ORGANIC DETECTION IN OCEAN WORLD ANALOGS WITH A TWO-STEP LASER DESORPTION/IONIZATION TIME-OF-FLIGHT MASS SPECTROMETER. K. Uckert[1], S. Getty[2], A. Grubisic[3], X. Li[4], A. W. Yu[2], M. E. Fahey[2], W. B. Brinckerhoff[2], S. X. Li[2], T. Cornish[5], B. Farcy[4], J. E. Elsila[2], [1]New Mexico State University (Department of Astronomy, Las Cruces, New Mexico 88003; kuckert@astronomy.nmsu.edu), [2]NASA Goddard Space Flight Center (8800 Greenbelt Road, Mailstop 699, Greenbelt, MD 20771), [3]University of Maryland (Department of Astronomy, College Park, MD 20742), [4]University of Maryland, Baltimore County (Baltimore, MD 21250), [5]C & E Research, Inc. (Columbia, MD 21045).

Introduction: The detection of organics on other planetary surfaces provides insight into the chemical and geological evolution of a Solar System body of interest and can inform our understanding of its potential habitability. In this study, we explore the analytical advantages offered by a prototype two-step laser desorption/ionization time-of-flight mass spectrometer (L2MS) by exploiting the resonance-enhanced desorption of analyte. We demonstrate the ability of the L2MS to detect hydrocarbons in organically-doped analog minerals, including cryogenic Ocean World-relevant ices and mixtures.

Methods & Instrumentation: L2MS is compatible with a future *in situ* science payload, and operates by generating a neutral plume of desorbed analyte with an IR desorption laser pulse, followed at a delay by an UV laser pulse, ionizing the plume. Desorption of analyte, including trace organic species, may be enhanced by selecting the wavelength of the IR desorption laser to coincide with IR absorption features associated with vibration transitions of minerals or organic functional groups. For the results presented here, we employ a breadboard mid-infrared (MIR) desorption laser (3.457 µm) with a discrete wavelength, selected to overlap the

C-H stretch vibrational transition of certain aromatic hydrocarbons. Additional selectivity to aromatic species is provided by the 266 nm UV ionization laser pulse via the UV resonance-enhanced multiphoton ionization effects [1]. The use of distinct laser wavelengths allows efficient coupling to the vibrational and electronic spectra of the analyte in independent desorption and ionization steps, mitigating excess energy that can lead to fragmentation during the ionization process and leading to selectivity that can aid in data interpretation.

In single-laser positive-ion laser desorption/ionization mass spectrometry (LDMS), salts frequently overwhelm the mass spectrum; in contrast, L2MS is insensitive to salt and other dominant inorganic cations and targets certain high-priority classes of organic molecules, such as polycyclic aromatic hydrocarbons, organic acids, amino acids, and nucleobases [2,3] in complex mixtures. A detailed description of the development, specifications, and sensitivity of this instrument has been reported previously [2,3,4].

To measure samples at cryogenic temperatures relevant to Ocean Worlds, such as Europa and Enceladus, we recently integrated a cooled sample stage into our L2MS testbed (Figure 2). A liquid nitrogen cooling loop is in thermal contact with the sample probe to provide
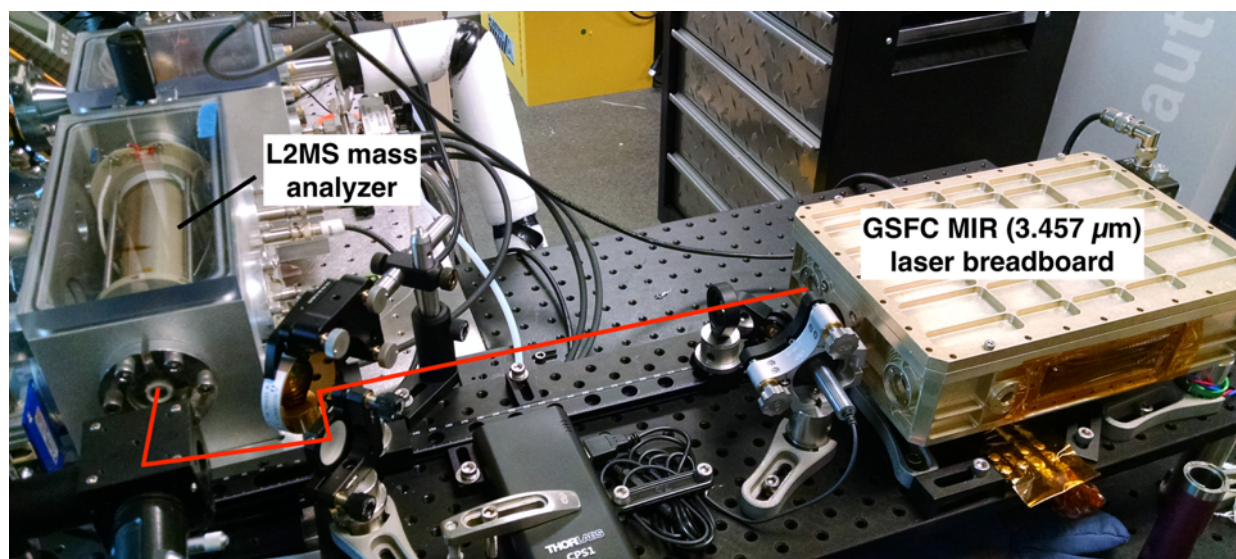

Figure 1: A photograph of the breadboard MIR laser (laser path in red) and the L2MS mass analyzer.

