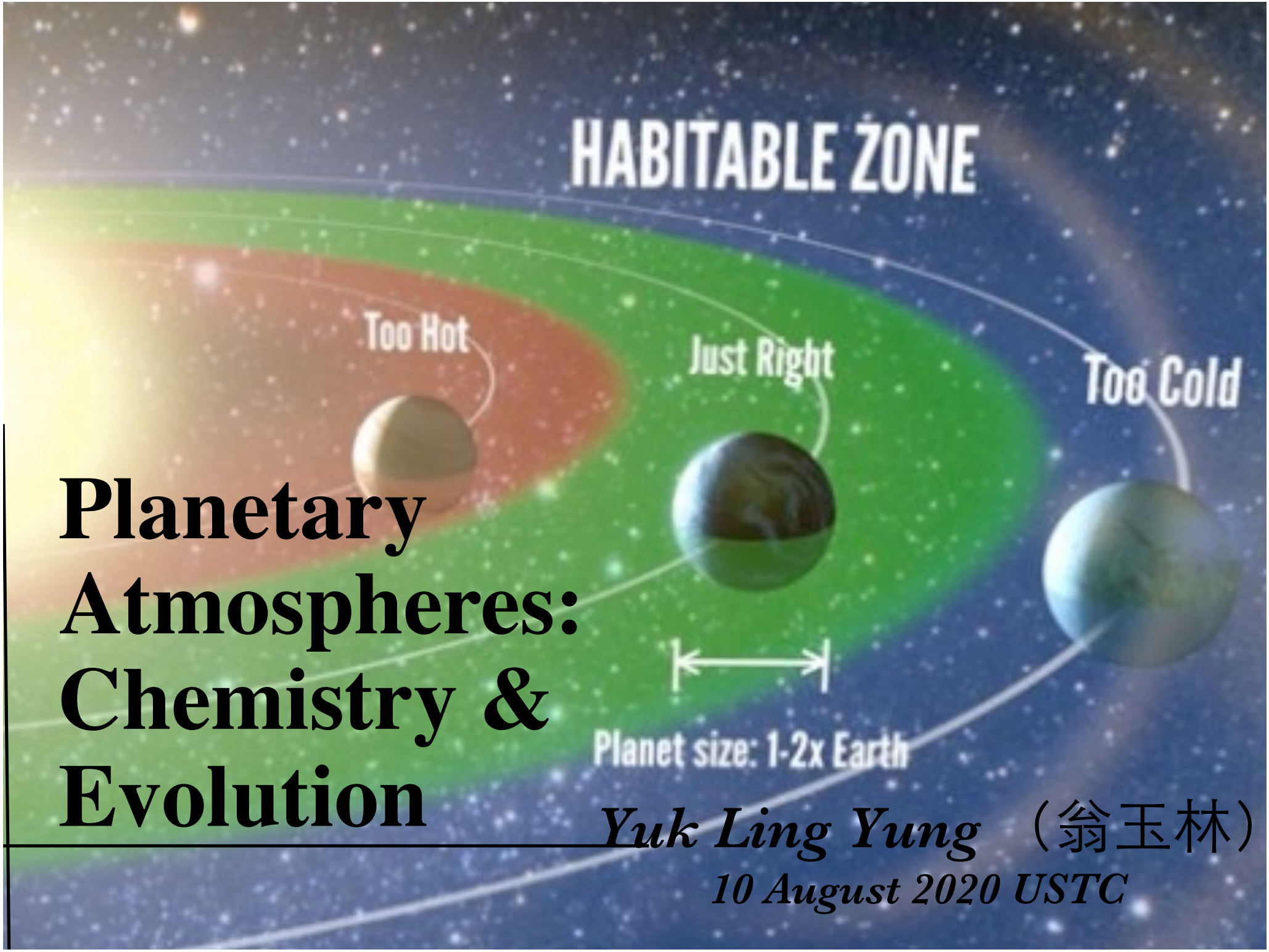


Planetary Atmospheres: Chemistry & Evolution

Yuk Ling Yung （翁玉林）

10 August 2020 USTC

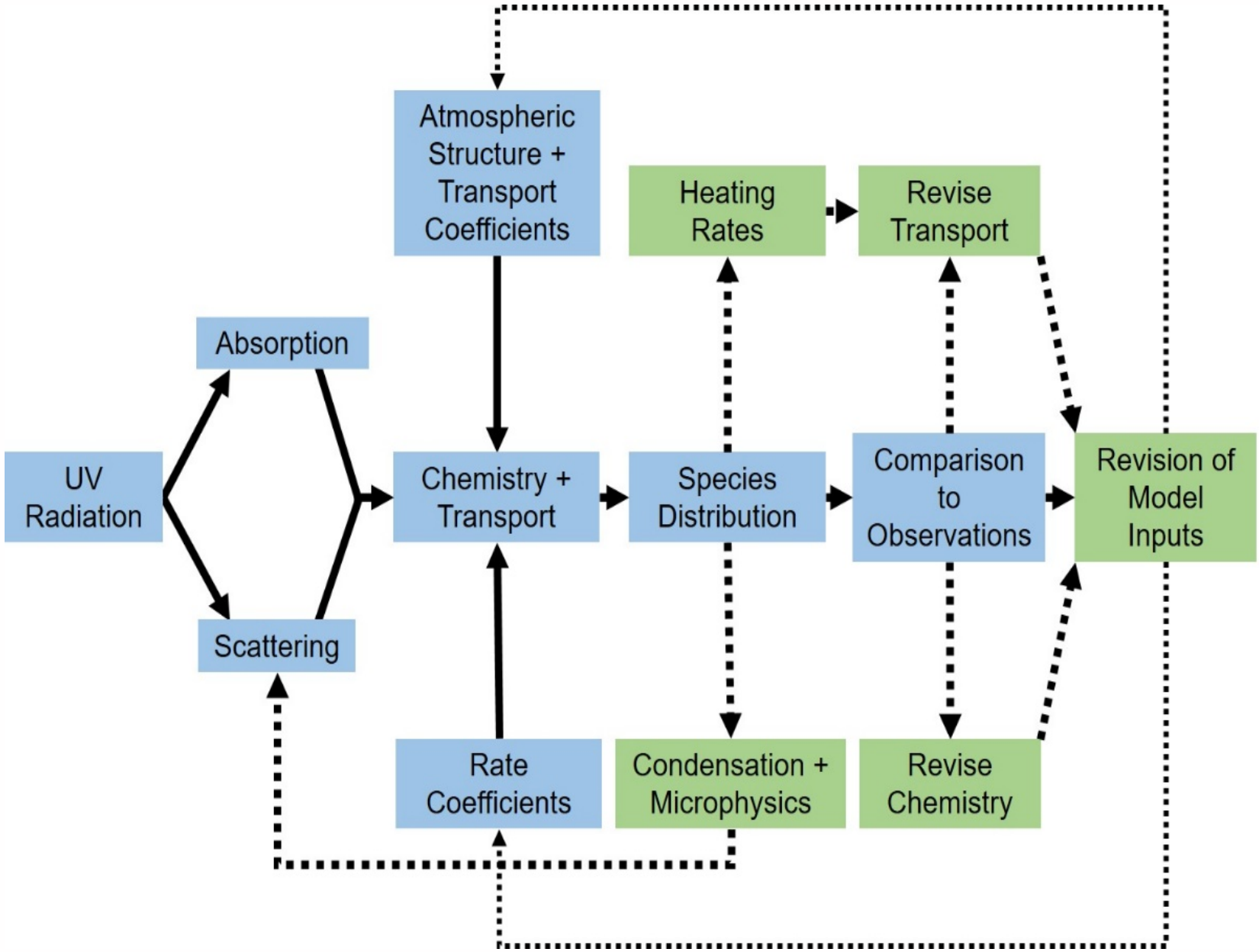
Comprehensive Chemical Model: KINETICS

- 1200 Species
- 20,000 reactions
- Coupled to aerosol microphysics
- Coupled to 1-D and 2-D transport

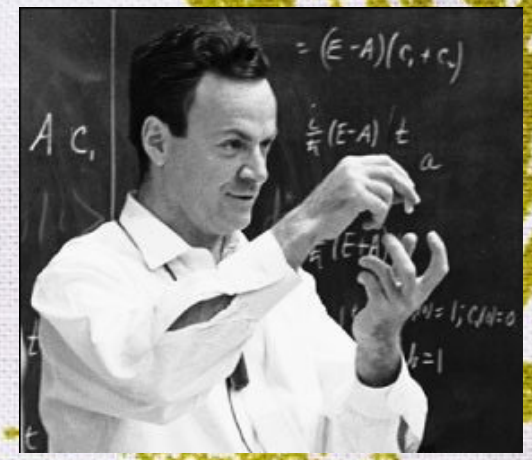


Mark Allen Run-Lie Shia Karen Willacy

- Applied to Solar System Planets, Earth as a Planet, Exoplanets and Planetary Evolution
- More than 100 refereed publications
- **Allen et al. (1981)**, Shia, Morgan, Weibel, Willacy + Students



Schematic diagram for the photochemical model KINETICS. The blue boxes constitute the core model. Green boxes are recent additions.



Nature uses only the longest threads to weave her patterns, so that each small piece of her fabric reveals the organization of the entire tapestry.

-Richard P. Feynman

I noted Kuiper's message that **terrestrial and planetary atmospheres**

share so much in common

that they can usefully be studied as a single field, each reinforcing ideas from the other. I have found this statement to be true and have echoed it, with the result that sometimes it is incorrectly attributed to me.

—Richard Goody, 2002

OUTLINE

1. **Terrestrial Planets: Mars, Venus and Earth**
2. Terrestrial Analogs: Titan, Pluto and Triton
3. Exoplanets Analogs
4. Habitability and Habitancy

On Mars

$$CO + OH \longrightarrow CO_2 + H$$

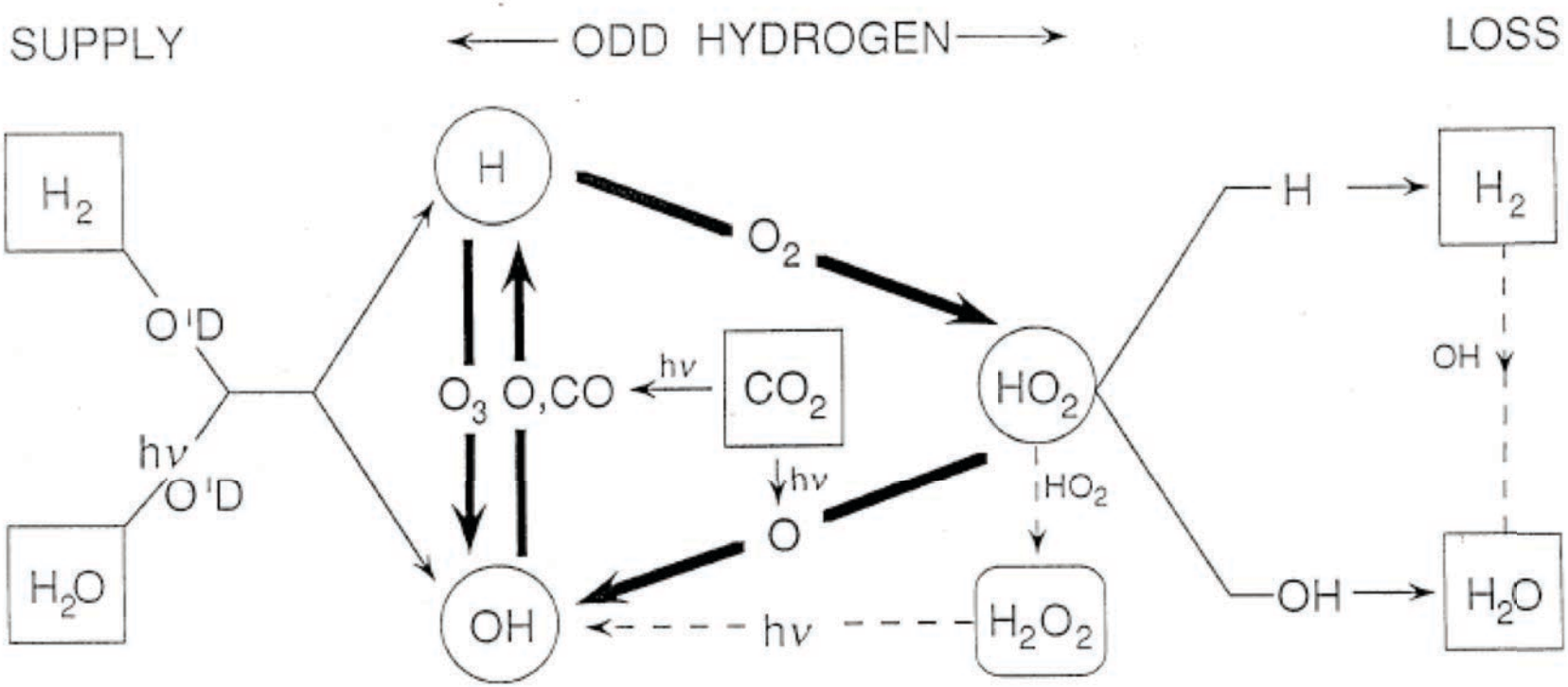
$$H + O_2 + M \longrightarrow HO_2 + M$$

$$HO_2 + O \longrightarrow OH + O_2$$

$$CO + O \longrightarrow CO_2$$

Prof. Michael McElroy
Harvard University

CO~0.1%, H_2O~10^{-4}



Classic Catalytic Cycles

McElroy and Donahue 1972

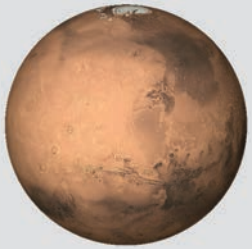
Parkinson and Hunten 1972

Applications to

Earth Mesosphere: Allen et al. 1981

M-Star Exomars: Tian et al. 2014; Gao et al. 2015

Everything should be made as simple as possible, but not simpler. *—Albert Einstein*



The atmosphere of Mars is the hydrogen atom of planetary atmospheres.

