Composition

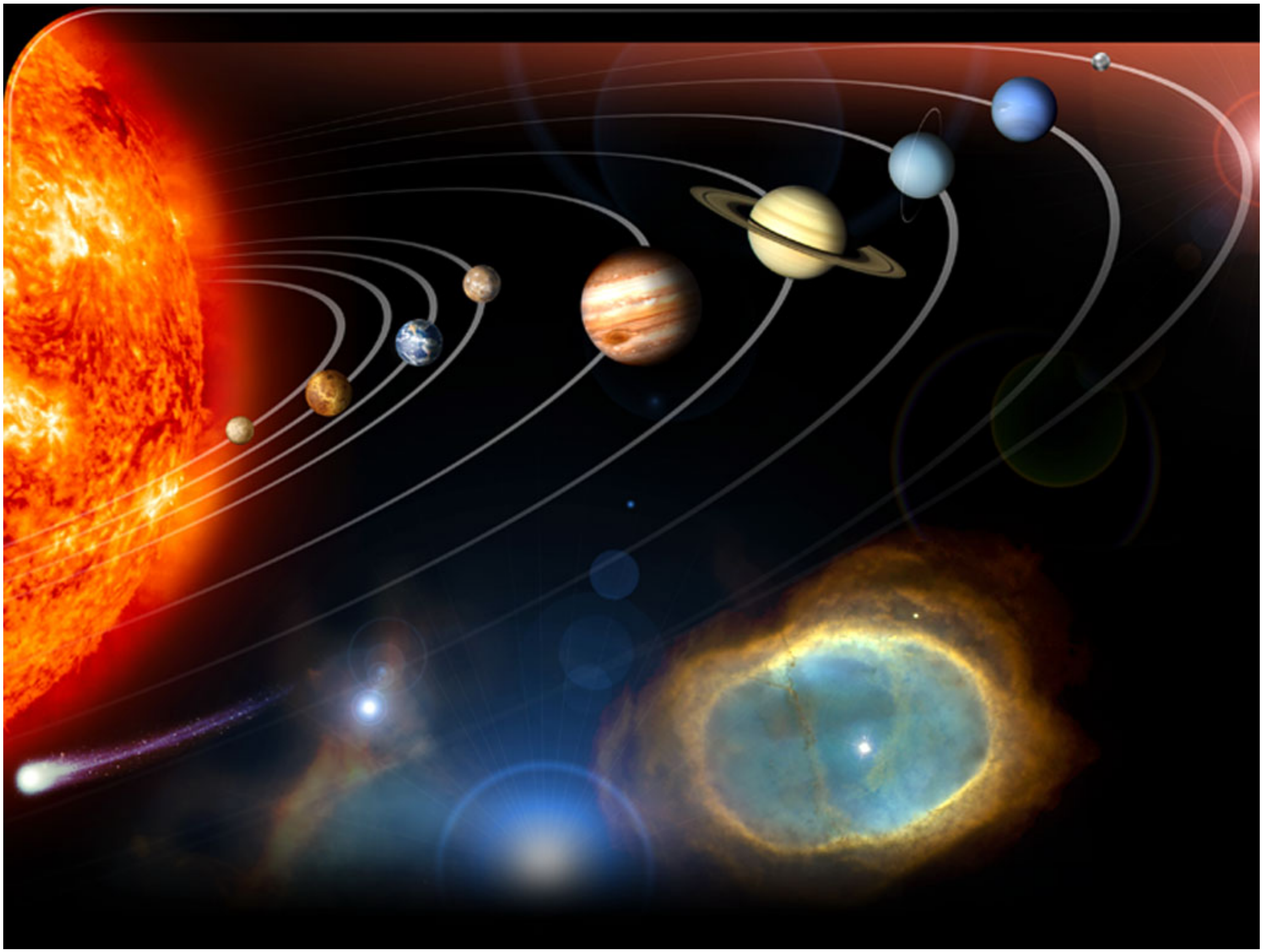
Sushil Atreya

Les Houches, 30 March 2010

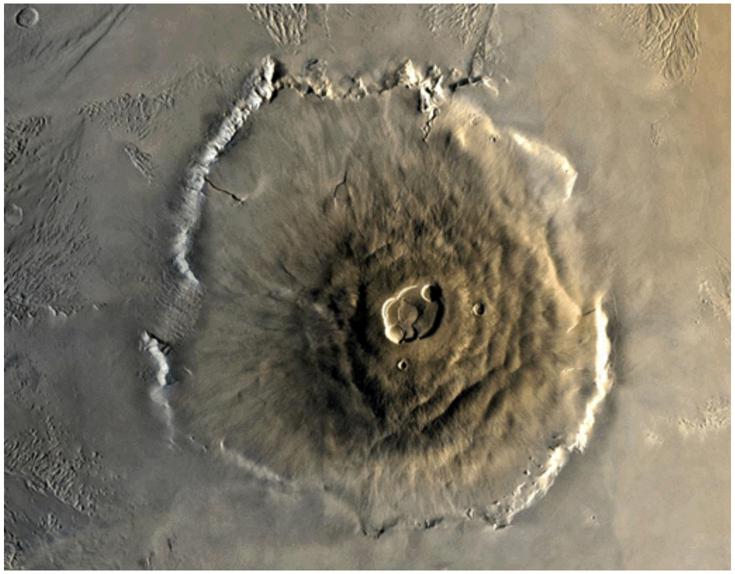
map

- ***Trace species***: what are they
- ***Formation*** (origin, source)?
- ***Destruction***: how, where, and how fast?
- ***Supply***: flux small or big?
- ***Meaning:*** *Habitability* - tests?
- ***Measurements***?

Our Solar System



Mars characteristics from recent observations



- Radius = 3396.2 km (Earth 6398 km)
- Density = 3.933 g/cm^3 (Earth 5.4 g/cm^3)
- **Semimajor Axis = 1.52 AU**
- Eccentricity = 0.0935
- Inclination = 25.2 degrees
- Orbital period = 686 days (Earth 365 d)
- Rotation period = 24.6229 hrs
- **Surface Gravity = 3.71 m/s^2**
- **Internal Magnetic Field: Negligible**
- Average Surface Temperature = 220 K (range 170-300 K)
- Surface Pressure 6.36 millibars (Earth 1013 mb, or 1 atmosphere)
- Satellites – Phobos and Deimos

mars atmosphere composition

species	mixing ratio
CO_2	95.32 %
N_2	2.7 %
^{40}Ar	1.6 %
O_2	0.13 %
CO	0.07 %
H_2O	1 - 100 pr-μm
O_3	0.01 – 0.8 ppm
H_2	15 ppm
2003 ***H_2O_2***	20-40 ppbv (*atmos.*)
2003 ***CH_4***	15 ppbv (global)

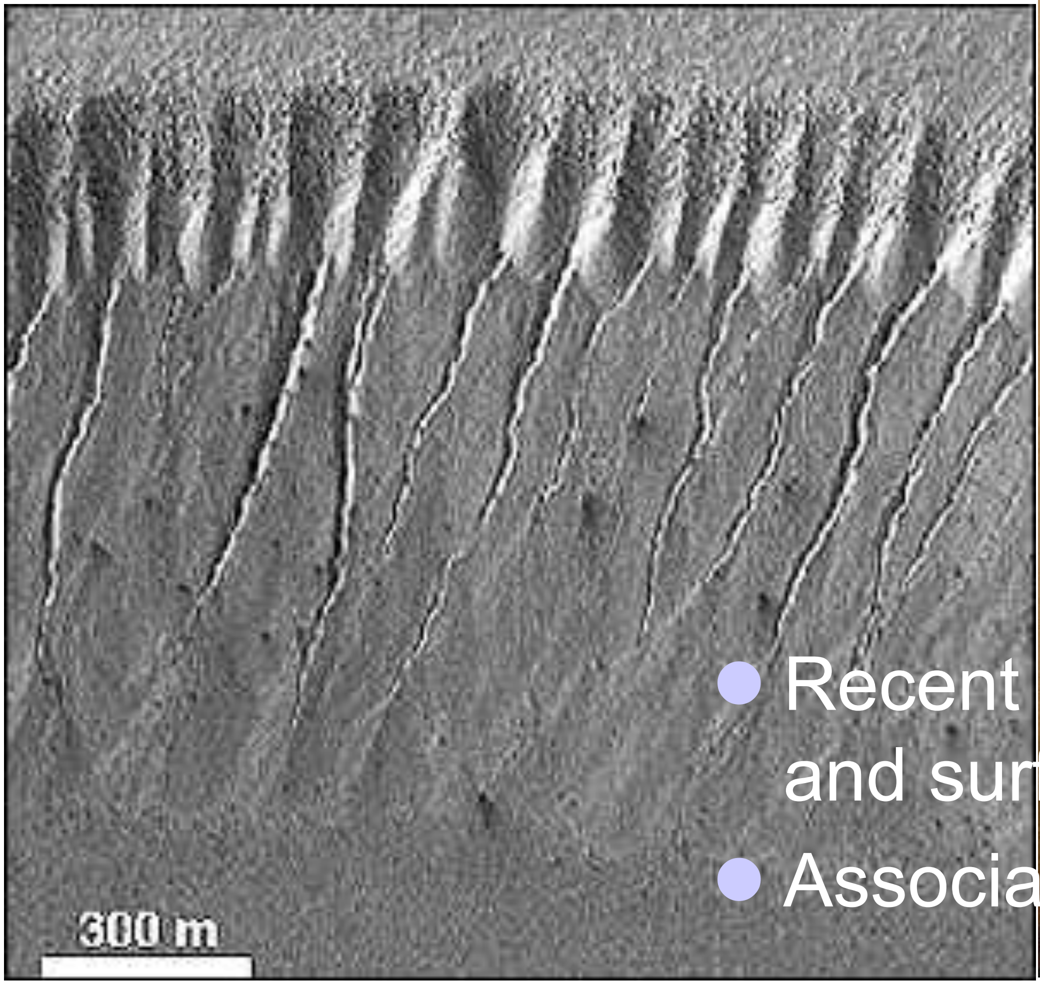
(Earth CFC's ~1 ppbv)

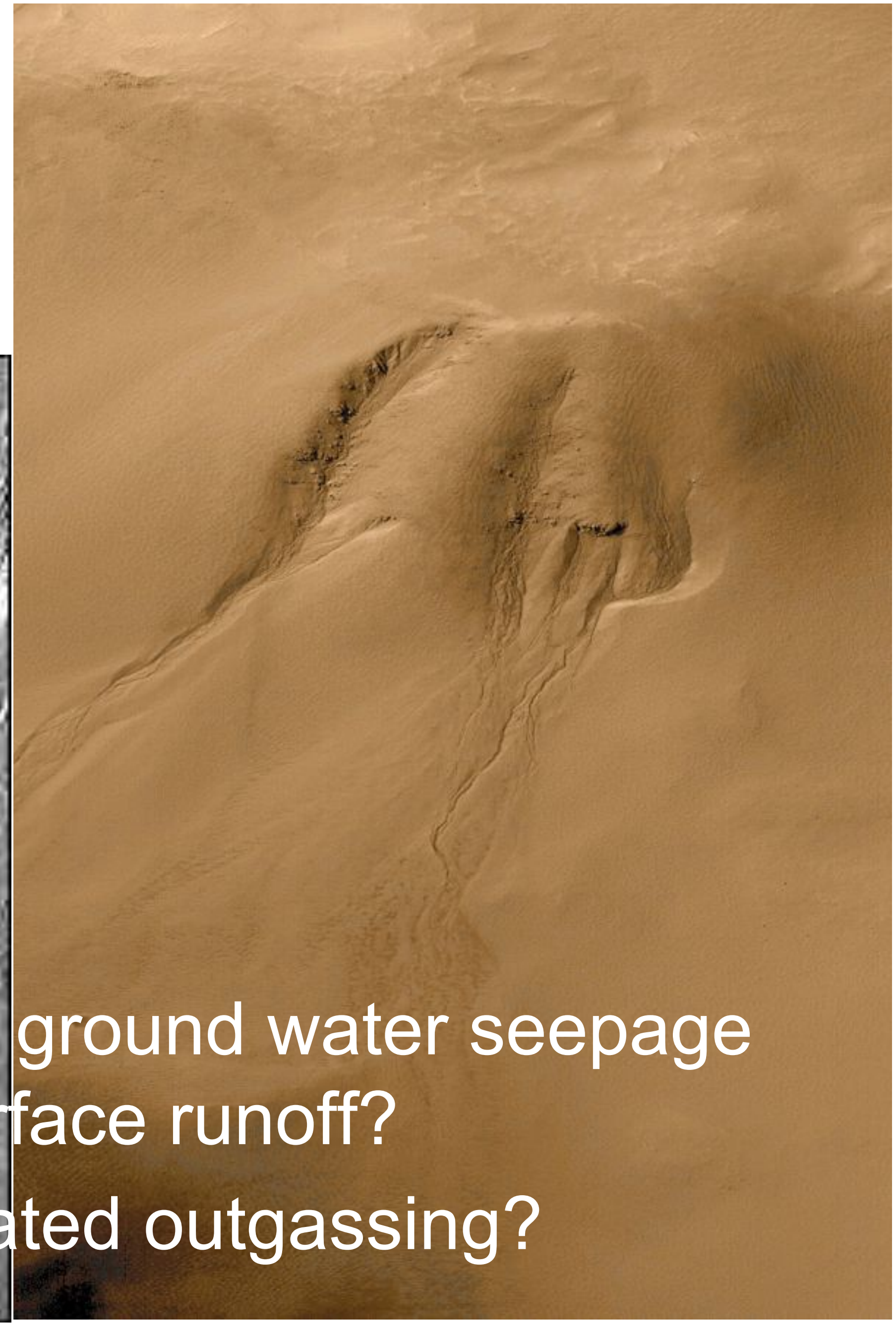
minor species	*upper limit*
N_2O	1 (-7)
NO_2	1 (-8)
C_2H_2	2 (-9)
C_2H_4	5 (-7)
C_2H_6	4 (-7)
SO_2	***1 (-9)***
H_2S	1 (-7)
HCl	2 (-9)

