Biosignature Identification in Habitable Martian Environments

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Timeline for the day

9.45	Room opens	
10:00	Welcome	Session 1: Searching for Biosignatures
10:08-10:35	Frances Westall (Keynote)	
10:35-10.48	J. L. Vago	Searching for Signs of Life with the ExoMars Rover: Why the mission is how it is.
10.48-11:01	S. McMahon	Biogenicity on Mars
11:01-11:14	A. Azua-Bustos	Inhabited subsurface wet smectites in the hyperarid core of the Atacama Desert as an analog for the search for life on Mars
11:14-11:19	M. C. Michael	Testing the habitability of distinct simulated martian environments
11:19-11:24	A. H. Stevens	Ambiguous biosignatures – the problems of identifying life in past habitable environments on Mars
11:24-11:29	S. Sharma	Simulated reaction networks involved in primitive organic reactions that serve as sources of potential biosignatures
	Question and Discussion	
11:34-11:47	F. Foucher	Detection of biosignatures on Mars using Raman spectroscopy
11:47-12.00	M. A. Sephton	Organic reactions and interactions with the minerals of Mars
12:00	Lunch	
12:40	Welcome back	Session 2: Biosignatures in Context
12:42-12:55	A. Parkes-Bowen	Using CaSSIS imagery to characterise and map the Oxia Planum Clay-bearing unit
12:55-13:08	A. C. O'Brien	Characterising Martian Meteoritic Organic Matter using Liquid Chromatography-Mass Spectrometry
13:08-13:21	M. McHugh	Characterising Carbon in Nakhla Meteorite Analogues using the Raman Laser Spectrometer Simulator
13:21-13:26	J. D. Campbell	Laboratory analogues for comparison with CRISM observations for detection of polycyclic aromatic hydrocarbons on Mars
13:26-13:31	S. M. R. Turner	Mineralogy of the Oxia Planum catchment area on Mars
13:31-13:36	G. Cann	Ares Wide search for Organics and Life over Jezero Crater and Oxia Planum
13:36-13:41	A. C. Fox	Position-Specific Isotope Analysis for Identifying Biosignatures in the Geologic Record: Implications for Intramolecular Isotopic Fractionation During Sorption
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13:49-13.55	Break	Session 3: Instruments and Exploration
13.55-14:08	H. N. Lerman	Raman spectroscopy on Mars: organics sensitivity levels
14:08-14:21	C. Schröder	Iron-rich X-ray amorphous material as a target to look for potential organic biosignatures
14:21-14:34	D. P. Glavin	The search for chiral asymmetry as a potential biosignature in samples from mars
14:34-14:39	J-P. de Vera	Lessons learned about biosignature research in Low Earth Orbit and in sediments and its relevance for Life detection missions within Martian sedimentary basins
14:39-14:44	I. Hutchinson	Bio-signature detection with the ExoMars Raman Laser Spectrometer (RLS)
14:44-14:49	R. B. Stabbins	Exploring the limits of VNIR Spectral Imaging of Natural Environments through End-End Simulations
14:49-15:54	M. Ángel Fernández-Martínez	The comprehensive 'MICRO-life detection platform' applied to in situ research at Mars and Icy Moons terrestrial analogs
	Question and Discussion	
15:00-15:28	Roger Wiens (Keynote)	Searches for martian organic materials with NASA's Perseverance rover
	Thank you and Close	
15:30	Room open for networking	
16:00	Ordinary meeting	

Contents

Session 1: Searching for Biosignatures (10.00 – 12.40)

1. Biosignatures for Mars

Frances Westall[1]

[1]*CNRS-Centre de Biophysique Moléculaire, Orléans, France*

The signatures of life as we know it (microbial life) comprise (1) physical structures (e.g. cells, colonies, biofilms, stromatolites); (2) organic molecules (e.g. their molecular/elemental composition; their structure); and (3) evidence of metabolic activity (e.g. isotopic fractionation, concentration of transition metals, biominerals…and more). Perhaps for extraterrestrial life we need to think about "agnostic signatures", *i.e.* generic signatures that indicate some kind of life, but not necessarily life as we know it, e.g. chemical complexity and molecular patterns, molecular complementarity, chemical fractionation, and disequilibrium chemistry and energy transfer.

The signatures of early life on Earth and the environments in which early life lived inform our search for life on Mars. Given the lack of permanent habitability on the planet and the phenomenon of punctuated habitability, life on Mars, if it appeared, will have been (and may still be) very primitive, using simple chemotrophic metabolisms (oxidation of organic or inorganic molecules as an energy source). Unless in a nutrient rich location, e.g. hydrothermal environment, chemotroph development is very limited and difficult to detect, even on the modern Earth. Their fossil biosignatures on Mars will be therefore even harder to detect. Context information from the micro to macroscale is also essential for reliably identifying signatures of life.

The ExoMars 2022 rover payload is a highly complementary suite of instruments that should provide all the necessary context information, as well as identification of potential signatures of life, if the Oxia Planum landing site was inhabited. I will demonstrate how this complementarity could work using examples of Mars-analogue fossil microbes from the Early Earth.

2. Searching for Signs of Life with the ExoMars Rover: Why the mission is how it is

J. L. Vago1, E. Sefton-Nash[1]*, P. Baglioni*[1]*, A. Haldemann*[1]*, the RSOWG*[3]*, the ExoMars Science Working Team, and the ExoMars Project Team,*

[1]*European Space Agency, ESTEC, the Netherlands (jorge.vago@esa.int),* [2]*IKI, Moscow, Russia,* [3]*Rover Science Operations Working Group: F. Altieri, E. Ammannito, A. Ball, M. Balme, W.-S. Benedix, T. Bontognali, J. Bridges, W. Brinckerhoff, J. R. Brucato, D. Bussi, J. Carter, V. Ciarletti, M. C. De Sanctis, F. Didot, Y. Dobrolenskiy, A. G. Fairén, P. Franceschetti, C. Freissinet, , T. Fornaro, F. Goesmann, N. Grand, A. Griffiths, S. Gupta, F. Haessig, A. Haldemann, E. Hauber, B. Hofmann, J.-L. Josset, L. Joudrier, G. Kminek, O. Korablev, D. Koschny, C. Quantin-Nataf, C. Leff, T. Lim, D. Loizeau, , G. López, A. Merlo, I. Mitrofanov, P. Mitschdoerfer, A. Moral Inza, N. Mozhina, S. Nikiforov, A. Pacifici, M. Patel, C. Pilorget, P. Poulakis, F. Raulin, D. Rodionov, O. Ruesch, N. Schmitz, C. Schröder, L. Seoane, S. Sijeström, S. Werner, F. Westall, , L. Whyte, A. Williams, R. Williams, Y. Yushtein, E. Zekri, C. Orgel, E. Sefton-Nash, and J. L. Vago*

ExoMars 2022 was conceived, from the very beginning, to answer one question: Was there ever life on Mars? All project design decisions have focused and continue to center on the achievement of this one scientific objective. This is particularly the case for the Rosalind Franklin rover. Putting the science team in the best possible position to search for physical and chemical biosignatures has led to:

1. The need to have a 2-m depth drill;
2. The choice of payload instruments (including the trade-offs we had to make).
3. The science potential and age of landing site.
4. The surface exploration strategy: which targets, how much traveling, and way the instruments will be used.

