Chemistry Models

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GPS Caltech

Sagan Exoplanet Summer Workshop
Jul 20 2009

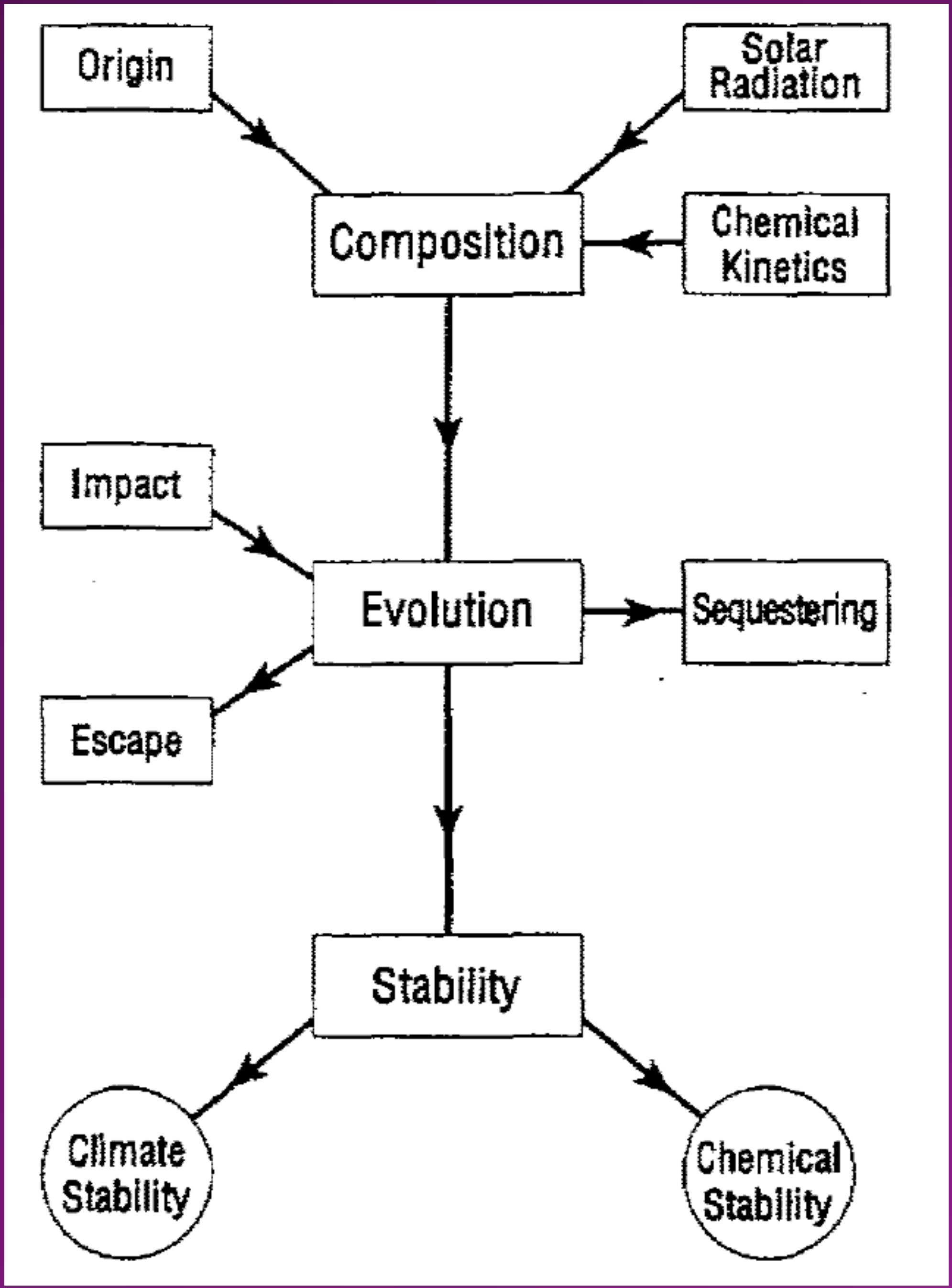
Models

Common photochemistry: hundreds of molecules, thousands of reactions

Transport: 1-D diffusion vertical

2-D advection

3-D general circulation model

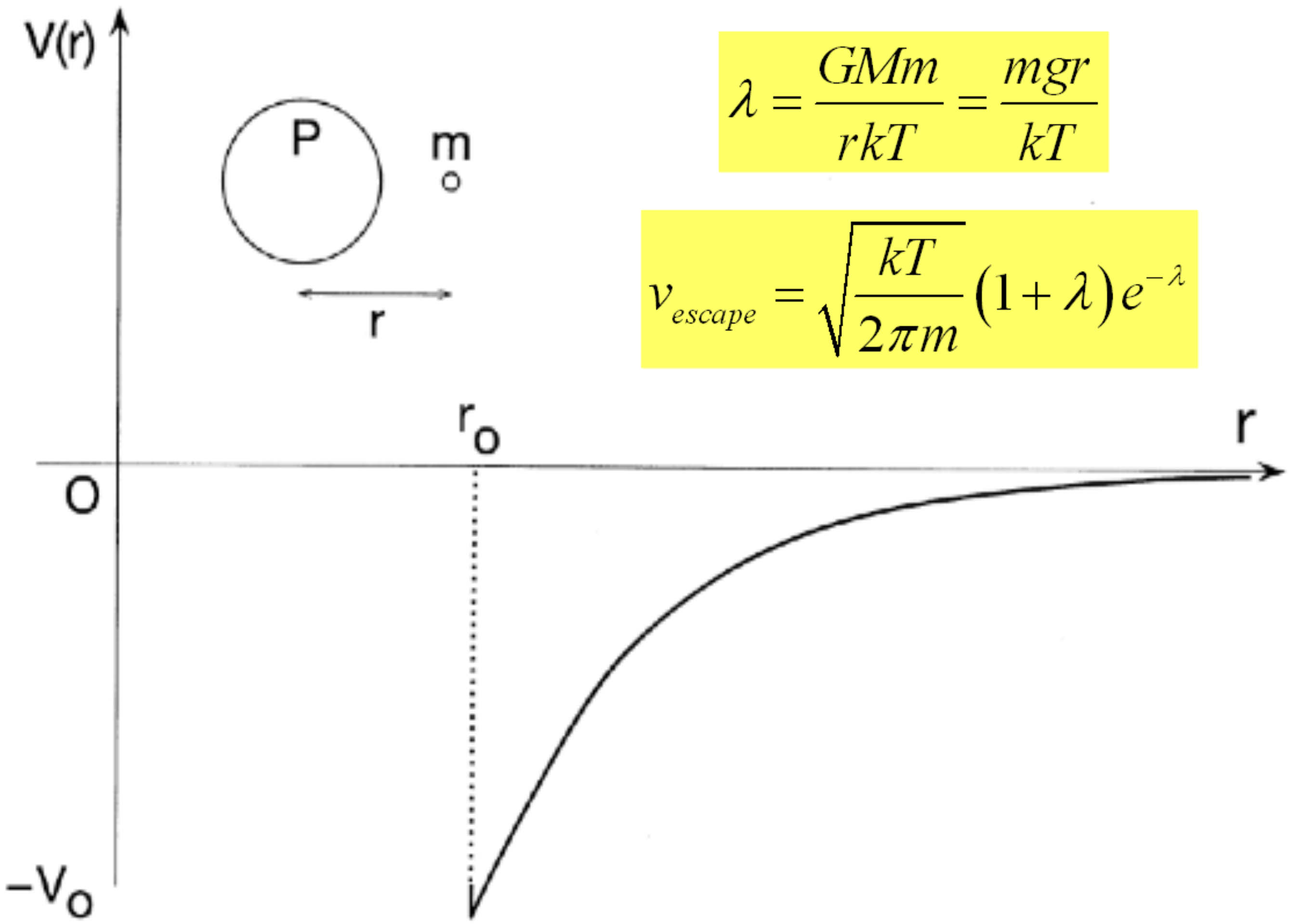


Yung and DeMore, 1999

Today's Outline

- Jupiter: The cosmic reference point
- Titan: Nature's Laboratory of Organic Synthesis
- Mars: Is Methane biologically produced?
- Earth: The cosmic end member
- Conclusions

Gravity and Escape



$$\lambda = \frac{GMm}{rkT} = \frac{mgr}{kT}$$

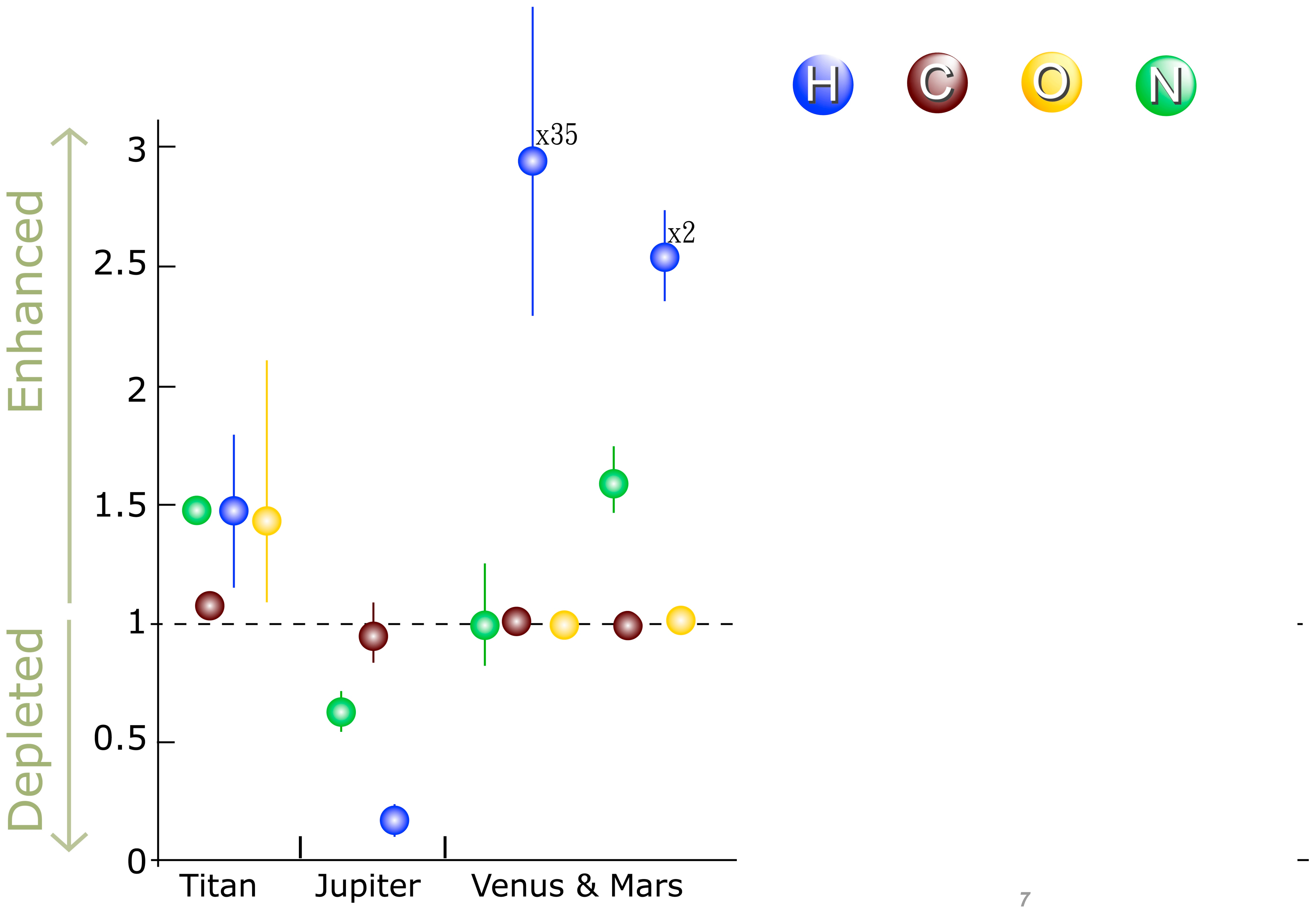
$$v_{escape} = \sqrt{\frac{kT}{2\pi m}}\left(1+\lambda\right)e^{-\lambda}$$

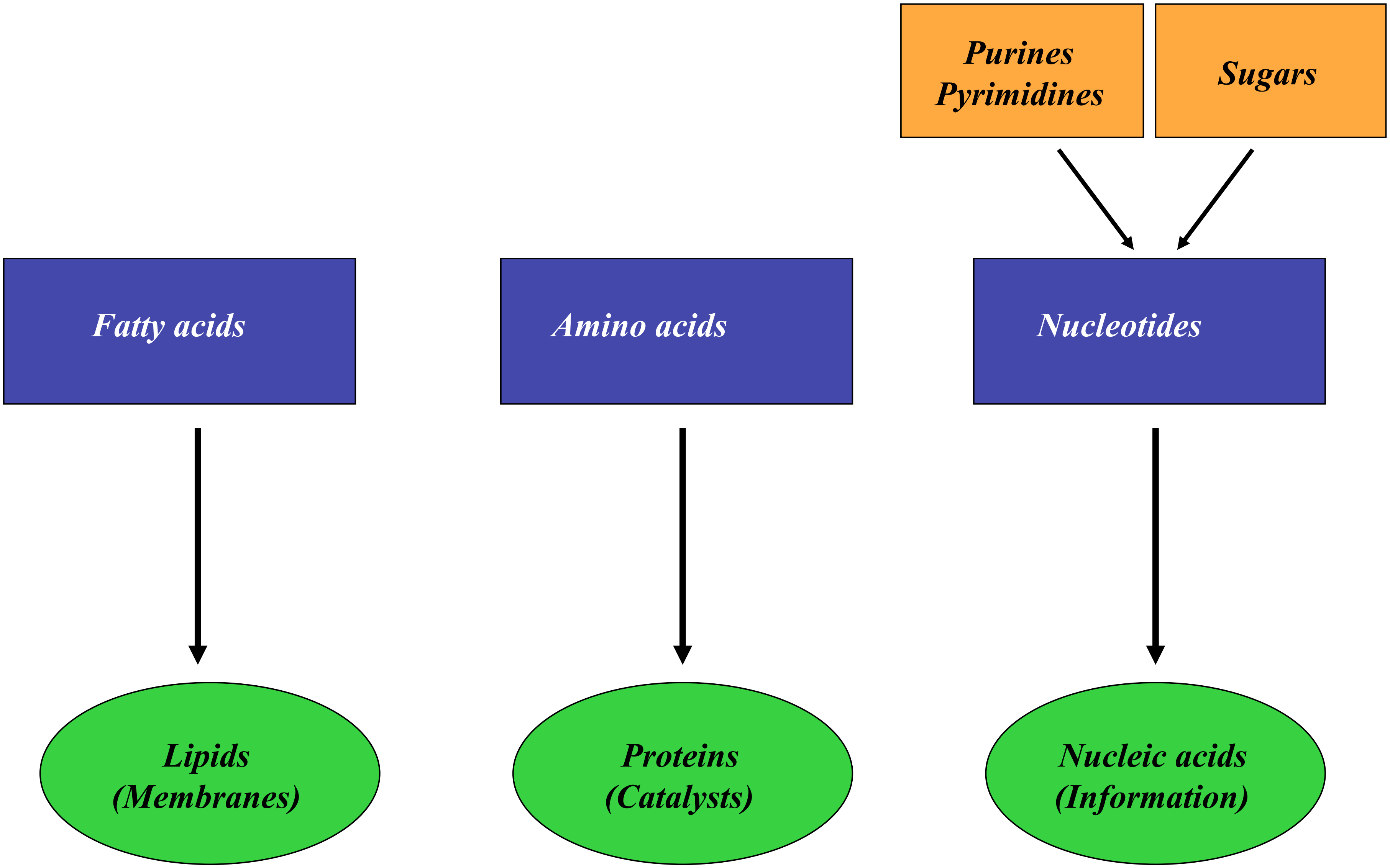
λ Determines Evolution

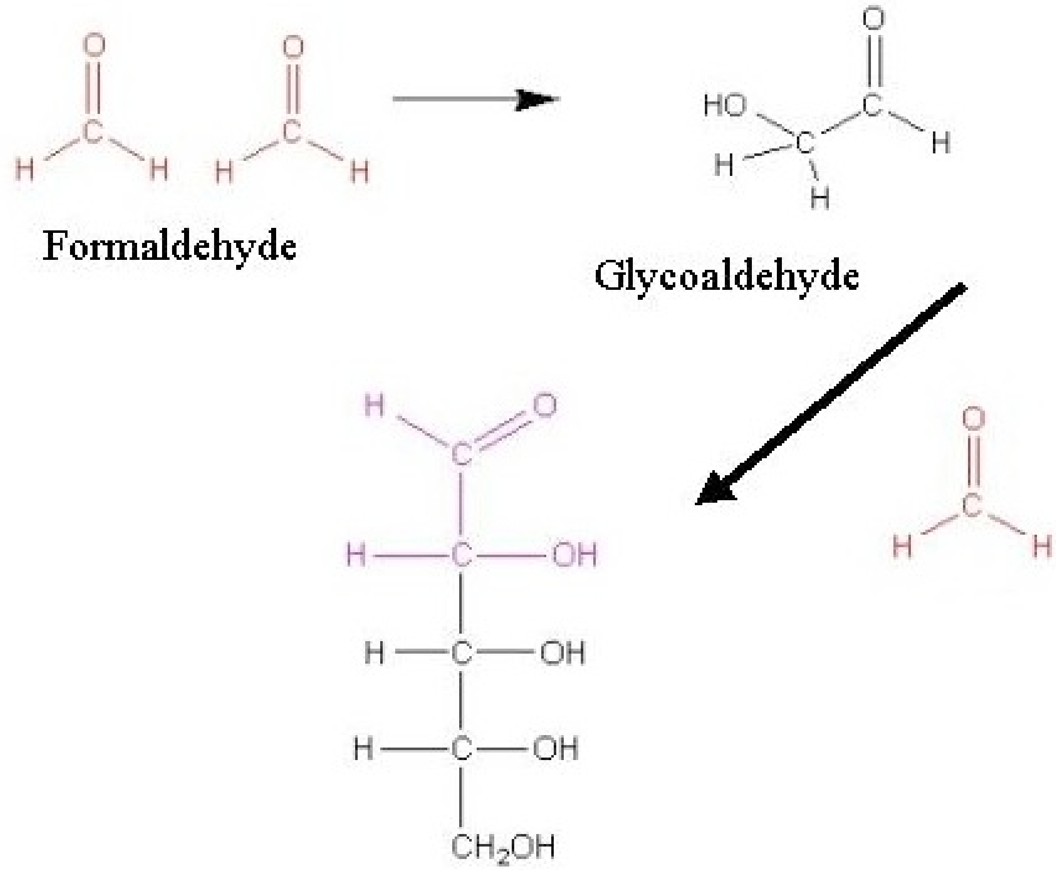
Table 1.6 Jeans escape parameters for hydrogen and oxygen atoms

Planetary body	Temperature[a] (K)	λ_H[b]	λ_O[b]	V_H[c] (cm s^{-1})	V_O[c] (cm s^{-1})
Jupiter	1200	165	2665	0	0
Saturn	400	162	2614	0	0
Uranus	810	33	531	1.6×10^{-8}	0
Neptune	540	61	977	1.7×10^{-20}	0
Titan	185	2.3	36	1.6×10^{4}	1.1×10^{-10}
Triton	95	1.3	22	2.2×10^{4}	5.7×10^{-5}
Pluto	100	0.9	14	2.8×10^{4}	0.11
Io	500	0.8	13	6.6×10^{4}	0.64
Mars	365	4.1	67	5.9×10^{3}	0
Venus	400	16.2	260	0.11	0
Earth	1200	6.3	100	1.7×10^{3}	0
Moon	390	0.9	14	5.5×10^{4}	0.22
Mercury	700	1.6	25	5.0×10^{4}	2.4×10^{-5}

