V Congresso Società Italiana di Astrobiologia
15-17 September 2015
Trieste, Italy

Disequilibrium in planetary atmospheres and the search for habitability

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

KROME better science through chemistry

Overview of this talk

- What is chemical disequilibrium
- How to calculate disequilibrium in chemical processes
- Atmospheric Disequilibrium of Earth
- Further applications

Introduction

What is chemical disequilibrium, and why should we use it

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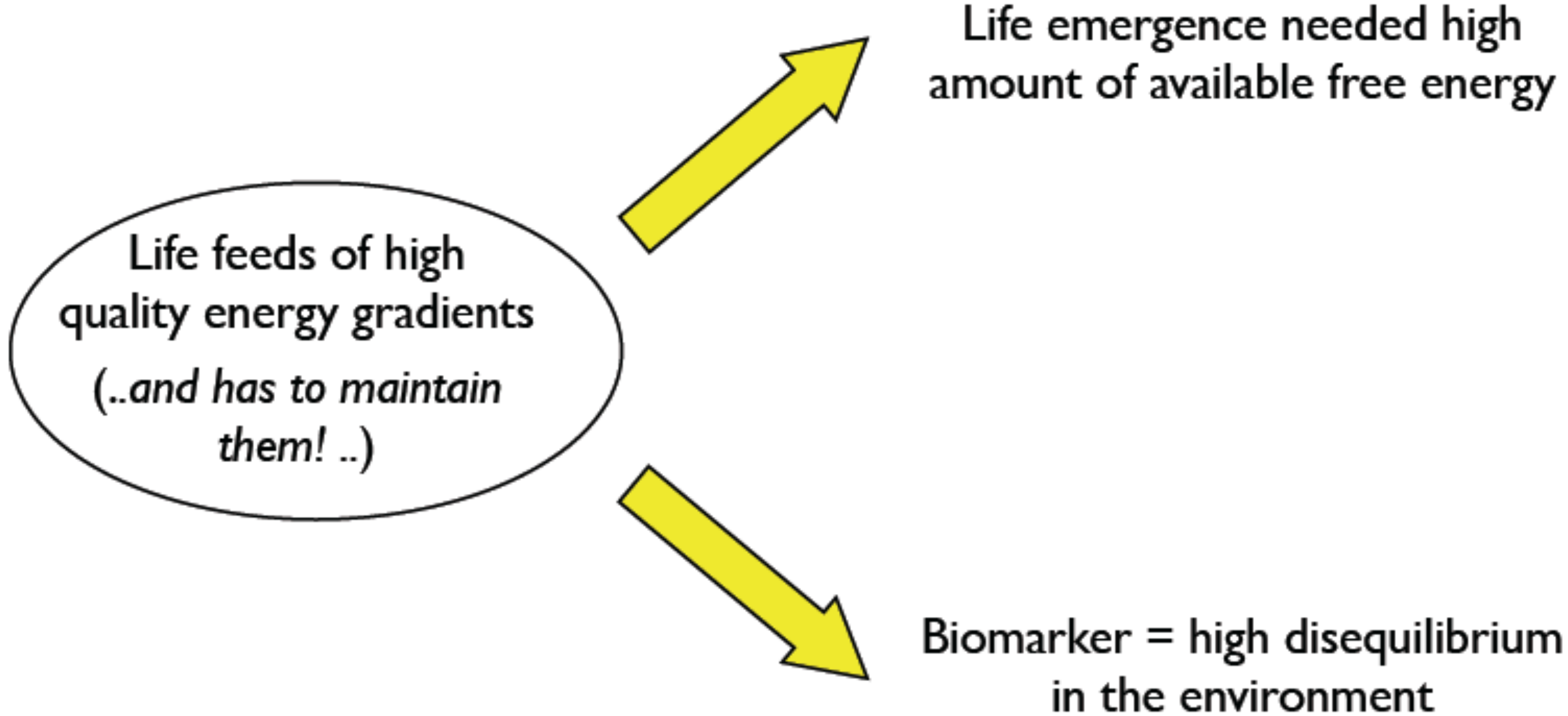
Titania may produce abiotic oxygen atmospheres on habitable exoplanets

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

Received: 31 March 2015
Accepted: 12 August 2015
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)

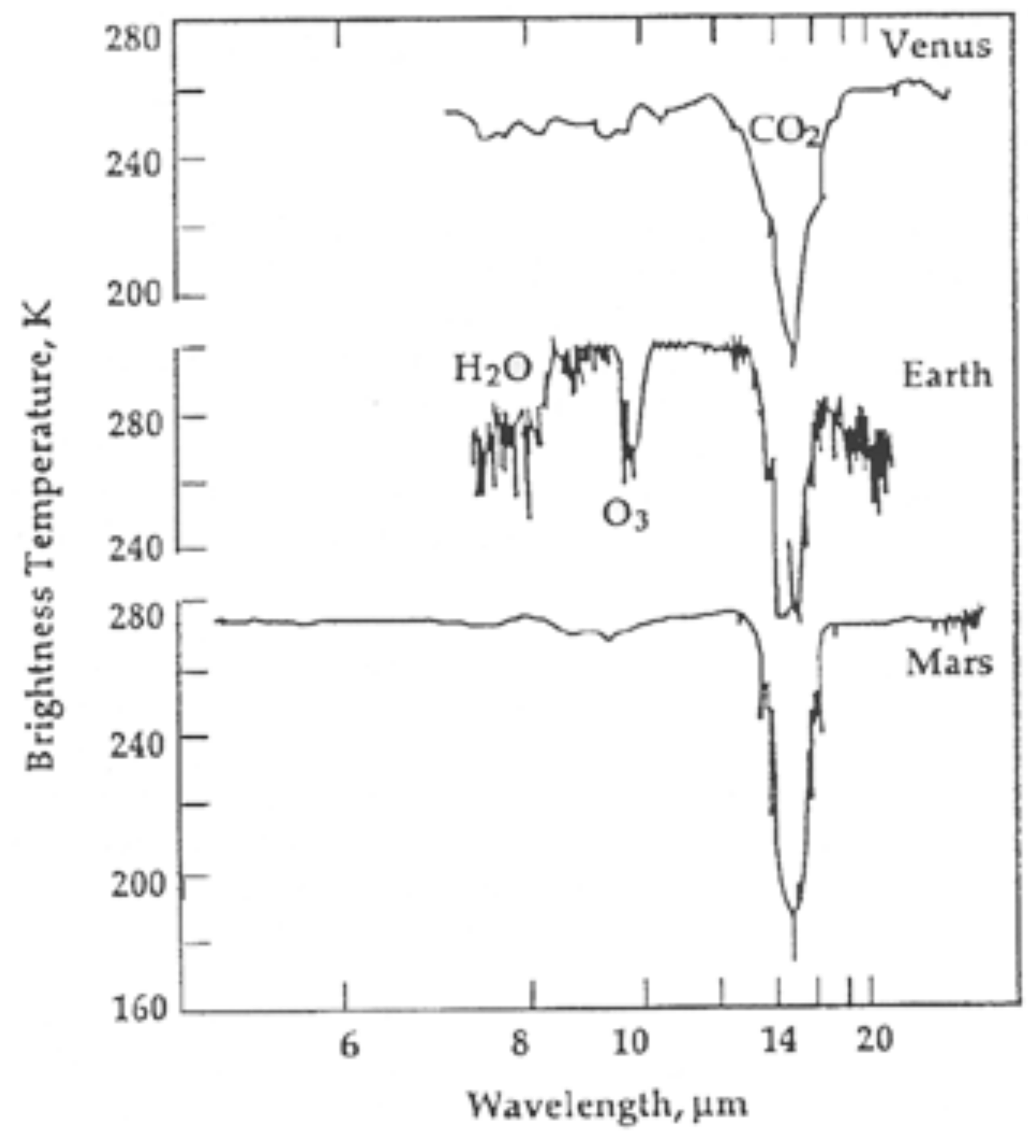
"Life feeds of high quality energy gradient" (Schrödinger, 1944)

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]

