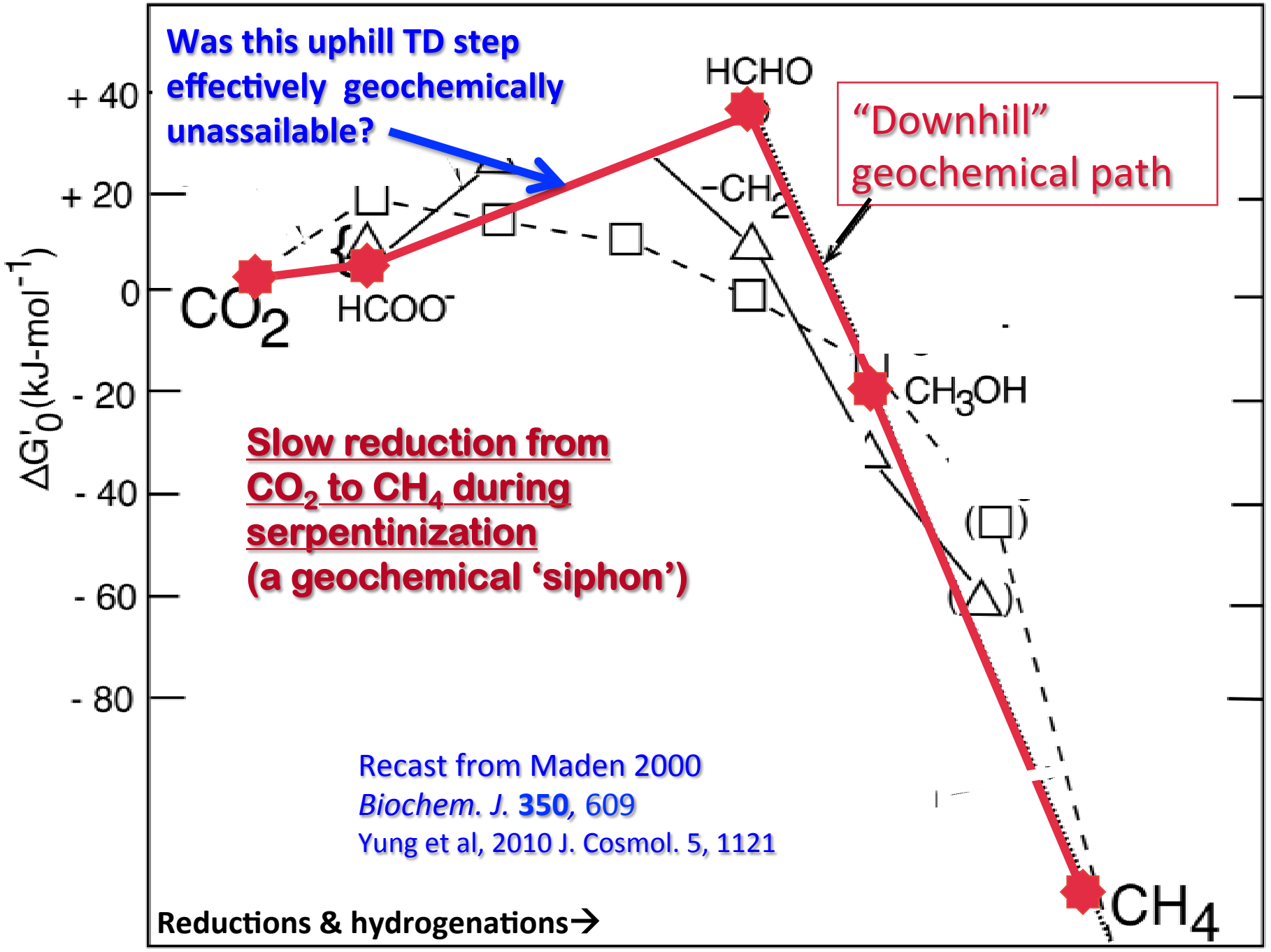
Beating the acetyl Co-A pathway to the origin of life

Michael Russell, Jet Propulsion Laboratory,

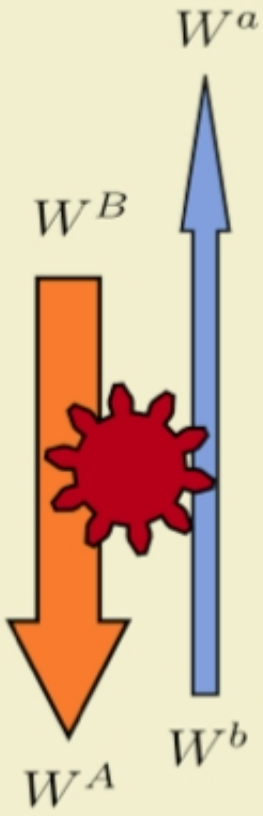
California Institute of Technology

Government sponsorship acknowledged


Was this uphill TD step effectively geochemically unassailable?
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
Yung et al, 2010 J. Cosmol. 5, 1121
Reductions & hydrogenations→

Abstract thermodynamics of a free energy converter: - a generalized "Atwood machine"

$$(S = k\,ln W)$$



$$W^A > W^B$$
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$$W^A \times W^a \geqslant W^B \times W^b$$
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$$S^A + S^a \geqslant S^B + S^b$$
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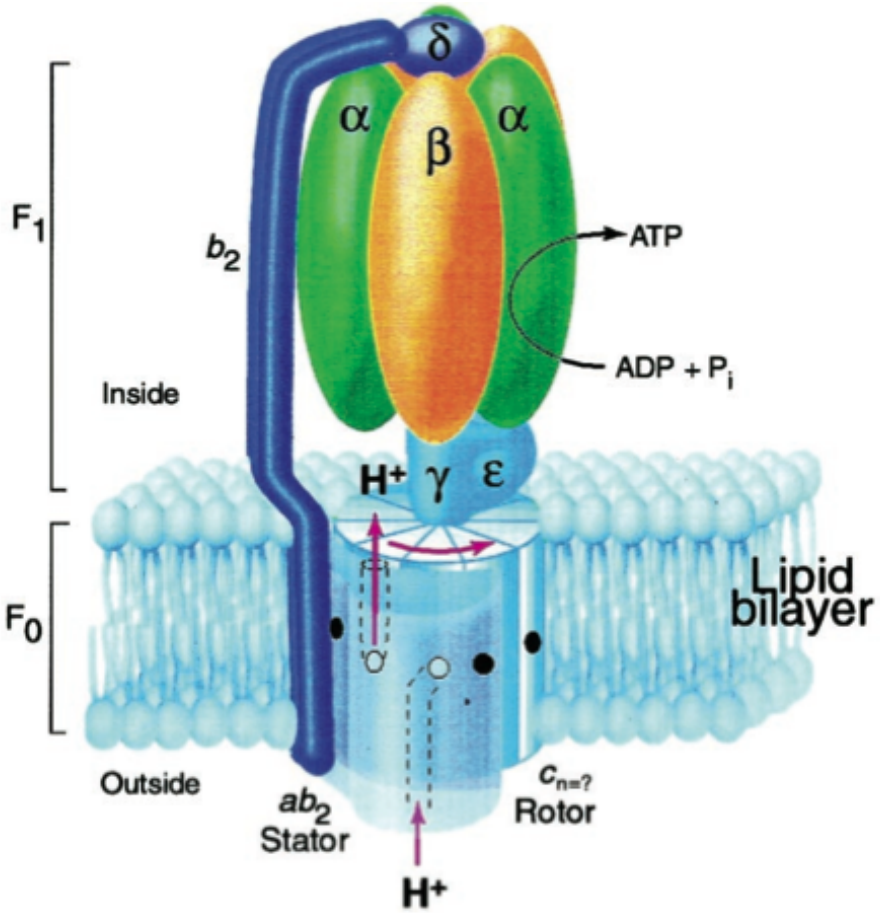
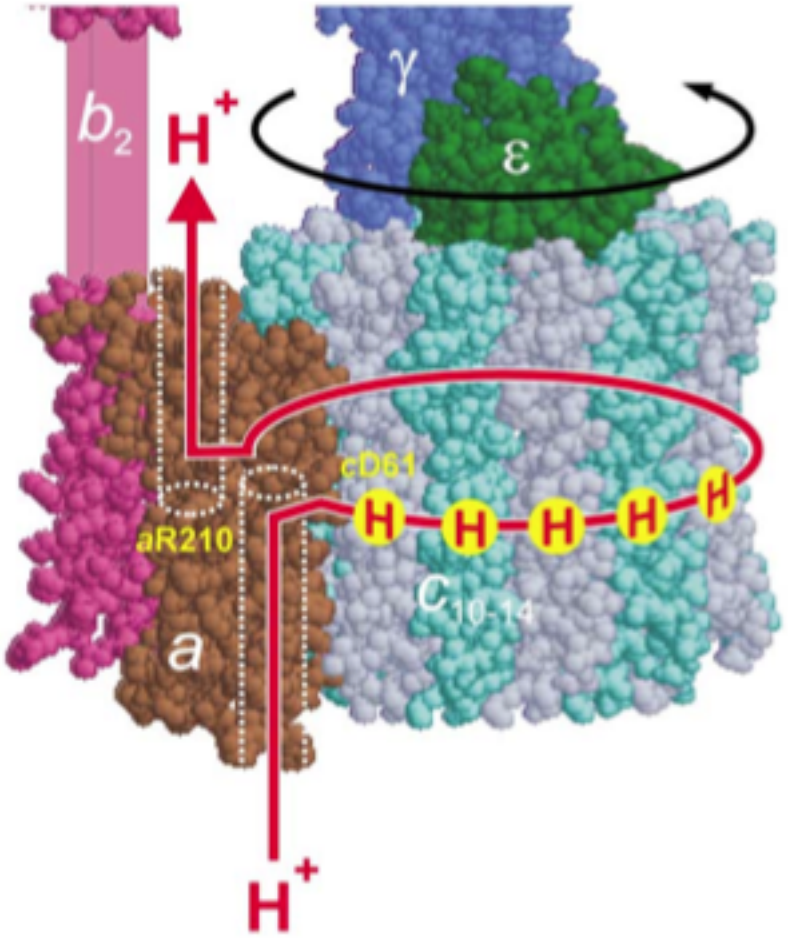
$$\Delta S^{driver} \geqslant -\Delta S^{driven}$$

Entropy is a measure of the number of particular microscopic arrangements of atoms that appear indistinguishable from a macroscopic perspective. ***Ludwig Boltzmann***

Branscomb & Russell, *Biochim Biophys Acta*, in press

The ATP synthase rotary engine

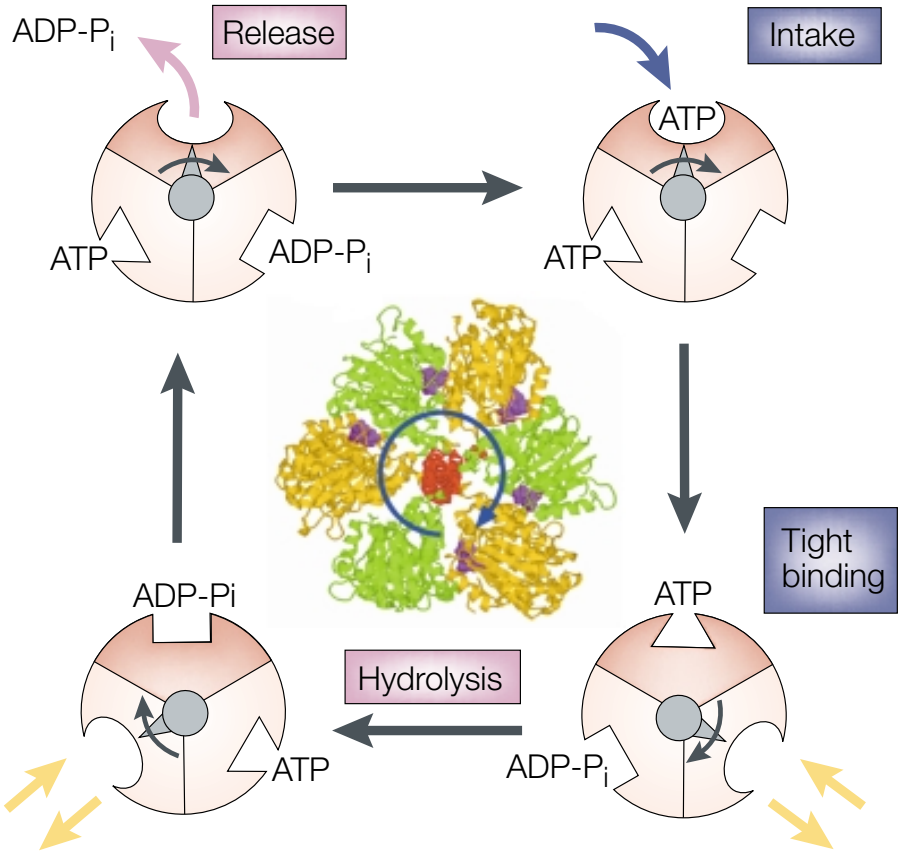




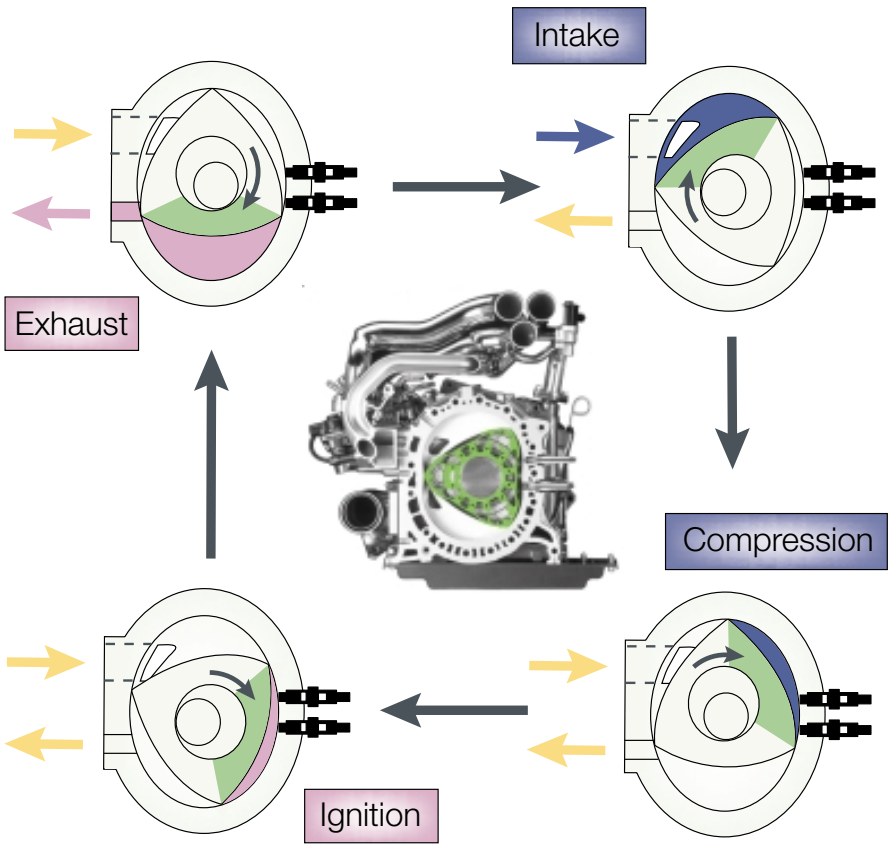
Jiang *et al.* (2001) *PNAS*, **98**, 4966-4971

