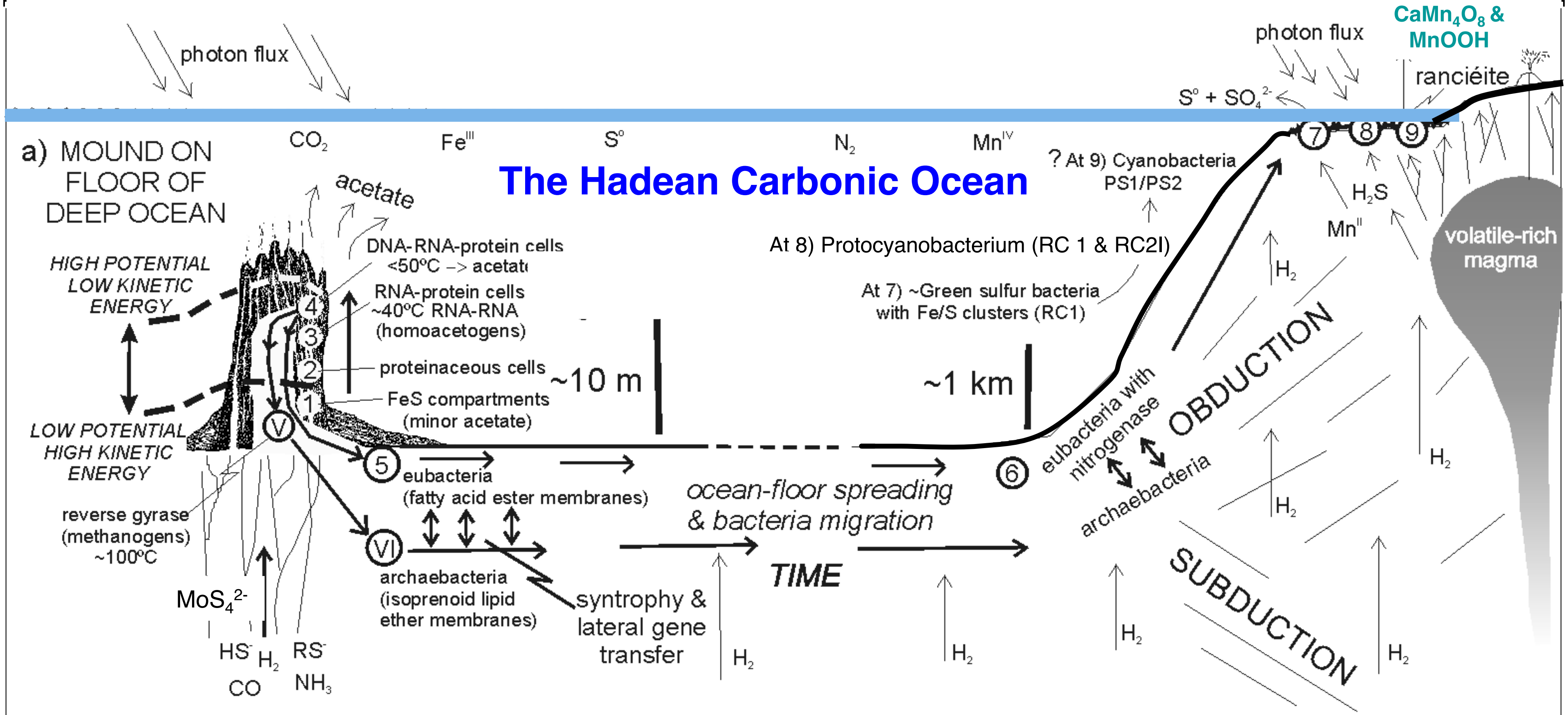
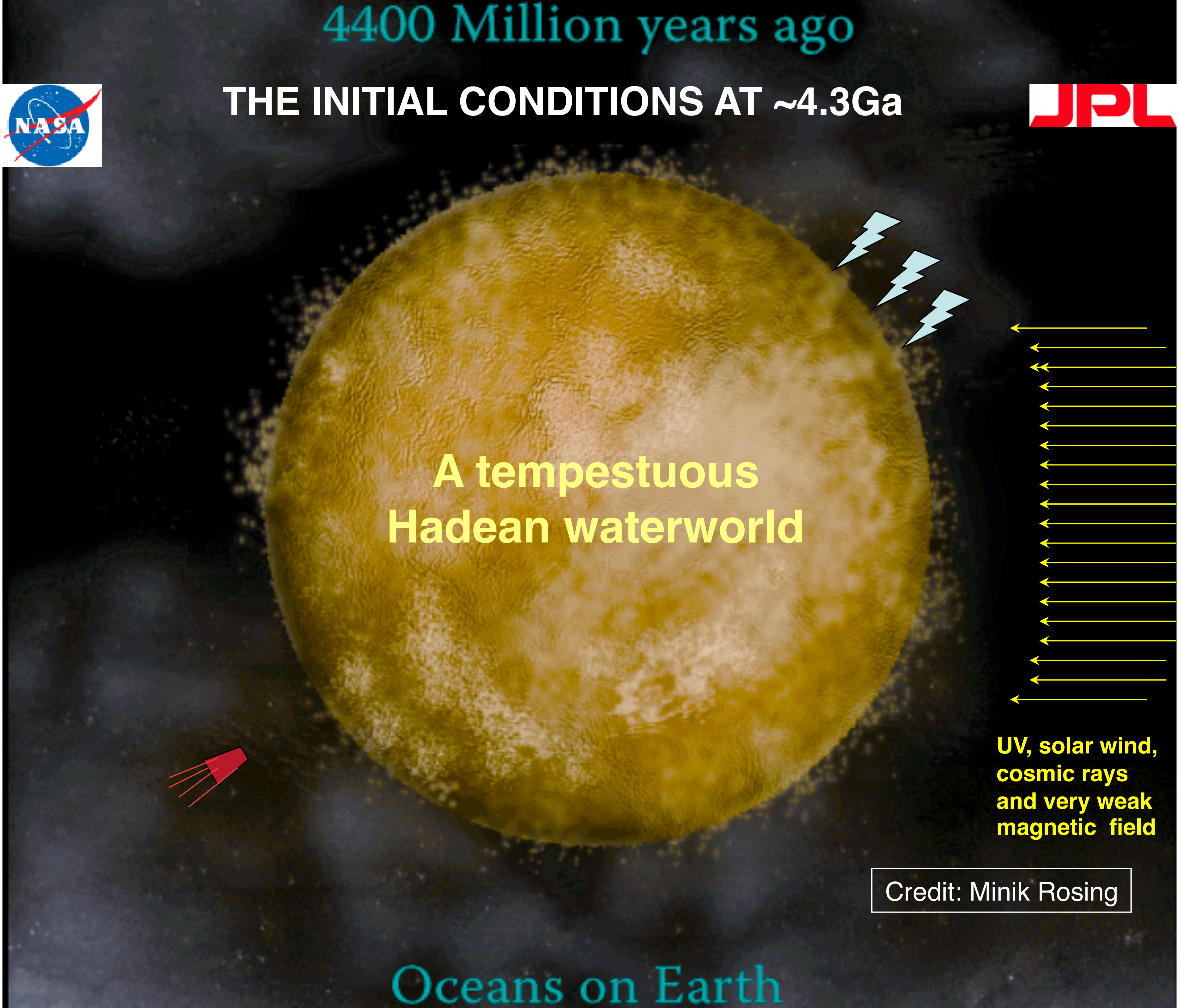
Why does life start, What does it do, Where will it be?



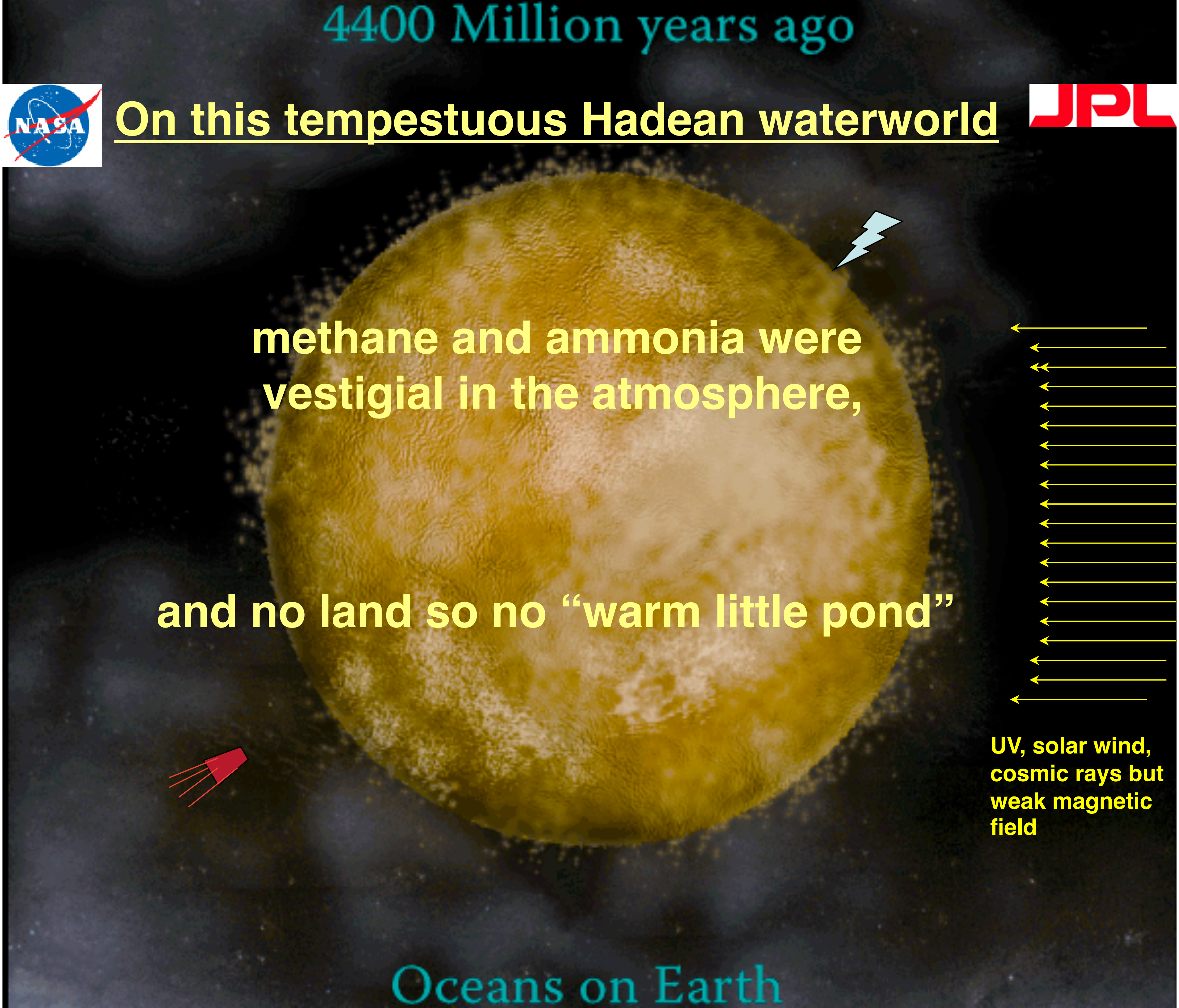
Chemosynthesis ← **atmospheric CO_2** → Oxygenic photosynthesis

H_2 from H_2O (Fe^0,Fe^{2+}) ☒ H_2 from H_2O (~$CaMn_4O_5$) ▽

Michael J Russell, JPL/Caltech


4400 Million years ago
THE INITIAL CONDITIONS AT ~4.3Ga
A tempestuous
Hadean waterworld
UV, solar wind,
cosmic rays
and very weak
magnetic field
Credit: Minik Rosing
Oceans on Earth

On this tempestuous Hadean waterworld



methane and ammonia were vestigial in the atmosphere,

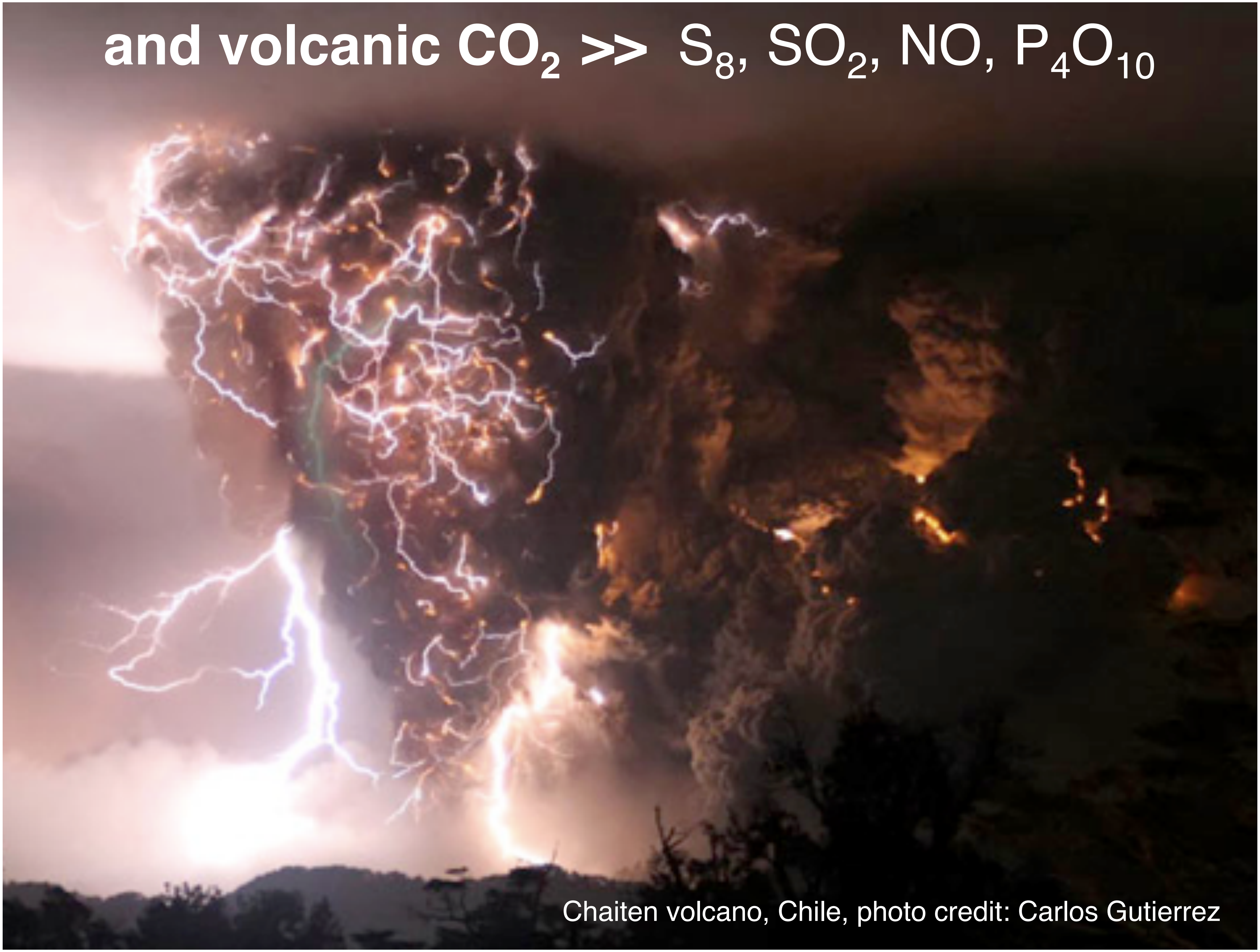
and no land so no "warm little pond"

UV, solar wind, cosmic rays but weak magnetic field

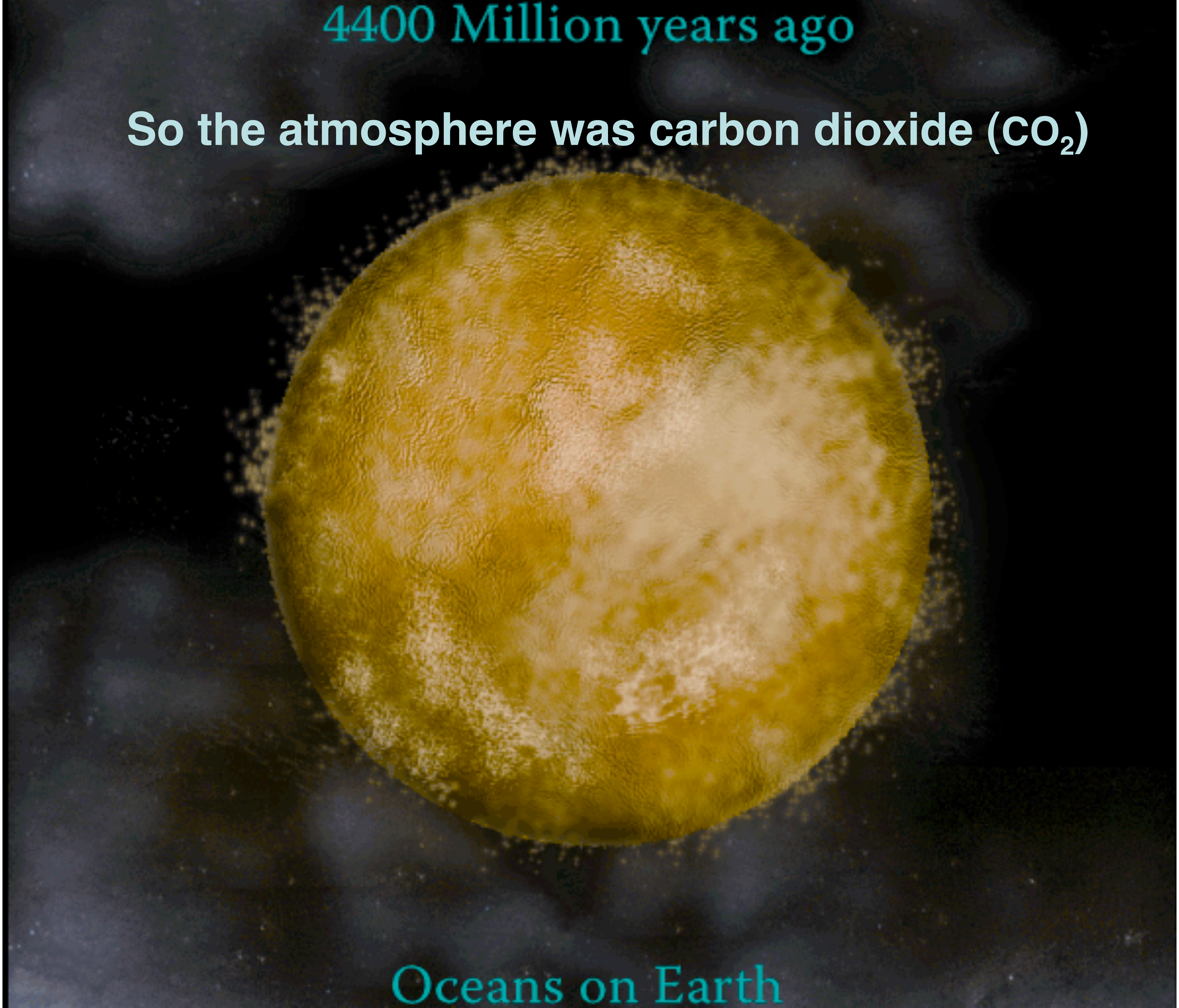

Getting the initial conditions
and the physics right
Susan Henry

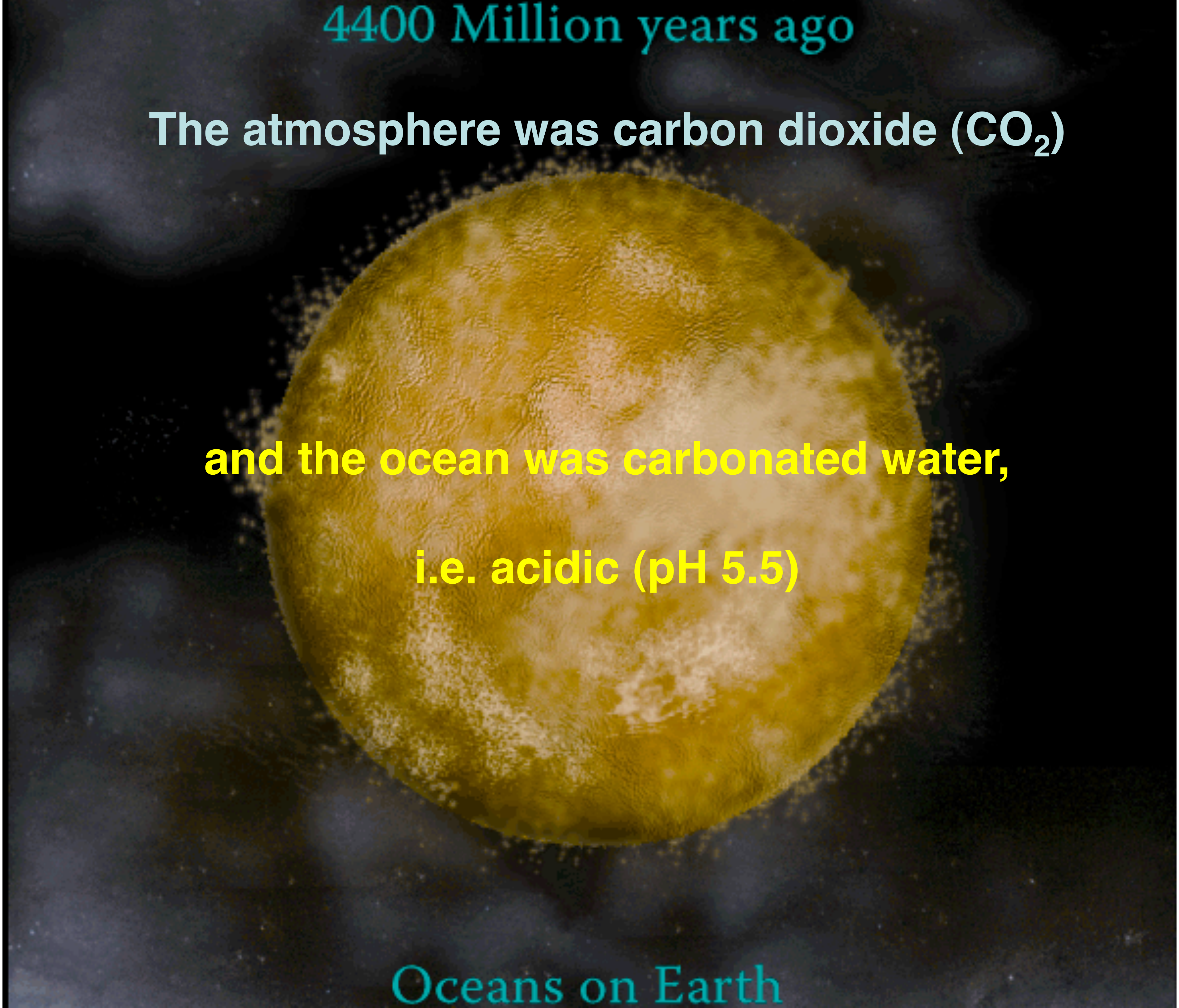

4400 Million years ago
The Earth produced hydrogen
from some of this water
H_2
Oceans on Earth

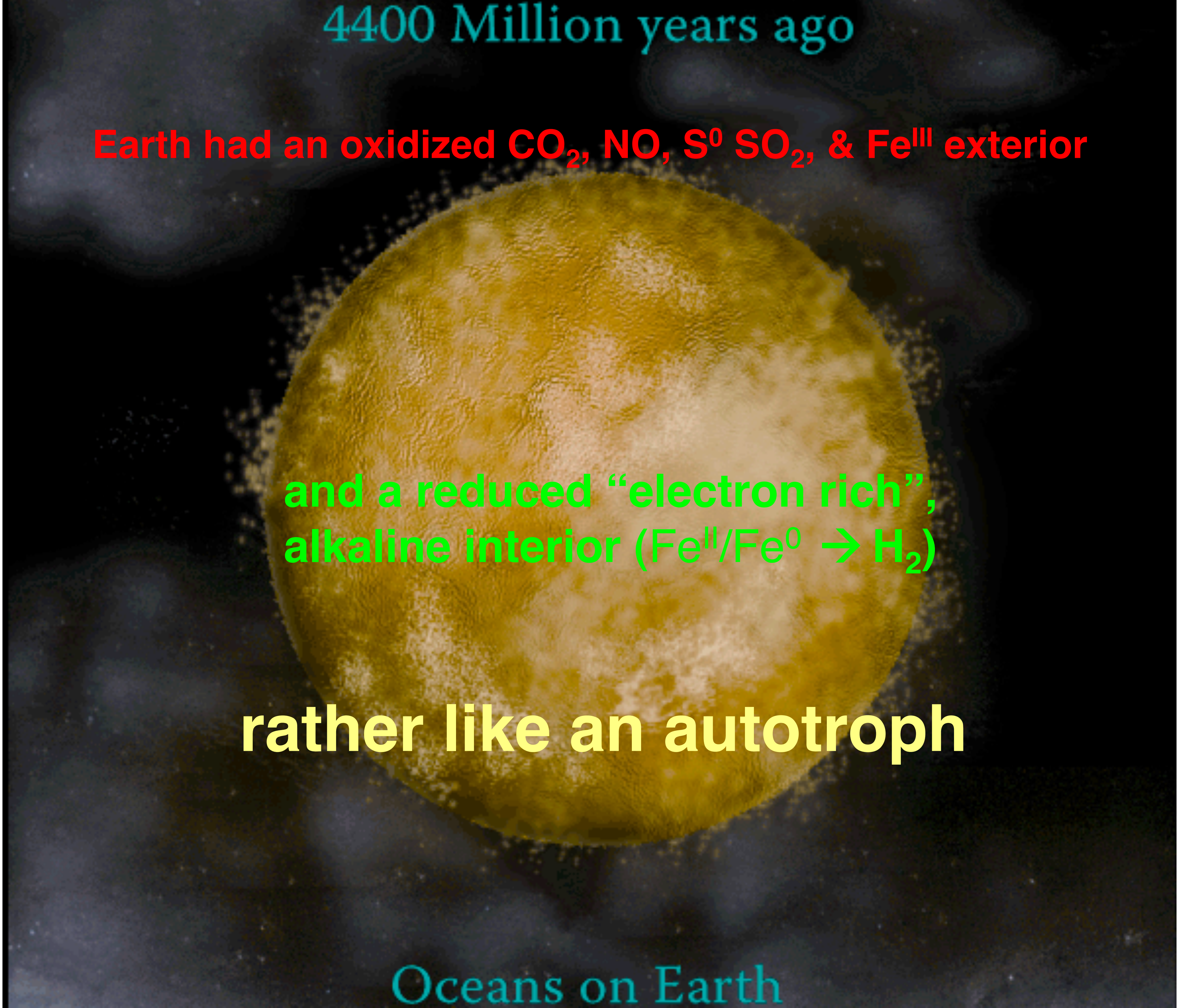
and volcanic CO_2 >> S_8, SO_2, NO, P_4O_{10}

