

Ion-Irradiation Induced Organic Refractory Residues from Nitrogen-rich Ices: Clues on the Isotopic Composition of the Organic Matter in UCAMMs.

J. Rojas¹, J. Duprat², E. Dartois³, T.-D. Wu⁴, C. Engrand¹, B. Augé⁵, Ph. Boduch⁶, H. Rothard⁶, M. Chabot¹, B. Guérin¹, J. Mathurin⁷, ¹ Univ. Paris-Saclay, CNRS/IN2P3, IJCLab, 91405 Orsay, France, ² IMPMC, CNRS-MNHN-Sorbonne Univ., 75005 Paris, France, ³ Univ. Paris-Saclay, CNRS, ISMO, 91405 Orsay, France, ⁴ Institut Curie, Univ. Paris-Saclay, CNRS, INSERM, 91405 Orsay, France, ⁵ IPAG, Univ. Grenoble Alpes, CNRS, 38000 Grenoble, France, ⁶ CIMAP, 14070 Caen, France, ⁷ Univ. Paris-Saclay, CNRS, ICP, 91405 Orsay, France

Introduction: Ultra Carbonaceous Antarctic MicroMeteorites (UCAMMs) are micrometeorites with a high carbonaceous abundance (C/Si ranging from 10 up to 10³) [1-6]. Their organic matter is N-rich, with isotopic heterogeneities in N and C, and exhibits extreme D/H ratios [2]. Despite their low abundance within the micrometeorite flux, UCAMMs represent a non-negligible source of exogenous unaltered carbon reaching Earth [7]. UCAMMs most probably originate from the surface of icy objects [2, 8] where the organic matter can be synthesized, at large heliocentric distance, by energetic processes such as Galactic Cosmic Rays (GCR) irradiation [9, 10]. In previous experiments, we showed the similarity of the IR signature and the D/H heterogeneities of UCAMMs with that observed in organic residues formed by swift ion irradiation of N-rich and D-rich ices mixed with hydrocarbons [9, 10]. We recently performed new irradiation experiments to study the transmission of light elements (H, C, N) isotopic heterogeneities from the ice to the irradiation-induced refractory residue. We also explored the impact of the ice chemical nature on the formation of the final organic residue.

Material and method: Ice irradiation experiments were performed with the ion beam (IRRSUD, 0.5-1 MeV/u) at GANIL (Caen, France). The IGLIAS experimental setup [9, 11] was used to form ice films by gas condensation on IR-transparent windows cooled down to 10K prior irradiation. A quadrupole mass spectrometer was used to monitor the gas phase during ice deposition, irradiation and subsequent sublimation. The ice evolution under irradiation was also monitored *in situ* with a Bruker Vertex 70v Fourier transform infrared (FTIR) spectrometer. Ice samples consisted in two $\approx 5 \mu\text{m}$ thick ice layers (¹⁴N₂-¹²CH₄ (90:10) or ¹⁴NH₃-¹²CH₄ (90:10)) deposited around a central layer isotopically labeled with ¹³C, ¹⁵N and/or D, forming an ice-sandwich [12]. The total thickness of the ice-sandwich was estimated from the fringe pattern observed in the IR spectra [13] and the central layer accounted for 1% to 4% of its volume, depending on the sample. Nine ice-sandwiches were irradiated during three experimental sessions with ⁵⁸Ni⁹⁺, ¹³⁶Xe¹⁹⁺ and ⁸⁶Kr¹⁵⁺ swift ion beams. The ion fluences used to irradiate the ice-sandwiches were adapted to the ion energies in order to reach doses ranging from 8 to 25 eV/molecules corresponding to tens to hundreds million years of exposure in the outer region of the solar system. At the end of the irradiation, the ice-sandwiches were slowly warmed up from 10K to 300K with a 0.1 - 0.5 K/min temperature ramp, leading to the sublimation of the volatile ices left and to the concentration of refractory organic residues on the substrate windows. The windows were subsequently transferred from the IGLIAS chamber to a specific holder to perform isotopic mapping with the NanoSIMS instrument. Analyses were performed on areas of about 50×50 μm^2 with a 7 pA Cs⁺ beam.

Results: Isotopic heterogeneities in D, N and C are observed at the micron scale in the organic residues, confirming the possibility to transfer isotopic heterogeneities from isotopically distinct ice layers to the irradiation-induced residue. Organic residues formed from ices with the same major composition of ¹⁴N₂-¹²CH₄ (90:10) share similar IR spectra, however we observed substantial differences on the morphology of the organic residues from one sample to another. The structure of the organic residue and the repartition of the D, ¹⁵N and ¹³C within the residue seems to be sensitive to the formation mechanisms. The presence of D, ¹⁵N and ¹³C enrichments in the residue around holes associated with bubbles formed during the annealing suggests that specific components of the residue's precursors can be concentrated during the residue's formation events. Ice-sandwiches where ammonia is the major component of the ice sandwich (¹⁴NH₃-¹²CH₄ (90:10)) have led to the formation of low quantity of organic residue, resulting from the sublimation of most of the irradiated material during the annealing. These results can provide new constraints on the formation of organic matter by irradiation of icy bodies' surfaces at large heliocentric distance.

References: [1] Duprat, J., et al. (2010). *Science*, 328, 742-745, [2] Dartois, E., et al. (2018). *Astronomy and Astrophysics*, 609, [3] Noguchi, T., et al. (2017). *Geochimica et Cosmochimica Acta*, 208, 119, [4] Dartois, E., et al. (2013). *Icarus*, 224, 243-252, [5] Rojas, J., et al. (2020). *LPS LI*, 1614, [6] Yabuta, H., et al. (2017). *Geochimica et Cosmochimica Acta*, 214, 172-190, [7] Rojas, J., et al. (2021). *Earth and Planetary Science Letters*, 560, 116794, [8] Dobrica, E., et al. (2010). *LPS XLI*, 1613, [9] Augé, B., et al. (2016). *Astronomy and Astrophysics*, 592, A99, [10] Augé, B., et al. (2019). *Astronomy and Astrophysics*, 627, A122, [11] Augé, B., et al. (2018). *Review of Scientific Instruments*, 89, 075105, [12] Rojas, J., et al. (2020). *LPS LI*, 1630, [13] Satorre, M. A., et al. (2008). *Planetary and Space Science*, 56, 1748-1752.