Methane and the Martian Habitability

Sushil Atreya
Paul Mahaffy
Chris Webster
Patrice Coll

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map

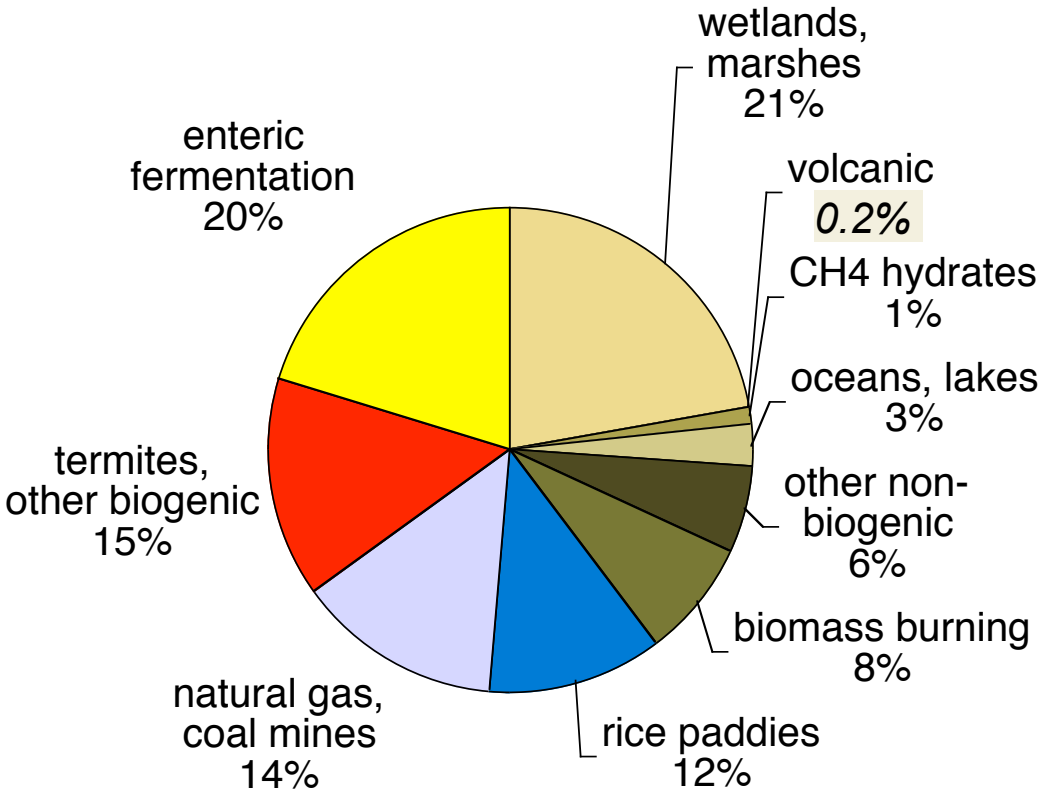
- ***Formation*** (i.e., origin, not source)?
- ***Destruction***: how, where, and how fast?
- ***Supply***: venting flux small or big?
- ***Habitability***: tests?
- ***Measurements***?

