Metrics to find life from remote sensing data & their limitations

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Outline

Part 1: Background: ideas of looking for life remotely

Part 2:

A) Looking at thermodynamic disequilibrium (in Gibbs energy/mole air) in Solar System atmospheres as a metric for life

B) the kinetics of disequilibrium

Part 3: Where we're going from here

PART 1:
Ideas for finding life remotely:

1. **Search for Extraterrestrial Intelligence (SETI)**
   legit approach, but not the focus of this talk/meeting

2. **Biogenic surfaces**
   microbial or multicellular pigments-discussed yesterday somewhat

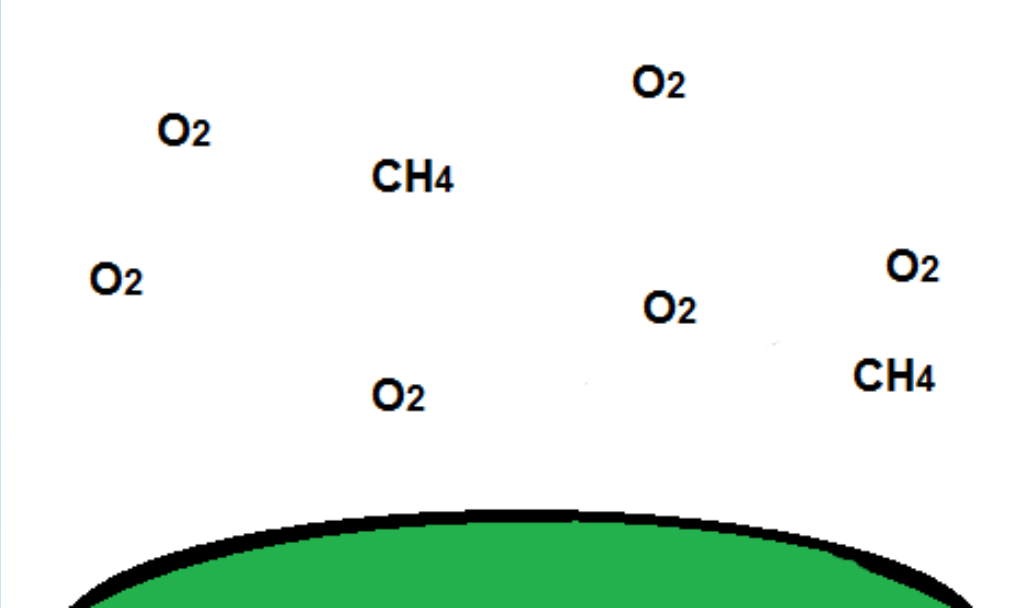
3. **Biogenic gases**
   Which gases? How many gases? What levels constitute life detection? Why chemical disequilibrium?

Chemical disequilibrium as a sign of life? Part 1

"*Kinetic instability in the context of local chemical and physical conditions…*" Joshua Lederberg (1965) *Nature*

More than one: "*Search for…compounds in the planet's atmosphere that are incompatible on a long-term basis*" James Lovelock (1965) *Nature*

"*gaseous oxygen…and atmospheric methane in extreme thermodynamic disequilibrium...are strongly suggestive of life on Earth*" Carl Sagan (1993) *Science*



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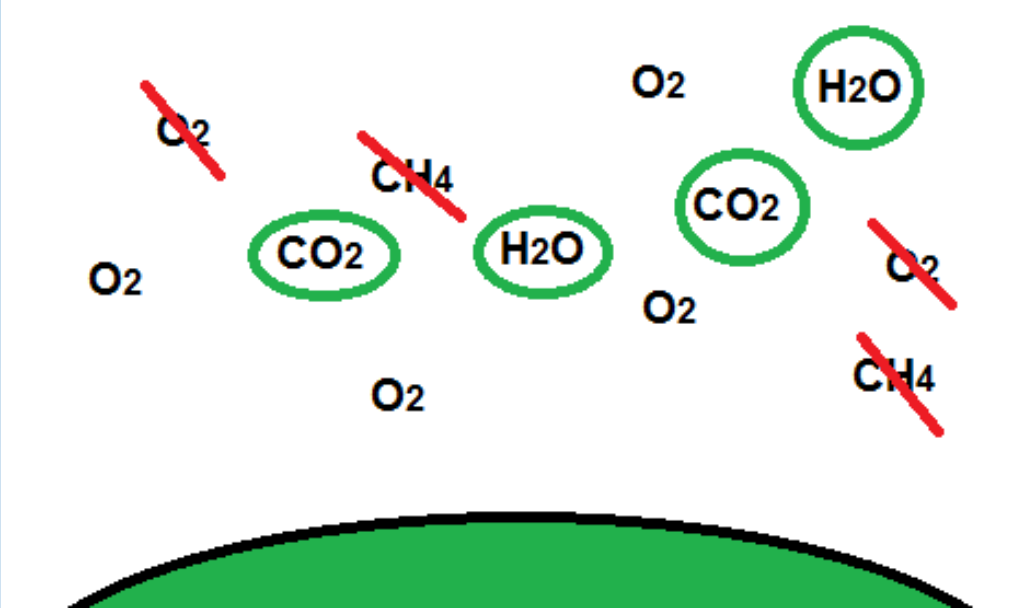

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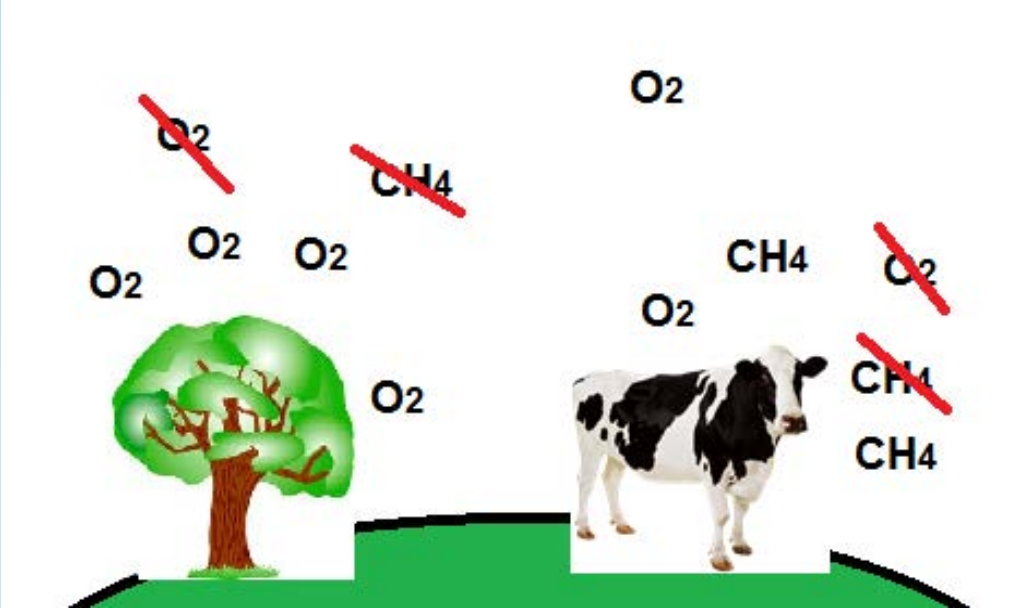
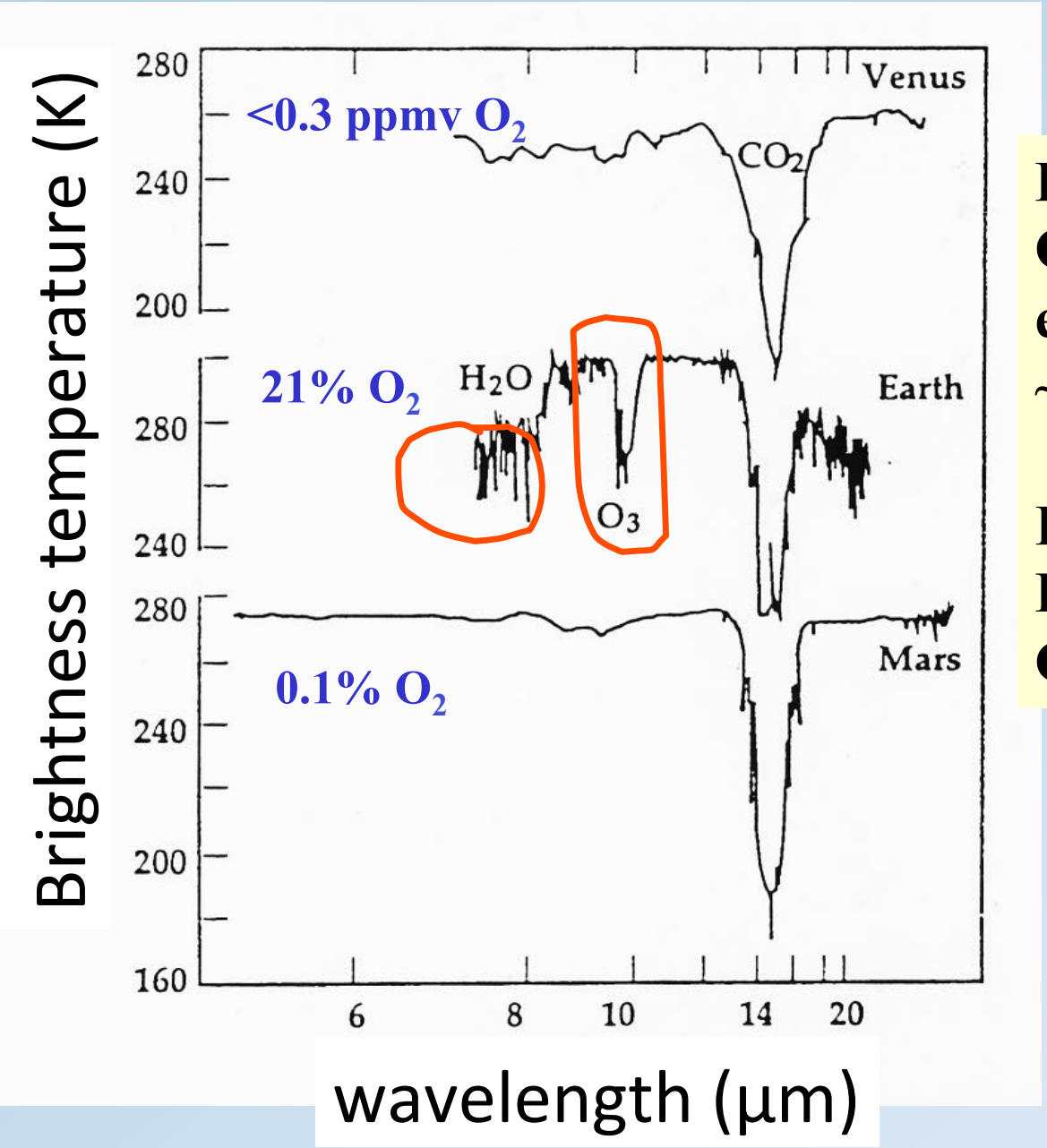