Yung and DeMore, 1999

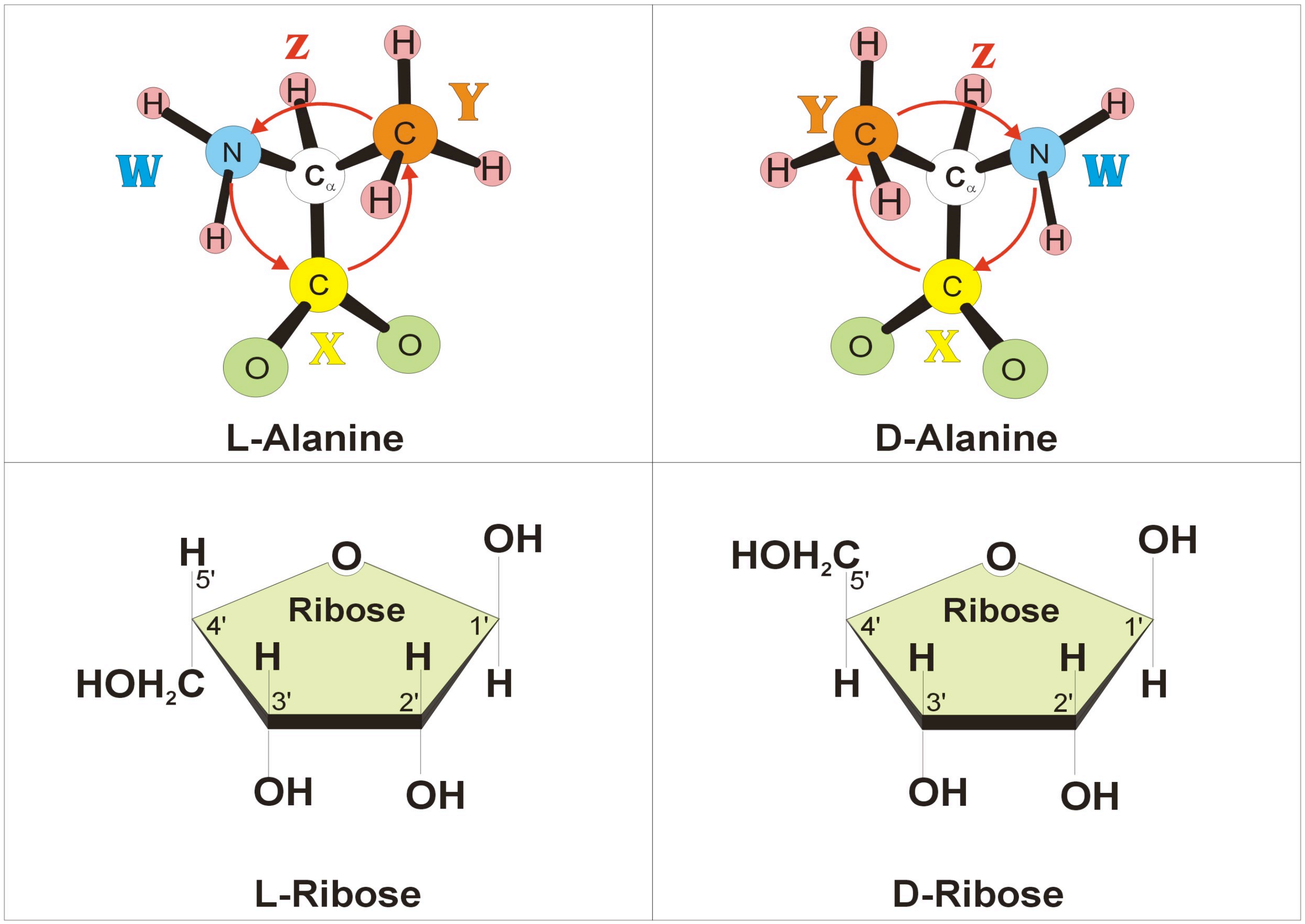

H
C
O
N
Enhanced
Depleted
3
2.5
2
1.5
1
0.5
0
x35
x2
Titan
Jupiter
Venus & Mars

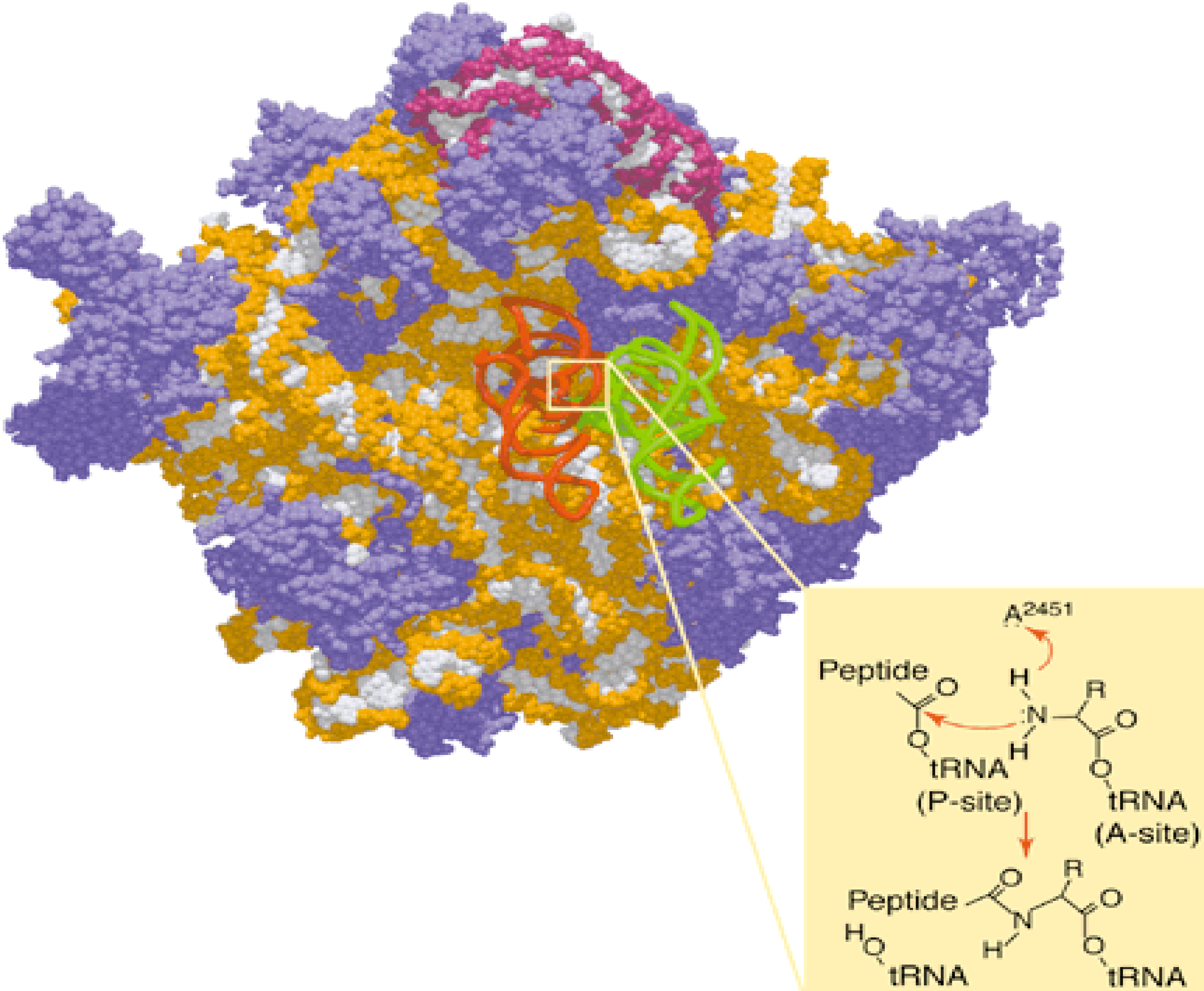

Purines
Pyrimidines
Sugars
Fatty acids
Amino acids
Nucleotides
Lipids
(Membranes)
Proteins
(Catalysts)
Nucleic acids
(Information)



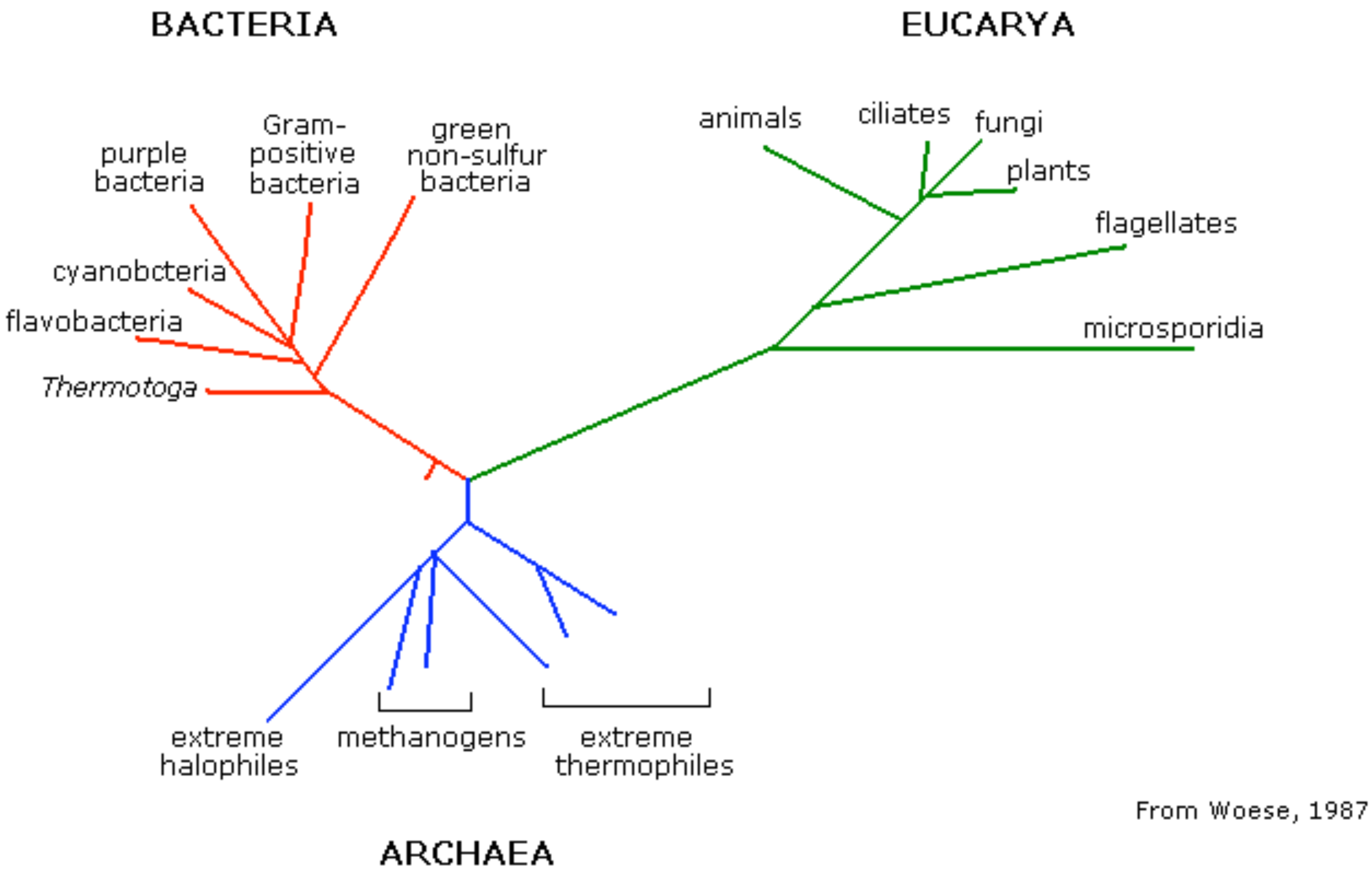
Ribose (D-enantiomer)

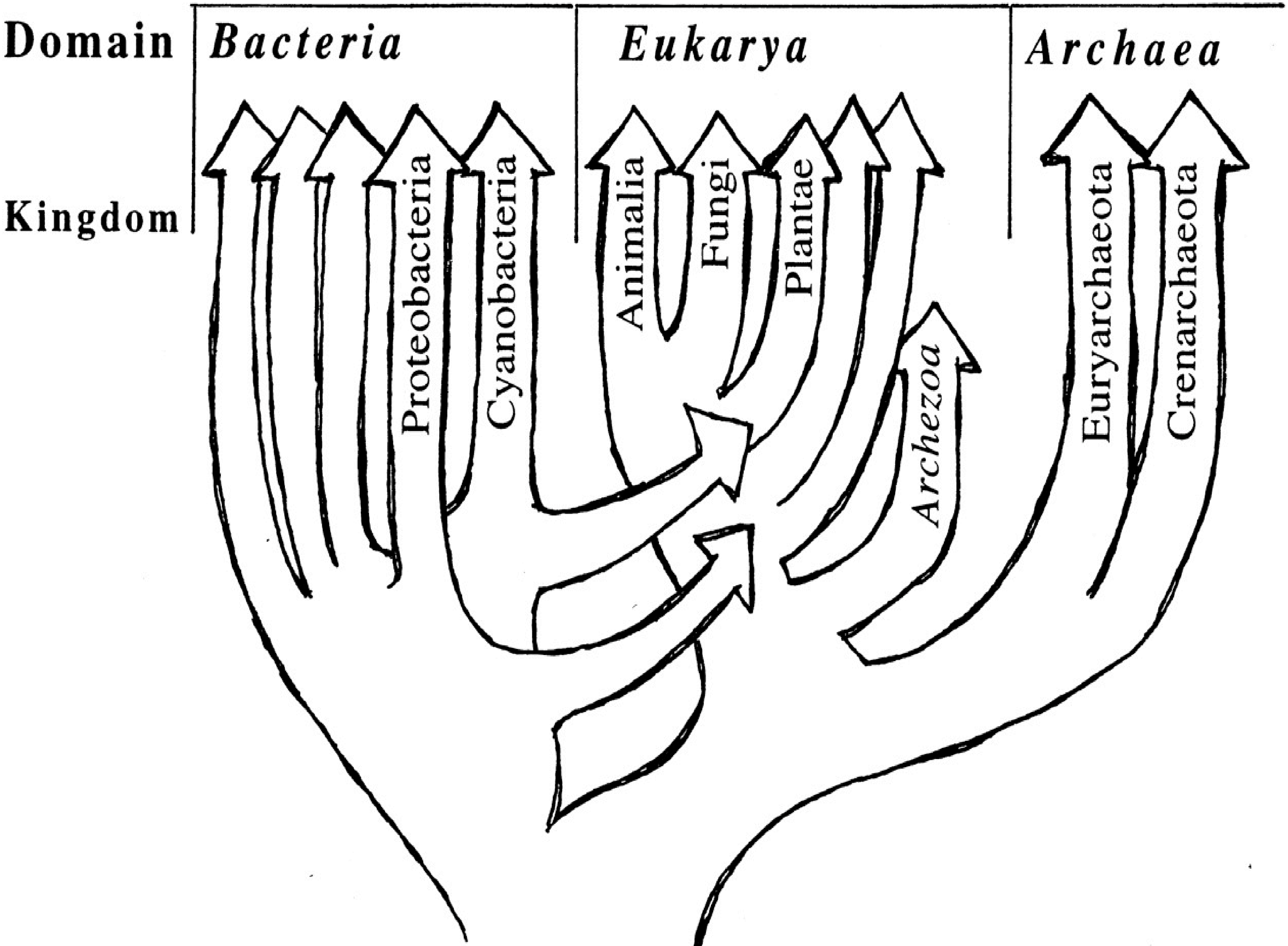
The chiral Molecules of Life

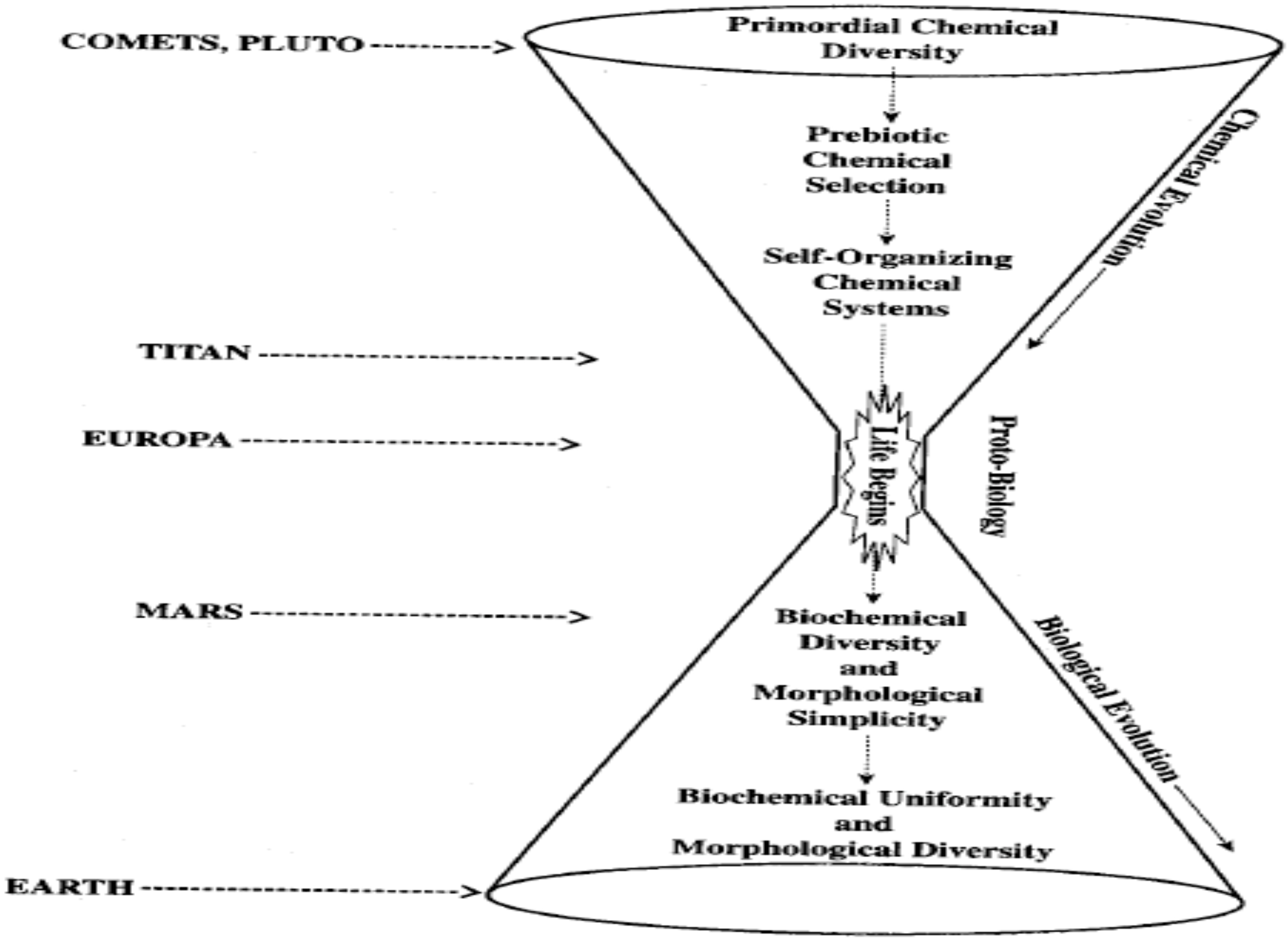




A2451
Peptide
H
N
H
R
O
O
O
tRNA
(P-site)
O
tRNA
(A-site)
Peptide
O
N
H
R
O
HO
tRNA
O
tRNA


BACTERIA
EUCARYA
purple bacteria
Gram-positive bacteria
green non-sulfur bacteria
cyanobcteria
flavobacteria
Thermotoga
animals
ciliates
fungi
plants
flagellates
microsporidia
extreme halophiles
methanogens
extreme thermophiles
ARCHAEA
From Woese, 1987


Domain
Kingdom
Bacteria
Eukarya
Archaea
Proteobacteria
Cyanobacteria
Animalia
Fungi
Plantae
Archezoa
Euryarchaeota
Crenarchaeota


COMETS, PLUTO
TITAN
EUROPA
MARS
EARTH
Primordial Chemical Diversity
Prebiotic Chemical Selection
Self-Organizing Chemical Systems
Life Begins
Biochemical Diversity and Morphological Simplicity
Biochemical Uniformity and Morphological Diversity
Chemical Evolution
Proto-Biology
Biological Evolution

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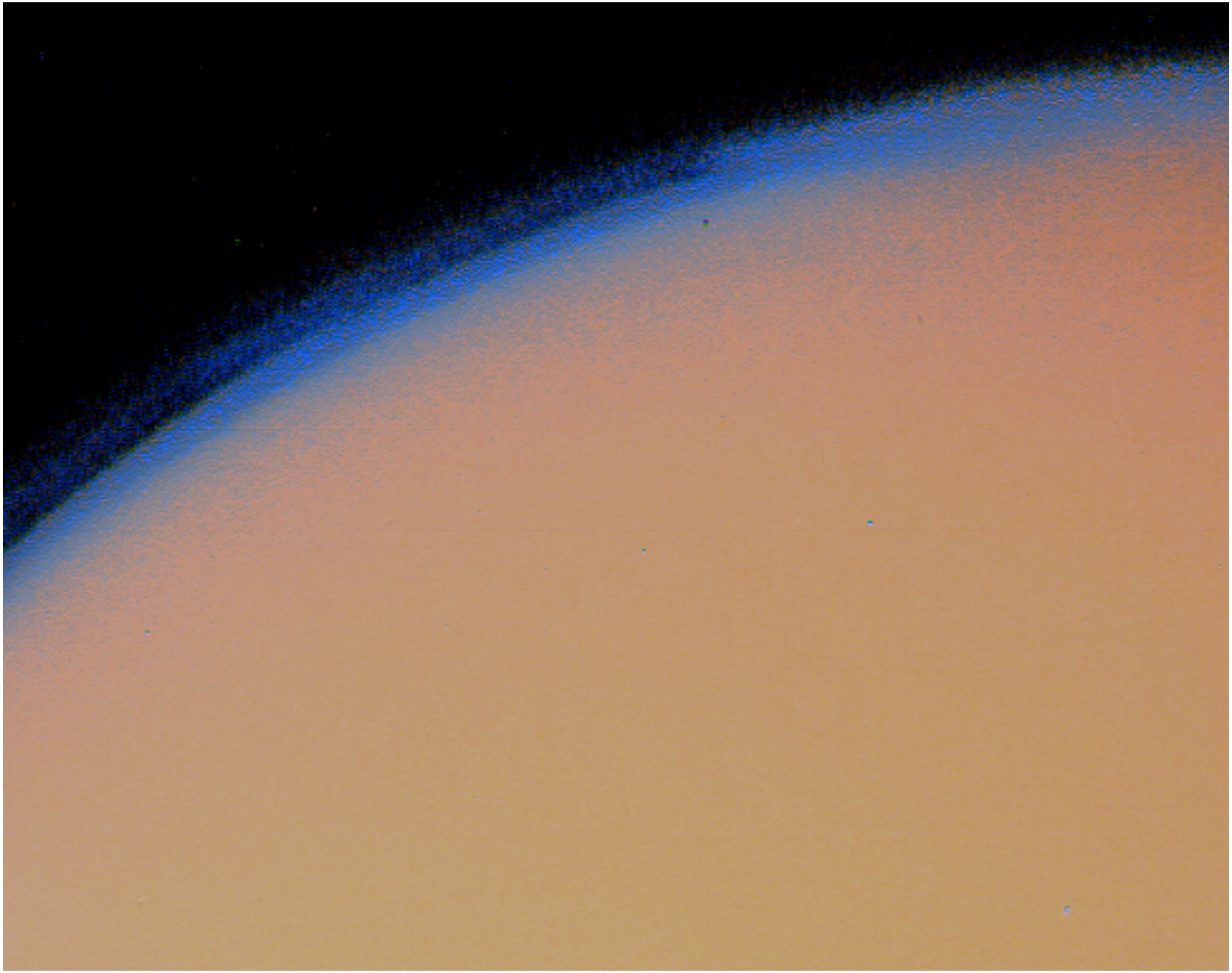
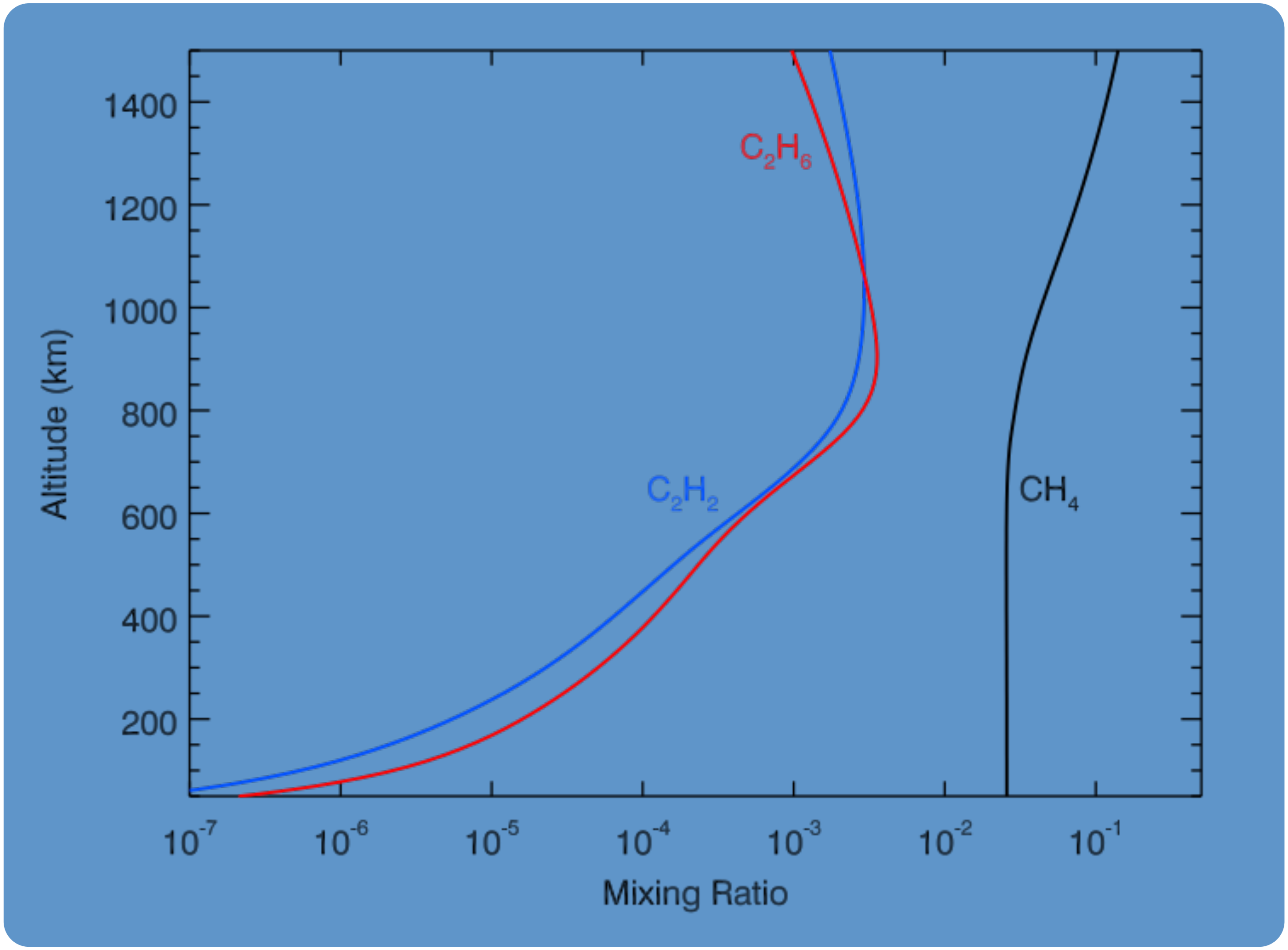
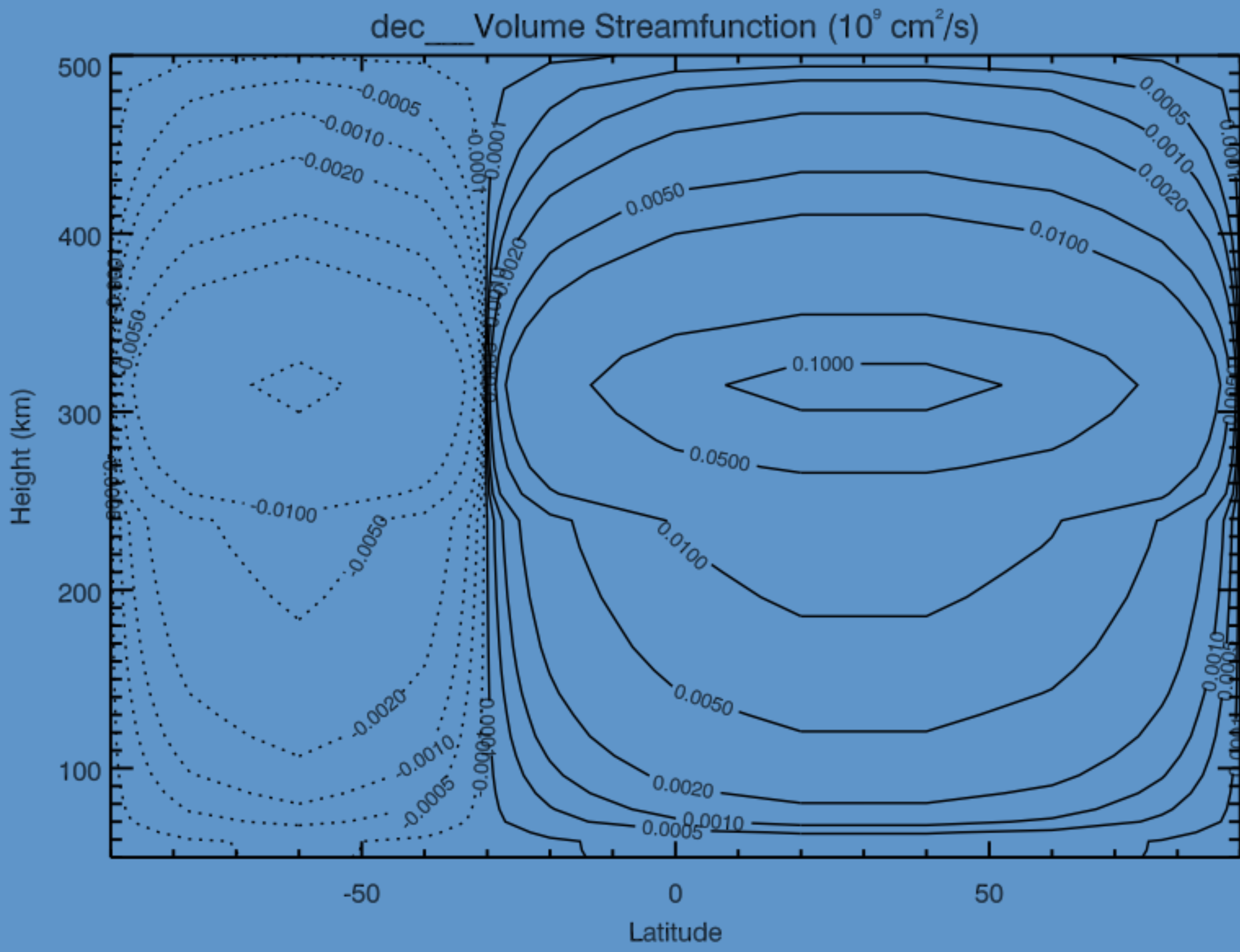


