Nano-infrared spectroscopy of Ryugu samples using AFM-IR measurement

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Introduction: In late 2020, samples of Ryugu (C-type) were collected from its asteroid and returned to Earth, led by the Japan Aerospace Exploration Agency (JAXA), thought to be similar in composition to CI chondrites ¹. Understanding how and under what conditions the organic matter interacted with inorganic phases, is a key step in hypothesizing the mechanism of accreted organic matter. This "fresh" carbonaceous material allows us to investigate the best preservation sample without terrestrial impact ². In addition, the "bulk" Ryugu samples also show some spectral reflectance bands corresponding to the NH-rich compounds ³. Altogether, our study aims to characterize the minerology, organic matter and the possible N-bearing molecule. To gain insight into fine meteorites matrices containing an interplay of ingredients at the sub-micro scale, it requires analytical techniques with the sub micrometer spatial resolution to separate their composition and understand their petrographic relations. Infrared spectroscopy (IR) is an effective method and a non-destructive technique for molecular-atomic scale vibrations of organic and inorganic compounds in the extra-terrestrial materials ^{4,5}. However, conventional IR spectrometers use mirror-based optics to focus the beam on the sample and thus the spatial resolution is limited by the diffraction limit. This IR diffraction limitation can be overcome by using AFM-IR (Atomic Force Microscopy-Infrared Spectroscopy), based on the combination of infrared spectroscopy and atomic force microscopy to efficiently distinguish spectral signatures of the different constituents ^{6,7}.

Our study aims to characterize two different grains of Ryugu that can be affected by the weathering space prepared by "Min-pet fine team" (Sand team)⁸ as crushed sample between two diamond windows, as well as two different Orgueil samples: one comes from the Paris Museum (Orgueil Museum) and the another one expected "fresher" kept in the sealed flask (Orgueil Flask) from collection of M. Bizzaro. Here, we report the comparison of AFM-IR results between Ryugu and Orgueil as a CI chondrite both in minerology and organic structure.

Samples preparation and methods: Two grains of Ryugu (P0032 and P0038), received from the Sand initial analysis team, were prepared by crushing $10 - 20 \mu m$ fragments between two diamond windows. As with Ryugu, the Orgueil Museum and Orgueil Flask samples were also pressed down to the appropriate thickness for AFM-IR measurement. Before AFM-IR analysis, all samples were performed the micro-FTIR analysis to select the region of interests (ROI).

IR spectroscopy and AFM-IR measurement: The micro-infrared spectra were first analyzed with a Bruker Hyperion 3000 infrared microscope. The nano-IR measurements were obtained with a Bruker nanoIR3s at IPAG (Grenoble, France), which includes an AFM probe capable of scanning the sample and generating topographic images at nm vertical resolution. The AFM-IR measurement can be performed in two acquisition modes: AFM and chemical imaging, and local, single point IR spectrum. First, the wavenumber is fixed and the tip moves along the surface to obtain the AFM topography and IR absorption at the given wavenumber. Second, the position of the tip is fixed and the IR laser is tuned to the possible spectral range ($2000 - 700 \text{ cm}^{-1}$ with the APE laser at IPAG) which provides the local absorption spectrum at the point of interest ⁶.

Results and Discussion: We are able to characterize two bulk grains of Ryugu with the region of interest $5 \times 5 \ \mu m^2$ (grain P0032) in the in Figure 1 and the ROI of $3 \times 3 \ \mu m^2$ (grain P0038) in Figure 2.





Figure 1. AFM-IR of a 5×5 μ m2 region of interest (ROI) acquired with the NanoIR3s at IPAG (Grenoble, France) of grain P0032. Left images: AFM image, the AFM-IR images of 1720 (red), 1450 (blue), 1100 (yellow), 1000 cm⁻¹ (green) corresponding to C=O, carbonate, sulfate and Si-O; and RGB (red, green, blue) composition image from the combination of three AFM-IR absorption images: 1720, 1450 and 1000 cm⁻¹ respectively. Right panel: comparison of local AFM-IR spectra on the carbonate rich area (in blue), and the phyllosilicate area (in green) with phyllosilicate signature of Orgueil Flask, μ -FTIR spectra of Ryugu, calcite and dolomite minerals.

