SOLID STATE MOLECULAR REACTORS IN SPACE

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Abstract. Lunar minerals and impact glasses, convert the polyatomic beam of solar wind (SW) ions into a flux of small molecules (*e.g.*, H_2, N_2, H_2O, CO, CO_2, CH_4, C_2H_4, C_2H_6, HCN, metal carbides and deuterides, etc.). They thus behave as "Solid State Molecular Reactors". Moreover, $\sim$100–200 μm size micrometeoroids (μMs) have also been exposed to the SW in the zodiacal cloud, before being captured by the Earth and recovered as Antarctic micrometeorites. They are mostly composed of a PAH-rich hydrous-carbonaceous material, which amplifies their power as molecular reactors. In particular, during the first $\sim$200 Myr of the post-lunar period, about 75% of the μMs have been melted and/or volatilized upon atmospheric entry. The release of their volatile species triggered a cosmic volcanism around the mesopause that ruled the formation of the early Earth's atmosphere and climate. Furthermore, a fraction of the μMs that survive unmelted upon atmospheric entry did settle on the proto-oceans floors. Upon further burial in sediments their constituent PAH-rich kerogen was cracked into abiotic oil, which generated giant oil slicks that fed prebiotic chemistry. Many stars, of all ages and types, are embedded into a secondary debris-disk loaded with ion implanted μMs. Some of them are expelled to the interstellar medium (ISM) where they behave first as "dormant-invisible" molecular reactors, until they became reactivated by various processes to synthesize interstellar molecules. This short paper only focus on some highlights of this research dealing with the synthesis of important interstellar molecules, including the most abundant ones (H_2 and CO) and H_2O, HCN and PAHs, all involved in prebiotic chemistry.

1 Introduction: Organic geochemistry of lunar molecular reactors

Lunar dust grains are unique reference samples for learning how to extrapolate the results of laboratory simulation experiments to cosmic dust grains, exposed in ultra-high vacuum ($\sim$10^{-13} torr) to beams of slow and fast ions. Left panel of

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Figure 1 shows the dark-field electron micrograph of a μm-size crystalline lunar feldspar grain, which was observed with a 3 MV high voltage transmission electron microscope by Christian Jouret. Radiation damage features due to the solar wind (SW) and solar energetic particles (SEPs) can be observed, which include -(i)- a darker rim with an average thickness of $\sim$40 nm that decorates an amorphous coating (AC) of SW radiation damage, and -(ii)- a high density of latent tracks of SEPs iron-group nuclei that are best observed as faint lines of dark contrast within the dotted yellow ellipse. The right panel of the same figure shows a zoomed–up detail of another grain, with the contrast enhanced to make the ion tracks more visible.

The identification of these features requires artificial ion implantations of terrestrial lunar analogs with both SW type ions (1 keV/amu) and fast Fe ions E$\sim$1 MeV/amu). Upon *in-situ* thermal annealing in the HVEM, the fossil SW-ACs and SEPs-tracks, as well as the artificial SW-ACs and Fe-tracks, did anneal at the same temperature ($\sim$700–800 °C). Moreover, the average thickness of the fossil ACs, of about 40 nm (see Figs. 1a, 1d, in Maurette 1976), corresponds to both that observed during artificial 1 keV/amu SW-implants, and to the projected damage range, $R_{pd} \sim 40$ nm, of 1 keV/amu SW ions in silicates, as estimated with the SRIM software.

In 1969, organic geochemists discovered that lunar dust grains returned by the Apollo 11 mission did only release small molecules (H_2O, CO, CH_4, and HCN, etc.) during either pyrolysis at moderate temperature (600 °C) or HF etching. They suggested that these molecules were likely produced during the implantation of high fluences of SW ions in the grains. We next helped testing the validity of this assumption while exposing successively $\sim$1 cm^2 flat surfaces of terrestrial analogs (ilmenite, oligoclase and a simulated lunar glass) to high fluence implants ($\sim$10^{15} to 2×10^{18} cm^{-2}) of "marked" isotopes of hydrogen (^{2}D), carbon (^{13}C) and nitrogen (^{15}N) ions, at energy of $\sim$ 1 keV/amu. The group of Al Burlingame (Space Science Laboratory, UC Berkeley) next showed (see Bibring *et al.* 1974) that the mixture of small molecules released upon heating and/or HF etching from these targets are very similar to the natural blend released from lunar dust grains (Simoneit *et al.* 1973).

