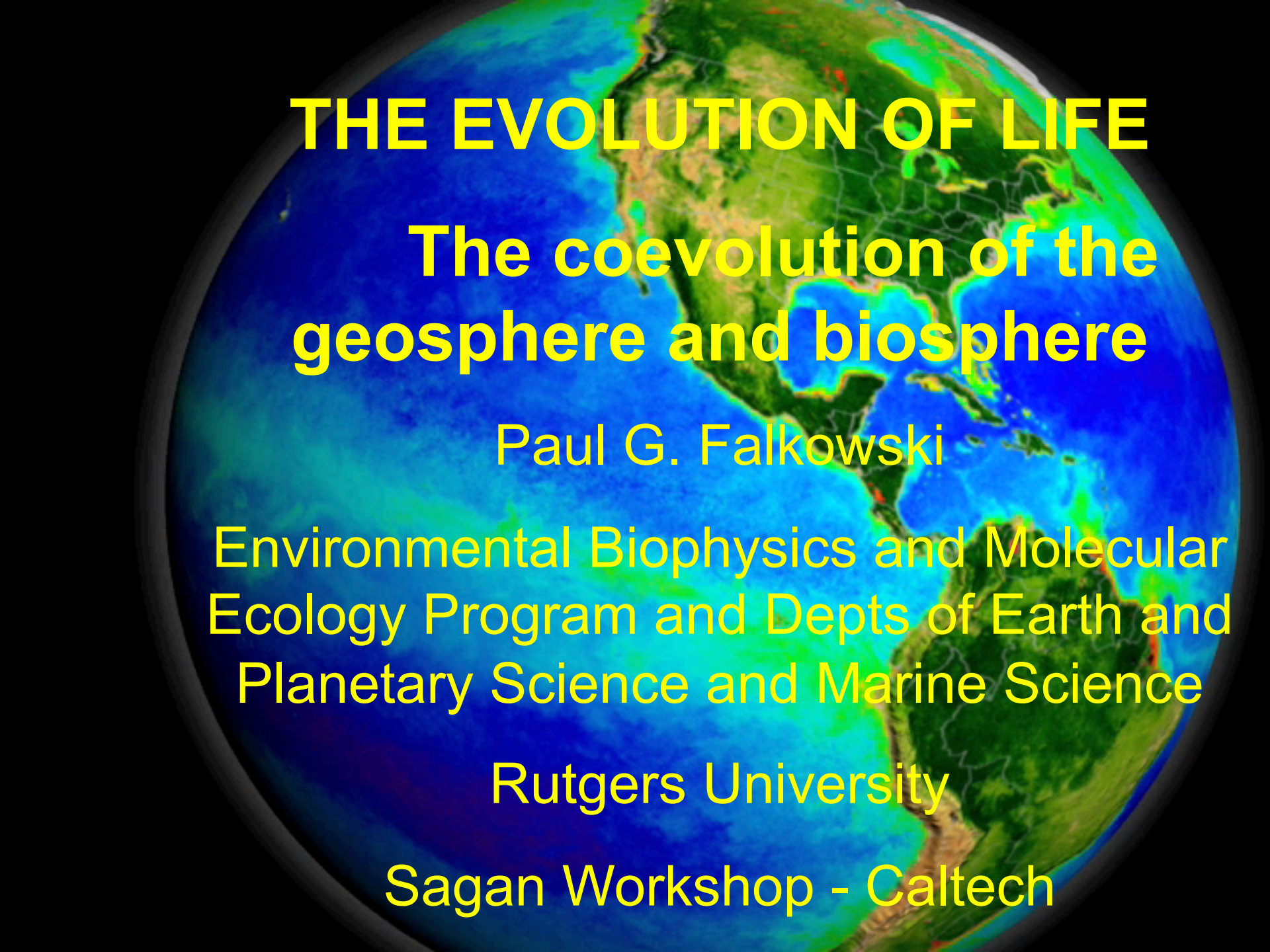


THE EVOLUTION OF LIFE

The coevolution of the geosphere and biosphere

Paul G. Falkowski

Environmental Biophysics and Molecular Ecology Program and Depts of Earth and Planetary Science and Marine Science