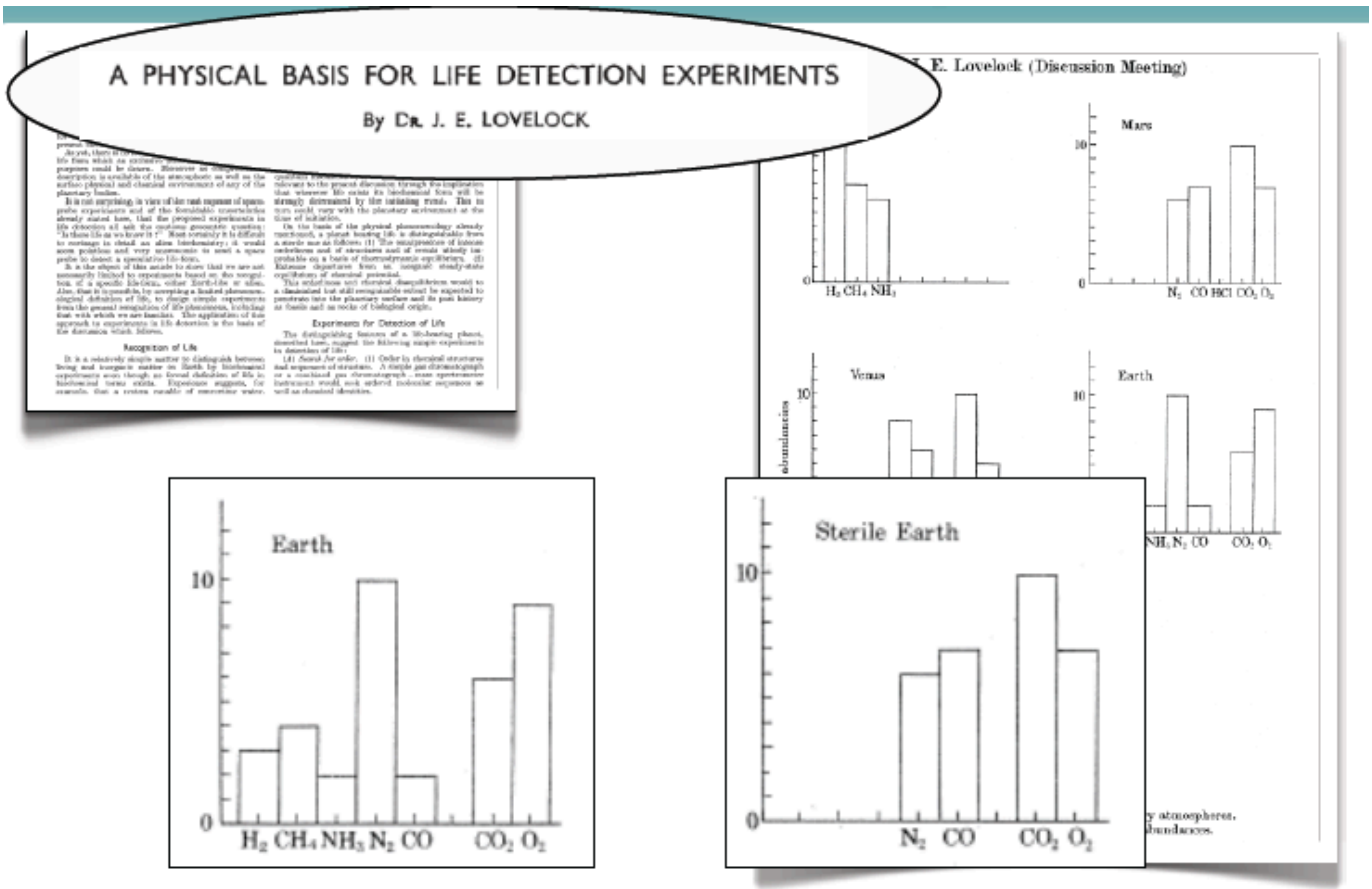


"*Once candidate disequilibria are identified, alternative explanations must be eliminated. Life is the hypothesis of last resort*" (Sagan et al., 1993)

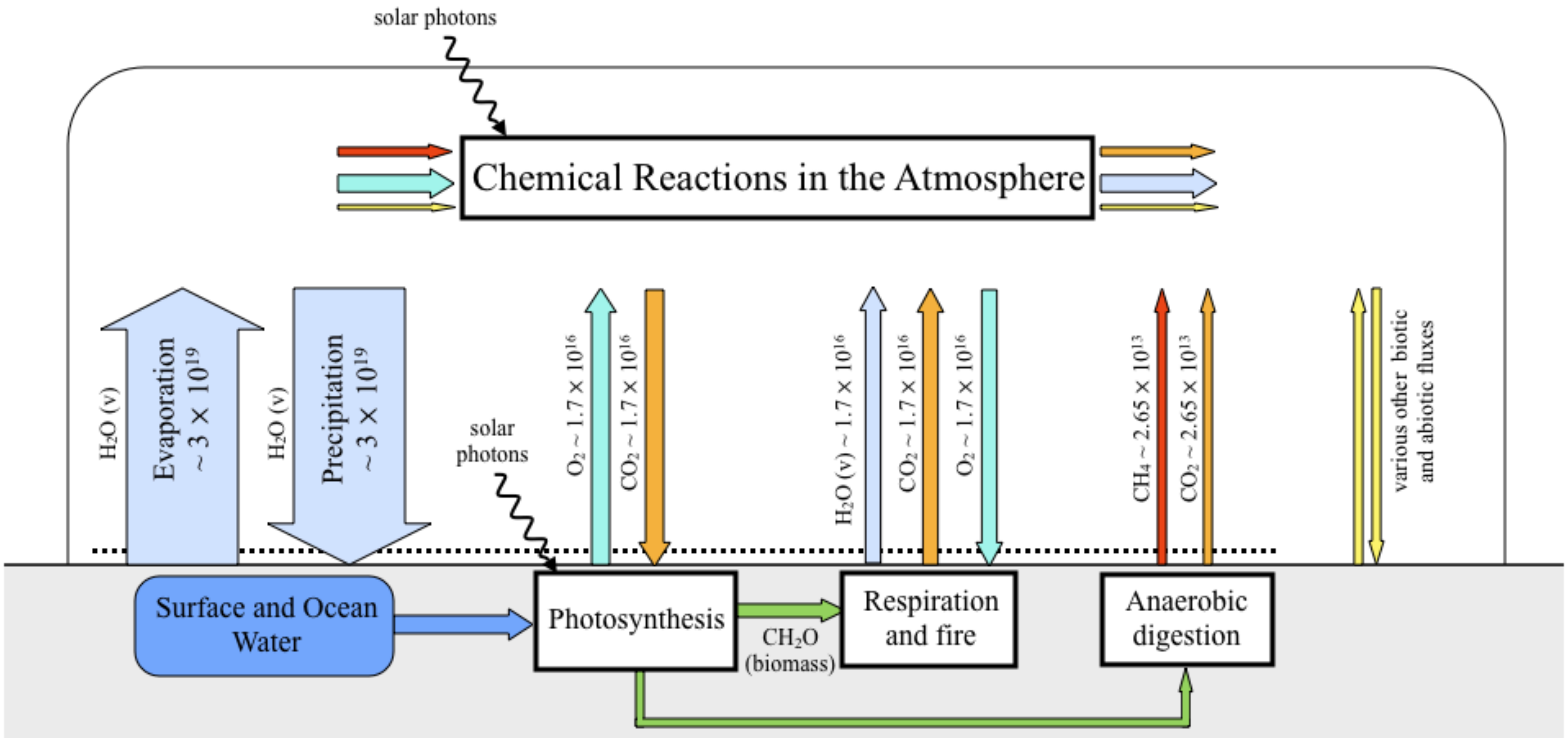
Simoncini E., Kleidon A., Gallori E., J. of Cosmology, Sept. 2010

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

Atmospheric Chemical Disequilibrium



Earth's methane disequilibrium



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

About 0.43 TW are given by living processes (animal enteric fermentation, 0.13TW; rice paddies 0.09TW).

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

Atmospheric Chemical Disequilibrium

$CO_2 + H_2O$ -> $CO + 3\ H_2$

$$\alpha(f_i, P) = \frac{f_{CH_4} f_{H_2O}}{f_{CO} f_{H_2}^3 P^2} = K_{eq}(T)$$

$$K_{eq}(T) = e^{-\Delta G/RT} = e^{-(\Delta H/RT - \Delta S/R)}$$

Line, M. R., Yung Y. L., ApJ 2013a
Line, M. R., Yung Y. L., ApJ 2013b
Line, M. R., Yung Y. L., ApJ 2013c

C\O ratio - Madhusudhan N., ApJ, 758:36, 2012

How to calculate (and compare) disequilibrium in chemical processes

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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:

$$d_iS/dt$$

Kondepudi & Prigogine, Modern Thermodynamics, 1998.

The extent of chemical disequilibrium

$$\frac{d_i S}{dt} = J \cdot X = \frac{d\xi}{dt} \cdot \frac{\alpha}{T}$$

Extent of reaction:

$$\xi(t) = \frac{[A]_0 - [A](t)}{\nu_A}$$

Chemical Affinity

$$\alpha(t) = -\left(\frac{\partial \Delta_r G(t)}{\partial \xi}\right)_{T,p}$$

It can be also written as:

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

R_f = forward rate

R_r = backward rate

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

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

www.kromepackage.org

Atmospheric disequilibrium of the Earth

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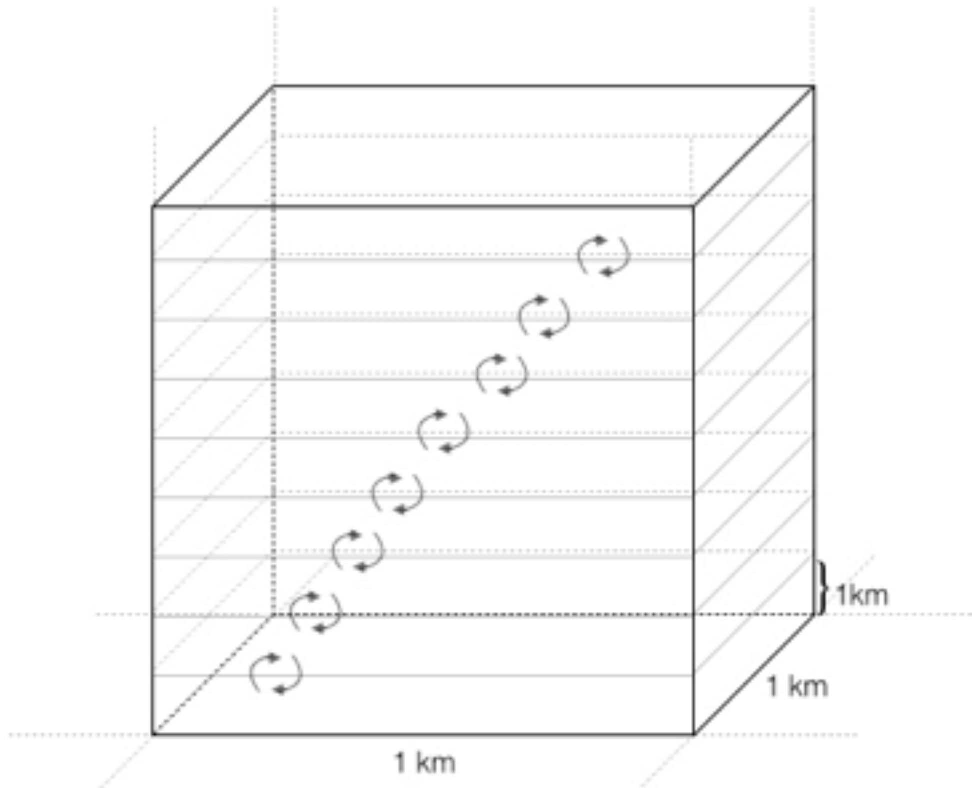
Earth Atmospheric Chemical Disequilibrium

