UNDERWATER LASER RAMAN SPECTROSCOPY FOR CHARACTERIZING ORGANIC CONTENT IN LAKES: IMPLICATIONS FOR TITAN EXPLORATION.

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Introduction: The search for evidence of life is a science priority for Mars and for the moons of the outer solar system. Biomarkers, and organic molecules – where distinguishable from abiotic sources – constitute one major source of such evidence. Laser Raman spectroscopy (LRS) has high detection sensitivity for all organic functional groups. The Raman spectroscopy of vibrations such S-S, C-H, C-O, C-N, N-O, N-H in amino acids, complex protein-like molecules, and pigments has been well studied in the context of astrobiological planetary exploration [1-9]. Such results demonstrate that LRS can be used to identify organic molecules and to determine their abundance within mineral matrices in both in-situ and ex-situ applications. The use of LRS for the characterization of organic molecules in aqueous solution is, comparatively, a much less explored subject [10,11].

Here, we describe the deployment of a field-portable LRS system in Laguna Negra, Chile; Laguna Negra is a glacial lake located in the Central Andes of Chile where planetary technologies, systems, and science exploration strategies are being developed and tested (see below). Two LRS deployments were made at the site. During these deployments we recorded 1000+ spectra from the lake's water. Over twenty samples were collected from the lake and analyzed in the laboratory using benchtop LRS instruments.

The data collected in the field and in the lab (1) demonstrates the feasibility of LRS to characterize the organic content of Laguna Negra through in-situ and ex-situ laboratory analyses, (2) establishes a mission-relevant path-to-flight for LRS as a powerful technique for astrobiological exploration, and (3) provides guidance for future development of LRS-based instrumentation for in-situ, real-time characterization of organic molecules in the context of planetary exploration.

Background: The ASTEP-funded Planetary Lake Lander (PLL) project aims to "develop and field test operational scenarios and systems relevant to future missions to the lakes and seas of Titan" [12]. In 2013, a LRS instrument was deployed, for the first time, at the PLL project field-site, Laguna Negra (33º37'25"/70º03'35W), in order to test the suitability of LRS for in-situ organic detection and provide insight on the organic diversity in the lake.

The field instrument is an Enwave Optronics EZ-Raman integrated Raman System. The system boasts a 532 nm laser for excitation, and a TE-cooled CCD spectrometer. The systems is battery-powered and is equipped with an optical fiber probe head. The probe head was retrofitted with a KOSI Immersion Optic accessory to enable analysis up to 50 cm below the lake's surface. Figure 1 shows a picture of the LRS system in Laguna Negra.

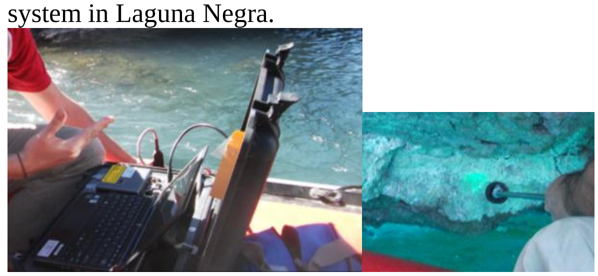

Figure 1: (left) EZ-Raman LRS system; (right) immersion optics – green reflection from laser source is visible

In-situ LRS analyses: We carried out two deployments of the LRS system described above during 13-18 December 2013. First, we used the immersion optics to probe the lake in different locations were diatoms and other algae were present. We recorded over two dozen spectra 10-50 cm below the surface during this deployment. The spectra were recorded in 1-second integration times. Figure 2 shows select spectra from this deployment. While the spectra show intense background interference from ambient light and sample fluorescence, the signal-to-noise of the spectra is high enough to observe Raman peaks across the spectral range.

The strong peaks at ~1150 and 1520 cm^{-1} observed in most of the spectra shown in Figure 2 are associated with the stretching modes of the C-C and C=C bonding in the β-carotene pigment [7]. Water-related O-H stretching modes occur in the >3200 cm^{-1} spectral region. Unfortunately, our field LRS system does not

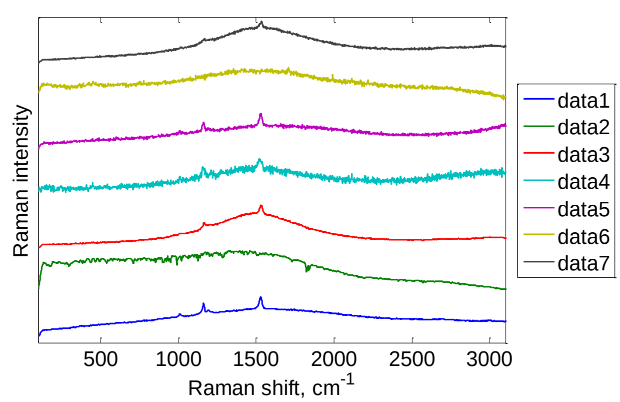

Figure 2. LRS spectra recorded in-situ in Laguna Negra

allow for analysis in that region. However, some spectra such as 'data5' show a slope around 3000 cm^{-1} that is likely due to the presence of very intense, and broad, OH peaks that reach into our spectral range. The 'data6' spectrum shows weak peaks at 390, 420, 450, 750, 758 cm^{-1}, which are related to Si-O vibrational modes; this particular sampling site featured turbid, tan-colored water.

