THE ISOTOPIC DIVERSITY OF ULTRACARBONACEOUS ANTARCTIC MICROMETEORITES, A COUPLED NANOSIMS AND AFMIR STUDY

J Rojas, J Duprat, L R Nittler, J Mathurin, E Dartois, C Engrand, N Bardin, A Dazzi, A Deniset-Besseau, M Godard, et al.

THE ISOTOPIC DIVERSITY OF ULTRACARBONACEOUS ANTARCTIC MICROMETEORITES, A COUPLED NANOSIMS AND AFMIR STUDY. J. Rojas[1], J. Duprat[1], L. R. Nittler[2], J. Mathurin[1], E. Dartois[3], C. Engrand[1], N. Bardin[1], A. Dazzi[4], A. Deniset-Besseau[4], M. Godard[1], J-L. Guerquin-Kern[6], B. Guerin[1], S. Mostefaoui[7], L. Rémusat[7], R. M. Stroud[5], T-D Wu[6]. [1]Univ. Paris-Saclay, CNRS, IJCLab, 91405 Orsay, France (Julien.Rojas@csnsm.in2p3.fr); [2]Department of Terrestrial Magnetism, Carnegie Institution of Washington, Washington, DC 20015, USA, [3]Univ. Paris-Saclay, CNRS, ISMO, 91405 Orsay, France, [4]Univ. Paris-Saclay, CNRS, LCP, 91405 Orsay, France, [5]Naval Research Laboratory, Washington, DC 20375, USA, [6]Institut Curie, PSL Research Univ., INSERM, U1196, 91405 Orsay, France. [7]IMPMC, CNRS, MNHN, Sorbonne Univ., 75005 Paris, France.

Introduction: Antarctic MicroMeteorites (AMMs) from the Concordia collection are collected in the snow of the central regions of Antarctica within the 20 to 500 µm size range [1]. UltraCarbonaceous AMMs (UCAMMs), accounting for about 1% of the AMMs, are mainly composed of nitrogen and deuterium-rich organic matter [2-5]. The UCAMMs characteristics suggest that they originate from the outer regions of the solar system [3, 6]. UCAMMs are also identified in Japanese collections [4, 5], one UCAMM from the Dome Fuji collection do not exhibit large deuterium excesses [5].

We present here the results from NanoSIMS studies on two UCAMMs from the Concordia collection: DC16-14-309 (hereafter DC16-309) and DC06-05-94 (hereafter DC06-94). DC16-309 was also recently studied to compare its isotopic heterogeneities with the chemical composition of organic materials measured by STXM-XANES/TEM [7] and AFM-IR [8, 9].

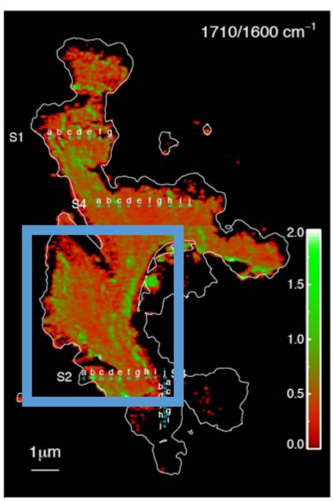

Figure 1: AFM-IR mapping of UCAMM DC16-309 showing the heterogeneity of the C=O/C=C ratios [8]. The blue zone is that analyzed by NanoSIMS.

Samples & methods: One fragment of UCAMM DC16-309 was embedded in sulfur, ultramicrotomed and the sections deposited on a diamond window. Figure 1 shows an AFM-IR image of fragment DC16-309b indicating the ratio of the 1710 cm^{-1} carbonyl (C=O) to the 1600 cm^{-1} (C=C) absorption bands [8]. The high spatial resolution of the AFM-IR technique allows identification of significant variations in this ratio at the sub-micron scale. After AFM-IR analysis, the sample was coated with 40 nm of gold for NanoSIMS analyses at the Carnegie Institution. The Cs^+ primary beam (10 pA) was rastered over 5×5 µm^2 and 128×128 pixel images were recorded with a dwell time of 2 ms/px. The hydrogen isotopic composition of DC16-309 was measured with the H^- and D^- secondary ions. A correction of the instrumental mass fractionation (IMF) was applied based on an in-house organic standard ($C_{30}H_{50}O$).

