

**A micro-Raman and X -ray study of erupted submarine pyroclasts from El Hierro (Spain)
and its astrobiological implications**

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Abstract

The analysis of volcanic samples with strong relation with astrobiology and with a possible connection to life evolution can give us clues about the bio-geochemical processes involved. In

this regard, the samples from the volcanic eruption from La Restinga (El Hierro, Spain) in 2011 have been studied by means of Raman spectroscopy. The research has been done in a complete Raman analysis identifying all the mineral phases and applying the most important Raman methods developed by other researchers to test the capabilities of the vibrational technique. The results showed that the Raman methods and mineral analysis are in strong agreement with the results obtained from other authors and techniques: the mineralization and organics detected correspond in the internal part (white interior) to amorphous silica, Fe-oxides, Ti-oxides, quartz, certain sulfates, carbonates, zeolites and organics. The external part (dark surface) mainly presents primary sequence mineralogy combined with some secondary alteration minerals like olivine, feldspar, pyroxene amorphous silica, Fe-oxide as well. Also, a comparison with other samples from other similar terrestrial analogs has been conducted, taking also into account the proposed hypothesis regarding the potential behavior of the pumice as a substrate for life evolution. The detailed mineralization measured from La Restinga eruption is coherent with the mineral phases and process discussed from the references. In this regard, the white internal part fulfills the conditions to work as an organic reservoir, confirmed by the detection of organic matter with Raman spectroscopy. The external layers of the samples work as a protection layer to protect the organics from decay in extreme conditions. Finally, here is demonstrated that the characteristics and advantages of Raman spectroscopy could help to assess and understand the possible biogenicity and alteration processes of any geological sample to be found on Mars.

Keywords: Raman, basalt, astrobiology, planetary science, hydrothermalism

1. Introduction

Several days after the start of the volcanic tremor on 10 October 2011 and the first visible evidences of the onset of the submarine eruption offshore El Hierro island (Spain), that took place two days later, abundant dark fragments of low bulk density (roughly $0,6 \text{ g/cm}^3$) resembling volcanic bombs appeared floating on the ocean surface at an approximate distance of about 3 km SSW of the coastal village of La Restinga, placed at the south point of the island (Becerril et al., 2015; Eugenio et al., 2014; Rodriguez-Losada et al., 2015). The fragments were

10 to 20 cm in its major axis and were formed by a light coloured glass, highly vesicular (bubble-rich) and low bulk density (about 0,3 to 0,4 g/cm³) as majoritarian material, covered by a thin dark crust of 1 cm or less, also of glassy nature, less porous and of higher bulk density (roughly 1,4 g/cm³) (Figure 1) (Martinez-Frias et al., 2012; Rodriguez-Losada et al., 2015). Mingling between both materials with quite clear limits can be observed. Identification of these pristine pyroclastic materials is of great interest to understand the glass formation processes from the magmas and the associated elements produced in these conditions under the water. On the other hand, regarding the point of view of the origin of life, the researchers have started to include the consideration of the link between life evolution and the changing planetary environment on Earth, since in general, the life is subjected to a variety of perturbations on the planetary surface. Special considerations are given to volcanism as it is the primary mechanism of geochemical changes and fluid migration at the planet's surface or in near subsurface; in this regard, the volcanism and life are inextricably linked.

Moreover, several hypotheses of the context for the emergence of life on Earth have been addressed in terms of theoretical and experimental chemistry in extremophile habitats, such as new hydrothermal vents and meteorite impact structures. However, one of the latest hypothesis is the consideration of pumice as a possible substrate for the origin of life, as they could have remarkable properties to become habitats for the earliest communities of micro-organisms (Brasier et al., 2011; Cavalazzi et al., 2011; Martinez-Frias et al., 2012; Westall et al., 2011). They have the highest surface-area-to-volume ratio known for any rock type, and they can float as rafts at the air-water interface. From the physicochemical point view, the pumice is exposed to an unusually wide variety of conditions, including dehydration, and they also have a remarkable ability to adsorb metals, organics and phosphates as well as to host organic catalysts (Brasier et al., 2011).

Concerning the detection technique for these materials, Raman spectroscopy is an excellent suited technique for the analysis at micrometric scale, as it provides an exact and completely non-destructive analysis for mineral phases identification at the mineral grain scale, being very

sensitive to temperature and pressure effects on the crystalline structure of minerals (Bost et al., 2015; Cote, 2018; Courrèges-Lacoste et al., 2007; Rull-Pérez and Martínez-Frias, 2006). Moreover, these features have converted Raman spectroscopy into one of the most demanded techniques for planetary research and space missions (Tarcea et al., 2008), including Mars (Beegle et al., 2015; Cote, 2018; Cote et al., 2018; Rull et al., 2017), Europa (Angel et al., 2012) and other icy moons (Sherwood et al., 2018), among others. The next ESA mission to Mars will feature the Raman Laser Spectrometer (RLS), one of the selected instruments included in the Analytical Laboratory Drawer (ALD) of the ESA ExoMars Rover. 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. Besides, RLS will focus on the search of past-present life which will be able to be acquired by their capabilities of organic detection. The RLS team has developed simulation tools and instrument prototypes for evaluating the future instrument performances, which have proved to be a useful method for maximizing the instrument capabilities (Bost et al., 2015, 2013; Foucher et al., 2013; Lopes-Reyes et al., 2013; Lopez-Reyes and Rull Pérez, 2017; Rull-Pérez and Martínez-Frias, 2006). In this work, a detailed Raman spectroscopic study has been performed in samples from La Restinga eruption provided by the Instituto Volcanológico de Canarias and the Museo de la Naturaleza y el Hombre (Tenerife). Furthermore, a complete spectroscopic analysis of La Restinga will improve our knowledge regarding the points of view discussed in the introduction and their possible link with the theory of the pumice working as the substrate for the origin of life, based on experimental results with Raman spectroscopy. The samples' physical properties have been characterized and analyzed by scanning electron microscopy and microscopic analysis. The density measurement has been carried out in the outer and internal fresh part. Also, a structural characterization performed by X-ray diffraction of the sample is presented. A comparison with other selected pumice samples from other terrestrial volcanic environments such as Tenerife (Spain) and Hawaii (USA) is performed on the current research. Furthermore, the samples have been compared with the astrobiological implications of submarine pumice in the evolution of life. The selected samples cover the required conditions to be considered as analogue samples

for a remarkable substrate for the origin of life proposed by (Brasier et al., 2011) and (Martinez-Frias et al., 2012).

2. Experimental setup and data analysis

The authorities responsible for their custody restricted the number of available samples for analysis. Nevertheless, it was enough to be able to perform the analysis both in the external surface of the samples and the freshly broken internal parts (see Figure 1). The Field emission scanning electron micrographs 130 (FE-SEM) were taken using a Hitachi S 4800 microscope at the University of La Laguna. The density measurements were performed using a Helium AccuPyc 1330 pycnometer. The powdered black external part of the sample and the white freshly broke internal part were measured on a PANalytical Empyrean diffractometer, and the crystallographic data were collected at room temperature by using Cu-K α radiation (λ -K α_1 = 1.5406 Å and λ -K α_2 = 1.5444 Å). The microscopic measurements were done by using an Eclipse Ci-L/S optical microscope.

