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Review

Spectroscopic study of terrestrial analogues to support rover missions to Mars – A Raman-centred review

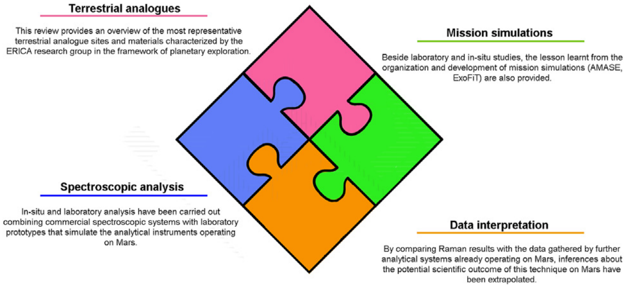
Fernando Rull [a, *], Marco Veneranda [a], Jose Antonio Manrique-Martinez [a], Aurelio Sanz-Arranz [a], Jesus Saiz [a], Jesús Medina [a], Andoni Moral [b], Carlos Perez [b], Laura Seoane [b], Emmanuel Lalla [c], Elena Charro [a], Jose Manuel Lopez [a], Luis Miguel Nieto [a], Guillermo Lopez-Reyes [a]

[a] University of Valladolid, Plaza de Santa Cruz 8, 47002, Valladolid, Spain
[b] National Institute for Aerospace Technology (INTA), Torrejón de Ardoz, Spain
[c] York University, Centre for Research in Earth and Space Science, Toronto, Canada

HIGHLIGHTS

- We present a review of the terrestrial analogue studies performed by the ERICA group.
- Details about planetary mission simulations are also provided.
- The main results gathered from the use of multiple analytical systems are compared.
- Pros and cons expected by the use of Raman spectrometers on Mars are presented.
- The work aims to support the interpretation of data returned from Mars2020 and ExoMars rovers.

GRAPHICAL ABSTRACT



Terrestrial analogues

This review provides an overview of the most representative terrestrial analogue sites and materials characterized by the ERICA research group in the framework of planetary exploration.

Mission simulations

Beside laboratory and in-situ studies, the lesson learnt from the organization and development of mission simulations (AMASE, ExoFiT) are also provided.

Spectroscopic analysis

In-situ and laboratory analysis have been carried out combining commercial spectroscopic systems with laboratory prototypes that simulate the analytical instruments operating on Mars.

Data interpretation

By comparing Raman results with the data gathered by further analytical systems already operating on Mars, inferences about the potential scientific outcome of this technique on Mars have been extrapolated.

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ABSTRACT

The 2020s could be called, with little doubt, the "Mars decade". No other period in space exploration history has experienced such interest in placing orbiters, rovers and landers on the Red Planet. In 2021 alone, the Emirates' first Mars Mission (the Hope orbiter), the Chinese Tianwen-1 mission (orbiter, lander and rover), and NASA's Mars 2020 Perseverance rover reached Mars. The ExoMars mission Rosalind Franklin rover is scheduled for launch in 2022. Beyond that, several other missions are proposed or under development. Among these, MMX to Phobos and the very important Mars Sample Return can be cited. One of the key mission objectives of the Mars 2020 and ExoMars 2022 missions is the detection of traces of potential past or present life. This detection relies to a great extent on the analytical results provided by complementary spectroscopic techniques. The development of these novel instruments has been carried out in step with the analytical study of terrestrial analogue sites and materials, which serve to test the scientific capabilities of spectroscopic prototypes while providing crucial information to better understand the geological processes that could have occurred on Mars. Being directly involved in the development of three of the first Raman spectrometers to be validated for space exploration missions (Mars 2020/SuperCam, ExoMars/RLS and RAX/MMX), the present review summarizes some of the most relevant spectroscopy-based analyses of terrestrial analogues carried out over the past two decades. Therefore, the present work describes the analytical results gathered from the study of some of the most

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* Corresponding author.
E-mail address: rull@fmc.uva.es (F. Rull).

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distinctive terrestrial analogues of Martian geological contexts, as well as the lessons learned mainly from ExoMars mission simulations conducted at representative analogue sites. Learning from the experience gained in the described studies, a general overview of the scientific outcome expected from the spectroscopic system developed for current and forthcoming planetary missions is provided.

Contents

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1. Introduction

Spectroscopic analytical techniques are acquiring increasing importance in the field of Mars exploration. Strictly focusing on ground instruments, elemental data have been successfully collected by alpha proton X-ray spectrometers (APXS) onboard the Pathfinder [1], Spirit [2], Opportunity [3] and Curiosity [4] rovers. With respect to the Mars Science Laboratory (MSL) mission, complementary elemental data were additionally collected by laser-induced breakdown spectroscopy (LIBS, ChemCam [5]) and X-ray fluorescence instruments (CheMin [6]) onboard the rover. Regarding mineralogical data, Mössbauer systems onboard Spirit [7] and Opportunity [8] rovers helped to shed light on the mineral phases composing Martian primary rocks and their alteration products.

Looking ahead, the Mars 2020 and ExoMars rover missions incorporate, among other spectroscopic techniques, the first Raman instruments to be validated for space exploration. On the one hand, the main objective of the ExoMars mission is to identify traces of life on Mars. To do so, the subsurface observations performed by the WISDOM (Water Ice and Subsurface Deposit Observation on Mars [9]) ground-penetrating radar will guide the drill of the Rosalind Franklin rover in the collection of geological samples down to a depth of 2 metres. The Sample and Preparation and Distribution System (SPDS [10]) will crush the geological materials and will deliver them to the Analytical Laboratory Drawer (ALD) located inside the body of the rover. Here, the molecular analysis performed by the Raman laser spectrometer (RLS [11,12]) will serve, together with complementary MicrOmega NIR data [13], to select the optimal targets to be characterized by the Mars Organic Molecule Analyser (MOMA) system [14].

On the other hand, the main objective of the Mars 2020 mission is to gather astrobiologically relevant samples and store them in tubes that will be sent back to Earth through the so-called Mars Sample Return mission [15]. In detail, the Perseverance rover will select the samples according to the spectroscopic data returned by a combination of remote and proximity science systems [16]. To do so, the SuperCam multi-suite instrument [17–19] performs remote Raman, LIBS, VISIR and fluorescence of Martian rocks and soils. Targets of high scientific interest are then further characterized by proximity instruments mounted on the robotic arm of the rover. In this case, the elemental data provided by PIXL (Planetary Instrument for X-ray Lithochemistry [20]) are complemented by the Raman spectra collected by Sherloc [21], a UV spectrometer whose design has been optimized for the detection of organics.

In addition, Raman spectrometers will be used on exploration missions that are currently under development (as is the case of the Raman spectrometer (RAX) onboard the JAXA-Martian Moons eXploration (MMX) rover that is scheduled to land on Phobos in 2025 [22–24]) and planning (Raman spectroscopy has been selected among the techniques necessary to meet the science goals outlined for the Europa Lander mission [25–27]).

In light of the increasing importance spectroscopic techniques (especially Raman) are acquiring in the field of space exploration, the analytical study of terrestrial analogue sites and materials using these techniques has become an essential tool to estimate the potential scientific outcome derived from their operation on Mars [28–30]. Furthermore, bearing strong analogies with Martian mineralogical/environmental contexts, the analysis of terrestrial analogues also helps to extrapolate important inferences about the geological and environmental evolution of the planet [31] and its past habitability [32].

Being involved at different levels in the development of SuperCam (Mars 2020 mission), RLS (ExoMars mission), and RAX (MMX mission) Raman spectrometers, the ERICA group (Raman and Infrared Spectroscopy applied to Cosmogeochemistry and Astrobiology) works in very close collaboration with INTA-CAB (National Institute for Aerospace Technology – Astrobiology Center) and several other laboratories in Spain and abroad to support the required technological advancements with the analytical study of representative terrestrial analogue sites and materials.

The spectroscopic-based analytical procedure used for these studies combines in situ analysis of the analogue site with the laboratory investigation of selected samples. In this framework, the analytical study of terrestrial analogue materials is generally carried out using a combination of commercial instruments and analytical prototypes simulating the scientific outcome of planetary instrumentation. In regard to Mars-related investigations, RLS-Sim, RAD-1 and SimulCam have been widely used to simulate RLS-FM and SuperCam operations. As described elsewhere [33], RLS-Sim is a laboratory simulator providing Raman spectra qualitatively comparable to the RLS-FM (flight model). Similar to RLS-Sim, RAD-1 is a portable RLS simulator that has been frequently used for the in situ investigation of terrestrial analogues [35]. In addition, SimulCam is a hybrid Raman-LIBS system that, similar to the Mars2020/SuperCam suite, is capable of performing complementary elemental and molecular analysis of remote targets [36]. In addition to representative prototypes, qualification (EQM) and spare (FS) models of the RLS system have also been used during ExoMars mission simulations [12]. Aiming to summarize and contextualize the numerous studies carried out in this field of research, the present review is organized as follows: first, the analytical results gathered from the most distinctive terrestrial analogues of Martian geological contexts are described. Then, the lessons learned from ExoMars mission simulations carried out at terrestrial analogue sites are described. This last aspect also covers the data treatment and database generation and management, which are essential tools to optimize the scientific information derived from Martian spectra. Finally, the potential scientific outcome that could derive from the forthcoming application of novel spectroscopic systems (especially Raman) in planetary missions is evaluated by comparison with complementary analytical instruments used in previous and current missions.

2. Terrestrial analogue sites

Scientific instruments for planetary exploration missions are the results of years of cutting-edge technological developments. Representative field trials are therefore needed to evaluate and optimize their analytical performances. Therefore, an increasing number of field trials are organized to gather insights about the potential scientific outcome of the scientific instruments that will serve, for example, to define the necessary hardware or software updates.

In light of the role the ERICA research group and its collaborators are playing in the development of spectroscopic tools onboard Mars 2020, ExoMars and MMX planetary missions, many field trips have been carried out to test the capabilities of analytical prototypes and compare their results with those provided by commercial instruments and complementary space-derived systems. Below, an overview of the research work carried out by the group at some of the most relevant terrestrial analogue sites is provided.

2.1. Jaroso Hydrothermal System (JHS, Spain)

One of the most interesting mineralogical discoveries achieved through the in situ exploration of Mars is the detection of iron oxyhydroxide and hydrated sulfate (alunite group) assemblages, with their crystallization associated with the past occurrence of large-scale hydrothermal systems [37–40]. Since the 1990s, an increasing number of researchers have analysed the mineralogy and tectonics of Jaroso Ravine (type locality for the mineral jarosite) to define the multiple mineralizing stages associated with both hypogenic and supergenic hydrothermal processes [41–44]. According to these studies, the Jaroso Hydrothermal System (JHS) outcrop is an important emplacement where 1) the detection capabilities of analytical instruments for space exploration missions can be tested and 2) constraints on hydrothermal processes that occurred on early Mars can be inferred from Ref. [41]. In this framework, a set of complementary in situ and laboratory studies of hydrothermal alteration deposits was carried out between 2004 and 2010 by an interdisciplinary scientific team that involved several members of both ERICA and INTA-CAB groups. Considering that the Mössbauer instrument onboard the Opportunity rover was the first instrument to detect jarosite ($KFe^{3+}3(SO_4)_2(OH)_6$) on Mars [45], this technique was used in combination with Raman spectroscopy to characterize the sulfate deposits found at the JHS. For that, a portable version of the Mössbauer flight instrument (MIMOS II) was used [46]. As detailed in multiple manuscripts [47–49], in addition to successfully identifying jarosite (see Fig. 1), the Mössbauer system detected additional sulfates, such as copiapite ($Fe^{2+}Fe4^{3+}(SO_4)(OH)_2\cdot 20H_2O$) and rozenite ($Fe_SO4\ 4H_2O$), together with minor amounts of iron oxides (goethite α-FeO(OH) and haematite Fe_2O_3) [47]. This association of minerals is very similar to those detected by the Opportunity rover at the Meridiani Planum [45], which underlines the strong analogy between this terrestrial analogue site and Martian geological contexts.