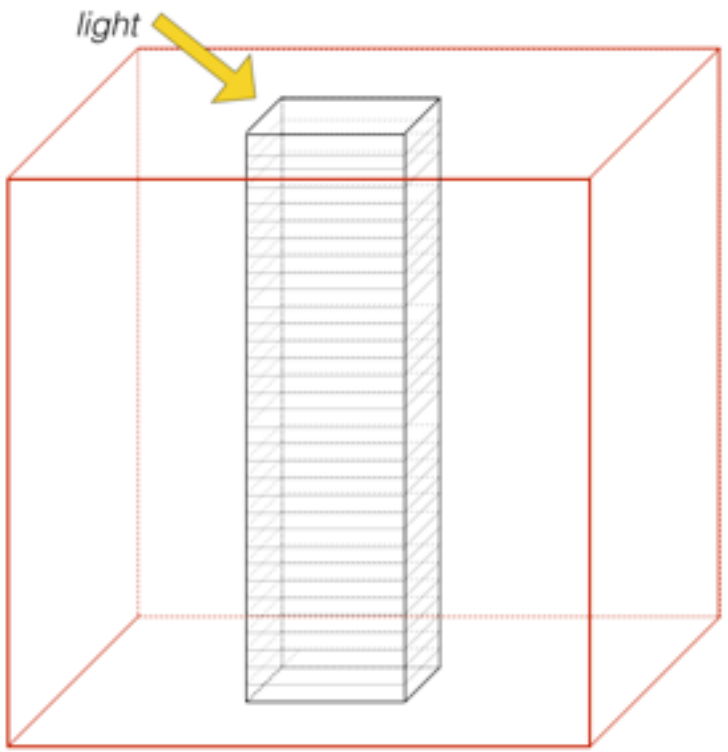
* Model: Kasting, J. F., and Donahue, T. M., J. Geophys. Res., 85,3255-3263. 1980 (K-80);

* 64 layers (~1km each);

* Eddy diffusion;

* Entropy production and the power dissipation:



