

5.1

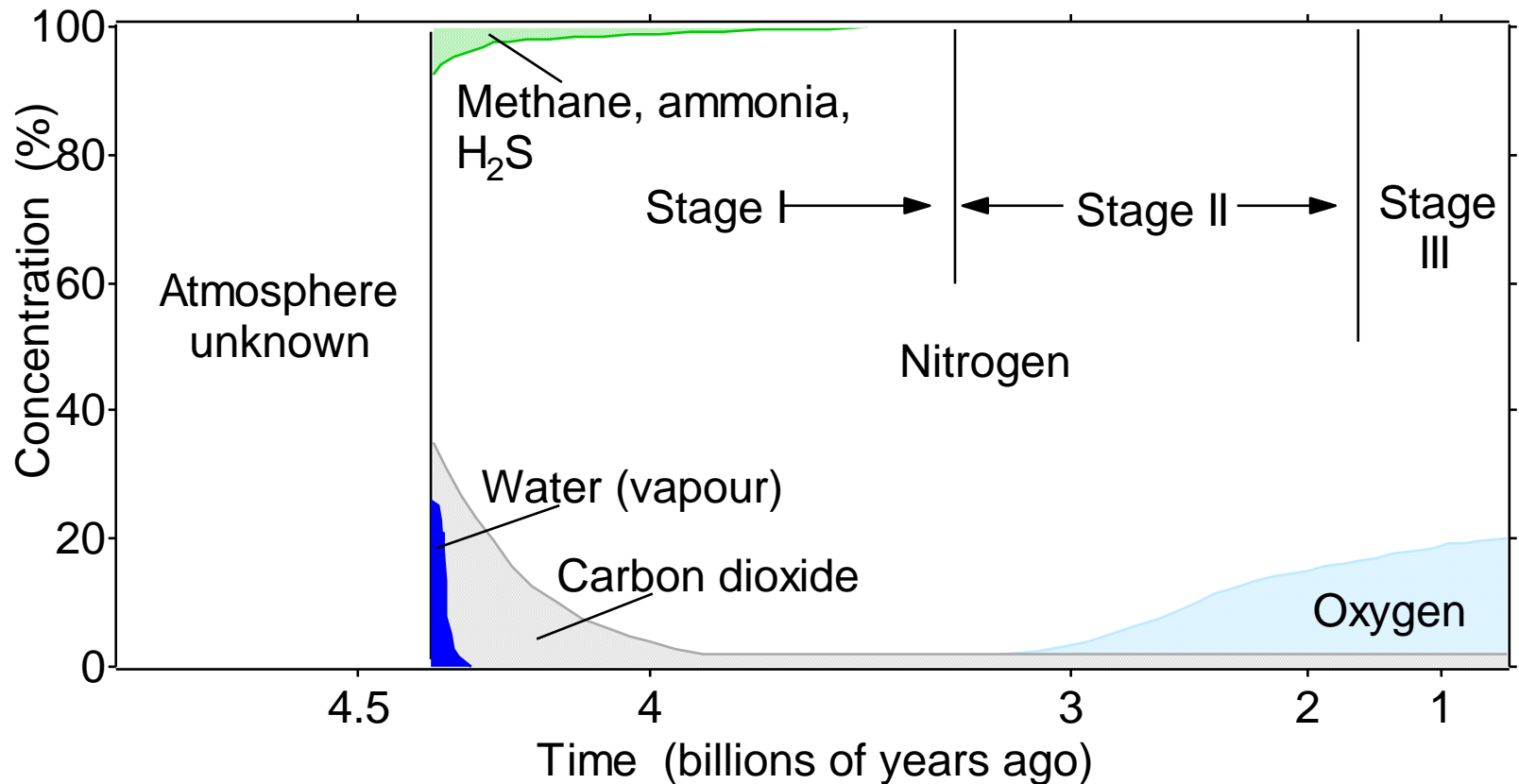
Lecture 5.1: Molecular dynamics, scale invariance and natural selection

- * Scale invariance occurs in atmospheric chemistry, aerosols, monomer sequences of amino acids in proteins, nucleotides in nucleic acids and their binding to lipids in membranes.
- * The folding of proteins and of a single loop in an RNA molecule obey fluctuation-dissipation theorems characteristic of maximum entropy production and power law behaviour.
- * Molecular clouds, the birth place of stars and solar systems, show scale invariance. Earth's atmosphere, uniquely among astrochemistries, is a scale-free network.
- * Does the thermodynamic formulation of scale invariance cast light on these observed results?
- * Is there a context for natural selection?

Geophysical Considerations for Origin of Life

- ¶ [Distance from sun](#): allows presence of liquid water for aeons.
- ¶ [Initial geochemical conditions](#): elementary (atomic), as now; molecular, evolved for atmosphere, ocean and surface.
- ¶ [Boundary conditions](#): anisotropies are gravity, rotation, solar beam and surface topography. Crust recycled via tectonics and volcanism.
- ¶ [Range of scales](#): 15 orders of magnitude from mean free path in surface air to planetary circumference, i.e. molecules to meteorology.
- ¶ [Non-equilibrium atmosphere](#): methane/ozone ratio is some 30 orders of magnitude from chemical thermodynamic equilibrium, equilibrium would be 0.2M nitric acid in the ocean. Air is also not at physical equilibrium (solar photons, winds, no LTE).
- ¶ [How to link molecular scale view of water and biology with the macroscopic scales of the planet's fluid envelope?](#) Equivalence of statistical thermodynamics with statistical multifractal scale invariance. Role of entropy and Gibbs free energy.

