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The ExoMars Mission: looking at our future and our past!

How did life evolved on Earth? Are we alone in the Universe? To which form of life are we progressing? These are three fundamental questions that humanity has asked itself for millennia. For decades, our closest neighbour, the rocky planet Mars has drawn all attention. It is therefore not surprising that the European Space Agency (ESA), in collaboration with the Russian Space Agency (Roscosmos) has put together an entire exploration program of the red planet: the ExoMars mission. The mission aims at documenting the possibility that life thrived on Mars some 3.5 billion years ago, and why not collect scientific evidence of certain extant form of life are still present in the subsurface of Mars. Here we ambition to sum up the ExoMars program and its scientific objectives. We discuss that, for the first time in the history of remote planetary exploration, the ExoMars rover was designed to include a miniaturised Raman spectrometer to examine materials that will be recovered from the surface down to two meter in the subsurface of Mars. Finally, a few words will be dedicated to our scientific activities in preparation for the ExoMars mission.

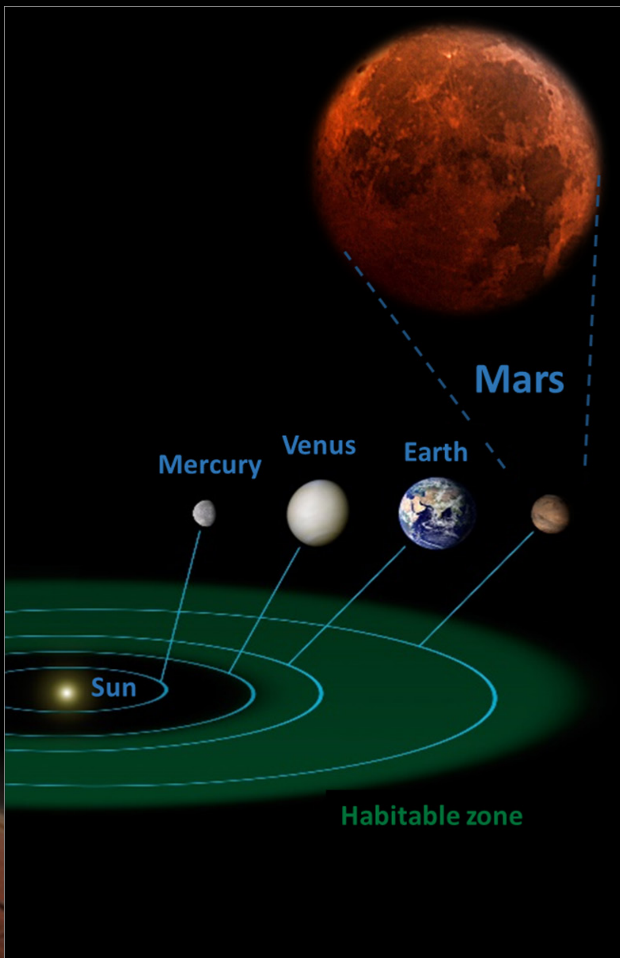

Figure 1. The habitable zone in the solar system (represented in green). The elliptic orbits of the four rocky planets of the solar system, Mercury, Venus, Earth and Mars are represented (adapted from images credited to NASA)

1. Mars, a potential host for life?

To answer to the question of whether Mars (Figure 1) could have hosted life anytime in the past, several mission were sent on Mars to explore the planet. Many were fruitful such as *Mars 3* (1971), *Viking* (1975), *Mars Pathfinder* (1996), *Phoenix* (2007), *Oportunity* and *Spirit* (2007) and finally *Mars Science Laboratory* (in 2011 with the rover *Curiosity* still active on the Martian surface). The missions enable to understand the composition of the atmosphere and the surface of the red planet, confirming that Mars is very similar to Earth in terms of geology [1].

One of the primary target of all missions was to follow the presence of water on Mars (would it be solid, liquid or gaseous), which is essential to the development of life as we understand it. Indeed liquid water is the universal solvent in which the fundamental chemical reactions of life take place, neither too fast nor too slow [2]. In a general point of view, the habitable zone around a star depends on the star itself, particularly on the energy that the star can irradiate to the planet. The habitable zone can be defined as a space where the distance to the star is long enough so that the planet is not too hot, and short enough so that the planet is not too cold (Figure 1) [3]. Actually Mars is located just at the border of the habitable zone of our solar system. In other words, the temperature on Mars would allow the presence of liquid water. For long, the topography suggested that liquid water was once flowing on Mars. In addition, evaporitic sediments (formed through the selective precipitation of minerals partially soluble in water) such as gypsum were identified on Mars [1]. At present, large amount of solid water are stored in the ice caps at both poles of Mars [4]. Recently, stains were observed down cliffs and crater walls, especially when the temperatures are increasing during summer time on Mars, strengthening the hypothesis that liquid water can still run at the surface of Mars, even if it is more likely as brines, which are concentrated salty aqueous solutions [5].

