

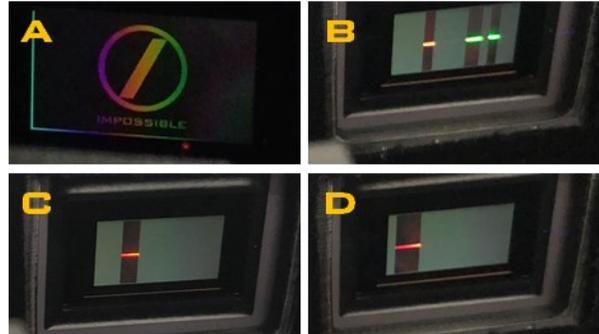
**ULTRA SENSITIVE RAMAN SPECTROMETER FOR PLANETARY SCIENCES.** P. Sobron,<sup>1,2</sup> E. Eshelman,<sup>1</sup> K. Simon,<sup>1</sup> L. Barge,<sup>3</sup> A. Davila,<sup>4</sup> M. Fahey,<sup>5</sup> A. Yu,<sup>5</sup> K. Zacny.<sup>6</sup> <sup>1</sup>Impossible Sensing, St. Louis, MO ([psobron@impossiblesensing.com](mailto:psobron@impossiblesensing.com)). <sup>2</sup>SETI Institute, Mountain View, CA. <sup>3</sup>NASA Jet Propulsion Laboratory, Pasadena, CA. <sup>4</sup>NASA ARC, Mtn View, CA. <sup>5</sup>NASA GSFC, Greenbelt, MD. <sup>6</sup>Honeybee Robotics, Pasadena, CA.

**The *i*SEE Innovation:** *i*SEE (*in-situ* Spectroscopic Europa Explorer) is a next-generation ultra-compact laser Raman Spectrometer with superior performance that meets the top-level scientific requirements of multiple planetary missions to the inner and outer Solar System. *i*SEE boasts an innovative combination of adaptive spatial coding optics and detector that enables unique measurements: *in-situ* chemical identification and sub-ppb quantitation of complex organic compounds, including pre-biotic compounds (e.g. amino acids); biomolecules (organic biomarkers such as proteins, lipids, and nucleic acid polymers); minerals; salts; volatiles.

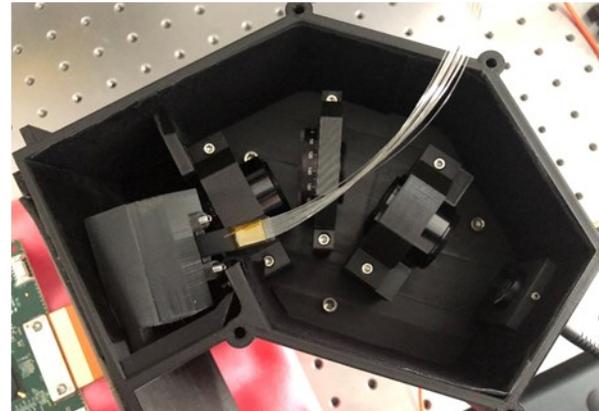
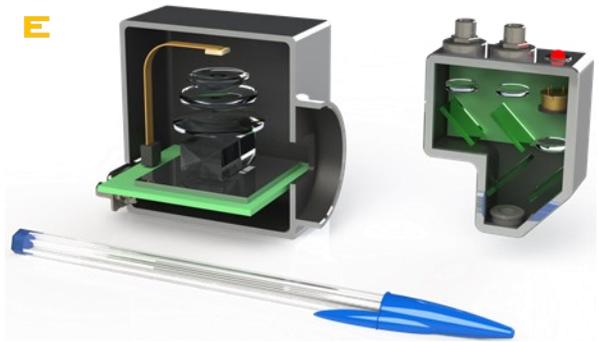
We are developing a small, versatile instrument that [1] addresses priority science goals in missions to several targets and with different spacecraft configurations (orbiters, flythroughs, landers, rovers) and [2] facilitates automated, unsupervised data acquisition and processing in a low-mass, compact deployable instrument with high data production; high scientific value of the returned data; and low operational costs.

Our architecture provides a 3-order of magnitude SNR enhancement relative to spaceflight and conventional compact Raman spectrometers, performs chemometric analysis, and calculates the composition of samples on the spectrometer itself, a particularly relevant feature in short duration missions with limited ground-in-the-loop feedback. This feature gives *i*SEE a remarkable operational advantage compared to CCD-based Raman systems: quantitative analysis can be implemented, in real-time, directly into the measurement process. CCD systems, on the other hand, require resource-intensive readout and subsequent spectral processing (peak area analysis).

Our team has integrated key subsystems of *i*SEE and critically evaluated their performance using standards. We have [1] developed *i*SEE Mk 1, a breadboard of a lander-mounted instrument suitable for remote *in-situ* science investigations; [2] demonstrated the ability of the breadboard to perform novel Raman astrobiological analysis in landed spacecraft, a TRL 2 to 4 advancement; [3] generated science-driven requirements for higher TRL versions of *i*SEE; [4] commenced a systematic Raman spectroscopic survey of planetary analog materials; [5] tested *i*SEE performance to detect a variety of low-concentration organic compounds; [6] commenced space qualification of key subsystems that will lead to *i*SEE Mk2, a TRL5/6 brassboard of our Raman instrument that paves the way for mission infusion of our technology.



[a] MEMS device enables on-chip quantitative Raman analysis of (among others) [b] amino acids and fatty acids; [c] hydration; [d] C-H bonds.