Weber & Senior (2003) *FEBS*, **544**, 61-70

Box 2 | **Rotary engines in the car and in the cell**

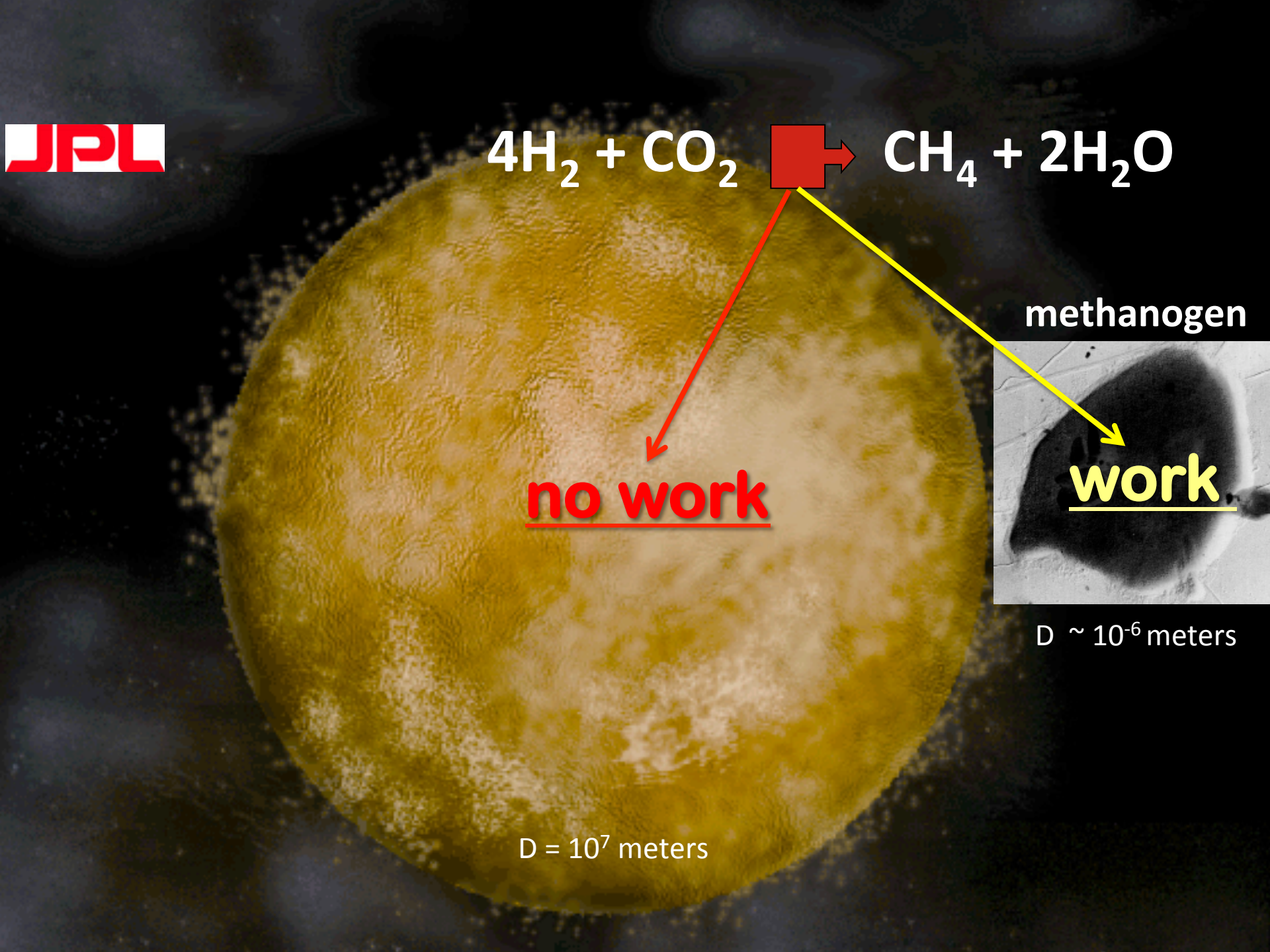


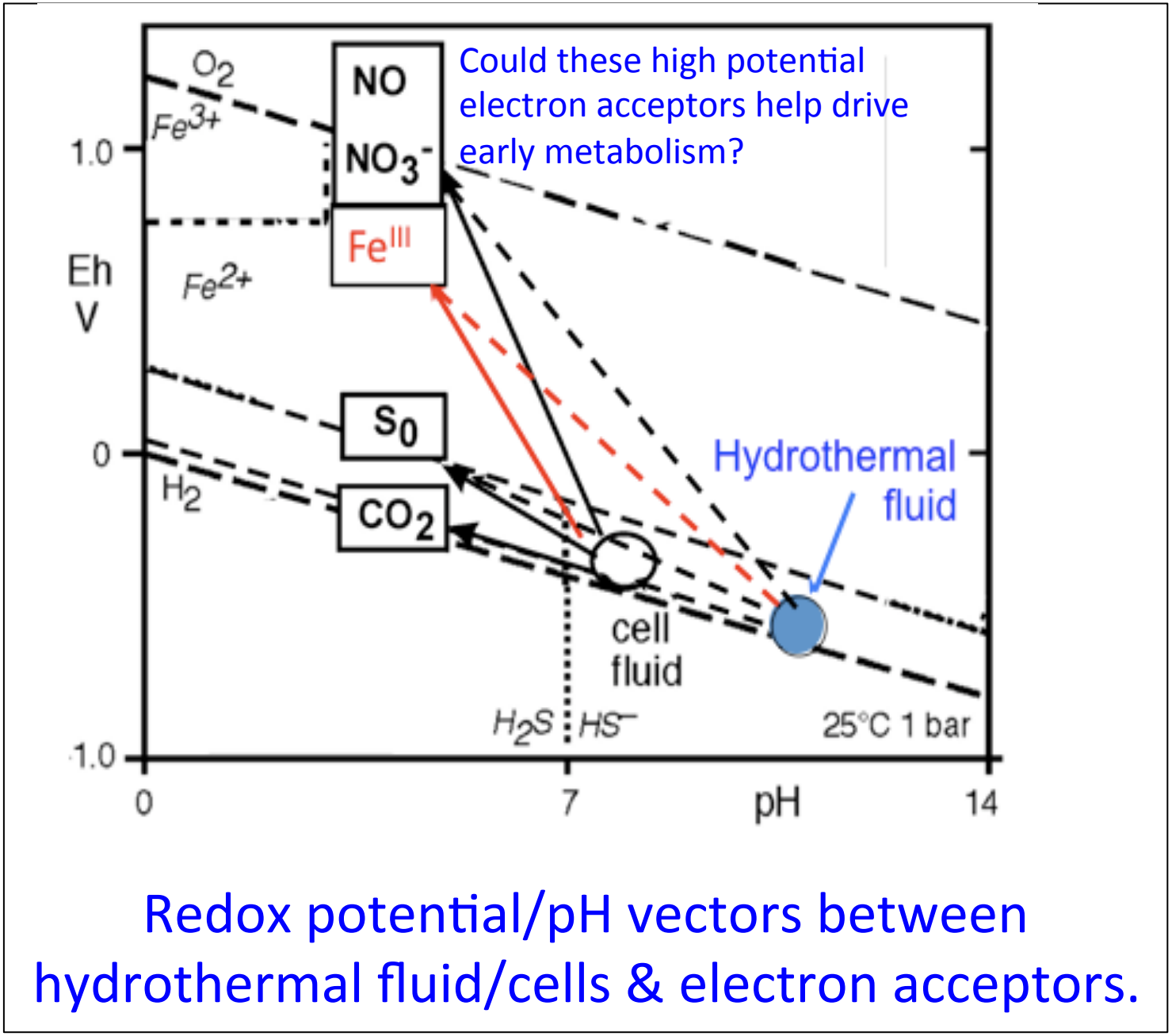
Wankel engine



ATP synthase — a marvellous rotary engine of the cell.

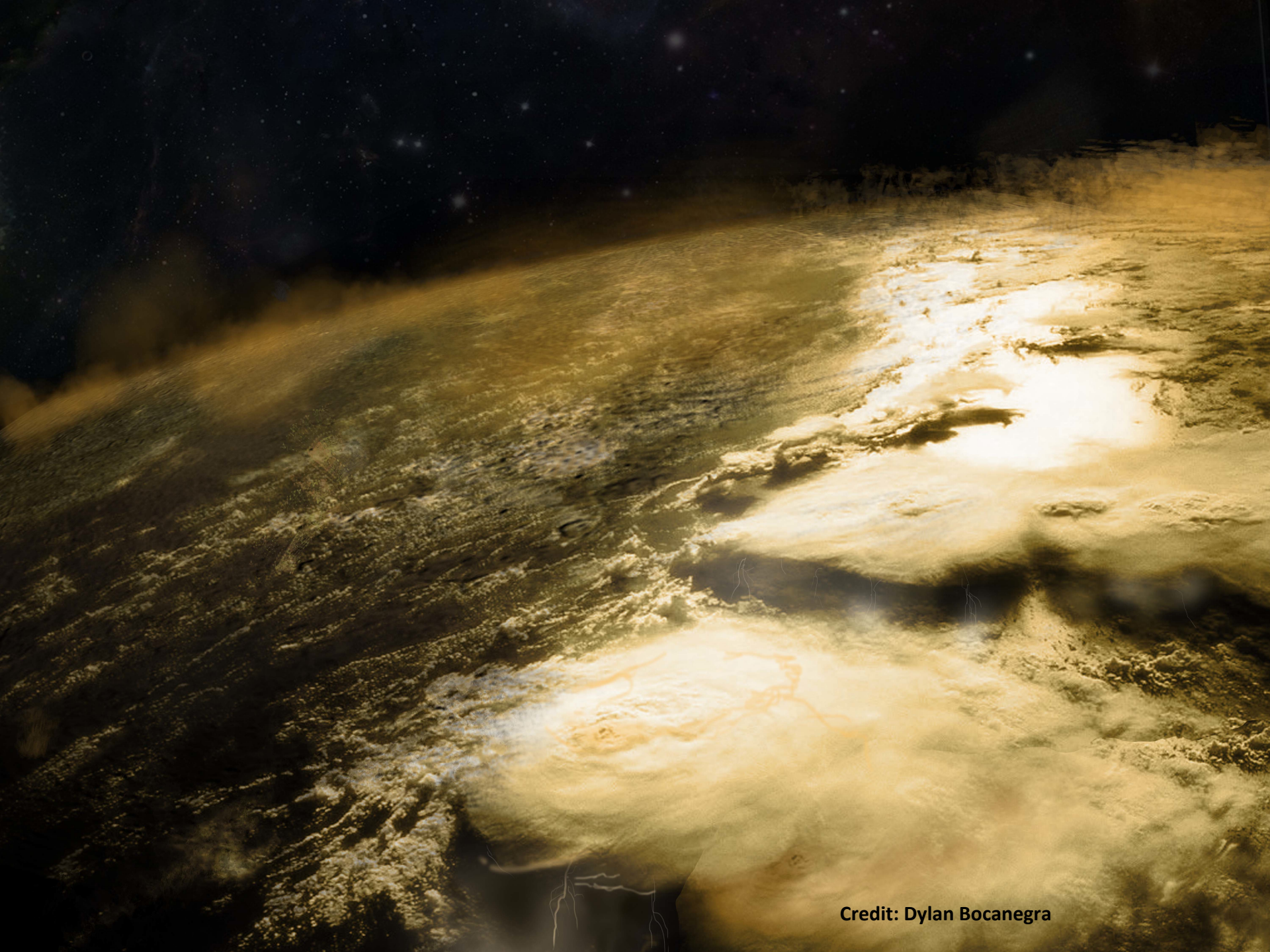
Yoshida, M., Muneyuki, E. and Hisabori, T. 2001,
Nature Reviews, Molecular Cell Biology, 2, 669-677.


$4H_2 + CO_2$
$CH_4 + 2H_2O$
methanogen
no work
work
D ~ 10^{-6} meters
D = 10^7 meters



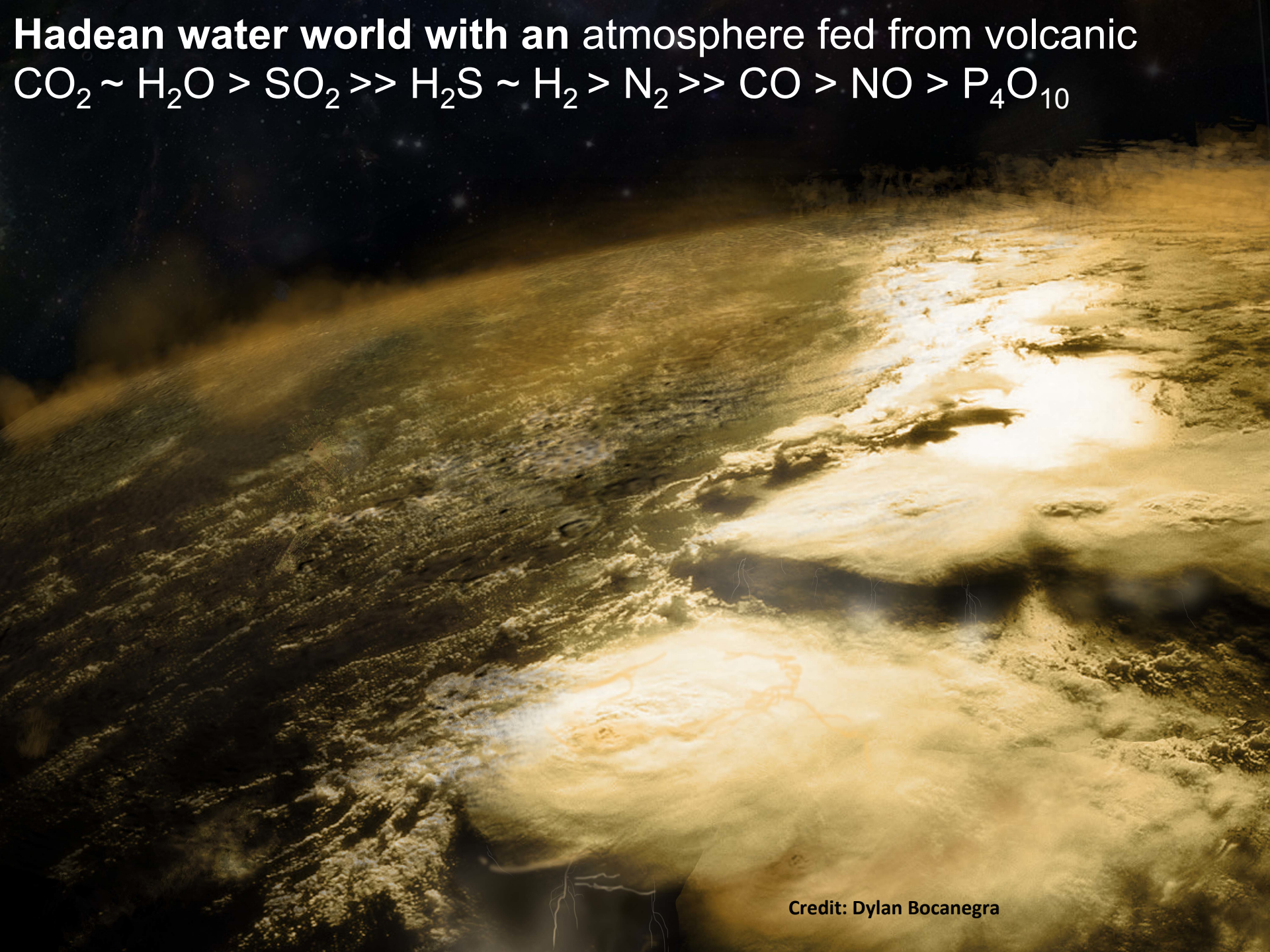
Redox potential/pH vectors between hydrothermal fluid/cells & electron acceptors.

Russell & Hall 2006 GSA Mem192, 1-32


Credit: Dylan Bocanegra

Hadean water world with an atmosphere fed from volcanic

$CO_2 \sim H_2O > SO_2 >> H_2S \sim H_2 > N_2 >> CO > NO > P_4O_{10}$

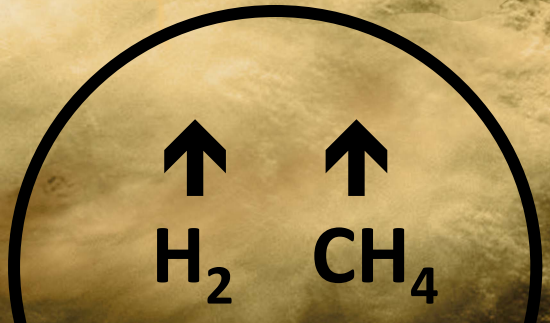


Credit: Dylan Bocanegra

$CO_2 \sim H_2O > SO_2 >> H_2S \sim H_2 > N_2 >> CO > NO > P_4O_{10}$

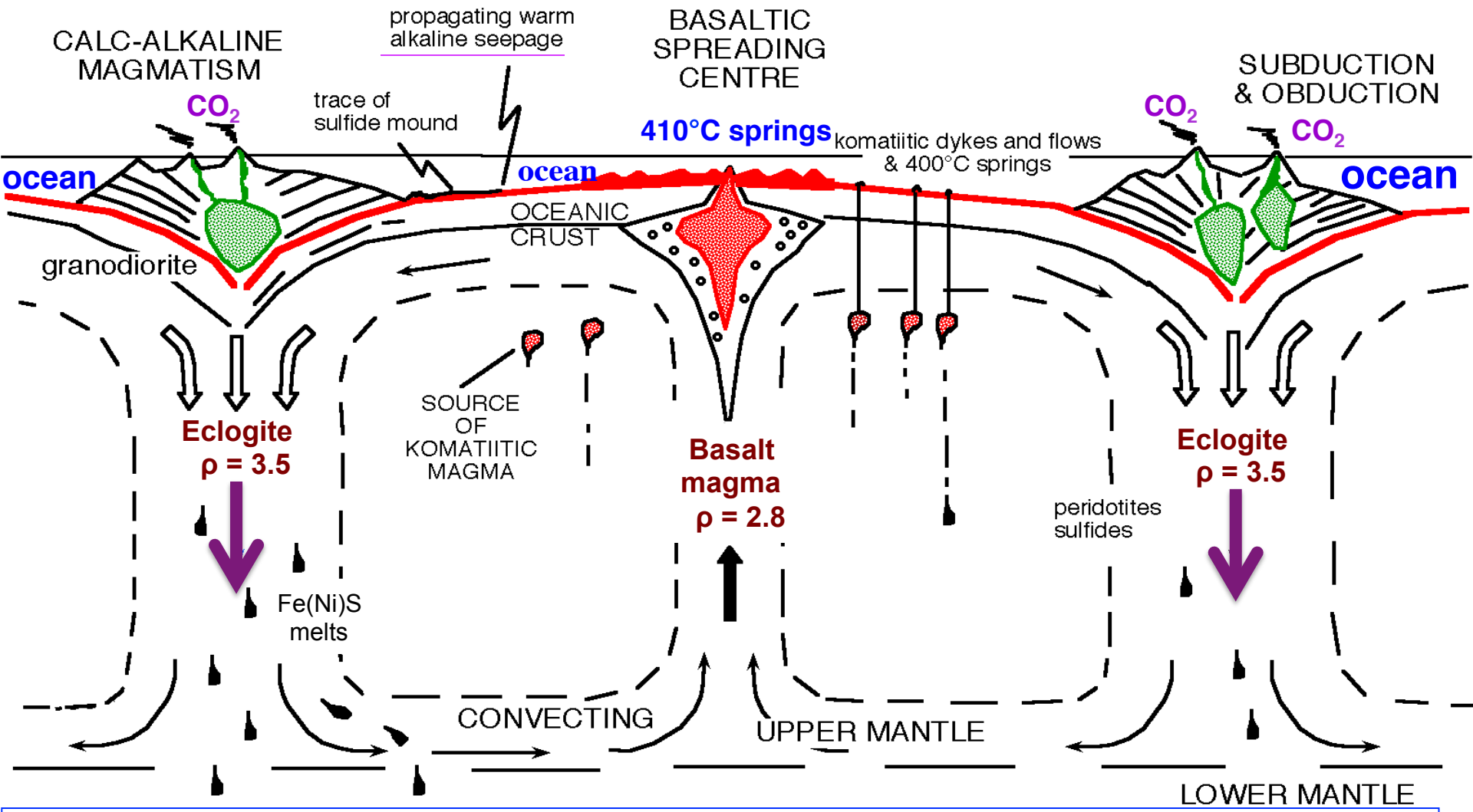
"The lab"

Prebiotic molecules



Autocatalytic mantle convection engine @ 4.4Ga

1 - 10 bars of CO_2



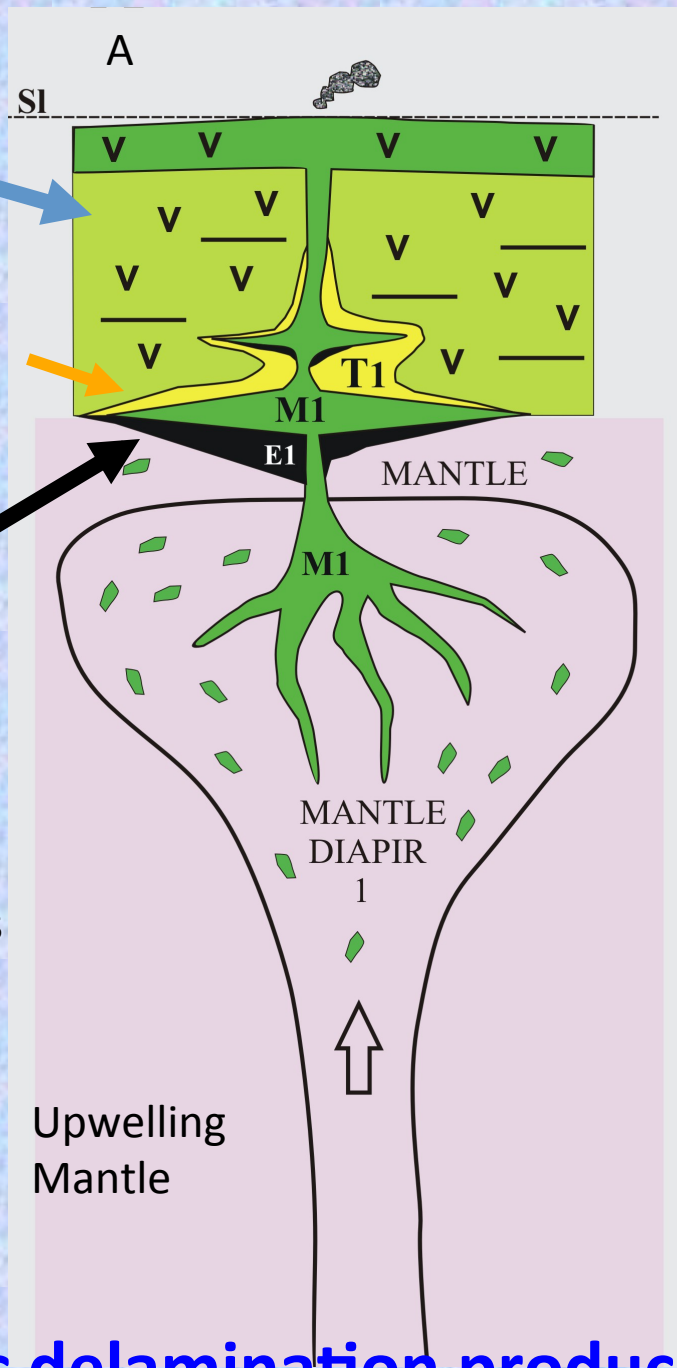
Russell & Hall 2006 GSA Mem192, 1-32, after Holmes 1931 Trans Geol Soc Glasgow 18, 559

