Raman-Mössbauer-XRD studies of selected samples from Los Azulejos outcrop: A possible analogue for assessing the alteration processes on Mars

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Abstract

The outcrop of "Los Azulejos" is visible at the interior of the Cañadas Caldera in Tenerife Island. It exhibits a great variety of alteration processes, which could be considered as terrestrial analogue for several geological processes on Mars. This outcrop is particularly interesting due to the content of clays, zeolite, iron oxides, and sulfates corresponding to a hydrothermal alteration catalogued as “Azulejos type alteration”. A detailed analysis by portable and laboratory Raman systems as well as other different techniques such as X ray diffraction (XRD) and Mössbauer spectroscopy have carried out (using twin-instruments from Martian lander missions: Mössbauer spectrometer MIMOS-II from the NASA-MER mission of 2001 and the XRD diffractometer from the NASA-MSL Curiosity mission of 2012). The mineral identification presents the following mineral species: magnetite, goethite, hematite, anatase, rutile, quartz, gregoryite, sulphate (thernardite and hexahydrite), diopside, feldspar, analacine, kaolinite and muscovite. Moreover, the in-situ Raman and Micro-Raman measurements have been done in order to compare the capabilities of the portable system specially focused for the next ESA Exo-Mars mission. The mineral detection confirms the sub-aerial alteration on the surface and the hydrothermal processes by the volcanic fluid circulations in the fresh part. Therefore, the secondary more abundant mineralization acts as the color agent of the rocks such as zeolite-illite group as bluish, feldspar and carbonate as whitish and iron oxide as redish. The XRD system was capable to detect a minor proportion of pyroxene, which is not visible by Raman and Mössbauer spectroscopy due to the “Los Azulejos” alteration of the parent material. Mössbauer spectroscopy was capable of detecting different types of iron-oxides ($Fe^{3+/2+}$-oxide phases). These studies emphasize the strength of the different

techniques and the working synergy of the three different techniques together for planetary space missions.

1. Introduction

Several volcanic places have been used as possible terrestrial analogues taking into account the volcanic activities and the huge variety of geological processes discovered on Mars heretofore (Chevrier and Mathé, 2007) such as Hawaiian Island, Marion Island, among others (Graham et al., 2015; Prinsloo et al., 2011). Considering the previous research, one of the most important alteration processes of volcanic materials on Martian surface are related to the hydrothermal processes (Merle et al., 2010). All the information yielded from the different missions such as MER-NASA mission (Mars Exploration Rover) (Rayl, 2014) and MSL-NASA-Curiosity mission (Mars Science Laboratory) (Kuhn, 2015a) has improved the understanding of the geological diversity of the planet. Also, the possibility of establishing new terrestrial environments as analogue test sites for future space missions such as ESA-ExoMars mission (Bost et al., 2015; Courrèges-Lacoste et al., 2007; Rull-Pérez and Martinez-Frias, 2006) and the future NASA mission in 2020 (Grossman, 2013) is needed. In this regard, new terrestrial volcanic analogue environments can provide new data which could be used for the interpretation of the geological history of Mars and the data collected by the different future space missions (Bishop et al., 2004; Lalla, 2014; Prinsloo et al., 2011). Special attention has to be paid to the mineralogy because it is the best indicator of the physical-chemical geo-processes and the paragenetic assemblages. Thus, the mineral diversity of new terrestrial analogues could allow the scientific community to increase the knowledge about the geological processes throughout the history of Mars (Mouginis-Mark and Robinson, 1992). Comparing the Martian mineralogy, it has been observed that it is as rich as the Earth mineralogy showing secondary mineralization

such as oxides, phyllosilicates, sulfates, carbonates, zeolites and clays (Chevrier and Mathé, 2007; Lalla et al., 2010; Minitti and Hamilton, 2010; Ruff, 2004). Secondary and accessory minerals have a paragenetic origin from hydrothermal reactions with the sub-surface fluids, water alteration, and sub-aerial processes. Nevertheless, there is a controversy about the detailed processes occurred on Mars, especially with the chemically weathered basalt (Mahaney et al., 2012). Thus, the use of natural samples from basaltic terrestrial analogues have been selected to perform future analysis on Mars relevant samples (with which the technology can be tested and improved).

