Measuring Methane on Mars
(from telescopes on Earth, from the surface of Mars, and from orbit around Mars)

Paul Mahaffy
NASA Goddard Space Flight Center
September 18, 2019

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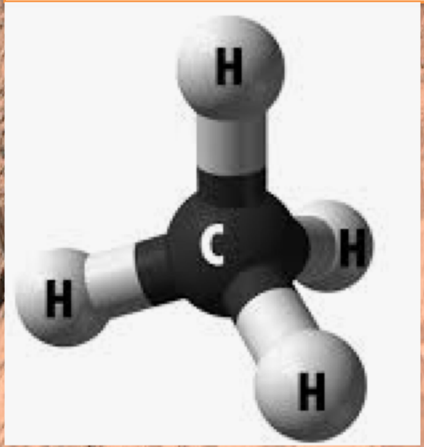
(from telescopes on Earth, from the surface of Mars, and from orbit around Mars)

The Martian METHANE MYSTERY

- Where does it come from?
- Why don't all the measurements agree?
- What does it all mean as we look for possible past or present life on Mars?



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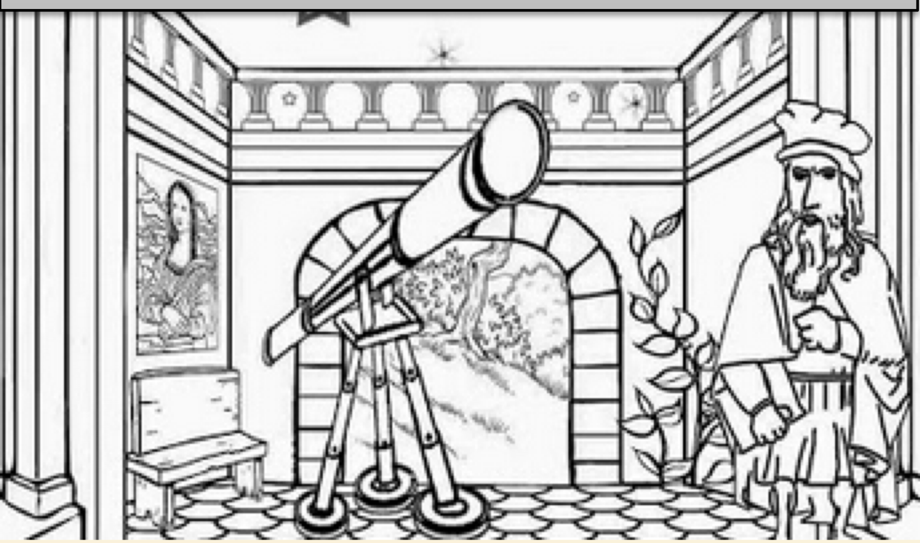
ARE WE ALONE IN THE UNIVERSE ?
WHERE AND HOW DO WE SEARCH FOR LIFE ?

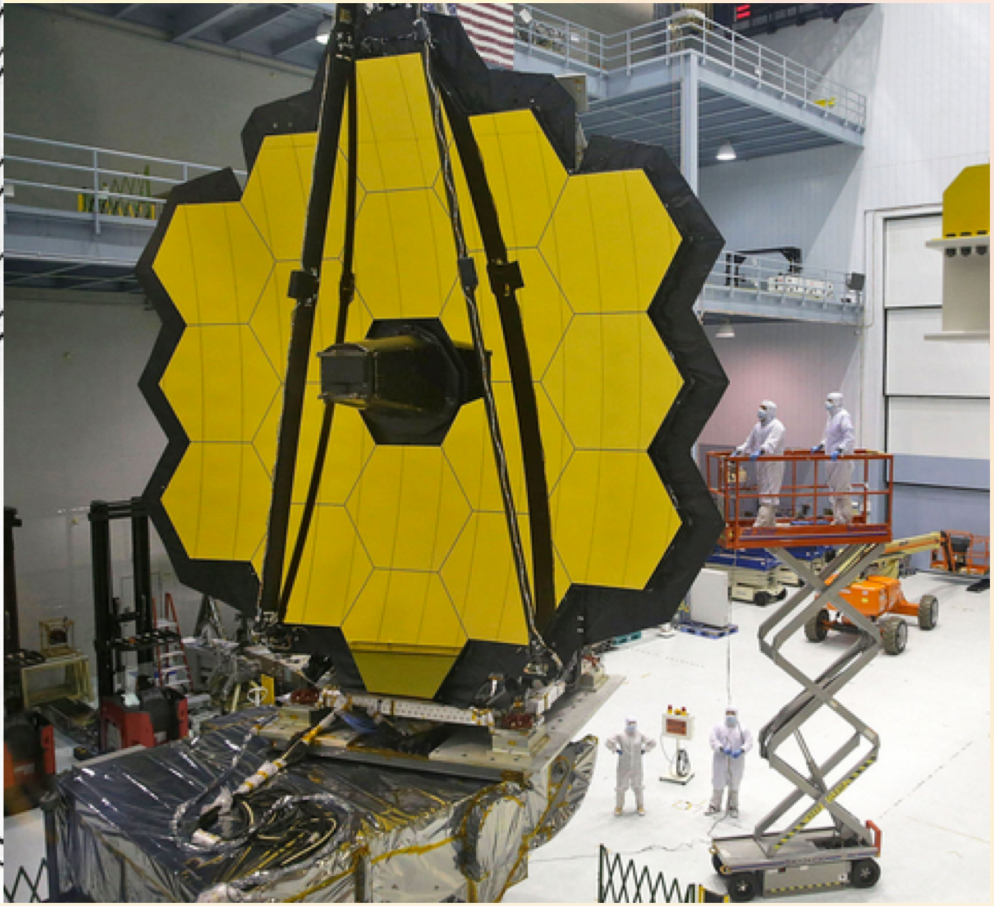
NASA's Strategic Objectives

- Discover the Secrets of the Universe
- Search for Life Elsewhere
- Safeguard and Improve Life on Earth

Currently there are ~4,000 confirmed planets in thousands of systems, with hundreds of systems having more than one planet.

Although Galileo could not detect methane with his 1610 telescope this measurement will be important for future exoplanet observations with big telescopes such as the James Webb and follow on space observatories.





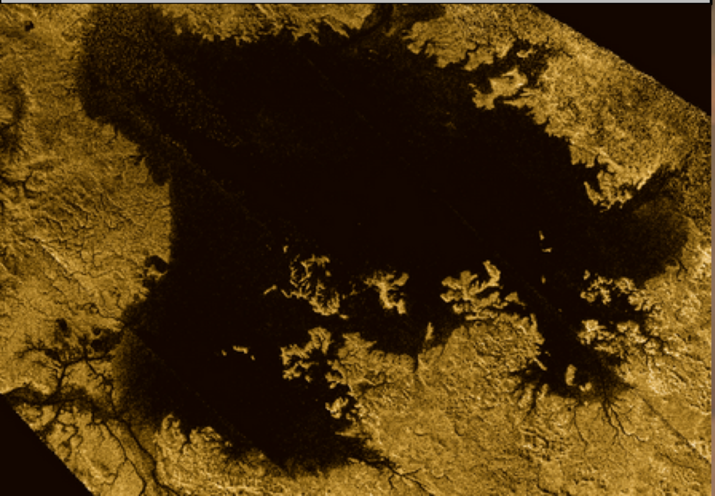
In our own solar system molecular biosignatures may reveal prebiotic chemistry or even the presence of present or past life in ocean worlds.

Measurements of methane in addition to complex organic molecules are an important element of this search

7/25/2018 Sub Glacial lake reported on Mars !

In our own solar system molecular biosignatures may reveal prebiotic chemistry or even the presence of present or past life in ocean worlds.

- Saturn's moon Titan has almost 5% methane in it's atmosphere.
- This carbon building block together with nitrogen and hydrogen leads to a rich organic chemistry.
- But Titan is so cold that there is methane rain and methane lakes such as Ligiea Mare shown below

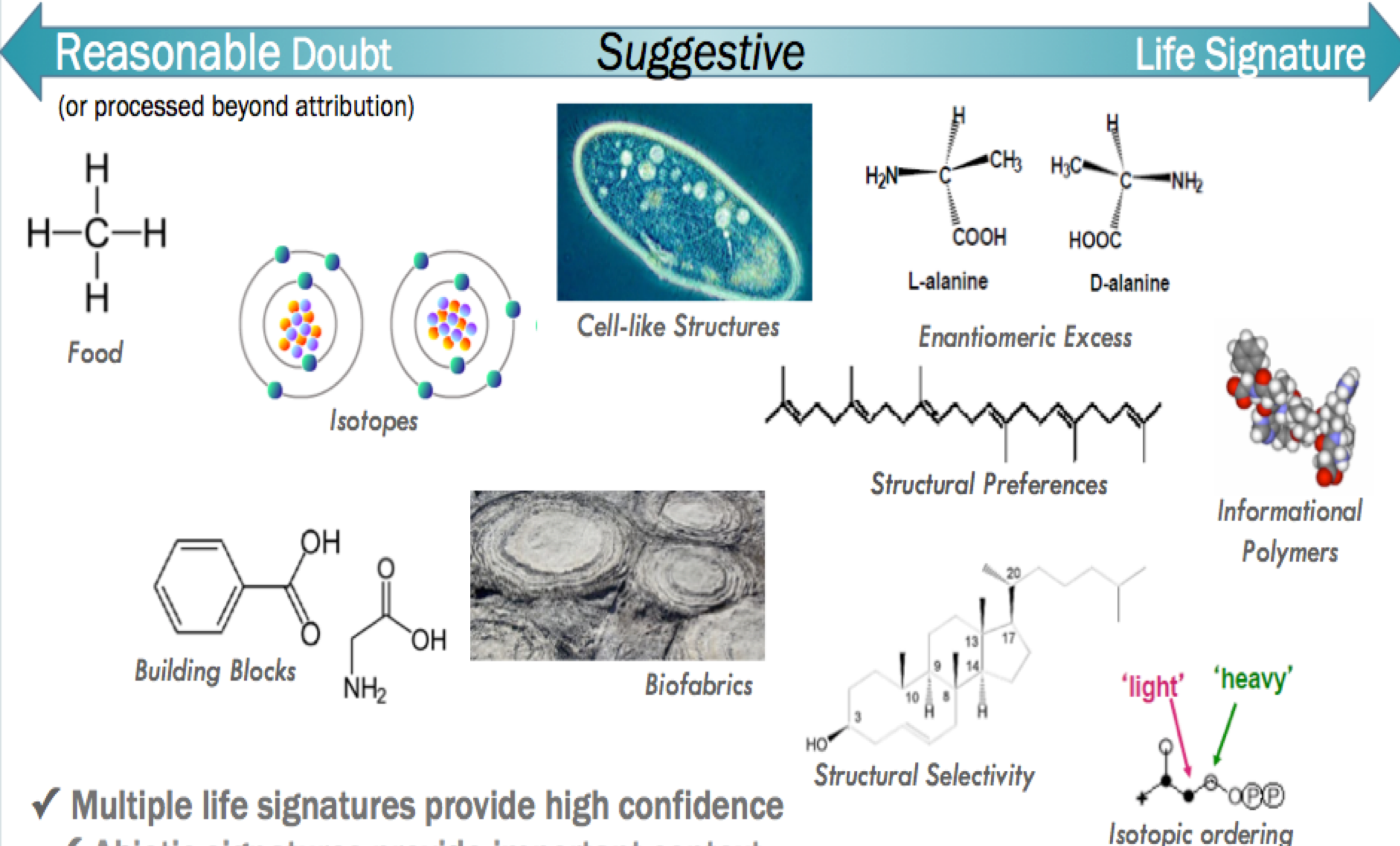


OCEAN WORLDS

Titan's hydrocarbon-rich surface looking for chemical complexity –

This rotocraft is being developed for NASA's latest New Frontier mission

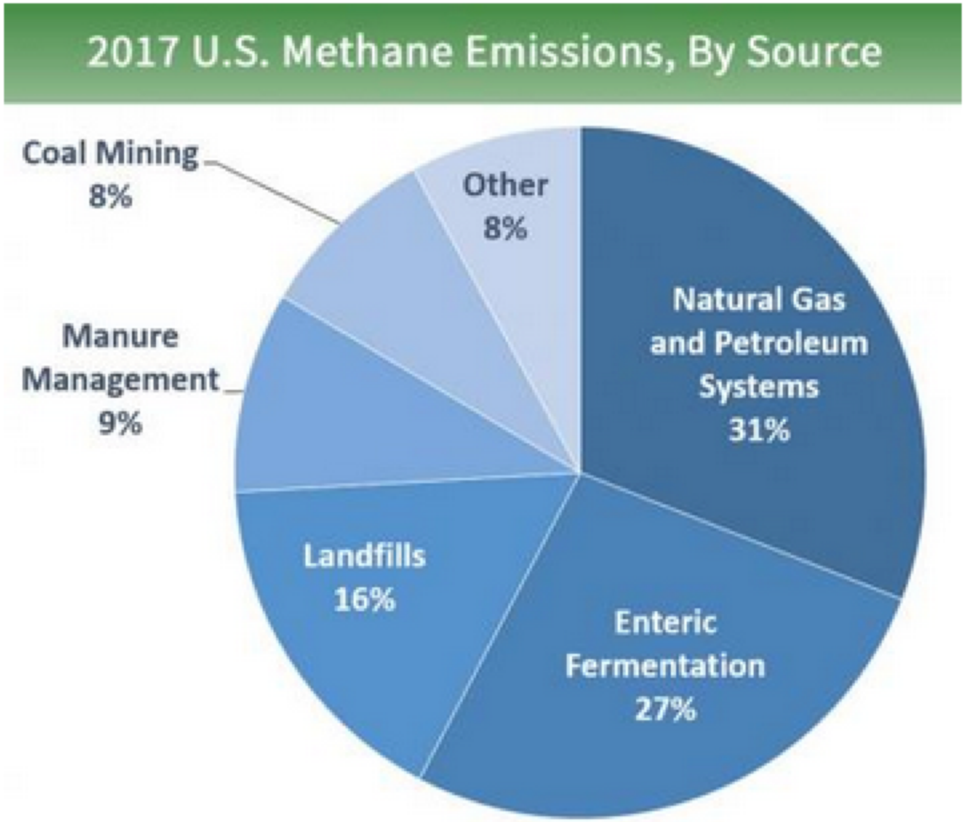
Measurements of simple molecules, their isotopes, and complex molecules all address the grand challenge to find extraterran life !



✓ **Multiple life signatures provide high confidence**

✓ **Abiotic signatures provide important context**

Most methane in Earth's atmosphere comes from human activity
Natural sources include volcanoes, methane clathrates, and permafrost



Note: All emission estimates from the *Inventory of U.S. Greenhouse Gas Emissions and Sinks: 1990–2017*.

Lifetime in Atmosphere: 12 years

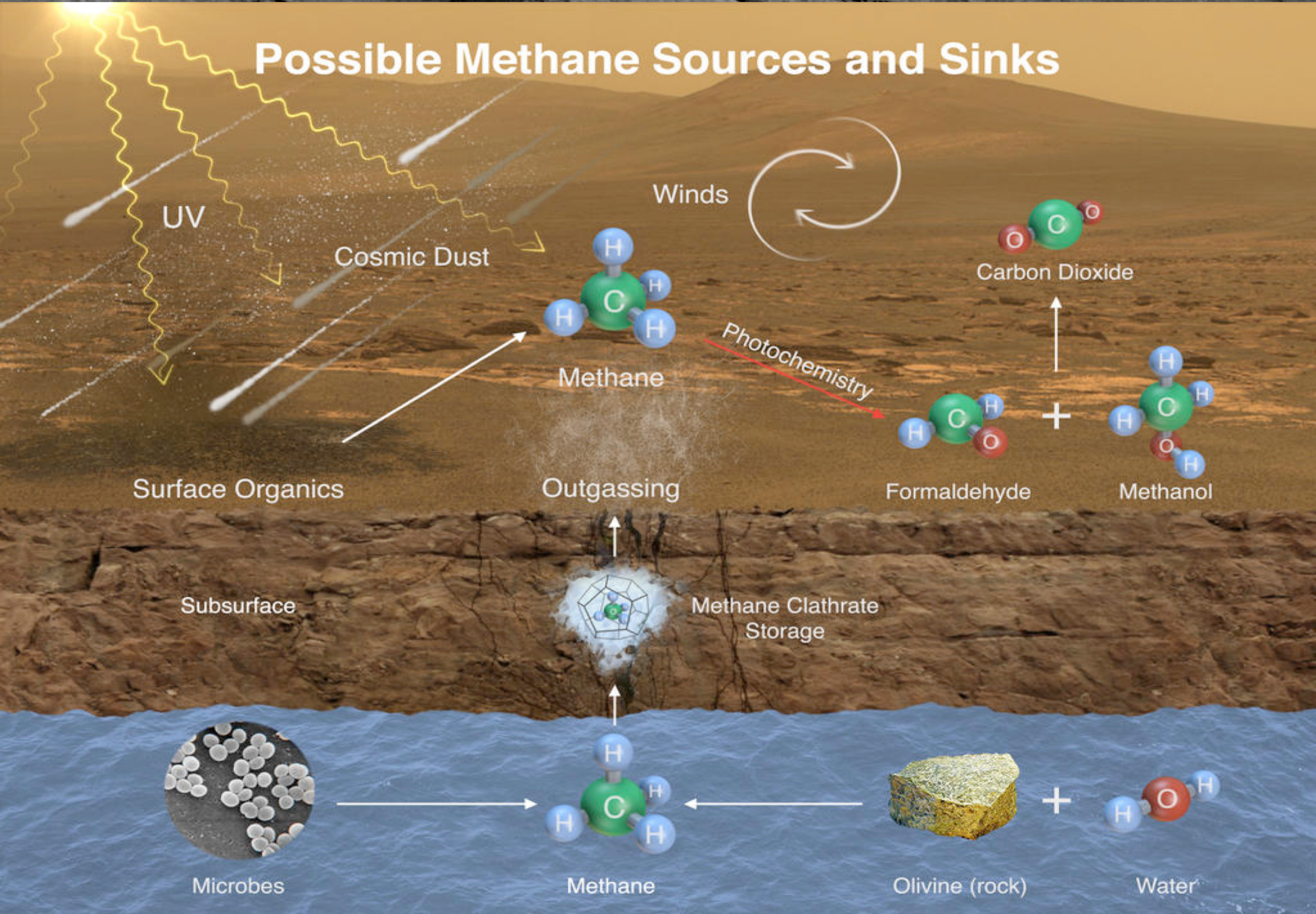
Global Warming Potential **(100-year)**: 25[1]

en.wikipedia.org/wiki/Enteric_fermentation

Ruminant animals are those that have a rumen. A rumen is a multichambered stomach found almost exclusively among some artiodactyl mammals, such cattle, deer, and camels, enabling them to eat cellulose-enhanced tough plants and grains that monogastric (i.e., "single-chambered stomached") animals, such as humans, dogs, and cats, cannot digest.

Enteric fermentation occurs when methane (CH_4) is produced in the rumen as microbial fermentation takes place. Over 200 species of microorganisms are present in the rumen, although only about 10% of these play an important role in digestion. Most of the CH_4 byproduct is belched by the animal, however, a small percentage of CH_4 is also produced in the large intestine and passed out as flatulence.