Venus

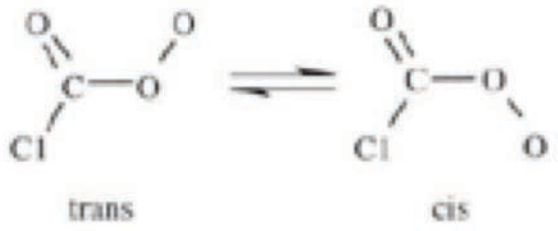
William DeMore

$$CO + Cl + M \longrightarrow ClCO + M$$

$$ClCO + O_2 + M \longrightarrow ClC(O)OO + M$$

$$ClC(O)OO + O \longrightarrow Cl + CO_2 + O_2$$

$$CO + O \longrightarrow CO_2$$



Yung and DeMore 1982

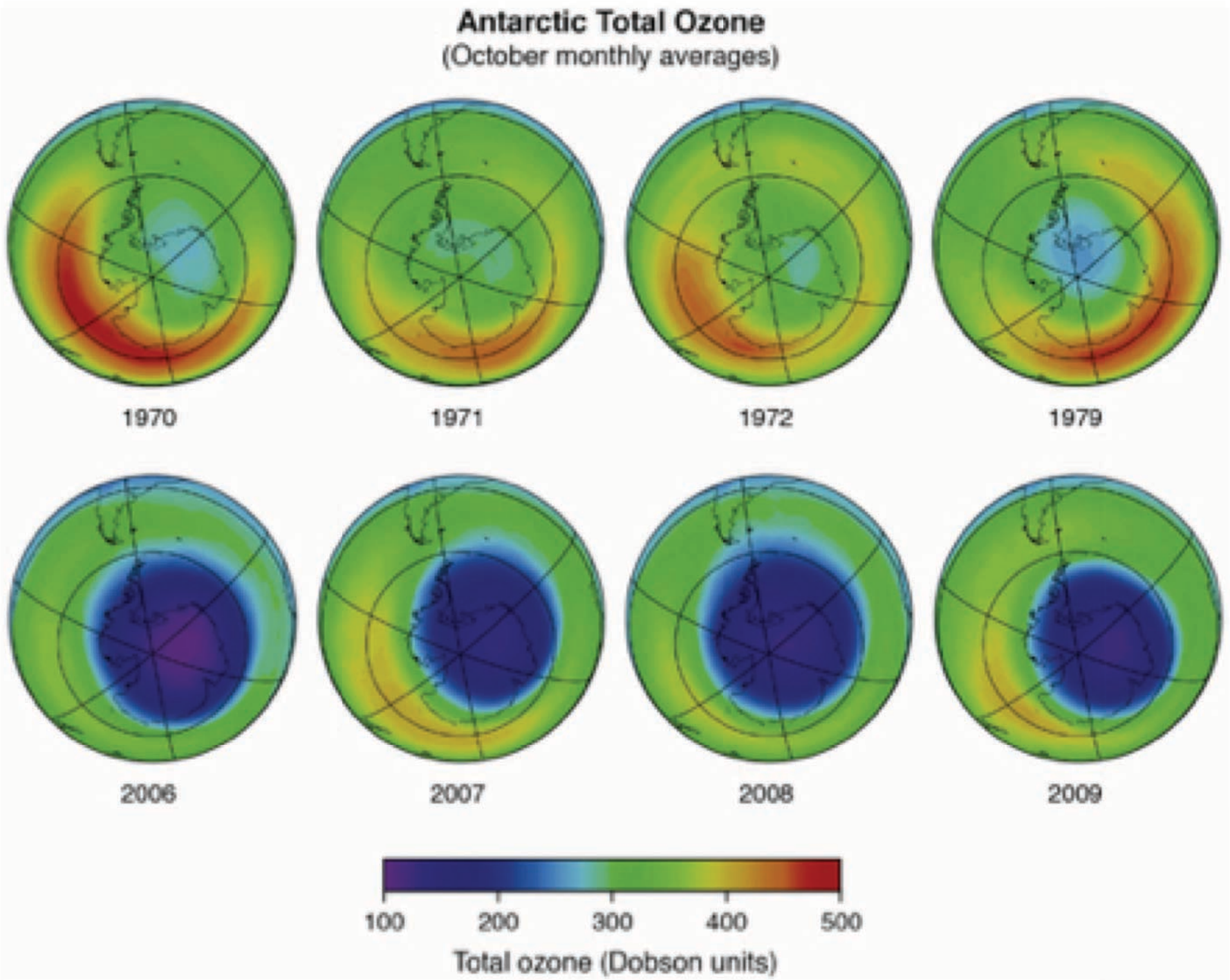
Pernice et al. 2004

Frank Mills ANU

CO~10^{-4}

HCl ~10^{-6}, Connes et. al 1967

Early work by Prinn, McElroy, Sze, Krasnopolsky



https://collidecolumn.wordpress.com/2012/09/15/when-worlds-collide-33-montreal-protocol-25-saluting-defenders-of-the-sky/

Chlorine Monoxide Dimer

Stan Sander

$$2[O_3 + Cl \longrightarrow ClO + O_2]$$

$$ClO + ClO + M \longrightarrow Cl_2O_2 + M$$

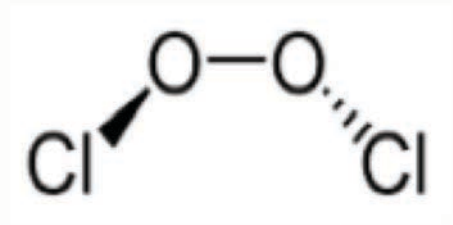
$$Cl_2O_2 + hv \longrightarrow ClOO + Cl$$

$$ClOO + M \longrightarrow Cl + O_2 + M$$

$$2O_3 \longrightarrow 3O_2$$

$O_3 \sim 10^{-5}$

$Cl_x \sim 10^{-9}$, from CFC



Sander, Friedl and Yung 1989

Solomon 1999 for Review

Outstanding Issues

Perchlorate on Mars

Nitrate on Mars

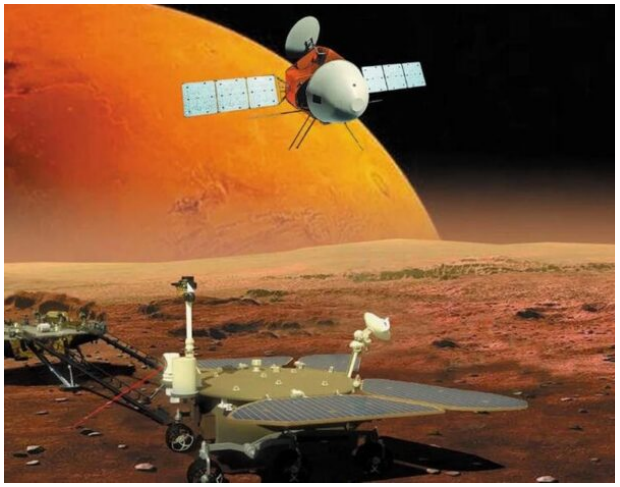
Mystery UV Absorber on Venus

Stability of Ancient CO_2 atmospheres

Chinese Space Missions

2020 July 23

Tianwen-1 (Mars)



Orbit, Land, Release a rover

Study the atmosphere, geology and magnetic properties of Mars

~2020 late October

Chang'e-5 probe (Moon)

Sample return mission

Aiming to return at least 2 kilograms of lunar soil and rock samples back to the Earth

OUTLINE

1. Terrestrial Planets: Mars, Venus and Earth
2. **Terrestrial Analogs: Titan, Pluto and Triton**
3. Exoplanets Analogs
4. Habitability and Habitancy

