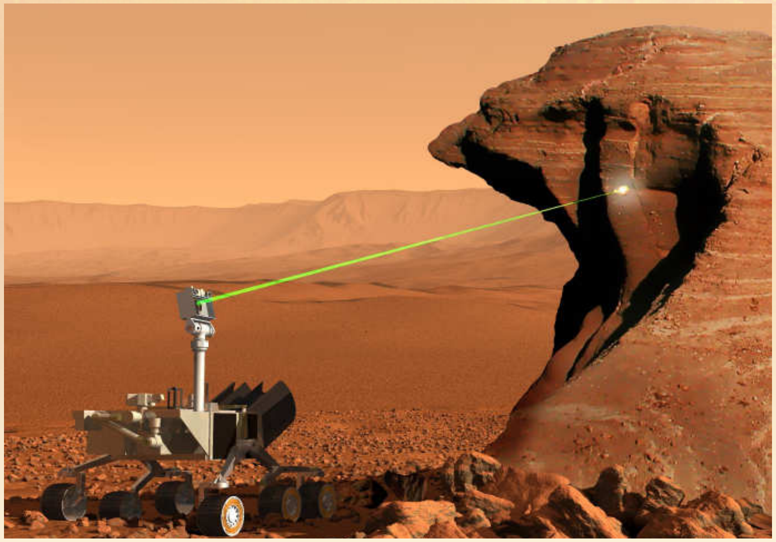
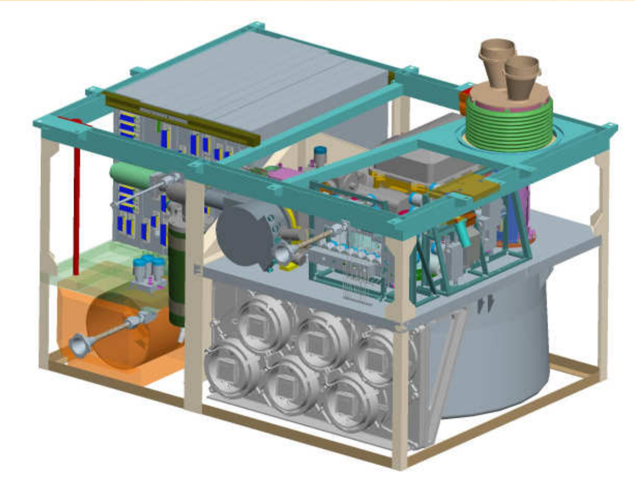
The Sample Analysis at Mars Suite and its METHANE Relevant Investigations

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

Joint ESA-ASI Workshop on Methane on Mars
ESA/ ESRIN Frascati, Italy
November 25-27th 2009





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

CoInvestigator	Institution	CoInvestigator	Institution	CoInvestigator	Institution
Paul Mahaffy, PI	NASA/GSFC	Andrew Steele	Carnegie Inst.	Toby Owen	U. Hawaii
Sushil Atreya	U. Michigan	Bruce Jakosky	U. Colorado	Bob Pepin	U. Minn.
Will Brinckerhoff	Johns Hopkins U.	John Jones	NASA/JSC	Francois Raulin	U. Parix XII
Michel Cabane	U. Paris/SA	Laurie Leshin	NASA/GSFC	Francois Robert	Museum Nat. Hist.
Patrice Coll	U. Paris XII	Chris McKay	NASA/Ames	James Scott	Carnegie Instit.
Pamela Conrad	JPL	Doug Ming	NASA/JSC	Steve Squyres	Cornell U.
Stephen Gorevan	Honeybee Robotics	Dick Morris	NASA/JSC	Chris Webster	JPL
Fred Goesmann	Max-Planck	R. Navarro-Gonzalez	U. Mexico	Color key → SAM hardware provider	

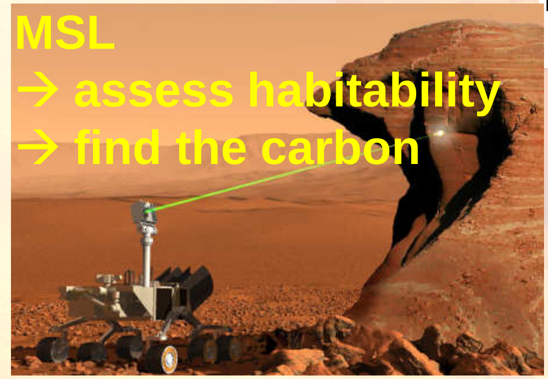
Collaborators: Mehdi Benna, Oliver Botta, Jason Dworkin, Jen Eigenbrode, Heather Franz, Daniel Glavin, Dan Harpold, Wayne Kasprzak, Heidi Manning, Kenneth Nealson, Alain Person, Claude Rodier, Robert Sternberg, Stephanie Stockman, Cyril Szopa, Meenakshi Wadhwa, Edward Vicenzi, Ah-San Wong, Jaime Demick, 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 CO_2.

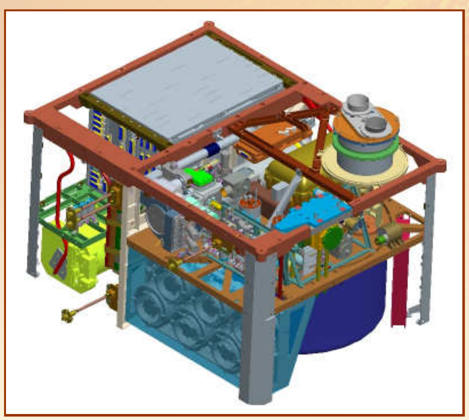
SAM Instruments and Major Subsystems

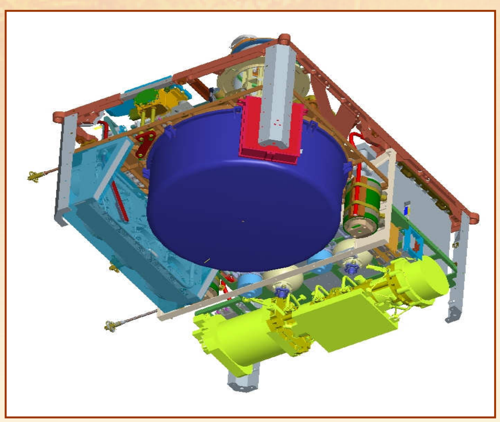
SAM is a Suite of 3 Instruments

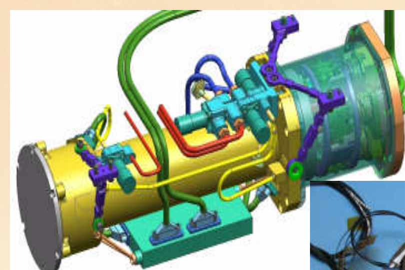
- **Quadrupole Mass Spectrometer (QMS) – Goddard Space Flight Center**
  - Molecular and isotopic composition in the 2-550 Dalton mass range for atmospheric and evolved gas samples
- **Gas Chromatograph (GC) - University of Paris, CNES**
  - Resolves complex mixtures of organics into separate components
- **Tunable Laser Spectrometer (TLS) – Jet Propulsion Laboratory**
  - Abundance and precision isotopic composition of CH_4, H_2O, and CO_2

SAM supporting subsystems

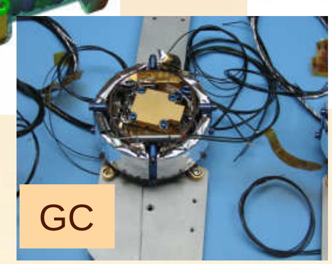
- **Gas Processing System (GPS) – Goddard Space Flight Center**
  - Includes valves, manifolds, carrier gas, enrichment cells, Wide Range Pump (WRP), and Pyrolysis Ovens
- **Sample Manipulation System (SMS) – Honeybee Robotics**
  - Positions 74 sample cups to below a sample inlet tube or into SAM pyrolysis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

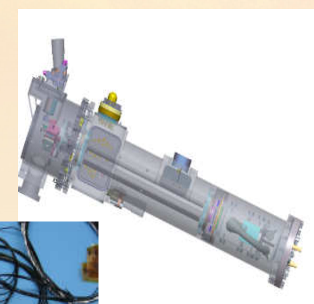






TLS





QMS

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 SO_2, H_2O, and 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 H_2O, O_2, N_2, Ar, O_3, H_2, and CH_4

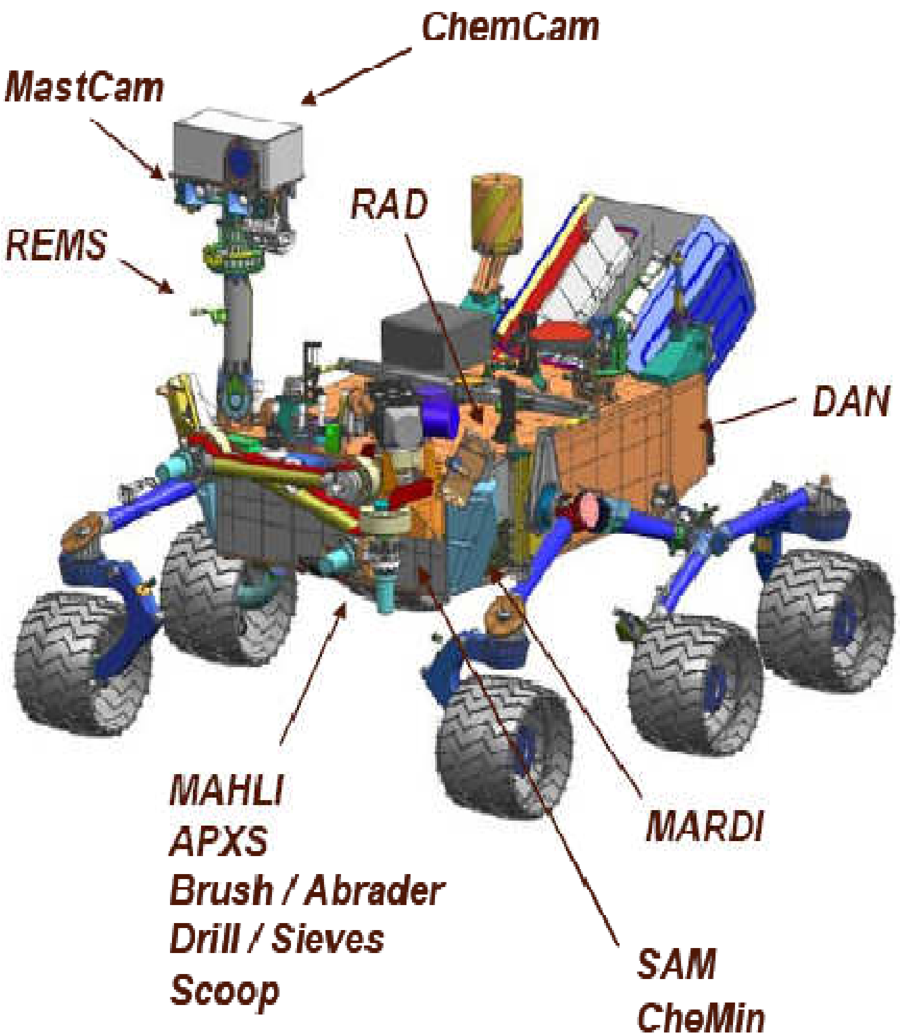
- **GOAL #5: Understand atmosphere & climate evolution through isotope measurements of noble gases & light elements**

