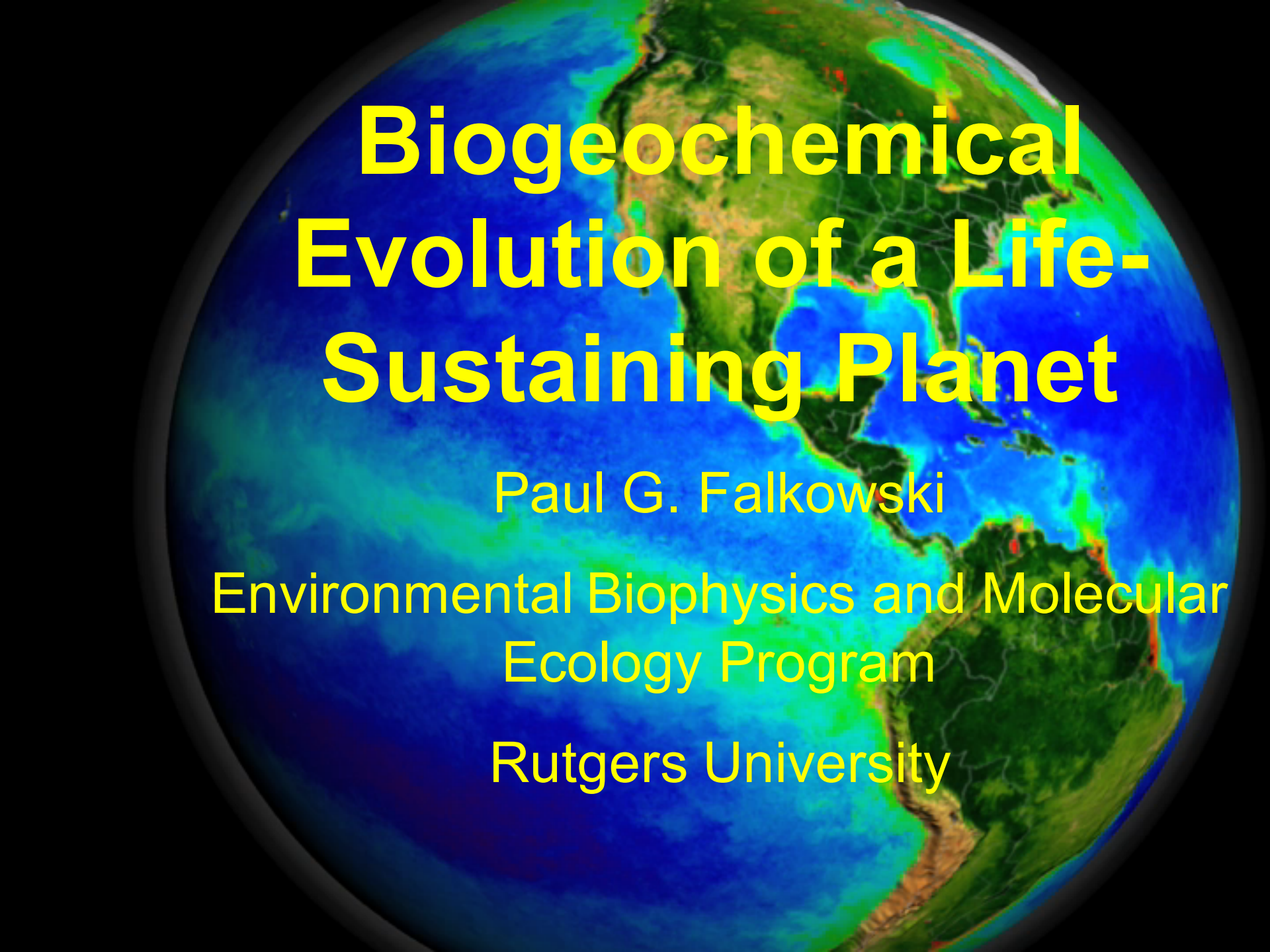

Biogeochemical Evolution of a Life-Sustaining Planet

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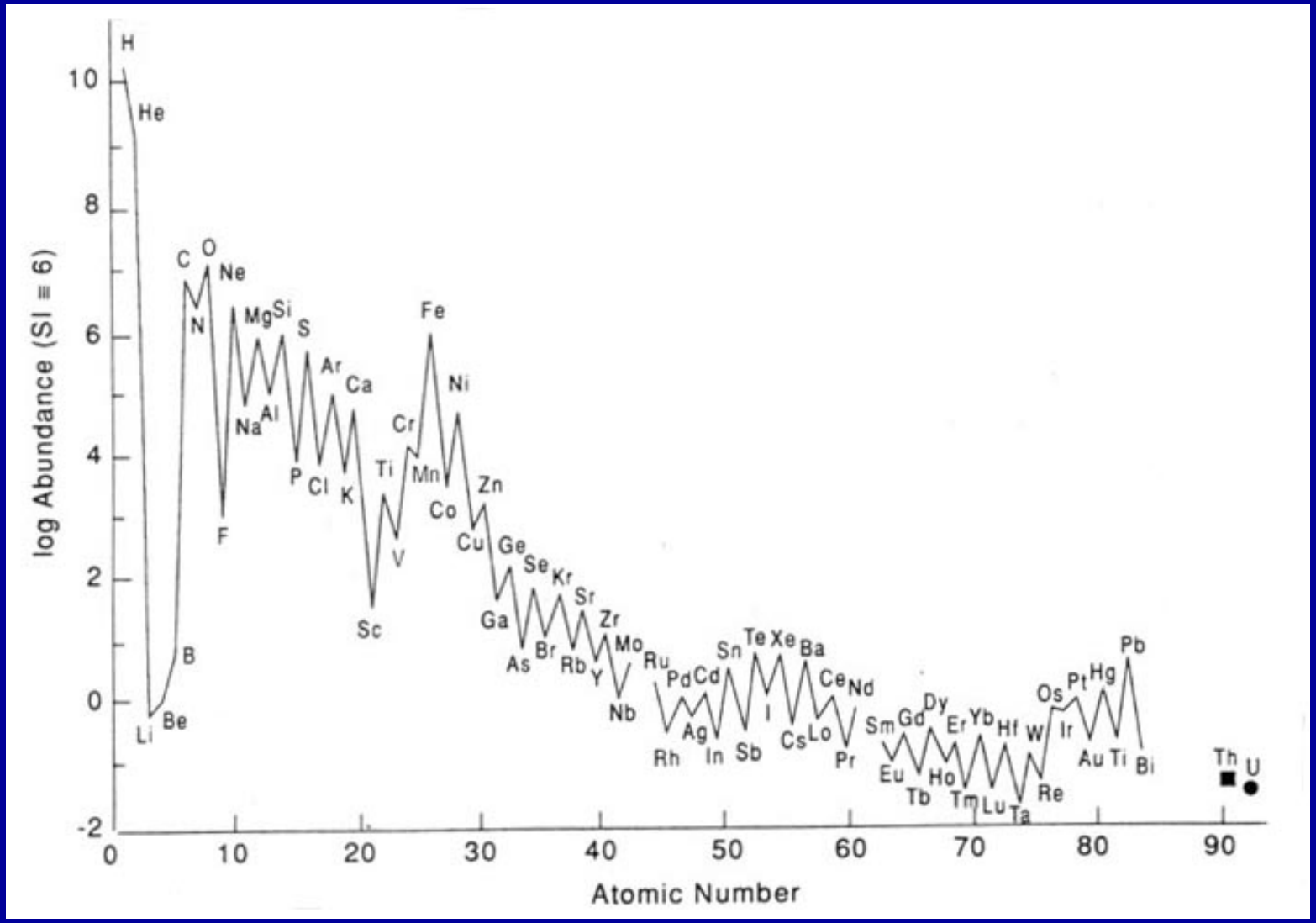
Rutgers University

LIFE'S ENGINES

How Microbes Made Earth Habitable

PAUL G. FALKOWSKI


log Abundance (Si ≡ 6)
10
8
6
4
2
0
-2
0
10
20
30
40
50
60
70
80
90
Atomic Number
H
He
Li
Be
B
C
N
O
Ne
F
Na
Mg
Al
Si
P
S
Cl
Ar
K
Ca
Sc
Ti
V
Cr
Mn
Fe
Co
Ni
Cu
Zn
Ga
Ge
As
Se
Br
Kr
Rb
Sr
Y
Zr
Nb
Mo
Ru
Rh
Pd
Ag
Cd
In
Sn
Sb
Te
I
Xe
Cs
Ba
La
Ce
Pr
Nd
Sm
Eu
Gd
Tb
Dy
Ho
Er
Tm
Yb
Lu
Hf
Ta
W
Re
Os
Ir
Pt
Au
Hg
Tl
Pb
Bi
Th
U

On Earth, the origin of life depended on the evolution of non-equilibrium redox chemistry that involves five of the The "Big Six"

H, C, N, O, P and S

And at least 54 other "trace elements"

Take Away 1
Life is Electric

- All organisms derive energy for growth and maintenance by moving electrons from a substrate to a product.
- All substrates and products must ultimately be cycled.
- Biological processes are paired (e.g., photosynthesis and respiration)

The ensemble of redox reactions are also coupled on a Planetary SCALE

Oxygenic Photosynthesis

$$2H_2O + CO_2 \longrightarrow (CH_2O)_n + O_2$$

Aerobic Respiration:

$$(CH_2O)_n + O_2 \longrightarrow 2H_2O + CO_2$$

The electron "marketplace"

Maintaining life on a planet requires recycling of electrons

What were the sources and sinks of electrons in the Archean and what are they today?