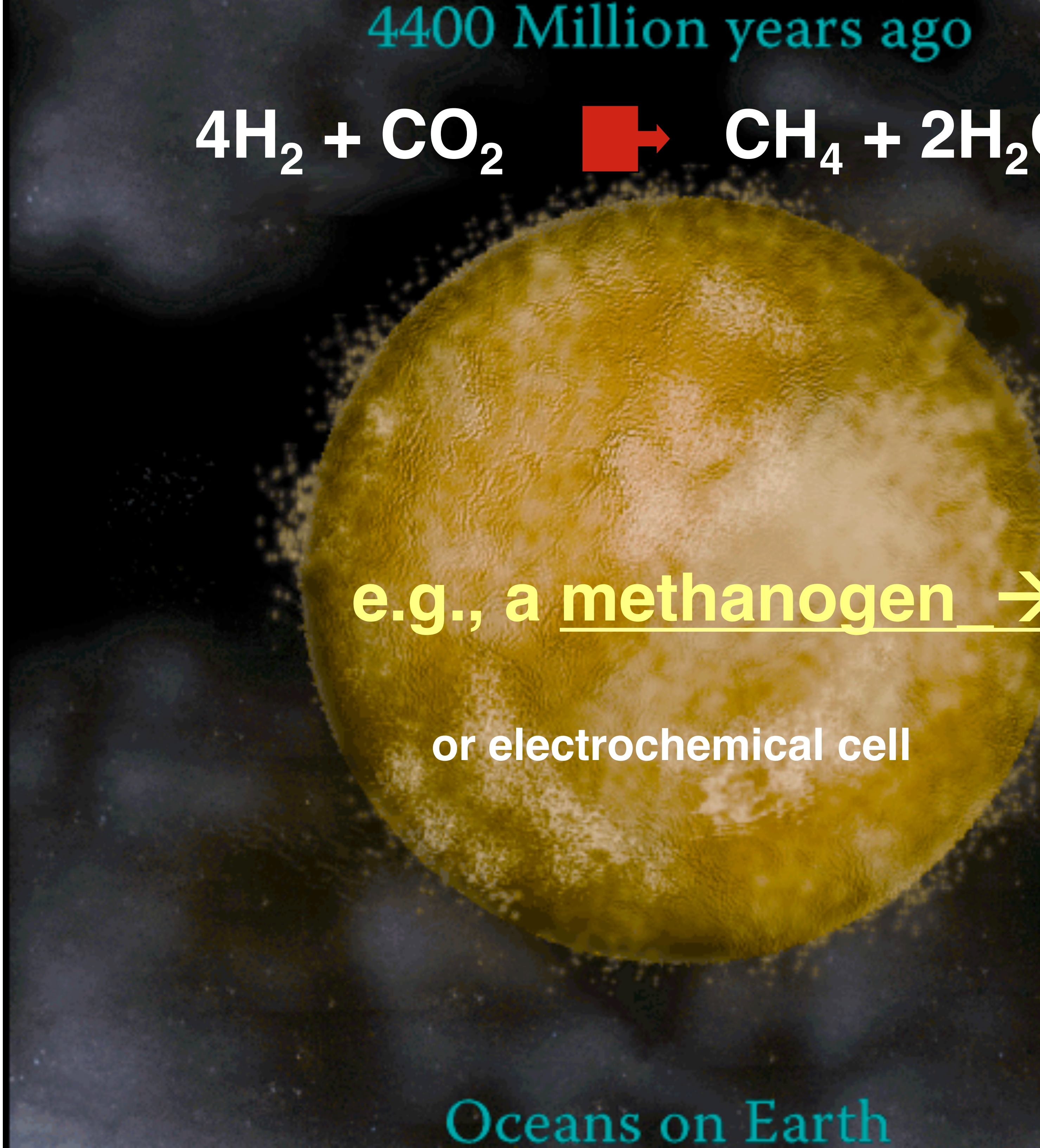


Chaiten volcano, Chile, photo credit: Carlos Gutierrez


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
Earth had an oxidized CO_2, NO, S^0 SO_2, & Fe^{III} exterior
and a reduced “electron rich”,
alkaline interior ($Fe^{II}/Fe^0 \rightarrow H_2$)
rather like an autotroph
Oceans on Earth



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

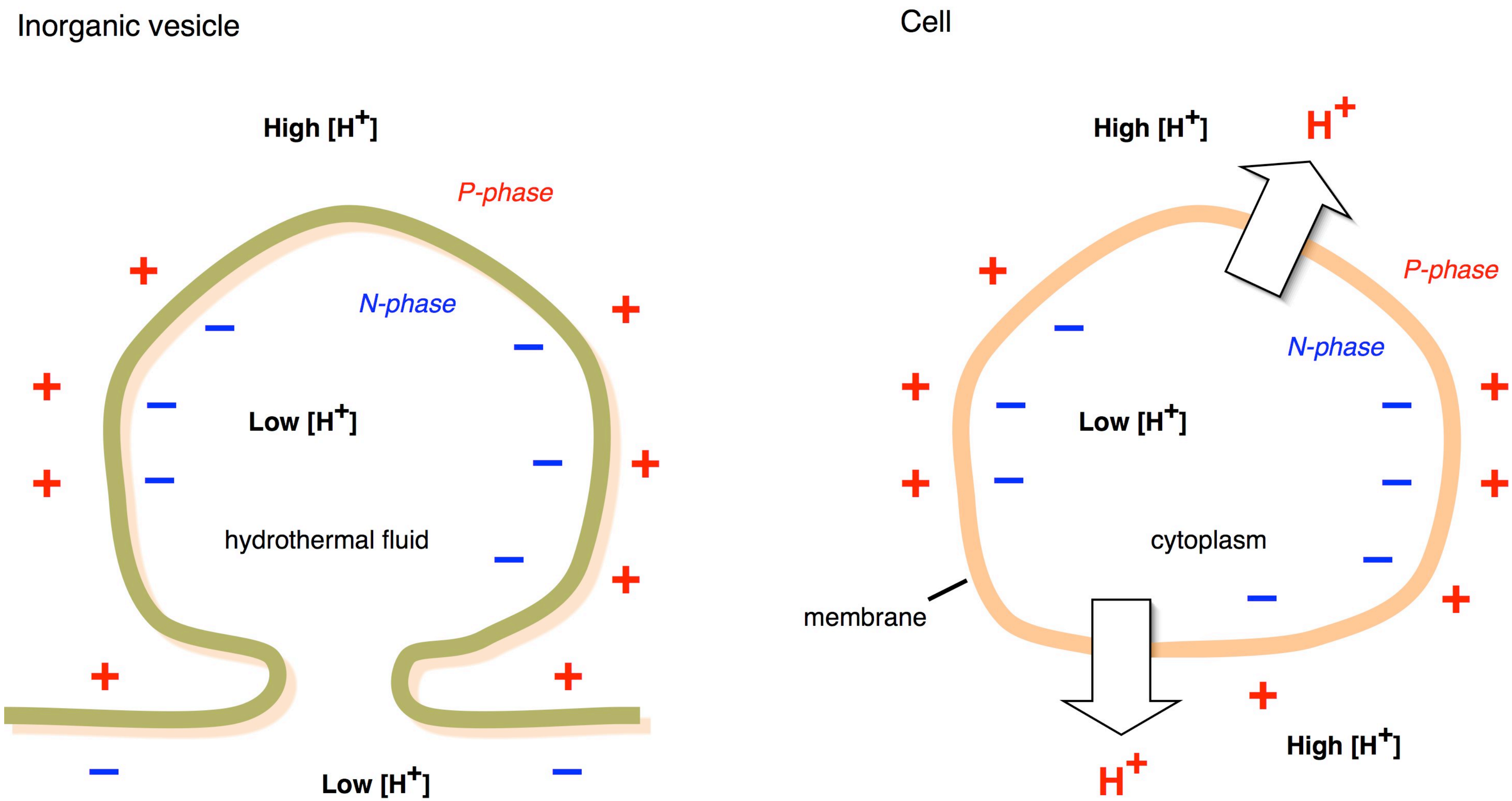
e.g., a <u>methanogen →</u>

or electrochemical cell

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

So can we imagine life just "bubbling off" from the surface?

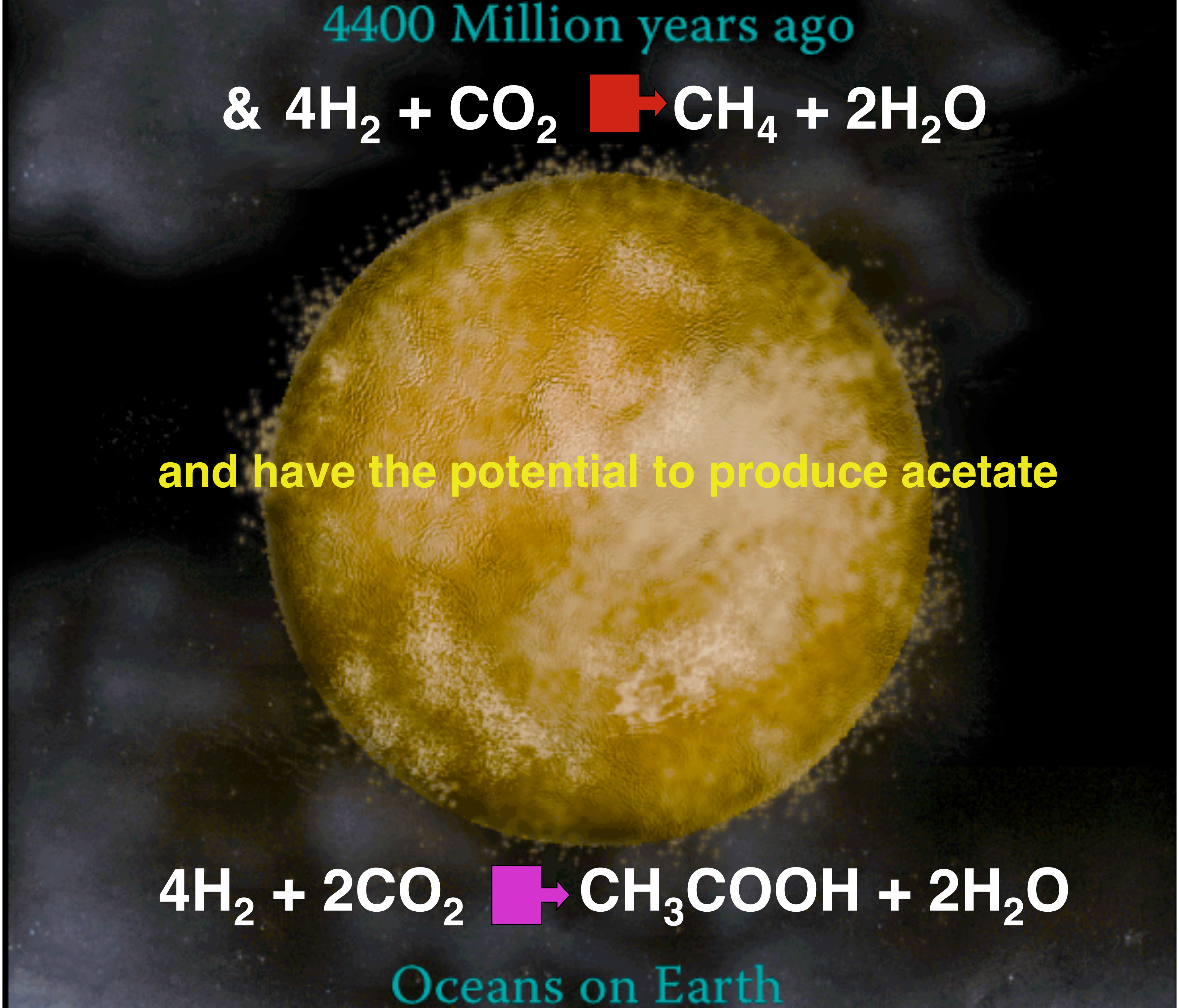
The bubbling off of life from the Earth' solid surface

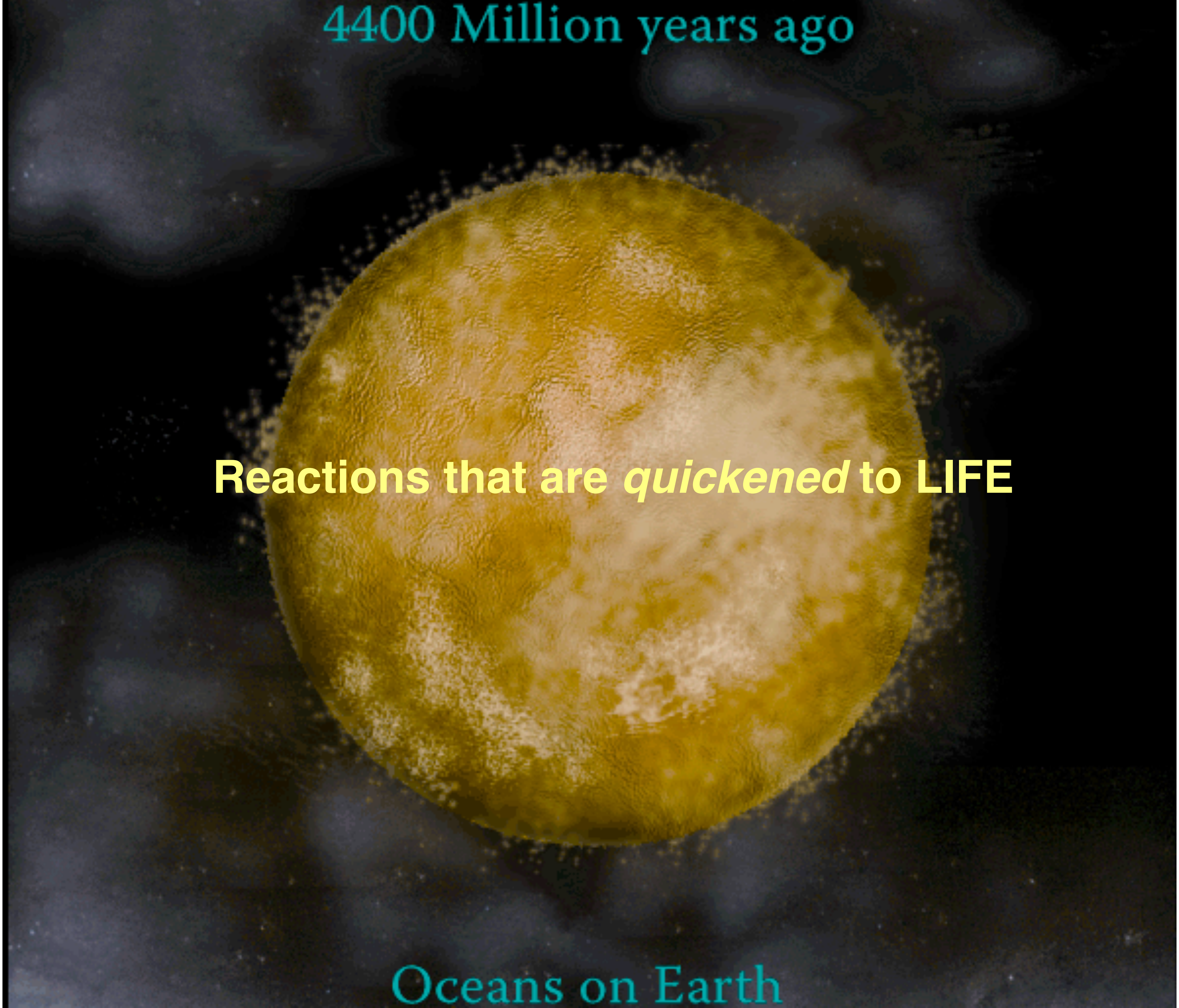


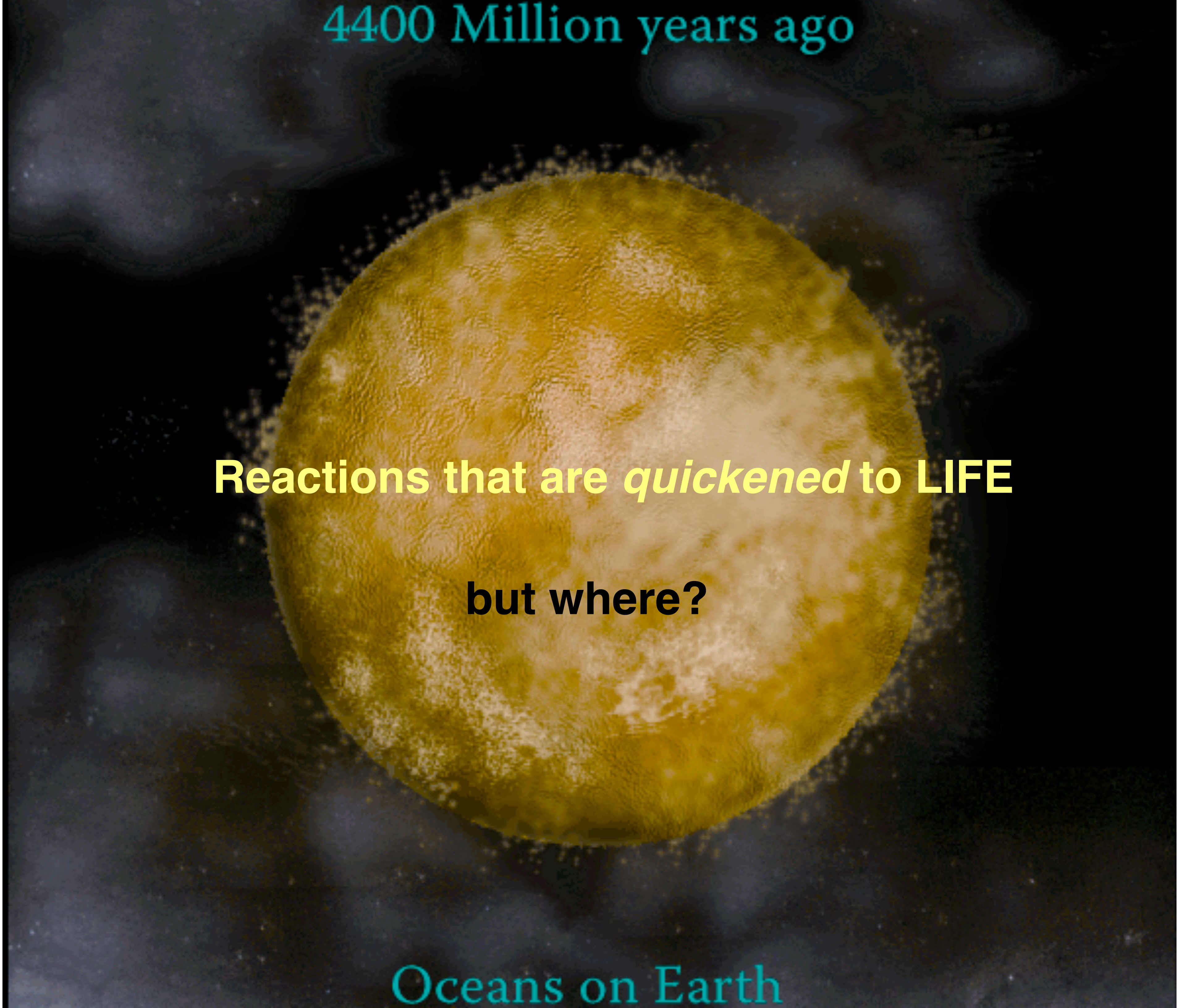
Left: Ambient protonmotive force across the boundary of hydrothermal mound and LUCA
Right: The proton-motive force of living cells descended from LUCA

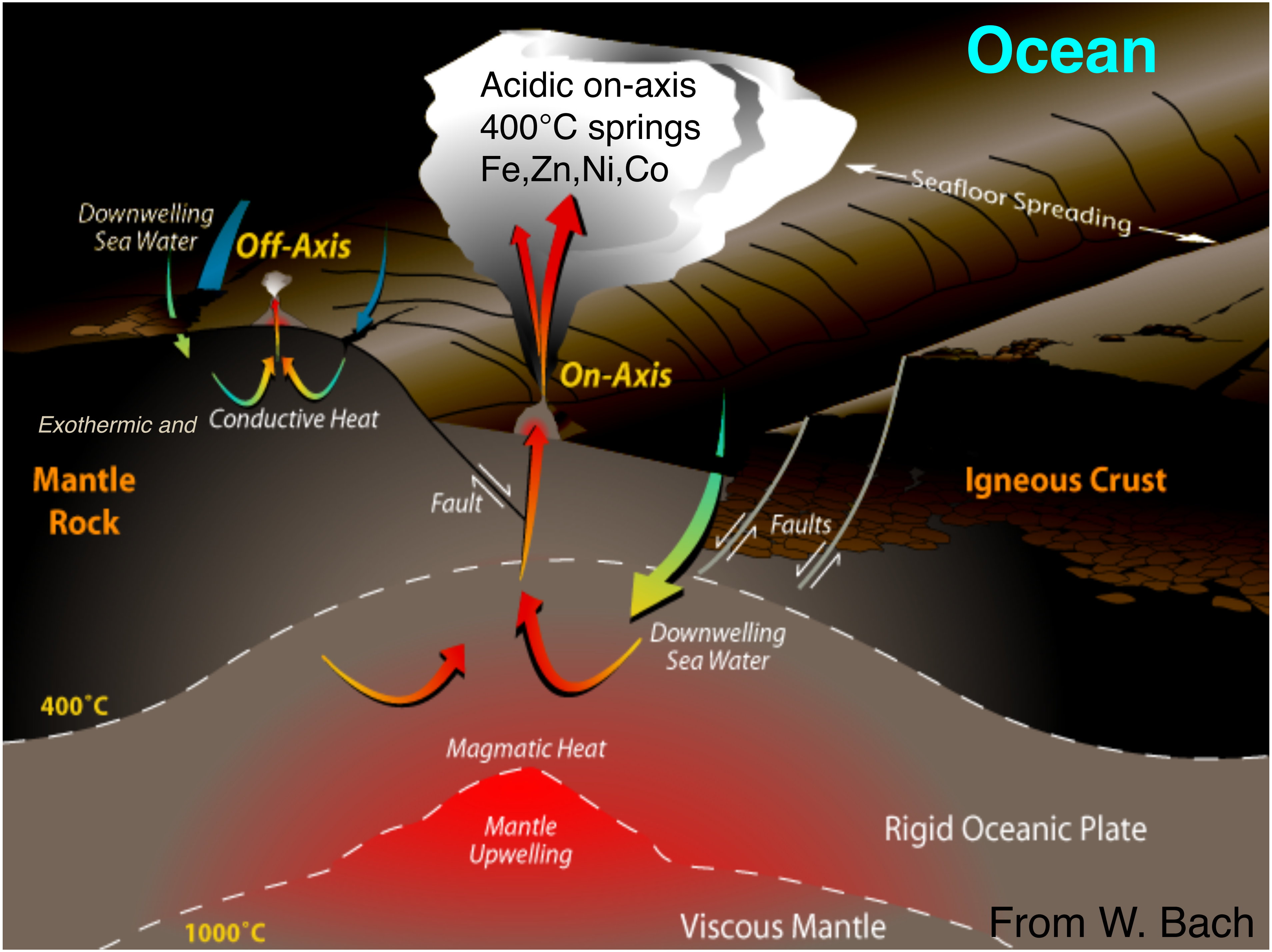
Lane et al. 2010, *BioEssays*, **32**, 271; Based on Russell et al. 1994, *JME*, **39**, 231 & Nitschke & Russell 2009, *JME*, **69**, 481


4400 Million years ago
& $4H_2 + CO_2 \rightarrow CH_4 + 2H_2O$
Hydrogen plus carbon dioxide react slowly to produce methane
Oceans on Earth


4400 Million years ago
& $4H_2 + CO_2 \rightarrow CH_4 + 2H_2O$
and have the potential to produce acetate
$4H_2 + 2CO_2 \rightarrow CH_3COOH + 2H_2O$
Oceans on Earth

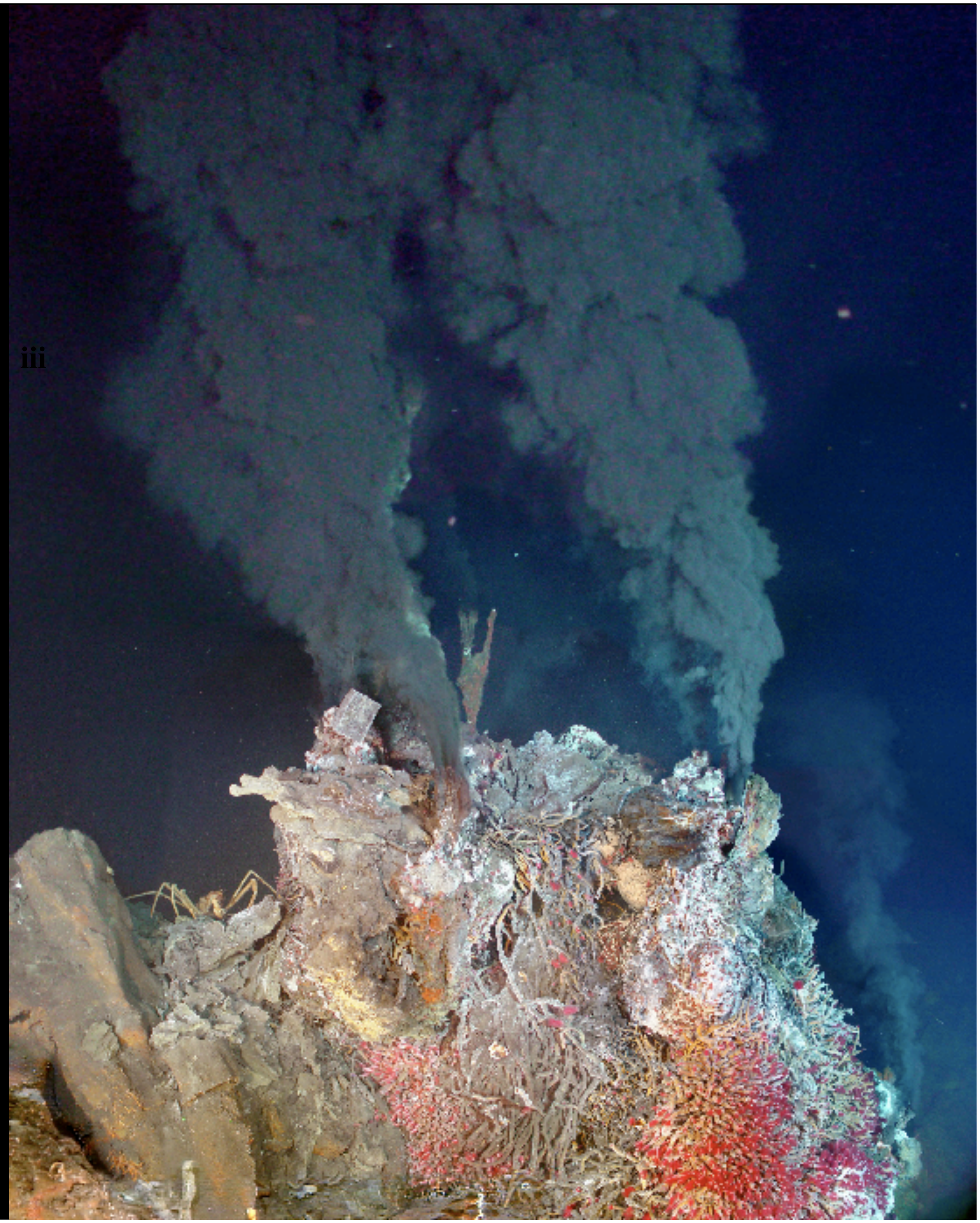

4400 Million years ago
Reactions that are *quickened* to LIFE
Oceans on Earth


4400 Million years ago
Reactions that are *quickened* to LIFE
but where?
Oceans on Earth

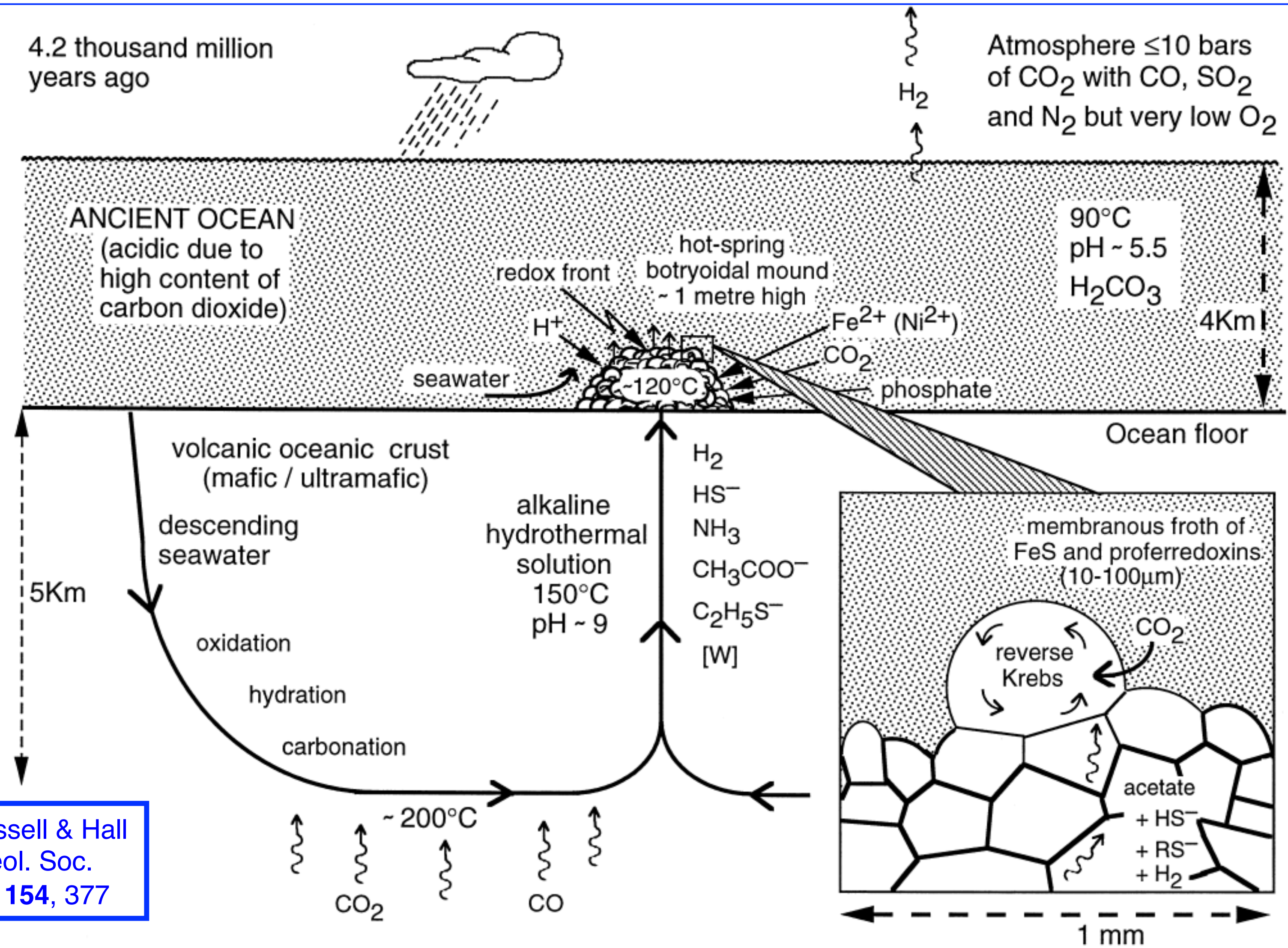

Ocean
Acidic on-axis
400°C springs
Fe,Zn,Ni,Co
Seafloor Spreading
Downwelling
Sea Water
Off-Axis
On-Axis
Exothermic and
Conductive Heat
Mantle
Rock
Igneous Crust
Fault
Faults
Downwelling
Sea Water
400˚C
Magmatic Heat
Mantle
Upwelling
Rigid Oceanic Plate
1000˚C
Viscous Mantle
From W. Bach

