NANO-INFRARED SPECTROSCOPY OF FUNCTIONAL CARBON GROUPS IN EXTRATERRESTRIAL KEROGENS.

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Introduction: Asteroids, which are the witnesses of the solar system formation, keep track of the different physico-chemical processes that occurred billions of years ago with little evolution over time. Through collisions, asteroids fragments be found on earth as meteorites, and studied to understand the chemical composition, geology and mineralogy of the parent asteroids leading to new insights on the formation of our solar system. Asteroids, therefore, can be contained different compositions organic matters (OM), silicates, sulfides, carbonates and water ice [1] Among the meteorite's classification, carbonaceous chondrites are of particular interest because they can contain up to 4 wt.% of organic matter, consisting both of insoluble and soluble compounds. To understand how and under which conditions OM has interacted with inorganic phases, is a key step hypotheses on the mechanism of the accreted OM. Therefore, to analyze organic matter without losing the petrographical information, a large set of techniques are available such as *Micro*-Fourier transform infrared spectroscopy, Raman spectroscopy, TEM and STXM. However, the main drawback of IR-related techniques is that they are limited by the diffraction limit and are particularly challenging for the study of intimately mixed organic and silicates such as found in IDPs, micrometeorite or meteorite matrices (grain size around hundreds of nanometers). In order to efficiently unmix spectral signatures of the different constituents, we apply here nano-IR spectroscopy a recently developed technique, having a spatial resolution beyond the diffraction limits can now be performed [2], [3]. Our study aims to characterize a suite of coals samples as analogues, two meteorites (CR2: Elephant Moraine 92042 (EET 99042) and CI: Orgueil) as well as their extracted Insoluble Organic Matter (IOM). The objectives are (i) investigate the OM/minerals evolution in the coals samples which are the known analogues of meteorites with IR imaging with spatial resolution beyond the conventional optical diffraction limit, (ii) document the IR spectra and IR imaging of IOMs extracted from their "bulk" materials and (iii) investigate the interaction between OM and minerals with nanometer spatial resolution in meteorites samples by NanoIR spectroscopy.

IR spectroscopy: Micro-infrared spectra were analyzed firstly with a Bruker Hyperion 3000 infrared microscope at IPAG. Point spectra were obtained on the sample with a typical beam size of 100 µm x 100 µm. Nano-IR measurement were obtained with a Brüker nanoIR-3s at the Institut de Planétologie et d'Astrophysique de Grenoble (Grenoble, France). Thus setup combines two complementary nanoscale IR techniques, AFM-IR and a scattering-SNOM. The AFM-IR technique results from the coupling of an Atomic Force Microscope (AFM) and a tunable infrared pulsed. This method is a powerful tool for the detection of organics within the sample, allowing nanoscale-resolution images and spectra. In addition, the nanoIR-3s allows mineral characterization using Scattering Scanning Near field Optical Microscopy (s-SNOM) giving information of the optical properties at a nanoscale region. For AFM-IR measurement, cantilever oscillation amplitude provide the equivalent the IR absorption [4]. While IR imaging was collected by fixing the wavenumbers and AFM images were also recorded during the mapping measurement to check of the sample thermal drift.

Sample and sample preparation: Three coal samples having different vitrinite reflectance from immature to mature coal level were studied (R_o from 0.33 to 2.8%). In addition, two primitive carbonaceous chondrites were investigated that are the CR chondrite EET 92042 (CR2) and the CI chondrite Orgueil (CI). In the case of the two chondrites, IOM was extracted at IPAG and analyzed with conventional and AFM-IR spectroscopies. In order to optimize Nano-IR measurements several sample preparations were tested. Samples were prepared as pressed between 2 diamond windows, and as slices cut with focus ion beam (FIB) or as section produced with Sulfur embedding ultramicrotomy [5].

Results: Our investigations of the optimum sample preparation revealed that all three preparations have their advantages and drawback. Pressing between diamonds windows provide an relatively rapid sample preparation technique, however the spatial information is somehow deformed by the pressing process. Good quality spectra were obtained for all samples using this preparation but IR maps were poor quality using the Tapping AFMIR Imaging due to the unflatten surface and thickness of sample. FIB and microtome preparations enable to preserve the petrographically context but are more longer to implement.

Figure 1 presents typical spectra obtained for a coal sample using AFM-IR, in the case of a sample prepared by Sulfur embedding ultramicrotomy in Kyushu University (Japan). Figure 1 also provide a composition image (RBG: Red, Blue and Green) obtained on that particular samples, color coded according to C=O (at 1700 cm^{-1}), C=C (1600 cm^{-1}), and Si-O vibrations (at 1040 cm^{-1}). Two major types of spectra are present in the sample, a spectra dominated by strong band at about 1040 cm^{-1} that we attribute to phyllosilicate (Si-O), and spectra with absorption at 1700, 1600, 1450 cm^{-1} that are attributed to complex organic matter. These results reveal the capability to obtain and unmix spectral signature of inorganic and organic species, and gives insights on the spatial resolution of the techniques, typically a few hundredth nanometer for this particular sample.

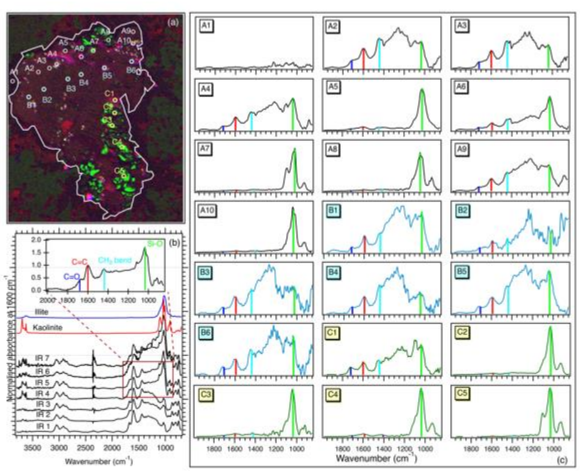

Figure 1. A composition image of OM at 1700, 1600 cm^{-1} and mineral at 1040 cm^{-1} associated with AFMIR spectral position in the 2000 – 850 cm^{-1} range, surrounding the image in comparison with the Micro-FTIR spectra. Note that the size if the analyzed area in (a) is of 10 × 12 μm^2.

Moreover, Figure 1 also presents a comparison of AFM-IR spectra to micro-IR spectral obtained on the same coal. This comparison reveal a good agreement between the spatially averaged signature obtained with micro-FTIR spectroscopy, and the individual phases signatures obtained with AFM-IR.

We will present at conference the whole dataset obtained so far, including a comparison of organic signatures of IOM and raw meteorite matrix, and then discuss our future plan of analysis.

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