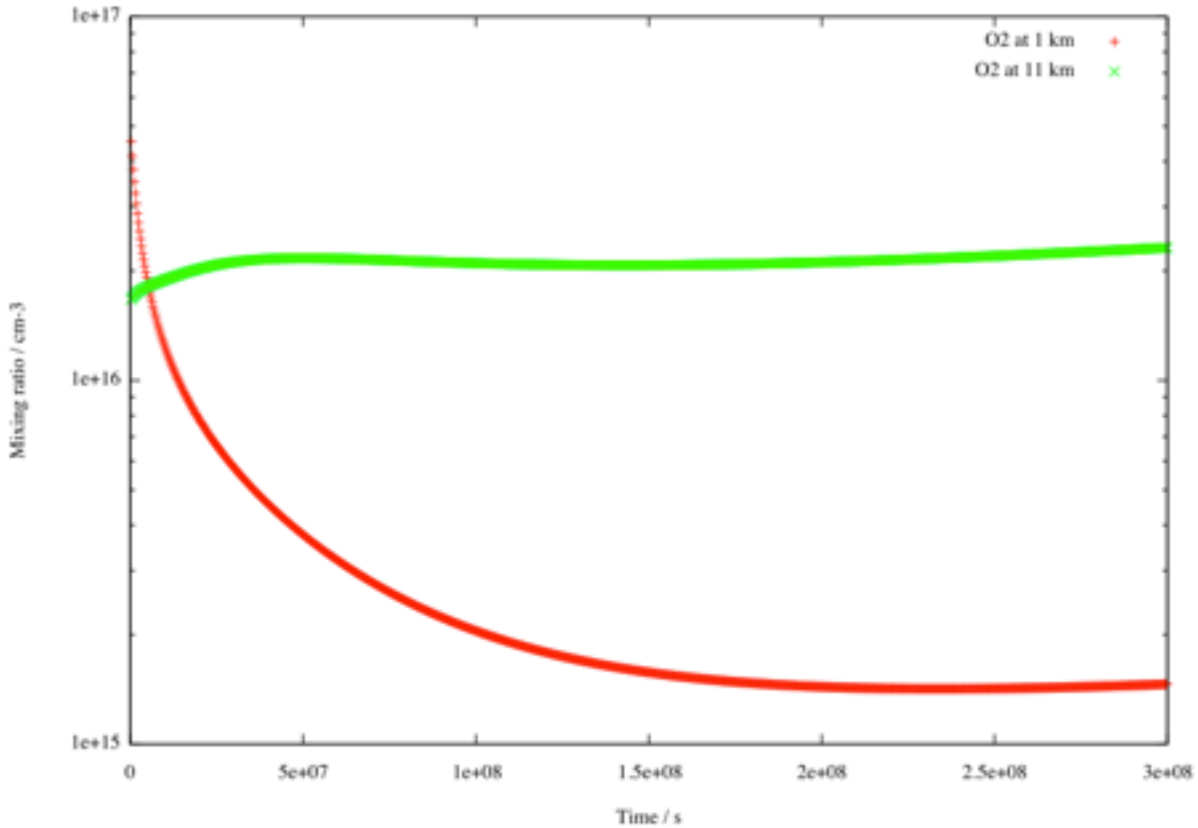


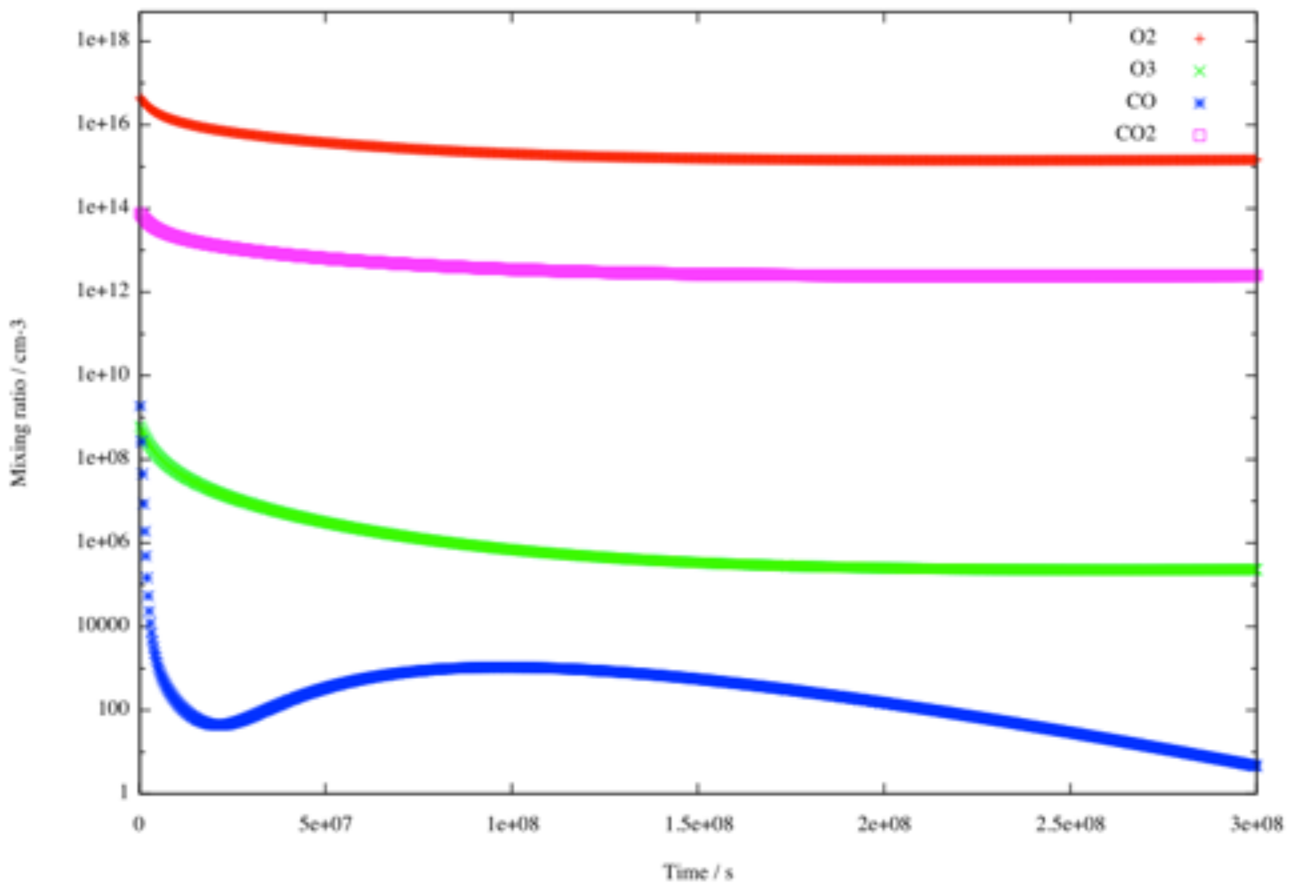
$$\sigma = \frac{d_i S}{dt}$$

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

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





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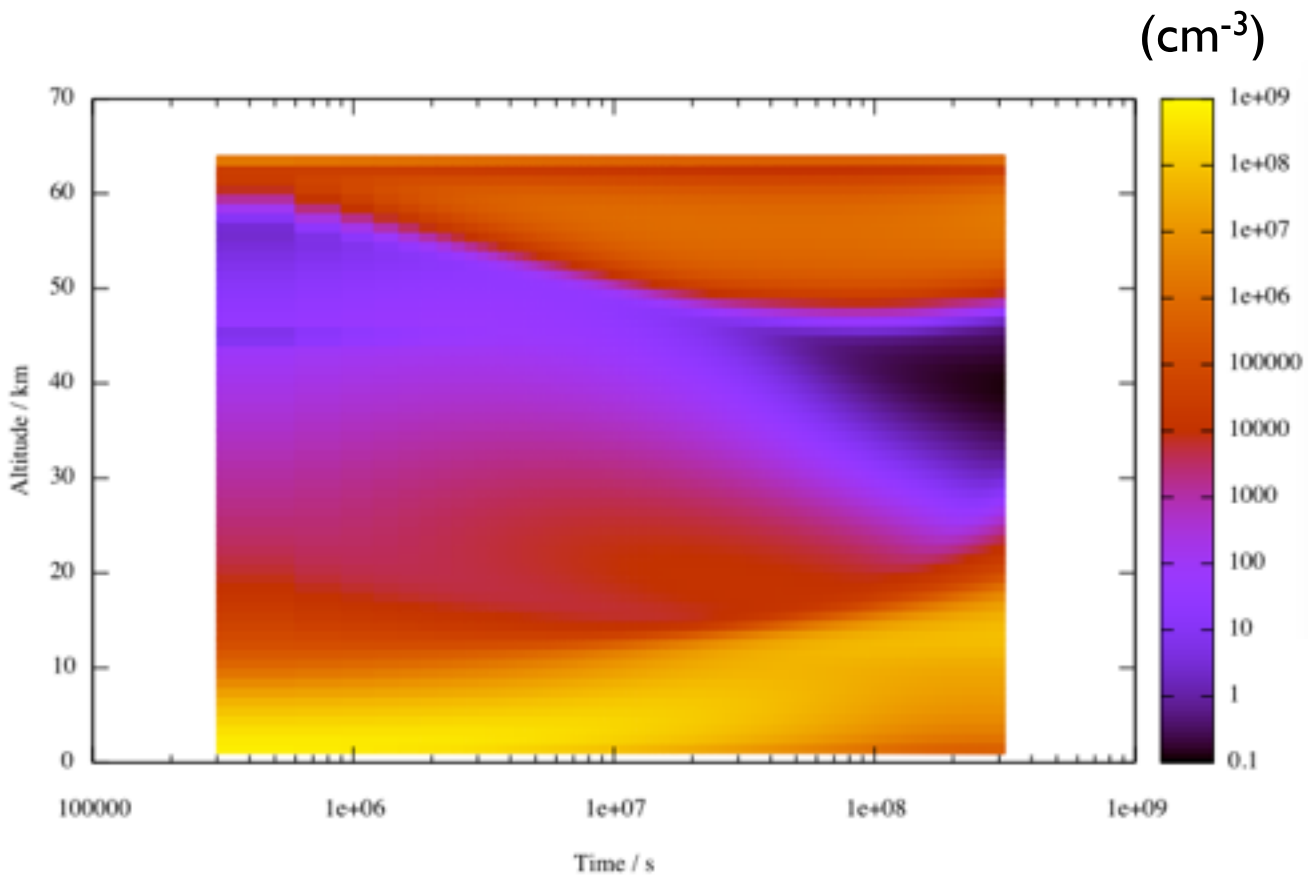
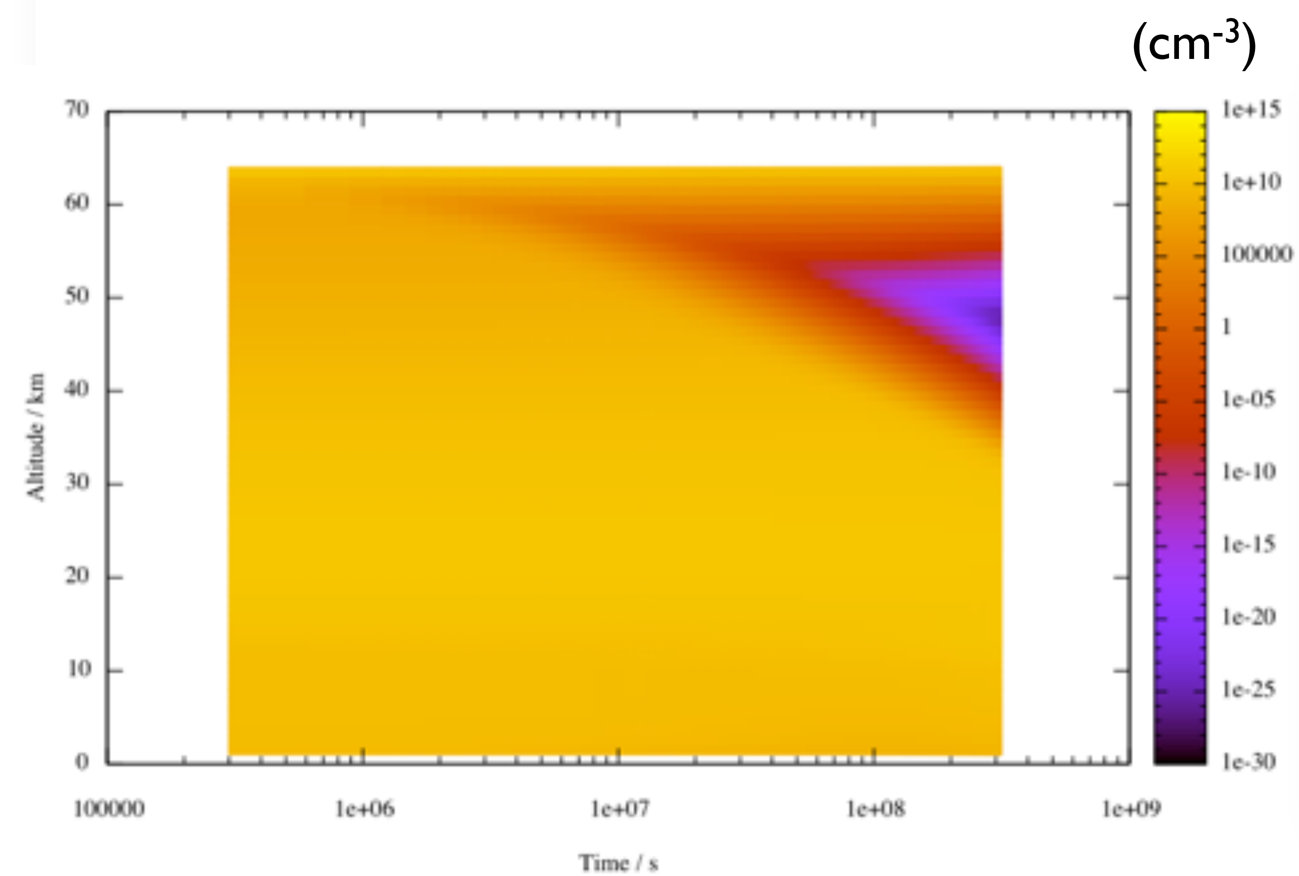
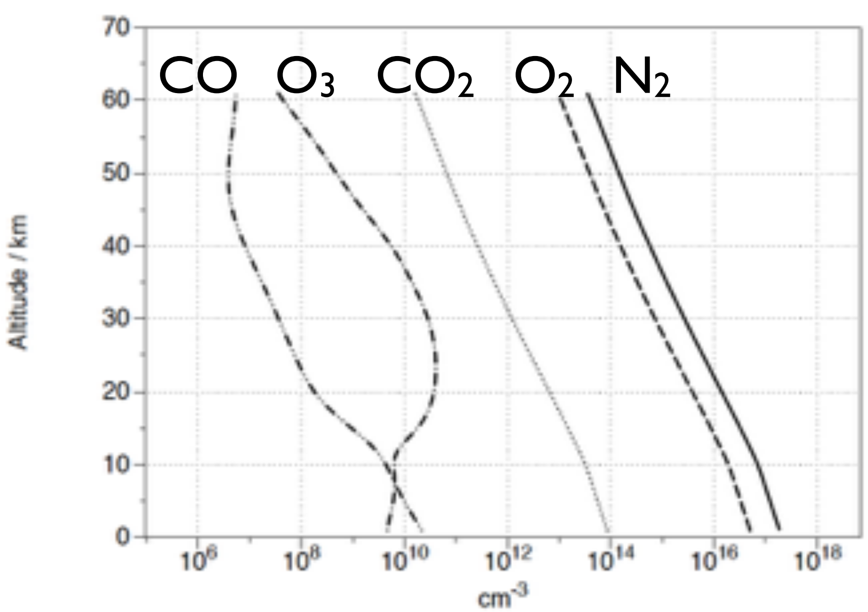
Earth Atmospheric Chemical Disequilibrium