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



>130 co-investigators in seven countries

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

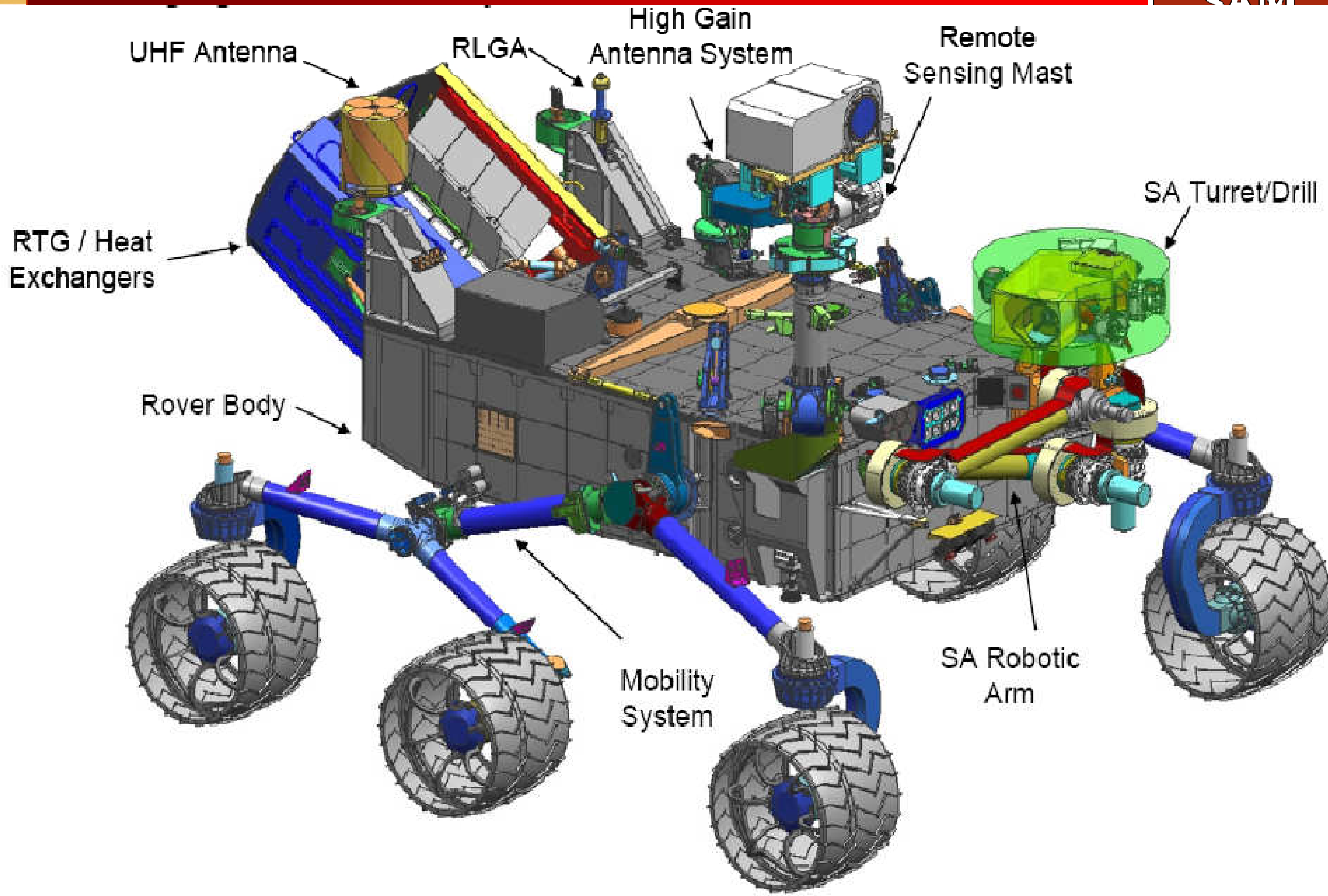
MARDI (M. Malin, MSSS) Descent imagery

REMS (L. Vázquez, CAB, Spain) - Meteorology / UV

RAD (D. Hassler, SwRI) - High-energy radiation

DAN (I. Mitrofanov, IKI, Russia) - Subsurface hydrogen

Other MSL elements

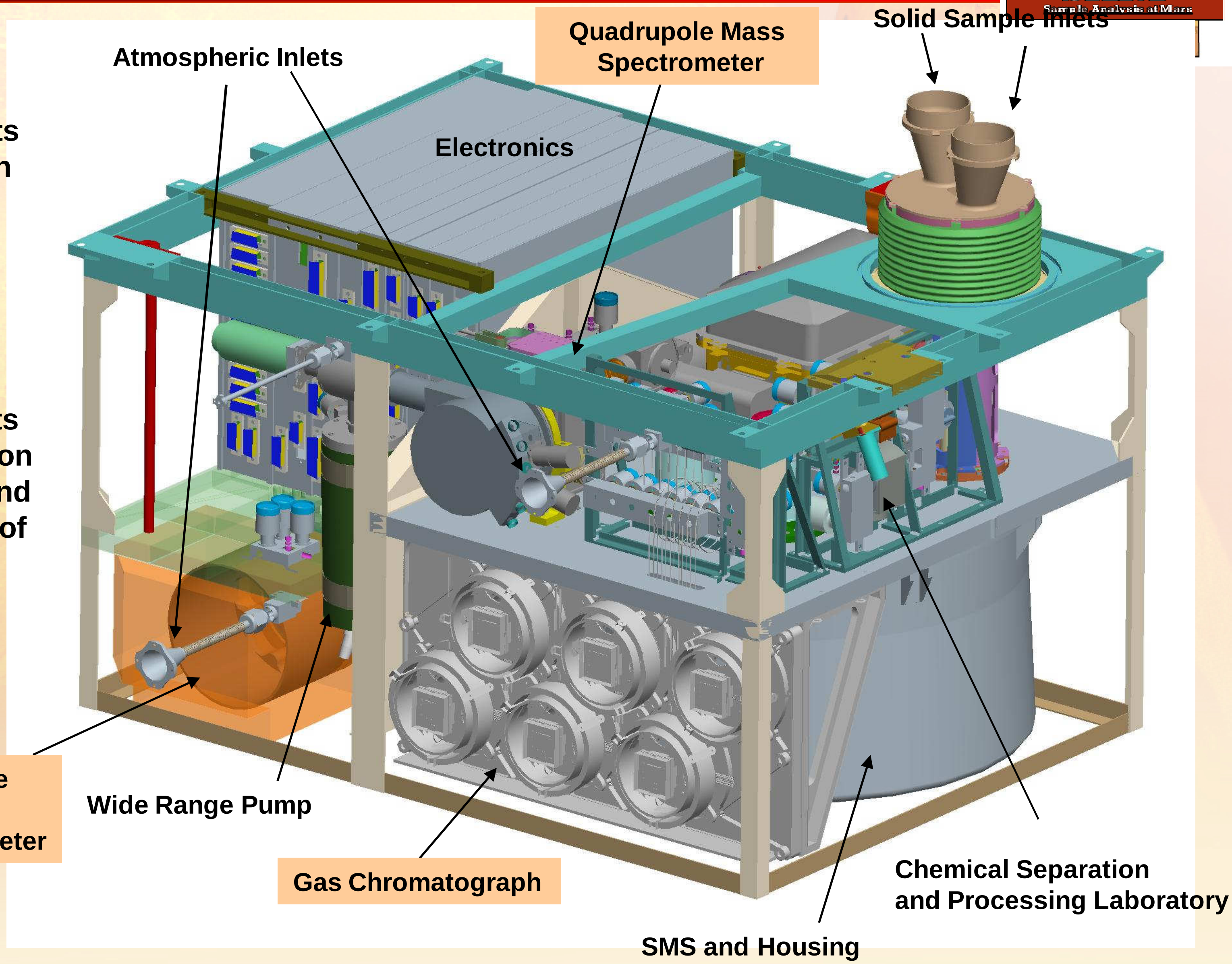


We anticipate the substantial benefit of an order of magnitude increase in payload mass resources !

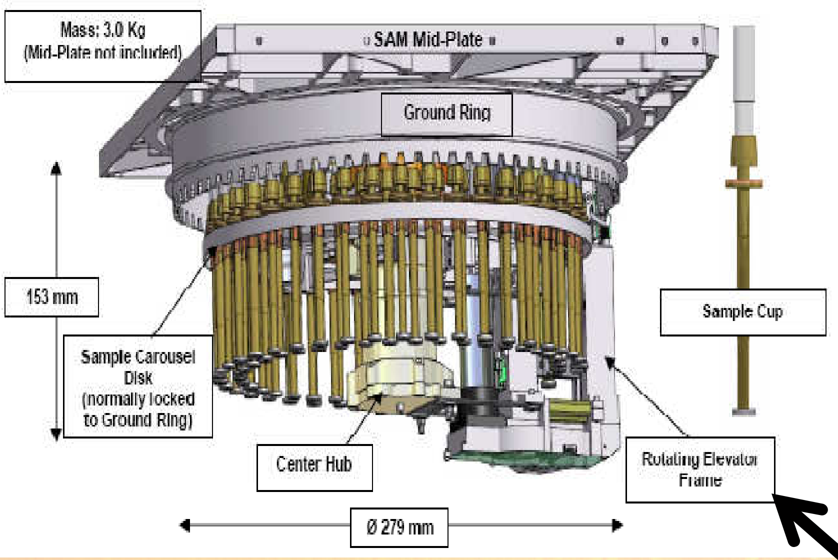
SAM Suite top assembly

Solid sample inlets penetrate through MSL top deck

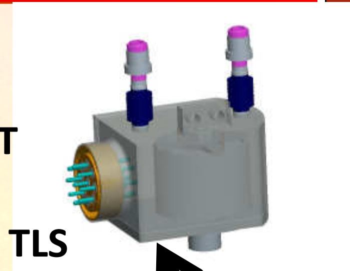
Atmospheric inlets and vents located on side of SAM box and penetrate +Y face of MSL WEB

