RAMAN SPECTROSCOPY TO DETECT ALTERATIONS IN VOLCANIC MINERAL PHASES DUE TO SHOCK AND ENVIRONMENTAL IMPACTS. C. Garcia-Florentino, J. Huidobro, L. Gomez-Nubla, I. Torre-Fdez, P. Ruiz-Galende, J. Aramendia, K. Castro, G. Arana, J. M. Madariaga, Department of Analytical Chemistry, University of the Basque Country UPV/EHU, P.O. Box 644 48080 Bilbao, Spain (kepa.castro@ehu.eus)

Introduction: Raman spectroscopy is one of the most promising analytical techniques among the non-destructive methods to characterize geological materials because inorganic and organic compounds containing covalent bonds are sensitive to this vibrational spectroscopic technique. Due to its capabilities, this technique will be implemented in the RLS instrument of the next Exomars2020 Mission as well as in two instruments of the Mars2020 Mission of NASA, the SuperCam remote sensing instrument and SHERLOC contact one.

Apart from the possibility of determining the inorganic and organic compounds of the Oxia Planum (Exomars2020) and Jezero crater and surroundings (Mars2020) on Mars, this technique is able to provide information about mineral phase transformations due to both, pressure generated in collisions or due to reactions in water and oxygen presence in the old Mars conditions. The approach considers that, if we have more than two/three mineral phases in the same spectrum (that means, both minerals are simultaneously present) and all of them are related by an alteration reaction, we have an evidence of the necessary environmental conditions to favor such reactions

To demonstrate such possibilities, this work present some examples on the capability of this technique to detect the simultaneous presence of related mineral phases in two meteorites.

Material and Methods: The Raman spectra have been collected with a Renishaw InVia Raman spectrometer, equiped with three different excitation lasers (785, 636 and 532 nm), a confocal Leica microscope (with different magnification lenses) and a Peltier cooled CCD detector. The spectral resolution is about 1 cm^{-1} and it has a motorized stage which allows performing automated high resolution Raman images.

The target samples were rock fragments from two meteorites, NWA11273 from the Moon and DaG735 from Mars.

Results: In the NWA11723, different spectra showing at the same time ilmenite ($FeTiO_3$) and anatase (TiO_2) were found (Figure 1). Anatase can arise from the alteration of ilmenite as the original compound was probably due to the pressure (around 20 GPa [1]) generated by the impact, followed by an oxidation to transform Fe(II) to Fe(III). This degradation reaction could also be identified on Mars because ilmenite is also an original compound on Mars rocks.

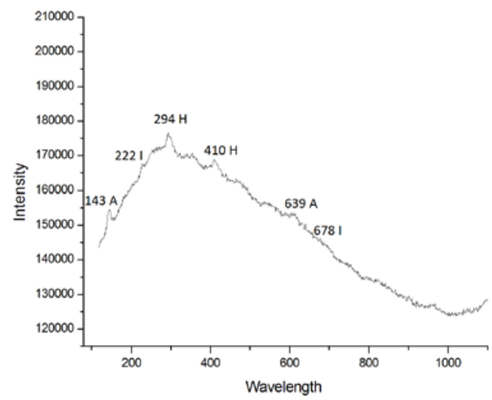

Figure 1.- Raman spectrum showing the simultaneous presence of ilmenite (I), anatase (A) and hematite (H).

The alteration reaction is shown in Eq.1 [2]. Looking at the intensity of the Raman bands, we can suggest that in the analysed spot ilmenite transformed mostly (low intensity bands to hematite plus anatase (higher intensity bands).

$$FeTiO_3 + ½O_2 \rightarrow TiO_2 + Fe_2O_3 \quad \text{Eq. 2}$$

Depending on the nature of the analysed spot, two non degraded/altered volcanic mineral can be detected, like Figure 2 shows. In this case, both olivine and enstatite are present in the nearly in the same proportion because the intensity of their Raman bands is similar.

