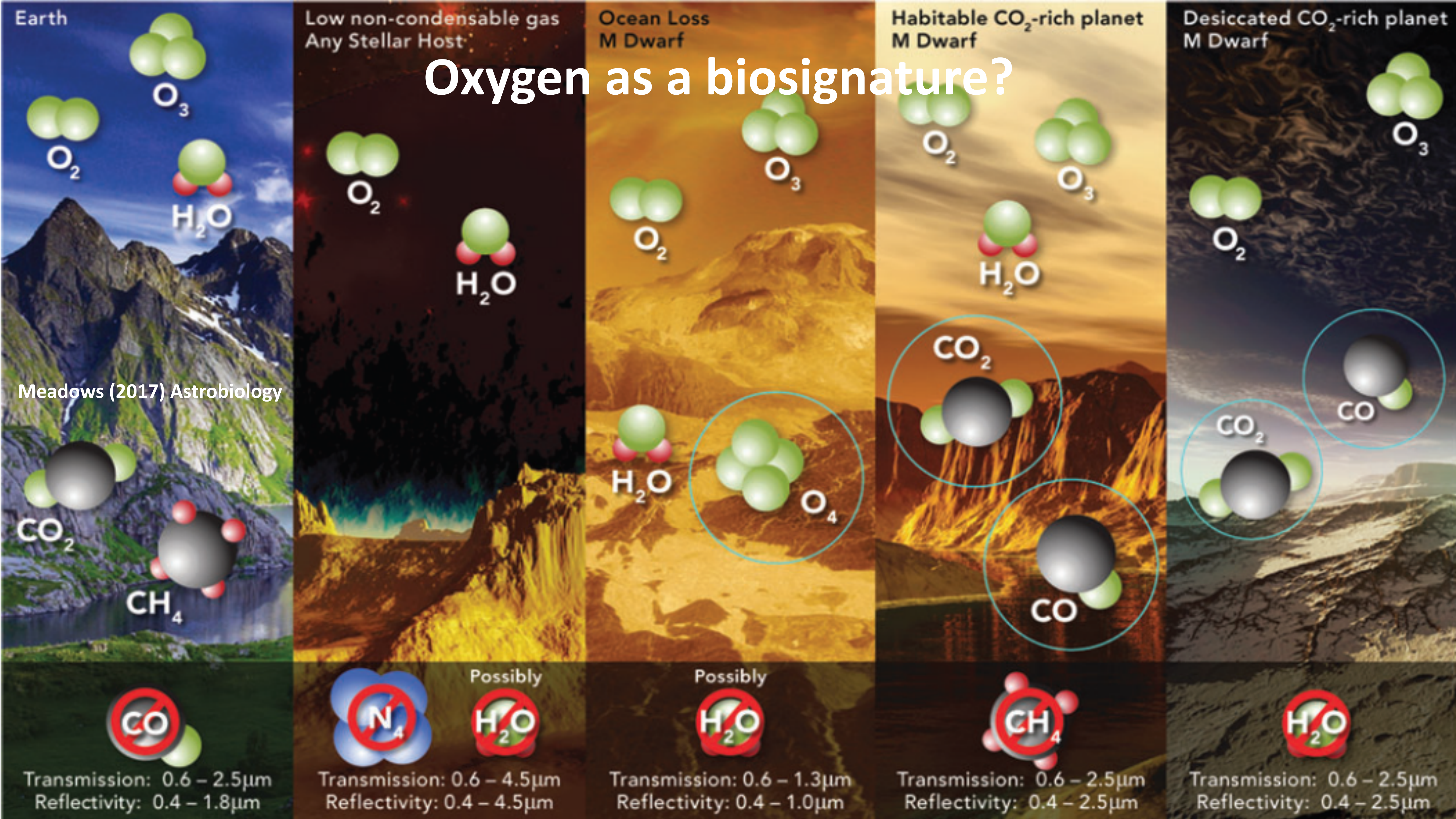
Disequilibrium biosignatures over Earth history and detecting life in anoxic atmospheres

Joshua Krissansen-Totton
University of Washington (soon UCSC)

Courtesy NASA/JPL-Caltech

Oxygen as a biosignature?



Meadows (2017) Astrobiology

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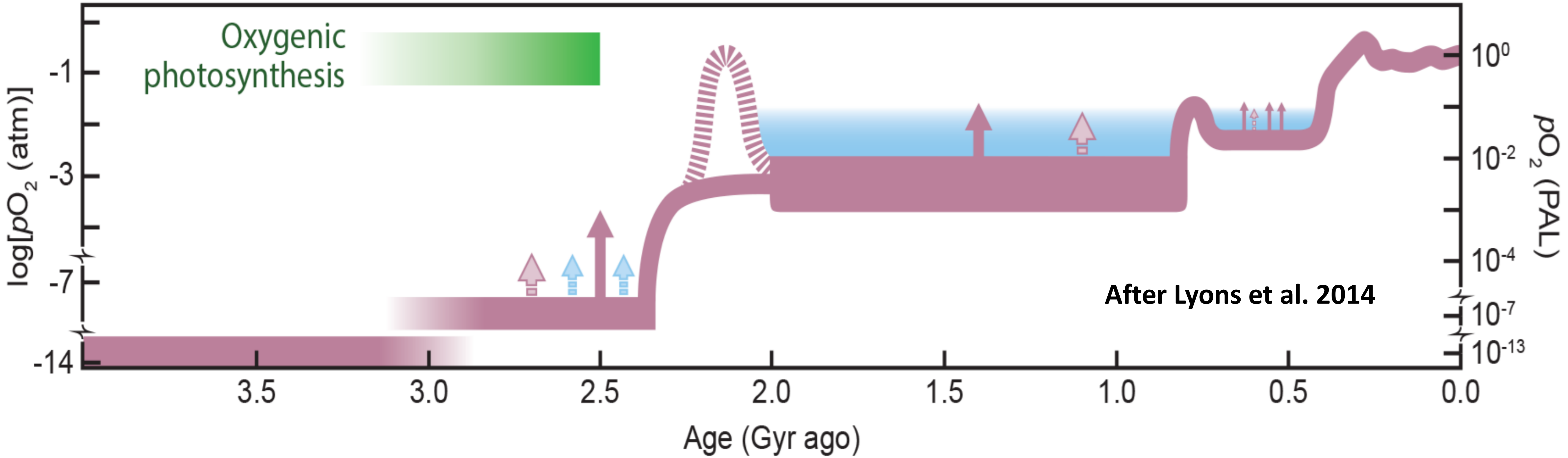
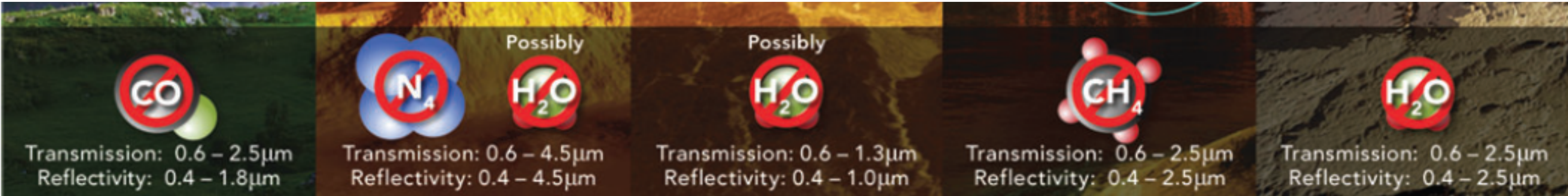


After Lyons et al. 2014



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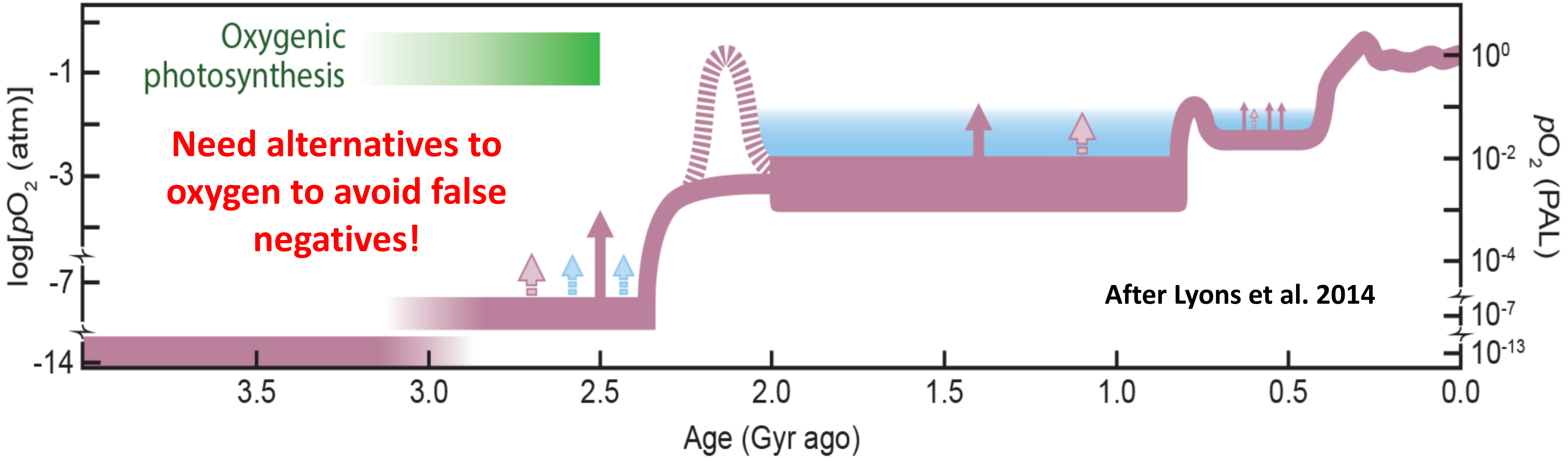
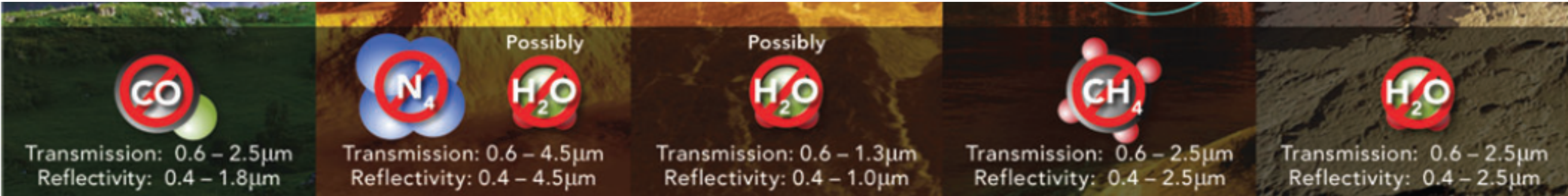


Need alternatives to oxygen to avoid false negatives!

After Lyons et al. 2014



Disequilibrium

The co-existence of incompatible species

Chemical disequilibrium as an exoplanet biosignature

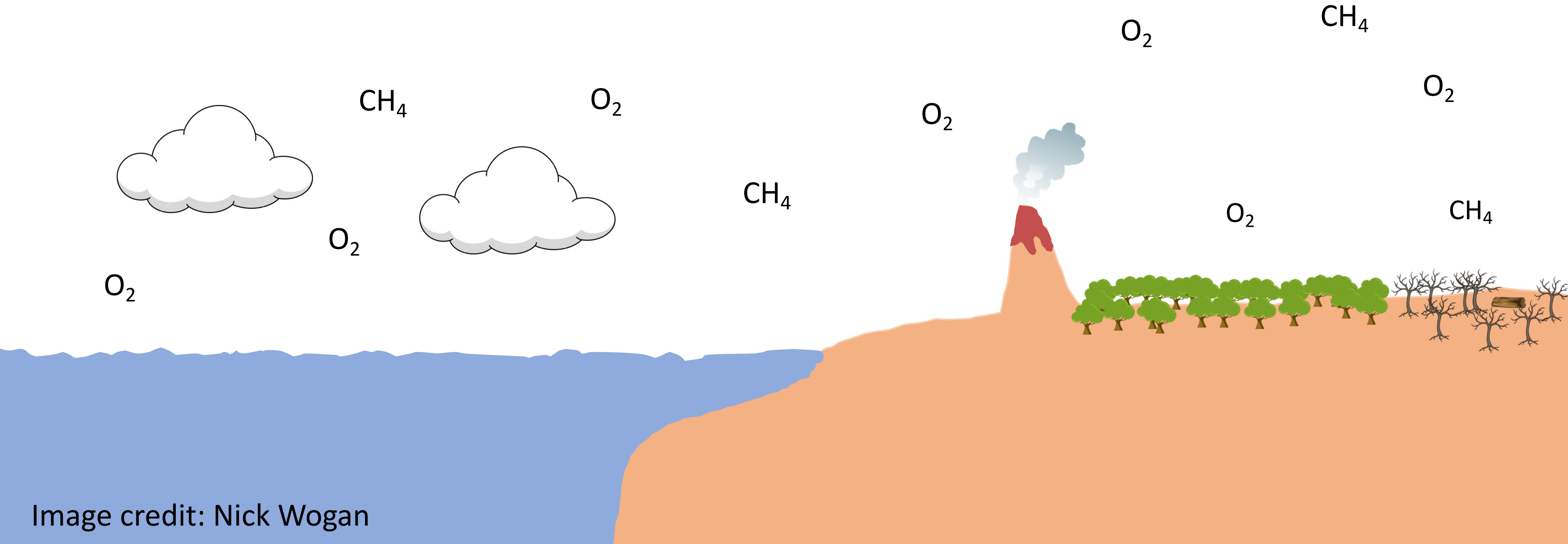
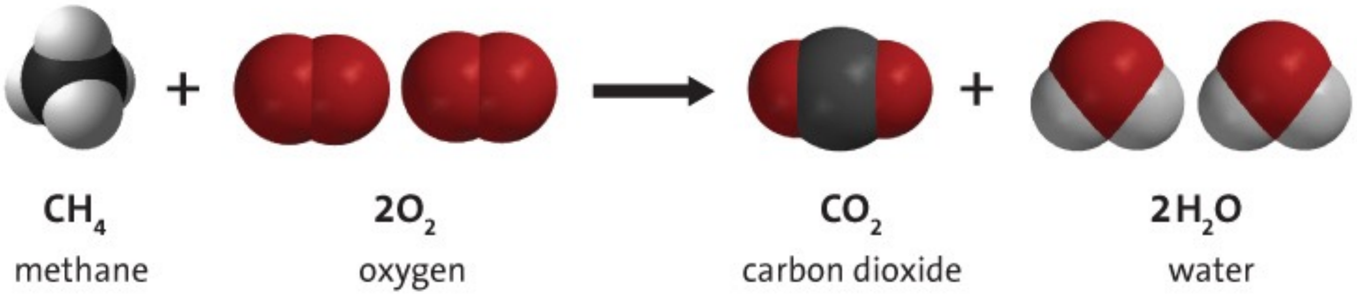
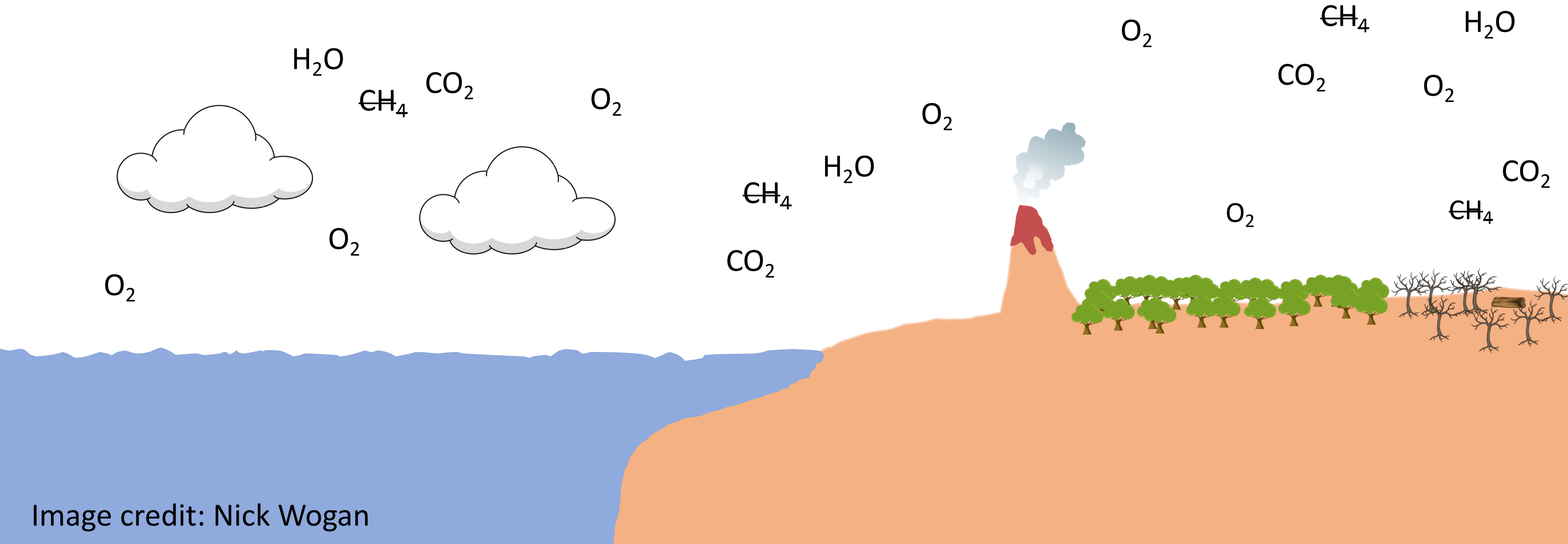


Image credit: Nick Wogan

Chemical disequilibrium as an exoplanet biosignature





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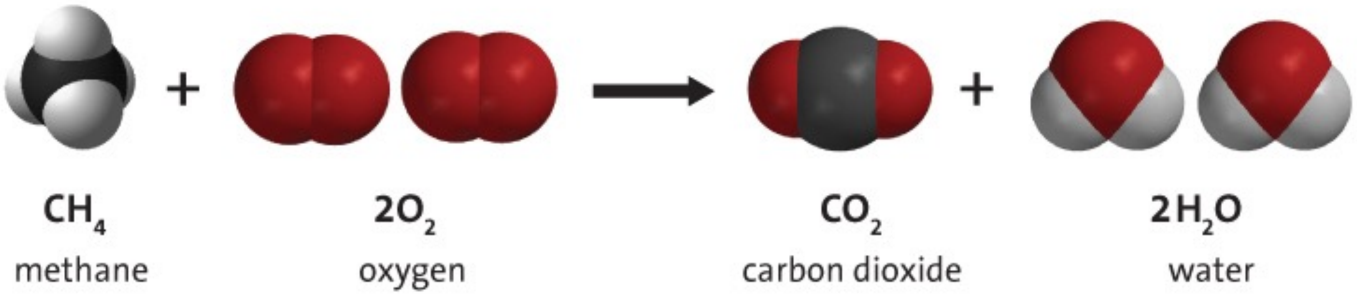
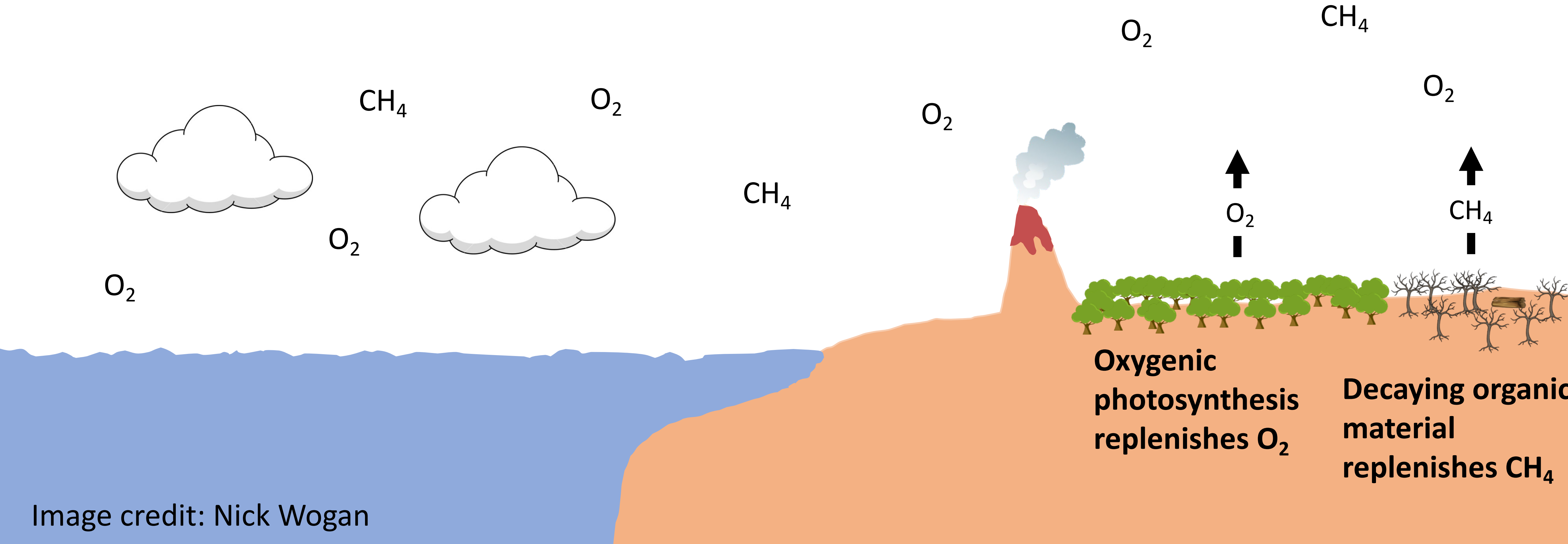




Oxygenic photosynthesis replenishes O_2

Decaying organic material replenishes CH_4

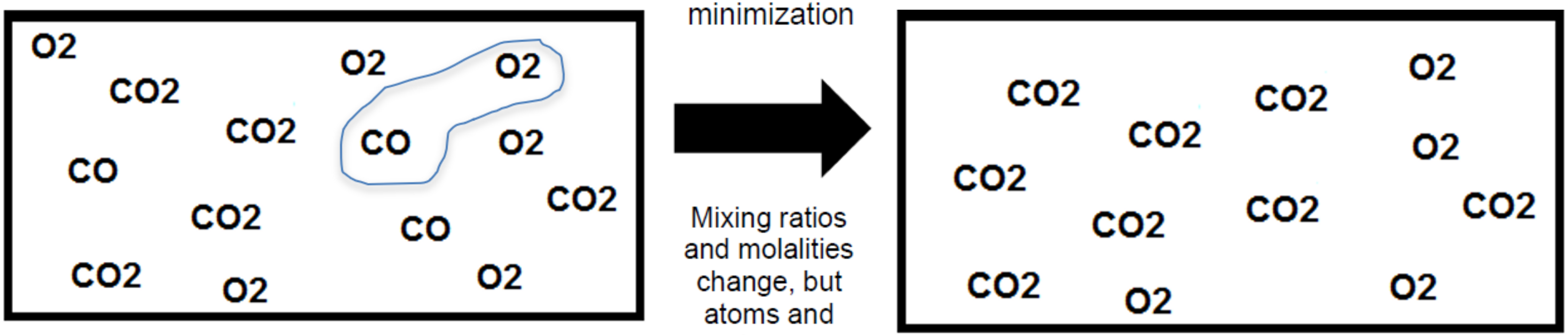
Image credit: Nick Wogan

Quantify chemical disequilibrium

Initial/Observed State

React to
equilibrium via
Gibbs energy
minimization

Equilibrium State



Mixing ratios
and molalities
change, but
atoms and
charge
conserved.

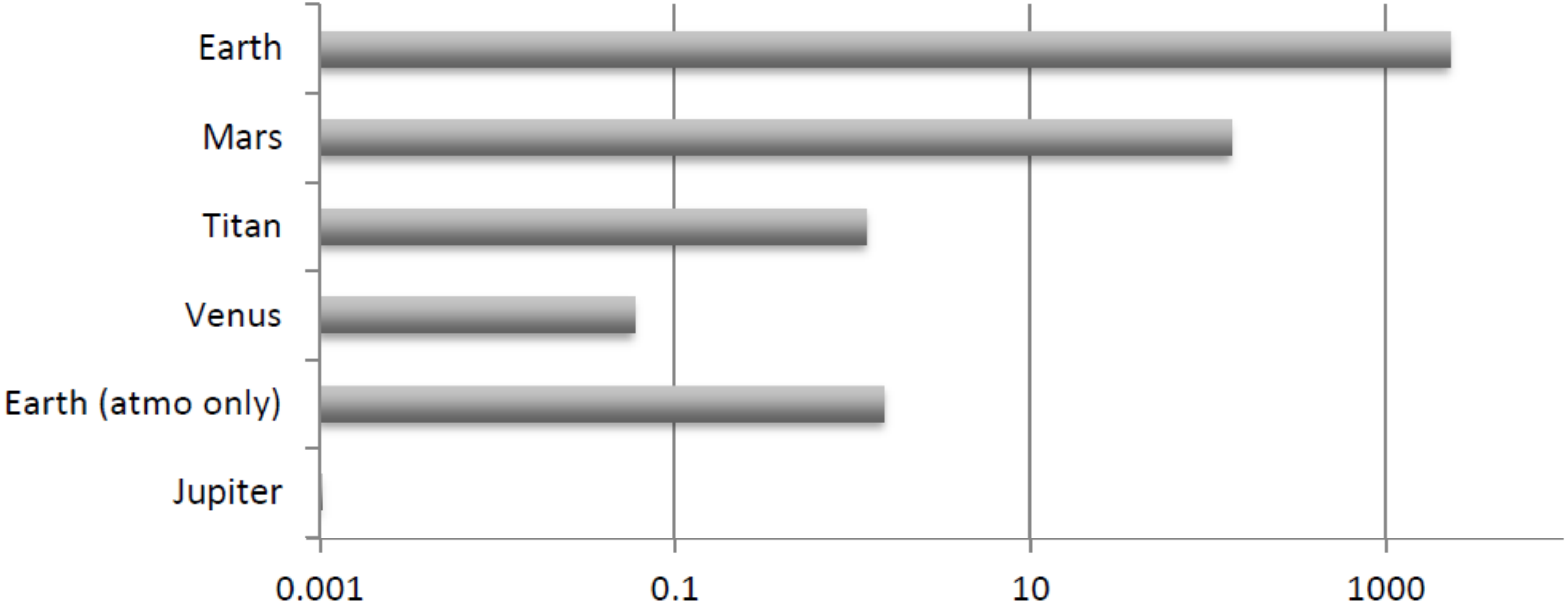
Gibbs energy of initial state, $G_{(T,P)}(\mathbf{n}_{\text{initial}})$

Gibbs energy of equilibrium state, $G_{(T,P)}(\mathbf{n}_{\text{final}})$

$$\boxed{\text{Available energy, } \Delta G = G_{(T,\mathrm{P})}(\mathit{initial}) - G_{(T,\mathrm{P})}(\mathit{equilibrium})}$$

Earth has largest disequilibrium in the solar system

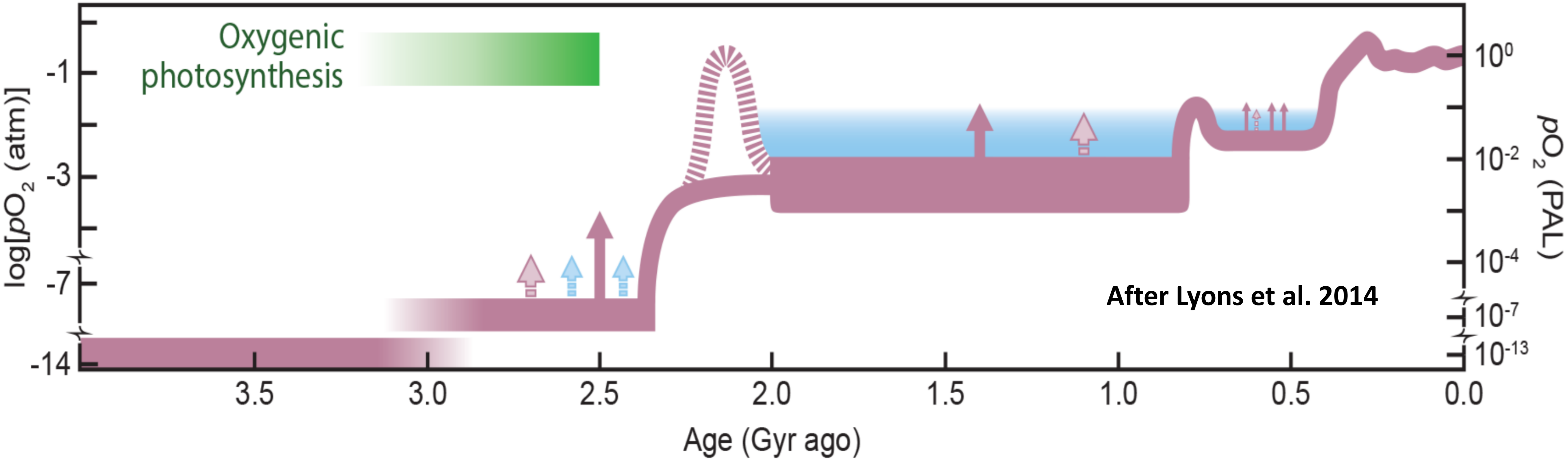
$$2N_2(g) + 5O_2(g) + 2H_2O(l) \rightleftharpoons 4H^+(aq) + 4NO_3^-(aq)$$



$\boxed{\text{Available energy, } \Delta G = G_{(T,\mathrm{P})}(initial) - G_{(T,\mathrm{P})}(equilibrium)}$ **(J/mol)**

J. Krissansen-Totton, D. Bergsman, D. C. Catling (2016) *Astrobiology* 16, 39-67

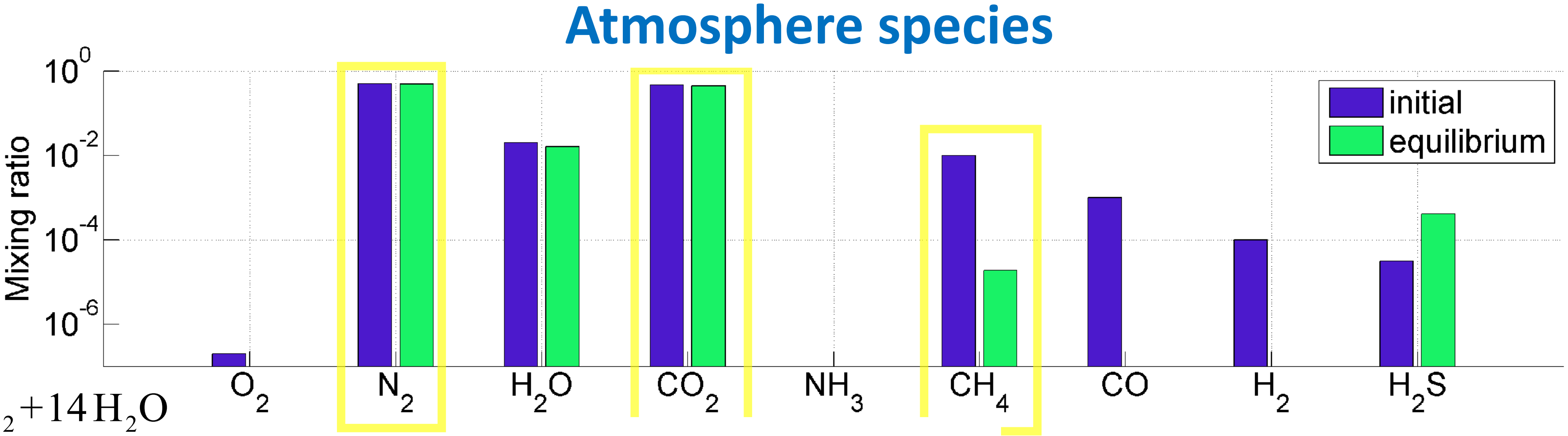
BUT O2-N2-H2O and O2/O3-CH4 are variations on oxygen as a biosignature!



