CARBONACEOUS PHASES AND MINERALOGY OF ULTRACARBONACEOUS ANTARCTIC MICROMETEORITES IDENTIFIED BY C- AND N-XANES/STXM AND TEM. C. Engrand[1], K. Benzerara[2], H. Leroux[3], J. Duprat[1], E. Dartois[4], N. Bardin[1] and L. Delauche[1]. [1]CSNSM, CNRS/IN2P3-Univ. Paris Sud, Bât 104, 91405 Orsay Campus, France (Cecile.Engrand@csnsm.in2p3.fr), [2]IMPMC, CNRS/Univ. Pierre et Marie Curie, Case postale 115, 4 place Jussieu, 75252 Paris Cedex 05, France, [3]UMET, CNRS/Univ. Lille1, 59655 Villeneuve d'Ascq, France, [4]IAS CNRS/INSU-Univ. Paris-Sud, Bât. 121, 91405 Orsay Campus, France.

Introduction: Ultracarbonaceous Antarctic Micrometeorites (UCAMMs) represent a unique sampling of primitive extraterrestrial matter (e.g., [1, 2]). They are dominated by carbonaceous matter containing large amounts of nitrogen (N/C atomic ratios up to 0.20) and showing high D/H ratios [2, 3].

We have investigated the microstructure and composition of carbonaceous matter and minerals in two UCAMMs by XANES analyses at the C and N K-edges using synchrotron-based scanning transmission X-ray microscopy (STXM), and by transmission electron microscopy (TEM).

Samples and methods: Two fragments of UCAMMs deposited on carbon tape (not embedded in epoxy) were sectioned by FIB at IEMN (Lille). DC06-07-18 (hereafter DC18) and DC05-06-65 (hereafter DC65) were collected from Dome C snow in 2006 at the CONCORDIA station in Antarctica. The 200 nm thick FIB sections were first analyzed by C- and N-XANES STXM analyses on beamline 11.0.2 at the ALS in Berkeley. O-XANES STXM analyses were also acquired but are not presented here. After synchrotron analyses, analytical transmission electron microscopy (TEM) was performed on the FIB sections at UMET (Lille). Previous studies on a complementary fragment of DC65 have revealed a bulk D/H ratio of $7.2 \pm 3.2 \times 10^{-4}$, a bulk $\delta^{15}N = 95 \pm 30‰$, and a N-rich carbonaceous matter with an average atomic N/C ratio of 0.12 [3]. The complementary characterization of DC18 is in progress.

Results: TEM analyses of DC18 reveal a significant proportion of minerals included in the carbonaceous matter (Fig. 1a). The C-XANES map indicates that two kinds of carbonaceous matter are present in DC18: an abundant smooth phase (bulk lighter area in Fig. 1b), and a carbonaceous phase that is associated with the minerals (irregular darker areas at the top and bottom right of Fig. 1b – hereafter quoted as "granular carbonaceous phase"). The N-XANES map at 406.9eV reveals that the smooth phase is nitrogen-rich whereas nitrogen is barely detectable in the granular carbonaceous phase of the mineral-rich area (Fig. 1c). Figures 2a and 2b show a detail of the C-XANES and N-XANES maps around the mineral-rich bottom area. These maps were obtained by spectral deconvolution of hyperspectral data at the C and N K-edges, illustrating the 2 different kinds of carbonaceous matter observed. The corresponding C-XANES and N-XANES spectra (Fig. 2c and 2d) reveal numerous functional groups in varying proportions, corresponding to aromatic carbon (C=C) at 285eV, nitrile (C≡N) at 286.6 and 399.8eV, ketone (C=O) at 286.6eV, carboxyl (O=C–O) at 288.5eV, imine (C=N) at 399.8eV, and amide (O=C–NH_x) at 401.5eV. The 290.5eV absorption feature in the granular carbon could suggest the presence of carbonates, but this has to be confirmed.

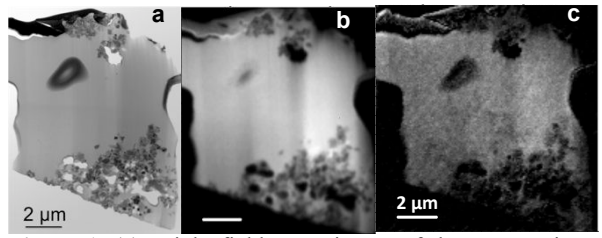

Figure 1: (a) Bright field TEM image of the FIB section of DC18 showing a significant abundance of minerals at the top and at the bottom right of the image; (b) C-XANES map of DC18; (c) N-XANES map of DC18. Vertical stripes reflect thickness variations of the FIB section.