The micro-Raman measurement of the samples was performed by using a microscope a Nikon Eclipse E600 optical microscope coupled with a spectrometer KOSI Holospec f/1.8i (best spectral resolution of 5 cm⁻¹) illuminated by a laser REO LSRP-3501 He-Ne (632.8 nm wavelength). The detection was performed by a CCD Andor DV420A-OE-130. The 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 with a Micro-Raman Prior Proscan II motorized stage in automatic mode 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 measured data was processed by a Gaussian curve fitting analysis for each band to obtain the correct band position of the different mineral phases on the spectra. Also, other spectral indicators such as peak intensity, area and bandwidth were calculated. The fitting was obtained with the commercial program Bruker OPUS and following the standard procedure: spectra smoothing,

background subtraction and correction, normalization and interactive curve fitting (by Levenberg-Marquardt or Local Least Squares methods). The mineral identification has been made according to the RRUFF database, Romanian Raman Database and other references that will be included in the discussion section (Buzgar et al., 2009; Downs et al., 2015).

3. Results

Scanning electron microscopy and Microscopic measurements

Figure 2 shows the results obtained by optical microscope and by Scanning electron microscopy. As it can be seen, the samples show a very high quantity of vesicles with different shapes, including tubular forms, spherical bubbles and cylindrical connections between the different shapes. These cylindrical connections seem to present several possible interconnections among all samples with different vesicle and bubble sizes, ranging from few μm up to 500 μm .

Helium Density measurements

The results of the density measurements of the white foamy core (WFC) shows highly porous amorphous structure with porosity between 78% to 80%, having a low bulk density (0.3 to 0.4 g/cm^3). On the other hand, the dust crust of the sample (DC) is less porous and has a higher bulk density (roughly 1.4 g/cm^3). The combined true density of both WFC and DC were determined by a helium pycnometer, giving values of 2.45 g/cm^3 and 2.89 g/cm^3 , respectively.

X ray analysis of the WFC and DC

The XRD analysis has been carried in the WFC and DC part. The results are shown on Figure 3. The internal part (WFC) presents mainly a glassy amorphous nature that can be observed by the broad bands along the diffractogram. Also, several minerals have been identified, including quartz (in silicate), barite (in sulfate) and halite (in salt rock).

On the external part (DC), the amorphous glassy behavior is less present than in the WFC part. The mineralogy determined on the surface confirms the volcanic origin of the sample based on

the existence of forsterite (olivine), augite (pyroxene), and magnetite (Fe-oxide). Also, traces of halite have been observed.

Raman identification of the samples mineralization

An overview of the spectral bands measured with Raman spectroscopy will be discussed following Dana's classification. Table 1 compiles the different detected minerals, presenting the most intense Raman band position of each compound.

The following sections present a detailed discussion of the Raman analysis for each mineral class, comparing the results in the external (DC) and internal white parts (WFC) of the samples, also taking into account the results from other analysis such as XRD previously performed on these samples, or comparing to data from the literature.

Fe-oxides

The Raman analysis of the Fe-oxide(-hydroxide) detected on the external and internal part corresponds to magnetite, maghemite, hematite, lepidocrocite and goethite. The analysis has been carried out with the band decorrelation based on Gaussian fitting. Goethite presents its main peak at 385cm^{-1} and others at 245, 299, 480, 550 and 681 cm^{-1} according to literature, e.g. (Hanesch, 2009; Rull et al., 2004). In the analysis performed on the samples, the principal vibration and the other detailed bands can be observed. These are combined with minor concentrations of other iron oxides such as maghemite (the band analysis is inset in Figure 4 and the results interpretation in the following paragraphs). Also, other impurities of amorphous silica, which is clearly in the spectra of the oxides in the WFC part, are detected, as shown in the pictures of Figure 4, where the area where the spectra were taken shows a surrounding matrix of this material.

Regarding the presence of maghemite, the band analysis shown in Figure 4 can be used to infer the potential presence of this mineral. The main bands presented by the maghemite minerals are located at 365 cm^{-1} (T_{2g}), 511 cm^{-1} (E_g), and 700 cm^{-1} (A_{1g}) corresponding to the Raman active phonon (Jubb and Allen, 2010). In our case, the band positions are located at: (a) 365, 522 and

700 cm^{-1} , (b) 500 and 697 cm^{-1} , and (c) 373, 513 and 704 cm^{-1} . The band assignment matches with the literature, e.g. (de Faria et al., 1997; Jubb and Allen, 2010), being the shifting in Raman shift possibly explained by the Gaussian fitting error. In the case of Figure 4.b, the non-detection of the 365 cm^{-1} (T_{2g}) could be explained by the poor scattering properties of maghemite (Jubb and Allen, 2010).

Hematite has well-established bands at 229 (A_{1g}), 249 (E_g), 295 (E_g), 302 (E_g), 414 (E_g), 500 (A_{1g}), 615 (E_g), 660 ($LO E_u$) and 1321 cm^{-1} (magnon interaction in hematite, e.g. (de Faria and Lopes, 2007)), according to references (Hanesch, 2009; Jubb and Allen, 2010; Prinsloo et al., 2011). Figure 5 presents the most intense vibrations of hematite as detected in two grains inside the WFC part of the sample (pictures of the grain-ores are inset). Also, this iron oxide phase has been found in combination with other ore-minerals such as magnetite or goethite-maghemite (as in Figure 4). Furthermore, in our case, the volcanic minerals such as amorphous silica are present in the Raman spectra of the local environment of the grains.

The other Fe-oxides commonly found in the WFC was magnetite, where the main vibrations are: 310 (T_{2g}), 554 (T_{2g}) and 665 (A_{1g}) according to references, e.g. (Hanesch, 2009; Jubb and Allen, 2010; Wang et al., 2004). The results obtained in some of the points by Gaussian fitting from Figure 5 as well as Figure 4 shows variation in the T_{2g} band from 539 to 550 cm^{-1} and in the A_{1g} from 655 to 667 cm^{-1} . The variation in the A_{1g} could be justified by a transformation of the main magnetite vibrational mode to hematite or ferrihydrite (non-detected on the samples), caused by temperature, pressure or water alteration. However, the shift of A_{1g} to higher values can also be caused by a transition from tetrahedral to an orthorhombic phase on an incipient oxidation process (Shebanova and Lazor, 2003). Also, other authors have confirmed that the co-existence of several bands in the order of 500 cm^{-1} , a low-intensity T_{2g} band values and the A_{1g} shifting to higher wavenumbers correspond to a transformation of magnetite to hematite (de Faria et al., 1997; de Faria and Lopes, 2007). (Wang et al., 2004) developed a general trend of dominant Raman peak position (at $\sim 660 \text{ cm}^{-1}$) related to the chemical composition and structural

behavior of the solid solution. It has been observed in the measured points a variation from magnetite in the values around 655 cm^{-1} and Ti-magnetite with band position at 665 cm^{-1} .

