

# NANOMETRE-SCALE INFRARED CHEMICAL IMAGING (AFM-IR) STUDY OF RYUGU SAMPLES RETURNED BY THE HAYABUSA 2 SPACE MISSION.

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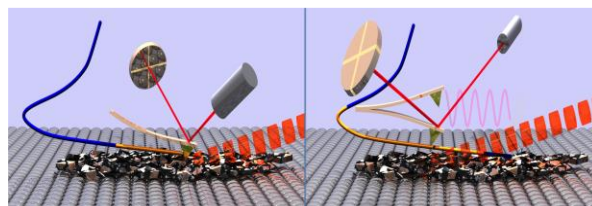
**Introduction:** The distribution of chemical bonds in organic matter (OM) of extraterrestrial samples (meteorites and micrometeorites) can be efficiently and non-destructively characterized using infrared (IR) vibrational spectroscopy ([1]). Conventional IR microscopy provides a global view of the dust grain physico-chemical composition but remains spatially limited by the diffraction. In state-of-the-art synchrotron-based  $\mu$ -IR microscopy typical spot sizes in the mid-IR range can, at best, sample a few  $\mu\text{m}$ . This spatial resolution limitation often hampers a direct comparison with complementary techniques such as isotopic imaging with NanoSIMS, TEM or STXM. Such IR diffraction limitation can be circumvented by using AFM-IR microscopy [2], allowing, for the first time, to directly compare the distribution of the associated chemical bonds at the sub-micron scale with the mineralogical, chemical and isotopic heterogeneities imaged by other techniques at the same scale.

In this study, we measured Ryugu samples by AFM-IR, showing the vibrational IR signatures at scales of 25 to 100 nm allowing the identification of the individual organic components at the sub  $\mu\text{m}$  scale. This work focuses on the analysis of OM of Ryugu samples that is intimately associated with minerals, revealing chemical heterogeneities (in the chemical bondings) of the OM at the nanoscale.

**Samples and methods:** AFM-IR is now a well-established microscopy technique in the vibrational field, combining an atomic force microscope (AFM) and a tunable IR illuminating source to detect photo-thermal effect and access chemical information [2]. This technique is applied in a wide diversity of scientific fields [3], and was recently used to analyze OM-rich extraterrestrial samples [4, 5].

Ryugu samples were received from the “IOM” and “Stone” initial analysis teams. Several samples from chamber A and chamber C, which were obtained at the

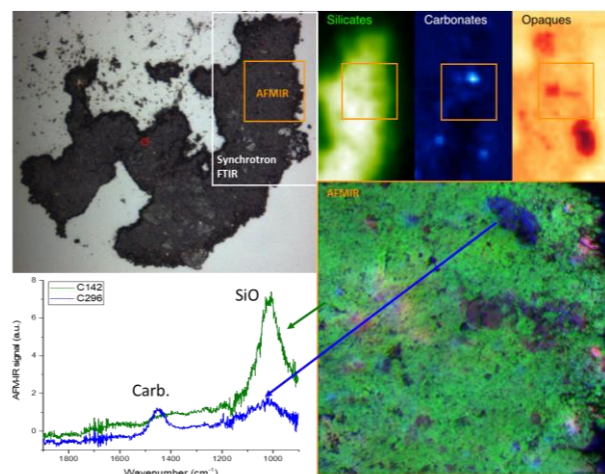
first and second touch-down sites, respectively, were prepared by crushing small fragments on diamond windows. Because of the high resolution of AFM-IR (tens of nanometers), regions of interest were first localized and selected using conventional and synchrotron IR microscopy [6].



**Figure 1:** Schematic view of the infrared (IR) nanospectroscopy (AFM-IR) technique, which measures the IR absorption of the sample upon tunable IR laser illumination, using an atomic force microscope – Left panel: Contact mode AFM-IR – the cantilever is in contact with the sample. Right panel: Tapping mode AFM-IR – the cantilever is vibrating and scanned across the sample [5].

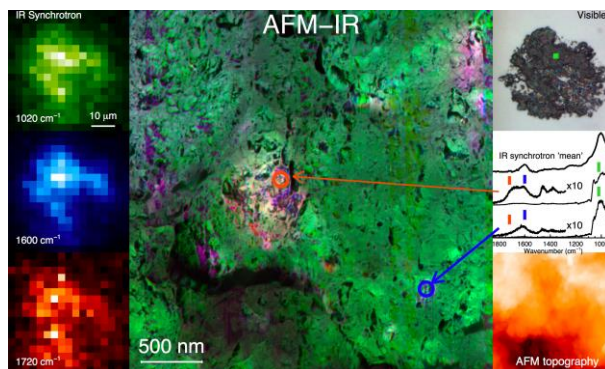
In this study, the AFM-IR measurements were performed using the AFM tapping mode with a top-down IR laser illumination on a standard NanoIR2 system (Fig. 1 – Right panel) and using the AFM contact mode on the new IconIR Bruker system (Fig. 1 – Left panel). In both cases, two kinds of acquisitions were carried out. First, the wavenumber is fixed and the tip moves along the surface, allowing to acquire simultaneously AFM topography and IR absorption map of the sample at a selected wavenumber. Second, the tip position is fixed on a sample position and the IR laser is tuned to explore the whole available spectral range (here  $1900\text{ cm}^{-1}$  –  $900\text{ cm}^{-1}$ ) giving access to local absorption spectra at the point of interest.

