THE RELEVANCE OF THE CREATION OF A RAMAN AND NIR SPECTROSCOPIC DATABASE FOR THE UPCOMING MARS MISSIONS. I. Torre-Fdez[1], P. Ruiz-Galende[1], J.M. Madariaga[1*], J. Aramendia[1], L. Gomez-Nubla[1], S. Fdez-Ortiz de Vallejuelo[1], J. Medina[2], K. Castro[1], M. Maguregui[1], G. Arana[1], V.G. Baonza[3], F. Rull[2], [1]University of the Basque Country (UPV/EHU), Bilbao, Spain, [2]University of Valladolid, Spain, [3]University Complutense, Madrid, Spain. (juanmanuel.madariaga@ehu.eus).

Introduction: The planetary exploration of the Solar System has increased during the last years, specially the Martian one. The next missions of ESA and NASA (Exomars2020 and Mars2020, respectively) are aimed at the exploration of the surface of Mars with a rover. Spectroscopic equipments are one of the main analytical instruments that the rover of both missions carry, due to the advantages that this kind of techniques offer for the Martian missions [1, 2]. Thus, the creation of a mineral spectroscopic database is mandatory improving and extending the current ones. With this pourpose, in this work different mineral groups were analysed by means of Raman spectroscopy and visible-near infrared (VNIR) spectroscopy, as they are two techniques that rovers of both missions will use.

Analyzed Samples: All the minerals analyzed for this work belong to the mineral collection of the Geominery Museum of the Spanish Geological and Miner Institute (IGME). Samples of silicates (cyclosilicates, phyllosilicates, inosilicates, nesosilicates, sorosilicates and tectosilicates), sulphates, carbonates, chromates, phosphates, sulfides, oxides, hydroxides and other minor mineral groups were analyzed. Altogether, 421 different mineral phases were analyzed.

Instruments And Methods: The mineral samples were measured by means of Raman and visible-near infrared spectroscopies for the molecular characerization. For Raman analysis two BWTEC (Newark, USA) systems were employed, one of them provided with a 785 nm excitation laser and the other one with a 532 nm laser. They were used coupled to a microscope with a 20x objective. In order to guarantee the accuracy of the spectra, a daily calibration of the instruments was performed using a silicon chip and its 520.5 cm^{-1} band. The integration times around 2-10 seconds ans 1-5 acumulations.

For visible near infrared (VNIR) measurements, a FieldSpec4 spectroradiometer (ASD Inc., Boulder, USA) was used. This instrument works in the 350-2500 nm wavelength range using a halogen lamp as a light source. The device uses three detectors for different spectroscopic ranges: 350-1000 nm (VNIR), 1000-1830 nm (SWIR1) and 1830-2500 nm (SWIR2). Sensor optimization and calibration was performed with a Spectralon white reference, which was scanned once before the measurement of each mineral, and each spectrum is the result of the average of 4 scans.

To check the purity of the analyzed minerals, elemental analysis of the mineral phases was performed by means of a handheld Energy Dispersive X-ray Fluorescence (EDXRF) analyzer XMET5100 (Oxford Instruments, Oxford, UK). The equipment is provided with a rhodium X-Ray tube as excitation source that works at a maximum voltage of 45 kV, with a high resolution silicon DRIFT detector (SDD). Measurement conditions for all samples were 50 seconds.

Results And Discussion: The main result of this work is the creation of a database of Raman and VNIR mineral spectra, with the support of the EDXRF elemental characterization. This database could be used for the proper interpretation of the spectra that the rovers of the Exomars2020 and Mars2020 missions will acquire. Due to the high amount of collected information, we present only 3 examples of 3 different analyzed minerals. The first one is raite, $(Na_4Mn^{2+}_3Ti_{0.25}Si_8O_{20}(OH)_2 \cdot 10H_2O$, Figure 1).
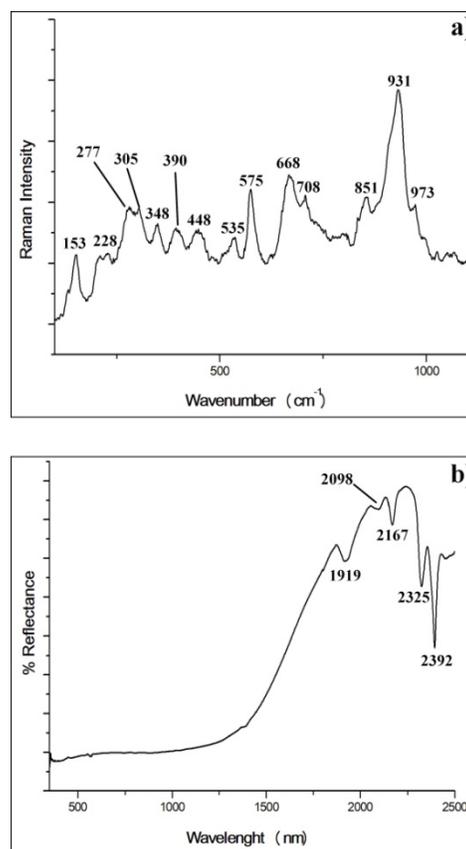

Figure 1. Raman and VNIR spectra of raite.