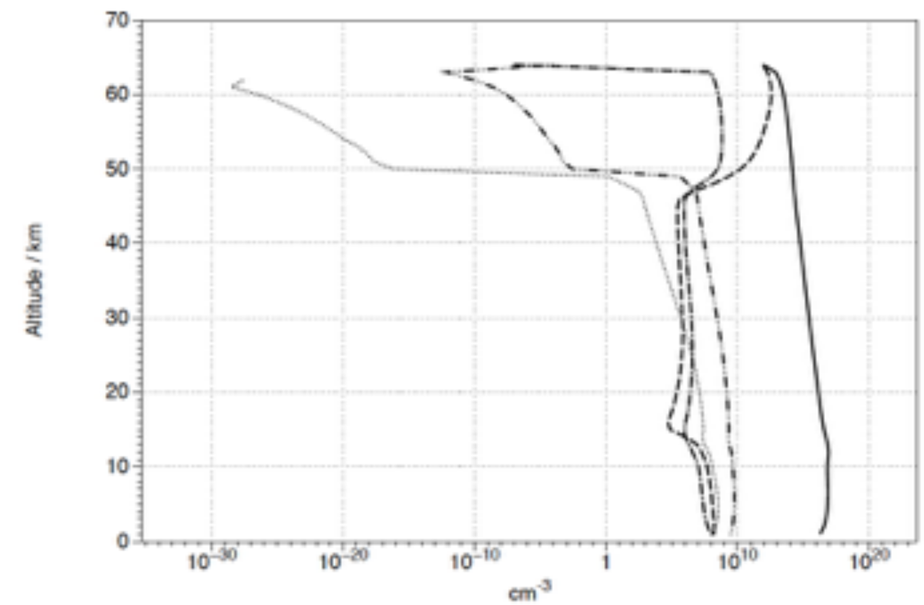
O_3



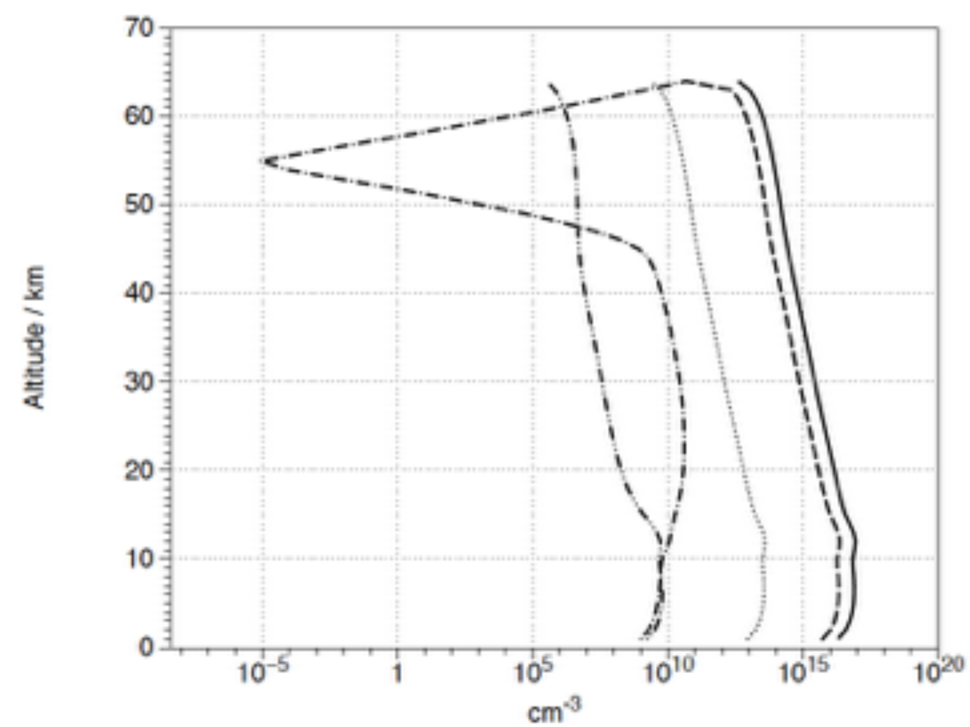
Earth Atmospheric Chemical Disequilibrium