mars atmosphere composition

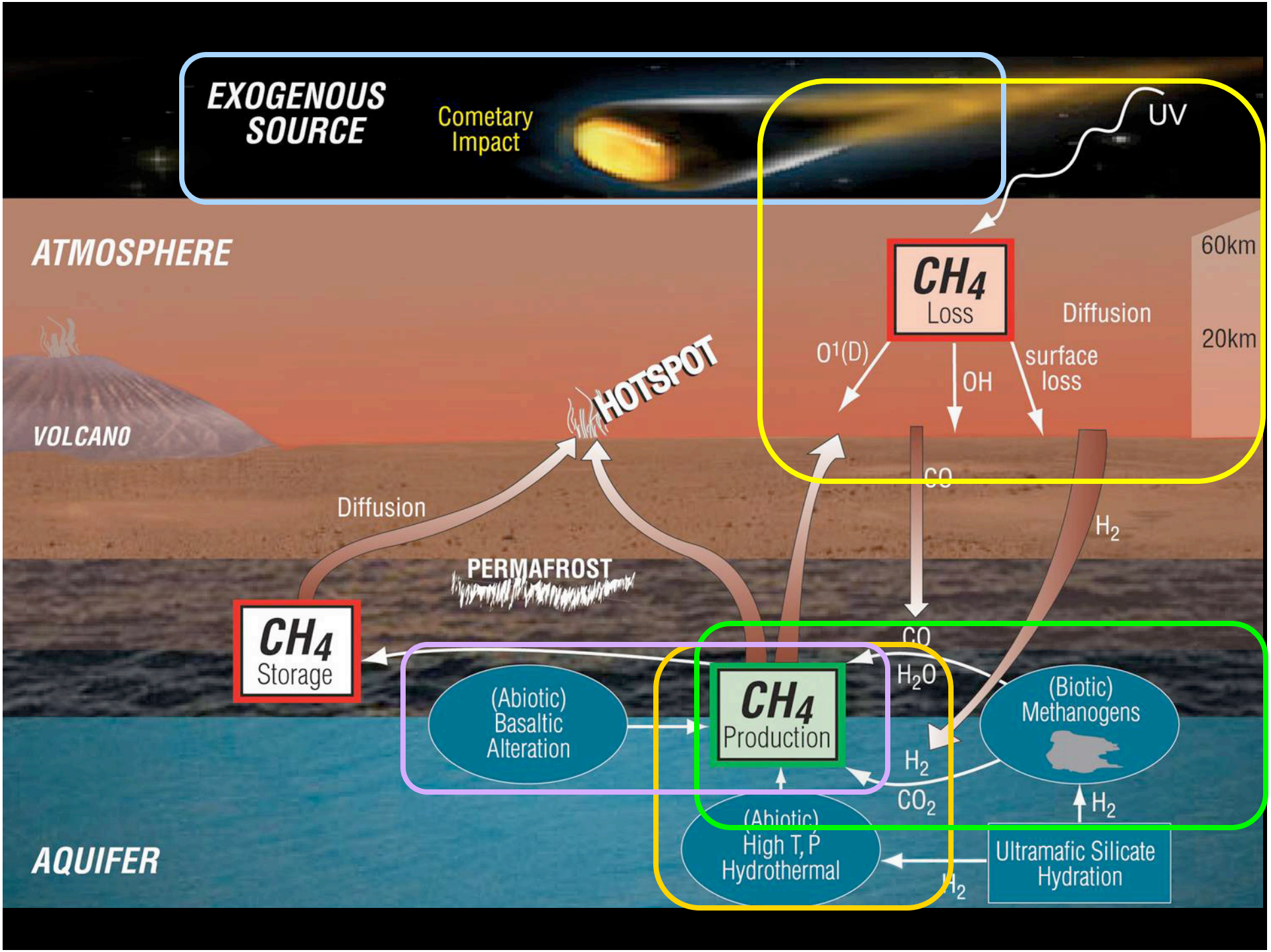
species	mixing ratio	minor species	*upper limit*
CO_2	95.32 %	N_2O	1 (-7)
N_2	2.7 %	NO_2	1 (-8)
^{40}Ar	1.6 %	C_2H_2	2 (-9)
O_2	0.13 %	C_2H_4	5 (-7)
CO	0.07 %	C_2H_6	4 (-7)
H_2O	1 - 100 pr-μm	SO_2	***1 (-9)***
O_3	0.01 – 0.8 ppm	H_2S	1 (-7)
H_2	15 ppm	HCl	2 (-9)
2003 H_2O_2	20-40 ppbv (*atmos.)*		
2003 CH_4	15 ppbv (global)		

surface pressure 6-10 mb

(Earth CFC's ~1 ppbv)