However, the presence of water is not sufficient to describe the habitability of a planet. Other crucial criteria such as the presence of an atmosphere, even a thin one, which is only feasible if the gravity is sufficient and yet not too strong. Although, Mars only owns a weak CO_2 rich atmosphere nowadays, a wetter atmosphere was present in the past, some 3.5 Ga ago. Since life was already developed on Earth at that period of time, it is plausible that life could have also developed on Mars. If any form of life survives on Mars, it would have adapted to the extreme conditions prevailing on Mars today: freezing temperature, high insolation and severe dryness. Indeed the thin Martian atmosphere cannot maintain a constant humidity nor can it shield the surface of Mars from the high UV and cosmic radiations. On Earth, microorganisms, known as extremophiles, had adapted to survive under extreme environmental conditions for life, comparable to those encountered on Mars [6]. They represent the terrestrial living systems that would be the closest to a possible existing Martian form of life. Amongst other protection strategies, they are able to dig into rocks or secrete pigments to shield themselves from deadly irradiations, they also excreted extracellular polymeric substances (EPS) mainly composed of polysaccharides and proteins forming a protective microenvironment against desiccation [7].

In addition, in order to develop and grow, microorganisms need energy and nutriments. Currently on Earth, many forms of life that we experience used the light and oxygen as a source of energy. However, some microorganisms are able to thrive under anaerobic condition (deprived from oxygen) and used redox reactions to power themselves, they are called chemotrophs. Relevant substances such as methane, sulphates and iron and manganese oxides were identified on Mars. Indeed, on Earth, extremophiles are able to retrieve water from hydrated mineral such as gypsum ($CaSO_4.2H_2O$) to survive extended period of dryness. Others promote redox reactions to power their metabolism, in particular redox reaction for the redox couples Fe^{2+}/Fe^{3+}, Mn^{2+}/Mn^{4+} and S^{2-}/SO_4^{2-}. Methane definitely indicates that organic carbon is available, a requirement for the chemistry of life as we understand it [8]. Yet methane is not necessarily formed by biotic processes and should never be considered a biomarker.

Nonetheless, despite Mars meets several criteria of habitability, the only way to be certain that life ever appeared on Mars is to search and bring scientific evidence on what happened and what is happening on Mars. Based on the recent technological advances and on the data already collected on Mars by previous missions (including the *Mars Science Laboratory* mission with the *Curiosity* rover) two new missions will be launched in 2020: the *ExoMars* mission (ESA in collaboration with Roscosmos) [9] and the *Mars 2020* mission (NASA) [10]. Both mission have similar scientific objectives and our discussion will focus on the *ExoMars* mission in the following lines.

2. Two phases of the ExoMars Mission

The *ExoMars* mission is part of the ESA's Aurora program, which objective is to propose and to implement robotic and inhabited exploration mission of solar system bodies holding putative traces of life. Specifically, the ExoMars mission is focused on Mars and was developed in two phases (Figure 2): the launch of the ExoMars Orbiter (TGO for Trace Gas Orbiter), which reached its orbital position in April 2018 at 400 km of altitude on Mars, and the ExoMars Rover, scheduled for launch in July 2020 [9].

