TIME-RESOLVED RAMAN AND LASER-INDUCED NATIVE FLUORESCENCE INVESTIGATIONS OF CARBONATE ROCKS AS AN ANALOGUE FOR MARTIAN CARBONATES. S. K. Sharma[1], C. P. McKay[2] and A. K. Misra[1], [1]Hawaii Institute of Geophysics and Planetology, Univ. of Hawaii, Honolulu, HI 96822, USA (sksharma@soest.hawaii.edu), [2]NASA Ames Research Center, Space Science Division, Moffett Field, CA 94035, USA.

Introduction: Hypolithic colonization of opaque dolomite rocks in the Arctic and Antarctic Polar Deserts [1] has motivated interest in the possibility of similar photo-synthetic organisms on Mars. Recent studies have identified carbonates on Mars at Nili Fossae [2-3], at Leighton crater [4], at the Phoenix landing site [5], at Gusev crater [6], and in several crater pits including Huygens basin [7]. Orbital detection of small carbonate outcrops on Mars has been possible recently using visible/near-infrared (VNIR) spectra acquired by the Compact Reconnaissance Imaging Spectrometer for Mars (CRISM) [8]. Carbonate rocks from the Little Red Hill site in the Mojave Desert in California, which contain iron oxide bearing coatings that greatly suppress the carbonate features of the underlying material have been proposed as potential analogues to the carbonates on Mars [9]. Tar-containing carbonate rocks from Devon Island in Canadian High Arctic, and colonized hypolith from Silver Lake, California are also considered as potential Martian Analogs [10-12]. We have investigated these three sets of carbonate rocks from the Mojave Desert, Devon Island and Silver Lake with time-resolved stand-off bio-imager [13], and Raman and LINF spectroscopic techniques to understand the organic and biosignatures in these rocks.

Experimental Methods: A bioimager instrument described elsewhere [13] was used to record the time-resolved photographs of various rocks investigated in this study. In brief, the standoff bio-imager consists of a regular 85 mm Nikon camera lens, a 532 nm notch filter and a gated ICCD camera. A small diode-pumped 532 nm YAG pulse laser with 0.1 mJ/pulse energy operating at 10 kHz was used to excite the targets placed at 2 m distance. A diverging lens was used to expand the laser beam diameter to 25 cm at 2 m distance where a variety of rocks were excited with the expanded beam. All images were recorded with 0.1 second integration time with all of the room lights turned on.

Time-resolved stand-off Raman and LINF spectroscopy experiments employed a Nd:YAG frequency doubled pulse laser operating at 15 Hz and with a maximum pulse energy of 24 mJ/pulse at 532nm. The pulse width of the laser pulses was 10 ns. A 10x beam expander was used to focus the 532 nm laser beams to 1-cm diameter spot onto the sample.

A stand-off Raman and LINF collection system described in earlier publications [14,15] was used for observing the scattered and fluorescence emission light from the samples located at a distance of 9-m from the system in the air. The light was analyzed with an intensified CCD detector operated in the gated mode. A series of combined Raman and LINF spectra were collected from the samples with 10-ns gate with varying delay time.

Results: Figure 1 shows the white-light and time-resolved photographs of rocks illuminated with a 532 nm pulsed laser recorded at 2 m distance. These samples include: 1. gypsum rock, from Freemont County, Colorado; 2. hematite-coated carbonate rock from the Little Red Hill site in the Mojave Desert, CA; 3. dolomite rock from Butte, Montana; 4. tar-containing dolomite from Devon Island in Canadian High Arctic; and 5. colonized carbonate hypolith on the top surface from Silver Lake, CA.

In Fig. 2, the white-light illuminated photograph (A) the gypsum rock (1) shows the brightest image

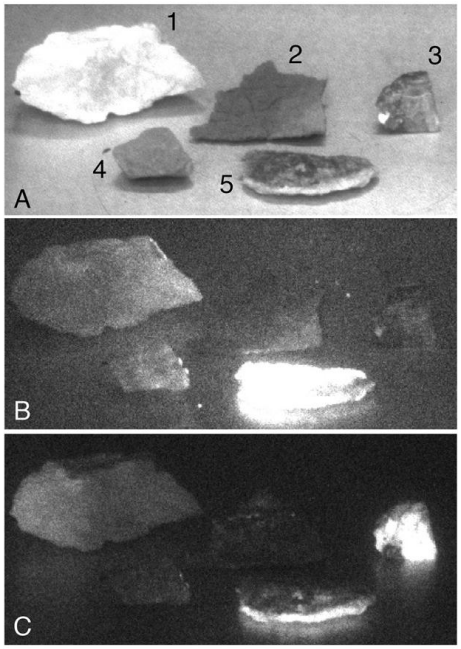

Fig. 1. Photographs of rock samples with 0.1 s exposure time at 2 m distance with gated ICCD camera with (A) White-light illumination; (B) with short life-time LINF (gated 200 ns) and (C) with long-life time LINF (4 ms gate) excited with 532 nm pulsed laser.