Modern incarnation: Biogenic gases in reflectance spectra



If photosynthesis ceased, O_2 decreases exponentially to <0.4% in ~10 m.y.

Proposed search to Earth-like exoplanets for O_2 and CH_4

Disequilibrium applies to waste biogenic gases, but it's nuanced:

1) All planetary atmospheres are in disequilibrium

- Geophysics competes with biology. How much?

2) Life feeds on disequilibrium so sometimes disequilibrium might mean "no one home" i.e.,

uneaten free food=> ~~no grad students~~

no life

Atmospheric disequilibrium as a biosignature on exoplanets?

DETECTING LIFE-BEARING EXTRASOLAR PLANETS WITH SPACE TELESCOPES

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Received 2007 October 7; accepted 2008 May 27

ABSTRACT

One of the promising methods to search for life on extrasolar planets (exoplanets) is to detect its signature in the chemical disequilibrium of exoplanet atmospheres. Spectra at the modest resolutions needed to search for methane, oxygen, carbon dioxide, or water will demand large collecting areas and large diameters to capture and isolate the light from planets in the habitable zones around the stars. Single telescopes with coronagraphs to isolate the light from

Remote Sensing of Planetary Properties and Biosignatures on Extrasolar Terrestrial Planets

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tures (e.g., complex organic molecules and cells). Life may be indicated by chemical disequilibria that cannot be explained solely by nonbiological processes. For example, a geologically active planet that exhales reduced volcanic gases can maintain detectable levels of atmospheric oxygen

Quantifying drivers of chemical disequilibrium: theory and application to methane in the Earth's atmosphere

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1965; Lippincott et al., 1966; Lovelock and Margulis, 1973; Sagan et al., 1993; Lenton, 1998). Disequilibrium by itself is not an unequivocal indicator of life, since it can also be caused by abiotic processes such as photochemistry or geothermally driven surface chemistry. In particular, photochemistry can produce substantial amounts of O_2 and O_3, as found in the Earth's stratosphere as well as on Venus

Some inconvenient truths about biosignatures involving two chemical species on Earth-like exoplanets

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Edited by Neta A. Bahcall, Princeton University, Princeton, NJ, and approved March 27, 2014 (received for review February 1, 2014)

The detection of strong thermochemical disequilibrium in the atmosphere of an extrasolar planet is thought to be a potential biosignature. In this article we present a previously unidentified kind of false positive that can mimic a disequilibrium or any other biosignature that involves two chemical species. We consider a sce-

a planet's atmosphere should not be considered as clear evidence for life. [Also note that the Earth might have never had a phase of strong, observable O_2/CH_4 disequilibrium (19).] There is a long list of abiotic sources that could also create a disequilibrium such as impacts (20), photochemistry (21), and geochemistry (14).

Remote life-detection criteria, habitable zone boundaries, and the frequency of Earth-like planets around M and late K stars

James F. Kasting[1], Ravikumar Kopparapu, Ramses M. Ramirez, and Chester E. Harman

sphere, as either methanogens would consume it (10), or alternatively acetogens would use it to produce acetate (11). So, the criterion of extreme thermodynamic equilibrium as a biomarker is directly contradicted.

FINDING EXTRATERRESTRIAL LIFE USING GROUND-BASED HIGH-DISPERSION SPECTROSCOPY

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Received 2012 October 8; accepted 2013 January 8; published 2013 February 5

ABSTRACT

Exoplanet observations promise one day to unveil the presence of extraterrestrial life. Atmospheric compounds in strong chemical disequilibrium would point to large-scale biological activity just as oxygen and methane do in the Earth's atmosphere. The cancellation of both the *Terrestrial Planet Finder* and *Darwin* missions means that it is unlikely that a dedicated space telescope to search for biomarker gases in exoplanet atmospheres will be

e.g., back-of-envelope estimate: CH_4 in fixed bulk air

$$CH_4 + 2O_2 \rightleftharpoons CO_2 + 2H_2O \quad \text{(net)}$$

$$\Delta G^0_{\text{reaction}} = \sum G^0_{\text{products}} - \sum G^0_{\text{reactants}} = -817.9 \text{ kJ mol}^{-1}$$

Negative: thermodynamically favored, with equilibrium constant for $b\text{B} + c\text{C} = g\text{G} + h\text{H}$ of

$$K_{eq,298\text{K}} = \frac{\text{activity product of products}}{\text{activity product of reactants}} = \frac{a_G{}^g a_H{}^h}{a_B{}^b a_C{}^c} = \exp\left(\frac{-\Delta G^0_{\text{reaction}}}{RT}\right)$$

Hence, equilibrium methane in 0.21 bar O_2 and 380 ppmv CO_2 is:

$$p_{\text{CH4}} \sim \frac{(p_{\text{CO2}})(a_{\text{H2O}})}{(p_{\text{O2}})^2 K_{eq}} = \frac{380 \times 10^{-6}}{(0.21)^2 \times 10^{143.29}} = 10^{-145} \text{ bar}$$

But actual CH_4 abundance is 1.8×10^{-6} bar

Equilibrium of each gas with *fixed* bulk air: O_2, N_2, CO_2, $H_2O(g)$

Gas	Abundance	Equilibrium abundance	Source	Detectable in *Galileo* NIR spectra of Earth?
CS_2	$10^{-11} – 10^{-10}$	~0	>80% Biology; + volcanic	
OCS	10^{-10}	~0	Biology + photochemistry	
SO_2	$10^{-11} – 10^{-10}$	~0	Volcanic + photochemistry	
CH_4	1.8×10^{-6}	10^{-145}	>90% biology; + geothermal	
NH_3	$10^{-10} – 10^{-9}$	10^{-60}	Biology	
O_3	$10^{-8} – 10^{-7}$	3×10^{-30}	Biology + photochemistry	
N_2O	3×10^{-7}	2×10^{-19}	Biology (+minor abiotic)	

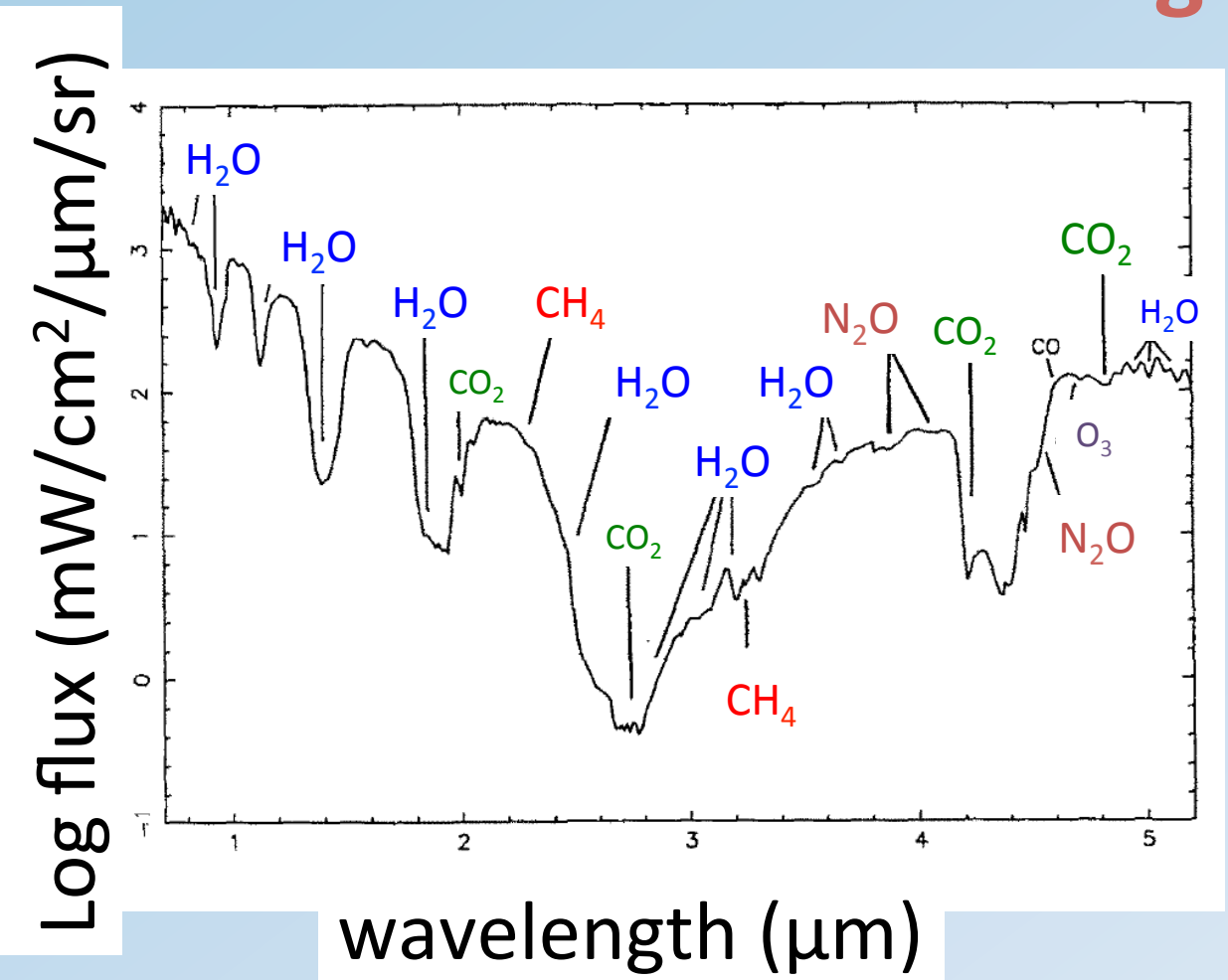
Note: Number of molecules in Earth's atmosphere ~10^{44}