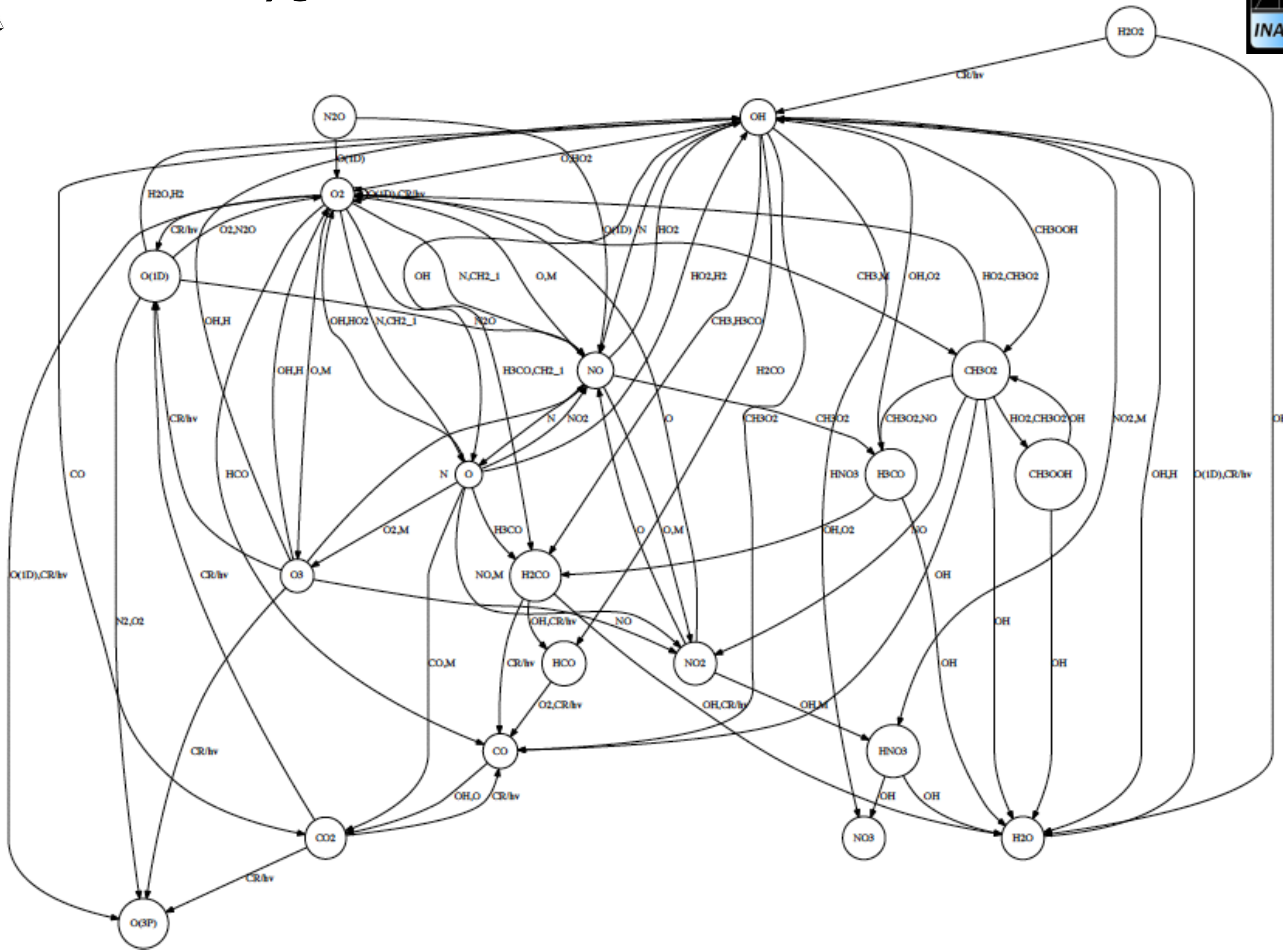
full model



no photochemistry



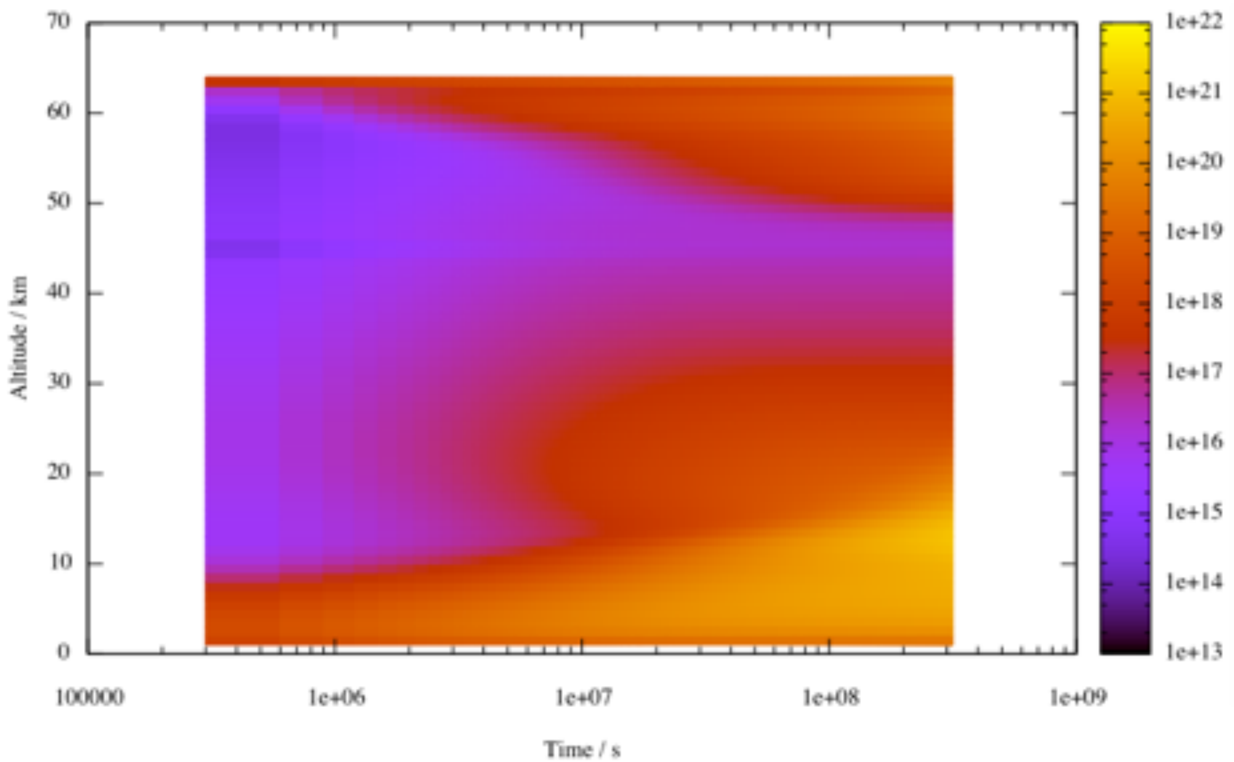
Oxygen reactions in the K-80 network



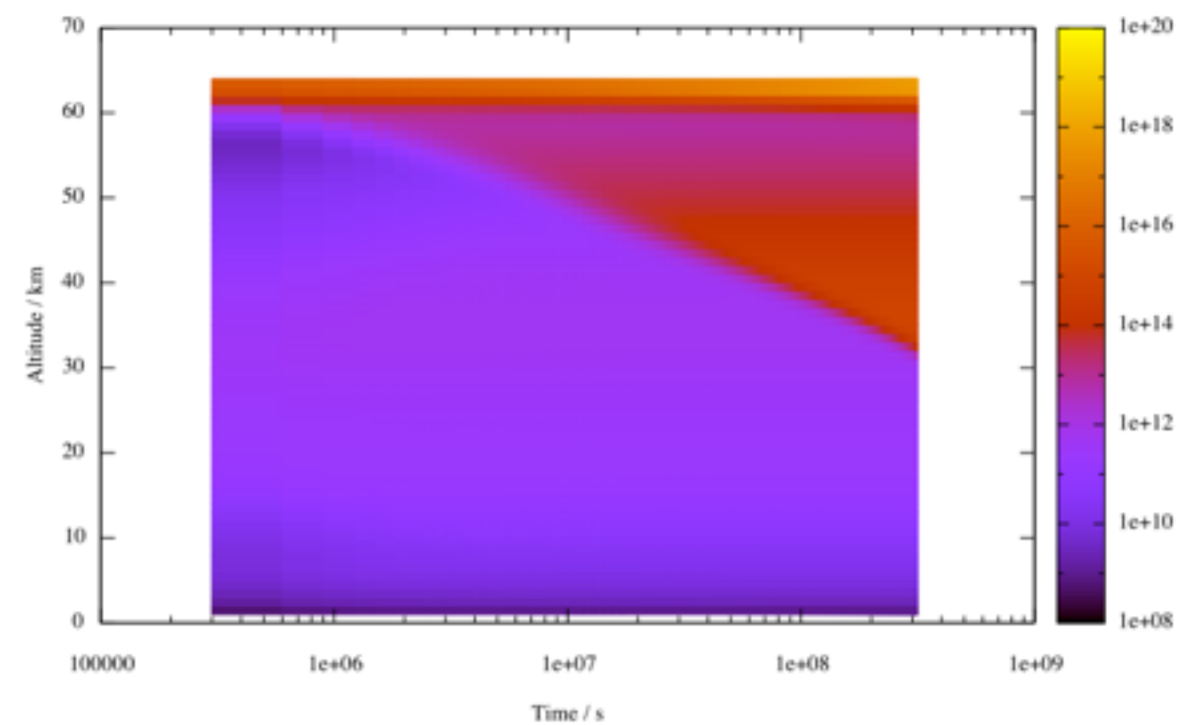
Earth Atmospheric Chemical Disequilibrium

The energetic structure

Present Earth



Present Earth
without photochemistry



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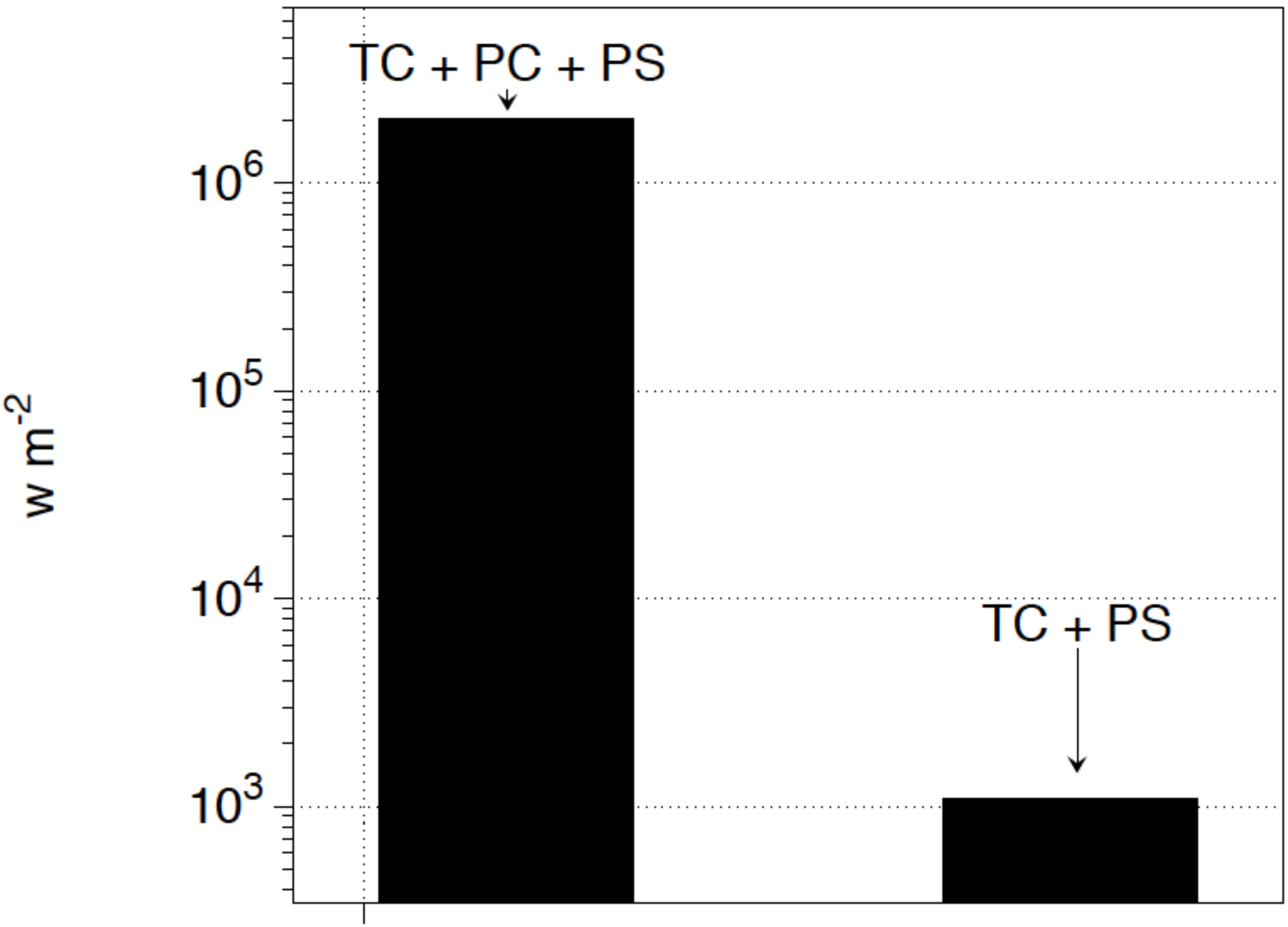
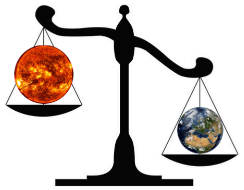
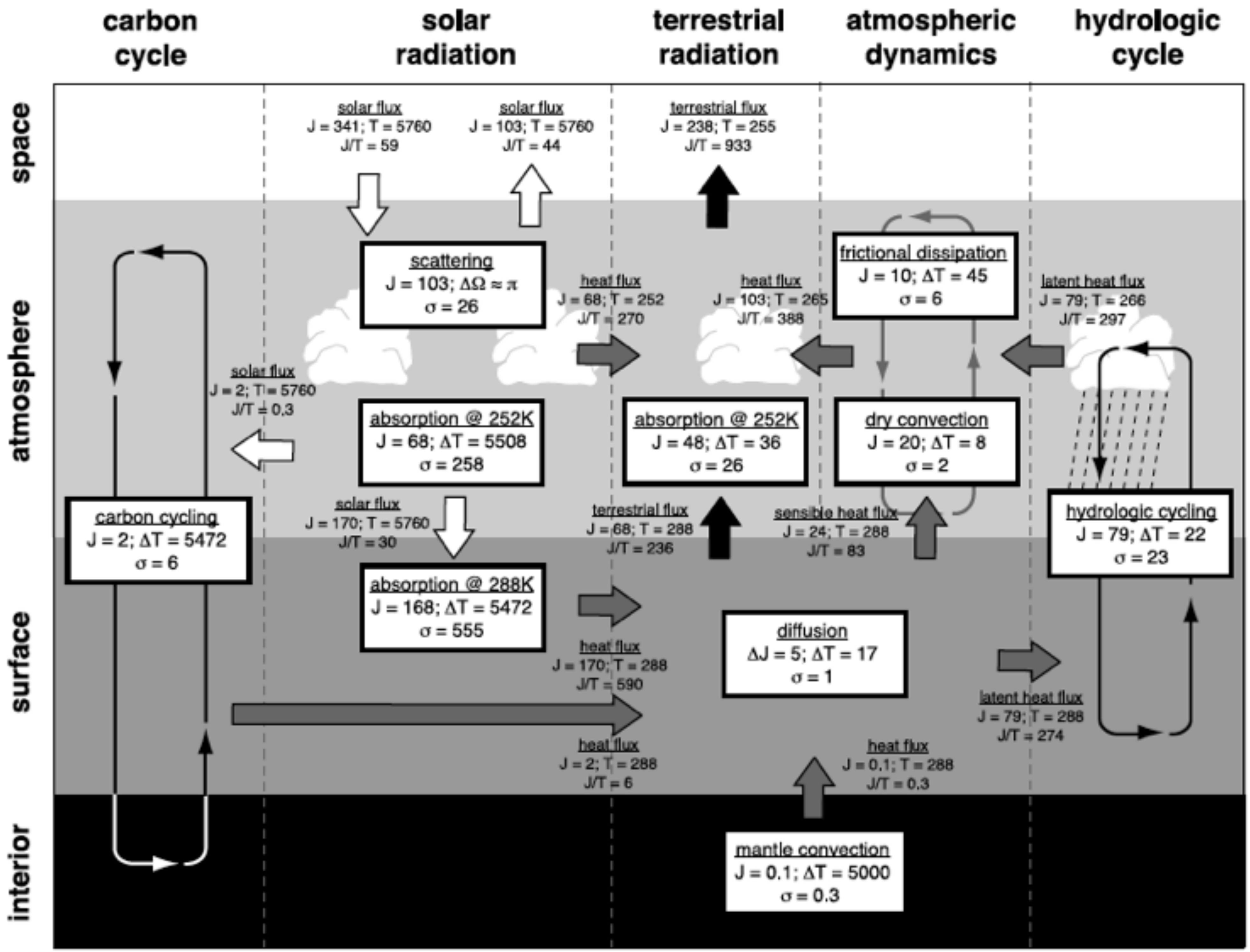
Earth Atmospheric Chemical Disequilibrium



