Observatoire Côte d'Azur - 18th March 2014

# Comparing atmospheric chemical disequilibrium of Earth and Mars to detect the traces of Life

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NASA ASTROBIOLOGY INSTITUTE

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

KROME better science through chemistry

INAF - Arcetri

# *Who I am*

* *Co-Chair of the "Thermodynamics, Disequilibrium and Evolution" NAI Focus Group*

* Astrophysical Observatory of Arcetri, INAF, Firenze, Italy
=> Atmospheric habitability; hydrothermal vents thermodynamics; life/habitability detection devices for space missions (May 2013)

* Centre of Astrobiology, INTA-CSIC, Madrid, Spain (2012)

* Max Planck for Biogeochemistry, Jena, Germany (2010 - 2012)

2010 PhD in Chemical Sciences *(Physical Chemistry; chemical oscillators; thermodynamics; excitable media)*.

2006 Master Degree in Chemistry for Sustainable Development *(Environmental Chemistry; "evolutive" thermodynamics; environmental accounting for land, productions and bioarchitecture)*.

2004 Bachelor Degree in Chemistry *(Green Chemistry; Supercritical fluids; Ionic Liquid; efficiency management)*.

(University of Siena, Italy)

## *Current projects*

- Atmospheric chemical disequilibrium
- Life emergence by *chemiosmosis* in hydrothermal vents
- Mars surface and sub-surface disequilibrium
- Adsorption of molecules on minerals
- Planetary protection

# Overview of this talk

- What is chemical disequilibrium

- How to calculate disequilibrium in chemical processes

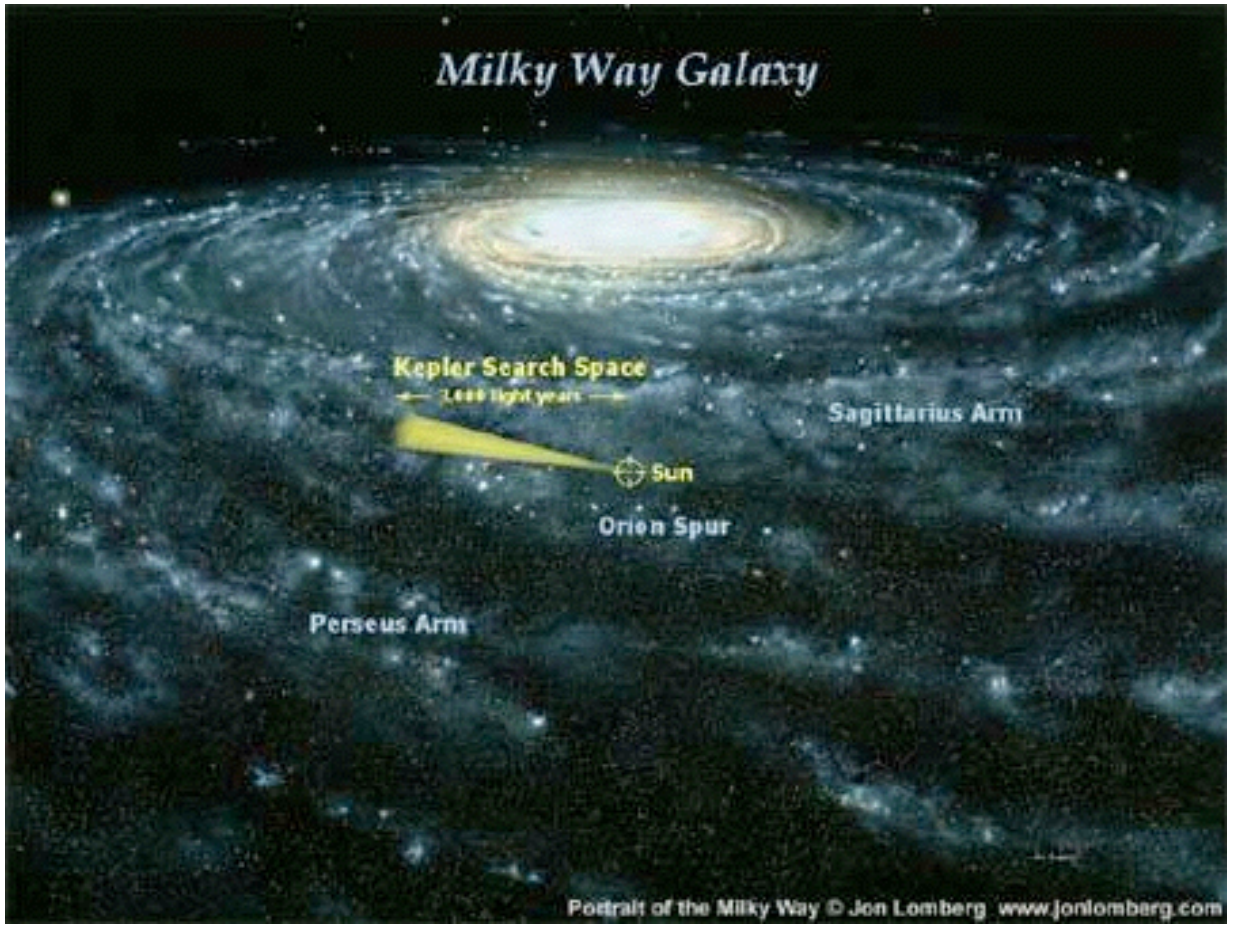
- Atmospheric Disequilibrium of Earth and Mars

Introduction

*What is chemical disequilibrium, and why should we use it*

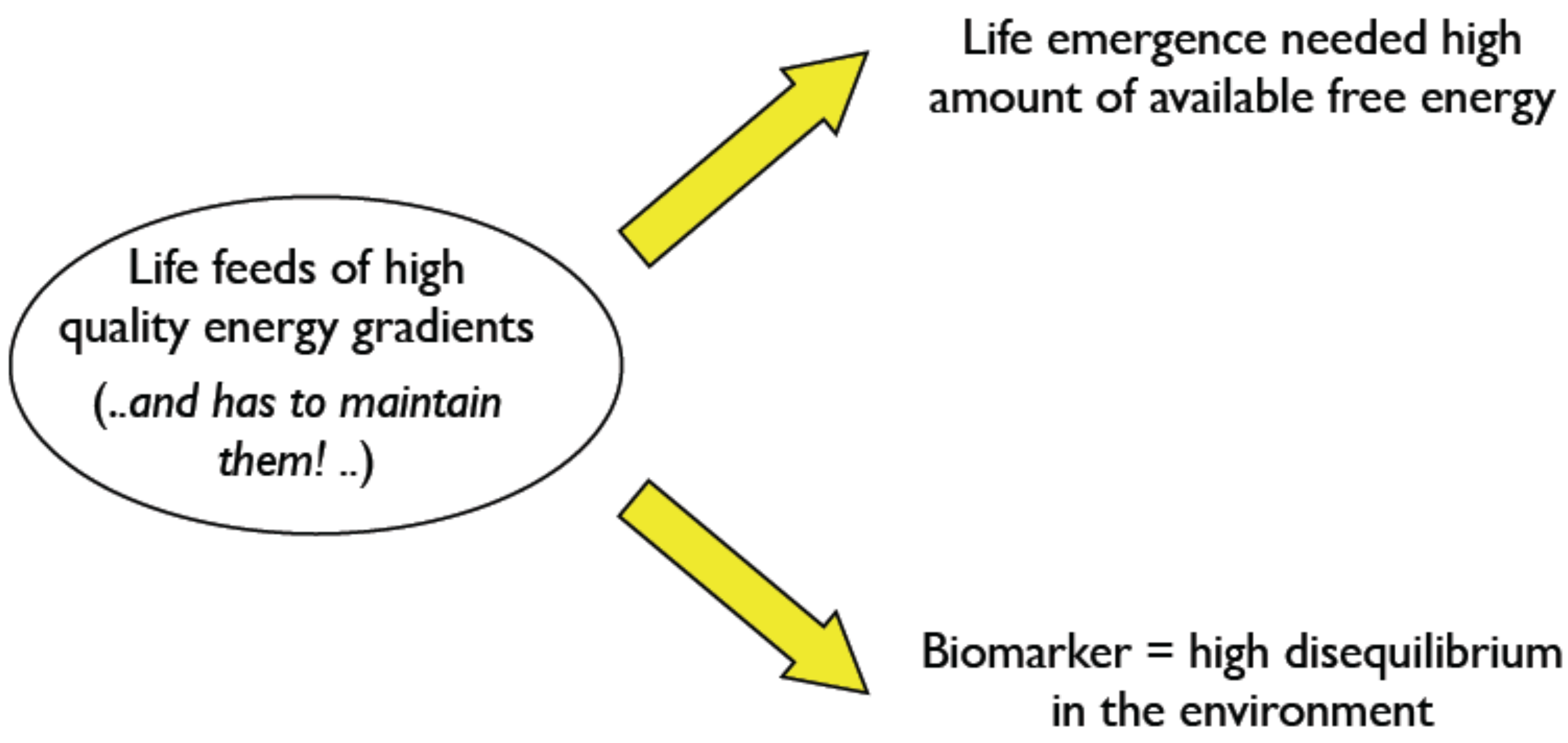
# Life and Biomarkers

- no signs for complex molecules
- simple molecules spectra




Jim E. Lovelock, *Nature* **207**, 568 (1965), about life:
"search for the presence of compounds in the planet's atmosphere that are incompatible on a long-term basis"

# Life & Disequilibrium

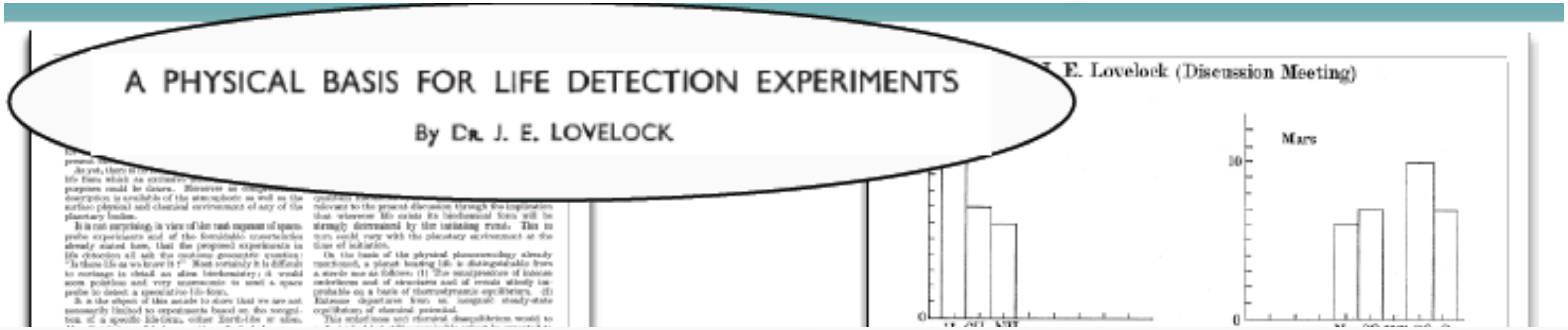



*"The general struggle for existence of animate being is struggle for entropy, which becomes available through the transition of energy from the hot sun to the cold earth"* (Boltzmann, 1886)

