IAS) allowing to work under improved experimental conditions. In view of the increasing amount of data arising from ever improved observation tools including earth and satellite based telescopes, and space probes such as JUICE, dedicated laboratory experiments are needed to interpret the observations. Well established and emerging experimental techniques [47] will help to understand formation of dust grains, icy mantles and their processing dust grain formation and processing (ice mantle chemistry, space weathering [48]) under astronomical conditions.

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References

[1] Allamandola L J, Bernstein M P, Sandford S A and Walker R L 1999 Evolution of interstellar Ices *Space Sci. Rev.* **90** 219–232

[2] Shen J C, Greenberg J M, Schutte W A and Van Dishoek E F 2004 Explosive chemical desorption in dense clouds *Astron. Astrophys.* **415** 203-215

[3] Hijazi H, Farenzena L S, Rothard H, Boduch P, Grande P L and da Silveira E F 2011 Cluster ion emission from LiF induced by MeV N^{q+} projectiles and ^{252}Cf fission fragments *Eur. Phys. J.* D **63** 391-400

[4] Collado V M, Farenzena L S, Ponciano C R, da Silveira E F and Wien K 2004 Ion desorption from frozen H_2O irradiated by MeV heavy ions *Surf. Sci.* **569** 149-162

[5] Farenzena L S, Iza P, Martinez R, Fernandez-Lima F A, Seperuelo Duarte E, Faraudo G, Ponciano C R, Homem M P G, Naves de Brito A, Wien K and da Silveira E F 2005 Electronic sputtering analysis of astrophysical ices *Earth Moon Planets* **97** 311-329

[6] Seperuelo Duarte E, Boduch P, Rothard H, Been T, Dartois E, Farenzena L S and da Silveira E F 2009 Heavy ion irradiation of condensed CO_2: sputtering and molecule formation *Astron. Astrophys.* **502** 599-603

[7] Seperuelo Duarte E, Domaracka A, Boduch P, Rothard H, Dartois E, and da Silveira E F 2010 Laboratory simulation of heavy ion cosmic ray interaction with condensed CO *Astron. Astrophys.* **512** A71

[8] Brown W L, Augustyniak W M, Marcantonio K J, Simmons E H, Boring J W, Johnson R E and Reimann C T 1984 Electronic sputtering of low temperature molecular solids *Nucl. Instrum. Meth.* B **1** 307-314

[9] Raut U and Baragiola R A 2013 Sputtering and molecular synthesis induced by 100 keV protons in condensed CO_2 and relevance to the outer Solar System *Astrophys. J.* **772** 53

[10] Dartois E, Ding J J, de Barros A L F, Boduch P, Brunetto R, Chabot M, Domaracka A, Godard M, Lv X Y, Mejía Guamán C F, Pino T, Rothard H, da Silveira E F and Thomas J C 2013 Swift heavy ions irradiation of water ice at MeV to GeV energies - Approaching true cosmic ray compaction *Astron. Astrophys.* **547** A97

[11] Boduch P, da Silveira E F, Domaracka A, Gomis O, Lv X Y, Palumbo M E, Pilling S, Rothard

H, Duarte E S and Strazzulla G 2011 Production of oxidants by ion bombardment of icy moons in the outer Solar System *Adv. Astron.* Article ID 327641

[12] Pilling S, Seperuelo Duarte E, Domaracka A, Rothard H, Boduch P and da Silveira E F 2010 Radiolysis of H_2O:CO_2 ices by energetic and heavy solar wind particles and cosmic ray analogs *Astron. Astrophys.* **523** A77

[13] Pilling S, Seperuelo Duarte E, da Silveira E F, Balanzat E, Rothard H, Domaracka A and Boduch P 2010 Radiolysis of ammonia-containing ices by energetic, heavy and highly charged ions inside dense astrophysical environments *Astron. Astrophys*. **509** A87

[14] Bordalo V, da Silveira E F, Lv X Y, Domaracka A, Rothard H, Seperuelo Duarte E and Boduch P 2013 Chemical processing of pure ammonia and ammonia-water ices induced by heavy ions *Astrophys. J.* **774** 105

