The Raman Laser Spectrometer on the ExoMars Rover Mission to Mars

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Outline

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  - Pasteur Payload
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  - Overview of the RLS
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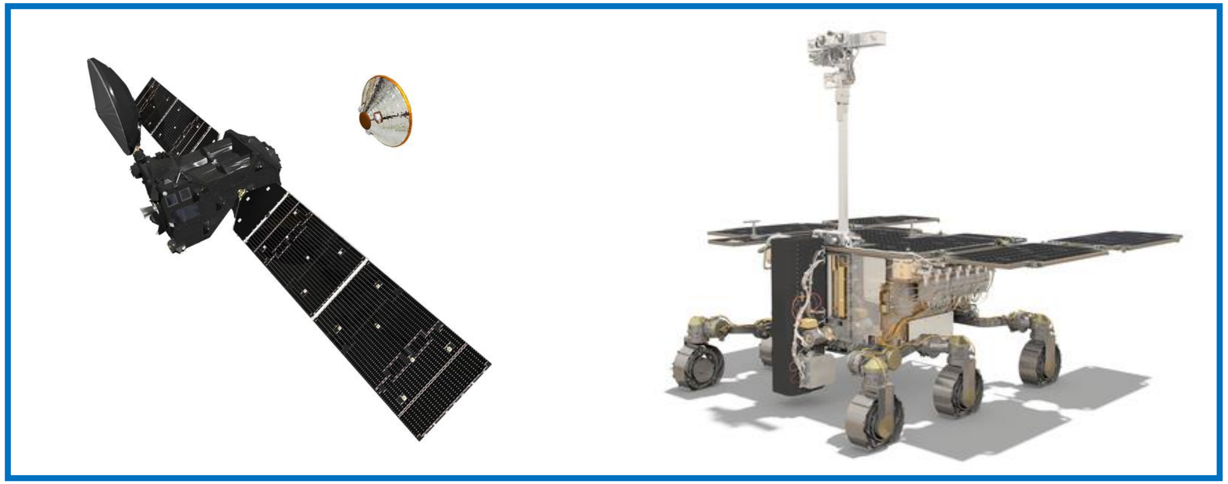
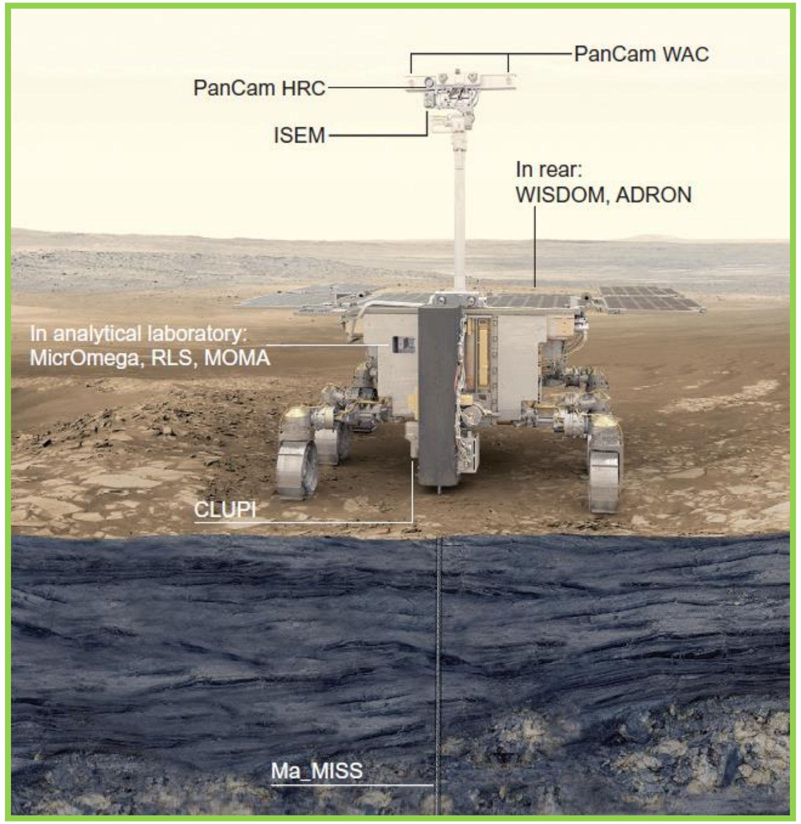
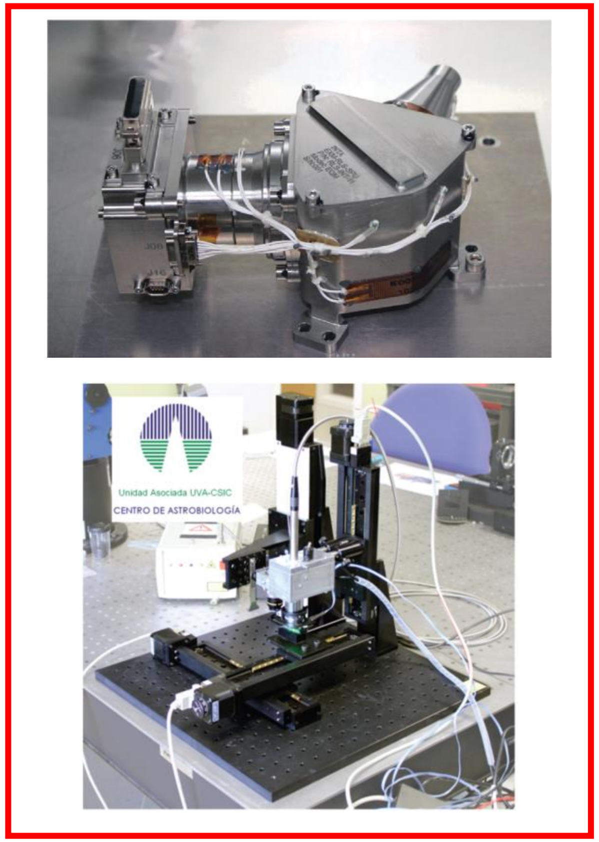
○ Final remarks







Introduction

The ExoMars program consists in two different missions: ExoMars 2016 and ExoMars 2022

1. **Scientific goals**:
   - ☐ Search for signs of past and/or present life on Mars
   - ☐ Investigate how geochemical environment varies
   - ☐ Investigate Martian atmospheric trace gases and their sources
2. *The ExoMars programme will demonstrate several essential flight and in-situ enabling technologies necessary for future exploration missions*.

ExoMars 2016:

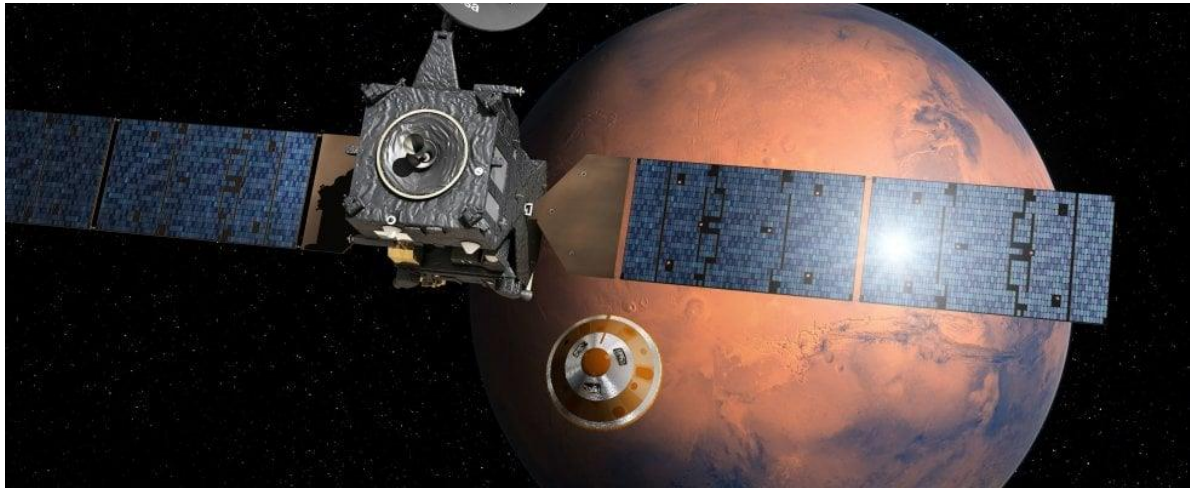
- Trace Gas Orbiter.
  - Investigations of the biological/geological origin of trace gases
  - Data relay for communications with the ExoMars 2022 rover
- Entry, Descent and landing demonstrator Module (Schiaparelli). *Landing failed*

ExoMars 2022:

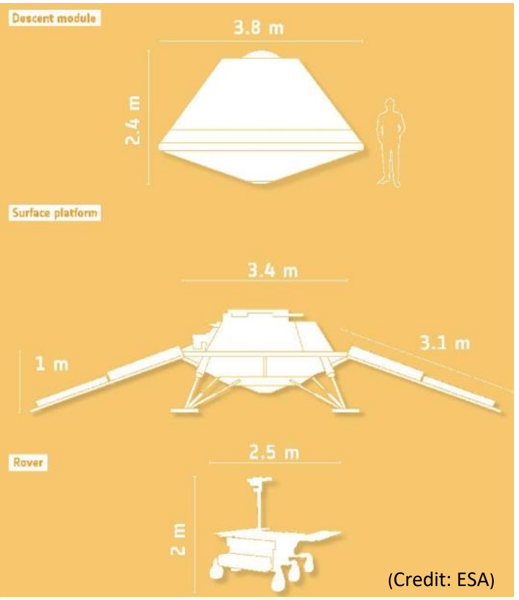
- Rosalind Franklin rover.
- Kazachok surface platform.
  - Long-term climate monitoring
  - Atmospheric investigations

ExoMars 2016

(Credit: ESA)



ExoMars 2022



(Credit: ESA)

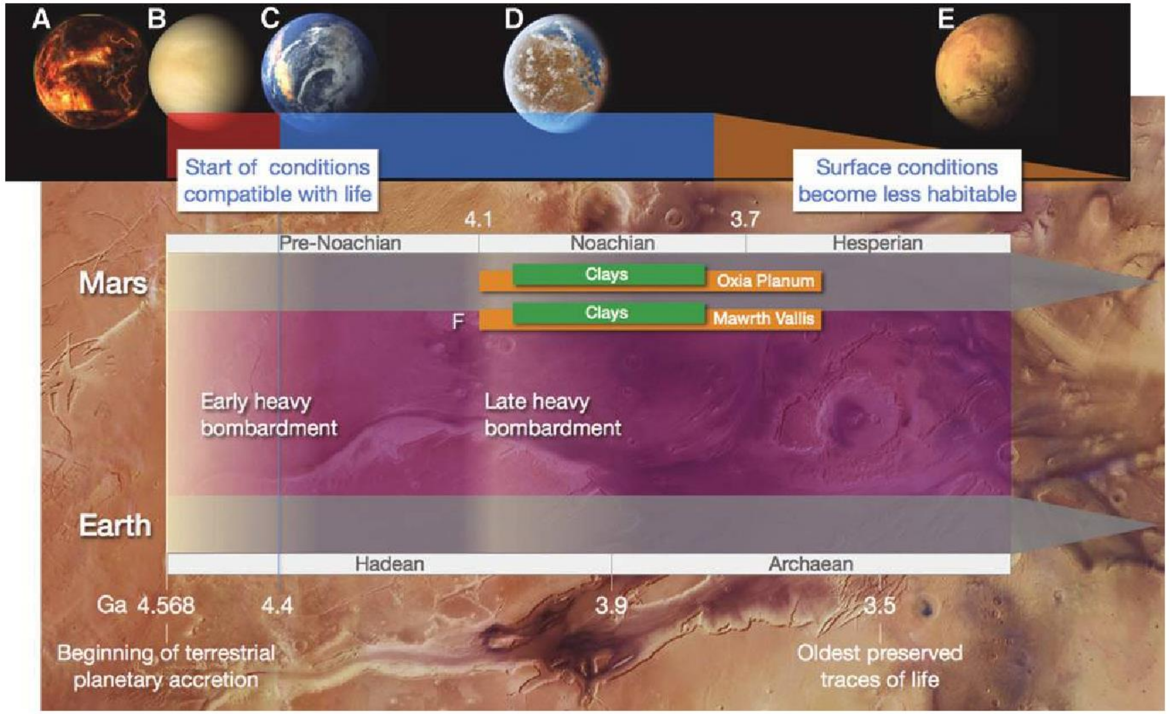
(Credit: ESA)