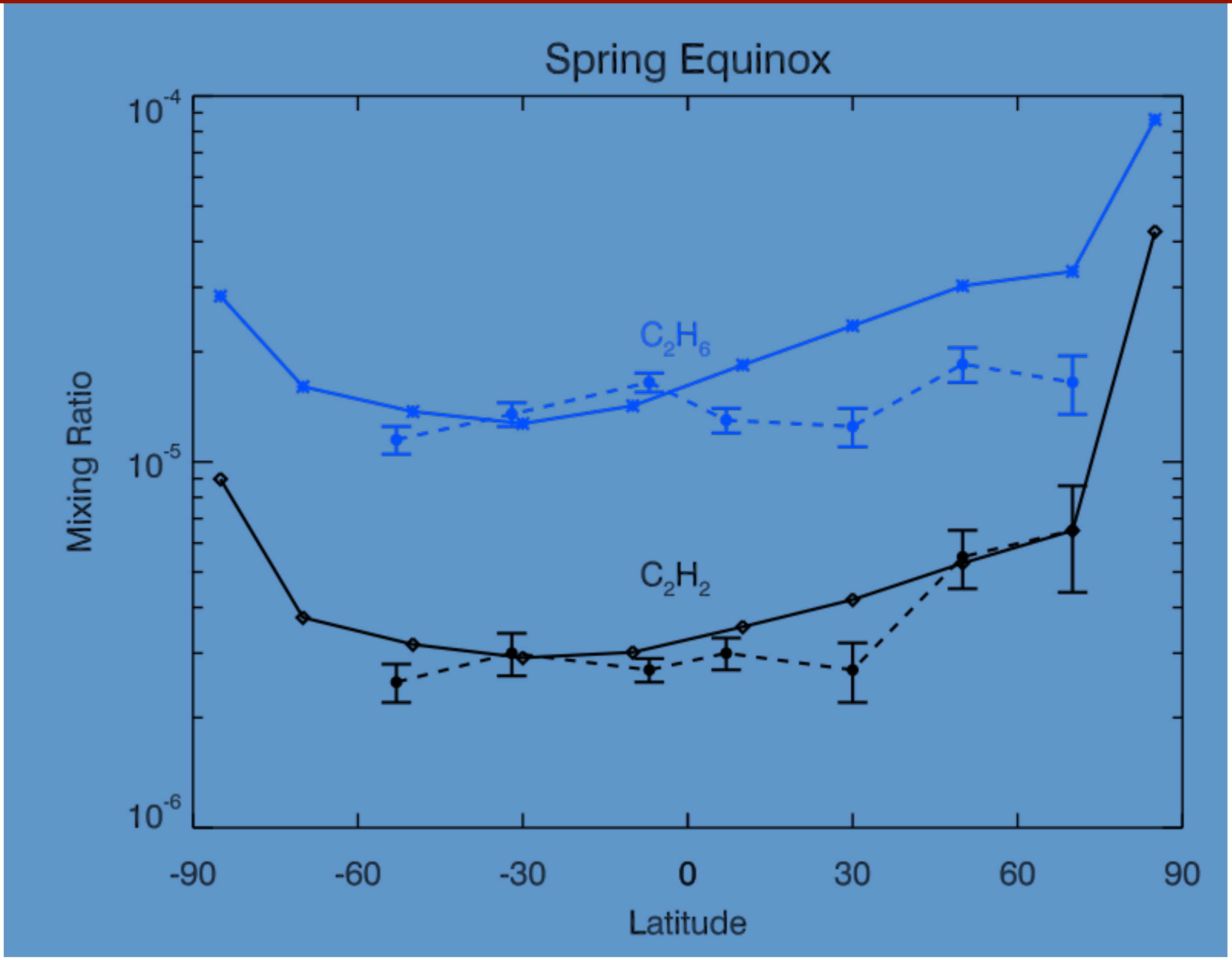
Hydrocarbons



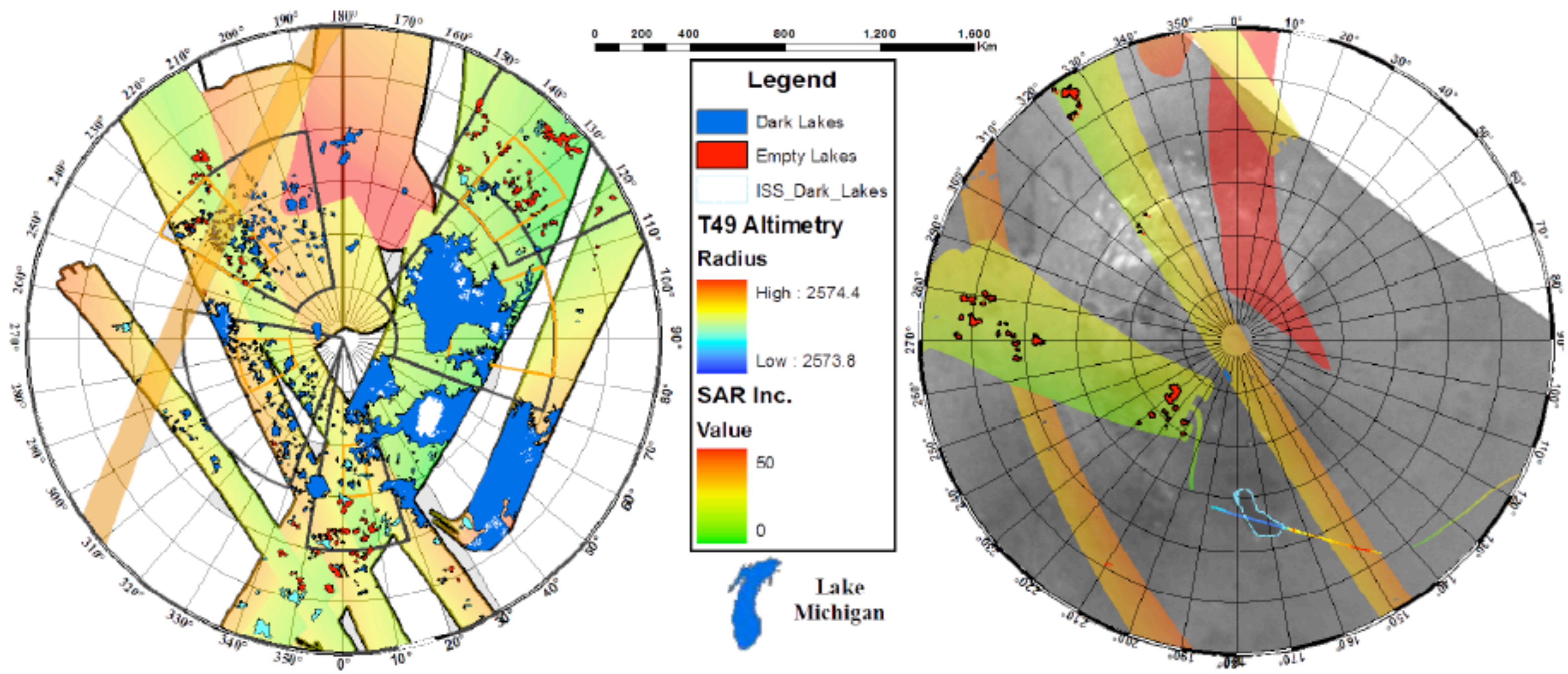
Winter Circulation



Hydrocarbon Gradients

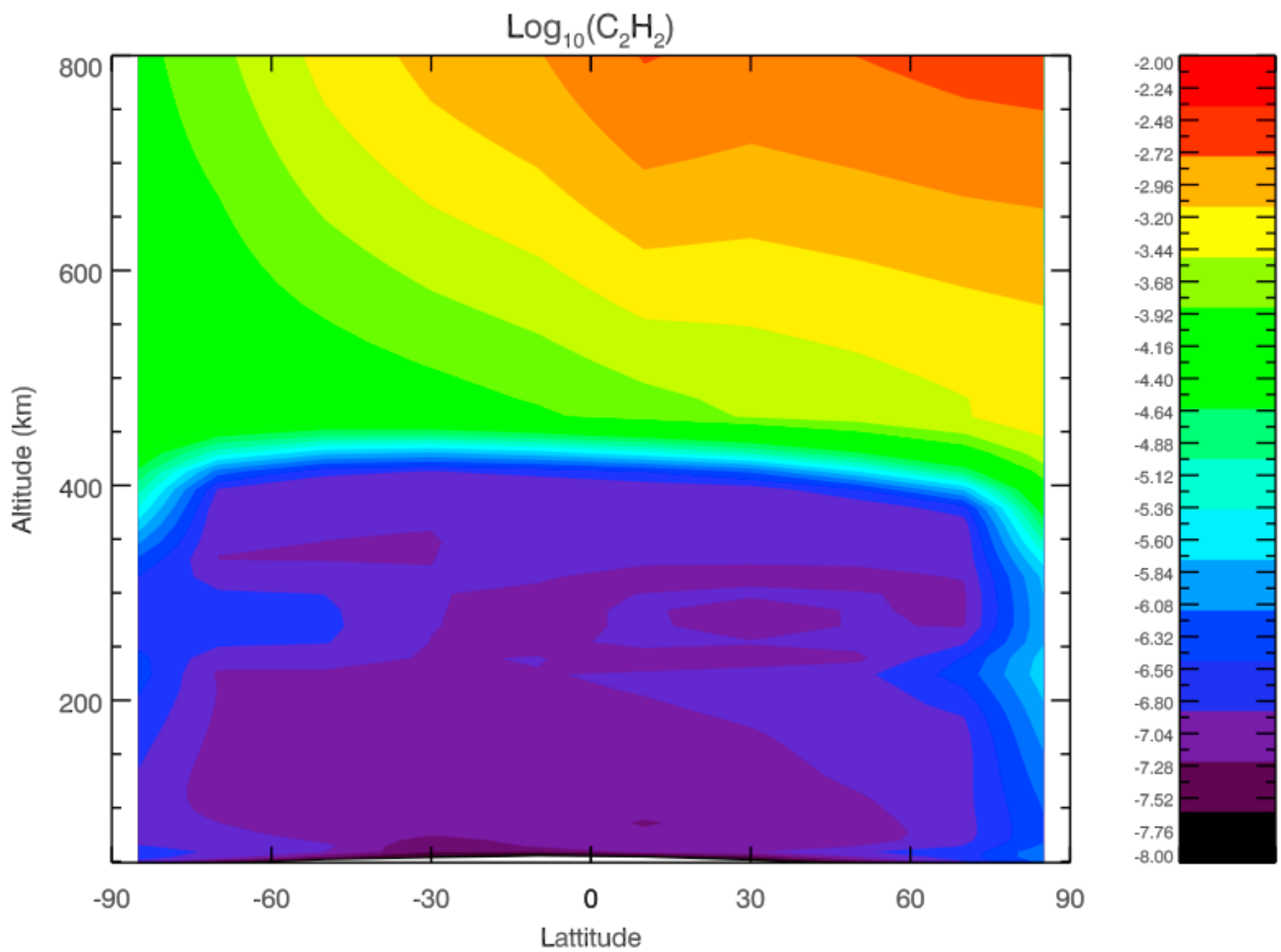


Images of Hydrocarbon Hydrology in Titan's Polar Regions

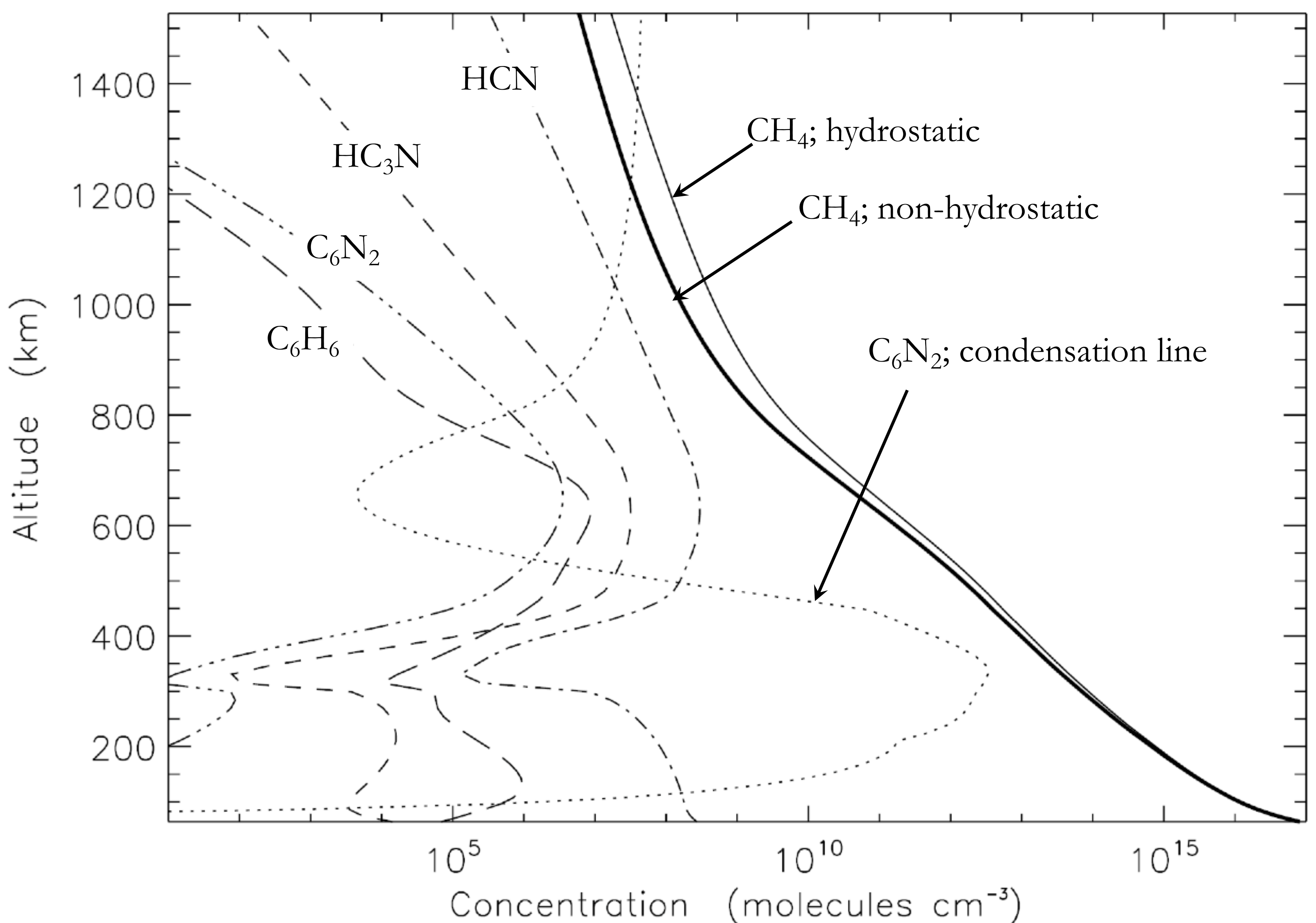


Alexander G. Hayes
Oded Aharonson, Charles Elachi, and the CRST

C_2H_2 Abundance



Photochemical results



Liang et al. 2007

- Mars: Gone with the (Solar) Wind

- Isotopic Fractionation

Kass and Yung Science 1995

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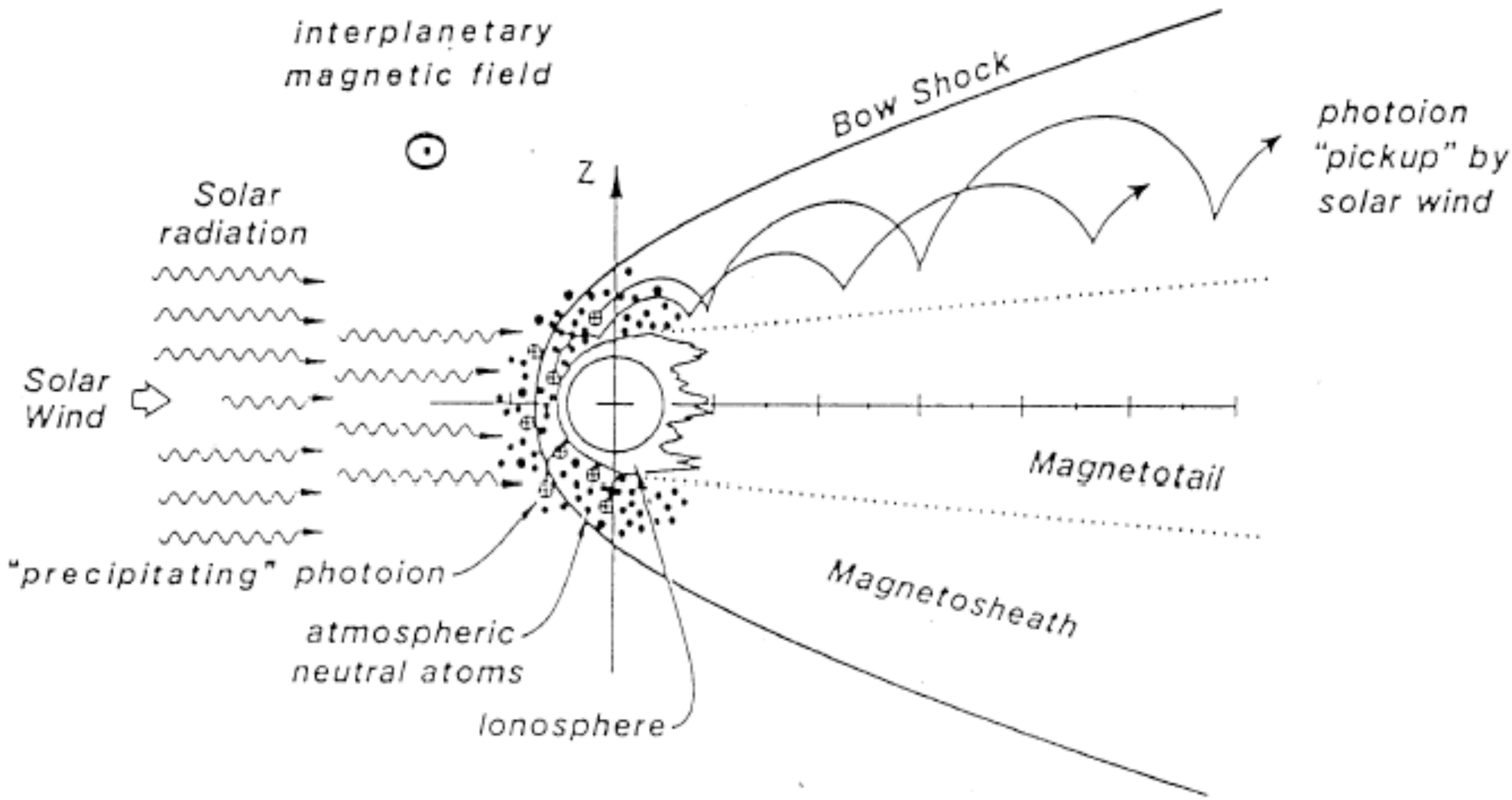
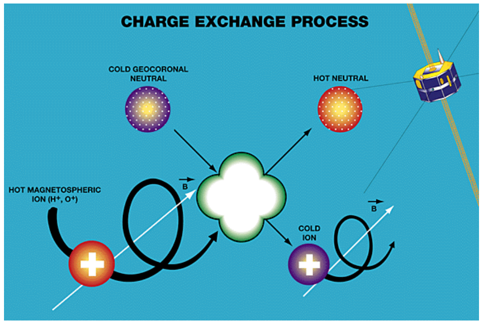
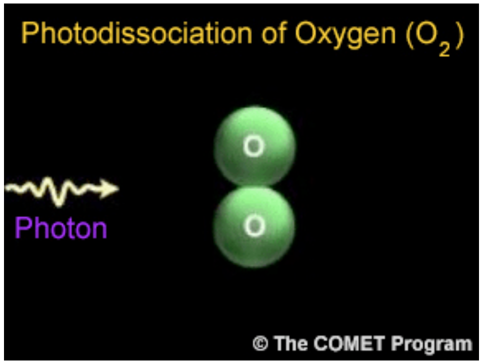

interplanetary
magnetic field
Bow Shock
photoion
"pickup" by
solar wind
Z
Solar
radiation
Solar
Wind
Magnetotail
Magnetosheath
"precipitating" photoion
atmospheric
neutral atoms
Ionosphere