As happens on Earth, jarosite on Mars may have precipitated from hydrothermal acidic (pH ˂4) solutions rich in heavy metals [50]. Despite low pH conditions, many chemolithoautotrophic and thermophilic microorganisms colonize these habitats [51]. In addition, jarosite shelters organic molecules from UV radiation, thus favouring the preservation of organic molecules [52]. For these reasons, jarosite deposits are among the most promising scientific targets for searching for signs of life on Mars.

As both ExoMars and Mars 2020 rovers are meant to select geological samples of high astrobiological relevance according to their mineralogical and geochemical composition, complementary Raman and LIBS analyses were additionally carried out. Analytical data gathered in situ and in the laboratory by means of Raman prototypes enabled the precise detection of jarosite with different cationic compositions (a characteristic Raman-LIBS spectrum is displayed in Fig. 2), copiapite, haematite and goethite, thus confirming the Mössbauer results. Furthermore, additional hydrothermal alteration products were also detected, including coquimbite ($Fe_2(SO_4)_3\cdot 9H_2O$), halotrichite ($Fe^{2+}Al_2(SO_4)_4\cdot 22H_2O$), gypsum ($CaSO_4\cdot H_2O$), barite ($Ba_SO_4$) and siderite ($FeCO_3$) [47,53,54]. These results successfully demonstrated the potential scientific outcome that could derive from the application of Raman spectroscopy during Martian exploration missions.

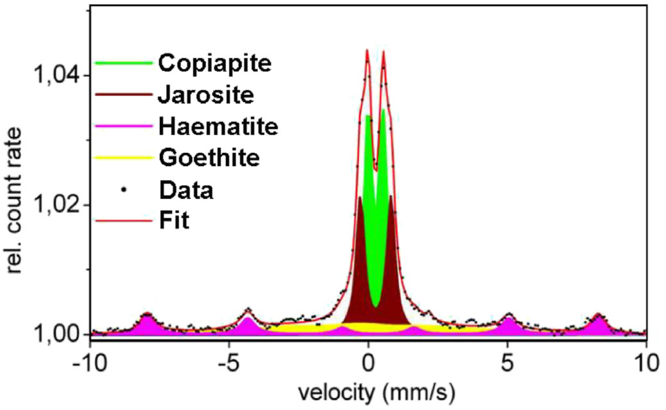

Fig. 1. Mössbauer spectra from JHS sulfate deposits, detecting the presence of jarosite, copiapite, haematite and goethite (from F. Rull et al., 2008 [47]).

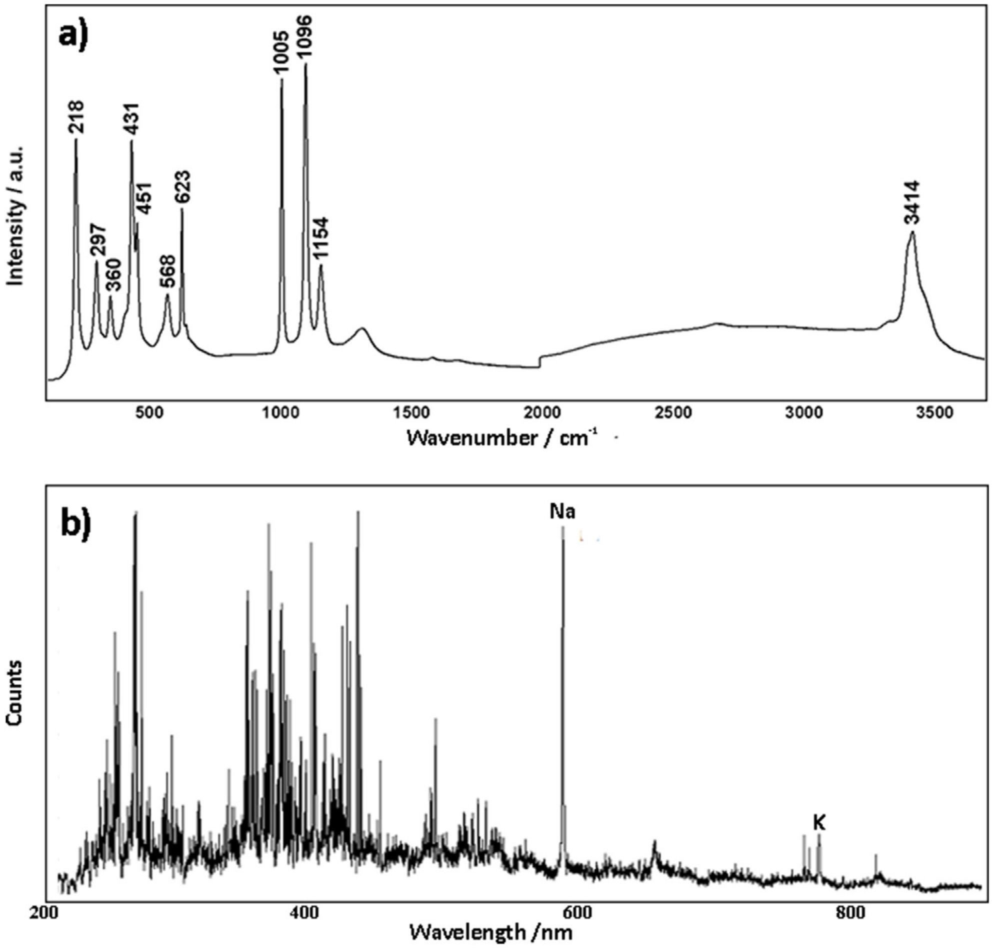

Fig. 2. Raman spectrum (a) and LIBS spectrum (b) of jarosite collected at the JHS and obtained in the laboratory. It is important to note the complementarity between the two techniques. From Raman, the mineral phase is precisely identified, and from LIBS, the precise cationic chemical composition is deduced.

The campaign of analysis carried out at the JHS also offered the opportunity to test, at a representative analogue site, the advantages provided by the combined use of Raman and LIBS systems. In this sense, by acquiring elemental and molecular data from the same spot of interest, it was possible to establish correlations between variations in the characteristic parameters of Raman peaks (position, width and intensity) and the elemental composition of the target. Thus, by means of the combined Raman-LIBS analysis of alunitic deposits, jarosite (rich in K) and natrojarosite (rich in Na) phases [55] were correctly discriminated. As presented in Fig. 2, the characteristic emission lines of sodium and potassium have often been detected in the same spot of interest, thus suggesting the presence of jarosite phases whose elemental composition falls within the K—Na solid solution. In this case, peak shifting detected by Raman analysis confirmed the presence of K—Na intermediate mineral phases, while the LIBS-based semiquantitative estimation provided detailed information regarding its geochemistry. As the LIBS spectra collected on Mars by the ChemCam instrument have been effectively used to estimate the elemental abundances of the analysed targets [56], this work suggests that the combined Raman-LIBS analysis performed by SuperCam could be used to extrapolate precise mineralogical and geochemical information about Martian rocks and soils. Additional analytical results, gathered from the use of complementary techniques (XRD, SEM and FTIR, among others) at the JHS, are presented elsewhere [54,57—59].

2.2. Rio Tinto (Spain)

As explained in Section 2.1, the iron-rich sulfate precipitation found on Mars is a very interesting scientific target to look for traces of past and/or present life. Therefore, the Rio Tinto Basin is widely considered the optimal terrestrial analogue site to test the capability of space-derived instrumentation to potentially detect biomarkers from extremophilic organisms. Rio Tinto is a 100 km-long river located in the Iberian Pyrite Belt, which is considered one of the largest sulfidic deposits in the world (mostly iron and copper sulfides). Partially as a consequence of mining activities, the red waters of the river (see Fig. 3) are characterized by highly acidic values (mean pH below 2.5) and a remarkable concentration of heavy metals (mostly Fe, Cu, Zn and As) [60,61].

Despite these extremophilic conditions, Rio Tinto presents high levels of microbial diversity. Among them, chemolithrophic organisms such as *Thiobacillus ferrooxidans* are partially responsible for sulfur compound reduction and ferrous iron oxidation [61,62], thus affecting the composition of the characteristic iron- and sulfate-bearing precipitates of Rio Tinto. Most recently, biomediated processes were also proven to occur in anaerobic conditions [63]. Due to the astrobiological relevance of this discovery, many research studies are currently focused on the analytical characterization of sulfate-rich precipitates by means of space-derived instruments [47,64]. As in the case of the JHS, the Mössbauer analysis of Rio Tinto samples has been complemented

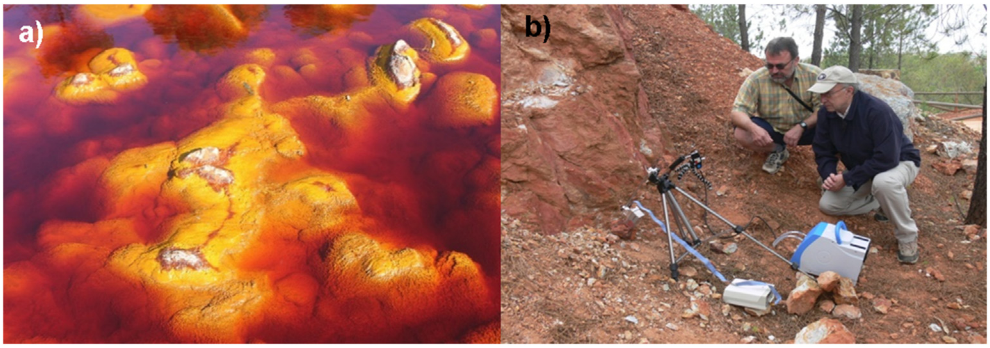

Fig. 3. a) Picture of Rio Tinto water and associated sulfate-rich precipitation. B) The Mösbauer MIMOS II instrument working in collaboration with a portable Raman system analysing Fe-bearing minerals at an outcrop.

by Raman investigations. The results gathered from Raman prototypes confirmed Mössbauer results while effectively detecting additional compounds, such as gypsum, jarosite and pyrite (FeS_2) [65,66] In the work of Sobron et al. (2014) [67], Raman results gathered from the study of Rio Tinto precipitates were compared with those provided by instruments employed in further exploration missions, such as the Terra X-ray diffractometer (commercial version of the XRD system onboard the Curiosity rover) and the FieldSpecProFR VNIR reflectance spectrometer (emulating the MicrOmega [13] system onboard the Rosalind Franklin rover). Compared with diffractometric results, the mineralogical heterogeneity of complex precipitate mixtures can be more effectively disclosed by combining Raman and VNIR analysis, which is the analytical strategy planned for the ExoMars mission. Nevertheless, the combination of these complementary techniques shows real potential for investigating precipitation sequences. Indeed, unlike Raman and VNIR instruments, whose excitation sources only probe the surface of the target, the gamma radiation used for Mössbauer spectroscopy penetrates deeper into the sample, thus enabling an in-depth mineralogical investigation. In this sense, the combination of complementary spectroscopic techniques delivers a level of depth-sensitive information, which could be used to extrapolate reliable inferences about the precipitation sequence.