This presentation will summarise how and why this came about and what, based on what we know about Oxia Planum today, we may expect to be able to study

3. Biogenicity on Mars

Sean McMahon[1]

[1]UK Centre for Astrobiology School of Physics and Astronomy & School of Geosciences University of Edinburgh

Any biosignatures detected by forthcoming Mars rovers will probably not correspond exactly to our “search images” and may be cryptic, ambiguous, and controversial. Indeed, it may be difficult to discriminate true signs of life from misleadlingly lifelike geochemical and morphological signals produced by abiotic processes on early Mars. Here, I will speculate about three (related) ways in which such “pseudobiosignatures” might have formed in Jezero Crater or at Oxia Planum: “prebiotic” organic chemistry, far-from-equilibrium inorganic chemical reactions, and sediment-water-organic interactions. Experimental work is needed to explore these processes in detail, but some useful predictions can be made already. Further, I will gently critique some of the approaches to biogenicity recommended by palaeobiologists, including strategies based on “biogenicity criteria” and on attempts to falsify over-specific “null hypotheses” for the abiotic origin of ambiguous features. Finally, I will propose a return to the concept of “dubiofossils” as an objective way to describe possible biosignatures provisionally; the utility of the concept will be illustrated with new examples of dubiofossils from Mars-analogue palaeoenvironments on Earth.

4. Inhabited subsurface wet smectites in the hyperarid core of the Atacama Desert as an analogue for the search for life on Mars

Armando Azua-Bustos[1,2]*, Alberto G. Fairén*[1,3]*, Carlos González Silva*[4]*, Daniel Carrizo*[1]*, Miguel Ángel Fernández-Martínez*[1,5]*, Cristián Arenas-Fajardo*[6]*, Maite Fernández-Sampedro*[1]*, Carolina Gil-Lozano*[1,7]*, Laura Sánchez-García*[1]*, Carmen Ascaso*[8]*, Jacek Wierzchos*[8]*, and Elizabeth B. Rampe*[9]*.*

[1]Centro de Astrobiología (CSIC-INTA), 28850 Madrid, Spain. [2]Instituto de Ciencias Biomédicas, Facultad de Ciencias de la Salud, Universidad Autónoma de Chile, Santiago, Chile. [3]Department of Astronomy, Cornell University, Ithaca 14853 NY, USA. [4]Facultad de Ciencias, Universidad de Tarapacá, Chile [5]Department of Natural Resource Sciences, McGill University, Quebec, Canada. [6]Atacama Research, Santiago, Chile. [7]Laboratory of Planetology and Geodynamics, Université de Nantes, 44322 France.

[8]Museo Nacional de Ciencias Naturales (CSIC), 28006 Madrid, Spain. [9]Astromaterials Research and Exploration Science Division, NASA Johnson Space Center, Houston, TX, USA.

The modern Martian surface is unlikely to be habitable due mainly to its extreme aridity. This is the reason why the hyperarid core of the Atacama Desert has been studied as an analog for the habitability of Mars for more than fifty years. Here we report a subsurface layer enriched in smectites in the hyperarid core of the Atacama. We discovered the clay-rich layer to be wet, a trait never observed before in this extremely dry region. Maintaining a high and constant water activity of 0.780, the clay-rich layer is located just 30 cm below the surface, completely isolated from the changing and extremely harsh subaerial conditions characteristic of the Atacama. The smectite-rich layer is inhabited by at least 30 halophilic species of metabolically active bacteria and archaea, unveiling a previously unreported habitat for microbial life under the surface of the driest place on Earth. The discovery of a diverse microbial community in smectite-rich subsurface layers in the hyperarid core of the Atacama, and the collection of biosignatures we have identified within the clays, suggest that similar shallow clay deposits on Mars may contain biosignatures easily reachable by current rovers and landers.

5. Testing the habitability of distinct simulated martian environments

MACEY, MICHAEL C.[1]; Ramkissoon, Nisha K.[1]; Pearson, Victoria K.[1], Schwenzer, Susanne P.[1], Karen Olsson-Francis[1]

1AstrobiologyOU, Open University, Milton Keynes, United Kingdom

Habitability of martian waters would have been partially determined by the chemistry arising from interactions with martian lithologies. In this study, the habitability of groundwater chemistries (based on basaltic, iron- and sulfur-enriched lithologies) and the resulting variation in biosignatures was investigated, with microbes from anaerobic estuarine sediment used as an inoculum. The microbial community was monitored by cell counts and 16S rRNA gene profiling. Changes in fluid and precipitate chemistries were measured using ICP-OES and IC, with changes over geological timescales modelled using CHIM-XPT. The fluid chemistries were shown to be habitable, with distinct patterns in cell abundance and growth phases between the chemistries. However, the same genera dominated (Acetobacterium, Desulfovibrio and Desulfosporomusa) regardless of the initial fluid chemistry. In the biotic test group, changes in fluid chemistry were the same in the three chemistries, with an enhanced concentration of aluminium and iron and the removal of sulfate. However, geochemical modelling of the fluids under abiotic conditions over geological timescales revealed similar changes to those in the biotic test groups. Therefore, these samples require further analysis to assess whether we can identify any potentially unambiguous biosignatures that could develop between geologically distinct sites.

6. Ambiguous biosignatures – the problems of identifying life in past habitable environments on Mars

Adam H. Stevens1 and Charles S. Cockell[1]

[1]UK Centre for Astrobiology School of Physics and Astronomy & School of Geosciences University of Edinburgh

The Perseverance and Rosalind Franklin rovers both aim to explore previously habitable martian environments typified by clay-rich geological systems created by past aqueous activity. We simulated a putative martian sedimentary biome using the Y-Mars analogue material (Stevens et al., 2018) inoculated with a terrestrial microbial community collected from anaerobic lacustrine sediments. Our simulation represents an optimistic scenario for the material sampled by future rovers – martian sedimentary material containing an active microbial community. We also prepared abiotic controls and samples with a single known species (Bacillus subtilis) to allow us to characterise the detectability of biosignatures in this environment.

