Introduction

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One contribution of 14 to a Theme Issue ‘Raman spectroscopy meets extremophiles on Earth and Mars: studies for successful search of life’.

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Recent studies relating to the analytical chemical characterization of terrestrial extremophiles reveal the presence of biomolecules that have been synthesized for the survival of the colonies in response to the extreme environmental conditions, where otherwise life could not exist. This is a vital part of the planned space missions now being undertaken to planets and their satellites in the search for extinct or extant life signatures in our Solar System. Extremophiles have existed on the Earth for some 3.8 Gyr and their interrogation indicates their strategic survival methods which can be associated and compared with extraterrestrial scenarios on Mars, Titan, Enceladus and Europa.

A key technique that has been proposed for the evaluation of potential biosignatures in geological matrices on such planetary missions is Raman spectroscopy; the adoption of miniaturized instrumentation on the forthcoming ESA/Roscosmos ExoMars and NASA 2020 Mars missions is now well advanced, and it is therefore opportune to consider the analytical results which might be anticipated from the deployment of this instrumentation on the planetary surface.

In this Thematic issue dedicated to the application of Raman spectroscopy for the characterization of biomolecular signatures in the search for life on Mars, several important critical stages can be revealed: perhaps the most important of these is the identification of Raman spectral biosignatures from terrestrial extremophilic colonies wherein survival strategies are dependent upon the synthesis of suites of protective biomolecules which facilitate the adaptation of the organisms to their geological desert niche environments and combat the...
destructive effects of desiccation, temperature and damaging ultraviolet radiation insolation. From these ongoing studies, a Raman spectral wavenumber database of key biomolecular signatures is being developed to facilitate the recognition of extinct or extant life in the surface and subsurface Martian regolith. Alongside these studies, some cutting-edge work is being undertaken for the identification of putative biomolecules which as yet have not been characterized spectroscopically but which could be present in unrecognized terrestrial and extraterrestrial scenarios: whereas a critically important family series of biomolecular signatures is provided by the polyene carotenoids (as exemplified in a detailed paper on this topic), of which several hundred are known with varying conjugated chain lengths, pendant methyls and end groups, that of scytonemin in contrast has been little studied beyond the parent molecule itself. A paper here reviews some scytonemin derivatives and their postulated low-energy complexes with iron that could be significant in cyanobacterial strategies for colonization survival in iron-rich environments such as that of Mars.

Whereas the understanding and recognition of these Raman spectral biosignatures form terrestrial extremophiles is paramount to the first deployment of a miniaturized spectrometer on Mars, of equal importance in the preparation for remote planetary surface and subsurface analytical interrogation is the behaviour and performance of the on-board rover vehicle instrumentation. A paper in this issue describes the challenges of the experimental instrumental approach and the construction of a flight-like prototype instrument which uses many of the novel features incorporated on the space mission: the existence of a limited number of portable Raman spectrometers available for terrestrial fieldwork affords an opportunity for testing and evaluation of the biomolecular signature recognition protocols which will be inestimable for the correct interpretation of spectral data from the space mission. Hence several papers here report comparisons of data acquired from extremophilic specimens using laboratory bench and portable instruments and also with an ExoMars flight-like prototype instrument—all of which enable an assessment to be made of the reliability and uniqueness of spectral data interpretation emanating from the wavenumber observations made in the field and in laboratories under different conditions of excitation wavelength, ambient conditions and spectral resolution.

It is realized that the preservation of biomolecular signatures of extinct life in a hostile environment, such as that of Mars over geological time frames extending over many million years or even billion years, will be susceptible to degradation particularly from the ultraviolet radiation, which penetrates to the planetary surface, the scarce availability of water and the chemical oxidative toxicity caused by the presence of perchlorates, hydroxyl radicals and peroxides. Hence, work is also being undertaken to gauge the extent and result of these degradation scenarios, where molecules such as chlorophyll, phycocyanins, carotenoids and scytonemin will have possibly degraded to carbon. The recognition of the presence of carbon, although not in itself providing mandatory evidence of former life because of the possibility of an abiotic origin, nevertheless would provide an intriguing discovery perhaps in association with other evidential material. This is a very important yet challenging aspect of analytical astrobiology which is now receiving considerable attention in the literature and is also addressed in this issue.

Finally, the issue concludes with a review paper on what has been described as the longest running yet still unsolved mystery in natural science which could have implications for extremophiles research: namely, the reported phenomenon of the will-o’-the-wisp, the eery sightings of flickering lights observed near marshland by travellers in desolate regions and often associated in historical literature with supernatural activities. Although first reported in the fourteenth century and commented upon by Isaac Newton in the early eighteenth century, this was first scientifically reviewed in the Philosophical Transactions of the Royal Society A but for which there is still no credible explanation. The identification of an ever-increasing number of extremophilic terrestrial scenarios which are being investigated currently using mobile and portable instrumentation means that the next sighting of this elusive natural phenomenon will perhaps generate their application in this direction and so provide a solution to this age-old mystery.