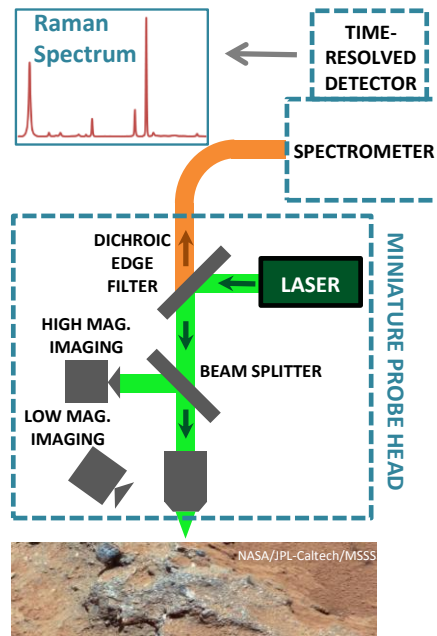


**TIME-RESOLVED RAMAN SPECTROSCOPY OF MARS ANALOG MINERALS AND ORGANICS.** J. Blackberg<sup>1</sup>, Y. Maruyama<sup>1</sup>, E. Alerstam<sup>1</sup>, C. Cochrane<sup>1</sup>, G.R. Rossman<sup>2</sup>, S. Shkolyar<sup>3</sup>, J. Farmer<sup>3</sup>, <sup>1</sup>Jet Propulsion Laboratory, California Institute of Technology, 4800 Oak Grove Dr., Pasadena, CA 91109, Jordana.blackberg@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>School of Earth and Space Exploration, Arizona State University, Tempe, AZ 85287

**Introduction:** We present recent developments in Raman spectroscopy for Mars surface analysis, targeting identification of both minerals and organics, preserving grain-scale geological context. A schematic of our instrument is shown in Figure 1.

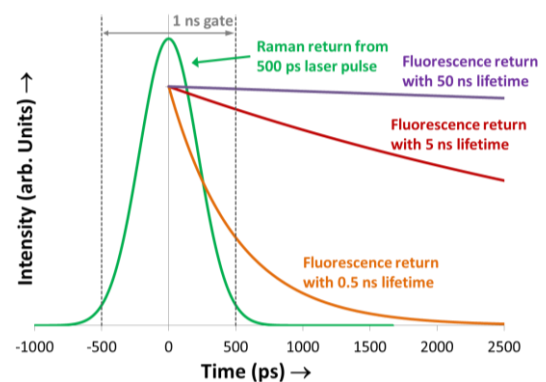


**Figure 1.** Schematic of a Time-Resolved Raman Spectrometer appropriate for a Mars rover. The miniature probe could be arm-mounted and the miniature spectrometer and detector could be located on the main rover body.

Raman spectroscopy has long been a candidate for the next generation of *in situ* planetary instruments, as it provides mineralogical structure and composition of nearly all crystalline minerals [1-3]. It can be performed in concert with microscopic imaging, preserving the geological context of mineral phases. In addition to minerals, Raman can identify organic materials, and has been used in the laboratory to analyze organics, for example those present in Martian meteorites [4]. In large part due to the ability to identify both minerals and organics, Raman spectroscopy has been included on the strawman payload identified by the Mars 2020 Science Definition Team [5].

However, several challenges exist when targeting mixed phase materials with Raman spectroscopy, particularly where organics are present. The primary challenge is that fluorescence often makes conventional 532 nm Raman spectroscopy of these samples impossi-

ble. Fortunately, it has become possible to take advantage of the fact that fluorescence can be distinguished from Raman processes in the time domain. Raman scattering is an instantaneous process while fluorescence processes are associated with decay times which vary from ps to ms. In natural mixed-phase samples, there can be several fluorescent phases, leading to both long lifetime (mineral) and short lifetime (organic) fluorescence. An illustration of fluorescence rejection using time resolved methods is shown in Figure 2. We have developed a time-resolved Raman spectrometer that builds on the widely used 532 nm Raman technique to provide a means for performing Raman spectroscopy without the background noise that is often generated by fluorescence.