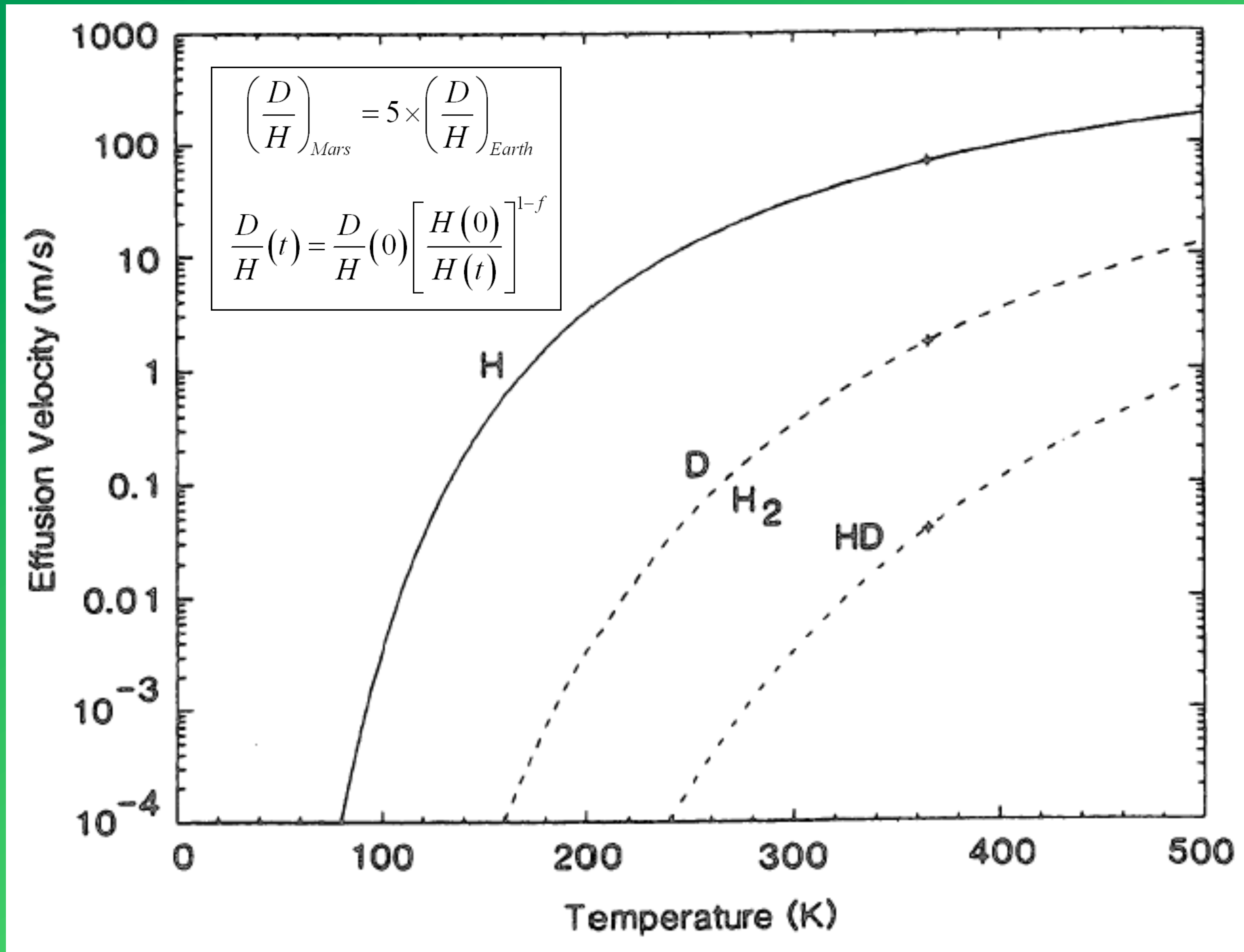
TABLE 1. Nonthermal Processes Leading to Escape*

PROCESS	EXAMPLES	PRODUCT†
1. Charge exchange	$H + H^{+}* \rightarrow H^{+} + H*$	N
	$O + H^{+}* \rightarrow O^{+} + H*$	N
2. Dissociative recombination	$O_2^{+} + e \rightarrow O* + O*$	N
	$OH^{+} + e \rightarrow O + H*$	N
3. Impact dissociation	$N_2 + e* \rightarrow N* + N*$	N
Photodissociation	$O_2 + h\nu \rightarrow O* + O*$	N
4. Ion-neutral reaction	$O* + H_2 \rightarrow OH^{+} + H*$	N
5. Sputtering or Knock-on	$O + O^{+*} \rightarrow O* + O^{+}*$	N
	$O* + H \rightarrow O* + H*$	N
6. Solar-wind pickup	$O + h\nu \rightarrow O^{+} + e$	I
	O^{+} picked up	I
7. Ion escape	$H^{+}*$ escapes	I
8. Electric field	$X^{+} + eV \rightarrow X^{+}*$	I





Escape and Rayleigh Distillation



$$\left(\frac{D}{H}\right)_{Mars} = 5 \times \left(\frac{D}{H}\right)_{Earth}$$

$$\frac{D}{H}(t) = \frac{D}{H}(0)\left[\frac{H(0)}{H(t)}\right]^{1-f}$$

Methane on Mars

* Spectroscopic detection
* Biological Production ?
* Geochemical Sources ?

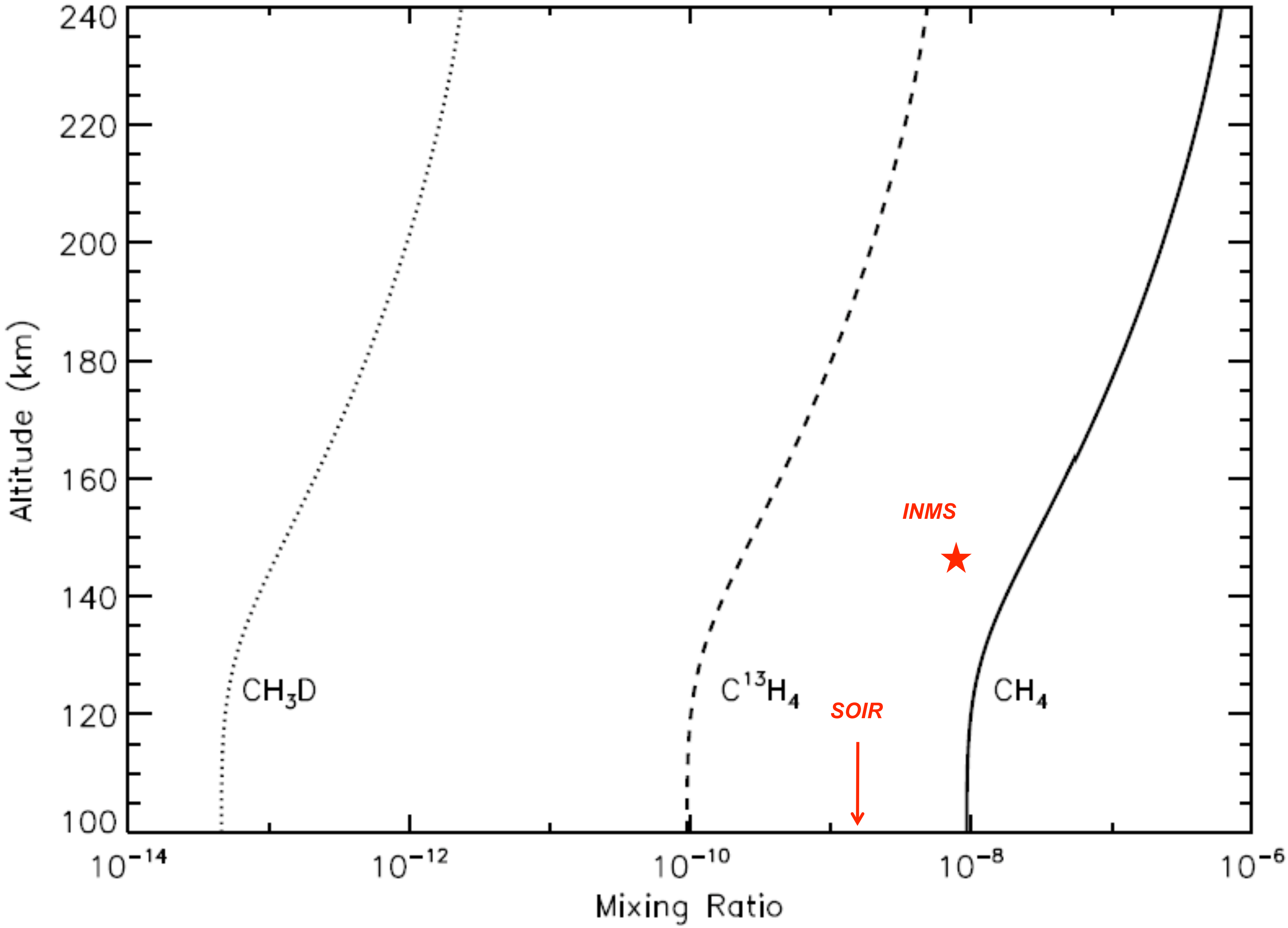
Mumma et al. 2009

Table 4

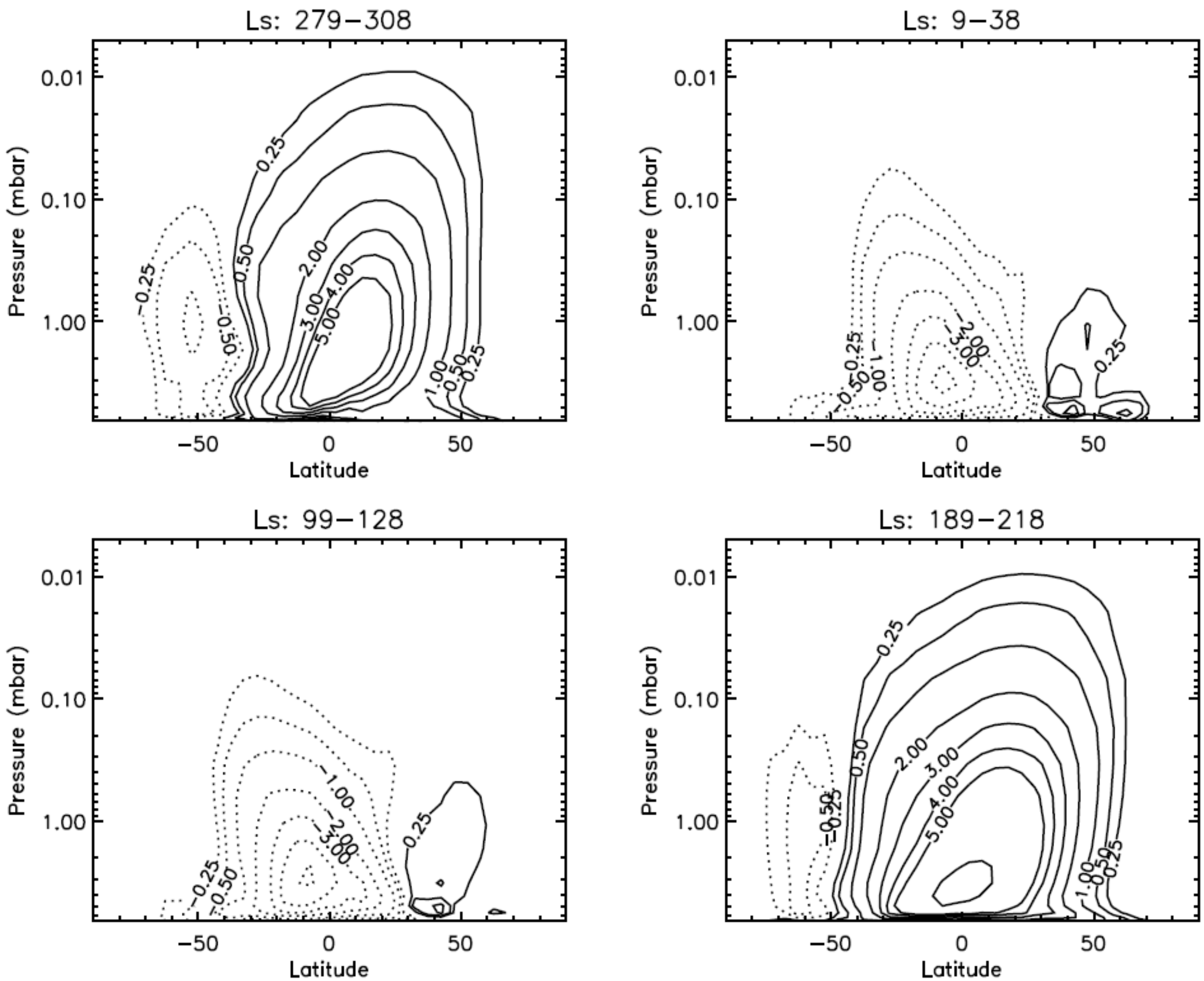
Column integrated loss rates and timescales for methane isotopologues

	$h\nu$ column rate ($cm^{-2}\,s^{-1}$)	τ (years)	OH column rate ($cm^{-2}\,s^{-1}$)	τ (years)	$O(^1D)$ column rate ($cm^{-2}\,s^{-1}$)	τ (years)
CH_4	1.700×10^5	430	1.098×10^5	665	6.702×10^4	1090
CH_3D	4.347×10^2	431	2.010×10^2	931	1.620×10^2	1155
$^{13}CH_4$	1.808×10^3	430	1.165×10^3	668	7.048×10^2	1104

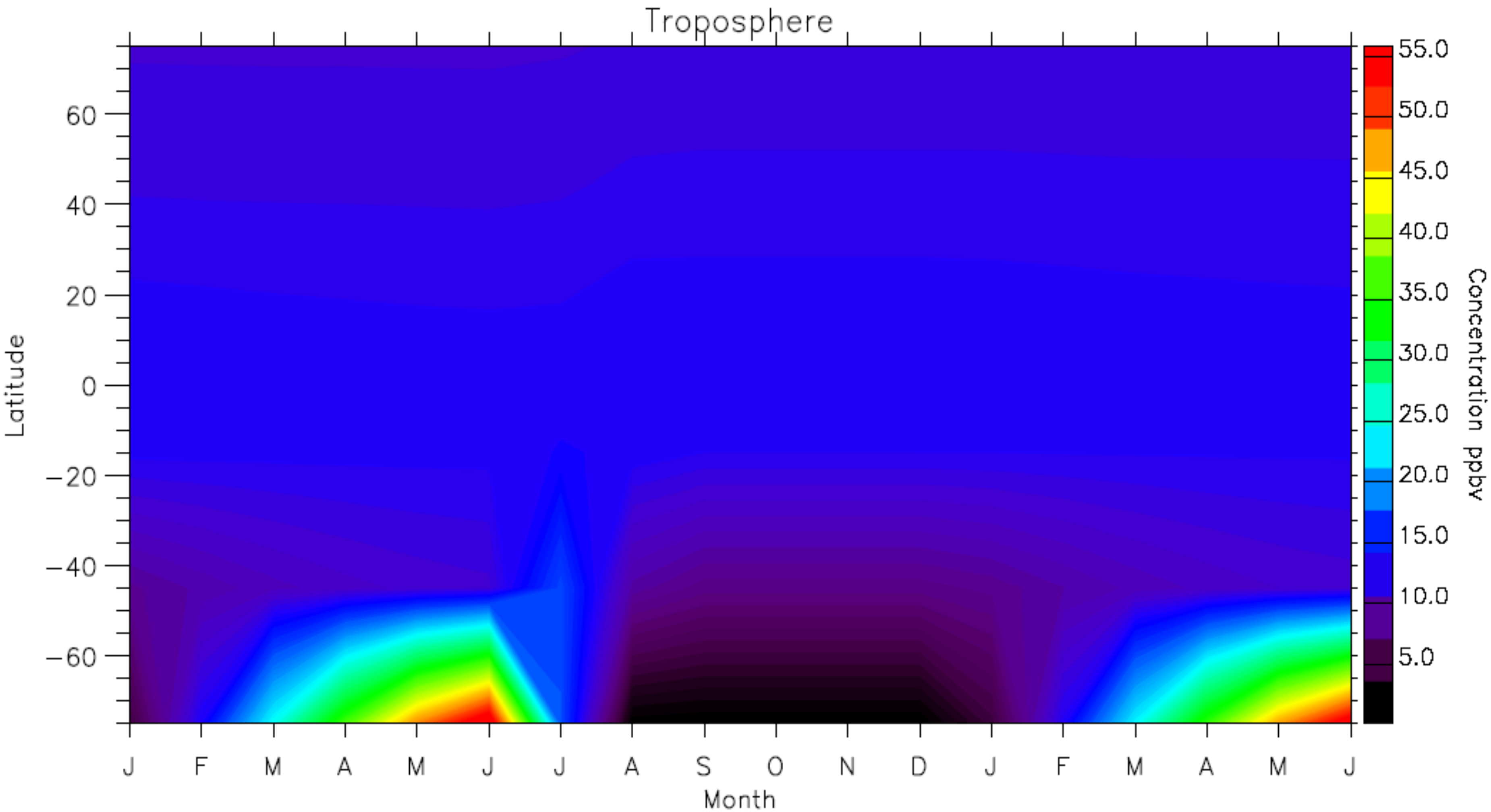
(Nair, Summers, Miller, and Yung, ICARUS, 2005)



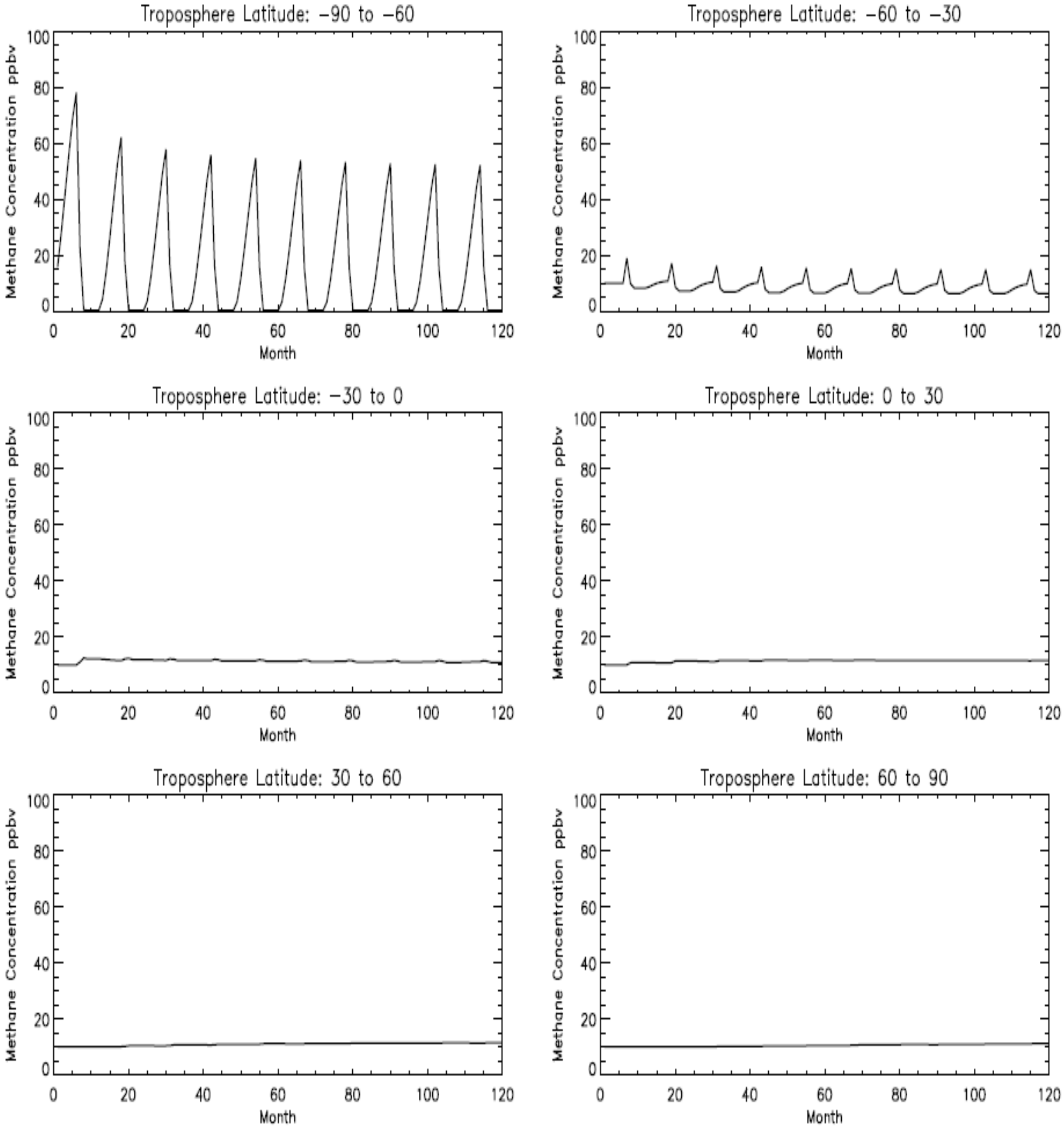
240
220
200
180
160
140
120
100
Altitude (km)
10^-14
10^-12
10^-10
10^-8
10^-6
Mixing Ratio
CH3D
C13H4
CH4
INMS
SOIR



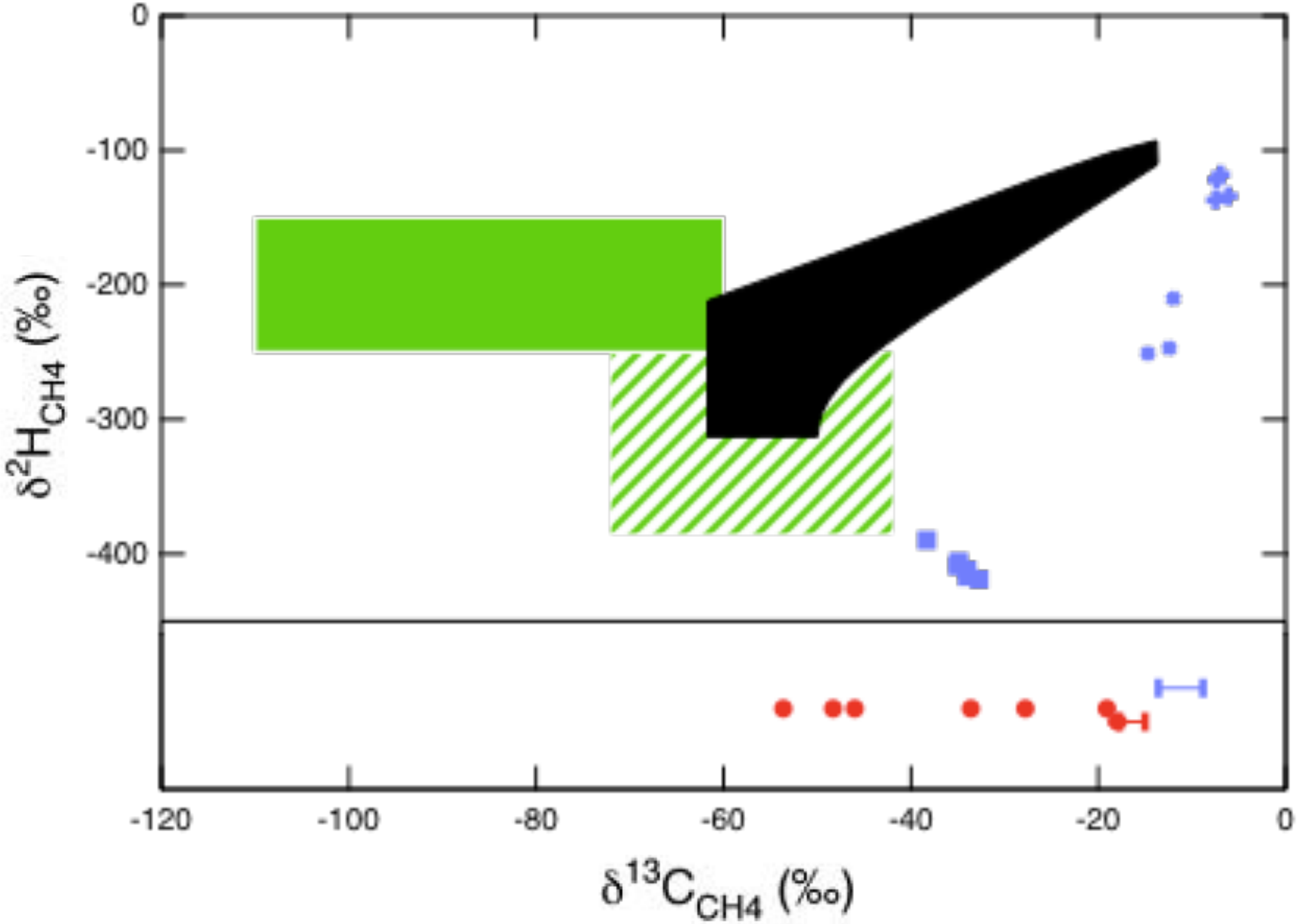
This shows the residual circulation of the stream function. The solid lines represent a clockwise flow and the dotted a counterclockwise flow. The top left graph is for January, the top right for April, the bottom left for July, and the bottom right for October.



