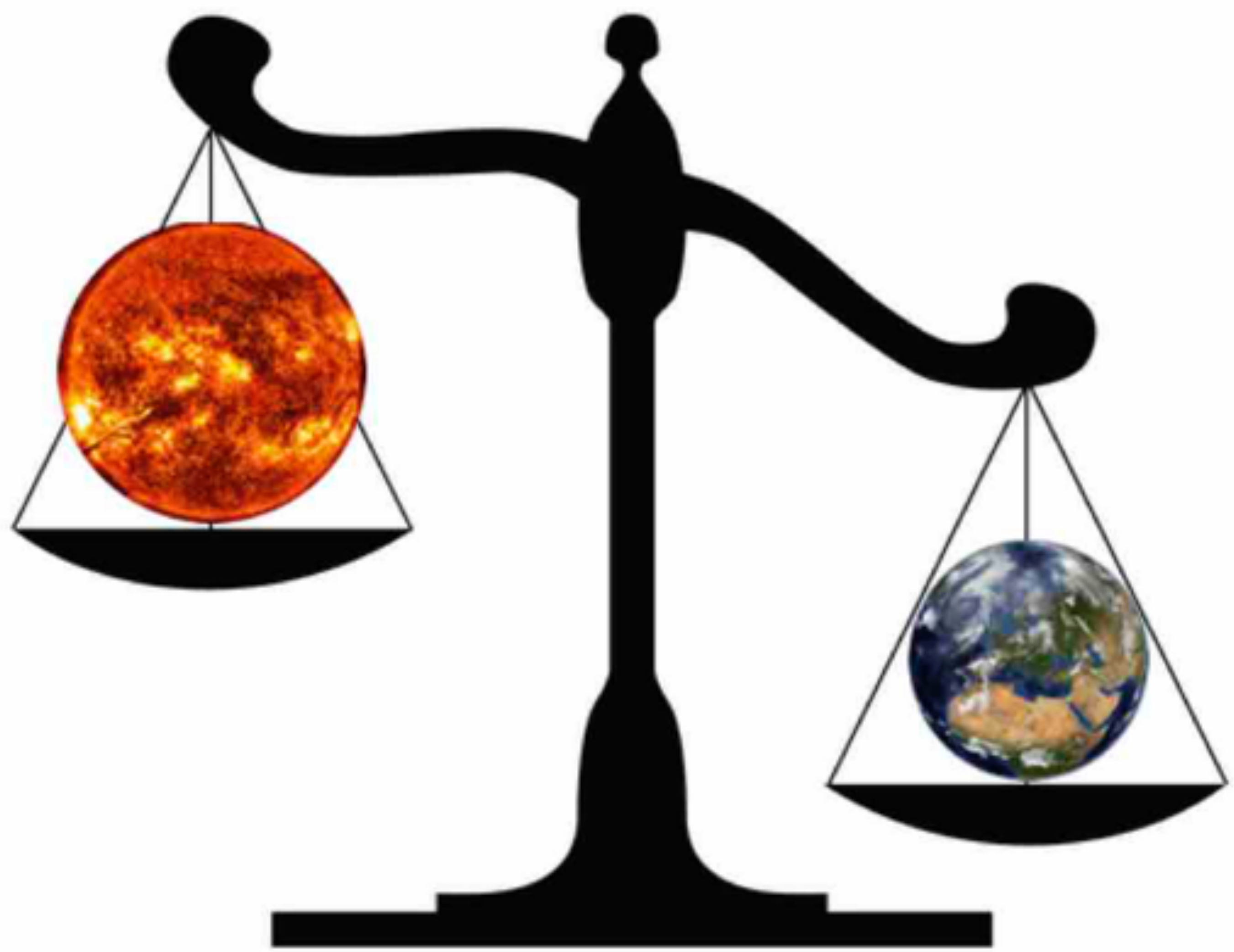
Exoplanetary Atmospheres and Habitability

Thermodynamics, Disequilibrium and Evolution focus group

12-16 October 2015
Observatoire Côte d'Azur, Nice, France



Disequilibrium in planetary atmospheres and the search for habitability

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NASA ASTROBIOLOGY INSTITUTE

Thermodynamics, Disequilibrium and Evolution (TDE) – *NAI Focus Group*

KROME better science through chemistry

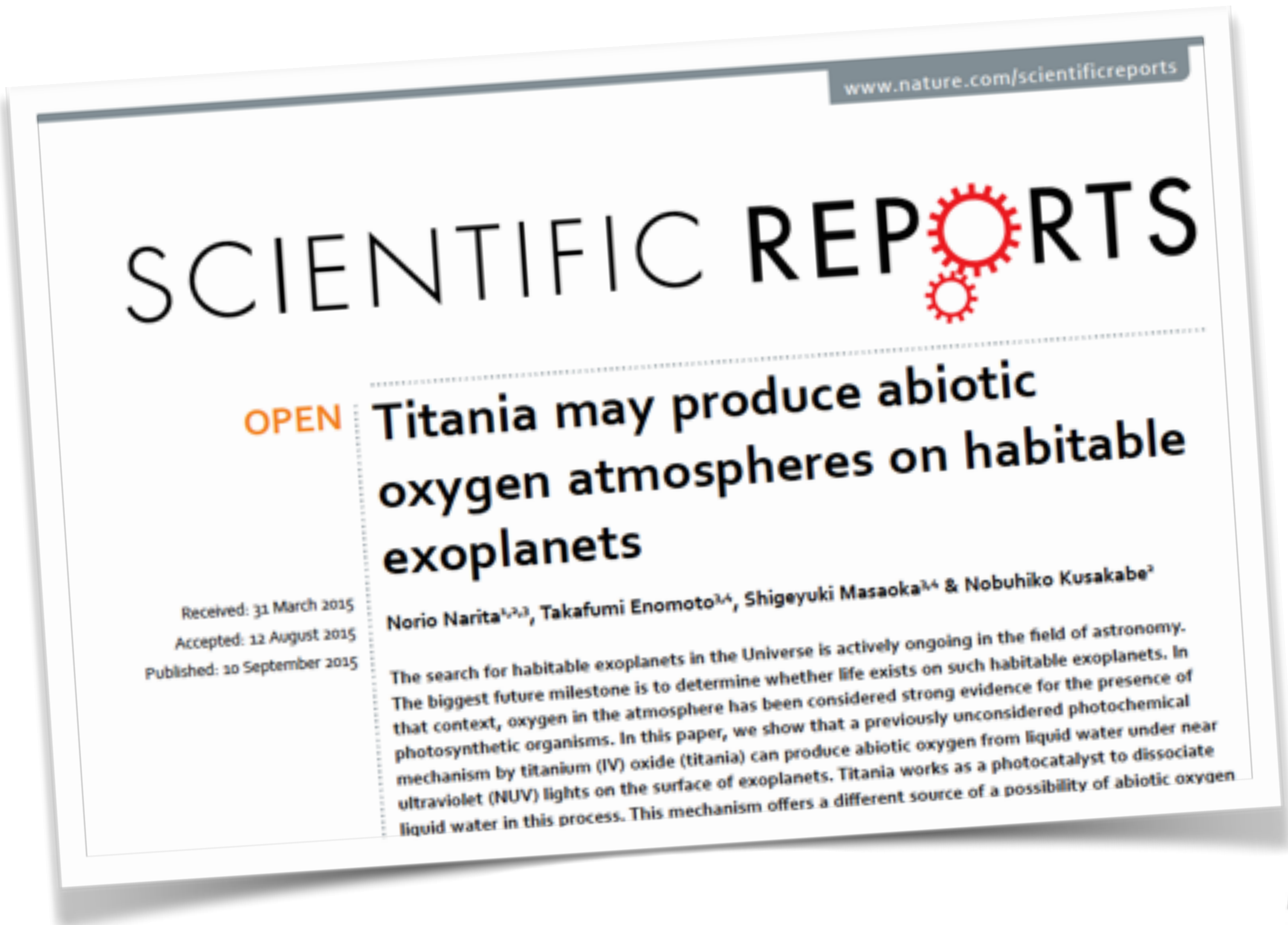
Overview of the talk

- Chemical disequilibrium and habitability
- Tools: correct calculation
- Applications:
  - Earth photochemistry (PC)
  - PC vs Photosynthesis (PS)
  - PC during geological history
  - Earth vs Mars
- Conclusions

Introduction

What is chemical disequilibrium, and why should we use it

Which biomarker?


www.nature.com/scientificreports

SCIENTIFIC REPORTS

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Titania may produce abiotic oxygen atmospheres on habitable exoplanets

Norio Narita[1,2,3], Takafumi Enomoto[3,4], Shigeyuki Masaoka[3,4] & Nobuhiko Kusakabe[2]

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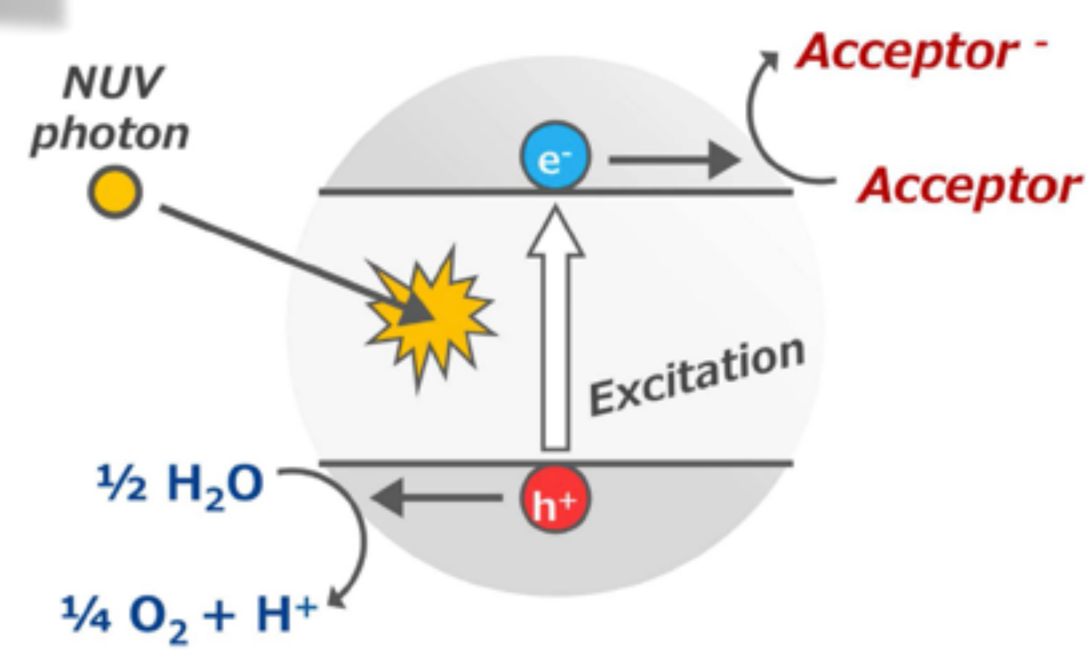
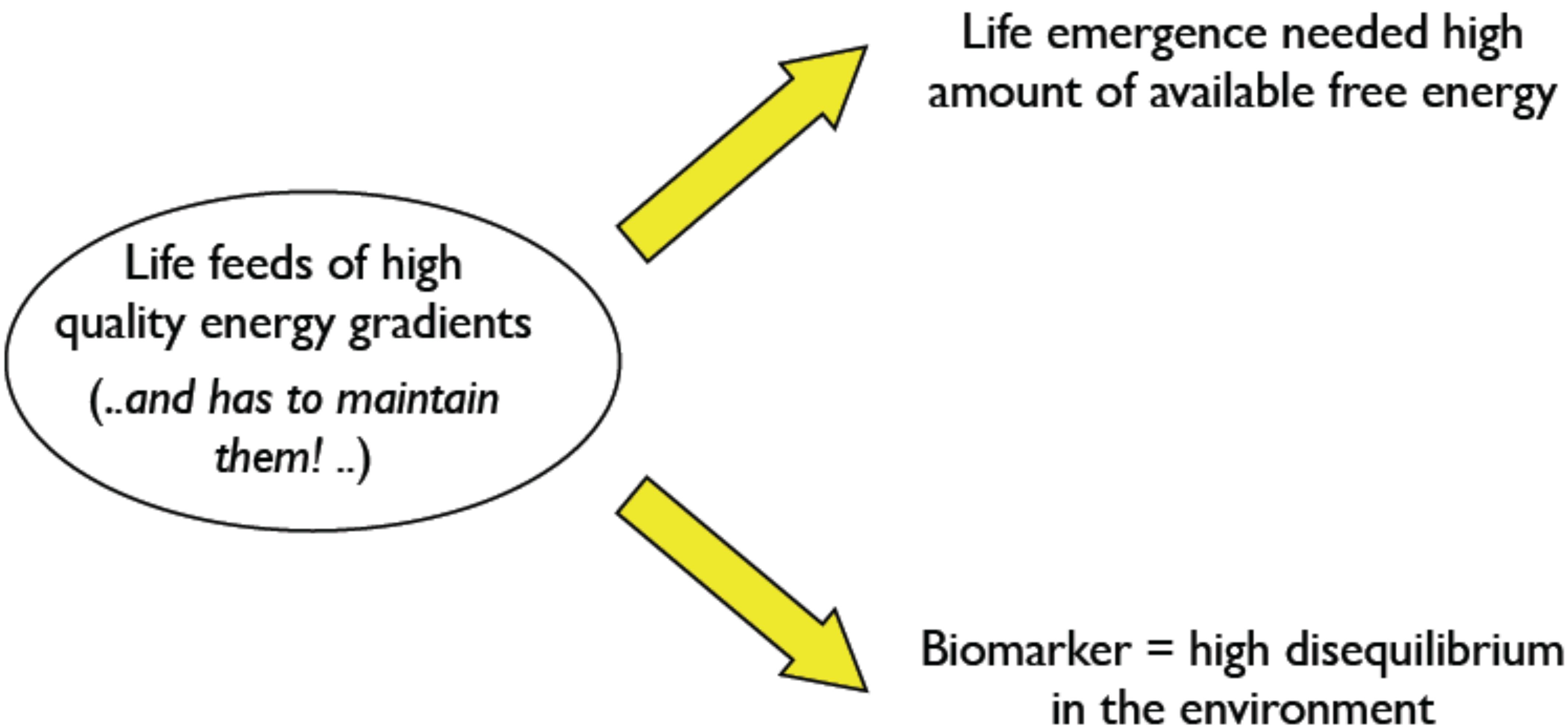
Published: 10 September 2015