The other Fe-oxide mineral present in the samples is lepidocrocite, and it presents conjunction of bands at 250, 348, 379, 528 and 650, 1054, and 1350 cm^{-1} , e.g. (Hanesch, 2009; Watanabe et al., 2008). The results obtained from the analyzed points (see Figure 5) shows similar results to those reported ($249, 350, 380, 529, 652$ and 1320 cm^{-1}). The broadening of the bands at 650 and 528 could be related to the existence of magnetite in the surrounding local environment.

The corresponding detection of the combination goethite-maghemite, lepidocrocite and magnetite could be related to processes under reducing weakly acid to weakly alkaline conditions, where the change of the pH during the eruption could be involved.

Ti-oxide

The detection of the polymorph titanium oxides such as rutile or anatase can be achieved by their major vibrational bands, being most common in volcanic environments. Anatase presents its main Raman peak positions in 393, 512 and 635 cm^{-1} , corresponding to the B_{1g} , A_{1g} and E_g active modes, e.g. (Balachandran and Eror, 1982; Lukačević et al., 2012). The TiO_2 rutile phase, on the other hand, presents the main band positions at 235 (B_{1g}), 448 (E_g), 609 (A_{1g}), and 810 cm^{-1} (B_{2g}) following the consulted references. In our results, the only Ti-oxide detected was the anatase by the main peaks at 393 and 512 cm^{-1} (Figure 5). However, some of the other features in the spectra was overlapped by other minerals phases, impairing a more in-depth study of these mineral phases.

Si-oxide

The chemical composition of quartz is SiO_2 . However, there can be several different kinds of crystal lattice variations. At ambient pressure, quartz has two types of crystal systems: α -quartz, a trigonal low-temperature form, and β -quartz, a hexagonal structure formed at high temperature, e.g. (Chemarin et al., 1996). The group factor analysis shows that the quartz presents $8E + 4A_1$ vibrational modes. The vibrational band commonly detected was the A_1 ,

assigned at 465 cm^{-1} approximately and in some cases $E_{(LO+TO)}$ at 127 cm^{-1} , as well as, the band A_1 (200 cm^{-1}) and E band (493 cm^{-1}) (Chemarin et al., 1996). The results from La Restinga samples show the detection of crystalline quartz in the WFC part (Figure 6). A_1 band is detected in positions varying from 462 to 463 cm^{-1} (error due to the Gaussian fitting). The second detected band was the shoulder E band around 492 to 493 cm^{-1} . The other two bands A_1 (at 200 cm^{-1}), and E_{LO+TO} (at 127 cm^{-1}) were not detected due to limitations of the system caused by the double Notch filter and the high fluorescence of the sample. (Enami et al., 2007) determined a way to obtain the residual pressure (retaining the tensile stress or remnants of the residual stress from its formation) by calibration curves and $\Delta\omega$ with standards. The function $\Delta\omega$ is defined as the difference in ω_1 and ω_2 between the α -quartz standard and the sample as $\Delta\omega_1 = \omega_{1\text{standard}} - \omega_{1\text{sample}}$ and $\Delta\omega_2 = \omega_{2\text{sample}} - \omega_{2\text{standard}}$. The values ω_1 is the distance from A_1 (at 464 cm^{-1}) to A_1 at 205 cm^{-1} , and ω_2 is the distance between A_1 (at 205 cm^{-1}) and E (at 127 cm^{-1}) (Enami et al., 2007). In our measurements, it was not possible to determine it due to the lack of the non-detected peaks at 205 and 127 cm^{-1} . The quartz formation does not seem to have a high-pressure formation according to previous results (Asell and Nicol, 1968). Instead, the WFC quartz minerals from La Restinga seem to have more dependence to temperature during its formation. According to (Dean et al., 1982), considering the A_1 band position, during temperature-driven formation the erupted quartz is between 350 to 380 K .

The DC analysis results plotted in Figure 6, show the existence of amorphous quartz broad bands centred at 463 cm^{-1} . Besides, the possible existence of amorphous silica behaviour (to be discussed below), can also be observed.

The transition phases between the DC and WFC part also present broad bands with several features and transition minerals as moganite. The main Raman band of the moganite, as analyzed from the reference samples from Gran Canaria Island (Spain), present several peaks centered at 501 (symmetric stretching-bending modes), 220 and 129 cm^{-1} , and also other groups of less intense bands in the ranges of 250 - 480 , 650 - 850 , and 1040 - 1210 cm^{-1} (Götze et al., 1998; Kingma and Hemley, 1994; Rodgers and Hampton, 2003). In some particular places of La

Restinga samples, the bands detected at 500 cm^{-1} , and the other broad bands in the range of 650-850, and $1040\text{-}1210\text{ cm}^{-1}$ approximately are spectral features on the Raman spectra that could belong to different mineralization of moganite. However, the moganite mineral seems to be in really small grain size, given that our detections were accompanied with other overlapping spectral bands such as quartz or amorphous silica. (Götze et al., 1998) studied the relative distribution of the moganite and quartz by the relative intensity of the symmetric stretching-bending modes I_{502}/I_{464} and developing a % concentration of moganite on a quartz matrix with the irradiation laser surface. In La Restinga samples, the transition between DC to WFC part shows values around 1 to 2 being assigned approximately from 5 to 10% (for a laser irradiation surface of $\sim 150\text{ }\mu\text{m}$). The Gaussian fitting on the external part (DC) shows a ratio of 0.06, this meaning almost 0% of moganite, the same happening on the WFC part (for a laser irradiation surface of $\sim 150\text{ }\mu\text{m}$). These results have to be interpreted carefully, due to the potential uncertainties that can be affecting the results such as the contribution of amorphous silica intensities to the moganite and/or the α -quartz Raman bands, as well as the random crystallographic orientation which results in an overlap of many different scattering geometries (Götze et al., 1998; Kingma and Hemley, 1994). Nevertheless, these results seem to indicate that the moganite minerals have only been detected on the transition phases of the samples.

Carbonates

The carbonates detected on the samples correspond mostly to calcite with the most intense vibrations at 285, 712 and 1085 cm^{-1} , e.g. (Buzgar and Apopei, 2009; Rividi et al., 2010). Other Ca-Mg-Fe carbonates could also be considered based on the symmetric stretching of the CO_3^- band, present in some samples between $1080\text{ and }1090\text{ cm}^{-1}$, but the other Raman active vibrations such as the symmetric bending or the external vibrations of the CO_3^- were not detected (Rividi et al., 2010; Rull et al., 2004) (Figure 4). The intensity of spectra shows the possibility of a shallow concentration of carbonate formation, which could have been formed in some specific points of the fresh part of the samples. The calibration methods developed by (Rividi et al., 2010) for carbonate materials are capable of determining and to track the

biologically derived carbonated structure. The method is based on studying the Raman-shift position of the most important bands around 1080-90, 700-10 and 290 cm^{-1} with the Mg/Mg+Fe concentration. However, in our results, the main Raman shift (cm^{-1}) positions are located below the limit of their calibrations curves used, confirming the non-existence of Fe or Mg concentration on the stoichiometry (Rividi et al., 2010).