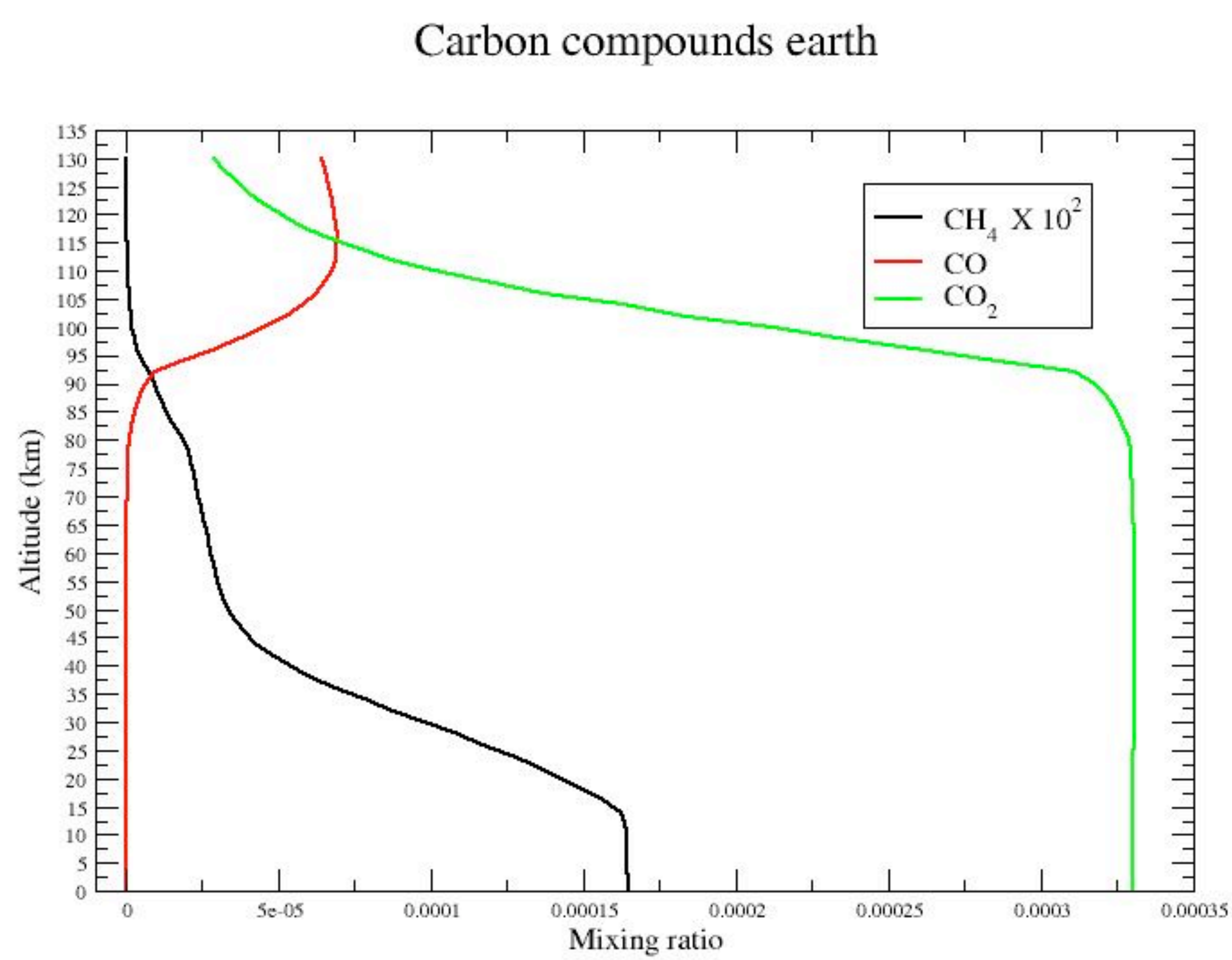
This is a 3D representation of the methane concentration on Mars for the BASE model simulation for months 36 to 54. It is evident that the most change occurs in the southern polar regions.

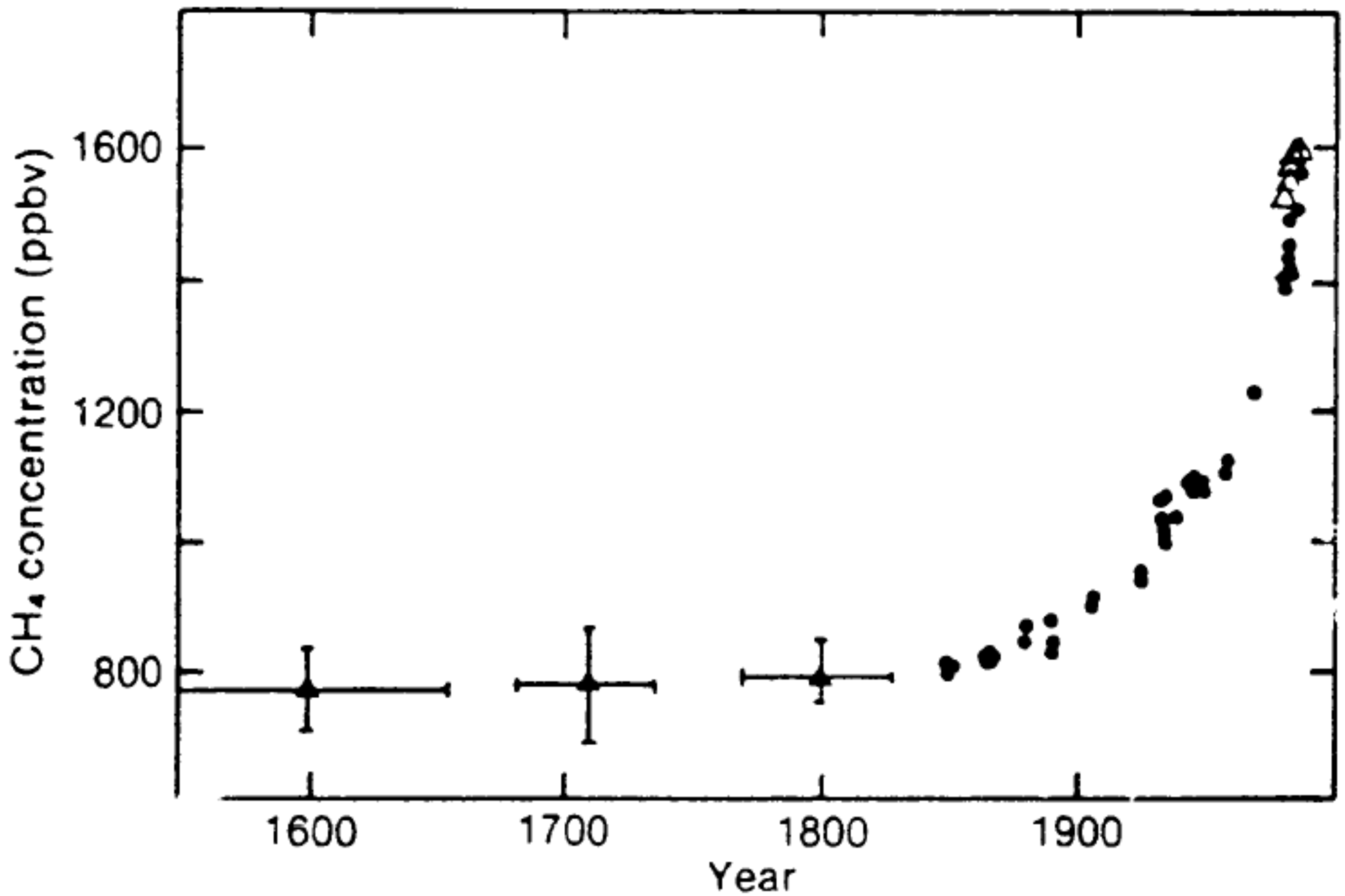


This shows the Methane concentration for 6 boxes in the troposphere. Of particular interest is the top left graph, which represents the Southern pole where the concentration changes dramatically as a result of condensation and evaporation of Carbon Dioxide.

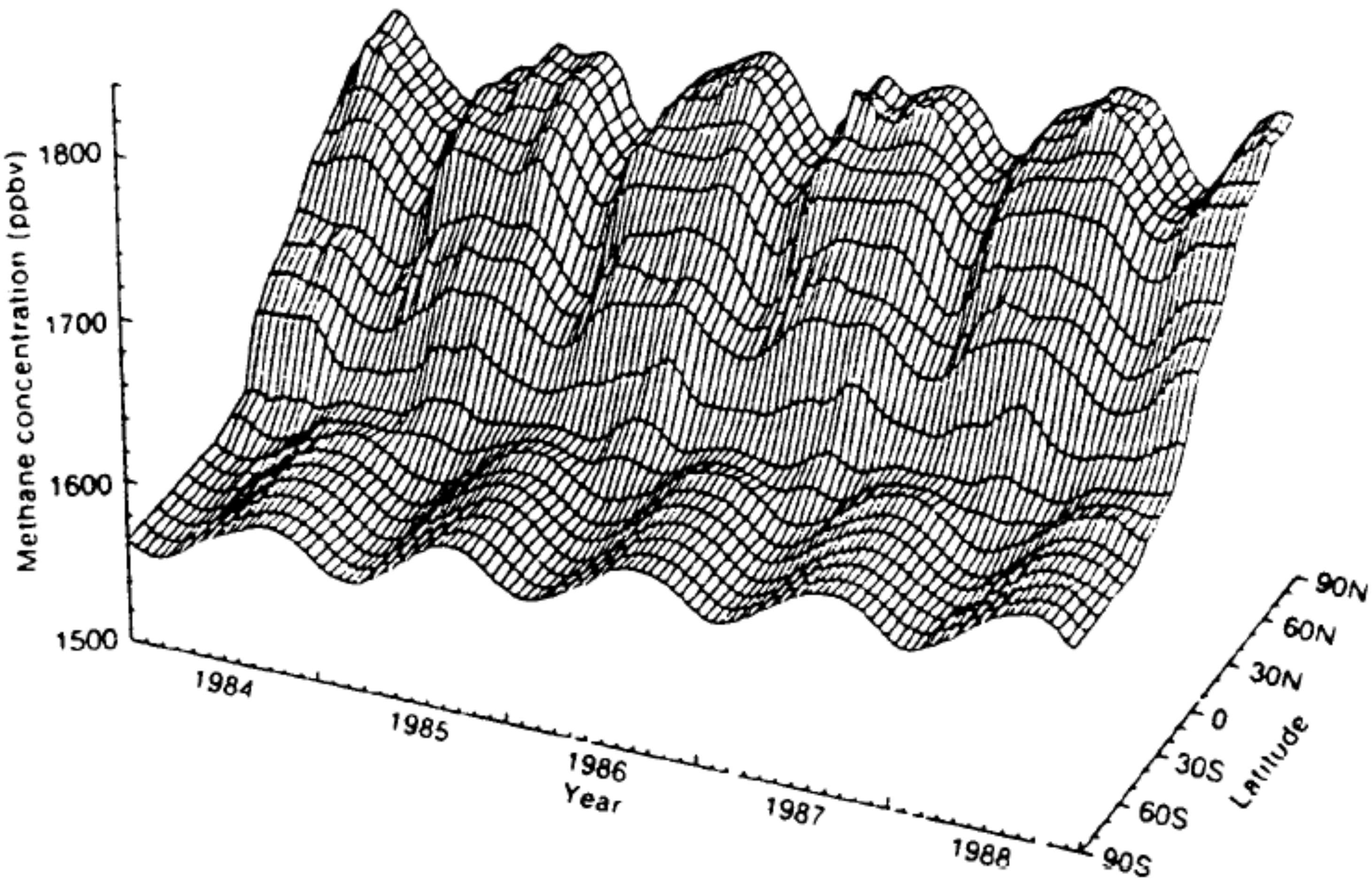


0
-100
-200
-300
-400
δ^2H_{CH4} (‰)
-120
-100
-80
-60
-40
-20
0
$\delta^{13}C_{CH4}$ (‰)


Carbon compounds earth
CH_4 X 10^2
CO
CO_2
Altitude (km)
Mixing ratio
0
5e-05
0.0001
0.00015
0.0002
0.00025
0.0003
0.00035

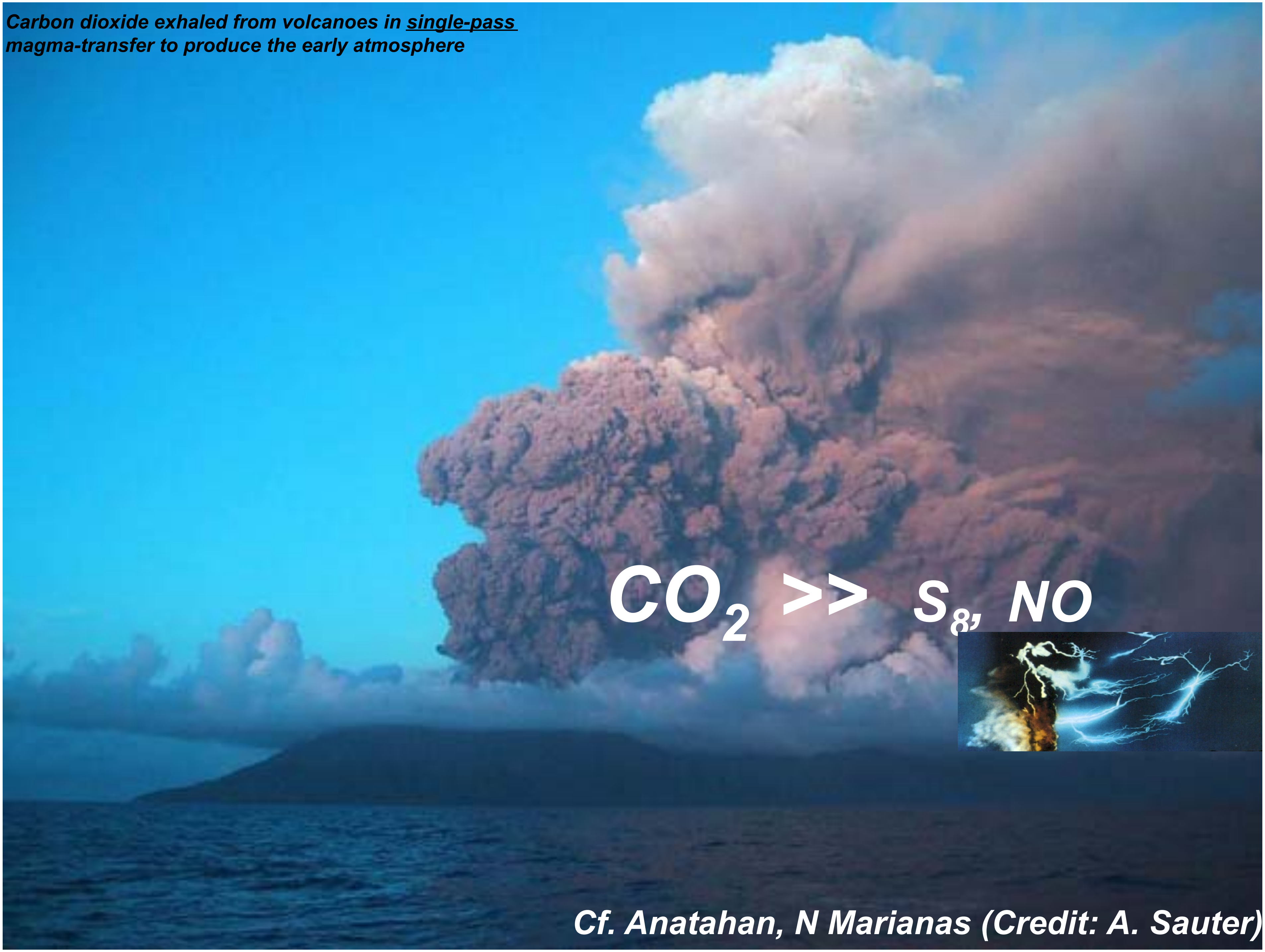


1600
1200
800
CH4 concentration (ppbv)
1600
1700
1800
1900
Year



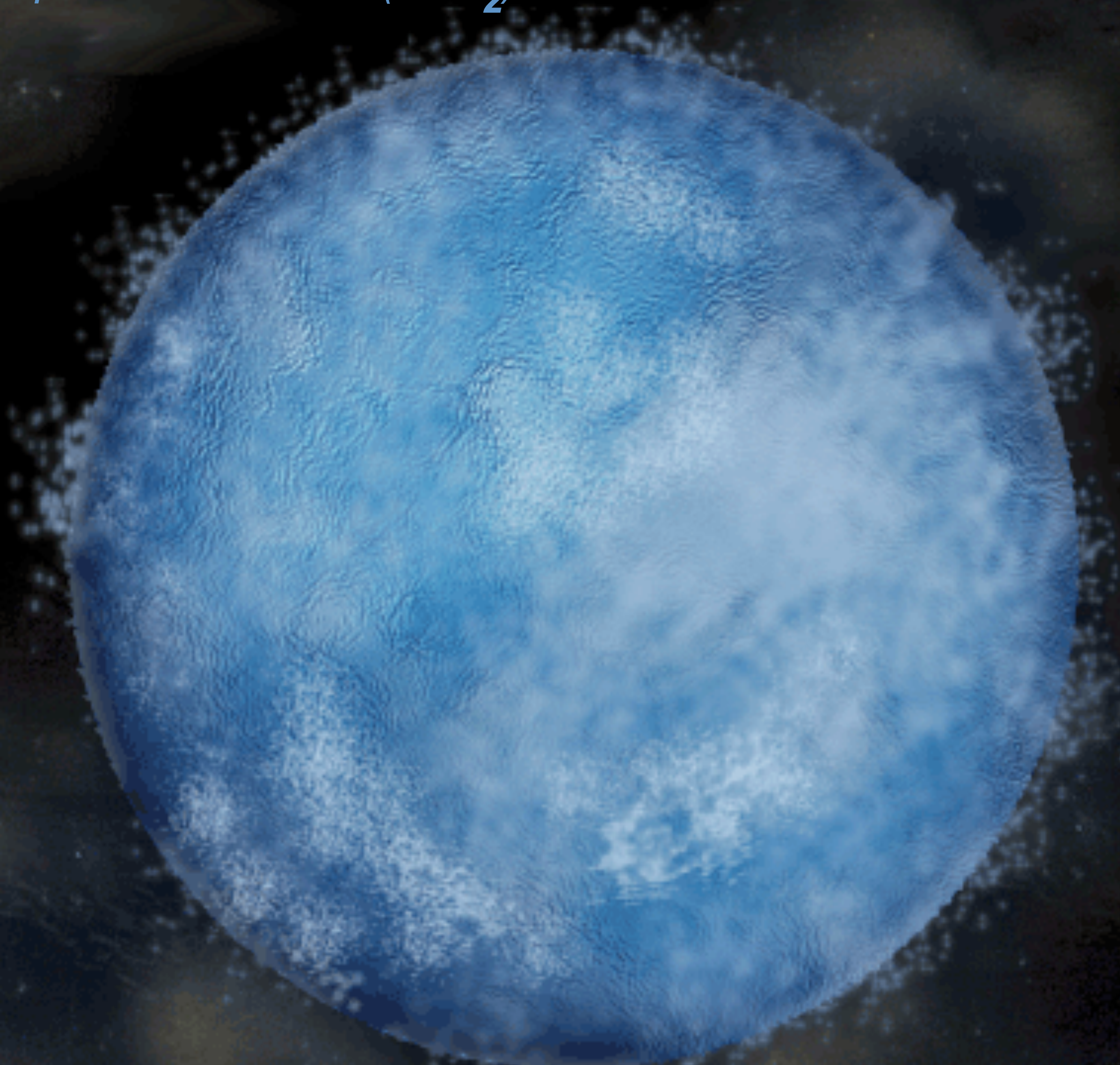
Methane concentration (ppbv)
1800
1700
1600
1500
1984
1985
1986
Year
1987
1988
90N
60N
30N
0
30S
60S
90S
Latitude


4400 Million years ago
NASA
JPL
The Earth produced hydrogen
from some of this water
H_2
Oceans on Earth


Carbon dioxide exhaled from volcanoes in <u>single-pass</u> magma-transfer to produce the early atmosphere
CO_2 >> S_8, NO
Cf. Anatahan, N Marianas (Credit: A. Sauter)

4400 Million years ago

So the atmosphere was carbon dioxide (CO_2)