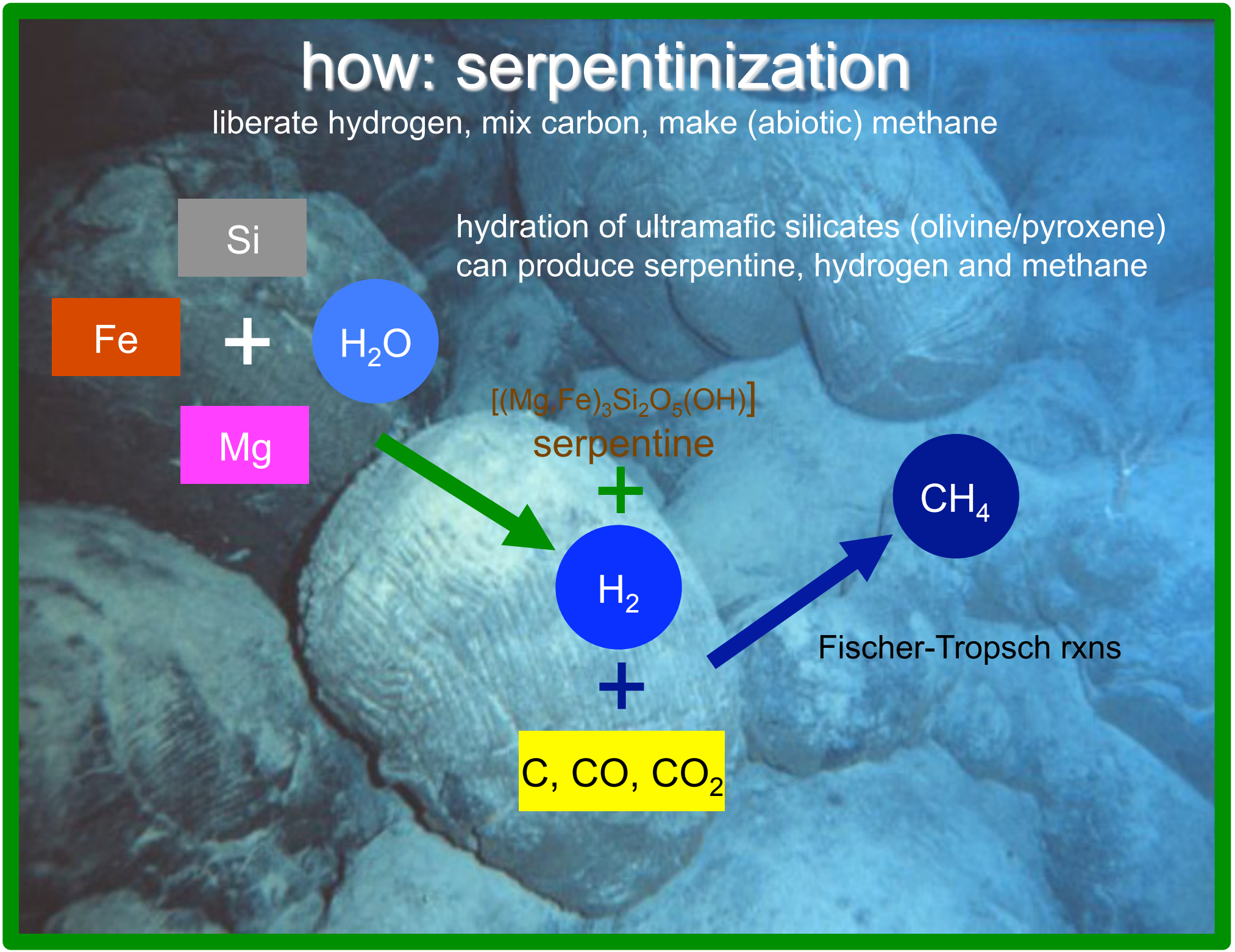


methane sources on Earth (1750 ppbv)

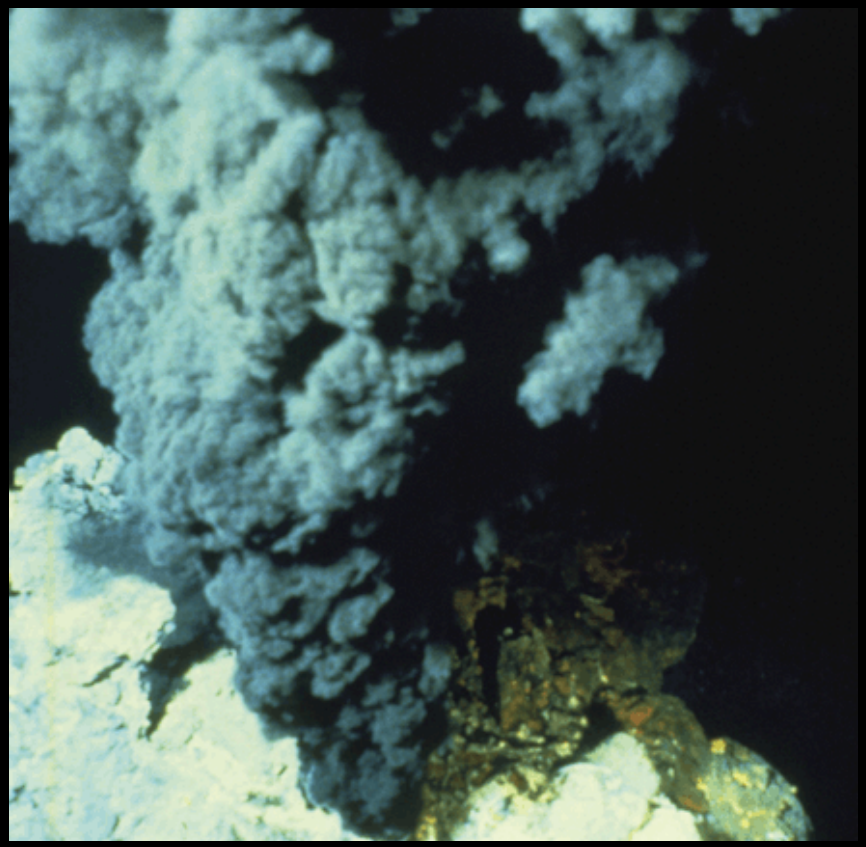

EXOGENOUS SOURCE
Cometary Impact
UV
ATMOSPHERE
60km
20km
CH4 Loss
Diffusion
O1(D)
OH
surface loss
HOTSPOT
VOLCANO
CO
Diffusion
H2
PERMAFROST
CH4 Storage
CO
H2O
(Abiotic) Basaltic Alteration
CH4 Production
(Biotic) Methanogens
H2
CO2
H2
(Abiotic) High T, P Hydrothermal
Ultramafic Silicate Hydration
H2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

how: serpentinization

liberate hydrogen, mix carbon, make (abiotic) methane



where: Black Smoker hydrothermal vents abiotic CH_4 by high temperature serpentinization



