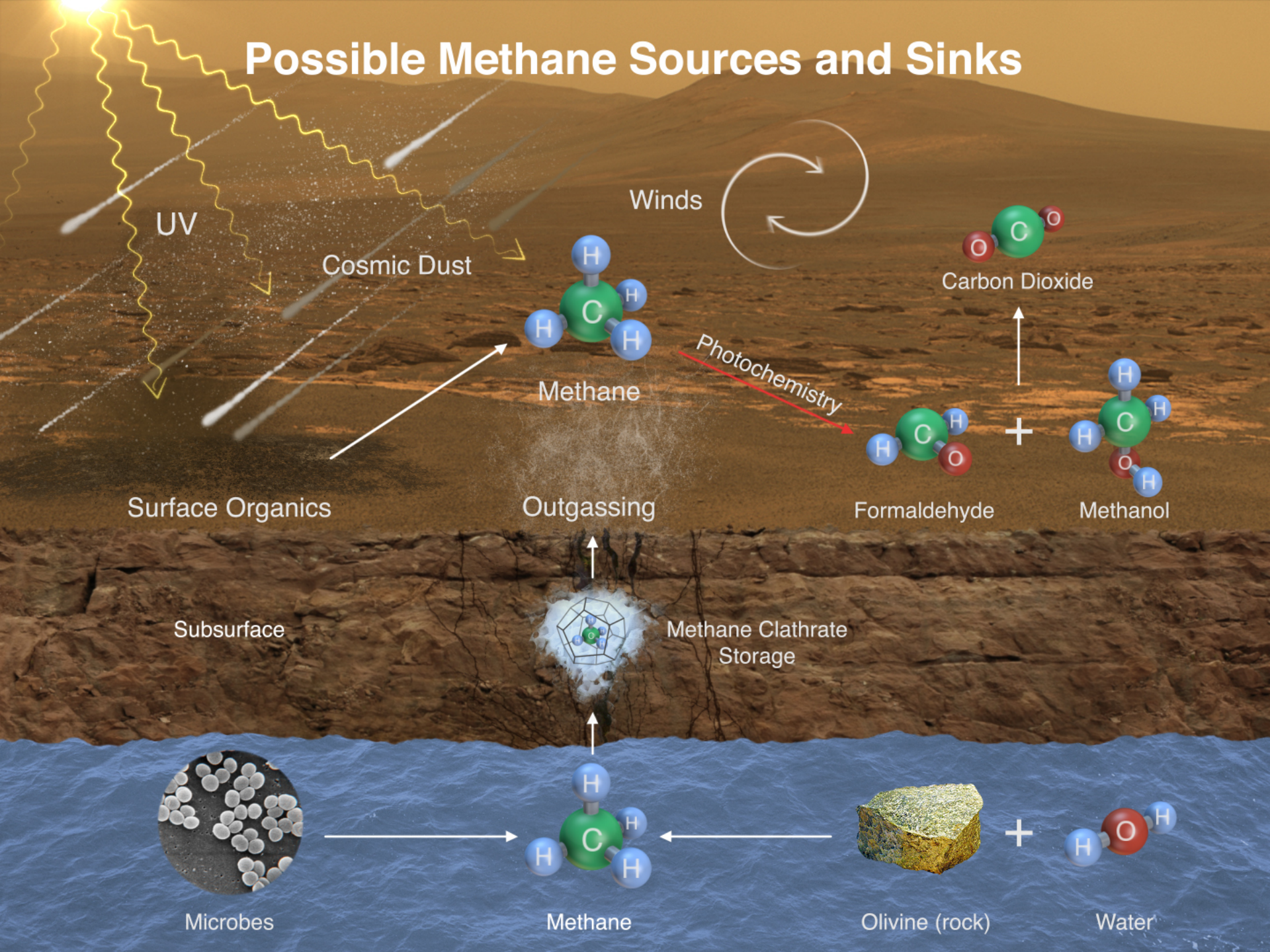
Sushil Atreya's slides for Yuk Yung presentation at Mars Methane Workshop, KISS

KISS 7-12 December 2015


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

Origin of Mars methane, now *or* in the past

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

  i.e. water-rock chemistry: serpentinization, followed by metal-catalyzed Fischer-Tropsch type reactions, or

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

  i.e. by enzymatic reduction of CO_2, or fermentation of organic matter in microbial metabolism

Both processes require (Liquid) water

subsurface aquifers, if CH_4 is recent

wetter, warmer past, if CH_4 is ancient

abiotic reaction pathways for CH_4: serpentinization yields H_2

Serpentinization Overview:

Olivine → Serpentine + Brucite + Magnetite + Methane

Feeder Reactions: hydration of ultramafic silicates

$6Fe_2SiO_4 + 7H_2O \rightarrow \mathbf{H_{2(aq)}} + 3Fe_3Si_2O_5(OH)_4 + Fe_3O_4$

or

$2Mg_2SiO_4 + 3H_2O \rightarrow Mg_3Si_2O_5(OH)_4 + Mg(OH)_2$

then:

$2Fe_3Si_2O_5(OH)_4 + 6Mg(OH)_2 \rightarrow \mathbf{2H_{2(aq)}} + 2Mg_3Si_2O_5(OH)_4 + 2Fe_3O_4 + 4\ H_2O$

serpentinization, then F-T: secondary CH_4 on Earth, Mars, Titan

H_2 liberated in previous reactions, combines with "carbon" in rocks, substrate, or that which diffuses from atmosphere, by metal-catalyzed (Cr, Fe, Mg…) Fischer-Tropsch type process:

$$(2n+1)H_{2(aq)} + nCO \rightarrow \mathbf{C_nH_{(2n+2)}} + nH_2O$$

or, $CO + 3H_{2(aq)} \rightarrow \mathbf{CH_4} + H_2O$

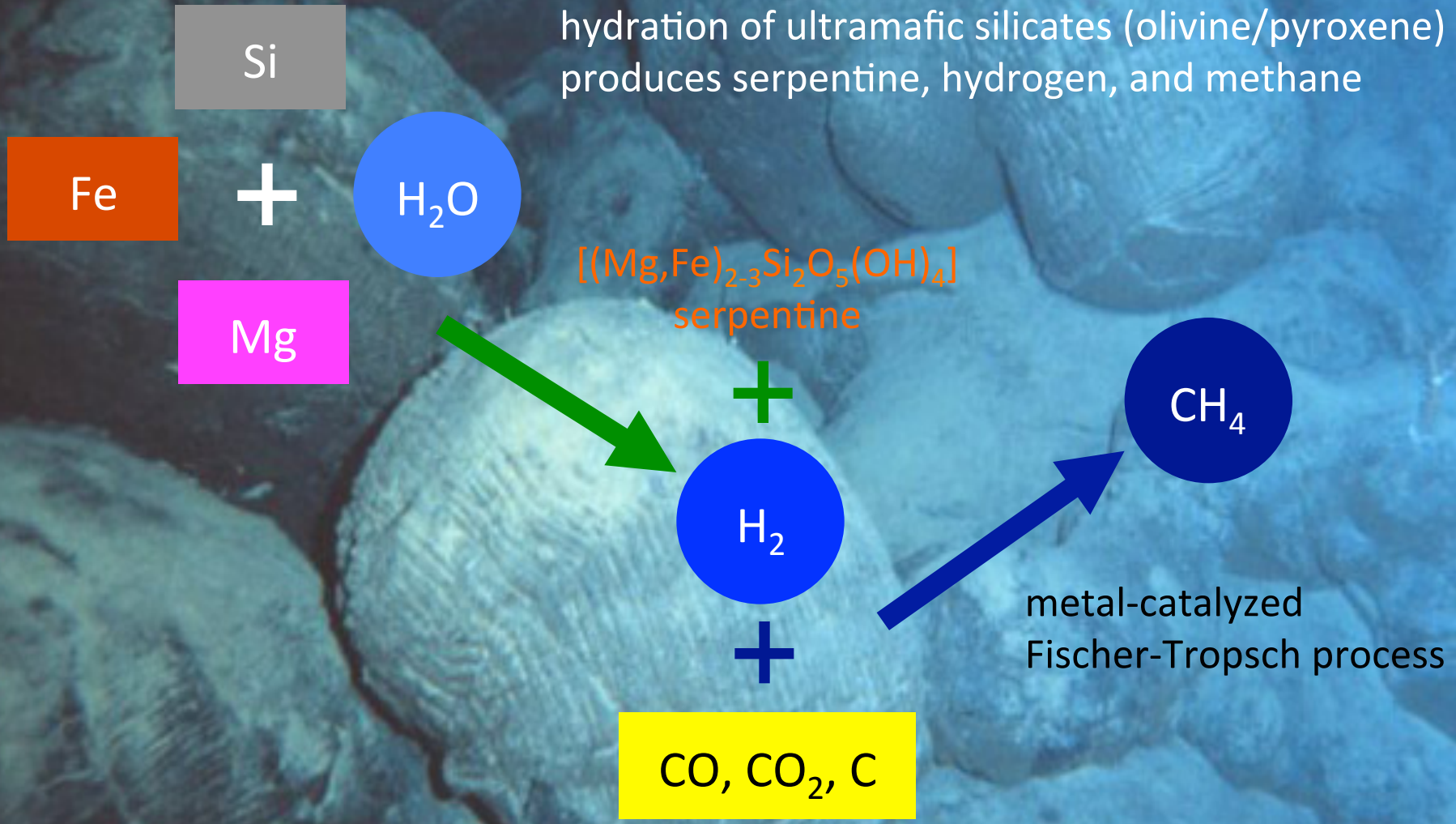
$C + 2H_{2(aq)} \rightarrow \mathbf{CH_4}$

