The Sample Analysis at Mars Suite and its METHANE Relevant Investigations

Paul Mahaffy (NASA Goddard Space Flight Center)
and the SAM Science team

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Topics

• SAM science team
• MSL mission science goals
• candidate landing sites
• SAM science goals
• MSL investigations and critical elements
• measurement capability of the SAM suite of instruments
• mitigation against terrestrial contamination
• SAM measurements that complement methane observations

Note: SAM’s TLS methane measurement specifics are described in Chris Webster’s presentation that follows
**SAM science team**

<table>
<thead>
<tr>
<th>CoInvestigator</th>
<th>Institution</th>
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<th>Institution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Paul Mahaffy, PI</td>
<td>NASA/GSFC</td>
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<tr>
<td>Will Brinckerhoff</td>
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<td>Honeybee Robotics</td>
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<td>Max-Planck</td>
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<td>U. Mexico</td>
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</tbody>
</table>

**Collaborators**: Mehdi Benna, Oliver Botta, Jason Dworkin, Jen Eigenbrode, Heather Franz, Daniel Glavin, Dan Harpold, Wayne Kasprzak, Heidi Manning, Kenneth Nealson, Alain Person, Claude Rodier, Robert Sternberg, Stephanie Stockman, Cyril Szopa, Meenakshi Wadhwa, Edward Vicenzi, Ah-San Wong, Jaime Demick, Guy Israel, Wes Huntress, Arnaud Bush

**Key team members for both development and surface op’s**: Eric Raaen, Florence Tan, Tom Nolan, Micah Johnson, Jason Feldman, Greg Flesch

**Recent addition to the EPO team**: Lora Bleacher

**Recent or soon-to-be additions to the GSFC research team**: Amy McAdam, Melissa Trainer, Fabian Stalaport, Alex Pavlov.
MSL’s core science goals

- **Assess biological potential of at least one target environment (past or present).**
  - Determine the nature and inventory of organic carbon compounds
  - Inventory the chemical building blocks of life (C, H, N, O, P, S)
  - Identify features that may record the actions of biologically-relevant processes

- **Characterize the geology of the landing region at all appropriate spatial scales**
  - Investigate the chemical, isotopic, and mineralogical composition of martian surface and near-surface geological materials
  - Interpret the processes that have formed and modified rocks and regolith

- **Investigate planetary processes that influence habitability**
  - Assess long-timescale (4-billion-year) atmospheric evolution processes.
  - Determine present state, distribution, and cycling of water and CO₂.
SAM Instruments and Major Subsystems

SAM is a Suite of 3 Instruments

- **Quadrupole Mass Spectrometer (QMS)** – Goddard Space Flight Center
  - Molecular and isotopic composition in the 2-550 Dalton mass range for atmospheric and evolved gas samples
- **Gas Chromatograph (GC)** - University of Paris, CNES
  - Resolves complex mixtures of organics into separate components
- **Tunable Laser Spectrometer (TLS)** – Jet Propulsion Laboratory
  - Abundance and precision isotopic composition of CH\(_4\), H\(_2\)O, and CO\(_2\)

SAM supporting subsystems

- **Gas Processing System (GPS)** – Goddard Space Flight Center
  - Includes valves, manifolds, carrier gas, enrichment cells, Wide Range Pump (WRP), and Pyrolysis Ovens
- **Sample Manipulation System (SMS)** – Honeybee Robotics
  - Positions 74 sample cups to below a sample inlet tube or into SAM pyrolysis ovens
- **Common Infrastructure Systems** – Goddard Space Flight Center
  - Electrical, Mechanical, Thermal, Flight Software
SAM Core Science Goals

- **GOAL #1**: Explore sources and destruction paths for carbon compounds
  
  Met by measurements of the identity and abundance of **organic molecules** and their distribution of oxidation states, molecular weights, and chemical structures

- **GOAL #2**: Search for organic compounds of biotic and prebiotic relevance including methane
  
  Met by measurements of:
  - **amino acids, nucleobases, carboxylic acids** by solvent extraction and chemical derivatization
  - **methane abundance** in the atmosphere & its $^{13}$C/$^{12}$C ratio with TLS.