Bringing all gases to equilibrium (Gibbs energy minimization formal solution):

Gas	Abundance	Equilibrium abundance	Source	Detectable in *Galileo* NIR spectra of Earth?
CH_4	1.8×10^{-6}	10^{-48}	>90% biology; + geothermal	
O_3	$10^{-8} – 10^{-7}$	2×10^{-30}	Biology + photochemistry	
N_2O	3×10^{-7}	3×10^{-20}	Biology (+minor abiotic)	

Note: Number of molecules in Earth's atmosphere ~10^{44}

Assuming estimates of gas abundances…e.g.,



Radiative transfer model + retrieval/fit

Invert bands of well-mixed gas (i.e., CO_2 @4.3µm; 4.8µm)

↓

Temperature-pressure profile

↓

CH_4, N_2O, H_2O, O_3 abundances, albeit non-unique vertical distribution

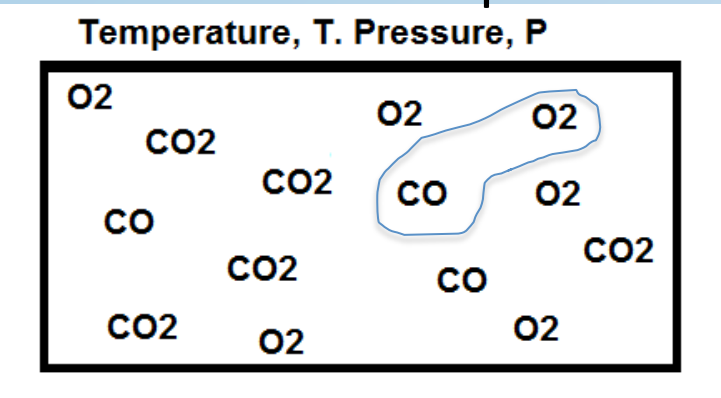
Galileo Near-IR Mapping Spectrometer (Drossart+, 1993)
NIMS' long-visible, O_2 band @0.76 µm => column O_2
I believe N_2 was assumed by Sagan+ (1993).

PART 2A:

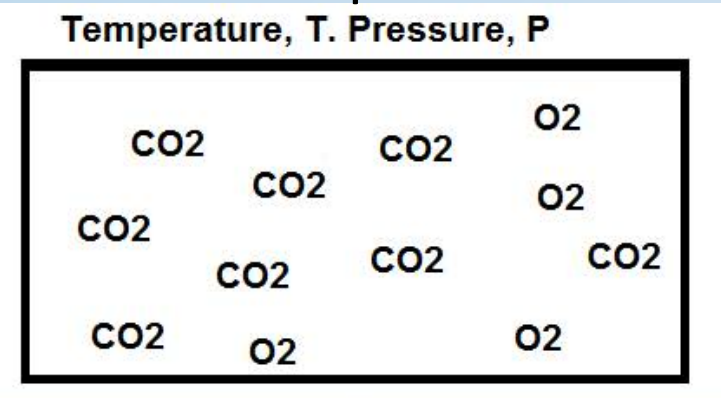
Does thermodynamic disequilibrium (in Gibbs energy/mole air) in Solar System atmospheres act as a metric for life?

Can quantify chemical disequilibrium

Observed atmosphere



Atmosphere if it were in chemical equilibrium



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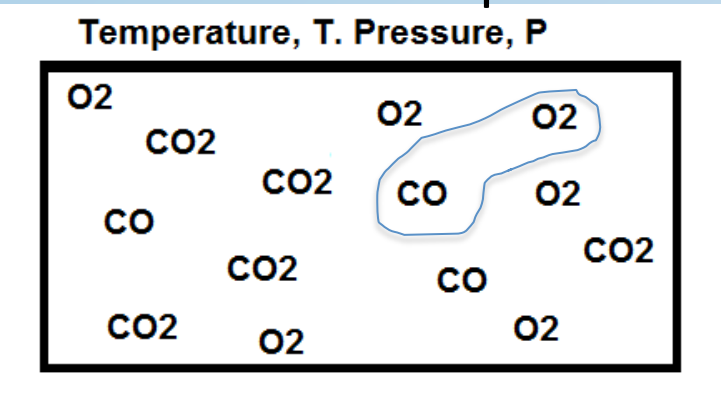

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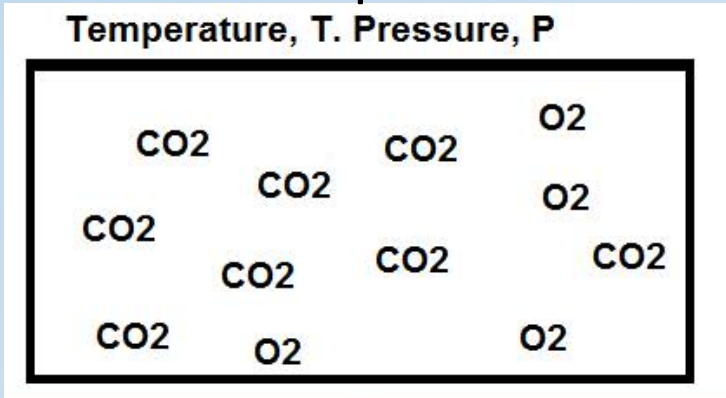


$$G_{(T,\mathrm{P})} = \sum_i n_i \left(G^{\circ}_{i\,(T,\mathrm{P}_r)} + RT\ln\left(\frac{P\gamma_i n_i}{n_{tot}}\right)\right)$$

moles gas *i*, activity coeff. γ_i

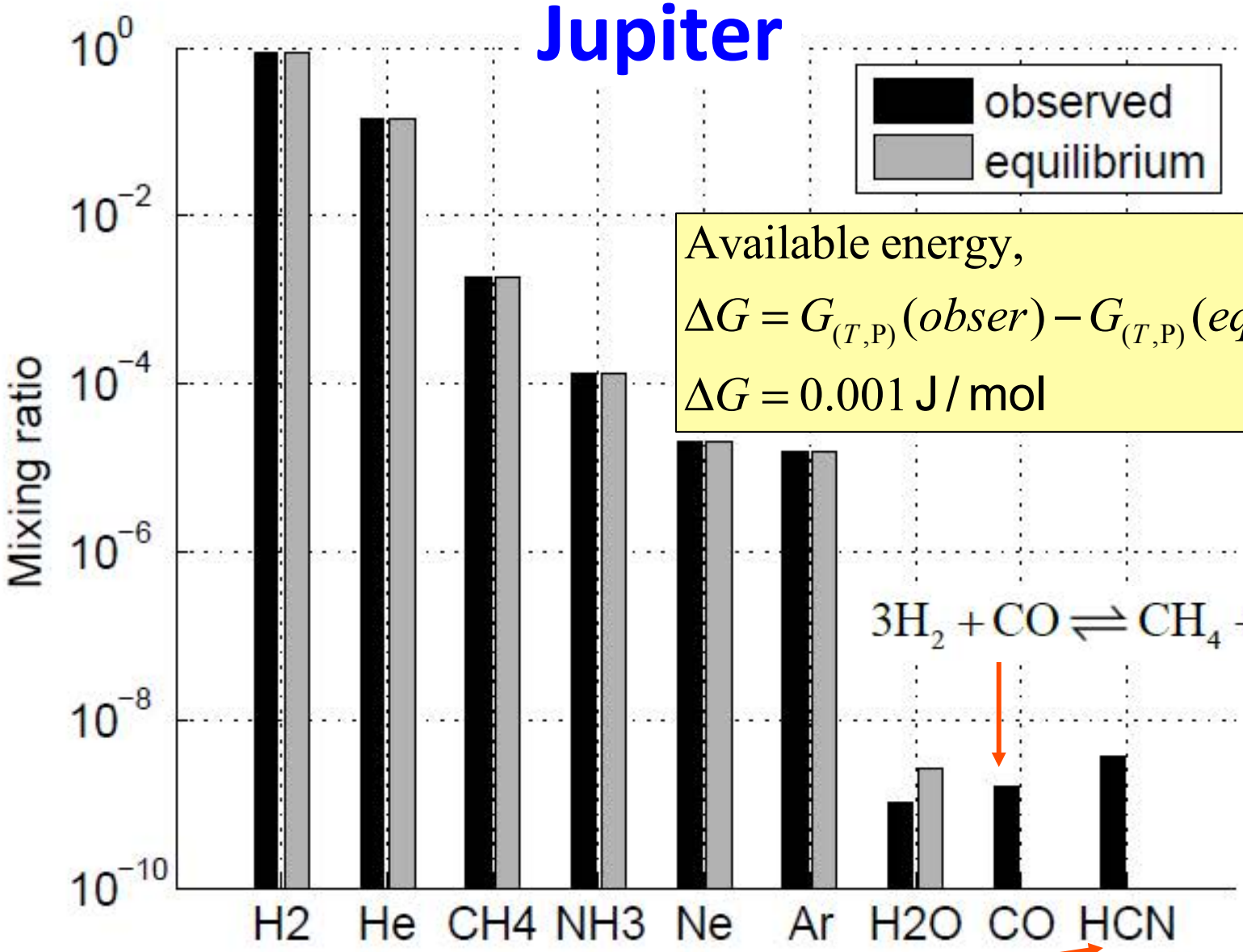
total moles air; do it for 1

We quantify disequilibrium as the change in Gibbs energy of the system during reaction to equilibrium:

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

Applied to Solar System atmospheres….