Although they're too hot, too acidic, too oxidized & too spasmodic for emergent life, 400°C springs do provide the trace elements (Fe, Ni, Zn, Mo, W, Co) that may be sequestered by metalloenzymes

Endeavor, NE Pacific
Credit: Delaney & Kelley

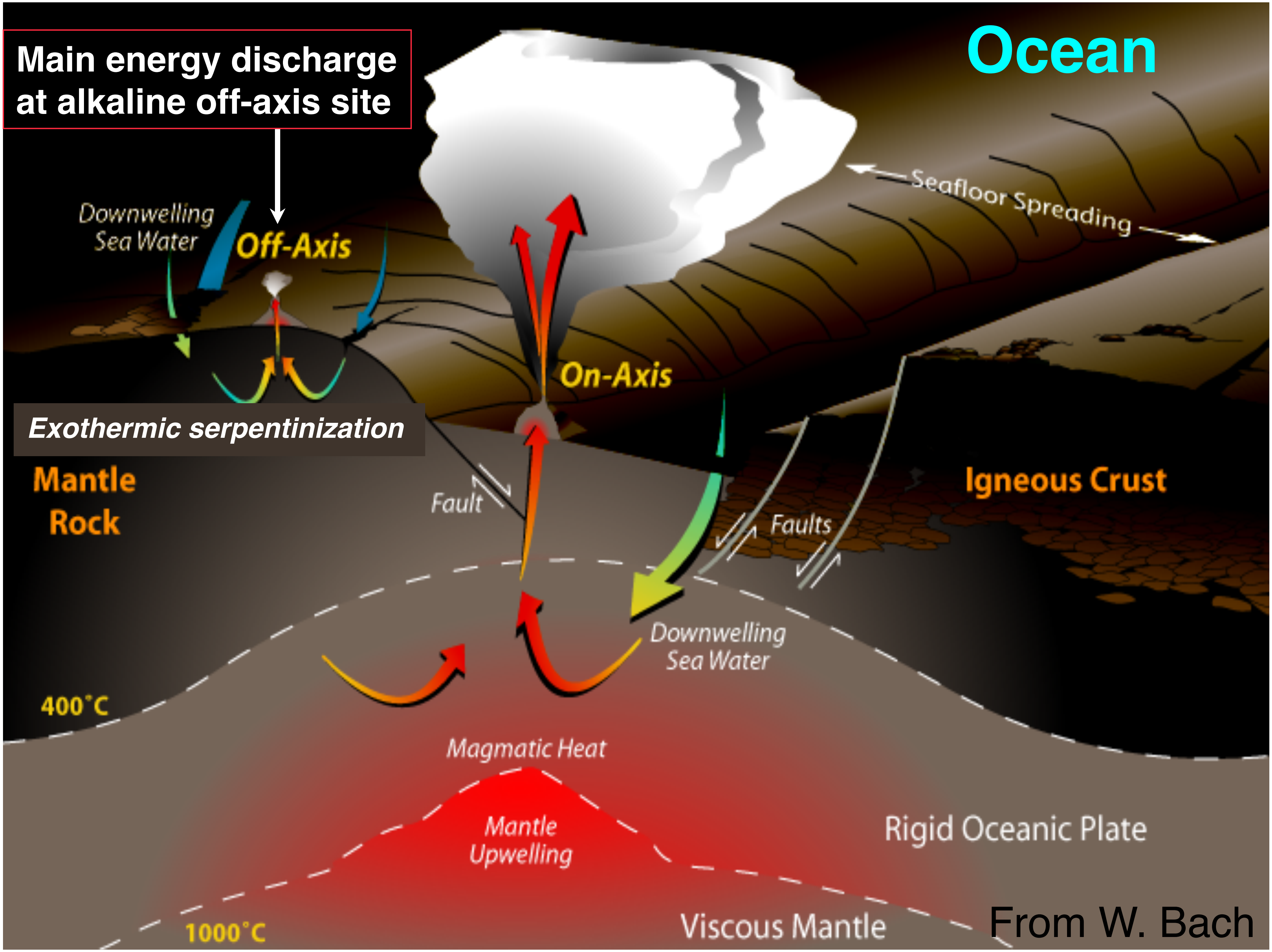


We have suggested that life emerged in cooler, alkaline springs away from oceanic spreading centers



e.g., Russell & Hall 1997 Geol. Soc. London, **154**, 377

i.e., from a low entropy feed


Main energy discharge
at alkaline off-axis site
Ocean
Downwelling
Sea Water
Off-Axis
Seafloor Spreading
On-Axis
Exothermic serpentinization
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 <u>SPRING</u>

$CaCO_3$

$Mg(OH)_2$

pH ≤12

T ≤94°C

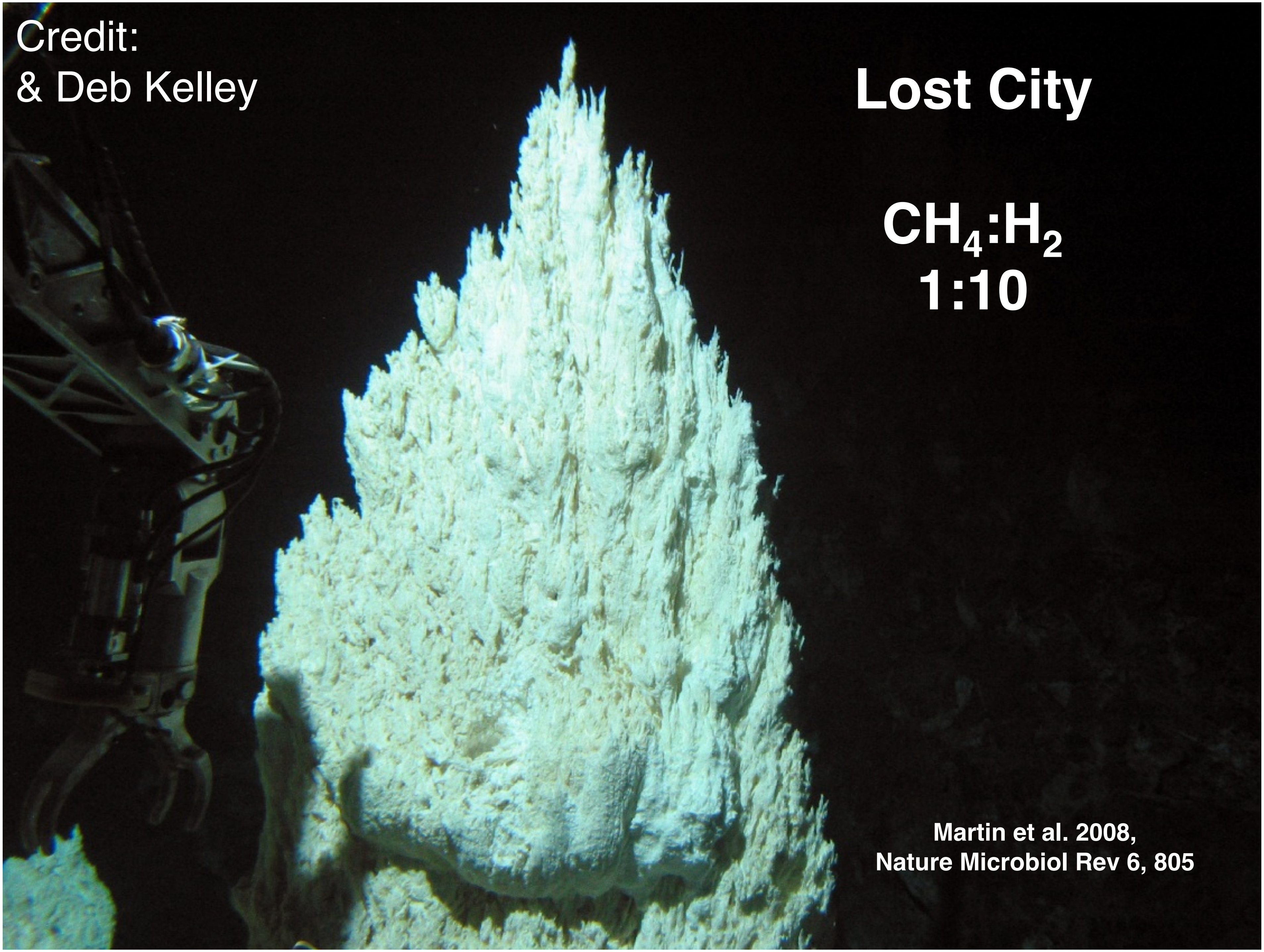
H_2 ≤15mmol

CH_4 ≤2mmol

<u>>30,000 years</u>

Kelley et al. 2001, Nature **412**, 145 & Science 2005, **307**,1428-1434.

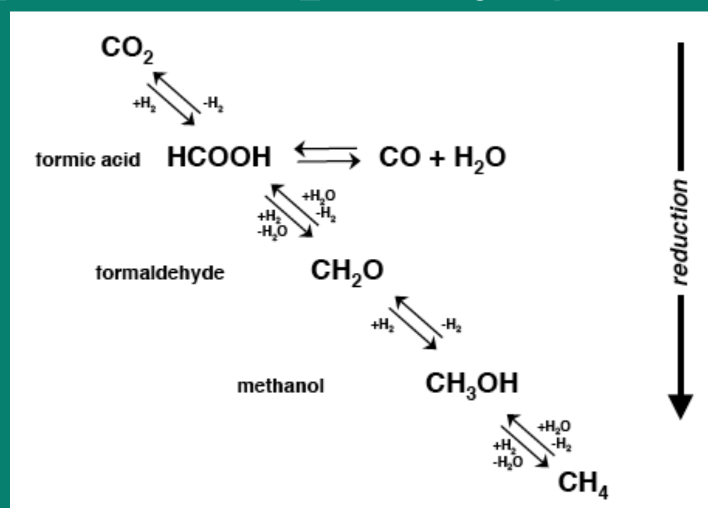
Martin et al. 2008, Nature Microbiol. Rev. **6**, 805-814.


Credit:
& Deb Kelley
Lost City
CH_4:H_2
1:10
Martin et al. 2008,
Nature Microbiol Rev 6, 805

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

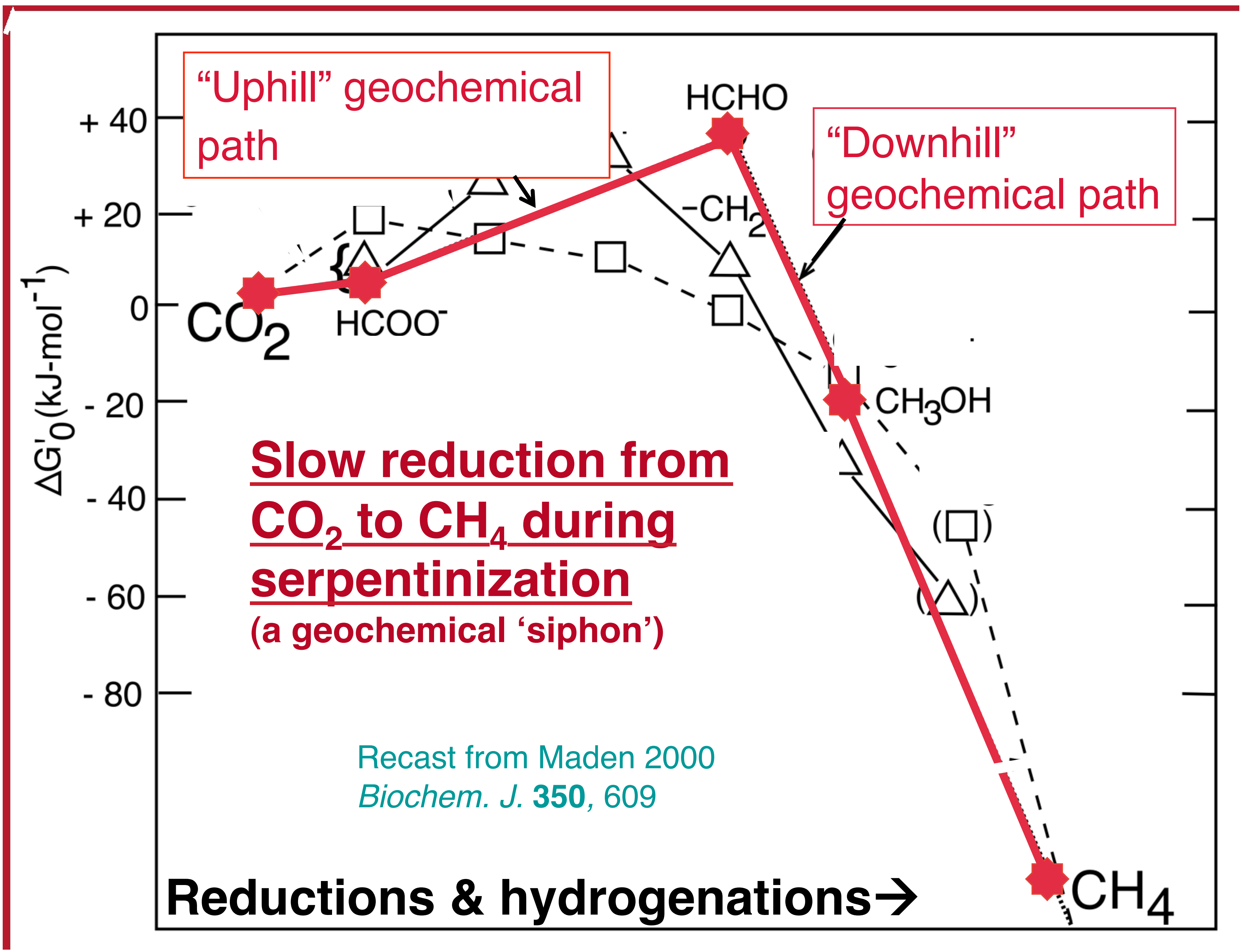
olivine + water → magnetite + serpentine + alkali + $H_2\uparrow$

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

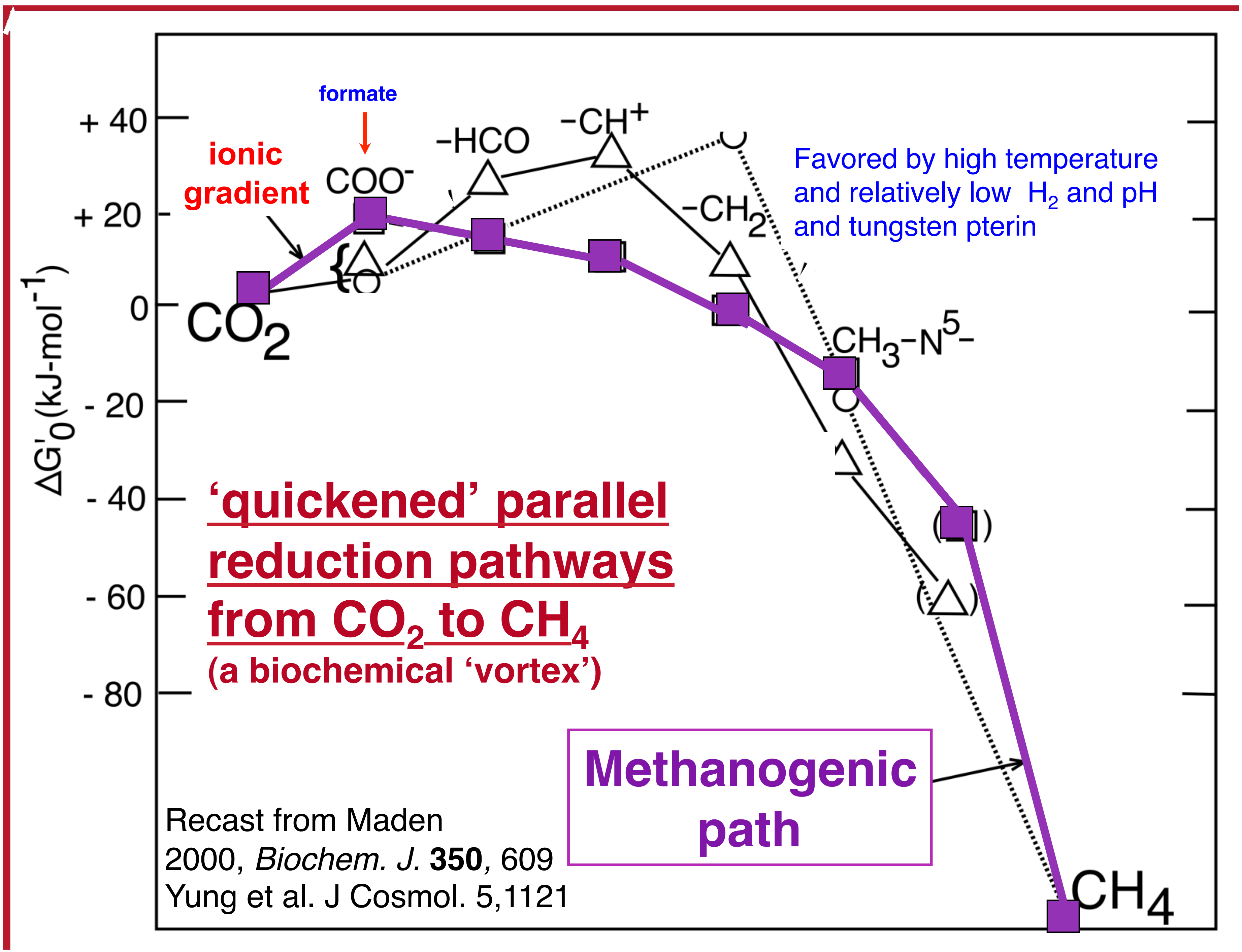


Single carbon redox reactions during serpentinization

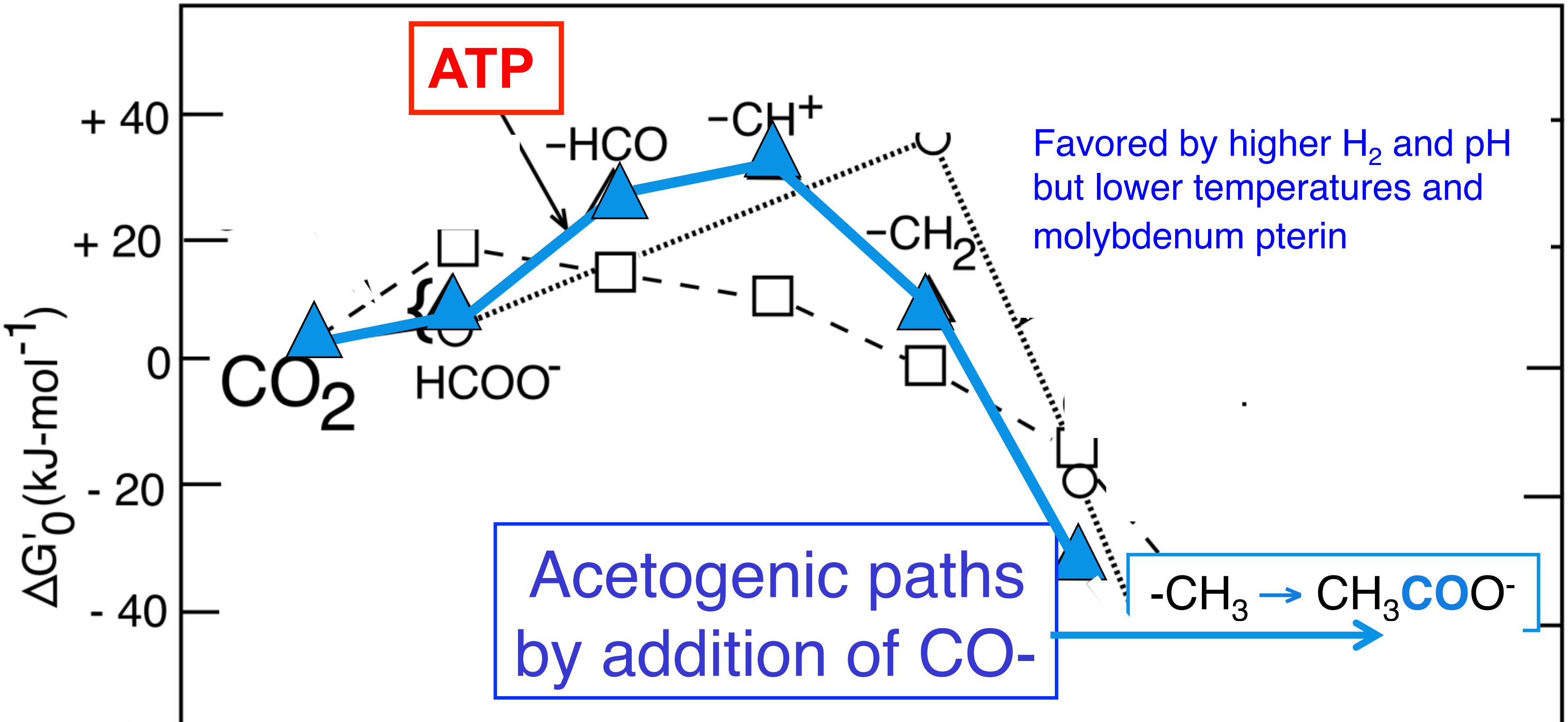
Seewald et al. 2006
GCA 70, 446



"Uphill" geochemical path
HCHO
"Downhill" geochemical path
+ 40
+ 20
0
- 20
- 40
- 60
- 80
$\Delta G'_0$ (kJ-mol^{-1})
CO_2
$HCOO^-$
$-CH_2$
CH_3OH
CH_4
Slow reduction from CO_2 to CH_4 during serpentinization
(a geochemical 'siphon')
Recast from Maden 2000
Biochem. J. **350**, 609
Reductions & hydrogenations→



formate
ionic
gradient
COO-
-HCO
-CH+
-CH2
CH3-N5-
CO2
CH4
+ 40
+ 20
0
- 20
- 40
- 60
- 80
ΔG'0(kJ-mol-1)
Favored by high temperature
and relatively low H2 and pH
and tungsten pterin
'quickened' parallel
reduction pathways
from CO2 to CH4
(a biochemical 'vortex')
Methanogenic
path
Recast from Maden
2000, Biochem. J. 350, 609
Yung et al. J Cosmol. 5,1121

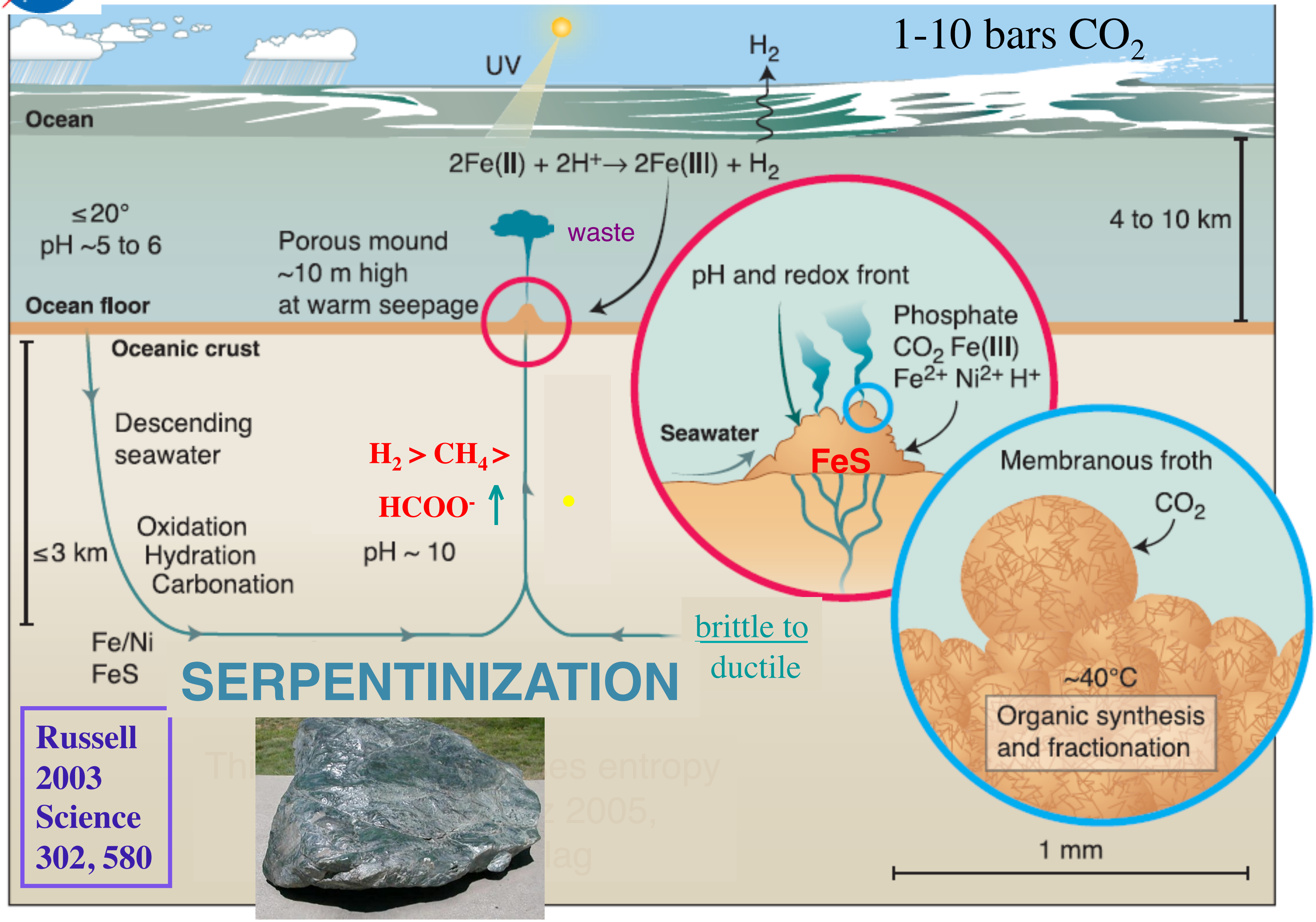


Single-pass reduction pathways from CO_2 to CH_3COO^-

(biochemical 'vortex')

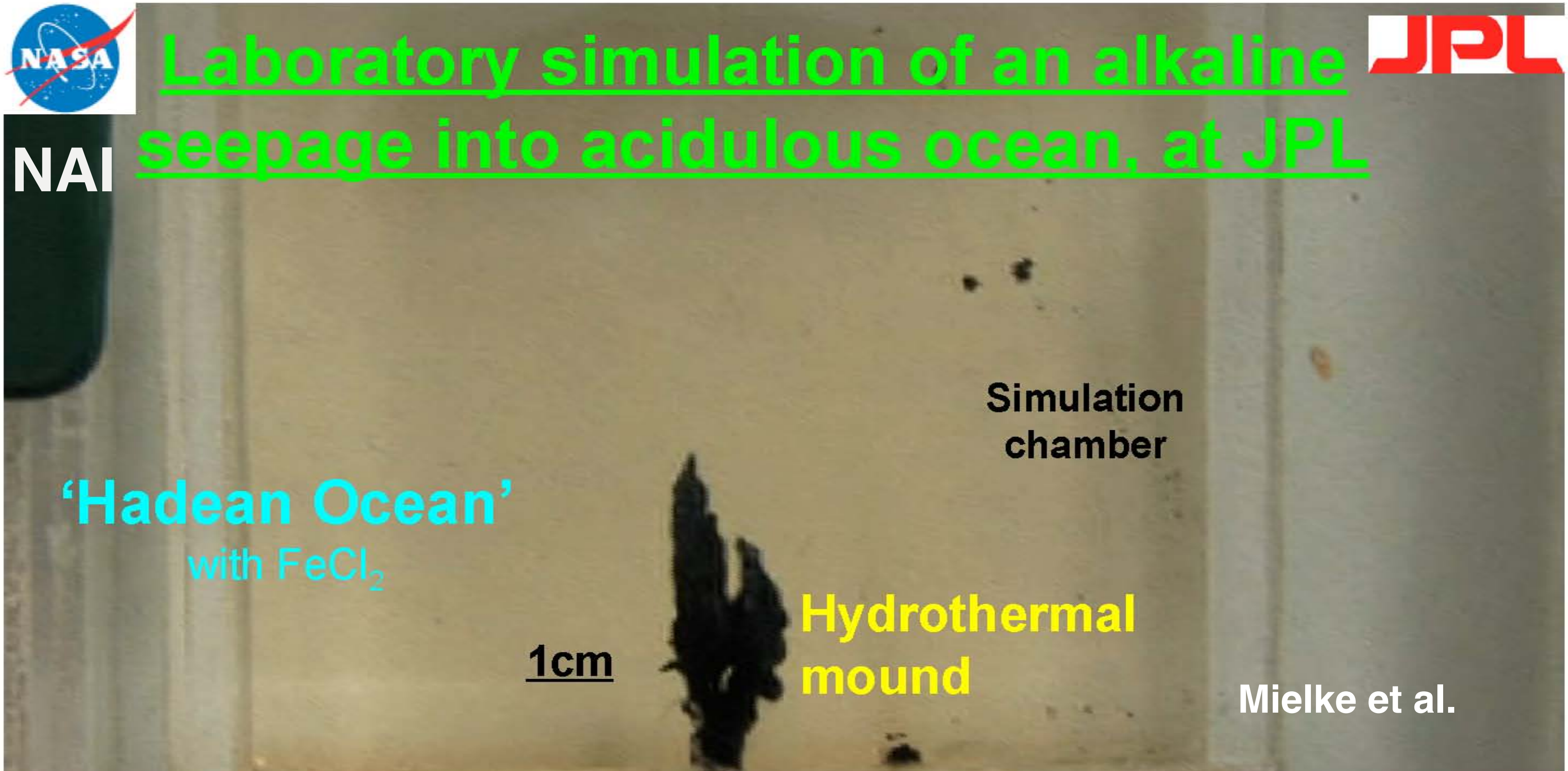
Recast from Maden 2000, *Biochem. J.* **350**, 609;

