ESO/M. Kornmesser

Theoretical Underpinnings of The Search for Life on Exoplanets

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LUNAR & PLANETARY LABORATORY

Life In The Universe

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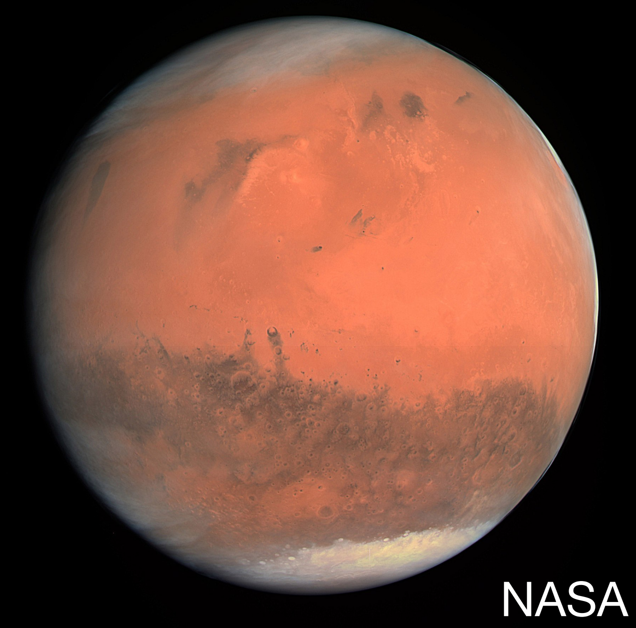
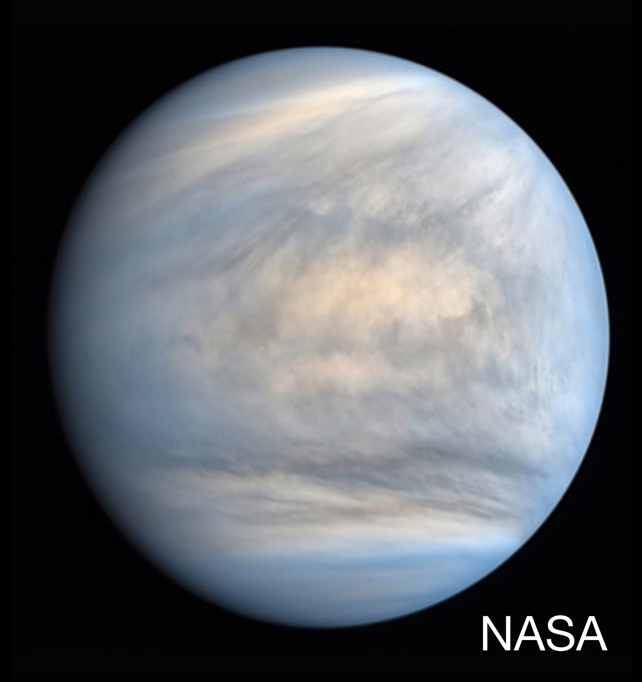
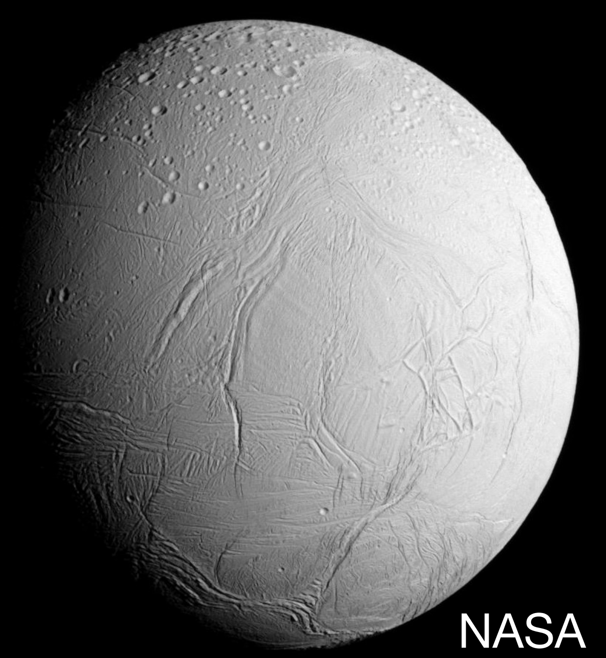
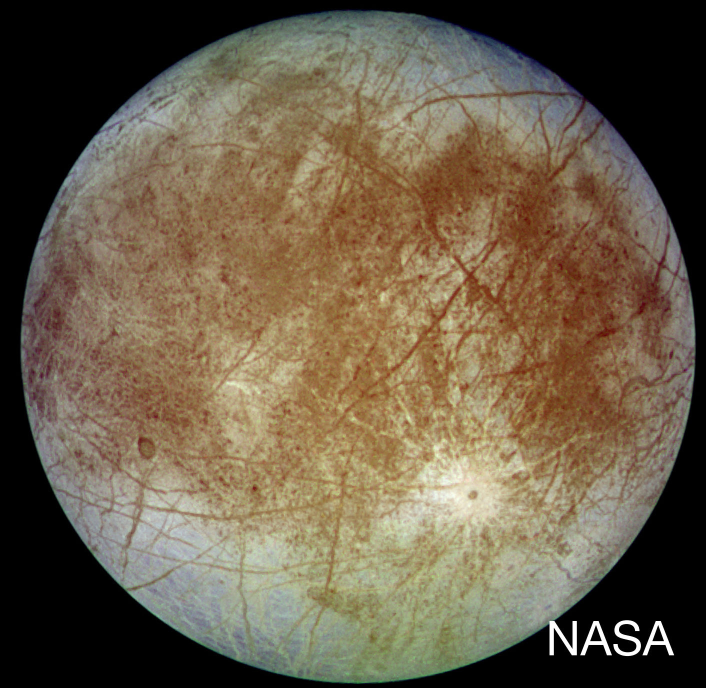
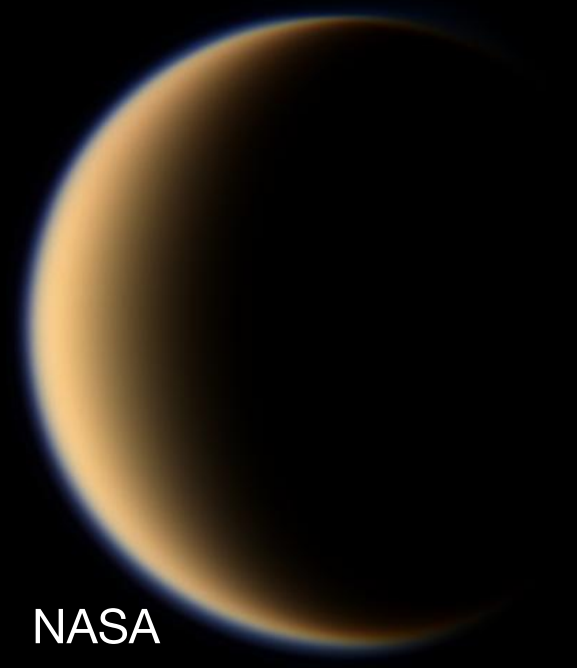
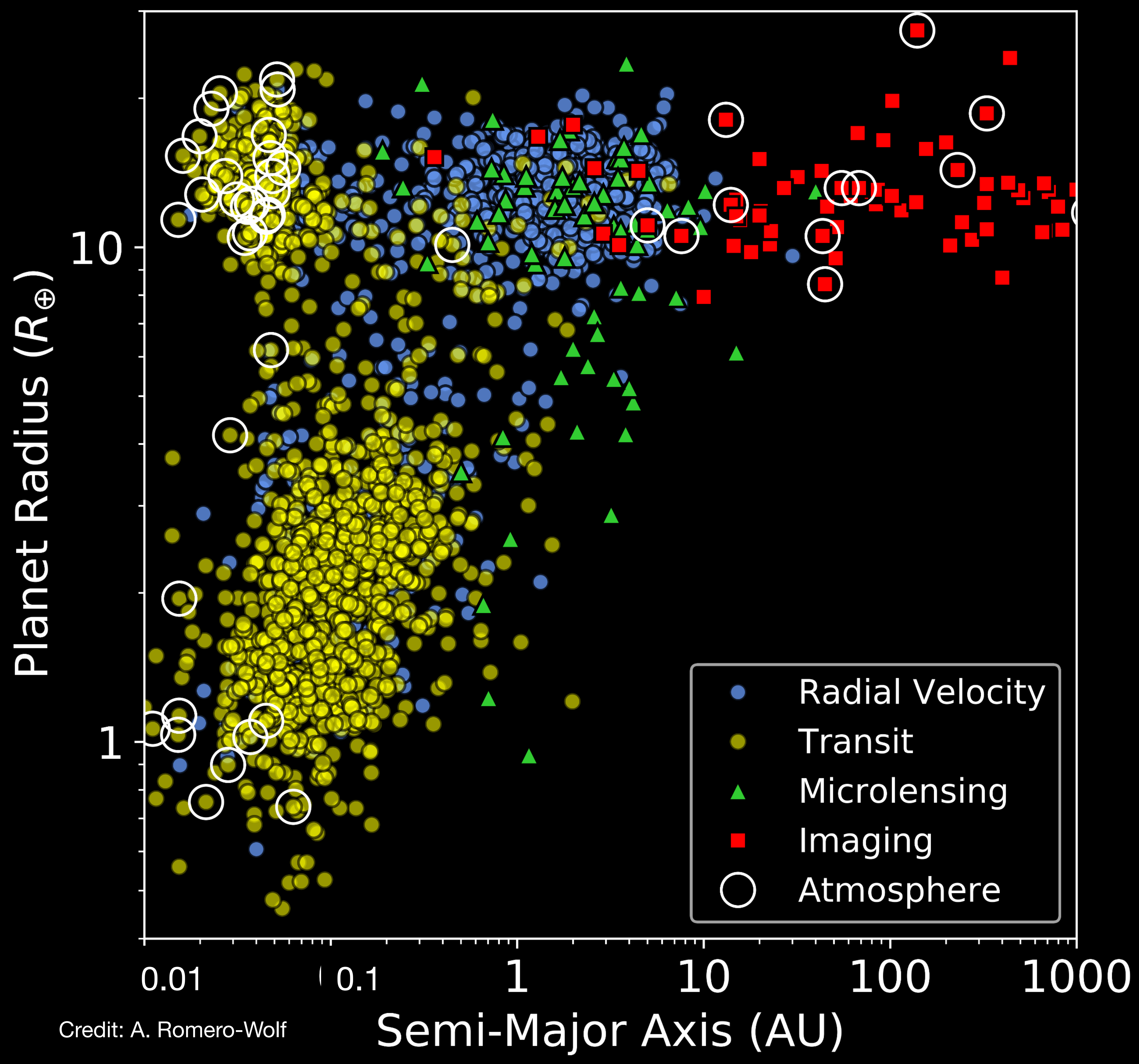




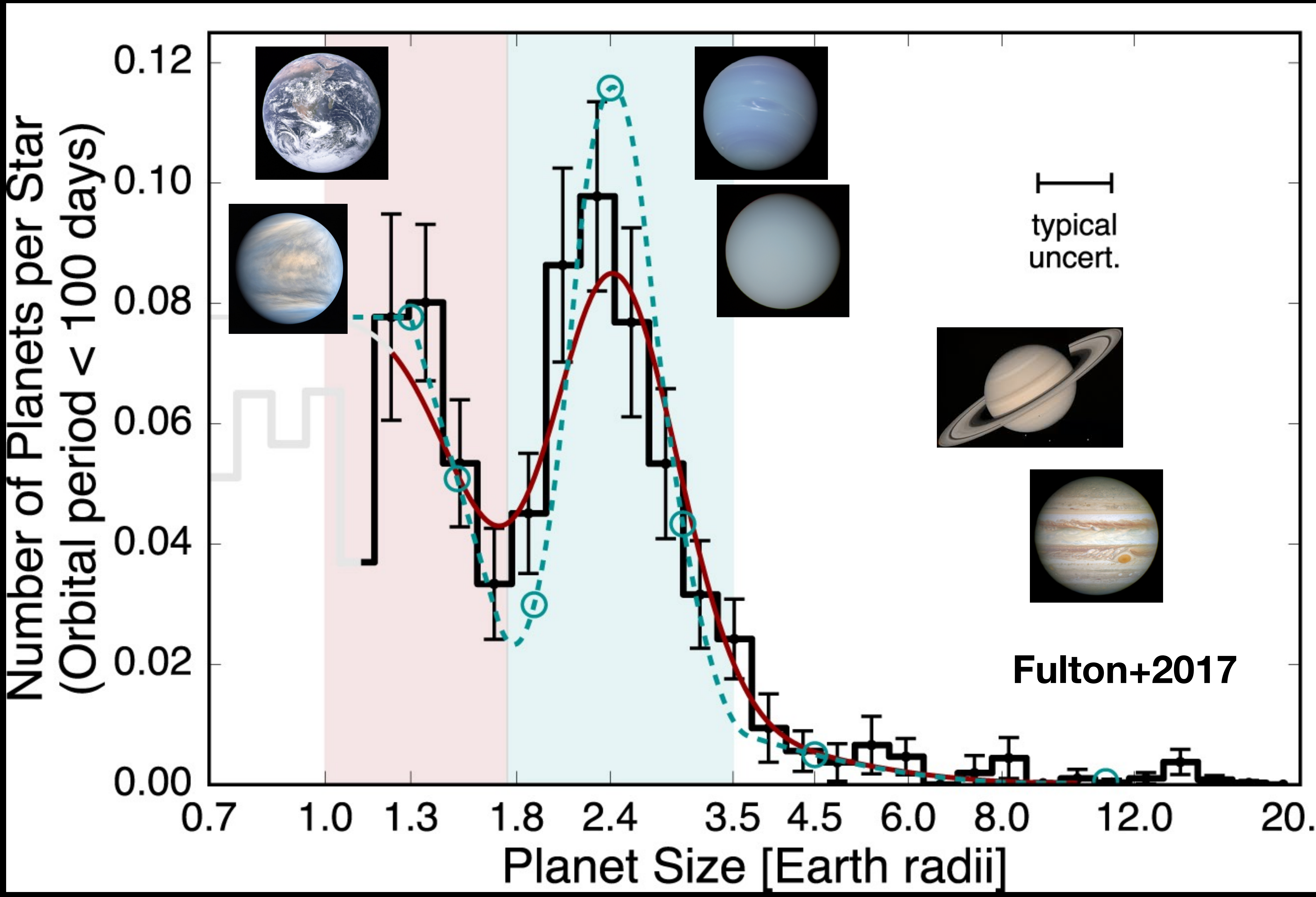


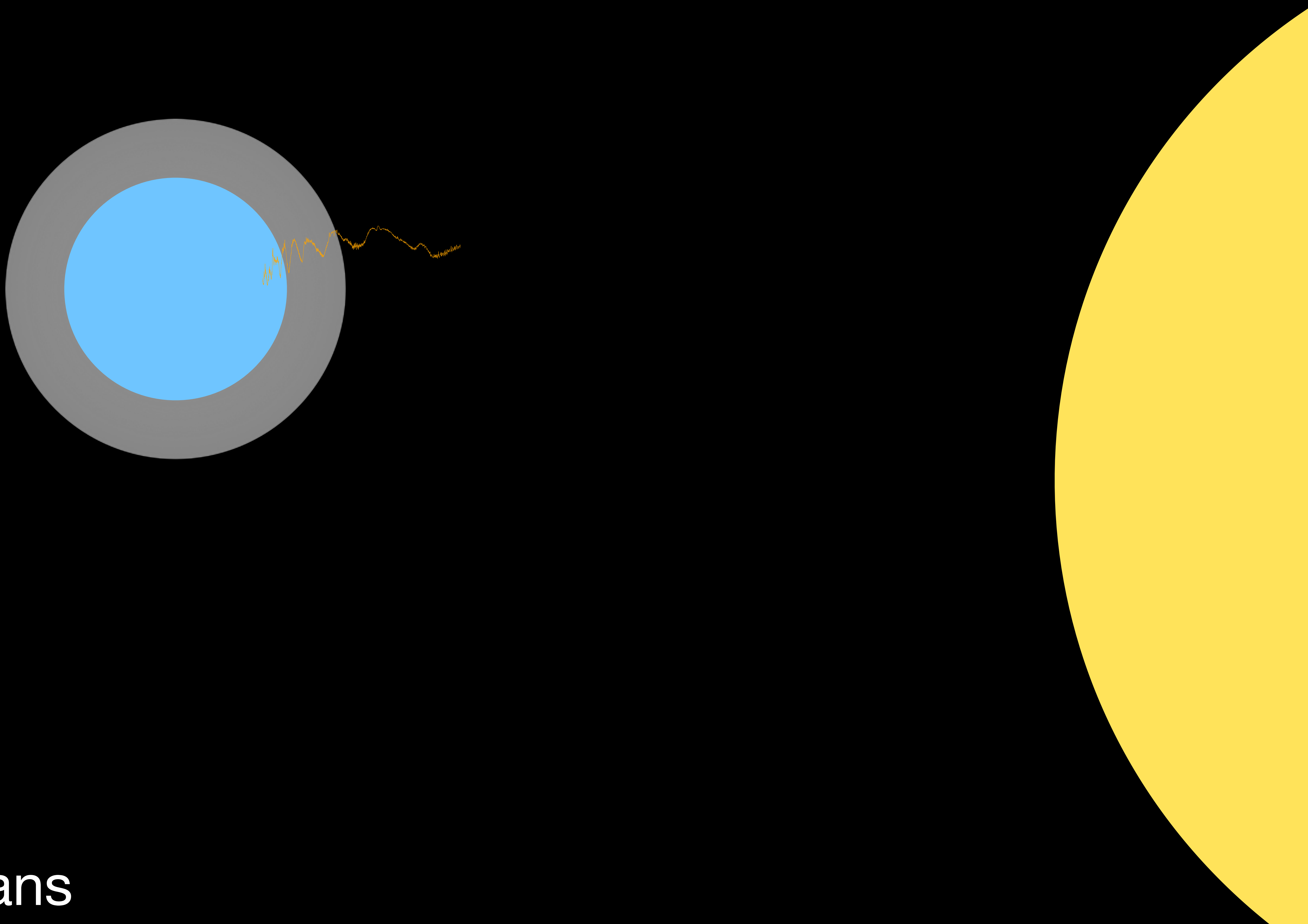






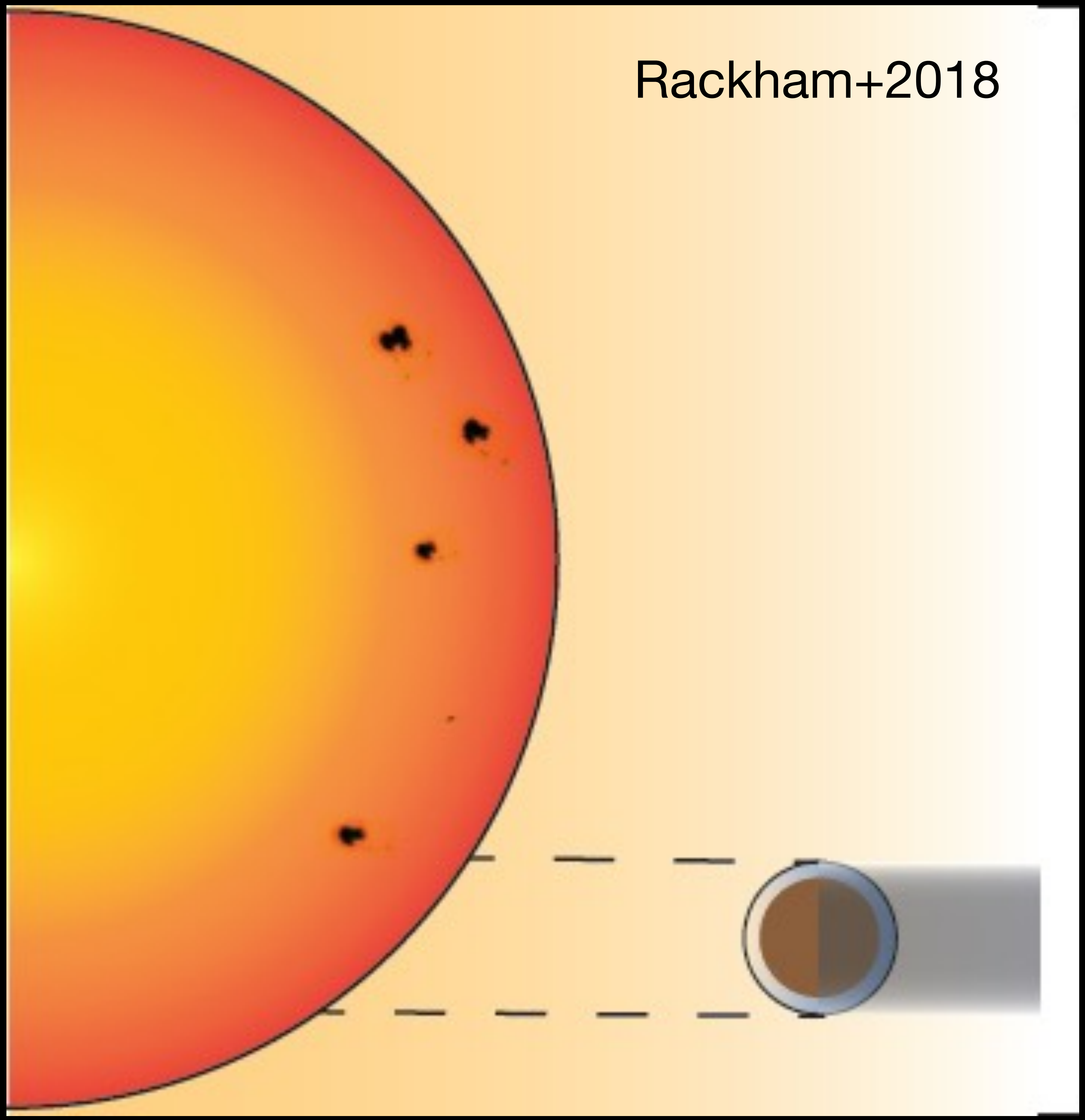
Credit: A. Romero-Wolf

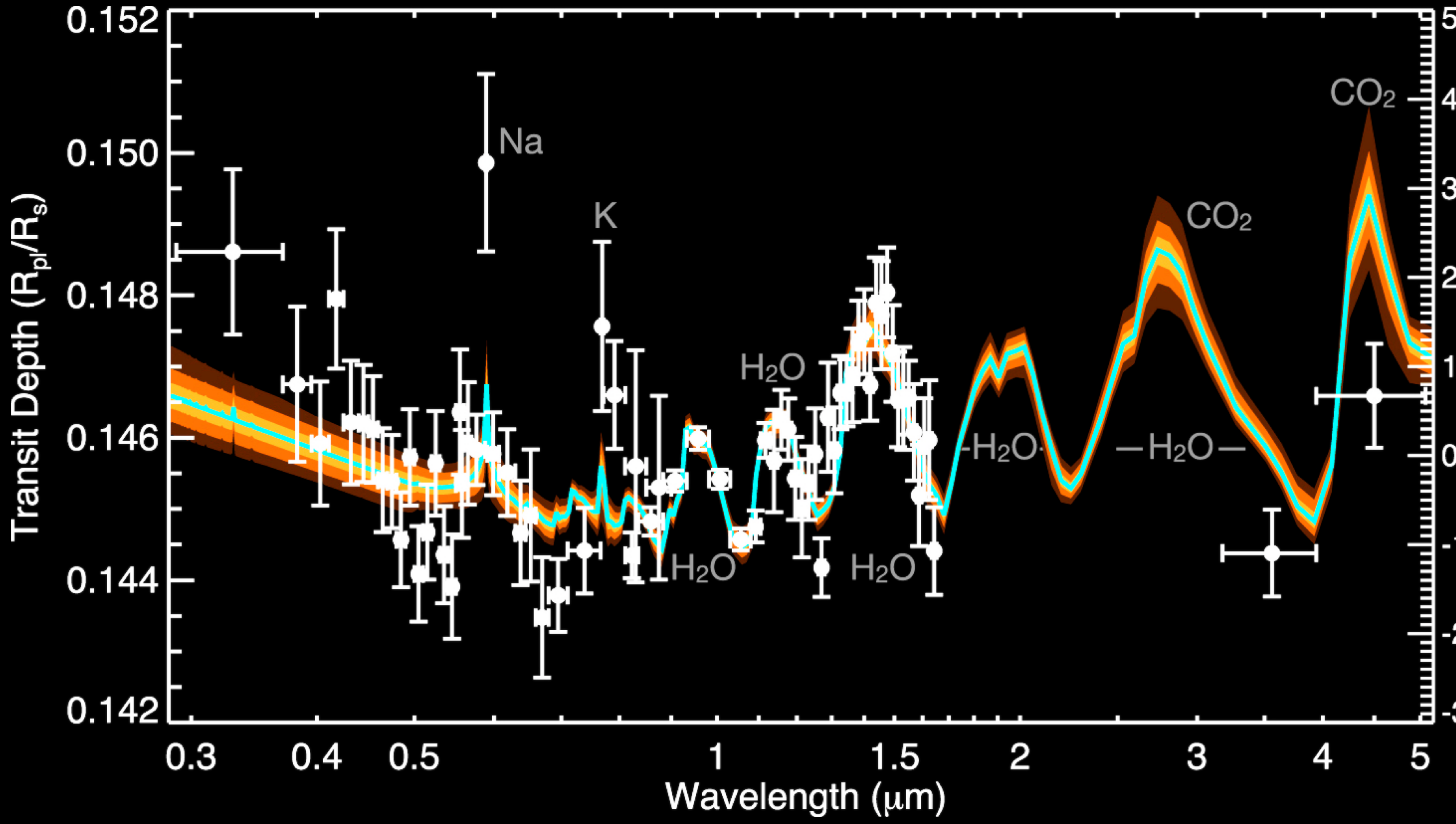




Slide & Animation: T. Mikal-Evans

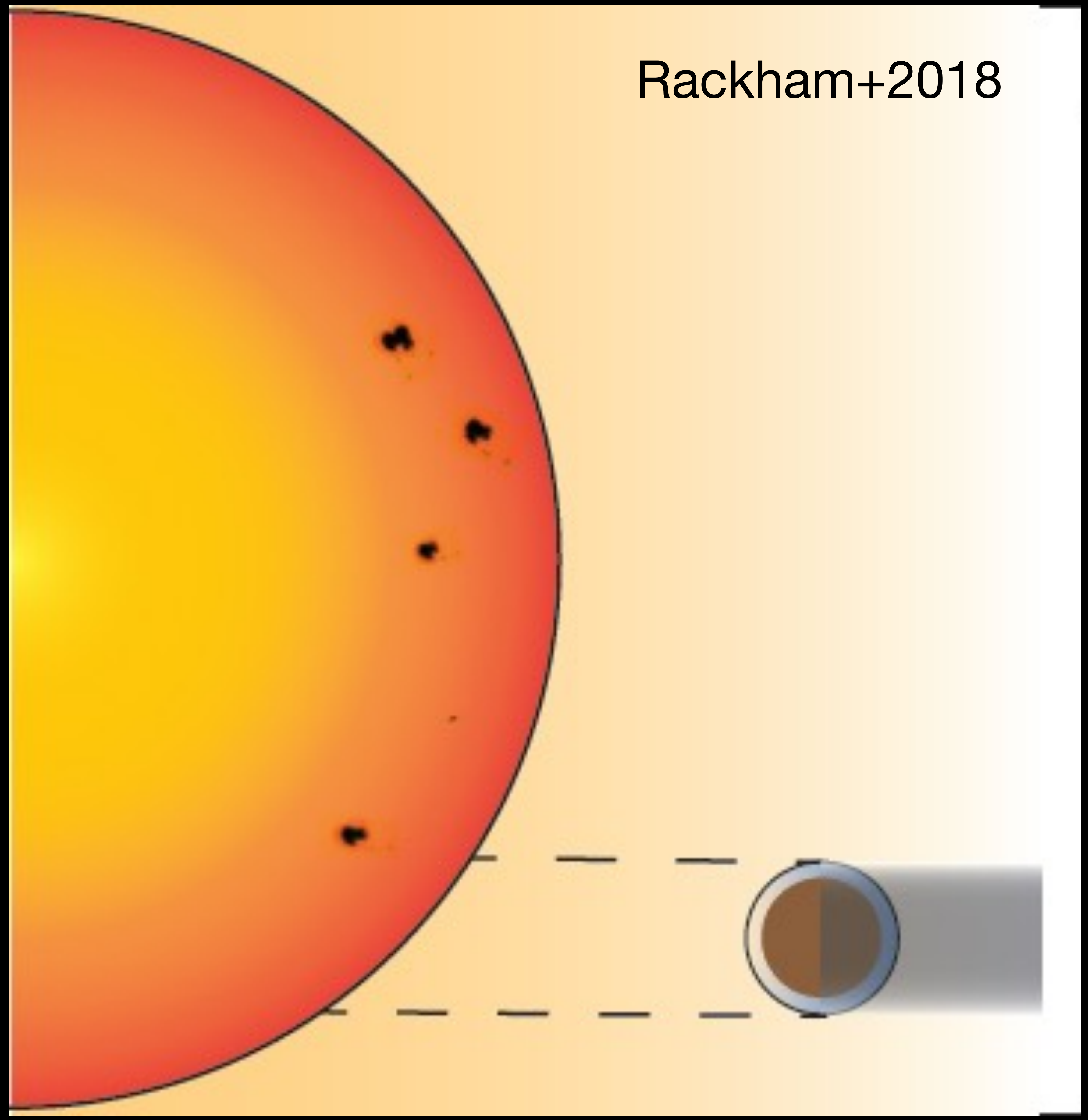
Exoplanet Spectroscopy Today

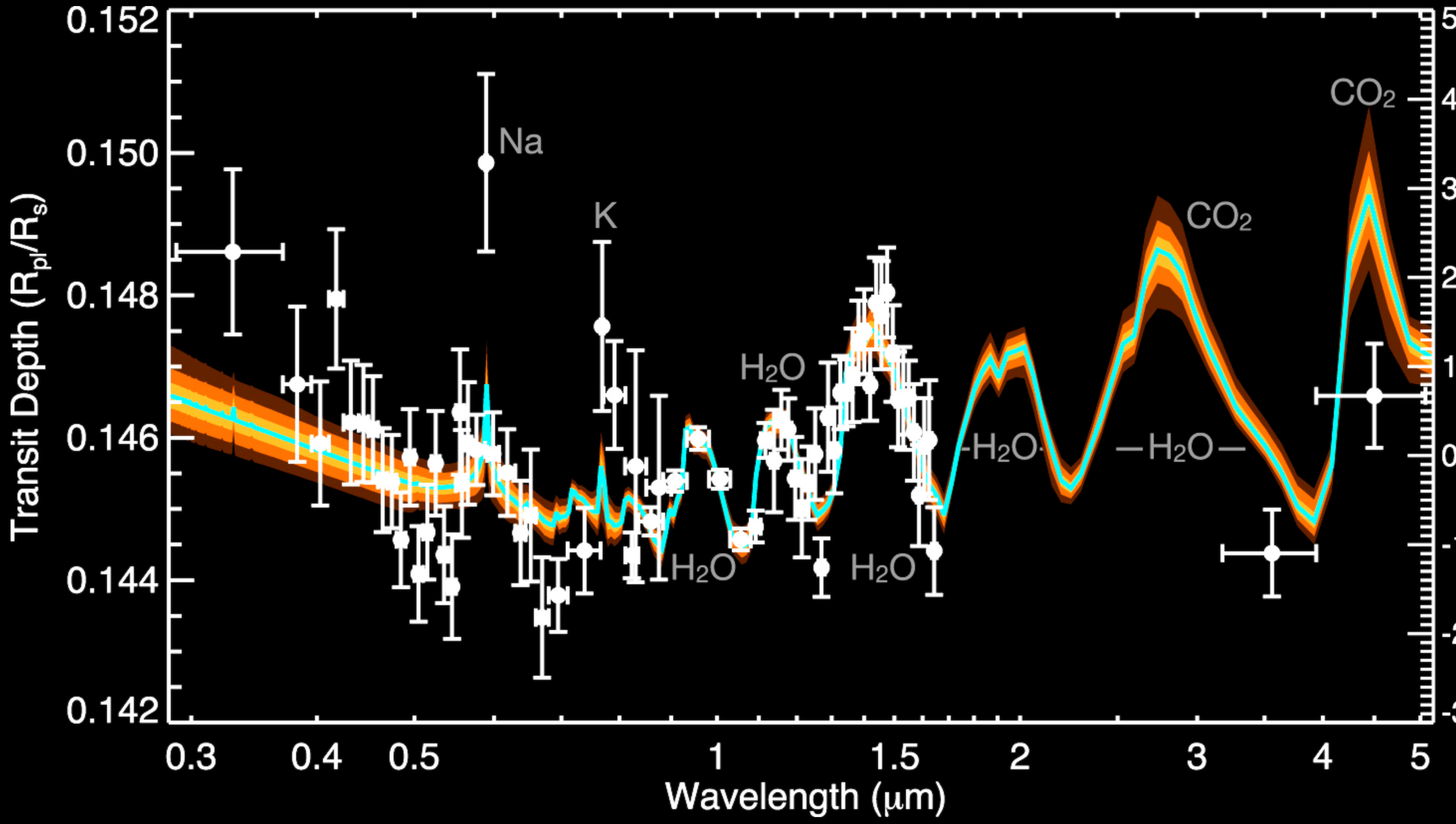




Wakeford et al. 2018

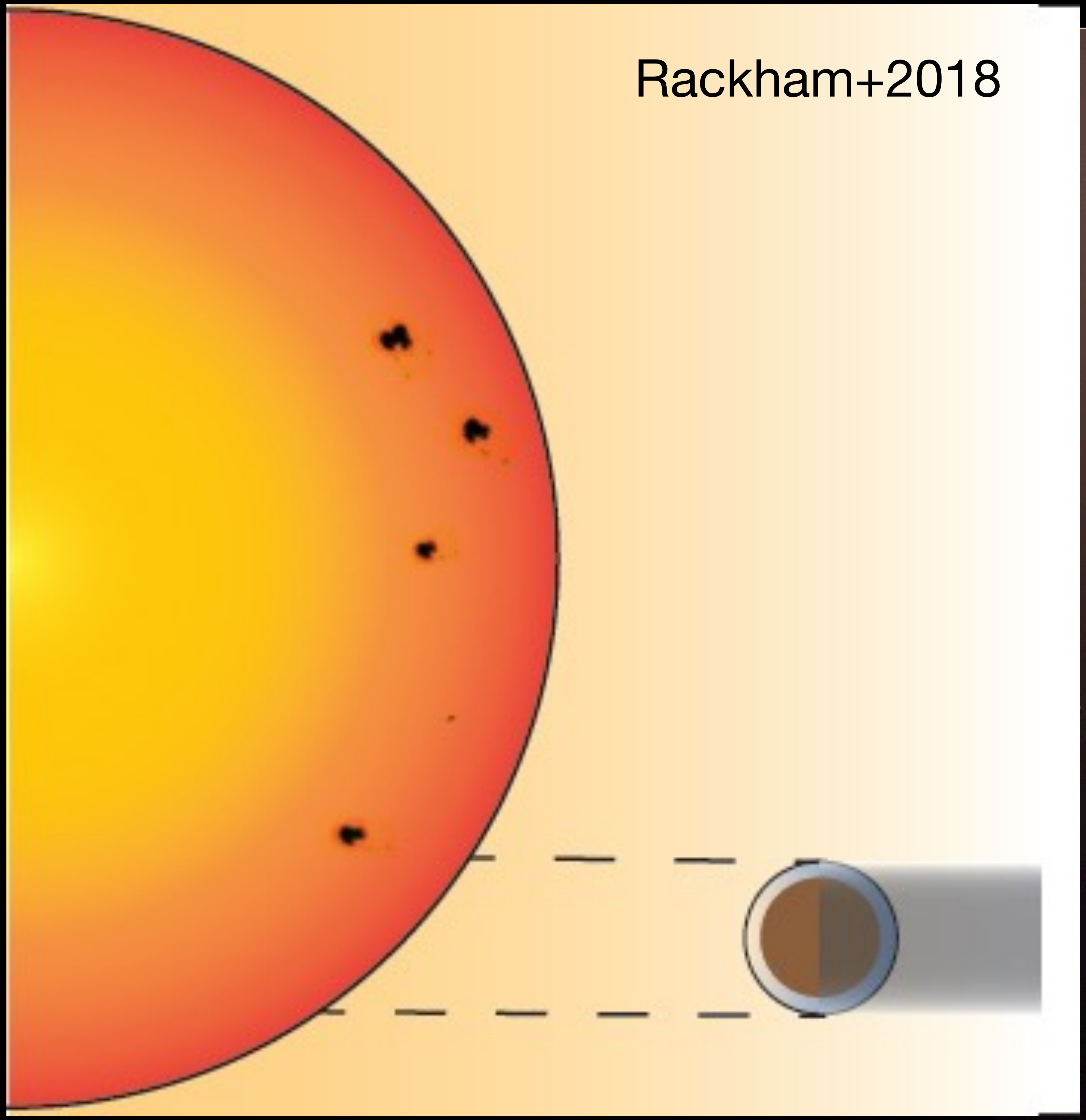
Exoplanet Spectroscopy ~~Today~~ *Yesterday*

