FINDING BIOSIGNATURES IN MARS ANALOG SAMPLES USING VISIBLE AND UV-GATED RAMAN SPECTROSCOPY, AND UV TIME-RESOLVED FLUORESCENCE SPECTROSCOPY.

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Introduction: The Mars 2020 mission marks the first step in NASA's plan to return Martian samples to Earth. This mission aims to analyze samples in situ and identify those with a high potential for having formed in a habitable environment and having captured and retained biosignatures.

The highest priority samples are likely to include aqueously formed sedimentary lithologies (such as sulfates, carbonates, silica, and clays) containing fossilized carbonaceous matter, or kerogen [1]. This is based on our knowledge of terrestrial kerogen, the most widespread and abundant biosignature representing the largest pool of organic matter on Earth [2].

Motivations and Methods: With MSR priorities in mind, we analyzed a diverse suite of natural, realistic analog samples chosen to represent diverse ancient habitable environments on Mars [1]. Samples included a hydrothermal chert; a siliceous mudstone; a carbonate- cemented marine sandstone; a laminated sulfate-carbonate evaporite; a lacustrine stromatolitic limestone; a lacustrine micritic carbonate; and a clay and magnesite-rich evaporitic mudstone. We explored data sets representing those that will be obtained for the first time on upcoming missions: Raman and laser-induced fluorescence spectroscopy. Our study investigated mineral and kerogen detections in our sample suite using two Raman spectrometers: a 532 nm (visible) continuous wave (V-CW) system and a 266 nm (UV) gated (UV-G) Raman system that is combined with a UV laser-induced time-resolved (UVLITR) fluorescence spectroscopy system.

Various studies have assessed the capabilities of Raman and fluorescence instruments for biosignature detection, including the system used in this study [3-5]. However, few have examined complex biosignatures expected on Mars, such as non-extracted kerogen in natural samples. In light of the upcoming Mars 2020 mission, it is crucial that Raman and fluorescence instrument performance is tested and methods optimized using natural, realistic analog samples containing non-extracted biosignatures, such as kerogen in our study's case.

Study Goals: The goals of this study were to (1) assess the effectiveness of time-gating compared to laser excitation wavelength optimization as a Raman-based fluorescence reduction strategy to enable successful caching of samples for MSR; (2) identify sample-specific issues which could challenge identification of our samples; and (3) assess the capabilities of UVLITR fluorescence spectroscopy for detecting kerogen in our sample suite.

Results: Results indicated that UV-G Raman was able to detect minerals and organics with higher confidence and without fluorescence interference as compared to V-CW Raman in most samples. UV excitation had more impact than time-gating on fluorescence mitigation. Two sample-dependent challenges arose with both Raman systems: success with V-CW Raman depended on lithotype and kerogen maturity, and the evaporitic mudstone sample complicated matrix and kerogen detections with both Raman systems. UVLITR fluorescence spectroscopy revealed two types of organic fluorescence in all samples.

Recommendations: In preparation for future MSR missions, our study offers recommendations for further work on Raman and fluorescence-based biosignature studies.

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