Raman Spectroscopy of Pillow Lavas from the Anaga zone – Tenerife Canary Island

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INTRODUCTION.

Some lava deposits have been reported on Mars by Martinez-Alonso et al (2008), showing similar characteristics to those of terrestrial pillow lavas. Pillow Lavas are an unequivocal sign of volcanism in an aqueous environment. Pillows are found in a wide variety of shapes including near-spherical bulbous pillows, flattened pillows, elongate and tubular pillows, and trapdoor pillows. They are probably the most abundant lava structural type on Earth. However, this kind of structure shares a concentric geometry and large central cavities, but they have differences in mineralogy, on the degree of crystallization, and the jointing. The main reason is that the interiors cool more slowly than the quenched glass rind, being more crystalline. Progressive crystallization at slower cooling rates toward the interior produces a variety of rock textures, and the interiors of large pillows may be almost entirely crystalline (Kenish et al., 1998). Studying and understanding the pillows lavas could help us to understand the past of Mars.

It has been proposed that Tenerife is an area of reference for carrying out research and technological studies with planetary and astrobiological implications (Rodriguez-Losada et al., 2000; Bustillo & Martinez-Frías, 2003; Lalla et al., 2010). These studies are mainly related with submarine and subaerial hydrothermal and weathering processes, which affected the primary volcanic mineralogy.

SPECTROSCOPIC TECHNIQUES.

Multispectral ranges and techniques are necessary in order to obtain ground truth information for the interpretation of rock and soil on Mars. Specially, the combination of Raman spectroscopy with LIBS and XRD, which are bound to be working jointly in future explorations on planetary Robotic Missions as ExoMars, which will bring Raman and XRD instruments onboard (Rull et al., 2006). They will provide comprehensive information about mineralogy taking into account different selection rules and particle sizes, vibrational and excitational information. Implementing an automatic mapping on the bulk sample surface with autofocus and auto adjustment of the acquisition parameters at each point, the potential of Raman technique on geological complex targets can be improved (Rull et al 2011).
Thus combining these techniques on terrestrial analogues environments (Natural Laboratories) could help us to learn about the planetary processes and test the technologies, methodologies and protocols to follow (Lacoste-Courreges et al., 2007).

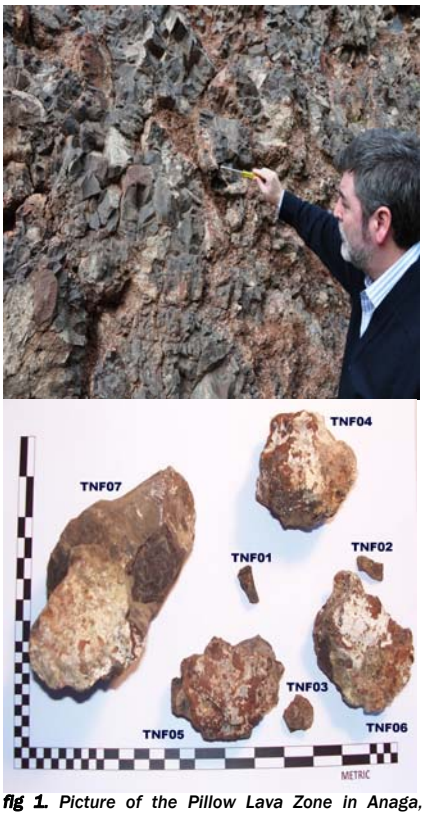

fig 1. *Picture of the Pillow Lava Zone in Anaga, Tenerife and picture of the Samples.*

EXPERIMENTAL SET-UP.

The mineralogical characterization of the sample was performed by micro-Raman Spectroscopy, using a microscope Nikon Eclipse E600 coupled to a spectrometer KOSI Holospec f/1.8i illuminated by a laser REO LSRP-3501, He-Ne 632.8 nm. The detection was performed with a CCD Andor DV420A-OE-130. Furthermore XRD (with XRD diffractometer Philips PW1710), IR-Spectroscopy (PerkinElmer Spectrum 100 FT-IR spectrometer) and L.I.B.S (Porta-Libs from Stellar Net) were used.
Raman mapping of the bulk surface of the sample were done by the ExoMars mission Operator simulator in automatic mode (532nm Laser with a spatial resolution of 2,5µm) (Rull et al., 2011).

RESULTS.

The Raman spectroscopy shows the presence of Plagioclase, Pyroxene, Magnetite, Hematite, Quartz, Olivine and hydrated secondary mineral such as carbonates. During the acquisition of Raman spectra, the preliminary results show a considerable peak width and a big contribution of fluorescence, which is caused by the alteration of the material and the amorphous structure (Fig. 2).

The XRD spectra determined the crystalline mineral phases included in the samples. The pillows contain significant amount of Plagioclase (silica-rich groundmass) and pyroxene. The results are coherent with those obtained by Raman spectroscopy showing an

palabras clave: Pillow Lavas, Espectroscopia Raman, Espectroscopia Infrarroja.

key words: Pillow Lavas, Raman Spectroscopy, IR Spectroscopy.

