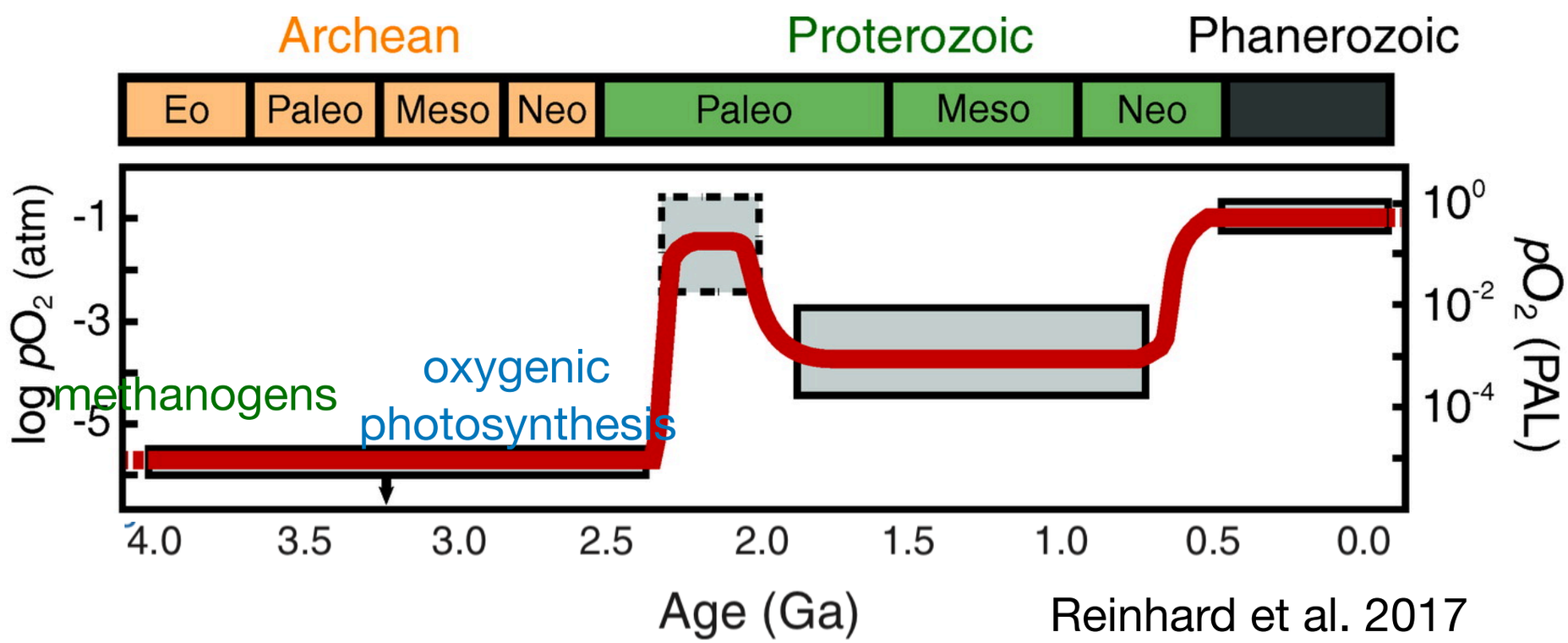
The 5th Chianti Topics International Focus Workshop

The evolution and stability of CO_2-CH_4-H_2O atmospheres

Shang-Min Tsai, R.J. Graham, Raymond Pierrehumbert

Biosignature gases



Reinhard et al. 2017

- Life exists long before O_2 buildup to a detectable level
- False positives (e.g., Segura et al. 2007, Hu et al. 2019)

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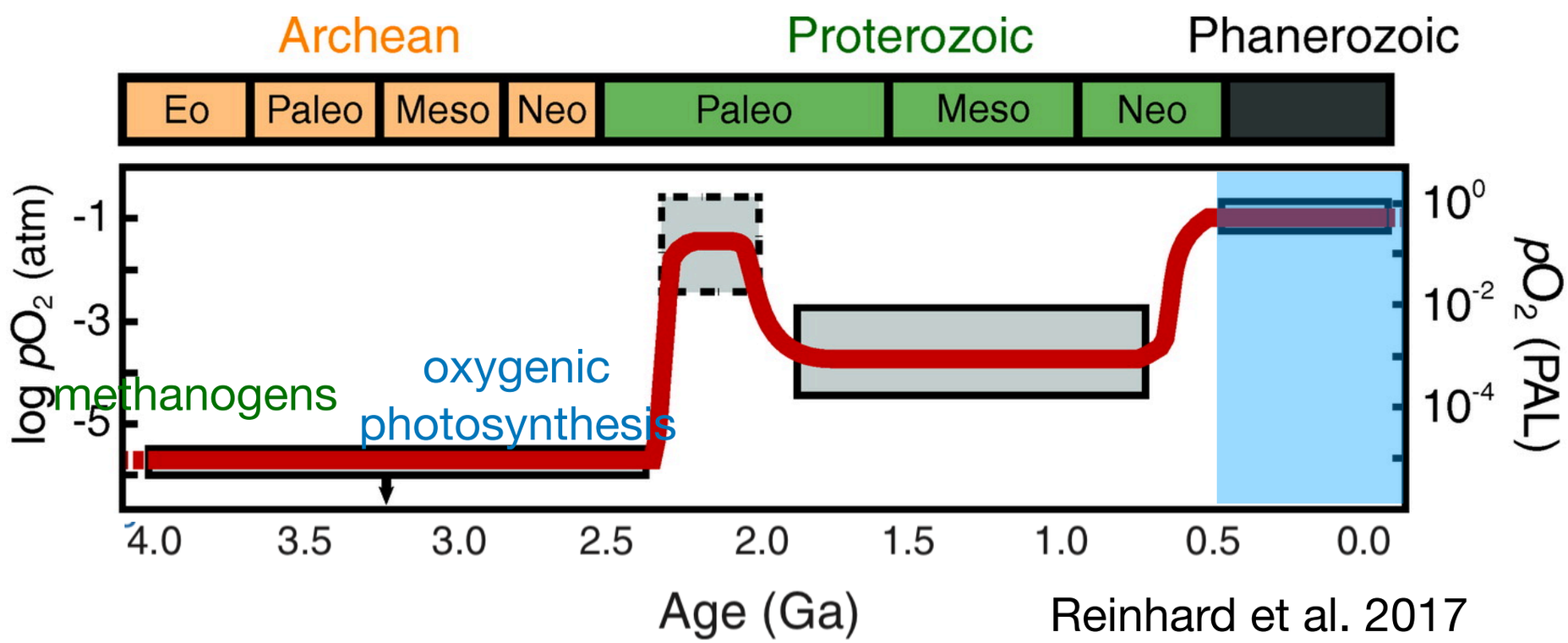

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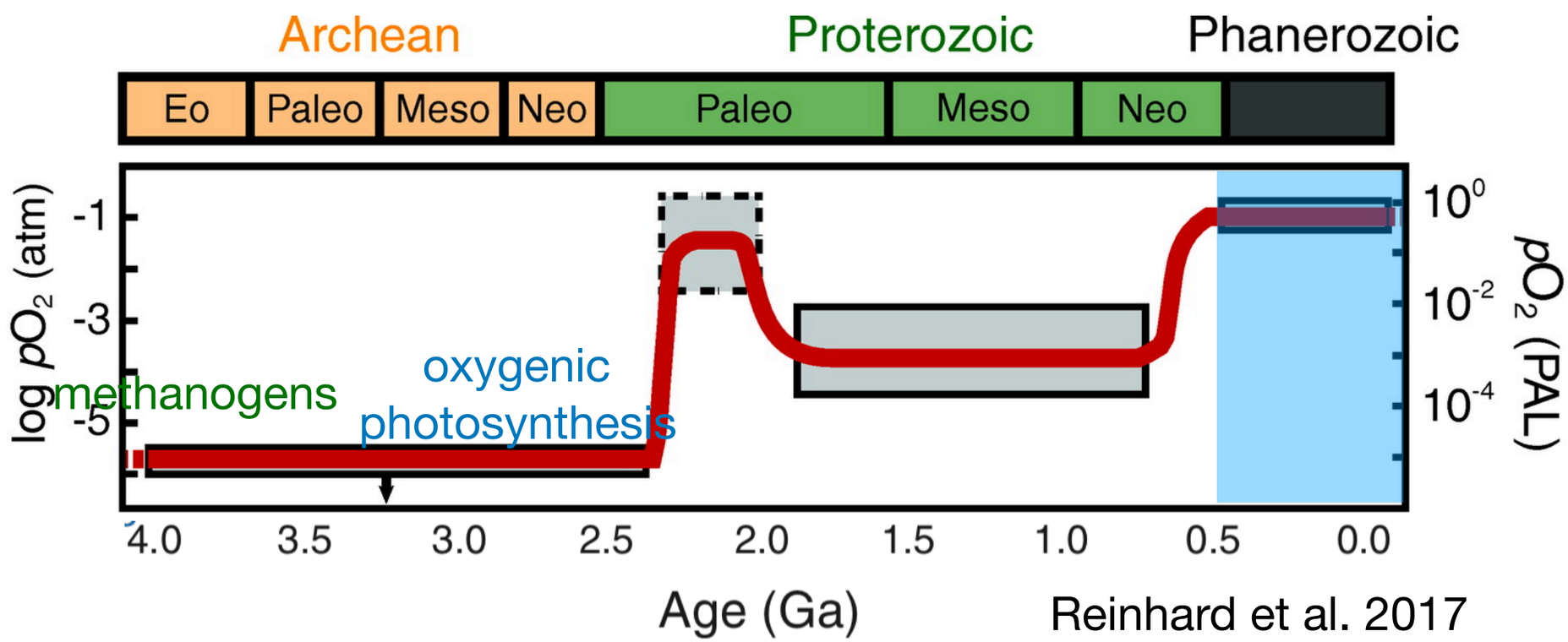

