REMOTE DETECTION OF MINERALS AND BIOMARKERS USING RALLF: A COMPACT RAMAN, ATMOSPHERIC LIDAR, LIBS AND FLUORESCENCE SENSOR. A. K. Misra[1], S. K. Sharma[1], M. N. Abedin[2], T. E. Acosta[1], J. N. Porter[1], D. E. Bates[1], P. G. Lucey[1], G. J. Taylor, and P. J. Mouginis-Mark[1]. [1]Hawaii Institute of Geophysics and Planetology, Univ. of Hawaii, Honolulu, HI 96822, USA; anupam@hawaii.edu, [2]NASA Langley Research Center, Hampton, VA 23681.

Overview: University of Hawaii (UH) in collaboration with NASA Langley Research Center has developed a compact portable sensor platform capable of performing remote Raman, LIBS, Fluorescence and lidar measurements from stand-off distances. The system using a 2.5 inch diameter telescope is capable of measuring Raman, LIBS, and fluorescence spectra of a mineral target from a distance of several meters with single laser shot excitation using a 532 nm, 30 mJ/pulse, 20 Hz laser. High quality Raman spectra providing unambiguous identification of various minerals and organics from 9 m distance in daytime can be recorded with 100 ns detection time. Similarly, the system is capable of recording LIBS and time-resolved fluorescence spectra using single laser shots. The spectra measured with 1 s integration time (= 20 laser shots) show significant improvement in signal to noise and provide very high quality spectra. The system also has lidar capability for atmospheric studies. The combined spectroscopy system has the advantage of rapid mineral analysis from a long stand-off distance without need for sample collection or preparation, and thus could be a technology appropriate for future Mars landers.

Among the various techniques for detecting water, ice, H_2O/OH bearing minerals and biominerals, Raman spectroscopy stands out as providing distinctive spectra for unambiguous identification of water and water-bearing minerals. The portable remote Raman instrument developed at UH has been shown earlier to detect water, ice, water-bearing minerals, and carbon in carbonate form from a distance of 10 to 50 m under bright day conditions with short integration time [1-4]. Over the years we have demonstrated that a large number of minerals including dark minerals such as augite, actinolite, antigorite, dravite, clinochlore, olivine, and minerals in Hawaiian basaltic rocks can be easily detected using our compact remote Raman systems [5].

We have previously demonstrated [6-8] that it is possible to combine both stand-off Raman and LIBS spectroscopy into one system that will produce and record Raman and LIBS spectra from a single sample at a distance. The synergy of combined stand-off Raman and LIBS technique provides a very powerful analytical instrument for planetary surface exploration.

In addition, the combined Raman and LIBS system also has the capability to perform time-resolved fluorescence spectroscopy. We have recently demonstrated that a new instrument known as "Stand-off Biofinder" can easily identify a biological material in a large search area in real time using time resolved fluorescence signals [9]. The task of finding a small amount of biological material or bio-minerals from a large collection of rocks and minerals on a planetary surface can be a very time consuming process for rovers/landers. The stand-off biofinder significantly improves the capability of a rover/lander to find bio-minerals and other bio-markers such as phyto pigments, nucleic acids and proteins from a stand-off distance providing detailed images of biological materials in real time.

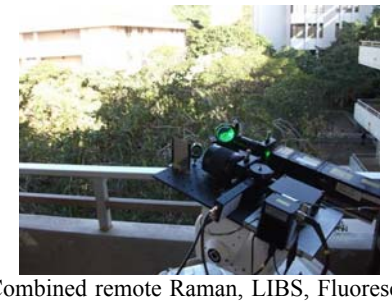

Fig.1: Combined remote Raman, LIBS, Fluorescenc and lidar sensor.

Experimental Set-up and Samples: The combined stand-off Raman, LIBS, Fluorescence and Lidar system uses a 2.5 inch telescope for collecting optical signals. A one inch diameter 532 nm notch filter is used in the back of the telescope to separate the lidar signal (Rayleigh scattered light). A frequency-doubled mini Nd:YAG pulsed 532 nm laser source is used to excite the target located at a remote distance. The scattered light generated by the target is collected and focused onto the slit of a compact spectrograph of size 10 cm (length) x 8.2 cm (width) x 5.2 cm (height). The spectrograph uses a custom HoloPlex grating and is equipped with a custom gated thermo-electrically cooled mini-ICCD detector. Figure 1 shows the combined stand-off system. All spectra were measured using a 50 micron slit with the intensified CCD in the gated mode under daylight conditions. Samples were placed 9 m away from the system. The rock-forming mineral samples were purchased from Ward's Natural Science Establishment, Inc., Rochester, New York. The Hawaiian basalt sample is from Hualalai Volcano, Hawaii.

Results: Figure 2 shows stand-off Raman spectra of gypsum, calcite, α-quartz and anatase from a distance

of 9 m with single pulse laser excitation and detection time of 100 ns. The plot shows three as-measured spectra for all minerals, illustrating the good signal to noise ratio and reproducibility of the system.

Figure 3 shows the stand-off LIBS measurement of Hawaiian basalt from Hualalai Volcano from a distance of 9 m with 1 second integration time using 532 nm pulsed laser with 30 mJ/pulse energy operating at 20 Hz. The stand-off LIBS spectrum of the lava rock shows the presence of Ca, Na, Fe, and Li elements. The broad features at 547-556 nm and 610-636 nm are CaO molecular bands. Figure 3 also illustrates that the sodium doublets observed at 588.99 and 589.59 nm are clearly resolved by the compact spectrograph.