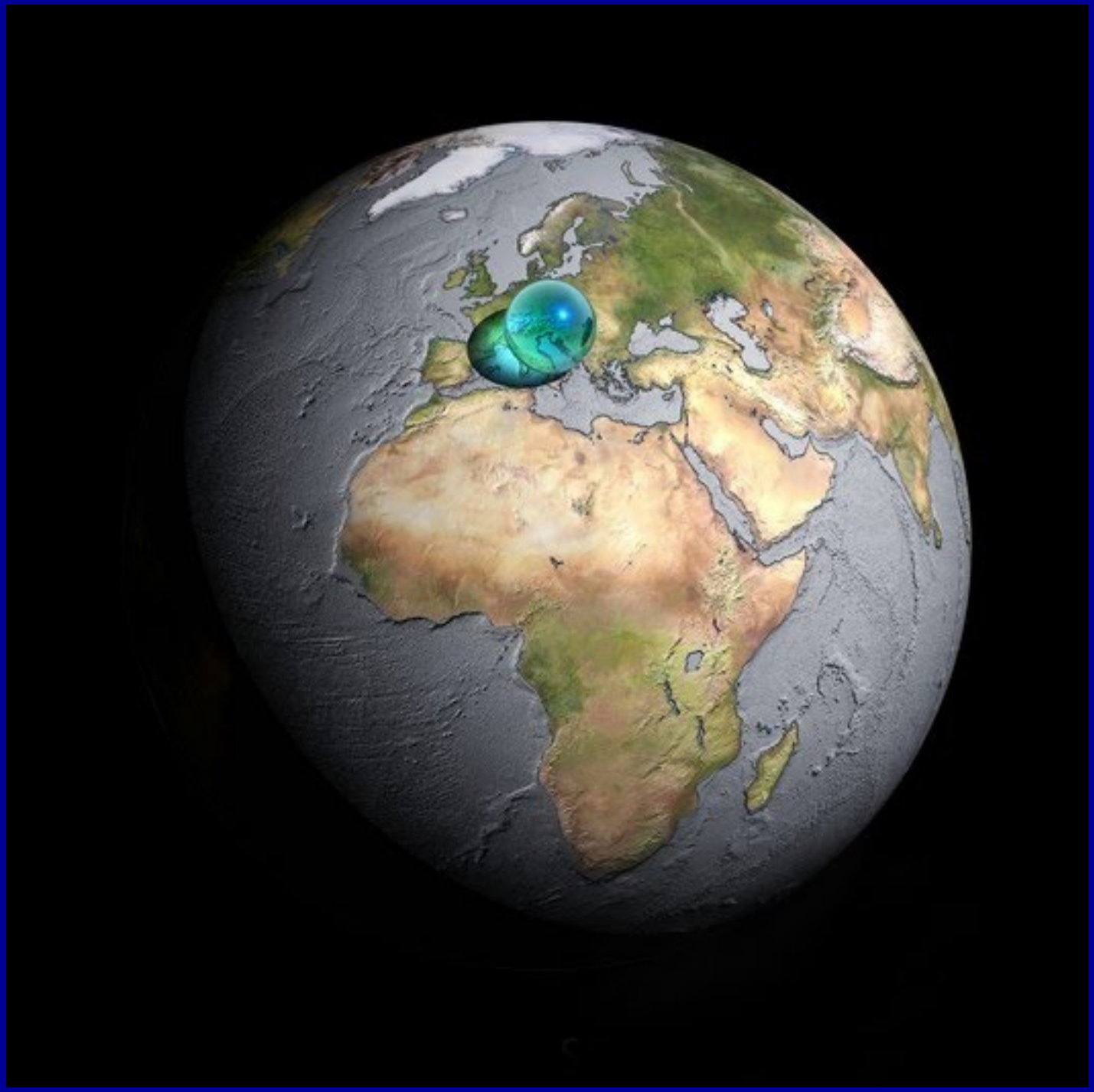
In the Archean Oceans …

- It was H_2, Fe(II), H_2S and CH_2O

The major source of electrons today is

LIQUID WATER

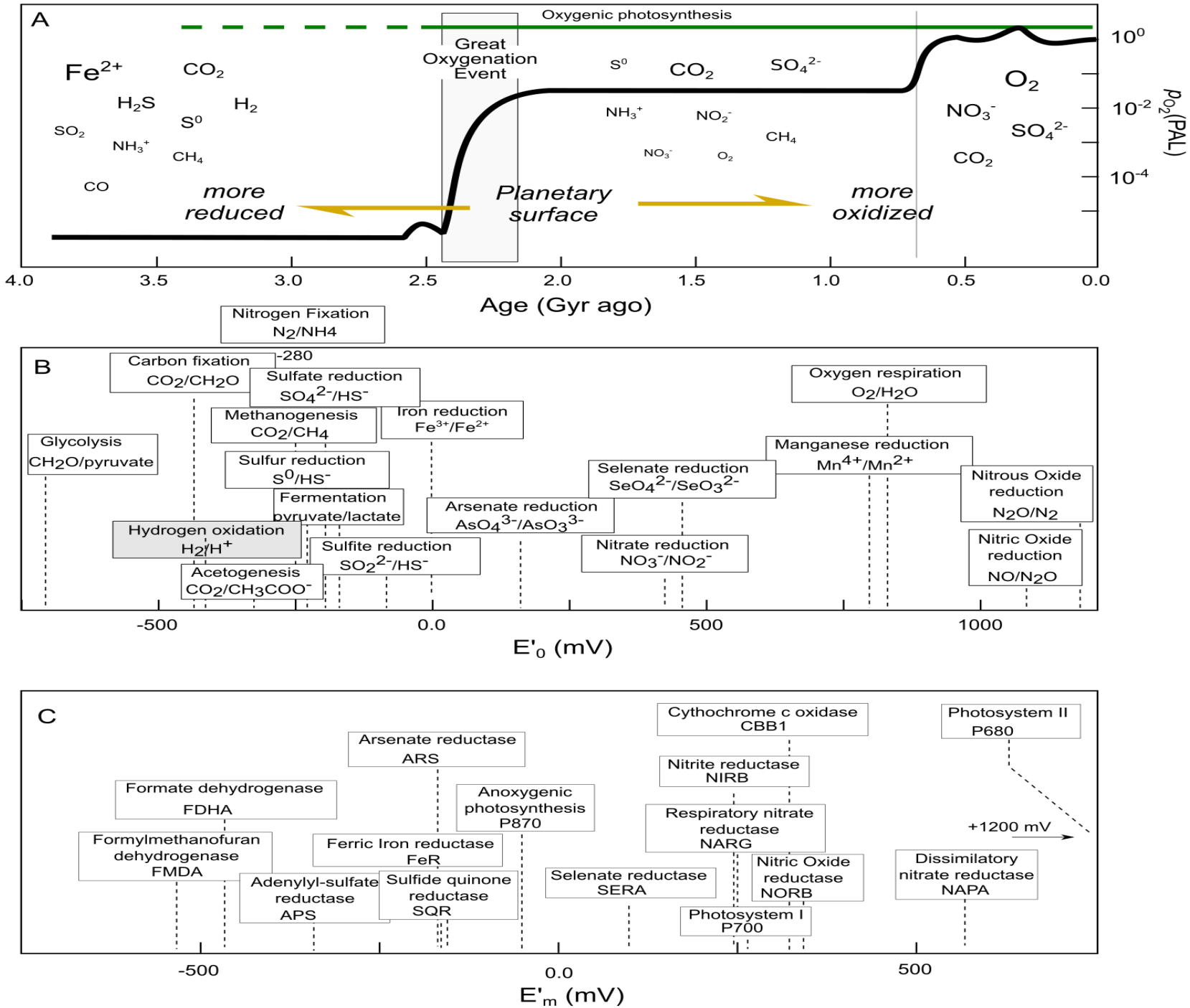
(H_2O)

