MARS ORGANIC MOLECULE ANALYZER (MOMA) FLIGHT MODEL QUALIFICATION. William B. Brinckerhoff[4], Veronica T. Pinnick[1], Ryan M. Danell[2], Friso H. W. van Amerom[3], Ricardo D. Arevalo, Jr.[1], Andrej Grubisic[1], Xiang Li[1], Caroline Freissinet[1], Zhiping Chu[1], Marco Castillo[1], Chris Johnson[1], Cyril Szopa[4], Fabien Stalport[5], Arnaud Buch[6], Tristan Allain[5], Noel Grand[5], Francois Raulin[5], Walter Goetz[7], Harald Steininger[7], Fred Goesmann[7], and the MOMA Team[1-8], [1]NASA Goddard Space Flight Center, 8800 Greenbelt Rd., Greenbelt, MD 20771; [2]Danell Consulting, Inc., Winterville, NC; [3]Mini Mass Consulting, Hyattsville, MD; [4]Laboratoire Atmosphères, Milieux, Observations Spatiales (LATMOS), Guyancourt, France; [5]Laboratoire Interuniversitaire des Systèms Atmosphériques (LISA), Univ. Paris-Est, Créteil, France; [6]Laboratoire de Génie des Procédés et Matériaux (LGPM), École Centrale Paris, Chatenay-Malabry, France; [7]Max Planck Institut für Sonnensystemforschung (MPS), Göttingen, Germany; [8]Laser Zentrum Hannover e.V. (LZH), Hannover, Germany.

Introduction: The Mars Organic Molecule Analyzer (MOMA) investigation on the 2020 ExoMars rover will examine the molecular composition of samples acquired from depths of up to two meters below the martian surface, where organics may have been protected from radiative and oxidative degradation [1,2]. The clay-rich rock exposures accessible in *Oxia Planum*, the preferred landing zone, will provide an excellent opportunity to sample ancient material for organics analysis. MOMA incorporates both pyrolysis-gas chromatography/mass spectrometry (pyr-GCMS) and laser desorption mass spectrometry (LDMS) modes of operation, and is designed to work in concert with the other investigations in the rover's Pasteur Payload, particularly the Raman [3] and MicrOmega [4] instruments that analyze common drill samples presented on a carousel. With two modes, MOMA detects compounds over a wide range of molecular weight, volatility, and mineralogical association [5].

Implementation of GCMS and LDMS Modes: GCMS mode is operated analogously to the Sample Analysis at Mars (SAM) investigation on Curiosity. Samples are sealed into ovens and heated to 850° C. Analyte gases, entrained in He, flow through the GC system to the MS. The GC includes two cooled hydrocarbon traps (Tenax and Carbosieve) that are opened after major water evolution (above 100° C) but prior to organic thermodesorption (from ~300° C up to > 500° C). Trapped organics are injected onto one of four columns and eluted over a temperature ramp to the MS electron ionization (EI) source. GCMS analyzes compounds of high-to-moderate volatility (enthalpies of vaporization $\Delta H_V \leq 50$ kJ mol^{-1}) such as alkanes, amines, and lighter carboxylic and amino acids and aromatic species. Derivatization agent present in some ovens enables detection of the higher ΔH_V and polar species over the full GCMS m/z range of 50-500 Da.

In LDMS mode, molecules are desorbed and ionized directly from powder samples with a pulsed UV laser (266 nm, 1 ns duration) at Mars ambient pressures. Parent molecular cations, and their fragments, enter the MS through a fast aperture valve that closes after ions are trapped, permitting the ion trap pressure to reduce to <10^{-3} Torr where the detectors can be operated. LDMS mode is designed to analyze compounds of moderate-to-low volatility (enthalpies of vaporization $\Delta H_V \geq 40$ kJ mol^{-1}) such as heavier carboxylic acids, aromatic species, chain-like compounds, and macromolecular organics. The nature of LDI permits some fraction of large "parent" molecules to desorb intact. As previously demonstrated, the pulsed LDMS mode is not strongly affected by the potentially oxidizing effects of heat-evolved perchlorates, simplifying analysis of nonvolatile organics [6].

Flight System Intergration and Test: The various flight instrument subsystems have been functionally tested and qualified at their respective institutions in preparation for flight model (FM) integration, test, and delivery to the rover in 2017. The flight MS completed earlier [7] has been integrated with an engineering model of the laser and with a commercial (Thermo) GC for both bench and Mars environmental chamber testing (Fig. 1) under stringent contamination and planetary protection controls.

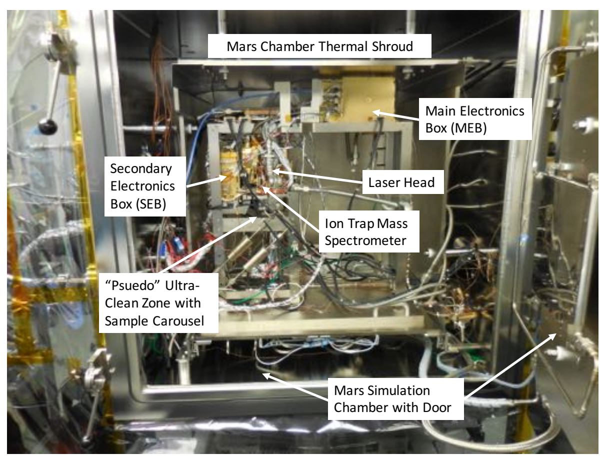

Fig. 1 Flight linear ion trap MS assembly with laser in Mars environment simulation chamber to match mechanical, thermal, pressure, and contamination level that MOMA will experience on the ExoMars rover. Configuration supports either external commercial GC, via gas feedthroughs, or flight model GC within the existing mechanical structure.