Composition of the Atmosphere

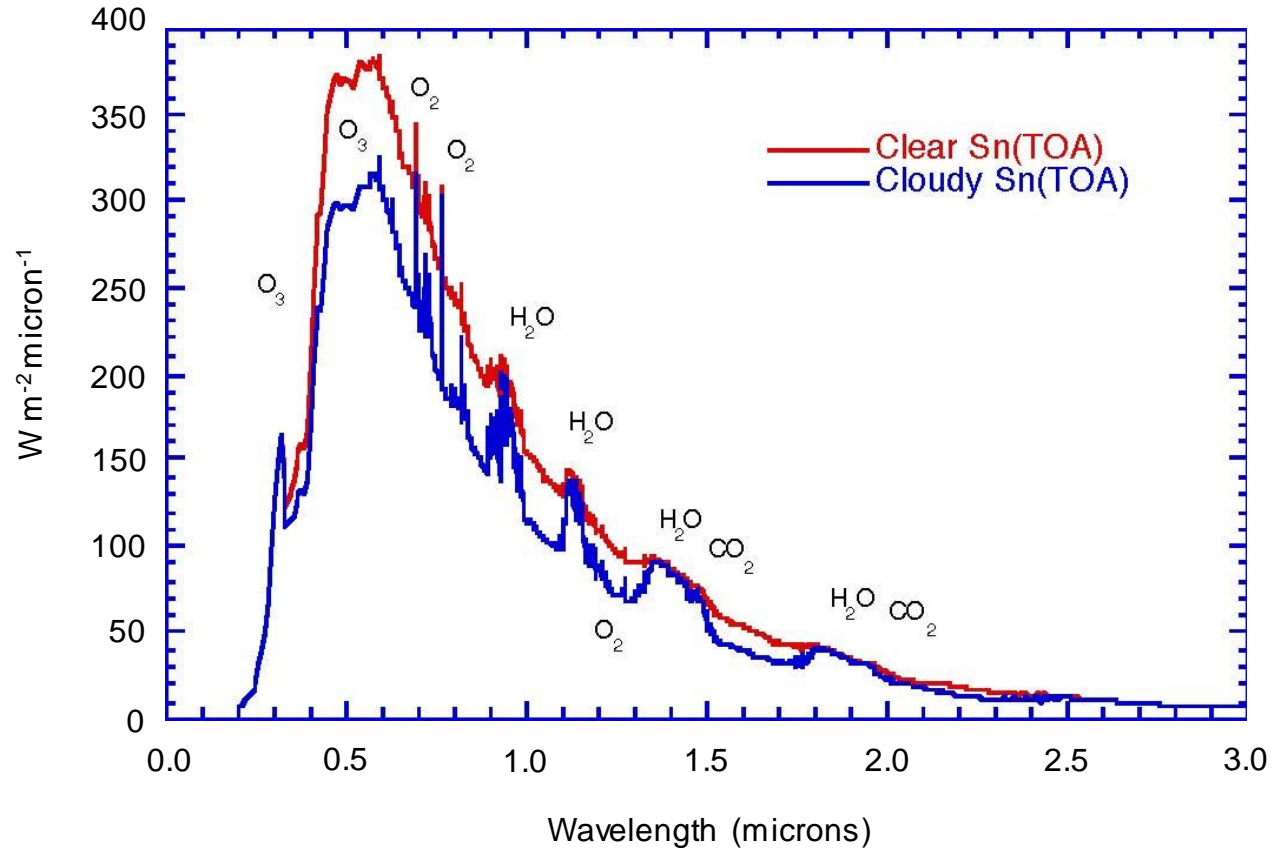


Williams & Fraústo da Silva, The Natural Selection of the Chemical Elements

Prebiotic Environment

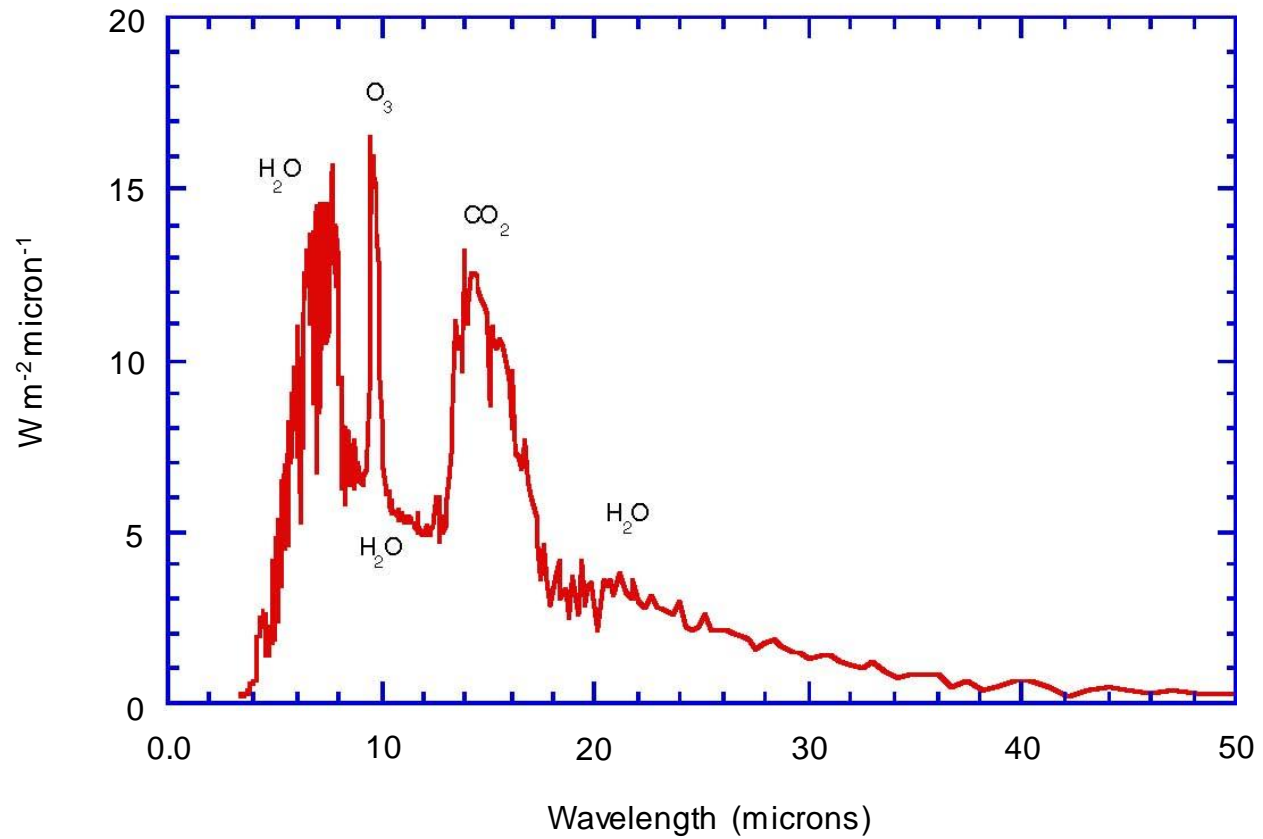
- * Wide, fluctuating range of radiation, temperature, humidity and wind fields.
- * Current atmosphere:
 - Temperature: -90° C to $+40^{\circ}$ C
 - Relative humidity: 0% to 100%
 - Solar radiation spectrum:
 - Virtually unattenuated from 175 nm to 1000 nm in upper stratosphere (residence time \approx years)
 - 6 months of darkness at the winter pole, continuous visible light for months at the summer pole