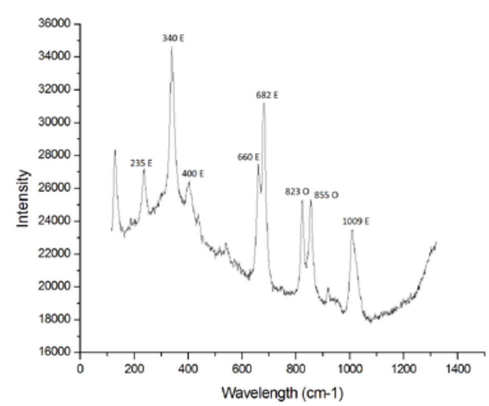

Figure 2.- Raman bands of enstatite (E) and olivine (O) found in the same spot of the NWA11273 meteorite.

The presence of anatase (the low mineral form of the titanium dioxide) suggests its formation in the ilmenite bearing unit of the parent body after the meteoroid impact to form the different fragments of the NWA11273 meteorite.

On the other hand, the simultaneous presence of pyroxene and hematite in some spectra taken from DaG735 meteorite (Figure 3) could be due to the degradation of an olivine in the presence of O_2 to the pyroxene and magnetite (Fe_3O_4).

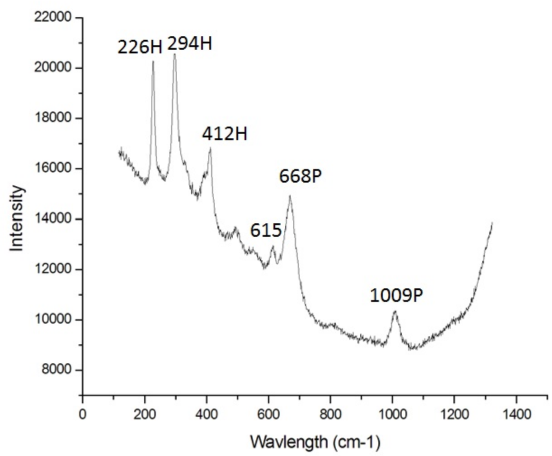

Figure 3. Simultaneous presence of hematite (H) and pyroxene (P) in the same spot of DaG735 meteorite

The general oxidation reaction could be the one reported in Eq. 2 [3]. Then magnetite easily degrades to hematite (Fe_2O_3) when in contact with oxygen.

$$6\ (M,Fe)_2SiO_4 + O_2 \rightarrow 3\ M_2Si_2O_6 + 2\ Fe_3O_4 \quad \text{Eq. 2}$$

Again, the similar intensities of the Raman bands of both compounds suggest a similar source for their formation, i.e. the reaction shown in Ep. 2.

In this particular case of the DaG735 meteorite, the alteration of the olivine comes probably from the presence of oxygen on Earth, i.e. it must be due to the terrestrial weathering of the meteorite. However, if this kind of degradations would be found on Mars, could be indicative of the alterations induced by the old presence of oxygen.

Conclusions: Raman spectroscopy can detect the simultaneous presence of even three mineral phases (or organic compounds in a mineral matrix) allowing to identify alteration processes of such minerals are interconnect by alteration reactions induced by pressure and/or environmental conditions.

The point-by-point analysis can be complemented with Raman images to see the distribution, nature and interactions of different minerals.

This spectroscopic information can be completed with other spectroscopic techniques like XRF, LIBS an VISIR Reflectance. This kind of collaborative spectroscopy is going to be tested in the forthcoming missions to Mars, because Exomasr2020 and Mars2020 integrate different spectroscopic techniques that will be analyzing the same spot when in Mars.

References: [1] Huidobro J. et al. et al. (2018) *LPSC2018*, Abstract #2476, [2] Liu L. G. (1975) *Phys Eart Planet Interiors, 10,* 167-176, [3] Rietmeijer F. J. M. (2009) *Astrophys J., 705,* 791-797.

Acknowledgements: C. Garcia-Florentino, L. Gomez-Nubla and J. Aramendia are gratefully to the UPV/EHU for their postdoc contracts. I. Torre-Fdez and P. Ruiz-Galende acknowledge their predoc contracts from the UPV/EHU. This work has been supported through the Exomars-Raman project (ref. ESP2017-87690-C3-1-R), funded by the Spanish Agency for Research AEI (MINECO-FEDER/UE).