PROBING THE ISOTOPIC COMPOSITION OF COMETARY ORGANIC MATTER WITH ULTRA-CARBONACEOUS ANTARCTIC MICROMETEORITES: A NANOSIMS STUDY. J. Rojas[1], J. Duprat[2], L. R. Nittler[3], E. Dartois[4], C. Engrand[1], N. Bardin[1], B. Guerin[1], L. Delauche[1], S. Mostefaoui[2], L. Rémusat[2], R. M. Stroud[5], T-D Wu[6]. [1]Univ. Paris-Saclay, CNRS, IJCLab, 91405 Orsay, France (Julien.Rojas@ijclab.in2p3.fr); [2]IMPMC, CNRS, MNHN, Sorbonne Univ., 75005 Paris, France [3]Earth and Planets Laboratory, Carnegie Institution of Washington, Washington, DC 20015, USA, [4]Univ. Paris-Saclay, CNRS, ISMO, 91405 Orsay, France, [5]Naval Research Laboratory, Washington, DC 20375, USA, [6]Institut Curie, PSL Research Univ., INSERM, U1196, 91405 Orsay, France.

Introduction: Ultracarbonaceous Antarctic micrometeorites (UCAMMs) are carbon-rich sub-millimeter particles that have been identified independently in the French and Japanese Antarctic micrometeorite collections [1, 2]. The low abundance of minerals and the high content of organic matter (OM) in UCAMMs [3] indicate that these objects originate from specific organic-rich parent bodies, most probably from the surface of cometary objects [4].

Laboratory experiments have demonstrated that irradiation of N_2-CH_4 ice mixtures (that are relevant to cometary ice mantles) by high energy heavy ions produces an organic residue with an infrared signature similar to that of UCAMMs' OM [5]. It is thus possible that Galactic Cosmic Ray (GCR) irradiation of N-rich ices at the surface of small icy bodies led to a refractory organic crust, after sublimation of the ices, with the chemical characteristics of UCAMMs. The study by Augé et al. [6] showed that this irradiation process cannot induce the high D/H values observed in UCAMMs. We thus proposed that the extreme D/H values in UCAMMs are rather inherited from the parent chemical (ice) reservoirs [6].

UCAMMs allow investigation of a pristine OM, most probably originating from the outer solar system, and poorly sampled by other interplanetary objects. The study of UCAMMs can thus shed light on the chemical and isotopic composition of volatile phases trapped in cometary ice mantles. We present here a comprehensive study of the H, N and C isotopic compositions on 6 fragments of 4 different UCAMMs.

Samples and method: UCAMMs DC06-05-94 (DC94), DC06-07-18 (DC18), DC06-14-309 (DC309) and DC06-04-43 (DC43) presented hereafter belong to the Concordia collection and were collected in ultra-clean snows around the Dome C station, Antarctica [7]. They were fragmented into several pieces and characterized by secondary electron microscopy and energy dispersive X-ray spectra (SEM/EDX). The isotopic imaging of these samples was performed with the NanoSIMS instruments at the Carnegie Earth and Planets Laboratory (EPL), the Museum national d'Histoire naturelle (MNHN) and the Institut Curie (IC/LMI). A fragment of UCAMM DC94 was crushed on a gold foil (final size ≈125×125µm²) and analyzed by NanoSIMS at MNHN and IC. Carbon isotopic data were acquired by collecting $^{12}C^-$ and $^{13}C^-$ ions with a primary Cs^+ beam of 1 pA. Nitrogen and hydrogen data were derived from the collection of $^{12}C^{14}N^-$, $^{12}C^{15}N^-$, $^{12}C_2H^-$, $^{12}C_2D^-$ ions with an 8-12 pA Cs^+ ion probe. The instrumental mass fractionations (IMF) were controlled with a type III kerogen, polystyrene standards and the natural anthracite DonH8 [8].

A fragment of UCAMM DC309 was embedded in sulfur and ultramicrotomed. A thin slice of DC309 was subsequently deposited on a diamond cell and slowly annealed to 50°C to remove the remaining sulfur. A 40 nm thick gold coating was added onto the slice to ensure proper charge evacuation during the NanoSIMS analyses. DC309 was previously characterized by IR nanospectroscopy (AFM-IR) [9]. The DC43 sample was prepared by pressing a fragment in a dedicated diamond cell and subsequently coated with a 20 nm gold layer. The 3 fragments of DC18 were prepared by crushing them on a gold foil. DC309, DC43 and DC18 were analyzed with the NanoSIMS at EPL, using a 10 µA Cs^+ primary beam. Hydrogen, carbon and nitrogen isotopic compositions were measured with the H^-, D^-, $^{12}C_2^-$, $^{12}C^{13}C^-$, $^{12}C^{14}N^-$, $^{12}C^{15}N^-$ ions. The IMF was controlled with an in-house standard $C_{30}H_{50}O$, insoluble organic matter (IOM) from CR chondrite Queen Alexandra Range 99177, SiC and Si_3N_4 standards.

Results and discussion: The H, N and C isotopic compositions are reported using the usual δ-notation as deviations from the standard mean ocean water D/H (V-SMOW), the atmospheric $^{15}N/^{14}N$ (Air) and the Pee-Dee belemnite $^{13}C/^{12}C$ (PDB). The bulk H, N and C isotopic compositions of the 4 UCAMMs, plotted on Fig. 1 (stars) and Fig. 2 (triangles), are substantially different from one another. Measurements on specific regions of interest (ROIs, on Fig. 1) show isotopic variations at scales of about 1-50 µm within individual UCAMM.