- **GOAL #3**: Reveal chemical and isotopic state of other light elements that are important for life as we know it on Earth
  
  Met by measurement of **inorganic gases** such as $\text{SO}_2$, $\text{H}_2\text{O}$, and $\text{CO}_2$ evolved from solid samples

- **GOAL #4**: Study habitability of Mars by atmospheric/surface interactions expressed in trace species compositions
  
  Met by measurement of:
  - abundance of multiple minor and **trace atmospheric species** including those with short photochemical atmospheric lifetimes
  - **diurnal and seasonal variation of atmospheric species** such as $\text{H}_2\text{O}$, $\text{O}_2$, $\text{N}_2$, $\text{Ar}$, $\text{O}_3$, $\text{H}_2$, and $\text{CH}_4$

- **GOAL #5**: Understand atmosphere & climate evolution through isotope measurements of noble gases & light elements
  
  Met by measurement in the atmosphere and in gas evolved from fines and powdered rocks
  - **isotope ratios for noble gases**
    - $^{13}$C/$^{12}$C, $^{15}$N/$^{14}$N, $^{18}$O/$^{16}$O, $^{17}$O/$^{16}$O, and D/H in simple compounds
  
  provides a database that constrains models of atmospheric evolution and identifies reservoirs of the light elements that contribute to the present atmosphere.
Ten Diverse MSL Science Investigations

REMOTE SENSING
MastCam (M. Malin, MSSS) - Color stereo imaging, atmospheric opacity
ChemCam (R. Wiens, LANL/CNES) – Chemical composition; remote micro-imaging

CONTACT INSTRUMENTS (ARM)
MAHLI (K. Edgett, MSSS) - Microscopic imaging
APXS (R. Gellert, U. Guelph, Canada) - Chemical composition

ANALYTICAL LABORATORY (ROVER BODY)
SAM (P. Mahaffy, GSFC/CNES) - Chemical and isotopic composition, including organics
CheMin (D. Blake, ARC) - Mineralogy

ENVIRONMENTAL CHARACTERIZATION
MARDI (M. Malin, MSSS) - Descent imagery
REMS (L. Vázquez, CAB, Spain) - Meteorology / UV
RAD (D. Hassler, SwRI) - High-energy radiation
DAN (I. Mitrofanov, IKI, Russia) - Subsurface hydrogen

>130 co-investigators in seven countries
Other MSL elements

- UHF Antenna
- RLGA
- High Gain Antenna System
- Remote Sensing Mast
- RTG / Heat Exchangers
- Rover Body
- Mobility System
- SA Turret/Drill
- SA Robotic Arm
We anticipate the substantial benefit of an order of magnitude increase in payload mass resources!
SAM Suite top assembly

Solid sample inlets penetrate through MSL top deck

Atmospheric inlets and vents located on side of SAM box and penetrate +Y face of MSL WEB

Tunable Laser Spectrometer

Quadrupole Mass Spectrometer

Solid Sample Inlets

Atmospheric Inlets

Electronics

Wide Range Pump

Gas Chromatograph

Chemical Separation and Processing Laboratory

SMS and Housing
SAM Processes both Rock and Atmospheric Samples

Getter utilized for methane enrichment pumps all gases EXCEPT CH\textsubscript{4} and noble gases – scrubbed gas is sent to TLS

- Martian rock & soil samples
- MSL sample processing & delivery system
- SAM Solid Sample Inlet
- Sample Manipulation System
- Sample Sealed in Ovens
  - gas extraction
    * derivatization
    * thermal processing
    * combustion
- Atmospheric samples
  - chemical separation & gas traps
    - GC
    - QMS
    - TLS
    - wide range pumps
3 core instruments provided an international collaboration between three different institutions:

- GC (Gas Chromatography)
- QMS (Quadrupole Mass Spectrometer)
- TLS (Time-of-Flight Mass Spectrometer)

**French contribution**

- GC from GSFC
- QMS from GSFC
- TLS from JPL

**Instruments Provided by Institutions**

- **NASA**:
  - MSL sample processing & delivery system
  - SAM Solid Sample Inlet
  - Sample Manipulation System
  - Sample Sealed in Ovens
  - Gas extraction
    - * derivatization
    - * thermal processing
    - * combustion

