INVESTIGATION OF ULTRACARBONACEOUS ANTARCTIC MICROMETEORITES BY ANALYTICAL TRANSMISSION ELECTRON MICROSCOPY. E. Dobrică[1], C. Engrand[1], H. Leroux[2], and J. Duprat[1], [1]CSNSM CNRS-Univ. Paris Sud, F-91405 Orsay Campus, France (Elena.Dobrica@csnsm.in2p3.fr), [2]LSPES CNRS-Univ. Sci. Techno., F-59655 Villeneuve d'Ascq, France.

Introduction: Despite the valuable data given by Wild 2 samples, our understanding of the conditions of cometary formation in the early solar system remain restricted. Ultracarbonaceous Antarctic Micrometeorites (UCAMMs) were identified in the CONCORDIA micrometeorite collection (2002, 2006) recovered from central Antarctic snow [1, 2]. UCAMMs are dominated by up to 85 vol% of carbonaceous material [3, 4] that exhibits large deuterium excesses [5]. They could represent cometary dust grains related to the CHON particles detected in comet Halley [6]. In this study we describe the mineralogy and petrology of 3 UCAMMs studied by transmission electron microscopy (TEM).

Samples and methods: Three UCAMMs (DC06-09-45, -19 and DC02-09-41, hereafter #45, #19 and #41) were identified according to their external aspect and their carbon content, by scanning electron microscopy (SEM) associated with energy dispersive X-ray spectroscopy (EDS). Ultramicrotomed sections of fragments of 2 particles (#45 - 53 µm, #19 - 58 µm) and of one entire sample (#41 - 48 µm) were studied using TEM. Grain compositions were obtained using EDS in the STEM configuration. The identification of minerals was based on chemical composition and electron diffraction patterns.

Results: All 3 UCAMMs are dominated by carbonaceous material in which are embedded small pockets (sizes ~1 µm) of mineral aggregates composed of silicates, Fe-Ni sulfides and metals, and amorphous material in diverse proportions. Within these aggregates, the iron sulfide sizes (avg. 90, 120 and 130 nm for #19, #41 and #45, respectively) are always smaller than that of silicates (avg. 175, 185 and 210 nm for #45, #19 and #41, respectively). Crystalline minerals (mostly Fe-Mg silicates) are abundant compared to amorphous material. The bulk compositions of the mineral assemblages are close to that of CI-chondrites, within a factor of 2. Olivines, pyroxenes, Fe sulfides and Fe-Ni metals are present in all UCAMMs but in different proportions. Low-Ca pyroxenes are always more abundant (4, 2 and 1.6 times) and larger (avg. 200, 220 and 260 nm) than olivines (avg. 165, 150, 170 nm) in #45, #19 and #41, respectively. The Fo content of olivines present a wide variation range with no preferential peak (#45 - Fo_{84-98}; #19- Fo_{59-100}; #41- Fo_{51-100}). Low-Ca pyroxenes present a wide composition range [Mg/(Mg+Fe) ratio] and several pronounced frequency peaks. UCAMM #45 (En_{57-100}) presents 2 frequency peaks at En_{92} and En_{100}, and #41 (En_{62-100}) at En_{96} and En_{100}. Particle #19 (En_{76-100}) shows only one frequency peak at En_{100}. Fe-Ni sulfides are dominated by low-Ni sulfides, but several small Fe-sulfides (40-90 nm) are Ni rich (up to ~24 at%). Kamacite and taenite (15 at%Ni) are found in all 3 samples but never in close association. Several differences were observed between two fragments of the same particle that we studied (#45 A and B). The first fragment (A) contains equilibrated silicates with Mg/(Mg+Fe) ratios ranging from 81 to 99, with a pronounced frequency peak around 89. The second fragment (B) contains unequilibrated minerals [Mg/(Mg+Fe) ratio 57-100]. Another difference between the 2 fragments is the grain size: #45A contains minerals twice smaller than #45B (A - avg. grain size 60 nm; B - 120 nm). Several Ca-rich pyroxenes and one perryite $(Ni_{5.0},Fe_{2.2})(Si_{2.2},P_{0.6})$ are found in fragment B. UCAMM #19 contains miscellaneous phases such as one enstatite whisker (En_{100}, 310 nm), ferrihydrite which occurs as rims of aggregates, one Mg-Al spinel, one Zn sulfide, Fe-Mn-Mg sulfides and several GEMS (Glass with Embedded Metal and Sulfides) embedded in the carbonaceous material. GEMS (70-345 nm, avg. 180 nm) are almost exclusively composed of nanometer-sized low Ni Fe-sulfides embedded in Mg-rich silicate glass. The bulk composition of 43 GEMS analyzed is chondritic for their major elements (within a factor of 2). All UCAMM GEMS fall in the S-rich region compared to GEMS in IDPs [7, 8]. In this sample #19 we also observed two adjacent composite objects with different compositions and mineralogy, embedded in the carbonaceous matter. One of them has a round shape resembling a micro-chondrule (380 nm diameter) with a porphyritic pyroxene-olivine (PPO) texture (Fig.1). It contains Mg-rich olivine (Fo_{99}) and pyroxene (En_{100}) in a glassy SiO_2-rich matrix. The second object is a polycrystalline equilibrated aggregate which contains olivine (Fo_{73-76}) and low-Ni iron sulfides (1 at%Ni). UCAMM #41 contains silicates enriched in minor elements. Glassy SiO_2-rich mesostasis is often seen between the crystalline grains. We identified one spheroid object resembling a chondrule with a porphyritic texture (373 nm) (Fig.2, a-d). It contains pyroxenes (En_{100}), low-Ni sulfides and kamacite (5 at%Ni), enclosed in a SiO_2-rich mesostasis. Pyroxenes occur as euhedral crystals with small inclusions of Fe-Ni metal. The micro-chondrule bulk com-