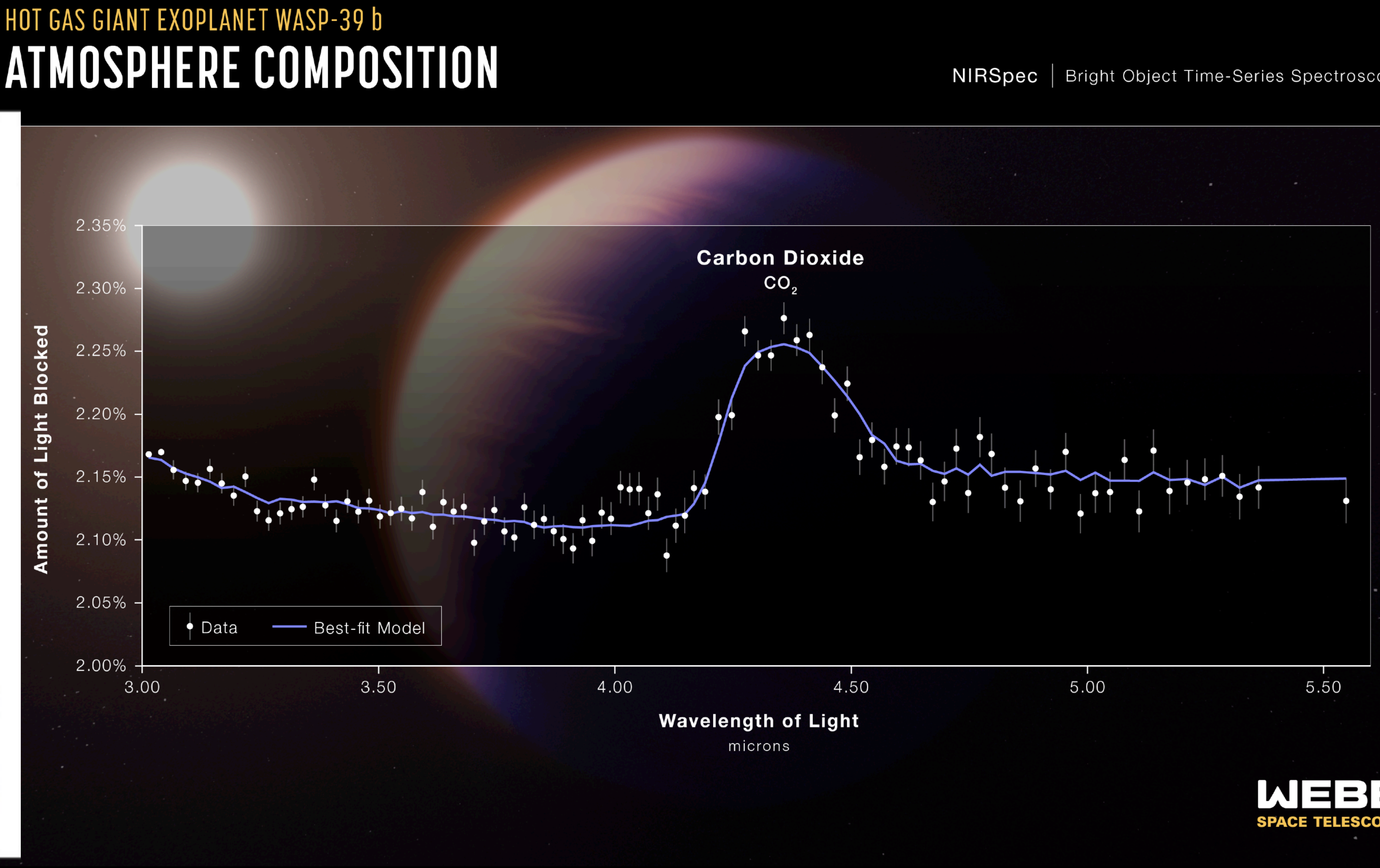




Wakeford et al. 2018

Exoplanet Spectroscopy Today



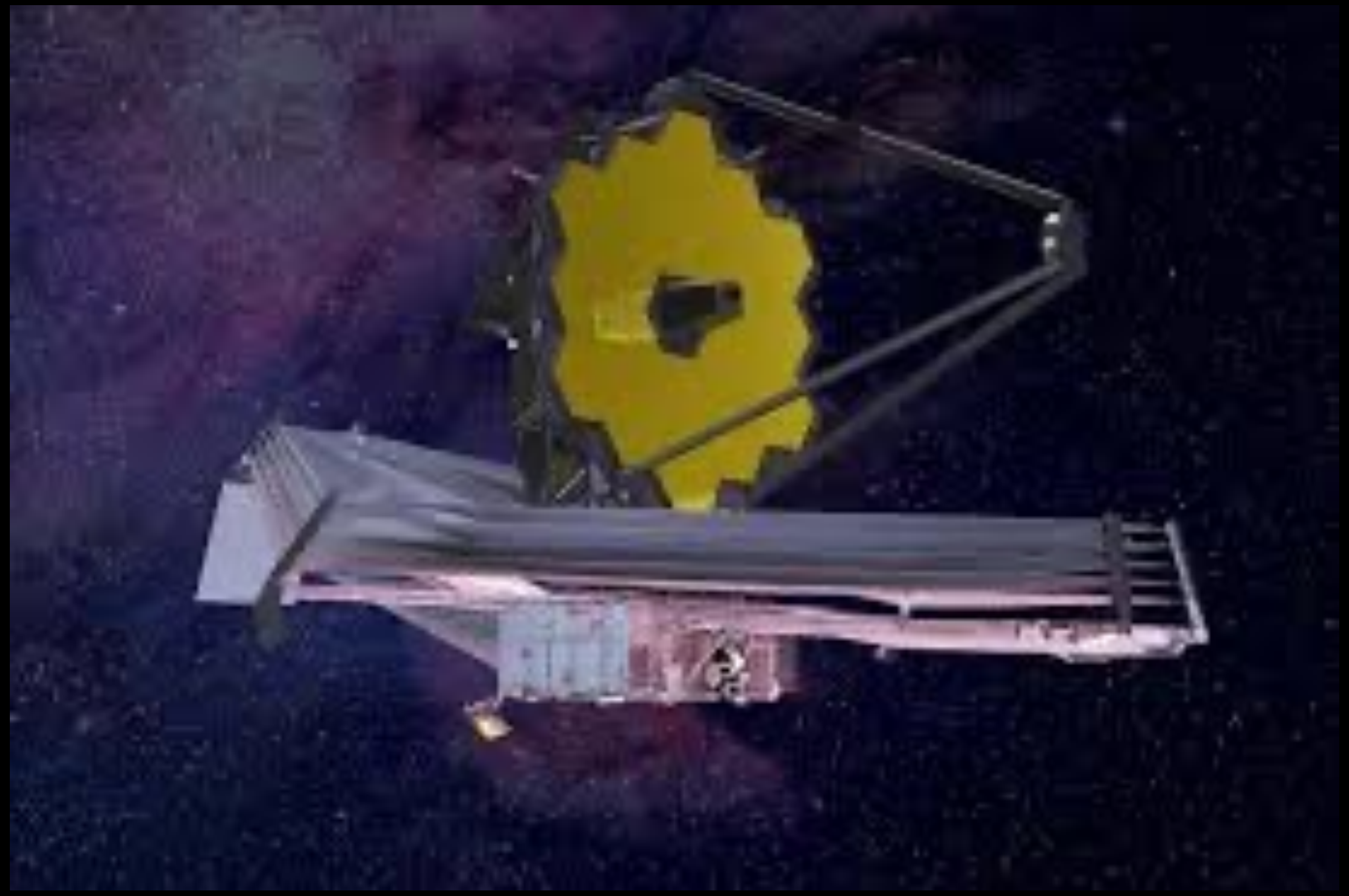


JWST Transiting Exoplanet Community Early Release Science Team 2022 *Nature*

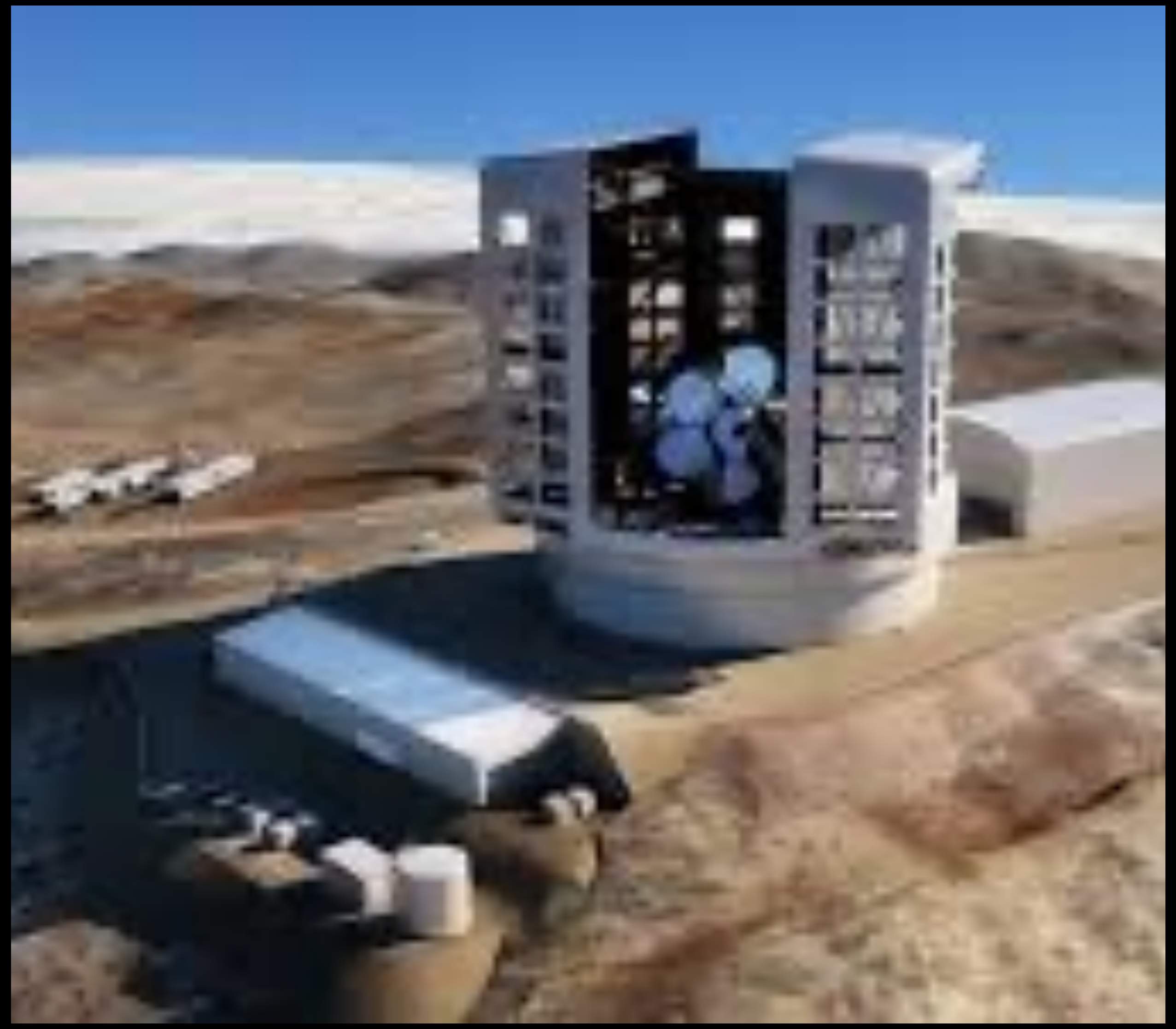
A Future Large Infrared/Optical/Ultraviolet Telescope Optimized for Observing Habitable Exoplanets and General Astrophysics (Highest Priority for Space Frontier Missions)

Inspired by the vision of searching for signatures of life on planets outside of our solar system… the priority recommendation in the frontier category for space is a large (~6 m diameter) IR/O/UV telescope with high-contrast (10^{-10}) imaging and spectroscopy.

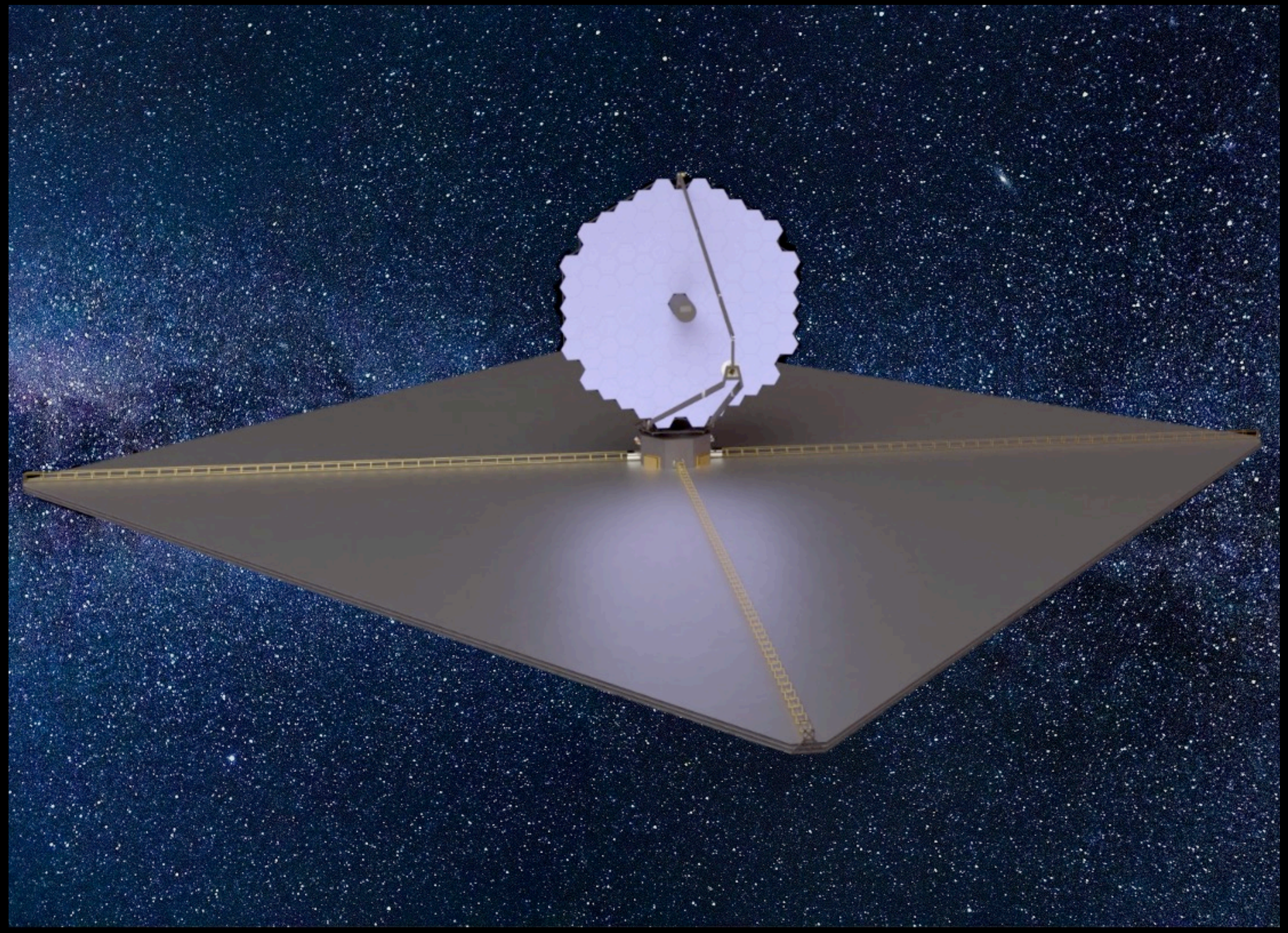
National Academy of Sciences (USA) 2021, *Pathways to Discovery in Astronomy and Astrophysics for the 2020s,* https://doi.org/10.17226/26141



JWST (NASA)

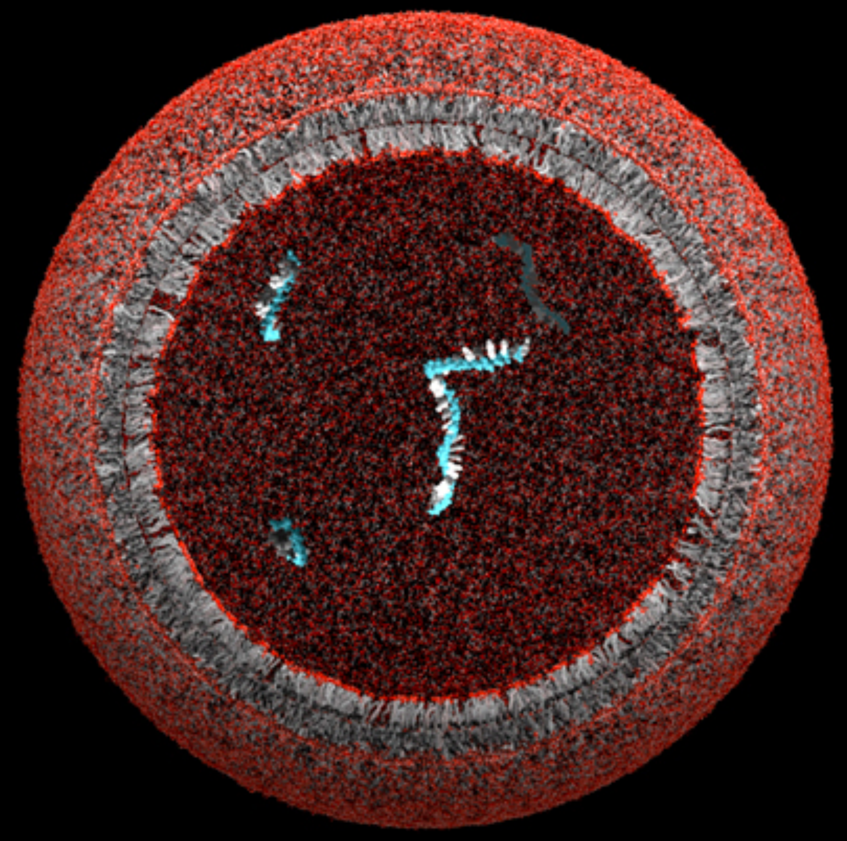


GMT (GMTO)



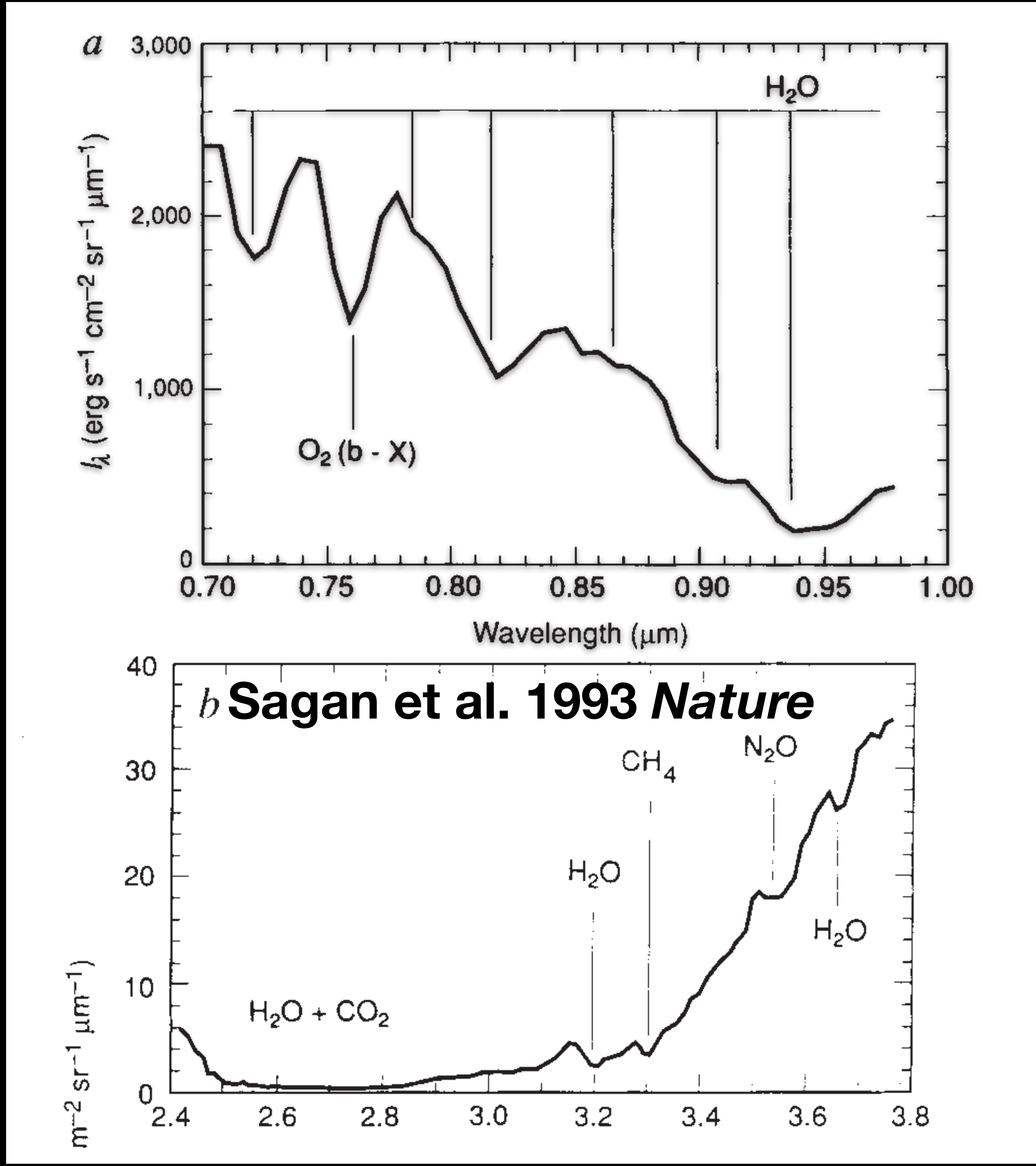
[L]UVOIR (NASA)

Life Can Alter Planetary Atmospheres



Exploringorigins.org

Is There Life on Earth?



Is There Life on Earth?

Sagan et al. 1993

Planet is rocky, temperate
Spectrum indicates H_2O, O_2, CH_4

Large flux of CH_4, O_2 required to explain observations

Known abiotic mechanisms do not explain inferred CH_4 flux, observed O_2

H_2O suggests habitability

Earth probably has life, but it’s pretty weird (organics in O_2?!)

Observation → **Interpretation** → **Conclusion**

"The planet is covered with large amounts of water…There is so much O_2 in the atmosphere as to cast doubt on the proposition that UV photodissociation of H_2O provides an adequate source…CH_4 is detected at ~1 ppm…only biological processes are likely to generate so large a disparity…but how plausible…[life generating]…a massive (and poisonous) [O_2] atmosphere…is an open question."

Sagan et al. 1993 *Nature*

Is There Life on Earth?

Sagan et al. 1993

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Observation → **Interpretation** → **Conclusion**

Recipe for Remote Life Detection

Measure atmospheric spectrum, bulk planetary/ stellar properties

Observation

Extensive Theoretical Infrastructure Required

Quantify production/loss fluxes of potentially biogenic gases implied by observations

Determine if known abiotic mechanisms can explain inferred gas fluxes

Use theories of (in)habitability to assess plausibility of biological explanation

Interpretation

Probabilistic constraint on presence of life

Conclusion

Three Illustrative Vignettes

Measure atmospheric spectrum, bulk planetary/ stellar properties

Observation

Theory, experiments, observations needed to build interpretive infrastructure

UV Irradiation on M-dwarf ... & Implications for A... s

Water Va... position of Early Atmospheres

Assessing Novel Biosignature Gases

UV Photochemistry

Interpretation

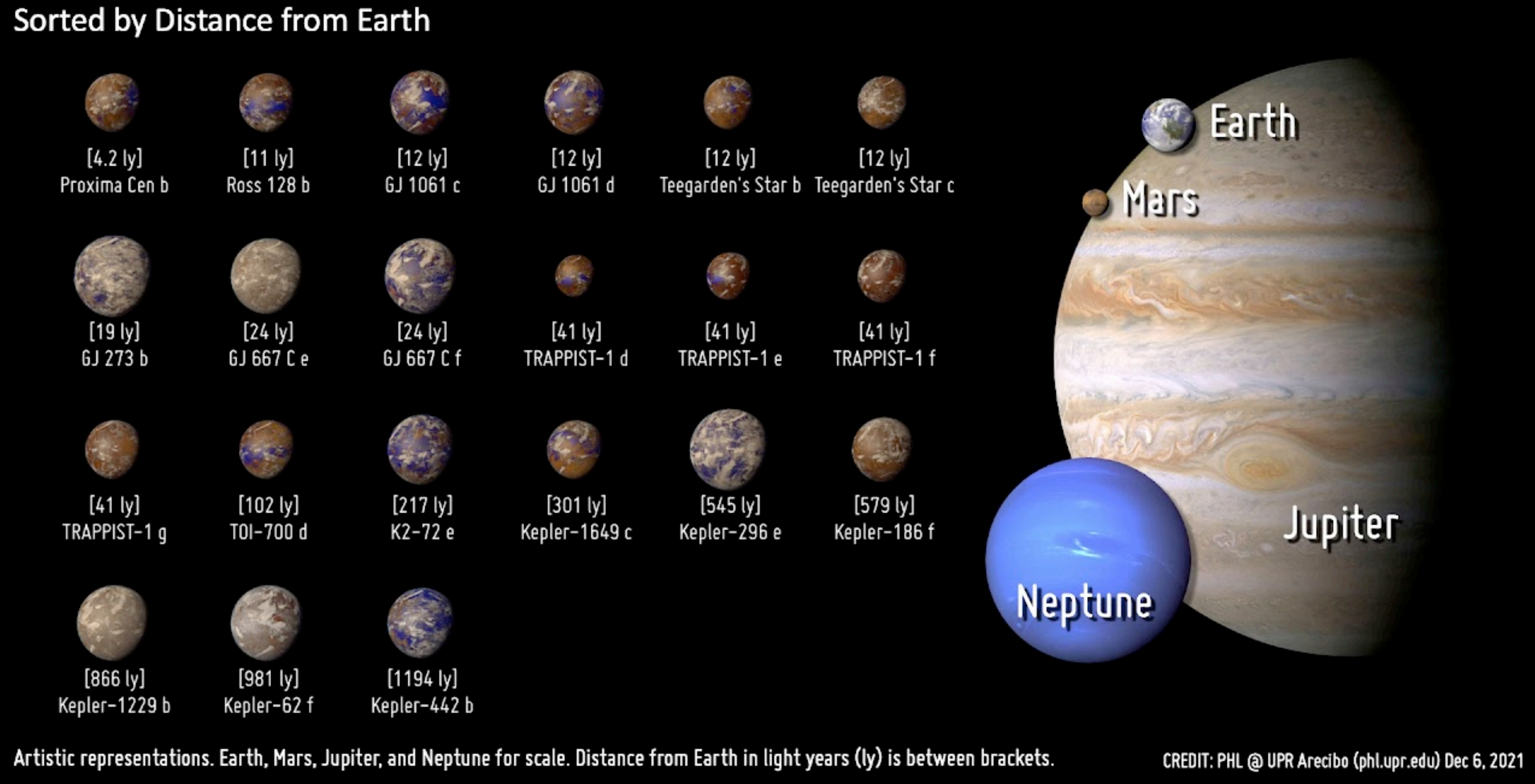
Probabilistic constraint on presence of life

Conclusion

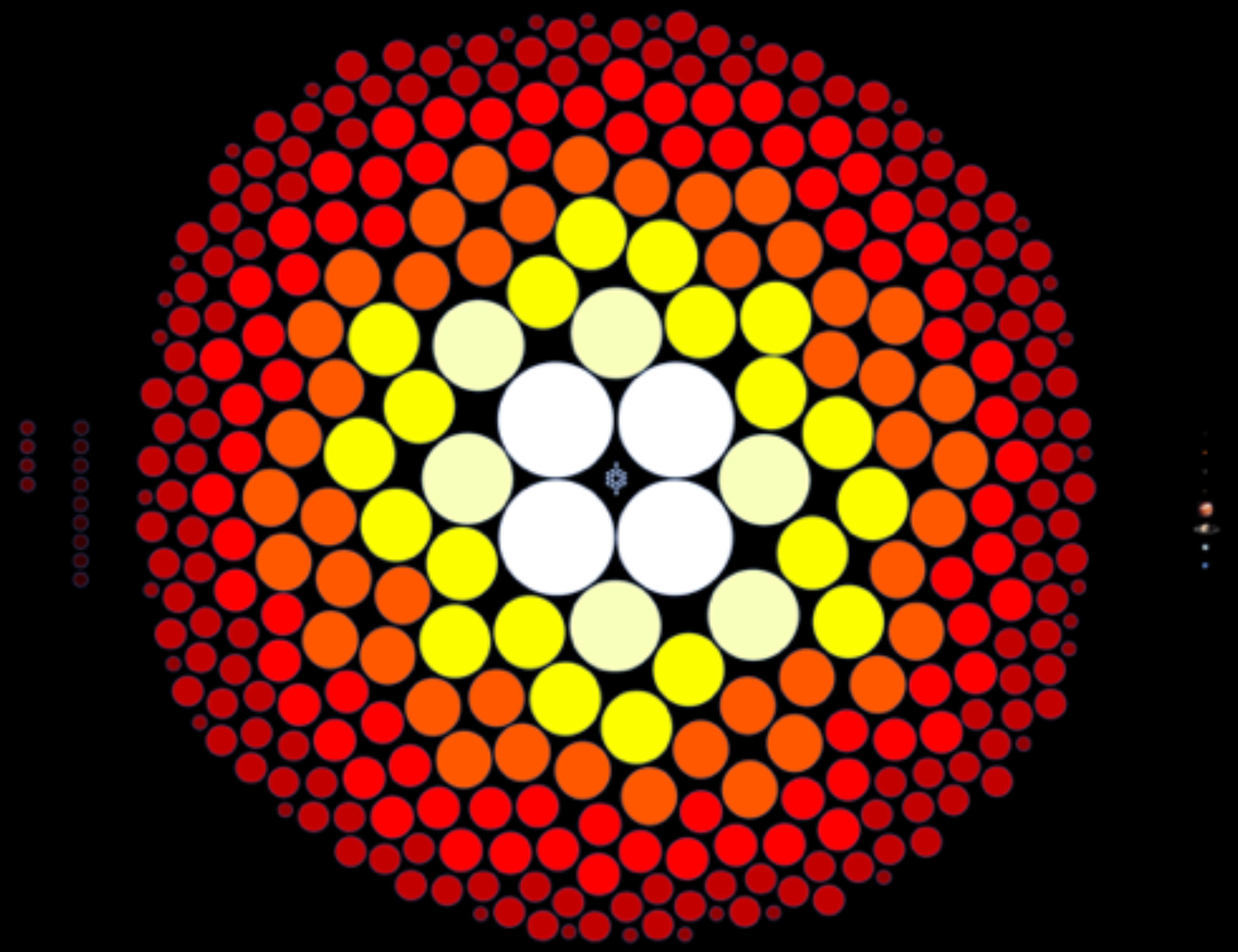
Photochemistry Influences Planetary Habitability

Rocky, Likely Temperate Exoplanets

Modified from PHL



M-Dwarfs: Only Practical Targets



RECONS Project

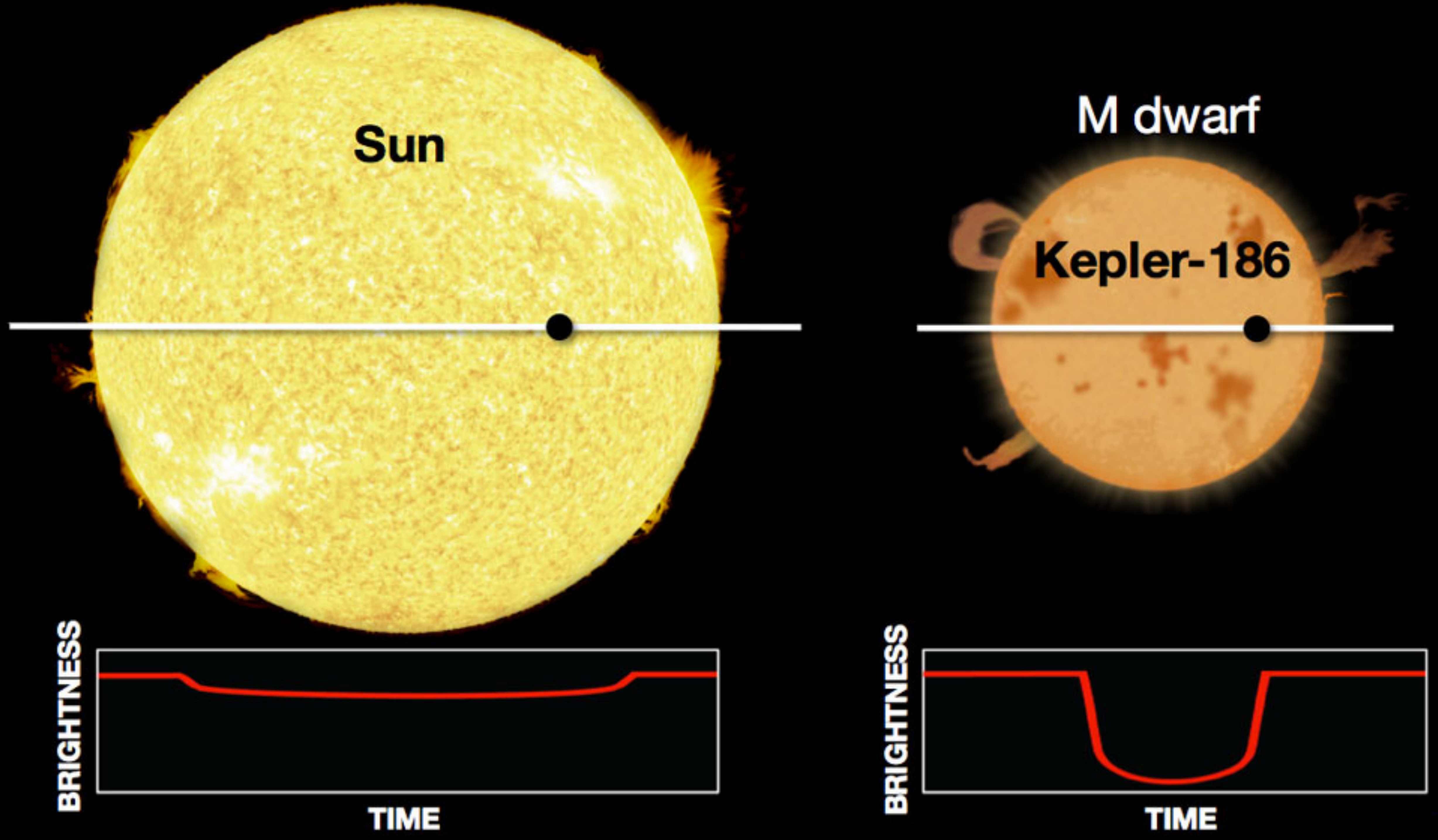
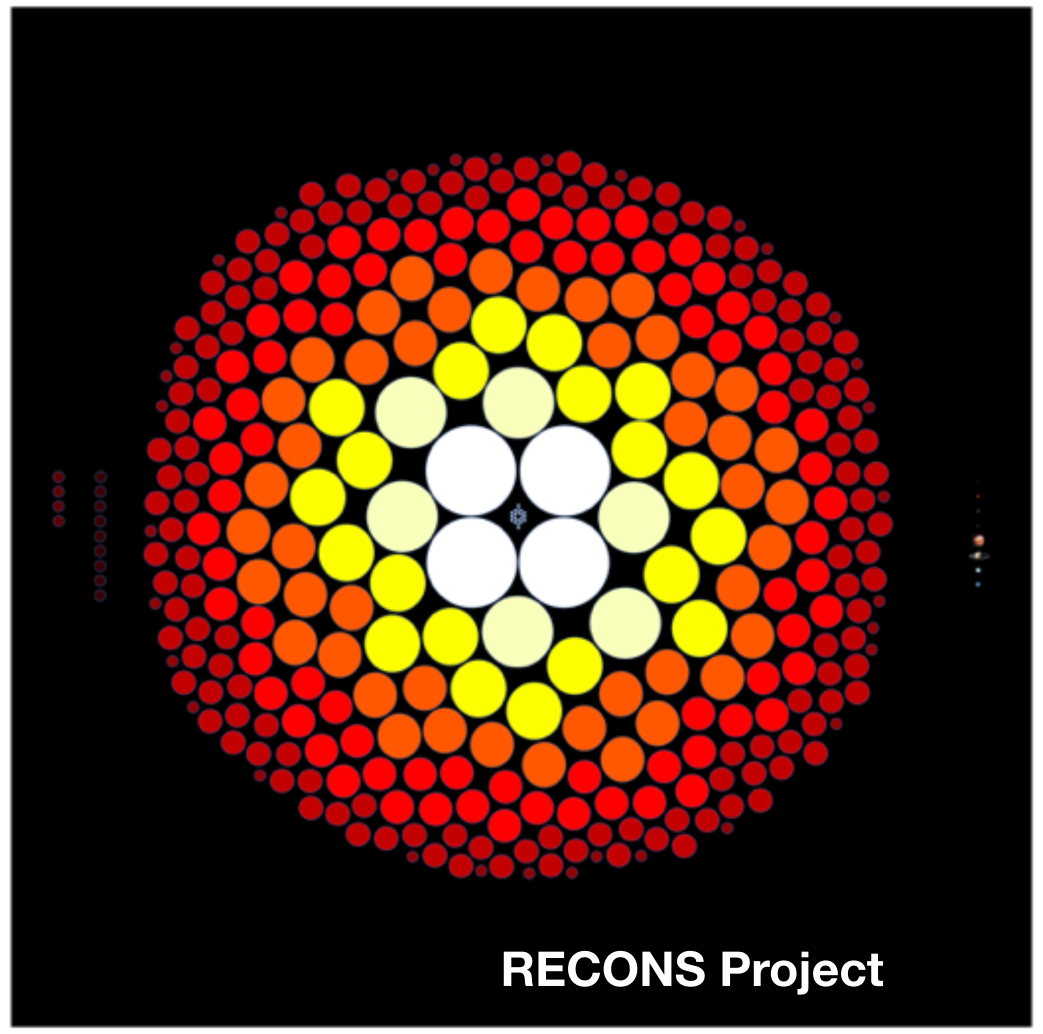
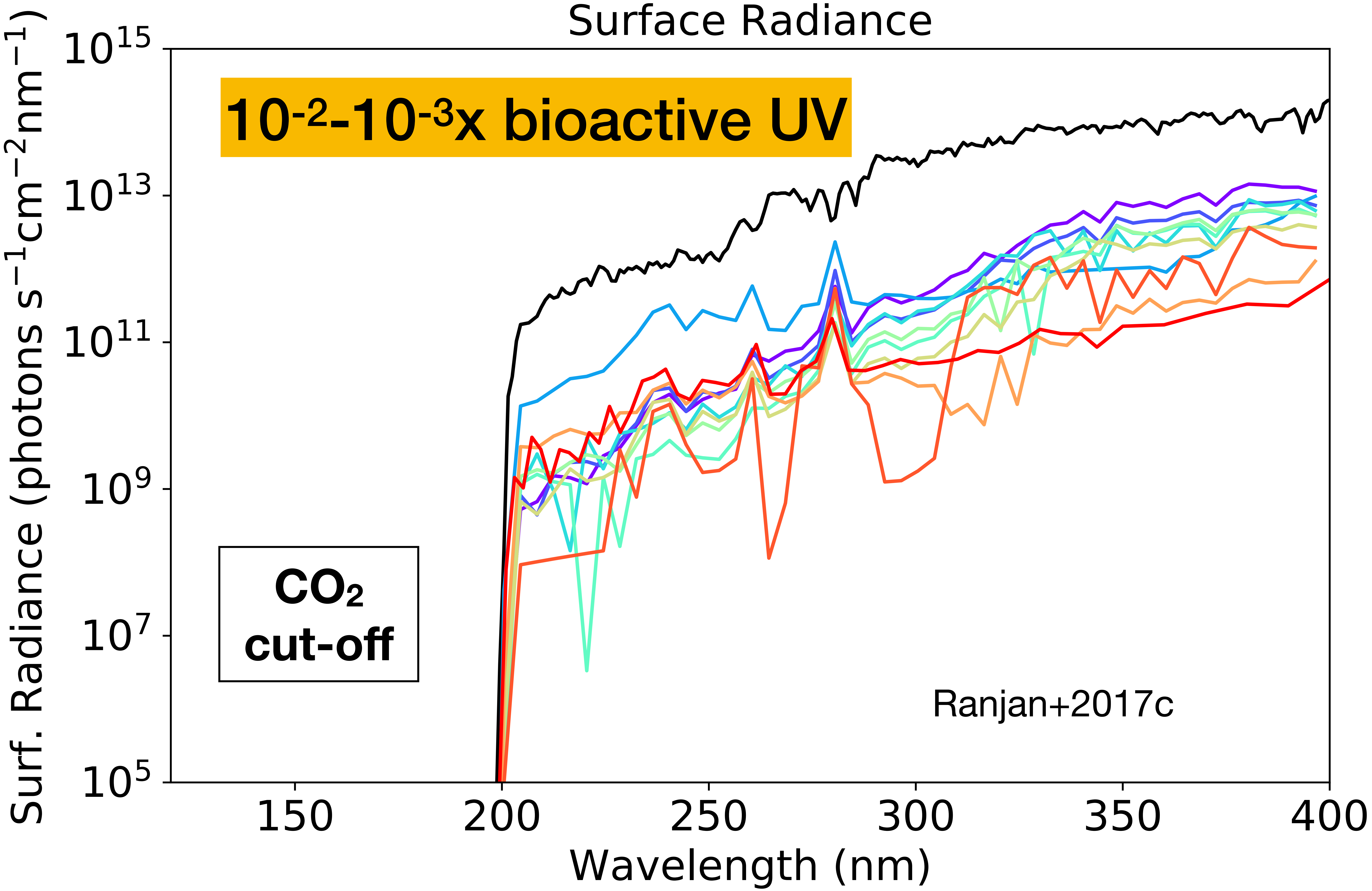


Image credit: W. Stenzel

M-Dwarf Planet Surfaces: UV-Poor





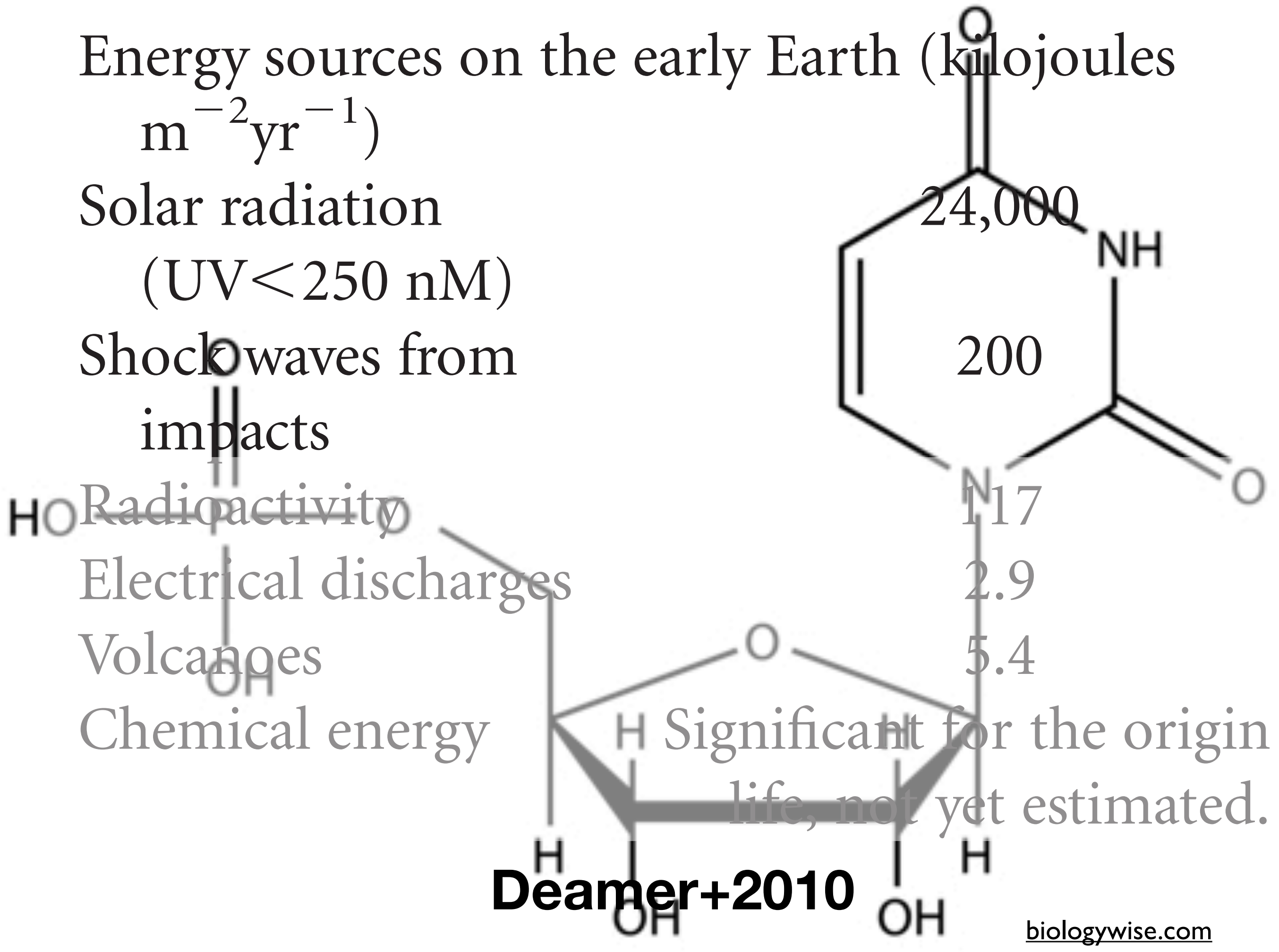
M-Dwarf UV Is Not Too High...