- **GSFC**:
  - QMS

- **JPL**:
  - TLS
SAM Conducts a Diverse Set of Chemical Analyses

<table>
<thead>
<tr>
<th>EXPERIMENT</th>
<th>WHAT EACH SAM EXPERIMENT DOES AND WHY</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Pyrolysis</strong> (61 quartz cups)</td>
<td>GENERAL SURVEY FOR ORGANIC COMPOUNDS - Sample in quartz cup is heated in a He gas flow and evolved gases monitored by the QMS – trapped organics are subsequently analyzed by GCMS using one of six columns. If evolved CO$_2$ from carbonates or H$_2$O from hydrates is produced, they can be isotopically analyzed by TLS.</td>
</tr>
<tr>
<td><strong>Derivatization</strong> (9 cups w/fluid)</td>
<td>ORGANICS OF SPECIAL INTEREST - Solvent extraction of organics and chemical derivatization (transformation of polar compounds such as amino acids, carboxylic acids, and even nucleobases into volatile compounds that can be analyzed by GCMS)</td>
</tr>
<tr>
<td><strong>Combustion</strong></td>
<td>$^{13}$C/$^{12}$C IN REFRACTORY CARBON – Oxygen from a SAM tank transforms macromolecular carbon into CO$_2$ in the SAM ovens at several hundred degrees – the CO$_2$ isotopic composition is analyzed by TLS</td>
</tr>
<tr>
<td><strong>Direct Atmospheric Sampling</strong></td>
<td>ATMOSPHERIC COMPOSITION VARIATIONS – the atmosphere is sampled by the QMS (wide survey) and the TLS on various temporal scales (diurnal and seasonal)</td>
</tr>
<tr>
<td>Atmospheric Sampling with Enrichment</td>
<td>ATMOSPHERIC TRACE SPECIES – trace species are enriched by the SAM traps and analyzed in the QMS</td>
</tr>
<tr>
<td>Atmospheric Methane with Enrichment</td>
<td>TRACE METHANE AND ITS ISOTOPE RATIOS – methane is enriched by the SAM set of getters and traps. Factors of 50-100 enrichment will be obtained and studies for greater enrichment are ongoing.</td>
</tr>
<tr>
<td>Atmospheric Noble Gas Enrichment</td>
<td>PRECISION NOBLE GAS ABUNDANCE AND ISOTOPE RATIOS – active gases are removed by getters and light and heavy noble gases separated. Noble gas measurements are secured by the QMS with static mass spectrometry</td>
</tr>
<tr>
<td><strong>In Situ Calibration</strong> (4 cups)</td>
<td>VERIFIES PERFORMANCE OF SAM ON MARS – both gas and solid calibration samples are used in situ as needed. Solid calibration samples are stored in sealed cups in SAM or in sealed containers that are sampled by the MSL sample acquisition system.</td>
</tr>
</tbody>
</table>

-3 cups w/fluorocarbs & inorganics + 1 cup calcite for terrestrial CO$_2$ validation
### SAM comparison with Viking GCMS

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Viking</th>
<th>SAM</th>
<th>Science Benefit</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Pyrolysis</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>No. of sample cups</td>
<td>3</td>
<td>74</td>
<td>More samples analyzed – each cup can be used multiple times</td>
</tr>
<tr>
<td>Temperature</td>
<td>50, 200, 350, or 500ºC</td>
<td>Continuous heating up to 1100ºC</td>
<td>Identification of mineral decomposition products</td>
</tr>
<tr>
<td><strong>Gas Chromatography</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Columns</td>
<td>Poly MPE-Tenax</td>
<td>Molsieve 5A carbo-bond, MXT 1,5, MXT PLOT U, RTX 5 Amine, Chirasil-Val</td>
<td>Analysis of a wider range of organics, noble gases, VOCs, derivatized compounds, enantiomers and amines</td>
</tr>
<tr>
<td>Derivatization</td>
<td>No</td>
<td>Yes, MTBSTFA</td>
<td>Transforms key organic biomarkers</td>
</tr>
<tr>
<td><strong>Mass Spectrometer</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mass range (Da)</td>
<td>12 - 200</td>
<td>2 - 535</td>
<td>ID of wider range of species; derivatized compounds</td>
</tr>
<tr>
<td>High throughput pumps</td>
<td>no</td>
<td>yes</td>
<td>Increase in sensitivity</td>
</tr>
<tr>
<td>Static/dynamic modes</td>
<td>Dynamic only</td>
<td>Static or dynamic</td>
<td>High precision noble gas isotopes</td>
</tr>
<tr>
<td>Direct EGA monitoring</td>
<td>no</td>
<td>yes</td>
<td>Detect complex, less volatile species</td>
</tr>
<tr>
<td><strong>Tunable Laser Spectrometer</strong></td>
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</tr>
<tr>
<td>CH$_4$</td>
<td>No TLS &amp; MS isobaric interference</td>
<td>Dedicated laser channels for CH$_4$ abundance</td>
<td>Enables detection of these important very trace species</td>
</tr>
<tr>
<td>Isotopes of C, O, H</td>
<td>No TLS &amp; MS isobaric interference</td>
<td>Isotopes of CO$_2$, H$_2$O, and CH$_4$</td>
<td>Great improvement in precision of isotope measurements for C, O, H</td>
</tr>
</tbody>
</table>
SAM integration/calibration took about a year – now finishing last of qualification tests

Integrated onto SAM frame and main deck
- Quadrupole Mass Spectrometer
- Tunable Laser Spectrometer
- 6 GC columns
- Sample Manipulation System
- 2 pyrolysis cells
- 16 Gas Processing System manifolds
- 2 high conductance valves
- 52 microvalves
- 51 gas line heaters
- combustion & cal gases
- 2 scrubbers and 2 getters
- hydrocarbon trap
- 2 turbomolecular pumps
- 2 He tanks pressurized to 2400 psi
- 4 heat pipes
- electronics stack
- ~ 600 m of harness wire
- Solid Sample Inlet Tubes
- thermal shields
SAM getting ready for thermal vacuum tests
October 2009 – fit checking a mechanical model of SAM into the MSL rover
Why 6 GC columns?

