A MICRO RAMAN STUDY OF THE ERUPTED PYROCLASTS FROM EL HIERRO (SPAIN)

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Introduction: Several days after the start of the submarine eruption of 10 October 2011 offshore El Hierro island, abundant dark fragments of low bulk density (roughly 0,6 gr/cm3) resembling volcanic bombs appeared floating on the ocean surface at an approximate distance of about 3 km SSW of the coastal village of La Restinga, placed at the south point of the island. The fragments are 10 to 20 centimeters in its major axis and are formed by a light colored glass, highly vesicular (bubble-rich) and low bulk density (about 0,3 to 0,4 g/cm3) as majoritarian material, covered by a thin dark crust of 1 cm or less, also of glassy nature, less porous and of higher bulk density (roughly 1,4 gr/cm3). Mingling between both materials with quite net limits can be observed. Identification of these pristine pyroclastic materials is of great interest to understand the glass formation processes from the magmas and the associated materials produced in these conditions under the water.

Raman spectroscopy is a very well suited technique for that analysis at micro scale provide it is completely non-destructive, very precise for mineral phase identification at mineral grain scale and very sensitive to temperature and pressure effects on the crystalline structure of minerals.

In this work a detailed Raman spectroscopic study has been performed in one piece of about 2x2 centimeters (see Fig.1) provided by the Instituto Volcanológico de Canarias and the Museo de la Naturaleza y el Hombre (Tenerife). This study is considered at our knowledge the first Raman analysis performed on these type of materials and the results obtained are presented and discussed.

Figure 1. Top: the sample anlysed in this study. Bottom: detail of the vesicular structure of the white area (silica glass).

Experimental: Raman spectroscopy was performed in the laboratory on the samples without any preparation using a Kaiser Raman spectrometer HoloSpec illuminated with a laser at 633 nm. Detection
was performed with an Andor CCD of 1024x256 pixels and a Raman probehead. The spectrometer is coupled by fiber optics to a Nikon Eclipse E600 microscope. Several objectives were used allowing a range of laser spots on sample between 30 and 10 μm diameter.

Spectra were also performed for comparison purposes with a prototype of the Raman spectrometer under development for ExoMars mission, now a joint NASA-ESA mission to be launched in 2018. This spectrometer is illuminated with a laser working at 532nm with a power on sample of 20mW and a spot diameter of 50 microns. And the detector is a Hamamatsu CCD of 2024x512 pixels. Detailed analysis on powder simulating the operation mode inside the ExoMars rover's analytical laboratory will be published separately.

Results: In Figure 1 the Raman spectra of the white area corresponding to the glassy silica in different crystalline states is depicted. The main broad bands at about 500 cm-1 (Si-O bending) and 1000 cm-1 (Si-O stretching) show different overlapped bands structure. In some cases spectra of well crystallised quartz is observed. The ratio between the band area of the 500 cm-1 and 100 cm-1 broad bands can be taken as a measure of the polymerization in the glassy structure.

The values found here differ in some extent showing the cooling process is not homogeneous at local scale. In Figure 2 spectra of different mineral phases detected mainly at the interface between the clear zone and the grey-dark zone are shown. These minerals are identified as oxides (hematite, magnetite and Ti-oxides), Mg and Na sulfates, forsterite and feldspars. Also partially graphitized carbon was detected, its origin is probably associated with the organic matter in the ocean trapped with the eruption.

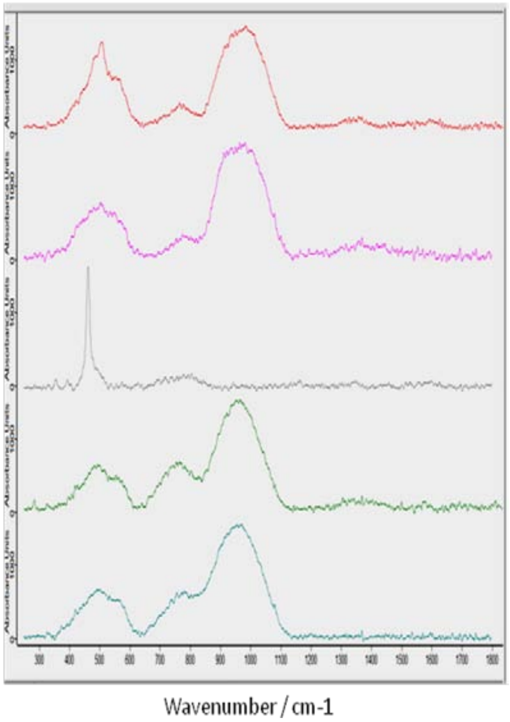

Figure 2. Raman spectra obtained in the white glassy area at different spots. Pure quartz with size of about 10 microns is detected in some cases inside the glass.

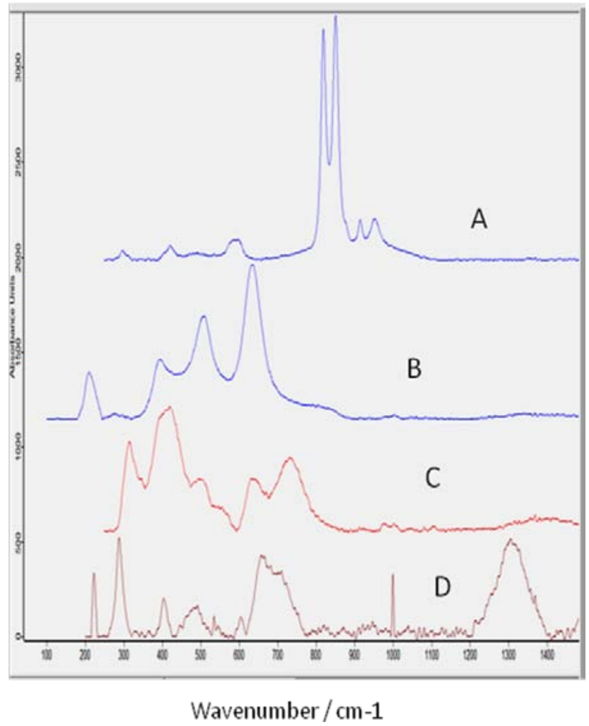

Figure 3. Raman spectra obtained at the dark area and at the interface with the white area. A: forsterite, B, C: a mixture of Fe and Ti oxides with some amount of plagioclase, D: hematite with Na Sulfate.

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