ACCESSING REFRACTORY MARTIAN ORGANICS USING THE MARS ORGANIC MOLECULE ANALYZER'S LASER DESORPTION MASS SPECTROMETRY EXPERIMENT.

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Introduction: The 2020 ExoMars Rover, currently targeted to the *Oxia Planum* region of Mars, will analyze the mineralogical and organic content of the surface and near subsurface, in its search for potential signs of life. *Oxia Planum* is rich in phyllosilicates and other rock and mineral types that have high preservation potential for complex organics that could reveal an ancient biosphere. Depth sampling using a 2 m drill will provide samples well-shielded from organic-degrading ionizing radiation, and potentially from harsh oxidative conditions, known at the surface [1]. This unprecedented opportunity to interrogate pristine organics calls for a versatile analytical suite, sensitive to organic molecular species over a wide range of molecular weights and volatilities. The Mars Organic Molecule Analyzer (MOMA) instrument answers this call by integrating two complementary experiments: pyrolysis gas chromatography mass spectrometry (pyr-GC-MS), with the option of chemical derivatization (analogous to the SAM instrument on the Curiosity rover) [2,3], as well as laser desorption mass spectrometry (LDMS) for nonvolatile compounds, which is new to spaceflight.

Implementation of LDMS on MOMA: During LDMS operations, powdered samples are irradiated under ambient Mars atmosphere. Molecules are desorbed and ionized in a single step using a pulsed UV laser (266 nm, 1 ns duration) and transferred to the mass spectrometer for analysis by a combination of electrostatic focusing and flow dynamics.

The unique benefit of LDMS is the ability to interrogate pristine Martian samples, without the need to chemically pre-treat samples. Prior studies have demonstrated successful MOMA-like LDMS on powders, cores, and thin sections [4, 5, 6]. These studies have proven the ability to detect and structurally characterize refractory organics by LDMS, even in the presence of up to 1 wt% calcium perchlorate, a highly oxidative chemical that is thought to be ubiquitous at the planet's surface [7]. (Hecht, Glavin2013)

SWIFT filtering for ion isolation and spectral deconvolution. The complexity of LDMS signatures that arise from analyses of unknown mineral-organic mixtures in Mars regolith requires sophisticated techniques to deconvolute spectra, and to provide structural information about analytes of interest. A major benefit of using an ion trap mass spectrometer is its ability to act as both an ion storage device and a mass filter. This allows the MOMA mass spectrometer to perform advanced ion manipulation experiments such as stored waveform inverse Fourier transform (SWIFT) experiments, where ions are isolated for up-concentration or for intended fragmentation during tandem mass spectrometric analyses (Fig.1) [6,8].

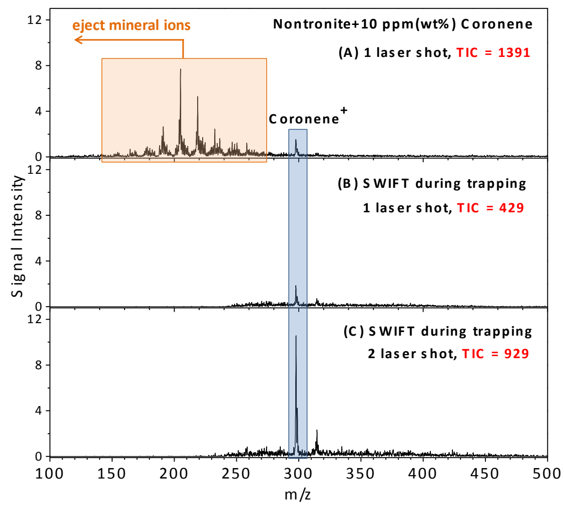

Fig. 1: (a) MOMA brassboard LDI spectrum of nontronite doped with 10 ppm coronene showing low mass contribution from mineral ions and (b) isolation of m/z 225-700 Da then (c) enhancement of the analyte signal with increased laser shots [8].

MS/MS analyses for molecular structural analyses. Tandem mass spectrometry (MS/MS) will be used during LDMS to probe species with molecular weights higher than those accessible by GCMS, where additional information is needed for structural elucidation,. In this experiment, SWIFT is used to isolate the ion, and a ramped amplitude single frequency excitation waveform induces collisions between the isolated molecule and the Mars CO_2 bath gas. These collisions allow for the fragmentation of molecules along expected fragmentation pathways.

References: [1] Pavlov, A.A. et al. (2012) GRL. [2] Freissinet, C. et al. (2017) this meeting. [3] Buch, A. et al. (2017) this meeting. [4] Grubisic, A. et al. (2016) ASMS. [5] Goetz, W. et al. (2017) LPSC. [6] Li, X. et al. (2015) Astrobiology. [7] Hecht et al. (2009) Science. [8] Li, X. et al. (2017) IJMS, submitted.