The search for habitable exoplanets in the Universe is actively ongoing in the field of astronomy. The biggest future milestone is to determine whether life exists on such habitable exoplanets. In that context, oxygen in the atmosphere has been considered strong evidence for the presence of photosynthetic organisms. In this paper, we show that a previously unconsidered photochemical mechanism by titanium (IV) oxide (titania) can produce abiotic oxygen from liquid water under near ultraviolet (NUV) lights on the surface of exoplanets. Titania works as a photocatalyst to dissociate liquid water in this process. This mechanism offers a different source of a possibility of abiotic oxygen



Life & Disequilibrium

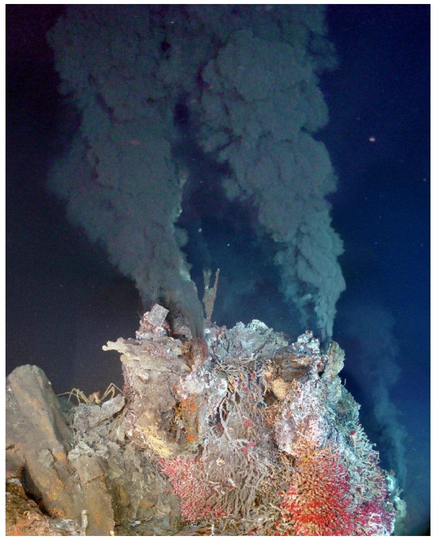


"The general struggle for existence of animate being is struggle for entropy, which becomes available through the transition of energy from the hot sun to the cold earth" (Boltzmann, 1886)

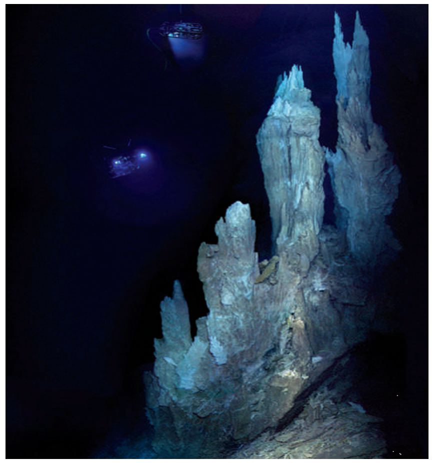
"Life feeds of high quality energy gradient" (Schrödinger, 1944)

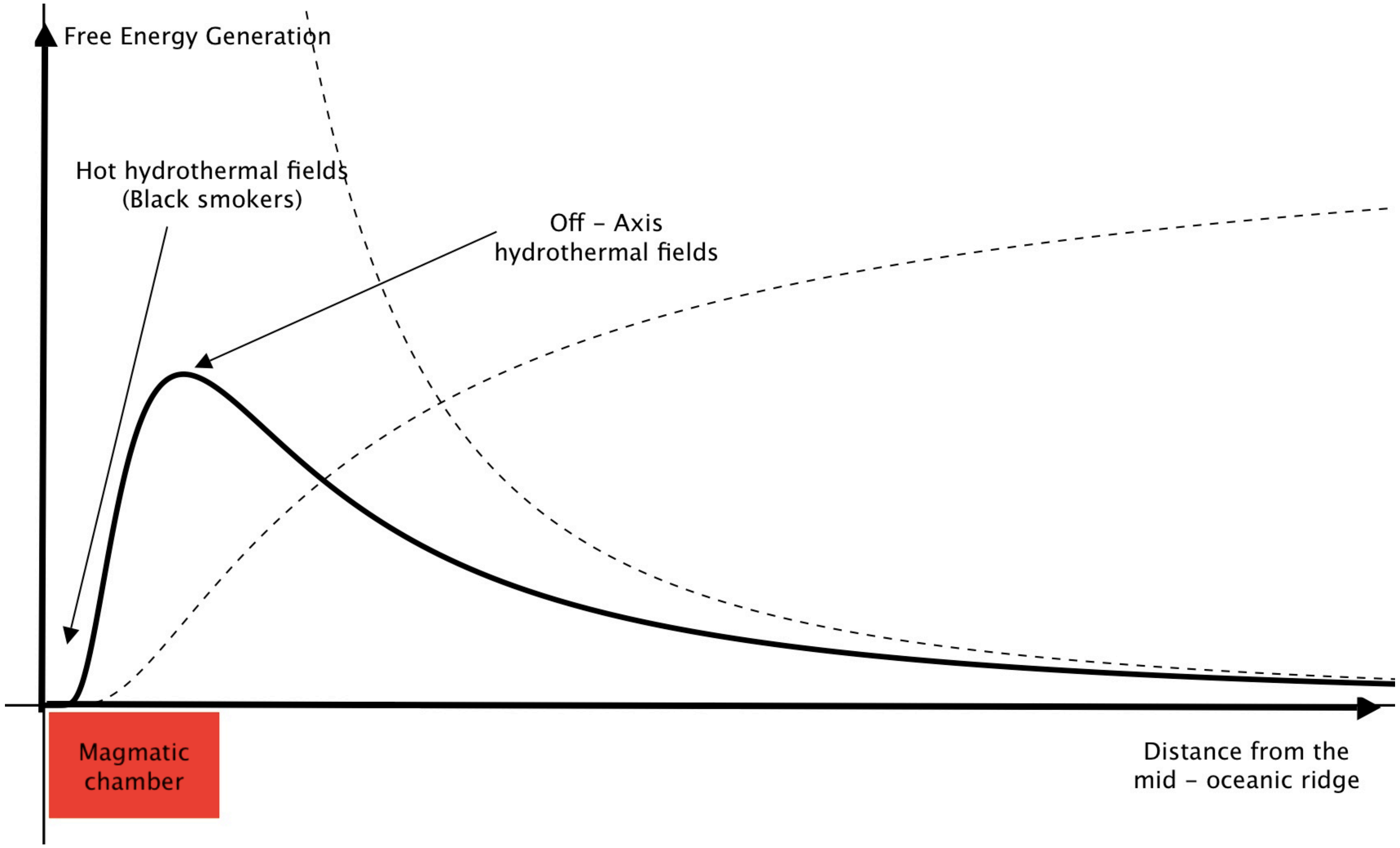
Modeling the thermodynamics of HV

Black smokers



"Lost City"

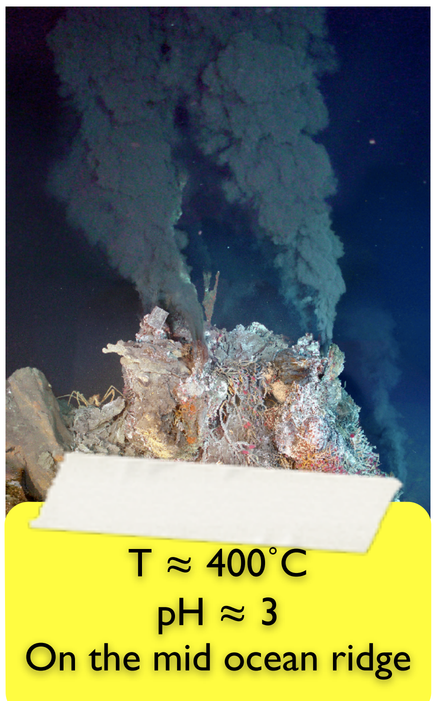




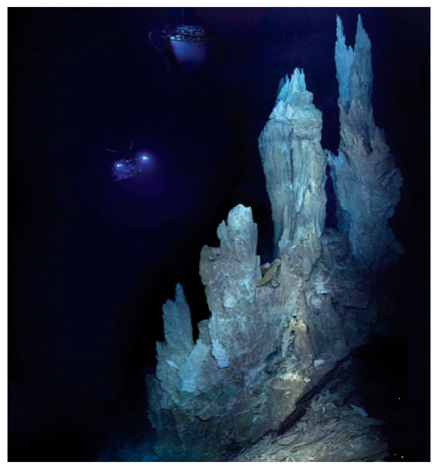
Simoncini E., Russell M. J., Kleidon A., OLEB 41, 529, 2012.

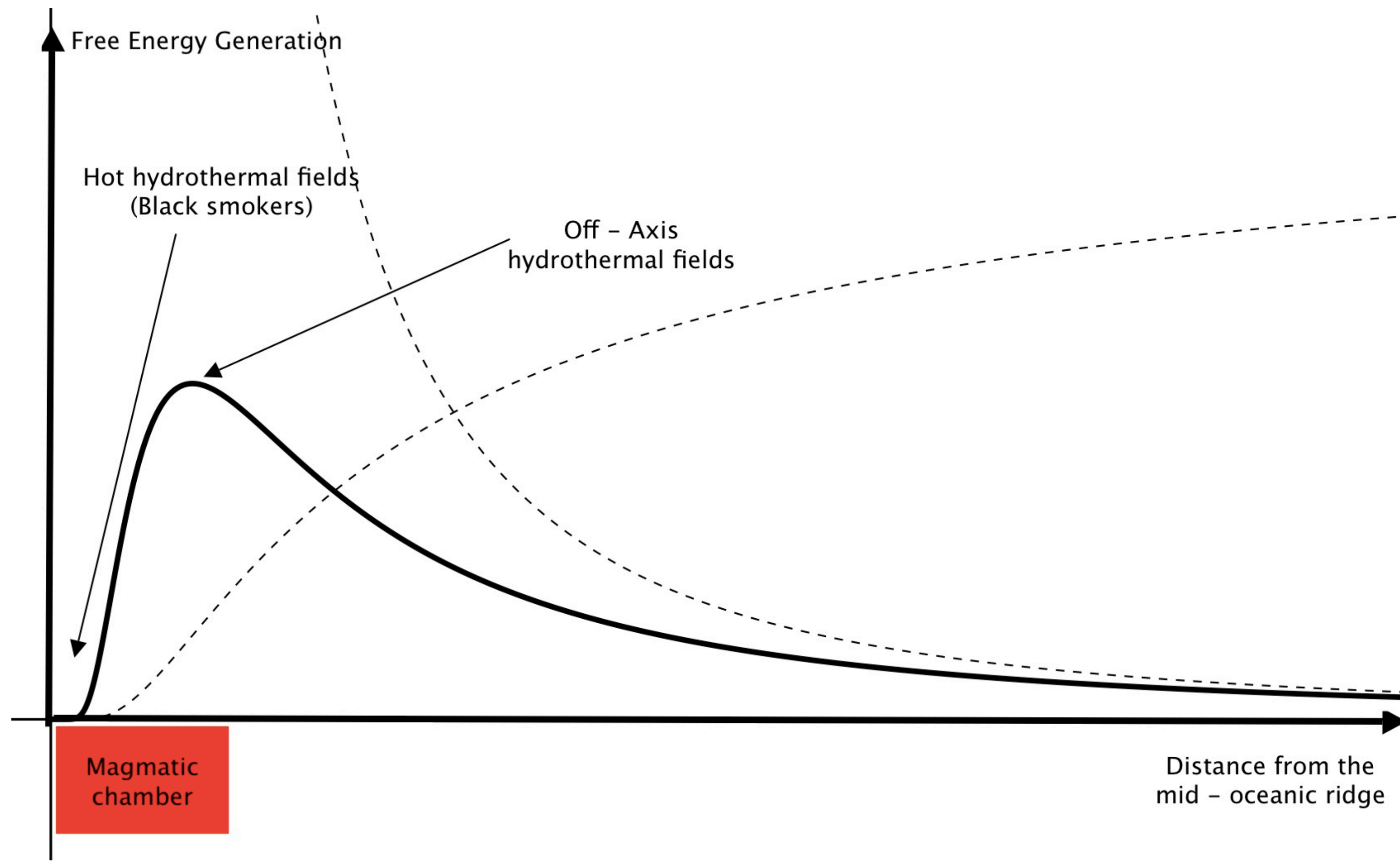
Modeling the thermodynamics of HV

Black smokers



“Lost City”

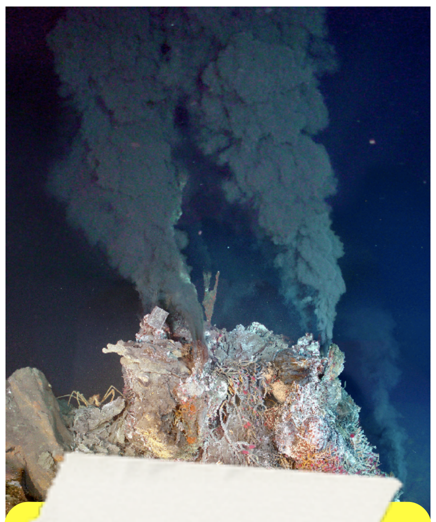




Simoncini E., Russell M. J., Kleidon A., OLEB 41, 529, 2012.