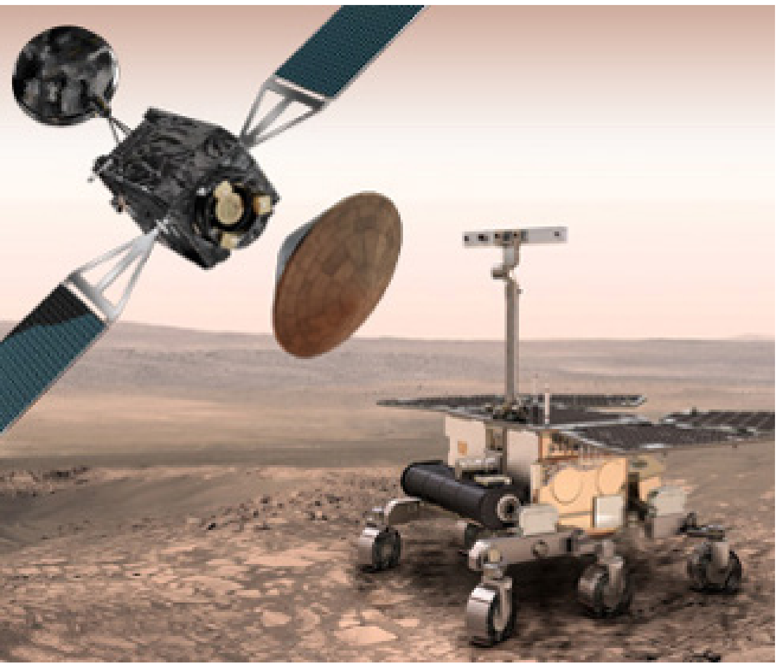

Figure 2. The ExoMars mission (ESA/Roscosmos) with the Trace Gas Orbiter (TGO), the *Schiaparelli* lander and the ExoMars rover (credit ESA)

The TGO orbiter was launched on the 14th of March 2016 and had started operating since March 2018. The orbiter is collecting data on trace gas in the Martian atmosphere, such as methane, water, nitrogen dioxide and acetylene, in order identify their origin with spectroscopic techniques operating in the infrared and in the ultraviolet region of wavelengths. The orbiter is also currently relaying data to support NASA landers on Mars. The TGO orbiter included the *Schiaparelli* lander, which goals were: studying the environment of the landing site (*Oxia Planum*, as one possible landing site recognised since 2015) with a suite of sensors (mainly meteorological instruments) and demonstrating that ESA was capable to successfully land instruments on Mars (capacity only demonstrated by the NASA and the Roscosmos). The *Schiaparelli* lander was successfully ejected from the TGO orbiter, and enter the Martian atmosphere, but unfortunately crashed on the Martian surface on the 19th of October 2017 due to an anomaly in the measurement and navigation system [11].

The ExoMars rover, scheduled for launch in 2020, will bring a suite of analytical instruments on Mars in order to document the habitability of Mars, but also to identify possible traces of life, whether extended or extinct, at the surface and within the subsurface. Indeed, and for the first time, the ExoMars rover will be provided with a drill able to recover samples from 2 meters down the surface of Mars. The specific sampling locations will be selected from data collected, on site but remotely, with panoramic and microscopic instruments:

- *PanCam*: a panoramic camera for digital mapping of Mars;
- *ISEM*: an infrared spectrometer to assess the mineralogy of the surface;
- *WISDOM*: a radar that penetrates the ground to characterise the stratigraphy below the rover, in particular to detect the presence of liquid water; and
- *Adron*: a neutron detector to interrogate the soil of Mars searching for hydrogen indicating the presence of hydrated and hydroxide minerals.

The collected samples, including those retrieved from the ground by the drill as powdered samples, will then be further interrogated by a suite of instruments on board of the rover:

- *CLUPI*: a high resolution camera to obtain coloured and close-up images from the samples;
- *Ma_Miss*: a multi-spectral camera within the drill to characterise the mineralogy and the hydration degree of the strata;
- *MicrOmega*: a visible and infrared spectrometer present also within the drill to determine the mineralogy of the layers on the Martian soil;
- *MOMA*: a mass spectrometer aiming at detecting possible biomarkers, recent or preserved in the soil, after volatilisation by pyrolysis; and
- *RLS*: a Raman spectrometer to characterise the geology and the possible presence of targeted biomarkers in samples collected at the surface or the sub-surface of Mars.

3. The RLS instrument, the first Raman spectrometer designed to study samples from the Martian sub-surface

The ExoMars mission stands out from previous mission by the deployment of the drill able to retrieve sample from 2 meters down the surface of Mars, but also by the implementation of a Raman spectrometer in the rover payload, the *Raman Laser Spectrometer* (RLS). The RLS instrument will interrogate the molecular composition of the samples [6] and has multiple scientific objectives:

- search of evidence of life, past or present;
- analyse the composition of rock and soil samples from the surface and sub-surface of Mars;
- determine the mineralogy, the chemistry and the origin of the surface of Mars; and
- document the distribution of water and the geochemistry as a function of the depth in the outer layers in the sub-surface of Mars.