Rio Tinto waters were sampled and used for laboratory experiments to better comprehend the precipitation sequence occurring at this analogue site. After measuring pH, conductivity and elemental composition [68], waters were poured into an evaporation chamber and used to reproduce the precipitation sequence occurring at Rio Tinto riverbanks [69,70]. The representative Raman spectra of some of the precipitated mineral phases are presented in Fig. 4. Similarly, microscale experiments were performed by analysing the Raman emissions proceeding from Rio Tinto water droplets during drying [69]. As presented by Rull et al. [71], a set of iron-rich mineral phases progressively formed by following a precipitation sequence that can be summarized as follows: ferricopiapite → coquimbite → copiapite → magnesiocopiapite → haematite → rozenite → szomolnokite → rhomboclase → metavoltine.

Beyond mineralogical studies, Raman spectroscopy was effectively employed to identify the potential presence of biomarkers. As presented by Edwards et al. (2007) [72], from the Raman characterization of mineral deposits collected at the edge of Rio Tinto water pools, organic compounds such as carotenoids, scytonemin and amino acids were detected, some of which could be related to the biological colonization of sulfate-rich precipitation materials.

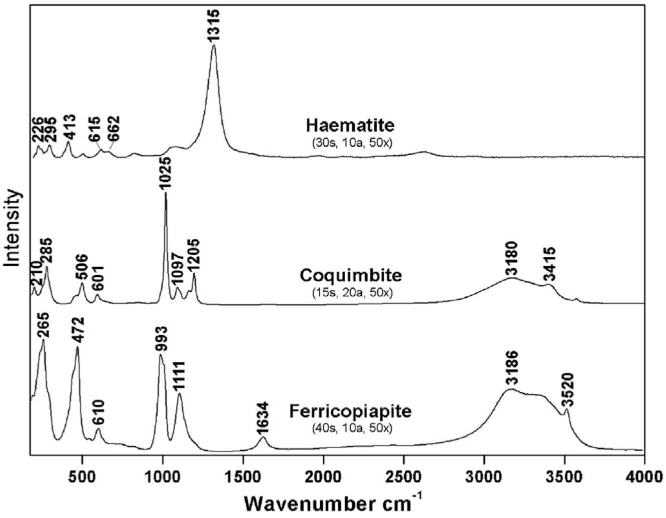

Fig. 4. Raman spectra of ferricopiapite, coquimbite and haematite phases precipitated during laboratory macroscale experiments after 1, 3 and 13 days. The experimental conditions (acquisition time, number of accumulations, and objective) set for each spectrum are provided between parentheses.

2.3. Barberton (South Africa)

Recording a geological history of approximately 500 million years, Barberton stratigraphy has been deeply analysed to extrapolate crucial information about the geological and environmental evolution of Earth during the Archean period [73–75]. In recent years, an increasing number of studies have presented Barberton as a potential analogue site of geological contexts that can be found on Mars [76] and other extraterrestrial bodies [77]. Within this field, two types of geological materials have attracted the interest of researchers.

On the one hand, komatiites from the Barberton Greenstone Belt are ultramafic rocks whose texture (spinifex) [78,79] and elemental composition (enriched in Mg) [76,80,81] make them surprisingly similar to Martian basalts. As geological materials of high interest for both geological and astrobiological studies, komatiite samples were collected from Barberton and used by the ExoMars team to assess the potential analytical capabilities of the spectroscopic systems onboard the Rosalind Franklin rover [82]. In addition to effectively identifying the main primary phases (olivine and amphiboles), water alteration products were also detected by Raman spectroscopy, including serpentine. It is well known that serpentinization generates hydrogen (H_2) and methane (CH_4, through the

Fischer-Tropsch reaction of H_2 with CO_2), which are energy sources that can fuel the metabolism of chemolithotrophic organisms [28,83,84]. Therefore, this work highlights the capability of this technique to detect secondary phases of high astrobiological interest.

On the other hand, the black and white banded chert found at Barberton is a silicified volcanic sediment of great astrobiological interest. Indeed, even though black and white layers share the same mineralogical composition (microquartz SiO_2), dark layers mainly differ by the high content of organic matter and carbonaceous material, whose deposition process has been described elsewhere [85]. As one of the oldest pieces of evidence for life on Earth (3.4 billion years ago), Westall and coworkers presented numerous studies in which layered chert samples from Barberton were employed as terrestrial analogue material for astrobiological studies [86–91]. Within this field of research, the ERICA research group carried out a set of studies mainly focused on the use of Raman spectrometers. While correctly characterizing the geological matrix (mainly quartz with trace amounts of anatase TiO_2 and dolomite $CaMg(CO_3)_2$ phases), the RLS-Sim was capable of clearly detecting the vibrational features of kerogen (Fig. 5), which is the organic matter preserved in black veins [92–94]. The detailed analysis of the D and G Raman bands of amorphous carbon allowed us to investigate the structural characteristics of kerogen, which are related to the “maturity process” undergone by the samples under the different geological processes. Nevertheless, these modified characteristics are not sufficient to determine the possible biogenic origin of the kerogen, which is an important challenge for Raman spectroscopy in investigating possible traces of life in these materials.

In light of the forthcoming missions to Mars, Barberton chert samples have been widely used to assess the capability of the RLS system to detect organic compounds in ancient geological matrices [11,33,95] and to evaluate how grain-size distribution affects the quality of Raman results [94].

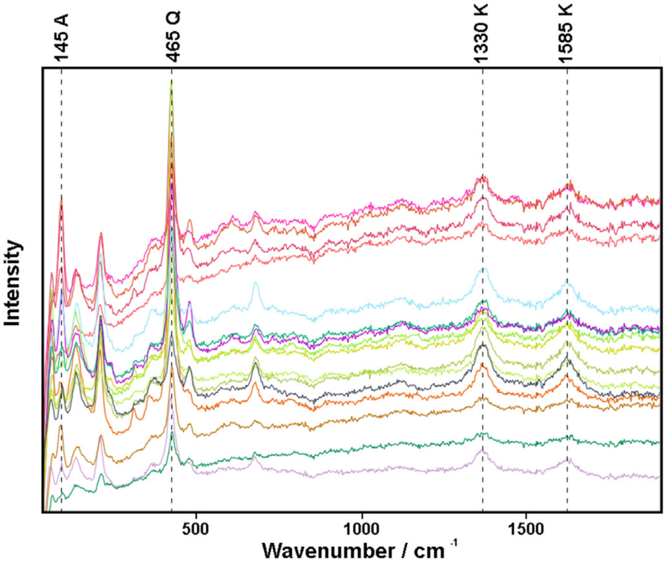

Fig. 5. Set of Raman spectra of a chert sample collected by means of the RLS-Sim in automatic mode (nominal RLS analytical cycle composed of 20 spectra gathered from different spots of interest). Kerogen (K) doublets at 1330 and 1585 cm^{-1} and quartz (Q) at 465 cm^{-1} are easily identified. Additional signatures from anatase (A, main peak at 145 cm^{-1}) are also detected.

2.4. Tenerife (Spain)

The volcanic complex of Tenerife (Spain) is also considered a mineralogical analogue of Mars. Located in the Atlantic Ocean, Tenerife is part of the Canary archipelago, which is composed of 7 main volcanic islands. Similar to other young volcanoes (e.g., those on the Hawaii and Galapagos islands), the volcanic complex of Tenerife presents many morphological features with strong similarities with the volcanoes observed on Mars [96–98]. Beyond morphological similarities, the mineralogical and geochemical composition of the basaltic rocks found at Tenerife and their alteration products are analogous to the Martian volcanic materials analysed by orbiters, landers and rovers [99]. Therefore, Tenerife has often been selected as an analogue site to explore the scientific capabilities of analytical techniques involved in planetary missions and to understand geological/biological processes that may have occurred on Mars. Within this field of research, the first investigations carried out by the ERICA group were mainly focused on the mineralogical and geochemical characterization of the geological units composing Tenerife's volcanic complex. Complementary in situ and laboratory results obtained by Raman, XRD, Mössbauer and FTIR systems helped to understand the multiple similarities between the geology of this site and Martian geological contexts [99,100].

In addition to analysing the composition of primary rocks, the same analytical procedure was also applied to the study of degradation products [101] by giving particular attention to the investigation of alteration processes related to the interaction with water. Thus, the volcanic complex of Tenerife displayed a great variety of water-related weathering, hydrothermal interactions and underwater alteration processes. As detailed in previous studies, these are some of the geological processes that could have favoured the potential proliferation of life forms on early Mars, when volcanic activity of the planet coexisted with the presence of liquid water on the surface [102,103]. In this framework, mineralogical studies have been recently performed by Lalla et al. (2015) at the Caldera de las Cañadas, an area displaying collapses and depressions whose geomorphology has many similarities with some of the volcanoes detected on Mars [104]. Beyond the mineralogical characterization of primary minerals, XRD, Mössbauer, XRF and Raman instruments were used to study the alteration products produced by the interaction of volcanic rocks with hydrothermal fluids. The effective detection of hydrothermal products (calcite $CaCO_3$, hidrotalcite $Mg_6Al_2(CO_3)(OH)_{16}\cdot 4(H_2O)$ and apatite $Ca_5(PO_4)_3(F,Cl,OH)$, among others) proves the capability of spectroscopic instruments to provide the mineralogical information necessary to optimize the selection of soil and rock samples to be analysed by the MOMA instrument onboard the ExoMars rover [14], or to be stored by the Mars 2020/Perseverance rover for the future Sample Return Mission [15,105].

Similarly, “Los Azulejos” is a colourful outcrop presenting bluish to greenish hydrothermal alteration layers. Thanks to spectroscopic (Raman and FTIR) and diffractometric (XRD) analyses carried out in situ and in the laboratory, the characteristic colours of this outcrop were proven to be provided by a combination of hydrothermal-mediated minerals such as analcime ($Na(Si_2Al)O_6\cdot H_2O$), smectite, sulfates and illite [99,106], most of which have been detected in putative hydrothermal systems on Mars [107].

In addition to in situ and laboratory analyses performed by commercial instruments, altered volcanic rocks were also studied in the laboratory by means of spectroscopic prototype systems. While detecting the main primary minerals (pyroxene and feldspar phases), the RLS-Sim was also capable of characterizing the main products of their alteration, including iron oxides, phosphates and carbonates (the most relevant spectra are provided in Fig. 6). This

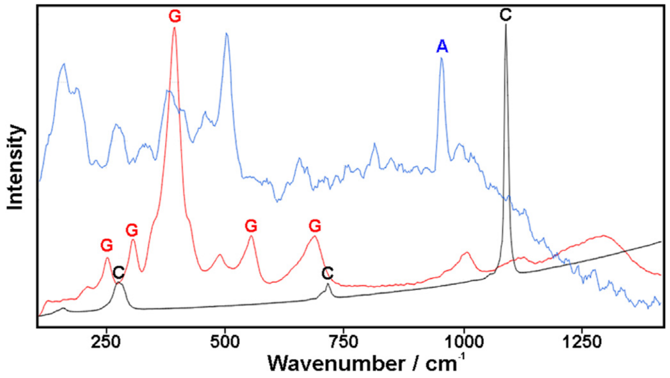

Fig. 6. Representative Raman spectra of calcite (C), goethite (G) and apatite (A) detected by means of RLS-Sim during the analysis of altered rocks sampled from the Los Azulejos outcrop.

investigation indirectly proved the capability of the RLS system onboard the Rosalind Franklin rover to identify mineralogical clues that could help fulfil the objectives of the ExoMars mission [108].