It has been demonstrated that Tenerife Island is an area of reference for carrying out research and technological studies with planetary and astrogeological implications (E.A. Lalla et al., 2015). Several places of the island have been selected considering the fluid-rock interactions caused by the weathering processes, the submarine and sub-aerial alteration, hydrothermalism and the geomorphological features (E. A. Lalla et al., 2015; E.A. Lalla et al., 2015)

The main motivation of this paper is to study and register a complete spectroscopic analysis (mainly by Raman spectroscopy) of the selected outcrop corresponding to “Los Azulejos”, which exhibit visible alterations from the original rocks (called Azulejos alteration type), and the results could be used as potential model substances for the original altered material on Mars. On the other hand, the data collected using twin-instrument from actual and future different space mission in terrestrial analogues could be also used for the next generation objectives in space exploration. Thus, the study is also focused to improve the strength of the Raman spectroscopy for space exploration and to complement the results with the capabilities of the XRD and Mössbauer techniques.

2. Geological setting

The Cañadas caldera, at the central part of Tenerife, formed by several collapse episodes of the Cañadas central volcanic edifice during several highly explosive eruptions of phonolitic magmas (Marti and Gudmundsson, 2000) (Figure 1). From the geo-chemical point of view, the Cañadas edifice has been and is also affected by active hydrothermal and fumaloric activities as well as CO_2 diffuse emission (Villasante-Marcos et al., 2014) which acted after the Caldera formation. The combination of the mechanical and geochemical processes produced a heterogeneous volcanic system, where really interesting specific outcrop could become a terrestrial analogue for instrument testing and contribute to the science development of new space missions. In this regard, one of the most interesting macro-structural formation is the called the outcrop of "Los Azulejos" (Figure 1), which forms a part of the Caldera wall. One of the most impressive features at this outcrop is the variety of the different processes involved (i.e. hydrothermal processes, argilization and parent mineralogical alteration) (Galindo et al., 2005; Villasante-Marcos et al., 2014). Galindo et al., have described these geological features indicating that the faults within "Los Azulejos" structure affect the igneous materials of the Cañadas edifice by the inclined and sub-vertical sheets intrusions formation. A variable displacement of the fault is reported in (Galindo et al., 2005). They also point out that the kinetic indicators such as the offset of stratigraphic layers, shear-cleavage structures in mylonitic foliation, among others, in combination with the CO_2 active diffuse degassing activities and the hydrothermal activities cause a huge variety of mineralogical species. The colored outcrop of Los Azulejos presents bluish, greenish, whitish, and yellowish colors (Figure 1). The bluish to greenish degradation corresponds to a combination of analcime and clay minerals such as smectite and illite. On the other hand, yellowish and blank coloration can be observed on the fumarolic structure and the argilization of the parent minerals. These colorations

present really interesting formations like mushrooms textures and veins circulation with sulfates and iron oxides mineral species (Bustillo, 1989; Galindo et al., 2005). The colors in the alteration correspond to a process called “Los Azulejos” type alteration and it is also present on other Canary Island graben formations such as Gran Canaria Island, Spain (Donoghue et al., 2008).

3. Analytical Techniques

3.1.In-situ portable instrumentation:

The Raman analyses were performed with an i-Raman device from B&W TEK Inc. designed to work at field conditions (Unidad Asociada UVa-CSIC al Centro de Astrobiología, Valladolid, Spain). The optical system was adapted and positioned in front of the samples using a mechanical positioner, which allows a surface mapping at near mineral grain scale (Figure 1). A baffle was used to minimize the solar light background. The excitation used was a laser with 532 nm wavelength, 15 mW power on the sample, a spot diameter of 85 μm and the best spectral resolution of 5 cm^{-1}. Some of the zones present a strong effect of the fluorescence, with inconclusive results and these samples have been carefully selected to carry out a Micro-Raman measurement at the Unidad Asociada UVa-CSIC al Centro de Astrobiología.