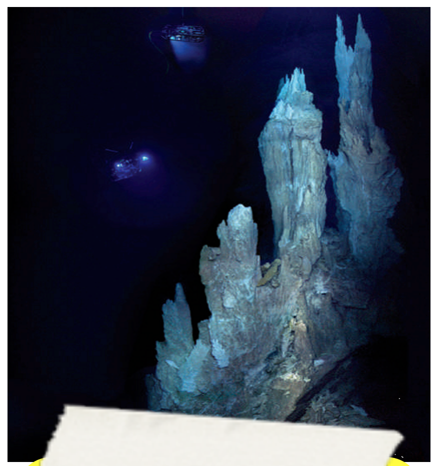
Modeling the thermodynamics of HV

Black smokers

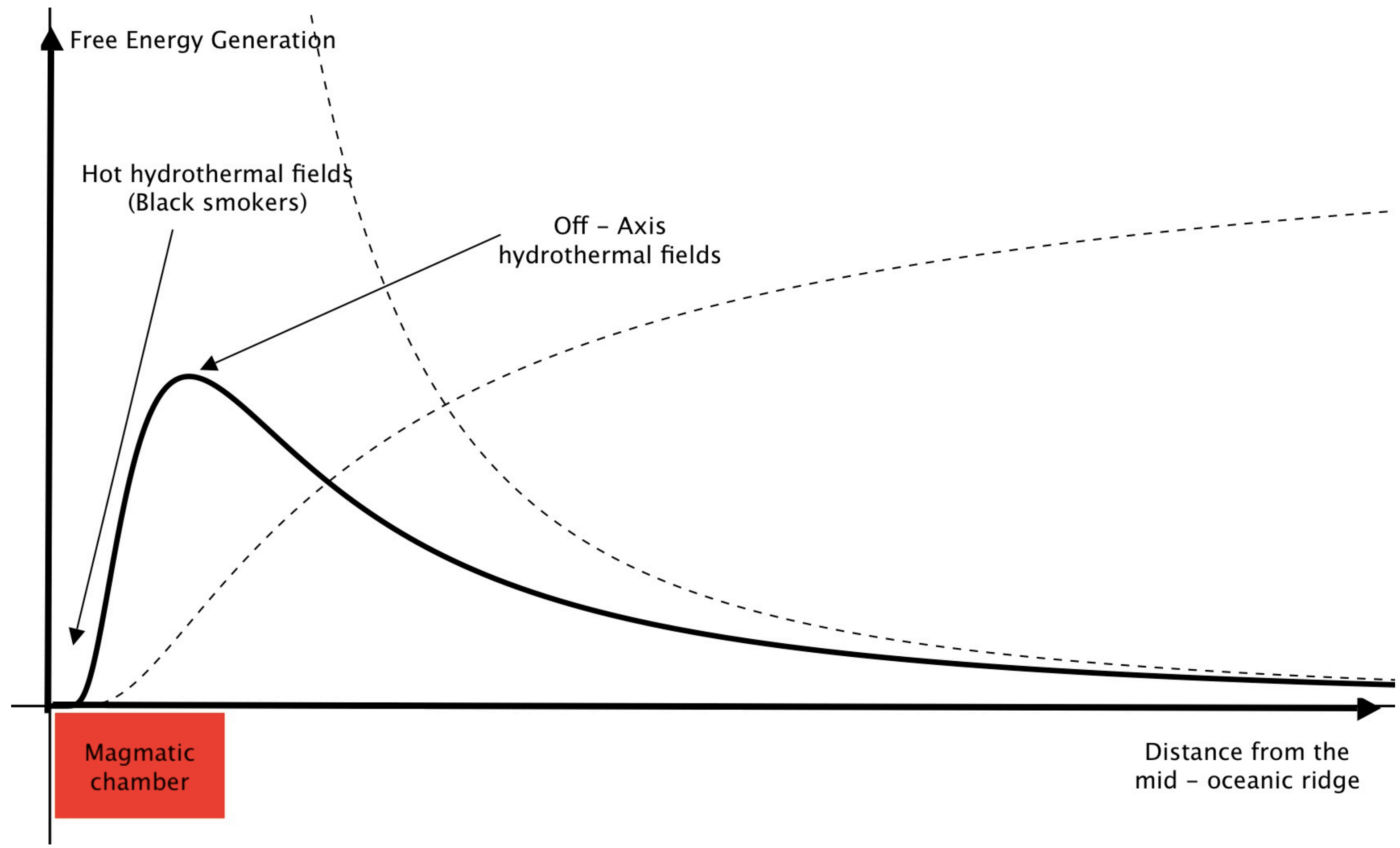


T ≈ 400°C
pH ≈ 3
On the mid ocean ridge

“Lost City”



T ≈ 75°C
≈15 km from mid - oceanic ridge
pH ≈ 11
Serpentinization



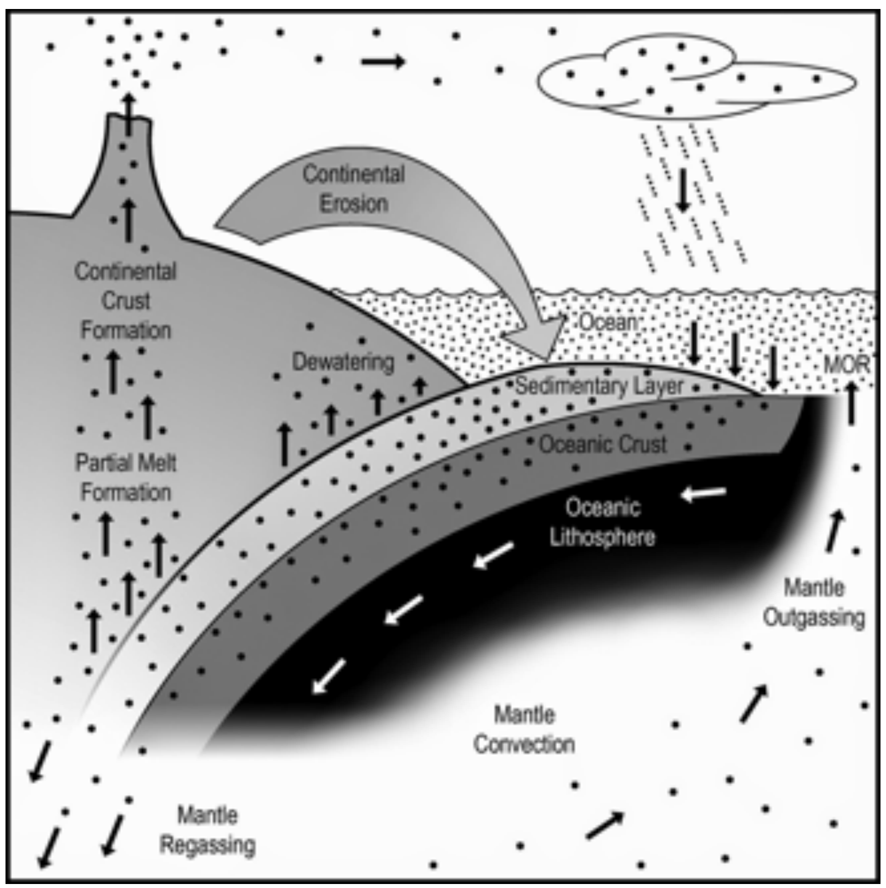
Simoncini E., Russell M. J., Kleidon A., OLEB 41, 529, 2012.

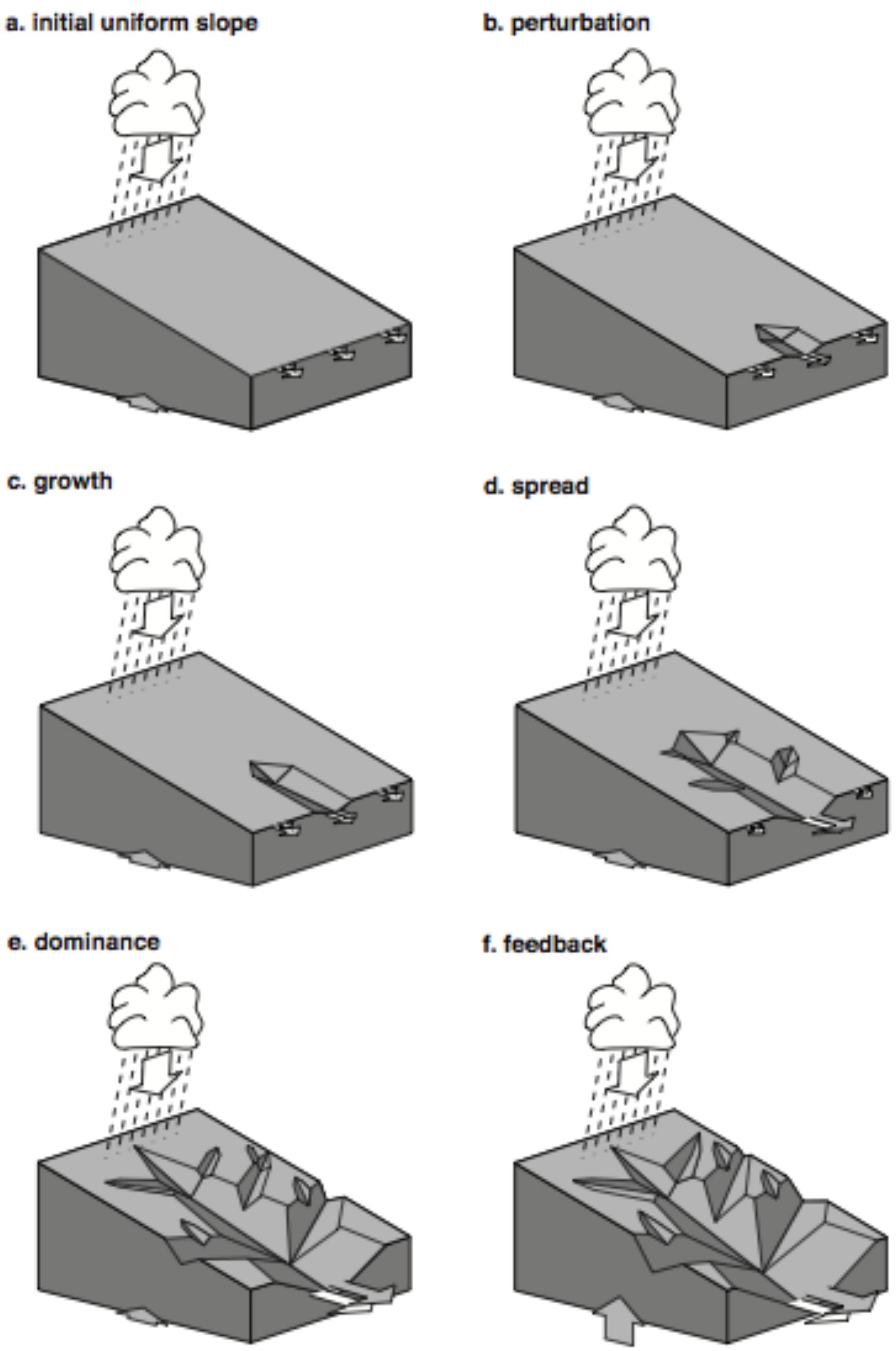
Life and Earth disequilibria

Geochemical cycles, continental crust formation [Rosing et al., 2006. Dyke et al., 2010]

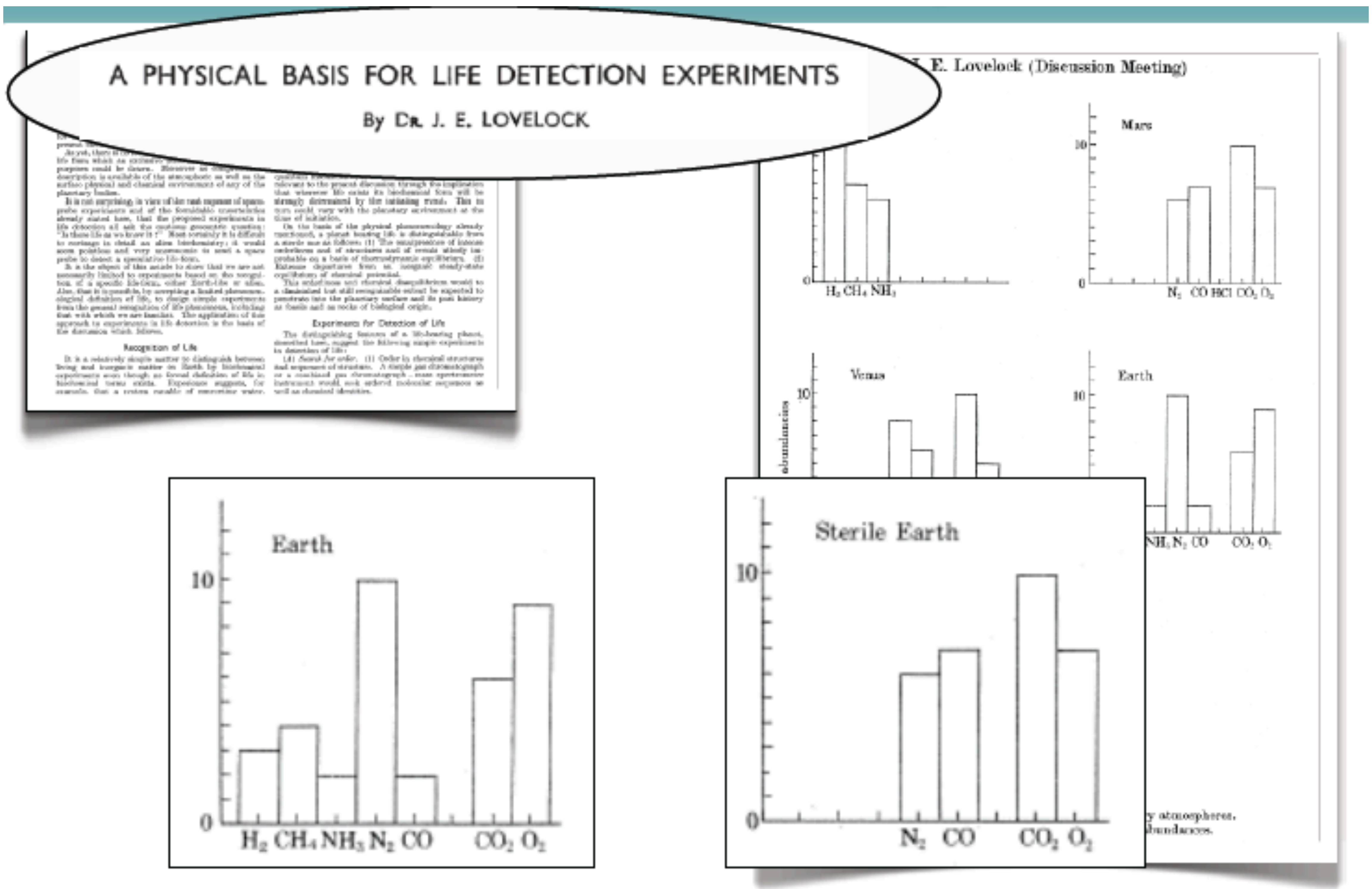
Rates of geochemical processes, silicate rock **weathering**, **carbon cycle** (=> Snowball Earth) [Schwartzman & Volk, 1989. Berner, 1997]

Topographic properties [Dietrich and Tayler Perron, 2006. Kleidon et al., 2012]