Capping and quickening serpentinization reactions

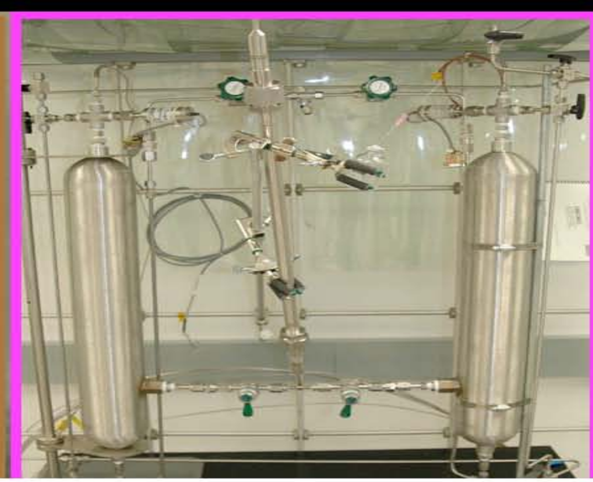


Laboratory simulation of an alkaline seepage into acidulous ocean, at JPL

NAI

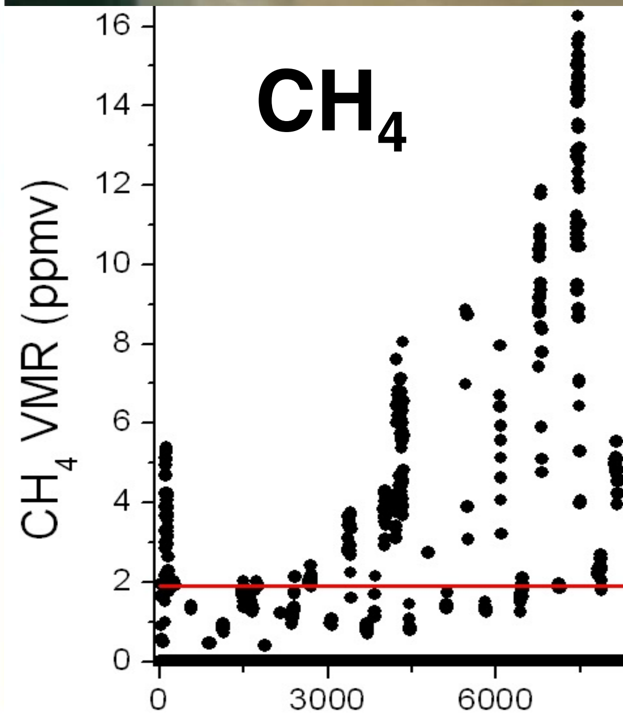


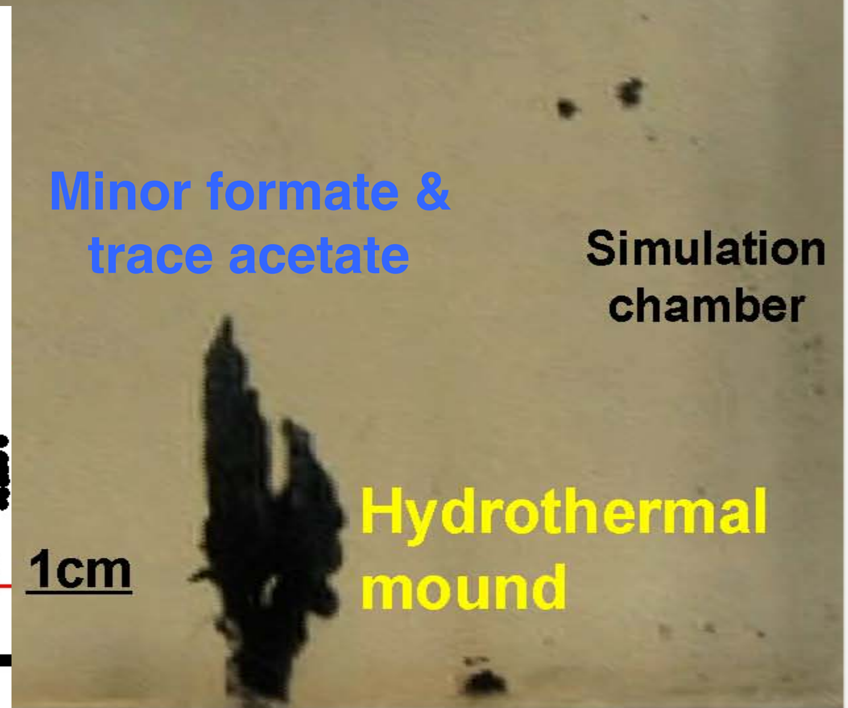
'ocean crust'

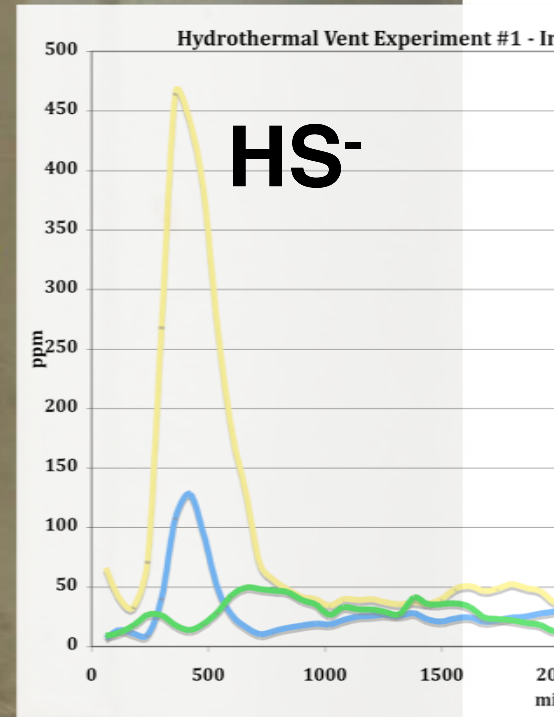


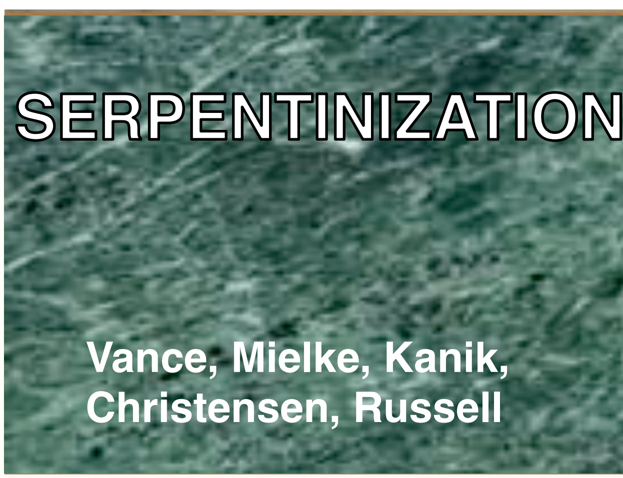
←Separate reactor experiment demonstrates sulfide delivery

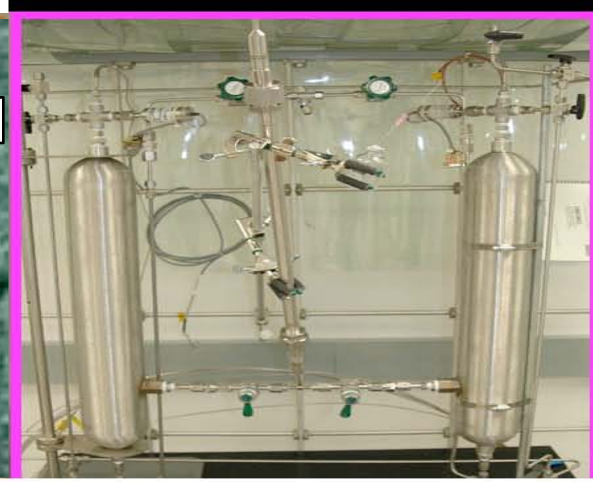
Laboratory simulation of an alkaline seepage into acidulous ocean, at JPL







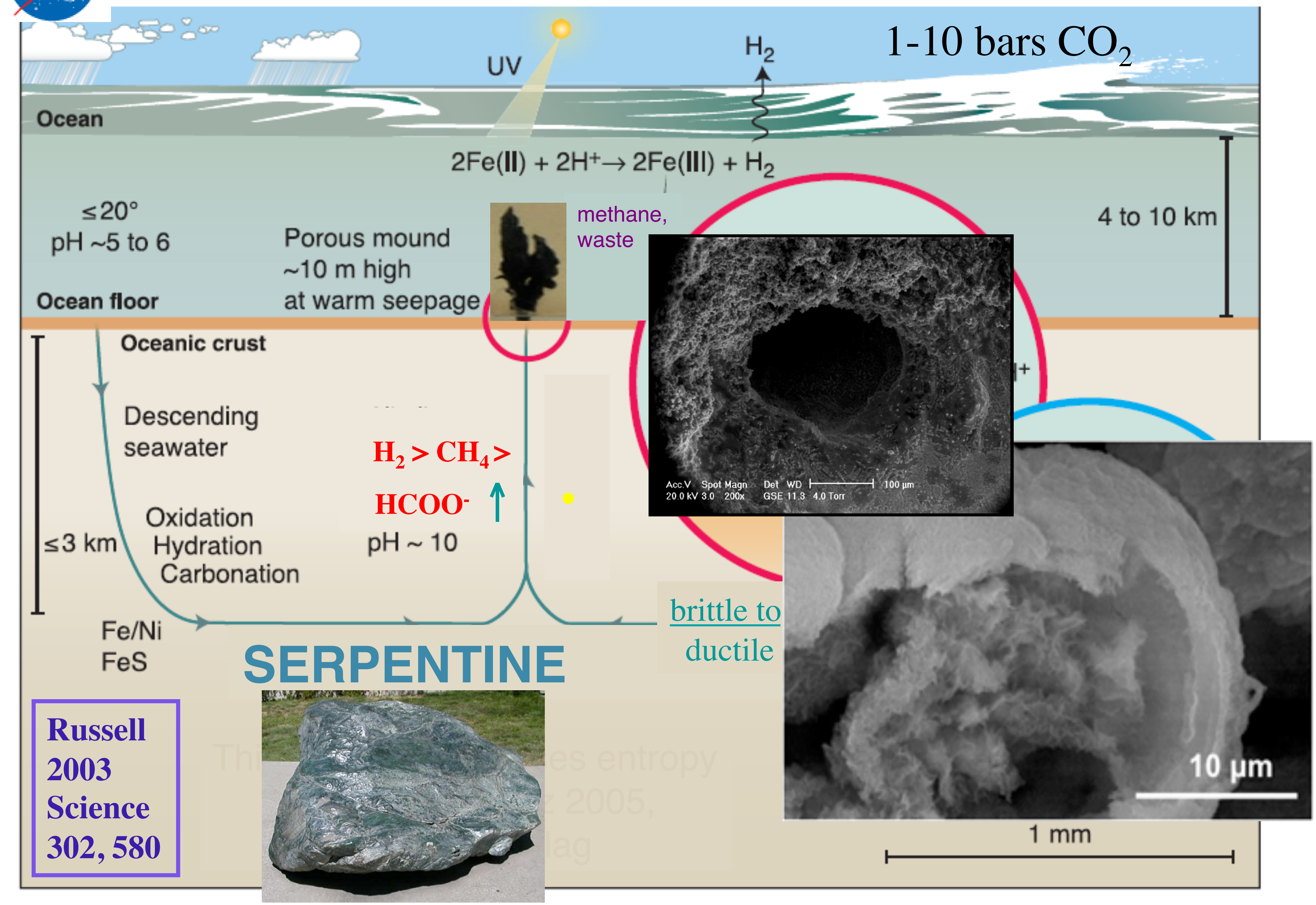




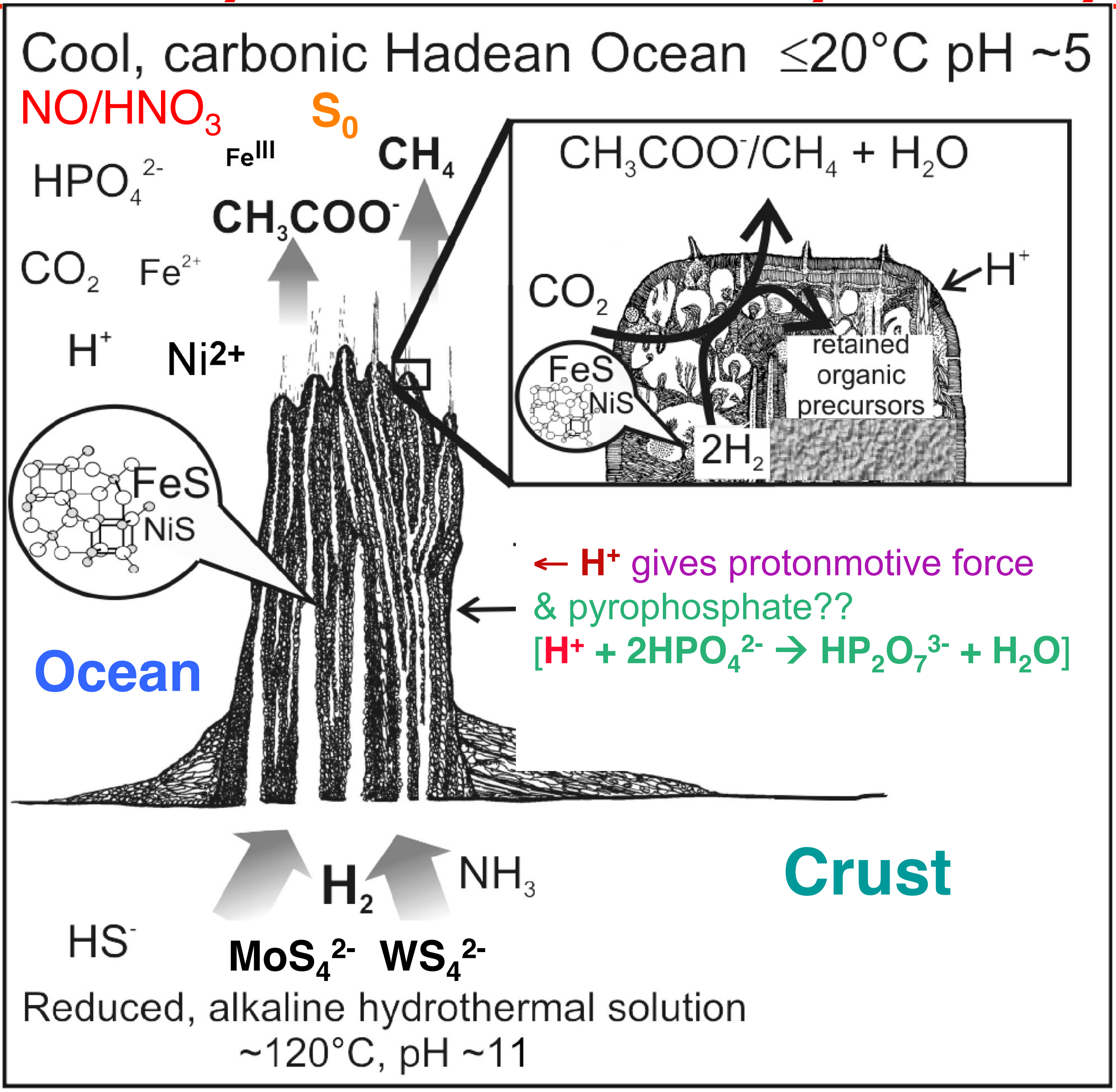
←Separate reactor experiment demonstrates sulfide delivery

Mielke, Kidd, Vance, Kanik, Russell

THE FIRST COMPARTMENTS



The Rocky Roots of the Acetyl-Coenzyme-A Pathway



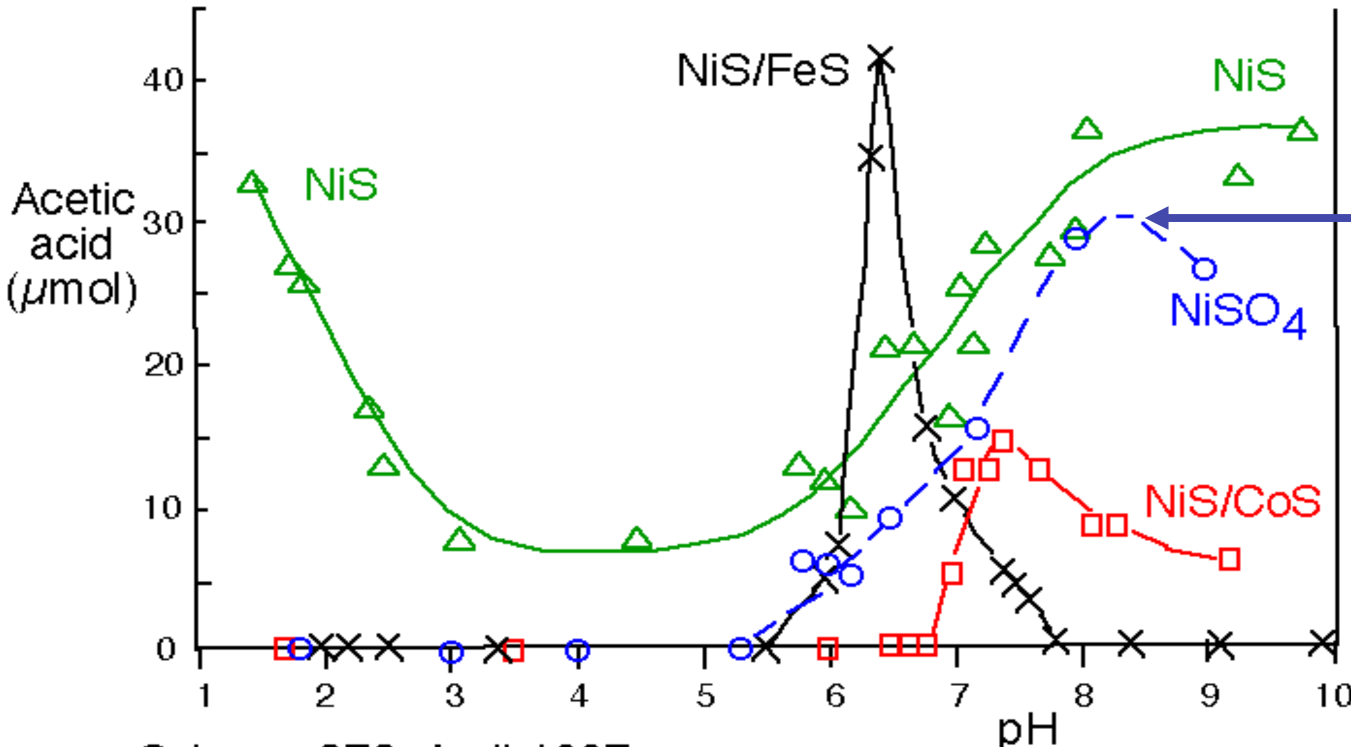
The hatchery of life

Russell & Martin 2004
TIBS, **29**, 358-363
Nitschke & Russell,
JME, **69**, 481

Assembly of methyl thio**acetate**

Huber & Wächtershäuser (1997) reaction

$$2CH_3SH + CO \xrightarrow[NiS/FeS]{100°C} CH_3CO(SCH_3) + H_2S$$



Science 276. April 1997

cf Acetyl-CoA synthase reaction

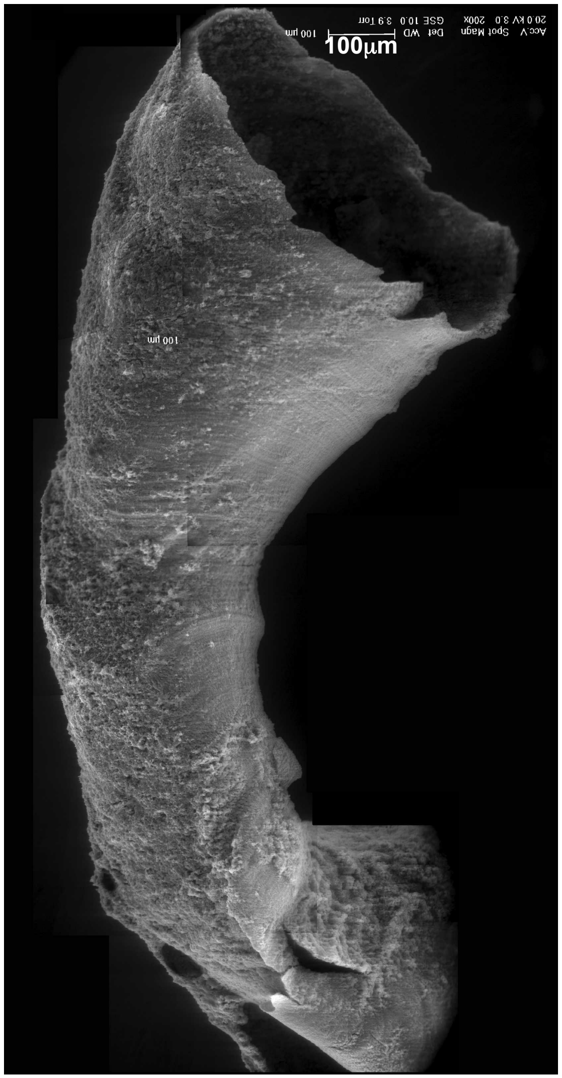
$$\underset{\text{corrin}}{CH_3} + CO + HSCoA \longrightarrow CH_3CO(SCoA)$$

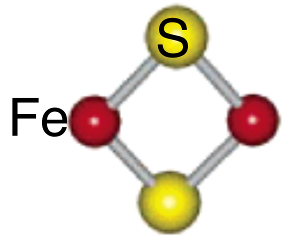
Promoted by alkaline conditions

NB.

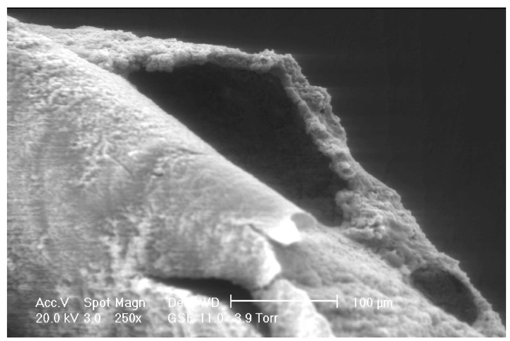
Nickel sulfate is also an effective catalyst so that the “pyrite-pulled” mechanism is irrelevant here

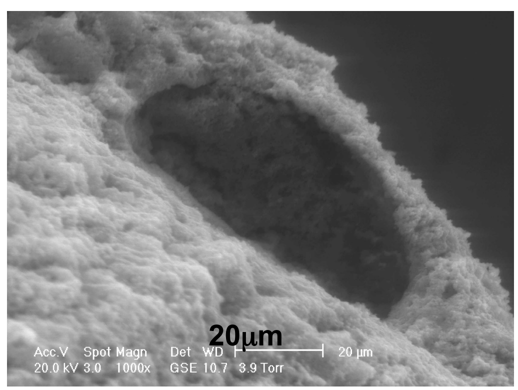
Mackinawite (FeS) comprises a portion of the first membrane