Sulfates

Our Raman measurements on the samples detected a large quantity of sulfate mineral species. Celestine could be identified, but others could not be correctly assigned due to the overlapping of the secondary mineral band vibrations. The most intense Raman band of celestine is found at 1003 (ν_1 symmetric stretching of the SO_4 tetrahedra) and the ones corresponding to the other vibrational modes are found at 641 (ν_4) and 1160 (ν_3) cm^{-1} , e.g. (Apopei and Buzgar, 2010). Celestine was found in the different freshly broken internal and external parts (Figure 7).

Also, other vibrations that apparently can be assigned to other sulfates have been found by bands around 982 to 983 (ν_1), 1014 (ν_2) and 1084 (ν_3) cm^{-1} . One possible assignation could correspond to barite with a very low concentration of Ba and enriched in Pb according to other authors and results obtained by XRD analysis in the previous section (Apopei and Buzgar, 2010; Lee et al., 2005). According to the theoretical results carried out by (Lee et al., 2005) in BaSO_4 - PbSO_4 solid solutions, the sulfate could correspond to barite mineral with 40 to 60 %mol: (Ba/(Ba+Pb)) in its stoichiometry. However, the results could also point to the existence of another common potassium calcium volcanic sulfate such as the syngenite. The diagenesis of the syngenite produces by volcanic sublimation on marine evaporitic deposits as well as in vein fillings in geothermal environments. Thus, the Raman results obtained were finally interpreted by assigning the intense vibration around 982 and 1002 cm^{-1} to syngenite's ν_1 symmetric stretching of the SO_4 tetrahedra. Also, the other vibrational modes at 1084 cm^{-1} could be assigned to the ν_3 (SO_4) from syngenite.

Phosphates

The phosphate detected on the samples was located in the micro-crevice between the WFC part and the DC part. The attempt to identify the phosphate was obtained by using the most important vibrational bands of the $(\text{PO}_4)^{3-}$. According to (Frost et al., 2013) and (Farmer, 1974), the main bands could be listed as follows: (1) the symmetric stretching vibration (ν_1) located in the region between 920 to 970 cm^{-1} , (2) the asymmetric stretching mode (ν_3) in the zone of 1000 to 1150 cm^{-1} , (3) the symmetric bending modes (ν_2) at around 460-480 cm^{-1} and finally (4) the symmetric bending modes (ν_4) located between 560 to 580 cm^{-1} . The Raman position of the bands can be shifted presumably due to different crystal structures, cation content or water content on the crystal lattice. As an example, in maricite phosphate, the cation content can change the crystal lattice structure and crystal size. (Litasov and Podgornykh, 2017) pointed out that the maricite's symmetric stretching vibration (ν_1) can present two main peaks in the region from 954 to 972 cm^{-1} or another Na-Fe-phosphate can present only one peak at 962 cm^{-1} . In this sense, our results detected match better to Na-Fe-phosphate, considering that the main peak (ν_1) is located at 960 cm^{-1} . Furthermore, the ν_2 and ν_4 bending bands are located at 437 and 572 cm^{-1} , agreeing with those reported by (Litasov and Podgornykh, 2017).

Comparing our results to another possible amorphous phosphate mineralization such as the Apatite, the results showed a shift on the main vibration (ν_1) from 4 to 8 cm^{-1} (e.g. apatite values at 962 cm^{-1}) and a shift of 10 cm^{-1} for the (ν_2) values (e.g. apatite values at 447 cm^{-1}) (Antonakos et al., 2007; Litasov and Podgornykh, 2017). However, apatite has been punctually found in WFC part surrounding possibly some iron ores as it can be observed in Figure 4.

Pyroxene group

The pyroxenes such as the augite, detected on the samples with XRD, were not detected with Raman spectroscopy, probably masked by other minerals such magnetite and the amorphous silicate with the broad bands present at 700 and 950 cm^{-1} .

Olivine group

Olivine was detected on the DC part of the samples, corresponding to forsterite. The main bands of forsterite are located at 820 and 850 cm^{-1} , e.g. (Chopelas, 1991). The forsterite Raman spectra also shows other vibrational modes: (1) the olivine lattice mode, both “translational and rotational” SiO_4 movements and the translational motions of the cations (Mg^{2+} , Fe^{2+}) in the crystal lattice in the region below 400 cm^{-1} ; (2) the internal bending vibrational modes of the SiO_4 ionic group around 400-700 cm^{-1} ; and (3) the internal stretching vibrational modes of the SiO_4 ionic group at the 700-1000 cm^{-1} region (Kuebler et al., 2006). The high-frequency peak of the olivine belongs to a combination of the symmetric and anti-symmetric stretching modes of SiO_4 units (Lam et al., 1990; Piriou and McMillan, 1983). The doublet at 820-850 cm^{-1} is commonly used to identify the different olivine phases (fayalite-forsterite) in the multi-phase spectrum. The relative peak height of the doublet and relative peak distances are a function of the crystal orientation and cation composition in the stoichiometry. Calibration methods for chemical, compositional and structural characterization of olivine mineral species have been developed according to the peak height and relative distance in Mg concentration ($\text{Mg\#}=\text{Mg}/(\text{Mg}+\text{Fe})$), e.g. (Kuebler et al., 2006; Mouri and Enami, 2008; Yasuzuka et al., 2009). The DC olivine part results point to low forsterite-olivine behavior detailed between 50 to 72% of Mg# concentration as per the following studies: (Kuebler et al., 2006) calibration curves point to Mg# between 50 to 62% of concentration (Fo_{50} to Fo_{62}), while (Mouri and Enami, 2008) calibration method provides an estimation of Mg# in the range of 56 to 72% of concentration (Fo_{56} to Fo_{72}).

Amorphous Silica

In the region WFC amorphous silica has been detected with a non-Silica lattice and depolymerized compositions that change depending on the Ca-Fe-Na-K cation contents. It has been proposed that most of the basaltic depolymerized glasses can be studied by dividing the spectra in three main: (1) The low wavenumber region (LW) between 250 to 650 cm^{-1} , (2) the mid-range wavenumber region (MW) from 650 to 850 cm^{-1} , and (3) the high wavenumber region (HG) in 850 to 1250 cm^{-1} (Di Genova et al., 2016, 2015). The LW region uses to present

the Raman vibrational bands from the bridging oxygen of the silicate tetrahedral network rings (Di Genova et al., 2016, 2015). Indeed, these vibrations can be associated with 3 to 8 rings. The second region (MW) mainly presents a possible combination of the Si-O stretching vibration from oxygen motion in the Si-O-Si plane, as well as the motion of the Si ions inside the oxygen cage at the crystal lattice (Di Genova et al., 2016, 2015). Finally, the HW region bands are assigned to the structural effect caused by the different cation concentration and its modification on cluster networking lattice (Di Genova et al., 2015). These are stretching vibrations of X-O bonds of the non-bridging oxygens (being X the cations as Si⁴⁺, Al³⁺, Fe³⁺).