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

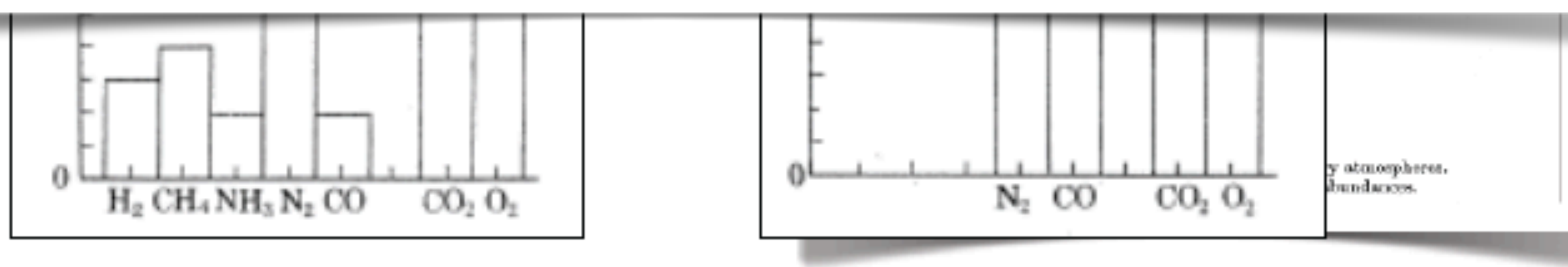
"*Once candidate disequilibria are identified, alternative explanations must be eliminated. Life is the hypothesis of last resort*" (Sagan et al., 1993)

# Atmospheric Chemical Disequilibrium

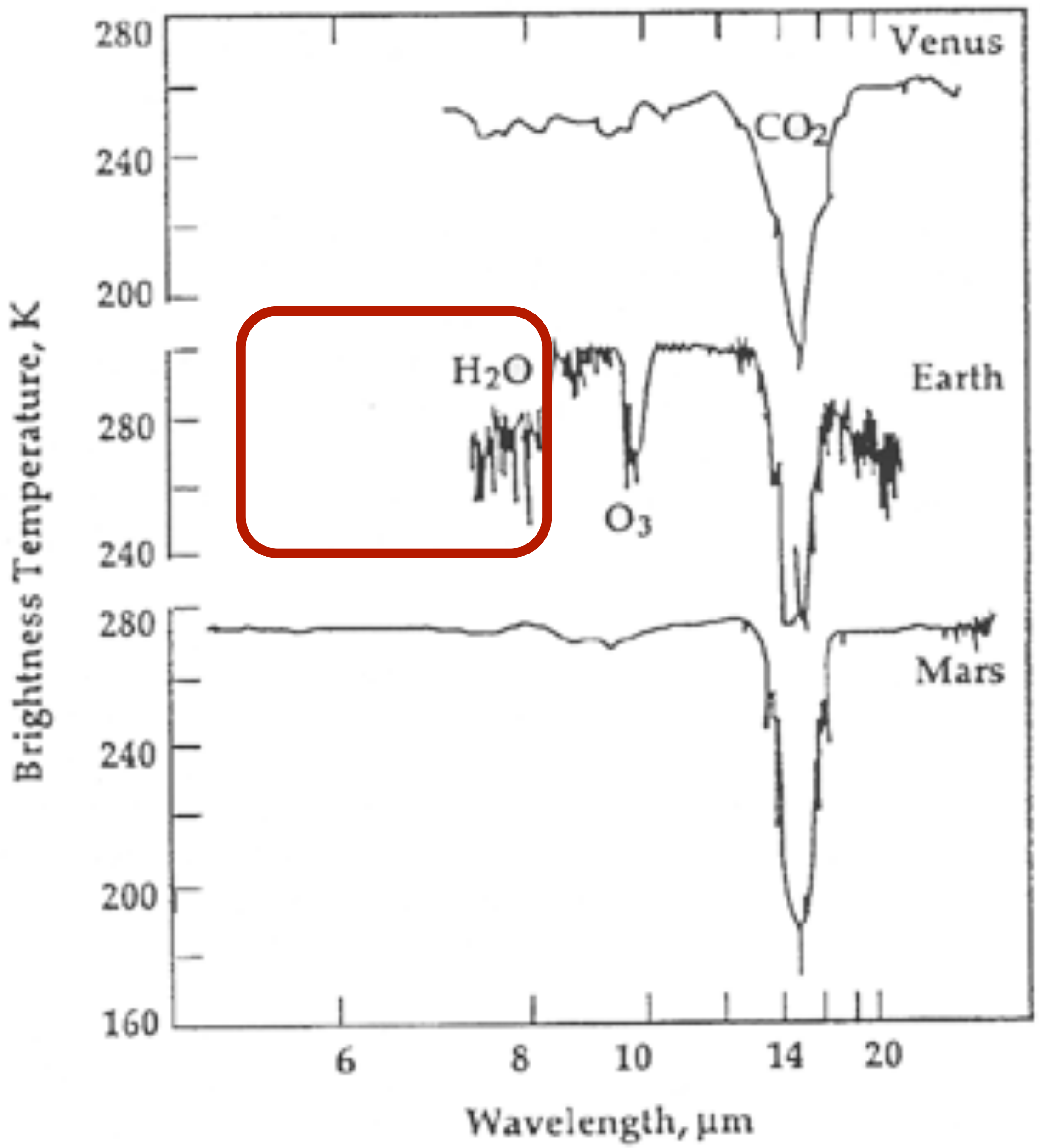



* Quantify the extent of chemical disequilibrium

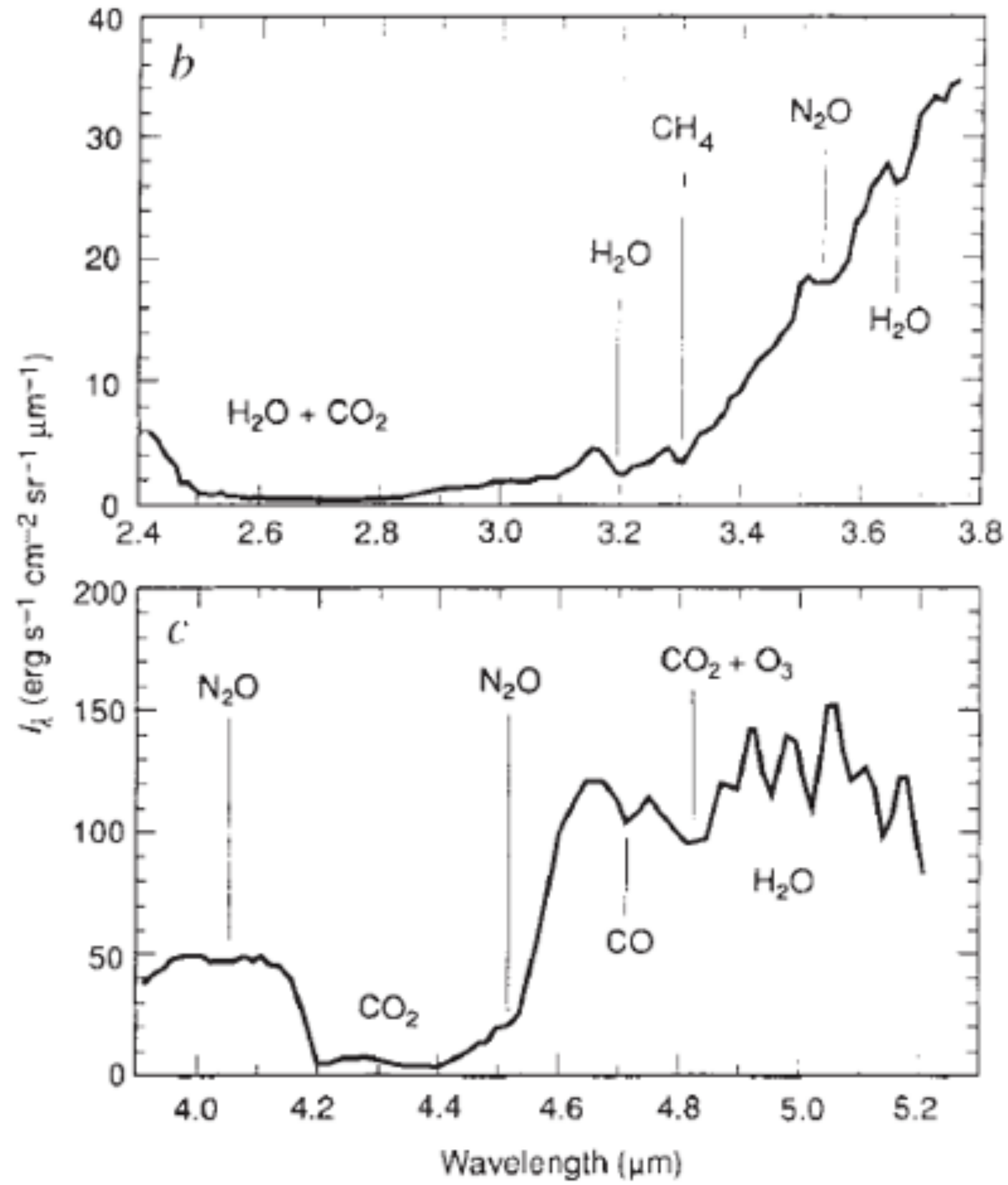
* Consider other kind of chemical disequilibrium and different sources:
  - Fast vertical mixing *vs.* chemical kinetics (Hot Jupiters)
  - $O_2/O_3$ in Mars, Venus