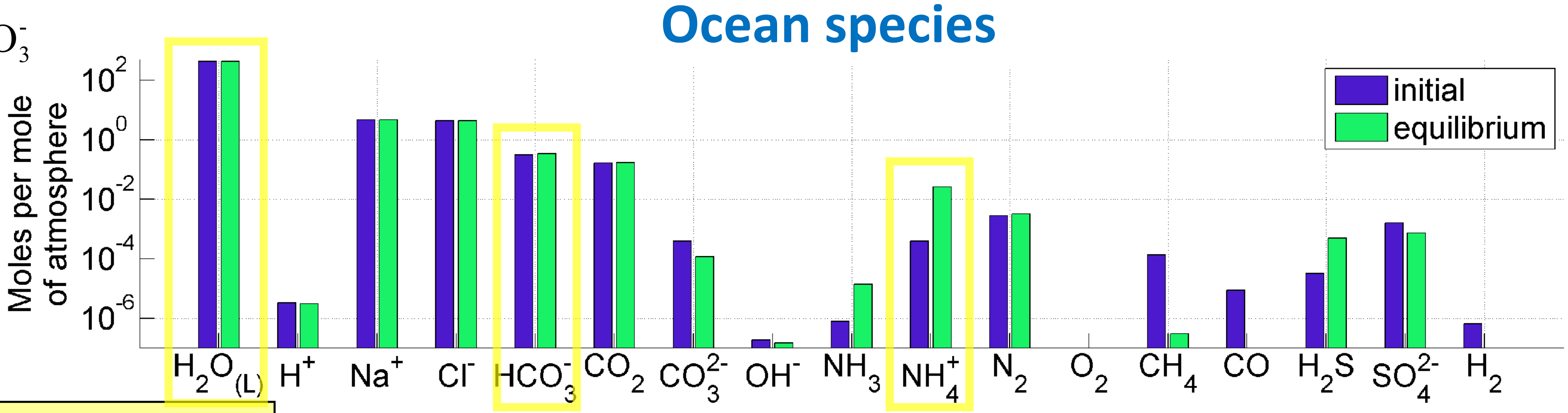
After Lyons et al. 2014

- The early Earth is the only example we have of an anoxic biosphere!

Archean atmosphere-ocean disequilibrium


Atmosphere species

$$5\,CO_2 + 3\,CH_4 + 4\,N_2 + 14\,H_2O$$
$$\rightarrow 8\,NH_4^+ + 8\,HCO_3^-$$


Ocean species

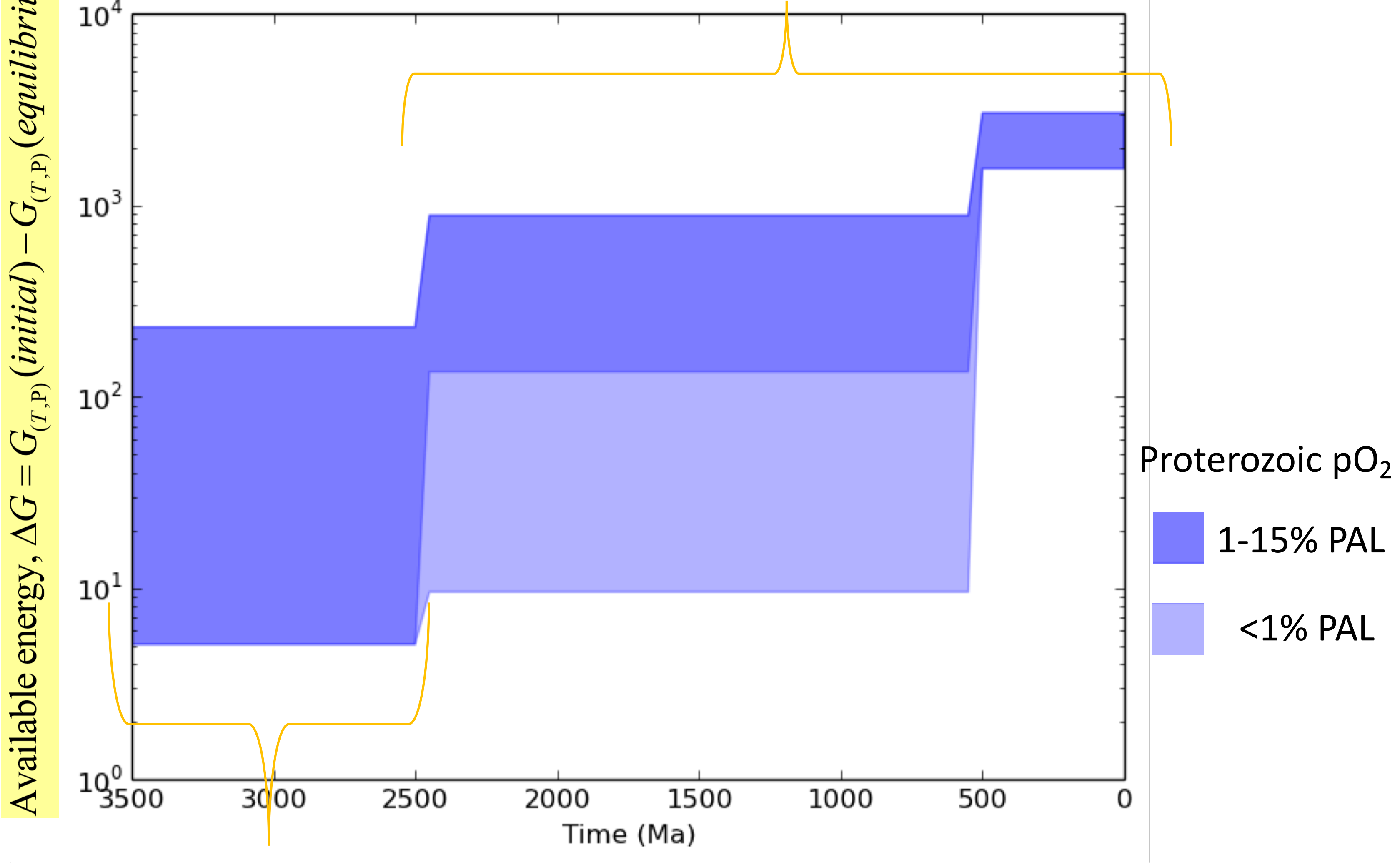
Available energy,

$$\Delta G = G_{(T,\mathrm{P})}(obser) - G_{(T,\mathrm{P})}(equil)$$

$$\Delta G < 231\ \mathrm{J/mol}$$

The Evolution of Earth’s thermodynamic disequilibrium

$$5\,O_2 + 2\,N_2 + 2\,H_2O \rightarrow 4\,H^+ + 4\,NO_3^-$$



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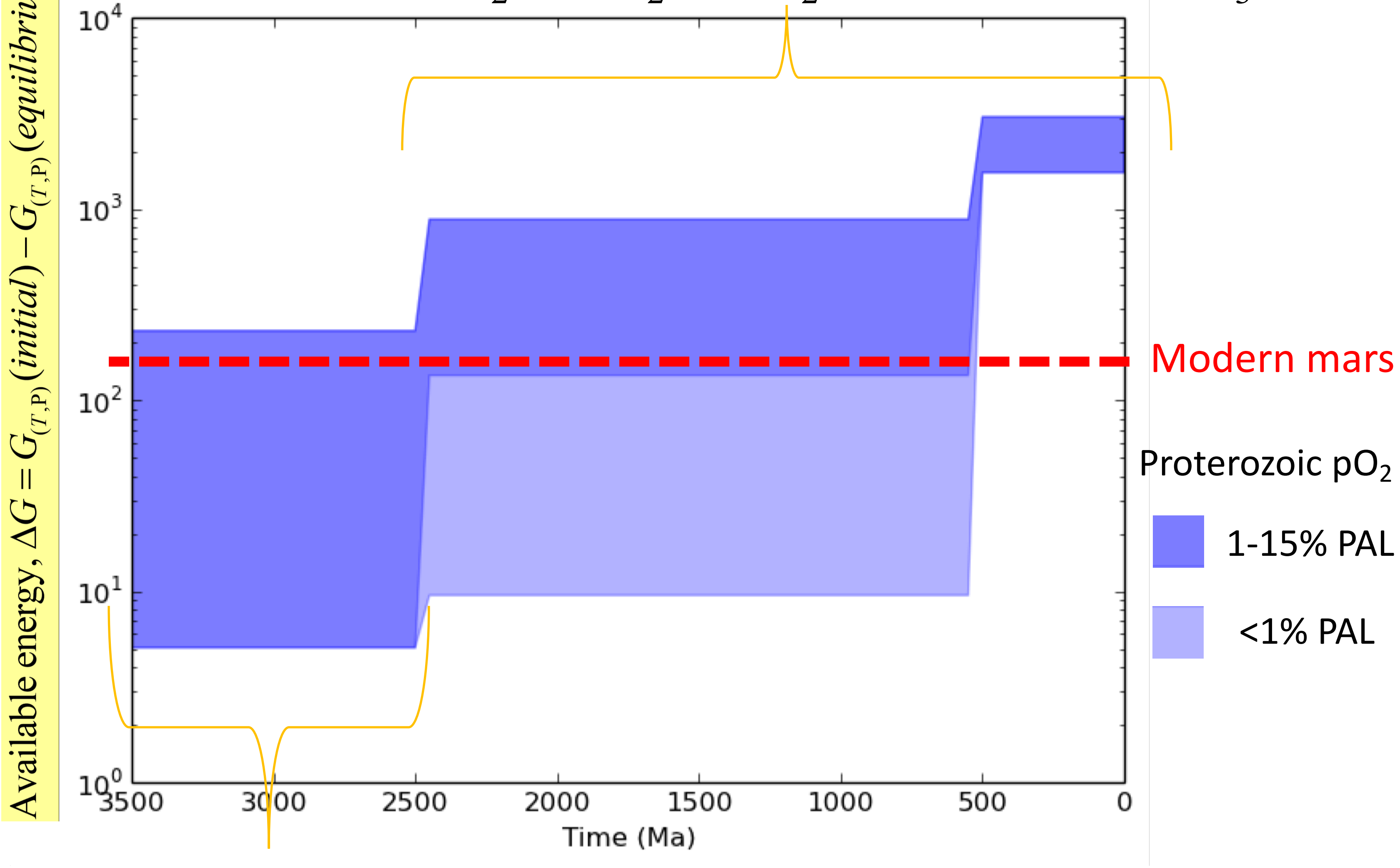

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Would a CH_4+CO_2 disequilibrium combination be a good exoplanet biosignature?

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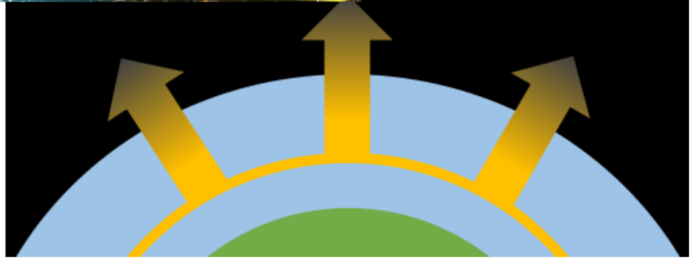
- CH_4 has short lifetime, perhaps ~30,000 yrs for diffusion limited escape.



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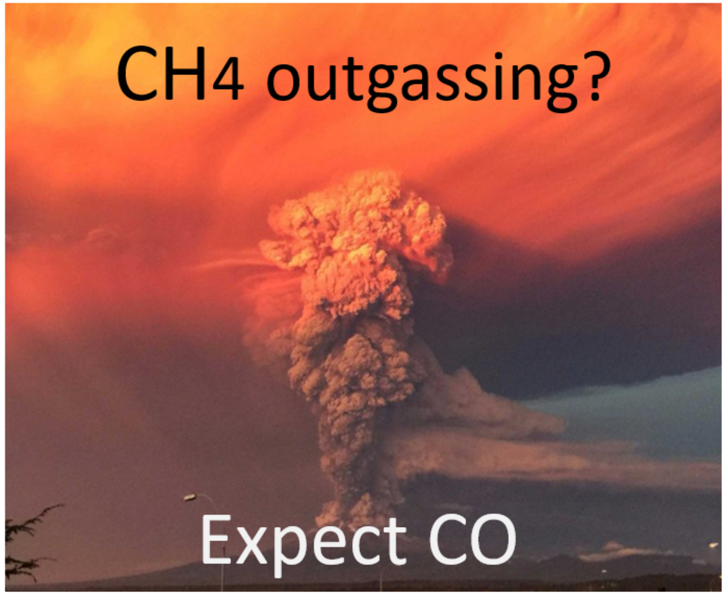
- Methanogenesis is an ancient and “primitive” metabolism

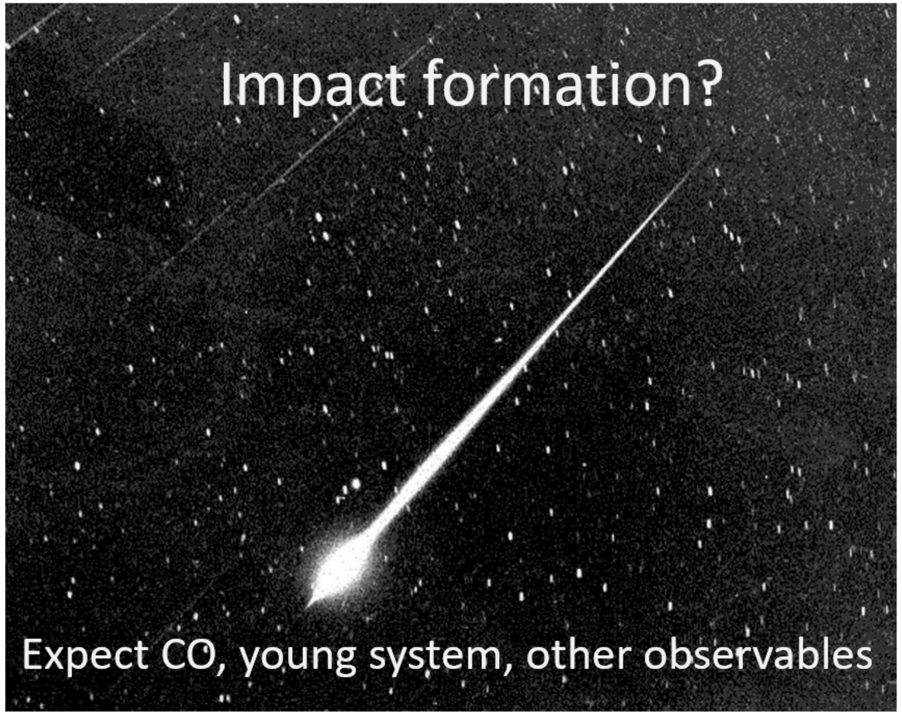
- CH_4 has short lifetime, perhaps ~30,000 yrs for diffusion limited escape.

- Would not expect CH_4+CO_2 atmospheres to persist without replenishing flux. Could there be large abiotic fluxes of CH_4?

Possible false positives for biogenic CH_4 + CO_2?


CH_4 outgassing?

Expect CO


Impact formation?

Expect CO, young system, other observables


Warm Titan?

CH_4 won't persist

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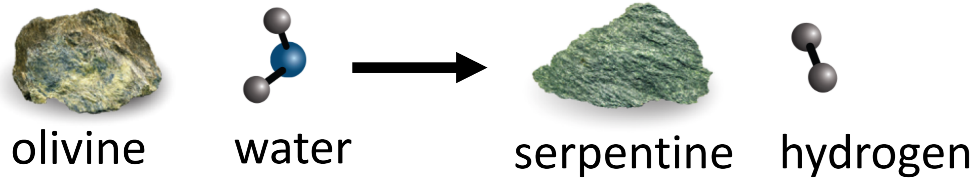
Serpentinization: Source of Hydrogen

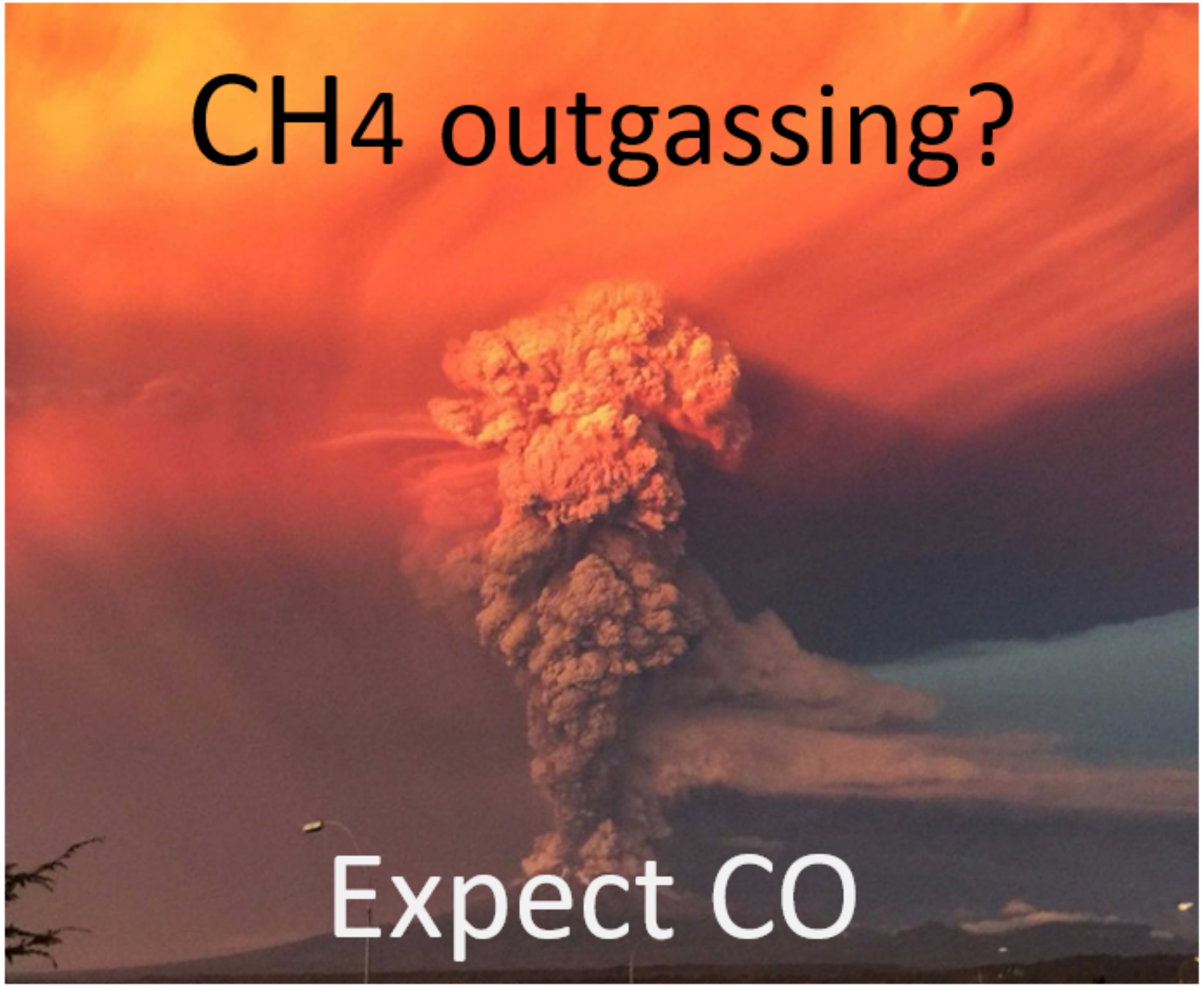


Credit: Jennifer Glass

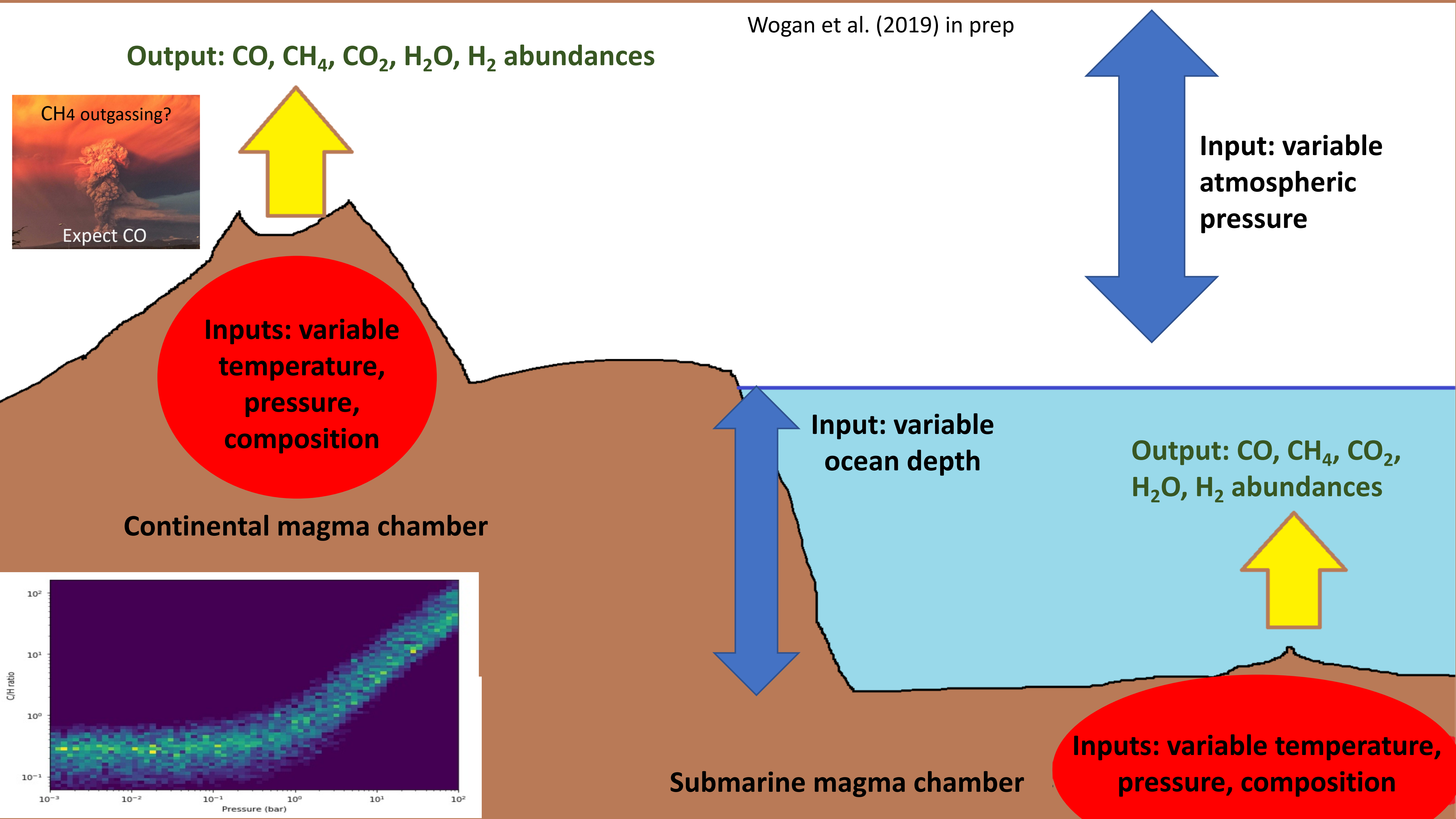
$$4H_2 + CO_2 \rightarrow CH_4 + 2H_2O$$

"Fischer-Tropsch Process" $$3H_2 + CO \rightarrow CH_4 + H_2O$$

Could a planet outgas CH_4 and CO_2?



Wogan et al. (2019) in prep



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Output: CO, CH_4, CO_2, H_2O, H_2 abundances

Input: variable atmospheric pressure

Inputs: variable temperature, pressure, composition

Continental magma chamber

Input: variable ocean depth

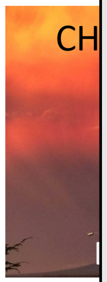
Output: CO, CH_4, CO_2, H_2O, H_2 abundances

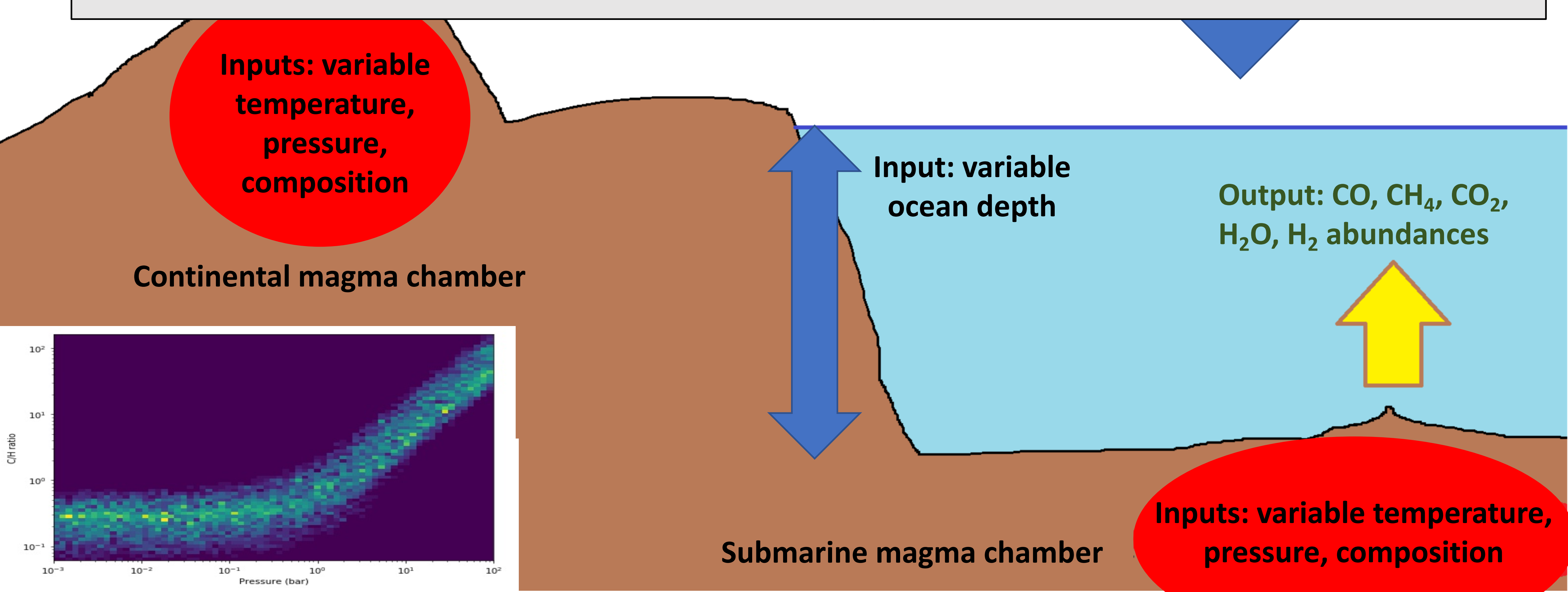
Submarine magma chamber

Inputs: variable temperature, pressure, composition

Wogan et al. (2019) in prep

Key outputs: CO/CO_2 and CO/CH_4 outgassing ratios





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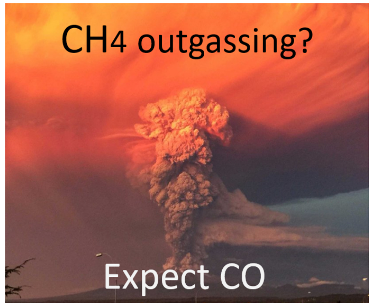