position is chondritic within a factor of 2 with the exception of Ni and S, which are 4 and 5 times more depleted than CI, respectively. The same #41 contains several aggregates composed of Fe-rich olivines and pyroxenes (typically Fo_{65} and En_{70}). One aggregate contains a large number of chromite crystals (20-95 nm) with euhedral habits (Fig.2, e-f). They are included in SiO_2-ich glassy mesostasis, next to Fe-rich olivines (Fo_{70-74}). The mesostasis is enriched in Al (5 at%), Fe (3 at%) and Ca (3 at%). Magnetite crystals are observed in this UCAMM.

Discussion: The mineral assemblages included in the carbonaceous matrix of these 3 UCAMMs show some similarities but also large differences. The UCAMMs contain abundant crystalline phases with a bulk chondritic composition. The high proportion of pyroxenes relative to olivines compared to carbonaceous chondrites may indicate that these samples were formed in a relatively reduced environment. All UCAMMs contain unequilibrated mineral assemblages with the exception of one fragment (A) of sample #45. Some UCAMMs contain oxidized phases, suggesting that the C-rich host collected different material formed under various oxidizing conditions. GEMS grains show similarities with those observed in IDPs which are considered to be the most primitive object of the solar system [9]. However, all GEMS in the UCAMMs are sulfur-rich when compared to GEMS in IDPs. This suggests that GEMS in UCAMMs may have undergone a sulfurization process [10] in the solar nebula in contrast to sulfur-poor GEMS in IDPs [7, 8]. Near-spherical shape objects similar to chondrules were observed in two UCAMMs (#19 and #41). The type 1 porphyritic pyroxene micro-chondrule in #41 presents a devitrified groundmass evidencing an event of heating and melting at subsolidus temperature (1430°C) followed by quenching. In these micro-chondrules, sulfur is 5 times more depleted than CI, but Fe-Ni sulfides are still present. This object probably evolved in an open system and experienced a peak temperature near the liquidus temperature (1550°C) [11]. Some mineral assemblages clearly displaying an igneous signature are likely fragments of chondrules, as observed in carbonaceous and ordinary chondrites [12]. Such small chondrules (250 nm) have already been observed in LL3 ordinary chondrites, although they are more Fe-rich compared to those observed in this #41 [13]. Fe-Ni metal is rare in UCAMMs like in the others cometary samples such as potentially cometary IDPs and Wild 2 samples [9, 14-16]. The abundance of sulfides compared to Fe-Ni metal may suggest that the samples have formed/evolved in a low H_2/H_2S environment [10].

