RAMAN MICROSPECTROSCOPY COUPLED TO SEM/EDS TO DETECT AND IDENTIFY ORGANIC MATTER IN IMPACT GLASSES, METEORITES AND TERRESTRIAL ANALOGS

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Abstract

In this work point-by-point Raman microspectroscopy, coupled to SEM/EDS, and Raman micro-imaging were employed as non-destructive techniques to detect the characteristics Raman bands corresponding to different Polycyclic Aromatic Hydrocarbons (PAHs), carboxylic acids and their metallic salts, kerogen and hydrocarbons. These determinations can be performed directly on the samples or on thin section preparations.

Several examples will be shown to demonstrate the adequacy of this technique to detect and identify (a) PAHs in Libyan Desert Glasses (LDG) and Darwin Glasses (DG), (b) carboxylic acids and its metallic salts from terrestrial weathering in Martian Meteorites like NWA 6148, as well as on LDG, DG and terrestrial analogs, (c) kerogen in LDG inclusions and terrestrial analogs.

Those identifications were corroborated by Py-GC/MS for non-polar organic compounds and Ionic Chromatography and GC-MS, in extracts obtained by leaching the polar organic molecules with Milli-Q water. Thus, Raman spectroscopy, that will be in the payload of both Exomars2020 (ESA) and Mars2020 (NASA) rovers, is a superb technique to measure organic compounds in impact glasses, meteorites and terrestrial analogs. We hope this success will be achieved soon on Mars.

1. Introduction

The presence of organic compounds in impact glasses, meteorites and terrestrial analogs can offer information about the area where they were formed, about the extraterrestrial body impacting on Earth as well as on the terrestrial weathering processes affecting the nature of the compounds found in these bodies. As these organic compounds are in minor concentrations, it is not easy to detect them by using non-destructive analytical techniques, other than the chromatographic ones usually employed.

Those organic molecules, including kerogen, are usually in the form of inclusions (in external and internal parts of samples), if they were trapped when formed, or in fissures/ cracks if they enter in the samples by means of terrestrial weathering processes.

In this work, we propose a new analytical strategy to detect organic molecules using Raman spectroscopy, coupled to SEM/EDS, in point-by-point mode or as Raman Imaging. Raman spectroscopy will be in the two rovers, Rosalind Franklin (ESA) and Mars2020 (NASA) that will operate on Mars after 2021, with the aim to search for (among others) organic compounds.

2. Experimental

2.1 Samples

Samples from two Impact Glasses, Libyan Desert Glass (LDG) and Darwin Glass (DG), and one stromatolite, as a terrestrial analog, were used before testing the methodology on a meteorite sample.

2.2 Instruments

The Renishaw InVia Raman spectrometer equipped with a 532 nm excitation diode laser and a high sensibility and low noise CCD detector (Peltier cooled) was used, having a mean spectral resolution of 1 cm^{-1} as wavenumber units. The nominal power of the laser can be modulated to avoid the thermo-decomposition of samples. The spectrometer has coupled a confocal microscope and different lenses of 5x, 20x and 50x were used. The calibration of the equipment was performed dayly with a silicon slice (520.5 cm^{-1} band). Spectra were acquired at 5 seconds and 1 accumulation using the 1800 l/mm grating while Raman images were taken with the HR-LineScan device through the Wire 4.2 software (Renishaw, UK).

The SEM/EDS measurements were performed with an EVO 40 Scanning Electron Microscope (Carl Zeiss NTS GmbH, Germany) coupled to an X-Max Energy-Dispersive X-Ray spectroscopy equipment (Oxford Instruments, Abingdon, Oxfordshire, UK).

3. Results

To avoid false positives, the thin and thick samples must be polished without using diamond powder and the glue must not be present in the spot areas. The Raman spectrum of the glue must be taken separately just to obtain its reference and confirm its absence in the spectra collected from samples.

The first step is the SEM/EDS screening to search for inclusions/bubbles and fissure/cracks. Fig. 1 shows an example obtained from a LDG sample.

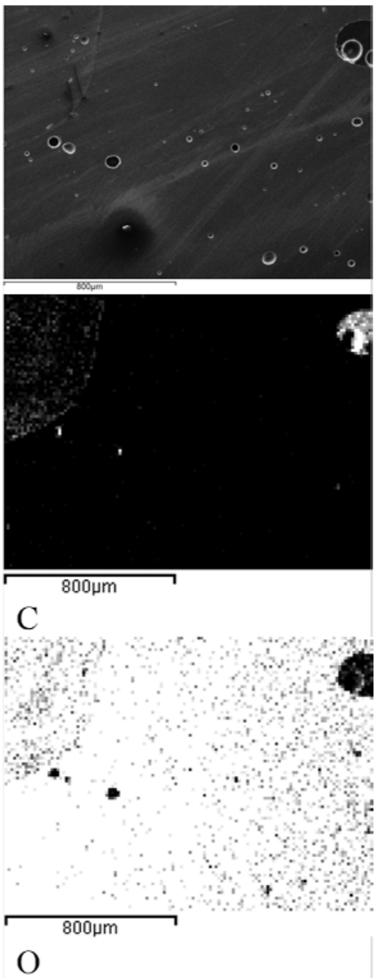

Figure 1. *SEM microphotograph and EDS maps of carbon and oxygen on a LDG thin section sample.*

As seen, most of the bubbles have not oxygen, but some have carbon. Those are good candidates for kerogen and/or aliphatic or aromatic hydrocarbons.

Then, the Raman microspectroscopic analysis must be perfomed on such bubbles to confirm if we have kerogen or an organic molecule. Fig. 2 shows such spectrum obtained on a sample of stromatolite.

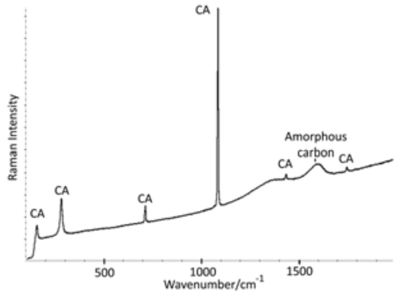

Figure 2. *Raman spectrum obtained on a bubble of an stromatolite showing the presence of amorphous carbon (kerogen) and calcite (CA) from the matrix*

Alternatively, if several bubbles are simultaneously present in the same micrometric area, Raman imaging can be performed, obtaining the distribution of the organic molecules, like Fig. 3 shows.

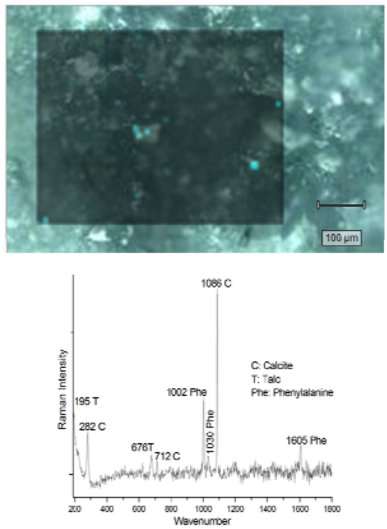

Figure 3. *Raman image on a 500x500 microns area showing five bubbles of Phenylalanine. Talc (T) and calcite (C) from the matrix are shown in the spectra*.

The identifications of organic molecules were corroborated by Py-GC/MS for non-polar organic compounds and Ionic Chromatography and GC-MS, in extracts obtained by leaching the polar organic molecules with Milli-Q water. Thus, Raman spectroscopy is a superb technique to identify organic compounds in impact glasses, meteorites and terrestrial analogs. We hope this success will be achieved soon on Mars.

4. Acknowledgments

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