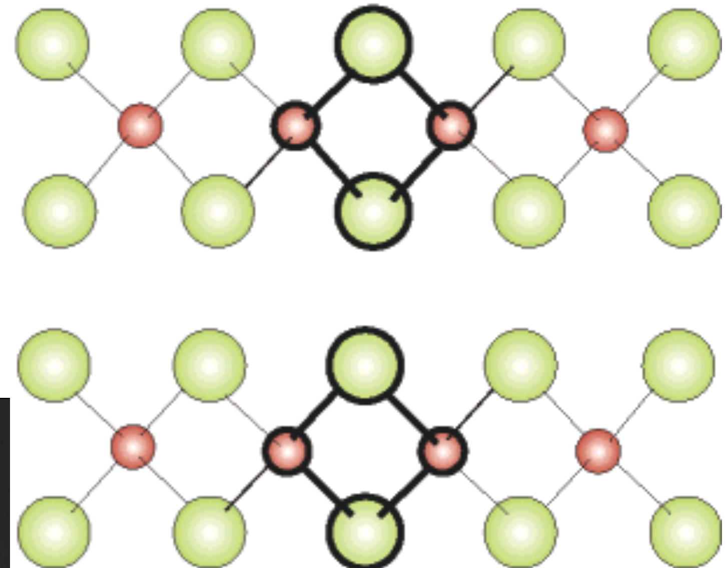




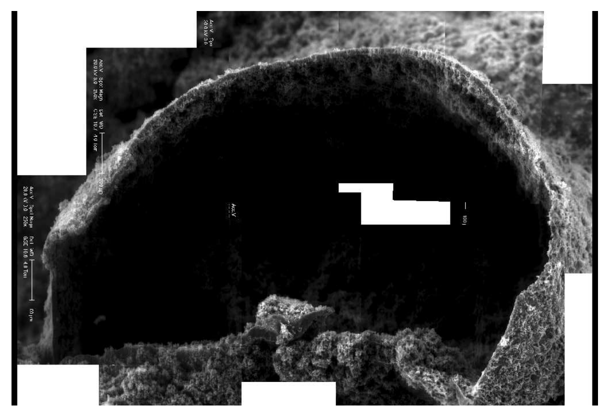
Fe_2S_2

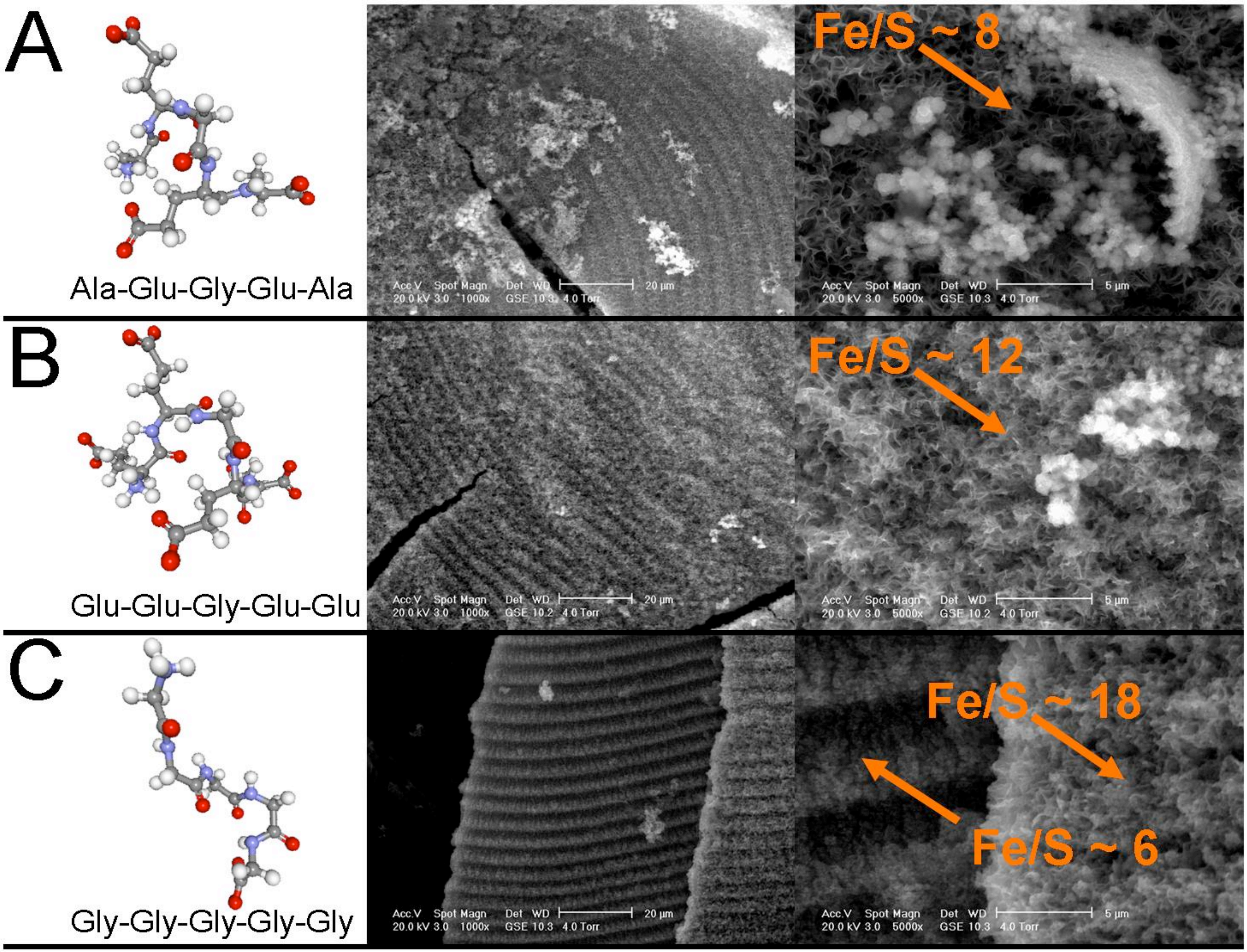






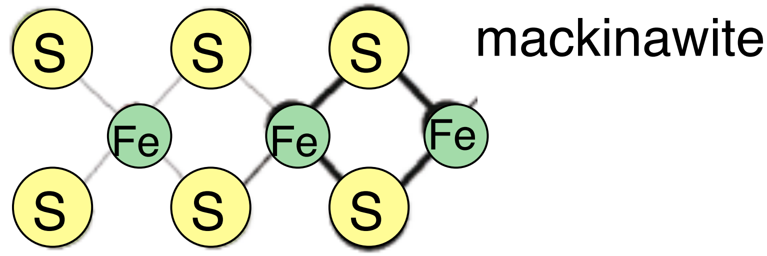
mackinawite

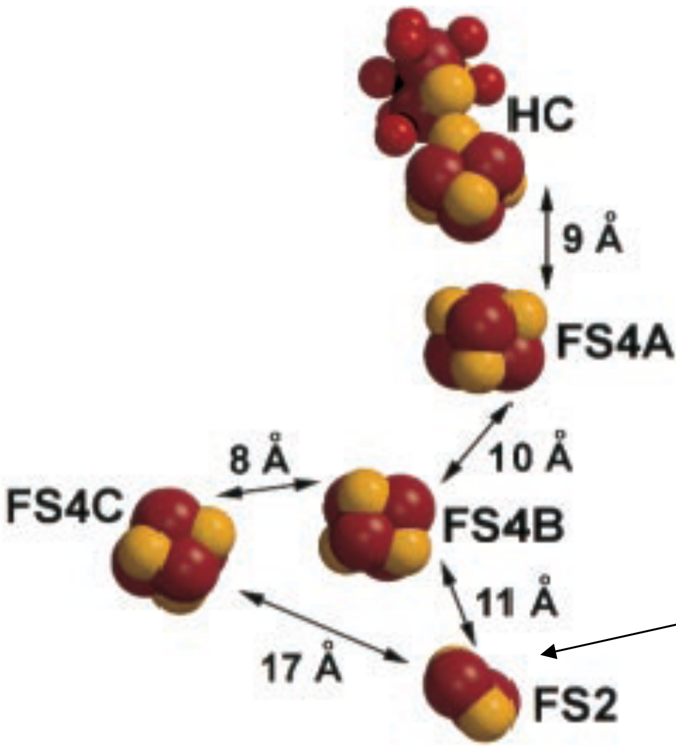


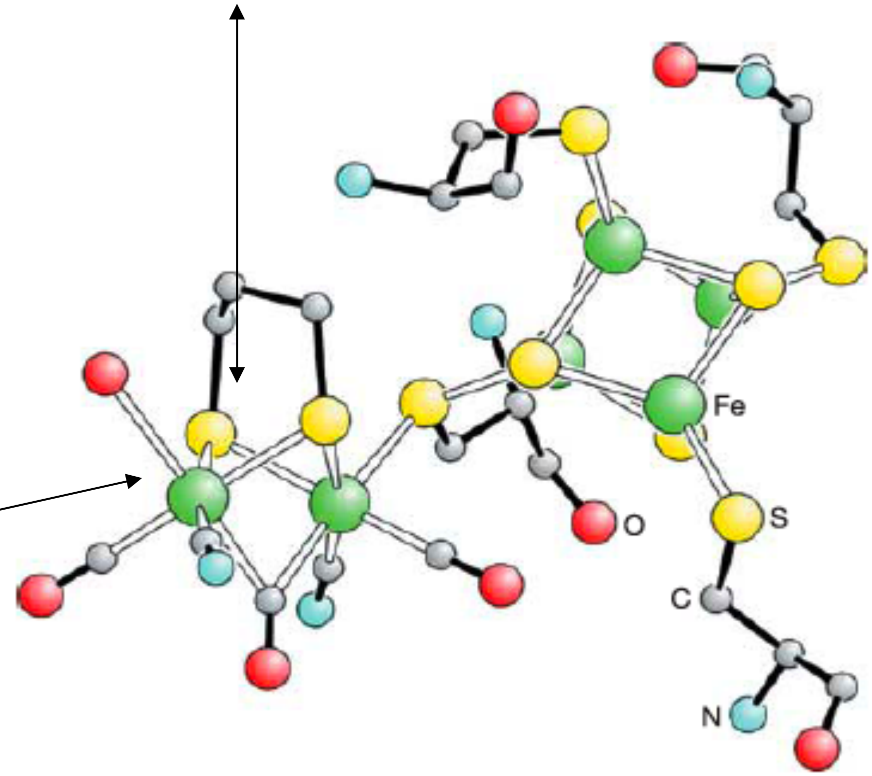

A
Ala-Glu-Gly-Glu-Ala
Fe/S ~ 8
B
Glu-Glu-Gly-Glu-Glu
Fe/S ~ 12
C
Gly-Gly-Gly-Gly-Gly
Fe/S ~ 18
Fe/S ~ 6

Could mackinawite act as a proto-hydrogenase?

$$H_2 \Leftrightarrow 2H^+ + 2e^-$$





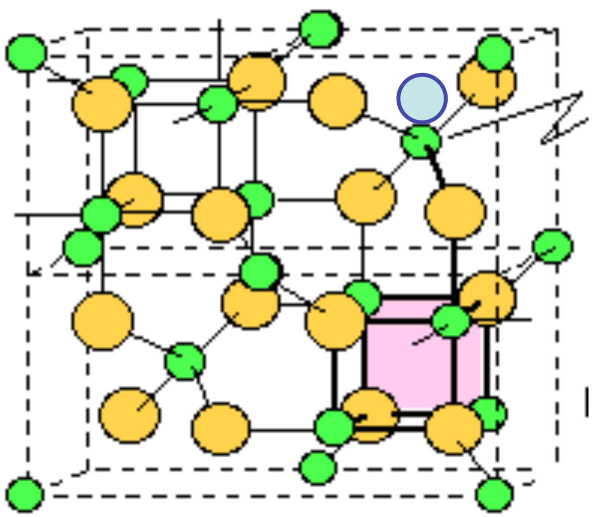


Peters et al, *Science* 1998, **282**:1853

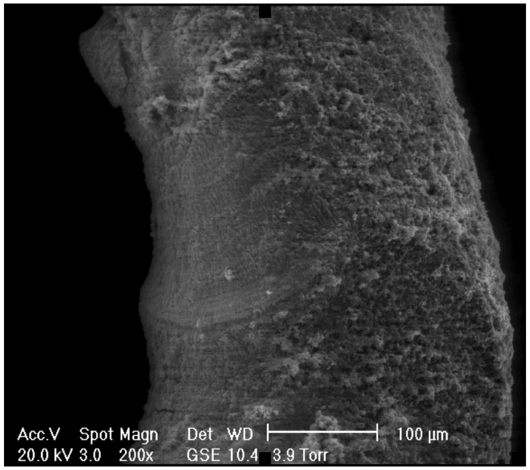
Composite structure of hydrogenase from *Clostridium* & *Desulfovibrio*
Tard et al., 2005 *Nature* **433**, 610

External H^+ could oxidize mackinawite (FeS) to greigite (Fe_3S_4) in the membrane

Greigite [Fe_5NiS_8]



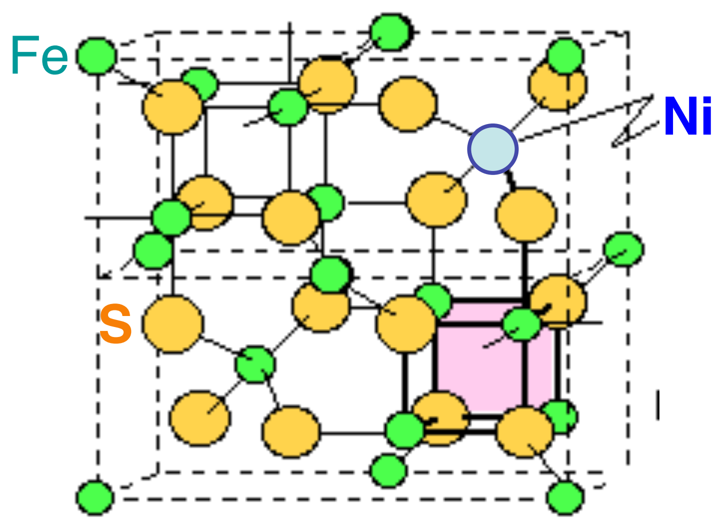
semiconducting
& ferrimagnetic

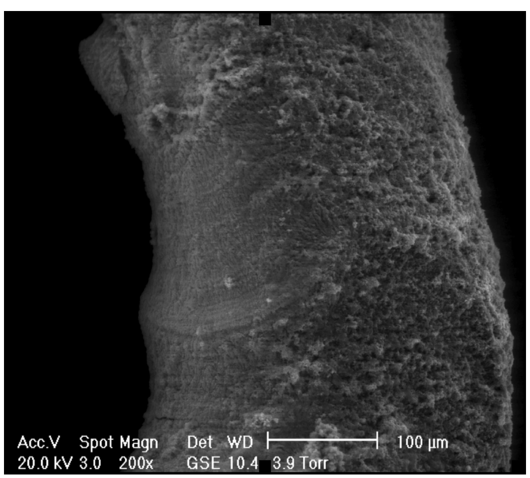


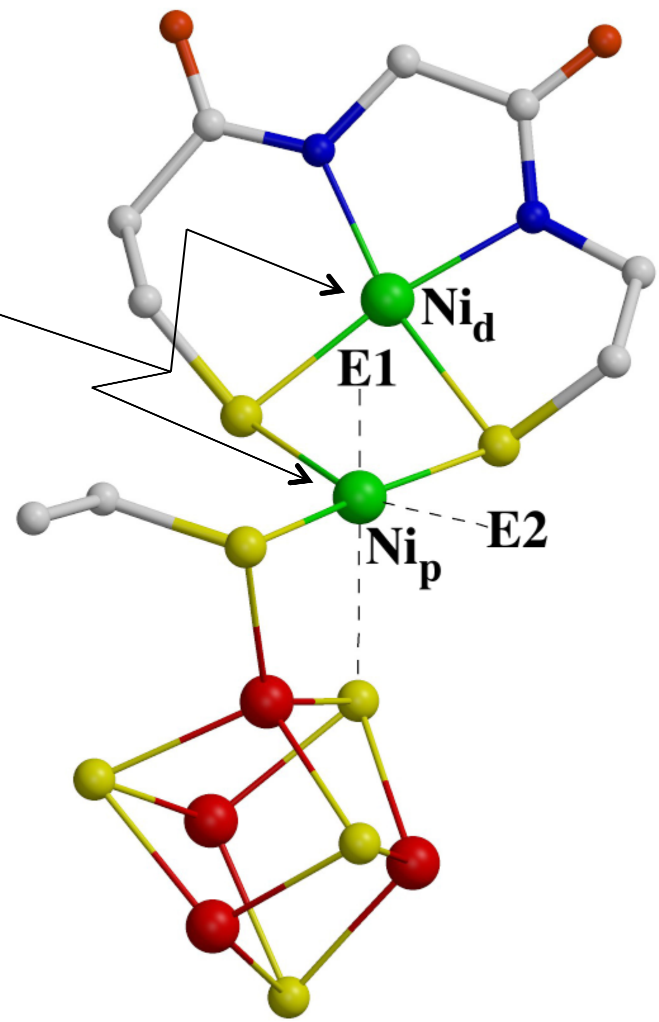
Rickard et al. 2001, EPSL, **189**, 85
Russell & Hall 2006 GSA Memoir, **198**, 1

Greigite compared to acetyl co-A synthase (ACS)

Greigite [Fe_5NiS_8]





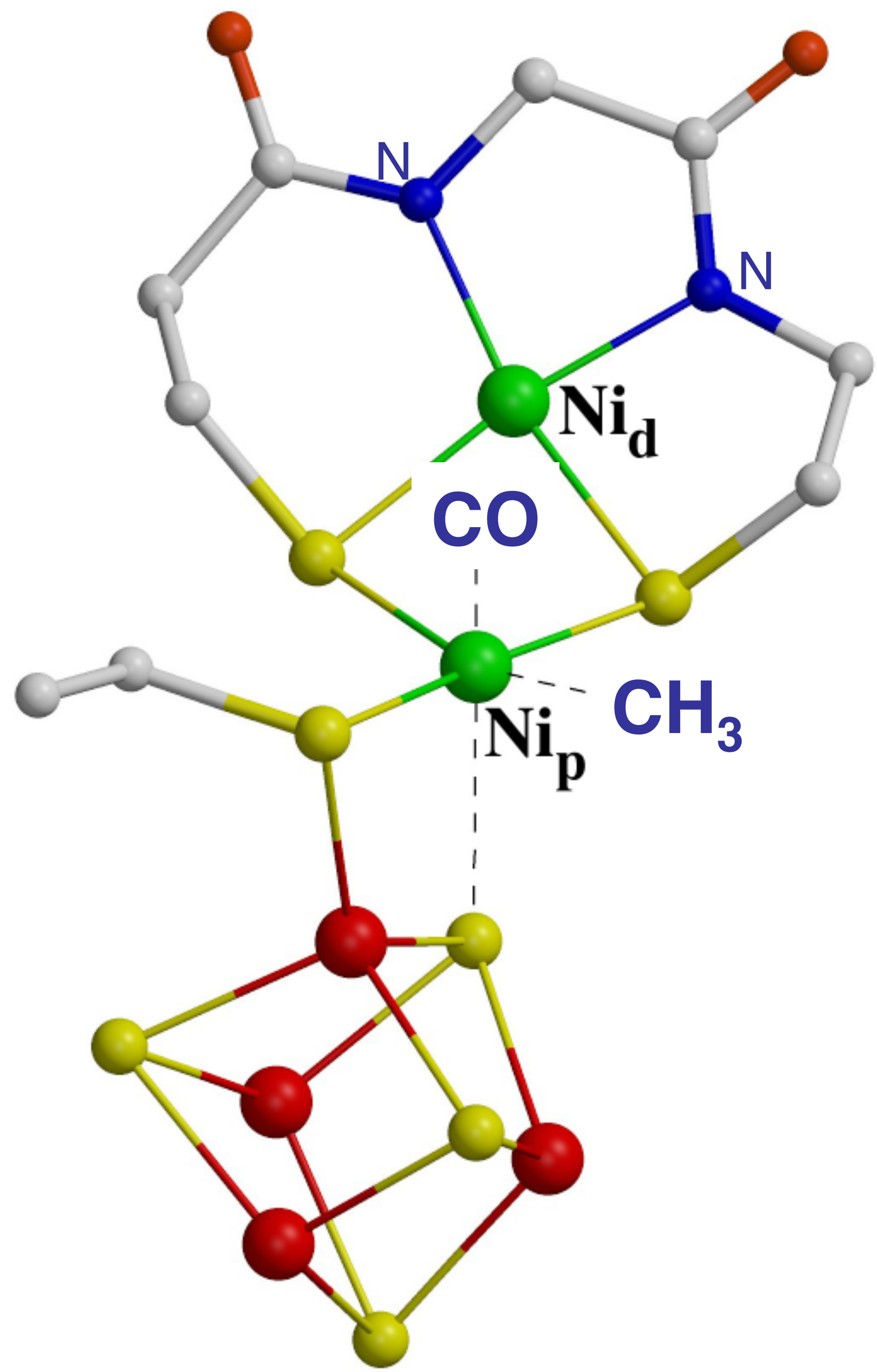


Volbeda and Fontecilla-Camps 2005,
Cordination Chemistry Reviews, **249**,1609-19

Acetyl-Coenzyme-A Synthetase **(ACS)** assembles:

$-CH_3 + -CO \Rightarrow H_3CCO-$

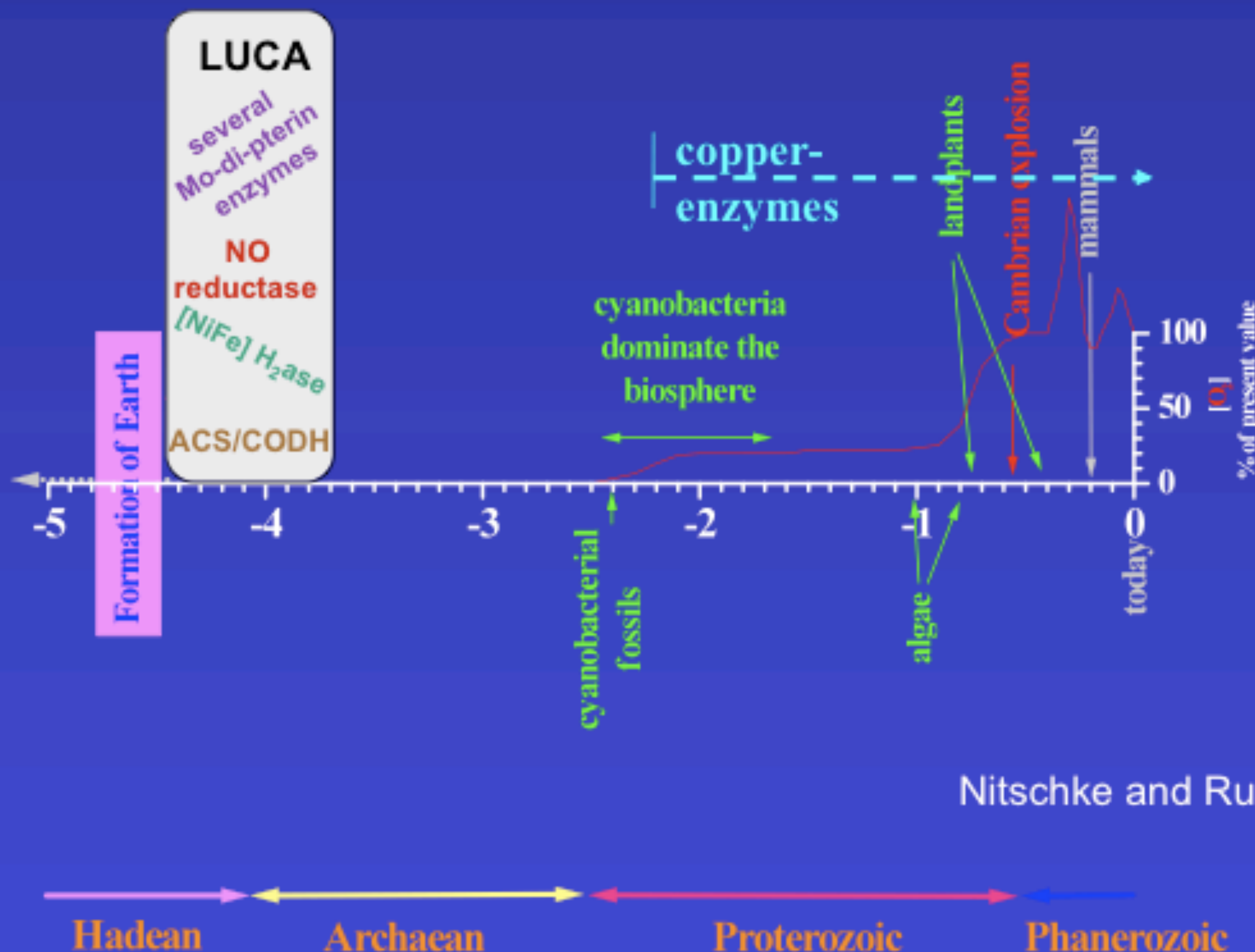
as $Ni^0 \leftarrow\rightarrow Ni^{II}$



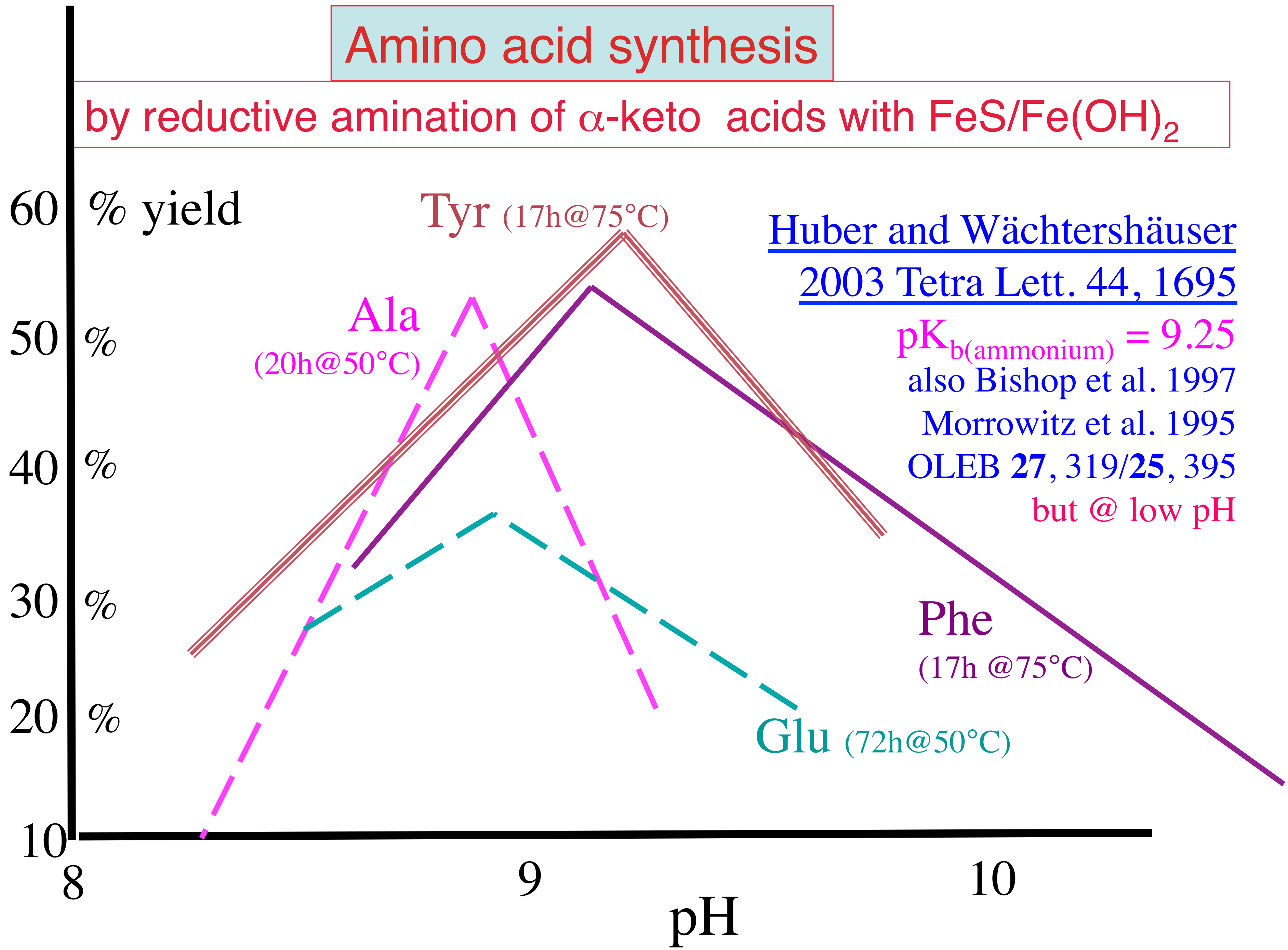
Volbeda & Fontecilla-Camps 2005
Coordin. Chem Rev. 249,1609

LUCA and post-LUCA enzymes

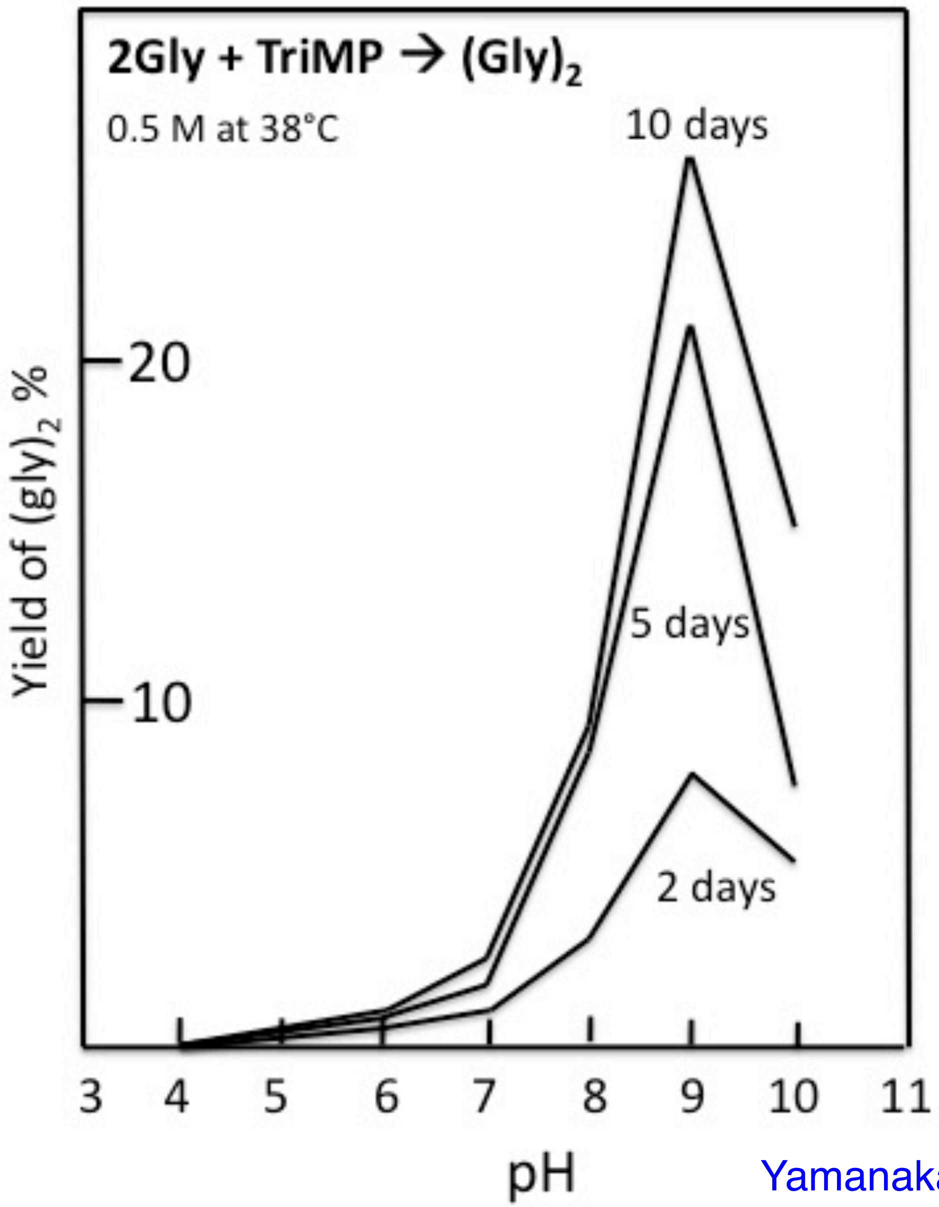
all enzymes dealing with autotrophic substrates are metalloproteins (except that for H_2S) and most of these are pre-LUCA

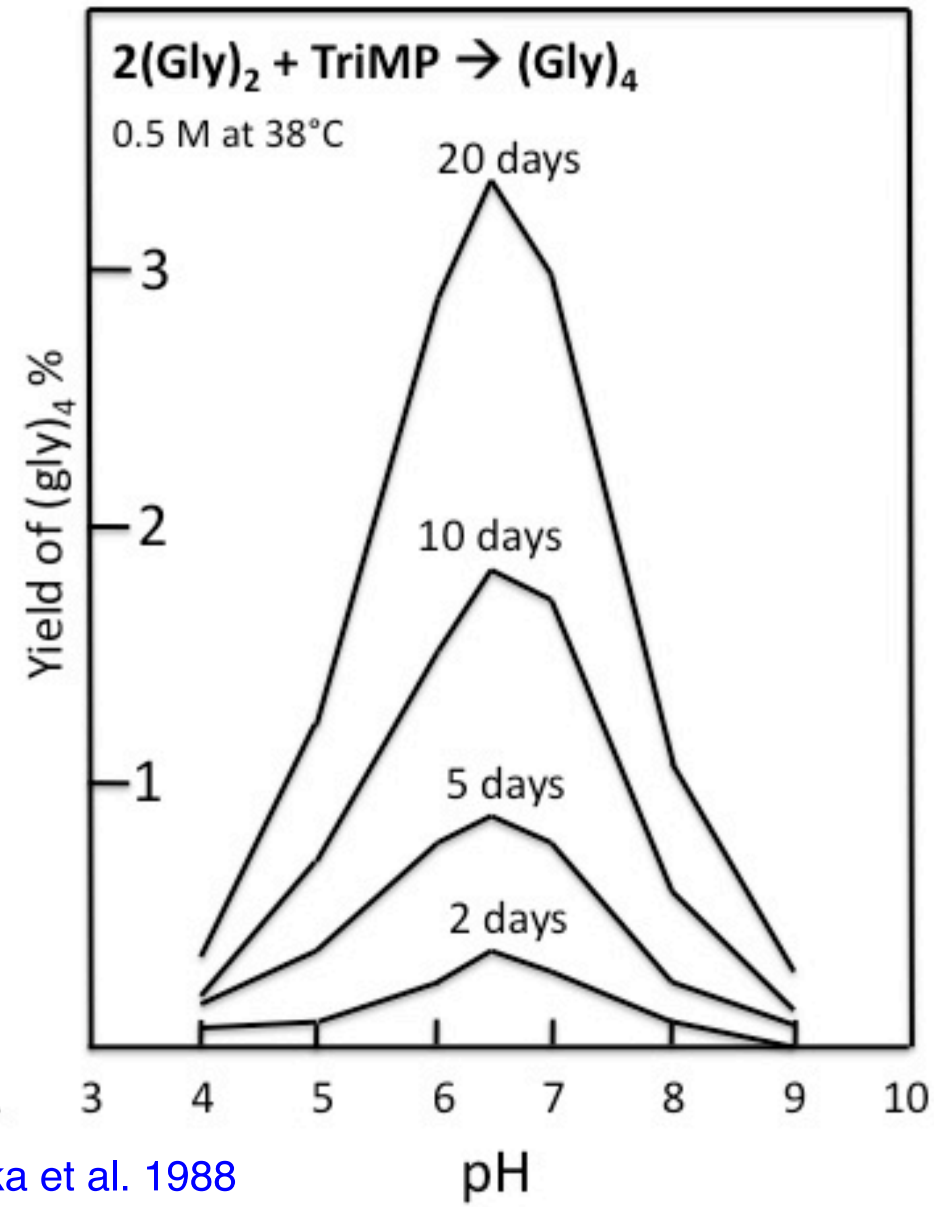


Nitschke and Russell, in prep.