temperatures sufficiently low as to mitigate sublimation of water ice mixtures under high vacuum conditions.
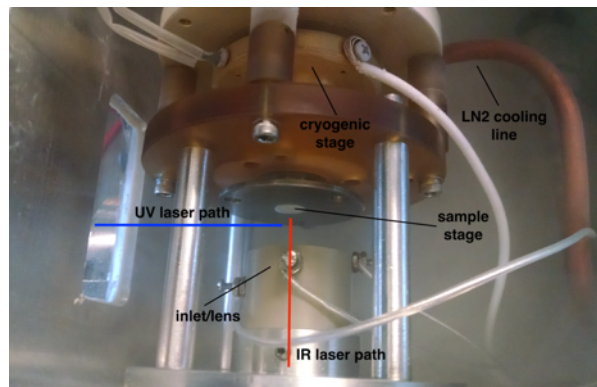

Figure 2: A photograph of the cold sample stage, including the orientation of the orthogonal IR (red) and UV (blue) laser paths relative to the sample.

Results: A mass spectrum of caffeic acid encapsulated by a thin layer of water ice is presented in Figure 3, and clearly shows the caffeic acid parent peak (m/z 180 Da). With excess ionization laser energy, minor diagnostic fragments are revealed to corroborate structural assignment of the base peak (m/z 163 Da: M-OH; m/z 136 Da: M-2•OH).
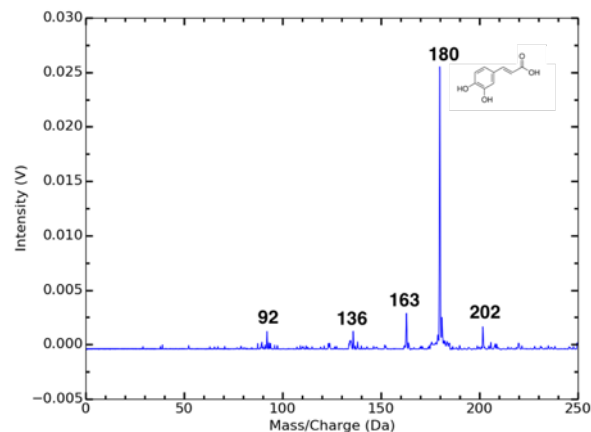

Figure 3: A mass spectrum of caffeic acid coated with water ice, measured at cryogenic temperatures.

We investigated the limit of detection of the L2MS by measuring caffeic acid ($C_9H_8O_4$) (Sigma Aldrich Co.) mixed with epsomite ($MgSO_4•7H_2O$) (Sigma Aldrich Co.) at several concentrations. Epsomite has been identified spectrally on Europa's surface [4], and may be sourced from the subsurface ocean [5], making it a relevant Europa analog salt for our laboratory studies.

Samples were prepared by adding a solution of caffeic acid dissolved in ethanol to epsomite powdered to a <150 μm grain size. We measured a quantity of the organic solution to achieve a 10,000 ppm (1 wt%), 1,000 ppm (0.1 wt%), and 100 ppm (0.01%) concentration series of caffeic acid in mineral concentration. The powdered mixture was dried, pressed onto a stainless steel stub, and mounted onto the sample probe.

The mass spectra of the caffeic acid epsomite mixtures are presented in Figure 4, showing the caffeic acid parent peak (m/z 180 Da) and common ionization fragments. An internal calibration standard, pyrene (m/z 202 Da) is also present in the spectrum. The limit of detection of caffeic acid embedded in a mineral matrix of the L2MS is approximately 20 ppm (assuming threshold signal-to-noise ratio > 10 is necessary for a detection) or better. Similar quantification of limits of detection will be pursued for a suite of organic analog compound classes in future work.
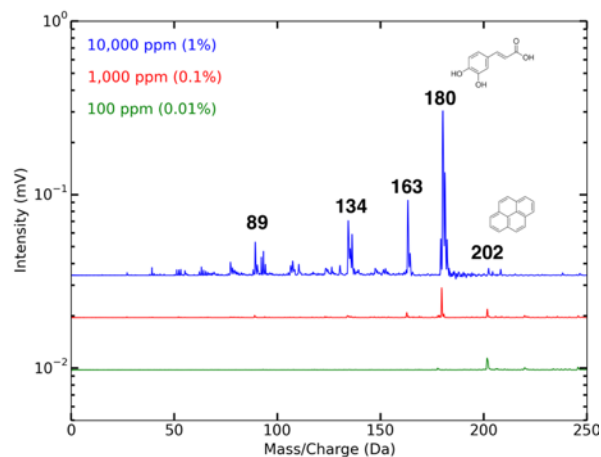

Figure 4: Mass spectra of caffeic acid in epsomite at various concentrations (1%, 0.1%, 0.01%).

Conclusions: We explore the resonance-enhanced detection of analyte on Ocean World analog samples with a two-step laser mass spectrometer to demonstrate the value of this technique in the *in situ* detection and characterization of the organic and molecular biosignature inventory on other planetary surfaces. L2MS has the potential to preserve high-molecular weight biosignatures against excessive fragmentation, and offers an analytical mode with selectivity to certain high-priority classes of organics that may be otherwise obscured in a complex mass spectrum.

References: [1] Han J. H., et al. (1988) *Science* 239(4847):1523 − 1525 [2] Getty S. A. et al. (2014) *Aerosp. Conf. Proc.*, 1 − 6. [3] Getty S. A. et al. (2013) *LPS XLIV*, Abstract #1719. [4] Getty S. A. et al. (2014) *International Workshop on Instrumentation for Planetary Missions*. [4] McCord T. B. et al. (2001) *JGR*, 106, 3311–3319. [5] Dalton III J. B. et al. (2012) *JGR: Planets,* 117:E3.