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

Eugenio Simoncini, John R. Brucato
Astrophysical Observatory of Arcetri - INAF, Firenze, Italy

Tommaso Grassi
Starplan, Copenhagen, Denmark / University of Rome - La Sapienza, Roma, Italy
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

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Introduction

What is chemical disequilibrium, and why should we use it
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 gradients” (Schrödinger, 1944)

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

![Graphs showing atmospheric chemical disequilibrium for Venus, Earth, and Mars.](http://www.astronomynotes.com/lifezone/s4.htm)
How to calculate (and compare) disequilibrium in chemical processes
Atmospheric Chemical Disequilibrium

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:

\[ \frac{dS}{dt} \]
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.

- 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:

\[ \mu_i = \mu_i(t) \]
The chemical potential and the reaction kinetics

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

\[ \text{CO} + \text{NO}_2 \rightleftharpoons \text{CO}_2 + \text{NO} \]

Atmospheric modeling with **KROME**

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

\[
A + B \rightleftharpoons C + D
\]

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

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

+ Calculate the entropy production

- 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

www.kromepackage.org
Diffusion and Kasting+80 chemical network (1D)

\[
\frac{\partial n_{ij}}{\partial t} = \zeta_j \frac{\partial^2 n_{ij}}{\partial z^2}
\]
$J \sim W \text{ m}^{-2}$
Earth far from equilibrium
Earth Atmospheric Chemical Disequilibrium

Our first calculation:


* 64 layers (~1km each);

* Eddy diffusion;

* Entropy production and the power dissipation:

\[ \sigma = \frac{d_i S}{dt} \]

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

First layer

Simoncini & Grassi, submitted to OLEB.
Simoncini, Brucato, Grassi, in preparation
Earth Atmospheric Chemical Disequilibrium

Simoncini & Grassi, submitted to OLEB.
Simoncini, Brucato, Grassi, in preparation
Earth Atmospheric Chemical Disequilibrium

The structure changes!

Simoncini, Brucato, Grassi, in preparation

Simoncini & Grassi, submitted to OLEB.
Earth Atmospheric Chemical Disequilibrium

Layer 1

Layer 64

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Mars Atmospheric Chemical Disequilibrium

Our first calculation:


* 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
Atmospheric Chemical Disequilibrium: Mars vs Earth

PE:
PE no photochemistry:

EE:
EE no photochemistry:

Mars:
Mars no photochemistry:

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

Atmospheric model 1 → Disequilibrium ID (DID) 1

Disequilibrium source A → a1 J/m²
Disequilibrium source B → b1 J/m²
Disequilibrium source C → c1 J/m²

DID 1 → Synthetic Spectra (SyS) 1

Atmospheric model 2 → Disequilibrium ID (DID) 2

Disequilibrium source A → a2 J/m²
Disequilibrium source B → b2 J/m²
Disequilibrium source C → c2 J/m²

DID 2 → SyS 2

... → ... →...

Atmospheric model n → DID n → SyS n
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 than 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!

T. Grassi, Università di Roma - La Sapienza, Rome, Italy.

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

S. O. Danielache, Sophia University, Tokio, Japan.

M. J. Russell, JPL, CalTech-NASA, Pasadena, CA, USA

S. Branciamore, Beckman Research Institute of City of Hope, CA, USA

A. Delgado-Bonal, J. Plá, T. Mendaza-de Cal, Maria Serrano, Centro de Astrobiologia, INTA-CSIC, Madrid, Spain

Kleidon, N. Virgo, Max Planck Institute for Biogeochemistry, Jena, Germany.


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