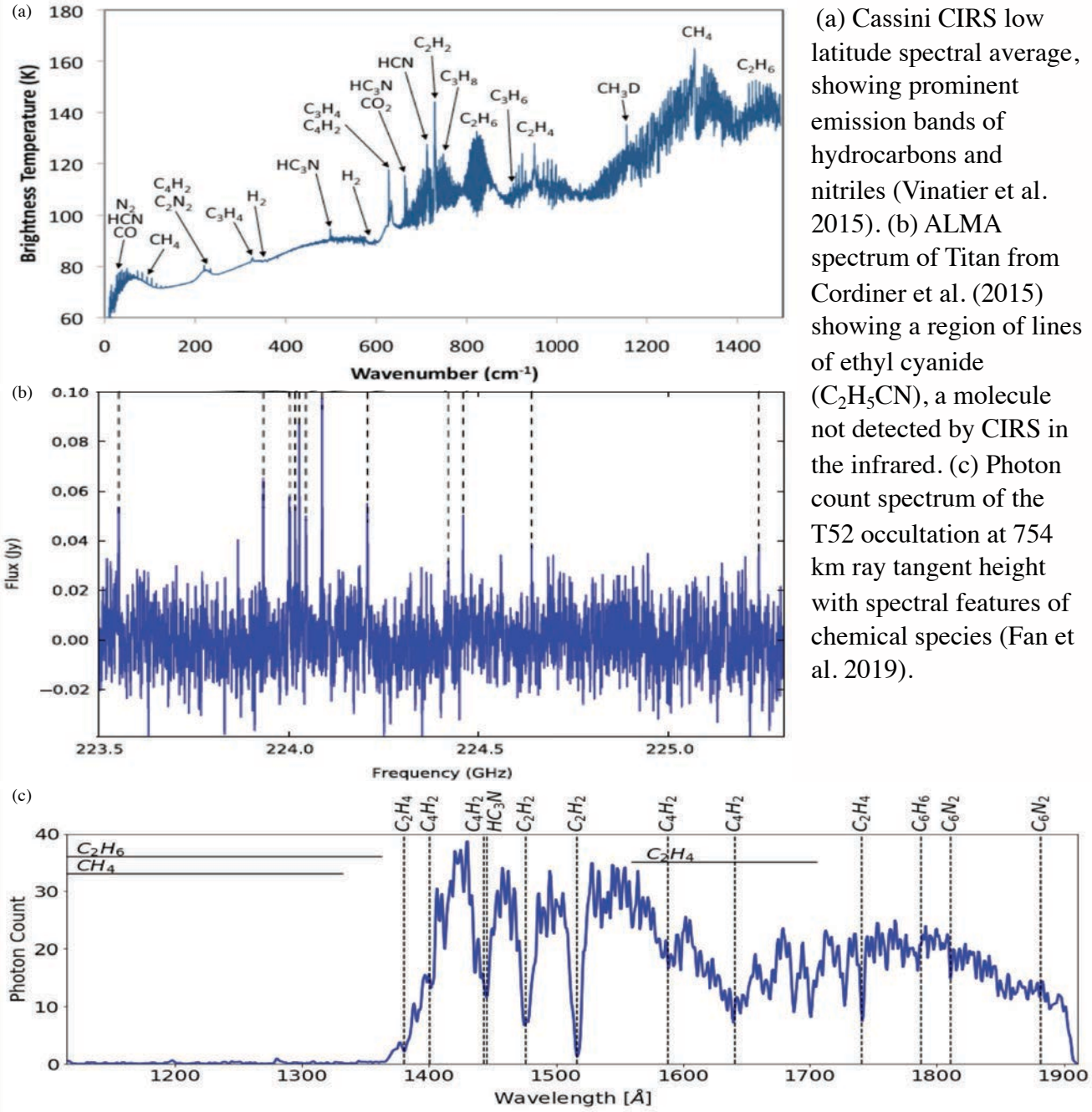
Randy Gladstone

Julie Moses

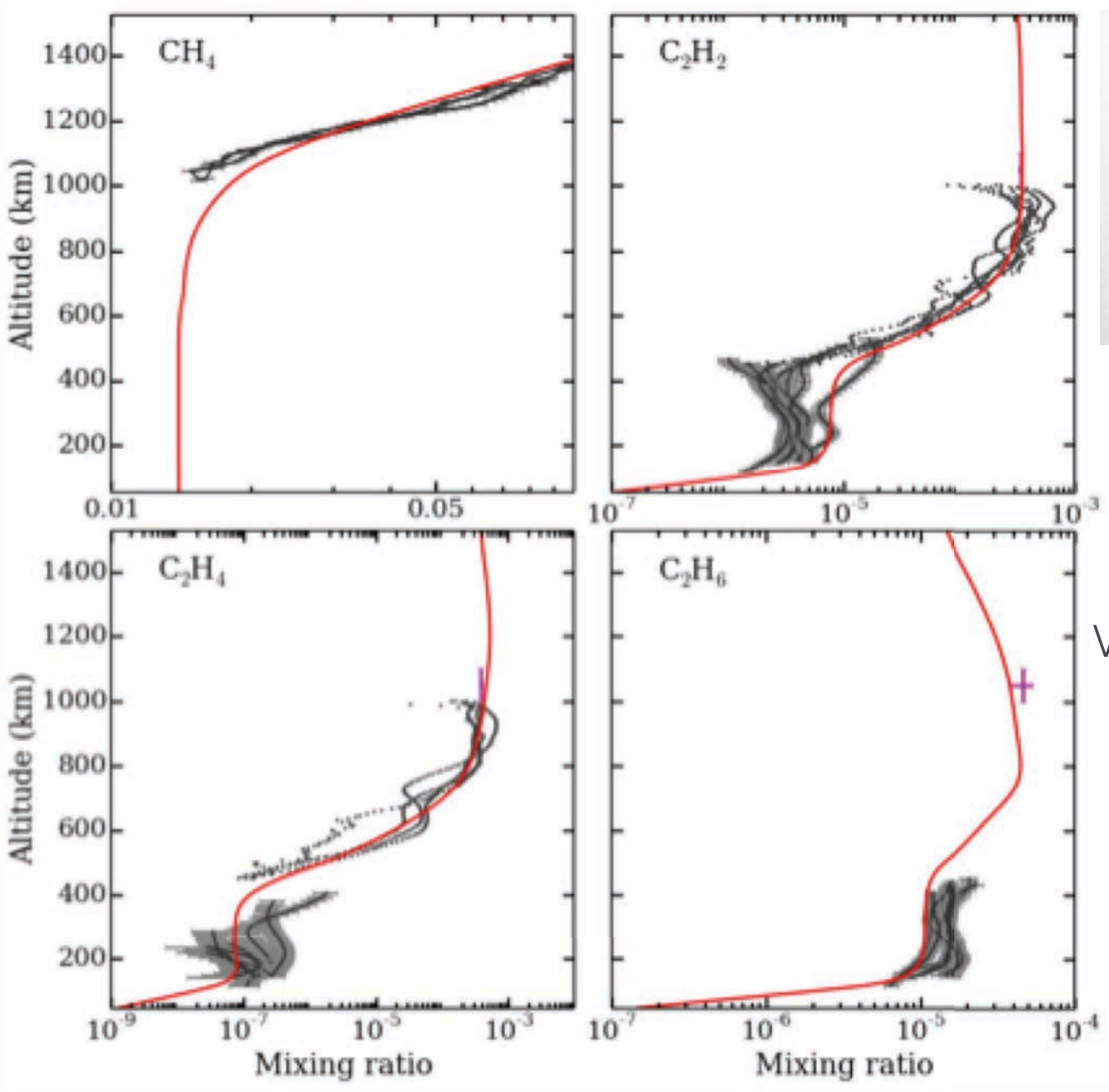
Strobel 1969, 1973

Gladstone et al. 1996

Moses et al. 2005



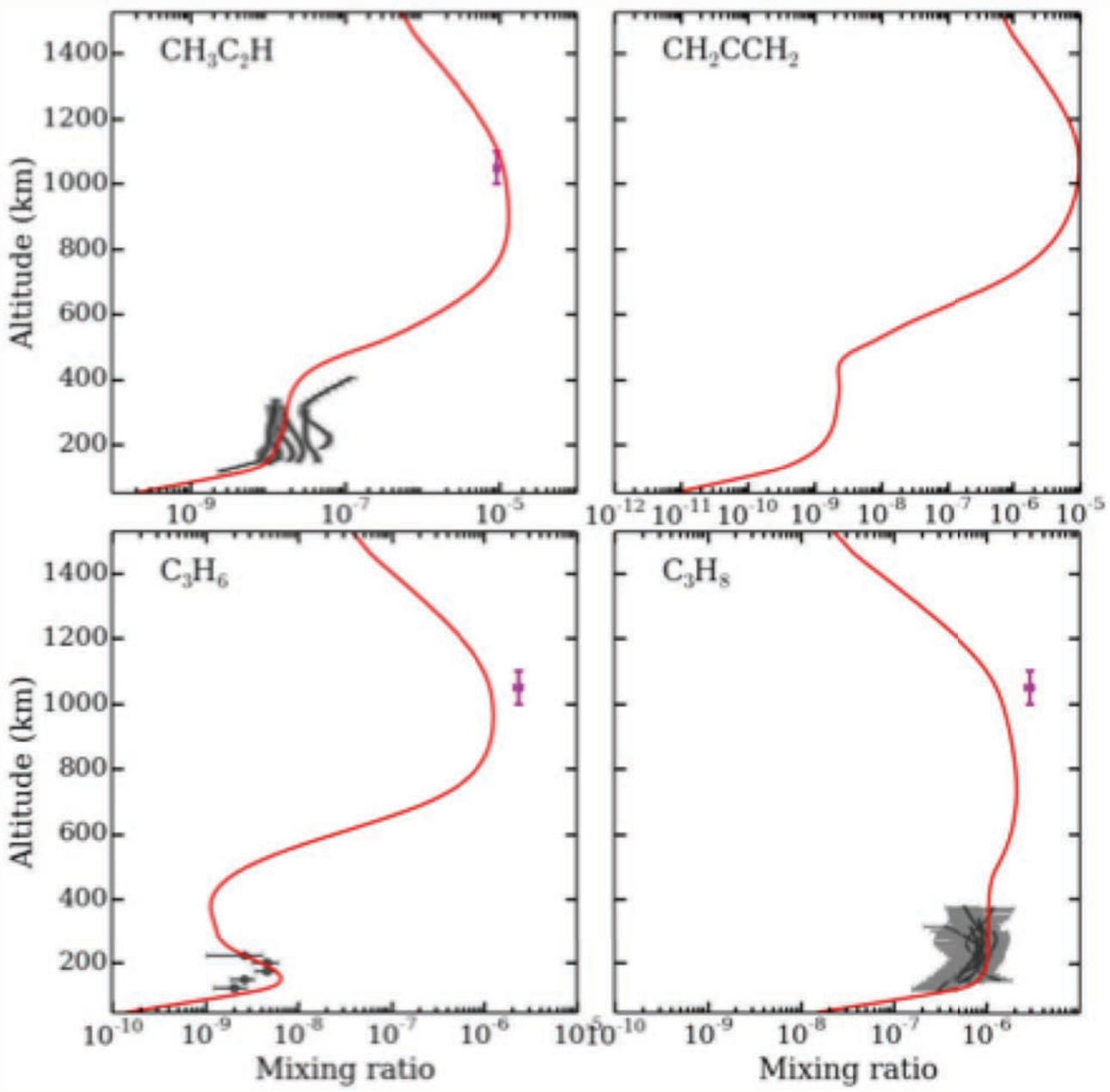
(a) Cassini CIRS low latitude spectral average, showing prominent emission bands of hydrocarbons and nitriles (Vinatier et al. 2015). (b) ALMA spectrum of Titan from Cordiner et al. (2015) showing a region of lines of ethyl cyanide (C_2H_5CN), a molecule not detected by CIRS in the infrared. (c) Photon count spectrum of the T52 occultation at 754 km ray tangent height with spectral features of chemical species (Fan et al. 2019).



Yung et al. 1984

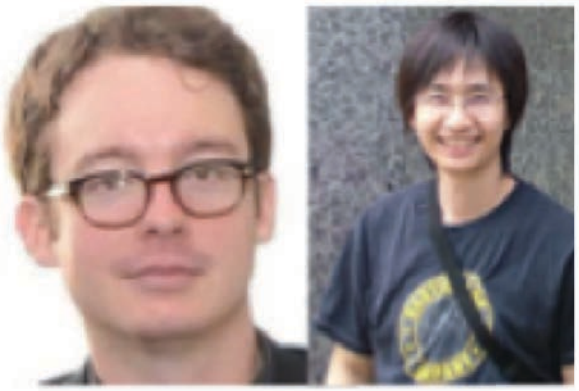
Li et al. 2014, 2015

Vuitton et al. 2007, 2008



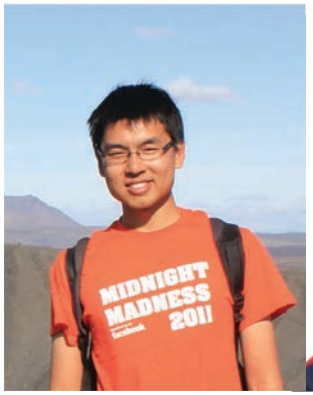
Titan is Nature's laboratory for organic synthesis, fulfilling the vision of Urey and Miller (1953)

However, the emergence of life requires more than that.

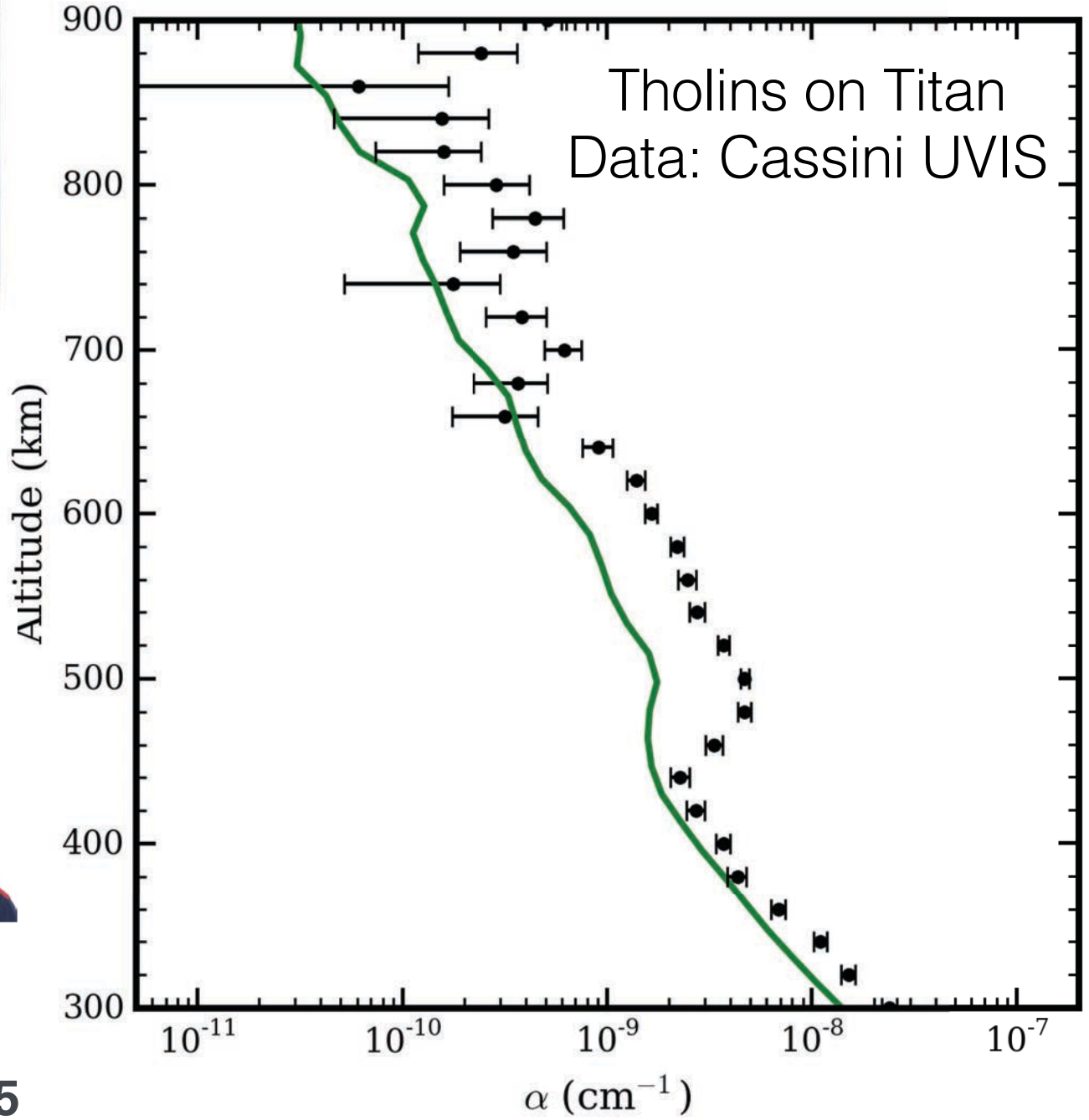


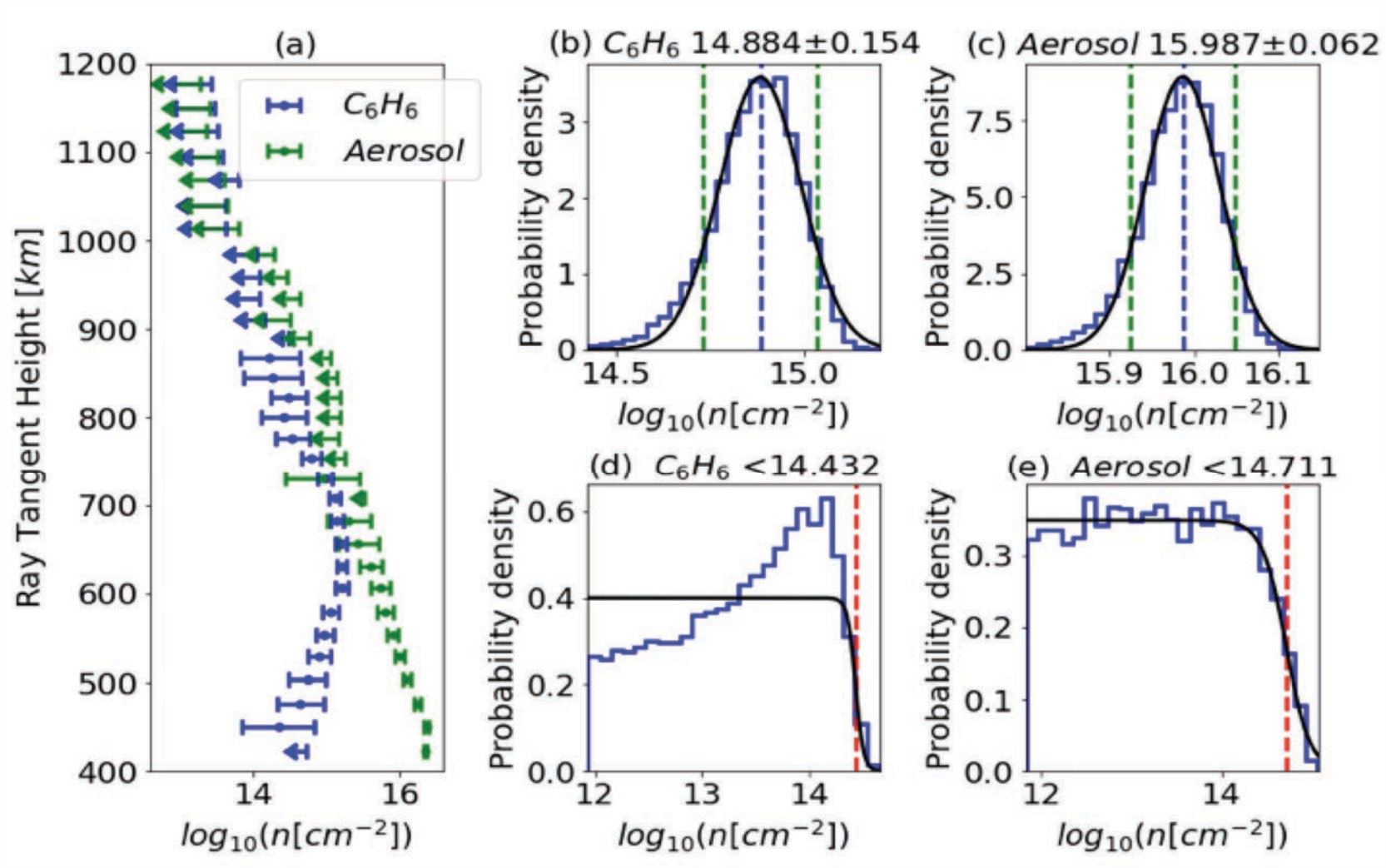
Josh Kammer Danie Liang

Peter Gao Siteng Fan



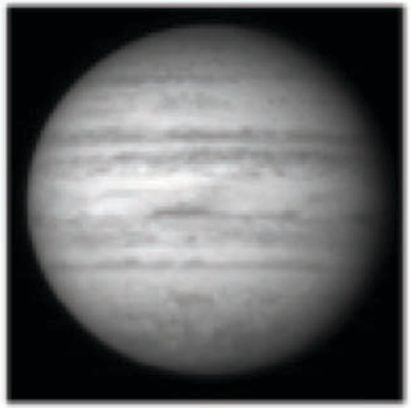
Liang et al. 2007
Lavvas et al. 2013
Kammer et al. 2015
Fan et a. 2019





(a) Line-of-sight (LOS) abundance of benzene and aerosol retrieved from occultation observation of Cassini-UVIS during T52 flyby. Error bars denote well-constrained LOS abundances, and arrows denote upper limits. (b) Probability density function of the LOS abundance of benzene at a ray tangent height of 529 km from T52 flyby. (c) Same as (b), but for aerosol. (d) and (e) Same as (b) and (c), respectively, but for 890 km. Fan et al. 2019.