surface pressure 6-10 mb

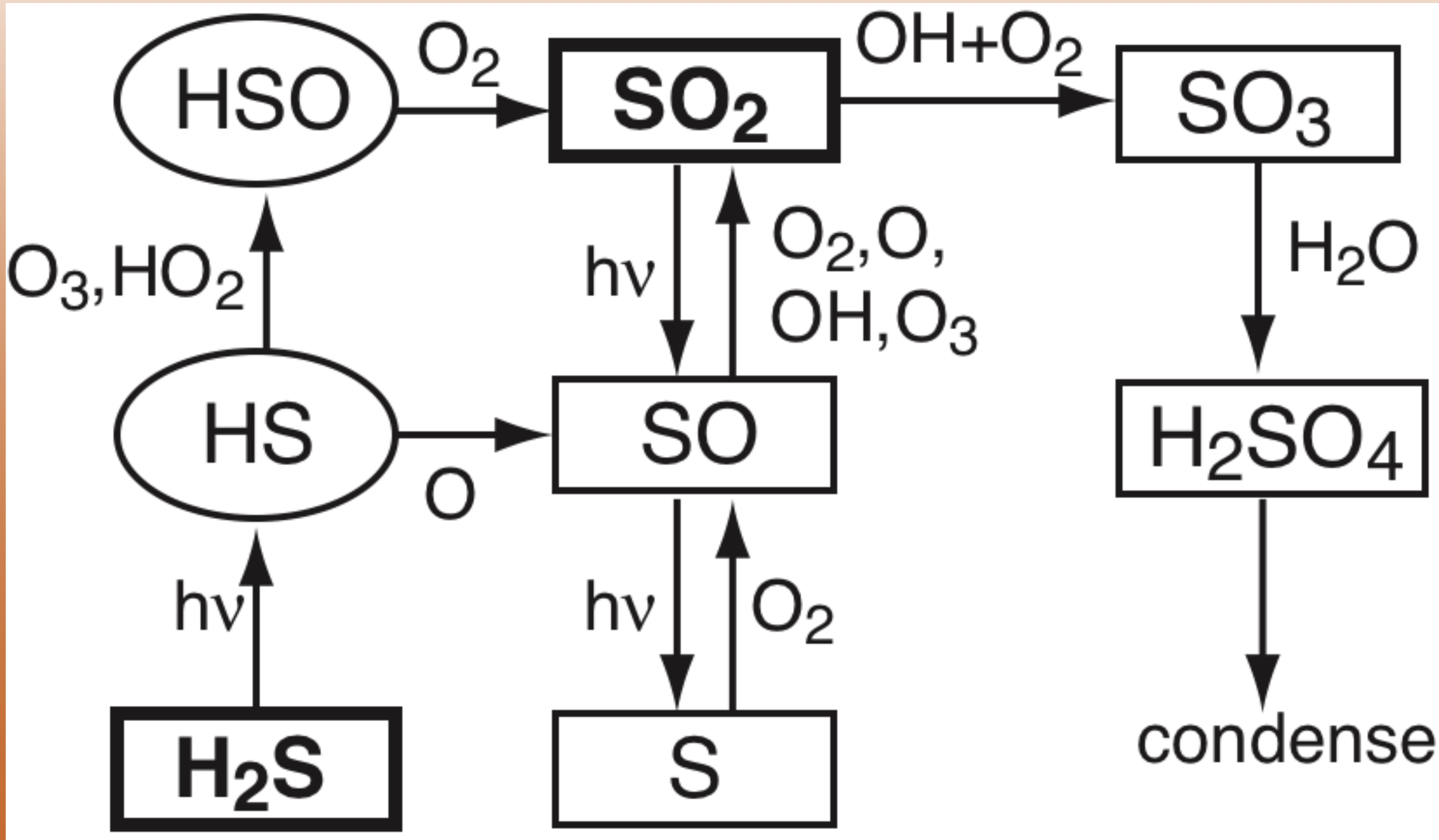
Possible outgassing on Mars?

(Mars Global Surveyor Images, 2000)





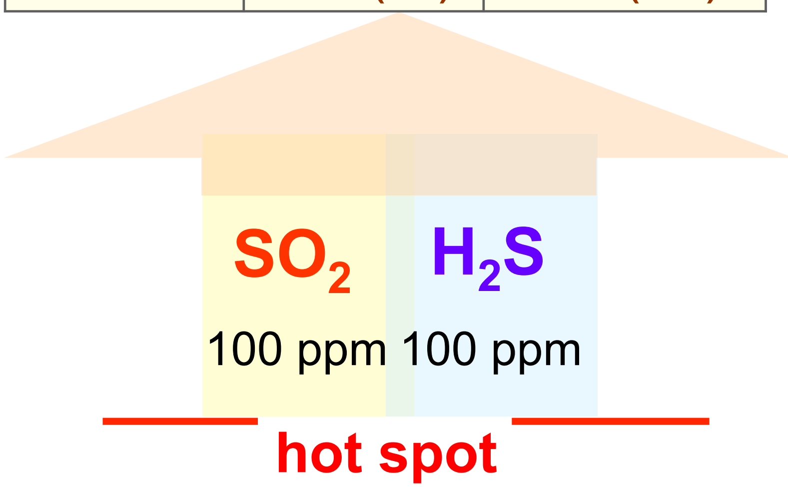
- Recent ground water seepage and surface runoff?
- Associated outgassing?

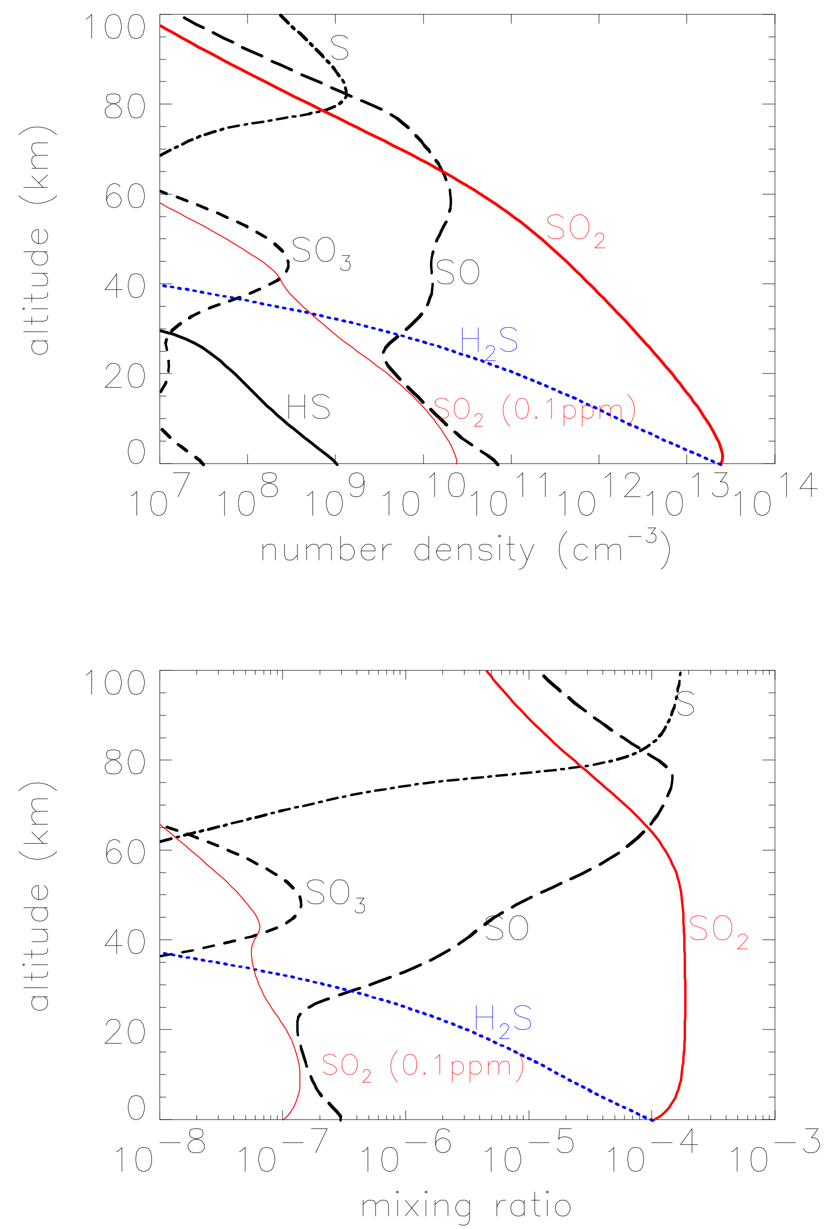


Hotspot sulfur chemistry

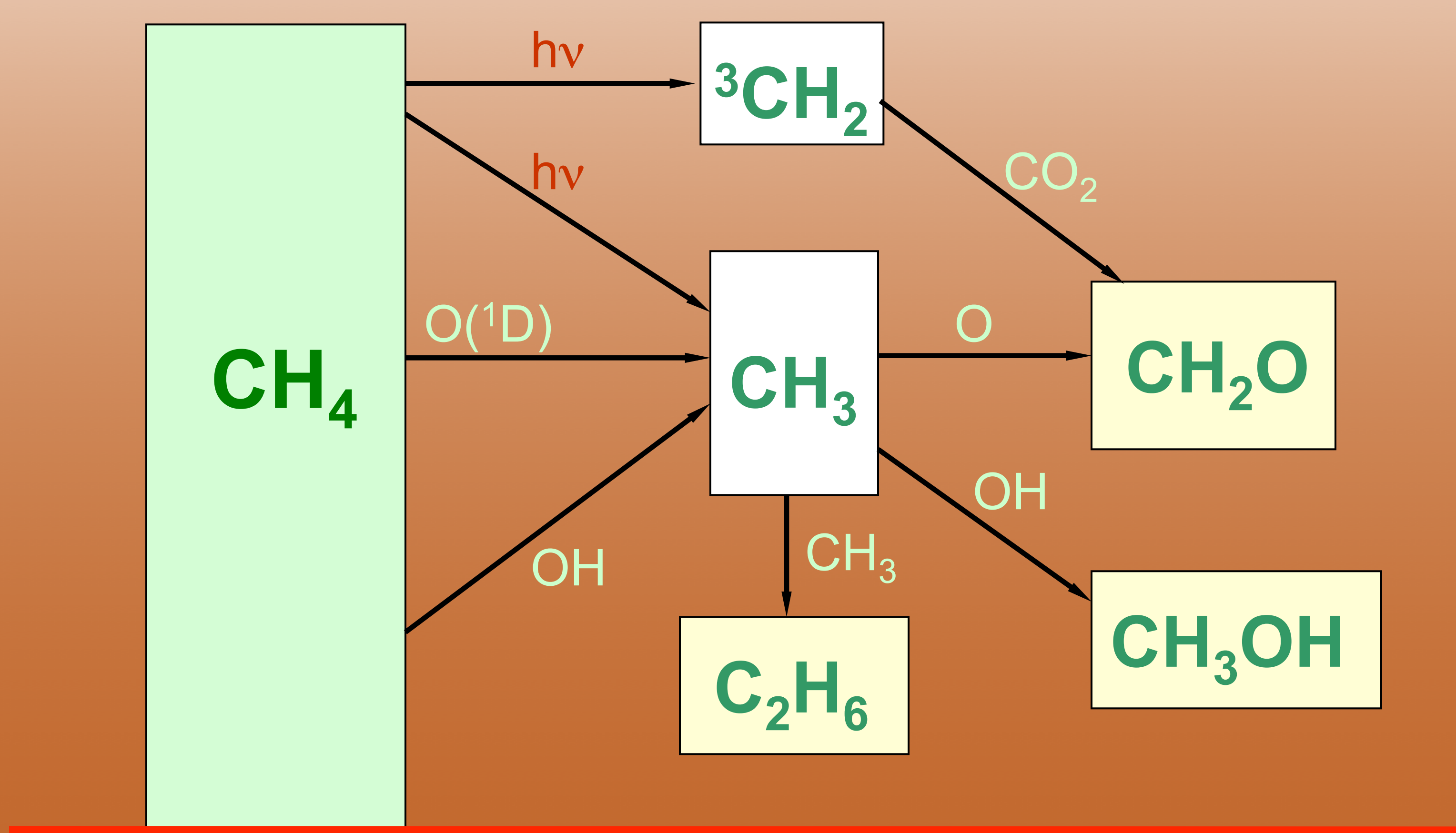
Sulfur Species

major species	mixing ratio (10 km)	column (cm^{-2})
SO_2	1.7 (-4)	1.8 (19)
H_2S	1.8 (-5)	7.4 (17)
SO	1.7 (-7)	7.8 (16)





Methane chemistry on Mars

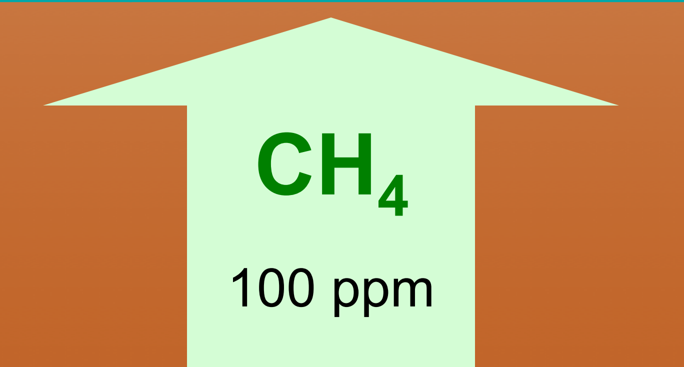


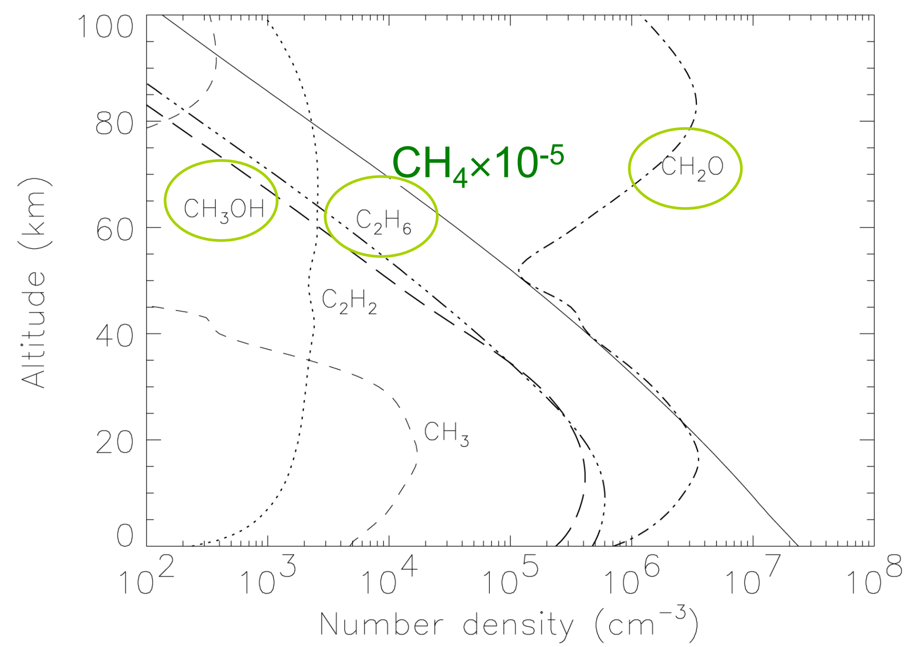
Flux from Mars surface

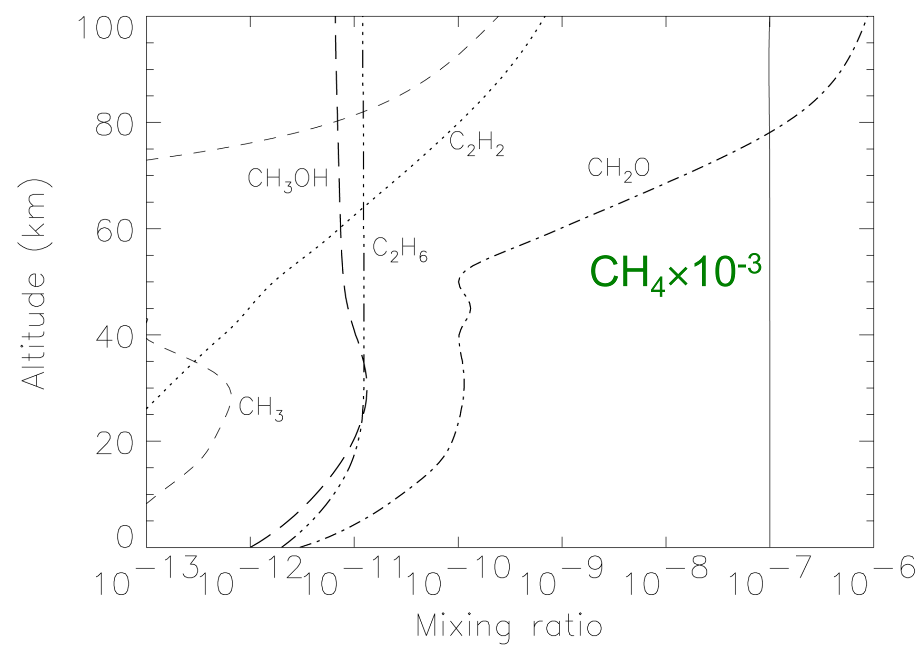
Photochemical Lifetime of methane 300-600 years