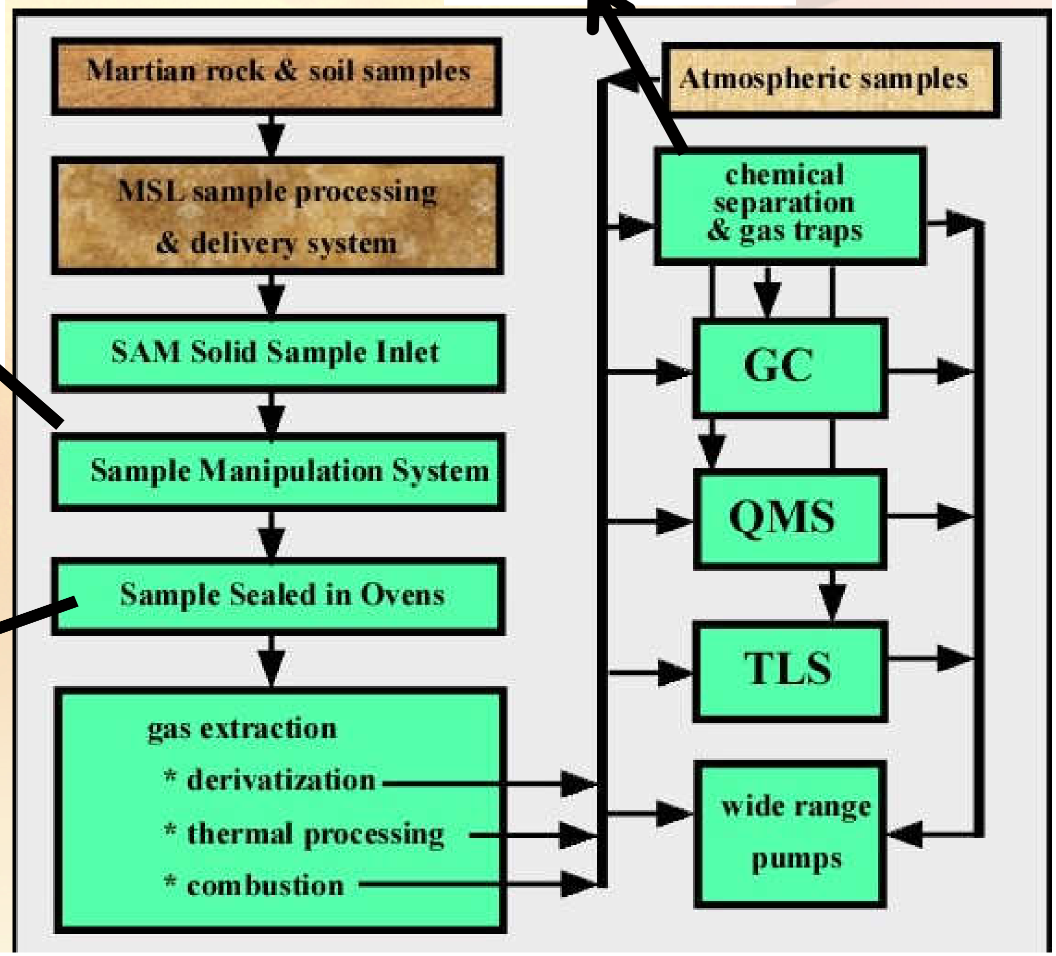


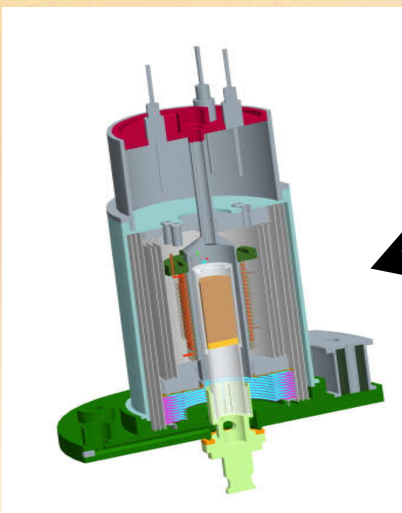
SAM Processes both Rock and Atmospheric Samples



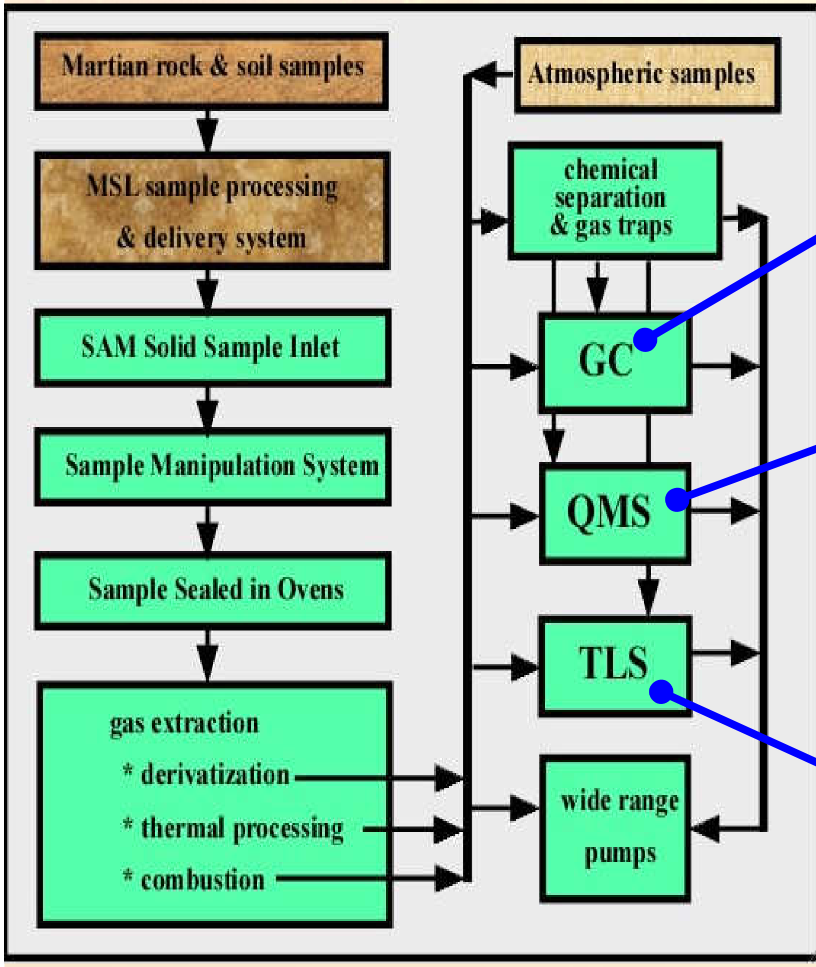
Getter utilized for methane enrichment pumps all gases EXCEPT CH_4 and noble gases – scrubbed gas is sent to TLS

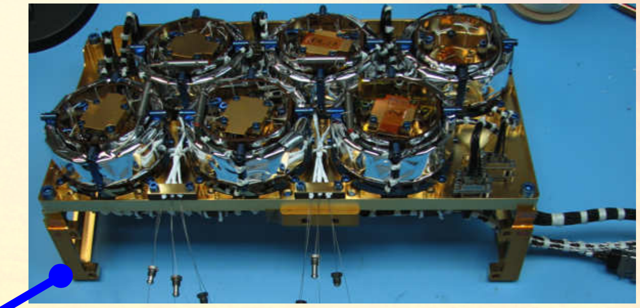






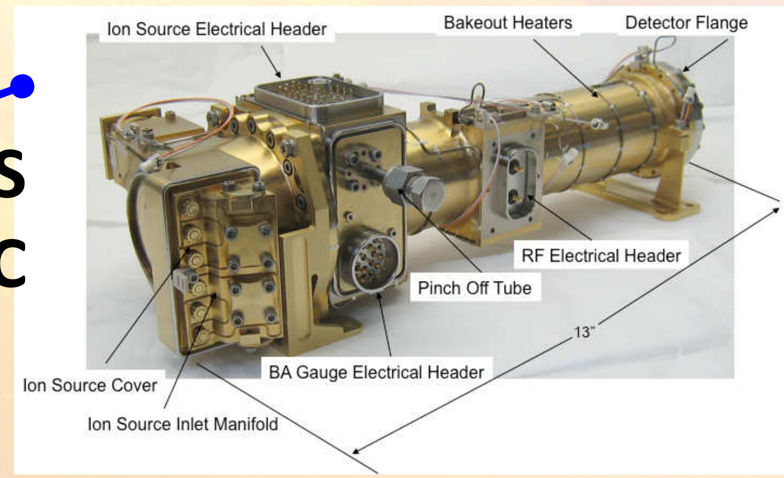
3 core instruments provided an international collaboration between three different institutions

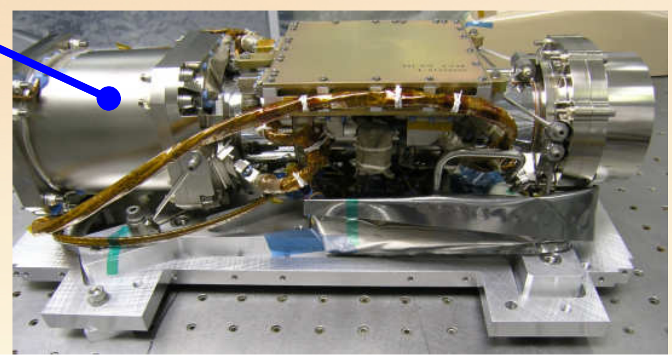




GC French contribution

QMS from GSFC





TLS from JPL

SAM Conducts a Diverse Set of Chemical Analyses

EXPERIMENT	WHAT EACH SAM EXPERIMENT DOES AND WHY
Pyrolysis *(61 quartz cups)*	**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_2O from hydrates is produced, they can be isotopically analyzed by TLS.
Derivatization *(9 cups w/fluid)*	**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)
Combustion	**$^{13}C/^{12}C$ 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
Direct Atmospheric Sampling	**ATMOSPHERIC COMPOSITION VARIATIONS** – the atmosphere is sampled by the QMS (wide survey) and the TLS on various temporal scales (diurnal and seasonal)
Atmospheric Sampling with Enrichment	**ATMOSPHERIC TRACE SPECIES** – trace species are enriched by the SAM traps and analyzed in the QMS
Atmospheric Methane with Enrichment	**TRACE METHANE AND ITS ISOTOPES** – 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.
Atmospheric Noble Gas Enrichment	**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
In Situ Calibration *(4 cups)*	**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. *-3 cups w/fluorocarbs &inorganics + 1 cup calcite for terrestrial CO_2 validation*