The Mössbauer spectra were collected with a copy of the MIMOS II spectrometer (MER) from the past NASA-MER-mission (AK Klingelhoefer, Mars Mössbauer Group, Mainz, Germany). The system has a Co 57/Rh source with an intensity of about 50 mCi. The measurements have been performed at room temperature and without sample preparation in a backscattering geometry.

The XRD system for the measurement was the Terra XRD diffractometer instrument (based on the MSL-CheMin concept, available at the Unidad Asociada UVa-CSIC al

Centro de Astrobiología with a detector of 1024 x 256 pixels, 2D peltier cooled CCD camera for XRD with a source of cobalt X-ray tube, working at 30 kV and 300 μA. For the XRD analysis, a preparation was necessary: powdering a minimum part of the samples (from 2 to 4 mg) and sieving with a granulometry lower than 150 μm. The XRD measurement and analysis were obtained using a 0.25° 2θ FWHM resolution, a 2θ spectral range of 5-55° and 200 accumulations with an exposition time of 15 seconds. The mineral identification software used was the Xpowder12 (Martin-Ramos, 2004)

3.2.Laboratory instrumentation:

The micro-Raman mineralogical characterization of the samples was performed with a Micro-Raman system from the Unidad Asociada UVa-CSIC, Valladolid, Spain. The system is composed by a microscope Nikon Eclipse E600 coupled to a spectrometer KOSI Holospec f/1.8i, with best spectral resolution of 5 cm^{-1}, illuminated by a laser REO LSRP-3501 He-Ne (632.8 nm wavelength). The detector was a CCD Andor DV420A-OE-130. The maximum laser power used on the sample was 14 mW with a minimum spot diameter of 15 μm. The Raman mapping of the bulk surface of the sample was done by the micro-Raman Prior Proscan II motorized stage in automatic mode in order to detect the different compositional mineralization. However, the optimum recording conditions were obtained by varying the laser power, microscope objective and the confocal spot size (XY instrument) as required for the different samples. The spectra were directly acquired on the sample material without any sample preparation.

The conventional X-ray diffraction analyses were carried out at University of Valladolid, Spain with a XRD diffractometer Philips PW1710 equipped with an automatic divergent slit graphite monochromator and Cu-anode. Experimental conditions: $Cu_{K\alpha}$ radiation, $\lambda = 0.154$ nm, a nickel filter, an aluminum sample-holder, 40

kV generator voltage, generator current 30 mA with a relation intensity of 0.5 (α_1/ α_2) and angle range (2θº) from 5 to 70º. The steps size applied is 0.02º and the identification have been done using Match! Program system, the crystallography Open Database (COD), the ICDD System (International Centre for Diffraction Data) in PDF-2 (Power Diffraction Files) and the JCPDS (Joint Committee on Powder diffraction Standards).

4. Results

3.1. Sample recollection and description

The samples from the different places of the in-situ analysis have been collected according to the coloration and characterized by the laboratory instrumentation at the Unidad Asociada UVa-CSIC and at Mars Mössbauer Group, Mainz, Germany. Moreover, the selected samples present different grain size, color, morphological characteristics, and stratigraphic position which are visually distinctive to the naked eyes and under microscope magnification. A total of 14 samples have been collected using a hammer and the blade of knife, and, also, carefully stored in plastic bags to avoid/minimize possible contamination. Table 1 presents the pictures, cataloguing, the general Raman analysis and XRD of each sample collection.

3.2 Raman Analysis

The in-situ Raman analysis can be observed in Figure 2 and the laboratory measurement is presented on the Figure 3. Moreover, the complete minerals species are depicted on Table 1. The identification of the mineral species has been done considering the following references: Fe-oxides (Jubb and Allen, 2010; Rull et al., 2007), Ti-oxides (Lukačević et al., 2012; Sekiya et al., 2001), Si-oxides (Karwowski et al., 2013; Zotov et al., 1999), carbonates (Buzgar and Apopei, 2009; Koura et al., 1996), sulfates (Buzgar et al., 2009; Chio et al., 2005), silicates (Freeman et al., 2008), zeolites (Chen

et al., 2007; Frost et al., 2014) and clays (Frost et al., 2001; Haley et al., 1982; Martens et al., 2002) (See Table 3). Also, the RUFF database and the Unidad Asociada spectra collection have been used for the identification (Downs et al., 2015).

