

LOCALIZATION AND CHARACTERIZATION OF ORGANIC MATTER WITHIN CM CHONDRITES BY TIME OF FLIGHT SECONDARY ION MASS SPECTROMETRY. Y. Arribard¹, M. Noun², S. Della-Negra³, B. Doisneau⁴, F. Daubisse³, D. Jacquet³, I. Ribaud³, R. Brunetto¹ and D. Baklouti¹, ¹Université Paris-Saclay, CNRS, Institut d'Astrophysique Spatiale, 91405, Orsay, France (yann.arribard@universite-paris-saclay.fr), ²Lebanese Atomic Energy Commission, NCSR, Beirut 11 -8281, Lebanon, ³IJCLab, CNRS/IN2P3, Université Paris-Saclay, F-91406, Orsay, France, ⁴IMPMC, MNHN, Sorbonne Université, CNRS, Paris, France.

Introduction: In order to understand the processes of formation and evolution of the organic matter in the Solar System, it is necessary to study the primitive matter of chondrites and their parent bodies, which are among the last witnesses of the early stage of the Solar System. The organic matter contained in chondrites has been largely studied after extraction [1, 2, 3, 4] and to a lesser extent, *in situ*, without extraction [5, 6]. *In situ* measurements have the advantage of revealing the spatial correlation between organic compounds and minerals.

In this study, we analyzed Cold Bokkeveld and Paris, a CM2.2 [7] and a CM2.7-2.9 [8,9] chondrite, respectively, with Time of Flight Secondary Ion Mass Spectrometry (TOF-SIMS). We previously analyzed the same samples by IR reflectance hyperspectral imaging (4000-800 cm^{-1} , 2.5-12.5 μm) and Raman spectroscopy for the localization and the identification of the mineral phases and the organic content [10]. TOF-SIMS has previously been used to study extraterrestrial materials and especially their organic content [11, 6, 12]. TOF-SIMS allows a better spatial resolution than IR reflectance spectroscopy and it is much more effective to characterize the organic compounds, in particular thanks to their fragmentation pattern. Moreover, it minimizes any alteration of the sample analyzed due to the low fluences applied and the low penetration depth of the ion beam (a few molecular layer). The aim of our study is to focus on the different families of organic compounds or fragments and their co-location with mineral phases in CMs with different degrees of hydration.

Materials and methods: The meteorite samples are freshly cut, unpolished, millimetric slices (see [10] for preparation protocol), kept under a clean and dry atmosphere. Following a protocol established in a previous work [6], the TOF-SIMS measurements were conducted using an ION-TOF V mass spectrometer (ION-TOF) on 500*500 μm^2 areas with a spatial resolution of 2 μm per pixel. The surfaces were analyzed by a Bi_3^+ ion beam at 25 keV preceded by a surface cleaning by argon clusters ($\text{Ar}_{1300-1900}$) at 5 to 10 keV with fluences of 8.10^{11} ions. cm^{-2} on the Cold Bokkeveld sample and 6.10^{11} ions. cm^{-2} on the Paris sample.

Results and discussion: TOF-SIMS measurements allow to confirm and refine the results obtained with IR hyperspectral imaging on the mineralogy of the samples' surfaces especially by looking at metallic cations and silicon, oxygen and sulfur ions.