2.5. Leka ophiolite complex (Norway)

By closely resembling the mineralogical and geochemical composition of mafic and ultramafic rocks detected on Mars by orbiters [109–112] and rovers [113–115], terrestrial ophiolites are widely considered optimal terrestrial analogue sites to investigate the water alteration of Martian igneous rocks [116–119]. Indeed, as is the case for terrestrial ophiolites, large areas of Mars present phyllosilicate features that are concordant with the putative water alteration of olivine-bearing rocks into serpentine phases [102,120].

As olivine-bearing rocks have been detected at both the ExoMars and Mars 2020 landing sites, it is important to assess to what degree the analytical tools onboard the Perseverance and Rosalind Franklin rovers can identify their potential serpentinization. Within this field of research, the Leka ophiolite complex (LOC) was selected as a very interesting analogue site to investigate the scientific outcome that could derive from the use of spectroscopic systems in similar Martian scenarios. Located in Norway, the LOC is the result of the uplift of the ancient ocean crust that occurred 497 Ma during Caledonian–Appalachian mountain belt formation [121]. Previous investigations confirmed that the LOC presents multiple altered and serpentinized peridotite (dunite and harzburgite) units [122–124], some of which have undergone severe serpentinization and carbonatation reactions [125].

Considering the astrobiological relevance that serpentinized ultramafic rocks could play in sustaining life proliferation on Mars [84], several terrestrial analogue samples were collected from the LOC to be analysed by instruments relevant for planetary missions. In detail, ultramafic rock fragments showing different degrees of serpentinization were characterized by Raman, NIR and LIBS systems. The obtained results were then compared with those provided by complementary diffractometric analysis.

In light of the forthcoming landing of the ExoMars rover at Oxia Planum, the combination of NIR and Raman analysis proved to be a promising analytical strategy for the mineralogical characterization of altered rocks on Mars. Indeed, as described in a dedicated manuscript, Raman investigations allowed the identification of main mineralogical phases and the discrimination between serpentine mineral phases, while NIR results provided complementary information about the nature of additional alteration products [30]. Furthermore, LIBS and Raman data collected from the same spot of interest proved that a deeper understanding of the detected mineral phases can be achieved by joining molecular and elemental information. In detail, knowing that the wavelength position of the main Raman double peak of olivine minerals shifts according to the iron/magnesium ratio of the crystal under study (forsterite (Fo, Mg_2SiO_4) and fayalite (Fa, Fe_2SiO_4), the end-members of the olivine solid solution [126]), an average composition between Fo87Fa13 and Fo92Fa08 was estimated by taking into consideration both the Raman peak position and the intensity ratio of LIBS Mg–Fe lines.

Focusing on Raman analysis, further studies were carried out to determine whether the serpentinization degree of the samples could be reliably estimated through univariate analysis of ExoMars-like Raman datasets (39 spectra collected from the same powdered sample). As represented in Fig. 7, external calibration curves were used to estimate the relative content of olivine and serpentine in the samples, obtaining concentration ratios that fit very well with XRD estimations. Therefore, the performed study suggested that the RLS could be used to perform a semiquantitative analysis of mineralogically heterogeneous targets on Mars.

2.6. Chesapeake bay impact crater (CBIS, USA)

Among the different typologies of terrestrial analogue sites, impact craters are particularly important, as they offer the opportunity to carry out important geological and astrobiological studies [127–129]. Indeed, impact craters have been selected as landing sites for many missions to Mars. This is the case for Spirit (Gusev crater [130]), Curiosity (Gale crater [131]), and Perseverance (Jezero crater [132]) exploration rovers. It is believed that impact craters on Mars and other celestial bodies could have offered the conditions for life proliferation. Indeed, the high temperatures generated by the impact of a bolide can last for thousands or even millions of years [133,134]. When the targeted surface contains water, these temperatures generate hydrothermal systems that provide the basic ingredients necessary to create and sustain biological activity. Furthermore, one of the oldest life forms found on Earth are

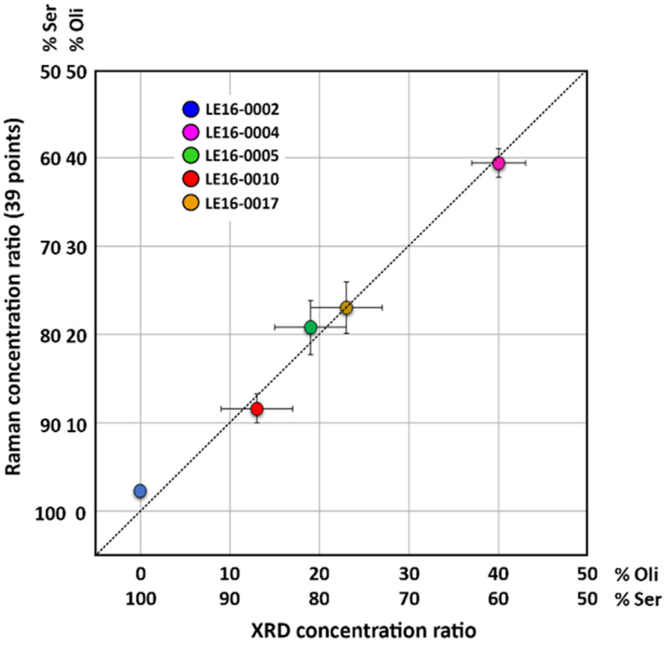

Fig. 7. Scatter plot comparing the concentration ratio of olivine and serpentine of Leka samples, calculated from the interpretation of XRD diffractograms and Raman datasets. The error bars show the quantification uncertainties for both techniques (from Veneranda et al. [83]).

putative fossilized microorganisms recently found in ancient hydrothermal vents, which can be dated to 3.77–4.28 billion years ago [135].

Thanks to the analysis of terrestrial craters, a series of morphological features have been identified that could be used to distinguish craters produced by a bolide impacting a wet surface from those produced in dry environments. As presented elsewhere [133], through the analysis of the high-resolution images gathered by the Mars Orbiter Camera wide-angle (MOC WA), several impact structures were identified whose morphology has strong similarities with the CBIS [136]. Knowing the repercussion that the scientific investigation of putative wet target impact craters on Mars and other planets could have in the potential identification of early forms of life, impact breccia samples selected from the ICDP-USGS Eyreville core [137] drilled at the centre of the CBIS were investigated in the laboratory to evaluate the scientific capabilities of Raman spectrometers to discriminate shock-induced metamorphism suffered by impact breccia minerals, as well as to detect hydrothermal alteration products.

As detailed in a dedicated paper [29], Raman investigations were carried out by combining commercial instruments with the RLS-Sim. Raman results were then compared with those provided by NIR and XRD systems. RLS-Sim effectively detected the main mineral phases observed by complementary analytical techniques and described in previous studies [137], including quartz, cristobalite (SiO_2), illite and feldspars ($(K,Na,Ca)(Si,Al)_4O_8$). In addition, additional minor compounds were also found (including haematite, coesite (SiO_2), ilmenite ($Fe^{2+}Ti^{4+}O_3$), barite and siderite), thus revealing a higher mineralogical complexity.

On the one hand, the discrimination of shocked quartz has a high scientific relevance for the forthcoming ExoMars mission, as it proves that the RLS could be able to identify the mineralogical evidence necessary to confirm the impact origin of a crater. As shown in Fig. 8, impact-induced shocked quartz was recognizable by the shifting of the main peak towards lower wavelengths [138]. The analysed quartz crystals presented different degrees of metamorphism: by increasing the shift of the main peak of quartz, the main Raman band became broader and asymmetrical.

On the other hand, barite (main peaks at 460, 617, 989 and 1144 cm^{-1}) and siderite (main peaks at 287 and 1090 cm^{-1}) were detected as minor phases (Fig. 9). Knowing that the formation of these mineral phases can occur under hydrothermal conditions [134,139], their detection can be seen as a mineralogical clue that could be used to detect potential postimpact hydrothermal systems. The identification of similar alteration features on Martian rocks would have a strong astrobiological relevance, as hydrothermal systems provide the chemical energy needed to sustain the metabolism of microbial forms of life [140].

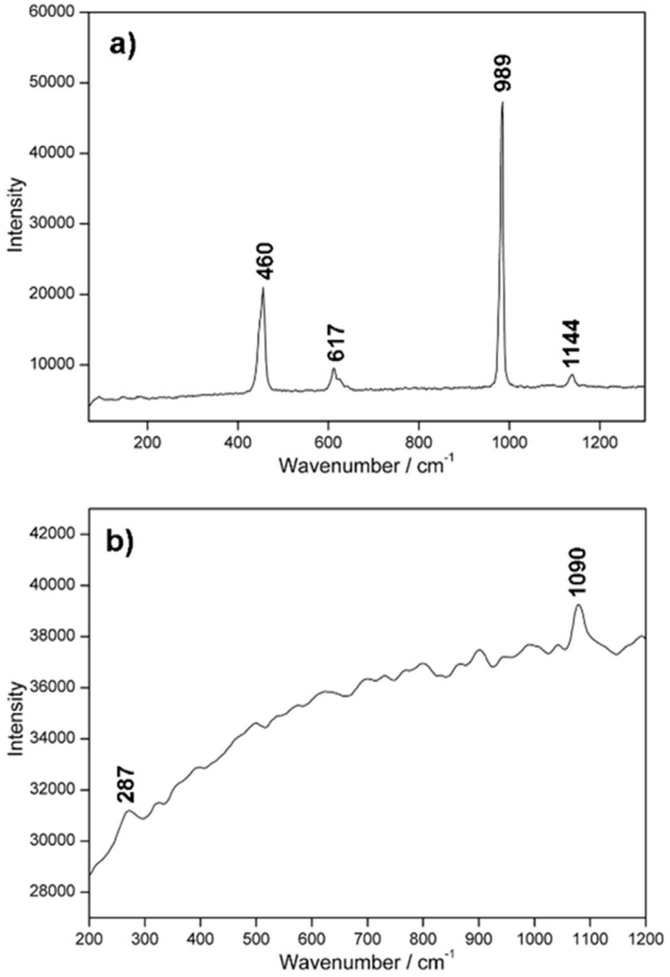

Fig. 9. Characteristic Raman spectra of barite (a) and siderite (b) collected from CBIS breccia samples using RLS-Sim.

On the whole, the analytical study of the CBIS as a terrestrial analogue site clearly demonstrates that Raman spectroscopy could play a key role in forthcoming planetary exploration missions, suggesting that the RLS ExoMars system could potentially be able to identify the mineralogical clues necessary to confirm the presence of wet-target impact craters on Mars.

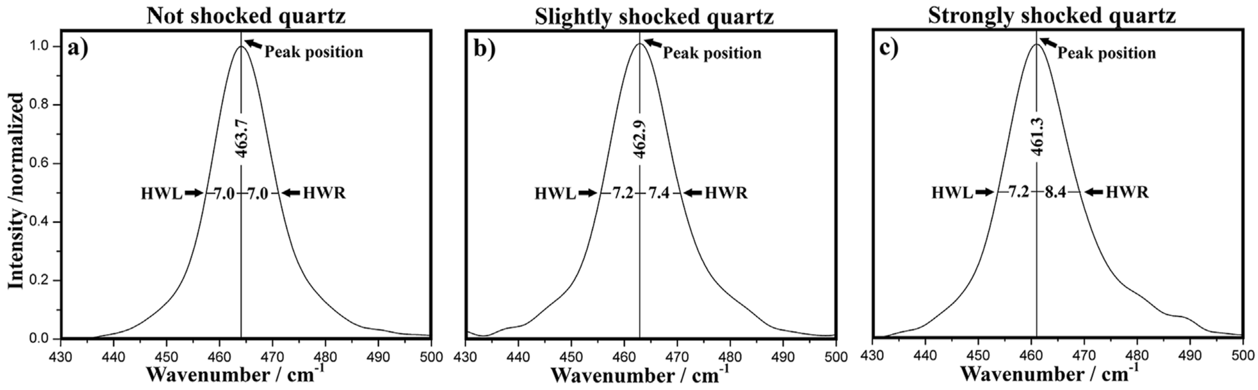

Fig. 8. Calculation of the main band parameter from characteristic spectra of a) not shocked, b) slightly shocked, and c) strongly shocked quartz (from Veneranda et al., 2019 [29]).

