Order from Order: How Life Emerged from a Convection-Driven Submarine Alkaline Vent

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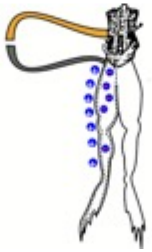
Galvani bequeathed us: Electrophysiology, Bioelectronics, Neuromuscular function, Motor nerves → Motors = (Nano)engines



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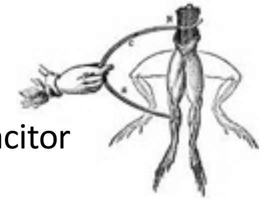
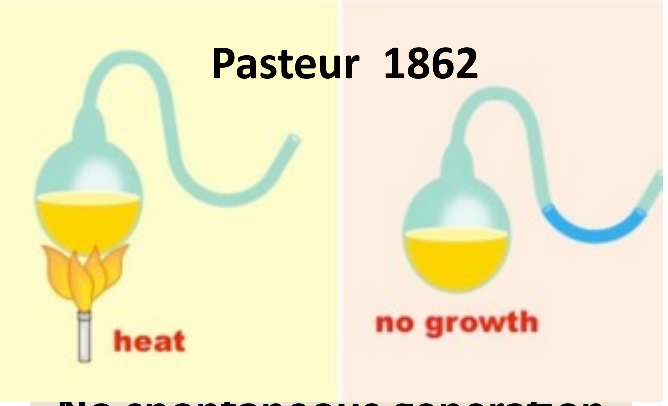
1782 and 1792

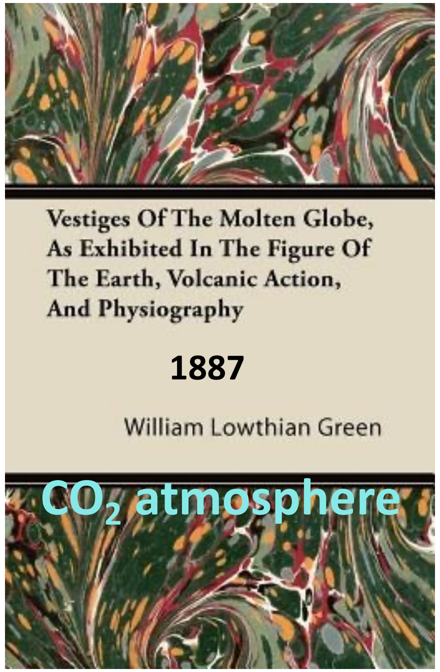
Using a Leydon Jar capacitor



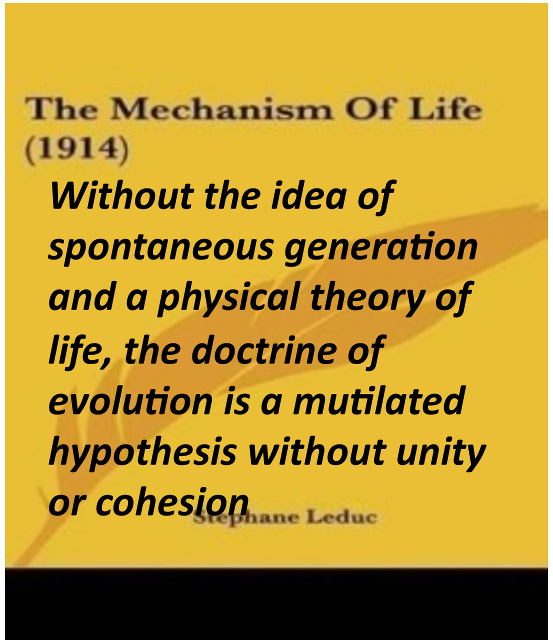
Piccolino 2006



No spontaneous generation of organic life



CO_2 atmosphere



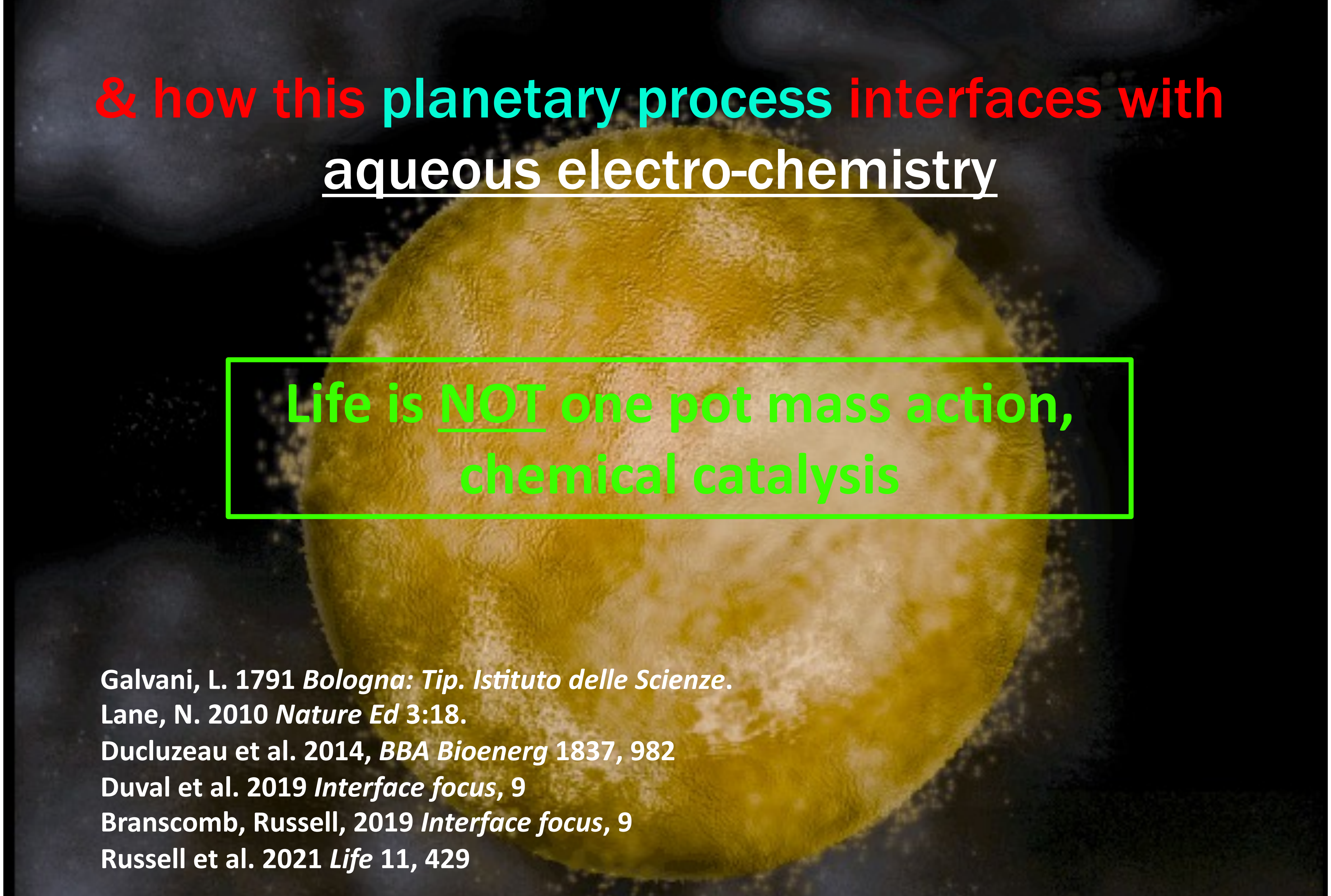
Without the idea of spontaneous generation and a physical theory of life, the doctrine of evolution is a mutilated hypothesis without unity or cohesion

“it is the inorganic elements that bring organic chemistry to life” Garner 1994

Beware of vitalism under new guises: e.g., organic soup, RNA World……

Life transcends chemistry! (Nick Lane)

Where is the wisdom we have lost in knowledge? Where is the knowledge we have lost in information?



& how this planetary process interfaces with <u>aqueous electro-chemistry</u>

Life is <u>NOT</u> one pot mass action, chemical catalysis

Galvani, L. 1791 *Bologna: Tip. Istituto delle Scienze*.
Lane, N. 2010 *Nature Ed* 3:18.
Ducluzeau et al. 2014, *BBA Bioenerg* 1837, 982
Duval et al. 2019 *Interface focus*, 9
Branscomb, Russell, 2019 *Interface focus*, 9
Russell et al. 2021 *Life* 11, 429

IMAGINE the initial conditions

Hard UV
Lightning
Impactors

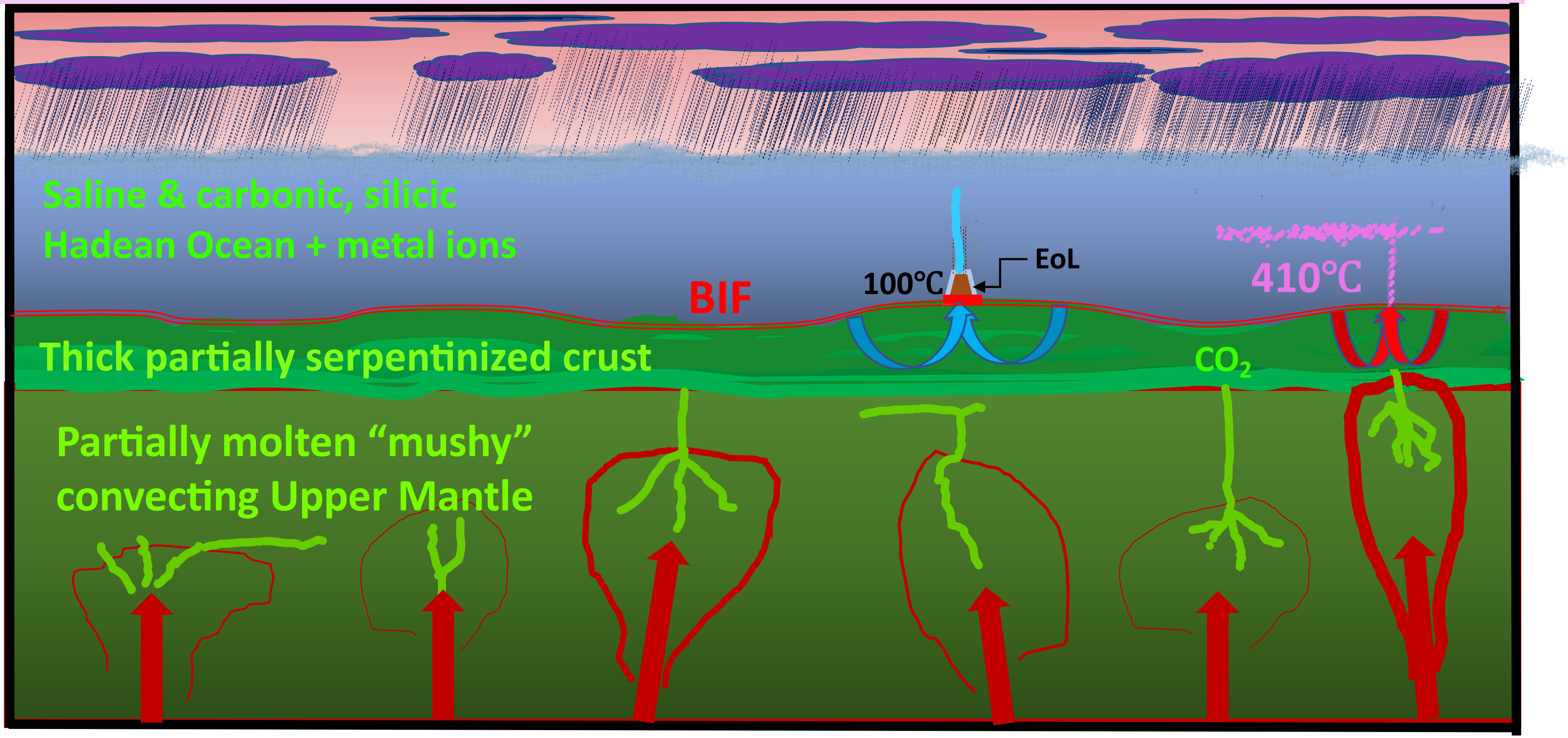
THERE WAS NO LAND 4.4Ga
when life onset

Just a turbulent torrential water world
whirling at > twice its present rate

The looming Moon!

Russell et al. 2014 *Astrobiology* 14, 308
Bartlett, Stevenson 2016 *Geophys Res Lett* 43, 5716
Monteux et al. 2020 *Geophys J Internl* 221, 1165
BUT NB. Monteux questioned by Korenaga 2021 *Life 11, 1142*

NO PART OF THE HADEAN CRUST BROKE THE OCEAN SURFACE



Note ordered hydrothermal convection cells

but no chimneys at 410°C

Russell 2021 The "Water Problem"(*sic*), the Illusory Pond and Life’s Submarine Emergence. *Life* 11, 429

Monteux et al. 2020 A Mushy Earth’s Mantle for more than 500 Myr. *Geophys J Internatl* 221, 1165

But see Korenaga 2021 *Life 11, 1142*

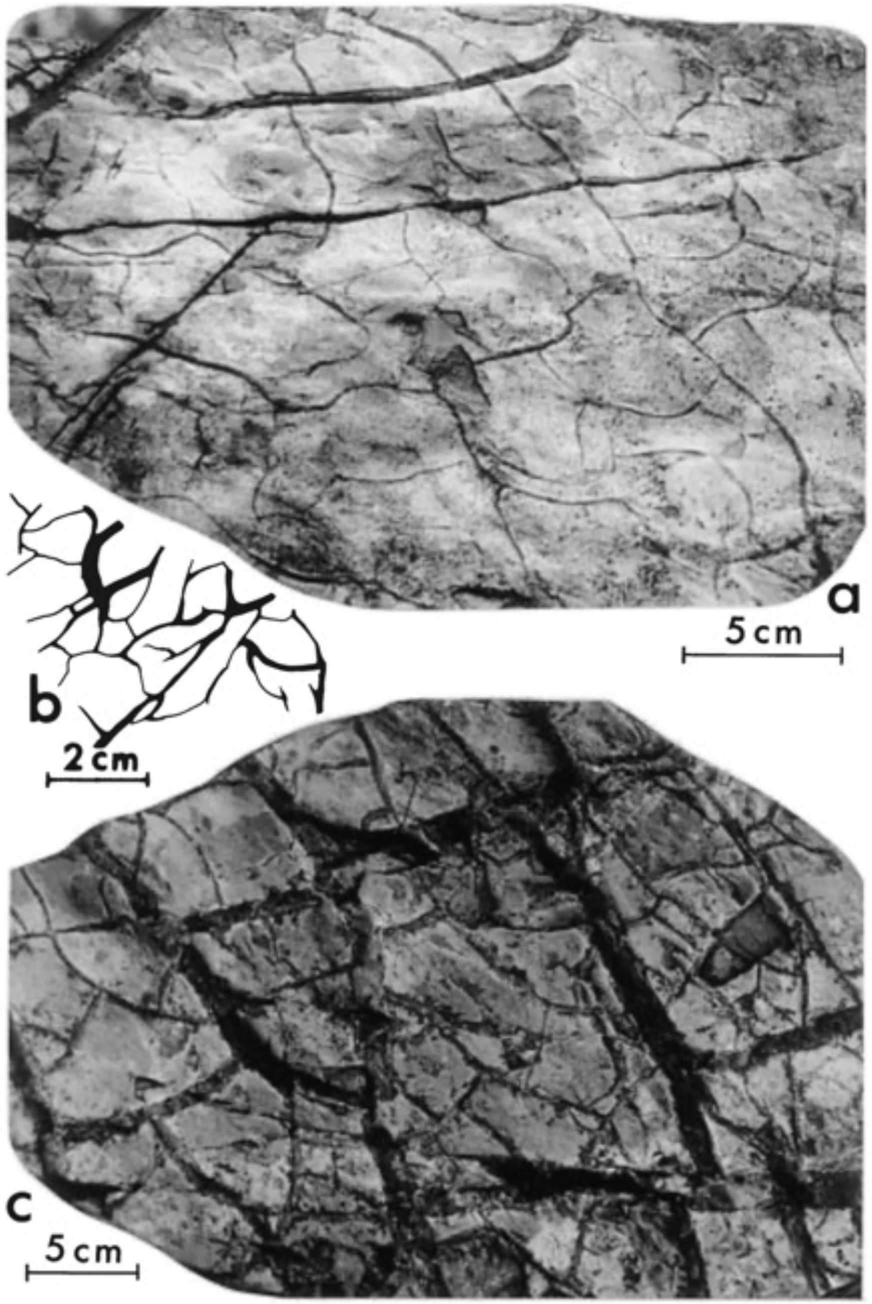
THERE WAS NO "WATER PROBLEM" IN THE DEPTHS OF THE HADEAN OCEAN!

e.g., Amorphous silica to chert and,
Dewatering cracks in the Marine Dalradian (late Proterozoic), Islay, W Scotland. Tanner 1998

and see
White, W.A. (1961) Colloid phenomena in the sedimentation of argillaceous rocks. J. Sedim. Petrol., 31, 560-570.