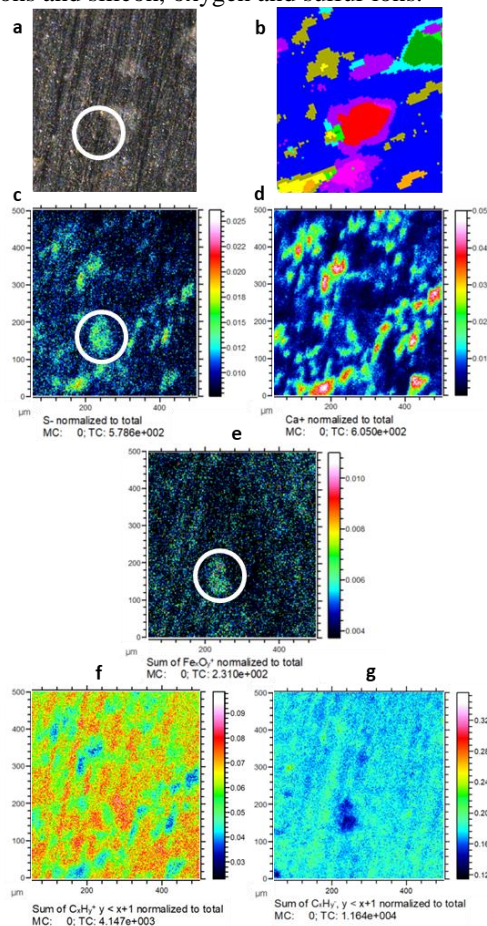


Figure 1: (a) optical image of the surface analyzed on a Cold Bokkeveld sample, (b) localization of the spectral families obtained with IR k-means clustering: regions dominated by phyllosilicates (dark blue), regions dominated by olivines (red), regions dominated by pyroxenes (green), regions dominated by phyllosilicates mixed to carbonates (orange), regions dominated by phyllosilicates mixed to sulfate (yellow and dark yellow), regions dominated by an olivine and phyllosilicate mixture (purple), regions dominated by an olivine and pyroxene mixture (light green), regions dominated by a pyroxene and phyllosilicate mixture (light blue) [10], TOF-SIMS mappings of ions S⁻ (c), Ca⁺ (d), FeO_y⁺ (e), C_xH_y⁺ (y < x+1) (f) and C_xH_y⁻ (y < x+1) (g) count normalized by the total count for each pixel.

For example, on the Cold Bokkeveld sample presented in Fig. 1, mapping S^- and Ca^+ (Fig. 1c and 1d) shows that these ions come from the sulfate-rich regions identified previously by IR measurements (yellow and dark yellow on Fig. 1b). Thus, the TOF-SIMS measurement implies that these sulfates are mainly calcium-rich.

On this same sample, a specific area, rich in iron oxide and sulfide (white circles in Fig. 1a, 1e and 1c) according to TOF-SIMS, appears close to an olivine-rich chondrule (in red in Fig. 1b). Due to the wavelength range of the IR detector used, these components cannot be directly identified in the IR spectra, except for their particular brightness. On the optical image, this region looks different from the bright apparent chondrule on its top right. TOF-SIMS analyzes the first molecular layers of a surface (10 – 100 nm in depth), whereas IR reflectance measurement goes more in depth (a few 100 nm up to a few μm). Thus, for this particular region of the sample, TOF-SIMS simply reveals the presence of iron sulfide and oxide sitting atop of the chondrule detected in the IR measurements.

By focusing on the organic peaks, we are able to study the different families of organic signatures and localize them.

For example, on the Cold Bokkeveld sample in Fig. 1, according to TOF-SIMS, $C_xH_y^+$ ($y < x+1$) organic fragments are widespread on the matrix and chondrules, but much less abundant on the sulfates, carbonates and the iron oxide inclusion (Fig. 1f and 1g). Thanks to Raman spectroscopy we found polyaromatic organic matter both in matrix and chondrules of this sample, and thanks to IR imaging we localized aliphatic-rich compounds mainly in the matrix [10]. The TOF-SIMS spatial distribution of $C_xH_y^+$ rather matches the location of the polyaromatic matter detected by Raman.

Conclusion: The first results extracted from TOF-SIMS measurements agree well with the previous IR imaging and Raman analyses and highlight the relative homogeneous repartition of polyaromatic organic moieties throughout the matrix and the chondrules in Cold Bokkeveld. The same tendency appears for the Paris meteorite sample studied. Work is in progress to perform a more detailed analyses of other organic fragments such as $C_xH_{2x+2}^+$, $C_xH_yN_z^+$ or $C_xH_yO_z^+$, which will provide interesting information on the location of the different families of organic compounds or fragments. The comparison between CM chondrites showing different stages of aqueous alteration will inform us about the formation and evolution process of organic matter.

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References: [1] Pizzalero S. et al. (2006) *Meteorites and the early solar System II*, 625-651. [2] Derenne S. et al. (2010) *Meteoritics & Planet. Sci.*, 45(9), 1461. [3] Alexander C.M.O.D. et al. (2017) *Geochemistry*, 77(2), 227-256. [4] Quirico E. et al. (2018) *Geochimica et Cosmochimica*, A241, 17-37. [5] Dionnet Z. et al. (2018), *Meteoritics & Planet. Sci.*, 53(12), 2608-2623. [6] Noun M. et al. (2019) *Life*, 9(2), 44. [7] Rubin A. et al (2007) *Geochimica et Cosmochimica*, A71(9), 2364-2382. [8] Hewins R.H. et al. (2014) *Geochimica et Cosmochimica*, A124, 190-222. [9] Marrochi Y. et al. (2014) *Meteoritics & Planet. Sci.*, 49(7), 1232-1249. [10] Arribard Y. et al. (2021) *Met-Soc 2021*, Abstract #6149. [11] Stephan T. (2001), *Planetary and Space Sci.*, 49, 859. [12] Siljestrom S. et al. (2021), *LPSC 2021*, Abstract #1468.