2 Desorption of molecules during ion implants

In 1975, Plasma Desorption Mass Spectrometry (see section 4, last paragraph) was already used to show that $\sim$ 100 MeV fission fragments from ^{252}Cf directly desorb DOH from D-implanted muscovite mica (Maurette *et al.* 1975). To further investigate this stimulated desorption, another set of the pre-implanted lunar analogs have been exposed to the 10 keV primary beam of Ar of the ionic analyzer built by G. Slodzian. This instrument gives the depth concentration profiles of all species released from the targets. J.P. Bibring observed a large variety of synthesized species ranging from ^{13}C-Mg to ^{13}C$_3$D$_8$, and including D$_2$, ^{15}N$_2$, D$_2$O, and ^{13}CO. However, ^{15}NO and ^{15}NO$_2$ were not detected (^{15}NO/^{13}CD $\leq 10^{-4}$).
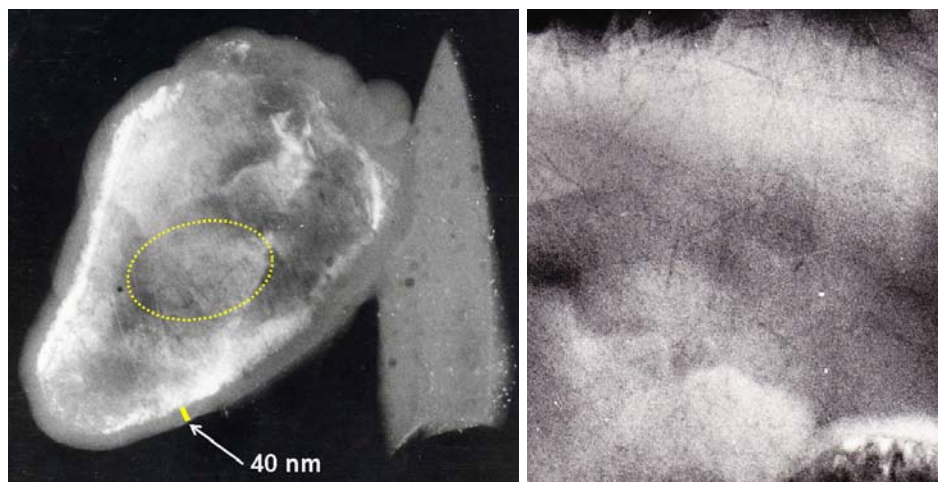
Fig. 1. *Left*: lunar Micron-size molecular reactor. The shard of impact glass stuck to the main grain has not been noticeably eroded by SW sputtering. Thus it has still not reach the critical saturation SW fluence to function as a molecular reactor. *Right*: detail of another dust grain with enhanced contrast to make ion tracks more visible to the untrained eye (the thin dark lines in the image).

This study could be extended to a primary beam of 3 keV deuterium, through the decisive help of W. Möller and his team (Max-Plank-Institute für Plasmaphysik, Garching). The three lunar analogs, as well as olivine, silicon, sapphire and a soda-lime glass, have been run with a sophisticated reaction chamber developed for understanding the interactions of a hot DT fusion plasma (T = ^{3}He) with the first wall of fusion reactors, at D and T energy in the keV to MeV range. This chamber is equipped with a quadrupole mass spectrometer on-line with both a 30 kV ion accelerator for deuterium implantation, and a 2.5 MV Van de Graaff accelerator for the analysis of the implanted targets with a 750 keV ^{3}He beam, through the D(^{3}He, α)H nuclear reaction. This reaction yields the residual concentration and depth concentration profile of the implanted deuterium. The mass spectrometer was tuned to detect simultaneously the release of D_2 and D_2O, which are considered as stumbling blocks in either the gas phase chemistry of the ISM (H_2) or prebiotic chemistry (H_2O).