Tanner, P. W. G. (1998). Interstratal dewatering origin for polygonal patterns of sand-filled cracks: a case study from late Proterozoic metasediments of Islay, Scotland. *Sedimentology*, *45*, 71-89.

McMahon, S., van Smeerdijk Hood, A., & McIlroy, D. (2017). The origin and occurrence of **subaqueous** sedimentary cracks. *Geological Society, London, Special Publications*, *448*, 285-309.

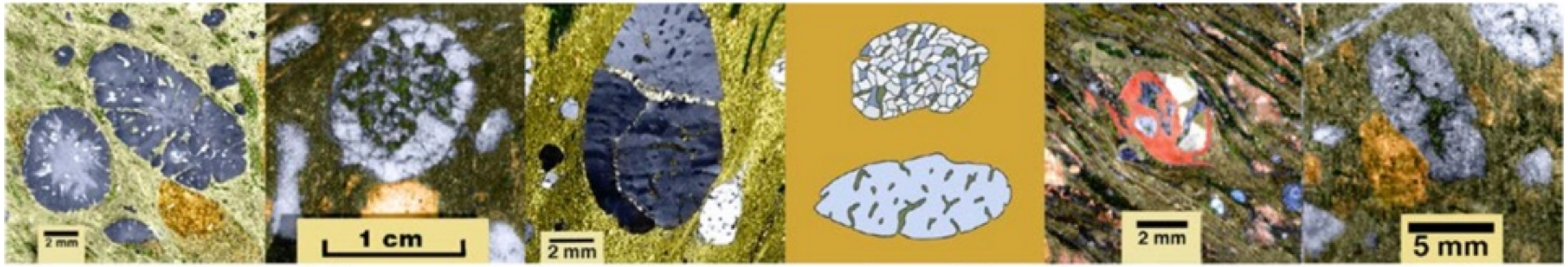


Cf. septarian nodule

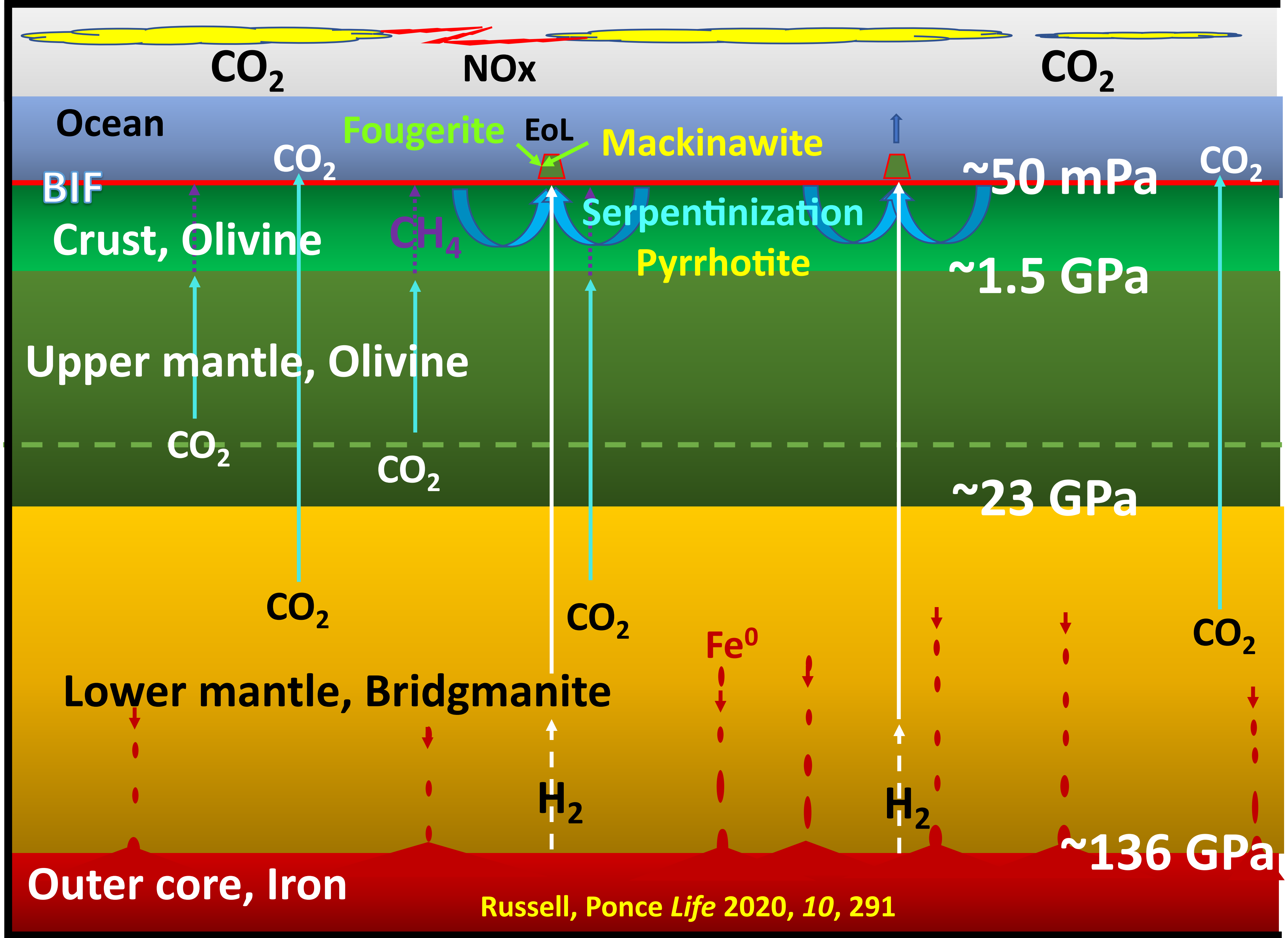
THERE WAS NO “WATER PROBLEM” IN THE DEPTHS OF THE HADEAN OCEAN!

e.g., Synerectic aging of silica gel → ~FeOOH Liesegang rings

Elliston, J. 2018 Hydration of Silica and Its Role in the Formation of Quartz Veins – Part 1. *Substantia* 2, 43-71.



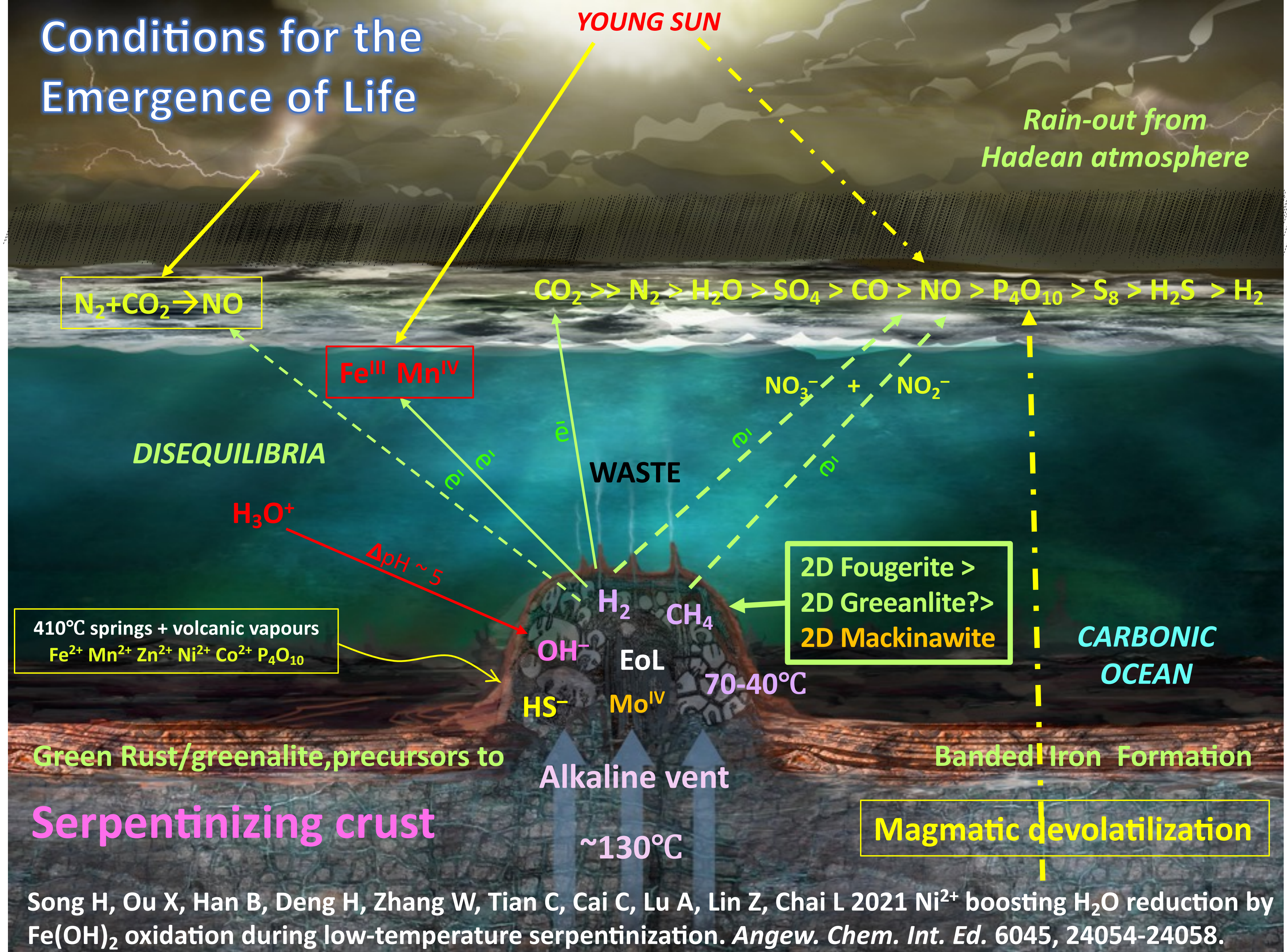
Syneresis shrinkage cracks in most porphyroid quartz ovoids are obvious



CO_2
NOx
CO_2
Ocean
CO_2
Fougerite
EoL
Mackinawite
~50 mPa
CO_2
BIF
Serpentinization
Crust, Olivine
CH_4
Pyrrhotite
~1.5 GPa
Upper mantle, Olivine
CO_2
CO_2
~23 GPa
CO_2
CO_2
Fe^0
CO_2
Lower mantle, Bridgmanite
H_2
H_2
~136 GPa
Outer core, Iron
Russell, Ponce *Life* 2020, *10*, 291

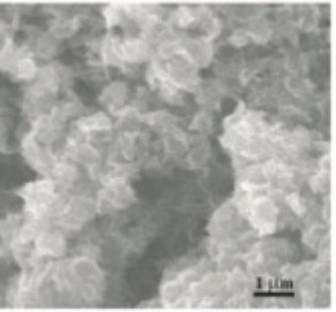
Submarine CO_2 bubbling up from magma at depth produces low pH seawater along a volcanic coast in the Phillipines

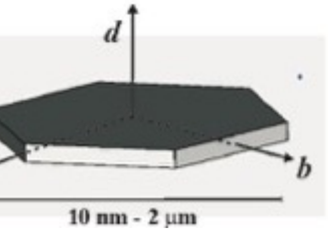
Cardenas et al. 2019. *Geophys Res Lett* GL085730.

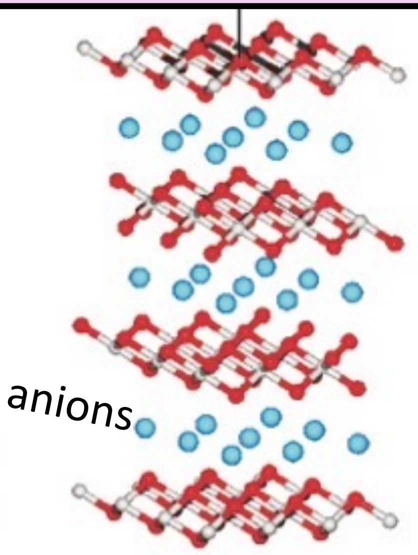

Conditions for the Emergence of Life
YOUNG SUN
Rain-out from Hadean atmosphere
$N_2 + CO_2 \rightarrow NO$
$CO_2 >> N_2 > H_2O > SO_4 > CO > NO > P_4O_{10} > S_8 > H_2S > H_2$
Fe^{III} Mn^{IV}
NO_3^- + NO_2^-
DISEQUILIBRIA
WASTE
H_3O^+
ΔpH ~ 5
2D Fougerite >
2D Greeanlite?>
2D Mackinawite
410℃ springs + volcanic vapours
Fe^{2+} Mn^{2+} Zn^{2+} Ni^{2+} Co^{2+} P_4O_{10}
H_2
CH_4
OH^-
EoL
HS^-
Mo^{IV}
70-40℃
CARBONIC OCEAN
Green Rust/greenalite,precursors to
Banded Iron Formation
Alkaline vent
Serpentinizing crust
~130℃
Magmatic devolatilization
Song H, Ou X, Han B, Deng H, Zhang W, Tian C, Cai C, Lu A, Lin Z, Chai L 2021 Ni^{2+} boosting H_2O reduction by $Fe(OH)_2$ oxidation during low-temperature serpentinization. *Angew. Chem. Int. Ed.* 6045, 24054-24058.