The iron oxides detected on the outcrop correspond to hematite, goethite and magnetite. The detection has been done considering the principal active Raman vibrations of each mineral. The vibrations exhibited by the magnetite were at 670, 550 and 300 cm^{-1} approximately which can be assigned to the following modes A_{1g}, T_{2g} and E_g vibrational modes (Jubb and Allen, 2010; Rull et al., 2007). In the case of the hematite, the Raman principal vibrations modes are produced at 225 (A_{1g}), 245 (E_g), 291 (E_g), 410 (E_g), 500 (A_{1g}) and 611 (E_g) cm^{-1} with the magnon at 1321 ($2E_u$) cm^{-1}. The goethite presents a combination of several vibrations at 244 (E_g), 299 (E_g), 385 (E_g), 480 (A_{1g}), 550 (A_{1g}) and 681 (E_g) cm^{-1} (Hanesch, 2009). The Ti-oxides detected on the different samples correspond to anatase and rutile. According to the factor group analysis, the anatase has six Raman active modes ($A_{1g} + 2B_{1g} + 3E_g$) allowed to appear at 145 (E_g), 200 (E_g), 393 (B_{1g}), 512 (A_{1g}), 520 (B_{1g}) and 640 cm^{-1} (E_g) (Rull et al., 2007). However, the rutile phase presents only 4 Raman-active modes at 235 (B_{1g}), 448 (E_g), 609 (A_{1g}) and 810 cm^{-1} (B_{2g}) (Rull et al., 2007; Sekiya et al., 2001).

The carbonate detected can correspond to hydrotalcite, being a Al-Mg rich hydrous carbonate, which have several modes at 237, 288, 484, 700, 1026, 1062, 1370 cm^{-1} according to the references (Frost et al., 2005). The most intense vibration correspond to the C-O stretching in CO_3 bonded to Al^{3+}-bound OH groups (1062 cm^{-1}) followed with a shoulder at 1050 cm^{-1} (caused by C-O stretching in CO_3 bonded to Mg^{2+}-bond OH group) and the peaks group at 720 to 650 cm^{-1} assigned to CO_3 in- plane bending mode. However, other authors (Buzgar and Apopei, 2009; Buzgar et al., 2009) present similar vibrations as the detected which can correspond to an anhydrous K-carbonate.

The vibrations can be attributed to a doublet at 1064 (vs) and 1048 (sh) cm^{-1} attributed to the $\nu_1(A_1)$ stretching modes- CO_3^{2-} , the 1306 and 701 cm^{-1} bands assigned to the $\nu_3(E')$ - symmetric CO stretching mode and $\nu_4(E')$ - COH bending mode (Buzgar and Apopei, 2009; Buzgar et al., 2009).

In the case of the sulfate, several mineral phases have been detected corresponding to the thernardite and hexahydrite that can be easily detected by the SO_4 vibrational modes and also by the H_2O vibrational bands. The peaks within water stretching and bending modes of the hexahydrite are shown at around 3450/3250 and 1650 cm^{-1} (Wang et al., 2006). However the major interest is more focused on the SO_4 vibrations at 983 (ν_1), 466 (ν_2), 1146 (ν_3) 610 (ν_1) and at 364 cm^{-1} (no detected) according to the other authors (Wang et al., 2006). On the other hand, the thernardite, which is an anhydrous sulfate, present the principal band at 991 (ν_1), a doublet 463/450 (ν_2), a triplet band 1110/1129/1153/ (ν_3) and other triplet 620/631/545 cm^{-1} (ν_1) (Wang et al., 2006). In our case, the thernardite has been better detected because it presents a better crystalline structure than the hexahydrite. This has been fairly compared with the RUFF database (Downs et al., 2015).