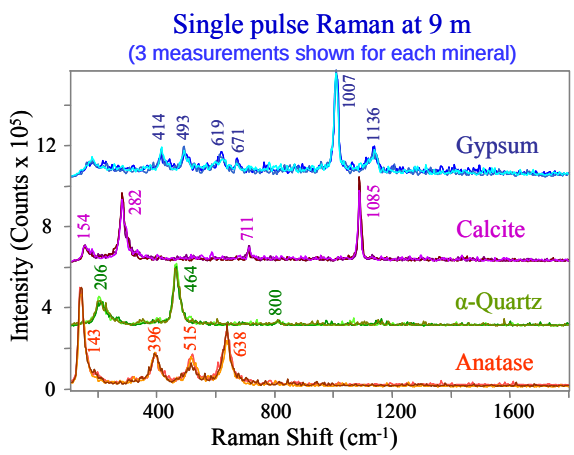

Fig. 2: Stand-off Raman spectra of various minerals from a distance of 9 m with single laser pulse excitation. The spectra have been vertically displaced for clarity.

Figure 4 illustrates the capability of the time-resolved fluorescence spectroscopy to work as a new instrument called "stand-off bio-finder" to distinguish biological materials from minerals backgrounds. In Fig. 4(a) it is hard to distinguish white seashell and eggshell residue over a white quartz rock and dark plant twigs over dark augite-rich rock. The time-resolved fluorescence photograph in Fig. 4(b) shows that the biomaterials stand-out as very bright objects due to their strong fast fluorescence and are easily identified.

Summary: We have developed a combined instrument capable of performing stand-off Raman, LIBS, fluorescence and lidar measurements using a 532 nm pulse laser and gated spectrograph with mini-ICCD. The data presented here shows the capability of the combined instrument using Raman, LIBS and fluorescence spectroscopies. Atmospheric lidar data [10] have also been collected and show range-resolved aerosols and clouds distribution and profiling. The combination of Raman, LIBS, fluorescence and lidar is extremely powerful, particularly in the role of reconnaissance of minerals, organic compounds, and elemental compositions of both surface targets and for characterizing dust, aerosols and clouds in the planetary atmosphere.

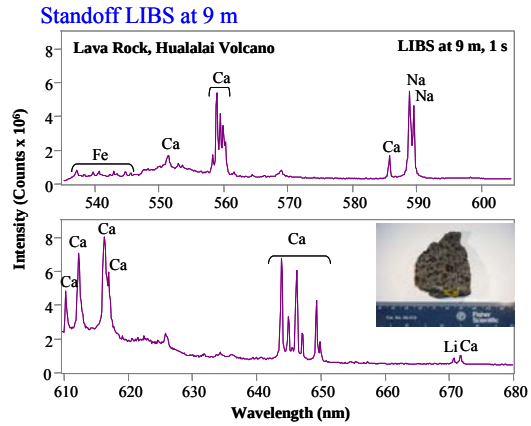

Fig. 3: Stand-off LIBS spectra of Hawaiian basaltic lava rock from a distance of 9 m with 1 s of integration time.

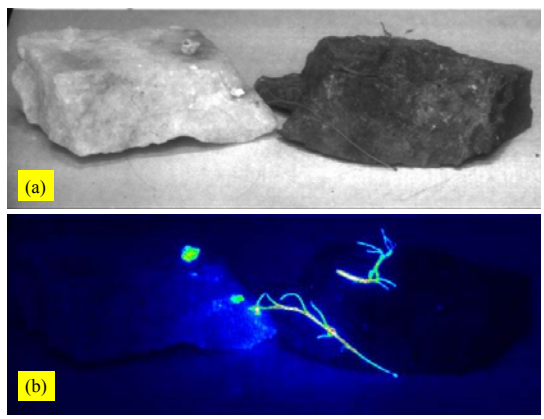

Fig. 4: Top: visible light image of two rocks with biologic samples. Bottom: Biofinder image of the same rocks showing strong organic and pigment fluorescence.

Acknowledgment: This work was supported in part by NASA under MIDP grant NNX08AR10G.

References: [1] Sharma, S.K., et al. (2002) *Appl. Spectrosc.*, **56,** 699-705. [2] Misra, A.K., et al. (2005) *Spectrochim. Acta,* **A 61**, 2281. [3] Misra, A.K., et al. (2006) *Appl. Spectrosc.*, **60**, 223-228. [4] Sharma, S.K., et al. (2011) *Spectrochim. Acta*, A **80**, 75-81. [5] Sharma, S.K. et al. (2010), *LPSC*, **41**, abstract #1443. [6] Wiens, R.C., et al. (2005) *Spectrochim Acta* A, **61**, 2324-2334. [7] Sharma, S.K., et al. (2009), *Spectrochim. Acta*, A **73**, 468-476. [8] Misra, A.K., et al. (2011) *Proc. SPIE*, **8032**, 80320Q. [9] Misra, A.K., et al. (2012) *LPSC*, **43**, abstract #1666. [10] Abedin, M.N. et al. (2012) LPSC, **43**, abstract #1219.