

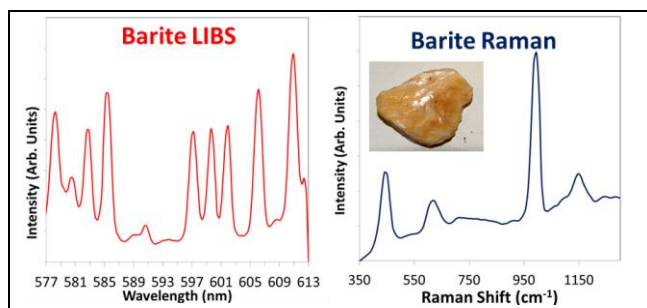
## MAXIMIZING SCIENCE RETURN FROM A SINGLE ON-SURFACE MINERALOGY TOOL: COMBINED RAMAN, LIBS, AND FLUORESCENCE SPECTROSCOPY

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**Introduction:** In this paper we present a single mineralogy tool with the potential for in-depth surface analyses that typically require the use of multiple techniques and instruments. We combine three techniques into one instrument: microscopic Raman spectroscopy, Laser Induced Breakdown Spectroscopy (LIBS) and fluorescence spectroscopy. Using this approach, we aim to maximize the science return for potential future landed missions to Mars, Phobos, and Deimos. In addition, these in-situ measurements will be needed to address the gaps in our understanding that must be filled before we embark on potential future human exploration of these bodies. Concerns about forward and backward contamination resulting from human interaction can be partially addressed by understanding the history of habitability on Mars and its moons. Microscopic characterization of the surfaces of these bodies can provide this information, which is largely absent today. For Phobos and Deimos, we do not have an understanding of even the basic surface geology that will be needed to design focused human-based scientific investigations on these bodies.

Future robotic exploration of Mars will be aimed at building on the wealth of knowledge acquired to date both from orbital and on-surface measurements (e.g. Mars Reconnaissance Orbiter, MER Rovers, and now MSL). For Phobos and Deimos, little is known about these bodies, which may or may not be geologically related to Mars. In all cases, the path to building a deep and comprehensive understanding of the geochemistry and mineralogy of these bodies compels us to employ microscopic analysis.

Geochemical and mineralogical studies require microscopic determination of the phases present, their composition, morphology, and in many cases isotope ratios. We present a single mineralogy tool with the potential to ascertain the first three simultaneously (a separate instrument will be required for isotope analysis). Of prime importance is the ability to determine structure and composition. The CheMin instrument on MSL uses X-ray diffraction (XRD) for this purpose; samples will be collected, powdered, and characterized on board the Curiosity rover. While XRD is the gold standard for determining crystalline phase, in its current incarnation



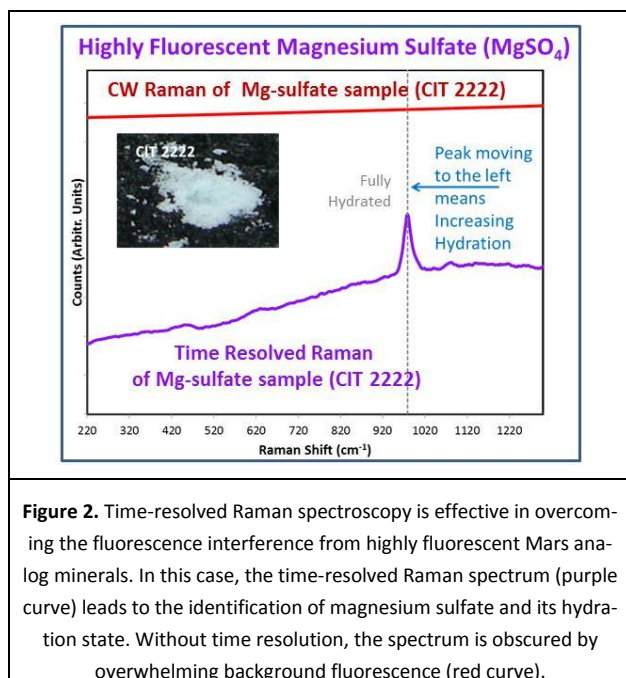
**Figure 1.** Raman and LIBS spectra collected using our time-resolved laser spectrometer with the 128x128 SPAD array. The instrumentation used to collect both spectra is identical. The only change in conditions between the two spectra is the laser power ( $\sim 10\times$  higher for the LIBS spectrum). The resolution of the spectra in this case is limited by the small size of the SPAD array. This is not a fundamental limitation, and future work will include a larger SPAD array and higher resolution.

it requires sample preparation and long measurement times.