# Atmospheric Chemical Disequilibrium and Life




*Earth*




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

# How to calculate (and compare) disequilibrium in chemical processes

# *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:

$$d_iS/dt$$

# *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:

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

$$R_f = \text{forward rate}$$

$$R_r = \text{backward rate}$$

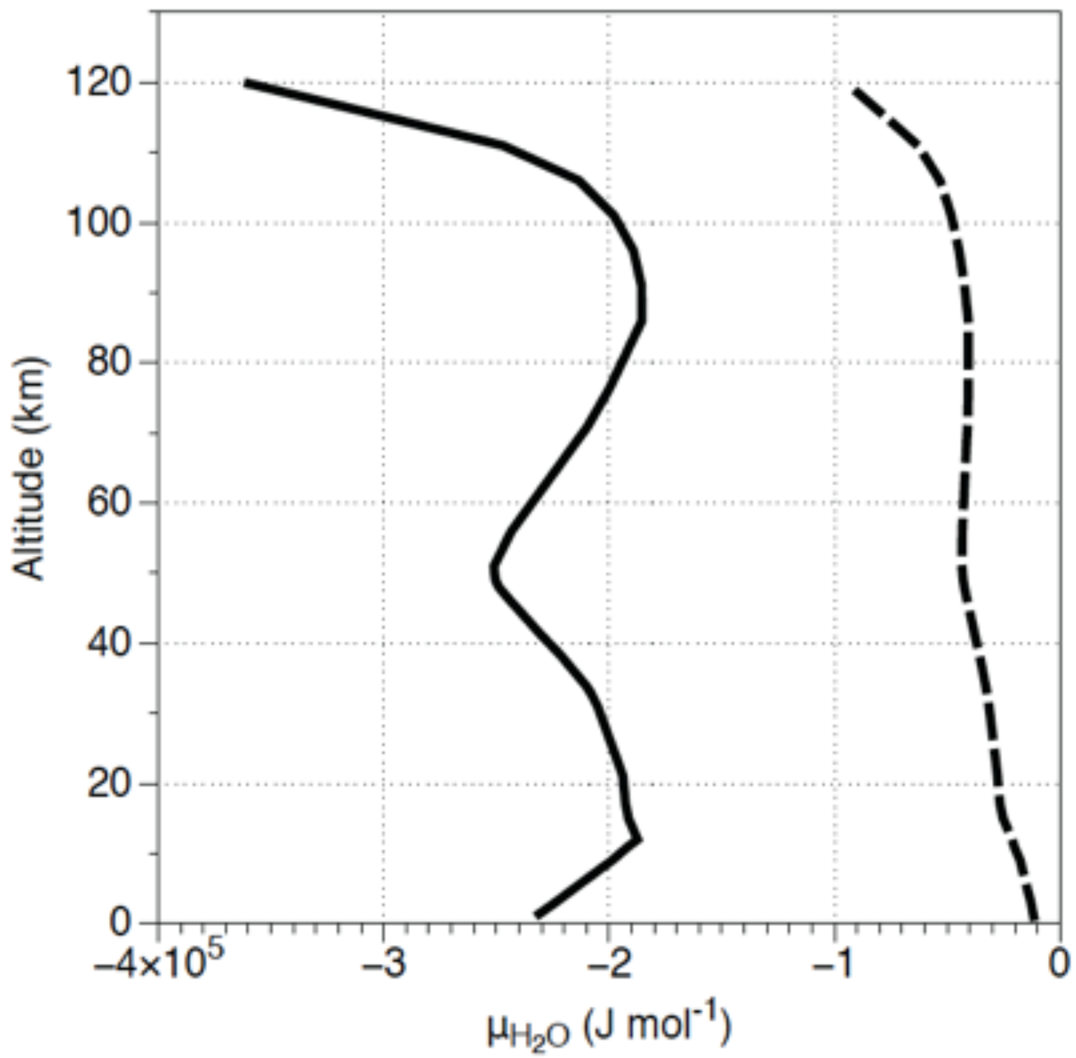
Simoncini E., Extent of chemical disequilibrium and planetary habitability, ***in prep.***


- Kondepudi & Prigogine, Modern Thermodynamics, 1998.
- Branscomb E. & Russell M. J., BBA, 2013.
- J. 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

# Application to atmospheric disequilibrium

# [ The chemical potential for gas mixtures ]

$$\mu_i(T,P,\chi_i) = \frac{T}{T_0}\mu_i^0 + \int_{p_0}^{p} V_{m,i}(T,p')dp' + T\int_{T_0}^{T} \frac{-h_i(T',p_0)}{T'^2}dT'$$




Key point:

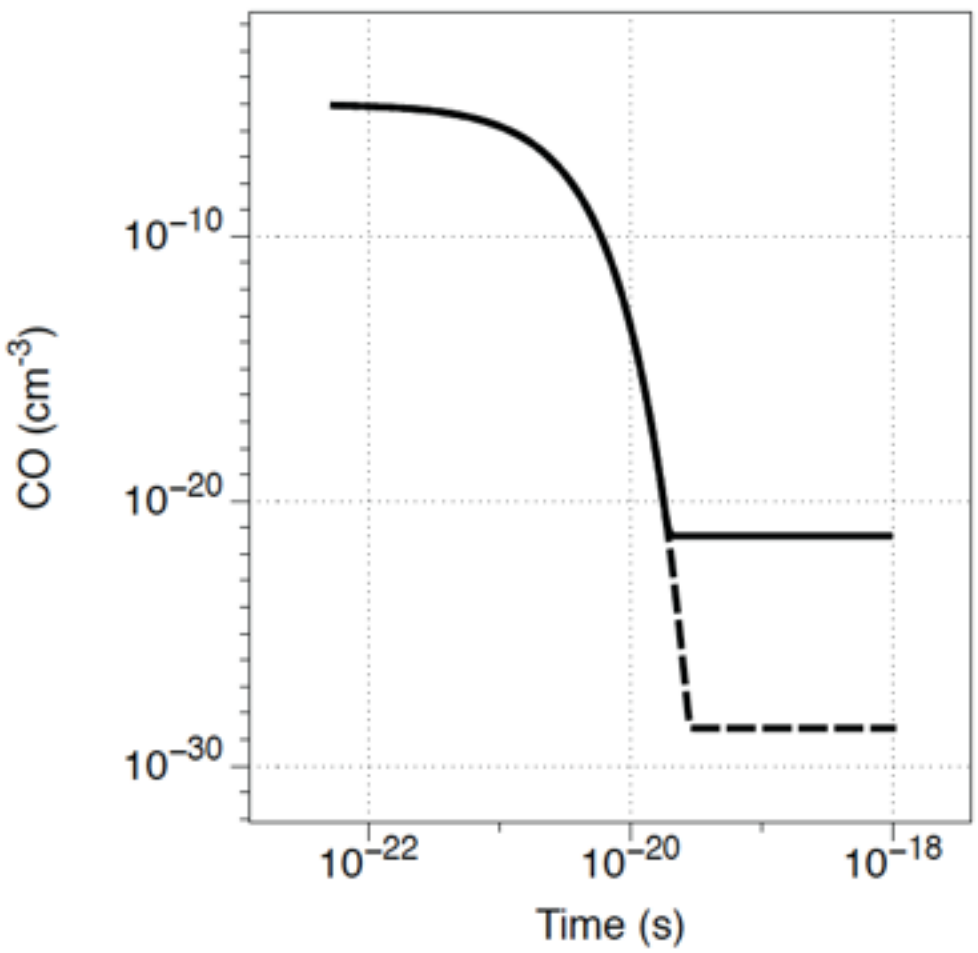
$$\mu_i = \mu_i(t)$$

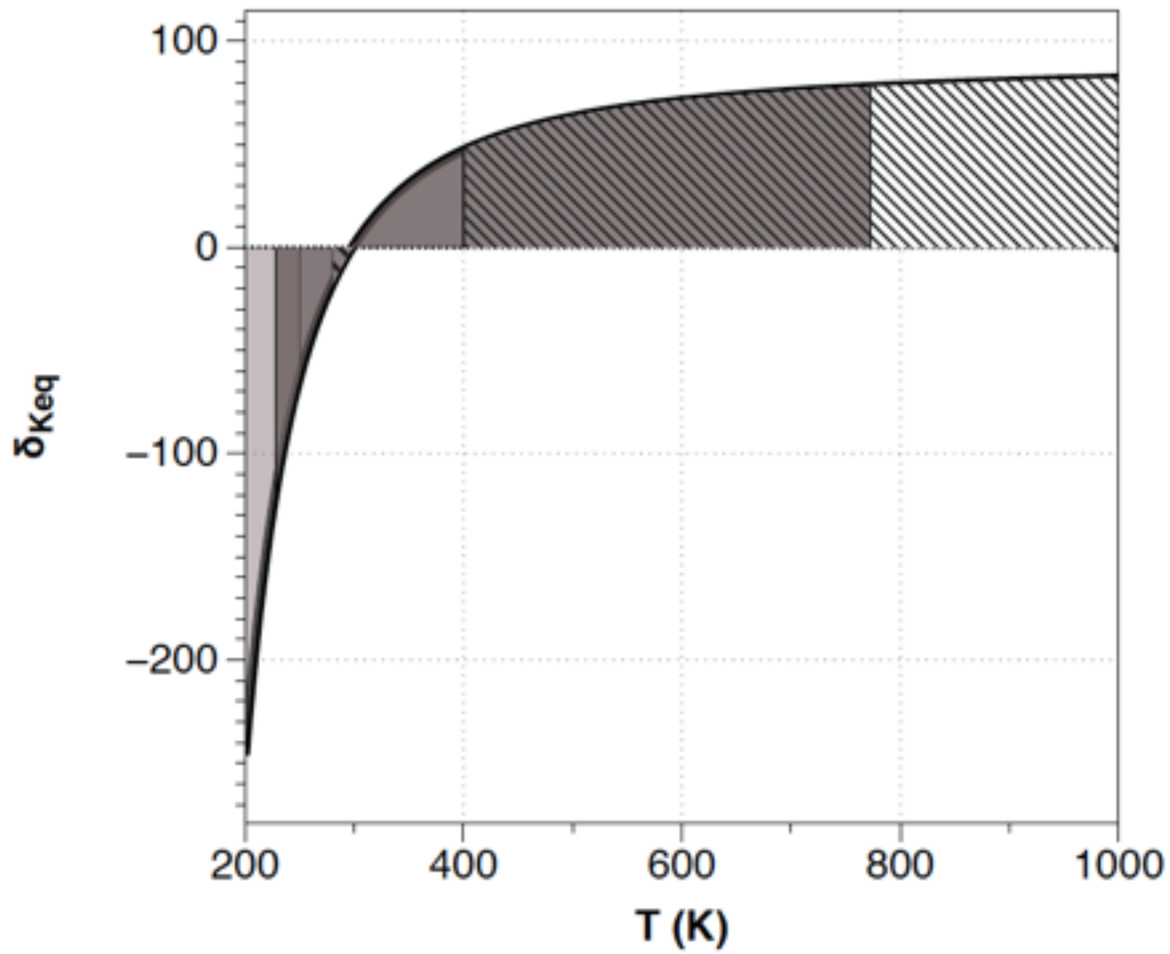

Simoncini E., Delgado-Bonal A., Submitted to Chem. Phys. Lett.
Kondepudi D., Prigogine I., Modern thermodynamics, 1998.
Chase, M. W. 1998, J. Phys. Chem. Ref. Data, Vol. 28.
NASA polynomials: http://www.me.berkeley.edu/gri_mech/data/nasa_plnm.html

# [ The chemical potential and the reaction kinetics ]

$$k_r = k_f \cdot exp\left[\frac{\Delta_R G^0}{R \cdot T_0} + K_R(T)\right]$$

$$CO + NO_2 \leftrightharpoons CO_2 + NO$$




Simoncini E., Delgado-Bonal A., Submitted to Chem. Phys. Lett.