$CO_{2(aq)} + 4H_{2(aq)} \rightarrow \mathbf{CH_4} + 2H_2O$

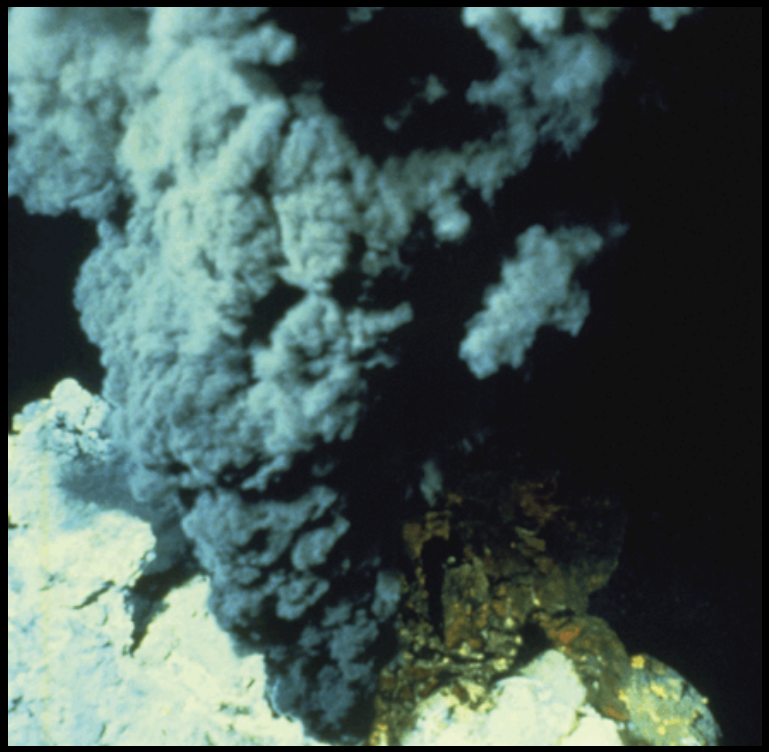
to produce methane and possibly alkanes

abiotic methane by serpentinization + F-T process:

liberate hydrogen, mix carbon, make methane on Earth, Mars, Titan



abiotic methane by *high* temperature serpentinization, e.g. *Black Smoker hydrothermal vents*



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)

abiotic methane by *low* temperature serpentinization: *Lost City*

- 15 km from Mid-Atlantic Ridge
- 30-90 C (120 C peridotite)
- highly alkaline (~ammonia, milk of magnesia)
- 20 m tall carbonate towers
- little sulfur minerals

(D. Kelly et al., *Science* 2005; James Cameron, *Aliens of the Deep)*

biochemical pathways of methanogenesis at Mars

Enzymatic reduction of Carbon to CH_4:

$4CO + 2H_2O \rightarrow CH_4 + 3CO_2$

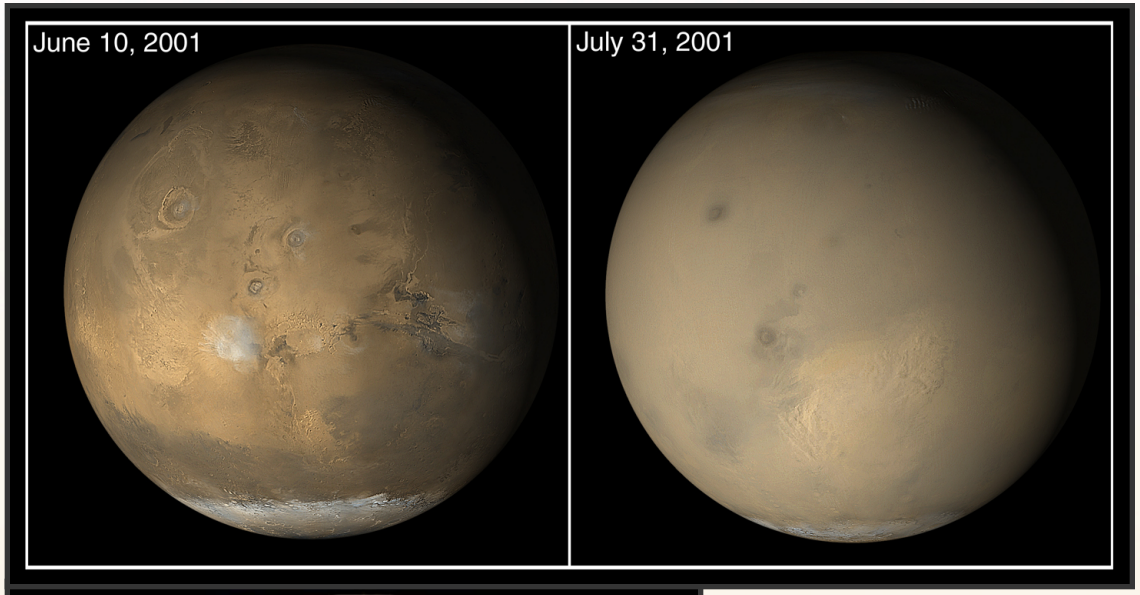
$4H_2 + CO_2 \rightarrow CH_4 + 2H_2O$

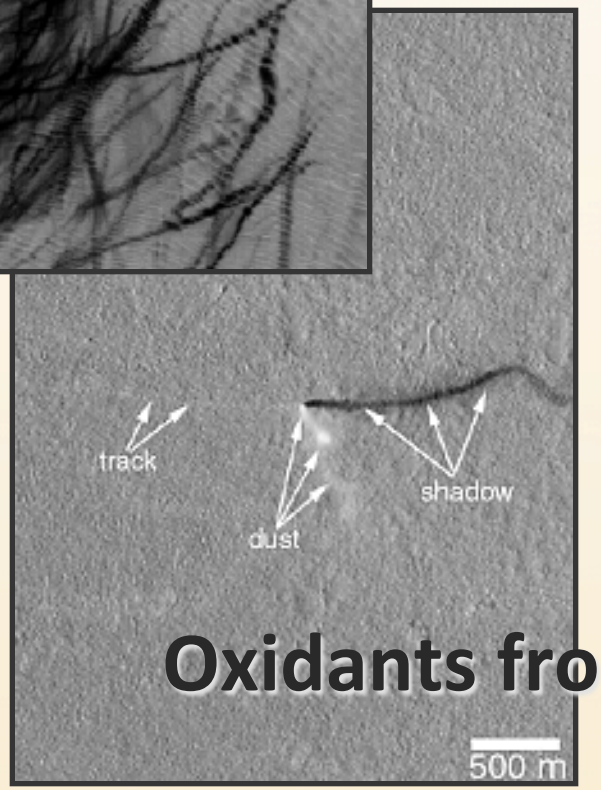
Fermentation:

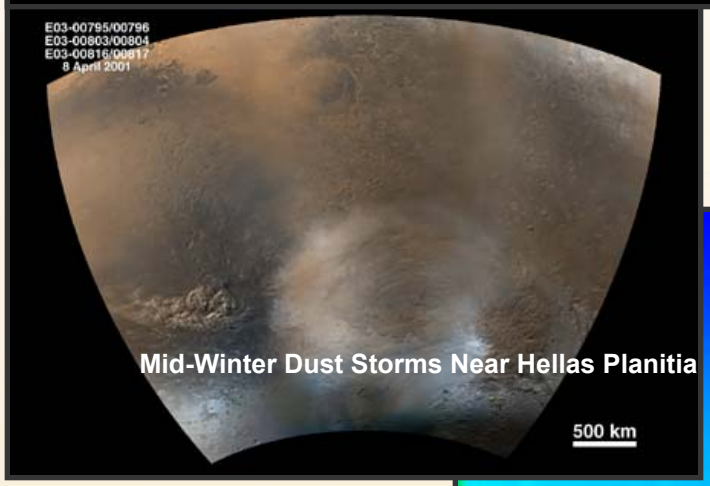
1. Organic matter → CH_3COOH (acetic acid)
2. CH_3COOH → $CH_4 + CO_2$