This on-line study reveals the intimate functioning of the seven molecular reactors (Borgesen *et al.* 1986). In a first group, including ilmenite, olivine, the alkalipoor LSG (0.02% K_2O), sapphire and silicon, a complete retention of D is observed as soon as the deuterium beam is turned on around a fluence of $\sim 10^{15}\,\mathrm{cm}^{-2}$. At increasing fluence, a sudden onset of deuterium re-emission (as D_2) is found around $1 \times 10^{17}\,\mathrm{cm}^{-2}$, which finally increases to 80–100% of the implanted deuterium around a saturation fluence, $\Phi_s \sim 10^{18}\,\mathrm{cm}^{-2}$. These major characteristics of the deuterium release have also been previously reported for metals (at low

temperature), and other targets at room temperature, including semiconductors, fused silica and a sintered powder of graphite, which did release both D_2, CD, C_2D and CD_4. During all the re-emission stage in the O-rich targets, the incoming D yields a D_2O / D production ratio of 10^{-4}, 3×10^{-4} and 2×10^{-5}, for ilmenite, oligoclase and the SLG, respectively.

However, both the Na-rich oligoclase and soda-lime glass show a very distinct behavior, as they start loosing (*i.e.*, synthesizing) D_2 at the onset of implantation (10^{15} cm^{-2}). They would be the best molecular reactors in a low ion flux environment. On a flat target, perpendicular to the anisotropic SW beam at 1 AU, this fluence is reached in a few months. However, a spherical grain on top of the surface of the Moon would require a longer exposure to accumulate the same fluence on each element of its surface, because the grain is partially shielded from the SW, *e.g.*, during the lunar night.

3   Hydrous-carbonaceous molecular reactors on the early earth

In 1975, we already suspected that lunar type molecular reactors might be effective in the ISM (*cf.*, last section in Maurette & Price 1975). In 1987, a much more powerful family of $\sim$100–200 μm size molecular reactors (*i.e.*, the hydrous-carbonaceous μMs) was discovered as Antarctica micrometeorites (see Maurette 2009, for the most recent review about collects and applications). Their marked similarities with the Wild-2 dust particles returned by the Stardust mission in January 2006 (Dobrica *et al.* 2009), further indicate that they likely originate from comets. This is further supported by IR observations, which revealed that contrarily to previous thoughts, comets are very efficient "dust machine gun" in the solar system (Lisse *et al.* 2004). Observations of comets P/Encke and P/IRAS with IR telescopes on the ISO and MSX spacecrafts show dust-to-gas mass loss ratios about 50 times larger than those inferred from measurement in the visible. These high mass-loss ratios, which were reconfirmed for comet Temple 1 during the Deep Impact mission, clearly show that comets are the major contributors of dust in the interplanetary medium.

After ejection, most of these 100 μm size cometary dust grains have been temporarily stored in the Zodiacal Cloud for duration of $\sim$200 000 yr (Raisbeck & Yiou 1989), and thus implanted with SW- and SEPs-ions. This cloud is probably a very faint remnant of the secondary debris-disk of the early Sun, which did exponentially decay until about 4 Ga ago, while triggering a period of early heavy bombardment of the Earth-Moon system (Greaves 2005).

About 99% of the Antarctica micrometeorites are only related to the most volatile-rich hydrous-carbonaceous chondrites, which are relatively rare (about 2–3% of the meteorite falls). Their major carbonaceous component is a kerogen composed of a mixture of PAH moieties and aliphatic hydrocarbons, and their constituent water (10 wt.%) is mostly stored in their major hydrous silicate, saponite, that starts dehydrating at $\sim$100°C. Upon atmospheric entry μMs would thus release solar wind implanted neon, but also molecules originating from their kerogen (N_2 and CO_2), hydrous silicates (H_2O), and metallic sulfides (SO_2).

These volatiles ended up making the early Earth's atmosphere (*i.e.*, before the formation of O_2), during the first $\sim$200 Myr of the post-lunar period, after the giant impact that did form the Moon (Maurette 2009). This impact did also close the formation time interval of the Earth, and blew-off the intractable pre-lunar atmosphere of the young Earth at a time when the Earth's mantle has already been extensively degassed. Therefore, after the impact, there was not enough volatile species left in the mantle to feed the formation of the massive early Earth's atmosphere, which required the delivery of total amounts of H_2O, CO_2 and SO_2 corresponding to partial pressures of about 270, 60 and 80 bars, respectively (today, CO_2 and SO_2 are mostly stored as carbonates in the crust and metallic sulfides in the upper mantle, respectively). This μMs origin of the atmosphere is strongly supported by the Ne/N_2 and the D/H ratios of Antarctic micrometeorites. They best fit the corresponding ratios observed in the air and the oceans, respectively, which are incompatible with all other models of atmosphere formation.