The Raman spectroscopy present several advantages for the remote exploration of a rocky planet. Raman spectroscopy is a non-destructive technique based on the inelastic scattering of light (Figure 3). Hence, the sample integrity is guaranteed and other analyses can be performed on the very same sample. In practice, a monochromatic laser beam is sent on the sample, the photons interact with the sample molecules (which undergo vibrational transitions), and eventually the molecules scatter the Raman light. The energy of the scattered photons are either increased or diminished by the energy required for the vibrational transitions taking place at the molecular level. The Raman spectrum obtained by resolving the scattered light intensity as a function of the wavenumber (shift from the laser line) is the fingerprint of the molecular substances analysed. Therefore, Raman spectroscopy enables to determine the molecular composition of inorganic compounds (such as minerals constituting rocks and soils), but also organic compounds (amongst them, some known as biomarkers can be specific of biological activities) without any particular preparation of the sample. It applies to study solids, liquids and gases likewise. While Raman spectroscopy was established for decades in research laboratories and military applications (e.g. for detection of potential explosive substances at customs) a number of technical challenges were to be resolved to send miniaturised instruments into space.

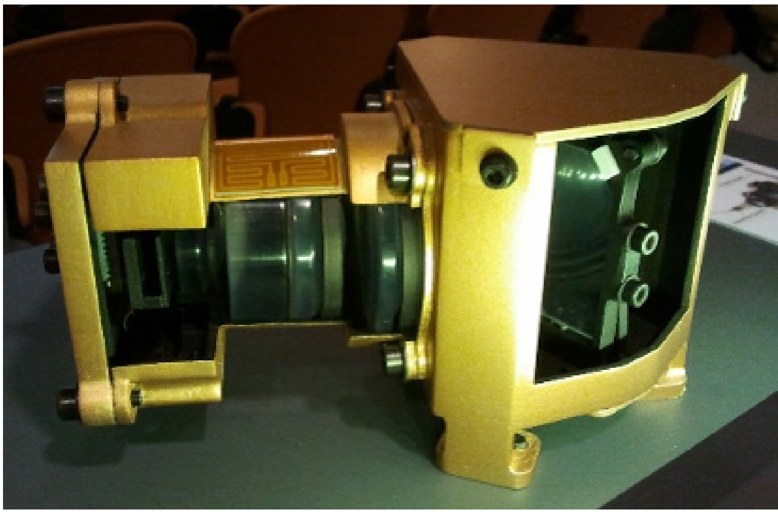

Figure 3. Raman analyses of a solid sample. The monochromatic laser beam (green) is sent on the sample, which scatters Rayleigh light (without any energy exchange, green lines) and Raman light (with energy exchange, blue and red lines)

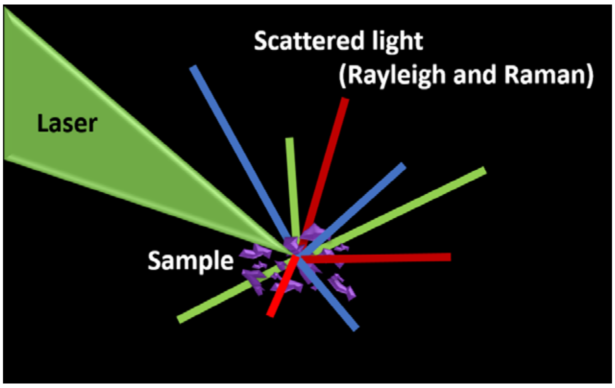

Figure 4. One of the optical prototypes of the ExoMars Raman Laser Spectrometer (RLS). Approximate dimensions 20x15x15 cm (length, width and height) (credit ESA)

Remote planetary exploration program requires robust instrumentation, resisting mechanical constrains. In addition, the CCD camera detector (2D capacitors arrays) should be operating properly, even after a long term exposition to ionising radiation (cosmic rays) during the journey from Earth to Mars, but also at the surface of Mars. The ExoMars Team at the University of Leicester was in charge of developing, characterising and providing the CCD camera for the RLS instrument (the optical parts shown in Figure 4 were developed in Spain). The detector has now been delivered and will be assembled in the rover for the launch. Beside the development of the CCD camera of the RLS instrument, the ExoMars Team at the University of Leicester is also interested in characterising the performances expected for the RLS instrument. In particular, the RLS and its prototypes should be capable of:

- detecting disordered carbon (including fossilised carbon) at low concentration levels;
- determining the origin of carbon (its degree of geological evolution);
- detecting organic molecules specifically produced through biological mechanisms (molecular biomarkers), again at low concentration levels;
- characterising the geological and bio-geological environment associated to the detection of carbon or biomarkers in natural samples.