On the results plotted in Figure 9, some of the different mapping points of amorphous silica from the WFC matrix of the samples can be observed. The LW Region (250-650 cm⁻¹) in La Restinga samples presents two broad bands at ~490 (*PeakA*) and ~570 cm⁻¹ (*PeakB*) that belong to the asymmetric bands (Di Genova et al., 2016, 2015). It has been reported that a shift of *PeakB* from values of 580 to lower values, as in our case, corresponds to a basaltic/basanite composition. On the other hand, the intensity values of *PeakB* and *PeakA* are assigned to the degree of crystallization, the more intense, the more crystallized and polymerized. In our results, there is no clear trend, showing that glass formation has probably been subjected to several processes such as water alteration and hydrothermalism (Lalla et al., 2015a; Zattin et al., 2007). Also, the different cation content and distribution is a strong indication that the sample has been conditioned to the local thermo-physical environment (temperature and cooling rates).

The MW Region on La Restinga samples presents only one broadband located around 730-760 cm⁻¹ which belongs to the Si-O symmetrical stretching. (Di Genova et al., 2016, 2015) reported a tendency behavior where low Raman-shift (700 cm⁻¹) belongs to basaltic/basanite glasses and high Raman-shift values (800 cm⁻¹) are the rhyolitic endmembers. In the results, there is a clear tendency to a more basaltic composition.

The HW wavenumber region of La Restinga samples presents two main fitting peaks located at ~960 and ~1035 cm⁻¹ that have been assigned to the asymmetric bands by (Di Genova et al., 2016, 2015). The expected values are agreeing with the previous results in the MW and LW

region, as well as the results from other authors (Di Genova et al., 2016, 2015). According to (Di Genova et al., 2016), the strong band asymmetric stretching bands for rhyolitic samples are located around 990 cm^{-1} with two shoulders at 1040 and 1150 cm^{-1} , and when SiO_2 content is decreased, the main band is shifted to lower values as $960\text{-}950\text{ cm}^{-1}$ with a shoulder 1035 cm^{-1} . Thus, the HW results in the samples also confirm their basaltic composition.

It is also important to mention that other points present different features preventing the confirmation of the general trend of Si-depolymerized glass, as it can be observed on Figure 9e and 9f, where the bands at LW and HW were not detected. That can be due to an interaction of the basaltic glass with the submarine environment, cutting off its complete formation. Alternatively, they could belong to another mineralization such as moganite, amorphous quartz or feldspar. However, any feldspar minerals would have been detected along the sample by considering the triplet-doublet bands at $450\text{-}515\text{ cm}^{-1}$ (Freeman et al., 2008), this not being the case.

(Di Genova et al., 2015) proposed a chemometric method in which the elemental composition of a Raman analogue sample can be inferred by a linear mixture model. In the proposed method, the original database is ordered concerning to SiO_2 concentration, so that the spectra corresponding to the highest and lowest concentrations are extracted. Each of the remaining spectra from the dataset is then expressed as a linear combination of these two end-member spectra to subsequently derive a mixture parameter for each spectrum mentioned above. The parameter is then used to fit a degree 2 polynomial to each element oxide. The derived models can then be used to estimate the oxide composition of an unknown sample using its' Raman spectrum. The full mathematical description can be seen on (Di Genova et al., 2015). In the case of La Restinga, we measured 7 Raman spectra from Figure 9, each of whose corresponding oxide composition was estimated using the described method. Table 2 summarizes the results of the model. We easily observe that 5 of the 7 estimates have very low variability concerning one another, and the other two have no variability up to the model's precision with respect to one another. Since each spectrum is taken at a distinct point on the sample, it is not unreasonable to

expect that the composition at any two points may differ in a nontrivial magnitude. Given the very obvious grouping of estimates into two partitions, we are confident that is precisely the case.

Organics

The sample shows a general trend of organic presence in the WFC and the intersection between the WFC and DC. In general, C-C vibrations present their main bands at 1350 (assigned to D₁ and D₂ bands), 1577 (assigned to G₁ band), and 1621 cm⁻¹. The D₁ and D₂ bands are found from 1300 to 1450 cm⁻¹, and the G₁ band can be observed at ~1580 cm⁻¹ with C-H bands at 1620-1630 cm⁻¹ approximately (Koura et al., 1996). The broadening of these specific bands always can show the degree of crystallization that can somehow be related to the fossilized or abiotic origin of the carbon, as carbon with organic origin presents amorphous behavior (Brolly et al., 2016). In La Restinga samples, the Gaussian fitting analysis shows a distinctly amorphous behavior coherent with the presence of C-C bands from organic matter (Figure 10). On the other hand, the C-H bands around 2900 to 3100 cm⁻¹ also support the organic origin of the C-C bands previously detected (Figure 10).

In order to distinguish the kind and origin of organic several possible types or organics were considered. One possible origin of the C-C and C-H detected bands could be from bacterias present in the water during the eruption and their bio-geointeraction. The selected Raman spectra plotted in Figure 10, compiles several a collection of Raman spectra from amino-acids (alanine and serine), saturated hydrocarbons (octacosane), fatty acids (stearic acid). Also, Figure 10 includes the Raman spectra of a bacteria's capable of producing magnetite by bio-geointeraction (named as geo-bacteria's) (Markovski et al., 2017). In the first stage, the comparison with the geo-bacteria shows that organics detected on the WFC part do not belong to the same type of bacteria. As it can be observed, the relative position of the C-C bands is shifted compared to the geo-bacteria on (Markovski et al., 2017). However, the spectral features could be coherent and it could match with bacterial behavior from previous studies if considering the following main bands: (1) the C-H stretching region bands on 2800-3000 cm⁻¹,

(2) the C-O deformation vibration region between 1300 to 1450 cm^{-1} and (3) the C=O stretching vibrational zone in 1650 to 1800 approximately (el-Kabbani et al., 1991; Kudelski, 2005). The samples present C-H peaks specifically located at 2853, 2903 and 2958 cm^{-1} , and, in some particular places around channels and internal fissures it has been detected other C-H bands located at ~ 2884 and other 2957 cm^{-1} . The octacosane and stearic acid have the C-H most intense bands at ~ 2850 and ~ 2890 cm^{-1} . Alanine presents the main C-H bands at ~ 2932 , ~ 2975 and ~ 3014 cm^{-1} and Serine at ~ 2961 and ~ 3000 cm^{-1} . The detected bands on the samples cannot be assigned to an amino-acid type (low carbon concentration) given the lack of bands around 1300 cm^{-1} . However, these bands are closer to those of octacosane and stearic acid, confirming a high concentration of carbon and hydrogen in the molecular structure of the samples.