followed by the dolomite rock (3), and the hematite-coated carbonate rock (2), the tar-containg carbonate rock (4) and the colonized carbonate hypolith appear darker on the surface. In time-resolved photograph (B) the colonized hyplith shows the brightest image because of presence of the hypolithon community on the surface of the dolomite rock that give rise to short-lived (<100 ns) LINF emission. In photograph (D) the dolomite rocks (3) appears brighter because of long-lived LINF emission from transition-metal ion impunities (e.g., Mn). The bottom part of the colonized carbonate hypolith also show bright image because of long-lived LINF in the carbonate rock.

Figure. 2 shows the time-resolved stand-off Raman and LINF spectra of the colonized hypolith surfaces excited with 532 nm laser at 9 m. The spectrum of white top surface of the colonized rock (Fig. 2 (a) low-

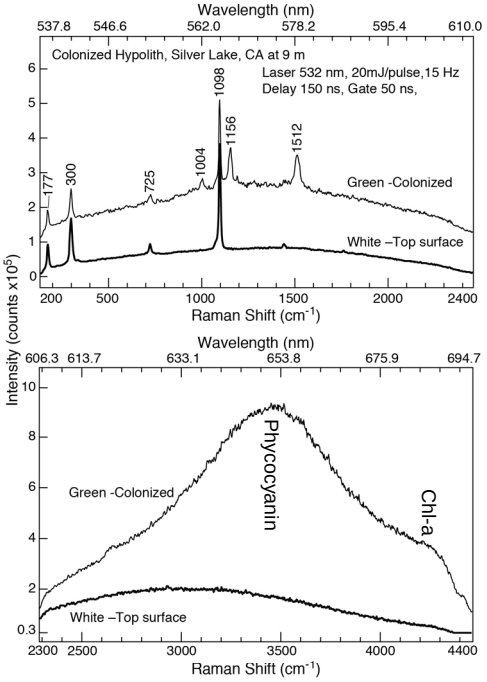

Fig. 2. Combined stand-off TR LINF and Raman spectra of colonized hyplolth from Silver Lake, CA. Laser 532 nm, 24 mJ/pulse, gate 50 ns, slit 100 εm.

er trace) contains the Raman fingerprint of dolomite at 177, 300, 725, and 1098 cm^{-1} and the colonized green surface has additional Raman lines at 1004, 1156 and 1512 cm^{-1} that are fingerprints of carotenoids (Fig. 2 a upper trace) [e.g., 15]. In Fig. 2 (b) the upper trace shows short-lived strong fluorescence bands centered at ~652 nm with a weak shoulder at ~688 nm. The 688 nm band is characteristic of chlorophyll-*a* pigment [15, 16], and the ~652 nm band indicates presence of another phytopigment phycocyanin [16] in the colonized hypolith. The top white side of the colonized dolomite rock shows much weak fluorescence centered at ~624 nm possibly indicating that some biogenic material might have diffused into the rock. This finding shows the potential of detecting colonized minerals and rock samples from their short lived (50 ns) fluorescence spectra. Time-resolved fluorescence spectra of tar containing carbonates from Arctic (Devon Island, Canadian High Arctic) at 9 m distance showed short-lived strong and broad fluorescence bands at ~564 and ~624 nm. Raman measurements with 785 and 255 nm laser excitations minimized the fluorescence from the tar containing carbonates and found the fingerprints of dolomite in these rocks. These measurements demonstrate that the TR LINF could be very useful in detecting biogenic materials in minerals and rocks on planetary surfaces.

Summary: We have demonstrated that a bioimager instrument can identify biogenic materials from their low (<100 ns) lifetime LINF emission photographs. A combined time-resolved stand-off Raman and LINF sytem can be used for verifying biogenic materials from their short lived fluorescence and could also identify the mineralogy of the rock from their Raman fingerprints. A combination of gated bioimager, and a gated stand-off Raman and LINF spectrometer will also be very useful for selecting samples from a lander/ rover for future Mars missions such as the Mars Astrobiology Explorer-Cacher (MAX-C) rover and Mars Sample Return Mission.

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