Moreover, a fraction of the μMs that did survive unmelted upon atmospheric entry with their full load of PAH-rich kerogen landed on the proto-oceans floors. They well fit the definition of good "source rocks" for the "economic exploitation" of petroleum, *i.e.*, fine clays with at least 0.5 wt.% of kerogen (Rondeel 2002). Therefore, they likely generated giant abiotic oil slicks that assisted prebiotic chemistry (Dias & Maurette 2007). In 1971, Dave Holland and collaborators (Lasaga *et al.* 1971) proposed a distinct type of primordial oil slick. But their oil was produced during the solar UV irradiation of a primordial methane and nitrogen atmosphere, which had soon to be disregarded.

4 Kerogen-rich molecular reactors in the ISM

Frank Shu (1982) pointed out that the extinction of visible starlight could be caused by "bricks". However, he cautioned that bricks cannot produce a reddening of starlight. The combination of true absorption and reddening of this starlight is thus attributed to grains that are slightly smaller ($\leq$0.4 μm) than the wavelengths of visible light in order to scatter blue light more efficiently than red light. This general extinction does not exclude the presence of $\geq$100 μm size "bricklets", which were injected from various stellar sources in the ISM. They could be made of the large diversity of solids that have the potential of desorbing molecules upon ion implants (Sect. 2), including hydrous carbonaceous micrometeoroids (see Sect. 3). All of them would start as somewhat dormant and invisible molecular reactors in the ISM, until they are re-activated by various processes (see next section).

In 1994, 15 Antarctica micrometeorites (*i.e.*, μMs) have been ranked on a scale of increasing thermal metamorphism upon atmospheric entry (Clemett *et al.* 1996). The PAH moieties of their constituent kerogen have been desorbed with the IR laser pulses of a double laser microscope equipped with a reflectron time-of-flight mass spectrometer (μL^{2}MS). A great diversity of PAH mass spectra were observed, from the simplest spectra of unmelted μMs (similar to that of the CM2-type Murchison chondrite) to the complex spectra of partially melted μMs that

mimic that of soot particles (see Figs. 4a to 4d, in Clemett *et al.* 1996). "Exotic" PAHs were also observed, such as vinyl PAHs that might have promoted interesting organometallic reactions.

McFarlane and co-workers invented the ^{252}Cf plasma desorption mass spectrometer, which allowed the determination of the molecular weight of large organic molecules, such as insulin, which desorbs "intact" from thin deposits irradiated with ∼100 MeV ^{252}Cf-fission fragments (Torgeson *et al.* 1974). Therefore, fast ions should also softly desorb PAHs from kerogen, like the IR laser pulses of the μL^{2}MS. We commented (Maurette *et al.* 2003) on the *in-situ* FTIR analysis of five organics irradiated with 10 MeV/amu ^{40}Ar ions, under oxygen free conditions (Reynaud *et al.* 2001). These materials loose the memory of their initial properties when the radiation dose exceeds ∼300 Mega-Grays, *i.e.*, after an exposure of about 10^4 yr to SEPs at 1 AU. They are all converted into an insoluble material dubbed as kerogen, which might desorb its PAH moieties in the ISM.

5   Summary and prospects

In the last 70 yr, an abundant literature was published about the main ingredients of dust evolution models in galaxies, including the synthesis of interstellar molecules (*cf.*, Dwek *et al.* 2009). Our studies show that many reaction channels are opened upon implantation of a **polyatomic** beam of fast ions in a great diversity of Solid State Molecular Reactors. A challenge is to check whether their easy-to-desorb and abundant species (*e.g.*, H$_2$, CO and PAHs), can help simplifying the chemical models proposed for the synthesis of interstellar molecules in the gas-phase, *"which contain thousands of reactions, many of which have not been studied theoretically or in the laboratory"* (quote from E.Herbst).

