TRANSMISSION ELECTRON MICROSCOPY OF ULTRACARBONACEOUS ANTARCTIC MICROMETEORITES OF POSSIBLE COMETARY ORIGIN. E. Dobrică[1], C. Engrand[1], H. Leroux[2], J.-N. Rouzaud[3], 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, [3]Lab. de Géologie, ENS-CNRS, 75231 Paris Cedex 5 France.

Introduction: UltraCarbonaceous Antarctic Micrometeorites (UCAMM) are a new type of fluffy, fragile particles, exceptionally rich in carbon. The samples were collected at Dome C near CONCORDIA station, in central Antarctica [1]. These particles are dominated by a very large amount of carbonaceous material, with concentrations up to ~ 50 wt%, even larger than that of anhydrous IDPs [2]. They are similar to those described by Nakamura et al. 2005 [3]. Large deuterium enrichments up to 30 times the solar value have been reported in UCAMMs [4], and their high carbon contents could relate them to the CHON particles detected in comet Halley [5]. In this work we performed transmission electron microscopy (TEM) analysis on two UCAMMs to study the associated silicates and sulfide mineralogy of this primitive carbonaceous material in order to shed light on the formation and evolution of these particles.

Samples and analytical procedure: The samples are first classified according to their external aspect and their carbon content by analytical scanning electron microscopy (SEM and associated EDX). Chemical compositions were measured by electron microprobe at CAMPARIS (Univ. Paris VI Jussieu) at 15 kV and 10 nA. We have studied two ultracarbonaceous Antarctic Micrometeorites (UCAMMs) (DC06-09-119 and DC06-09-45) by analytical and high resolution transmission electron microscopy. Sample DC06-09-45 was mounted in epoxy (EMBed-812) and then sliced by ultramicrotomy. Thin sections were analyzed by TEM using a Tecnai G2-20 (LaB6 filament, 200 kV) equipped with EDX. Electron energy-loss spectroscopy (EELS) spectra have been acquired around the absorption edge of carbon (284 eV). A second UCAMM sample (DC06-09-119) was crushed between two glass slides. The powder was transferred onto C-lacey TEM support grids (Cu) for high resolution TEM characterization using a Jeol 2011 (200 kV).

Results and discussion: From a total of 31 fine-grained fluffy (FgF) AMMs, we have identified by SEM-EDX analysis five ultracarbonaceous particles that contain up to 50 wt% carbonaceous matter. The particles exhibit a fluffy texture with a high porosity. Their average size ranges from 40 to 275 µm. HRTEM investigations show that the carbonaceous matter is highly disorganized but non *stricto sensu* amorphous since this carbonaceous matter is made of nanometre sized misoriented graphene layers (Fig. 1). This observation is confirmed by EELS results and by Raman spectroscopy investigation [6]. Graphitic nanodomains with total sizes of ~1 000 nm^2, have been observed included in the amorphous-like carbonaceous material (~15 µm^2), but their abundance is insignificant with regard to the disorganized carbonaceous material.

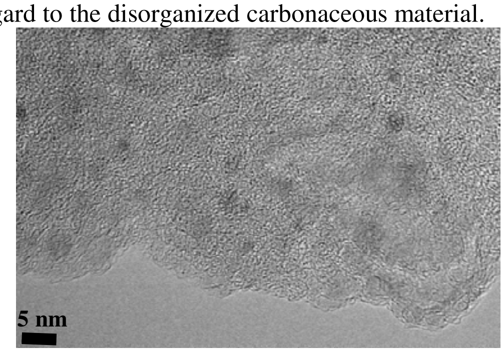

Figure 1: HRTEM image of UCAMM disordered, carbonaceous matter. The dark spots are nanometric crystals not yet identified.

UCAMMs contain up to five times more highly disordered, C-rich material, than crystalline phases. Mineral phases identified by SEM-EDX analysis include Mg-rich olivines and pyroxenes, anorthite, sulphides, Fe-Ni alloy and carbonates. In general, all carbonates are calcite grains and have euhedral shapes. The larger calcite crystal identified so far is ~7 µm in its longest dimension. Electron microprobe analysis revealed some low-iron, manganese-enriched (LIME) pyroxenes in an UCAMM (DC06-09-45), containing 1.7 wt% MnO. These Mn-rich minerals are surrounded by large enstatite crystals that contain less than 0.5 wt% MnO. LIME minerals are abundant in IDPs but extremely rare in other meteoritic objects. It was proposed that this type of minerals could form by condensation from a gas of solar composition [7].

TEM investigations show that UCAMMs contains small pockets of a complex mixture of fine-grained assemblages of minerals of ~1 µm in diameter, surrounded by an amorphous-like carbonaceous material. The grain that we sliced by ultramicrotomy was ~11 µm in diameter (Fig. 2). We have determined the average composition of the UCAMM mineral assemblages by summing the EDX measurements of large scanned areas (~19 µm^2). The element abundances for Mg, S, Cr, Fe and Ni are consistent with the CI composition [8]. These elemental abundances fall in the same range as that of Wild 2 samples [9]. UCAMMs are enriched in Mn and Ca relative to Wild 2 samples by a factor of 5 and 2, respectively [9].

