COSMIC IRRADIATION OF CARBONACEOUS MATERIAL IN SPACE AND PREBIOTIC CHEMISTRY.

M.Maurette[1], E.Balanzat[2], J.Duprat[1]. [1]CSNSM, 91406 Orsay-Campus, France; [2]CIRIL, BP 5133, 14070 Caen, France.

Reprocessed organics in meteorites and "sporadic" micrometeorites. In 2001, G.Bada quoted the possibility that the doses of ionizing radiation deposited in hydrous-carbonaceous chondrites (HCCs) during their exposure in space to $\approx$1 GeV/amu galactic cosmic rays (GCRs) would be sufficient to alter their carbonaceous matter. The effects of heavy ion irradiations ($\approx$10 MeV/amu ^{40}Ar) on the IR spectrum of various organics have been studied by a French group [1], including one of us (E. B.), at the GANIL accelerator. Irradiations and in situ IR analysis were performed under oxygen free conditions. Published results on polystyrene and hydrogenated carbon nanoparticles, as well as unpublished data on polycarbonate and polyethylene, indicate that, as soon as the irradiation dose in Grays (Gy) exceeds a critical value, $\Omega_C \approx$300 MGy, all irradiated materials are degraded into an insoluble organic (dubbed as "kerogen") and loose the memory of their initial properties.

From both the fluence ($\approx$1 p.cm^{-2}.s^{-1}) and the energy ($\approx$1 GeV/amu) of GCRs (their nuclear cascades penetrate up to depths of a few meters in rocks) it can be deduced that the dose deposited in a carbonaceous meteorite exceeds Ω_C, when its "cosmic ray exposure age" in space is larger than 10 Myr. But solar energetic particles (SEPs) with a much smaller energy of $\approx$10 MeV/amu cannot produce any measurable effects in meteorites because their penetration in rocks is about 100 μm. Consequently, their radiation effects are lost during ablation upon atmospheric entry.

The situation is sharply different for the $\approx$100–200 μm sized micrometeorites of the sporadic flux, such as those sampled in the collection of Antarctic micrometeorites (AMMs). Their entire volume is irradiated by SEPs nuclei. Their exposure ages in the interplanetary medium are much shorter than those of meteorites ─they were inferred from ^{10}Be contents in AMMs indicating ages ranging from $\approx$1000 up to a few times 10,000 centuries [2]. But their fluence ($\approx$100 p.cm^{-2}.s^{-1}) and ionization energy loss rate are much higher than the corresponding value noted for GCRs. Consequently, Ω_C is reached in MMs after only a few hundred centuries of exposure in space.

The major conclusion inferred from these estimates of radiation doses is that the constituent organics of both HCCs and "sporadic" MMs have been severely degraded during their flight times to the Earth. These predictions are comforted by previous observations showing that kerogen is the dominant carbonaceous matter in both HCCs [3] and AMMs [4]. This challenges previous conclusions about the major role of complex organics delivered by meteorites and micrometeorites in the prebiotic chemistry of life on the early Earth, because kerogen is considered as very inert. There are at least two approaches to tackle this challenge. One could either: ─ focus on the more pristine material delivered by "shower" micrometeorites (MMs), or; ─ exploit some odd properties of kerogen carried by sporadic MMs.

The pristine carbonaceous component of "shower" micrometeorites. Micrometeorites (MMs) mostly originate from the "sporadic" flux. But there is also a minor component of "shower" MMs deposited during meteors showers produced when the Earth intersects the dusty orbits of comets. The best known and most intense "Leonid" showers originates from comet Temple-Tuttle. Since 1999, dynamicists have developed accurate models to predict the arrival time of this shower within about 15 minutes [5]. This validates these models, and consequently their prediction that "shower" MMs are released from their parent comets at most a few centuries before their capture by the Earth. Their exposure to SEPs ions is too short to produce noticeable radiation effects. They would be the only extraterrestrial material captured by the Earth that might contain pristine organics for prebiotic chemistry.

Mass flux of "invisible" shower micrometeorites. Shower MMs are considered in the size range ($\approx$100-400μm) where $\approx$99% of the mass of the sporadic micrometeorite flux is concentrated. They are too small to give visible meteors. Their average yearly mass flux, Φ_s (number of tons delivered to the whole Earth's), is rather tricky to estimate. Difficulties arise from both their highly anisotropic delivery to the Earth and the chaotic variations of both the duration and the intensity of the few strongest showers (i.e., "storms") observed since 1960. In contrast, that of the permanent sporadic flux of micrometeorites ($\Phi_0 \approx$ 40,000 tons / yr) has been measured with various techniques [6].

