Advanced Resolution Organic Molecule Analyzer (AROMA): Simulations, Development and Initial Testing of a Linear Ion Trap-Orbitrap Instrument for Space. R. Arevalo Jr.[1], R. M. Danell[2], C. Gundersen[3], L. Hovmand[4], A. Southard[5], F. Tan[1], A. Grubisic[6], W. B. Brinckerhoff[1], S. A. Getty[1], P. Mahaffy[1], H. Cottin[7], C. Briois[8], F. Colin[8], C. Szopa[9], V. Vuitton[10], A. Makarov[11], and M. Reinhardt-Szyba[11]; [1]NASA GSFC (USA), (ricardo.d.arevalo@nasa.gov), [2]Danell Consulting, Inc. (USA), [3]AMU Engineering (USA), [4]Linear Labs, LLC (USA), [5]USRA (USA), [6]UMBC (USA), [7]LISA (FR), [8]LCP2E (FR), [9]LATMOS (FR), [10]IPAG (FR), [11]Thermo (DE)

Introduction: In collaboration with Thermo Bremen and the French CosmOrbitrap Consortium, NASA GSFC is developing a highly capable mass spectrometer instrument suite that will transform our understanding of cryogenic, potentially organic-rich planetary targets, such as comets, Jupiter's Europa, and Saturn's moons, Enceladus and Titan. This comprehensive, in situ investigation, funded through the ROSES PICASSO Program, promises versatile and high-performance instrumentation capable of:

1. Quantitative measurements of trace levels (e.g., ≤ ppmw) of organic and inorganic compounds over a wide range of volatility, ionization potential and molecular weight;
2. Selective isolation of targeted mass ranges for enhanced signal-to-noise (and by extension limits-of-detection) and controlled ion manipulation and ejection;
3. Induced fragmentation of parent molecules and structural analysis of daughter ions via tandem mass spectrometry (i.e., MS^n operations) for the differentiation of isomers; and,
4. Mass discrimination and disambiguation of isotopologues and organic and inorganic isobaric interferences with high-resolution ($m/\Delta m \geq$ 50,000) and mass accuracy.

In order to achieve these analytical capabilities, the AROMA instrument combines a mature linear ion trap (LIT) developed at NASA GSFC for the MOMA flight instrument and further augmented through MatISSE efforts (P-I: Brinckerhoff), and an Orbitrap™ mass analyzer adapted for spaceflight by a consortium of French laboratories which is capable of separating isobaric interferences with a resolving power as high as $m/\Delta m \geq 100{,}000$ (FWHM at m/z 100, 1 Hz scan rate; [1]). Together, this powerful combination (**Fig. 1**) will redefine our capabilities to identify complicated organic signatures unambiguously, and assign molecular structures with functional specificity. The primary analytical challenges that will be addressed in this effort are: i) ejection of tight ion packets (≤ µs pulse widths) from a spaceflight LIT; ii) ion collimation and beam steering via simple ion optics; and, iii) analysis of injected ions at suitably high mass resolution (goal: $m/\Delta m \geq 50{,}000$, FWHM at m/z 100 Da) in an Orbitrap™ with limited resources and/or in challenging environments.

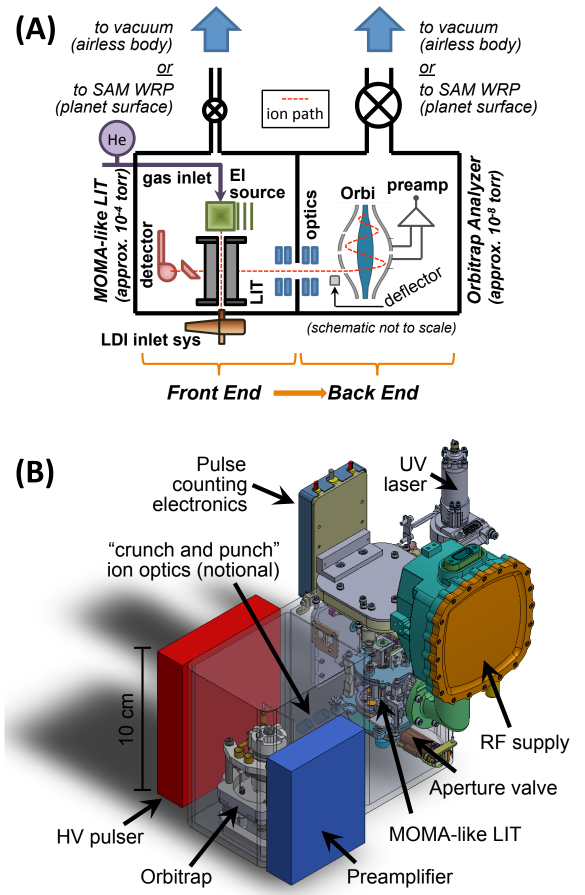

Fig. 1. (A) Schematic representation and (B) 3D model of one possible AROMA flight configuration, including heritage electron ionization (EI) and laser desorption/ionization (LDI) sources, thereby supporting the analysis of gas and solid phases, respectively. A particular flight implementation will require a trade of required mass resolution versus analyzer base pressure and other factors. Greater mass, volume and energy can lead to higher mass resolving powers. As shown, the AROMA concept is estimated at <10 kg and requires <40 W average power (the addition of one or more pumps would increase both mass and power requirements).

