SOURCE AND EVOLUTION OF ORGANIC MATTER IN AQUEOUSLY ALTERED CARBONACEOUS CHONDRITES. B. Laurent[1], J.Maillard[2], C.Afonso[2], G.Danger[3], P.Giusti[4] and L.Remusat[1] [1]Muséum National d'Histoire Naturelle, Sorbonne Université, UMR CNRS 7590, Institut de minéralogie, de physique des matériaux et de cosmochimie, Paris, France (boris.laurent@mnhn.fr). [2]Normandie Université, COBRA UMR 6014 et FR 3038 Univ Rouen, France. [3]Aix Marseille Université, CNRS, PIIM, Marseille, France. [4]International Joint Laboratory–iC2MC, TotalEnergies - TRTG Refining and Chemicals, Gonfreville l'Orcher, 76700 Harfleur, France.

Introduction: Primitive carbonaceous chondrites offer a unique window into the formation of C-complex asteroids. Among these meteorites, the CM class of carbonaceous chondrites have been preferred targets for organic matter investigations [1,2]. In CMs, most of the carbon resides in a form of insoluble macromolecule, the IOM. The IOM structure is constituted by small aromatic units connected by short and branched aliphatic chains resulting in a high degree of cross-linking [3]. Beside an unparalleled diversity, the organic content in the IOM shows heterogeneity down to the micrometer scale, as revealed by the occurrence of D and ^{15}N-rich hot spots [4,5]. The molecular diversity and isotope heterogeneities could result from the accretion of organic particles having experienced different environments in the protosolar nebula [6,7,8]. As shown by the mineralogy, CM parent-body has experienced significant aqueous alteration [9]. It is then fundamental to assess the effects of the asteroidal evolution on the IOM. Consequently, extended circulation of fluids may have blurred the imprint of the organic precursor. The comparative study of CMs exhibiting various degrees of alteration is decisive to establish or to rebut the possibility of a common organic precursor, potentially preserved from the effects of the accretion processes. To investigate the influence of the hydrothermal alteration on the molecular diversity of the IOM, our study extends to newly CM chondrite falls to evaluate if molecular distributions are comparable within different parent bodies and if different sources of IOM precursors could have been accreted on them.

Samples and Methods: We have applied laser desorption ionization coupled with ultra-high-resolution mass spectrometry – LDI-FTICR. A unique attribute of LDI is the ability to analyze IOM, although only a fraction of IOM is likely to be ionized under the laser beam. FTICR-MS offers unparalleled performances in term of isobaric resolution, mass accuracy and dynamic range [10], optimal for the analysis complex molecular mixtures. This technique has been recently proven successful at unravelling the molecular diversity of Paris IOM [11]. Recent falls such as Aguas Zarcas (CM2.2[12], Costa Rica, 2019), Mukundpura (CM2.0 [13], India, 2017) and Kolang (CM1/2 [14], Indonesia, 2020) were selected as the main CM samples. IOM from Orgueil (CI1) and the ungrouped Tarda (C2 ungrouped [15], Morocco, 2021) were also investigated. The new results are compared to those acquired previously on Paris [15]. For all meteorite samples, the insoluble organic matter from each chondrite were isolated through solvent washing and HF/HCl leaching. LDI-FTICR analyses were performed on a SolariX XR equipped with a 12T superconducting magnet. Laser ionization parameters were tuned according to a previous work [16].

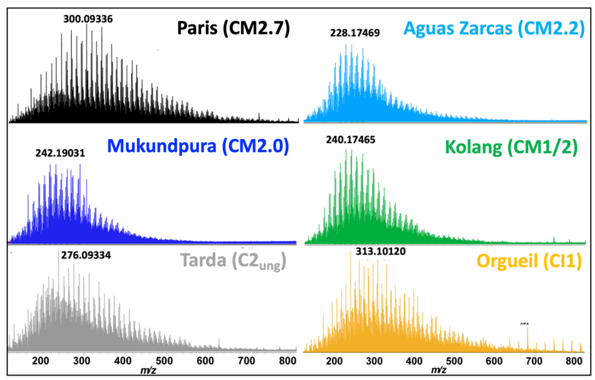

Figure 1. FTICR mass spectra obtained for Paris, Aguas Zarcas Mukundpura and Kolang CM chondrites, as well as Tarda C2 chondrite, and Orgueil CI chondrite.

