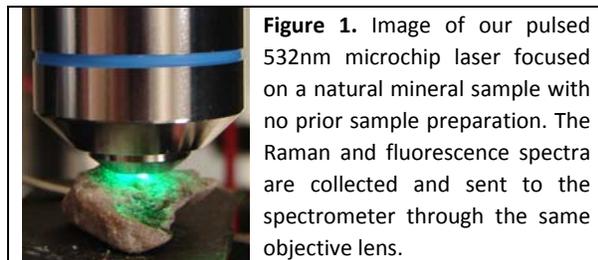


**On-Surface Planetary Mineralogy Using Time Resolved Raman and Fluorescence Spectroscopy.** J. Blackberg<sup>1</sup> and G.R.Rossman<sup>2</sup>, <sup>1</sup>Jet Propulsion Laboratory, California Institute of Technology, 4800 Oak Grove Dr., Pasadena, CA 91109, Jordana.blackberg@jpl.nasa.gov, <sup>2</sup>California Institute of Technology, Division of Geological and Planetary Sciences, Pasadena, California 91125, grr@gps.caltech.edu

**Introduction:** Laser Raman spectroscopy offers the exciting opportunity to interrogate rocks in their natural geological context, preserving the mineral constituents along with their textural and morphological information (Figure 1). Microscopic Raman spectroscopy is a nondestructive means of generating two dimensional maps of mineralogy on the order of grain sizes. Because of its versatility, Raman spectroscopy has developed as a prime candidate for *in situ* exploration of planetary bodies (e.g. Mars, Venus, the Moon, the moons of Mars – Phobos and Deimos, asteroids) as well as pre-selection of rock and soil samples for cache and return missions. Laser Raman spectroscopy is a widely used method in the laboratory, and more recently in the field, for structural analysis of minerals. Large databases of Raman spectra of minerals are under development to enable rapid mineral identification, for example the RRUFF project [1].



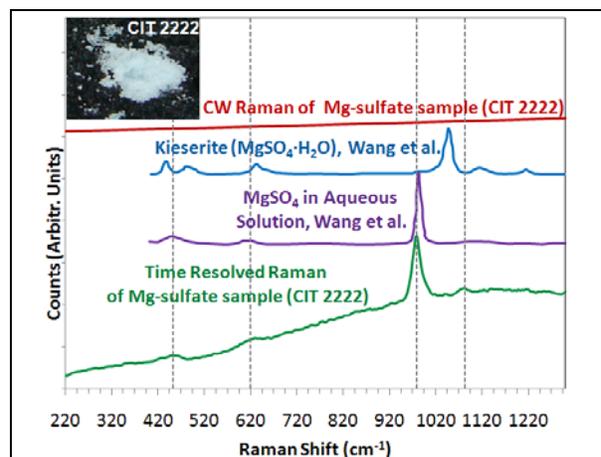
**Figure 1.** Image of our pulsed 532nm microchip laser focused on a natural mineral sample with no prior sample preparation. The Raman and fluorescence spectra are collected and sent to the spectrometer through the same objective lens.

Traditional continuous wave green Raman is the primary technique used in the laboratory for mineralogical analysis. However, in many circumstances Raman is impossible to obtain due to large interfering fluorescence from trace impurities overlapping the Raman region of the spectrum. We discuss the use of time resolved spectroscopy to obtain Raman spectra under even the most extreme fluorescence conditions [2]. Since Raman occurs instantaneously with the laser pulse, and fluorescence decay times vary from picoseconds to milliseconds, it is possible to separate out the Raman from many possible fluorescence centers using time resolution.

In addition to obtaining fluorescence-free Raman, time-resolved spectroscopy allows us to collect the complete time spectrum, which can also include complementary fluorescence and laser induced breakdown spectroscopy (LIBS) spectra when performed under the appropriate conditions.

**Planetary mineralogy:** Raman spectroscopy is under consideration for a host of landed planetary missions aimed at definitive mineralogical studies. Mars

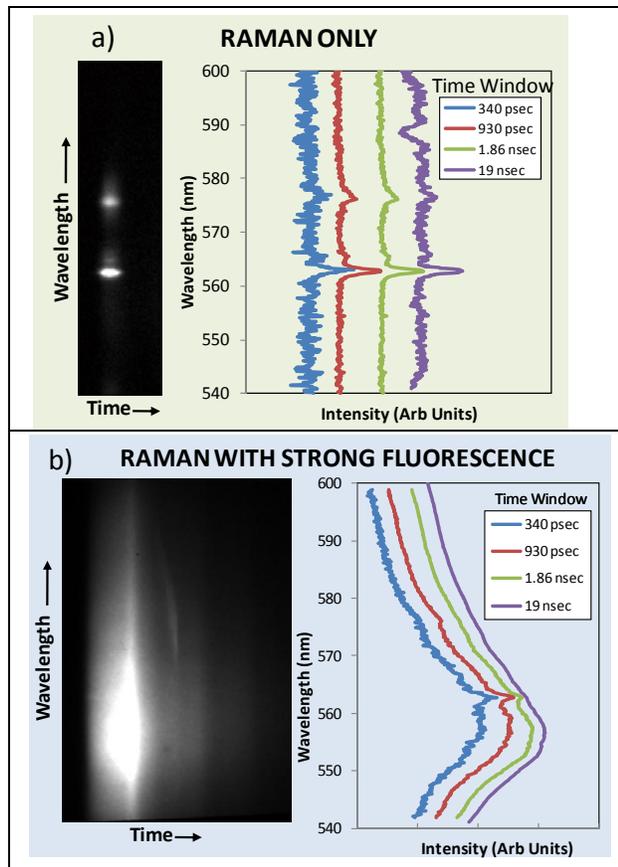
mineralogy has primarily been inferred from both orbital and lander data. Evidence for an early water rich history is supported by the probable presence of altered minerals such as goethite, jarosite, Fe-, Mg-, and Ca- sulfates, hydrated sulfates (e.g., kieserite), phyllosilicates (e.g., montmorillonite clays), and Fe-, Mg-, and Ca- carbonates [3]. However, with the exception of Fe-bearing sulfates, hematite, and goethite identified by the MER Mössbauer instrument there have been no alteration phases unambiguously identified by



