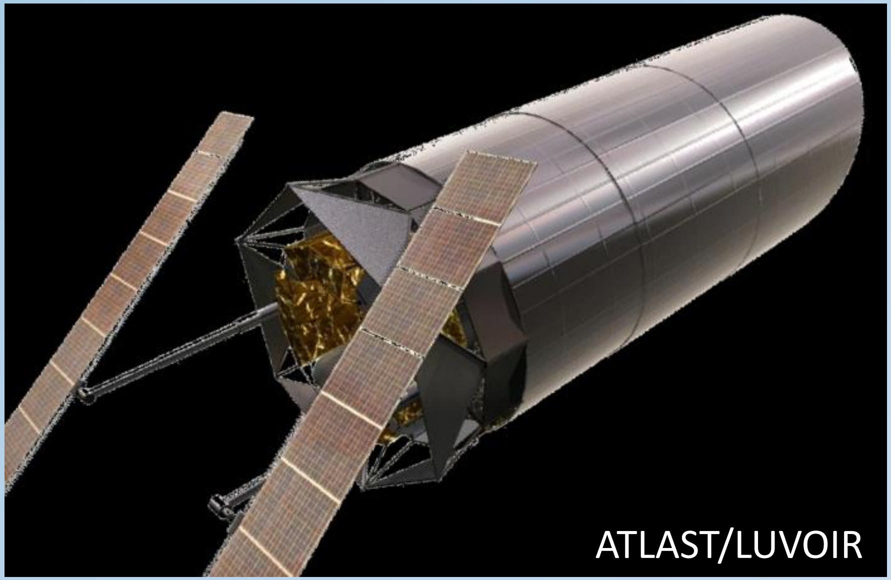
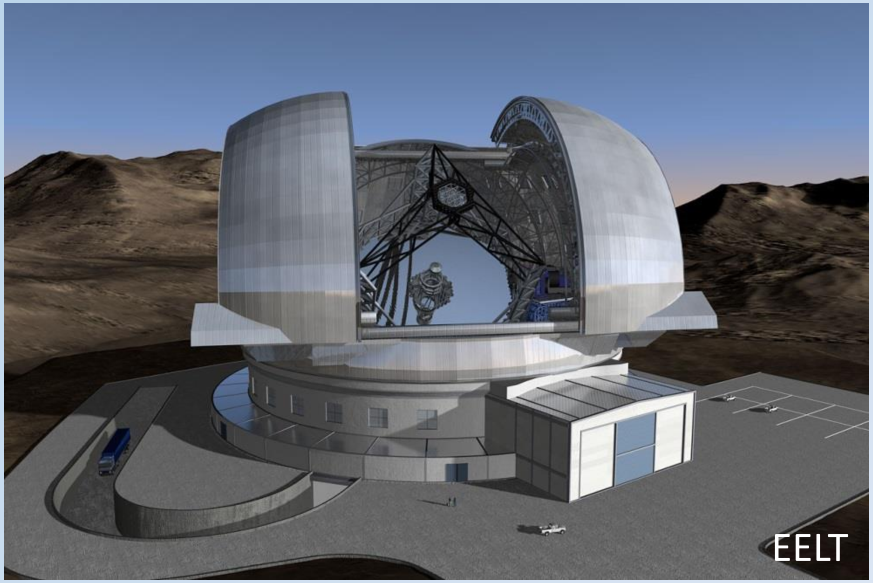
On detecting biospheres from thermodynamic disequilibrium in planetary atmospheres

Joshua Krissansen-Totton, David Bergsman and David Catling
Department of Earth and Space Sciences / Astrobiology Program
University of Washington, Seattle

Basic question:

How do we detect life on exoplanets from telescope observations?



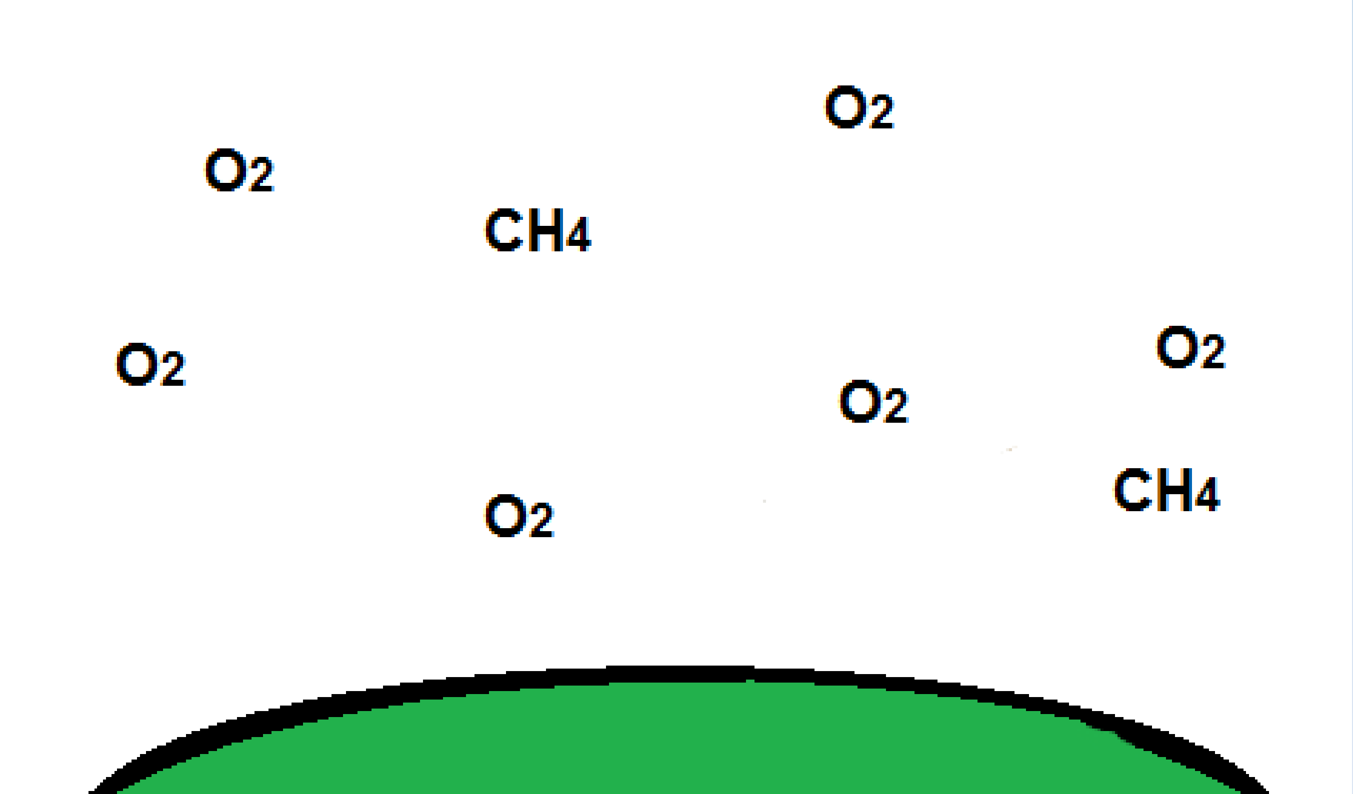


Chemical disequilibrium as a sign of life?

James Lovelock (1965), Joshua Lederberg (1965) *Nature*

- "*Kinetic instability in the context of local chemical and physical conditions…*" *Lederberg*

- "*Search for…compounds in the planet's atmosphere that are incompatible on a long-term basis*" *Lovelock*



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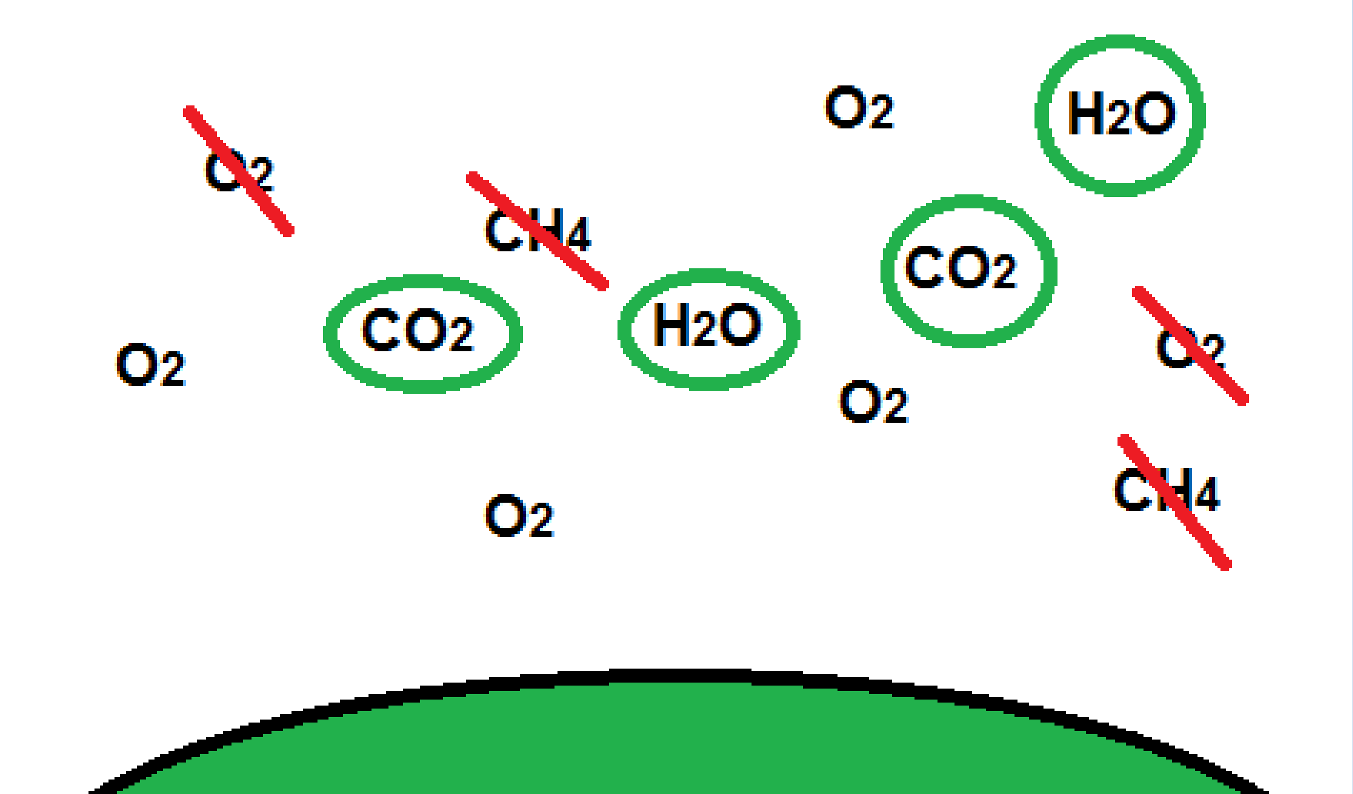