Nett Shortwave: solar flux beam is low entropy



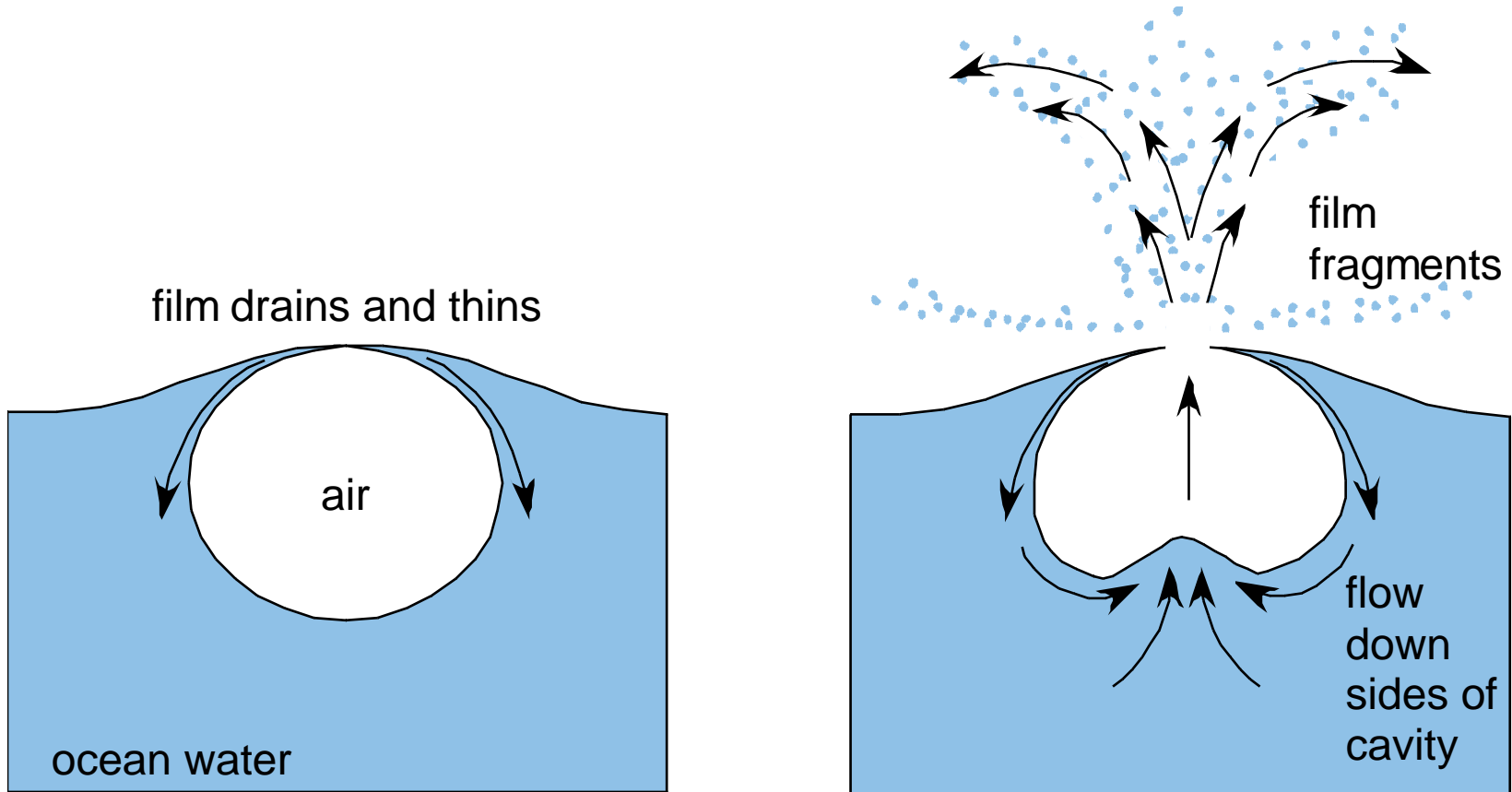
Kiehl and Trenberth (1997)

Greenhouse Effect: IR flux out is high entropy



Kiehl and Trenberth (1997)