Amino acid synthesis
by reductive amination of α-keto acids with FeS/Fe(OH)2
60 % yield
50 %
40 %
30 %
20 %
10
8
9
10
pH
Tyr (17h@75°C)
Ala (20h@50°C)
Phe (17h @75°C)
Glu (72h@50°C)
Huber and Wächtershäuser
2003 Tetra Lett. 44, 1695
pKb(ammonium) = 9.25
also Bishop et al. 1997
Morrowitz et al. 1995
OLEB 27, 319/25, 395
but @ low pH

Condensation of oligoglycines with trimetaphosphate

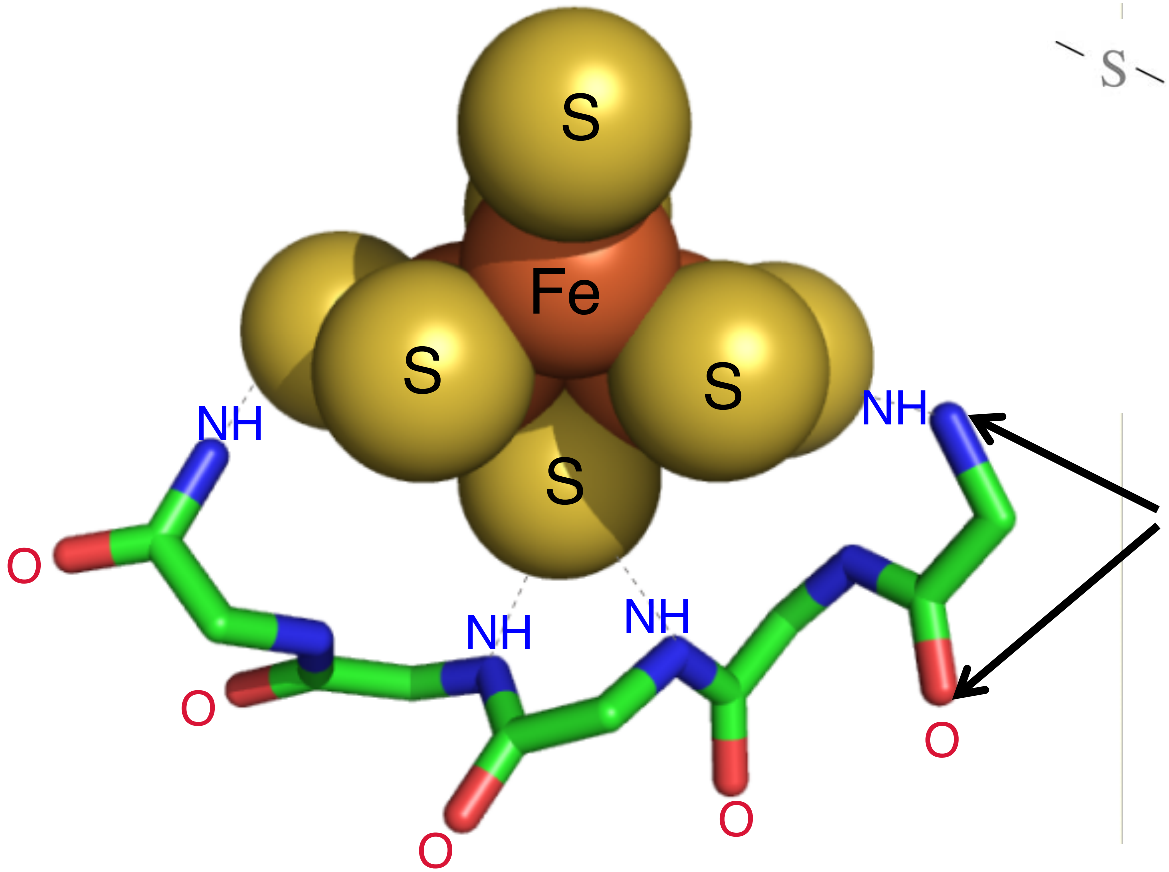


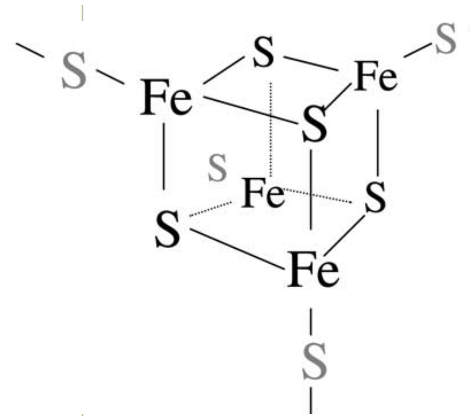


Yamanaka et al. 1988
OLEB 18, 165

The beginning of the peptide takeover?

Fe_3S_4 “egg” bound to RLRLR ***nest*** (cf. a ferredoxin)

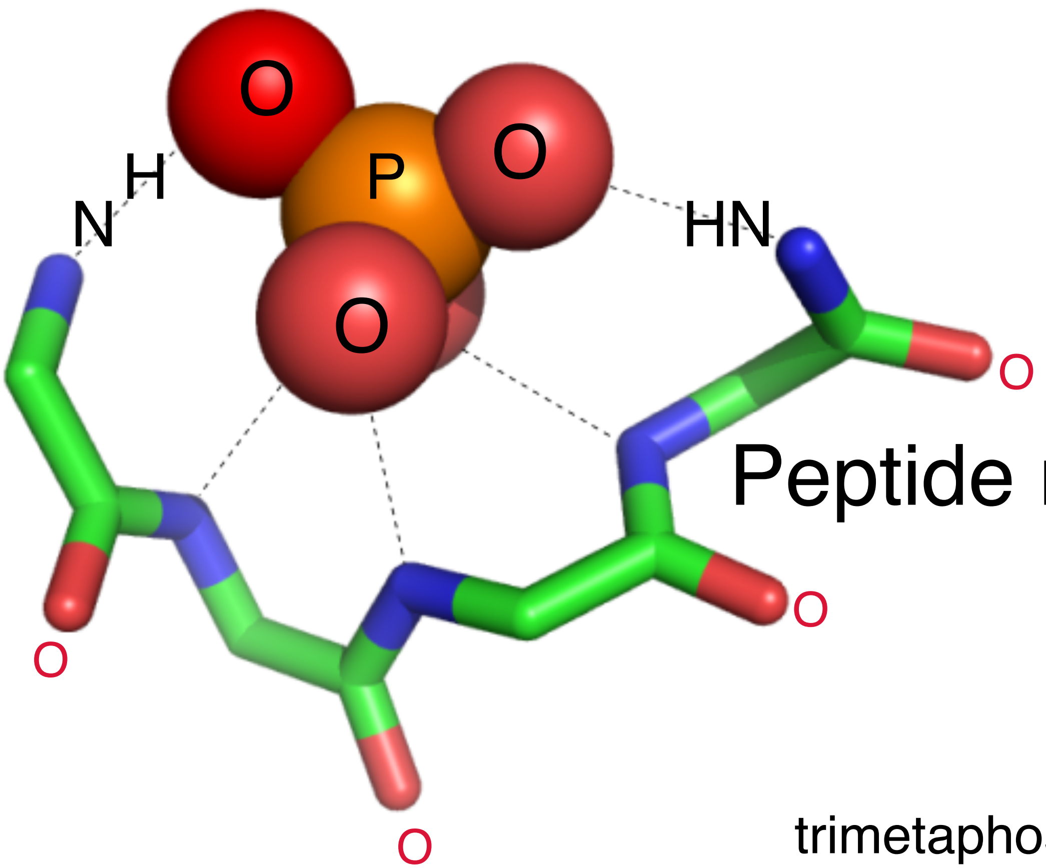




Milner-White & Russell 2008 Biology Direct, 3, 3

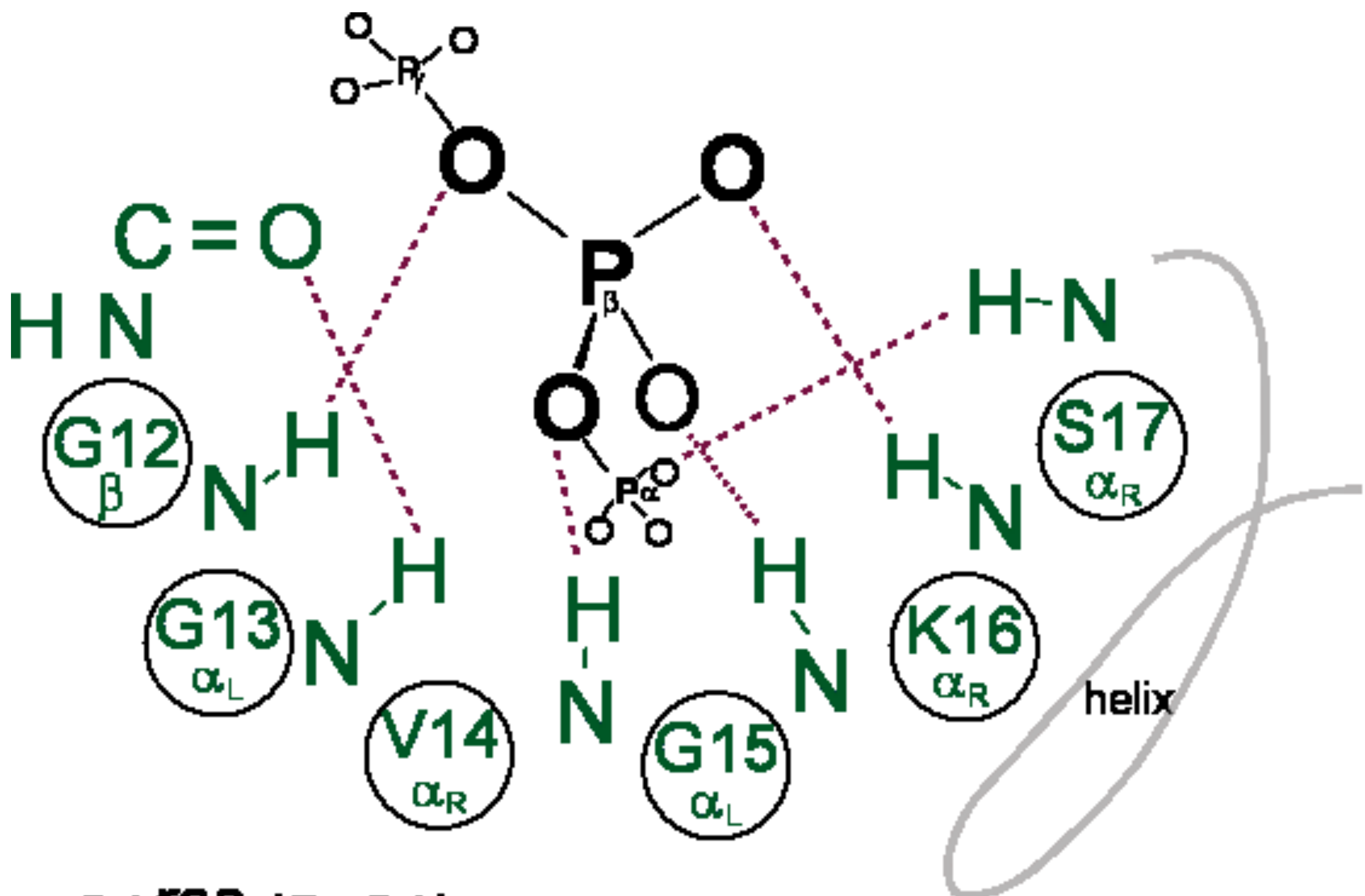
Phosphate (PO_4^{3-}) “egg” in an LRLR peptide nest (cf. the P loop)

Milner-White & Russell 2008 Biology Direct, 3, 3



trimetaphosphate + glycine + alanine →
dipeptide at 36% yield + >> tripeptide
at pH 7-8 and 70°C

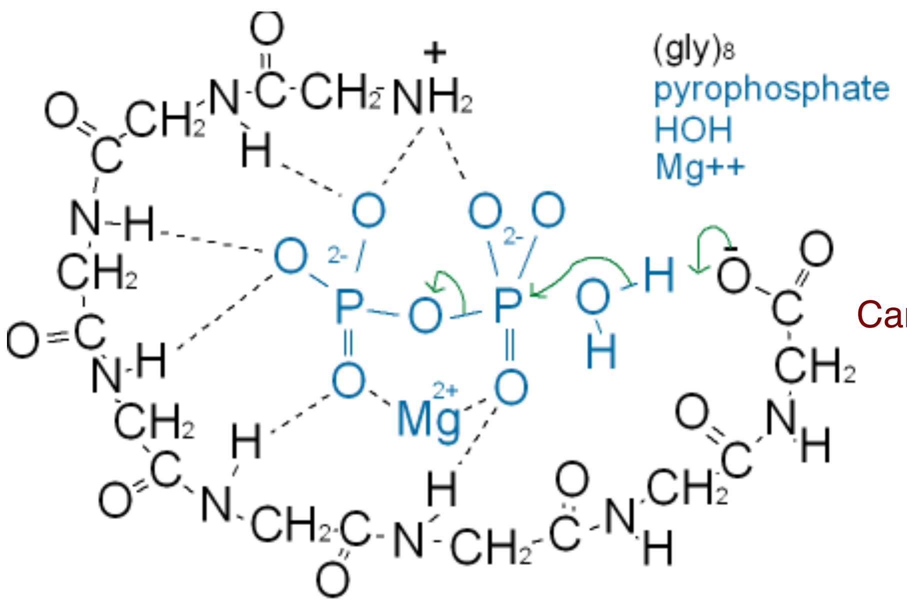
Rabinowitz et al. 1969



p21*ras* (5p21)
LRLR nest at residues 13-16
N-terminus of α-helix at residues 15-22
Type II β-turn at residues 12-13

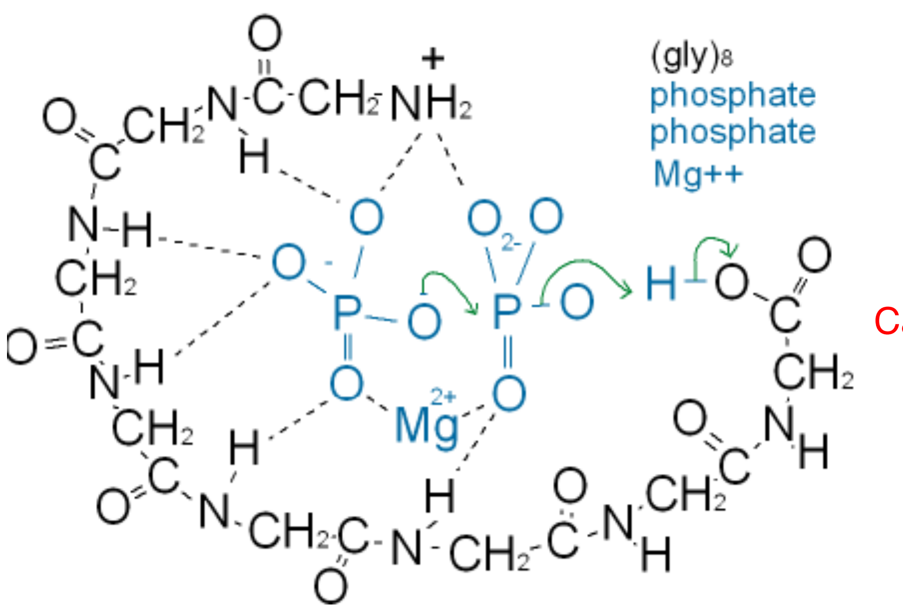
How short peptides may catalyze phosphoryl transfer

H⁺-pyrophosphatase
GXXXXGKX



Carboxyl group acts as base

$$PPi \rightarrow Pi + Pi$$

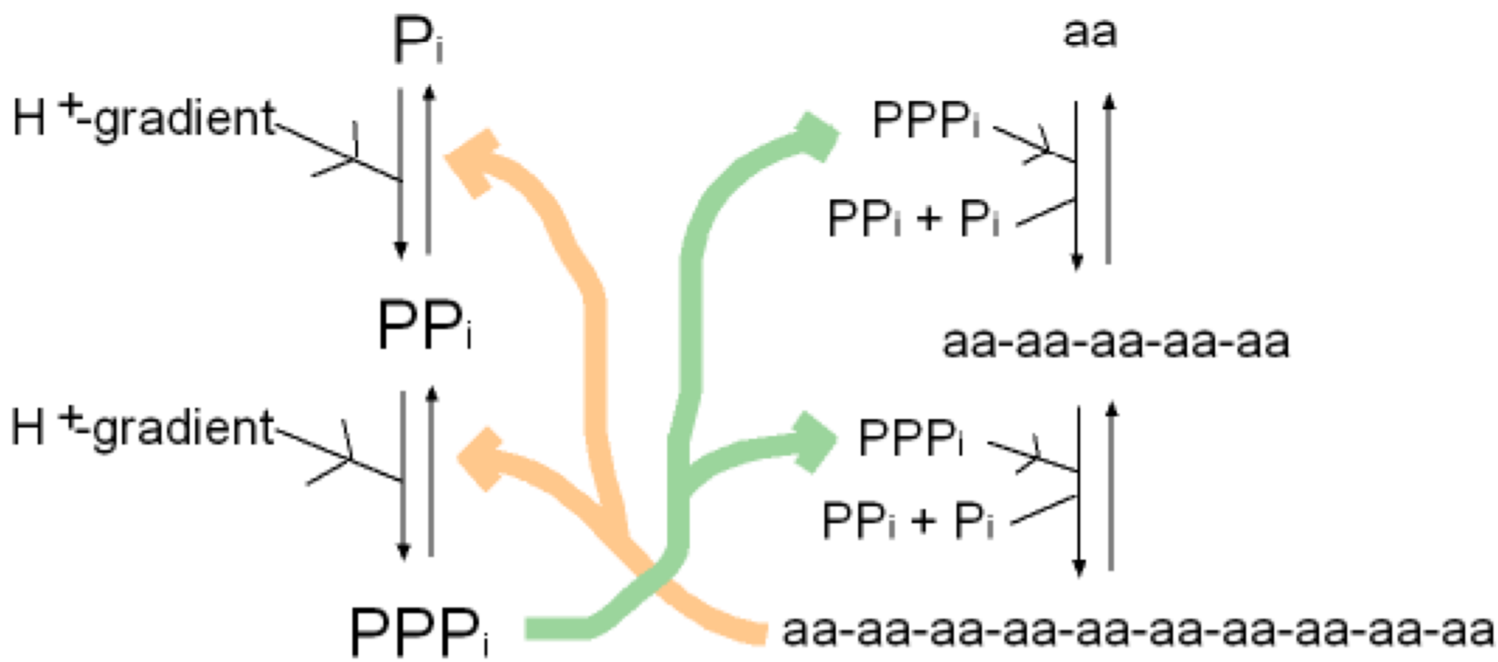


Carboxyl group acts as acid

$$Pi + Pi \rightarrow PPi$$

Milner-White, E.J. and Russell, M.J. (2010).
http://journalofcosmology.com/Abiogenesis100.html

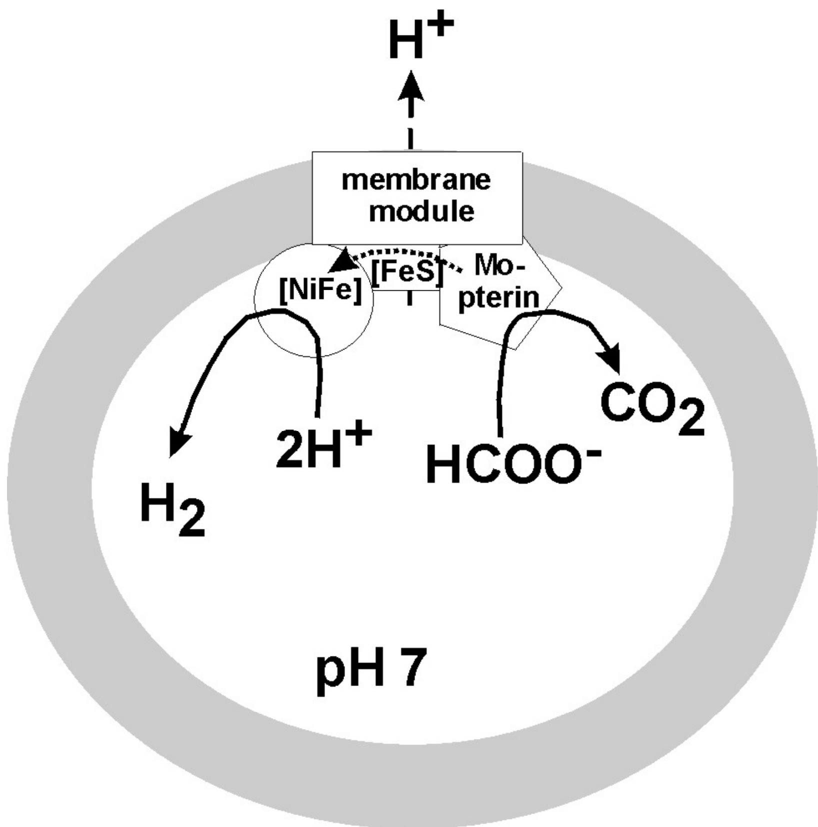
Protein - Polyphosphate Synergy



The decapeptide aa-aa-aa-aa-aa-aa-aa-aa-aa-aa acts as an enzyme that, driven by a proton gradient, phosphorylates phosphate to form pyrophosphate. The same enzyme phosphorylates pyrophosphate to form triphophate.

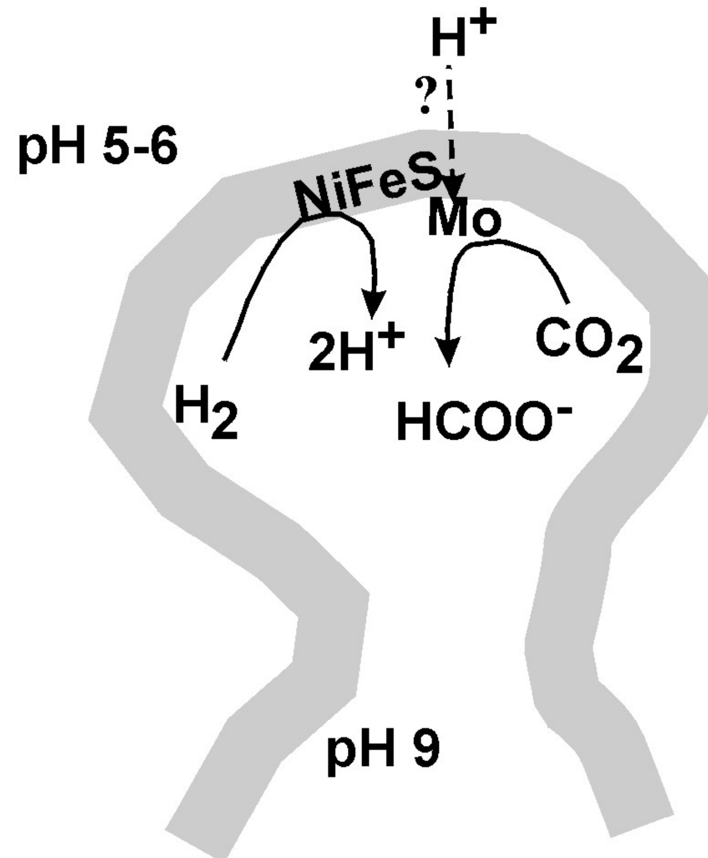
Triphosphate reacts with amino acids and phosphorylates them, giving rise to polypeptides after their dephosphorylation. In so doing it becomes hydrolyzed to phosphate and pyrophosphate.

The effect is synergy between protein and polyphosphates. Polyphosphates are required for making polypeptides and polypeptides catalyze polyphosphate formation.