Conclusion: Some mineral aggregates present in these UCAMMs have been processed in the inner solar nebula. They show similarities with what is observed in IDPs of probable cometary origin and with Stardust samples. The study of these particles of probable cometary origin reinforce the asteroid (carbonaceous chondrite)- comet continuum and supports the presence of large radial mixing in the early solar nebula.

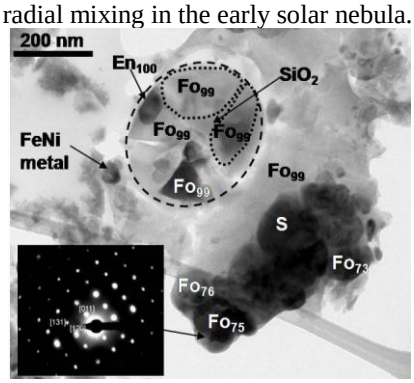

Figure 1. TEM bright field image of UCAMM DC06-09-19 showing the presence of a micro-chondrule (dashed line) containing Mg-rich olivines and pyroxenes in a glassy mesostasis (SiO_2). A Fe-rich metal was found close to it.

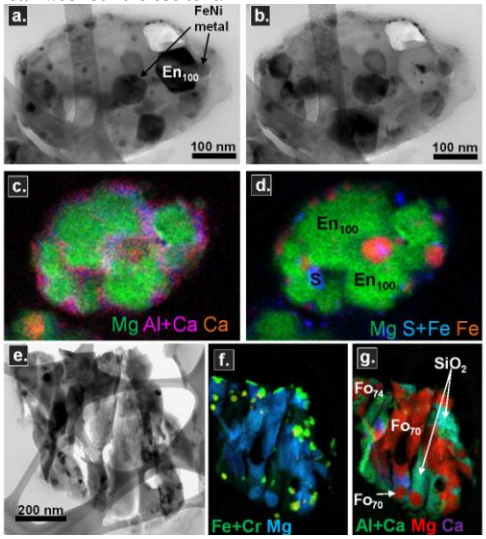

Figure 2. Bright field TEM images of 2 mineral aggregates from UCAMM DC02-09-41 (a, b-different tilts; and e) and stacked EDX elemental distribution maps for different elements (c-d, f-g; the color significations are different in each image).

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References: [1] Dobrică E., *et al.* (2009) *LPS* **XXXX**, #1534. [2] Duprat J., *et al.* (2007) *Adv. Space Res.* **39**, 605-611.[3] Nakamura T., *et al.* (2005) *Meteoritics Planet. Sci.* **40**, 5046.[4] Dobrică E., *et al.* (2008) *Meteoritics Planet. Sci.* **43**(7), A38-A38.[5] Duprat J., *et al.* (2009) *LPS* **XL**, #1724.[6] Lawler M.E. and Brownlee D.E. (1992) *Nature* **359**, 810-812.[7]Keller L.P. and Messenger S. (2004) *LPS* **XXXV**, #1985.[8] Keller L.P., *et al.* (2005) *LPS* **XXXVI**, #2088.[9] Bradley J.P. (1994) *GCA* **58**, 2123-2134.[10] Lauretta D.S., *et al.* (1998) *Meteoritics Planet. Sci.* **33**, 821.[11] Yu Y., *et al.* (1996) *Chondrules and the Protoplanetary Disk*.[12] Johnson C.A. and Prinz M. (1991) *GCA* **55**, 893-904.[13] Rubin A.E., *et al.* (1982) *GCA* **46**, 1763-1776.[14] Fraundorf P. (1981) *GCA* **45**, 915-937.[15] Chi M., *et al.* (2007) *LPS* **XXXVIII**, #2010.[16] Leroux H., *et al.* (2008) *Meteoritics Planet. Sci.* **43**(1-2), 97-120.