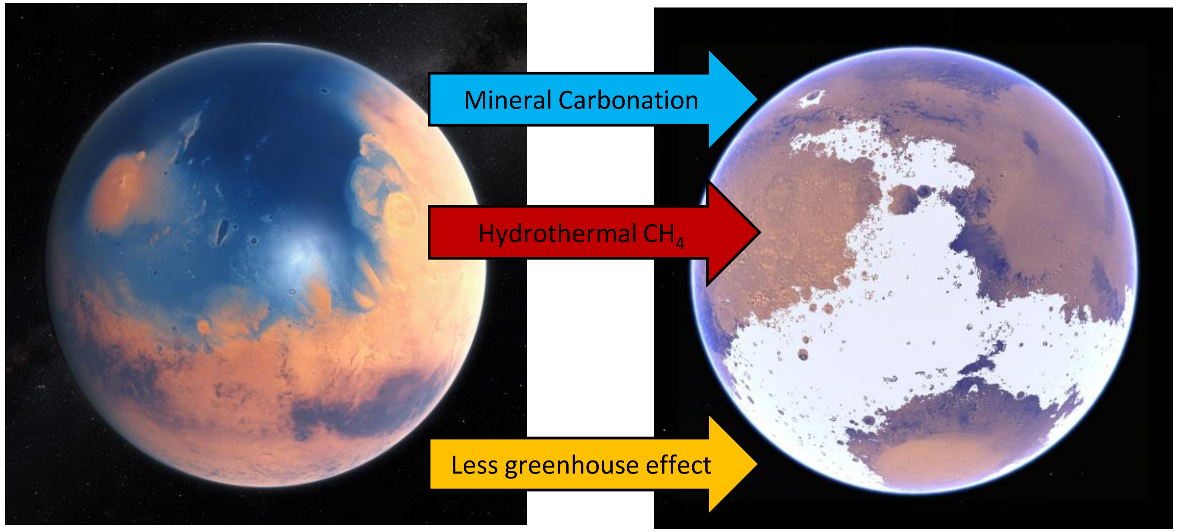
Searching for past life on Mars

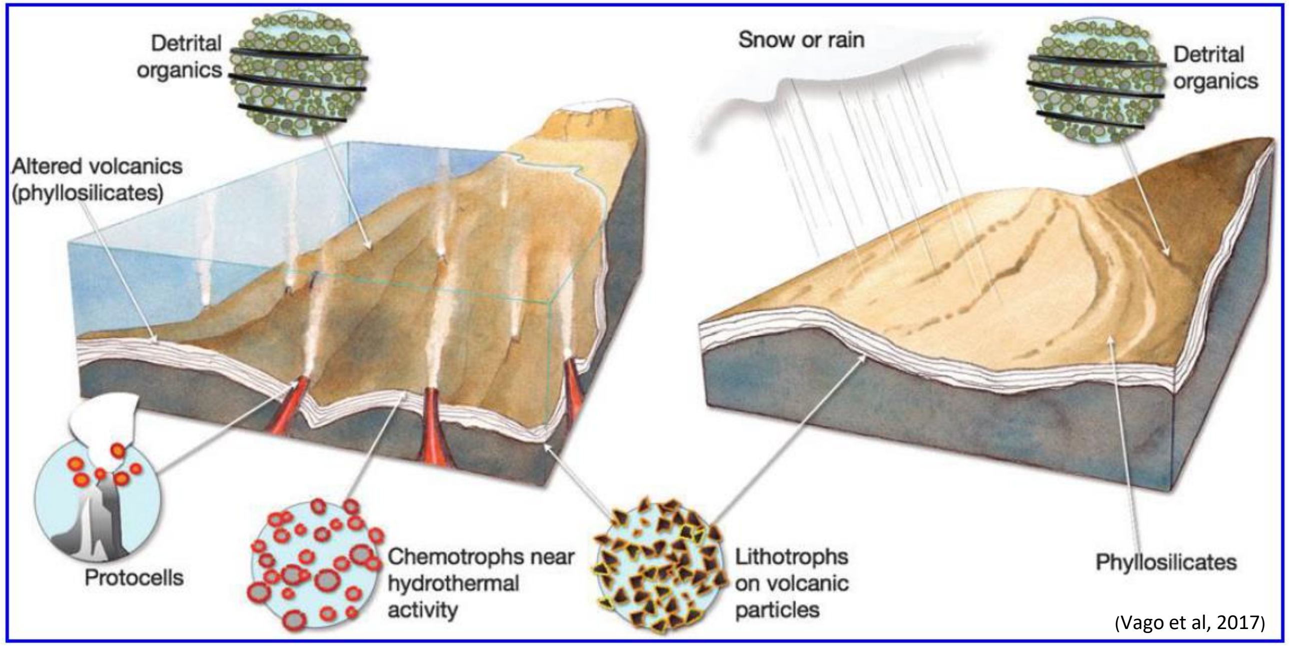
Similar to the Earth, ≈4.45 Gyr ago Mars could also have formed a primordial H_2O-rich atmosphere, which trough condensation, could have create a global warm ocean (or large bodies of water)

Due to decreasing greenhouse effect, for a good part of its early history, Mars could have looked like a colder version of present-day Iceland. **Nevertheless, this does not constitute a serious impediment for the possible appearance of life since abundant subglacial and submerged volcanic/hydrothermal activity.**

(Vago et al, 2017)







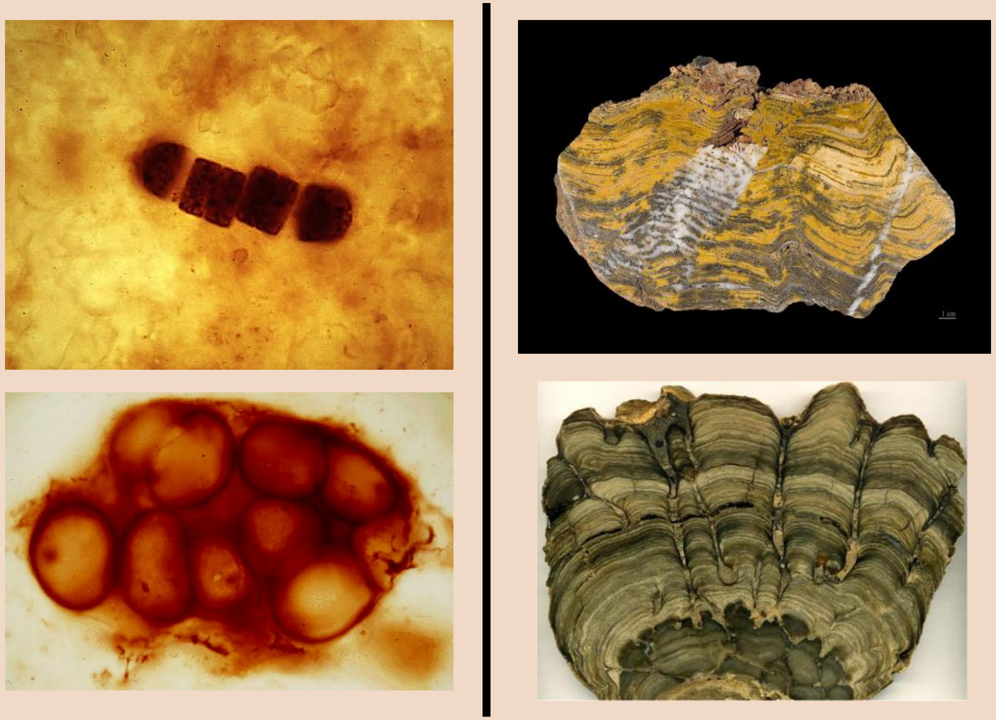
(Vago et al, 2017)

What to search?

We need to search for "**biosignatures**", i.e. any substance (an element, isotope, or molecule) or phenomenon that provides scientific evidence of past or present life

Morphological Biosignatures

Carbonaceous remains of microbial colonies and biofilms trapped in sediments encased in mineral cement



Chemical Biosignatures

Organic material possibly preserved in extensive, organic-rich sedimentary deposits

Primary biomolecules:

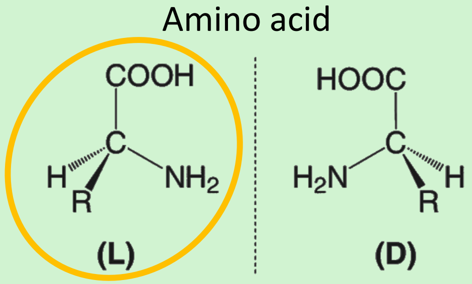
- ○ *Lipids (membranes)*
- ○ Amino acid
- ○ Proteins
- ○ Nucleic acids
- ○ Carbohydrates
- ○ Intermediary metabolites

Degrade quickly once microbes die

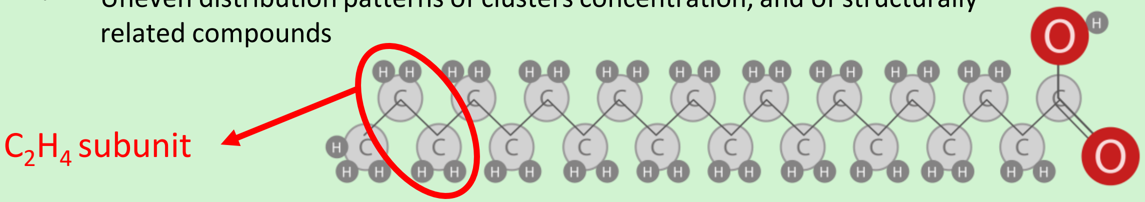
Diagenesis

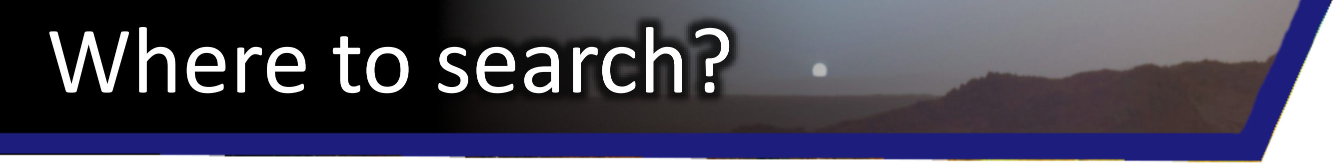
Macromolecular organic matter
(e.g. Kerogen)

- ➢ *Isomerism selectivity*
  - **Enantiomeric excess**: life forms synthesize exclusively one enantiomer (e.g: l-amino acids)
  - Diastereoisomeric preference
  - Structural isomer preference



- ➢ *Molecular weight fingerprints*
  - **Repeating constitutional subunits**: enzymes synthesizing fatty acids attaching one subgroup at a time (C_2H_4)
  - Uneven distribution patterns of clusters concentration, and of structurally related compounds

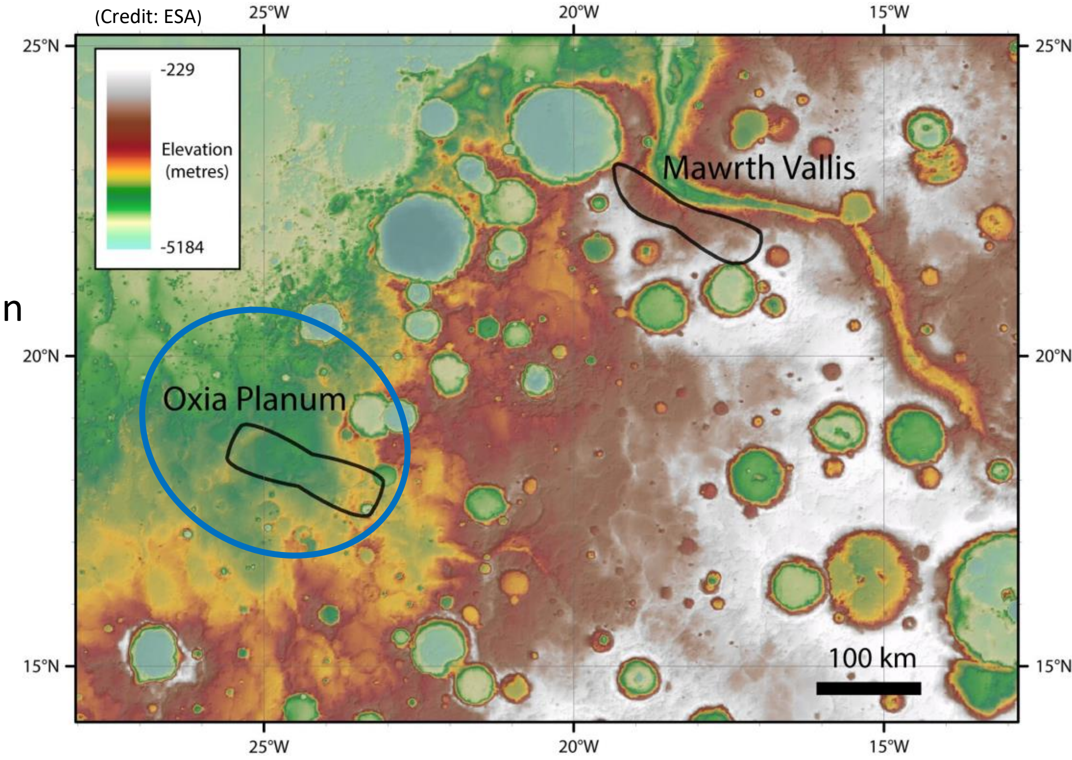




Where to search?