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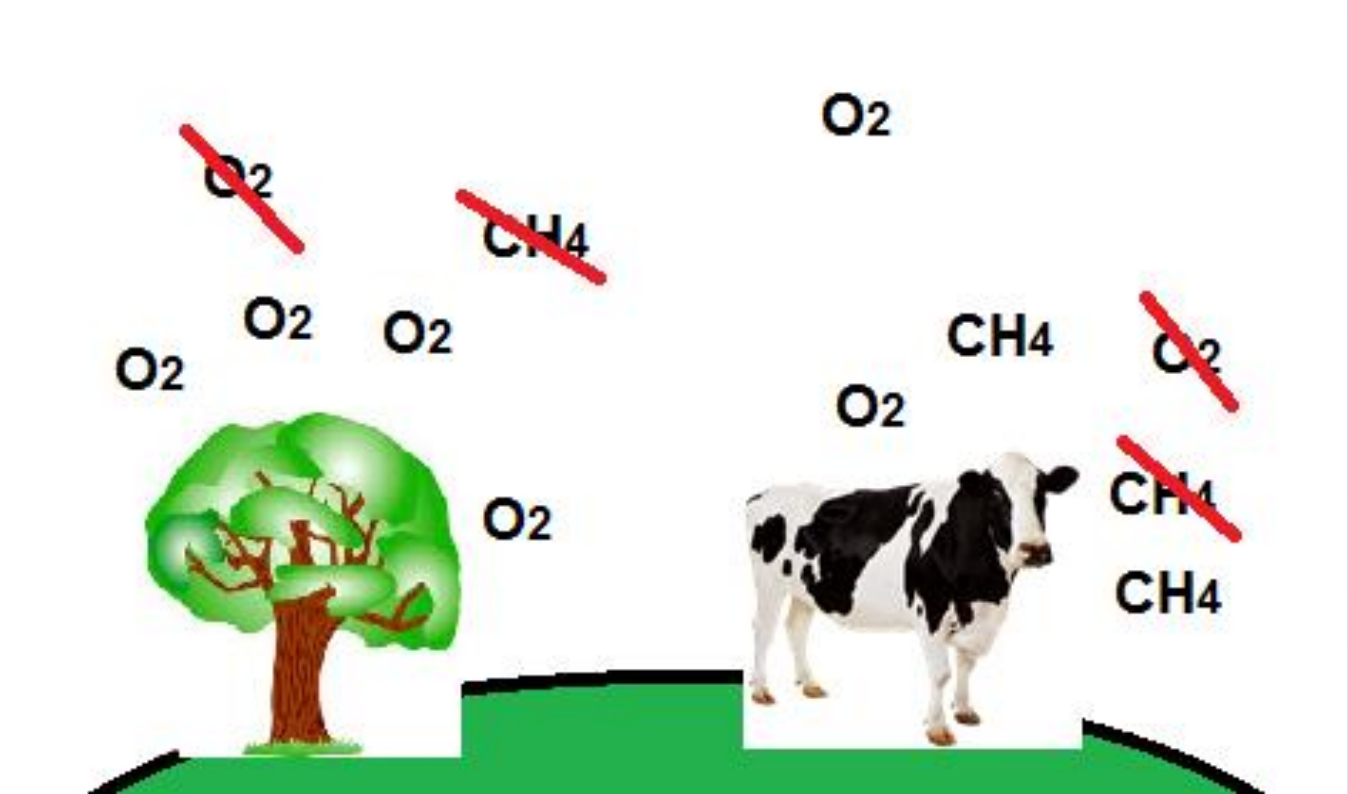

Atmospheric disequilibrium as a biosignature on exoplanets?

DETECTING LIFE-BEARING EXTRASOLAR PLANETS WITH SPACE TELESCOPES

STEVEN V. W. BECKWITH[1,2,3]
University of California, 1111 Franklin Street, Oakland, CA 94607-5200; steven.beckwith@ucop.edu
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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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© Mary Ann Liebert, Inc.

DAVID J. DES MARAIS,[1] MARTIN O. HARWIT,[2] KENNETH W. JUCKS,[3] JAMES F. KASTING,[4] DOUGLAS N.C. LIN,[5] JONATHAN I. LUNINE,[6] JEAN SCHNEIDER,[7] SARA SEAGER,[8] WESLEY A. TRAUB,[3] and NEVILLE J. WOOLF[6]

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

E. Simoncini[1,2], N. Virgo[1], and A. Kleidon[1]
[1]Max-Planck-Institute for Biogeochemistry, Hans-Knöll-Str. 10, 07745 Jena, Germany
[2]INAF, Astrophysical Observatory of Arcetri, 50124, Arcetri, Firenze, Italy

Correspondence to: E. Simoncini (simoncin@arcetri.astro.it)

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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

PNAS

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

Hanno Rein[a,1], Yuka Fujii[b], and David S. Spiegel[c]

[a]Department of Environmental and Physical Sciences, University of Toronto, Toronto, ON, Canada M1C 1A4; [b]Earth-Life Science Institute, Tokyo Institute of Technology, Ookayama, Meguro, Tokyo 152-8550, Japan; and [c]Astrophysics Department, Institute for Advanced Study, Princeton, NJ 08540

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

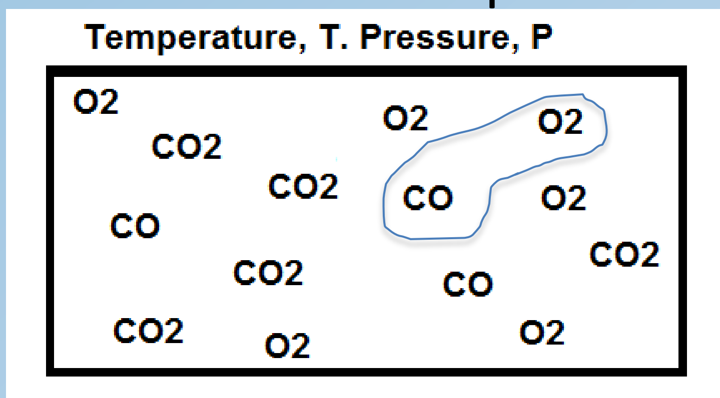
I. A. G. SNELLEN[1], R. J. DE KOK[2], R. LE POOLE[1], M. BROGI[1], AND J. BIRKBY[1]
[1] Leiden Observatory, Leiden University, Postbus 9513, 2300-RA Leiden, The Netherlands
[2] SRON, Sorbonnelaan 2, 3584-CA Utrecht, The Netherlands
Received 2012 October 8; accepted 2013 January 8; published 2013 February 5

ABSTRACT

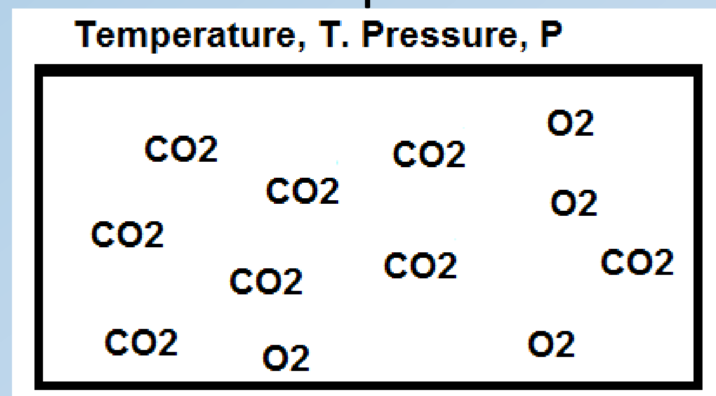
Exoplanet observations promise one day to unveil the presence of extraterrestrial life. Atmospheric compounds in strong chemical disequilibrium would point to large-scale biological activity just as oxygen and methane do in the Earth's atmosphere. The cancellation of both the *Terrestrial Planet Finder*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

Quantifying chemical disequilibrium

Observed atmosphere



Atmosphere if it were in chemical equilibrium



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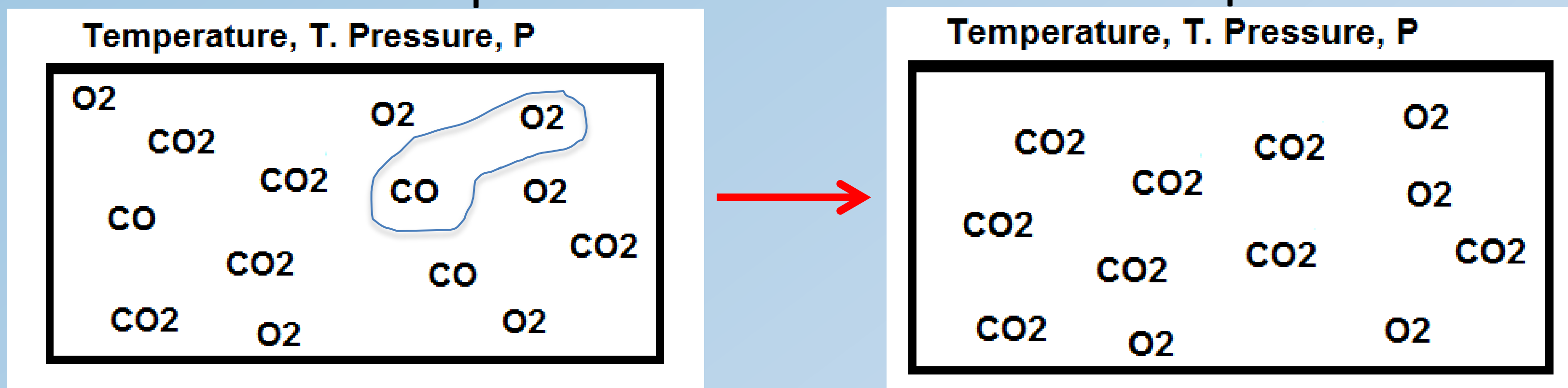


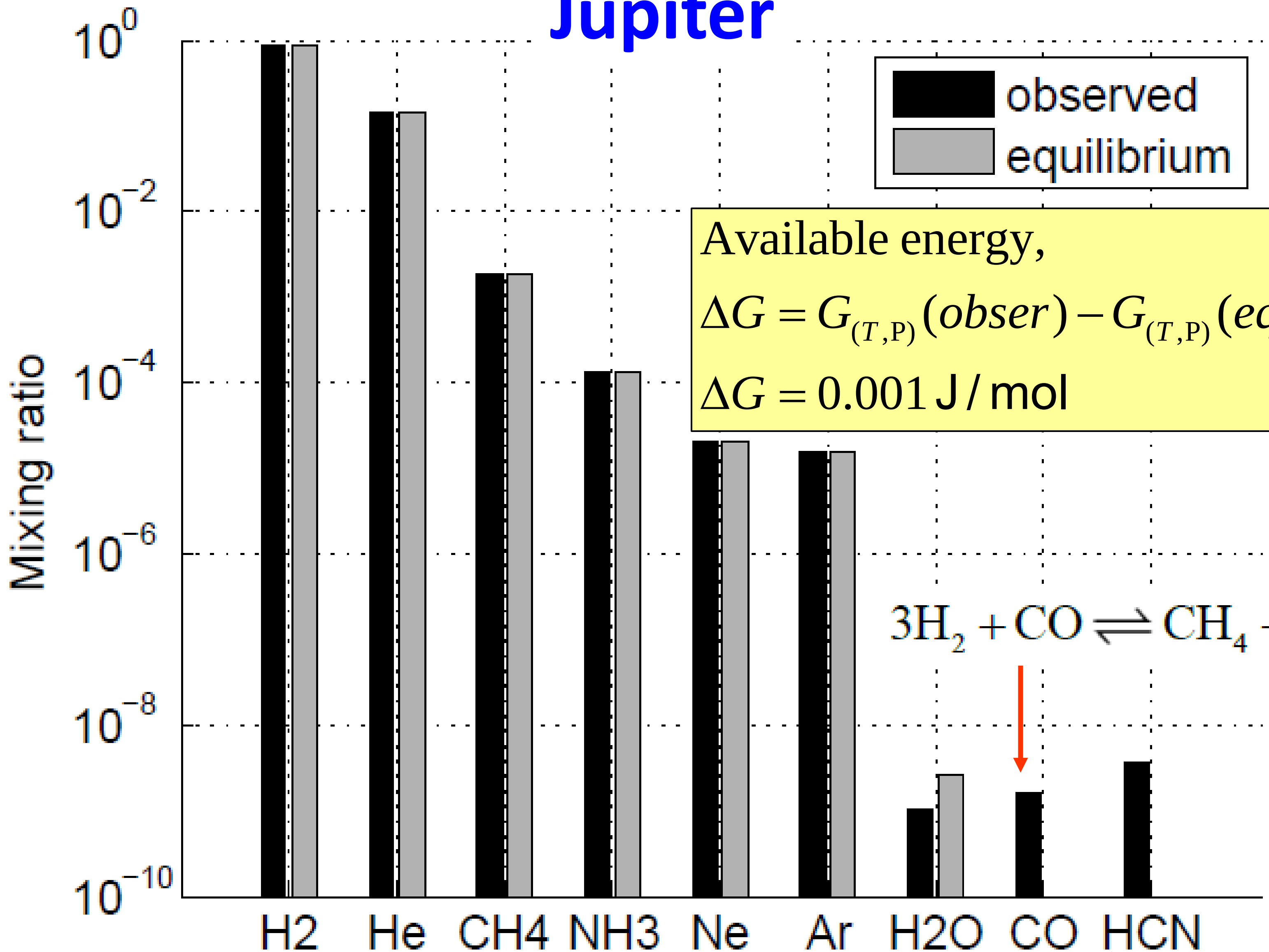
$$G_{(T,\mathrm{P})} = \sum_i n_i \left(G^{\circ}_{i\,(T,\mathrm{P}_r)} + RT \ln\left(\frac{P\gamma_i n_i}{n_{tot}}\right)\right)$$

