AFM-IR study of carbonaceous chondrites and Ryugu samples returned by the Hayabusa 2 space mission

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Background – The distribution of chemical bonds in organic matter (OM) of interplanetary samples (meteorites and micrometeorites) can be efficiently and non-destructively characterized using infrared (IR) vibrational spectroscopy. Conventional IR microscopy provides a global view of the dust grain physico-chemical composition but remains spatially limited by diffraction [1]. In state-of-the-art synchrotron-based μ-FTIR microscopy, spot sizes of a few microns at best can be achieved in the mid- IR range. Such diffraction limited sampling can be circumvented by using AFM-IR microscopy [2], allowing, for the first time, to compare the distribution of chemical bonds at the sub-micron scale.

Methods – AFM-IR is now a well-established microscopy technique in the vibrational field, combining an atomic force microscope (AFM) and a tunable IR laser source to record the photo-thermal effect and access chemical information at the sub-micrometric scale [3]. This technique is applied in a wide diversity of scientific fields, and was recently used to analyze OM-rich extraterrestrial samples [2], [4]. As AFM-IR reaches a high resolution (tens of nanometers) compared to the size of the studied objects (few tens to hundreds of microns), regions of interest were first localized and selected using conventional and synchrotron FTIR microscopy.

Results – Firstly results were obtained on carbonaceous chondrites which were prepared without chemical pre-treatment. The extended analyses give a complete insight on the different chemical components involved in these meteoritic samples. The study has then been extended to more precious samples from the Japanese space mission Hayabusa2, that returned samples from the primitive asteroid Ryugu. Ryugu samples were received from the "IOM" and "Stone" initial analysis teams led by Dr. H. Yabuta and Dr. T. Nakamura, respectively. Several samples from two different sample chambers (A and C, corresponding to two different collecting sites) were prepared by crushing small fragments on diamond windows. The analyzed areas were chosen based on previous µ-FTIR synchrotron analyses. It was then possible to localize OM inclusions in samples from chamber A (not shown here) and chamber C (Fig. 1) using the same method than presented in Fig. 1. Figure 2 presents the signal from the Si-O stretching mode of the silicates (1020 cm^{-1} - in green) and that from the OM contributions of the C=C absorption (1600 cm^{-1} - in blue) and C=O absorption (1720 cm^{-1} - in red). It shows that the OM

inclusions recorded by AFM-IR range from 50 nm to 500 nm in size, and that chemical heterogeneities are observed at small scales: parts of the inclusions seem to exhibit local enrichment in C=O (redder) while other a local enrichment in C=C (bluer). This is confirmed by the local IR spectra which show locally different C=C and C=O contributions.

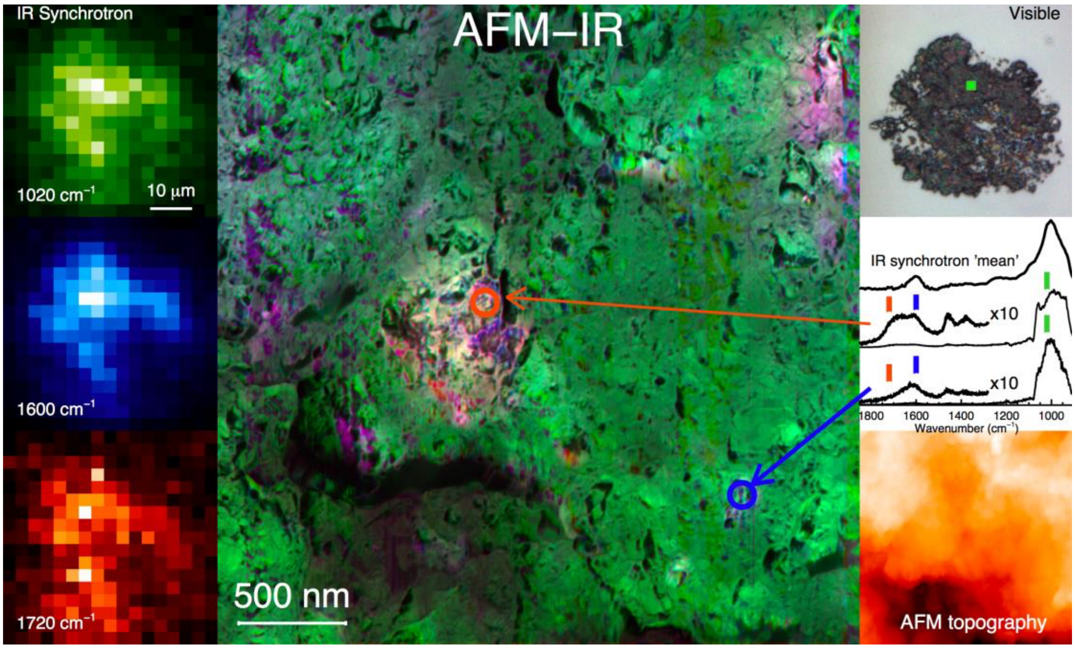

Fig. 2. AFM-IR study of chamber C sample C109-04, in the context of µFTIR maps. Left panels: maps obtained by transmission synchrotron µFTIR and corresponding to the absorption of Si-O (silicates at 1020 cm-1, green), C=C (1600 cm-1, blue) and C=O (1720 cm-1, red) – Middle panel: 3 x 3 µm RGB composite image combining the AFM-IR absorption mapping obtained at same wavenumber (and corresponding colors) as the µFTIR synchrotron maps. The size of the image corresponds to that of one pixel in the synchrotron µFTIR maps – Right panels: Top: optical image of the crushed sample; Middle (from top to bottom spectra): average µFTIR 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 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 x 3 µm area studied in AFM-IR

Conclusions – The AFM-IR technique appears as an optimal method to study the physico-chemical characteristics of meteoritic samples below submicrometric scale. Both on chondritic meteorites and Ryugu samples, measurements demonstrate the presence of organic inclusions intimately mixed with minerals at the sub-micron scale. Focusing on the OM-rich zones of Ryugu samples it is possible to unveil, without any chemical treatment, heterogeneities in the IR signature of the chemical bondings in the OM, such as local C=O enrichment with spots of a few tens of nm.

References

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