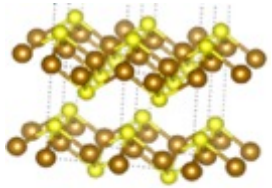
Submarine alkaline springs then and now

2D complex green rust mineral ~$Fe_2(OH)_5.H_2O$



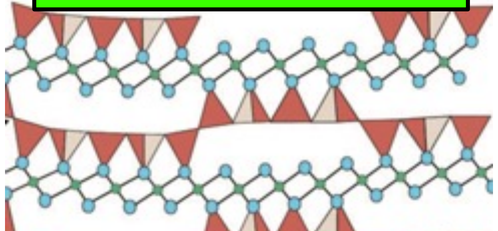




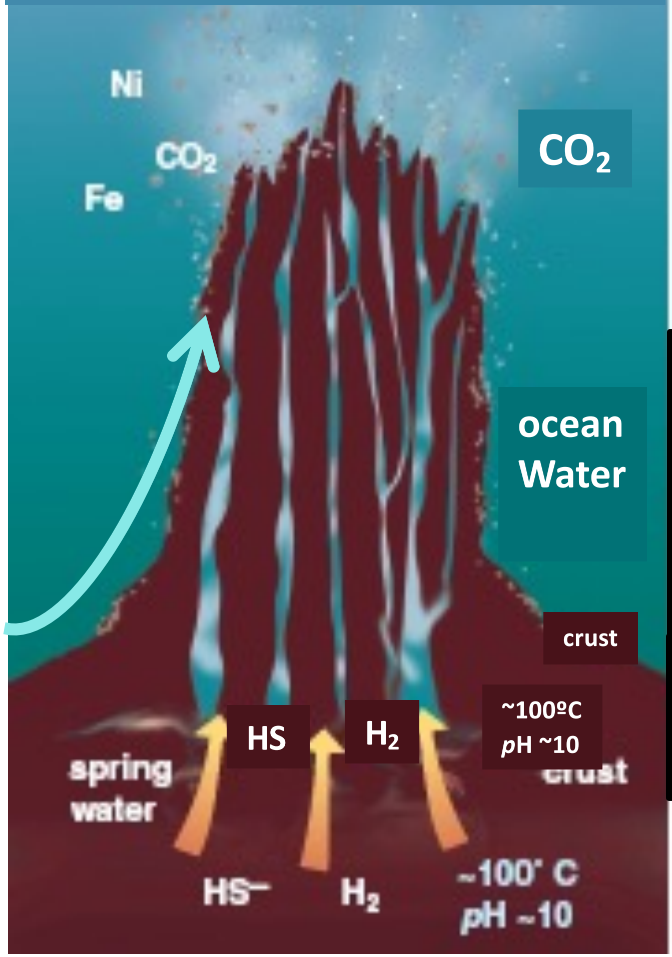


2D subsidiary Mackinawite FeS

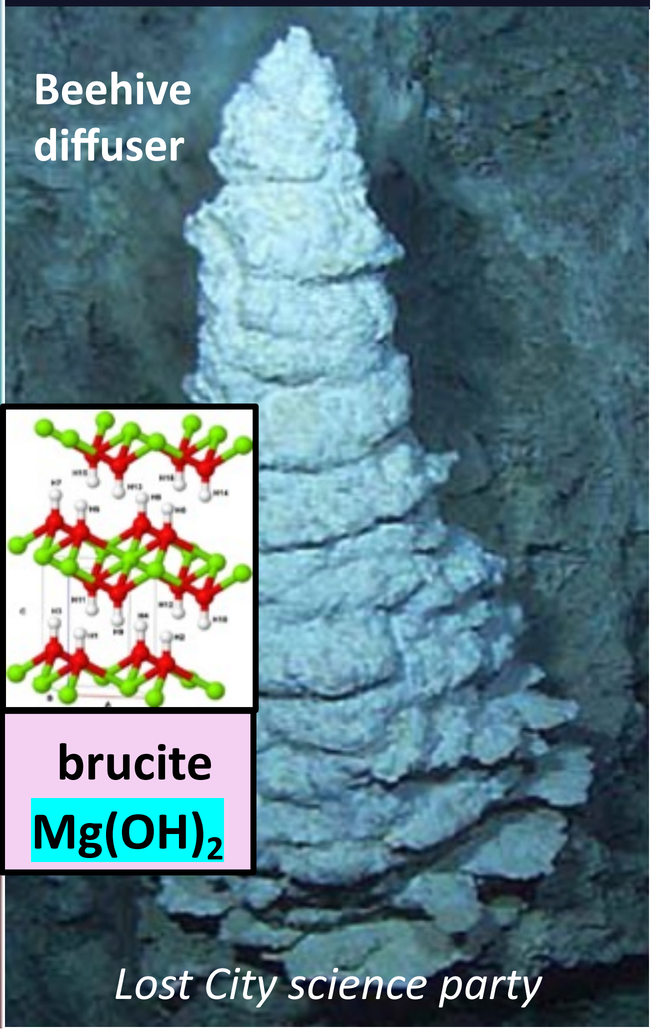
Greenalite $Fe_2^{2+/3+}.3Si_2O_5(OH)_4$



4.4 Ga alkaline hydrothermal vent "hatchery of life" Russell et al 1989, 2003



Lost City alkaline vent Kelley et al. 2001 & see Russell et al 1989



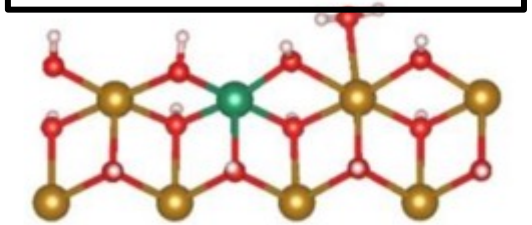
brucite $Mg(OH)_2$

Jochym et al. 2010. *J. Phys: Cond. Matter* 22 445403; Duval et al. 2019. *Interface Focus*. 20190063; White et al. 2015. *Earth Planet Sci. Lett. 430*, 105; Rasmussen et al. 2021 *Astrobiology* 21, 246

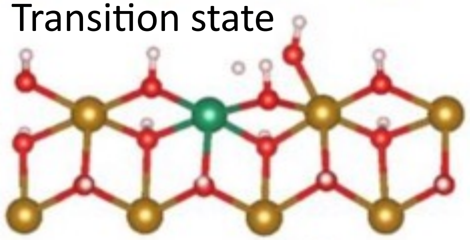
Ni^{2+} Boosting H_2O Reduction by $Fe(OH)_2$ Oxidation during Low-Temperature Serpentinization
Song et al. 2021

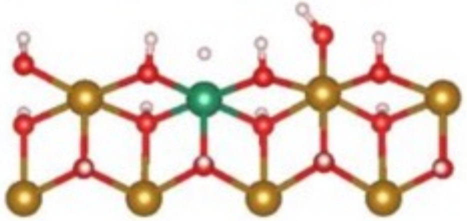
Origin of hydrothermal H2

Water adsorption

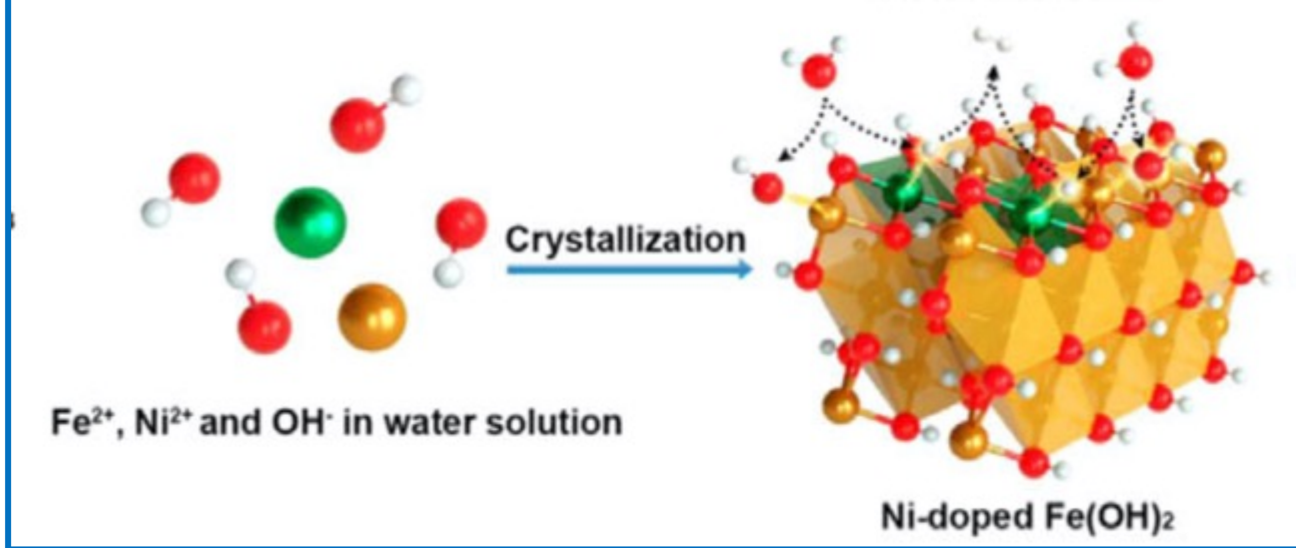


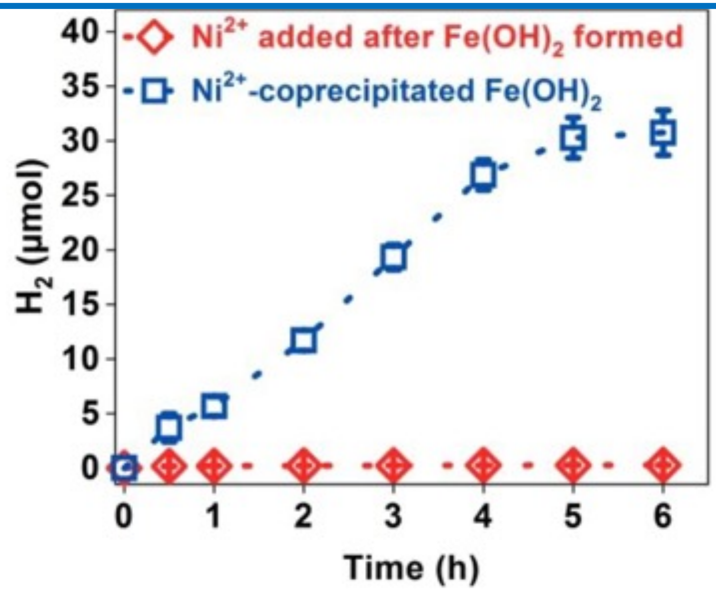
Transition state





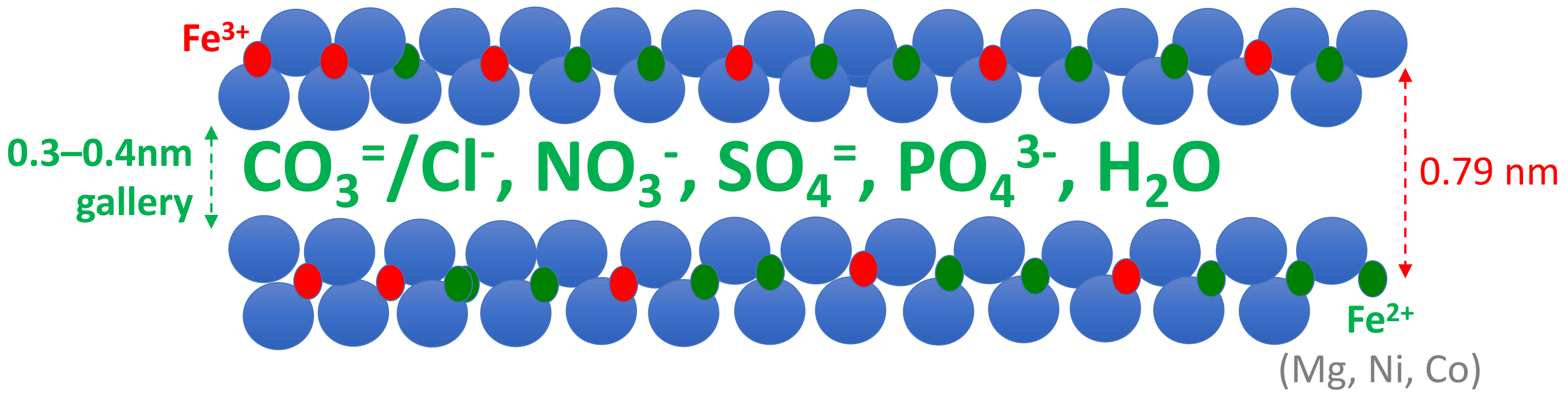
Dissociation





Song H, Ou X, Han B, Deng H, Zhang W, Tian C, Cai C, Lu A, Lin Z, Chai L 2021 Ni^{2+} boosting H_2O reduction by $Fe(OH)_2$ oxidation during low-temperature serpentinization. *Angew. Chem. Int. Ed.* 6045, 24054-24058.

Green rust: THE ALREADY-COMPLEX PRECURSOR OF THE CELL?



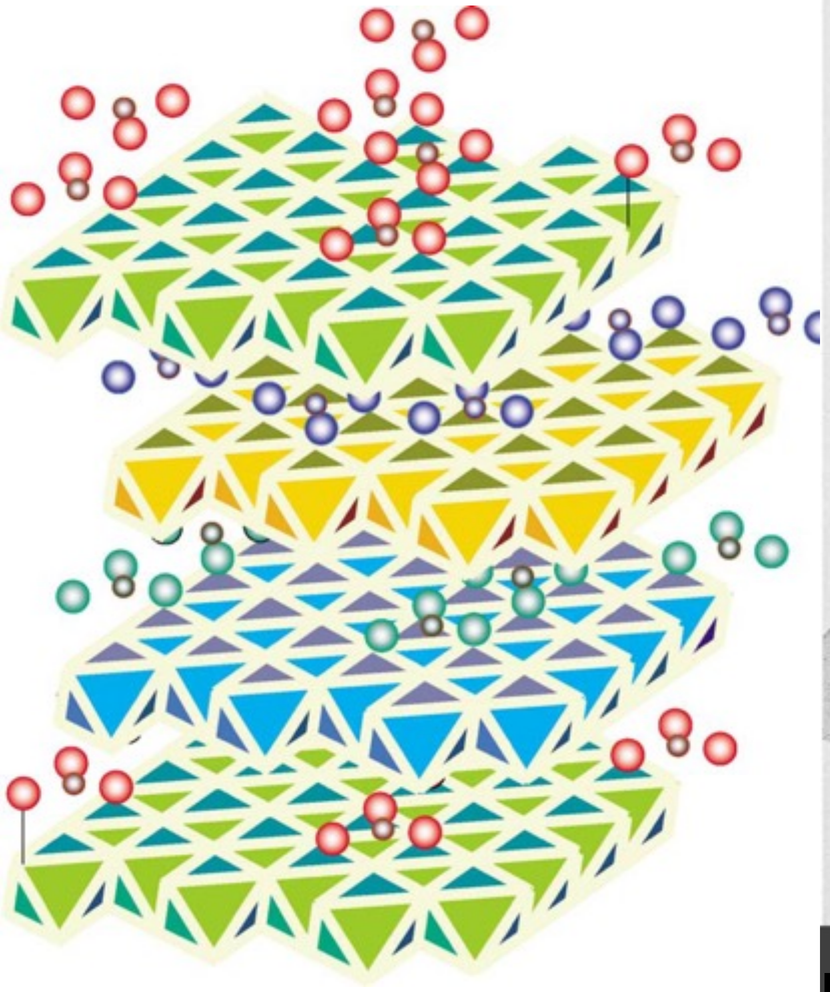
$$Fe^{2+}{}_4Fe^{3+}{}_2(OH)_{12}CO_3.3H_2O \Leftrightarrow Fe^{2+}{}_2Fe^{3+}{}_4(OH)_{10}CO_3.3H_2O + H_2 + 2\bar{e}$$

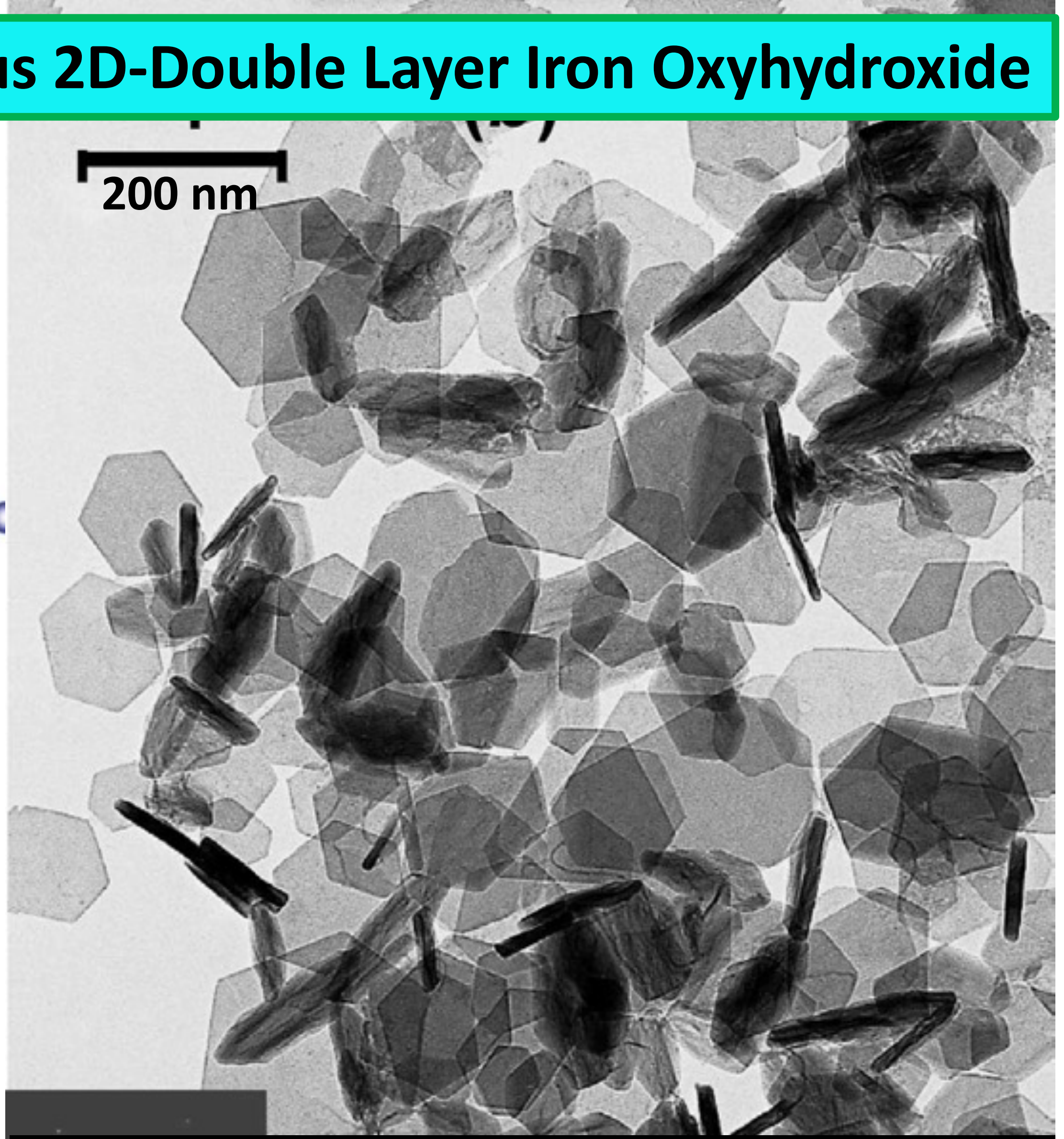
Fougerite (green rust) is a “soft” 2D-anionic clay hosting ionic substitutes, & capable of conformational change in response to its “hard” solid electrolyte properties