[e] *i*SEE ultra-compact footprint enables accommodation in small lander and rovers [f]

***i*SEE Performance:** Figure G shows a spectrum of a cryoconite powder sample we used to determine the sensitivity of the Mk1 design to trace organics and biosignatures within the sample matrix. We detected carbon bands. The overall detection limit requirement of the instrument is approximately at ppb level. However, because pure compounds were not present at ppm levels, a common characteristic of most organics from natural samples, individual organic species were not identifiable with Raman spectroscopy. Additionally, the lack of individual organic species detection could be because organics in the samples were a complex mixture, which is known generally to reduce the overall Raman signal that is generated or induce a large background fluorescence response that is not specific to any one type of compound.

Only two carbon-related bands were detected at wavelengths 1300 and 1600  $\text{cm}^{-1}$ , which are carbon disordered “D” and graphitic “G” bands. These bands were detected in 4 out of 10 sampling points. The G band at 1600  $\text{cm}^{-1}$  is due to the in-plane vibration of aromatic carbons, and the 1300  $\text{cm}^{-1}$  band, highlighted in the figure, is an intense and broad band seen in poorly ordered carbon.

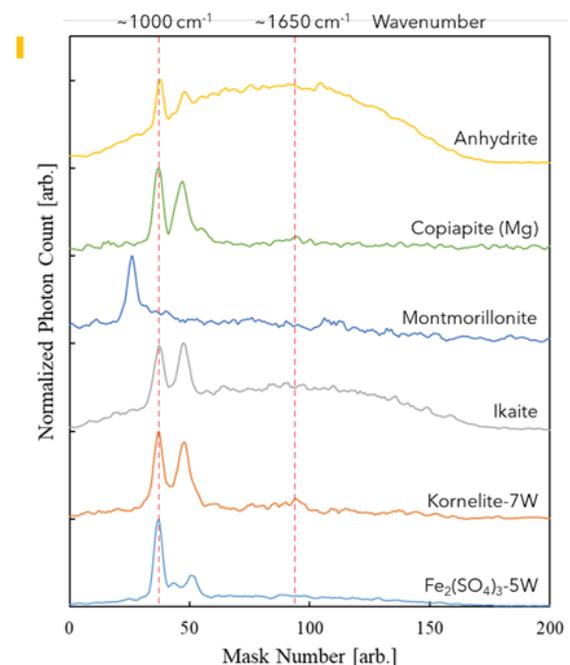
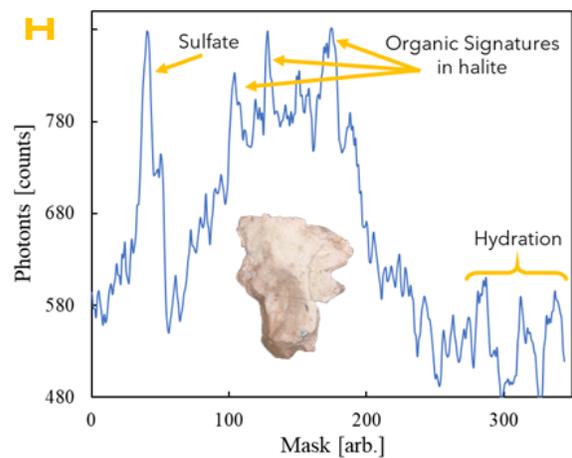
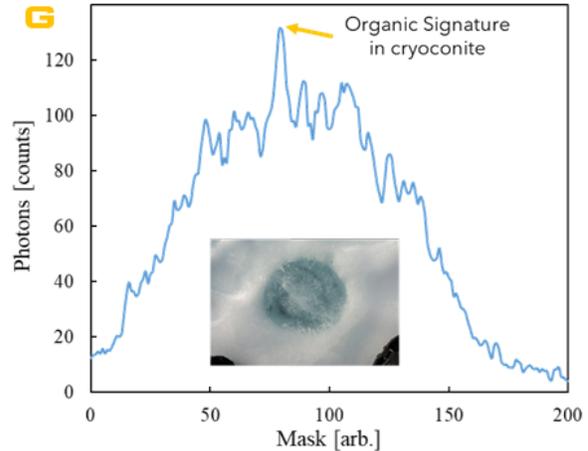
We performed measurements on a sample from the hyper arid core of the Atacama Desert to determine the distribution of microbial colonies, organic matter, and potential biosignatures within the salt matrix (Figure H). Our analyses demonstrated that *i*SEE is sensitive to the presence of trace organic compounds through the spectral signatures of CH, CN, CO, OH molecules; bacterotene and chlorophyll in multiple spots through unique Raman spectral signatures of molecular bonds in the organic compounds; other bio-related materials included degraded carbon (kerogen), scytonemin, alanine, and other yet-unidentified amino acids.

Understanding spatial heterogeneity is important to assess biosignature detectability in the absence of visual clues. In our case study, microbial colonies show spectral patterns distinct from the surrounding salt matrix. In one instance we identified a green colony of cyanobacteria whose Raman spectra includes the chromophore carotene. Reconstructions of Raman wavelengths appear homogeneously distributed and confined to the interior of the colony, consistent with living cells.

Finally, we performed measurements on a variety of sample standards and planetary analogs including sulfates, clays, and media with trace organics. Figure I shows a subset of relevant spectra recorded during testing.

**Next steps:** Demonstrate classification and quantitation of complex organic compounds, minerals/ices, and volatiles.

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Three case studies demonstrating the performance of *i*SEE Mk1. [g] Trace organic compounds detected in natural cryoconite. [h] Gypsum, hydration, and trace organics in natural salt; [i] Materials of interest in planetary sciences.