

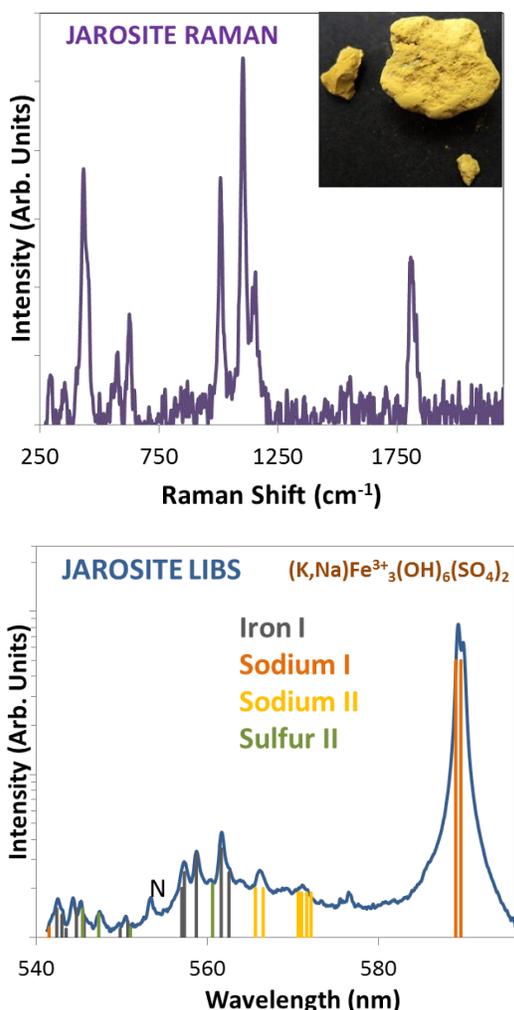
**COMBINED RAMAN AND LIBS FOR PLANETARY SURFACE EXPLORATION: ENHANCED SCIENCE RETURN ENABLED BY TIME-RESOLVED LASER SPECTROSCOPY.** J. Blacksb<sup>1</sup>, Y. Maruyama<sup>3</sup>, M. Choukroun<sup>1</sup>, E. Charbon<sup>3</sup>, G.R. Rossman<sup>2</sup>, <sup>1</sup>Jet Propulsion Laboratory, California Institute of Technology, 4800 Oak Grove Dr., Pasadena, CA 91109, Jordana.blacksb@jpl.nasa.gov, <sup>2</sup>California Institute of Technology, Division of Geological and Planetary Sciences, Pasadena, California 91125, grr@gps.caltech.edu, <sup>3</sup>Circuits and Systems, Delft University of Technology, Delft, The Netherlands, y.maruyama@tudelft.nl.

**Introduction:** In this paper we present a mineralogy tool that could potentially perform both phase and elemental analysis on rock, soil, and regolith in an undisturbed natural geological setting. Such measurements are typically achieved by the use of multiple techniques and instruments. New developments in the field of time-resolved laser spectroscopy have opened up the possibility of highly capable combined Raman

and Laser Induced Breakdown Spectroscopy (LIBS) instruments suitable for planetary environments [1,2]. With recent progress in miniature pulsed microchip lasers and solid-state time-resolved detectors, we could achieve significant reduction in size, weight, power, and overall complexity of these instruments. This would place them on par with instruments that do not have time resolution, but with the ability to provide enhanced science return. An example of combined phase and elemental analysis (Raman and LIBS) obtained using our time-resolved instrument is shown in figure 1.

The geochemistry and mineralogy of a planetary body tell a story of its' history and evolution. Evidence from on-surface measurements allows us to piece together that story by measuring 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). The compelling science goals of on-surface missions underscore the need for on-surface instruments that can perform comprehensive analysis at the scale of individual grains. These grains can often be on the order of microns in scale. The versatility of our combined technique makes it relevant to the exploration of any solid solar system body. Some specific examples of relevant bodies and potential science return are:

- \* *Mars* – In depth mineralogy capabilities using microscopic contextual measurements can elucidate the evolution of Mars including proposed models of early aqueous alteration. This approach can also be used to study regions of recently emerging scientific interest such as those containing possible present-day brines on the surface of Mars [3]. Such measurements will also help us address gaps in our understanding that must be filled before we embark on potential future human exploration.
- \* *Phobos and Deimos* – Surface geology of Mars' moons can inform about origins and aid in designing focused human-based scientific investigations on these bodies. The origins of these moons are currently unknown with theories suggesting possible capture of primitive asteroids, or accretion of ejecta from a Mars impact. Little is known about their