**Figure 2.** The Raman spectrum of this naturally occurring magnesium sulfate sample from Strassfurt, Germany was completely obscured by fluorescence when measured using a CW Raman spectrometer (red curve). Using time-resolved Raman spectroscopy (green curve) we were able to identify magnesium sulfate as well as determine the mineral hydration state of our sample. This is one example of the use of time resolved spectroscopy for highly fluorescent Mars-relevant minerals. Several other pertinent examples will be presented. [Ref: Wang et al., *Geochimica et Cosmochimica Acta*, 70 (24), 2006]

*in situ* instruments to date. An *in situ* Raman spectrometer would be able to definitively determine the mineralogy of nearly all crystalline phases on Mars, and indeed is proposed for the ExoMars and Max-C rovers in 2018 [4]. Because many of these altered minerals are known to exhibit a strong fluorescence, the use of time resolution would be expected to significantly improve the number of successful measurements on Mars. Figure 2 shows an example where we have used time resolved Raman spectroscopy to identify a hydrated magnesium sulfate phase in a highly fluorescent sample. Sulfates are an important class of altered min-

erals inferred on Mars; for example magnesium sulfate is likely to be present in the Columbia Hills and Meridiani Planum outcrops. Part of the appeal of Raman spectroscopy as an *in situ* planetary tool is its applicability to mineralogy in diverse planetary environments. In addition to Mars, it is under consideration for *in situ* missions to Venus, Mars' moons, the Earth's moon, and asteroids. Examples of how time resolved Raman can be used in these highly varied environments will be presented as well.



**Figure 3.** Demonstration of our ability to distinguish Raman and fluorescence in the presence of short lifetime fluorophores. The streak camera images are on the left and spectra taken from the images averaged over the indicated time windows from 340 psec to 19 nsec are shown on the right. a) Data from pure methanol showing the methanol Raman peaks with no associated fluorescence or background. b) Rhodamine 6G diluted to  $10^{-7}$ M in methanol. Despite overwhelming fluorescence, the methanol Raman is still visible if observed at  $t < 2$  nsec. This data indicates that with the current system, we could easily distinguish Raman for a mineral with a similar fluorescence lifetime to Rhodamine, or  $< 3.9$  nsec. We would expect to see Raman even for shorter fluorescence lifetimes.

**Time Resolved Raman and Fluorescence laboratory instrument:** We demonstrate the use of a 532 nm pulsed miniature microchip laser and a streak camera (Axis Photonique) operating with the laser and sweep electronics synchronized to collect time resolved Raman and fluorescence spectra. The streak camera allows the collection of Raman and fluorescence together while preserving the time resolution information. The benefit of this approach is that a small and inexpensive low pulse energy laser (microchip laser) can be used, and that we do not incur CCD read noise with every pulse which significantly improves signal to noise ratio (SNR). Since only the return is synchronized with the laser, background light is eliminated, allowing for daylight operation. Additionally, our streak camera system is capable of picosecond resolution, essential for distinguishing Raman and fluorescence in samples containing impurities with short fluorescence lifetimes. For example, figure 3 demonstrates that we can distinguish Raman spectra from a sample with fluorescence lifetime of less than 3.9 nsec.

**Planetary Instrument Challenges:** *In situ* instruments face many challenges that do not affect the design of state-of-the-art laboratory instruments. These include extreme conditions (temperature, pressure, etc.), restricted payload sizes, and the need to be highly automated, withstand vibration testing, varying radiation environments, and planetary protection requirements. For some missions long acquisition times may not be possible, for example asteroid touch-and-go and Venus surface lander missions. Despite the many challenges, there is an important role for on-surface Raman spectrometers in both *in situ* and sample selection for cache and return missions. The key subsystems of potential risk are the pulsed microchip laser and time resolved detector. Estimates will be discussed which suggest that a miniature and robust time resolved Raman system is within reach for establishing a versatile and definitive planetary mineralogy tool.

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**References:** [1] <http://rruff.info/> [2] J. Blacksberg, G. Rossman, and A. Gleckler (2010) *Applied Optics*, 49 (26), 4951-4962, [3] D.W. Ming et al. (2008) in *The Martian Surface: Composition, Mineralogy and Physical Properties*, J.F. Bell III, ed., 519-540 [4] J.A. Grant et al. (2010) *Astrobiology* 10 (7), 663-685