BUT methane by itself on Mars is not a biosignature



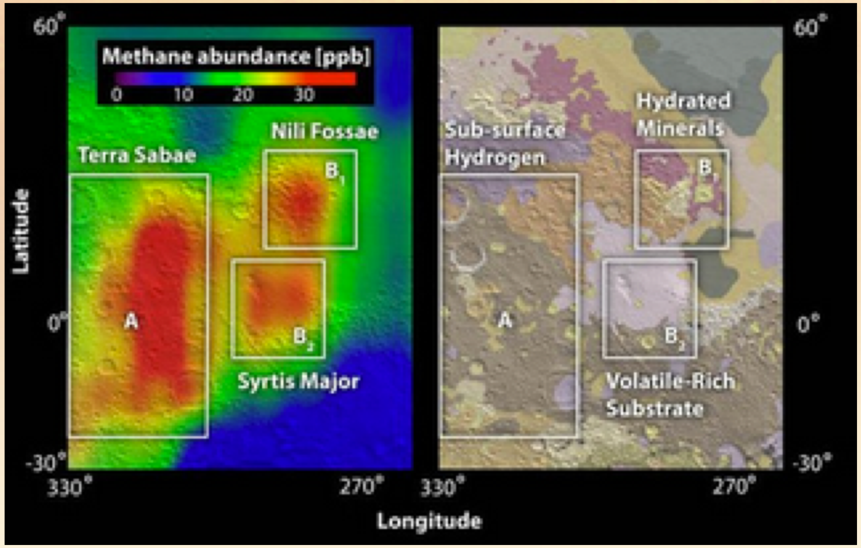
The search for martian methane from telescopes on Earth and from ESA's Mars Express Planetary Fourier Spectrometer

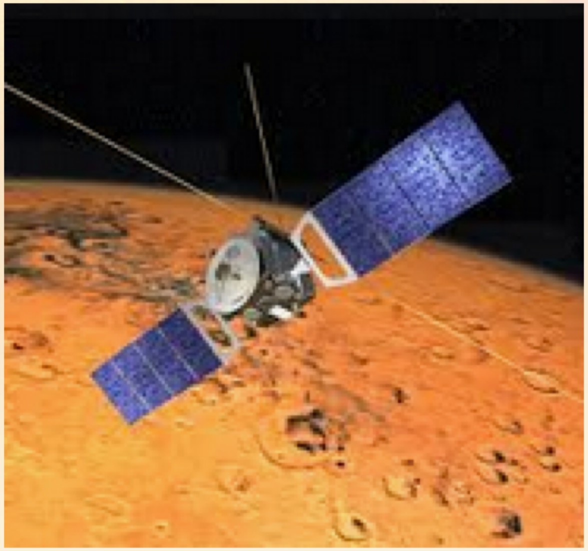
Michael Mumma et al. from 2004 observations
- 10's of parts per billion enhanced in regions of changing topography and over Valles Marineris

Vladimir Kranopolski et al., from another telescope
- 10 ppb suggesting 270 tons of CH_4 produced per year with an atmospheric lifetime of 340 years

Geronimo Villanueva et al.from later observations
- Upper limit of 7 ppb

Vittorio Formisano et al. from Mars Express
- 15 ppb secured by averaging more than 15,000 spectra
- Suggested source was northern cap summer release





These observations immediately raised some great questions

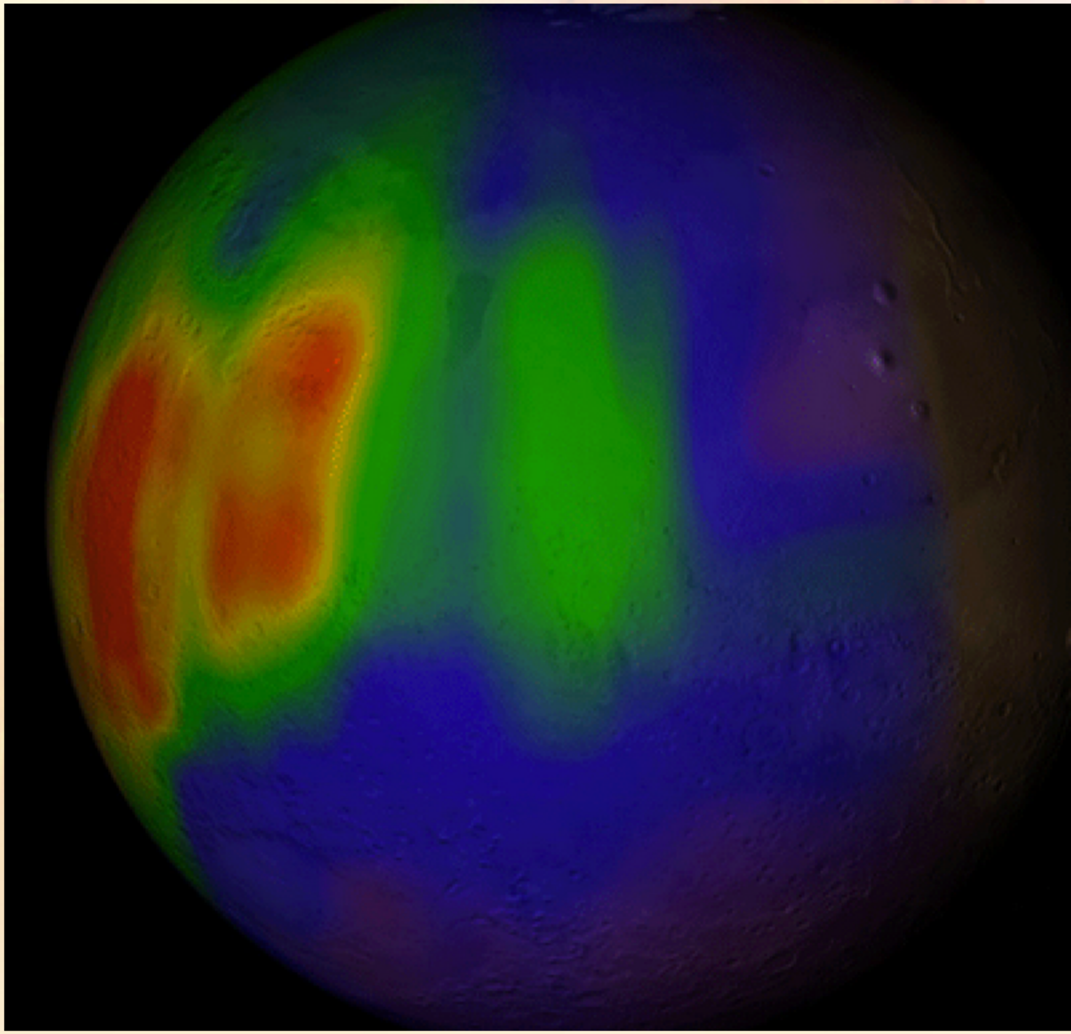
Mischna et al.
LeFevre and Forget

How could you have these gradients if the methane lifetime is really greater than 300 years?

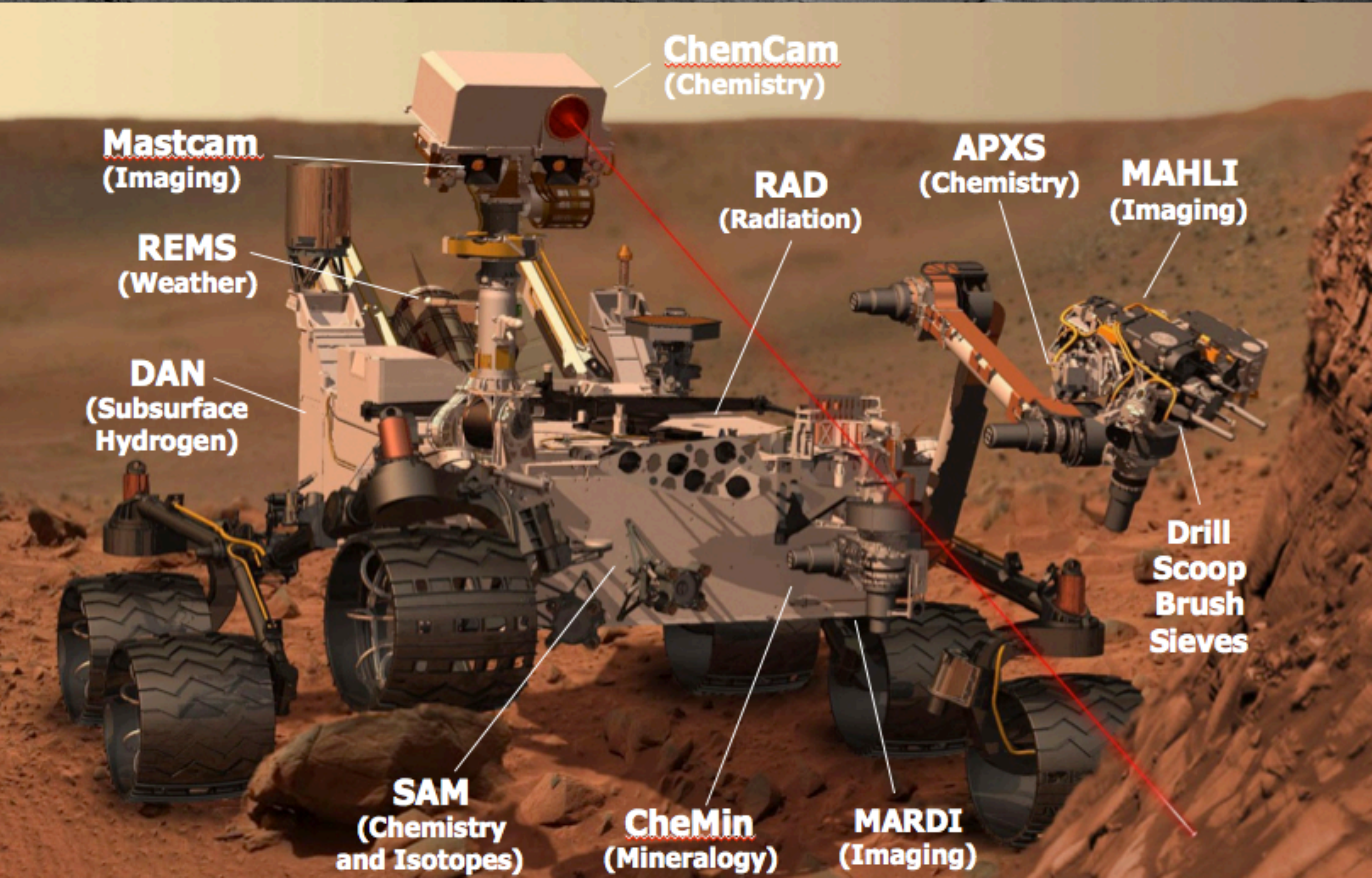
Would not a persistent plume require a release over months and a faster decay than photochemistry would allow?

Zahnle et al.
Was the terrestrial methane properly accounted for?

If chemical oxidation what was the source of the oxygen since over thousands of years the atmospheric oxygen would be consumed?

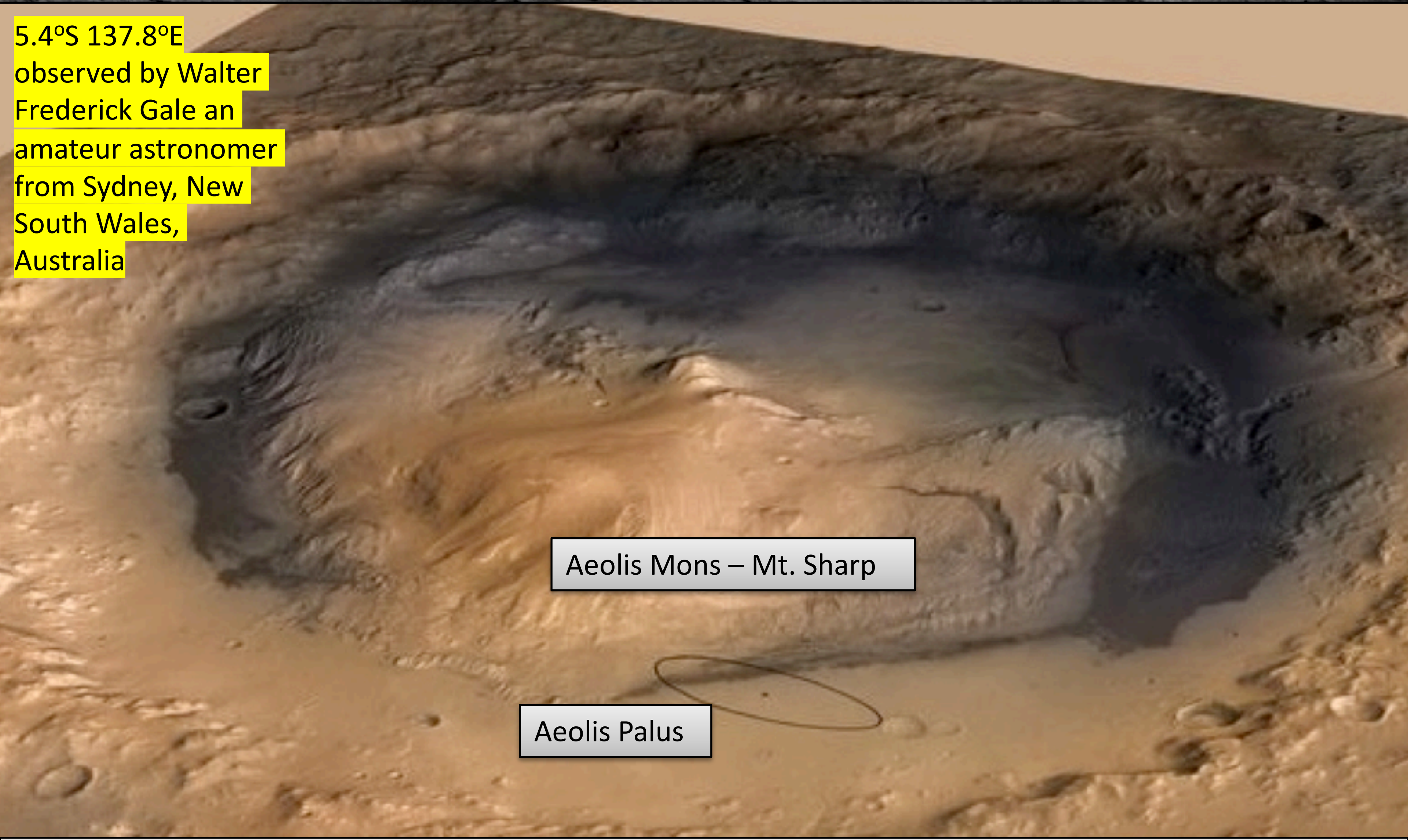


Curiosity's primary scientific goal is to explore and quantitatively assess a local region on Mars' surface as a potential habitat for life, past or present.



CAN ORGANICS FROM A CRATER FORMED MORE THAN BE PRESERVED ON MARS ???

5.4°S 137.8°E observed by Walter Frederick Gale an amateur astronomer from Sydney, New South Wales, Australia



Gale Crater is a 150 km diameter crater with a central 5 km high mound

Curiosity's primary scientific goal is to explore and quantitatively assess a local region on Mars' surface as a potential habitat for life, past or present.

Methane is only one of the measurements that give insight into chemical processes related to possible life on early Mars when surface water was more abundant

(1) Mineralogy and geology
→ **what is it telling us about the ancient crater environment ?**

(2) Isotopic composition of light elements
→ **is isotopic fractionation from biological or physical/chemical processes ?**

(3) Age of formation of rocks
→ **how long have aqueous conditions persisted on Mars ?**

(4) Cosmic radiation of surface materials
→ **are near surface organics preserved from cosmic radiation ?**

(5) Clays, perchlorates, sulfates, and hydrated minerals
→ **do chemical environments enable preservation or destruction of organics ?**

(6) Organic compounds extracted from soils and rocks
→ **what have we learned so far ?**

(7) Atmospheric composition and methane
→ **what does methane have to do with present or past life?**

Sample Analysis at Mars (SAM) Instrument Suite

SAM suite instruments and major subsystems:

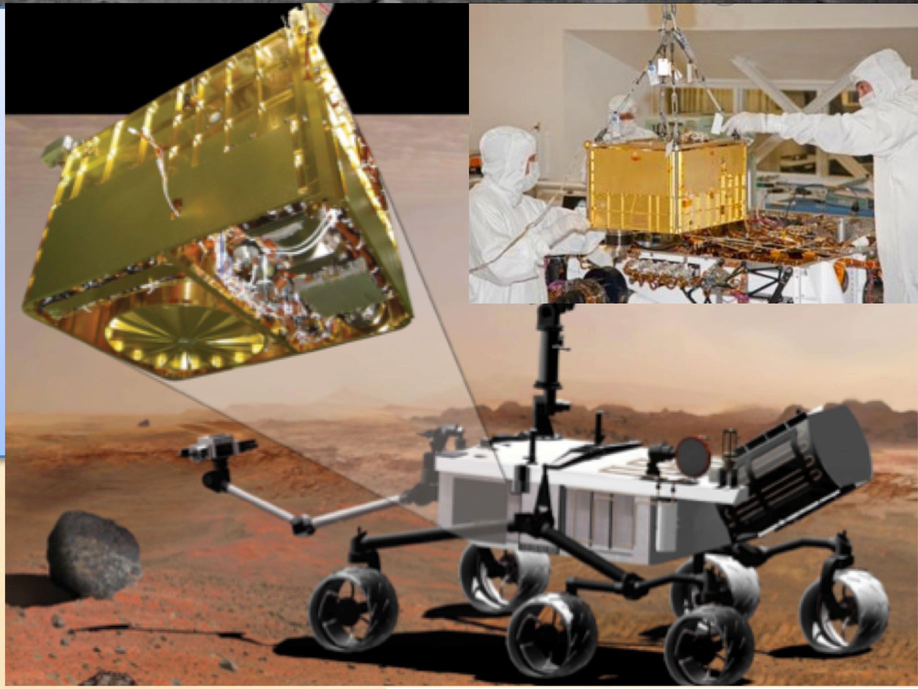
Quadrupole Mass Spectrometer-NASA GSFC

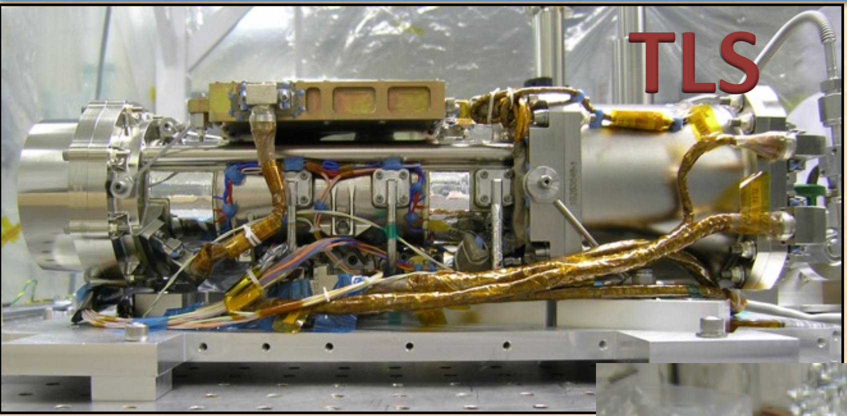
Gas Chromatograph-University of Paris, France