Hydrocarbons

major species	mixing ratio (10 km)	column (cm^{-2})
CH_4	1.0 (-4)	1.0 (19)
CH_2O	2.8 (-11)	1.6 (13)
CH_3OH	4.3 (-12)	8.2 (11)
C_2H_6	6.4 (-12)	9.6 (11)





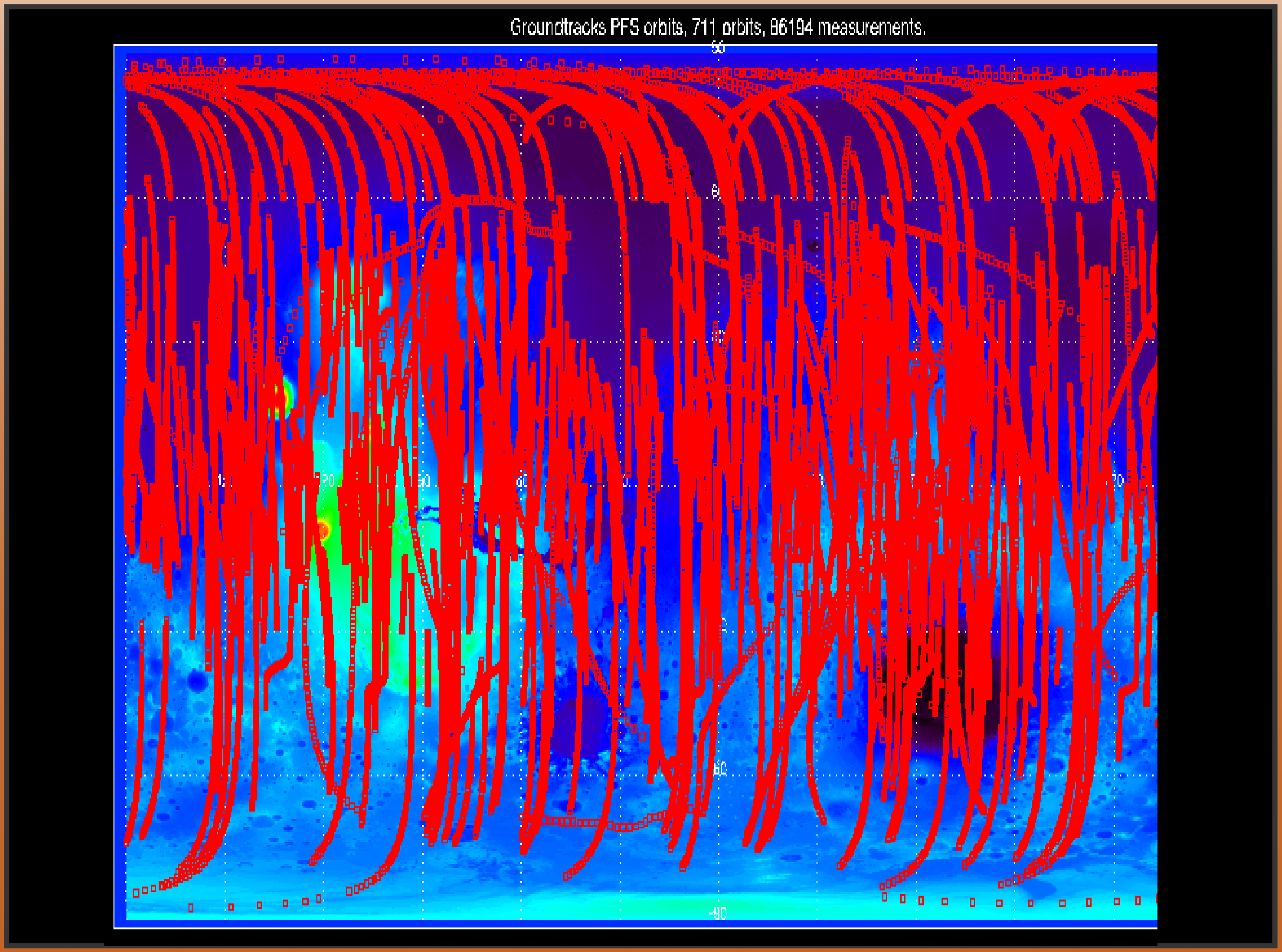


Possible Detectable Species - Model

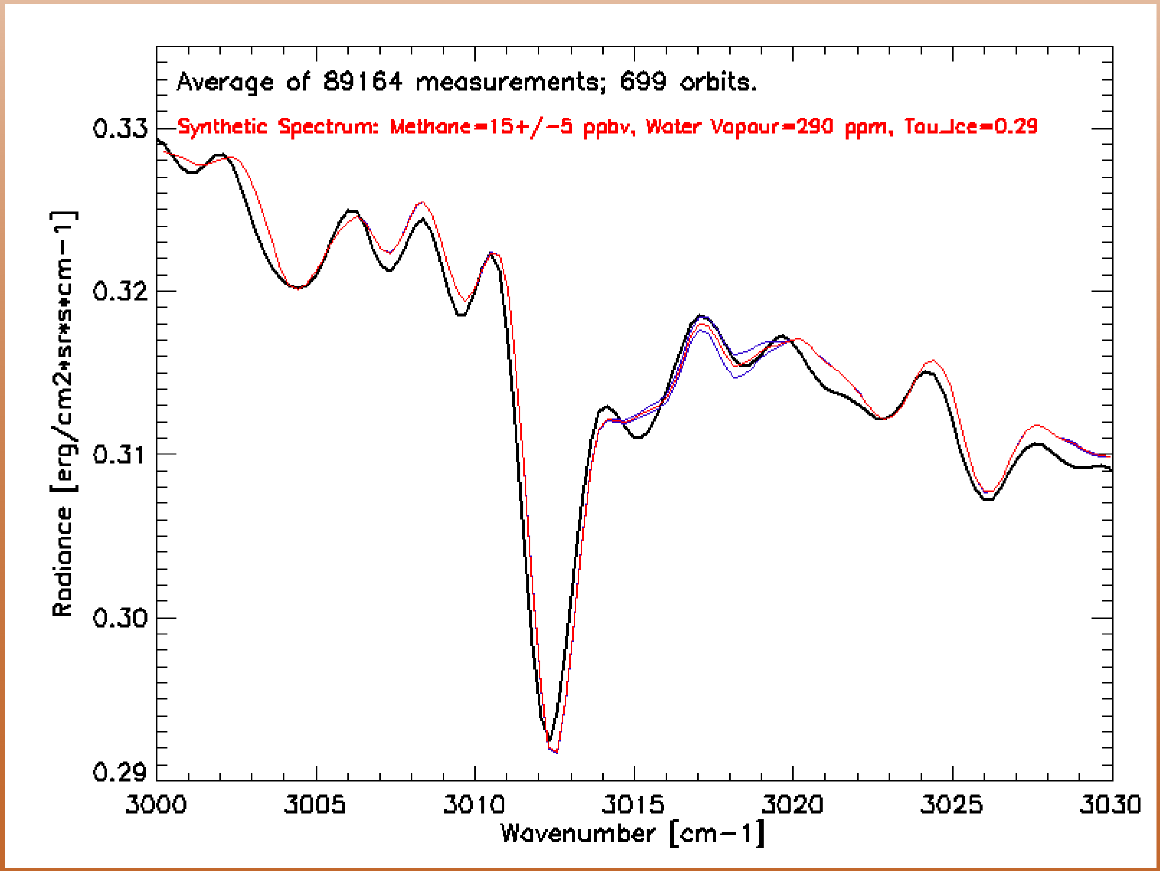
(100 ppm outgassing of SO_2, H_2S, CH_4)

Species	Mixing ratio (10 km)	Column abundance (cm^{-2})	Photochemical lifetime
SO_2	1.7 (-4)	1.8 (19)	40 days
H_2S	1.8 (-5)	7.4 (17)	9 days
SO	1.7 (-7)	7.8 (16)	4.6 hours
CH_4	1.0 (-4)	1.0 (19)	670 years
CH_2O	2.8 (-11)	1.6 (13)	7.5 hours
CH_3OH	4.3 (-12)	8.2 (11)	74 days
C_2H_6	6.4 (-12)	9.6 (11)	25 days

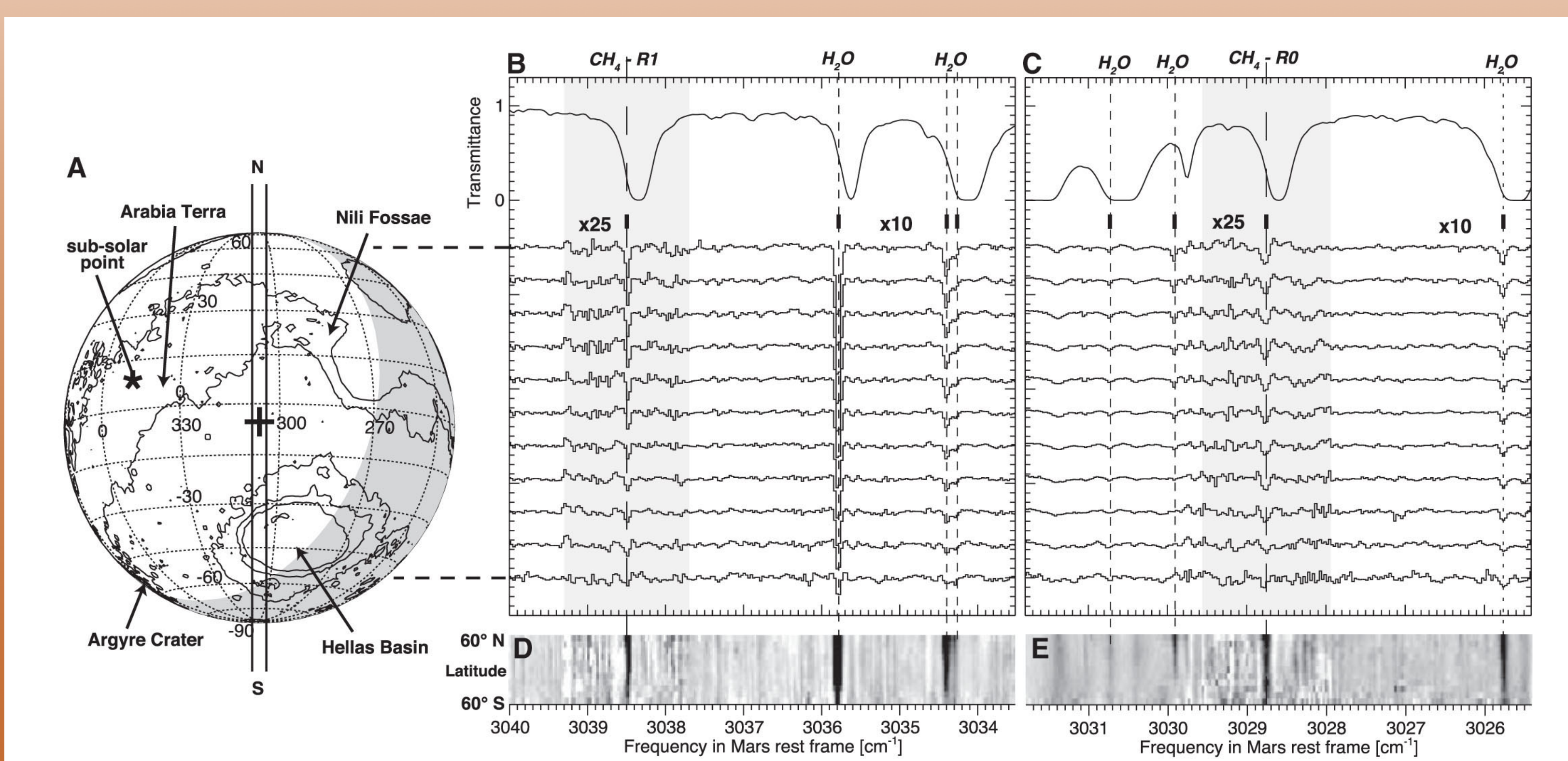
Mars Express PFS orbit ground-tracks



global average methane: 14±5 ppbv



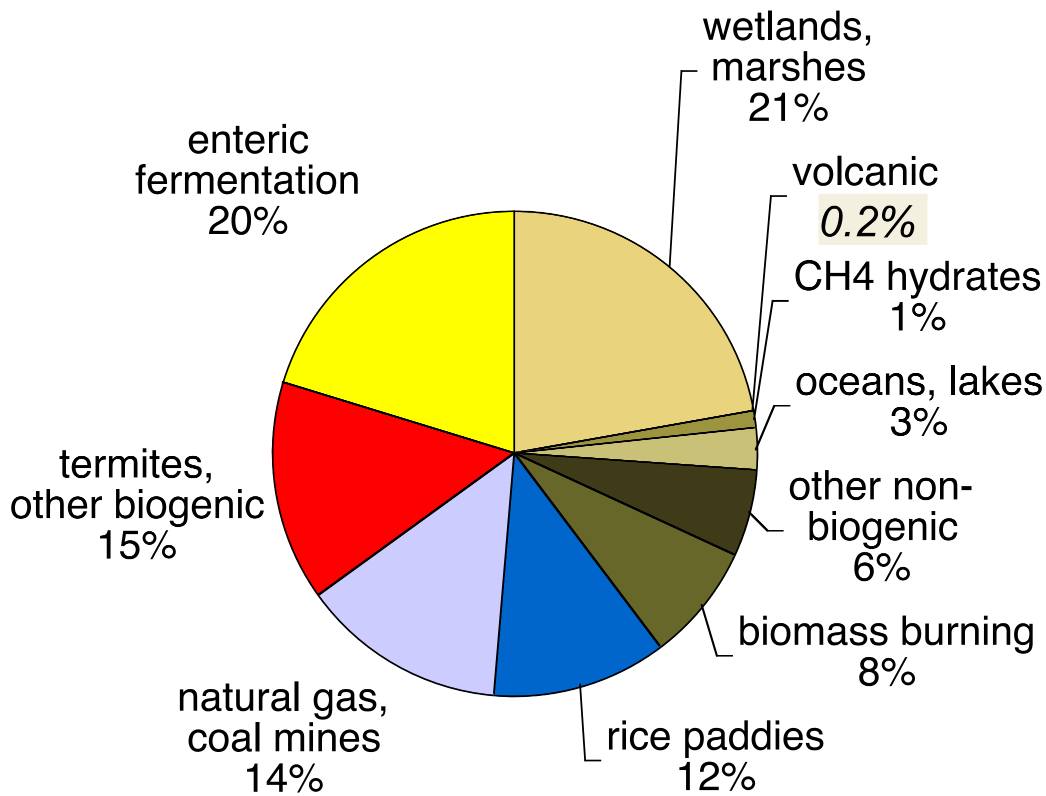
Mars Express PFS (Formisano et al., 2004; Geminale et al., 2007)