4. Terrestrial analogue samples, cases study in preparation for ExoMars

A significant phase for the development of scientific instrument dedicated to space exploration missions is the characterisation of the apparatus performances (both technical and scientific). To do so, the scientists often use natural samples representative of the target samples. In the case of Mars, besides meteorites that were exposed to extreme temperatures and pressures, there is no natural samples available on Earth. However, several locations on Earth present some degree of similarity with the Martian environment in terms of geology, high UV-irradiation, desiccation or, extreme temperatures. In these extreme condition habitats, microorganisms are even identified as thriving on or within substrates such as rocks, soils and bio-geological formation. These bio-geological samples, also known as analogue samples, are often identified by geologists and (astro)biologists to support the design of planetary exploration instrumentation.

The ExoMars Team at the University of Leicester and the Laboratory of Inorganic Analytical Chemistry at the University of Liege are studying numerous of these analogues samples. Using miniaturised instruments (operating with experimental parameters similar to those for the RLS instrument) and highly performant benchtop confocal instruments, analogues samples are interrogated to (a) characterise the performances of the instruments, and (b) better understand the preservation of bio-organic matter when buried in particular mineralogical substrates. Among other analogue samples, basalts containing carbonaceous matter that underwent different geological processes, evoparite that are formations resulting of the precipitation of minerals such as sulphates and carbonates and very often colonised by microorganisms [12,13], silicified rock outcrops with endolithic colonies (inhabiting the rocks) [14], and desert varnishes [15, 16]. A selection of analogues samples is presented in Figure 5.

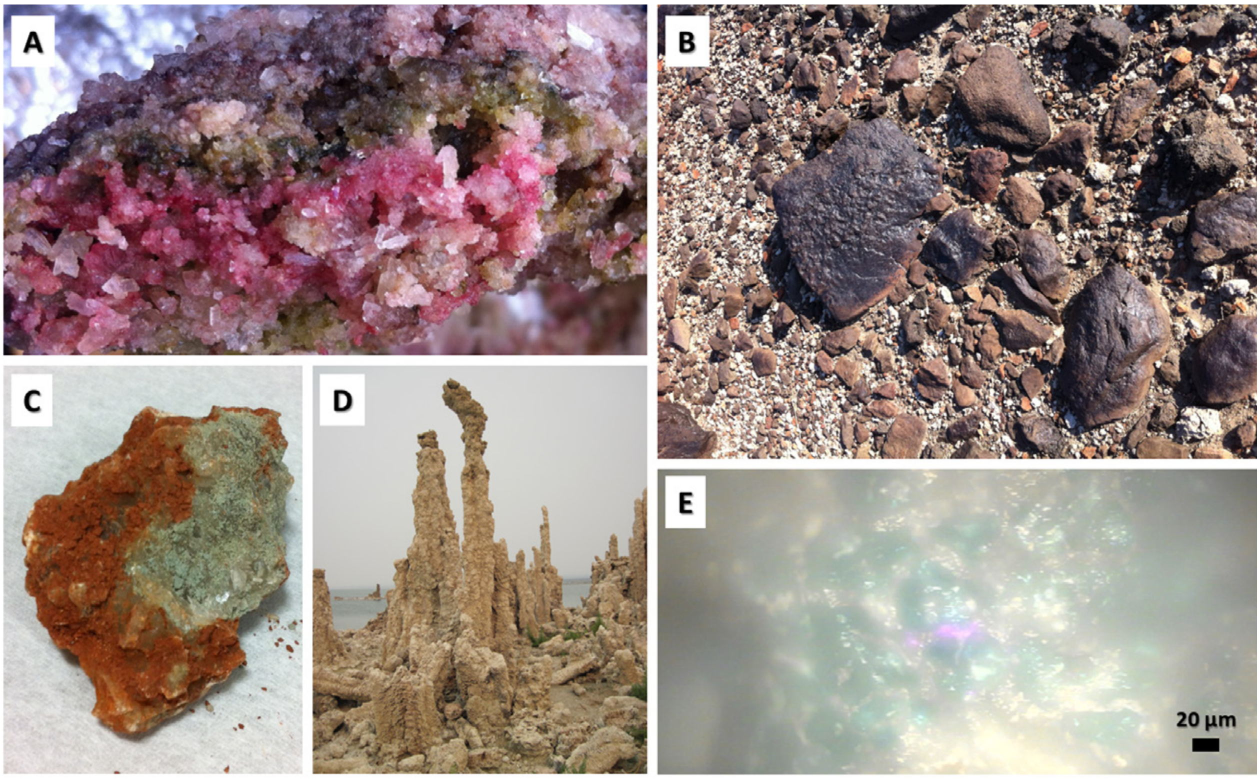

Figure 5. A selection of terrestrial bio-geological analogue samples for Mars exploration: (A) colonised bentic crust of gypsum, Israel; (B) rocks covered with desert varnish, California; (C) colonised ferric sulfate; (D) preserved colonised submarine vents, California; and (E) microorganism colony in feldspar, Antarctica