# Atmospheric modeling with KROME

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

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

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

—> A package to solve ODEs for the kinetics of hundreds of reactions (like in atmospheres)

+ Calculate the entropy production

Grassi et al., MNRAS 2014 + http://arxiv.org/abs/1311.1070

# KROME

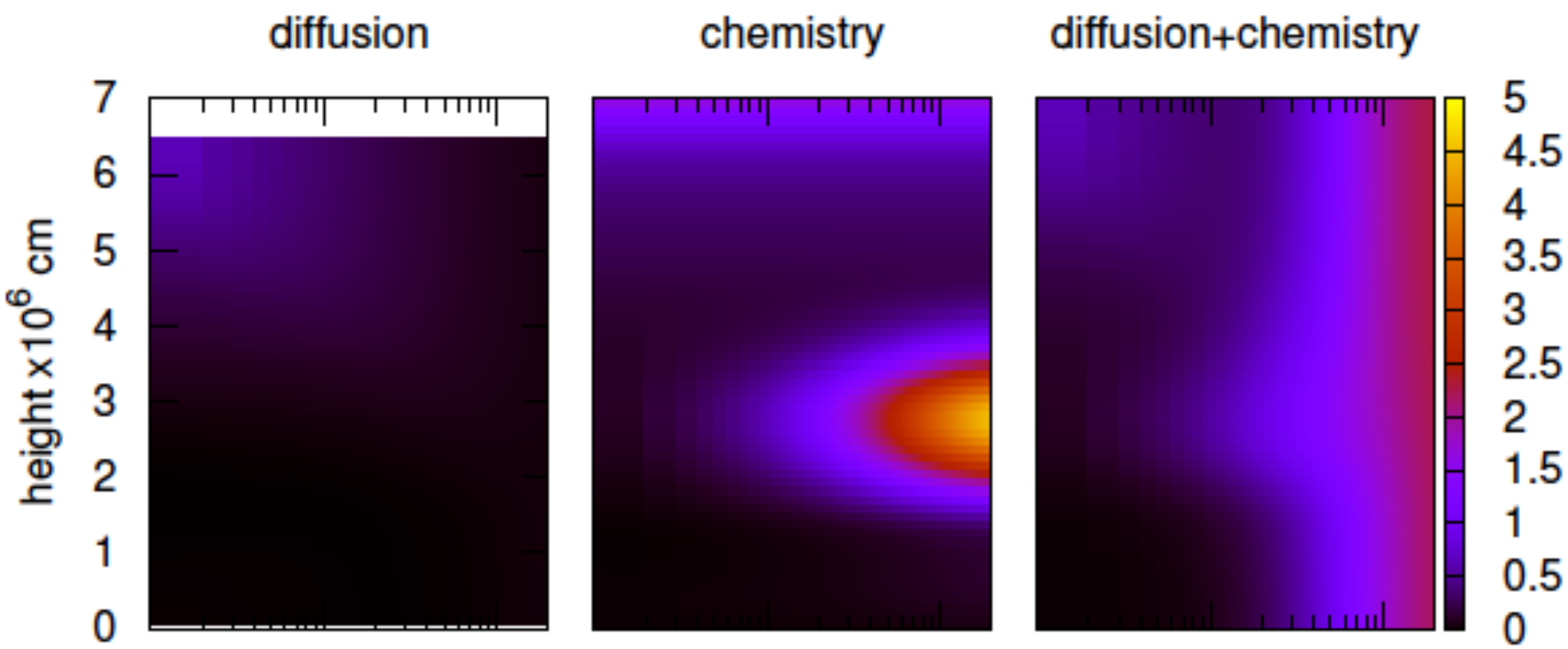
better science through chemistry

- 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

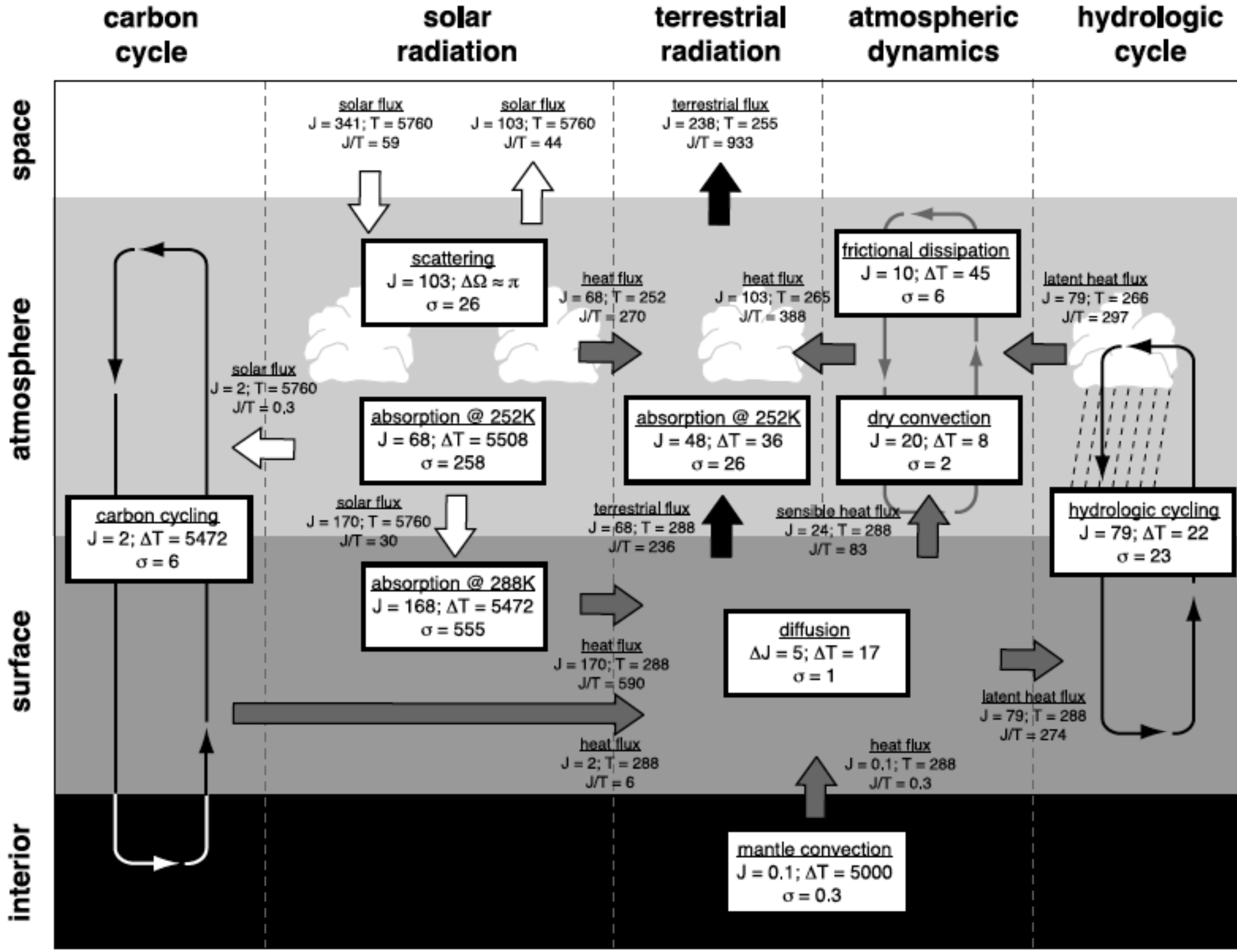
Diffusion and Kasting+80 chemical network (1D)

$$\frac{\partial n_{ij}}{\partial t} = \zeta_j \frac{\partial^2 n_{ij}}{\partial z^2}$$




www.kromepackage.org

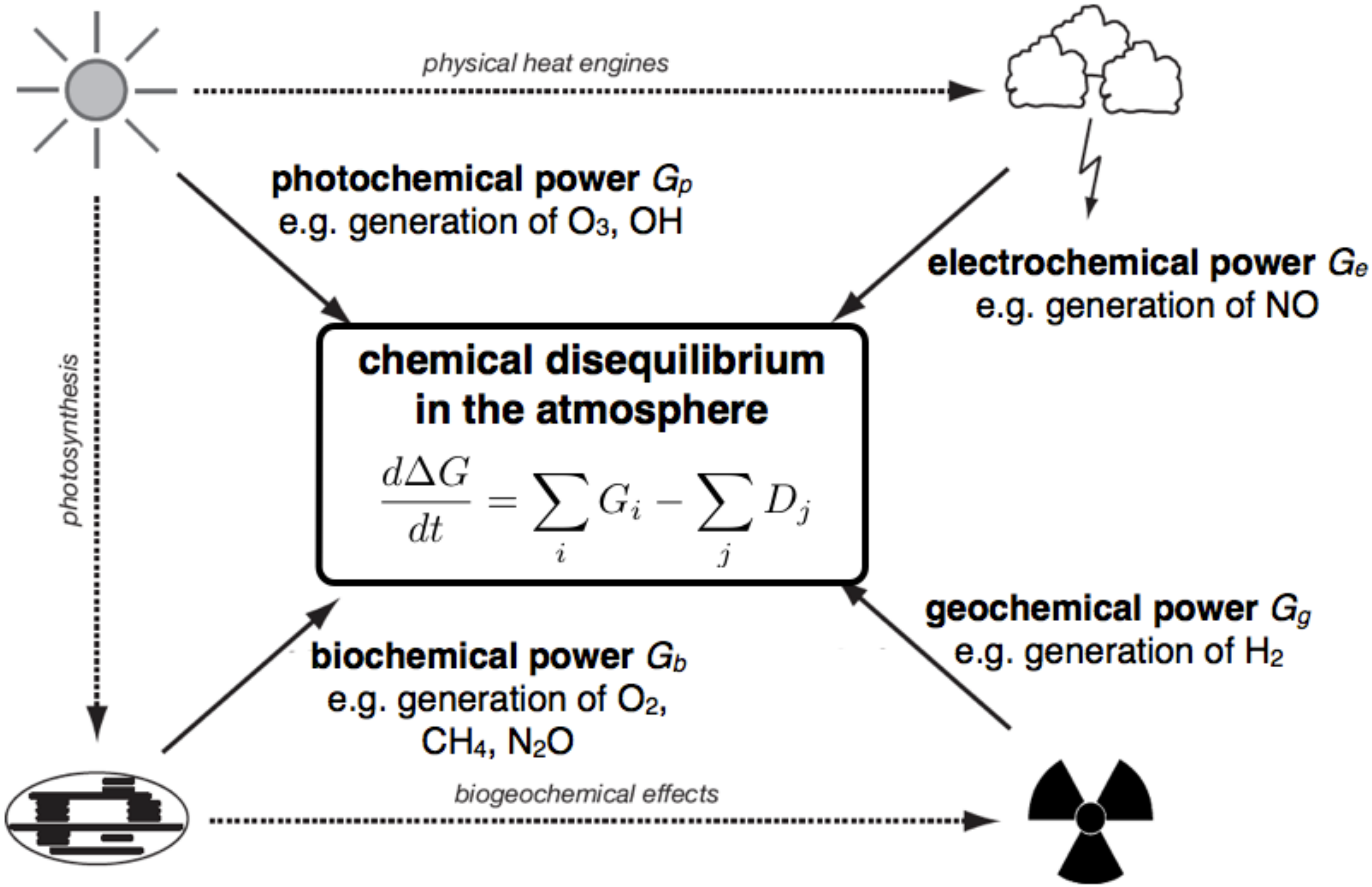
# Earth Powers




$J \sim W\ m^{-2}$

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

# *Earth far from equilibrium*



# Earth Atmospheric Chemical Disequilibrium

Our first calculation:

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

* 64 layers (~1km each);

* Eddy diffusion;

* Entropy production and the power dissipation:

$$\sigma = \frac{d_i S}{dt} \qquad \frac{\sigma \times T}{A_{Earth}} \sim W m^{-2}$$

Simoncini & Grassi, submitted to OLEB.
Simoncini, Brucato, Grassi, in preparation
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

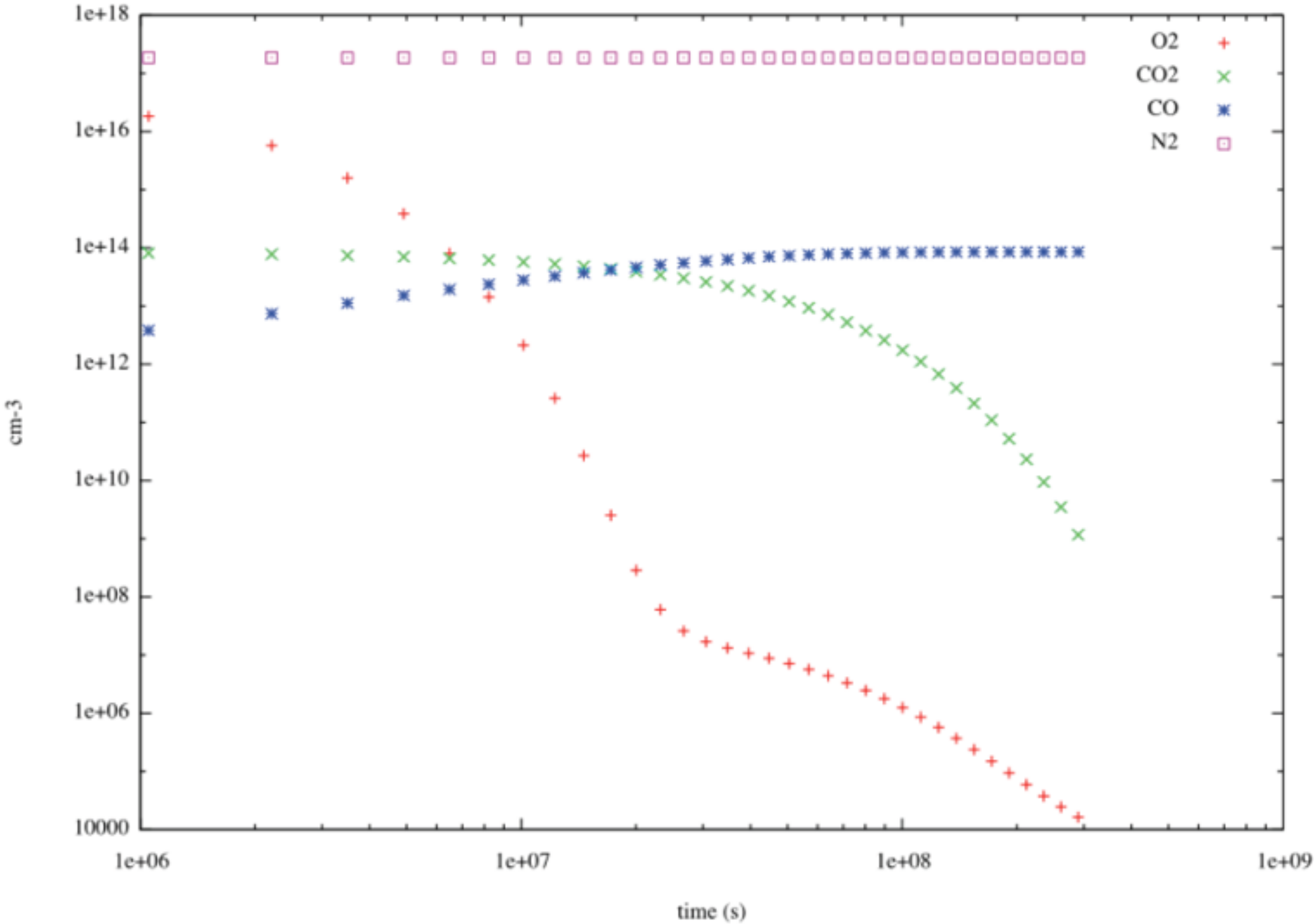
Different runs of K-80 model:

- With and without photochemistry
- With and without eddy diffusion
- Low O2, O3, high CO2 = pseudo pre-photosynthesis Earth

*Simoncini & Grassi, submitted to OLEB.*

# Earth Atmospheric Chemical Disequilibrium

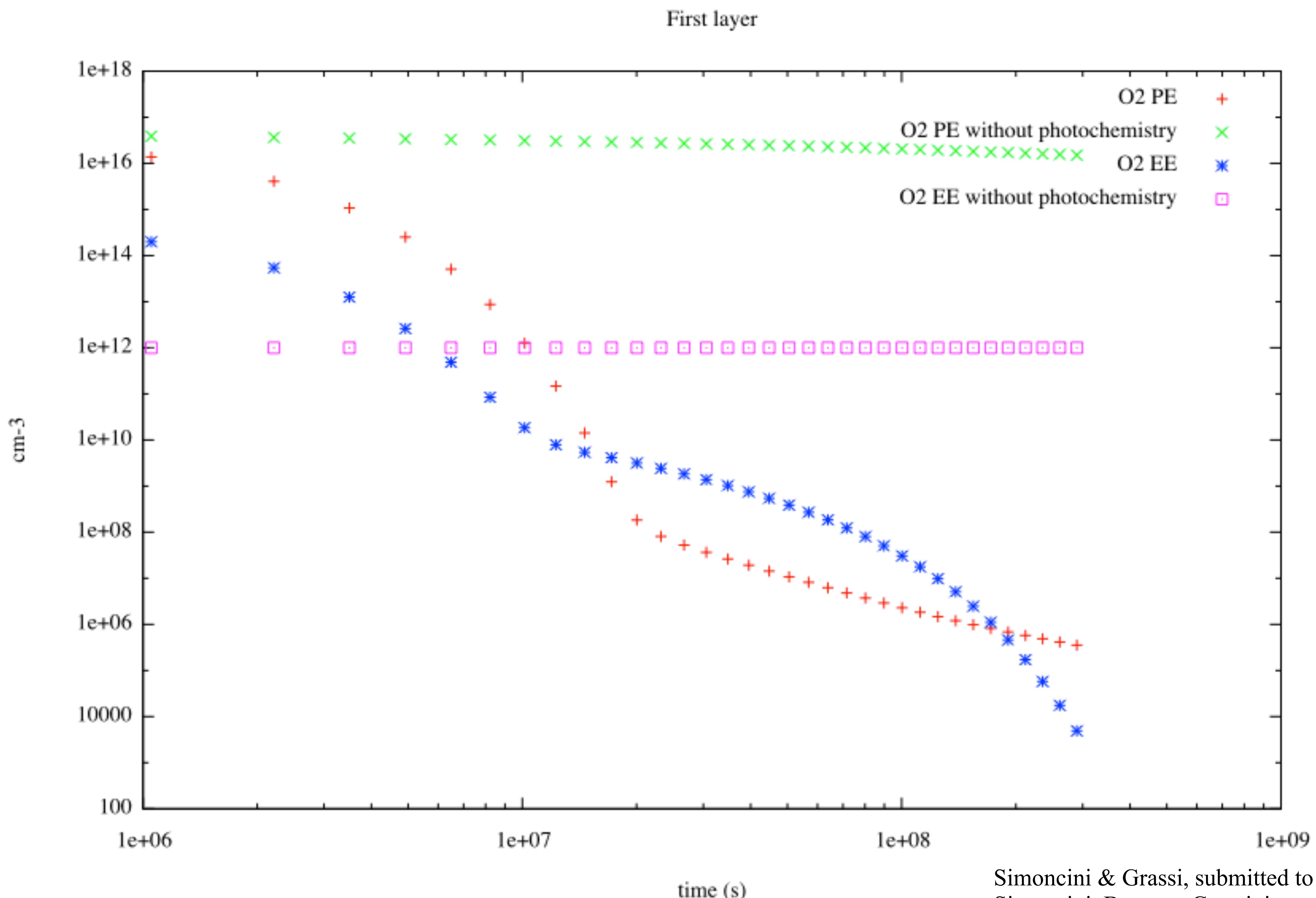
## *Column model + KROME: species evolution*