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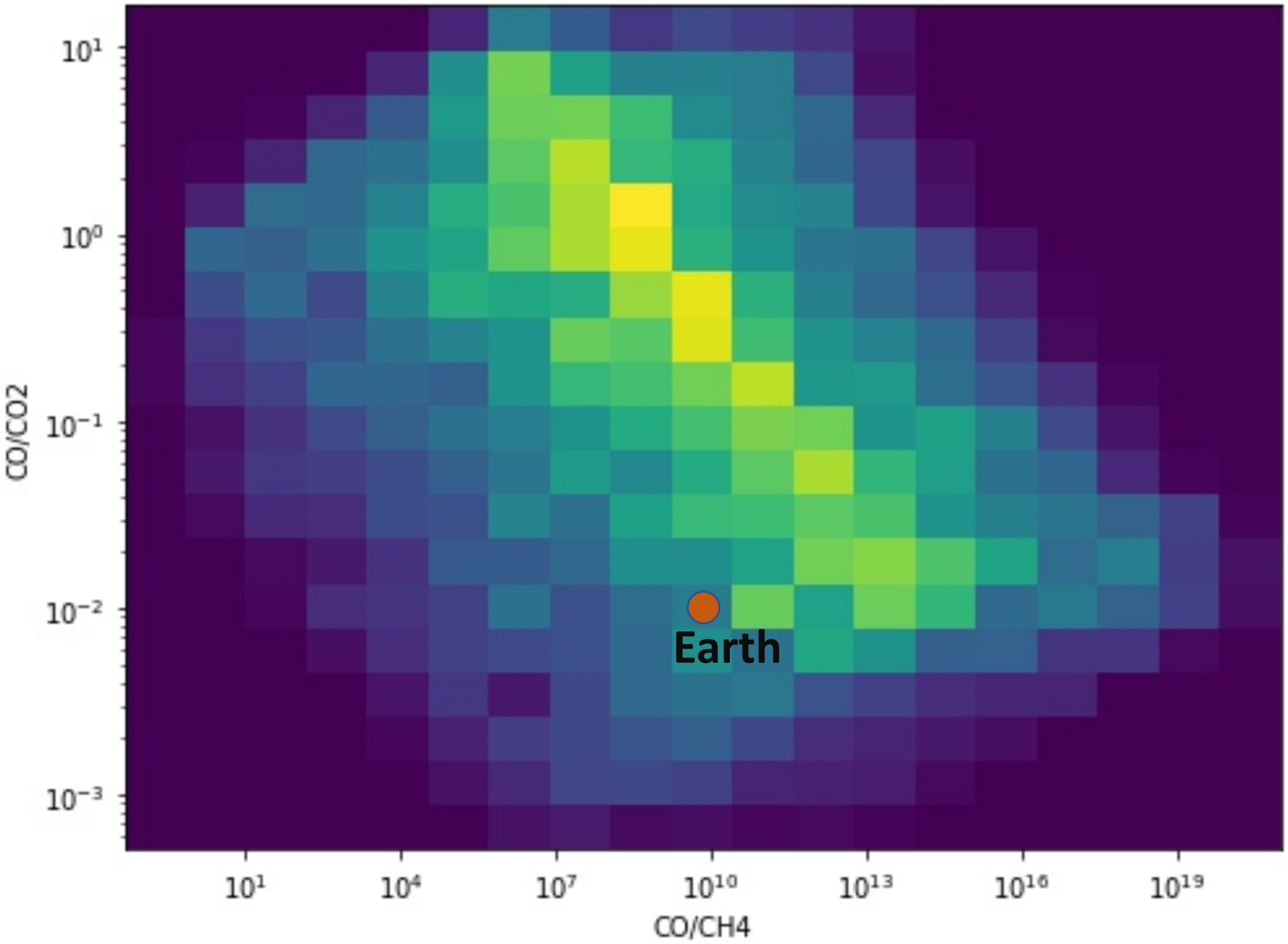
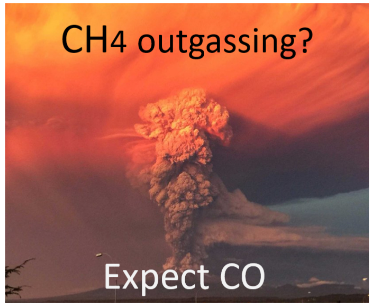


Key point: simultaneous outgassing of CO_2 and CH_4 without CO is very unlikely



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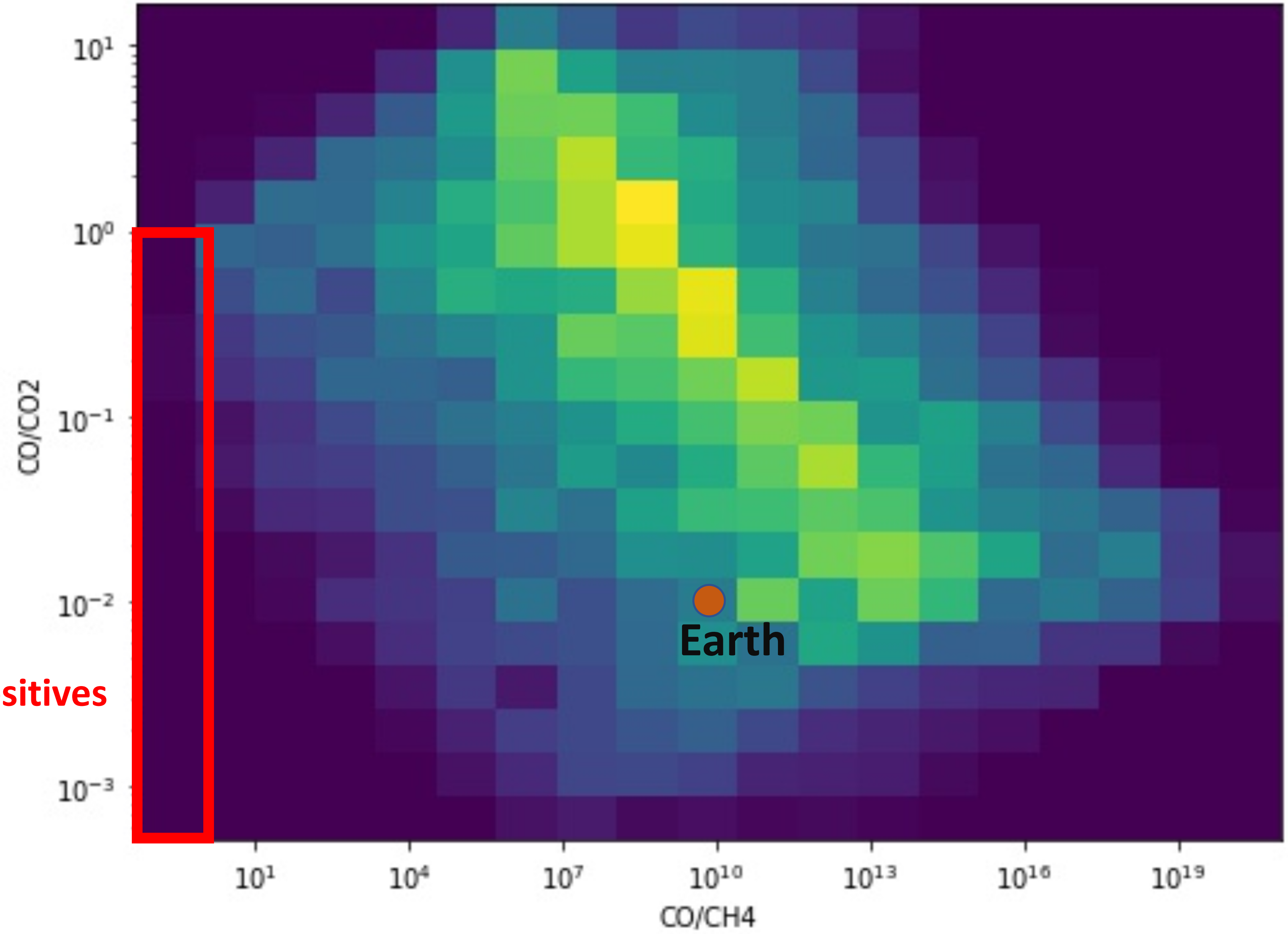

Possible false positives

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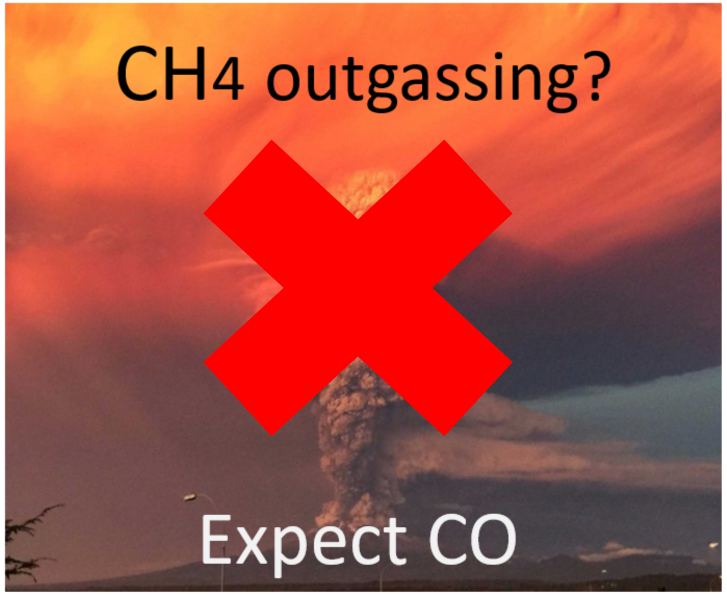

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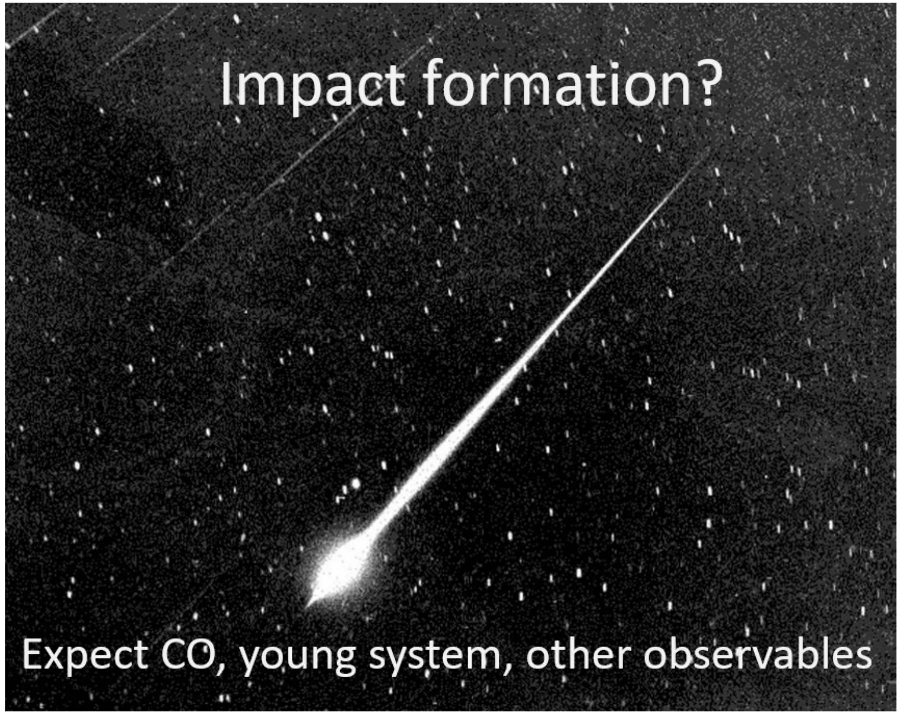

Impact formation?

Expect CO, young system, other observables

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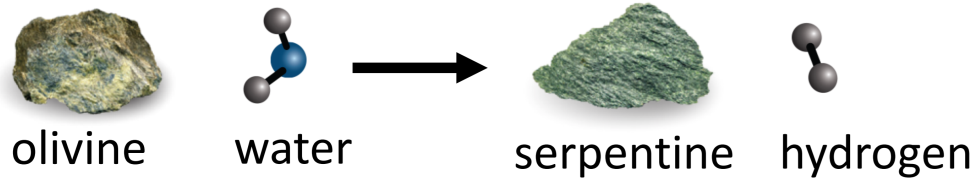
Serpentinization: Source of Hydrogen



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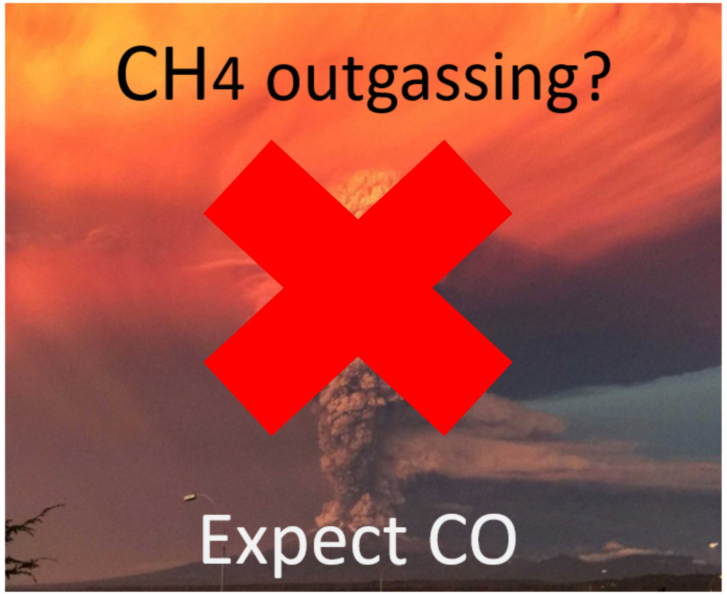

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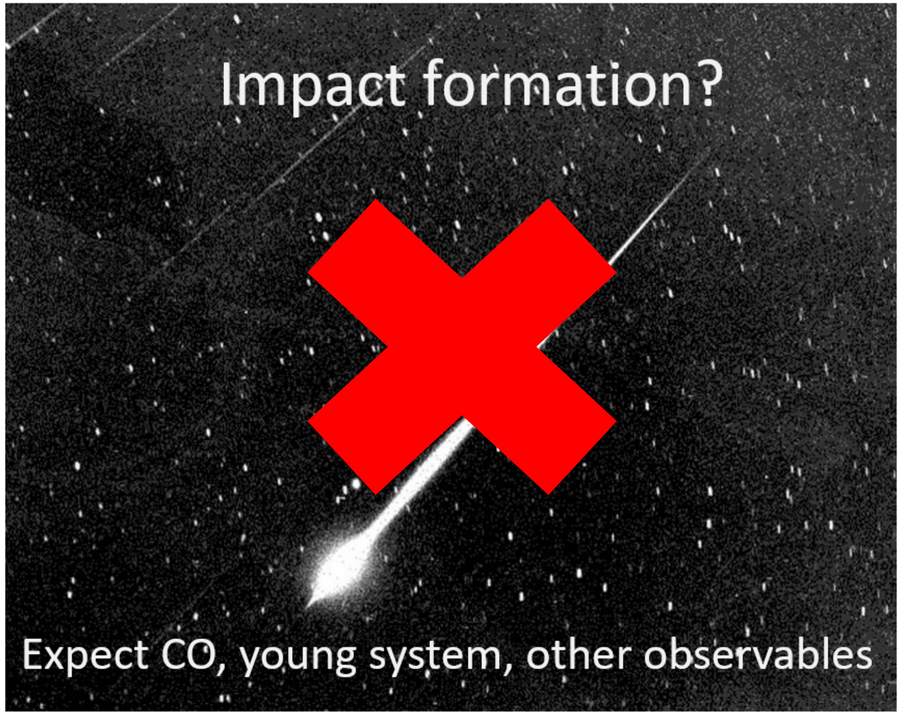

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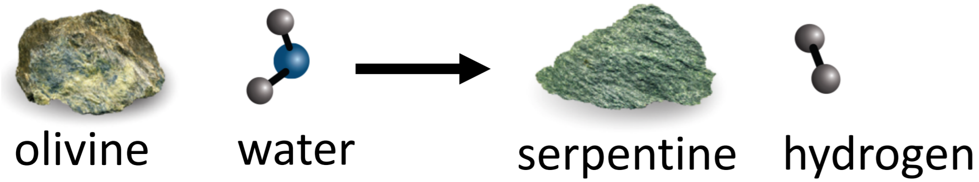

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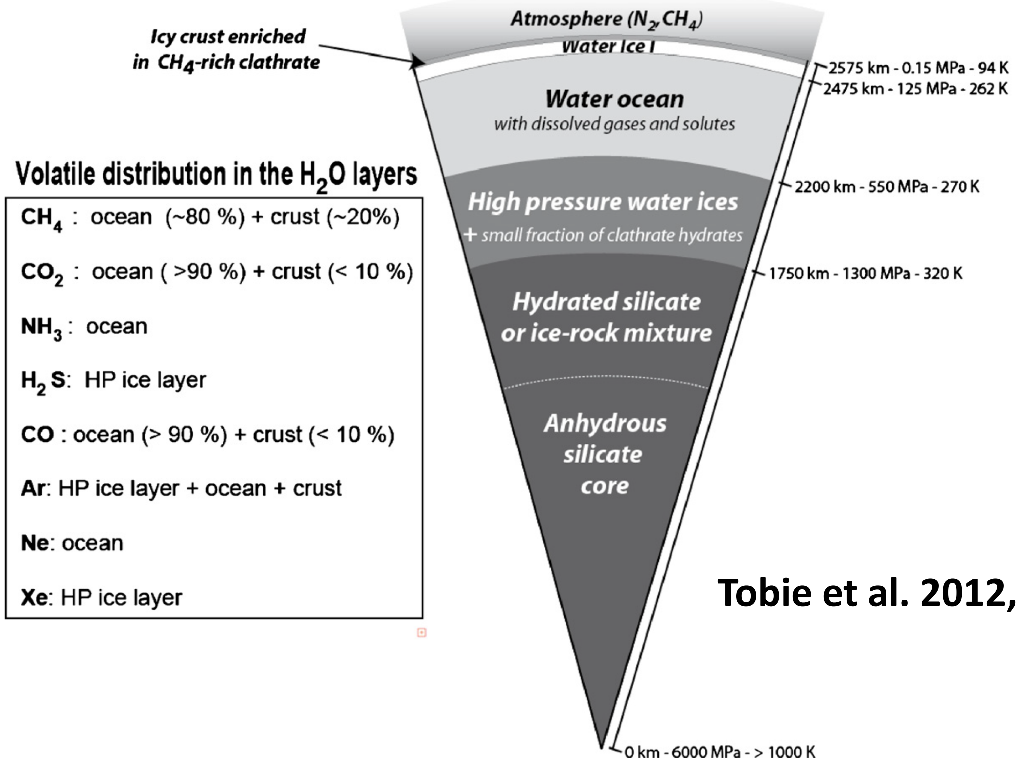


Volatile distribution in the H_2O layers

CH_4 : ocean (~80 %) + crust (~20%)

CO_2 : ocean (>90 %) + crust (< 10 %)

NH_3 : ocean

H_2S: HP ice layer

CO : ocean (> 90 %) + crust (< 10 %)

Ar: HP ice layer + ocean + crust

Ne: ocean

Xe: HP ice layer

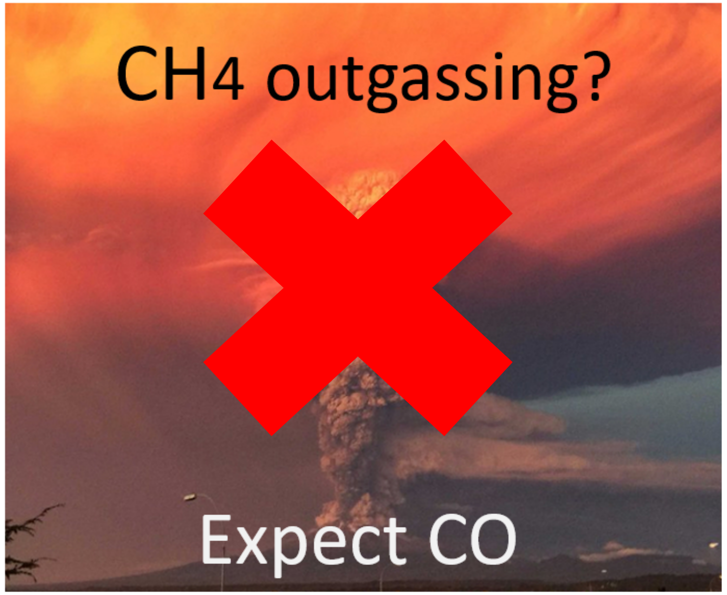
Figure 2. Possible present-day structure of Titan's interior and estimated volatile distribution within the thick H_2O mantle. The radius, temperature, and pressure of each interface are only indicative.

Tobie et al. 2012, ApJ

Table: Estimated photochemical lifetimes of CH_4 for Earth-sized planets with surface oceans of varying size, and Titan-like initial volatile inventories.

Mass of surface ocean (wt% planet mass)	0.1 wt% water	1.0 wt% water	10 wt% water	50 wt% water
Lifetime of CH_4 (Myr)	2	20	200	1000

Possible false positives for biogenic CH_4 + CO_2?



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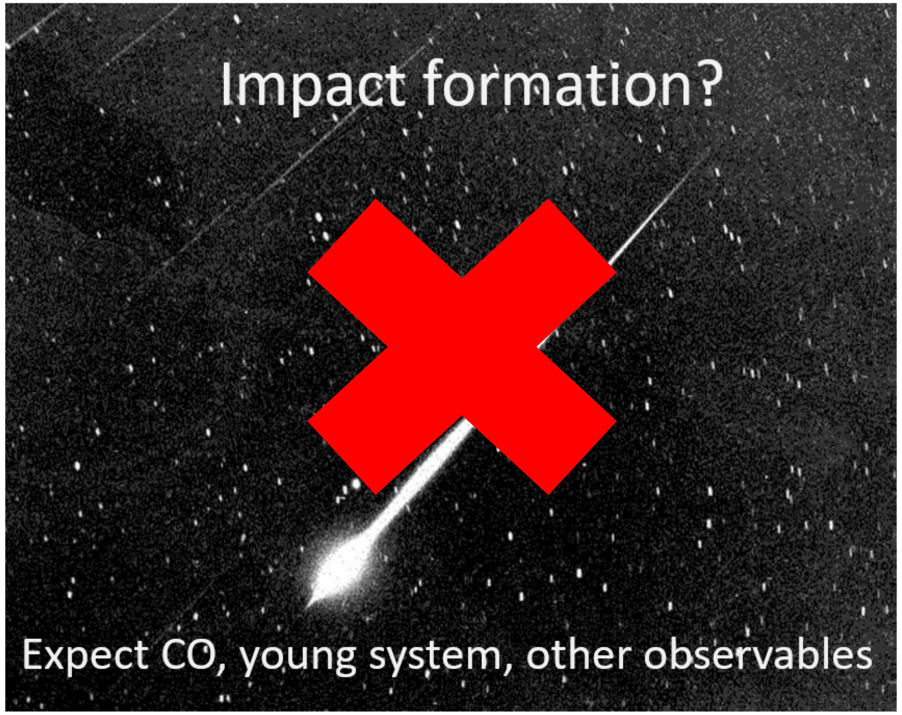

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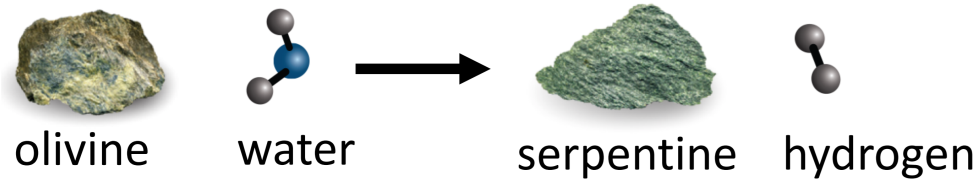

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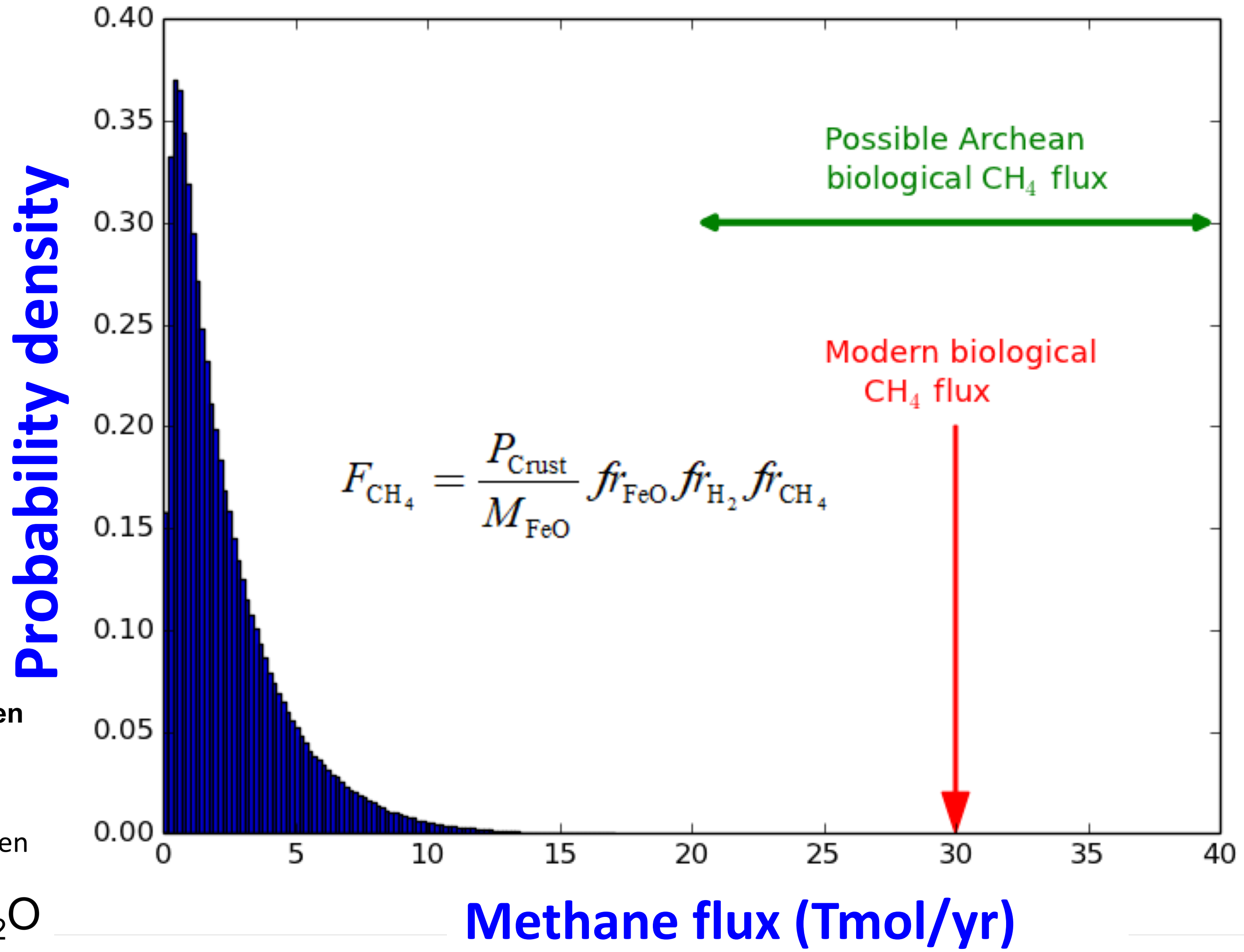
Maximum abiotic methane from serpentinization << biological fluxes



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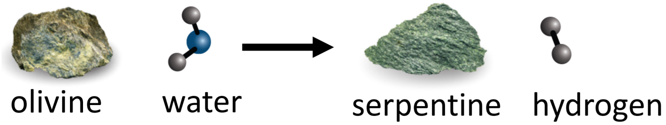

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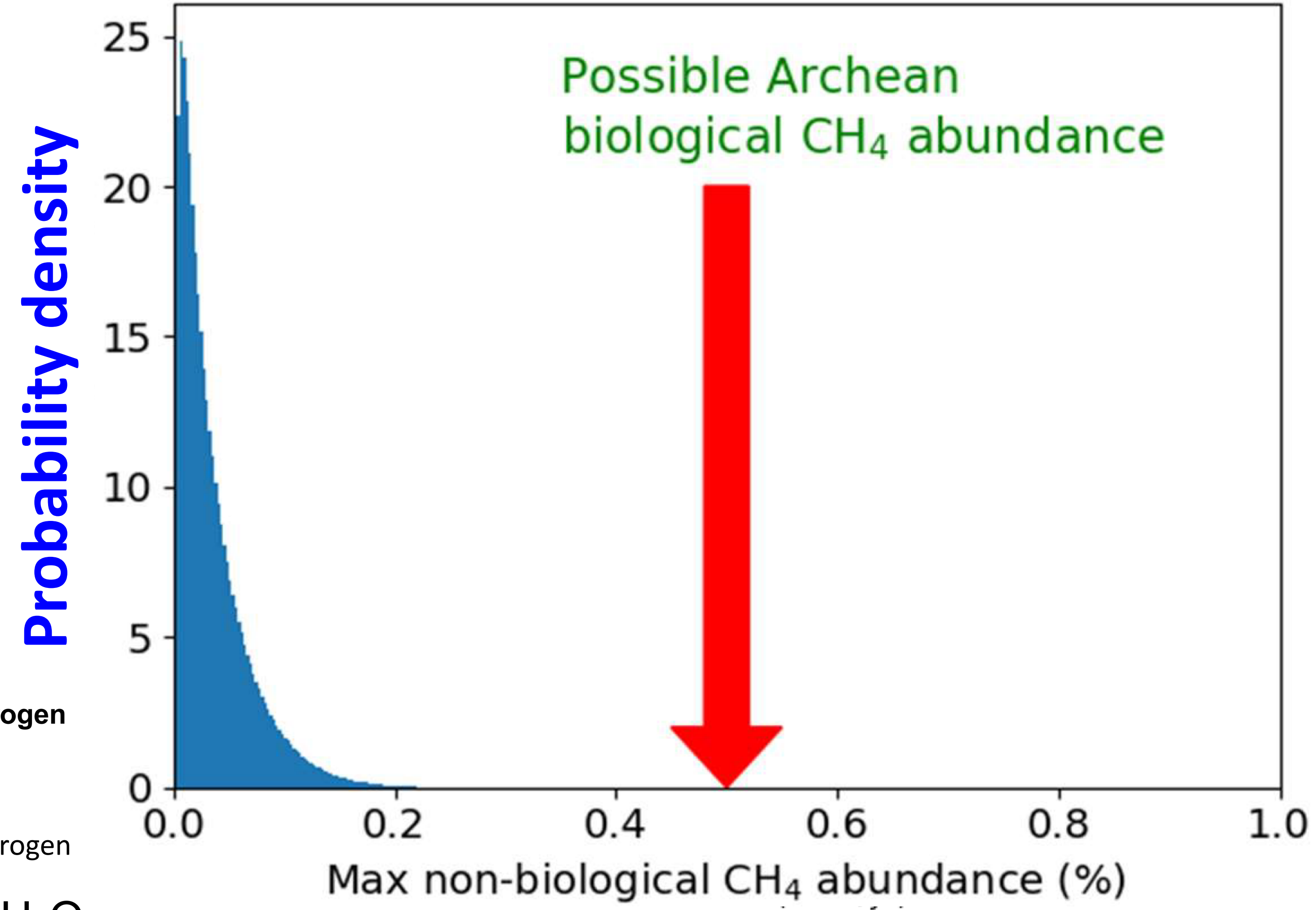