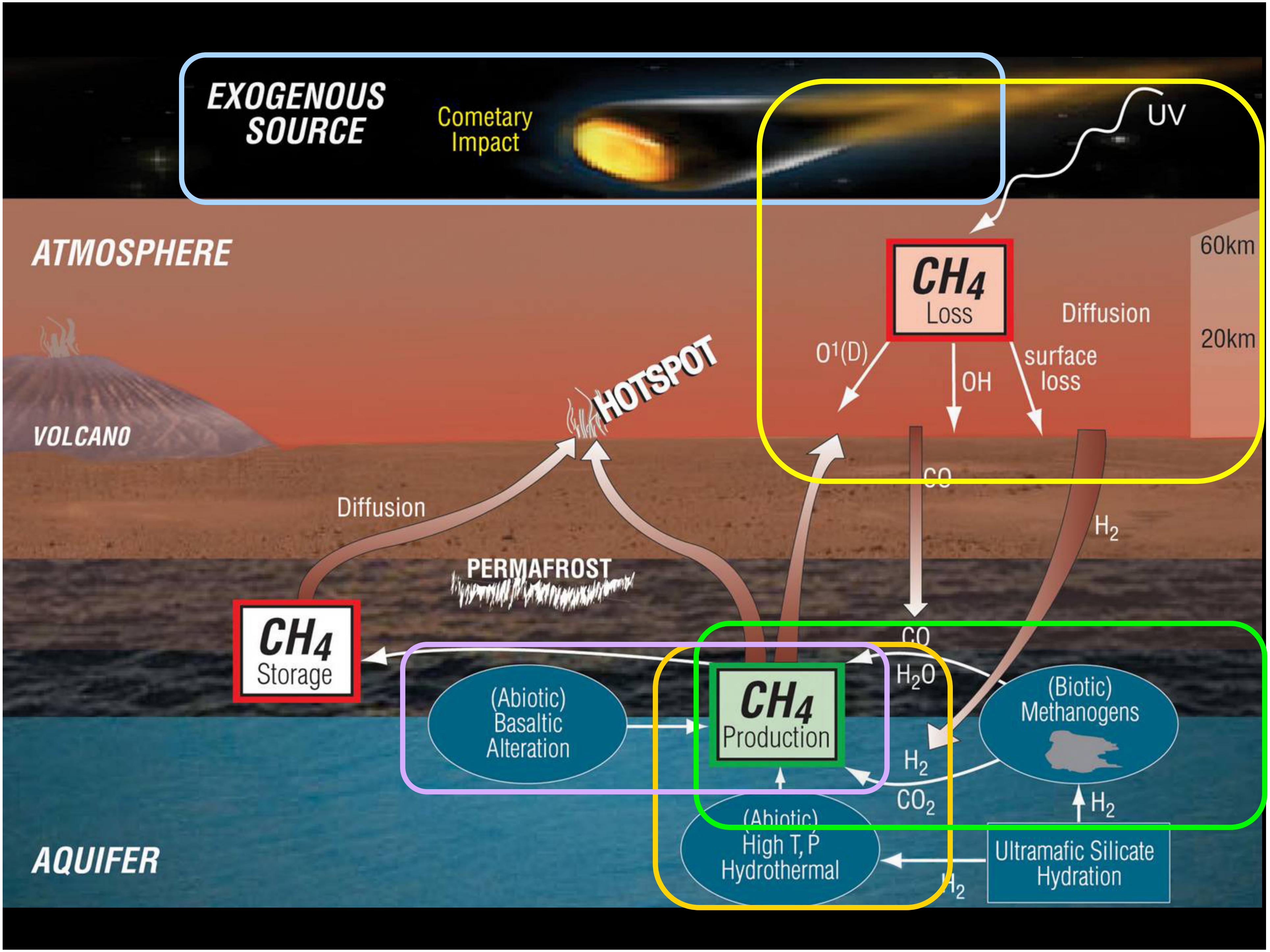
IRTF & Keck 2 (Mumma et al., 2009)

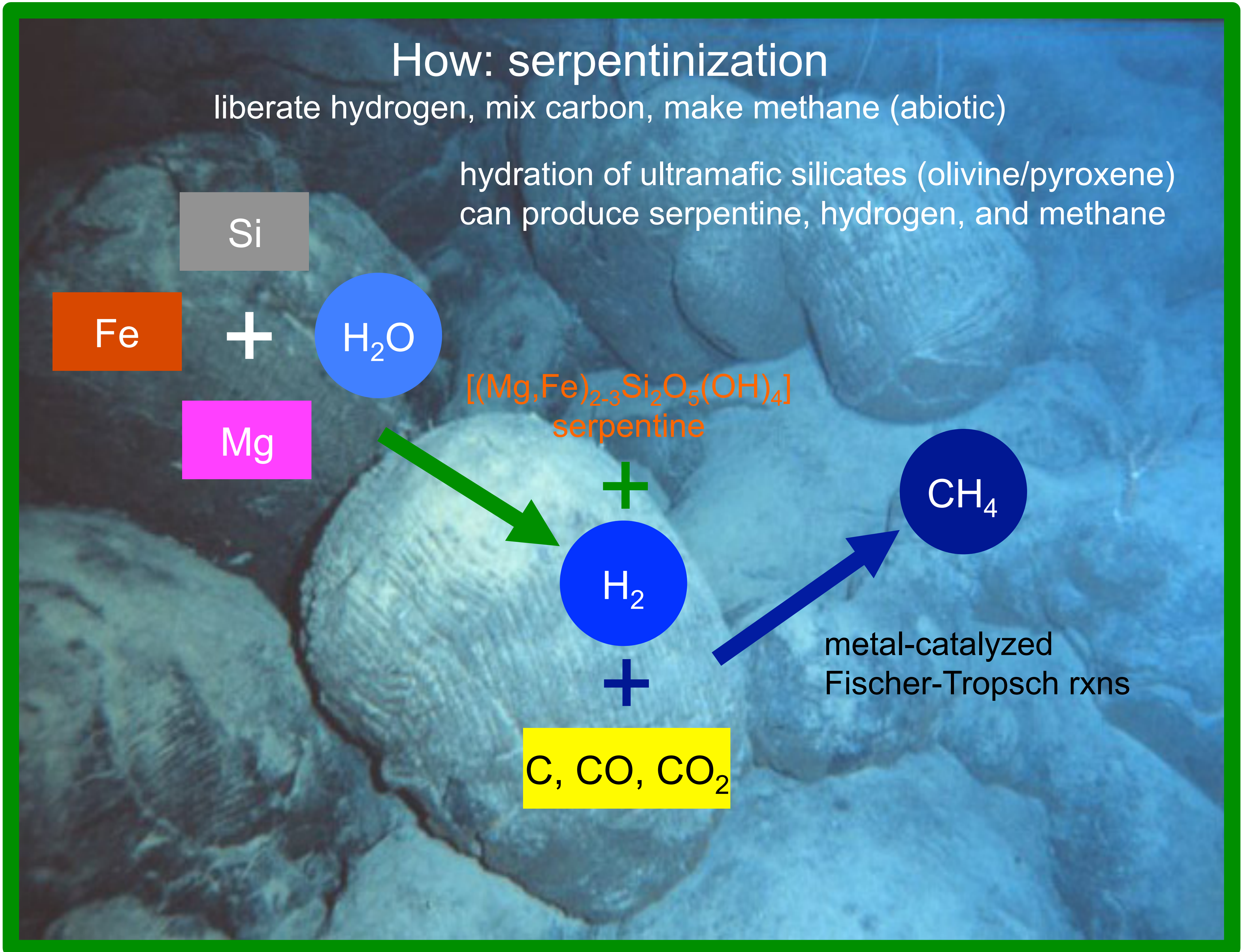
mars methane: significant findings

- MEX/PFS (>500,000 spectra; 3018 cm^{-1}; Formisano et al., 2003-present)
  - average 14±5 ppbv; non uniform; *footprint ≥1000 km*
  - max: 35-50 ppbv; *hotspots* - Arabia Terra, Elysium Plenum, N-pole
  - min: <10 ppbv; hints of seasonal variability
- CSHELL/IRTF, NIRSPEC/Keck-2 (R0, R1; Mumma et al., 2003-2006)
  - average 10-20 ppbv; non uniform, *footprint ~800 km*
  - max: ~35 ppbv; east of Arabia Terra, Nili Fossae, SE Syrtis Major
  - *in plumes* when present; transient
- CFHT/ FTS (3018 cm^{-1}; Krasnopolsky et al., 2004)
  - global average only: 10 ppb (<30 ppbv from later observations)

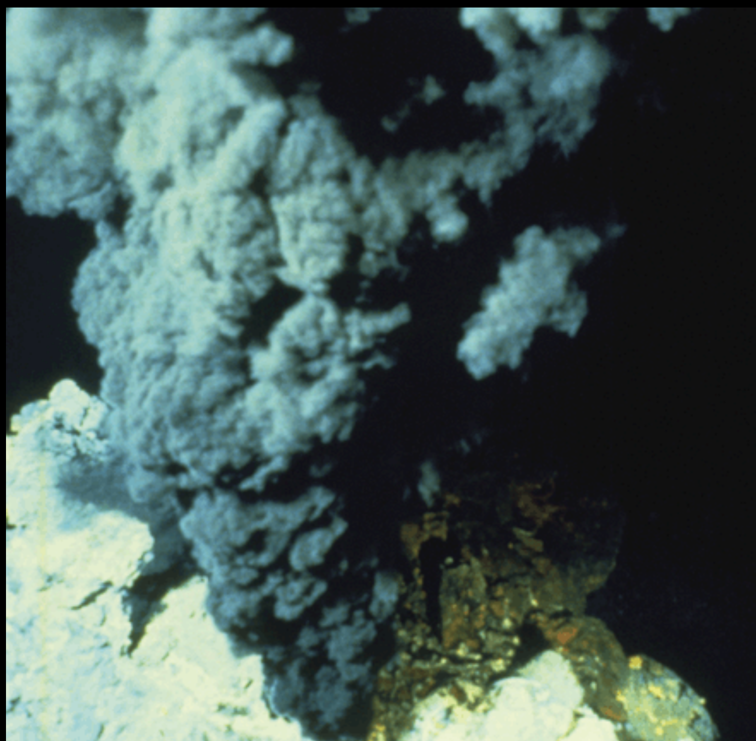


methane sources on Earth (1750 ppbv)


EXOGENOUS SOURCE
Cometary Impact
UV
ATMOSPHERE
60km
20km
CH4 Loss
Diffusion
O1(D)
OH
surface loss
HOTSPOT
VOLCANO
Diffusion
CO
H2
PERMAFROST
CH4 Storage
CO
H2O
CH4 Production
(Abiotic) Basaltic Alteration
(Biotic) Methanogens
H2
CO2
H2
(Abiotic) High T, P Hydrothermal
Ultramafic Silicate Hydration
H2
AQUIFER


How: serpentinization
liberate hydrogen, mix carbon, make methane (abiotic)
hydration of ultramafic silicates (olivine/pyroxene)
can produce serpentine, hydrogen, and methane
Si
Fe
+
H_2O
Mg
$[(Mg,Fe)_{2\text{-}3}Si_2O_5(OH)_4]$
serpentine
+
H_2
+
C, CO, CO_2
CH_4
metal-catalyzed
Fischer-Tropsch rxns

Where (on Earth): Black Smoker hydrothermal vents abiotic CH_4 by *high* temperature serpentinization



Mid Atlantic Ridge

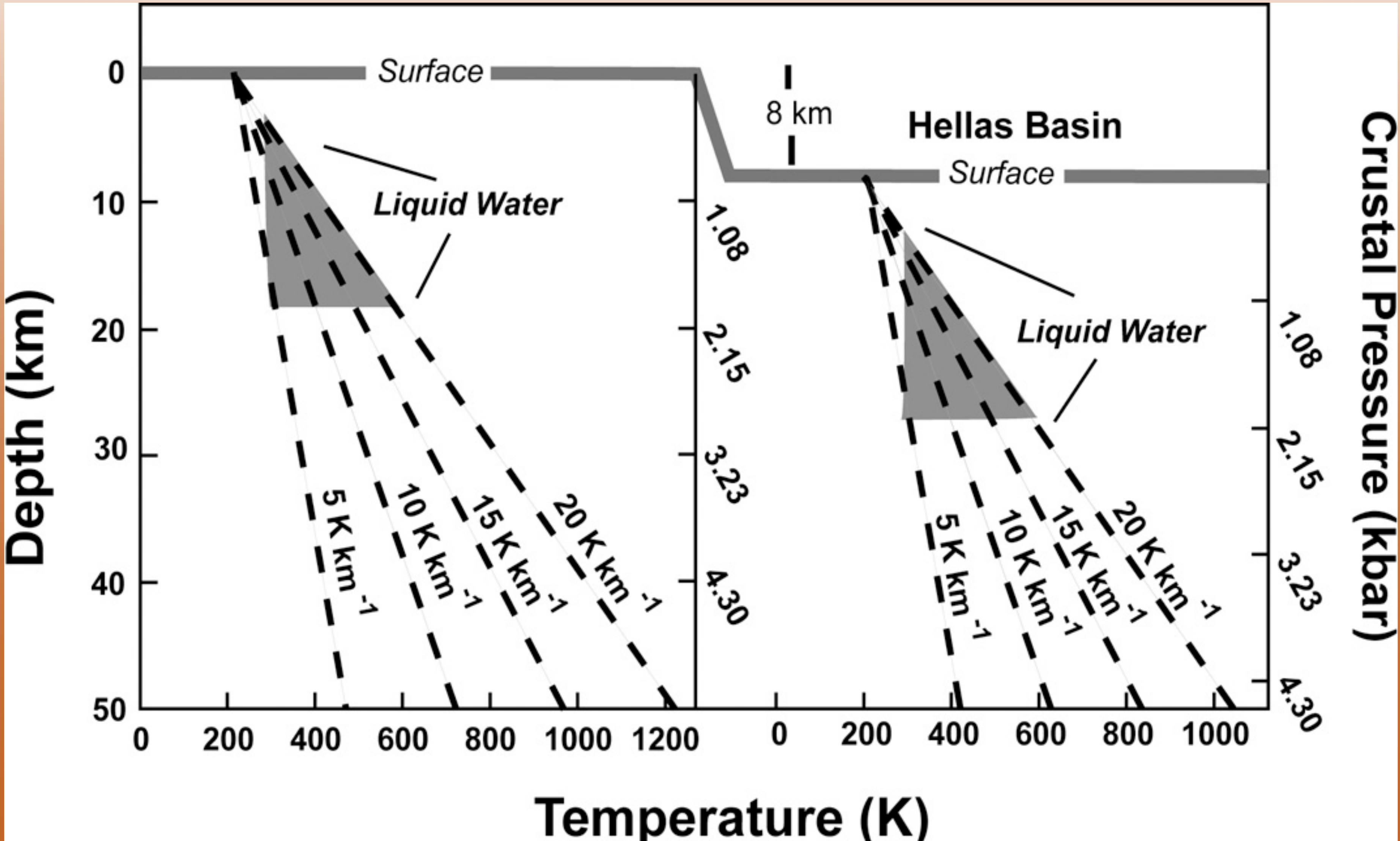
Juan De Fuca Ridge	
depth	*2222 m*
exit temp	*342 C*
pressure	*200 bar*
chimney ht.	*10 m*

300-500 C, sulfur-rich, highly acidic (~lemon juice)

