Nanoscale infrared characterization (AFM-IR) of Ryugu samples returned by the Hayabusa-2 space mission

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The distribution of chemical bonds in organic matter (OM) of interplanetary samples (meteorites and micrometeorites) can be efficiently and non-destructively characterized using infrared vibrational spectroscopy (FTIR) [1]. Conventional FTIR 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 FTIR microscopy, the typical spot sizes in the mid-IR range can, at best, sample a few µm. This spatial resolution limitation often hampers a direct comparison with complementary techniques such as isotopic imaging with NanoSIMS, transmission electron or X-ray microscopy. Such IR diffraction limitation can be circumvented using AFM-IR microscopy [2]. 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. This technique is applied in a wide diversity of scientific fields [3] and we recently used it to analyze various extraterrestrial samples [4-8]. For this study the tunable IR illuminating source is a QCL laser with a spectral range from 1900 cm^{-1} – 900 cm^{-1} with a top-down illumination. This configuration allows two modes of acquisition. In the first one, the wavenumber is fixed and the tip moves along the surface, allowing to acquire simultaneously AFM topography and an IR absorption map of the sample at the selected wavenumber. In the second one, the tip position is fixed on a sample position and the IR laser is tuned to explore the whole available spectral range of the QCL laser, giving access to local IR spectra at the point of interest.

Ryugu samples from chamber A (surface) and chamber C (sub-surface) were received from the "IOM" and "Stone" Hayabusa2 initial analysis teams. Several samples from chambers A and C were prepared by crushing small fragments on diamond windows, down to a thickness of ~1 µm. Because of the high resolution of AFM-IR (tens of nanometers), regions of interest were first localized and selected using synchrotron-based FTIR microscopy [8].
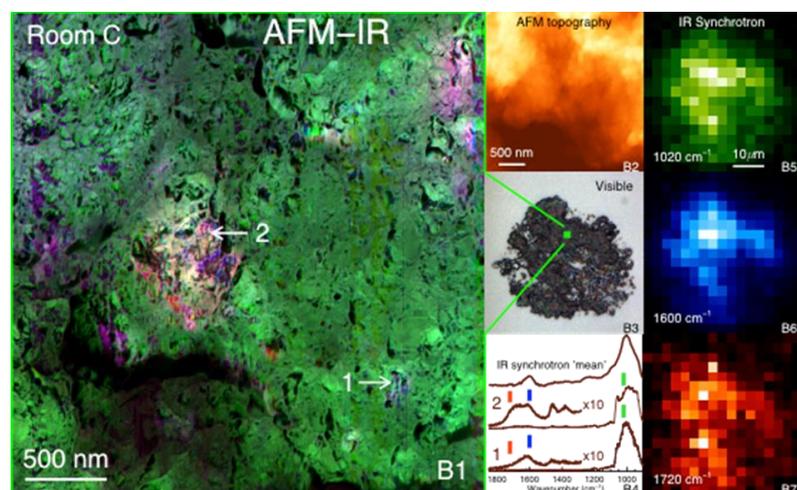
Figure 1: Study of chamber C sample C109-04. B1: 3 x 3 µm RGB composite image combining the AFM-IR absorption mapping obtained at different wavenumbers corresponding to the absorption of Si-O silicates (1020 cm^{-1}, green), C=C (1600 cm^{-1}, blue) and C=O (1720 cm^{-1}, red). The size of the image here corresponds to the size of one pixel in the synchrotron maps - B2: AFM topography of the 3 x 3 µm area studied in AFM-IR - B3: optical image - B4: from top to bottom : 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 cm^{-1}, on the locations highlighted by arrows in B1. The red, blue and green dashes indicate the wavenumber positions of the IR mapping with the same color - B5-B7: IR maps obtained by transmission synchrotron µFTIR at same wavenumber (and corresponding colors) as the AFM-IR maps. Adapted from [7]

A large-scale map (20 µm x 20 µm) was first recorded to characterize the main components' distribution within the sample with a spatial resolution of ~75 nm [8]. As the OM contribution in the IR spectra is weaker than that of minerals, highly spatially resolved maps of 3 x 3 µm in size were acquired with a lateral spatial resolution of ~25 nm. It was then possible to localize OM inclusions in the samples (Fig.1 – B1) by comparing the signal from the Si-O of the silicates (Fig. 1 – B1 in green) and that from the OM contributions of the C=C absorption (Fig. 1 – B1 in blue) and C=O absorption (Fig. 1 – B1 in red). On the larger OM inclusion displayed in Fig. 1 – B1, 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) or in C=C (bluer). Local AFM-IR spectra were recorded on these spots, showing locally different C=C and C=O contributions (Fig.1 – B4) [7].