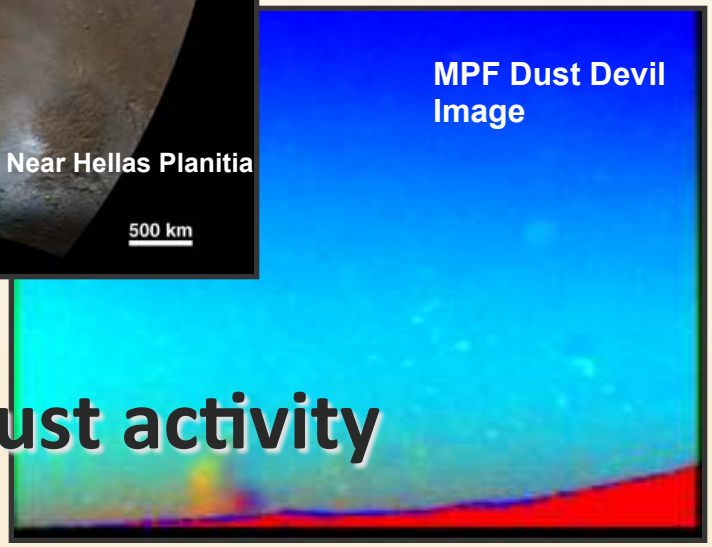
Liquid water required as medium & solvent

aeolian triboelectricity









Oxidants from martian dust activity

organics and oxidants don't get along

- **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:**

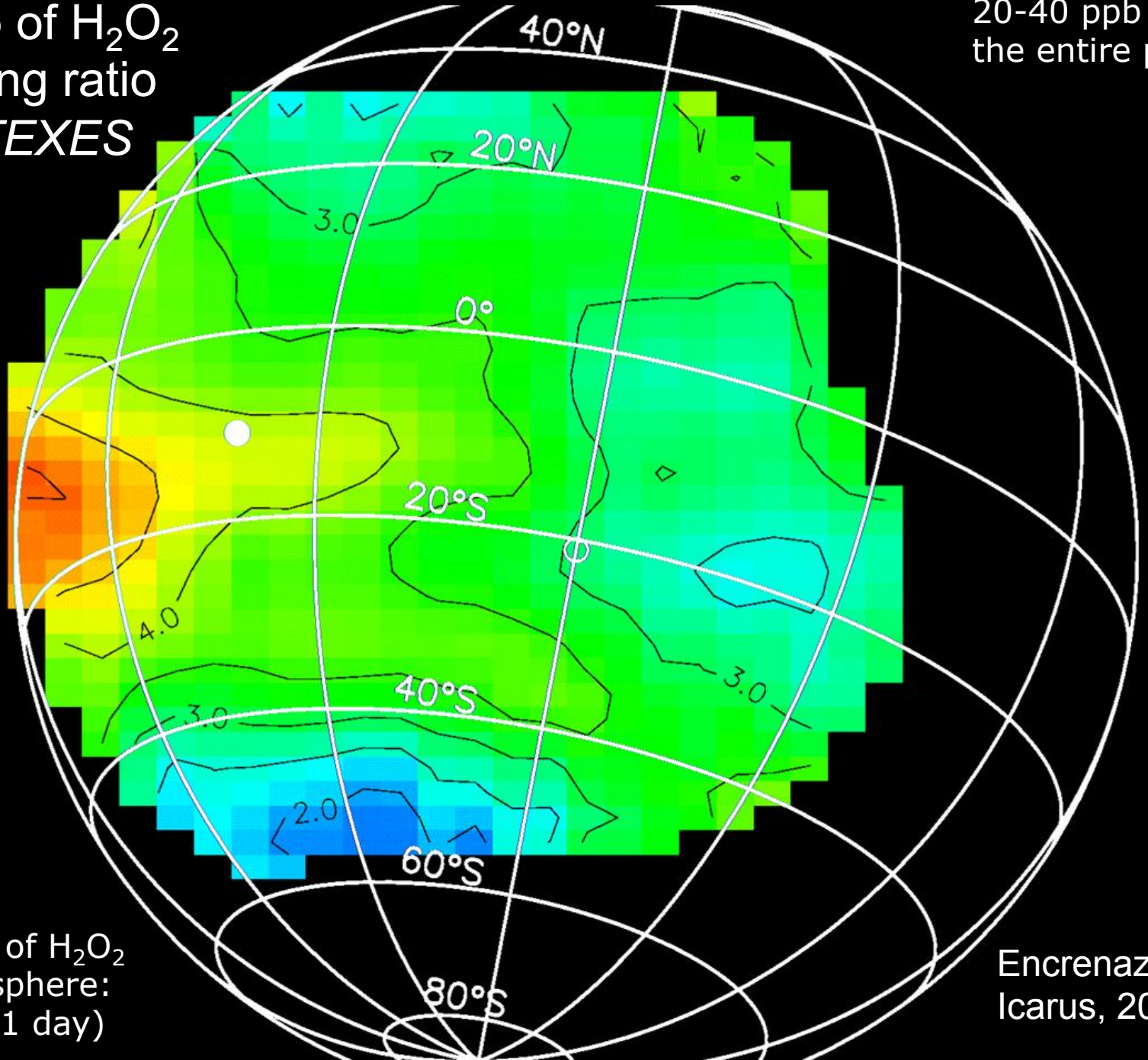
  ***surface* oxidant ; required amount 20-250 *ppmv* H_2O_2**

