THE CHALLENGE TO SEARCH FOR ORGANICS AND BIOSIGNATURES ON MARS BY THE EXOMARS-2020 ROVER.

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Introduction: The ESA/Roskosmos Exomars-2020 rover shall be launched on July 24, 2020 and land in Western Arabia Terra [1], Mars, in April 2021. The goals of the mission, in order of priority, are: (i) to search for signs of past and present life on Mars, and (ii) to characterize the water/geochemical environment as a function of depth in the shallow subsurface (ESA, 2016: http://exploration.esa.int/jump.cfm?oid=45082). These goals shall be accomplished over 7-8 months of mission operations and within less than 5 km from the rover's landing site by the following set of tools & instruments: (1) remote sensing instruments to characterize surface (NIR reflectance spectrometer & cameras) and subsurface (radar & neutron spectrometer) nearby the rover, (2) a drill to acquire samples down to 2 m below the surface, and (3) analytical instruments (MicrOmega, a microscopic NIR reflectance spectrometer, RLS [Raman Laser Spectrometer] & MOMA [Mars Organic Molecule Analyzer]) to characterize crushed drill cores [1]. This abstract demonstrates how these instruments are going to be used, which science questions will be addressed, and which questions are beyond the scope of this mission.

Analytical instruments onboard ExoMars-2020: Figure 1 shows the spatial arrangement of the analytical instruments (MicrOmega, RLS, MOMA) in the body of the rover. A subsurface drill core is deposited in the sample port, then crushed and eventually delivered to the refillable sample container that is mounted on the sample carousel. Then it can be investigated by the analytical instruments *in this order*: (i) MicrOmega [2] to detect mafic and alteration phases (as well as some specific organic molecules) at high resolution 20 µm/px within a Field of View 5 x 5 mm^2, (ii) RLS [3] to identify mineral phases and organic compounds within an area 50 µm across, and (iii) MOMA [4, 5] to detect and identify volatile and refractory organics within an area ~300 µm across. Organic blanks (Figure 1) will define the instruments' background (terrestrial organic contaminants). All parts of the rover that are in contact with Martian samples (sample path, refillable container, ovens *etc.*) are sterile (as per *Category-4b* Planetary Protection rules [1]) as a result of the above stated mission goals.

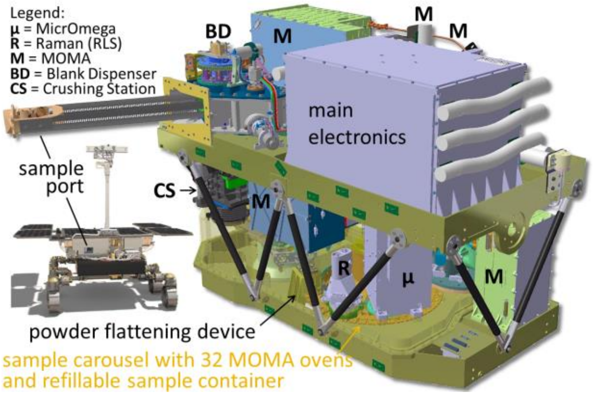

***Figure 1** ExoMars-2020 rover with sample port and analytical instruments in the rover body. Modified from [1].*

Problems of detecting Martian organics and how they are addressed by ExoMars-2020: Martian rocks do contain indigenous organic carbon at ppm level as shown by calculations on meteoritic influx and numerous analyses of SNC meteorites ([6] and refs. therein). However, only recently, it has been possible to detect and characterize sub-ppm levels of Martian organic compounds by the SAM instrument onboard the MSL Curiosity rover [7, 8]. So far a number of facts have limited *in-situ* detection of organics [5]: (i) *Cosmic radiation* (high-energy protons & α-particles) negatively affects biopreservation by steadily fragmenting, cross-linking and oxidizing organics and by depleting the upper 2 m of the Martian surface in organics. It has been shown that the presence of water greatly accelerates this process [9]. Even though hydrous minerals are useful (and widely accepted) proxies for ancient habitability and thus attractive targets for *in-situ* exploration by landers & rovers, these same minerals within the radiation-bathed zone may be "the worst place to look for intact ancient organic molecules on Mars" [9]. (ii) Pyrolysis (> 200-250°C), the preferred organic analysis technique on landed missions so far, leads to (partial) *combustion* of organic compounds due to oxygen release by heated perchlorate (up to 1 wt% in surface rocks & soils). (iii) Pyrolysis does not allow for efficient *extraction* of organic compounds from their host minerals (*e.g.* clays). ExoMars-2020 addresses these problems. Concerning (i): Samples can be acquired down to a depth of 2 meters which is the typical spatial scale for transitioning from radiation-bathed to radiation-free subsurface. Concerning (ii-iii): MOMA offers next to pyrolysis several other experimental techniques (Figure 2) that are insensitive (or much less sensitive) to the presence of perchlorates: (a) LDI (Laser Desorption & Ionization) and (b) several forms of low-T chemical processing of Martian samples (addition of a derivatization agent) that increases the volatility of certain key organic compounds such that they become detectable by Gas Chromatography-Mass Spectrometry (GC-MS). Indeed, LDI has been shown to be insensitive to perchlorates [10]. The same applies to the derivatization techniques, either because they occur at temperatures below the decomposition of perchlorates (such as DMF-DMA, Figure 2) or the derivatization agent protects organics by scavenging short-lived oxidizing radicals that are released during thermal decomposition of perchlorates.