Mid Atlantic Ridge

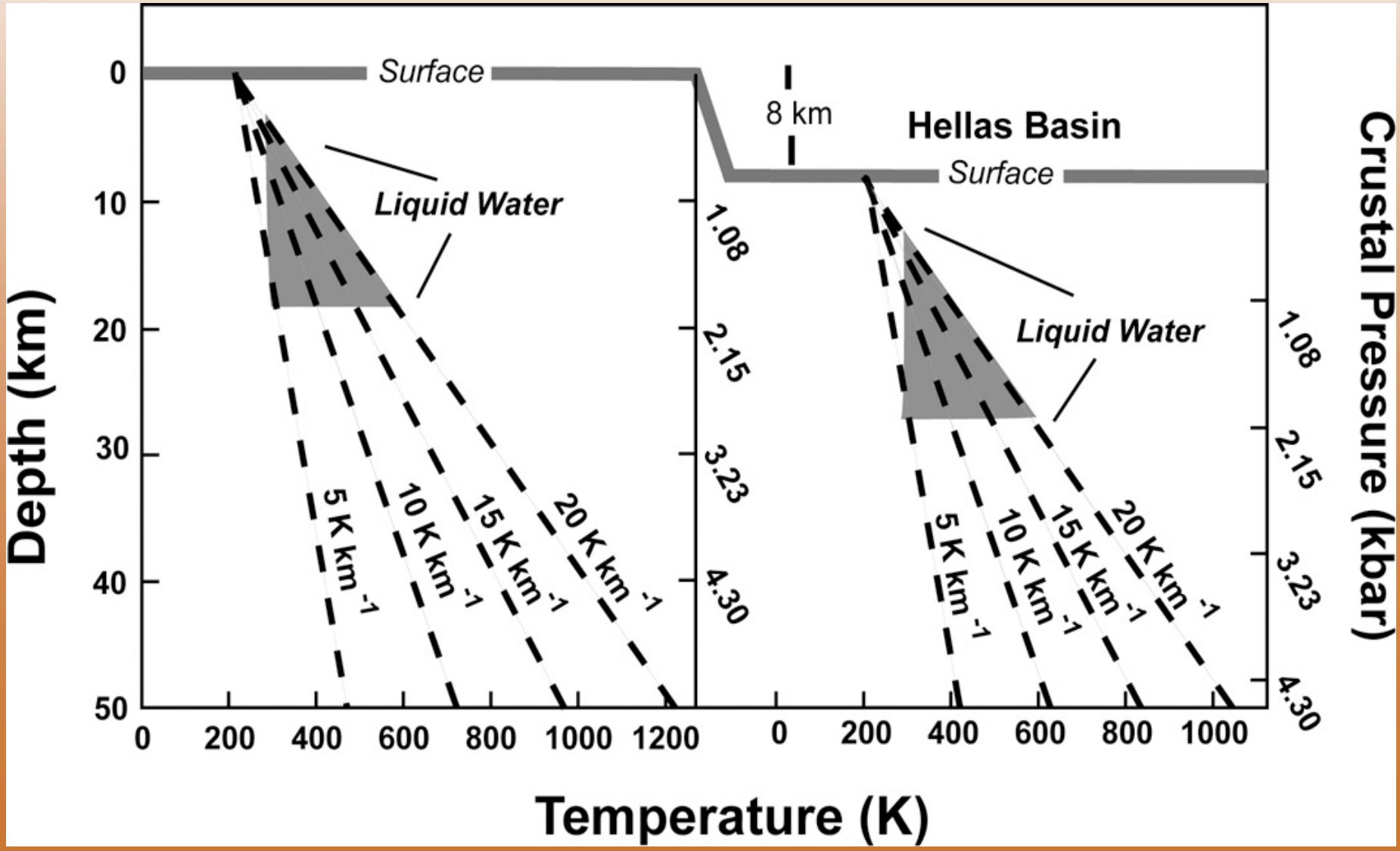
Juan De Fuca Ridge
depth 2222 m
exit temp 342 C
pressure 200 bar
chimney ht. 10 m

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

where: Lost City
abiotic CH_4 by low temperature serpentinization

- 15 km from Mid_Atlantic Ridge
- 30-90 C
- highly alkaline (ammonia, m.o.m.)
- 20m high carbonate towers
- little sulfur minerals

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



(Oze,Sharma, 2005)

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)

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.]