The bulk compositions of DC309 and DC18 are δD ≈ 6800‰, $\delta^{15}N$ ≈ -120‰, $\delta^{13}C$ ≈ 30‰ and δD ≈ 950‰, $\delta^{15}N$ ≈ -120‰, respectively. No ^{13}C data are available for DC18. DC309 and DC18 are characterized by a low bulk $\delta^{15}N$ i.e. lower than values commonly reported in extraterrestrial OM [10-12]. The bulk $\delta^{15}N$ and $\delta^{13}C$ of DC309 are close to that measured in a chondritic-porous IDP (i.e. CP-IDP "Eliot", hatched circle in Fig. 2) for which a cometary origin was proposed [12].

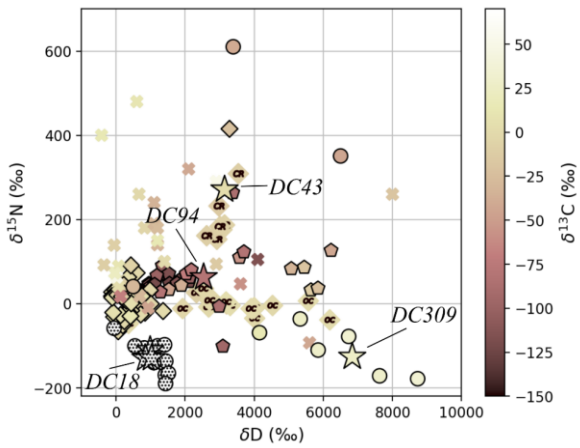

Fig. 1: Bulk δD, δ^{15}N and δ^{13}C measured in 4 UCAMMs (stars) compared with values from IDPs (crosses, [11]) and meteoritic IOM (diamonds, [10]). Measurements on specific ROIs are plotted with pentagons (DC94), hexagons (DC43), octagons (DC309) and circles (DC18). The black to yellow color scale indicates the δ^{13}C value. CR and OC stands for CR chondrites and ordinary chondrites, respectively [10].

The bulk composition of DC94 is δD ≈ 2500‰, δ^{15}N ≈ 60‰, comparable with that of several IOMs and IDPs while its δ^{13}C ≈ -90‰ is strikingly lower than commonly observed. Comparable δ^{13}C values are reported in some IDPs [11] but in less spatially extended areas. DC43 has δD ≈ 3100‰, δ^{15}N ≈ 270‰ and δ^{13}C ≈ -10‰, similar to the isotopic composition of the IOM extracted from CR chondrites [10].

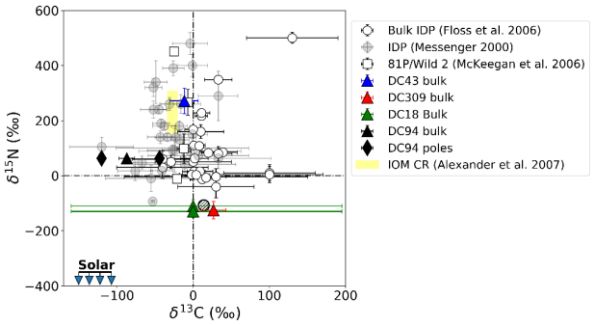

Fig. 2: Bulk δ^{13}C and δ^{15}N measured in 4 UCAMMs (triangles) compared to measurements on IDPs [11, 12], IOM [10] and grains from 81P/Wild 2 [13]. The hatched circle stands for the CP-IDP Eliot that share a very similar texture and isotopic composition with DC309. Black diamonds indicate two distinct poles observed in DC94. The solar composition is plotted for comparisons [14].

Correlations of H, N and C isotopic heterogeneities. The isotopic imaging on ROIs within individual UCAMMs reveals correlations at a 1-50 µm scale between δD and δ^{15}N in DC309 and δD and δ^{13}C in DC94. Laboratory experiments showed the possibility of transferring isotopic heterogeneities from an irradiated ice film to the induced refractory residue [6, 15]. Micron scale isotopic heterogeneities in UCAMMs could thus result from isotopic heterogeneities in their ice precursors that were irradiated by GCR ions.

Conclusion: The NanoSIMS analyses of the OM in UCAMMs reveal a diversity of H, N and C bulk isotopic compositions. Chemical data previously acquired on UCAMMs by STXM-XANES [16] led to the identification of 3 types of OM within UCAMMs, with one phase characterized by high N/C ratios, up to about 0.2 (type III in [16]). The OM of DC309 and DC18 appears to be N-rich (N/C ≈ 0.07-0.17) and ^{15}N-depleted while the OM of DC94 and DC43 has a less N-rich composition (N/C ≈ 0.04-0.05) and an isotopic signature closer to that of IDPs and IOM from meteorites. These two end-members (Fig. 2) are probably representative of two kinds of OMs formed under distinct local conditions in the disk. N and C isotopic fractionation is predicted to occur within the evolving protoplanetary disk according to numerical models [17, 18]. The isotopic signature of UCAMMs may reflect the composition of different chemical species existing at this stage of evolution, preserved under the form of ice mantles at the surface of their parent bodies. Investigating local variations of the OM isotopic composition can thus help to understand the isotopic diversity of the precursor ices from which these specific cometary organic components have formed. The comparison of these objects with the surface samples from asteroids Ryugu and Bennu, returned by the Hayabusa2 and OSIRIS-REx missions, will help to better understand the family bonds between asteroids and comets and the origin of their OM.

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