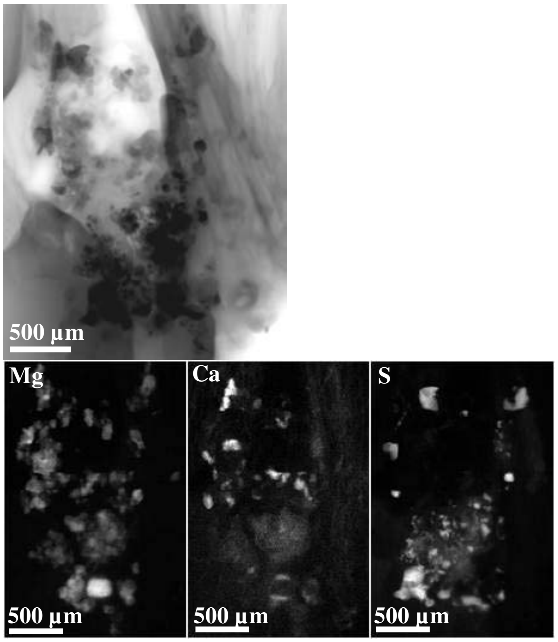

Figure 2: Bright-field STEM image (top) and EDX elemental distribution maps for Mg, Ca and S (bottom) of 07-08-06 (UCAMM) thin section. In general, the distribution of Mg and Ca correlate well with silicates (olivine, enstatite for the Mg map and diopside for Ca map) and S with Fe-Ni sulphides.

The mineral assemblages observed at the TEM scale consist of a fine-scale mixture of silicate, iron-sulfide and metal phases. The grain size ranges from 10 nm to 400 nm, with an average of ~80 nm. They represent only ~15 % in volume compared to the carbon-rich amorphous-like material. The silicates are highly dominated by crystalline phases, including olivine, low-Ca pyroxene and diopside. Fe-Ni sulphides are abundant, with sizes between 10 nm and 200 nm, and dominated by low-Ni iron-sulfides (Fig. 3). Only one Ni-rich sulphide (22 wt% Ni - pentlandite) was identified. The UCAMM compositions of sulphides, measured by STEM-EDX analysis are similar to that of micron-sized crystals measured by electron microprobe [10]. Fe,Ni alloy (kamacite) is present but rare (5x less abundant than sulphides).

Conclusion: UCAMM particles have no counterpart in all meteorites classes. They likely originate from the outer regions of the solar nebulae (i.e. of potential cometary origin). The particles studied by TEM consist of a highly disordered carbonaceous matrix containing clusters of complex fine-grained assemblages of minerals. Most of the small individual components are crystalline with dominant olivine, low-Ca pyroxene, diopside and iron-sulfide. Their sizes range from a few nanometers to half a micron in size and their average composition is close to that of CI-chondrites. The fine-grained assemblages, the disordered nature of the carbonaceous matter and their CI-like composition support the idea that these minerals are likely unprocessed material. The assemblages are close to what is encountered in Wild 2 material found into track walls in the aerogel collectors of the Stardust mission [9].

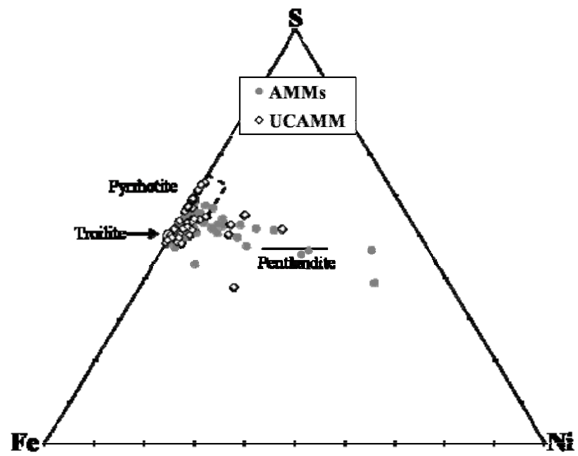

Figure 3: Fe-Ni-S ternary diagram (at.%) for sulphides enclosed in the carbonaceous matter of UCAMMs (open diamonds). The UCAMM data are compared with electron microprobe measurements of Fe-Ni sulphides in other samples mounted in polished sections (filled grey circles) [10].

The presence of carbonates and pentlandite enclosed in the amorphous-like carbonaceous matrix is puzzling since these phases are typical of aqueous alteration in meteorites. It has been shown recently that carbonates can form by non-equilibrium vapor phase condensation [11], and thus they could be the product of solar nebula processing in the gas phase [12]. The relative abundances of sulphides with regard to Fe, Ni alloys may suggest that the samples have formed/evolved, rapidly (~200 years) in an extremely rich H_2/H_2S gas mixtures environment [13]. The occurrence of LIME mineral phases, refractory minerals and carbonates within UCAMMs, with chemical signatures similar to asteroidal and cometary materials, support the idea that a large-scale dust mixing took place in the early solar nebula [14].

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