*Simoncini & Grassi, submitted to OLEB.*

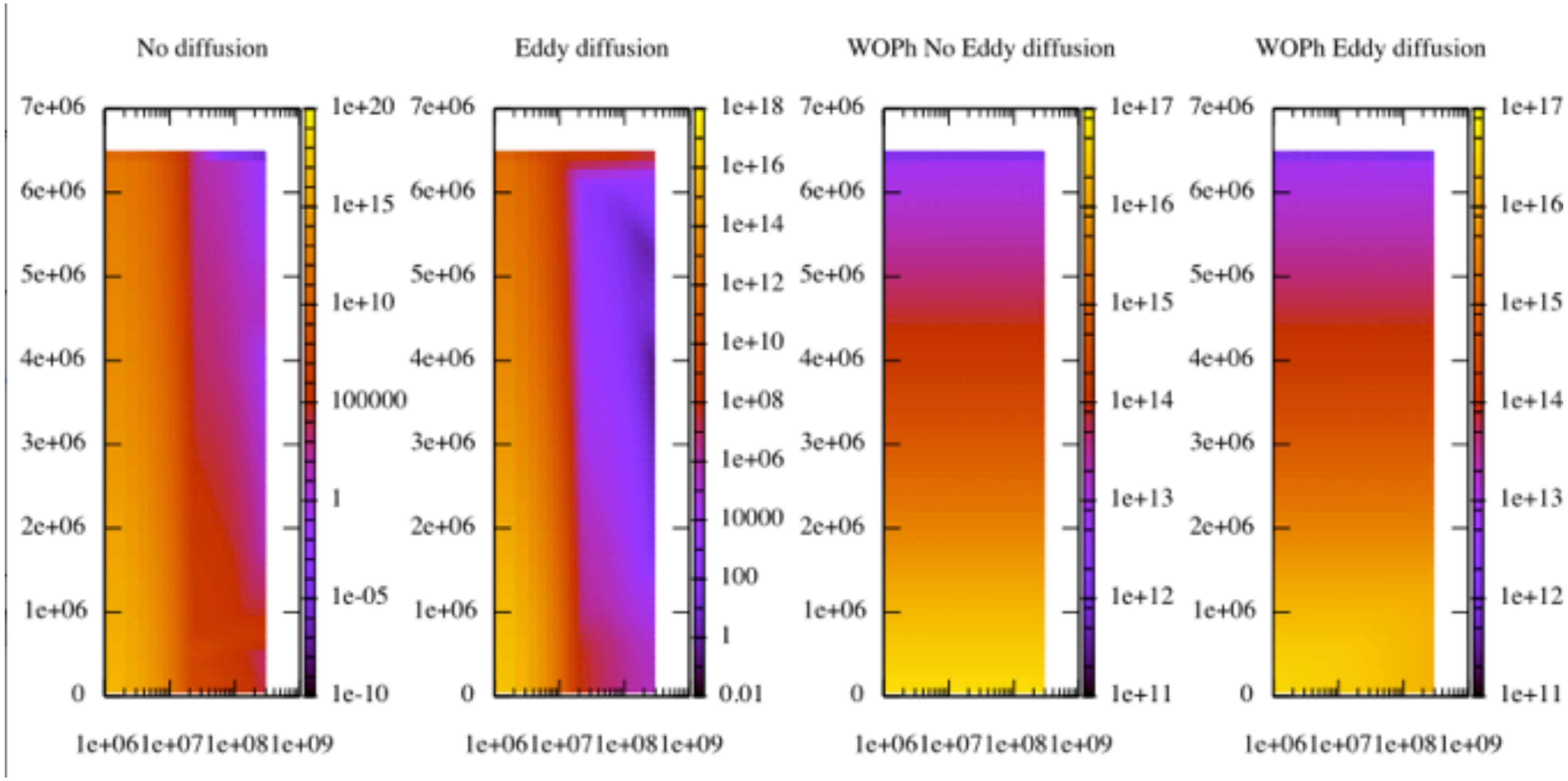
# Earth Atmospheric Chemical Disequilibrium

## *Column model + KROME: species evolution*

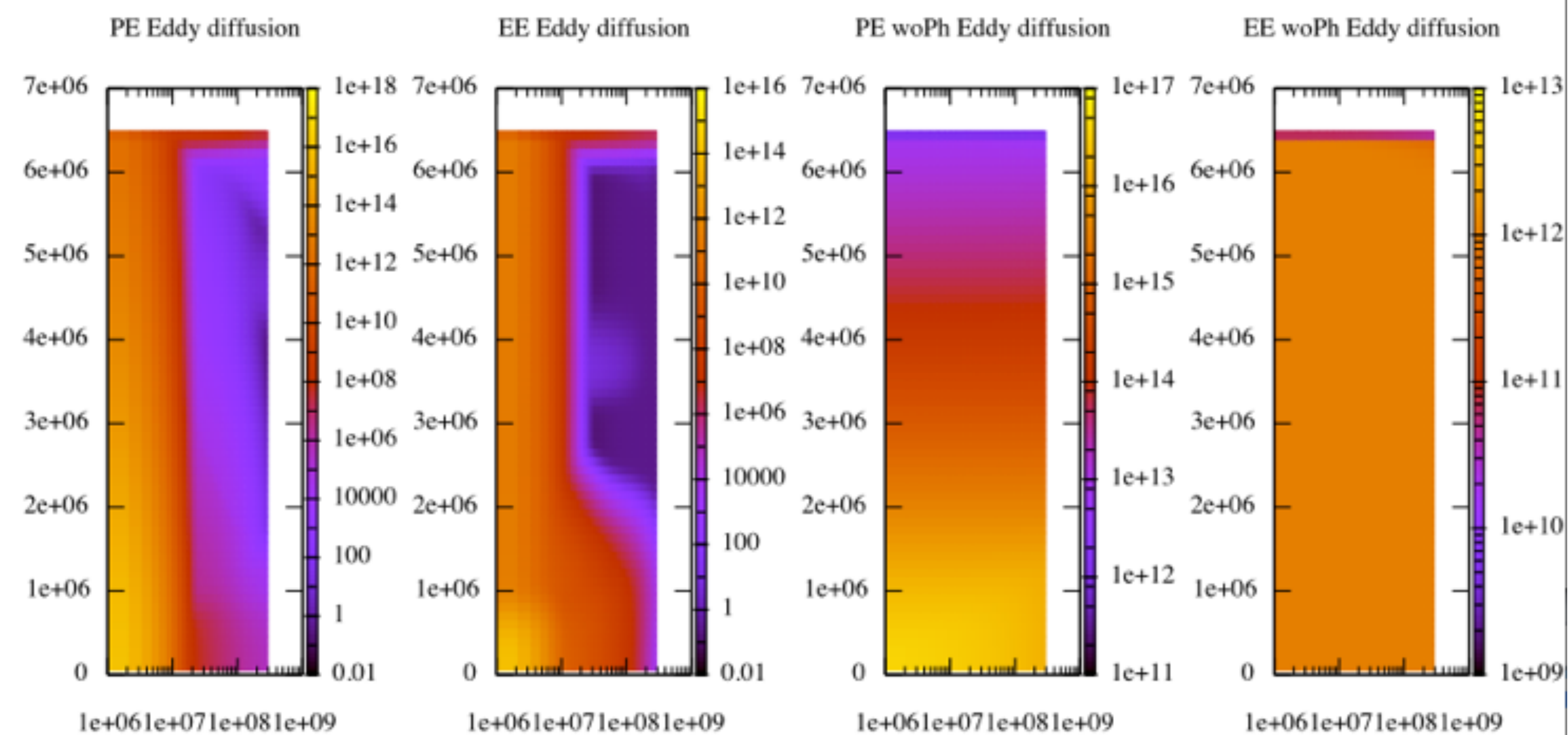



Simoncini & Grassi, submitted to OLEB.
Simoncini, Brucato, Grassi, in preparation

# Earth Atmospheric Chemical Disequilibrium



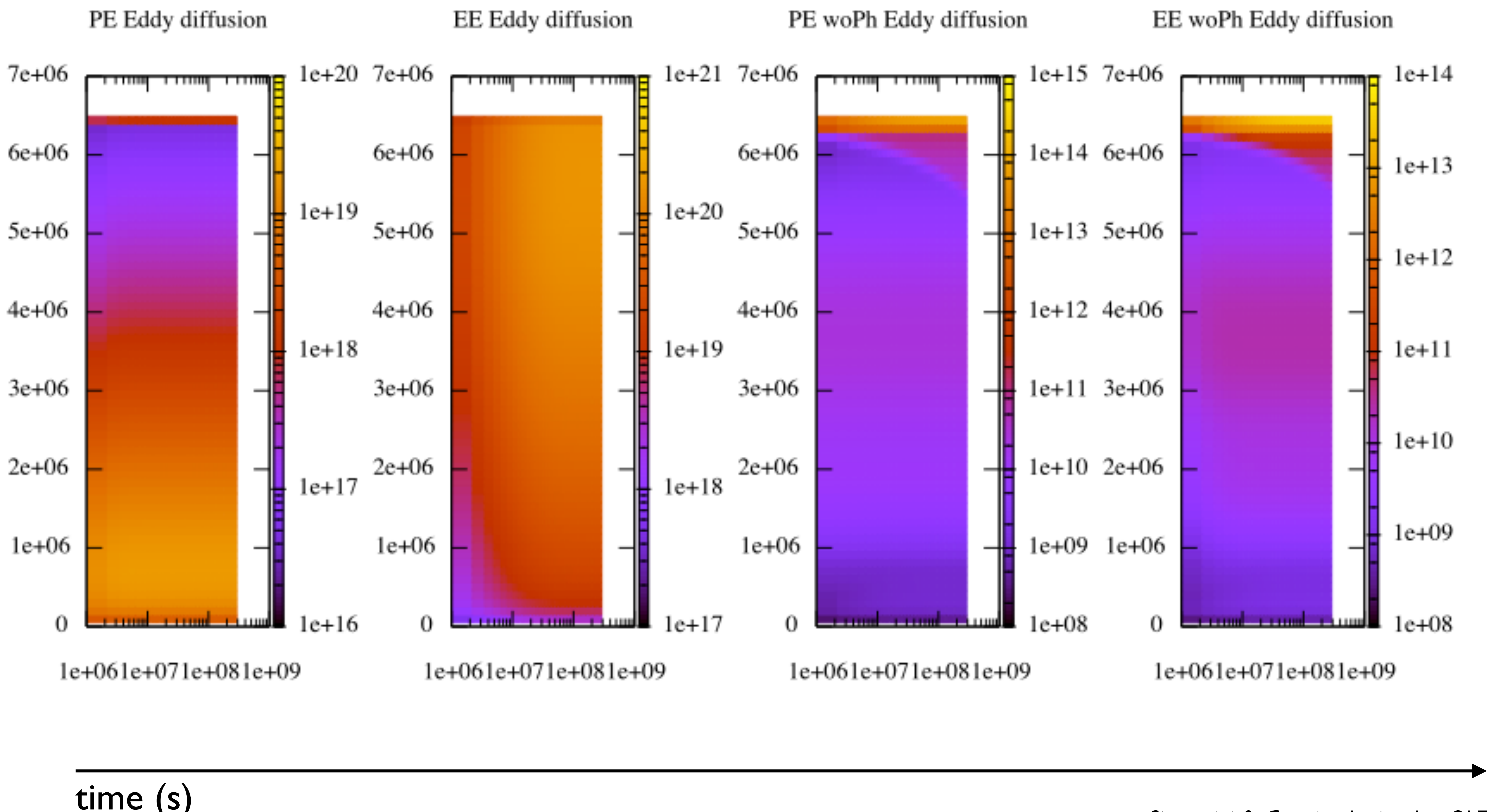

O2




*Simoncini & Grassi, submitted to OLEB.*
*Simoncini, Brucato, Grassi, in preparation*