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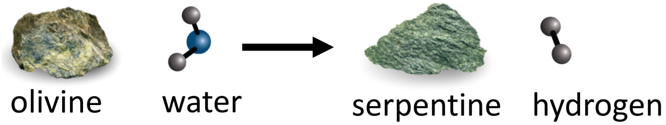

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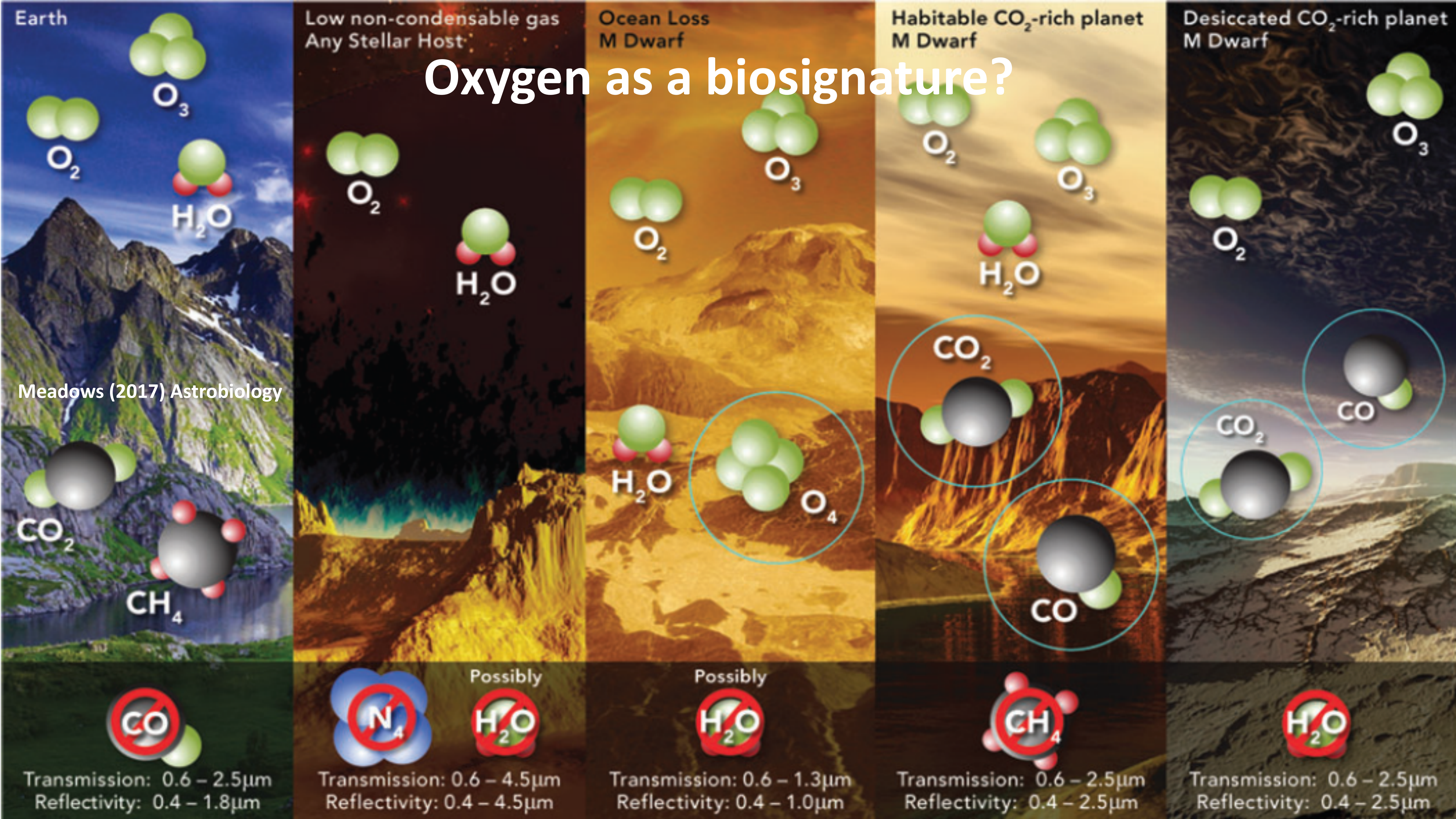
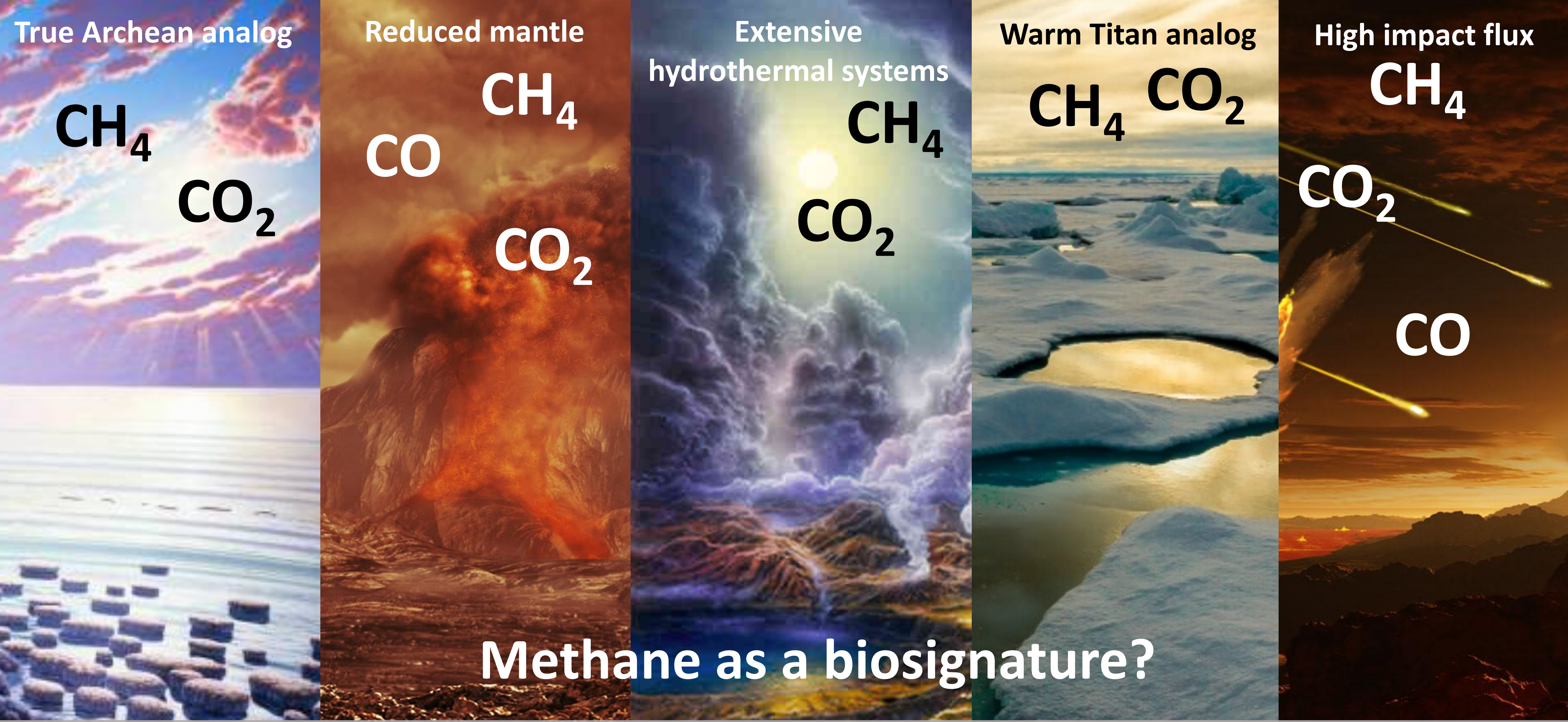
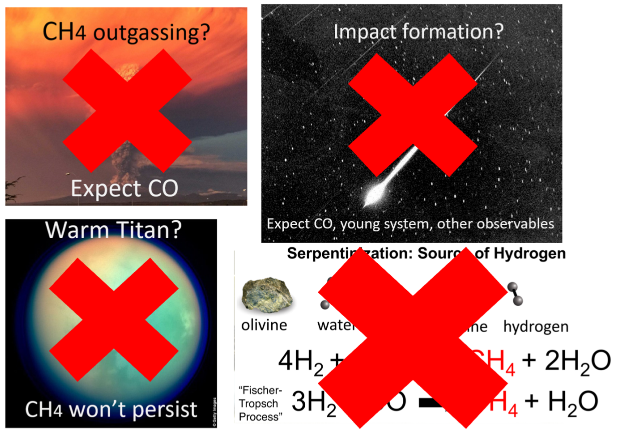


Meadows (2017) Astrobiology

Methane as a biosignature?



True Archean analog	Reduced mantle	Extensive hydrothermal systems	Warm Titan analog	High impact flux
CH_4 CO_2	CH_4 CO CO_2	CH_4 CO_2	CH_4 CO_2	CH_4 CO_2 CO
~~CO~~	CO	$pCH_4 < 0.1$ %	Low bulk density Limited lifetime	Transient Debris disk? Young system?



The bottom line:

The simultaneous detection of atmospheric CO_2 and >1 part per thousand CH_4 (and little/no CO) on a habitable planet is a promising disequilibrium biosignature.

Also: CO_2/CH_4 pair more common O_2/O_3 biosignatures?

Is this detectable with the James Webb Space Telescope?

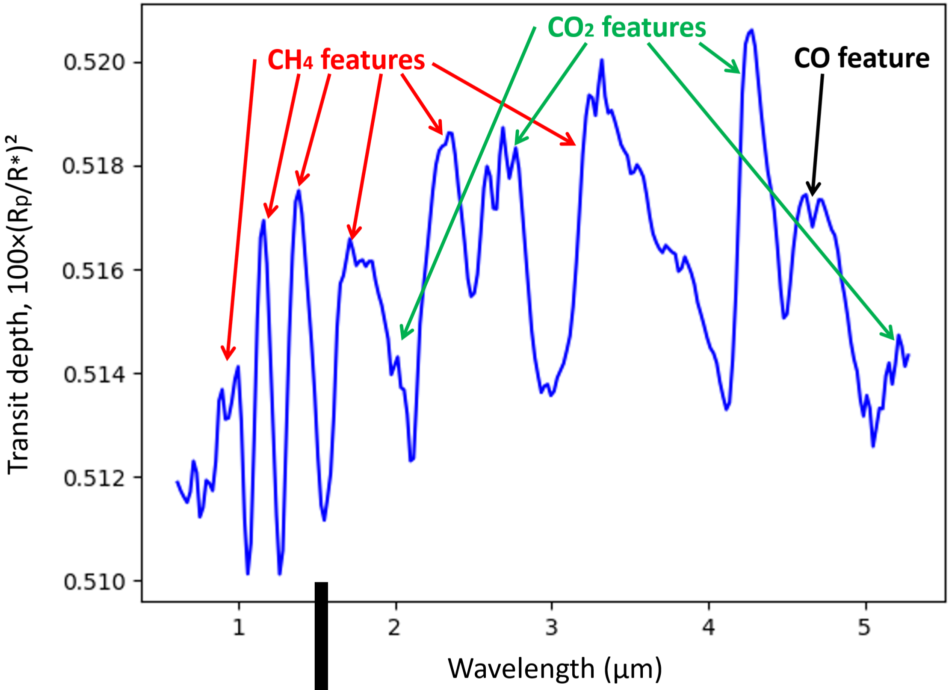
The inverse problem

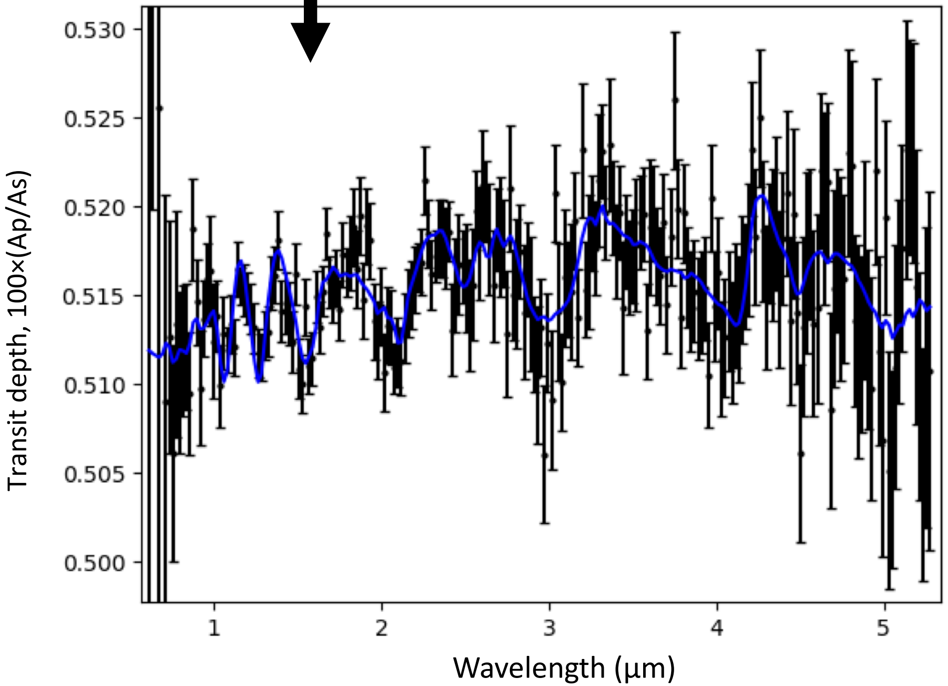
Archean Earth-like composition (no haze)

Mass = 0.772 M_{Earth}
Radius = 0.91 R_{Earth}
pCO_2 = 5%
pCH_4 = 0.5%
pCO = 0%
pH_2O = 1%
T_strat = 200 K
P_surf = 1 bar

Forward model

NEMESIS





Instrument simulator: PandExo described in Batalha et al. (2017) *PASP*

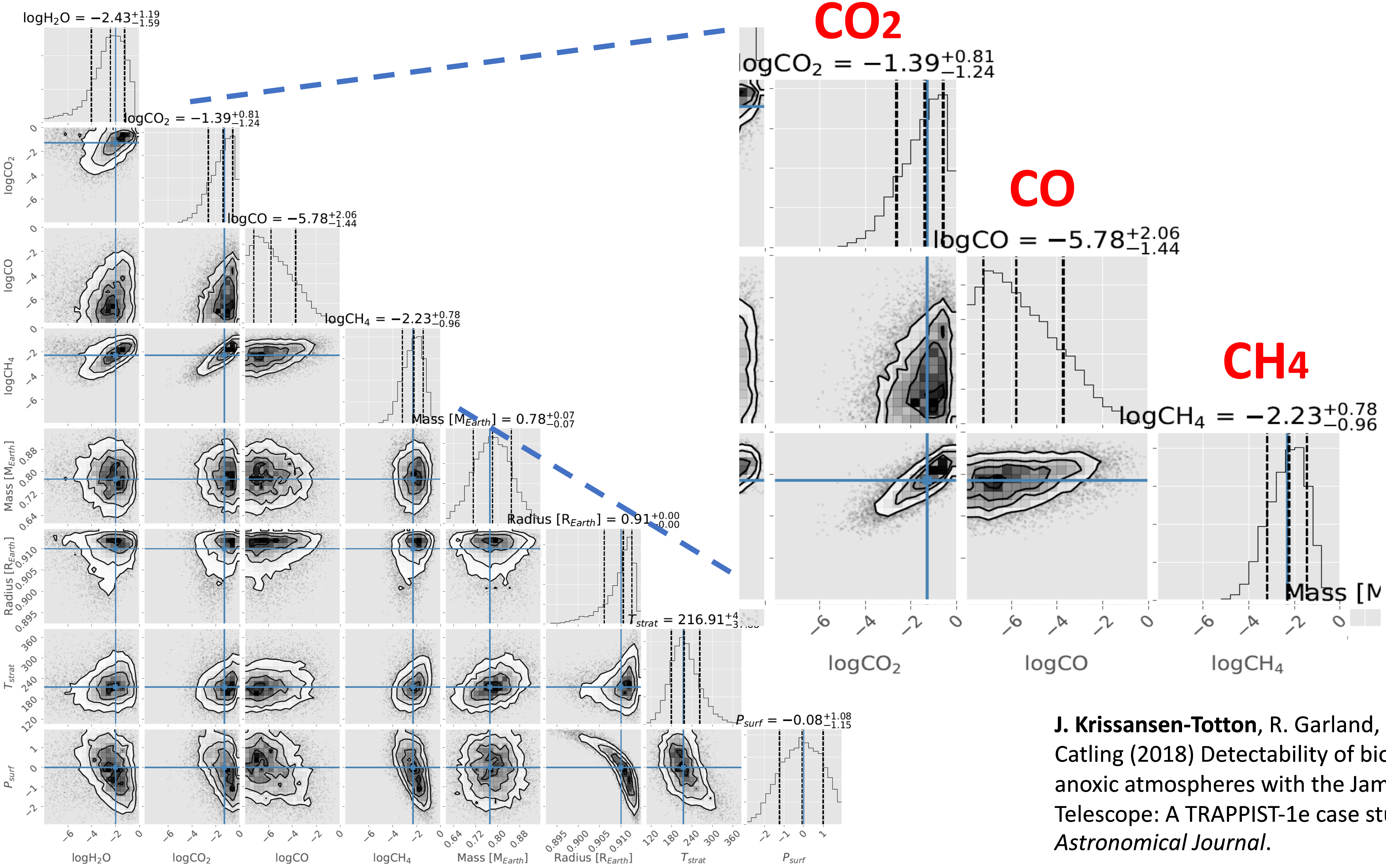
JWST simulator

Solve inverse problem

Mass = 0.81±0.2 M_{Earth}
Radius = 0.901±0.003 R_{Earth}
pCO_2 = 3±2%
pCH_4 = 0.3±0.29%
pCO = 0.001±0.0002%
pH_2O = 0.5±0.48%
T_strat = 188±54 K
P_surf = 2.3±1.3 bar

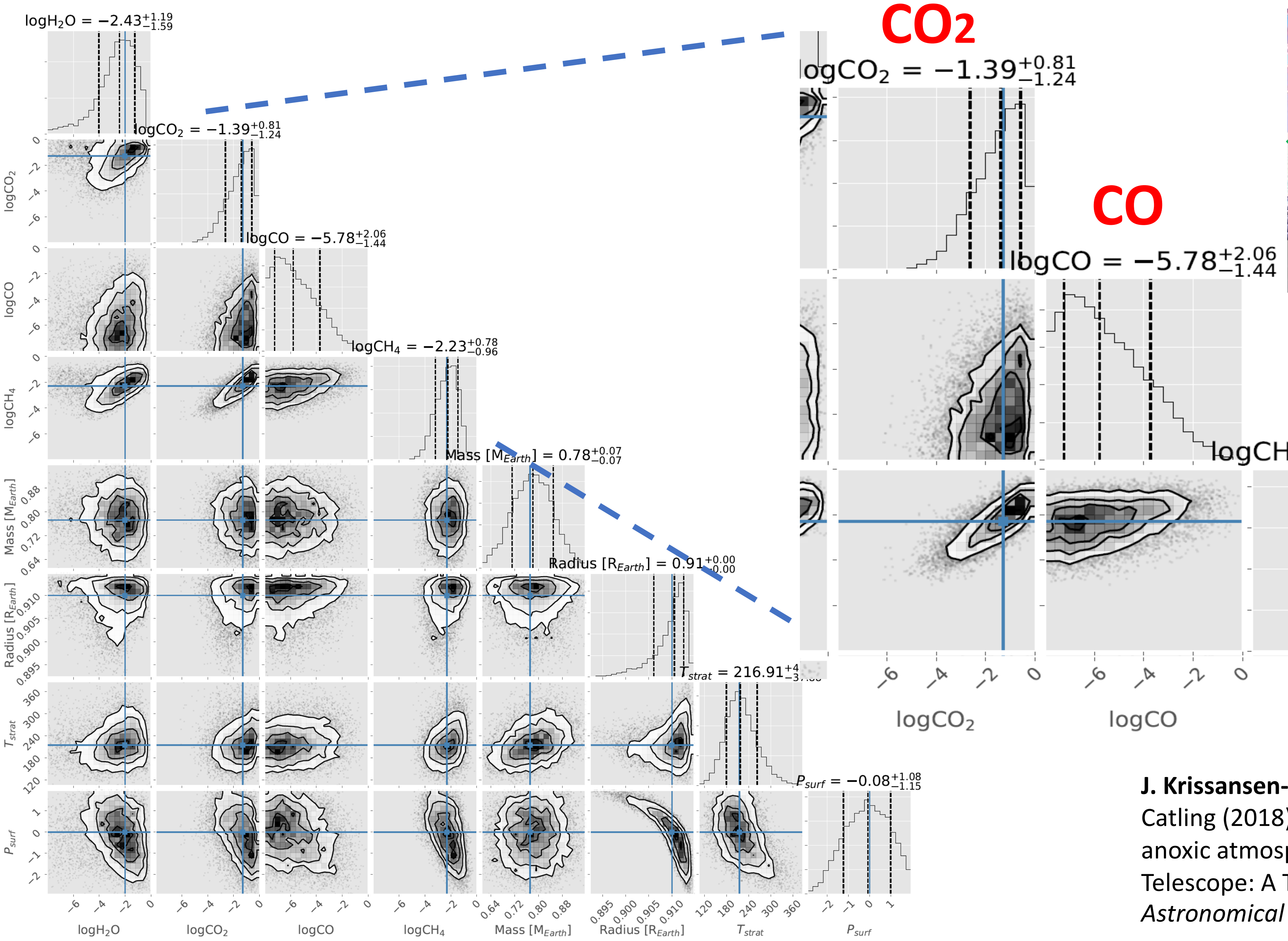
Compare to "true" properties

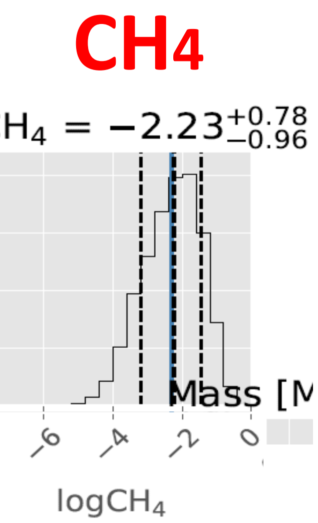
Results: Observing TRAPPIST-1e with James Webb for 10 transits

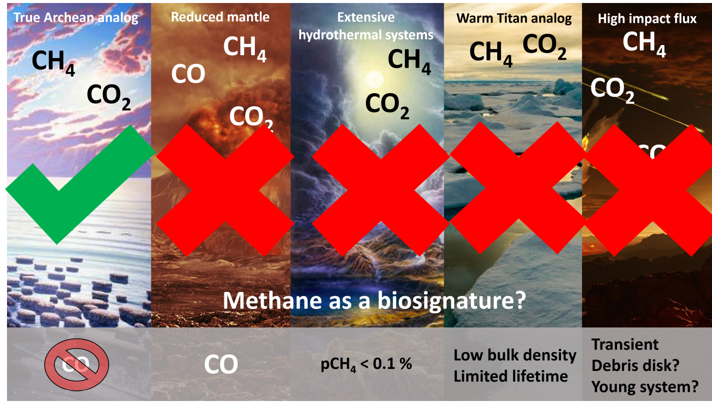


J. Krissansen-Totton, R. Garland, P. Irwin, D. C. Catling (2018) Detectability of biosignatures in anoxic atmospheres with the James Webb Space Telescope: A TRAPPIST-1e case study, *The Astronomical Journal*.

Results: Observing TRAPPIST-1e with James Webb for 10 transits







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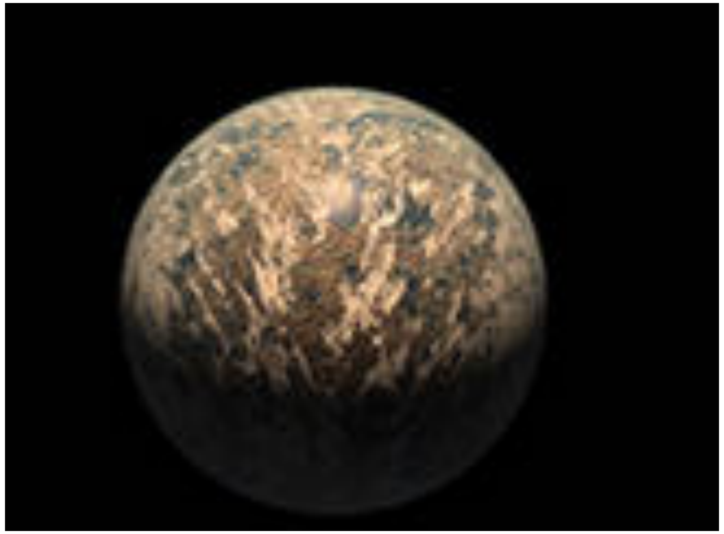
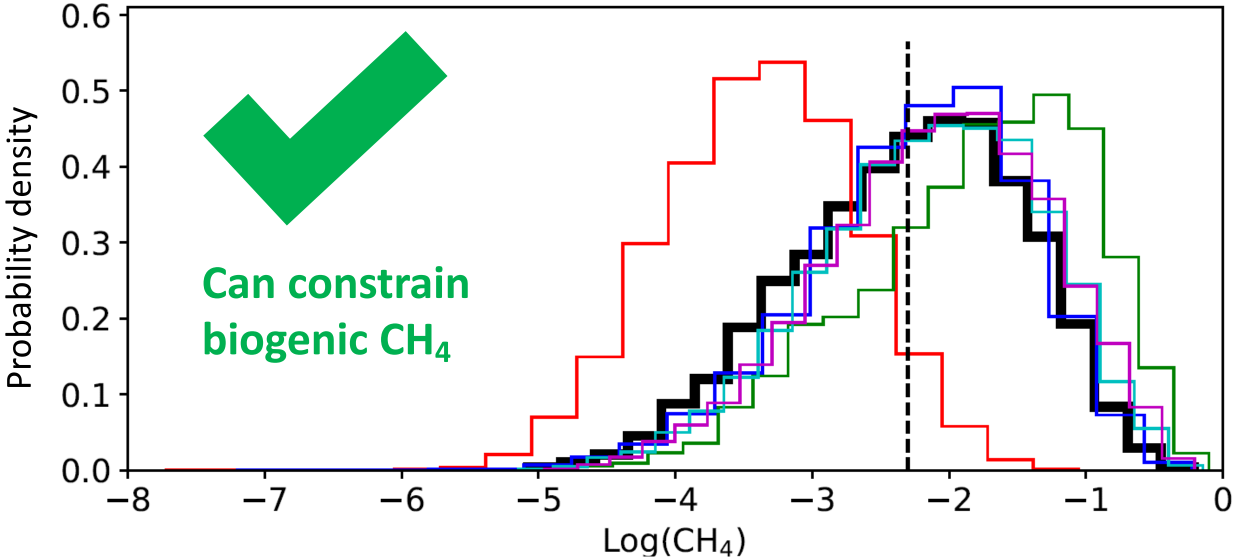
Is CH_4+CO_2 biosignature easier to observe than O_3?