Discussion of the results

A complete structural, imaging and vibrational characterization have been carried out. The dominant mineralogy detected is summarized in Table 1. There was detected different mineral species which belongs to primary and secondary mineralization, water/submarine and hydrothermal processes.

The Fe-oxides and oxy-hydroxides detected such as hematite, goethite, lepidocrocite and altered magnetite is a combined precipitation process which depends on several factors from abiotic and probably from biological factors. The main the abiotic factors are the pH, Eh, temperature and precipitation rates that are strongly related to a hydrothermal process with the ambient seawater during the emission. In La Restinga emission, the chemical and mineralogical compositions have been limited by a mixing of hydrothermal fluid mixed with the sea water. Also, the high pH and Eh from volatile gasses perhaps decreases the temperature, in the local environment, to increase the probability of Fe-oxyhydroxide formation (Perez-Torrado et al., 2012; Rodriguez-Losada et al., 2015). These hypotheses can be confirmed by the amorphous silica and quartz which are form a low hydrothermal fluidic temperature formation. Also, the high variety of sulfates detected also is reflected in the high gasses emitted during the process. The geo-bacteria's use the Fe-oxides and Fe-carbonates as energy sources and generate Fe(III)

oxi-hydroxide or low-crystalline magnetite as the final product from the bio-geointeraction with energy sources (Markovski et al., 2017; Veeramani et al., 2011). The reported combinations of (siderite-magnetite-hematite-non-crystalline-goethite, as well as, (ferrihydrite-goethite-lepidocrocite-magnetite) or (goethite-hematite-maghemite-magnetite-akaganeite) are importantly dependent of the biological mechanism (Ahn et al., 2012; Hansel et al., 2005; Markovski et al., 2017). However, in La Restinga emission, the possible bio-geo-mineralization detected cannot be confirmed, but it should not be discarded due to the fast mineralization occurred in days.

The detection of the anatase and rutile on the samples has not been reported yet on these samples. However, the detection can change from sample to sample and given the large quantity. It has been reported that the compositional zoning reflects substantial changes in Mg, Ti, Al and Si contents (Meletlidis et al., 2015). As an example, (Meletlidis et al., 2015) reported that cores and rim are differed for Ti/Si cation ratio relative (Meletlidis et al., 2015). In some cases, the cores show low values of Ti/Si (0.03) and the rims reflects values of 0.07.

The quartz detected by XRD and Raman spectroscopy is in agreement with the other results obtained previously (Rodríguez-Losada et al., 2015; Troll et al., 2012). The existence of the quartz on the sample has to be taken with caution due to several hypotheses to be considered. In one hand, (Rodríguez-Losada et al., 2015) proposed that it is possible to find examples of Canarian volcanic rocks that contain quartz and jasper. Indeed jasper veins, small quartz cavities were found in other eruption from the Canary Islands, where the mineralization was the result of hydrothermal mineralization from the interaction of hydrothermal fluids, ambient sea water and different cooling rates (Rodríguez-Losada et al., 2000). On the other hand, the igneous rocks from El Hierro Island do not contain quartz crystals as an initial formation (Troll et al., 2012). (Troll et al., 2012) proposed that the source of the quartz crystals found on the samples is from African sand plumes. These sand plumes transport considerable quantities of Aeolian dust (fine-grain) that lately is deposited in Canarian archipelago creating a complex system of quartz-rich sedimentation with the oceanic background. In any case, and without any consideration of its

origin, the Raman spectroscopy was able to confirm the alteration caused by the sea-water environment, and temperature cooling rates by the shift to lower Raman values (WFC) and broad-bands on the (DC) part.

Comparing to the Raman spectroscopy, XRD powder diffraction technique was not capable of identifying the diffraction pattern of moganite because of two main factors on the limitation of the technique and limit of detection. In the first case, the moganite presents a similar diffraction pattern like quartz (Rodgers and Cressey, 2001). On the other hand, the samples present a shallow concentration or unanticipated and also it has been detected in some specific locations in the samples. The presence of moganite surrounding the quartz has been obtained for the spot size where the Raman measurement has been carried out. The laser spot has a 15 μm diameter and an irradiation surface of 152 μm^2). In the Raman section, we discussed that there are several uncertainties according to Raman bands intensity, as random crystallographic orientation, and the overlapping of many different scattering geometries that could affect the full detection of the moganite. From our point of view, the Raman result about the moganite could neither be fully confirmed nor disproved.

The carbonate detected on La Restinga samples from our research in Raman spectroscopy confirms that they are Ca-carbonate. Furthermore, the calibration curves have shown that they have a high content of Ca in the carbonate stoichiometry (Ca-Mg-Fe) by the non-detection of Fe and Mg. (Troll et al., 2012) and (Perez-Torrado et al., 2012) have confirmed the detection of aggregates of calcite in the WFC part.

The phosphates detected could correspond to a $\text{Na}_2\text{Fe}(\text{Mg,Ca})(\text{PO}_4)_2$ phosphate, as it has reported on previously (Litasov and Podgornykh, 2017), matching with our results. Nevertheless, the origin could become from a particular formation, a hydrothermal alteration, or sea-weathering cation process during the emission.

The great variety of sulfate detected on the samples are in general agreement with the other authors, e.g. (Perez-Torrado et al., 2012; Rodriguez-Losada et al., 2015; Troll et al., 2012). The

barite results are confirmed by the XRD analysis previously analyzed. However, the mineral cation content has not been presented or reported. In this sense, the Raman spectroscopy was capable of quantifying 40 to 60 %mol: (Ba/(Ba+Pb)) in the stoichiometry of the barite. Other common mineral detected mineral detected was the celestine minerals (SrSO_4) not reported by other research. The previous research results confirm a high content Sr and Ba trace elements (Perez-Torrado et al., 2012; Rodriguez-Losada et al., 2015; Troll et al., 2012). Indeed, the Sr^{2+} and Ba^{2+} sulfate precipitation have been reported to be ones of the few marine authigenic minerals forms in the water column with marine sediments around hydrothermal vents and submarine emissions (Griffith and Paytan, 2012; Zaczek et al., 2015). The method for the precipitation of barite and sulfate inside La Restinga sample could occur when the Ba/Sr-rich hydrothermal fluid, SO_4 from seawater-gasified by the on-going emission exceed the maximum solubility proportion of the mixed fluid. Finally, the final sulfates are deposited in the WFC part vesicles and veins.

Also, syngenite has been obtained by Raman spectroscopy considering the main bands at 982 and 1003 cm^{-1} . The determination of the diagenesis of the syngenite follows a complex mechanism formation that depends on the potassium concentration, ion sulfate, intermediates phases, temperature cooling rates and the amount of ambient-sea water in vesicles of the samples. However, it has been found that syngenite is a widespread mineral found in other volcanic systems- Haleakala volcano, Maui, in Hawaii or Vesuvius, Campania, and in the Cesano geothermal field, Latium, Italy.

