Identifying High Priority Fossil Biosignatures in Mars Analog Materials Using Raman Spectroscopy

Svetlana Shkolyar[1], Jack Farmer[1], and Jordana Blacksberg[2].

[1]School of Earth and Space Exploration, Arizona State University, Tempe, AZ
[2]Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA

Mars sample return has been identified as a top priority in the planetary science decadal survey. A Mars sample selection and caching mission would likely be the first step in this endeavor. Such a mission would aim to select aqueously formed sedimentary rock samples present at a selected site on Mars, and prioritize them for return to Earth, based upon their enhanced potential for biosignature capture and preservation. If evidence of past life is found, it is likely to come via the identification of fossilized carbonaceous matter of biological origin (called kerogen) from detailed analyses of samples in terrestrial laboratories, following their return to Earth. The total amount of materials returned from Mars will be restricted. For an effective sample return for Astrobiology, it will be essential to select, *in situ*, those samples with the highest potential for biosignature preservation. Raman spectroscopy is a favored method for analyzing materials *in situ* based on its capability to provide information about both mineralogy and organic matter present in a rock as kerogen. To better understand the complexities of identifying kerogen in high priority aqueous lithologies that are analogs for Mars, we performed a pilot study using Raman spectroscopy. Samples used for the study were also characterized by X-ray Diffraction and thin section petrography to provide independent assessments of mineralogy and micropaleontology, and to map the distribution of kerogenous fossil materials present. Study samples included a wide range of relevant Mars analog materials representing a broad range of mineral compositions (i.e., silica, carbonates, sulfates, and clays) and kerogen maturities, over a time span of Archaean to Holocene. The study revealed that reliable kerogen identification in high priority target lithologies for Mars can be impeded by high background fluorescence originating from both long (>10 ns to ms) and short (<1 ns) lifetime effects arising from organic matter in the samples and the surrounding mineral matrixes. Certain lithotypes displayed consistently low background fluorescence, which enhanced both mineral identifications and organic matter detection. For example, kerogen preserved in a fine-grained cherts, such as chert dike samples from the Archaean Strelley Pool chert of western Australia, were not highly fluorescent (Fig. 1). One possible reason for the lower fluorescence in these examples may be the fluorescence-quenching effects of increased concentrations of poly-aromatic hydrocarbons present in some types of diagenetically mature kerogen [Bertrand et al, 1985]. In contrast, kerogen-containing carbonate lithotypes often showed strong fluorescence, resulting from contributions of both immature kerogen, and the surrounding carbonate matrix, thus, making reliable kerogen detection in such lithologies challenging using Raman. An example of a sample exhibiting high fluorescence background include carbonate lithotypes such as Holocene age stromatolitic limestones from Walker Lake (NV), shown in Fig. 1. Both carbonate and chert lithologies are the most common host rocks for the Precambrian microfossil record on Earth and are high-priority targets for sample selection on Mars [Farmer and Des Marais, 1997]. Work by Blacksberg et al [2013; 2014] shows the potential of time-resolved Raman spectroscopy to reduce fluorescence and improve the ability to detect kerogen and minerals. This study recommends (1) further research to better understand how to reduce fluorescence

interference in challenging, but high-priority lithologies and (2) continued science-driven exploration of sample-dependent issues using Raman spectroscopy as a tool for sample selection for caching on Mars.

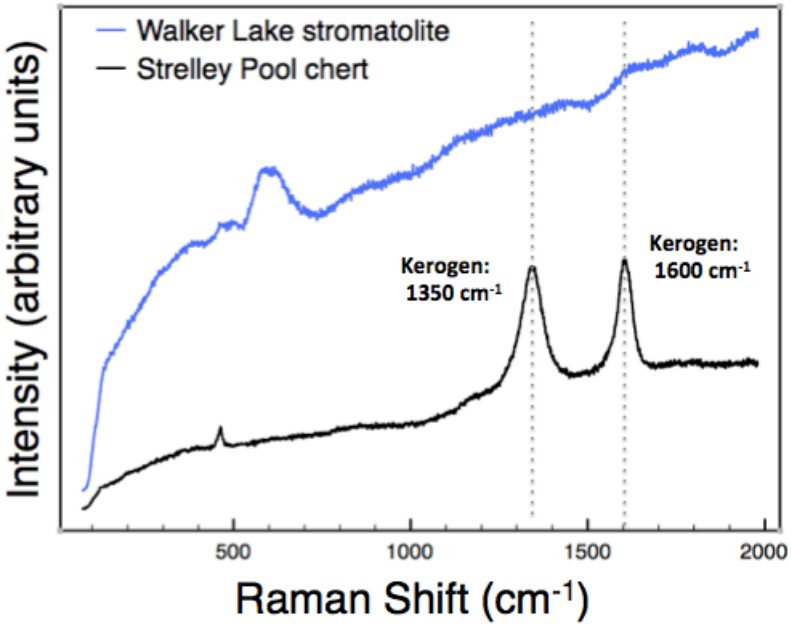

Fig. 1. Continuous Wave (conventional) Raman spectra for a carbonate-hosted stromatolite exhibiting high fluorescence and a quartz-hosted chert exhibiting low fluorescence. Kerogen, identified by peaks at 1350 cm^{-1} and 1600 cm^{-1} is visible in the chert but not the stromatolite, due to fluorescence.

References

Bertrand, P., J.-L. Pittion, and C. Bertrand. (1985). Fluorescence of sedimentary organic matter in relation to its chemical composition. *Advances in Organic Geochemistry*, 10, p. 641-7.

Blacksberg, J., Y. Maruyama, E. Alerstam, C. Cochrane, G.R. Rossman, S. Shkolyar, and J. Farmer. (2014). Time-resolved Raman spectroscopy of mars analog minerals and organics, *45th Lunar and Planetary Science Conference*, Abstract #1544.

Blacksberg, J., E.Alerstam, Y. Maruyama, E. Charbon, G.R. Rossman, S. Shkolyar, and J.D. Farmer. (2013). Planetary surface exploration using Raman spectroscopy for minerals and organics, *2013 Fall Meeting of the American Geophysical Union Conference,* Abstract # P51G-1803.

Farmer, J. D., and D. J. Des Marais. (1999). Exploring for a record of ancient Martian life, *J. Geophys. Res*., 104(E11), p. 26,977–26,995.