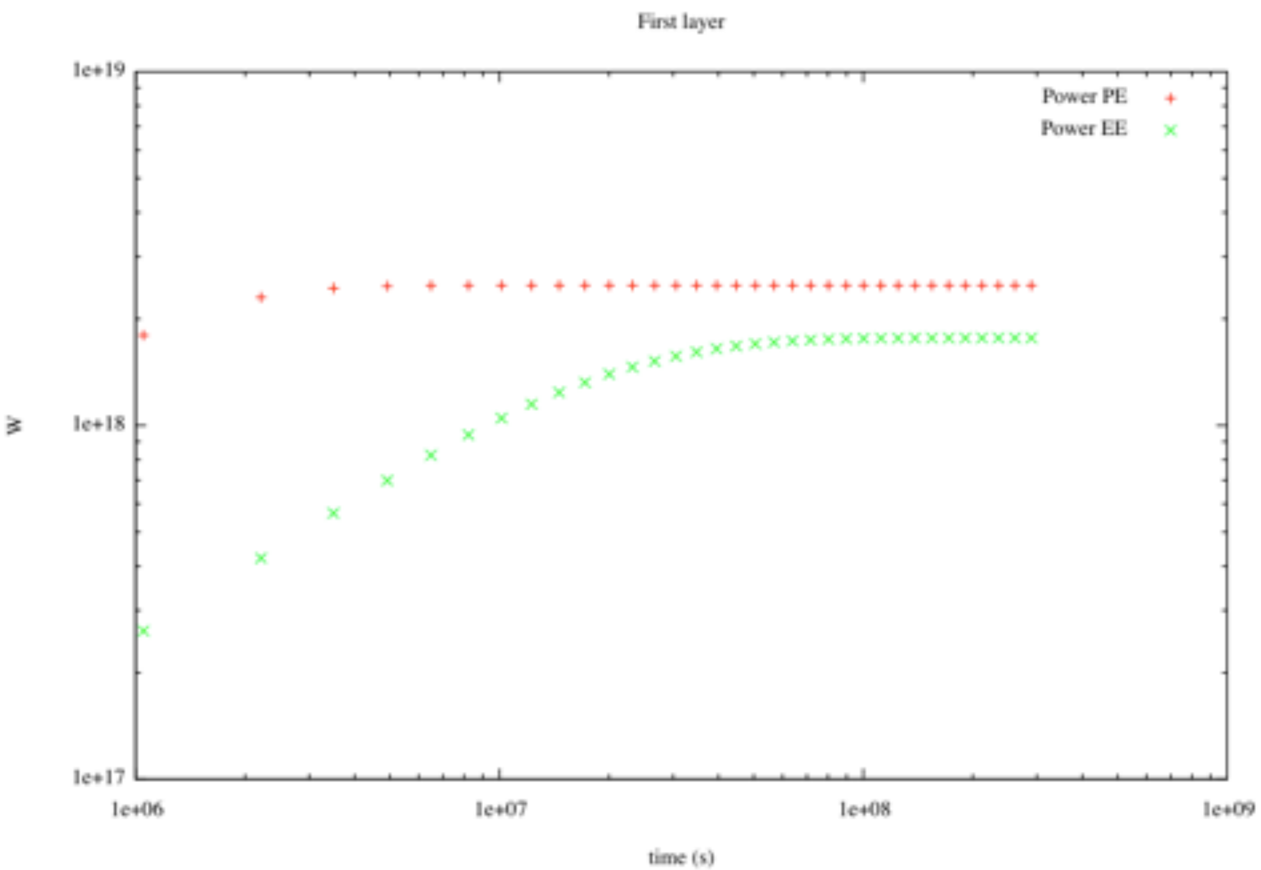
# Earth Atmospheric Chemical Disequilibrium

*The structure changes!*

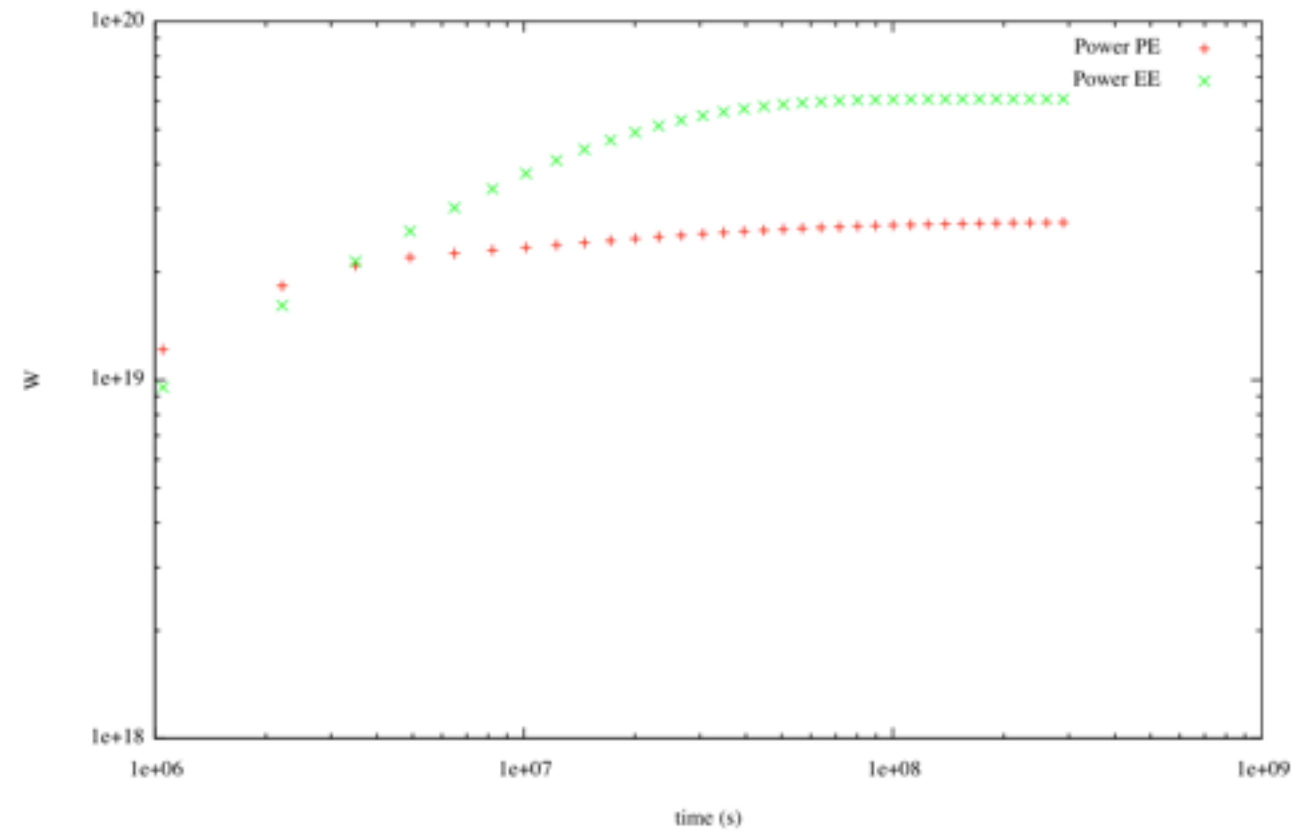



*Simoncini & Grassi, submitted to OLEB.*
*Simoncini, Brucato, Grassi, in preparation*

# Earth Atmospheric Chemical Disequilibrium




*Layer 1*




*Layer 64*

*Simoncini & Grassi, submitted to OLEB.*
*Simoncini, Brucato, Grassi, in preparation*

# Mars Atmospheric Chemical Disequilibrium

Our first calculation:

* Model: Zahnle K., Haberle R. M., Catling D. C., Kasting J. F., JGR 113, 2008

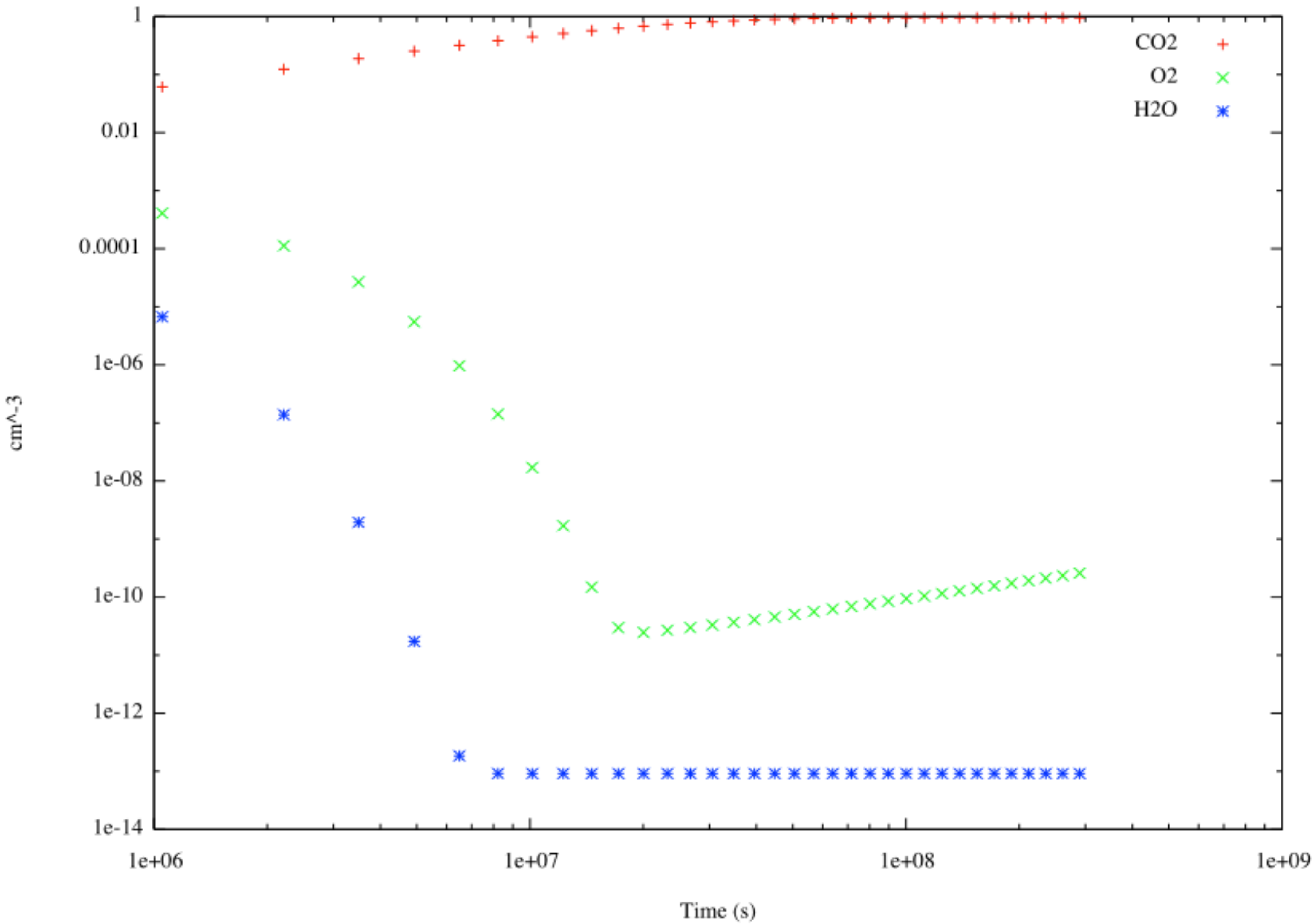
* 142 layers;