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

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

Applied to Solar System atmospheres….

Jupiter



Available energy,

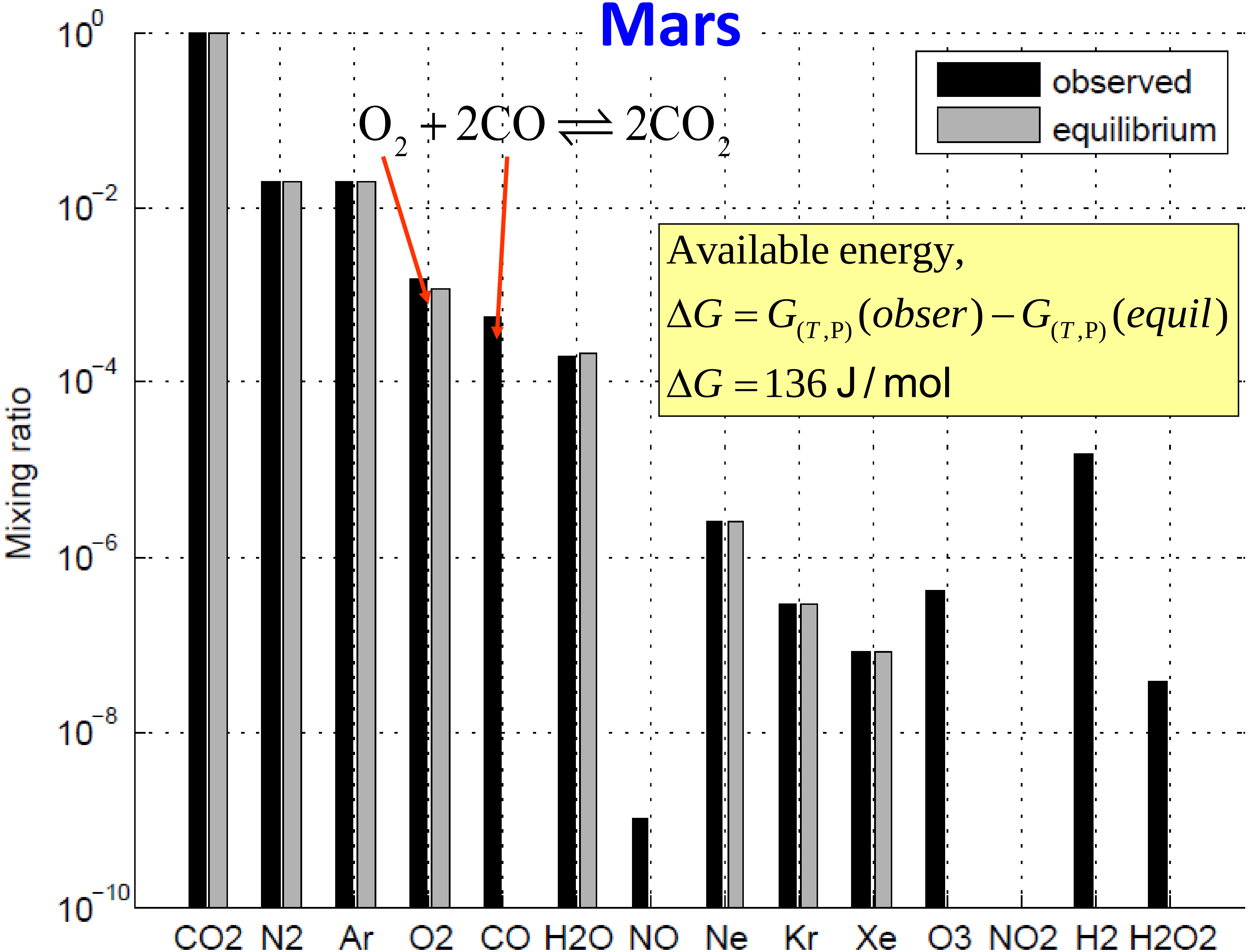
$$\Delta G = G_{(T,P)}(obser) - G_{(T,P)}(equil)$$

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

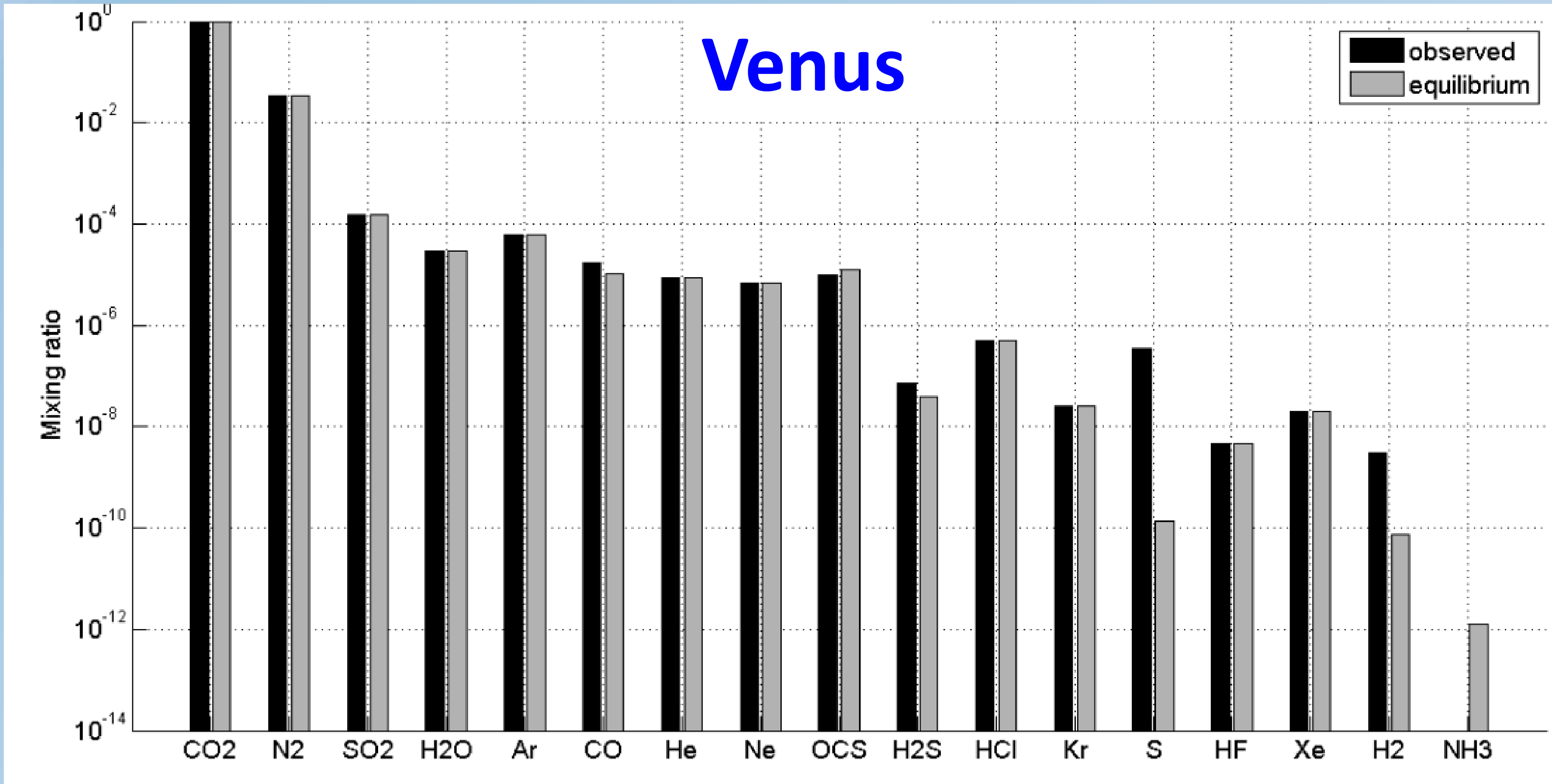
$$3H_2 + CO \rightleftharpoons CH_4 + H_2O$$

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

Mars



Mixing ratio
10^0
10^-2
10^-4
10^-6
10^-8
10^-10
CO2 N2 Ar O2 CO H2O NO Ne Kr Xe O3 NO2 H2 H2O2
observed
equilibrium
$O_2 + 2CO \rightleftharpoons 2CO_2$
Available energy,
$\Delta G = G_{(T,P)}(obser) - G_{(T,P)}(equil)$
$\Delta G = 136$ J / mol