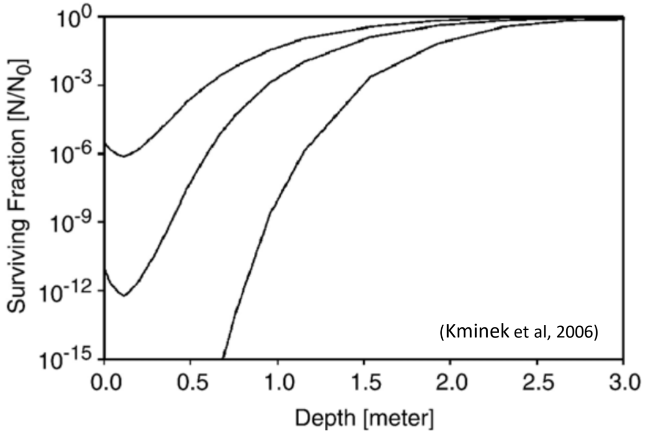
The absence of a recent global plate tectonics on Mars increases the probability that rapidly buried, ancient sedimentary rocks (possibly hosting microorganisms) may have been spared thermal alteration and been shielded from ionizing radiation damage until uncovered by eolian erosion relatively recently.

<u>We need to search for “Sweet spot” in Mars’ geologic history: areas with prolonged, low-energy, water-rich environments able to receive, host, and propagate microorganisms.</u>


(Credit: ESA)

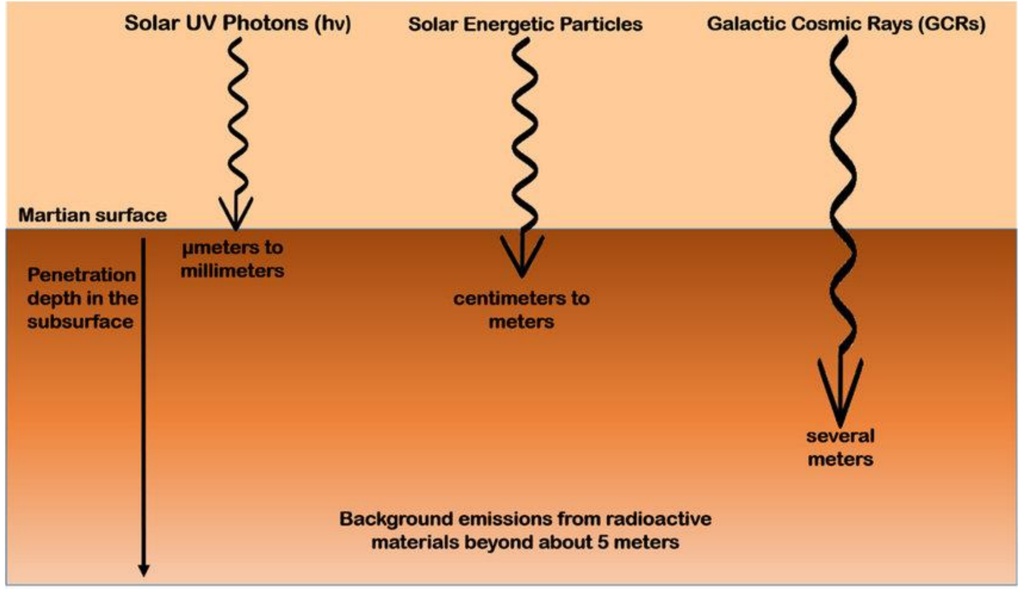
Once landed the rover must search for biosignature underground

1. UV radiation is higher than Earth’s and it quickly damage biomolecules.
2. UV-induced photochemistry produces reactive oxidants that can destroy chemical biosignatures
3. Ionizing radiation penetrates into the uppermost meters of the planet’s subsurface slowly degrading organic compounds.
4. Avoid superficial dust deposits generated by eolian transport. This material has been processed by UV radiation, ionizing radiation, and potential oxidants



(Kminek et al, 2006)

Fig. 2. Depth dependent surviving fraction of amino acids after being exposed half (top), one (middle), and three billion years (lower curve) to the ionizing radiation in the Martian subsurface.


Solar UV Photons (hν)

Solar Energetic Particles

Galactic Cosmic Rays (GCRs)

Martian surface

Penetration depth in the subsurface

μmeters to millimeters

centimeters to meters

several meters

Background emissions from radioactive materials beyond about 5 meters

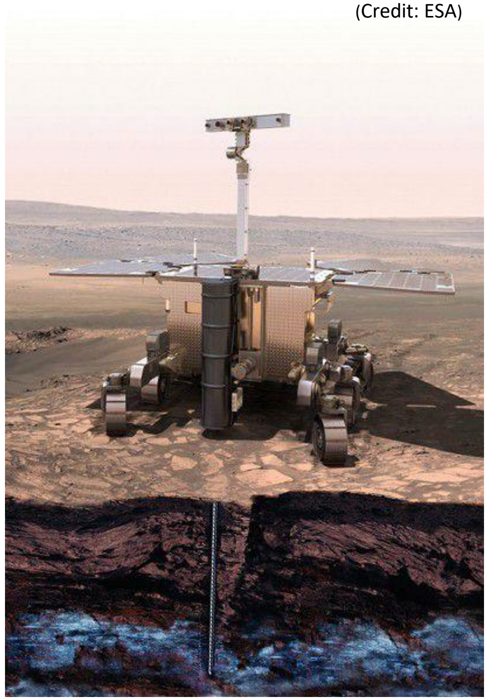
The Rosalind Franklin rover

The Rosalind Franklin rover will be the first European rover to land on Mars

Properties

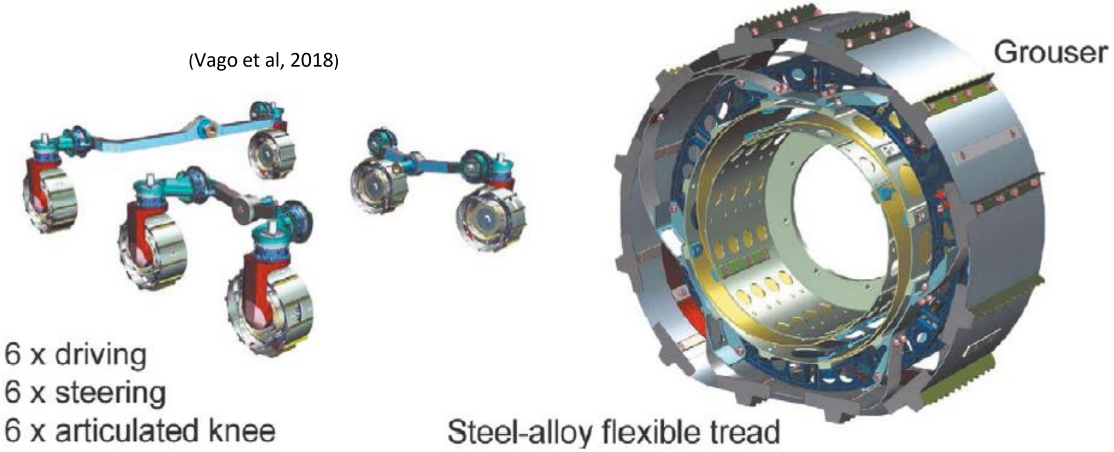
- *Mass*: 310 Kg + 26 Kg payload
- *Rover kinematic config*: 6x6x6 wheels
- *Power*: Solar array electric power
- *Distance covered*: 70m/sol
- *Expected rover lifetime*: 218 sol (≈7 months)
- *Lunch date*: “September 2022”

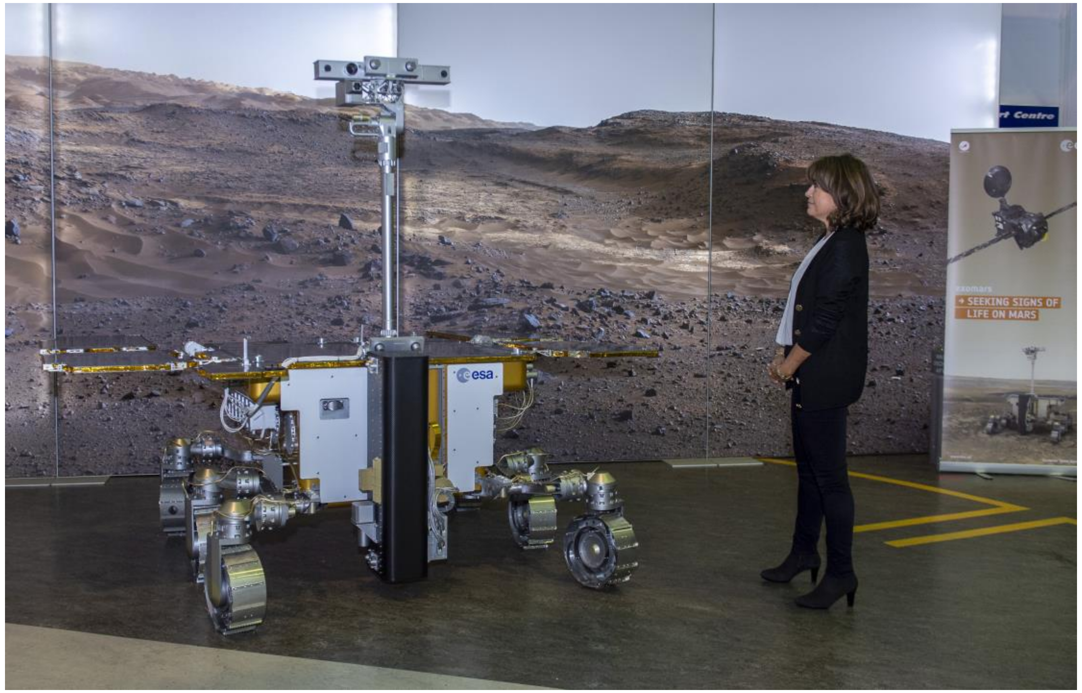
(Credit: ESA)



See backup slides for the Reference Surface Mission

(Vago et al, 2018)





(Credit: ESA)

Pasteur payload

The rover’s Pasteur payload will produce comprehensive sets of measurements capable of providing reliable evidence for, or against, the existence of a range of biosignatures at each search location.