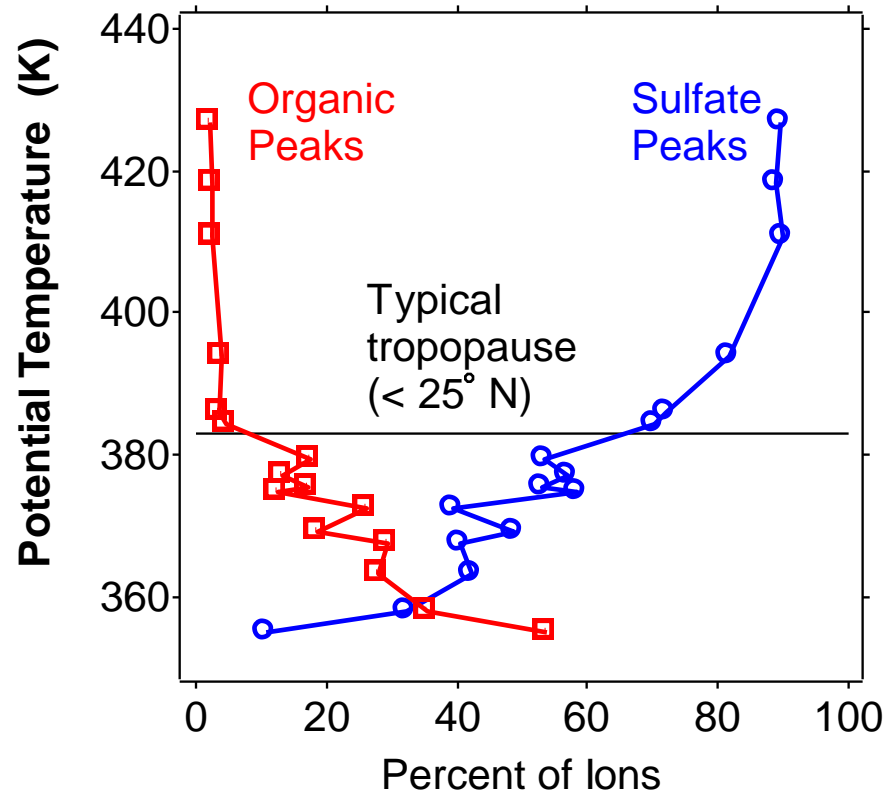
Aerosol from the Ocean



Wave-breaking produces bubbles near the sea surface.

Mass Spectra of Aerosols

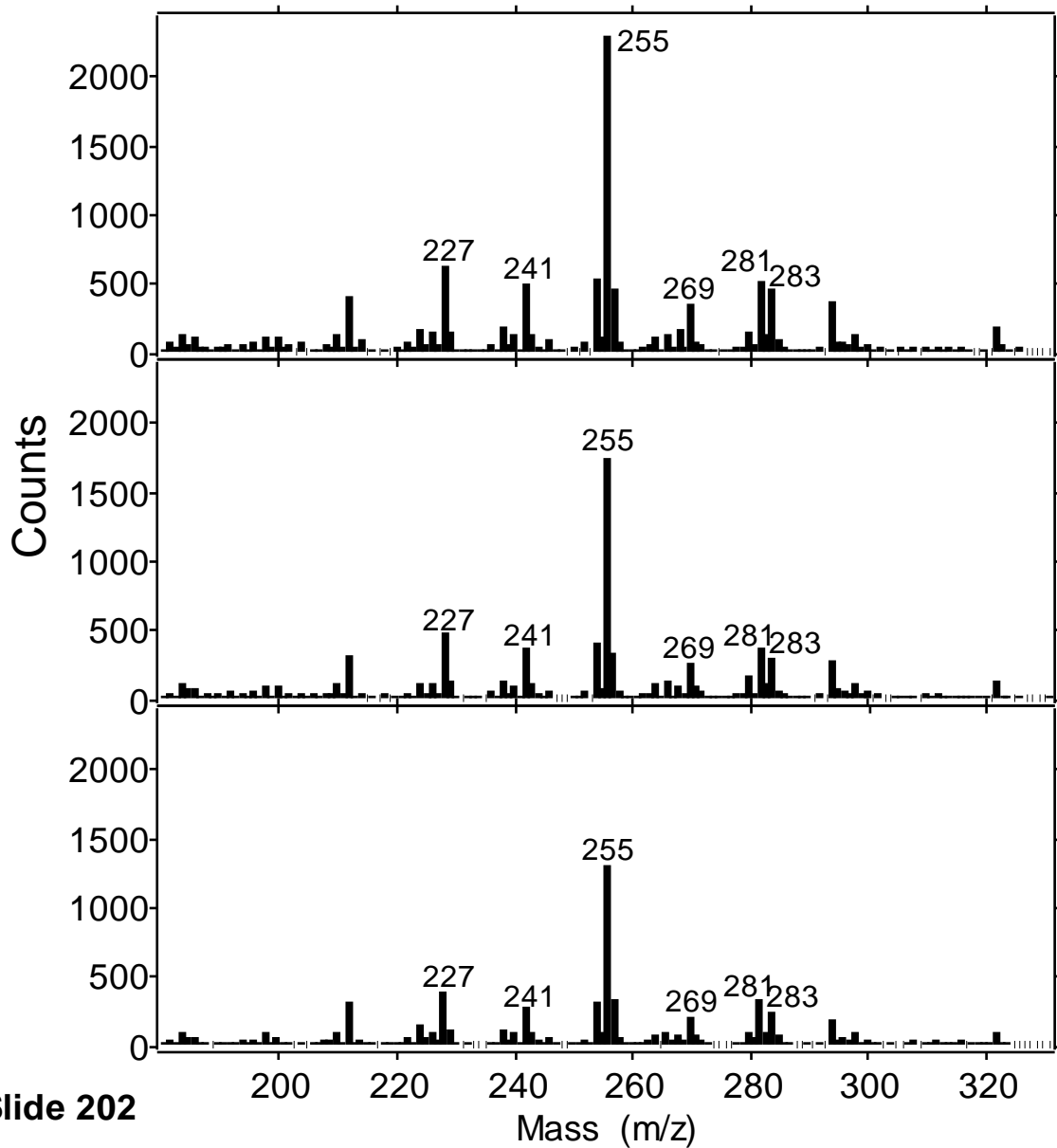
- WB57F Aerosol Mission (WAM); Houston, 1998.
- Particle Analysis by Laser Mass Spectrometry (PALMS)
- Individual particles are $\approx 50\%$ by mass organic material in upper tropical troposphere.