& can mediate gradient-driven coupling mechanisms in confined viscous hydrous 2D spaces

Arrhenius et al. 1997 *J Theor Biol* 187, 503; Génin et al. 2006 *Solid State Sci* 8, 1330;
Etique et al. 2016 *Geobiology, 14*, 237-254; Russell 2018 *Life* 8, 35;
Duval et al. 2019 *Interface Focus* 20190063; Sun et al. 2021 *Geochem. Trans.* 22, 1-10

Green rust, a heterogeneous 2D-Double Layer Iron Oxyhydroxide

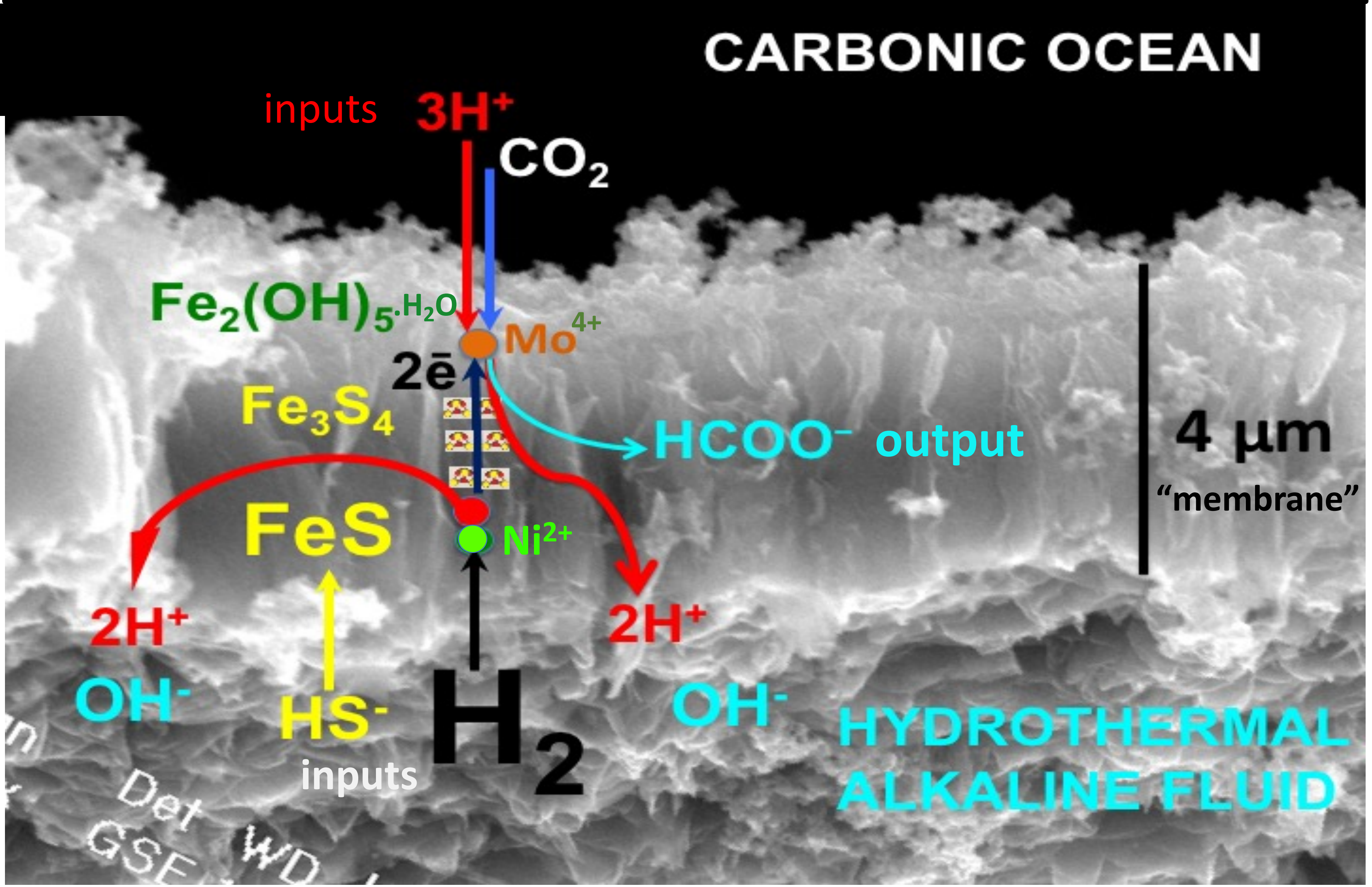




Mass precipitation of green rust
Fe II–III hydroxy-carbonate
Génin et al. 2005 *Solid State Sci* 7:545

Note, the **confined water** in the GR interlayers, i.e., no “water problem”!

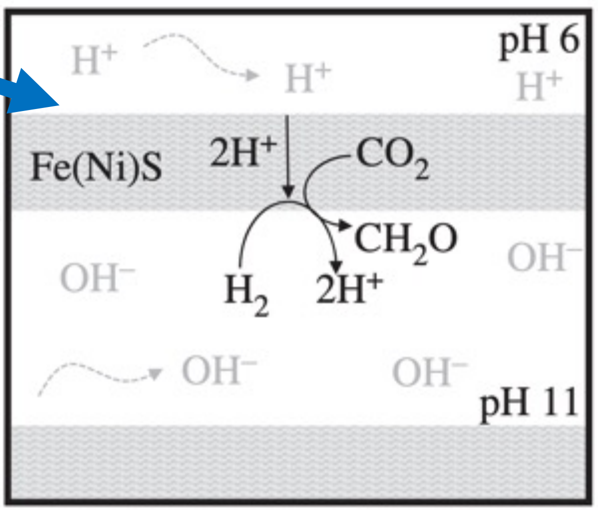
ENGINE 1: HYPOTHETICAL HYDROGENATION OF CO_2 TO FORMATE



Branscomb, Russell 2013; Vasiliadou et al. 2019; Then see Hudson et al. 2020 *PNAS* 117, 22873

CO_2 reduction to formate by H_2 and H^+

via **vectorial** electrochemistry in a microfluidic reactor



Vasiliadou et al. 2019*** *Interface Focus* 9:2019 0063

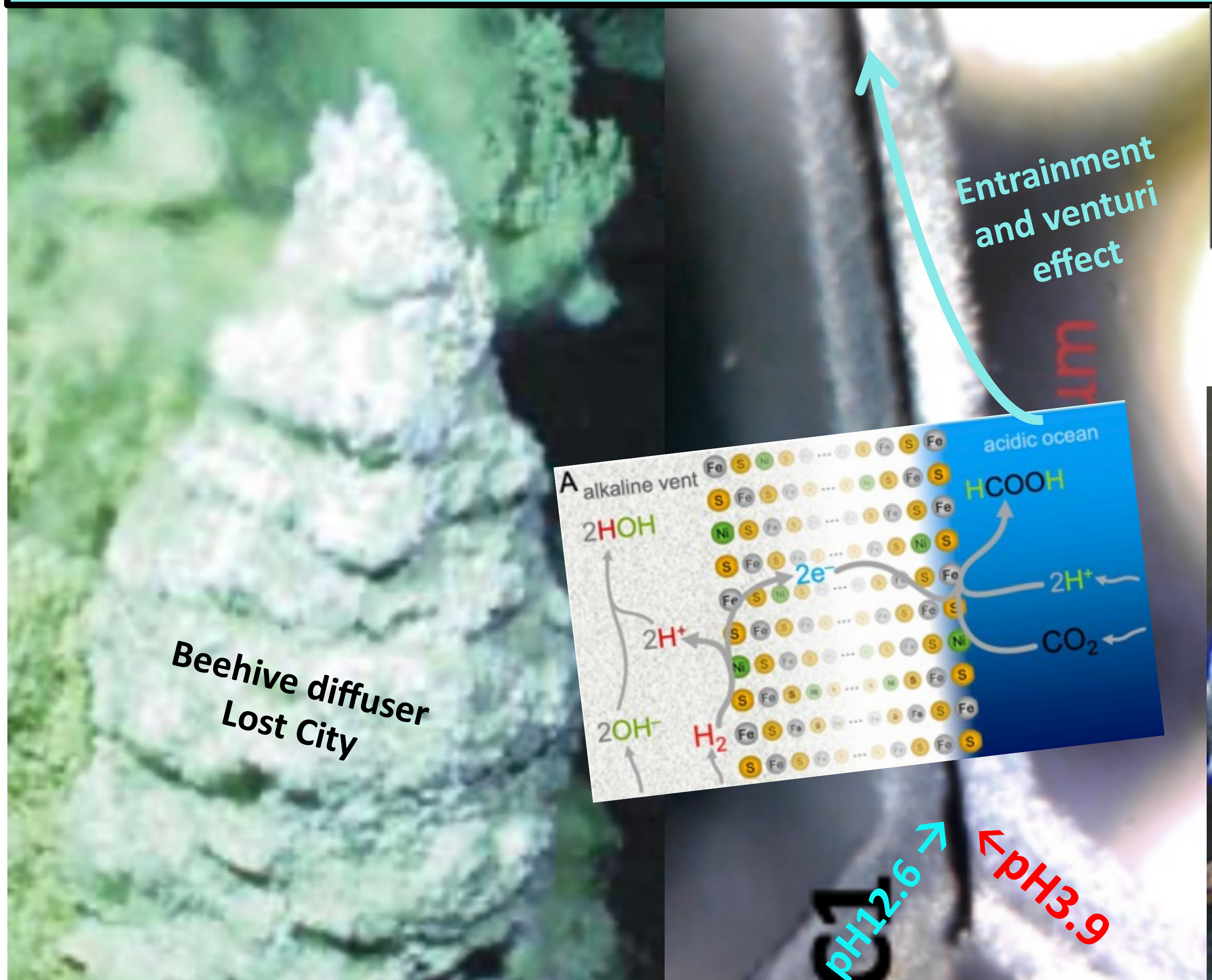
H^+ flux is $2X10^6$ faster than OH^- flux

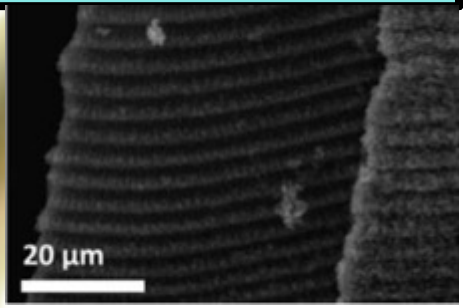
Sojo et al. 2014 *PLoS Biol.* 12

Hudson et al. 2020, *PNAS* 117, 22873-22879,

CO_2 reduction driven by a pH gradient

Hudson et al. 2020, *PNAS* 117, 22873-22879





Mielke et al. 2011
Astrobio

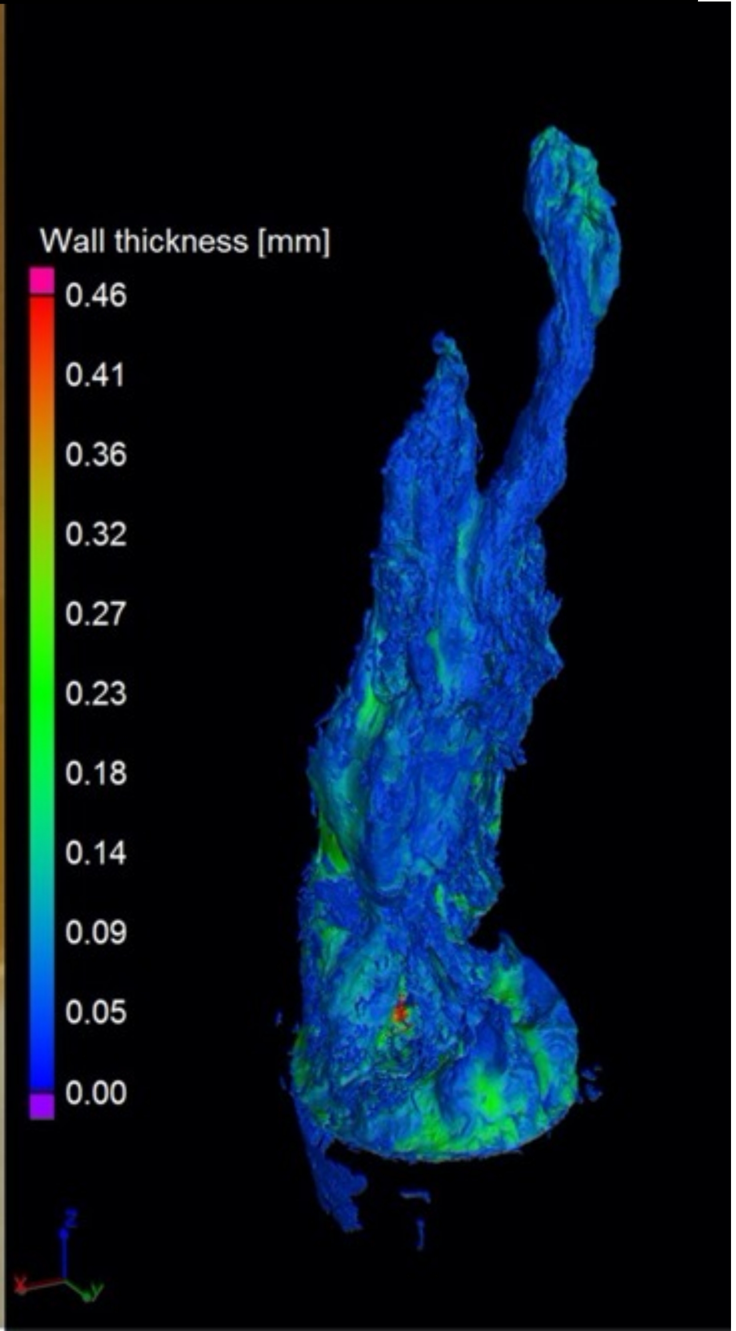
Wheeler et al. 2013 Moytirra. *Geochem/phys/syst.* 14.10 4170