Panoramic instruments

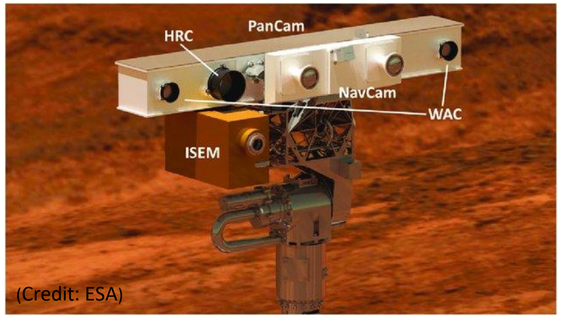
Characterize the rover’s geologic context. Typical scales span from panoramic (100m) to 1m

PanCam (Panoramic camera):
two wide-angle stereo cameras and one HR camera to investigate the rover’s environment and geology, and for target selection and for rock textural studies.

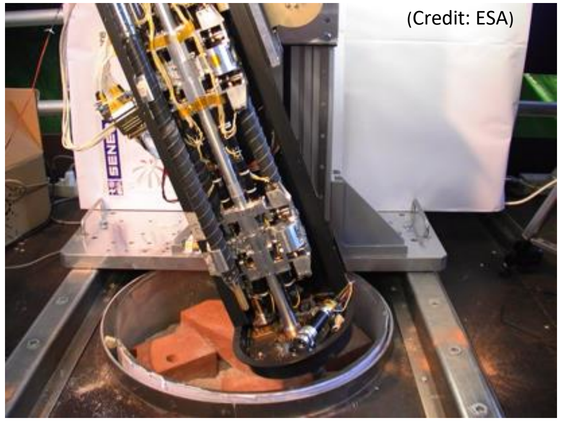
ISEM (IR spectrometer):
bulk mineralogy characterization, remote identification of water-related minerals

WISDOM (GPR):
subsurface stratigraphy down to 3m depth

ADRON (Neutron detector):
determine the level of subsurface hydration and the possible presence of an ice fraction to 1m depth



(Credit: ESA)



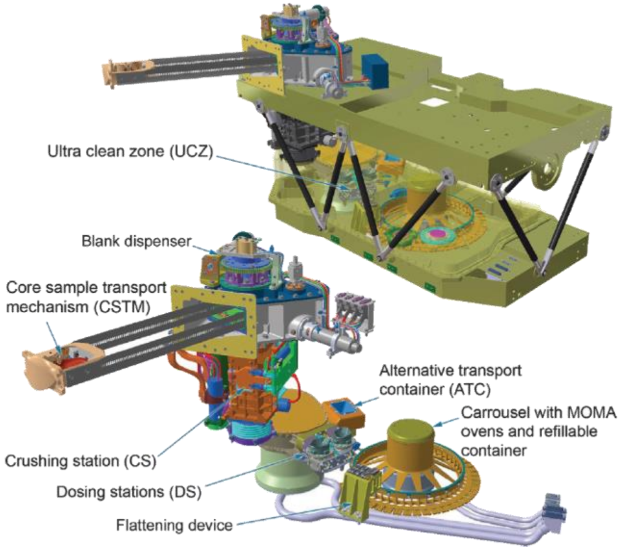
(Credit: ESA)

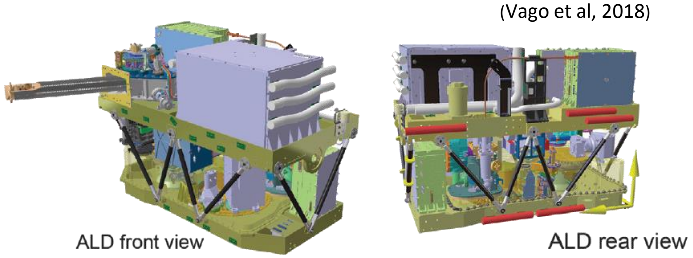
Contact instruments

Investigate outcrops, rocks, and soils. Understand local depositional environment and search for morphological biosignatures

CLUPI (Close-up imager):
study rock targets at close range (50cm) with submillimeter resolution. Search for morphological biosignatures, such as biolamination

Ma_MISS (IR spectrometer in drill):
for conducting mineralogical studies in the drillborehole’s walls





(Vago et al, 2018)

Support subsystems

Essential devices devoted to acquisition and preparation of samples to be studied in the analytic laboratory.
Mission’s ability to break new scientific ground depends on these two subsystems

Subsurface drill:
Retrieve samples from 0 to 2m depth. Includes a blank sample, temperature sensors, and an IR spectrometer (Ma_MISS)

SPDS:
Sample preparation and distribution system receive a samples from the drill system, produce particulate materials preserving the organic and water fractions, and presents it to all analytic laboratory instruments

Analytic laboratory

Perform detailed analysis of each collected sample.

1. Sample crushing, and visual plus spectroscopic investigation.
2. Search for organic molecules.
3. In case interesting results, perform more in-depth analyses

MicrOmega:
Examine crushed sample material to characterize structure and composition at grain-size level. Help point the laser-based instruments

Raman Laser Spectrometer (RLS):
Identify mineral phases at grain scale in the crushed sample material, determine their composition, and establish the presence of carbon

MOMA (LD+Der-TV GCMS):
Conduct broad-range, high sensitivity search for organic molecules. Organics extraction: (1) laser-desorption and (2) thermal volatilization, with or without derivatization agents, separation using four gas chromatograph columns. Identification of the evolved organic molecules achieved with an ion-trap MS

The Raman Laser Spectrometer

Scientific objectives for the RLS

1. Identify organic compound and search for life;
2. Identify mineral products and indicators of biologic activity;
3. Characterize mineral phases produced by water related processes;
4. Characterize igneous minerals and their alteration products;
5. Characterize the water/geochemical environment as a function of depth in the shallow subsurface

Raman laser spectrometer components

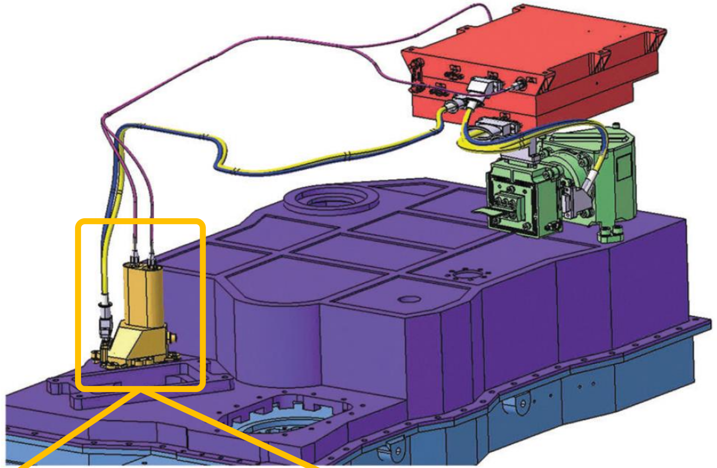
Optical head unit (iOH)
Double purpose: focusing the incident laser on the sample with a 50 μm spot diameter and collect the scattered radiation

Electrical harness (EH)
The various elements of the EH have been designed to connect (electrically and optically) the RLS instrument's main units (SPU, iOH, and ICEU)

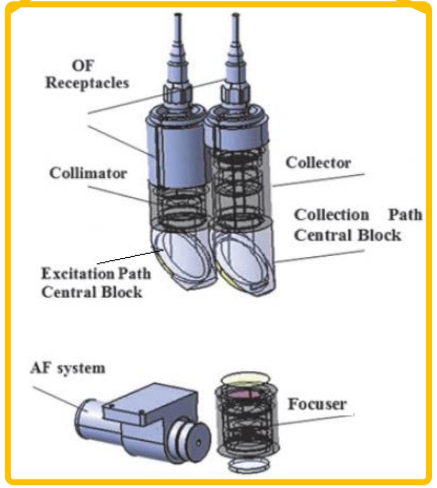
Spectrometer unit (SPU)
Transmission spectrograph that disperses Raman signal that is projected on the CCD

Calibration target (CT)
1-mm-diameter disk sample of PET used for RLS instrument calibration. PET shows a sufficient number of fine bands but also have good mechanical, thermal, and low outgassing properties

Electronics control unit (ICEU)
Contains the excitation unit (laser: 532nm continuous wave) and its control. Include also the power board responsible for managing the rover-provided +28V primary voltage.

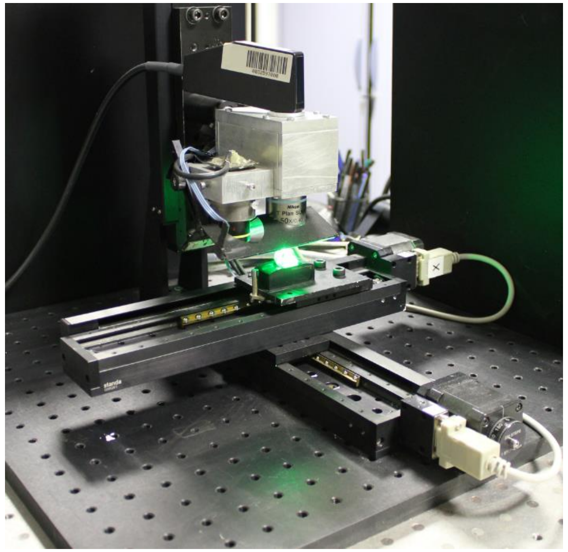


(Rull et al, 2017)



RLS ExoMars Simulator

Not "*exact*" copy used for lab tests.
Continuous laser source 532nm
Laser power output (20 mW)
Range of analysis (70–4200 cm^{-1})
Spot of analysis (≈50 μm)
Spectral resolution (6–10 cm^{-1})
Working distance (≈15 mm)



Raman Spectroscopy

Raman spectroscopy is based on the **Raman effect** consisting of inelastic scattering of photons.

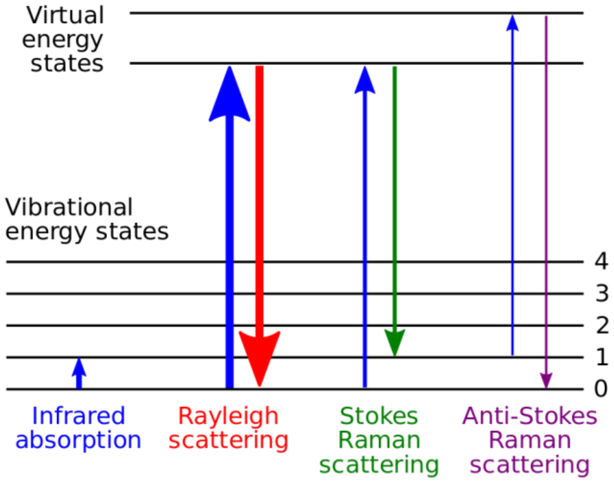
$$\hbar\omega_i + M_i(E_i) \rightarrow M_f(E_f) + \hbar\omega_s$$

Anti-Stokes Raman Scattering

$$\hbar\omega_s > \hbar\omega_i$$

Stokes Raman Scattering

$$\hbar\omega_s < \hbar\omega_i$$



Classic vibrational Raman effect (see backup slides)

$$\vec{p} = \vec{\mu_0} + \sum_{n=1}^{Q} \left(\frac{\partial\vec{\mu}}{\partial q_n}\right)_0 q_{n0}\cos(\omega_n t) + \alpha_{ij}(0)\vec{E}_0\cos(\omega t) +$$

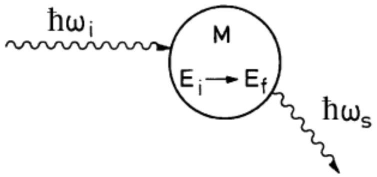
IR spectrum Rayleigh scattering

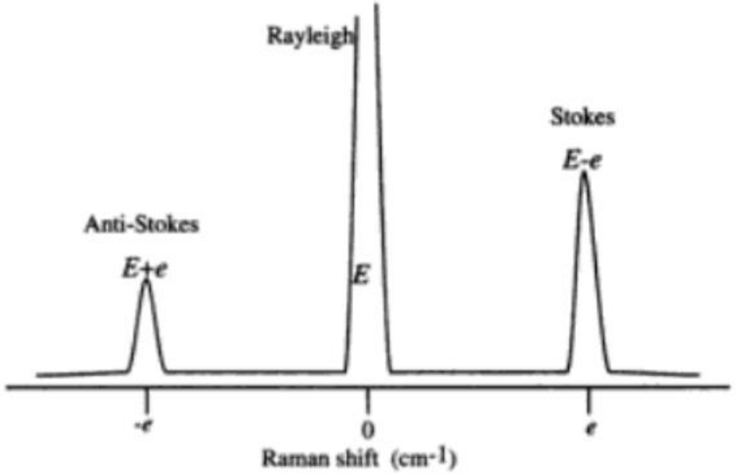
$$+ \frac{1}{2}\vec{E}_0 \sum_{n=1}^{Q} \left(\frac{\partial\alpha_{ij}}{\partial q_n}\right)_0 q_{n_0}[\cos(\omega+\omega_n)t + \cos(\omega-\omega_n)t]$$