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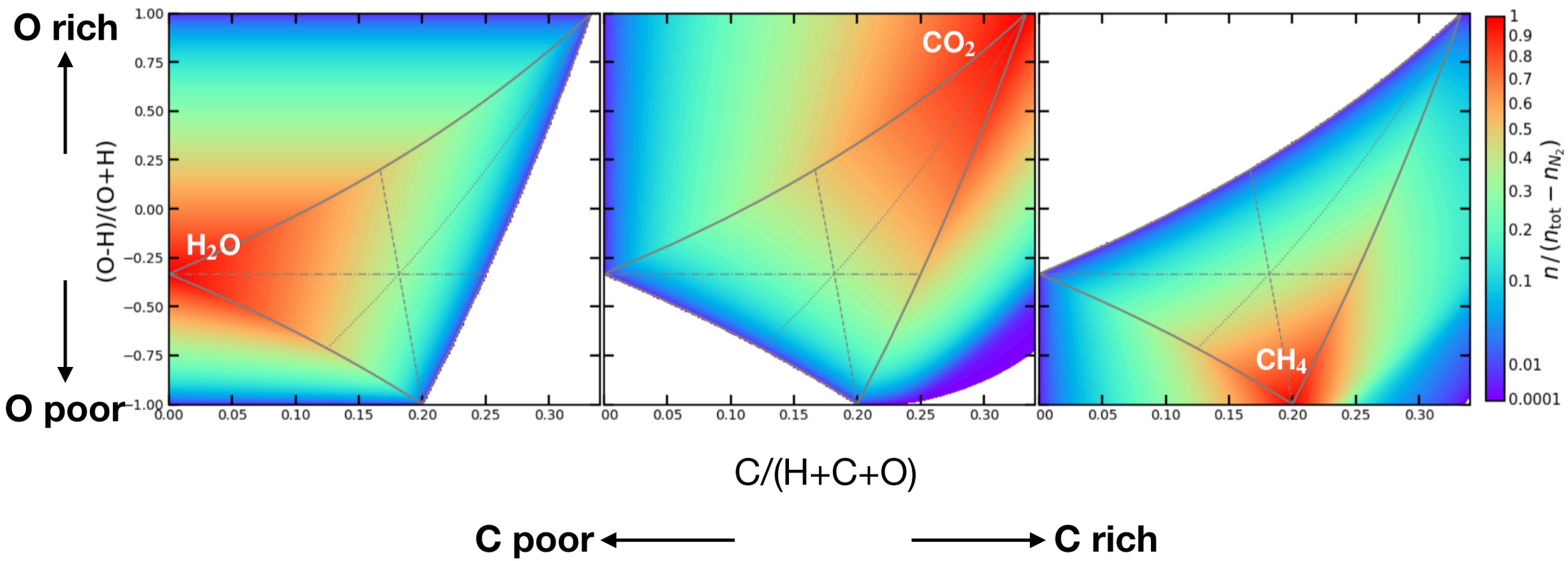
A more general biosignature: chemical disequilibrium

In the Archean, CH_4 produced by microbes contributes the most to disequilibrium. CH_4—CO_2 disequilibrium is a detectable biosignature for anoxic atmospheres

Krissansen-Totton et al. 2018

CH_4 and CO_2 as major components (> 10%) in chemical equilibrium



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Woitke et al. 2020

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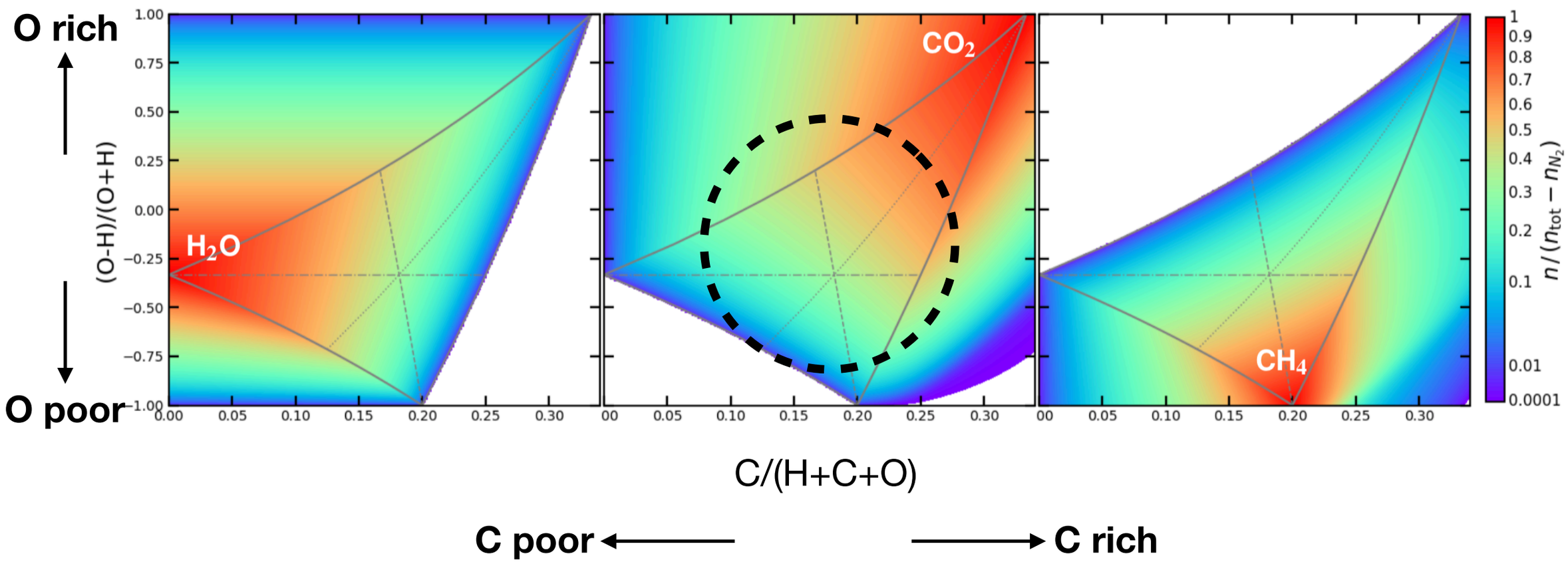

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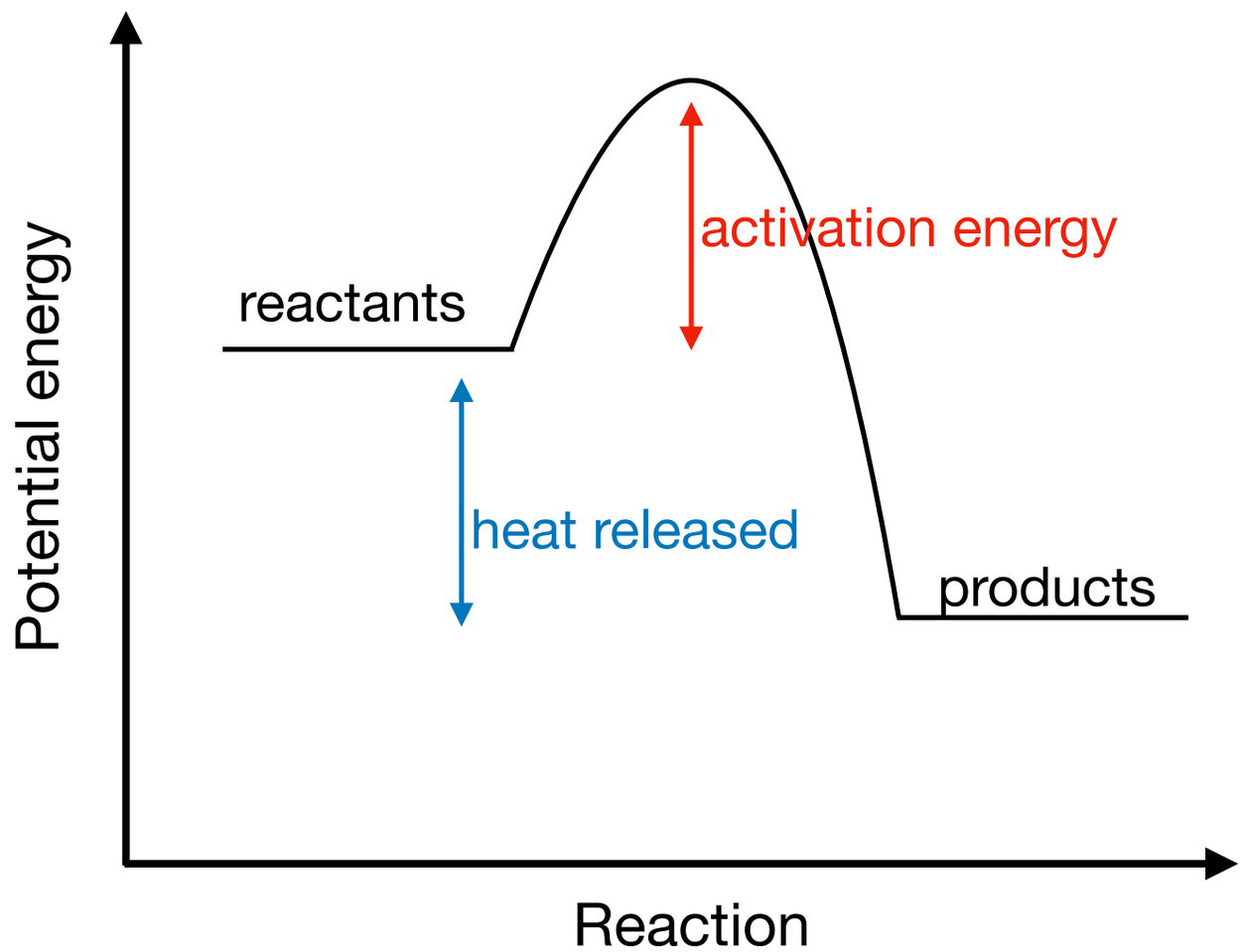