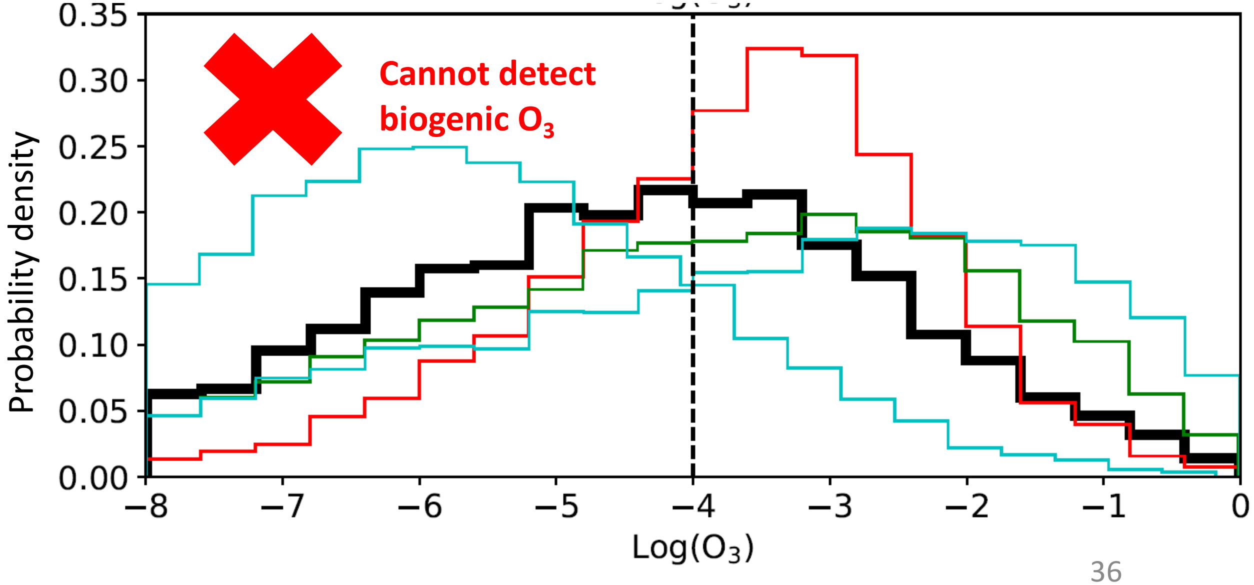


JWST observing an early Earth analog



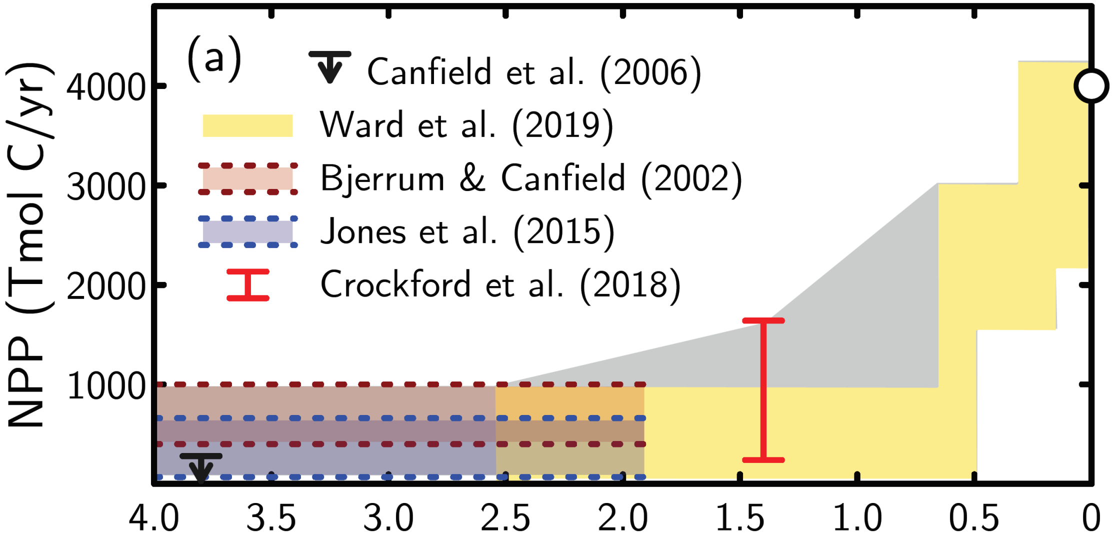
Can constrain biogenic CH_4

JWST observing a modern Earth analog in thermal IR



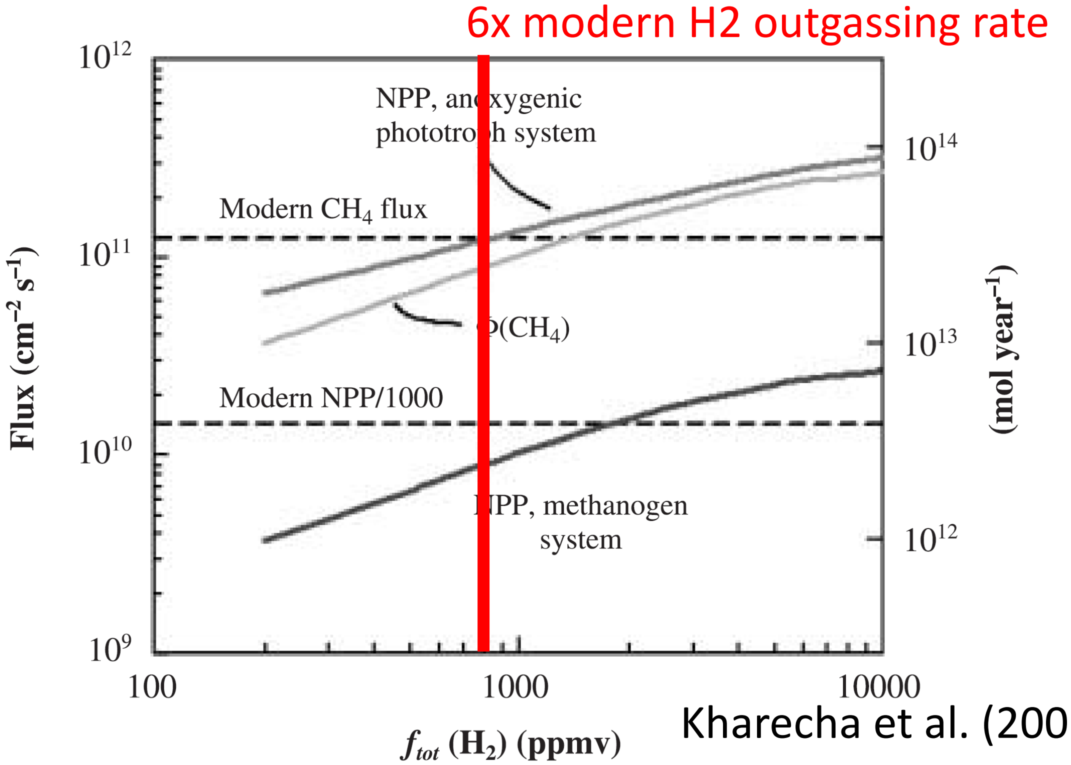
Cannot detect biogenic O_3

Reasons to be cautious…

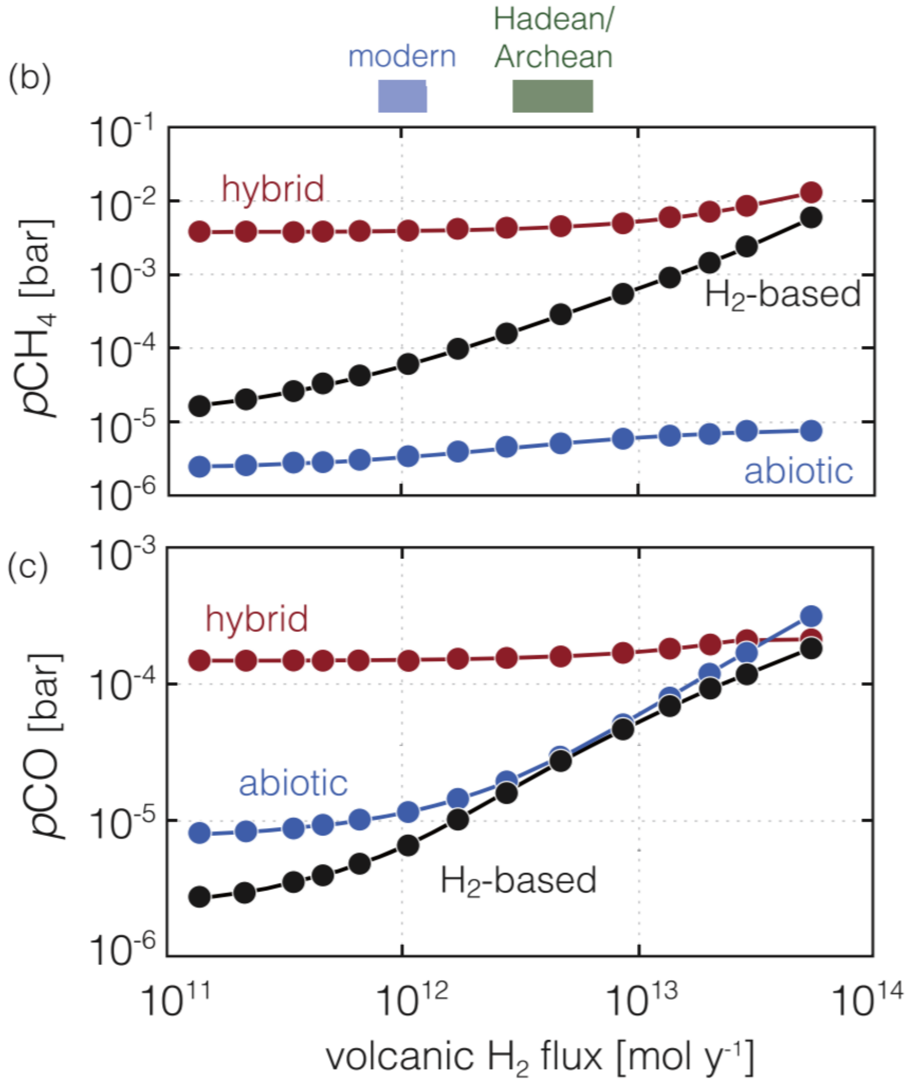


Would low productivity preclude Archean-like CH4+CO2 biosignatures?

- If oxygenic photosynthesis has evolved -> **definitely not**
- If anoxygenic photosynthesis has evolved -> **probably not**
- If purely chemoautotrophic -> **depends on H_2 flux**



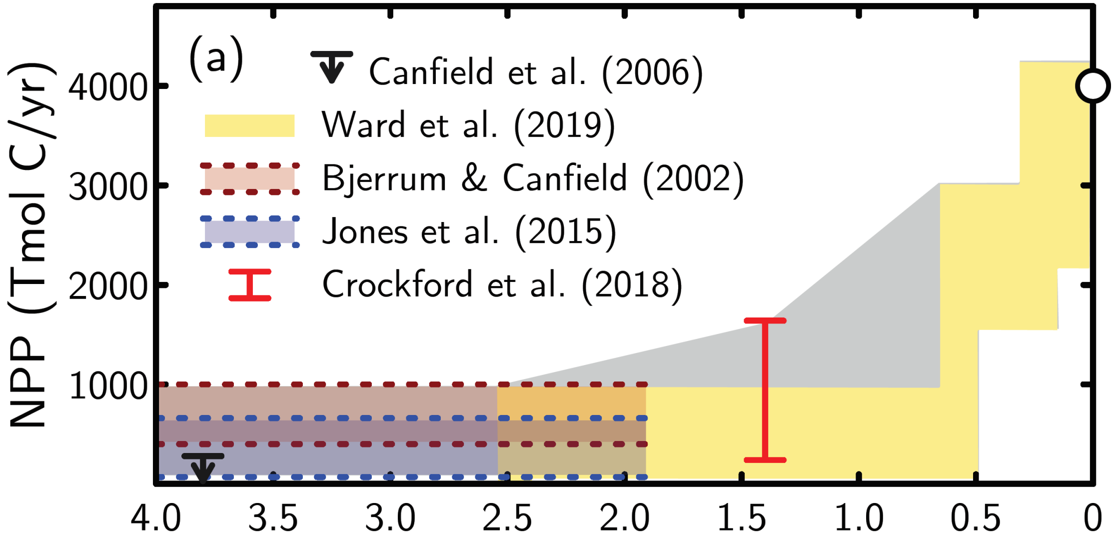
Kharecha et al. (2005) Geobiology



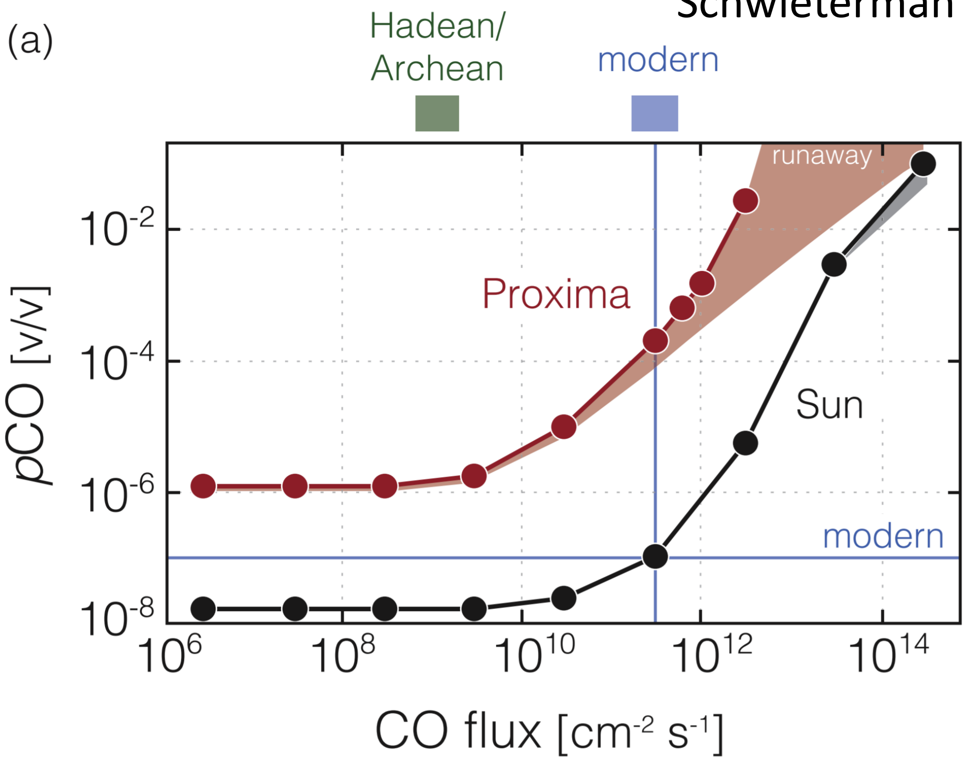
- Empirical evidence from Xe isotopes (Zahnle et al. 2019)

Schwieterman et al. (2019) ApJ

Reasons to be cautious…

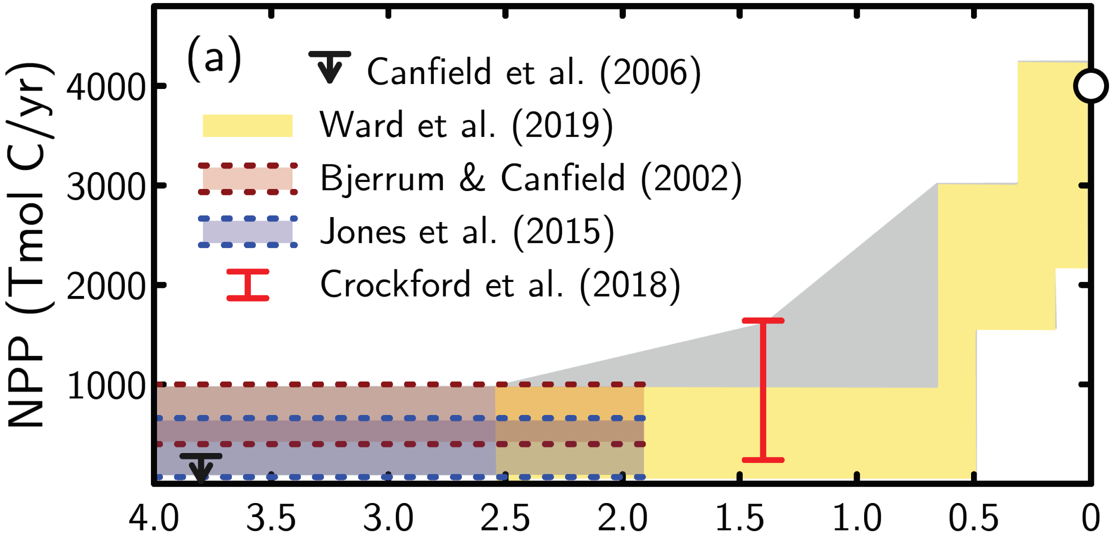


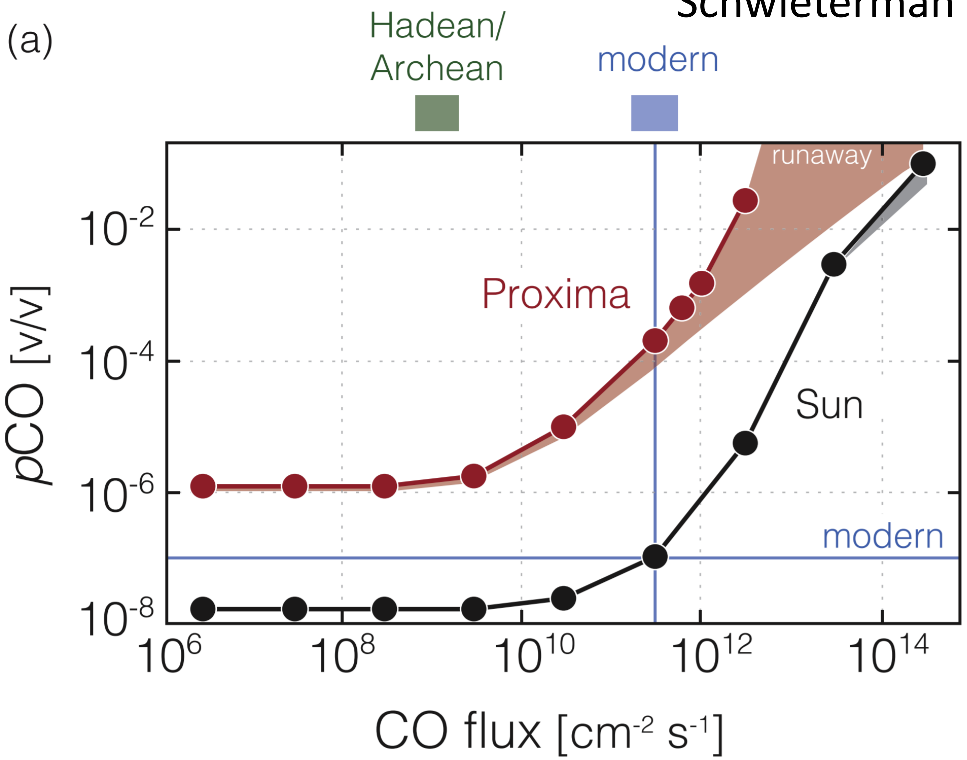
Schwieterman et al. (2019) ApJ



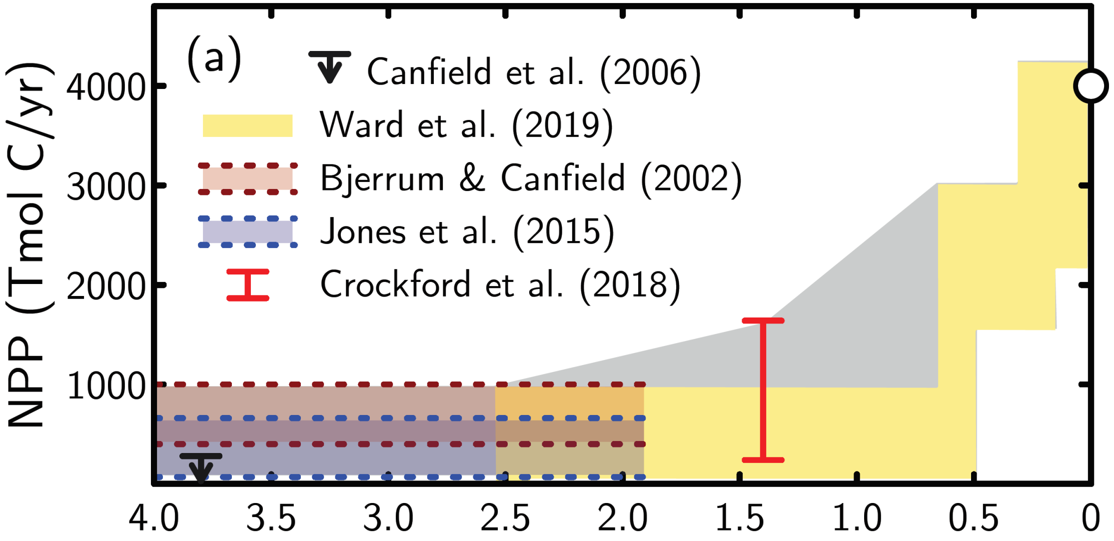
Reasons to be cautious…

Schwieterman et al. (2019) ApJ





Reasons to be cautious...



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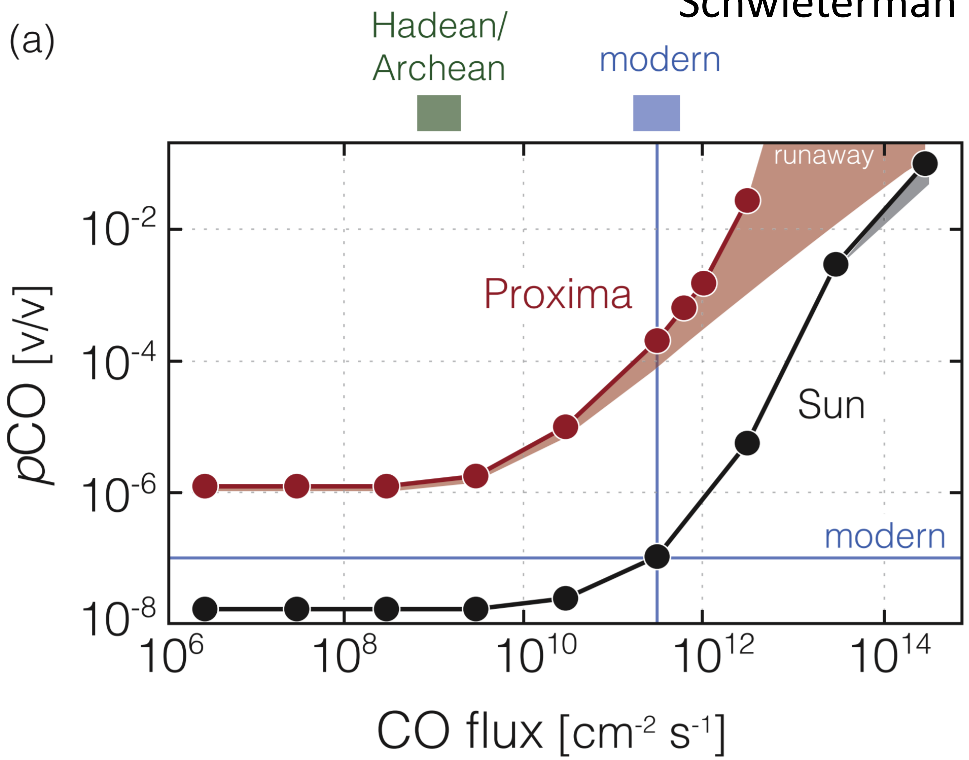
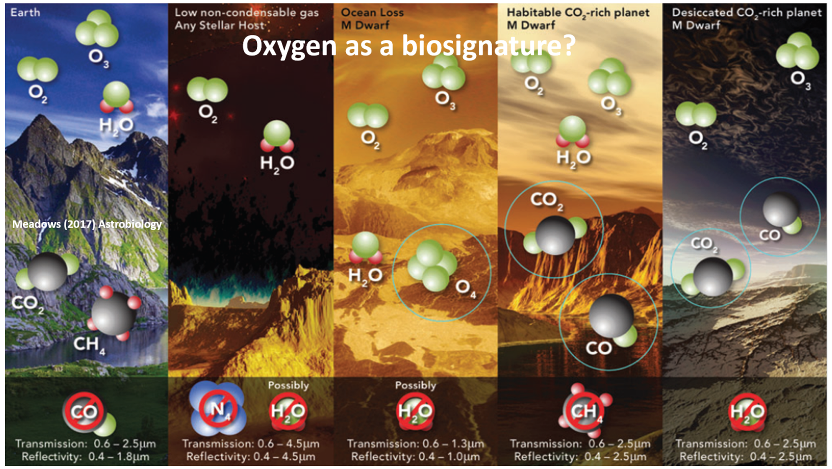
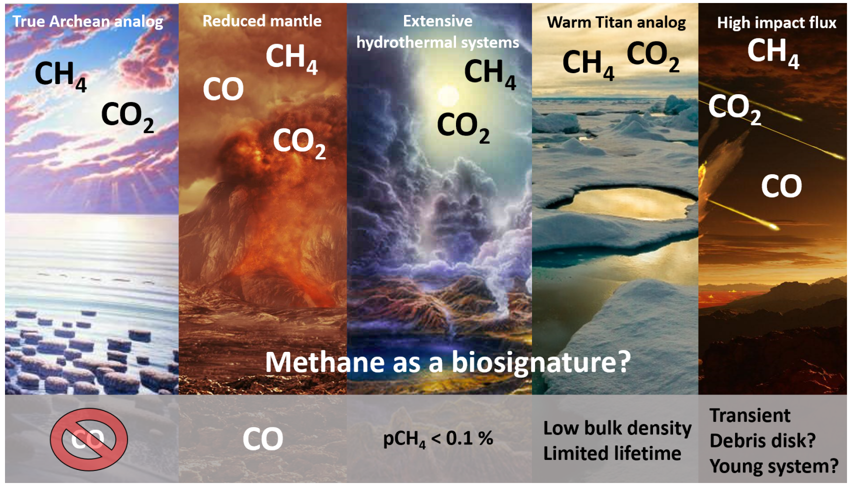




Oxygen as a biosignature?

Meadows (2017) Astrobiology

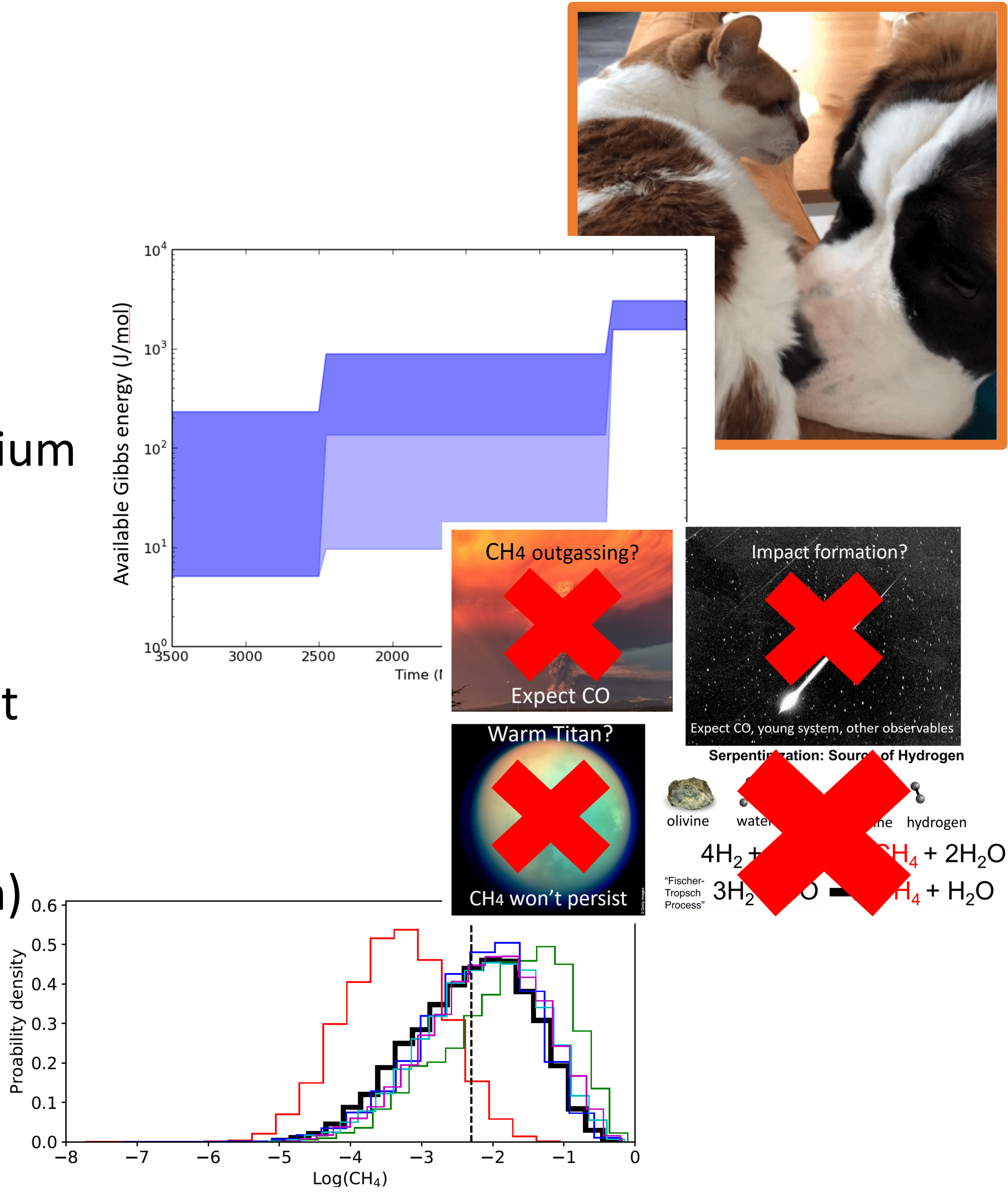
Vs.



Methane as a biosignature?

Conclusions

- Chemical disequilibrium is a useful conceptual framework for thinking about exoplanet biosignatures.
- The Earth has had a sizeable biogenic disequilibrium in its atmosphere-ocean system throughout its history.
- The coexistence of carbon dioxide and abundant methane is difficult to explain with known non-biological processes and could be a compelling exoplanet biosignature (as it was in the Archean)
- This biosignature combination is potentially detectable with JWST



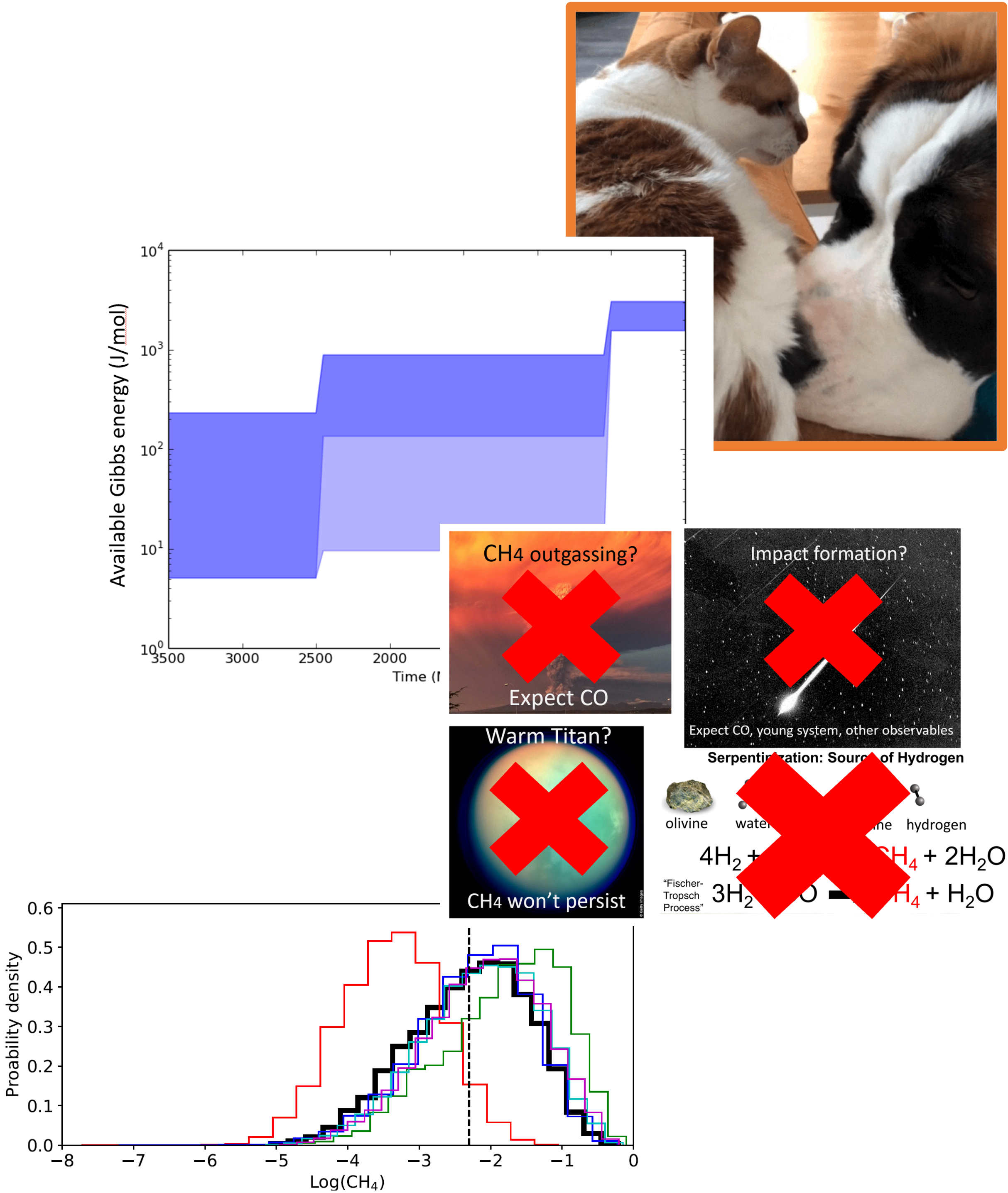
Thanks!