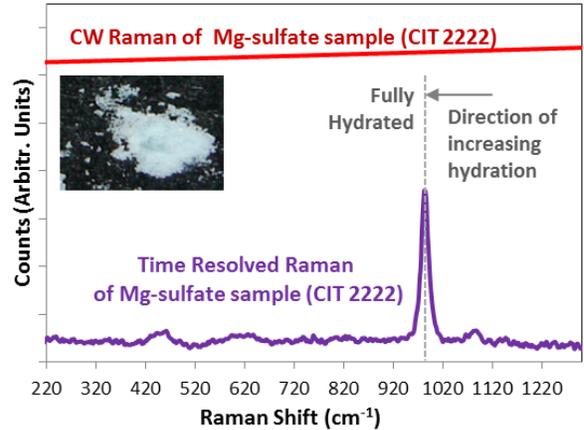
**Figure 1.** Raman and LIBS of a natural jarosite sample taken using our time-resolved spectrometer. The instrumentation used to collect both spectra is identical, with the laser power ~ 10× higher for the LIBS spectrum. These spectra reveal a sample representative of the jarosite - natrojarosite series where Na substitutes for some of the K.

mineralogy due to relatively featureless remote reflectance spectra.

- \* *Comets and Asteroids* –In many cases, little to nothing is known about the mineralogy of these bodies. For example Jupiter Trojans and D-type objects exhibit featureless infrared reflectance spectra when observed by remote measurements. Our proposed technique is very powerful for these primitive bodies where mineralogy can help us tell the story of solar system origins and evolution. For example, a detailed microscopic analysis of the phases present (especially when tied in with complementary isotopic analysis) can constrain the conditions under which they formed and their subsequent histories.

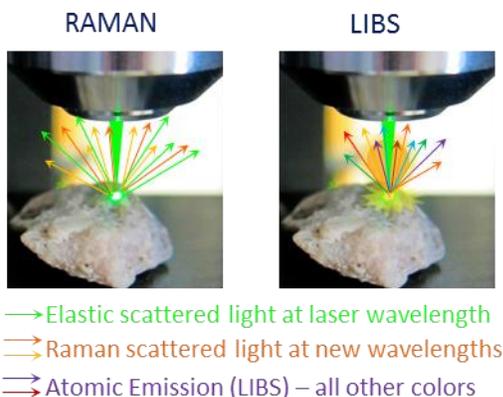
For mineralogical studies, determination of phase and structure are of prime importance. The CheMin instrument on MSL uses XRD for this purpose; samples will be collected, powdered, and characterized onboard the curiosity Rover. XRD is considered the gold standard for determining crystalline phase. Future XRD instruments are likely to become ever more functional as techniques are developed that can circumvent sample preparation and offer analysis of powders as well as large grained single crystals [4]. Alternately, laser spectroscopic techniques that are inherently non-contact and non-destructive have gained a lot of traction over the past decade [5-7]. 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. For example, a Raman spectrometer has been selected on the payload of the ExoMars rover [8]. Raman is fast, non-destructive, can provide phase identification for most crystalline materials, and in many cases, can provide significant compositional information. The laser source can be focused to a very small spot size (~ 1-5  $\mu\text{m}$ ) comparable to mineralogical grains. It lends itself easily to combination with microscopic imaging, retaining the context of the natural mineral setting. LIBS provides elemental abundances, thus its combination with Raman provides detailed geochemical information.

**Combined Microscopic Raman and LIBS:** By adding time-resolution to Raman spectroscopy we open a whole new realm of capability. We can exploit the different time scales of the various laser-induced scattering and emission processes that occur. Since Raman emission is virtually instantaneous, while fluorescence (and LIBS) occurs over longer timescales, a fast time-resolved detector can be used to distinguish spectra from these processes. The main advantages are:



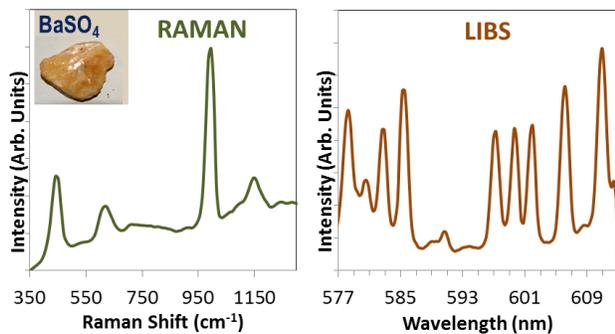
**Figure 2.** Time-resolved Raman spectroscopy is effective in overcoming the fluorescence interference from highly fluorescent Mars analog minerals. In this case, the time-resolved Raman spectrum (purple curve) leads to the identification of magnesium sulfate and its hydration state. Without time resolution,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

1. *Fluorescence elimination:* 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). For example, figure 2 shows the Raman spectrum for a highly fluorescent natural magnesium sulfate sample. The fluorescence is separated out in time and could potentially provide further useful information (e.g. fluorescence lifetime of the fluorophors present in the sample).
2. *Daylight operation:* Rejection of background light is a natural consequence of this approach.
3. *Simultaneous LIBS:* The simultaneous Raman and LIBS capability of the instrument is illustrated by the cartoon in figure 3. Using the same instrument configuration, if we increase the pulsed laser power by approximately a factor of 10, we can create a plasma at the surface of the target material. As the plasma expands and heats up, a bright broadband emission is generated. This background decays and gives way to atomic emission lines that are characteristic of the elements present. In a typical LIBS instrument, the background decay occurs over the microsecond time scale. In our setup, due to the lower laser energy and shorter pulse width we observe the background decay in a few nanoseconds with atomic emission lines that are sustained for ~100 ns.



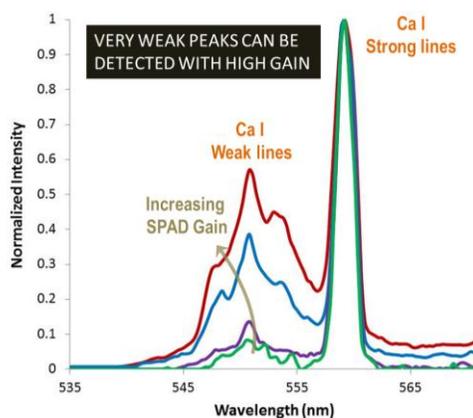
**Figure 3.** Cartoon illustrating microscopic Raman and LIBS. Both processes are initiated with a kHz pulsed microchip laser with pulse width  $\sim 400$  ps. The laser pulse energy is  $\sim 10 \mu\text{J}$  for LIBS and  $1 \mu\text{J}$  for Raman. In the LIBS process, a plasma is created near the sample surface.

**Advances in time-resolved detectors:** Background fluorescence in minerals exists over a range of time-scales. Fluorescence lifetimes typically vary from ns to ms. For maximum fluorescence rejection, we require sub-ns time resolution. Until recently, detectors with sub-ns time resolution have relied primarily on photocathode-based detectors such as streak cameras which are relatively large and delicate with high power consumption. They are therefore not best 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 [9]. The use of a solid state time-resolved detector offers a significant reduction in size, weight, power, and overall complexity - making time resolved detection feasible for planetary applications. Our demonstration of this technology used a  $128 \times 128$  SPAD array for proof-of-concept. Raman and LIBS spectra of a natural barite sample obtained using this



**Figure 4.** Raman and LIBS spectra collected using our time-resolved laser spectrometer with the  $128 \times 128$  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).

SPAD are shown in figure 4. Using this detector, we can also employ gain adjustment to our advantage. This is particularly relevant to LIBS where we may wish to operate over a narrower wavelength range in order to obtain higher spectral resolution. In this case the chip gain can be increased in order to enhance the signal-to-noise ratio for very weak peaks (figure 5). Automatic on-chip gain adjustment that would take advantage of this extended dynamic range is possible. We will present the latest results on SPAD development for this application; this includes future work that aims to incorporate a larger detector array of format similar to a CCD that is standard in many laboratory instruments.



**Figure 5.** Calcium atomic emission lines generated during LIBS and detected using the  $128 \times 128$  SPAD array. By increasing the gain on the SPAD chip, weaker lines that are not typically visible can be detected with a high signal-to-noise ratio.

**Acknowledgements:** The research described here was carried out at the Jet Propulsion Laboratory, California Institute of Technology, under a contract with the National Aeronautics and Space Administration (NASA). Continuous-wave Raman measurements were performed at the Mineral Spectroscopy Laboratory at the California Institute of Technology. SPAD development was performed at Delft University of Technology.

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