storm electric fields (triboelectricity) change near-surface chemistry

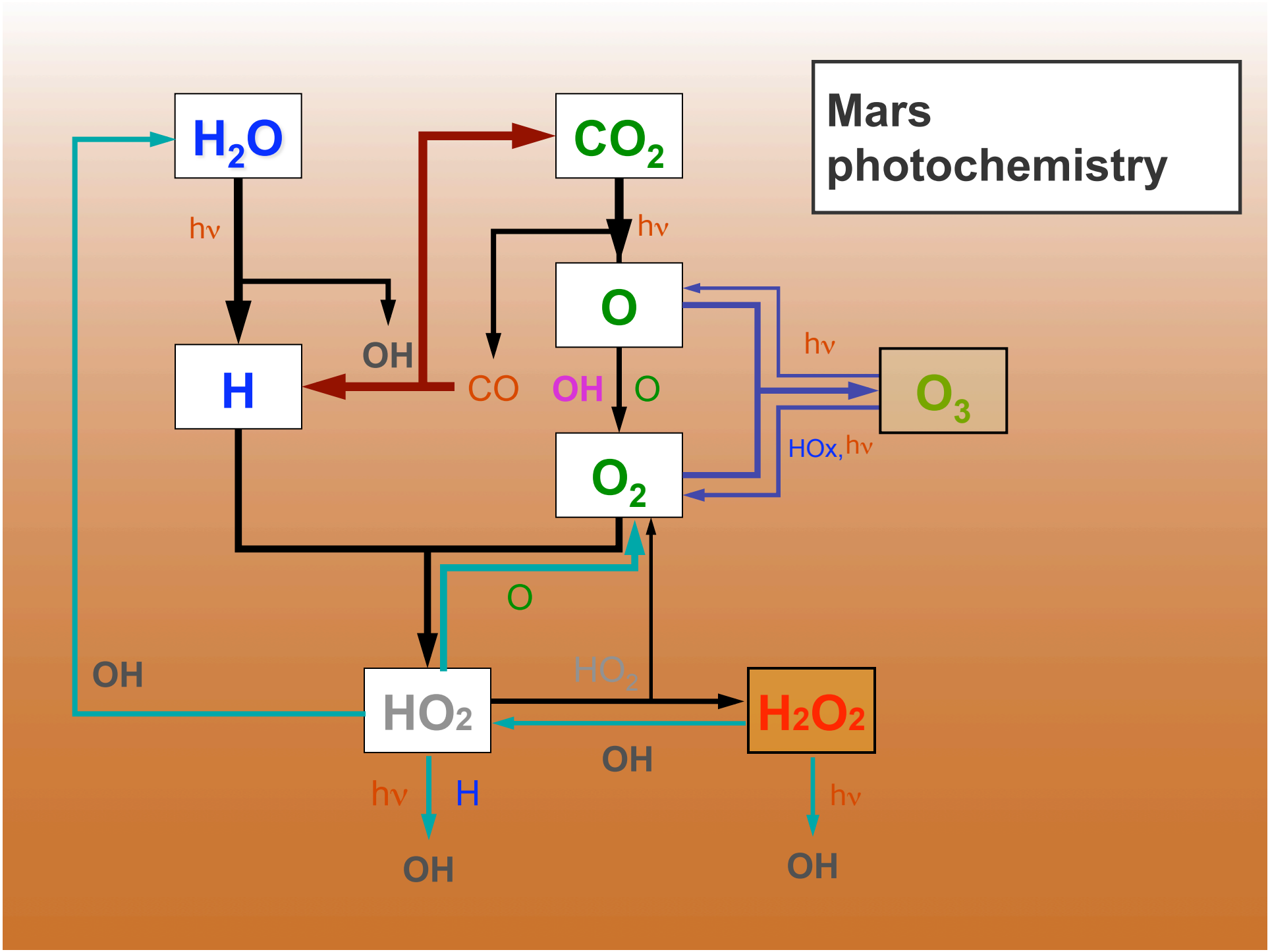
→ 5-25 kV/m* electrostatic fields generated in Martian aeolian processes, i.e. in convective dust storms and dust devils