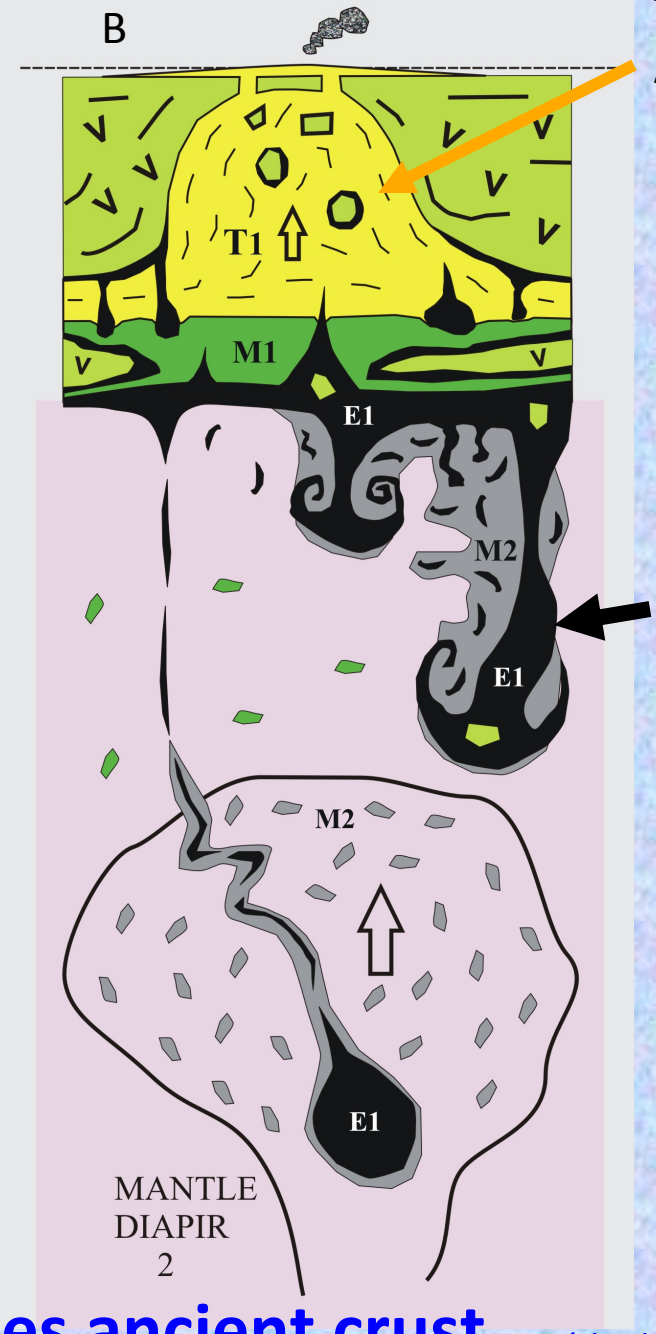
Thick Oceanic Plateau

Tonalitic Anatectites

Eclogitic Restites

Melt 1 Segregates Ascends & Underplates





Tonalitic Anatectites Rise (PCO)

Eclogitic Restites Delaminate Mix = Melt 2

Catalytic delamination produces ancient crust

Bédard 2006 *GCA* **70**, 1188

Abstract thermodynamics of a free energy converter: - a generalized "Atwood machine"

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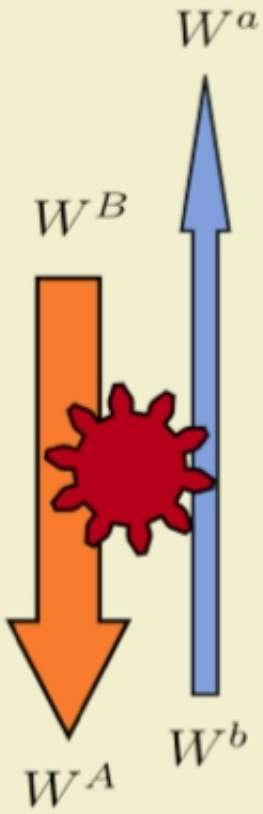

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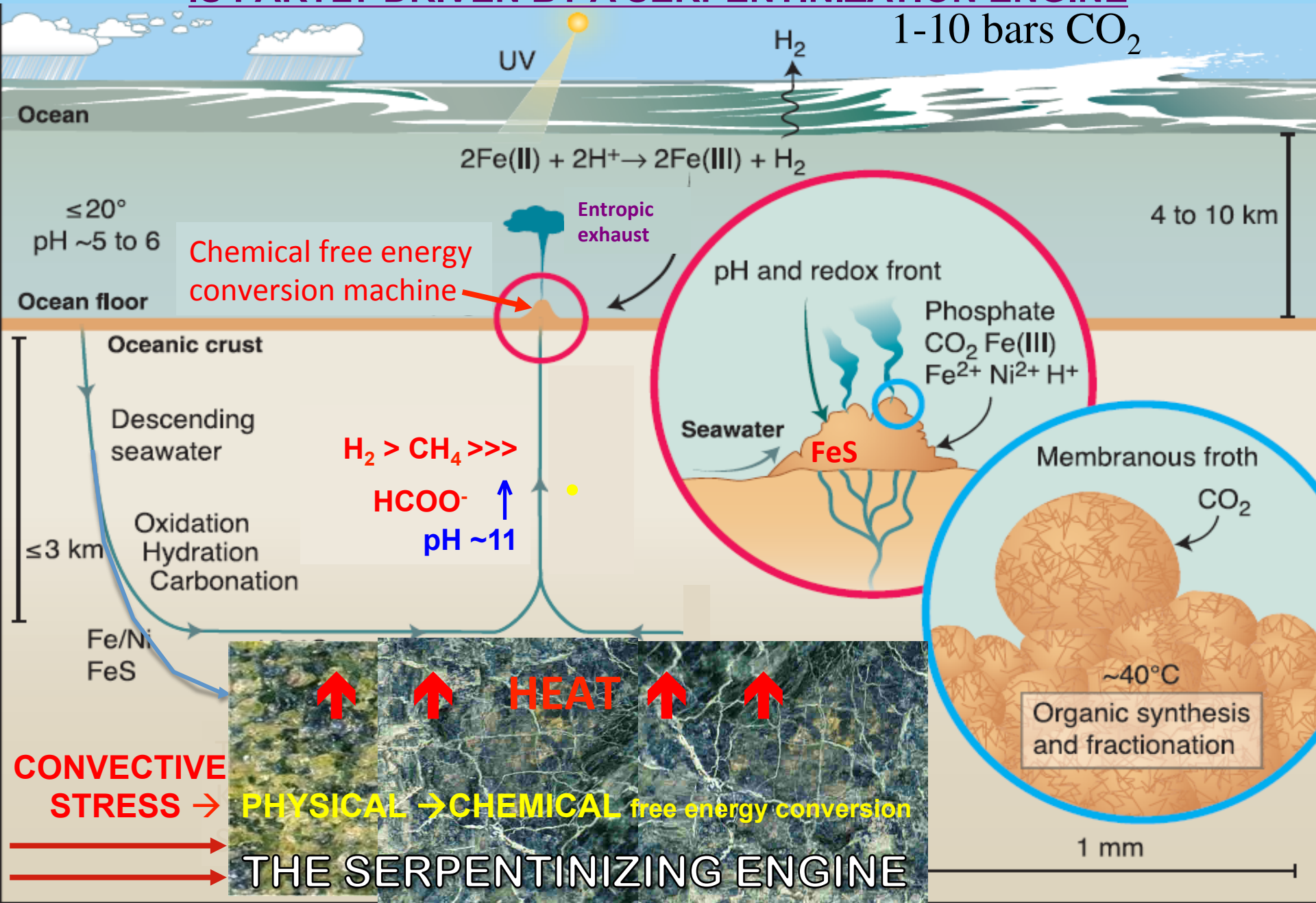
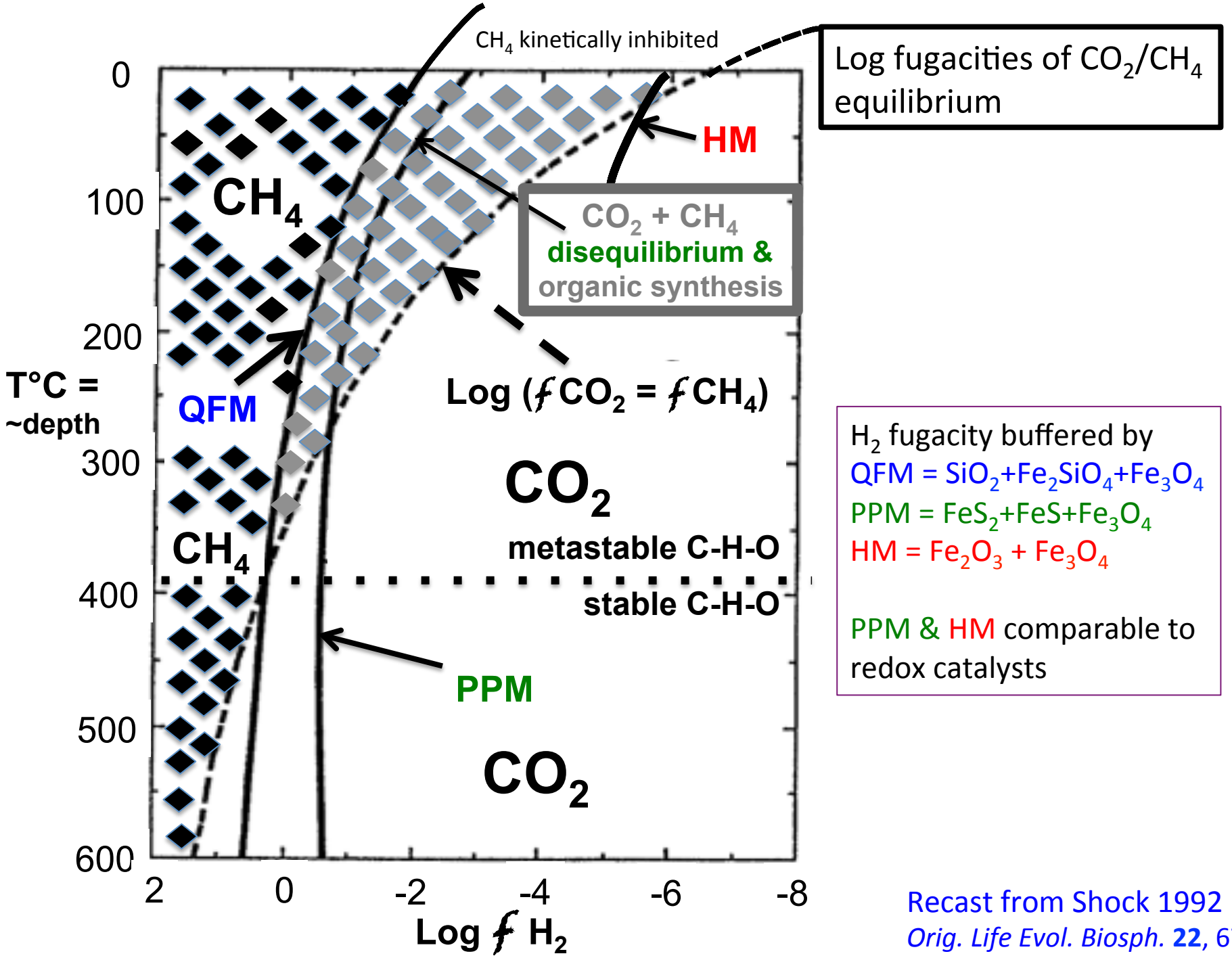
Branscomb & Russell, *Biochim Biophys Acta*, in press

MODERATE TEMPERATURE HYDROTHERMAL CONVECTION IS PARTLY DRIVEN BY A SERPENTINIZATION ENGINE

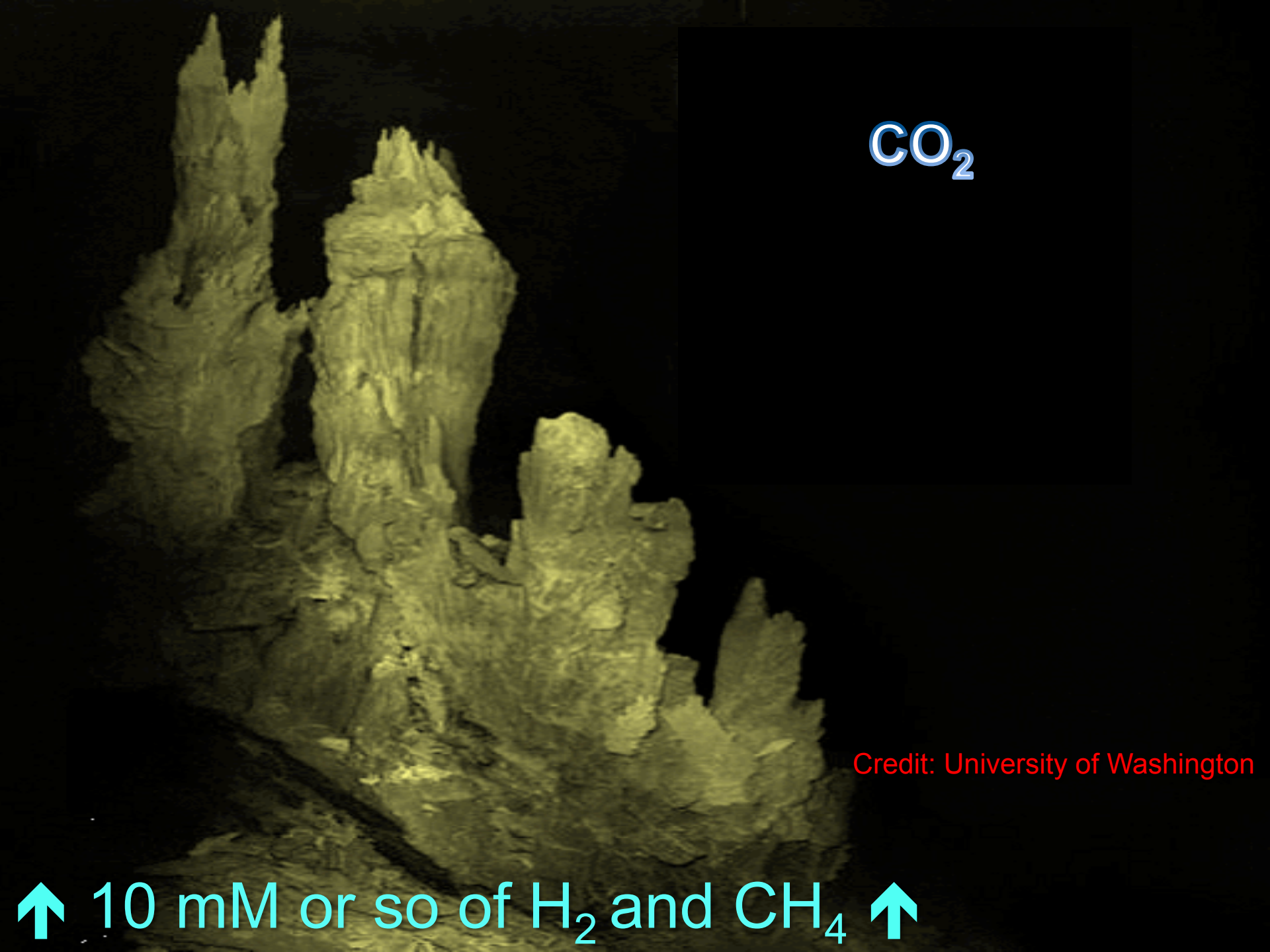


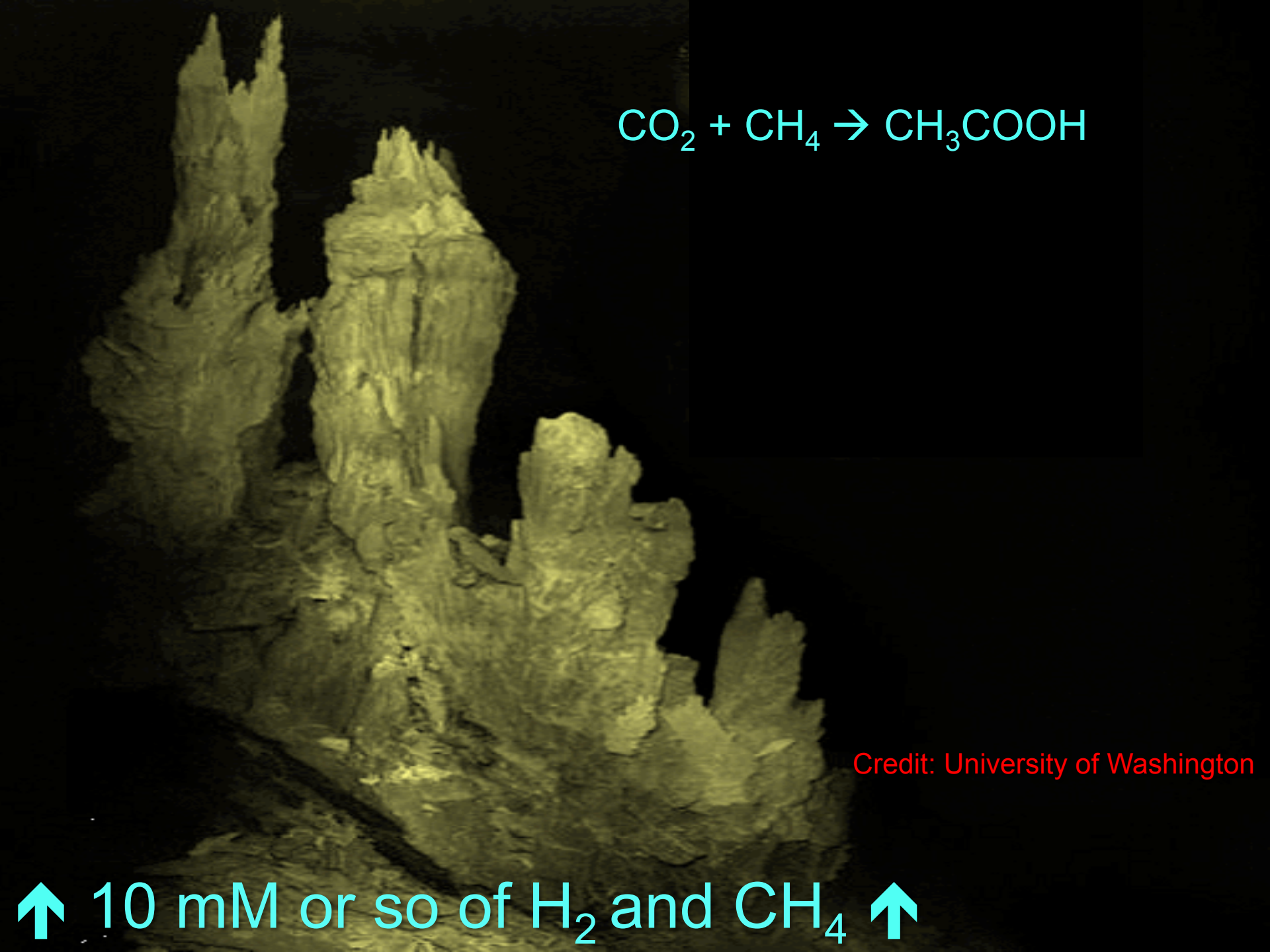


H_2 fugacity buffered by
QFM = SiO_2+Fe_2SiO_4+Fe_3O_4
PPM = FeS_2+FeS+Fe_3O_4
HM = Fe_2O_3 + Fe_3O_4