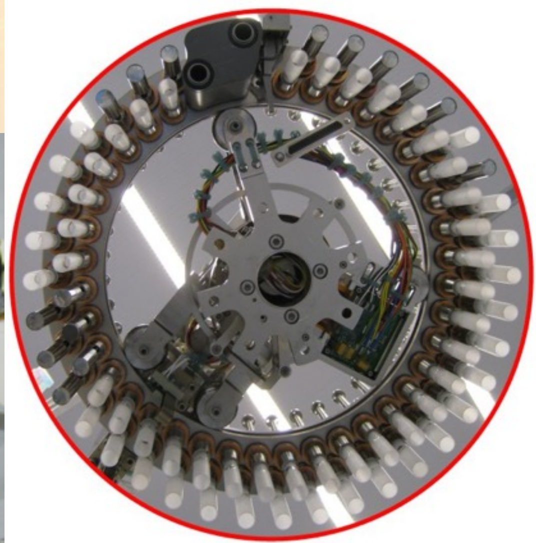
Tunable Laser Spectrometer-JPL

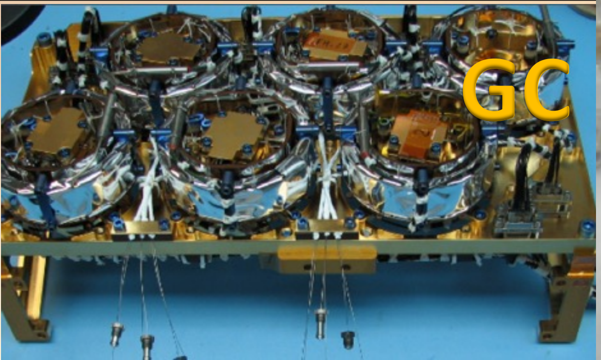
Gas Processing System-NASA GSFC

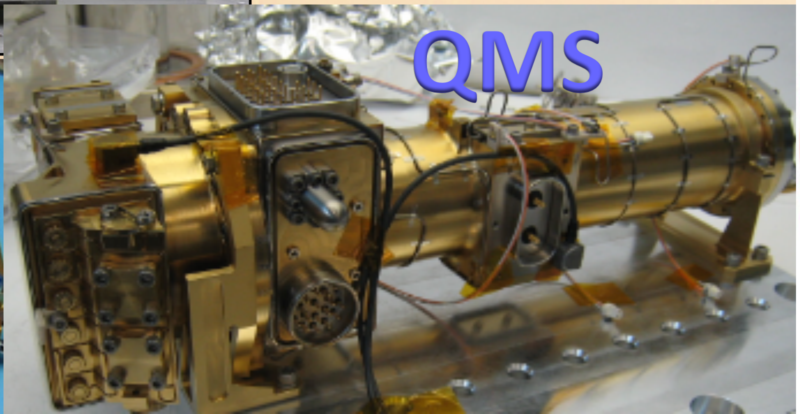
Sample Manipulation System-Honeybee Robotics

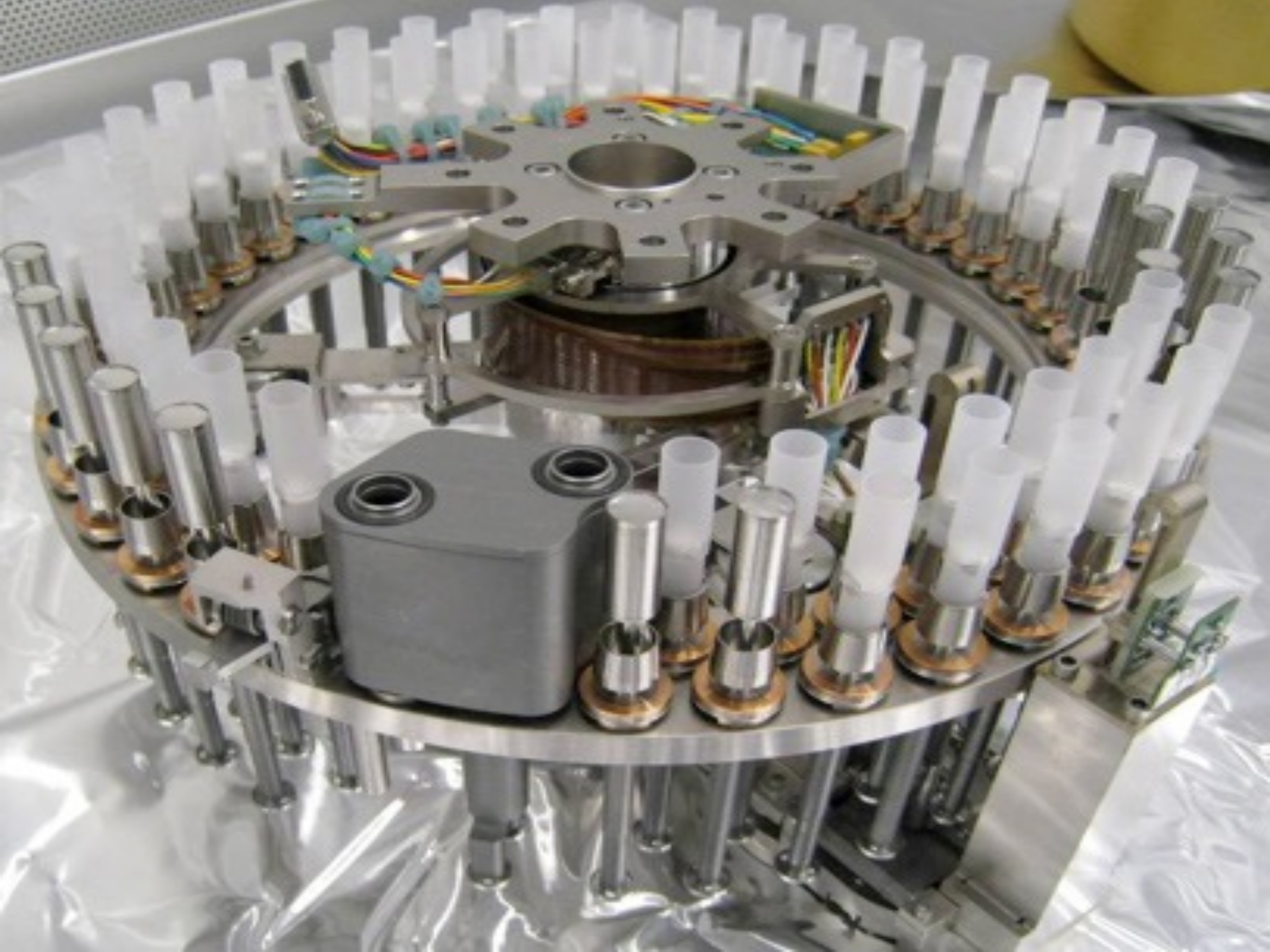




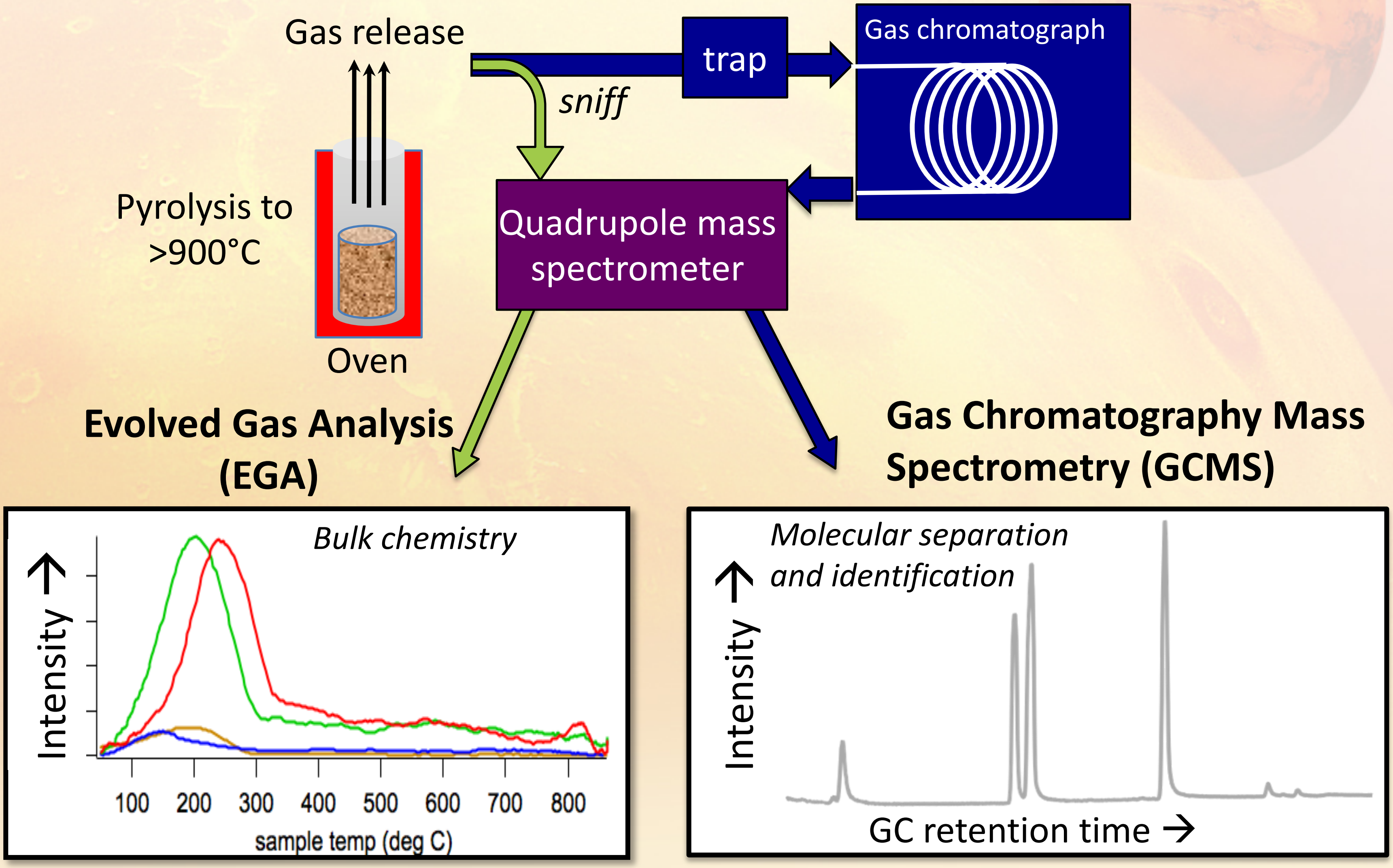






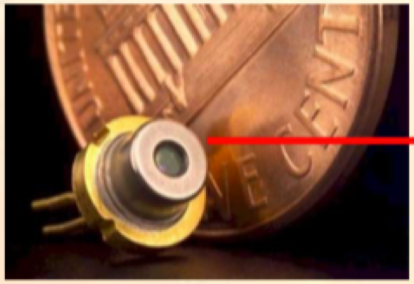


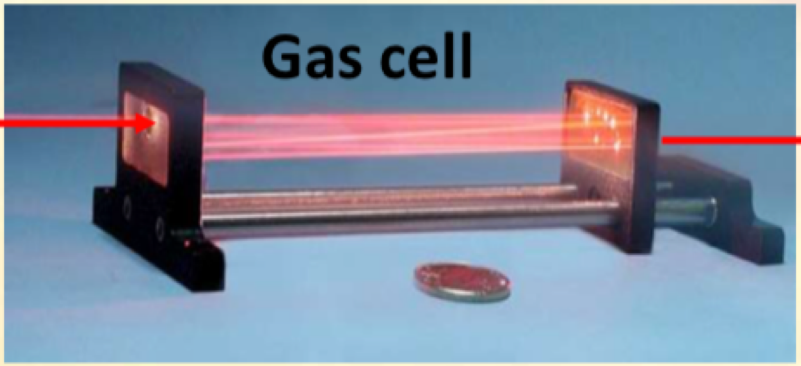
SAM Detects Volatiles Released from Sample



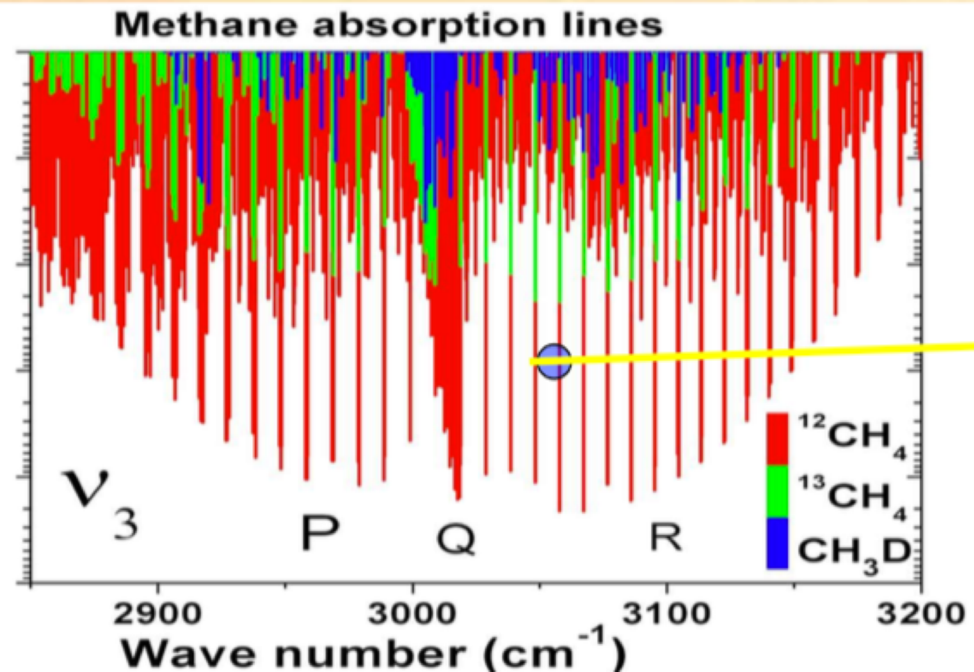
Credit: J. Eigenbrode

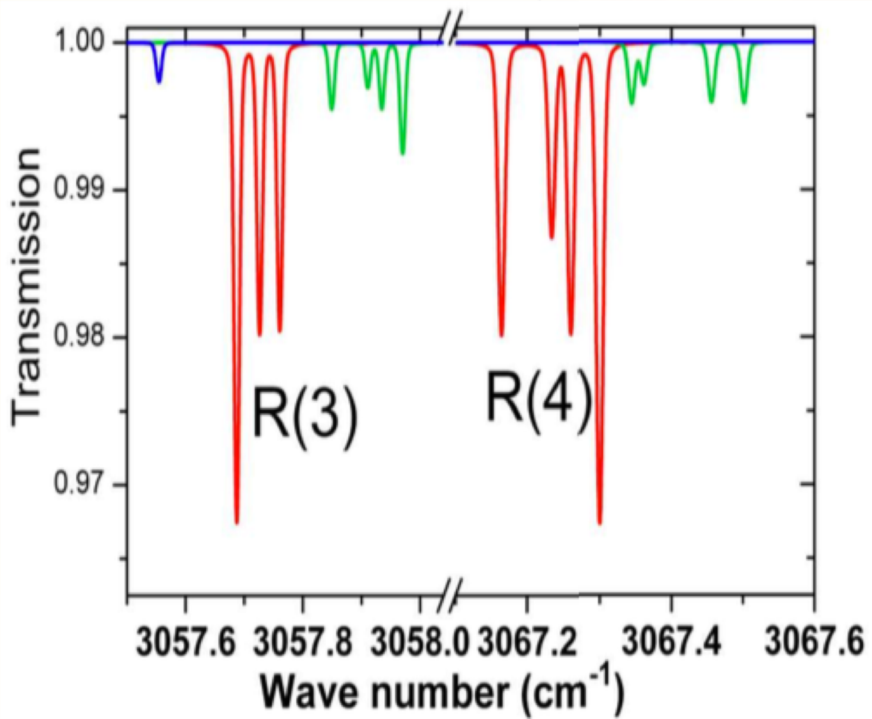
SAM's Tunable Laser Spectrometer (TLS) methane detector

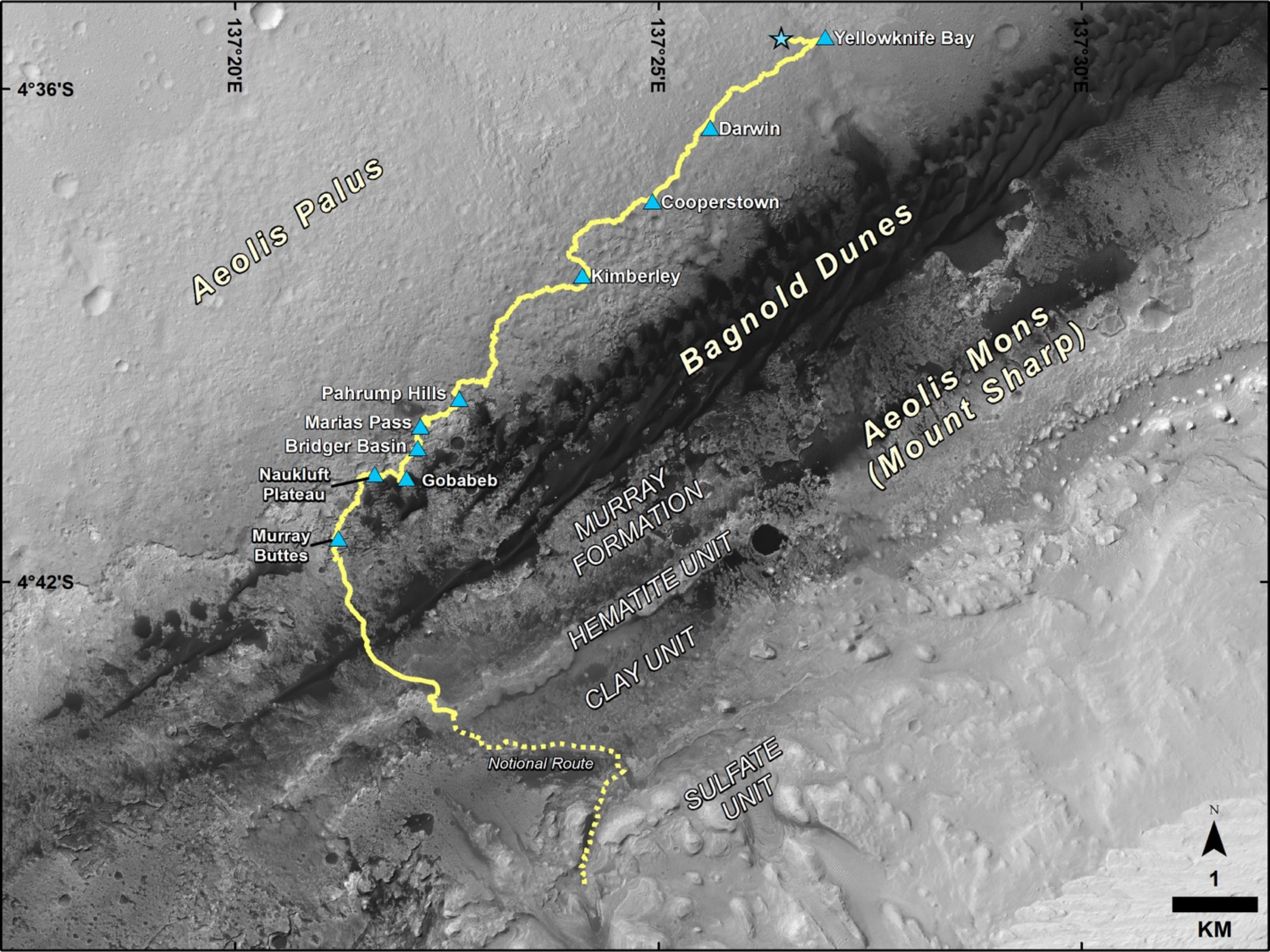

Tunable laser 1-12 µm




Detector






137°20'E
137°25'E
137°30'E
4°36'S
4°42'S
Yellowknife Bay
Darwin
Cooperstown
Kimberley
Aeolis Palus
Bagnold Dunes
Aeolis Mons
(Mount Sharp)
Pahrump Hills
Marias Pass
Bridger Basin
Naukluft
Plateau
Gobabeb
Murray
Buttes
MURRAY
FORMATION
HEMATITE UNIT
CLAY UNIT
Notional Route
SULFATE
UNIT
N
1
KM


John Klein
Sol 182
Cumberland
Sol 279
Windjana
Sol 621
Confidence Hills
Sol 759
Mojave
Sol 882
Telegraph Peak
Sol 908
Buckskin
Sol 1060
Big Sky
Sol 1119
Greenhorn
Sol 1137
Lubango
Sol 1320
Okoruso
Sol 1332
Oudam
Sol 1361
Marimba
Sol 1422
Quela
Sol 11464
Sebina
Sol 1495
MAHLI images credit
NASA/MSSS/ JPL
arranged by
Lakdawalia &
Sorenson

Curiosity's primary scientific goal is to explore and quantitatively assess a local region on Mars' surface as a potential habitat for life, past or present.