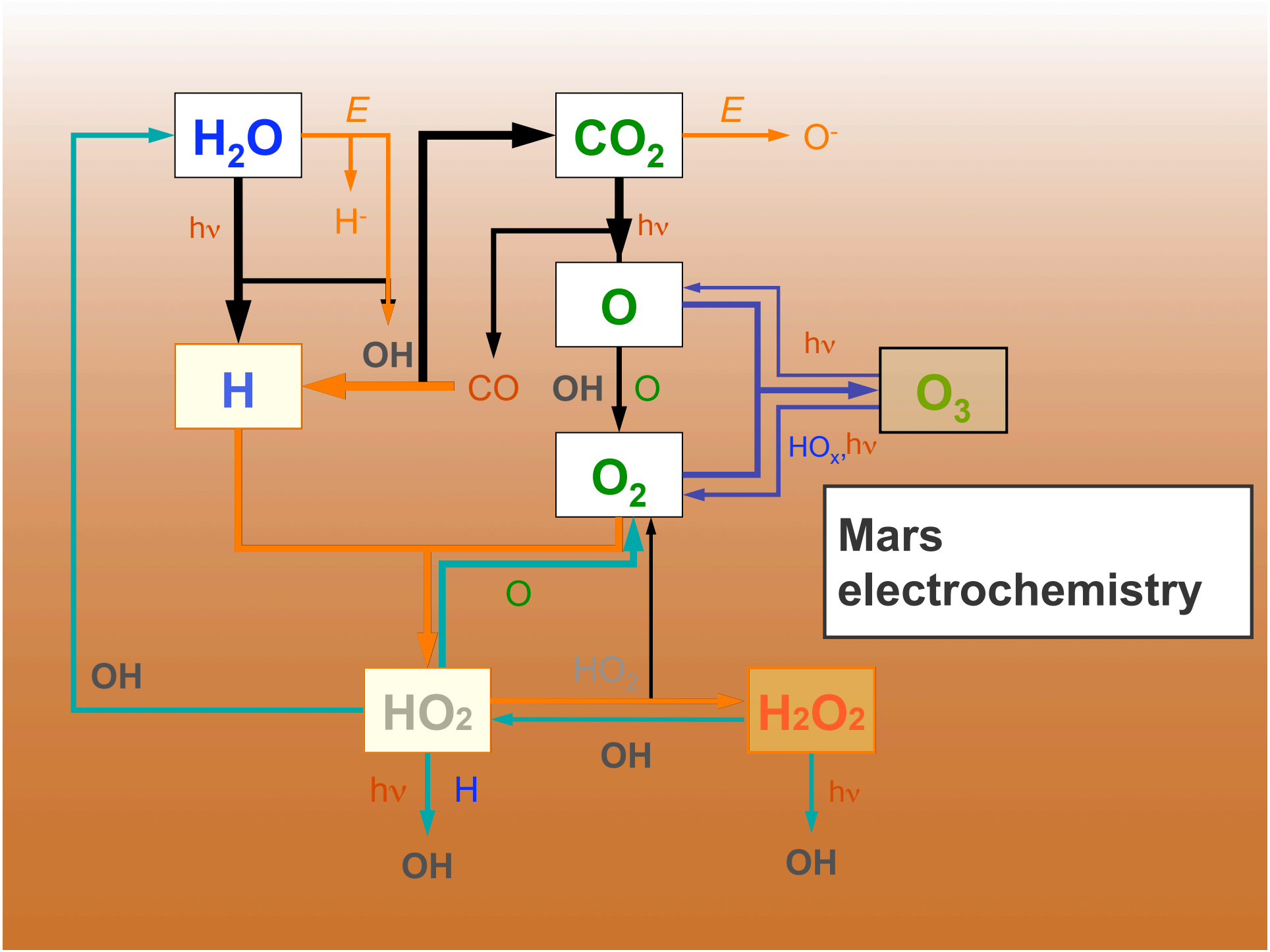
→ CO/O-, OH/H- ion pairs* produced→

→ 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
O
H
OH
CO
OH
O
hν
O3
HOx, hν
O2
O
OH
HO2
HO2
H2O2
OH
hν
H
hν
OH
OH


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

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**

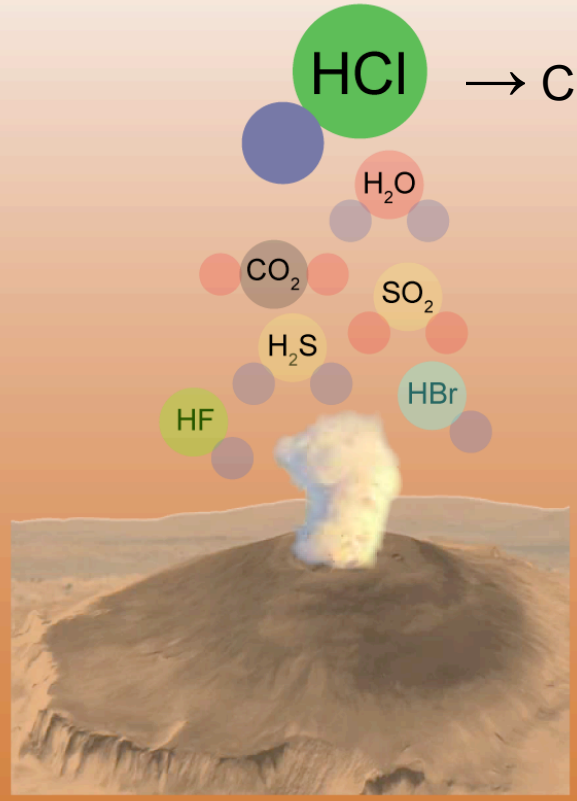
→ **methane*, by OH, HO_2 and superoxides from H_2O_2***

→ ***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



$\longrightarrow$ Cl

volcano

(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) $\rightarrow$ $Mg(ClO_4)_2$, $K(ClO_4)$, …

+surface minerals

brine

	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)