Faces of Aerosols (high latitudes)



Xi (Arthur) Zhang

Fractal Aggregates

(e.g., Titan aerosols,
West and Smith, 1991;
Tomasko et al. 2008)

Zhang, West, Banfield, Yung 2013

Horst et al. 2012

Trainer et al. 2006

Autocatalysis

Direct Photolysis ($\lambda < 140$ nm)

$$2[CH_4 + h\nu \longrightarrow CH_3 + H]$$

$$CH_3 + CH_3 + M \longrightarrow C_2H_6 + M$$

$$2CH_4 \longrightarrow C_2H_6 + 2H$$

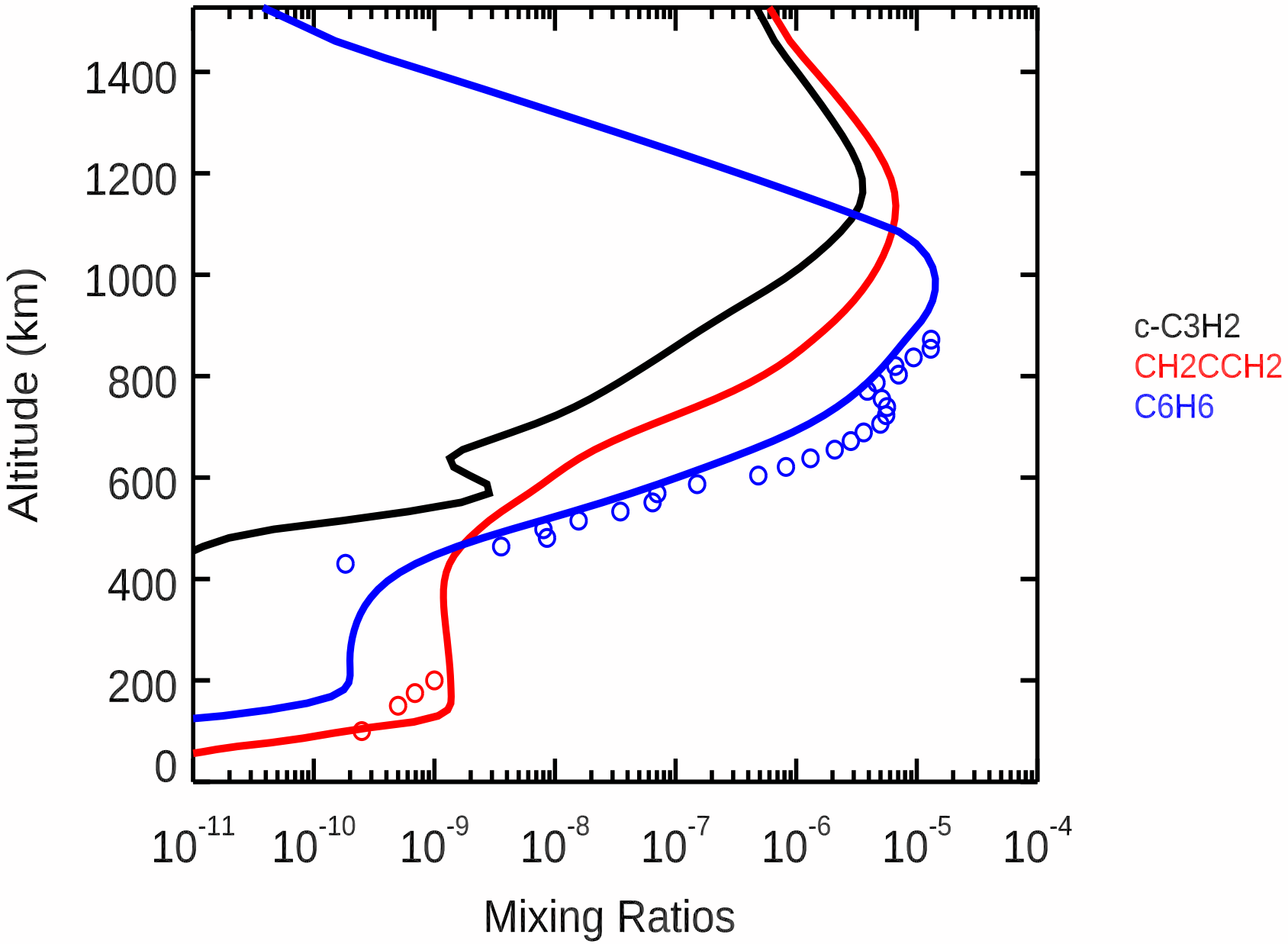
Autocatalysis ($\lambda < 200$ nm)

$$C_2H_2 + h\nu \longrightarrow C_2H + H$$

$$C_2H + CH_4 \longrightarrow CH_3 + C_2H_2$$

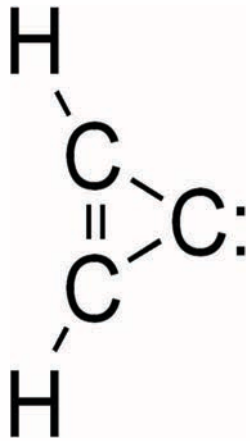
$$CH_4 \longrightarrow CH_3 + H$$

Allen, Pinto and Yung 1982

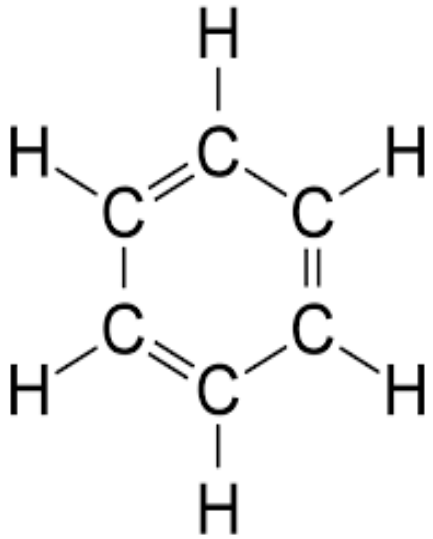


Mixing ratios of *c*-C_3H_2, CH_2CCH_2 and C_6H_6 from KINETICS (Willacy and Yung 2020). Detailed profile for is not yet available for *c*-C_3H_2; observed column abundance in within a factor of 3 of our model. See text for the sources of observed data. Willacy and Yung 2020.

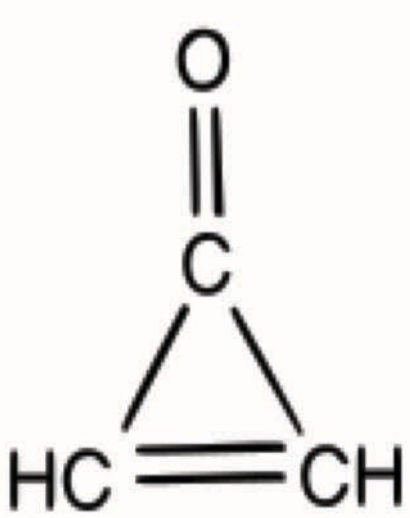
a)



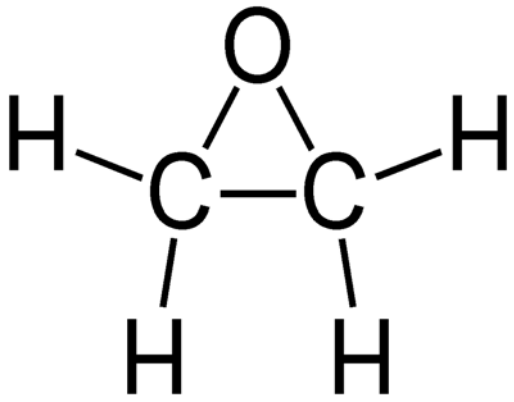
b)



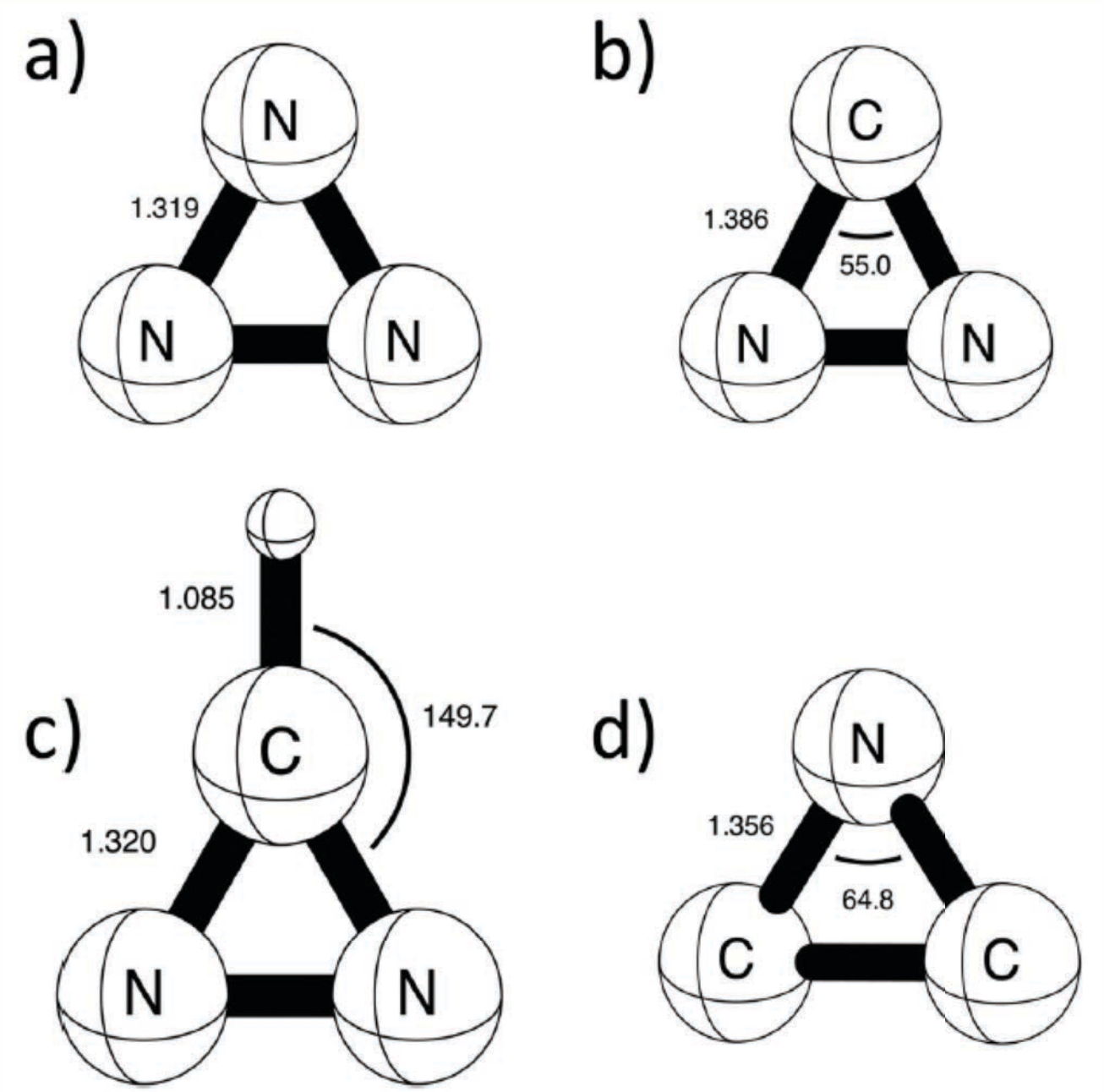
c)



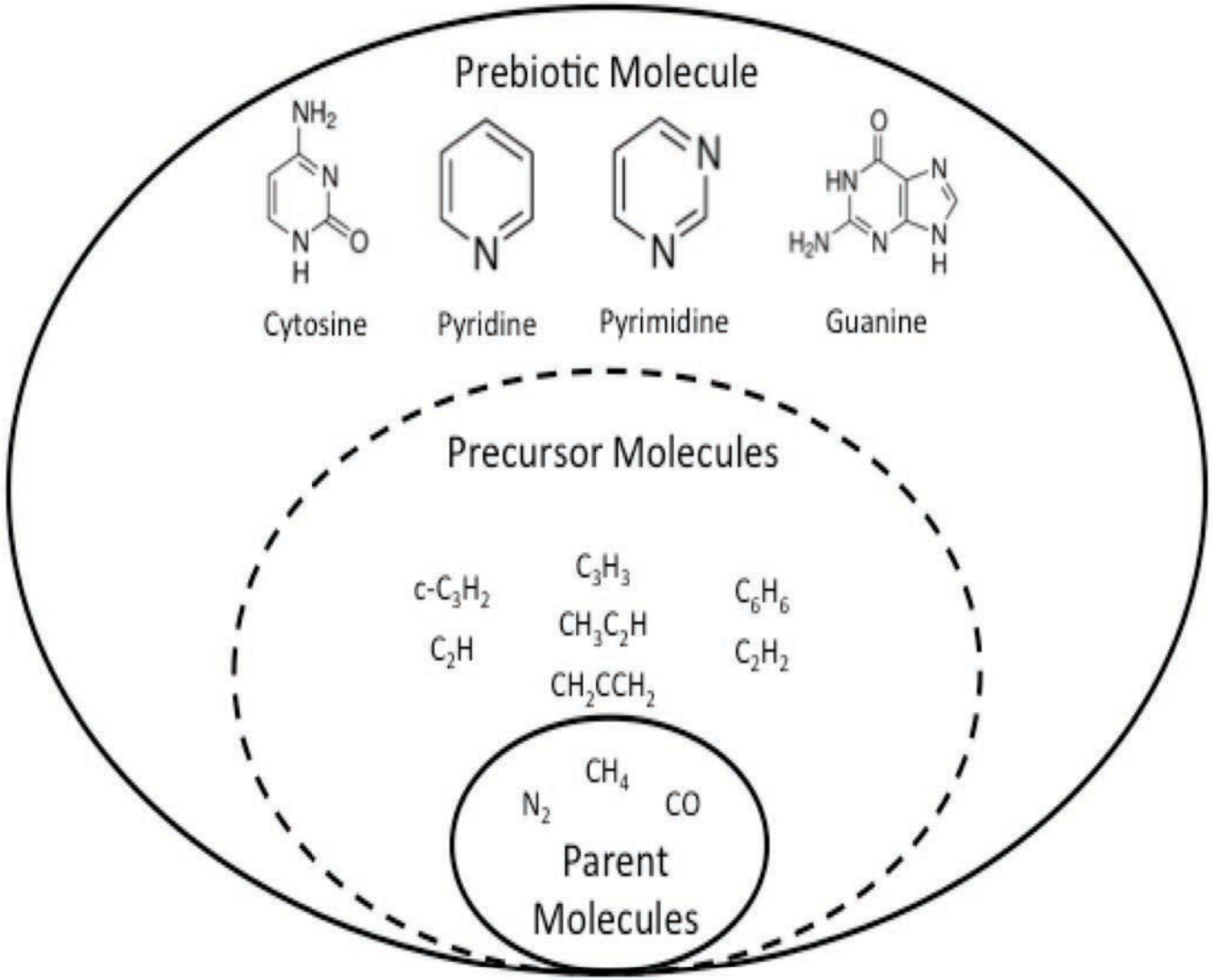
d)



(a) *c*-C_3H_2 cyclopropenylidene (b) C_6H_6 benzene (c) *c*-C_3H_2O cyclopropenone (d) *c*-C_2H_4O ethylene oxide.



Structure of molecules isoelectronic to *c*-C_3H_2: (a) *c*-N_3^+ (b) c-CNN (c) $HCNN^+$ (d) c-CNC^-. Fortenberry et al. (2017).



Grand vision for organic synthesis on Titan. For simplicity, only a small number of representative molecules are shown. Based on Sebree et al. (2018).