The identification process of the feldspars and plagioclases has been done based on a band fitting method to overcome the overlapping of Raman signals with other mineral species. The classification method developed by other authors was applied (Freeman et al., 2008), where the strongest vibrational bands are produced by the structure of SiO_4 of tecto-silicate group and it is characterized by triplet or doublet bands located on the 450–515 cm^{-1} region with the strongest peak is at 505–515 cm^{-1}. Also, other vibrational regions have been considered for the correct mineral identification such as: (1) the rotational-translational modes (200–400 cm^{-1}); (2) the deformation modes of the tetrahedral (600–800 cm^{-1}); and (3) the region of the vibrational stretching mode of the

tetrahedral structure 900–1200 cm^{-1} (Freeman et al., 2008). However, this identification depends upon the sample under analysis due to some of the spectra matches with the references in some case, but in others were necessary the use of the RUFF database (Downs et al., 2015). The different types of feldspars are indicative of different cation contents in the solid solution expected in basaltic material formation.

The analcime present the main following vibrations: (1) the water librations E_g at 390 cm^{-1}; (2) the O—(Al, Si)—O bending E_g at 480 cm^{-1}; (3) the (Al, Si)—O stretching F_{2g} in the 1100 cm^{-1} (Frost et al., 2014). Concerning the clays, two types were detected: (1) kaolinite and (2) muscovite. The first clay (kaolinite) vibrations matches with the results from other measurements carried out by other authors. The main Raman bands are at 290, 406 and 700 cm^{-1} that are assigned to: the lattice vibrations, the Al-O-Al vibrations (symmetrical stretching vibrations are the strongest vibrations) and the Si-O-Si vibrations at the teatrahedral site (Haley et al., 1982). For last, the kaolinite present several active Raman bands at 258, 333, 393, 461, 510 and 640 cm^{-1} (Frost et al., 2001)

3.3 XRD diffraction analysis

The XRD analyses of several samples are shown in Figure 4 and 5. The identifications have been obtained by pattern matching and taking into consideration the main bands of the diffractograms using the methods aforementioned. Also, the analysis of both diffraction systems converges that they present several crystalline structures with some minor amorphous phases. Furthermore, the results have been compared with other commercial standard patterns. However, the XRD could detect other mineral structure like the diopside, which can be related due to a very low proportion or a low crystal size for the Raman techniques. For the different samples, the majority of the mineral phases have been obtained being similar to the Raman measurements

3.4. Mössbauer Spectroscopy

Mössbauer spectroscopy analysis has been performed measuring the different colored areas of the samples as done with XRD. The hyperfine parameter, derived from the data is depicted in Table 3 and Figure 6. The different sub-spectral areas obtained by a band fitting from the different samples show Fe oxide-content. Moreover, the $Fe^{3+/2+}$ oxide phases present on the different samples have a similar isomer shift (IS), quadrupole splitting (QS) and spectral line width (Fleischer et al., 2012). The observed presence of hematite, magnetite goethite and oxide phase with different degrees of crystallinity have been also confirmed by Raman analyses and XRD.

5. Discussion of the results

The Raman analysis shows the primary mineralization and it is also confirmed by XRD measurement such as the feldspar. On the other hand, the Fe-oxides has been confirmed by Mössbauer spectroscopy like the hematite, magnetite and goethite. The Raman identifications have been done carefully by the peak assignment of the principal bands, by several methods developed by other authors, and, also by comparison with internal and external database. The analysis in-situ shows, in several case, strong activities of fluorescence maybe caused by external contamination due to biological activities or saturation caused by large exposition. However, other difficulties have to be considered from the technological point of view such as that some constituents from basaltic rocks have their own fluorescence (Bathgate et al., 2015). In this regard, other authors proposed to stablish specific methodologies for the identification and the diagnosis of the peaks in order to mitigate this effect (Bathgate et al., 2015; Wang et al., 1994). But, in the case of remote planetary laboratories, they cannot applied because of the limitation in the capabilities. Thus, a greater understanding and greater quantity of in-situ spectra from terrestrial analogues are needed for the success of the future space