Laboratory grown green rust (fougerite) chimneys

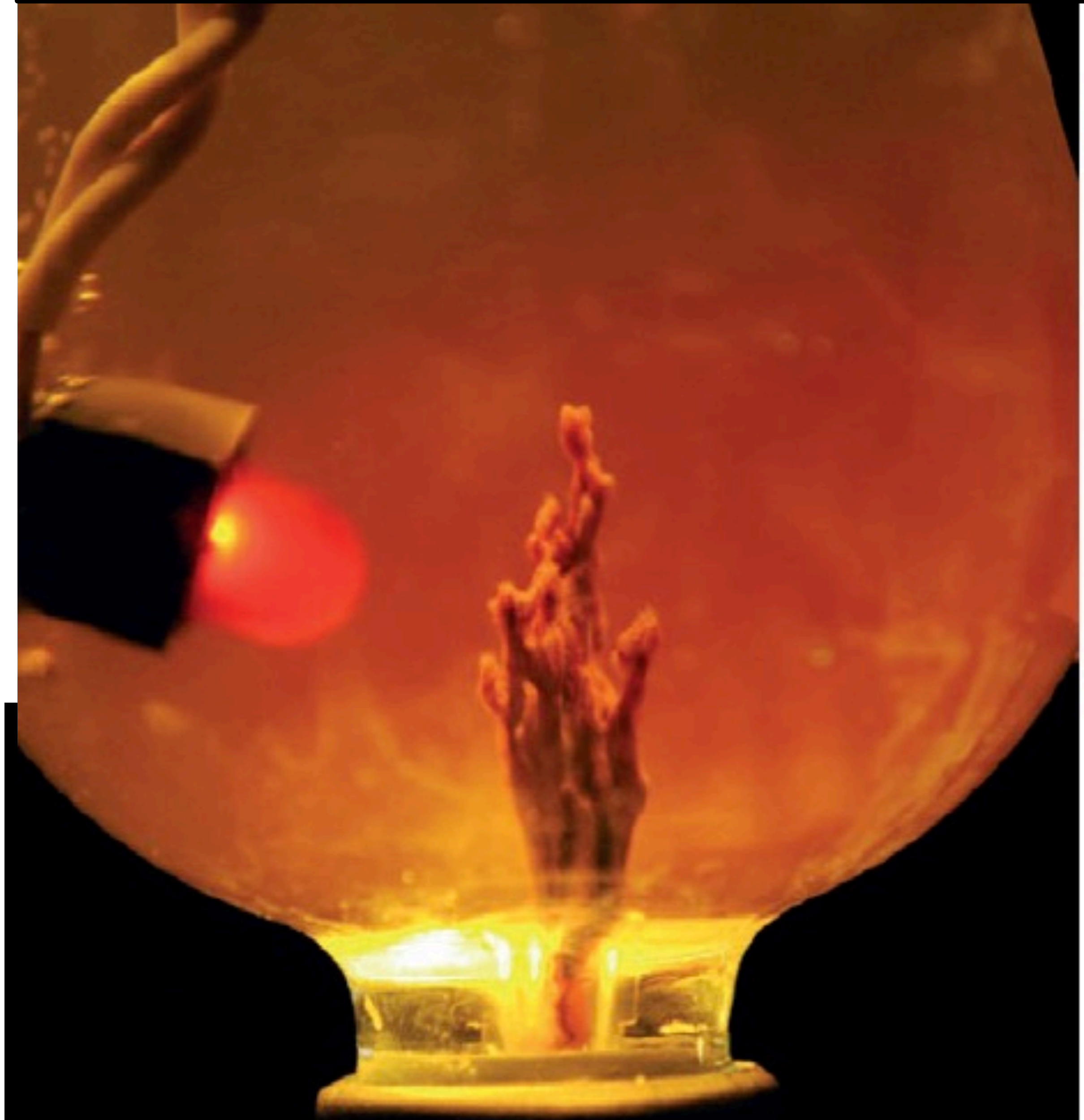
2D-$Fe_2(OH)_5.H_2O$
wall 10-40 μm thick

comprising ~50 – 200 complex ~ 200 nm nanocrysts orthogonal with wall

Barge et al. 2020, 3D-analysis of simulated prebiotic hydrothermal chimney. *ACS Earth Space Chem.* 4.9, 1663



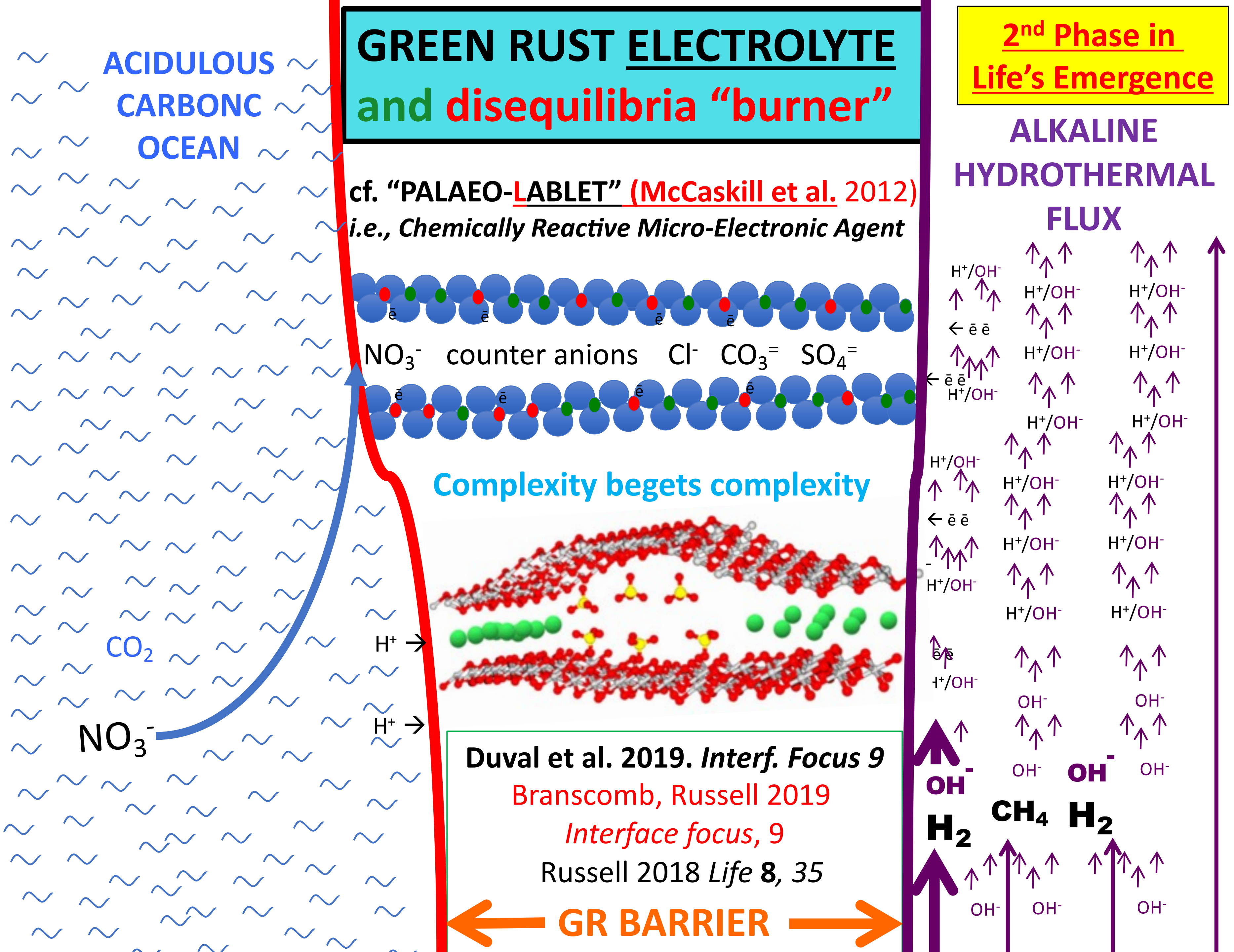
Systems produce the billions electrons/sec required by life

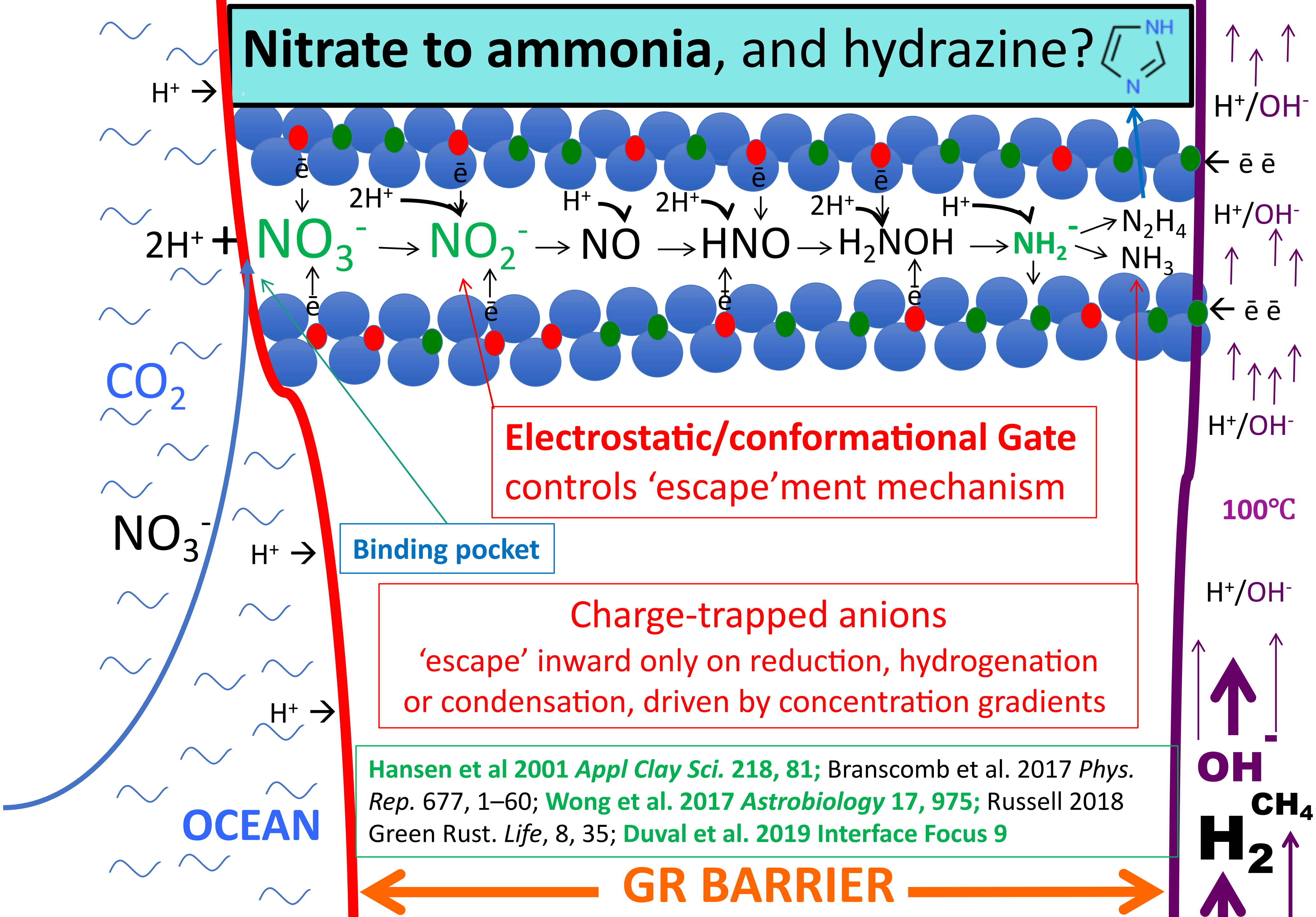


Barge et al. 2015 *Angew Chem Int Ed* 54:8184

Submarine power-plant

Yamamoto et al. 2013
Generation of Electricity and Illumination by an Environmental Fuel Cell in Deep-Sea Hydrothermal Vents. 52: 10758

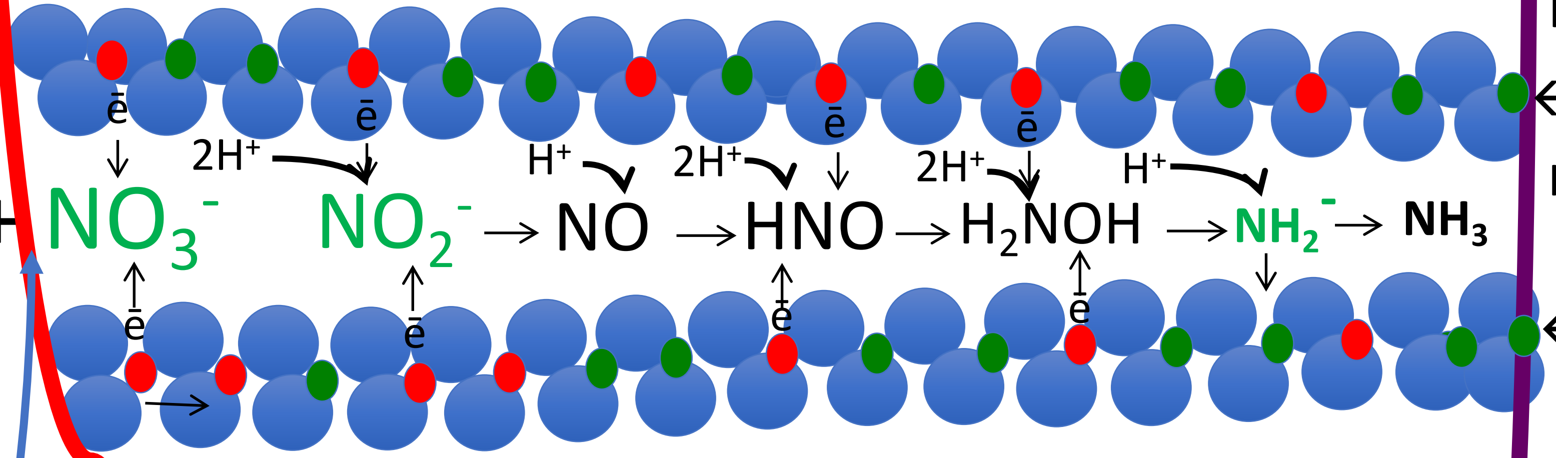

GREEN RUST ELECTROLYTE
and disequilibria "burner"
2nd Phase in Life's Emergence
ACIDULOUS CARBONC OCEAN
ALKALINE HYDROTHERMAL FLUX
cf. "PALAEO-LABLET" (McCaskill et al. 2012)
i.e., Chemically Reactive Micro-Electronic Agent
NO3- counter anions Cl- CO3= SO4=
Complexity begets complexity
CO2
NO3-
H+ →
H+ →
H+/OH-
← ē ē
OH-
OH
CH4
H2
Duval et al. 2019. Interf. Focus 9
Branscomb, Russell 2019
Interface focus, 9
Russell 2018 Life 8, 35
GR BARRIER



Nitrate to ammonia, and hydrazine?
NH
N
H+
H+/OH-
ē ē
2H+ + NO3-
2H+
NO2-
H+
NO
2H+
HNO
2H+
H2NOH
H+
NH2-
N2H4
NH3
ē
CO2
Electrostatic/conformational Gate
controls 'escape'ment mechanism
100°C
NO3-
Binding pocket
Charge-trapped anions
'escape' inward only on reduction, hydrogenation
or condensation, driven by concentration gradients
Hansen et al 2001 Appl Clay Sci. 218, 81; Branscomb et al. 2017 Phys. Rep. 677, 1–60; Wong et al. 2017 Astrobiology 17, 975; Russell 2018 Green Rust. Life, 8, 35; Duval et al. 2019 Interface Focus 9
OH-
CH4
H2
OCEAN
GR BARRIER