[15] de Barros A L F, Bordalo V, Seperuelo Duarte E, da Silveira E F, Domaracka A, Rothard H and Boduch 2011 Cosmic ray impact on astrophysical ices: Laboratory studies on heavy ion irradiation of methane *Astron. Astrophys.* **531** A160

[16] Mejía C F, de Barros A L F, Bordalo V, da Silveira E F, Boduch P, Domaracka A and Rothard H 2013 Radiolysis of methane ice at 15 K by MeV O, Fe and Zn ions *Mon. Not. R. Astron. Soc.* **433** 2368–2379

[17] de Barros A L F, Domaracka A, Andrade D P P, Boduch P, Rothard H and da Silveira E F 2011 Radiolysis of frozen methanol by heavy cosmic ray and energetic solar particle analogues ions *Mon. Not. R. Astron. Soc.* **418** 1363–1374

[18] de Barros A L F, da Silveira E F, Rothard H, Langlinay T and Boduch P 2014 Chemical and physical effects induced by heavy cosmic ray analogs on frozen methanol and water ice mixtures ions *Mon. Not. R. Astron. Soc.* **443** 2733-2745

[19] Andrade D P P, de Barros A L F, Pilling S, Domaracka A, Rothard H, Boduch P and da Silveira E F 2013 Chemical reactions induced in frozen formic acid by heavy ion cosmic rays ions *Mon. Not. R. Astron. Soc.* **430** 787-796

[20] Bergantini A, Pilling S, Rothard H, Boduch P and Andrade D P P 2014 Processing of formic acid-containing ice by heavy and energetic cosmic ray analogues ions *Mon. Not. R. Astron. Soc.* **437** 2720–2727

[21] de Barros A L F, da Silveira E F, Pilling S, Domaracka A, Boduch P and Rothard H 2014 Processing of low content carbon interstellar ice analog by cosmic rays: Implications on the chemistry around oxygen-rich stars ions *Mon. Not. R. Astron. Soc.* **438** 2026-2035

[22] Pilling S, Andrade D P P, da Silveira E F, Rothard H, Domaracka A and Boduch P 2012 Formation of unsaturated hydrocarbons in interstellar ice analogs by cosmic ray ions *Mon. Not. R. Astron. Soc.* **423** 2209–2221

[23] Andrade D P P, A. L. F. de Barros A L F, Ding J J, Rothard H, Boduch P and da Silveira E F 2014 Acetone degradation by cosmic rays in the solar neighborhood and in the galactic centre ions *Mon. Not. R. Astron. Soc.* **444** 3792 -3801

[24] Bernstein M P, Dworkin J P, Sandford S A, Cooper G W and Allamandola L J 2002 Racemic amino acids from the ultraviolet photolysis of interstellar ice analogues *Nature* **416** 401-403

[25] Muñoz Caro G M, Meierhenrich U J, Schutte W A, Barbier B, Arcones Segovia A, Rosenbauer H, Thiemann W H-P, Brack A and Greenberg J M 2002 Amino acids from ultraviolet irradiation of interstellar ice analogues *Nature* **416** 403-406

[26] Palumbo M E 2006 Formation of compact solid water after ion irradiation at 15 K *Astron. Astrophys.* **453** 903-909

[27] Fama M, Loeffler M J, Raut U and Baragiola R A 2010 Radiation-induced amorphization of crystalline ice *Icarus* **207** 314-319

[28] Strazzulla G 2011 Cosmic ion bombardment of the icy moons of Jupiter *Nucl. Instrum. Meth.* B **269** 842–851

[29] Lv X Y, de Barros A, Boduch P, Bordalo V, da Silveira EF, Domaracka A, Fulvio D, Hunniford CA, Langlinay T, Mason N, McCullogh R, Palumbo M E, Pilling S, Rothard H and

Strazzulla G 2012 Implantation of multiply charged carbon ions in water ice *Astron. Astrophys.* **546** A81

[30] Ding J J, Boduch, P Domaracka A, Guillous S, Langlinay T, Lv X Y, Palumbo M E, Rothard H and Strazzulla G 2013 Implantation of multiply charged sulfur ions in water ice *Icarus* **226** 860

[31] Lv X Y, Boduch P, Ding J J, Domaracka A, Langlinay T, Palumbo M E, Rothard H and Strazzulla G 2014 Sulfur implantation in CO and CO_2 ices ions *Mon. Not. R. Astron. Soc.* **438** 922-929