Jupiter



Available energy,

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

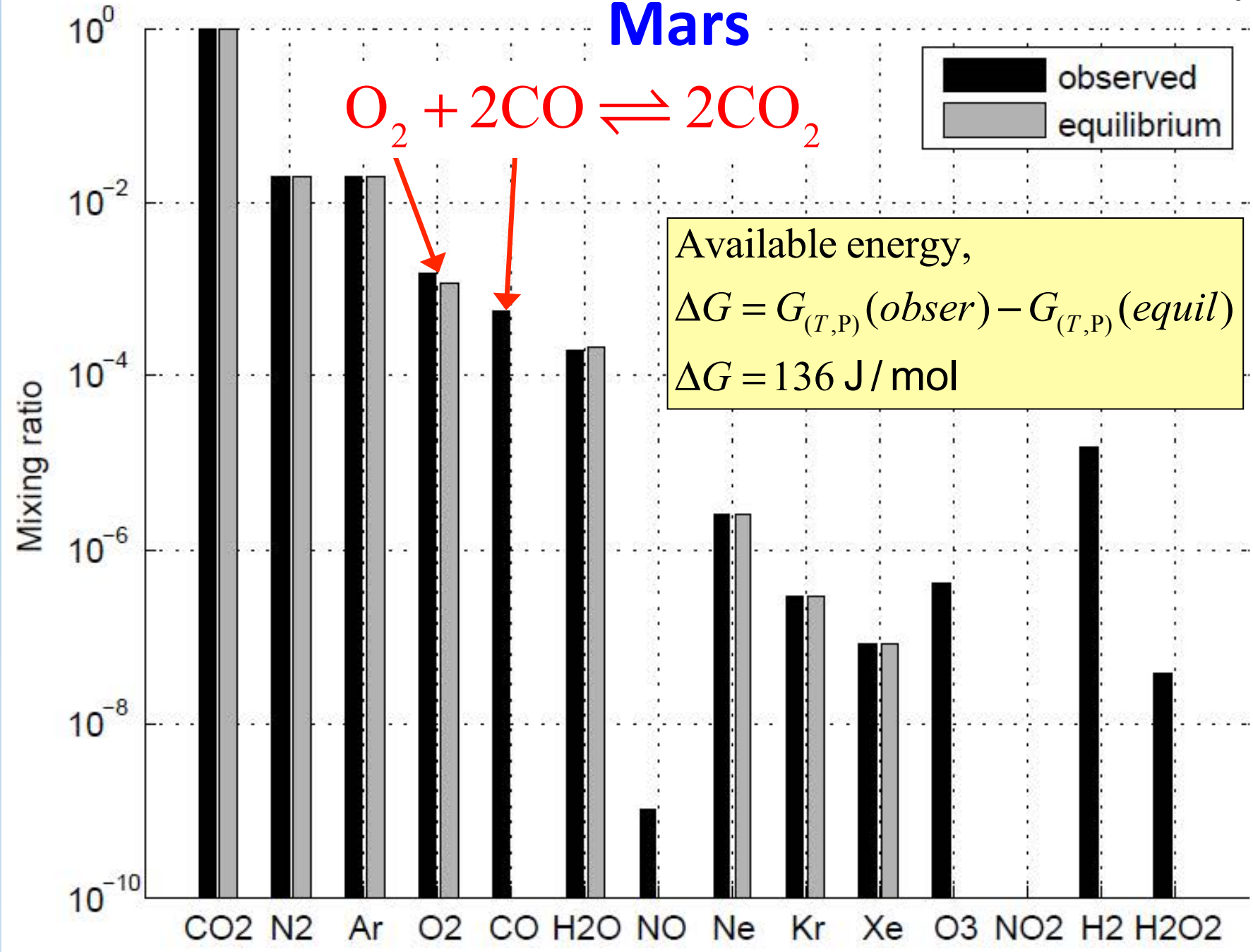
$$\Delta G = 0.001\ \mathrm{J/mol}$$

$$3H_2 + CO \rightleftharpoons CH_4 + H_2O$$

$$3H_2(g) + HCN(g) \rightleftharpoons CH_4(g) + NH_3(g)$$

Mars

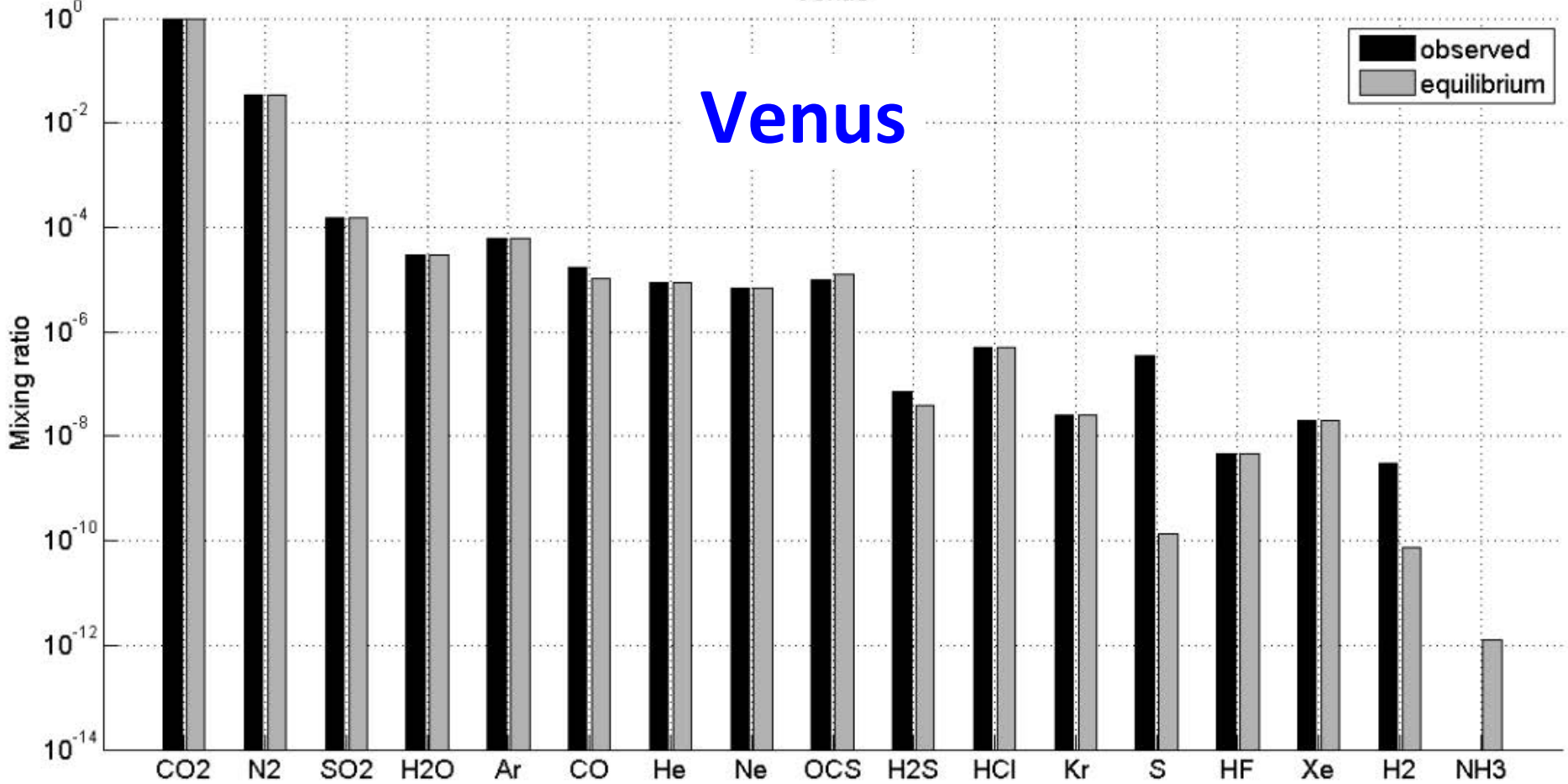
$$O_2 + 2CO \rightleftharpoons 2CO_2$$



Available energy,

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

$$\Delta G = 136\ \mathrm{J/mol}$$



Available energy,

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

$$\Delta G = 0.06\ \mathrm{J/mol}$$