Where (on Earth): Lost City
abiotic CH_4 by *low* temperature serpentinization

- 15 km from Mid-Atlantic Ridge
- 30-90 C
- highly alkaline (~ammonia, milk of magnesia)
- 20m high carbonate towers
- little sulfur minerals

mars geotherms: liquid water stable in 2-25 km, 20-300 C

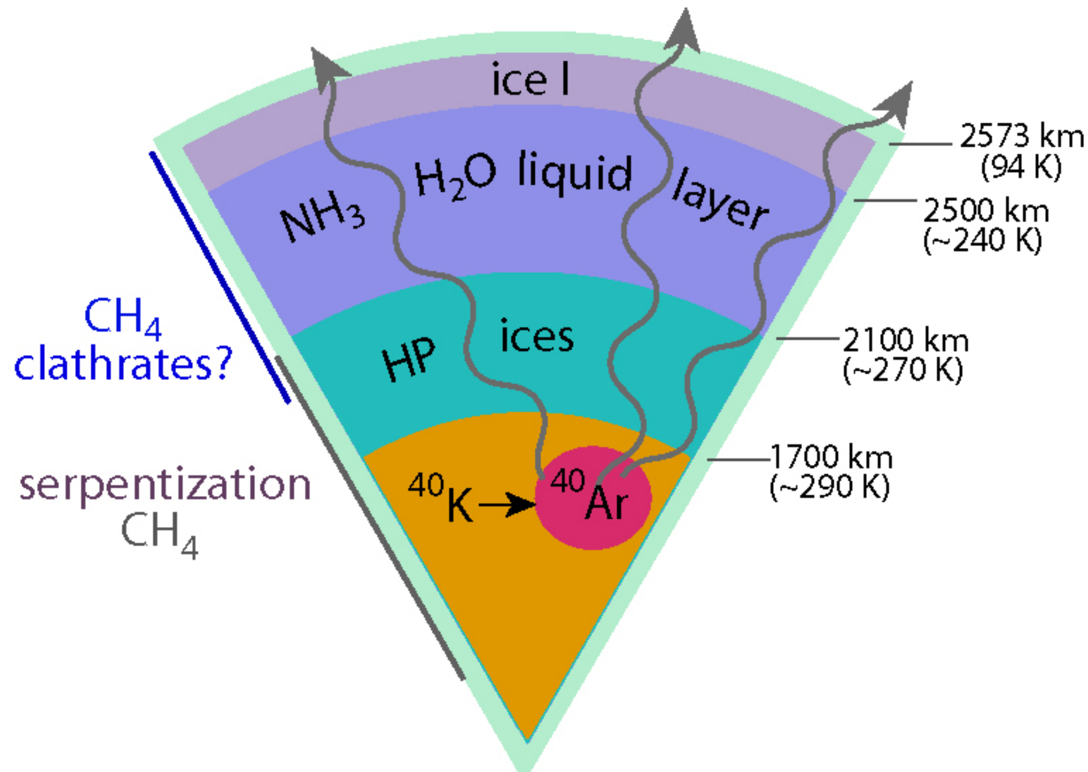


(Oze,Sharma, 2005)

Outgassing at Titan

- ^{40}Ar detection ($^{40}K \rightarrow {}^{40}Ar$ 1.3 Gyr half-life)
- cryovolcanism
- CO (VIMS)

→CH_4 outgassing



(interior structure, after Grasset et al.)

methane *origin*, now or in the past

- ***Geologic*** (or hydrogeochemical)

  i.e. water-rock chemistry, involving serpentinization and metal-catalyzed Fischer-Tropsch type reactions, or

- ***Biogenic*** (microbial methanogenesis)

  i.e. by enzymatic reduction of CO_2 , or fermentation of organic matter by microbes in the metabolic process

Liquid water essential to both

(subsurface aquifers, if CH_4 produced recently)

source strength: shorter life, bigger flux

- **Photochemical loss:** long life, small source flux
  - 300-600 yrs, ~200 ton/yr → uniform methane

- **Reactive surface:** faster loss, i.e. ~one year lifetime, requiring much bigger source flux

- **Surface loss due to oxidants**
  - ***peroxide*** (very reactive), i.e.
    resulting hydroxyl, hydroperoxy (HO_2), superoxides
  - ***perchlorates*** (very stable, but reactive with free Cl)

organics and oxidants don't mix

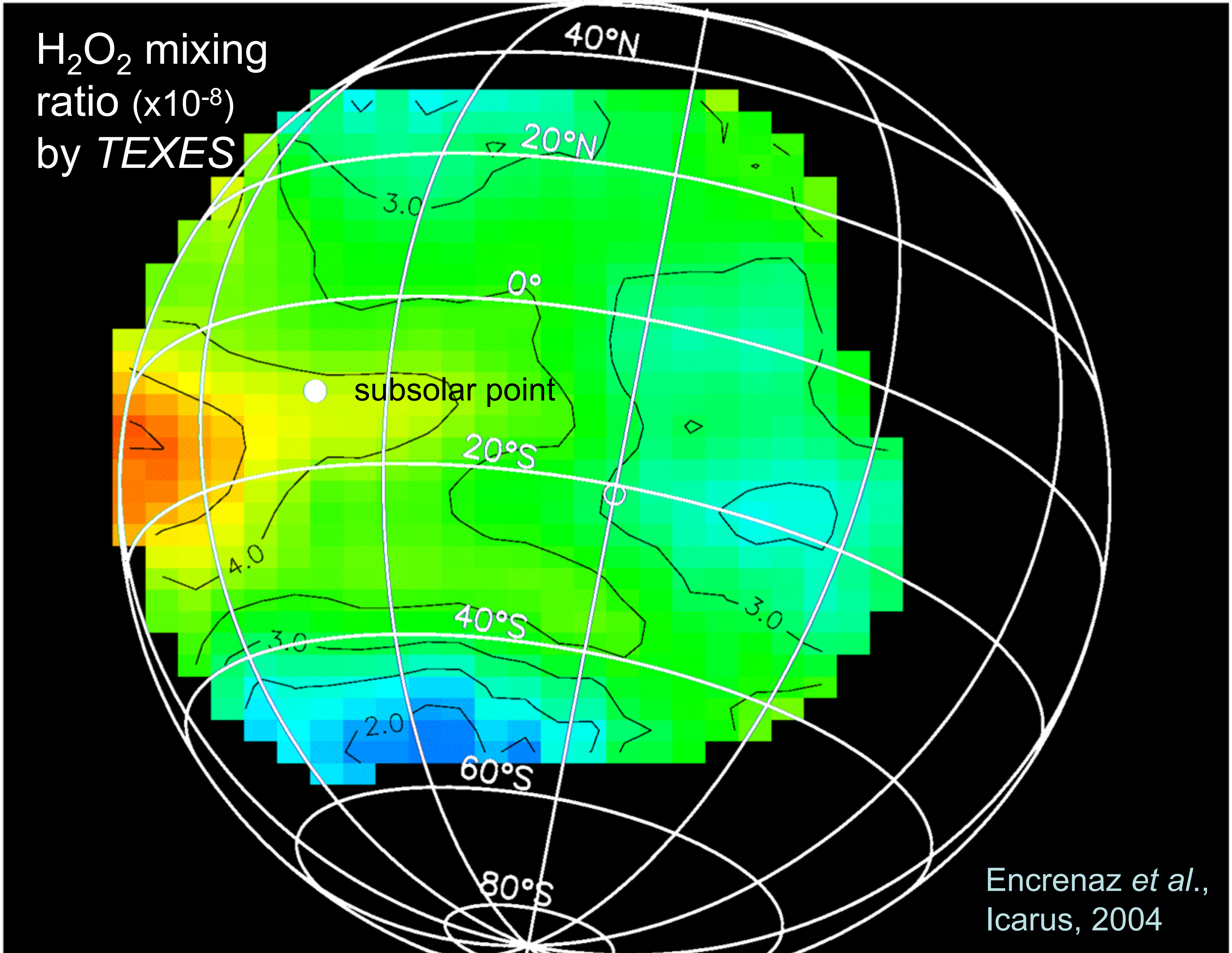
- **Viking (1976) Life Sciences Experiments (LSE)**
  - **GCMS: no organics found in Martian soil --**
    - **Indigenous; or externally delivered by meteorites, IDPs, comets**
  - **GEX: nutrients & H_2O added, O_2 released rapidly:**

    ***surface* oxidant ; required amount 20-250 *ppm* H_2O_2**

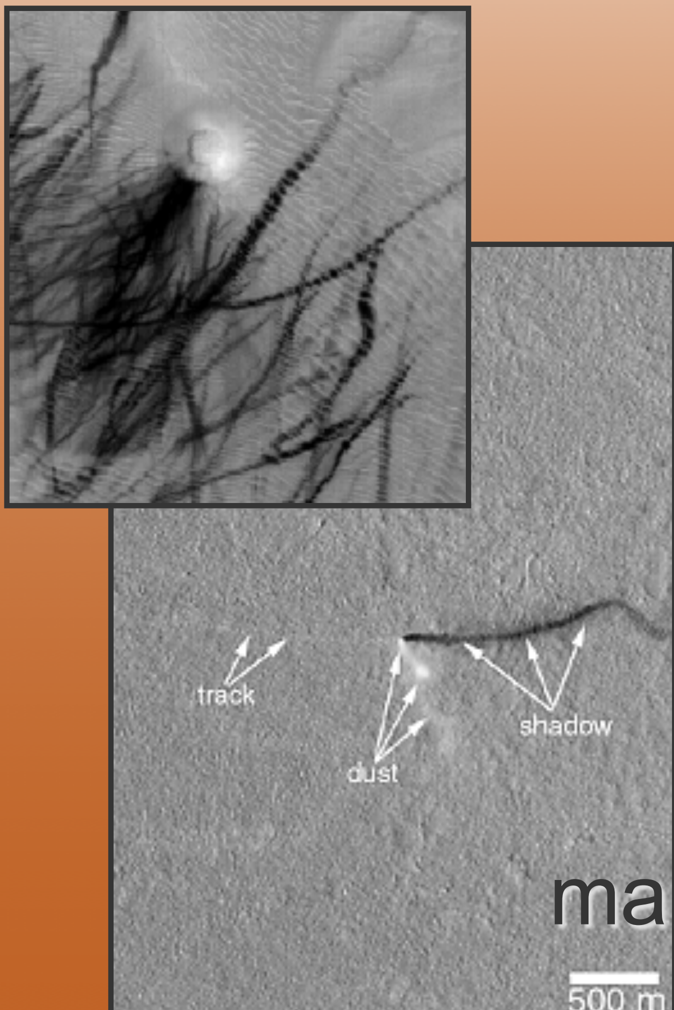
    (Oyama, 1977; Hunten, 1979; Huguenin, 1982)

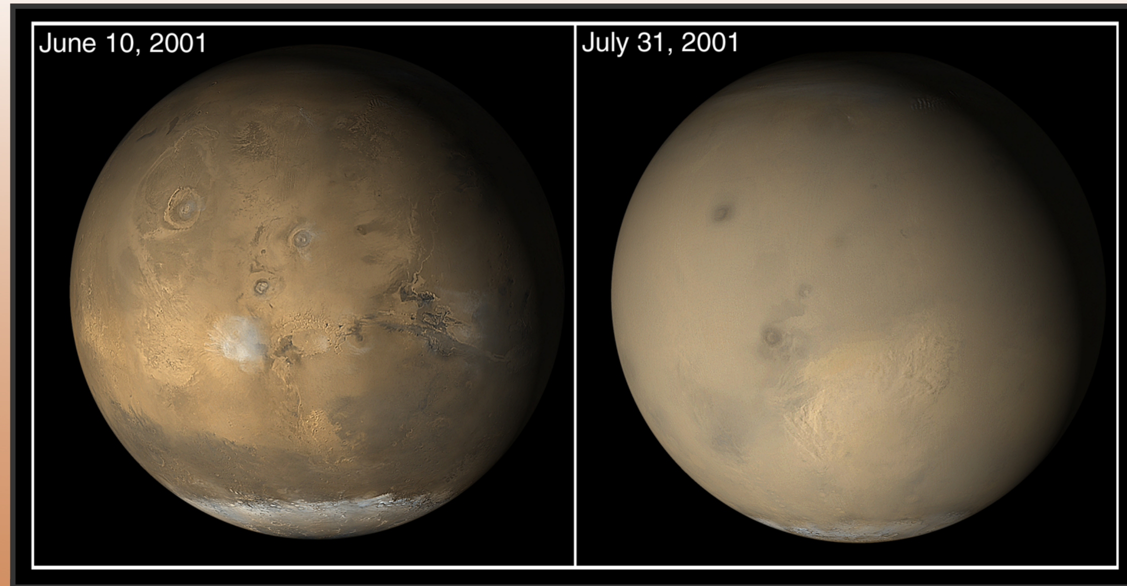
- **In 2003, 20-40 *ppb* H_2O_2 in *atmosphere* detected, but is *too low by a factor of 100-1000* compared to LSE requirement**

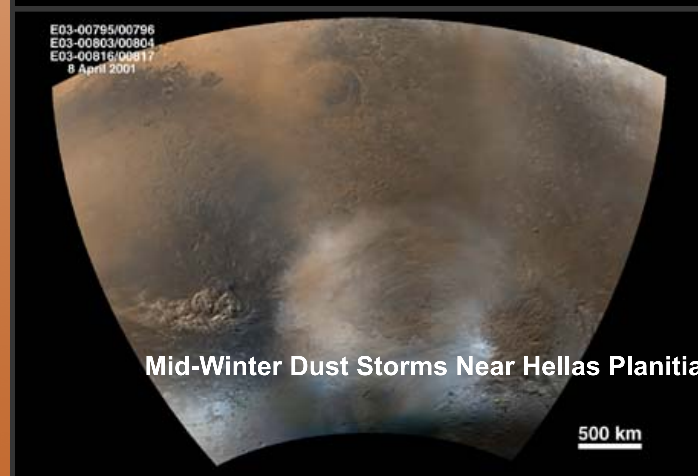
[H_2O_2 detection: submm 362.156 GH,
Clancy et al,; IR (8.04 – 8.13 μm) Encrenaz, et al.]

