Mass Spectrometry on Future Mars Landers. W. B. Brinckerhoff[1], P. R. Mahaffy[1], and the MSL/SAM and ExoMars/MOMA Investigation Teams, [1]Code 699 Planetary Environments Laboratory, NASA Goddard Space Flight Center, Greenbelt, MD 20771, william.b.brinckerhoff@nasa.gov paul.r.mahaffy@nasa.gov

Introduction: Mass spectrometry investigations on the 2011 Mars Science Laboratory (MSL) and the 2018 ExoMars missions will address core science objectives related to the potential habitability of their landing site environments and more generally the near-surface organic inventory of Mars. The analysis of complex solid samples by mass spectrometry is a well-known approach that can provide a broad and sensitive survey of organic and inorganic compounds as well as supportive data for mineralogical analysis. The science value of such compositional information is maximized when one appreciates the particular opportunities and limitations of *in situ* analysis with resource-constrained instrumentation in the context of a complete science payload and applied to materials found in a particular environment. The Sample Analysis at Mars (SAM) investigation on MSL and the Mars Organic Molecule Analyzer (MOMA) investigation on ExoMars will thus benefit from and inform broad-based analog field site work linked to the Mars environments where such analysis will occur.

Mission Description: The SAM investigation [1] merges the capabilities of a quadrupole mass spectrometer (QMS) with those of a gas chromatograph (GC) and a tunable laser spectrometer (TLS), supported by a seventy-four cup solid sample manipulation system (SMS) and an extensive chemical separation and processing laboratory (CSPL). SAM analyzes the chemical and isotopic composition of both the martian atmosphere and particulate samples introduced from the MSL sample acquisition-sample analysis and handling (SA-SPaH) system through solid sample inlet tubes and into the quartz sample cups. Gas is extracted from solid samples via pyrolysis (with selectable options for derivatization, thermochemolysis, and combustion). Gas may be sampled directly by the 2-550 Da mass-to-charge (m/z) range QMS or preprocessed in the CSPL to concentrate organics or noble gases. It may additionally be routed into the GC or the TLS. The six column GC not only has its own detectors, but also can operate together with the QMS as a gas chromatograph mass spectrometer (GCMS). The GCMS detection limit surpasses the part per billion mission requirement for organic detection. The TLS is a two-channel Herriott cell design spectrometer that provides detection of CH_4, H_2O, and CO_2 and the isotope ratios $^{13}C/^{12}C$, $^{18}O/^{16}O$, and $^{17}O/^{16}O$ in carbon dioxide, D/H in water, and $^{13}C/^{12}C$ in methane. The TLS sensitivity for atmospheric gas is < 1 ppb and the detection limit can be substantially reduced by methane enrichment in SAM's CSPL. SAM thus provides a broad investigation of organic and inorganic species and their isotopes in solid and atmospheric samples. In the context of the full MSL payload including chemical and mineralogical analysis tools such as CheMin, ChemCam, and APXS, the SAM investigation will directly support the assessment of potential habitability of an environment characterized by evidence of ancient hydrologic, depositional, and preservational features, to be selected later this year. SAM has participated in analog field campaigns such as the Antarctic Mars Analog Svalbard Expedition (AMASE) supported by the Astrobiology Science and Technology for Exploring Planets (ASTEP) program as well as MSL-sponsored field tests, and is involved in an intensive ongoing development of mass spectral libraries using standard and analog materials representative of potential landing site composition.

The MOMA investigation led by the Max Planck Institute for Solar System Explortaion (MPS) merges the capabilities of a GCMS and a laser desorption MS into a single miniaturized instrument incorporated into the Analytical Laboratory Drawer (ALD) of the ExoMars rover. The rover is significantly smaller than MSL and as such provides a more focused set of measurements, aligned to support the top science objective of the search for signs of life on Mars. A significant advancement offered by ExoMars is a drill that obtains samples from depths of up to two meters below the surface, which in some cases may be substantially better for survival of complex organics than the highly degradational surface environment. Crushed samples are delivered to instruments including MOMA via rover-provided sample manipulation facilities within the ALD. In MOMA particulate samples are loaded into small oven cups and pyrolyzed analogous to SAM. Evolved gas is transported to the (multiplexed) four-column MOMA GC provided by the same French team that provided the SAM GC, incorporating some advancements such as a high density valve assembly. Both derivatization and thermochemolysis are baselined for a fraction of the oven cups to permit volatilization and survival of organics that are more readily fragmented or oxidized under the pyrolysis protocol. GC effluent is directed into a highly-miniaturized ion trap mass spectrometer (ITMS) with electron ionization that supports an m/z range of 2 kDa and which can be operated in tandem mass spectrometry (MS/MS) mode to provide additional information on molecular structure. In addition, MOMA incorporates the ability to analyze solid samples provided on a tray at Mars ambient pressure using pulsed laser desorption/ionization (LDI) and an ion optical scheme that brings prompt laser ions into the ITMS. The LDI mode offers complementary information on the more nonvolatile organic and elemental composition of the sample, with the possibility of directly detecting higher molecular weight species that may be indicative of the survival of complex organics in the near surface of Mars. MOMA has begun to participate in analog field campaigns such as AMASE and the team is particularly interested in opportunities for collaborative field work in support of ExoMars objectives. Analog sites and materials representing potentially Mars-like microenvironments (phyllosilicate-rich deposits, cryptoendolithic communities, varnishes, brines/ices, etc.) for preservation of both extinct and extant or dormant habitats are a strong need going forward to optimize the application of the complementary MOMA mass spectrometry techniques on ExoMars.

References:

[1] Mahaffy P. M. (2009) *Geochem. News, GN141*, The Geochemical Society (http://www.geochemsoc.org/publications/geochemicalnews/gn141oct09/)