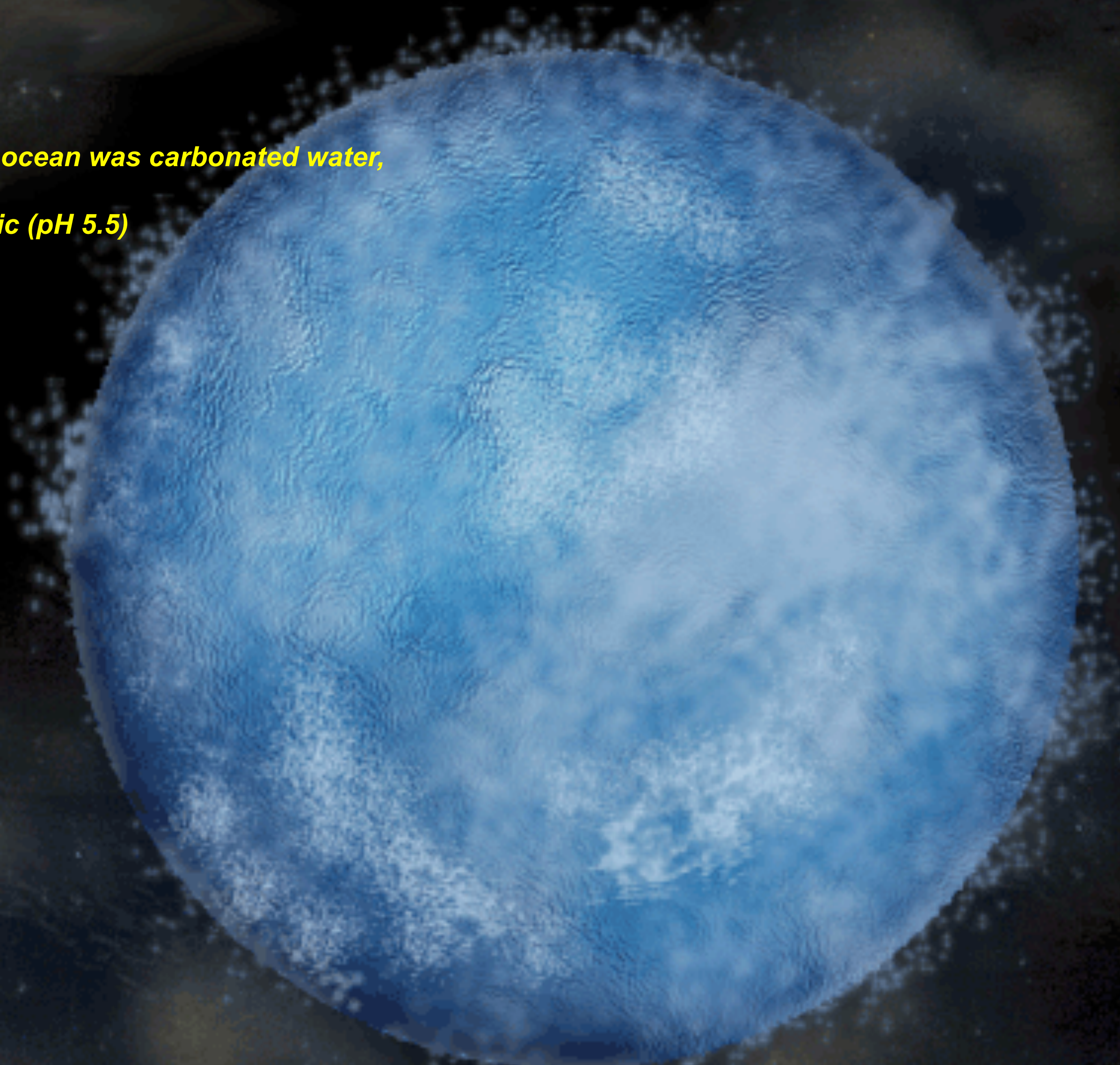
Oceans on Earth

4400 Million years ago

The atmosphere was carbon dioxide (CO_2)

and the ocean was carbonated water,

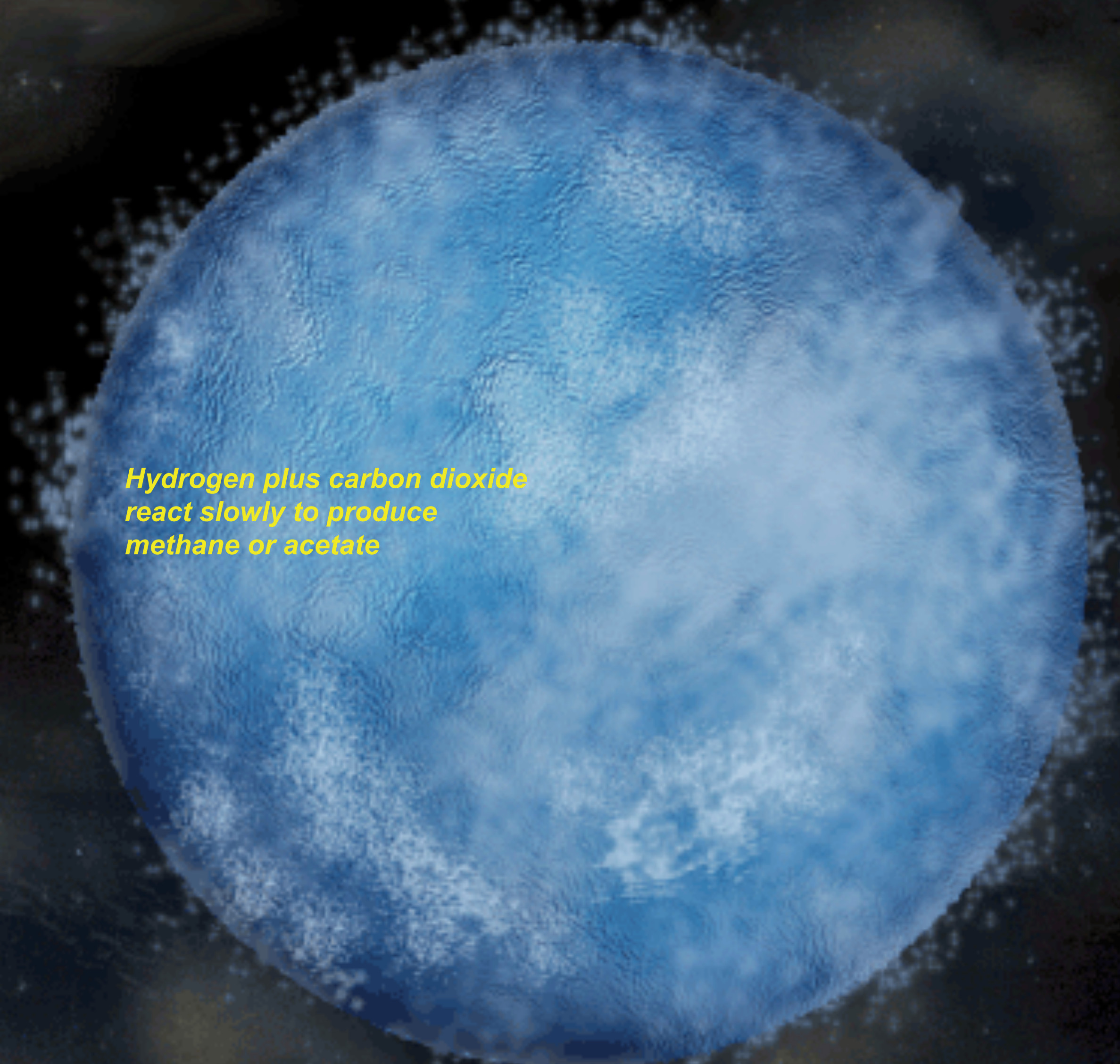
i.e. acidic (pH 5.5)



Oceans on Earth

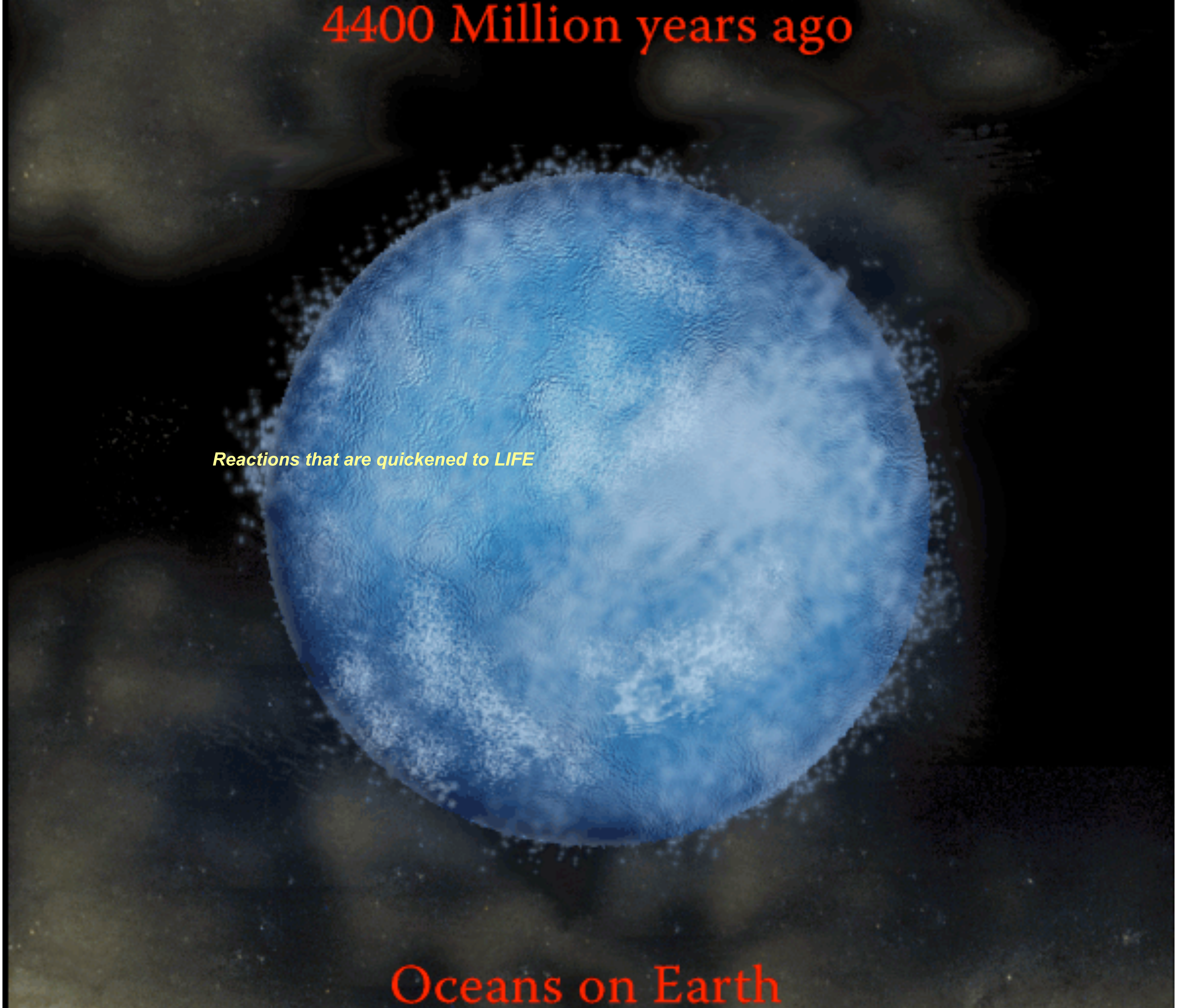
4400 Million years ago

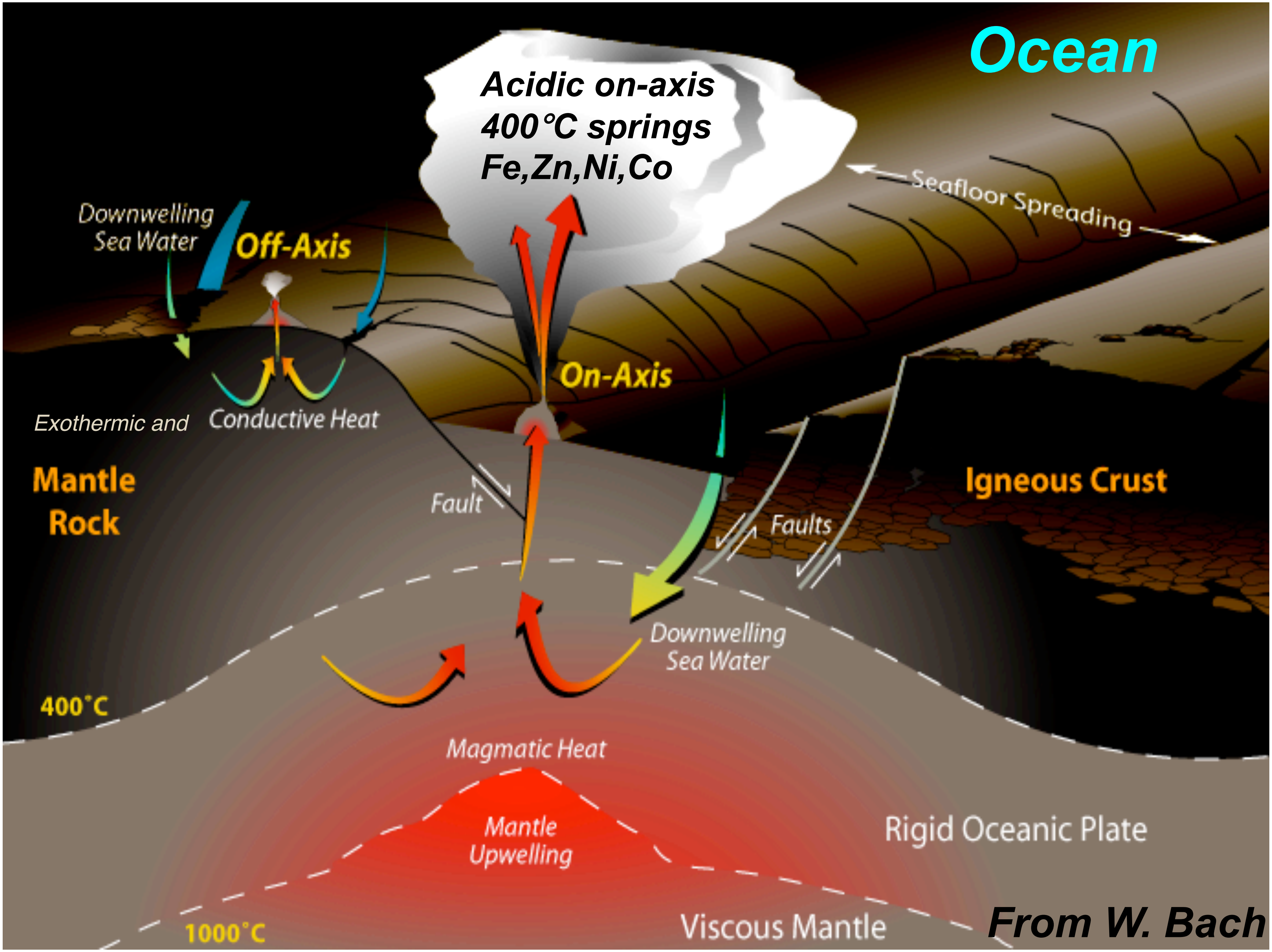
$$\& \; 4H_2 + CO_2 \rightarrow CH_4 + 2H_2O$$



$$4H_2 + 2CO_2 \rightarrow CH_3COOH + 2H_2O$$

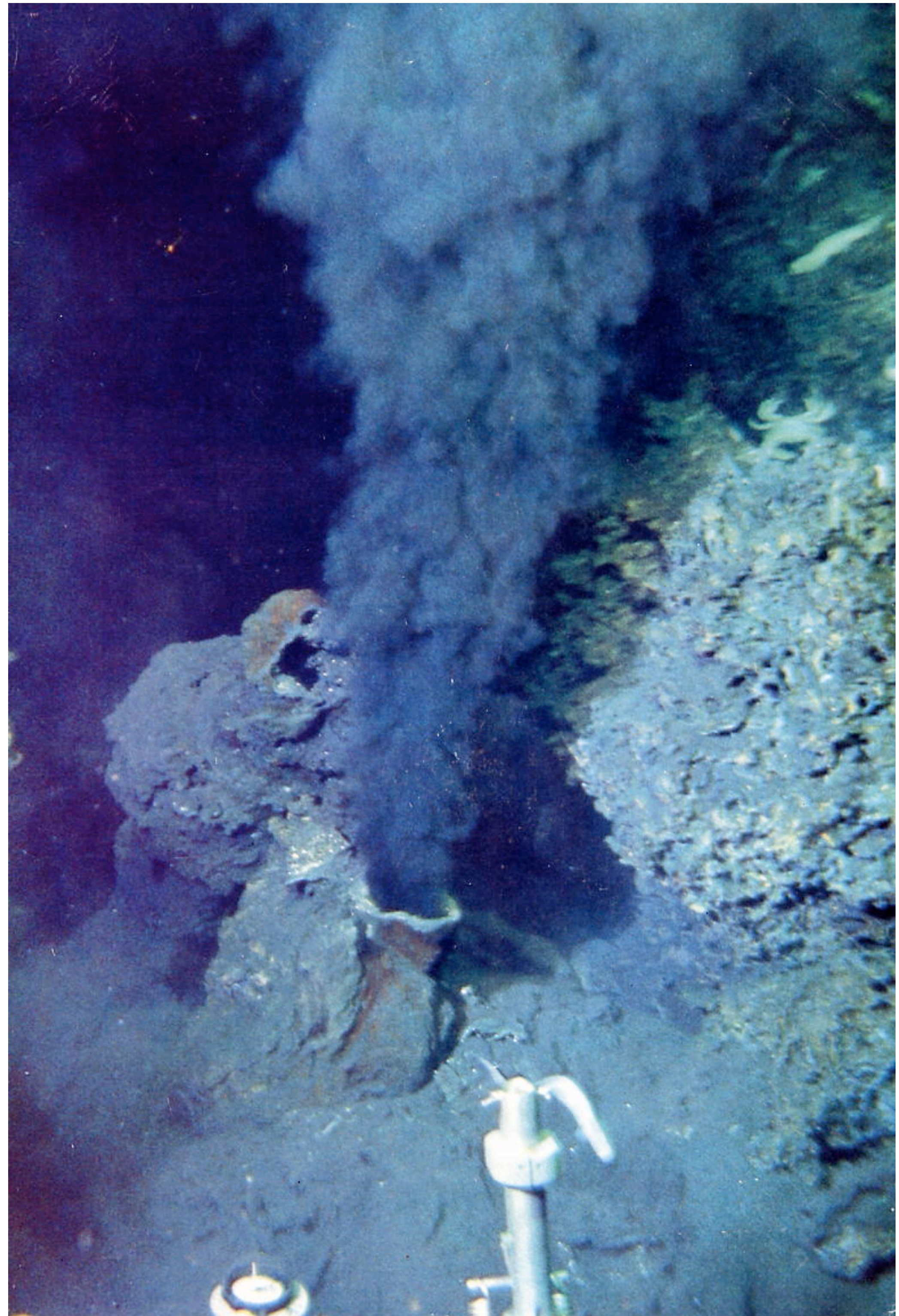
Oceans on Earth

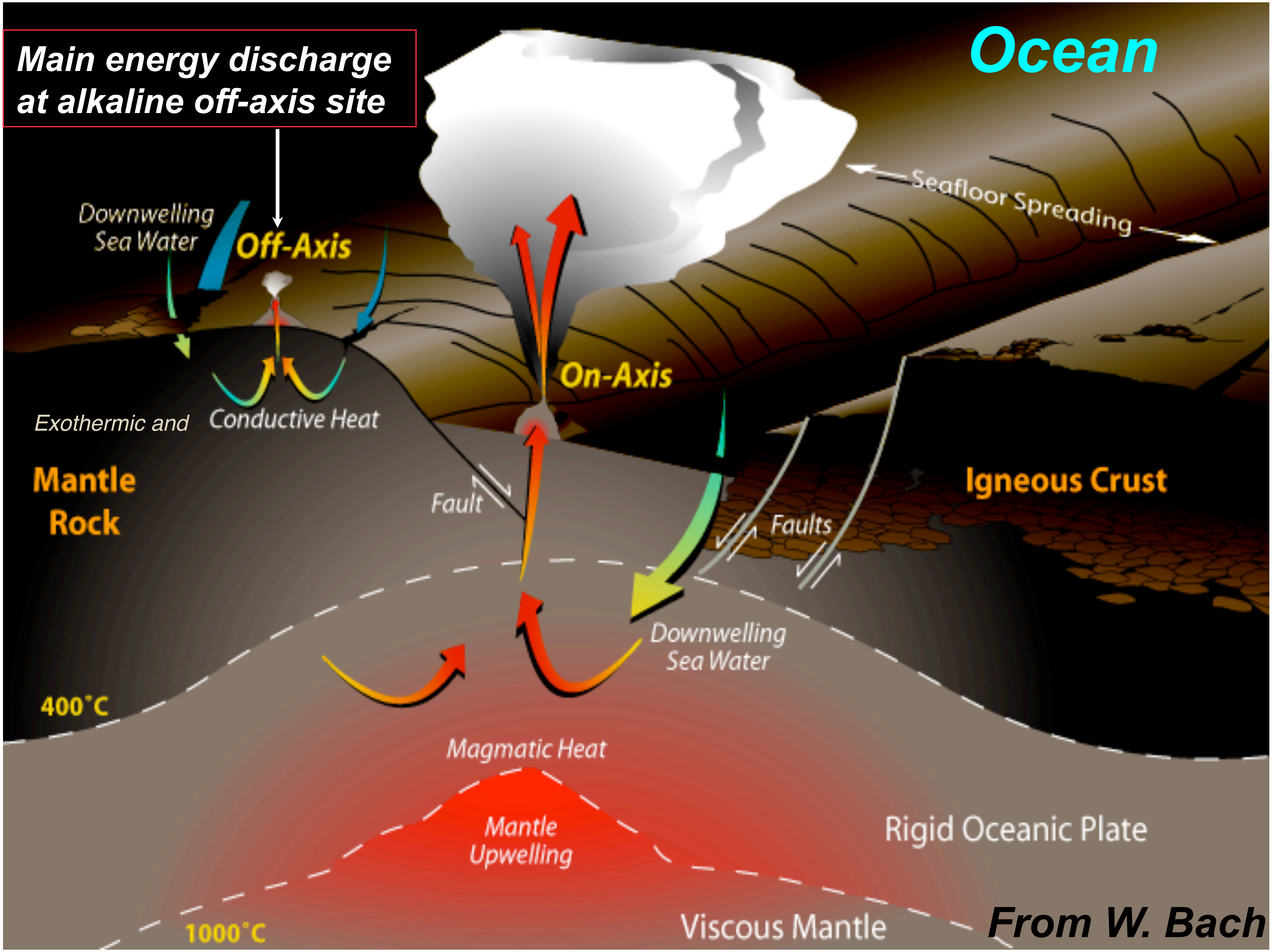

4400 Million years ago
Reactions that are quickened to LIFE
Oceans on Earth


Ocean
Acidic on-axis
400°C springs
Fe,Zn,Ni,Co
Seafloor Spreading
Downwelling
Sea Water
Off-Axis
On-Axis
Exothermic and
Conductive Heat
Mantle
Rock
Igneous Crust
Fault
Faults
Downwelling
Sea Water
400°C
Magmatic Heat
Mantle
Upwelling
Rigid Oceanic Plate
1000°C
Viscous Mantle
From W. Bach

Black Smoker at 360 C, pH ~3.4 East Pacific Rise

Too hot,
too acidic,
too oxidized &
too spasmodic




Main energy discharge
at alkaline off-axis site
Ocean
Downwelling
Sea Water
Off-Axis
Seafloor Spreading
On-Axis
Exothermic and
Conductive Heat
Mantle
Rock
Fault
Igneous Crust
Faults
Downwelling
Sea Water
400˚C
Magmatic Heat
Mantle
Upwelling
Rigid Oceanic Plate
1000˚C
Viscous Mantle
From W. Bach