Preliminary tests of the GCMS mode using calibration gases have demonstrated as-expected functional performance in for resolution, acquisition rate, sensitivity, and fragmentation patterns. A four-component hydrocarbon mix (butane, pentane, hexane, and benzene) was injected at the appropriate concentrations and rate onto the 20 m × 0.25 mm × 0.25 µm Restek CLP GC column, matching Mars-like MOMA pyrolysis and GC operation, to test GC-specific trapping and retention characteristics (Figure 2). The spectrum in the lower plot was found to closely match the fragmentation pattern known for hexane during its column elution. The limit of detection (LOD) requirement of 1 pmol s^{-1} is readily met and will be revisited for different compounds and with higher fidelity GC configurations.

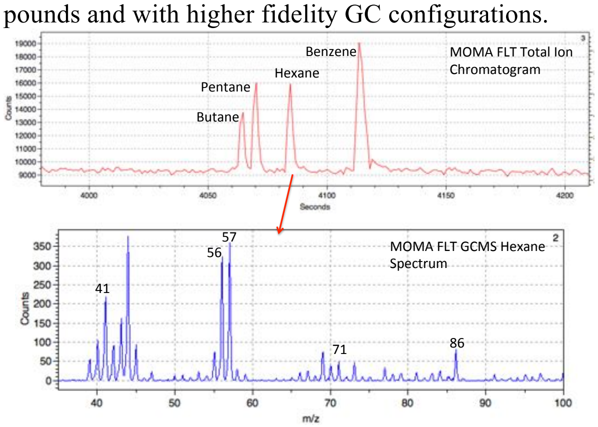

Fig. 2 Flight MOMA GCMS total ion chromatogram (top) shows nominal detection of hydrocarbons in He. The hexane GC peak is sampled with multiple EI spectra such as shown (bottom) with its characteristic fragmentation pattern.

The flight Tapping Station, which seals pyrolysis ovens on the carousel, and the flight GC have been assembled (Figure 3) and are undergoing functional testing. A flight GCMS coupling is planned, but limited to the activities critical to verify MOMA/GCMS without significant contamination exposure. Additional end-to-end characterization will be conducted using the engineering units and, as in the case of the Sample Analysis at Mars (SAM) investigation, a testbed model assembled from spare flight components.

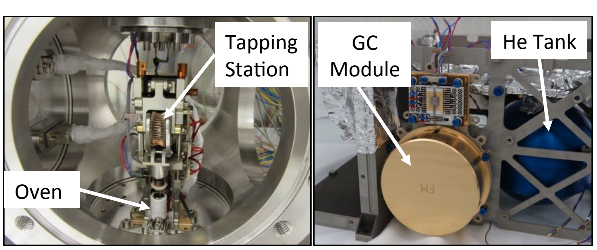

Fig. 3 The flight models of the Tapping Station (left; to seal pyrolysis ovens) and the GC subsystem (right) have been assembled and are undergoing "ultra-clean" functional tests.

The flight model has been tested in LDMS mode, initially with the engineering unit laser, verifying ion transmission, sensitivity, resolution, and accuracy requirements over the mass range up to 1000 Da. A calibration target of solid CsI will be delivered to Mars with MOMA and used to track and correct any drift of m/z position or mass bias of sensitivity. Only the most trace-level concentrations of selected organics are used, rarely, to perform critical verification of the MOMA limit of detection for nonvolatile compounds in the FM. Figure 4 demonstrates the flight MS readily produces an accurate spectrum of the aromatic Rhodamine 6G calibrant, present at 50 femtomoles per mm^2, with a signal-to-noise ratio over 100 at the base peak of m/z 443. As such the observed performance in this test is more than 1000 times better than the overall LDMS requirement of 1 pmol mm^{-2} Additional tests of the FM with other selected gases and samples are underway to complete the verification of all operational parameters, including use of MS/MS and SWIFT protocols [8]. In parallel, the engineering unit LDMS is used to characterize and develop libraries of the response to a range of Mars-relevant mineral matrices [9]. Following a thorough cleaning and continued background and procedural blank tracking scans, the flight laser will be integrated to the flight ion trap MS, and the full system will undergo final Mars thermal vacuum testing prior to delivery to the rover.

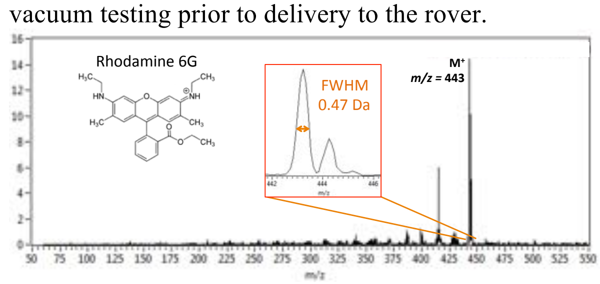

Fig. 4 Flight mass spectrometer in laser desorption/ionization mode achieves ~femtomole per mm^2 limit of detection per spectrum for a nonvolatile aromatic organic compound.

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