Available energy,

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

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

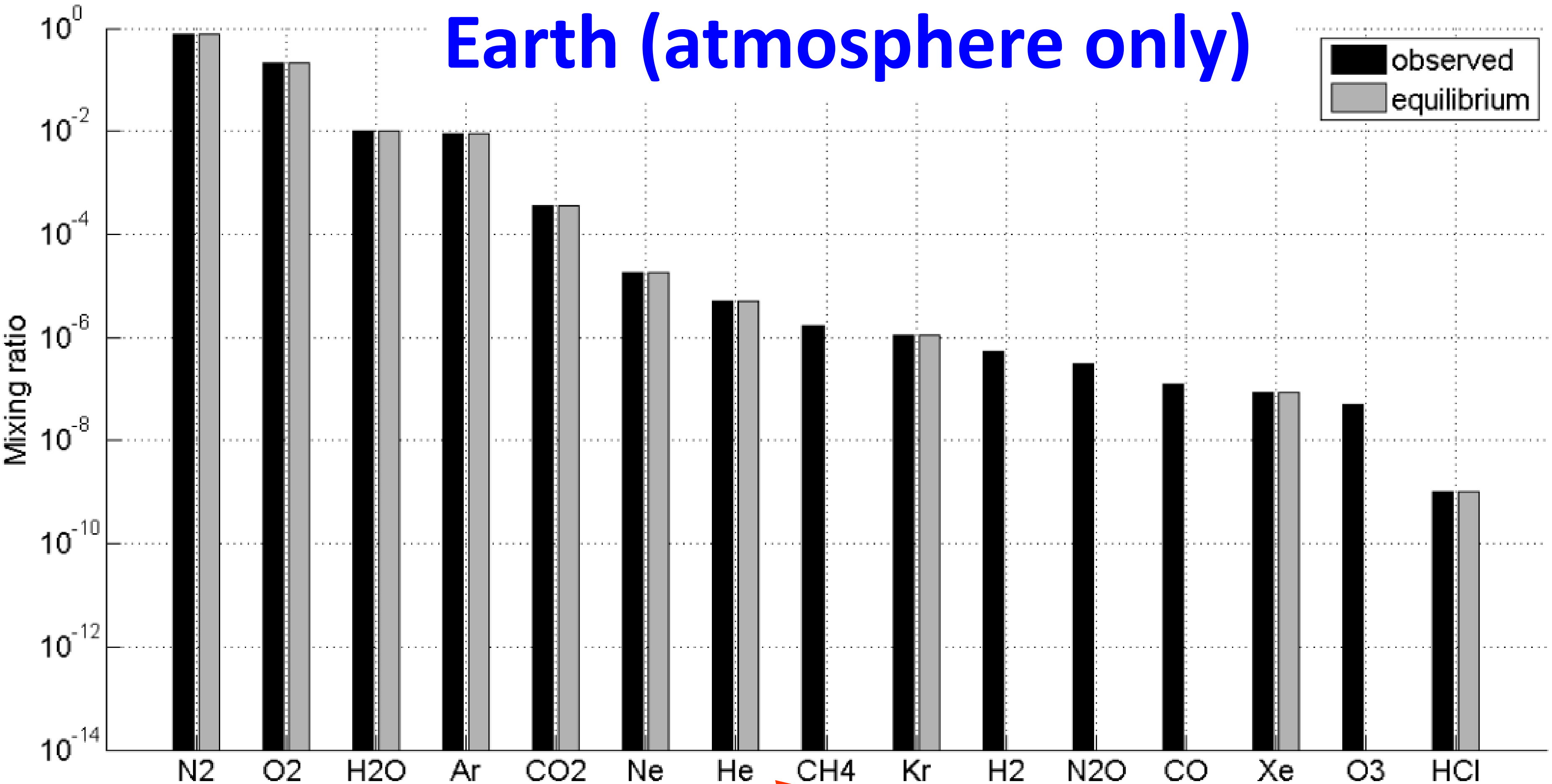
$$H_2S + CO_2 \rightleftharpoons H_2O + OCS$$

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

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

$$H_2 + S \rightleftharpoons H_2S$$

Earth (atmosphere only)



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

Available energy,

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

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


Typical surface of Mars

Typical surface of planet Earth

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

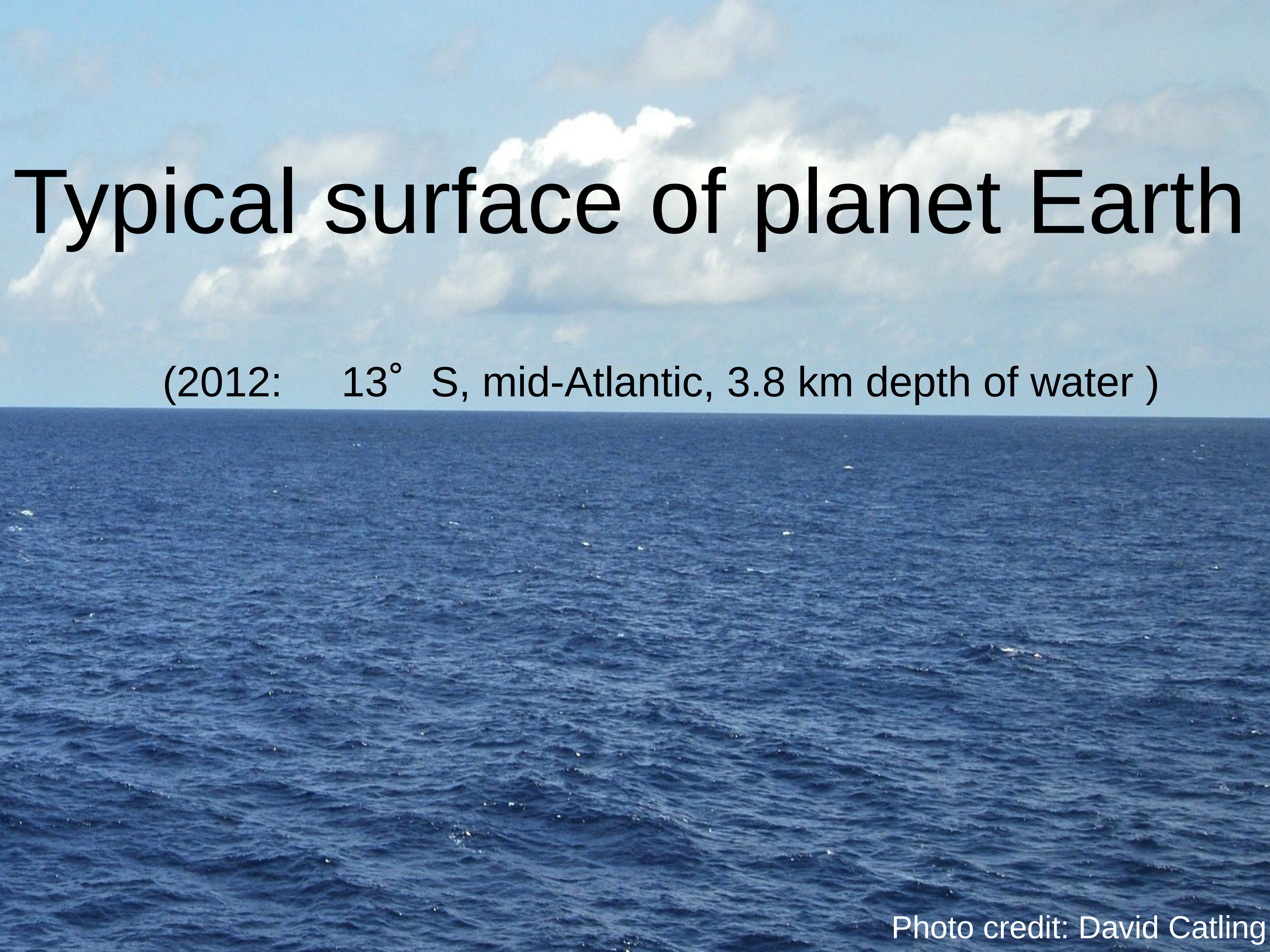
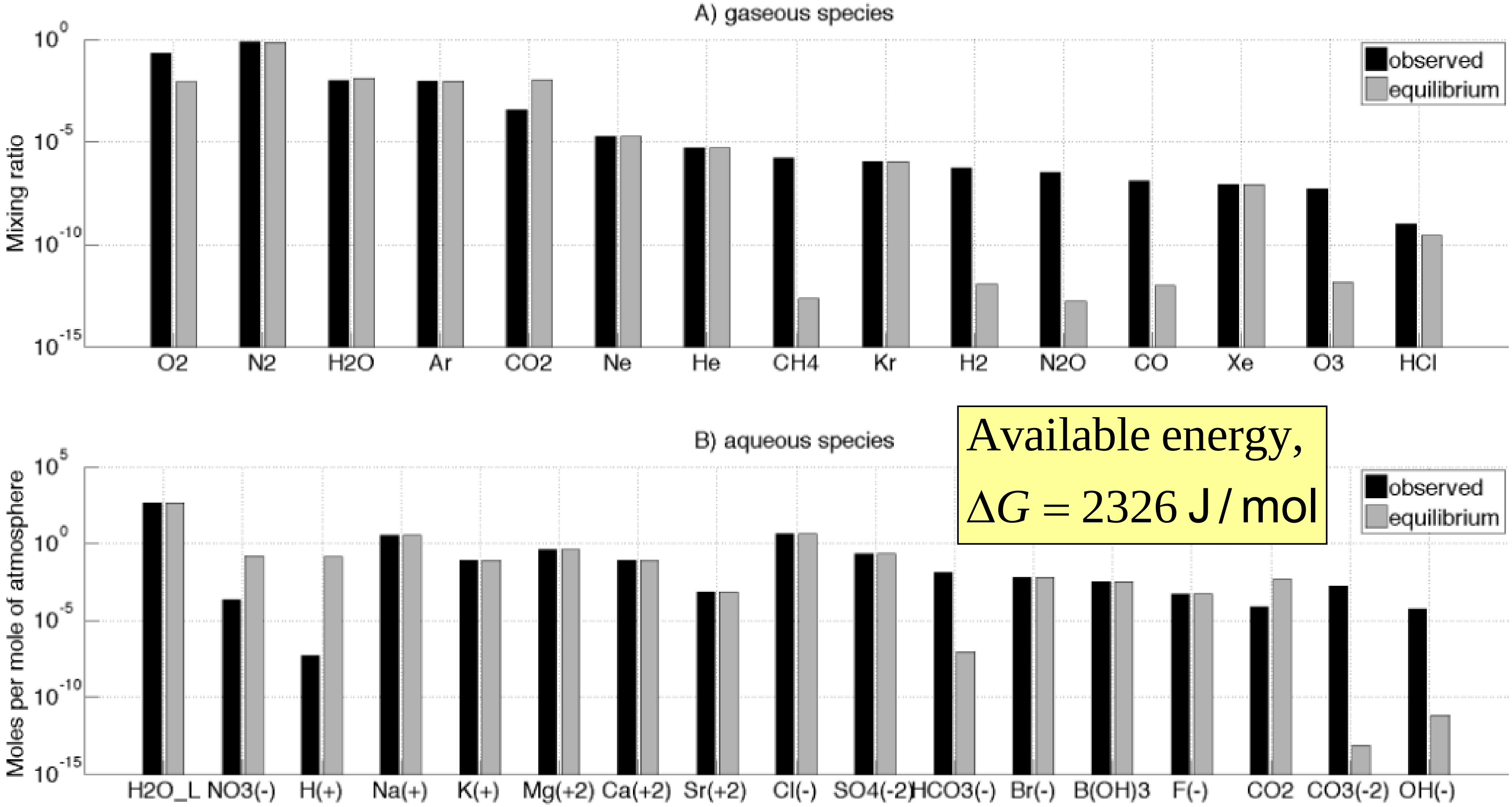


Photo credit: David Catling

Earth (atmosphere-ocean fluid envelope)