ALKALINE SUBMARINE SPRING

$CaCO_3$

$Mg(OH)_2$

pH ≤11

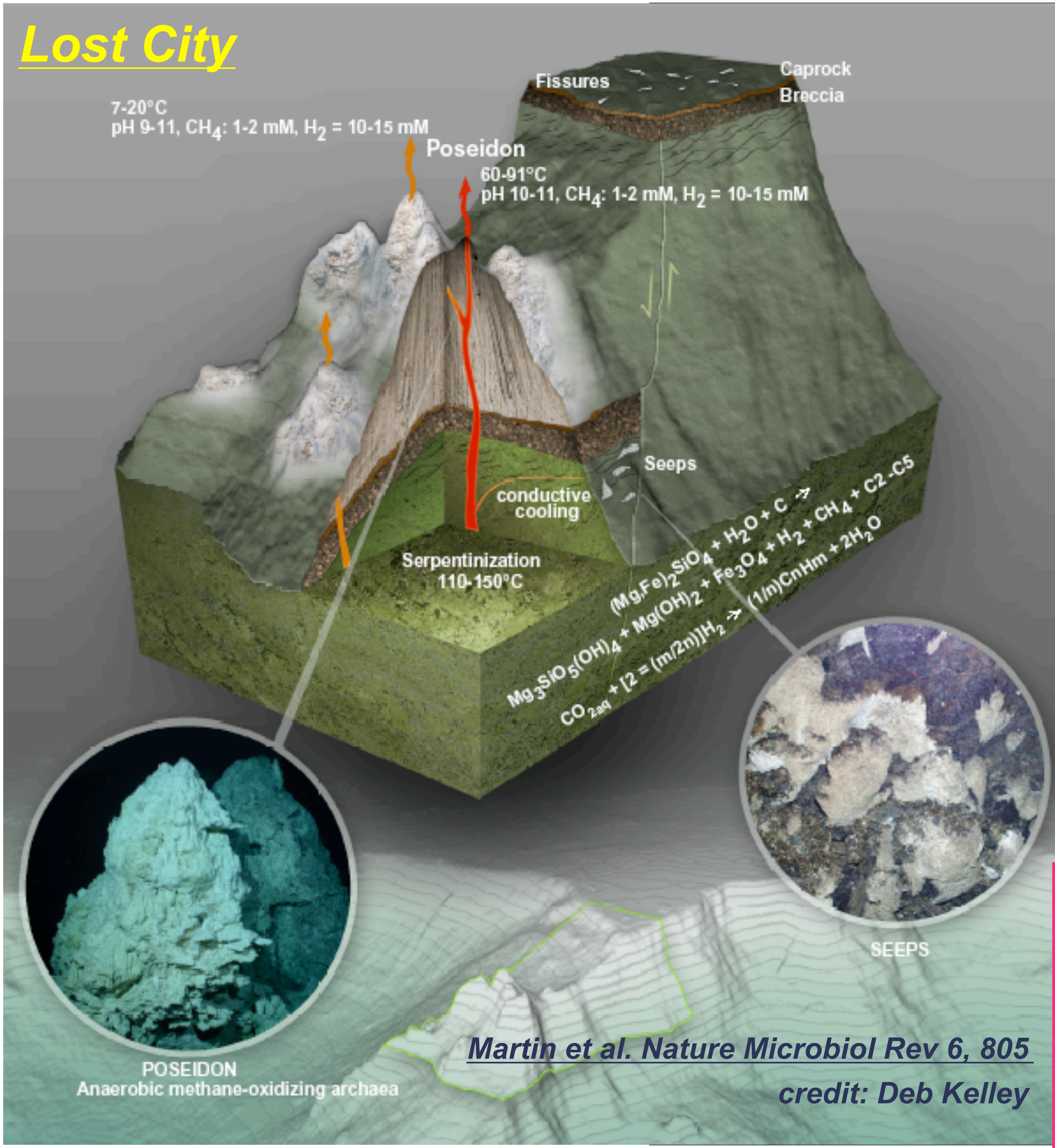
T ≤91°C

H_2 ≤15mmol

~100,000 years

Kelley et al. 2001, Nature 412, 145
Science 2005, 307
Früh-Green + 2003, Science 301, 495
Ludwig et al. 2005 EOS, 86,V51B-1487

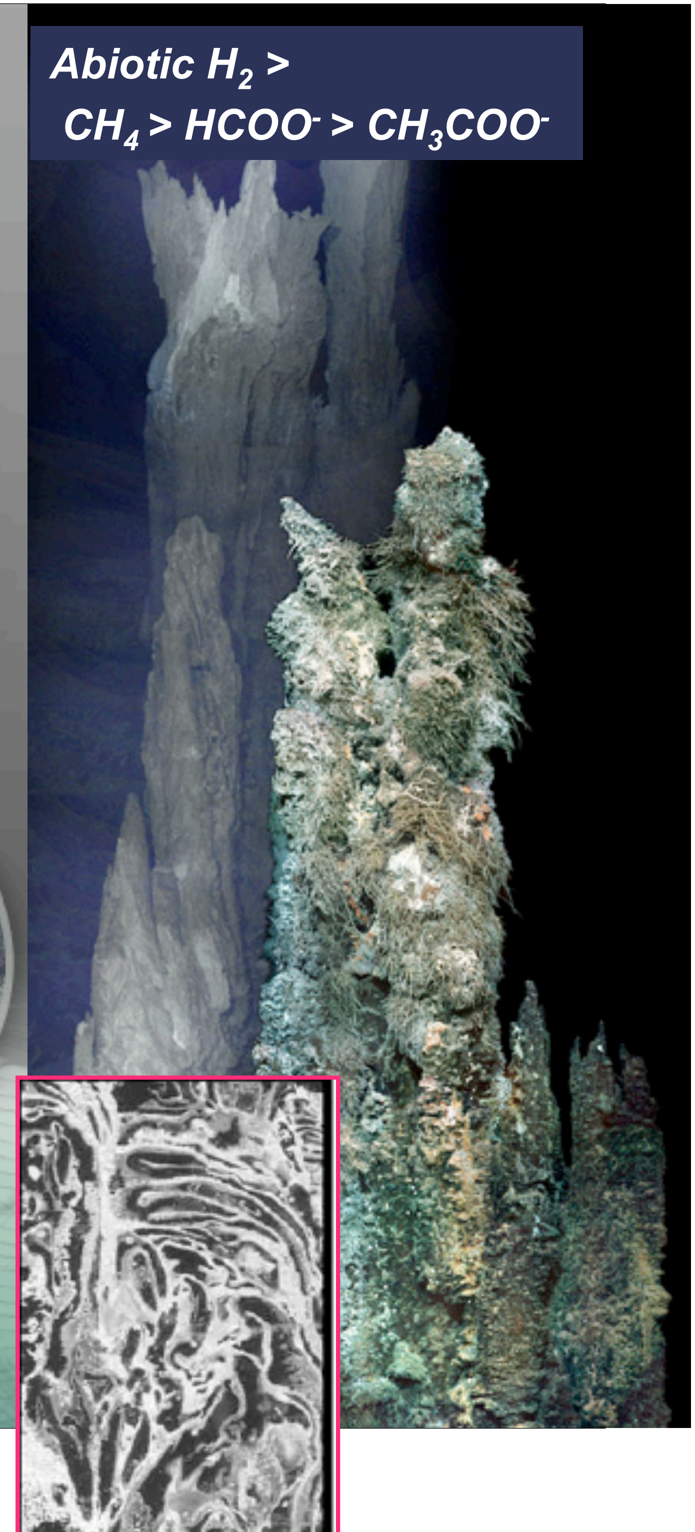
Lost City



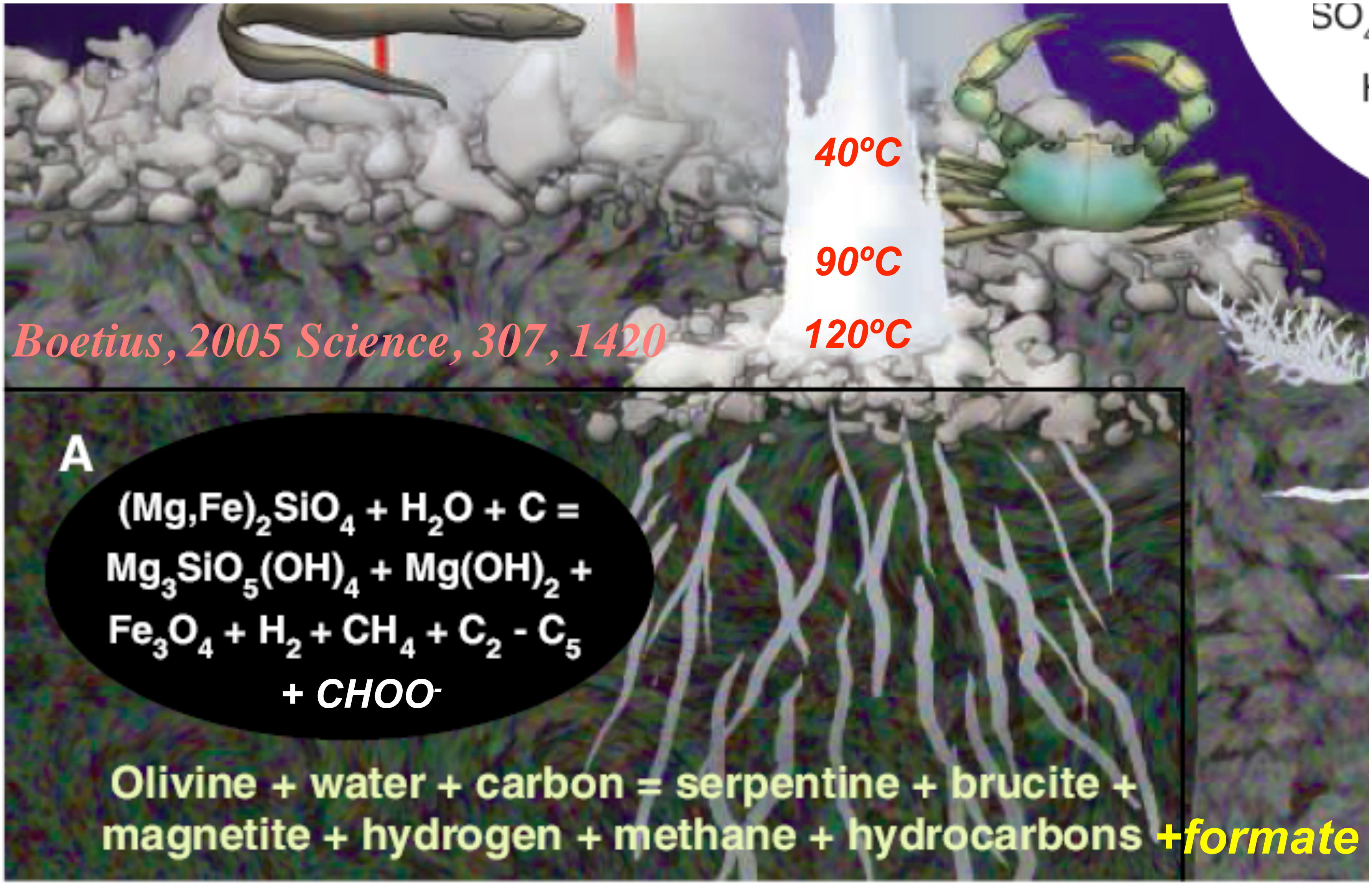
Martin et al. Nature Microbiol Rev 6, 805

credit: Deb Kelley

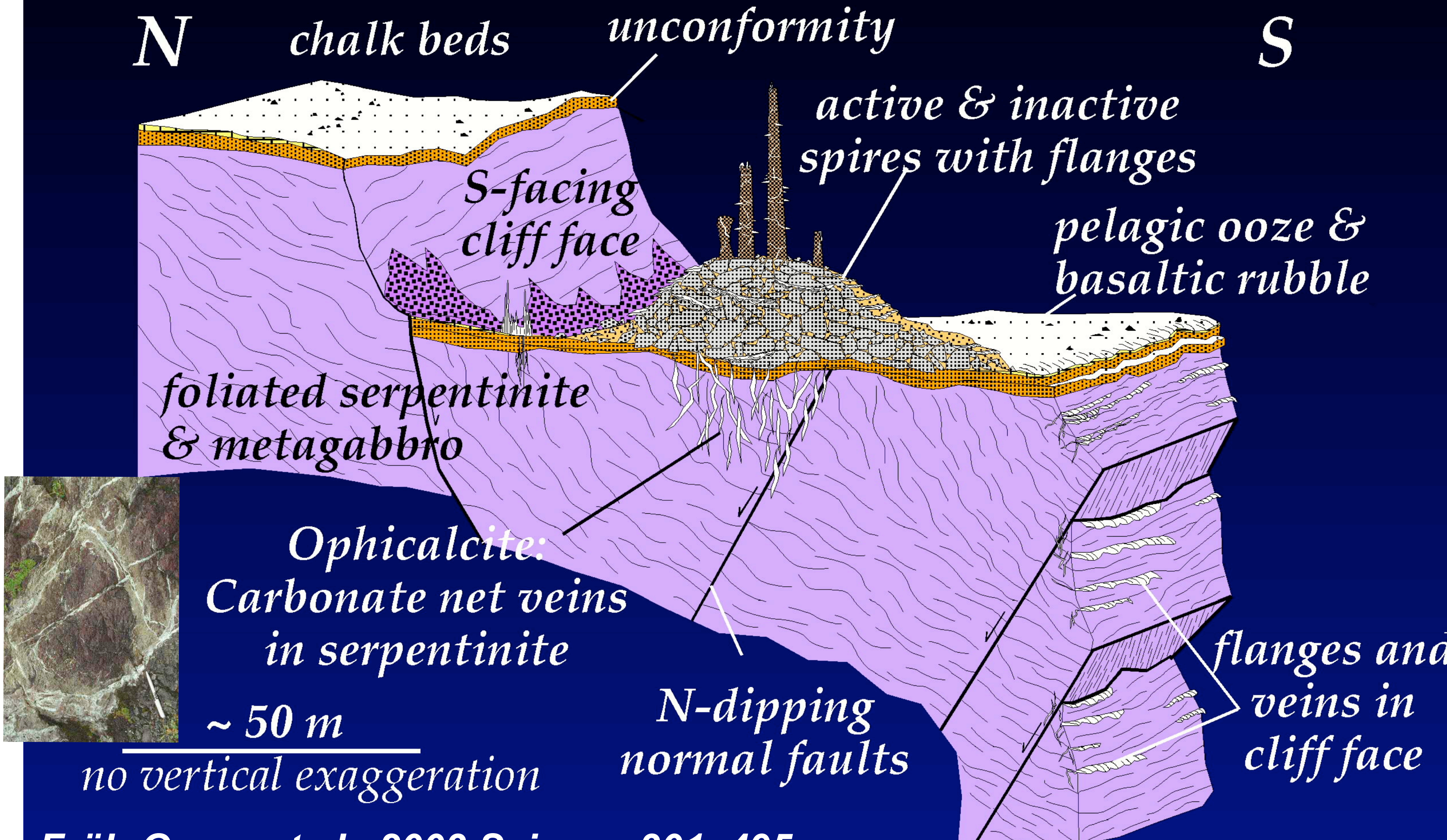
Abiotic H_2 > CH_4 > $HCOO^-$ > CH_3COO^-



Serpentinization Reactions



Lost City Vent Field
MAR 30°N



Früh-Green et al., 2003 Science 301, 495

Serpentinite

$Mg_{2.85}Fe_{0.15}Si_2O_5(OH)_4$

overall reaction:

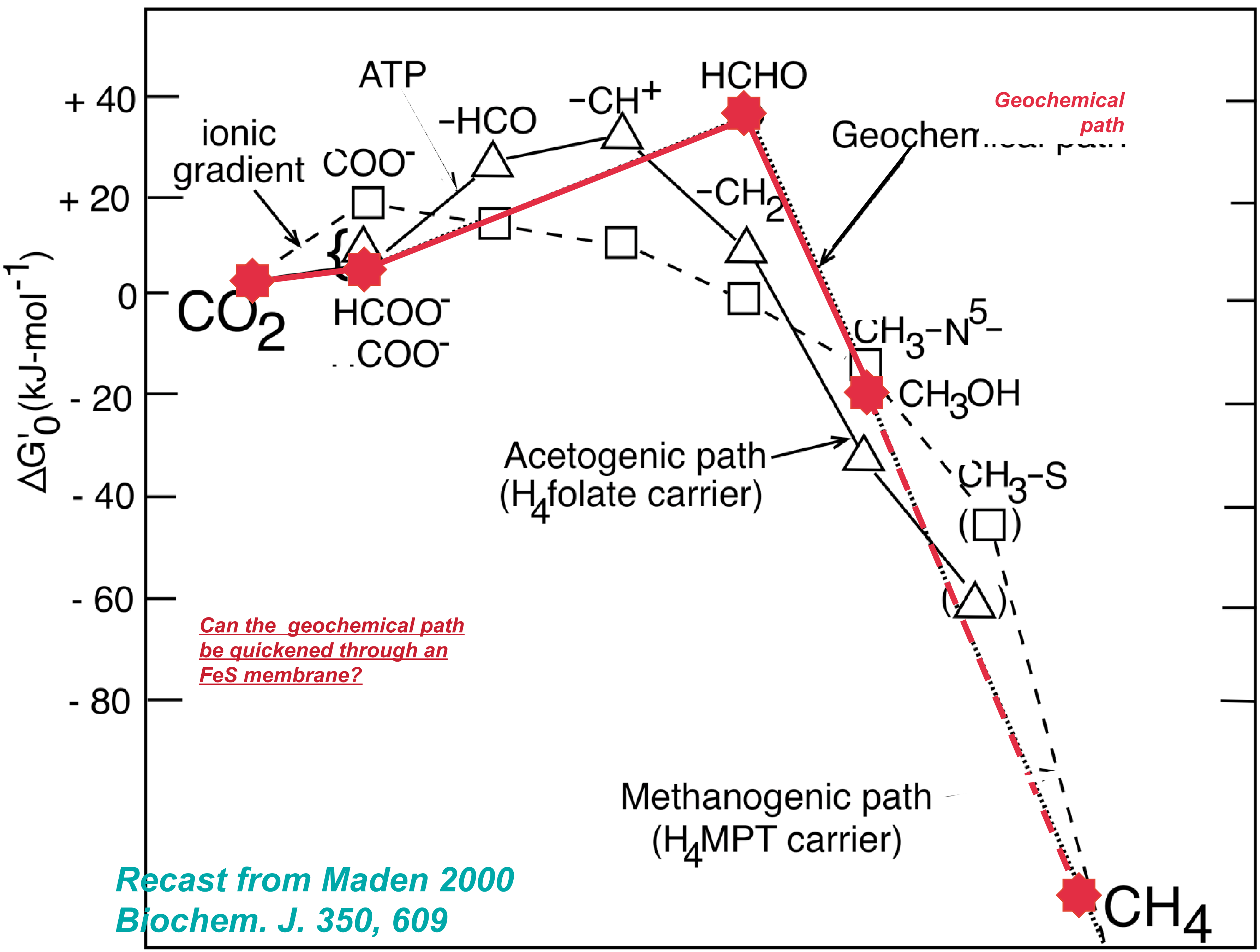
olivine + water → magnetite + serpentine + alkali + $H_2\uparrow$

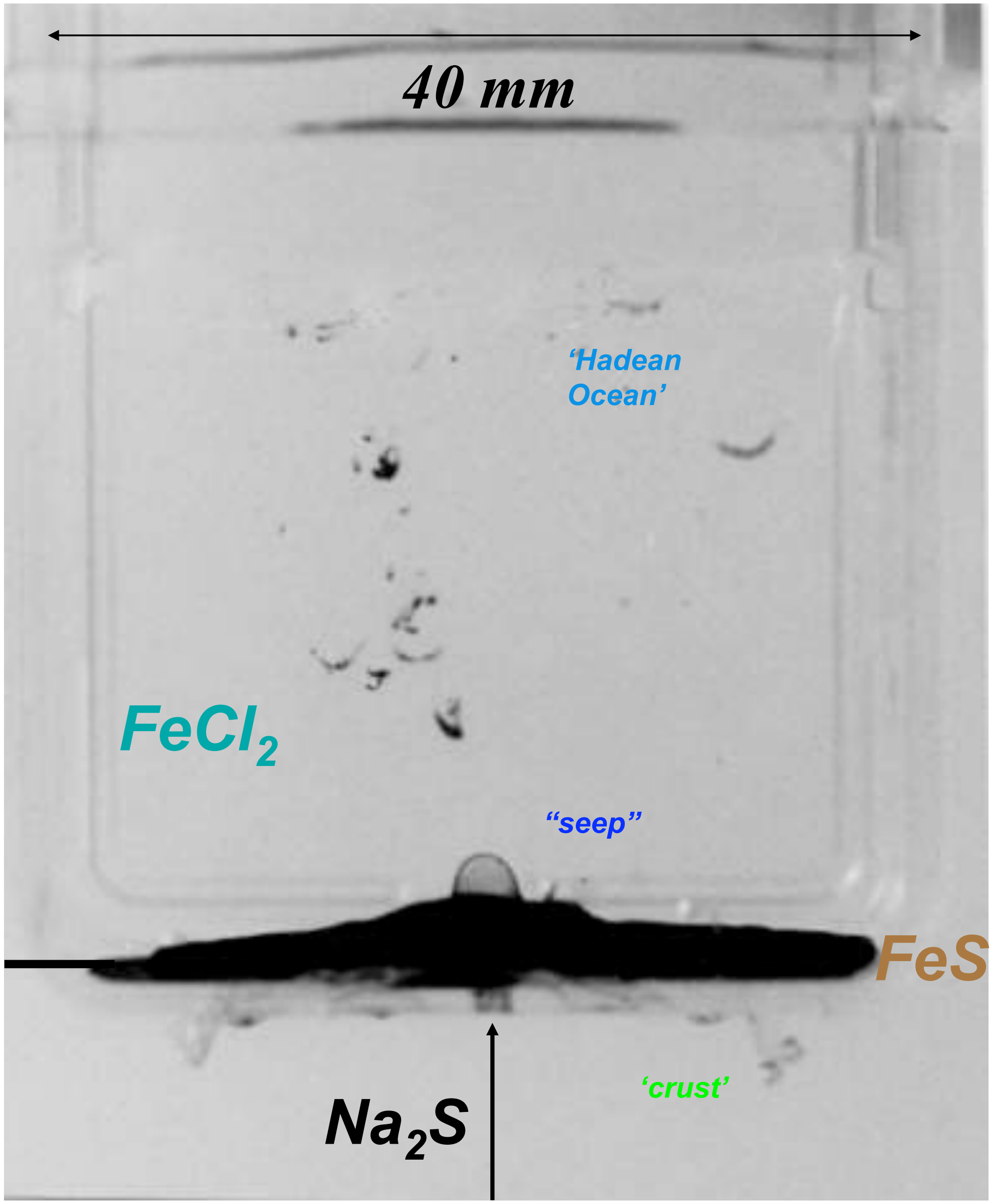
$$3MgFeSiO_4 + 4H_2O \rightarrow 3SiO_2 + Fe_3O_4 + 3Mg^{2+} + 6OH^- + H_2\uparrow$$

and $CH_4 > HCOO^- > CH_3COO^-$

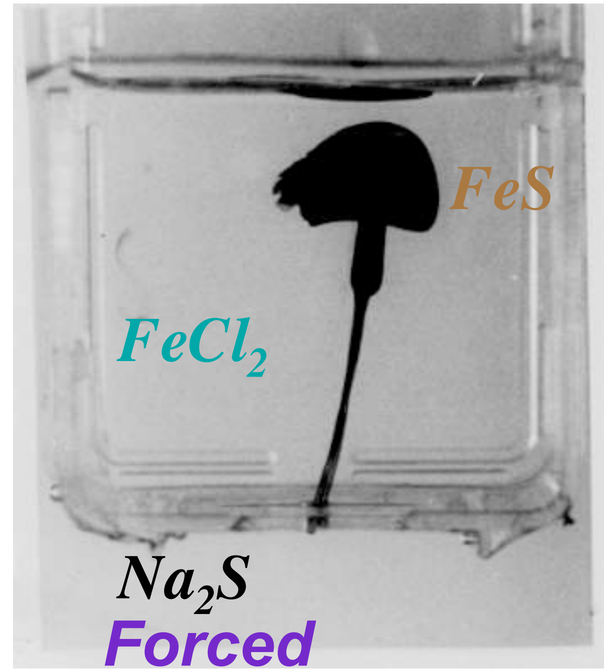
Bach et al. 2006 Geophys. Res. Lett, 33, L1330

