ISOTOPIC ANALYSES OF ION IRRADIATION-INDUCED ORGANIC RESIDUES, CLUES ON THE FORMATION OF ORGANICS FROM UCAMMS. J. Rojas1, J. Duprat1, E. Dartois2, T-D Wu2, C. Engrand1, B. Augé2, J. Mathurin1, B. Guerin1, J-L. Guerquin-Kern1, Ph. Boduch2, H. Rothard3. 1 Univ. Paris-Saclay, CNRS, IJCLab, 91405 Orsay, France. (Julien.Rojas@csnsm.in2p3.fr); 2 Univ. Paris-Saclay, CNRS, ISMO, 91405 Orsay, France. 3 Institut Curie, PSL Research University, INSERM, U1196, 91405 Orsay, France. 4 IPAG UGA/CNRS Grenoble France. 5 CIMAP (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 isotopically 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).

The ices sandwiches were irradiated at 8K with 33 MeV Ni9+ ions up to a fluence of 1015 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 sublime 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-
rganic 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 20x20μm² (256x256 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, 12C18N and 13C15N 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/12C12 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 20x20 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 13C14N 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, CD3 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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References: