Mars Atmospheric Chemistry and Methane Measurements

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[Contributions from SAM team (PI Paul Mahaffy) including Sushil Atreya]

KISS Study on

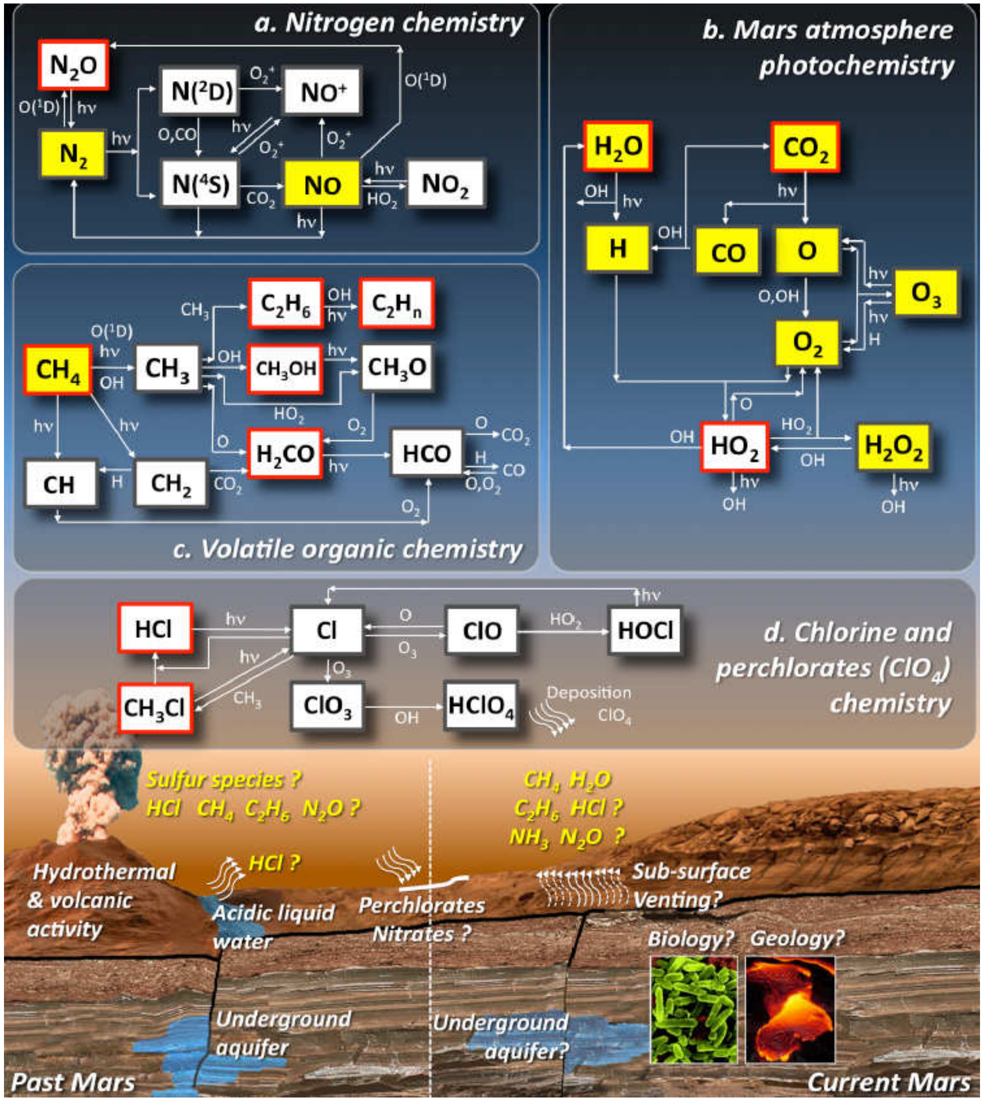
Methane On Mars

December 7th - 11th 2015

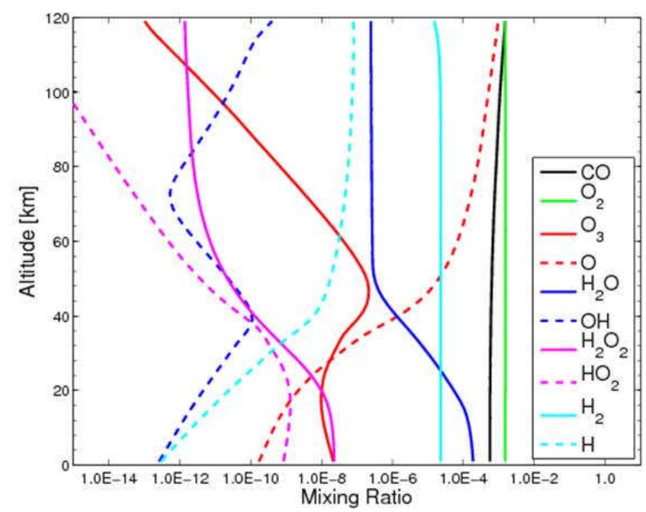
Mars Atmosphere Today

- Typical surface pressures 6-8 mbar, scale height 11 km, surface temperatures ~210 K
- Even when above freezing temperature, surface pressure too low for liquid water to form.
- Mainly CO_2 (96%), argon-40 (2%), nitrogen (2%), oxygen (0.15%) and CO (0.06%) – *Viking, SAM*
- Each pole in continuous darkness during winter, when up to 25% of CO_2 condenses at caps, subliming back into atmosphere in spring to produce seasonal cycles in pressure and composition.
- Local dust clouds, global dust storms every 2 years, cirrus, frost- MRO
- Thin ozone layer above Mars southern pole in winter
- Trace gases detected: H_2O, O_3, CH_4, H_2O_2,

Mars Atmospheric Photochemistry



- Villanueva et al. *Icarus*, 2012
- Atreya, Wong, Catling
- Yung et al.



Example of photochemical model output

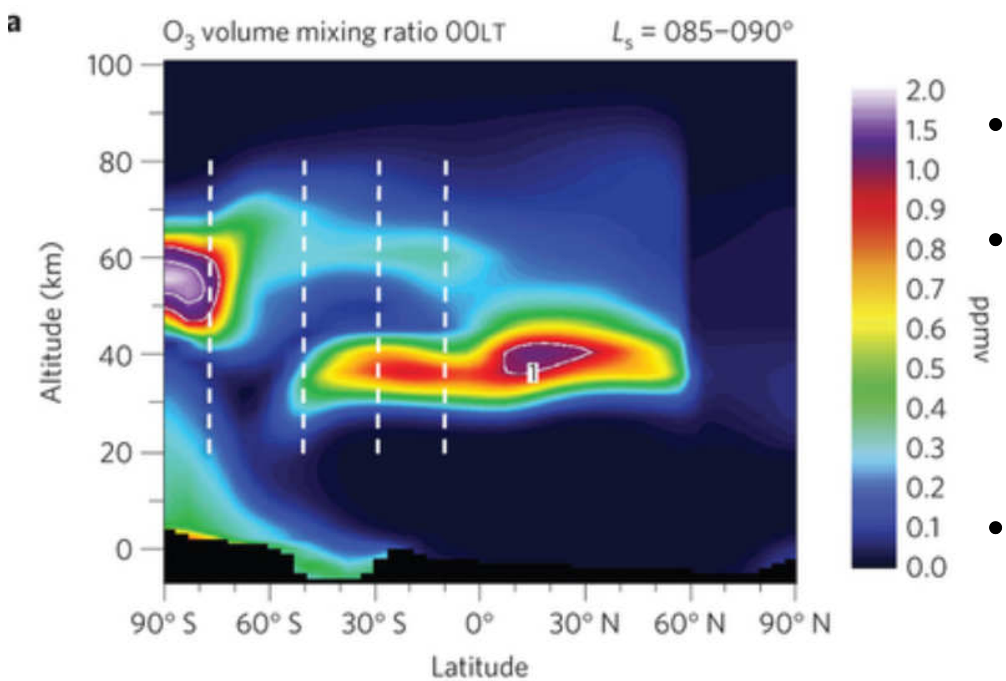
Sci-News.com

HOME ASTRONOMY SPACE EXPLORATION ARCHAEOLOGY PALEONTOLOGY BIOLOGY PH

Scientists Discover Third Ozone Layer in Atmosphere of Mars

Sep 30, 2013 by Editors

« PREVIOU



- Known ozone layers near surface and at 40-60 km
- Montmessin and Lefevre (Nat. Geosciences 2013) use SPICAM-MEX data to discover 3rd ozone layer at 30-70 km over southern winter pole
- Recombination of O atoms from CO2 photolysis, then transport

Mars Atmospheric Loss

- McElroy 1972; McElroy + Nier + Yung 1976
- Viking 1976 nitrogen isotope enrichment provided evidence of atmospheric loss
- Toby Owen D/H and hydrogen escape: *Science 24 June 1988: 1767.*

Deuterium on Mars: The Abundance of HDO and the Value of D/H

TOBIAS OWEN, JEAN PIERRE MAILLARD, CATHERINE DE BERGH, BARRY L. LUTZ

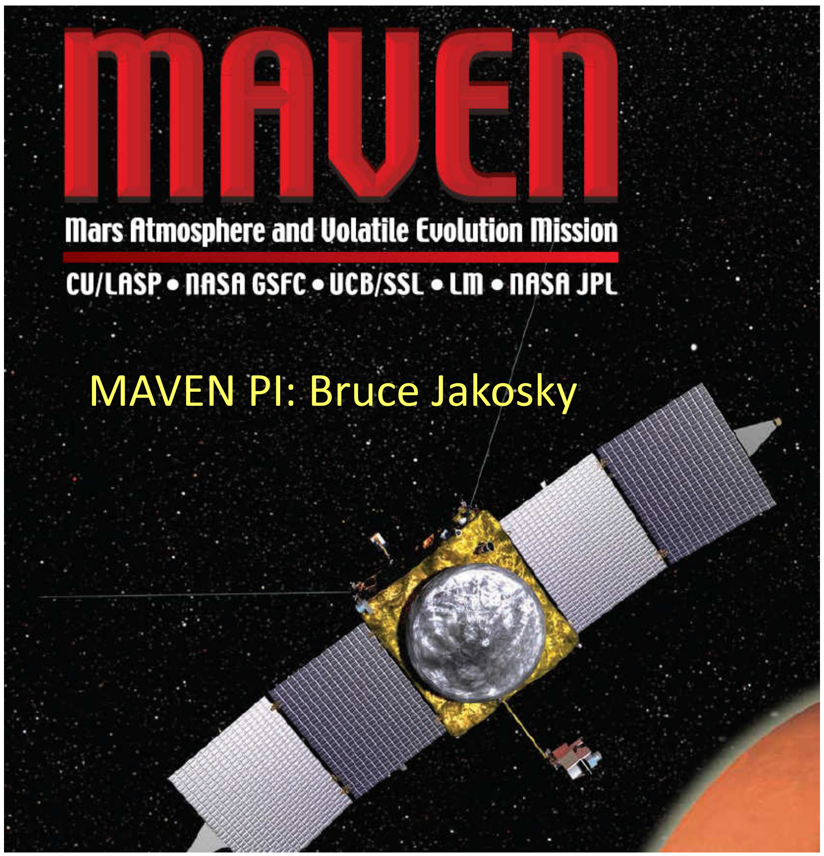
Deuterium on Mars has been detected by the resolution of several Doppler-shifted lines of HDO near 3.7 micrometers in the planet's spectrum. The ratio of deuterium to hydrogen is $(9 \pm 4) \times 10^{-4}$; the abundance of H_2O was derived from lines near 1.1 micrometers. This ratio is enriched on Mars over the telluric value by a factor of 6 ± 3. The enrichment implies that hydrogen escaped more rapidly from Mars in the past than it does now, consistent with a dense and warm ancient atmosphere on the planet.

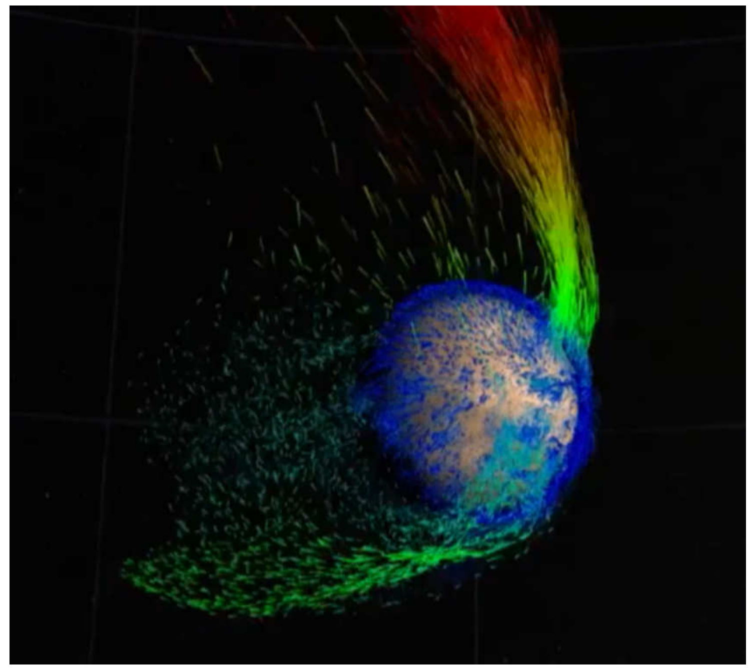
- Mars once had a thicker atmosphere and surface liquid water, lost through:
  - Planet's core cooled and solidified (70% density of Earth), losing magnetic field ~4 Gya
  - Catastrophic collision with large body arrested dynamo effect?
  - Gradual erosion by
    - Jeans KE escape
    - Photochemical production of ions that join with e- to reach escape velocities
    - Solar wind pickup and acceleration of ions along solar wind magnetic field, some returning to atmosphere to energize heavier neutrals to escape in sputtering process.

Ongoing Processes in the Upper Atmosphere

MAVEN 2013:

- Upper atmosphere, ionosphere, magnetosphere
- Response to solar and solar-wind events
- Ability of atmospheric molecules and atoms to escape to space





March 2015 interplanetary coronal mass ejection impact -> Large enhancement in escape rate of ions to space.
Jakosky et al. *Science* 350, Nov 2015.

SAM Atmospheric Isotope Ratios -synergy of mass spectrometry *vs* spectroscopy

A suite of 8 isotope ratios show early atmospheric escape

Isotopes	Mars value ‰	Instrument	Reference
$\delta^{38}Ar_{Sun}$	310 ± 31	QMS	Atreya et al. (2013, *GRL*)
$\delta^{40}Ar_{Earth}$	5,419 ± 1013	QMS	Mahaffy et al. (2013, *Science*)
$\delta^{15}N_{Earth}$	572 ± 82	QMS	Wong et al. (2013, *GRL*)
$\delta^{13}C_{VPDB}$	45 ± 12	QMS	Mahaffy et al. (2013, *Science*)
$\delta^{13}C_{VPDB}$	46 ± 4	TLS	Webster et al. (2013, *Science*)
$\delta^{18}O_{SMOW}$	48 ± 5	“	“ “
$\delta^{17}O_{SMOW}$	24 ± 5	“	“ “
$\delta^{13}C\delta^{18}O$	109 ± 31	“	“ “
δD_{SMOW}	4,950 ± 1080	“	“ “
“	4,231 ± 33	“	Leshin et al. (2013, *Science*; updated)

Atmosphere-surface Interactions

nature COMMUNICATIONS

ARTICLE

Received 17 Jul 2015 | Accepted 26 Oct 2015 | Published 24 Nov 2015 DOI: 10.1038/ncomms10003 OPEN

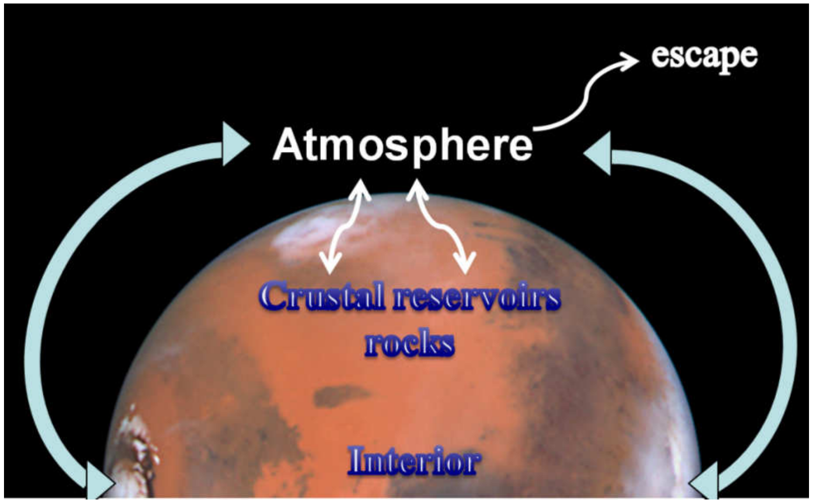
Tracing the fate of carbon and the atmospheric evolution of Mars

Renyu Hu[1,2], David M. Kass[1], Bethany L. Ehlmann[1,2] & Yuk L. Yung[1,2]

- Current day atmospheric d^{13}C in CO_2 (+46 per mil) is the result of the history of atmospheric loss (^{13}C enrichment) and carbonate deposition (^{13}C depletion)
- Hu et al. show that escape of C via CO photodissociation and sputtering enriches ^{13}C, a process partially compensated by moderate carbonate precipitation.

Keck Institute for Space Studies

Martian Atmosphere Shows Significant Early Loss



Jakosky and Phillips, Nature 412, July 2001:

- Up to 90% of the original volatile inventory was lost 3.8 billion years ago from impact ejection;
- ~2/3 of water lost to space
- D/H, $^{15}N/^{14}N$, $^{13}C/^{12}C$ show enrichments over mantle values

Noachian **Hesperian** **Amazonian**

4.6 **4.0** **3.7** **1.0** **0 Gya**

Hydrodynamic escape, impact ejection of atmosphere

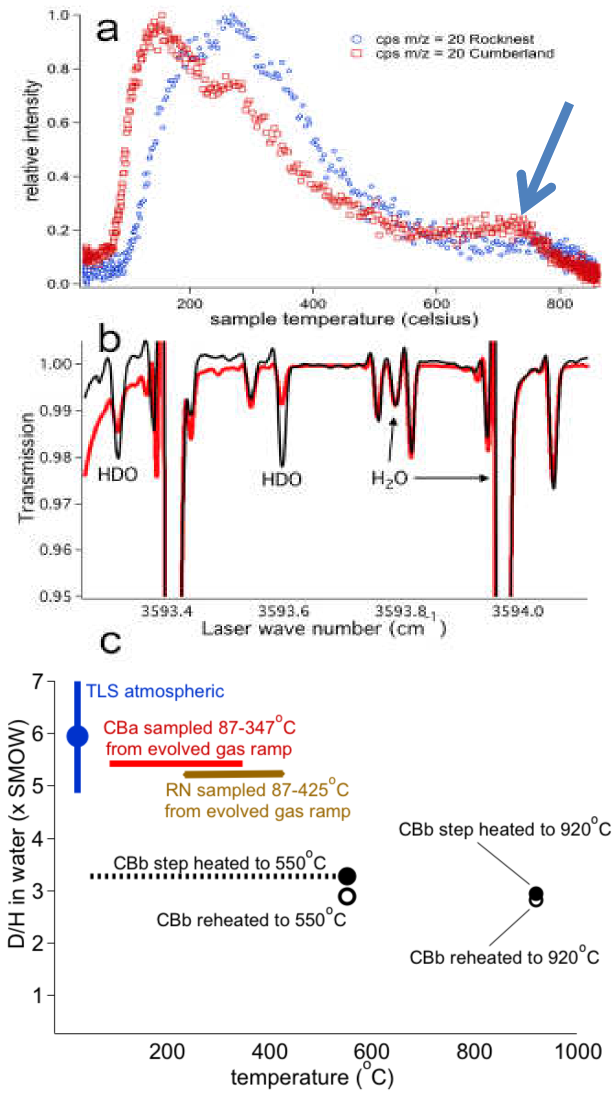
Carbonate deposition

Curiosity

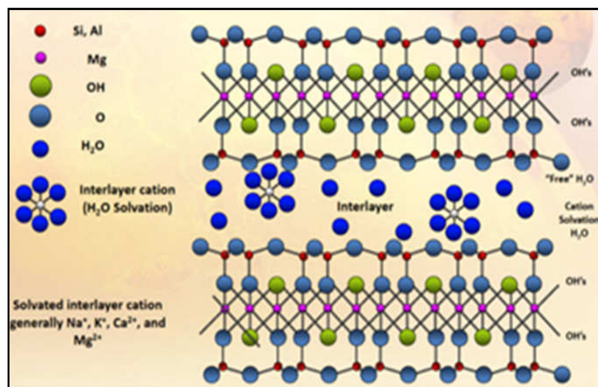
ALH84001 — **Meteoric record** — Nakhla — EETA79001

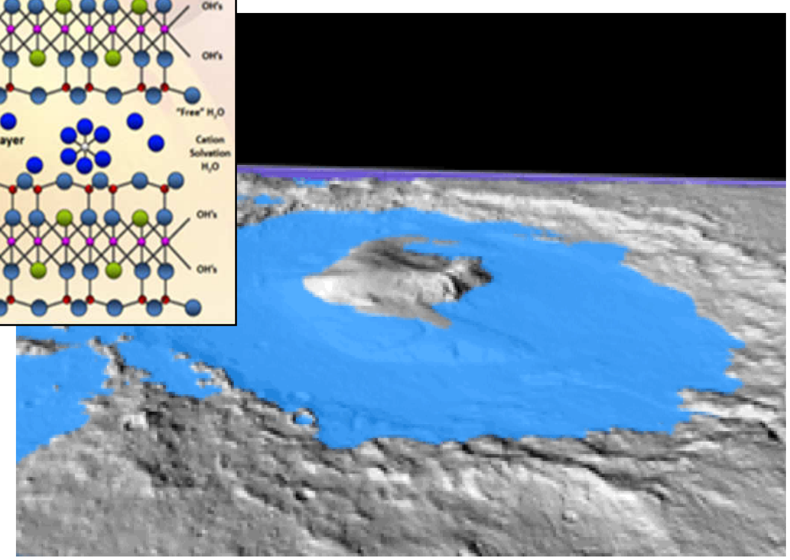
D/H ratio in Yellowknife Bay Mudstone

-Mahaffy et al. *Science* Dec 2014

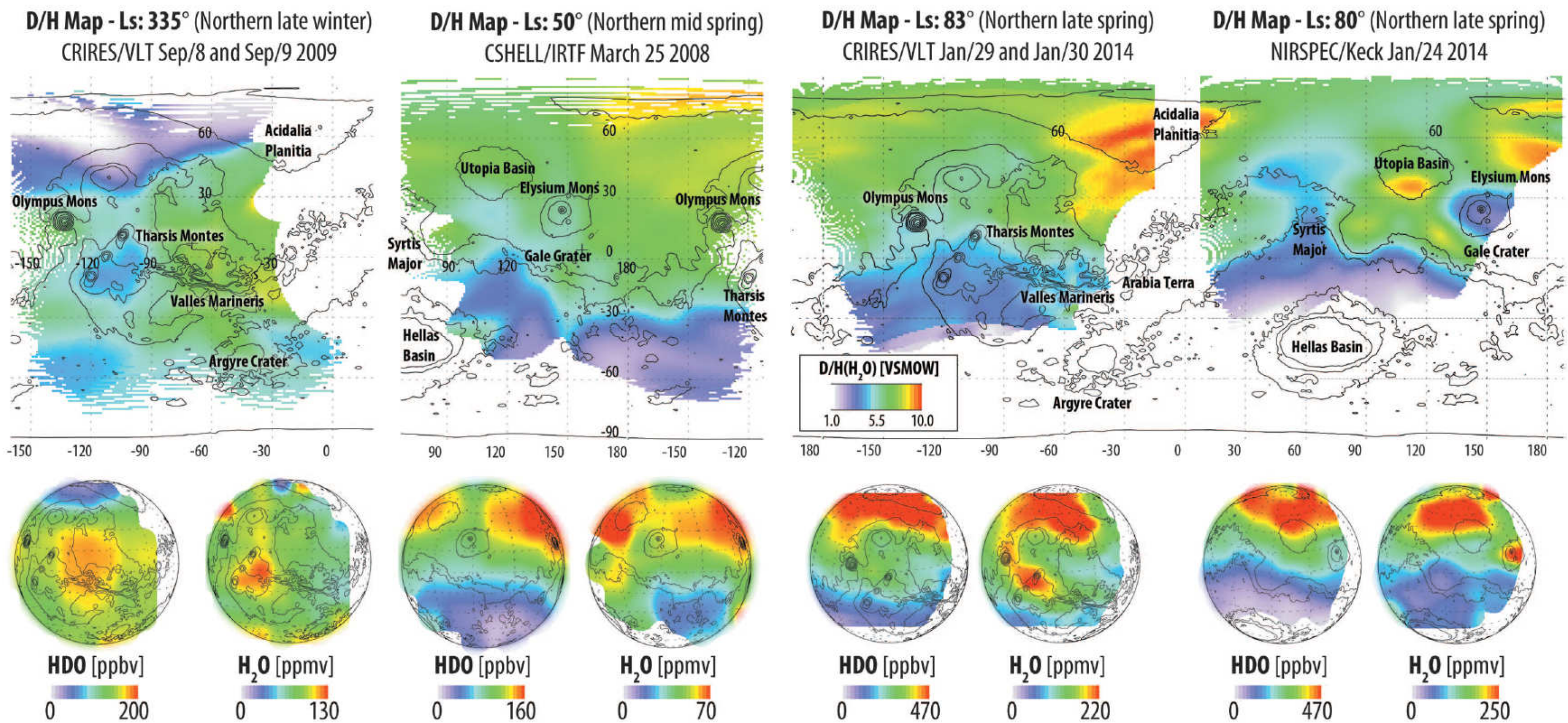


- D/H from both evolved water (TLS) and hydrogen (QMS) at 3 x SMOW.
- Low D/H in bound OH in clays formed 2.9-3.5 Gya (Hesperian) shows that considerable water was lost both before and after this point.
- GEL at Cumberland mudstone formation ~150m compared to ~50m today.





Earth-based Observations- H_2O and HDO

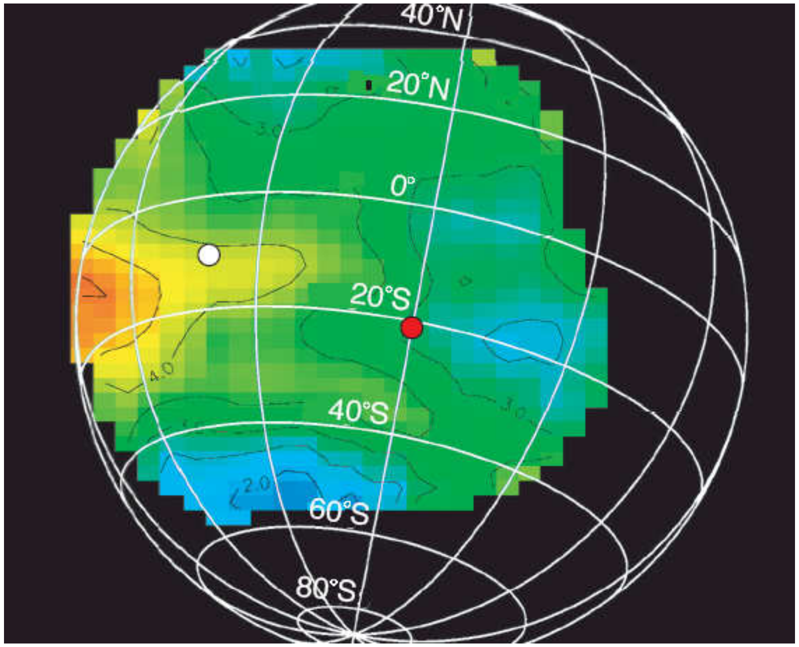


Villanueva et al., *Science* 348, 218-221, 2014

Earth-based Observations – H_2O_2

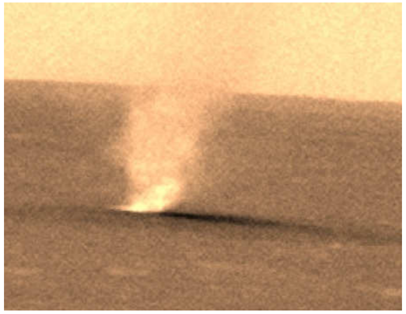
Therese Encrenaz (Paris Observatory) et al., *Icarus*, 2004

- Discovered 40 ppbv H_2O_2 on Mars at subsolar point (white dot) in summer time using the 3 m NASA IRTF at Hawaii
- Spatial and seasonal variations

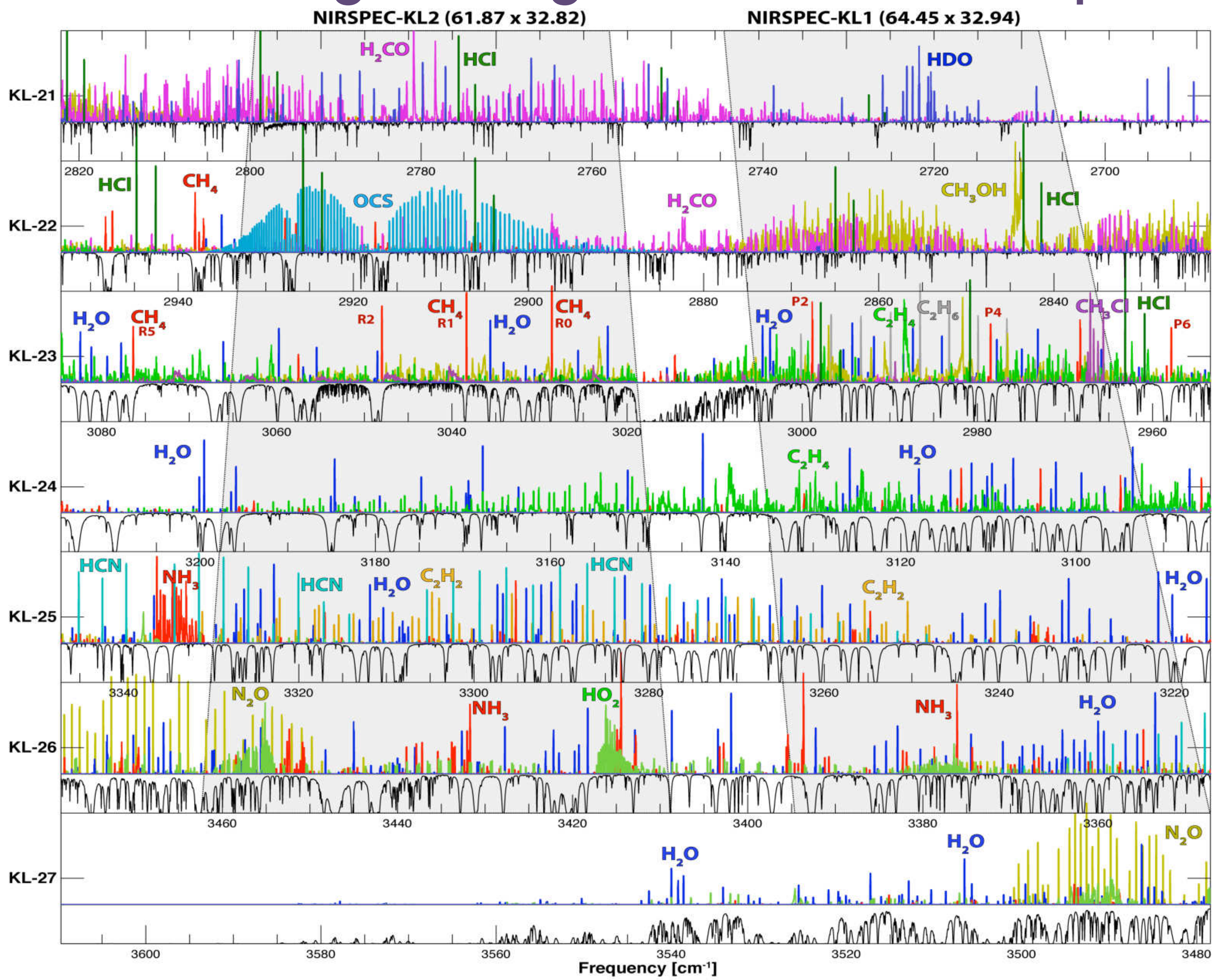


Martian dust devils, electrochemistry and oxidants

Sushil Atreya et al. (2006) – Large turboelectric fields in dust storms can produce greatly enhanced OH and therefore H_2O_2. Resulting superoxides and other oxidants could destroy methane gas and form formaldehyde or methanol.

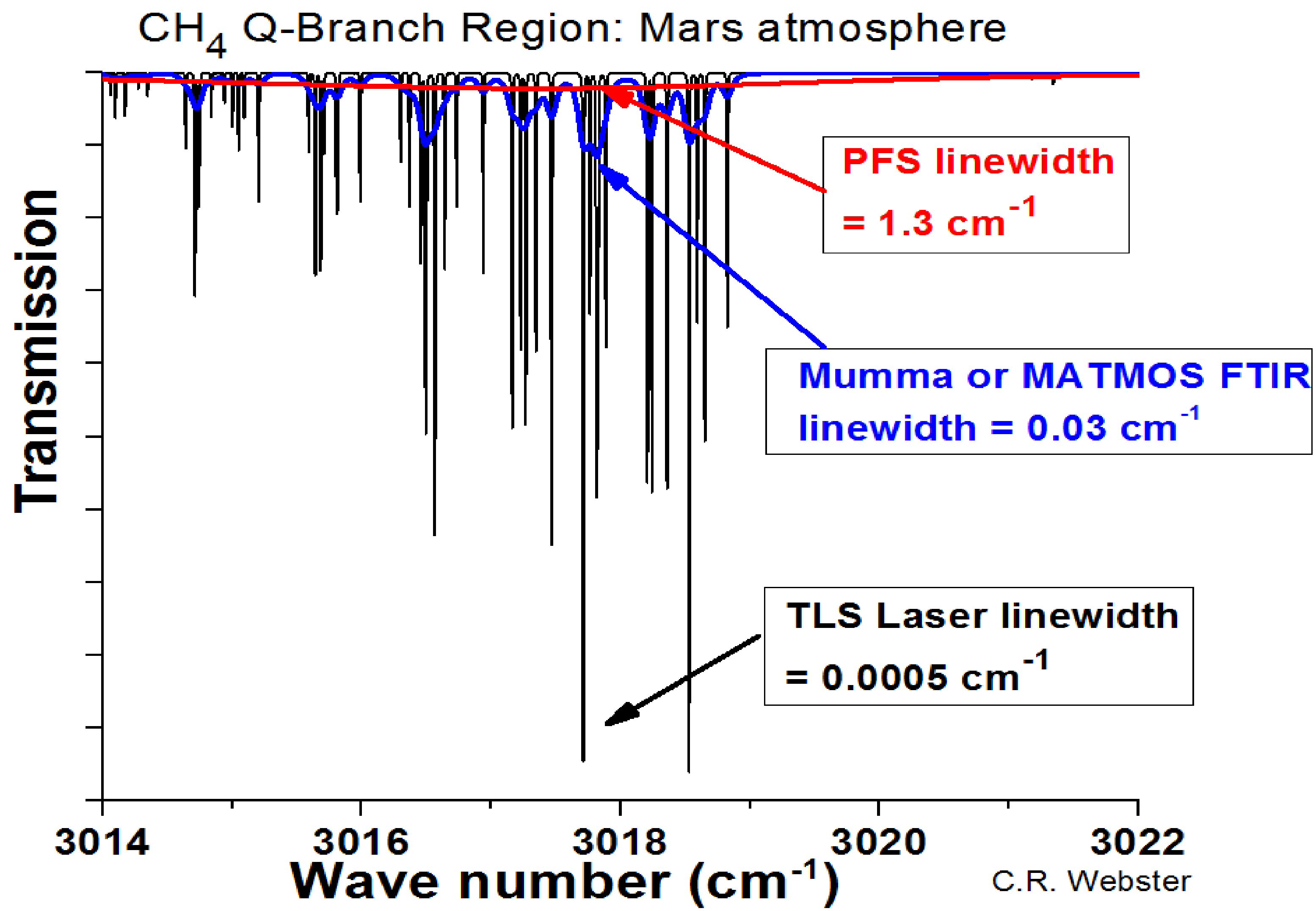


Looking through Earth's Atmosphere



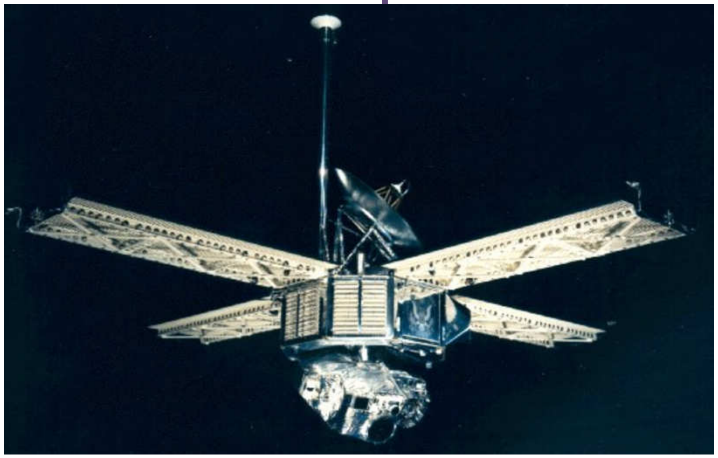
Villanueva et al. *Icarus*, 2012

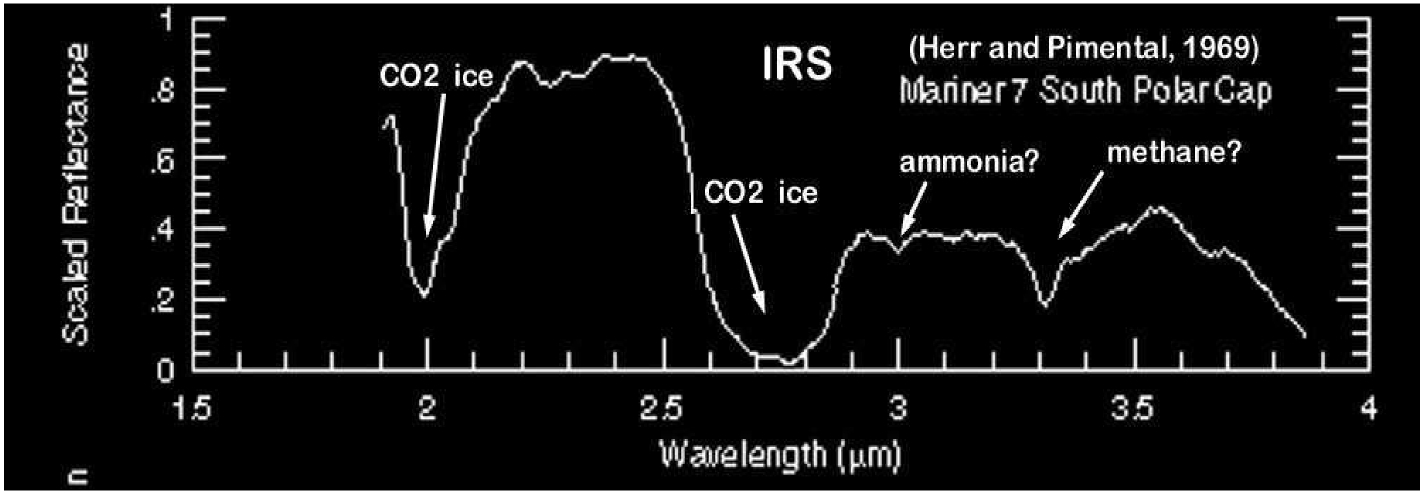
Spectral Resolution

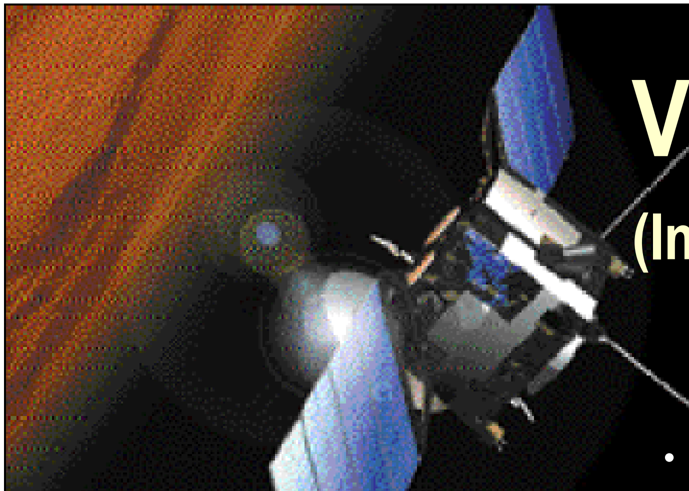


Earth-based Observations – CH_4?

- Aug 1969 – One week after Moon landing- in JPL's Von Karman auditorium…. Walter Cronkite
- Mariners 6 and 7 IRS (PI George Pimental) announced discovery of significant NH_3 and CH_4 on Mars………..later retracted….



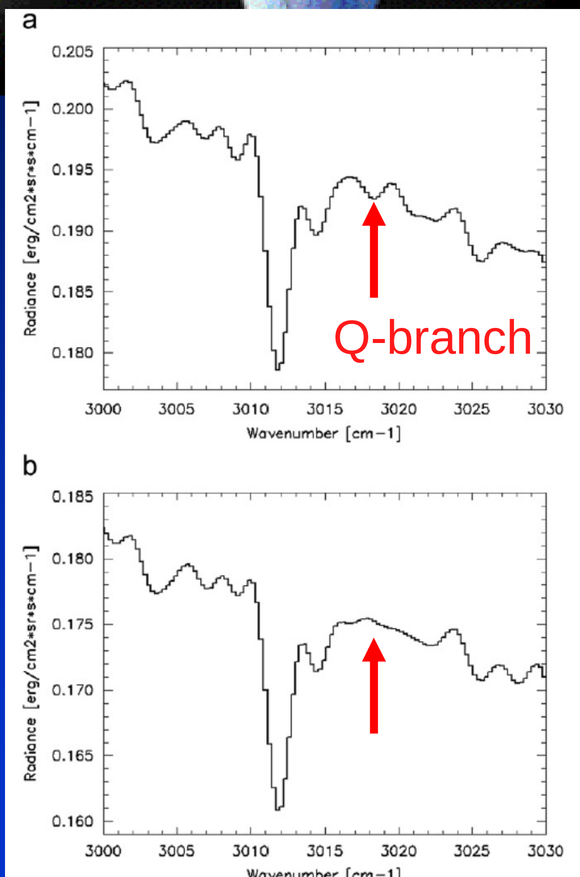




Vittorio Formisano et al.

(Institute of Physics & Interplanetary Space)

Geminale et al. PSS 59 (2011) 137–148

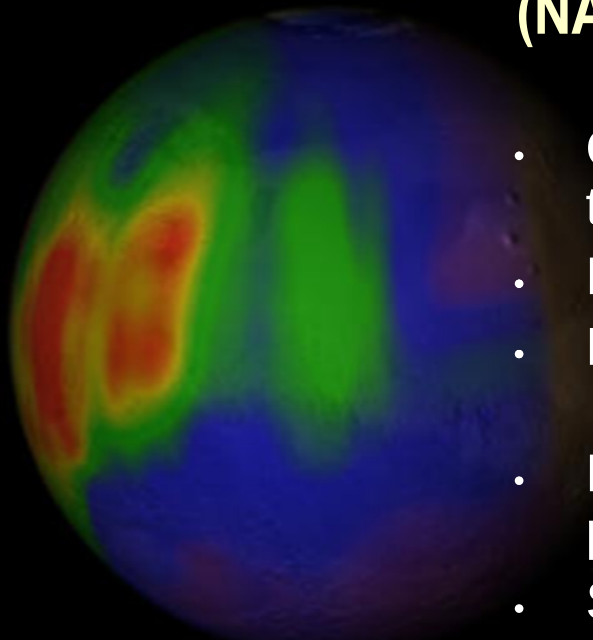


- Planetary Fourier Spectrometer on ESA's Mars Express
- Designed to measure vertical profiles of CO_2 and column H_2O, CO, CH_4 and H_2CO

- Detected 15 ± 5 ppbv CH_4 in the Martian atmosphere by averaging 15,687 spectra
- CH_4 signatures in 9 lines (!)
- CH_4 mixing ratio variable from 0 to 40 ppbv
- CH_4 and H_2O emanate from 3 locations: Arabia Terra, Elysium Planum, and Arcadia-Memnomia

- Conclude source is northern cap, whose summertime release is sufficient to explain global mean of 15 ± 5 ppbv.

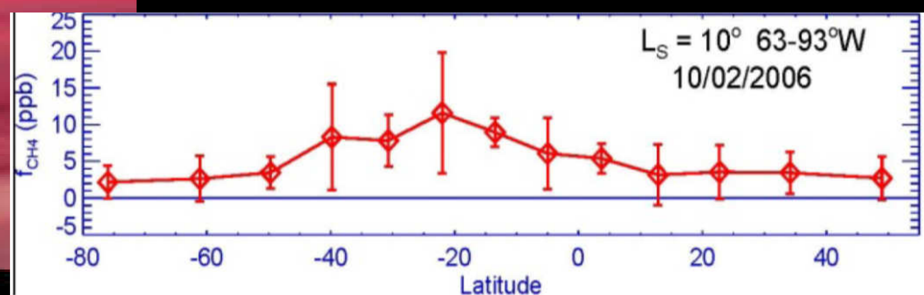
Michael J. Mumma et al.
(NASA GSFC) -2004



- Observations mainly from the 8 m Gemini South telescope in Chile (& NASA's IRTF, Mauna Kea)
- Relies on Doppler shifts
- Multiple spectral features of CH_4 seen
  - Need to subtract Earth CH_4
- Lower amounts at the higher latitudes – 20-60 ppbv
- Significant *enhancement at equatorial regions* – up to 40 ppbv – in region of changing topography - transition highlands to plain, scarps, cliff faces
- Enhancement also over deep rift Valles Marineris – steep high cliffs
- Is methane diffusing under the permafrost and emerging at cliff faces or fissures?

Vladimir Krasnopolski et al.
(Catholic University) et al. *Icarus* 2004, EPSC 2011

- Ground-based FTIR (Canada-France-Hawaii telescope on Mauna Kea, Hawaii) looking at 40% of Mars disk
- Detected 10 ± 3 ppbv CH_4 in Mars atmosphere where lifetime is 340 years
- 270 tons CH_4 therefore produced per year
- Concluded that observed CH_4 is from methanogenesis by living subterranean organisms (Martian biota scarce and sterile except oases)



Keck INSTITUTE FOR SPACE STUDIES

- **Conflicting results – from 0 ppbv to 60 ppbv**
- **Differing distributions – uniform distribution to high local variations- and widely differing interpretations**

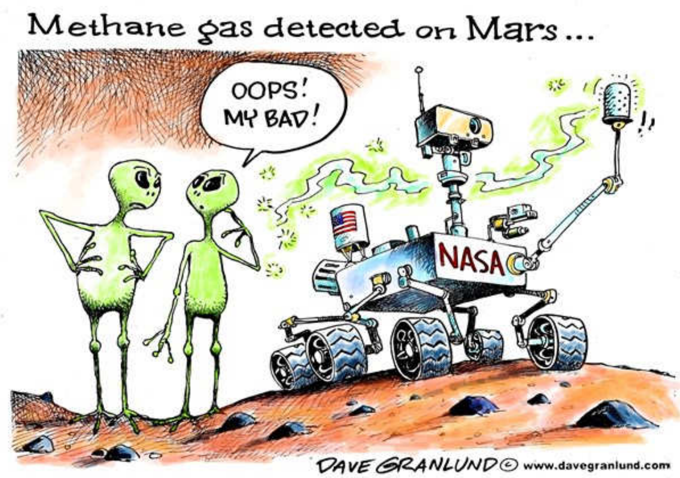
nature Vol 460 | 6 August 2009 | doi:10.1038/nature08228

LETTERS

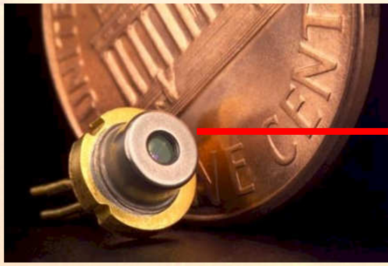
Observed variations of methane on Mars unexplained by known atmospheric chemistry and physics

Franck Lefèvre[1] & François Forget[2]

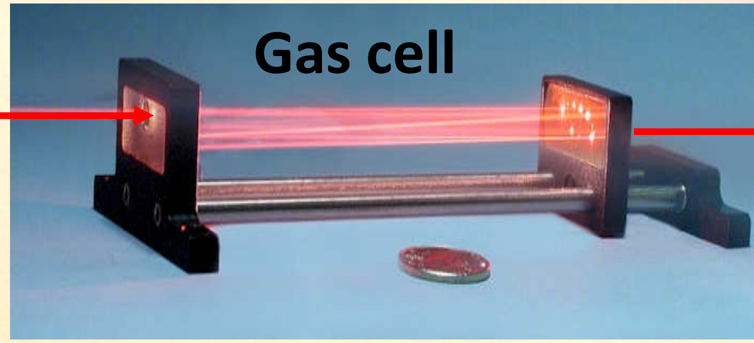
So what did TLS-SAM on Curiosity see?

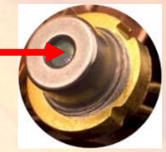


TLS – Tunable Laser Absorption Spectroscopy

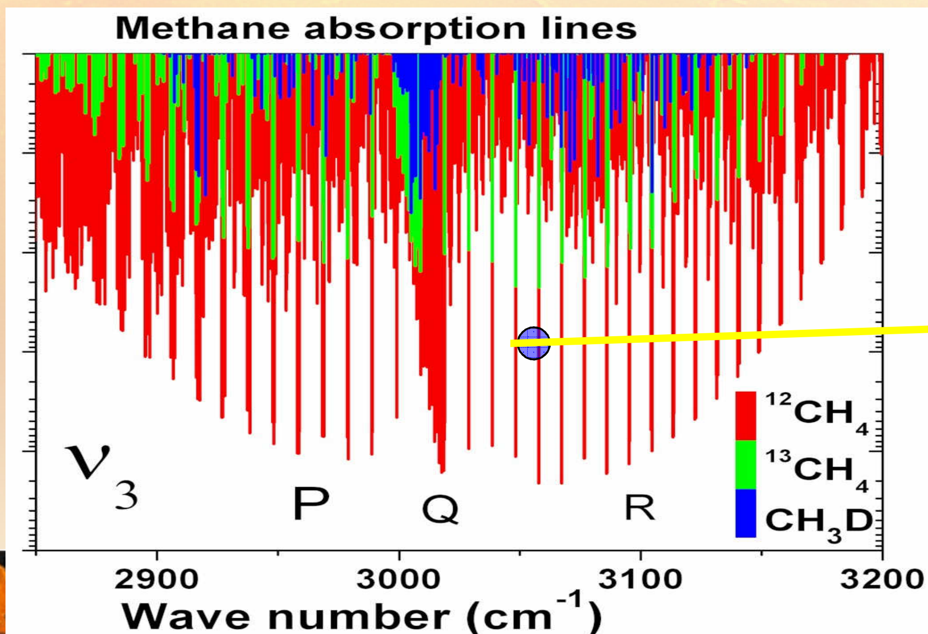


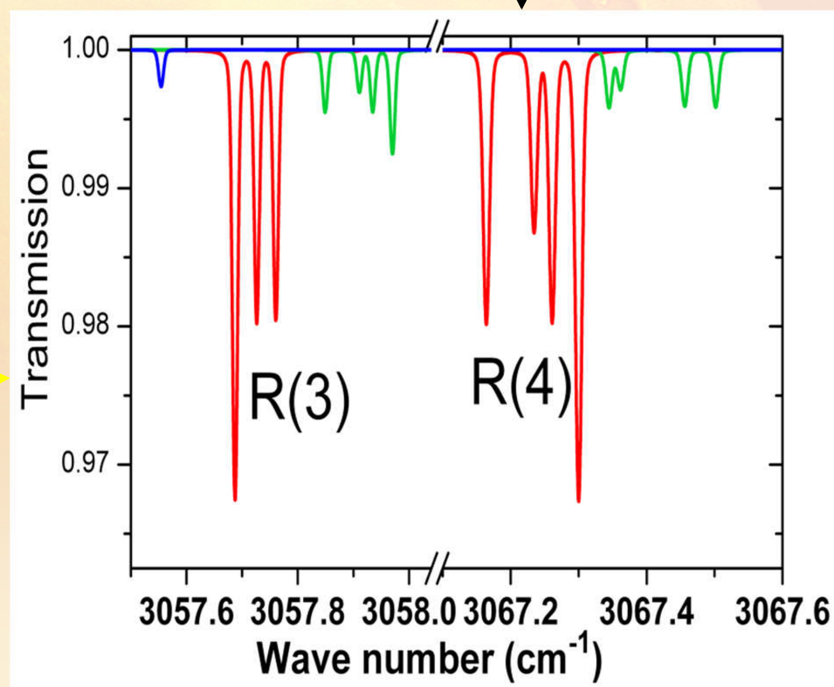
Tunable laser 1-12 µm



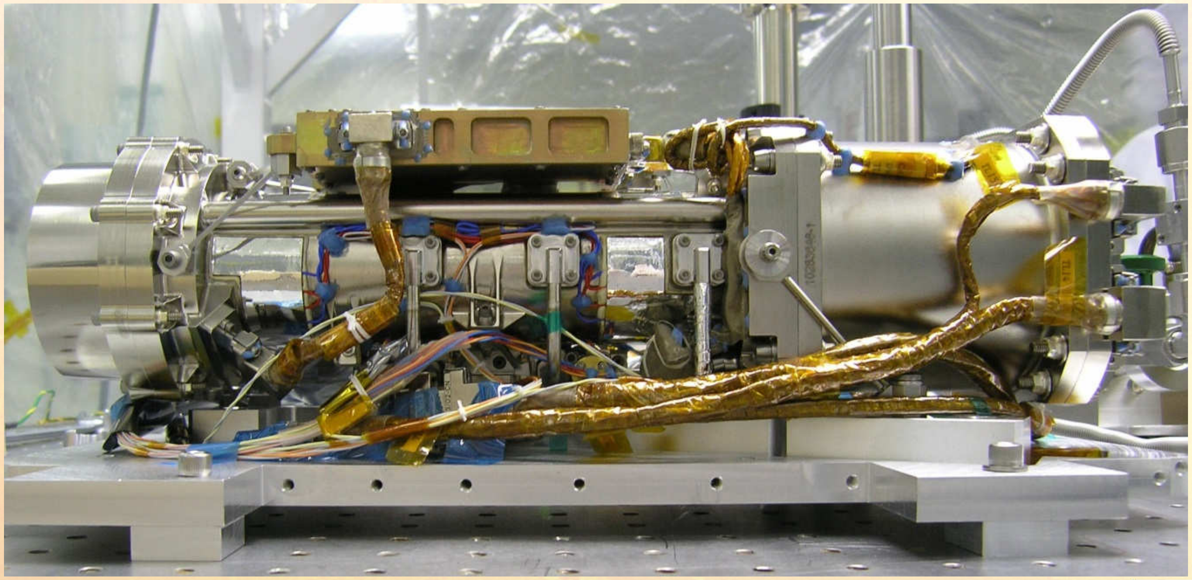


Detector

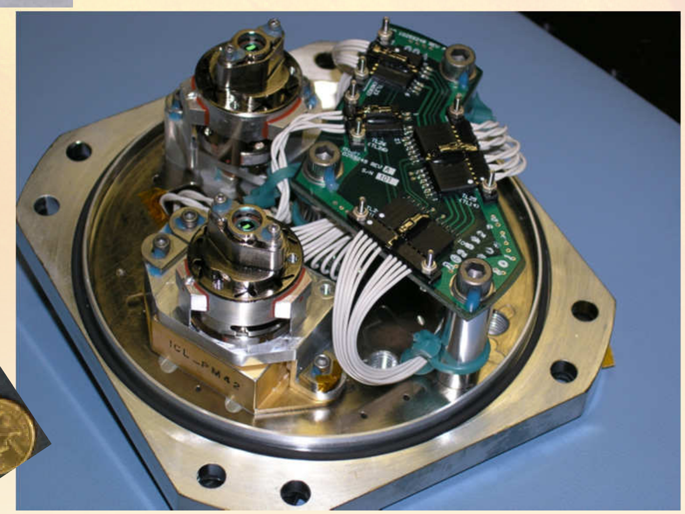




Tunable Laser Spectrometer (TLS)



Mass = 3.3 kg

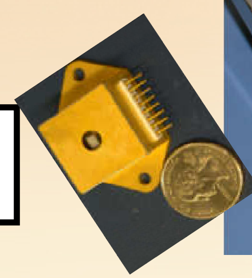


Near-IR TDL from
Nanoplus, Germany

2.78 µm

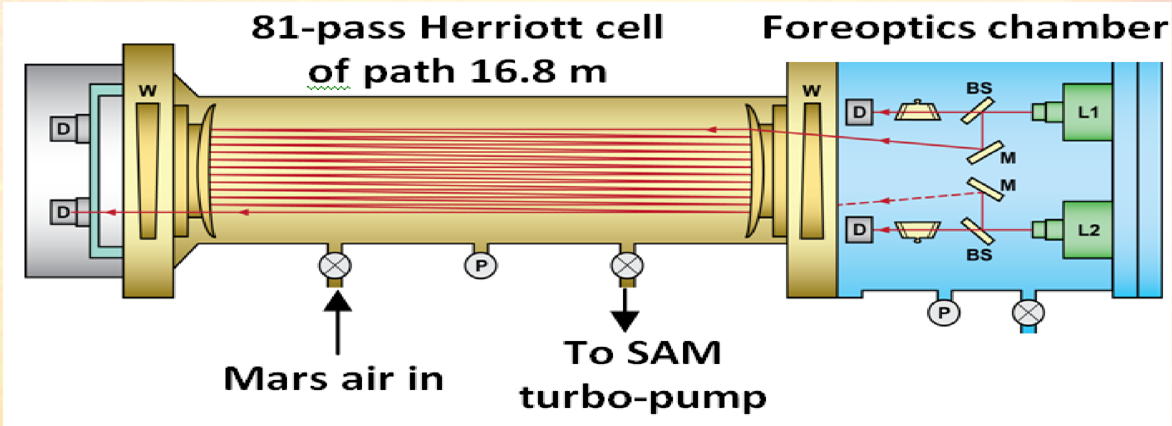
IC laser from MDL-JPL

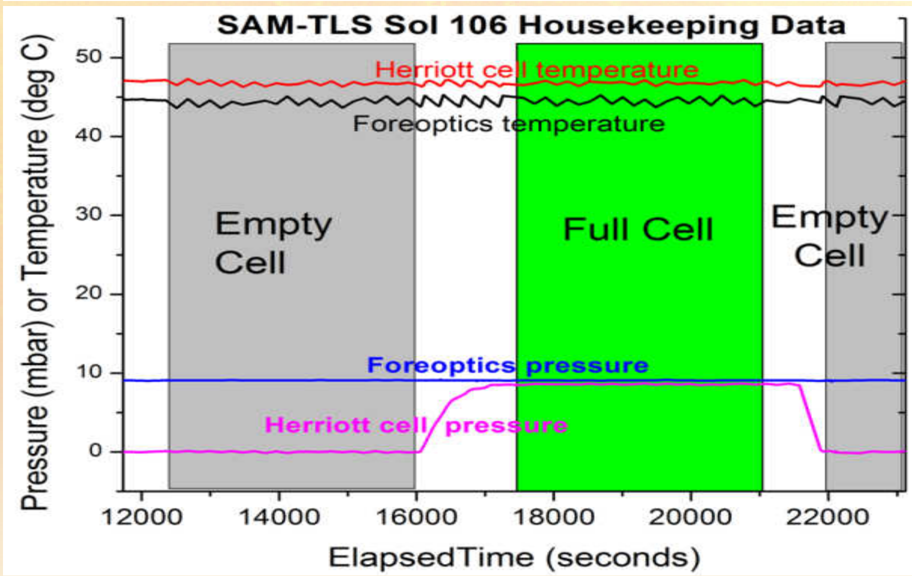
3.27 µm



TLS-SAM Methane Search

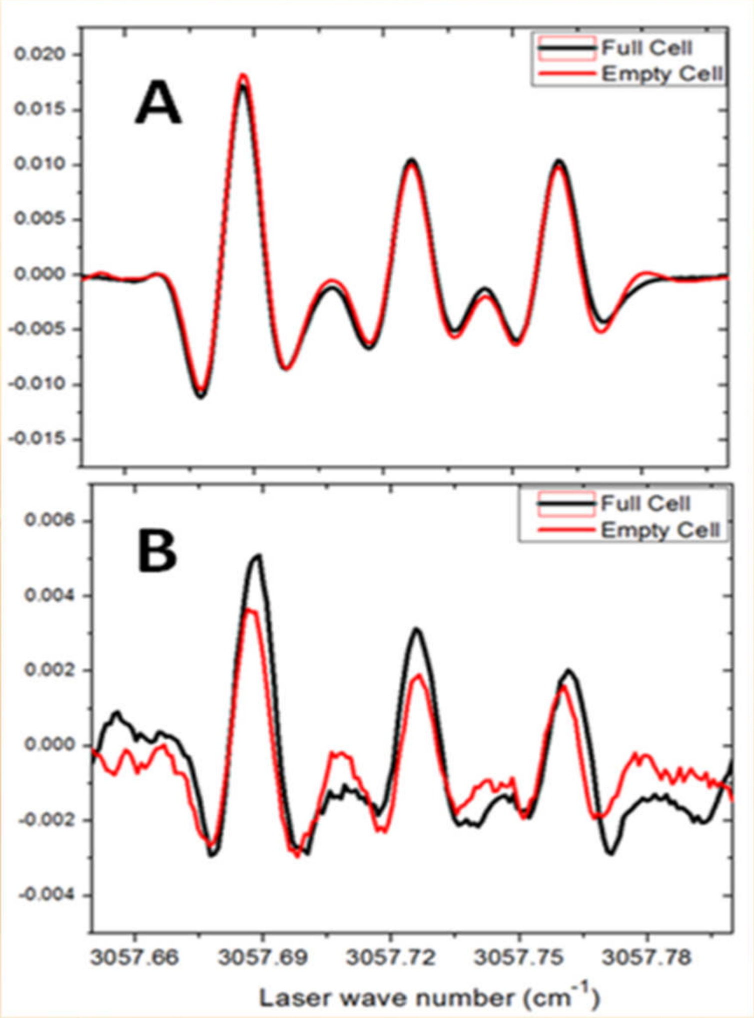
- Fore-optics chamber contains residual terrestrial air
- Use “difference method” comparing full sample cell to empty sample cell

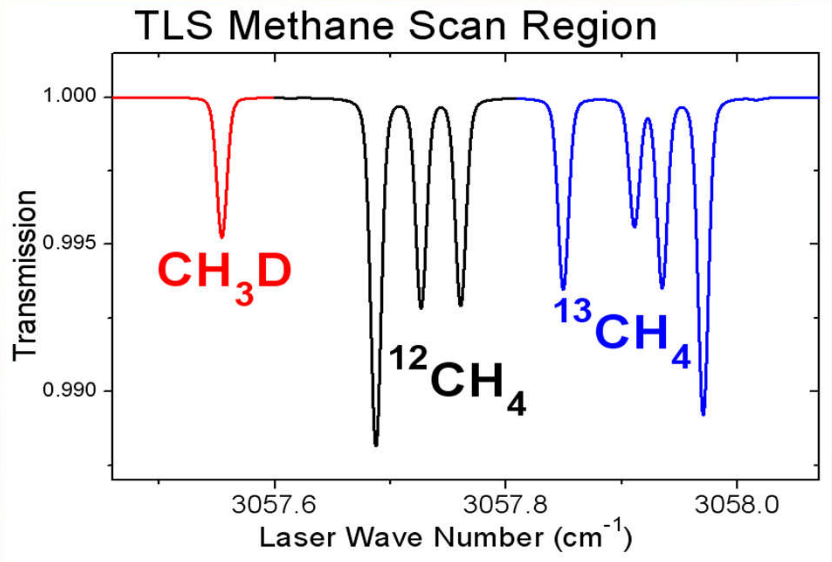




Enrichment x 23 achieved by flowing input over Linde 13X CO_2 scrubber.

Direct Ingest Spectra

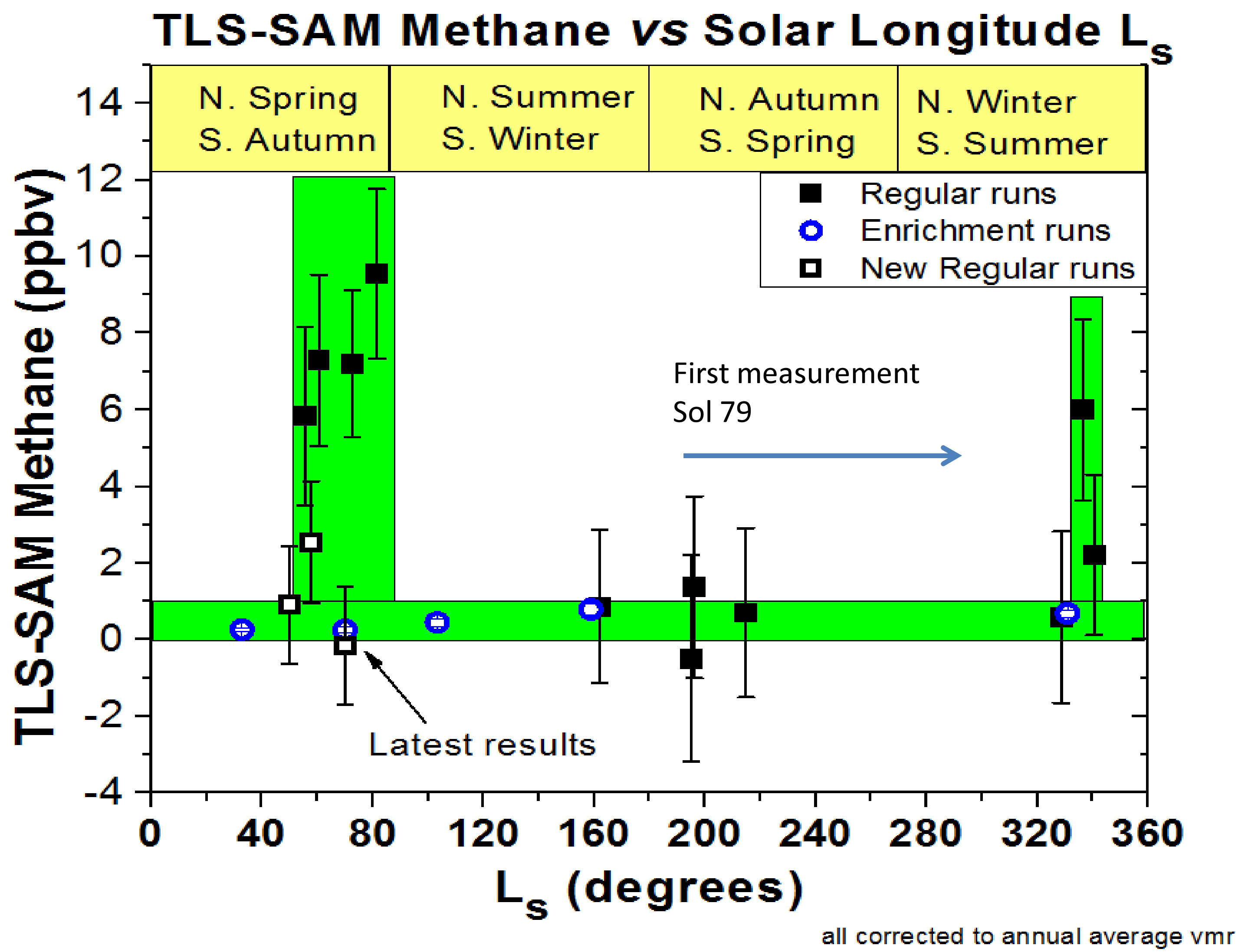




A. "Low methane" from Sols 79, 81, 106, 292, 313 and 684;

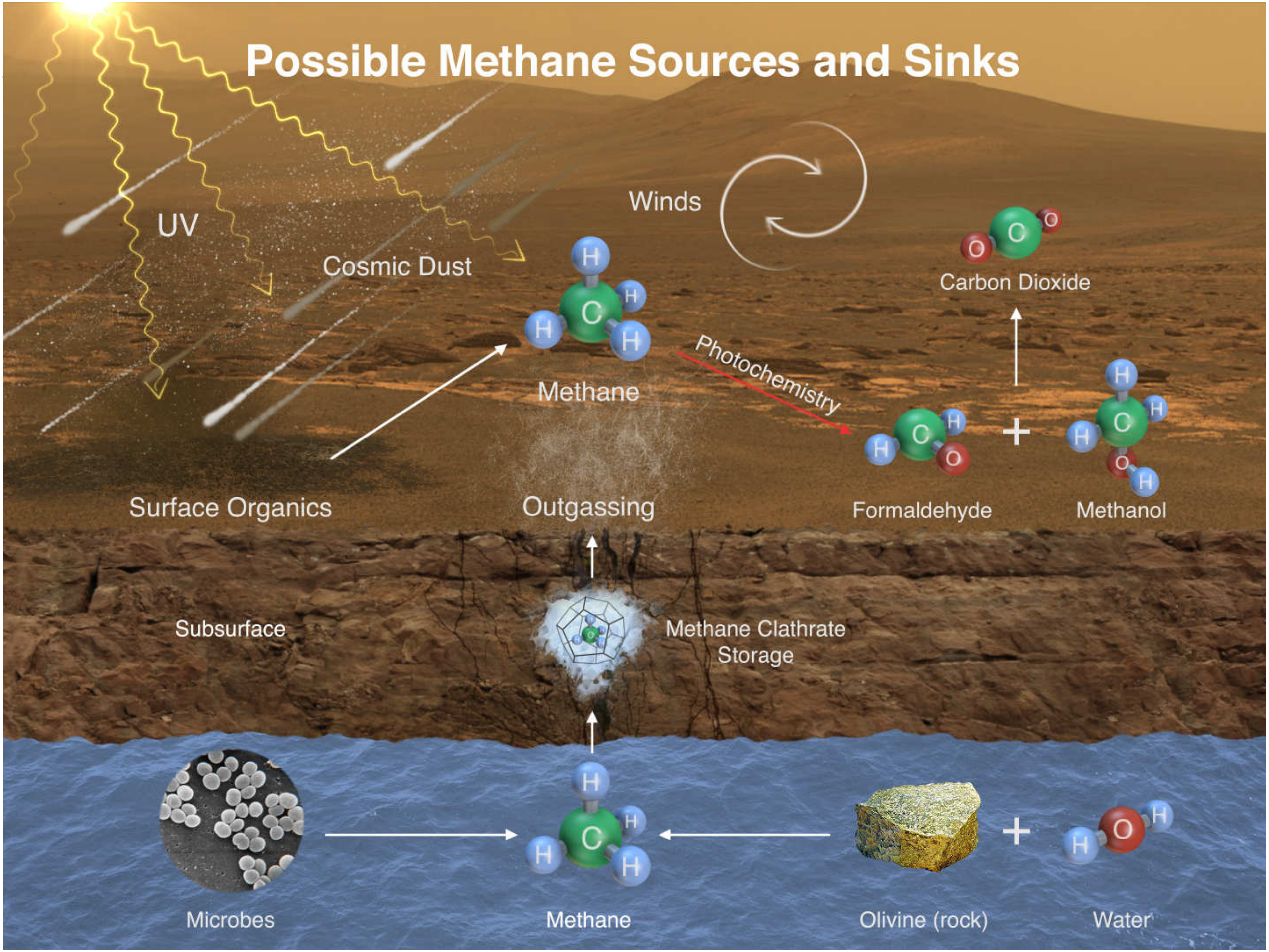
B. "High methane" from Sol 474 only

“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



Possible Methane Sources and Sinks
UV
Cosmic Dust
Winds
Carbon Dioxide
Methane
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

<u>Hu…..Yung group (2015):</u>

- 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 – expect *seasona*l dependence (?)

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; Bak et al. EPL 2015 in press).- could explain the fast disappearance of methane.

TLS-SAM Low Methane Background

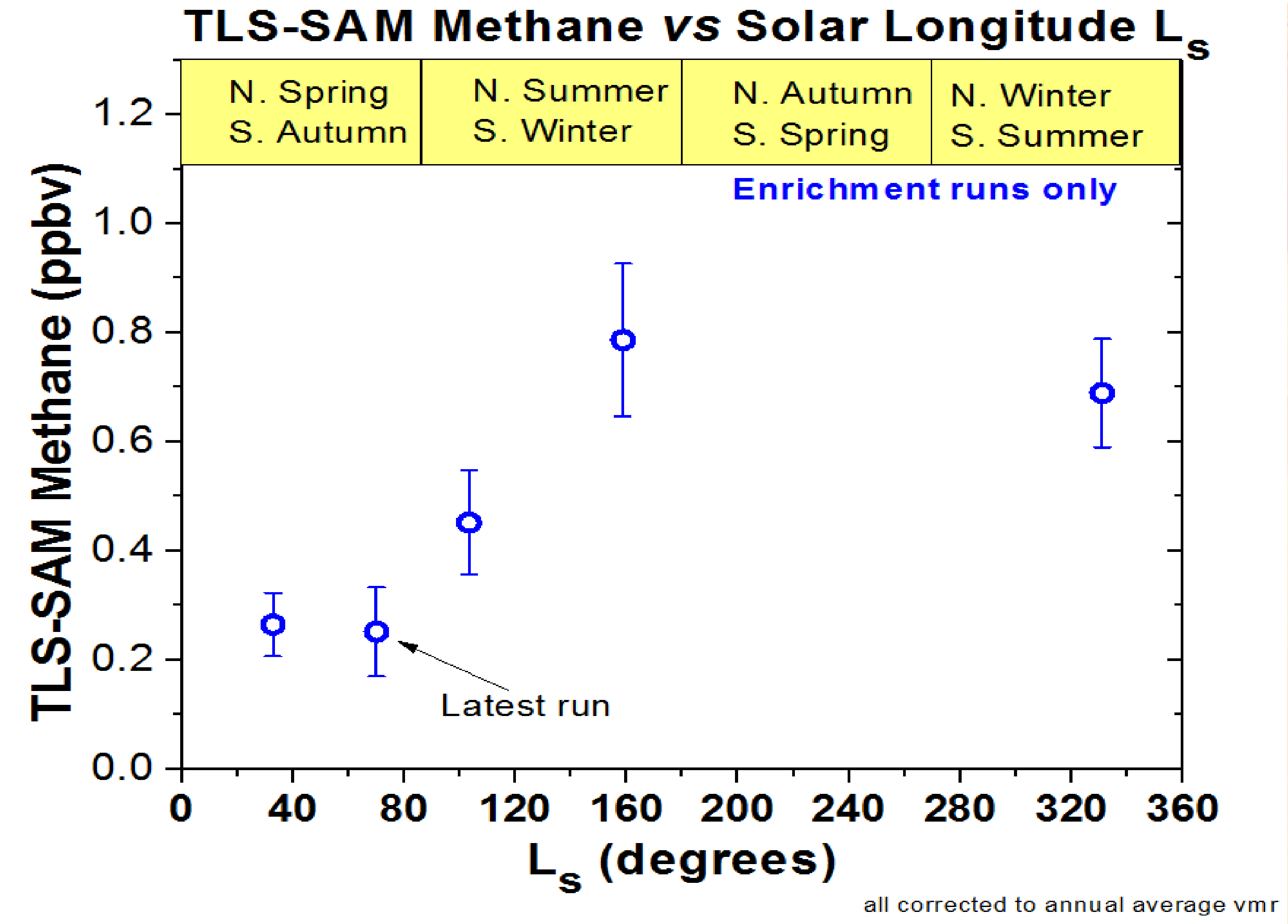
A contribution from a variety of sources?

Consider UV degradation of surface material

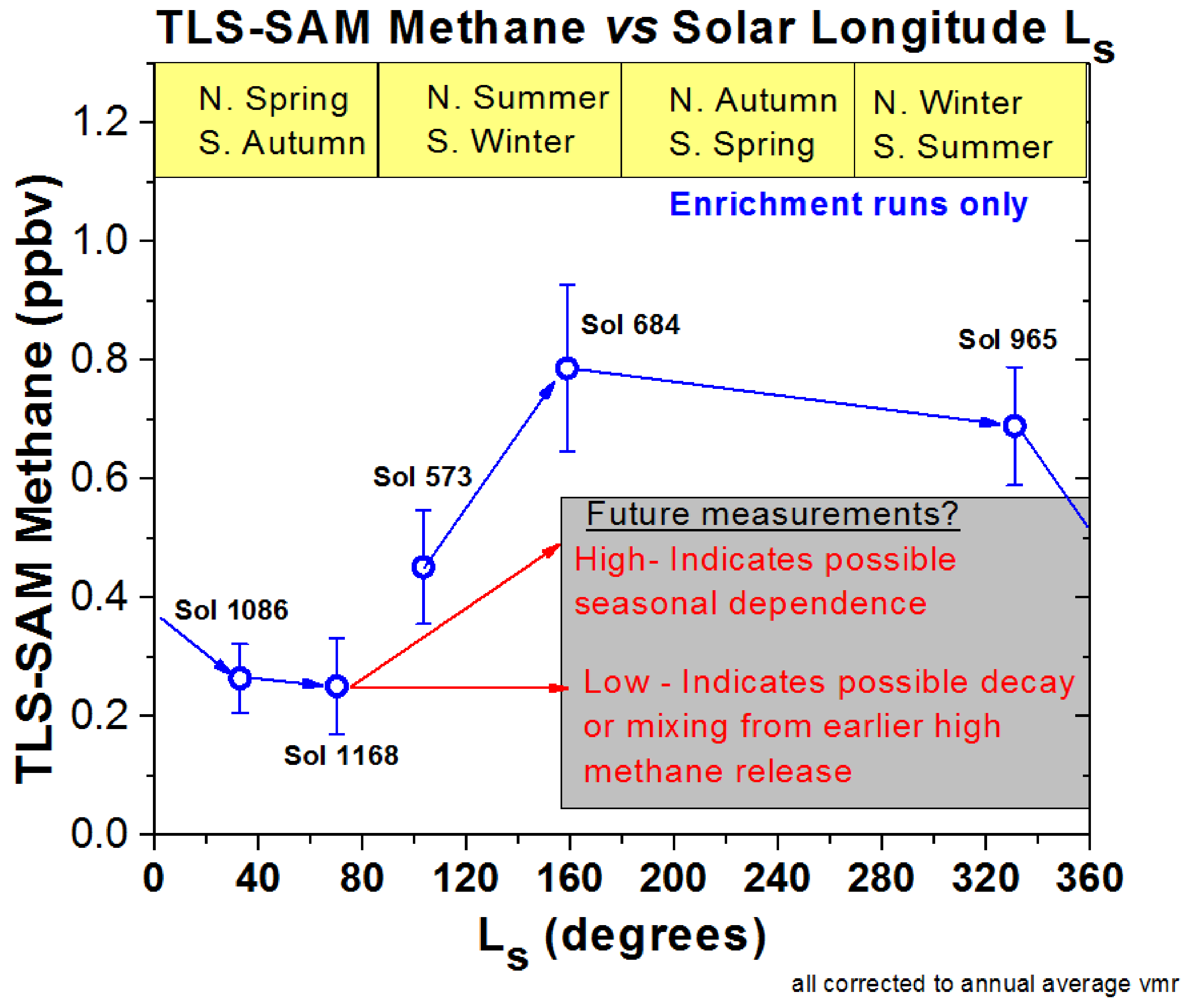
- Surface meteoric material: micrometeorites from accreted IDP, and carbonaceous chondrites containing few wt% organic matter;
- Accreted IDP's deliver 90% of organic C with average C content of 10%- a carbon-limited (not UV) process.

- 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 < model prediction of ~2.2 ppbv
  - Therefore infall amount, C conversion efficiency or organic content is overestimated by factor of ~3.
  - But lab measurements do NOT accurately simulate Mars conditions, such as inclusion of surface oxidants
- Steady infall/conversion cannot explain large episodic bursts.

TLS-SAM Low Methane Background



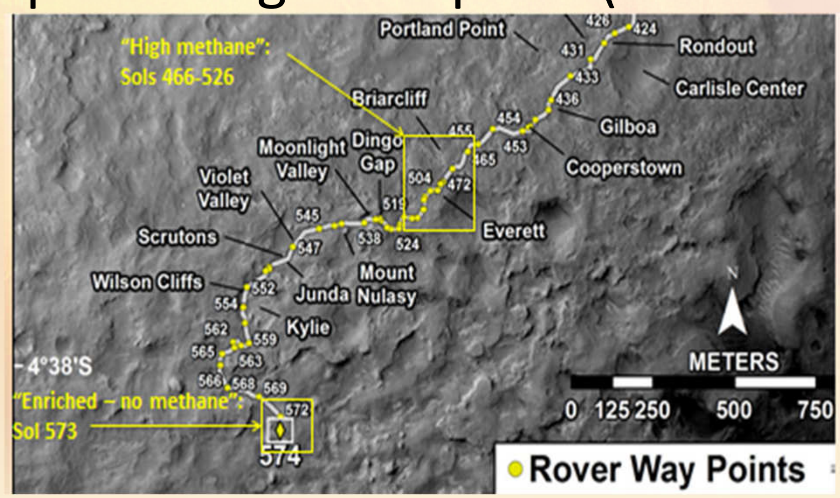
New mean value = 0.5 ppbv


TLS-SAM Methane vs Solar Longitude L_s
N. Spring S. Autumn
N. Summer S. Winter
N. Autumn S. Spring
N. Winter S. Summer
Enrichment runs only
Sol 684
Sol 965
Sol 573
Sol 1086
Sol 1168
Future measurements?
High- Indicates possible seasonal dependence
Low - Indicates possible decay or mixing from earlier high methane release
TLS-SAM Methane (ppbv)
1.2
1.0
0.8
0.6
0.4
0.2
0.0
0
40
80
120
160
200
240
280
320
360
L_s (degrees)
all corrected to annual average vmr

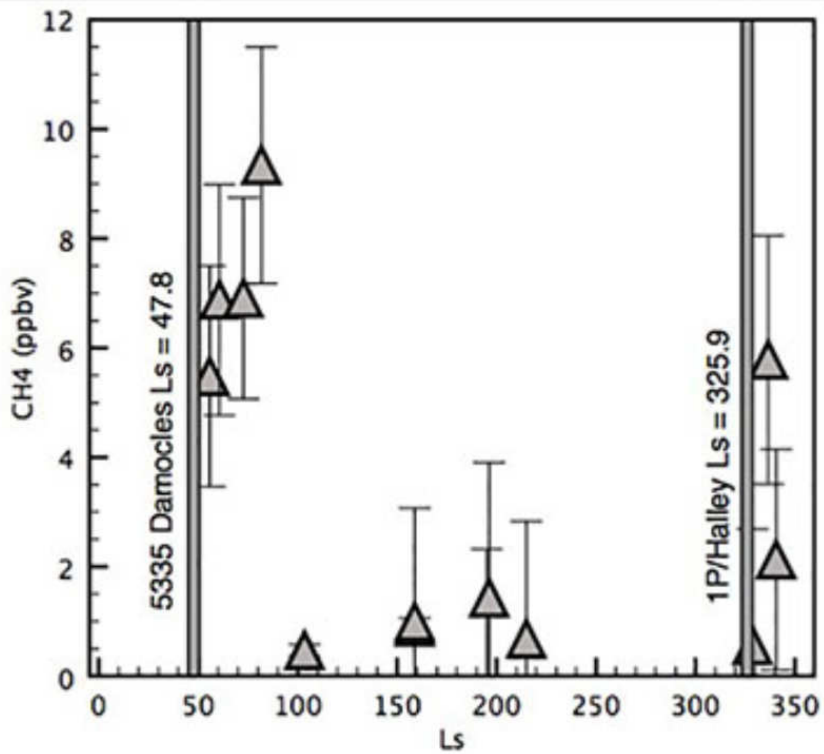
TLS-SAM High Methane

- 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.
- Anti-correlations with column water, oxygen **now ruled out.**
- Consistent with a small local source producing a temporal (not location) change.
- Wind fields and daytime

increase indicate source to the north.



Encounters with Cometary Debris Fields?



Geochemical Perspectives Letters v2, n1 | doi: 10.7185/geochemlet.1602. Dec 2015.

- Could "meteor showers" deliver macromolecular carbon MMC that produces CH4 under UV photolysis- possibly at higher altitudes?
- Maarten-Roos/ Atreya 2015 conclude no correlation with cometary debris/meteoritic infall.
- Fries et al. (GPL, 2015) use data from PFS, Mumma, MSL to show possible dependence on cometary debris encounters
  - *But more recent TLS-SAM measurements show no repetition.*

Local Source Within Gale Crater?

Tracking the MSL-SAM methane detection source location
Through Mars Regional Atmospheric Modeling System (MRAMS)

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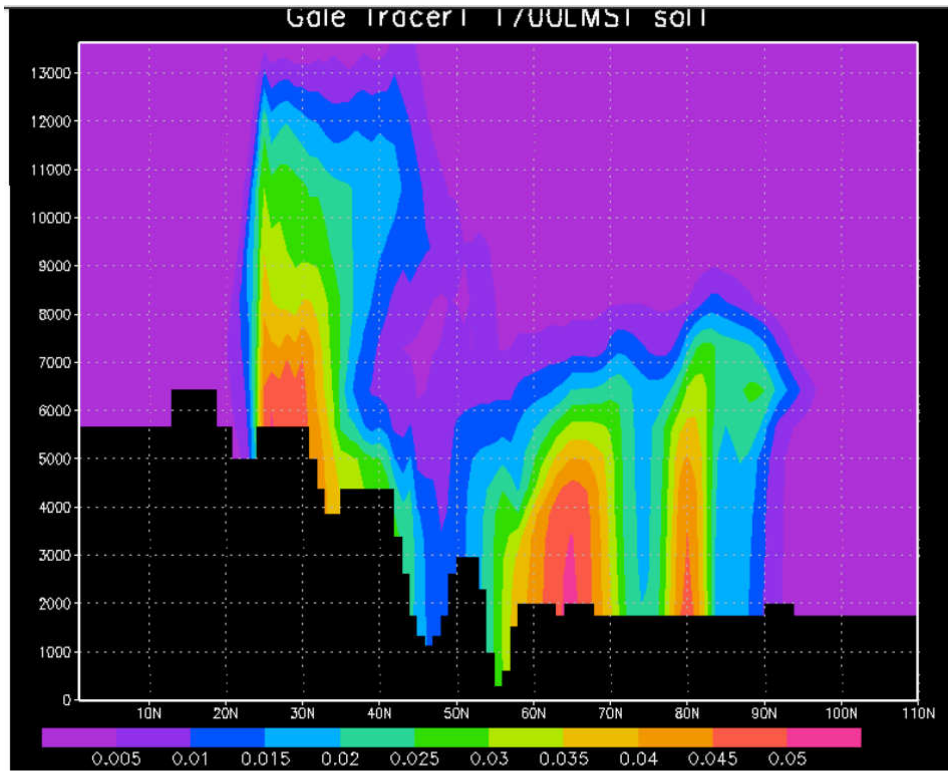
EGU Abstract 2016

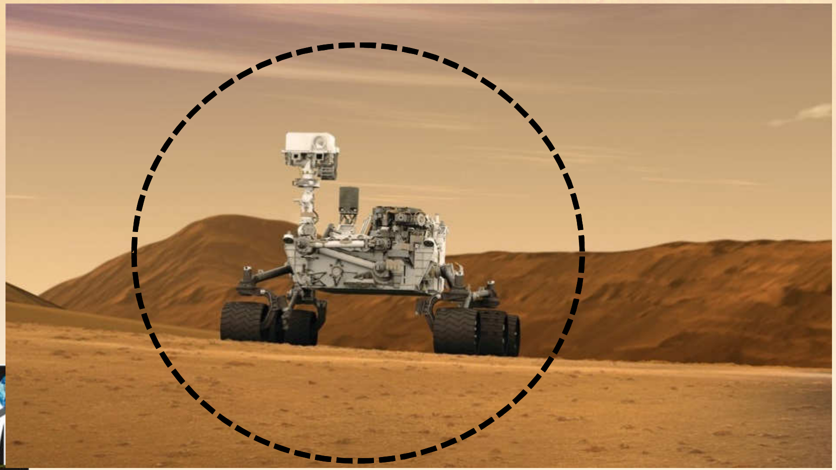


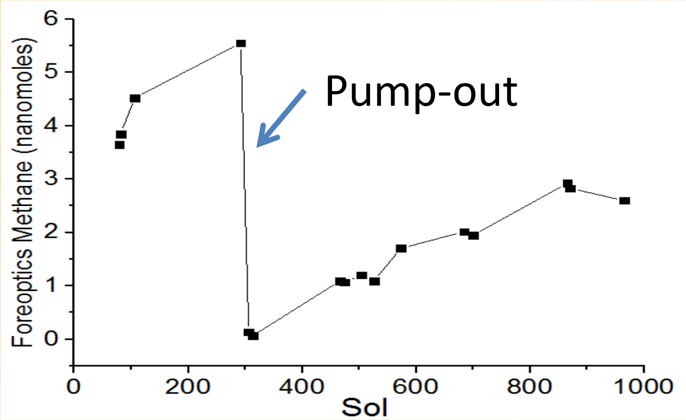
- Modeling supports local source within Gale Crater with existing chemistry, OR
- Source outside Gale Crater with subsequent deep mixing and rapid destruction

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.





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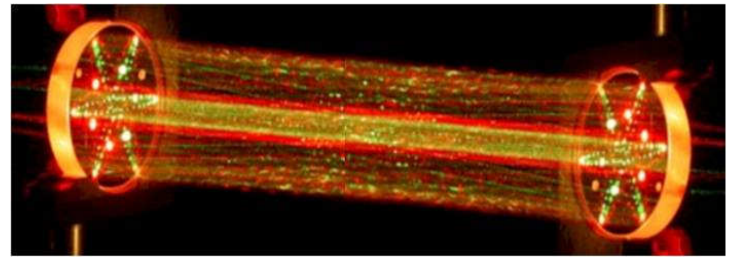
TLS-SAM Methane Results Summary

- The very low background level of methane (~0.7 ppbv) could result from the UV degradation of surface organics, but is 3 times lower than model predictions. A geological or biological source cannot be determined. A seasonal dependence or time decay may be evident.
- The sudden spike in methane (~7 ppbv) indicates a release from either modern production or from storage of older methane in clathrates. Higher daytime values suggest a northerly source. No obvious correlations with oxygen, other species, meteoritic infall, cometary debris. Seasonal repetition not observed.
- The sudden rise in methane and the fact that it came back down quickly indicate the source was most likely relatively localized and small.
- These observations of methane are suggestive of a *currently active Mars*.

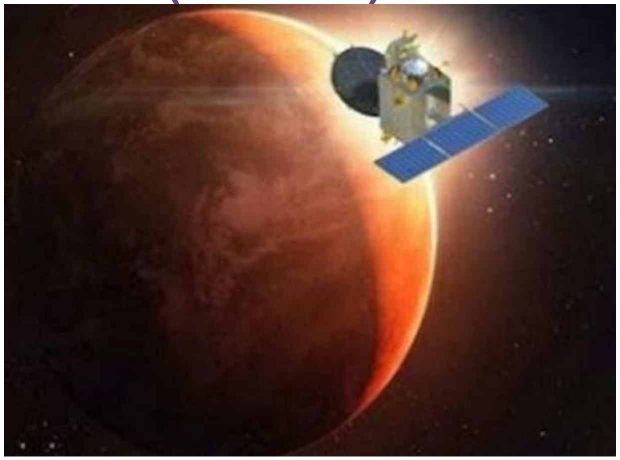
Advanced TLS Instruments for Mars Methane Isotope Measurements

- TLS-SAM-MSL (Webster, Mahaffy)
  - Sensitivity 0.1 ppbv with enrichment



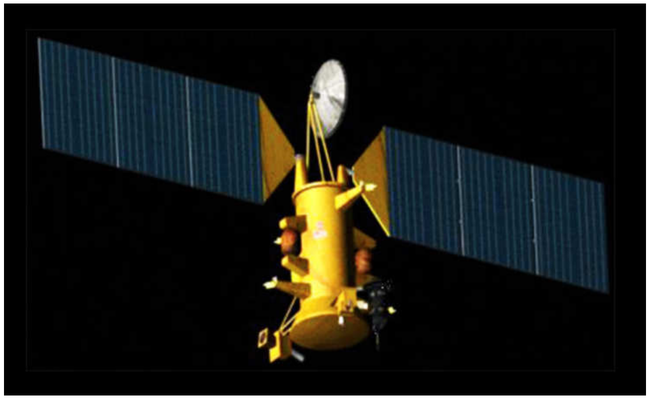
- Enhanced pathlength digital TLS (Webster, Flesch et al. JPL)
  - Sensitivity 20 pptv with enrichment
- Cavity Ringdown TLS (Okamura (Caltech), Christensen (JPL))
  - Sensitivity 10 pptv
- Integrated Cavity Output Spectroscopy (ICOS)- Vinogradov (IKI, Russia) for ExoMars 2018 Lander
  - Sensitivity <50 pptv

MOM's Methane Sensor for Mars (MSM)



- ISRO's first planetary mission after successful Chandrayaan Moon mission
- Entered Mars orbit Sep 2014
- Methane spectrometer will subtract solar reflectance at 1.65 µm from that at 3.3 µm to produce column CH_4 in a global map.
- Sensitivity undetermined, expected 10 ppbv

NOMAD on ExoMars Orbiter



- Nadir and Occultation for MArs Discovery (NOMAD) – two instruments, echelle grating, 0.2-0.4 cm^{-1} resolution
- PI is Ann Vandaele, Belgian Institute for Space Aeronomy
- Expected detectivity of ~25 pptv in solar occultation, and 11 ppbv in nadir view.

MATMOS on ExoMars (Mars 2022+?)

- Solar occultation orbiting FTIR with 0.03 cm^{-1} spectral resolution
- Long pathlength (~10 km), high vertical resolution
- Huge number of spectral lines, IR bands, many molecules simultaneously
- PI's Paul Wennberg (Caltech) and Vicky Hipkin (Canadian Space Agency), with Drummond, Toon, Allen, Blavier, Brown, Kleinbohl, Abbatt, Lollar, Strong, Walker, Bernath, Clancy, Coutis, DesMarais, Eiler, Yung, Encrenaz, McConnell