DEVELOPMENT OF ANALYTICAL PROTOCOLS FOR ORGANICS AND ISOTOPES ANALYSIS ON THE 2009 MARS SCIENCE LABORTORY. P. R. Mahaffy¹ and the SAM team, ¹NASA Goddard Space Flight Center (GSFC), Greenbelt, MD 20771.

Introduction: The Mars Science Laboratory, under development for launch in 2009, is designed explore and quantitatively asses a local region on Mars as a potential habitat for present or past life. Its ambitious goals are to (1) assess the past or present **biological potential** of the target environment, (2) to characterize the **geology and geochemistry at the MSL landing site,** and (3) to investigate **planetary processes that influence habitability.** The planned capabilities of the rover payload will enable a comprehensive search for organic molecules, a determination of definitive mineralogy of sampled rocks and fines, chemical and isotopic analysis of both atmospheric and solid samples, and precision isotope measurements of several volatile elements. A range of contact and remote surface and subsurface survey tools will establish context for these measurements and will facilitate sample identification and selection. The Sample Analysis at Mars (SAM) suite of MSL addresses several of the mission's core measurement goals. It includes a gas chromatograph, a mass spectrometer, and a tunable laser spectrometer. These instruments will be designed to analyze either atmospheric samples or gases extracted from solid phase samples such as rocks and fines. We will describe the range of measurement protocols under development and study by the SAM engineering and science teams for use on the surface of Mars.

Overview of MSL Architecture: The MSL rover has a substantially larger payload capability (-75 kg) than any other landed Mars mission, to date. Its currently planned ability to access latitudes between 60 N and 60 S below +2 km above the mean surface altitude, opens up a vastly increased range of possible landing sites. The rover mobility cabability is expected to be greater than 20 km and the planned nominal mission lifetime is one Mars year. On the surface of Mars, remote-sensing instruments will rapidly characterize the environment and identify target regions. The MSL mobility will enable it to access these targets and sample them with contact instruments. If the targets are judged worthy of further study a sample acquisition and processing system will prepare samples for more detailed analysis. Fractions of these processed samples will be delivered into the MSL Analytical Labortory for analysis by the mineralogy experiment and by SAM. MSL may spend several sols at a site and then traverse some distance to a new site for another round of analysis.

Figure I. A conceptual design for the Mars Science Laboratory show counter clockwise from the top left: the mast camera (MastCam); the laser induced breakdown chemistry and micro-imaging experiment (ChemCam); the Radiation Assessment Detector (RAD); the Alpha Particle X-Ray Spectrometer (APXS); the Mars Hand Lens Imager (MAHLI), the sample acquisition and processing system (SA/SPaH); the Mars Descent Imager (MARDI); the Chemistry and Mineralogy (CheMin) experiment; the Sample Analysis at Mars (SAM) experiment; the Dynamic Albedo of Neutrons (DAN) experiment; the Ultra High Frequency (UHF) system for communication with orbiting spacecraft; and the High Gain Antena (HGA) for direct communication to Earth. Image courtesy of the MSL Project at the Jet Propulsion Laboratory.

Overview of the SAM suite investigation: The SAM science goals are to

- Search for organic compounds of biotic and prebiotic relevance and explore sources and destruction paths for carbon compounds.
- Reveal chemical state of other light elements that are important for life as we know it on Earth *0*
- Study habitability of Mars by measuring oxidants such as hydrogen peroxide
- Investigate atmosphere and climate evolution through isotope measurements of noble gases and light elements

The three SAM instruments analyze gases extracted or evolved from solid phase samples or sampled directly from the atmosphere. The quadrupole mass spectrometer (QMS) obtains molecular and isotopic composition in the 2-535 Dalton mass range for atmospheric and evolved gas samples, the gas chromatograph (GC)

resolves complex mixtures of organics into separate components, and the tunable laser spectrometer (TSL) obtains abundance and precision isotopic composition of CH₄, H₂O, CO₂, N₂O, and H₂O₂. The SAM instruments are supported by subsystems that chemically or physically process solid or gaseous samples. These include; a Chemical Separation and Processing Laboratory (CSPL) that includes valves, manifolds, carrier gas, enrichment cells, and ovens; a Sample Manipulation System (SMS) that positions one of 74 sample cups to below a sample inlet tube or into on of two SAM pyrolysis ovens; and two Wide Range Pumps

Figure 2. The present concept for the packaging of the SAM suite elements is illustrated. The suite is somewhat isolated from the Mars environment inside the MSL warm electronics box.

(WRP), that are hybrid turbomolecular/drag pump servicing the QMS, TLS, GC, and CSPL.

The SAM pyrolysis system is able to heat a few milligrams of sample from ambient temperature to approximately 1100°C using a linear temperature ramp. Gases are rapidly removed from the sample by an inert helium carrier gas, They are first analyzed directly by the QMS and TLS and then again after completion of the pyrolysis by release of organics trapped on a high surface area adsorbant into a GC column. The controlled sample heating also enables analysis of simple inorganic gases, such as $CO₂$, H₂O, and SO₂ that provide information on mineral type and the degree of mineral alteration by weathering. In a complementary experiment, low temperature solvent extraction of organics is followed by chemical derivatization prior to the GCMS analysis for detection of a wider range of organic compounds including carboxylic acids, amino acids, and even nucleobases if there are present in Mars samples.

SAM experiment types: Nine detailed SAM measurement sequences have been defined, to date, as a set of experiments that would be repeated over the course of the landed mission to meet the SAM investigation objectives. There are:

- Pyrolysis (ambient to Il00"C) with direct QMS and TLS evolved gas analysis and GCMS analysis for released organics 1)
- Chemical derivatization for analysis of fragile, low volatility, or polar organic molecules 2)
- Solid sample calibration and sample blank analysis 3)
- Direct atmospheric sampling to obtain diurnal and seasonal composition variations 4)
- Atmospheric sampling with enrichment for trace species *5)*
- Atmospheric sampling with methane specific enrichment protocol 6)
- Atmospheric noble gas elemental and isotopic composition protocol 7)
- Stepped combustion of solid samples to sample non-volatile carbon 8)
- 9) Calibration gas sampling

The detailed development of these experiment sequences serves as a tool to study the accomadation of the SAM Suite measurements with MSL operations. For example, we plan to implement the SAM pyrolysis experiments at night when the MSL platform is stationary. This has the additional benefit of minimizing temperature perturbations of the sample prior to thermal processing in the SAM ovens where the evolved gases can be sampled. Atmospheric sampling, however, will be carried out over the duration of the mission but both day and night to obtain adequate sampling of diurnal and seasonal variations in composition and isotope ratios.

Analysis of Mars analogues: Evaluation of the protocols described continues on a variety of Mars analog samples. These include soils from the driest regions of the Atacama desert [I], meteoretic samples, and Hawaii Mars analog soils from Mauna Kea [2] such as Jarositic Tephra, Palagonitic Tephra, and Phyllosilicate-rich Tephra that exhibit a variety of weathering alterations.

References: (1) Navarro-González, R., Rainey, F.A., Molina, P., Bagaley, D.R., Hollen, B.J., Rosa, J., Small, A.M., Quinn, R.C., Grunthaner, F.J, Cáceres, L., Gomez-Silva, B., and McKay, C.P., "Mars-Like Soils in the Atacama Desert, Chile, and the **Dry** Limit of Microbial Life", Science 7, 1018-1021 (2003). [2] Ming, D.W. et al., "The search for water and other volatile-bearing phases on Mars: Mauna Kea volcano as an analog", LPSC XXXIV, 1800 (2003).