AT LAST, PROOF OF LIFE ON MARS! I SEE A STARBUCKS!
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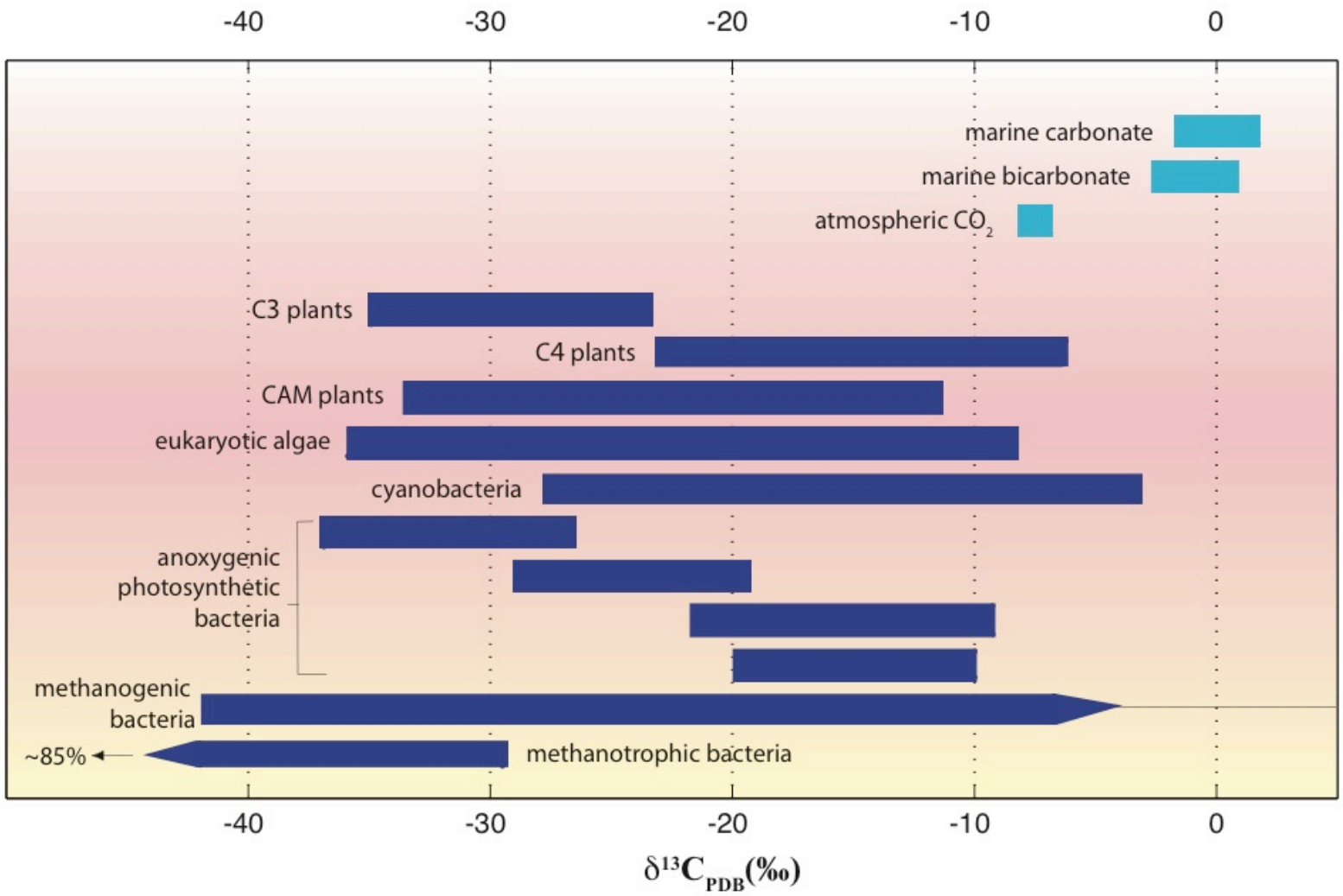
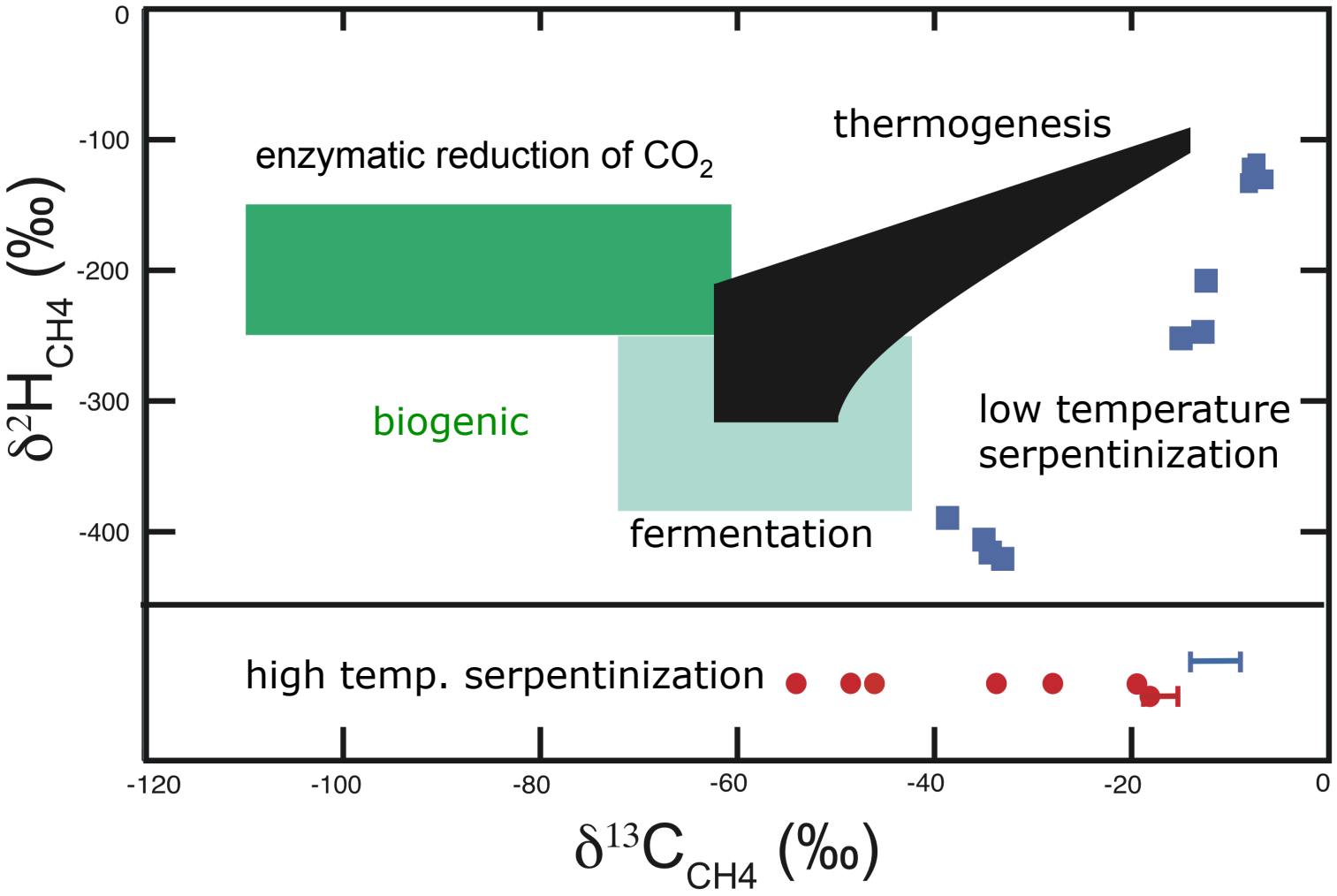
Organic (living) vs. Inorganic ^{13}C carbon isotope V-PDB $^{12}C/^{13}C=89.4$