The olivine detected on the sample by Raman spectroscopy and confirmed by XRD is forsterite. The analysis is in agreement with the other samples analyzed by other authors, e.g. (Perez-Torrado et al., 2012; Rodriguez-Losada et al., 2015; Troll et al., 2012). In our case, olivine was only found in DC part, indeed (Troll et al., 2012) found a notable absence of primary igneous minerals (olivine, pyroxene, feldspar, amphibole) from the XRD analysis. Also, (Meletlidis et al., 2015) confirmed that the olivine occurred as isolated phenocrysts in the intersectal texture between WFC and DC of the samples. The calibration curves from our results show that the

olivine corresponds to a FO_{50} to FO_{72} . In comparison to (Meletlidis et al., 2015), their results show a bigger Mg# concentration FO_{70-88} . Nevertheless, the results can vary from sample to sample and the day of emission/sampling.

The amorphous silica analyzed by the band fitting method proposed by (Di Genova et al., 2016, 2015) allowed to distinguish and confirm its basaltic/basanitic behavior. However, it has to be noticed that few samples were analyzed by Raman spectroscopy and the methods used from reference have been developed by using glasses in the following tendency: Basalt/Basanite, basaltic andesite, andesite, dacite and rhyolite.

Indeed, the analysis carried out showed strong amorphous behavior. Also, it is not the purpose of this work to analyze trace elements and the analysis of total alkalis versus silica diagram. Nonetheless, the aim of this research is in part to show the capabilities of Raman spectroscopy for geochemistry. In future research, more samples could be analyzed in order to have a reliable comparison with past results such as (Meletlidis et al., 2015; Troll et al., 2012)

Comparison with other pumice and submarine emission

A comparison with other terrestrial pumice from Hawaii and Tenerife and submarine pillow lavas from Tenerife is necessary to understand the difference of mineralization.

The information and analysis from the pillow lavas used for comparison have been already reported by (Lalla et al., 2015a). The most advanced feature of the pillow lavas is they are the most notable sign of submarine volcanism during the island formation. During the pillow lavas formation, the volcanic activity becomes violent where a combination of water interaction, gas emission, continuous magma eruption create this peculiar formation (Lalla et al., 2015a). The primary mineralization has been obtained by Raman spectroscopy, XRD and SEM-EDX reported are compiled in Table 3 and Figure 11. The results can be compared due to similar equipment and methods have been applied along both, the current and previous (Lalla et al., 2015a).

The other terrestrial pumice samples came from Güimar Valley in the southern part of the island. The selected sample belongs to a recent volcanic group eruption with a global age lower than ten thousand years (Lalla et al., 2015b). The outcrop where the samples were collected is constituted by a big cone, and it associated lava field that extends to the coast. A general description of the materials can be resumed as basaltic with other small basaltic enclaves, like an islet (Lalla et al., 2015b). The most remarkable of the area are the processes of hydrothermal, subaerial, submarine alteration and the interaction of ancient materials with the most recent volcanic fluids (Lalla et al., 2015b). The primary mineralization has been obtained by Raman spectroscopy, XRD and FT-IR reported are compiled in Table 3 and Figure 12

The Hawaiian pumice belongs to the ESA-ExoMars Raman database collection and the PTAL on the Unidad Asociada UVA-CSIC. The Raman analysis is also compiled in Table 3 and Figure 13.

When the two terrestrial pumices from the Canary Island, it can be observed the two relevant points. The first point on the current comparison is the terrestrial pumice (Güimar Valley) presents a more notable concentration of primary igneous minerals (i.e. olivine, pyroxene, feldspar, amphibole). The secondary mineralization detected on the Güimar Valley belongs mainly to a subaerial alteration process or weathering.

The second point that came to light, when the Hawaiian terrestrial pumice is compared, has a similar behavior in the sense of the amorphous silica. Also, it has been found at some point the possible existence of organics or amorphous carbon, but with not so high concentration as La Restinga sample. Furthermore, the organics on the Hawaiian cannot be well determined due to the lack of C-H peaks at around $2900-3000\text{ cm}^{-1}$. The spectra could confirm that the detected bands could be generated by amorphous carbon or graphitic material. The carbonates and sulfates present on Hawaiian terrestrial pumice have a big possibility to come from a weathering process.

For last, the Pillow lavas from Anaga also present a more notable concentration of primary igneous mineralization as the Güimar Valley pumice as well. The secondary mineralization found like the oxides and carbonates are less abundant in variety and quantity as it can be observed on (Lalla et al., 2015a) and presented in Table 3. The most possible cause is the kind of volcanic emission and rock-forming of samples collected. Since their physical shape and structure, up to now the origin of these “floating stones” has been vigorously debated among researchers and it is still ongoing with new insight. Indeed one possible origin of this unique emission, as other researcher proposed, could be the mixing and hybridization of two magmas from distinct mantle reservoirs, among others (Martinez-Frias et al., 2012; Meletlidis et al., 2015; Rodriguez-Losada et al., 2015). Contrary to La Restinga eruption, the pillow presented on Table 3 has followed the magmatic formation of pillow lavas, which it is well documented and studied (Lalla et al., 2015a; Sigurdsson et al., 1999).

However, the comparison done along this section has been made to focus which kind of volcanic samples (with the corresponding mineralization), volcanic emission/eruption kind and the alteration processes (sub-aerial, weathering, submarine, hydrothermal) could cover the hypothesis of (Brasier et al., 2011). La Restinga emission presents a more variety of mineral composition, as it can be observed in Table 3 in general perspectives, especially in secondary materials. The minerals presented on the Raman section and Table 1 and 2 shows a very high different elemental composition. They could be potentially used for organometallic catalysts of organic sedimentary material (Brasier et al., 2011). Among, the most notable catalysts, it should be mentioned that the secondary minerals like phosphate, Fe-oxide and Ti-oxide among others. In the primitive ocean on Earth, the early crust presented a more notably volcanic activity, and this abundance of hydrothermal veins fed the seafloor with carbonaceous cherts were rich in barium sulfate and iron sulfate that emerged from vents (Brasier et al., 2011; Cavalazzi et al., 2011; Martinez-Frias et al., 2012; Nna-Mvondo and Martinez-Frias, 2007). In this sense, the carbonates and sulfates from La Restinga eruption could be used as young modern analog materials for such hypothesis and to carry future experiments.

Implications on the astrobiological hypothesis

The detections of the organics along the samples and their comparison with the proposed standards (amino acids and high hydrocarbons materials) and geo-bacteria as well, allowed assigning their origin and organic kind. The measurements have shown that Raman bands of the organics may belong to a bacterium from the sediments. The main feature is that C-H bands are located closely to 2800 cm^{-1} , where the complex organics such as bacteria or fatty acids present this strong bands. Assuming that the assignation proposed by (el-Kabbani et al., 1991), (Kudelski, 2005) and (Markovski et al., 2017) the bands on the other regions belong to the C-O and C=O vibrational bands.