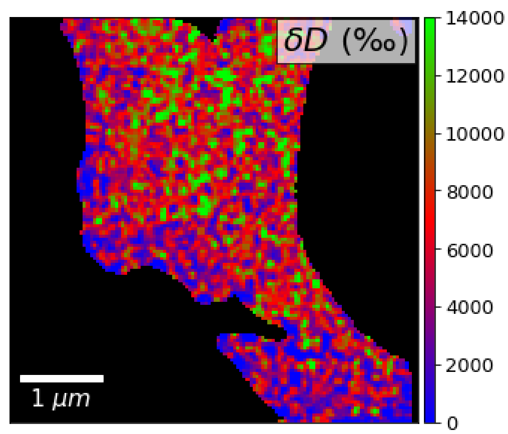

Figure 2: Hydrogen isotopic composition (expressed as δD with respect to VSMOW) mapping in a central zone of UCAMM DC16-309b (blue zone in Figure.1).

The D/H images of DC06-94 was measured on the NanoSIMS instrument at Institut Curie using the C_2D^-/C_2H^- ratio imaging, with a primary Cs^+ ion beam at 16 keV following the protocol detailed in [10]. Multi-frame scanning images were acquired over a 50×50 µm^2 area (512 × 512 pixels). The probe dwell time was 0.5 ms/px and the typical counting rate for C_2H^- was 154 000 c.s^{-1}. The IMF calibration was carried out according to the procedure described in [11] by the use of standards with known D/H values. The carbon isotopic data were obtained on the NanoSIMS instrument at

IMPMC/MNHN. The $^{13}C/^{12}C$ map were derived from the $^{13}C^-$ and $^{12}C^-$ secondary ion emissions, using a 16 keV Cs^+ primary beam rastered over a 20×20 µm² area (256×256 pixels). Multi-frame images were acquired with a dwell time of 1 ms/pix and the average counting rate for $^{12}C^-$ was 128 400 c.s^{-1}. A type III kerogen was used for the IMF calibration. In order to study correlations between the $^{13}C/^{12}C$ and D/H ratio an alignment procedure was applied based on C_2^- and $^{12}C^-$ images. The $^{13}C^-$ and $^{12}C^-$ images were rotated and their size slightly rescaled to match with that of C_2H^- and C_2D^-.

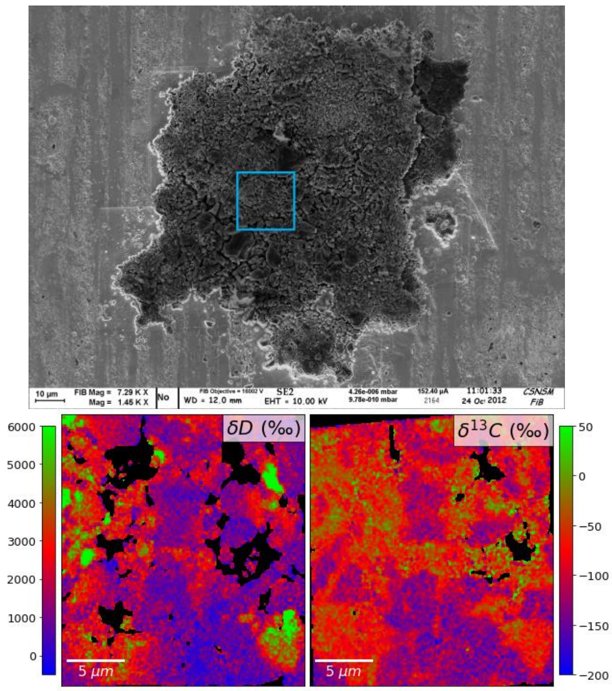

Figure 3. Top: secondary electron image of UCAMM DC06-94. Bottom: Deuterium and ^{13}C excess with respect to SMOW and PDB values measured by NanoSIMS in the blue area (top).