Earth Powers

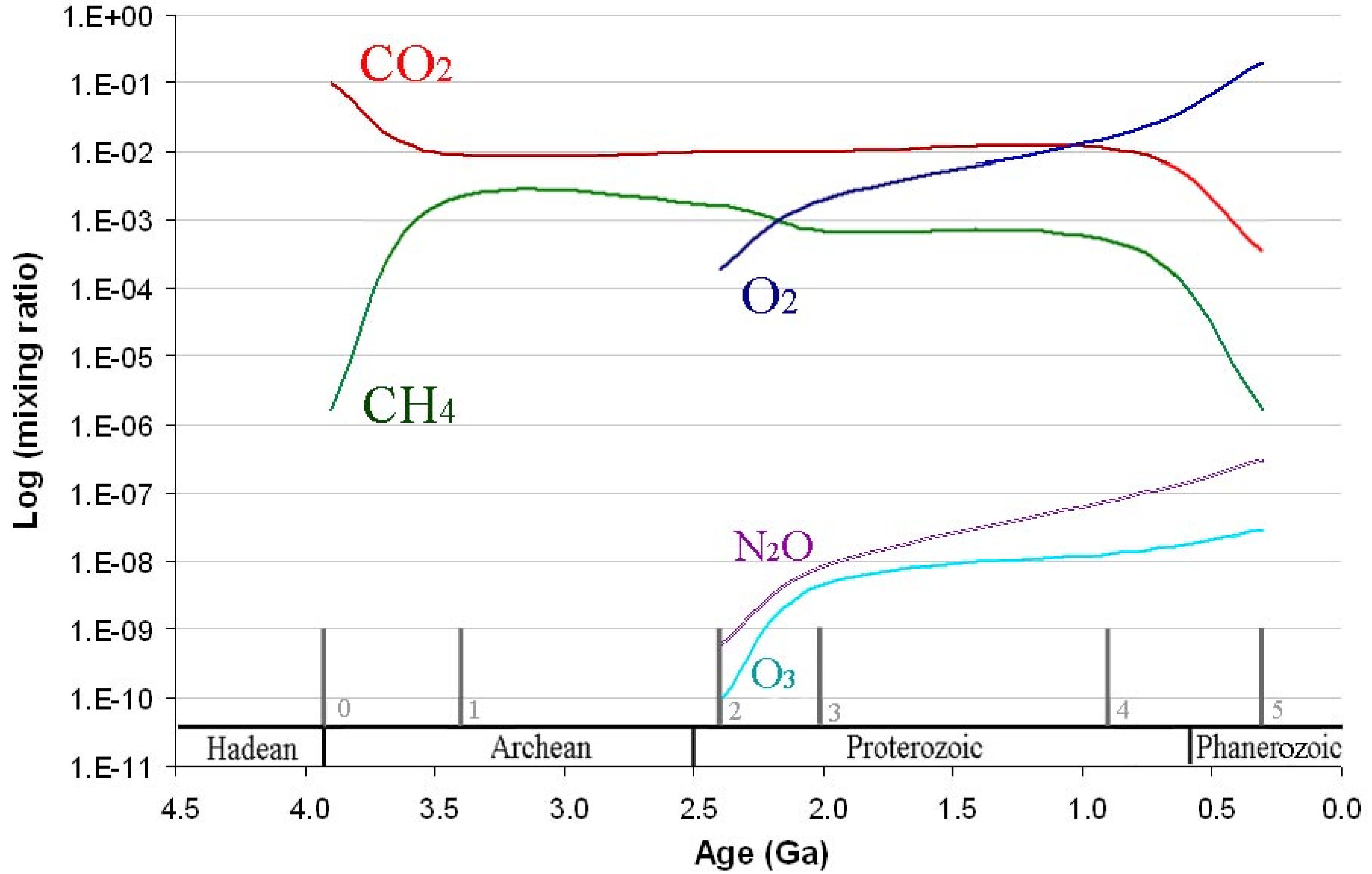




J ~W m^{-2}

Kleidon A., Physics of Life Reviews, 7, 2010. 424-460

Earth Atmospheric Chemical Disequilibrium

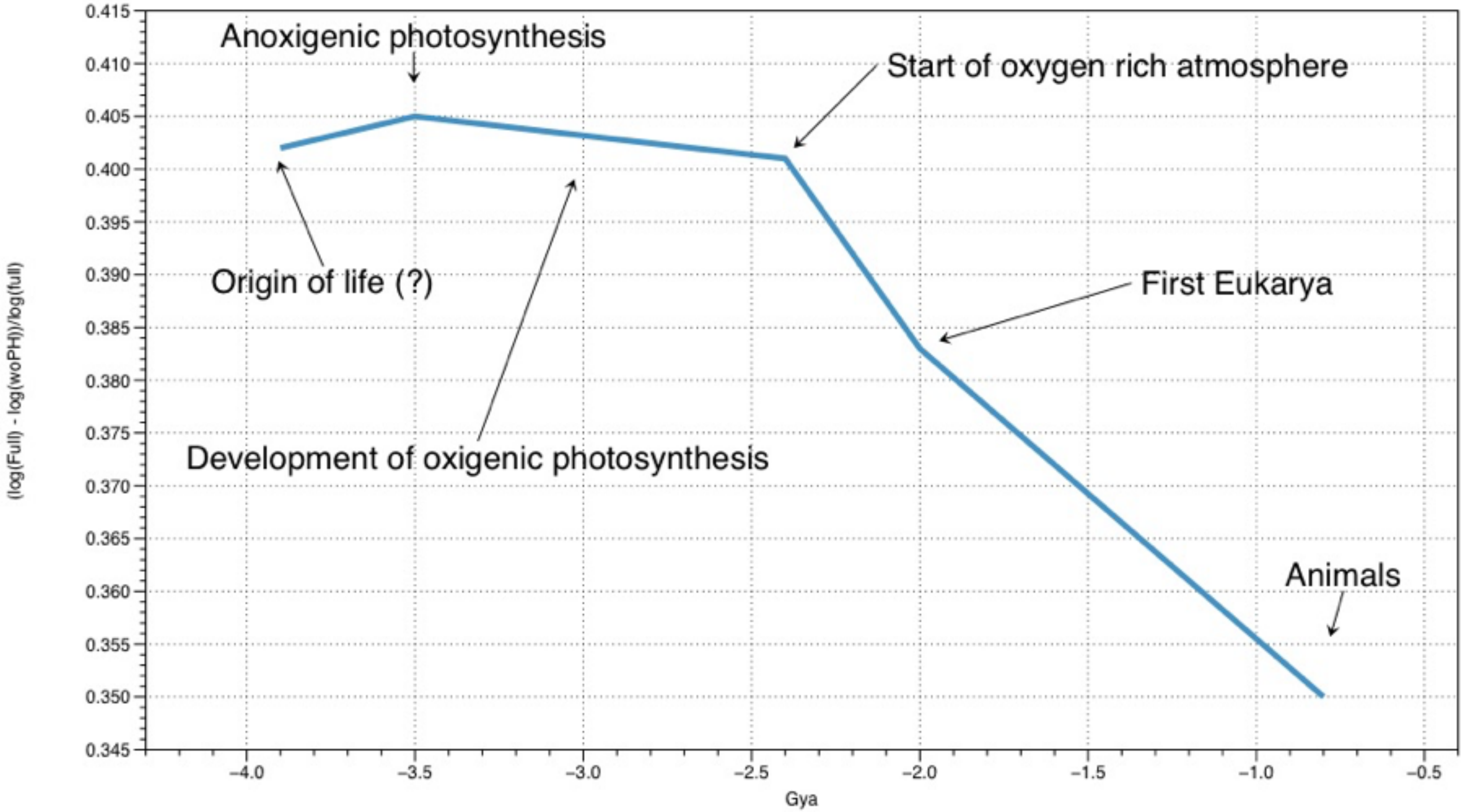


Epoch	Age (Ga)	CO_2 (mixing ratio)	CH_4 (mixing ratio)	O_2 (mixing ratio)	O_3 (mixing ratio)	N_2O (mixing ratio)
0	3.9	1.00E-01	1.65E-06	0	0	0
1	3.5	1.00E-02	1.65E-03	0	0	0
2	2.4	1.00E-02	7.07E-03	2.10E-04	8.47E-11	5.71E-10
3	2.0	1.00E-02	1.65E-03	2.10E-03	4.24E-09	8.37E-09
4	0.8	1.00E-02	4.15E-04	2.10E-02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