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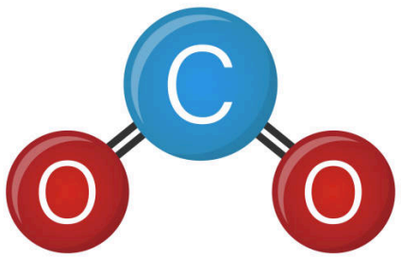
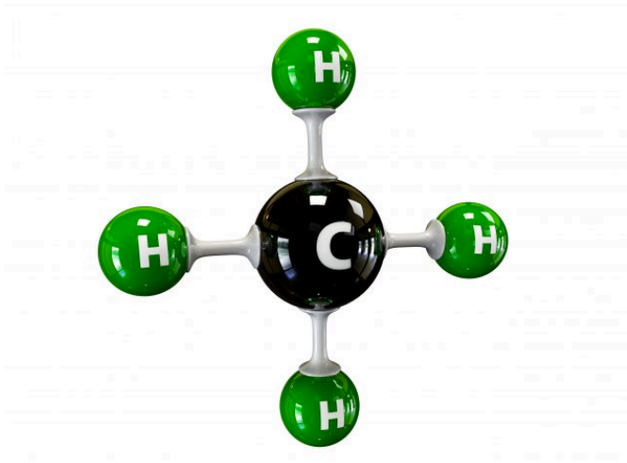
Questions to address

1. Can a CO_2-CH_4-H_2O-N_2 atmosphere form abiotically?

2. Is a CO_2-CH_4-H_2O-N_2 atmosphere stable?

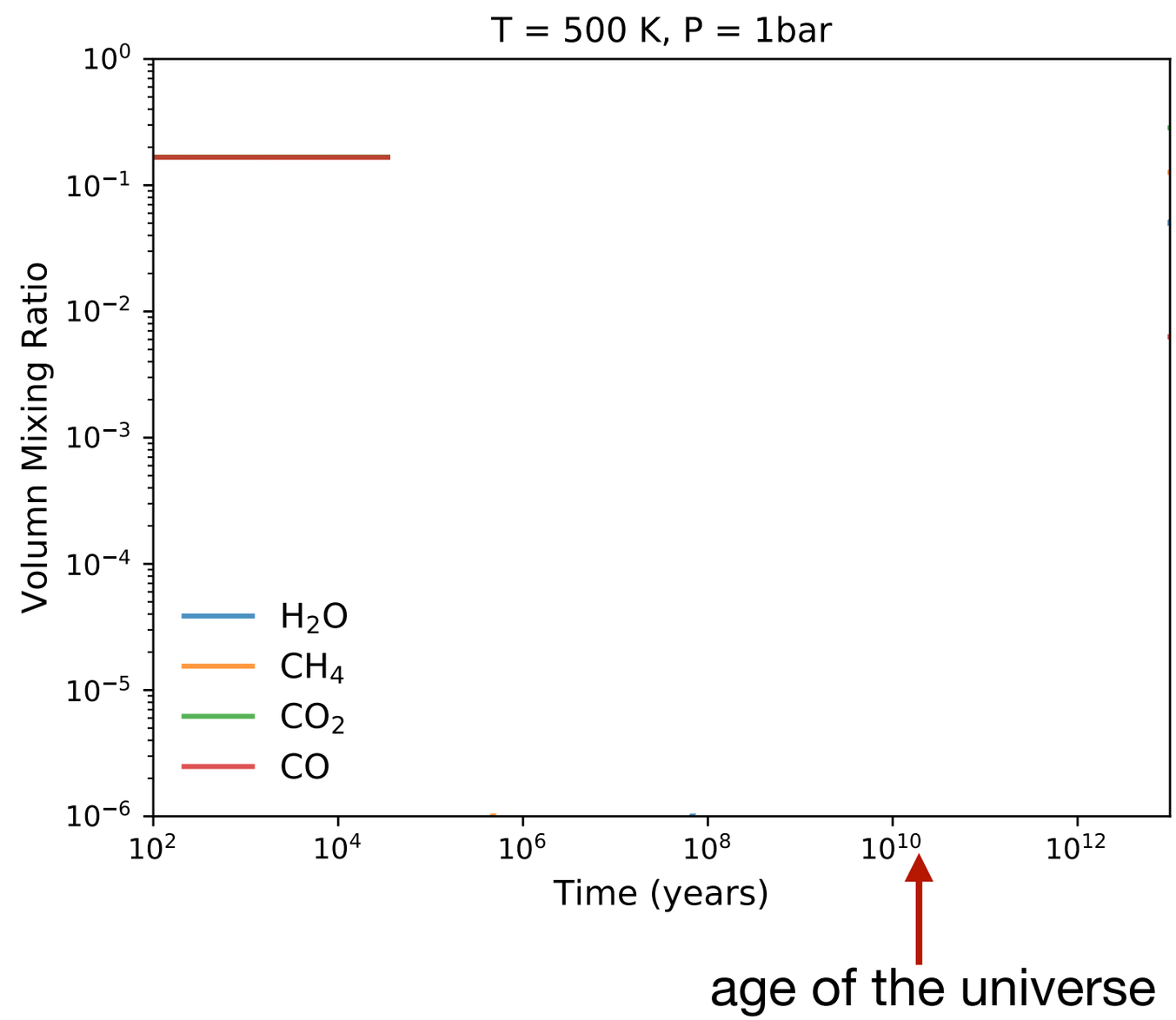
3. Is the CO_2-CH_4 pair a good biosignature for anoxic atmospheres?





Thermochemical equilibrium is too slow to be relevant

Started with a mixture of the same elemental abundance as that in Woitke et al. 2020 but with all the carbon in CO_2 and CO



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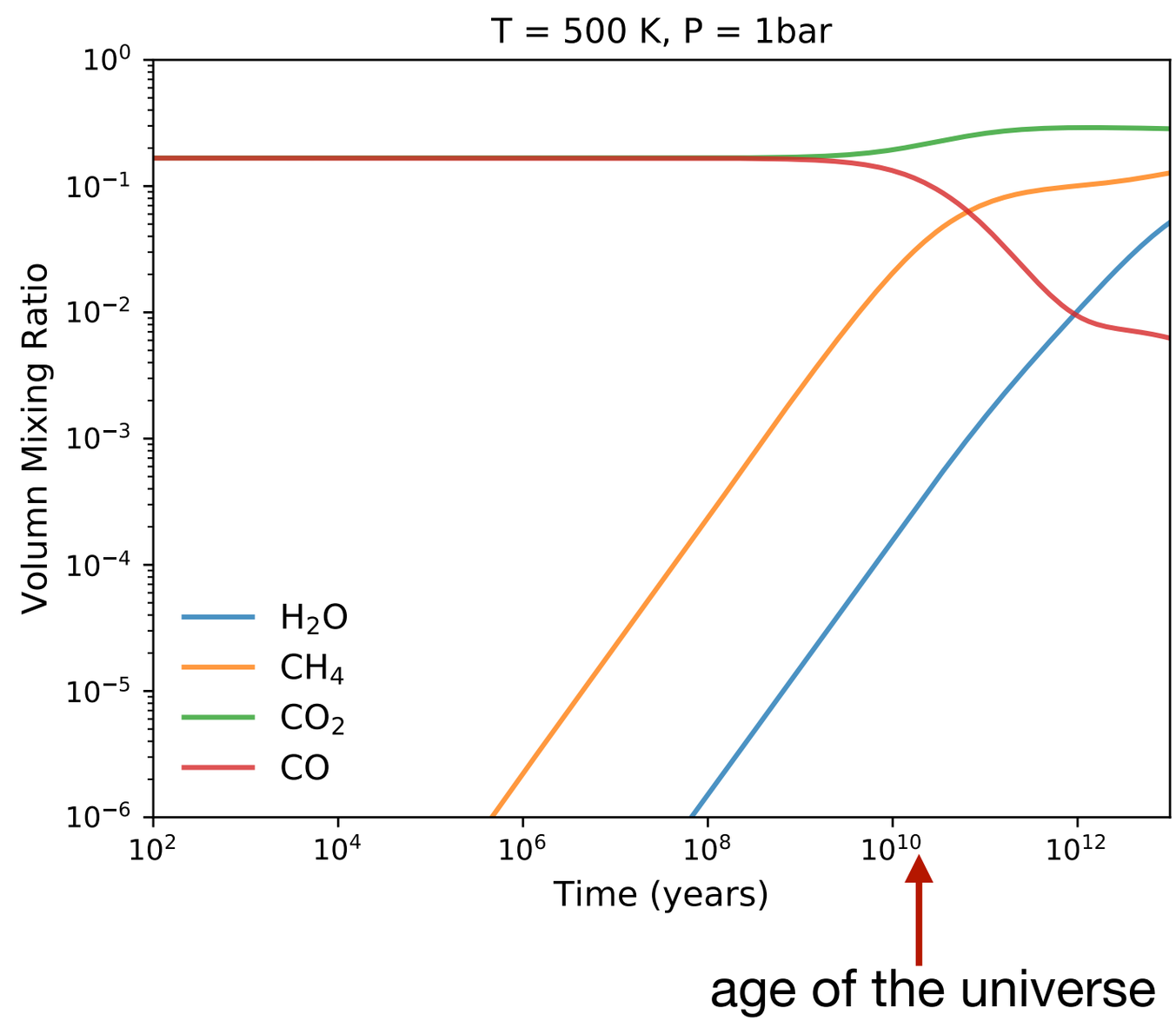