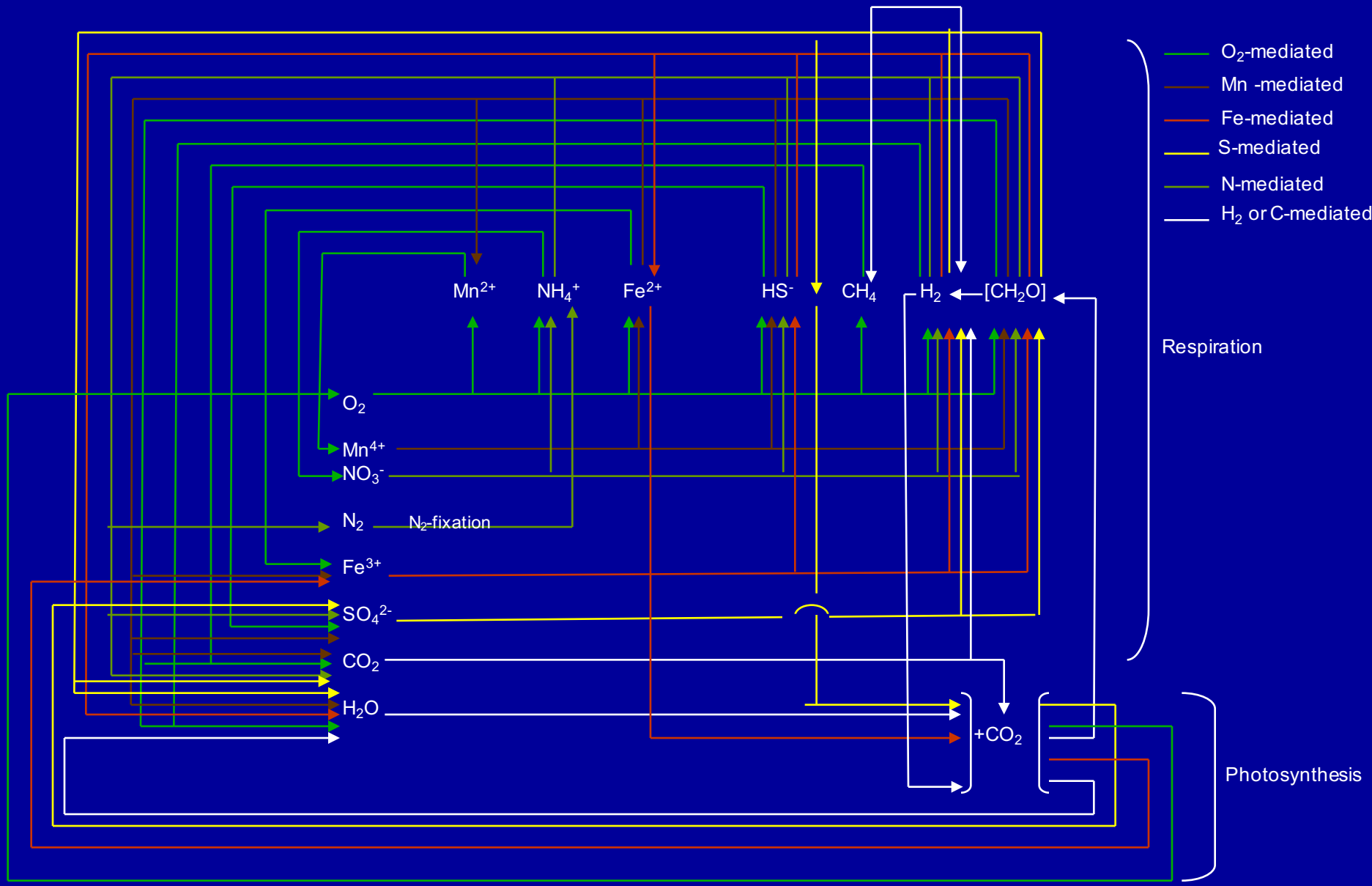


Take Away 2 – as per Vernadsky

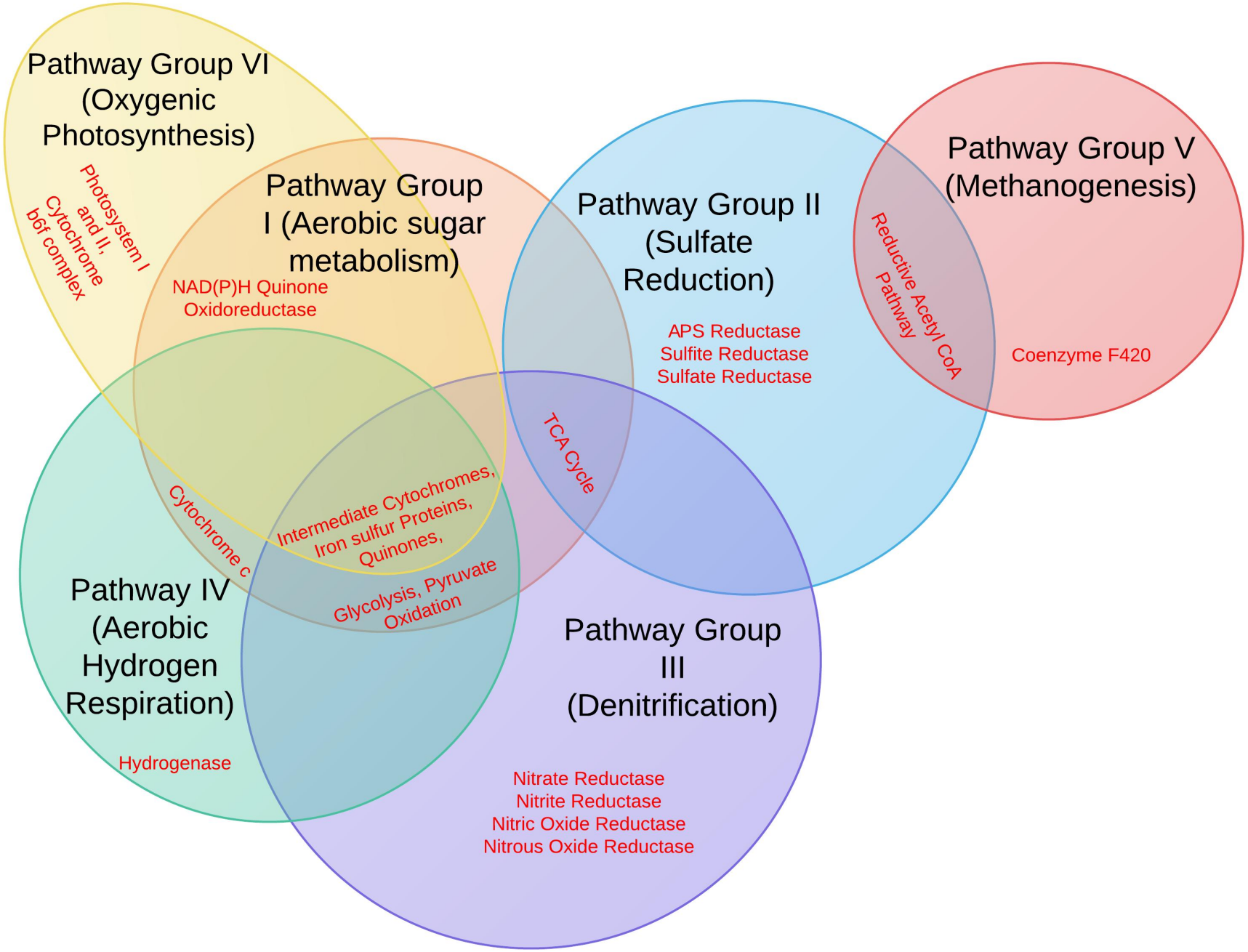
All living organsisms on Earth exchange a gas with their environment – via redox reactions

Many of the core metabolic processes are related to gas exhange reactions


A
Oxygenic photosynthesis
Great Oxygenation Event
Fe2+
CO2
H2S
H2
S0
SO2
NH3+
CH4
CO
S0
CO2
SO42-
NH3+
NO2-
CH4
NO3-
O2
O2
NO3-
SO42-
CO2
more reduced
Planetary surface
more oxidized
10^0
10^-2
10^-4
pO2(PAL)
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
Age (Gyr ago)
B
Nitrogen Fixation N2/NH4
-280
Carbon fixation CO2/CH2O
Sulfate reduction SO4 2-/HS-
Methanogenesis CO2/CH4
Iron reduction Fe3+/Fe2+
Oxygen respiration O2/H2O
Glycolysis CH2O/pyruvate
Sulfur reduction S0/HS-
Manganese reduction Mn4+/Mn2+
Selenate reduction SeO4 2-/SeO3 2-
Nitrous Oxide reduction N2O/N2
Fermentation pyruvate/lactate
Arsenate reduction AsO4 3-/AsO3 3-
Hydrogen oxidation H2/H+
Sulfite reduction SO2 2-/HS-
Nitrate reduction NO3-/NO2-
Nitric Oxide reduction NO/N2O
Acetogenesis CO2/CH3COO-
-500
0.0
500
1000
E'0 (mV)
C
Cythochrome c oxidase CBB1
Photosystem II P680
Arsenate reductase ARS
Nitrite reductase NIRB
Formate dehydrogenase FDHA
Anoxygenic photosynthesis P870
Respiratory nitrate reductase NARG
+1200 mV
Formylmethanofuran dehydrogenase FMDA
Ferric Iron reductase FeR
Nitric Oxide reductase NORB
Dissimilatory nitrate reductase NAPA
Adenylyl-sulfate reductase APS
Sulfide quinone reductase SQR
Selenate reductase SERA
Photosystem I P700
-500
0.0
500
E'm (mV)



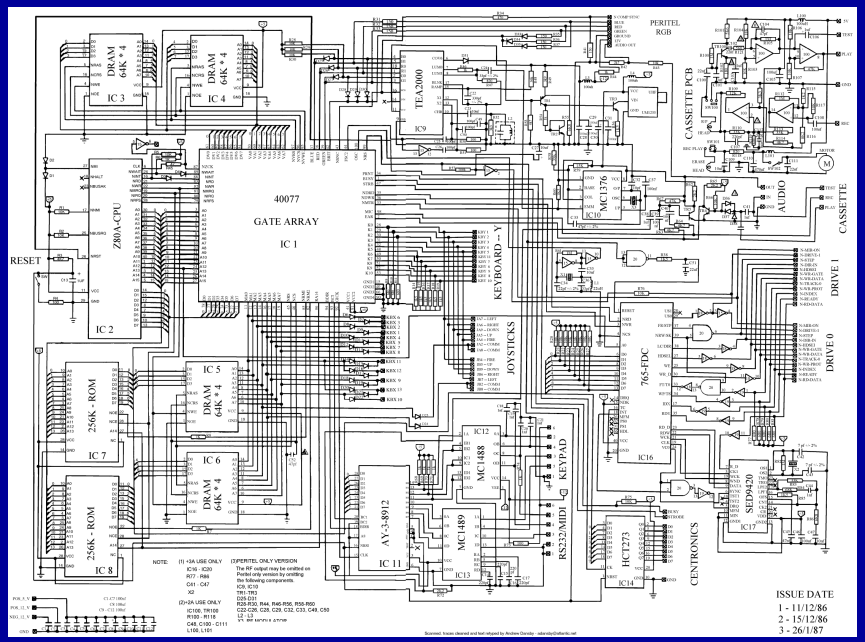
Falkowski, Fenchel and Delong, Science, 2008

