ON THE ORIGIN OF ORGANICS IN ULTRACARBONACEOUS ANTARCTIC MICROMETEORITES (UCAMMS), IRRADIATION OF N-RICH ICES IN THE OUTER SOLAR SYSTEM.

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Introduction: The origin of interplanetary organic matter (OM) is still debated, considering either a direct heritage from the parent molecular cloud or processes in the solar protoplanetary disk. Large hydrogen fractionation, i.e. deuterium (D) excesses, can result from ion-molecule reactions at low temperature. Such reactions can produce molecular reservoirs with extreme D/H ratios (e.g. H_2D^+), that may be transferred to other gas phase molecules then to ices and, eventually, to refractory organic phases [e.g. 1]. Most approaches consider that the high D/H component result from ion-molecule reactions at early stages (i.e. prior planetary formation) in the low temperature and dense gas-phase of the protosolar cloud or in the outer regions of the protoplanetary disk [2,3]. Some recent studies showed that, more limited, D enrichments may also result from intense irradiation of organics by electrons or X-rays [4-6].

Samples & methods : It is possible to recover from Antarctic ice and snow Ultra-Carbonaceous Antarctic Micrometeorites (UCAMMs) that exhibit exceptional OM concentrations associated with extreme D excesses [7,8]. Deciphering the D enrichment mechanism of the OM of UCAMMs can help placing constraints on the formation process of this specific interplanetary organic matter.

Formation of organic matter can occur at later stages of solar system evolution, when small bodies such as asteroids or comets are already formed. The irradiation by Galactic Cosmic Rays (GCR) of the (sub-)surface of icy objects can explain the characteristics of specific organic components observed in carbon rich interplanetary dust such as UCAMMs [9,10]. The D/H ratio imaging performed on UCAMMs fragments reveals the spatial heterogeneities of the D excesses and the presence of distinct OM components (e.g. Fig 1 and [8,11]). A major component of UCAMM OM also exhibit N/C ratio substantially higher than that observed in insoluble organic matter (IOM) or bulk analysis from chondrites [9, 12-15]. A recent IR and Raman survey of eight UCAMMs confirmed that the OM components observed in UCAMMs are different from that of IOM extracted from carbonaceous chondrites [15]. The fact that some UCAMM OM components exhibit high N/C ratio (similar or even above the inferred value for the interstellar medium) while containing less O than meteoritic IOM requires a specific process involving the incorporation of substantial amounts of N in their organic component in a specific O poorer environment. This formation reservoir of UCAMMs has to be highly depleted in minerals to explain the unusually high C/Si of these particles.

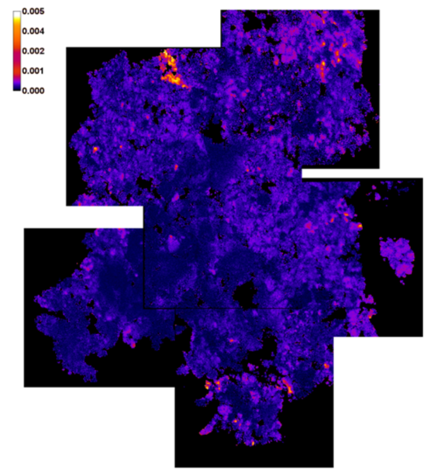

Figure 1 : Mosaic of NanoSIMs maps of the D/H ratio in an UCAMM fragment (DC94). Each square is 50 x50 µm^2.

Large reservoirs of N_2 and CH_4 ices occur at the (sub-)surface of remote icy objects, as recently imaged by the New-Horizon space probe [16]. These ices endure irradiation by GCR. Recent experiments performed at the heavy ion accelerator in GANIL (Caen, France) demonstrated that irradiation of N_2-CH_4 ices by such high-energy ions produces a N-rich refractory organic residue that could be the precursor of the OM observed in UCAMMs [10]. We pursued these experiments to: i) evaluate the D-enrichment levels induced by the irradiation of ices starting with a normal isotopic composition, and ii) study the characteristic D/H spatial heterogeneities in an organic residue produced by irradiation of an ice mixture including an initial D-rich layer. These results are part of an article by Augé et al. in preparation [17].

Irradiation experiments were performed at GANIL using the new experimental set-up IGLIAS [18] consisting of an ultra-high vacuum chamber coupled to a cryogenic sample holder. Ice samples were deposited from CH_4 and N_2 gas condensation on IR-transparent windows. The first organic residue was obtained from irradiation of N_2-CH_4 (90:10) ices at 10K and exposed to 92 MeV Xe ion beam. The D/H ratio of the CH_4

molecule of this first sample was measured and had a value of (126±1)x10^{-6} (i.e δD_{CH4}=-189±2‰) slightly below the V-SMOW value. The second ice sample consisted of a very thin layer of CD_4 ice deposited between two thicker layers of N_2-CH_4 (90:10) ices. It was exposed to 88 MeV Xe ion beam. The initial bulk D/H ratio of the D-rich ice sample (D/H_{Ice2} = 0.08 ± 0.02) was inferred using the integrated absorbance of methane and heavy methane IR bands.