O'Malley-James & Kaltenegger 2019

...But May Be Too Low

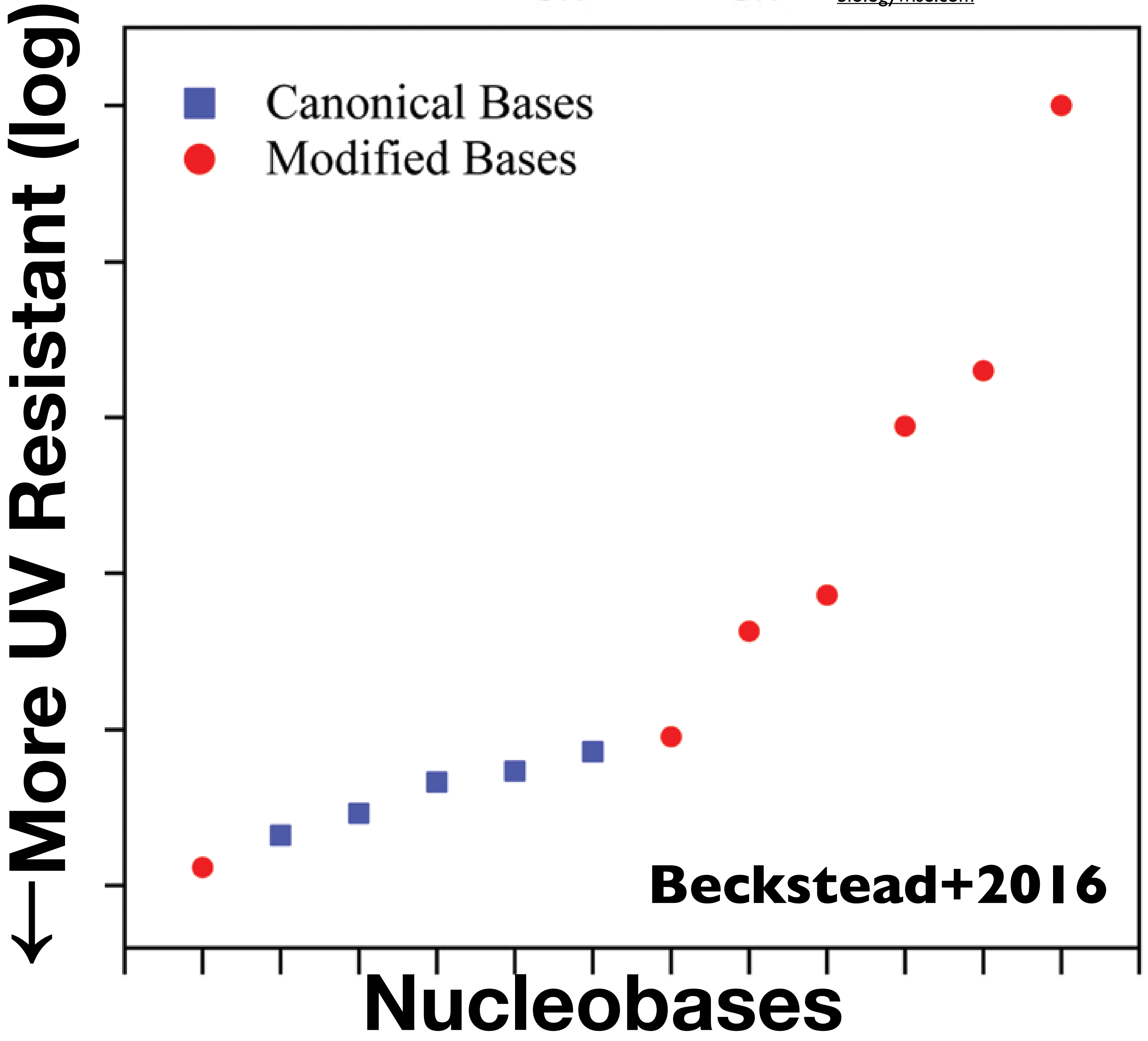
Prebiotic Relevance of UV

- **Experimental**: Shown to drive diverse syntheses (reviewed e.g., Green et al. 2021)
- **Theoretical**: Most abundant energy source; directly affect electronic states of molecules (Deamer et al. 2010; Pascal 2012)
- **Historical**: Biogenic nucleobases show evidence of high-UV selection pressure (Beckstead et al. 2016)



Energy sources on the early Earth (kilojoules $m^{-2}yr^{-1}$)	
Solar radiation (UV<250 nM)	24,000
Shock waves from impacts	200
Radioactivity	117
Electrical discharges	2.9
Volcanoes	5.4
Chemical energy	Significant for the origin of life, not yet estimated.

Deamer+2010

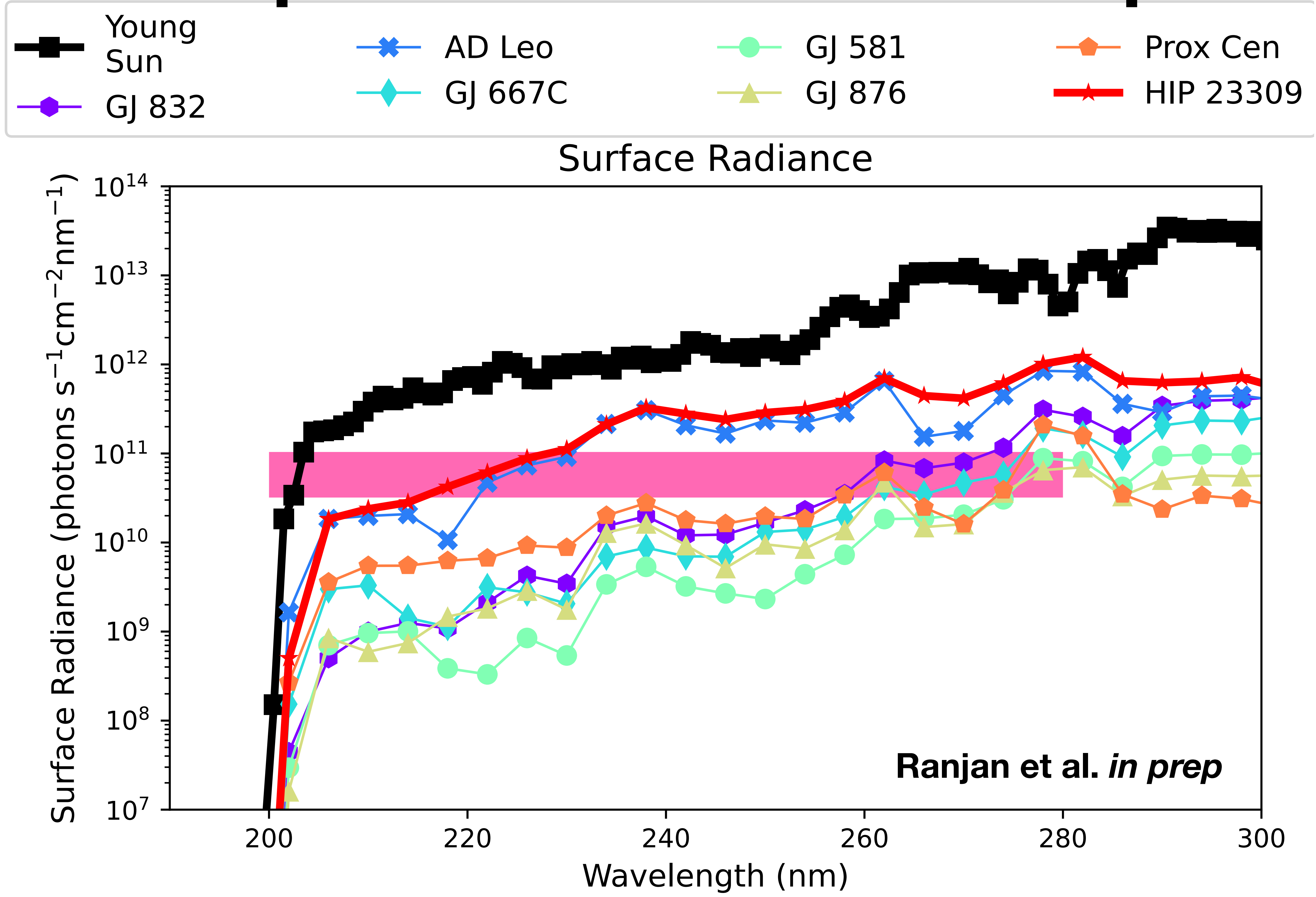


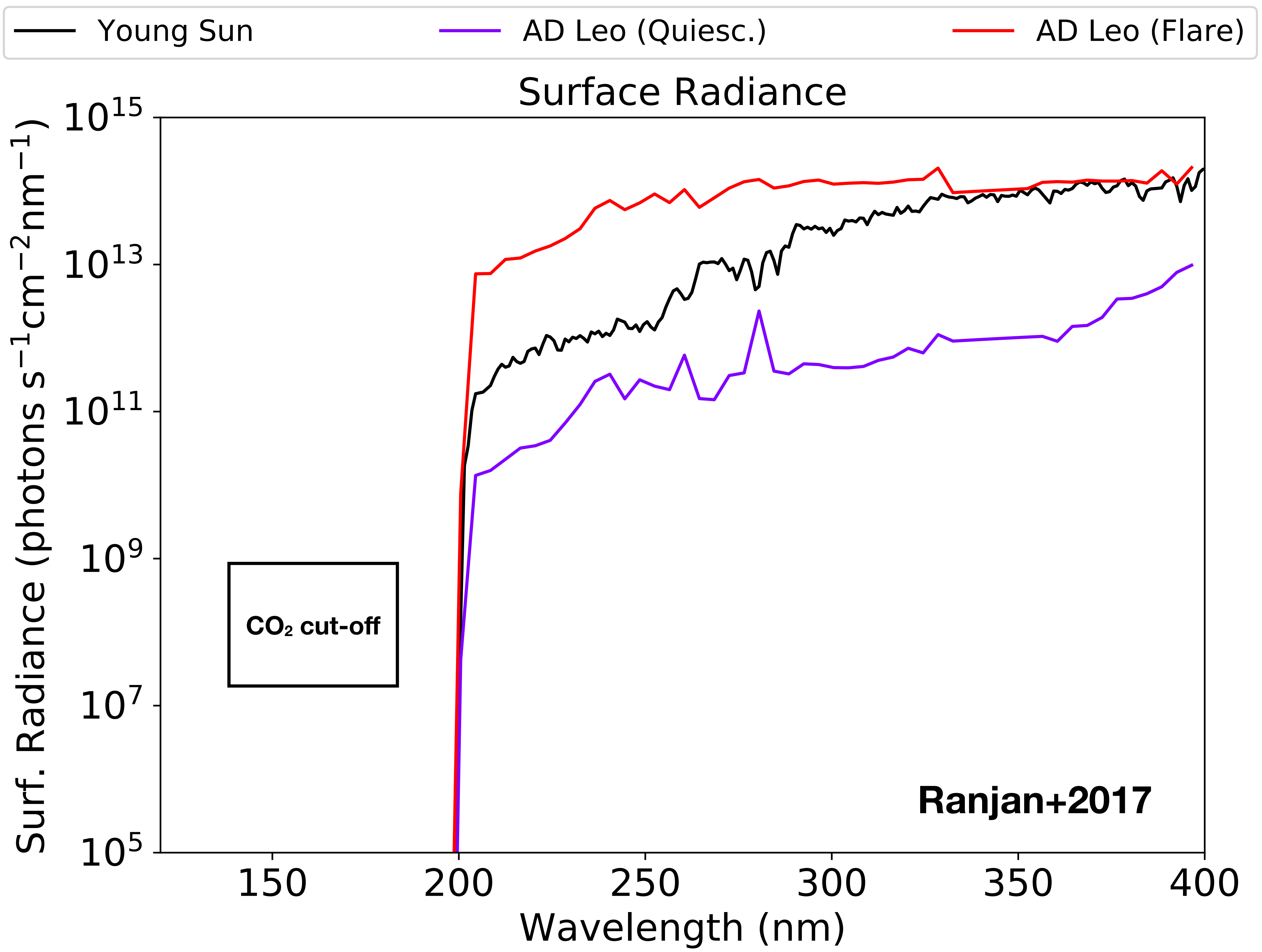
M-dwarf Planets: Is UV Required To Start Life?

- UV-driven ribonucleotide synthesis fails under steady-state M-dwarf UV (all M's, Rimmer et al. 2018; some M's, Ranjan et al. *in prep*)

- Flares (Ranjan et al. 2017c, Guenther et al. 2020)?

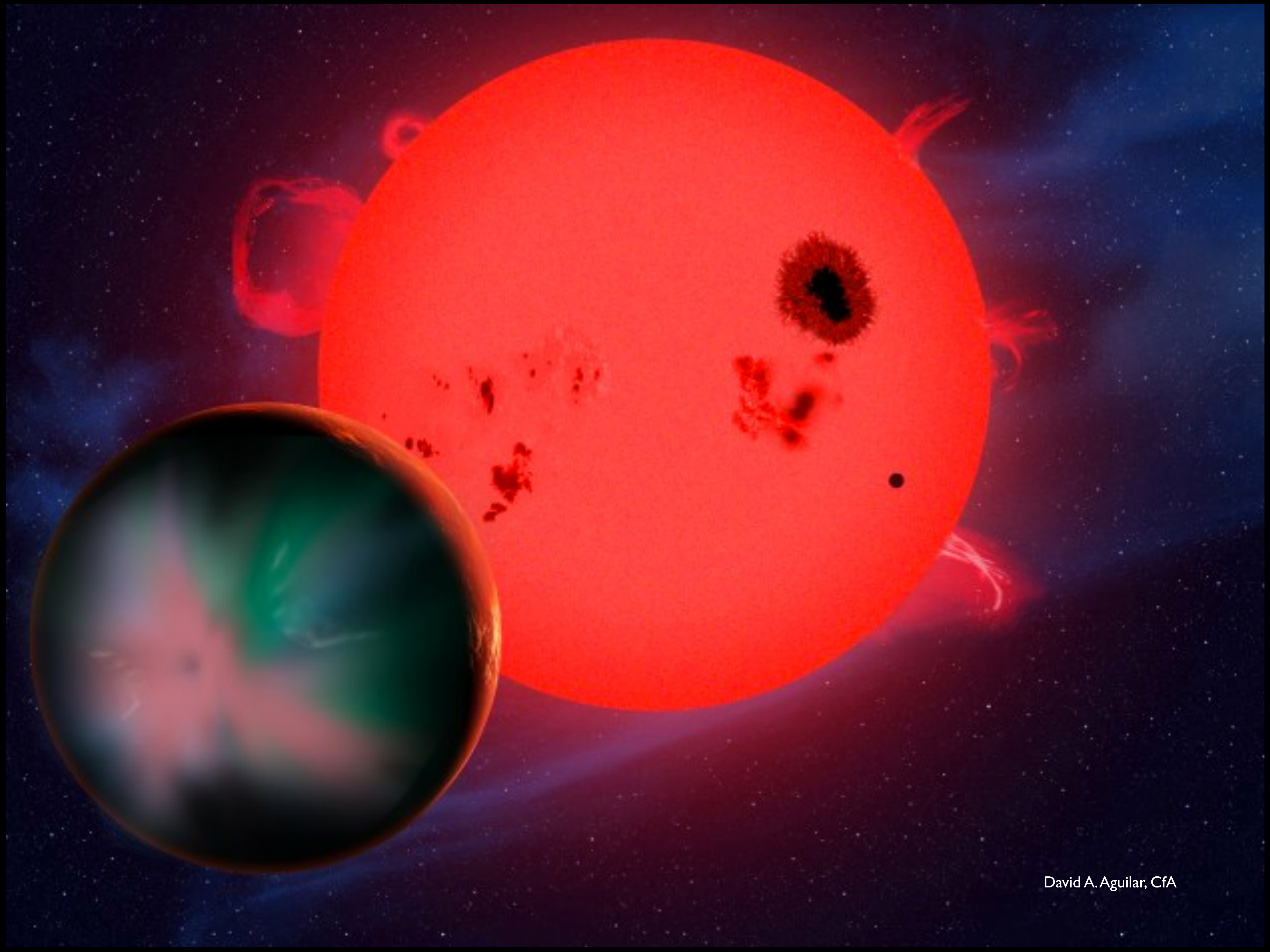
  - If not: **potential test for UV-dependent theories of abiogenesis**





Takeaways

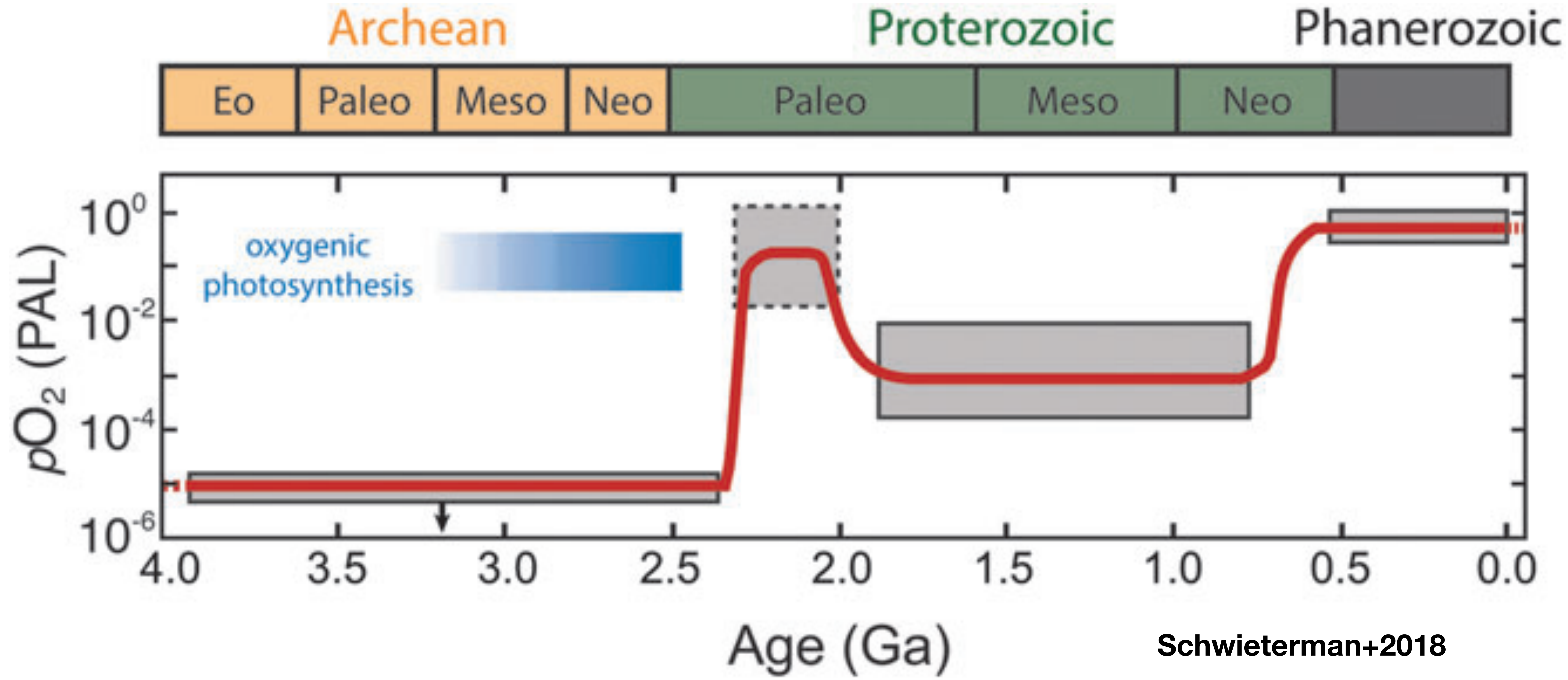
- UV irradiation influences habitability
- M-dwarf planets: low UV. OK for habitability, but abiogenesis?
  - Can flares compensate?
  - Potential opportunity to **use exoplanets to test origins-of life-theories**



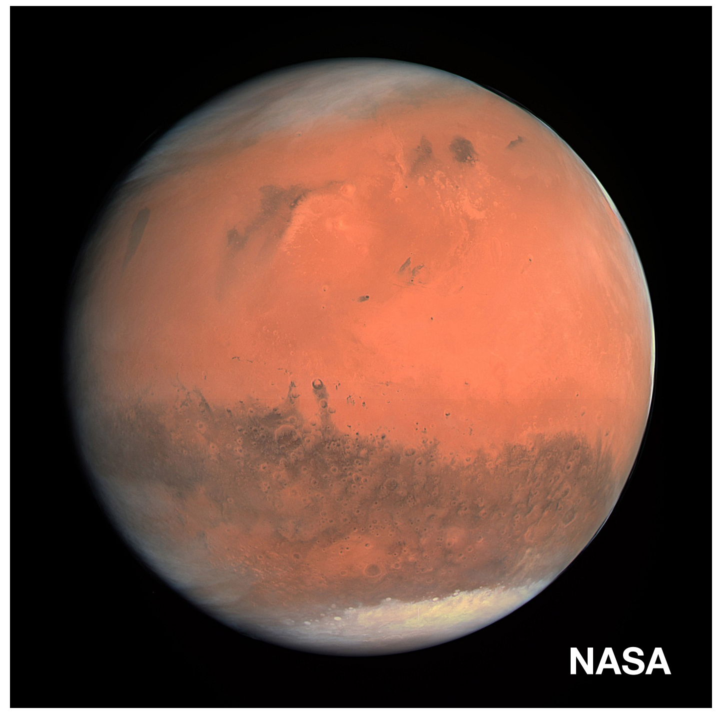
Photochemistry Sets the Atmospheres of Early Earth-Like Planets

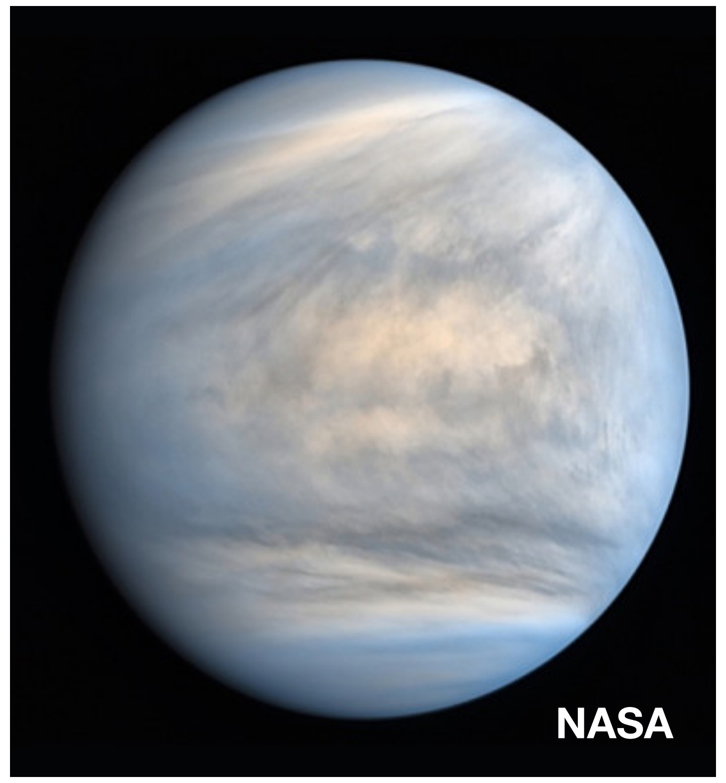
Early Earth-Like Planets

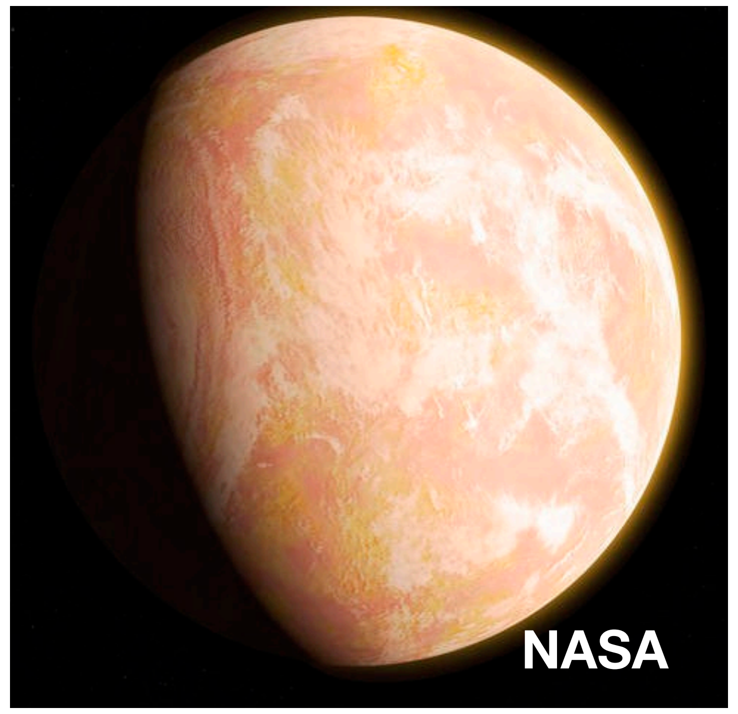
- Anoxic CO_2-N_2 atmosphere
    - <u>Rule</u> in the SS: Mars, Venus, early Earth
- Prebiotic Earth; biosignature null hypothesis



Schwieterman+2018







Photochemistry of CO_2-N_2 Atmospheres

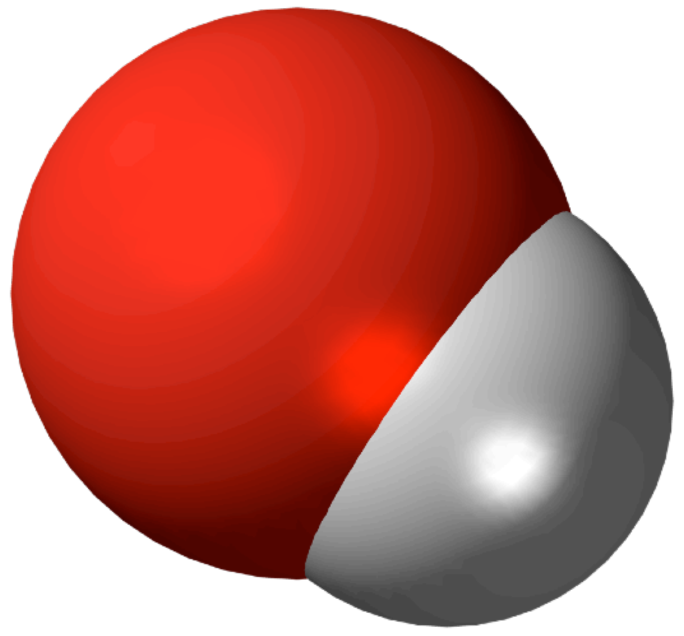
- OH controls buildup of spectrally-active species (CH_4, SO_2, N_2O…; Crutzen+1991)
- OH controls atmospheric stability (c.f. Mars; McElroy+1972)
- OH source: H_2O photolysis

$$CO_2 + h\nu \rightarrow CO + O$$
$$O + O + M \rightarrow O_2 + M$$

BUT

$$CO + OH \rightarrow CO_2 + H$$
$$O_2 + H + M \rightarrow HO_2 + M$$
$$\underline{HO_2 + O \rightarrow O_2 + OH}$$
$$\text{Net: } CO + O \rightarrow CO_2$$

$$H_2O + h\nu \rightarrow H + OH$$



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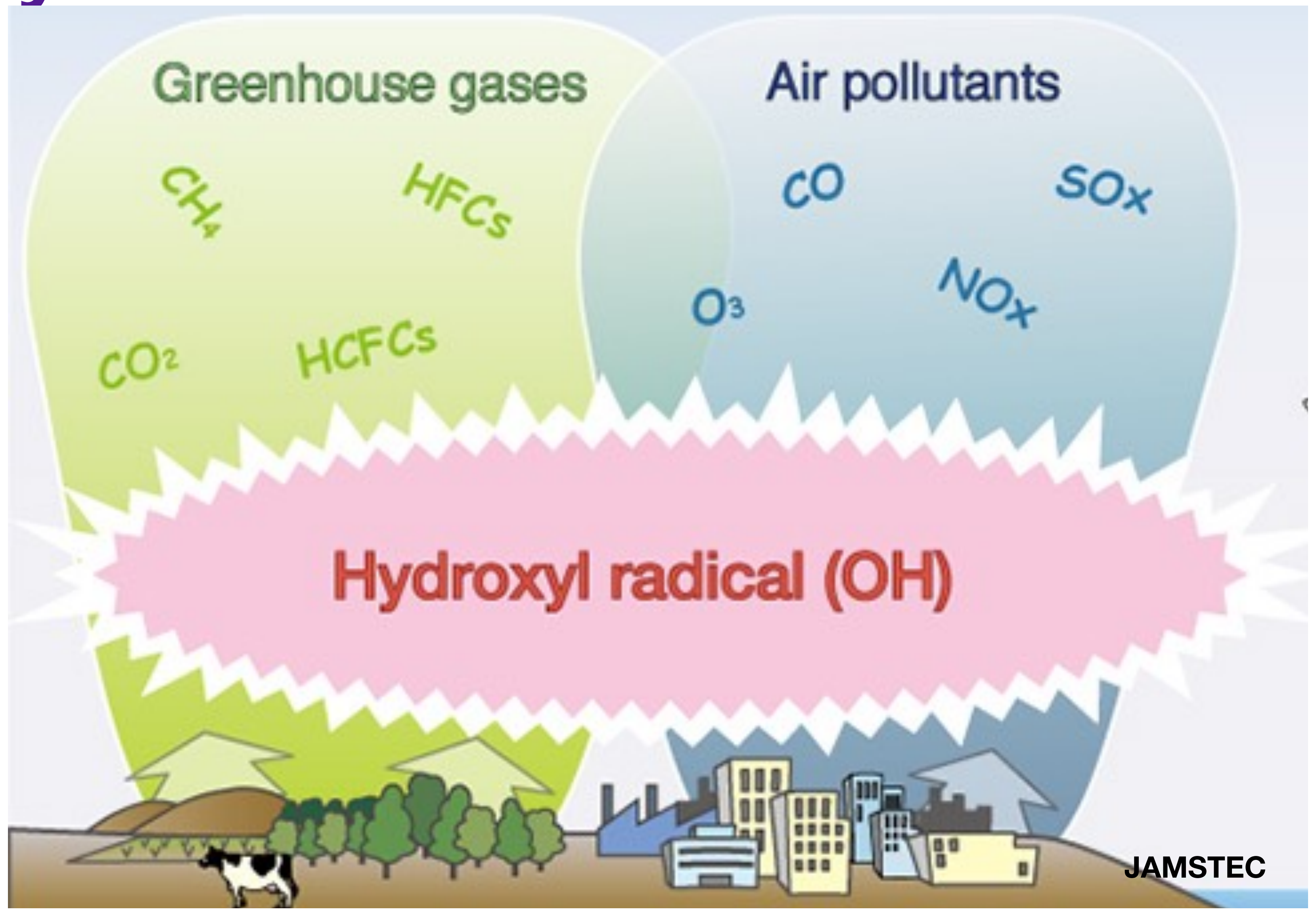
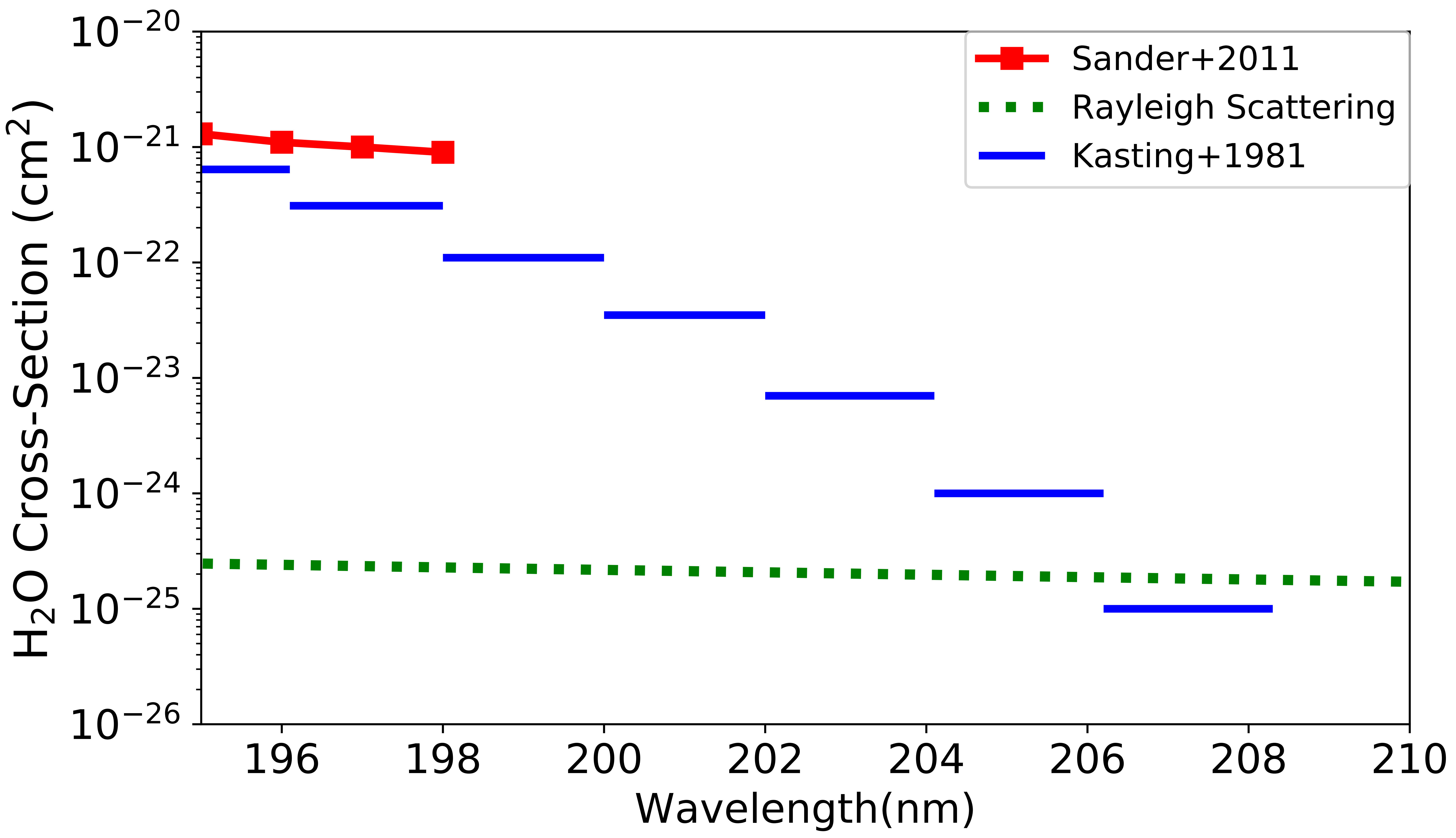
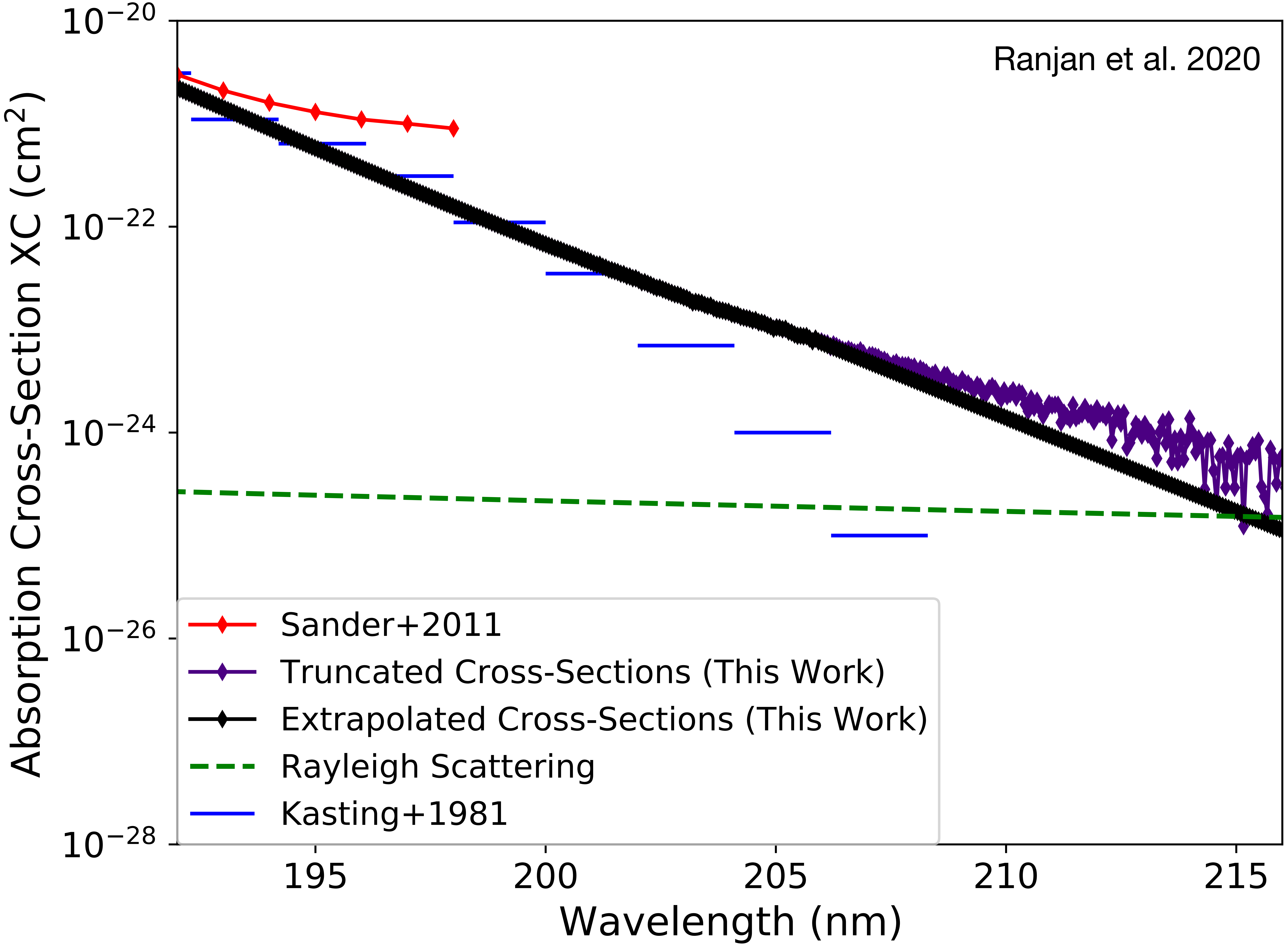