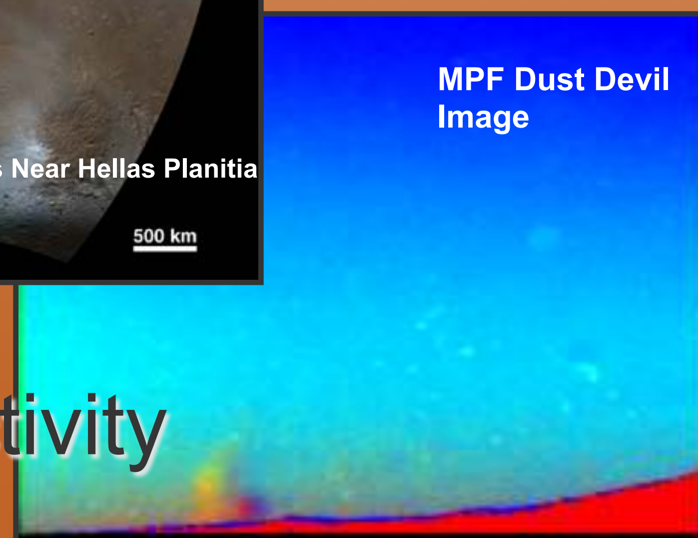

H_2O_2 mixing ratio ($x10^{-8}$) by *TEXES*
40°N
20°N
0°
20°S
40°S
60°S
80°S
3.0
4.0
3.0
2.0
3.0
subsolar point
Encrenaz *et al*., Icarus, 2004

aeolian triboelectricity



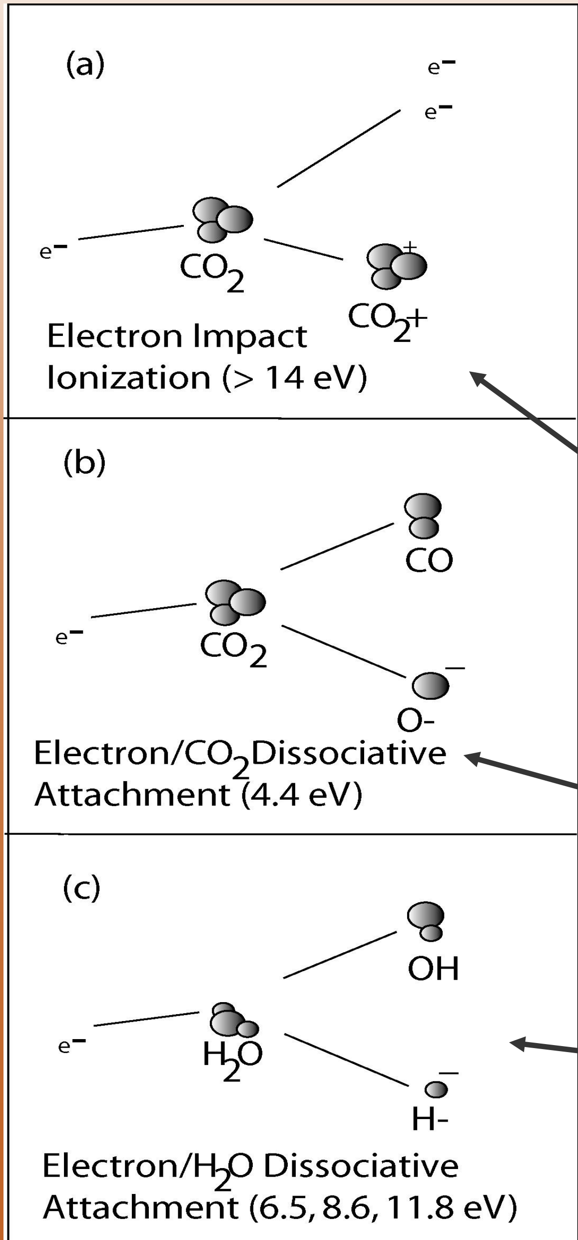






martian dust activity

enhanced species production in dust storm collisional plasmas



- three new product sets results from the energetic electron population [Delory et al. '06; Farrell et al, '07]
- production of CO_2^+ (> 14 eV)
  $e + CO_2 \rightarrow 2e + CO_2^+$
- production of CO/O- (~4.4 eV)
  $e + CO_2 \rightarrow CO + O^-$
- production of OH/H^- (~6.5 eV)
  $e + H_2O \rightarrow OH + H^-$

storm electric fields (triboelectricity) change near-surface chemistry

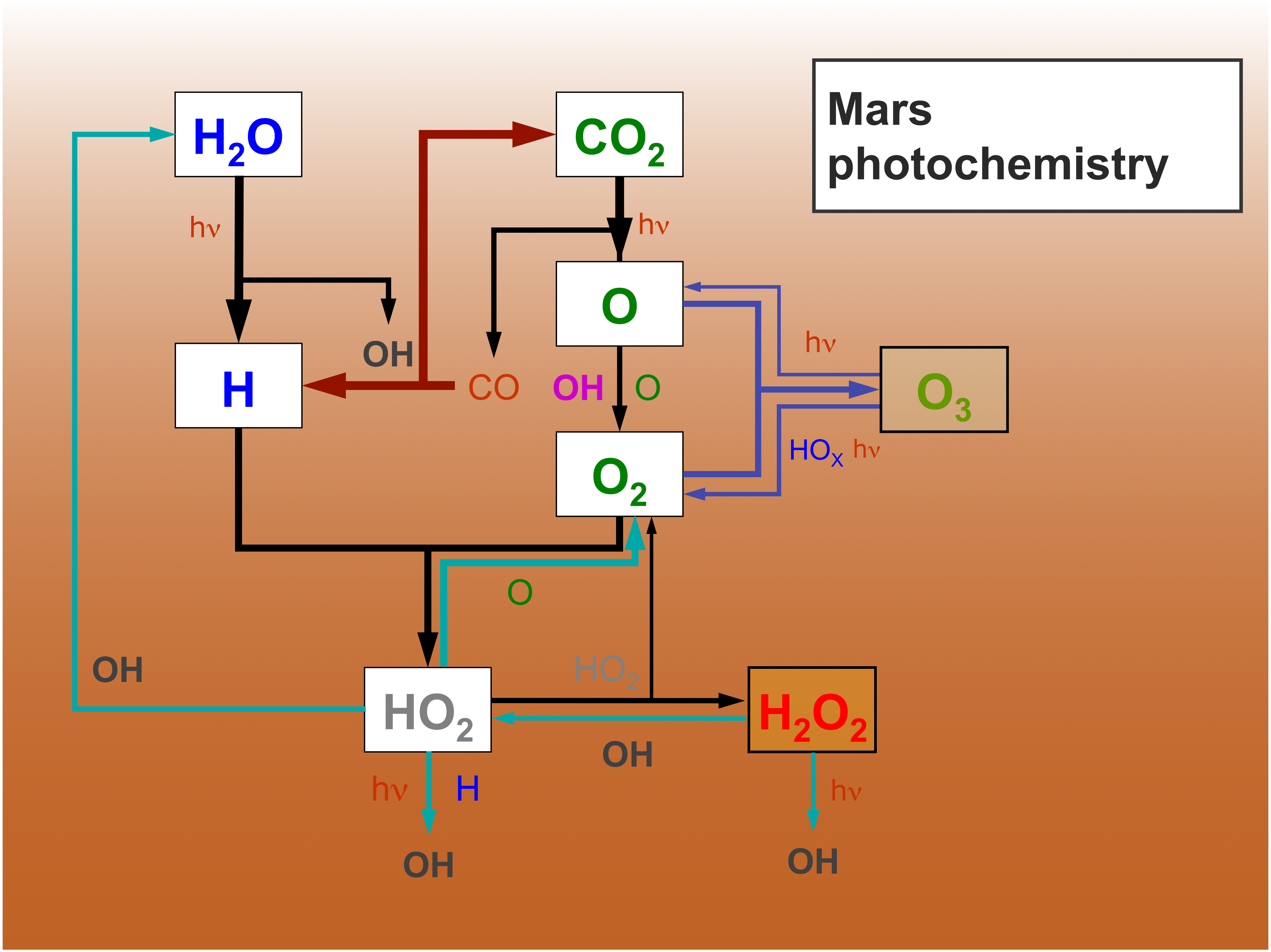
→ 5-25 kV/m[*] electrostatic fields generated in Martian aeolian processes, i.e. in convective dust storms and dust devils

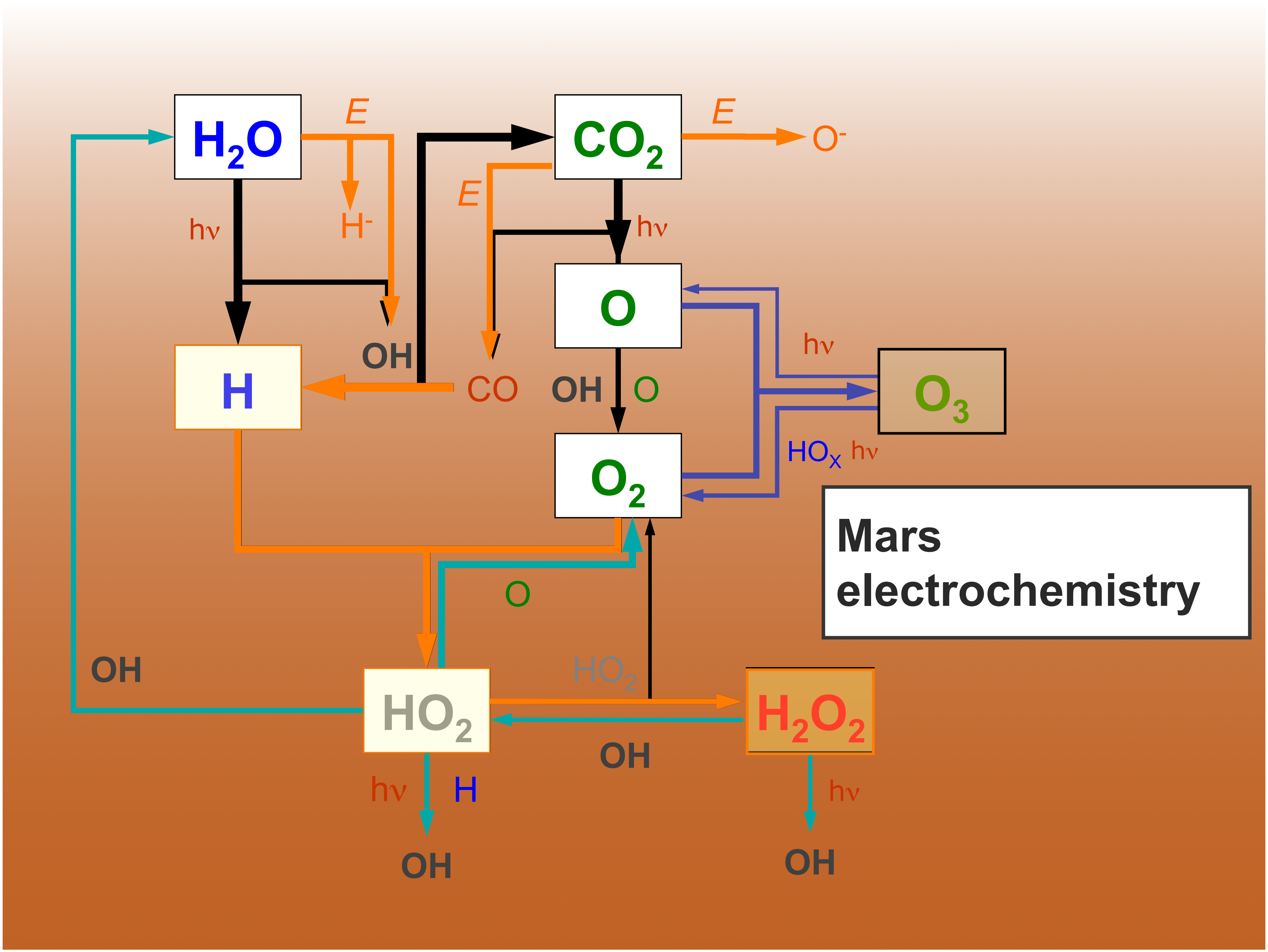
→ CO/O-, OH/H- ion pairs[*] produced→

→ H_2O_2 enhanced substantially by electrochemistry over photochemical source[**]

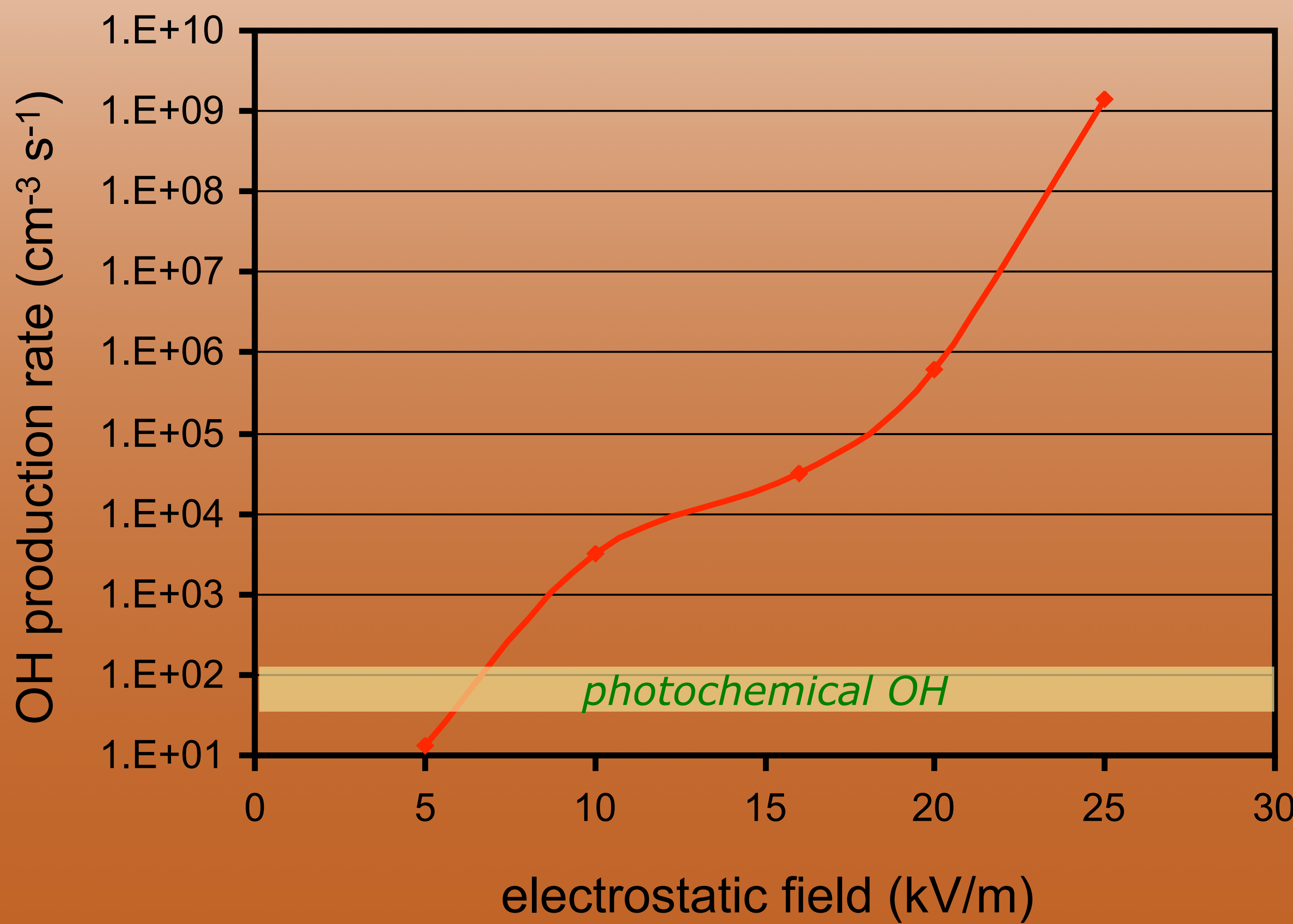
[*]Delory,et al. 2006, Farrell et al. 2007, Jackson 2009