Samples were characterized biologically using fluorescent cell counting and DNA sequencing and were then analysed using a variety of biosignature detection techniques relevant to the ExoMars rover. The microbial community, under comparable levels of endogenous organic carbon as detected by MSL was diverse but with a low total biomass and was highly dispersed throughout the material. Some of the notable taxa present were presumptive iron-reducers, anoxygenic phototrophs, and heterotrophs. Biosignatures were not detectable in bulk measurements but finer-scale techniques were able to consistently measure potential biosignatures at micrometre scales in biological samples that were not present in abiotic controls. In this presentation we will discuss these results and how the ambiguity of these potential signatures can help guide sampling and analysis methods for planned and future Mars life detection missions.

7. Simulated reaction networks involved in primitive organic reactions that serve as sources of potential biosignatures

Siddhant Sharma[1], Henderson (Jim) Cleaves[1, 2]

[1]Blue Marble Institute of Space Science, USA, [2]Earth Life Science Institute - ELSI, Tokyo Institute of Technology, Japan

Complex chemical reaction networks grow exponentially in terms of the chemical diversity they can generate, the products of these reaction networks can serve as potential biosignatures in Martian environments. We used an automated, rule-based reaction generation to simulate the reaction network generated during the alkaline hydrolysis of glucose, which is a well studied reaction providing ample data for ground-truthing. We applied graph transformation rules based on well-documented reaction mechanisms and restricted by applying various constraints to the outputs, such as disallowed output structural motifs. We used isomorphism tests to match the output molecular structures to experimentally reported structures as a test of the completeness of our methods. The reaction network was further assessed for the existence of potentially autocatalytic loops, whose components might contribute to biosignature identification. This was done by loading the network topology (nodes being compounds and edges being reactions) into a graph database where pattern matching queries could be executed to search for patterns of interest. This work demonstrate efficient methods for finding reaction pathways and autocatalysis in modeled, in silico reaction networks, enabling comprehensive studies of origins of life as well as the identification of primitive organic compounds as potential biosignatures in Martianenvironments.

8. Detection of biosignatures on Mars using Raman spectroscopy

Frédéric Foucher[1] (frederic.foucher@cnrs.fr) and Frances Westall[1]

[1]Centre de Biophysique Moléculaire, UPR 4301, CNRS, rue Charles Sadron, CS80054, 45071Orléans Cedex2, France,

Raman spectroscopy is able to detect both organic and mineral phases and is very sensitive to carbonaceous matter and biomolecules. It is thus particularly suited for the detection of biosignatures associated with present or ancient life. Thus, in the framework of the future missions to Mars dedicated to the search for traces of life on Mars (Mars 2020, NASA; ExoMars 2022, ESA/RosCosmos; Mars Sample Return, NASA/ESA), this method is extremely useful. Nevertheless, the sample preparation systems and the Raman spectrometers on-board the rovers are limited with respect to laboratory devices. These differences must be considered in preparation of these future missions.

In this presentation, the different aspects of Raman spectroscopy applied to biosignature characterisation will be described. The search for these biosignatures in situ on Mars and during the analyses of the samples brought back to Earth will then be discussed.

9. Organic reactions and interactions with the minerals of Mars

Mark A. Sephton[1], Jonathan Tan[1], Sam Royle[1], Wren Montgomery[1] and Jonathan Watson[1]

[1]Department of Earth Science and Engineering. Imperial College London,

Mars is not the Earth. The minerology of the red planet contains inorganic components that aggressively deter organic preservation including perchlorates along with iron-containing clays, oxides and oxyhydroxides. The minerals of Mars, therefore, present a challenge for missions that aim to detect organic evidence of past life on our nearest planetary neighbour. Fortunately, Mars analogue sites on Earth provide opportunities to simulate the mechanisms of organic preservation on Mars and the potential to develop mitigation strategies for future attempts at seeking evidence of past Mars life. Mars organic preservation steps require a greater understanding. Areas of research explored include how the entombment of organic remains relies on mineral components generated in habitable settings, how the storage of organic matter in the subsurface of Mars is hampered by the kinetics of organic-mineral interactions, how the exhumation of organic-containing rocks can introduce preservation bias, and how analyses of organic-containing samples can lead to further degradation. The Imperial College Organic Geochemistry group has been addressing these issues and providing suggested mitigation and interpretation strategies to help with the search for past life on Mars.

Session 2: Biosignatures in Context (12.40 – 13.50)

10. Using CaSSIS imagery to characterise and map the Oxia Planum Clay-bearing unit

Adam Parkes Bowen[1] (acdpb1@le.ac.uk), Lucia Mandon[2], John Bridges[1], Cathy Quantin-Nataf[2], Livio Tornabene[3], James Page[1], Jemima Briggs[1], Nicolas Thomas[4], and Gabriele Cremonese[5]

[1]Space Research Centre, University of Leicester, UK, [2]Université de Lyon, France, [3]CPSX, Western University, Canada, [4]Universität Bern, Switzerland, [5]Astronomical Observatory of Padova-INAF, Italy

Our current understanding of the extent of the clay unit at Oxia Planum is based in large part on spectroscopy data from the OMEGA and CRISM instruments. While this has been useful in identifying candidate clays at the site, as well as for creating a broad map of the unit, these maps are limited by the nature of the instruments used to create them. Much of the mapping has been done using 300m/pixel OMEGA or 100m/pixel CRISM data, and, even with small portions of the landing site having 18m/pixel CRISM hyperspectral data available, the existing clay maps are insufficient for anything but the most high-level traverse planning of the rover.

Use of Colour and Stereo Surface Imaging System (CaSSIS) imagery[1] offers a way to improve this. Work carried out by members of the CaSSIS team showed that certain CaSSIS band ratios can identify the presence of ferric/ferrous minerals[2]. In a more recent study currently going through review[3], CaSSIS, along with co-analysis from CRISM and HiRISE colour imagery, identified that at least two spectrally and morphologically distinct subunits make up the Oxia clay unit. These were a lower member, appearing orange in HiRISE colour imagery, showing metre-scale fracturing and spectral signatures of Fe/Mg-rich clay minerals associated with hematite; and an upper member, blue in HiRISE colour, showing decametre scale fracturing with an Fe/Mg-rich clay mineral/olivine signature.