Models Discrepant

Old σ_{H2O} NUV Prescriptions

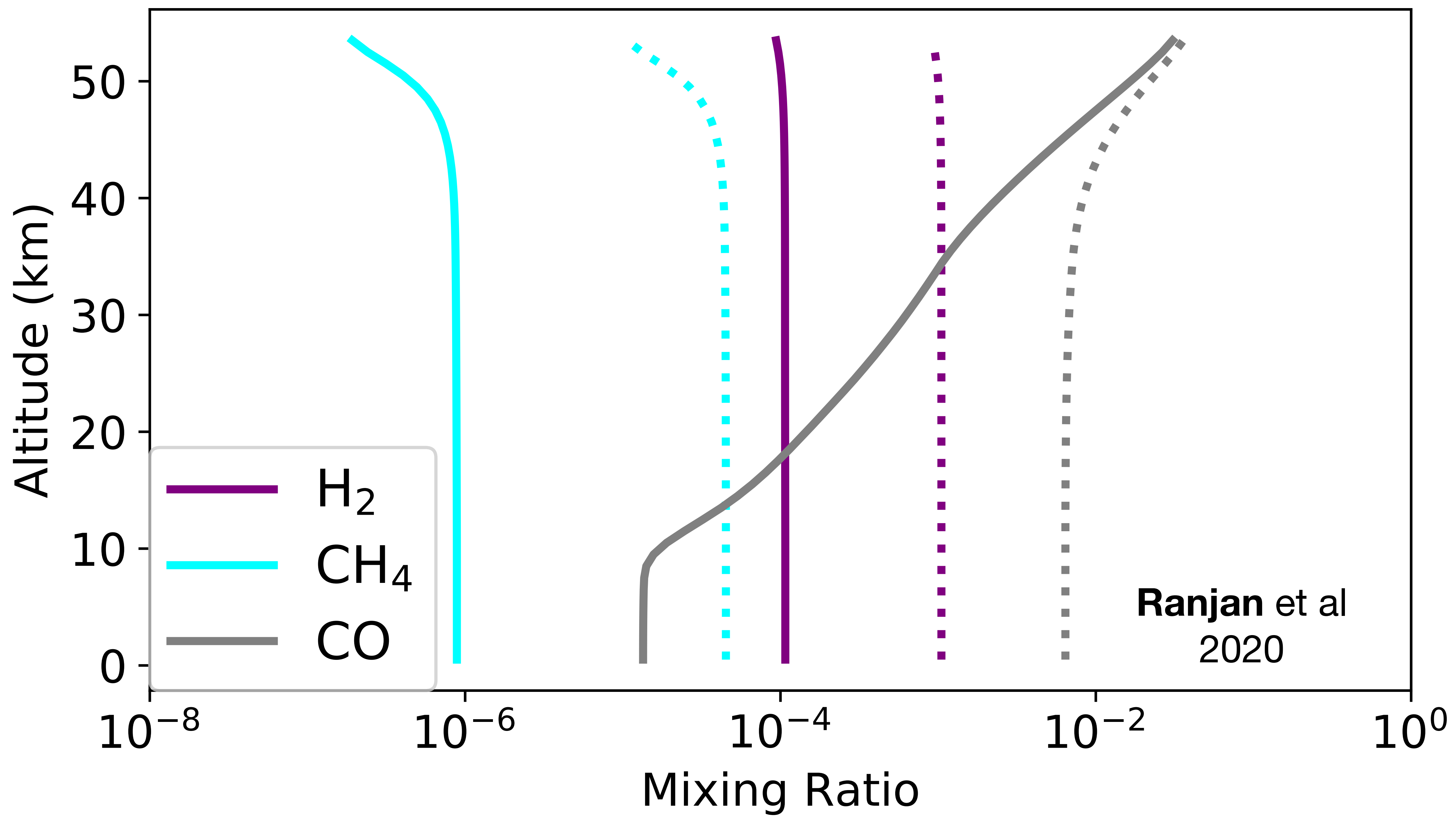


(New) σ_{H2O} NUV Measurements



Photochemical Implications

- **10^{-3}**x decrease in pCO. (H_2, CH_4 may also be reduced)
- No abiotic O_2 (removes O_2 biosignature false-positive)
- Fate of H_2: chemistry, not escape
  - **5**x increase in prebiotic organic production (CH_2O, formaldehyde)



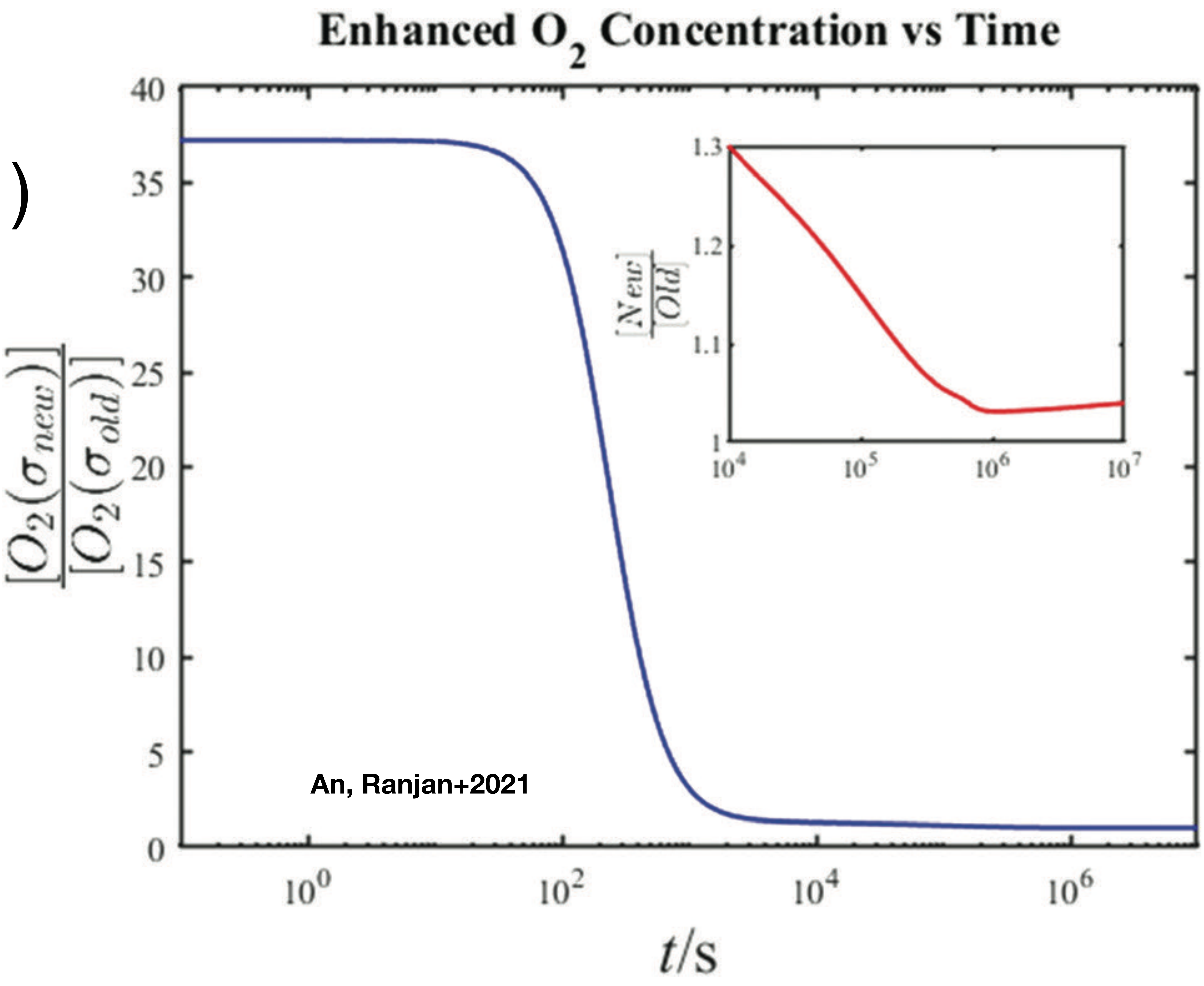
Is O_2 a robust sign of life?

7 OOM

$\phi_{H_2} = \phi_{CH_4} = 0$ cm^{-2} s^{-1}	r_{CO}	r_{O_2}
Uncorrected model	3.7E-2	1.5E-3
Sander et al. (2011) H_2O	1.6E-2	2.1E-4
Extrapolated H_2O (this work)	1.6E-5	3.4E-11

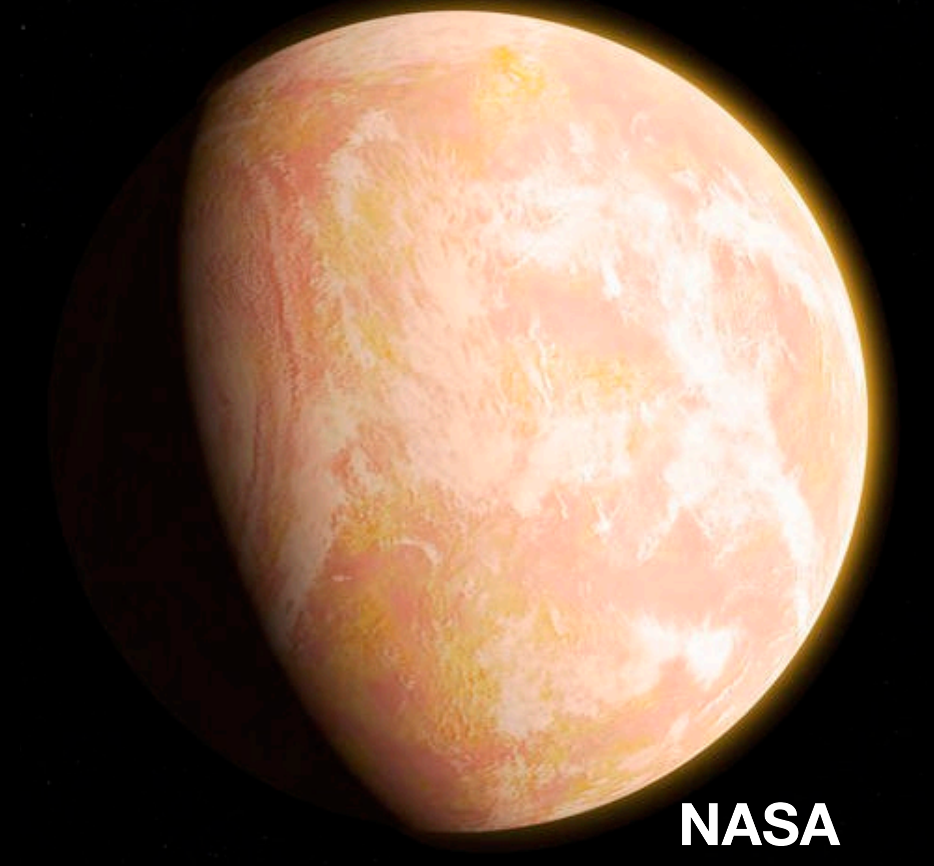
Many Photochemical Uncertainties Remain

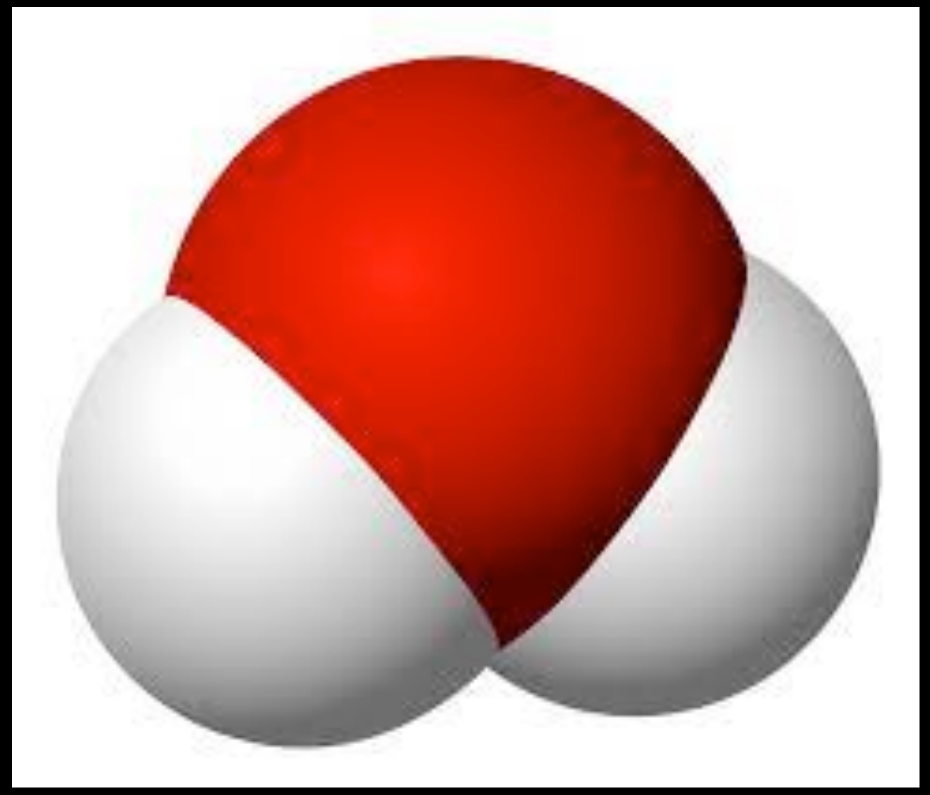
- New EUV H_2O photolysis channel (90-110 nm; An, Ranjan et al. 2021)
  H_2O + hν → H + H +O
  - Astrochemical implications
  - Potentially relevant to exo-mesospheric chemistry?
- σ_{CH4}, σ_{HSO}, σ_{HNO}…



Takeaways

- Many basic photochemical parameters are underconstrained, limiting efficacy of photochemical models for exoplanets
  - NUV σ_{H2O}: higher than assumed, large photochemical implications
  - New H_2O EUV photodissociation channel
  - Etc…
- Much work is required to prepare our photochemical models for biosignature search



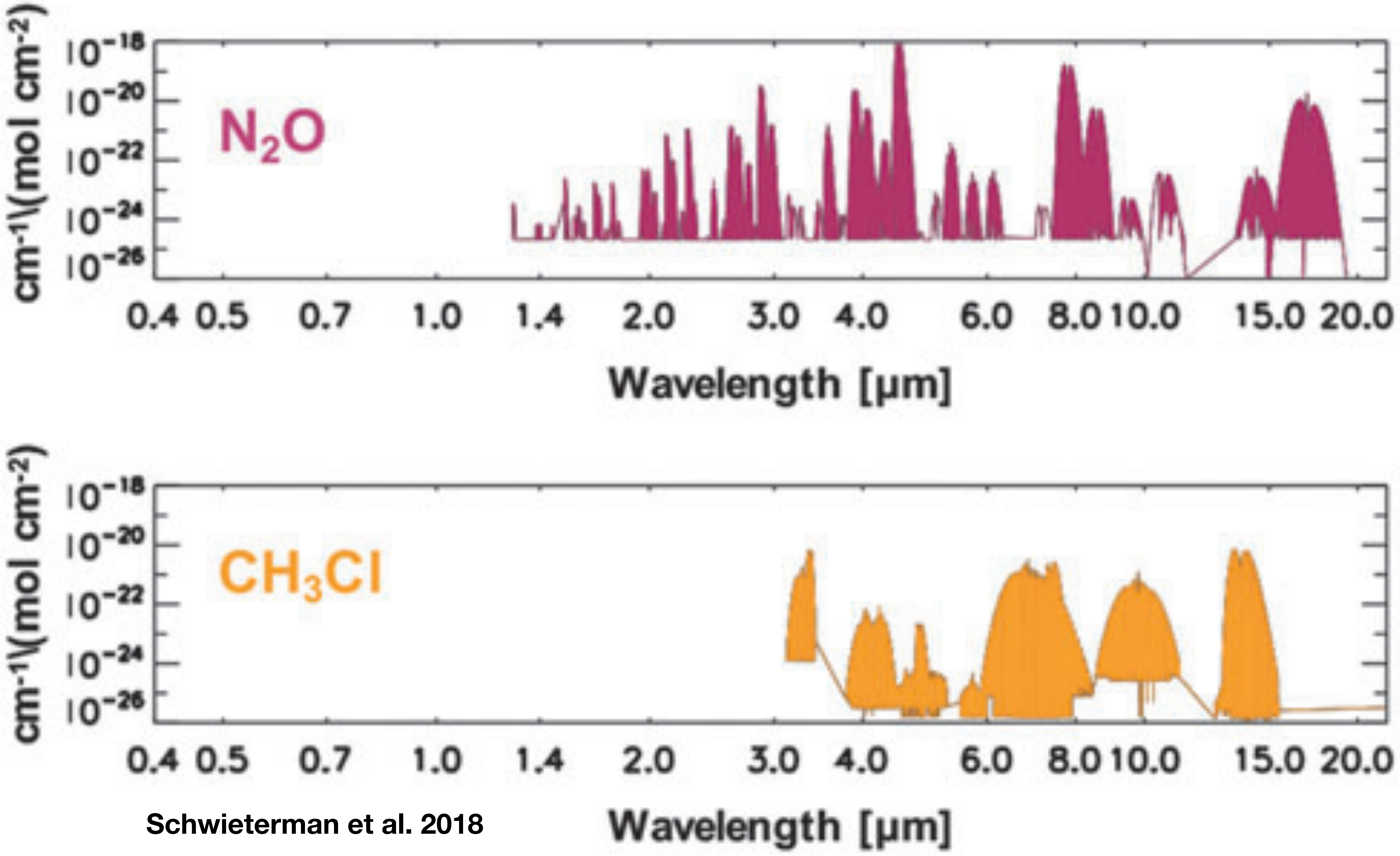


Photochemistry Controls the Detectability of Biosignature Gases

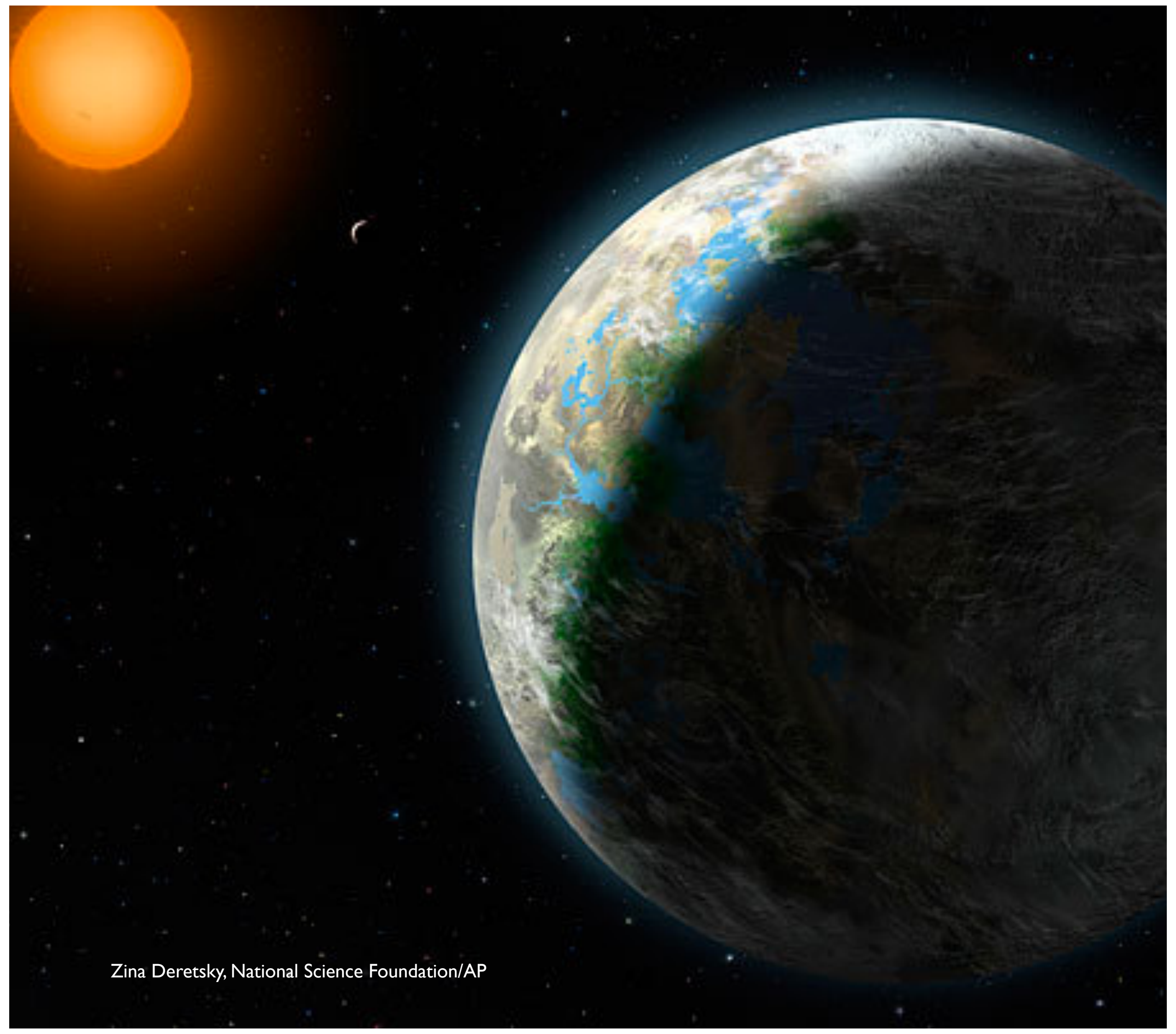
Zina Deretsky, National Science Foundation/AP

The Ideal Biosignature Gas…

- Is spectrally distinguishable
- Has no abiotic false positives
- Accumulates to detectable levels



Schwieterman et al. 2018



…Has not yet been identified

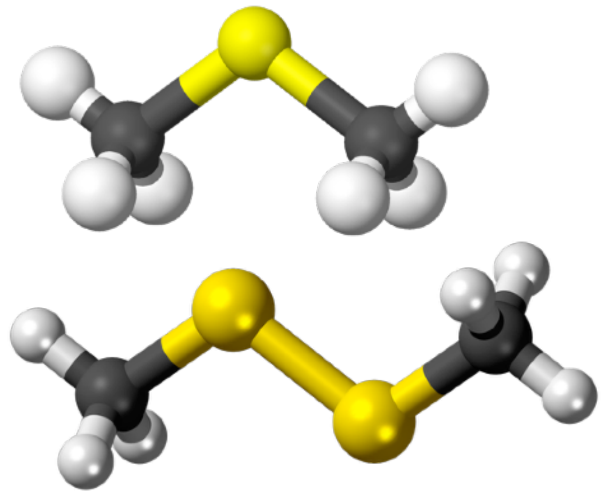
Oxygen
(O_2)

Ozone
(O_3)

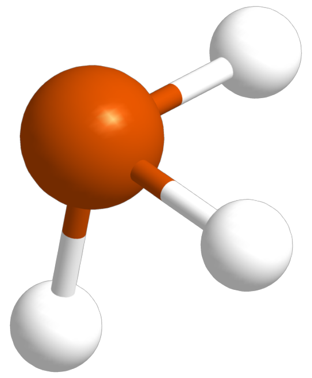
Methane
(CH_4)

Nitrous Oxide
(N_2O)

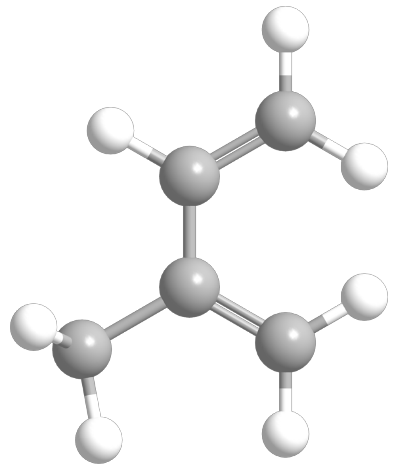
Novel Biosignature Gases: Too Reactive?



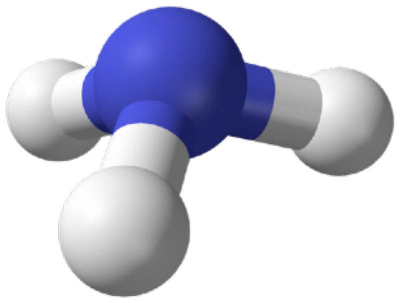
Organosulfurs
(DMS, DMDS)



Phosphine
(PH_3)



Isoprene
(C_5H_8)



Ammonia
(NH_3)

Wikimedia
commons

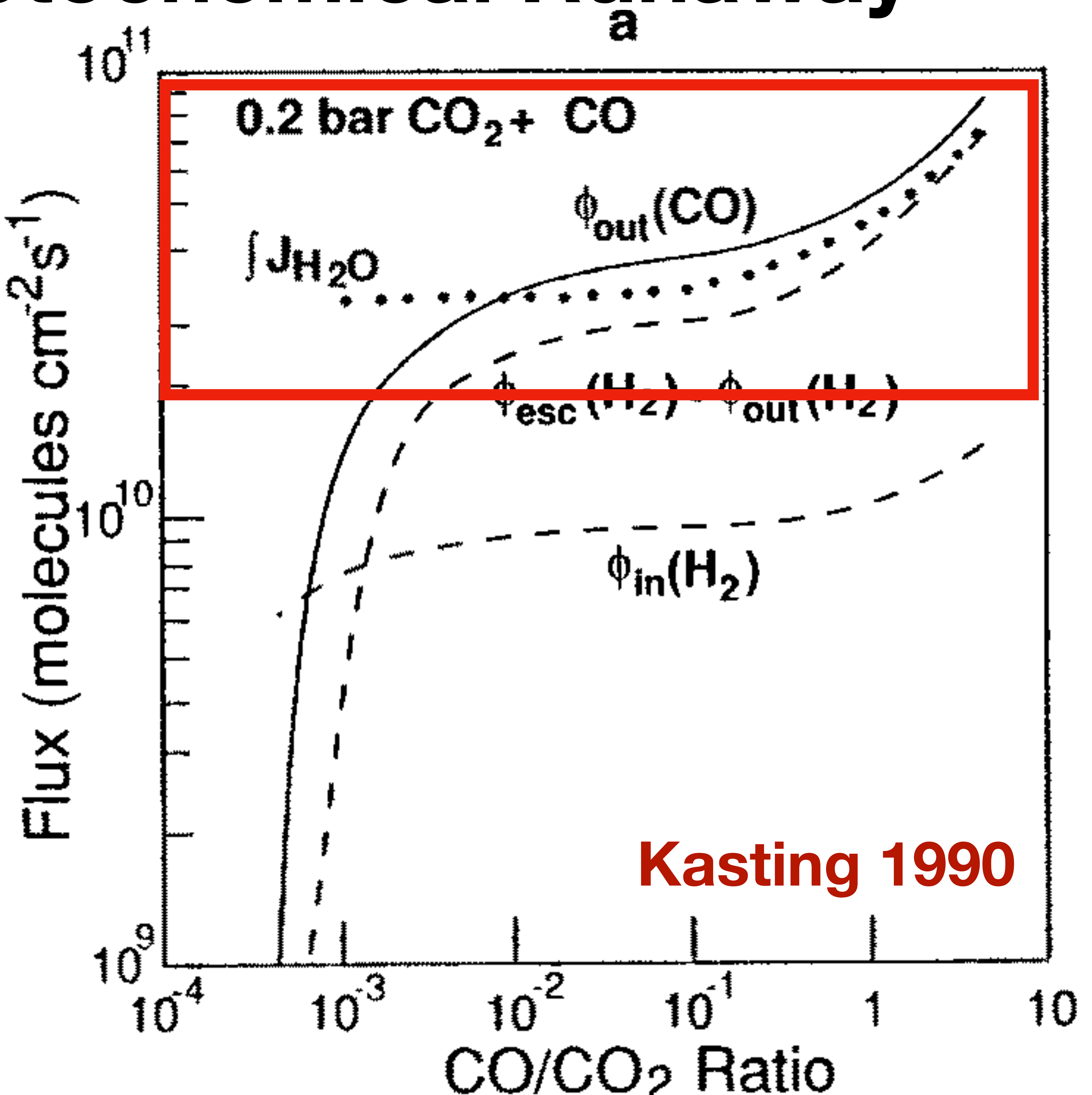
A Ray of Hope: Photochemical Runaway

$CO + OH \rightarrow CO_2 + O$

$\boxed{H_2O + h\nu} \rightarrow OH + H$

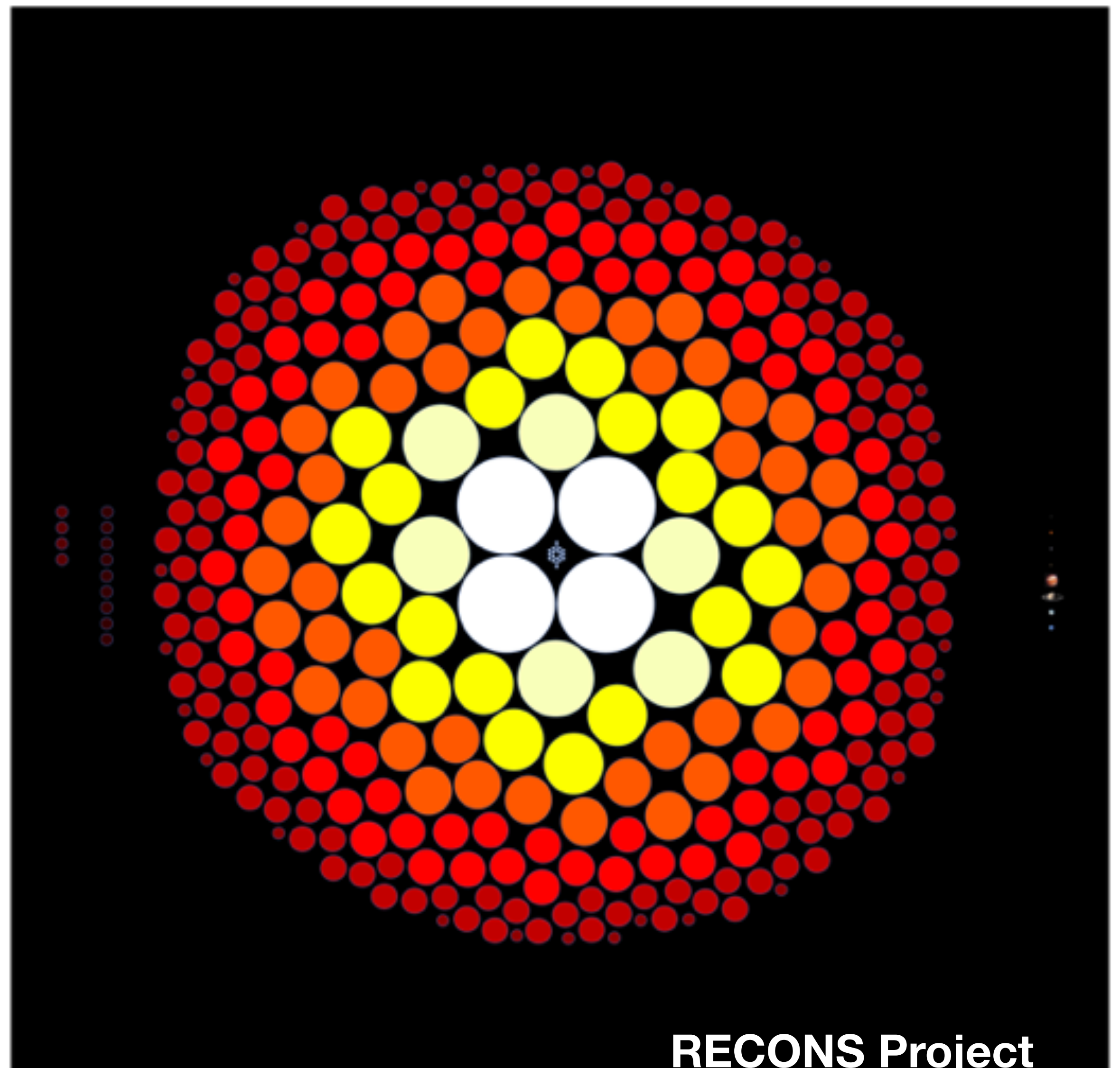
Finite

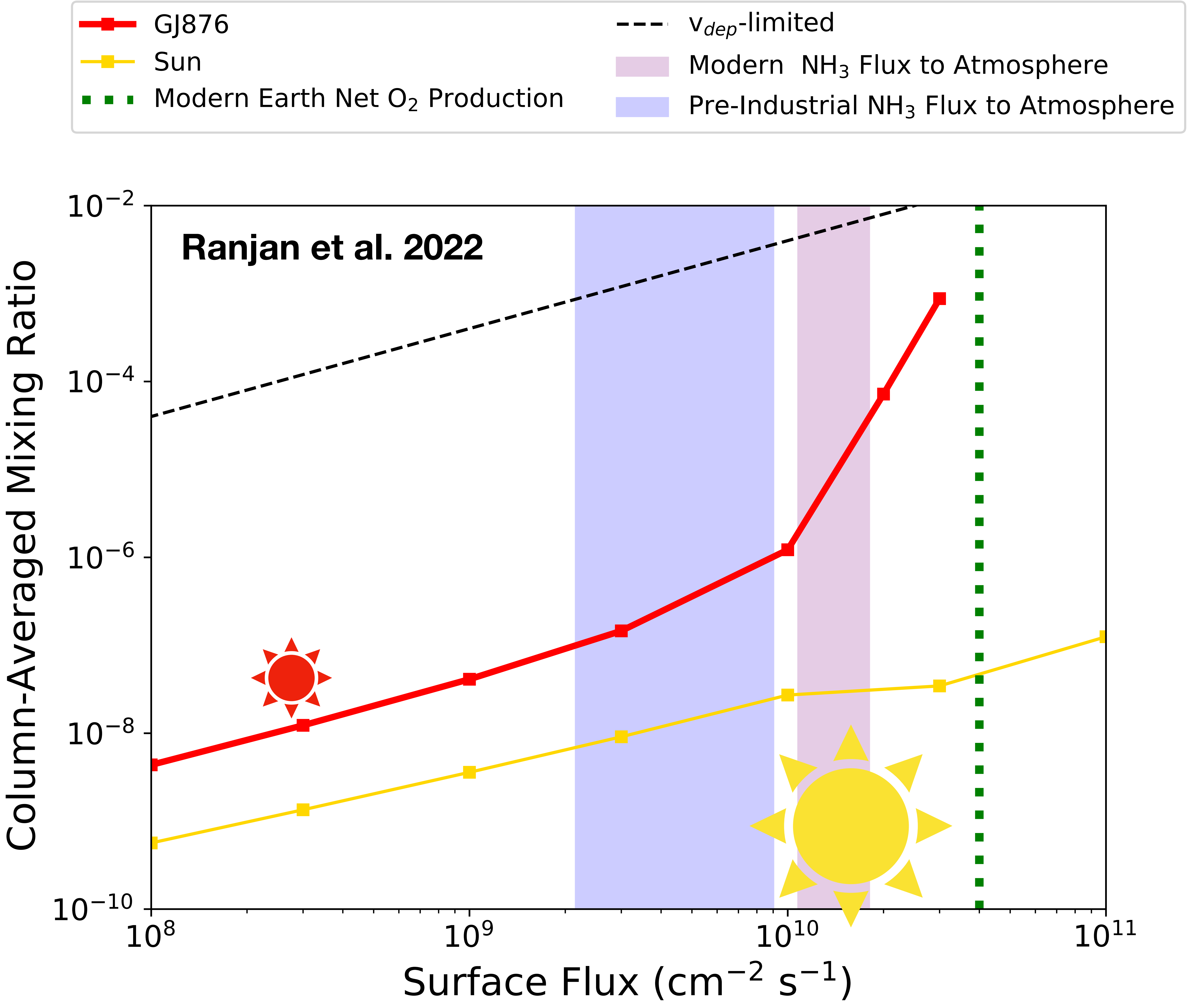
- The ability of an atmosphere to photochemically cleanse itself of trace gases is <u>finite</u>
- If a gas is emitted at fluxes exceeding this threshold, it <u>runs away</u> until limited by surface processes