missions. On the other hand, the XRD supplementary technique have shown to be more powerful than the Raman techniques in the mineral identification with a 88% success rate than 77% rate. Nevertheless, if the fluorescence effect is eliminated on Raman techniques, it can be possible to achieve 90% success rate (Bathgate et al., 2015). The main motivation of using a 532 nm portable Raman system is due to the Raman Laser System (RLS) onboard on the ESA-ExoMars that will be working with the same wavelength. In this regard, previous studies using the RLS simulator working at 532 nm shows that the system was capable of detecting the secondary materials, which are related with the different alteration processes. However, the laser power has to be chosen carefully as a trade-off between general instrument performance and the risk of damaging thermolabile mineral species (Lalla et al., 2013).

In the geological considerations, the analogue outcrop presented shows strong mineral similarities with the long term and earliest volcanology of Mars. In this point of view, the Martian surface present extensive partial melting mineral with unaltered basalt and low evidence of evolved siliceous rocks. The main justification is the absence of plate tectonics on the Martian surface that prevent the cycling of material as found on Earth (Christensen et al., 2003; Kuhn, 2015b; Sigurdsson et al., 1999). However, the earliest Martian volcanic activity, in the recent discoveries, has been more influenced by explosive eruptions. Thus, the large quantities of volatiles or the present of ground water have been responsible for hydrothermal and fumarolic activities with its mineral alteration (Chevrier and Mathé, 2007; Mangold et al., 2007). In this regard, the fumarolic activity and their diffuse emission processes presented on the outcrop of "Los Azulejos" with the formation of hydrothermal sulfate minerals could be used as parent model for the alteration processes aforementioned. The sulfates are products of the interaction of magmatic fluids, volcanic gases (H_2S and SO_2) and the surrounding rocks.

They can be of interest for future studies and to increase our knowledge of the processes occurred over the Martian geological time. Taking into account the recent space missions like NASA-Curiosity mission and NASA-MER-mission, where twins instrument have been used in this investigation, present similar mineral phases (Anderson et al., 2015; Klingelhöfer et al., 2003). Moreover, the minerals detected on Mars are in accordance with our investigations on the outcrop of "Los azulejos", and this could be of importance for future testing of Raman spectrometers of Martian automatic laboratories. Our Raman results encourage a continue development for Raman systems in space science and for the Mars exploration. A comparison of the different techniques is available on the Table 4 showing the capabilities of the Raman spectroscopy applied to the geological context, where in the combination with the other techniques they are capable to obtain a full detail of the mineralogy and the geological process occurred on the selected target.

6. Conclusions

Different measurements have been performed by in-situ and laboratory Raman spectroscopic techniques, X-ray diffractometers and Mössbauer spectrometer for the very first time on the outcrop of "Los Azulejos", through a complete analysis of the mineralogy. Regarding to this, its possible relation to Mars based on its possible alteration processes has been also studied. Crystalline primary phases such as pyroxene, feldspar, oxides, as well as secondary minerals like carbonate, Fe-oxides/oxy-hydroxides, sulfates, zeolites, and clays have been confirmed by Raman spectroscopy and XRD analyses. Moreover, the Mössbauer spectroscopy also detected Fe-oxides and other amorphous $Fe^{3+/2+}$ oxide phases as a result of hydrothermal alteration. The phases of mineral species described along the paper are similar to those reported on other volcanic terrestrial analogue materials and Martian observations. The possibility to

distinguish between different alteration processes by Raman spectroscopy will help us to deduce the rock-process formation by the combined processes occurred on "Los Azulejos" outcrop and its possible extension to Mars. Thus, the enlargement of knowledge on terrestrial analogues provide an aid and a relevant knowledge support for the planetary research field, especially when astrogeological implications are addressed. The results reveal that Raman technique, XRD and Mössbauer spectroscopy are powerful and robust systems. The three techniques in combination will be suitable for a complete identification of alteration processes inferred on Mars. In this regard, the measurements support the continued endeavors of the system developments for the Mars exploration on the future space mission such as the Raman Laser Spectrometer (RLS) included in the ESA Exo-Mars Mission. However, a continued improvement of the Raman technique is needed for the improvement of the future space missions

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