This work also showed that the ferric detections within band ratioed CaSSIS imagery correlated very well with CRISM clay detections. It was also shown that the lower member appears much more ferric in CaSSIS imagery than the upper member. Following this study CaSSIS, in conjunction with HiRISE greyscale imagery to observe fracture size, are being used to map these sub-units. As CaSSIS has a higher resolution at 4.5m/pixel, and will have near 100% coverage of the landing site by the time of the rover's launch, CaSSIS can be used to create a clay map with improved resolution and coverage in comparison to what is currently available.

References; 1; Thomas, N., et al. (2017). "The Colour and Stereo Surface Imaging System (CaSSIS) for the ExoMars Trace Gas Orbiter." Space Science Reviews 212(3-4): 1897-1944. 2; Tornabene, L. L., et al. (2017). "Image Simulation and Assessment of the Colour and Spatial Capabilities of the Colour and Stereo Surface Imaging System (CaSSIS) on the ExoMars Trace Gas Orbiter." Space Science Reviews 214(1). 3; L. Mandon, A. P. B., C. Quantin-Nataf, J. C. Bridges, J. Carter, L. Pan (in review). "Spectral Diversity and Stratigraphy of the Clay-Bearing Unit at the Exomars 2020 Landing Site Oxia Planum." Astrobiology

11. Characterising Martian Meteoritic Organic Matter using Liquid Chromatography- Mass Spectrometry

A. C. O'Brien[1] (a.obrien.1@research.gla.ac.uk), L. J. Hallis[1], A. Tait[2], D. Morrison[3], P. Ascough[3], A. Steele[4], L. Daly[1], M. R. Lee[1]

[1]University of Glasgow, [2]Monash University, [3]Scottish Universities Environmental Research Centre, [4]Carnegie Institute of Washington Geophysical Laboratory

A key aim in the assessment of martian habitability is the availability of organic matter (OM), since organics form the basis of all terrestrial life. The Rosalind Franklin and Perseverance rovers are both equipped with substantial instrument suites designed for the detection of organics. Furthermore, Perseverance will be caching some of the most promising biomarker-containing soil samples ready for in depth analysis on Earth, due to the greater range of techniques that can be used. Prior to Mars Sample Return we must have robust protocols in place to maximise the scientific understanding from samples.

Many martian meteorites contain OM in the form of macromolecular carbon hosted in igneous minerals; data analysis from the SAM instrument onboard Curiosity has shown similar OM is present at Gale Crater. Previous work has used spectroscopic techniques such as Raman spectroscopy and XANES to detect individual inclusions of martian meteoritic OM *in-situ* in thin sections. These techniques determine the presence of organics and suggestions of structure e.g. identification of organic functional groups with XANES, but not full molecular structure.

Recently, we have been developing and testing protocols to use bulk analysis mass spectrometry techniques to detect and fully characterise OM in crushed powders of the martian meteorites Lafayette and Nakhla, as well as martian analogues and simulants. OM was extracted using organic solvents hexane, dichloromethane and methanol. These extractions were then analysed using liquid chromatography mass spectrometry (LC-MS).

Through comprehensive addition of blanks throughout the process, as well as comparison with terrestrial analogues and simulants, we were able to rule out lab contaminants and identified a number of possible martian organics. One such molecule was butanesulfonate, a sulfur-containing hydrocarbon. Finding molecules such as this is a promising result since the Curiosity rover detected thiophenes – sulfonated ring structures – in 2018. We hope to revisit these samples to attempt to obtain deuterium/hydrogen ratios to determine whether or not they are martian. We also detected some likely terrestrial contaminants, some of which may help constrain the unknown fall scenario of the Lafayette meteorite. We also investigated the oxidising effect of perchlorate salts on (non-martian) meteoritic OM by treating crushed samples of Jbilet Winselwan, a CM2 carbonaceous chondrite, before extracting the OM. We found the OM content varied hugely with perchlorate concentration, with some molecules increasing with perchlorate concentration and others decreasing with perchlorate concentration.

12. Characterising Carbon in Nakhla Meteorite Analogues using the Raman Laser Spectrometer Simulator

Melissa McHugh[1], I.B. Hutchinson[1], H.N. Lerman[1], H.G.M. Edwards[1], J. Parnell[2], A. Moral, C. Perez[3], G. Lopez-Reyes[4], F. Rull[4]

[1]University of Leicester, [2]University of Aberdeen, [3]INTA, Madrid [4]Centre de Astrobiologia, Valladolid

In preparation for the launch of ExoMar's Rosaline Franklin rover in 2022, the Raman Laser Spectrometer (RLS) instrument team have been characterising the response of the instrument and its sensitivity limits to key target materials such as carbonaceous material (important for understanding the preservation or alteration of organic material).

This study focuses on reduced carbon within basaltic material, analogous to that expected at Oxia Planum. Simple reduced carbon structures are expected to be present on the Martian surface as a result of volcanic erosion, meteor bombardment or as a product of ancient biological processes. Veinlets of carbonaceous matter have also been observed in Nakhla meteorites and have been highlighted as evidence for reduced carbon on Mars.

Here we present the Raman analysis of a Nakhla meteorite analogue sample recovered from an area of ancient carbon-bearing lava flow in the UK using the RLS Simulator, located at the Centre de Astrobiologia. The basaltic sample contains a large quantity of embedded organic carbon, thermally altered through geological processes. We discuss how the thermal history of the sample might affect the Raman spectra observed, review the level to which such signatures can be identified by a flight representative instrument, and hence infer how the performance of the RLS during mission operations.

13. Laboratory analogues for comparison with CRISM observations for detection of polycyclic aromatic hydrocarbons on MarsTitle

Jacqueline D. Campbell[1], Bernard Schmitt[2], Olivier Brissaud[2] and Jan- Peter Muller[1]

[1]Imaging Group, Mullard Space Science Laboratory, UK, [2]l'Institut de Planétologie et d'Astrophysique de Grenoble

A series of laboratory experiments was carried out in order to generate a diagnostic infrared (IR) spectrum for Polycyclic Aromatic Hydrocarbons (PAHs) of astrobiological interest in the context of the Martian South Polar Residual Cap (SPRC) and Recurring Slope Lineae (RSL).