**Results:** Using the NanoIR2 system, it was possible to analyze large area ( $20 \times 20 \mu\text{m}$ ) to characterize the main components of the sample i.e. mineral phases and carbonates with a spatial resolution  $\sim 75\text{ nm}$  (Fig. 2).



**Figure 2:** AFM-IR study of a 20x20  $\mu\text{m}$  area acquired with the nanoIR2 system (chamber A sample A0108-15) – Upper left panel: Optical image of the sample with localization of synchrotron (white square) and AFM-IR (orange square) analysis – Upper right panels: IR mapping obtained from synchrotron IR microscopy acquisition and corresponding to the absorption of Si-O silicates ( $1020\text{ cm}^{-1}$ , green), carbonates ( $1450\text{ cm}^{-1}$ , blue) and opaques (drop in the transmitted IR signal) – Lower right panel: RGB composite images combining the AFM-IR absorption mapping Si-O silicates ( $1020\text{ cm}^{-1}$ , green), carbonates ( $1450\text{ cm}^{-1}$ , blue) and C=O ( $1720\text{ cm}^{-1}$ , red), opaques as contributing to each wavenumbers and appear in pink in the image – Lower left panel: comparison of local spectra obtained by AFM-IR on a silicate rich area (in green) and carbonate rich area (in blue).

As OM contribution is weaker than mineral and carbonates ones, a localized and highly resolved analysis was made using the IconIR system (Fig. 3). Maps of  $3\times 3\text{ }\mu\text{m}$  (which roughly correspond to one pixel of the best conventional IR synchrotron acquisition) at a spatial resolution of  $\sim 25\text{ nm}$  were acquired. The areas were chosen based on previous  $\mu\text{-FTIR}$  synchrotron measurements analysis. It was then possible to localize OM inclusions in samples from chamber A (not shown here) and chamber C (Fig. 3) by comparing the signal from the Si-O of the silicates (in green) and that from the OM contributions of the C=C absorption (in blue) and C=O absorption (in red). The OM inclusions characterized by AFM-IR range from  $50\text{ nm}$  to  $500\text{ nm}$  in size. On the larger inclusion displayed in Fig. 3, the OM signal is a mix between C=C and C=O (which appears in purple), but chemical heterogeneities are observed at small scales: parts of the inclusion seem to exhibit local enrichment in C=O (redder) while other a local enrichment in C=C (bluer). Local AFM-IR spectra were recorded on these spots, showing locally different C=C and C=O contributions.



**Figure 3:** Study of chamber C sample C109-04 with the Bruker IconIR, in the context of  $\mu\text{FTIR}$  maps. Left panels: IR maps obtained by transmission synchrotron  $\mu\text{FTIR}$  and corresponding to the absorption of Si-O silicates ( $1020\text{ cm}^{-1}$ , green), C=C ( $1600\text{ cm}^{-1}$ , blue) and C=O ( $1720\text{ cm}^{-1}$ , red) – Middle panel:  $3\times 3\text{ }\mu\text{m}$  RGB composite image combining the AFM-IR absorption mapping obtained at same wavenumber (and corresponding colors) as the IR synchrotron maps. The size of the image here corresponds to the size of one pixel in the synchrotron maps – Right panels: Top: optical image; Middle (from top to bottom spectra): average IR synchrotron spectra obtained on the whole sample, local spectra obtained by AFM-IR highlighting the presence of OM with and without a C=O signature at  $1720\text{ cm}^{-1}$ ). The red, blue and green dashes indicate the wavenumber positions of the IR mapping with the same color; Bottom: AFM topography of the  $3\times 3\text{ }\mu\text{m}$  area studied in AFM-IR

**Conclusions:** AFM-IR measurements demonstrate the presence of organic inclusions intimately mixed with minerals in Ryugu samples at the sub-micron scale.

Focusing on the OM-rich zones of Ryugu samples it is possible to unveil, without any chemical treatment, the IR signature in the chemical bondings of chemical OM heterogeneities, such as local C=O enrichment with spots of a few tens of nm, directly on the whole rock samples.

The results also provide insight into the distribution of organic functionalities of the OM in whole rock that will be compared to IOM extracts from chamber A and chamber C samples.

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**References:** [1] Dartois E. et al. (2018) *A&A* 609, A65. [2] Dazzi A. et al (2005), *Opt. Lett.*, 30, 2388. [3] Dazzi A. and Prater C. (2017), *Chem. Rev.* 117, 5146. [4] Kebukawa Y. et al. (2019) *PNAS* 116, 753. [5] Mathurin J. et al. (2019), *A&A.*, 622, A160. [6] Dartois et al. this meeting.