Atmospheric Chemical Disequilibrium

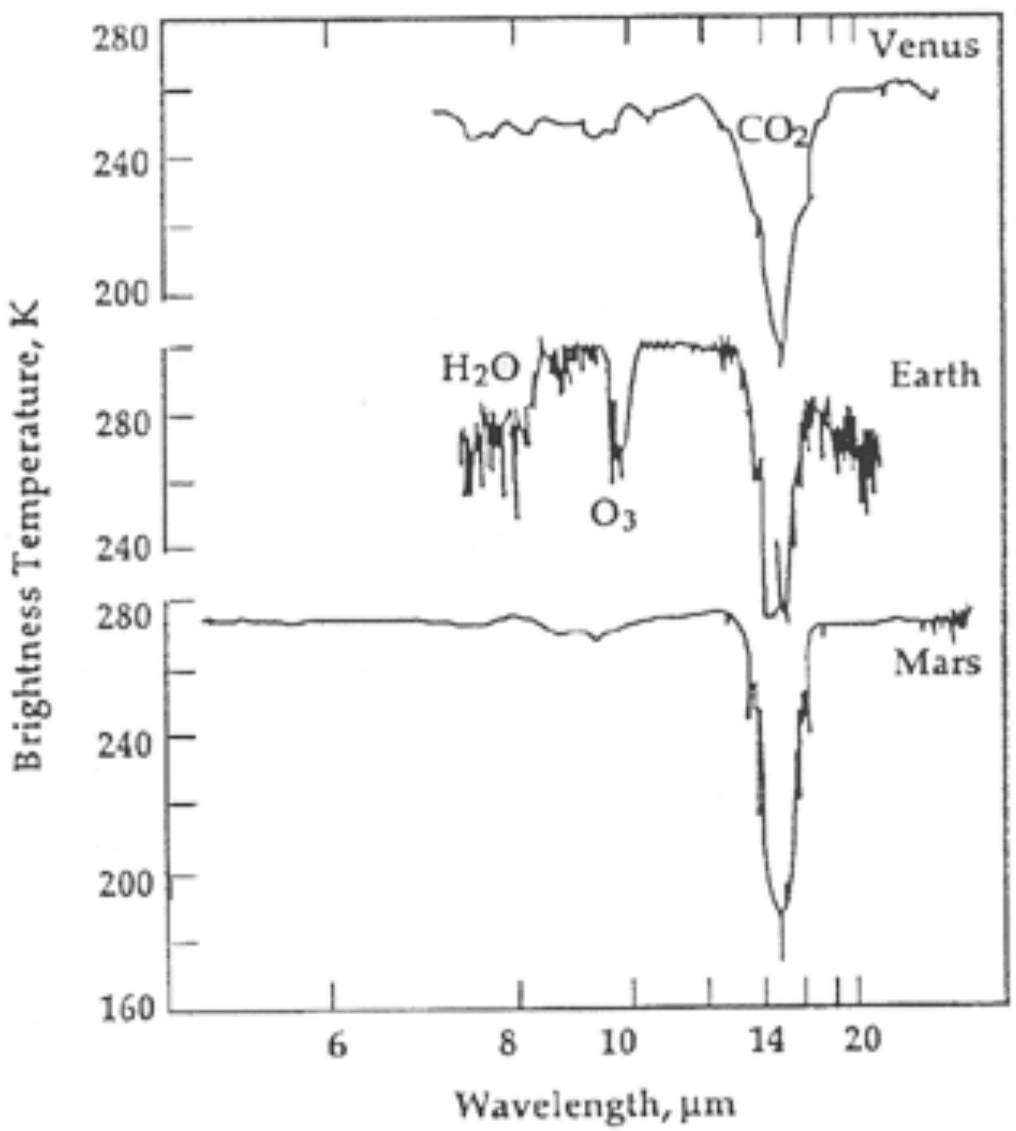


Life and Earth disequilibria

The emergence of life allowed the use of more degrees of freedom associated to geological and atmospheric cycles, and consequently the generation of more free energy from the same initial energy sources.

The Earth atmosphere [Lovelock 1965; 1975. Hitchcock and Lovelock, 1967]

Co-evolution of Earth geochemical cycles and life [Grenfell et al., 2010. Lammer et al., 2010]



"*Once candidate disequilibria are identified, alternative explanations must be eliminated. Life is the hypothesis of last resort*" (Sagan et al., 1993)

Simoncini E., Kleidon A., Gallori E., J. of Cosmology, Sept. 2010

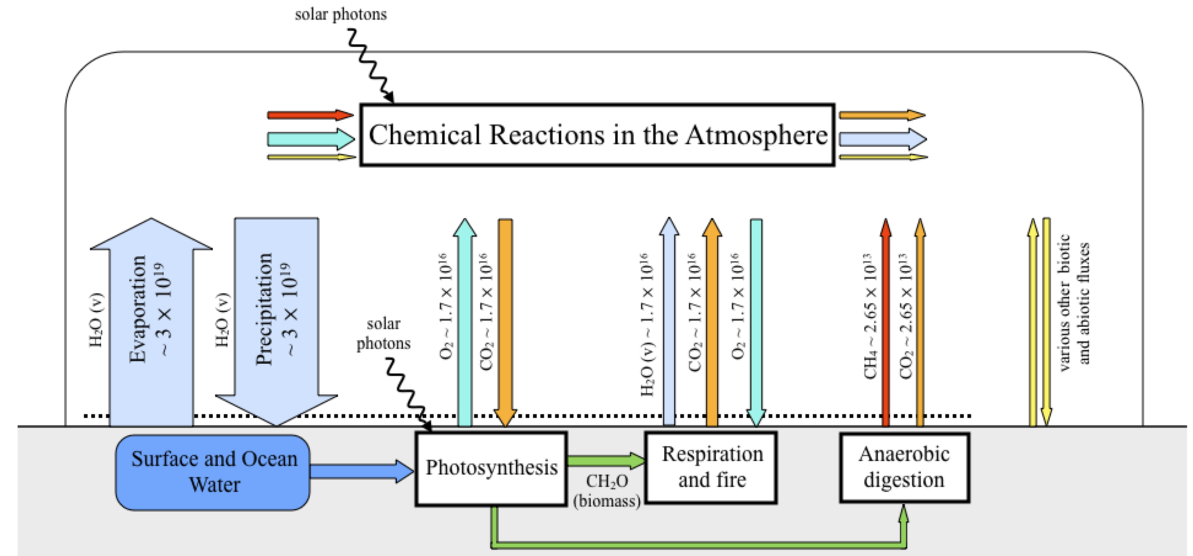
http://www.astronomynotes.com/lifezone/s4.htm

Earth's methane disequilibrium

Simoncini, E., Virgo, N., Kleidon, A., Earth Syst. Dynam., 4, 317-331. 2013.

Earth’s methane disequilibrium

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



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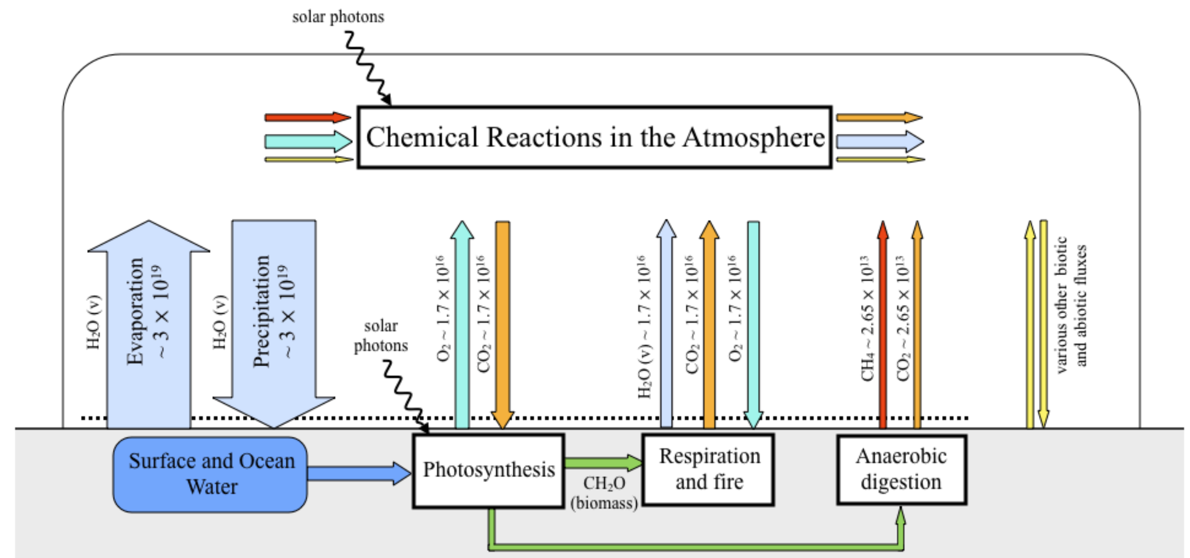

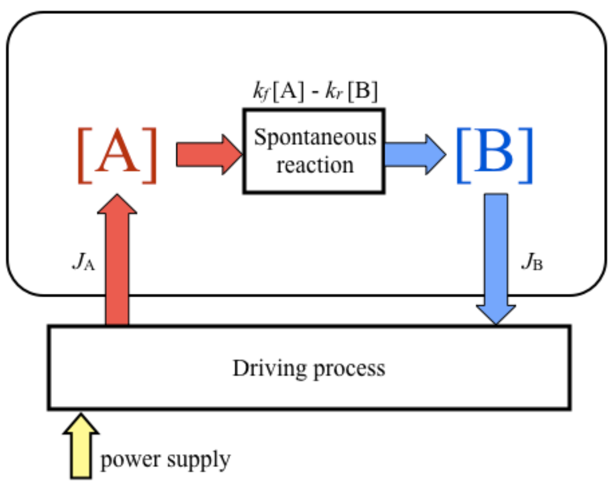

$$\frac{d[A]}{dt} = j_A - k_f[A] + k_r[B]$$

$$\frac{d[B]}{dt} = j_B + k_f[A] - k_r[B] = -\frac{d[A]}{dt}.$$

$$\Delta G = \Delta G^{\circ} + RT \log \frac{[B]}{[A]} = RT \log \frac{1-[A]}{K_{\mathrm{eq}}[A]}$$

Simoncini, E., Virgo, N., Kleidon, A., Earth Syst. Dynam., 4, 317-331. 2013.

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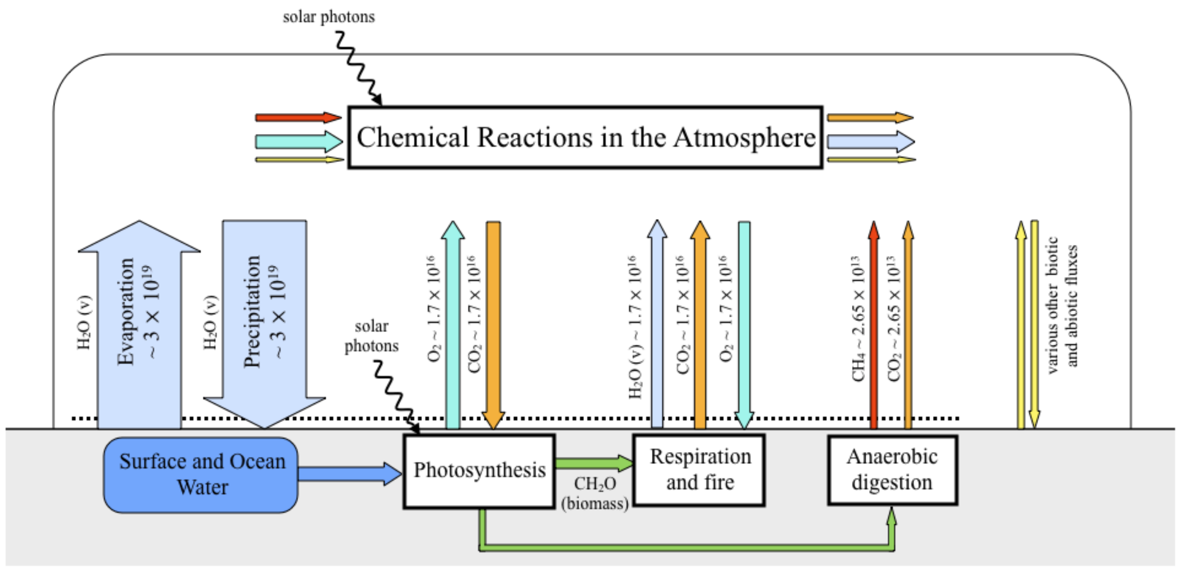

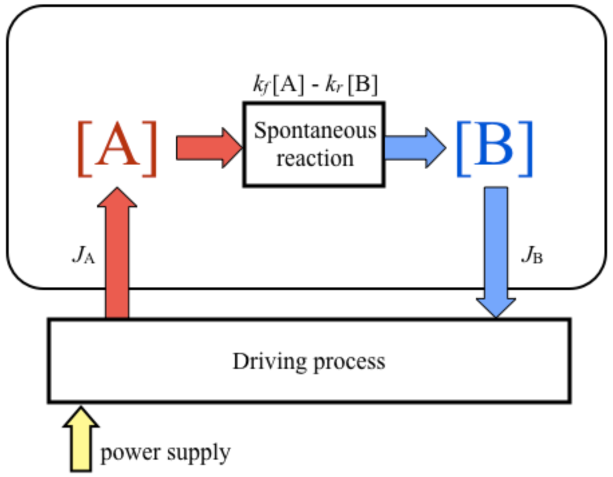

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$$\Delta G = \Delta G^\circ + RT\log\frac{[B]}{[A]} = RT\log\frac{1-[A]}{K_{eq}[A]}$$

The contemporaneous presence of O_2 and CH_4 into the Earth's atmosphere is maintained by ~ 0.67 TW

~ 0.43 TW are given by living processes (animal enteric ferm.: 0.13TW; rice paddies 0.09TW).

Incoming (sunlight): 175000 TW, of which 215 TW extracted globally by photosynthesis

Simoncini, E., Virgo, N., Kleidon, A., Earth Syst. Dynam., 4, 317-331. 2013.