One could postulate that Φ_s and Φ_0 are both proportional to the hourly rates, HR_s and HR_0, of visible meteors relevant to particles with sizes $\geq$1mm, and measured in the shower and sporadic flux, respectively. Consequently, $\Phi_s / \Phi_0 \approx HR_s / HR_0$. But the orbits of the smallest and invisible shower particles are preferentially widely spread along the dusty cometary orbit by non gravitational forces. Thus, they get separated from the more concentrated clusters and/or "filaments" of big particles. Consequently, the proportionality between Φ_s and HR_s is not known. We did play with the differential mass distributions of both the sporadic and shower particles (averaged for several showers), reported by Hughes in the $\approx$10 μm–10 cm size range [see fig. 8, in ref. 7]. We got: $\Phi_s / \Phi_0 \approx 0.034$ x (HR_s / HR_0).

Next, we averaged the HR_s / HR_0 ratio since 1960, when Radar measurements started to extend the direct observation of meteors down to a particle size of about 100 μm. As the value relevant to the sporadic meteors ($HR_0 \approx$10) is constant with time, we had only to assess the average value of HR_s. Since 1960, the most intense "storms" were the "Leonids", which occurred twice: ─ in 1966, with a peak intensity HR_s (peak) $\approx$10^5, that lasted about 5 hours, and; ─ during five years (between 1998-2002) with an average HR_s (peak) $\approx$2000, effective over an integrated duration of $\approx$10 hours. Moreover, 6 much less intense "recurrent" cometary showers, with HR_s (peak) $\leq$ 120, are observed each year in the Northern hemisphere. But their peak intensity lasts between 2 and 8 days, and not only for a few hours. Thus, they still noticeably feed the flux of shower micrometeorites. By summing up the average yearly contributions of both storm and recurrent shower meteors since 1960, we first deduce that the relative abundance (i.e., HR_s / HR_0) of large shower particles with sizes $\geq$1 mm in the sporadic flux is $\approx$50%. Then, the relationship given in the previous section yields a value $\Phi_s / \Phi_0 \approx$2%. But recent

IRRADIATION OF CARBONACEOUS MATERIAL IN SPACE. M.Maurette et al

continuous monitoring of meteor showers with radiotelescopes reveal that the peak intensity of the Radar meteors in a given storm and/or shower lasts much longer ($\approx$2 days) than that of the visible meteors ($\approx$2 hours). Moreover, additional showers have their radiant in the Southern hemisphere. So, this value of 2% is a lower limit which might reach $\approx$10%.

Shower micrometeorites in prebiotic chemistry. This mass of "pristine" shower carbonaceous material was delivered to the early Earth during a period of "late heavy bombardment" (*LHBomb*), when the micrometeorite flux was greatly enhanced. With the arithmetic of accretion described in the next section, we get a total amount of unmelted shower MMs deposited on the early Earth during the *LHBomb* of $\geq 3.10^{22}$ g.

Their organics were probably more pristine and reactive than kerogen. Each one of these micrometeorites could have functioned as a tiny chemical reactor, that synthesized complex organics for the prebiotic chemistry of life [8]. The huge amount of "shower" unmelted MMs thus delivered during the *LHBomb*, was equivalent to at least a $\geq$20 m thick layer all around the early Earth. But we have no clues about the nature of these pristine organics, and thus about the functioning of their host micrometeorite reactor in the hot environment of the early Earth. Therefore, their chemical reaction networks in the early atmosphere and/or water cannot be assessed. This reinforces the interest of our attempts to recover Leonid shower MMs from both Greenland and Antarctica snow [9], as to investigate such pristine organics. We next explore whether the "inert" kerogen of sporadic MMs might have independently contributed to prebiotic chemistry.

Sporadic micrometeoritic in prebiotic chemistry. The functioning of sporadic MMs as chemical reactors was probably quenched by the irradiation reprocessing of their constituent organics into kerogen. But sporadic MMs also released their kerogen during atmospheric entry. This mostly occurred during the post-lunar *"PHBomb"*, extending over a time interval of $\approx$500 Myr after the formation of the Moon by a giant Mars-sized impact. This cataclysmic impact did blew off the complex pre-lunar atmosphere of the Earth, including water. A new post-lunar atmosphere was generated by a total mass of "juvenile" sporadic micrometeorites of $\approx$5 x 10^{24} g, showing a composition astonishingly similar to that of AMMs [10]. The same arithmetic yielded the mass of unmelted shower MMs quoted here above, just remembering that only $\approx$25% of the $\geq$100 µm micrometeorites survive unmelted after atmospheric entry [11].

