NANOSCALE COMPARISON BETWEEN ORGANIC MATTER AND MINERALS OF RYUGU SAMPLES, CI-LIKE ANTARCTIC MICROMETEORITES (AMMs), AQUEOUSLY ALTERED METEORITES AND UCAMMS: A PROBE TO STUDY THE ASTEROID-COMET CONTINUUM.

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Introduction: Micrometeorites are pristine materials that give insights into the evolution of the Solar System. They are the dominant extraterrestrial mass input on Earth nowadays [1]. They can be efficiently collected in Antarctica (Antarctic micrometeorites – AMMs [2, 3]). Among AMMs, a rare type of organic rich micrometeorites with a very probable cometary origin was identified, the UCAMMs [4]. CI chondrites constitute pristine solar system material, having chemical composition closest to the solar photosphere, although their mineralogy was altered by secondary processes. In 2019, the Japanese mission Hayabusa2 sampled *Ryugu*, a Cb-type asteroid, both at the surface and sub-surface [5, 6]. The *Ryugu* samples brought back on Dec. 6, 2020 contain a significant level of insoluble organic matter [7] and show striking similarities with CI chondrites [8, 9]. We investigate here the relationships between *Ryugu* samples, CI-like AMMs, UCAMMs, CI chondrites (Orgueil, Flensburg) and the CM2.1 Winchcombe meteorite. We measured the infra-red signature of their organic matter by IR microscopy (µFTIR) and IR nanospectroscopy (AFM-IR). The comparison between these samples allows to assess a possible effect of atmospheric entry and exposition to the terrestrial atmosphere, and to investigate the differences between their parent bodies.

Materials and methods: Eleven samples were selected for this study, including two particles from whole-rock *Ryugu* samples obtained through the first Hayabusa2 AO (A0194 and C0058). Additionally, fragments of four CI-like AMMs (DC16-11-429, DC16-11-430, DC16-11-436, DC16-14-315) [10] were selected in the Concordia collection (hereafter DC16-429, DC16-430, DC16-436, DC16-315). Their selection was based on analytical scanning electron microscopy (SEM-EDX) that revealed their aqueously altered mineralogy and the presence of framboidal magnetite. This study includes data on two new UCAMMs (DC19-01-201 and DC19-02-59, hereafter DC19-201 and DC19-59) identified from the Concordia collection, and fragments from CI meteorites Orgueil and Flensburg [11] and CM2.1 meteorite Winchcombe [12]. For IR studies, one (or several) fragment(s) of each sample was flattened to a thickness of ~1 µm in custom-made diamond cells. They were analyzed by infrared transmission (µFTIR) microspectroscopy on the SMIS beamline at synchrotron SOLEIL (France) in April and November 2022. For µFTIR, the synchrotron beam was coupled to a Thermo Fisher Scientific continuum IR microscope to obtain hyperspectral maps with a spot resolution of 6x6 µm and a 3 µm spatial sampling step. These µFTIR maps were used to select areas to be subsequently analyzed by IR nanospectroscopy (AFM-IR) at much higher spatial resolution. The AFM-IR data were obtained in July and December 2022, with a Bruker IconIR coupled to a multi-chip Quantum Cascade Laser (QCL, Daylight Solutions) covering the mid-IR range from 900 cm^{-1} to 1900 cm^{-1}. For each sample (except for C0058 and DC19-59 to be analyzed soon), we acquired 20 x 20 µm maps at 1020, 1460, 1600, 1640, 1730, and 1850 cm^{-1}, corresponding to silicates, carbonates or CHx, C=C, OH, C=O and continuum absorption bands, respectively. Smaller maps down to 3x3 $µm^2$ with a spatial resolution of ~ 50 nm were subsequently acquired on selected areas.

Results: At the µFTIR level, the compositions of all samples exhibit heterogeneities, both intra and inter-samples. Except for UCAMMs that are dominated by organic matter, µFTIR measurements of all samples show that they are dominated by a phyllosilicate-rich matrix mixed with organic matter showing C=C, C=O and CHx bonds' signatures. Noticeably, in Flensburg the structural OH band at ~3670 cm^{-1} is strong, with only a faint broad band signing the presence of molecular water. The two UCAMM fragments are dominated by organic matter with the signature of C=C, N-H and C=O bonds and no significant signature of mineral phases. Carbonates are observed in Orgueil spectra, whereas they are rare in CI-like AMMs, and not found in µFTIR spectra of Ryugu samples, Flensburg and Winchcombe.