UWastrobiology

NExScI

VPL

NASA



CH4 outgassing?

Expect CO

Impact formation?

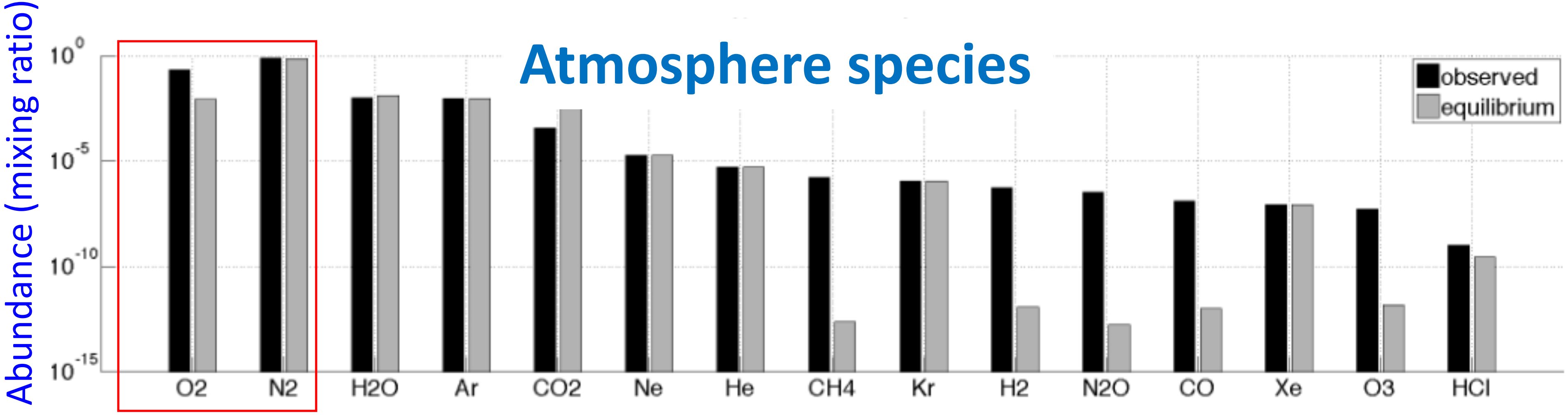
Expect CO, young system, other observables

Warm Titan?

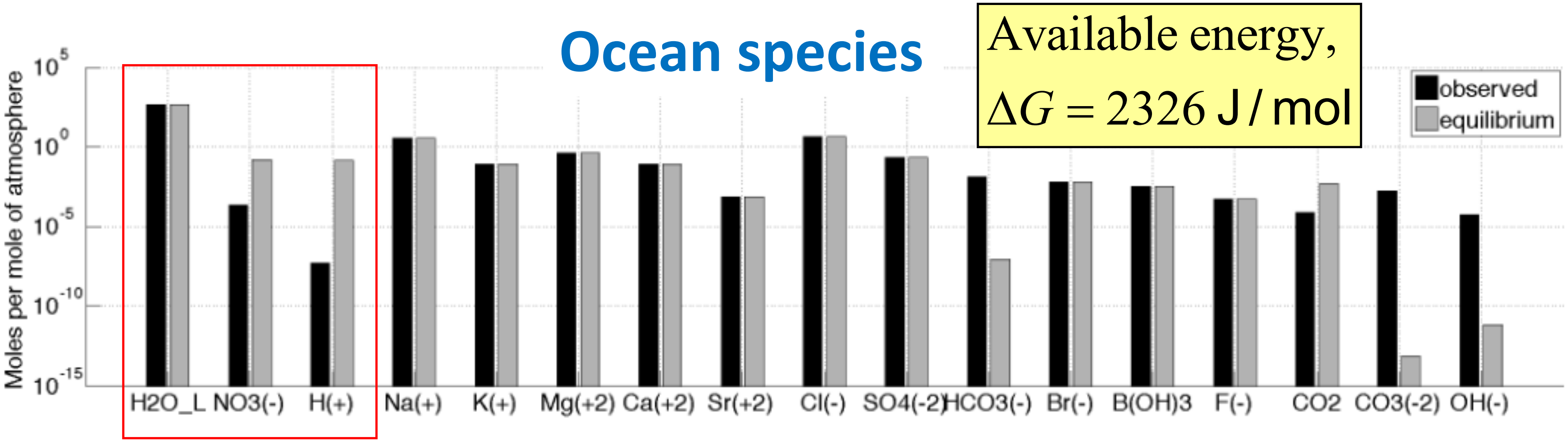
CH4 won't persist

Serpentin zation: Sour of Hydrogen

Earth (atmosphere-ocean fluid envelope)



Atmosphere species



Ocean species

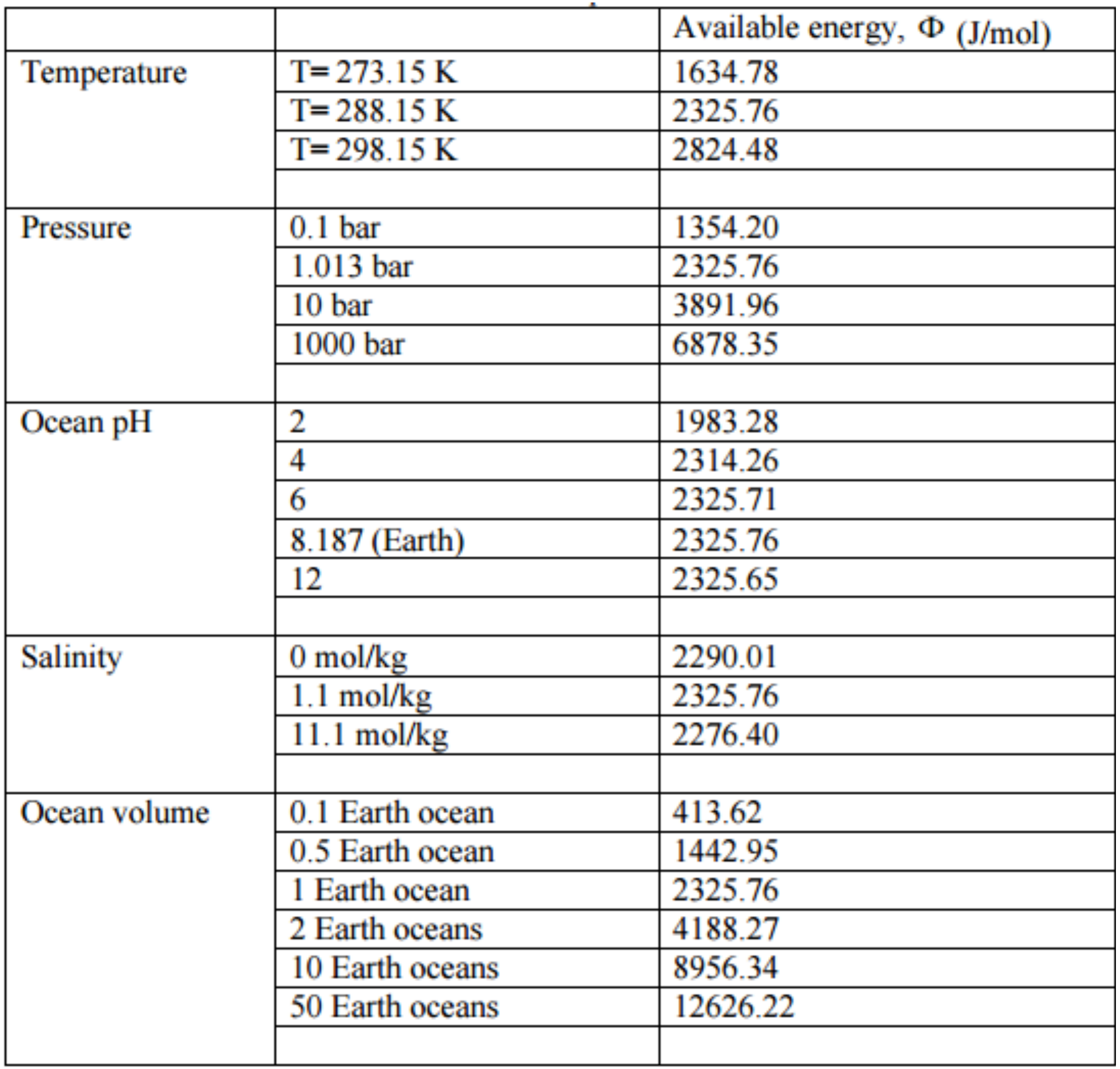
Available energy,

$\Delta G = 2326 \text{ J/mol}$

$$2\text{N}_2(\text{g}) + 5\text{O}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l}) \rightleftharpoons 4\text{H}^+(\text{aq}) + 4\text{NO}_3^-(\text{aq})$$

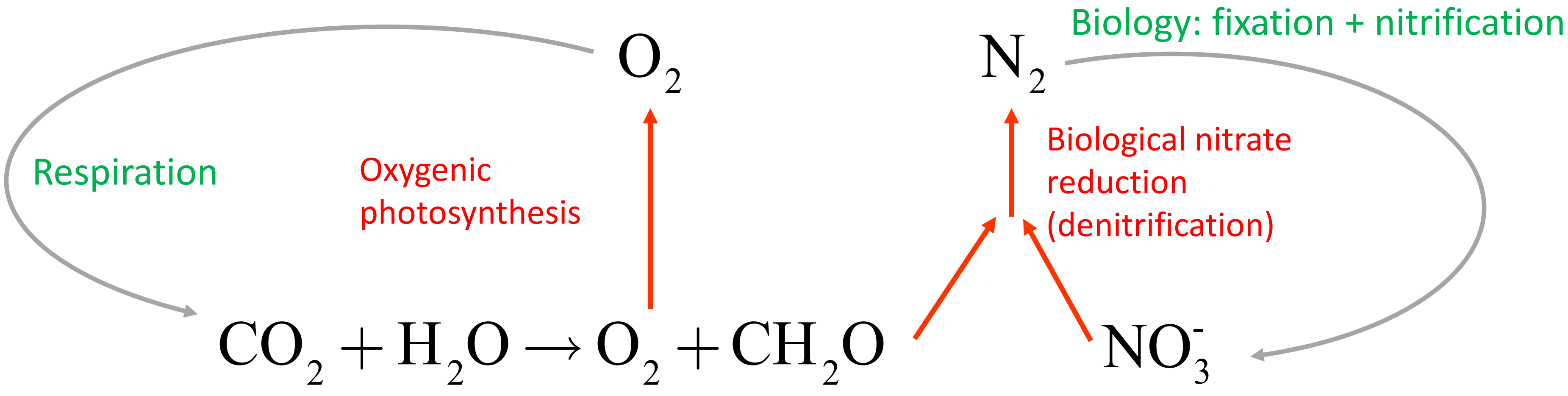
Gilbert Lewis (1923): “starting with air and water…nitric acid should form. It is to be hoped that nature will not discover a catalyst for this reaction, which would… turn the oceans into dilute nitric acid”.

Sensitivity test



		Available energy, Φ (J/mol)
Temperature	T= 273.15 K	1634.78
	T= 288.15 K	2325.76
	T= 298.15 K	2824.48
Pressure	0.1 bar	1354.20
	1.013 bar	2325.76
	10 bar	3891.96
	1000 bar	6878.35
Ocean pH	2	1983.28
	4	2314.26
	6	2325.71
	8.187 (Earth)	2325.76
	12	2325.65
Salinity	0 mol/kg	2290.01
	1.1 mol/kg	2325.76
	11.1 mol/kg	2276.40
Ocean volume	0.1 Earth ocean	413.62
	0.5 Earth ocean	1442.95
	1 Earth ocean	2325.76
	2 Earth oceans	4188.27
	10 Earth oceans	8956.34
	50 Earth oceans	12626.22

What does disequilibrium mean?



O_2

N_2

Biology: fixation + nitrification

Respiration

Oxygenic photosynthesis

Biological nitrate reduction (denitrification)

$$CO_2 + H_2O \rightarrow O_2 + CH_2O$$

NO_3^-

- In the absence of life, lightning would convert all oxygen to nitrate within a few million years.
- Thus the coexistence of N2, O2 and liquid water is a more compelling biosignature than O2 alone.

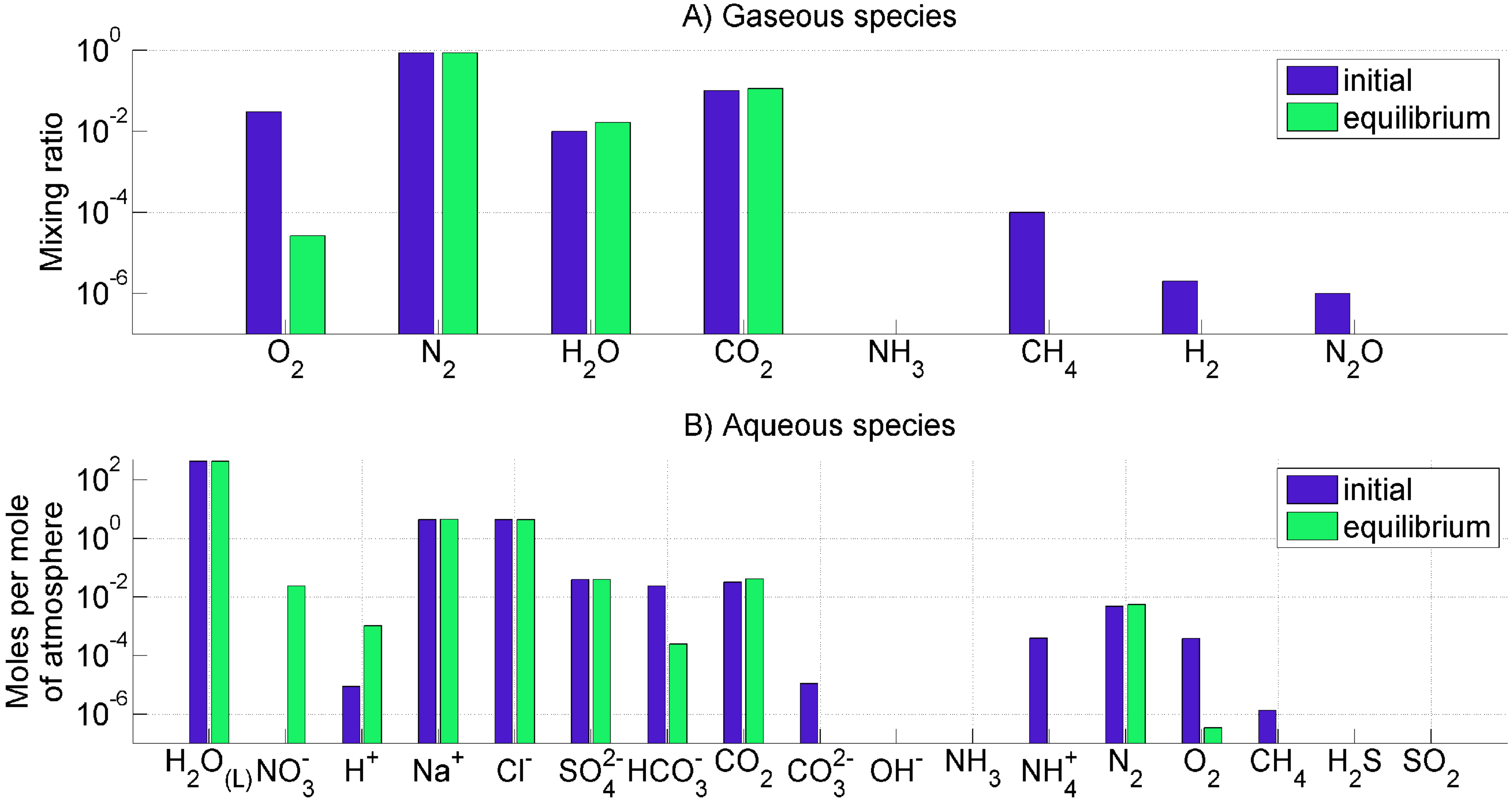
Krissansen-Totton, J., D. S. Bergsman, and D. C. Catling (2016), On detecting biospheres from chemical thermodynamic disequilibrium in planetary atmospheres, *Astrobiology*, *16*(1), 39-67.

Composition of the early Earth

	Archean range			Proterozoic range		
Atmospheric species	Mixing ratio		Reference/Explanation	Mixing ratio		Reference/Explanation
	Min. diseq.	Max diseq.		Min. diseq.	Max diseq.	
N_2(g)	0.98	0.5	Mixing ratios sum to 1. But see also Som et al. 2016; Marty et al. 2013	0.99	0.86	Mixing ratios sum to 1.
O_2(g)	1×10^{-10}	2×10^{-7}	Zahnle et al. 2006	0.0001	0.03	Lyons et al. 2014
CH_4(g)	0.0001	0.01	Kasting and Brown 1998	3×10^{-6}	1×10^{-4}	Olson et al. 2016
CO_2(g)	0.001	0.5	Sheldon 2006; Kanzaki 2015	0.0001	0.1	Sheldon 2006; Kanzaki 2015
H_2(g)	0	0.0001	Kharecha et al. 2005	0	2×10^{-6}	Segura et al. 2003
N_2O(g)	0	0	No denitrification	0	1×10^{-6}	Roberson et al. 2011
NH_3(g)	0	1×10^{-9}	Pavlov et al. 2001	0	0	NA
O_3(g)	0	0	Negligible	0	0	Negligible
CO(g)	0	0.001	Kharecha et al. 2005	0	2×10^{-7}	Segura et al. 2003
Ocean species	Molality (mmoles/kg)		Reference/Explanation	Molality (mmoles/kg)		Reference/Explanation
	Min. diseq.	Max diseq.		Min. diseq.	Max diseq.	
Na(+)	550	586	Charge balance	547	549	Charge balance
Cl(-)	546	546	Modern value	546	546	Modern value
SO_4(2-)	0	0.2	Olson	0.25	5	Olson
H_2S	0	0.004	Euxinic oceans like Black Sea	0	0.004	Euxinic oceans like Black Sea
NH_4(+)	0	0.050	Set by P (N fixation evolved early)	0	0.050	Set by P
NO_3(-)	0	0	Anoxic bulk ocean	0	0	Anoxic bulk ocean
ALK	4	40	Krissansen-Totton*	1.0	3.0	Krissansen-Totton*
pH	5.0	8.0	Carbon chemistry equilibrium**	6.0	8.0	Carbon chemistry equilibrium**

Proterozoic atmosphere-ocean disequilibrium

$$5O_2 + 2N_2 + 2H_2O \rightarrow 4H^+ + 4NO_3^-$$



$$2O_2 + CH_4 \rightarrow CO_2 + 2H_2O$$

Available energy,

$$\Delta G = G_{(T,P)}(obser) - G_{(T,P)}(equil)$$

$$\Delta G = 884 \text{ J/mol}$$

$$2O_2 + H_2S \rightarrow 2H^+ + SO_4^{2-}$$

$$3O_2 + 4NH_4^+ \rightarrow 4H^+ + 2N_2 + 6H_2O$$

Proterozoic atmosphere-ocean disequilibrium

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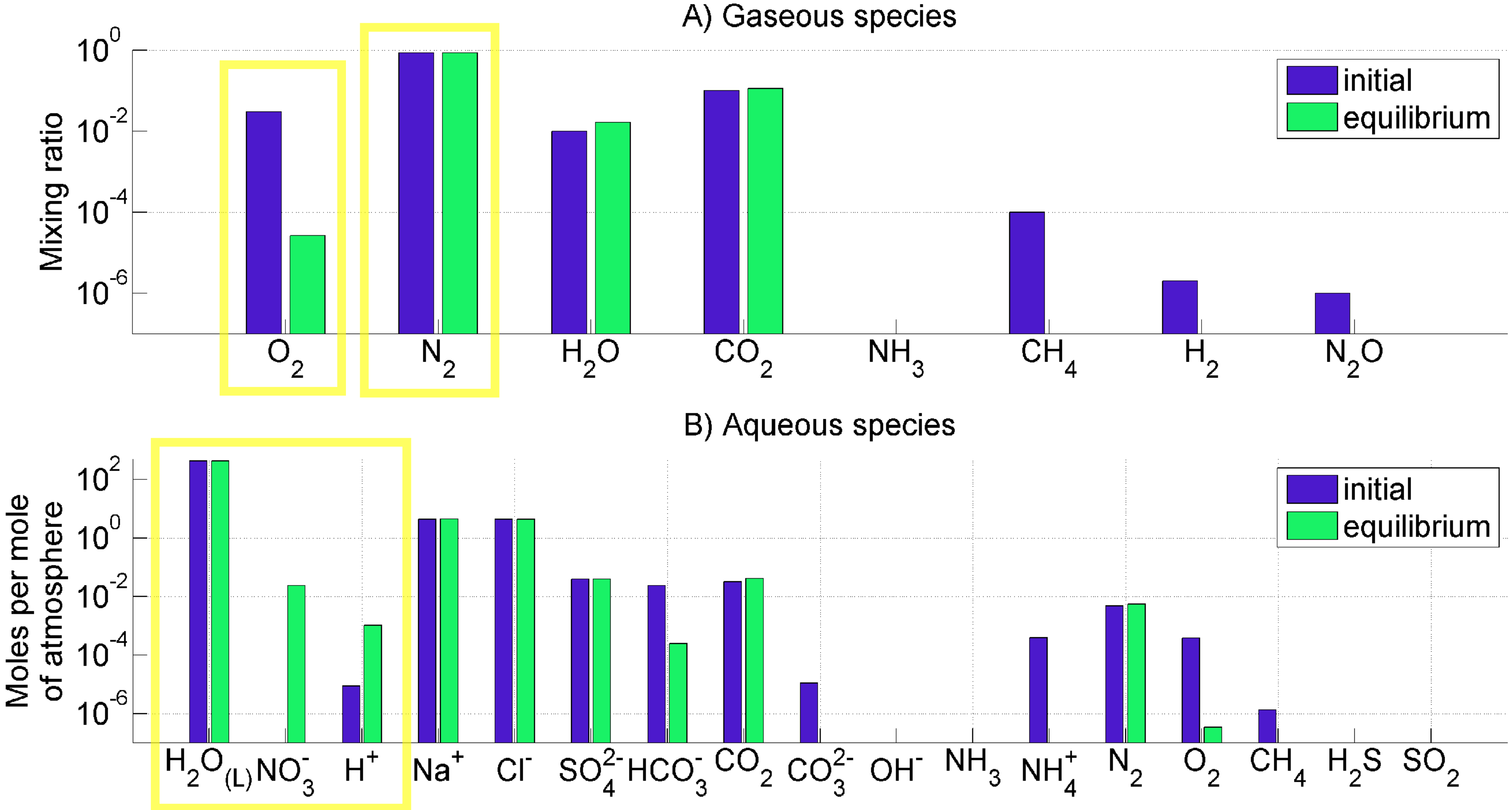

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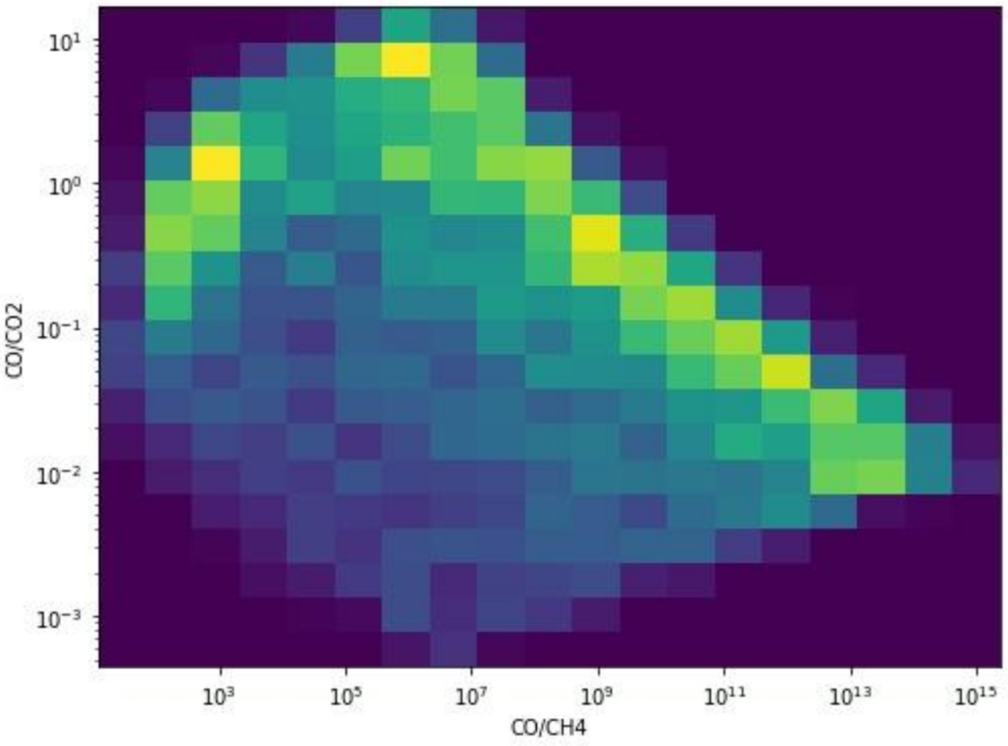
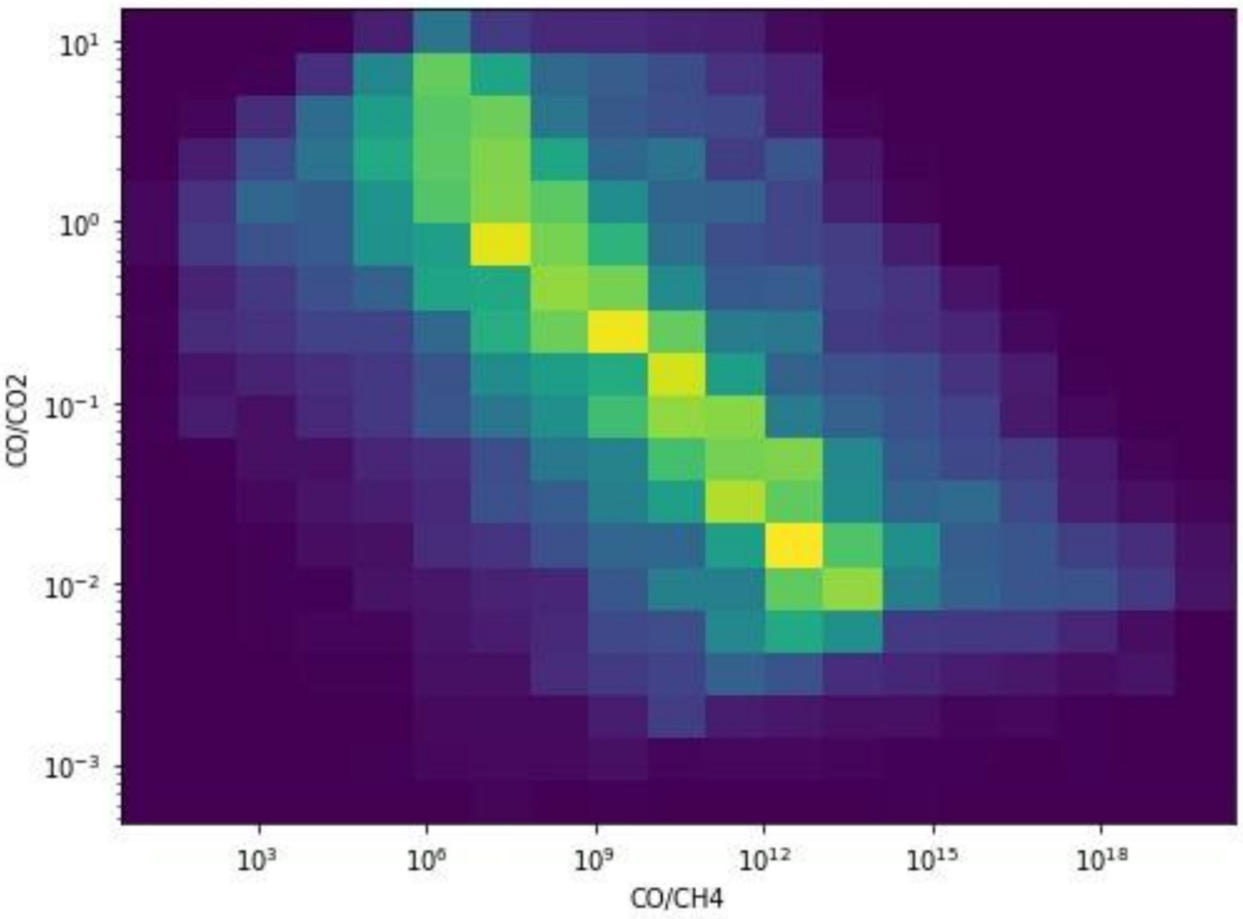
Ocean worlds, 100-1000 bar

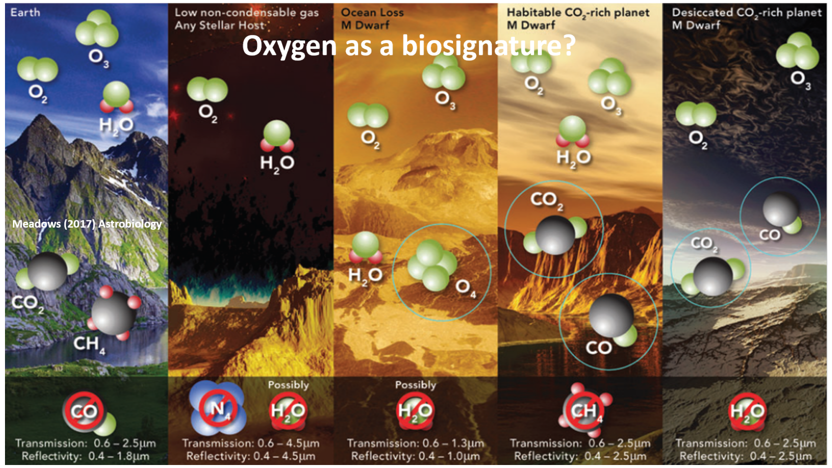


Submarine + subaerial outgassing, 0.01-100 bar



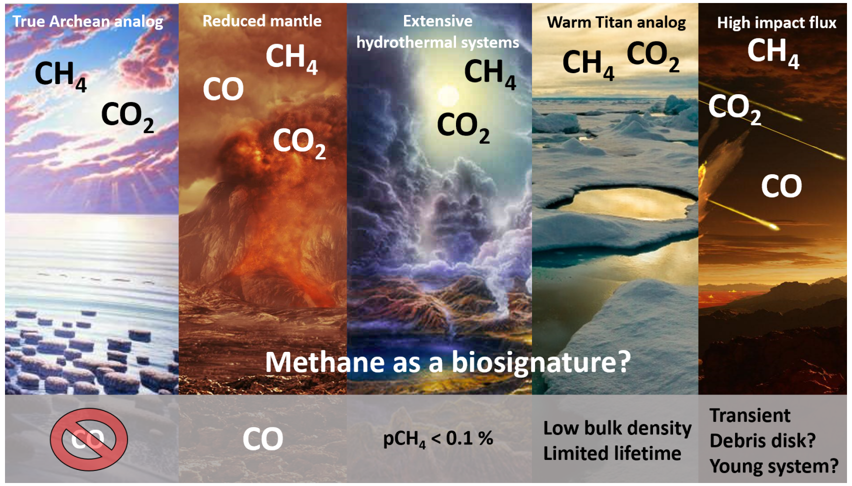
fO2: -4.5 to 2.0 FMQ, magma chamber 800-1200 bar, also varied CO2 and H2O composition host rock but secondary effect.