Measurements that give insight into chemical processes related to possible life on early Mars when surface water was more abundant

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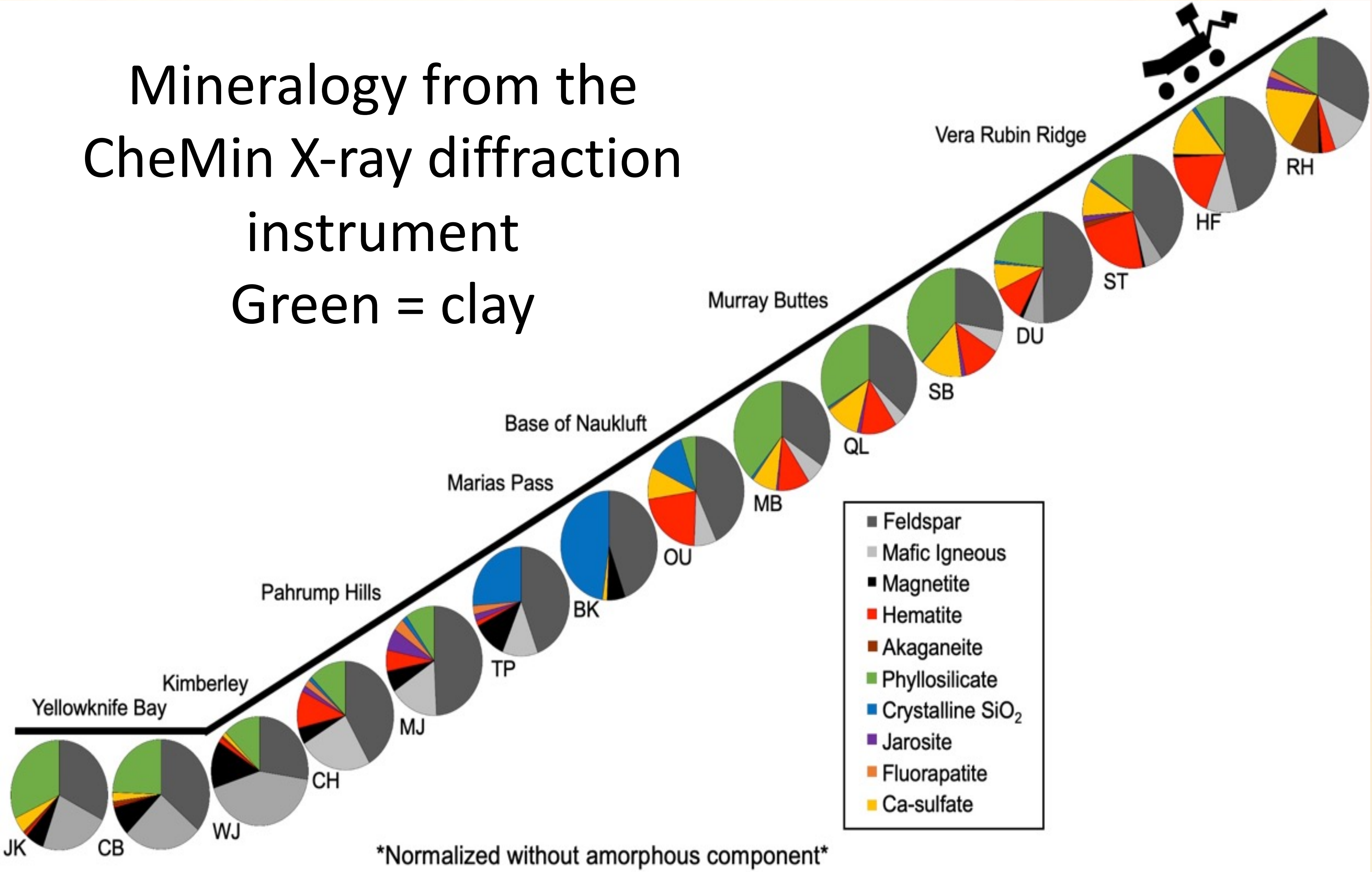
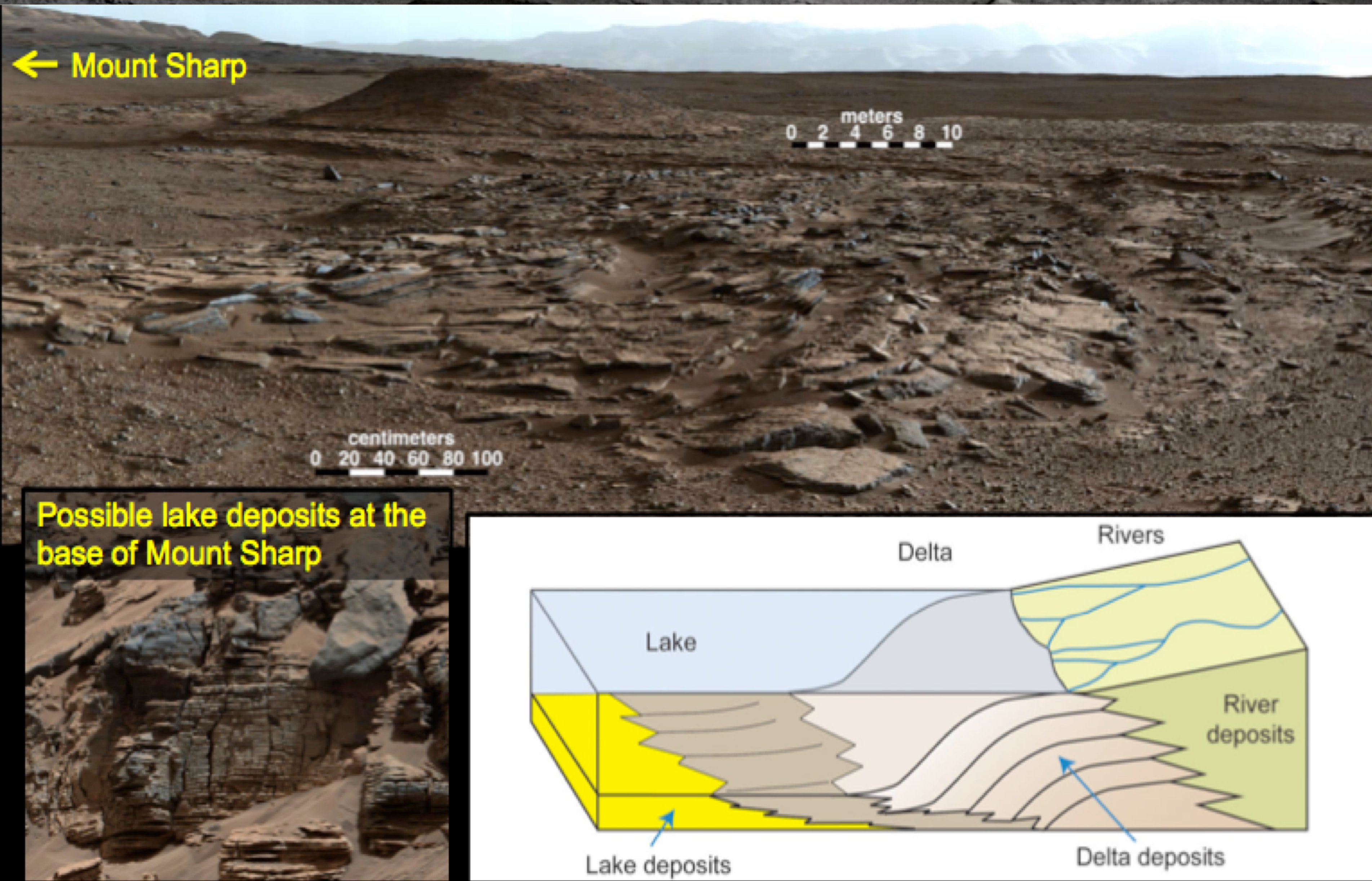
→ **what does methane have to do with present or past life?**

Changes in mineralogy with elevation → differences in sediment source regions, rock-forming processes, and subsequent alteration.

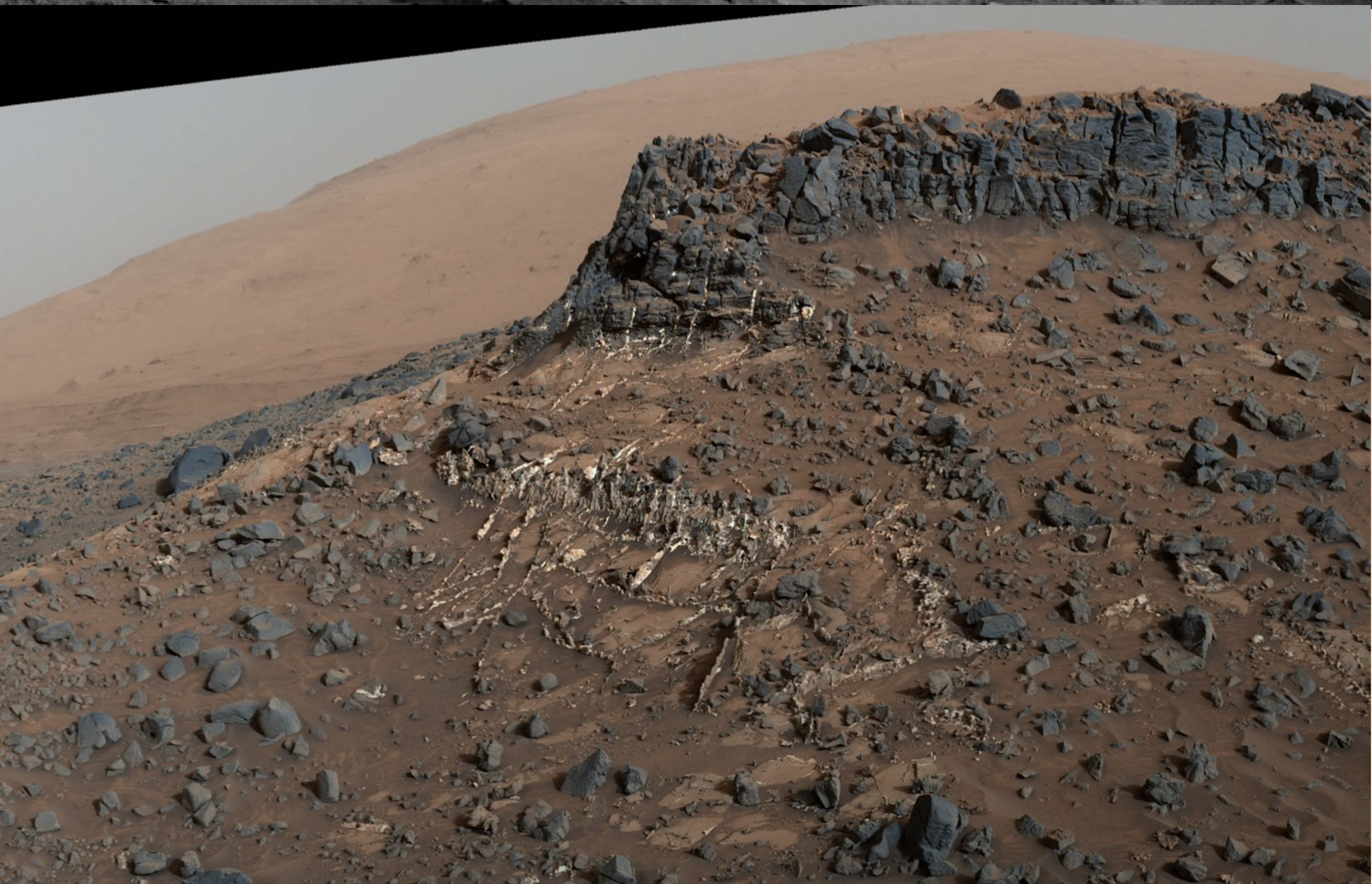
Mineralogy from the CheMin X-ray diffraction instrument
Green = clay



Sandstone beds on Gale Crater's plains indicate water-driven transport of sediment, building lower Mount Sharp from lake deposits



Mineral ($CaSO_4$ & B-rich) veins of fill fractures within the lake-formed mudstone → multiple generations of interaction with liquid water



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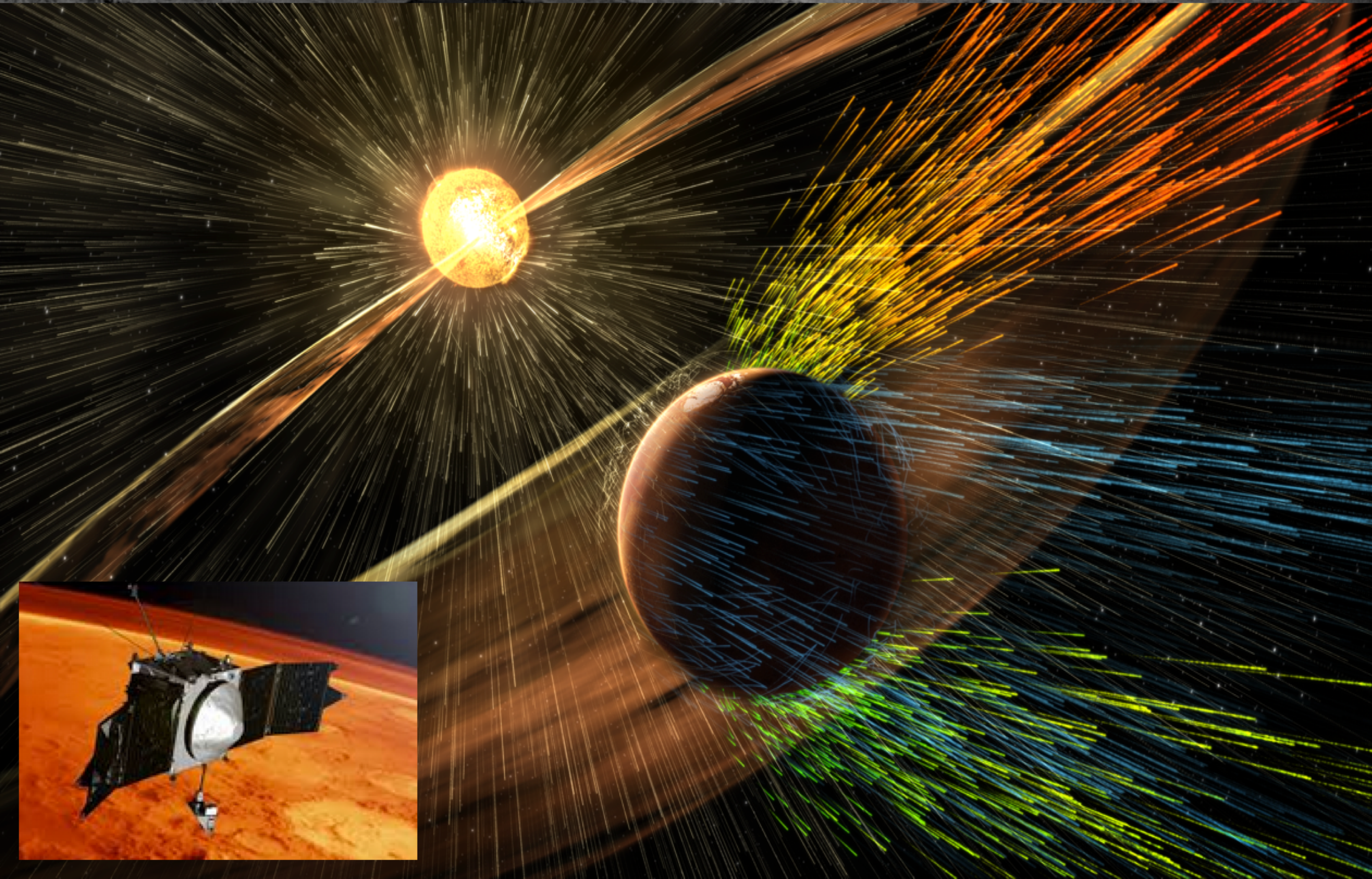
MSL and MAVEN exploring martian atmospheric loss over time. Atmospheric H, C, O, N, Ar, & Xe isotopes dominated by atmospheric escape processes



This is now

D/H and geological evidence suggests

THAT WAS THEN

P.R. Mahaffy and 26 CoAuthors, The imprint of atmospheric evolution in the D/H of Hesperian clay minerals on Mars, Science 23, 412-414 (2015).

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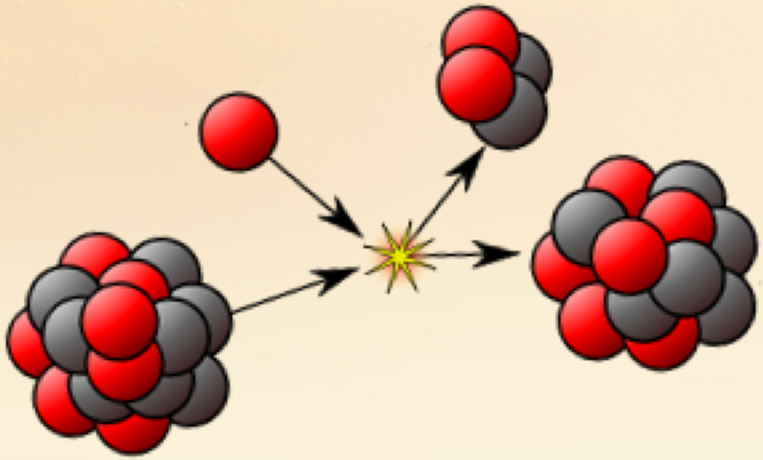
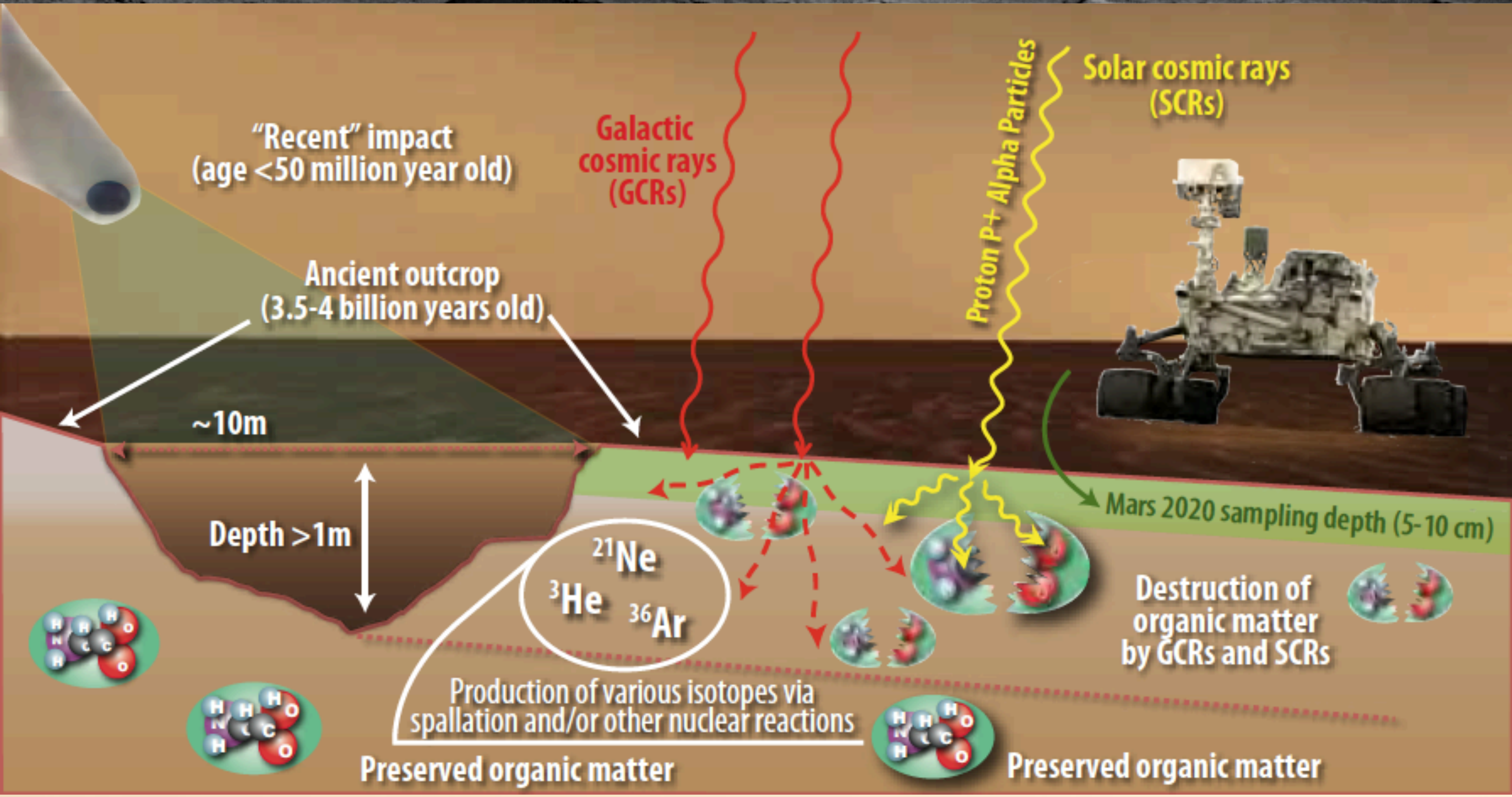
COSMIC RADIATION

- ^{3}He, ^{21}Ne, ^{36}Ar in Martian rocks can be produced only by Cosmic Rays (protons, alpha particles, etc.)
- CRs bombard Martian surface and cause nuclear reactions in the top few meters
- ^{3}He, ^{21}Ne – "spallation"; ^{36}Ar – "neutron capture"
- The more ^{3}He, ^{21}Ne, ^{36}Ar are in the rock the longer CR exposure of that rock had to be.

