**Raman-LIBS Data Fusion for Ocean World Exploration.** L. E. Rodriguez[1], A. G. Yanchilina[2], S. Lamm[1,3], K. H. Simon[2], E. J. Eshelman[2], C. Sudlik[2], O. Pochettino[2], D. S. Kelley[4], R. E. Price[5], P. S. Sobron[2], L. M. Barge[1], [1]NASA Jet Propulsion Laboratory, California Institute of Technology, 4800 Oak Grove Drive, Pasadena, CA, 91109 (Laura.Rodriguez@jpl.nasa.gov), [2]Impossible Sensing, St. Louis, Missouri, [3]Department of Geology, Kansas State University, [4]School of Oceanography, University of Washington, Box 357940, Seattle, WA 98195, USA, [5]Stony Brook University, School of Marine and Atmospheric Sciences (SoMAS), Stony Brook, New York 11794, USA.

**Introduction:** Ocean Worlds such as Europa and Enceladus are prime targets in the search for extraterrestrial life as they have an abundance of liquid water and are likely to host geochemical gradients which can serve as an energy source to sustain life [1]. Importantly, strong geochemical gradients are most likely to form wherever hot fluids interact with rocky crust — conditions that also favor the formation of hydrothermal vents. In Earth's oceans, hydrothermal vents are hotspots of geochemical and biological activity, which may have generated conditions that facilitated abiogenesis on a prebiotic world [2,3]. Hence, hydrothermal vents on Ocean Worlds are a promising locale to search for extraterrestrial life.

In this work we explored the feasibility of using Raman and Laser Induced Breakdown Spectroscopy (LIBS) both as stand-alone techniques and concatenated together (known as data fusion [4]) to characterize the organic geochemistry of hydrothermal vent samples and precipitates collected adjacent to vent sites. Notably, both techniques are complementary: Raman provides information regarding the minerology and/or organics present within the system whereas LIBS is generally used to discern the elemental composition. Raman is better suited for analysis of lighter-colored minerals (e.g. calcite, barite, anhydrite) because darker-colored minerals (e.g. hematite, magnetite, pyrite, galena) generate poor Raman signals; the reverse is true for LIBS. Importantly, LIBS is also the only field technique that can detect biogenic elements (CHONPS). Given that life concentrates these elements relative to the surrounding environment, identifying CHONPS hotspots using LIBS may be a feasible strategy to search for life.

**Methods:** Samples (Table 1) from the Roane chimney in the Mothra Hydrothermal Field (Juan de Fuca Ridge), Strytan Hydrothermal Field (Eyjafjord, Iceland), Ambitle Island (Papua New Guinea), Kueishantao hydrothermal field (Taiwan), La Calcara, Panarea Island (Italy), and standards for minerals commonly found at such sites were analyzed using a Raman (Dual in-situ Spectroscopy and coring (DiSCO)) and LIBS (Spectrogrid) system specifically designed for space flight by Impossible Sensing. Both Spectrogrid and DiSCO employ a 1064 nm pulsed fiber optic laser; for Raman spectroscopy the laser is frequency-doubled to give a 515 nm laser. High resolution 6 x 6 mm maps were generated using a liquid lens that enables autofocusing of the laser without the use of any movable parts [5]. Preprocessing (background subtraction, baseline correction, denoising) and data analysis of the spectra were carried out using R software. To confirm elemental, mineralogical, and organic trends, pieces of select hydrothermal vent samples were sent to Activation Laboratories, Ltd. (Actlabs) in Toronto, Ontario to determine total carbon (TC), total inorganic carbon (TIC), and total organic carbon (TOC) content and perform Inductively coupled plasma atomic emission spectroscopy (ICP-OES) and X-ray diffraction (XRD) analysis.

**Table 1.** Field samples characterized in this study.

| Sample Type | Field Site | Major Minerals |
|---|---|---|
| Vent precipitate | Roane: Mothra Hydrothermal Field, Juan de Fuca Ridge | pyrite, chalcopyrite, barite, galena, sphalerite, wurtzite, amorphous silica |
| Vent precipitate | Strytan Hydrothermal Field, Eyjafjord, Iceland | saponite |
| Precipitate on Elephant Ear coral | Ambitle Island, Papua New Guinea | ferrihydrite |
| Cementing sediment | Ambitle Island, Papua New Guinea | aragonite |
| Sulfur balls | Kueishantao hydrothermal field, Taiwan | sulfur |
| Hard crust | La Calcara, Panarea Island, Italy | anhydrite |

**Preliminary Results:** LIBS is highly sensitive to matrix effects; thus, obtaining accurate concentrations for elements of interest via univariate analysis can be difficult to achieve. Fortunately there are workarounds to matrix effects using supervised learning techniques such as Partial Least Squares (PLS). We have found that LIBS analyses of Roane samples yielded elemental trends consistent with previous work [6,7] as well as ICP-OES analysis. In addition, we have shown that matrix effects can be leveraged to deduce mineralogical gradients within these complex geochemical systems using a technique known as Multivariate Curve Resolution – Alternating Least Squares (MCR-ALS [8]; Fig. 1). Importantly, this technique does not require *a priori* information about the sample.

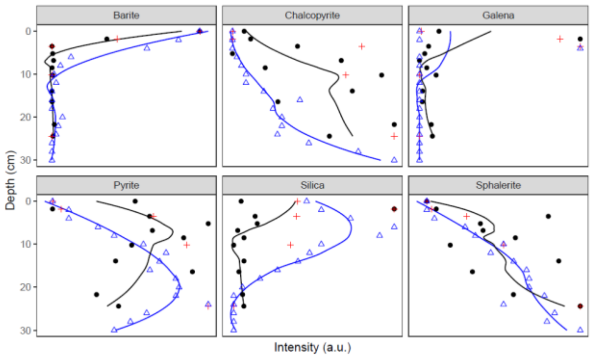


**Figure 1.** In general, mineralogical gradients deduced from MCR of LIBS spectra agree with that from gold-standard techniques. Individual data points and moving average trend lines are plotted against depth into the chimney (0 = exterior): black dots (MCR results); blue triangles (based off SEM data from a different Roane sample [6]); red crosses (XRD). (Rodriguez et al. 2021, in prep. [9])

**Ongoing Work:** We are currently analyzing Raman maps generated via DiSCO. In our preliminary analysis of the Roane samples we have identified hydroxyl-apatite in the exterior samples; this finding was surprising given that apatite was not discovered in previous analysis of these samples by scanning electron microscopy [6] or XRD [this work].

We will ground truth the organic and geochemical trends discerned from Raman analysis with the ICP-OES, TOC, and TIC data we have collected. We will also present our efforts to leverage the known elemental, mineralogical, TOC, and TIC content in the samples to develop machine learning models (e.g. MCR-ALS, PLS, hierarchical clustering, K-means clustering) to discern features diagnostic of CHONPS hotspots and organic content in Raman and LIBS alone, as well as Raman-LIBS fused data sets.

**Significance:** We have generated high resolution Raman and LIBS maps using instruments designed specifically for spaceflight. Preliminary analysis has shown that in using novel chemometric techniques, LIBS alone is sufficient for discerning elemental and mineralogical trends within hydrothermal vent precipitates. Given the mission heritage of these instruments (Raman and LIBS are on NASA's *Perseverance* Mars rover; LIBS is also on NASA's *Curiosity* rover), these techniques are promising in the search for life on Ocean Worlds. It is thus critical to understand the full capabilities and limitations of Raman and LIBS on Ocean World relevant samples, which require the exploration of novel data science tools.

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