Earth, Moon, and Planets (2023) 127:2
https://doi.org/10.1007/s11038-023-09550-4

Ion Implantation and Chemical Cycles in the Icy Galilean Satellites

G. Strazzulla[1] · M. E. Palumbo[1] · P. Boduch[2] · H. Rothard[2]

Received: 27 January 2023 / Accepted: 31 May 2023 / Published online: 13 June 2023

Abstract

An essential requisite for the appearance and permanence of life on Earth is the onset of a continuous "cycling" of some key atoms and molecules. Cycling of elements probably also occurs on other objects and is driven by biological or a-biological processing. Here we investigate the cycling of some species in the icy Galilean satellites that are exposed to the intense fluxes of energetic particles coming from the Jupiter magnetosphere. Among the most studied effects of particle bombardment, there is the production of molecules not originally present in the sample. These newly synthesized species are irradiated as well and in some circumstances can re-form the original species, giving rise to a "cycle". Here we discuss the cycling of some atoms (C, N, O, S) incorporated in molecules observed on the surface of the icy Galilean satellites.

The results indicate that cycling of carbon atoms starts with solid elemental carbon. Irradiated in the presence of water ice, carbon dioxide is produced and forms carbonic acid and other organics whose irradiation re-produces carbon dioxide and solid carbon. The effect on nitrogen atoms is limited to a continuous cycle among nitrogen oxides (e.g. NO_2 produces NO, and N_2O).

Oxygen is mostly incorporated in water ice. When irradiated, the large majority of the water molecular fragments recombine to re-form water molecules.

The sulfur cycle occurs among SO_2 (that cannot be produced by ion irradiation only), sulfuric acid and elemental sulfur.

The results are discussed in view of their relevance to the expected space observations of the JWST telescope (NASA, ESA, CSA) and the JUICE (ESA) spacecraft.

Keywords Icy satellites · Ion implantation · IR spectroscopy · Radiolysis

---

✉ G. Strazzulla
giovanni.strazzulla@inaf.it

M. E. Palumbo
maria.palumbo@inaf.it

[1] INAF-Osservatorio Astrofisico di Catania, Via Santa Sofia 78, Catania 95123, Italy

[2] Centre de Recherche sur les Ions, les Matériaux et la Photonique Normandie Univ, ENSICAEN, UNICAEN, CEA, CNRS, CIMAP, Caen 14000, France

1 Introduction

An essential requisite for the appearance, evolution and permanence of life on Earth is the onset of a continuous "cycling" of some key atoms and molecules, in particular carbon and water. On Earth such "cycles" imply a continuous conversion of e.g. carbon atoms from a molecule to another (e.g. CO_2 that is transformed in sugars by photosynthesis) or by a continuous conversion of e.g. water molecules from solid to liquid to gaseous phases. Cycling of elements is also believed to occur on other planetary objects and merits to be investigated in order to understand the ecosystems in other worlds that in some instances could bring up biological evolution.

The recycling of atoms and molecules is driven by biological and/or physical and/or chemical processing.

In this paper we discuss the cycling of some atoms (C, N, O, S) incorporated in molecules observed on the surface of the icy satellites of Jupiter driven by the processing of the surfaces by irradiation of energetic ions accelerated in the giant magnetosphere of the planet.

It is well known that ices on the surfaces of the satellites of planets in the outer Solar System are exposed to the intense fluxes of energetic ions and electrons mostly coming from the magnetospheres of their planets. The most spectacular is Jupiter's giant magnetosphere in which the icy Galilean satellites are embedded and subjected to intense bombardment by ions such as H^+, S^{n+} and O^{n+}, and by energetic electrons (e.g. Cooper et al. 2001).

By depositing energy to target species, ions and electrons are able to release momentum to nuclei or to break chemical bonds and cause ionizations and excitations. Thus species can be expelled (sputtered), the structure of the ice (crystalline/amorphous, porous/compact) can be changed and new chemical species can be formed by the recombination of fragments. The detailed qualitative and often quantitative knowledge of some of those effects has been possible on the basis of detailed specific laboratory experiments performed in many laboratories in the world. For a specific review on the effects induced on the icy satellites of outer planets see Strazzulla (2011) and Baragiola et al. (2013); for a more general review on the space weathering of Solar System bodies that includes the icy satellites see Bennett et al. (2013) and Brunetto et al. (2015). These experiments are still in progress and represent a mandatory need to understand what is observed and/or to program new observations.

This is particularly relevant in view of the present and upcoming space missions. The James Webb Space Telescope (JWST) carries four instruments of unprecedented sensitivity and spectral resolution that cover a wide spectral range from the optical to the infrared (0.6−28.3 µm; see e.g. McElwain et al. 2020). The JWST has been successfully launched on 25 December 2021 and has already performed many exciting observations in several fields of astronomy. Just as an example, interstellar ices have been observed and spectra of unprecedented quality have been obtained (e.g. McClure et al. 2023). Enceladus, an icy satellite of Saturn has been observed and the results have been submitted for publication (Villanueva et al. 2023a). Also spectra of some of the icy satellites of Jupiter have been obtained. The data are presently under analysis and those obtained for Europa in the near IR (NIRSpec) have already been submitted for publication (Villanueva et al. 2023b).

In addition the ESA space mission JUpiter ICy moons Explorer (JUICE) will make detailed observations of Jupiter and of Ganymede, Callisto, and Europa (Banks 2012). On board JUICE two instruments will perform spectroscopic observations: the UV imaging Spectrograph (UVS, 55−210 nm), and the Moons And Jupiter Imaging Spectrometer

(MAJIS, 400–5400 nm). The spacecraft was launched on 14 April 2023 and will reach Jupiter after a journey of 8 years. Also relevant is to mention the forthcoming NASA's Europa Clipper spacecraft that will be launched in October 2024 and arrive at Jupiter in April 2030. Also in this case the scientific instruments include UV and Vis-IR spectrometers (https://europa.nasa.gov/).

2 Ion Irradiation Effects

Experimental results have shown that ion irradiation of ices causes the erosion of the target (sputtering; e.g. Johnson et al. 2008). This is a well-studied phenomenon and data concerning sputtering yields exist for a wide range of combinations of projectile energy and target composition. One of the important findings having been confirmed over five orders of magnitude of projectile energy (Seperuelo Duarte et al. 2010), is that when the energy deposition is dominated by ionizations and excitation (electronic energy loss) the sputtering yields scale as the square of the electronic energy loss. This is a very well known quantity easily calculated by available codes for all of the target composition-projectile combinations (e.g. Ziegler et al. 2008). Sputtered species include mostly neutral atoms and molecules but also ionized species (these latter include clusters and still deserve further studies; see e.g. Martinez et al. 2019). The released species can be lost to space or can populate the exospheres of the icy satellites (e.g. Plainaki et al. 2015). In the next years it will be important to have further data on the nature of the species released by ion irradiation of realistic ice mixtures, as well as their yields and energy and angular distribution. These results could in fact drive the interpretation of data that will be obtained by space missions (e.g. JUICE).