Raman effect

Line intensities

$$I_s = N_i(E_i)\sigma^R_{i\rightarrow f}(\alpha_{ij})I_L$$





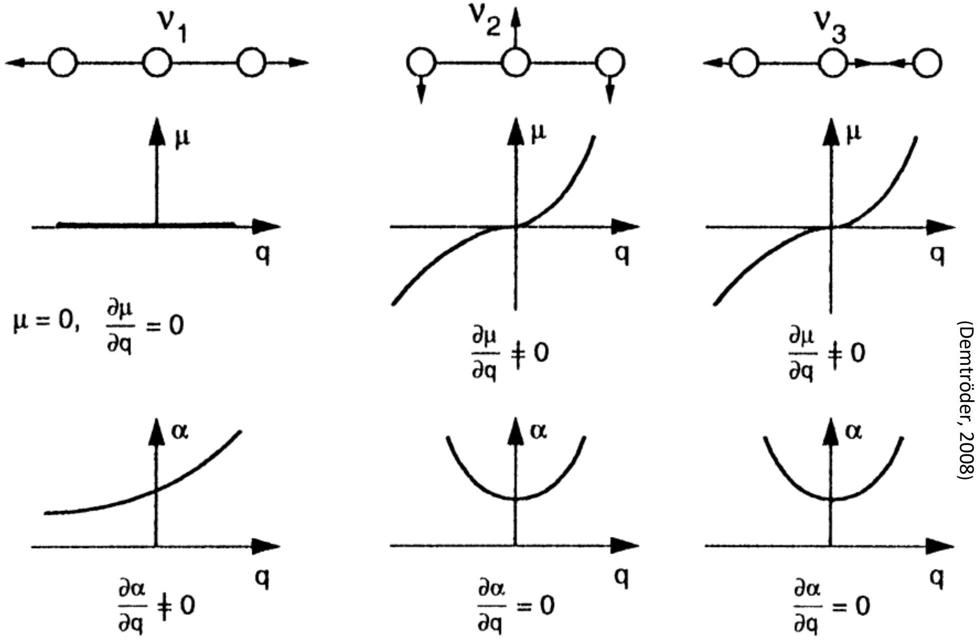
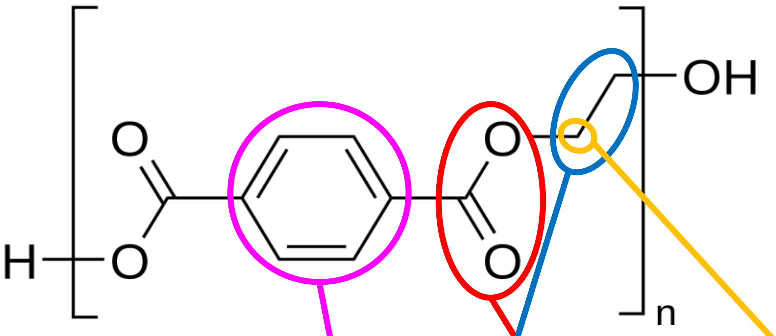


Fig. 3.2. Dependence $\partial\boldsymbol{\mu}/\partial q$ of dipole moment and $\partial\alpha/\partial q$ of polarizability on the normal vibrations of the CO_2 molecule

(Demtröder, 2008)

Raman spectrum example

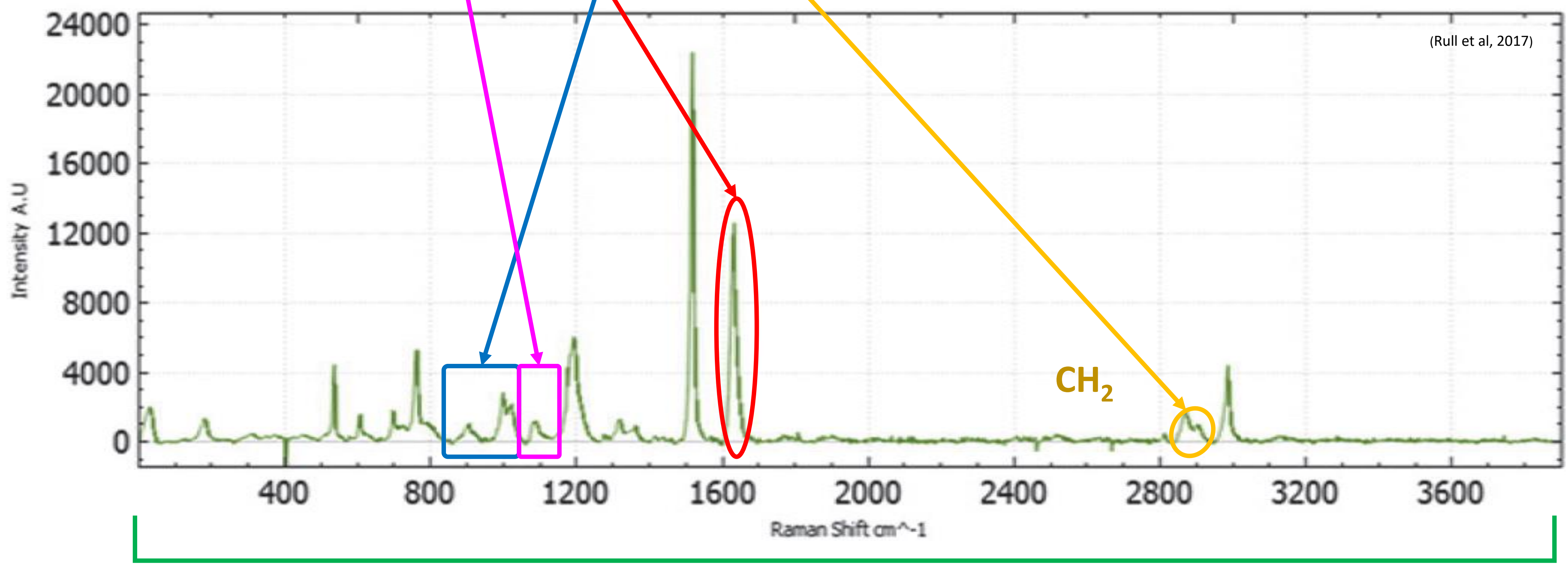
Polyethylene terephthalate (PET)



(Rull et al, 2017)

The molecular structure can be complex, generating not straightforward Raman spectra.

Usually, some peaks can trace the presence of functional subgroups



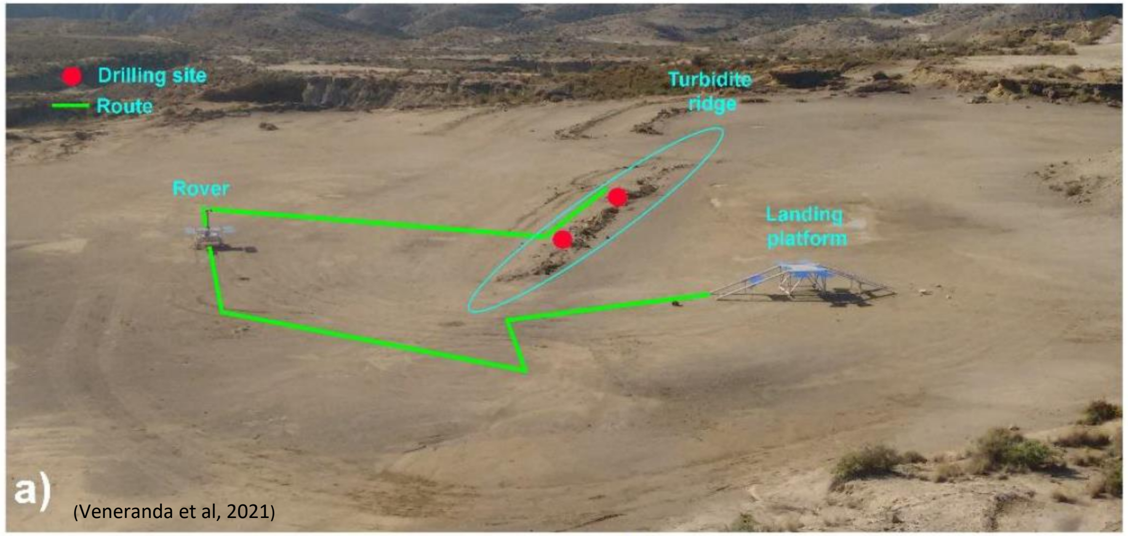
RLS spectral range: 70-4000 cm $^{-1}$

Test on the field (I)

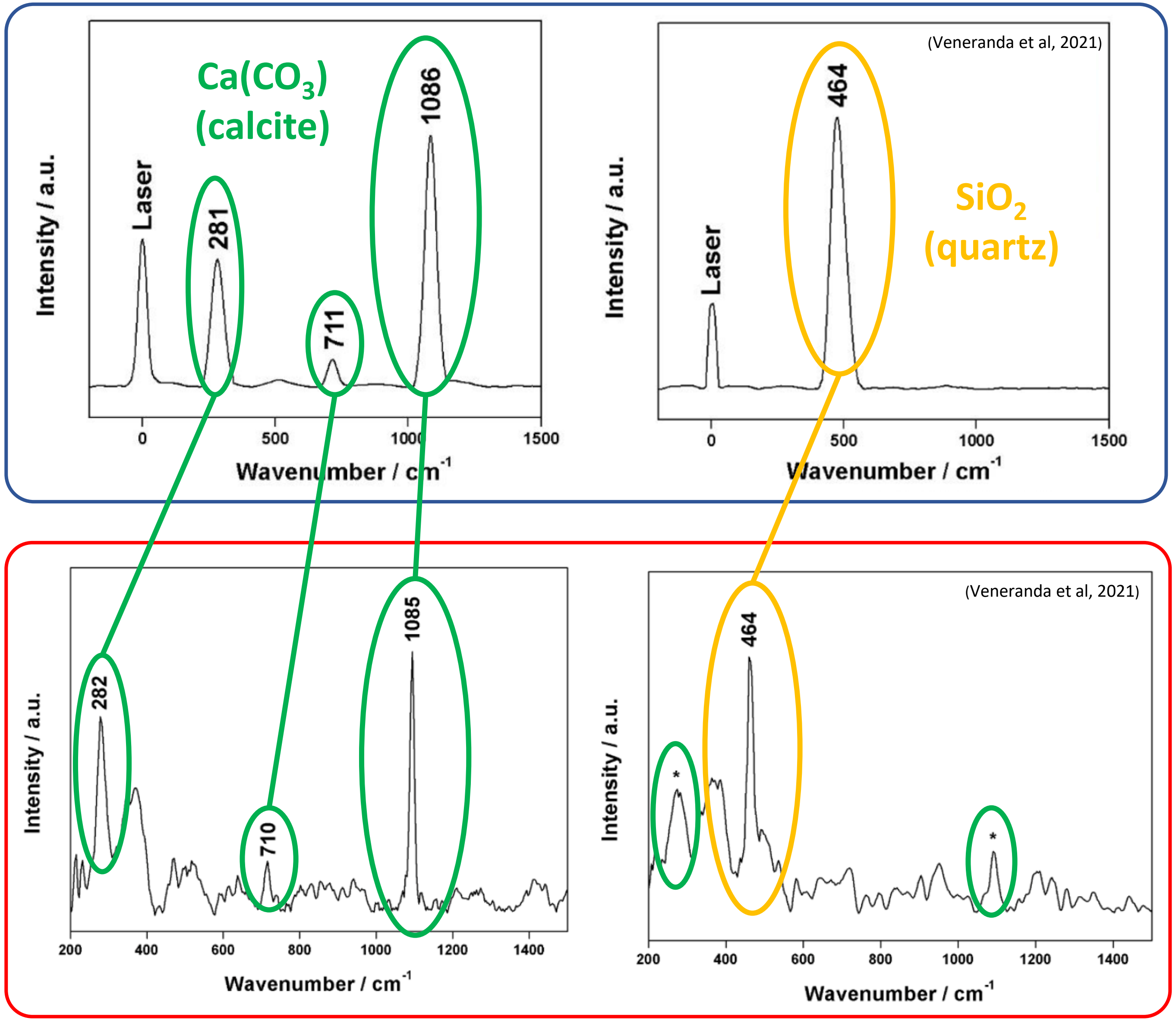
Among the various tests for the RLS, one consists in analyzing samples from the Tabernas Desert (Spain). Sample analysis has been done both **in-situ** and in laboratory. **Results are coherent with the expected mineralogic studies of the region**

RLS engineering and qualification model (RLS EQM-2)
Perfect copy of the RLS fight model (same structure).
Unfortunately, RLS EQM-2 was not working under Martian temperature conditions → spectral resolution and SNR lower than RLS FM spectra from Mars

Raman Demonstrator (RAD1)
Portable emulator of the RLS (not a perfect copy, similar to the RLS simulator)



(Veneranda et al, 2021)



(Veneranda et al, 2021)

(Veneranda et al, 2021)

Test on the field (II)

Result for sample analysis in laboratory

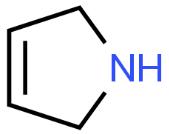
The collected sample have been also analyzed in lab using the RLS simulator (under more stable condition).