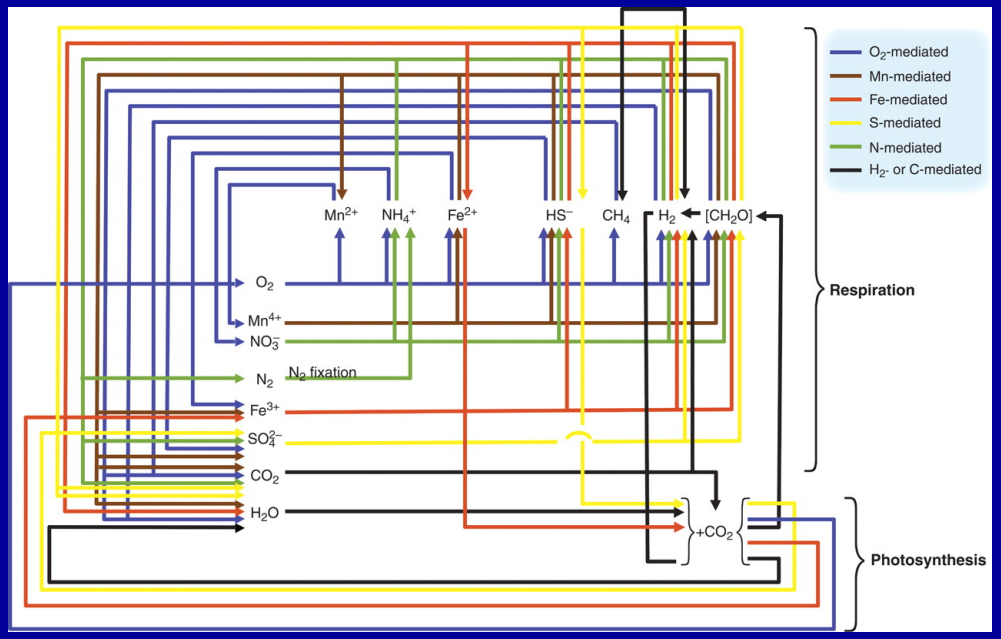

Pathway Group VI (Oxygenic Photosynthesis)
Photosystem I and II, Cytochrome b6f complex
Pathway Group I (Aerobic sugar metabolism)
NAD(P)H Quinone Oxidoreductase
Pathway Group II (Sulfate Reduction)
APS Reductase
Sulfite Reductase
Sulfate Reductase
Pathway Group V (Methanogenesis)
Reductive Acetyl CoA Pathway
Coenzyme F420
TCA Cycle
Cytochrome c
Intermediate Cytochromes, Iron sulfur Proteins, Quinones,
Glycolysis, Pyruvate Oxidation
Pathway IV (Aerobic Hydrogen Respiration)
Hydrogenase
Pathway Group III (Denitrification)
Nitrate Reductase
Nitrite Reductase
Nitric Oxide Reductase
Nitrous Oxide Reductase

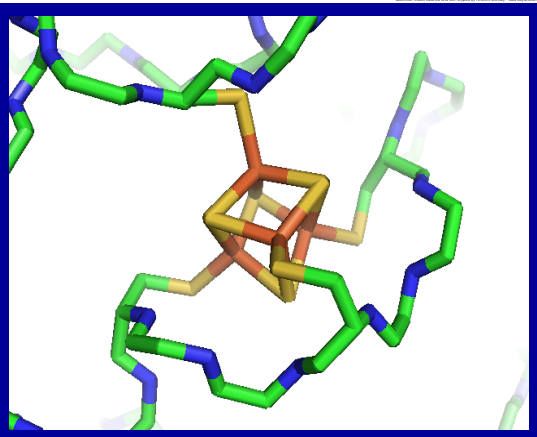
Take Away 3 – The processes are not that complicated

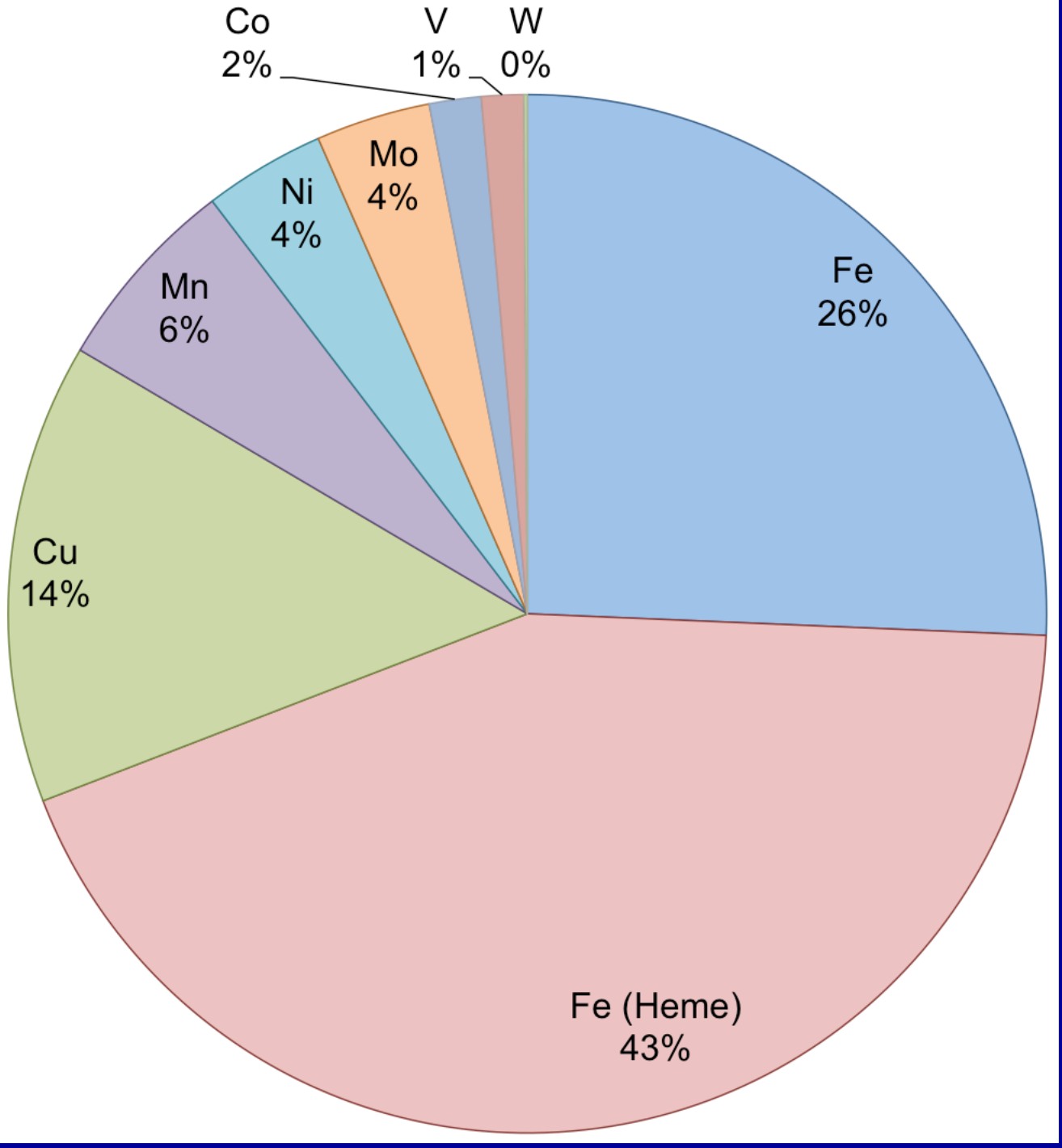
This metabolic map implies there are only about **400** core genes responsible for all electron transport reactions on the planet!

Metals in protein "transistors"