Recent studies carried out by (Zaczek et al., 2015) confirmed unequivocally that the youngest pre-island sediment is located beneath El Hierro Island. The calcareous identified nanofossils are coccolithophores that secrete small calcite platelets and carbonates. The detected carbonates could be considered as a reliable stratigraphic biomarker and also bio-marker for the search of life in this kind of volcanic material substrate (Brasier et al., 2011; Zaczek et al., 2015). Furthermore, (Zaczek et al., 2015) reported other nanofossils could compatible with *Prediscosphaera sp.*, *Prediscosphaera cretacea*, *Retecapsasp.*, *Retecapsa crenulata*, *Watznaueria sp.*, *Watznaueria fossacincta*, *Watznaueria ovata*, *Watznaueria barnesiae*, *Watznaueria manivitiaie*, *Bukryolithus ambiguus*, *Eiffellithus turriseiffelii*, *Eprolithus floralis*, and *Rhagodiscus asper*. This fossil variation assemblage range from the Cretaceous (~100 Ma) to the Pliocene (~2.5 Ma) period, presenting the age progression for the onset of volcanism in Canary Island. From (Zaczek et al., 2015) result, it has been confirmed that magma migrated laterally along the sediment base through lateral channel flows and acquiring the different sediment (with the nanofossils). Later, the rapid melting, pumiceous behavior and high quantity of gasses emitted allowed the rapid incorporation and assimilation of the sediment and organic matter into the samples (lowest and highest sediment from the El-Hierro sedimentary pile) (Zaczek et al., 2015). Remarkably, this process could be considered as a modern example

for the organic incorporation on the glassy volcanic pumice (Brasier et al., 2011) and (Martinez-Frias et al., 2012) hypotheses.

(Brasier et al., 2011) proposed the hypothesis that the submarine pumice must fulfill the following three summarized requirements: (1) The rocks must have area-to-volume ratio highest than any other rock type, (2) the volcanic rock should float at the level of sea and (3) the samples should be exposed to an unusually wide variety of conditions (Brasier et al., 2011). The first condition proposed is completed fulfilled by really low density measured of the whole samples being among 2.45 g/cm^3 and 2.89 g/cm^3 . Also, the SEM measurements revealed a high porous substrate with different vesicle size interconnected as (Brasier et al., 2011) proposed. The bacteria were commonly found forming possible future microbial colonies, already proposed and having a maximal area for the effective surface chemical reaction.

On the other hand, the second condition was confirmed by the several days of material that appeared floating. The vesicles interconnected were filled with the volcanic gasses emitted during the process. (Brasier et al., 2011) suggested, from last evidence, that pumices from submarine emission or eruptions could suffer a saturation of water, in combination magmatic steam and the continuous agitation at the ocean forming a unique internal atmosphere. This suggestion can be confirmed by the detection of the different sulfates and halite along the sample. Also, the interconnected vesicles act as a barrier from the UV-effects such as photodissociation or photodegradation, and the floating properties allowed to be on the water-air interface creating a stable thermal condition (Brasier et al., 2011).

Furthermore, in the visual perspective, another feature to be considered is that the DC part is black-colored allowing, possibly in the future, to absorb the external radiation, transported heat to the internal WFC. Thus, this energy transfer in radiation could also help to make steady thermal conditions.

(Brasier et al., 2011) proposed that floating pumice could be exposed to unusual conditions on the primitive Earth during the volcanic activities. Some of the proposed effects could be the

Leiden frost boiling, effect triboelectric and electrical discharges that could generate Miller-Urey synthesis (Brasier et al., 2011; Lazcano and Miller, 1996). After these processes, the pumice floating samples were coated by Ti-oxide and the UV light could create a photo-catalysis on the samples with a final product of hydrogen ions from water, hydrocarbons, and phosphorus (Brasier et al., 2011; Lazar et al., 2012). In this case, the analyzed samples show the existence of the different Ti-oxide as rutile and anatase with high accumulation of organics, confirming the initial proposed conditions for possible future photo-catalysis. However, the other assumptions of chemo-physical effects for the thousands of years like evaporitic effects, salinity variations, hydration, or dehydration that could assist the polymerization of sugar, lipids and amino-acids cannot be confirmed given the youth of the samples (Brasier et al., 2011).

The volcanic minerals that could be as catalysts proposed by (Brasier et al., 2011) and generated by hydrothermal activities are present in La Restinga samples (Barbieri and Cavalazzi, 2014). The list of minerals and material proposed were carbonaceous material, barium sulfate, iron sulfate, phosphate, clays, Ti-oxide and microporous zeolites (Brasier et al., 2011). The different minerals proposed will follow a different path to carry out the catalysis and also it depends on the physic-chemical conditions of the process. However, La Restinga samples almost have different mineral and materials like the sulfate, Ti-oxide and phosphates. Again, the youth of the samples did not allow the formation of the zeolites and clays because they will need longer time in a water-saturated environment to be formed.

Conclusions

For the very first time, some selected samples from La Restinga eruption (El Hierro) has been thoroughly analyzed by Raman spectroscopy with other supporting methods such as Scanning electron microscopy, optical microscopy and X-ray diffraction. The vibrational analysis carried mainly by Raman spectroscopy allowed to detect Fe-oxide, Ti-oxide, quartz and Si-oxide, carbonates, sulfates, phosphates, pyroxene and olivine. Some of the minerals were already reported from the literature, and previous research carried out before. However, other new minerals have been detected and not reported like the lepidocrocite, the possible existence of

moganite and the Ca-carbonate. The detected sulfates, like syngenite and barite, have an origin due to the interaction of volcanic emission and interaction among the magma, degassing and water. Also, other phosphate was detected punctually and not reported. The correct identification of the minerals presented has been using Gaussian fitting procedure and stoichiometric methods developed on Raman spectroscopy.

A detailed analysis of the organic detected material has been carried from the samples with a comparison with other organic standards and bacteria confirming the incorporation of the organic sediments, nanofossils and other submarine bacterias during the pumice formation. The detected results enforce the survival of the bacterias during the hydrothermal processes and to become the substrate for the evolution of possible future life.

The comparison with other pumice samples and submarine emission sample from same archipelago (Tenerife, Spain) and another volcanic outcrop (Hawaii, USA) have shown a wider variety of mineralogy, alteration processes and higher properties as a possible substrate for the evolution of life. These primary considerations have been done using the (Brasier et al., 2011) and (Martinez-Frias et al., 2012) hypotheses about the hydrothermal processes significance in astrobiology. In this regard, the measurements support the continued endeavors of developments in Raman spectroscopy research for Mars exploration on the future space mission such as the RLS to be onboard on ExoMars and SHERLOC on Mar 2020. Also, the analysis of Raman spectroscopy in synergy with other laboratory methods will enforce the methods and protocols of Raman analysis in the detection of life for future space systems in Mars and Icy Moons.

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