Calibration expts | Solid Sample expts | Gas expts

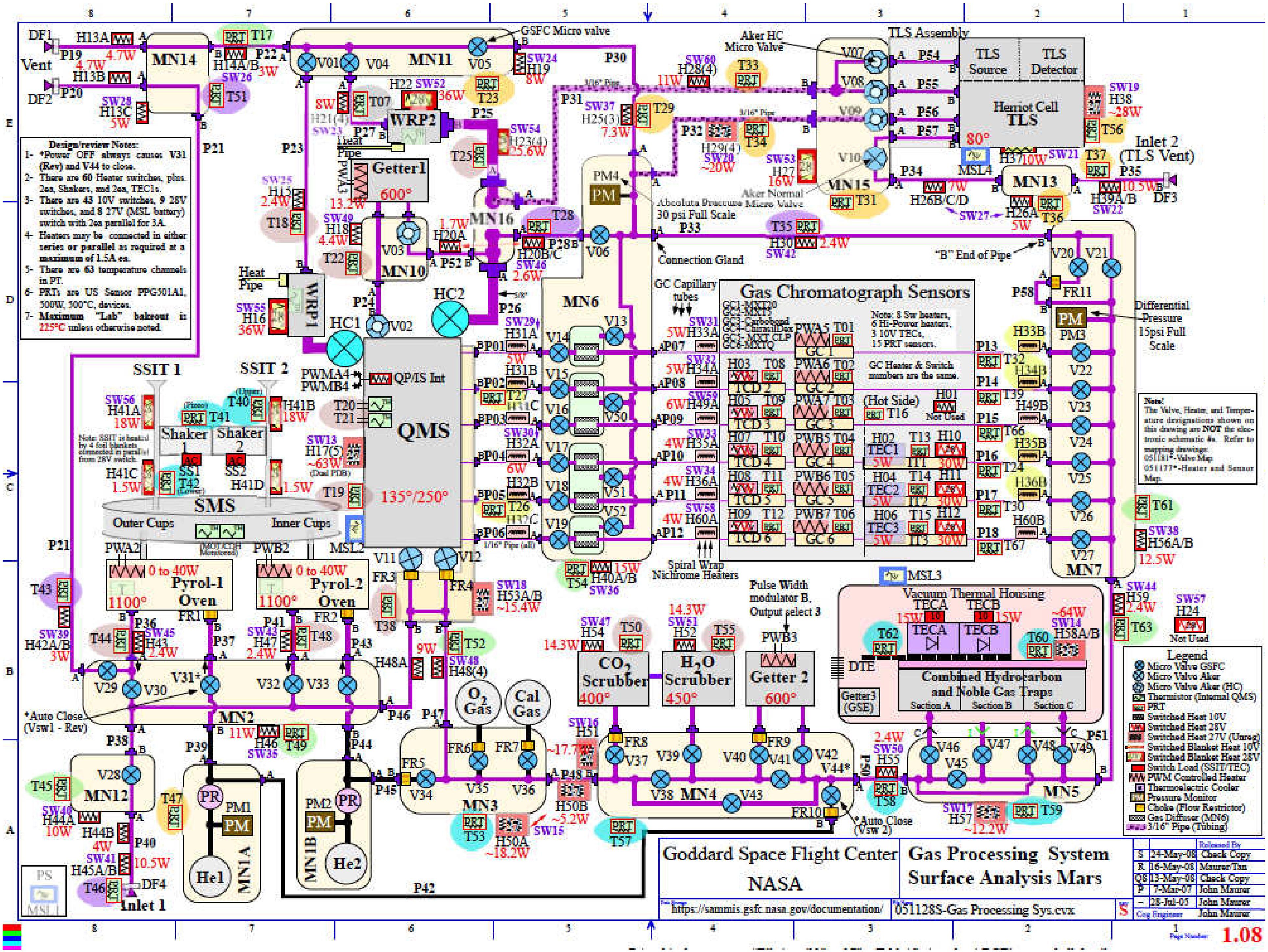
SAM comparison with Viking GCMS

Parameter	Viking	SAM	Science Benefit
Pyrolysis			
No. of sample cups	3	74	More samples analyzed – each cup can be used multiple times
Temperature	50, 200, 350, or 500ºC	Continuous heating up to 1100ºC	Identification of mineral decomposition products
Gas Chromatography			
Columns	Poly MPE-Tenax	Molsieve 5A carbo-bond, MXT 1,5, MXT PLOT U, RTX 5 Amine, Chirasil-Val	Analysis of a wider range of organics, noble gases, VOCs, derivatized compounds, enantiomers and amines
Derivatization	No	Yes, MTBSTFA	Transforms key organic biomarkers
Mass Spectrometer			
Mass range (Da)	12 - 200	2 - 535	ID of wider range of species; derivatized compounds
High throughput pumps	no	yes	Increase in sensitivity
Static/dynamic modes	Dynamic only	Static or dynamic	High precision noble gas isotopes
Direct EGA monitoring	no	yes	Detect complex, less volatile species
Tunable Laser Spectrometer			
CH_4	No TLS & MS isobaric interference	Dedicated laser channels for CH_4 abundance	Enables detection of these important very trace species
Isotopes of C, O, H	No TLS & MS isobaric interference	Isotopes of CO_2, H_2O, and CH_4	Great improvement in precision of isotope measurements for C, O, H

SAM integration/calibration took about a year – now finishing last of qualification tests

Integrated onto SAM frame and main deck

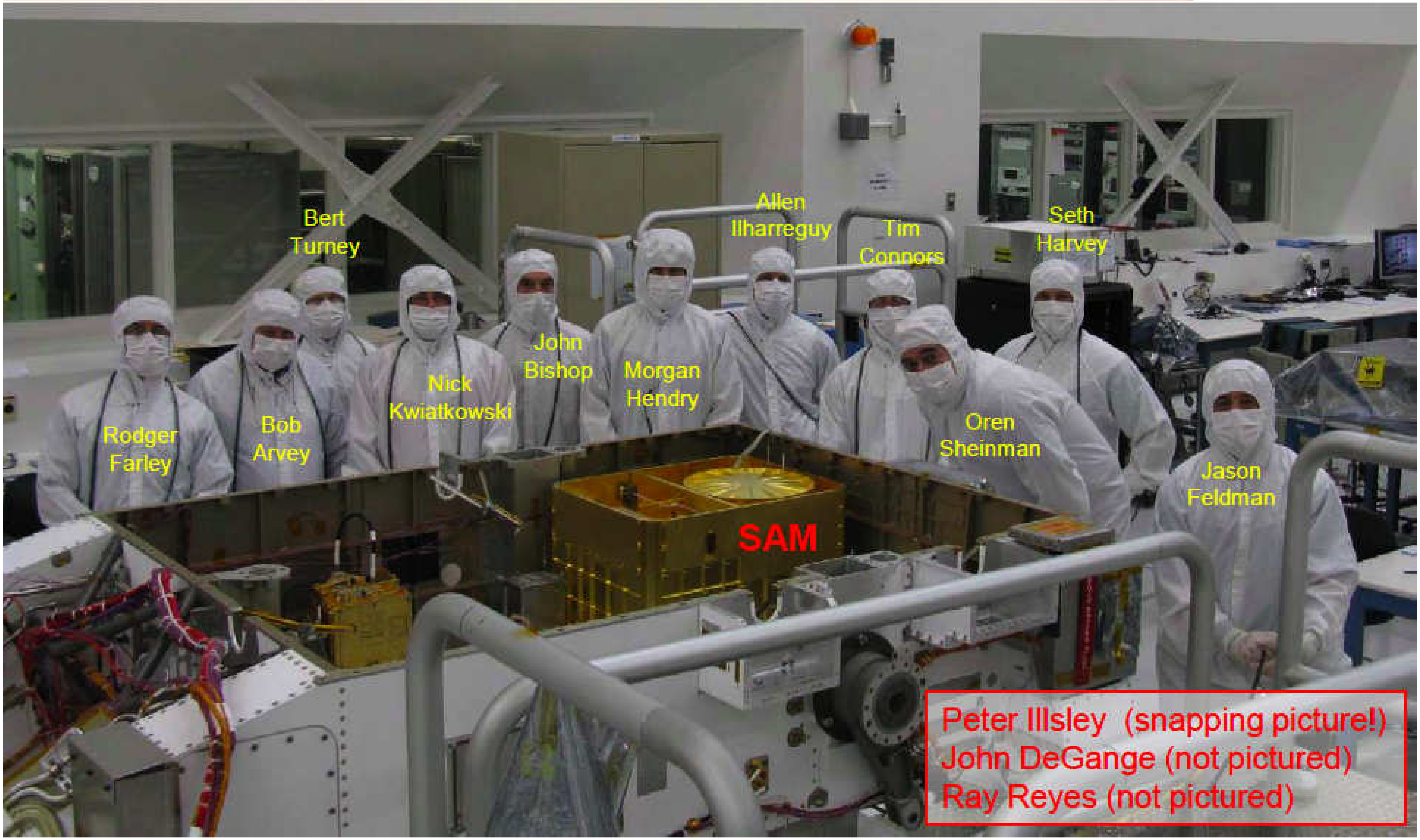
- Quadrupole Mass Spectrometer
- Tunable Laser Spectrometer
- 6 GC columns
- Sample Manipulation System
- 2 pyrolysis cells
- 16 Gas Processing System manifolds
- 2 high conductance valves
- 52 microvalves
- 51 gas line heaters
- combustion & cal gases
- 2 scrubbers and 2 getters
- hydrocarbon trap
- 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