Energetic processing by ions as well as electrons also produces a number of non-thermal chemical reactions that drive the formation of molecules initially not present in the target. If the initial targets contain C-bearing species the chemical inventory of the newly produced species is extremely variegated and complex molecules as well as organic refractory residues are produced as evidenced by several laboratory experiments using different techniques. For reviews see e.g. Hudson et al. (2008), and Allodi et al. (2013). Numerous experiments have been performed on icy mixtures made of O, C, and N bearing species. They are particularly relevant to understand the chemical and physical phenomena that drive the evolution of ices in the interstellar medium (e.g. Palumbo et al. 2000; Modica and Palumbo 2010) as well as the formation of an organic crust on comets and trans-Neptunian objects (Strazzulla et al. 2003a), and the color of TNOs (Brunetto et al. 2006; Kaňuchová et al. 2012).

The surfaces of icy satellites in the outer Solar System are dominated by water ice and hydrated materials (e.g. sulfuric acid on Europa, Dalton et al. 2013). Minor amounts of other species such as H_2O_2 (e.g. on Europa, Carlson et al. 1999b; Ganymede and Callisto, Hendrix et al. 1999), SO_2 (e.g. on Ganymede and Callisto, McCord et al. 1997) and CO_2 (e.g. on Ganymede and Callisto, McCord et al. 1997) and organic compounds (e.g. on Callisto, McCord et al. 1997) are also observed. However, it is probable that the number of compounds present at the surface (and below) is much greater than observable at the surface by spectroscopic techniques from remote observations. Irradiation by the abundant fluxes of energetic ions and electrons (see e.g. Bennett et al. 2013 and references therein) drive a chemical evolution (radiolysis) that could have produced some of the observed species and others that have not yet been observed in the solid and/or in the gas phase.

An example of the radiolysis effects is the synthesis of hydrogen peroxide that has been found on the surface of Europa (Carlson et al. 1999b), Ganymede, and Callisto (Hendrix et al. 1999). Several groups have studied the formation of hydrogen peroxide by ion bombardment of water ice (Moore and Hudson 2000; Gomis et al. 2004; Loeffler et al. 2006): the results support the idea that ion irradiation is the primary mechanism responsible for the formation of hydrogen peroxide on the surface of icy Galilean satellites.

Ion irradiation has also been suggested to be responsible for the formation of O_2 and O_3 observed on Ganymede (Johnson and Jesser 1997), via the dissociation of water molecules and diffusive loss of hydrogen with retention of oxygen. Laboratory experiments on ion (Teolis et al. 2006; Boduch et al. 2016) and electron (Jones et al. 2014) irradiation of ices made of mixtures of water with O_2 or CO_2 confirmed the synthesis of ozone and evidenced that the shape of the UV absorption band does not reproduce the observed feature on Ganymede for which an additional component, unknown at present, is requested.

Finally, the projectile itself can be included in the new species formed (this effects is often referred to as ion implantation). Several experimental investigations have indeed focused on implantation of reactive ions in thick ice samples (thicker than the penetration depth of impinging ions). As an example, carbon dioxide (CO_2) is formed after implantation of C ions in H_2O ice (e.g. Strazzulla et al. 2003b; Lv et al. 2012) and sulfur dioxide (SO_2) is formed after S ion implantation in CO and CO_2 ice samples (Lv et al. 2014). It is important to note that in the latter case the implantation experiments have been conducted at low temperatures (10–20 K) that are appropriate to interstellar ices. Additional experiments by Mifsud et al. (2022) confirmed that SO_2 is formed after S implantation into CO_2 ice at 20 K, but not at 70 K. They conclude that this process is likely not a reasonable mechanism for SO_2 formation on the icy Galilean satellites.

3 Molecular Cycles

Here we present some recent experimental results obtained at the Laboratorio di Astrofisica Sperimentale (LASp), INAF-Osservatorio Astrofisico di Catania (Italy) and at Grand Accélérateur National d'Ions Lourds (GANIL), Caen (France). The experiments have been performed following the experimental procedures already described elsewhere. In Table 1 we summarize the experiments presented in this manuscript and the reference where the experimental procedure is described in details.

3.1 C-bearing Species

The carbon bearing species identified on the surfaces of the icy satellites of Jupiter include elemental carbon, carbon dioxide (CO_2), carbonates and an organic refractory dark material.

Several experiments have addressed the possibility of formation of carbon dioxide by energetic processing. Two types of experiments have been conducted. The first concerns the implantation of 30 keV carbon ions (C^{n+}, $n=1$–3) in water ice deposited at low temperatures (Strazzulla et al. 2003b; Lv et al. 2012).

By using FTIR spectroscopy, it has been demonstrated that CO_2 is efficiently produced. As an example, Fig. 1 shows the spectrum ($2300-2050\ cm^{-1}$) of water ice as deposited at 80 K and after implantation of 30 keV $^{13}C^{3+}$ at different ion fluences (ions/cm^2). The spectra

Table 1 List of the experiments conducted in the laboratories of Catania and/or Caen, whose results are here used to prepare the figures and discussed to support the idea of molecular cycles on the icy Galilean satellites

sample (temperature)	Ion (energy)	Laboratory	reference
H_2O (80 K)	$^{13}C^{3+}$ (30 keV)	GANIL	Lv et al. (2012)
Asphaltite (80 K)	He^+ (30 keV)	LASp	Strazzulla and Moroz (2005)
H_2O on asphaltite (16 K)	He^+ (30 keV)	LASp	Strazzulla and Moroz (2005)
$H_2O:CO_2$ (16 K)	He^+ (200 keV)	LASp	Strazzulla et al. (2005)
CO_2 (16 K)	H^+ (50 keV)	LASp	Brucato et al. (1997)
$H_2O:N_2:O_2$ (15 K)	$^{13}C^{2+}$ (30 keV)	GANIL	Boduch et al. (2012)
H_2O (80 K)	S^{7+} (105 keV)	GANIL	Ding et al. (2013)
$H_2O:SO_2$ (80 K)	He^+ (30 keV)	LASp	Kaňuchová et al. (2017)