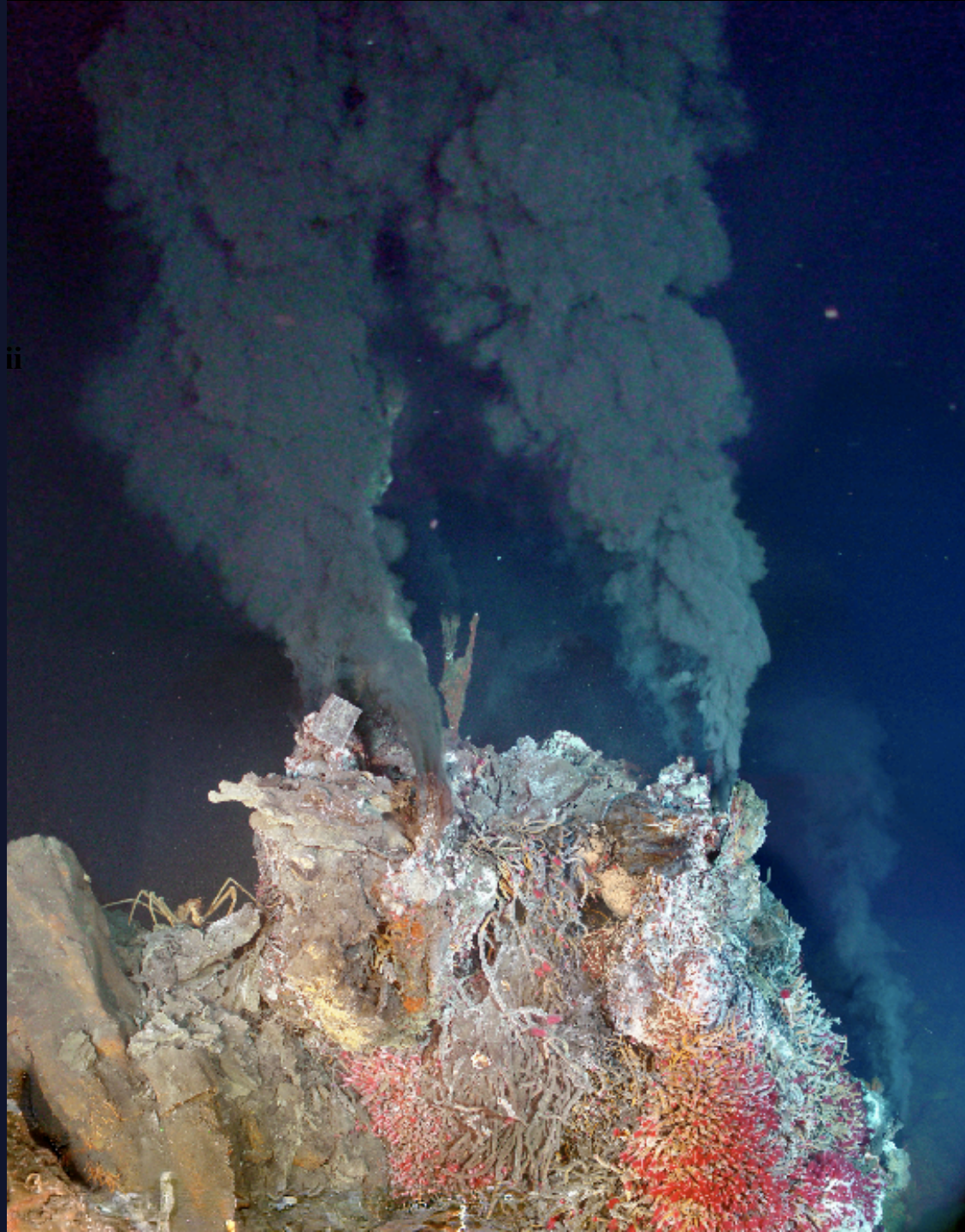
PPM & HM comparable to redox catalysts

Recast from Shock 1992
Orig. Life Evol. Biosph. **22**, 67


CO_2
Credit: University of Washington
↑ 10 mM or so of H_2 and CH_4 ↑

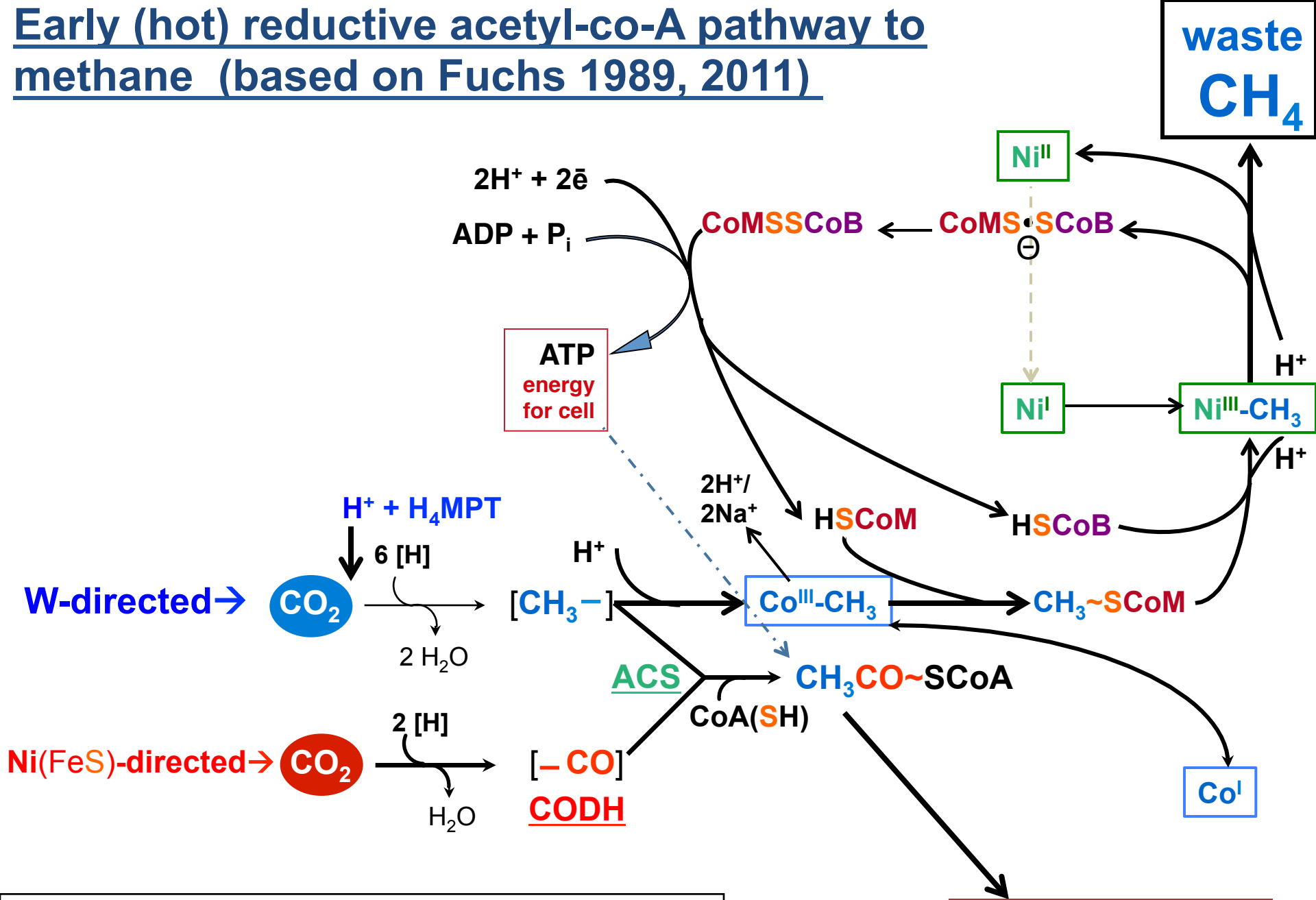

$CO_2 + CH_4 \rightarrow CH_3COOH$
Credit: University of Washington
↑ 10 mM or so of H_2 and CH_4 ↑

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

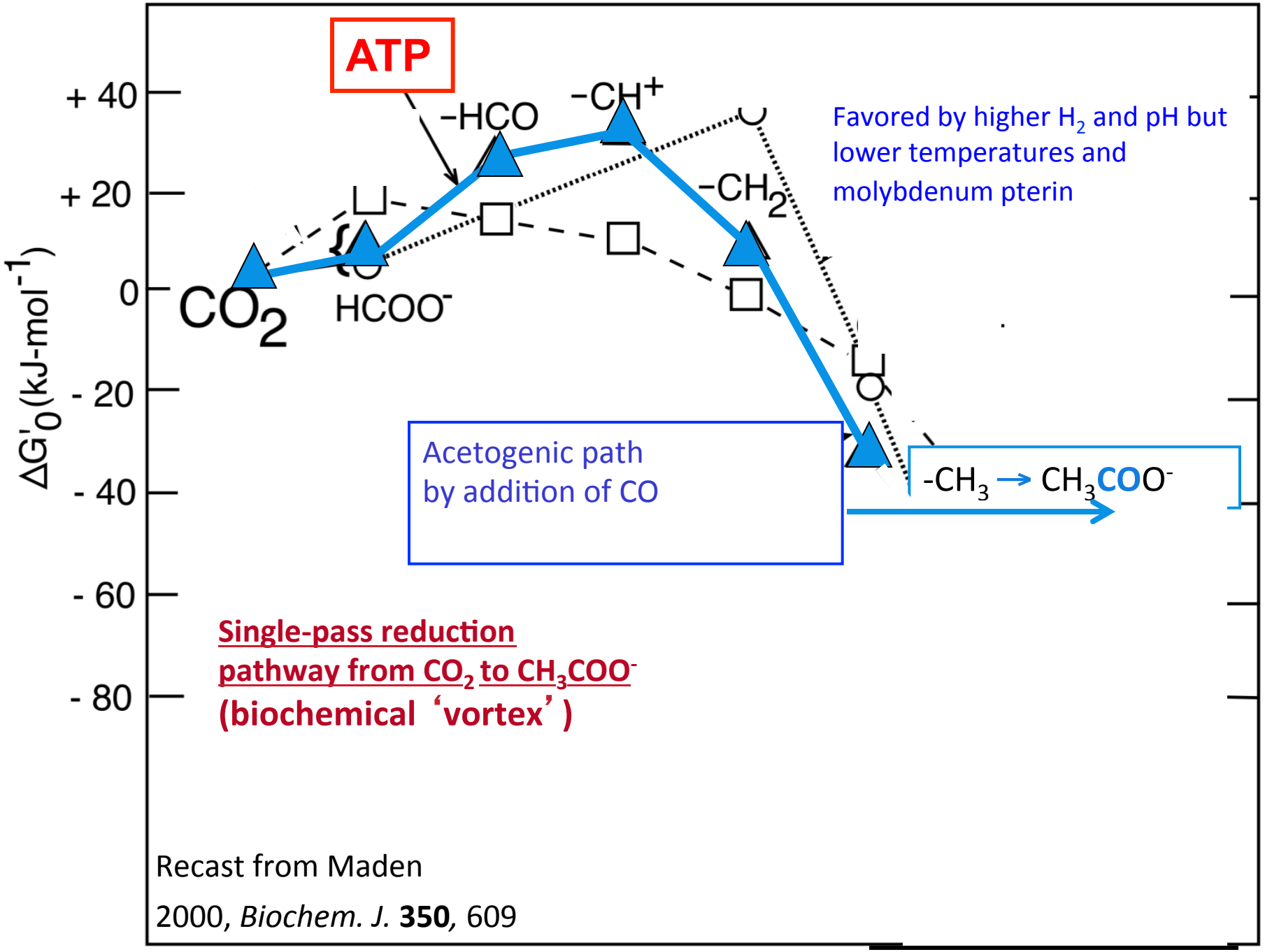


Endeavor, NE Pacific
Credit: Delaney & Kelley

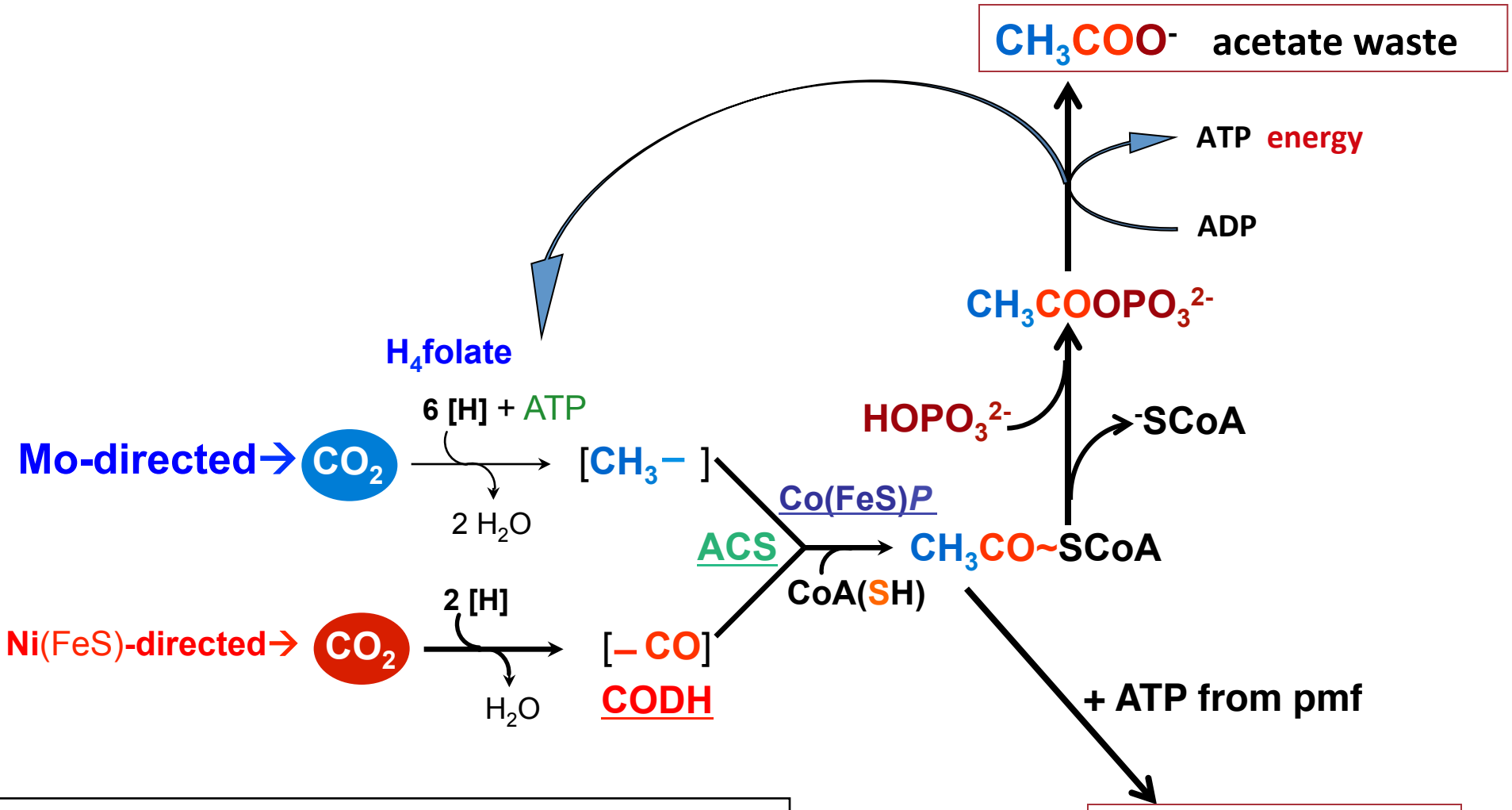
Early (hot) reductive acetyl-co-A pathway to methane (based on Fuchs 1989, 2011)



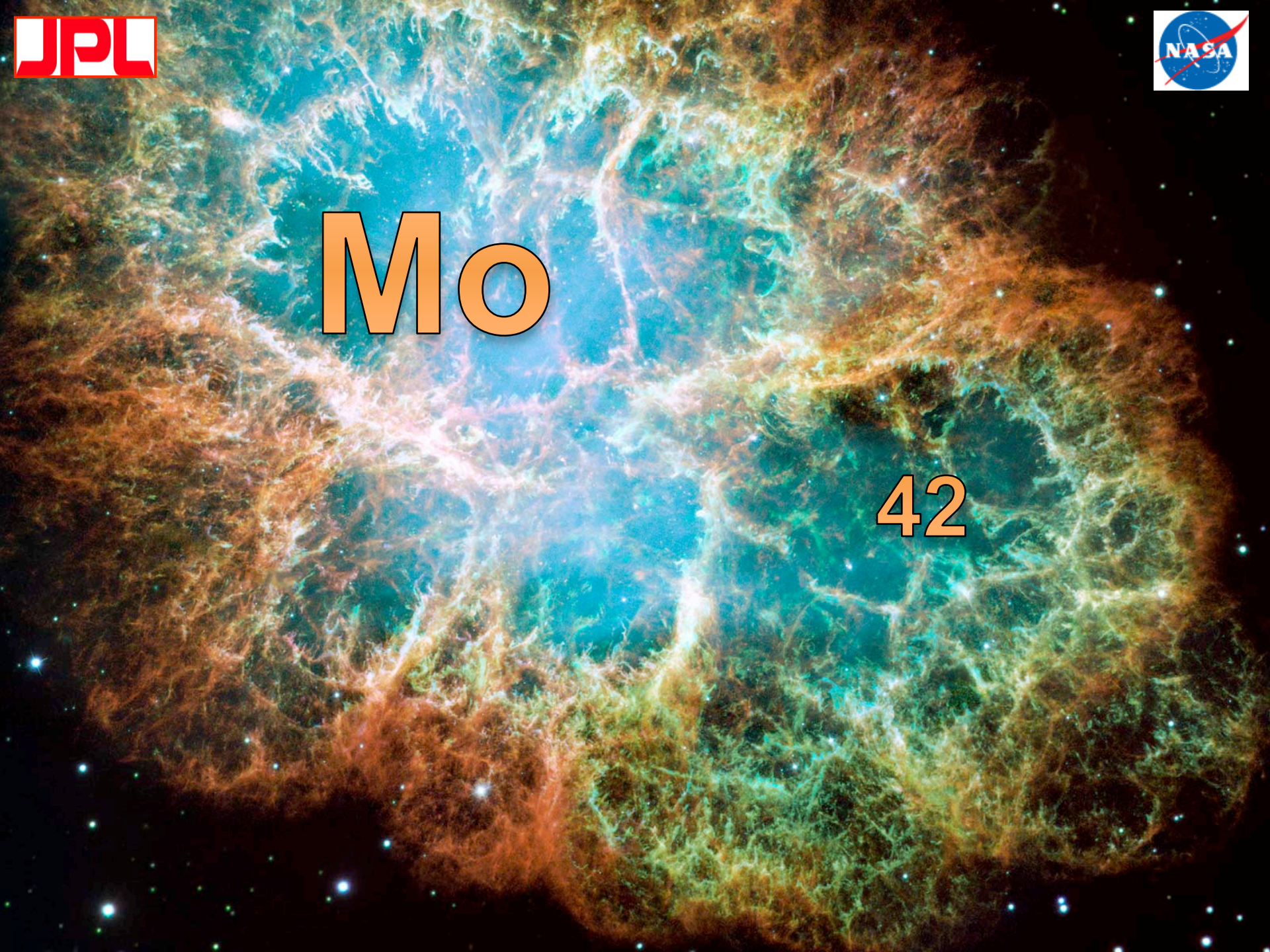
Grabarse et al. 2001, J Mol Biol 309, 315 &
Fuchs, G. 1989, *in* Autotrophic Bacteria 365


ATP
+ 40
+ 20
0
- 20
- 40
- 60
- 80
$\Delta G'_0$(kJ-mol^{-1})
CO_2
-HCO
$HCOO^-$
$-CH^+$
$-CH_2$
Favored by higher H_2 and pH but lower temperatures and molybdenum pterin
Acetogenic path by addition of CO
$-CH_3 \rightarrow CH_3COO^-$
Single-pass reduction pathway from CO_2 to CH_3COO^- (biochemical 'vortex')
Recast from Maden 2000, *Biochem. J.* **350**, 609

