RAMAN ANALYSIS OF BASALTIC SAMPLES FROM TENERIFE ISLAND (CAÑADAS, AZULEJOS, AND HISTORICAL ERUPTIONS) WITH THE EXOMARS RLS INSTRUMENT. E. Lalla[1], G. Lopez-Reyes[1], F. Rull[1], J. Medina[1], J.Martinez-Frías[1], A. Sansano[1] and R. Navarro. [1]Unidad Asociada UVA-CSIC al Centro de Astrobiología, Valladolid, Spain (**lallaea@cab.inta-csic.es**)

Introduction: Prior in-situ planetary missions have proved to be a useful method for providing in-situ mineral characterization and rock identification on planetary surfaces to better understand the evolution and habitability of Mars. The future ESA Exomars mission will focus on "Searching for evidence of past and present life on Mars" and to characterize the water/geochemical environment as a function of depth in the shallow subsurface [1].

The Raman Laser Spectrometer (RLS) is one of the selected instruments included in the Analytical Laboratory Drawer (ALD) of the rover, as Raman spectroscopy is considered a key technique by ESA due to its ability to perform a combination of petrology, mineralogy and geochemistry at the same spot [2]. This will provide new means to add knowledge of the past evolution of Mars. In order to maximize the instrument capabilities, it has been necessary to develop simulation tools and instrument prototypes for evaluating the instrument performances in the framework of the unmanned operation mode of the rover. This experiments allow us to evaluate the instrument capabilities and to study its limitations. The instrument will perform an automatic linear mapping on a powdered sample, autofocusing on the surface and auto-adjusting the acquisition parameters at each point. With this methodology, the geological context of the samples is lost. However, the potential of the Raman technique on geological complex targets can be improved in some aspects with respect to the analysis on bulk samples, and with respect to manned analysis, as for example, pseudo-quantification of abundances [3] or detection of minor phases present on the sample [4].

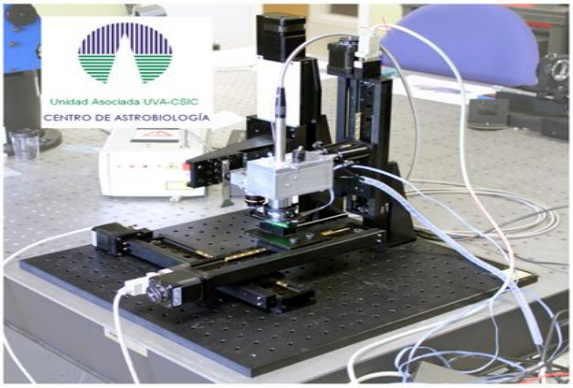

Figure 1. Picture of the RLS Simulator at the Unidad Asociada UVA-CSIC al Centro de Astrobiología

Natural samples from basaltic terrestrial analogues have been selected to perform analysis on Mars-relevant samples (with which the technology can be tested and improved). The Tenerife Island is an area of reference for carrying out research and technological studies with planetary and astrobiological implications. Several places of the Island have been selected considering the relevant volcanic activity and episodes: the fluid-rock interactions caused by the weathering processes, the submarine and sub-aerial hydrothermal alterations and the geomorphological features [5, 6, 7].

This work presents the results obtained with the RLS instrument on these samples, and compares them with the characterization performed with laboratory instruments.

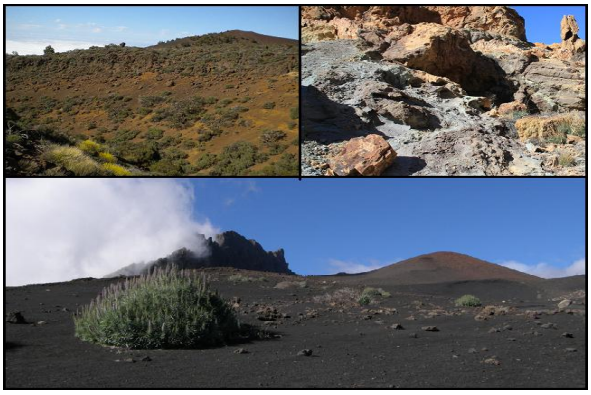

Figure 2. Picture of the sites from Tenerife Island

Experimental setup: The laboratory mineralogical characterization of the samples (in bulk mode) 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 DV420AOE- 130. The acquisition parameters on the micro-Raman system were: 30 second integration time, 10 accumulations and laser power varying depending on the sample. In addition, X-ray diffraction was performed on the samples (with XRD diffractometer Philips PW1710). Raman automatic mappings of the powdered surface of each sample were done by the ExoMars RLS Simulator in automatic mode (acquiring a total of 30 spectra per sample, with automatically calculated integration time and number of accumulations at each point. Laser wavelength: 532 nm. Spot size: 50 microns.). The number of