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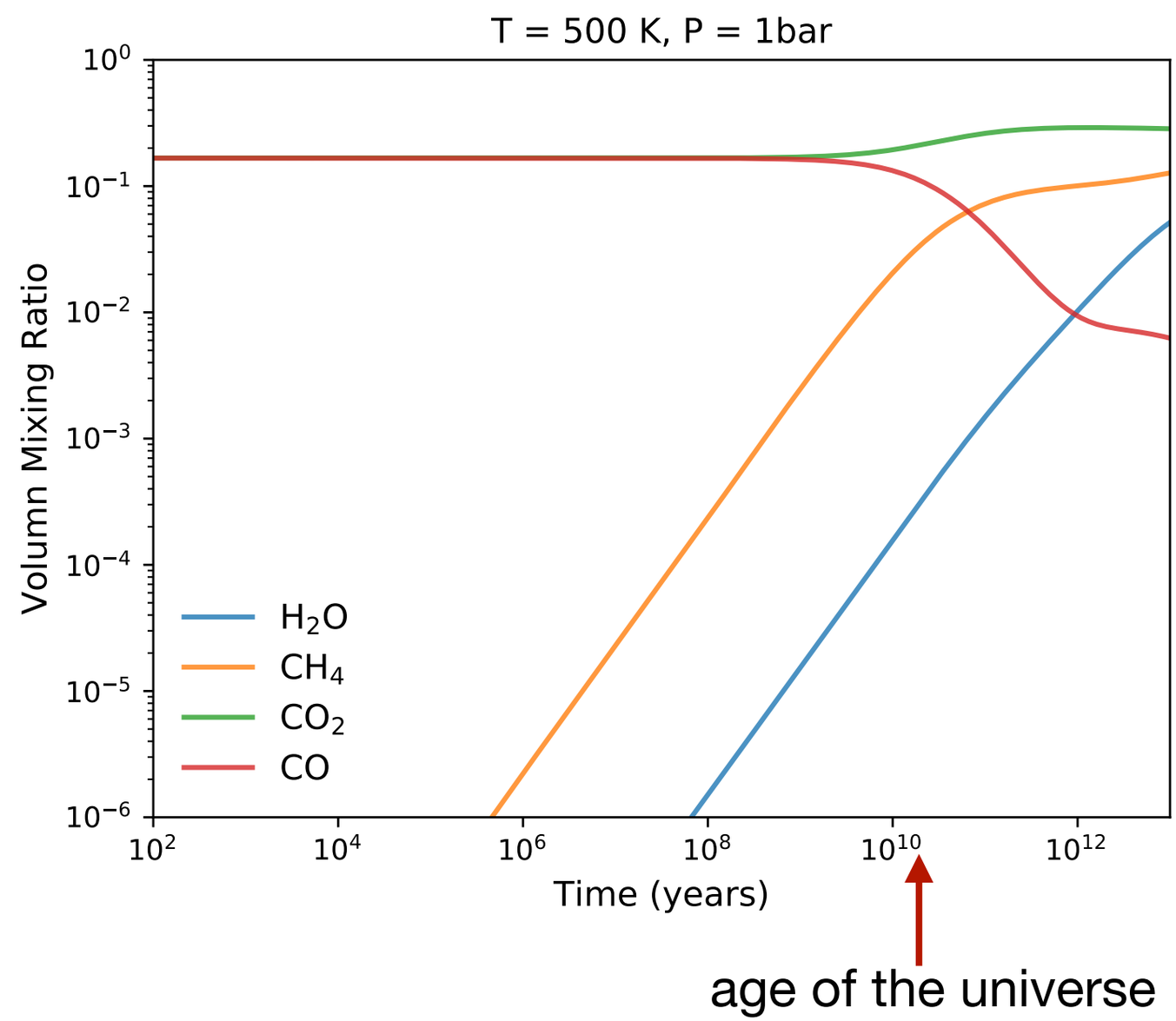

Without catalysts, equilibrium chemistry is irrelevant in the context of CO_2-CH_4 false positives

Quenched from a hotter state

- a plausible thermodynamical path to form CO_2-CH_4: **inheriting the compositions at a higher temperature**

- As the atmosphere cools down from the final accretion or impact, the composition can be quenched from a hotter equilibrium state (Zahnle et al. 2020, Itcovitz et al. 2022) after the kinetics shuts off

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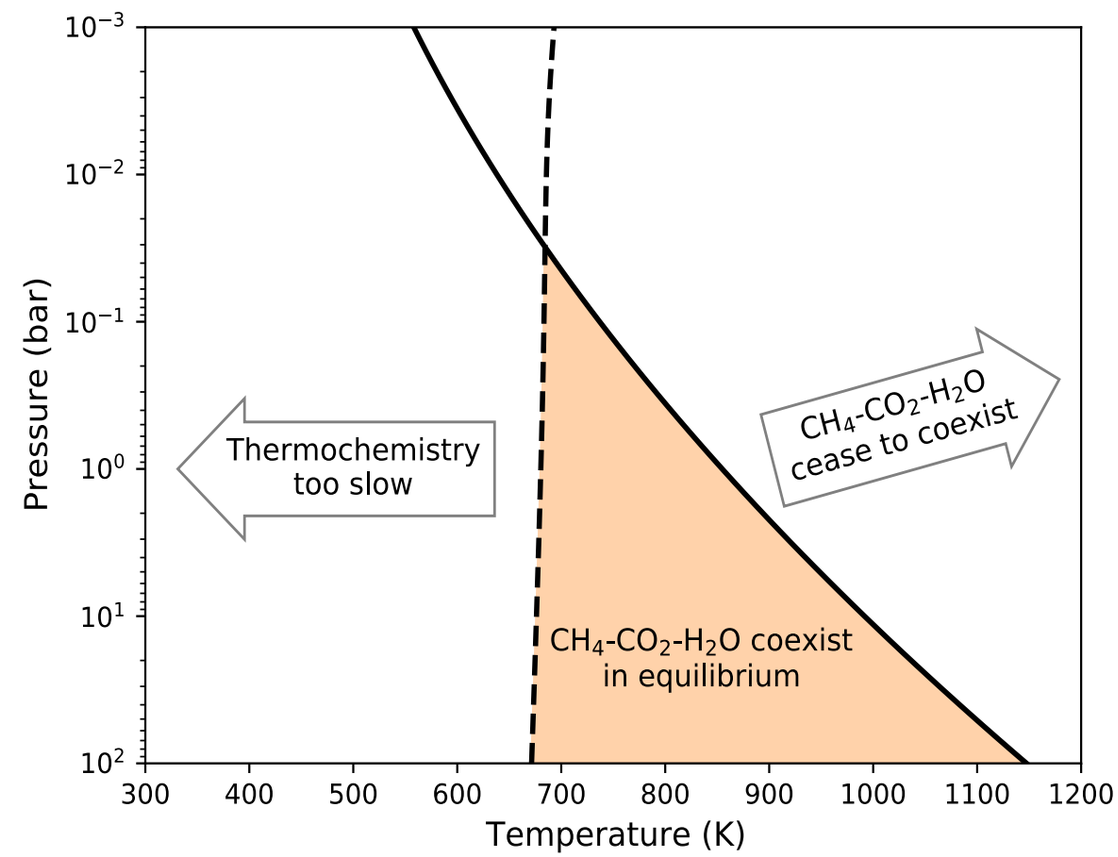
- catch: CH_4 is not stable at high T