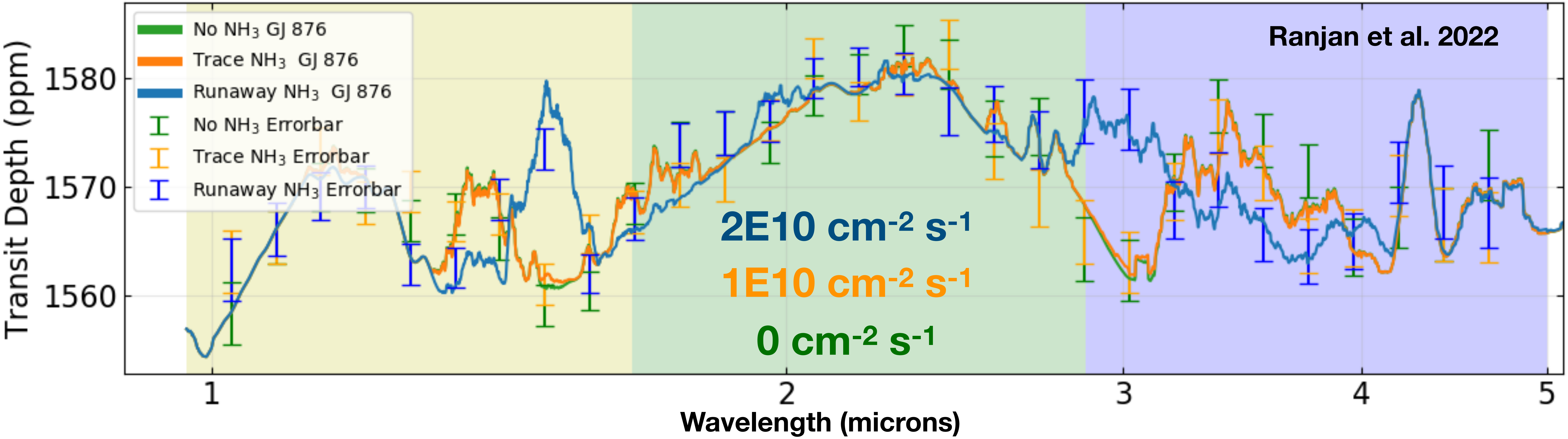
NH_3 Undergoes Runaway around M-Dwarfs

- Case study: NH_3 in H_2-N_2 atmosphere ("Cold Haber World", Seager et al. 2013)
- NH_3: Reactive, well-studied, <u>not</u> for excellence as biosignature (Huang et al. 2022)



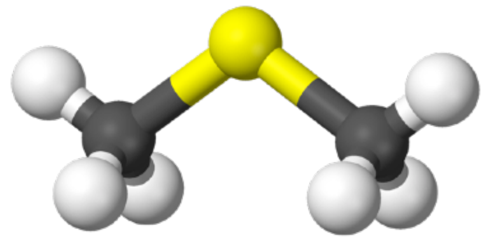
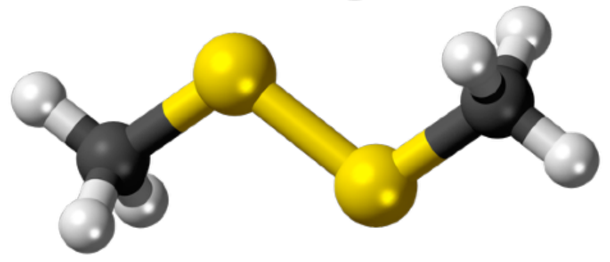
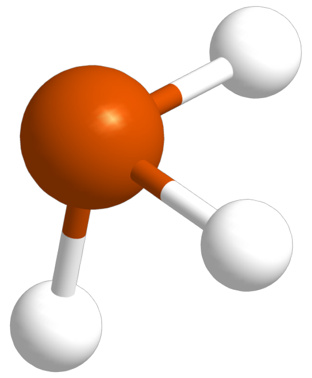
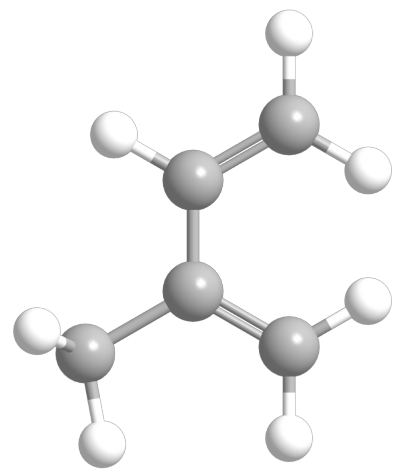
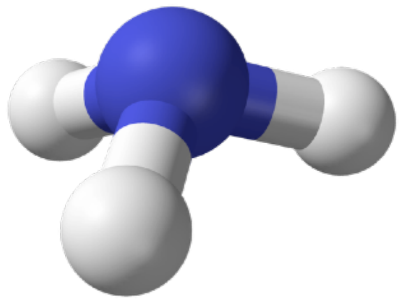


Runaway Makes NH_3 Detectable



2 JWST Transits
Super-Earth (1.5 R_E)
GJ876 stellar properties

Novel Biosignature Gases: Too Reactive?

		Spectral Features	False Positive Potential (Known)	Atmospheric Accumulation	Ref
 	**Organosulfurs (DMS, DMDS)**	Good	Low	Bad	Domagal-Goldman et al. 2011
	**Phosphine (PH_3)**	Good	Low	Bad	Sousa-Silva **et al.** 2020
	**Isoprene (C_5H_8)**	Moderate	Low	Bad	Zhan **et al.** 2021
	**Ammonia (NH_3)**	Good	Low	Bad	Seager et al. 2013, Huang **et al.** 2021

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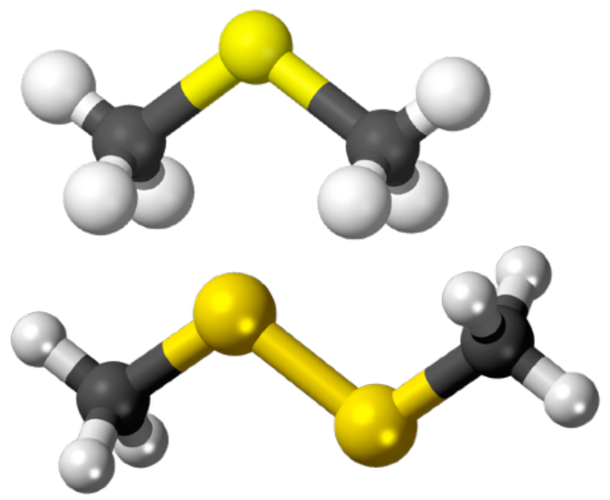
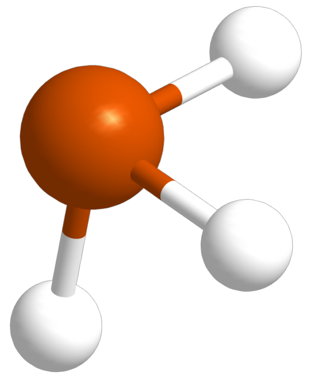
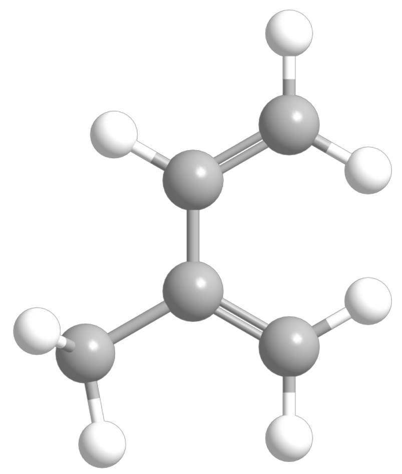
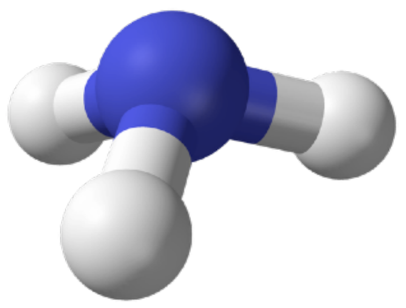
Runaway Makes Reactive Gases Detectable

		Spectral Features	False Positive Potential (Known)	Atmospheric Accumulation	Ref
	**Organosulfurs (DMS, DMDS)**	Good	Low	?	Domagal-Goldman et al. 2011
	**Phosphine (PH_3)**	Good	Low	**Detectable in Runaway**	Sousa-Silva **et al.** 2020
	**Isoprene (C_5H_8)**	Moderate	Low	**Detectable in Runaway**	Zhan **et al.** 2021
	**Ammonia (NH_3)**	Good	Low	**Detectable in Runaway**	Seager et al. 2013, Huang **et al.** 2021

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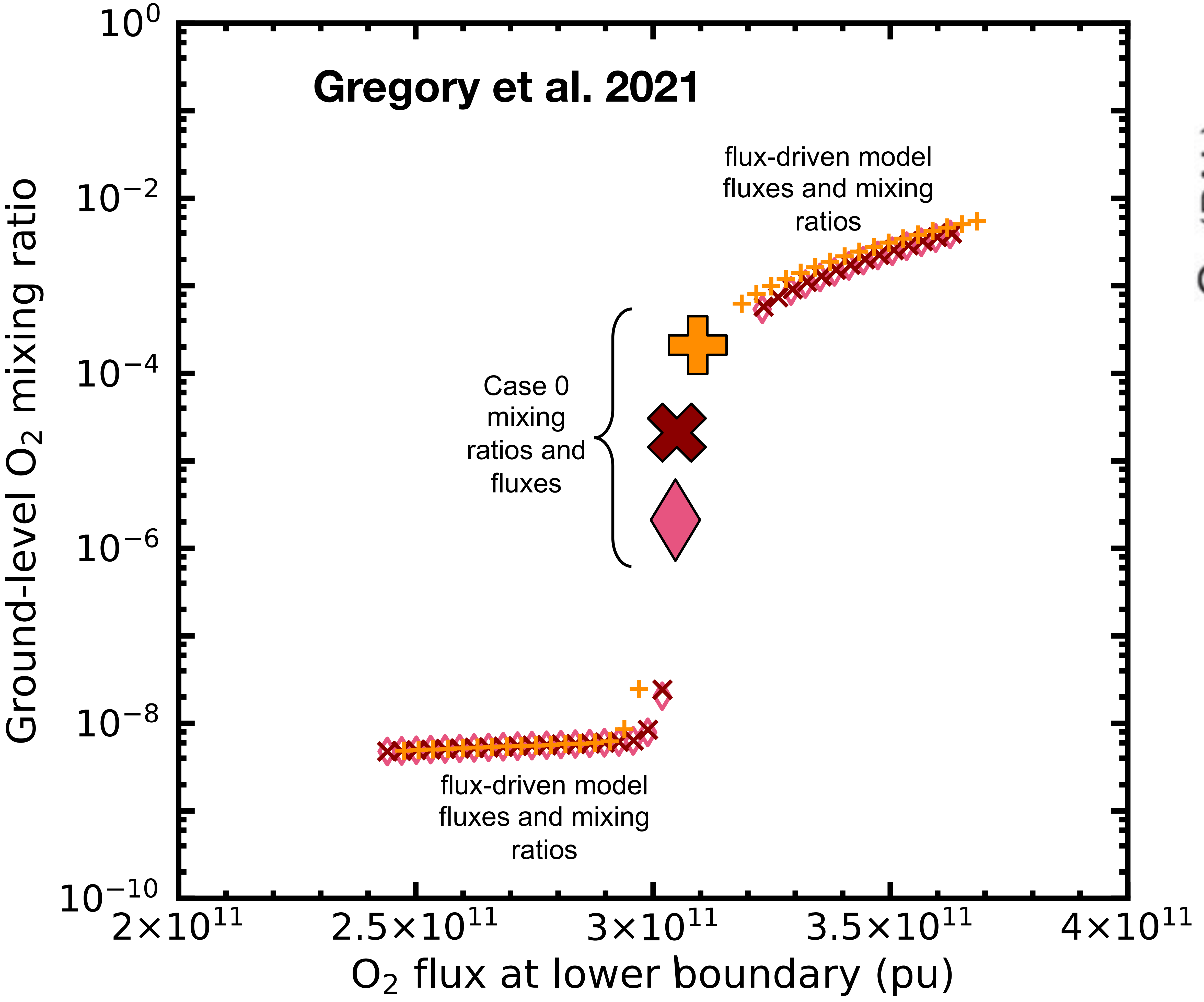
Runaway is a General Prediction

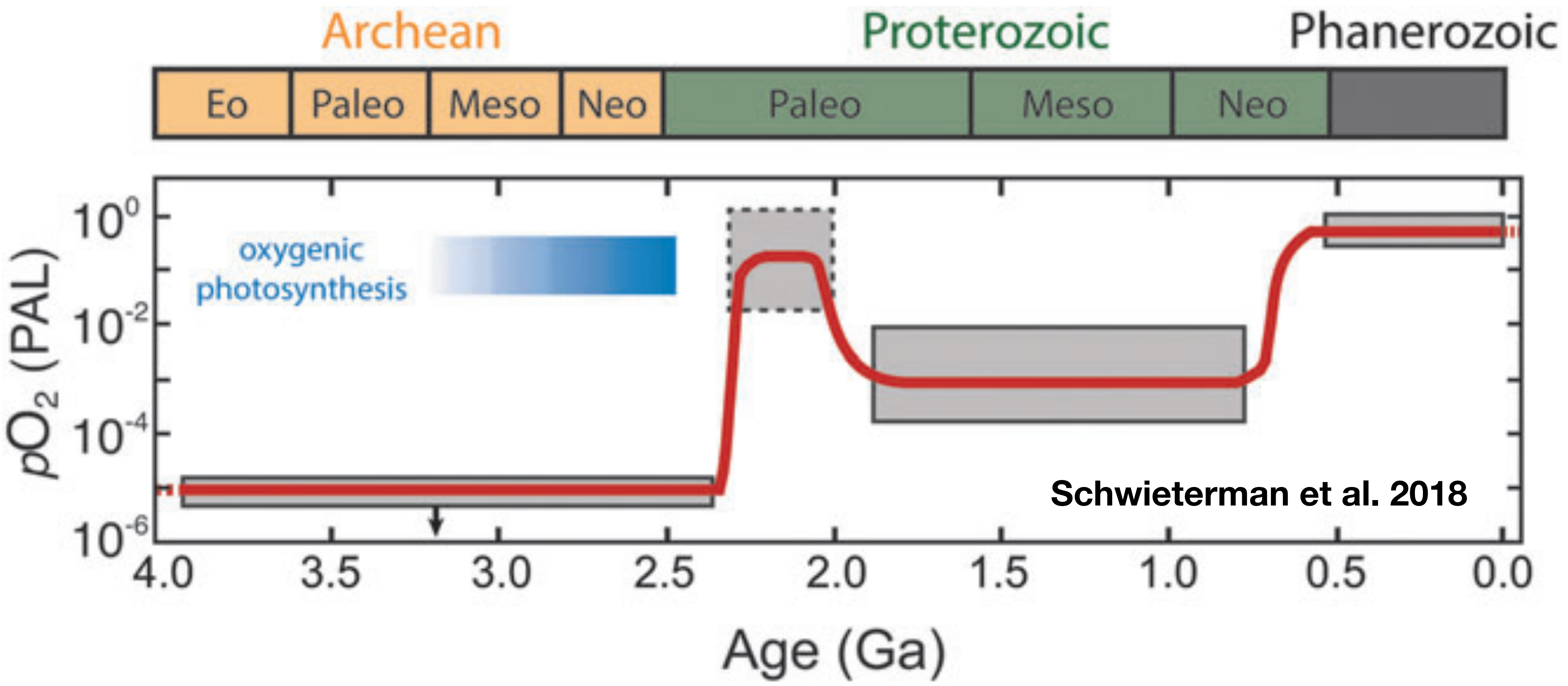
CO
Zahnle 1986
Kasting 1990, 2014
Schwieterman et al. 2019

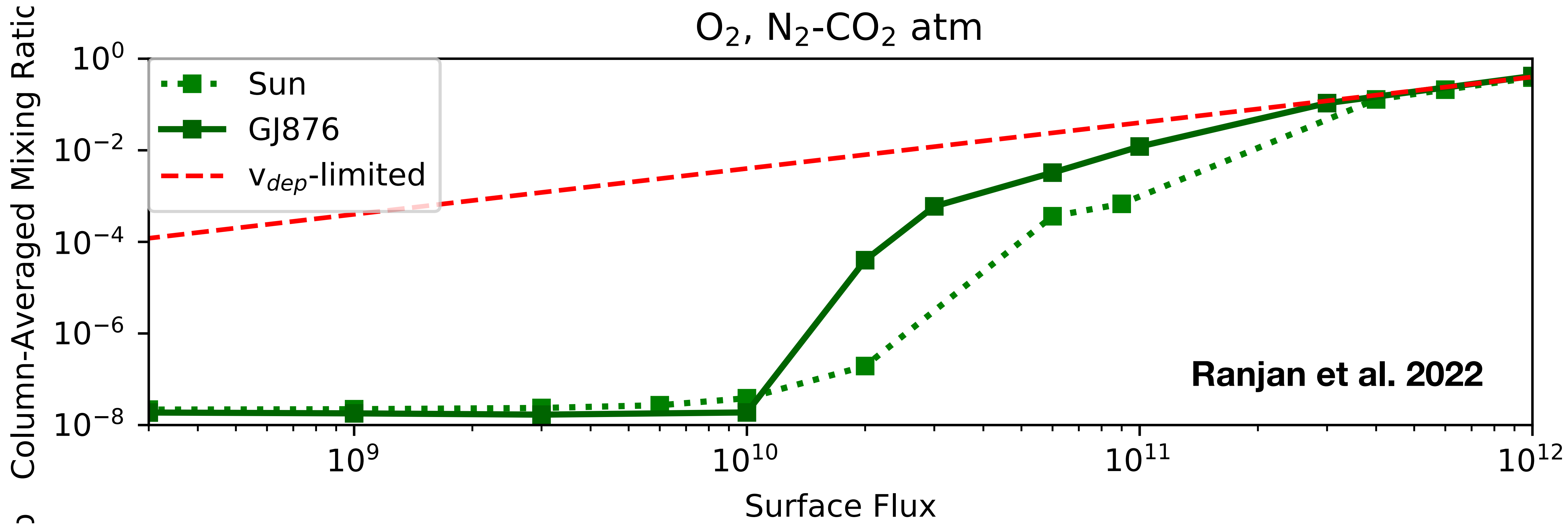
O_2
Gregory et al. 2021

- Also CH_4 (Prather 1996; Pavlov et al. 2003, Segura et al. 2005, Ranjan et al. 2022)

O_2 on Earth: Actualized Runaway

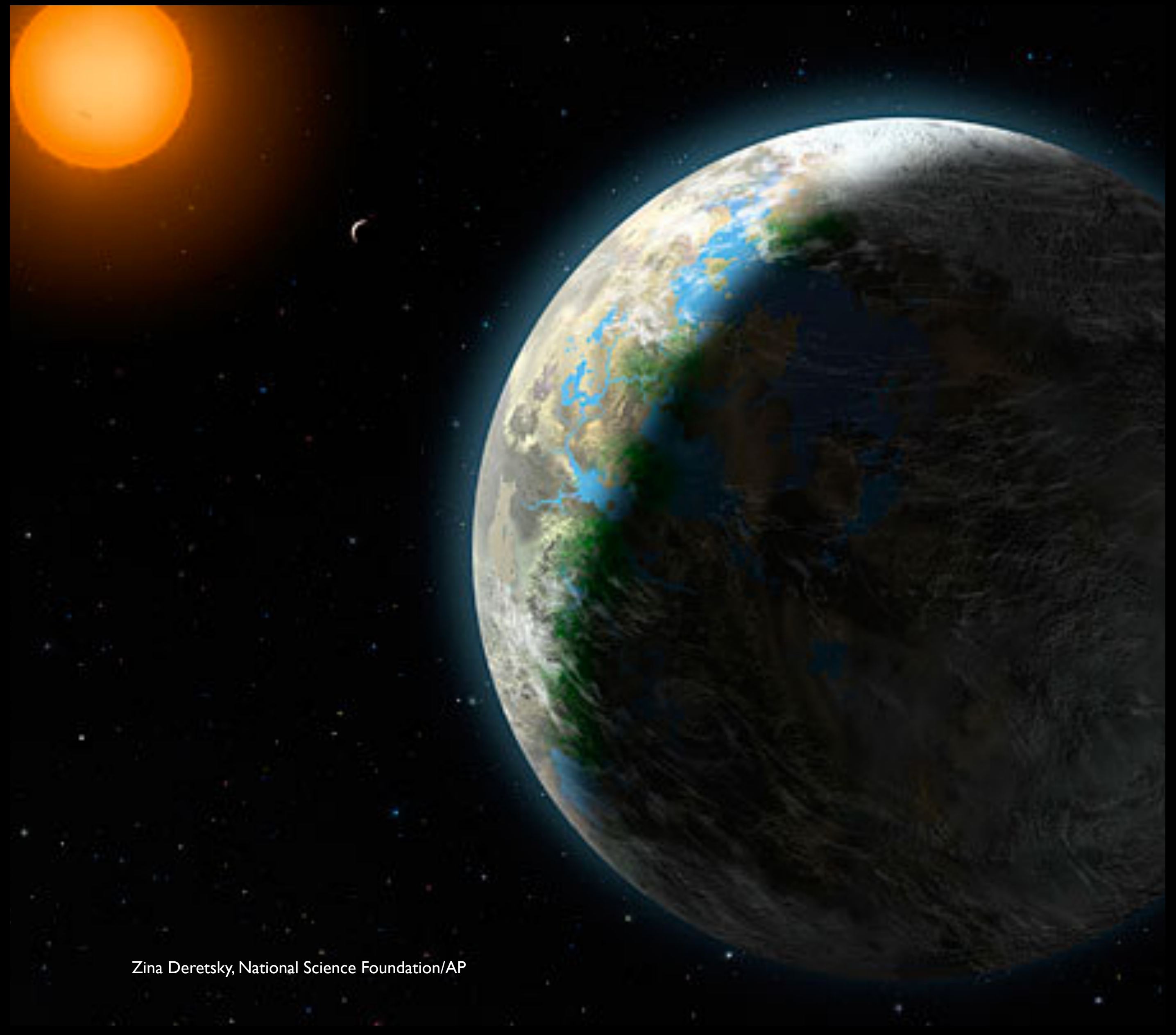






Takeaways

- No “perfect” biosignature
  - Conventional (e.g., N_2O): elevated false positive potential
  - Unconventional (e.g., C_5H_8): very reactive
- Reactive gases: potentially detectable with JWST via <u>photochemical runaway</u>
  - Broad catalog of potential biomarkers: not necessarily reliant on evolution of O_2 photosynthesis



Recipe for Remote Life Detection

Measure atmospheric spectrum, bulk planetary/ stellar properties

Extensive Theoretical Infrastructure Required

Quantify production/loss fluxes of potentially biogenic gases implied by observations

Determine if known abiotic mechanisms can explain inferred gas fluxes

Use theories of (in)habitability to assess plausibility of biological explanation

Probabilistic constraint on presence of life

Observation → **Interpretation** → **Conclusion**

Future Work

Measure atmospheric spectrum, bulk planetary/ stellar properties

Theory, experiments, observations needed to build interpretive infrastructure

Theory, lab work to catalog (1) which biosignature gases to look for, (2) where to look for them, (3) how to discriminate false positives

Theory and lab work to build robust photochemical models

Theory, observational, lab work to refine theories of habitability, abiogenesis, extract priors

Probabilistic constraint on presence of life

Observation → Interpretation → Conclusion

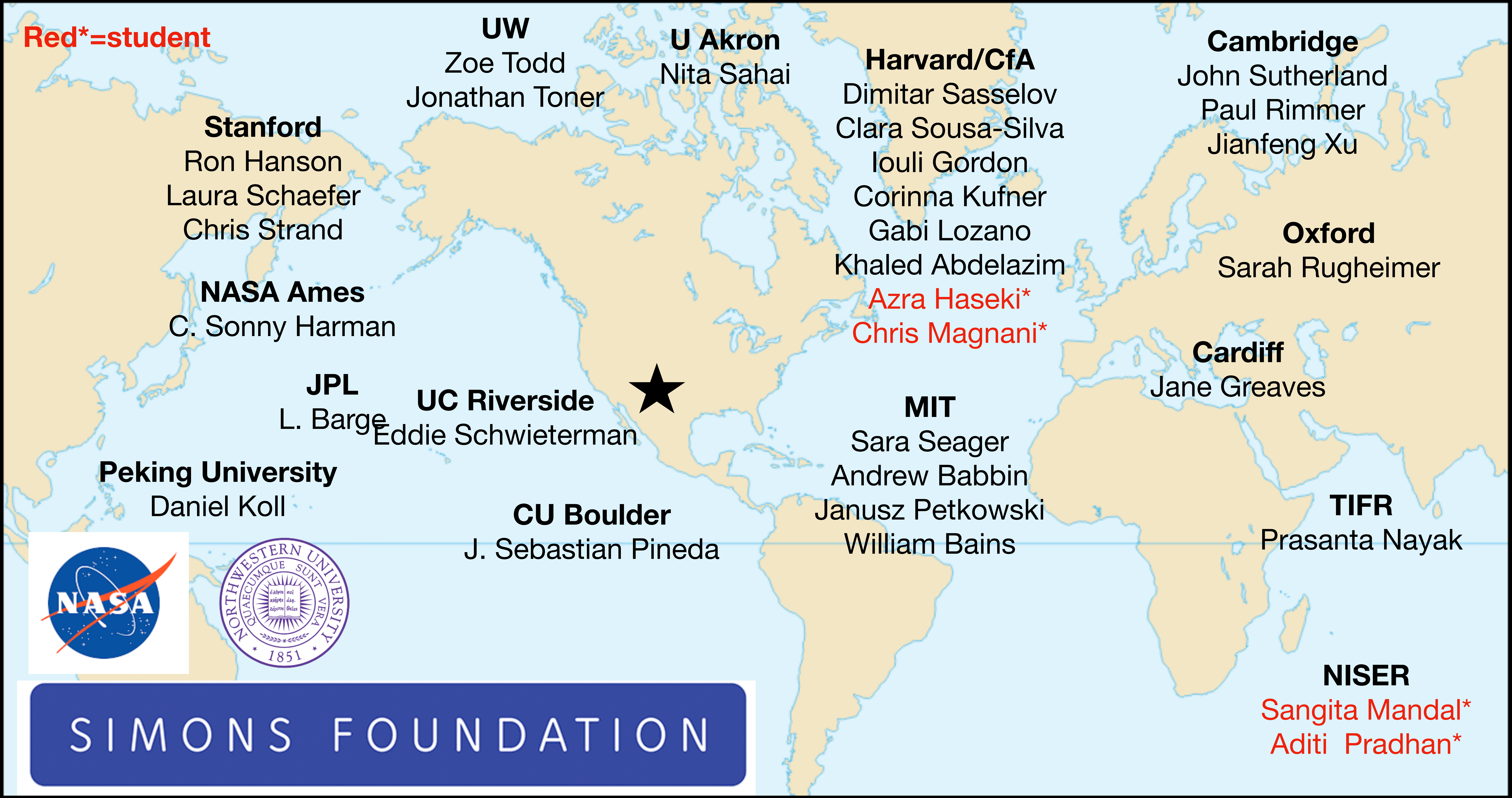
Summary

- Temperate rocky planets orbiting other stars are common, and we will measure their atmospheric spectra within the next few decades.
- Constraining exoplanet life from atmospheric spectra requires intense interpretive intervention
  - Photochemical models (characterize potential biosignatures)
  - Geochemical models (understand geological false positives)
  - Theories of origin & endurance of life (Bayesian interpretation of putative biosignature)
- Theoretical, laboratory, and observational work is required to build this interpretive infrastructure

Life on Earth may be the result of a common process, or it may require such an unusual set of circumstances that we are the only living beings within our part of the galaxy, or even in the universe. Either answer is profound…The coming decades will set humanity down a path to determine whether we are alone.

National Academy of Sciences (USA) 2021, *Pathways to Discovery in Astronomy and Astrophysics for the 2020s*, https://doi.org/10.17226/26141

(Partial) Acknowledgements



Summary

- Temperate rocky planets orbiting other stars are common, and we will measure their atmospheric spectra within the next few decades.
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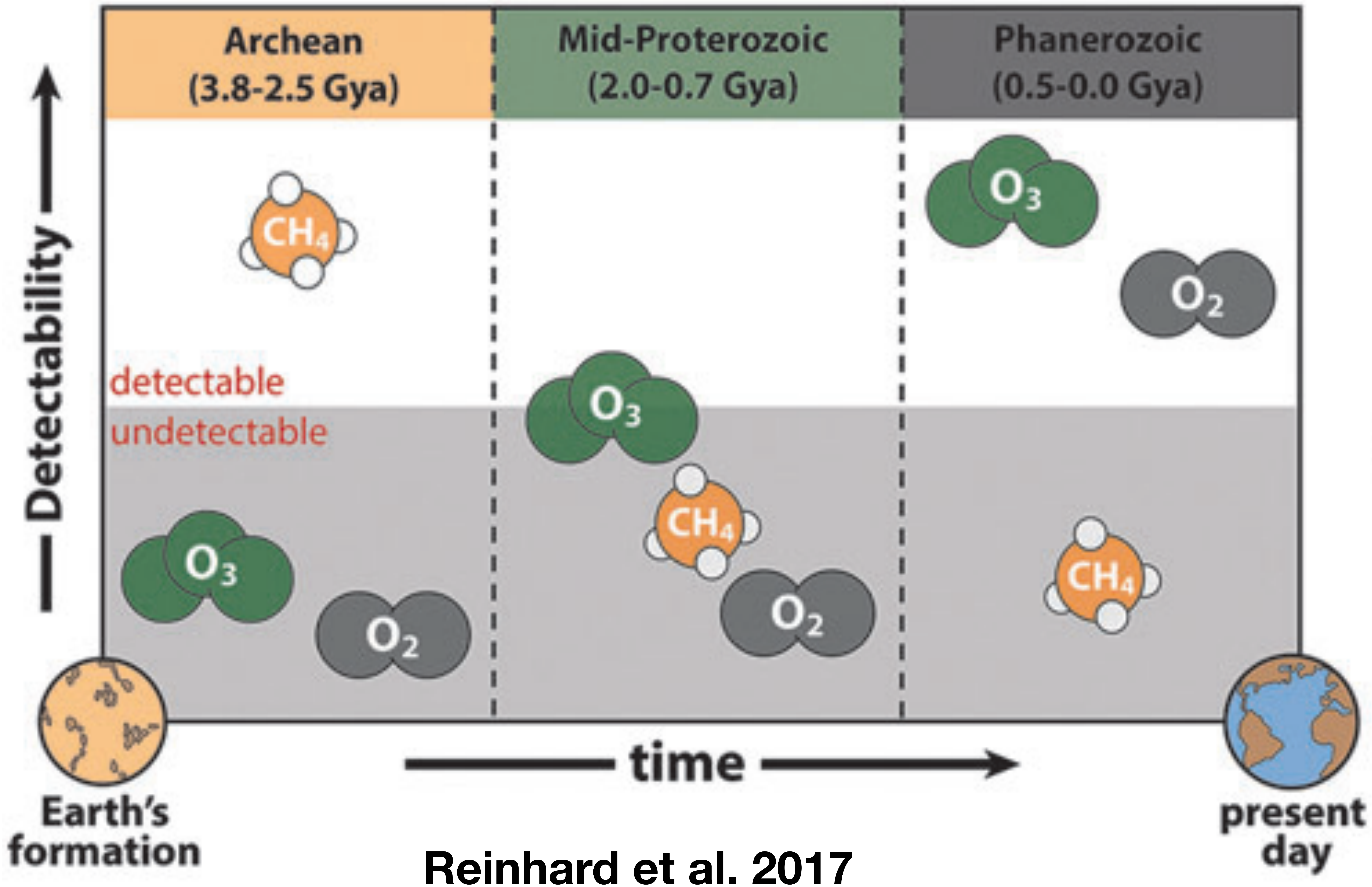
Backup Slides

Canonical Biosignature: CH_4 + O_2 (+ H_2O) [Sagan et al. 1993]



Reinhard et al. 2017

Runaway:Thermodynamically Forbidden?