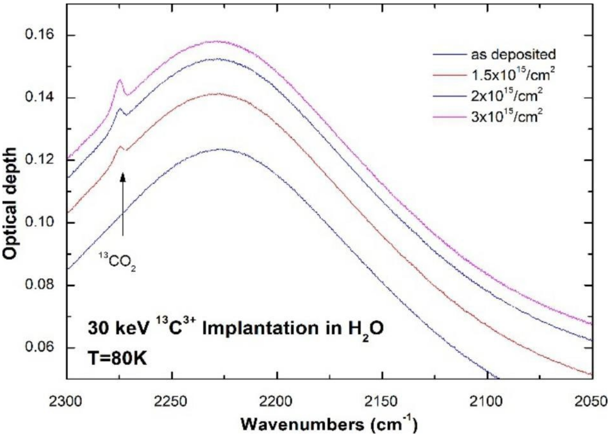

Fig. 1 FTIR spectrum (2300−2050 cm^{-1}) of water ice as deposited at 80 K and after implantation of 30 keV $^{13}C^{3+}$ at different ion fluences (ions/cm^2) (Lv et al. 2012)

evidence the presence of a band centered at about 2200 cm^{-1}. This is attributed to the combination mode of water ice and the formation of a band at 2277 cm^{-1} due to a fundamental vibration mode of $^{13}CO_2$ (see e.g. Gerakines et al. 1995, Strazzulla et al. 2005, Seperuelo Duarte et al. 2010) formed because of implantation of energetic carbon ions. The measured implantation yields are in the range of 0.32–0.57 CO_2 molecules per ion. The measured yield is independent of the temperature (15–80 K) of the ice. The flux of (keV–MeV) C-ions at the surface of Europa has been estimated to be about 1.8×10^6 C ions cm^{-2} s^{-1} (Cooper et al. 2001). Using the experimental values for the production yield (0.4–0.5 CO_2 molecules/ion) it is possible to calculate the time necessary to produce a column density of 3×10^{17} molecules cm^{-2} that is the CO_2 column density estimated at Europa (e.g. McCord et al. 1997). This time scale results to be of the order of $1.0–1.3\times10^4$ years. This time is much larger than the estimated time scale for the production of carbon dioxide by ion bombardment of water ice on top of carbonaceous materials (see below).

Consequently, the conclusion is that although a relevant quantity of CO_2 is produced by carbon ion implantation, this cannot be the dominant formation mechanism at Europa.

The second type of experiment has been devoted to the investigation of the formation of CO_2 and other C-bearing molecules by ion bombardment of water ice deposited on top of solid carbonaceous targets. Several different carbonaceous substrates have been used among which organic residues obtained after ion irradiation of frozen hydrocarbon rich ices (Gomis and Strazzulla 2005), amorphous carbon with different amount of hydrogen content (Mennella et al. 2004) and bitumens such as asphaltite (Strazzulla and Moroz 2005). A schematic view of the experimental concept is shown in the inset of Fig. 2. Figure 2 refers, as an example, to a water ice layer formed by vapor deposition on an asphaltite substrate. The ice thickness (~1000 Å) is lower than the penetration depth of the used ions so that an induced mixing can occur at the ice-solid interface.

Asphaltite, a natural complex hydrocarbon, exhibits both aliphatic and aromatic structures considered representative of complex organic materials present in astrophysical objects (Moroz et al. 2004). FTIR spectra (in the $2600-1975\ \text{cm}^{-1}$ region) of three samples are presented in Fig. 2. In detail: a not irradiated asphaltite substrate (16 K, full line), an irradiated (1.5×10^{16} He^+ ions/cm^2) asphaltite substrate (80 K, dashed line) and an irradiated (1.5×10^{16} He^+ ions/cm^2) sample of a water ice layer (1.8×10^{17} molecules/cm^2) deposited on top of an asphaltite substrate (16 K, connected dots). Upon irradiation the formation of new bands is evident. The one at $2341\ \text{cm}^{-1}$ is easily attributed to the $C=O$ stretching mode in CO_2, the one at $2135\ \text{cm}^{-1}$ is due to $C\equiv O$ stretching mode in CO, and the one at $2110\ \text{cm}^{-1}$ has been attributed to $C\equiv C$ in carbynoids (Strazzulla and Moroz 2005). When water ice is not deposited only the latter feature at $2110\ \text{cm}^{-1}$ appears after irradiation of pure asphaltite.

It has been demonstrated that magnetospheric ion bombardment of carbonaceous grains embedded in water ice dominated porous regolith that characterize the surface of icy Galilean satellites shaped by interplanetary meteoroid impacts (Johnson et al. 2004) is able to produce the quantity of CO_2 detected on the surfaces of the icy Galilean satellites (Gomis and Strazzulla 2005).

Thus whatever is the nature of the carbonaceous material (from amorphous carbon to complex hydrocarbons) and its origin (native or delivered by comets and micrometeor-

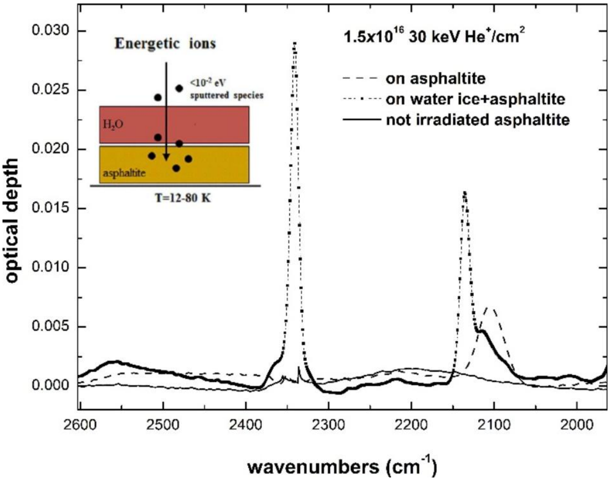

Fig. 2 FTIR spectra ($2600-1975\ \text{cm}^{-1}$) of three samples: a not irradiated asphaltite substrate (16 K, full line), an irradiated (1.5×10^{16} He^+ ions/cm^2) asphaltite substrate (80 K, dashed line) and an irradiated (1.5×10^{16} He^+ ions/cm^2) sample of a water ice layer (1.8×10^{17} molecules/cm^2) deposited on top of an asphaltite substrate (16 K, connected dots) (Strazzulla and Moroz 2005)

ites) on the surface of the icy Galilean satellites, magnetospheric ion bombardment is able to produce enough quantity of carbon dioxide to explain the observations. CO_2 in turn is subjected to ion irradiation whose effects have been studied in the laboratory (Moore and Khanna 1991; Brucato et al. 1997; DelloRusso et al. 1993; Gerakines et al. 2000; Strazzulla et al. 2005; Zheng and Kaiser 2007; Peeters et al. 2010; Pilling et al. 2010; Boduch et al. 2011; Jones et al. 2014) either for pure CO_2 as it could occur by segregation in spotted areas of the satellite's surface or mixed with other ices, mainly water ice. The results indicate that in presence of H-bearing species (e.g. water) mixed with carbon dioxide or of H atoms implanted in pure CO_2, carbonic acid (H_2CO_3) is easily produced along with many other organic molecules. Examples are shown in the two panels of Fig. 3. The top panel exhibits FTIR spectra of a mixture (H_2O:CO_2 = 1:1) as deposited and after irradiation with 3×10^{14} He^+ ions/cm^2. The synthesis of carbonic acid is easily recognized; the bottom panel exhibits FTIR spectra of a thick layer (several micrometers) of pure CO_2 as deposited and after implantation with 3×10^{15} H^+ ions/cm^2 from which the formation of CO_3, HCO and H_2CO_3 is evident.