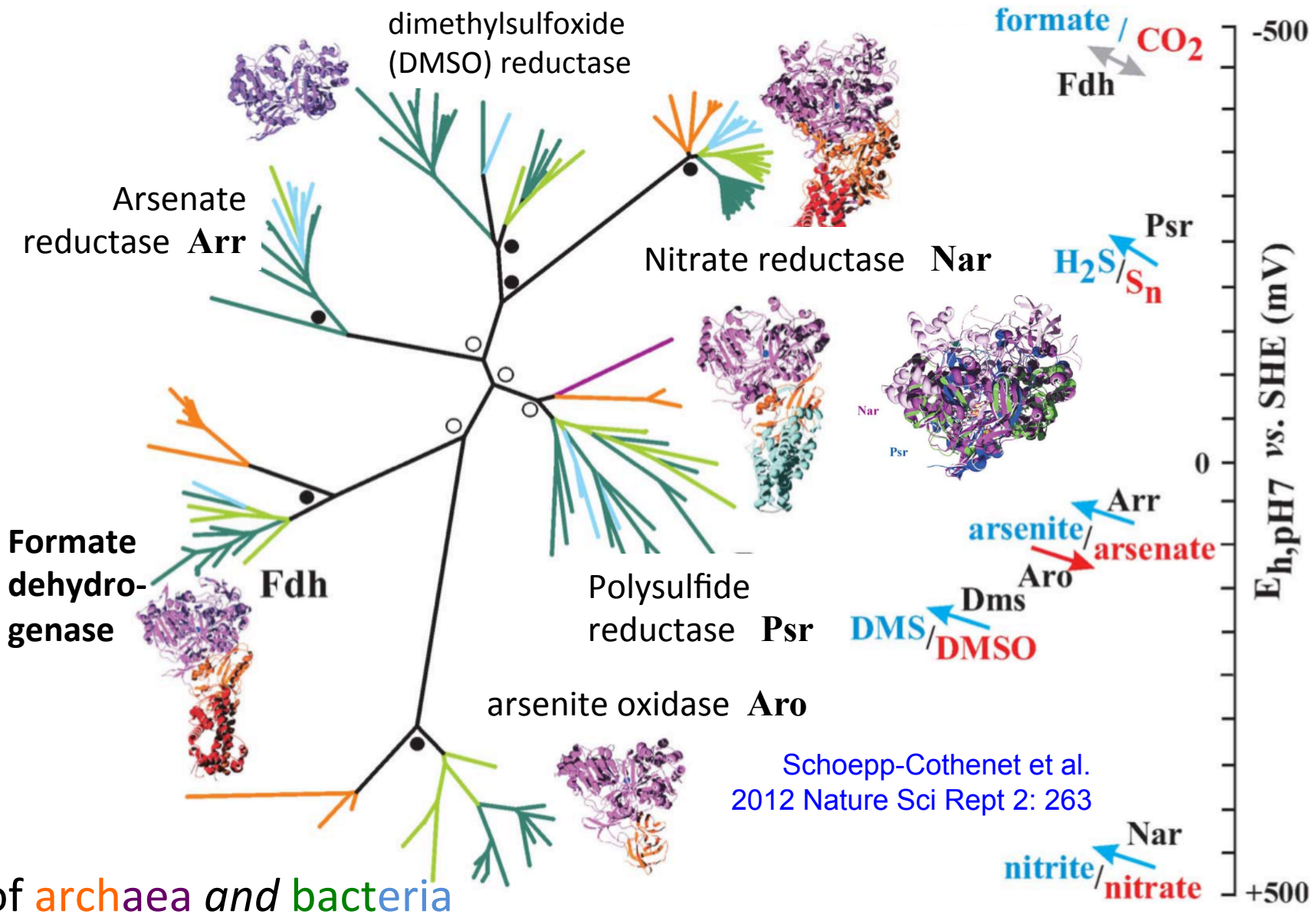
Reductive acetyl-co-A pathway to acetate



Fuchs, G. 1989, *in* Autotrophic Bacteria, Schlegel & Bowien, WI, Science Tech.

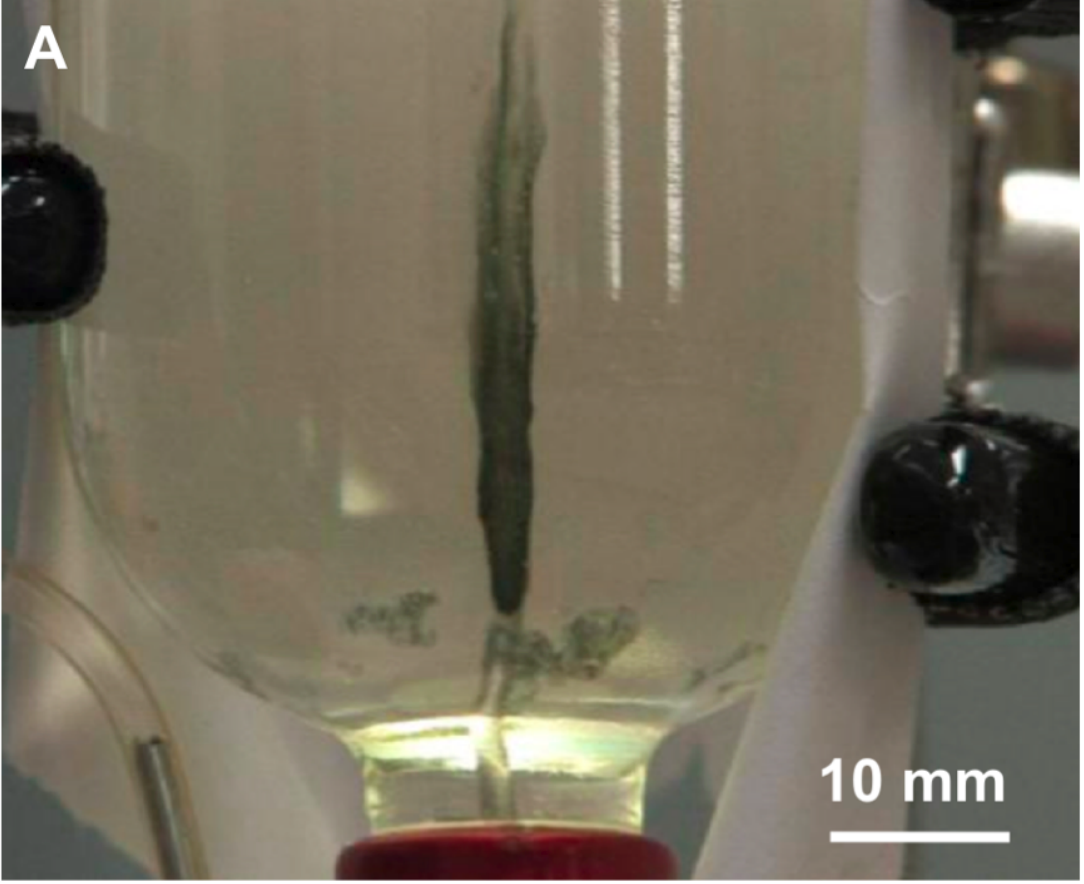

Mo
42

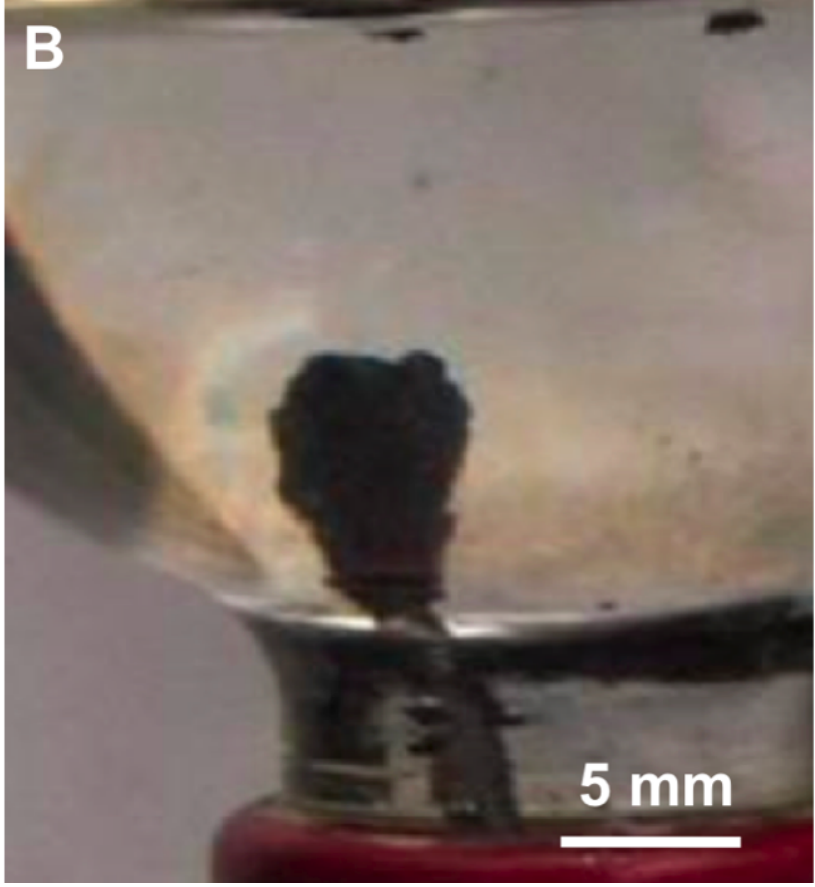
Phylogenetic tree of the **C**omplex **I**ron **S**ulfur **M**olybdenum enzymes



Schoepp-Cothenet et al.
2012 Nature Sci Rept 2: 263

of archaea *and* bacteria





A. Rapid injection of reactor effluent into 'Hadean Ocean' favors inorganic chimney growth
B. Slow injection rate favors inorganic bubbles and geodes

Both precipitates are a mixture of hydrosilicates, ferrous hydroxide and minor FeS (mackinawite)

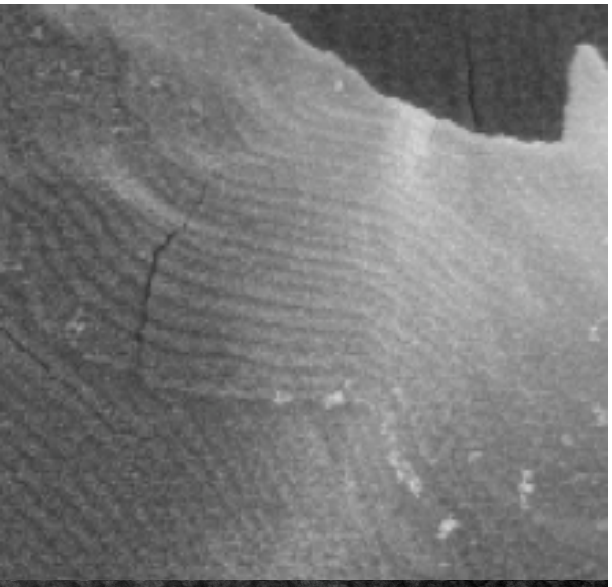
Mielke et al. 2010 Astrobiology 10, 799-810

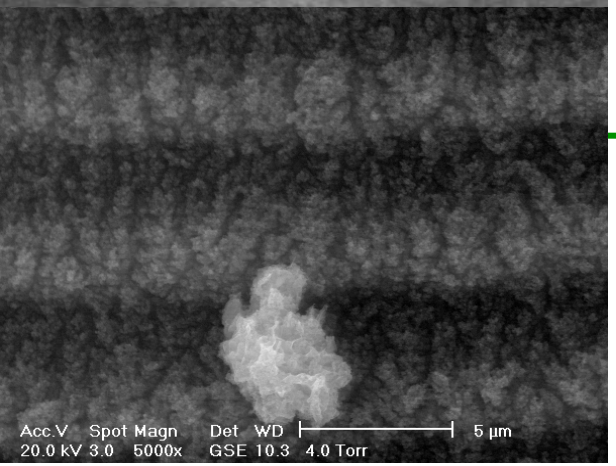
NAI

JPL

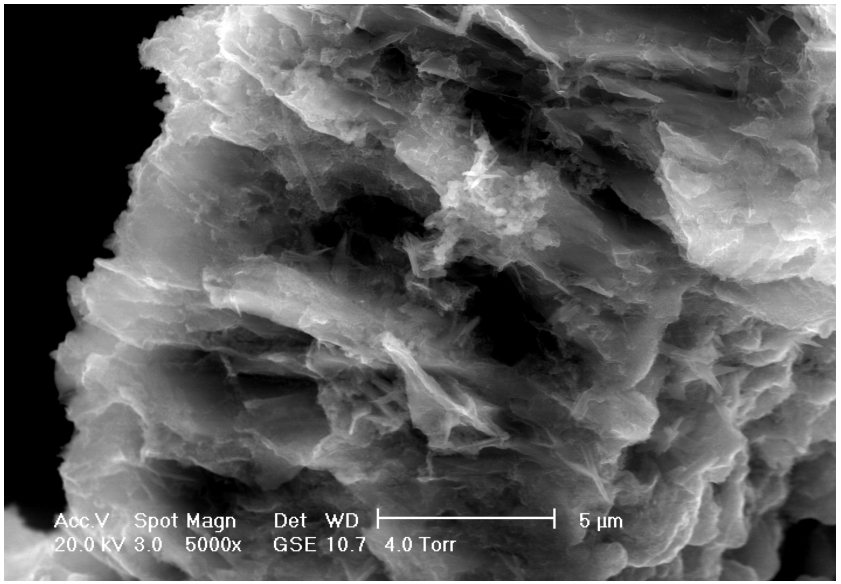
Inorganic membrane structure and composition

$Fe(OH)_2$ flanges to exterior

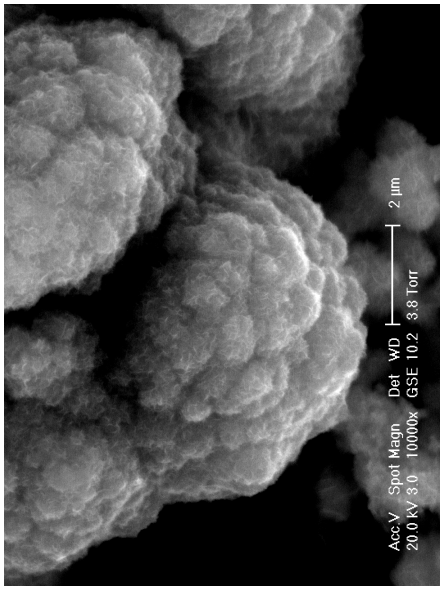




Porous cross-section of FeS & $Fe(OH)_2$



Internal Fe_3S_4 framboids

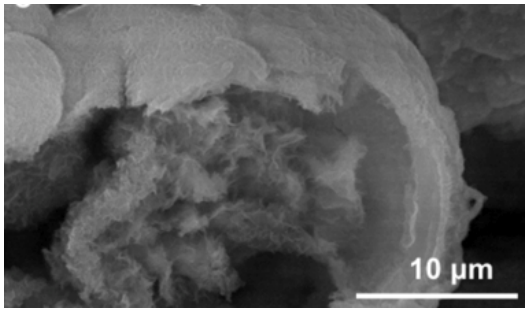


$Fe(OH)_2$ ← **alkaline flow**

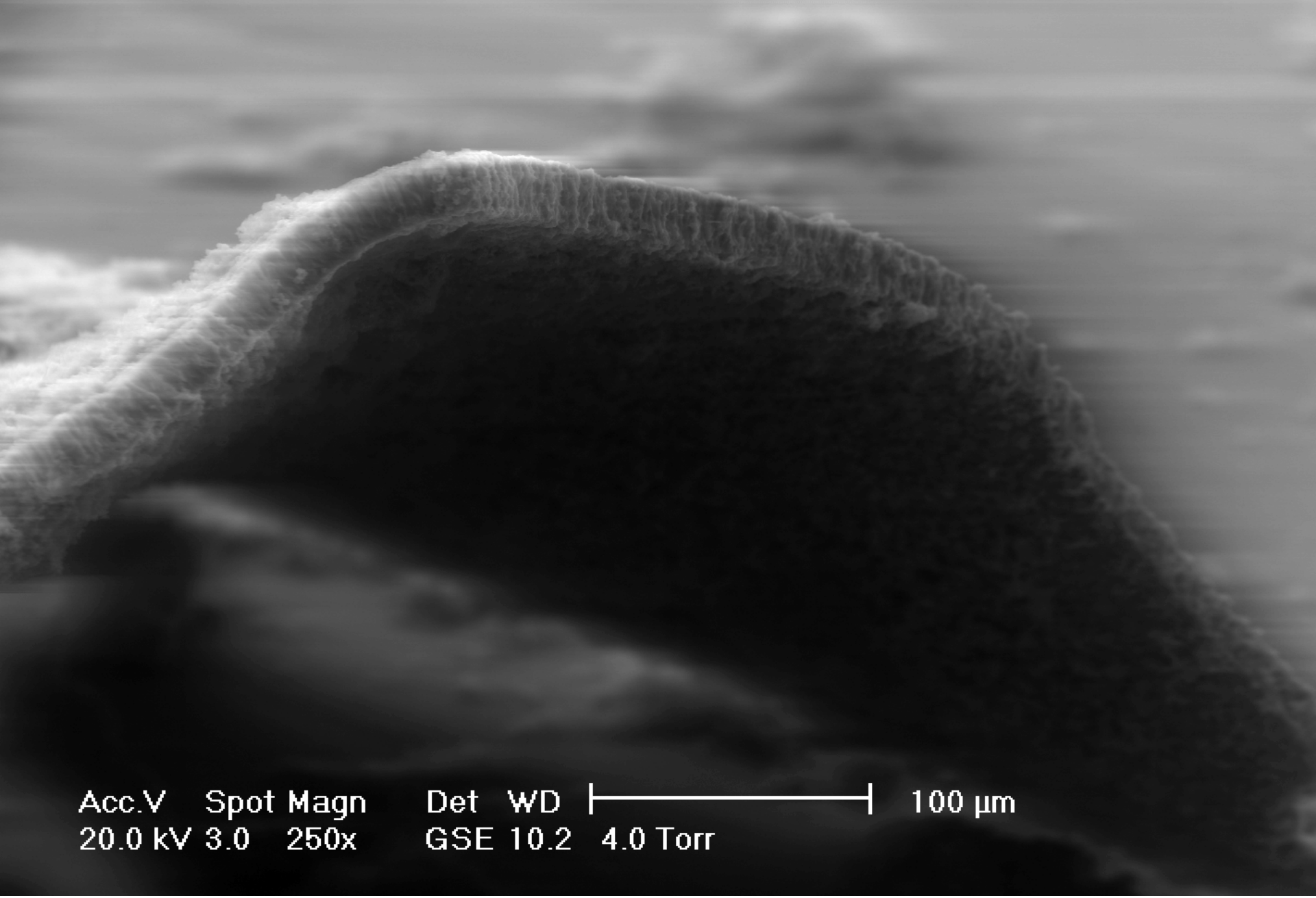
central divider, $Fe(OH)_2$/FeS — Steep gradients

acidic counterflow → **framboids**

Two-way transport

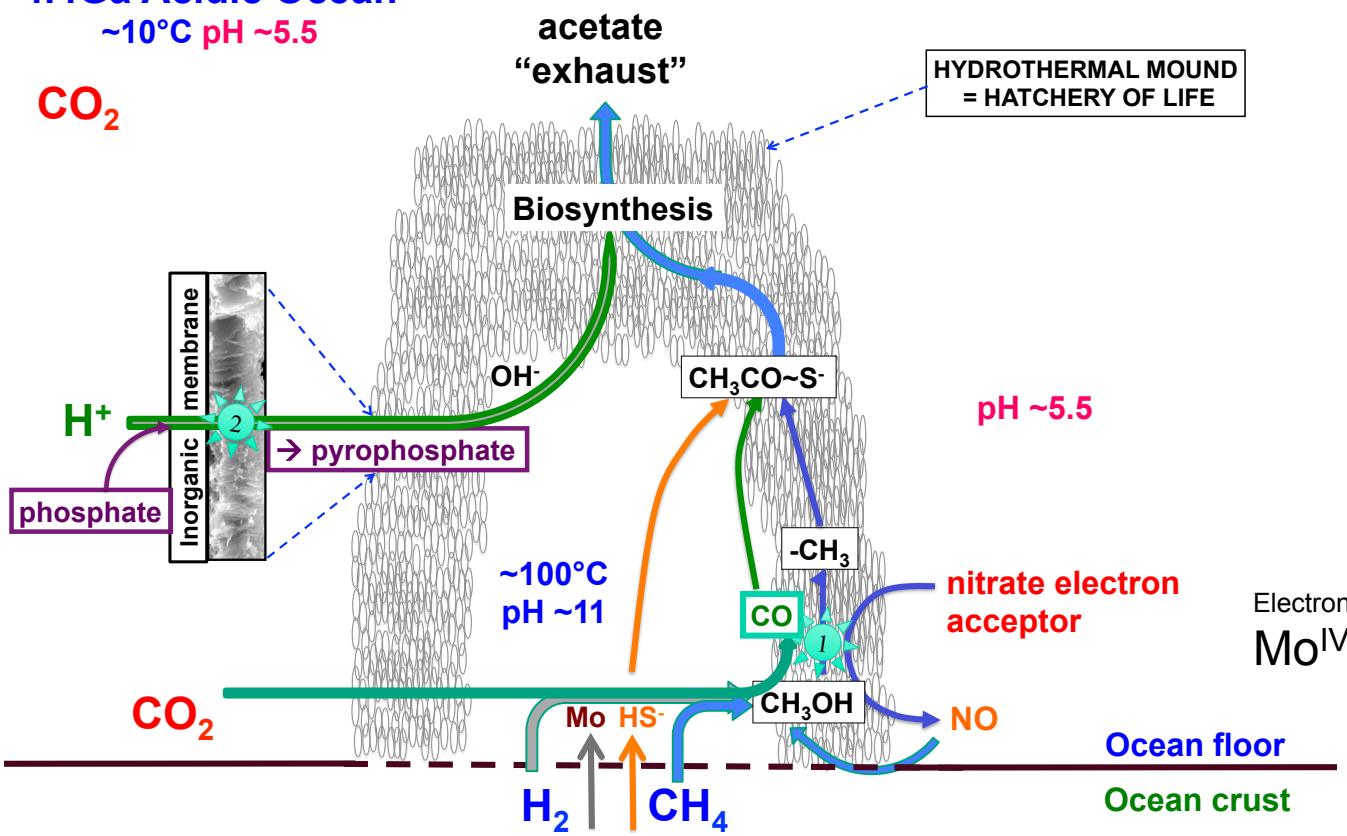


Large porous membrane structure prefigures the first biofilms?