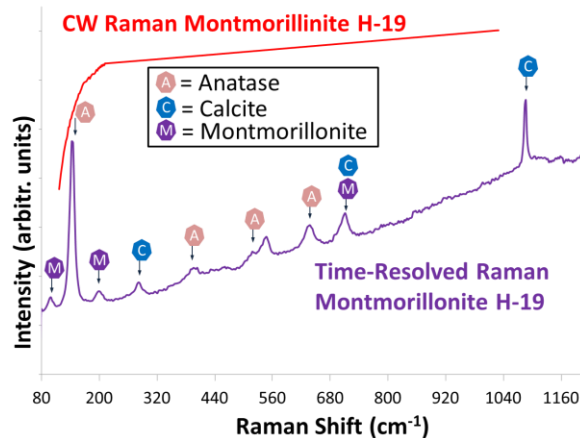
**Figure 2.** Illustration of fluorescence rejection with time-resolved Raman spectroscopy, where only the signal that falls within the chosen time gate is collected. Mineral fluorescence is typically long-lifetime ( $\mu\text{s}$  to  $\text{ms}$ ) and is easily rejected using a 1 ns gate. Organics present a greater challenge as they often exhibit faster fluorescence lifetimes (ps to ns) as illustrated in the orange and red curves.

It is now well understood that Mars once contained habitable environments, such as those explored by Curiosity in Gale Crater [6]. Minerals associated with sedimentary deposits and aqueous alteration, such as phyllosilicates and sulfates, have been identified from orbit as well as *in situ*, and most recently by Curiosity with its suite of tools [7]. Future missions will be aimed at seeking samples for return to Earth, likely from similar habitable environments, that are most likely to contain evidence of past life. Once these regions are identified, Raman spectroscopy has the potential to map out minerals on the grain scale and potentially find evidence for organics that would be essential to priori-

tizing samples for cache and return. We present Raman spectra of Mars analog minerals, indicating that fluorescence is indeed problematic, but can be mitigated using time-resolved techniques.

### Raman spectra of Mars analog samples:

We present time-resolved Raman spectra of Mars analog samples such as clays and sulfates, and compare the results to those obtained with conventional continuous wave (CW) Raman spectroscopy. Figure 3 shows Raman spectra for a montmorillonite clay sample, where several phases are revealed with time-resolved Raman. Conventional Raman, in this case, was unsuccessful due to high background fluorescence. Figure 4 shows a time-resolved Raman spectrum of an organic-rich sample in which carbonates and kerogen, a fossil biosignature, can be identified [8].

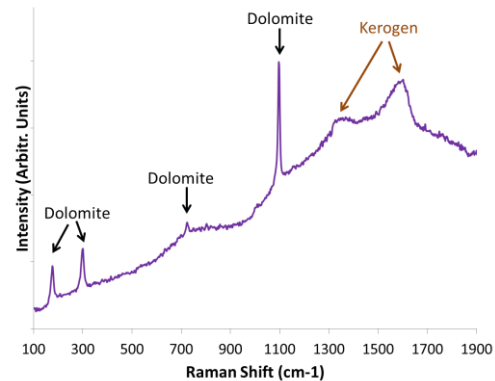


**Figure 3.** Raman spectra of montmorillonite clay standard H-19. The conventional Raman spectrum with a 514 nm laser exhibits high fluorescence that saturates the detector, and therefore no Raman peaks. The time-resolved spectrum reveals several phases: montmorillonite, anatase, and calcite.

### Instrument Development:

Time-resolved detection is enabled by a 500 ps pulsed laser and a recently-developed solid state Single-Photon Avalanche Diode (SPAD) detector array based on Complementary Metal-Oxide Semiconductor (CMOS) technology [9,10]. Using this compact SPAD array, we have demonstrated that we can achieve equal or greater sensitivity to that achieved with traditional photocathode-based detectors such as streak cameras [11]. 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. We will present recent developments in optical design and microscopic imaging that enhance signal-to-noise while maximizing contextual information. We will also discuss methods for improving identification of unknown minerals with classi-

fication algorithms that use Raman databases such as the RRUFF database [12].



**Figure 4.** Time-resolved Raman spectrum of an organic-rich sample from the Castille Formation, Delaware Basin, Texas contain fossilized organic matter in the form of kerogen.

Finally, we will discuss future improvements for optimizing the signal-to-noise performance of the time-resolved Raman instrument for dark samples and those containing organics. For example, kerogen and other fossilized biosignatures present a challenge in that they often exhibit short lifetime fluorescence, they can be dark and thus susceptible to laser damage. We will discuss potential advancements that may greatly improve our ability to identify these challenging samples by making use of higher repetition rate lasers (MHz) with lower energy per pulse that are currently under development.

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