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NANOMETRE-SCALE INFRARED CHEMICAL IMAGING (AFM-IR) OF ORGANIC MATTER IN ULTRA-CARBONACEOUS ANTARCTIC MICROMETEORITES (UCAMMS) AND FUTURE ANALYSES OF HAYABUSA 2 SAMPLES. J. Mathurin¹, E. Dartois², C. Engrand¹, J. Duprat¹, A. Deniset-Besseau³, A. Dazzi³, Y. Kebukawa⁴, T. Noguchi⁵, D. Troadec⁶. ¹Univ. Paris-Saclay, CNRS, IJCLab, France (jerie-mathurin@u-psud.fr), ²Univ. Paris-Saclay, CNRS, ISMO, France, ³Univ. Paris-Saclay, CNRS, ICP, France, ⁴Faculty of Engineering, Yokohama National University, Japan, ⁵Kyushu University, Japan, ⁶IEMN, Univ. Lille, France.

Introduction: The chemical composition of organic matter (OM) in interplanetary samples (meteorites and micrometeorites) is suitably characterized by the distribution of the different chemical bonds using infrared (IR) vibrational spectroscopy (see e.g. [1]). Classical IR microscopy provides a global view of the dust grain chemical structure content but remains limited by the diffraction, with typical spot sizes sampling a few micrometers in the mid-IR range. This spatial resolution limitation is well above that of complementary techniques such as isotopic imaging with NanoSIMS or transmission electron or X-ray microscopy techniques. These techniques reveal mineralogical, chemical and isotopic heterogeneities at the sub-micron scale but do not give full access to the distribution of the various chemical bonds. The IR diffraction limitation can be circumvented by using AFM-IR microscopy. This technique opens a new window for studies of OM at ten to tens of nanometer scales and will be of importance for studies of the samples from carbonaceous asteroid *Ryugu*, returned by the Hayabusa 2 space probe in December 2020.

AFM-IR is now a well-established microscopy technique in the vibrational field. It combines an atomic force microscope (AFM) and a tunable IR source to detect photo-thermal effect and access chemical information down to a nanoscale resolution [2]. This technique is now applied in a wide diversity of scientific fields [3], and was recently used to analyze extraterrestrial OM [4, 5]. We report here on recent results obtained on imaging two UltraCarbonaceous Antarctic MicroMeteorites (UCAMMs) using AFM-IR [5]. A small fraction of the Antarctic micrometeorites from the Concordia collection consists in UCAMMs, particles with extreme concentrations in OM, most of them exhibiting large deuterium excesses [6]. UCAMMs are also found in Japanese interplanetary dust collections [7-9]. These UCAMMs most likely originate from the surface of small icy bodies in the outer regions of the solar system [1,6,7,10]. The large OM fraction of UCAMMs (considerably higher than in the most carbon-rich meteorites) enables direct analyses without the pre-treatment generally applied to extract the OM from other meteoritic samples, and give access to unaltered chemical maps of the intimate association of minerals and organics.

Samples and methods: Two UCAMM fragments from the Concordia collection were analyzed by AFM-IR: DC06-07-18 (hereafter DC06-18) and DC16-14-309 (hereafter DC16-309). DC06-18 was prepared by crushing a small fragment on a diamond window. DC06-309 was ultramicrotomed after embedding in sulfur; sulfur was then sublimated from the sections overnight in a desiccator at about 50°C. After AFM-IR analysis, complementary high resolution scanning electron microscopy images and EDX spectral maps of elements from C to Fe were obtained on the samples.

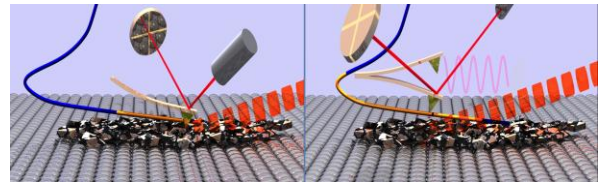


Figure 1: Schematic view of the AFM-IR technique in contact (left panel) and tapping (right panel) modes. The interaction potential normal to the surface is illustrated by the colored line. The approximate excursion ranges on this interaction potential for the two AFM modes are shown in yellow. In contact mode, the tip is in close contact with the surface and explores mainly the repulsive potential. In tapping mode, the cantilever oscillates and approaches the surface only for a short time, oscillating back and forth on the potential curve.

We used two different AFM-IR setups: i) contact mode setup where the AFM tip stays in contact with the sample (Fig. 1 left panel), and ii) tapping mode setup where the AFM tip is oscillating at the surface of the sample (Fig. 1 right panel). The latter mode is more adapted to the AFM-IR imaging on loosely bound samples. AFM-IR maps were acquired in contact mode for DC06-18 and tapping mode for DC16-309. In both setups, two acquisition modes are possible. In the first mode, the emission 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. In the second mode, the tip position's is fixed and the IR laser is tuned to explore the whole spectral range (here $1900\text{ cm}^{-1} - 1350\text{ cm}^{-1}$) giving access to local absorption spectra at the point of interest.