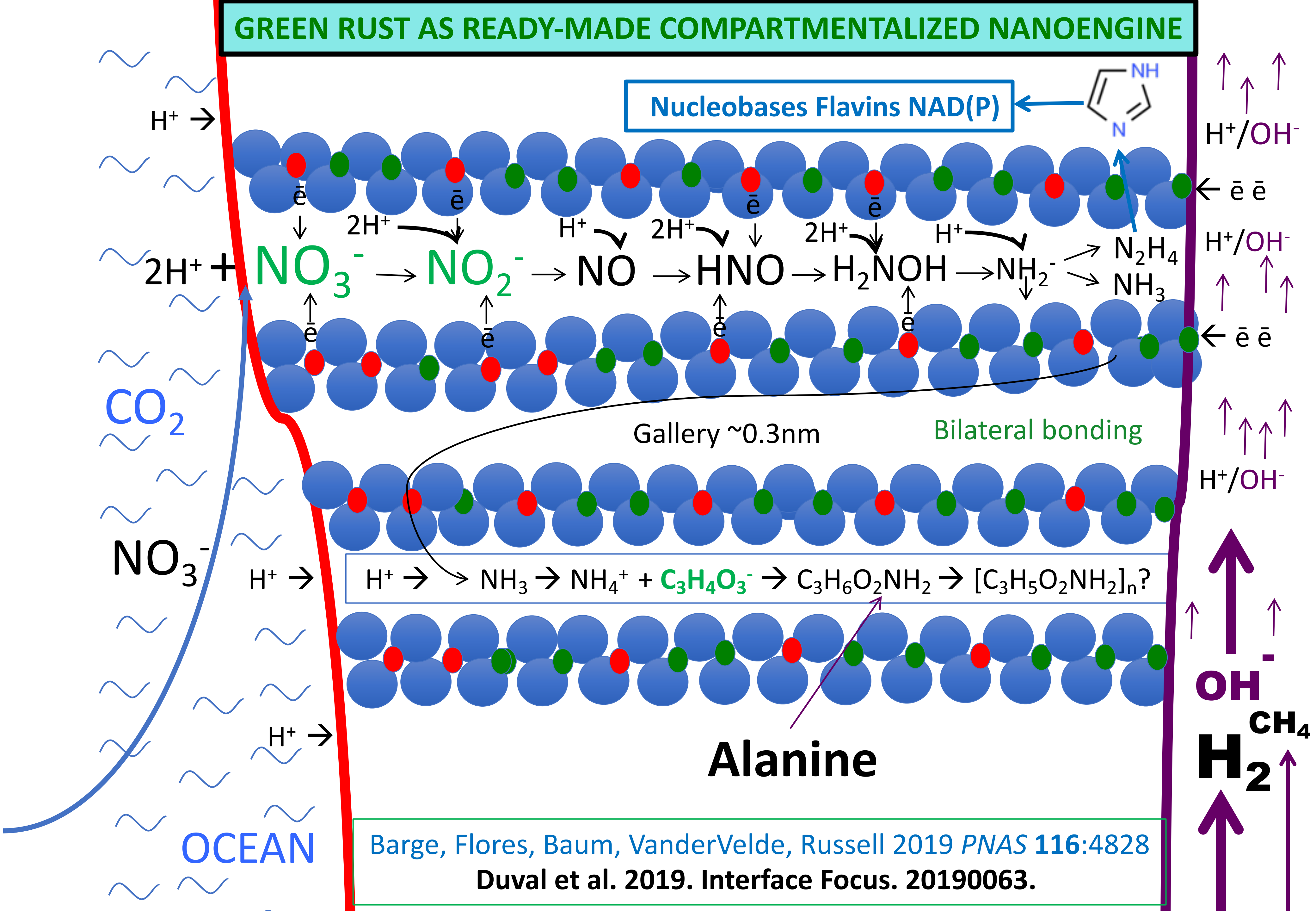
“proton gradients enable cellular metabolism to **transcend chemistry**” Lane

flux-force linear conversions, i.e., where the flux ∝ thermodynamic force

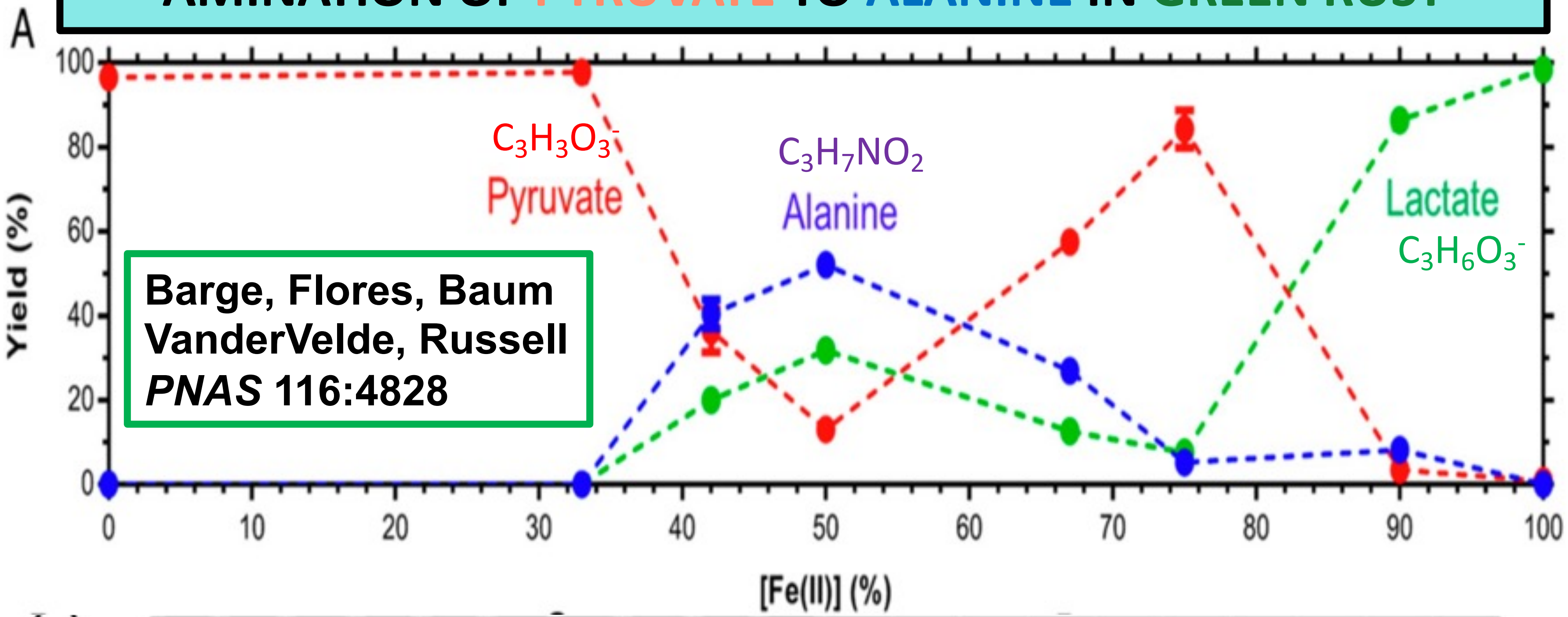


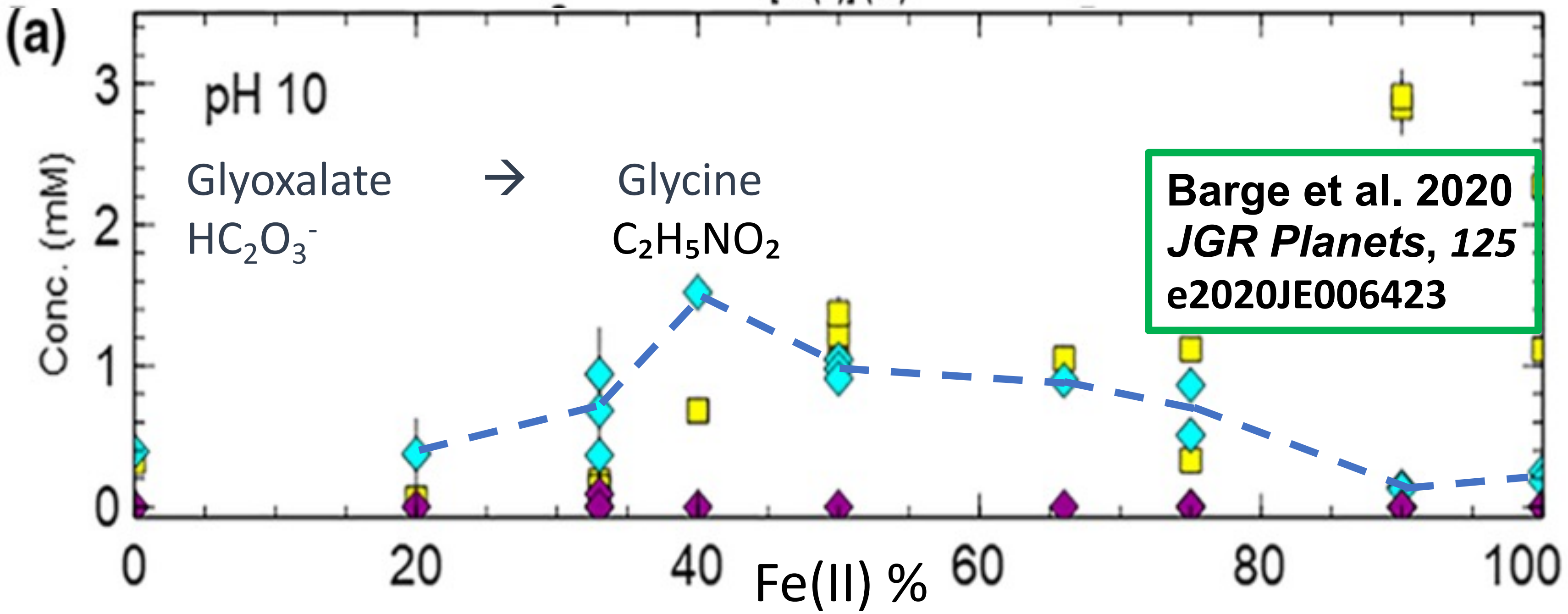
peristaltic GR layers govern an interlayer regime where water is so viscous that the thermodynamic force imposes a linear proportionality to flux as in *enzymes*

Branscomb, Russell 2019 *Interface focus, 9*;
Astumian 2007 *Phys. Chem. Chem. Phys. 9*, 5067–5083.
Lane 2010 *Nature Education* 3, 2.
Hansen et al. 2001 *Appl. Clay Sci.* 218, 81–91.
Stucki 1980 *Eur. J. Biochem*. 109, 269–283.
Onsager 1931 *Phys. Rev.* 37, 405–426.

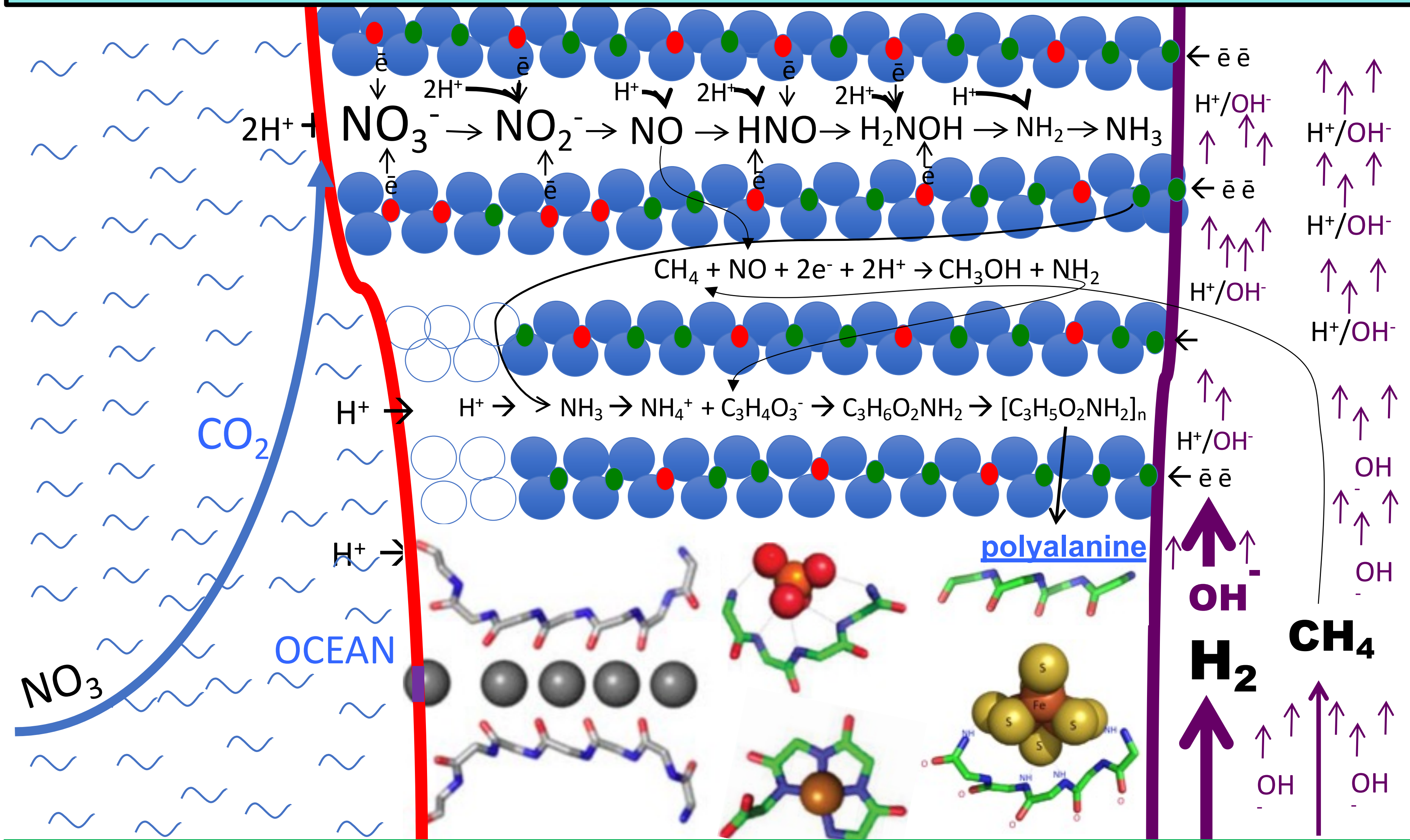

GREEN RUST AS READY-MADE COMPARTMENTALIZED NANOENGINE
Nucleobases Flavins NAD(P)
NH
N
H+ →
H+/OH-
ē ē
ē
2H+
H+
2H+
2H+
H+
2H+ + NO3- → NO2- → NO → HNO → H2NOH → NH2- → N2H4
NH3
H+/OH-
ē ē
CO2
Gallery ~0.3nm
Bilateral bonding
H+/OH-
NO3-
H+ →
H+ → NH3 → NH4+ + C3H4O3- → C3H6O2NH2 → [C3H5O2NH2]n?
OH-
CH4
H2
H+ →
Alanine
OCEAN
Barge, Flores, Baum, VanderVelde, Russell 2019 PNAS 116:4828
Duval et al. 2019. Interface Focus. 20190063.

AMINATION OF PYRUVATE TO ALANINE IN GREEN RUST





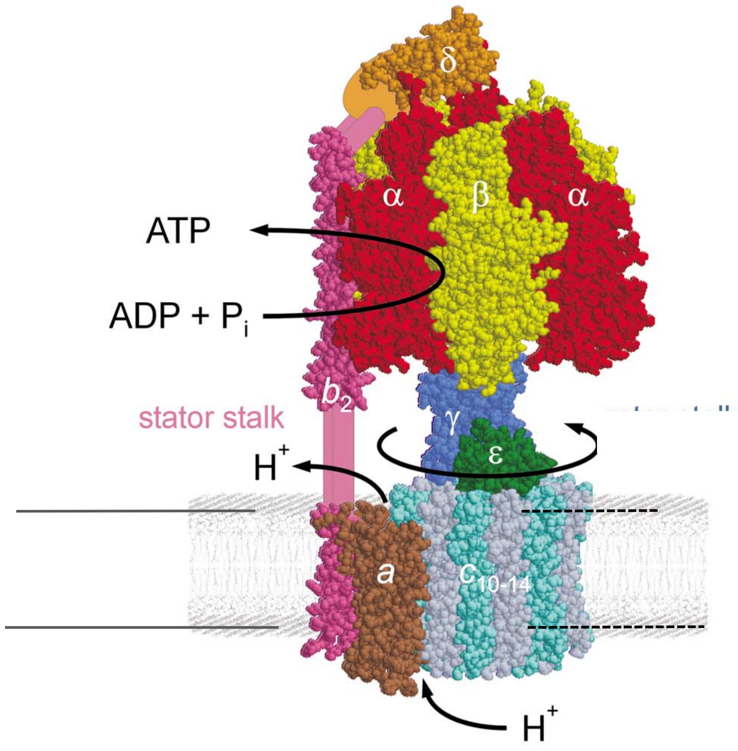
PROTOMETABOLIST TO ORGANC TAKEOVER?