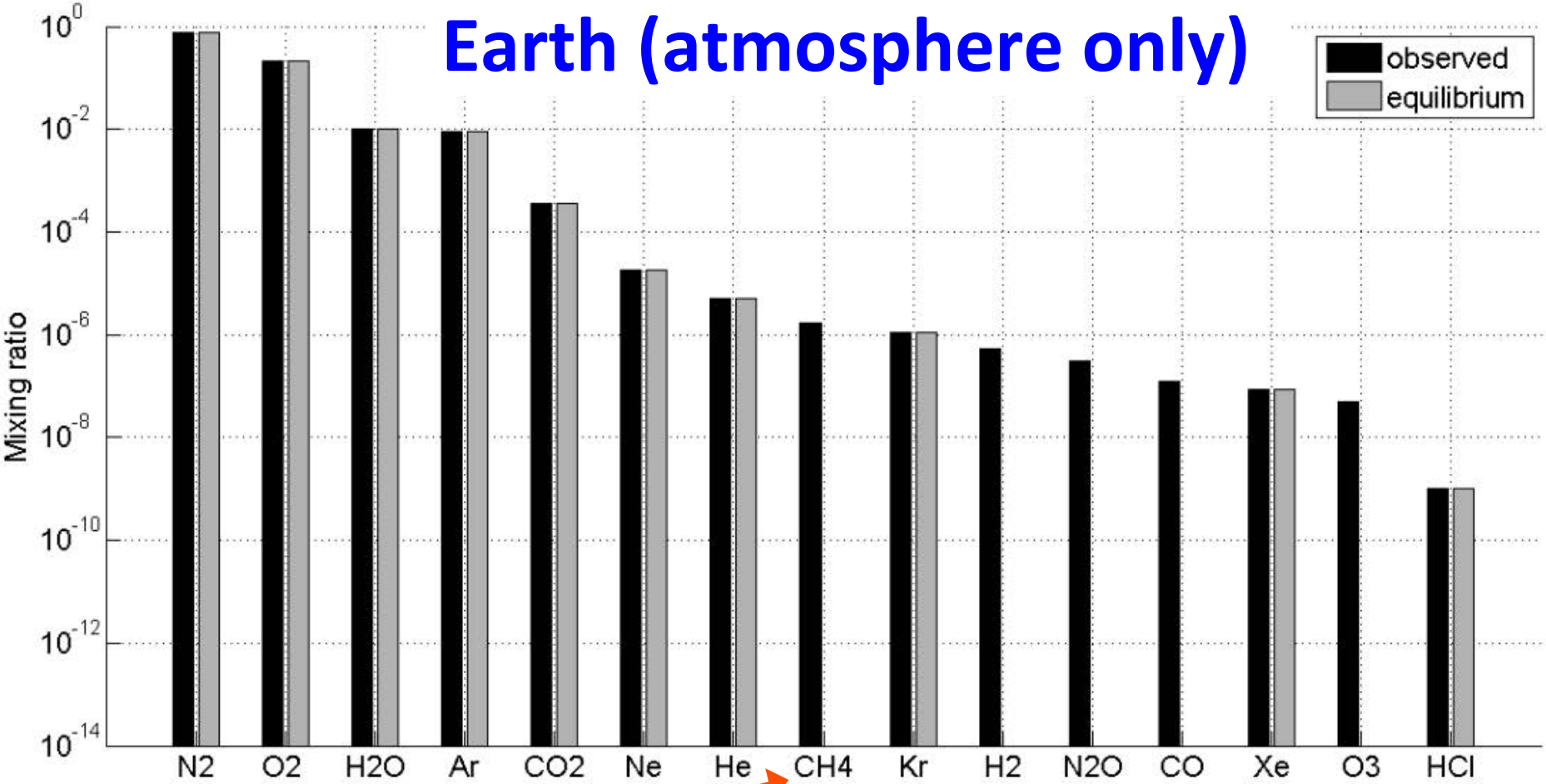
$$H_2S + CO_2 \rightleftharpoons H_2O + OCS$$

$$3CO + SO_2 \rightleftharpoons 2CO_2 + OCS$$

$$2CO_2 + S \rightleftharpoons SO_2 + 2CO$$

$$H_2 + S \rightleftharpoons H_2S$$

Earth (atmosphere only)



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

Available energy,

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

$$\Delta G = 1.5\ \mathrm{J/mol}$$

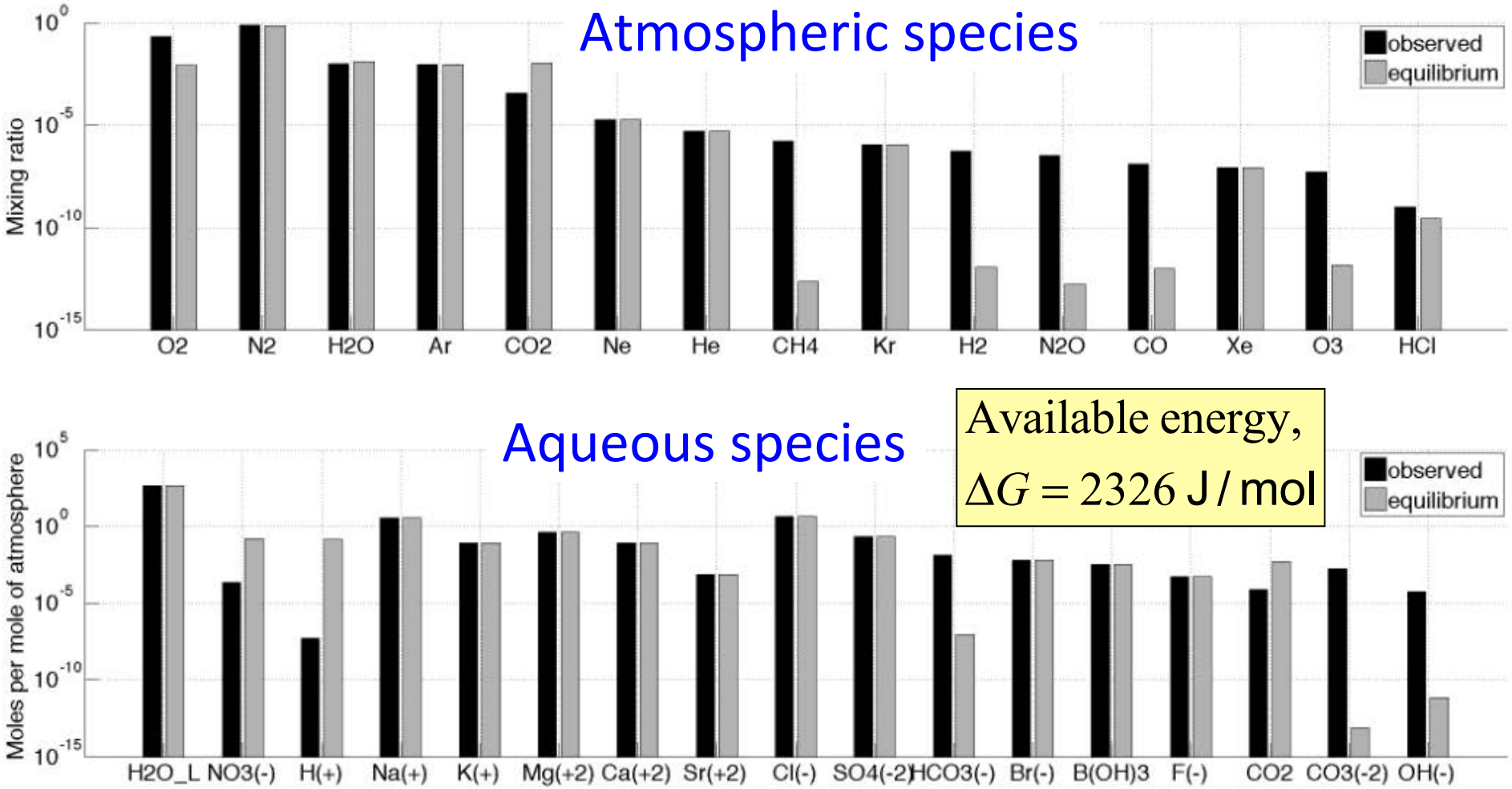
Typical surface of Mars

Typical surface of planet Earth

(2012: 13°S, mid-Atlantic, 3.8 km depth of water)