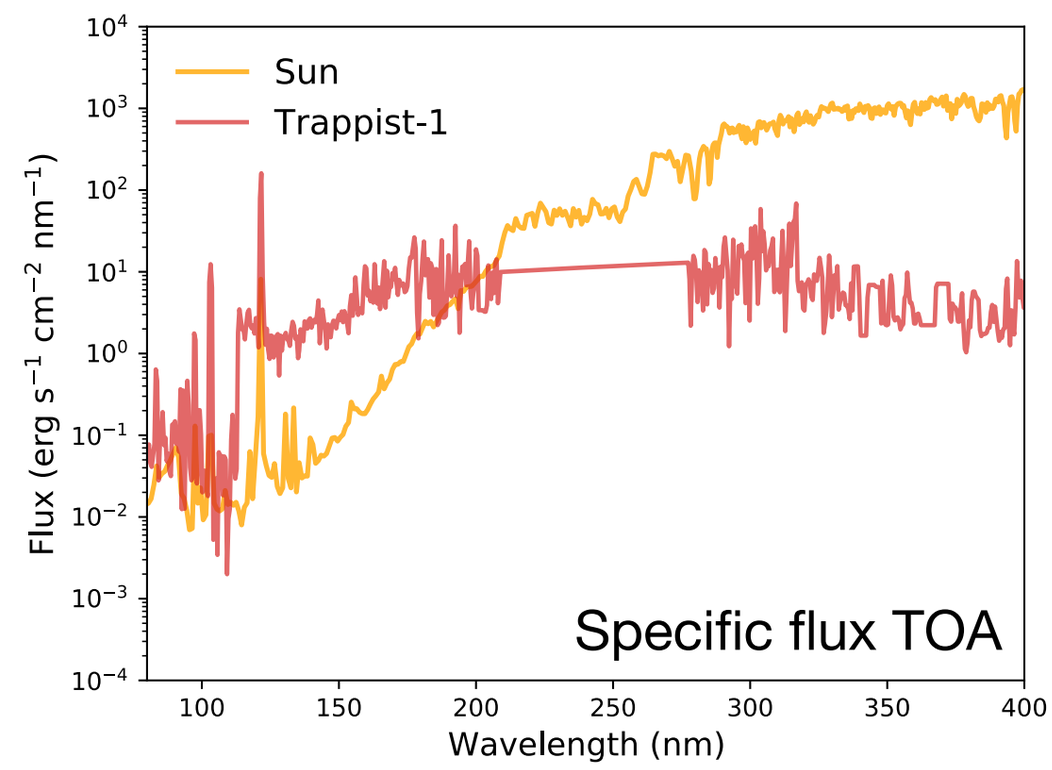


Coupled climate-photochemistry

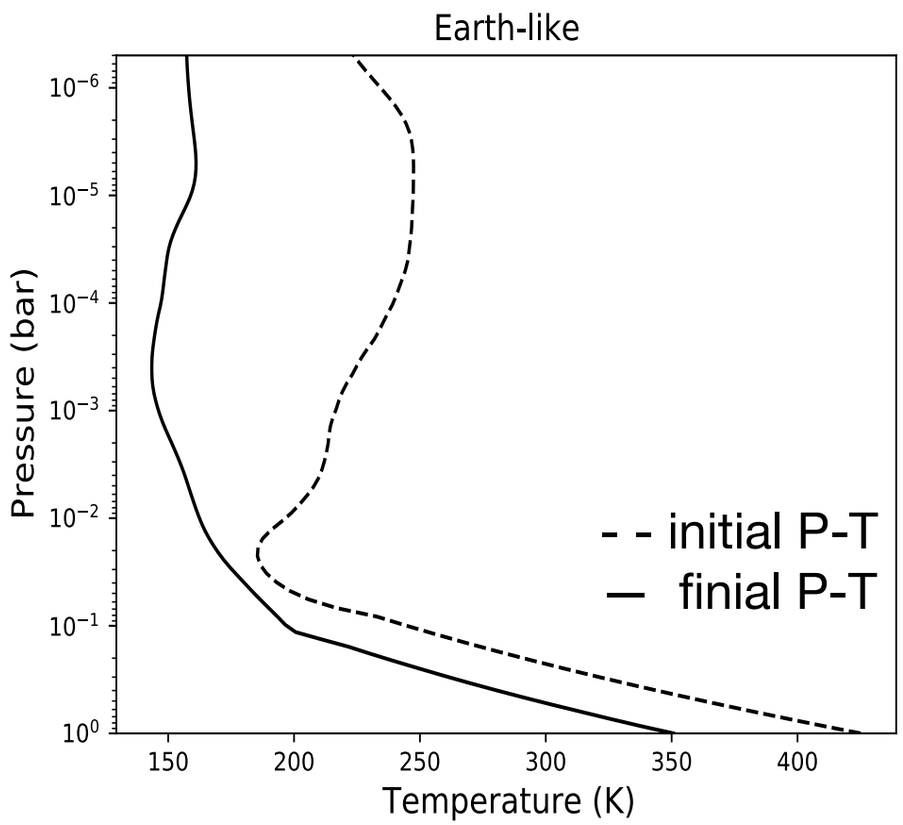
- Coupled radiative transfer (HELIOS) + photochemistry (VULCAN) model
- VULCAN: 75 species and ~900 reactions — validated for gas giants and Earth (Tsai et al. 2017, Tsai et al. 2021)
- Iterate until a radiative-convective and photochemical equilibrium state
- All runs started with 25% of CH_4, CO_2, H_2O, and N_2 assuming surface H_2O is fixed by ocean reservoirs

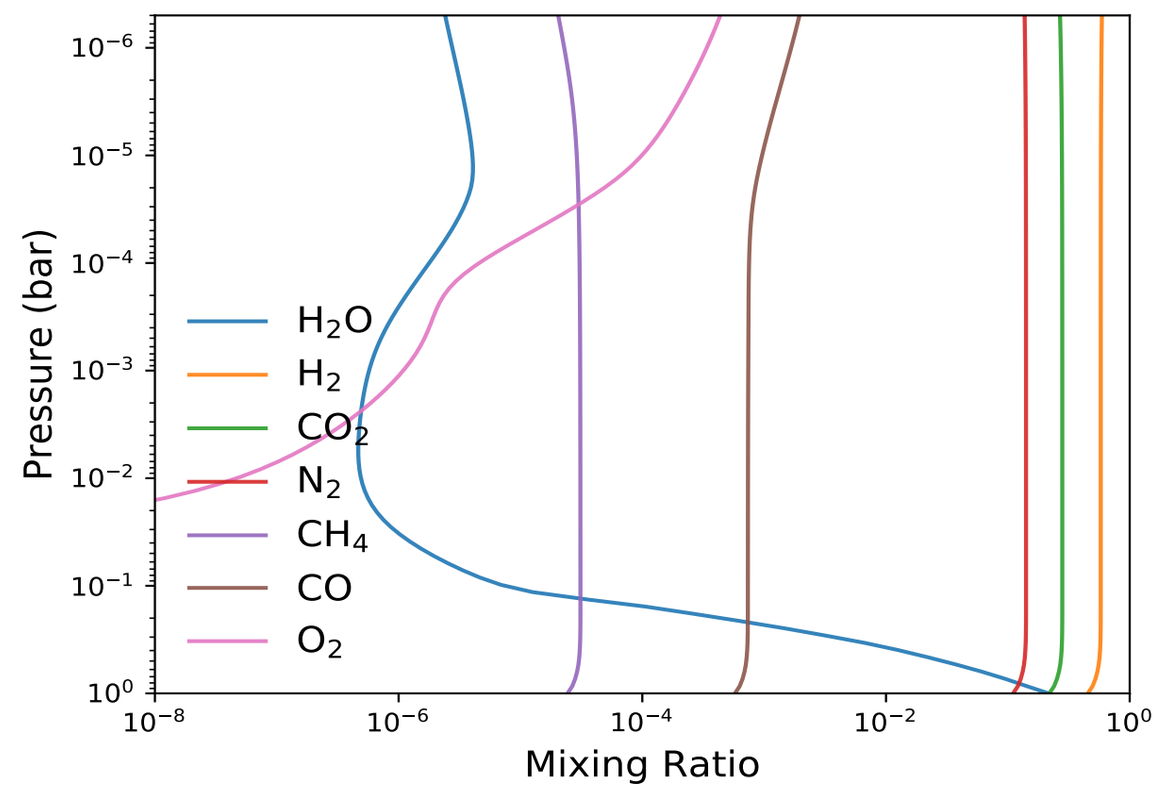
— Earth-like insolation

— Trappist-1e



Results: Earth-like





- CH_4 destroyed down to about “Archean levels”
- [CO] > [CH_4] ([CO] << [CH_4] in chemical equilibrium)
- H_2 runaway: H is liberated from CH_4 and H_2O

