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ISOTOPIC ANALYSES OF ION IRRADIATION-INDUCED ORGANIC RESIDUES, CLUES ON THE FORMATION OF ORGANICS FROM UCAMMS. J. Rojas¹, J. Duprat¹, E. Dartois², T-D Wu³, C. Engrand¹, B. Augé⁴, J. Mathurin¹, B. Guerin¹, J-L. Guerquin-Kern³, Ph. Boduch⁵, H. Rothard⁵. ¹Univ. Paris-Saclay, CNRS, IJCLab, 91405 Orsay, France (Julien.Rojas@cnsnm.in2p3.fr); ²Univ. Paris-Saclay, CNRS, ISMO, 91405 Orsay, France, ³Institut Curie, PSL Research University, INSERM, U1196, 91405 Orsay, France, ⁴IPAG UGA/CNRS Grenoble France, ⁵CIMAP (CEA/CNRS/ENSICAEN/Université de Caen-Basse Normandie), BP 5133, 14070 Caen Cedex 05, France.

Introduction: UltraCarbonaceous Antarctic MicroMeteorites (UCAMMs) are interplanetary dust particles that exhibit large concentrations of organic matter with high N concentrations and extreme D/H ratios [1-4]. The mineralogy, the elemental and isotopic composition of UCAMMs indicate that they most likely originate from the cometary reservoir [1, 2, 5]. Most UCAMMs exhibit large variations on D/H, ¹⁵N/¹⁴N and ¹³C/¹²C ratios at the micron or sub-micron scale. These isotopic fractionations are carried by the organic matter and their origin is still an open question.

We showed that the precursors of UCAMMs can be formed by irradiation with high energy ions of N-rich ice mixtures with hydrocarbons, a process likely to take place at the surface of icy bodies orbiting beyond a nitrogen snow line and irradiated by galactic cosmic rays [2, 6]. Recent experimental simulations showed that the irradiation itself does not induce large D fractionation, but that the refractory organic residue resulting from irradiation of isotopically heterogeneous ice mixtures can exhibit large D/H spatial variation at the micron scale [7]. We performed a new series of experiments on D, ¹⁵N and ¹³C labelled ices to study the transmission of the isotopic labelled ice layers to the irradiation-induced residue.

Material and method: Irradiation experiments of ices were conducted with the low-energy beam (Irrsud, 0.5-1 MeV/n) at GANIL (Caen, France). We used the IGLIAS experimental set-up [8] which allows to deposit and irradiate complex ice films mixtures on substrate windows held at temperatures ranging from 8K to 300K (Figure 1). The evolution of the ices during the irradiation was monitored *in situ* with a Bruker Vertex 70v Fourier transform infrared (FTIR) spectrometer. The gas mixtures deposited are controlled with a Quadrupole Mass Spectrometer (QMS). We followed the same protocol as described in [7]. We first irradiated a mixture of ices made of two equally thick layers of ¹⁴N₂-CH₄ (90:10) of about 5 μm each surrounding a thin layer of isotopically labeled (in D, ¹³C and ¹⁵N) ice with a thickness of about 0.2 μm. The ice films were formed by gas injections on ZnSe windows at 8K. The thickness of the central isotopically labeled ice layer was estimated from the volume of gases injected (i.e. 2% of the total thickness). The overall thickness of the ice sandwiches (11 μm) were

determined from the interference fringe patterns on the IR spectra taken *in situ* [7, 9]. In the first experiment (hereafter referred as sandwich Sd#1) the isotopically labeled central ice layer was ¹⁵N₂-CD₄ (90:10). In the second experiment (sandwich Sd#2) the central isotopically labeled layer was ¹⁵N₂-CD₄-¹³CO (80:10:10).



Figure 1 : Target windows holder of the IGLIAS set-up. The isotopic labeled gases are condensed at 8K on each window prior to irradiation. ZnSe IR-transparent windows (yellow window covered with a brown residue) are used, allowing IR spectroscopy monitoring during the irradiation.

The ices sandwiches were irradiated at 8K with 33 MeV Ni⁹⁺ ions up to a fluence of 10¹³ ions/cm². The duration of each irradiation was about 2 hours. The ion projected range estimated with the SRIM code [10] was about 23 μm, i.e. larger than the sample total thickness, allowing the high energy Ni⁹⁺ ions to interact with the entire ice film. At the end of the irradiation, we applied a very slow temperature ramp to the samples (0.1 K/min from 8K to 70K, 0.2 K/min from 70K to 80K, 0.3 K/min from 80K to 140K and 0.5 K/min from 140K to 300K) to allow the remaining ice to sublimate and to bring the irradiation induced residue to room temperature. IR and mass spectra were recorded by the FTIR spectrometer and the QMS prior and along each irradiation to monitor the evolution of the sample. During the warming up of the sample, a FTIR spectrum of Sd#1 sample was acquired every 15 minutes.