2.7. El Soplao Cave (Spain)

Based on the detailed analysis of high-resolution images collected from orbit, recent studies have indicated the presence of basaltic caves and lava tubes beneath the surface of Mars [141,142]. This discovery increased the interest of the scientific community in the analysis of terrestrial caves as potential analogue sites for astrobiological studies. Indeed, caves ensure thermal stability and protection from UV radiation. This, together with the potential preservation of high humidity levels, makes Martian caves an optimal site to look for microbial forms of life [142]. Although the exploration of caves has not been defined as a scientific objective of Mars 2020 and ExoMars rovers, the analytical study of terrestrial analogues is necessary to develop and optimize analytical procedures to implement for future exploration missions (in particular those paving the way for human exploration). In this sense, an increasing number of scientific articles can be found in the literature on this topic [143,144].

Among the terrestrial sites considered very interesting analogues for potential extraterrestrial contexts, El Soplao Cave (Cantabria, Spain) stands out for having critical relevance for astrobiological studies [145,146].

In situ spectroscopic and diffractometric analyses (Fig. 10), combined with complementary laboratory studies of selected samples, were carried out to determine the ancient climate of the cave and to determine its evolution over time. For example, the formation of the characteristic Mg—Fe crusts found in El Soplao Cave has been interpreted as the result of dry precipitation of metallic ions lixiviated from detrital material accumulated during prior turbulent flooding events [145]. Further information regarding speleothem genesis and the climate evolution of this cave is provided elsewhere [146,147].

Beyond paleoclimatic studies, the high astrobiological relevance of El Soplao Cave is driven by the recent discovery of stromatolite formations [148]. Stromatolites are laminated sedimentary structures whose formation is mediated by microbial activity and represent some of the most ancient evidence of life on Earth [149,150]. Composed of alternating layers of sediments and organic matter, the analytical study of potential stromatolite formations on Mars has been established as a scientific target of primary importance for the identification of life traces. Therefore, numerous studies have recently focused on the study of terrestrial stromatolites by means of analytical instruments relevant for space exploration [151–154]. Compared with other terrestrial analogue sites, El Soplao Cave provides the first reported case of stromatolite formation occurring in the total absence of light, thus mediated by the biogenic activity of chemolithotrophic bacteria [155,156]. Considering the astrobiological relevance of this discovery, spectroscopic analysis of stromatolite samples was carried out to disclose their mineralogical composition [157,158]. In situ and laboratory Raman investigations helped detect Mn-oxide minerals, such as birnessite ($Mn_2O_4 \cdot 1.5H_2O$), superposing broad bands between 550 and 650 cm^{-1} [159] (Fig. 11) and hausmannite (Mn_3O_4,

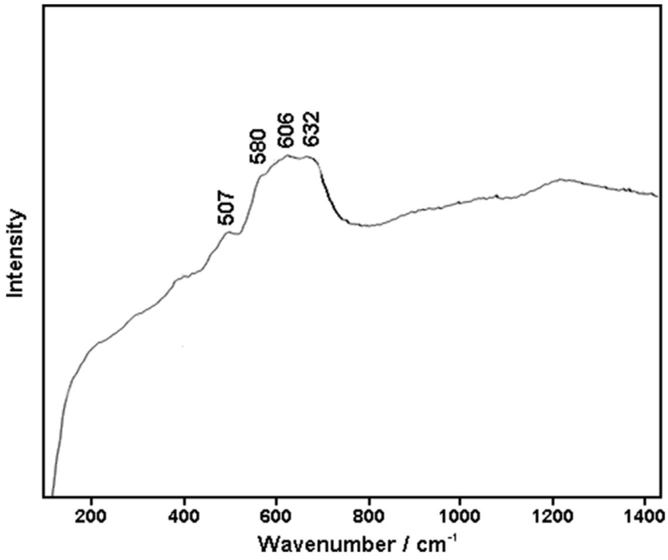

Fig. 11. Raman spectrum of birnessite ($Mn_2O_4 \cdot 1.5H_2O$), collected by means of a laboratory system from a stromatolite sample collected at El Soplao Cave. Compared with reference standards [159,161], the Raman spectrum displays a stronger contribution of the deconvoluted band located at 606 cm^{-1}.

Fig. 10. In situ Raman characterization of speleothems found at El Soplao Cave.

main peak at 659 cm^{-1} together with weak signals between 290 and 380 cm^{-1} [160]), as major components of these biogenic structures, together with additional minor phases [155]. Thus, spectroscopic analysis of El Soplao helped to deepen the knowledge regarding biogeochemical processes occurring in caves and underlined the importance of including Raman spectroscopy in the development of astrobiologically relevant exploration strategies.

3. Planetary mission simulations

Analytical campaigns carried out at terrestrial analogue sites offer the opportunity to reliably evaluate the potential outcome of scientific instruments developed in the framework of planetary exploration. However, real space missions present additional challenges that need to be faced. For example, one of the biggest concerns is coordinating the navigation of the rover by relying only on remotely collected data and adapting its route to unanticipated events that could endanger its safety. In addition, it is necessary to refine the coordinated work of the different teams controlling the analytical instruments onboard the rover, thus maximizing the science return of the mission. Knowing that mistakes during real planetary missions can be very costly, the involved personnel need to be trained in the coordinated management of navigation and scientific instruments. In the case of analytical systems, it is also necessary to develop and test tailored protocols and tools that could help minimize human intervention. Therefore, instrument development occurs together with the realization of mission trials where team members can train on how to face the abovementioned challenges. In this framework, the ERICA research group joined multiple mission simulations, the most important of which are described in the following section.

3.1. Arctic Mars analogue svalbard expedition, AMASE (svalbard, Norway)

Svalbard is an archipelago of small islands located 1000 km from the North Pole. The mineralogical variability of the islands, combined with the extreme environmental conditions they present, make this an ideal area where to test instruments for planetary exploration [162]. Since the beginning of 2000, Svalbard periodically hosts crews of researchers from different disciplines to collaborate to carry out mission simulations named the Artic Mars Analogue Svalbard Expedition (AMASE). As explained elsewhere, AMASE expeditions are meant to 1) test the hardware robustness and analytical performance of prototype instruments for space exploration under extreme cold conditions [164,165], 2) conduct astrobiological-relevant experiments [166], and 3) refine analytical procedures and sample collection protocols [167].

As part of the AMASE team, from 2007 to 2011, the ERICA group carried out Martian-like analytical experiments by combining in situ analysis with the detailed study of samples in the laboratory. The research activities were aimed at pursuing the two objectives summarized below.

- *Testing cutting-edge spectroscopic technologies*

The first expeditions gave the opportunity to operate, in a representative Martian analogue site, novel spectroscopic prototypes for their potential use in surface planetary missions. In detail, from 2007 to 2009, the ERICA group joined the AMASE scientist crews (including researchers from the University of Leeds, Cornell University, Caltech, NASA and ESA, among others) to test laboratory-assembled remote Raman and Raman-LIBS systems. As the results of conceptual and technological developments started in 2004, these instruments were used for the elemental and molecular characterization of remote targets.

Beyond confirming the suitability of remote LIBS analysis, AMASE trials helped prove the feasibility of remote Raman detection of molecular compounds from up to 150 metres of distance [168]. Together with the technological advances presented by other research groups [169], the results achieved in these trials contributed to settling the conceptual knowledge necessary for the design and development of remote Raman-LIBS instruments for space exploration, as is the case of the SuperCam instrument onboard the NASA/Perseverance rover [170].

- *Performing research of high astrobiological relevance*

Belonging to the Svalbard Archipelago, Spitsbergen Island presents carbonate precipitation on basaltic rocks that has been related to hydrothermal processes that occurred during the Pleistocene when the Sverrefjell Volcano erupted through a layer of ice [171]. Considering that 1) the coexistence of liquid water and warm temperature favour the proliferation of microbial life [172] and 2) the carbonate deposits found at Gusev Crater by the Mars Exploration Rover Spirit [173] were interpreted as the result of hydrothermal processes having strong analogies with the one described above [174], the AMASE expeditions served to carry out analytical experiments of high astrobiological relevance.

As presented by Rull et al. (2011) [168], a combined Raman-LIBS system was successfully used to investigate basaltic rocks and carbonate precipitation from a distance of 15 metres. Focusing on molecular results, Raman spectra successfully identified the main mineral phases of the volcanic targets (pyroxene and feldspars, among others) and detected mixtures of carbonate minerals (calcite, dolomite and magnesite $MgCO_3$). Based on in situ analysis, geological samples were also collected for analysis in the laboratory. Here, XRD data were compared with the results gathered from the use of Raman simulators that were assembled to provide spectra qualitatively comparable to those expected by the RLS system onboard the ExoMars mission. In addition to detecting the main mineral phases, in situ Raman analysis of altered rocks from Svalbard enabled us to identify the vibrational features of beta-carotene (Fig. 12), thus further confirming that the RLS system could potentially detect organic compounds on Mars.

Beyond Mars-related studies, natural ice icebergs were also studied to assess the potentiality of remote Raman spectrometers for the in situ exploration of icy extraterrestrial bodies, as is the case of the Europa Lander mission proposed by NASA (according to the updated Europa Lander concept, Raman spectroscopy was selected as one of the techniques necessary to meet the science goals outlined for the mission [25]). In this context, the results presented by Rull et al. (2011) [175] proved that Raman remote systems can be used to analyse icy targets, allowing the detection of spectral changes that can be related to structural modifications induced by the condition of ice formation (e.g., temperature and pressure). Indeed, as shown in Fig. 13, the intensity of the Raman spectra proved to be affected by the transparency of the targeted ice [175].

3.2. ExoMars-like Field Testing, ExoFiT (tabernas, Spain)

The ExoMars-like Field Testing (ExoFiT) trials [176] were organized by AIRBUS and ESA to train the ExoMars operation team to manage the engineering and scientific challenges arising from the remote control of the Rosalind Franklin rover soon to be operating at Oxia Planum. The first trial, carried out in 2018, consisted of manoeuvring an emulator of the Rosalind Franklin rover in the Taberna Desert (Spain) by following the instructions provided by the Remote Control Centre (RCC) team that operated the simulation (from UK) by only relying on the data returned by its panoramic instruments.