Results and Discussion: The high resolving power (2.160.000 at *m/z* 200) allows the resolution of a large number of signals on each spectrum (figure 1). On average, 10000 molecular formulas were assigned in each chondrite. The spectral spread or the position of the base peak (the most intense signal) are indicative of molecular diversity. Altered CM2 Mukundpura, Aguas Zarcas and Kolang exhibit similar spectral shape, with maximum intensity around *m/z* 240. Paris spectrum is the widest, with the largest diversity of detected compounds (Kolang the lowest), and has distinctive patterns present over *m/z* 400. The Orgueil spectrum show some similarities with Paris, while its maximum is around *m/z* 310, while the shape of Tarda spectrum appears as in between Paris and Orgueil.

To sort out the large dataset, a principal component analysis (PCA) was performed (fig.2). The four regions are separated by a first component, PC1, that explains >83% of the differences and that is related to the saturation (H/C), and another one, PC2, linked to the relative oxygen content. The altered CM2 are grouped together in the compositional space, whereas Paris and Kolang were found to be isolated. While being described as a CM1/2, Kolang occupies its own quadrant, with little similarities to Aguas Zarcas and Mukundpura. More surprising is the joined presence of Tarda and Orgueil in the same quadrant, although they are not related to CMs. This indicate that ungrouped C2 like Tarda differ from CM2 subtype [13]. Remarkably, Paris shows the highest dispersion in compositional space, as its IOM may have preserved a certain chemical heterogeneity from the sources of IOM precursors. The minimal heterogeneity in altered CMs (and its absence in Kolang) may result from fluid circulation, as previously considered for the large homogenization of the functional groups content in Murchison and Orgueil [17].

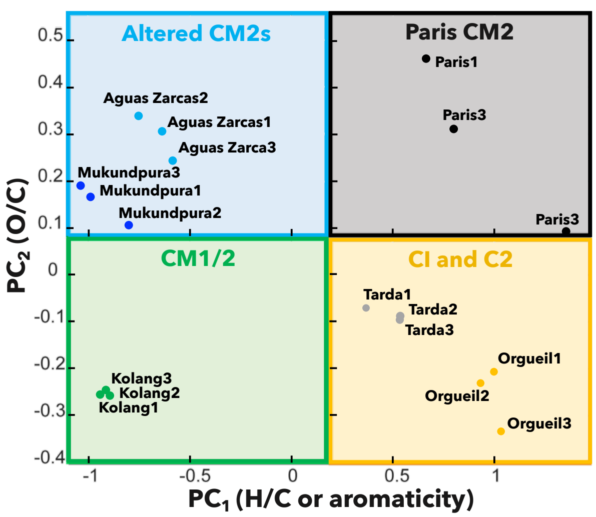

Figure 2. Principal components analysis of IOM mass spectra of CM2 Paris (black), Aguas Zarcas and Mukundpura (blue), CM1/2 Kolang (green), as well as C2 Tarda and CI Orgueil (yellow).

Aqueous alteration appears to promote aromatization (figure 2), and to homogenize IOM molecular features. With increasing alteration, oxygen-bearing groups are lost (Kolang); this is counter-intuitive. As only the oxygen-bearing groups sensitive to laser ablation (LDI) can be measured here, we only accessed a portion easily from the macromolecule. Hence, their behaviour may not be representative of the entire IOM. For objects with similar alteration index (e.g. Mukundpura/Tarda) but spatially isolated in the compositional space (figure 2), the difference may reside in the precursor nature. Different parent-bodies should be considered for CMs and CI, and possibly a similarity of precursor with Tarda (C2), as they share similar spectra shapes (figure 1) and proximity in the PCA analysis.

Ultra-high-resolution mass spectrometer (FTICR-MS) offers a new perspective on the study of the chondritic organic matter. It enables the simultaneous study of molecular diversity resulting whether from asteroidal processes or from different parent-bodies. Molecular diversity in the primitive chondrites cannot be explained solely by the secondary processes taking place during the asteroidal phase. A part of this diversity is also linked directly to the organic precursor and its location in the solar system.

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