MSL Observations of Mars Methane

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Committee on Astrobiology and Planetary Science (CAPS)

Space Sciences Board

Beckman Center, Irvine CA

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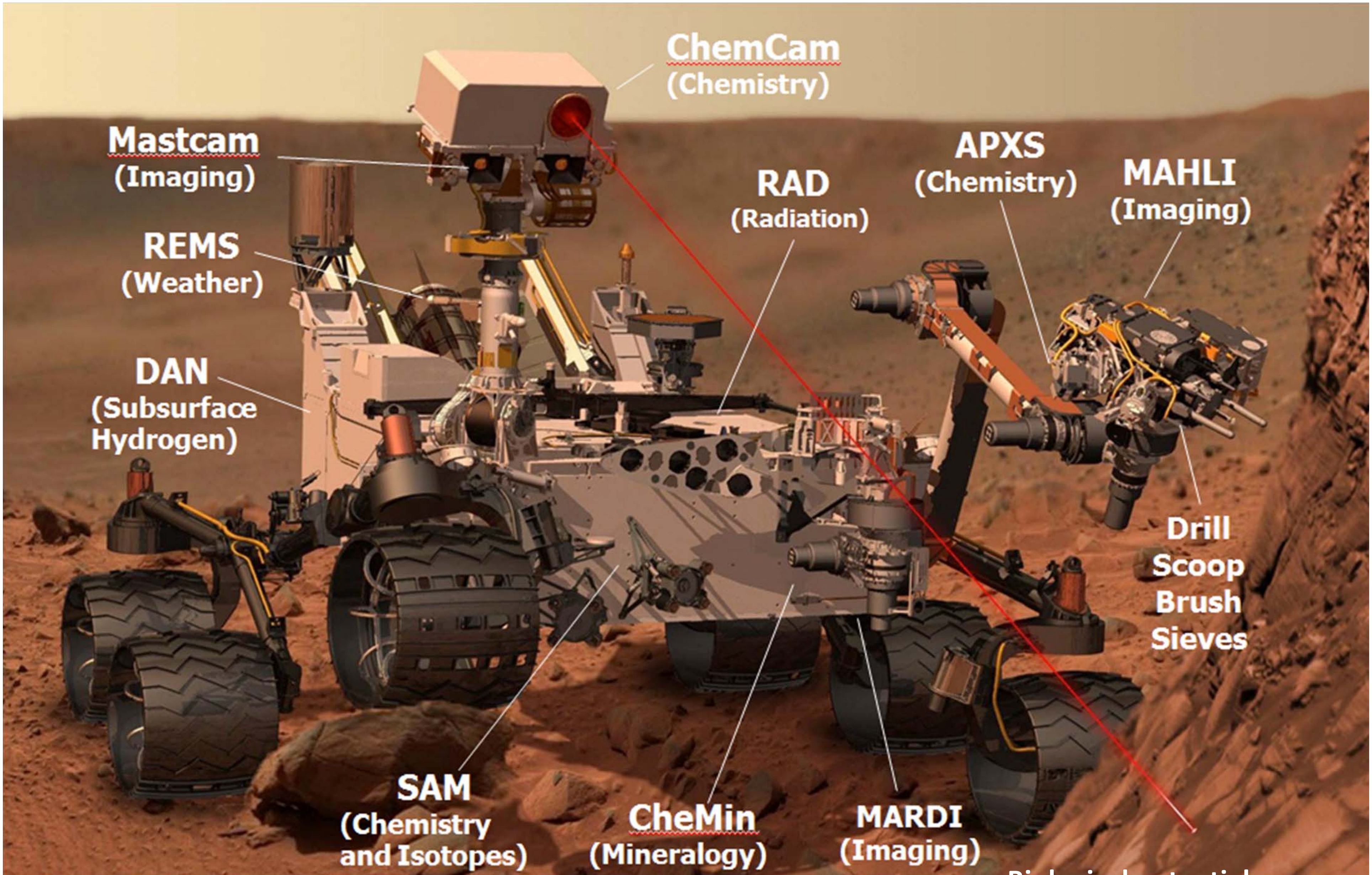


CURIOSITY

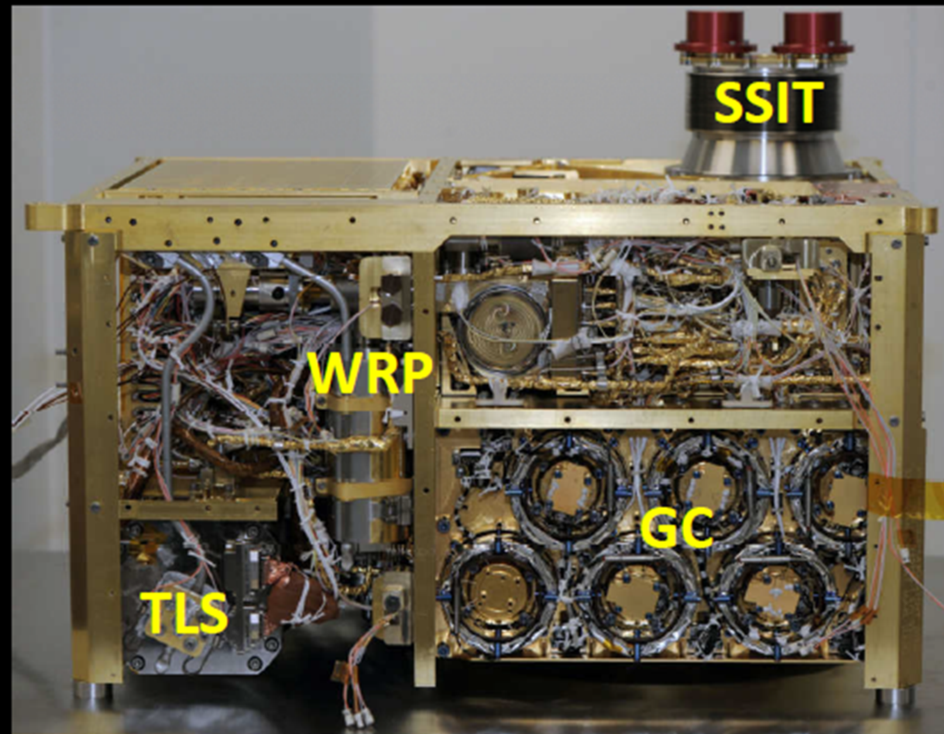
Curiosity's Science Payload

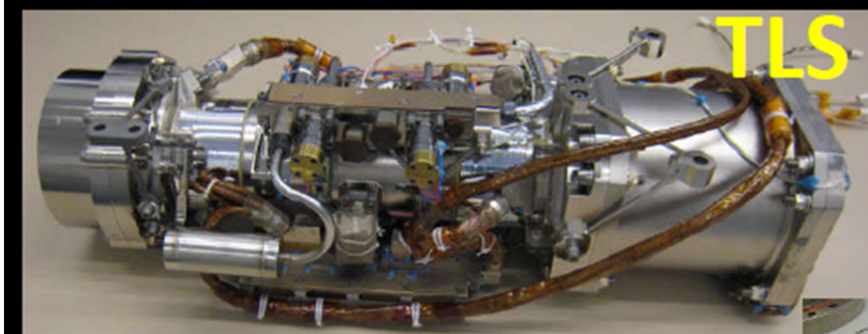
- Biological potential
- Geology and geochemistry
- Role of water
- Surface radiation

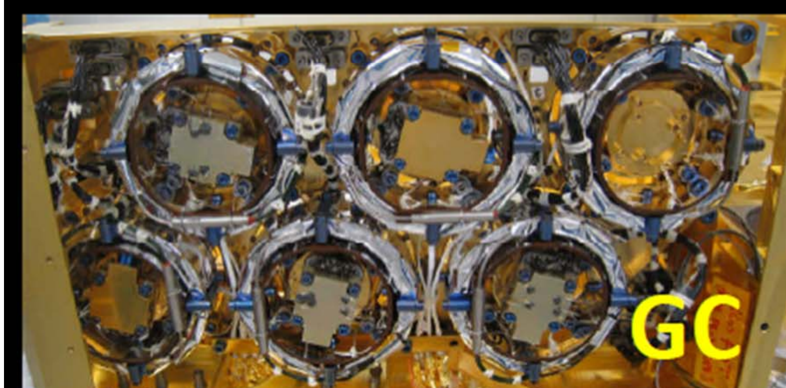
SAM Instrument Suite

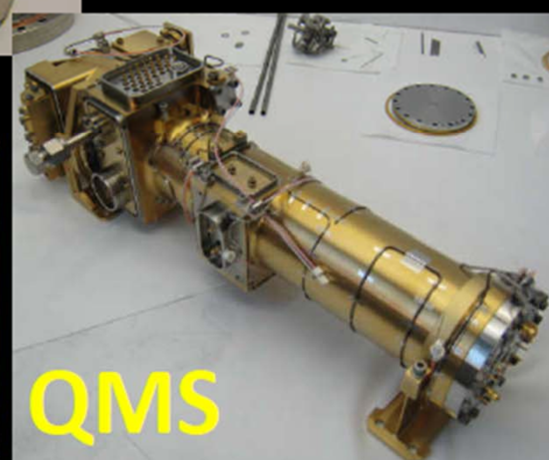
SAM Suite Instruments and Major Subsystems

- Quadrupole Mass Spectrometer
- 6-column Gas Chromatograph
- 2-channel Tunable Laser Spectrometer
- Gas Processing System
- Sample Manipulation System









SAM is the most sophisticated planetary instrument suite ever flown

- 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 at 2400 psi
- 4 heat pipes
- Electronics stack
- ~ 600 m of harness wire
- Solid Sample Inlet Tubes
- Thermal shields

SAM PI is **Paul Mahaffy**, NASA GSFC
GC lead is **Michel Cabane**, Univ. Paris
TLS lead is **Chris Webster**, JPL

Consumables: WRP to 7 yrs, 74 cups reusable, traps to 25 yrs, He to 9 yrs

SAM Experiment Sequences & Surface Operations- Paul Mahaffy

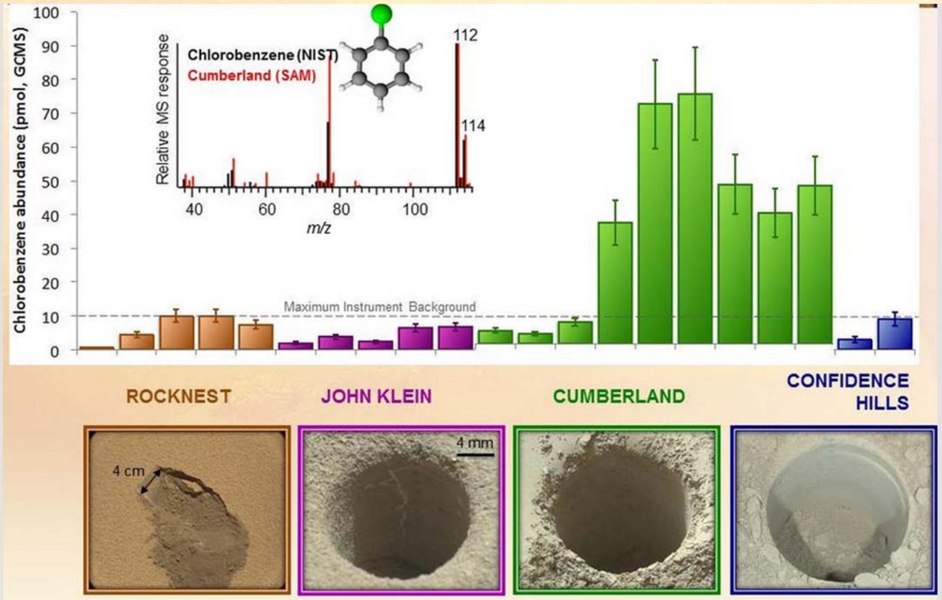
Experiment	Inst. Used		Frequency
1. Pyrolysis with Preconditioning	QMS, GC, TLS		Science driven
2. Derivatization	QMS, GC		Science driven
3. Solid Sample Calibration	QMS, GC, TLS		6, 12, and 18 months after landing, or as needed
4. Atmospheric Sampling (direct)	QMS, TLS		Once per month
5. Atmospheric Sampling with Enrichment (using traps)	QMS, TLS		Once per month
6. Atmospheric Methane Enrichment	TLS		Once per month; more if science driven
7. Atmospheric Noble Gas Enrichment	QMS		Once prior to 1st pyrolysis +5 more times during mission
8. Combustion (Pyrolysis with preconditioning and oxidation	QMS, TLS		Must be done in 1st 6 mos
9. Calibration Gas Sampling	QMS, TLS, GC		Once a month

Calibration expts — Solid Sample expts — Gas expts

SAM surface operations are primarily to be conducted at night during sols dedicated to the analytical suite (both SAM and CheMin).

SAM has produced high-impact science

1. Detection of organics (chlorobenzene) from a drilled mudstone – *Freissinet et al., Eigenbrode et al.*
2. Detection of atmospheric methane at low background levels and in an episodic release ten times this value- *Webster et al.*
3. Age-dating of rocks in Gale crater and the determination of surface exposure times: -*Farley et al.*
   - K-Ar age of 4.21 ± 0.35 B years for rocks in crater rim
   - Cosmic-ray–produced ^{3}He, ^{21}Ne, and ^{36}Ar yield surface exposure ages of 78 ± 30 Myrs



SAM has produced high-impact science

4. The D/H measurement in Hesperian clay mudstone reveals the history of water loss on Mars- *Mahaffy et al.*
   – Low D/H of 3xSMOW in bound OH in clays formed 2.9-3.5 Gya (Hesperian) shows that considerable water was lost both before and after the lakebed formed.
   – GEL at Cumberland mudstone formation ~150m compared to ~50m today.

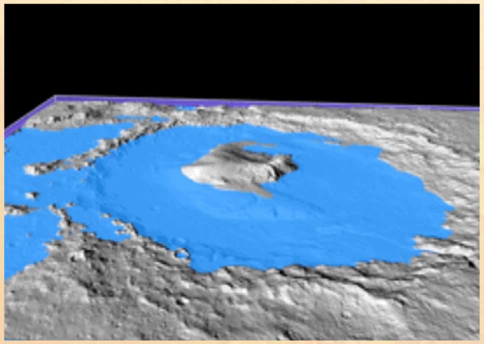


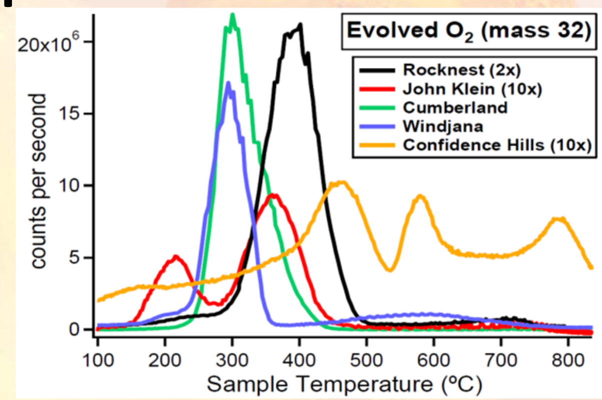
Table 1. Carbon dioxide isotope ratios ‰ ± 2 SEM (standard error of the mean). *, not measured.

Measurement	$\delta^{13}C$	$\delta^{18}O$	$\delta^{17}O$	$\delta^{13}C^{18}O$
SAM-TLS	46 ± 4	48 ± 5	24 ± 5	109 ± 31
SAM-QMS (*3*)	45 ± 12	*	*	*
Phoenix lander (*12*)	−2.5 ± 4.3	31.0 ± 5.7	*	*
Viking Neutral Mass Spectrometer (*11*)	23 ± 43	7 ± 44	*	*
SNC meteorites (*8, 12, 32*)	36 ± 10	3.9–5.4 ± 0.1	~0.53* $\delta^{18}O$	~ $\delta^{13}C$+ $\delta^{18}O$
ALH84001 meteoritic carbonate range (*30, 31*)	27 to 64	−9 to 26	~0.53* $\delta^{18}O$	~ $\delta^{13}C$+ $\delta^{18}O$
ALH84001 meteoritic carbonate mean value (*31*)	46 ± 8	4.6 ± 1.2	*	*

5. Isotopic measurements in noble gases, C, H, N, and O demonstrate atmospheric loss- *Mahaffy et al., Webster et al., Atreya et al., Wong et al.*
   - $^{13}CO_2$ measurements rewrite the chapter on atmospheric evolution whereby escape of carbon via CO photodissociation and sputtering enriches ^{13}C in the Martian atmosphere, partially compensated by moderate carbonate precipitation.
     - Hu, Kass, Ehlmann, Yung 2015.

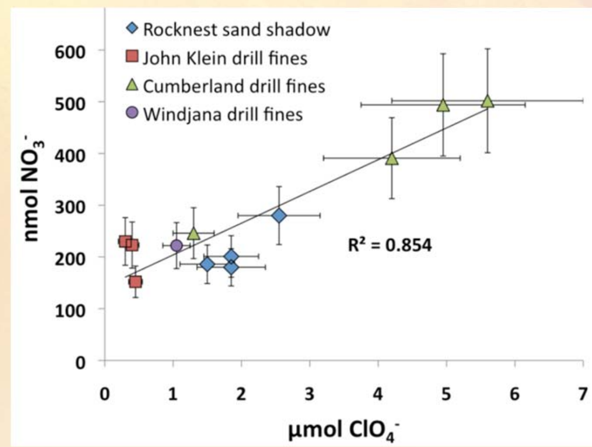
SAM has produced high-impact science

6. The detection of oxychlorine species evolved from rock samples (SAM evolved O_2 correlates with APXS chlorine) ties to perchlorate existence – *Ming et al., Archer et al., Leshin et al.*

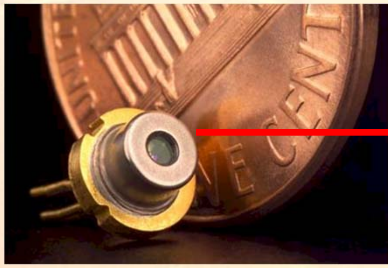


7. The measurement of isotopic ratios in Xe isotopes that reveal the very earliest period of massive atmospheric loss- *Conrad et al.*

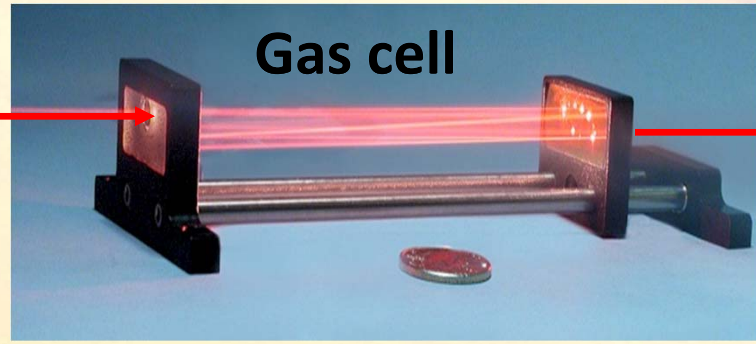
8. Detection of nitrates- Very low ratio of nitrate/perchlorate implies nitrogen fixation from impacts long ago before escape and without return to atmosphere, and dominance of continued perchlorate production *-Stern et al.*

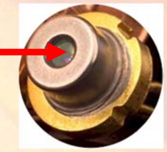


TLS – Tunable Laser Absorption Spectroscopy

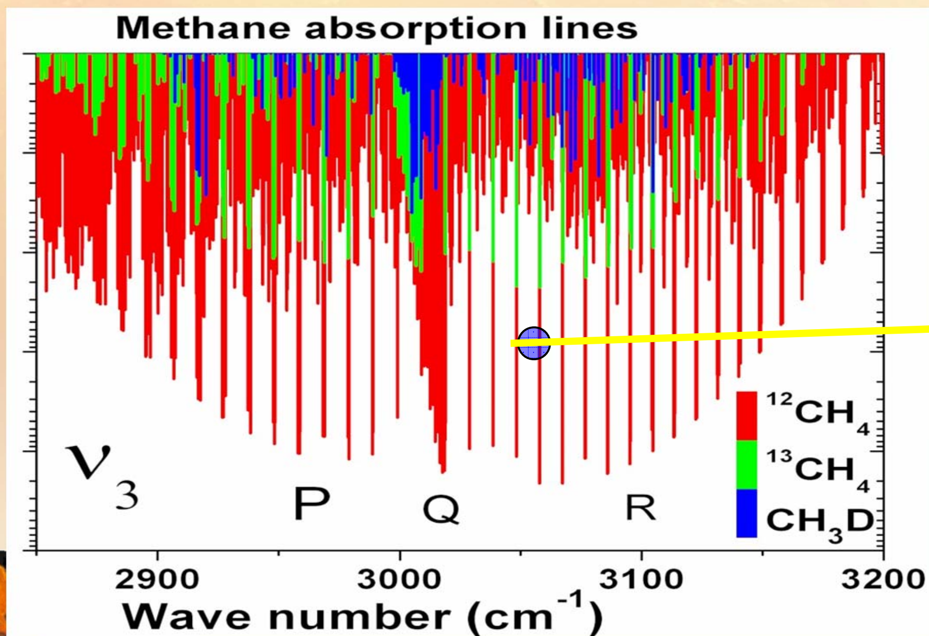


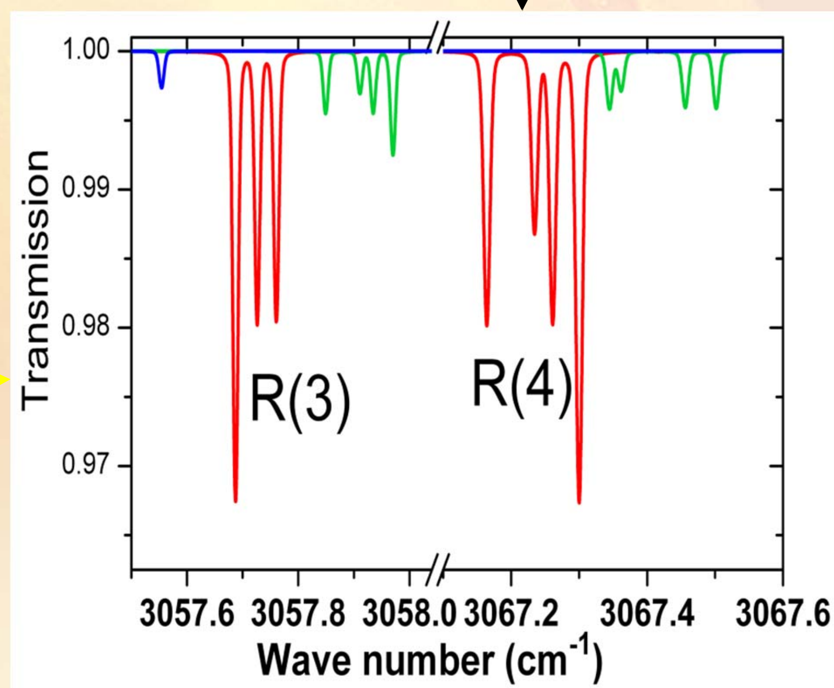
Tunable laser 1-12 µm



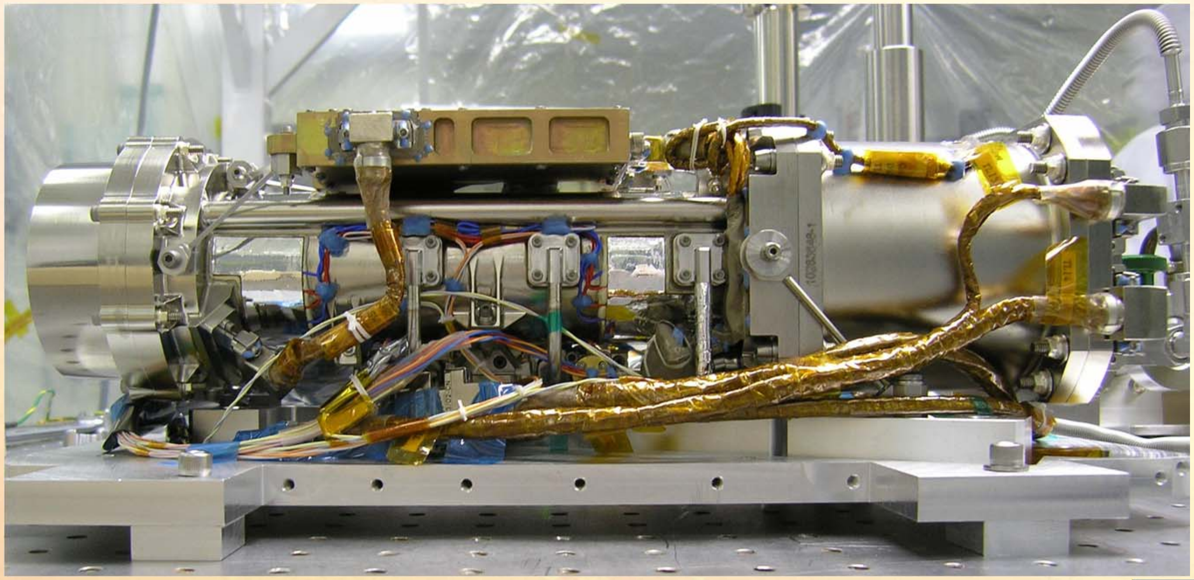


Detector





Tunable Laser Spectrometer (TLS)



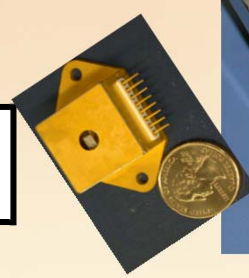
Mass = 3.3 kg

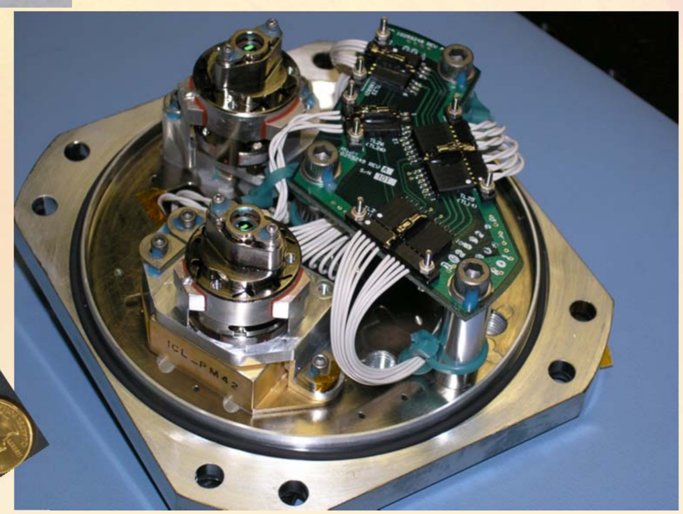
Near-IR TDL from Nanoplus, Germany

2.78 µm

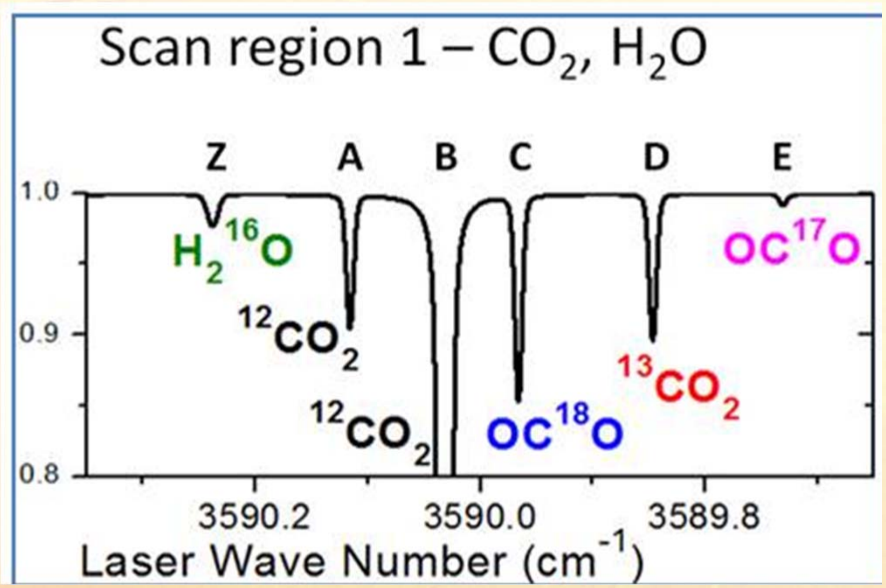
IC laser from MDL-JPL

3.27 µm

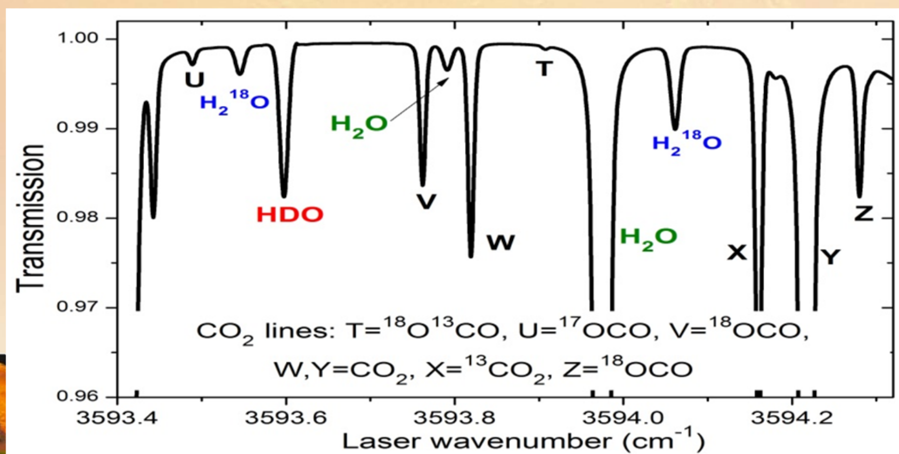


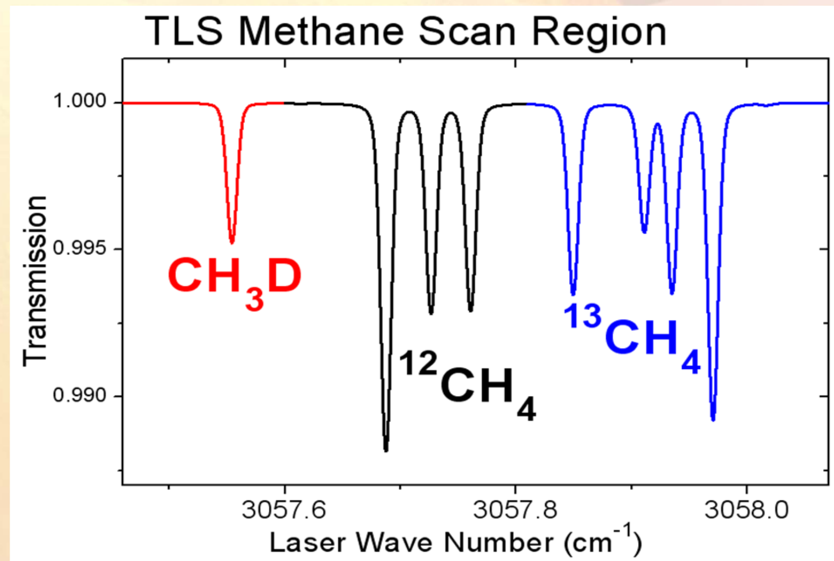


TLS Spectral Regions

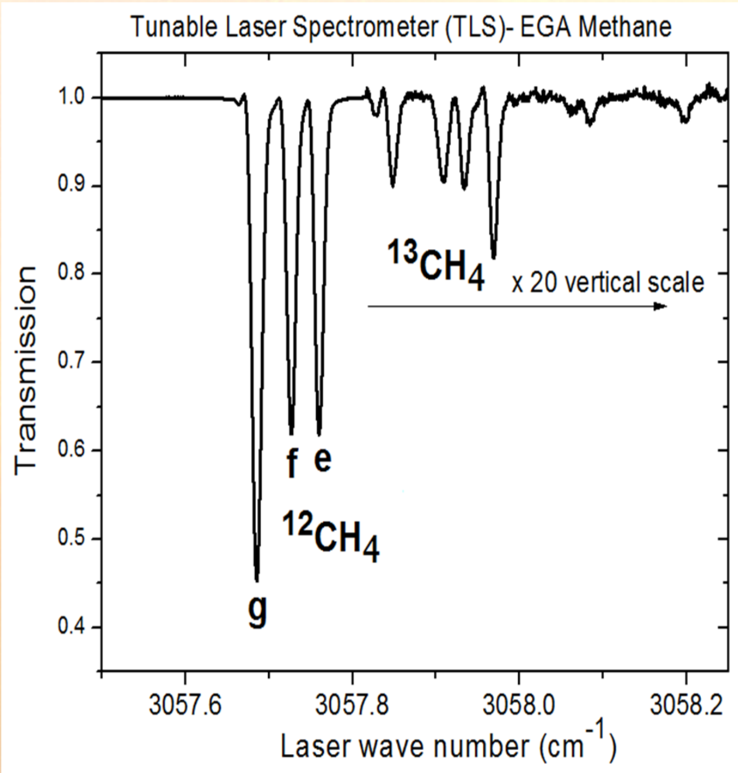


Scan region 2 – H_2O, CO_2

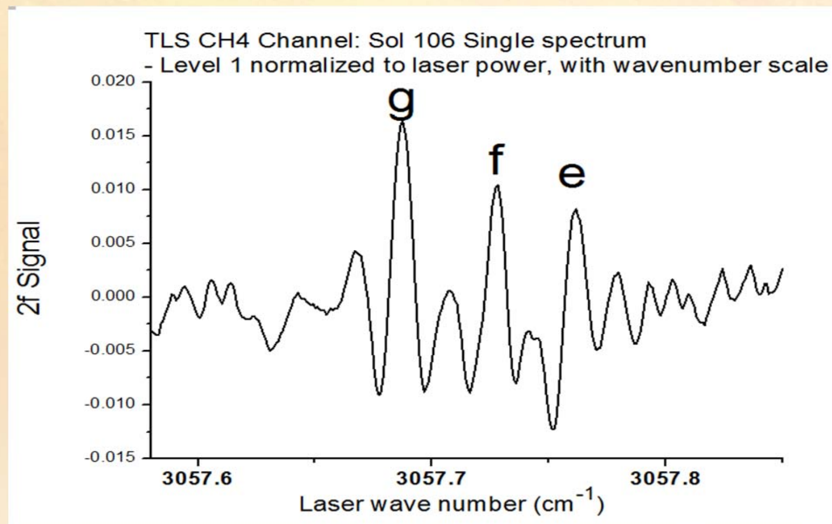




Observed TLS CH_4 Spectra

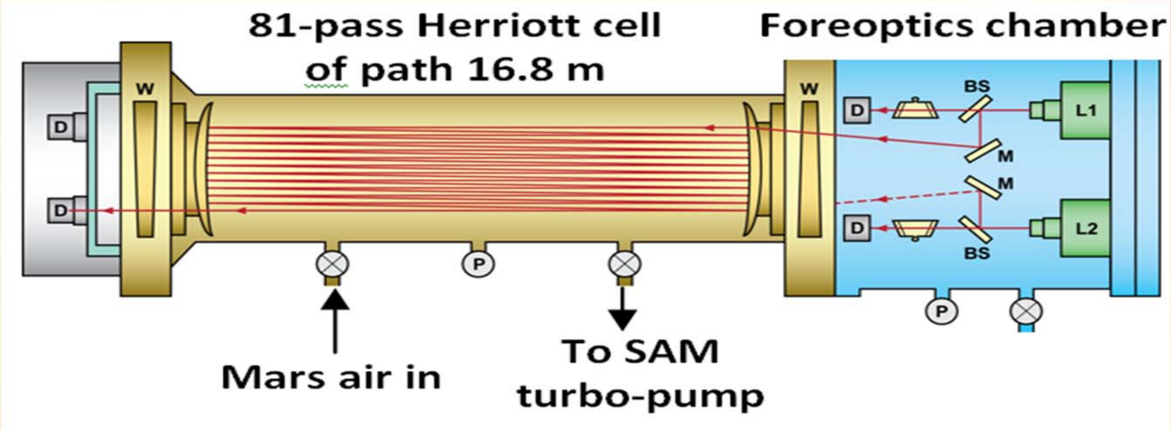


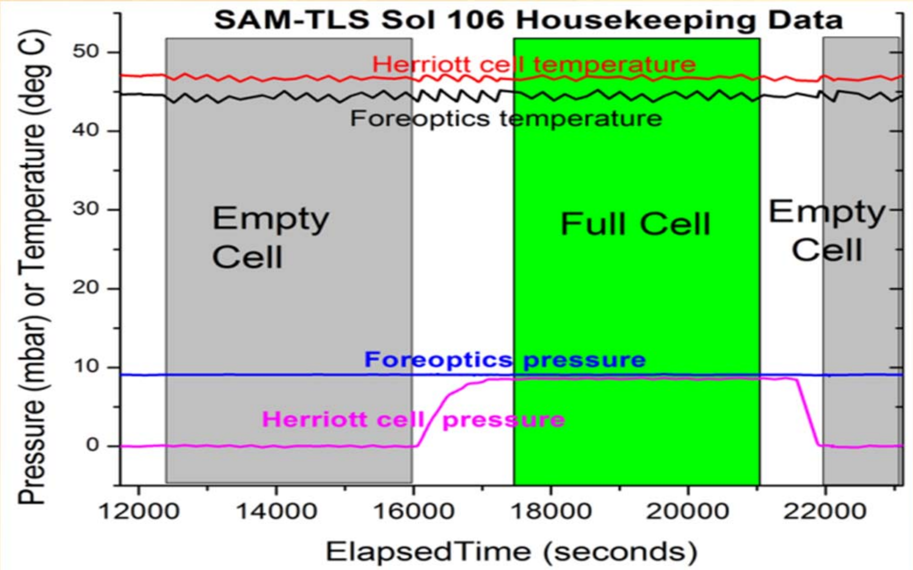
- Atmospheric measurements are interleaved between EGA experiments that show high (~100 ppmv) methane
  - Proves that our scan region is robust
- Atmospheric methane measurements have very low SNR spectra and require second-harmonic 2f detection



TLS-SAM Methane Search

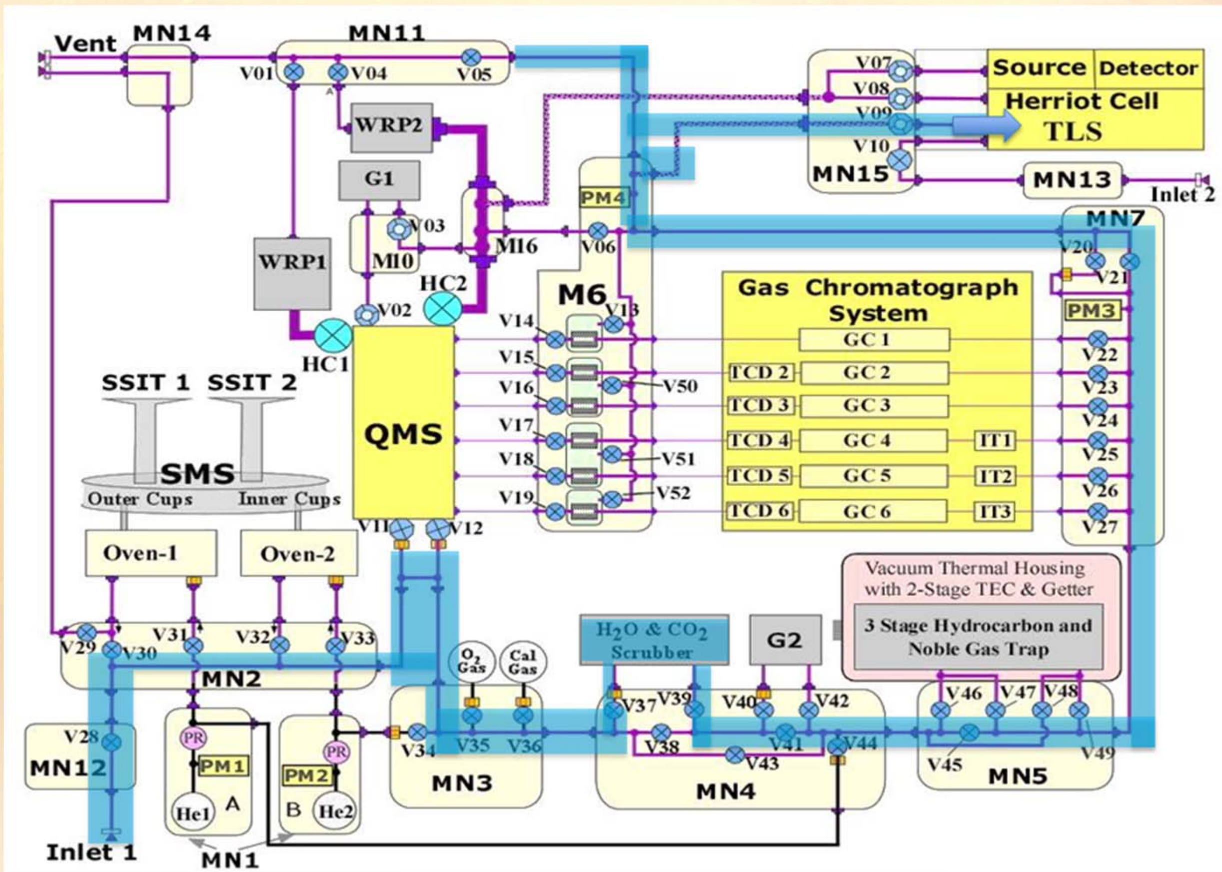
- Fore-optics chamber contains residual terrestrial air
- Use “difference method” comparing full sample cell to empty sample cell



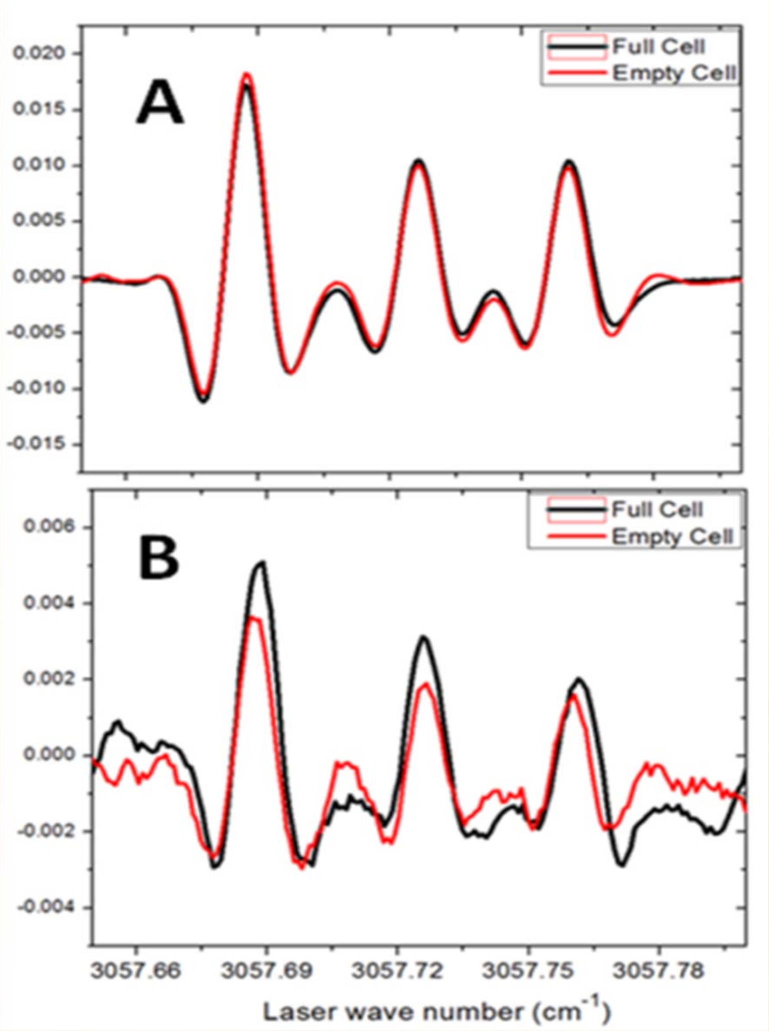


SAM Methane Enrichment

- Preconditioning of scrubbers: Heat to >200 ^{o}C for ~1hr, keep lines at 50^{o}C.
- CO_2 scrubber is Linde 13X molecular sieve material.
- Inlet 1 allows Mars atmosphere to pass slowly over scrubbers until TLS cell is at 90% of Mars ambient (~7 mbar) or 2 hrs have gone by.
- Enrichment factor is 23 ± 2 from Test Bed runs.



TLS-SAM Spectra



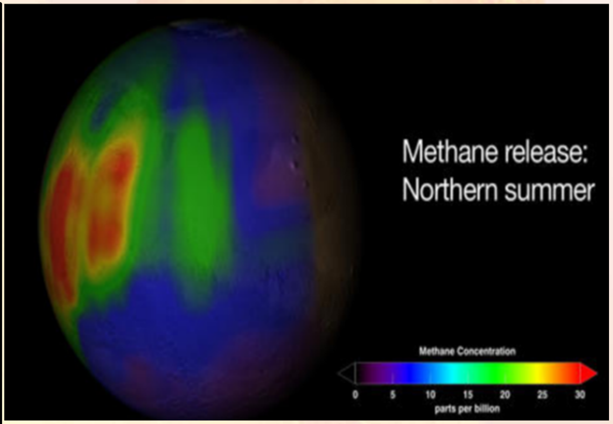
Visual comparison between full and empty cell average spectra:

A. "Low methane" from Sols 79, 81, 106, 292, 313 and 684;

B. "High methane" from Sol 474 only

Mars Methane

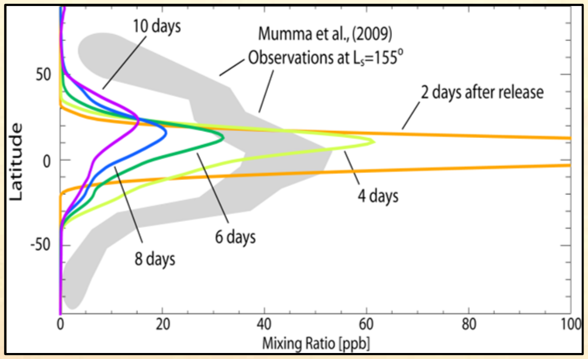
• PFS on MEX (Formisano et al. 2004) reported a global abundance of 10 ±5 ppbv (later updated to 15 ppbv) in localized sources with a summer max of ~45 ppbv in the north polar region;
• CFHT observations of 2003 (Mumma et al. 2009) reported plumes from discrete sources with a summer max of ~45 ppbv;
• TES on MRO (Fonti and Marzo, 2010) reported intermittent localized amounts between 5 to 60 ppbv;

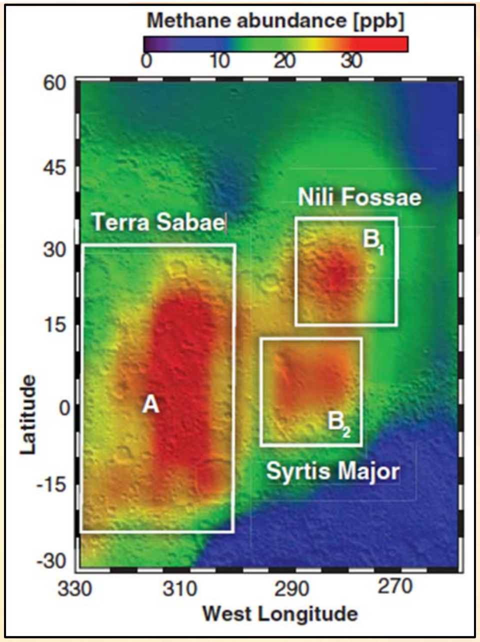


The observed spatial and temporal distribution of Mars methane has defied explanation with known chemistry and photochemical lifetime.

Puzzlement over Observations

- Sharp gradients for a long-lived (300 yr) tracer!
- Mischna et al. 2011: Plume would have to be less than 6 days old!
- Need steady release and fast decay.



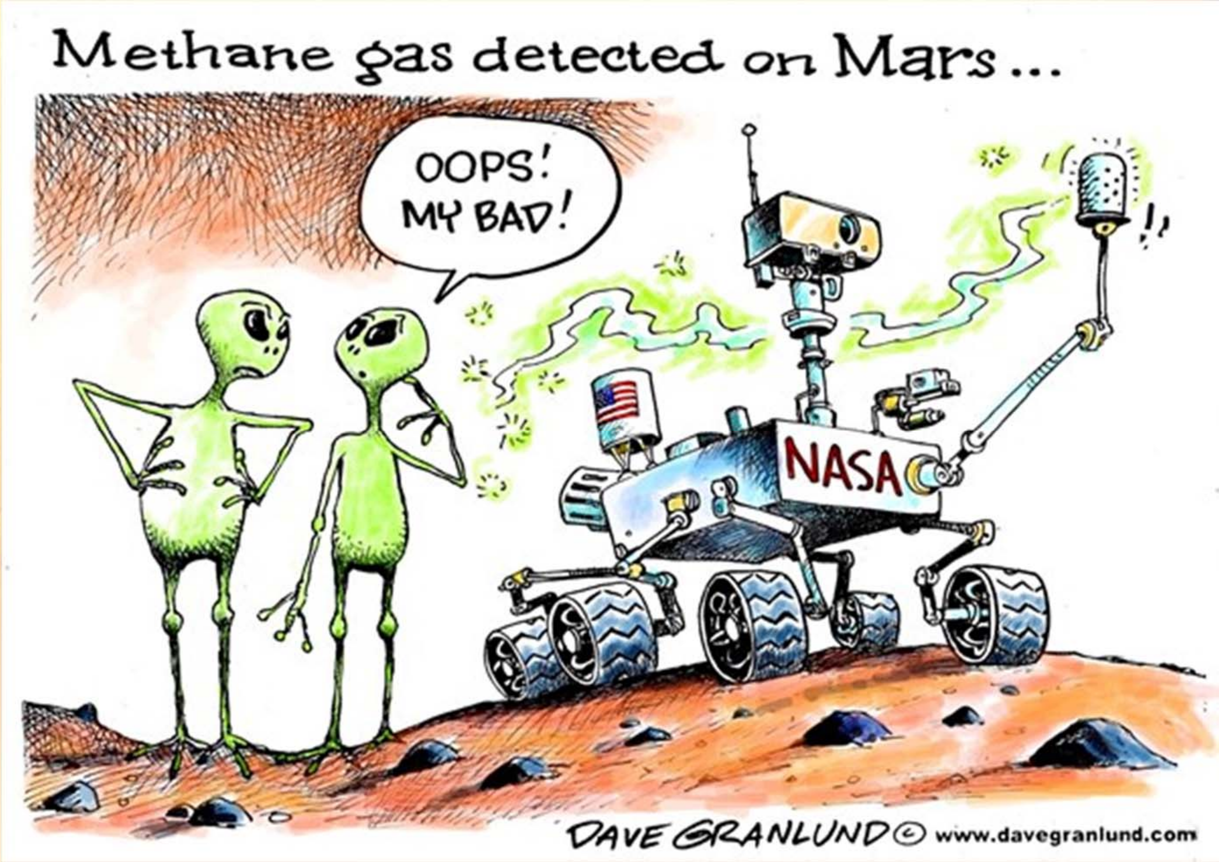


- LeFevre and Forget: Need 200 day lifetime and fast destruction!

Zahnle et al. 2011:

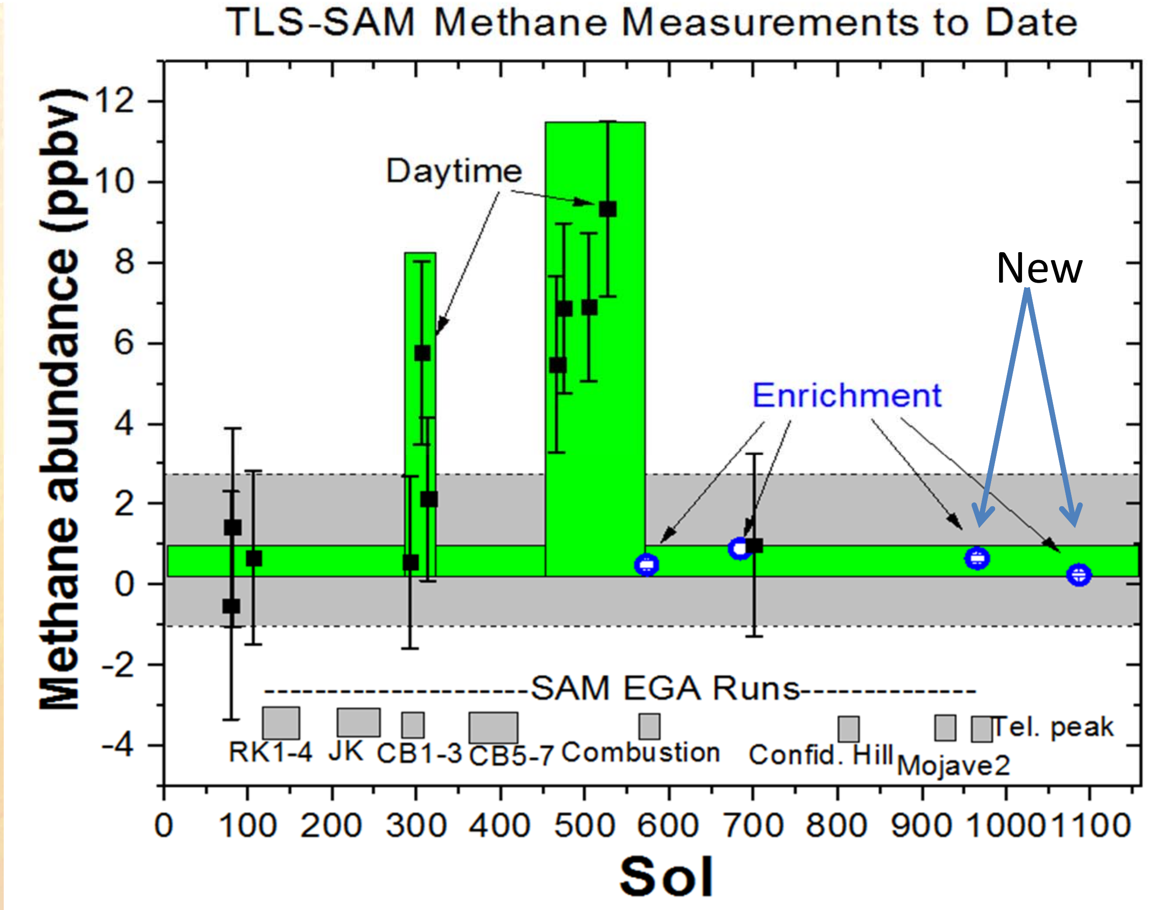
- Mumma observations of R0 and R1 in redshift avoid terrestrial isotopic overlap, but report only an upper limit of 3 ppbv.
- No known mechanism for destroying CH_4 chemically on Mars. But if so, CH_4 oxidation would deplete the O_2 in Mars's atmosphere in <10,000 years unless balanced by an equally large unknown source of oxidizing power.

Mars methane – what TLS-SAM observes from the Curiosity rover



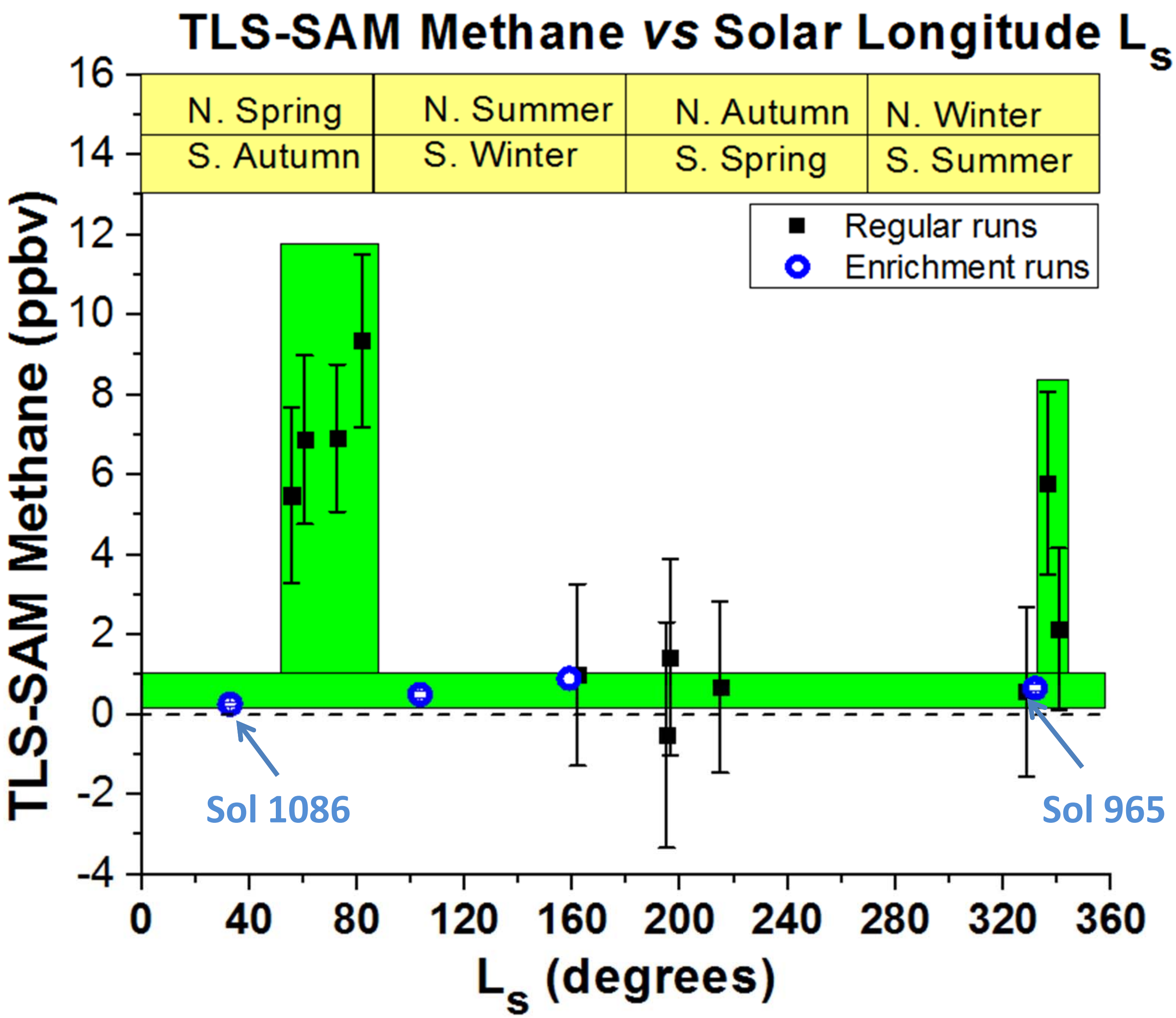
TLS-SAM Methane Measurements

"Mars Methane Detection and Variability at Gale Crater", Webster et al., *Science*, **347**, 415-417 (2015).

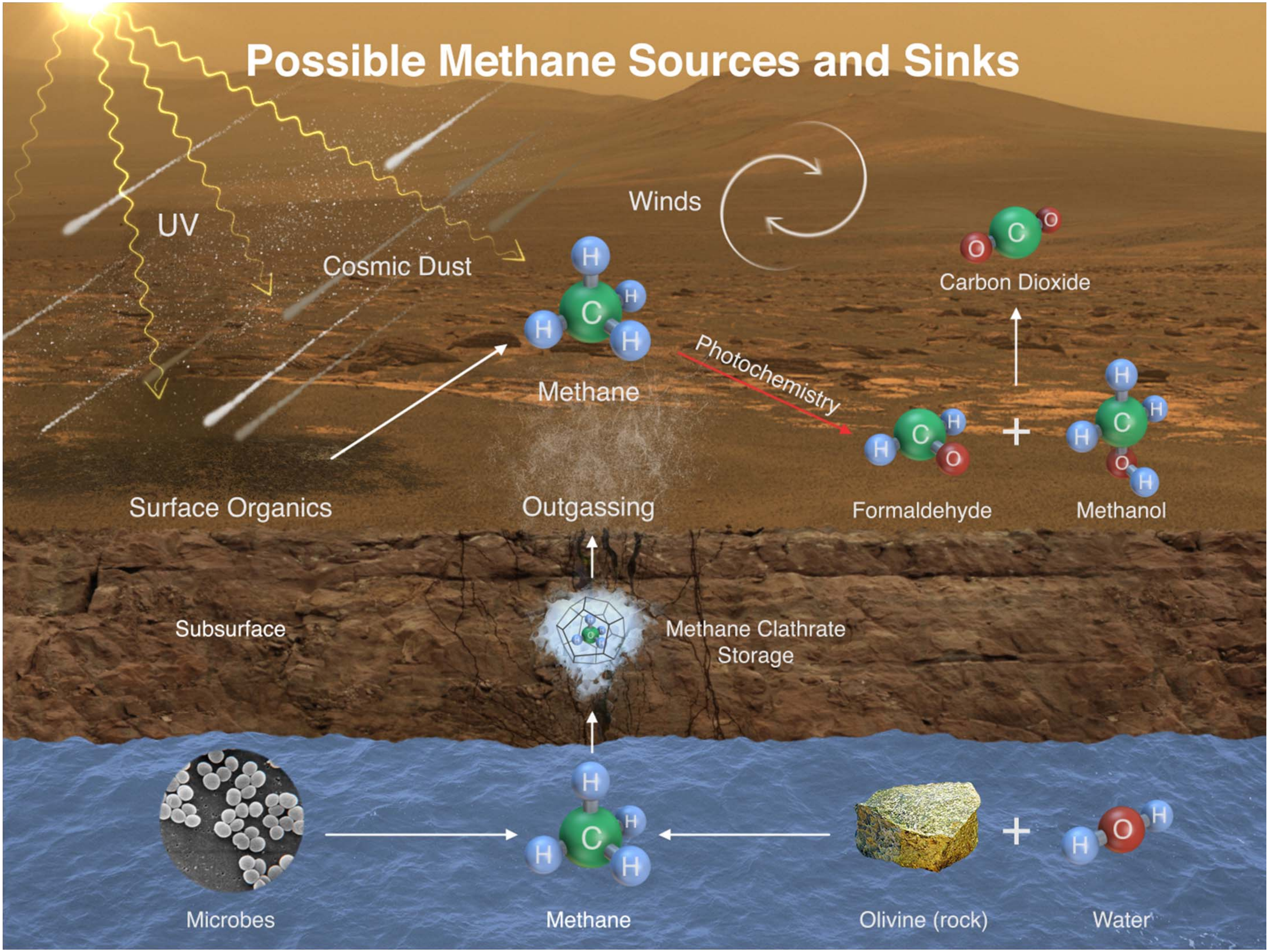


Science **paper 2015:**

"Low CH_4" (enrichment):	**= 0.69 ±0.25 (95% CI) ppbv**
"High CH_4" (regular):	**= 7.2 ±2.1 (95% CI) ppbv**



TLS-SAM Methane vs Solar Longitude Ls
N. Spring
S. Autumn
N. Summer
S. Winter
N. Autumn
S. Spring
N. Winter
S. Summer
Regular runs
Enrichment runs
TLS-SAM Methane (ppbv)
16
14
12
10
8
6
4
2
0
-2
-4
0
40
80
120
160
200
240
280
320
360
Ls (degrees)
Sol 1086
Sol 965



Possible Methane Sources and Sinks
UV
Cosmic Dust
Winds
H
C
H
H
H
Methane
Carbon Dioxide
O
C
O
Photochemistry
Formaldehyde
Methanol
Surface Organics
Outgassing
Subsurface
Methane Clathrate
Storage
Microbes
Methane
Olivine (rock)
Water

Methane sources to consider

- Unknown photochemical processes in the atmosphere that may involve dust (heterogeneous chemistry)
- Geological production such as serpentinization of olivine
- UV degradation of IDP’s, meteoritically-delivered organics
- Release from gas trapped in subsurface clathrates
- Release from regolith-adsorbed gas
- Erosion of basalt with methane inclusions
- Geothermal production
- Production from sub-surface methanogens

Hu…..Yung group (2015):

- Release following deliquescence of perchlorate salts
- Microorganism release of methane from organic decay in solution
- Deep subsurface aquifers that produce bursts of methane as a result of freezing and thawing of the permafrost as in the Arctic

Methane sinks

- Photochemical processes (Krashnopolsky et al., 2004) UV +OH oxidation
- Electrical discharges in dust devils (Farrell et al., 2006)
- Reactions with oxidants in the soil (Atreya et al., 2006).
- Wind erosion of quartz grains - Methane is removed by reactions with abraded silicates, which leads to covalent $\equiv Si\text{-}CH_3$ bonds and thus an enrichment of the soil with reduced carbon (Jensen et al., 2014).- could explain the fast disappearance of methane.

TLS-SAM Low Methane Background

A contribution from a variety of sources?

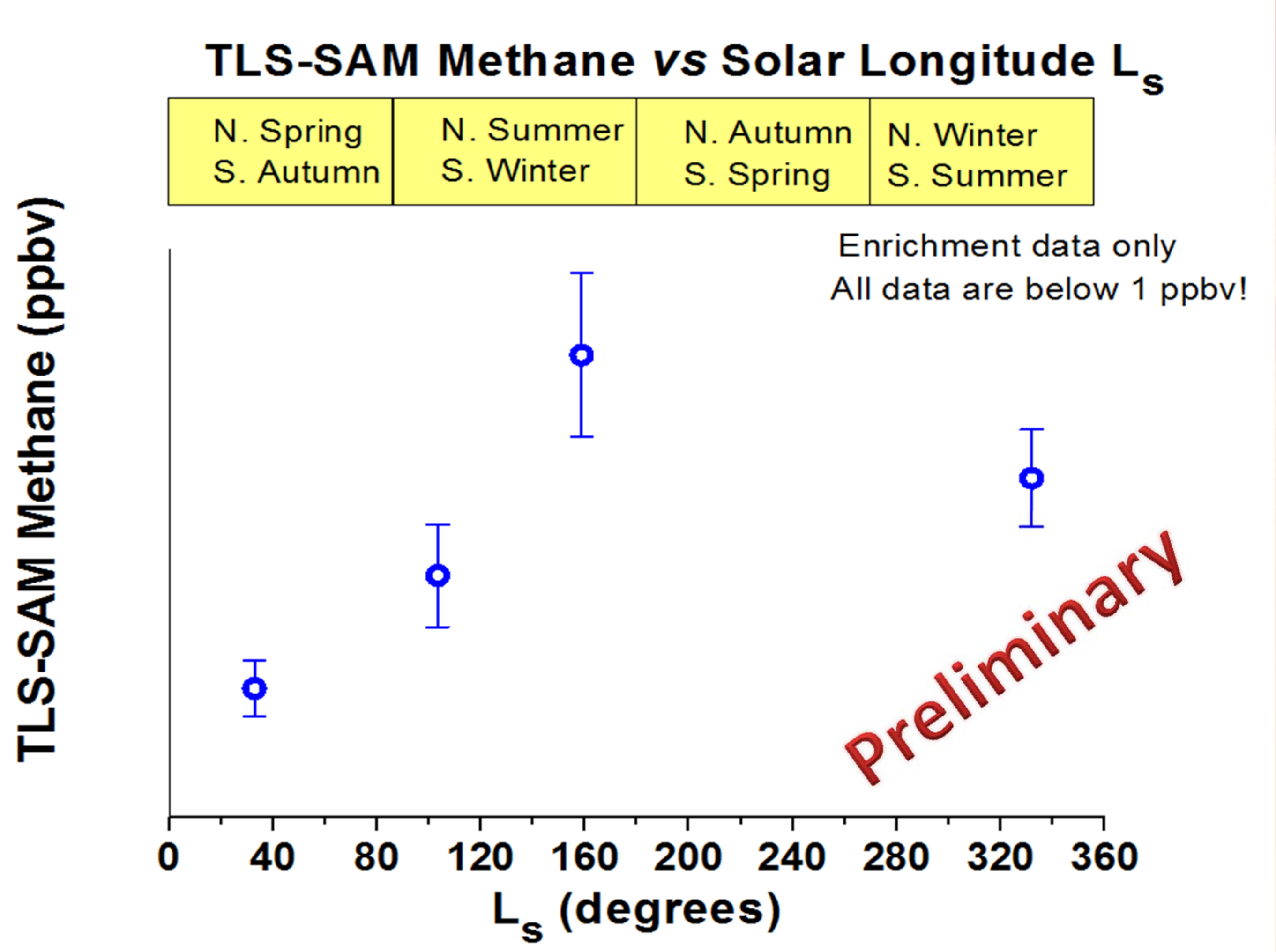
Consider UV degradation of surface material

- Surface meteoric material: micrometeorites from accreted IDP, and carbonaceous chondrites containing few wt% organic matter;
- Accreted IDP's deliver 90% of organic C with average C content of 10%- a carbon-limited (not UV) process.

- UV/CH_4 model of Schuerger et al. (2012) predicts
  - Over geological time, a present day 2.2 ppbv methane for 20% conversion efficiencies of 10 wt% C material
  - Very small diurnal/seasonal changes (daily input is 0.02 pptv)
- TLS-SAM background level is ~3 times lower than model prediction of ~2.2 ppbv
  - Therefore infall amount, C conversion efficiency or organic content is overestimated by factor of ~3.

TLS-SAM Low Methane Background

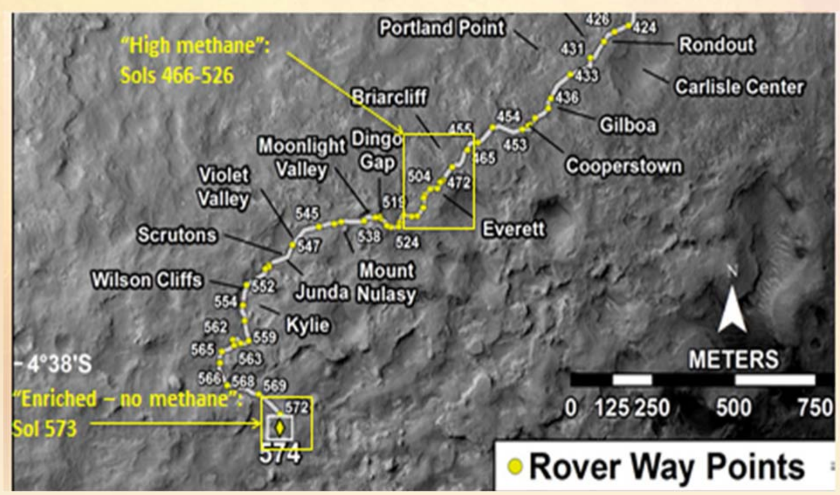
- SAM methane enrichment opens new window into background methane variation!
- Investigating correlations with REMS UV, dust opacity, etc.



TLS-SAM High Methane

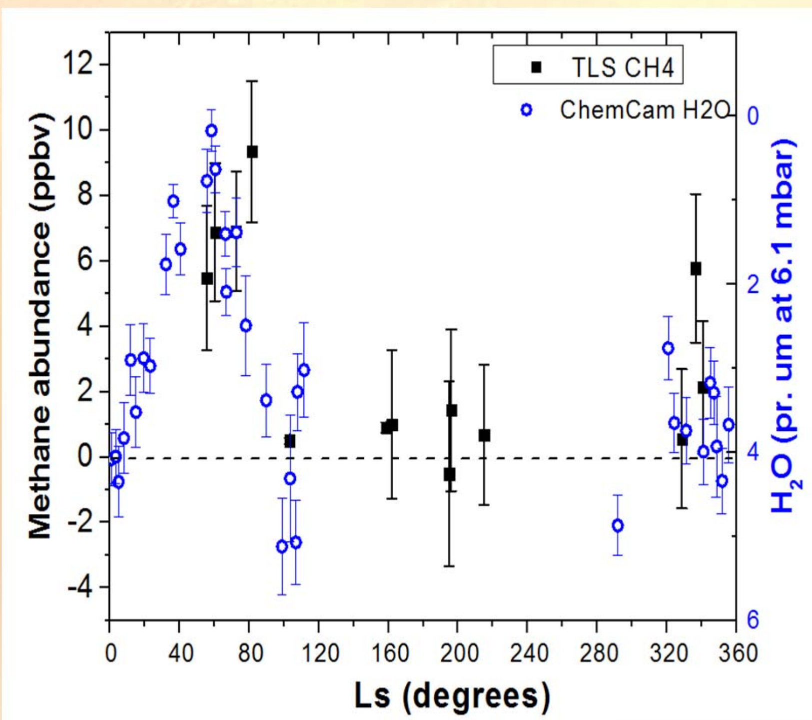
- High methane of ~7 ppbv is within range of UV/CH_4 model predictions if transported from region of airburst/bolide, but MRO shows no measurable impacts at Gale Crater since landing.
- No correlations with pressure, surface/air temperature, opacity, UV flux, in situ H_2O, surface mineralogy/composition.
- Intriguing anti-correlations with *column* water, oxygen.
- Consistent with a small local source producing a temporal (not location) change.
- Wind fields and daytime

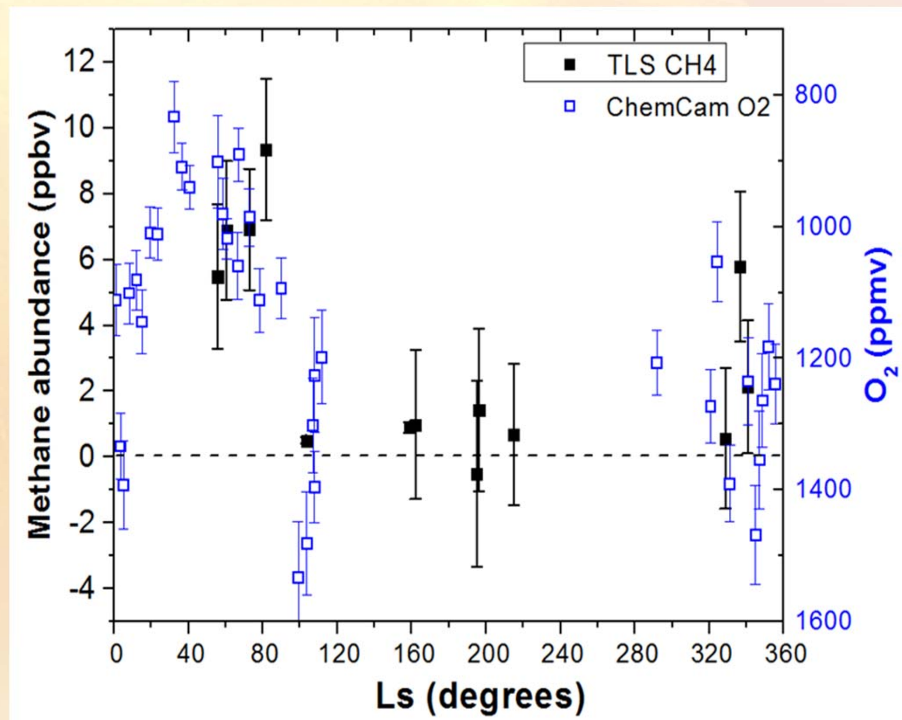
increase indicate source to the north



High Methane- Correlations?

- No clear correlation with ground/air temperature, relative humidity, dust/aerosol opacity, atmospheric pressure, radiation levels, inlet pointing
- Possible anti-correlation with column abundances of water, oxygen, but recent Sol 1086 data rule out correlation of high CH_4 with low O_2 unless time delay in effect.





Questions Considered

1. Does the Hcell contains residual gas left over from prior EGA runs that generated CH_4?
   - Cell is pumped to <0.007 mbar, so 10 ppmv CH4 in 10 mbar He could leave 7 ppbv for the first of 4 high results, but cell is first pumped out and again in between runs.
   - No EGA is done in between the 4 runs, and the second and third pump-outs would reduce this to negligible values, so hard to see why the 4 points remain identically high.
   - Also, several earlier measurements made after RN, JK are low, not high.
2. The CH_4 scans are often made after the CO_2-volume expansion. Is it possible that the volume expansion with heated areas produces CH_4 from the reaction of Mars atmosphere with MTBSTFA, and then we incompletely pump this out prior to the subsequent methane ingest?
   - This could be happening for the first high point only, and produce up to a few ppbv methane in the Hcell, but this would become part of the "empty cell" scans that then precede the methane scans, so would be subtracted from the ingest full cell result anyway. Also we'd see a difference in the before and after empty cell scans, which we don't.

Questions Considered

3. Is there is a coating (MTBSTFA or reaction products) inside the Hcell that emits CH_4 after reacting with Mars atmosphere? This coating could have built up over time, and was cleaned/removed by the combustion run leading to the lower CH_4 values in the subsequent (enriched plus hybrid) runs. The empty cell would not show CH_4 that would appear once Mars gas oxidants ingested.

4. Is there any correlation with wheel damage or terrain traversed?

5. Is the Curiosity Rover, instruments within, or the TLS foreoptics chamber producing a methane cloud around the Rover?

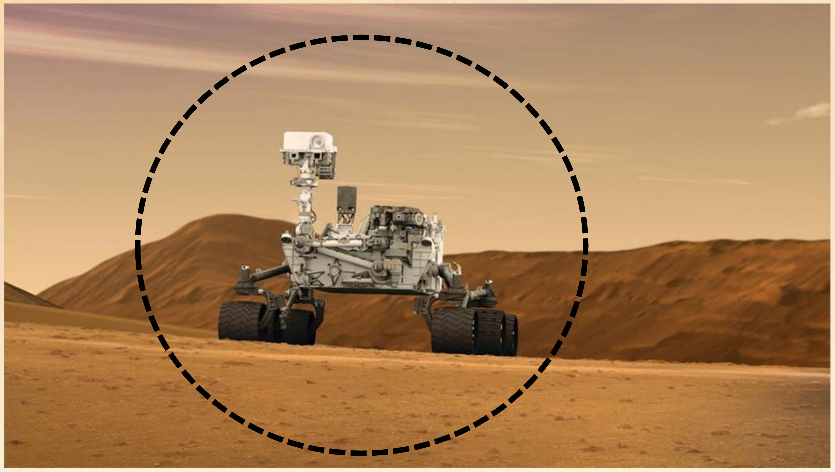
Coating Concern Ruled Out

- There is no evidence of a coating/film that formed in the TLS Hcell
  - Laser light levels show mirror reflectivity is unchanged within 12 ppm, and could accommodate a 10^{-3} monolayer at most
- The earlier CH_4 data do not show any increase after 15 EGA runs (RN, JK, CB1-3, BK's), with the high CH_4 occurring only after an additional 3 EGA runs (CB5-7).
- The TLS Hcell only occasionally sees the EGA experiment. TLS receives a "temperature cut" only ONCE per EGA run - not continuously - and this is a single 400 cc plug of mainly He at 10 mbar with EGA products, fed to TLS in minutes.
- It is difficult to identify atmospheric reactants and chemistry that would react with a methyl-propene-like film inside the Hcell to produce methane.
  - Eigenbrode lab study simulated deposition of pyrolysis products from MTBSTFA on the liner of the GC inlet (held at conditions similar to TLS inlet) and then exposed them to 30% H2O2 in water (at similar conditions expected for TLS) – no methane generated.

Methane source from Curiosity?

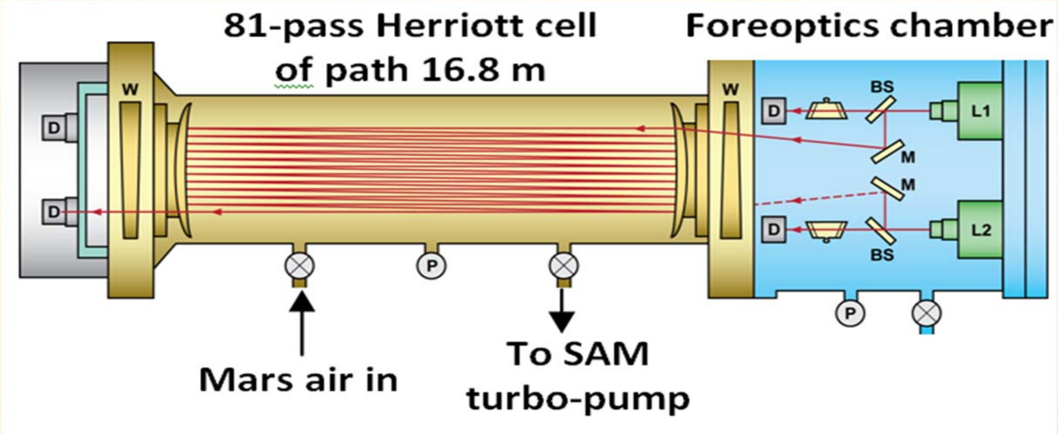
"Zahnle, who was also critical of the 2003 and 2004 methane reports, said that it wouldn't take much from the rover to lead scientists astray. After all, the rover contains within a chamber some methane at a concentration 1,000 times higher than the puff supposedly found in Mars' atmosphere. Curiosity's methane comes from Earth"
– Discovery News

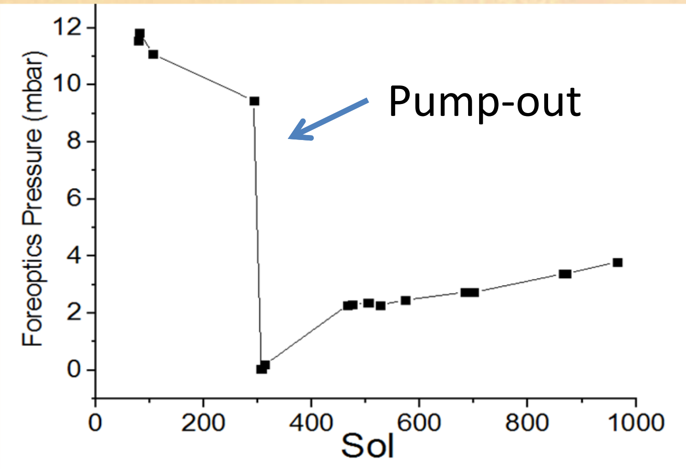
- TLS foreoptics chamber contains ~12 ppmv methane, or ~2 nanomoles CH_4, or ~10^{15} molecules.
- A 10-m diam sphere around the rover with 7 ppbv methane contains 1 micromole of methane, or ~10^{18} molecules.
- If surface winds are only ~1m/sec, sphere volume is replenished in 10 secs, so to sustain high methane for 2 months, would need a source of ~5 x 10^{23} molecules!
- Also, foreoptics chamber CH_4 content shows no evidence of loss over time.

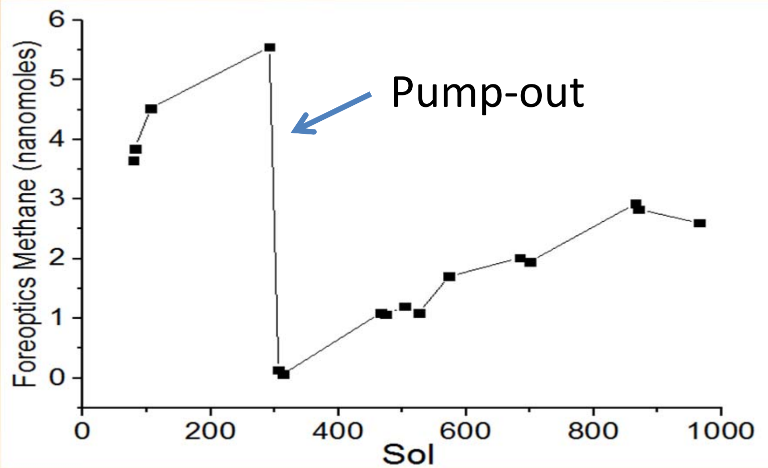


TLS Foreoptics Chamber Shows No Loss of Methane

- Foreoptics pressure, temperature are measured directly
- Foreopics methane is measured by internal detector, and empty (Herriott) cell values







TLS-SAM Methane Results

- The very low background level of methane could result from the UV degradation of surface organics, geology or biology, or their combination.
- The sudden spike in methane seen by the TLS indicates a release from either modern production or from storage of older methane in clathrates.
- The sudden rise in methane and the fact that it came back down quickly indicate the source was most likely relatively localized and small. Also, because our daytime values are somewhat higher, the wind field in and around Gale Crater indicates a northerly source.
- These observations of methane are strongly suggestive of a *currently active Mars*.

Measurements over next few months will determine if seasonal repetition !