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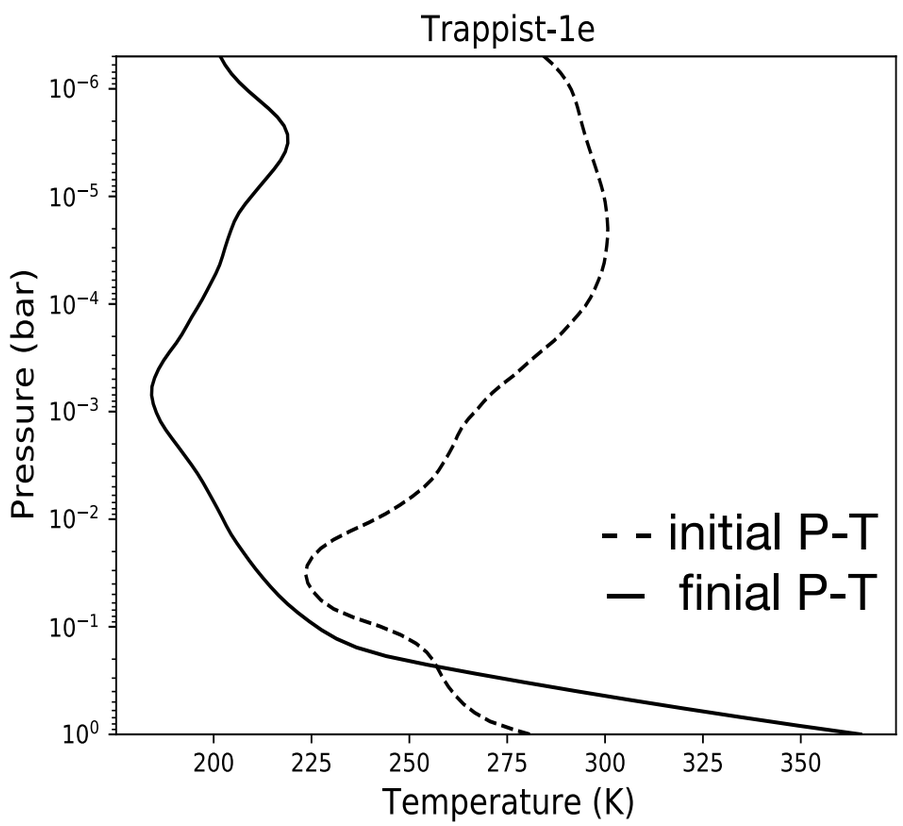

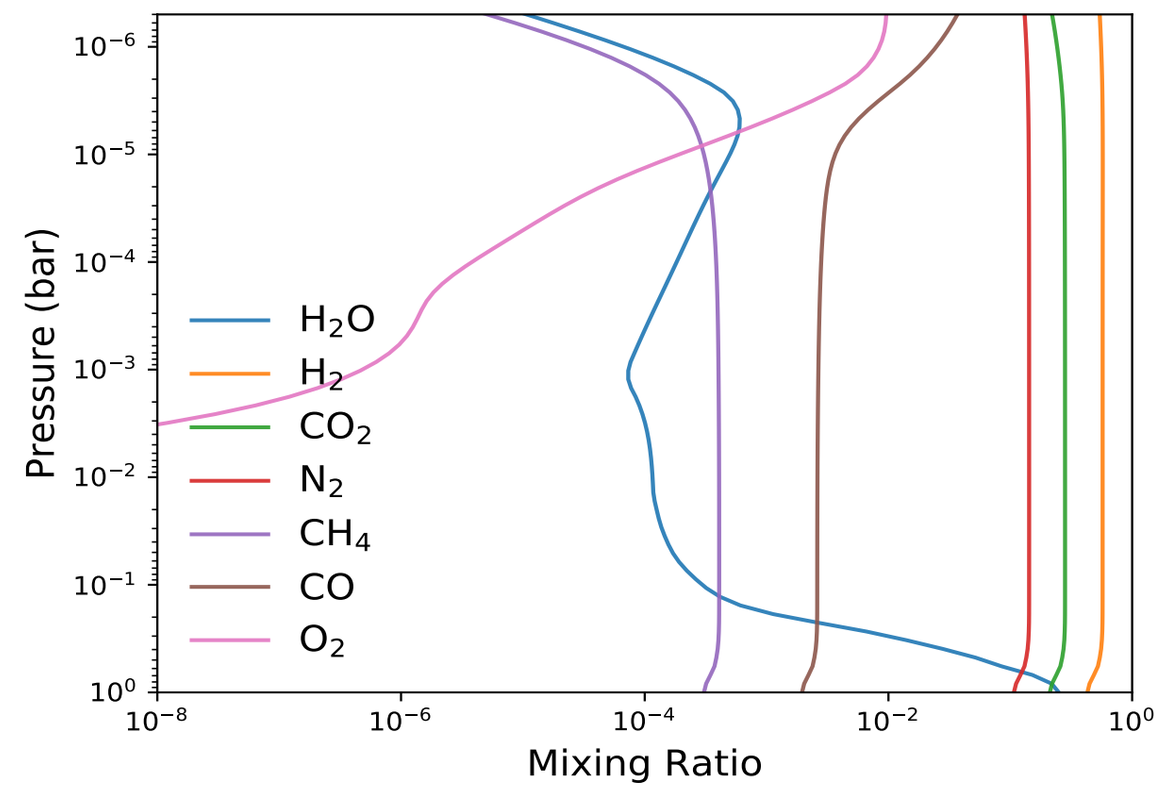

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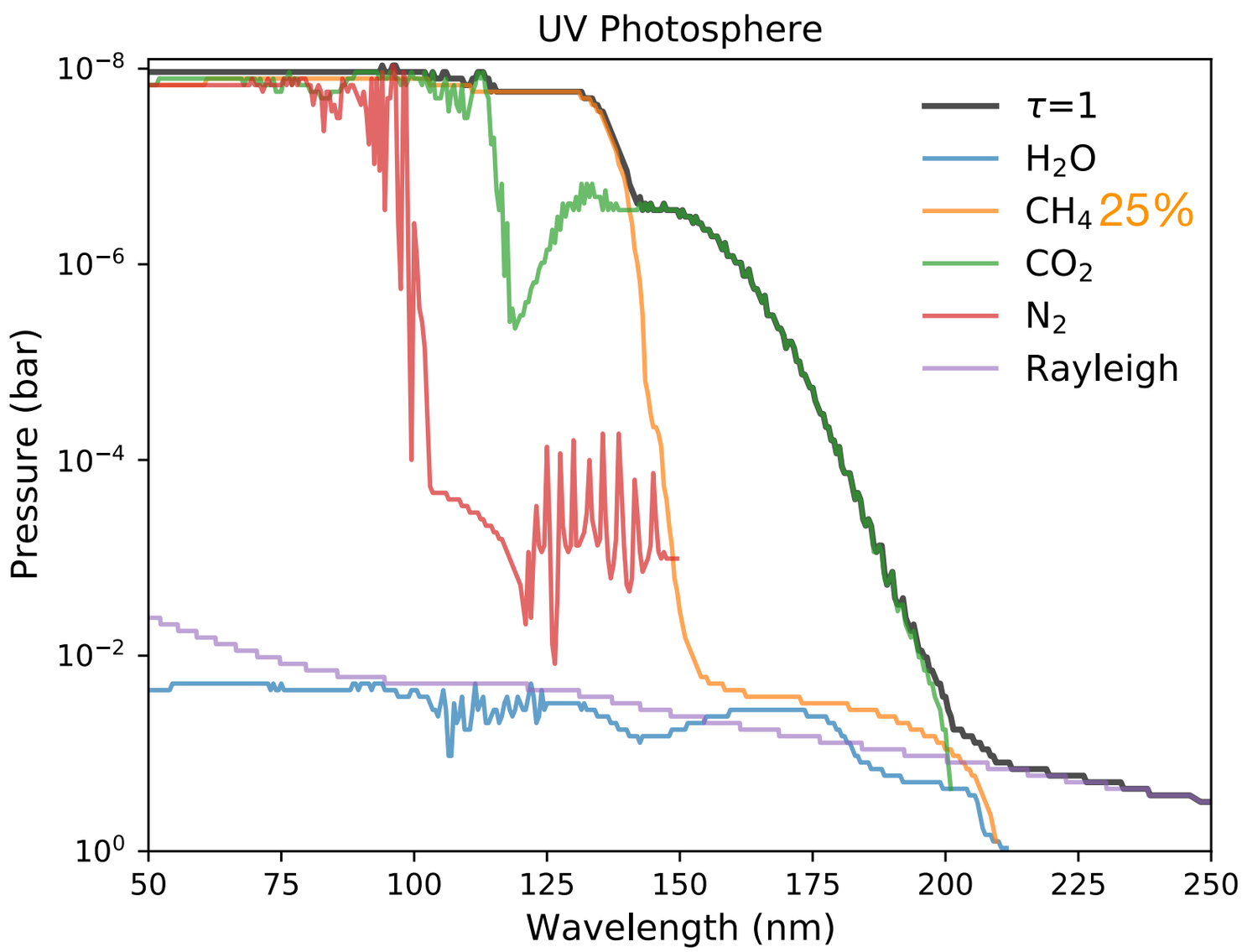
Limited by the dissociation around Lyman-α



When $[CH_4] > 10^{-3}$:

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CH

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CO, CO2

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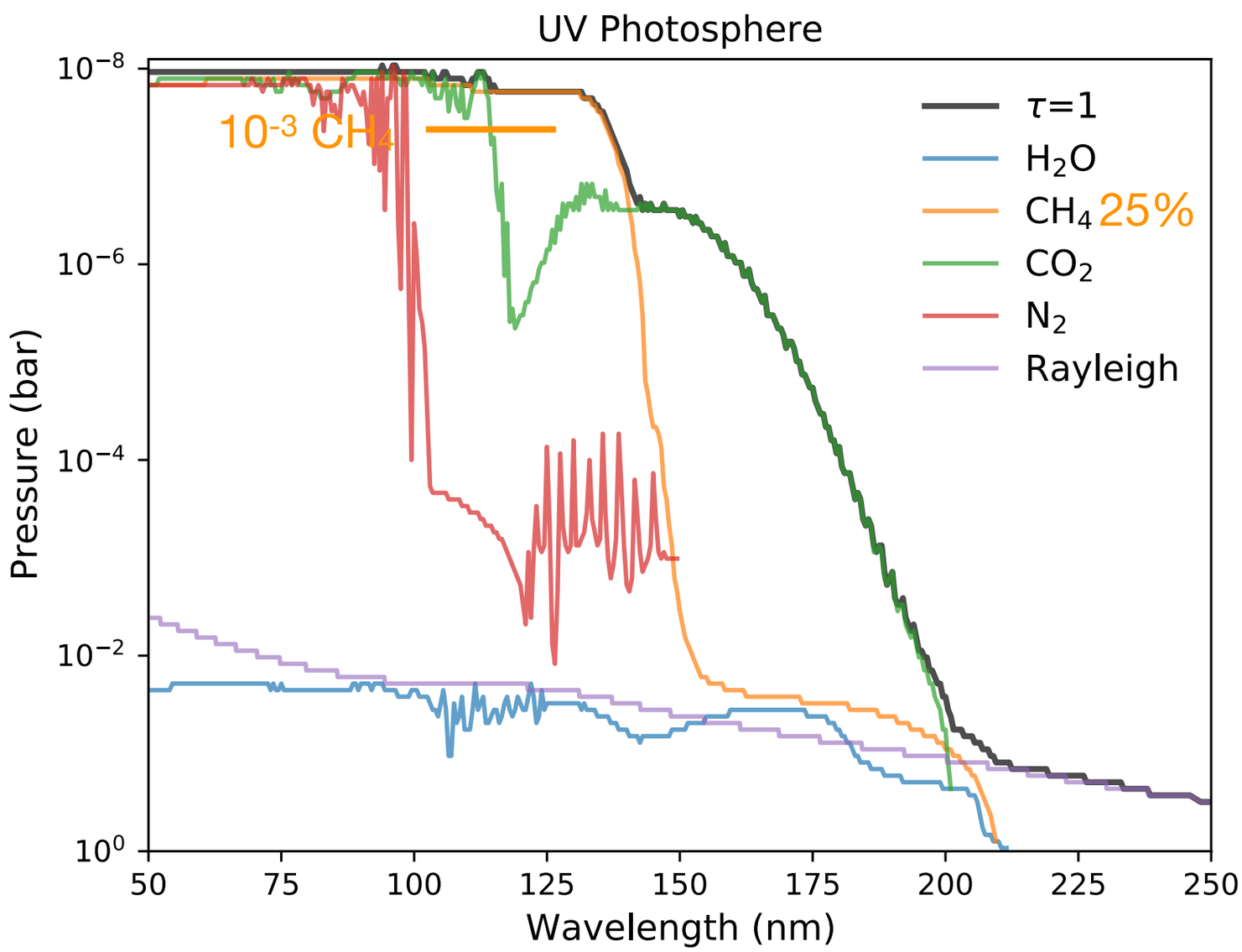

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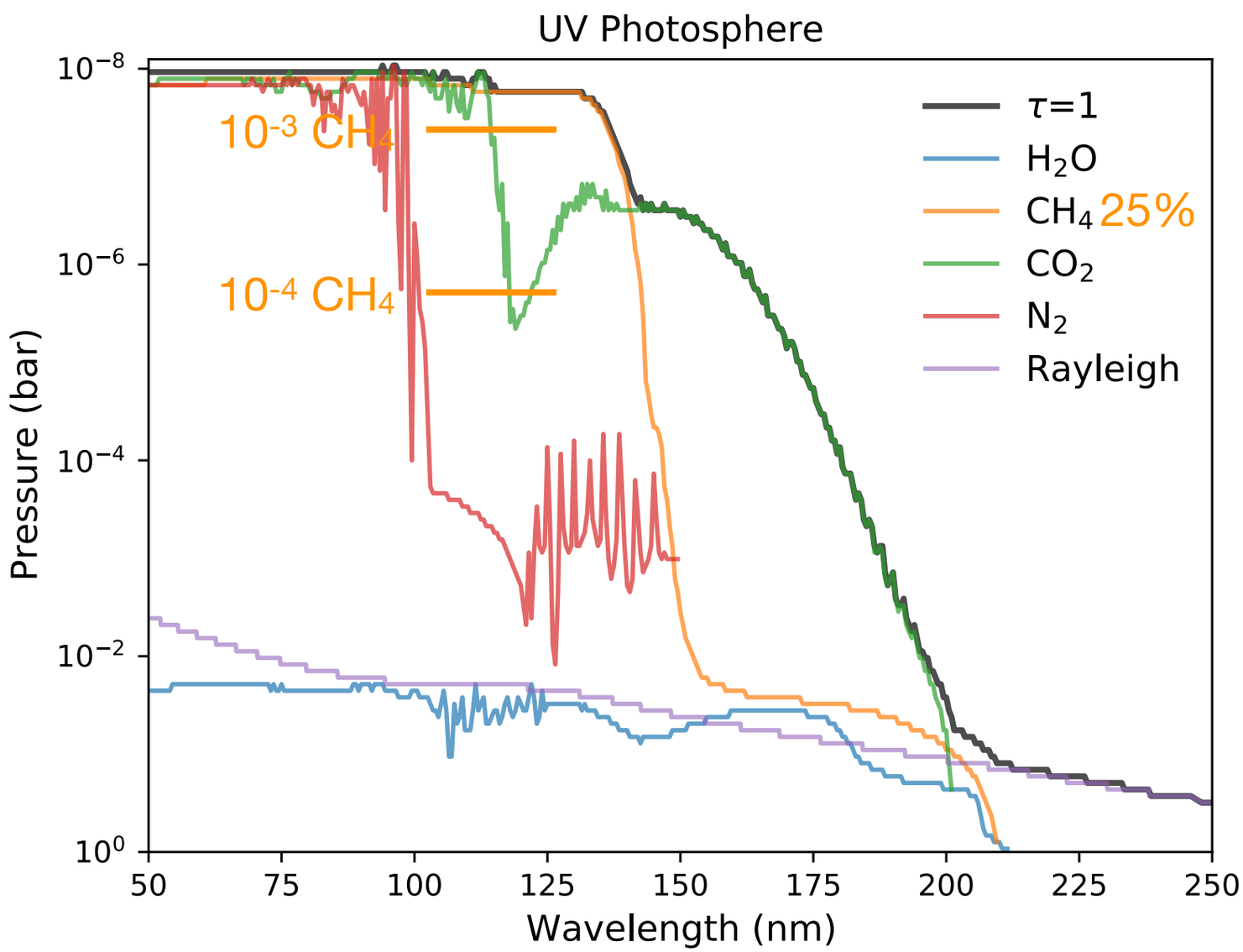