Even relatively short exposure to cosmic rays can transform most of the organic compounds



COSMIC RAY EXPOSURE AGE - but this radiation can also transform organic compounds

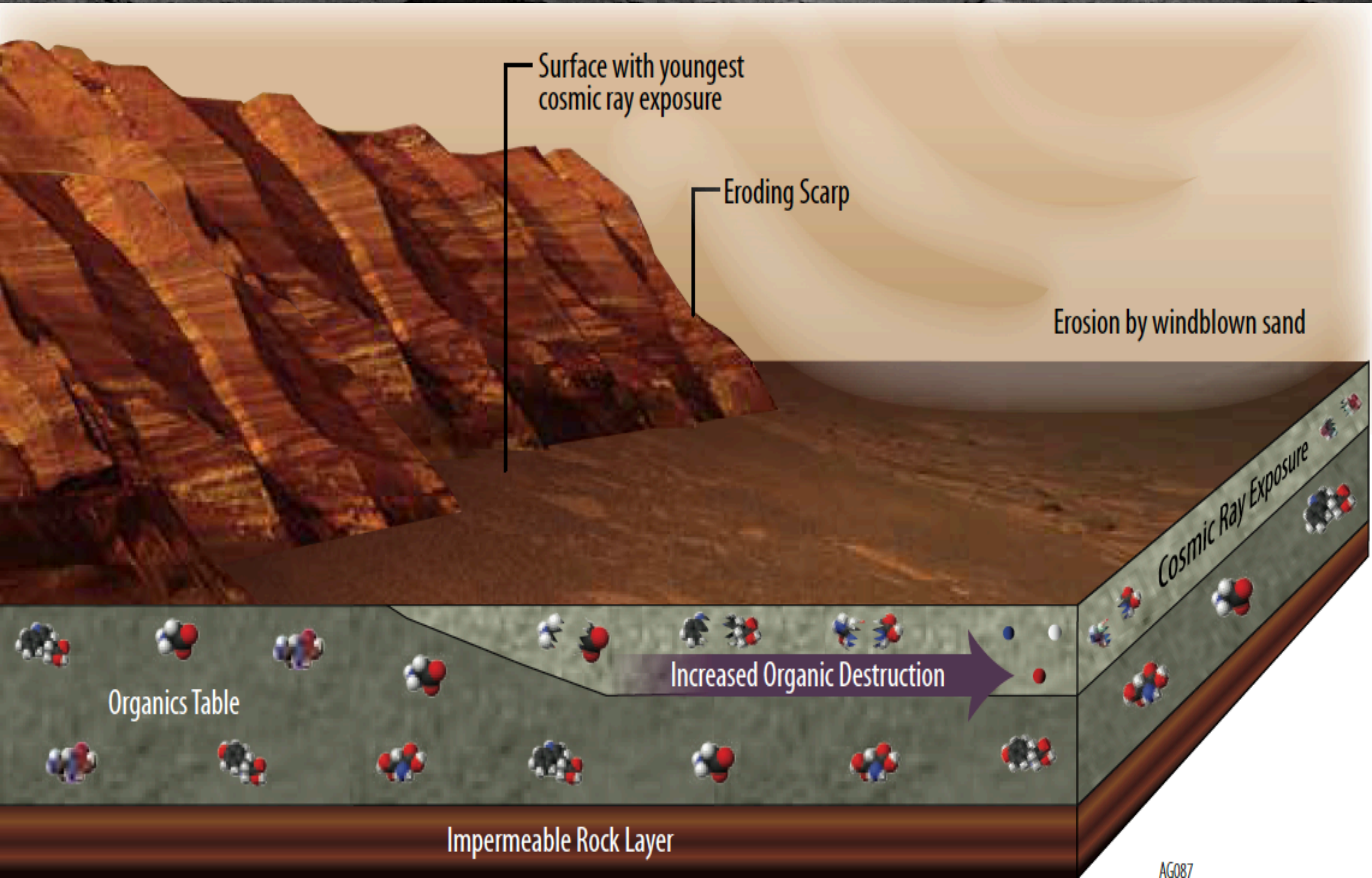


Nuclear spallation - ^{3}He from many elements; ^{21}Ne – Mg, Al, Si; ^{36}Ar – Ca, K

Neutron capture – ^{36}Ar from ^{35}Cl, ^{80}Kr from Br; ^{128}Xe from I

INDEPENDENT EXPOSURE AGE RESULTS (Ma) = ^{3}He 72$\pm$15, ^{21}Ne 84$\pm$28, ^{36}Ar 78$\pm$24

SAM noble gas measurements are pointing toward the best locations to search for minimally transformed organic compounds



First *in situ* rock formation age experiment on another planet

Sample Mass		0.135 ± 0.018 g
K-Ar System		$\pm 1\sigma$
K_2O (wt %)	0.50	0.08
^{40}Ar (nmol/g)	11.95	1.71
K-Ar Age (Ga)	4.21	0.35

Conclusion – rock sediment that washed down from the rim of Gale Crater was formed ~4.2 billion years ago – this consistent with crater densities

A 2-step K/Ar chronology measurement on a drilled sample containing jarosite gave an age of 2.12±0.36 billion years for this mineral

→ fluvial activity in Gale crater long after fluvial activity had been supposed to cease !!

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Formation

Microbes or meteoritic infall?

Concentration & lithification

Initial preservation and diagenesis

ionizing radiation?

Water, oxidants, salts, heat

Subsurface alteration

Surface alteration

ionizing radiation

Loss during analysis (e.g. chemical reactions)

Organics and taphonomic windows – it's what survives that counts!

A challenge with the detection and characterization of organics by SAM is an exploration the conditions that led to their preservation, i.e., their taphonomic windows

From SAM Evolved Gas (EGA) Experiment → noble gases, organic & inorganic compounds & many isotopes

Evolved gases

H_2O – from hydrated minerals, adsorbed water, or clays

SO_2 & H_2S - from sulfates & sulfides

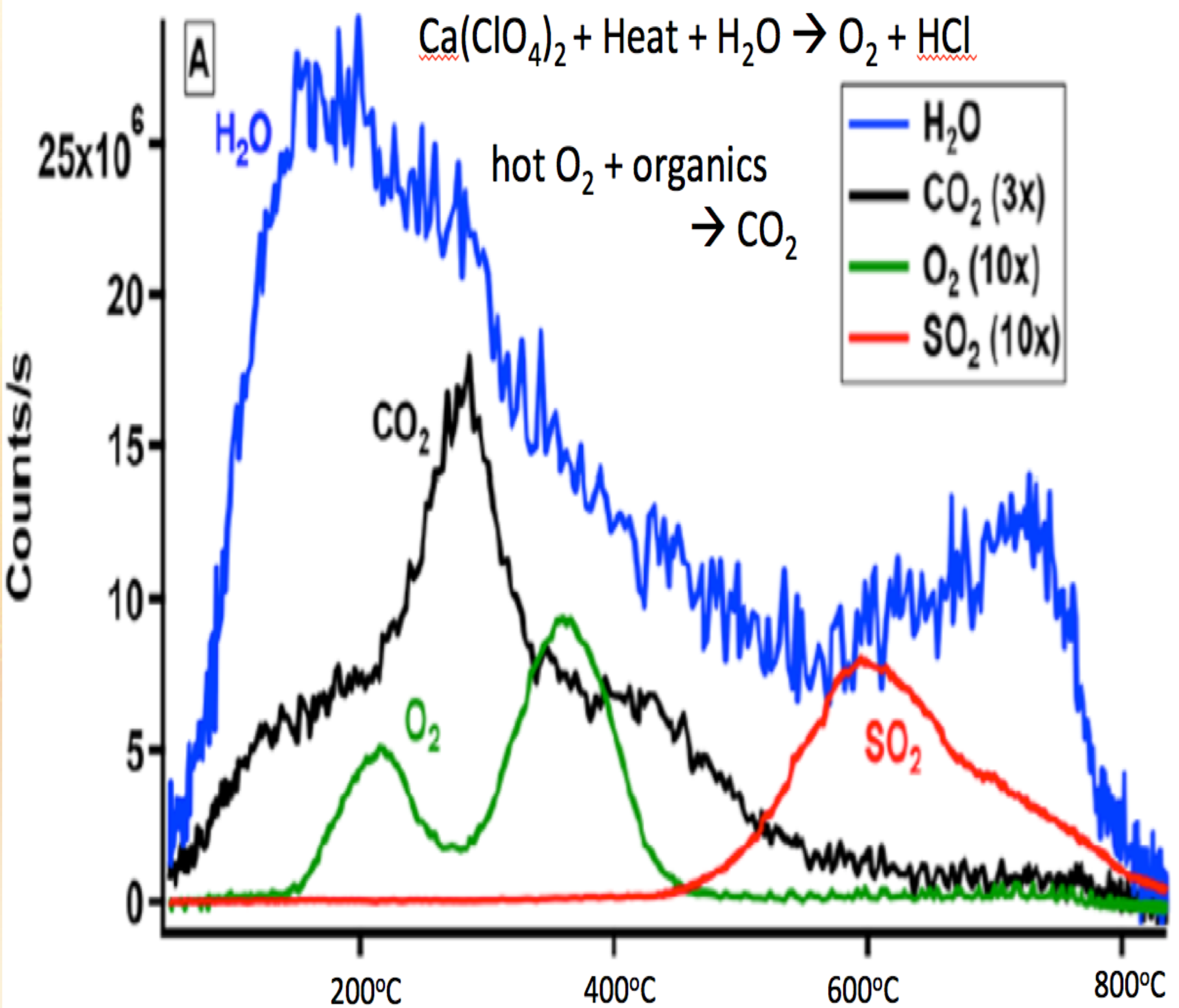
O_2 & HCl - from perchlorates or oxychlorine compounds

NO - from nitrates

He, Ar, Ne – rock formation & exposure age determinations

CO_2 & CO – from carbonates or combusted organics

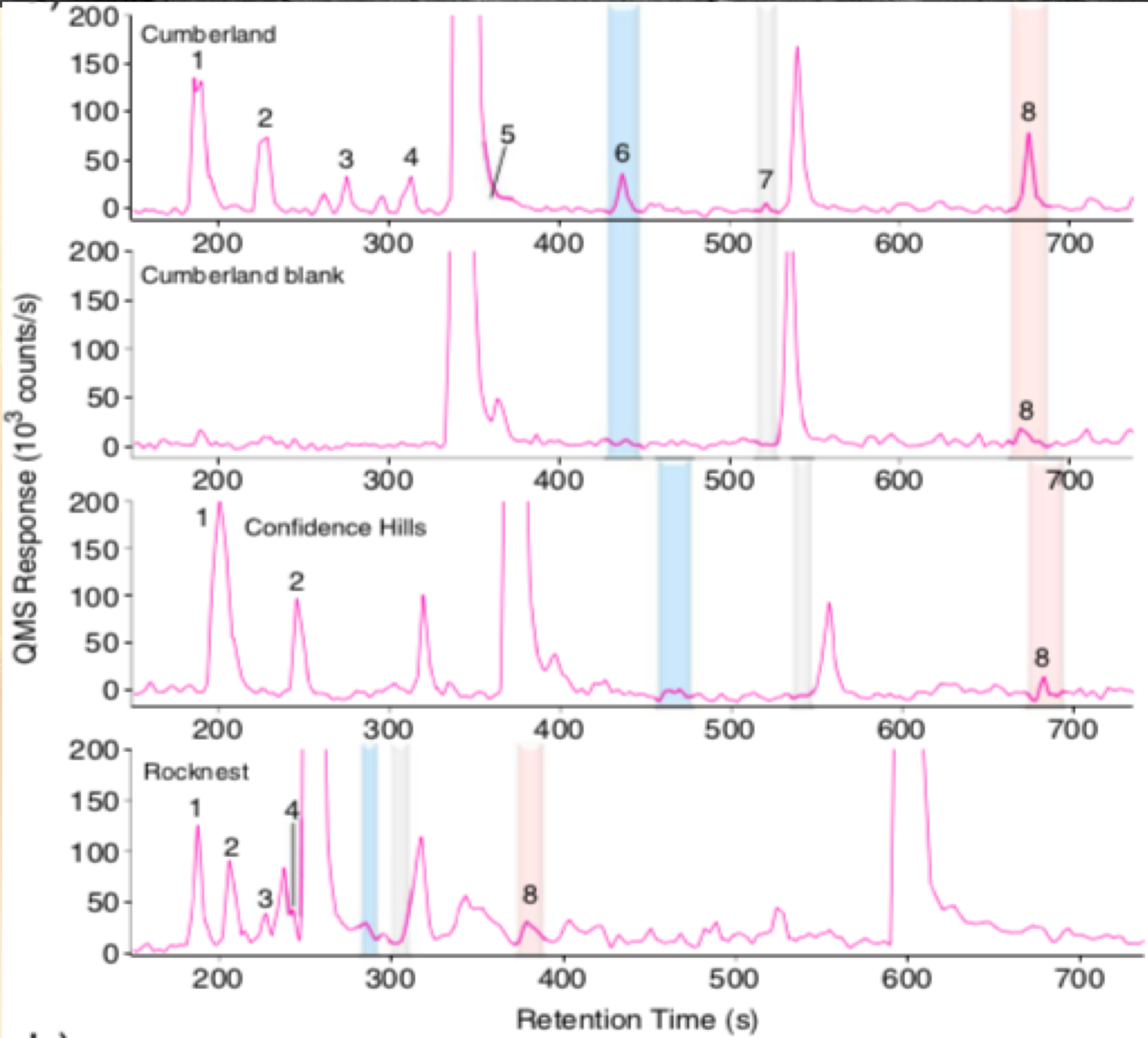
Organics (incl. CH_4)



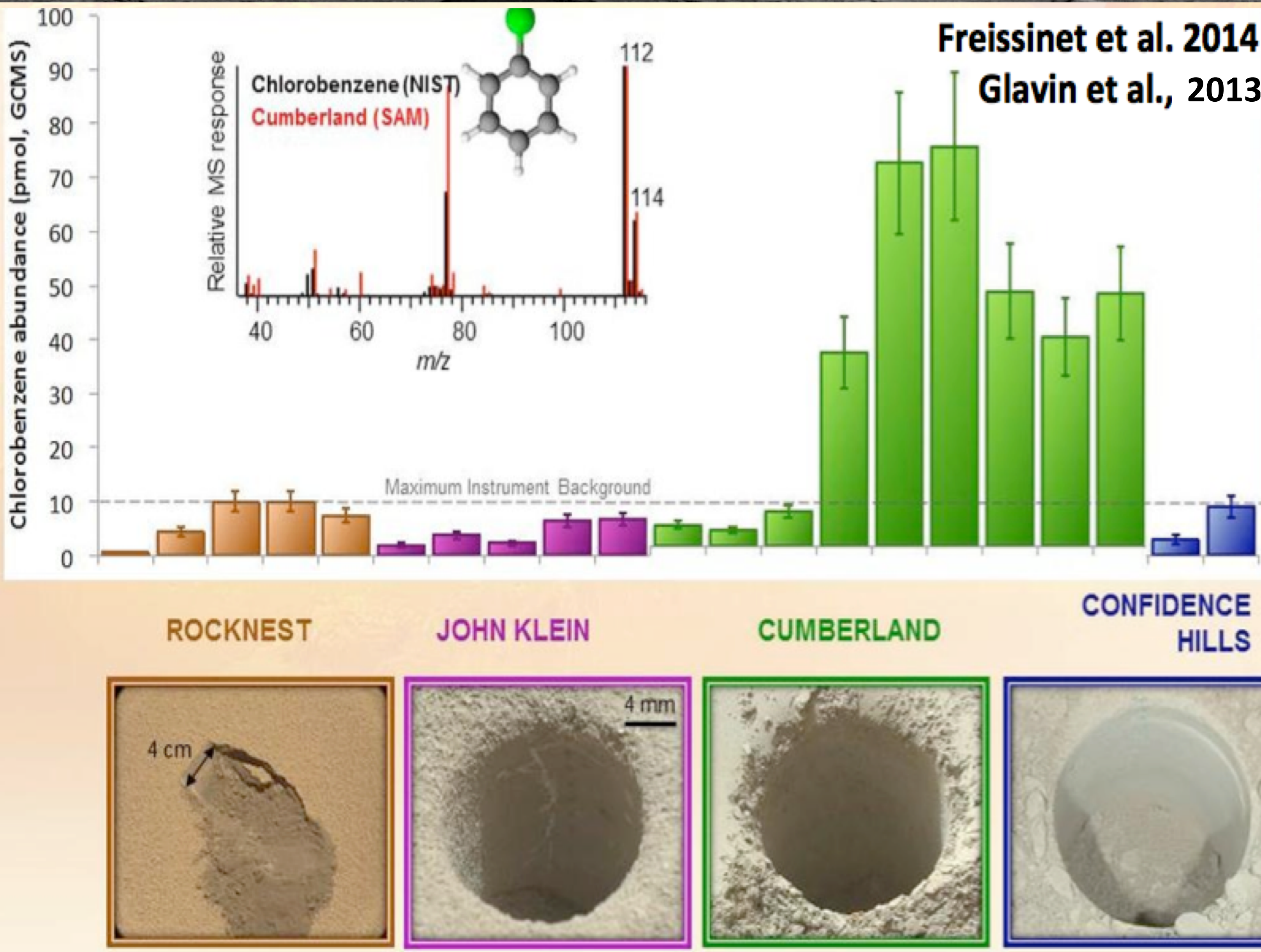
SAM chromatograms and SAM GCMS identification of chlorohydrocarbons validated with retention times on SAM TB