Found many inorganic and organic compounds!

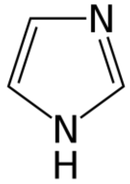
Rutile → indicator of hydrothermal alteration processes

Found also biomarkers!!!

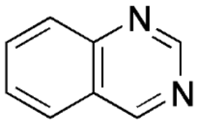
Excitation of $-NH_3$ and $=NH_2$ functional groups or vibration of nitrogen-heterocyclic compounds



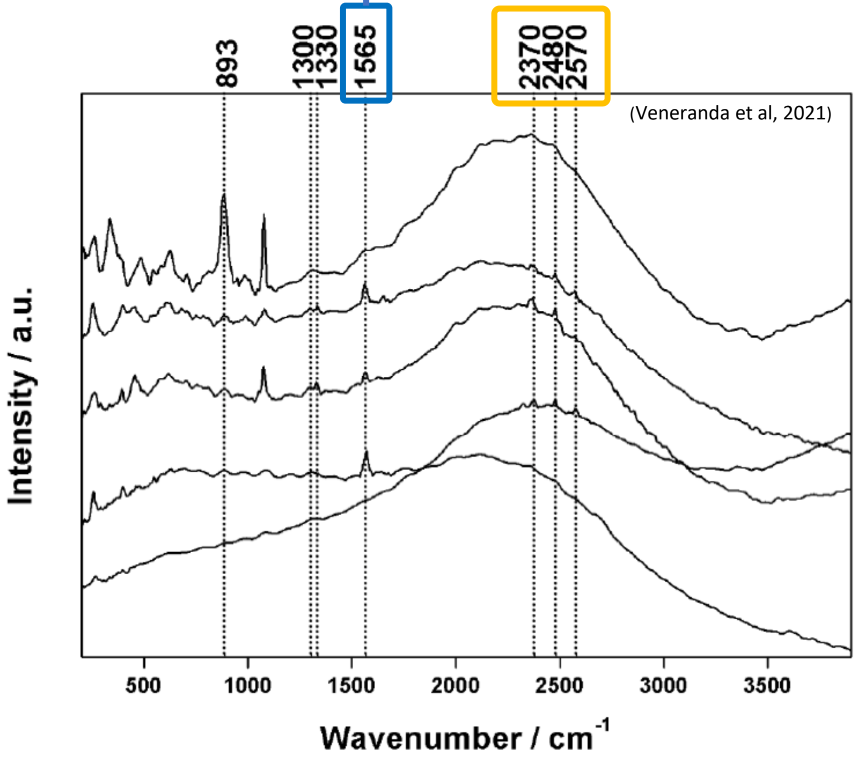
Pyrroline



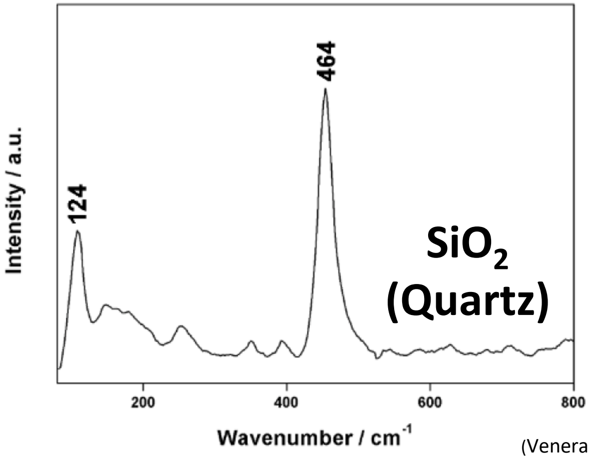
Imidazole

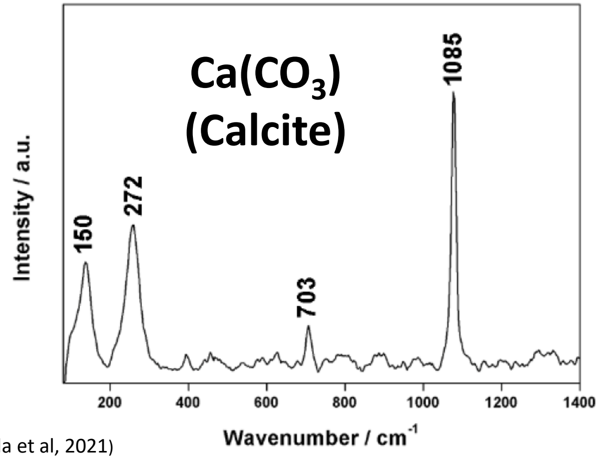


Quinazoline



(Veneranda et al, 2021)





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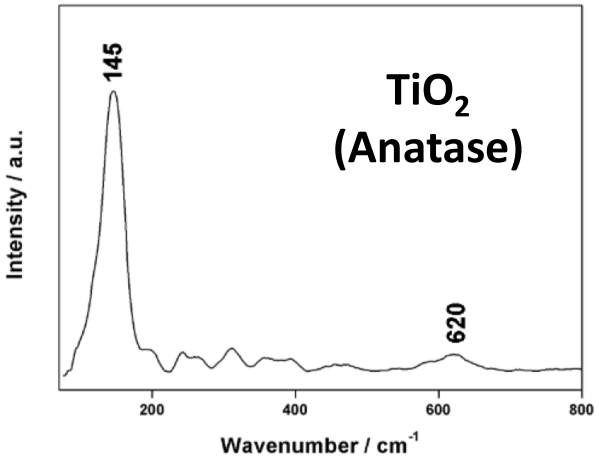
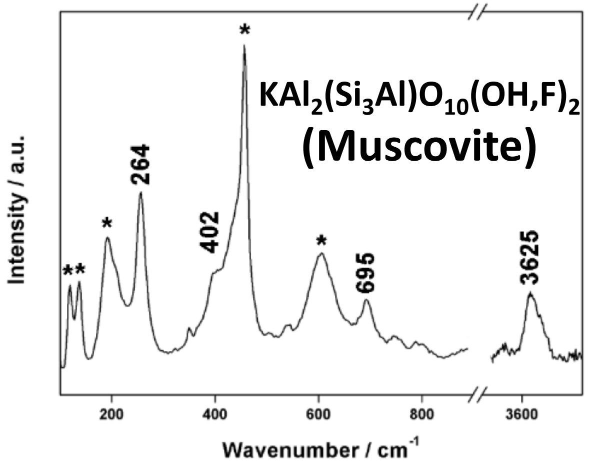
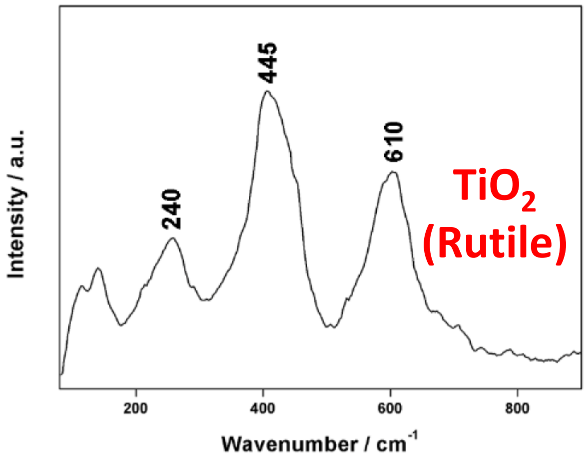
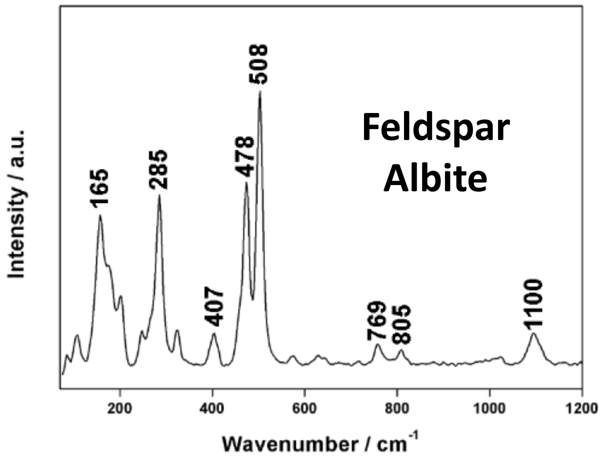








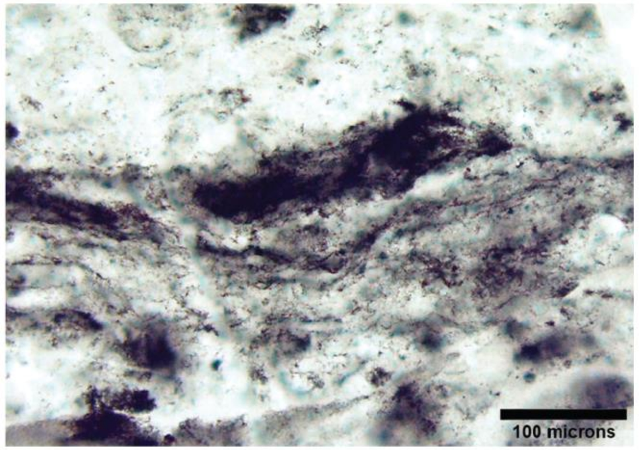
Performance lab tests

Additional performance tests have been performed on specific minerals similar to those expected at the landing site.