In the first grain, P0032, AFM-IR images at different wavenumber were obtained at 1720, 1450, 1100 and 1000 cm⁻¹ in the left panel corresponding to carbonyl (C=O), carbonate, sulfate and phyllosilicate (Si-O), respectively (Figure 1). The three maps of 1720, 1450 and 1000 cm⁻¹ wavenumber were overlaid in the RGB composite image, allowed us to identify the two different domain compositions in the mapped area: the green area can be distinguished by a strong absorption at 1000 cm⁻¹ attributed to the presence of phyllosilicate; the blue/purple area shows a strong absorption at 1450 cm⁻¹ related to carbonate. Numerous spectra were obtained across this ROI shown in the right panel and compared to AFM-IR spectra of Orgueil Flask, dolomite, calcite and μ -FTIR of the same P0032 grain. Spectrum A, the average of hundreds of spectra in the green region shows signature at 1020 cm⁻¹ corresponding to phyllosilicate (e.g., saponite, serpentine). Compared to the Orgueil phyllosilicate spectra, Ryugu is lack of a sulfate signature at 1100 cm⁻¹. However, we observed that some purple areas have stronger absorption at 1100 cm⁻¹ and AFM-IR spectra also confirm the two peaks at 1100 and 840 cm⁻¹ (B spectrum). This Ryugu sample was collected in the fine-grained fraction, affected by space weathering ⁸, the phyllosilicate-rich region can be modified. C spectrum in the blue region suggests the presence of carbonate with two strong signatures at 1440 and 860 cm⁻¹, all indicative of dolomite or calcite.

In the second Ryugu grain, P0038, we first collected the different images at 1720 (red), 1450 (blue) and 1000 cm⁻¹ (green) in ROI of $20 \times 20 \ \mu\text{m}^2$ and overlaid them in the RGB composite image in the upper left panel. We found a ~ 1µmdiameter globule with strong absorption at 1720 cm⁻¹ corresponding to C=O in the organic material (Figure 2). Therefore, the ROI of $3\times3 \ \mu\text{m}^2$ was selected to obtain the different images at 1720, 1600, 1450 and 1000 cm⁻¹. The RGB composite (combined between the images at 1720, 1450 and 1000 cm⁻¹) show an organic globule in red with strong absorption at 1720 cm⁻¹. Later, the contact AFM-IR spectra also confirm the presence of organic matter with two distinct features at 1720 and 1610 cm⁻¹ corresponding to C=O and C=C, respectively. Although the AFM-IR images only show the strong organic appearance, the AFM-IR spectra of organic globule still mixes with the minerals. Compared to the organic matter obtained at Orgueil described in ⁹, the Ryugu organic material is more aromatic. The more diffuse organic may present in this ROI but still finely mixed with phyllosilicate.



Figure 2. AFM-IR of a 3×3 µm² region of interest (ROI) acquired with the NanoIR3s at IPAG (Grenoble, France) of grain P0038 from the RGB image of 20×20 µm² region on the upper left panel. Right images: AFM image, the AFM-IR images of 1720 (red), 1600 (pink), 1450 (blue), 1000 cm⁻¹ (green) corresponding to C=O, C=C, CO₃/CH₂ bend, and Si-O; and RGB (red, green, blue) composition image from the combination of three AFM-IR absorption images: 1720, 1450 and 1000 cm⁻¹, respectively. Lower left panel: comparison of local AFM-IR spectra on the organic globule (red), and the phyllosilicate area (green) with organic matter of Orgueil and µ-FTIR spectra of Ryugu.

Conclusion: The complete results and discussion of this study will be presented at the conference. So far, we confirm that the AFM-IR technique allows us to disentangle the IR signatures of phyllosilicate, carbonate and organic matter in Ryugu at the sub-micron scale. In minerology, compared to Orgueil, the sulfate signatures almost absent from the phyllosilicate, but some modifications in Si-O-rich areas were observed. In the organic structure, the weak organic signature is diffuse and significantly intermixed with phyllosilicate, similar to the diffuse organic of Orgueil. A 1 μ m-organic globule was also observed with clear C=O and C=C features in its structure. This organic matter globule is more aromatic compared to the organic matter in Orgueil meteorites.

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