Program Schedule: In Phase I of this investigation, the team at NASA GSFC will build a dedicated Orbitrap™ testbed to allow for continuous experimental characterization/tuning of this high-resolution mass analyzer to understand the effect of a number of external variables, including the following:

- Pressures of 10^{-7} – 10^{-9} Torr (impact: pumping requirements);
- Ion pulse widths from 100 ns up to 2 μs (impact: ion source requirements);
- Ion residence times up to 1 s (impact: mass resolution, duty cycle and energy);
- < 3 kV voltage on the central electrode (impact: instrument power); and,
- Incident energy of the ions from 500 – 1500 eV (impact: ion optical interface design).

In Phase II NASA GSFC will define the LIT mechanical and electrical interfaces with the CosmOrbitrap subsystem, and build up the LIT assembly and vacuum housing analogous to previous efforts with MOMA prototype instruments. However, rather than employing redundant detector assemblies in a stand alone LIT, one of the ion ejection pathways will direct ions into an array of collimating optics and low-conductance apertures that will interface to the CosmOrbitrap chamber. Once the build is complete, we will verify the analytical capabilities of the LIT subsystem, including sensitivity (limit-of-detection), SWIFT mass excitation (isolation of targeted mass ranges), tandem mass spectrometry (MS^n) operations., and functionality as an ion injection trap (comparable to the C-Trap found in commercial instruments [2]).

In Phase III we will conduct multiple test campaigns with the French CosmOrbitrap Consortium to define system-level analytical capabilities and verify AROMA functional requirements of the fully coupled instrument.

Results: The design of the Phase I Orbitrap™ testbed chamber for use at GSFC has recently been completed and the build of this system is currently underway. As stated above, the purpose of this configuration is to test the effect of various operating parameters on the performance of the Orbitrap™ mass analyzer.

Complete ion optical simulations have been completed of the Phase 1 configuration and the relevant parameters required for successful ion injection have been investigated (**Fig 2**). These models have served to inform the design of this configuration and will also be integrated with a similar model of ion ejection from the LIT to aid in the Phase II system design.

Of particular interest is the effect of operating pressure on the resulting Orbitrap™ mass spectrum, as this will impact the pumping requirements (and therefore mass, volume and power) for a flight system. The CosmOrbitrap portion of our team has recently demonstrated that full performance ($m/\Delta m \geq 100{,}000$) can be maintained at pressures up to 10^{-8} Torr, indicating that ultra high vacuum is not required for many potential applications [1].

A second very important parameter for this coupled LIT/Orbitrap™ instrument is the ion packet pulse width, and its impact on the achievable performance of the instrument (particularly mass range and resolution). In contrast to the CosmOrbitrap system in France, the GSFC testbed employs an ion gun for generating pulsed beams of ions for injection into the Orbitrap™. This allows direct testing of the ion pulse width and its interaction with the other Orbitrap™ operational parameters, and informs the requirements for ion ejection from the LIT. Initial data from these key tests are expected to be available for presentation at the meeting.

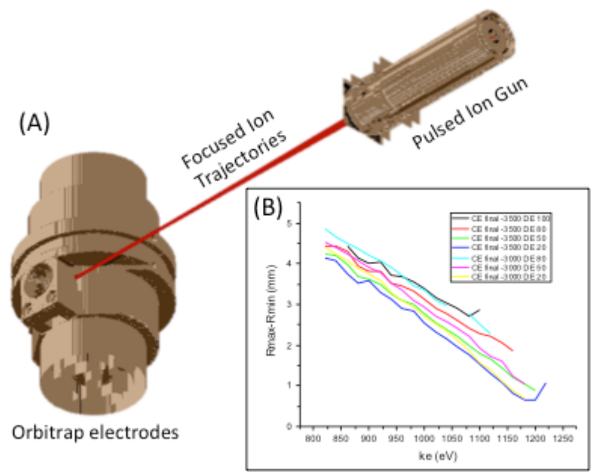

Fig. 2. (A) SIMION model of Phase I testbed configuration. (B) Simulation results showing range of acceptable ion kinetic energies at various Orbitrap electrode operating voltages.

Future Directions: Through the strategic partnership established between NASA GSFC, the French CosmOrbitrap Consrtium and Thermo Bremen, other instrument configurations relying on the CosmOrbitrap analyzer have been submitted for potential funding to complement the AROMA investigation described here. One such concept, the Femtosecond Laser Analysis of Viable Organic Reservoirs (FLAVOR) instrument, promises to characterize the organic and inorganic inventory of planetary materials via in situ stoichiometric laser sampling without contacting or thermally degrading the sample.

References: [1] Briois, C., et al. (2016) *PSS, in press.* [2] Zubarev, R. A. and Makarov, A. (2013) *Anal Chem.*