Acc.V Spot Magn Det WD 100 µm
20.0 kV 3.0 250x GSE 10.2 4.0 Torr

4.4Ga Acidic Ocean

~10°C pH ~5.5



Electron bifurcation cluster

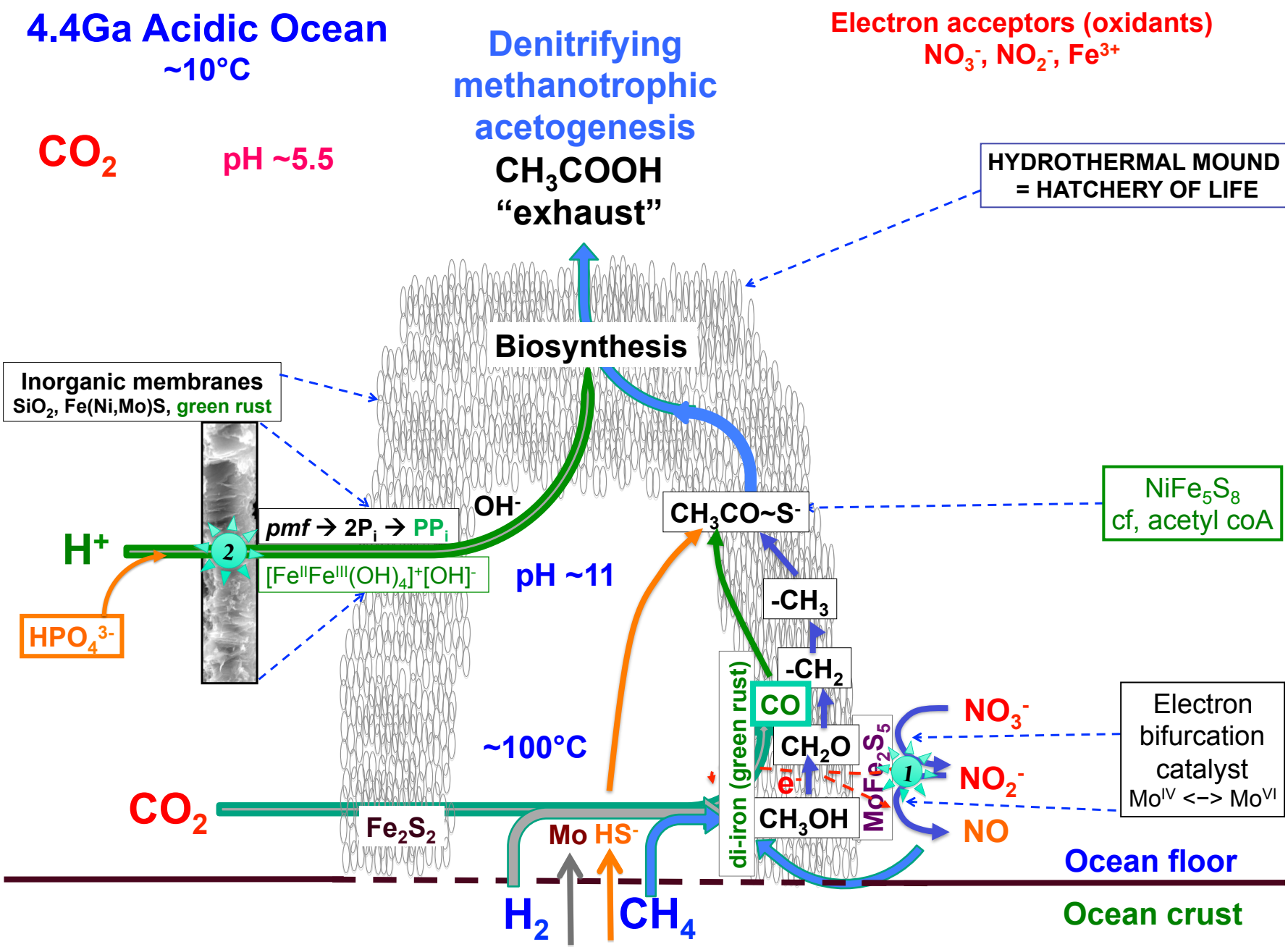
$Mo^{IV/VI}{}_2Fe_3S^{0/2-}{}_9$

Serpentinization produces electron donors in alkaline hydrothermal fluid

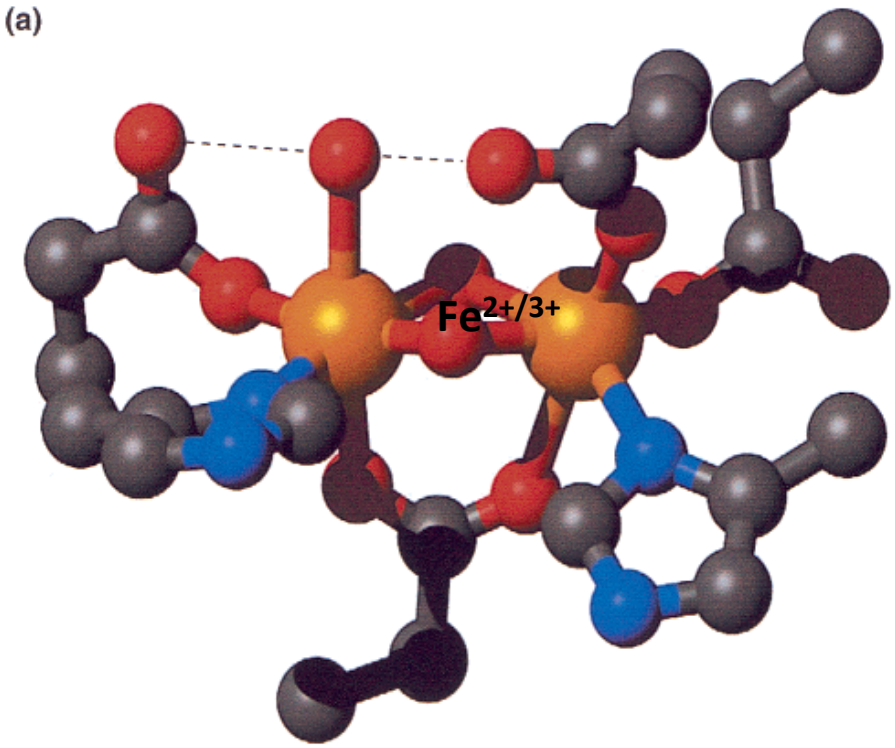
Chemical free energy (*disequilibria*) derived from serpentinization

Physical free energy from the mantle convection engine

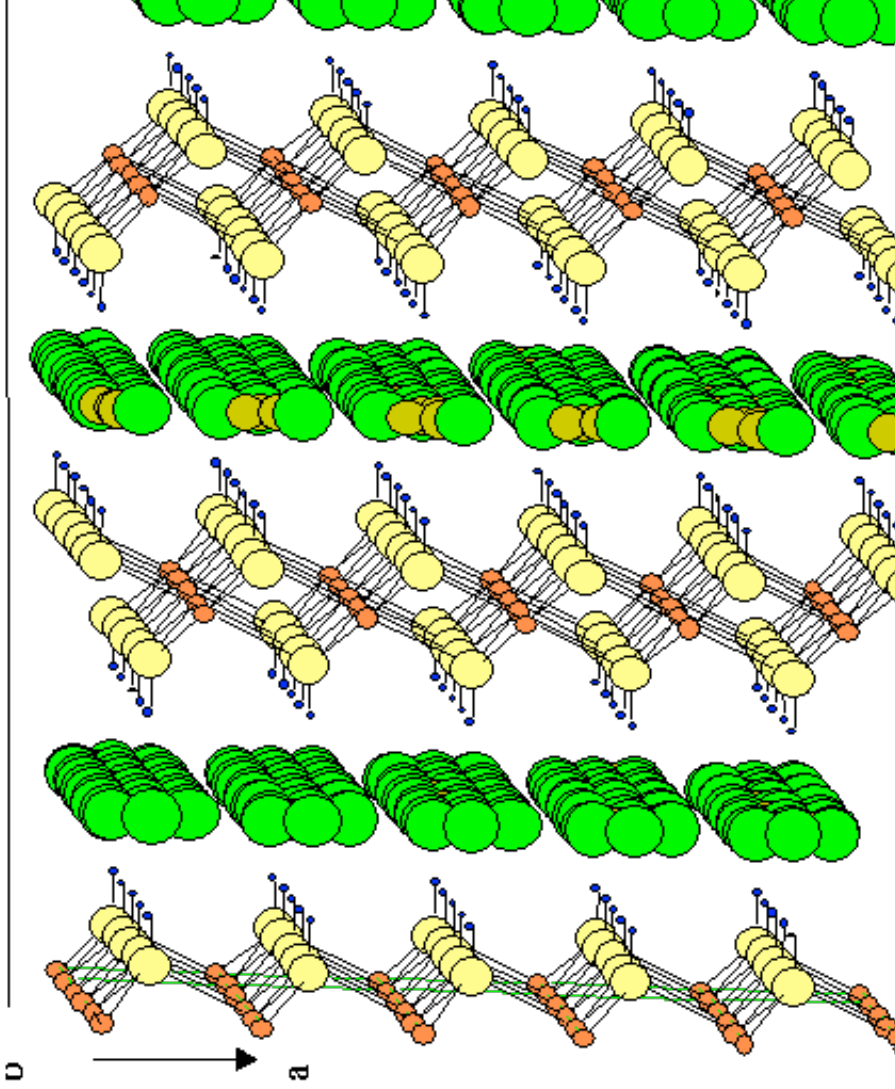
Russell, Nitschke, Branscomb
Trans R Soc London, in press


4.4Ga Acidic Ocean
~10°C
Denitrifying methanotrophic acetogenesis
Electron acceptors (oxidants)
NO_3^-, NO_2^-, Fe^{3+}
CO_2
pH ~5.5
CH_3COOH "exhaust"
HYDROTHERMAL MOUND = HATCHERY OF LIFE
Biosynthesis
Inorganic membranes
SiO_2, Fe(Ni,Mo)S, green rust
$NiFe_5S_8$ cf, acetyl coA
H^+
HPO_4^{3-}
pmf → $2P_i$ → PP_i
$[Fe^{II}Fe^{III}(OH)_4]^+[OH]^-$
OH^-
pH ~11
$CH_3CO{\sim}S^-$
$-CH_3$
$-CH_2$
CO
CH_2O
CH_3OH
di-iron (green rust)
$MoFe_2S_5$
e^-
NO_3^-
NO_2^-
NO
Electron bifurcation catalyst
Mo^{IV} <–> Mo^{VI}
~100°C
CO_2
Fe_2S_2
Mo HS^-
H_2
CH_4
Ocean floor
Ocean crust
Serpentinization produces electron donors in alkaline hydrothermal fluid

Methane Monooxygenase



Baik et al. *Chem. Rev.* **2003,** *103,* 2385

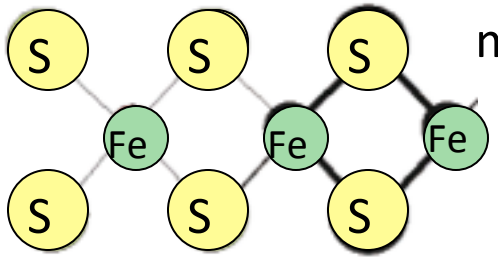


Green Rust

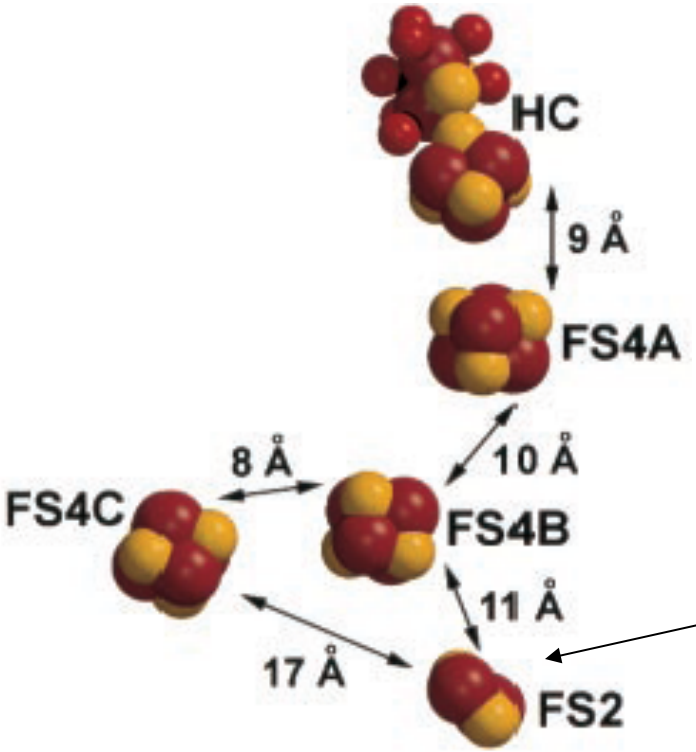
~$[Fe^{II}Fe^{III}(OH)_4]^+[OH]^-$

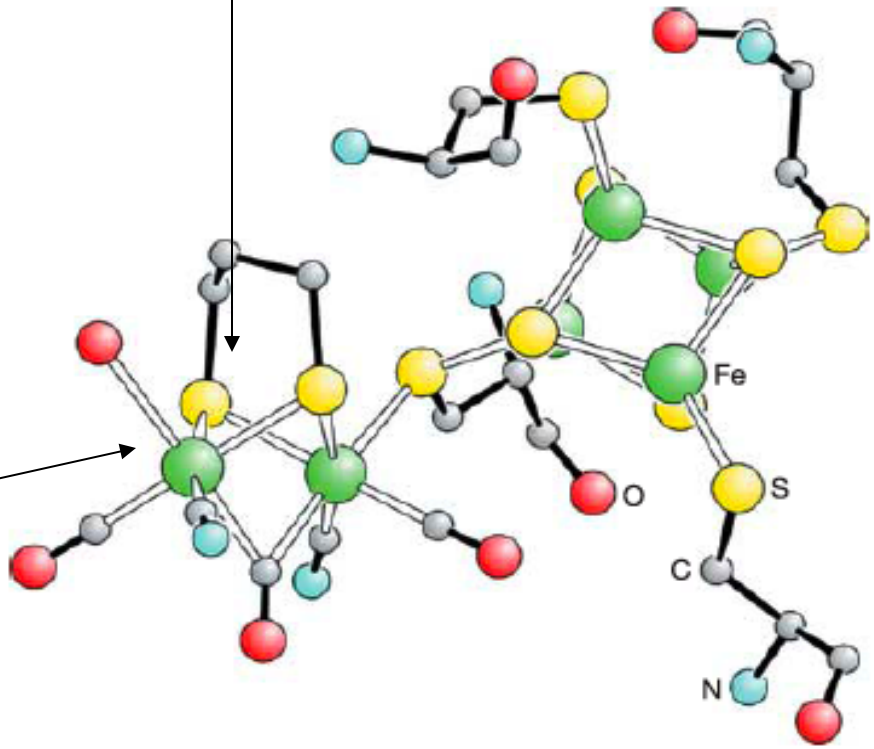
Could mackinawite act as a proto-hydrogenase?