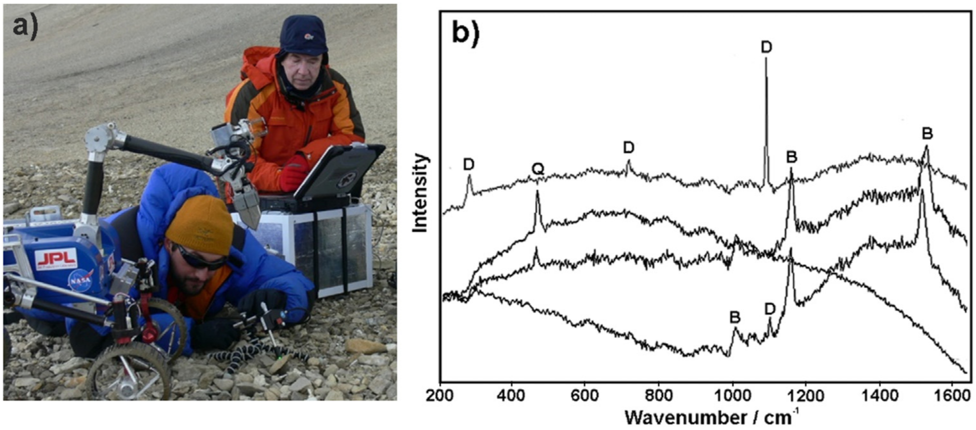

Fig. 12. a) In situ Raman investigation of altered carbonates found on Svalbard in collaboration with the microimager located on the JPL rover prototype. b) Raman spectra obtained during in situ analysis (D = dolomite, Q = quartz, and B = beta-carotene). (Picture credits JPL-UVA-FR).

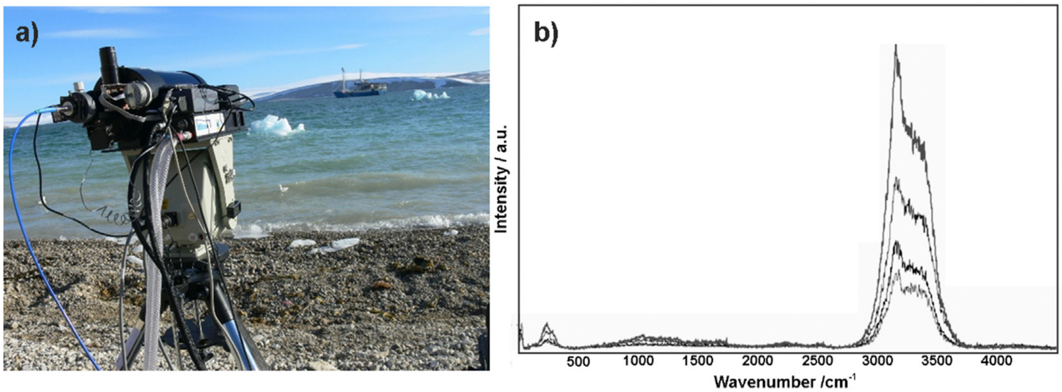

Fig. 13. a) Remote Raman analysis of icebergs. b) Raman spectra of translucent (high intensity) and opaque (low intensity) ice targets collected at a 40 m distance (from Rull et al. [175]).

During 9 Martian sols, a broad range of rover activities were simulated. In detail, panoramic cameras were used to investigate the surroundings. After descending the landing platform, the rover emulator was driven towards areas of high scientific interest. A combination of surface (CLUPI [177]) and subsurface (WISDOM radar [9]) investigations was then performed to identify the optimal drilling sites. After drilling, subsoil samples were crushed and analysed by the RLS team, which was represented by researchers and technical personnel from the University of Valladolid (UVa) and INTA.

As seen in Fig. 14, the location selected for the trial was a flat area covered by sand-silt deposits with sporadic boulders and an elongated multilayered ridge outcropping at the centre of the plain.

In addition to presenting a landscape very similar to what Rosalind Franklin is expected to find at the landing site, two additional characteristics made the selected area a perfect analogue site where to test the analytical tools of the rover. Similar to the fine-clay deposit covering 80% of the landing ellipse, the particle size distribution of the regolith ground found in the Tabernas Desert is dominated by silt-clay particles [178–180]. Knowing that the analysis of fine-grained samples causes an increase in the background level and peak width, together with a decrease in the signal-to-noise ratio (SNR) [94], this trial served to evaluate to what extent sample granulometry could affect the quality of RLS spectra. Furthermore, previous studies demonstrated that despite the arid environment, the surface of the Tabernas Desert is characterized by the proliferation of microorganisms [179], which makes it the perfect site where to test the ability of Raman spectrometers to detect the presence of biomarkers.

As explained in the introduction section, the fulfilment of the ExoMars main objective (to find potential biosignatures on Mars) will strongly rely on spectroscopic investigations of geological samples performed by MicrOmega and RLS spectroscopic systems. To simulate RLS operations at the analogue site, Raman analysis was carried out by means of the RAD-1 system (Raman Demonstrator), which is a portable spectrometer that follows the same geometrical concept and spectral characteristics of the RLS-FM. Additional in situ analyses were performed using the RLS qualification model (EQM-2), a replicate of the RLS-FM that has been assembled to demonstrate the ability of the instrument to fulfil the scientific capabilities required by the mission [12]. RAD-1 and EQM-2 data were then complemented by additional laboratory analysis. In this sense, the RLS-Sim was used to replicate the complete analytical cycle (39 spectra per sample) established for RLS during nominal operation on Mars. The entire set of Raman data was finally compared with the mineralogical results gathered from the diffractometric analysis of powdered samples, which was carried out through Terra (from Olympus), an XRD system that made use of the same technology developed by NASA for the MSL/Curiosity rover mission (CheMin instrument) [181].

- Raman analysis of drilled cores

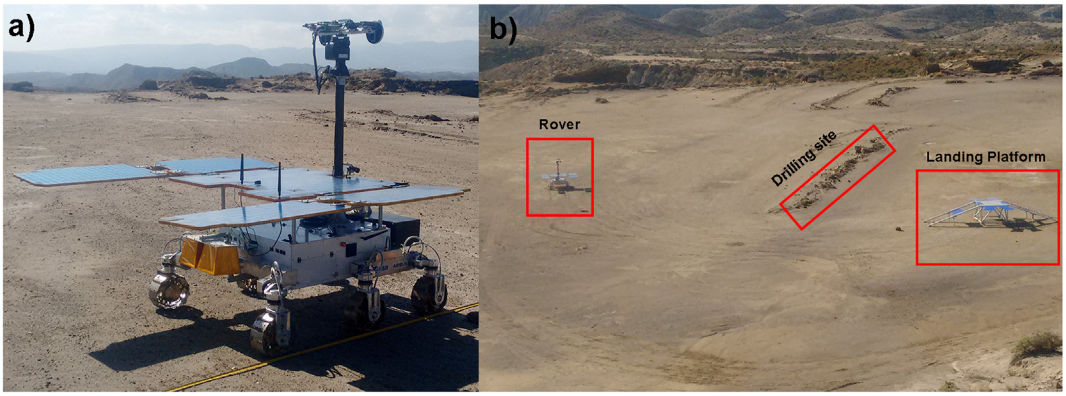

Fig. 14. a) Close-up image of the Rosalind Franklin rover's emulator (Charlie) used during ExoFiT trials. b) Panoramic view of the area selected for the mission simulation.

During the mission simulation operation cycle, two cores were drilled (TDC1 and TDC2). Prior to analysis, geological samples were crushed and sieved to replicate the granulometry of the powdered material produced by the ExoMars crusher. After flattening, the RAD-1 and EQM-2 systems were used to analyse between 6 and 8 spots per sample, with just a small fraction of the dataset the RLS gathered during nominal operation on Mars (20–39 analysis) [182].

Through RAD-1 analysis, quartz (main peak at 464 cm^{-1}) was found to be the main mineralogical phase in both drilled cores. In addition, peaks of medium intensity from calcite (281, 711 and 1086 cm^{-1}) and rutile (146 cm^{-1}) were also observed. The same samples were further characterized at the site by means of the RLS-EQM2 system, which confirmed the detection of quartz and calcite in both drilled cores (Fig. 15) [35]. Thus, the in situ Raman results fit very well with the mineralogical studies previously performed in this area, which confirmed that these mineral compounds are among the main components of the soil in the Tabernas Desert [183].

With regard to laboratory studies, powdered samples were placed on a replicate of the *ExoMars* refillable sample holder, and after flattening, point-by-point 39 spectra were automatically collected by the RLS-Sim. In addition to confirming the detection of the abovementioned minerals, the higher number of spectra per sample enabled the detection of additional minor compounds, such as muscovite (264, 402, 695 and 3625 cm^{-1}), anatase (240, 445 and 610 cm^{-1}) and plagioclase (165, 285, 407, 478, 508, 769, 805 and 1100 cm^{-1}). The main Raman spectra collected in the laboratory are provided in a dedicated manuscript [184]. Among them, the detection of muscovite is particularly interesting, as the detection (by RLS and MicrOmega) and further analysis (by MOMA) of phyllosilicate minerals has been established as the highest priority targets for fulfilment of the astrobiological goals of the ExoMars 2022 mission. Overall, the Raman results fit very well with the X-ray diffractograms, which detected quartz, calcite and phyllosilicate (chlorite and muscovite) as the main mineral phases of both drilled cores [184].

In addition to the characterization of inorganic compounds, Raman analysis of subsoil samples enabled the identification of vibrational features potentially derived from organic functional groups (893, 1300, 1330, 1565, 2370, 2480 and 2570 cm^{-1}). Knowing that the Tabernas Desert has many mineralogical and environmental similarities with Oxia Planum, the detection of organics in both drilled cores is a very promising result, as it proves that the RLS system could be able to detect crucial analytical clues for the selection of potential biomarker-bearing mineralogical samples on Mars.

3.3. *ExoMars-like Field Testing, ExoFiT (Atacama Desert, Chile)*

To further train the ExoMars team in enhancing collaboration practices between instrument working groups, a second ExoFiT trial was organized in the Atacama Desert (Chile, February 2019). As in the case of the previous ExoFiT simulation, the Charlie rover performed complex sequences of scientific operations by following the ExoMars Reference Surface Mission (RSM) [185]. As seen in Fig. 16, the Martian landscape of this region (combined with the hyperarid climate) makes this the ideal location where to test rovers [186–188] and analytical systems [189–191] for Martian exploration.

The site selected for the ExoFit trial is located in the region of Antofagasta, approximately 11 km west of the ESO Paranal observatory. According to previous studies, the mineralogy of the selected area is characterized by granodiorites, andesite and gabbro rocks [192], while phyllosilicates, iron oxides and evaporitic minerals can be found as alteration products. This region displays strong levels of thermal excursion and surface ultraviolet (UV) irradiance (>1100 W/m^2) [193], together with extremely low values of humidity (5–20%) and rainfall (an average of 10 mm per year) [194], which makes it one of the best terrestrial analogue sites to verify the capability of analytical instruments developed for astrobiological-related studies to detect organics. Indeed, it is well known that extremophile microorganisms proliferate in the subsurface of the Atacama Desert by relying on analogue metabolic mechanisms similar to those that may occur or may have occurred on Mars [195–197]· Therefore, Vitek and coworkers performed several in situ analyses to assess the capability of Raman spectroscopy to detect organic compounds in Atacama geological samples, obtaining encouraging results [198–200].

Taking a step forward in this field of study, during the second ExoFiT trial, the RLS science team was able to carry out Raman studies very closely following the real operation protocol established for the ExoMars mission. For that, the portable RAD-1 system used in Chile presented numerous hardware and software updates that allowed us to more faithfully replicate RLS-FM operations on Mars.