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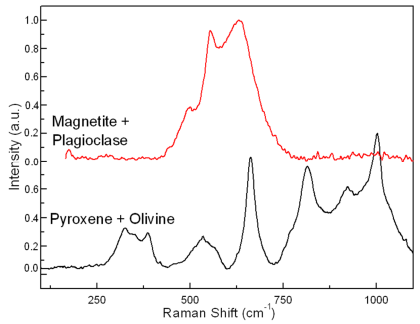


fig 2. *Raman Spectrum of Pillow Lava. Shown two spectra of the crystal matrix. The Original fluorescence was corrected.*

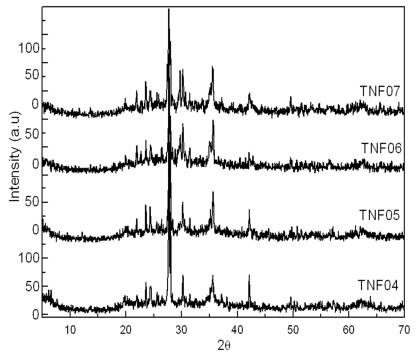


fig 3*. XRD Diffractograms of the Pillow Lavas Samples.*

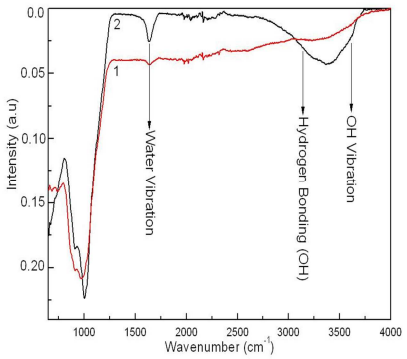
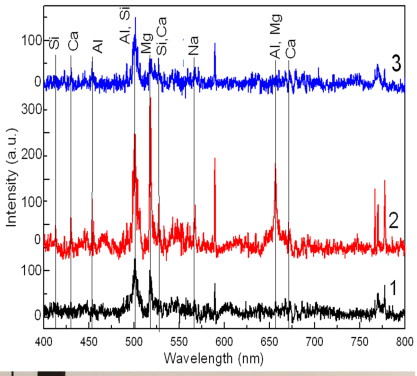


fig 4*. ATR-FTIR Infrared Spectra of Pillow Lava. (1) Internal Surface of the Sample (2) External Surface of the Sample.*

amorphous structure (Fig. 3).

It is well known that IR-Spectroscopy is more sensitive to the OH and H_2O vibrations than the Raman spectroscopy it can be seen directly by the hydrogen bonding of the OH and the water vibration. These are consequence of the water-rock interaction due to the hydrothermal activities (Fig. 4).

On the other hand, LIBS of the different zones of the samples, both external and internal zones, has demonstrated that some elements like Fe, Si, Mg, Al and Ca may be lost or added, during the formation and alteration of the pillow



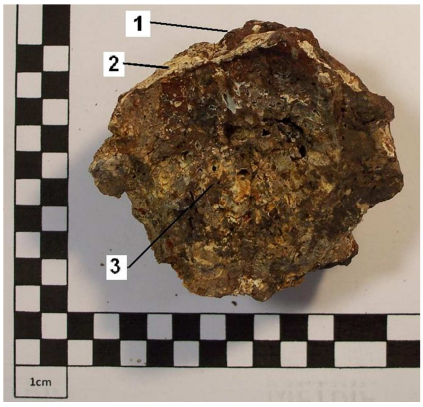


fig 5*. Laser Induced Breakdown Spectrometry of Pillow Lava Sample. On the Spectra is only shown the most intense peaks. (1) Brown External Face (2) White External Face (3) Red-Brown Internal Face.*

lava (Fig. 5). The peak identification has been done by direct comparison with reference samples.

CONCLUSION.

The results show that the groundmass is plagioclase material with clino-pyroxene. Olivine phenocrysts are also observed from the host matrix, but only with Raman Spectroscopy. The secondary mineralogy (Calcite), replacing the primary phases suggest a relatively low temperature alteration (<100ºC). The structure is very amorphous and it can easily be altered. The processes, mainly the hydration of the groundmass and ion exchange, are due to the action of percolating groundwater in the sub-aerial environment or to the action of sea water in the case of submarine environment.

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REFERENCES.

Bustillo, M.A., Martínez-Frías, J. (2003): Green Opals in Hydrothermalized basalts (Tenerife Island, Spain). Alteration and aging of silica pseudoglass. Journal of noncrystalline solids, ***323****, 27-33.*

Kennish, M.J., Lutz, R.A (1998): Morphology and distribution of Lava flows on mid-ocean ridges a review. Earth-Science Reviews, ***43****, 63-90.*

Lacoste-Courreges, G.B., Ahlers, B., Rull, F. (2007): Combined Raman Spectrometer/LIBS for the next ESA Mission to Mars. Spectrochim. Acta A, ***68****, 1023-1028.*

Lalla, E., Sansano, A, Sanz, A., Alonso, P., Medina, J., Martinez-Frías, J., Rull, F. (2010): Espectroscopía Raman de Basaltos correspondientes al Volcán de las Arenas, Tenerife. Macla, ***13****, 129-130.*

Martínez-Alonso, S, Mellon, M.T., Banks, M.E., Keszthelyi, L.P., McEwen, M.E., The HiRISE Team (2008): Evidence of volcanic and glacial activity in Chryse and Acidalia Planitiae, Mars. Icarus, ***212****, 597-621.*

Rodríguez-Losada, J.A., Martínez-Frías J., Bustillo, M.A., Delgado, A., Hernández-Pacheco, A., De la Fuente Krauss, J.V. (2000): The hydrothermally altered ankaramite basalts of Punta Poyata (Tenerife, Canary Islands). J. Volcanol. Geother. Res., ***103****, 367-376.*

Rull, F., Martinez-Frías, J. (2006): Raman Spectroscopy goes to Mars. Spectroscopy Europe, ***18****, 1.*

Rull, F., Maurice, S., Diaz, E., Tato, C., Pacros, A., The RLS Team (2011): The Raman Laser Spectrometer (RLS) on the Exomars 2018 Rover Mission. The 42nd Lunar and Planetary Science Conference, 2400.