PAHs are a group of chemical compounds considered to be a 'building block' for life and can also be a biomarker for extant life. While they are abundant on Earth and throughout space, PAHs have not been discovered on Mars. Dynamic SPRC and RSL features may expose material that has previously been shielded from harmful UV radiation, and are therefore candidate sites for PAH detection using orbital hyperspectral imaging. Here we use the parameters of the (Compact Reconnaissance Imaging Spectrometer for Mars) CRISM instrument as a basis for the laboratory experiments, to constrain the detectability limit of PAHs, and to establish PAH spectral features at wavelengths other than the well-known absorption features previously established.

The detectability limit of PAHs was established within SPRC and RSL laboratory analogues, end member spectra have been derived for all components of interest, and new diagnostic absorption features for PAHs have been recorded at a number of wavelengths. For RSL analogues, we found that drying brines within soil samples increased the detectability of PAHs compared with soil samples devoid of salt. This work provides the data necessary to improve interpretation of orbital data and will form the basis of research of dynamic features on Mars in order to detect organic material, and contribute to the search for habitable environments on Mars.

14. Mineralogy of the Oxia Planum catchment area on Mars

S. M. R. Turner[1] and P. Fawdon[2]

[1]AstrobiologyOU, School of Environment, Earth and Ecosystem Sciences, Faculty of Science, Technology, Engineering and Mathematics, The Open University, Milton Keynes, UK. [2]School of Physical Sciences, Faculty of Science, Technology, Engineering and Mathematics, The Open University, Milton Keynes, UK.

The European Space Agency's ExoMars Rosalind Franklin rover is scheduled to launch in 2022, with the goals of searching for signs of past and present life on Mars by investigating the geochemical environment in the shallow subsurface and characterising the surface environment [1]. The selected landing site for the mission, Oxia Planum, is a clay bearing plain approximately 200 km wide at the margin of Chryse Planitia [2]. Remote sensing with OMEGA and CRISM spectral datasets have previously been used to identify a widespread, mid-noachian Fe/Mg-clay unit overlain by younger, late-noachian aged delta-fan enriched in silica to the south-east [3,4,5]. The delta-fan has been identified as an outlet for a large catchment area which spans ~2.1 × 10^5 km^2 [6]. In this presentation we show early results of CRISM spectral analysis of the Oxia Planum catchment area, with comparisons to reported findings within the ExoMars rover landing ellipses. This work aims to develop the geological context for the clay detections within the ExoMars rover landing site, and may have implications for biomarkers as these may have formed in the catchment area and transported into the landing site.

[1] Vago, J.L., et al., 2017. Astrobiology, 17(6-7), pp.471-510. [2] Quantin-Nataf, C., et al., 2019. Ninth International Conference on Mars. LPI Contrib. No. 2089, pp. 6317. [3] Carter, J., et al., 2019. EPSC Abstracts Vol. 13, No. 445. [4] Carter, J., et al., 2016. LPSC Vol. 47, No.2064. [5] Turner, S.M.R., and Bridges, J.C., 2017. LPSC Vol. 48, No.2228. [6] Fawdon, P., et al., 2019. LPSC Vol. 50, No.2356.

15. Ares Wide search for Organics and Life over Jezero Crater and Oxia Planum

George Cann[1] (george.cann.15@ucl.ac.uk), Ahmed Al-Rafaie[2], Ingo Waldmann[2], Dave Walton[1], and Jan-Peter Muller[1]

[1]Imaging Group, Mullard Space Science Laboratory, Department of Space and Climate Physics, University College London, London, UK. Email. [2]Department of Physics and Astronomy, University College London, London, UK.

Since its tentative detection in 2003[1, 2], the nature of methane, CH_4 (a possible biosignature), on Mars has caused controversy [3, 4]. The discrepancy between surface and orbital CH_4 measurements, significantly constrains the mechanisms of production and destruction, that are needed to corroborate the measurements[5][6]. Abiotic and biotic sources of CH_4 having been suggested to explain the detection, ranging from Fischer-Tropsch-type (FTT) reactions to methanogenesis by methanogenic archaea [7, 8].

Here we consider the Martian atmosphere over Jezero Crater and Oxia Planum, with regard to the search for organics and life, using the Ares atmospheric retrieval code [9]. Ares is an extension of the TauREx3 exoplanetary atmospheric retrieval framework [10, 11], designed for retrieving trace gases from the European Space Agency's (ESA) ExoMars Trace Gas Orbiter (TGO) Nadir and Occultation for MArs Discovery (NOMAD) instrument, for Solar Occultation (SO) channel measurements.

We will present how Ares may help to unravel the true nature of CH_4, through producing marginalised and conditional posterior distributions of Ares forward model parameters (e.g. temperature, trace gas abundances, etc.), which can in turn be used to map correlations between these parameters. In addition to CH4 we discuss the search for possible signals of derivatives, namely methanol, CH_3OH, and formaldehyde, H_2CO [12]. Finally, we examine how dimensionality reduction methods, such as Uniform Manifold Approximation and Projection (UMAP) [13], could be applied with Ares posteriors to separate mechanisms for trace gas production and destruction.

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16. Position-Specific Isotope Analysis for Identifying Biosignatures in the Geologic Record: Implications for Intramolecular Isotopic Fractionation During Sorption

A. C. Fox[1], E. Martineau[2,3], G. S. Remaud3, and Katherine H. Freeman[1]*

[1]Pennsylvania State University, University Park, Pennsylvania, USA, [2]SpectroMaitrise, CAPACITÉS, 26, bd Vincent Gâche - 44200 Nantes, France, [3]Université de Nantes, CNRS, CEISAM UMR 6230, F-44000 Nantes, France

Intramolecular isotope patterns reflect the synthetic pathway of organic molecules, and may prove to be a valuable tool in studying the origins of extraterrestrial organic material. However, intramolecular isotope patterns are also sensitive to interactions occurring between organic material and its environment, such as sorption to mineral surfaces. Sorption is a key process that both protects organics from oxidation and aids in their polymerization into complex molecules. Sorption interactions are driven by a combination of intermolecular forces between organic molecules and mineral surfaces, which may be influenced by isotopic substitutions. While global (whole-molecule) C isotope fractionation associated with sorption is small (< 1 ‰), larger fractionation of C isotopes (> 2 ‰) was observed for specific positions within a molecule during chromatographic separation, indicating that fractionation during sorption is likely more significant at positions interacting with the surface. To quantify the position-specific isotopic fractionation, we used quantitative isotopic 13C NMR to measure position-specific C isotopic distributions within glycine, L-alanine, L -serine, L -leucine, and L -phenylalanine sorbed to an ice surface from an aqueous solution. Isotopic differences up 8.5 ‰ at functional sites were observed between sorbed and free amino acids, suggesting that sorption can alter primary isotopic patterns associated with their synthesis. Further, position-specific isotopic fractionation appears to reflect the orientation of an amino acid on the ice surface. Sorbed amino acids with non-polar side chains displayed a large 13C-depletion in the carboxyl carbon, consistent with hydrogen bonding between the carboxyl group and hydroxyl groups on the ice surface. Hydrogen bonding at the carboxyl carbon lessens its electron density and promotes peptide bond formation via nucleophilic attack by another amino acid, which could explain the dominance of amino acids with non-polar side chains in modern proteins.