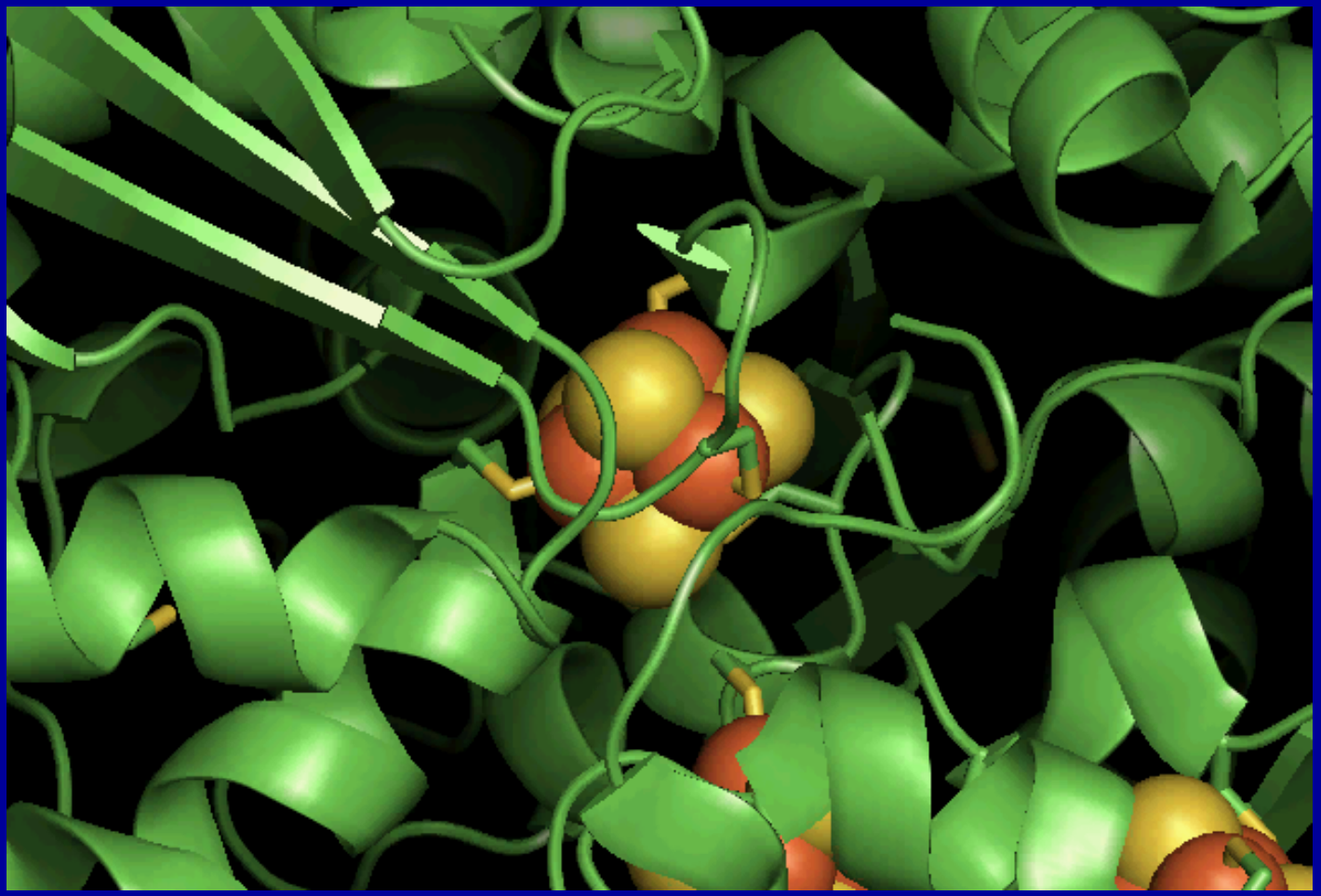





Co
2%
V
1%
W
0%
Mo
4%
Ni
4%
Mn
6%
Fe
26%
Cu
14%
Fe (Heme)
43%

ferredoxin

scandium	titanium	vanadium	chromium	manganese	iron	cobalt	nickel	copper	zinc
21	22	23	24	25	26	27	28	29	30
Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
44.956	47.867	50.942	51.996	54.938	55.845	58.933	58.693	63.546	65.39
yttrium	zirconium	niobium	molybdenum	technetium	ruthenium	rhodium	palladium	silver	cadmium
39	40	41	42	43	44	45	46	47	48
Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
88.906	91.224	92.906	95.94	[98]	101.07	102.91	106.42	107.87	112.41
lutetium	hafnium	tantalum	tungsten	rhenium	osmium	iridium	platinum	gold	mercury
71	72	73	74	75	76	77	78	79	80
Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
174.97	178.49	180.95	183.84	186.21	190.23	192.22	195.08	196.97	200.59



nitrogenase

scandium	titanium	vanadium	chromium	manganese	iron	cobalt	nickel	copper	zinc
21	22	23	24	25	26	27	28	29	30
Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
44.956	47.867	50.942	51.996	54.938	55.845	58.933	58.693	63.546	65.39
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71	72	73	74	75	76	77	78	79	80
Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
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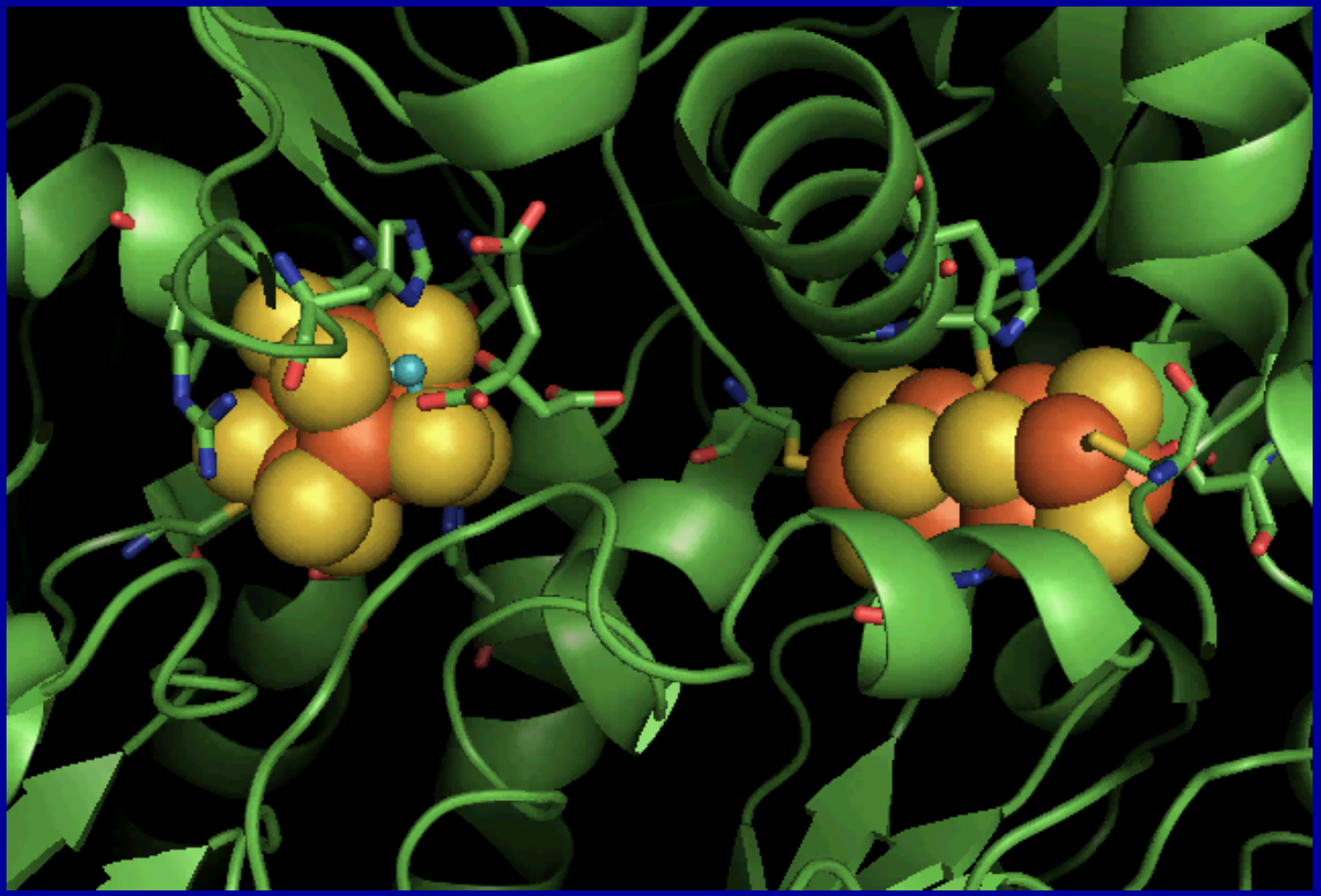
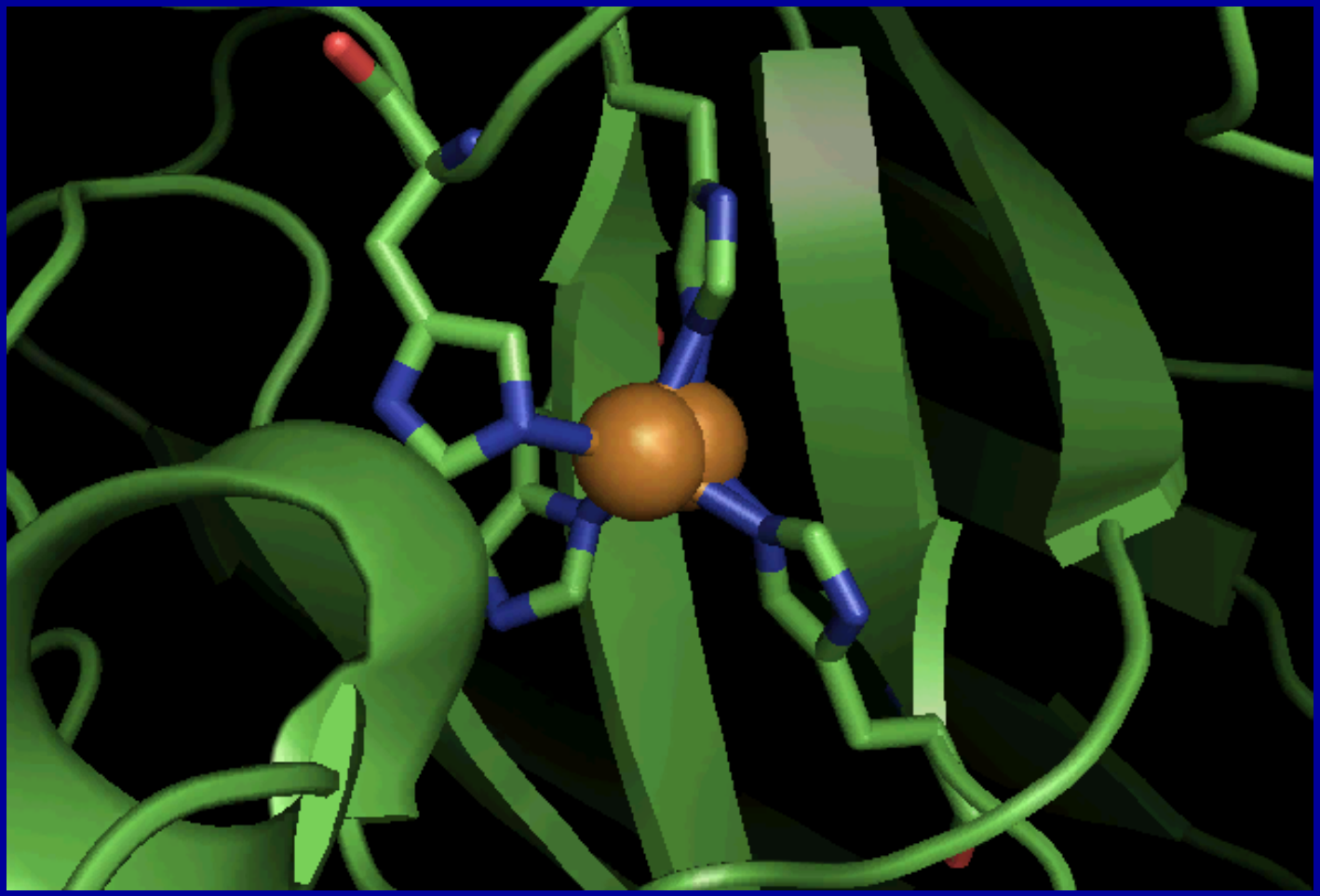