The formation of carbonic acid is particularly relevant because it has been many times suggested to be present at the surfaces of the Jovian moons (McCord et al. 1997; Carlson et al. 2002, 2005; Johnson et al. 2004; Peeters et al. 2010). In addition carbonic acid is a precursor of other organic molecules (e.g. formaldehyde) and of carbonates when in presence of Ca or Na bearing species.

Carbonic acid itself has been irradiated in the laboratory with energetic electrons (5 keV) at a temperature of 80 K (Jones et al. 2014). The results indicate that energetic processing of carbonic acid mainly produces CO_2 and H_2O i.e. the same species used to form it. It is worth mentioning that the re-produced carbon dioxide exhibits an IR band that very well matches with that observed on Callisto (Jones et al. 2014).

Thus the "carbon cycle" is closed as schematically shown in Fig. 4: solid elemental carbon, in presence of water ice and subjected to energetic processing, produces carbon dioxide that forms carbonic acid and other organics (and possibly carbonates) whose irradiation reproduces carbon dioxide and solid carbon.

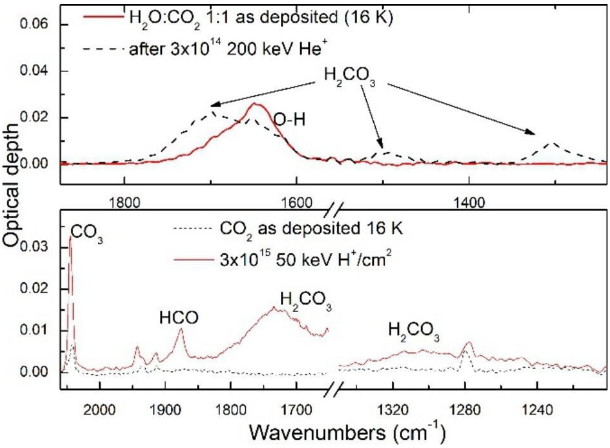

Fig. 3 Top panel: FTIR spectra (1860−1250 cm^{-1}) of a mixture H_2O:CO_2 (1:1) as deposited and after irradiation with 3×10^{14} He^+ ions/cm^2. Bottom panel: FTIR spectra (in two spectral regions) of a thick layer (several micrometers) of pure CO_2 as deposited and after implantation with 3×10^{15} H^+ ions/cm^2 (Strazzulla et al. 2005)

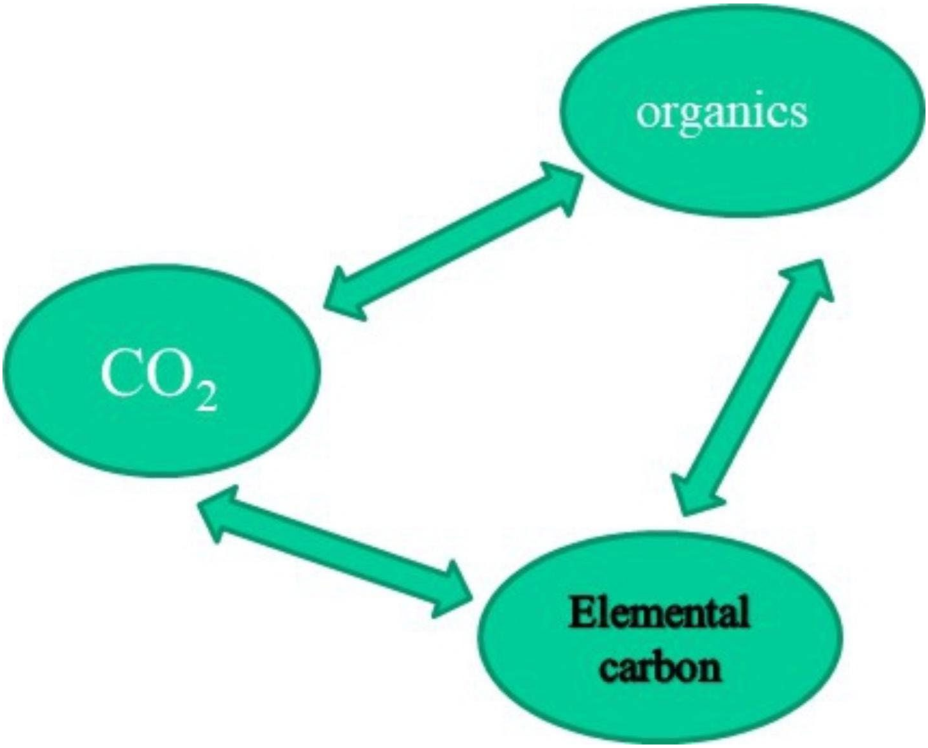

Fig. 4 Schematic view of the "carbon cycle" as discussed in the text

3.2 N-bearing Species

At present, nitrogen bearing molecules have not been firmly detected in the solid phase on the surface of icy Galilean satellites although the presence of CN bearing species on Ganymede and Callisto has been suggested by McCord et al. (1997). This is probably due to observational difficulties, however, their presence is highly probable. The presence in the solid state is supported by the observation of a number of gaseous species in the exospheres and in particular in the plumes of Enceladus (Waite et al. 2009) that include NH_3, N_2, and HCN. It should be noted that the signal at mass 28u detected by the Cassini INMS assigned to N_2 could be due also to CO. Based on these findings Teolis et al. (2017) suggested that a Europa plume source, if present, might produce a global exosphere whose composition would be similar to that of Enceladus. Let us assume that the nitrogen bearing species NH_3, N_2, and HCN are present in the exosphere and, as a consequence, on the surface of Europa and/or Ganymede and/or Callisto. Then the question relevant to this paper is if NH_3, N_2 and HCN can be "cycled" under the action of energetic processing. It is important to note that N_2 is so volatile that cannot survive as a pure solid species on the icy surface of Jovian satellites. It could however be formed "in situ" by ion (see e.g. the results obtained after irradiation of ammonia ice by Parent et al. 2009) or electron (see e.g. the results obtained after irradiation of NO_2 and mixtures NO:N_2O by Ioppolo et al. 2020) bombardment and remain trapped in a more refractory species.

Experimental results have demonstrated that after ion irradiation of icy mixtures containing NH_3 or N_2 mixed with oxygen bearing molecules (e.g. H_2O and/or O_2) and carbon bearing species (e.g. CH_4) a plethora of new species are formed that include CO, CO_2, OCN^-, HCN and nitrogen oxides (N_2O, NO, NO_2) (e.g. Fedoseev et al. 2018).

It has been demonstrated in dedicated experiments (see Fig. 5 after Boduch et al. 2012) that nitrogen oxides and carbon bearing molecules are also formed when the source of carbon is exogenous e.g. energetic carbon ions coming from the magnetosphere are implanted in the icy surfaces. On the other hand, implantation of energetic nitrogen ions in pure water ice does not produce detectable quantity of nitrogen oxides (Strazzulla et al. 2003b).