Qualitative

Runaway produces high temperatures and metabolite concentrations, meaning it will self-inhibit (Segura et al. 2005; Rugheimer et al. 2015, 2018)

$\boxed{\mathbf{CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O}}$

Quantitative

$\Delta G_{reac}(T, C_i) \leq -20$ kJ mol^{-1} (Hoehler 2004)

[Metabolism energetically profitable]

$P_{me}(T)/\Delta G_{reac}(T, C_i) < 10^{-4}$ mol g^{-1} s^{-1} (Seager+2013 & refs therein)

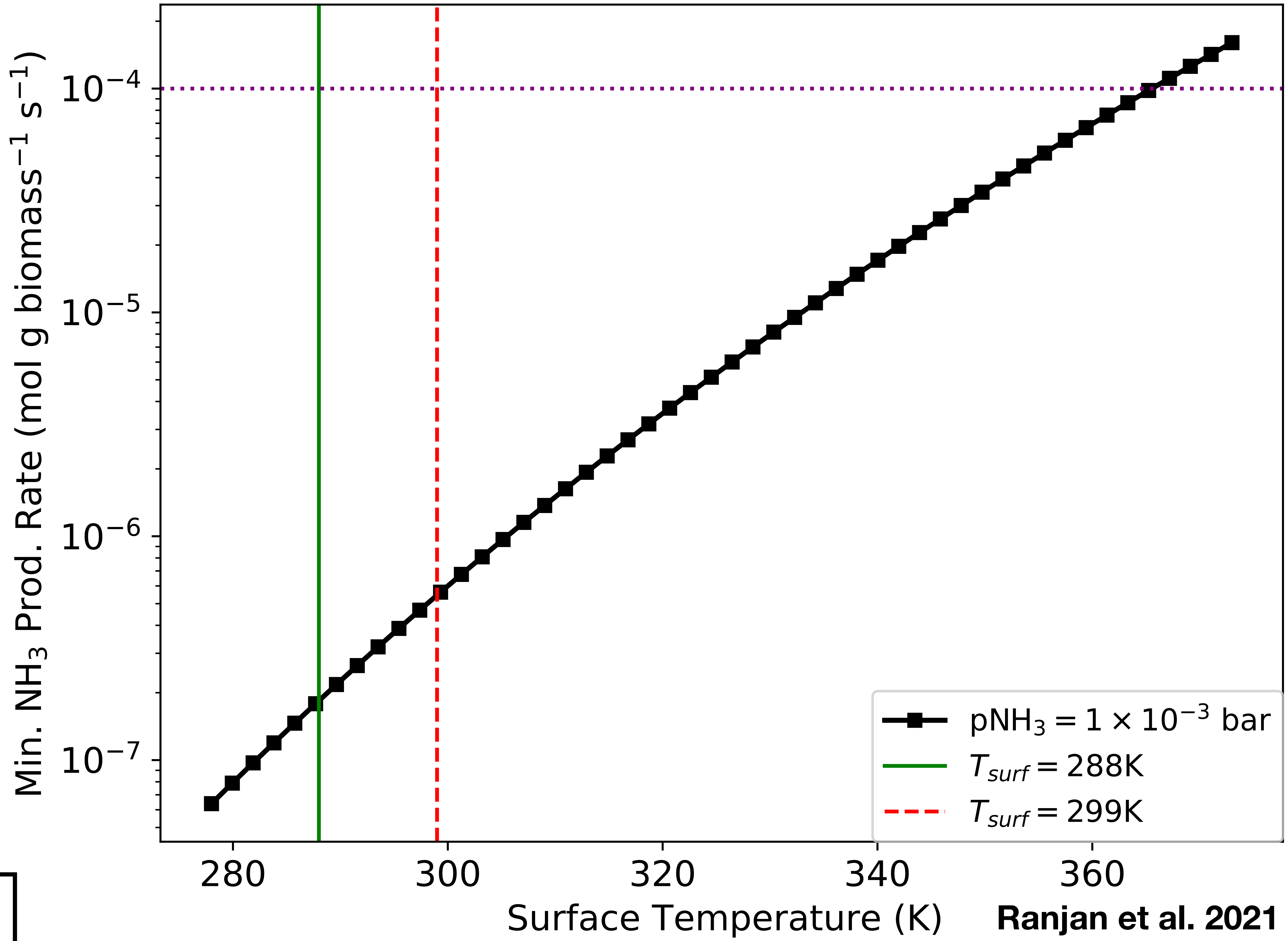
[Metabolite production rate plausible]

Runaway:Thermodynamically Allowed

- CH_4 runaway self-inhibits for **modern Earth**, but not **early Earth**
- NH_3 runaway allowed for N_2-H_2 atmosphere

$\boxed{N_2 + 3H_2 \rightarrow 2NH_3}$

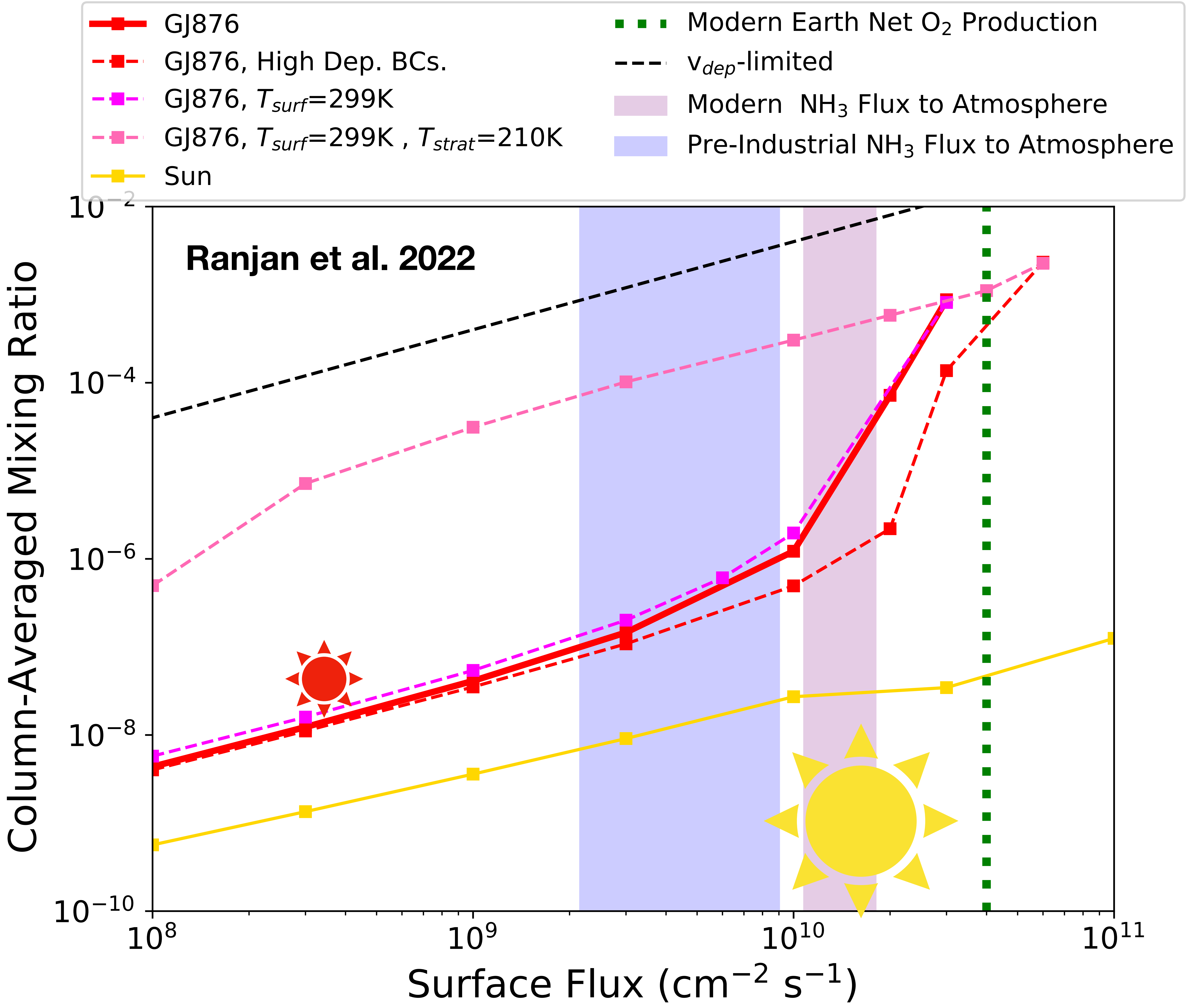
$\boxed{CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O}$



Ranjan et al. 2021

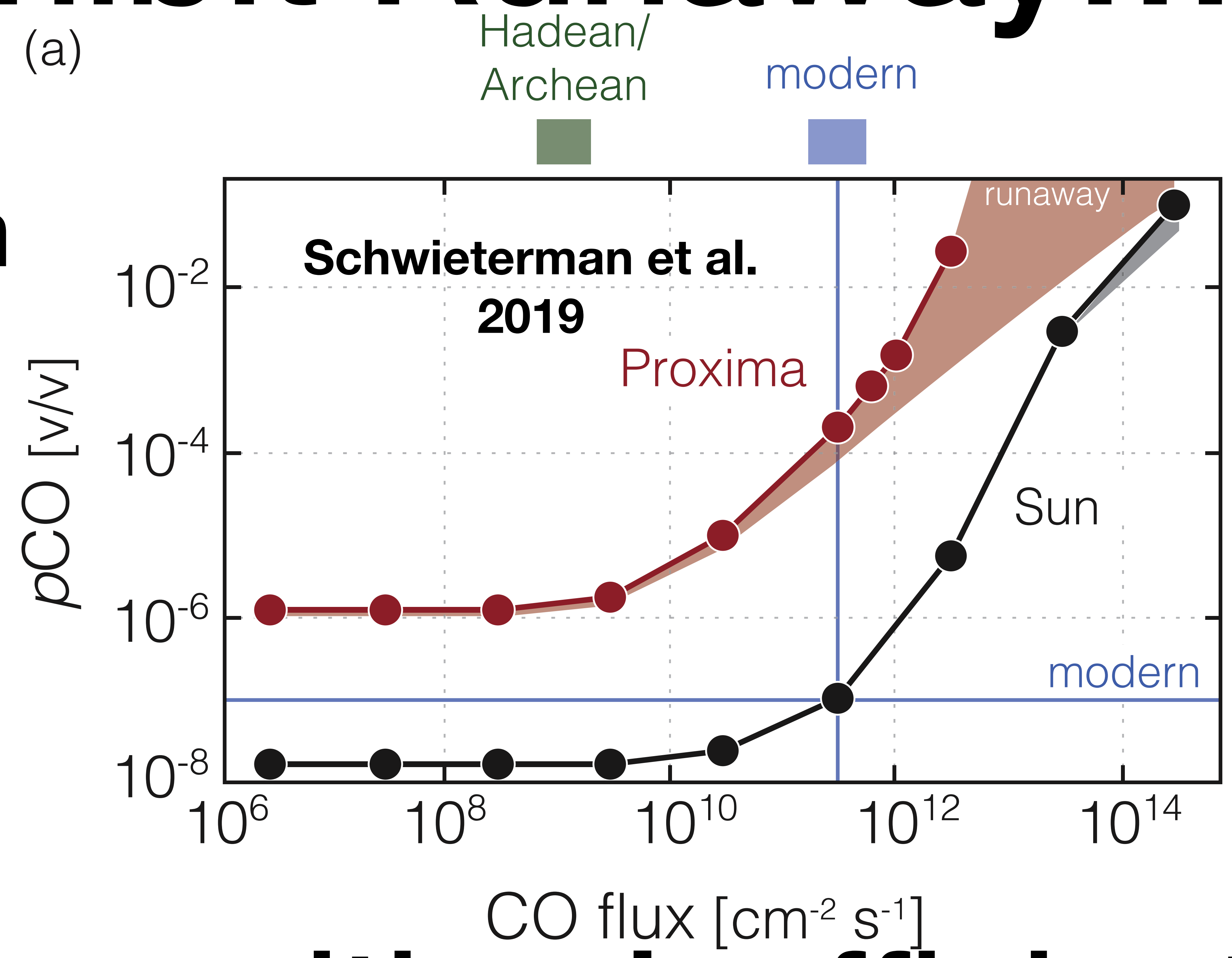
NH_3 Runaway is Robust to Boundary Conditions

- Case study: NH_3 in H_2-N_2 atmosphere ("Cold Haber World", Seager et al. 2013)
- NH_3: Reactive and well-studied, <u>not</u> for excellence as biosignature (Huang et al. 2022)



Surface Deposition <u>Can</u> Inhibit Runaway…

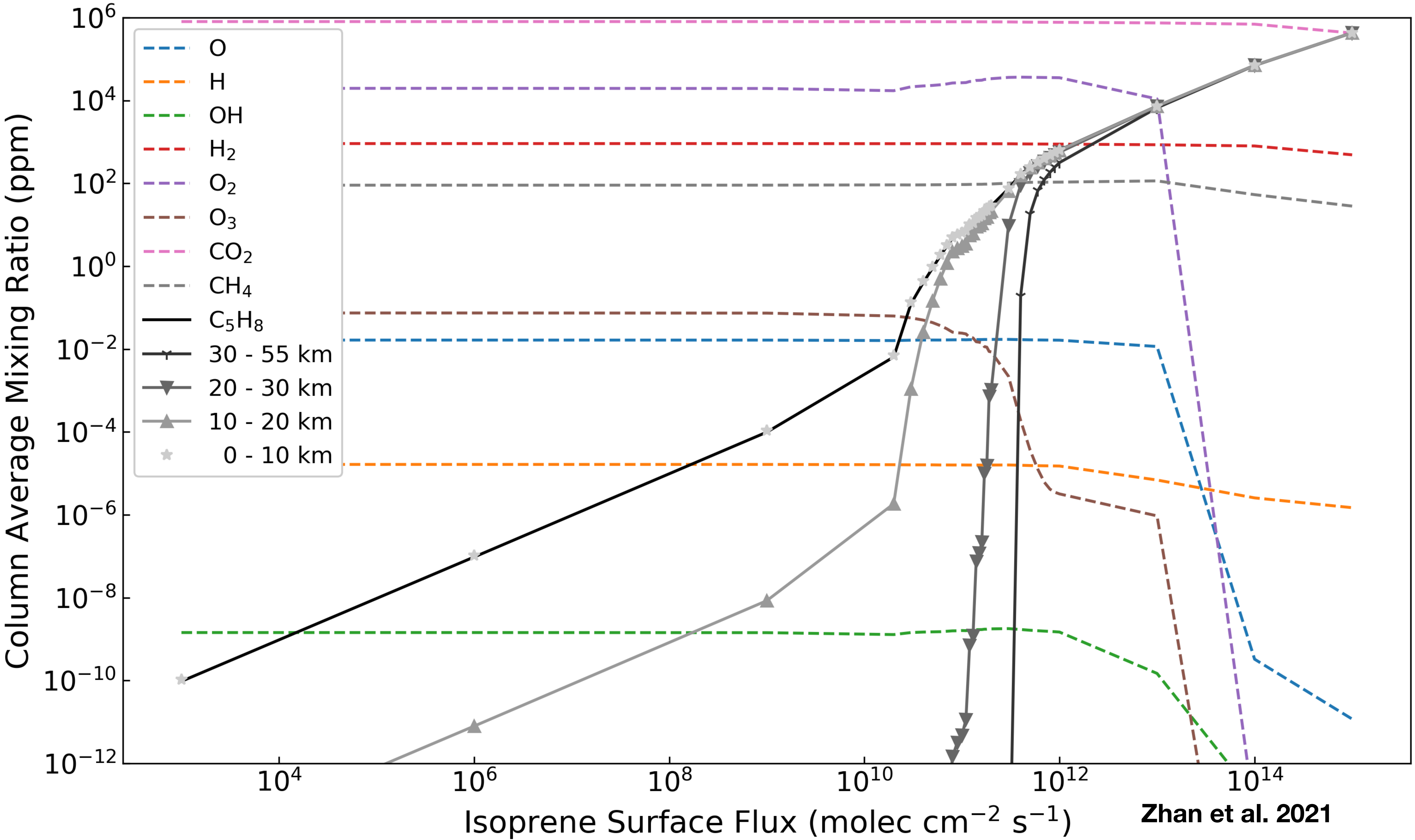
- E.g., NH_3 undetectable if surface deposition efficient (Huang et al. 2022)
- Surface deposition inefficient for insoluble gases (e.g., CO; Kharecha et al. 2005, Schwieterman et al. 2019)



…Biology Can <u>Make</u> Surface Deposition Inefficient

- Modern Earth: $v_{O2,eff}$ = **10^{-8}** cm s^{-1} vs **10^{-4}** cm s^{-1} allowed by theory (Kharecha et al. 2005)
- O_2 has saturated surface, making O_2 deposition inefficient (Daines et al 2017, Galvez et al 2020)

$$\boxed{\Phi_{gas} = r_{gas} n_{atm} v_{dep,gas}}$$

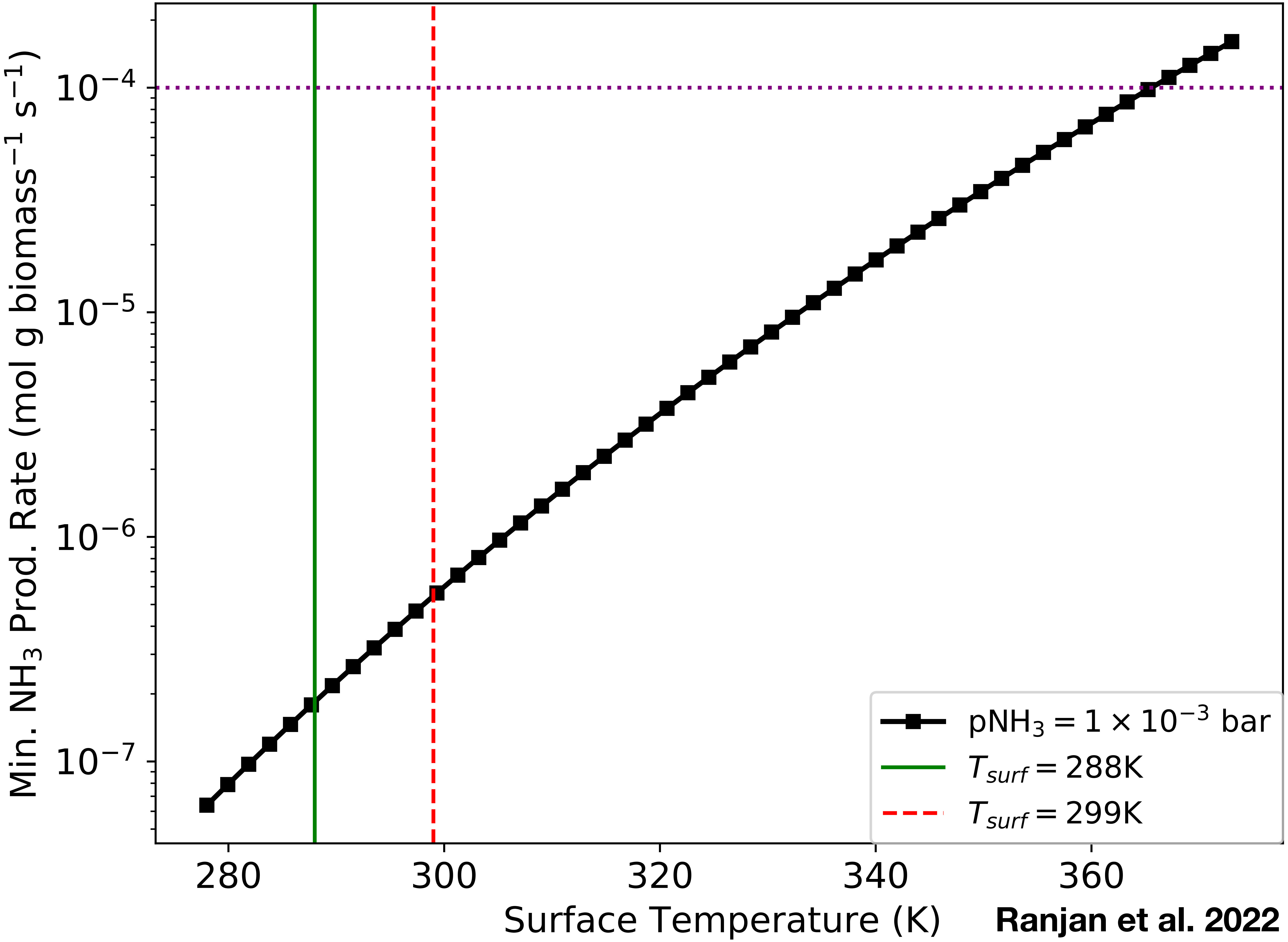


O
H
OH
H_2
O_2
O_3
CO_2
CH_4
C_5H_8
30 - 55 km
20 - 30 km
10 - 20 km
0 - 10 km
Column Average Mixing Ratio (ppm)
Isoprene Surface Flux (molec cm^{-2} s^{-1})
Zhan et al. 2021

Runaway:Thermodynamically Allowed

$N_2 + 3H_2 \rightarrow 2NH_3$

- NH_3 runaway: thermodynamically allowed



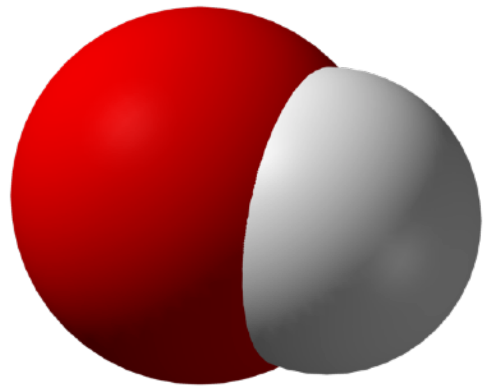
Ranjan et al. 2022

σ_{H2O} controls OH (anoxic)…

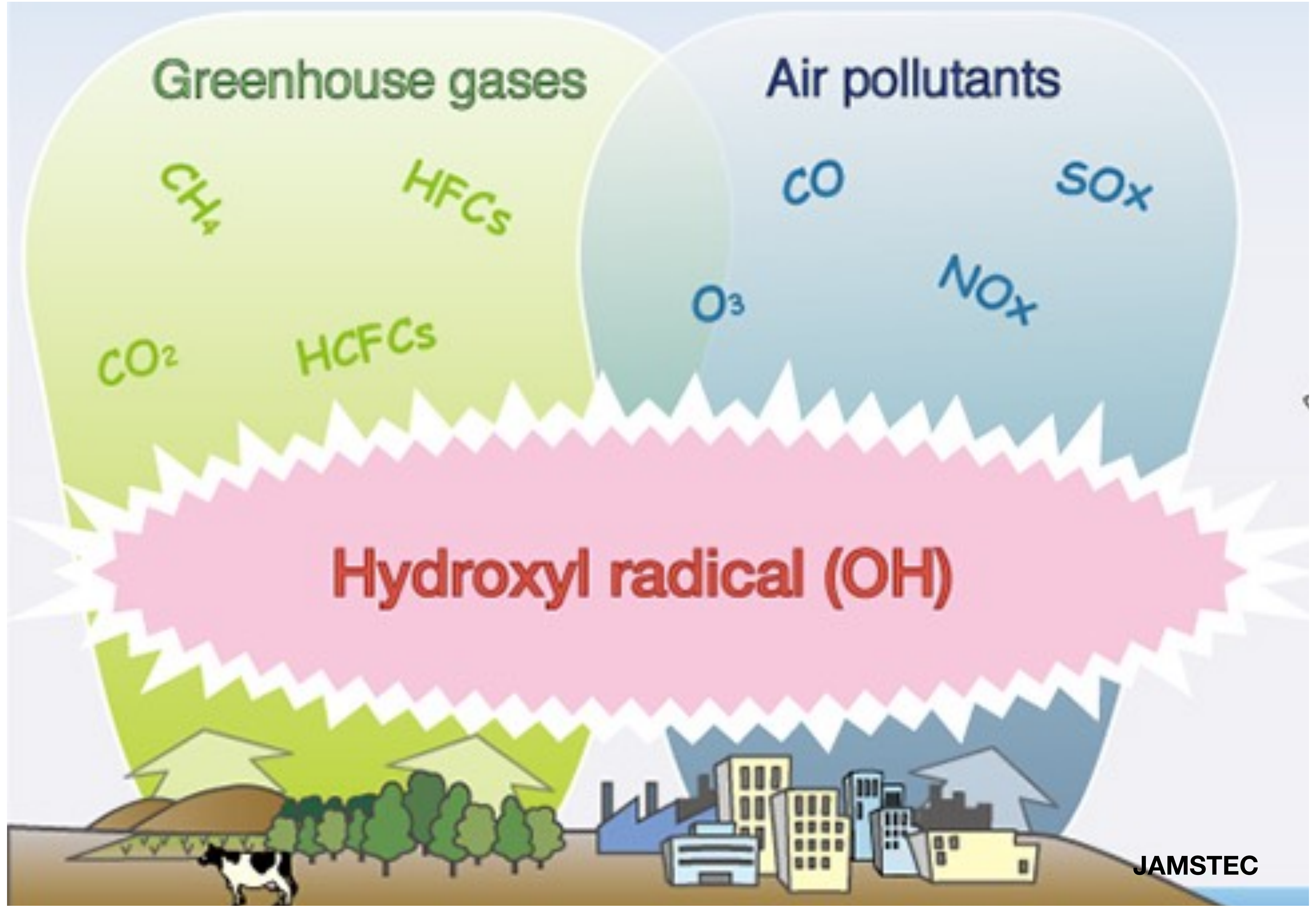
Anoxic Atmospheres
$H_2O + h\nu \rightarrow H + \underline{OH}$

Oxic Atmospheres
$O_3 + h\nu \rightarrow O(^1D) + O_2$
$O(^1D) + H_2O \rightarrow 2\underline{OH}$

…OH Controls Atm. Composition


Wikimedia Commons

- OH controls composition (CH_4, CO, SO_2, etc…)
- OH controls stability (CO_2-rich, e.g. Mars)



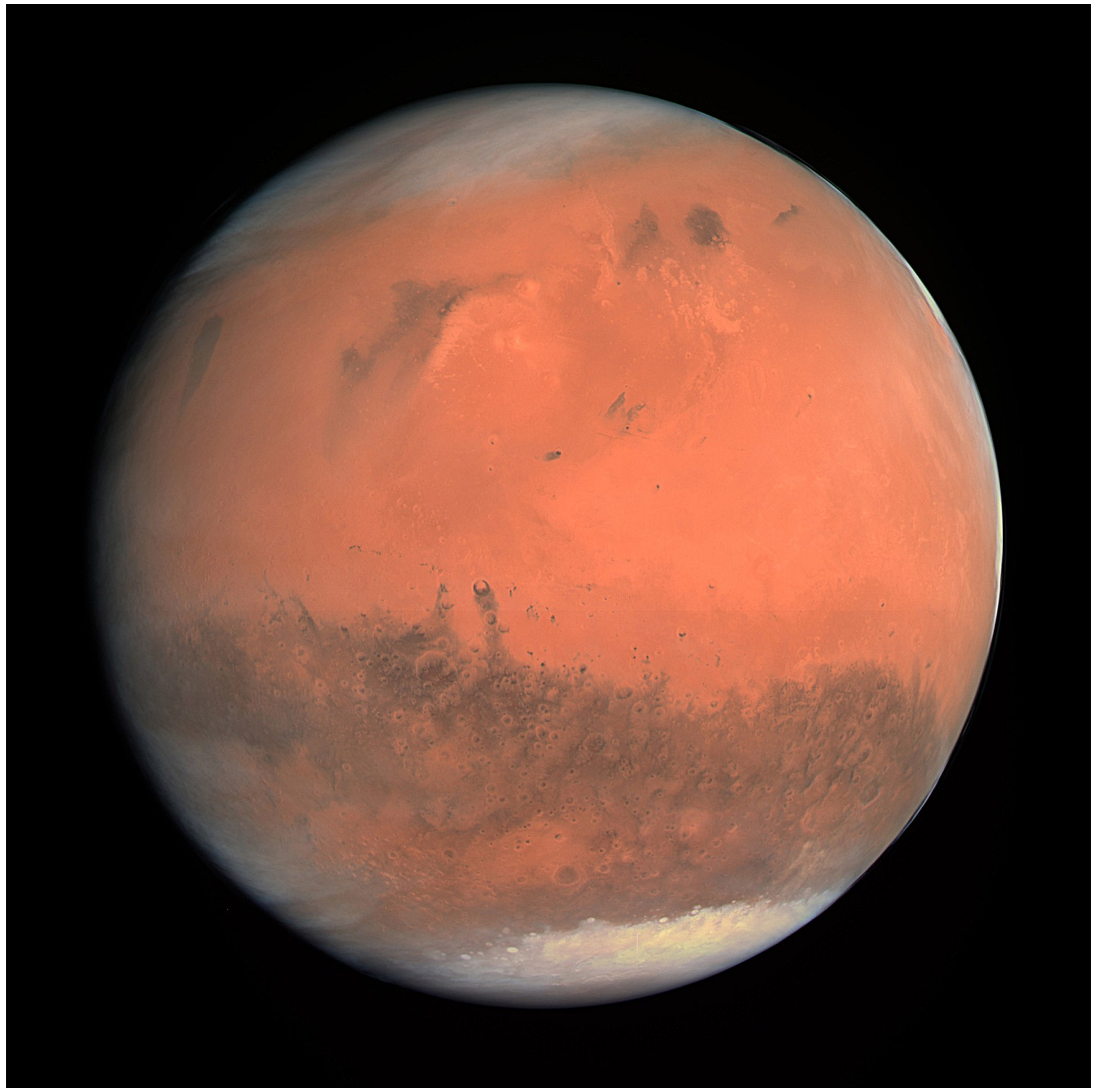
Basic Problem

$$CO_2 + h\nu \rightarrow CO + O$$

$$CO + O \not\rightarrow CO_2$$

$$O + O + M \rightarrow O_2 + M$$
$$CO + O + M \rightarrow CO_2 + M$$

Mars



NASA

Trace $H_2O + h\nu$ Stabilizes Martian CO_2

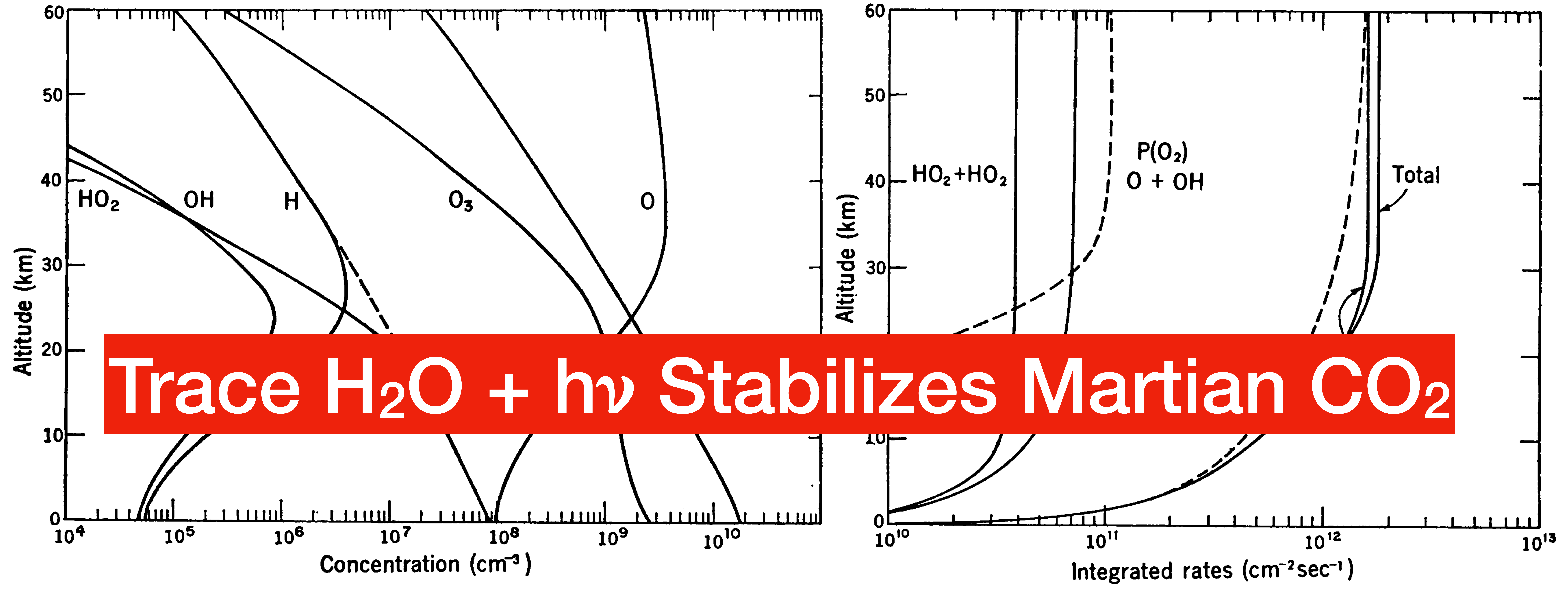
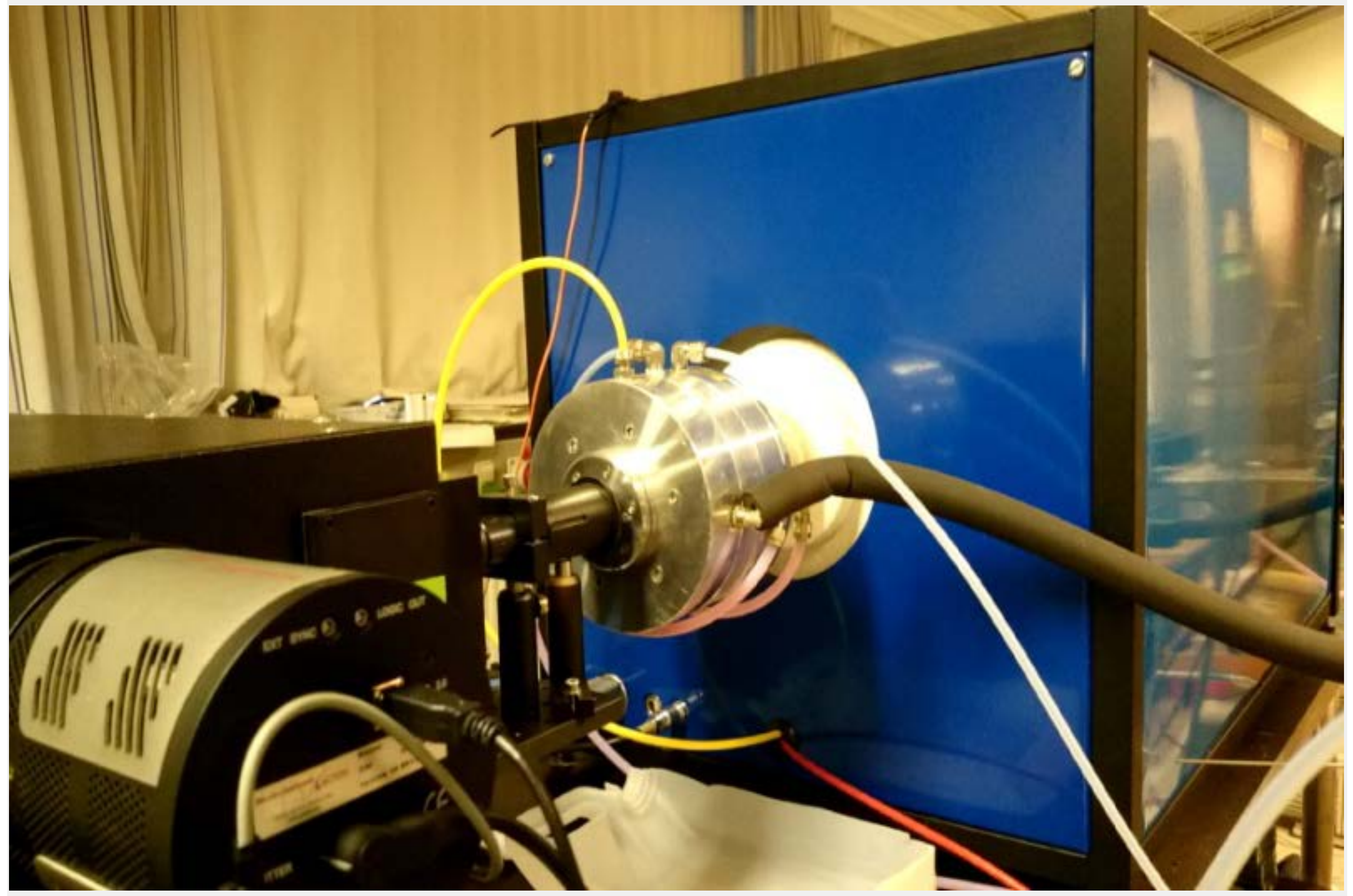


Fig. 1 (left). Concentrations of principal constituents in the martian atmosphere. The surface temperature is 220°K. The eddy diffusion coefficient is 1.5×10^8 cm² sec⁻¹. The curve for odd hydrogen, shown as a broken line between the portions labeled HO_2 and H, is plotted for a density of odd hydrogen 5×10^{-10} times the CO_2 density. The O_2 and CO densities are, respectively, 1.3×10^{-3} and 8×10^{-4} times the CO_2 density. Fig. 2 (right). Integrated rates of reactions important in CO_2 and O_2 formation and loss. The rates are integrated from the martian surface to height z. The curve labeled P(O) is the integrated photolysis rate for CO_2. The contribution from $O + O + CO_2$ is only 2.3×10^9 cm² sec⁻¹ and is not shown.

McElroy & Donahue 1971

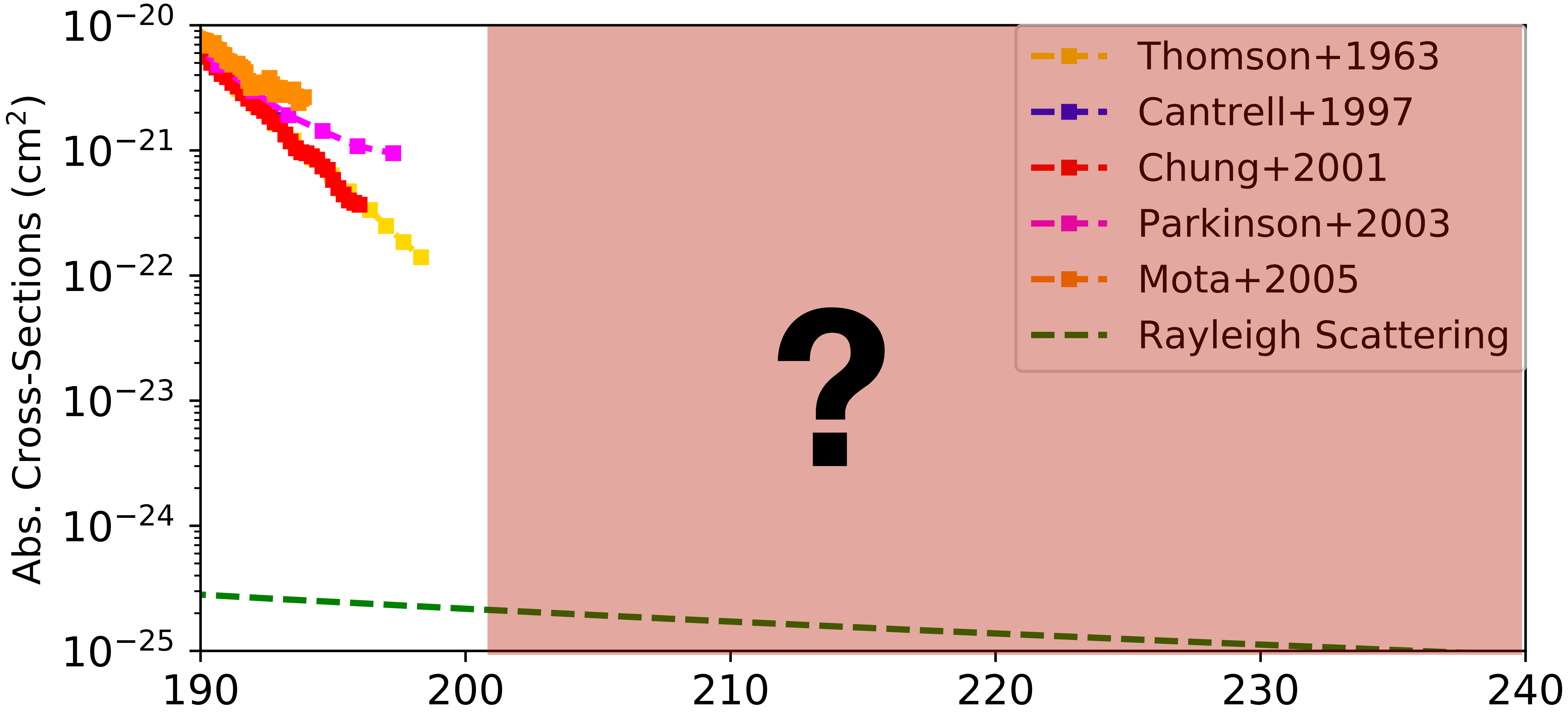
Measuring σ_{H2O}

- Gas flow cell measurements @ 292 K
  - Anoxic (N_2 purged); sub-saturation H_2O
  - Triplicate measurements
- **First NUV** (>200 nm) **H_2O cross-sections ever measured at habitable conditions** (T<373K)