MOMA experiments and their interpretation: MOMA is a highly versatile instrument that can be run in many different ways, some of them presented in Figure 3. Interpretation of mass spectra may be straightforward, but interpretation of MOMA data on a high level is challenging. MOMA will search primarily for signs of ancient life (as preserved in sediments) [4, 5]. In some cases MOMA may be able to distinguish between current and extinct life, although this capability is beyond the instrument requirements.

Assuming positive detection of organic material MOMA's most important goals will be [4, 5]: (1) to assess if the abundances of macromolecular carbon, poly-aromatic hydrocarbons (PAH) & kerogen (as potentially detected by LDI) vary differently on a given spatial scale than those in meteorites, and (2) to assess if potential organic compounds (detected by any MOMA operational mode, Figure 2) are biogenic or abiogenic. Strong chemical biosignatures include (a) an even-to-odd bias in fatty-acids carbon-chain lengths within a fairly limited range of molecular weights, (b) an enantiomeric excess of chiral molecules (such as amino acids or sugars), and (c) the detection of specific high-molecular-weight organic compounds, *e.g.* terpenoids (including hopanes) or peptides [4]. Several (or even all) of these biosignatures and a favorable geologic context will be required to make the claim of signs of ancient life in Martian sediments.

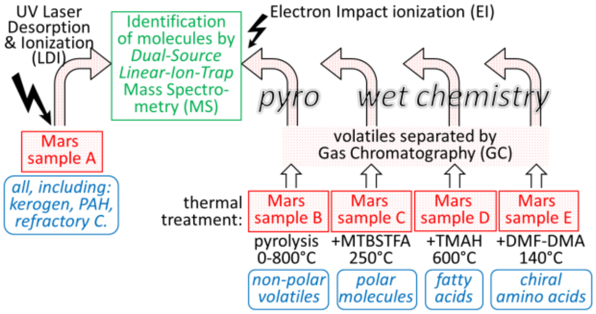

Figure 2 *Overview of MOMA operational modes. Left part: LD-MS mode (grain surface analysis), right part: GC-MS modes (grain bulk analysis), three of them involving a derivatization agent (DMF-DMA or MTBSTFA or TMAH; N,N-**d**i**m**ethyl**f**ormamide-**d**i**m**ethyl **a**cetal, N,N-**m**ethyl**t**ert-**b**utyl-dimethyl**s**ilyl**t**ri**f**luoro**a**cetamide, **t**etra**m**ethyl**a**mmonium **h**ydroxide). "Mars samples" (red): aliquots of crushed drill core. Blue boxes: potential organic target compounds.*

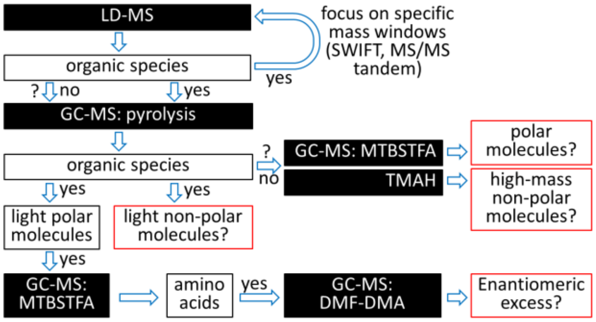

Figure 3 *MOMA decision tree. Modified from [4]. Black-filled rectangles refer to MOMA techniques (Figure 2). Red framed boxes mark the end of an analytical thread.*

Conclusions: The ExoMars-2020 rover has a highly synergetic payload for mineral identification and unprecedented detection & characterization of organic compounds. The project is currently in Flight hardware building & (mainly) testing phase and set for launch in July 2020. By virtue of its payload the mission will have a high science potential in preparation of the next step: Mars Sample Return (MSR)!

References: [1] Vago J. L. et al. (2017) *Astrobiology*, *17*, 471-511. [2] Bibring J.-P. et al. (2017) *Astrobiology*, *17*, 621-627. [3] Rull F. et al. (2017) *Astrobiology*, *17*, 627-655. [4] Goesmann F. et al. (2017) *Astrobiology*, *17*, 655-686. [5] Goetz W. et al. (2016) *Intern. J. Astrobiology*, 15, 239-250. [6] Steininger H. et al. (2012) *Planet. Sp. Sci.*, 71, 9-17. [7] Mahaffy P. R. et al. (2012), *Space Sci. Rev.*, 170, 401-478. [8] Freissinet C. et al. (2015) *J. Geophys. Res. Planets*, 120, doi:10.1002/2014JE004737. [9] Pavlov A. A. et al. (2016) *LPS XLVII*, #2577. [10] Li X. et al. (2015) *Astrobiology*, 15, 104–110.