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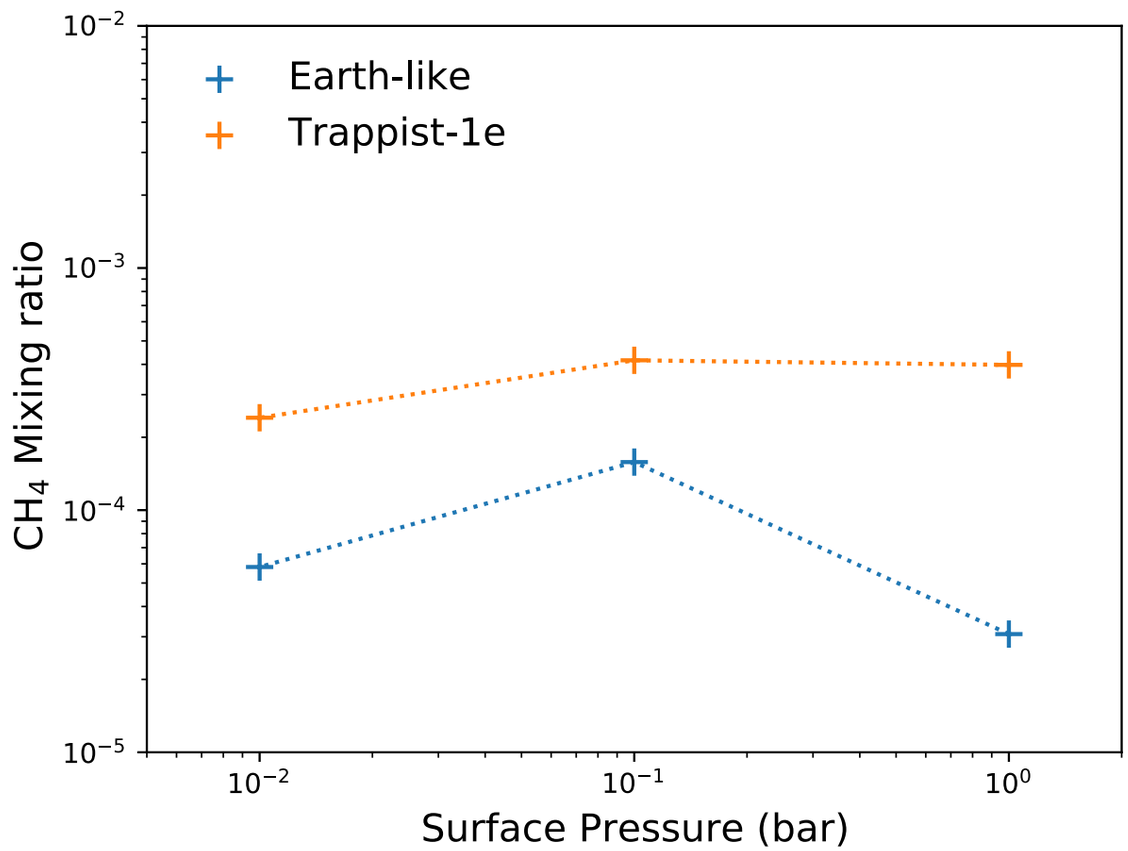
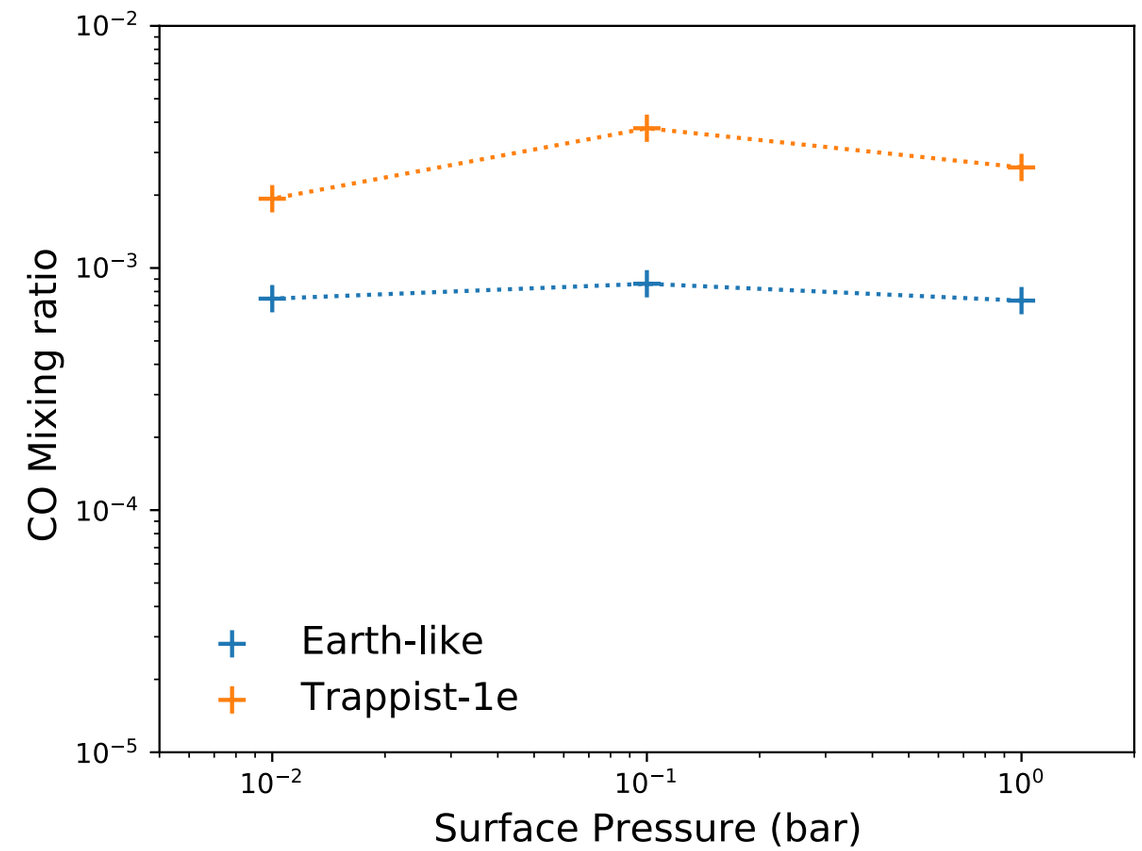
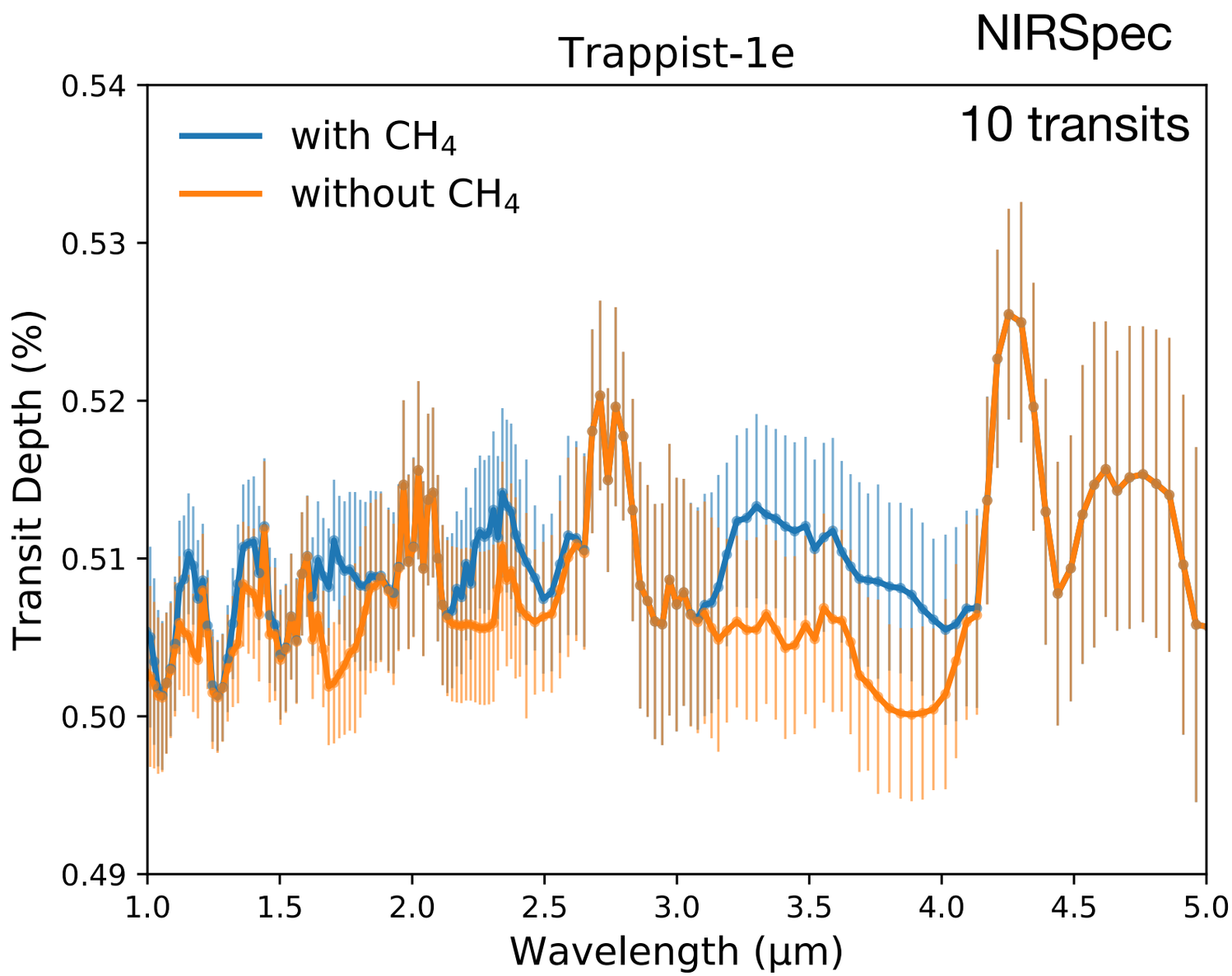
Insensitivity to the surface pressure





Synthetic spectra



e.g., Krissansen-Totton et al. 2018, Mikal-Evans 2022

Summary

1. A CO_2-CH_4-H_2O-N_2 atmosphere can originate from **quenching following a hotter state**

2. CH_4 is generally not stable against photolysis but can still maintain close to Archean biogenic CH_4 levels (10 — 1000 ppmv)

3. It is worth rethinking CO_2-CH_4 as a biosignature pair since CO_2 and CH_4 **can coexist in photochemical equilibrium** without biological sources

But what about haze?

- The initial CH_4-rich environment favors organic haze formation but $CH_4/CO_2 \leq 0.001$ in the steady state (In Archean Earth, organic haze could form when $CH_4/CO_2 >$ **0.1**)

- Fractal hazes can shield UV

- Future work coupling microphysics + photochemistry to include the feedback