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

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

[H_2O_2 detection in 2003: Clancy et al. submm 362.156 GH; Encrenaz, et al. IR (8.04 – 8.13 μm)]

map of H_2O_2 mixing ratio by *TEXES*

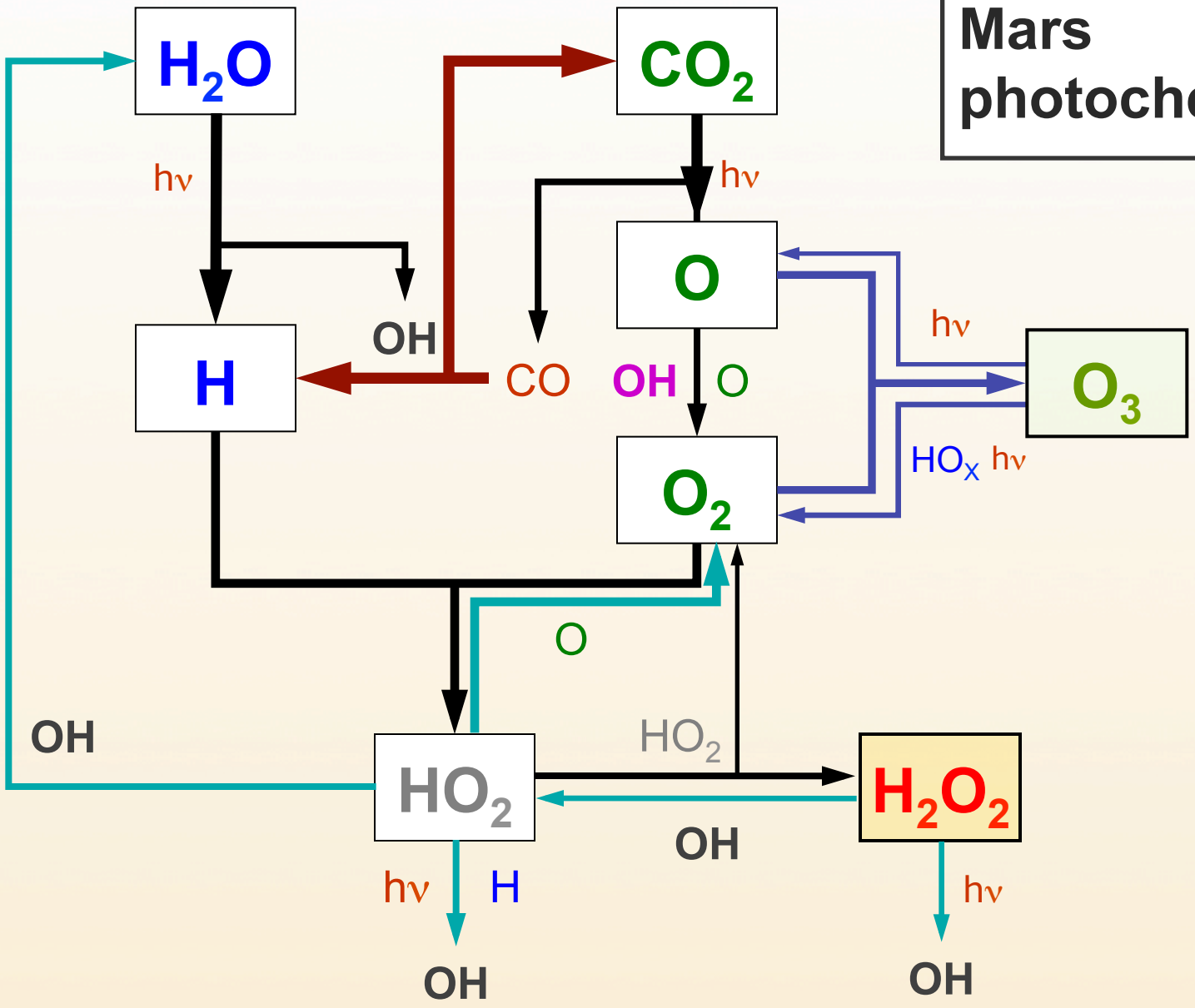


20-40 ppb over the entire planet

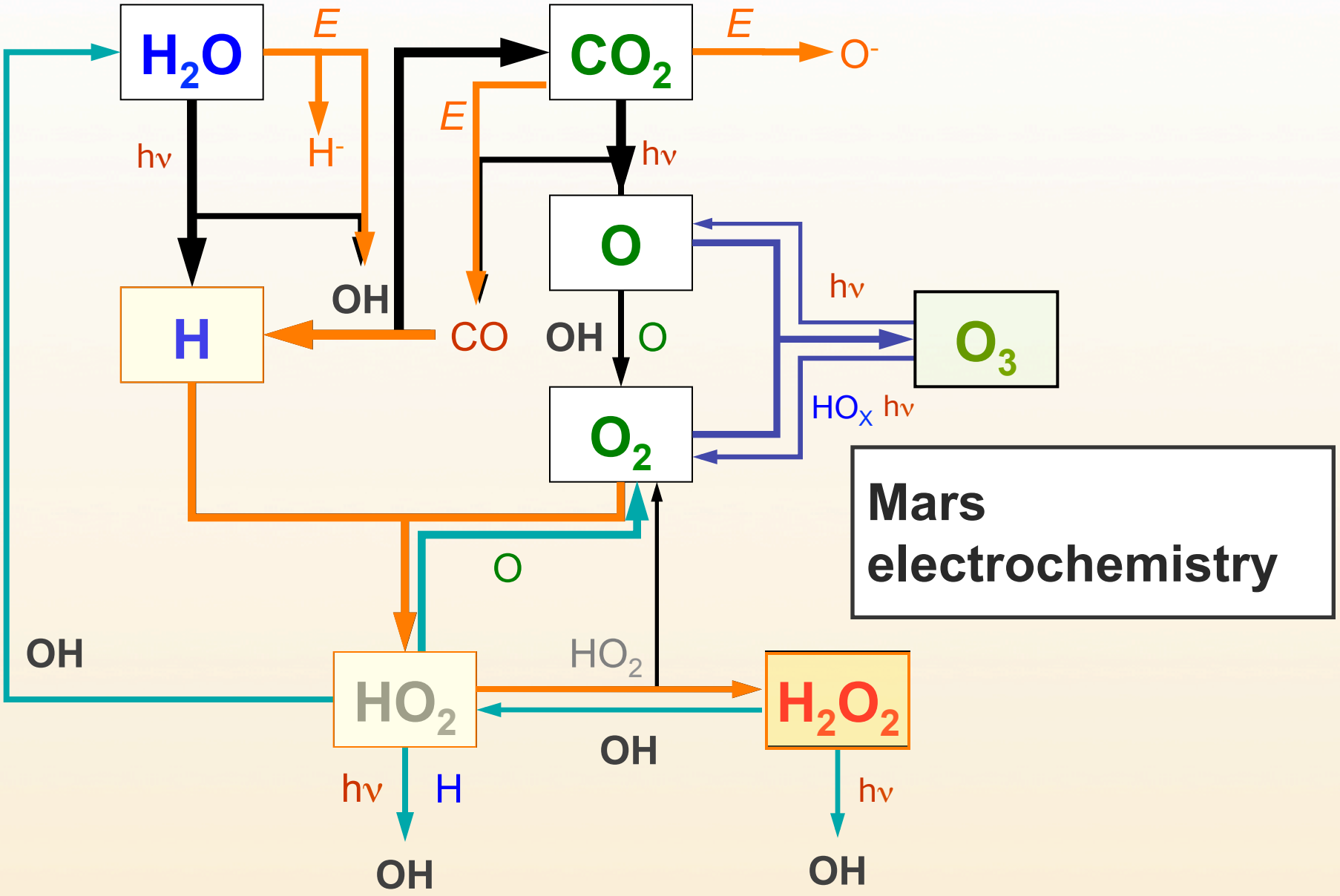
Lifetime of H_2O_2 in atmosphere: short (~1 day)