Another challenge is to identify the dominant process that can activate molecular desorption from the "dormant" molecular reactors in the ISM. All previous processes, including those listed by Maurette & Price in 1975, might be fully superseded by the high flux of low energy (2–20 MeV/amu) galactic cosmic rays (LOWs) if McCall and co-workers are right (McCall 2010). They reported challenging papers (*e.g.*, Indriolo *et al.* 2009) dealing in particular with the determination of the high degree of ionization of the diffuse ISM (as inferred from the H$_3^+$ ion) and the production rates of Li, Be, B and gamma-rays. They tested multiple LOWs energy spectra and found only two spectra that best fitted the corresponding observations.

I selected their simplest "broken power-law" distribution of cosmic rays in relativistic momentum, reproduced in Figure 2, that represents a differential number flux, Φ_p [particles cm^{-2}s^{-1}sr^{-1} (GeV/n)$^{-1}$]. Nick Indriolo has kindly computed the corresponding integrated flux of protons, in the three energy ranges considered in this paper: Δ_1 (0.002–1GeV/n); Δ_2 (2–20 MeV/n) and Δ_3 (5–20 MeV/n). The corresponding "integral" proton fluxes (number cm^{-2} s^{-1} sr^{-1}) are about 3.7, 1.5, and 0.9, for Δ_1, Δ_2, and Δ_3, respectively. For grains smaller than the projected range of 2 MeV/n LOWs in silicates (about 42 μm and 18 μm for H and
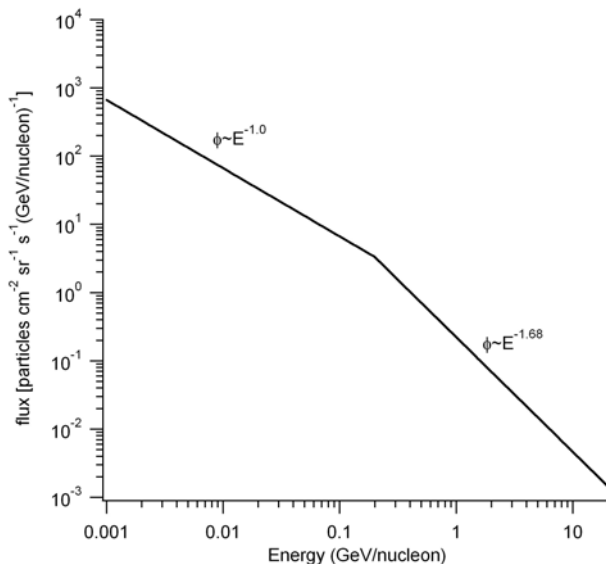
Fig. 2. Possible energy spectrum of low energy cosmic rays in the ISM (Courtesy N. Indriolo).

Fe, respectively), and which include all "visible" grains with sizes $\leq 1\,\mu m$ in the ISM, this value has to be multiplied by 4π because the LOWs flux is isotropic.

The lifetime of a large dust grain in the ISM is about 3×10^7 yr, cycling several times between dense and diffuse clouds (see *e.g.* Tielens 2005). With the resulting flux of 20 protons $cm^{-2}s^{-1}$ (in the 2–20 MeV/n range) the kerogen simulation experiments discussed in section 4 predict that the organic component of the visible grains would be transformed into kerogen in $\sim 10^5$ yr of exposure in the diffuse interstellar clouds. Furthermore, artificial implants of Fe and Ar ions, show that crystalline silicates, would be rendered amorphous by a fluence of $\geq 10^{11}$ VH cm^{-2} at the very low temperatures of the ISM, which quench the diffusion induced annealing of atomic defects. Considering a low energy cutoff value of 5 MeV/n required for the penetration of VH ions in the diffuse clouds, the Indriolo predicted proton flux (11 cm^{-2} s^{-1}) corresponds to an exposure of $\sim 3 \times 10^7$ yr and $\sim 10^6$ yr in the ISM, for a solar VH/H ratio (10^{-5}) and the 30 times higher ratio measured for ≥ 1 GeV/n GCRs, respectively. A reasonable VH/H ratio just a few times higher than solar would insure that *in the diffuse ISM, crystalline silicates would be rare but PAHs quite abundant.*

The Mcfarlane desorption mass spectrometer can measure PAH desorption yields of kerogen-rich materials, which are required to extrapolate the desorption model to the ISM. The presence of abundant "bricklets" along the orbits of comets is brightly signaled by meteor showers. However, the ISM bricklets have still to be detected.

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