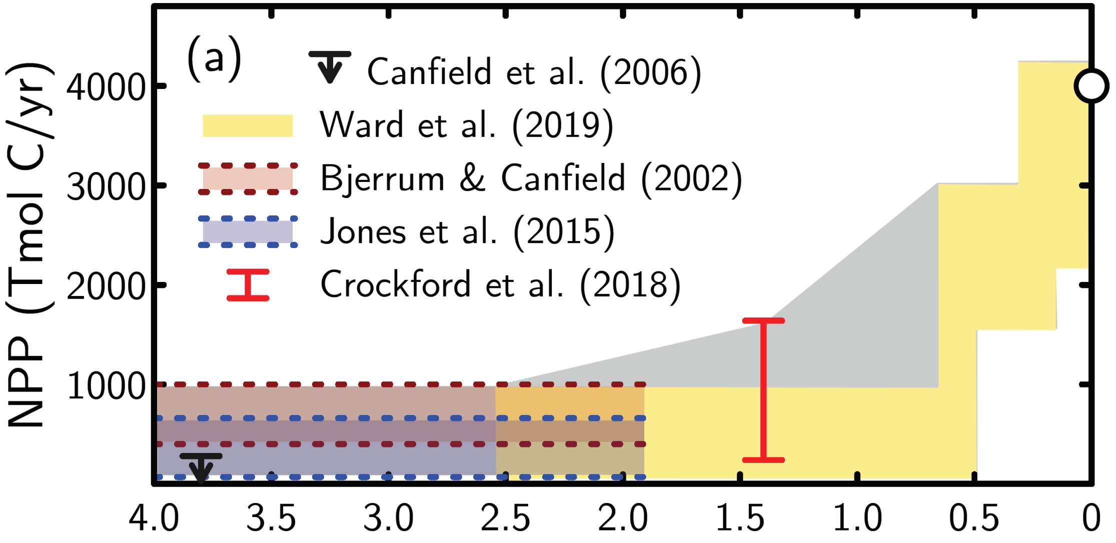
Reasons to be cautious…


Oxygen as a biosignature?

Meadows (2017) Astrobiology

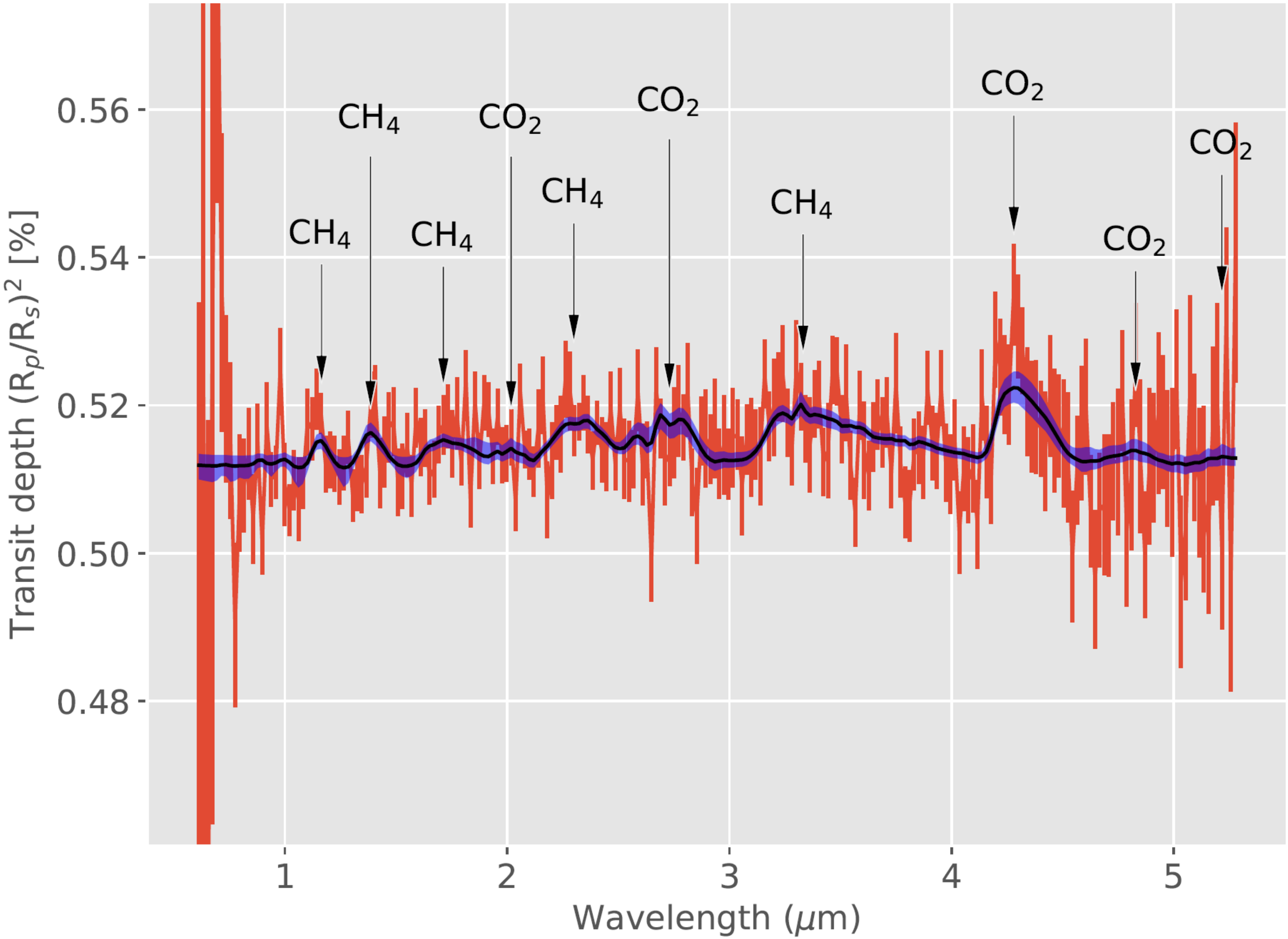
Vs.


Methane as a biosignature?



Failures of imagination

TRAPPIST-1e, NIRSpec prism on JWST, 10 transits



J. Krissansen-Totton, R. Garland, P. Irwin, D. C. Catling (2018) Detectability of biosignatures in anoxic atmospheres with the James Webb Space Telescope: A TRAPPIST-1e case study, *The Astronomical Journal*.

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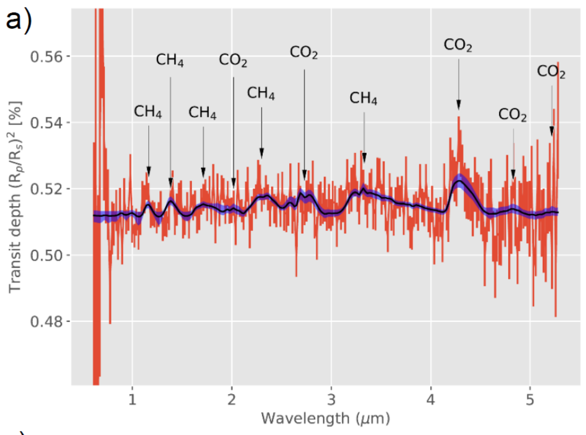
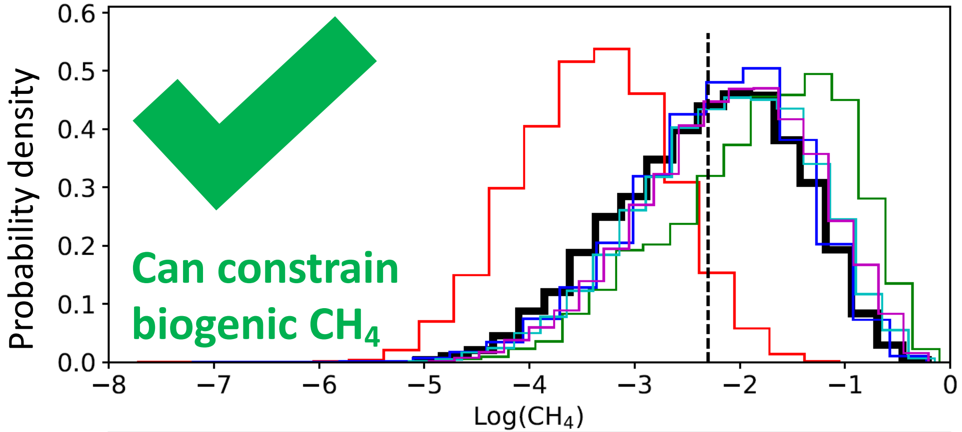
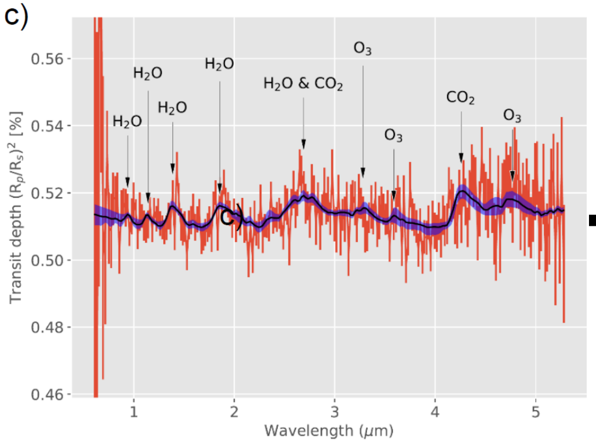


JWST observing an early Earth analog

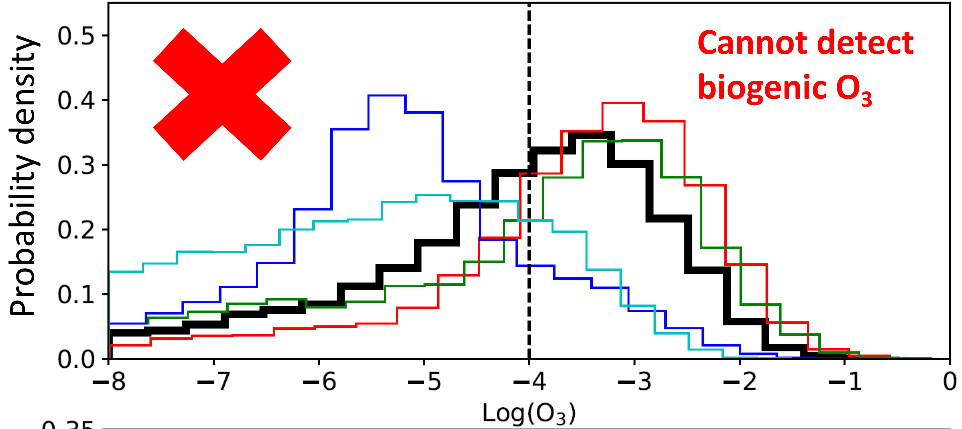


✓

Can constrain biogenic CH_4

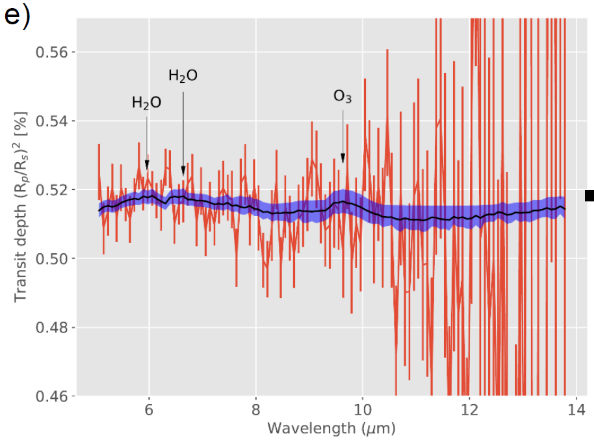


JWST observing a modern Earth analog in the NIR

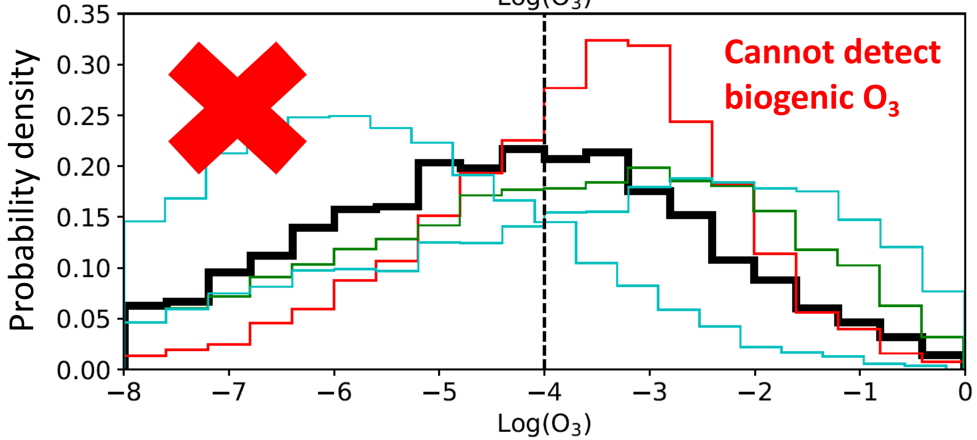


✗

Cannot detect biogenic O_3

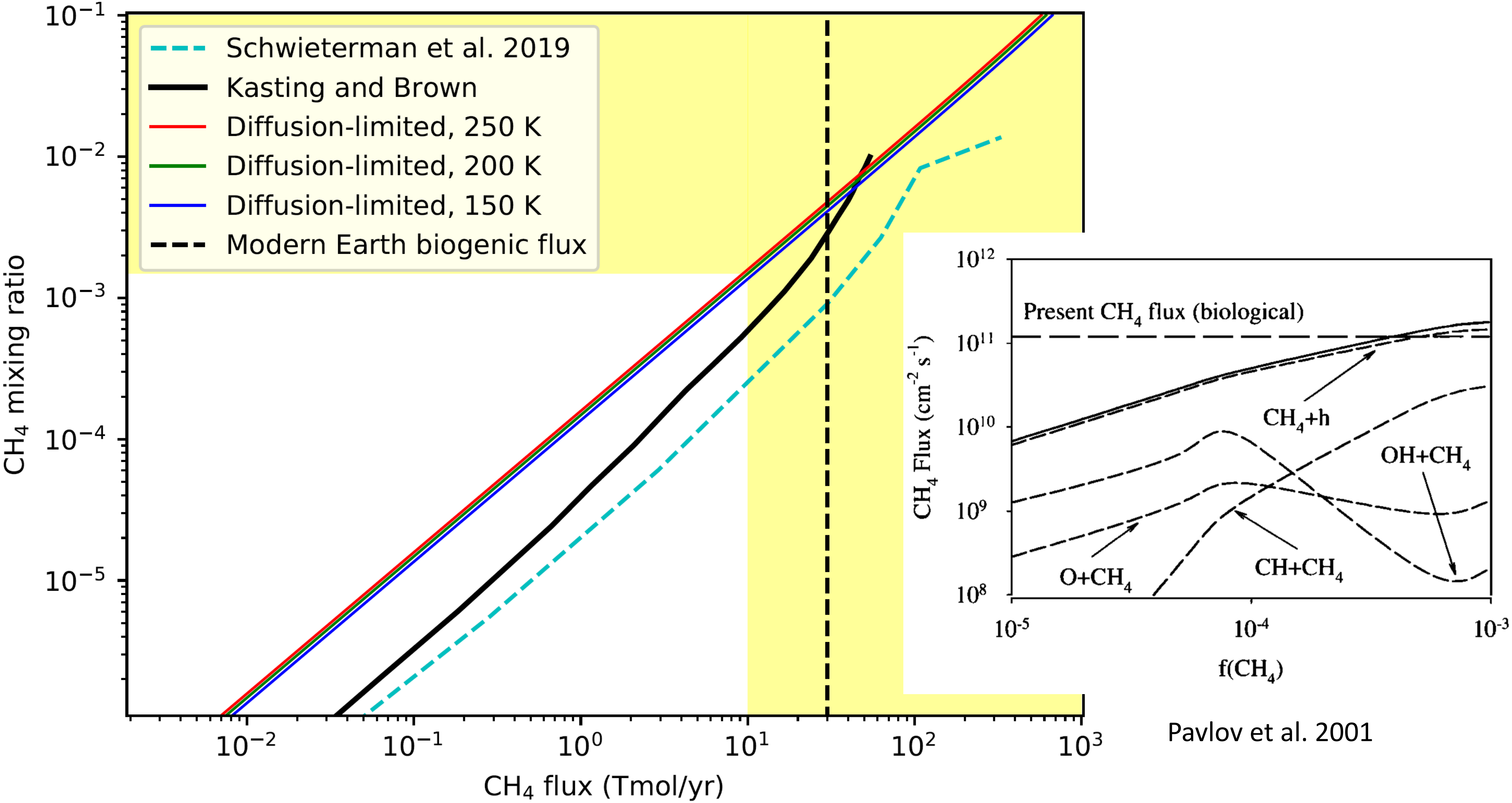


JWST observing a modern Earth analog in thermal IR

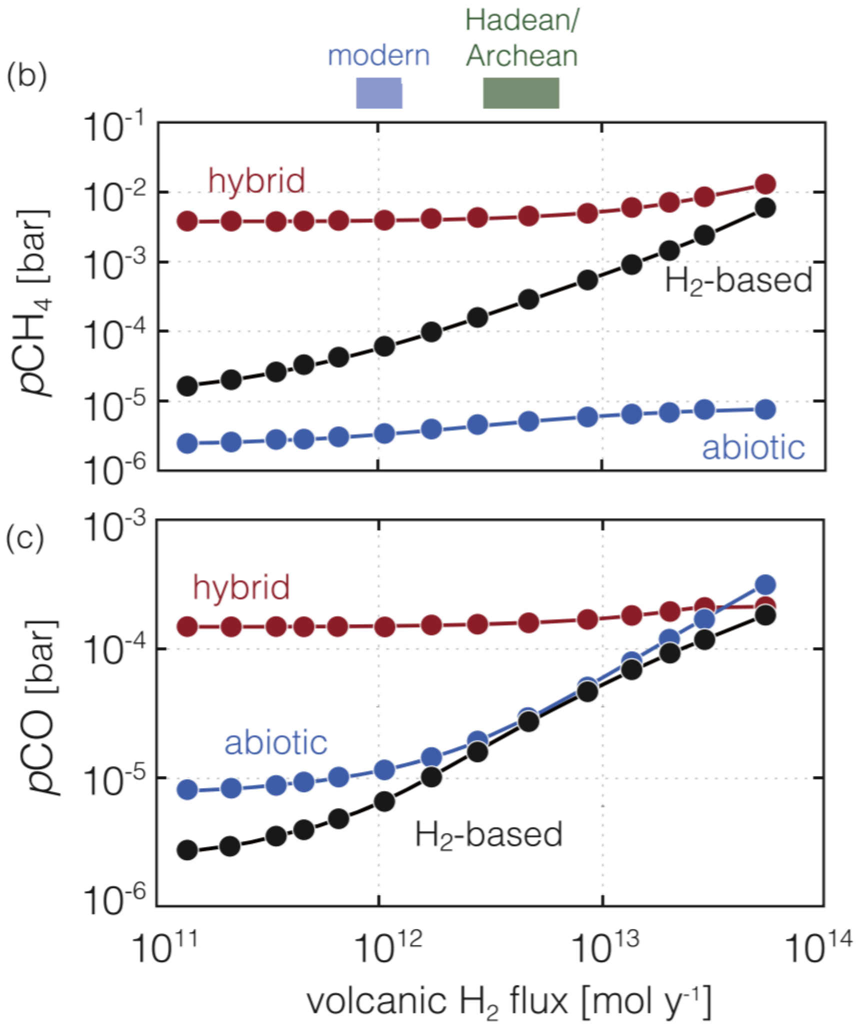


✗

Cannot detect biogenic O_3



Pavlov et al. 2001



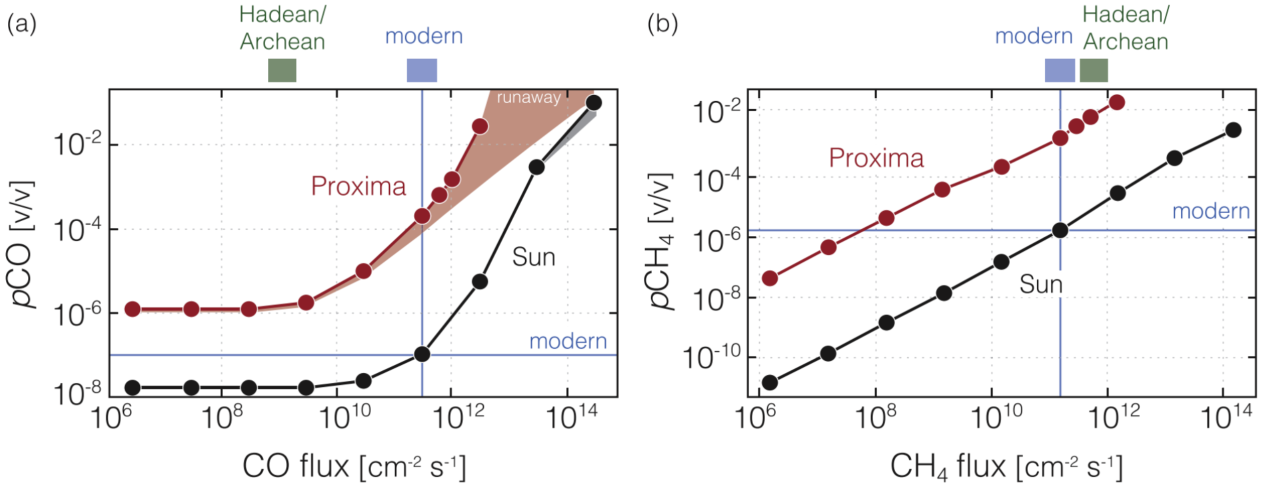
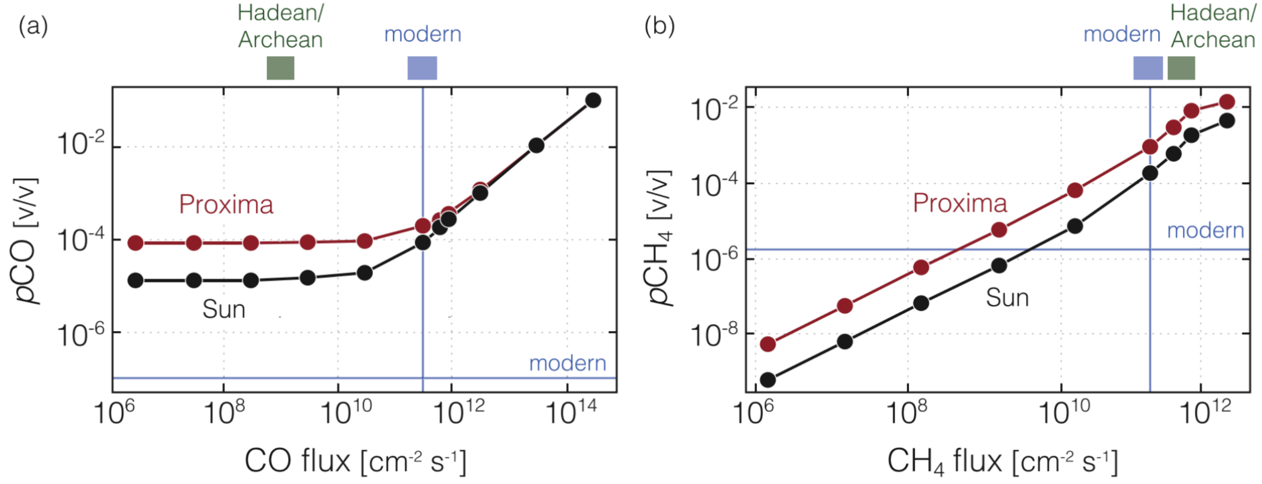
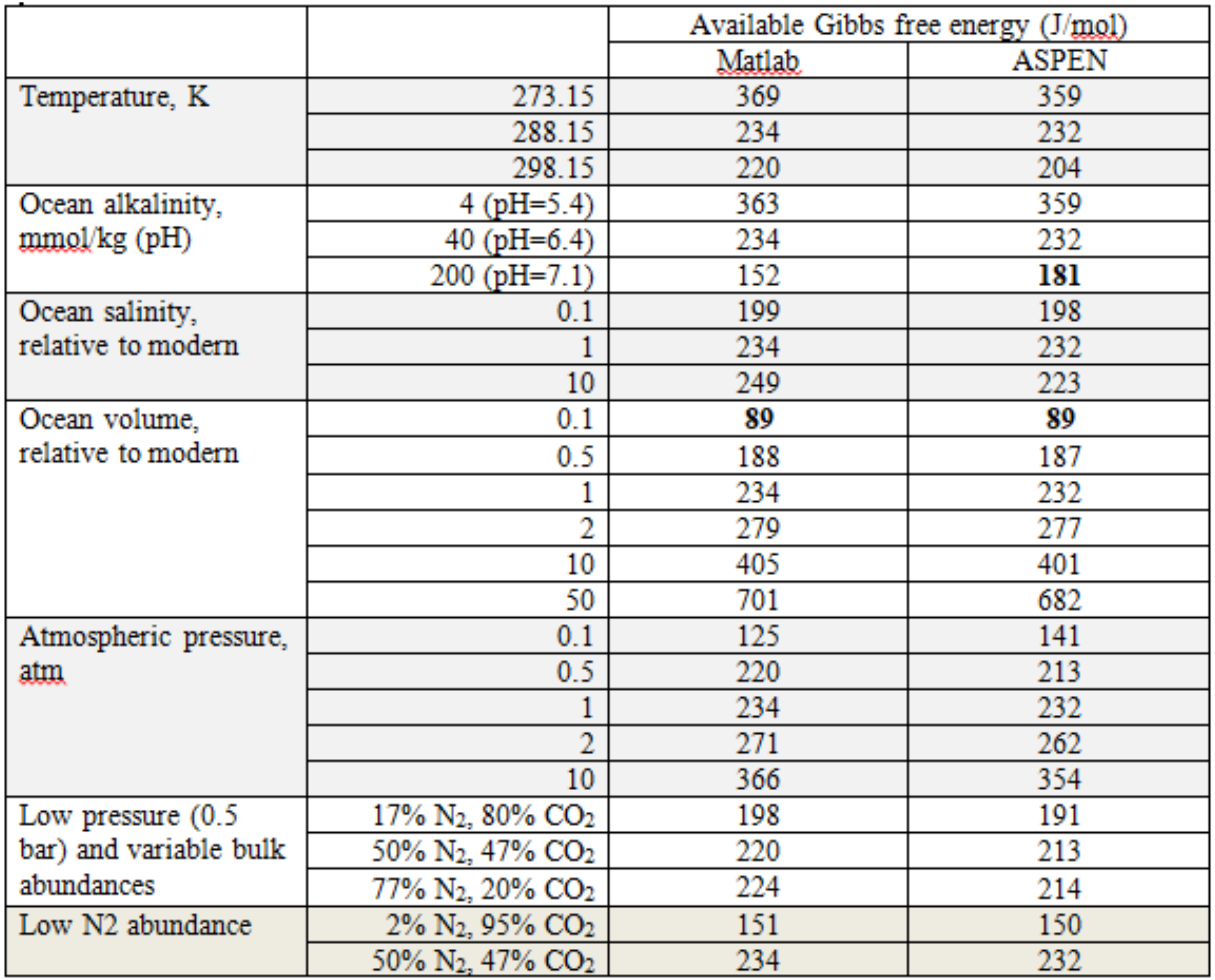


Figure 2. Atmospheric mixing ratios of CO (a) and CH_4 (b) as a function of surface molecular fluxes for oxygen-rich, modern Earth-like atmospheres. Results are shown for both the Sun (black) and the M-star Proxima Centauri (red). Horizontal line shows mixing ratios for each gas in the modern atmosphere, while modern and estimated Hadean/Archean fluxes of CO and CH_4 are shown above each panel. The shaded ranges in (a) depict results for models assuming only an upward molecular flux of CO (upper end) and assuming both an upward molecular flux and the maximum possible deposition velocity of 1.2×10^{-4} cm s^{-1} (lower end). Note that for the highest surface fluxes around Proxima Centauri the atmosphere enters a "CO runaway." Atmospheric pCO$_2$ is fixed at 360 ppm ($\sim 3.6 \times 10^{-4}$ bar) in all calculations.