superoxide dismutase

scandium	titanium	vanadium	chromium	manganese	iron	cobalt	nickel	copper	zinc
21	22	23	24	25	26	27	28	29	30
Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
44.956	47.867	50.942	51.996	54.938	55.845	58.933	58.693	63.546	65.39
yttrium	zirconium	niobium	molybdenum	technetium	ruthenium	rhodium	palladium	silver	cadmium
39	40	41	42	43	44	45	46	47	48
Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
88.906	91.224	92.906	95.94	[98]	101.07	102.91	106.42	107.87	112.41
lutetium	hafnium	tantalum	tungsten	rhenium	osmium	iridium	platinum	gold	mercury
71	72	73	74	75	76	77	78	79	80
Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
174.97	178.49	180.95	183.84	186.21	190.23	192.22	195.08	196.97	200.59



superoxide dismutase

scandium	titanium	vanadium	chromium	manganese	iron	cobalt	nickel	copper	zinc
21	22	23	24	25	26	27	28	29	30
Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
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71	72	73	74	75	76	77	78	79	80
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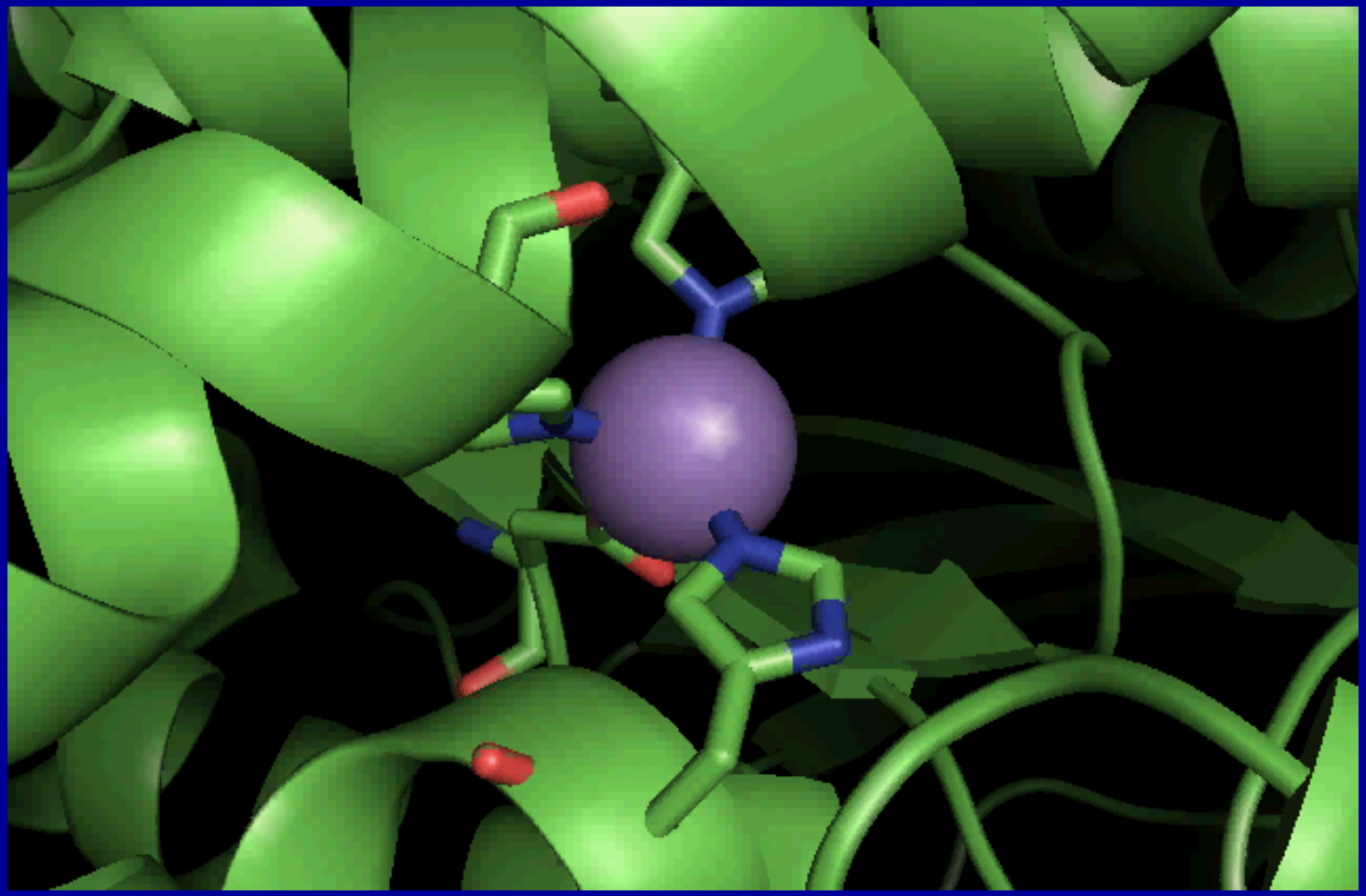
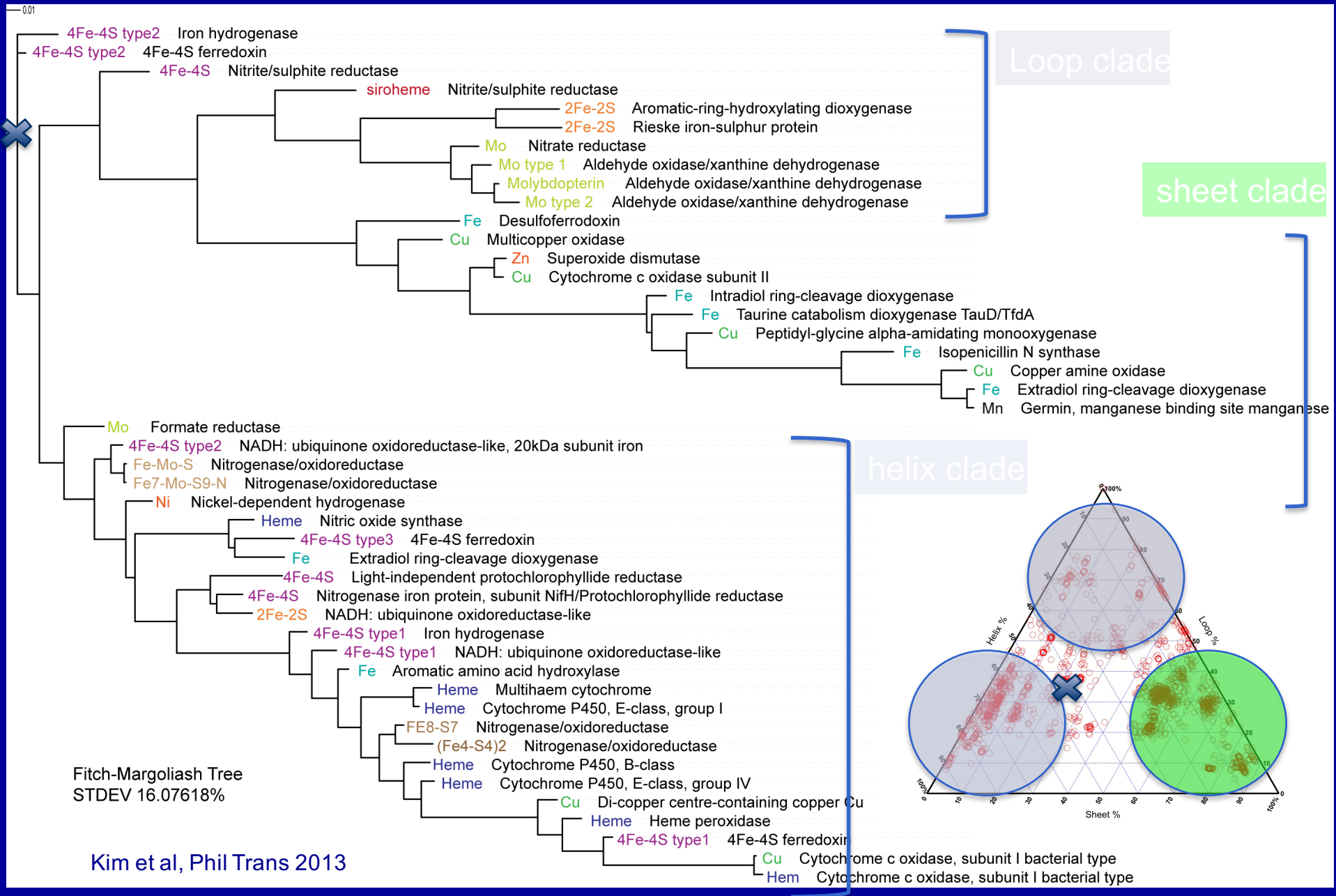
174.97	178.49	180.95	183.84	186.21	190.23	192.22	195.08	196.97	200.59



Motifs

- There appear to be only 35 motifs in all of the extant electron transfer reactions in nature.
- Decifering the evolutionary history of these motifs is one of the grand challenges of science.