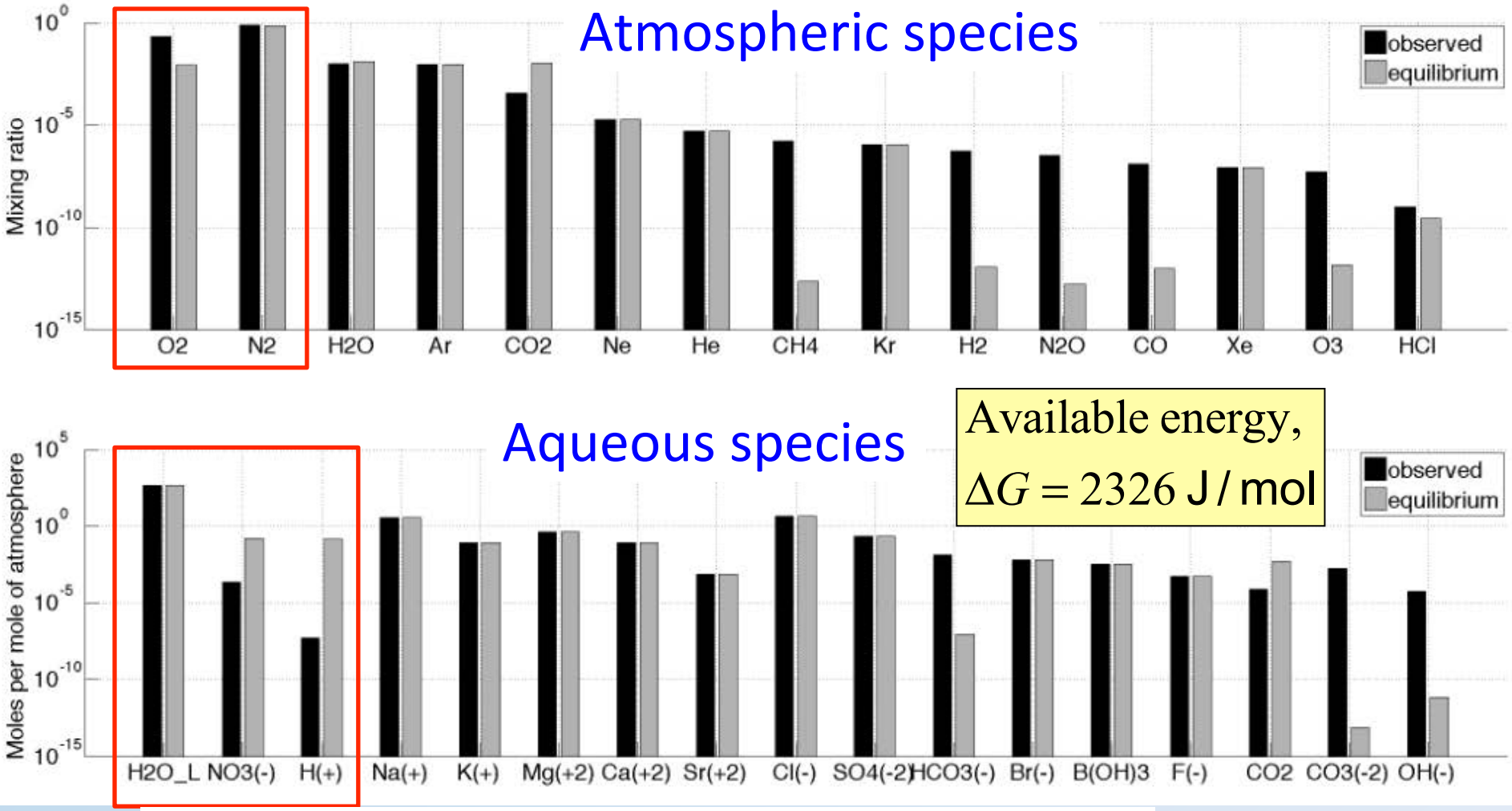
Photo on way to Ascension Island from St. Helena: David Catling

Earth (atmosphere-ocean fluid envelope)



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".

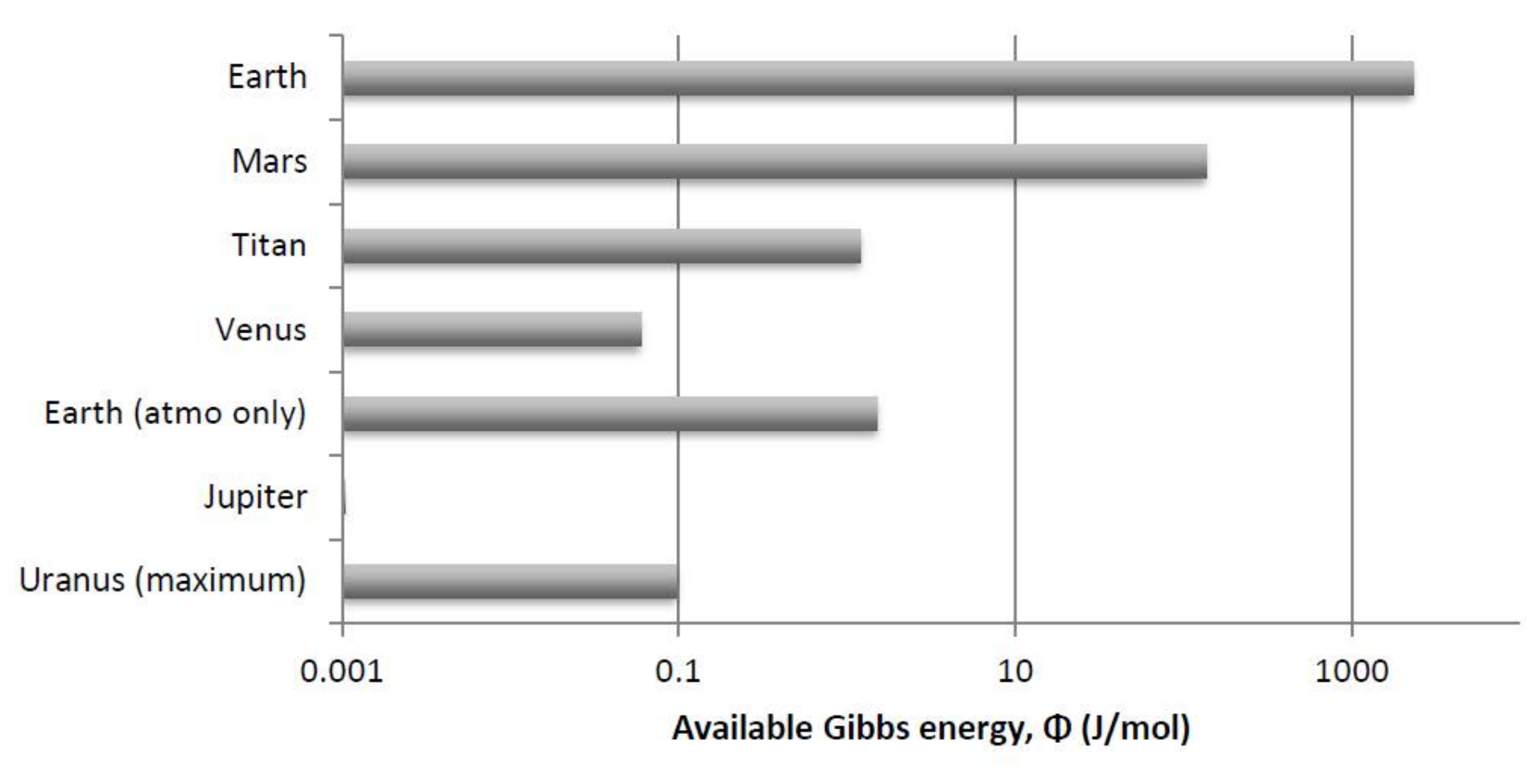
Earth (atmosphere-ocean fluid envelope)



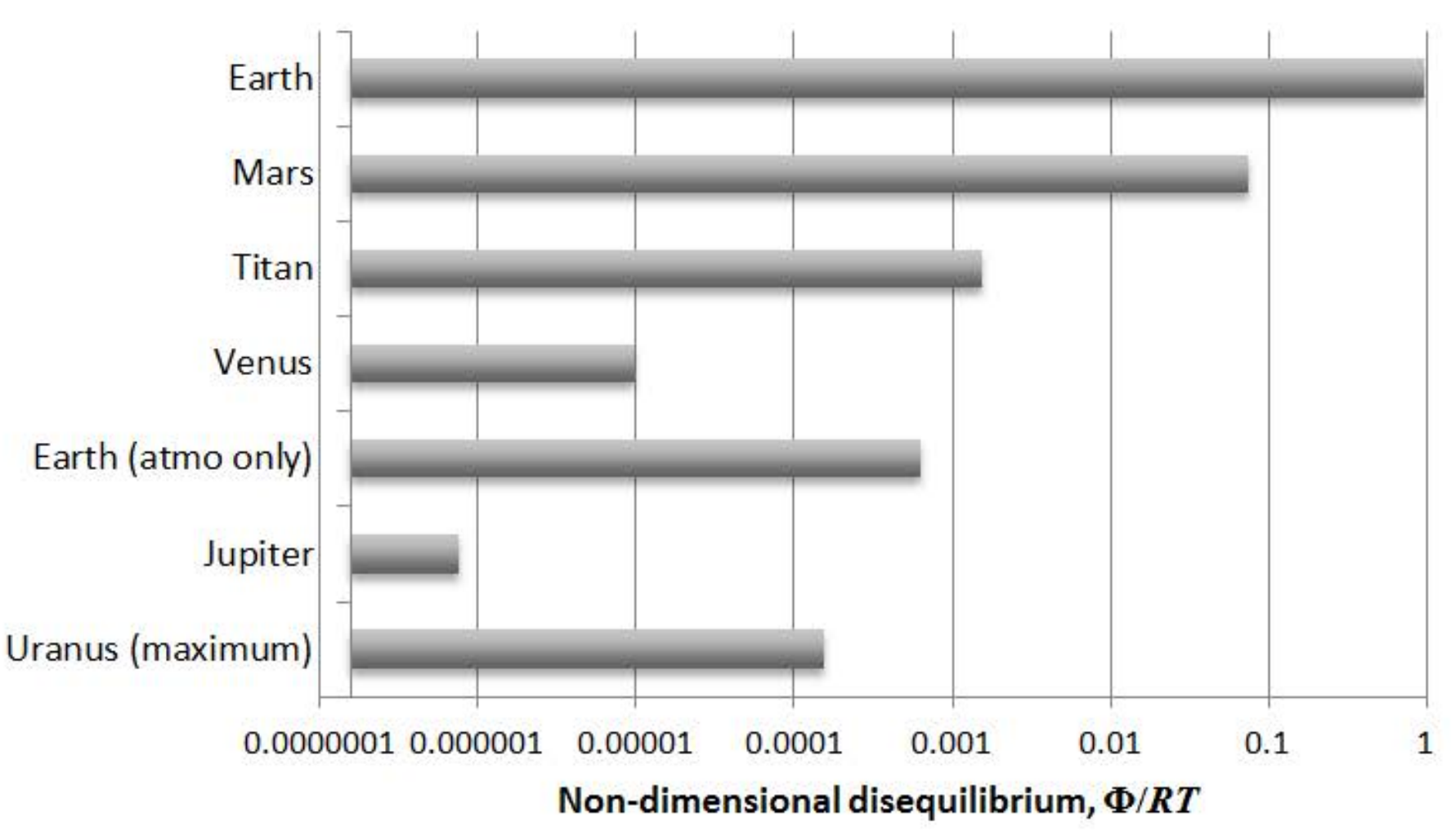
$$2N_2(g) + 5O_2(g) + 2H_2O(l) \rightleftharpoons 4H^+(aq) + 4NO_3^-(aq)$$

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".