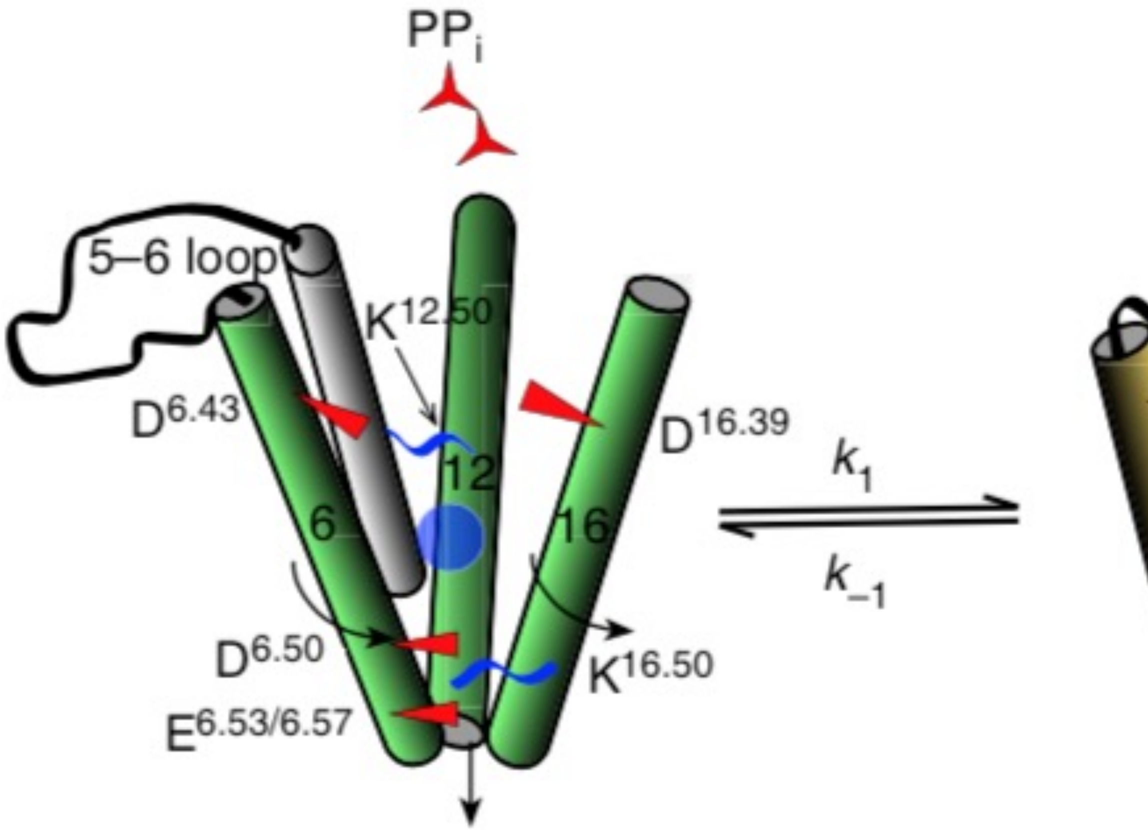
Nitschke et al. 2013 **Antiquity of metalloenzymes** *BBA-Bioenergetics*, *1827*, 871-881.
Branscomb, Russell 2019 **On the beneficent thickness of water**. *Interface focus*, 9
Milner-White 2019 **Protein three-dimensional structures at 'OoL'.** *Interface focus*, 9, 0057
Jordan et al. 2021 **assembly of redox-active Fe-S clusters at low conc^tn of cys.** *Nature comm* 12, 1

ATPase is too complicated to produce the pyrophosphate bond,
but a pyrophosphatase (Pi→Ppi) is much simpler

“inside”

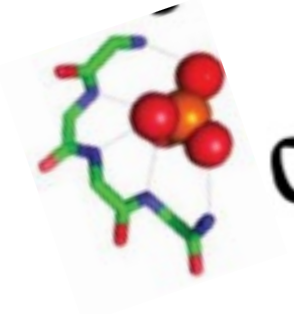


“outside”

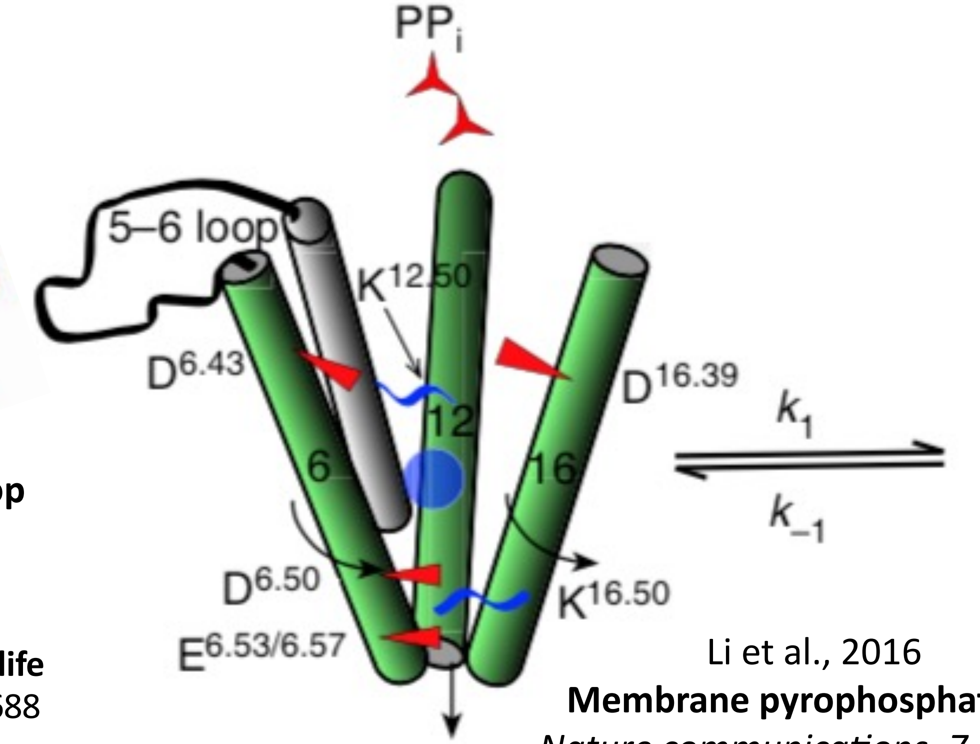


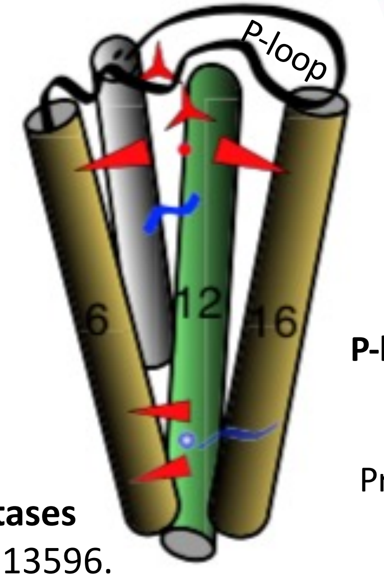
Something simpler than ATPase **is** needed at origin of life

Simpler membrane pyrophosphatase pumps can also produce PPi, the energy currency of the cell

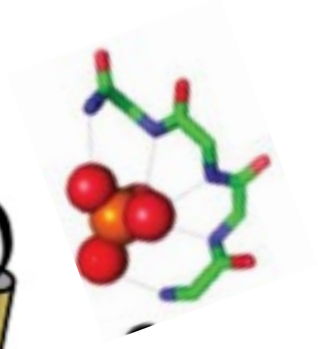


Natural P-loop
Milner-White, Russell, 2011
Peptide era & emergence of life
Genes 2, 671-688





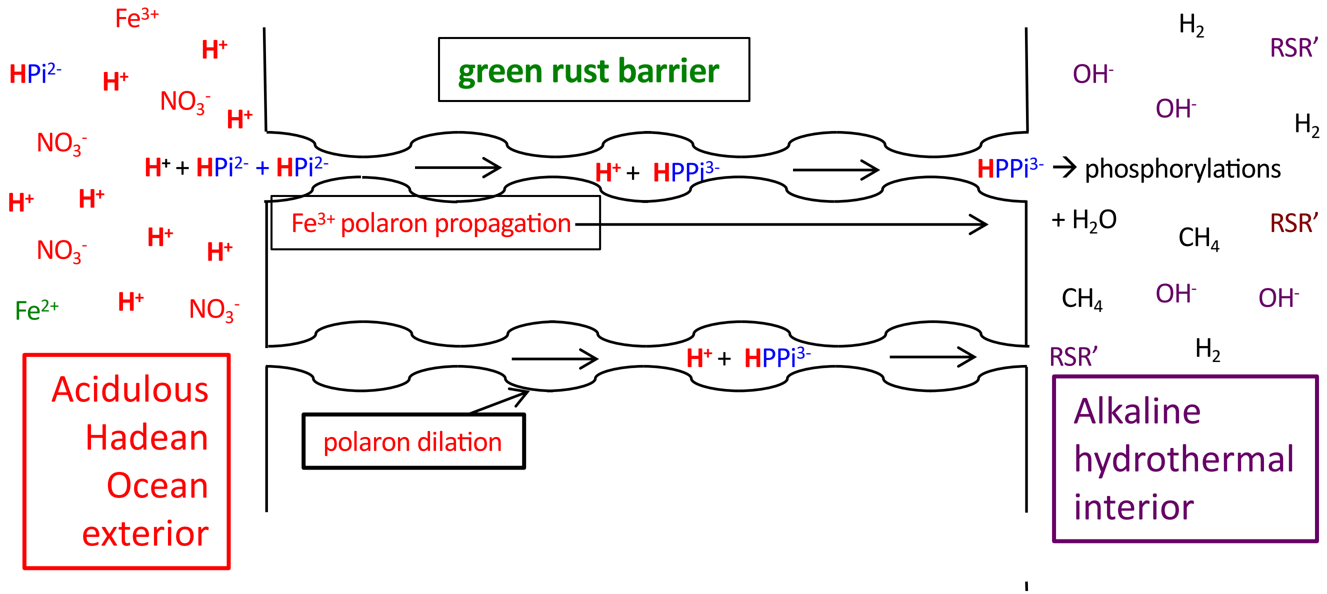
Li et al., 2016
Membrane pyrophosphatases
Nature communications, *7*, 13596.



Bianchi et al. 2012
P-loop nest binds inorganic phosphate
Proteins 80:1418

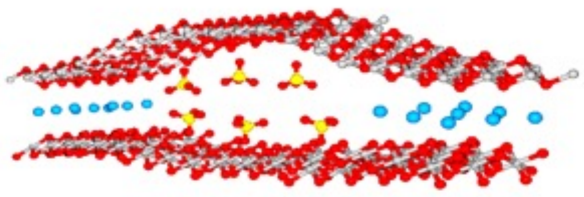
Ferric green rust as speculative H^+-pyrophosphatase

Russell, Nitschke, Branscomb, 2013, The inevitable journey to being.
Phil. Trans. R. Soc. Lond. B. Biol. Sci., 368, 20120254.

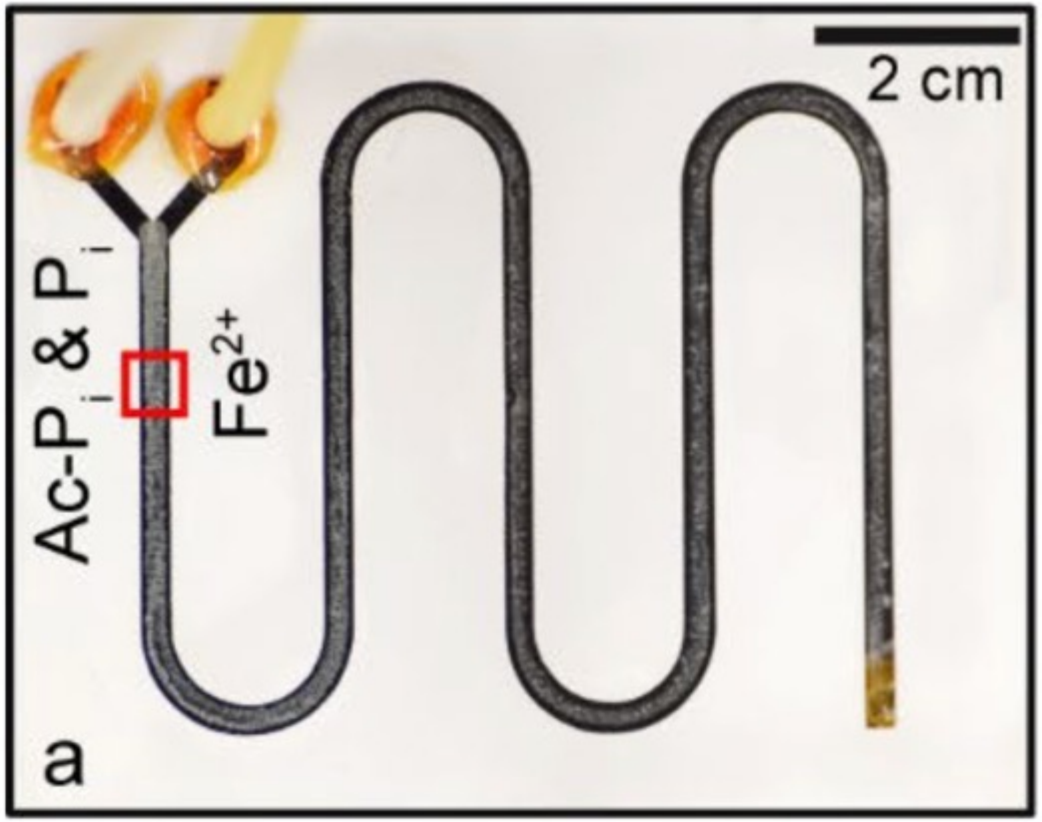


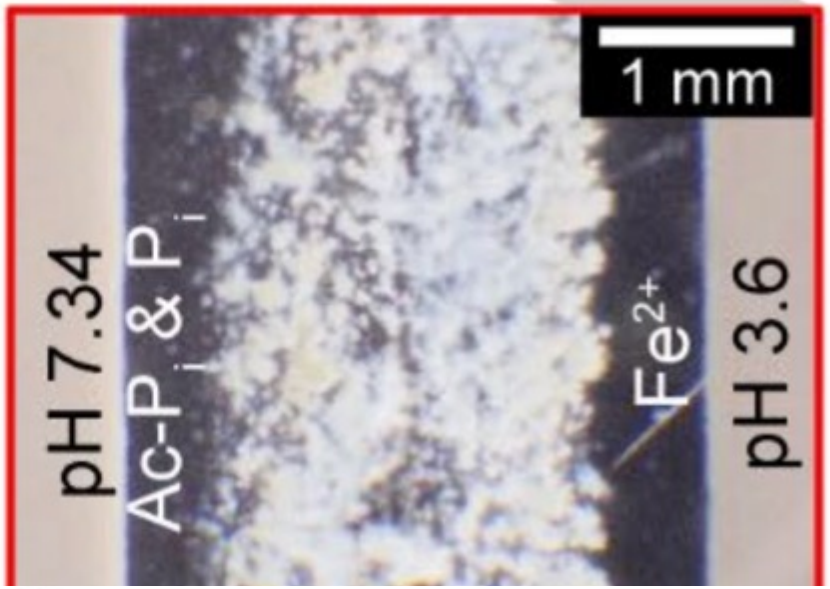
Duval et al. 2019. *Interface Focus,* 20190063.