Nitrogen oxides and other N-bearing species are in turn processed by the same projectiles but this does not induce a "cycle". The original ammonia is not re-formed and the majority of the most volatile species (hydrogen, N_2 and O_2) are not retained in the ice at the temperatures appropriate for the icy Galilean satellites (70–140 K). The only possibility for a nitrogen cycle may be the case of nitrogen oxides: proton irradiation of NO_2 produces the formation of NO (Fulvio et al. 2019); on the other hand, NO_2 is formed in irradiated NO ice (Ioppolo et al. 2020). Similarly, irradiation of N_2O produces NO (Fulvio et al. 2019), and irradiation of NO induces the formation of N_2O (Ioppolo et al. 2020).

The ESA JUICE mission will certainly provide a great step forward to the investigation of the presence of nitrogen bearing species. Nitrogen oxides should be searched for because, as said, they are easily formed after radiolysis of appropriate ice mixtures.

3.3 O-bearing Species (the H_2O case)

The cycles of many O-bearing species are discussed in the sections dedicated to C- N- and S-bearing molecules (e.g. N-oxides, CO_2, SO_2). Thus in this section we discuss the case of water ice.

Water ice is the dominant species on the surfaces of icy Galilean satellites. Each incoming ion having energies between 10 and 1000 keV, breaks 10^3–10^5 bonds along its track and a number of new molecules can be formed per single incoming ion by recombination of fragments of the irradiated species (e.g. H_2O_2 in the case of water irradiation). In the case of

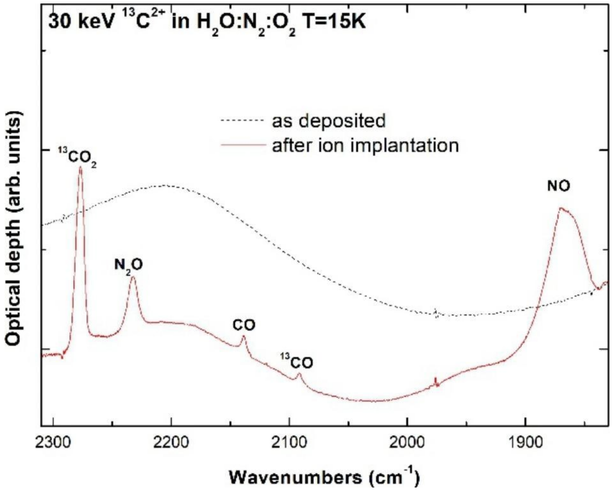

Fig. 5 FTIR spectra of a mixture H_2O:N_2:O_2 = 1:1:1 at 15 K before and after implantation of 30 keV $^{13}C^{2+}$ ions. The continuum is due to the interference pattern of the IR beam that passes through the icy film. (Note: the appearance of ^{12}CO is due to the presence of $^{12}CO_2$ contaminant)

water the large majority of the molecular fragments recombine to re-form water molecules. The production of hydrogen peroxide increases exponentially and reaches an equilibrium at about 1–2% into respect to water ice (Gomis et al. 2004). We can then consider the case of water ice as instantaneous re-cycling that allows water ice to survive as such over energetic processing. This is one of the (many) peculiar properties of water. In contrast, the same does not occur for ammonia or methane: ammonia irradiation produces N_2 and loss of hydrogen (e.g. Parent et al. 2009); methane irradiation produces polymerization and species of progressively higher molecular weight (e.g. Foti et al. 1984).

3.4 S-bearing Species

The sulfur bearing species that have been identified or suggested to be present on the surfaces of the icy satellites of Jupiter include sulfur dioxide (SO_2), sulfuric acid (H_2SO_4), sulfates such as $MgSO_4.6(H_2O)$ and $Na_2Mg(SO_4)_2.4(H_2O)$, and elemental sulfur (e.g. Ligier et al. 2019; Carlson et al. 1999a).

A large number of experiments have been performed to study energetic processing of S-bearing frozen species. Similarly to what was done with CO_2, also the potential formation of SO_2 has been investigated with two kinds of experiments that have been conducted: (i) irradiation of water ice on top of sulfurous solid materials and (ii) implantation of energetic sulfur ions in water ice.

Ion irradiation of thin water ice layers deposited on top of a solid sulfurous material has not given evidence of an efficient formation of SO_2 (Gomis and Strazzulla 2008). Only an upper limit has been obtained that lead those authors to conclude that radiolysis of mixtures of water ice and refractory sulfurous materials is not the primary formation mechanism responsible for the SO_2 presence on the surfaces of the icy Galilean satellites.

Experiments of sulfur ion implantation in water ice have been performed by using 200 keV singly ionized ions (Strazzulla et al. 2007) and 35–176 keV S^{q+} (q = 7, 9, 11) multicharged ions (Ding et al. 2013).

Figure 6 shows the spectra of water ice deposited at 80 K before and after implantation of 105 keV S^{7+} ions. The experimental results indicate that implantation produces hydrated sulfuric acid with high efficiency (for the bands assignment see Table 2). The yields (mol-

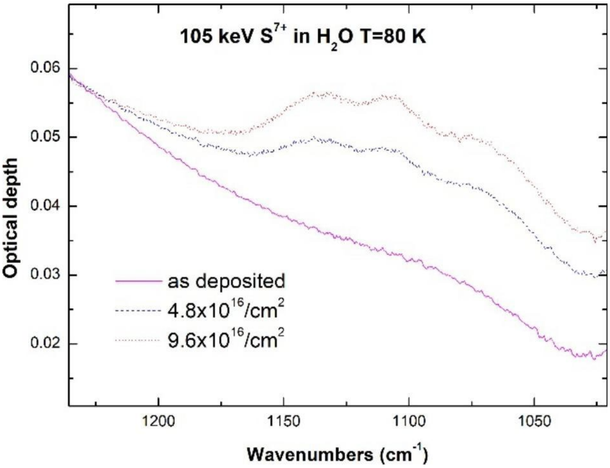

Fig. 6 FTIR spectra (1250 – 1000 cm^{-1}) of water ice as deposited at 80 K and after implantation of 105 keV S^{7+} at two different ion fluences (ions/cm^2)

ecules produced/ion) range from 0.12 for 35 keV ions to 0.64 for 200 keV ions. No evidence for the formation of SO_2 and H_2S has been found.

The results indicate also that sulfur ion implantation cannot explain the presence of SO_2 as it was proposed before (Lane et al. 1981; Noll et al. 1995, 1997; McCord et al. 1997). Nevertheless, it is the dominant formation mechanism of hydrated sulfuric acid at Europa as suggested before (Carlson et al. 1999a, 2002).