The Primordial Soup

Russell et al. 2014

* Soup
* Clay
* Hydrothermal Vents

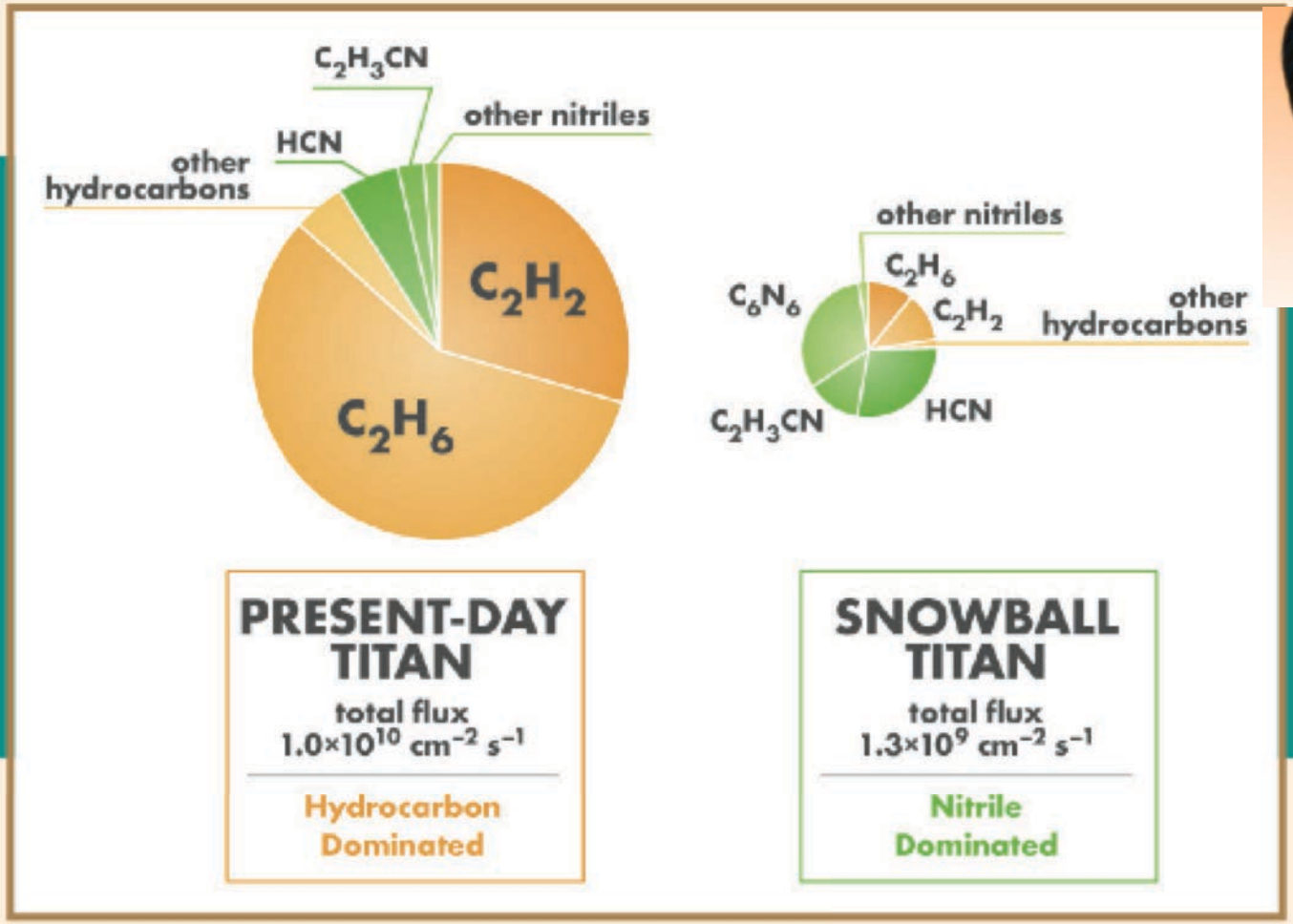
Lunine, Stevenson and Yung 1983

Ethane Ocean on Titan

It is proposed that Saturn's satellite Titan is covered by an ocean one to several kilometers deep consisting mainly of ethane.

> The dog did nothing in the nighttime.
>
> That was the curious incident.
>
> —*Sherlock Holmes*

CARBON MASS FLUX



michael l. wong

Wong, Gladstone and Yung 2015

Lorenz, McKay and Lunine 1997

@MIQUAI #TITAN #PLUTO #TTT3

Pluto Col (HCN) ~10^{14} cm^{-2}

Outstanding Issues


Randy Gladstone
& Mike Summers
Is Pluto a Proxy for Snowball Titan?

Jim Lyons
Is Triton more similar to Pluto than to Titan?

Lyons, Allen and Yung 1992

OUTLINE

1. Terrestrial Planets: Mars, Venus and Earth
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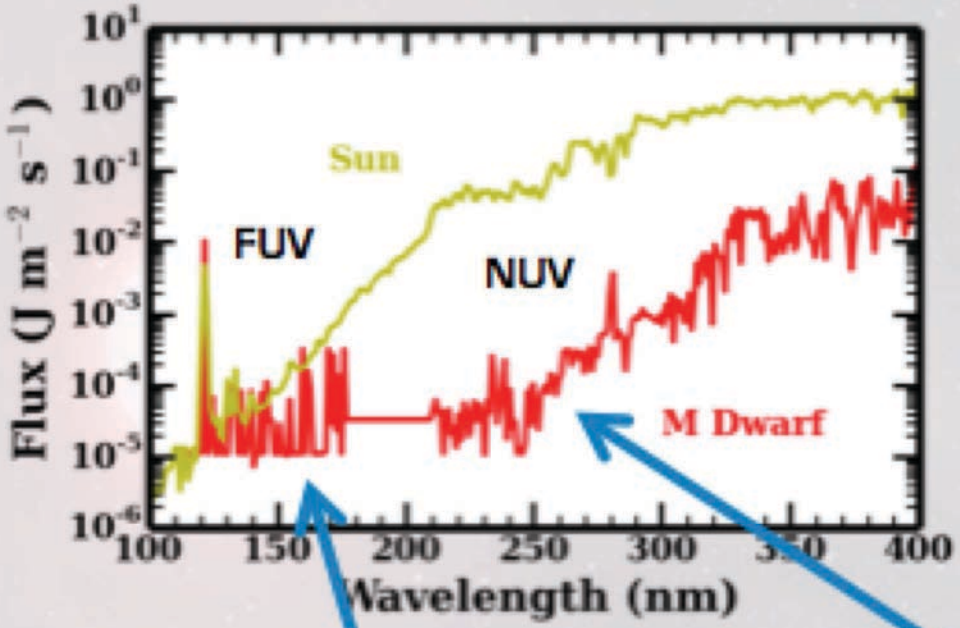
3. **Exoplanets Analogs**
4. Habitability and Habitancy