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



mackinawite



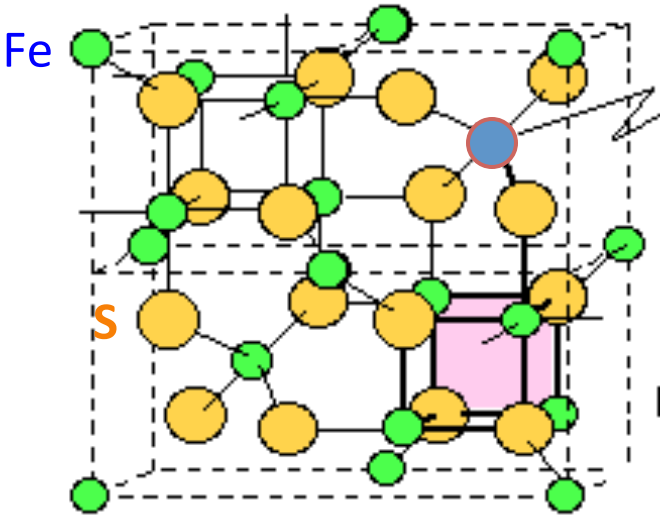


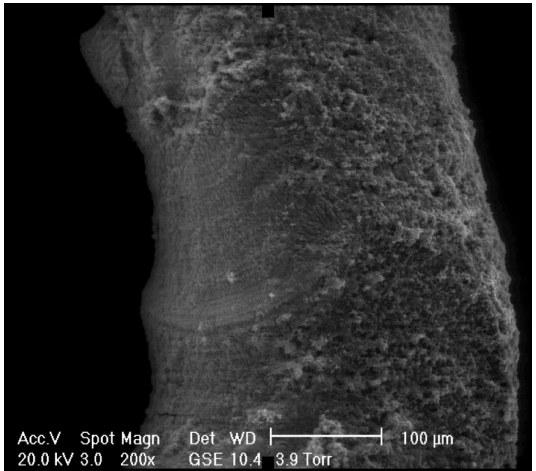
Peters et al, *Science* 1998, **282**:1853
McGlynn et al, 2009, Dalton Trans. **22**, 4274

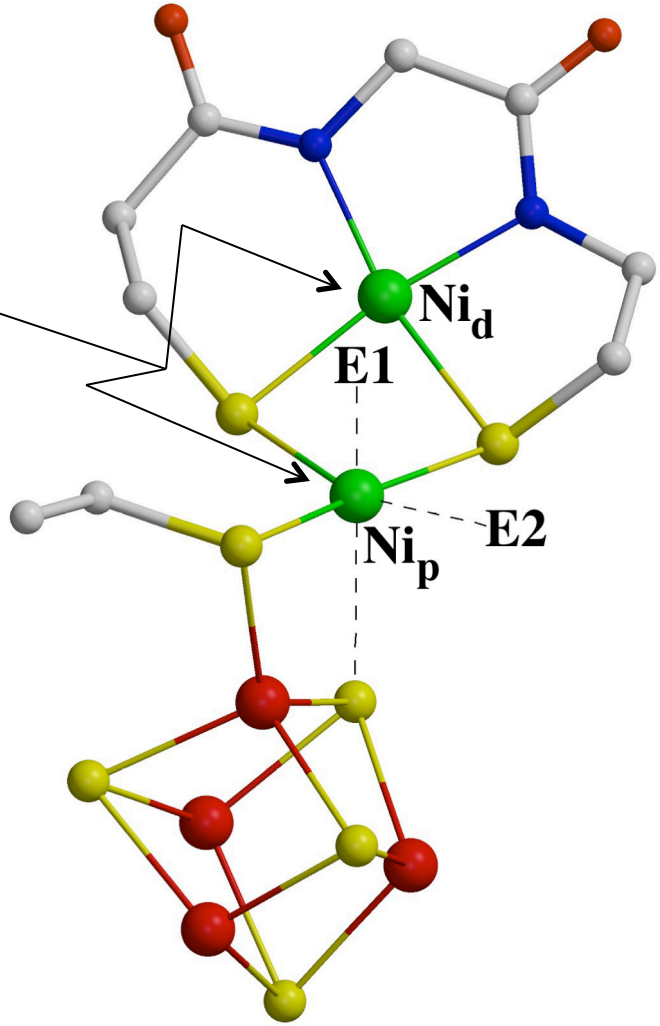
Composite structure of hydrogenase from *Clostridium* & *Desulfovibrio*
Tard et al., 2005 *Nature* **433**, 610

Greigite compared to acetyl co-A synthase (ACS)

Greigite [Fe_5NiS_8]



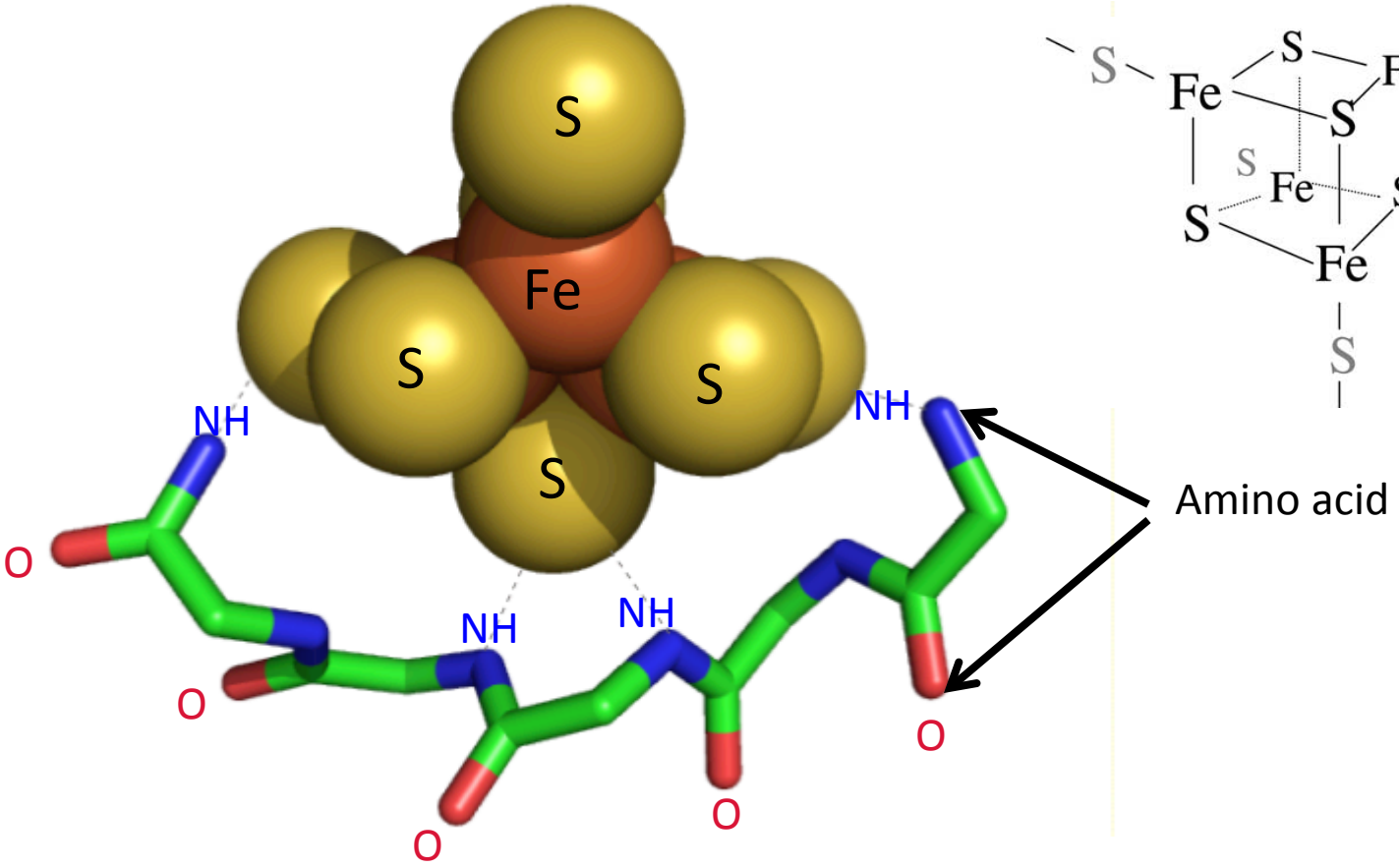




Volbeda and Fontecilla-Camps 2005, Cordination Chemistry Reviews, **249**,1609-19

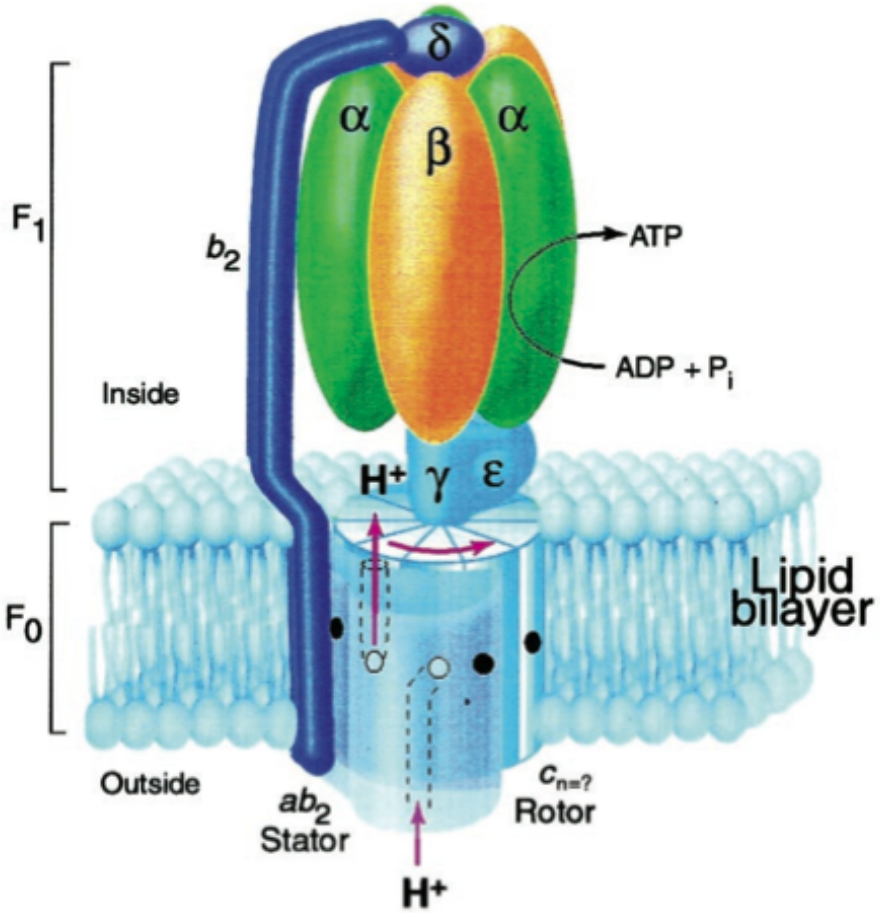
The beginning of the peptide takeover?

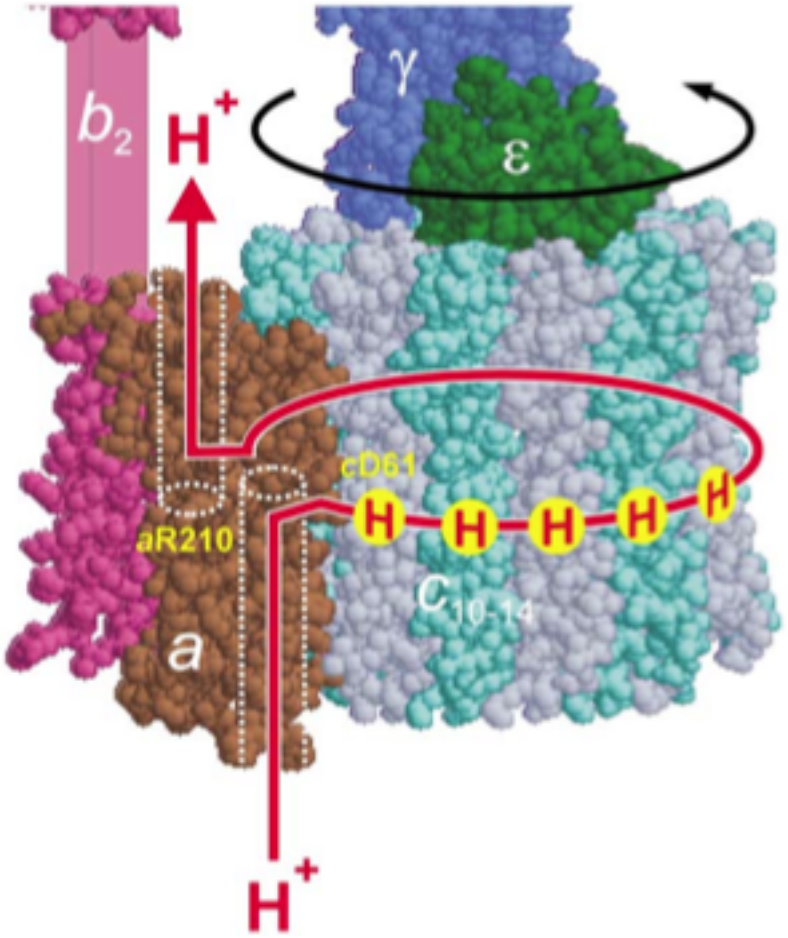
Fe_3S_4 "egg" bound to RLRLR ***nest*** (cf. a ferredoxin)



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

The ATP synthase rotary engine

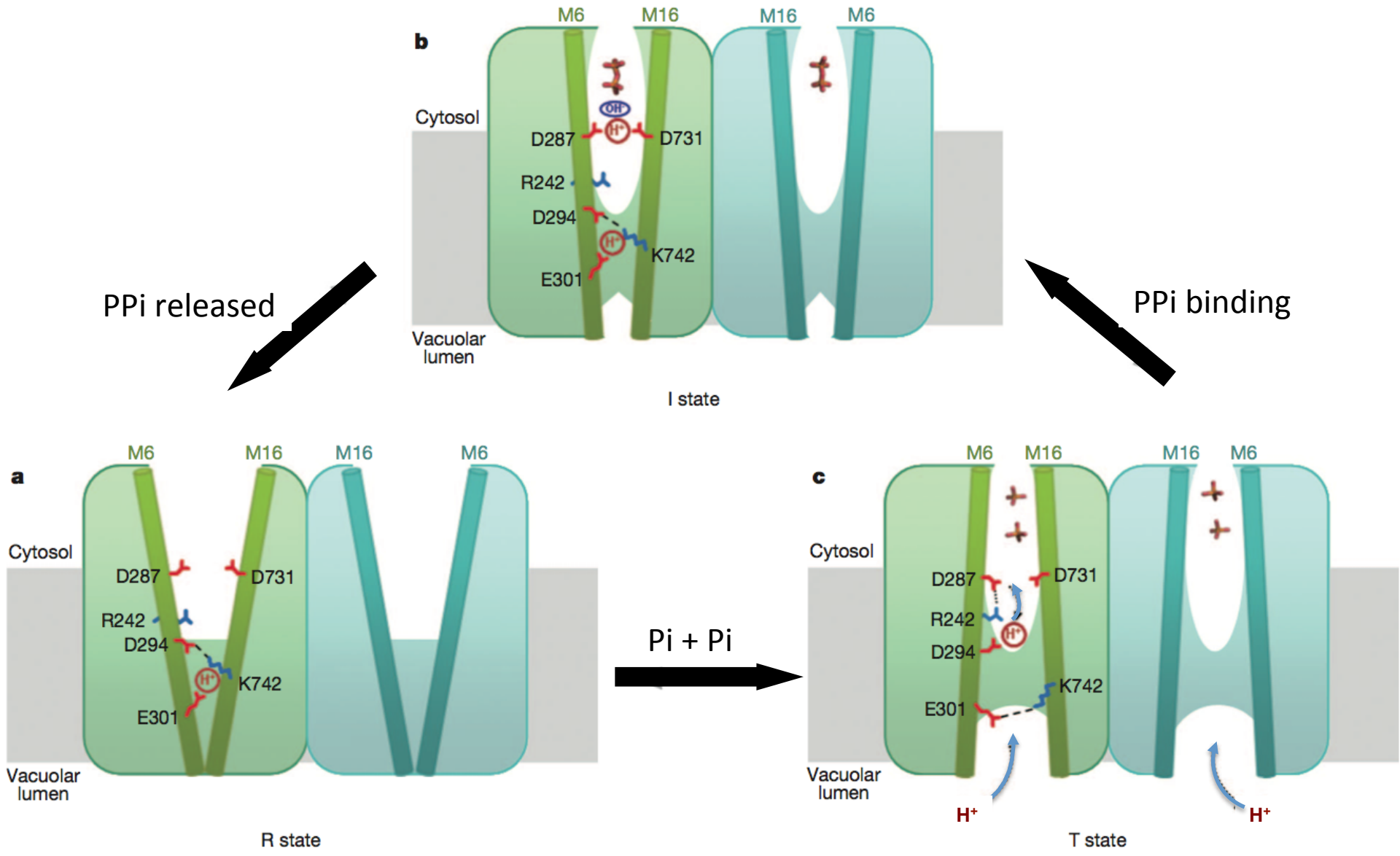




Jiang *et al.* (2001) *PNAS*, **98**, 4966-4971

Weber & Senior (2003) *FEBS*, **544**, 61-70

membrane-embedded H⁺-translocating pyrophosphatase



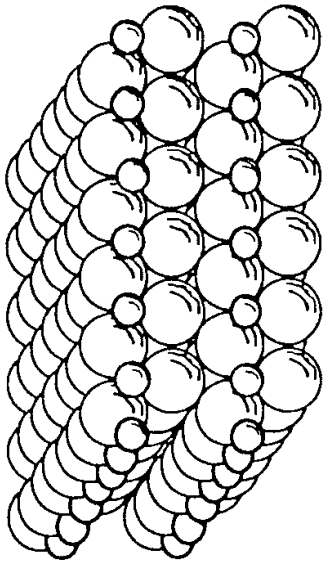
Lin *et al.*, 2012, *Nature* **484**, 399-403

$Fe(OH)_2$ → green rust as putative proto H^+-pyrophosphatse

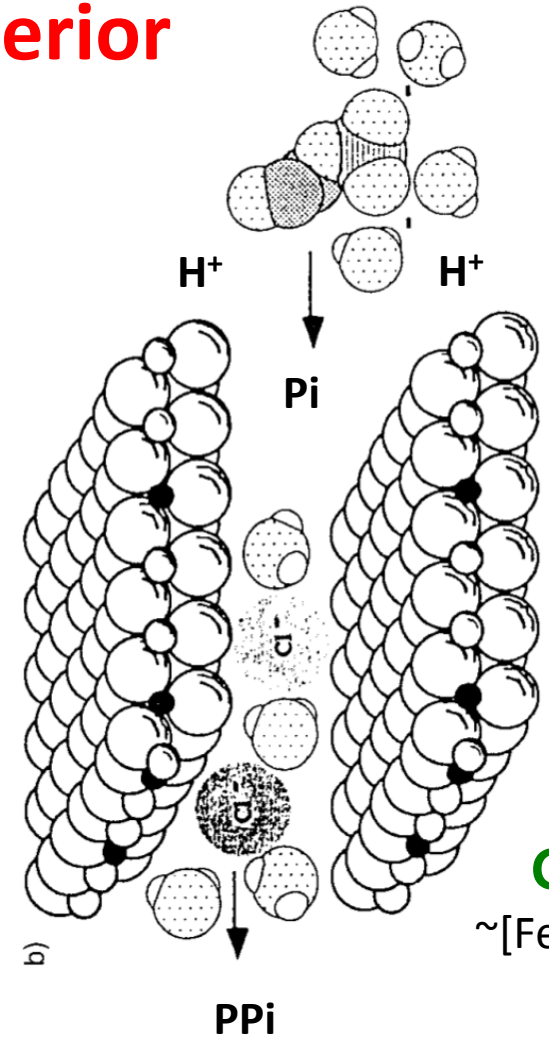
Acidulous oxidizing exterior

e.g. nitrate

$Fe^{II}(OH)_2$



$Fe^{2+} \rightarrow Fe^{2+/3+}$



Green Rust

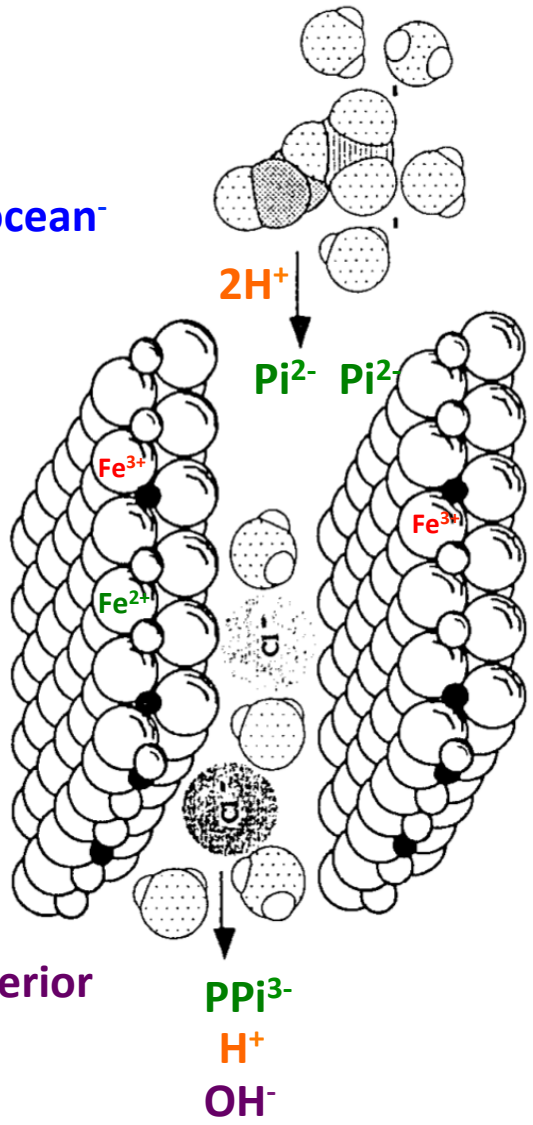
$\sim[Fe^{II}Fe^{III}(OH)_4]^+[OH]^-$

Alkaline reduced interior

Arrhenius **2003** *Helv. Chim. Acta*, *86*, 1569

ENGINE 2: MAKING PYROPHOSPHATE (PPi)