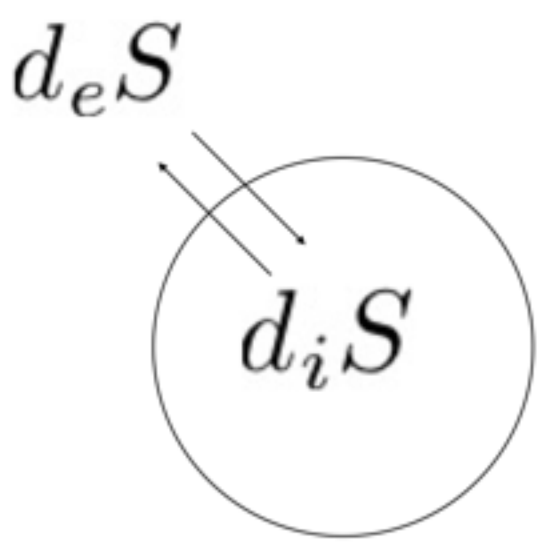
How to calculate (and compare) disequilibrium in chemical processes

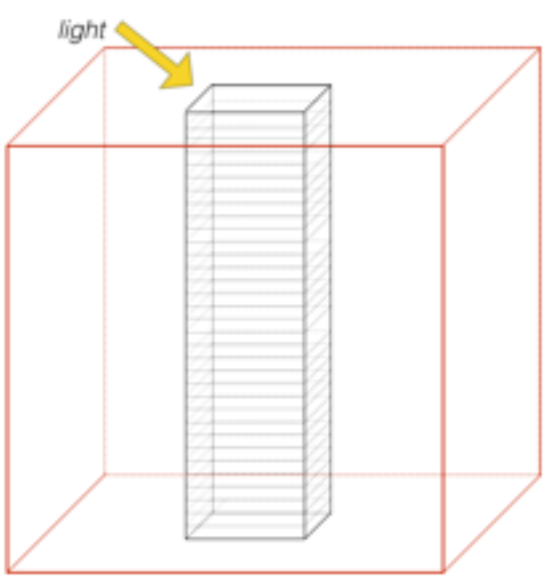
Exoplanetary Atmospheres and Habitability
TDE, 15/10/2015, Observatoire Côte d'Azur, Nice, France

The extent of chemical disequilibrium

In order to measure the extent of disequilibrium, we have to deal with the thermodynamics of non-equilibrium (irreversible) processes.

The distance of a system from its equilibrium condition (i.e. the measure of its irreversibility) is given by the entropy production within a system (d_iS).



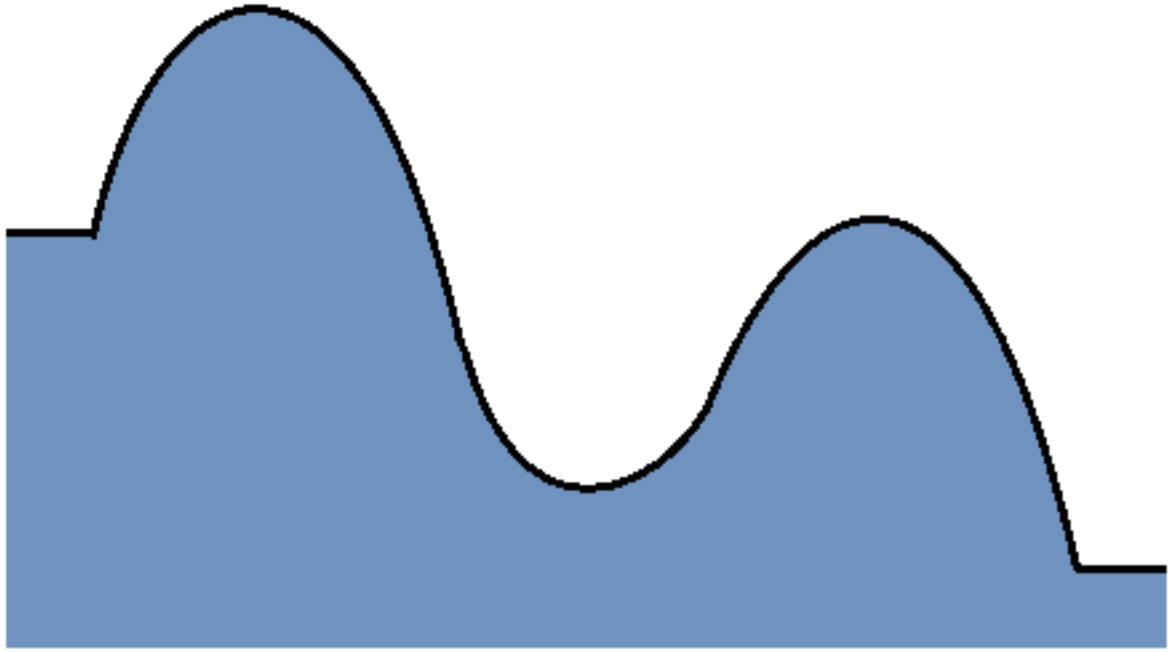


Kondepudi & Prigogine, Modern Thermodynamics, 1998.

Atmospheric Chemical Disequilibrium

$$\int_{begin}^{end} \frac{\partial_i S}{\partial t} dt \neq \Delta S \Big|_{begin}^{end}$$

$$\frac{dS}{dt}\Big|_{t_{equilibrium}}$$



The extent of chemical disequilibrium

$$\frac{d_i S}{dt} = R \cdot (R_f - R_r) \cdot ln\left(\frac{R_f}{R_r}\right)$$

R_f = forward rate $\qquad$ R_r = backward rate

$$\mathrm{A + B \leftrightharpoons C + D}$$

$$\frac{d_i S}{dt} = R(k_f[A]_t[B]_t - k_r[C]_t[D]_t)ln\left(\frac{k_f[A]_t[B]_t}{k_r[C]_t[D]_t}\right)$$

Kondepudi & Prigogine, Modern Thermodynamics, 1998.
Stucki, The Optimal Efficiency and the Economic Degrees of Coupling of Oxidative Phosphorylation. Eur. J. Biochem, 109, 269-283, 1980
Caplan and Essig, Bioenergetics and linear nonequilibrium thermodynamics; the steady state, 1999

KROME

better science through chemistry

- Python pre-processor provides Fortran routines
- Creates modules from chemical network
- Dust evolution, cooling heating photoionization
- Large test suite
- Highly optimized, fast solvers
- Open source, bitbucket community
- Grassi T. et al., MNRAS 2014. doi:10.1093/mnras/stu114

=> *Tommaso Grassi's talk*

www.kromepackage.org

Atmospheric disequilibrium of the Earth

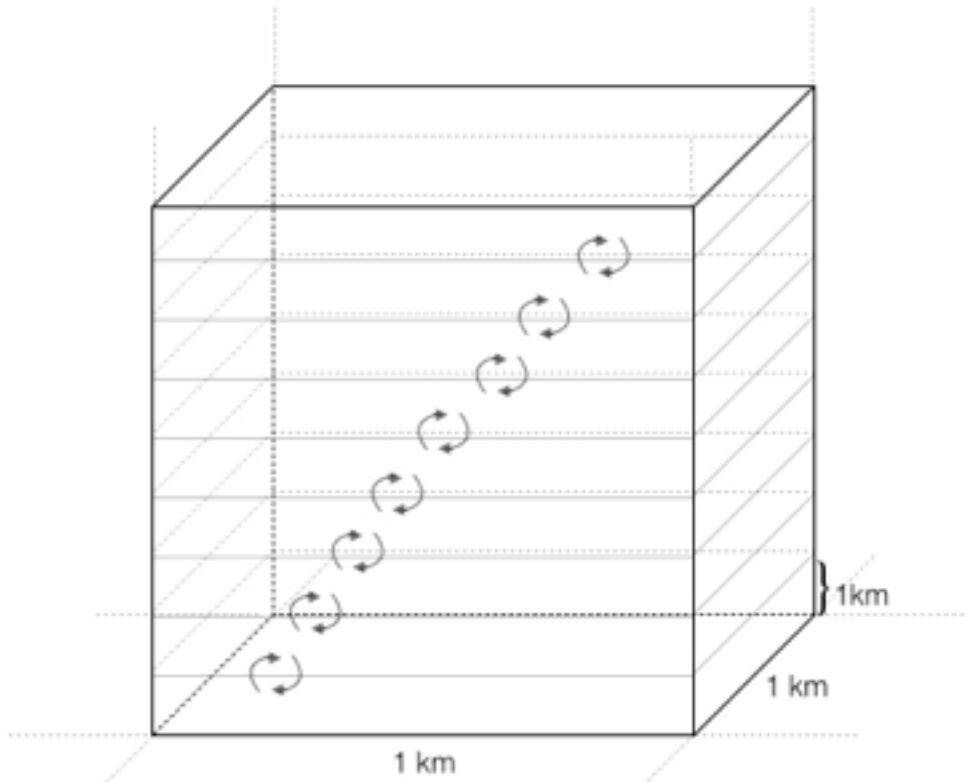
Earth Atmospheric Chemical Disequilibrium

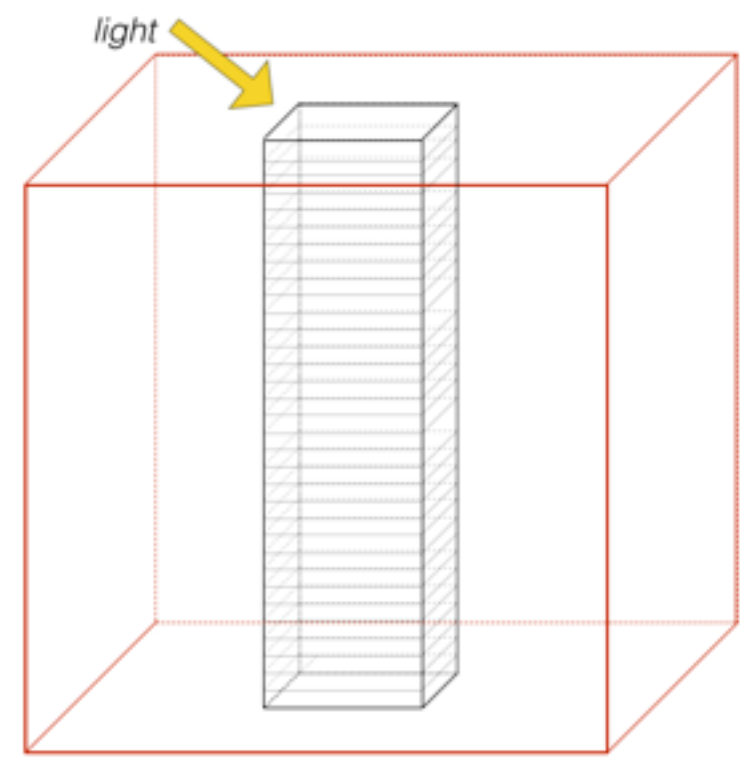
* Model: Kasting, J. F., and Donahue, T. M., J. Geophys. Res., 85,3255-3263. 1980 (K-80);

* 64 layers (~1km each);

* Eddy diffusion;

* Entropy production and the power dissipation:





$$\sigma = \frac{d_i S}{dt}$$

$$\frac{\sigma \times T}{A_{Earth}} \sim W m^{-2}$$

Simoncini, Brucato, Grassi, sub. to OLEB
S. O. Danielache, E. Simoncini,Y. Ueno, Archean Atmospheres Modeled with the KROME Chemistry Package, JPGU 2014
Simonicni E., Virgo N., Kleidon A., Quantifying drivers of chemical disequilibrium: theory and application to methane in the Earth's atmosphere. Earth System Dynamics 4, 1-15, 2013.
Angerhausen D., Sapers H., Simoncini E., and coworkers, An astrobiological experiment to explore the habitability of tidally locked M-Dwarf planets, IAU 2013 Proceedings.

Earth Atmospheric Chemical Disequilibrium

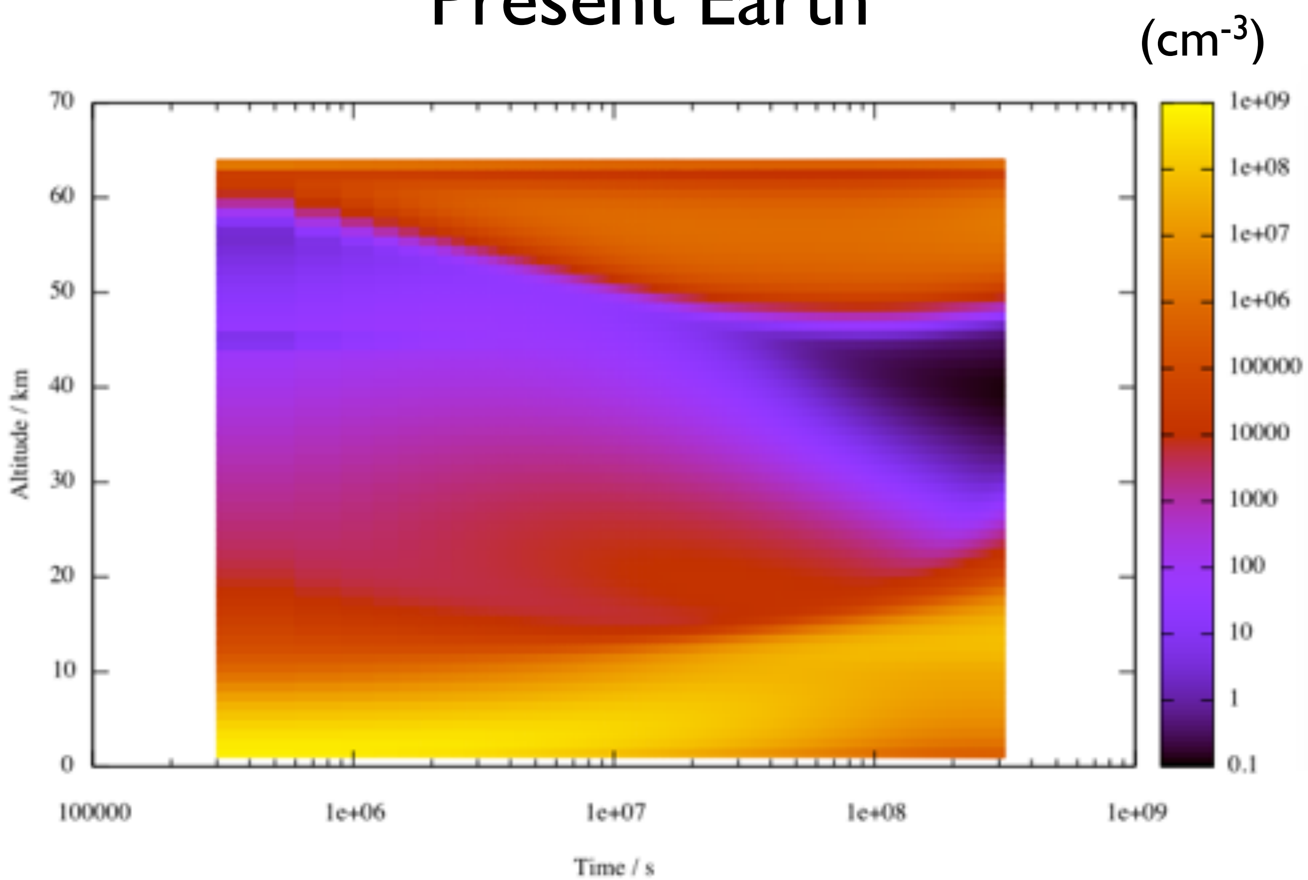
Different runs of K-80 model:

- Effect of photochemistry (PC)
- Effect of eddy diffusion (ED)
- Effect of photosynthesis' products (PS)
- Several points during the Earth history

Simoncini, Brucato, Grassi, sub. to OLEB

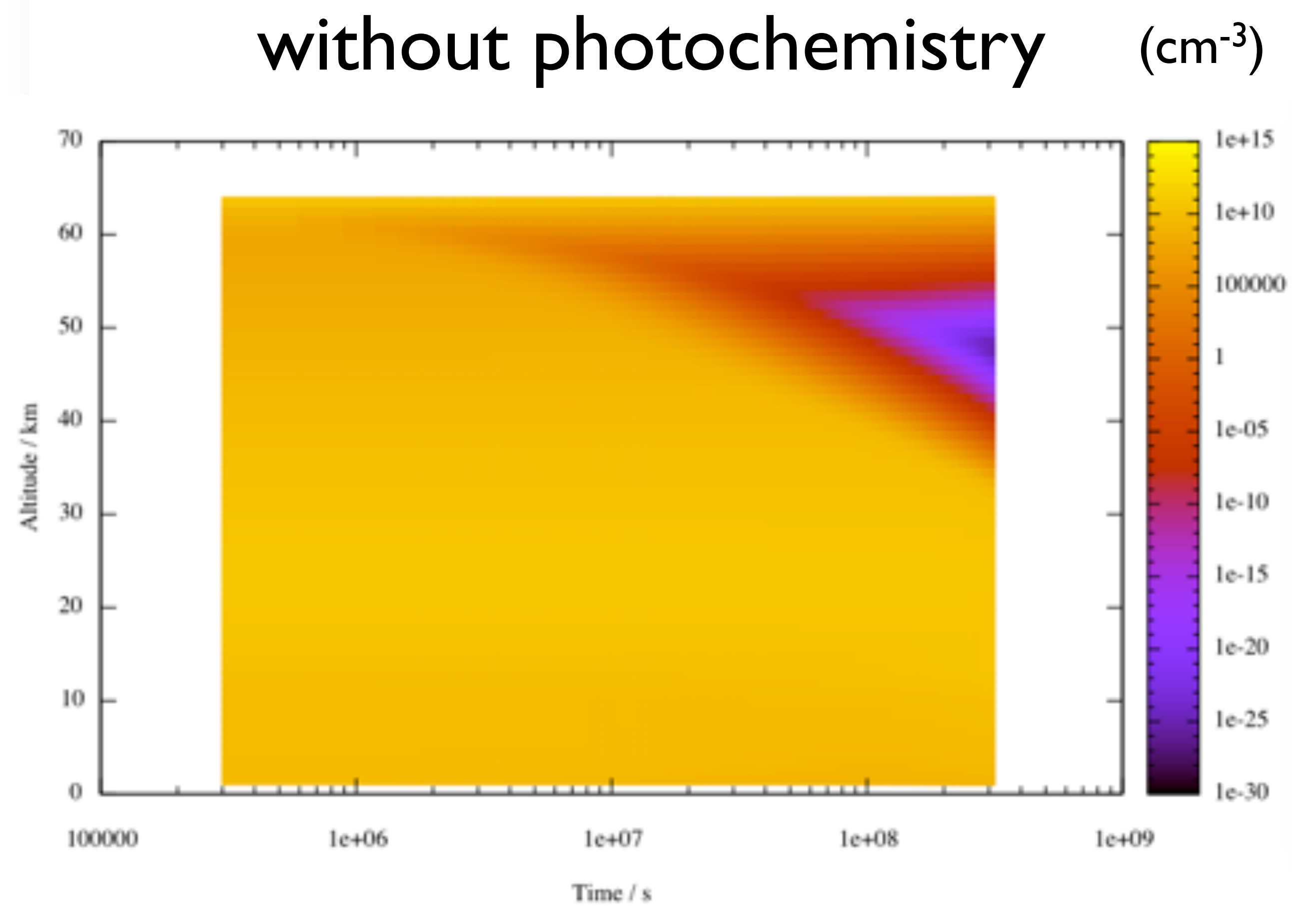
Earth Atmospheric Chemical Disequilibrium

Present Earth



O_3

Present Earth
without photochemistry



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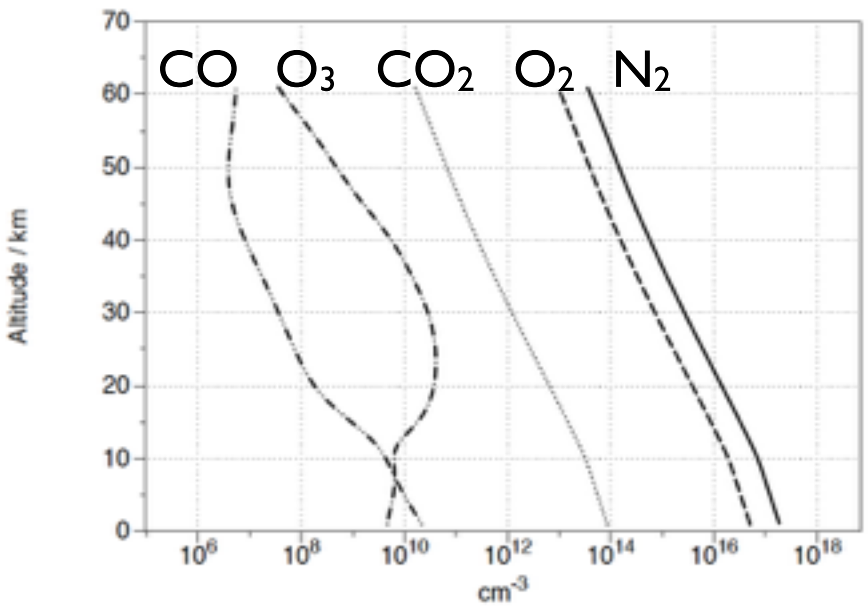
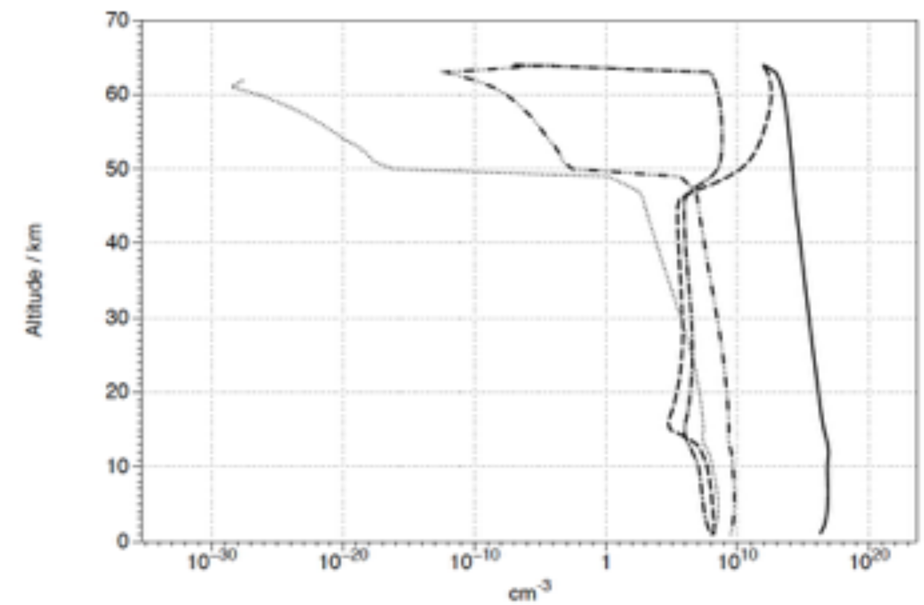
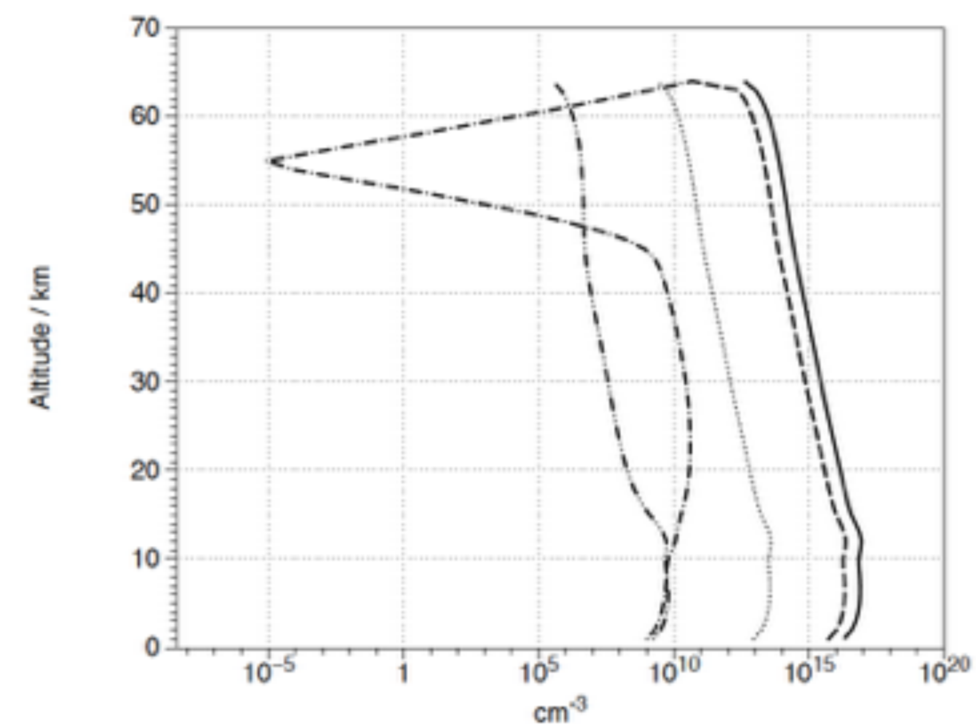
Earth Atmospheric Chemical Disequilibrium



full model



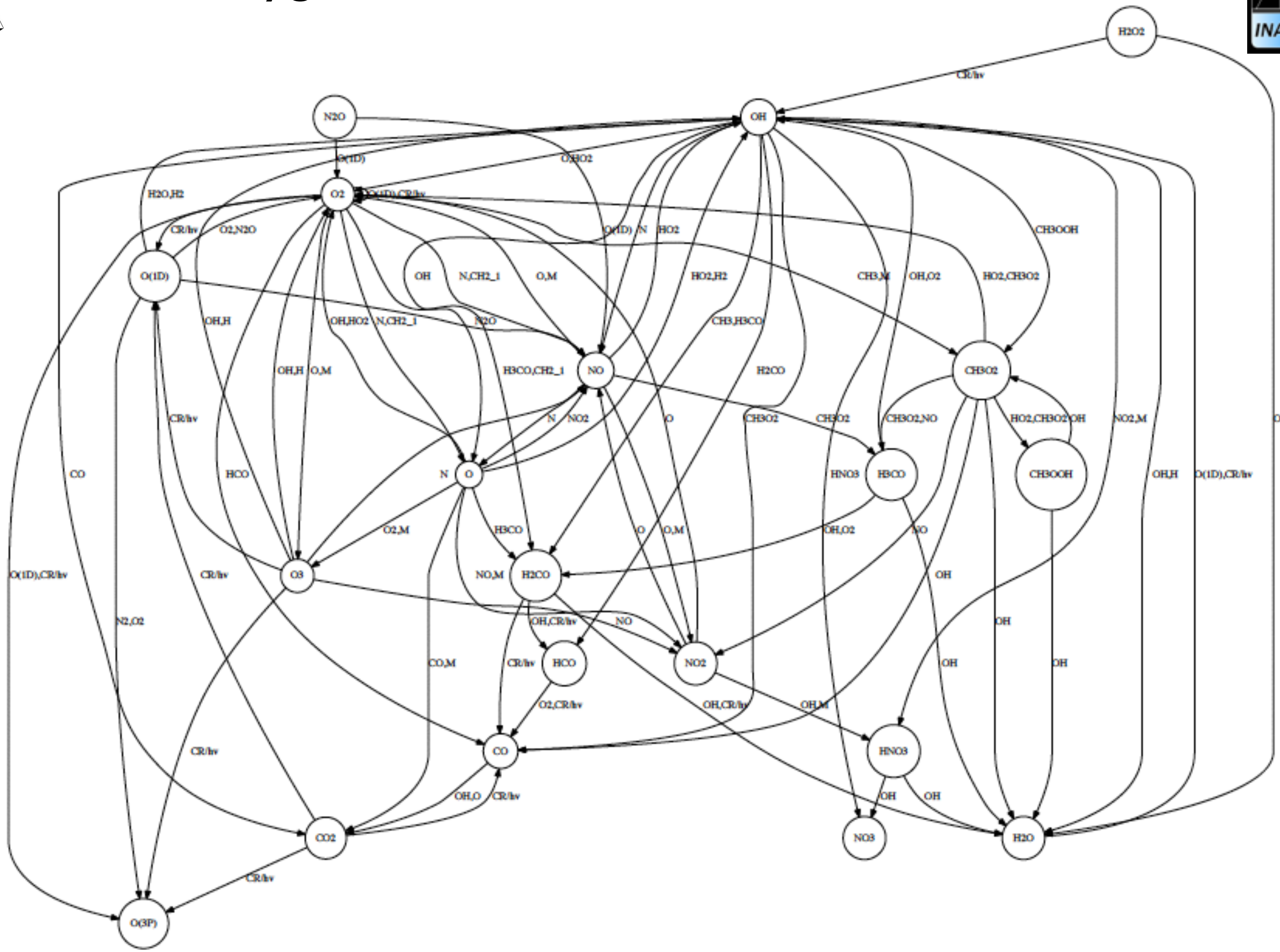
no photochemistry



KROME better science through chemistry

Simoncini, Brucato, Grassi, sub. to OLEB

Oxygen reactions in the K-80 network



Simoncini, Brucato, Grassi, sub. to OLEB

Simoncini, Brucato, Grassi, sub. to OLEB

Earth Atmospheric Chemical Disequilibrium

Reaction	σ / W
$H_2O + h\nu \rightarrow H + OH$	2.45×10^{-1}
$H + O_2 + M \leftrightharpoons HO_2 + M$	2.36×10^{-1}
$OH + HO_2 \leftrightharpoons H_2O + O_2$	1.12×10^{-1}
$H_2O_2 + h\nu \rightarrow 2OH$	1.42×10^{-2}
$HO_2 + HO_2 \leftrightharpoons H_2O_2 + O_2$	4.45×10^{-3}