After irradiation and annealing to room temperature, the substrate windows were extracted from the IGLIAS chamber and mounted on a dedicated holder to perform NanoSIMS analyses on the refractory or-

ganic residue. We deposited a 40 nm thick gold coating on the windows to allow efficient charge evacuations during NanoSIMS measurements. Measurements were made with a 7 pA Cs⁺ primary beam on 20×20 μm² (256×256 pixels) areas in multi-frames acquisition mode with a dwell time of 33 ms per frame. For the analysis of the Sd#1 residue, the 4 detectors were set to detect simultaneously CH⁻, CD⁻, ¹²C¹⁴N⁻ and ¹²C¹⁵N⁻ secondary ions. For the Sd#2 residue, we used 3 detectors collecting CH⁻, CD⁻, ¹²C¹⁴N⁻ secondary ions and the last one, set at *m/z*=27, was set to a peak switching mode, alternatively counting ¹²C¹⁵N⁻ and ¹³C¹⁴N⁻ secondary ions. Thereby, we acquired quasi-simultaneous maps of ¹²C¹⁵N⁻ and ¹³C¹⁴N⁻ emissions, allowing a direct comparison of the hydrogen, carbon and nitrogen isotopic spatial variations. We performed additional measurements of ¹³C/¹²C ratios using both ¹³C¹⁴N⁻/¹²C¹⁴N⁻ and the ¹³C¹²C⁻/¹²C₂⁻ secondary ions ratios to ensure that the contribution of ¹¹B¹⁶O⁻ to the ¹³C¹⁴N⁻ signal at *m/z*=27 was negligible. We performed 5 maps on Sd#1 and 9 maps on Sd#2. On each analysis, about 300 consecutive frames were acquired prior to the apparition of large charging effects observed due to the erosion of the residue and the insulating nature of the ZnSe windows.

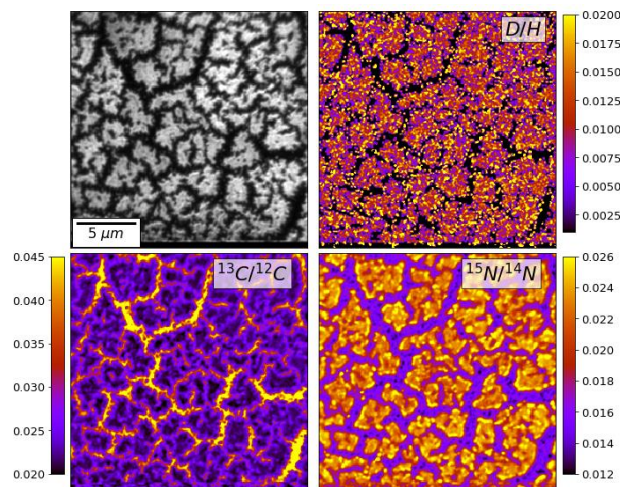


Figure 2. Isotopic ratio images on a same 20×20 μm² zone of the Sd#2 residue obtained with D, ¹⁵N, and ¹³C labeled ices. From top left to bottom right: the ¹²C¹⁴N⁻ direct image, D/H, ¹³C/¹²C and ¹⁵N/¹⁴N ratio images.

Results: The organic residues formed by the irradiation of the ices mixture tend to concentrate in micron-scale “islands” that contrast with “valleys” where the ¹²C¹⁴N⁻ ion emission is much lower (Figure 2, top-left). The low bulk abundance of D in the initial ices resulted in rather large statistical variations on the D/H images.

The behavior of the D/H and ¹⁵N/¹⁴N ratios were found similar for both Sd#1 and Sd#2 samples. D/H and ¹⁵N/¹⁴N isotopic ratios exhibit higher values on the material from the islands than in the valleys (Figure 2, top and bottom right). The matter from the islands exhibits ¹⁵N/¹⁴N spatial variations. Such variations were previously reported in D/H [7]. These experiments thus indicate that the irradiation of a D- and ¹⁵N-labeled ice sandwich forms heterogeneous units in D and ¹⁵N. The D-rich and ¹⁵N-rich units obtained through the irradiation appear to behave similarly. The D/H and ¹⁵N/¹⁴N ratios remain stable along the 300 consecutive frames.

On the Sd#2 residue, the spatial repartition of the ¹³C enrichments follows a pattern opposite to that of D and ¹⁵N : the valleys exhibit larger ¹³C/¹²C ratios than the islands (Figure 2, bottom left). The sequential evolution of the ¹³C/¹²C ratios with the frames indicates that the ¹³C-rich material is mostly concentrated in a layer of matter in the organic residue located below its surface, suggesting that the mixing of the carbon atoms from the ¹³CO ice layer was not as extensive as that of hydrogen and nitrogen atoms from the ¹⁵N₂-CD₄ ices. Additional ¹⁶O⁻ NanoSIMS measurements indicate that ¹³C and ¹⁶O are spatially correlated.

The marked difference between the D/H, ¹⁵N/¹⁴N and ¹³C/¹²C images suggest that, during the residue formation process, carbon atoms had a lower diffusion rate than hydrogen and nitrogen atoms, when initially present as ¹³CO, CD₄ and ¹⁵N₂, respectively. These results confirm that the organics resulting from the irradiation of complex ice mixture can keep a memory of the isotopic heterogeneities of the initial ices. The isotopic heterogeneities observed in UCAMMs may therefore provide clues on the isotopic composition of the complex ices layers at the surface of their parent bodies and underline the diversity of the organic phases in UCAMMs.

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