

A C-, N-, O-XANES/STXM AND TEM STUDY OF ORGANIC MATTER AND MINERALS IN ULTRACARBONACEOUS ANTARCTIC MICROMETEORITES (UCAMMs).

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Introduction: Ultracarbonaceous Antarctic Micrometeorites (UCAMMs) represent a unique sampling of pristine interplanetary dust from the outer regions of the solar system [1, 2]. They are dominated by organic matter with extreme D/H ratios [2] and a bulk abundance of nitrogen (N/C atomic ratios up to 0.2) higher than meteorite insoluble organic matter (IOM) [2, 3].

We investigated the microstructure and composition of the organic matter and embedded minerals in two UCAMMs using transmission electron microscopy (TEM) and X-ray absorption near edge structure (XANES) spectroscopy analyses at the C and N K-edges, in combination with synchrotron-based scanning transmission X-ray microscopy (STXM).

Samples and methods: The UCAMMs DC06-07-41 (hereafter DC41) and DC06-04-43 (hereafter DC43) were collected from Dome C snow close to the CONCORDIA station in Antarctica. The fragments were deposited on carbon tape, carbon coated and subsequently sectioned by Focused Ion Beam (FIB) milling at IEMN (Lille). The 100 nm thick FIB sections were first analyzed by XANES STXM at the C-, N- and O- K edges on the HERMES beamline at the synchrotron SOLEIL in Saclay. After synchrotron analyses, analytical TEM was performed on the same sections at UMET (Lille) using FEI Tecnai G2 20 and FEI TITAN Themis 300.

Results and discussion: DC41 is dominated by organic matter with dusty patches and μm -sized silicates. It is texturally similar to another UCAMM (DC65) analyzed in a previous work [4].

The organic matter of DC43 (Fig.1) contains μm -sized Mg-rich pyroxene aggregates, Fe-Ni metal, Ni-poor Fe sulfides and abundant Glass with Embedded Metal and Sulfides (GEMS - [5, 6]) inclusions (Fig.1b). The nature of these minerals is similar to those reported in previous TEM studies of UCAMMs, although the pyroxenes crystals observed in this fragment of DC43 are larger [7, 8].

Figure 2 shows a TEM view (a), a C-XANES map at 293.2eV (b) and a N-XANES map at 406.9eV(c) of one area in DC43. We identified three carbonaceous phases (see Fig 2a). Phases 1 and 2 appear as smooth

organic phases, while the organic matter of phase 3 contains dusty patches.

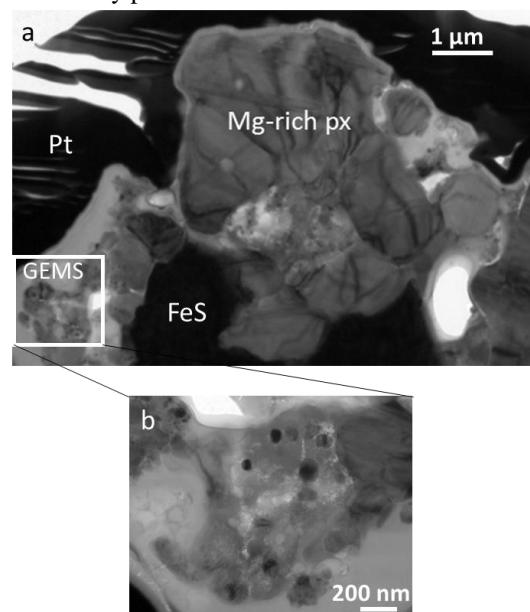


Figure 1 : a) large scale bright field TEM image of part of the DC43 fragment (Pt is platinum from the sample preparation); b) detail of GEMS embedded in DC43 organic matter.

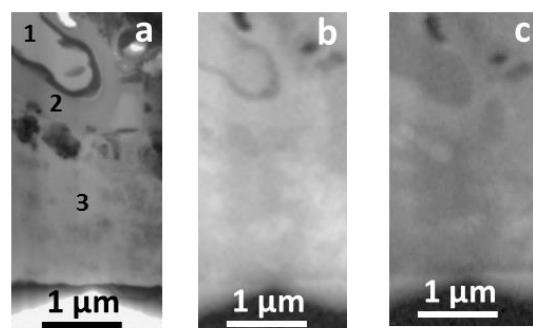


Figure 2 : (a) Bright field TEM image of the FIB section of DC43; (b) C-XANES map of DC43; (c) N-XANES map of DC43.

The N-XANES map shows that only phase 2 is nitrogen-rich whereas phases 1 and 3 are N-poor (Fig. 2c). Phases 1 and 3 share a similar C- and N-XANES

signature (Fig. 3 a and c) and differ by the presence of the dusty patches in phase 3. C- and N-XANES maps of DC41 also show organic phases similar to the DC43 phase 2 (N-rich) and 3 (N-poor with dusty patches). These results are consistent with those about organic phases observed in DC65 in a previous work [4].