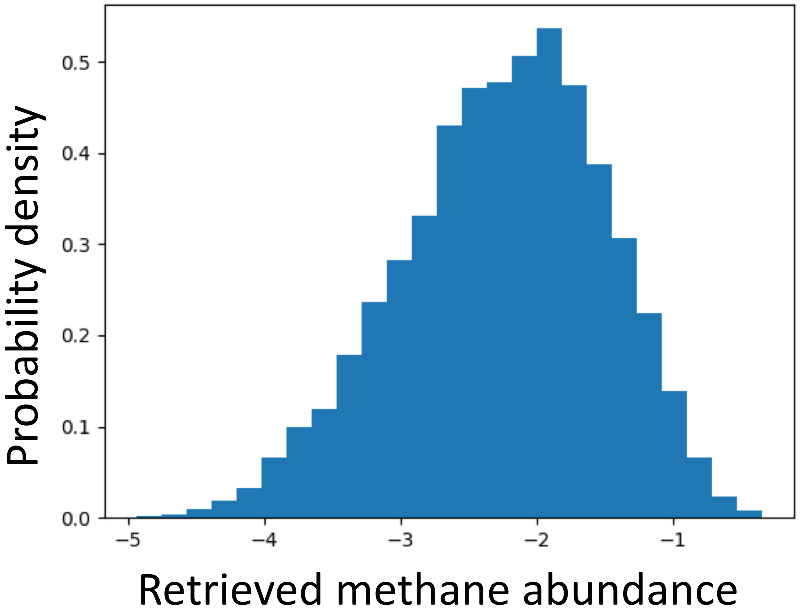


Archean sensitivity test



		Available Gibbs free energy (J/mol)	
		Matlab	ASPEN
Temperature, K	273.15	369	359
	288.15	234	232
	298.15	220	204
Ocean alkalinity, mmol/kg (pH)	4 (pH=5.4)	363	359
	40 (pH=6.4)	234	232
	200 (pH=7.1)	152	**181**
Ocean salinity, relative to modern	0.1	199	198
	1	234	232
	10	249	223
Ocean volume, relative to modern	0.1	**89**	**89**
	0.5	188	187
	1	234	232
	2	279	277
	10	405	401
	50	701	682
Atmospheric pressure, atm	0.1	125	141
	0.5	220	213
	1	234	232
	2	271	262
	10	366	354
Low pressure (0.5 bar) and variable bulk abundances	17% N_2, 80% CO_2	198	191
	50% N_2, 47% CO_2	220	213
	77% N_2, 20% CO_2	224	214
Low N2 abundance	2% N_2, 95% CO_2	151	150
	50% N_2, 47% CO_2	234	232

Getting from methane abundances to Pr(life)



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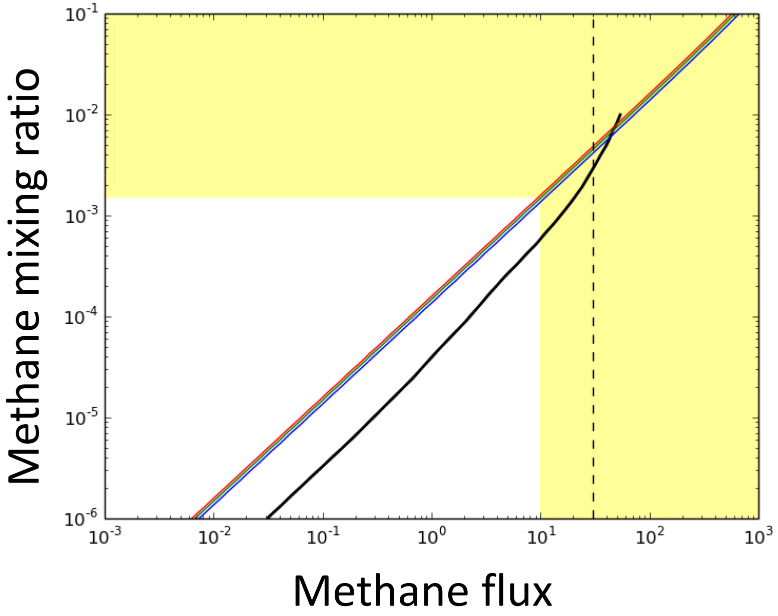

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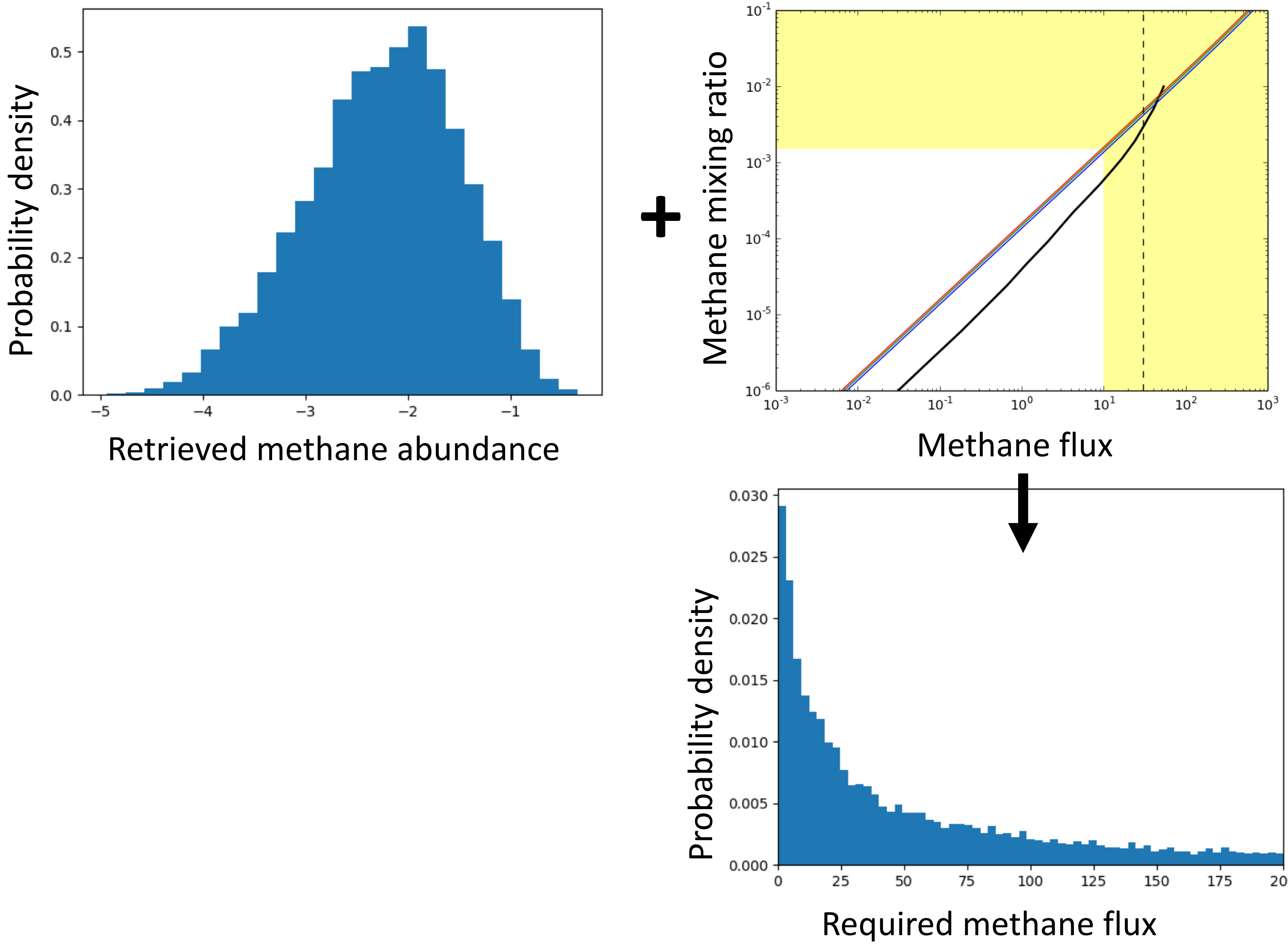

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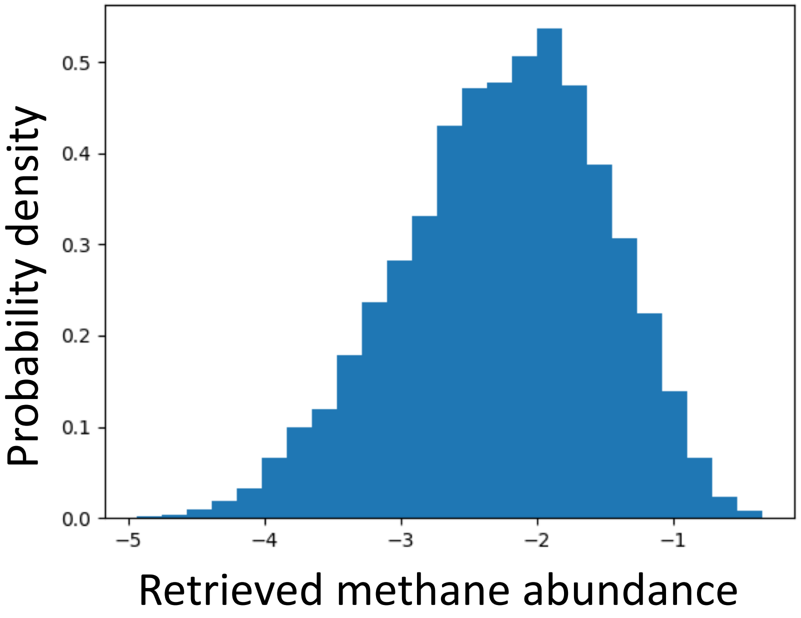
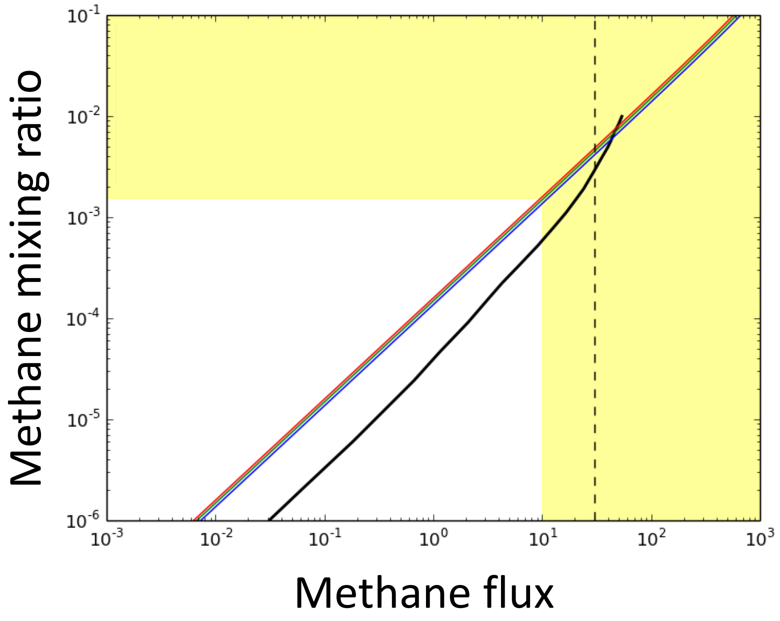
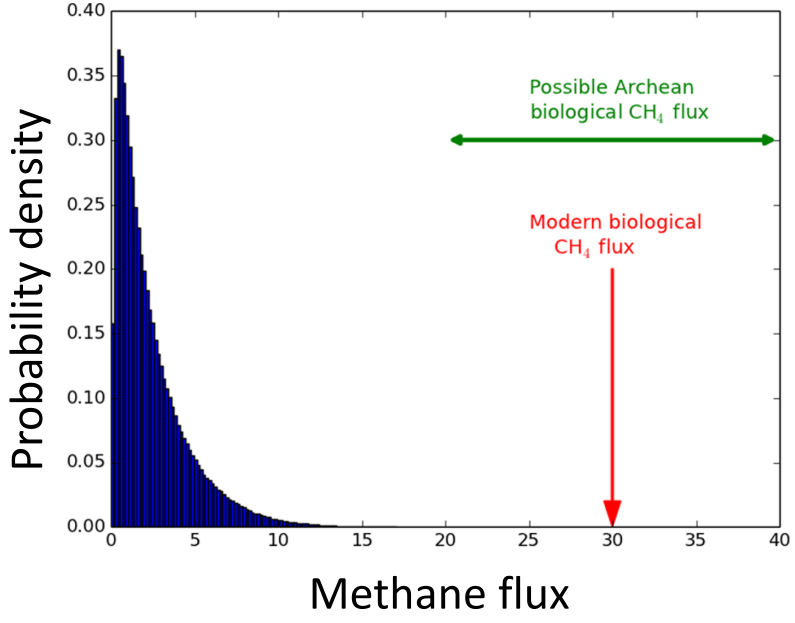
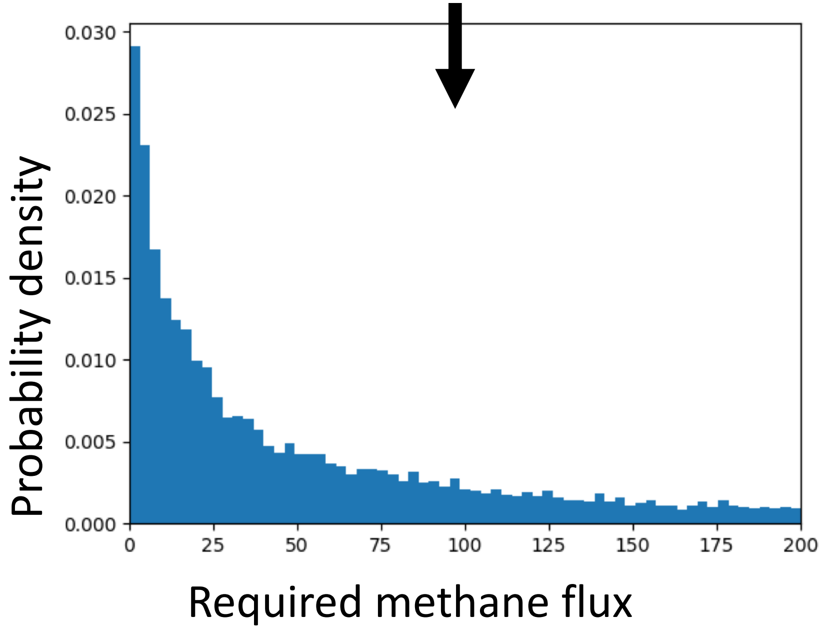


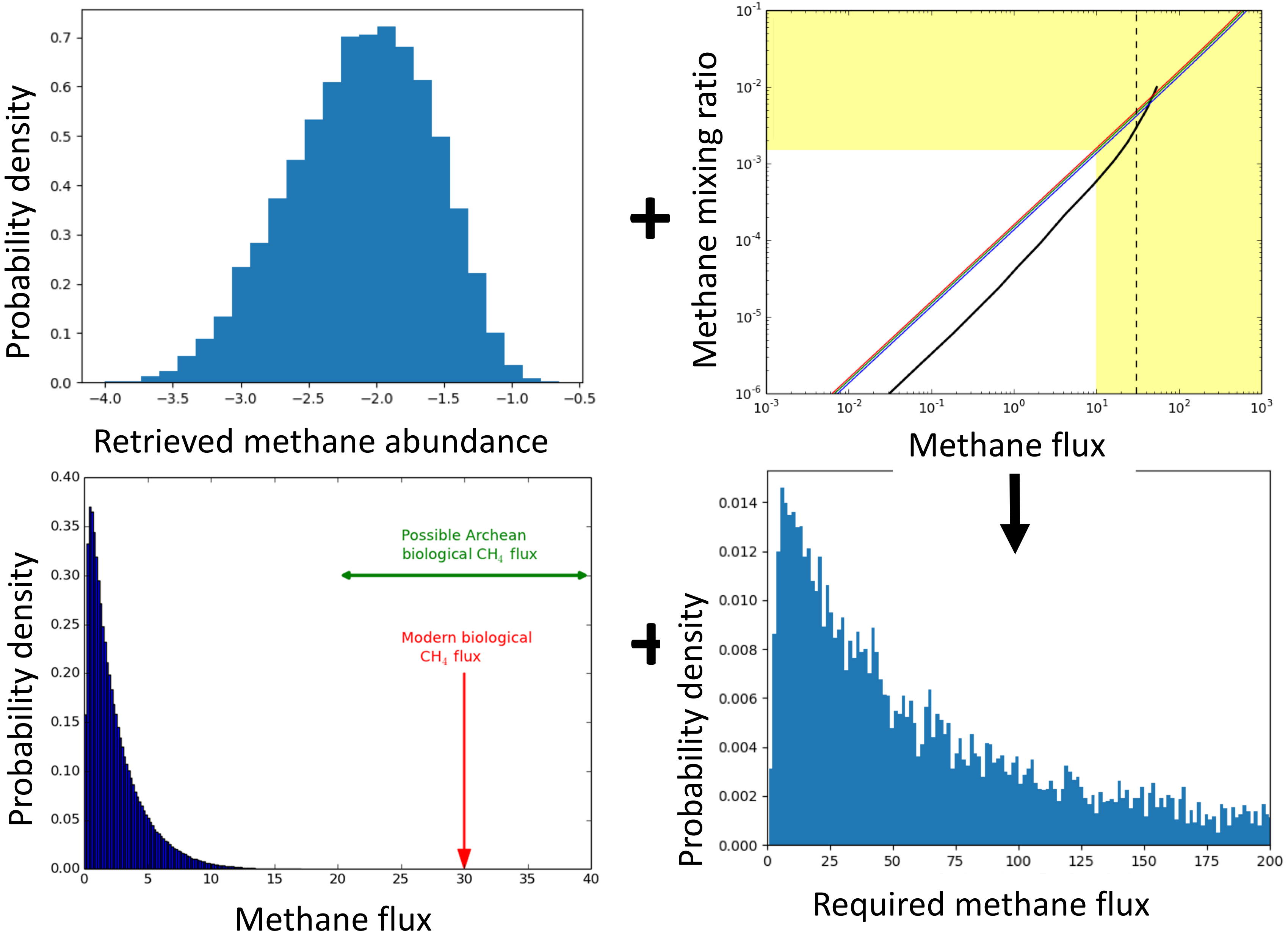






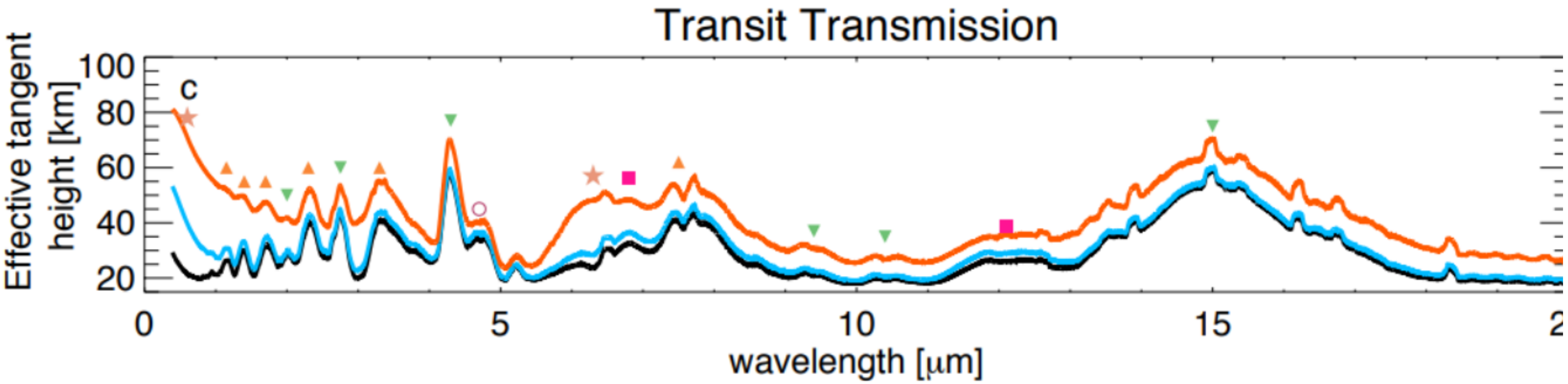
Pr(explain with known abiotic process) = 9% **Typical 10** orbit case

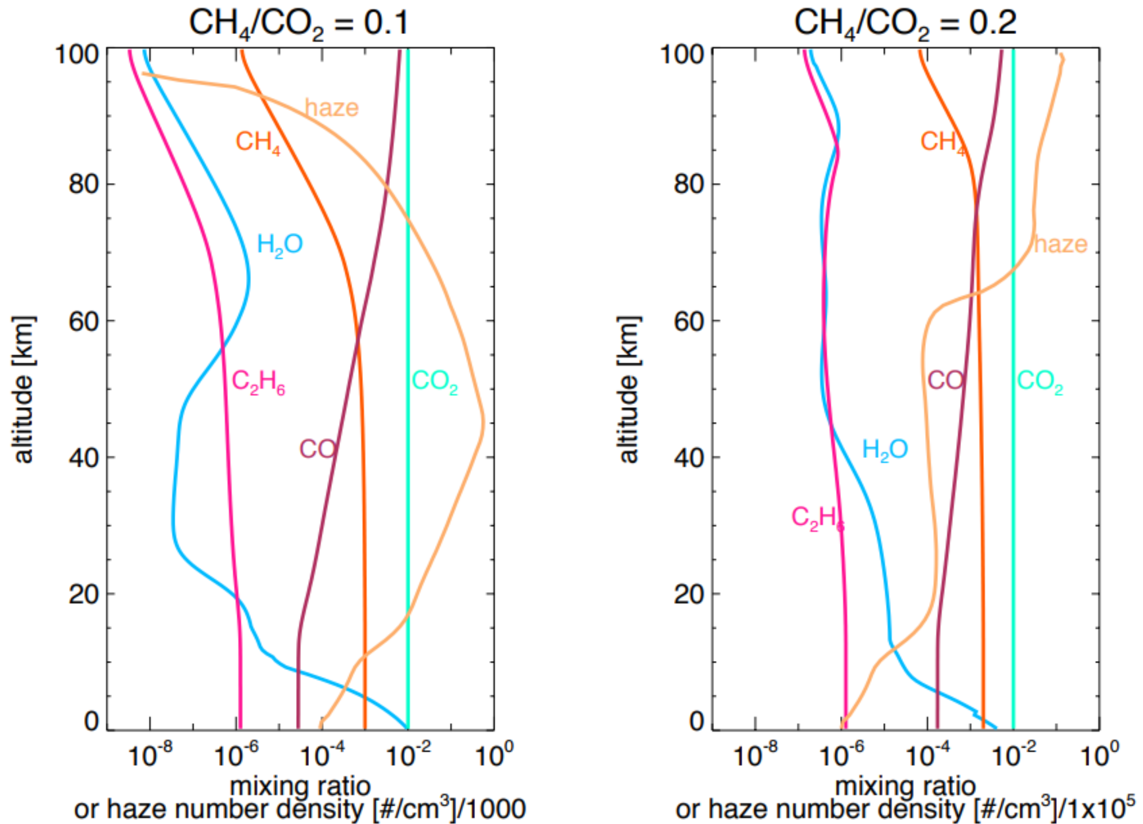
Getting from methane abundances to Pr(life)



→ **Pr(explain with known abiotic process) = 2%** **50 orbit case**

Haze and vertical profiles





Arney et al. 2016 *Astrobiology*

Nested Sampling Retrieval algorithm

$$\Pr(\mathbf{\Theta}|\mathbf{D},H) = \frac{\Pr(\mathbf{D}|\,\mathbf{\Theta},H)\,\Pr(\mathbf{\Theta}|H)}{\Pr(\mathbf{D}|H)}$$

where $\Pr(\mathbf{\Theta}|\mathbf{D},H) \equiv P(\mathbf{\Theta})$ is the posterior probability distribution of the parameters, $\Pr(\mathbf{D}|\mathbf{\Theta},H) \equiv L(\mathbf{\Theta})$ is the likelihood, $\Pr(\mathbf{\Theta}|H) \equiv \pi(\mathbf{\Theta})$ is the prior, and $\Pr(\mathbf{D}|H) \equiv \mathcal{Z}$ is the Bayesian evidence.

$$\mathcal{Z} = \int \mathcal{L}(\mathbf{\Theta})\pi(\mathbf{\Theta})d^D\mathbf{\Theta}$$

Transform this horrible integral into a 1D integral over prior volume:

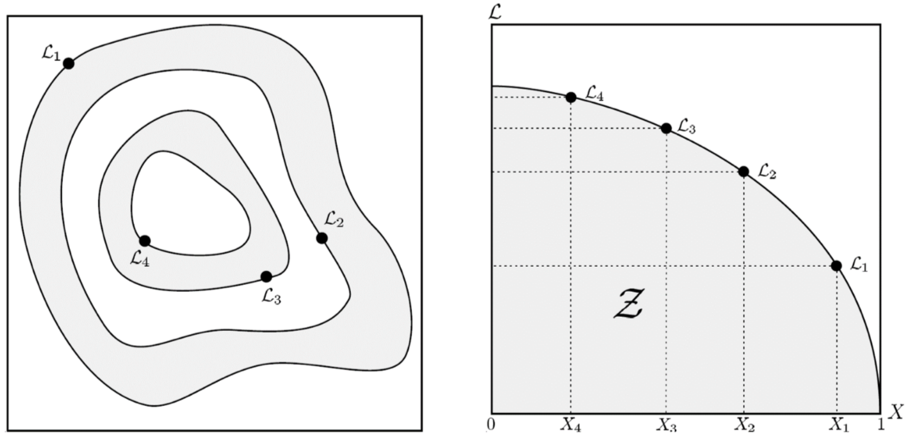
$$X(\lambda) = \int_{L(\mathbf{\Theta})>\lambda} \pi(\mathbf{\Theta})d^D\mathbf{\Theta},$$

$$\mathcal{Z} = \int_0^1 L(X)dX.$$

Can then calculate Bayesian evidence as summation over likelihood contours:

Feroz and Hobson 2008, *MNRAS*

$$0 < X_M < \cdots < X_2 < X_1 < X_0 = 1,$$

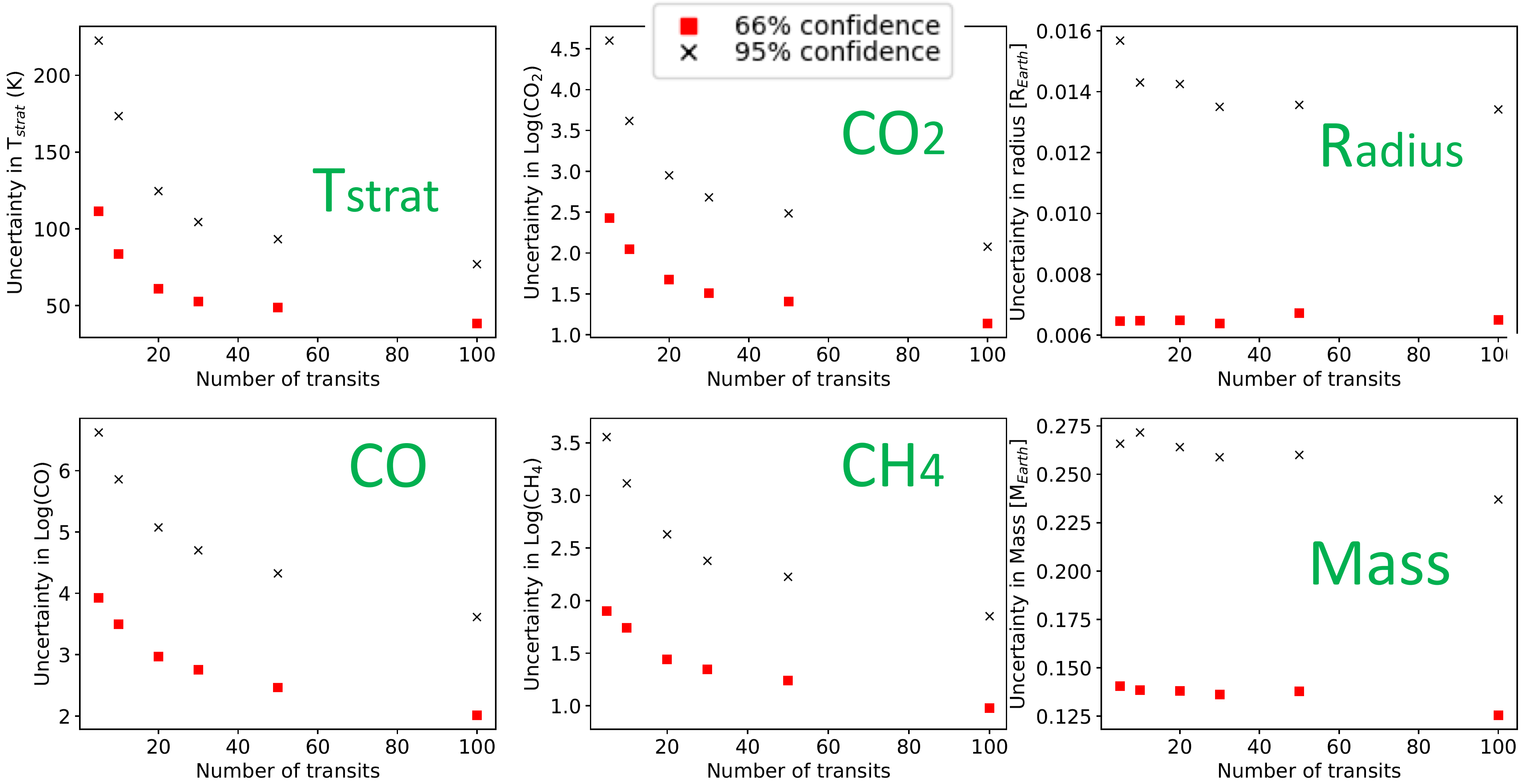


$$\mathcal{Z} = \sum_{i=1}^{M} L_i w_i.$$

Posteriors can then be easily calculated: $p_i = \frac{L_i w_i}{\mathcal{Z}}.$

Nested Sampling Produces same posteriors as MCMC

Does observing more transits help?



What about clouds?

Archean Earth-like Trappist-1e with Earth-like, grey clouds (10 transits with NIRSpec)

No clouds

With clouds

“True” values