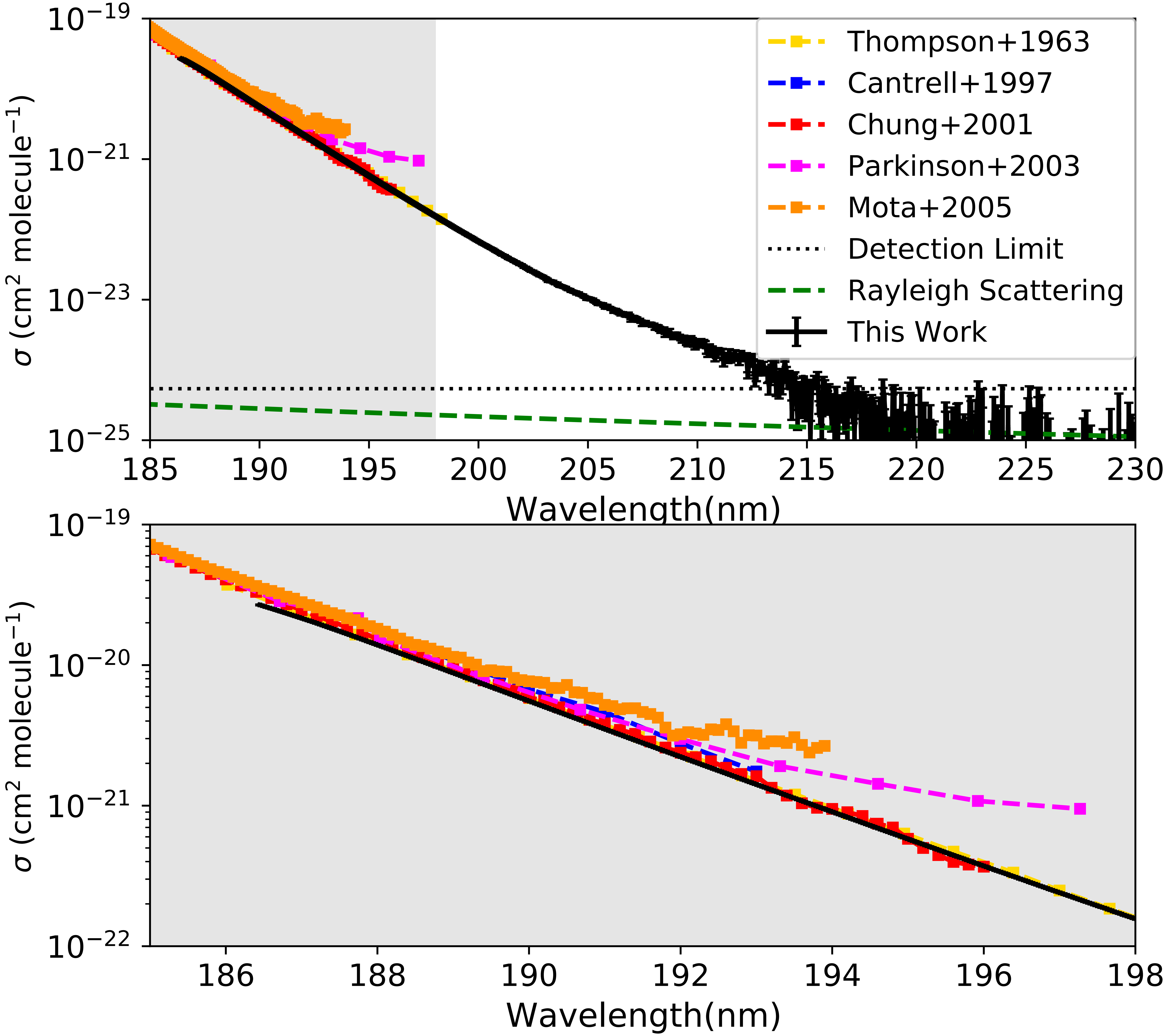


A. Fateev

Technical University of Denmark DTU



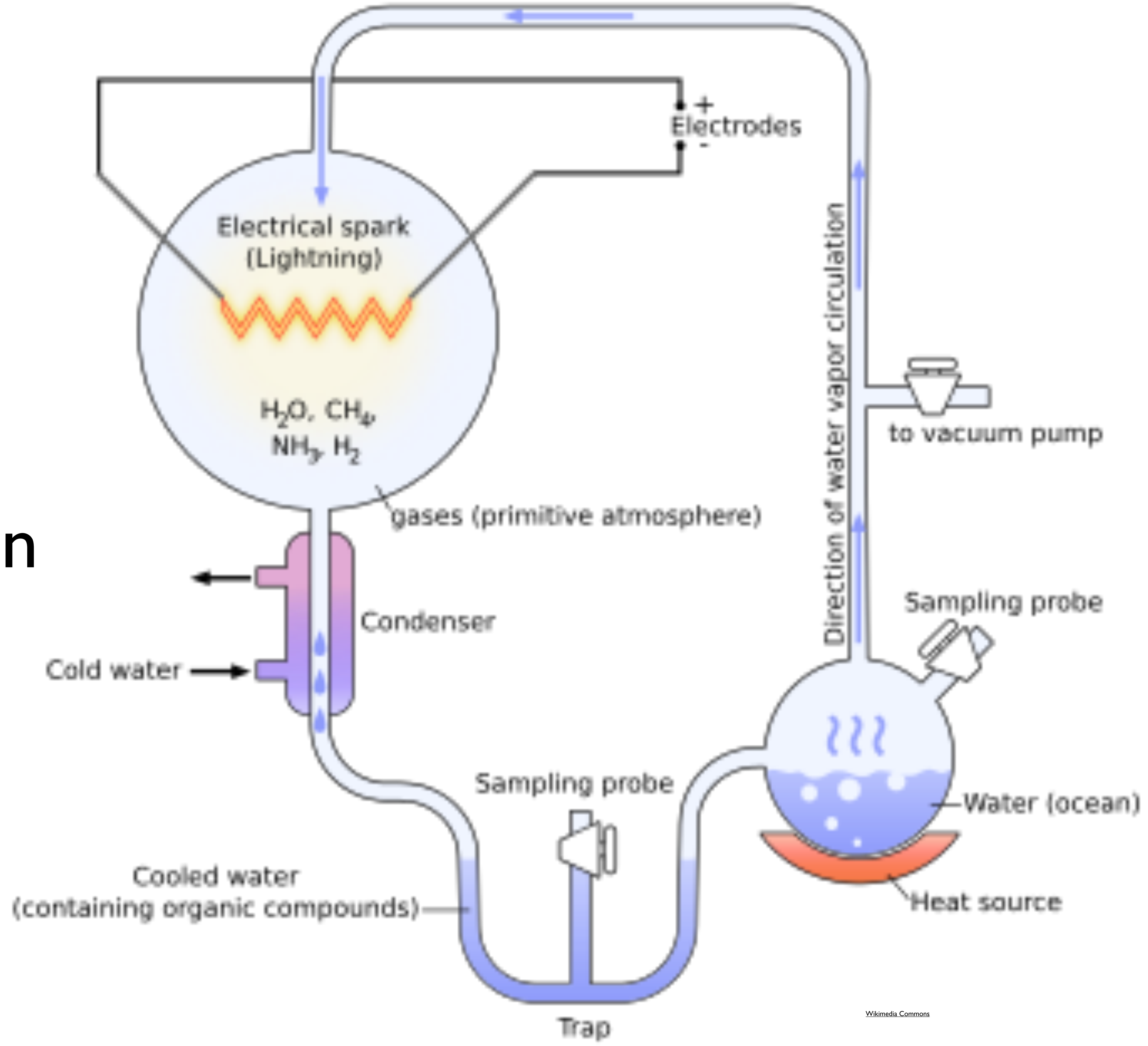
Thomson+1963
Cantrell+1997
Chung+2001
Parkinson+2003
Mota+2005
Rayleigh Scattering
?
Abs. Cross-Sections (cm^2)
10^{-20}
10^{-21}
10^{-22}
10^{-23}
10^{-24}
10^{-25}
190
200
210
220
230
240



Thompson+1963
Cantrell+1997
Chung+2001
Parkinson+2003
Mota+2005
Detection Limit
Rayleigh Scattering
This Work
σ (cm^2 molecule^{-1})
10^{-19}
10^{-21}
10^{-23}
10^{-25}
185
190
195
200
205
210
215
220
225
230
Wavelength(nm)
σ (cm^2 molecule^{-1})
10^{-19}
10^{-20}
10^{-21}
10^{-22}
186
188
190
192
194
196
198
Wavelength(nm)

1950s: Miller-Urey Synthesis

- 1952: Abiotic amino acids
- 1961: abiotic nucleobases
- Simple AA, nucleobases, sugars: synthesized readily on Earth, in space
- Raw materials+energy=life?



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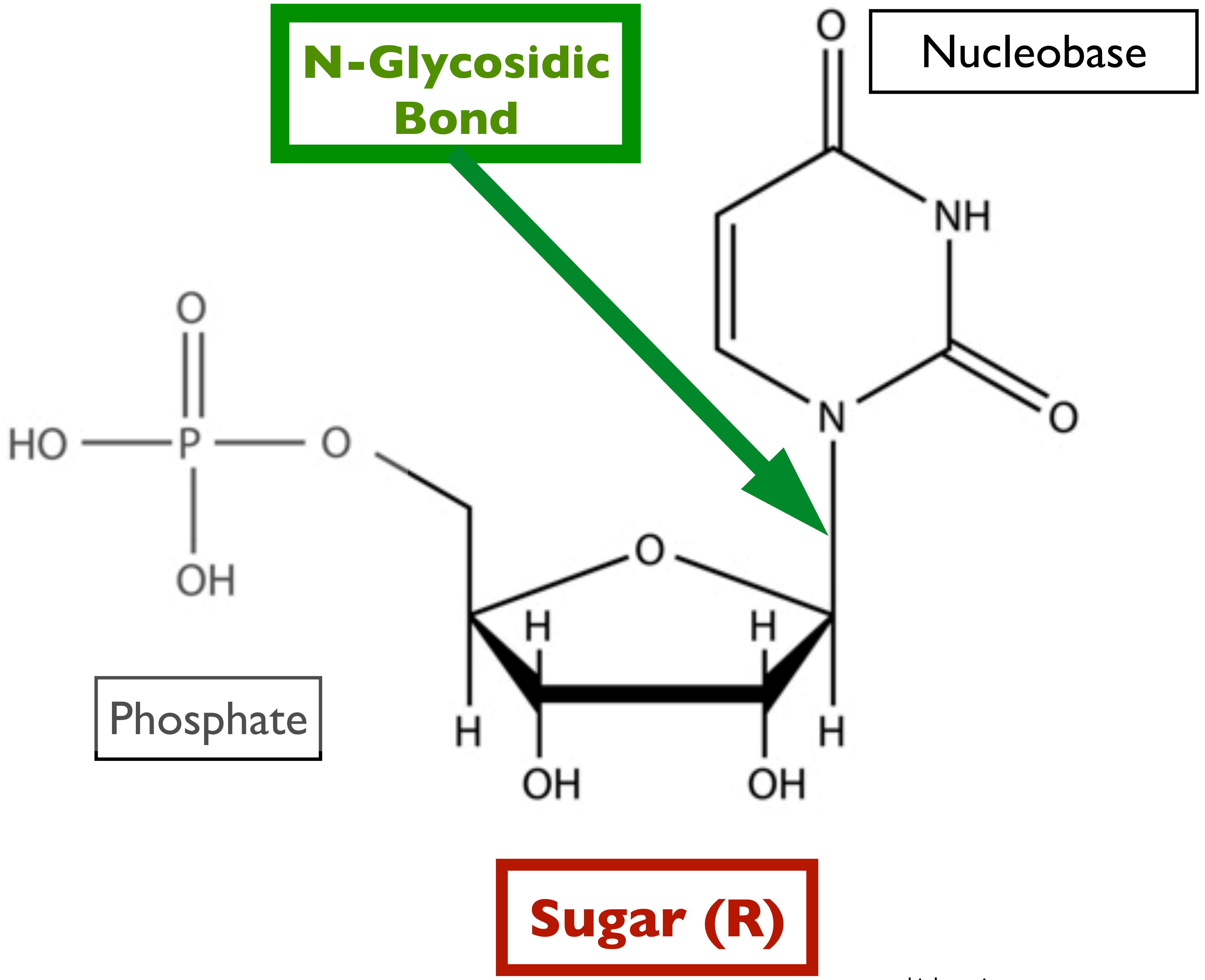
'70s-2000s: Challenges

- AA: no complex AAs, no polymerization,no bioselectivity
- Sugars: asphaltization problem
- Nucleic acids (RNA)
  - Potential key to origin of life (RNA world)
  - Nucleobases, but no nucleo<u>tides</u>

$$(CH_2O)_n + CH_2O \rightarrow (CH_2O)_{n+1}$$

Wikimedia commons



biologywise.com

2009-present: Advances

- 2009: Prebiotic path to U, C nucleotides
- 2012: Prebiotic path to 2, 3-C sugars
- 2015: Reaction network (U, C, sugars, amino acids, lipid precursors)
- Key pathway requirements
  - Liquid water, HCN, phosphate
  - **UV light, sulfidic anions** (e.g, HS^-, HSO_3^-)**, NOx** (NO_2^-, NO_3^-)

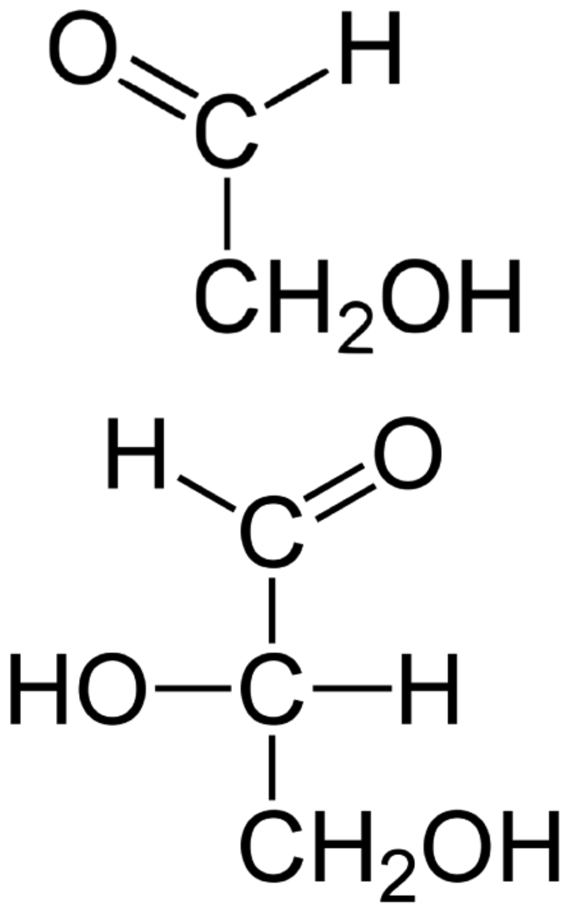
U, C, other pyrimidines $\xrightarrow[\text{Amplification}]{h\nu}$ U, C

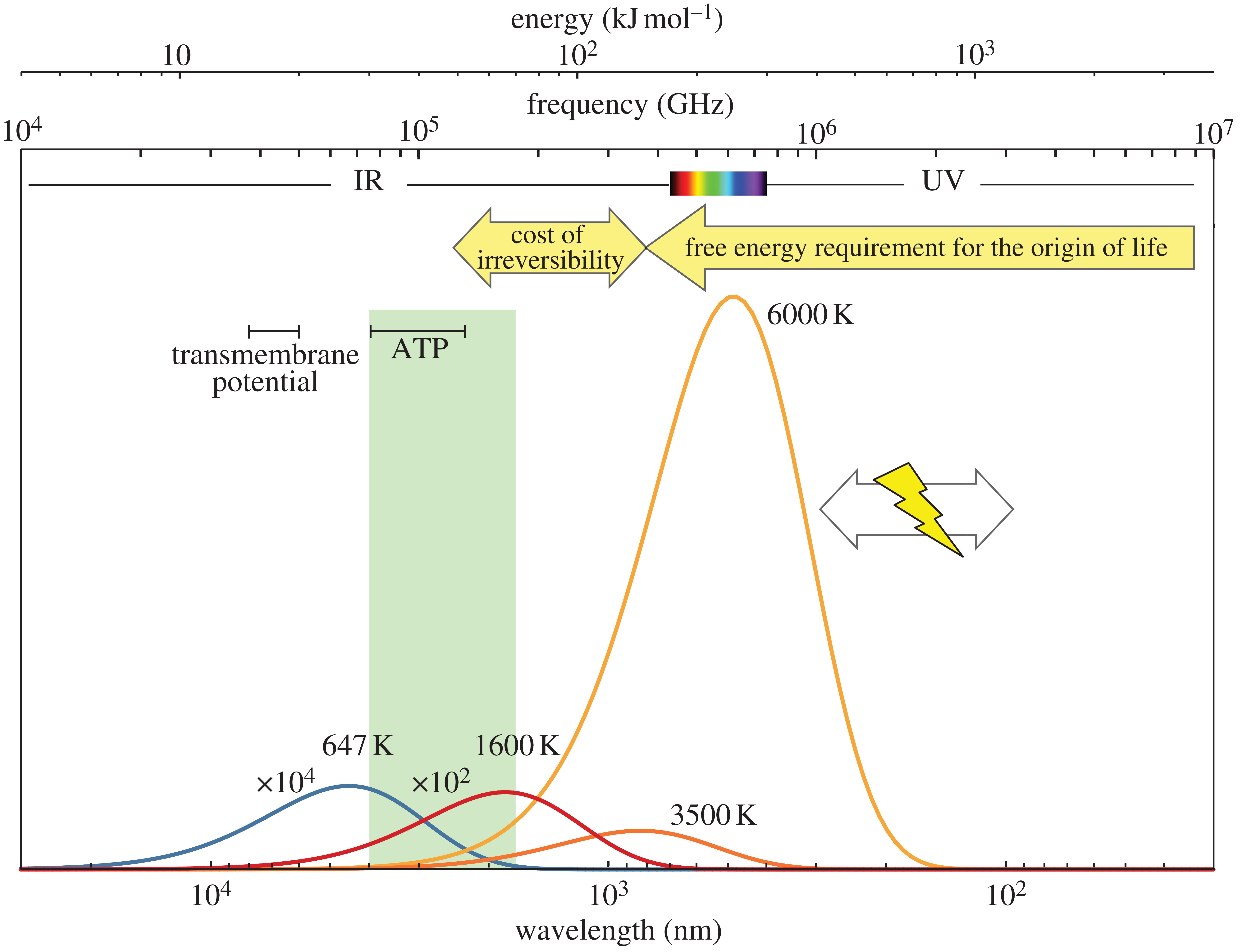
Formose Reaction (nonselective)

Wikimedia Commons

vs

Cyanosulfidic Pathways (selective)




energy (kJ mol−1)
10
10^2
10^3
frequency (GHz)
10^4
10^5
10^6
10^7
IR
UV
cost of irreversibility
free energy requirement for the origin of life
6000 K
transmembrane potential
ATP
647 K
1600 K
×10^4
×10^2
3500 K
10^4
10^3
10^2
wavelength (nm)

Pascal+2013

UV Light: Foe…or Friend?

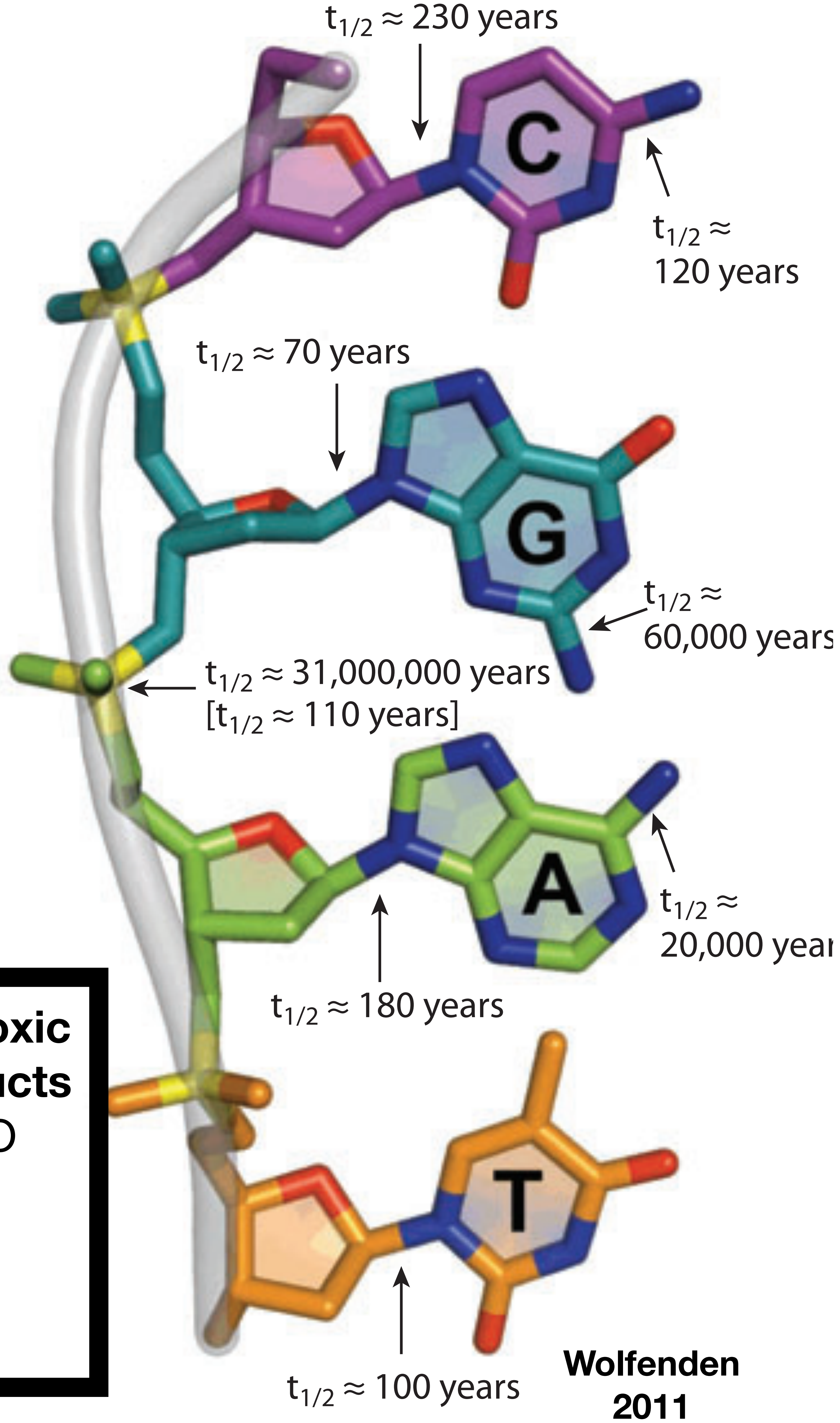
- O_2: requires sophisticated machinery (Adele 2002, Horandl+2018)
- H_2O: corrodes proteins, nucleic acids (NRC+2007; Benner 2014, Adam+2018)
- Key: does “good” outweigh “bad”?

Aerobic/Facultive Microbes

O_2 → **Metabolism** → **Toxic Products** → **Detoxifying Pathways** → **Nontoxic Products**

Toxic Products	Detoxifying Pathways	Nontoxic Products
O_2-	Superoxide dismutase	H_2O
OH·	Catalase	O_2
O_2·	Peroxidase	
H_2O_2		

After https://www.ifmed.uniba.sk/fileadmin/ilf/Pracoviska/ustav-mikrobiologie-a-imunologie/ANAEROBIC_BACTERIA.pdf



Wolfenden 2011

UV: Abundant on Early Earth

- **Experimental**: Shown to drive diverse syntheses (Sagan+1971, Rosenberg+2008, Powner+2009, Barks+2010, Sarker+2013, Patel+2015, Bonfio+2017, etc…)
- **Theoretical**: Most abundant energy source; directly affect electronic states of molecules (Deamer+2010, Pascal+2012)
- **Historical**: Biogenic nucleobases show evidence of high-UV selection pressure (Rios & Tor 2013, Beckstead+2016)

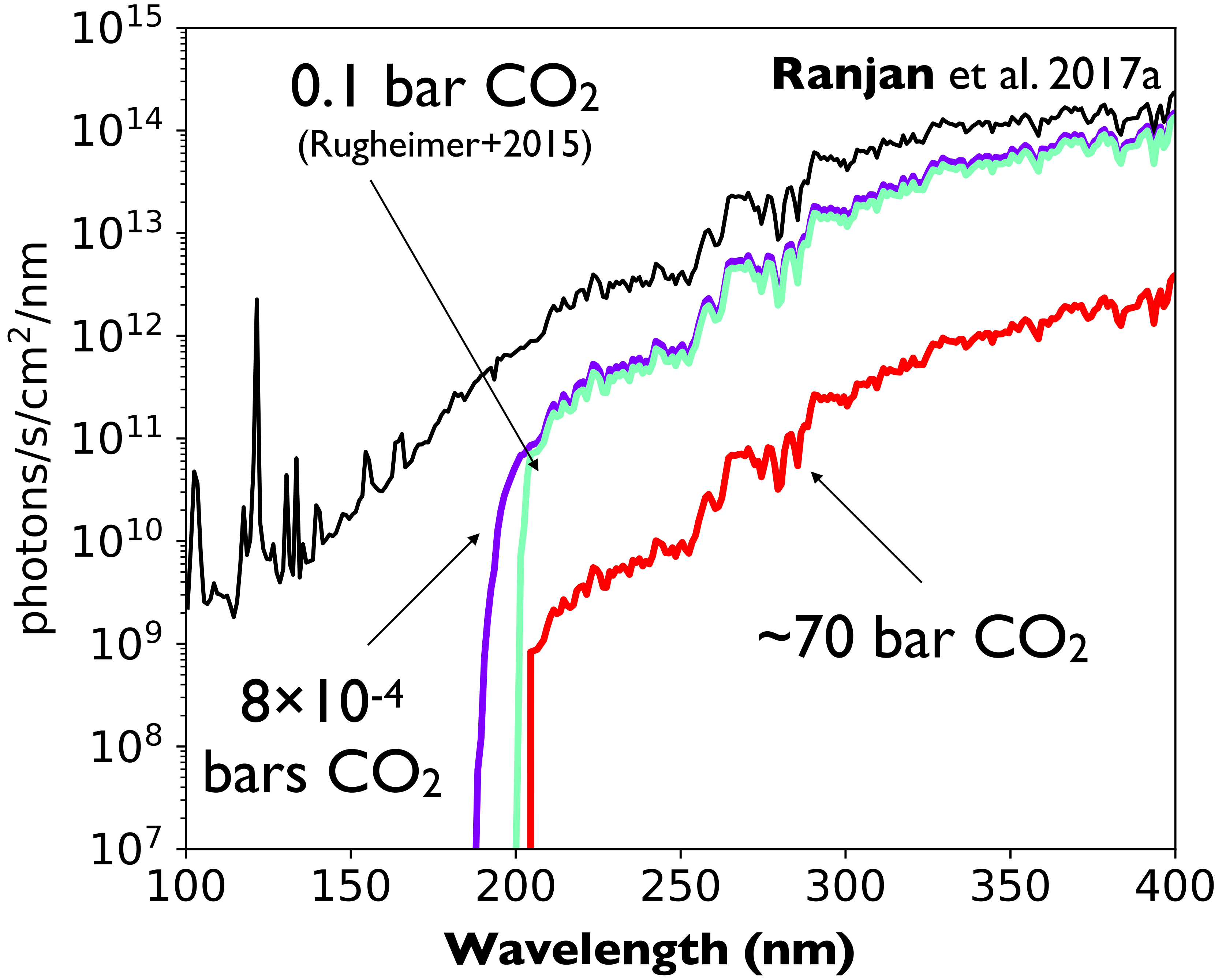
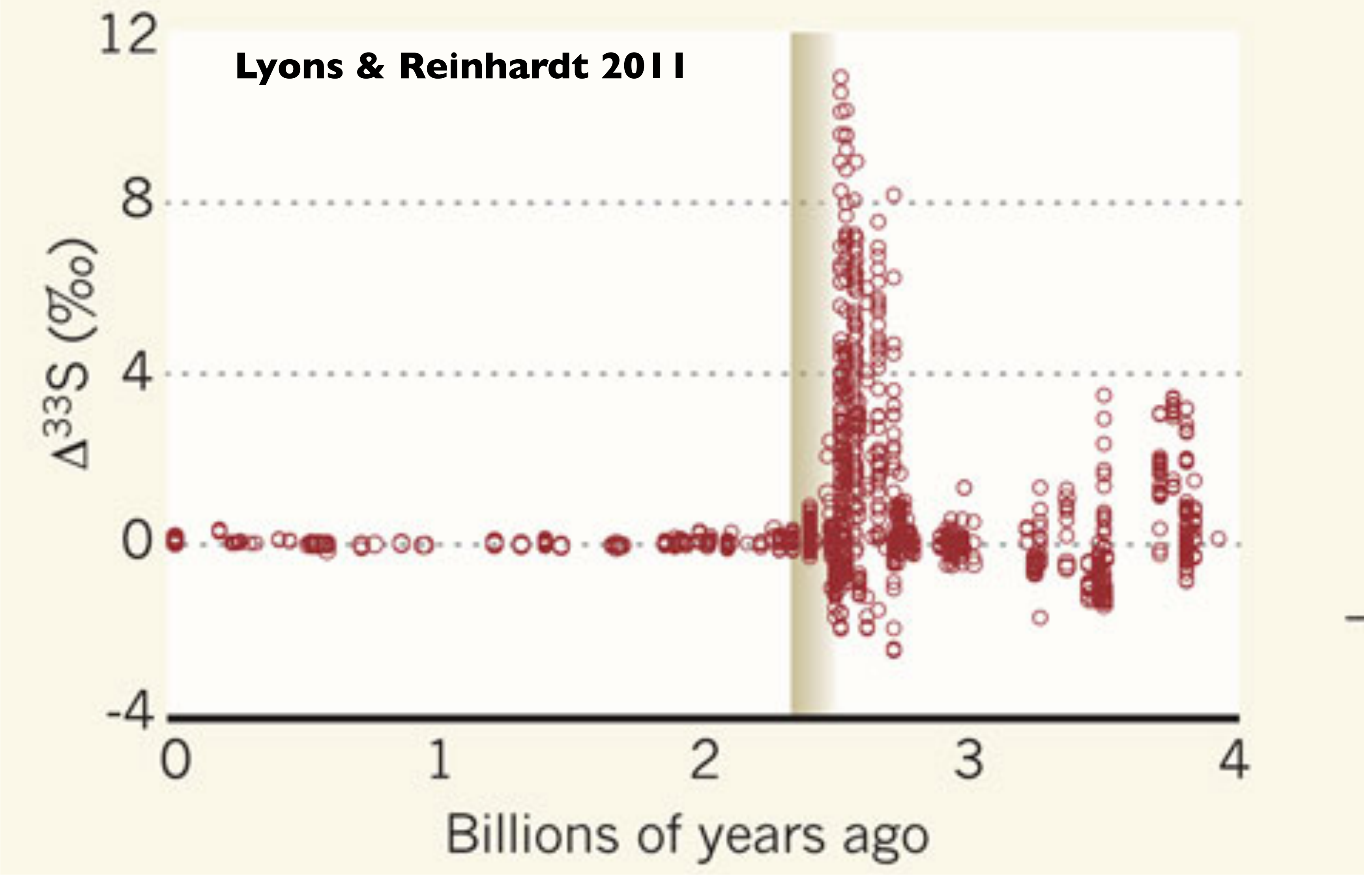


Table 1. Most of the energy flux on the early Earth was in the form of light energy from the sun, just as it is today.

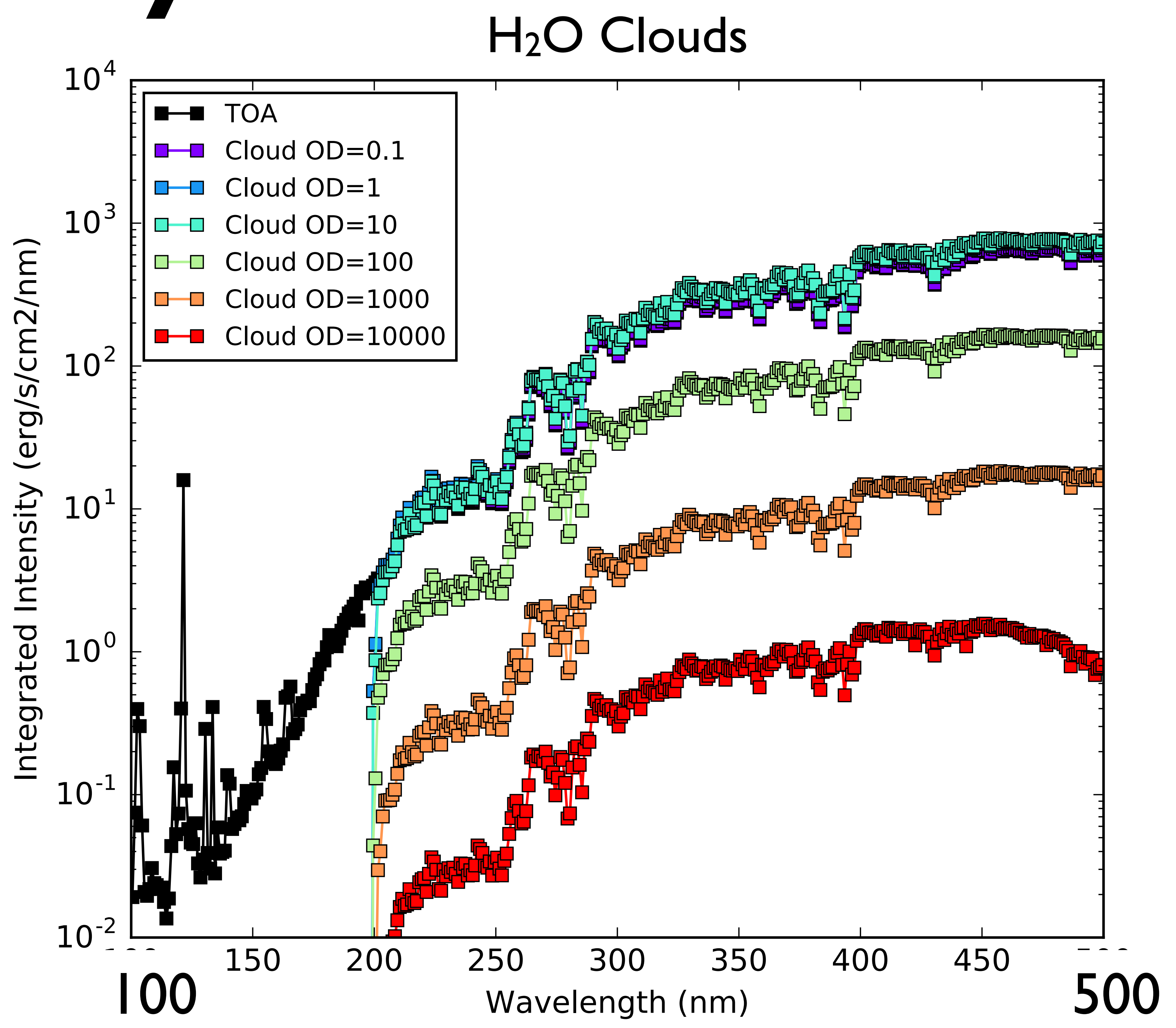
Energy sources on the early Earth (kilojoules $m^{-2}yr^{-1}$)	
Solar radiation (UV<250 nM)	24,000
Shock waves from impacts	200
Radioactivity	117
Electrical discharges	2.9
Volcanoes	5.4
Chemical energy	Significant for the origin of life, not yet estimated.

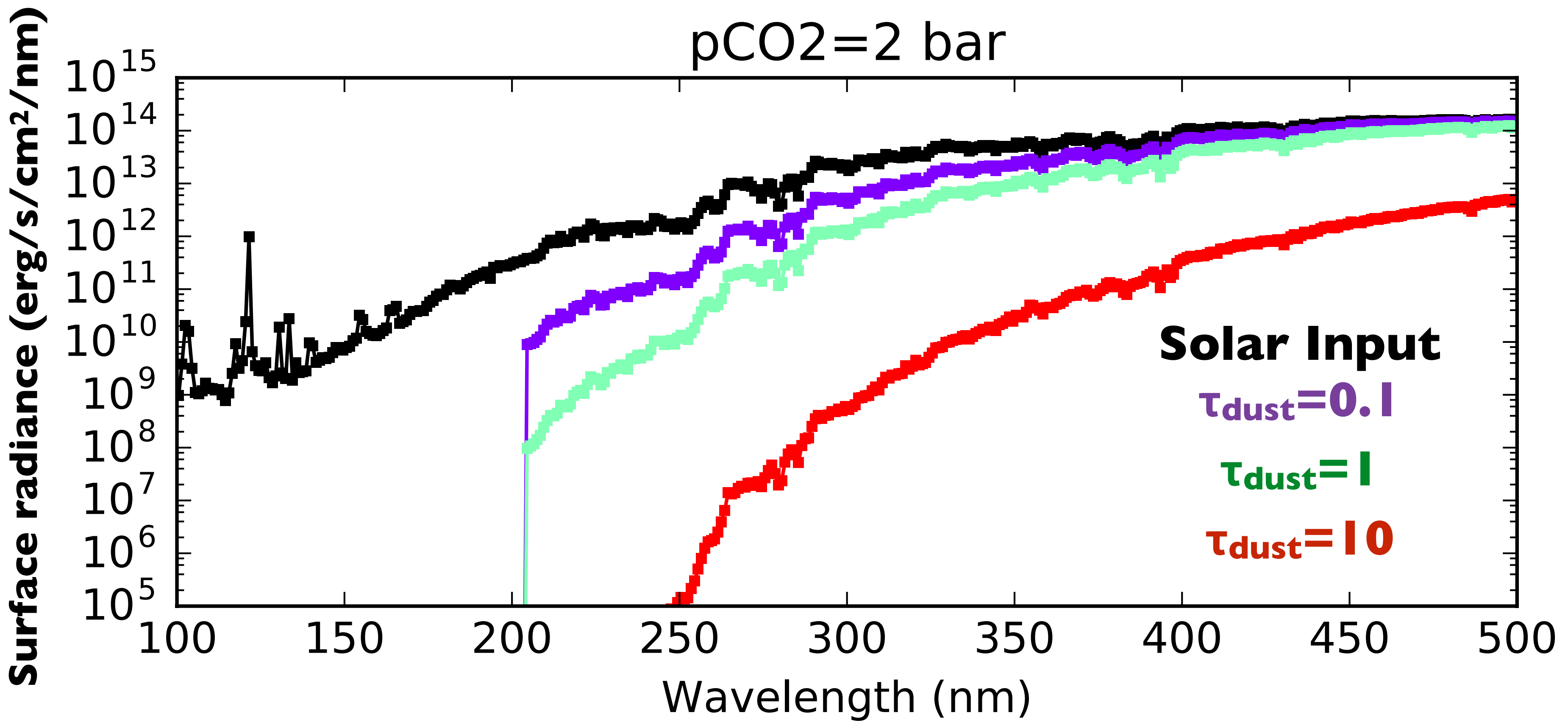
Deamer & Weber 2010



Early Mars: Probably Similar

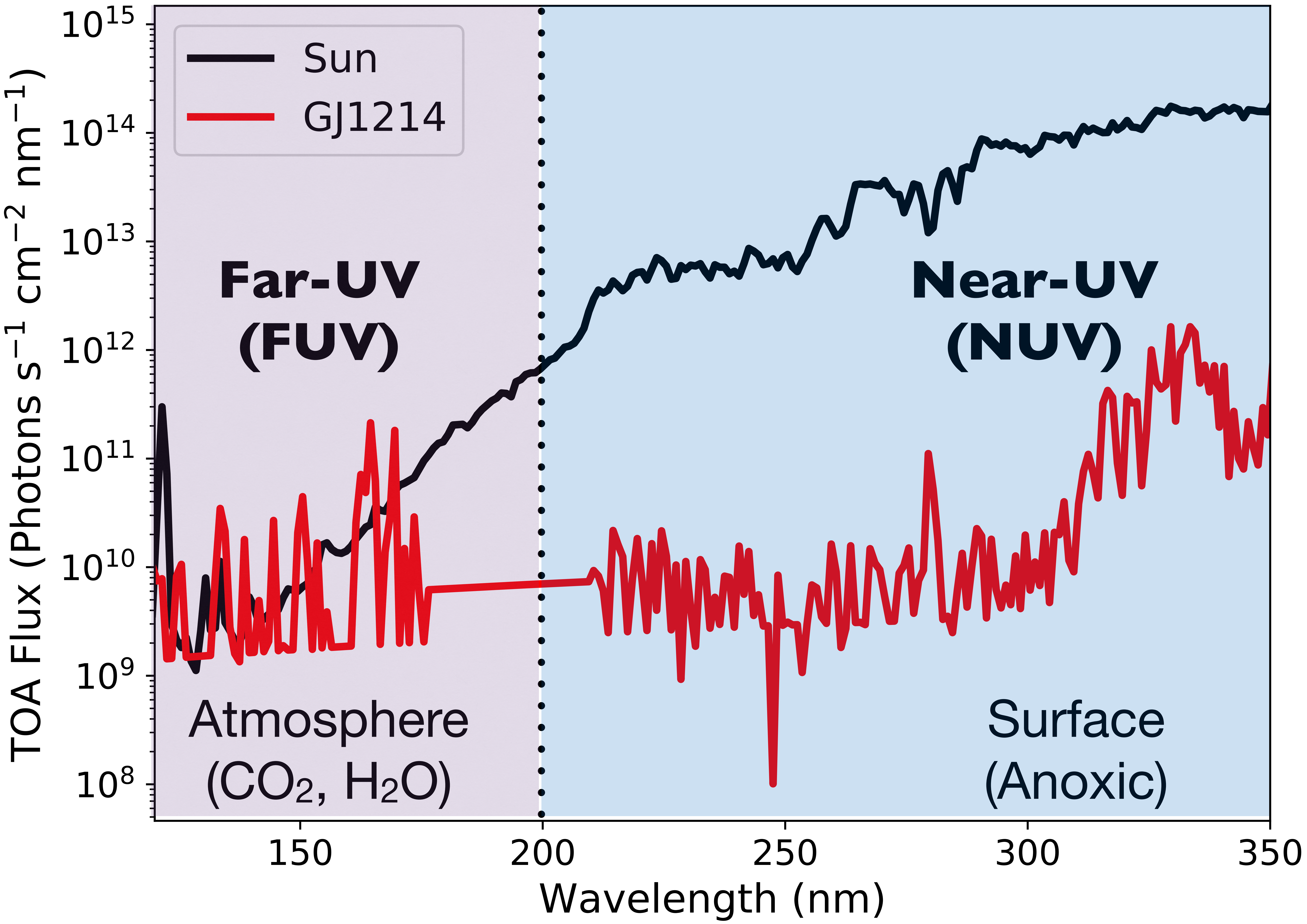
- Clouds: Implausibly thick decks required to affect surface UV
- SO_2/H_2S: need $\geq 10^{-6}$ bar; only transiently possible
- Dust: τ=1-10 can scrub UV; τ~0.5 today
  - More modelling required