Further experiments have been conducted by irradiating either pure SO_2 or SO_2 mixed with other species such as water ice (Moore et al. 2007; Kaňuchová et al. 2017). An example of the obtained results is given in Fig. 7 that shows the FTIR spectra ($1300-850\ \mathrm{cm}^{-1}$) of a $H_2O:SO_2$ (1:1) mixture at 80 K before and after irradiation (3.5×10^{14} He^+ ions/cm^2). For comparison the sulfuric acid band observed after S implantation in water ice is also shown (arbitrary units).

From Fig. 7 we see that the intensity of the two SO_2 bands (at 1325 and 1150 cm^{-1}) decreases after irradiation and a number of species are produced as testified by the appearance of new bands in the spectrum. The identified species are listed in Table 2. It is also relevant to note that the experiments conducted by different laboratories evidenced the formation of a sulfurous residue (often called elemental sulfur) after irradiation of SO_2 bearing ices (Moore et al. 2007; Kaňuchová et al. 2017).

It is interesting to note that the IR signatures in the $1150-1000\ \mathrm{cm}^{-1}$ region due to sulfur implantation are different from those observed after irradiation of $H_2O:SO_2$ mixtures (see Fig. 7; Table 2) and thus the two processes are potentially distinguishable by astronomical observations with e.g. James Webb Space Telescope.

The idea of the radiolytic sulfur cycle isn't new (see e.g. Figure 1 in Carlson et al. 2002). The results discussed in this paper confirm and extend the possibility of the cycle. A significant difference is the role of implanted sulfur that prevalently forms sulfuric acid and not SO_2 as previously thought.

In summary the "sulfur cycle" is schematically shown in Fig. 8. The cycle needs, however, a source of SO_2 at the surface of the icy satellites that could be endogenic (e.g. cryo volcanism) or exogenic (e.g. SO_2 coming from Io). Sulfur ion implantation produces abundant sulfuric acid and possibly other sulfates that are also produced by ion irradiation of

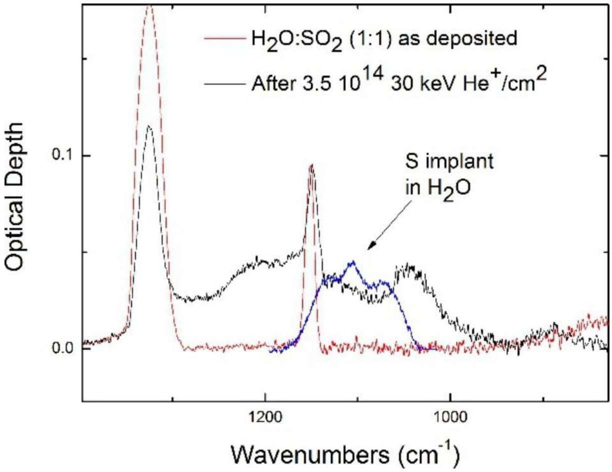

Fig. 7 FTIR spectra ($1350-850\ \mathrm{cm}^{-1}$) of a $H_2O:SO_2$ (1:1) mixture at 80 K before and after irradiation by 3.5×10^{14} He^+ ions/cm^2. For comparison the sulfuric acid band observed after S implantation in water ice is also shown (arbitrary units)

Table 2 Peak position and assignment of the bands identified in the spectra of various S-bearing samples discussed in the text

Peak position cm^{-1}	Assignment	Process/Ice	Ref.
982	SO_2^{4-}	$H^+ \rightarrow H_2O:SO_2$	Moore et al. (2007)
1044	HSO_3^-, HSO_4^-	$He^+ \rightarrow H_2O:SO_2$	Kaňuchová et al. (2017)
1052	HSO_4^-	$H^+ \rightarrow H_2O:SO_2$	Moore et al. (2007)
1070	SO_2^{2-}	implantation, $S^{7+} \rightarrow H_2O$	Ding et al. (2013)
1105	HSO_4^-	implantation, $S^{7+} \rightarrow H_2O$	Ding et al. (2013)
1110	SO_4^{2-}	$H^+ \rightarrow H_2O:SO_2$	Moore et al. (2007)
1120	SO_4^{2-} ?	$He^+ \rightarrow H_2O:SO_2$	Kaňuchová et al. (2017)
1135	H_2SO_4	implantation, $S^{7+} \rightarrow H_2O$	Ding et al. (2013)
1200	poly SO_3	$He^+ \rightarrow H_2O:SO_2$	Kaňuchová et al. (2017)
1235	HSO_3^-, HSO_4^-	$H^+ \rightarrow H_2O:SO_2$	Moore et al. (2007)

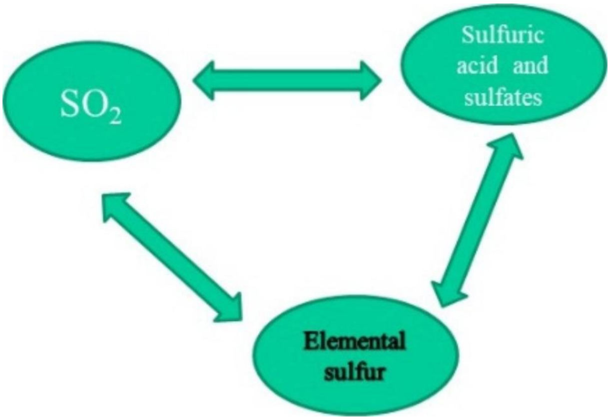

Fig. 8 Schematic view of the so called "sulfur cycle" as discussed in the text

SO_2. Solid elemental sulfur is in turn a residue of the irradiation processes of the other sulfur species.

4 Conclusions

In this paper we have re-analyzed several experiments performed in the laboratories of Catania (Italy) and Caen (France) concerning the chemical and physical effects induced by bombardment of energetic ions on frozen gases relevant to the surface of icy Galilean satellites. In particular the discussed results give a comprehensive picture of elemental cycles driven by those processes.

We believe that the results will be useful in the immediate to interpret the observations that are presently coming from JWST and to prepare at best the observational plan of the instrument MAJIS on board of the European mission JUICE.

One of the objective of the present and future observations will be the study of the abundance and distribution of frozen CO_2 on the surfaces of the icy satellites and the results presented here would significantly contribute to understand its origin (endogenous vs. exogenous) and drive the search for the other species of the here proposed carbon cycle.

In the case of Europa a fundamental observational effort would be the spectral search for the sulfuric acid features. If detected the experimental results described here would give clues on its formation mechanism (e.g. sulfur implantation vs. SO_2 precursor).

At the time of the preparation of this manuscript, only the NIRSpec (0.6-5 µm) instrument on board JWST has already observed Europa and Callisto (and Enceladus in the Saturnian system). The spectra relative to Europa have been processed and the first results submitted for publication (Villanueva et al. 2023b).

Acknowledgements We are grateful to the staff of GANIL and CIMAP, and in particular to T. Been, C. Grygiel, and J. M. Ramillon for their invaluable assistance during the experiments.
GS acknowledges support under the ASI-INAF agreement 2018-25-HH.0.
This work was supported by the Italian Istituto Nazionale di Astrofisica, the Italian Space Agency and the Normandy Region.