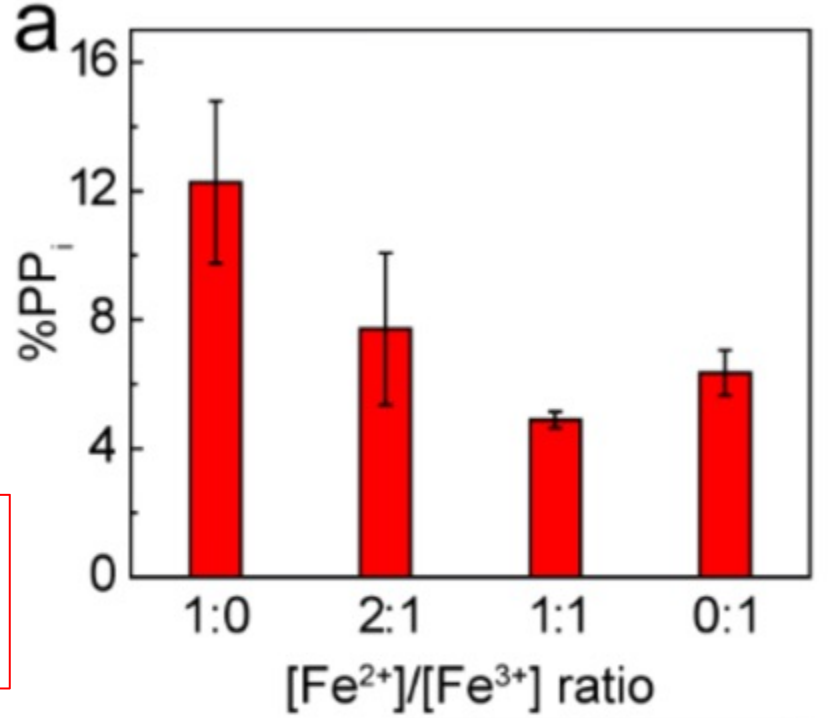
Branscomb & Russell. 2019.
On the beneficent thickness of water
Interface Focus, 9, 20190061.



Microfluidic Production of Pyrophosphate Catalyzed by Mineral Membranes with Steep pH Gradients





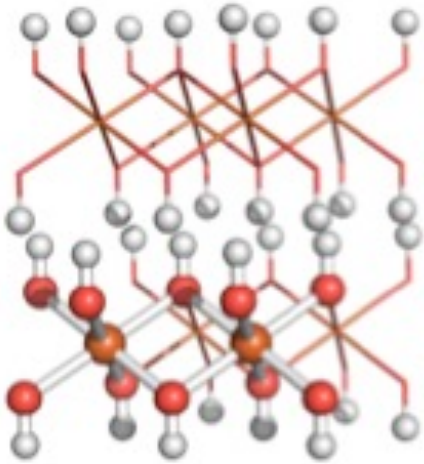


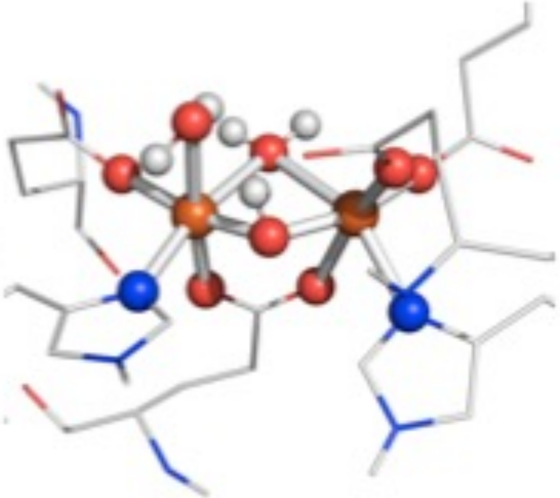
Qingpu Wang, Laura M. Barge, Oliver Steinbock, 2019, *Chemistry–A European Journal* 25: 4732

$$\mathbf{HPO_4^{2-} + CH_3COPO_4^{2-} + H^+ \Leftrightarrow HP_2O_7^{3-} + CH_3COOH}$$

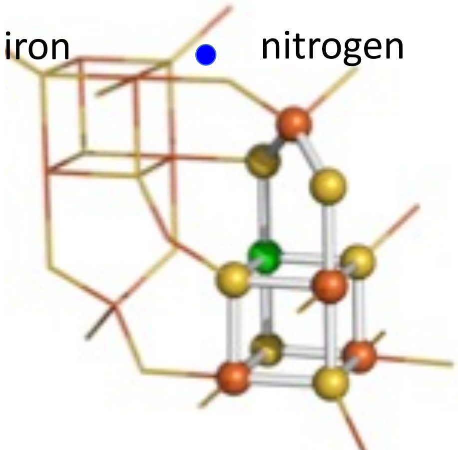
but Whicher et al. 2018 *OLEB* 48, 159:show production of acetyl phosphate – a phosphorylating agent – from thioacetate in water!

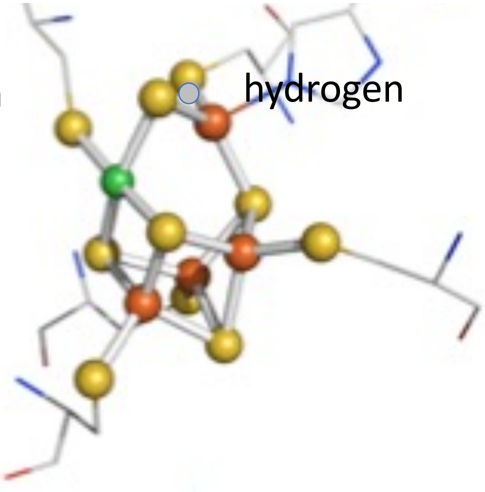
Structure of Green Rust and Methane Monooxygenase active site





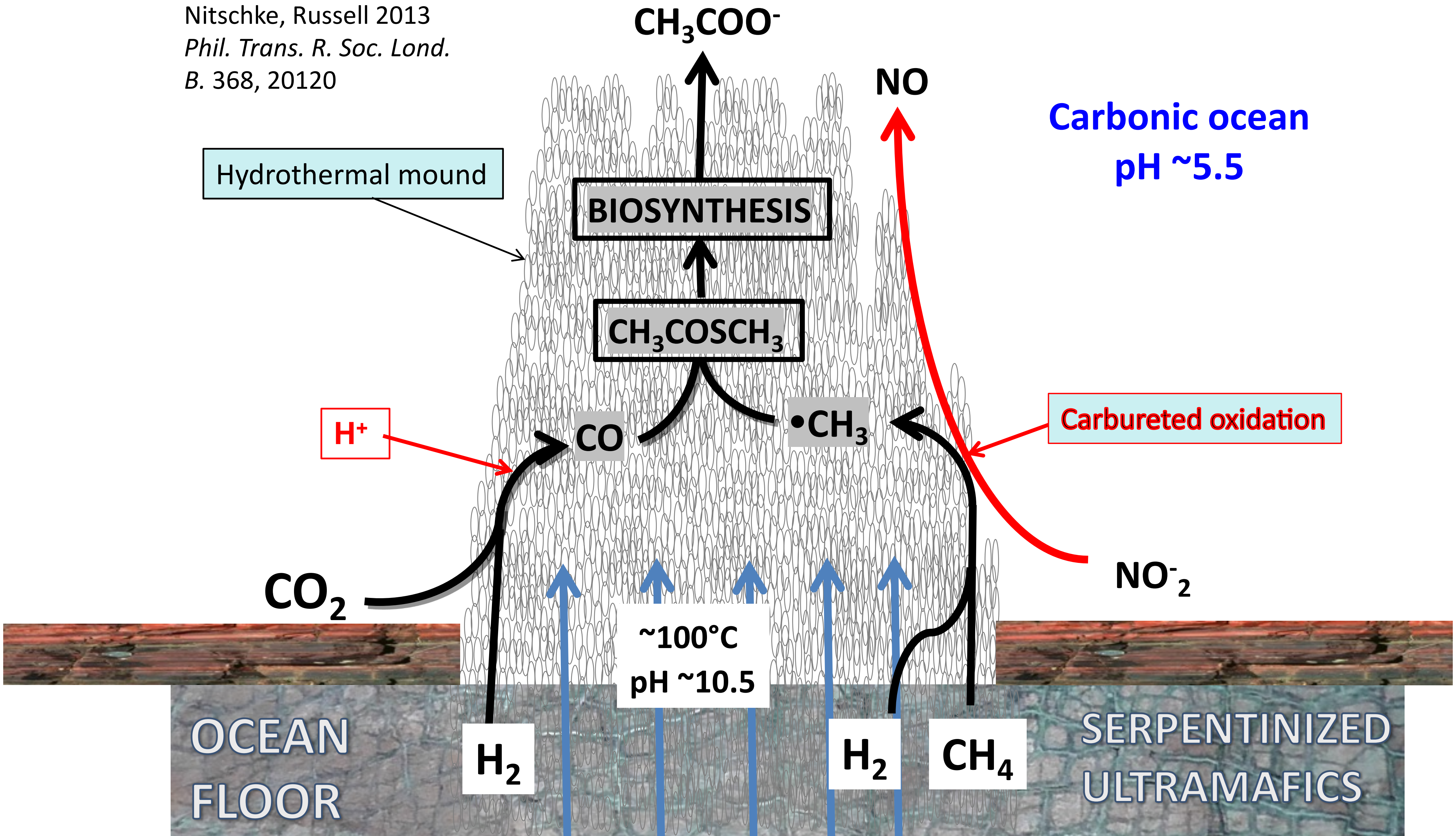
iron nitrogen oxygen hydrogen



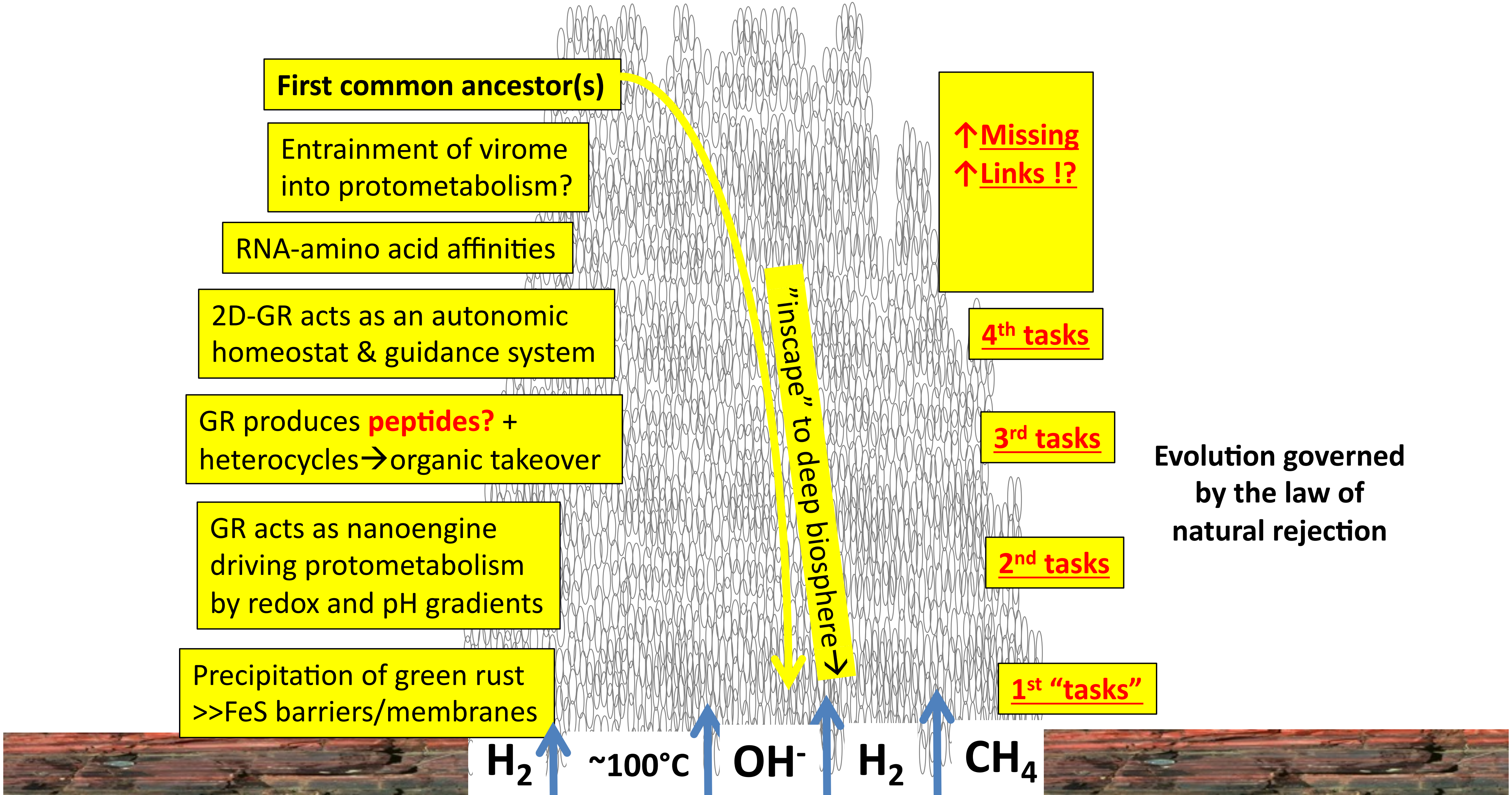


The denitrifying methanotrophic acetogenic pathway

Nitschke, Russell 2013
Phil. Trans. R. Soc. Lond. B. 368, 20120

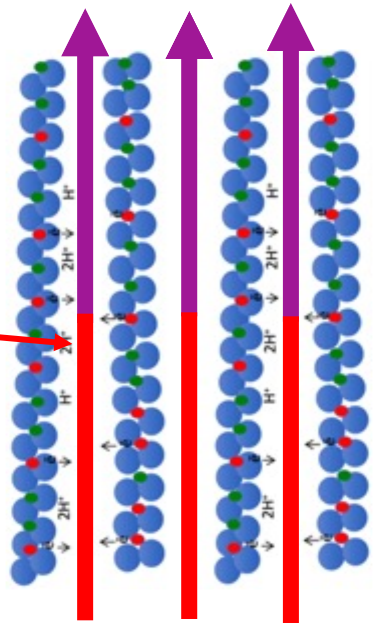


Gain of function during the emergence of life through complexification driven by incremental increases in stochastic entropy production



Summary cartoon: green rust interlayers resolving disequilibria at the vent & trapping the prebiotic product

WASTE



Order creation = emerging metabolism

Rechargable GR has Functional Sequence Complexity with potential as multi-'purpose' transistors and computing nanoengines [cf. Trixler, 2021].

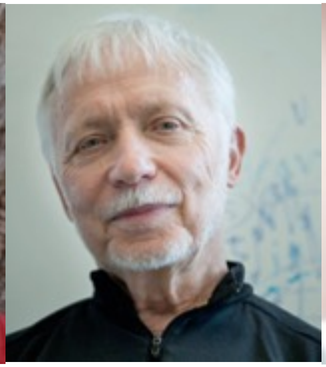
GR

Disequilibria at the vent/
'entropy disproportionation'

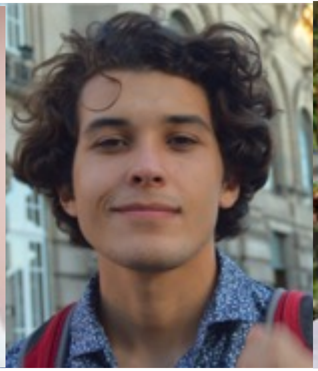
Branscomb, Russell 2019 **On the beneficent thickness of water**. *Interface focus*, 9
Russell 2018 Green rust: The **simple** organizing 'seed' of all life? *Life*, 8, 35
Duval et al. 2019 Fougerite: The **not so simple** progenitor of the first cells. *Interface focus*, 9

Collaborators – with appreciation!


Wolfgang Nitschke


Elbert Branscomb


Simon Duval


Orion Farr


Kilian Zuchan


Julyan Cartwright


Alessandro Minguzzi


Alberto Vertova


Francesco Panico


Sara Pellegrino


James Milner-White


Adrian Ponce