As an example, desert varnishes are dark mineral coating (Figure 6), typically below one hundred of microns in thickness, covering rocks in desert places, either hot or cold [17]. There are only found in geologically stable environments (where minimal erosion occurs) and can cover small rocks to entire cliff sides. Rich in iron and manganese oxides as well as in clays, desert varnishes are recognised as analogue samples. Indeed, comparable mineral formations were recently identified on Mars by the *Curiosity* rover [18]. On Earth, desert varnishes are often associated with extremophiles such as manganese-oxidative bacteria, cyanobacteria and microfungi. Hence, desert varnishes represent a habitable substrate enabling the surviving of these microorganisms in extreme environmental stresses, such as low nutrient abundance, high desiccation and high UV-insolation. However, whether the microorganisms take an active part or not in the formation of desert varnish is still unclear. Therefore, the recognition of desert varnish cannot be regarded as evidence of life. Yet, we demonstrated that Raman spectroscopy is a suitable technique to describe the mineralogy of several samples of desert varnish from Death Valley, in California. The presence of carotenoid pigments (such as b-carotene, Figure 6) was also achieved on desert varnish using Raman spectroscopy. Actually carotenoid are very active in Raman spectroscopy when a green laser is used (as the ExoMars 532 nm laser) and have been early identified as a target biomarker to search for during planetary exploration. Indeed, it is found in association with various extremophile colonies [13,19]. Since the half-life time of carotenoids under irradiation is quite short, their detection at the surface of Mars would mean that an active source of carotenoid is present.

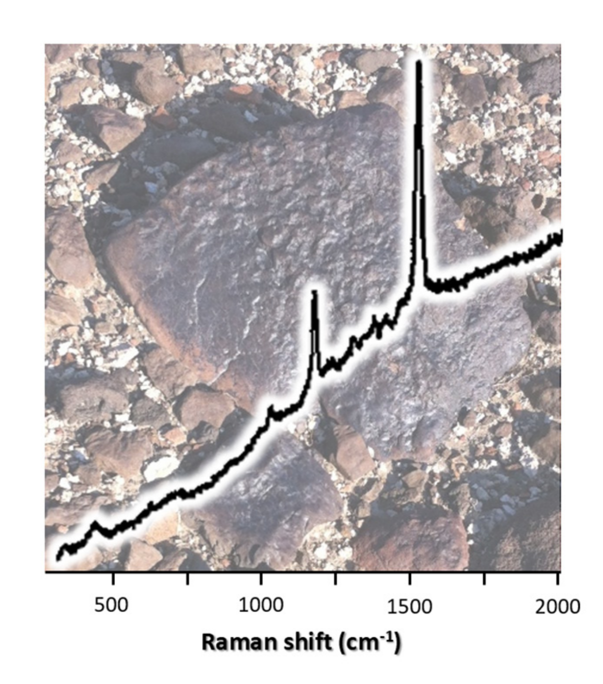

Figure 6. Desert varnish from Death Valley, California and a Raman spectrum of carotenoid detected at (1005, 1150 and 1510 cm^{-1}) is association with quartz (detected at 465 cm^{-1}) within the mineral coating

5. Conclusion

During the ExoMars mission, the RLS instrument would be the first Raman spectrometer in space for analysing the sub-surface of Mars. According to the scientific objectives of the ExoMars mission, the RSL instrument was designed to interrogate the molecular composition (inorganic and organic) of a rocky sample delivered by the ExoMars drill. In preparation for the ExoMars mission (launch in 2020), analogue samples sharing similarities with expected Martian samples (in terms of molecular composition and/or environment conditions) are thoroughly interrogated, using miniaturised prototype instruments (with operating parameters similar to the RLS). The prototypes demonstrate their scientific value in characterising the habitability of a geological substrate (linked to its mineralogy) and detecting molecular evidence of life either extinct (a molecular sight in the past) or extant (a molecular vision in the future).

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