Elements Observed During WAM Flights (1998)

		most						many			common			some		rare		maybe			
H																				He	
Li	Be											B	C	N	O	F				Ne	
Na	Mg											Al	Si	P	S	Cl				Ar	
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br				Kr	
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I				Xe	
Cs	Ba	*	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At				Rn	
Fr	Ra	*																			
La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu							
Ac	Th	Pa	U																		

TOF-SIMS Spectra



- Successive negative ion spectra (120 s duration) of same marine aerosol.

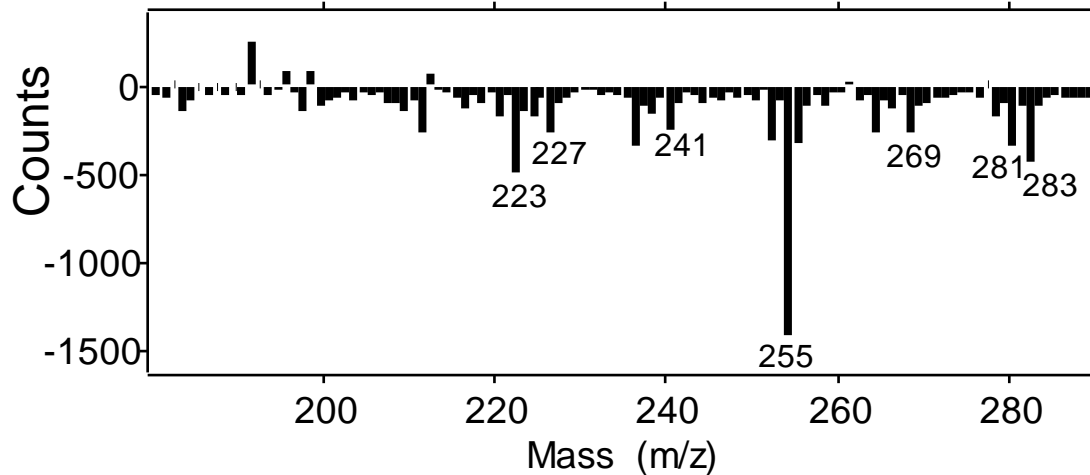
- Palmitic acid most abundant.

- During gallium ion bombardment, C₁₄-C₁₈ fatty acid peaks decline.

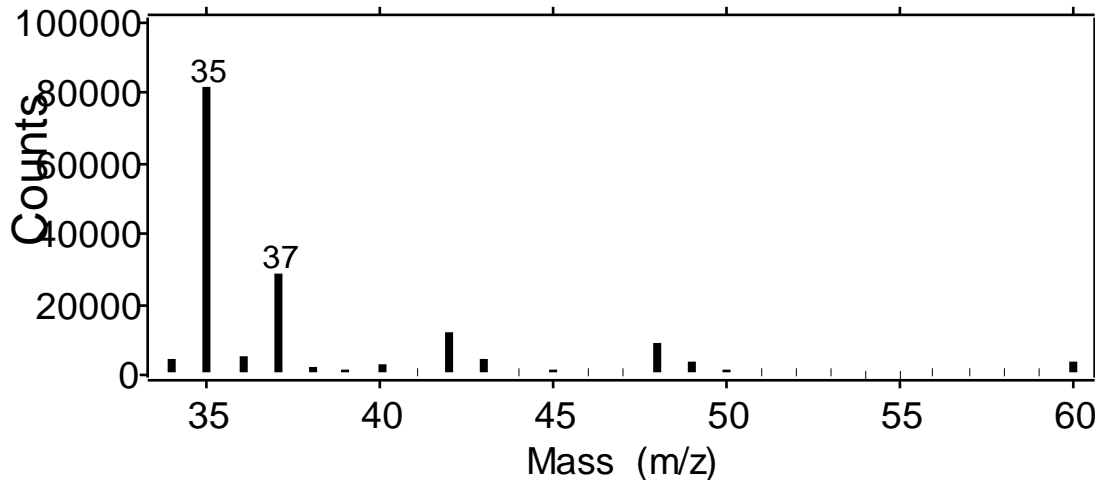
- Outer parts of aerosol are composed of these fatty acids.

Changes Induced by Sputtering

- TOF-SIMS peaks of chlorine (35 & 37) and palmitic acid (255).