Josefsdal Chert (Barberton Greenstone Belt, South Africa)
Hydrothermally-silicified volcanic sediments (among the oldest sedimentary rocks on Earth). <u>They contain the silicified, carbonaceous traces of primitive life forms considered as analogues of primitive life that may have appeared on Mars</u>

Carbonate breccia (Svalbard, Norway)
Carbonates deposited by magnesium-rich, <u>hot hydrothermal waters</u> associated with volcanic activity that cemented basaltic breccia fragments. <u>Considered the closest terrestrial analogs of Martian carbonates found by the Spirit</u>

Synthetic sample
Test performed on synthetic mixture of Gypsum and Calcite. Successfully identified both compound down to 1% of concentration



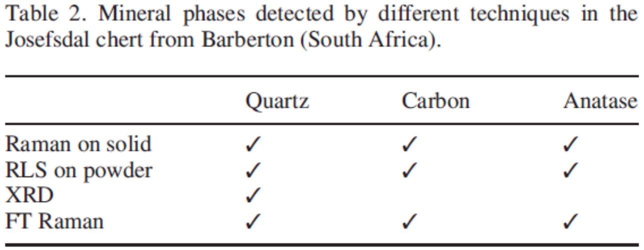
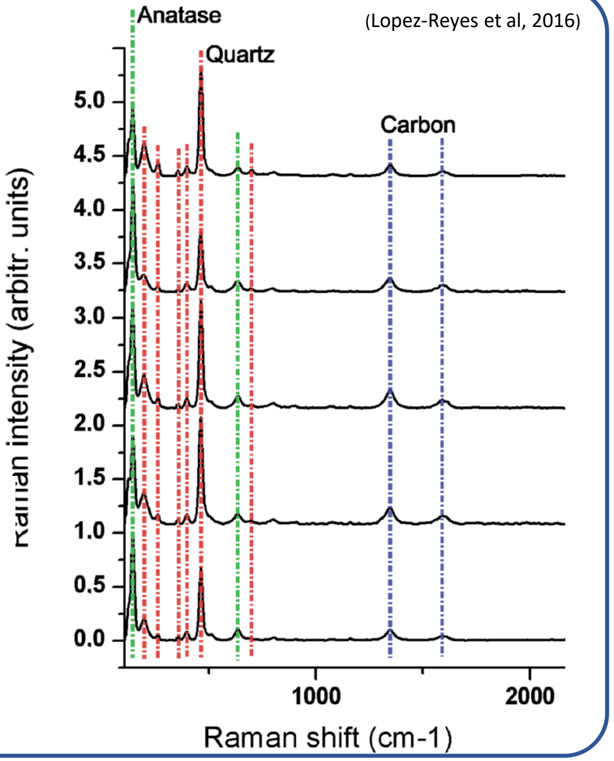
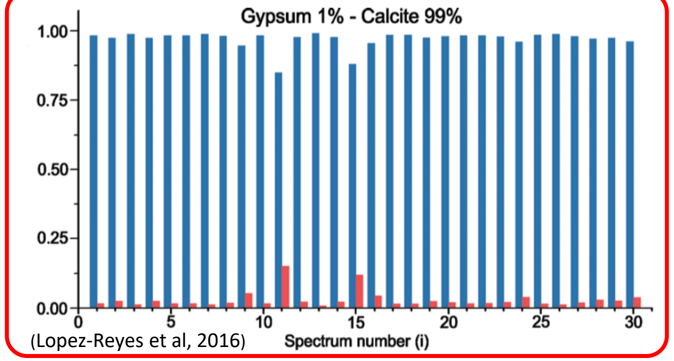


Table 2. Mineral phases detected by different techniques in the Josefsdal chert from Barberton (South Africa).

	Quartz	Carbon	Anatase
Raman on solid	✓	✓	✓
RLS on powder	✓	✓	✓
XRD	✓		
FT Raman	✓	✓	✓



(Lopez-Reyes et al, 2016)



(Lopez-Reyes et al, 2016)

(Lopez-Reyes et al, 2016)

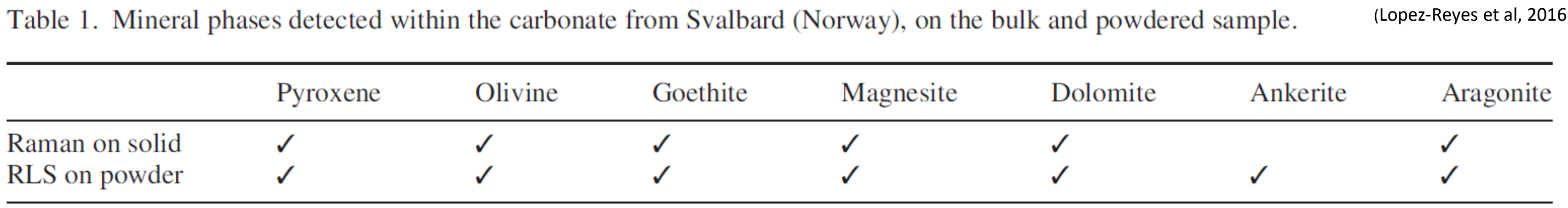


Table 1. Mineral phases detected within the carbonate from Svalbard (Norway), on the bulk and powdered sample.

(Lopez-Reyes et al, 2016)

	Pyroxene	Olivine	Goethite	Magnesite	Dolomite	Ankerite	Aragonite
Raman on solid	✓	✓	✓	✓	✓		✓
RLS on powder	✓	✓	✓	✓	✓	✓	✓

Mission Lunch

<u>The lunch of ExoMars 2022 was expected for 20th September 2022 (window closing on 1st October 2022)</u>

ExoMars is a mission developed in close collaboration with Roscomos (Russian space agency). Because of the Russian aggression towards Ukraine, all collaborations between ESA and Roscomos have been interrupted.

At present, it is unlikely that ExoMars 2022 will be lunched for the expected date.

Josef Aschbacher @AschbacherJosef · 17 mar

Over the past two days, our Member States discussed the impact of the war in Ukraine on ESA's space programmes. Together, we took a tough – but necessary – decision to suspend the launch of ExoMars foreseen for September with Roscosmos, and to study options for a way forward.

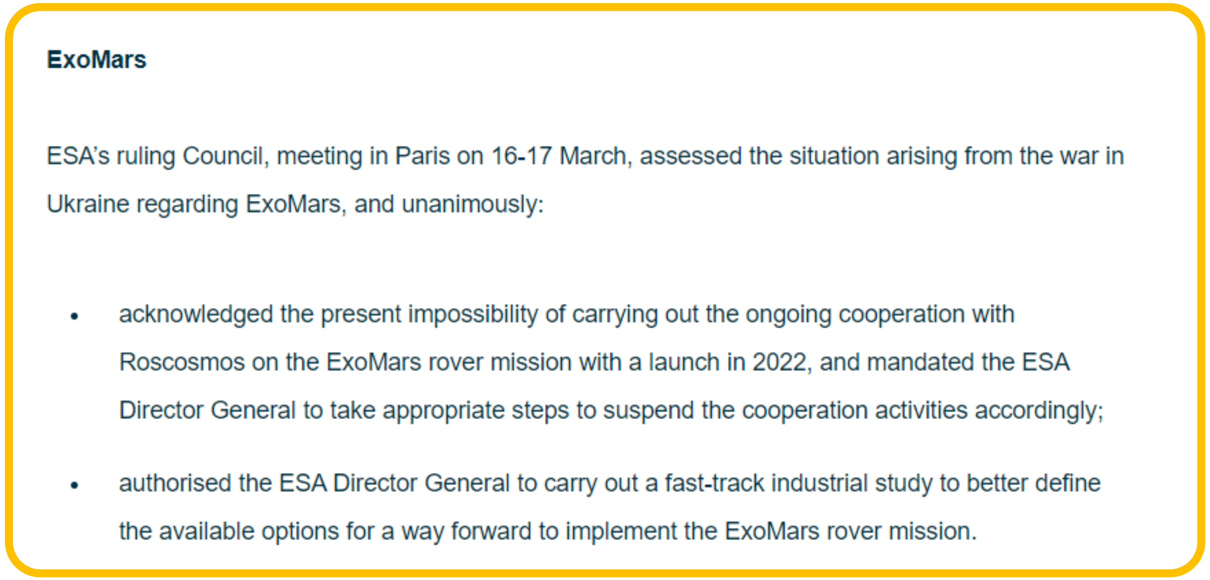
> **ESA** @esa · 17 mar
>
> Statement from ESA Council, 17 March 2022, on the situation arising from the war in Ukraine regarding #ExoMars and other ESA programmes 👉 esa.int/Newsroom/Press...

(Credit: ESA)

Nº 9–2022: ExoMars suspended

17 March 2022

As an intergovernmental organisation mandated to develop and implement space programmes in full respect with European values, we deeply deplore the human casualties and tragic consequences of the aggression towards Ukraine. While recognising the impact on scientific exploration of space, ESA is fully aligned with the sanctions imposed on Russia by its Member States.



ExoMars

ESA's ruling Council, meeting in Paris on 16-17 March, assessed the situation arising from the war in Ukraine regarding ExoMars, and unanimously:

- acknowledged the present impossibility of carrying out the ongoing cooperation with Roscosmos on the ExoMars rover mission with a launch in 2022, and mandated the ESA Director General to take appropriate steps to suspend the cooperation activities accordingly;
- authorised the ESA Director General to carry out a fast-track industrial study to better define the available options for a way forward to implement the ExoMars rover mission.

Final Remarks

☐ ExoMars programme goals:

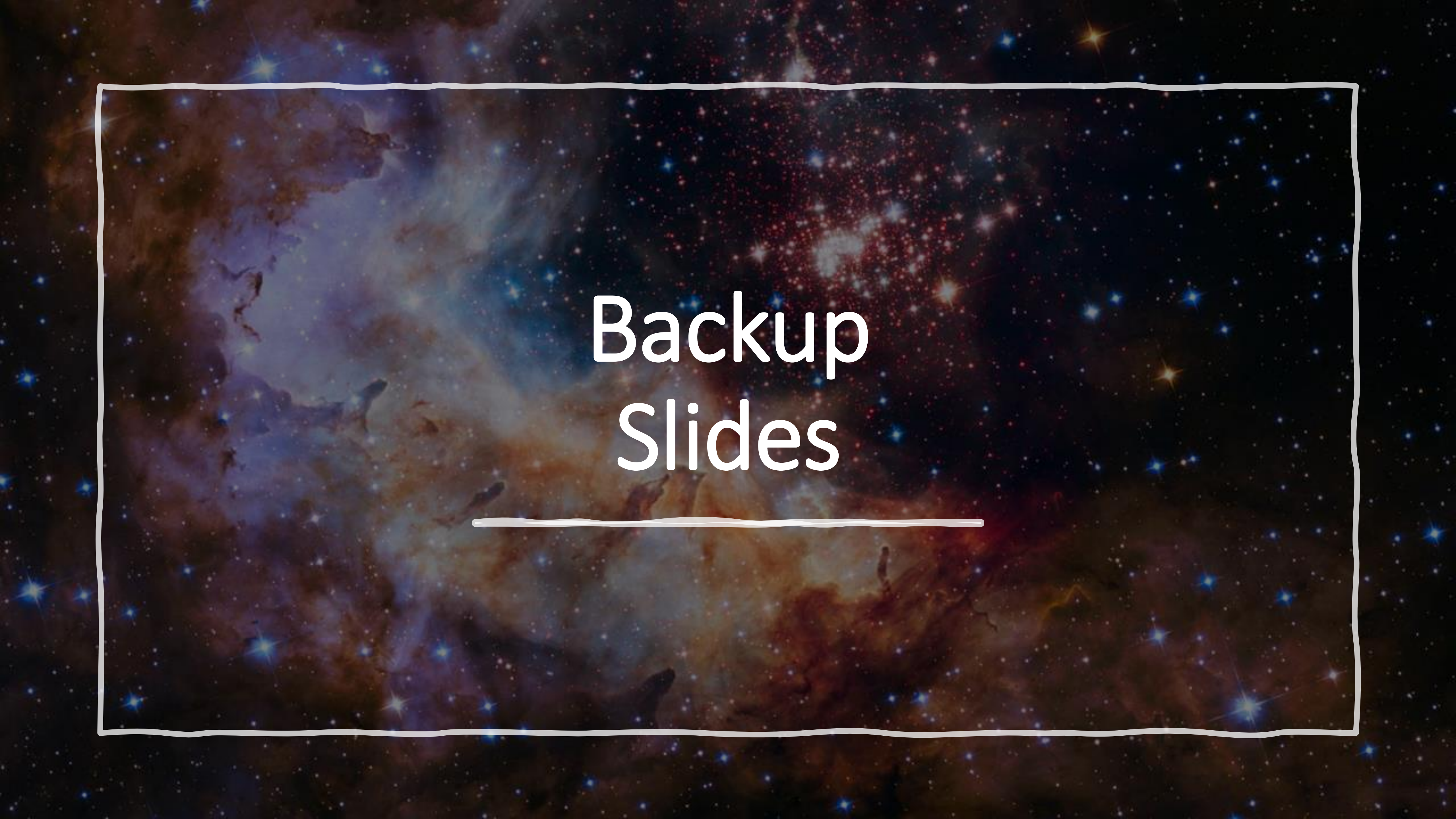
- Search for signs of past and present life on Mars
- Investigate how geochemical environment varies
- Investigate Martian atmospheric trace gases and their sources
- Demonstrate several essential flight and in-situ enabling technologies necessary for future exploration missions.

