TOF-SIMS analyses of an Ultracarbonaceous MicroMeteorite: preparation of Rosetta-COSIMA studies in 2014.

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Introduction: Micrometeorites of probable cometary origin were recently discovered in the Concordia micrometeorite collection [1]. These UltraCarbonaceous Antarctic Micrometeorites (UCAMMs) are dominated by organic matter, up to 80% in volume, and do not exhibit signs of alteration by the passage through the Earth's atmosphere. The UCAMM organic matter is available for laboratory analyses without need for chemical purification, and its hydrogen isotopic composition shows extreme D enrichments, supporting a formation in the cold regions of the protoplanetary disk. Previous studies have also shown the disorganized state of this organic matter [2], and its close association with pockets of mineral aggregates [3]. We started time-of-flight secondary ion mass spectrometry (TOF-SIMS) analyses on one UCAMM fragment to get more insights on the composition of its organic matter.

UCAMMs are crucial samples for the preparation of the ESA spatial mission Rosetta that will reach comet 67P/Churyumov-Gerasimenko (67P/C-G) in 2014. COSIMA onboard the Rosetta spacecraft is a TOF-SIMS that will analyze the dust grains of comet 67P/C-G [4]. The interpretation of TOF-SIMS data obtained by COSIMA will be a complex task due to the intimate mixture of minerals and organic matter expected in cometary grains [5]. We used Antarctic micrometeorites as cometary proxies to optimize the scientific return of COSIMA [6].

Materials and Methods: One UCAMM (DC-06-05-94, hereafter UCAMM-94) was fragmented and a piece of it was pressed on a 1 cm^2 gold foil identical to a target which will collect cometary grains in space for COSIMA analyses. One fragment of a chondritic fine-grained micrometeorite (DC-06-09-148, hereafter AMM-148) was also pressed on a gold foil for comparative analyses. High mass resolution TOF-SIMS analyses in both positive ($M/\Delta M \sim 10{,}000$) and negative ($M/\Delta M \sim 7{,}000$) mode were performed with an IONTOF-TOF-SIMS 5 mass spectrometer at CRMD (France) for both samples, followed by analyses of UCAMM-94 with the COSIMA reference model (RM) at MPS Lindau (Germany). Clusters of Bi_3^+ primary ions were used at CRMD while the COSIMA-RM used an In^+ primary ion beam. EDX maps at 15 kV of the UCAMM were subsequently acquired with a LEO1350 SEM at CSNSM.

Results and discussion: EDX spectral maps show the complex composition and structure of UCAMM-94 (Fig.1). Highly rich in C (Fig. 1a), UCAMM 94 shows Mg-rich silicates (Fig. 1b), Fe-Ni sulfides (Fig. 1c) dispersed in its whole volume, with sizes up to ~10 µm. In addition, , P-rich inclusions (estimated fomula $Fe_{2.5}Ni_{0.5}P$, i.e. possibly schreibersite) were observed (bright spots in Fig. 1d top right).

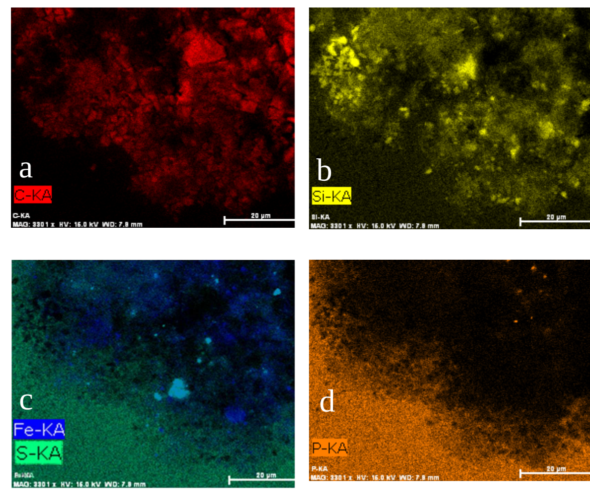

Fig. 1. Close-up EDX maps of UCAMM 94, representing about a quarter of the whole micrometeorite. Scale bar is 20 µm. The UCAMM edges are clear in the C map (a). Mg-rich silicates (b) and Fe-Ni sulfides [light-blue inclusions in (c)] are widespread. P rich-inclusions (d) are probably schreibersite (estimated formula $Fe_{2.5}Ni_{0.5}P$).

Positive spectra of AMM-148 obtained with the TOF-SIMS 5 show major peaks corresponding to Al, Ca, Mg, Fe, and Si, the rock forming elements. These elements also contribute to the highest peaks in UCAMM-94 positive spectra, with the addition of an intense C^+ peak. The comparison of negative spectra for UCAMM-94 and AMM-148 shows that N-bearing organic species clearly dominate in the case of UCAMM-94, with CN^- as the dominant peak (Fig. 1). Aliphatic compounds are not abundant in the spectra, and hydrocarbons are often associated with O atoms (like C_2H_3O). Phosphorus observed in EDX maps as probable schreibersite inclusions, is present in TOF-SIMS spectra as PO_2^- and PO_3^-. Sulfur bearing species are also observed in negative spectra, as CO_2S^-, S^-, $CHSO_2^-$, HS^-, SO^-, SO_2^-, SOH^-.