Results: Figure 2a shows the local absorption at different wavenumbers on a microtomed section of UCAMM DC06-309, each wavenumber corresponding

to the specific absorption of a given chemical bond. The AFM-IR maps reveal the heterogeneity of the absorption of the C=O (1710 cm^{-1} , in green) and C=C (1600 cm^{-1} , in red) bonds. Based on these maps, ratio of different absorptions can be obtained to map the functional group diversity. Figure 2b shows the ratio of the C=O bond (green) versus the C=C bond (red). This ratio shows heterogeneities appearing as patches of tens to hundreds of nanometers in size. The size of these heterogeneities is consistent with complementary results obtained by STXM-XANES for UCAMMs [9, 11, 12]. Local spectra were also acquired (Figure 2c) to allow a spectral identification of vibrational signatures at very fine scale. The heterogeneity of such signatures escape detection in a classical diffraction-limited IR analysis with typical sampling of several microns in size. AFM-IR also allowed the identification of a sub-micrometric contaminant brought during the sample preparation of DC16-309, as observed at 1460 cm^{-1} (light blue in Fig. 2a and spectra lines S2 & S3 in Fig. 2c) (see [5]).

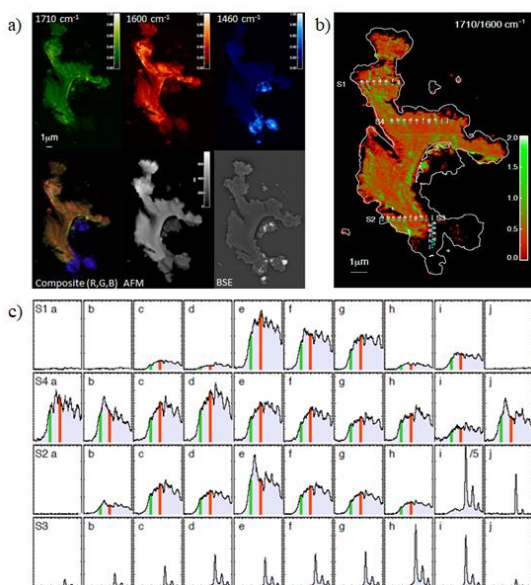


Figure 2: AFM-IR study of UCAMM DC16-309. a) AFMIR maps recorded at 1710 cm^{-1} (green), 1600 cm^{-1} (red), and 1460 cm^{-1} (blue), composite (red, green, blue) image of the three maps, and AFM height and back-scattered electron (BSE) images, b) ratio of the AFM-IR maps at 1710 and 1600 cm^{-1} . The white isocontour delineates the height corresponding to 5% of the maximum height measured by the AFM tip, c) AFM-IR spectral maps labelled S1 to S4, performed in selected locations shown on the (b) map in the $1900\text{--}1350\text{ cm}^{-1}$ range. Vertical green and red lines on (c) mark the 1710 cm^{-1} and 1600 cm^{-1} wavenumber positions.

Conclusions and outlook for the analysis of Hayabusa 2 samples: The chemical functional group diversity of OM in UCAMMs without pre-treatment can be quantitatively characterized at a sub-micron

scale by AFM-IR [5]. Using this technique with an extended spectral range should increase the outcome of the chemical characterization of the OM and will better define the association (and potential interaction) between the OM and the minerals in the sample.

In addition to the preliminary work by Kebukawa et al. [4], this first study paves the way for the development of AFM-IR studies of different extraterrestrial objects such as carbonaceous chondrites. More recently, we successfully applied AFM-IR in tapping mode to carbonaceous chondrites for the first time. To prepare the analysis of Hayabusa 2 samples, a preliminary study of the Jbilet Winselwan (heated CM2) carbonaceous chondrite was performed, and heterogeneous distribution of C=O and C=C was observed (Figure 3). One of the main objectives of these investigations is to develop an upfront and dedicated expertise on complex materials such as extraterrestrial samples, to fully apply the AFMIR technique on the samples soon returned by the Hayabusa 2 mission.

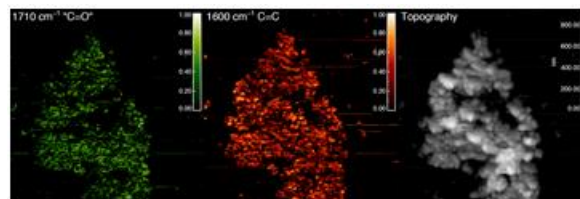


Figure 3: AFM-IR study of Jbilet Winselwan (heated CM2) carbonaceous chondrite - AFMIR maps recorded at 1710 cm^{-1} (green), 1600 cm^{-1} (red) and AFM height

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