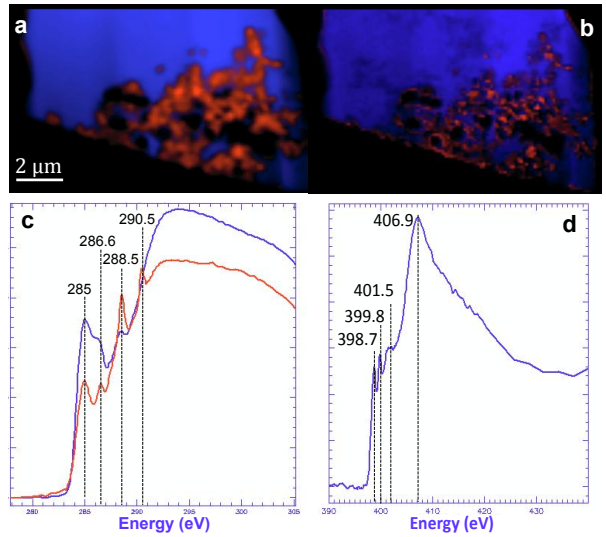

Figure 2: XANES study of DC18: (a & c) False color C-XANES map and typical spectra for the smooth carbon (in blue) and for granular carbon (in red). (b & d) False color N-XANES map and spectrum for smooth carbon in blue (the N abundance in the granular carbon is too low to identify the functional entities). The identification of functional groups at the C and N K-edges used the compilation by [4] (see text).

The mineralogy of DC18 is dominated by sub-µm sized Mg-rich olivines and pyroxenes, Ca-rich pyroxenes, Fe-Ni metal, Fe-sulfides and abundant GEMS inclusions (Glass with Embedded Metal and Sulfides - [5]) (Fig.3). It is compatible with that of other UCAMMs previously analyzed by TEM [6].

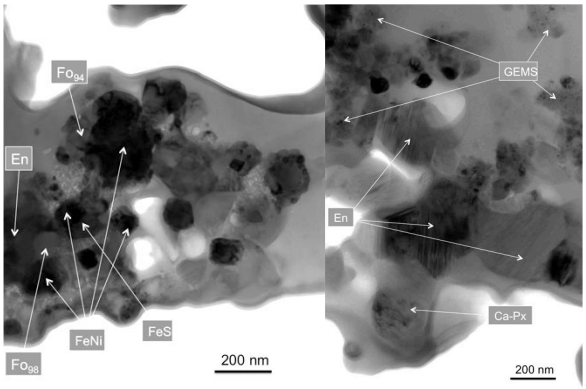

Figure 3: Bright field TEM images of DC18 showing in particular the large abundance of GEMS inclusions.

The TEM study of the DC65 FIB section (Fig. 4) revealed that the sample is constituted of two different carbonaceous phases without any embedded inorganic component, except for some dusty patches (arrows in Fig. 4) that are more S-rich (but with no Fe) than the surrounding carbonaceous phases. This very low mineral content is in good agreement with previous studies on another fragment of DC65 [3].

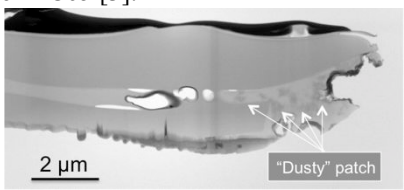

Figure 4: Bright field TEM image of the DC65 FIB section.

C- and N-XANES STXM maps of DC65 obtained by spectral deconvolution suggest the presence of three carbonaceous phases (Fig. 5): the smooth carbonaceous phase (Fig. 5c in red) contains higher amounts of N than that containing the dusty patches (blue and green in Fig. 5c). The phases shown in blue and green on Fig. 5c have the same N-XANES spectroscopic signature (Figs. 5d and 5f in blue).

For both DC18 and DC65, the smooth carbonaceous phase is characterized by aromatic carbon, high amounts of N (presence of imine, nitrile, and amide functional groups), and low amounts of oxygen in the form of ketone and carboxyl functions. In contrast, the granular carbonaceous phase in DC18 and in DC65 is associated with mineral compounds and is characterized by low nitrogen contents and high amounts of O-bearing functional groups (ketone and carboxyl).