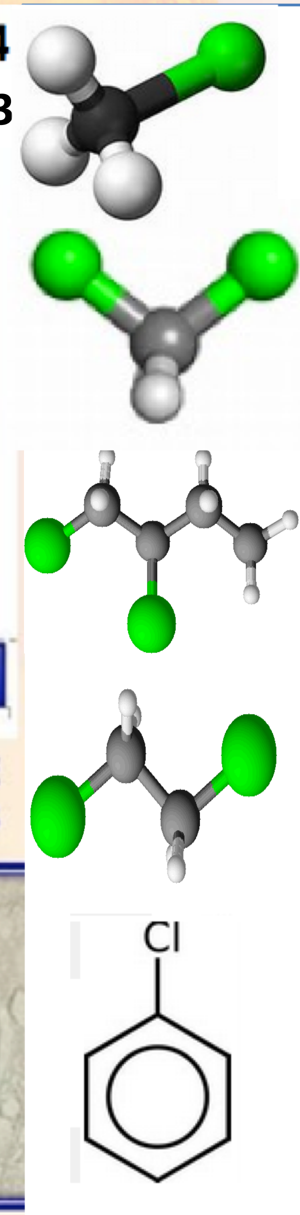
1: chloromethane
2: dichloromethane
3: trichloromethane,
4: carbon tetrachloride
5: 1,2-dichloroethane
6: 1,2-dichloropropane
7: 1,2-dichlorobutane
8: chlorobenzene

Reconstructed chromatograms
m/z 52 × 2 +
m/z 84 +
m/z 83 × 8 +
m/z 117×35 +
m/z 63×8 +
m/z 90×10 +
m/z 112×7

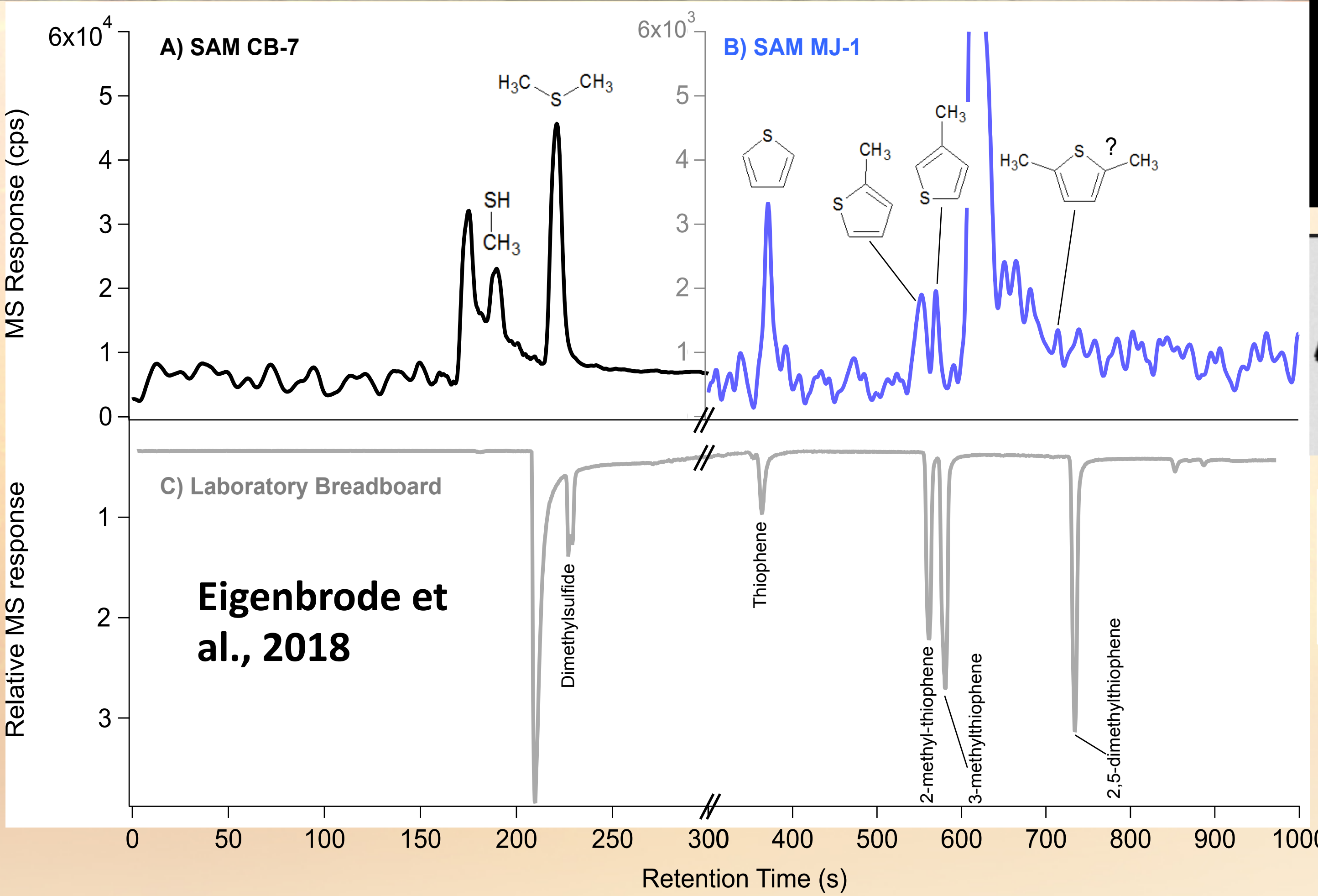


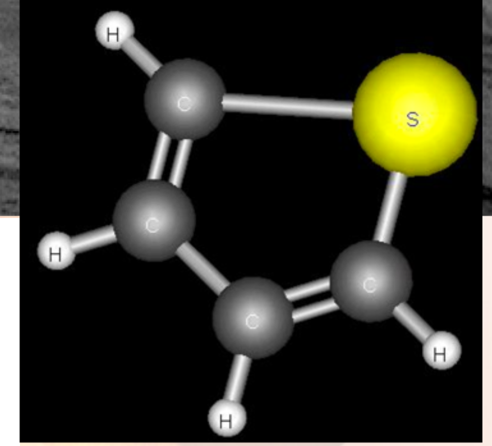
SAM has a special focus on carbon compounds
SAM GCMS – chlorobenzene and dichlorinated alkanes

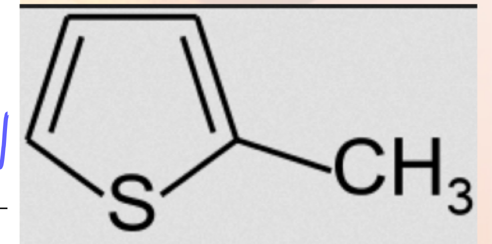


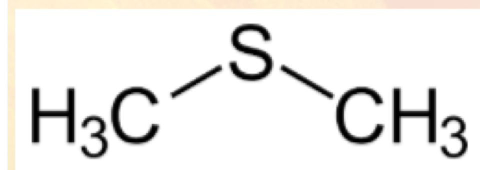


S-containing compounds without Cl !





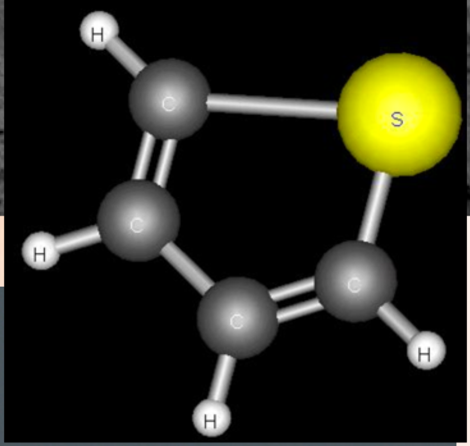


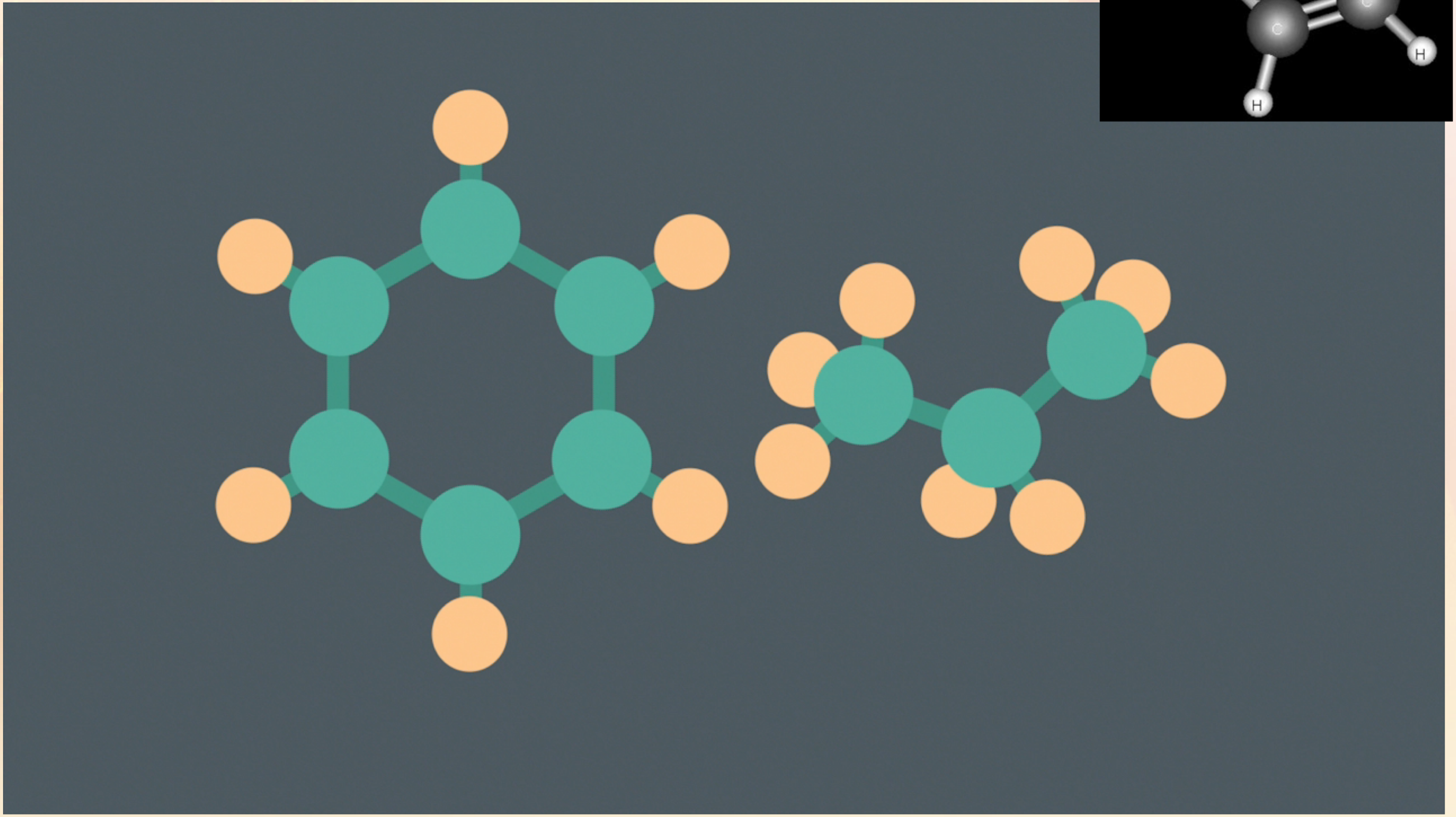


CH_3SH

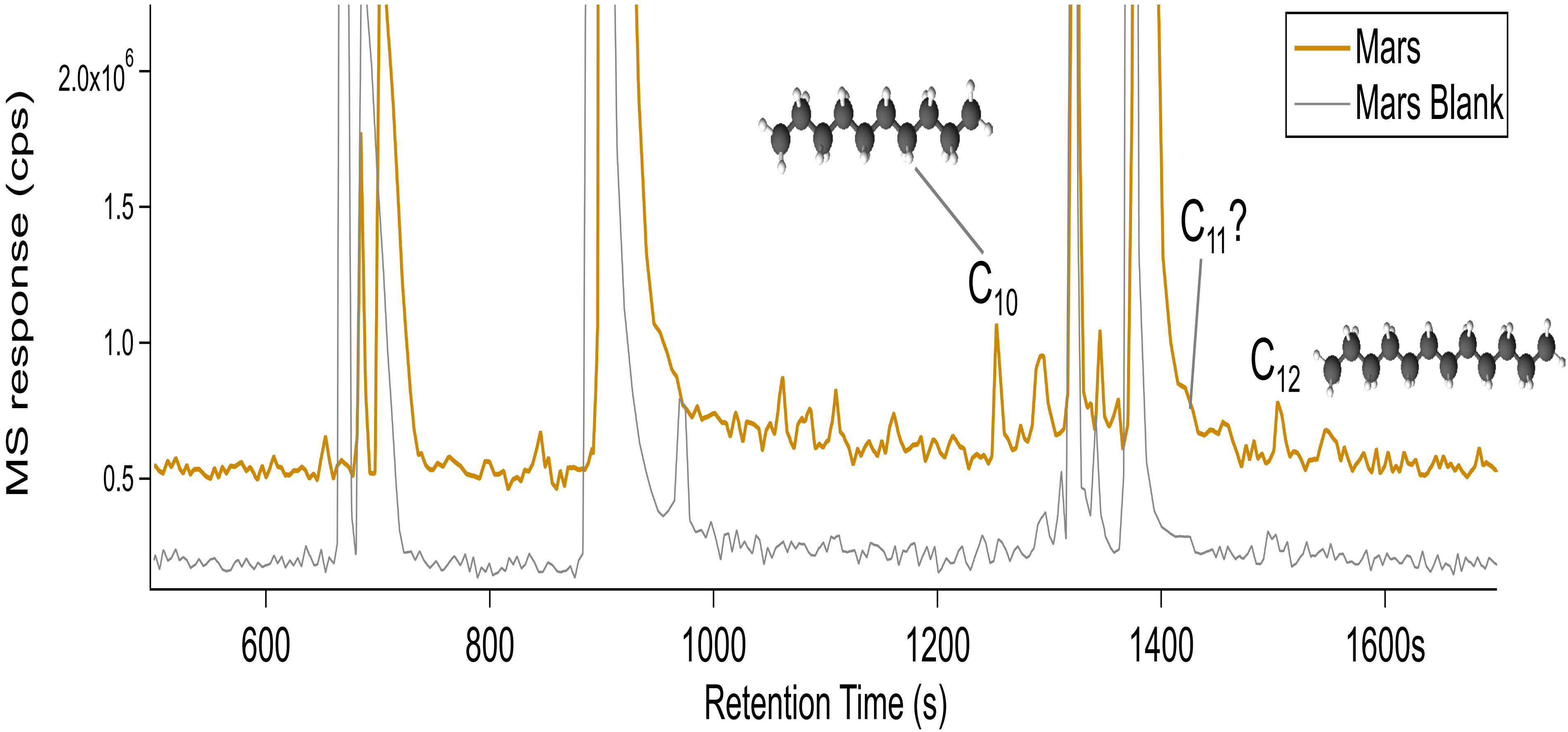
- ✓ Thiophene, methyl and di-methyl thiophene, dimethylsulfide, methanethiol
- ✓ Seen in CB high temperature cut & Mojave (MJ) wide temperature cut.
- ✓ MJ in Murray formation at Parhump Hills - lower mount outcrop at Gale.

S-containing compounds without Cl and evidence of macromolecules !





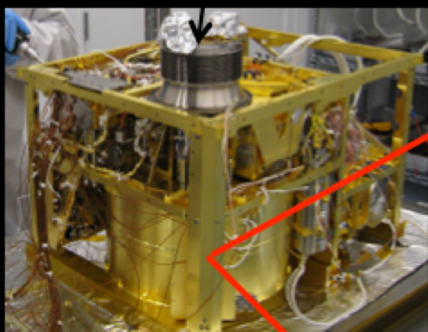
Long chain alkanes from a Cumberland "doggy bag" sample!



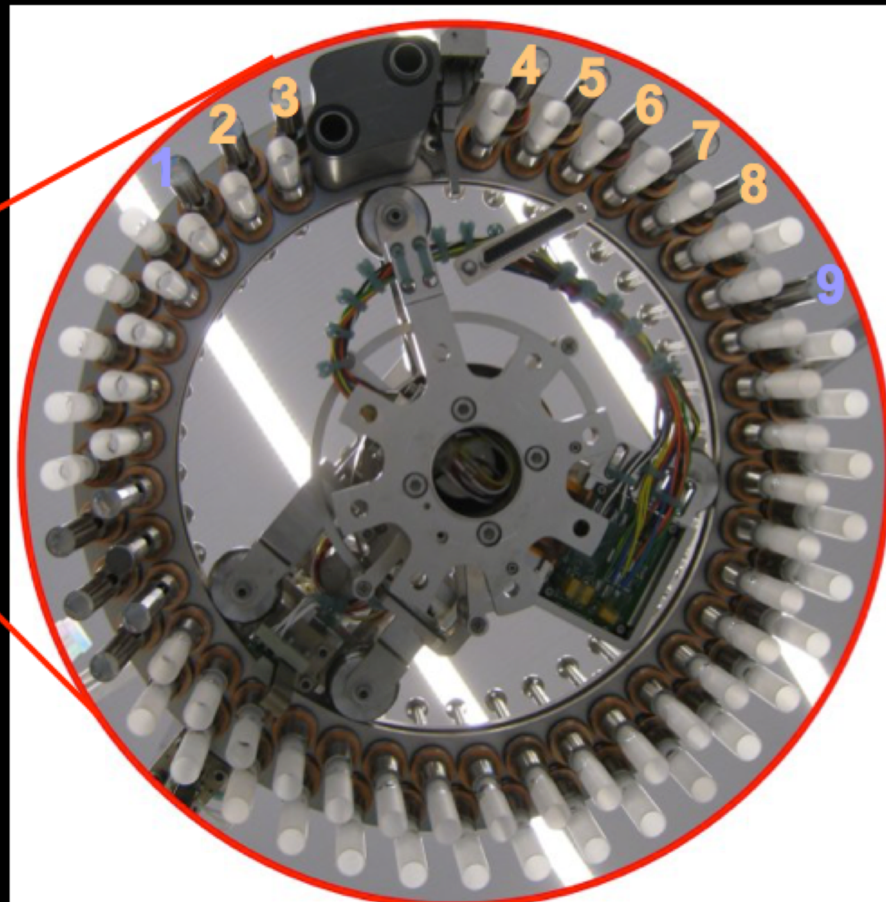
Are decane and dodecane decomposition products of fatty acids?