In the past decade, fundamental mineralogy tools employing laser spectroscopic techniques (e.g. Raman, LIBS) have been the subject of increasing attention and development [e.g., 1, 2, 3]. Raman spectroscopy yields information similar to XRD in a non-destructive manner and without sample preparation. It is often considered the next important tool for a host of planetary surface missions. A Raman spectrometer has been selected on the payload of the ExoMars rover [4], and is included in a proposed mission to Mars' moon Deimos [5]. It can provide phase identification for most crystalline materials, and in many cases, significant compositional information. It is fast and non-destructive. The laser source can be focused to a very small spot size ( $\sim 1\text{-}5\ \mu\text{m}$ ) comparable to mineralogical grains. And lastly, it can be combined with microscopic imaging to retain the context of the natural mineral setting. LIBS provides elemental abundances, thus its combination with Raman provides detailed geochemical information.

### Proposed Instrument & Techniques:

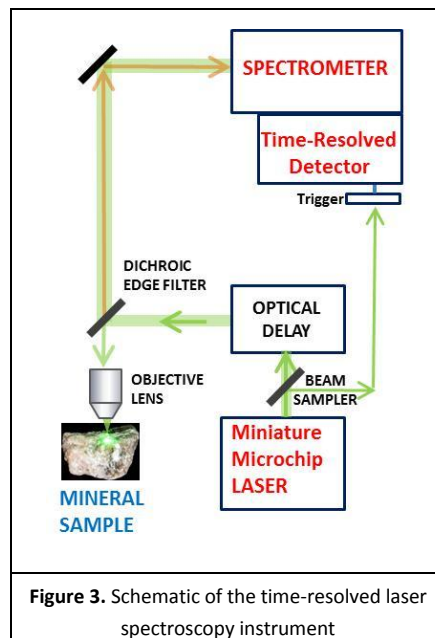
With time-resolved Raman spectroscopy, we can realize all of the benefits of Raman, with additional advantages [6]. Using a picosecond-scale pulsed laser and a fast time-resolved detector we can simultaneously collect spectra from Raman, Laser Induced



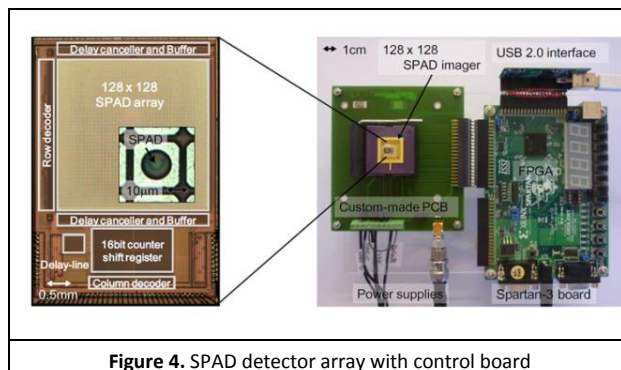
**Figure 2.** Time-resolved Raman spectroscopy is effective in overcoming the fluorescence interference from highly fluorescent Mars analog minerals. In this case, the time-resolved Raman spectrum (purple curve) leads to the identification of magnesium sulfate and its hydration state. Without time resolution, the spectrum is obscured by overwhelming background fluorescence (red curve).

Breakdown Spectroscopy (LIBS), and fluorescence emissions that are separated in time due to the unique decay times of each process. An example of Raman and LIBS obtained with our instrument is shown in figure 1. First, we can collect Raman spectra with high signal-to-noise ratio even in the presence of large background fluorescence that is often associated with altered minerals (e.g. clays, sulfates, phosphates) – see figure 2. This fluorescence is separated out in time providing further potentially useful information (e.g. fluorescence lifetime of the fluorophors). Finally, we obtain a new form of microscopic LIBS along with the Raman spectra. This can be accomplished by small changes in the laser energy between scans. A schematic of the instrument is shown in figure 3.

Until recently, detectors with sub-ns time resolution relied primarily on photocathode-based detectors which are relatively large and delicate with high power consumption. They are therefore not well suited for planetary instruments. The detector technology that makes this instrument possible is a newly developed Single-Photon Avalanche Diode (SPAD) sensor array based on Complementary Metal-Oxide Semiconductor (CMOS) technology [7]. The use of a solid state time-resolved detector offers a significant reduction in size, weight, power, and overall complexity, putting it on par with instruments that do not have time resolution, while providing enhanced science return. Our first demonstration used a 128x128 SPAD array for proof-of-concept (figure 4). Future work aims to incorporate a larger detector array of format similar to a CCD that is standard in many laboratory instruments.



**Figure 3.** Schematic of the time-resolved laser spectroscopy instrument



**Figure 4.** SPAD detector array with control board

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