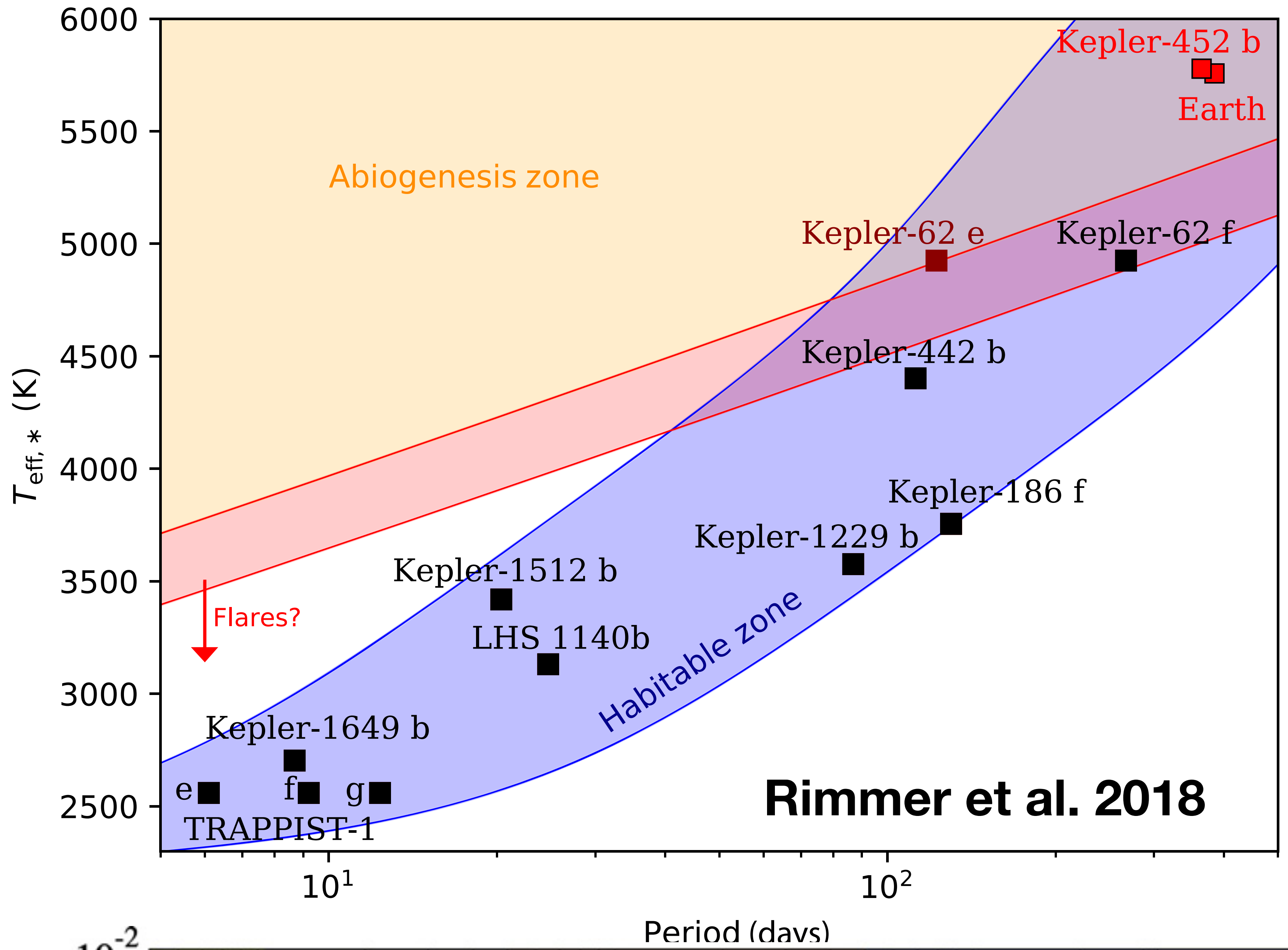
Ranjan et al. (2017), Astrobiology, 17, 687

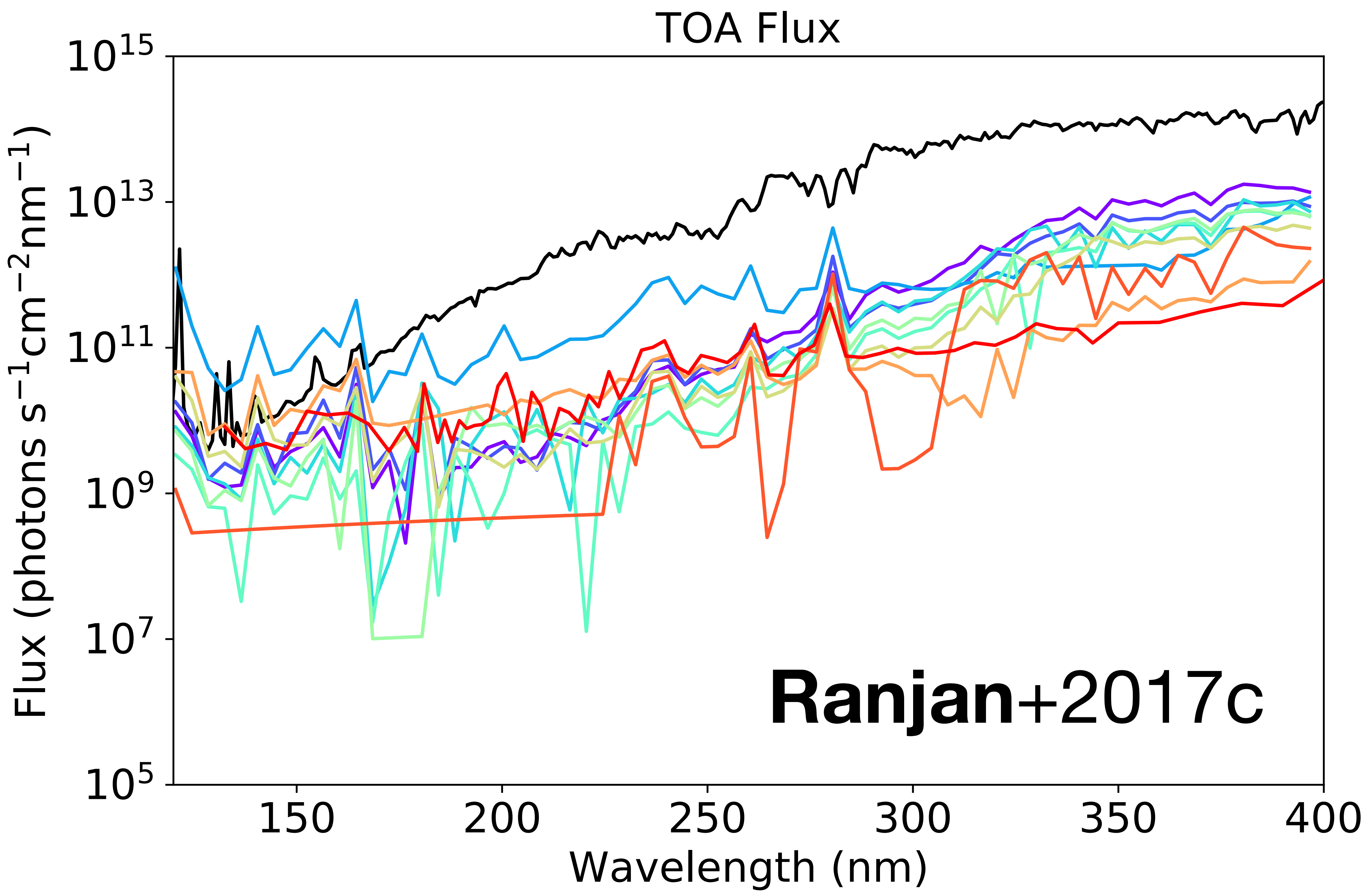
UV Light: An Orientation

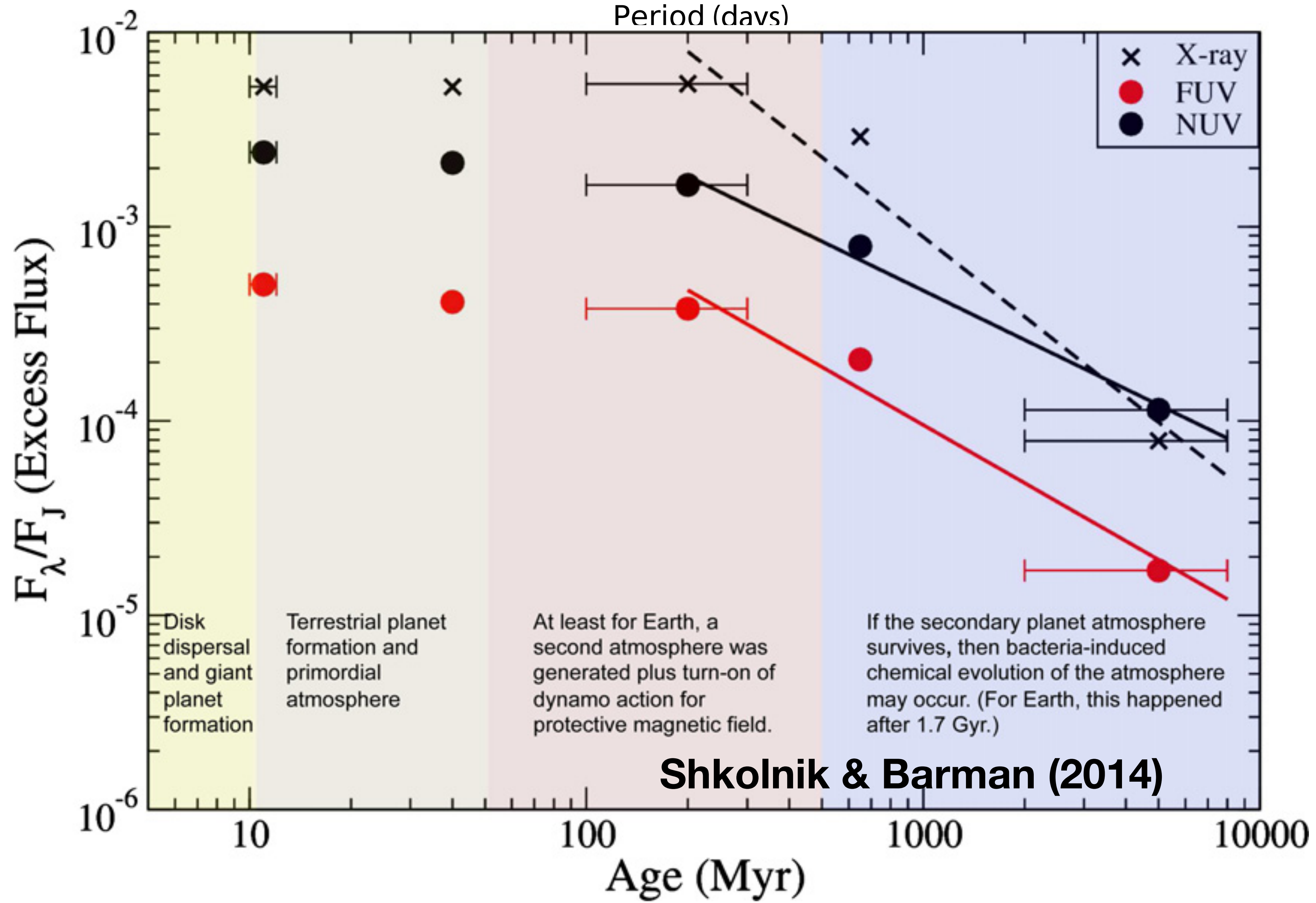


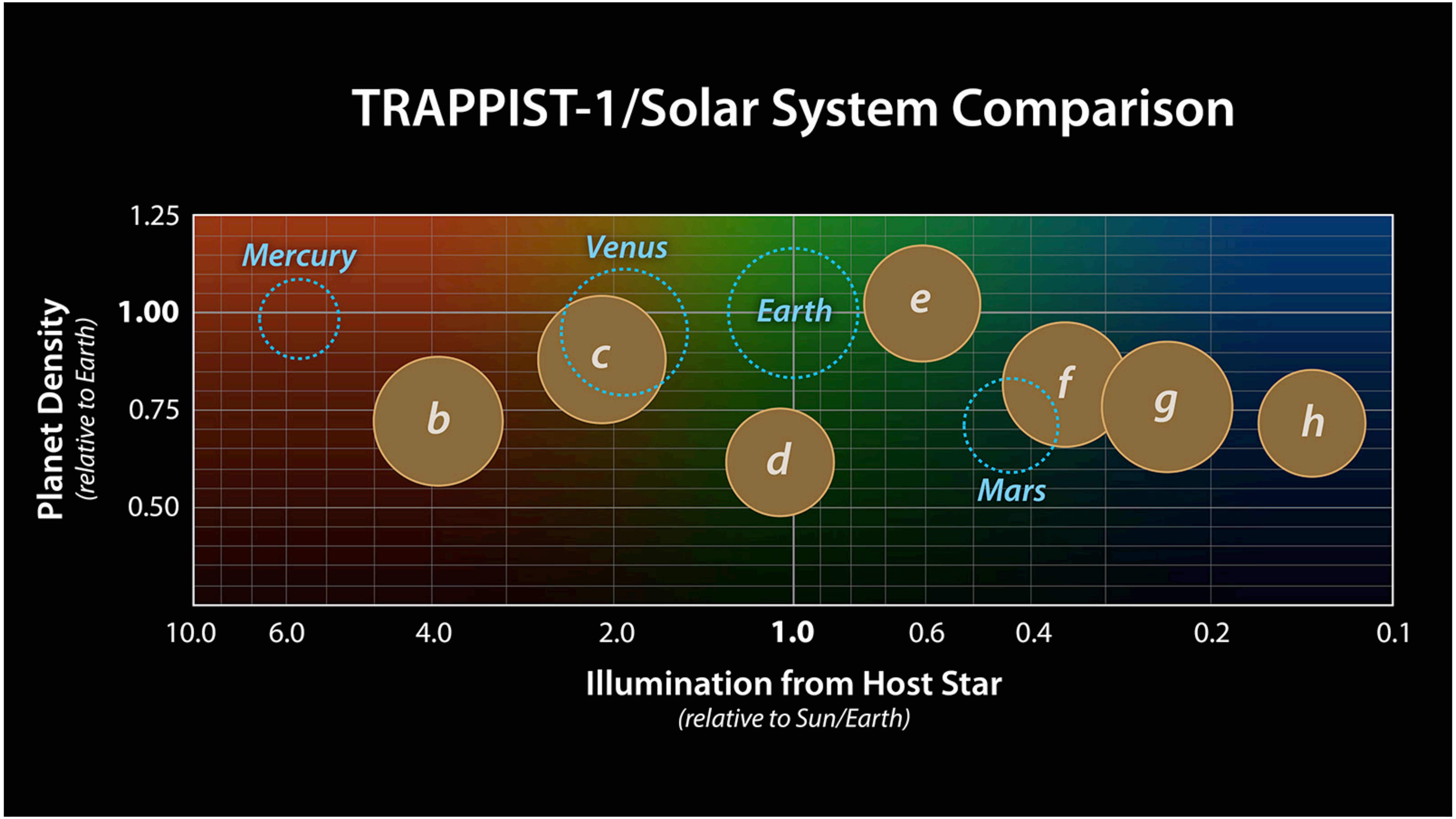
Is UV Required for Abiogenesis?

- Better atmospheric transmission modelling
- Evolution of low-mass star SED
- Reprocessing of high-energy radiation



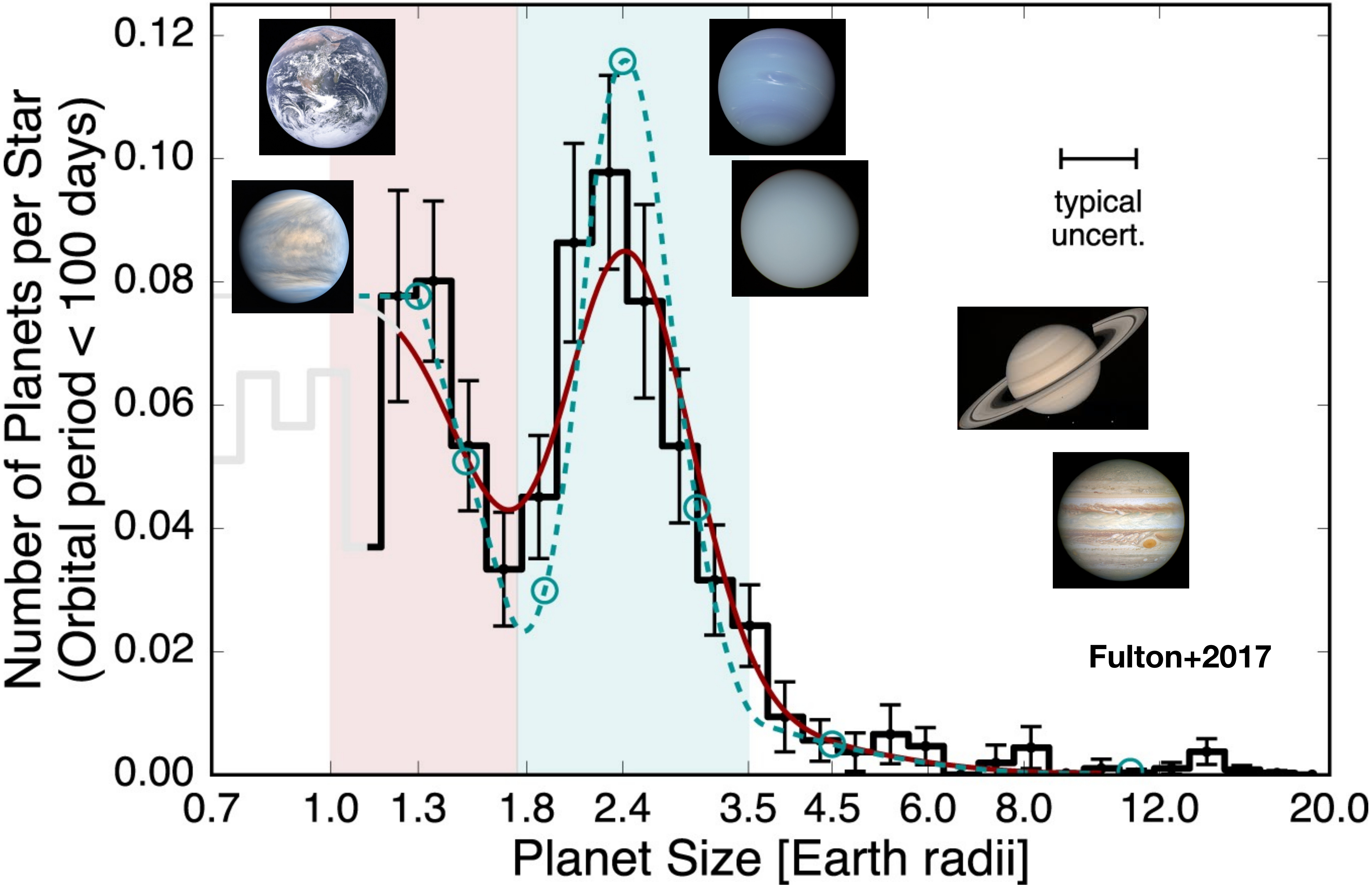






NASA/JPL-Caltech

Potential Diversity of Rocky Exoplanets



Anoxic Biochemistry is Understudied

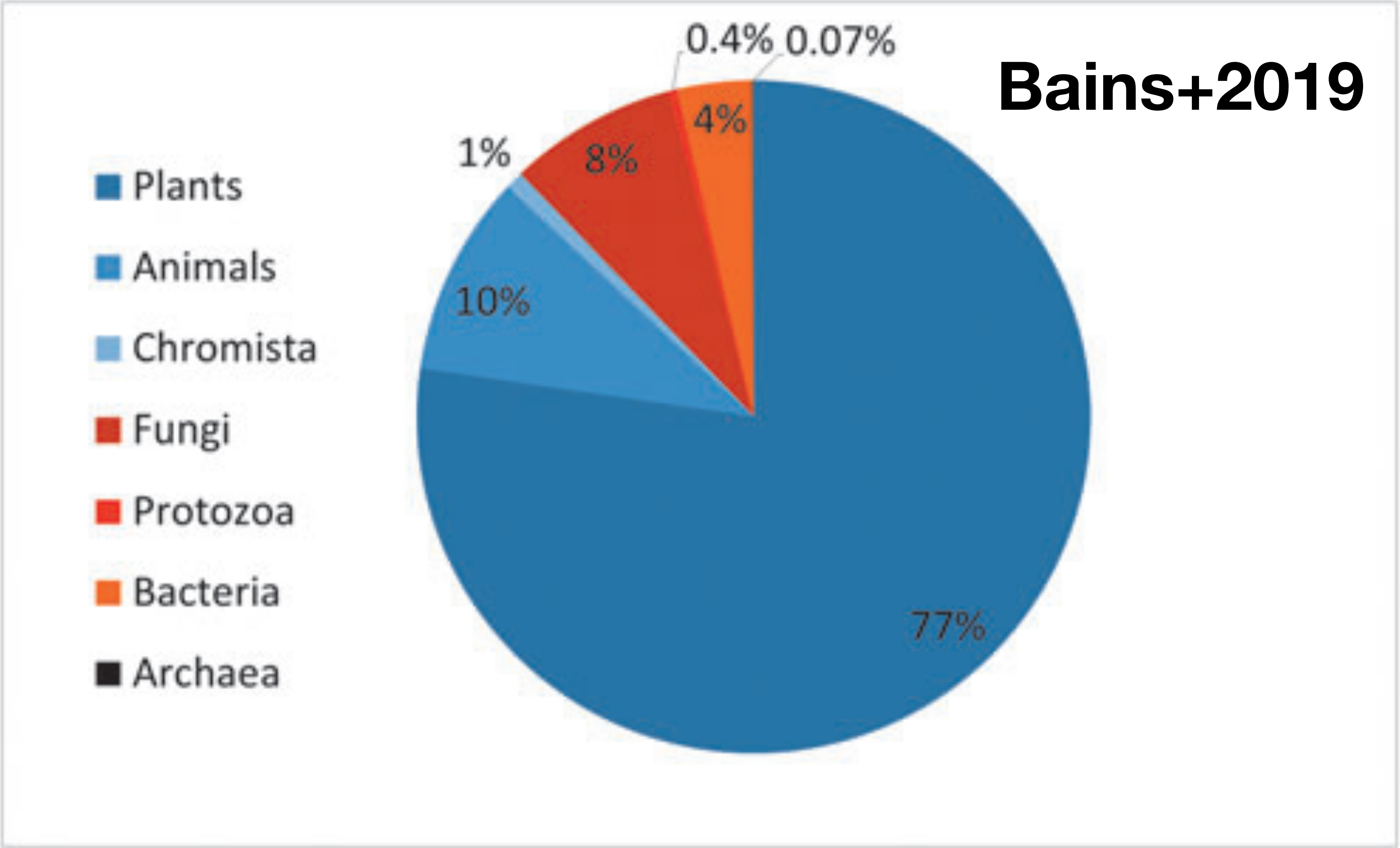


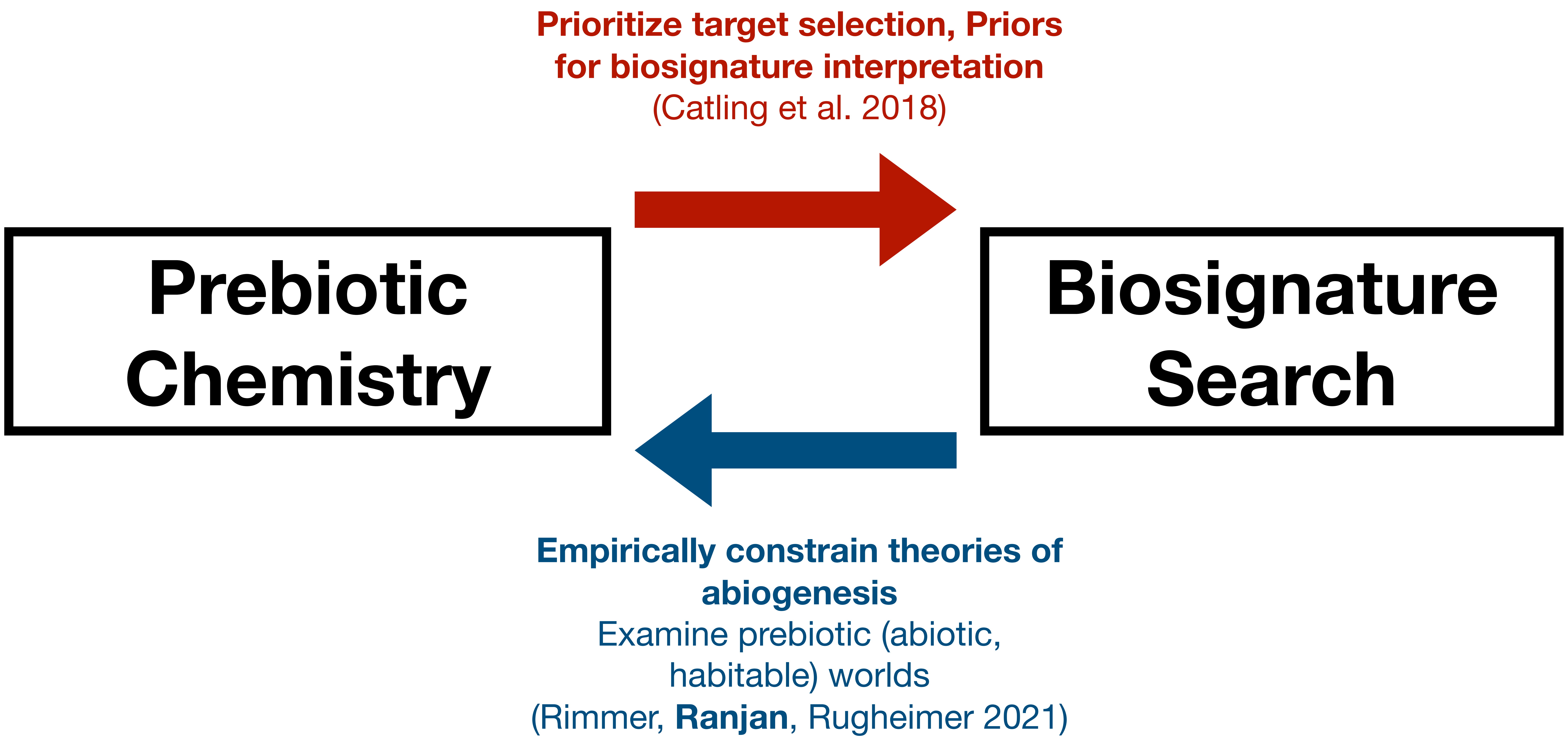
FIG. 1. The distribution of source organisms of known natural products shows a strong bias of the search for natural compounds toward aerobic organisms. At least 88% and maybe as much as 99% of all natural products are extracted from aerobic source organisms. Distribution of source organisms is shown on the example of publicly available UNPD natural product database (Gu *et al.*, 2013). Sources that are obligately aerobic are colored blue. Fungi, protozoa, and bacteria can be aerobic or anaerobic, depending on species or growth condition (shown in red). Archaea, which are predominantly anaerobic, are shown in black, but only represent 0.07% of originating species. The fraction of the biosphere on Earth that is anaerobic is unknown, however, the distribution of source organisms above it not typical of the biosphere, in which between 30% and 50% of the biomass is known to be bacterial (Whitman *et al.*, 1998). A substantial fraction, possibly 30%, of the total biomass on Earth is represented by the ocean floor sedimentary bacteria, almost all of which are anaerobic (Kallmeyer *et al.*, 2012). If biosynthesis of trivalent phosphorus-containing natural chemicals is strictly dependent on an anoxic environment, it is likely that more of such molecules are going to be discovered in anaerobic source organisms.

“There are two overarching goals in exoplanet science…

Goal 1 is to understand the formation and evolution of planetary system…

Goal 2 is to learn enough about the properties of exoplanets to identify potentially habitable environments and their frequency, and connect these environments to the planetary systems in which they reside. <u>Furthermore, scientists need to distinguish between the signatures of life and those of nonbiological processes, and search for signatures of life on worlds orbiting other stars.</u>”

National Academy of Sciences (USA) 2018, http://nap.edu/25187

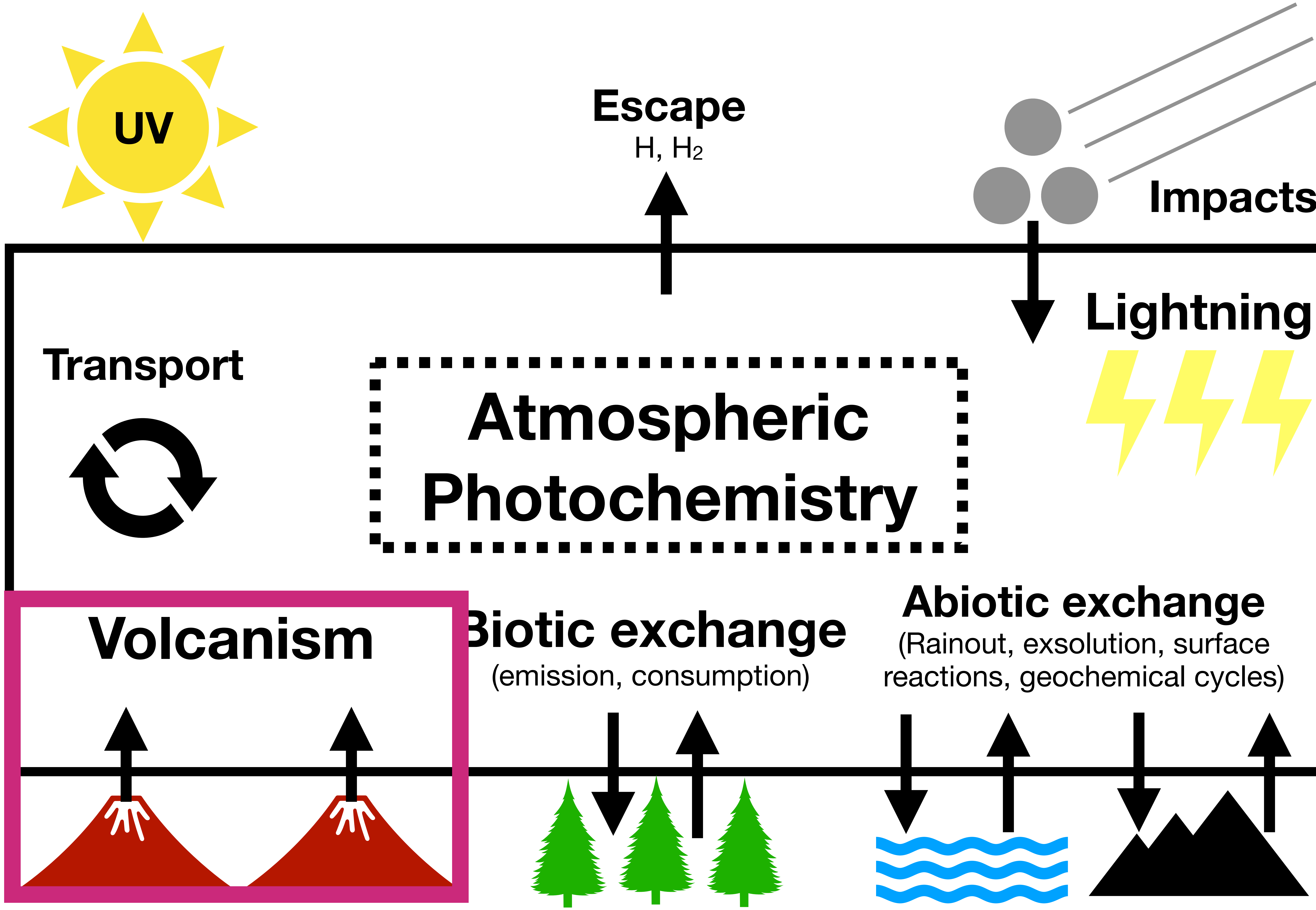


Prioritize target selection, Priors for biosignature interpretation
(Catling et al. 2018)
Prebiotic Chemistry
Biosignature Search
Empirically constrain theories of abiogenesis
Examine prebiotic (abiotic, habitable) worlds
(Rimmer, **Ranjan**, Rugheimer 2021)

Recipe for Remote Life Detection Flowchart

Potential Diversity of Rocky Exo-Volcanism

- How does exo-volcanism vary with: Temperature, Pressure, oxygen fugacity, volatile loading?
- Photochemical probe of underlying planet?
- Biosignature false positive/negatives?



Potential PhD Project

Present and future NASA missions promise a wealth of measurements that contain the answers to the two overarching goals of understanding planets and searching for life. But the scientific implications of these data will not be fully realized without a thriving and engaged community in related fields of theoretical, laboratory, and observational science.

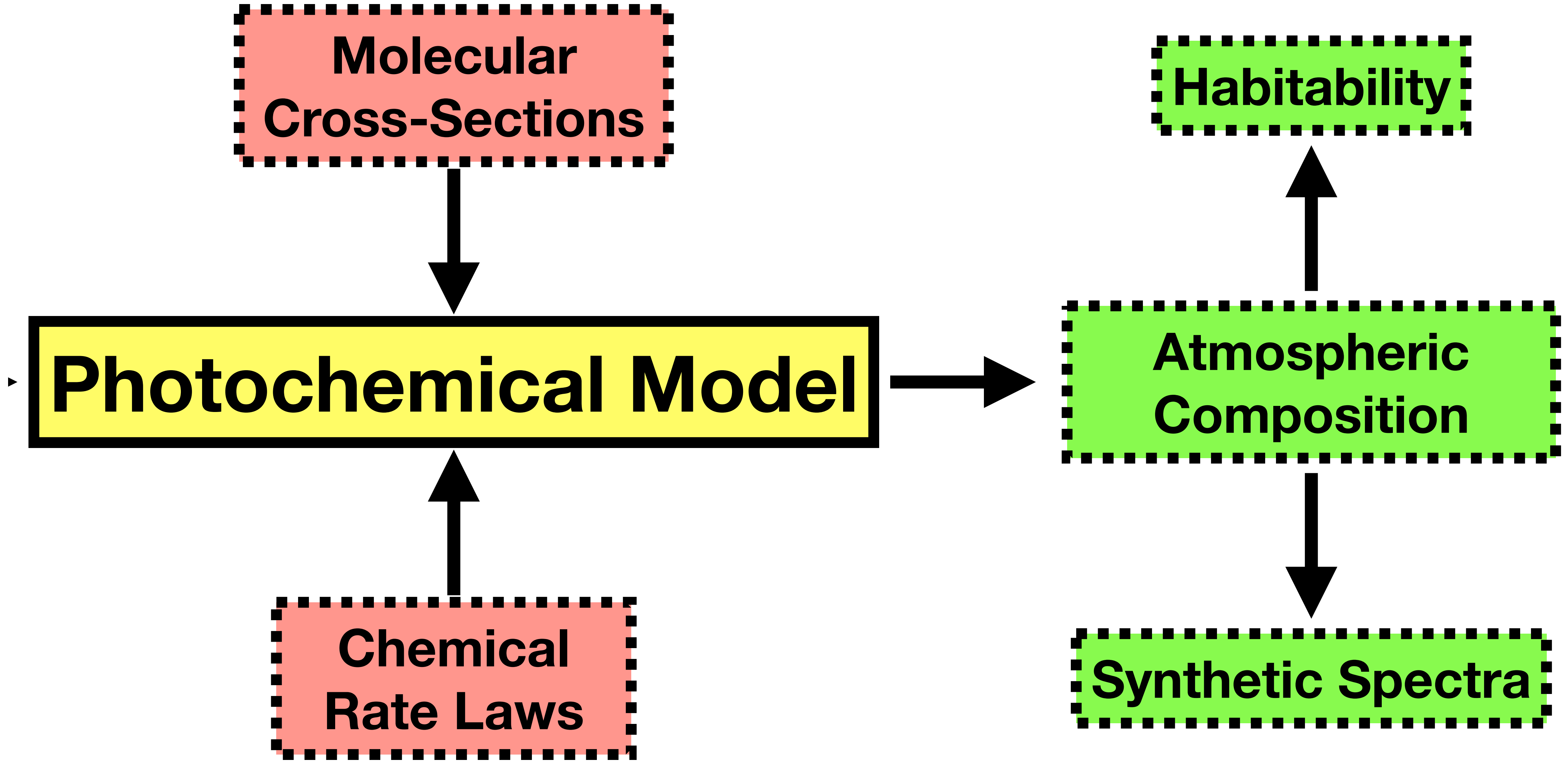
Finding: Theoretical models are essential to plan and interpret observations of exoplanets.

Finding: The limited laboratory and ab initio data covering the parameter space relevant to exoplanets is a barrier to accurate models of exoplanet atmospheres and interiors.

Finding: Understanding of exoplanets is limited by measurements of the properties of the parent stars.

National Academy of Sciences (USA) 2018, *Exoplanet Science Strategy,* http://nap.edu/25187

Experimental Constraints to Improve Terrestrial Exoplanet Photochemical Models (ExCITE-PM)



CENTER FOR ASTROPHYSICS HARVARD & SMITHSONIAN

- Identify, rectify weaknesses in rocky planet photochemical models (e.g., **Ranjan** et al. 2020)

- First iteration **funded** (XRP, \$660k, SPI: Ranjan).

  - Initial focus: O_2 and S on TRAPPIST planets