Design/review Notes:
1- *Power OFF always causes V31 (Rev) and V44 to close.
2- There are 60 Heater switches, plus 2ea, Shakers, and 2ea, TEC1s.
3- There are 43 10V switches, 9 28V switches, and 8 27V (MSL battery) switch with 2ea parallel for 3A.
4- Heaters may be connected in either series or parallel as required at a maximum of 1.5A ea.
5- There are 63 temperature channels in PT.
6- PRTs are US Sensor PPG501A1, 500W, 500°C, devices.
7- Maximum "Lab" bakeout is 225°C unless otherwise noted.
TLS Assembly
TLS Source
TLS Detector
Herriot Cell TLS
80°
Inlet 2 (TLS Vent)
Inlet 1
Vent
QMS
135°/250°
Getter1
600°
SSIT 1
SSIT 2
SMS
Outer Cups
Inner Cups
Pyrol-1 Oven
Pyrol-2 Oven
1100°
0 to 40W
Note: SSIT is heated by 4 foil blankets connected in parallel from 28V switch.
Gas Chromatograph Sensors
Note: 8 Sw heaters, 6 Hi-Power heaters, 3 10V TECs, 15 PRT sensors.
GC Heater & Switch numbers are the same.
GC Capillary tubes
Spiral Wrap Nichrome Heaters
Pulse Width modulator B, Output select 3
Vacuum Thermal Housing
Combined Hydrocarbon and Noble Gas Traps
Section A
Section B
Section C
CO2 Scrubber
400°
H2O Scrubber
450°
Getter 2
600°
Getter3 (GSE)
O2 Gas
Cal Gas
He1
He2
GSFC Micro valve
Aker HC Micro Valve
Aker Normal
Absolute Pressure Micro Valve
30 psi Full Scale
Connection Gland
"B" End of Pipe
Differential Pressure 15psi Full Scale
*Auto Close (Vsw1 - Rev)
*Auto Close (Vsw 2)
Note! The Valve, Heater, and Temperature designations shown on this drawing are NOT the electronic schematic #s. Refer to mapping drawings: 051181*-Valve Map 051177*-Heater and Sensor Map.
Legend
Micro Valve GSFC
Micro Valve Aker
Micro Valve Aker (HC)
Thermistor (Internal QMS)
PRT
Switched Heat 10V
Switched Heat 28V
Switched Heat 27V (Unreg)
Switched Blanket Heat 10V
Switched Blanket Heat 28V
Switch Load (SSIT/TEC)
PWM Controlled Heater
Thermoelectric Cooler
Pressure Monitor
Choke (Flow Restrictor)
Gas Diffuser (MN6)
3/16" Pipe (Tubing)
Goddard Space Flight Center
NASA
Gas Processing System
Surface Analysis Mars
https://sammis.gsfc.nasa.gov/documentation/
051128S-Gas Processing Sys.cvx
S 24-May-08 Check Copy
R 16-May-08 Maurer/Tan
Q8 13-May-08 Check Copy
P 7-Mar-07 John Maurer
- 28-Jul-05 John Maurer
Cog Engineer John Maurer
1.08

SAM getting ready for thermal vacuum tests

October 2009 – fit checking a mechanical model of SAM into the MSL rover



Why 6 GC columns ?

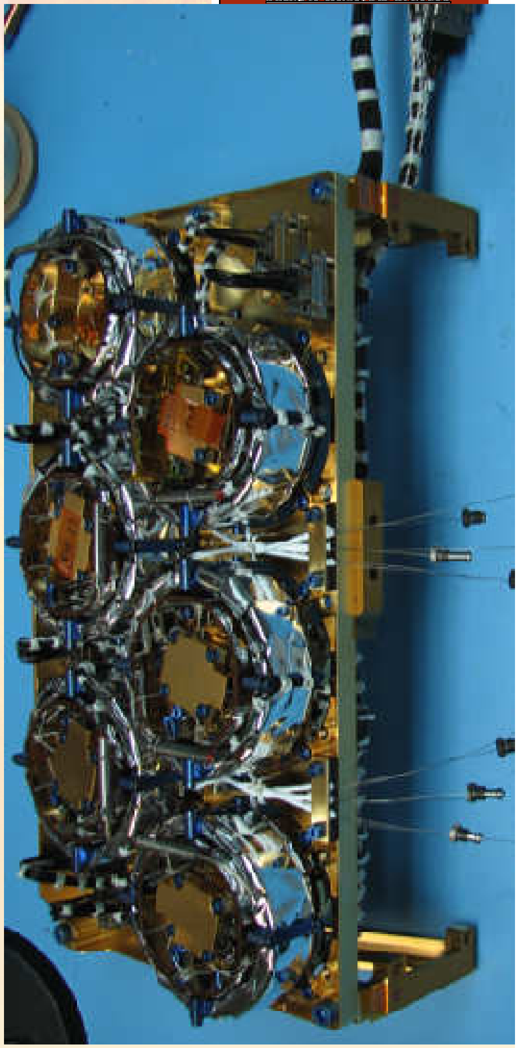
<u>Column 1 :</u> devoted to "atmospheric gases", as rare Gases (Kr, Ar...) + N_2
+ O_2 + CO + CO_2 + H_2O + CH_4 (!!);

<u>Column 2 :</u> devoted to low molecular weight VOC (C_1-C_3) and sulfured compounds (SO_2...);

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

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

<u>Column 6 :</u> devoted to chiral compounds, could be also a backup if one of the (3+4 columns) couple fails.

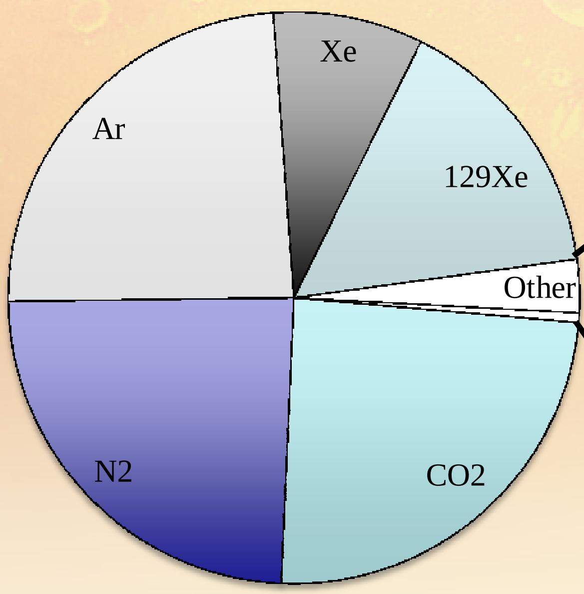


SAM Gas Calibration Cell - Composition

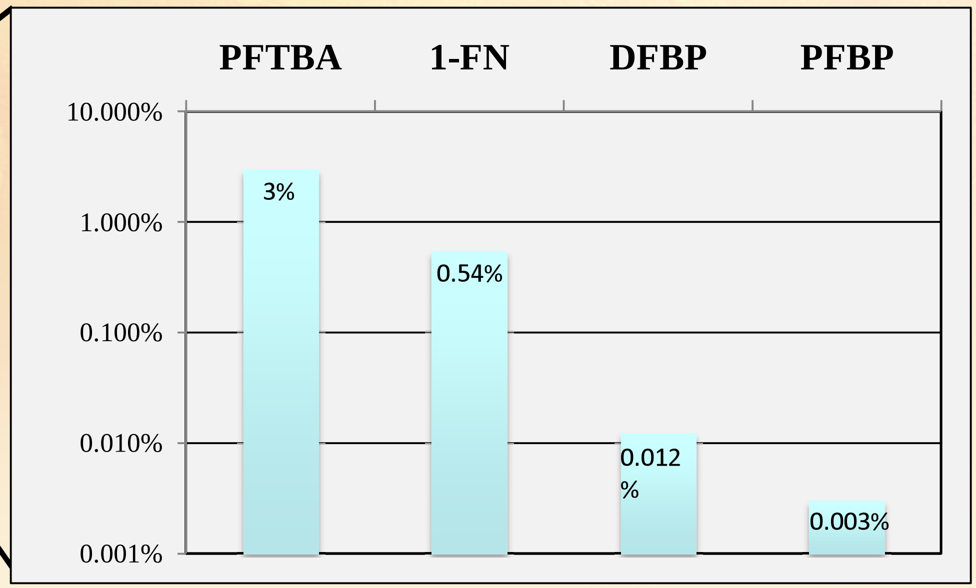
- Strong contrast to Mars composition
- Xe strongly enriched in ^{129}Xe to contrast with Mars Xe
- Mole fraction of calibration fluoro compounds in gas phase in cell set by cell temperature

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

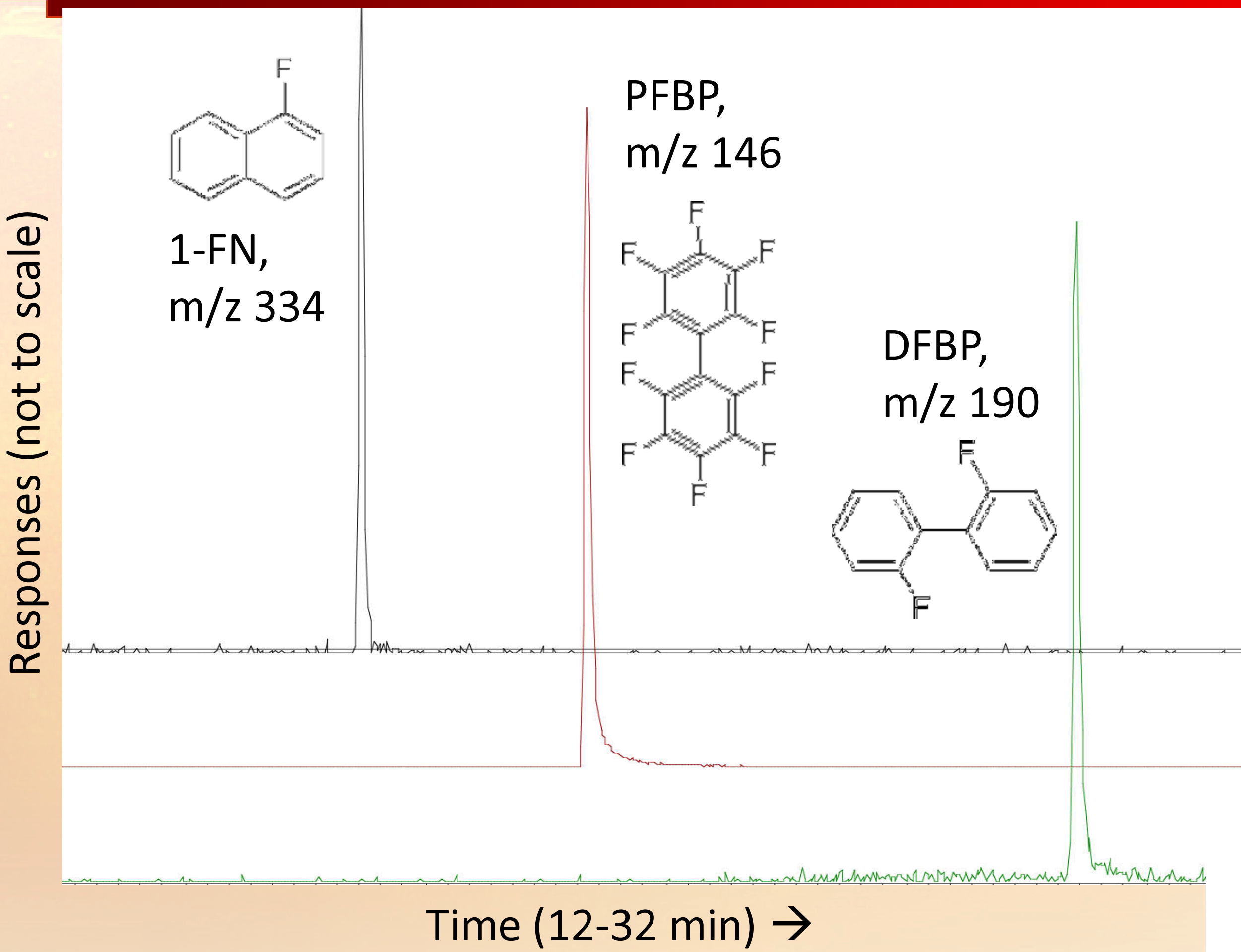
Total Composition (Mole Fraction)



Mole fractions for higher-molecular- weight, calibration compounds



High molecular weight calibrants

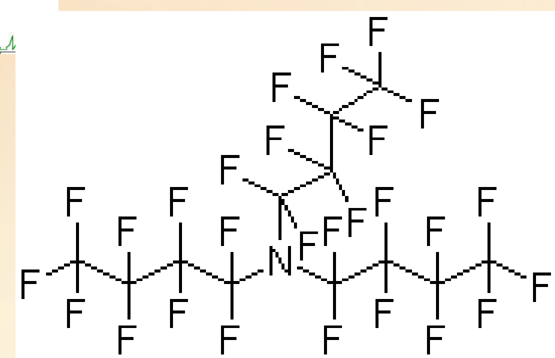


GCMS ion chromatograms of 250 µl gas removed from a practice cell via syringe at 100-120ºC.