The low abundance of aliphatic hydrocarbons observed in the negative spectra are compatible with the polyaromatic nature of the UCAMM organic matter, as determined by Raman and TEM on complementary samples [2, 3]. The low aliphaticity of the UCAMM organic matter is also in agreement with the high C/H ratios determined by NanoSIMS [1].

Although at lower mass resolution (M/ΔM ~ 3000), N- and S-bearing species can also be found in the RM negative spectra of UCAMM-94 (Fig. 3). Positive spectra acquired with the COSIMA RM show a peak distribution dominated by the rock forming elements (Mg, Al, Si, Fe).

Carbon, nitrogen, and oxygen isotopic compositions can be inferred from the TOF-SIMS 5 negative spectra. The calculated values are around terrestrial value within analytical errors, except for $\delta^{15}N$ = (207 ± 87)‰ (2σ) that is closer to the solar value [7, 8], and $\delta^{18}O$ that is slightly negative at the two sigma level [$\delta^{18}O$ = (-63±31)‰]. Such isotopic compositions are difficult to assess with the RM data, due to the lower mass resolution, and will require further developments.

References: [1] Duprat J., *et al.* (2010) *Science* **328**, 742-745. [2] Dobrică E., *et al.* (2011) *Meteoritics & Planetary Science* **46**, 1363-1375. [3] Dobrică E., *et al.* (2012) *Geochimica et Cosmochimica Acta* **76**, 68-82. [4] Kissel J., *et al.* (2007) *Space Science Reviews* **128**, 823-867. [5] Fomenkova M.N., *et al.* (1992) *Science* **258**, 266-269. [6] Engrand C., *et al.* (2007) *MAPS* **42 suppl.**, A42.

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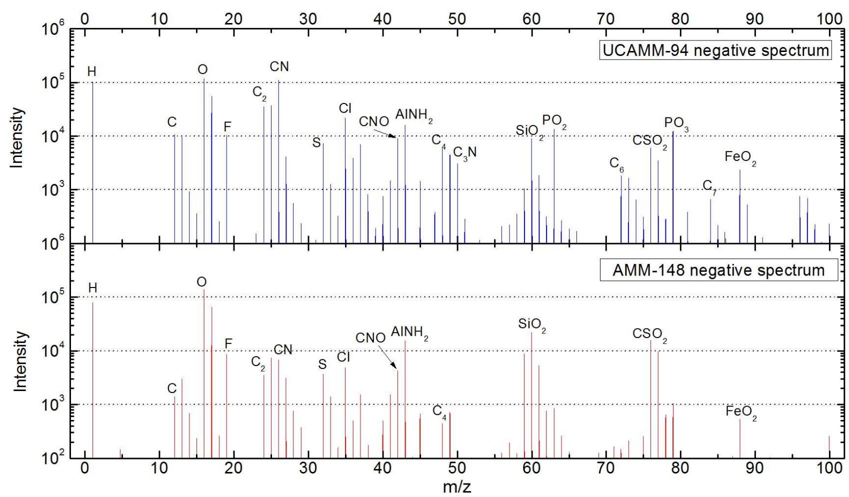

Fig. 2. Comparison on a logarithmic scale of negative secondary ion spectra for UCAMM-94 (top) and AMM-148 (bottom). The UCAMM spectra is dominated by organic species like CN^- and exhibit in particular P- and S-bearing species.

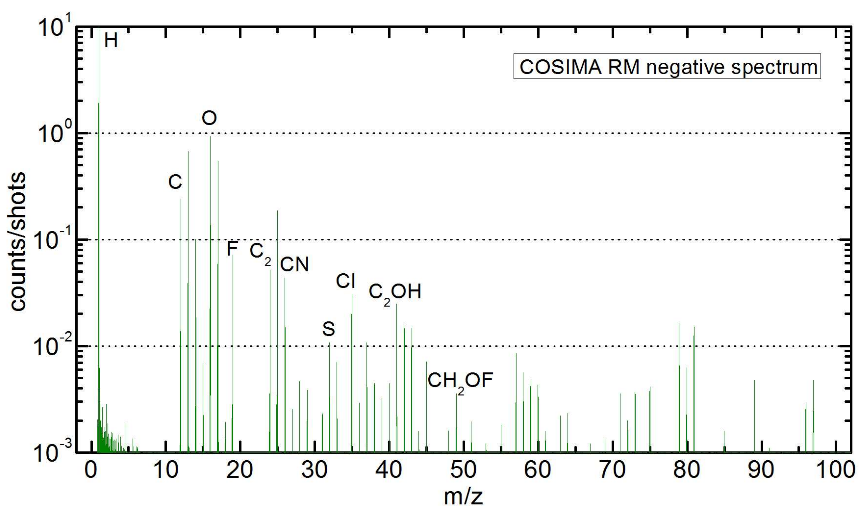

Fig. 3. Example of negative secondary ion spectrum obtained on UCAMM-94 with the reference model (RM) of the TOF-SIMS COSIMA instrument.