Double layer hydroxide:
e.g., **green rust** $[Fe^{II}_3Fe^{III}(OH)_8]^+[Cl{\cdot}3H_2O]^-$
or
$[Fe^{II}Fe^{II}(OH)_4]^+[OH]^-$

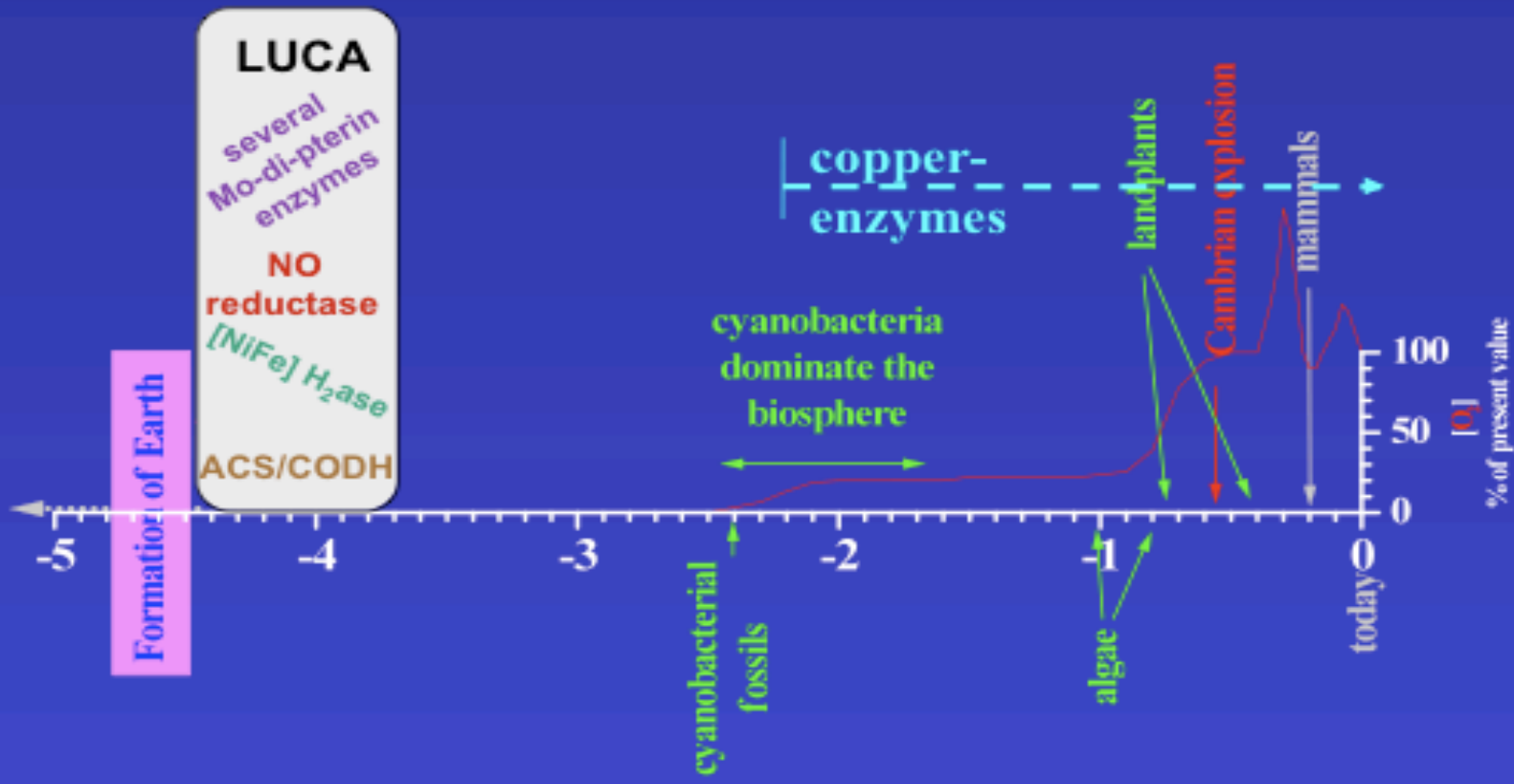


Crystals and Life

Arrhenius 2003 *Helvetica Chimica Acta*, 86, 1569

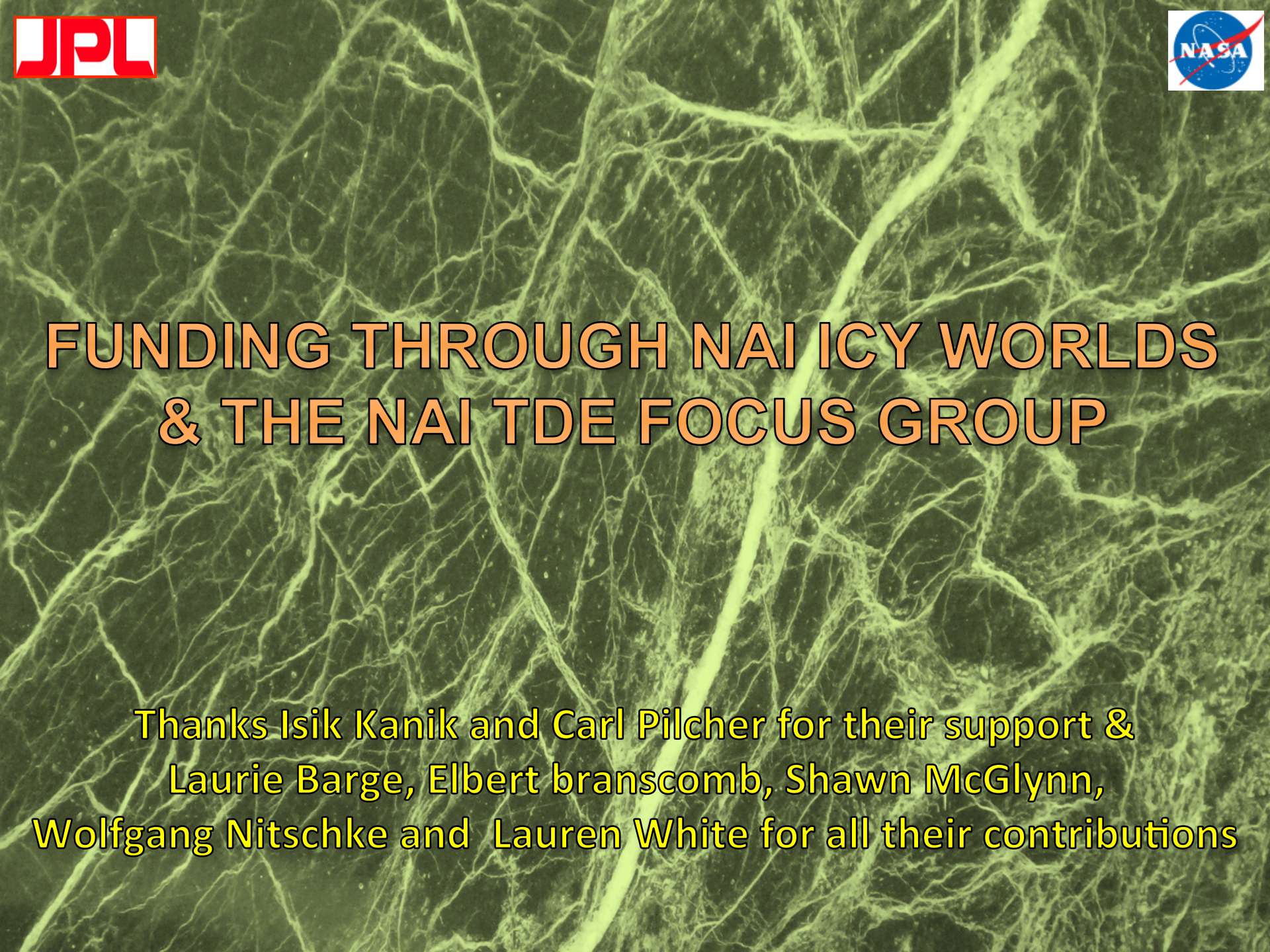
LUCA and post-LUCA enzymes

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.

Hadean | Archaean | Proterozoic | Phanerozoic



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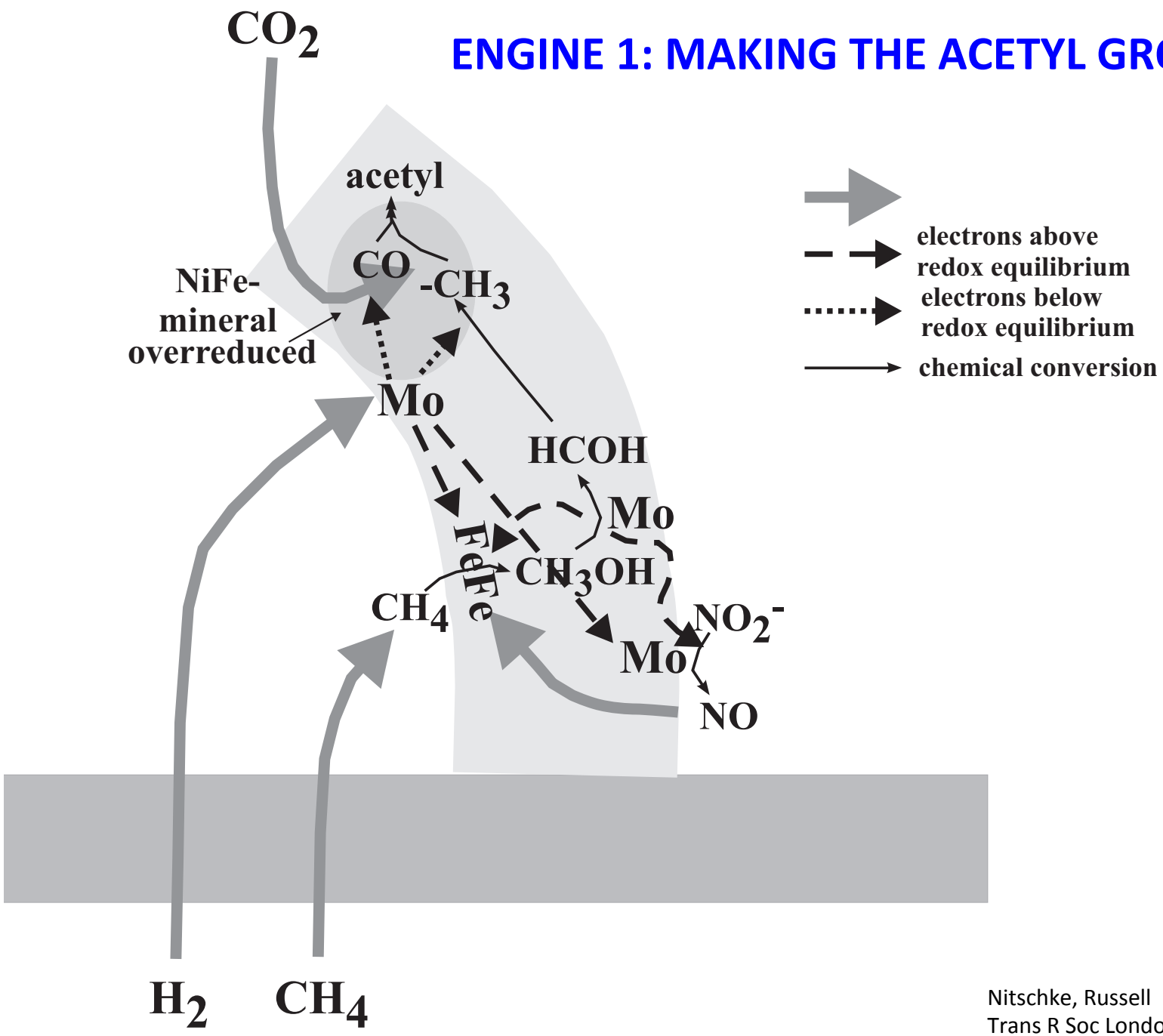
Laurie Barge, Elbert branscomb, Shawn McGlynn,
Wolfgang Nitschke and Lauren White for all their contributions

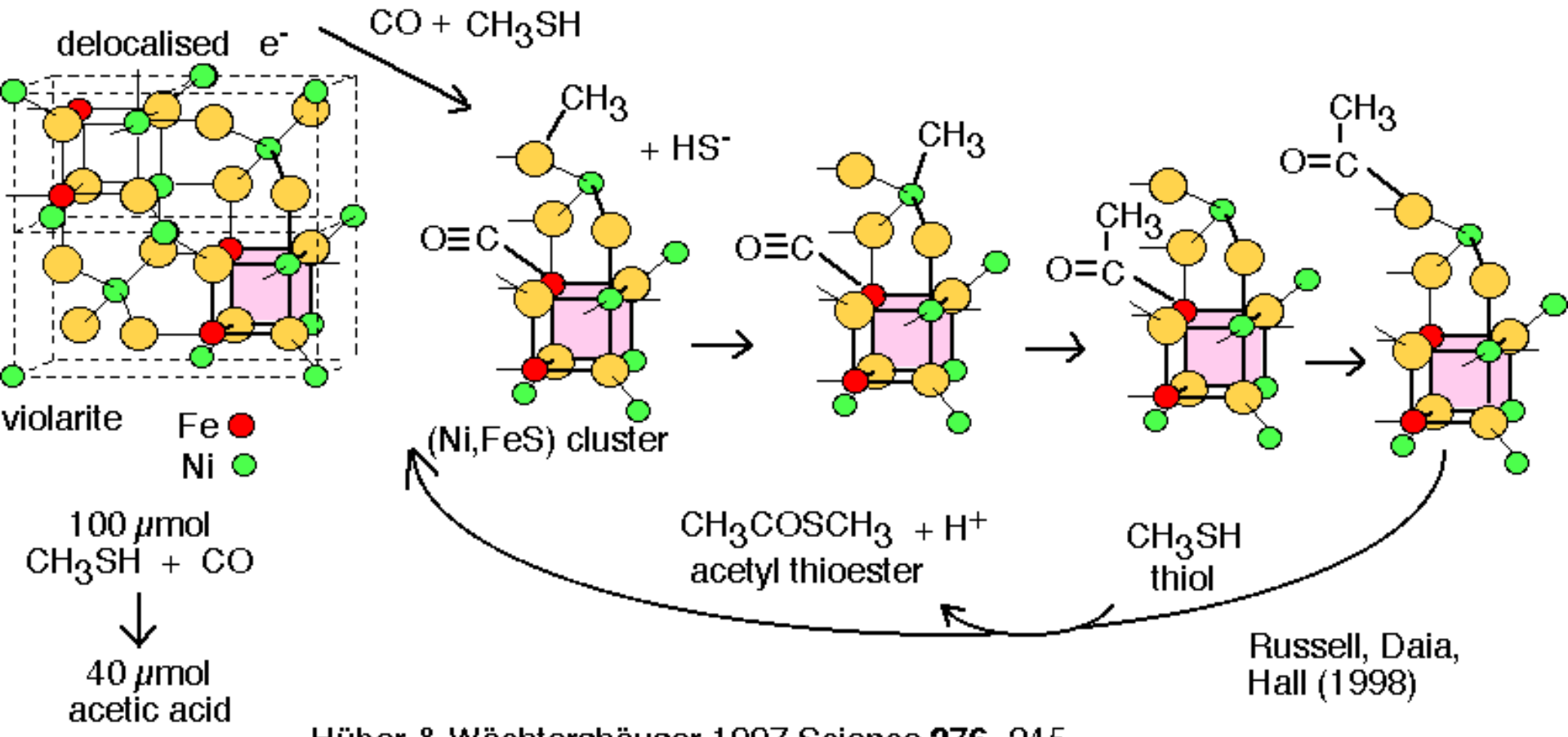
ENGINE 1: MAKING THE ACETYL GROUP



Nitschke, Russell
Trans R Soc London, in press

Notional mechanism for prebiotic acetyl synthesis
on Ni_2FeS_4 in FeS membrane

cf. Qiu *et al* Science **264**, 817. & Turner *et al (in press)*

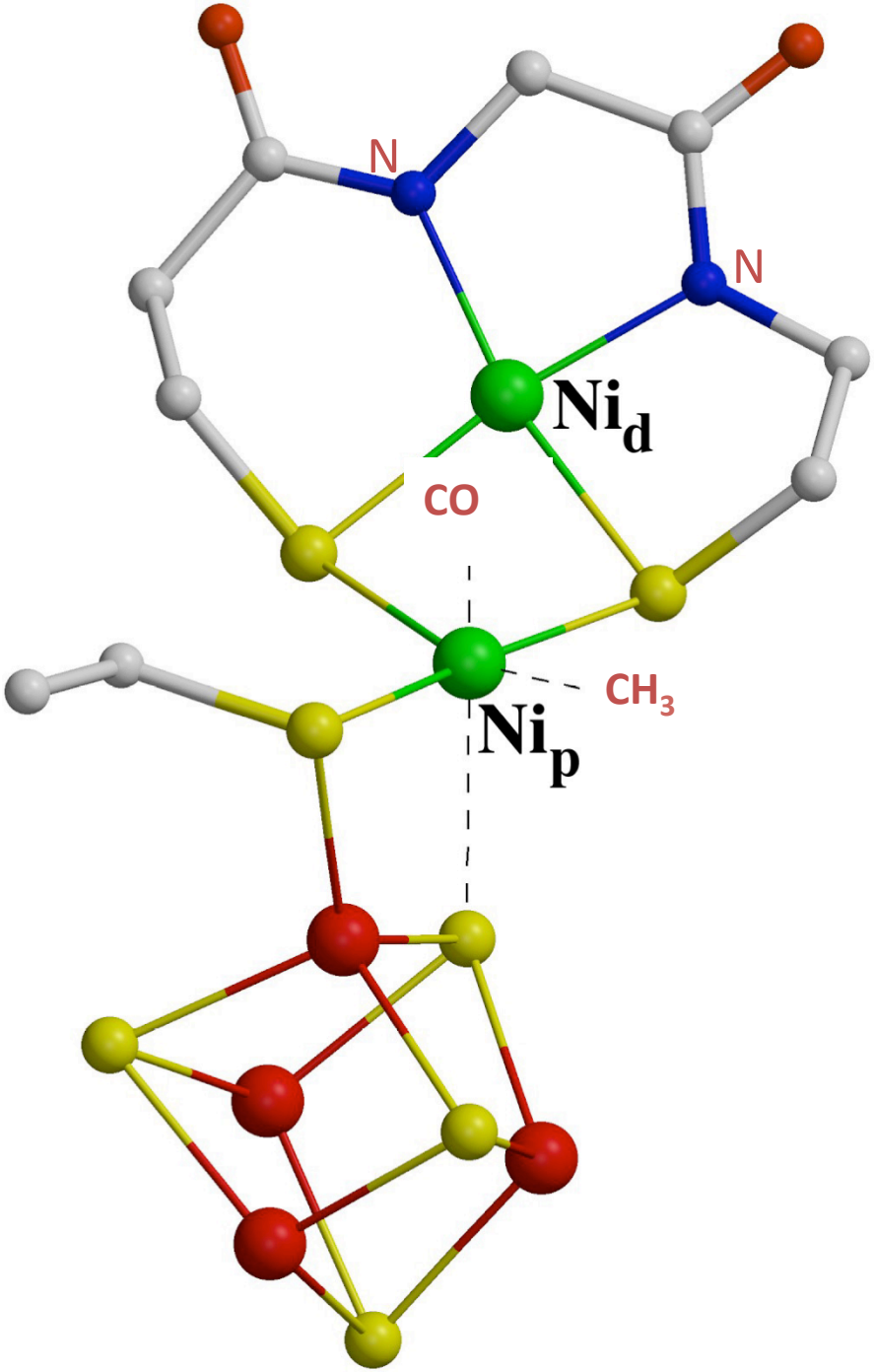


Hüber & Wächtershäuser 1997 Science **276**, 245

Acetyl-Coenzyme-A Synthetase (ACS) assembles:

$-CH_3 + -CO \Rightarrow H_3CCO-$

as $Ni^0 \leftrightarrow Ni^{II}$



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