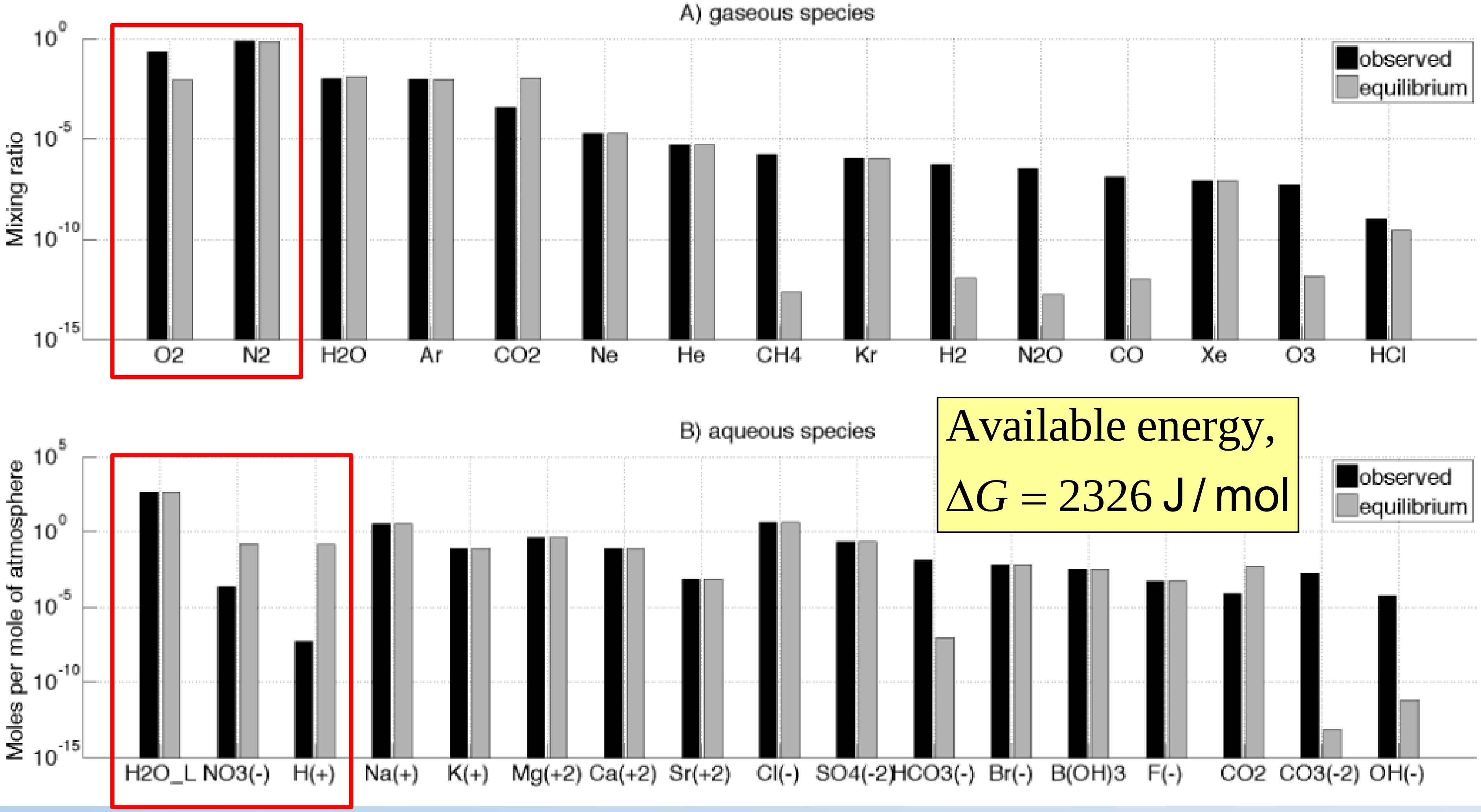
Available energy,

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

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

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 (atmosphere-ocean fluid envelope)



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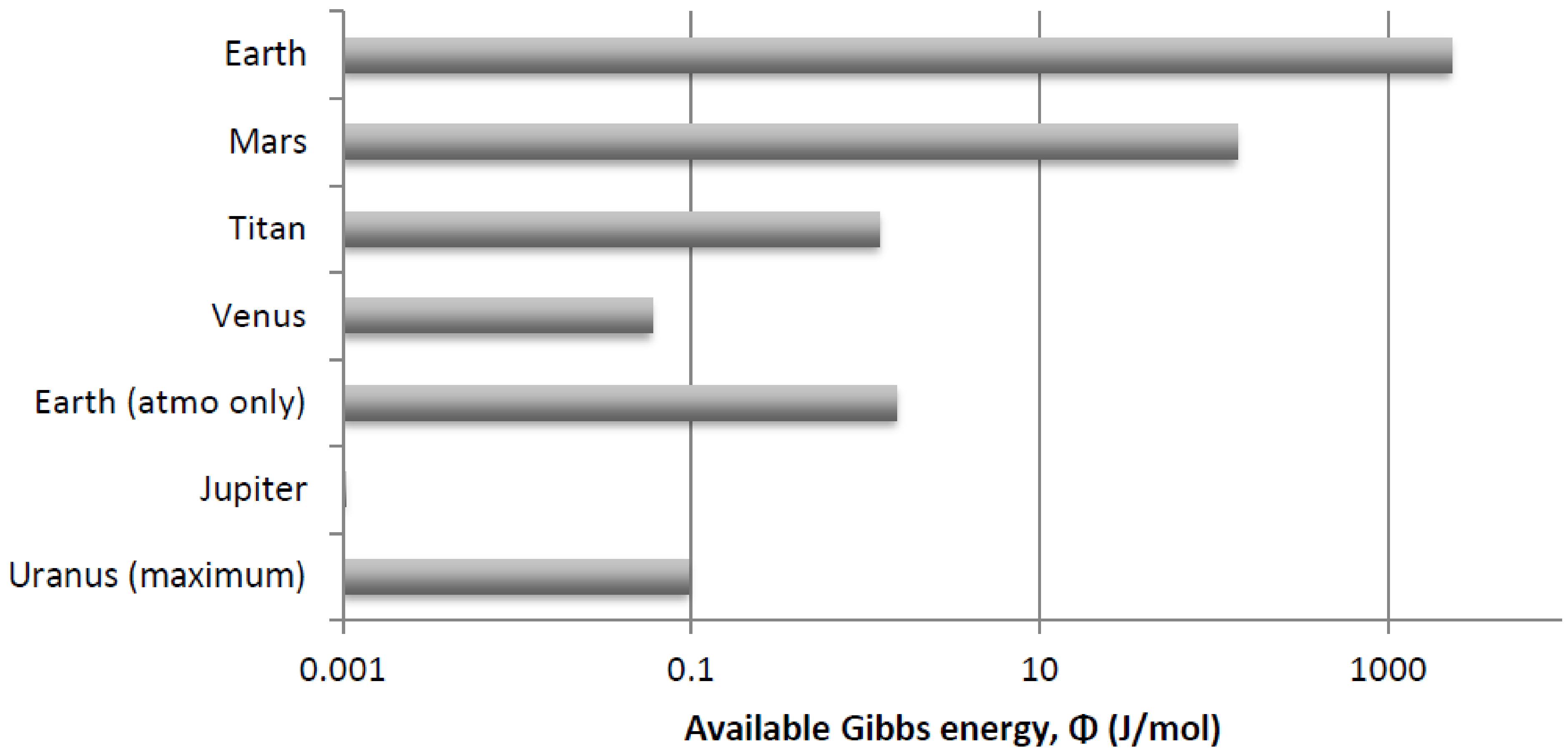
Earth has largest disequilibrium in the solar system



Contrast with kinetic disequilibrium

- *Simoncini* et al. 2013 calculate the minimum power required to maintain the biogenic oxygen-methane disequilibrium in Earth’s atmosphere = **0.67 TW.** *This is a flux metric (kinetic disequilibrium).*

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- We find the disequilibrium in Earth's atmosphere is 1.5 J/mol, and of this 1.3 J/mol is attributable to oxygen and methane (2.34×10^{20} J). *This is a reservoir metric (thermodynamic disequilibrium)*.

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- Comparison: If we assume a 10 year lifetime of methane in the atmosphere then we find the "power" is **0.74 TW**. **The two approaches are consistent!**

Is this practical for exoplanets?

- For exoplanets, **thermodynamic disequilibrium** could be computed directly from observations without any assumptions about gas fluxes.

- Bulk abundance, oceans, and total pressure are observational challenges, but have been considered by the Virtual Planetary Lab:
  - N_2 from N_2-N_2 dimer absorption, 4.3 µm (Schwieterman et al., 2015).
  - Ocean presence from glint + spectra (e.g., Robinson et al., 2010; 2014).
  - Pressure from O_2-O_2 dimer, 1.06 & 1.27 µm (Misra et al., 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

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	10 bar	3891.96
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Salinity	0 mol/kg	2290.01
	1.1 mol/kg	2325.76
	11.1 mol/kg	2276.40

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Temperature	T= 273.15 K	1634.78
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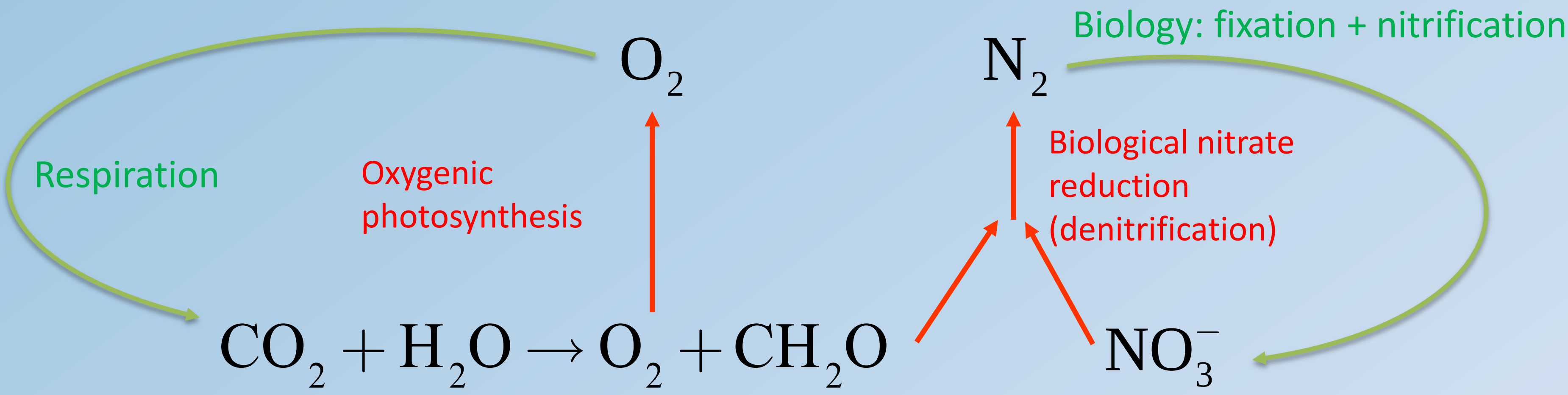
	12	2325.65
Salinity	0 mol/kg	2290.01
	1.1 mol/kg	2325.76
	11.1 mol/kg	2276.40
Ocean volume	0.1 Earth ocean	413.62
	0.5 Earth ocean	1442.95
	1 Earth ocean	2325.76
	2 Earth oceans	4188.27
	10 Earth oceans	8956.34
	50 Earth oceans	12626.22

See extra slides

What does disequilibrium mean?

- Sometimes thermodynamic disequilibrium means life.