Based on this first measurement, a more complete analysis of various samples was conducted either on whole-rock samples or on IOM extracted from chambers A and C samples [9]. The results obtained not only confirmed the heterogeneity of the OM distribution already observed but also highlight the fact that OM is mainly distributed in two phases, a diffuse organic component intimately mixed with the mineral matrix and nanoglobule-like organic particles (Fig. 2). These particles are texturally resembling nanoglobules present in primitive meteorites and were identified in both whole-rock and IOM samples from chambers A and C Ryugu samples. The local IR spectra of nanoglobule-like particles also clearly show enhanced carbonyl (C=O) and CH contributions with respect to the diffuse organic matter in Ryugu whole-rock and IOM residue (Fig. 2 – (c)). Such spectra are compatible with that of organic residues formed from UV or ion irradiated ices at low temperatures, simulating the environment of the outer regions of the protoplanetary disk, or in the protosolar cloud.
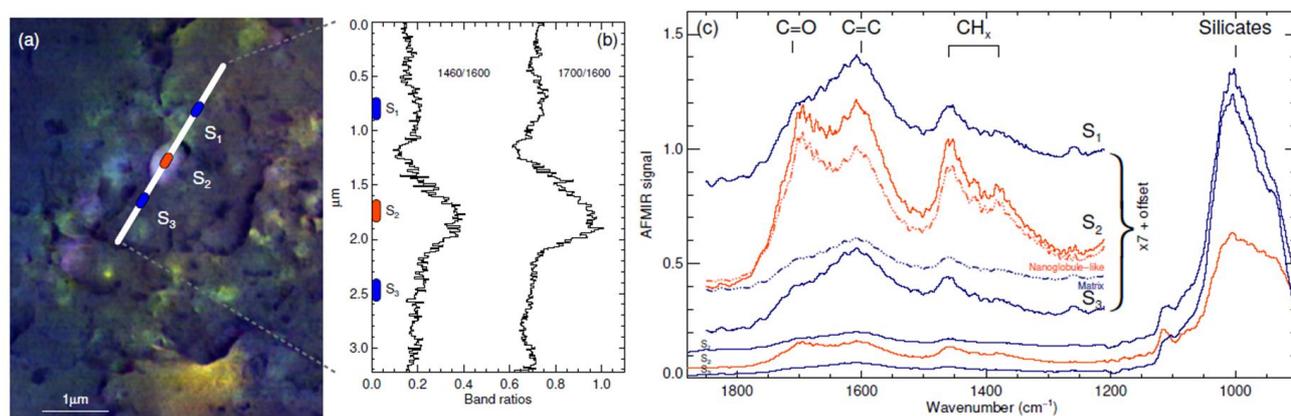
Figure 2: Whole-rock Ryugu sample A0108-19. (a) RGB image of the region including an organic nanoglobule-like particle (C=O at 1720 cm^{-1} in red, C=C at 1600 cm^{-1} in green, CH$_X$ at 1460 cm^{-1} minus 1520 cm^{-1} in blue). The white line shows the location of individual AFM-IR spectra taken across the nanoglobule-like feature. The colored dots (S1 to S3) correspond to average spectra taken on each side (S1 and S3 in blue) and on the nanoglobule-like feature (S2 in red). (b) Intensity ratios corresponding to CH$_X$/C=C (1460 cm^{-1}/1600 cm^{-1}) and C=O/C=C (1700 cm^{-1}/1600 cm^{-1}) along the white line shown in (a). The location of the S1 to S3 spectra is recalled on the left axis. (c) Average spectra on each side (blue, S1 and S3) and on the nanoglobule-like feature (red, S2). The red dot-dashed line spectrum labelled 'Nanoglobule-like' is obtained by scaling the average of S1 and S3 spectra to the same silicate band intensity as in the S2 spectra, and by subtracting this scaled spectrum from S2. The resulting 'Nanoglobule-like' spectrum is thus freed from the matrix contribution underneath the globule. The nanoglobule-like spectrum shows elevated CH$_X$ signal (intense methyl and methylene deformation modes at ~1460 cm^{-1} and ~1370 cm^{-1}), as well as high carbonyl contributions around 1700 cm^{-1}. The blue dot-dashed line spectrum labelled 'Matrix' corresponds to the expected contribution from the matrix for equivalent probe depth as for the nanoglobule-like spectrum. Adapted from [9].

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 as well as the sub-micrometric spatial distribution of the different components. This study shows that OM exists in (at least) two forms in Ryugu samples, as a diffuse phase in the minerals matrix, and as isolated inclusions resembling nanoglobules.

References
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