State rock of California

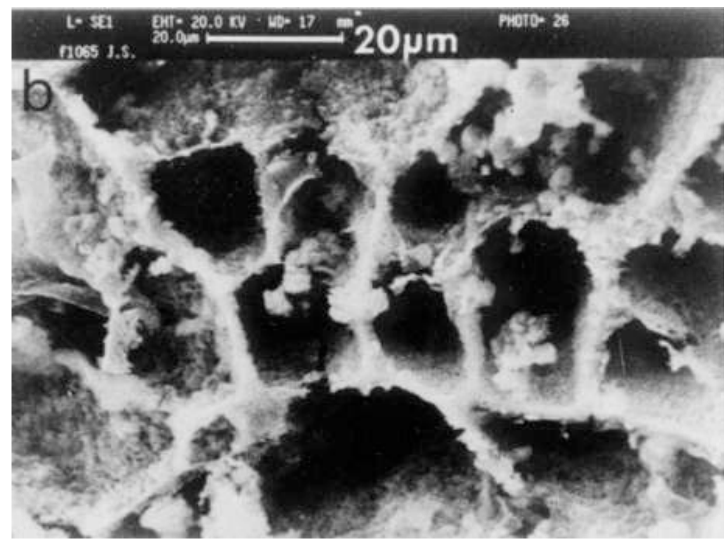

ΔG'0(kJ-mol-1)
+ 40
+ 20
0
- 20
- 40
- 60
- 80
ionic gradient
ATP
COO-
-HCO
-CH+
HCHO
-CH2
CO2
HCOO-
COO-
CH3-N5-
CH3OH
CH3-S
Geochemical path
Acetogenic path
(H4folate carrier)
Methanogenic path
(H4MPT carrier)
CH4
Can the geochemical path be quickened through an FeS membrane?
Recast from Maden 2000
Biochem. J. 350, 609



Simulation of an alkaline seepage into acidulous ocean



Forced injection

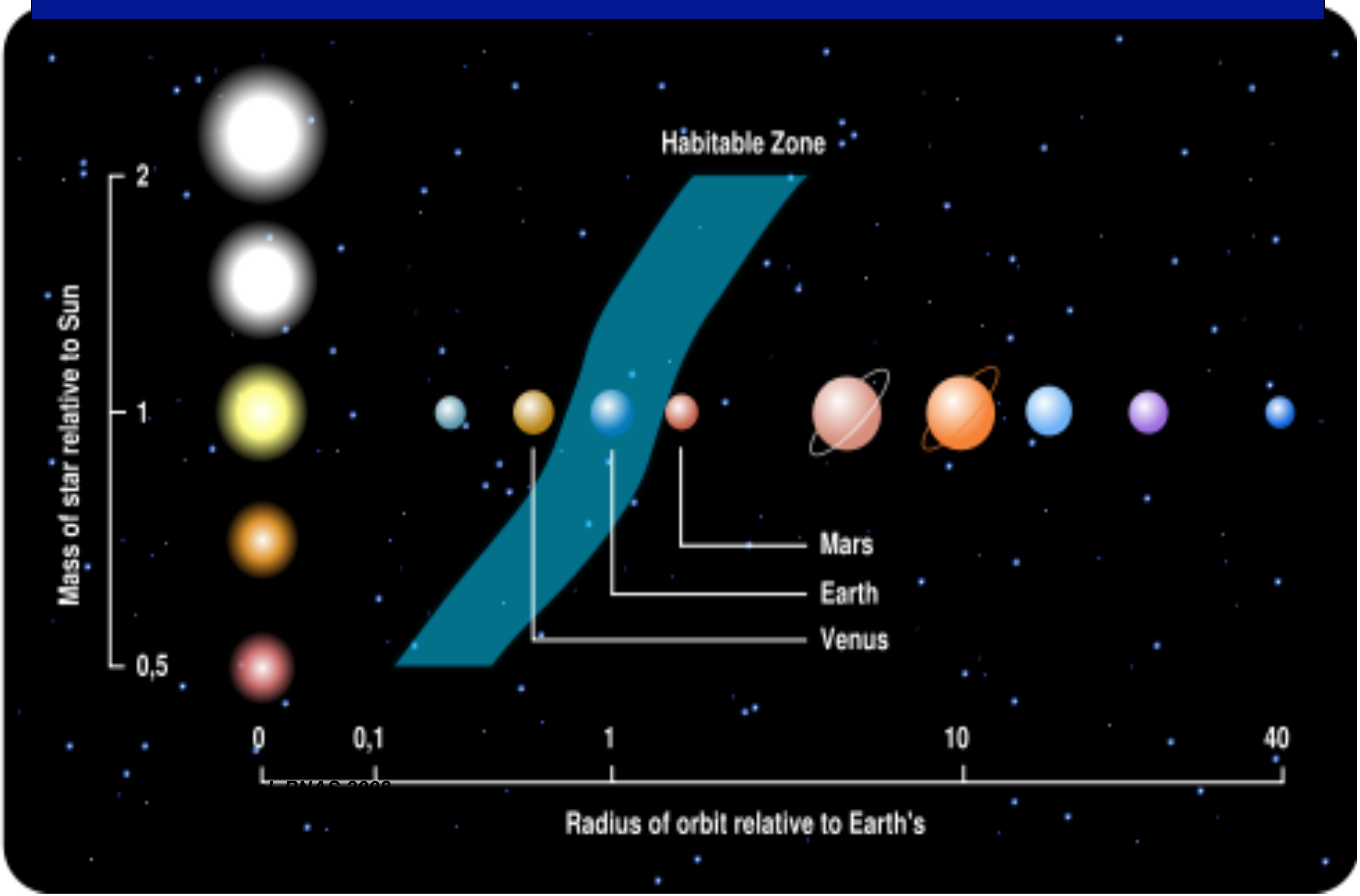


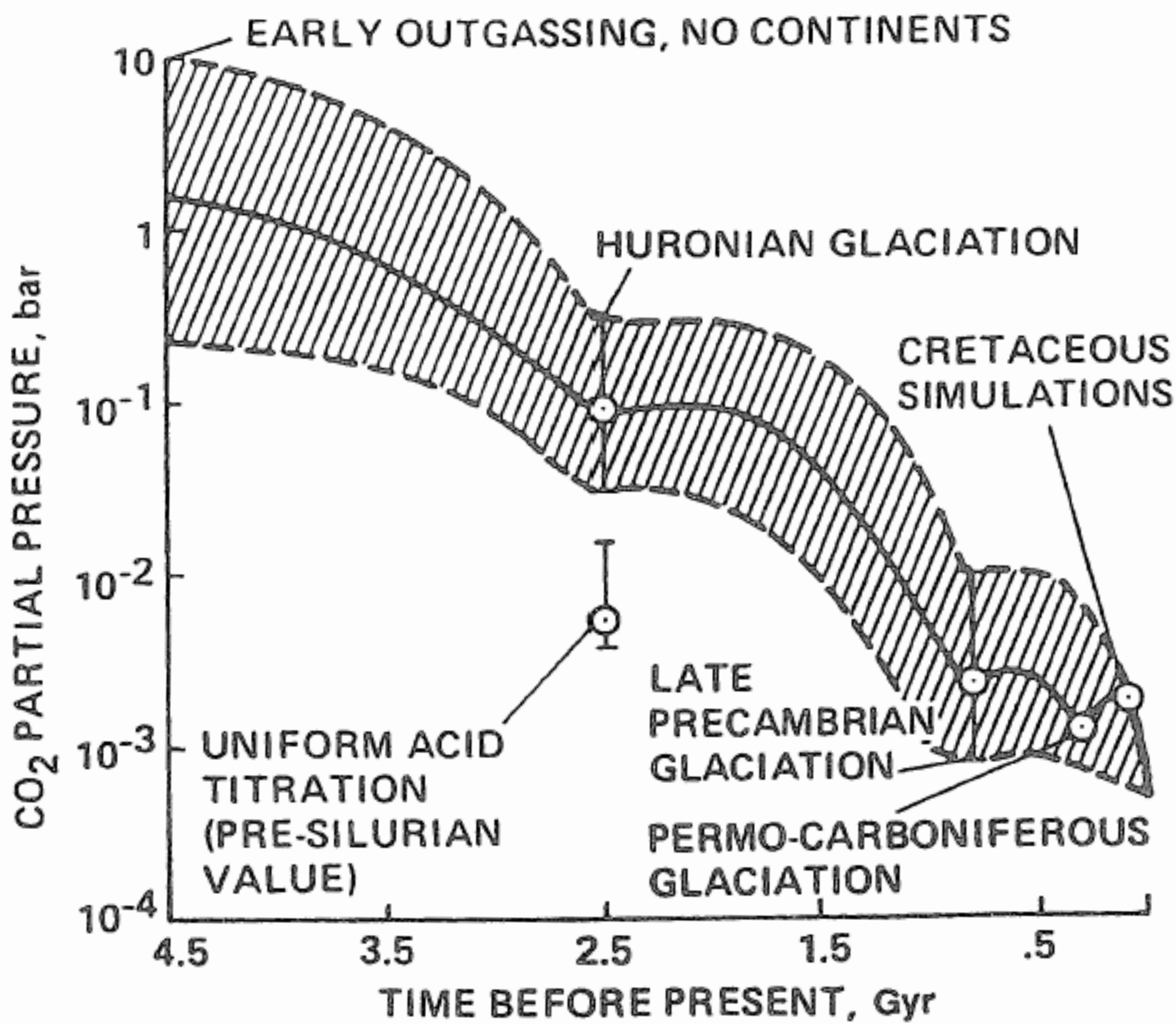
FeS compartments

Today's Outline

- Jupiter: The cosmic reference point
- Titan: Nature's Laboratory of Organic Synthesis
- Mars: Is Methane biologically produced?
- Earth: The cosmic end member
- Conclusions

Habitable Zone





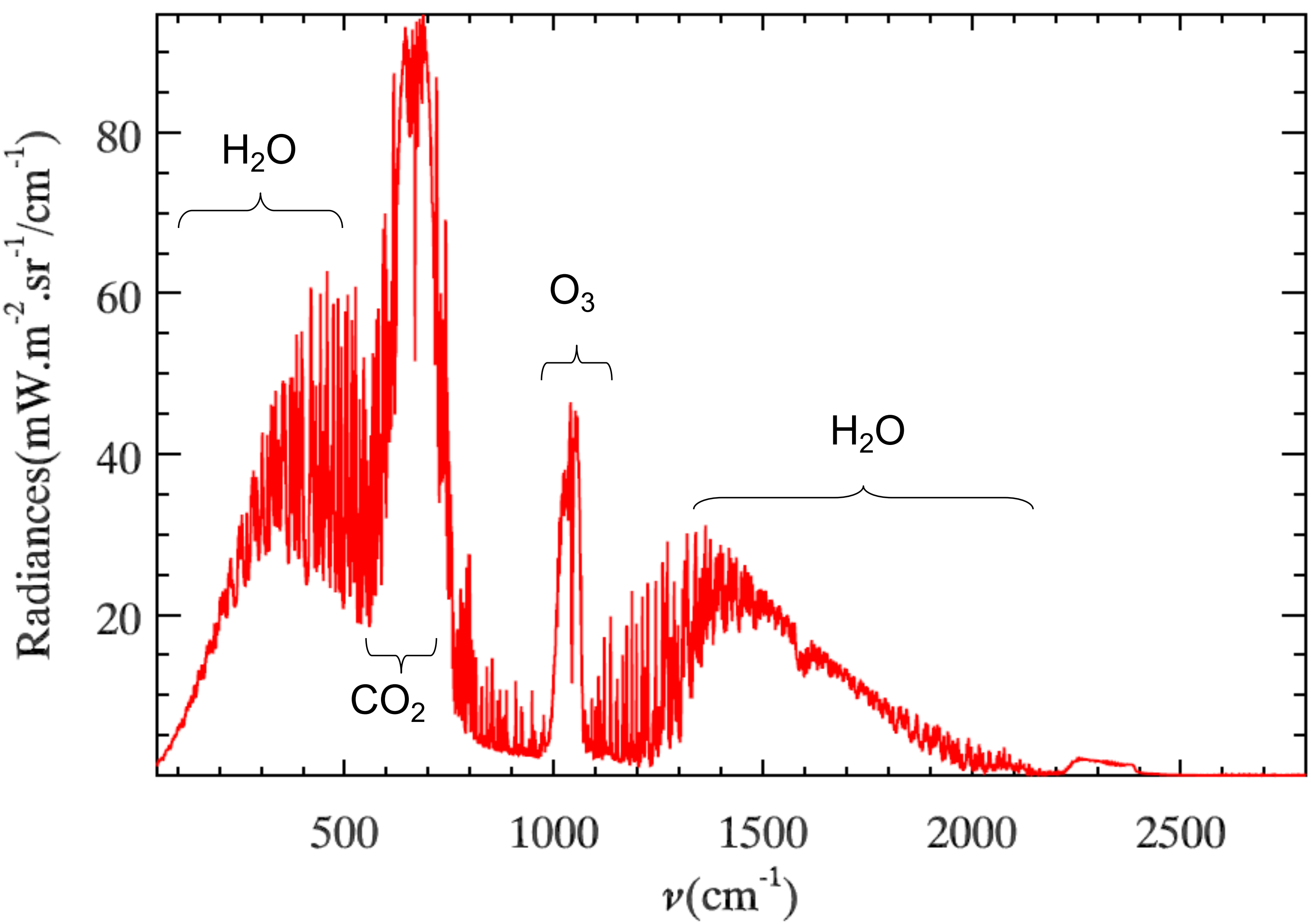
EARLY OUTGASSING, NO CONTINENTS
HURONIAN GLACIATION
CRETACEOUS SIMULATIONS
LATE PRECAMBRIAN GLACIATION
UNIFORM ACID TITRATION (PRE-SILURIAN VALUE)
PERMO-CARBONIFEROUS GLACIATION
CO_2 PARTIAL PRESSURE, bar
10
1
10^{-1}
10^{-2}
10^{-3}
10^{-4}
4.5
3.5
2.5
1.5
.5
TIME BEFORE PRESENT, Gyr

❖Earth (Snowball, Gaia Lifeboat)

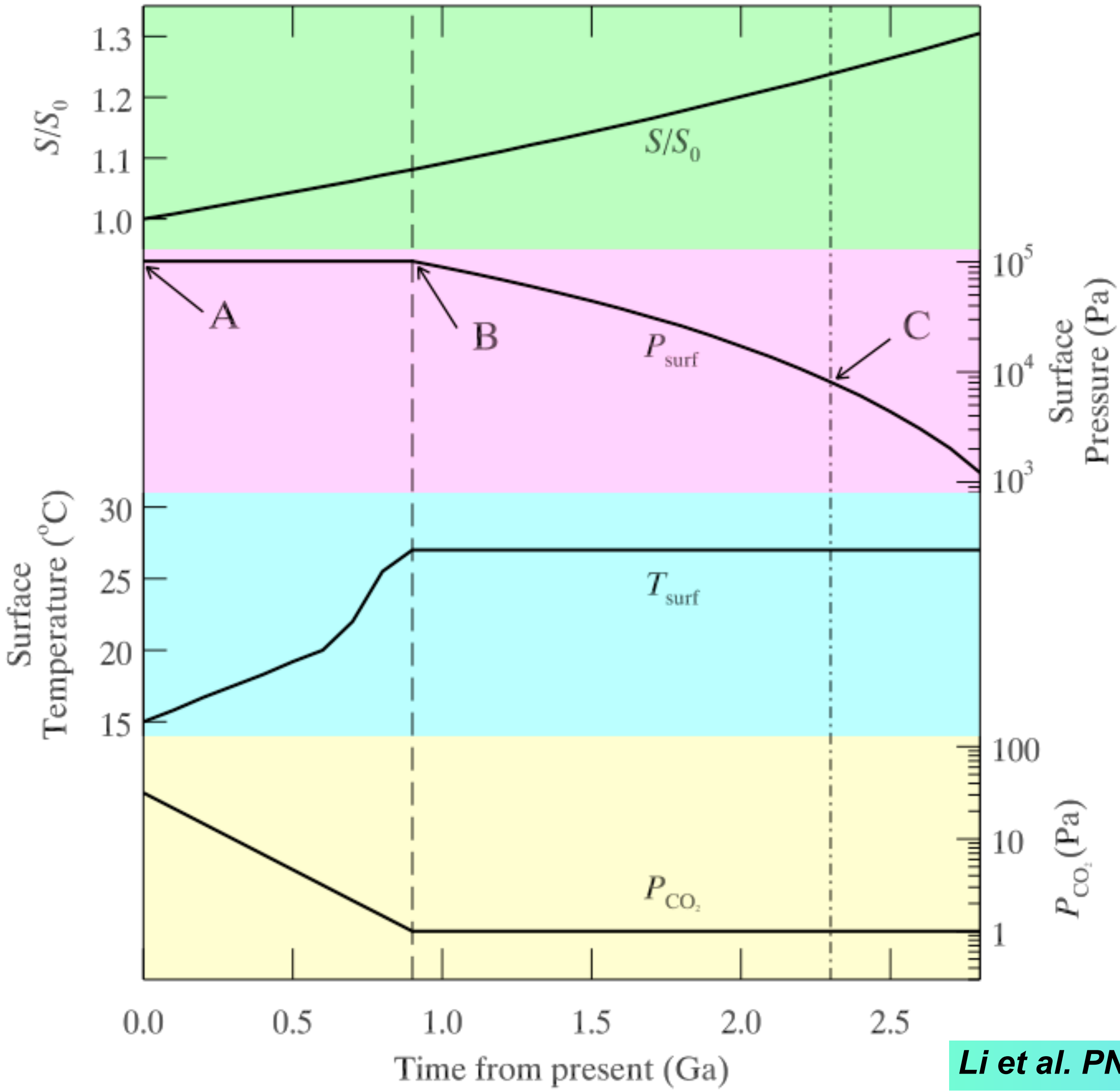
Liang et al. PNAS 2007

Li et al. PNAS 2009 (in press)

Absorption in Earth's Atmosphere

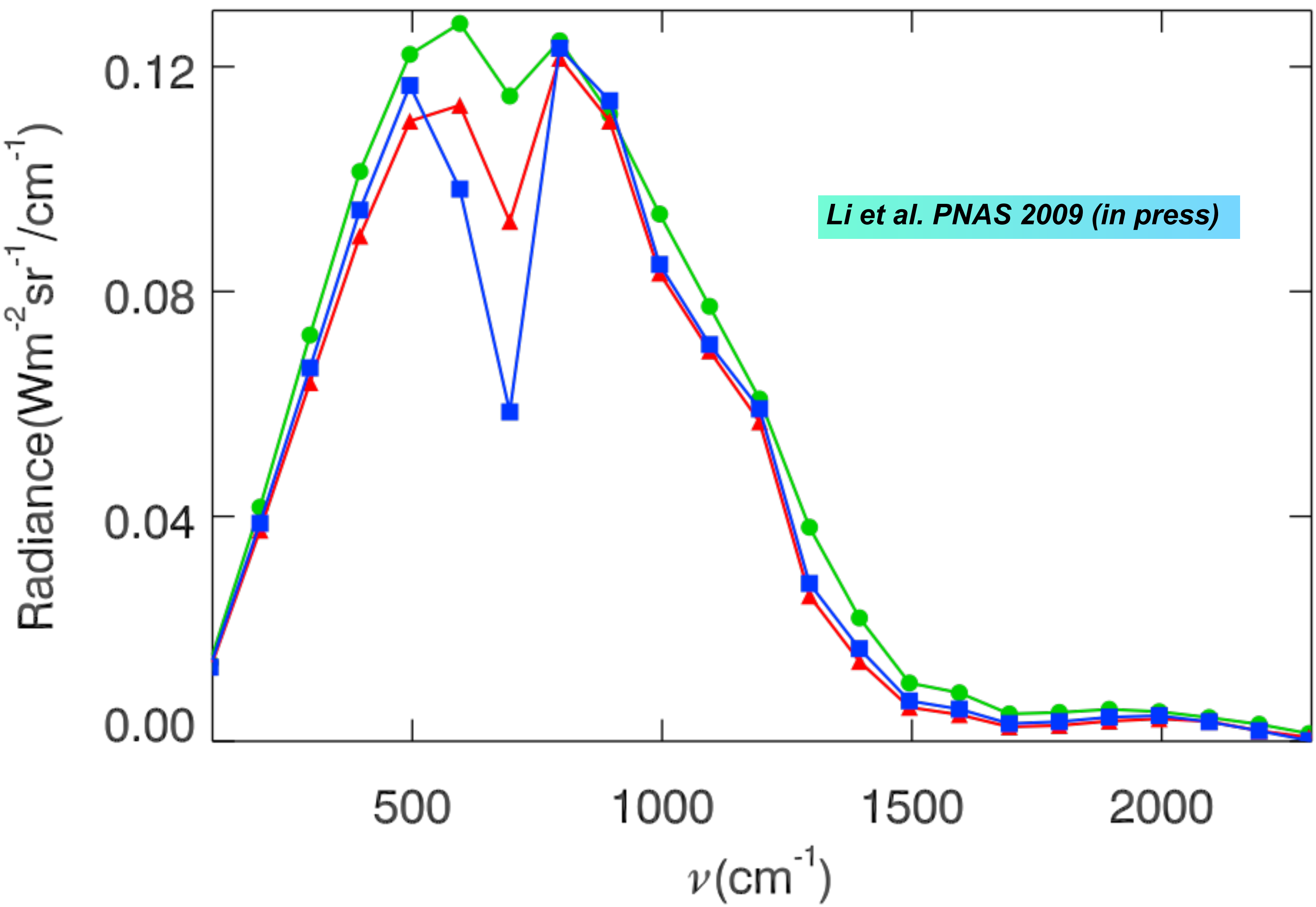


Extending the Lifespan by Regulating Pressure



Li et al. PNAS 2009 (in press)

Testable Hypothesis



Conclusions: Chemistry

Planets have evolved

Isotopic composition provides clues

Look of life supporting chemistry

Thanks

- Yung's Group at Caltech,
- Liang (Taiwan), Jiang (U Houston)
- Lunine's book 2004
- Prof Michael Russell
- NASA/JPL
- NSF
- ESA