Both mixtures were irradiated with a similar total dose of 19 eV.molecule^{-1}, corresponding to about 100 million years of exposure to GCR in the outer solar system. After irradiation of the ices, a slow warming-up was performed to room temperature, and the residues were transferred under vacuum for NanoSIMS analyses at Institut Curie in Orsay. The samples were covered with 20 nm of gold for charge evacuation. The D/H was measured from CD^-/CH^- ratio imaging using a primary Cs^+ ion beam at 16 keV using the high mass resolution protocol detailed in [19]. Multi-stack scanning images were acquired over a field of view of 60x60 µm^2 area, with a definition of 256 x 256 pixels. The probe dwell time was 0.5 ms per pixel and the typical counting rate for CH^- was 50 000 cs^{-1}. The instrumental mass fractionation calibration was obtained using the procedure and the standards described in [20].

Results & Discussion : The D/H ratio of the residue obtained after irradiation of the first ice sample (consisting in non-isotopically labelled N_2-CH_4 ices) revealed moderate D enrichment relative to V-SMOW value (δD_{Res1}=150±100 ‰, i.e D/H_{Res1} = (180 ± 20) x10^{-6}). As the initial ice was slightly depleted in D, this result indicate that the upper limit on the isotopic fractionation induced by irradiation is probably at most a few hundred ‰ (about 400‰). Although heavy ion irradiation may have induced a moderate increase of the D/H ratio in the organic refractory molecules, the resulting D/H ratio remains much smaller than that usually observed in D-rich components of interplanetary OM and is not compatible with the large D-excesses observed in interplanetary dust particles or UCAMMs organics, implying that their hydrogen fractionation must be related to another process.

The second sample (i.e the residue resulting from the D-rich ice mixture) does exhibit large D-enrichments and pronounced D/H spatial heterogeneities (Fig. 2). The average D/H ratio of the residue is D/H_{Res2} = 0.11 ± 0.01 that is, as expected, compatible with that of the original ice mixture (D/H_{Ice2}). However, large D/H heterogeneities are observed at the micron scale in this residue (Fig 2) demonstrating that that large spatial isotopic heterogeneities can result from irradiation of layers of ices with different D/H ratios. The fact that the residue exhibits such micron-sized D-rich areas make irradiation of heterogeneous ices a promising process to reproduce the D/H ratio distribution observed in the OM of UCAMMs. This indicates that organics with highly heterogeneous D/H ratios can be obtained by irradiation of ices resulting from condensation of different gaseous reservoirs with distinct hydrogen isotopic composition at the surface of remote parent bodies from the outer solar system.

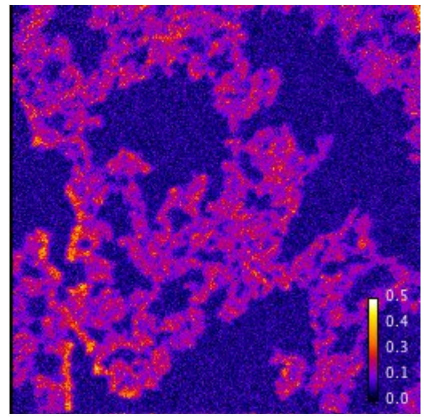

Figure 2 : D/H ratio NanoSIMS image of the organic residue obtained by irradiation of an ice mixture including a D-rich layer [17]. The size of the image is 60x60 µm^2.

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References: [1] Aikawa, Y., et al. *A&A*. 2002. 622-632.; [2] Remusat, L., et al., EPSL 2006. **243**: 15-25.; [3] Alexander, C.M.O.D., et al. Chemie der Erde / Geo., 2017. **77**: 227-256.; [4] De Gregorio, B.T., et al., GCA 2010. **74**: 4454-4470.; [5] Laurent, B., et al., Nature Com. 2015. **6**.; [6] Gavilan, L., et al., ApJ 2017. **840**.; [7] Nakamura, T. et al., Meteoritics, 2005. **40** Suppl #5046.; [8] Duprat, J., et al., Science 2010. **328**: 742-745; [9] Dartois, E., et al., Icarus 2013. **224**: 243-252; [10] Augé, B., et al., A&A 2016. **592**; [11] Bardin, N., et al., LPSC 2014. **45**: 2647; [12] Yabuta, H., et al., LPSC 2012. **43**: 2239; [13] Yabuta, H., et al., M&PS Suppl., 2012. **75**; [14] Yabuta, H., et al., GCA 2017. **214**: 172-190; [15] Dartois, E., et al., A&A 2018. **609**; [16] Grundy, W.M., et al., Science, 2016. **351**.; [17] Augé, B., et al., A&A 2019. **in prep**.; [18] Augé, B., et al., Rev. of Sci. Instr. 2018. **89**.; [19] Slodzian, G., et al., M&M 2014. **20**: 577-581 and NIMB 2017. **412**: 123-173; [20] Bardin, N., et al., IJMS 2015. **393**: 17-24.