Earth has largest disequilibrium in the solar system



Earth has largest disequilibrium in the solar system



Only on Earth is available energy ≈ thermal energy of air

Is this practical for exoplanets?

- For exoplanets, **thermodynamic disequilibrium** (in principle) could be computed from observations without assumptions about gas fluxes.

- Bulk abundance, oceans, and total pressure are observational challenges, but have been considered:
  - **N_2 from N_2-N_2 dimer absorption, 4.3 µm** (Schwieterman+ 2015).
  - **Ocean presence from specular glint + H_2O-rich spectra** (e.g., Lack of glint on Mars: Phillips (1863) *Proc. Roy Soc. Lond.*; Sagan+ 1993; Robinson+ 2010; 2014)
  - **Pressure from O_2-O_2 dimer, 1.06 & 1.27 µm** (Misra+ 2014).

- Sensitivity tests to difficult-to-observe variables in the calculation show **relative insensitivity**

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

Sensitivity test

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Pressure	0.1 bar	1354.20
	1.013 bar	2325.76
	10 bar	3891.96
	1000 bar	6878.35

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Pressure	0.1 bar	1354.20
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	1000 bar	6878.35
Ocean pH	2	1983.28
	4	2314.26
	6	2325.71
	8.187 (Earth)	2325.76
	12	2325.65

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Ocean pH	2	1983.28
	4	2314.26
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	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

Sensitivity test

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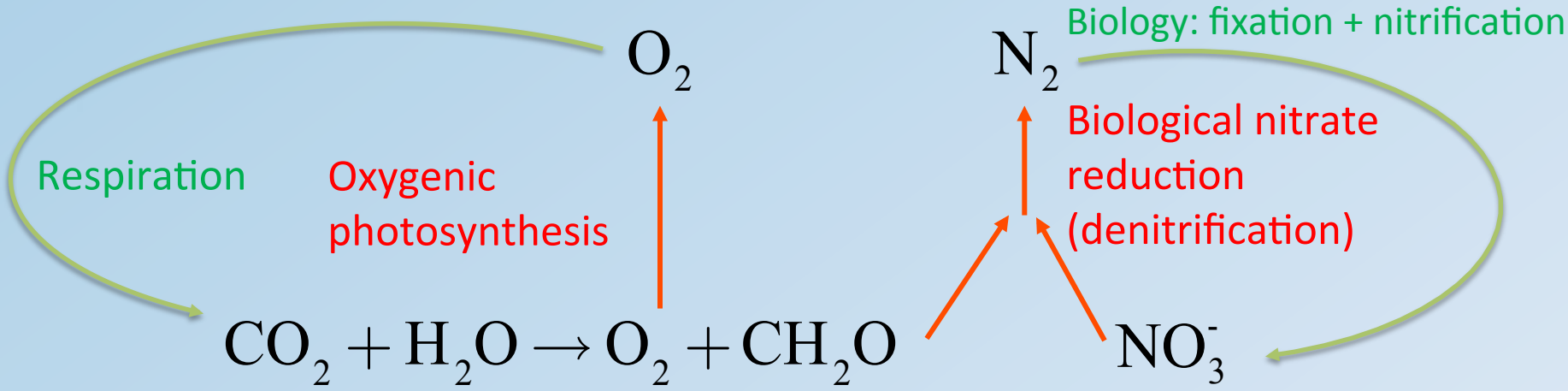
	8.187 (Earth)	2325.76
	12	2325.65
Salinity	0 mol/kg	2290.01
	1.1 mol/kg	2325.76
	11.1 mol/kg	2276.40
Ocean volume	0.1 Earth ocean	413.62
	0.5 Earth ocean	1442.95
	1 Earth ocean	2325.76
	2 Earth oceans	4188.27
	10 Earth oceans	8956.34
	50 Earth oceans	12626.22

(extra slides)

What does disequilibrium mean?

- Sometimes thermodynamic disequilibrium means life.



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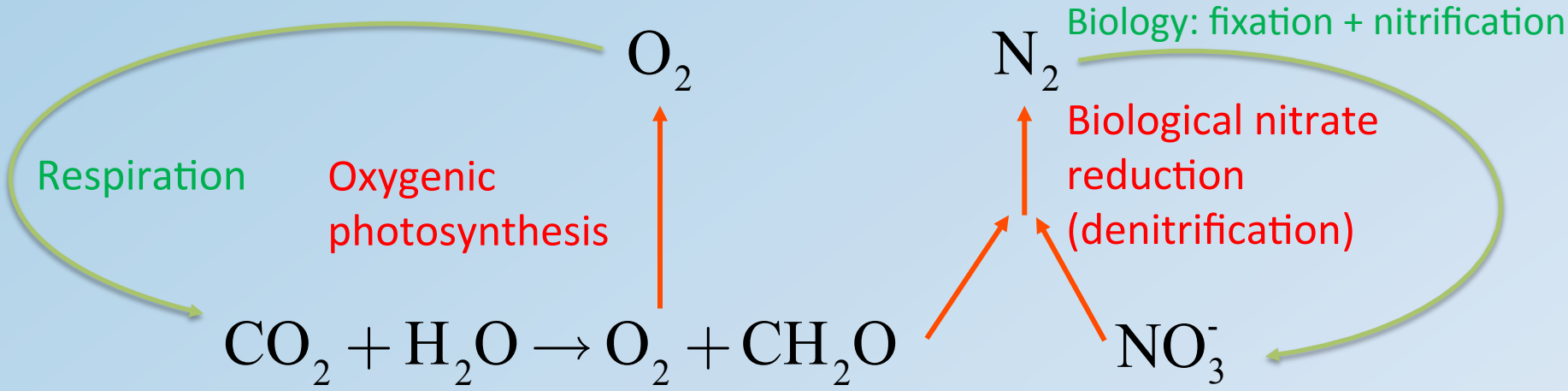


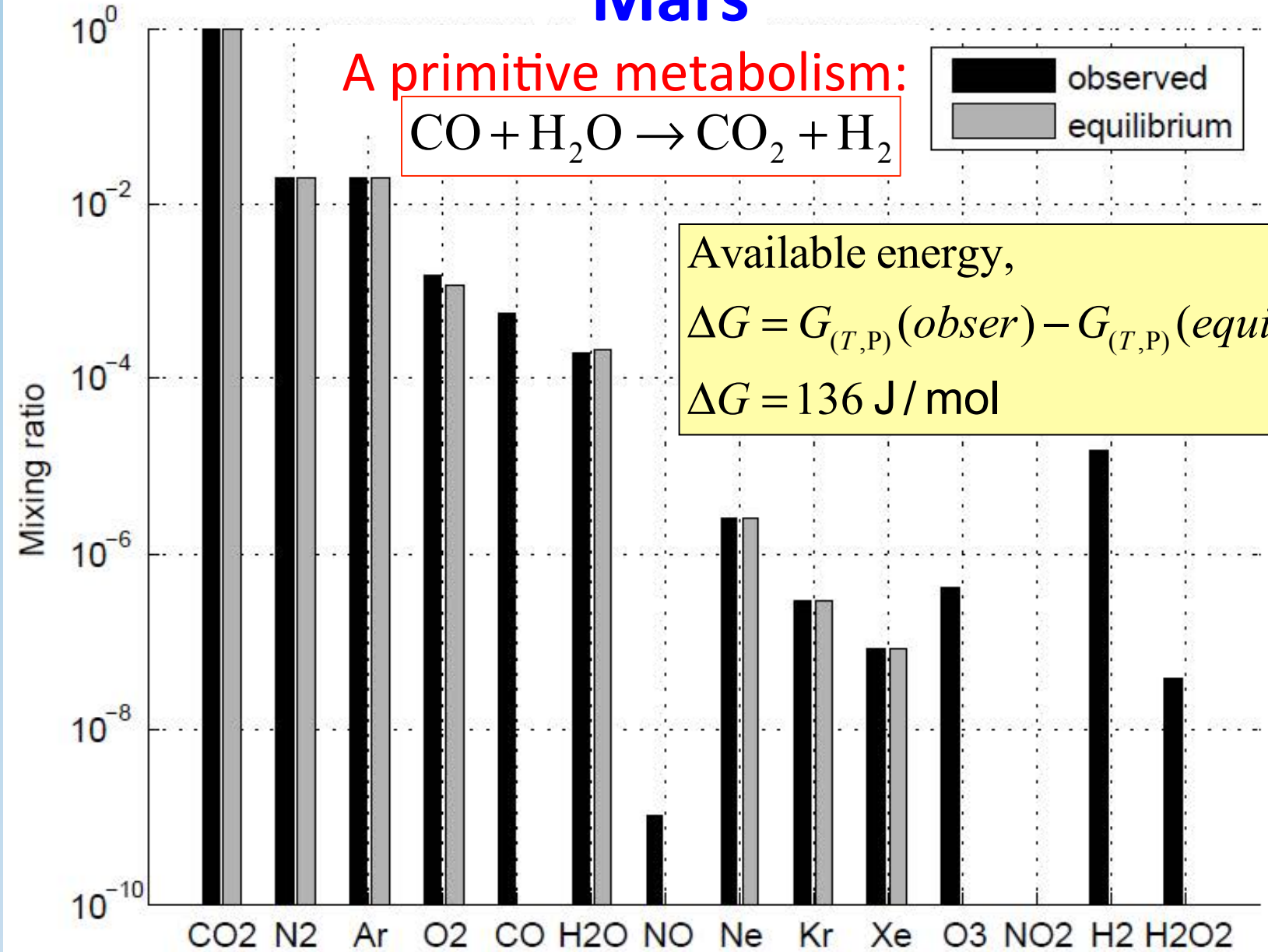
- But sometimes thermodynamic disequilibrium means the absence of life (**anti-biosignature**).