- Raman analysis of drilled cores

During the mission simulation, two cores were also drilled. In this case, each core (DC1 and DC2) was divided into two parts (upper UP and lower LP, respectively); therefore, the multi-analytical study was carried out on a total of 4 samples, which were previously crushed and sieved to replicate the granulometry produced by the ExoMars crusher. For the case of the Tabernas Desert,

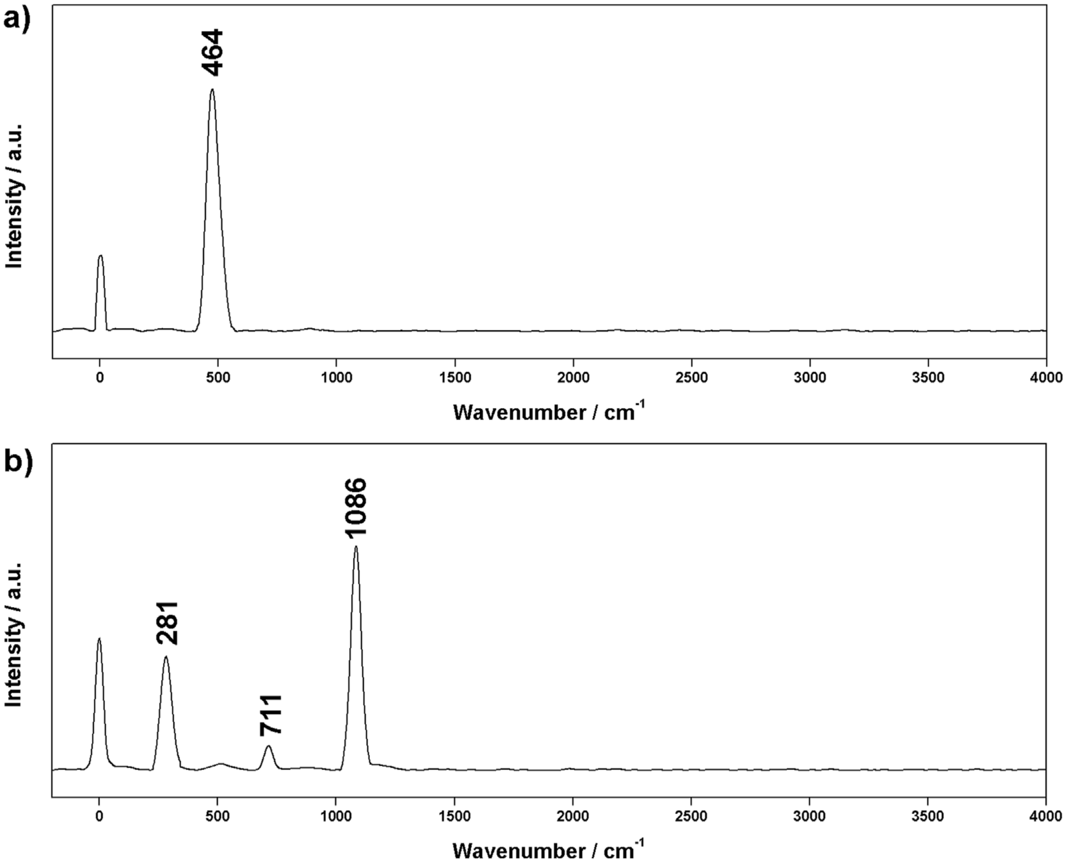

Fig. 15. Representative Raman spectra of quartz (a) and calcite (b) collected at the site by means of the EQM-2 system from the study of the TDC1 drilled core. The presented spectra were submitted to baseline correction by using the dedicated spectral tool of IDAT/SpectPro software (from Veneranda et al. [184]).

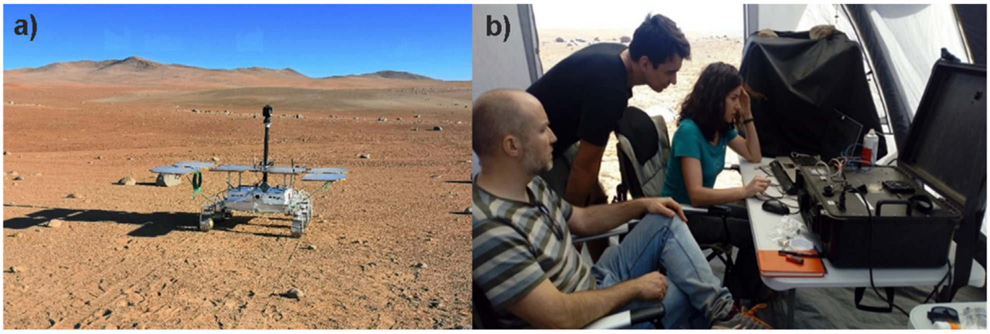

Fig. 16. a) Panoramic view of the Rosalind Franklin rover's simulator (Charlie) operating in the Atacama Desert (Chile). b) The RAD-1 prototype obtaining Raman spectra from the powdered core samples.

the strict time constraint imposed by the real mission simulation allowed only between 6 and 8 spots per sample to be analysed in situ.

As seen in Table 1, the in situ Raman analysis allowed us to identify feldspar in both ADC1 samples, while a more complex mineralogy was detected in the ADC2 core. In detail, the characteristic peaks of quartz and calcite were identified in the ADC2-UP sample, whereas quartz, feldspar, amphibole, and phyllosilicate were observed in ADC2-LP. Regarding laboratory analysis, the 39 spectra per sample analysed by means of the RLS-Sims proved that by increasing the number of spots of analysis, a more detailed comprehension of the mineralogical composition of the material under study can be reached. Therefore, quartz, feldspar, anatase and phyllosilicate were detected in all samples [35]. Depending on the sample under analysis, amphibole and phyllosilicate were also detected together with evaporitic minerals (gypsum and calcite, see Table 1). On the whole, the mineralogical results obtained from the interpretation of Raman datasets fit very well the information extrapolated from X-ray diffractograms [35].

As seen in Table 1, spectroscopic analysis also detected vibrational peaks that can be assigned organic compounds. Specifically, peaks at 1340, 2190, 2250, 2800 and 2850 cm^{-1} (among others) were detected in the two ADC1 samples by RLS-Sim, while in the ADC2-UP sample, they were only detected by in situ analysis with the RAD-1 instrument [35]. Similar samples on Mars would be considered optimal candidates for MOMA analysis, as this

Table 1
Comparison of Raman (RLS-Sim and RAD1) and XRD results obtained from the study of Atacama core samples.

Sample	quartz	feldspar	anatase	amphibole	phyllosilicate	gypsum	anhydrite	calcite	haematite	organics
ADC2-UP (0–15 cm)	x ◊ o	x o	x o	x o	x o	x o	o	x ◊o		◊
ADC2LP (15–30 cm)	x ◊ o	x ◊ o	x	◊	x ◊ o			x o		
ADC1-UP (0–15 cm)	x o	x ◊ o	x	x o	x o			x		x
ADC1-LP (15–30 cm)	x o	x ◊ o	x		x o				o	x

x = RLS ExoMars Simulator, ◊ = Rad1, o = XRD.

instrument would be able to assess their biotic or abiotic origin.

On the one hand, the detection of organic features proves the capability of the RLS to support MOMA analysis by optimizing sample selection. On the other hand, considering that organics in sample ADC2-UP were only detected by RAD-1 proves that the 39 spots analysed by the RLS-Sim were not sufficient to ensure the detection of trace compounds potentially preserved within the mineralogical matrix. Therefore, this test was extremely useful for the RLS team, as it suggests that more than one cycle of analysis per sample should be considered when subsoil materials of high scientific interest (e.g., rich in potential biomarker-bearing minerals, as is the case with phyllosilicates) will be collected by the Rosalind Franklin rover on Mars.

4. Discussion

Placing Raman spectroscopy at the centre of this discussion, the first part of this section evaluates the pros and cons expected by the application of this technique in planetary missions. To do so, the potential scientific outcome of Raman systems is compared with that provided by molecular and mineralogical techniques already operating on Mars. Starting with Mössbauer spectroscopy, it is well known that the analytical systems onboard both Spirit and Opportunity Mars Exploration Rovers enabled us to deeply probe the composition of Fe-bearing materials found at the landing sites [7]. Mössbauer analysis of Martian rocks and soils identified a large number of new mineral phases, thus providing information of key importance to reconstruct the geological and mineralogical evolution of the planet. For example, the detection of alunite and jarosite minerals shed light on the past occurrence of superficial acidic waters at the surface of Mars, which is an extremely important discovery for the field of astrobiology research [8]. Although Raman is sensitive to a great variety of iron oxides, hydroxides and additional Fe-bearing phases, Mössbauer spectroscopy often provides more detailed information about the electronic structure and geometry of the investigated molecule. However, the ability of the Mössbauer technique to accurately analyse Fe-bearing minerals is partially countered by the inability to detect Fe-free minerals. In this sense, the main advantage of Raman spectroscopy is the ability to detect any mineral phase that undergoes a change in molecular polarizability as it vibrates, regardless of its elemental composition. The combined Mössbauer-Raman investigations carried out at the JHS, Rio Tinto and Tenerife terrestrial analogue sites demonstrated the complementarity between the two techniques. In light of current and future missions, the greater versatility of Raman spectroscopy can be particularly useful when investigating heterogeneous geological environments [64,99]. This is the case for the Mars2020 rover, which, after analysing Jezero crater bedrocks and phyllosilicate-bearing deposits, will target the Mg-rich carbonate units detected at the crater rim [16].

In addition to Mössbauer spectroscopy, much of the current knowledge about Martian mineralogy at a micrometric scale is due to the CheMin XRF-XRD system onboard the Curiosity rover, which has been operating at the Gale crater since 2012 [201]. As it allows the identification of any kind of crystal structure, X-ray diffractometry is the primary method for the mineralogical characterization of rocks and soils. Despite being particularly suitable for planetary exploration missions, the detection limit of the technique allows minor and trace compounds to often pass undetected. In the case of CheMin, the miniaturization of the components, the simplified geometry and the low energy consumption requirements causes the estimated detection limit of the instrument to be approximately 3% [130,202,203].

By investigating the selected target at a micrometric scale, Raman spectroscopy is capable of punctually detecting minor compounds that are below the detection limit of XRD. The numerous cases of study in which terrestrial analogue materials have been characterized by both diffractometric and Raman instruments helped demonstrate that Raman spectroscopy is often capable of identifying additional minor phases provided that the number of observed spots on the sample is sufficient. The detection of minor compounds is relevant, as they can supply very valuable information about the formation and/or alteration processes of the geological sample under analysis. Knowing the RLS system onboard the Rosalind Franklin rover will nominally perform between 20 and 39 point-by-point observations on the sample surface [204], the Raman investigations to be carried out in the framework of the ExoMars mission should allow the identification of both major and minor phases composing Martian rocks and soils. In this sense, the mission simulations carried out in Almeria and Atacama (see Section 3) proved that the higher the number of Raman analyses carried out on a powdered sample is, the greater the probability of completely disclosing its mineralogical heterogeneities. For this reason, when a sample of high scientific-astrobiological interest is processed by the ExoMars analytical payload, running more than one cycle of analysis should be considered. Another observed difference from XRD analysis is the difficulty of identifying amorphous systems with this last technique [205]. Raman spectroscopy can handle these materials, although important difficulties arise when fluorescence appears, which is very often present in clay minerals.

Furthermore, compared with Mössbauer spectroscopy and XRD, the greater advantage of Raman spectroscopy is the ability to additionally detect organic compounds (e.g., biomarkers), which makes it suitable for astrobiological studies. Indeed, we presented numerous cases in which Raman prototypes simulating the scientific capability of RLS and SuperCam enabled the detection of organic features from terrestrial analogue samples, as was the case in the Barberton, Rio Tinto, Svalbard and Atacama samples. This characteristic makes Raman spectroscopy particularly suitable for the fulfilment of Mars2020 and ExoMars missions, whose main objective is to determine if life ever took hold on Mars [16,95].