analyzed samples are the following: (1) 12 samples from Cañadas zone, (2) 6 samples from Azulejos outcrop and (3) 4 samples from Arenas Volcano. On the manned Micro-Raman analysis, between 40 and 50 spectra have been obtained at interesting spots selected by the operator in the bulk sample. On the RLS simulator analysis, 30 spectra were obtained with irradiances of 0.25 and 1 kW/cm^2. The acquisition parameters were autojusted at each point.

Result: On table 1, A summary of the mineral species and phases on the chosen zones identified by Micro-Raman instrument and XRD in comparison with the Exomars prototype simulator is compiled.

Mineral Species and Phases	Las Cañadas		Los Azulejos		Las Arenas	
	MR	RLS	MR	RLS	MR	RLS
Olivine (Forsterite)	X	X			X	X
Plagioclase and Feldspar	X	X	X	X	X	X
Pyroxene	X	X			X	X
Fe-Oxides	X	X	X	X	X	X
Ti-Oxides	X	X	X	X		
FeTi- Spinels	X	X				
Phosphate		X			X	X
Quartz	X	X	X	X		
Clays	X		X			
Sulphates			X	X	X	
Carbonates	X			X	X	X
Zeolite	X		X		X	
Carbon/Graphite	X	X	X	X		X
Organics	X	X				X
Alterated silicate	X	X				
Actinolite	X	X				

Table1. Summary of the mineral species detected on the Cañadas outcrop, Azulejos outcrop and Arenas Volcano by Micro-Raman analysis and Automatic Raman Analysis**.** RLS (RLS Simulator in automatic mode) and MR (Conventional micro-Raman and XRD)

As it can be seen, the result of the automatic mode shows good results comparing to the manned sample characterization, as all the principal mineral phases and secondary mineral species were detected in both analysis. Furthermore, there are certain differences between the analysis which are generated due to: (1) The manned Raman analysis where achieved on compact bulk sample and the automatic where achived from powdered samples under 250 µm; (2) sometimes, the detection result is punctual (such as the sulphates in the Arenas volcano, see table 1) and it is not general in all the samples; and (3) on the automatic mode, the measurements have been done by varying the laser power between two irradiance levels to evaluate the quenching effect in thermolabile samples such as goethite, certain sulphates or some carbonaceous material.

By performing a simple statistic of mineral identification (Mineral detected/Total of Minerals species) achieved by the Micro-Raman+XRD and RLS simulator, the result in Table 2 is obtained.

Percentage of Identification	Las Cañadas		Los Azulejos		Las Arenas	
	RLS	MR	RLS	MR	RLS	MR
Percetage of Mineral species detected	80	93	77	88	90	70

Table 2. Percentage of the mineral phases detected by the RLS simulator (RLS) and micro-Raman+XRD (MR). (Mineral detected/Total mineral phases).

Conclusions: The RLS Exomars simulator results are similar to those obtained by micro-Raman, where the magmatic differentiation following the Bowen´s reaction has been detected. On the other hand, RLS was capable of detecting the secondary materials, which are related with the different alteration processes (see Table 1 and 2). The powder analysis in some case means that the spatial distribution of species is lost. However, comparing to manned bulk analysis, some superficial very minor phases can be lost, while others, not visually differenticable, can be detected easier on the automatic analysis of the powder. In addition, in automated analysis, powdered samples increase the chances to detect minor phases with respect to bulk. The laser power has to be chosen carefully as a trade-off between general instrument performance and the risk of damaging thermolabile mineral species. The results here presented endeavour to use the Raman spectroscopy for the future exploration of Mars.

Reference: [1] Rull, F.; et al, *42nd LPSC*, #2400. [2] Rull, F and Martinez-Frías, J. (2000), *Spect. Europe*, 18, 1. [3] Lopez-Reyes, G. et al. (2012), *GeoRaman Xth*, 151-152. [4] Foucher, F. et al. *GeoRaman Xth*, 143-144. [5] Lalla, E., et al (2010) *Macla* 13, p. 129-130. [6] Lalla E., et al (2011) *Macla* 15, p. 119-120. [7] Rull F. (2012), *43rd LPSC* #2882.