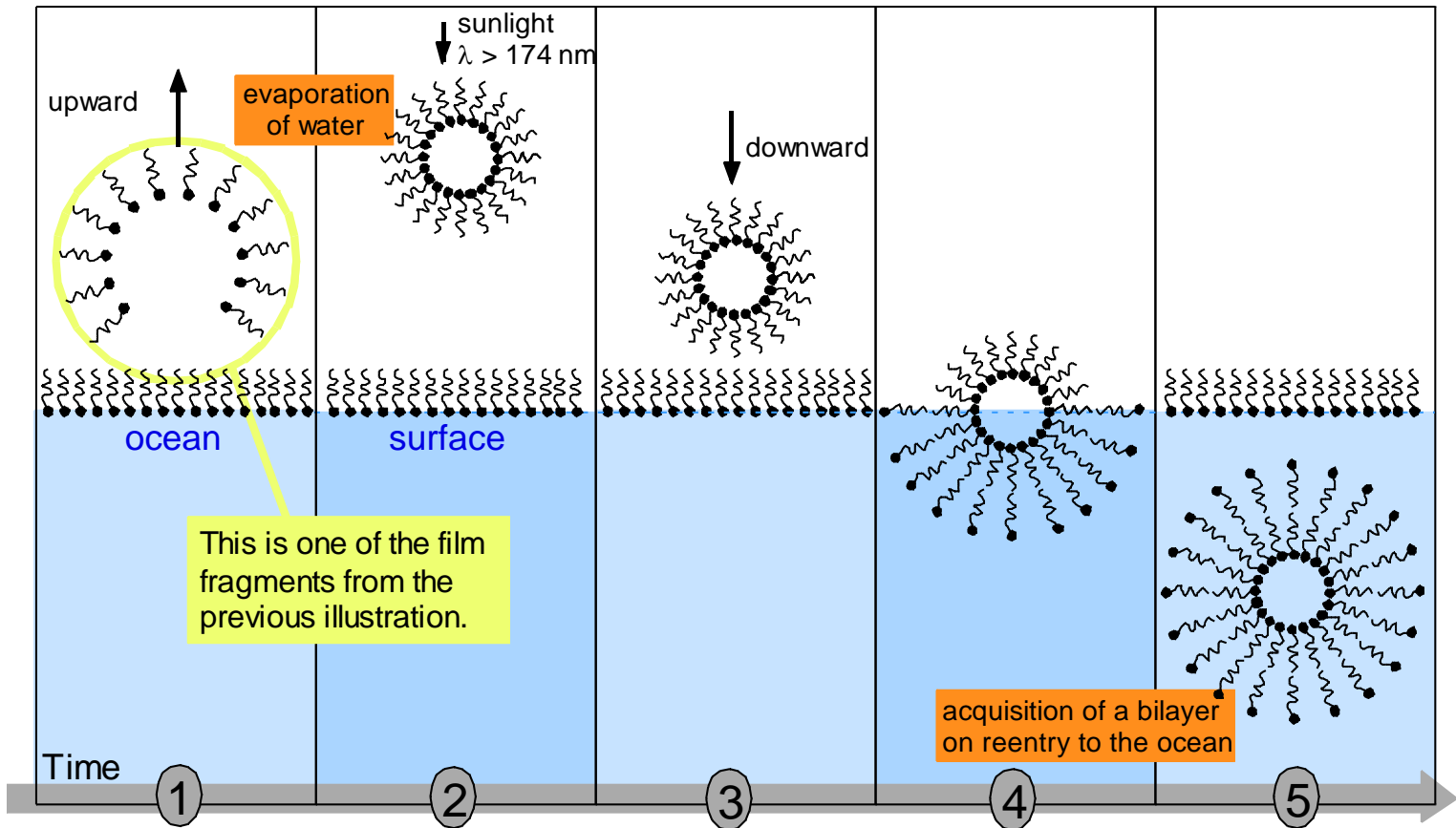


- Vertical bars show signs and intensities of changes induced by sputtering.



- Peaks from fatty acids on the surface decrease, accompanied by an increase of chlorine peaks in the interior.

Sea-Air-Sea Journey



Scale Invariance and Statistical Multifractality

$$S_q(r; \Psi) = \langle |\Psi(x+r) - \Psi(x)|^q \rangle$$

↑ q^{th} order structure function S of variable $\Psi(x)$

If a plot of $\log S_q$ vs. $\log(r)$ is linear with slope $\zeta(q)$, then $\zeta(q)$ is a scaling exponent for $\Psi(x)$, which therefore has scale invariance and power law PDFs.

Define

$$H_q = \zeta(q)/q$$

Further define

$$H = H_q + K(q)/q$$

We will be interested in $K(q)$ and H

To obtain $K(q)$, consider $\Psi(x)$ to have been observed at finite intervals $x = 1, 2, 3, \dots, x_{\max}$ and define:-

$$\varepsilon(1, x) = \{ |\Psi(x+1) - \Psi(x)| \} / \langle |\Psi(x+1) - \Psi(x)| \rangle$$

for $x = 1, 2, 3, \dots, x_{\max}$

$$\varepsilon(r, x) = (1/r) \sum_{j=x}^{x+r-1} \varepsilon(1, j)$$

for $x = 1, 2, 3, \dots, x_{\max} - r$

then a plot of $\log \langle \varepsilon(r, x) \rangle^q$ vs $\log r$ has slope $-K(q)$ and a plot of $-K(q)$ vs q shows a convex function with $K(0) = K(1) = 0$.

We can now note equivalences between scale invariance and statistical thermodynamics.

Formal equivalences between **scale invariant** (r.h.s.)
and **statistical thermodynamic** (l.h.s.) variables

$$T = 1/qk_{\text{Boltzmann}}$$

temperature

$$f = e^{-K(q)}$$

partition function

$$G = -K(q)/q$$

Gibbs free energy

This offers possible links:

molecular scale



statistical thermodynamics



macroscopic scale invariant observables

Occurrences of Scale Invariance

- * Monomer sequences in proteins and nucleic acids.
- * Distributions of proteins and lipids in membranes.
- * Folding of proteins and their binding to lipid rafts.
- * Folding, unfolding & re-folding of a 'hairpin' in a single RNA molecule.
- * All atmospheric variables observed to date.
- * Plankton spatial distributions.
- * Ocean waves and sea ice.
- * Earth's atmospheric chemistry is a **scale-free network**, like cellular biochemistry but unlike any other planet and unlike interstellar molecular clouds. *Solé & Munteanu, Europhys. Lett. 68, 170 (2004)*. [Lovelock: Gaia Hypothesis]

Tests: *Does $K(q)/q$ converge?*
 Has it been minimized?

SCALE FREE NETWORKS

¶ Still under mathematical development

¶ Molecules as nodes, reactions as connections

¶ The probability $P(k)$ of a node (molecule) having k connections (reactions) is

$$P(k) \approx ck^{-\gamma}$$

where typically $2 < \gamma < 3$

To work, need a few nodes (molecules) among many that have many connections (reactions).

