Geochemical Characterization Of A Terrestial Martian Analogue: The Submarine Volcano Of Meñakoz (Biscay, Spain) P. Ruiz-Galende, I. Torre-Fdez, G. Arana*, J. Aramendia, L. Gomez-Nubla, S. Fdez-Ortiz de Vallejuelo, K. Castro, J. M. Madariaga, Department of Analytical Chemistry, University of the Basque Country UPV/EHU, P.O.Box 644, 48080 Bilbao, Spain. (gorka.arana@ehu.eus)

Introduction: The next Mars missions that will be carried out by NASA and ESA in 2020 will probably land in Jezero crater and Mawrth Vallis respectively, which are among the largest exposures of phyllosilicates on Mars [1]. These compounds are the most likely products of chemical weathering or hydrothermal alteration on Mars, and they are considered indicator of aqueous weathering processes of magmatic rocks [2]. For the proper interpretation of the results to be obtained by the rovers that will be sent by the mentioned missions, the development of databases becomes crucial. This fact implies the study of terrestrial Martian analogues that play an important role in the knowledge of the origin and geological features observed on Mars. For that reason and due to its volcanic origin, in this research work, the old submarine volcano of Meñakoz, an outcrop located in Biscay (northern Spain), has been studied and proposed here as a Martian analogue. In this site, the volcanic minerals alternated with the old marine sediments showing a similar sequence to that found in Jezero or Mawrth Vallis that have a sequence of volcanic minerals coming from the near eruptions of volcanoes, associated with sediments that can have different origin such as basaltic alteration.

Geological setting: Meñakoz outcrop (Figure 1) is situated at the Alpine syncline of Biscay and it is characterized by a sequence of volcanic rocks and Cretaceous sediments. It represents a submarine volcano scenario where the outcrop arises from an underwater volcano and due to its eruption emerged from the sea. This volcanic scenario shows typical characteristics of this type of submarine eruptions conditions, such as pillow lavas, megapillows and pyroclastic deposits, which have been suffering several weathering processes during the last 60 My. The existence of vesicles and pyroclastic materials leads to think that volcanism developed underwater at the depth at which alkaline magma causes eruptions [3]. In order to assess if the similarities on the origin are reflected in the geochemical composition of both emplacements, different samples of Meñakoz were analyzed by techniques included in the missions by NASA and ESA to Mars in 2020.

Samples: Samples were collected from different emplacements of Meñakoz due to the differences observed between several areas. There were mainly two type of samples: those affected by the water and wave's impacts, and those extracted from the cliff affected by runoff. These samples have different colours being green and white the most common ones, that are characteristic of these basaltic rocks.

Figure 1. Location of Meñakoz outcrop and detail of the pillow lava formation

Instruments and methods: With the aim of characterizing this analogue, spectroscopic techniques were used. Raman and near infrared (NIR) spectroscopies are two of the techniques that will go on-board the rovers in the next planetary missions. Therefore, they were selected to characterize the samples collected in Meñakoz.

Results: As was expected, phyllosilicates were the major minerals detected by the mentioned techniques in the Meñakoz samples.

Celadonite ($K(Mg,Fe^{2+})(Fe^{3+},Al)(Si_4O_{10})(OH)_2$) was detected in green areas. Its NIR spectrum shows bands that correspond to the Metal-OH vibrations (2245, 2314 and 2354 nm) and bands related to the presence of iron: Fe^{2+}-Fe^{3+} charge transfer band (764 nm) and Fe^{2+} crystal-field transition bands (926 and 1119 nm) with a possible additional contribution from Fe^{3+} ligand-field transitions to the first one. Moreover, vibration of OH group (1413 nm) and combination bands of H_2O (1910 and 1969 nm) demonstrate the presence of water.

In the case of the Raman spectrum, bands consistent with the presence of glauconite could be recorded. Both minerals have similar composition (Fe^{2+}-bearing micas) but with different formation mechanisms. Celadonite is formed from volcanic materials in low-pressure and temperature environment [4]. In contrast, glauconite is formed in marine sediments and is less abundant than the first one.

Celadonite has been detected on Mars by the CheMin instrument of the Curiosity rover [5]. It could have been formed on Mars due to a big impact that generated temperature gradients and hydrothermal alterations [6].

Some other silicates such as kaolinite ($Al_2Si_2O_5(OH)_4$, Figure 3) were detected only by NIR spectroscopy with a doublet at 2163 and 2205 nm and a triplet at 2323, 2358 and 2386 nm, which are characteristic features of this compound. Kaolinite is formed by the decomposition of feldspars [7] and it was observed on Mars by Compact Reconnaissance Imaging Spectrometer for Mars (CRISM) in Mawrth Vallis [8].

Moreover, some weathering products such as goethite (α-FeOOH, Figure 2) could be identified by Raman spectroscopy. This iron oxyhydroxide arises from weathering of natural iron-containing minerals such as lepidocrocite or silicates (like in this case) [9]. Although it has not been reported to be present on Mars surface, it could help in the possible future detections of this mineral.

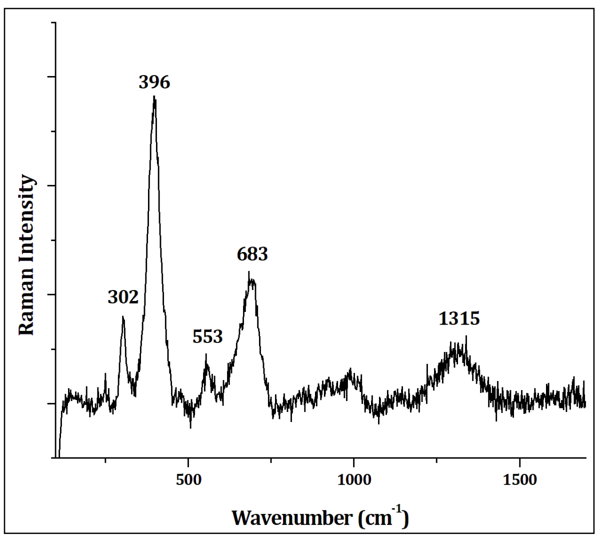

Figure 2. Raman spectrum of goethite.

Conclusions: As can be seen, compounds that have been reported to be present on Mars were identified in the proposed analogue. Phyllosilicates, as one of the most important family of weathered basaltic rocks, can help in the comprehension of their formation mechanism on Martian surface and, on the other hand, the necessity of water for their formation makes possible to state that in some moment of the history of Mars the water could be present.

Moreover, in this work we have demonstrated the complementarity of NIR and Raman spectroscopies, supporting their results each other as in the case of celadonite and glauconite. However, it has to take into account that some compounds, like goethite, can be detected by Raman and not by NIR. On the other hand, there are compounds detected by NIR and not by Raman, like kaolinite in our case. This fact is interesting because both techniques are necessary to achieve a complete characterization of this kind of samples being a right decision for the proper geochemical characterization of Mars surface and its analogues.

Finally, compounds such as goethite, that have been found in Meñakoz, are not reported to be present on Mars. Due to this fact, Meñakoz could help as a database for future discoveries regarding these alteration minerals and as they arise from weathering processes, helping in the understanding of the weathering mechanisms.

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