Results : *The DC16-309: a coupled AFMIR-NanoSIMS study.* Figure 2 shows the D anomalies in the zone reported in blue on the IR map of Figure 1. DC16-309 exhibits large D excesses with an average D/H ratio of $(1.1 \pm 0.6)\times10^{-3}$, i.e. $\delta D = 6100 \pm 3600‰$ relative to standard mean ocean water (SMOW). These large D/H ratios are comparable to that observed in previous UCAMMs from the Concordia collection [2, 3]. By contrast, there is no obvious correlation between the D-rich zones revealed by the NanoSIMS and the 1710/1600 cm^{-1} ratio from the AFM-IR image, suggesting that the D-rich component is not related to specific C=O/C=C ratios.

DC06-94 : NanoSIMS, $^{13}C/^{12}C$ – D/H correlations. The average D/H in the image (Figure 3) is D/H = $(4.45\pm1.48)\times10^{-4}$ (i.e. $\delta D = 1860 \pm 950$ ‰) that is in agreement with $(5.4\pm0.4)\times10^{-4}$ measured in the bulk of DC06-94 in previous studies [11]. The average $^{13}C/^{12}C$ of the image is $^{13}C/^{12}C = (1.02\pm0.03)\times10^{-2}$ (i.e $\delta^{13}C$ = -90 ± 28 ‰ with respect to the Pee Dee Belemnite value, Figure 3). The comparison of hydrogen and carbon isotopic maps reveals correlations between cold and hot D/H and $^{13}C/^{12}C$ zones. First, one can distinguish a "cold" pole characterized by the lowest D/H (i.e. $\delta D <$ 1000 ‰) that is also characterized by the lowest $^{13}C/^{12}C$ ratios, with $\delta^{13}C$ lower than -100 ‰. By contrast, the "hot" endmember characterized by the highest D/H (i.e. $\delta D >$ 1000 ‰) has the highest $^{13}C/^{12}C$, with $\delta^{13}C$ greater than -100 ‰. Within this "hot" zone, some areas exhibit extreme D-rich spots (with δD ranging from 4000 up to 6000 ‰). The $\delta^{13}C$ of these D-rich spots is not significantly greater than that of other parts of the hot zone.

Conclusion: Thanks to the coupling of NanoSIMS with the novel AFM-IR technique it is possible to perform extensive characterization of the organic matter on a same sample at tens to hundreds of nm spatial resolution, giving an insight on the link between isotopic enrichment and chemical composition. Although correlations are seen between the isotopic composition of different organics components in grains (hydrogen and carbon in DC06-94), these correlations are not common to all UCAMMs. The large D excesses appear to be common in most UCAMMs confirming a formation in the outer regions of the solar system. UCAMMs organics do not exhibit the same IR signatures, nor the same isotopic variations as those seen in primitive chondrites, confirming that UCAMMs are probing a different organic reservoir than that sampled by primitive chondrites.

Acknowledgements: This work is supported by ANR COMETOR, CNRS, LabEx P2IO, IN2P3, INSU, Univ. Paris-Saclay, DIM-ACAV and CNES. The micrometeorites were collected at Concordia Station with the support of the French Polar Institute (IPEV).

References

[1] Duprat, J., et al. (2007). *Adv. Space Res.*, 39, 605-611. [2] Duprat, J., et al. (2010). *Science*, 328, 742-745. [3] Dartois, E., et al. (2013). *Icarus*, 224, 243-252. [4] Nakamura, T., et al. (2005). *MAPS*, 40 Suppl., #5046. [5] Yabuta, H., et al. (2017). *GCA*, 214, 172-190. [6] Augé, B., et al. (2016). *A&A*, 592. [7] Guérin, B., et al. (2020). *This meeting.* [8] Mathurin, J., et al. (2019). *A&A*, 622, A160. [9] Mathurin, J., et al. (2020). *This meeting.* [10] Bardin, N., et al. (2015). *Int. J. Mass Spectrom.*, 393, 17-24. [11] Bardin, N., et al. (2014). *LPS XLV*, 2647.