Session 3: Instruments and Exploration (13.55 – 15:30)

17. Raman spectroscopy on Mars: organics sensitivity levels.

H.N. Lerman1, I.B. Hutchinson1 Melissa McHugh1, H.G.M. Edwards1, J. Parnell2, A. Moral, C. Perez3, G. Lopez-Reyes4, C. Cockell[4]

[1]University of Leicester, [2]INTA, Madrid, [3]Centre de Astrobiologia, Valladolid, [4]University of Edinburgh,

In 2018, Oxia Planum was selected as the most suitable landing site for ExoMars2022 rover, given its primary scientific objective, which is to search for signs of past or present life on the surface and in the shallow sub surface. Orbital data from the region suggest substantial evidence for long-term water activity and potentially habitable conditions, such as a substantial clay unit that contains smectites (Fe/Mg-rich saponite) which are considered to be likely sites for organic material preservation. Raman spectroscopy is a powerful analytical technique that is sensitive to the specific molecular composition and chemical structure of a material, including the hydration states related to the environmental condition. It is therefore a high priority technique for searching for biomarkers, organics, and other signs of life processes, which may be preferentially preserved at Oxia Planum, i.e. through identification of spectral bands in the 1150 - 2000 cm^{-1} range. Specifically, the Raman technique is sensitive to the pigments that organisms produce to enable them to survive within the environment, and is able to identify biomolecules. The Raman spectrometer on-board the Rosalind Franklin rover utilises a green laser, since this wavelength produces an optimal response from organic materials, and in this presentation, we report on data obtained with early versions of the flight spectrometer, that highlight the sensitivity levels of the instrument to such molecules (e.g. analysis of: organic/clay, carotenoids, and CHNOPS relevant samples).

18. Iron-rich X-ray amorphous material as a target to look for potential organic biosignatures

Christian Schröder[1] *(christian.schroeder@stir.ac.uk)*

[1]Biological and Environmental Sciences, University of Stirling, Stirling FK9 4LA,

Iron minerals play a key role in the sequestration of carbon. Over 20% of organic carbon in sediments on Earth is directly bound to reactive iron phases (Lalonde et al. 2012), also dubbed the Rusty Carbon Sink. The organic matter-iron mineral complexes mutually stabilize each other against organic matter degradation and mineral transformation, whereby the iron species involved often occur in nanoparticulate and X-ray amorphous forms (Schröder et al. 2016). Upon diagenesis, however, the redox properties of iron facilitate the oxidation of organic matter (Posth et al. 2013; Schröder et al. 2016; Sephton paper). On that basis, a good target for the search for potential organic biosignatures would be rich in nanophase iron phases and X-ray amorphous minerals. Aqueously altered rocks and soils investigated in Gusev crater and at Meridiani Planum on Mars contain abundant nanophase iron oxides (e.g. Morris et al. 2019), and 20-60 wt% of minerals in fluvio-lacustrine deposits in Gale crater are X-ray amorphous and this amorphous phase is rich in iron (e.g. Rampe et al. 2017, 2019). Similar deposits should be targeted in Jezero crater and at Oxia Planum to look for organic biosignatures.

Lalonde, K., et al., (2012), Preservation of organic matter in sediments promoted by iron, *Nature*, Morris, R.V., et al., (2019), Chapter 27: Iron Mineralogy, Oxidation State, and Alteration on Mars from Mössbauer Spectroscopy at Gusev Crater and Meridiani Planum, *Remote Compositional Analysis: Techniques for Understanding Spectroscopy, Mineralogy, and Geochemistry of Planetary Surfaces*, Posth, N.R., et al., (2013), Simulating Precambrian banded iron formation diagenesis, *Chemical Geology*, Rampe, E.B., et al., (2017), Mineralogy of an ancient lacustrine mudstone succession from the Murray formation, Gale crater, Mars, *Earth and Planetary Science Letters*, Rampe, E.B., et al., (2019), The mineralogical record of ancient fluvio-lacustrine environments in Gale crater as measured by the MSL CheMin instrument, Abstract # 6054, Ninth International Conference on Mars, Schröder, C., I. et al., (2016a), The biogeochemical iron cycle and astrobiology, *Hyperfine Interactions,* Tan, J. and M.A. Sephton (2020), Organic Records of Early Life on Mars: The Role of Iron, Burial, and Kinetics on Preservation, *Astrobiology*.

19. The Search For Chiral Asymmetry as a Potential Biosignature in Samples From Mars

D. P. Glavin[1], A. S. Burton[2], J. E. Elsila[1], J. C. Aponte[1,3], and J. P. Dworkin[1]

[1]NASA Goddard Space Flight Center, Greenbelt MD, USA, [2]NASA Johnson Space Center, Houston TX, USA, [3]Catholic University of America, Washington DC, USA.

The search for evidence of extraterrestrial life in our solar system is currently guided by our understanding of terrestrial biology and its associated biosignatures. The observed homochirality in all life on Earth, that is, the predominance of “left-handed” or L-amino acids and “right-handed” or D-sugars, is a unique property of life that is crucial for molecular recognition, enzymatic function, information storage and structure and is thought to be a prerequisite for the origin or early evolution of life. Therefore, the detection of L- or D-enantiomeric excesses of chiral amino acids and sugars could be a powerful indicator of extant or extinct life on Mars or other habitable environments in our solar system. The exploration of habitable environments on Mars, including an assessment of the preservation potential for complex organics of either abiotic or biological origin, remains a key goal of both current and future Mars missions. Now with the unambiguous detection of indigenous organic matter in sedimentary rocks on Mars [1-3], NASA’s Curiosity rover has significantly advanced our understanding of the preservation of potential chemical biosignatures in the martian near surface. Although amino acids have not yet been identified by *in situ* measurements on Mars, if they were present, it is expected that amino acid hydrolysis and racemization would be very slow and any chiral or isotopic signatures from an extinct martian biota could be preserved for billions of years, given the extremely cold and dry surface conditions [4]. One of ESA’s Rosalind Franklin rover payload instruments called the Mars Organic Molecule Analyzer (MOMA) includes a wet chemistry package capable of measuring the enantiomeric ratios of any chiral amino acids present at part-per-million concentrations or higher [5].