As the analytical investigation of unknown mineralogical samples can benefit from the combined use of multiple analytical techniques, the scientific outcome of Raman analysis can be optimized by complementary molecular and/or elemental data. In this sense, both Mars 2020 and ExoMars missions will provide the opportunity to investigate the same target with complementary analytical systems. As the subsoil samples collected by the ExoMars rover will be characterized by both Raman and NIR spectrometers, many of the studies presented in Section 2 had the purpose of determining the advantages provided by the combined use of these two techniques. For example, the multianalytical investigation of terrestrial analogue samples from Rio Tinto, LOC and CBIS proves the different sensitivity of the two spectroscopic systems towards the detection of specific mineral phases, making the mineralogical results obtained from the interpretation of both Raman and NIR data more complete than those achieved by using only one of the two instruments. In the case of the future ExoMars mission, it should be highlighted that the MicrOmega system will map areas of 5×5 mm^2 of the powdered samples with a spatial sampling of 20 μm per pixel [13]. This offers a great advantage for Raman investigations since the raster of spots analysed by the RLS can be selected by taking into account NIR results [206].

Looking at the Mars 2020 mission, remote (SuperCam [18]) and proximity (Sherloc [21]) Raman analyses the Perseverance rover is performing on Mars are supported by the elemental information provided by LIBS and XRF analysis, respectively. In the case of the SuperCam analytical suite, additional spectroscopic information can be gathered in VISIR and fluorescence modes. As the ERICA research group took part in the development of the SuperCam instrument [17], several terrestrial analogue materials were investigated by hybrid Raman-LIBS remote systems. Technically, the analysis of terrestrial analogues proved that combined spectroscopic instrumentations provide great advantages in terms of mass and volume requirements, which are key parameters to consider in the development of space exploration instruments. Analytically, hybrid Raman-LIBS systems afford advantages, as both molecular and elemental data can be gathered from the same spot of interest. As described in the examples provided in Section 2, remote Raman-LIBS analysis helps to optimize the geochemical and mineralogical characterization of the samples under analysis. Therefore, the combination of the two spectroscopic methods will help gather key information for the selection of soil and rock samples to be returned to Earth [207].

From a broader perspective, this review highlights that the analysis of terrestrial analogue materials represents a cornerstone tool to constrain and predict the potential scientific outcome of analytical instruments for planetary exploration. In this sense, the ERICA research group is collaborating with an international consortium in the development of the Planetary Terrestrial Analogue Library (PTAL). Funded by the European Union's Horizon 2020 research and innovation programme, the PTAL project aims at supporting forthcoming space missions to Mars and other extraterrestrial bodies by providing the scientific community with XRD, LIBS, Raman and NIR data collected by over 100 different terrestrial analogue materials [208–210]. In addition to PTAL, the research group is also building a novel database of pure mineral phases that are relevant for Mars exploration. Called Analytical Database of Martian Minerals (ADaMM), a collection of more than 300 different mineral phases is being analysed by combining the use of diffractometric and spectroscopic instruments providing results qualitatively comparable to the analytical systems (soon) operating on Mars [212]. In addition to analogue/mineral databases, the ERICA research group aims to additionally support rover missions through the development of tailored software that is meant to facilitate the analysis and interpretation of the spectroscopic data gathered on Mars. For example, through the PTAL and ADaMM platforms, a downloadable version of IDAT/SpectPro software will be provided to the scientific community [36,213]. Developed in the framework of the ExoMars mission to receive, decodify, calibrate and verify the telemetries generated by the RLS on Mars, further details about this novel analytical tool will be provided in a dedicated manuscript.

5. Perspectives

In light of the forthcoming deployment of novel spectroscopic techniques on Mars, the analytical study of terrestrial analogue sites and materials gains importance. As summarized in Section 2, the spectroscopic-based characterization of representative terrestrial analogues of Martian geological contexts helps to shed light on the potential scientific outcome that could derive from the operation of Raman systems on Mars. In detail, the mentioned studies confirm the capability of this spectroscopic technique to gather mineralogical data qualitatively comparable to those provided by further analytical techniques that have been successfully employed on Mars in previous rover missions (e.g., Mössbauer and X-ray diffractometry). Compared with these, Raman spectrometers proved to effectively detect organics within analogue geological samples, thus confirming the potential key role this technique could play in the fulfilment of the main objective of both ExoMars and Mars 2020 missions: to detect clues of past or present life on Mars. Furthermore, the multianalytical investigation of terrestrial analogue materials confirmed the complementarity of Raman spectroscopy with NIR and LIBS systems, thus providing crucial information for the proper interpretation of the data returned by the Perseverance and Rosalind Franklin rovers. In addition to analysing the scientific capabilities of spectroscopic instruments, mission simulations described in Section 3 offered the opportunity to optimize the synergistic collaboration between instrument working groups and to practice with real mission issues. While confirming the complementarity between spectroscopic techniques, the experience gained by participating in mission simulations helped refine the analytical protocols to follow during nominal operations on Mars.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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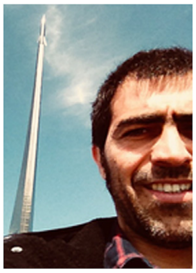


Andoni Gaizka Moral: He currently works at Instituto Nacional de Técnica Aerospacial (Spain). Main research in Astrobiology, Aerospace Engineering and Optics Engineering. Project Manager of the 'Raman Laser Spectrometer' (RLS) Instrument for ESA's ExoMars 2020 Rover'. Project Manager of the 'Raman Laser Assembly' (RLA) of the Raman Instrument of the JAXA-DLR MMX mission. Project Manager of the 'Signs Of LIfe Detection' (SOLID) instrument for the NASA Icebreaker Mission Proposal. He co-authored 16 articles in SCI journals and more than 20 conference abstracts and book chapters.

J. Aurelio Sanz-Arranz: He is a member of the ERICA research group from the University of Valladolid.He is collaborating in multiple projects related to planetary exploration and provides analytical support to research lines developed in the framework of the ESA/ExoMars and NASA/Mars 2020 missions.As "Raman craftsman" specialist his professional activity is principally devoted to Raman analysis of many kind of organic and inorganic compounds, including minerals, terrestrial analogues and materials of cultural interest.He co-authored 34 SCI papers, 6 papers in no-SCI journals, 5 book chapters, and 102 conference abstracts.

Elena Charro: She obtained her Ph.D. in Physical Chemistry from the University of Valladolid (UVa, Spain) in 1993 in the field of microwave spectroscopy and was appointed Postdoctoral Fellow in the Department of Applied Mathematics of Queen's University of Belfast (UK) in 1998 working in the field of photoionization process in species of astrophysical interest and fusion plasmas. In 2018 she became Full Professor at UVa. Her main research topics are: Microwave spectroscopy, Atomic Spectra Calculations in Fusion Plasma of Astrophysical Interest (30 publications), Determination of Natural Radionuclides in Soils and Soil Organic Carbon studies.

Fernando Rull: He is the founder and coordinator of Erica Research Group. Since 1989 Fernando Rull is Chair Professor of Crystallography and Mineralogy in the University of Valladolid. He has over 20 years of experience in the development of spectroscopic instruments and in their application to the study of terrestrial analogue materials. He co-authored over 240 papers in SCI journals and more than 150 conference abstracts. Currently Fernando Rull is PI of the Raman Laser Spectrometer (RLS) of the ExoMars mission, and co-PI of SuperCam and RAX instruments for the Mars2020 and MMX missions (to Mars and Phobos, respectively).

Guillermo Lopez-Reyes: Postdoctoral researcher at the University of Valladolid, he works on the development of spectroscopic instruments and data analysis techniques for planetary exploration missions. He is the Science Operations responsible of the RLS Raman spectrometer onboard the ESA ExoMars rover. He is also collaborator of the SuperCam Raman/LIBS spectrometer on NASA Mars 2020 and member of the Raman spectrometer RAX Scientific Team on JAXA MMX. He has 39 indexed publications, 120+ contributions to International conferences; 200+ documents and technical reports for the more than 15 projects in which he has participated.

Jesus Medina: PhD. in Chemistry, and Professor of the Condensed Matter Physics, Crystallography and Mineralogy Department of the University of Valladolid. His major research areas are mineralogy and planetary science. He has been collaborating in the development of spectroscopic instrumentation for planetary exploration and in the analytical characterization of terrestrial analogue sites. Member of the ERICA research group, he co-authored over 50 articles in SCI journals and more than 100 conference abstracts.

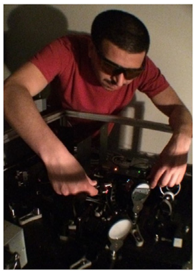
Jesus Saiz: Jesus Saiz is a telecommunications systems technician currently working for the ERICA group from the University of Valladolid. He is the ground software developer of the RLS (Raman Laser Spectrometer) instrument of the ExoMars2022 mission, as well as developer of the PTAL(Planetary Terrestrial Analogues Library) platform of the European Commission project within Horizon 2020 program. He co-authored more than 20 and participated as a speaker at several international conferences and social dissemination activities.

Laura Seoane: She is a space systems engineer at INTA with more than 15 years of experience in satellites and space instruments development. She has been deeply involved in the INTA Small Satellites Program, performing a wide range of activities, from System Engineering to Operations, HW/SW development, and AIV at board, unit and satellite level. During the last six years, she has been mainly focused on the development of the RLS (Raman Laser Spectrometer) instrument for the ExoMars 2022 mission, in charge of the on-board SW and Operations. She co-authored more than 20 publications in peer-reviewed journals and conferences.

Luis Miguel Nieto: He is professor of Theoretical Physics at the University of Valladolid, developing lines of research in Mathematical Physics, such as “Mathematical modeling of graphene and other metamaterials”, “Safe quantum communications” or “Integrability, symmetries and non-linear dynamics of classical and quantum systems”.He has published 125 articles in indexed journals, having participated in 50 research projects. In 2018 he received the Award from the Social Council of the University of Valladolid for all his activity. He is referee of 15 scientific journals and coordinates predoctoral and postdoctoral research activities. He has been Vice Chancellor and currently heads the Department of Theoretical Physics.

Marco Veneranda: With a PhD in analytical chemistry, he works as postdoctoral researcher at the University of Valladolid (UVa). He is directly involved in many research projects related to Mars exploration. As an official member of Operations and Science Support teams of both ESA/ExoMars (RLS) and NASA/Mars 2020 (SuperCam) missions, his current research interests include the spectroscopic analysis of Martian-relevant rocks and the development of novel Raman semi-quantification strategies and Raman-LIBS chemometric tools for Mars exploration. He co-authored over 35 articles in SCI journals and more than 40 conference abstracts.

Carlos Pérez Canora: He currently works at Instituto Nacional de Técnica Aerospacial (Spain) with more than 15 years of experience in space instruments development. Main research in Astrobiology, Aerospace Engineering and Optics Engineering. System Engineering of the ‘Raman Laser Spectrometer’ (RLS) Instrument for ESA's ExoMars 2020 Rover’. System Engineering of the ‘Raman Laser Assembly’ (RLA) of the Raman Instrument of the JAXA-DLR MMX mission. He co-authored 12 articles in SCI journals and more than 20 conference abstracts and book chapters.



Emmanuel Lalla: Emmanuel Lalla is a Research Associate at York University, where he leads and collaborates on science and technology development projects for space exploration. In 2021 he became co-PI of several projects funded by the Canadian Space Agency, where he engages in knowledge transfer activities among research institutions and industry at all technology readiness levels. He received his Ph.D. in Physics from the University of Valladolid, Spain, and worked as a researcher at several institutions in Europe before coming to Canada. He is a research collaborator of the Raman Laser Spectrometer at ExoMars Mission, currently scheduled for flight in 2022.