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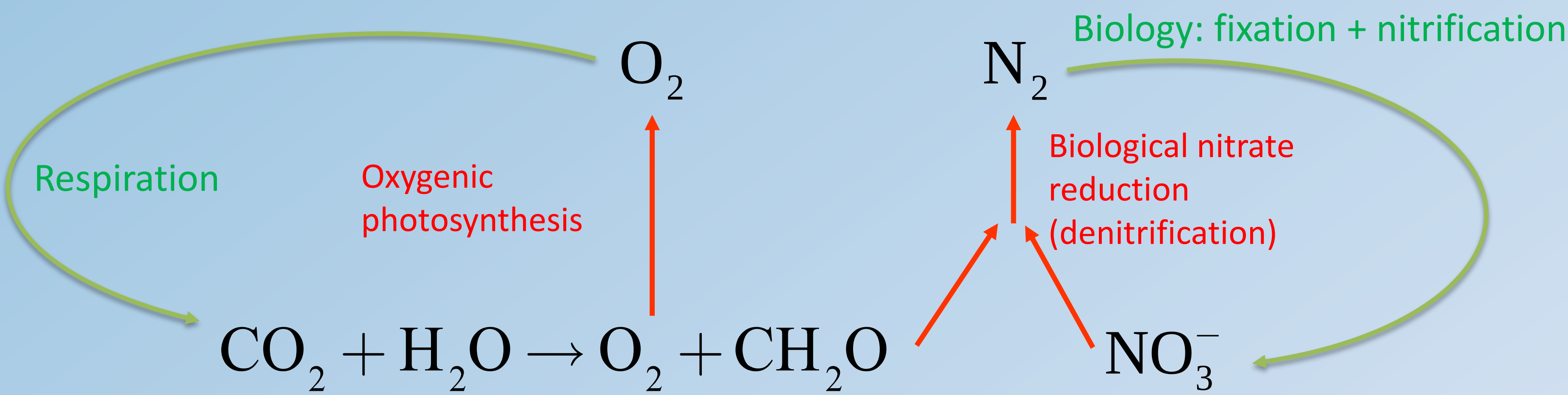
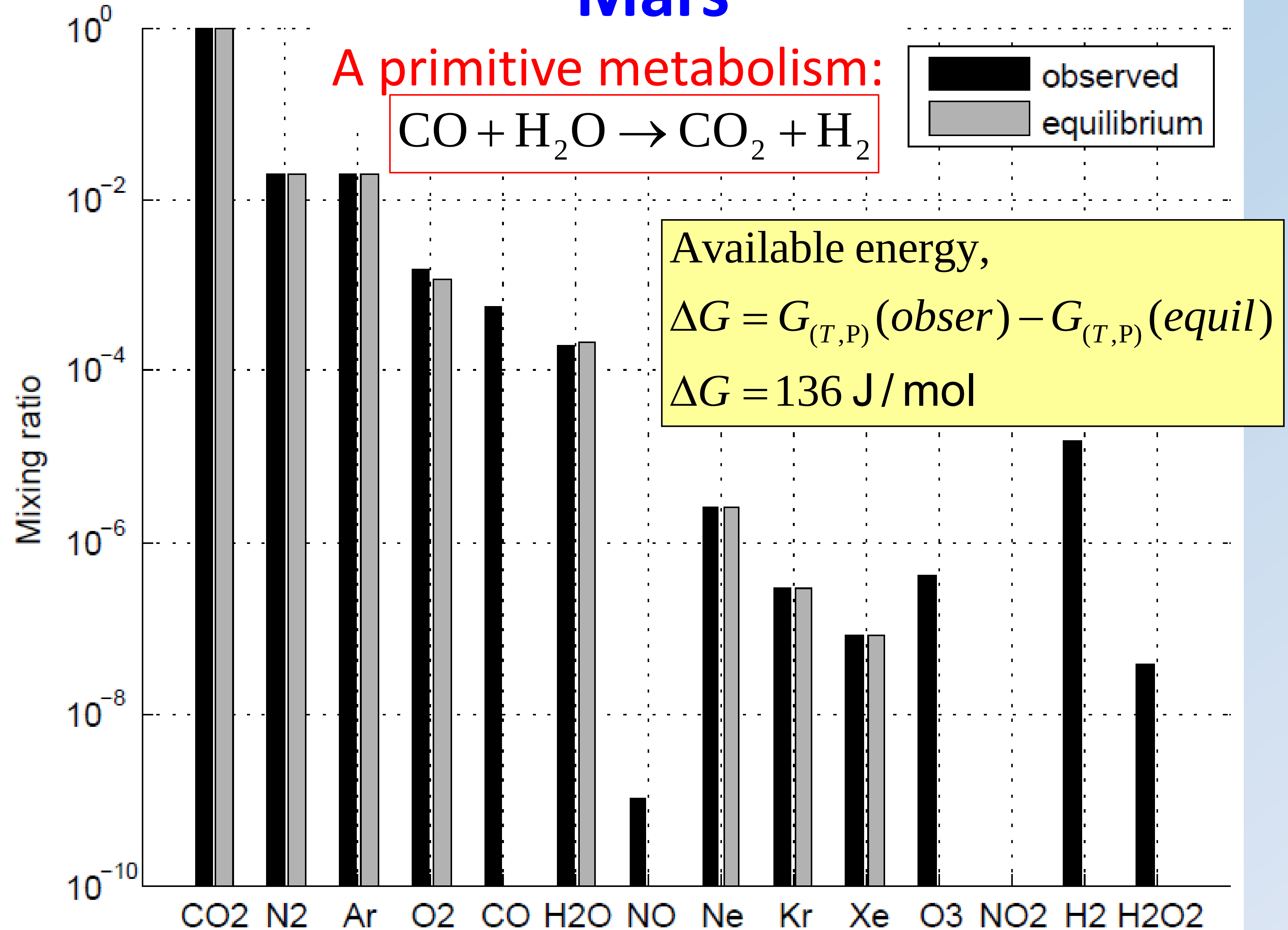


- Sometimes thermodynamic disequilibrium means the absence of life (**antibiosignature**). Large available energy = an “uneaten free lunch” -> no life exists.

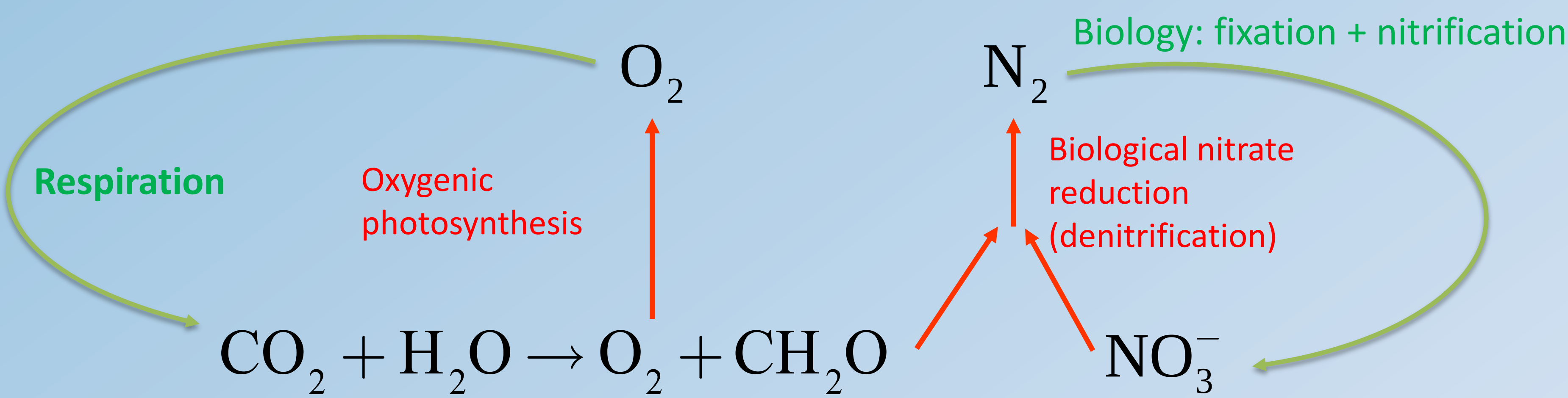
Mars



Overabundant CO suggests no life today on the surface of Mars. (Weiss et al. 2000; Zahnle et al. 2011)

What does disequilibrium mean?

- Sometimes thermodynamic disequilibrium means life.



- Sometimes thermodynamic disequilibrium means the absence of life (**antibiosignature**). 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**.

Conclusions

- Earth has the largest thermodynamic 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 any assumptions about gas fluxes.

Thanks!

Acknowledgements

- Johnathan D. Toner
- Kathryn Cogert
- Chris Glein

On detecting biospheres from thermodynamic disequilibrium in planetary atmospheres

Joshua Krissansen-Totton, David Bergsman, David Catling, in press, *Astrobiology* 15(12) http://arxiv.org/abs/1503.08249

Code and associated databases will be made public upon publication

Extra slides

Methods

Gas phase:

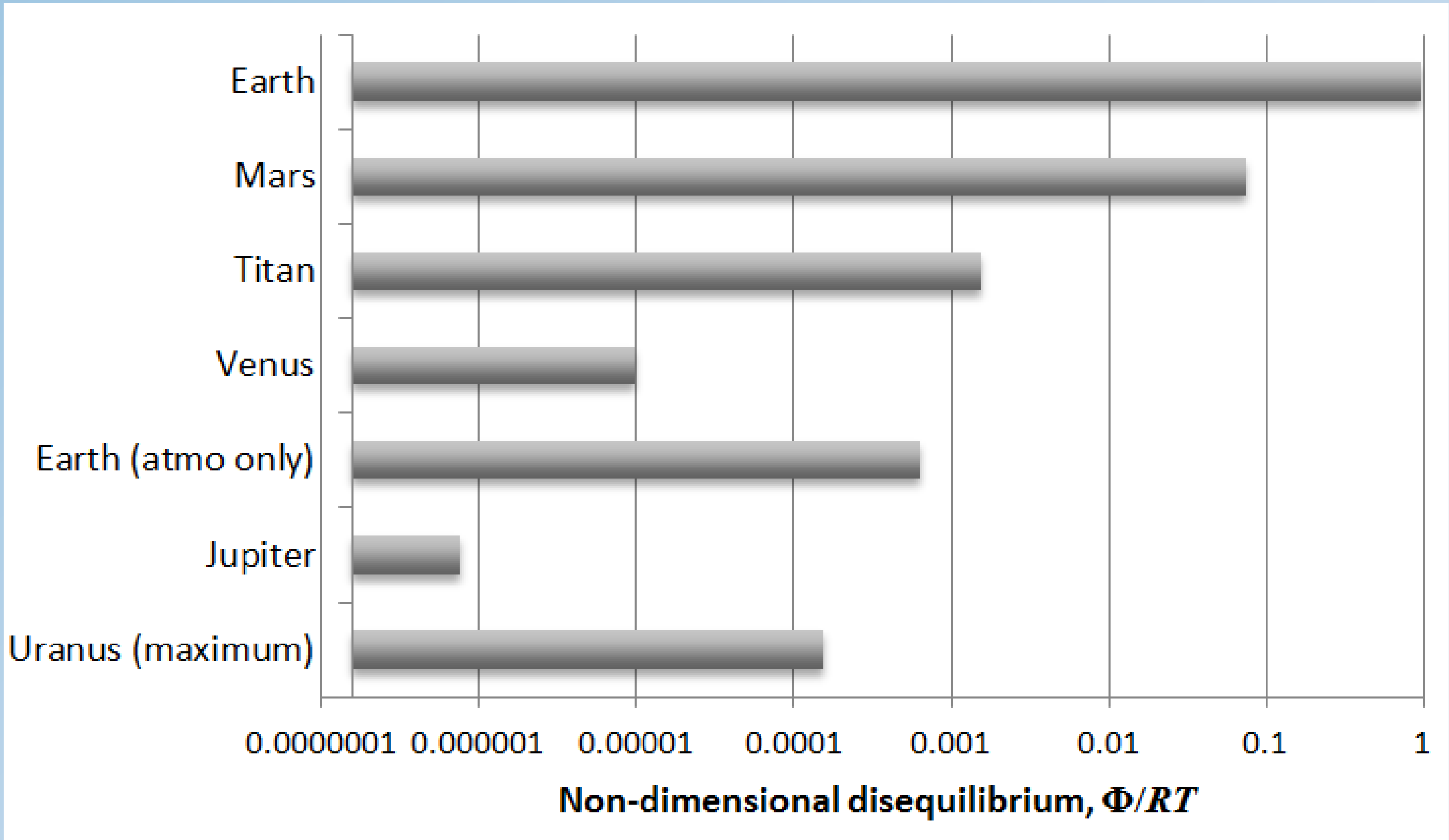
$$G_{(T,P)} = \sum_i n_i \left(G^{\circ}_{i\,(T,P_r)} + RT\ln\left(\frac{P\gamma_i n_i}{n_{tot}}\right)\right)$$