ExoMars

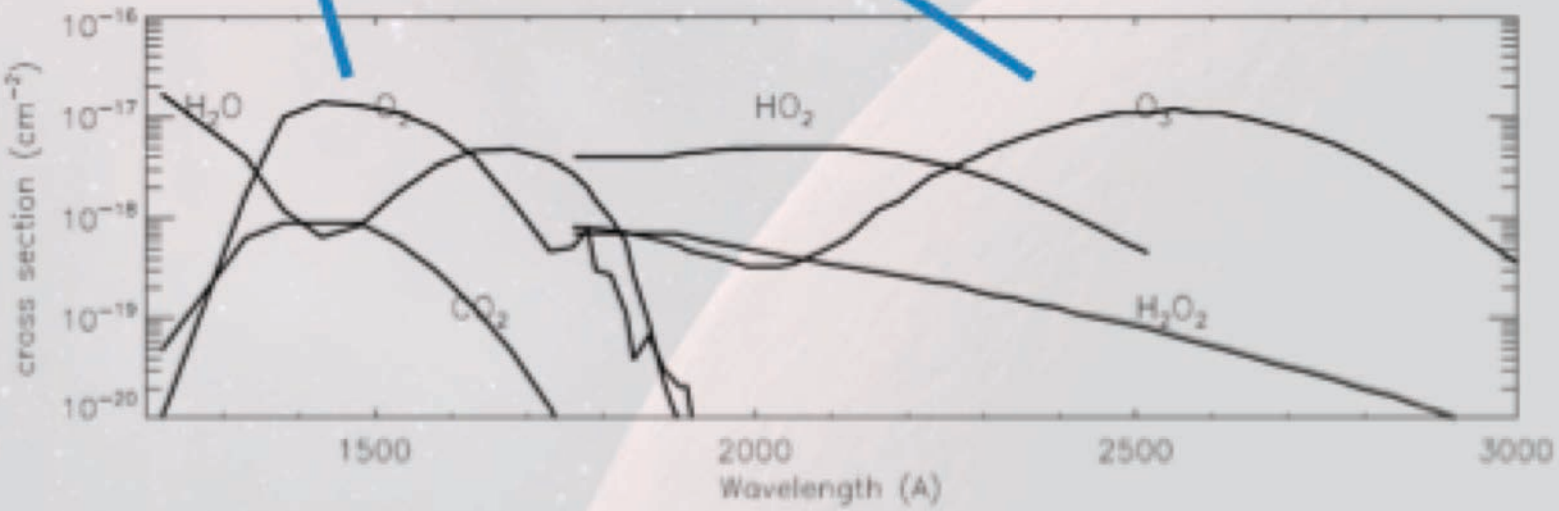


$HO_2 + O \rightarrow O_2 + OH$

$H + O_2 + M \rightarrow HO_2 + M$

$OH + CO \rightarrow CO_2 + H$

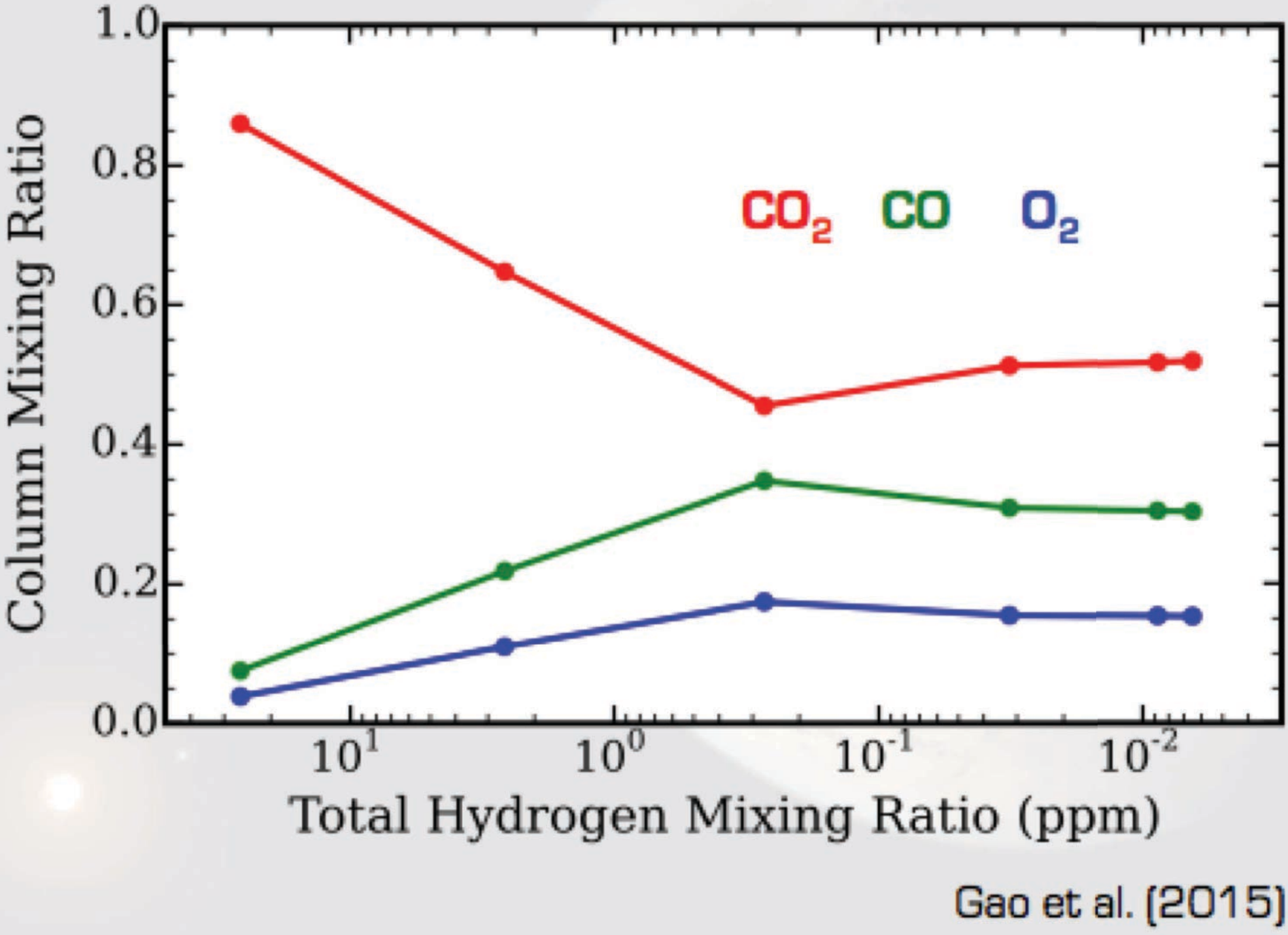
$CO + O \rightarrow CO_2$



Tian et al. 2014

Gao et al. 2015

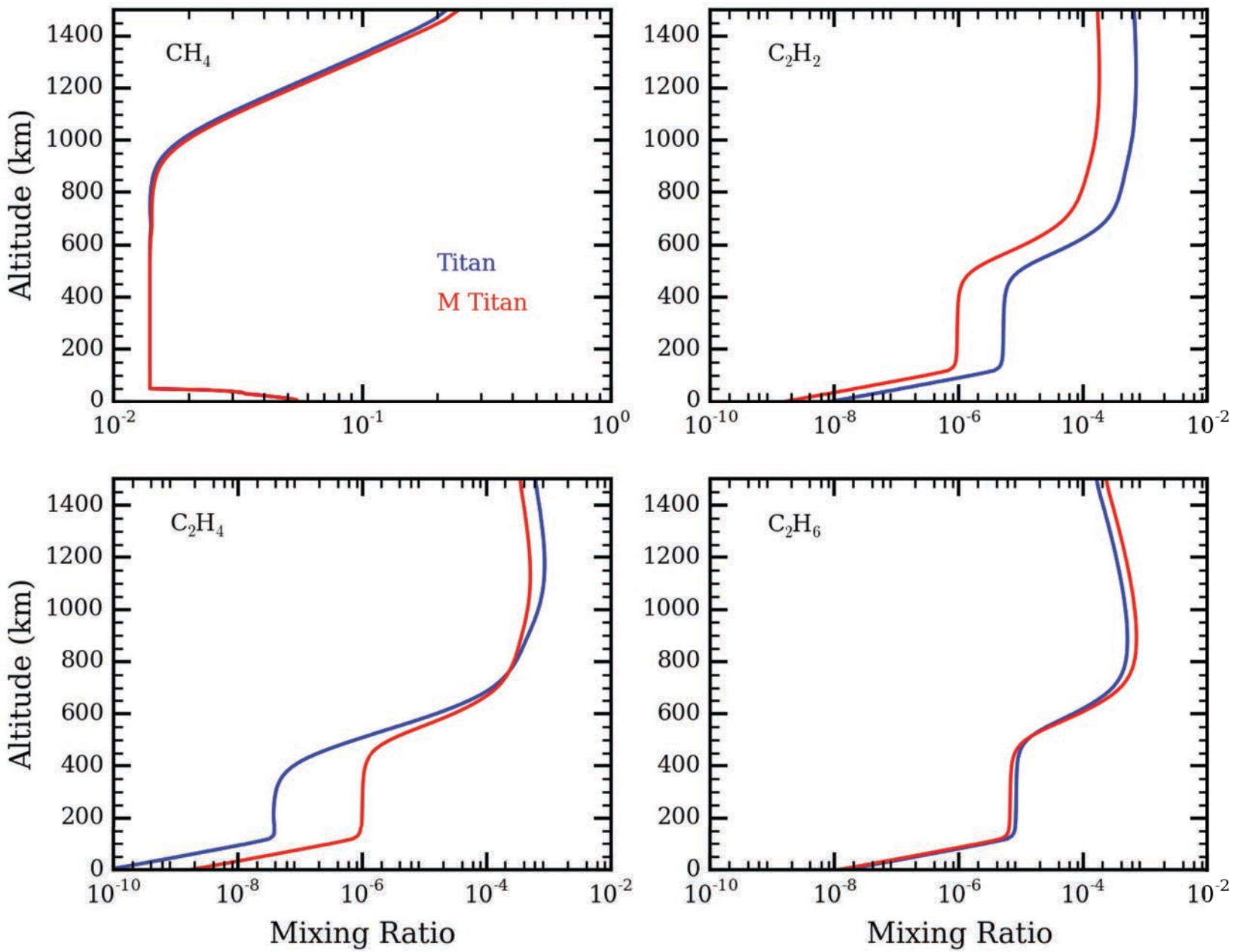
Exomars



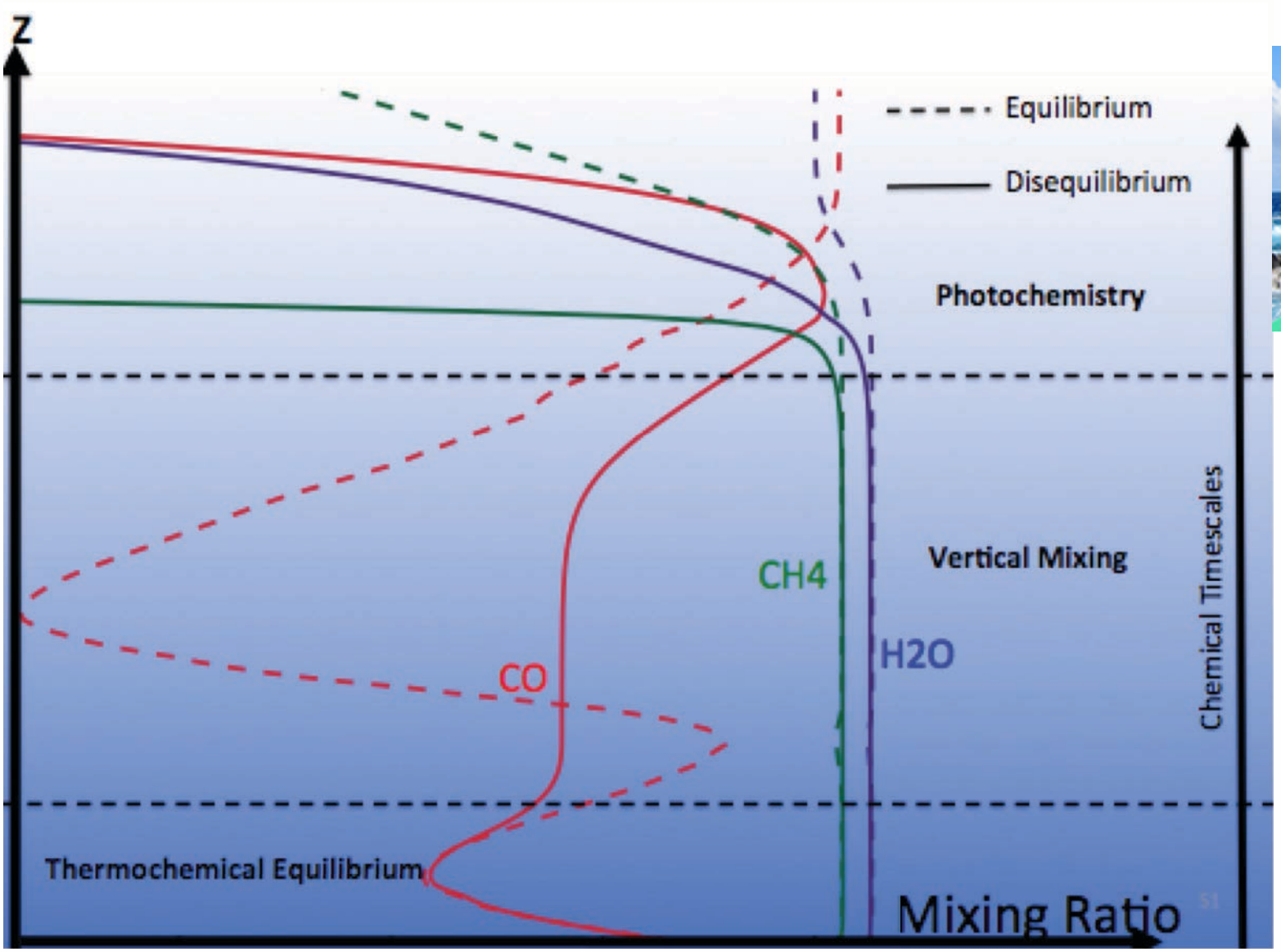
Gao et al. (2015)

ExoTitan

Gao and Yung 2015



Hot Jupiters: Equilibrium and Disequilibrium Chemistry

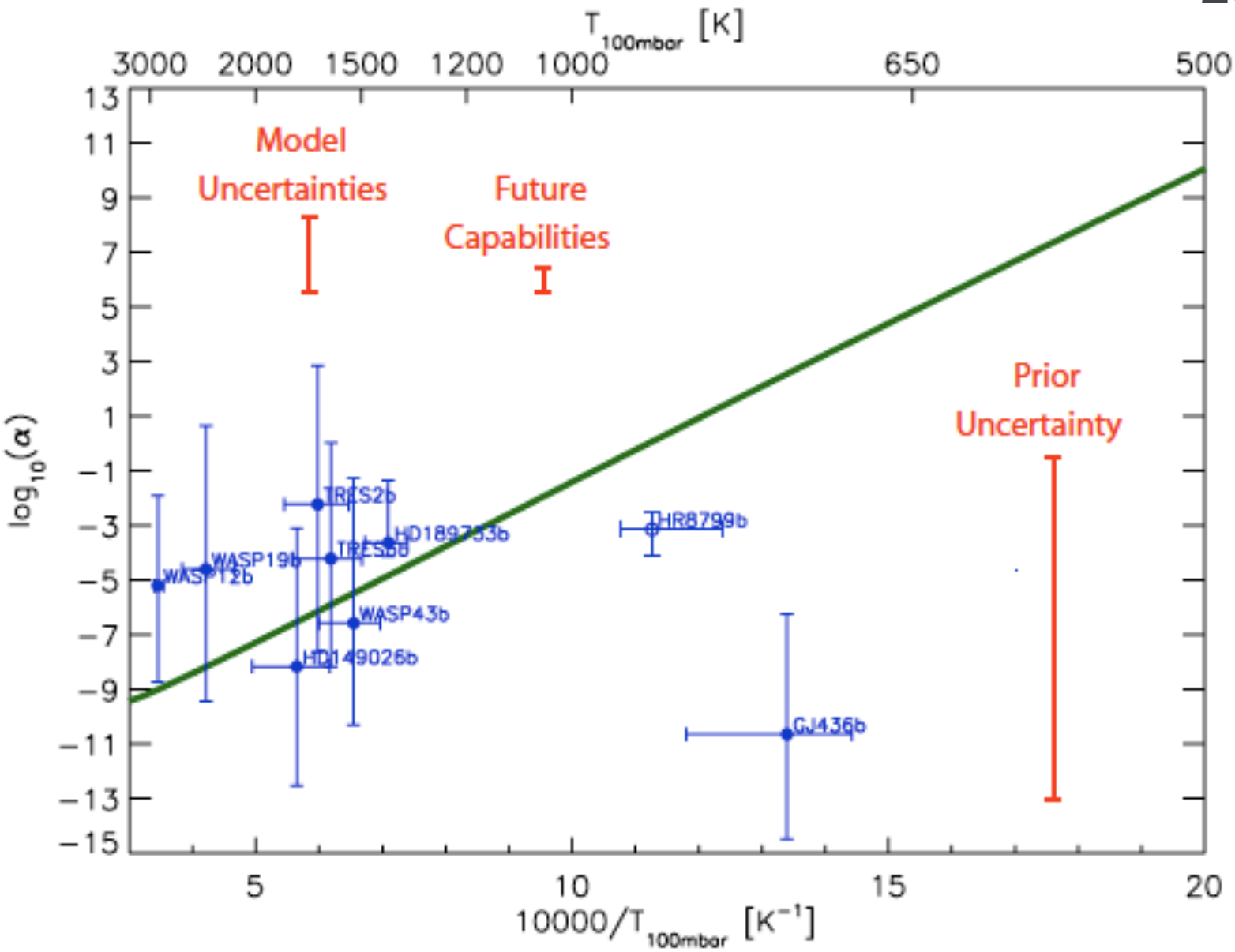


Mike Line

Exoplanet like HD189733b

Test of Equilibrium Chemistry

Line and Yung 2013



Outstanding Issue:

Are we alone?

Sanxingdui Museum
Sichuan, China

OUTLINE

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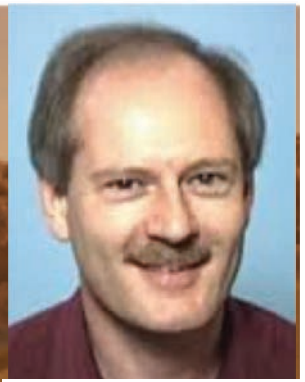
4. **Habitability and Habitancy**

Was Mars Habitable?