PE
(reaction per layer)

PEnoPC
(reaction per layer)

Reaction	σ / W m^{-2}
$CH_3O_2 + HO_2 \leftrightharpoons CH_3OOH + O_2$	3.75×10^{-13}
$CH_3 + O_2 + M \leftrightharpoons CH_3O_2 + M$	3.31×10^{-14}
$NO_2 + OH + M \leftrightharpoons HNO_3 + M$	3.22×10^{-14}
$CH_3 + OH \leftrightharpoons H_2CO + H_2$	1.38×10^{-14}
$O(1D) + N_2 \leftrightharpoons O(3P) + N_2$	4.27×10^{-20}

Simulation run for 3.15e7 sec (KROME)

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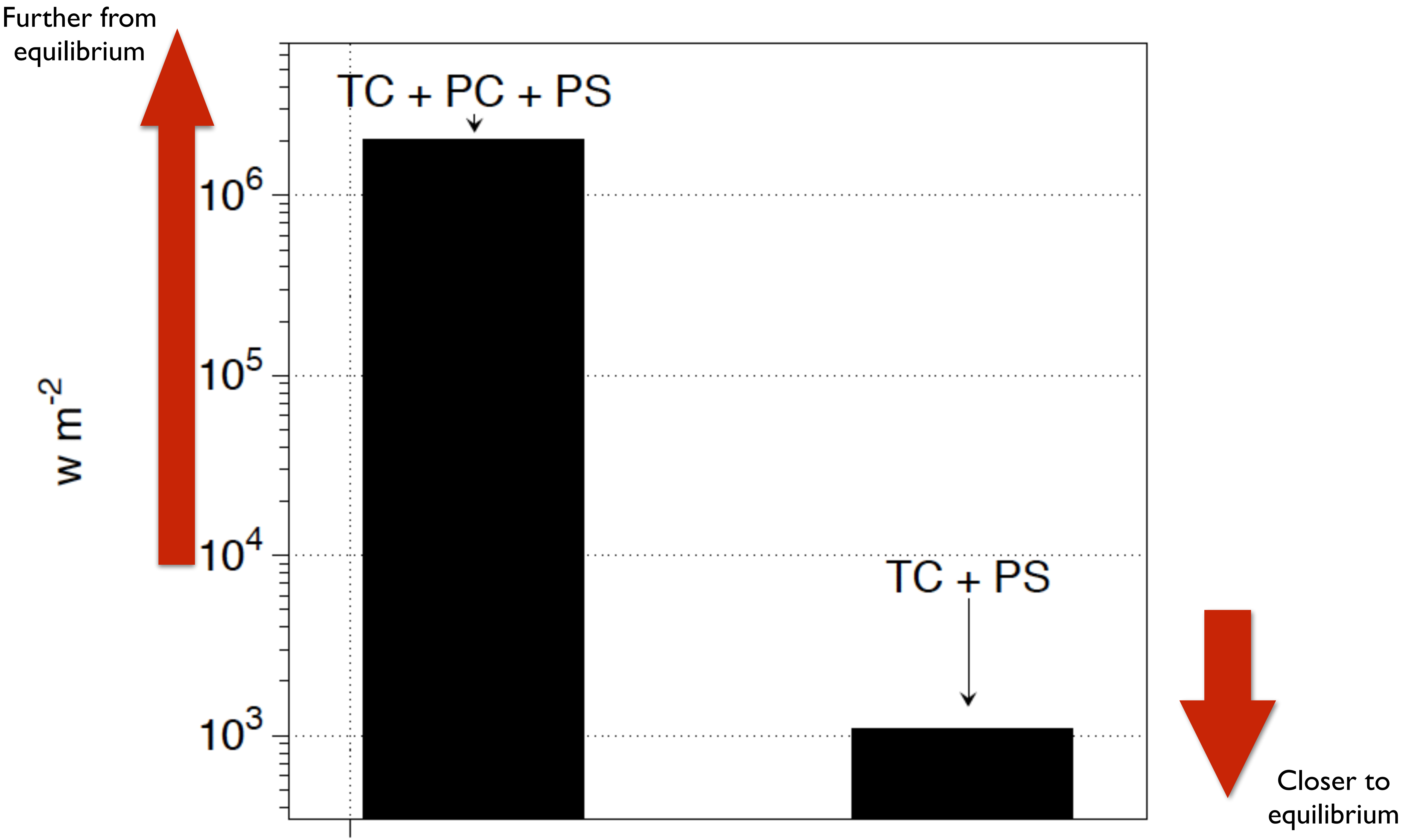
Earth Atmospheric Chemical Disequilibrium



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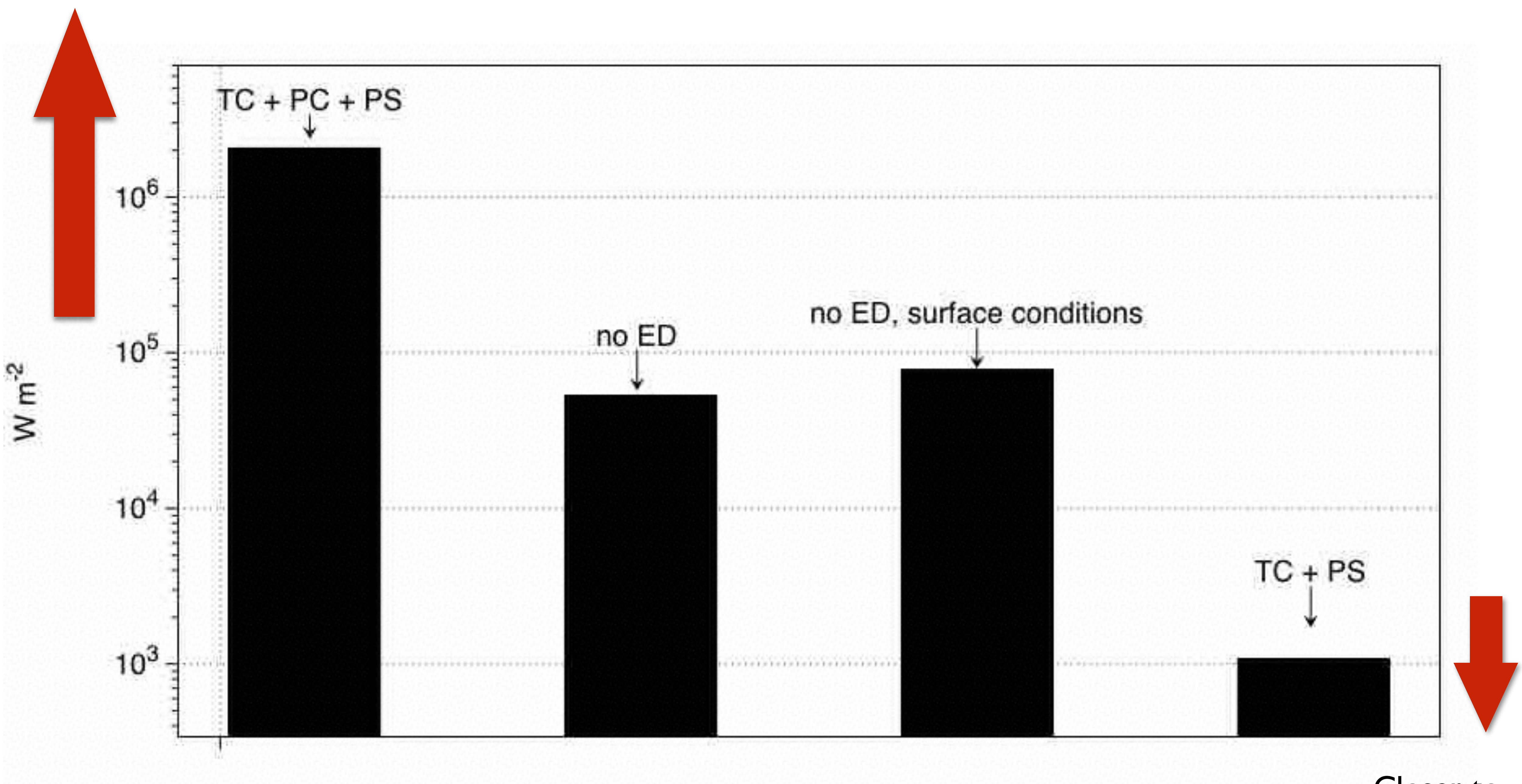
Earth Atmospheric Chemical Disequilibrium

Further from equilibrium



Closer to equilibrium

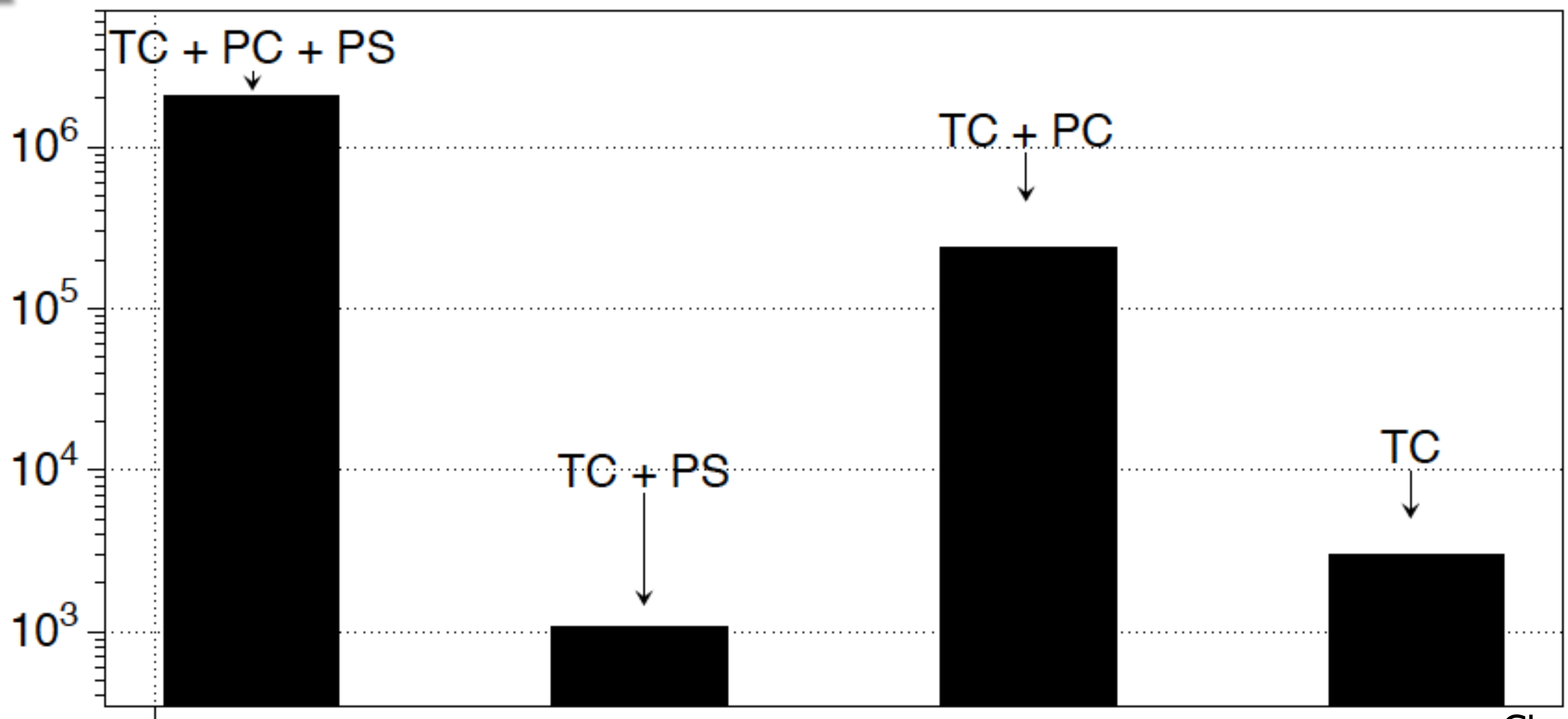
Simoncini, Brucato, Grassi, sub. to OLEB