Aqueous:

$$\Delta G_{(T,P)} = \sum_i c_i n_i + \sum_\alpha \sum_{i\in\alpha} n_i RT\ln(n_i / n_\alpha) - \sum_{j=aqueous\ species} n_j RT\ln(n_w / n_{aq})$$

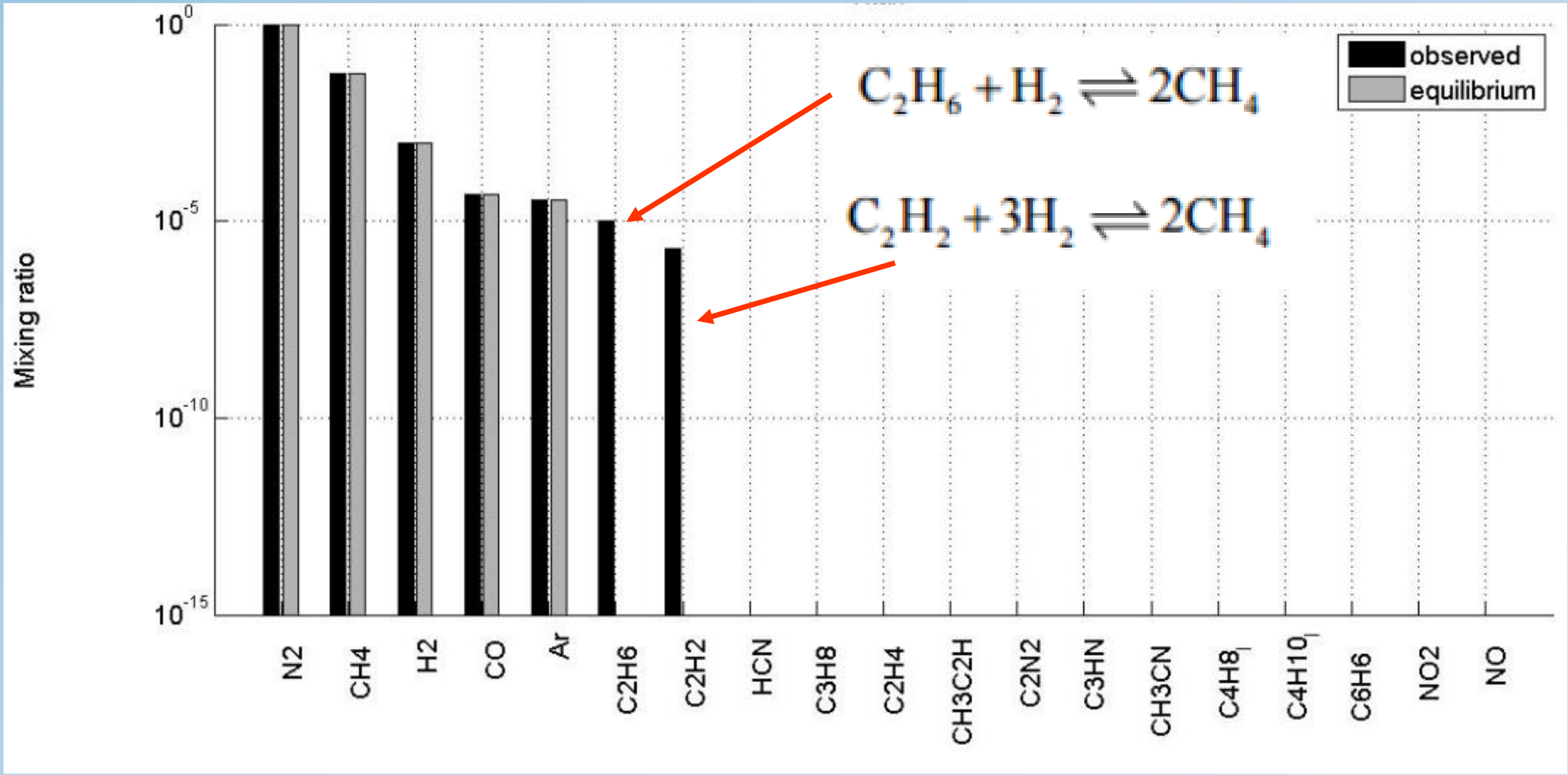
$$c_i = \begin{cases} \Delta_f G^{\circ}_{i\,(T,P)} + RT\ln(\gamma_{fi}) + RT\ln(P), & i \in gas \\ \Delta_f G^{\circ}_{i\,(T,P)} + RT\ln(\gamma_{aw}), & i \in water \\ \Delta_f G^{\circ}_{i\,(T,P)} + RT\ln(\gamma_{ai}) + RT\ln(55.5084), & i \in aqueous \end{cases}$$

Earth has largest disequilibrium in the solar system



Only on Earth is available energy ≈ thermal energy of air

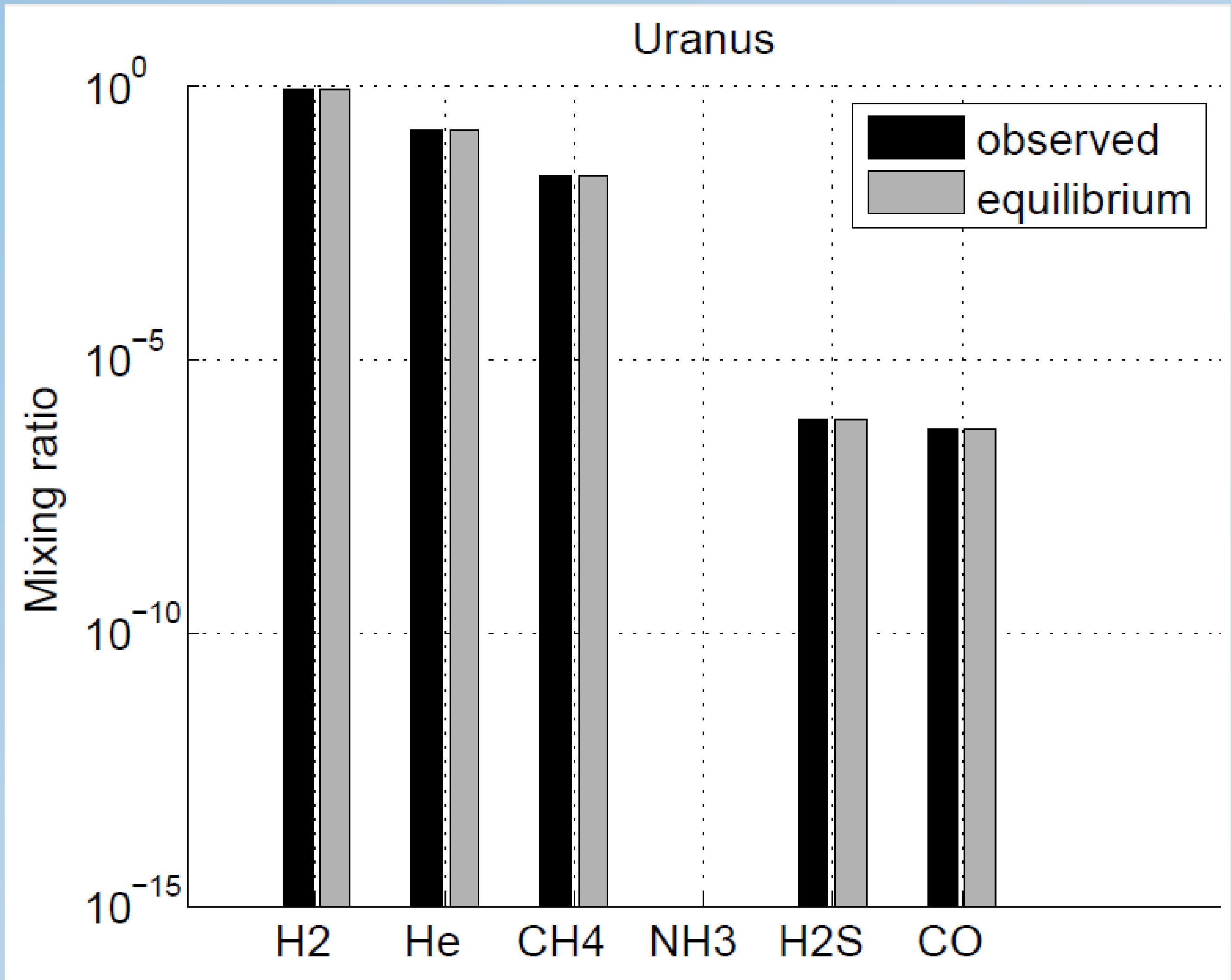
Titan



Available energy,

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

$$\Delta G = 1.2\ \mathrm{J/mol}$$



Available energy,

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

$$\Delta G = 0\ \mathrm{J/mol}$$

Can ocean volume be constrained remotely?

Ocean detection from **glint** (Robinson et al. 2010), **polarization** (Zugger et al. 2010).

Surface ocean fraction from **time resolved photometry** (Cowan *et al.* 2009; Cowan and Strait 2013; Fujii and Kawahara 2012).

Ocean volume from **thermal inertia** (Gaidos and Williams 2004).