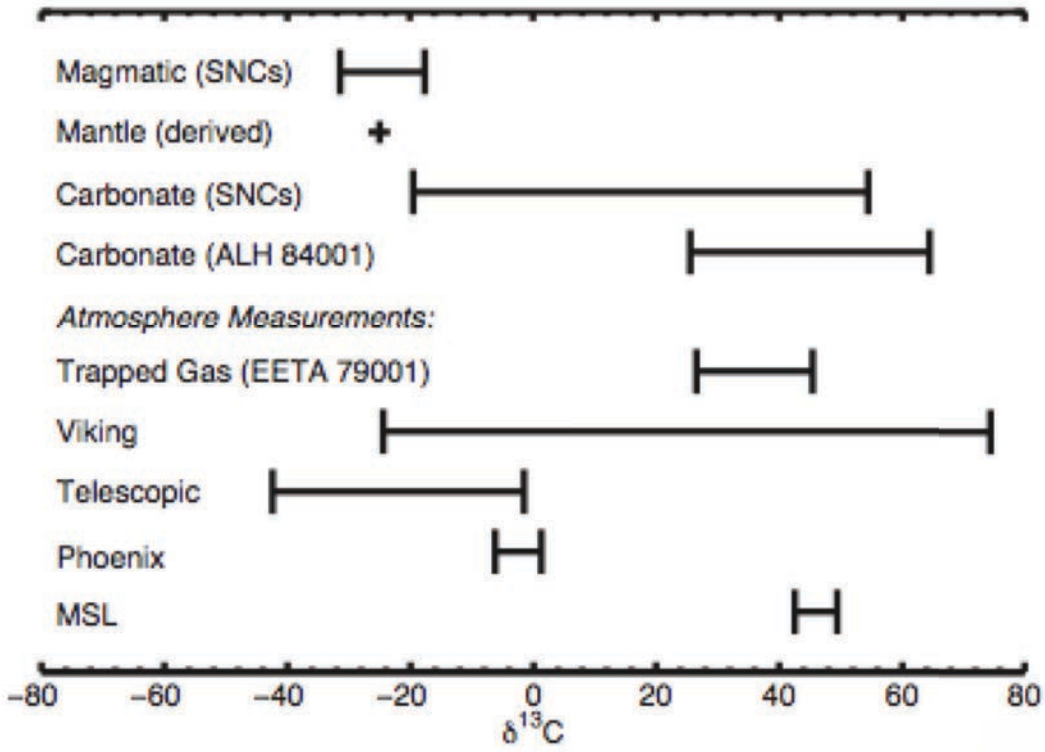
Chris Webster

Paul Mahaffy

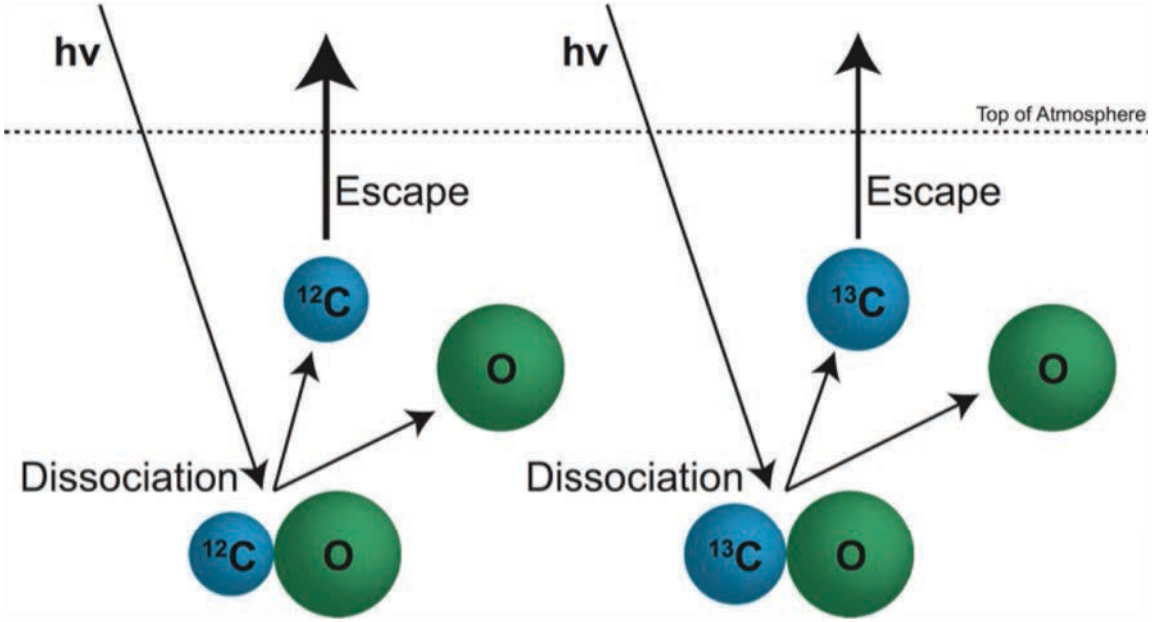
Renyu Hu

JPL

Carbon Isotopic Signatures of Mars



Carbon Escape via CO Photodissociation



Hu, Kass, Ehlmann and Yung 2015

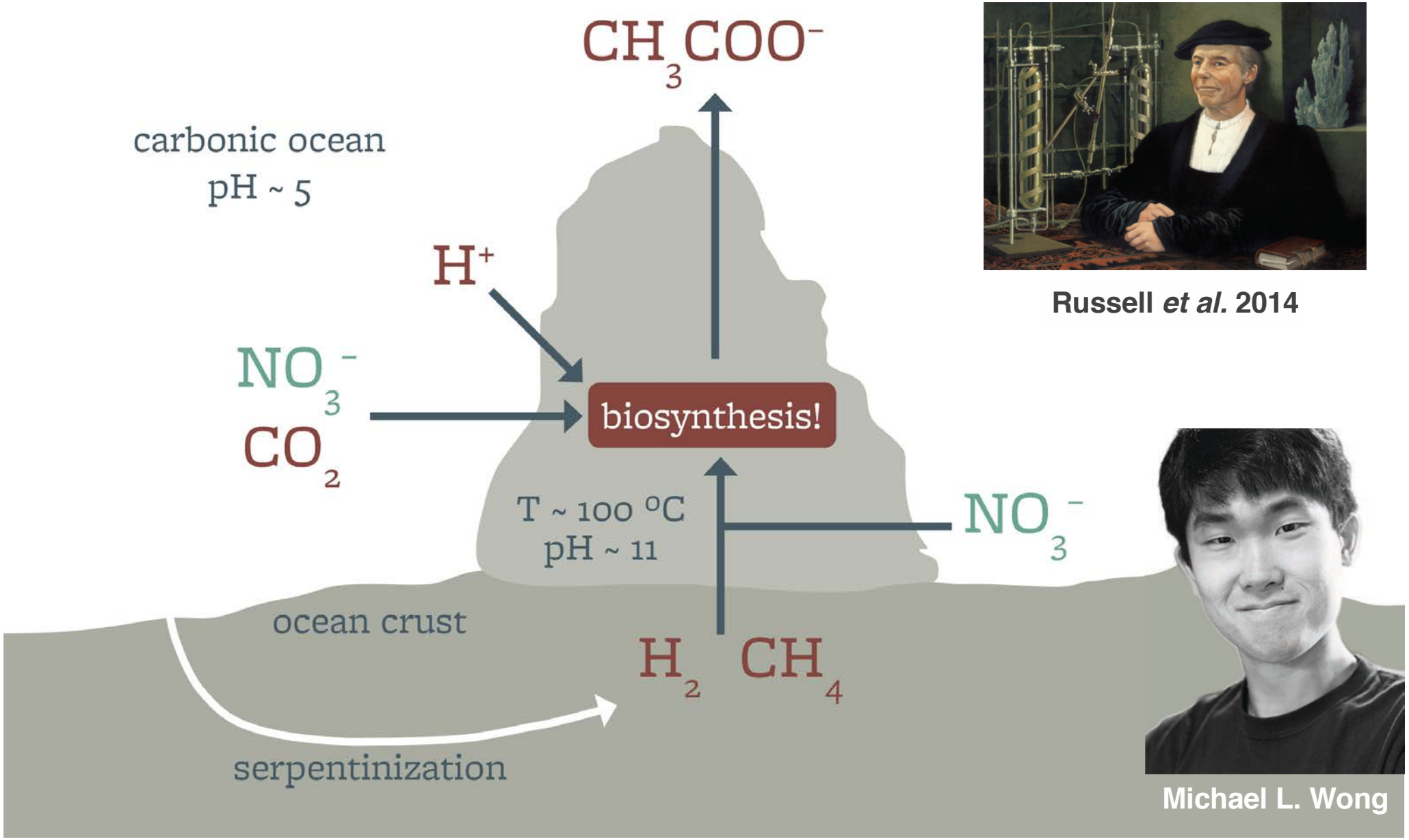
A Moderately Dense Early Atmosphere

- An upper limit of 0.9 bar can be derived from when carbonate formed in the subsurface
- Or 1.7 bar when carbonate in surface lakes

The atmosphere does not collapse, allowing transient melting, runoff, and low-temperature hydrological cycles

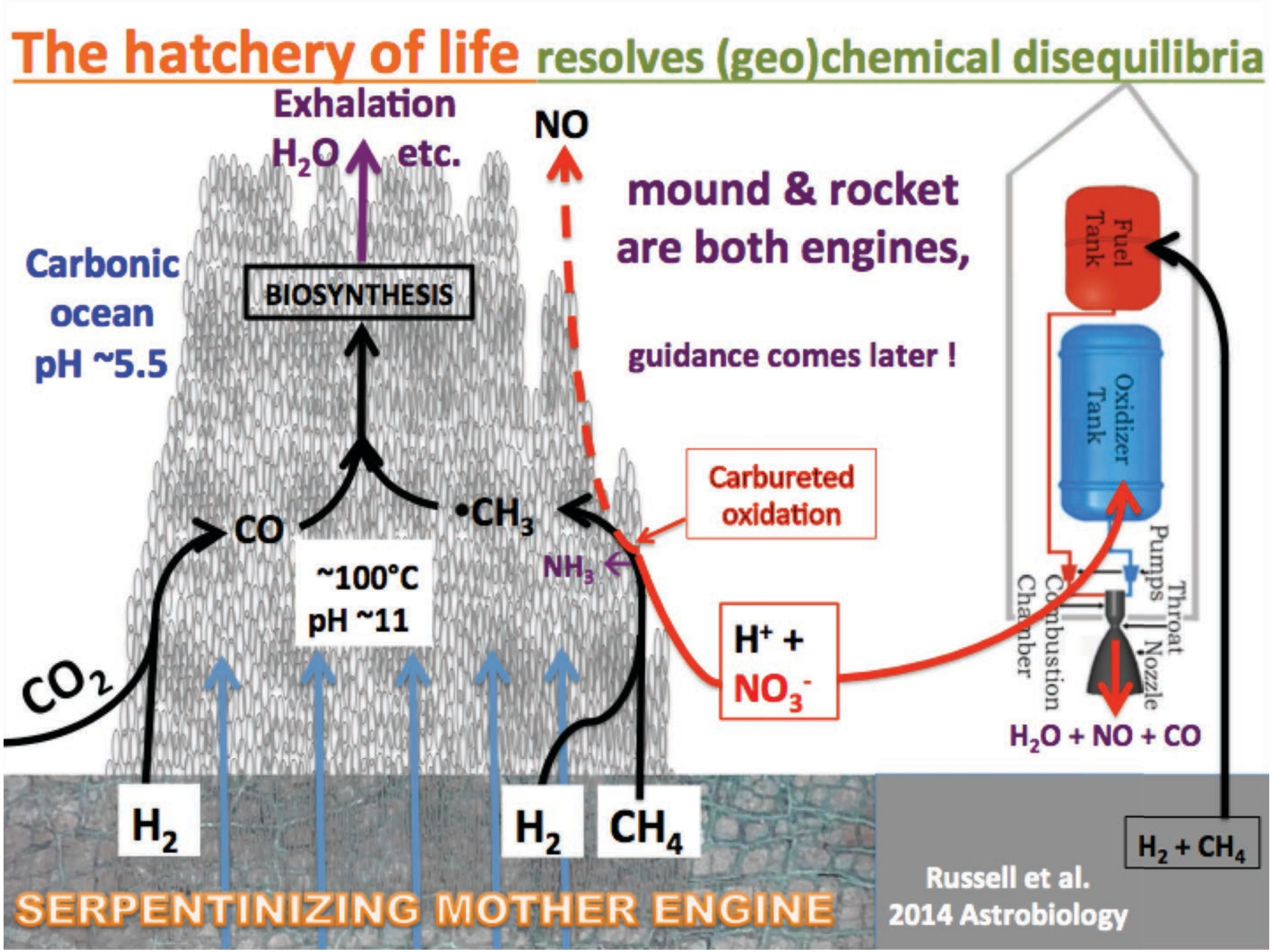
Forget et al. 2013; Kite et al. 2014; Hu et al. 2015

How did Life Start on Earth?

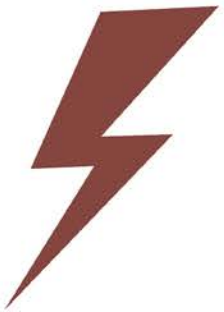


Russell *et al.* 2014

Michael L. Wong


The hatchery of life resolves (geo)chemical disequilibria
Exhalation
H_2O etc.
NO
mound & rocket
are both engines,
guidance comes later !
Carbonic
ocean
pH ~5.5
BIOSYNTHESIS
Carbureted
oxidation
$\bullet CH_3$
CO
CO_2
~100°C
pH ~11
NH_3
$H^+ +$
NO_3^-
Fuel Tank
Oxidizer Tank
Pumps
Throat
Nozzle
Combustion Chamber
$H_2O + NO + CO$
H_2
H_2
CH_4
$H_2 + CH_4$
SERPENTINIZING MOTHER ENGINE
Russell et al.
2014 Astrobiology

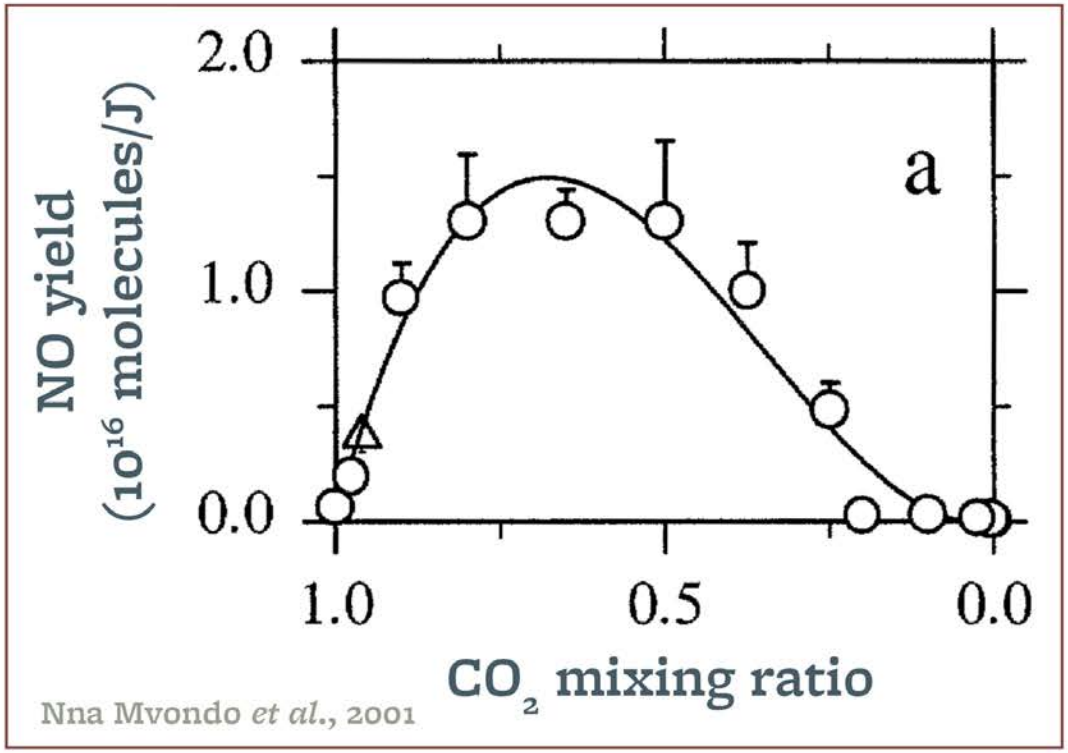
Lightning Estimates



$$CO_2 \rightarrow CO + O$$
$$N_2 + O \rightarrow \mathbf{NO} + N$$
$$N + CO_2 \rightarrow \mathbf{NO} + CO$$