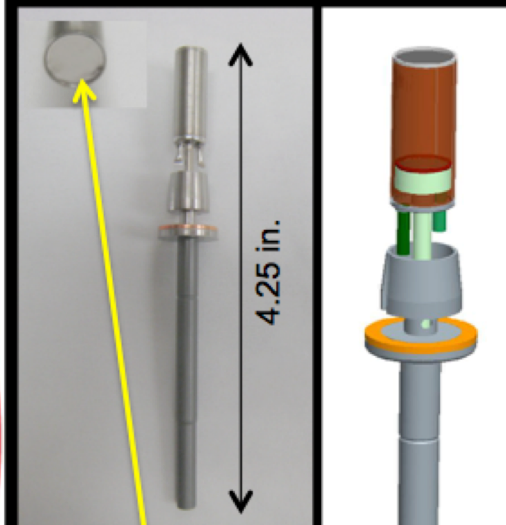
Wet chemistry cups – OD = use of residual vapor in the SMS and long exposures to sample to enable MTBSTFA Rx

Nine cups for low temperature extraction targeting less volatile organic compounds

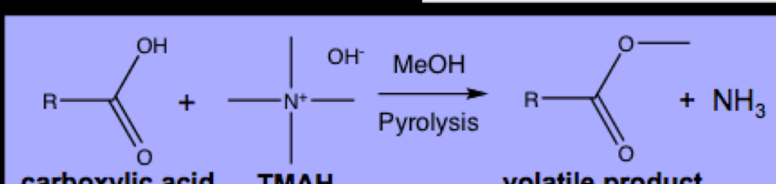


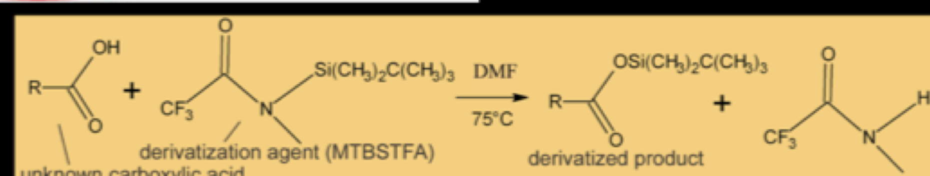
Several unidentified heavy organics showing up in OD runs





Foil cap designed for puncture using pin – Mars sample dropped into solvent filled cup through inlet tube



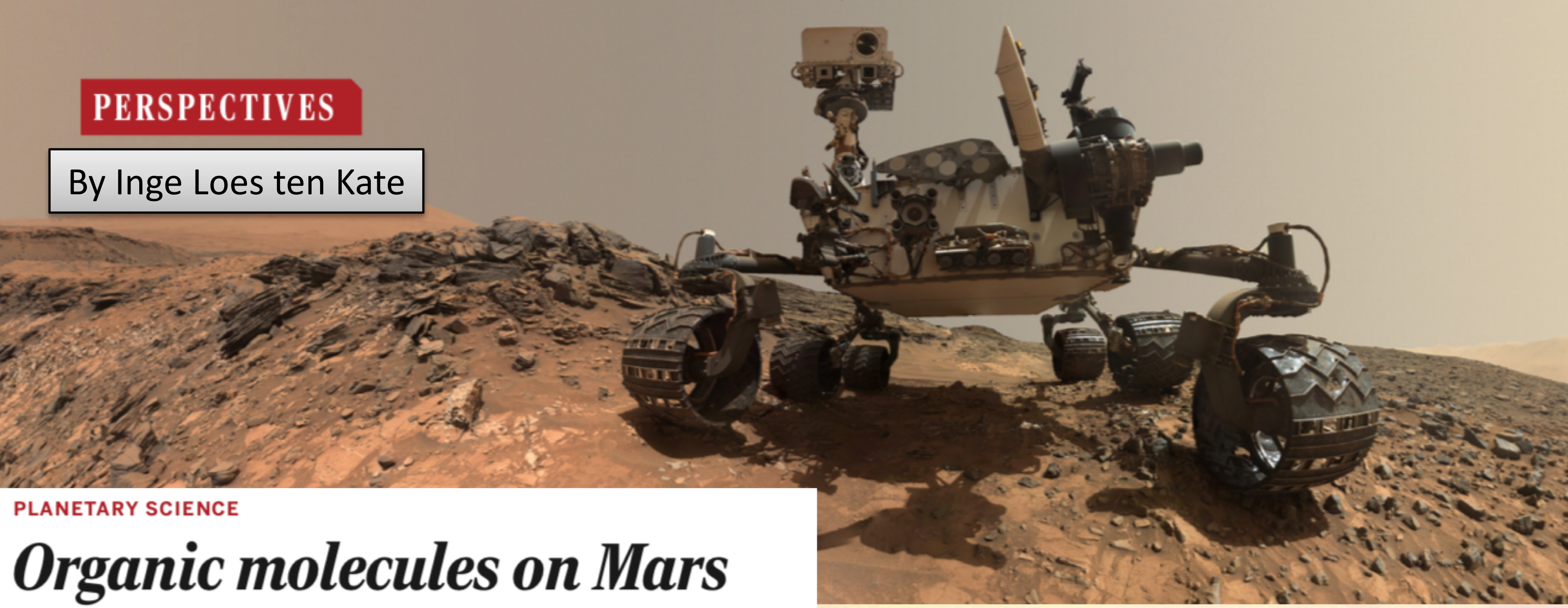


TMAH: Tetramethylammonium hydroxide

MTBSTFA: *N*-(*tert*-butyldimethylsilyl)-*N*-methyltrifluoroacetamide

PERSPECTIVES

By Inge Loes ten Kate



PLANETARY SCIENCE

Organic molecules on Mars

Data from the Curiosity rover provide evidence for organic molecules in ancient martian rocks and in the atmosphere

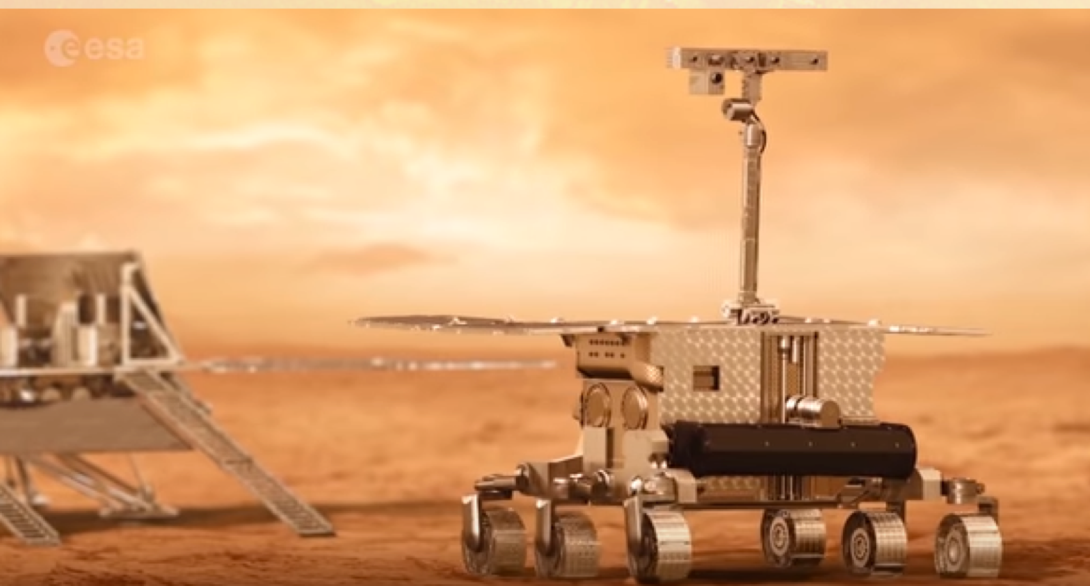
The detection of organic molecules and methane on Mars has far-ranging implications in light of potential past life on Mars. Curiosity has shown that Gale crater was habitable around 3.5 billion years ago (15), with conditions comparable to those on the early Earth, where life evolved around that time. The question of whether life might have originated or existed on Mars is a lot more opportune now that we know that organic molecules were present on its surface at that time.

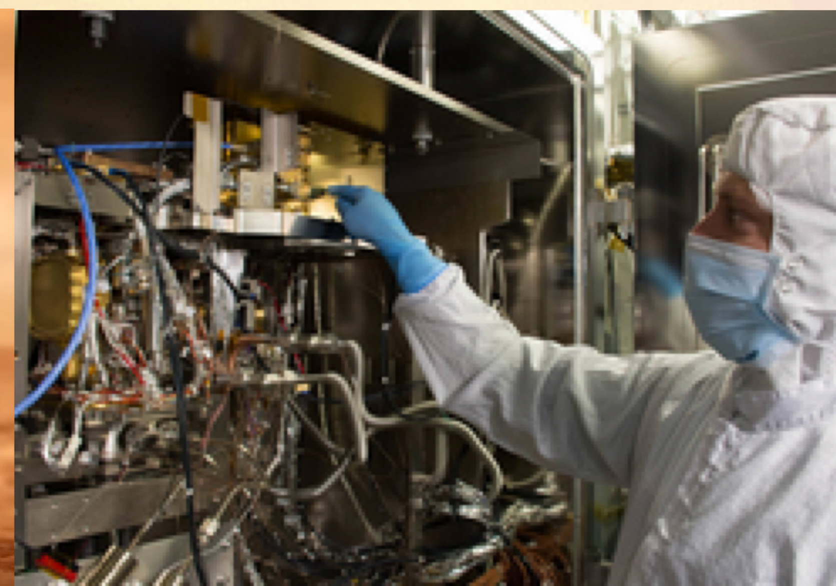
Planetary goals for mass spectrometry are moving toward direct detection of molecular biosignatures

Example -The MOMA investigation is the first direct search for martian life since the Viking landers in 1976. MOMA-MS just delivered to ESA from Goddard.

MOMA-MS advanced capabilities and development notes

- Laser ablation mass spectrometry will be a planetary first
- Tandem mass spectrometry enables more robust analysis of complex molecular structures and provides a new capability for future missions
- GCMS with derivatization (DMF-DMA) for enantiomeric separations
- Significant contribution to international collaborations in the search for life





Curiosity's primary scientific goal is to explore and quantitatively assess a local region on Mars' surface as a potential habitat for life, past or present.

Measurements that give insight into chemical processes related to possible life on early Mars when surface water was more abundant

(1) Mineralogy and geology

→ **what is it telling us about the ancient crater environment ?**

(2) Isotopic composition of light elements

→ **is isotopic fractionation from biological or physical/chemical processes ?**

(3) Age of formation of rocks

→ **how long have aqueous conditions persisted on Mars ?**

(4) Cosmic radiation of surface materials

→ **are near surface organics preserved from cosmic radiation ?**

(5) Clays, perchlorates, sulfates, and hydrated minerals

→ **do chemical environments enable preservation or destruction of organics ?**

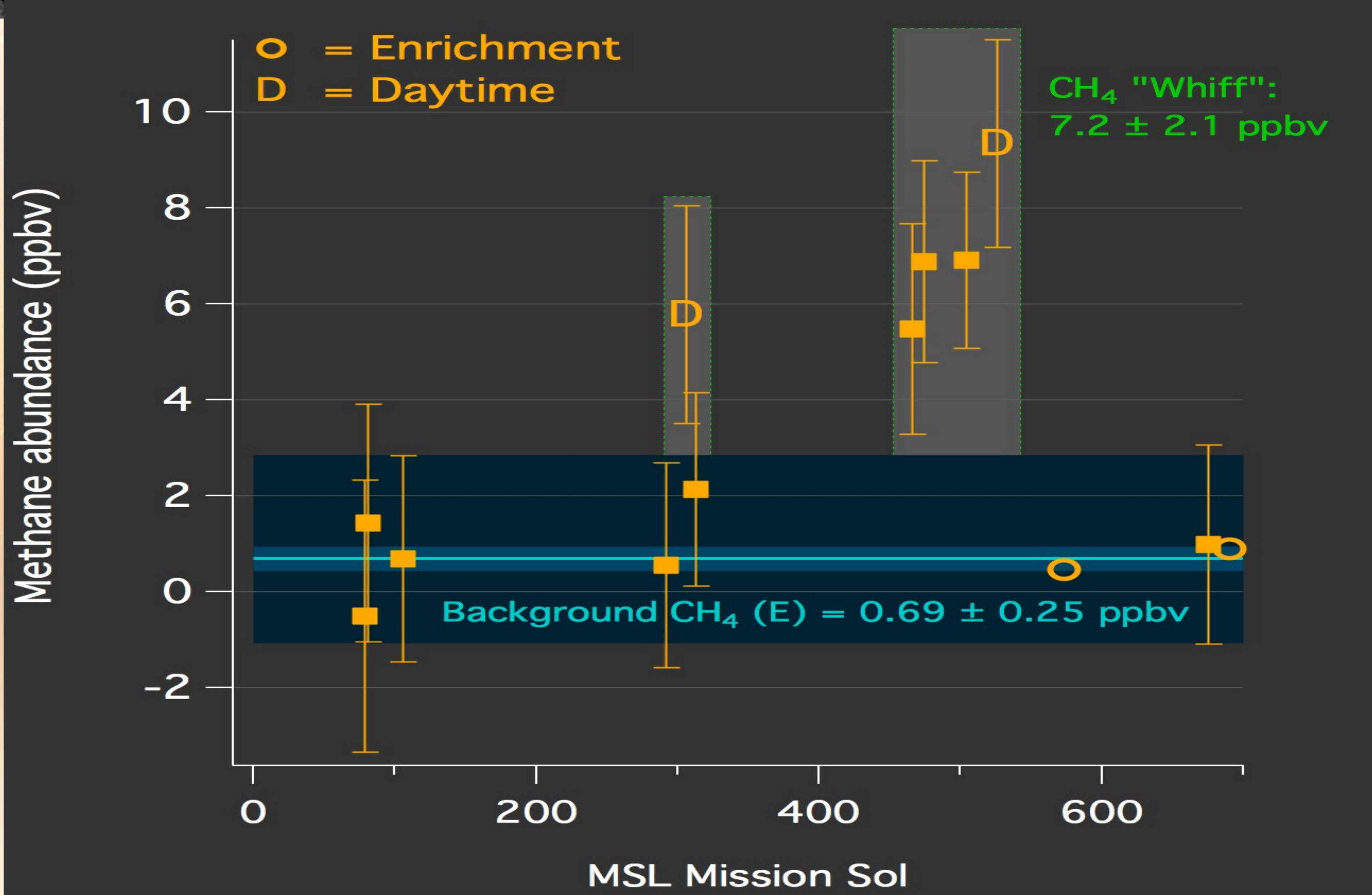
(6) Organic compounds extracted from soils and rocks

→ **what have we learned so far ?**

(7) Atmospheric composition and methane

→ **what does methane have to do with present or past life?**

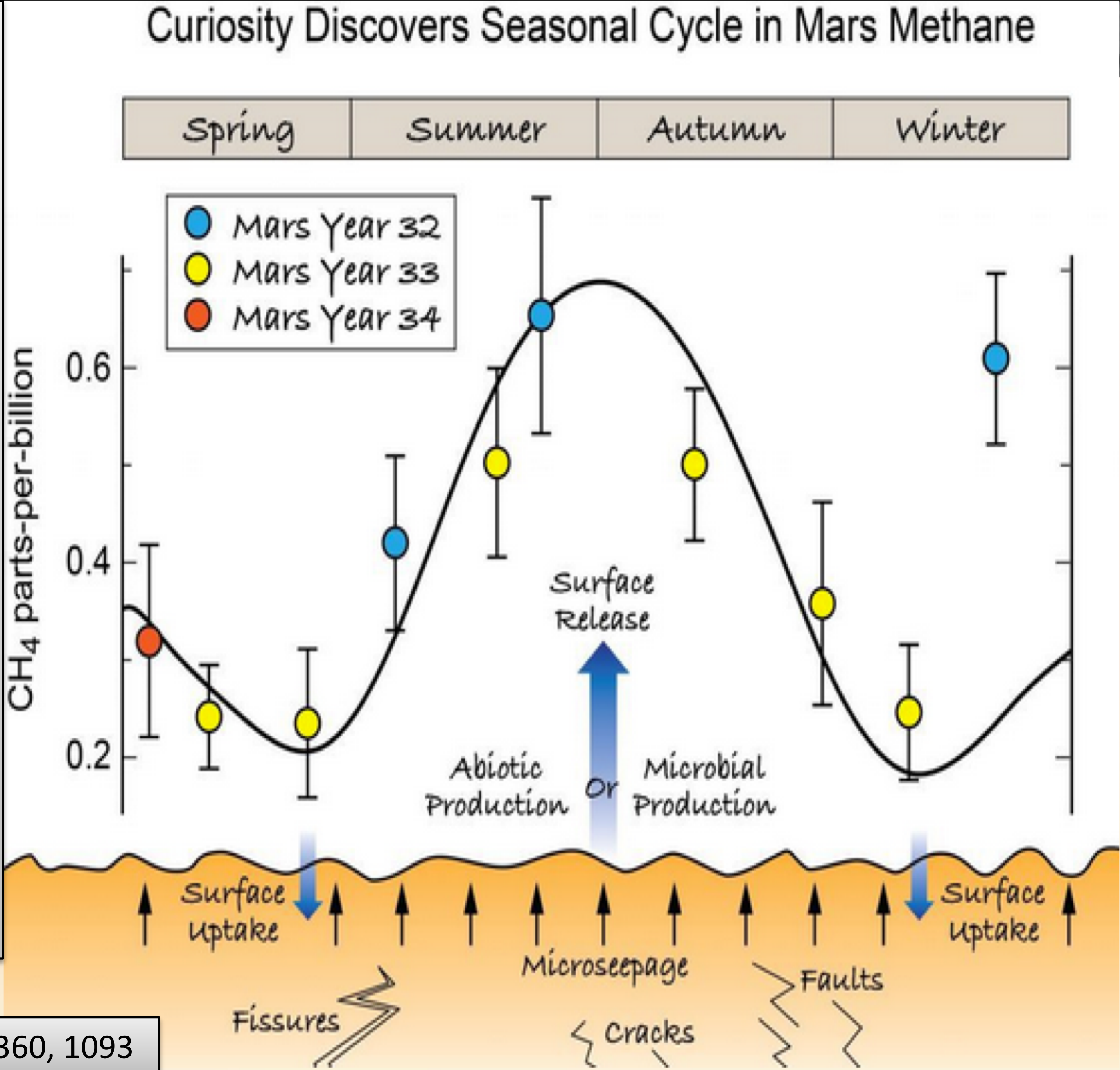
Methane "spikes" early in the mission



SAM's commanding language allows us great flexibility in generation of new sequences on Mars as we make discoveries – we keep a duplicate SAM operational at NASA Goddard to test these scripts

Atmospheric composition using both QMS & TLS

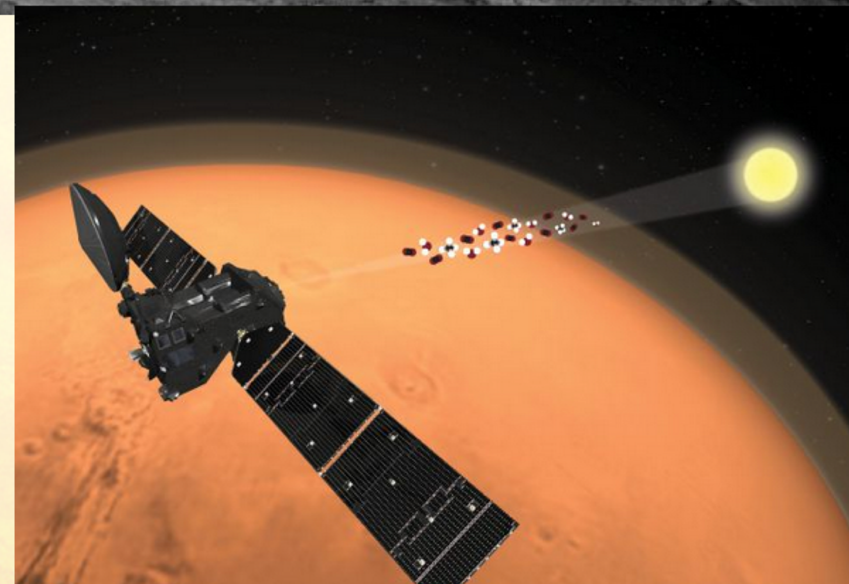
- Seasonal variations in mixing ratios of major atmospheric gases CO_2, N_2, Ar, O_2, and CO
- "Spikes" in methane mixing ratio to 5-10 ppn
- With enrichment sub-ppb levels and seasonal trends.