Encrenaz *et al*., Icarus, 2004

Mars photochemistry

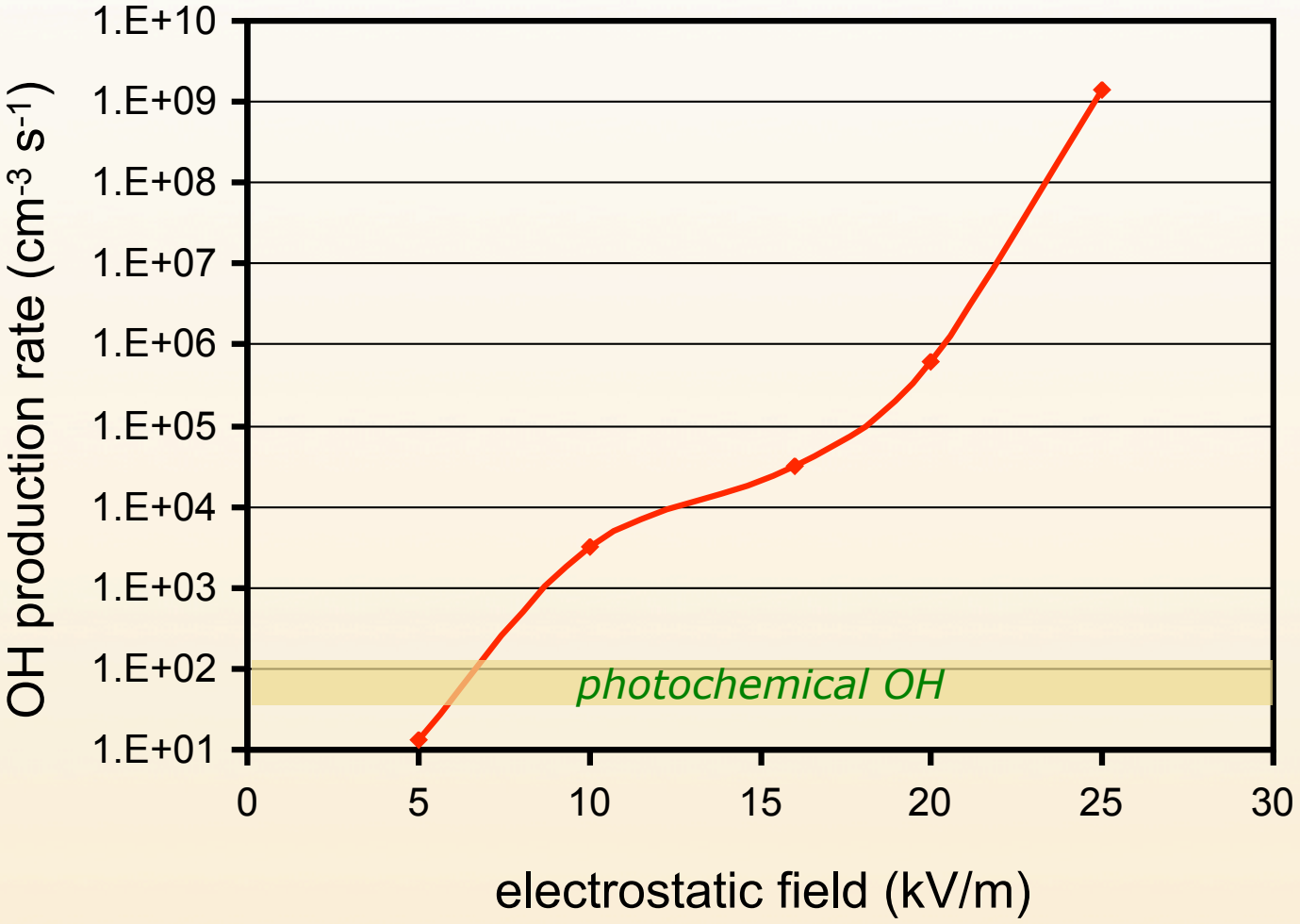


Atreya et al., 2007



Atreya et al., 2007

hydroxyl by electrochemistry



Atreya et al., 2007

storm electric fields make peroxide; peroxide could destroy surface organics (directly) and methane *(indirectly)*

→ Electrochemical H_2O_2 up to 10,000x photochemical H_2O_2 →

→ H_2O_2 "snow" → H_2O_2 diffuses into regolith →

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

→ *Superoxides (O_2-, etc.),hydroxyl, hydroperoxy (HO_2), etc. form in soil rxns*

Hydrogen peroxide can destroy

→ **surface organics, directly, and**

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

→ ***would recycle the excess CO to CO_2 lost to triboelectricity***

Radiolysis of ice → small qtys. of H_2O_2, as on Europa, Ganymede & Callisto

Open question: ***How much H_2O_2 is sequestered in the surface/regolith, and what type of superoxides are present?*** [TLS H_2O_2 channel was dropped to cut cost]

**Atreya, et al., 2006 (Electrochemistry model); Delory et al., 2006 (Plasma model)