Mixed-acid fermentation
(*via* formate hydrogenlyase)
Reaction generates H_2 & CO_2

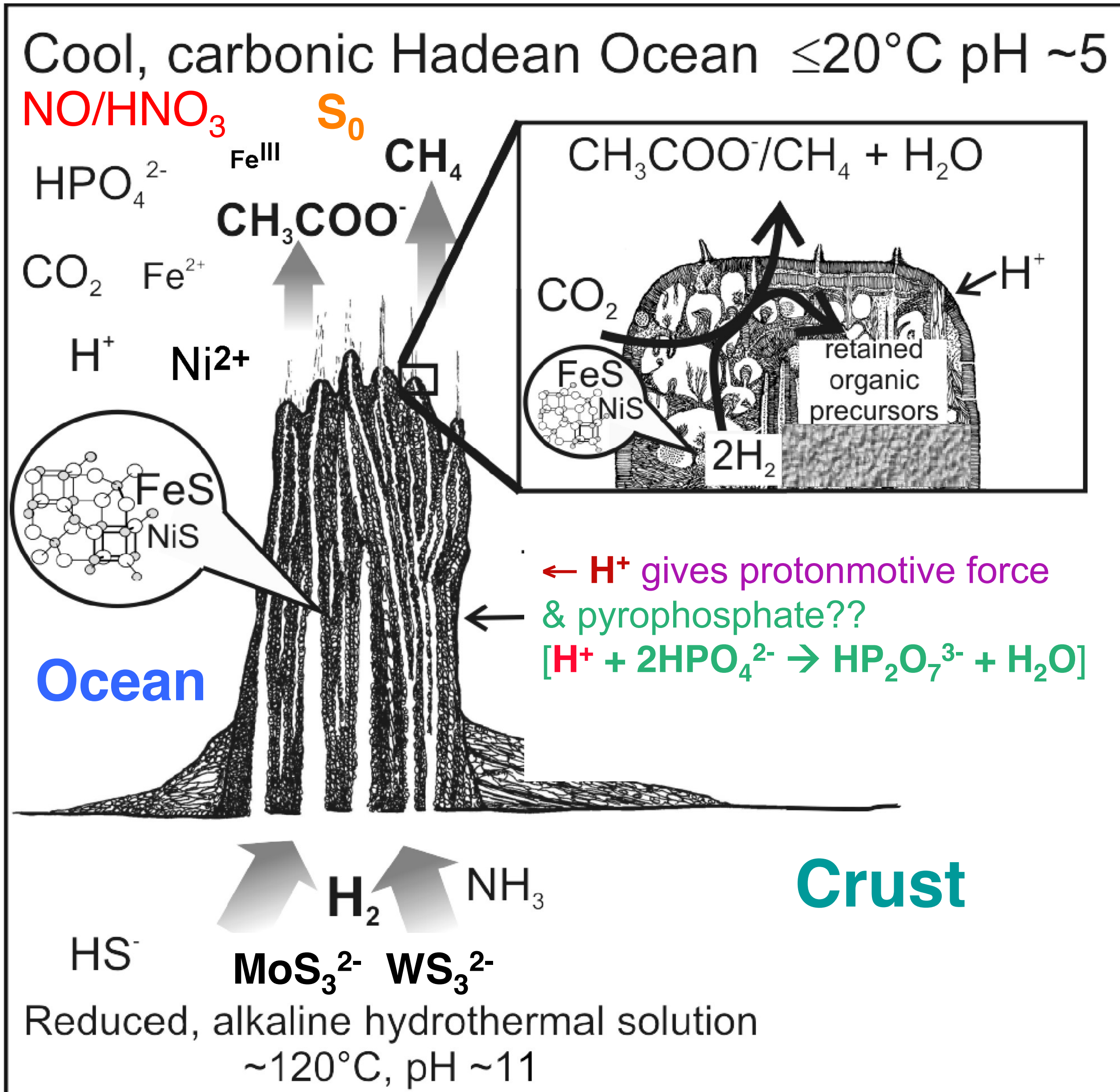
Andrews et al. 1997 *Microbiol*, **143**, 3633



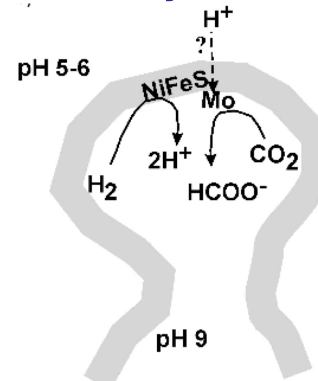
Inverse of the same scheme to explain the origin of metabolism
Reaction generates formate?
Other reductions are downhill

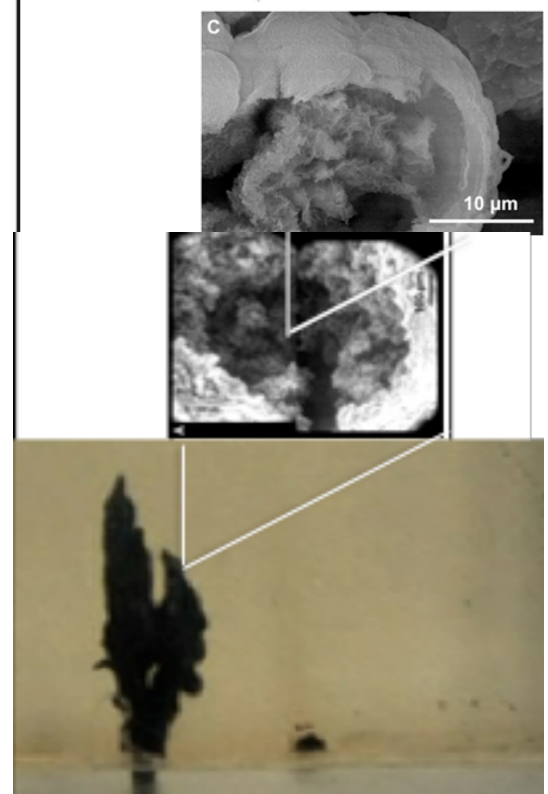
Nitschke & Russell, *JME*, **69**, 481,

The Rocky Roots of the Acetyl-Coenzyme-A Pathway

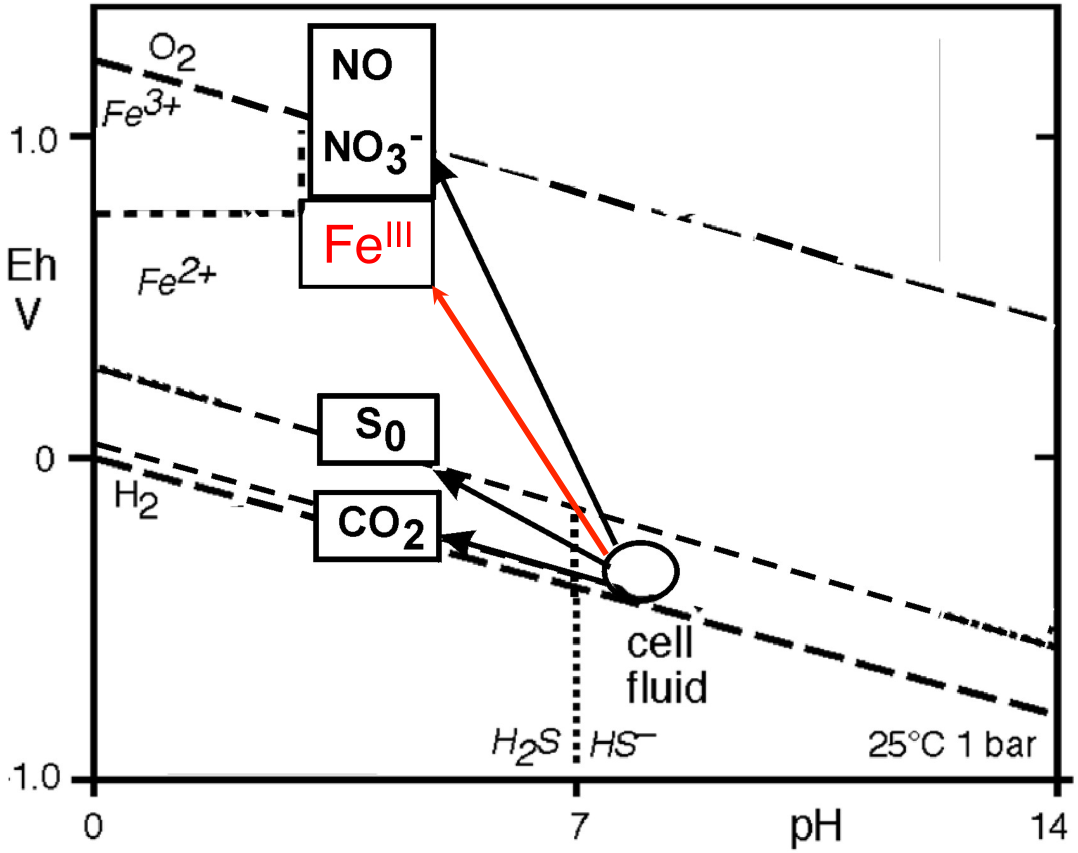


The hatchery of life





Russell & Martin 2004 *TIBS* **29**, 358-363, Nitschke & Russell, JME, 69, 481-496

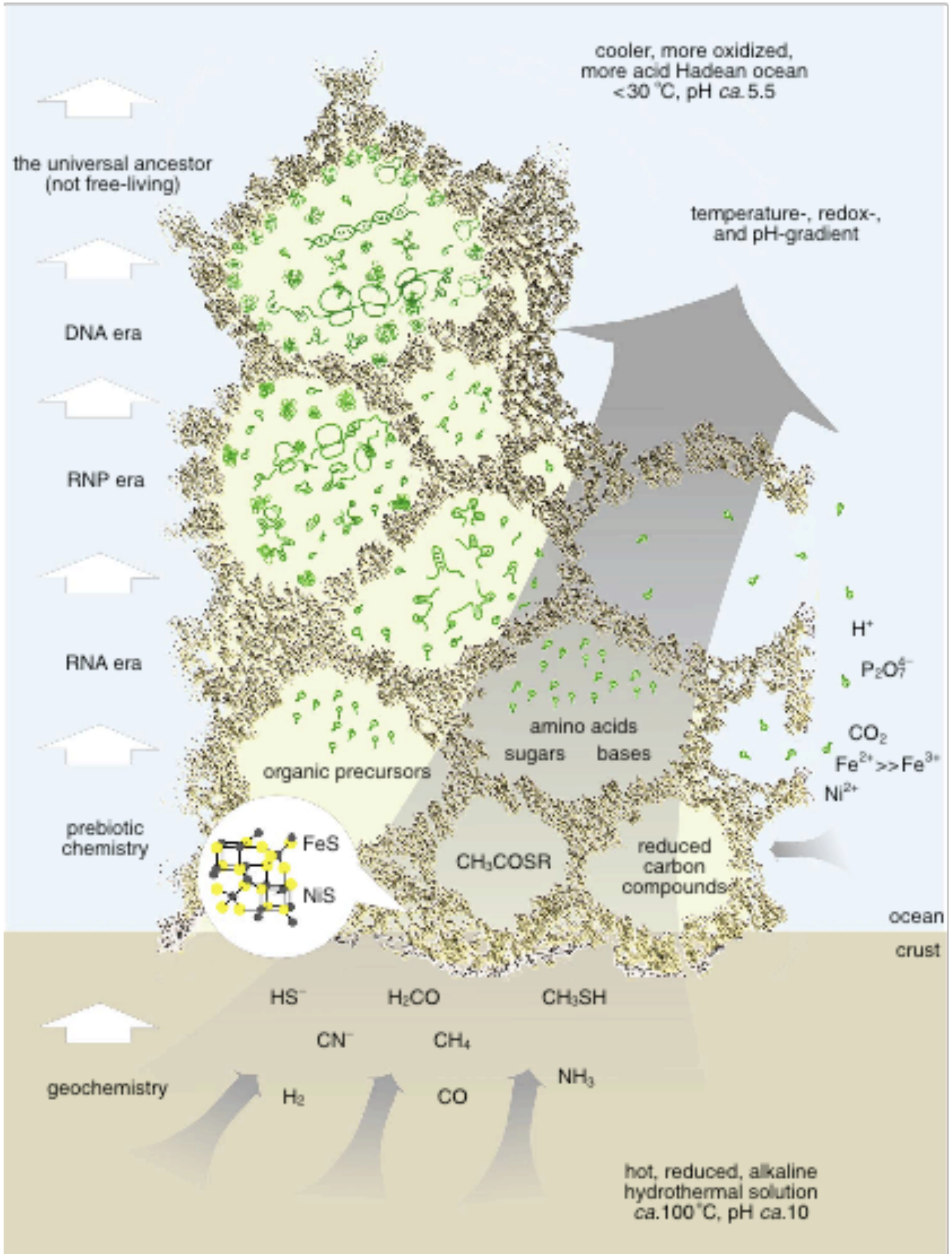


Provision of energy (and **H_2**) through respiration:

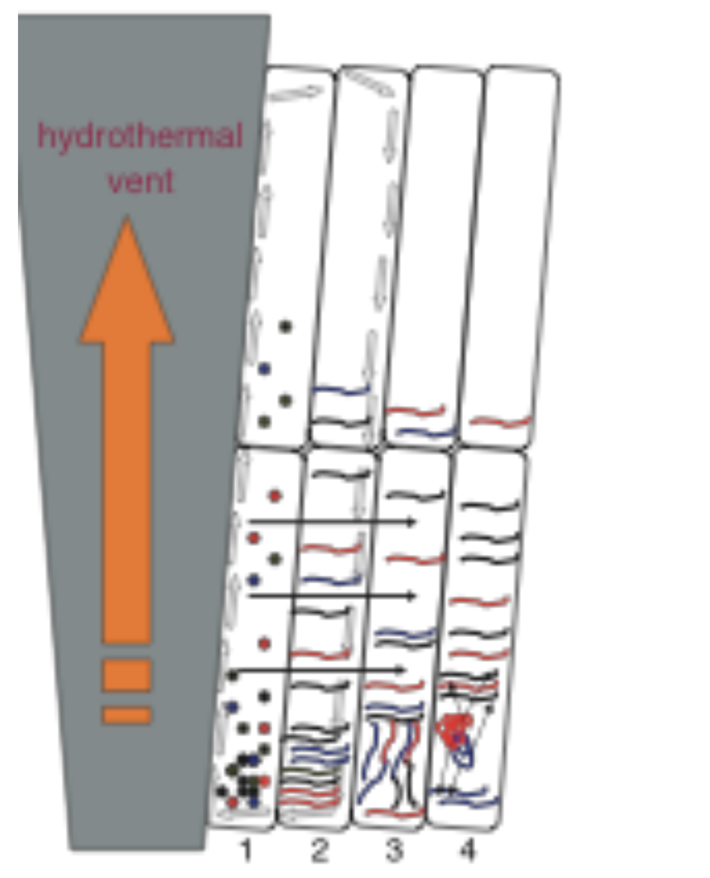
via a **Mo** cofactor one electron is transfer to high potential electron acceptor leaving the other high energy electron to reduce **CO_2** to **COO^-** and the hydride generates **$HCOO^-$**

$$\mathbf{Mo^{IV}} \Rightarrow Mo^{V} \Rightarrow \mathbf{Mo^{VI}}$$

Ducluzeau et al. 2009, TiBS, 34, 9
Nitschke & Russell, JME, 69, 481

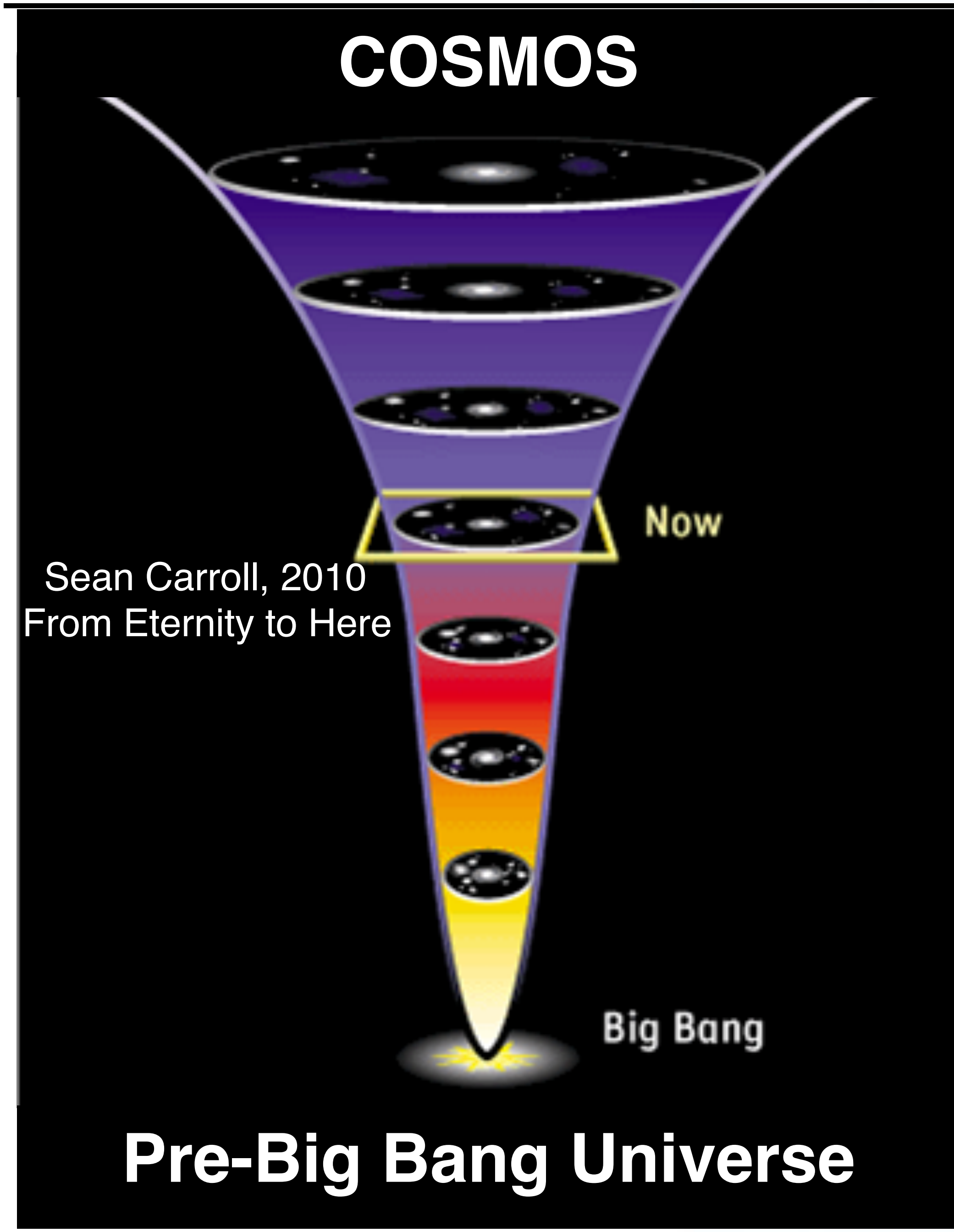


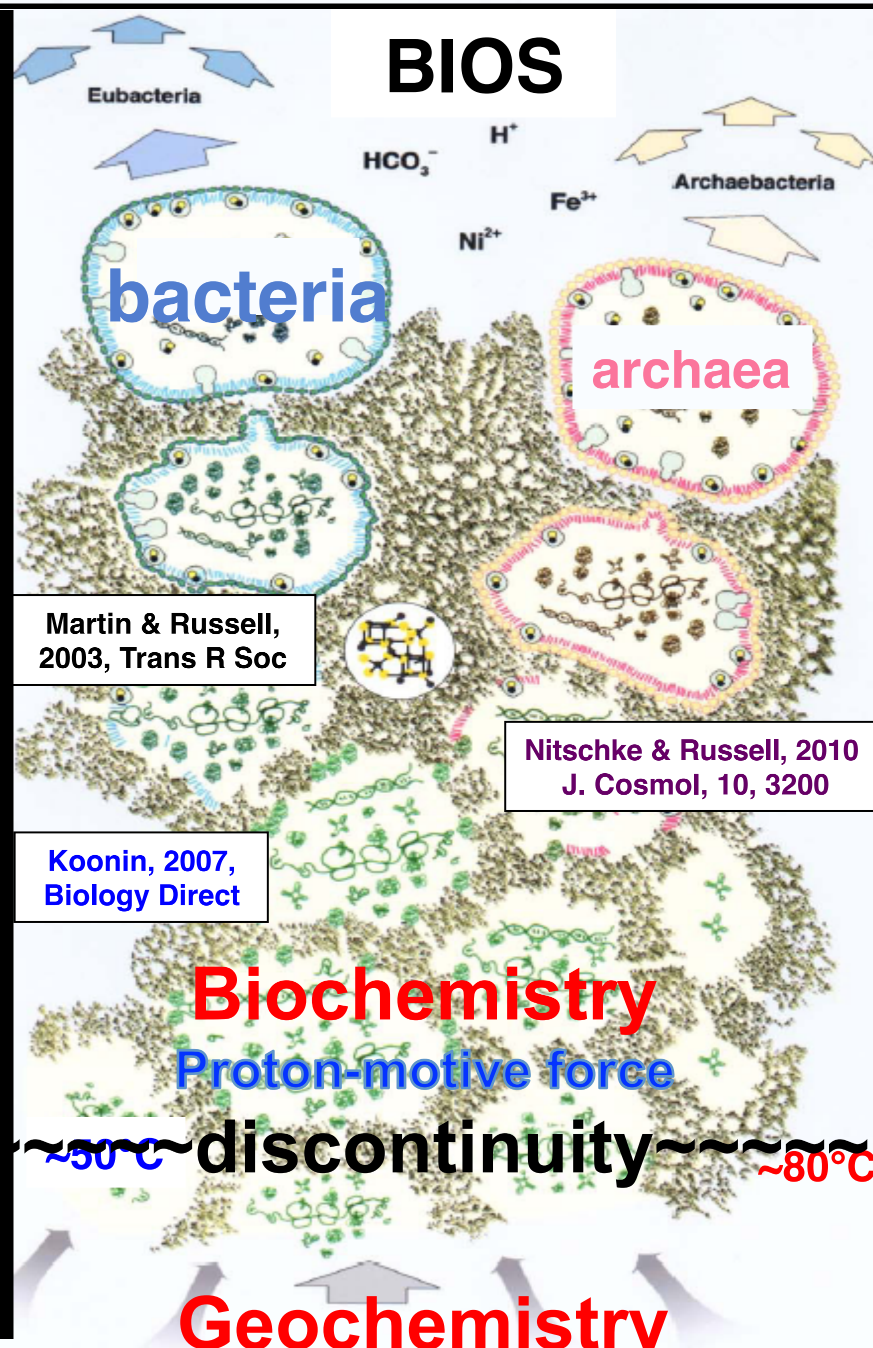
An RNA-reactor for the emergence of life



Koonin, 2007, PNAS, 104, 9105
Martin, Russell, 2003, Trans R Soc London B362, 1887
Baaske et al. PNAS, 104, 9346

EMERGENCE OF DISSIPATIVE STRUCTURES





CO_2 hydrogenation mechanisms quicken, complexify & tend to take over with time

1. Serpentinization (redox and heat) → CH_4

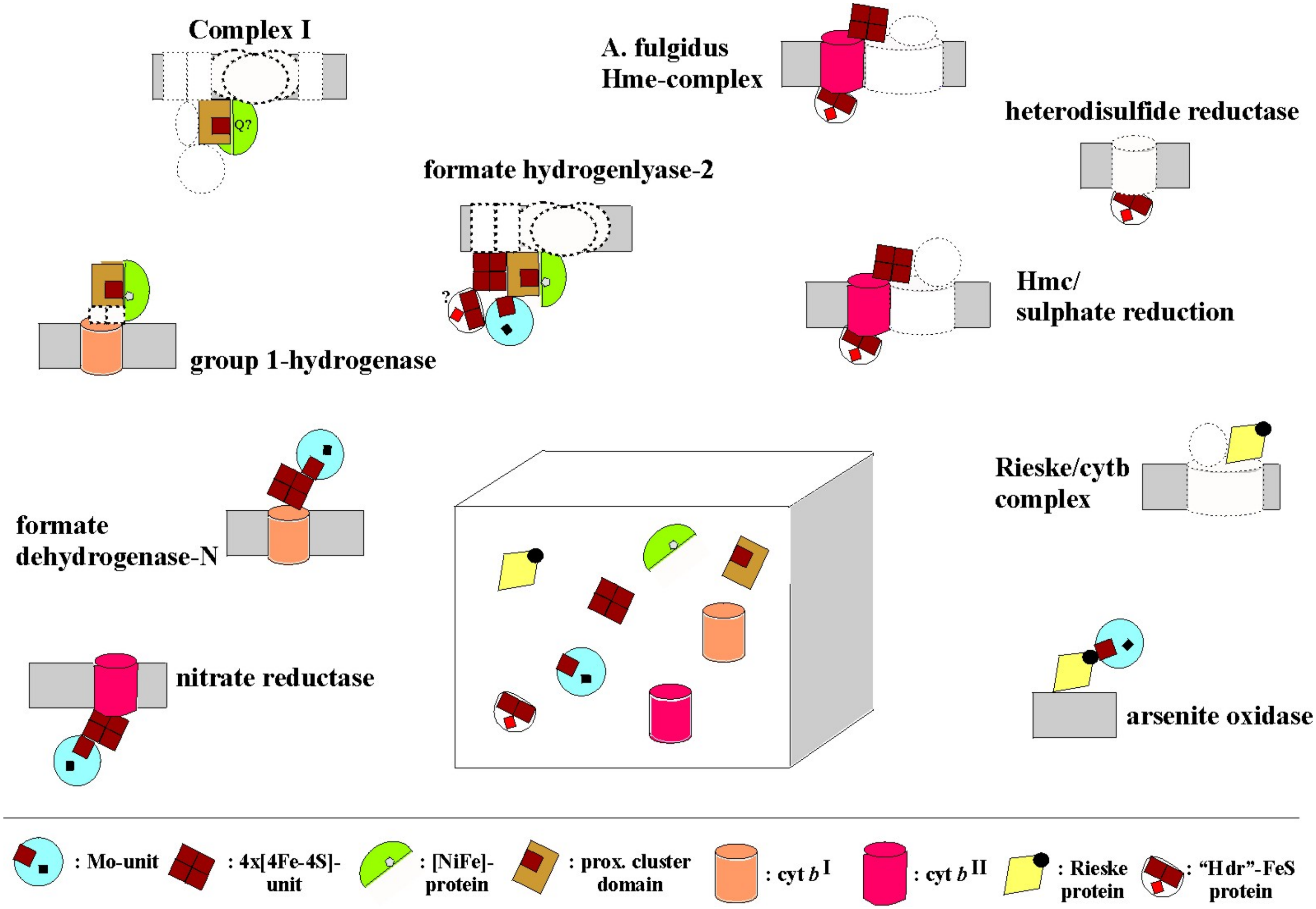
----------------------------------life emerges----------------------------------

2. Bacterial acetogenesis (H_2, pmf, ATP) → CH_3COO^-

3. Archae-methanogenesis (H_2, pmf, Co-B, Co-M)→ much CH_4

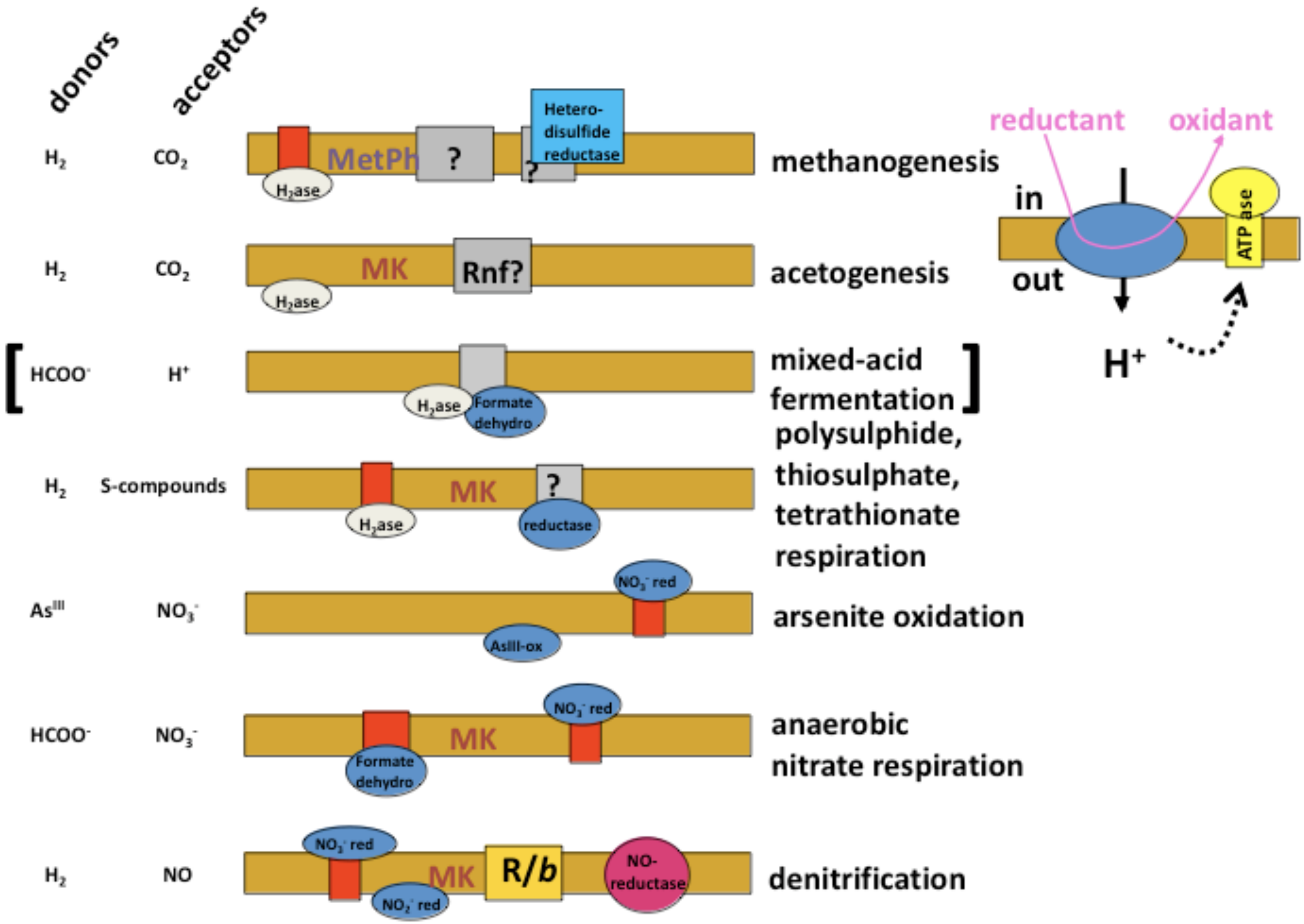
4. Archaeal then bacterial sulfate reduction → $H_2S + CH_3COO^-$