Author Contributions G.S. and M.E.P. performed the experiments at LASp and reduced the experimental data. P.B. and H.R. performed the experiments at GANIL and reduced the experimental data. G.S. wrote the main manuscript. All the authors reviewed the manuscript.
The experimental data here discussed are available from the corresponding author on reasonable request.

Funding The authors have no relevant financial or non-financial interests to disclose.
Open access funding provided by Istituto Nazionale di Astrofisica within the CRUI-CARE Agreement.

Declarations

Competing Interests The authors declare no competing interests.

References

M.A. Allodi, 21 colleagues: Complementary and emerging techniques for Astrophysical Ices processed in the Laboratory. Space Sci. Rev. **180**, 101–175 (2013)

M. Banks, JUICE mission picked for launch. Phys. World. **25**(06), 6 (2012). https://doi.org/10.1088/2058-7058/25/06/10

R.A. Baragiola, M.A. Famá, M.J. Loeffler, M.E. Palumbo, U. Raut, J. Shi, G. Strazzulla, Radiation Effects in Water Ice in the Outer Solar System, in The Science of Solar System Ices, M.S. Gudipati, J.Castillo Rogez Eds, Astrophysics and Space Science Library, 356 Springer Science, New York, p. 527 (2013)

C.J. Bennett, C. Pirim, T.M. Orlando, Chem. Rev. **113**, 9086 (2013)

P. Boduch, E.F. da Silveira, A. Domaracka, O. Gomis, X.Y. Lv, M.E. Palumbo, S. Pilling, H. Rothard, E. Seperuelo Duarte, G. Strazzulla, AdAst, Article id 327641 (2011)

P. Boduch, A. Domaracka, D. Fulvio, T. Langlinay, X.Y. Lv, M.E. Palumbo, H. Rothard, G. Strazzulla, *A&A*, 544, A30 (2012)

P. Boduch, R. Brunetto, J.J. Ding, A. Domaracka, Z. Kaňuchová, M.E. Palumbo, H. Rothard, G. Strazzulla, *Icarus*, 277, 424 (2016)

J.R. Brucato, M.E. Palumbo, G. Strazzulla, *Icarus*, 125, 135 (1997)

R. Brunetto, M.A. Barucci, E. Dotto, G. Strazzulla, ApJ. **644**, 646 (2006)

R. Brunetto, M.J. Loeffler, D. Nesvorny, S. Sasaki, G. Strazzulla, Asteroid surface alteration by space weathering processes. Asteroids IV 597–616 (2015)

R.W. Carlson, M.S. Anderson, R.E. Johnson, M.B. Schulman, A.H. Yavrouian, *Icarus*, 157, 456 (2002)

R.W. Carlson, M.S. Anderson, R.E. Johnson, W.D. Smythe, A.R. Hendrix, C.A. Barth, L.A. Soderblom, G.B. Hansen, T.B. McCord, J.B. Dalton, R.N. Clark, J.H. Shirley, A.C. Ocampo, D.L. Matson, Sci, **283**, 2062 (1999b)

R.W. Carlson, K.P. Hand, P.A. Gerakines, M.H. Moore, R.L. Hudson, BAAS **37**, 751 (2005)

J.F. Cooper, R.E. Johnson, B.H. Mauk, H.B. Garrett, N. Gehrels, *Icarus*, 149, 133 (2001)

R.W. Carlson, R.E. Johnson, M.S. Anderson, Sci. **286**, 97 (1999a)

J.B. Dalton, T. Cassidy, C. Paranicas, J.H. Shirley, L.M. Prockter, L.W. Kamp, PlSpSci. **77**, 45 (2013)

N. DelloRusso, R.K. Khanna, M.H. Moore, *JGRE*, 98, 5505 (1993)

J.J. Ding, P. Boduch, A. Domaracka, S. Guillous, T. Langlinay, X.Y. Lv, M.E. Palumbo, H. Rothard, G. Strazzulla, Icarus. **226**, 860 (2013)

G. Fedoseev, C. Scirè, G.A. Baratta, M.E. Palumbo, *MNRAS*, 475, 1819 (2018)

G. Foti, L. Calcagno, K.L. Sheng, G. Strazzulla, *Nat*, 310, 126 (1984)

D. Fulvio, G.A. Baratta, B. Sivaraman, N.J. Mason, E.F. da Silveira, A.L.F. de Barros, O. Pandoli, G. Strazzulla, M.E. Palumbo, MNRAS **483**, 381 (2019)

P.A. Gerakines, W.A. Schutte, J.M. Greenberg, ApJL. **344**, L171 (1995)

P.A. Gerakines, M.H. Moore, R.L. Hudson, *A&A*, 357, 793 (2000)

O. Gomis, M.A. Satorre, G. Strazzulla, G. Leto, : *PlSpSc*, 52, 371. (2004)

O. Gomis, G. Strazzulla, *Icarus*, 177, 570 (2005)

O. Gomis, G. Strazzulla, *Icarus*, 194, 146 (2008)

A.R. Hendrix, C.A. Barth1, F. Stewart, A.I. Hord, C.W. Lane, A.L., LPS XXX, 2043 (1999)

R.L. Hudson, M.E. Palumbo, G. Strazzulla, M.H. Moore, J.F. Cooper, S.J. Sturner, Laboratory Studies of the Chemistry of Transneptunian object surface materials. Solar Syst. Beyond Neptune 507 (2008)

S. Ioppolo, Z. Kaňuchová, R.L. James, A. Dawes, N.C. Jones, S.V. Hoffmann, N.J. Mason, G. Strazzulla, *A&A*, 641, A154 (2020)

R.E. Johnson, W.A. Jesser, ApJL. **480**, L79 (1997)

R.E. Johnson, M. Famá, M. Liu, R.A. Baragiola, E.C. Sittler, H.T. Smith, PlSpSci. **56**, 1238 (2008)

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

B.M. Jones, R.I. Kaiser, G. Strazzulla, ApJ, 781, id. 85, 11 pp (2014)

Z. Kaňuchová, P. Boduch, A. Domaracka, M.E. Palumbo, H. Rothard, G. Strazzulla, A&A **604**, A68 (2017)

Z. Kaňuchová, R. Brunetto, M. Melita, G. Strazzulla, Icarus **221**, 12 (2012)

A.L. Lane, R.M. Nelson, D.L. Matson, Nature. **292**, 38 (1981)

N. Ligier, C. Paranicas, J. Carter, F. Poulet, W.M. Calvin, T.A. Nordheim, C. Snodgrass, L. Ferellec, Icarus, 333, 496L (2019)

M.J. Loeffler, U. Raut, R.A. Baragiola, R.W. Carlson, Icarus, 180, 265L (2006)

X.Y. Lv, P. Boduch, J.J. Ding, A. Domaracka, T. Langlinay, M.E. Palumbo, H. Rothard, G. Strazzulla, MNRAS **438**, 922 (2014)