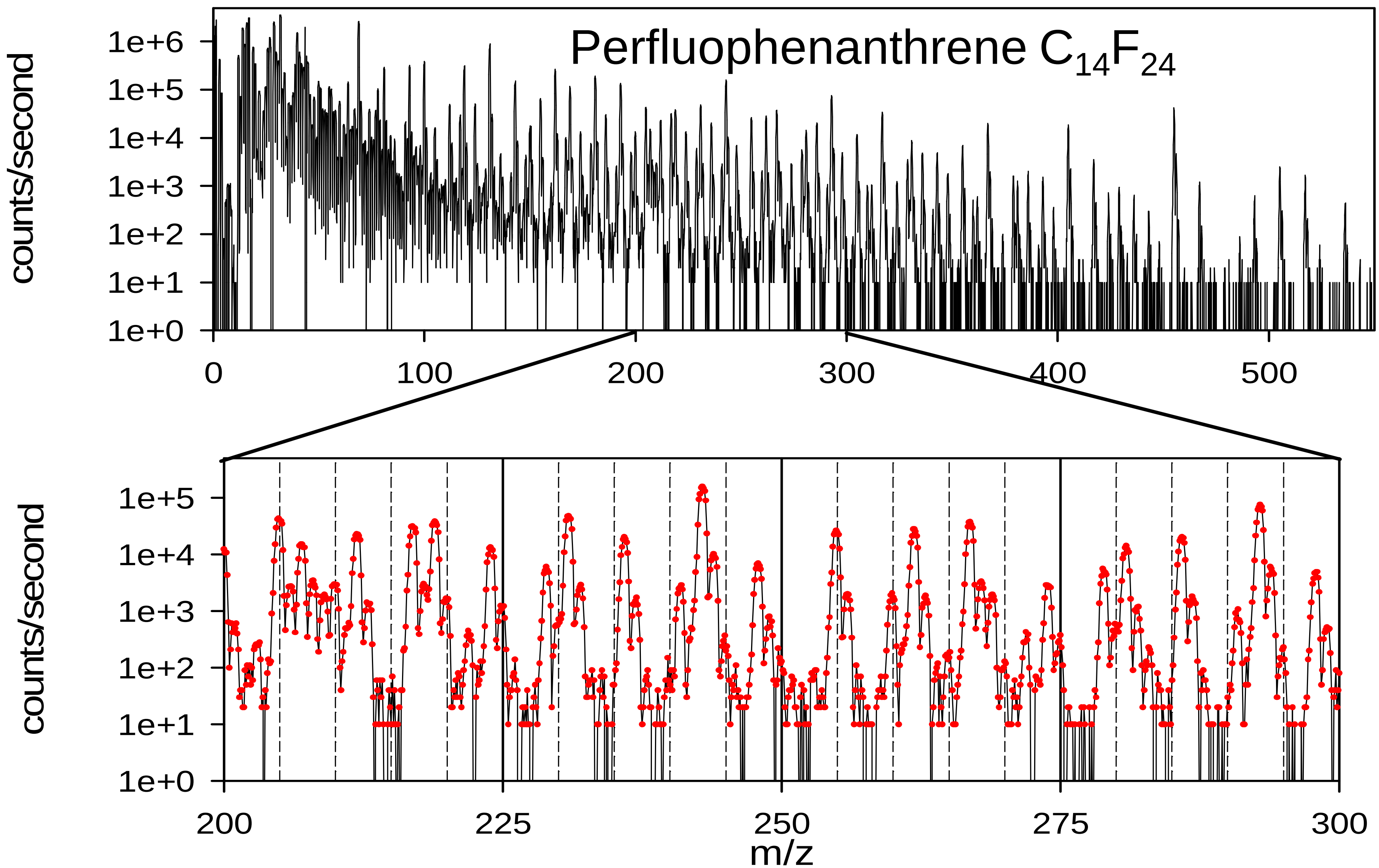
- Practice cell tests demonstrate our method for adding calibrants to cell works.
- Calibrants can be easily separated on RTX-5 column.

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

Perfluorotributylamine

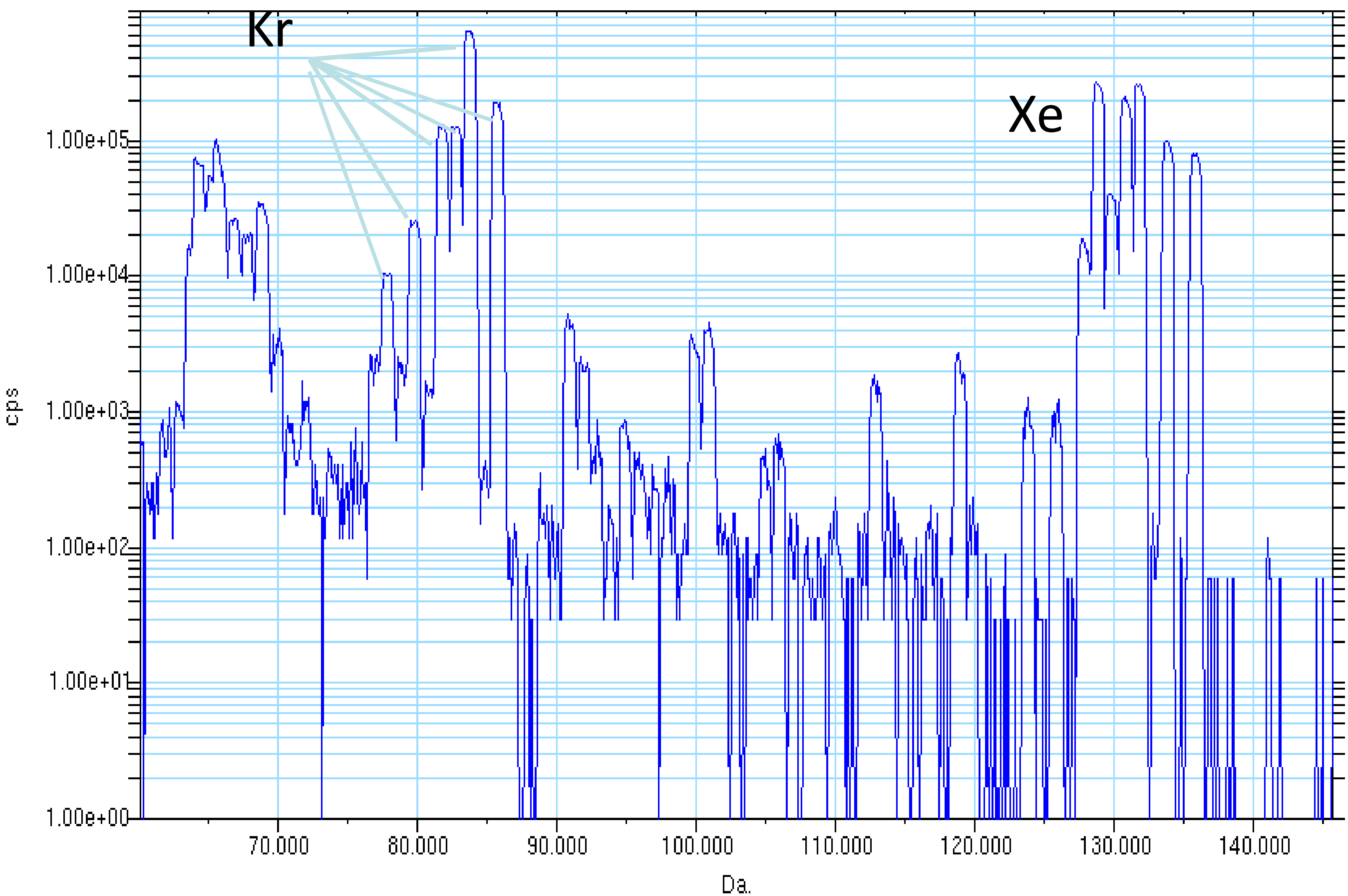


SAM QMS flight instrument (FM) performance demonstrated with high MW fluorocarbon