Presence of continents provides a maximum ocean depth due to **limits of rock strength** (Cowan and Abbot 2014)

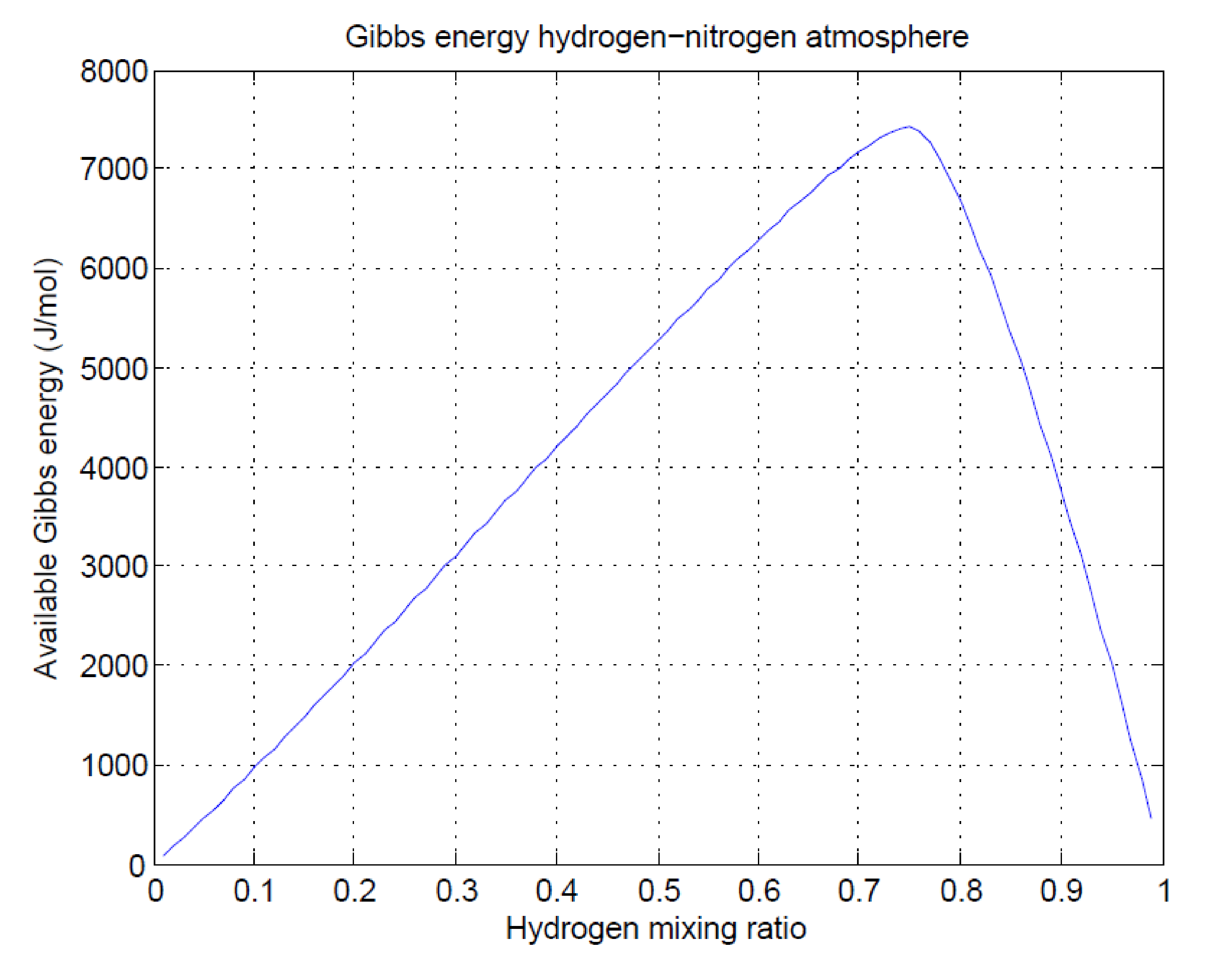
Dynamic topography could constrain **minimum ocean depth?**

For ~1000 km deep oceans, ocean volume possibly constrained by **mass-radius observations**.

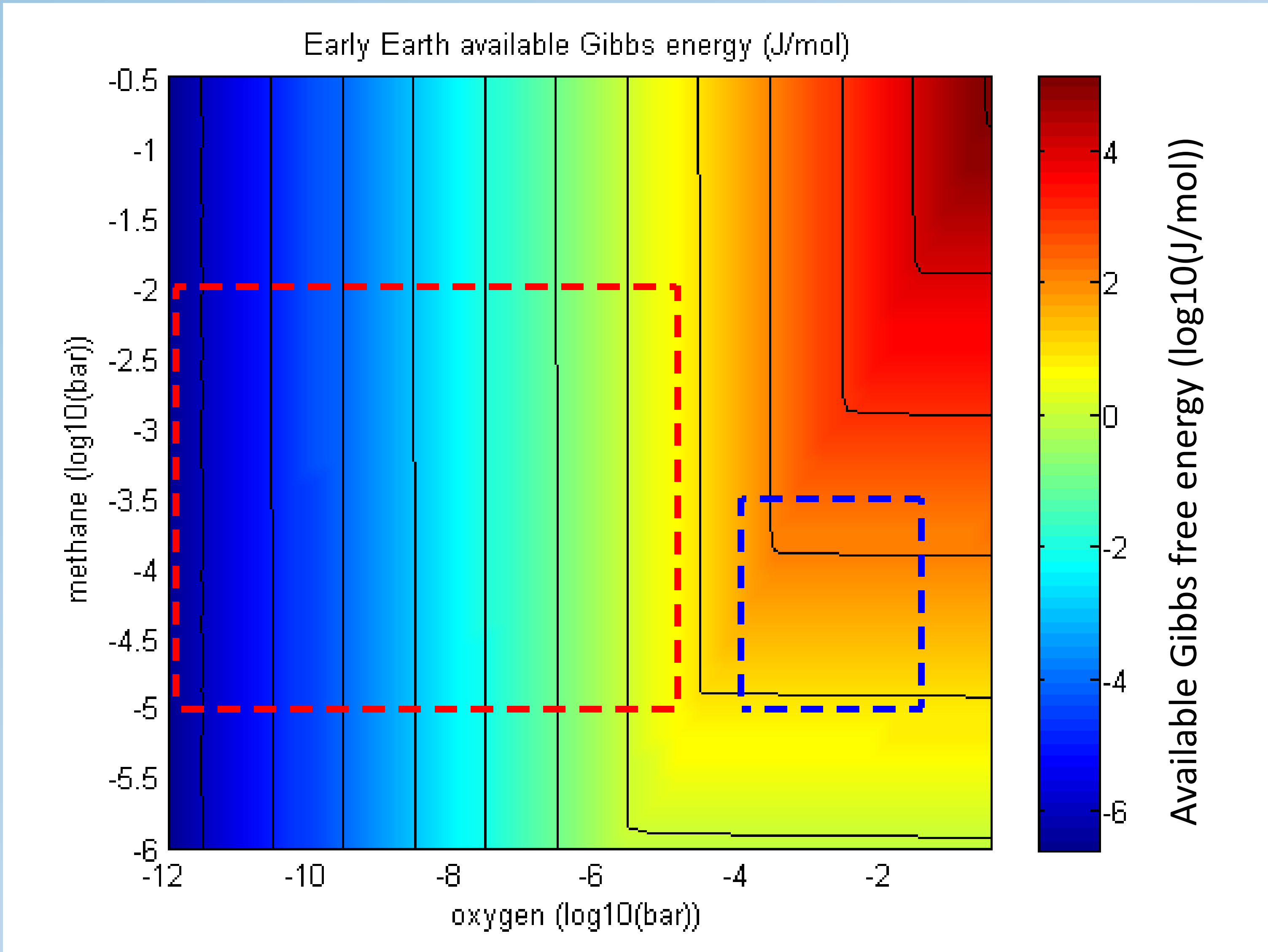
Validation

	Available Gibbs energy, Φ (J/mol of atmosphere)	Validation, Φ (J/mol of atmosphere)		Lovelock and Kaplan (1975), Φ (J/mol of atmosphere)
		Semi-analytic approximation	Aspen Plus	
Venus	0.059598	0.0565586	0.060099	5
Earth(atm)	1.51348	1.5072	1.52564	Not reported
Earth	2325.76	1723.65*	2348*	55000
Mars	136.3485	136.8070	136.3506	13
Jupiter	0.001032077	0.00103205	0.0010228	<1
Titan	1.2126495	1.212617	1.208787	Not reported
Uranus**	0.0971394	0.0983	0.09713801	Not reported

H2-N2 Super Earth

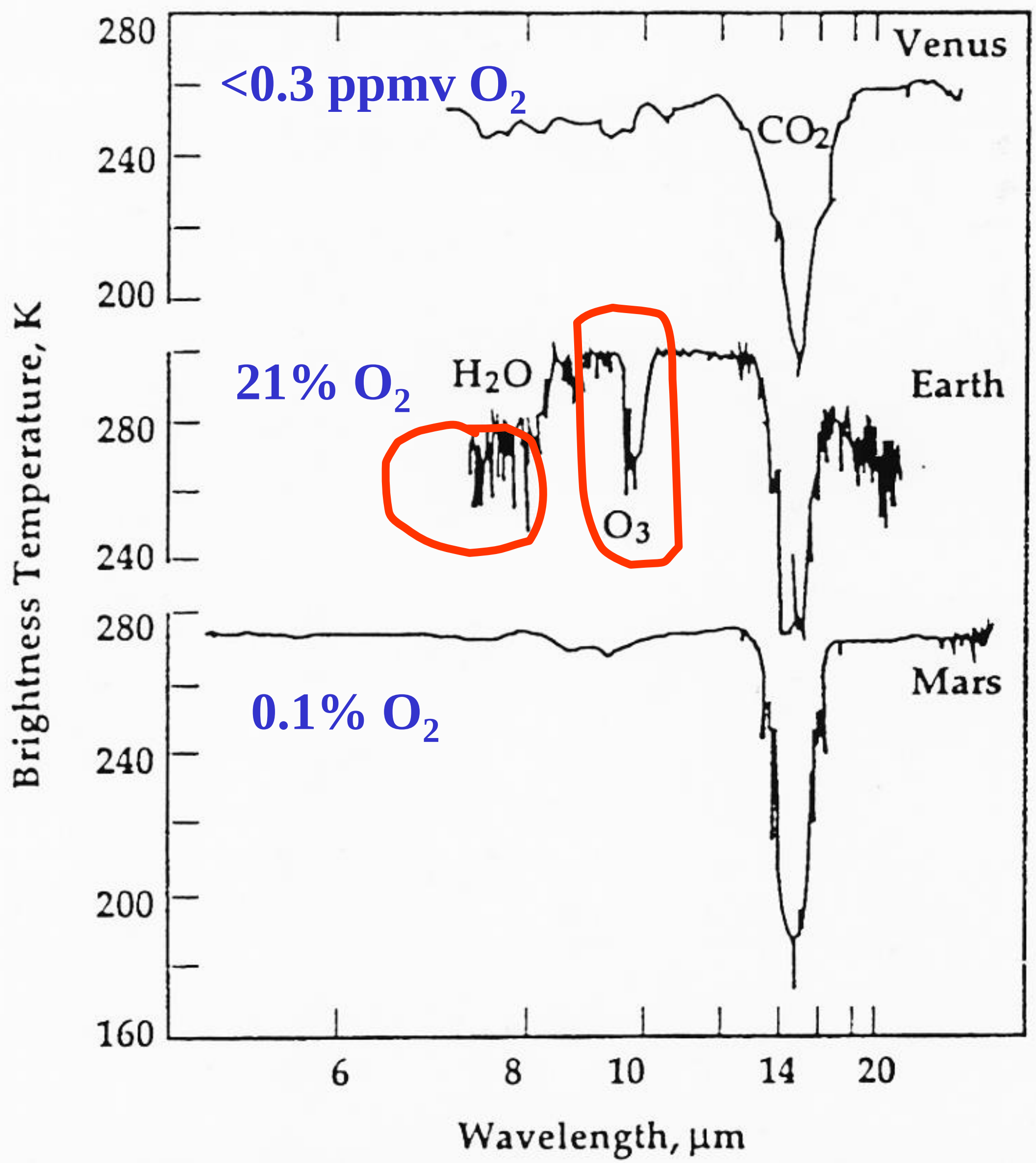


Early Earth



Early Earth available Gibbs energy (J/mol)
-0.5
-1
-1.5
-2
-2.5
-3
-3.5
-4
-4.5
-5
-5.5
-6
methane (log10(bar))
-12
-10
-8
-6
-4
-2
oxygen (log10(bar))
4
2
0
-2
-4
-6
Available Gibbs free energy (log10(J/mol))

Modern incarnation: Biogenic gases in spectra



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

Proposed telescopes to search Earth-like exoplanets for O_2 and perhaps 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