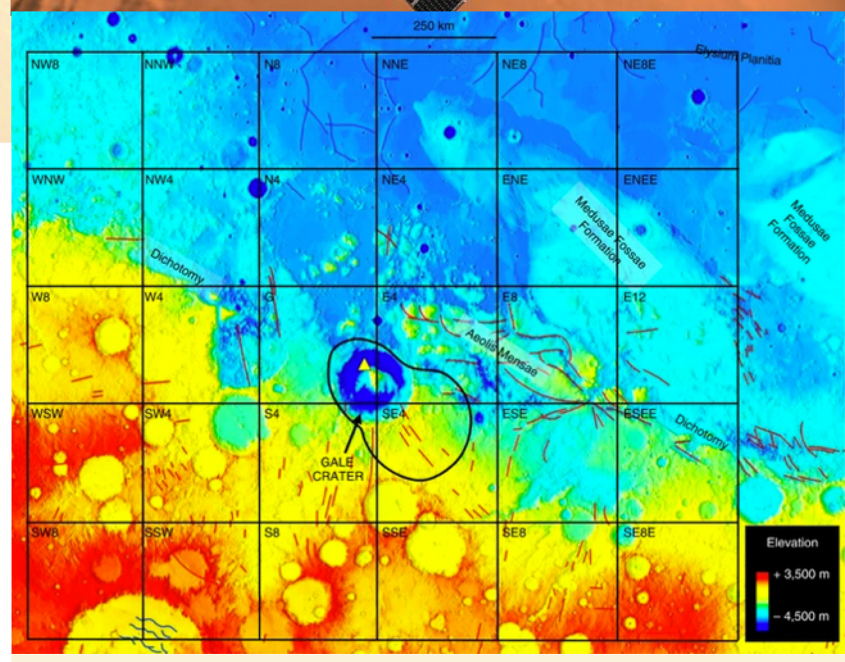


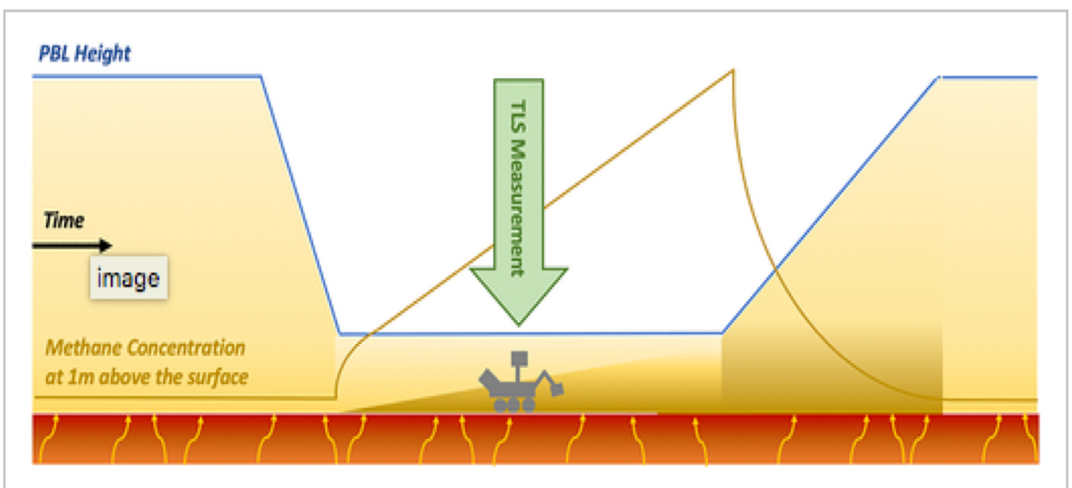
Webster et al., Science (2018) 360, 1093

The methane mystery persists - 2019 developments

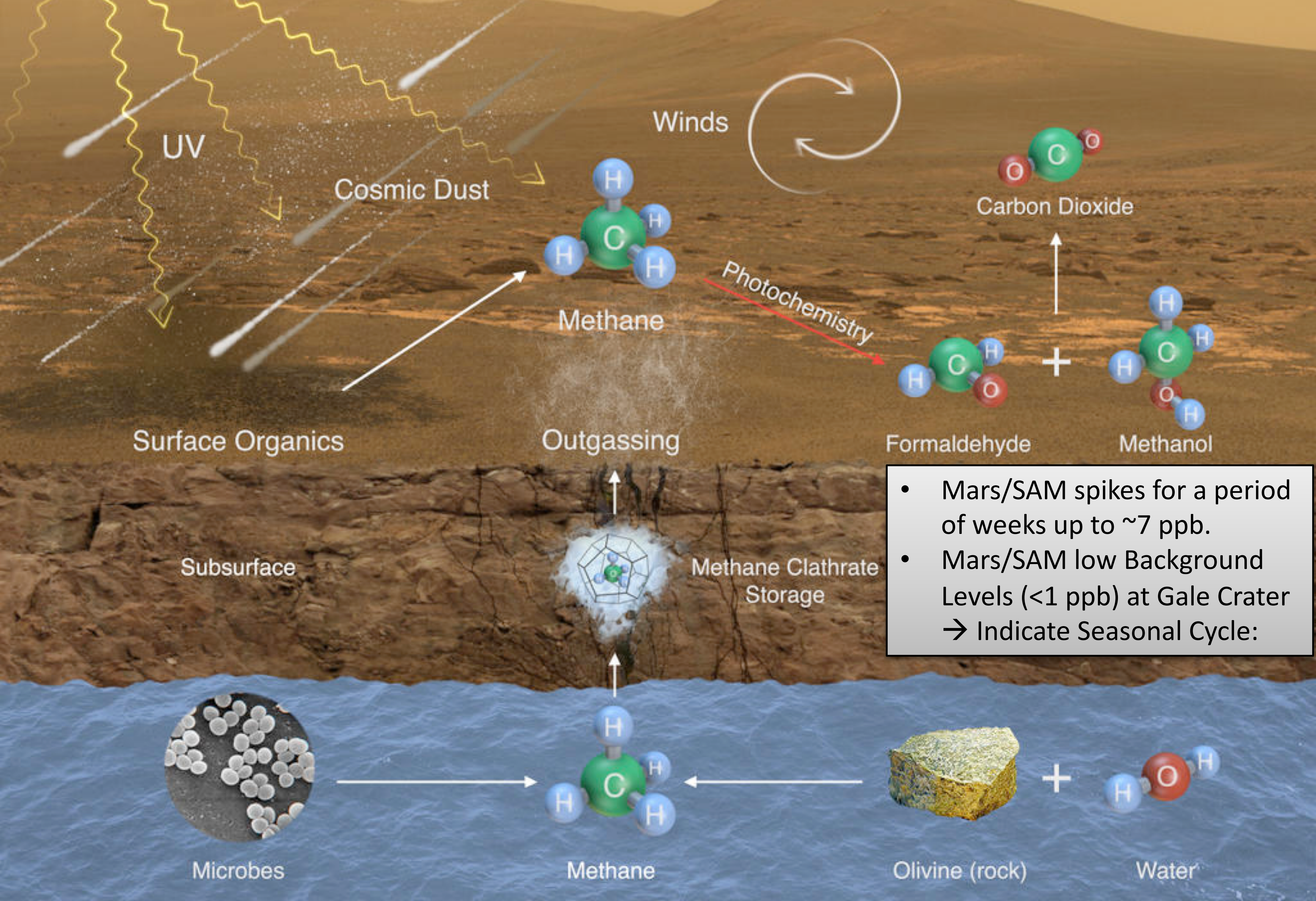
1) ESA's Trace Gas Orbiter gets to work and finds very low upper limits only of methane
2) ESA's Mars Express PFS instrument reports finding methane near Gale crater at the time of a previous Curiosity TLS methane spike
3) A model of methane seep in Gale crater (Moores et al.) predicts methane accumulation at night near the surface
4) Curiosity conducts an experiment to test the Moores theory but instead finds the biggest methane spike yet on the surface ~20 ppb





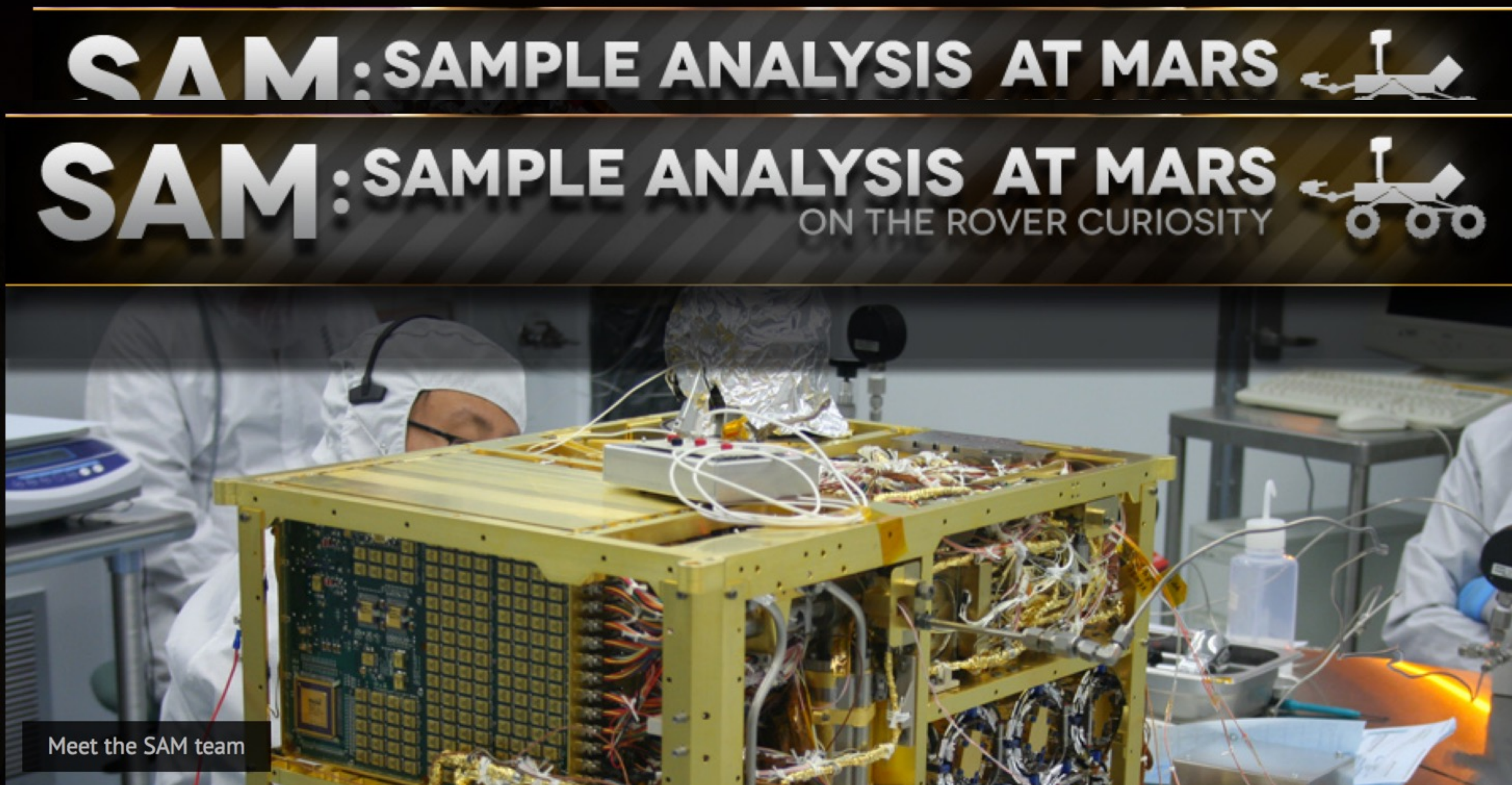


Possible Methane Sources and Sinks



- Mars/SAM spikes for a period of weeks up to ~7 ppb.
- Mars/SAM low Background Levels (<1 ppb) at Gale Crater → Indicate Seasonal Cycle:

http://ssed.gsfc.nasa.gov/sam/



http://ssed.gsfc.nasa.gov/sam/

The Martians sent out a patrol
To see what was doing one sol.
They got a big thrill
To see over a hill
Curiosity taking a stroll

Curiosity limerick by Dr. J.T. Nolan

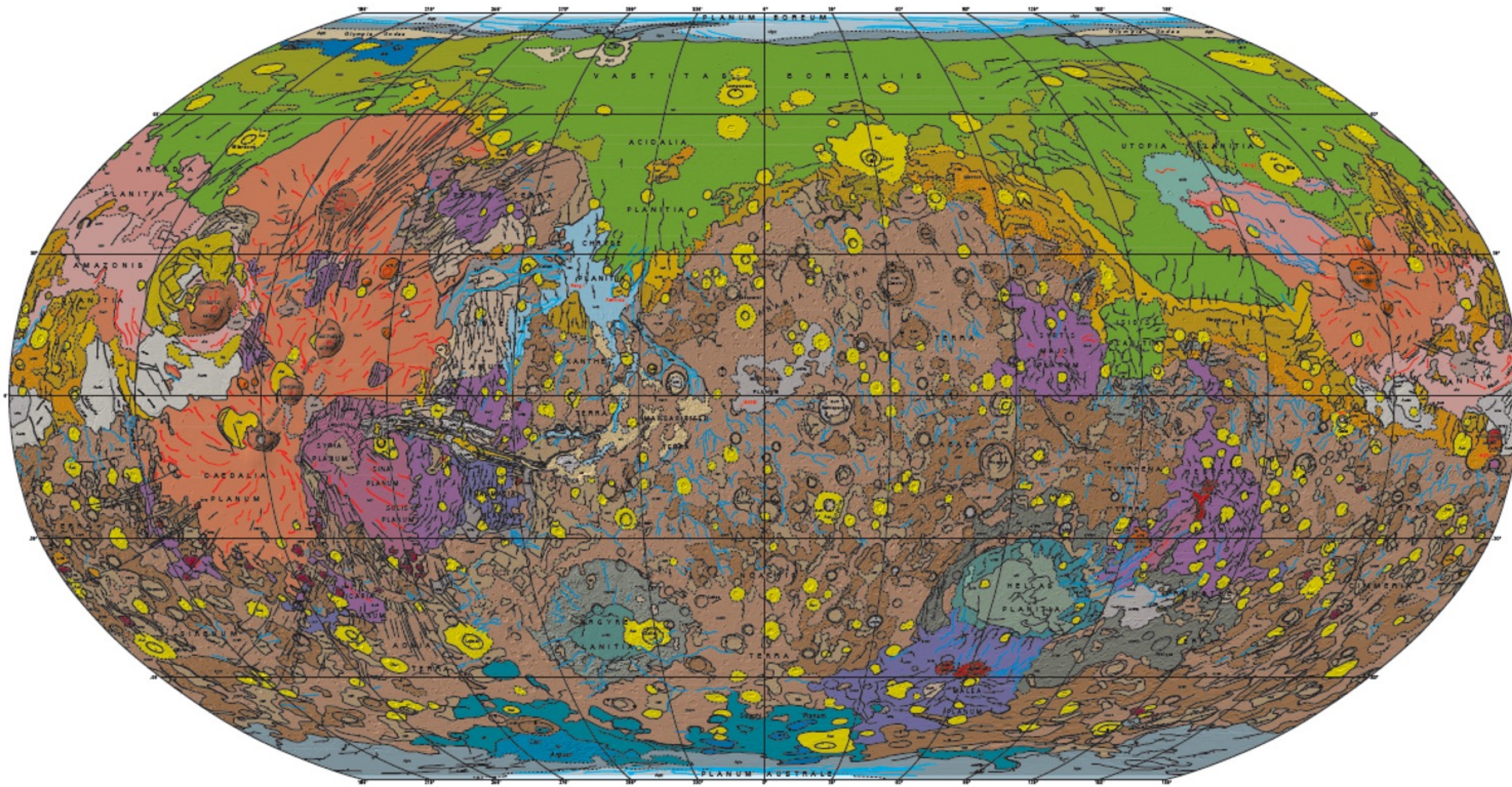
Curiosity now in the clay unit will continue to study the Layers, Canyons, and Buttes of Mount Sharp

backup

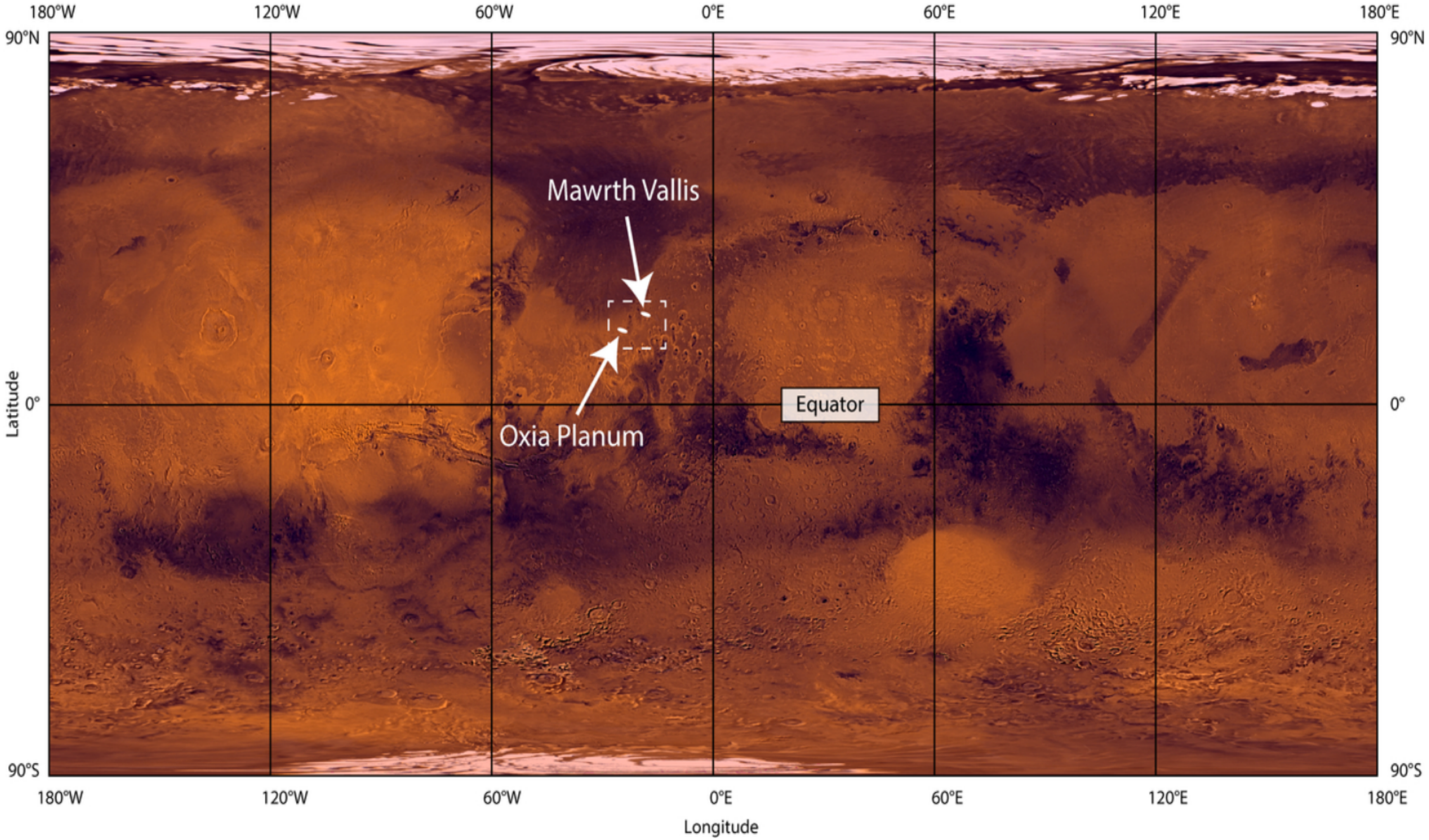
In contrast to Earth where much of the first billion years is obliterated – on Mars half the surface is old

Geologic Map of Mars

By Kenneth L. Tanaka, James A. Skinner, Jr., James M. Dohm, Rossman P. Irwin, III, Eric J. Kolb, Corey M. Fortezzo, Thomas Platz, Gregory G. Michael, and Trent M. Hare



Ancient Noachian site Oxia Planum is the selected landing site for the Roslind Franklin rover



Clay rich material recently exposed giving a window into very early Mars

An entirely different world preserved from ancient times may be revealed in the martian subsurface