This huge "sporadic" mass contains $\approx$2.5 wt.% of organic carbon [12] mostly associated to kerogen [4]. This can be translated into a total quantity of kerogen before atmospheric entry of $\approx 10^{23}$ g, equivalent to a $\approx$200 m thick layer around the Earth. This is an upper limit because kerogen was partially lost by processes such as volatilization. But other reactions can modify any type of kerogen in the atmosphere, such as those reported about 15 years ago [13], for the constituent PAHs (Polycyclic Aromatic Hydrocarbons) of terrestrial kerogen. These reactions likely apply to sporadic MMs, where kerogen contains PAHs moieties with substituted side chains [14]. But $\approx$75% of the micrometeorites are volatilized and/or degassed during atmospheric entry. Such processes generate a kind of

micrometeoric "smoke", partially fed with both the constituent water of micrometeorites, and hydrogenated carbon particles resulting from the complete degradation of their kerogen. A fraction of this water is photodissociated into oxygen and OH radicals, which generate hydrogen upon recombination. The carbon particles can then react with these thermalized species in the ionosphere as to regenerate new varieties of reactive kerogen, with substitution side chains on the carbon skeleton. These varieties would be even more complex and less compact than the initial kerogen.

"Kerogenetics" in early prebiotic soups. The complex fate of micrometeoritic kerogen has not been traced back, yet. We are stuck with a science fiction scenario to describe its plausible role in prebiotic chemistry (i.e., a field where such types of scenarios are rather frequent anyway), that just yields a few guidelines for future works. It relies on three plausible assumptions: — some fraction of this reprocessed micrometeoritic "smoke" kerogen was deposited in early seas as colloidal particles; — the least compact and lightest varieties were preferentially enriched in the top layers of the early oceans functioning as decantation filters; — a fraction of this extended "foam" of light kerogen particles subsequently aggregated into some huge kerogen "mats".

As kerogen is insoluble in most acids and organic solvents, these kerogen foam and/or mats were probably quite durable. Did they floated and drifted for a very long time in the hot dilute prebiotic soup of the early oceans, while being constantly agitated and "aerated"? They should have been made of a wide variety of building units, reflecting that of the entry conditions of sporadic MMs in the atmosphere. They could have behaved as gigantic chemical reactors, collecting and absorbing first into their texture organics already existing in the dilute prebiotic "soup "of the early oceans —the remarkable absorption behavior of kerogen is well documented for varieties dubbed as "active coals" [15]. Furthermore, the atmospheric reprocessing of kerogen likely introduced reactive side chains such as vinyl groups in the carbon skeleton of kerogen. They could have interacted with atmospheric species such a nitrogen, which got excited in the spectacular *"persistent trails"* of the largest meteors [5], where a glow discharge chemistry operates.

References: [1] Reynaud et al (2001) *Spectrochemica Acta* **A57**, 797; [2] Raisbeck and Yiou (1989) *Meteoritics* **24**, 318; [3] Cronin (1998) In Brack (Ed.) *The molecular origin of life* (Cambridge Univ. Press), pp. 119-146; [4] Matrajt et al (2001) *Meteoritics Planet. Sci.* **36**, A127; [5] Jenniskens (2001) In *"Interplanetary Dust"* (Springer, Berlin), pp. 233-252; [6] Love and Brownlee, (1993) *Science* **262**, 550; [7] Hughes (1994) In *"The Cosmic Dust Connection"* (Kluwer Acad. Publishers), pp. 357-398; [8] Maurette (1998) In Brack (Ed.) *The molecular origin of life* (Cambridge Univ. Press), pp. 147-186; [9] Duprat et al (2001) *LPSC* **32**, A1773, CD-ROM; [10] Maurette et al (2001) In, Gargaud et al (Eds) *Environnement de la Terre primitive* (Presses Univ. Bordeaux), pp. 99-127; [11] Duprat et al (2003) this abstract volume; [12] Engrand and Maurette (1998) *Meteoritics Planet. Sci.* **33**, 565; [13] Schmidt (1987) In *"PAHs and Astrophysics"* (Reidel Publi. Co.) pp.149-164; [14] Clemett et al (1998) *Origin Life Evol. Biosphere* **28**; [15] Cookson (1980) *Carbon Adsorption Handbook* (Ann Harbor Sci. Publishers), pp. 241-280.