Considerations for the collection of Raman spectra of potential Martian biosignatures

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The search for signatures of life termed "biosignatures" is one of the major goals of astrobiological exploration programs of the National Aeronautics and Space Administration (NASA) and the European Space Agency (ESA). A biosignature is defined as an object, chemical substance, and or pattern whose origin requires formation by biology alone.[1] Organic compounds formed exclusively by biological processes whose formation is virtually unachievable in the absence of life can hence act as biosignatures. Examples of potential bio-organic molecular structures with this goal in mind are defined by their functionality, such functionality being fundamental to all organisms. Furthermore, it is desirable to target molecules that are clearly distinguished from abiogenic organic compounds that are widely distributed throughout the cosmos. Potential molecules that could serve as biomarker compounds to target include: DNA/ RNA, chlorophyll, carotenoids/ retinal-protein complexes, bacteriohopanetretol, and steroids which are exclusively formed by biological processes.[2] Organic compounds that do not fall under the above definition of biomarkers are proteins, amino acids, aliphatic hydrocarbons and polycyclic aromatic hydrocarbons as they can be synthesized by biological and non-biological processes.

Currently, there is debate as to what would be the best choice of the wavelength of laser line used for sample excitation for Raman spectroscopy in astrobiological prospecting. Possible wavelengths of laser lines that have been proposed are 244 nm (e.g., useful for DNA and proteins), 514.5 and 532 nm (e.g., useful for resonance enhancement of carotenoids, and minerals), and 785 nm (e.g., useful for organics and minerals). Thus far, the Mars Microbeam Raman Spectrometer (MMRS) developed by Washington University in St. Louis and Jet Propulsion Laboratory uses a low-power mode 532 nm laser for sample excitation.[3] Recently, the 532 nm excitation wavelength has also selected for the ESA's Raman system (Raman Laser Spectroscopy RLS) for the upcoming ExoMars mission. Given the above considerations for the unequivocal detection of life on Mars by targeting organic compounds of biological origin, the best choice of wavelength of excitation is still 532 nm. This excitation wavelength has proven to be useful when analyzing carotenoids (one of the above targeted biomarkers) due to its coincidence with an electronic transition in carotenoids, which results in the Raman resonance effect and thus significantly enhances the Raman signal.[4] Additionally, this wavelength is best for mineral analysis.

Here we present Raman spectra collected on solid β-carotene, various concentrations of β-carotene solutions (Figure 1), and various weight per weight percentages of β-carotene mixed in with carbonate and sulfate minerals over a range of laser excitation wavelengths. We employed the same collection parameters for excitations ranging from 325, 488, 514, 532, 785, and 1064 nm. We show that the optimal laser excitation source is 488, 514 and 532 nm.

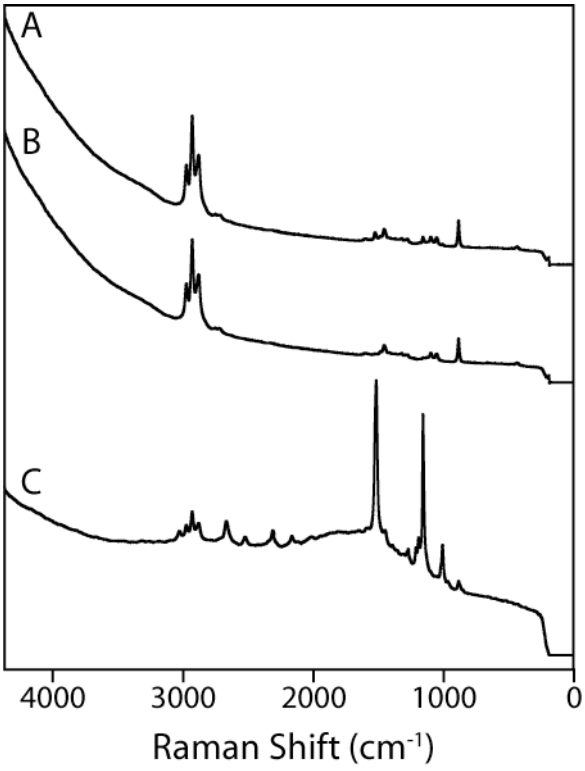

Figure 1: Raman spectra of various concentrations of β-carotene collected at 532 nm. A: 8.2×10^{-7} moles of β-carotene, B: 8.2×10^{-8} moles b-carotene, C: 4.1×10^{-5} moles of β-carotene.

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