Earth Atmospheric Chemical Disequilibrium

Uncoupling the effects of photochemistry and photosynthesis

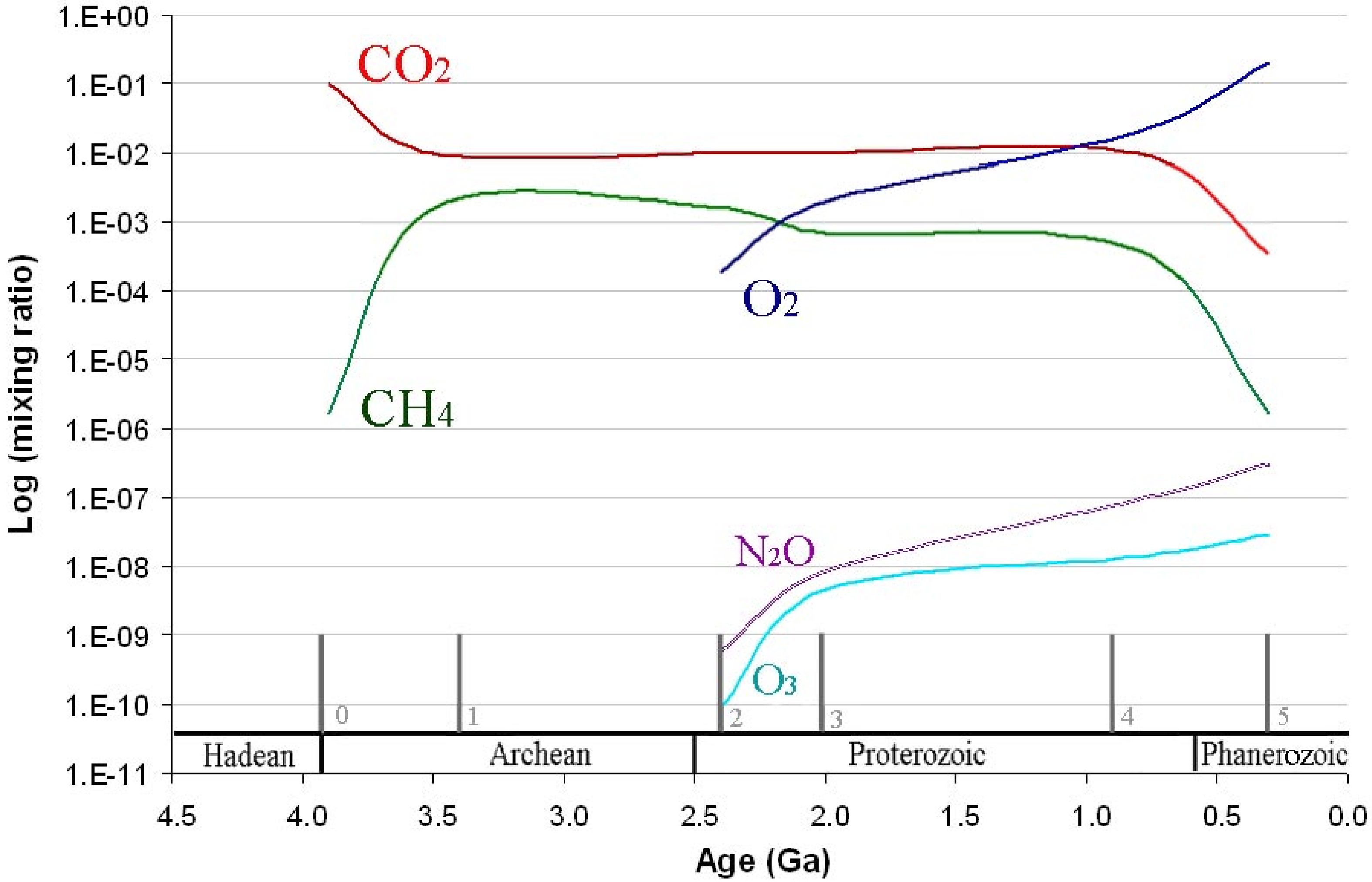
(O_2, O_3, CO_2, H_2O, CH_4)

Further from equilibrium



Closer to equilibrium

Earth Atmospheric Chemical Disequilibrium

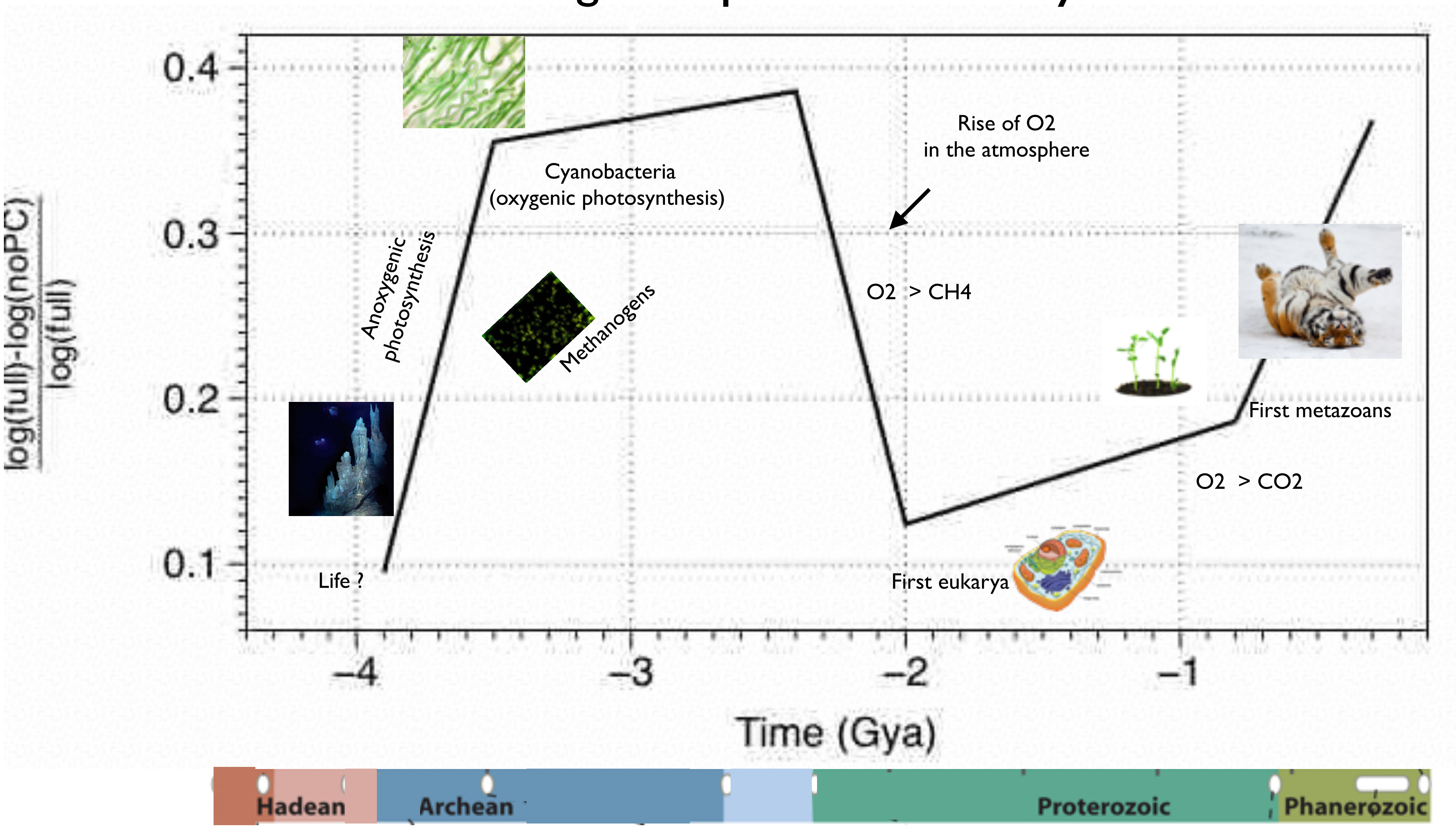


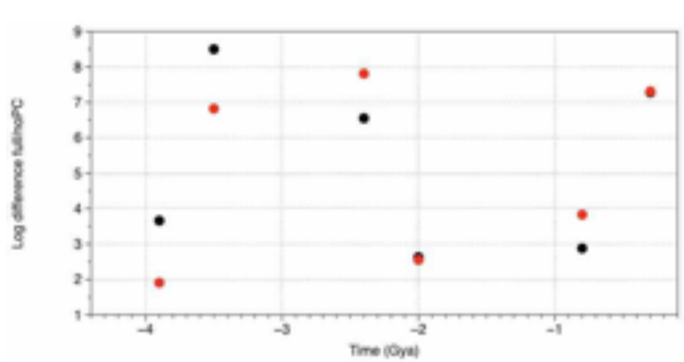
Epoch	Age (Ga)	CO_2 (mixing ratio)	CH_4 (mixing ratio)	O_2 (mixing ratio)	O_3 (mixing ratio)	N_2O (mixing ratio)
0	3.9	1.00E-01	1.65E-06	0	0	0
1	3.5	1.00E-02	1.65E-03	0	0	0
2	2.4	1.00E-02	7.07E-03	2.10E-04	8.47E-11	5.71E-10
3	2.0	1.00E-02	1.65E-03	2.10E-03	4.24E-09	8.37E-09
4	0.8	1.00E-02	4.15E-04	2.10E-02	1.36E-08	9.15E-08
5	0.3	3.65E-04	1.65E-06	2.10E-01	3.00E-08	3.00E-07

Simoncini, Brucato, Grassi, sub. to OLEB
Kaltenegger et al., ApJ 658, 598, 2007
Kasting, J. F., Scientific American Magazine; 80 2004

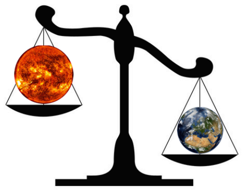
Earth Atmospheric Chemical Disequilibrium

Life origin and development
The *weight* of photochemistry



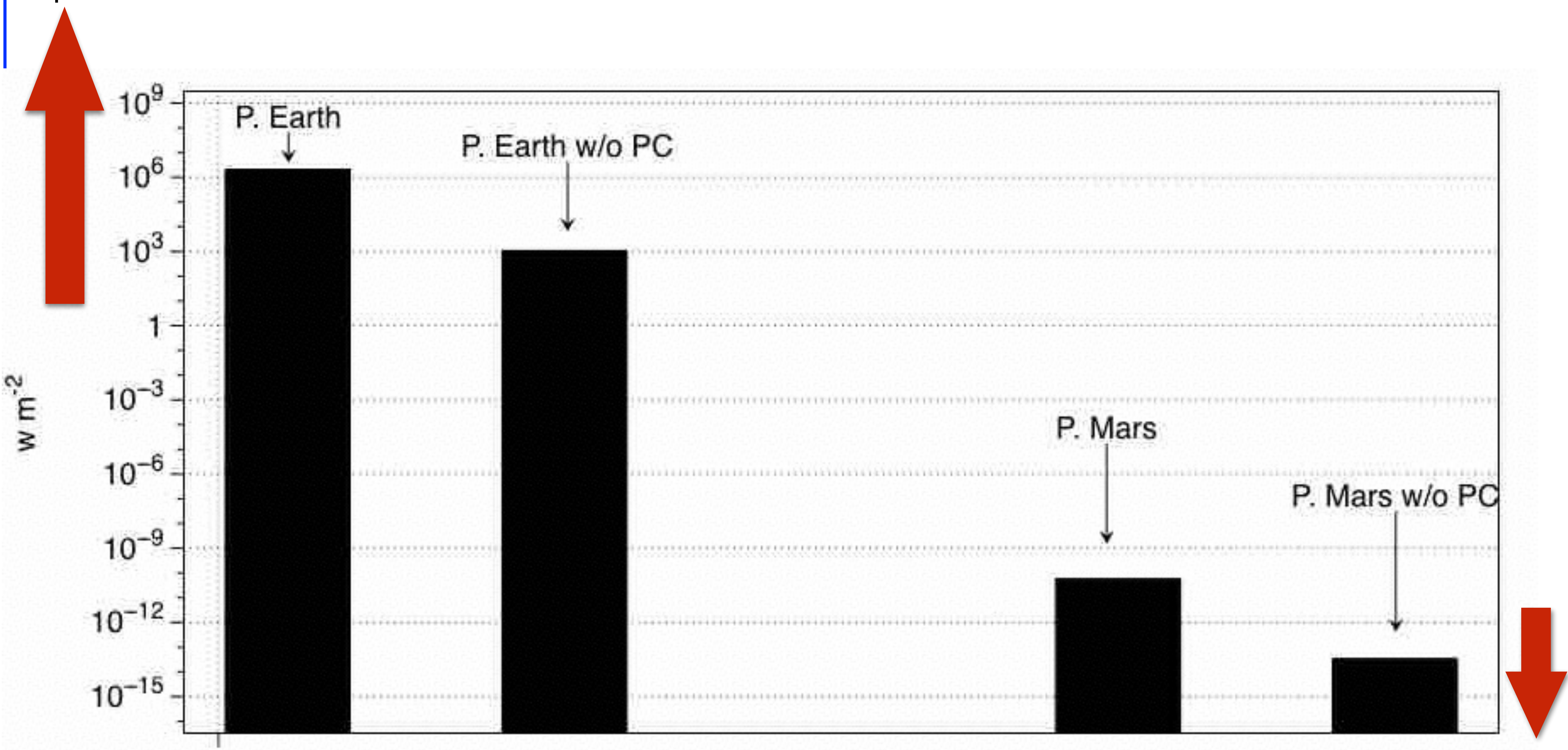


The entropy production at different moment of the runs.
The parameter shown above is plotted with different run times (full dots vs. red dots).



Atmospheric Chemical Disequilibrium: *Mars vs Earth*

Further from equilibrium



Closer to equilibrium

After 1 year

Simoncini, Brucato, Grassi, in preparation
Zahnle K., et al., JGR 113, 2008

Atmospheric extent of disequilibrium

Further studies

-> Mars atmosphere
-> Earth + fluxes (steady state)
-> Earth + simplified biosphere (decading L-V model)
-> Analysis of reaction pathways
-> Deeper analysis of sulfur chemistry
-> Influence of Sun luminosity variability

basis for habitability studies

-> Atmospheric spectra
-> Rocky and warm/hot exoplanets (new models)
-> Other Solar System planets and moons

Summary

- Entropy production is able to compute and uncouple the effect of different processes on the physico - chemical state of a planetary atmosphere
- Photochemistry has a main role in atmospheric disequilibrium
- The "disequilibrium footprint" of photosynthesis and photochemistry can be uncoupled
- Life uses free energy - otherwise used by photochemistry - to build up biomass
- Planets with a "disequilibrium footprint" by photochemistry lower than expected, are easier candidate to host complex chemical processes [¿life?]
- Mars disequilibrium is very very low

Grazie per l'attenzione!

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