Discussion: The XANES signatures at the C and N K-edges are compatible with those of Stardust Samples [4 and refs. therein], reinforcing the cometary origin of UCAMMs. Coupled TEM and C- and N-XANES maps in 2 UCAMMs allow to shed light on the close association of minerals and organics in well preserved cometary dust.

The large amount of GEMS inclusions, as well as the presence of Fe sulfides in DC18 stress the very good state of preservation of UCAMMs collected from snow. The presence of N-rich and N-poor carbonaceous phases in the 2 UCAMMs is in agreement with that reported by [7, 8] in one UCAMM from the Dome Fuji collection. In both DC18 and DC65, the smooth carbonaceous phase is N-rich and devoid of minerals. This phase may have been formed and processed by irradiation of N_2 and CH_4-rich ices at the surface of large bodies in the outer regions of the protoplanetary disk [3]. Averaged over the UCAMM fragment, the N-rich carbonaceous matter dominates the N-poor carbonaceous phases, which is compatible with the large N bulk content of UCAMMs analyzed so far by IR and NanoSIMS [3].

The N-poor carbonaceous phases in DC18 and DC65 are associated with mineral compounds (particularly for DC18). These minerals were formed and processed in the inner regions of the protoplanetary disk and later distributed up to the external regions by radial mixing [9, 10], suggesting that the N-rich and N-poor carbonaceous matter of UCAMMs may have formed by different mechanisms and/or in different locale in the protoplanetary disk.

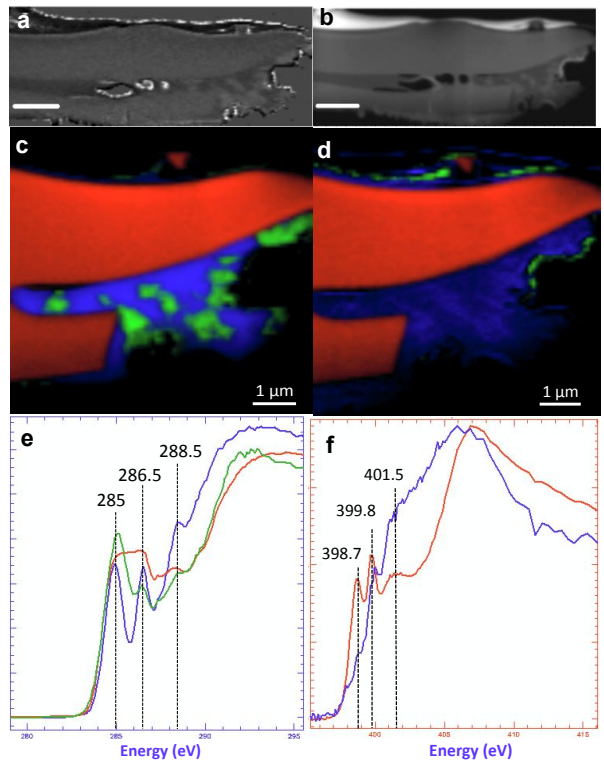

Figure 5: (a & b) C- and N-XANES maps of DC65 FIB section (scalebar is 2µm). (c & d) detail of C- and N-XANES map in false color showing 3 distinct phases for the C-XANES and 2 phases for the N-XANES map, with corresponding color-coded spectra (e & f).

Acknowledgments: We thank CNRS, ANR-2010-BLAN-0502 contract, DIM-ACAV, IPEV and CNES for support.

References: [1] Nakamura T., *et al.* (2005) *MAPS* **40 Suppl.**, #5046. [2] Duprat J., *et al.* (2010) *Science* **328**, 742-745. [3] Dartois E., *et al.* (2013) *Icarus* **224**, 243-252. [4] De Gregorio B.T., *et al.* (2011) *MAPS* **46**, 1376-1396. [5] Bradley J.P. (2013) *GCA* **107**, 336-340. [6] Dobrică E., *et al.* (2012) *GCA* **76**, 68-82. [7] Yabuta H., *et al.* (2012) *MAPS Suppl.* **75**, 5196. [8] Yabuta H., *et al.* (2012) *LPSC* **XLIII**, #2239. [9] Bockelée-Morvan D., *et al.* (2002) *A&A* **384**, 1107-1118. [10] Ciesla F.J. and Sandford S.A. (2012) *Science* **336**, 452-454.