[**]Atreya, et al. 2006

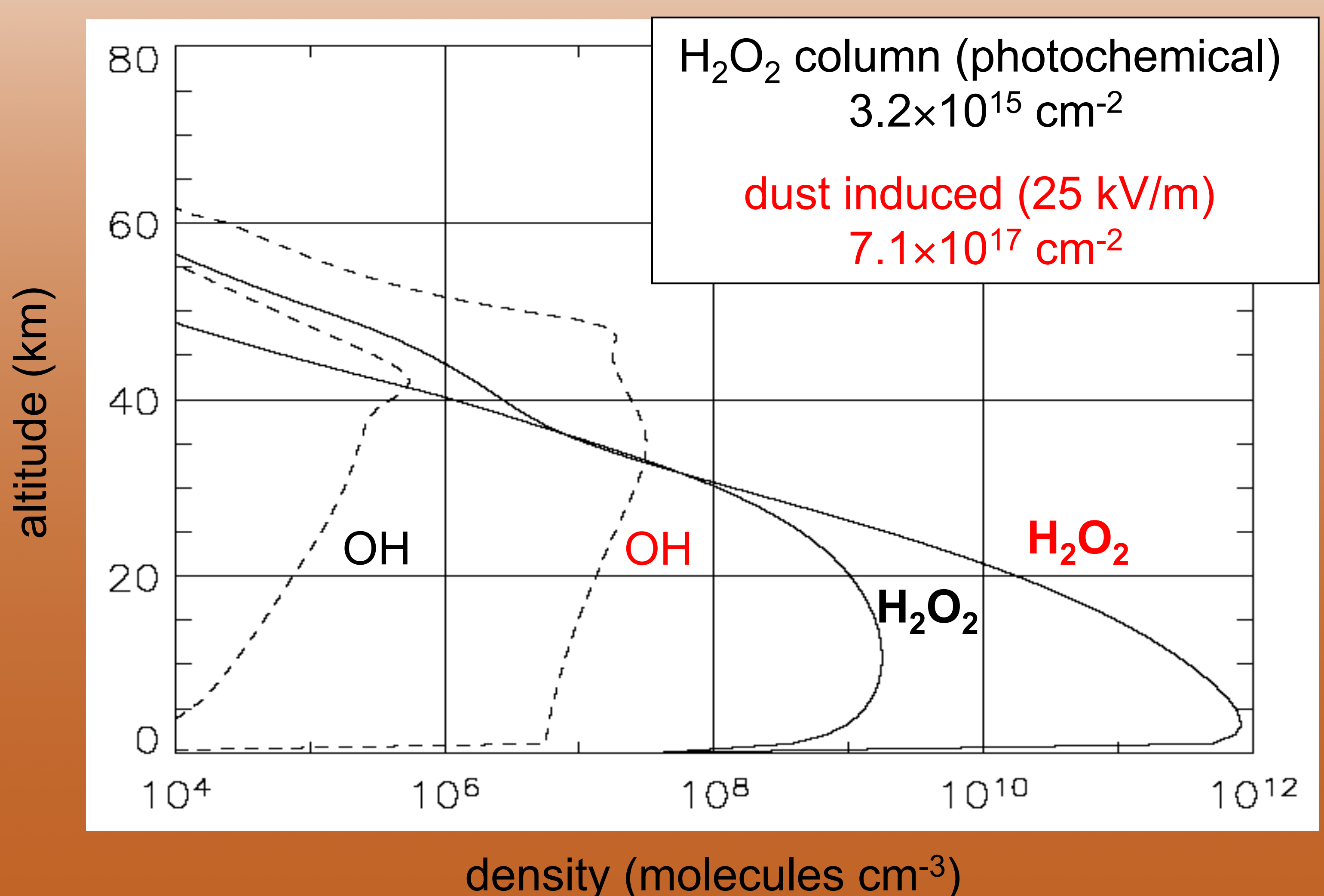

Mars photochemistry
H2O
CO2
hν
hν
OH
O
H
CO
OH
O
hν
O3
O2
HOx hν
O
OH
HO2
HO2
H2O2
OH
hν
H
hν
OH
OH


H2O
E
H-
hν
OH
CO2
E
O-
E
hν
CO
H
O
hν
O3
OH
O
O2
HOx hν
Mars electrochemistry
O
OH
HO2
HO2
H2O2
OH
hν
H
OH
hν
OH

dust-induced OH production



model profiles of OH, H_2O_2



storm electric fields make peroxide; peroxide & products destroy surface organics and methane

→ 10,000x enhancement of H_2O_2 over photochemical source** →

→ H_2O_2 "snow" → H_2O_2 into regolith

→ H_2O_2 in regolith lives long, up to millions of years (M. Bullock, 1996), compared to *less than* one day in atmosphere

→ *superoxides/ hydroxyl/ hydroperoxy (HO_2) generated in soil*

→ **rapid destruction of surface organics (directly), and of**

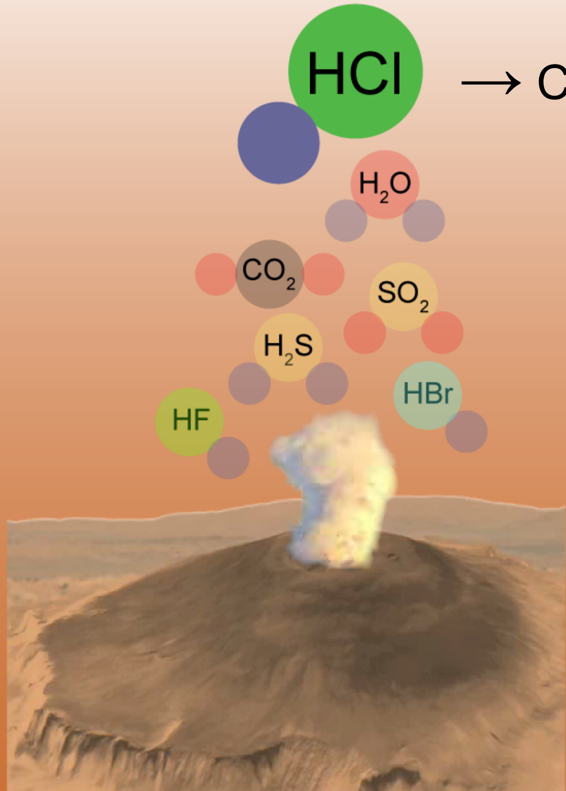
→ **methane*, by OH, HO_2 and superoxides* from H_2O_2**

→ ***excess CO recycles the CO_2 lost to triboelectricity***

Radiolysis of ice also produces H_2O_2, as on Europa, Ganymede & Callisto

**Atreya, et al. 2006

perchlorate (ClO_4^-) on Mars and Earth



$\rightarrow$ Cl

(odd)chlorine + (odd)oxygen $\rightarrow$ ClO, OClO, ClO_3

ClO_3 + OH $\rightarrow$ $H(ClO_4)$

ClO + H_2SO_4 $\rightarrow$ $H(ClO_4)$ + …

OClO + OClO +hν $\rightarrow$ $Cl(ClO_4)$

(H or Cl)ClO_4 (dry deposition) +surface minerals $\rightarrow$ $Mg(ClO_4)_2$, $K(ClO_4)$, …

brine

volcano

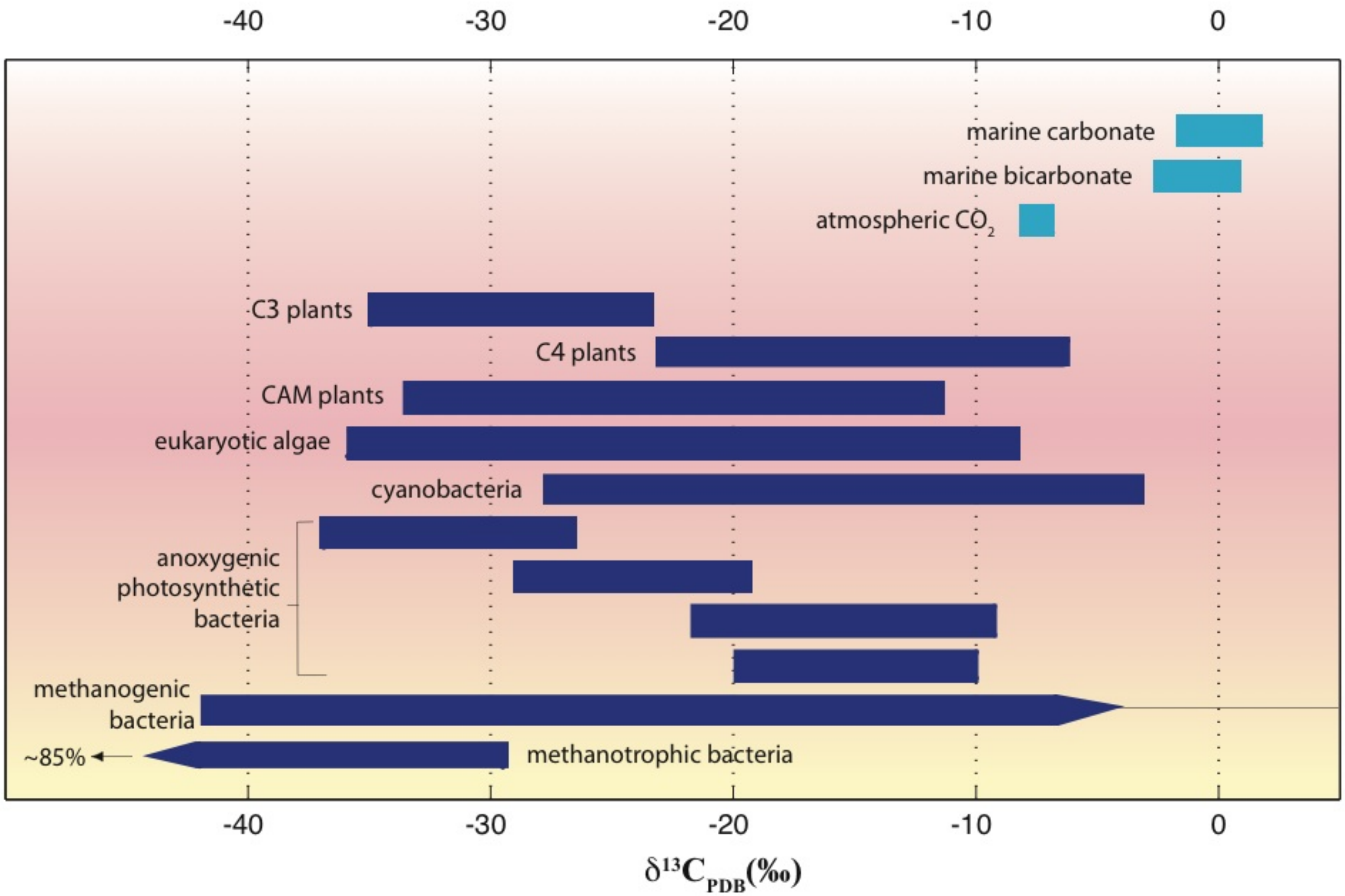
	Mars	*Earth*
where	north polar region	Atacama, Bolivia, Texas
how much	0.3 – 0.6 wt%	0.03 – 0.6 wt% (Atacama)
dry period	?	5-15 Myr (Atacama)