☐ ExoMars rover is equipped with state-of-the-art instrumentation allowing analysis of the Martian soil as never done before

☐ Included in the rover's Pasteur payload there is the first ever Raman spectrometer (RLS) used in space exploration. The main objective of RLS are:

- Identify organic compound and search for life;
- Identify mineral products and indicators of biologic activity;
- Characterize mineral phases produced by water related processes;
- Characterize igneous minerals and their alteration products;
- Characterize the water/geochemical environment as a function of depth in the shallow subsurface

☐ In-situ and lab test of several Martian-like samples with RLS have successfully proven the suitability of RLS to complete the required scientific objective



Backup Slides

Reference surface mission

After deployment and moving away from the landing site the rover will commence the operation for the **Experimental Cycle** where all the Pasteur instruments will be use for the analysis.

Sol 4-6 expected analysis sequence

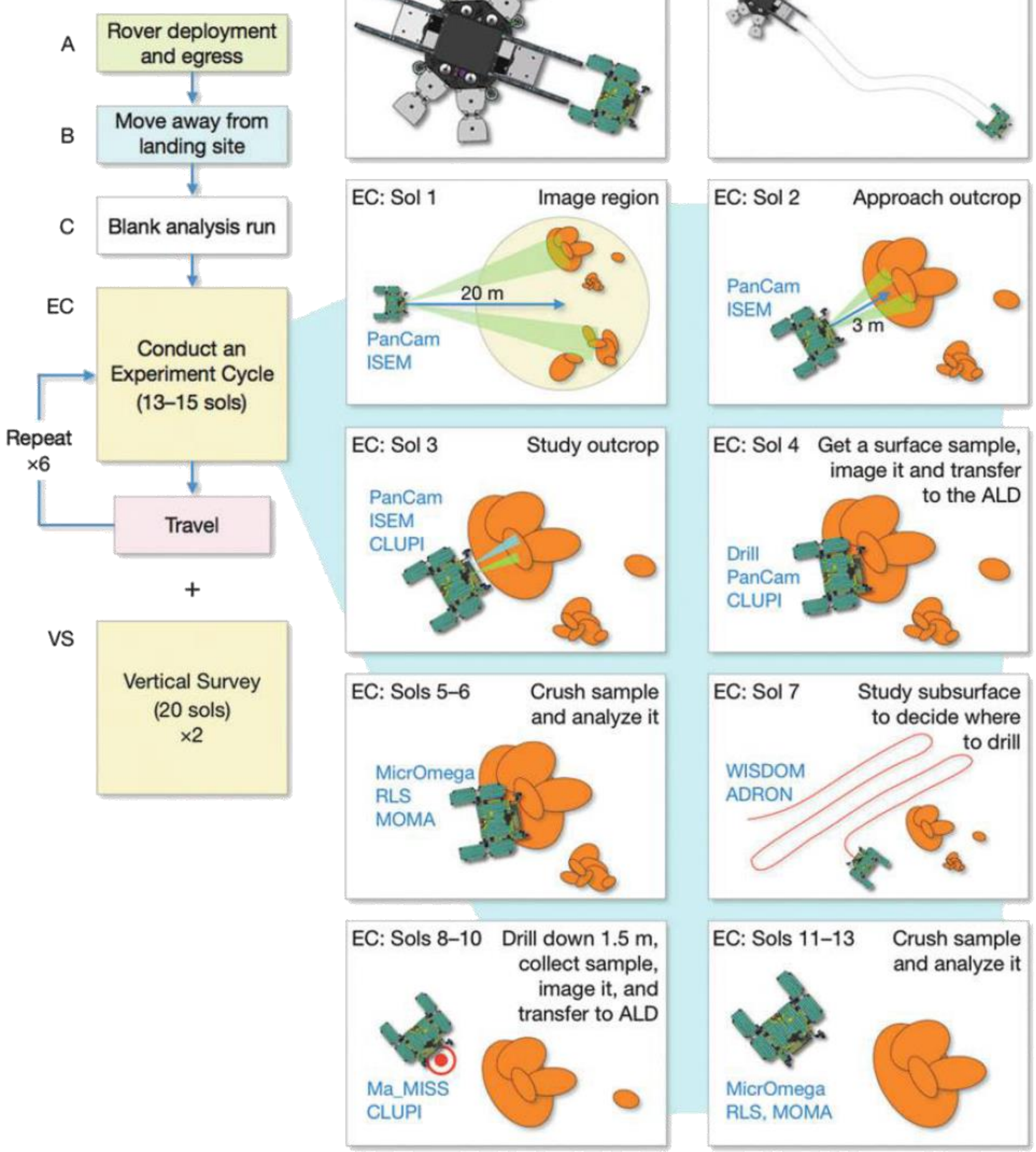
Sample collection
(Sample preparation and distribution system)

Sample crushing
(Sample preparation and distribution system)

RLS+MOMA+LDMS **analysis**

In the first stage, RLS is essential to seek for possible presence of organic material, in order to understand if MOMA and LDMS analysis are necessary or not (slow analysis)

(Vago et al, 2017)



Raman Spectroscopy

Raman spectroscopy is based on the **Raman effect** consisting of inelastic scattering of photons.

Classic vibrational Raman effect

$\vec{p} = \overrightarrow{\mu_0} + \tilde{\alpha}\vec{E}$ Molecule dipole moment (permanent+induced)

$\vec{E} = \vec{E}_0 \cos(\omega t)$ Incident wave

$q_{n_0}(t) = q_{n_0}\cos(\omega_n t)$ Coordinates of nuclear displacement

$$\mu = \vec{\mu}(0) + \sum_{n=1}^{Q}\left(\frac{\partial\vec{\mu}}{\partial q_n}\right)_0 q_n$$

$$\alpha_{ij}(q) = \alpha_{ij}(0) + \sum_{n=1}^{Q}\left(\frac{\partial\alpha_{ij}}{\partial q_n}\right)_0 q_n$$

If electronic charge distribution is determined by the nuclear positions (adjusts “instantaneously”) we can expand the dipole moment and polarizability into Taylor series

$$\vec{p} = \overrightarrow{\mu_0} + \sum_{n=1}^{Q}\left(\frac{\partial\vec{\mu}}{\partial q_n}\right)_0 q_{n0}\cos(\omega_n t) + \alpha_{ij}(0)\vec{E}_0\cos(\omega t) +$$

IR spectrum Rayleigh scattering

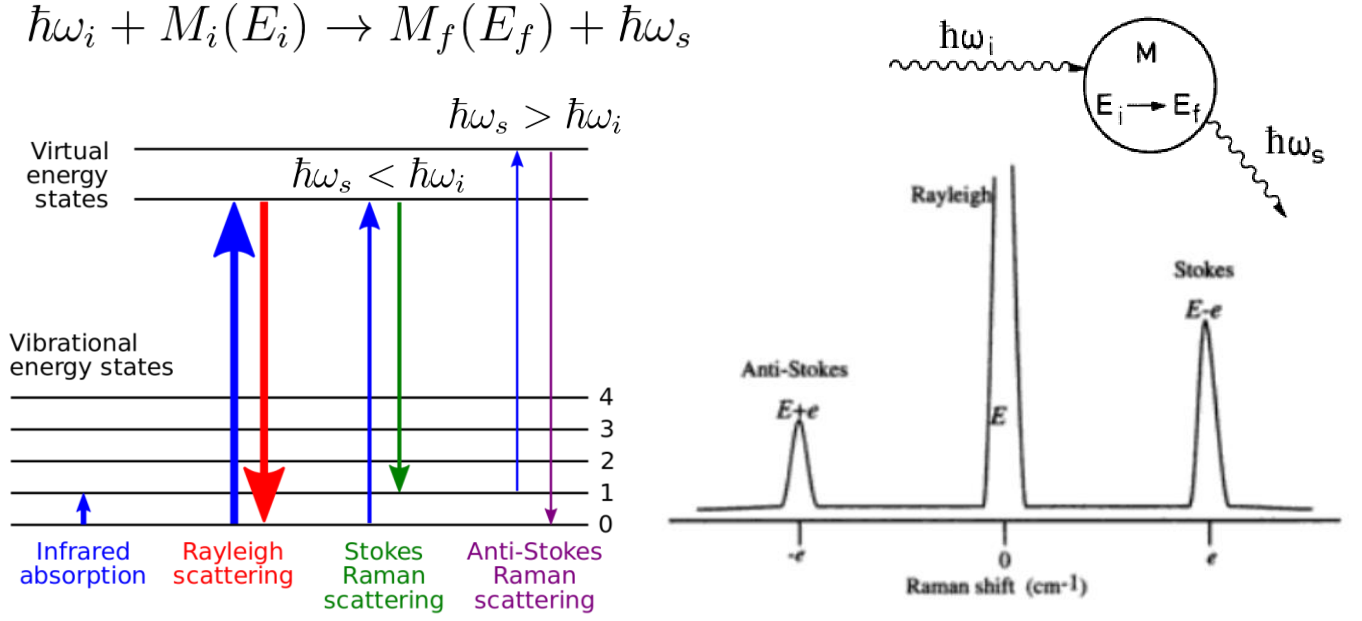
$$+\frac{1}{2}\vec{E}_0\sum_{n=1}^{Q}\left(\frac{\partial\alpha_{ij}}{\partial q_n}\right)_0 q_{n_0}[\cos(\omega+\omega_n)t + \cos(\omega-\omega_n)t]$$

Raman effect

Line intensities

$$I_s = N_i(E_i)\sigma^R_{i\to f}(\alpha_{ij})I_L$$

$$\hbar\omega_i + M_i(E_i) \to M_f(E_f) + \hbar\omega_s$$



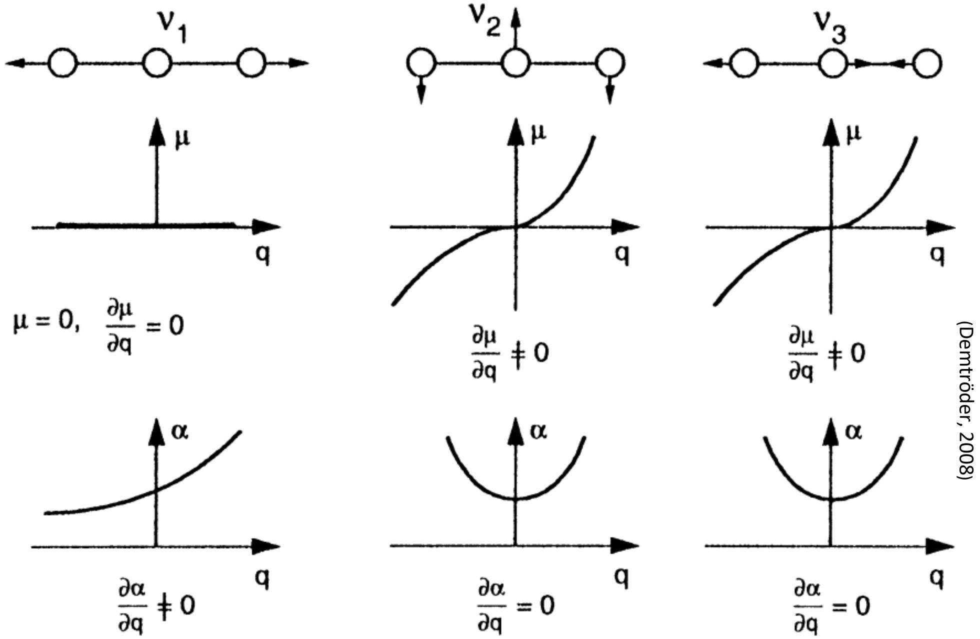


Fig. 3.2. Dependence $\partial\mu/\partial q$ of dipole moment and $\partial\alpha/\partial q$ of polarizability on the normal vibrations of the CO_2 molecule

(Demtröder, 2008)