[32] McCord T B, Carlson R W, Smythe W D, Hansen G B, Clark R N, Hibbitts C A, Fanale F P, Granahan J C, Segura M, Matson D L, Johnson T V and Martin P D 1997 Organics and other molecules in the surfaces of Callisto and Ganymede *Science* **278** 271

[33] Hage W, Liedl K R, Hallbrucker A and Mayer E 1998 Carbonic acid in the gas phase and its astrophysical relevance *Science* **279** 1332

[34] McCord T B, Hansen G B, Clark R N, Martin P D, Hibbitts C A, Fanale F P, Granahan J C, Segura M, Matson D L, Johnson T V, Carlson R W, Smythe W D and Danielson G E 1998 Non-water-ice constituents in the surface material of the icy Galilean satellites from the Galileo near-infrared mapping spectrometer investigation *J. Geophys. Res.* **103** 8603

[35] Carlson R W, Johnson R E and Anderson M S 1999 Sulfuric acid on Europa and the radiolytic sulfur cycle *Science* **286** 97

[36] Johnson R E, Carlson R W, Cooper J F, Paranicas C, Moore M H and Wong M C 2004 *Jupiter: Planet, Satellites, and Magnetosphere* ed F Bagenal, W McKinnon and T Dowling (Cambridge Univ. Press, Cambridge, UK) p. 485

[37] Hibbitts C A, Klemaszewski J E, McCord T B, Hansen G B and Greeley R 2002 CO_2-rich impact craters on Callisto *J. Geophys. Res.* E **107** 5084

[38] Hibbitts C A, Pappalardo R T, Hansen G B and McCord T B 2003 Carbon dioxide on Ganymede *J. Geophys. Res.* E **108** 5036

[39] Cooper J F, Johnson R E, Mauk B H, Garrett H B and Gehrels N 2001 Energetic ion and electron irradiation of the icy Galilean satellites *Icarus* **149** 133

[40] Gomis O and Strazzulla G 2005 CO_2 production by ion irradiation of H_2O ice on top of carbonaceous materials and its relevance to the Galilean satellites *Icarus* **177** 570

[41] Strazzulla G, Baratta G, Leto G, Gomis O 2007 Hydrate sulfuric acid after sulfur implantation in water ice *Icarus* **192** 623

[42] Dalton J B, Cassidy T, Paranicas C, Shirley J H, Prockter L M and Kamp L W 2013 Exogenic controls on sulfuric acid hydrate production at the surface of Europa Planet *Space Sci.* **77** 45

[43] Lane AL, Nelson R M and Matson D L 1981 Evidence for sulfur implantation in Europa’s UV absorption band *Nature* **292** 38

[44] Sack N J, Johnson R E, Boring J W and Baragiola R A 1992 The effect of magnetospheric ion bombardment on the reflectance of Europa's surface *Icarus* **100** 534

[45] Muñoz Caro G M, Dartois E, Boduch P, Rothard H, Domaracka A and Jiménez-Escobar A 2014 High energy ion versus UV irradiation of methanol:ammonia ice - Formation of common organic products *Astron. Astrophys.* **566** A93

[46] Portugal W, Pilling S, Boduch P, Rothard P and Andrade D P P 2014 Radiolysis of amino acids by heavy and energetic cosmic ray analogs in simulated space environments : α-glycine zwitterion form ions *Mon. Not. R. Astron. Soc.* **441** 3209–3225

[47] Allodi M A, Baragiola R A, Baratta G A, Barucci M A, Blake G A, Boduch P, Brucato J R, Contreras C, Cuylle S H, Fulvio D, Gudipati M S, Ioppolo S, Kaňuchová Z, Lignell A, Linnartz H, Palumbo M E, Raut U, Rothard H, Salama F, Savchenko E V, Sciamma-O'Brien E and Strazzulla G 2013 Complementary and emerging techniques for astrophysical ices processed in the laboratory *Space Sci. Rev.* **180** 101-175

[48] Bennett C J, Pirim C and Orlando T M 2013 Space-weathering of Solar System bodies: a laboratory perspective *Chem. Rev.* **113** 9086−9150