A secondary structural tree of EC1 proteins

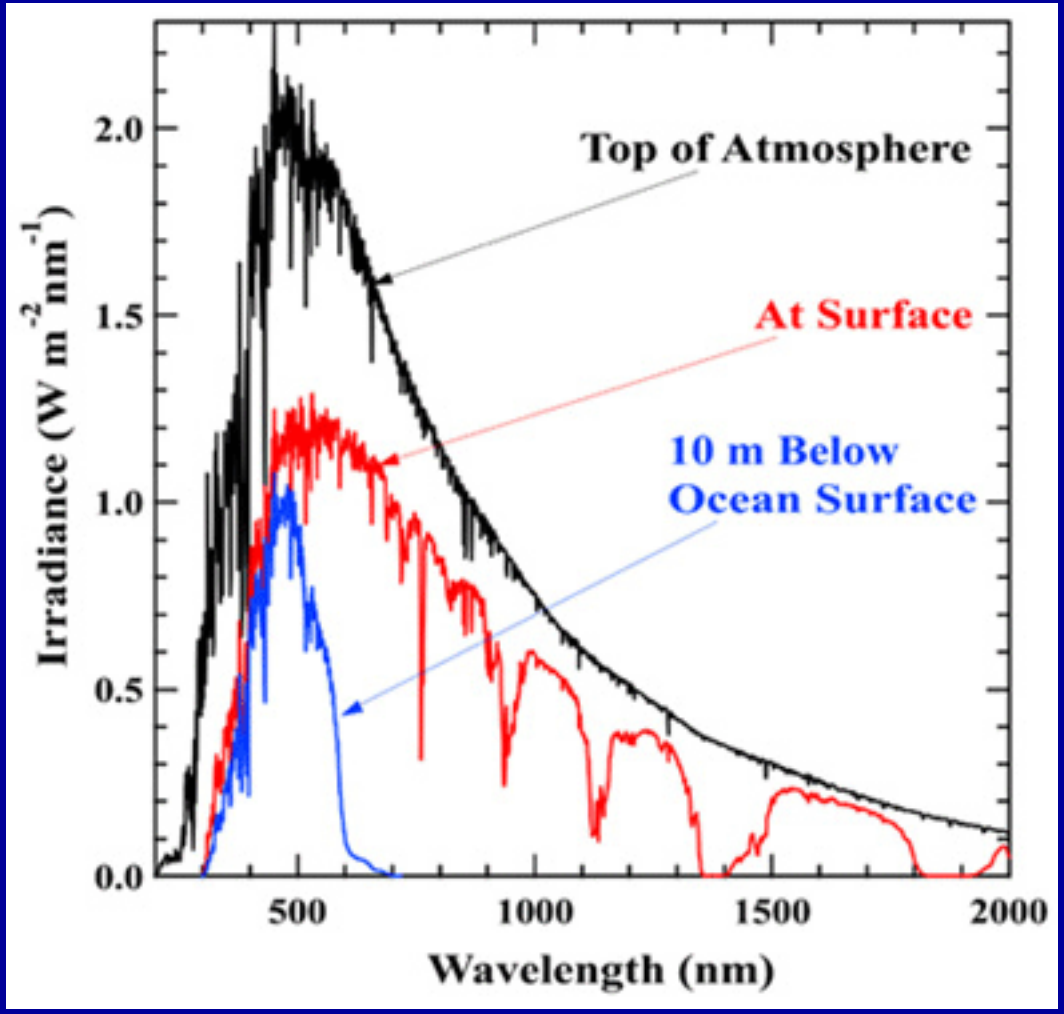


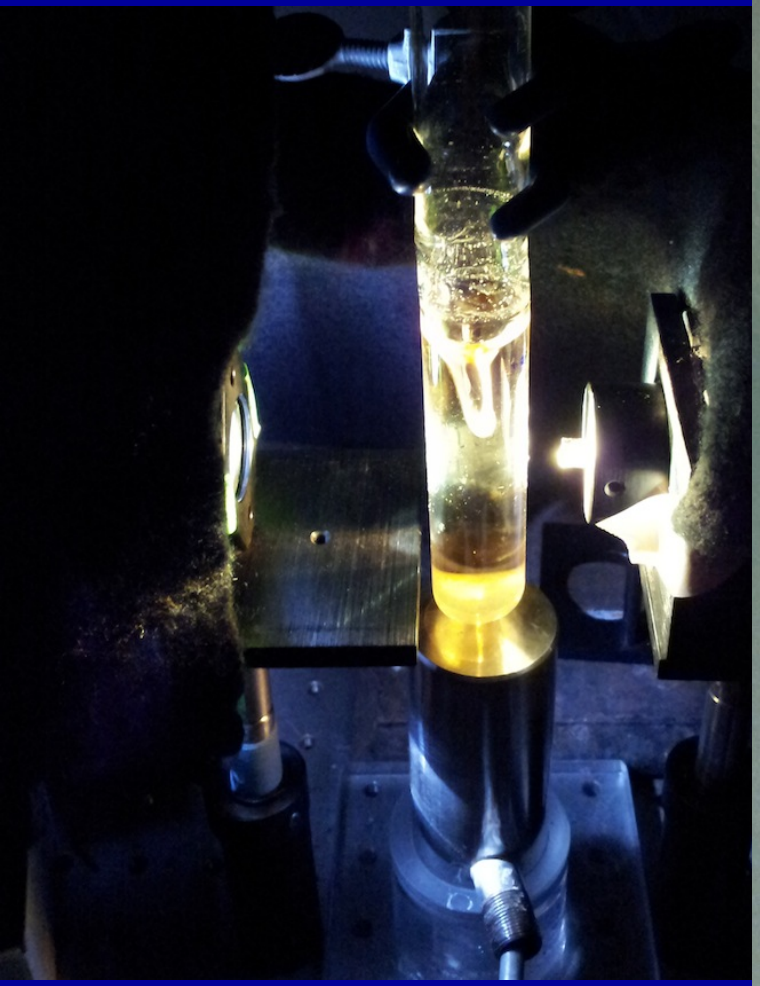
Fitch-Margoliash Tree
STDEV 16.07618%

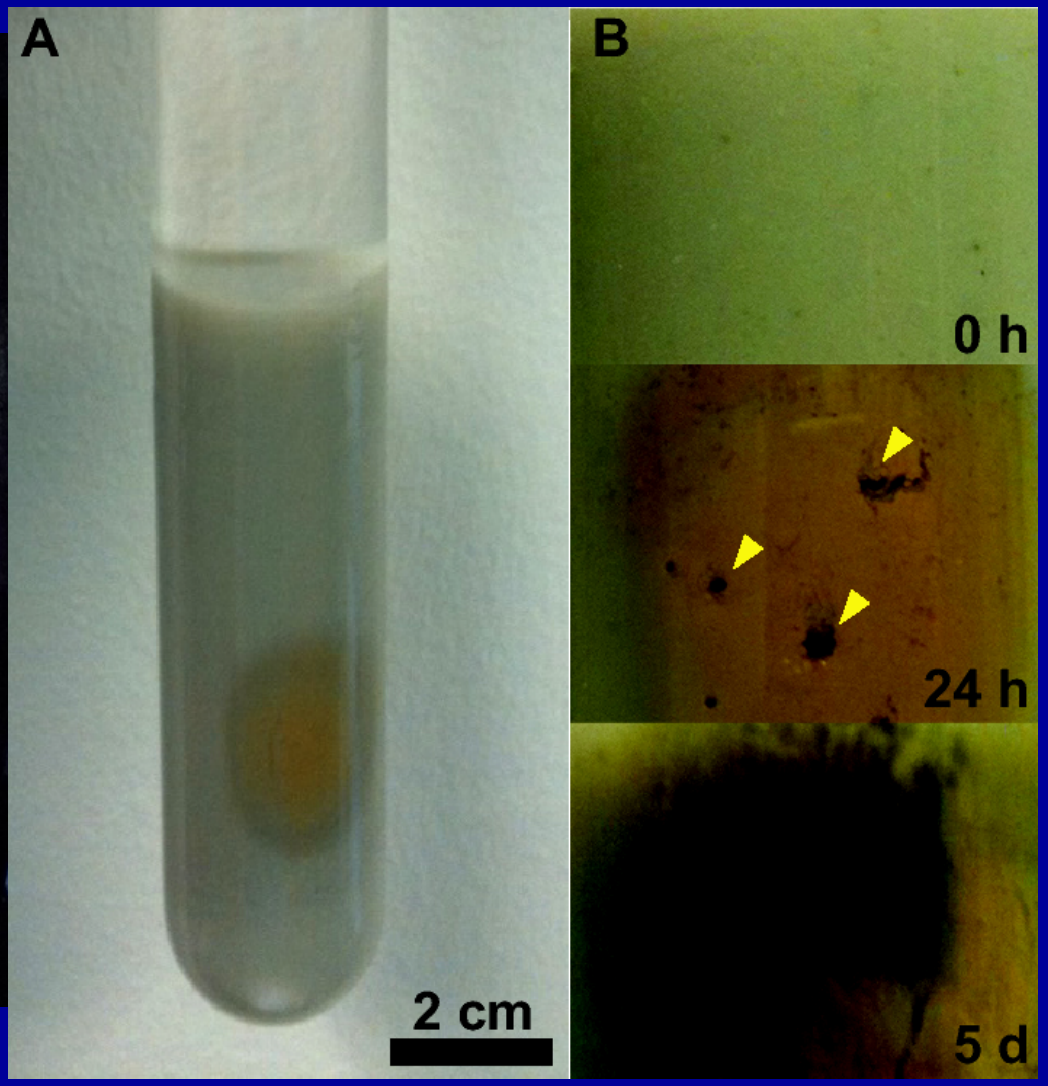
Kim et al, Phil Trans 2013

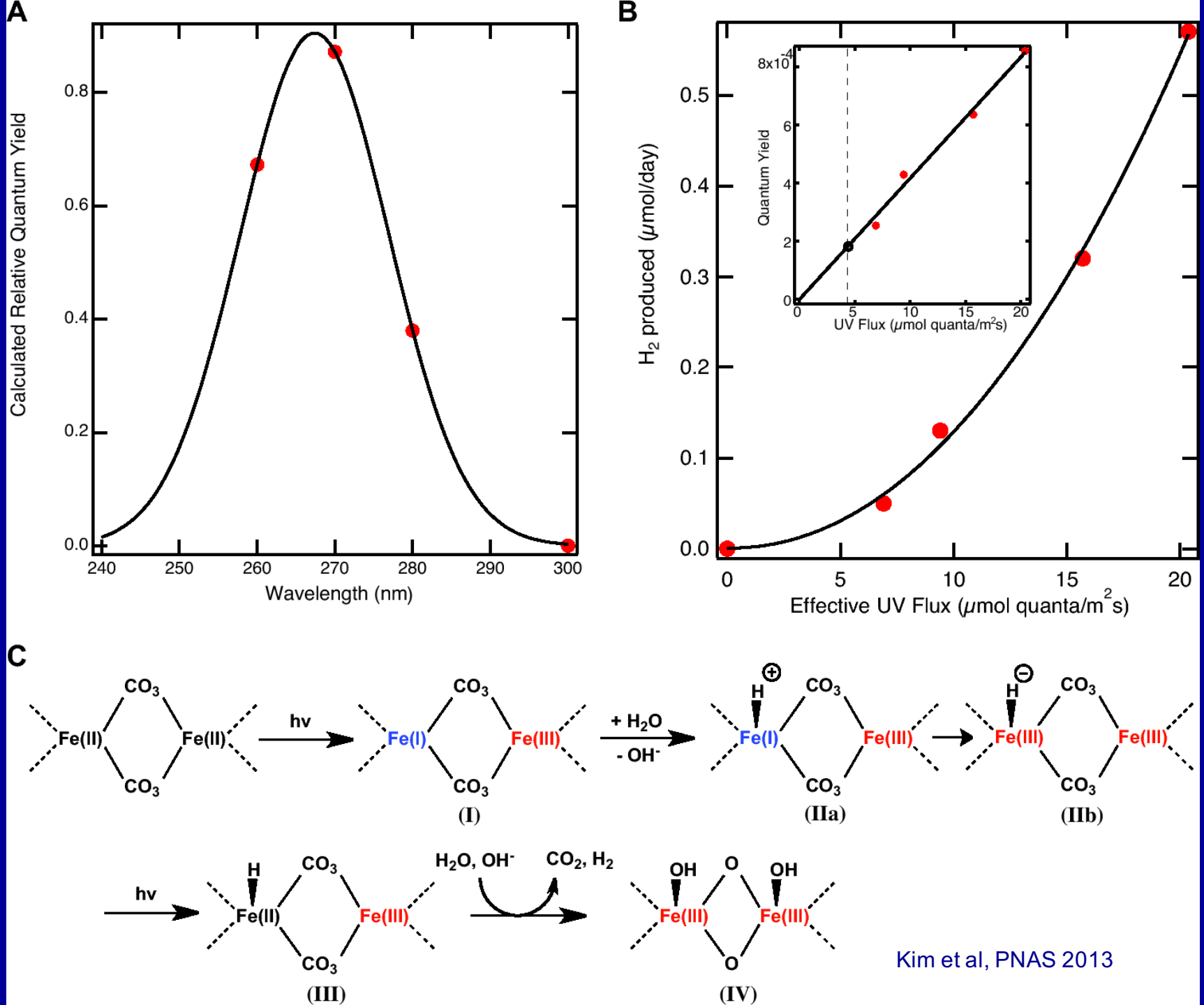
Take Away 4

- On Earth, the electron transfer reactions are almost entirely driven by Light


Top of Atmosphere
At Surface
10 m Below
Ocean Surface
Irradiance (W m-2 nm-1)
Wavelength (nm)
0.0
0.5
1.0
1.5
2.0
500
1000
1500
2000




A
2 cm
B
0 h
24 h
5 d



Kim et al, PNAS 2013

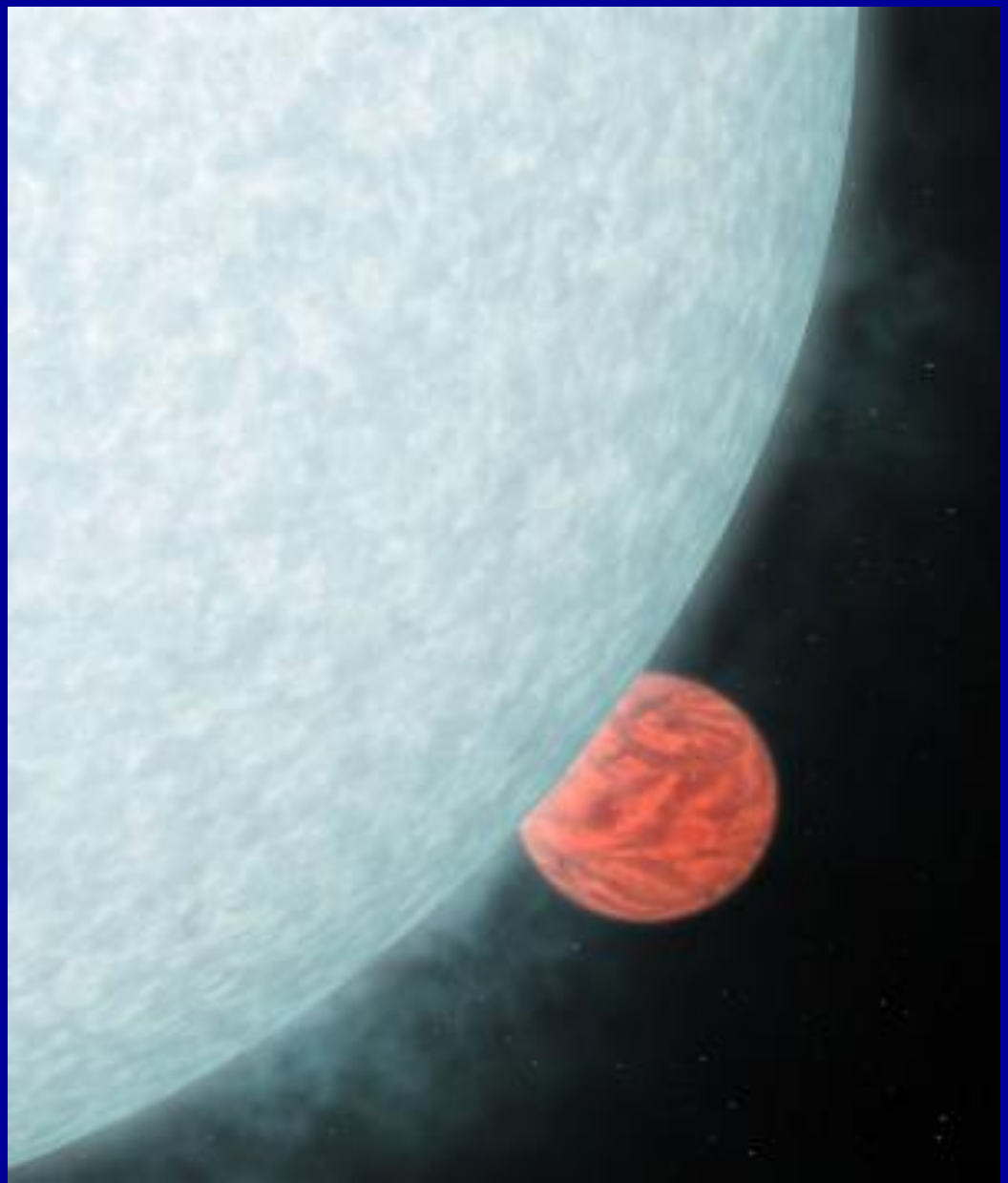
Type	H_2 flux ($x10^{11}$ mol yr^{-1})	Reference
Subaerial volcanoes	0.9 – 3.4	Canfield
Ocean crust serpentiniation	0.8 – 1.3	Canfield
Mid-ocean ridge volcanoes	0.07 – 0.27	Canfield
Total H_2 flux	1.8 – 5.0	Canfield
Siderite Photooxidation	2.0	This work
Type	H_2 flux (pmol $cm^{-2}min^{-1}$)	Reference
Volcanic outgassing	0.92	Tian & Toon
Siderite photooxidation	3.8	This work

Conclusions

1. In the first ca. 2.5 Ga of Earth's history, nature invested heavily in R&D from which a "core" set of metabolic machines evolved.
2. All of the key metabolic processes were developed in prokaryotes
3. There are approximately 400 core metabolic genes that make biological electrons flow across the planet world.
4. These metabolic sequences are coupled on local and planetary scales to facilitate an electron market between C, N, O, and S.
5. The electronic potential is driven by light

Terrestrial Planet Finder

Glows from other planets




Thank you!