5. Bacterial oxygenic photosynthesis (photons) → O_2

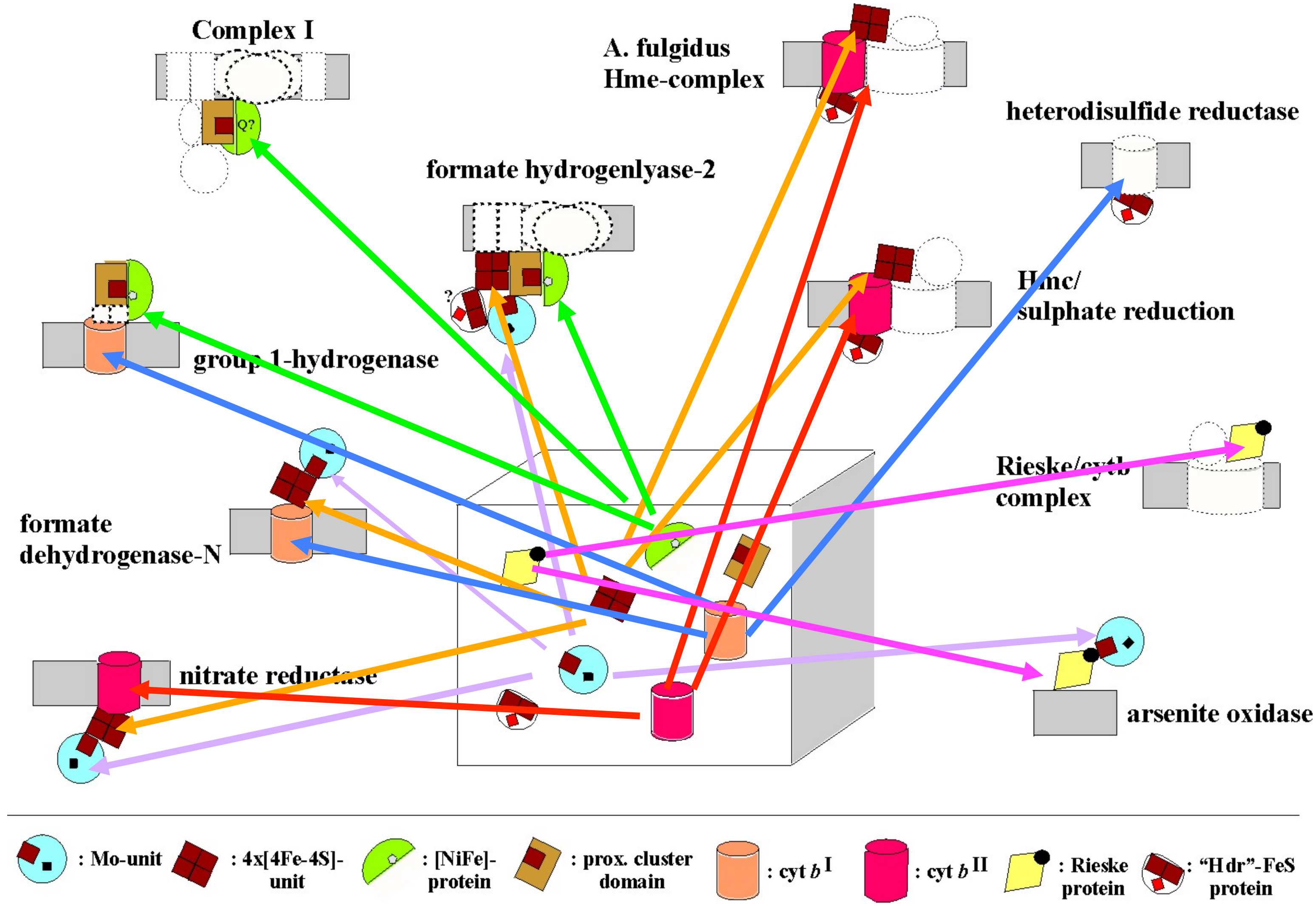


"The redox protein construction kit"

Baymann *et al.* (2003) Phil.Trans. R. Soc. B 358, 267-274



donors
acceptors
H2
CO2
Hetero-disulfide reductase
MetPh
?
H2ase
methanogenesis
reductant
oxidant
in
out
ATP ase
H+
H2
CO2
MK
Rnf?
acetogenesis
HCOO-
H+
H2ase
Formate dehydro
mixed-acid fermentation
H2
S-compounds
MK
?
reductase
polysulphide, thiosulphate, tetrathionate respiration
AsIII
NO3-
NO3- red
AsIII-ox
arsenite oxidation
HCOO-
NO3-
MK
Formate dehydro
anaerobic nitrate respiration
H2
NO
NO3- red
NO2- red
MK
R/b
NO-reductase
denitrification



"The redox protein construction kit"

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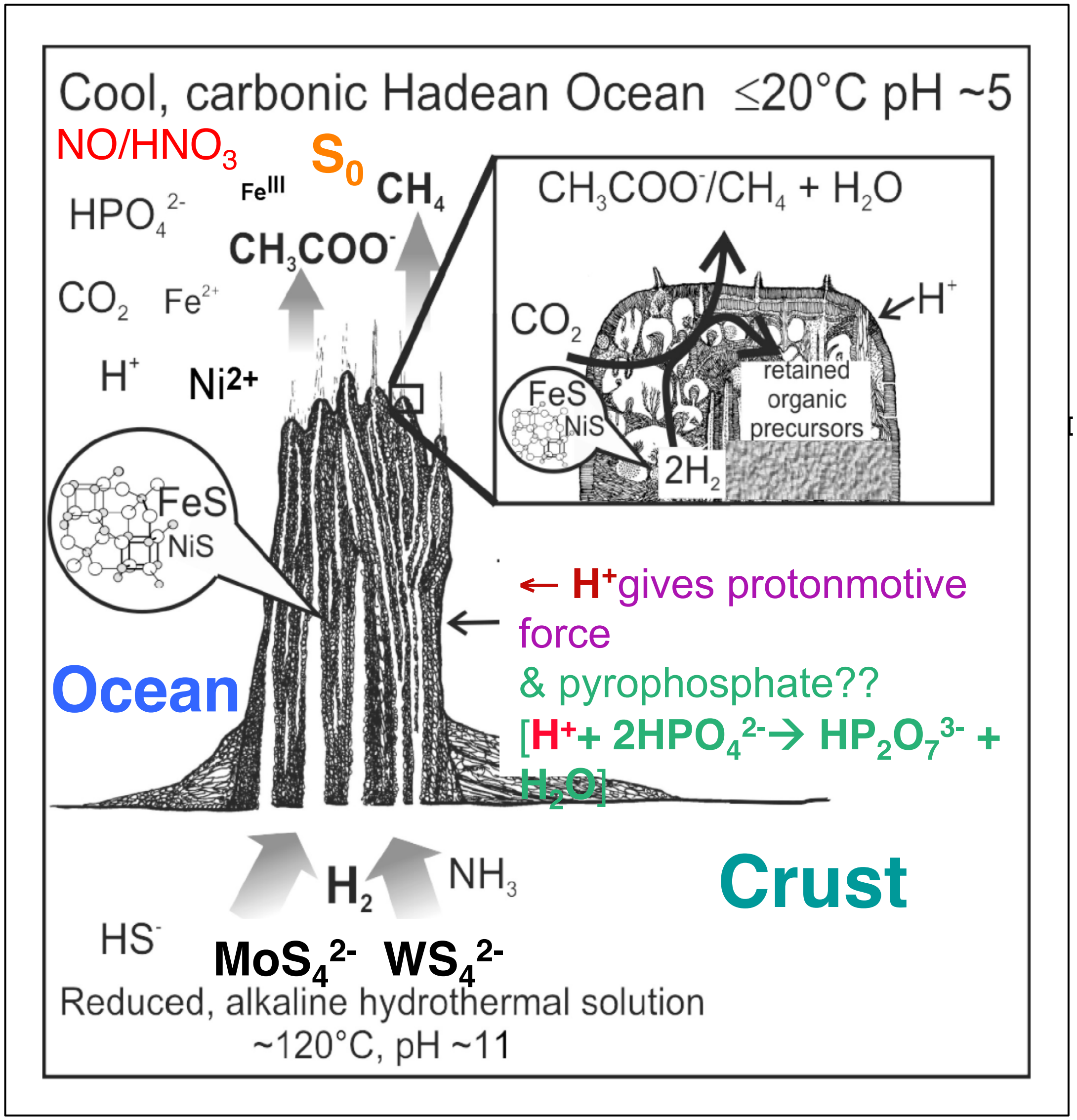
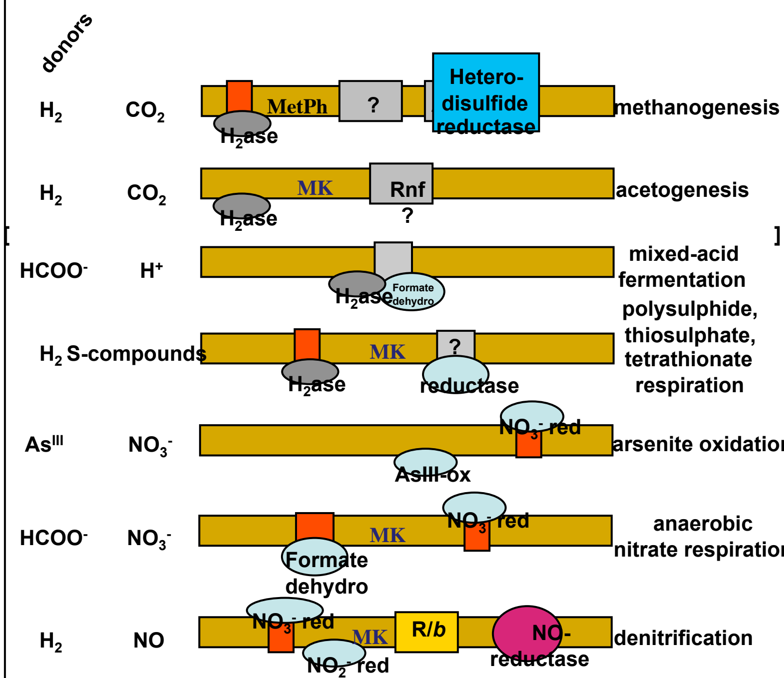
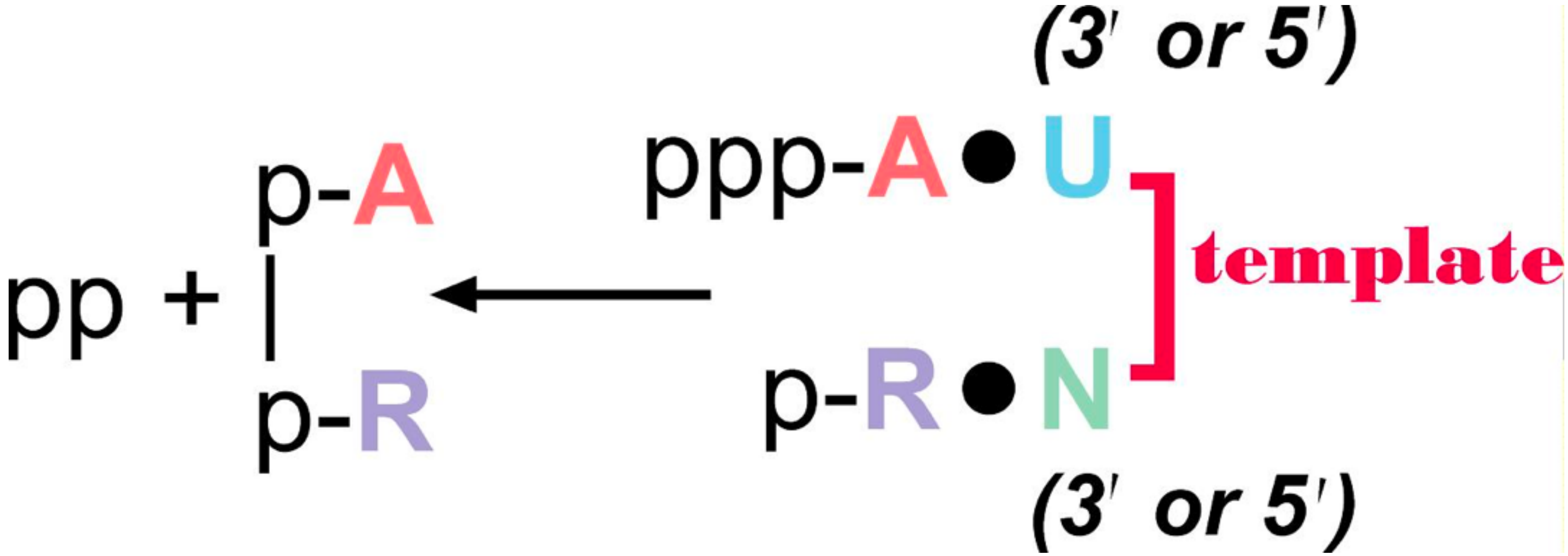




The energy metabolism pathways predicted by molecular phylogeny to be ancient correspond mostly to those of the alkaline vent model

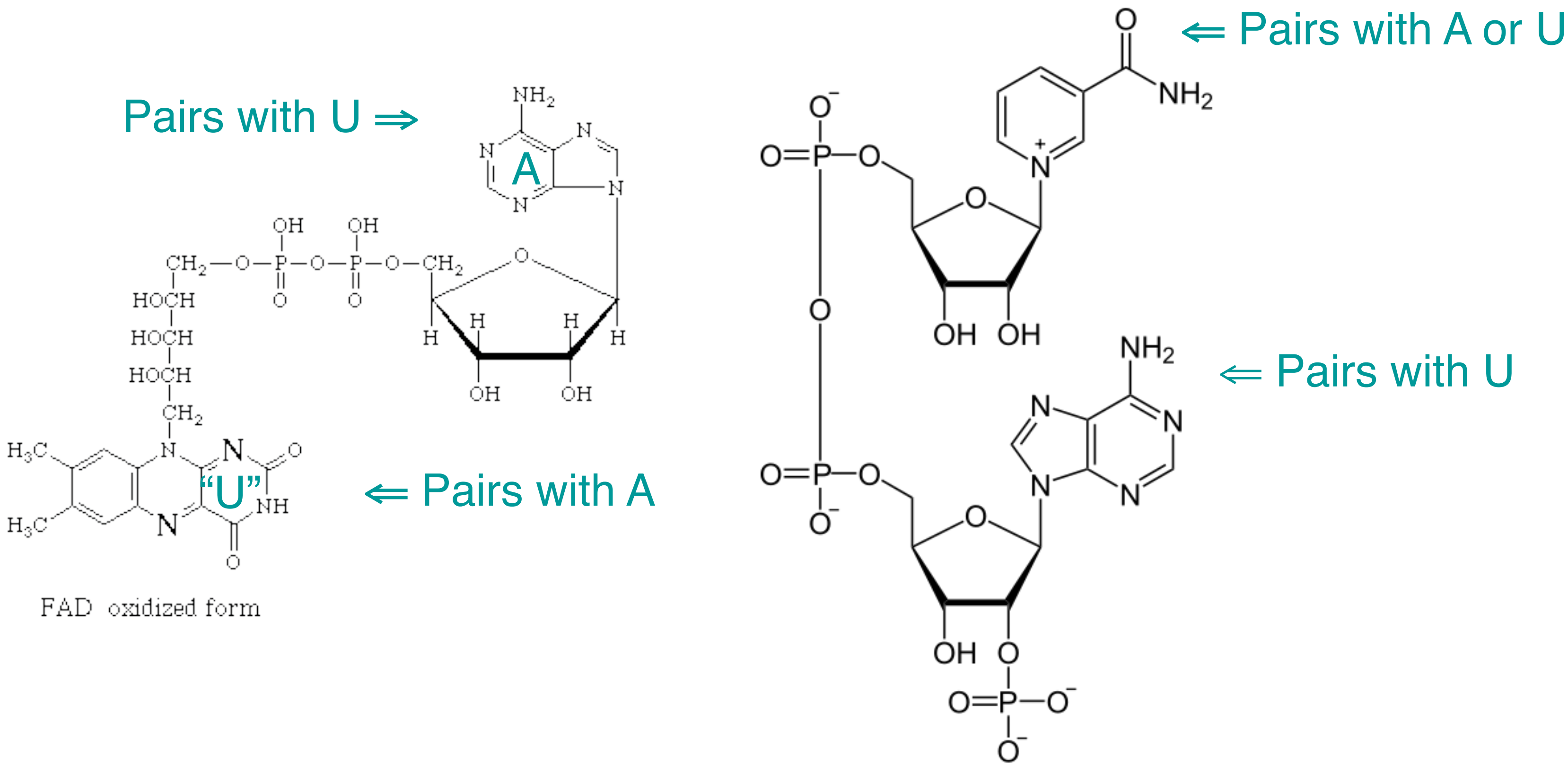
Did small catalysts replicate?



R is nicotinamide nucleotide or a congener
N is its complement.

Yarus, M. 2010, in *RNA world IV*, T. Cech, R. Gesteland, J. Atkinset, eds. CSH Lab

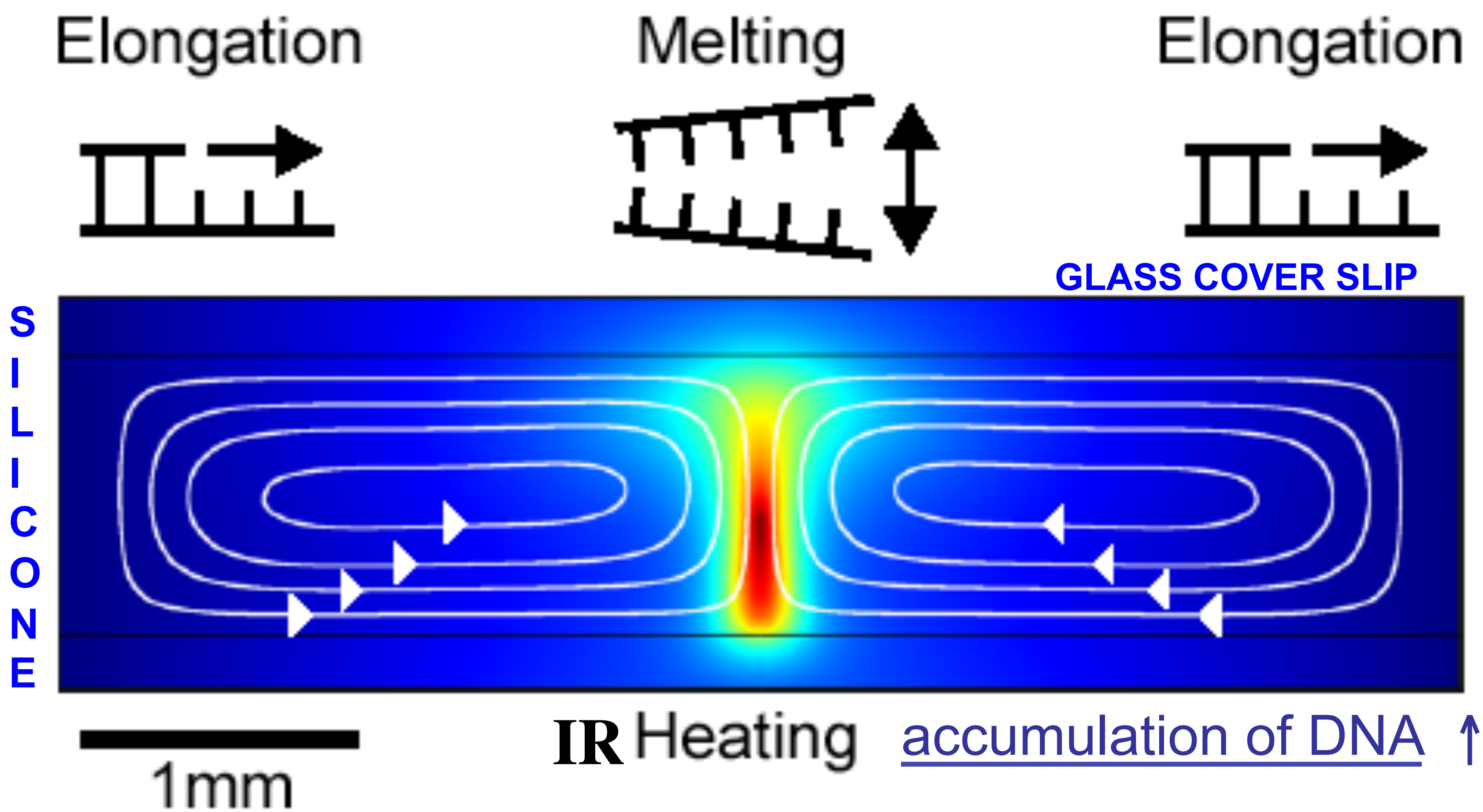
Possible base pairing with cofactors



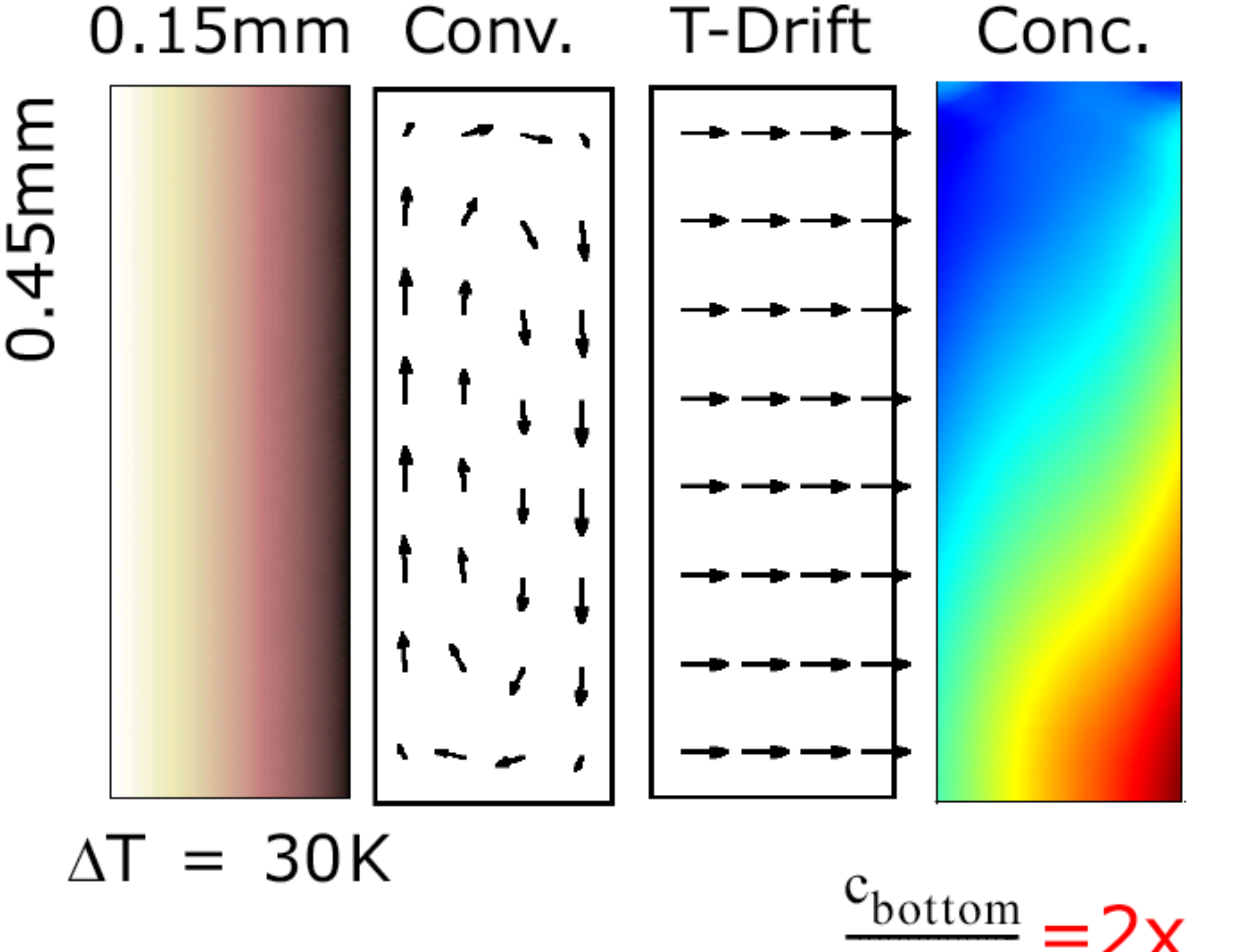
FAD **NADP**

Yarus, M. (2010). Getting past the RNA world: the initial Darwinian ancestor. In: Cech, T., Gesteland, R., Atkins, J. (Eds), RNA world IV, CSH Lab Press.

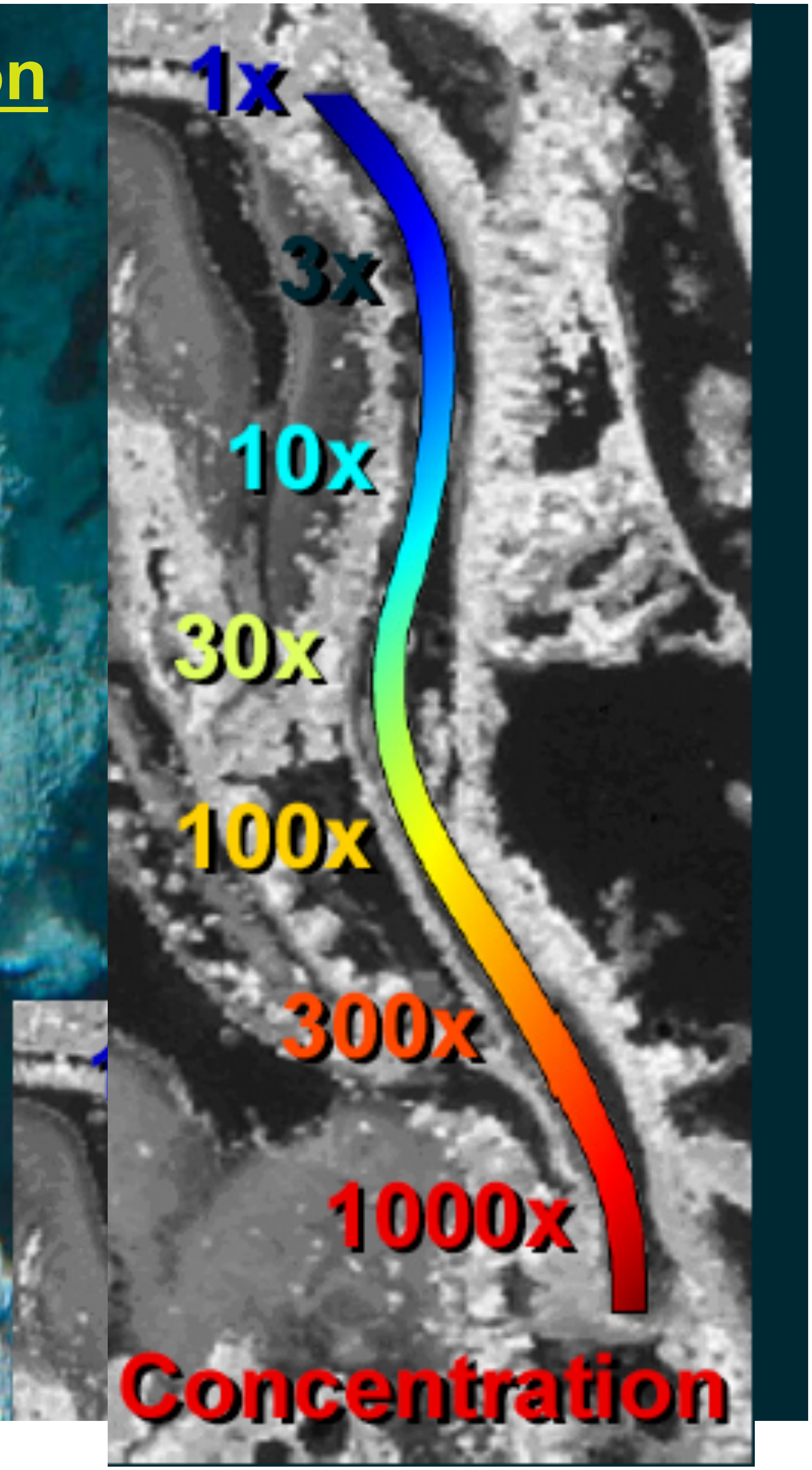
Polymerase chain reaction by convection and thermophoretic accumulation



Braun et al., 2003, Physical Review Letters 91, 158103.


0.15mm
Conv.
T-Drift
Conc.
0.45mm
ΔT = 30K
c_bottom
=2x

Thermophoretic concentration of polymers



Baaske et al. PNAS, 104, 9346