For the second deployment of our LRS system, we attached the Raman head and its immersion optics to an YSI 6-Series water quality sondes in order to record collocated data on the lake's water temperature, turbidity, chlorophyll content, pH, and LRS-derived organic content. The dual water quality-LRS sonde was fixed to the starboard side of a Zodiac and immersed 15 cm in the lake (Figure 3). We then traversed Laguna Negra for over two hours recording near real-time data with the sonde. An extended description of this experiment is available in [13]. We recorded a total of 919 LRS spectra at 5-second intervals. All of the LRS spectra were processed using automated routines in order to determine the variability in peak intensity as a function of time. Figure 3 shows the variation of the intensity of the eight peaks with most variability within our dataset. Specifically, these peaks are located at ~140, 200, 450, 750, 1150, 1520, 2228, and 3080 cm^{-1}. We have tentatively assigned these peaks to vibrational modes of water, organic compounds (carotenoids and chlorophyll), and clays dissolved in water.

Laboratory analyses: We have carried out LRS analyses of samples from Laguna Negra in the laboratory using three different systems: two conventional Raman systems that use 532 (Horiba Jobin-Yvon equipped with an Elforlight G4 series laser) and 785 nm (BWTek Prime T spectrometer with integrated laser source) as excitation wavelengths, respectively, and a FT-Raman Bruker RFS100/S instrument (1064 nm excitation). By way of an example, Figure 4 shows the Raman spectra recorded with the FT-Raman; Raman signals are enhanced with this instrument due to suppressed fluorescence with a 1064 nm excitation source. These spectra confirm the presence of β-carotene as a major component of the organic samples. We have also identified triglycerides and chlorophyll in some of the samples, although the associated Raman peaks are relatively much weaker than those of the carotenoid pigment.

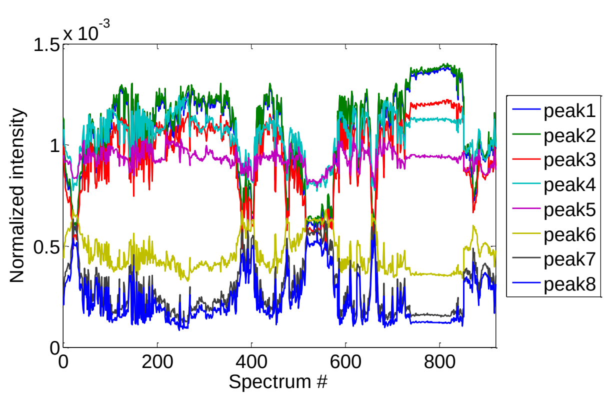

Figure 3. LRS spectra recorded during a traverse

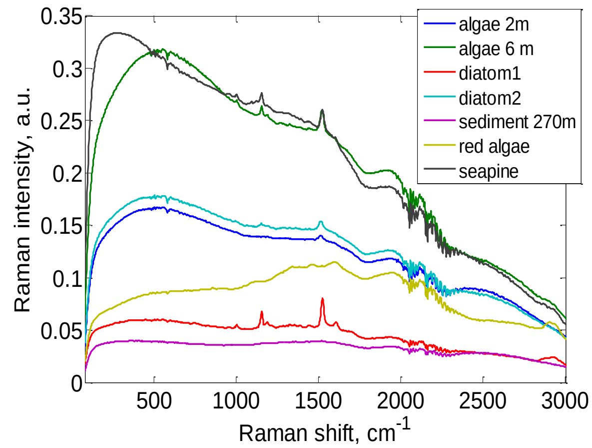

Figure 4. LRS spectra of select Laguna Negra organic samples recorded in the laboratory

Summary and implications: We have used LRS for characterizing the organic content of the lake through real-time, in-situ analyses and through lab analyses of returned samples. Pigments such as β-carotene and fatty acids (triglycerides) were identified as major components of the organic samples. Their relative abundance can be calculated along a traverse in the lake and at various depths.

In light of the above results, LRS may offer a strategic advantage for Titan surface lake exploration. It could provide a critical element in the development of adaptive science payload packages and exploration strategies in communication- and bandwidth-limited missions [12].

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