Life as we know it produces methane,

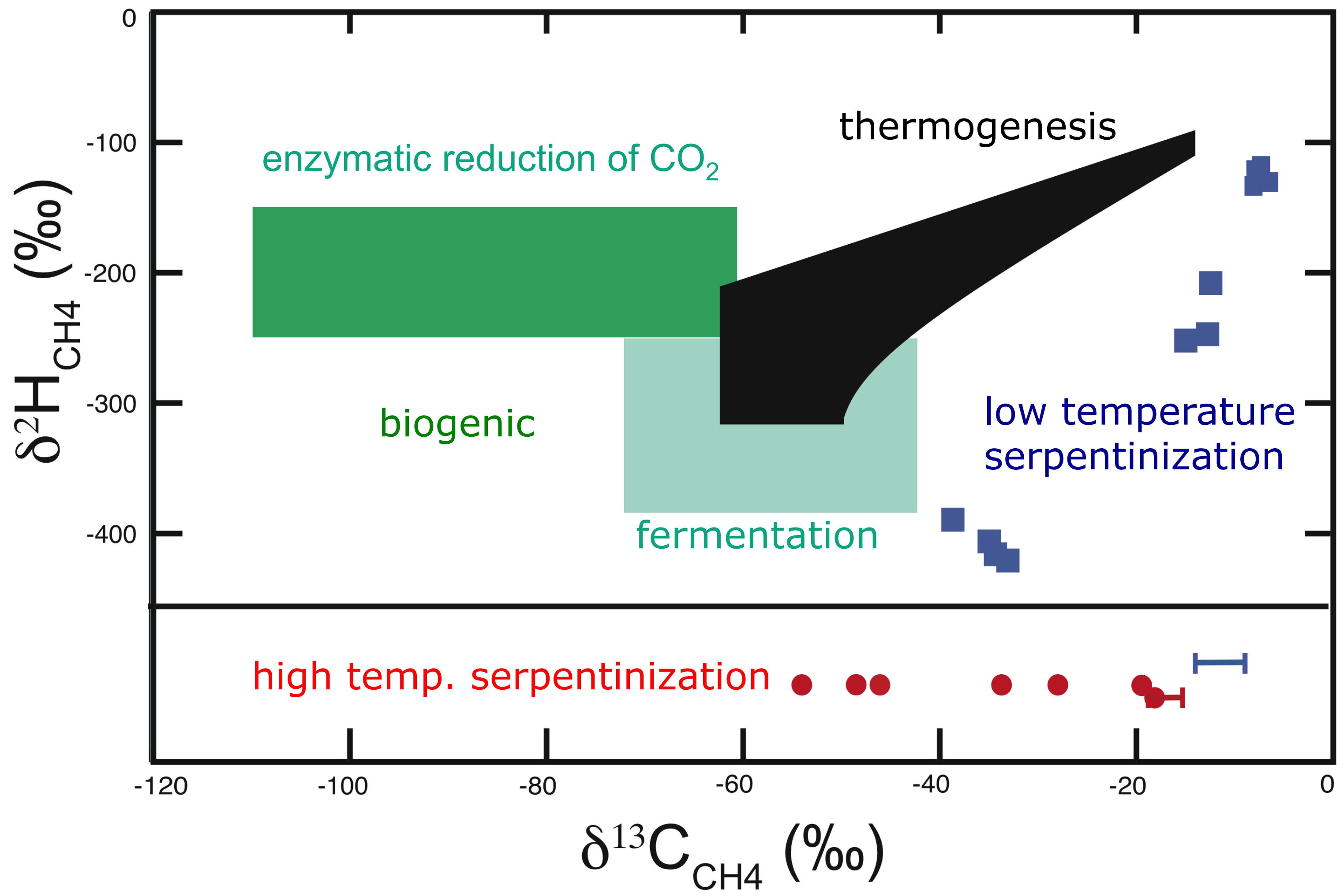
but

presence of methane does not by itself imply presence of life

Organic (living) vs. Inorganic ^{13}C carbon isotope V-PDB $^{12}C/^{13}C=89.4$

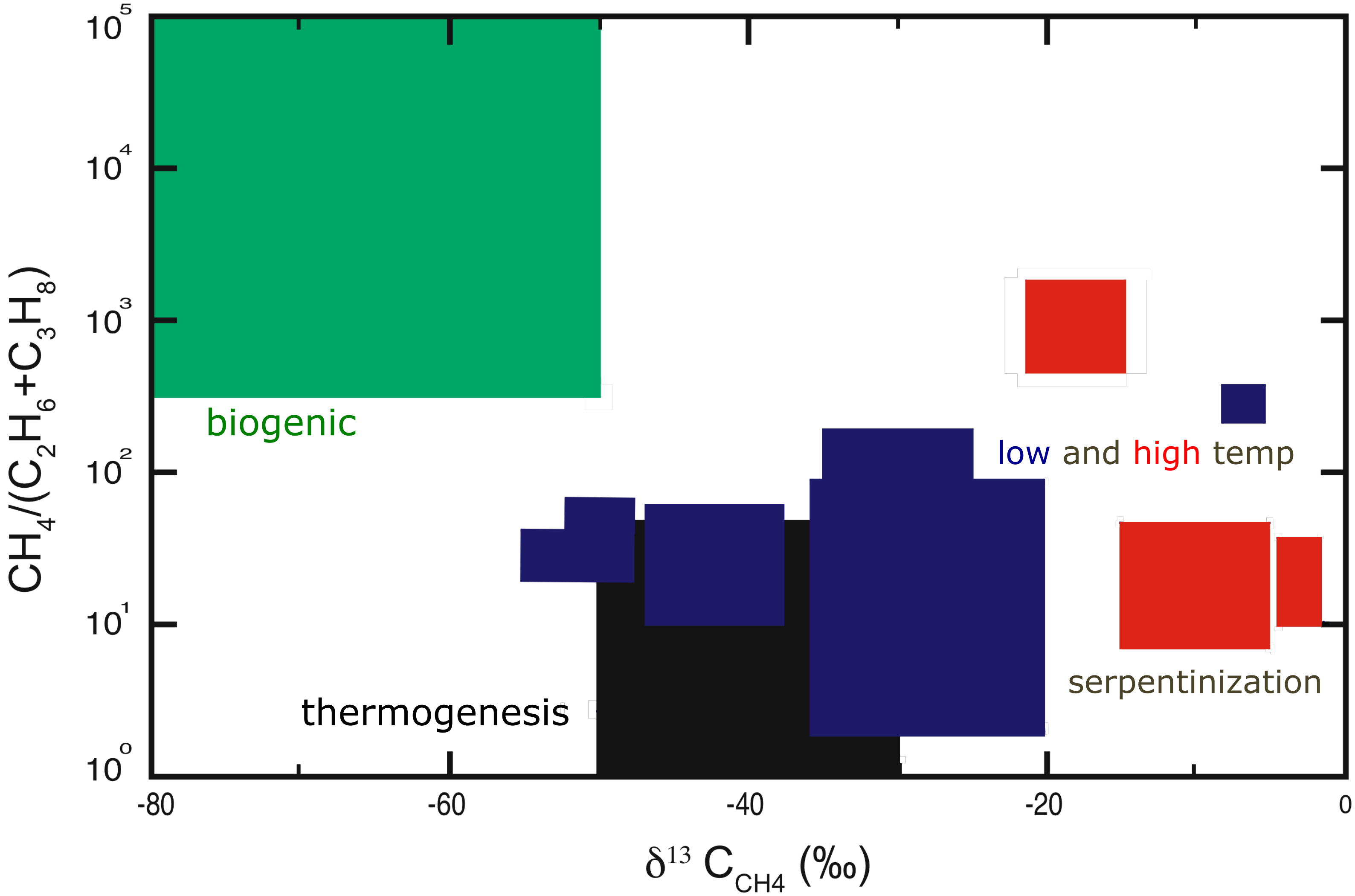


δ^2H vs $\delta^{13}C$ in CH_4



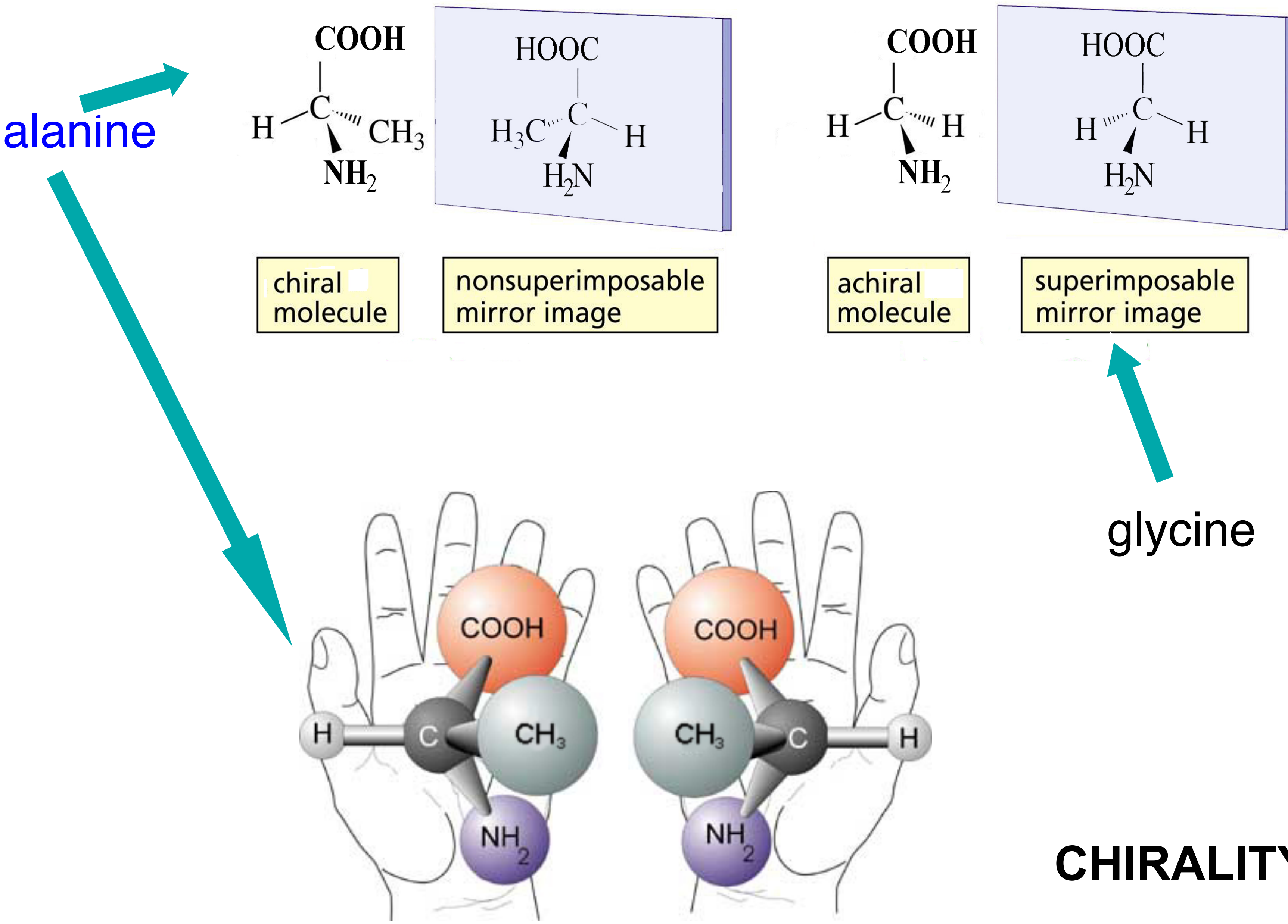
(adapted from M. Allen/ T. Onstott/ Sherwood-Lollar)

ratio of methane/(ethane + propane) with $\delta^{13}C$ (methane)

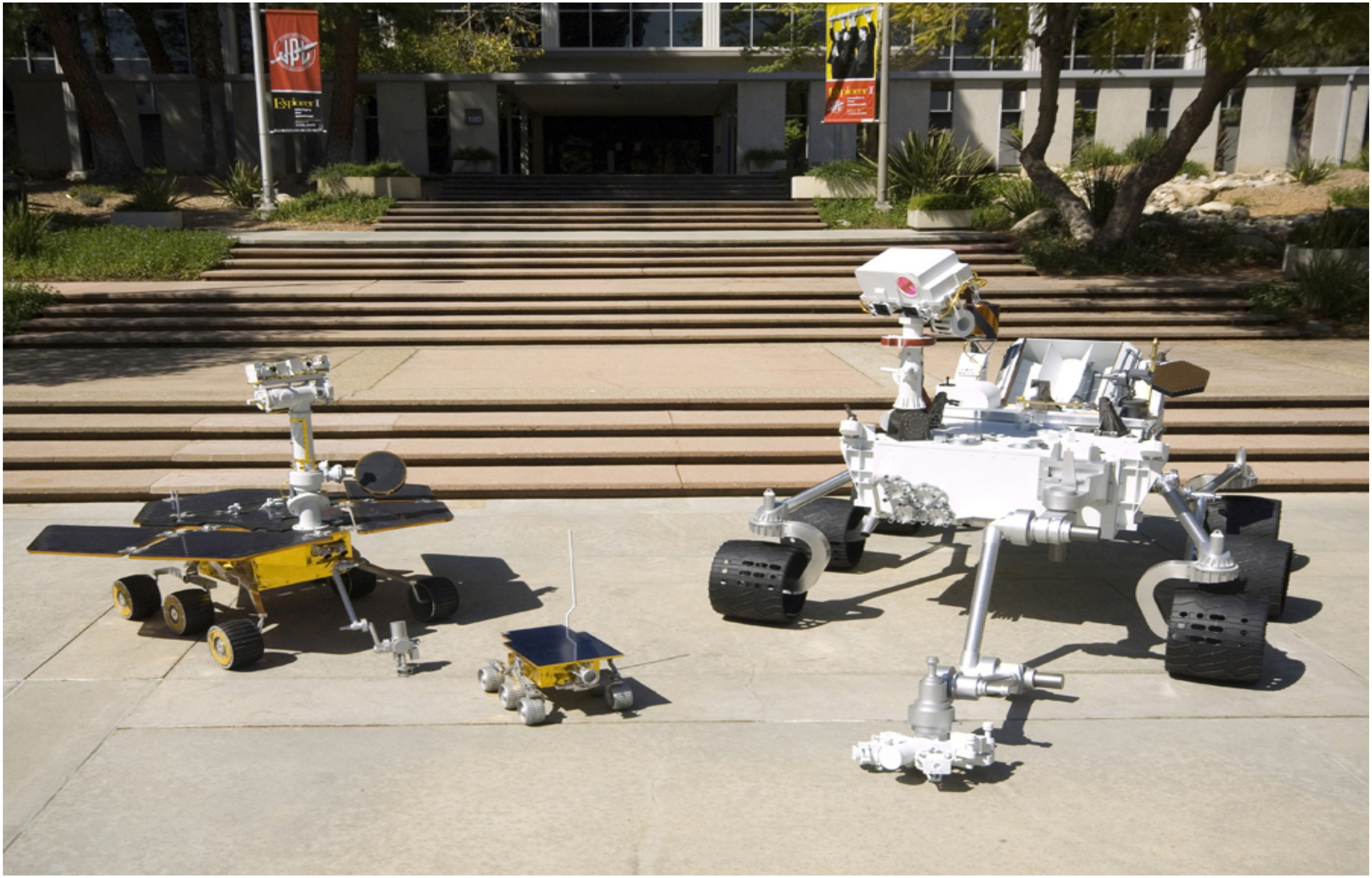


(after M. Allen/ Horita, Berndt)

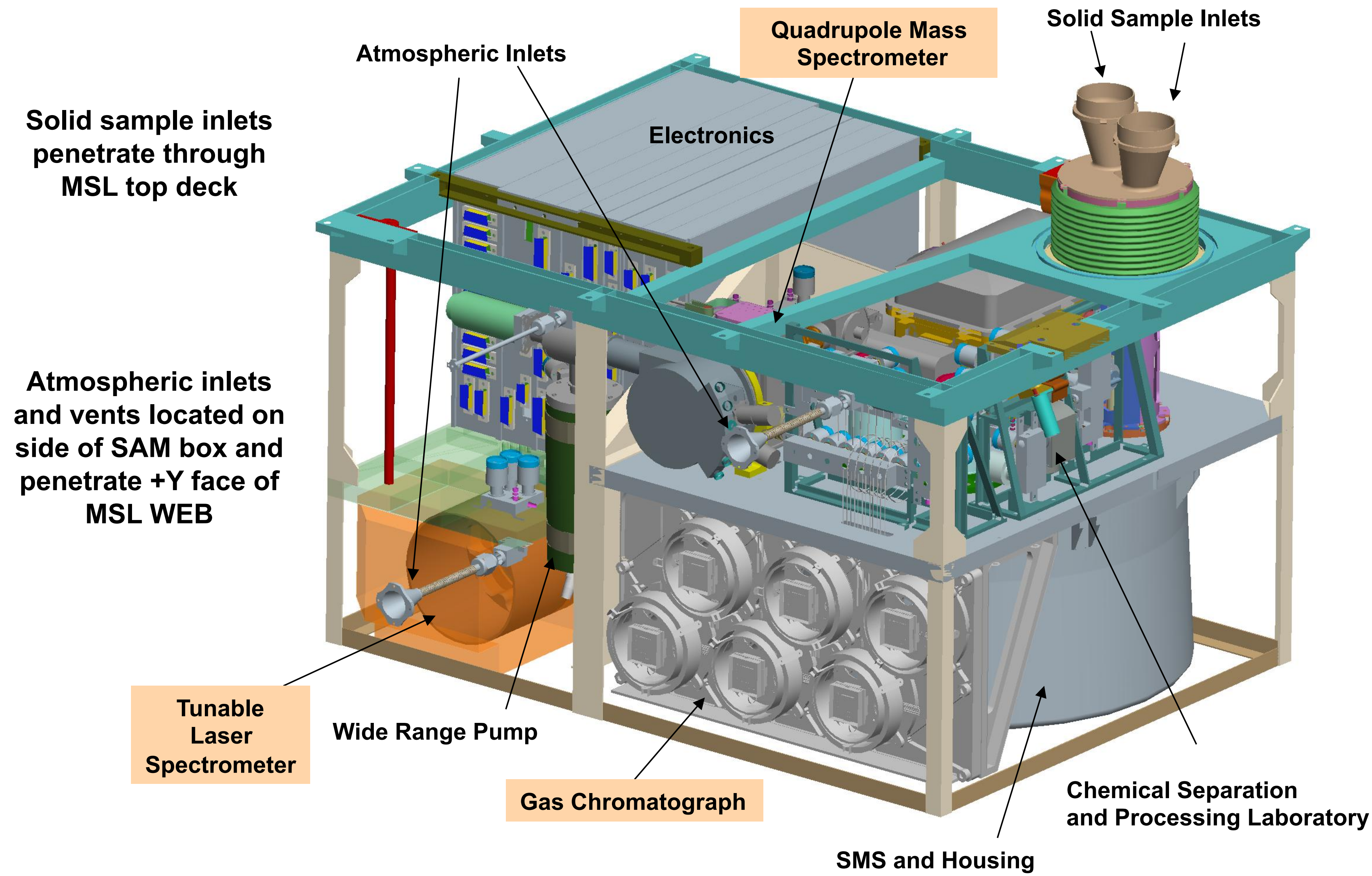
CHIRALITY


alanine
COOH
H
C
CH3
NH2
HOOC
H3C
H
H2N
chiral molecule
nonsuperimposable mirror image
COOH
H
C
H
NH2
HOOC
H
C
H
H2N
achiral molecule
superimposable mirror image
glycine
COOH
H
C
CH3
NH2
COOH
CH3
C
H
NH2

MER, Sojourner, MSL at JPL Science Fair



SAM Suite top assembly



take home

- ***Map of Trace Constituents*** in solid & gas samples, including methane, but not limited to it, essential to address key questions of Mars, such as habitability, and extinct or extant life
- ***Find the Organics***
- ***Isotopes of C, S, O, etc.*** also essential
- ***Conext: Mineralogical, Geologic, Environmental*** essential
- ***??****Surface oxidation state, surface-atmosphere-interior coupling over geologic time, electric fields at surface and in atmosphere, are some of the big unknowns, that still need addressing*

MSL and ExoMars will address some of the above

?

- atreya@umich.edu
- pdf’s of pubs: my website (google sushil atreya)
- Scientific American article, “Mystery of Methane on Mars and Titan”: ask or email me