Raite is a phyllosilicate mineral with a orthorhombic crystal system. There is not any Raman or VNIR spectrum in the literature of this mineral. This mineral could be present in the surface of Mars, as it is a phyllosilicate [3] and, as such, it could be of interest to have these spectra in the database.

The second example is hisingerite ($Fe^{3+}_2(Si_2O_5)(OH)_4 \cdot 2H_2O$, Figure 2). This mineral is a phyllosilicate formed by the weathering or hydrothermal alteration of most sulfide and silicate minerals. Hisingerite, along with other minerals, may be formed due to deuteritic alteration of iron rich basalts. Its detection in Mars, could help on the knowledge of the history of its surface [4].
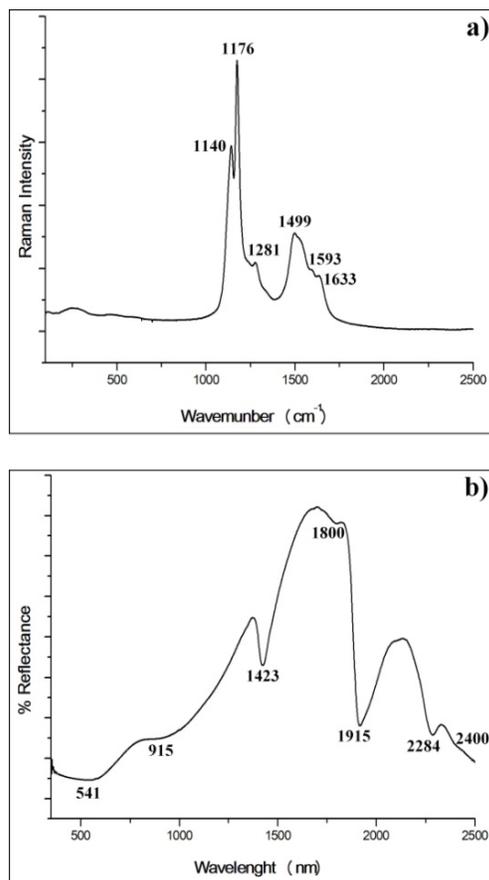

Figure 2. Raman and VNIR spectra of hisingerite.

The last example is linerite ($PbCu(SO_4)(OH)_2$, Figure 3), from which there is not a VNIR spectrum in the literature. It is a sulphate that is formed by the oxidation of lead or copper ores [5]. As it is known, lead or copper ores could be present in Mars [6]. This fact means that if this mineral was found in Mars, it would confirm a past oxidant atmosphere, which would be a key factor to support the theory of a possible life development in the past of the planet.
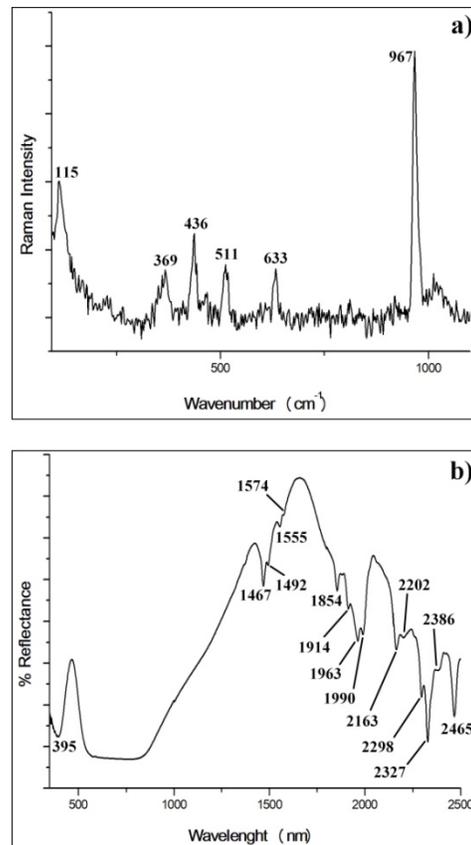

Figure 3. Raman and VNIR spectra of linarite.

Conclusions: Considering the amount of the collected spectra, this database will provide very useful information for the interpretation of the results provided by the rovers of the missions Exomars2020 and Mars2020. As it has been mentioned, there is still not enough Raman and/or VNIR spectroscopic information about minerals that could be of high relevance in the study of Mars. With this database, this lack of knowledge will be reduced.

References: [1] Bibring, J.P. et al. (2017) *Astrobiology, 17,* 621-626. [2] Rull, F. et al. (2017) *Astrobiology, 17,* 627-654. [3] Bishop, J. L. et al. (2008) *Science, 321,* 830-833. [4] Burns, R. G. (1986) *Nature, 320,* 55-56. [5] Adul-Samad, F. et al. (1982) *Transition Met. Chem., 7,* 32-37. [6] Burns R. G. and Fisher D. S. (1990) *J. Geophys. Res., 95,* 14415-14421.