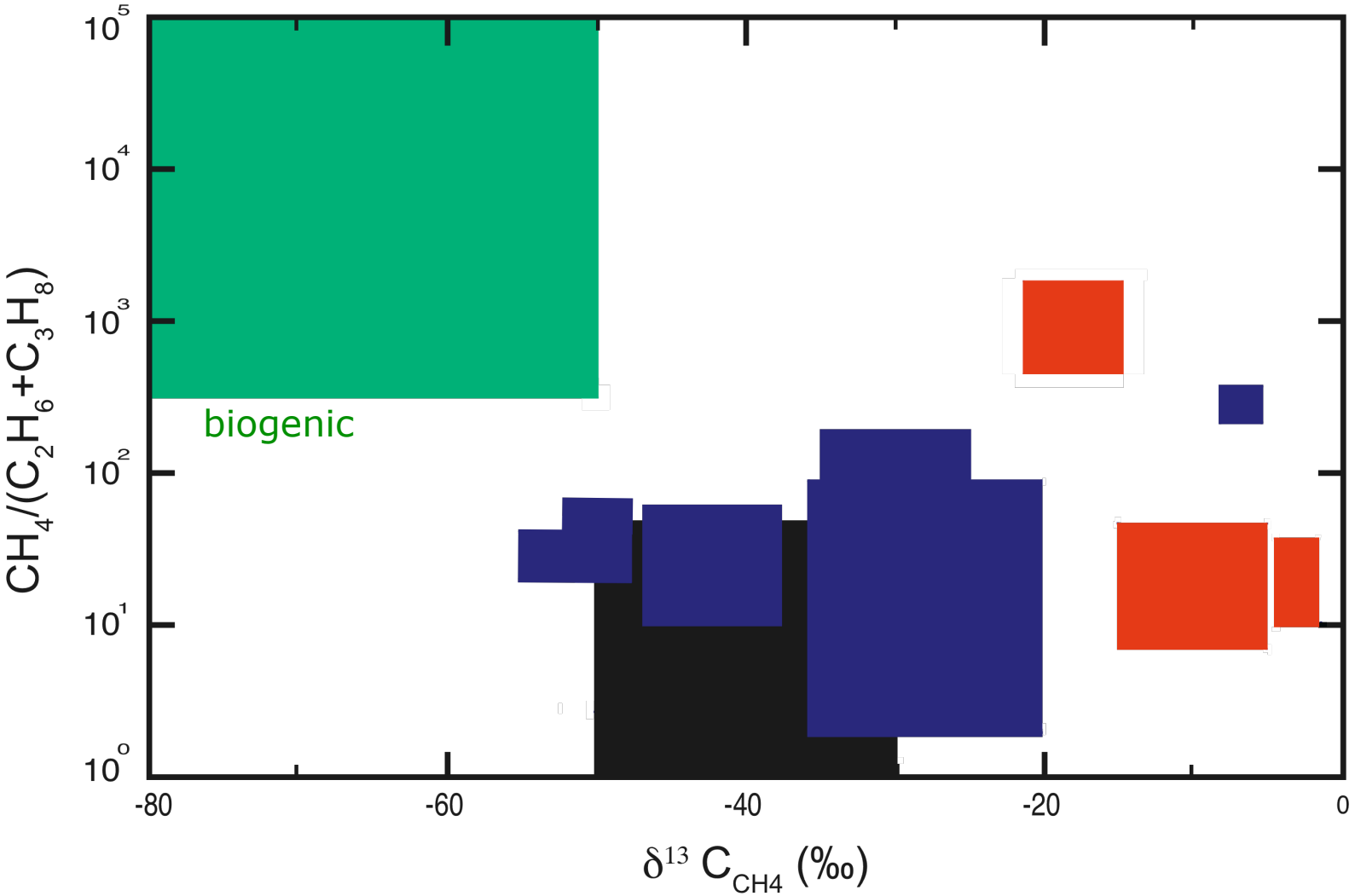


δ^2H vs $\delta^{13}C$ in CH_4



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

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



(after M. Allen/ Horita, Berndt)

habitability: what must be measured

- ***Methane*** to *1 ppbv*, and its ***map***,
- ***Localize*** the vent/s to within a *few tens of kilometers*
- ***C-isotopes*** in methane
- ***Reference*** (inorganic) C-isotope (e.g. CO_2 in air)
- ***Alkanes***: ethane, propane, butane
- ***Organics***: find them, their chirality, $^{12}C/^{13}C$ in evolved CH_4
  Context *:* geochemical, geological, environmental
- *plus more: D/H, $^{18}O/^{17}O/^{16}O$, $^{34}S/^{32}S$, trace gases, etc.*

take home

- ***Methane*** is necessary, but not sufficient, for proving habitability, or extinct or extant life on Mars
- ***Geology and biology*** are equally plausible, and both require
- ***Liquid water***, to produce methane
- ***Related data*** on multiple isotopes and trace gases in solid and gas samples, mineralogical/environmental context, etc., essential to nail the origin of methane and habitability of Mars

MSL and ExoMars are only a start

?

- 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