AFM-IR allows to investigate the observed heterogeneities at the 50 nm level. CI-like AMMs are very different from one another. AFM-IR measurements of DC16-436 present phyllosilicates, carbonates with sizes from 100 nm up to 1 µm, low organic content. DC16-430 is quite homogeneous at the nano-scale with diffuse organic matter scattered among the matrix. Carbonates are seen at the µFTIR level but not in the areas analyzed by AFM-IR. DC16-315 AFM-IR maps are dominated by phyllosilicate, with organic patches (Figure 1) and widespread low organic content (rich in C=C), as shown in average spectrum in Fig. 1. Magnetite inclusions but no carbonates were identified in DC16-315. DC16-429 consists of a phyllosilicate matrix (without organics nor carbonate), and a variety of magnetite inclusions (platelets, framboids) observable at the nano-scale. The AFM-IR spectra of CI-like AMMs, Orgueil and *Ryugu* A0194 sample present a phyllosilicate absorption at ~1020 cm^{-1}, suggesting a dominant contribution of saponite, while that of Flensburg and Winchcombe is at ~950 cm^{-1}, compatible with the presence of serpentine. All the CI-like AMMs, Orgueil, Flensburg and *Ryugu* A0194 sample present opaque minerals consisting of magnetites and Fe sulfides. DC16-436 is the only sample showing pure carbonate phases. A sulfate absorption band around 1120 cm^{-1} is observed in AFM-IR spectra of *Ryugu* sample A0194, AMM DC16-315, UCAMM DC19-201, Orgueil and Flensburg, but is not found in other CI-like AMMs and Winchcombe.

All samples except for DC16-315 and Orgueil show the presence of a widespread and diffuse organic matter in the matrix. In Flensburg, the µFTIR spectra exhibited C=C, C=O, CHx signature, which are seen at a weak level by AFM-IR, suggesting a very diffuse and low quantity of organic matter. In addition, *Ryugu* sample A0194, AMMs DC16-430 and DC16-315, Winchcombe and Orgueil contain well-defined organic patches with sizes ranging from 500 nm to 1 µm in Orgueil and DC16-430, 1-2 µm in *Ryugu* A0194 sample and CI-like AMM DC16-315, and from 2 to 3 µm in Winchcombe. No organic patch was identified within Flensburg. UCAMM DC19-201 presents an organic matrix, enriched in NH with low C=C, C=O and CHx signatures, a faint sulfate signal but shows no phyllosilicate, nor carbonate, which is consistent with previous study [13].

Discussion: The AFM-IR analyses show different distributions and chemical compositions of the organic matter in the meteorites. Winchcombe and Flensburg do present diffuse organic matter, while Orgueil does not. On the other hand, Orgueil and Winchcombe contain organic patches, while Flensburg does not. The weak AFM-IR organic signal of Flensburg is compatible with its rather low carbon content, as measured by [10]. Winchcombe presents larger organic patches than Orgueil. On the basis of AFM-IR analyses, Ryugu A0194 sample shares some similarities with each of the three meteorites analyzed, but with no perfect match. So far, *Ryugu* A0194 does not seem more similar to Flensburg than to Orgueil, as would have been expected from the recent recovery of Flensburg. The four AMMs studied have different characteristics. It is noticed that DC16-315 shows similarities with Orgueil: they are mostly composed by a phyllosilicate matrix with organics being mostly localized in ~1 µm organic patches. Also, DC16-429 shares similarities with Flensburg. As expected, UCAMMs represent a unique class of objects, as they most probably originate from comets.

Conclusion and further investigations: The diversity of organic matter components contained in *Ryugu* samples, CI-like AMMs, Orgueil and Flensburg (CI1), Winchcombe (CM2.1) and UCAMMs can reflects multiple origins or different post-accretional processes. Nano-scale regions of interest containing organic matter within this set of diverse objects were identified and will be analyzed by NanoSIMS to allow the comparison between IR spectroscopy and isotopic ratio measurements at the nano scale, and get a better insight on the information on the region(s) and processes that led to the formation of organic matter in the early solar system.

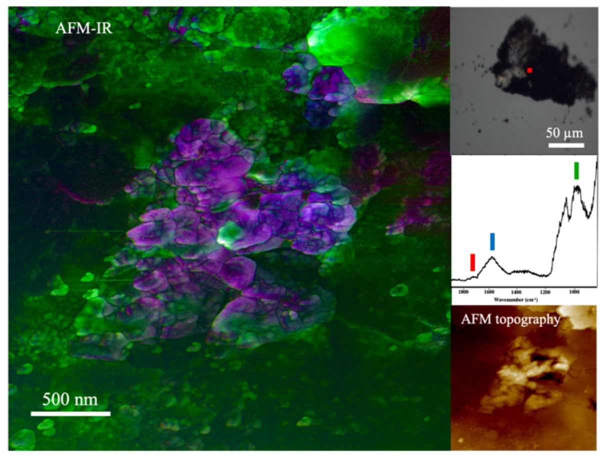

Figure 1: *DC16-14-315 composite RGB map acquired by AFM-IR. Red: C=O, green = phyllosilicates, blue = C=C. Top right: optical image of the sample. The red dot indicates the 3x3µm AFM-IR map position. Middle right: Average spectrum of the map. Bottom right: AFM topography.*

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