Simoncini, Brucato, Grassi, in preparation
Kaltenegger et al., ApJ 658, 598, 2007

Further studies

-> Earth + fluxes (steady state)
-> Earth + simplified biosphere (not stable LV model)
-> Analysis of reaction pathways
-> Deeper analysis of sulfur chemistry
-> Influence of Sun luminosity variability

basis for habitability studies

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

KROME + Planetary Atmosphere Applications

Modeling exoplanets with KROME

+ Y. Miguel
Observatoire de Côte d’Azur, Nice, France

Miguel, Y, Simoncini, E., *in prep.*

Hot rocky exoplanet

* $M = 10 \cdot M_e$
* Star = Sun (T_{superf} = 5777 K)
* T ~ 2200 K (temperature profile by Ito et al., *ApJ* **801** 144, 2015)
* 30 species from accretion (Y. Miguel code)
  —> part of them condensates

* Build-up abundances and pressure profile using the Scale Height:

$$H = \frac{k_b T}{M g}$$

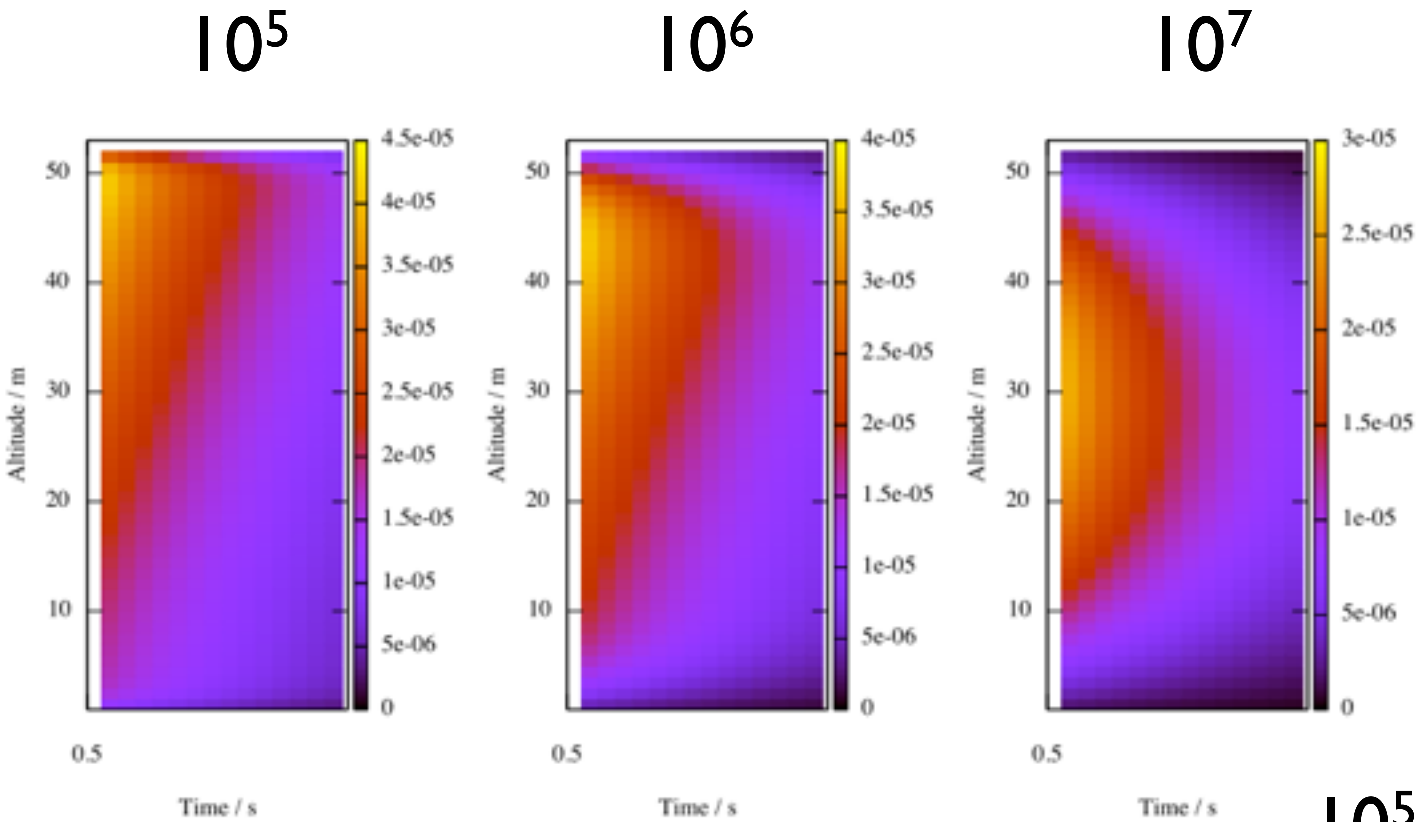
* Using the T, p conditions, take out not gaseous species
* $K_{zz} = 10^6$ (low Martian atmosphere)
* Build-up the network: NIST, KIDA, exoplanets literature, Mercury atmosphere

Miguel, Y, Simoncini, E., *in prep.*

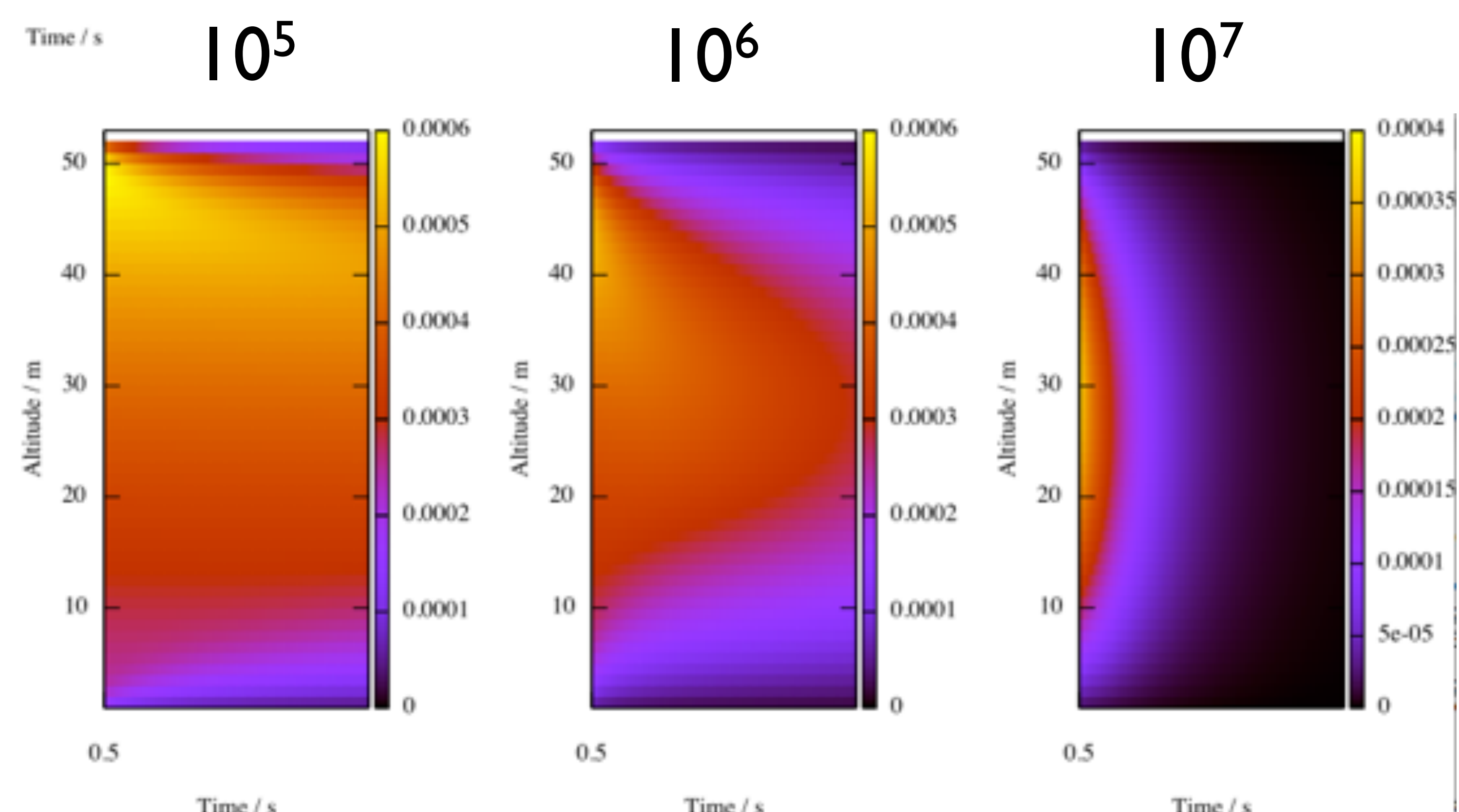
=> 45 reactions

Hot rocky exoplanet: effect of diffusion

$K_{zz} \sim$ cm^2 /s



O_2



Na

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Miguel, Y, Simoncini, E., *in prep.*

Grazie per l'attenzione!

J. R. Brucato, Astrophysical Observatory of Arcetri - INAF, Firenze, Italy

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...And all the members of the TDE Focus Group