Yung and McElroy 1979

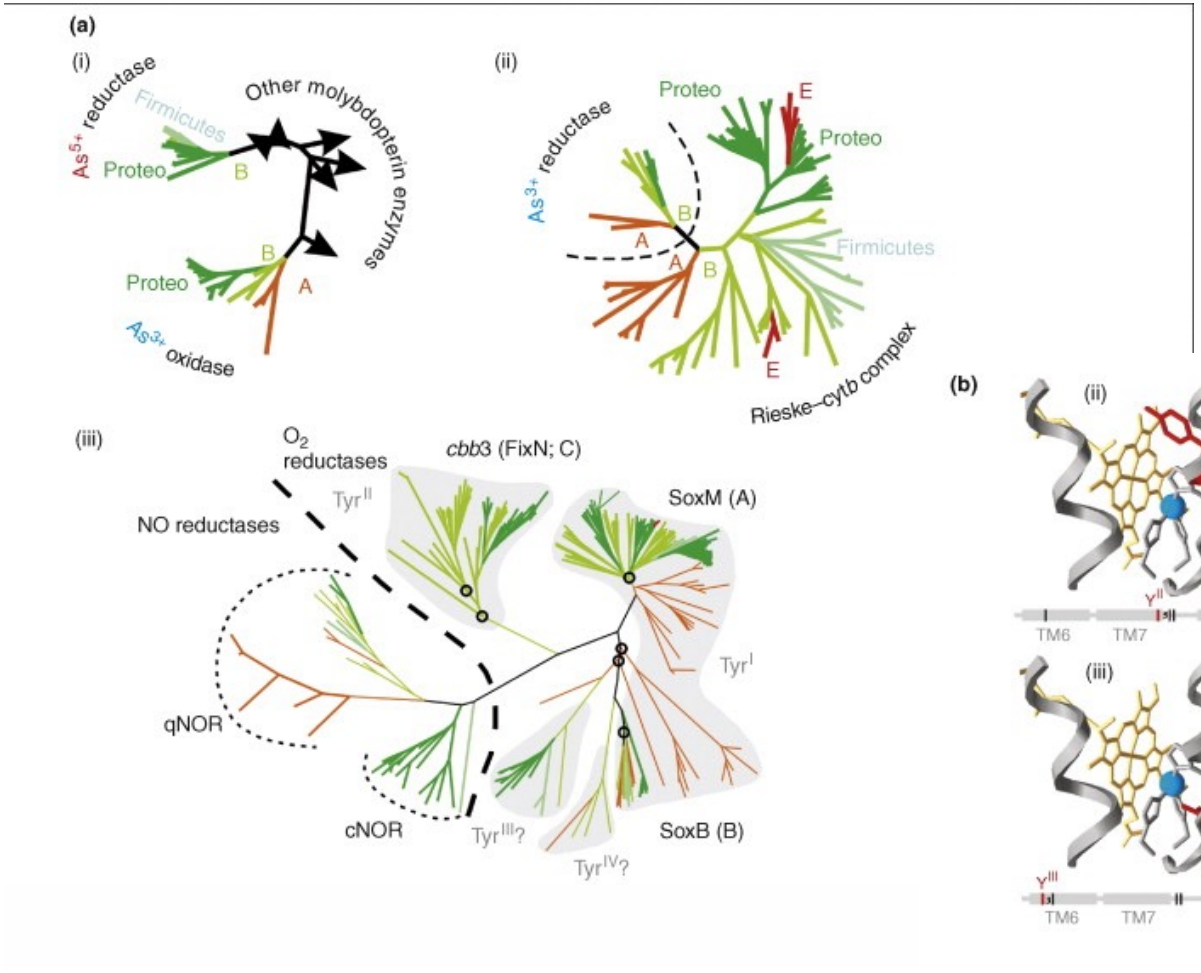
Ben Charnay
VPL



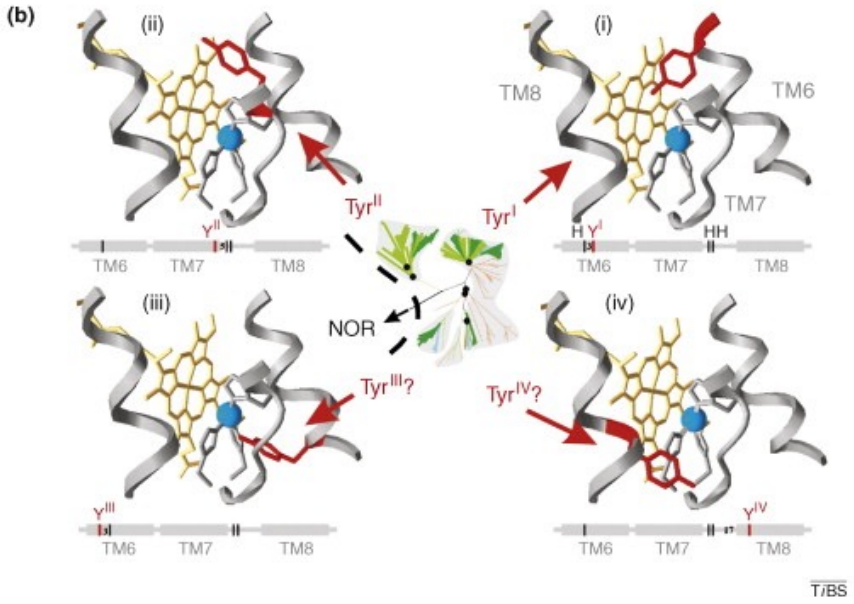
~5 × 10^9 J flash^{-1}
(present day)

flash rate ∝ precip. rate × CAPE
(Romps *et al.* 2014)

Why Nitrate?

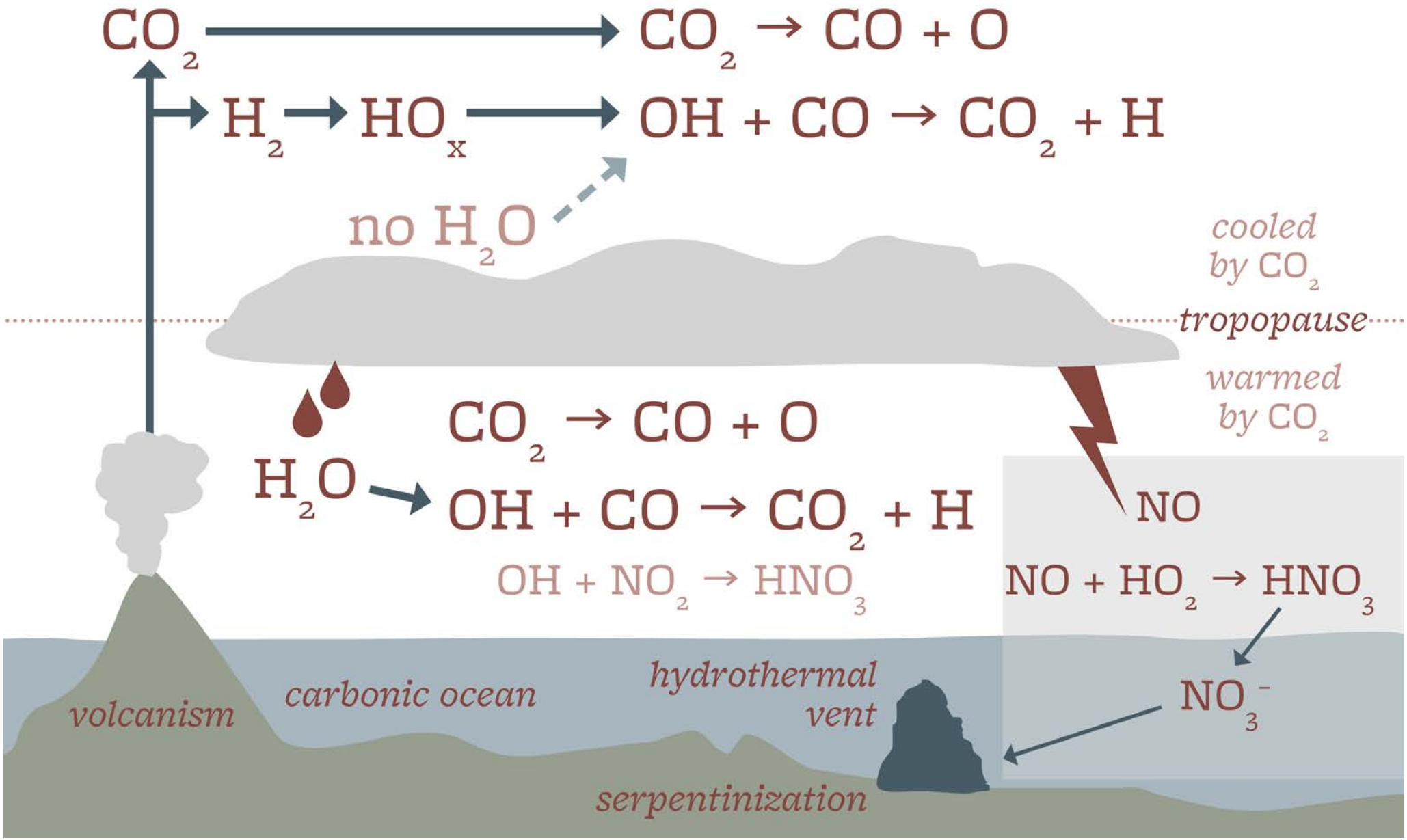


Enzyme that uses NO_3^-
Pre-LUCA
Nitschke et al. 2013

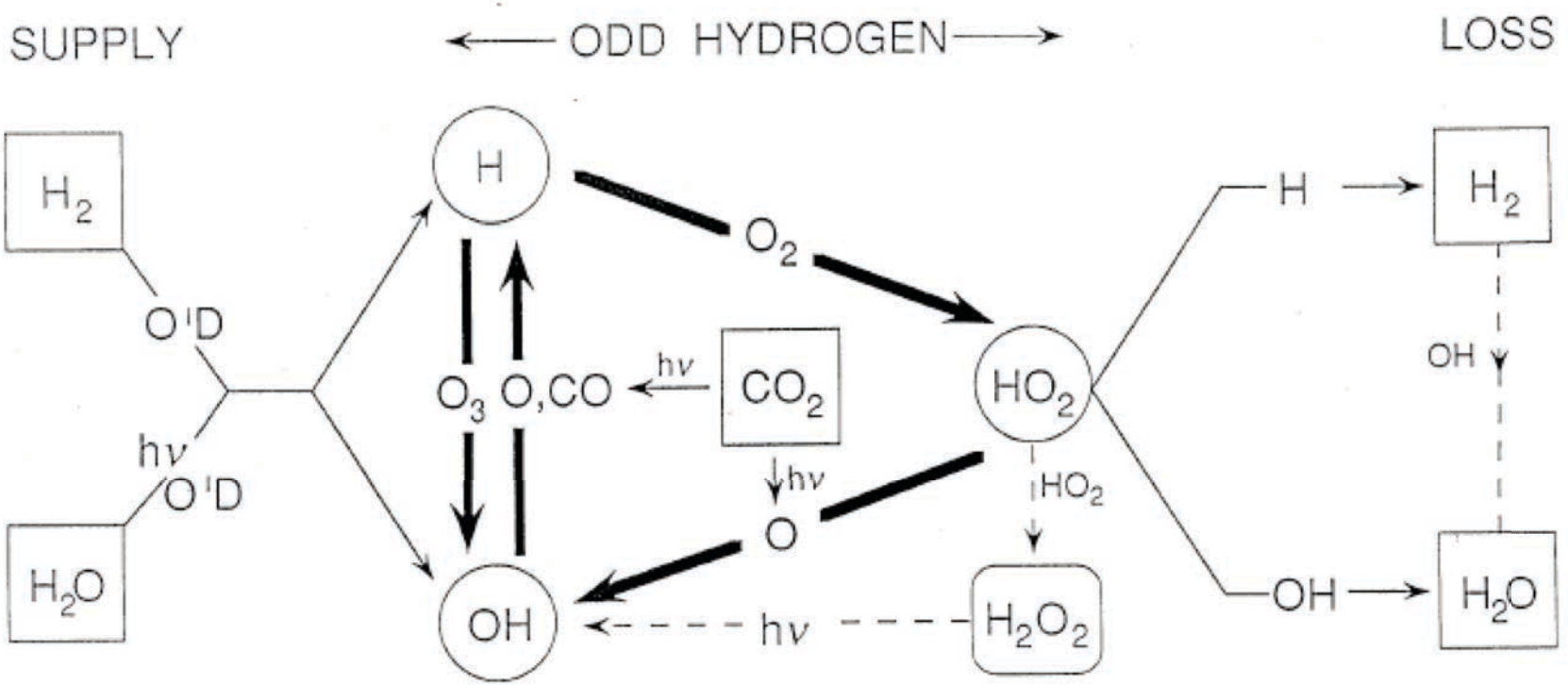


Duclzeau et al. 2009

Emergence of Life is Ineluctable on a Habitable Planet!



Wong, Russell, Charnay, Yung 2017, Adams et al. 2020, Astrobiology



Classic Catalytic Cycles

McElroy and Donahue 1972

Parkinson and Hunten 1972

Applications to

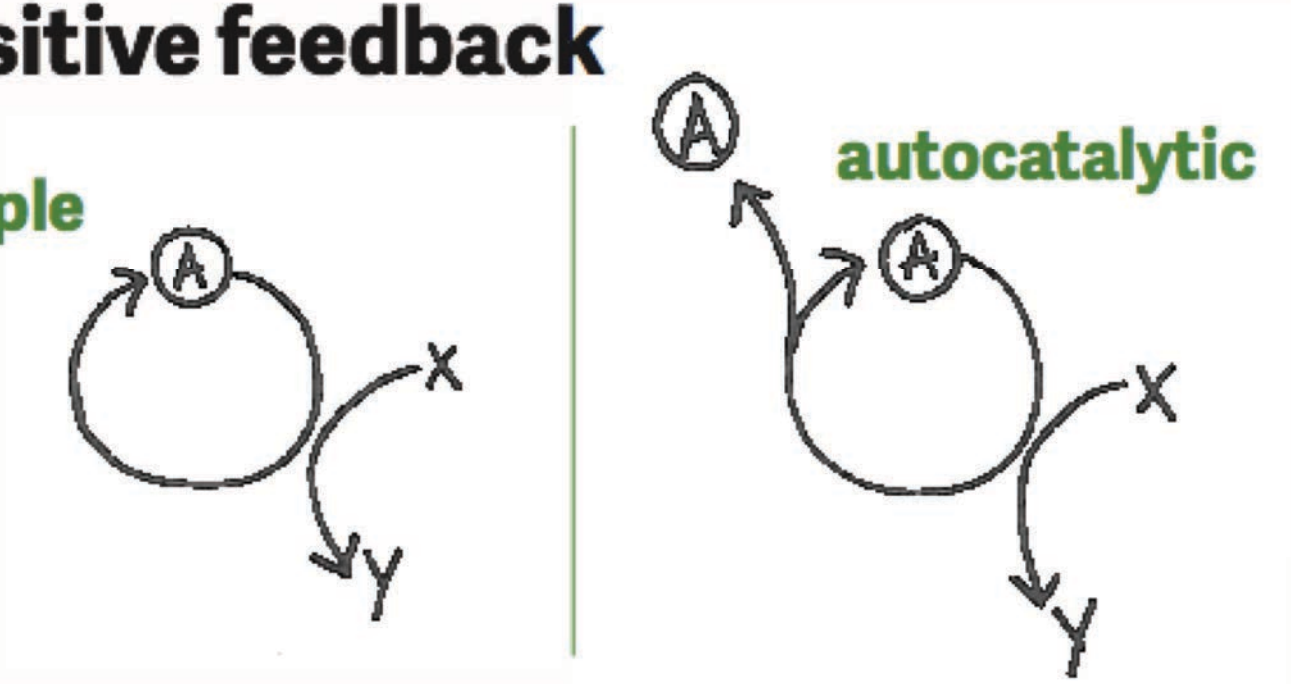
Earth Mesosphere: Allen et al. 1981

M-Star Exomars: Tian et al. 2014; Gao et al. 2015

Also solves an outstanding puzzle of Zahnle et al. 2008

Autocatalysis

A positive feedback



Autocatalysis important for all three central subsystems of life:

self-maintenence, self-replication, self-reproduction

“Twenty-first century astronomers are

uniquely positioned

to study the evolution of the Universe in order to relate causally the physical conditions during the Big Bang to the development of RNA and DNA.

—Riccardo Giacconi
Nobel Prize in Physics, 200

Photo Credit: Brandon Carroll

Chinese Space Missions

~2023

Chang'e-6 (Moon)

Lunar south pole
sample return

~2030

Mars sample return mission

Asteroid Exploration

Jovian system exploration

Life is the **ultimate poetry of the universe** written using the alphabet of molecules.

浣溪沙: 遊楚天台 (1)

極目沉思憶此台

中原問鼎壯之哉 (2)

黃河飲馬鐵花開 (3)

國運千年斯永盛

神州萬里楚惟才

章華風韻自天來 (4)

(1) 在武漢東湖區。
(2) 楚莊王八年 (前606年): 問鼎中原。
(3) 楚莊王十七年 (前597年): 楚擊敗中原超霸晉, 飲馬黃河。
(4) 章華台, 楚天台古名。