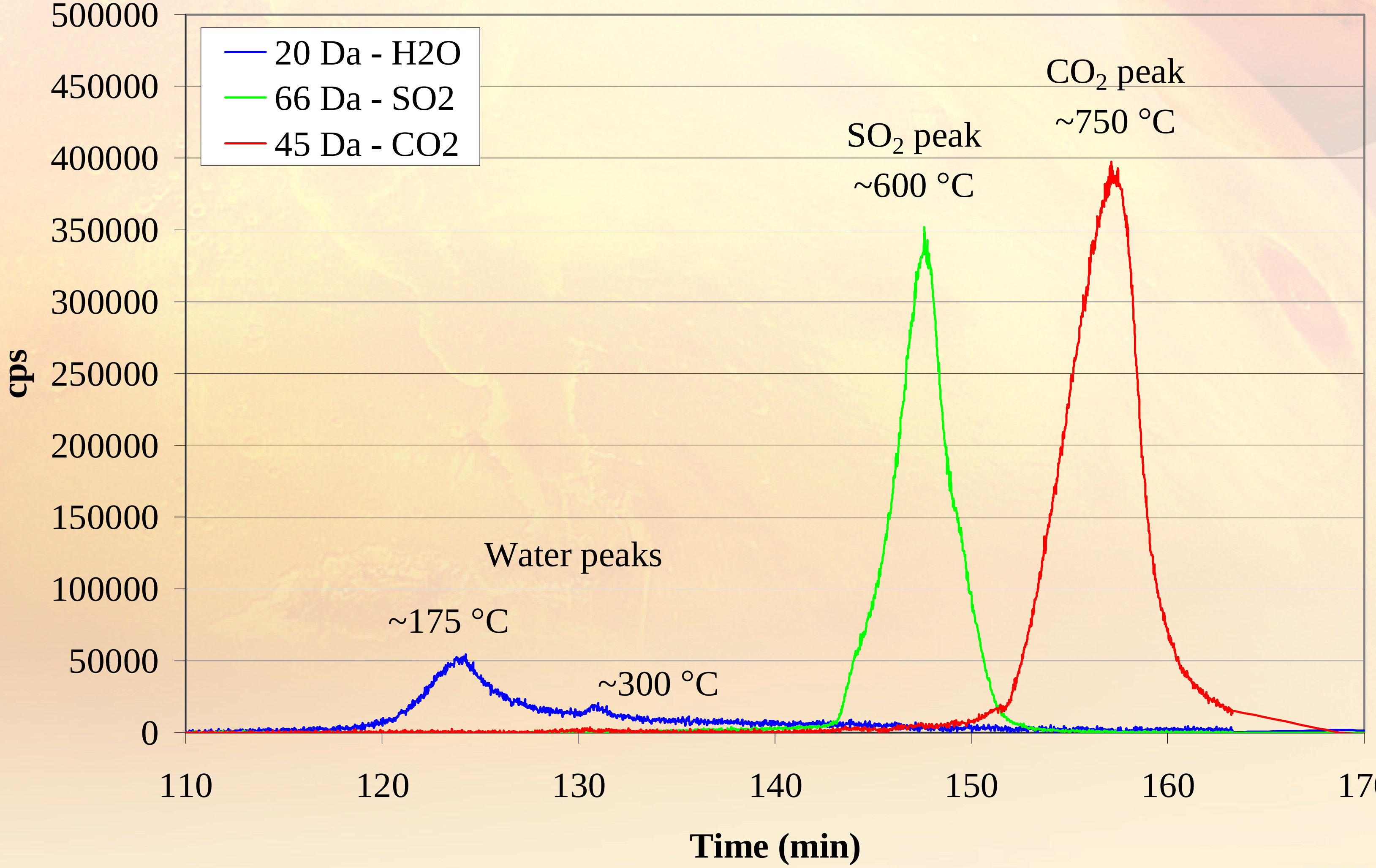
Calibration spectrum of Kr and Xe

Noble gases to be measured both from the atmosphere and thermally evolved from solids

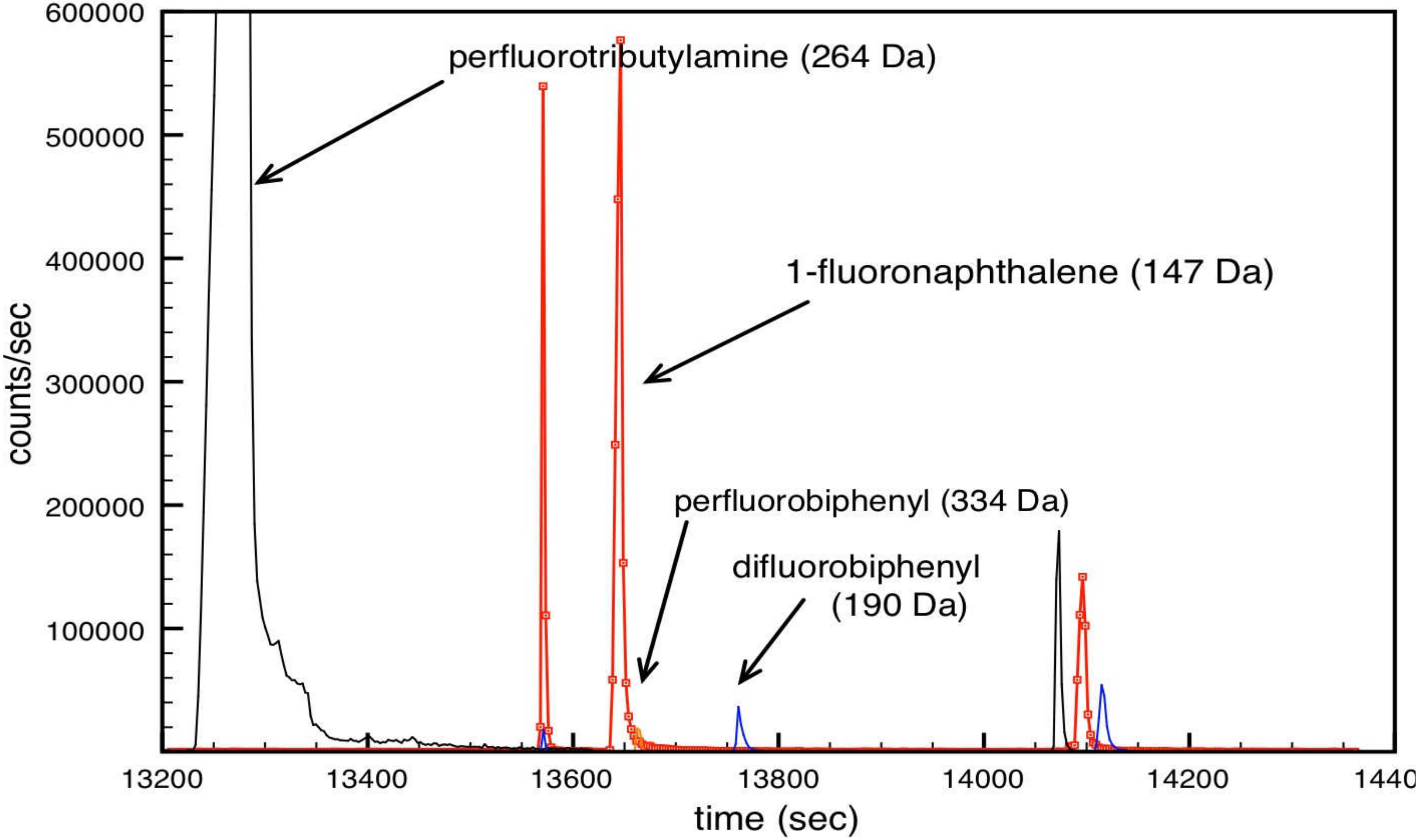


Evolved gas calibration with solid mineral samples
Sample heated from ambient to 950 C

SAM FM Calibration Calcite and Melanterite EGA – 1/22/2009



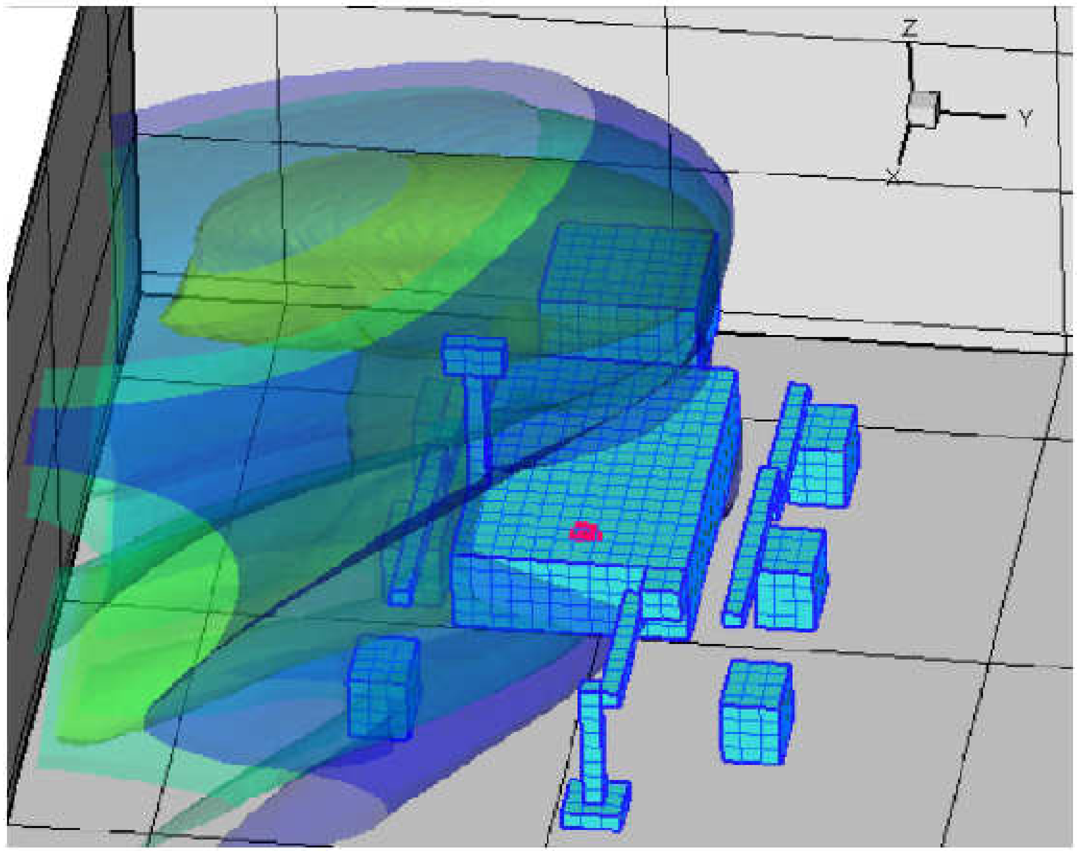
GCMS from FM Comprehensive Performance Test
(use of fluorocarbons to eliminate confusion with Mars organics)



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)

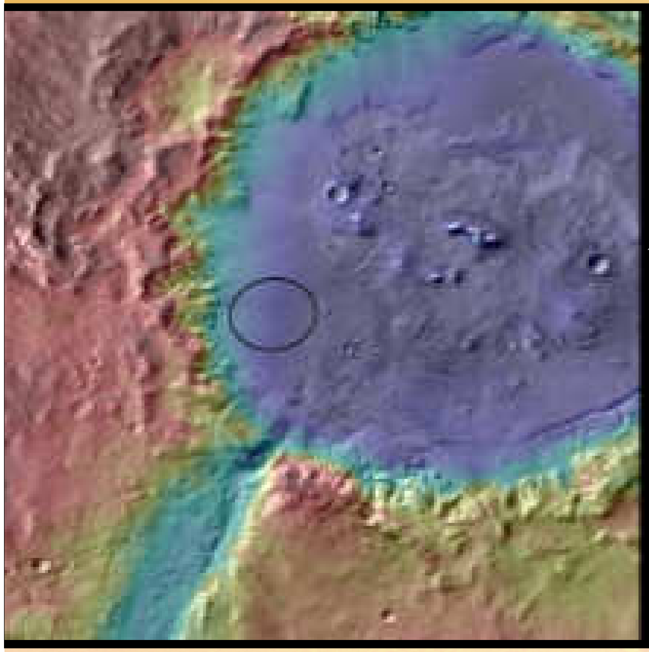


Results of an example calculation showing surfaces of 100 ppb, 10 ppb, and 1 ppb densit for a contaminant emanating from a vent, not shown, located at the right rear of the rover body. The outermost contour corresponds to 1 ppb, the innermost contour to 100 ppb.