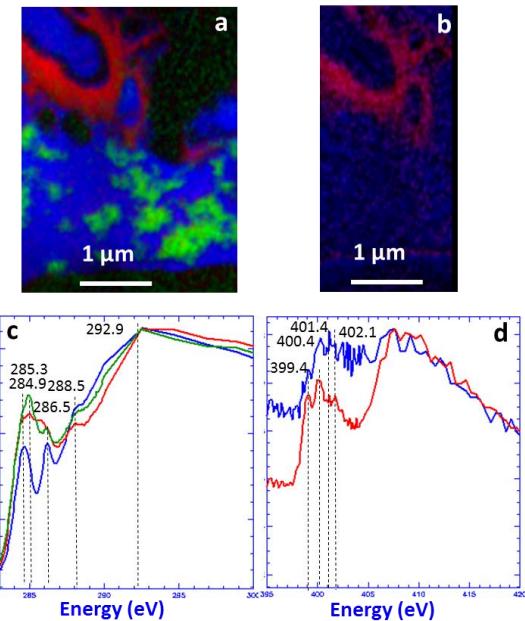


Figure 3 : (a & c) False color C-XANES map and typical spectra showing three distinct organic phases in DC43. (b & d) False color N-XANES map and corresponding typical spectra for DC43.

Figure 3 shows XANES map of the three components at the C and N edges: i) in red the nitrogen-rich smooth phase (Phase 2 in Fig. 2a), ii) in blue the nitrogen-poor phases 1 and 3 in Fig. 2a; iii) in green, the dusty patches in phase 3.

Using the functional groups positions compilation by [9], the C-XANES and N-XANES spectra from Fig. 3c and 3d exhibit absorptions corresponding to: alkene carbon ($C=C$) at 284.9 eV, aromatic carbon ($C=C$) at 285.3 eV, nitrile ($C\equiv N$) at 286.5 and 400.4eV, ketone ($C=O$) at 286.5 eV, carboxyl ($O=C-O$) at 288.5 eV, imine ($C=N$) at 399.4 eV, amide ($O=C-NHx$) at 401.4eV and pyrrole (C_4H_4NH) at 402.1eV.

This study confirms the presence of several types of organic matter in UCAMMs [4, 10]. The smooth N-rich organic phase contains no mineral (phase 2), while the N-poor organic phase is associated with minerals and dusty patches. The N-poor organic matter associated with dusty patches in DC43 (phase 3) contains abundant GEMS inclusions. The smooth N-poor organic phase in DC43 (phase 1) was observed in the previous UCAMMs from the Concordia collection.

DC43 contain a large polycrystalline inclusion of Mg-rich pyroxene (dominant), Mg-rich olivine (minor), troilite and Fe-Ni metal. The presence of triple junctions at grain boundaries between the pyroxene grains strongly suggest an assemblage processed at high temperature. This polyphased inclusions is thus most probably originating from the inner part of the solar system. At the edge of the assemblage, the pyroxene grains display a disordered rim typically 50 nm thick. In addition, the pyroxene contains abundant solar flare tracks. It is the first time that irradiation damages (i.e. disordered rims and irradiation tracks) are observed in Antarctic micrometeorites. The disordered rim is most probably due to low energy particles irradiation (solar wind) whereas the tracks likely result from irradiation by solar energetic particles (SEP).

The assemblage of such diverse organic and mineral phases traces back the dynamical history of both minerals and the organic phases in the protosolar nebula. The smooth N-rich organic phase was probably formed by irradiation of N_2 - and CH_4 -rich ices at the surface of the parent bodies beyond the nitrogen snowline, i.e. at large heliocentric distance in the protoplanetary disk [3, 11]. The occurrence of abundant GEMS in the N-poor organic phase suggests that this organic phase also originated from the cold regions of the protoplanetary disk. By contrast, the Mg-rich pyroxenes were formed and aggregated in the inner solar system, and subsequently transported to the UCAMM formation region (the outer regions of the protoplanetary disk). They were then incorporated into the N-rich ices/organic phase and ices/organic phases containing the GEMS inclusions. The presence of solar irradiation damages in crystalline silicates put a stringent constraint on the transport mechanism to preserve these features (i.e. it must be at low temperature).

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References: [1] Nakamura T., *et al.* (2005) *MAPS & Suppl.*, #5046. [2] Duprat J., *et al.* (2010) *Science* **328**, 742-745. [3] Dartois E., *et al.* (2013) *Icarus* **224**, 243-252. [4] Engrand C., *et al.* (2015) *LPSC* **46**, #1902. [5] Bradley J.P. (1994) *Science* **265**, 925. [6] Keller L.P. and Messenger S. (2011) *GCA* **75**, 5336. [7] Dobrică E., *et al.* (2012) *GCA* **76**, 68-82. [8] Bradley J.P., *et al.* (2014) *LPSC* **45**, #1178. [9] Alleon J., *et al.* (2016) *Nat. Comm.* **7**, 11977. [10] Yabuta H., *et al.* (2012) *LPSC* **43**, #2239. [11] Augé B., *et al.* (2016) *A&A* **592**, A99.