The complexity and limited duration of spaceflight operations and the known analytical challenges associated with *in situ* extraction and characterization of trace reduced organic compounds in ancient rocks make it challenging to determine the origins of martian organic matter found to date. Coordinated state-of-the-art laboratory measurements of returned samples from Mars that include spatially resolved chemical, mineralogical, and isotopic studies and molecule-specific isotopic and enantiomeric measurements will be required to firmly establish whether the complex organic matter detected on Mars comes from biotic or abiotic sources. Ultimately, sample return may be our best chance of identifying chemical biosignatures from a past or present martian biota, if one ever existed on Mars. NASA’s Perseverance rover will collect dozens of surface sample cores for possible future return to Earth by NASA and ESA. Here we review our current knowledge of the distributions and enantiomeric and isotopic compositions of non-biological amino acids found in meteorites compared to terrestrial biochemistry and propose a set of measurement criteria that should be used to help establish the origin of any chiral asymmetry detected in samples from Mars [6].

References: [1] Eigenbrode, J. L. *et al.* (2018) *Science* 360: 1096-1100. [2] Freissinet, C. *et al.* (2015) *J. Geophys. Res. Planet.* 120: 495-514. [3] Szopa, C. *et al.* (2020) *Astrobiology* 20: 292-306. [4] Bada, J. L. and McDonald, G. D. (1995) *Icarus* 114: 139-143. [5] Goesmann, F. *et al.* (2017) *Astrobiology* 17: 655-685. [6] Glavin, D. P. *et al.* (2020) *Chemical Reviews* 120: 4660-4689.

20. Lessons learned about biosignature research in Low Earth Orbit and in sediments and its relevance for Life detection missions within Martian sedimentary basins

Jean-Pierre de Vera[1], Mickael Baqué[1], Ernst Hauber[1], Nicole Schmitz[1], Ute Böttger[2] and the BIOMEX and BioSigN life detection teams[3]

[1]German Aerospace Center (DLR), Institute of Planetary Research, Astrobiological Laboratories, Berlin, [2]German Aerospace Center (DLR), Institute of Optical Sensor Systems, Berlin, [3]International Group of the BIOMEX consortium from 30 different institutes, 12 nations and 3 continents

Present Mars is mainly a hostile planet, and in particular for life as we know it. But still today habitable niches could be present even close to the surface. A number of observations but also experiments in different laboratories and in space are indicating that such kind of habitable environments could even be close to the surface. We will present results on the habitability of present or past Mars, the limits of life and also on selected biosignatures with relevance to Mars and in particular to the next landing sites of the two missions ExoMars and Mars 2020 with sediment environments of former lakes or even oceans. Those selected biosignatures which were also tested to space and simulated Mars-like conditions directly on the outer side of the International Space Station during the BIOMEX experiment and also foreseen to be used for the next space exposure experiment BioSigN will be a contribution to the discussion how and to what extent we should investigate organic molecules originating directly from life or entire cells, allowing finally well based in situ analysis, interpretation and final conclusions on Mars. This should allow us to come closer to respond to the question: was or is there Life on Mars, or was it never been able to originate and evolve in this harsh environment.

21. Bio-signature detection with the ExoMars Raman Laser Spectrometer (RLS)

Ian Hutchinson[1], Melissa McHugh[1], Hannah Lerman[1] & Howell Edwards[1], Cedric Malherbe[2], Lucas Demaret[2], Andoni Moral Inza[3] & Carlos Perez[3]

[1]University of Leicester, UK, [2]University of Liege, Belgium, [3]INTA, Madrid

The Raman Laser Spectrometer is one of three analytical instruments located inside the body of the ExoMars rover. The excitation wavelength of the instrument (532 nm) is well suited to the detection and identification of biomolecules and the same wavelength has been selected for the Raman mode of the SuperCam instrument on NASA's Perseverance rover. Small cores extracted from the subsurface of Mars by the ExoMars drill will be crushed into fine grains and passed to the Analytical Laboratory Drawer for detailed interrogation. The RLS optics focus the excitation beam into a 50um spot on the surface of the sample (using an auto-focus mechanism) and scanning modes are implemented by micro-stepping the sample delivery system. In this presentation we describe the fundamental bio-signature detection capabilities of the RLS instrument and present the data obtained with flight instrumentation from a broad range of martian analogue samples (specifically selected to enable the performance of the instrument to be optimised during ground based mission preparation activities). Specific studies include carotenoids with iron oxide and clays, fumaroles and Antarctica feldspars.

22. Exploring the limits of VNIR Spectral Imaging of Natural Environments through End-End Simulations

R.B. Stabbins[1] (rstabbins@nhm.ac.uk), P. Grindrod[1], S. Motaghian[1], A. D. Griffiths[2,3], A. J. Coates[2,3], and the PanCam Science Team

[1]Division of Mineral & Planetary Sciences, Natural History Museum, London, [2]Mullard Space Science Laboratory, University College London, [3]Centre for Planetary Sciences at UCL/Birkbeck

A number of geochemical features that relate to biosignature formation and preservation in an environment, such as oxidation and hydration states, are observable in reflected visible and near-infrared light. These features can be mapped, to an extent, by the multi-spectral mast-mounted stereo cameras of the PanCam Wide-Angle Cameras (ExoMars) [1] and Mastcam-Z (Mars2020) [2]. Whilst the capabilities of these imaging systems have been demonstrated through the deployment of emulators at Mars-analogue field sites [3,4,5], the breadth and numerical precision of such investigations are limited by the field-site contents, and discrepancies between emulator and flight model properties. Here we use hyperspectral radiometric ray-tracing and spectral imaging system simulations to describe and demonstrate some limiting factors involved in capturing and analysing spectral images of natural environments. Scene simulation removes the combinatorial limitations of physical environments, including mineral diversity and distribution, whilst instrument simulation allows for the response of flight-models, including noise limits, to be comprehensively and economically investigated. In addition to demonstrating the visual perception afforded by these cameras, the simulation software provides a framework for synthesising the spatial distribution of a target (i.e. a biosignature perquisite) against a background (i.e. Mars soil or dust), and predicting the signal of this target in an image product, depending on external factors such as viewing geometries and illumination. We invite the community to suggest further use-cases for the simulation tool, relating to the detection of biosignature environmental prerequisites.