  Large available energy = an “uneaten free lunch” -> no life exists or “no one home”

Mars

A primitive metabolism:

$$CO + H_2O \rightarrow CO_2 + H_2$$



Available energy,

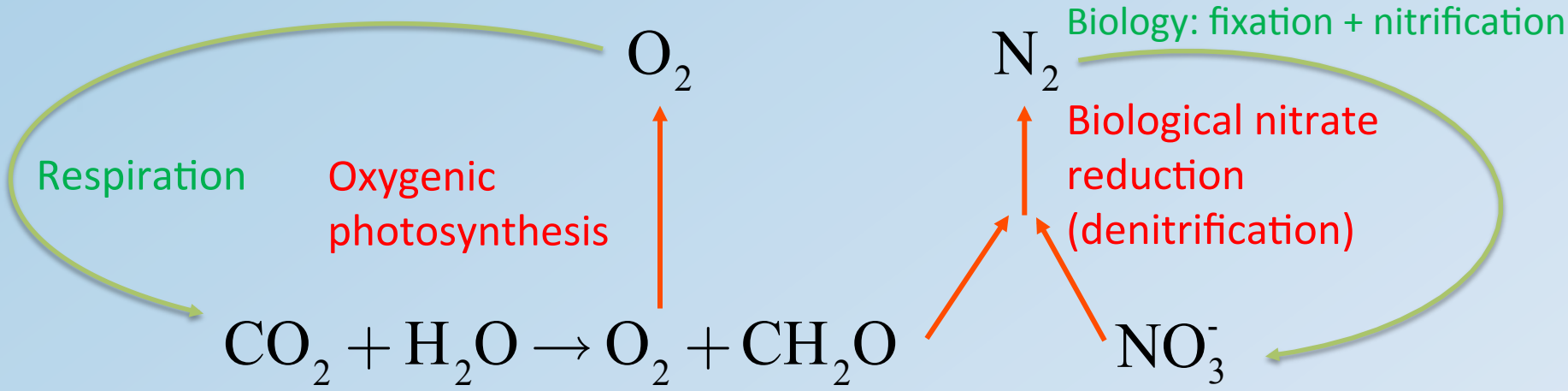
$$\Delta G = G_{(T,P)}(obser) - G_{(T,P)}(equil)$$

$$\Delta G = 136 \text{ J/mol}$$

Much CO => no life today on the surface of Mars. (Weiss et al. 2000; Zahnle et al. 2011). We calculate: ≤100 blue whales equiv. CO-eating biomass in subsurface.

What does disequilibrium mean?

- Sometimes thermodynamic disequilibrium means life.



- But sometimes thermodynamic disequilibrium means the absence of life: **anti-biosignature**. Large available energy = an "uneaten free lunch" -> no life exists.

- **Conclusion**: a single number metric like available energy has to be considered judiciously – **in context**.

PART 2B (brief)

Kinetic metrics

Lifetimes, sources, sinks

Concentration C; $\frac{\partial C}{\partial t} = -\lambda t \Rightarrow C = C_0 \exp(-\lambda t)$ => Lifetime = 1/λ

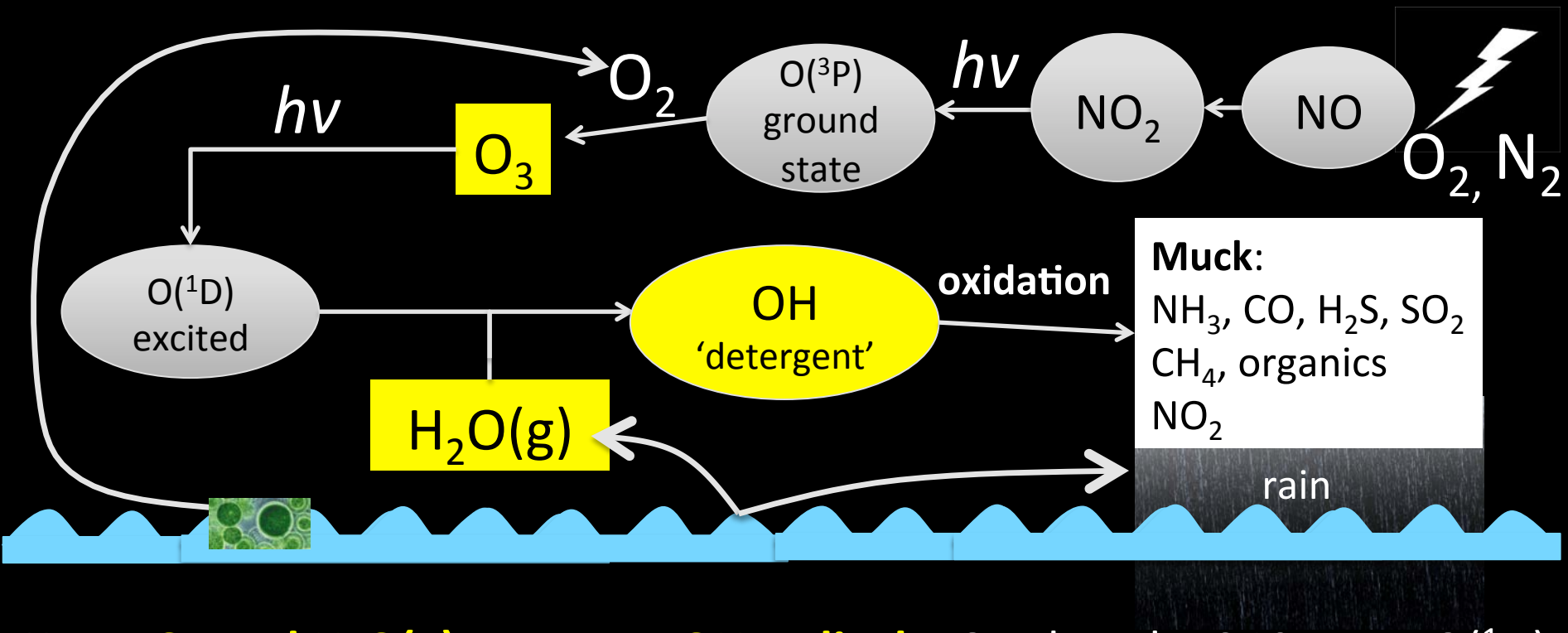
λ calculated from photochemical sinks. Examples below.

	abundance	lifetime (years)	Source (Tmol/ yr)	Abiotic fraction
CH_4	1.8 ppmv	10	30	<10%
N_2O	0.3 ppmv	120	~1	negligible

To estimate source = sink, need to know:

1) CH_4 + OH loss of CH_4
2) Mainly N_2O photolysis loss in stratosphere (plus some $N_2O + O(^1D)$)

To know OH sink on CH_4 need to know…



Keys: O_3 and $H_2O(g)$ generate OH radicals; O_3 photol. <340 nm ->$O(^1D)$

$$H_2O + O(^1D) \rightarrow OH + OH$$

OH oxidizes muck => air transparent to visible (no significant haze at alt.)

Schematic: Essentials of Earth's tropospheric chemistry: See review: D. C. Catling (2015) Planetary Atmospheres in *Treatise on Geophysics* (2nd Ed.), vol 10, Elsevier, New York, 429-472.

Kinetics => Source fluxes

Bottom lines:

1) We get a source flux from balancing a sink flux, which requires a knowledge of the atmospheric chemistry beyond that for thermodynamic equilibrium from bulk gases

2) Abiotic vs. biotic source flux is still a question of degree:

- plausible biomass?
- implausible abiotic flux?

Part 3: Future work

1) Current to-do list: more diseqm cases; *kinetic* metrics
- deducing unusual gas fluxes, given expected lifetimes
- ways to quantify this; metrics

2) The full shebang with a Bayesian approach:

spectrum→ inversion → gases +/- errors → metrics +/- errors → probability of whether life is present

=Project of VPL/UW astrobiology PhD student Josh Krissansen-Totton:

Summary

- Earth has the largest disequilibrium in the Solar System, which **is biogenic**.

- The other Solar System planets have smaller disequilibria maintained by abiotic processes.

- For exoplanets, thermodynamic disequilibrium could be computed directly from observations without assumptions about gas fluxes. An imperfect tool but one for the toolbox; key (dis)equilibria inform obs.

- Kinetic metrics are another avenue: means assessing plausibility of biogenic vs. abiotic gas fluxes

Some references:

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

2) J. Krissansen-Totton+, Is the Pale Blue Dot unique? Optimized photometric bands for identifying Earth-like planets. *Astrophy. J.* 817, 31, 2016.

Shameless plug for researcher-level book, coming soon:

D. C. Catling & J. F. Kasting (2017) ***Atmospheric Evolution on Inhabited and Lifeless Worlds***, Cambridge University Press. ~500 pages, ~2600 references.