**Column 1**: devoted to "atmospheric gases", as rare Gases (Kr, Ar...) + N2 + O2 + CO + CO2 + H2O + CH4 (!!);

**Column 2**: devoted to low molecular weight VOC (C1-C3) and sulfured compounds (SO2...);

**Columns 3 and 4**: Classical or “universal" columns that give access to a wide range of products- devoted to pyrolysis products and lighter derivatized products;

**Column 5**: devoted to products produced by derivatization (they are heavy after this sample preparation and need a specific column);

**Column 6**: devoted to chiral compounds, could be also a backup if one of the (3+4 columns) couple fails.
SAM Gas Calibration Cell - Composition

- Strong contrast to Mars composition
- Xe strongly enriched in $^{129}\text{Xe}$ to contrast with Mars Xe
- Mole fraction of calibration fluoro compounds in gas phase in cell set by cell temperature

When a small volume of calibration mix is injected into the SAM manifold – verification of GCMS performance at the sub ppb level is achieved

Mole fractions for higher-molecular-weight, calibration compounds

- PFTBA: 3%
- 1-FN: 0.54%
- DFBP: 0.012%
- PFBP: 0.003%
High molecular weight calibrants

GCMS ion chromatograms of 250 µl gas removed from a practice cell via syringe at 100-120ºC.

• Practice cell tests demonstrate our method for adding calibrants to cell works.

• Calibrants can be easily separated on RTX-5 column.

1-FN: 1-fluoronaphthalene
PFBP: perfluorobiphenyl
DFBP: 2,2-difluorobiphenyl

1-FN, m/z 334
PFBP, m/z 146
DFBP, m/z 190

Perfluorotributylamine
SAM QMS flight instrument (FM) performance demonstrated with high MW fluorocarbon Perfluophenanthrene $\text{C}_{14}\text{F}_{24}$
Calibration spectrum of Kr and Xe
Noble gases to be measured both from the atmosphere and thermally evolved from solids
Evolved gas calibration with solid mineral samples
Sample heated from ambient to 950°C

SAM FM Calibration Calcite and Melanterite EGA – 1/22/2009
GCMS from FM Comprehensive Performance Test
(use of fluorocarbons to eliminate confusion with Mars organics)
Contamination model, materials archive, and SAM library

Model of MSL contamination transport includes Mars winds and thermal plume from RTG

Materials archive & library
SAM team has analyzed volatile outgassing from numerous MSL materials and is creating a library of organics from MSL that may show up on Mars (dozens of GCMS pyrolysis runs and hundreds of compounds)

SAM environmental chamber duplicates T and P conditions on Mars – second round of qualification to start in January 2010
Prime MSL Landing Sites from multiple open MSL landing site workshops

**Holden crater:**
bedrock outcrops, alluvial fans, rich history of aqueous processing

**Eberswalde crater:**
well defined delta suggests long duration water flow

**Mawrth:**
strong CRISM and OMEGA signatures of Fe/Mg and Al phyllosilicates – may be good preservation environment for organics

**Gale crater:**
diversity of mineralogy in well defined layered sequences that could be traversed by MSL
MSL landing sites and methane hot spots

Eberswalde Crater (24°S, 327°E, -1.5 km)
Gale Crater (4.5°S, 137°E, -4.5 km)
Holden Crater (26°S, 325°E, -1.9 km)
Mawrth Vallis (24°N, 341°E, -2.2 km)

Additional methane maps from future Mars Express and ground based observations will be useful in providing an additional discriminating factor for MSL landing site selection

From Mumma et al.
Mars methane sources will only be revealed with a RANGE of chemical and isotopic measurements

Deep terrestrial methane sources are likely MIXED abiotic and biotic. To provide signatures of source type, a range of measurements and their temporal variations are needed:

For example, Sherwood Lollar et al., 2006 point to ENDMEMBER signatures

• ratio of CH₄ to C₂H₆ and C3 and C4 compounds
• δH vs. δ¹³C in methane, ethane, and C3 and C4 compounds
• temporal variations of δH vs. δ¹³C in methane
• ratio of H₂ to CH₄
• CH₄/C₂+ vs. δ¹³C in methane

SAM could utilize

• ¹³C/¹²C and D/H measurement in methane (if methane present in sufficient abundance)
• correlation of ¹³C/¹²C in methane and D/H measurement in H₂O
• ratio of methane to heavier hydrocarbons (best measurements for C4 and heavier compounds)
• combustion of refractory carbon to possibly reveal ¹³C/¹²C in source material
• seasonal and diurnal measurements of methane abundance in one surface region to contribute to understanding of sources and sinks.

TLS contribution to this analysis will be described in the next talk