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23. The comprehensive ‘MICRO-life detection platform’ applied to in situ research at Mars and Icy Moons terrestrial analogs

Miguel Ángel Fernández-Martínez[1], Isabelle Raymond-Bouchard[1], Catherine Maggiori[1], Louis-Jacques Bourdages[1], David Touchette[1], Brady O’Connor[1], Olivia Blenner-Hasset[1], Felix Denomme[2], Alex Ellery[2] and Lyle G. Whyte[1, 3]

[1]Natural Resource Sciences, McGill University - Macdonald Campus, Sainte-Anne-de-Bellevue, Quebec, Canada; [2]Mechanical and Aerospace Engineering, Carleton University, Ottawa, Ontario, Canada, [3]McGill Space Institute, McGill University, Montreal, Quebec, Canada

Here we present the MICRO-life detection platform, a comprehensive, multi-technique instrumentation for molecular microbial ecology studies. This platform already includes three complementary tools that, in the next future, would be operated at once without any human intervention. The main instrument included within the platform is Oxford Nanopore MinION, a fully portable device (Fig. 1A) able to carry out real-time analysis of DNA, RNA, proteins and other smaller molecules. With it, feasible sequence data can be obtained within 48 h from natural samples with only ~ 0.001 ng of DNA. Complimentary to the MinION, MICRO-life detection platform also includes the Microfluidic microbial activity microassay (µMAMA), a multi-well plate based on redox-indicator dyes chemically associated to the substrates for microbial activity detection (Fig. 1B). Together with both instruments, a multi-well culture plate named Cryo-iPlate, is included to remain at the field site to allow inoculated microorganisms to grow under exactly the same conditions of the environment from where they were sampled (Fig. 1C), thus potentially increasing the total number of culturable microorganisms present on a field sample from 0.1-1% to 20-30%. An automated mechanic Ice Drill (Fig. 1D) for permafrost and soil perforation is also being included in the platform to automatically supply samples to the different instruments, including a nucleic acids’ extraction self-designed instrument (‘MagLysis’ tool) which extractions will be directly transferred to MinION. The different instruments have been successfully field tested in Mars and icy moon analogue sites in the Canadian high Arctic and we are currently attempting to combine and automate the different components into an integrated platform. Our initial investigations have indicated that this biosignature detection platform has strong potential for future robotic and human planetary exploration missions.

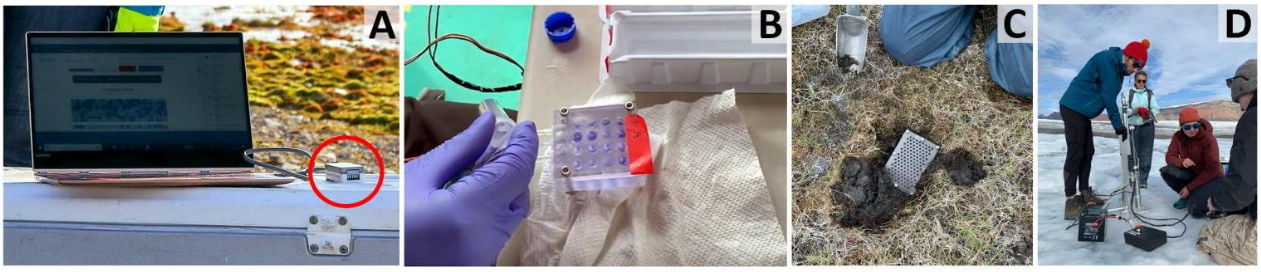

Figure 1: *MICRO-life detection platform techniques employed in situ. A) Sequencing with MinION (red circle) at a High Arctic sampling site; B) µMAMA plate being used at McGill Arctic Research Station; C) Culturing with Cryo-iPlate in the High Arctic; D) Ice Drill on a sampling expedition.*

24. Searches for martian organic materials with NASA’s Perseverance rover

Roger C. Wiens

Los Alamos National Laboratory (+ co-authors to be acknowledged at the talk)

Organic materials have been definitively identified and characterized on Mars by the SAM instrument on the Curiosity rover. The sampled material originated < 6 cm below the surface, and in spite of the extensive radiation environment, complex organic molecules were observed, including decane and dodecane. Most of the SAM experiments are challenged by the difficulty of mobilizing representative abundances of organics in their original form, especially given the presence of perchlorates and other oxidizing species in some of the samples. More recent use of derivitization agents may provide more clues to the abundances and nature of organic materials on Mars. The MSL rover has observed other evidence of strongly oxidizing conditions in the past, sufficient to precipitate manganese oxides out of groundwater. Such large redox gradients represent a potential source of energy for primitive organisms, and build on the scenario of a habitable environment on Mars existing well into the Hesperian period.

The Perseverance rover that is currently on its way to Mars provides new instrumentation for exploration of organic signatures and their sources. These include two Raman + fluorescence spectrometers that operate in vastly different ways. SuperCam’s Raman spectrometer operates remotely, from the rover’s mast, using a pulsed 532 nm laser beam and 10 ns spectral time resolution for time-resolved luminescence and Raman spectroscopy, focusing on mineralogy but also capable of observing organic materials. The SHERLOC instrument uses a deep-UV (248 nm) laser to excite Raman signals below 265 nm and fluorescence signals above that wavelength, focusing on organic materials but also with mineral-detection capabilities. The SHERLOC fine-scale measurements will be complemented by fine-scale elemental composition mapping by the arm-mounted PIXL instrument.

The ultimate study of organics on Mars will involve the return of samples from Mars, to be initiated by Perseverance’s collection and caching drill-core samples. The Perseverance team is developing protocols for comprehensive in-situ characterization of the drill sites with the rover instruments. Thirty-eight sterile tubes are mounted in the belly of the rover for sample collection. This talk will describe the primary Perseverance instruments involved in the search for organic materials, and the plan for collecting drill-core samples.

Contacts and links

Nisha Ramkissoon (nisha.ramkissoon@open.ac.uk) – The Open University

Peter Fawdon (peter.fawdon@open.ac.uk) – The Open University

Louisa Preston – Natural History Museum

Mark Buchell – Universty of Kent

https://ras.ac.uk/events-and-meetings/ras-meetings/biosignature-identification-habitable-martian-environments

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