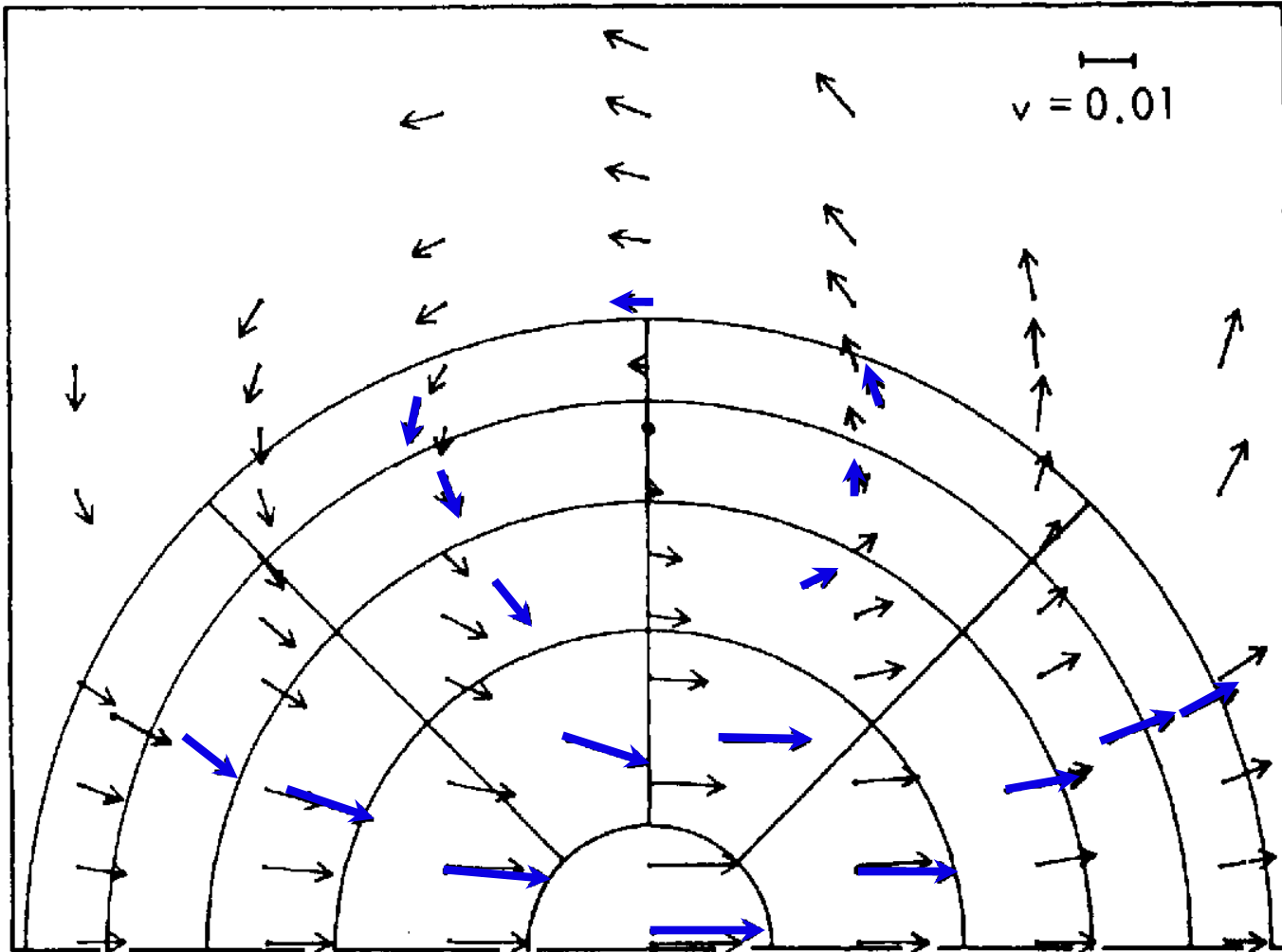
Examples:

OH in current atmosphere

ATP, pyruvic acid in metabolic chemistry

Alder & Wainwright: MD and Hydrodynamics

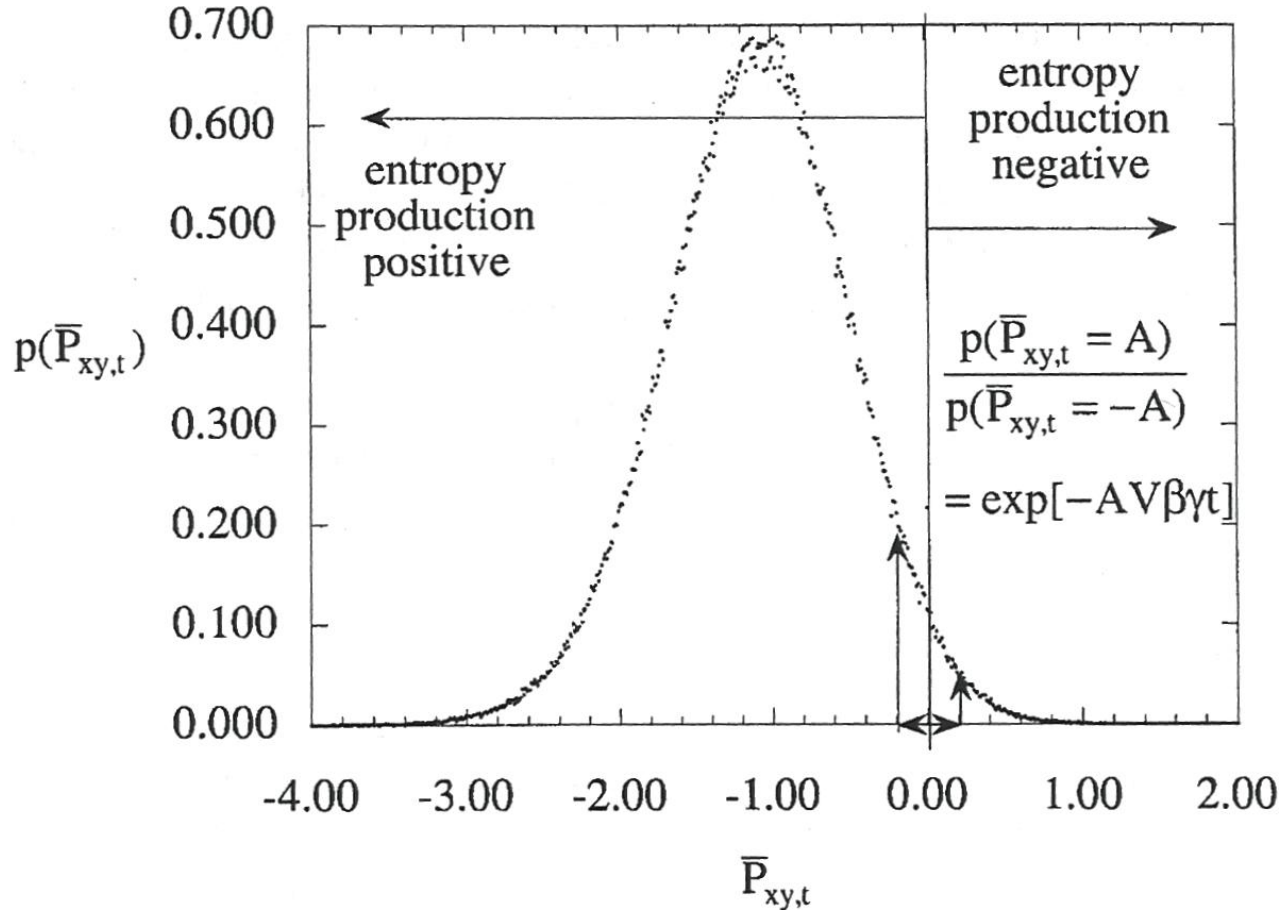
Phys. Rev. A, 1, 18-21 (1970)



Evans & Searles (2002), *Adv. Phys.*, 51,1529-1585. The minority high speed molecules, produce organization ('flow') while the average majority produce dissipation ('temperature').

The Fluctuation Theorem

$t = 0.1, \gamma = 0.5$



Fast Molecules Generate Vorticity

Under the action of a dis-equilibrating force, e.g. a flux, a thermalized population of Maxwellian molecules generates vortices ('ring currents'). The fast molecules cause high number density ahead and leave low number density behind, causing a vortex. The over-populated tail in the molecular speed PDF interactively sustains the vortex. *Hydrodynamics has emerged from Maxwellian molecules reacting to a flux on molecular scales of time and space, 10^{-8} m and 10^{-12} s.* [B J Alder]

Consequence: no local thermal equilibrium.

Recent work: molecular dynamics & fluid simulations have same scaling.

- * **Molecules compete for a finite resource** - translational energy
- * **Variation** - as the molecules collide and exchange energy
- * **Memory** - the emergent, organized fluid flow propagates
- * These are the 3 defining requirements of natural selection

IS NATURAL SELECTION AN INHERENT MOLECULAR PROPERTY?

Hypothesis: scale invariance has utility in examining the emergence of natural selection

- ¶ Earth's atmospheric chemistry is a scale-free network, like cell metabolism but unlike any other known planetary atmosphere or astrochemistry.
- ¶ If scaling exponent $-K(q)/q$ exists for a set of observations, its minimization can be a test for its thermodynamic status (Gibbs free energy criterion).
- ¶ The most energetic molecules cause organization, while the average ones accomplish dissipation and permit operational non-equilibrium temperature.
- ¶ Scale invariance corresponds to dissipation: scale selectivity would correspond to organization, which emerges after entropy production has been maximized.
- ¶ The emergence of natural selection is an expression of the boundary conditions combined with the operation of the above principles.

e. g.

aerosol fission & fusion, size distributions
propagation of organized flow
source & sink thermodynamics of atmospheric chemistry
monomer sequences in proteins & nucleic acids

are examples from the present status of Earth.

Possible Experimentally Testable Phenomena

- ¶ The propagation of organized behaviour by the most energetic molecules constitutes a very simple form of selectivity and hence “memory”. Is this the most primitive, molecular form of natural selection?
- ¶ Scale invariance is a consequence of dissipation, linking microscopic and macroscopic scales. Convergence and minimization of scaling exponent ratio $-K(q)/q$ constitutes sufficiency.
- ¶ Do present day airborne bacteria and viruses mutate via atmospheric photochemistry? ($h\nu$, OH, HO₂, NO_x, O₃, RO_x, halogen chemistry). Do they undergo fusion and/or fission? Do they interact with aerosols?
- ¶ Can contemporary “one pot” chemistry experiments aimed at nucleic acid and protein genesis be usefully examined by scale free network and multifractal scale invariance analysis?
- ¶ Is “junk” DNA simply the entropy price paid for the organized (genetically functional) sequences? Recent evidence suggests not.

Lecture 5.1: Summary

* Scale invariance exists on all scales from molecules to molecular clouds.

* Scale free networks have been found only in cellular biochemistry and Earth's atmosphere. [A new view of Lovelock's Gaia hypothesis?]

* Consistent with the thermodynamic formulation of scale invariance and the molecular dynamics interpretation of natural selection.

E C Griffith, A F Tuck & V Vaida (2012), Ocean-atmosphere interactions in the emergence of complexity in simple chemical systems, *Accounts of Chemical Research*, **NN**, nnn-*nnn*, doi:10.1021/ar300027q.

E C Griffith & V Vaida (2012), In situ observation of peptide bond formation at the water-air interface, *Proceedings of the National Academy of Sciences*, **NN**, nnnn-*nnnn*, doi: 10.1073/pnas.1210029109.