* No diffusion

* With and without photochemistry

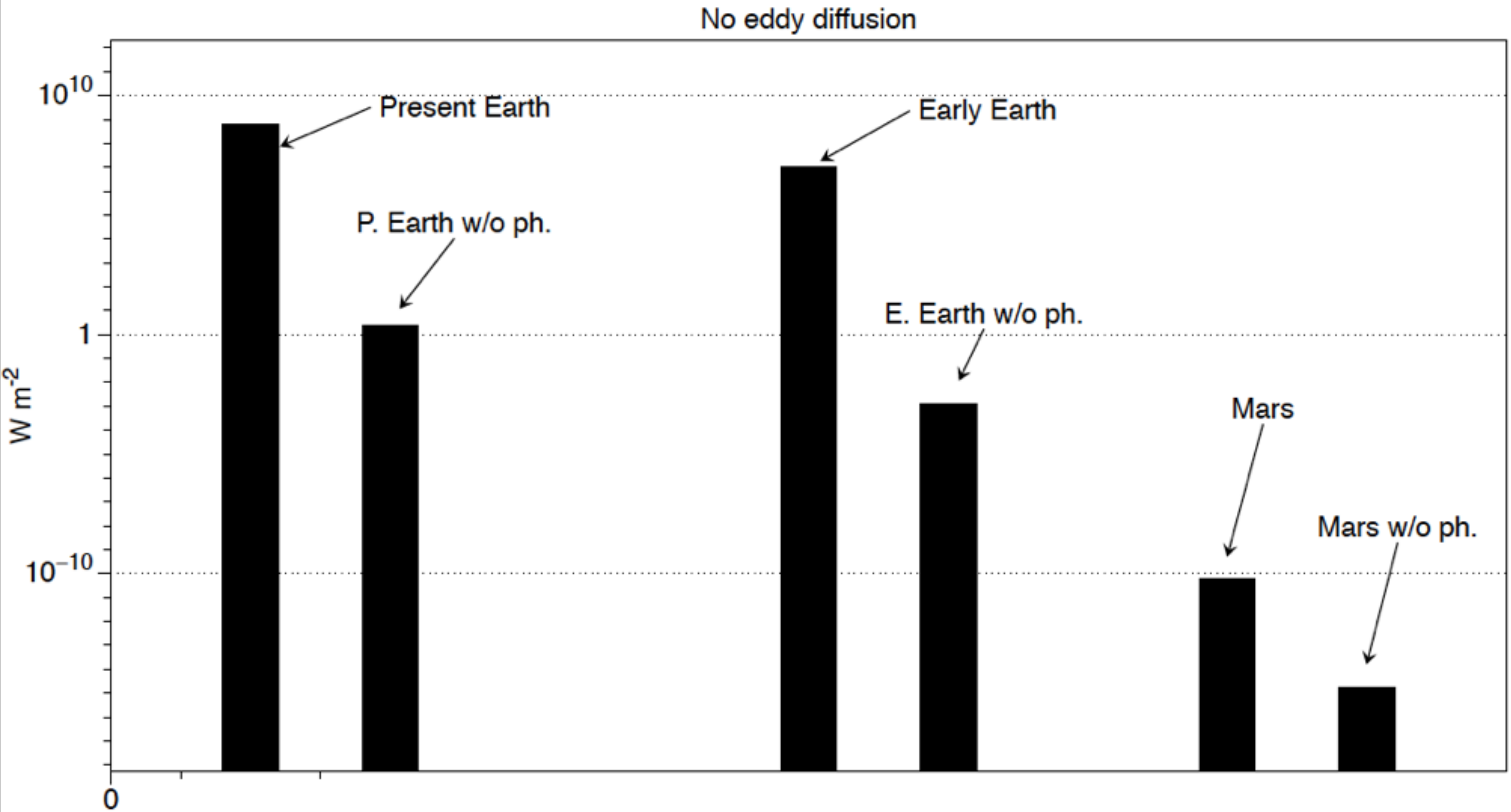
* Entropy production and the power dissipation.

# Mars Atmospheric Chemical Disequilibrium




*Simoncini & Grassi, submitted to OLEB.*
*Simoncini, Brucato, Grassi, in preparation*

# Atmospheric Chemical Disequilibrium: Mars vs Earth




After 10 years

*Simoncini & Grassi, submitted to OLEB.*
*Simoncini, Brucato, Grassi, in preparation*

# Atmospheric Chemical Disequilibrium: Mars vs Earth

| | |
|---|---|
| PE: | 3.34 E23 W |
| PE no photochemistry: | 1.56 E3 W |
| EE: | 2.68 E6 W |
| EE no photochemistry: | 1.17 E2 W |
| Mars: | 8.70 E3 W |
| Mars no photochemistry: | 2.59 E-1 W |

*Simoncini & Grassi, submitted to OLEB.*
*Simoncini, Brucato, Grassi, in preparation*

# Atmospheric Chemical Disequilibrium: Mars vs Earth

Results:

* The effect on the atmospheric chemical disequilibrium attributable to the biosphere is very higher than the one due to photochemistry (some orders of magnitude).

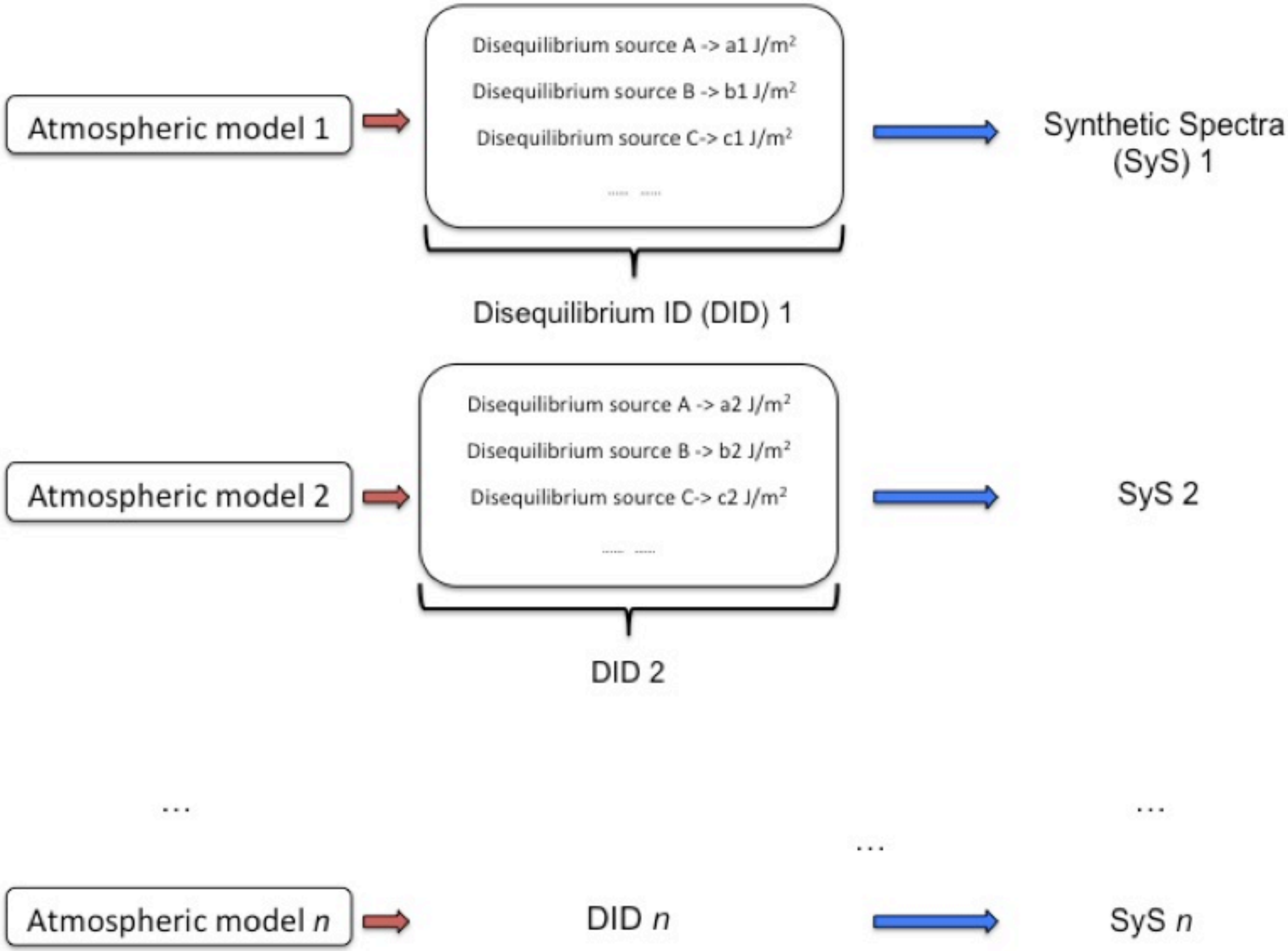
* Life and photochemistry are strongly linked in their effects. However, we found that the effect of photochemistry is enhanced by the biosphere.

* Mars disequilibrium is more then 10 orders of magnitude lower compared to present and pre-photosynthesis Earth!

# Perspectives

- Comparison of entropy production between planets ( better link with the concept of "habitability" )
- Comparison between different power sources (photochemistry, fast vertical mixing, geological degassing, and life as the last option). Give a range of the maximum energy that can be dissipated by each process.
- Application to different geological moments of Earth history (computing different effects of life)
- Application to any typology of exoplanet, connecting a disequilibrium characterization of a modeled planet/moon with its synthetic spectra. This will make the entropic analysis able to be compared with observed spectra.

# Perspectives



# Summary and outlook

- Calculate the extent of disequilibrium: no need of steady-state assumption
- KROME applied to disequilibrium calculations
- Reduce the selection of habitable planets to those which present high chemical disequilibrium (not attributable to any other process but life)

- Capability to separate the effect of each source of disequilibrium
- Life processes and photochemistry interact
- Mars disequilibrium is more then 10 orders of magnitude lower compared to present and pre-photosynthesis Earth

- Enhance precision for photochemical and early Earth's models

# *Thanks for your attention!*

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*.. and all members of the TDE Focus Group - NASA Astrobiology Institute*