X.Y. Lv, A.L.F. de Barros, P. Boduch, V. Bordalo, da E.F. Silveira, A. Domaracka, D. Fulvio, C.A. Hunniford, T. Langlinay, N.J. Mason, R.W. McCullough, M.E. Palumbo, S. Pilling, H. Rothard, G. Strazzulla, A&A **546**, A81 (2012)

R. Martinez, A.N. Agnihotri, P. Boduch, A. Domaracka, D. Fulvio, G. Muniz, M.E. Palumbo, H. Rothard, G. Strazzulla, JPCA, **123**, 8001 M, (2019)

M.K. McClure, W.R.M. Rocha, K.M. Pontoppidan, N. Crouzet, L.E.U. Chu, E. Dartois, T. Lamberts, J.A. Noble, Y.J. Pendleton, G. Perotti, D. Qasim, M.G. Rachid, Z.L. Smith, F. Sun, T.L. Beck, A.C.A. Boogert, W.A. Brown, P. Caselli, S.B. Charnley, H.M. Cuppen, H. Dickinson, M.N. Drozdovskaya, E. Egami, J. Erkal, H. Fraser, R.T. Garrod, D. Harsono, S. Ioppolo, I. Jiménez-Serra, M. Jin, J.K. Jørgensen, L.E. Kristensen, D.C. Lis, M.R.S. McCoustra, B.A. McGuire, G.J. Melnick, K.I. Öberg, M.E. Palumbo, T. Shimonishi, A. Sturm, E.F. van Dischoeck, H. Linnartz, Nat Astron **7**, 431 (2023)

T.B. McCord, R. Carlson, W. Smythe, G. Hansen, R. Clark, C. Hibbitts, F. Fanale, J. Granahan, M. Segura, D. Matson, T. Johnson, P. Martin, Science. **278**, 271 (1997)

M.W. McElwain, L.D. Feinberg, R.A. Kimble, C.W. Bowers, J. Scott Knight, M.B. Niedner, M.D. Perrin, J.R. Rigby, E.C. Smith, C.C. Stark, J.C. Mather, "Status of the James Webb Space Telescope mission,“ Proc. SPIE 11443, Space Telescopes and Instrumentation 2020: Optical, Infrared, and Millimeter Wave, 114430T (15 December 2020)

V. Mennella, M.E. Palumbo, G.A. Baratta, ApJ. **615**, 1073 (2004)

D.V. Mifsud, Z. Kaňuchová, P. Herczku, Z. Juhász, S.T.S. Kovács, G. Lakatos, K.K. Rahul, R. Rácz, B. Sulik, S. Biri, I. Rajta, I. Vajda, S. Ioppolo, R.W. McCullough, Mason, N. J.: GeoRL 49, e2022GL100698 (2022)

P. Modica, M.E. Palumbo, *A&A*, 519, A22 (2010)

M.H. Moore, R.L. Hudson, Icarus **145**, 282 (2000)

M.H. Moore, R.L. Hudson, R.W. Carlson, Icarus, 189, 409 (2007)

M.H. Moore, R.K. Khanna, AcSpA, 47, 255 (1991)

L. Moroz, G. Baratta, G. Strazzulla, L. Starukhina, E. Dotto, M.A. Barucci, G. Arnold, E. Distefano, Icarus. **170**, 214 (2004)

K.S. Noll, H.A. Weaver, A.M. Gonnella, JGR. **100**, 19057 (1995)

K.S. Noll, R.E. Johnson, M.A. McGrath, Caldwell, J. J. : GRL. **24**, 1139 (1997)

M.E. Palumbo, Y.J. Pendleton, G. Strazzulla, ApJ. **542**, 890 (2000)

P. Parent, F. Bournel, J. Lasne, S. Lacombe, G. Strazzulla, S. Gardonio, S. Lizzit, J.-P. Kappler, L. Joly, Laffon, C.: JChemPhys 131, 154308 (2009)

Z. Peeters, R.L. Hudson, M.H. Moore, A. Lewis, Icarus **210**, 480 (2010)

S. Pilling, E.S. Duarte, da E.F. Silveira, E. Balanzat, H. Rothard, A. Domaracka, P. Boduch, *A&A*, 523, A77/1 (2010)

C. Plainaki, A. Milillo, S. Massetti, A. Mura, X. Jia, S. Orsini, V. Mangano, De E. Angelis, R. Rispoli, Icarus. **245**, 306 (2015)

E. Seperuelo Duarte, A. Domaracka, P. Boduch, H. Rothard, E. Dartois, da E.F. Silveira, *A&A* 512, A71 (2010)

G. Strazzulla, NIMB **269**, 842 (2011)

G. Strazzulla, L. Moroz, *A&A* 434, 593 (2005)

G. Strazzulla, J.F. Cooper, E.R. Christian, R.E. Johnson, Comptes Rendus Physique, Academie des Sciences, Paris 4, 791 (2003a)

G. Strazzulla, G. Leto, O. Gomis, M.A. Satorre, Icarus. **164**, 163 (2003b)

G. Strazzulla, G. Leto, F. Spinella, O. Gomis, Astrobiology. **5**, 612 (2005)

G. Strazzulla, G.A. Baratta, G. Leto, O. Gomis, Icarus. **192**, 623 (2007)

B.D. Teolis, M.J. Loeffler, U. Raut, M. Fama, R.A. Baragiola, ApJ. **644**, L141 (2006)

B.D. Teolis, D.Y. Wyrick, A. Bouquet, B.A. Magee, J.H. Waite, Icarus. **284**, 18T (2017)

G.L. Villanueva, H.B. Hammel, S.N. Milam, V. Kofman, S. Faggi, C.R. Glein, R. Cartwright, L. Roth, K.P. Hand, L. Paganini, J. Spencer, J. Stansberry, B. Holler, N. Rowe-Gurney, S. Protopapa, G. Strazzulla, G. Liuzzi, G. Cruz-Mermy, E. Moutamid, M. Hedman, M. Denny, K.; NatAs, submitted (2023a)

G.L. Villanueva, H.B. Hammel, S.N. Milam, S. Faggi, V. Kofman, L. Roth, K.P. Hand, L. Paganini, J. Stansberry, J. Spencer, S. Protopapa, G. Strazzulla, Cruz-Mermy, G., C.R. Glein, R. Cartwright, G. Liuzzi, Science, submitted (2023b)

J.H. Jr. Waite, W.S. Lewis, B.A. Magee, J.I. Lunine, W.B. McKinnon, C.R. Glein, O. Mousis, D.T. Young, T. Brockwell, J. Westlake, M.-J. Nguyen, B.D. Teolis, H.B. Niemann, R.L. McNutt, M. Perry, Ip, W.-H.: Nature 460, 487 (2009)

W. Zheng, R.I. Kaiser, CPL, 450, 55 (2007)

J.F. Ziegler, J.P. Biersack, M.D. Ziegler, *The Stopping and Range of ions in Solids* (Pergamon Press, New York, 2008)