Ten Kate, I.L., Canham, J.S., Conrad, P. G, Errigo, T., Katz, I, and Mahaffy, P.R., Impact of Terrestrial Contamination on Organic Measurements from the Mars Science Laboratory, ***Astrobiology*** 8, 571-582 (2008).

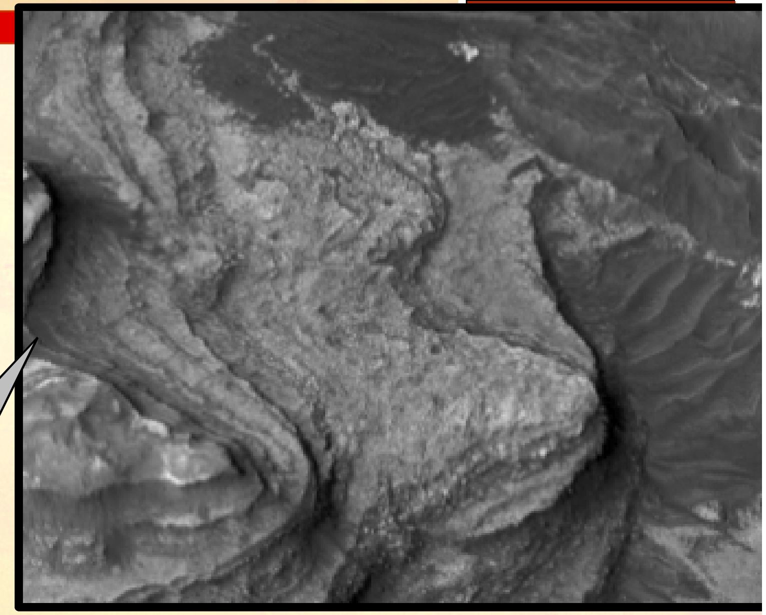
SAM environmental chamber duplicates T and P conditions on Mars – second round of qualification to start in January 2010

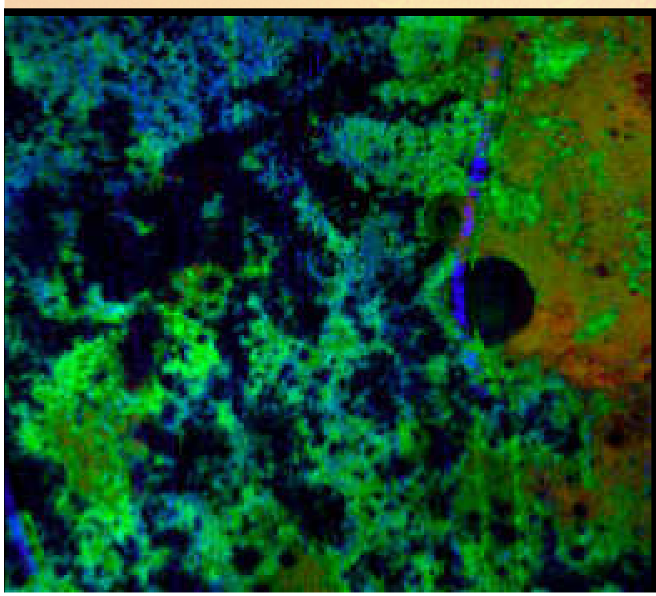
Prime MSL Landing Sites from multiple open MSL landing site workshops



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

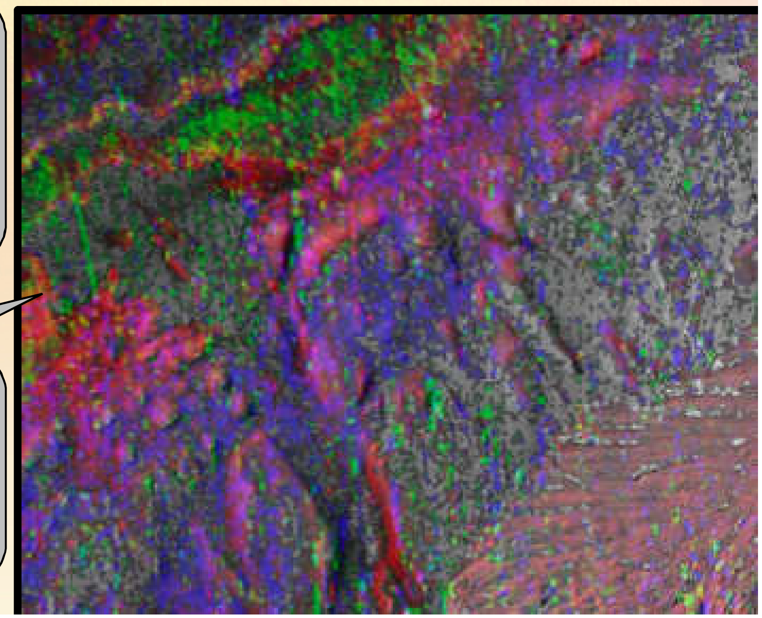
Eberswalde crater: well defined delta suggests long duration water flow



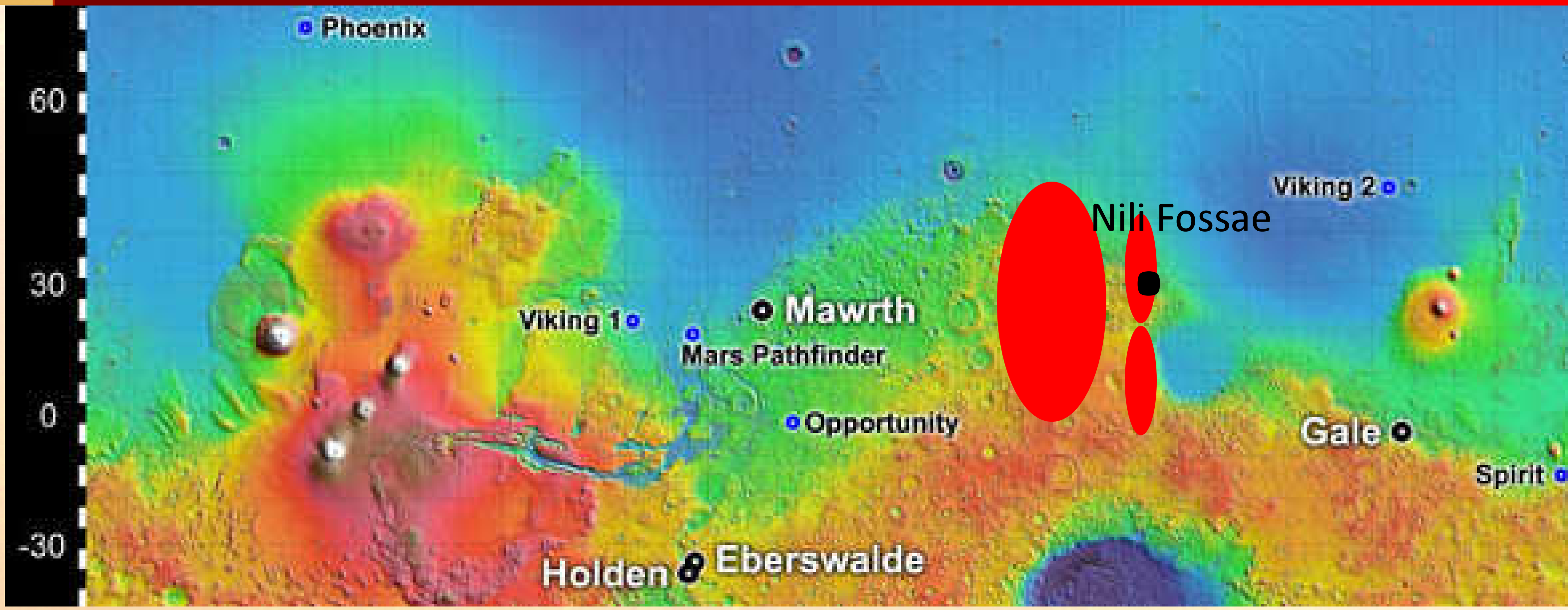


Mawrth: strong CRISM and OMEGA signatures of Fe/Mg and Al phylosilicates – may be good preservation environment for organics

Gale crater: diversity of mineralogy in well defined layered sequences that could be traversed by MSL

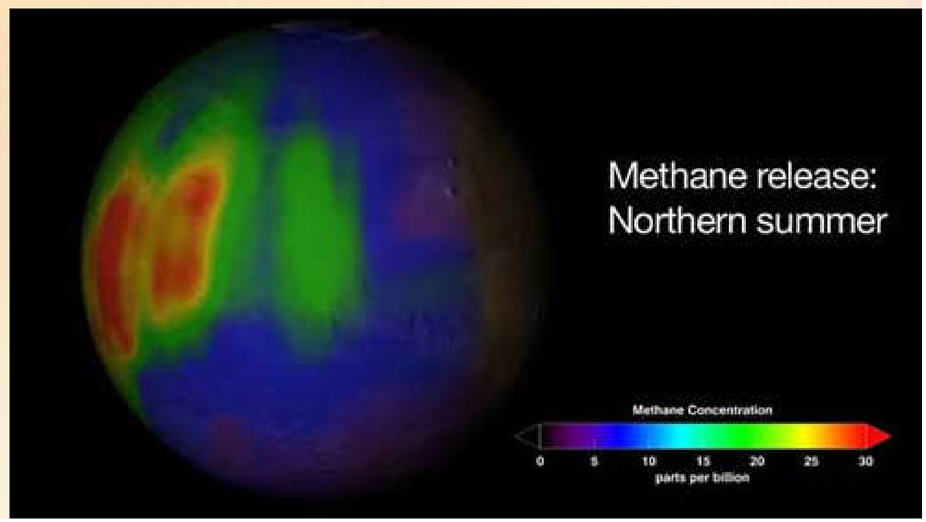


MSL landing sites and methane hot spots



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)

From Mumma et al.



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

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 CH_4 to C_2H_6 and C3 and C4 compounds
- δH vs. δ^{13}C in methane, ethane, and C3 and C4 compounds
- temporal variations of δH vs. δ^{13}C in methane
- ratio of H_2 to CH_4
- CH_4/C_2+ vs. δ^{13}C in methane

SAM could utilize

- $^{13}C/^{12}C$ and D/H measurement in methane (if methane present in sufficient abundance)
- correlation of $^{13}C/^{12}C$ in methane and D/H measurement in H_2O
- ratio of methane to heavier hydrocarbons (best measurements for C4 and heavier compounds)
- combustion of refractory carbon to possibly reveal $^{13}C/^{12}C$ 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