Rutgers University

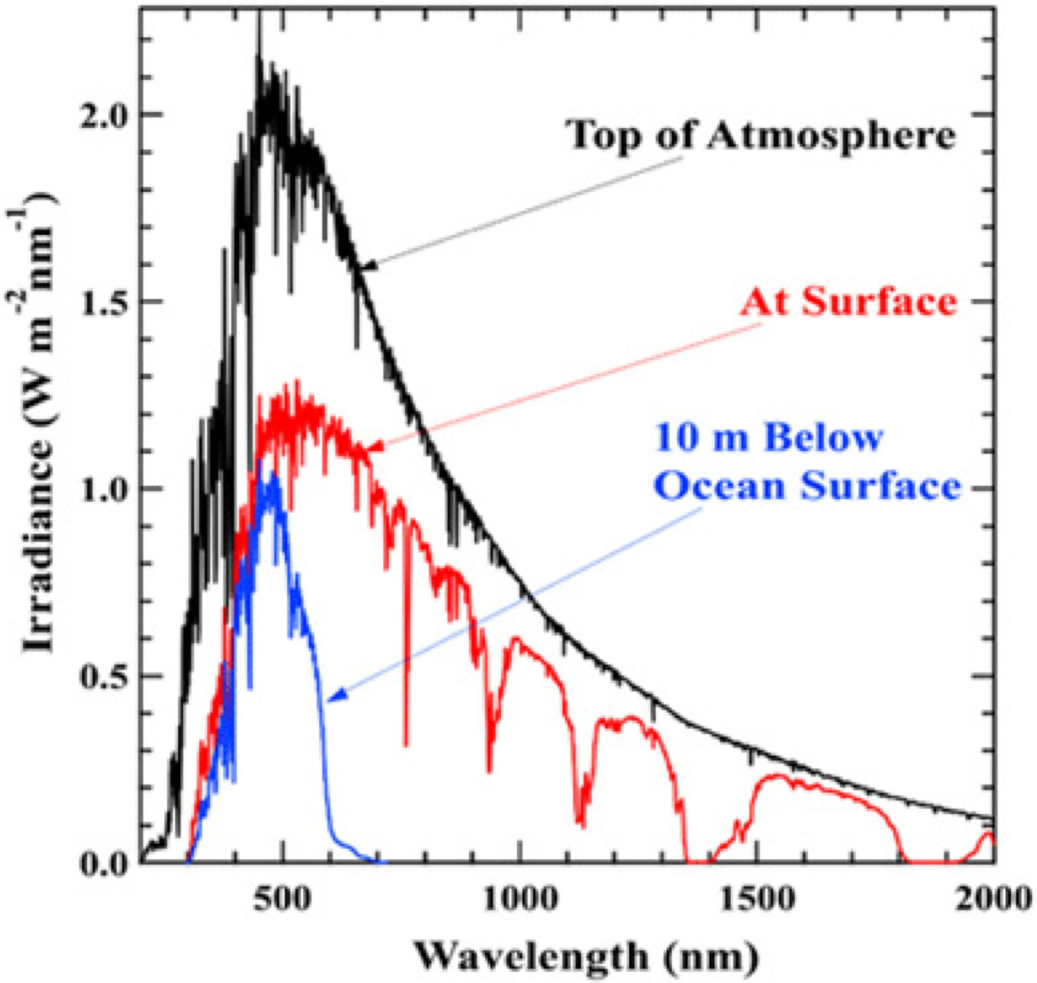
Sagan Workshop - Caltech

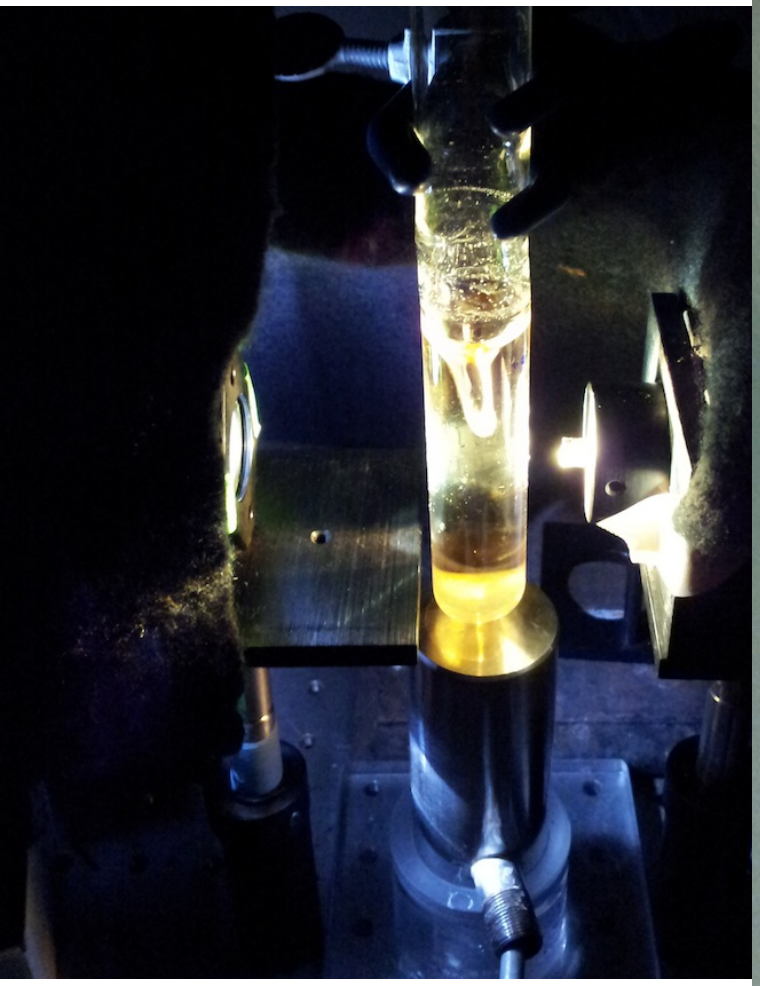
e·nig·ma

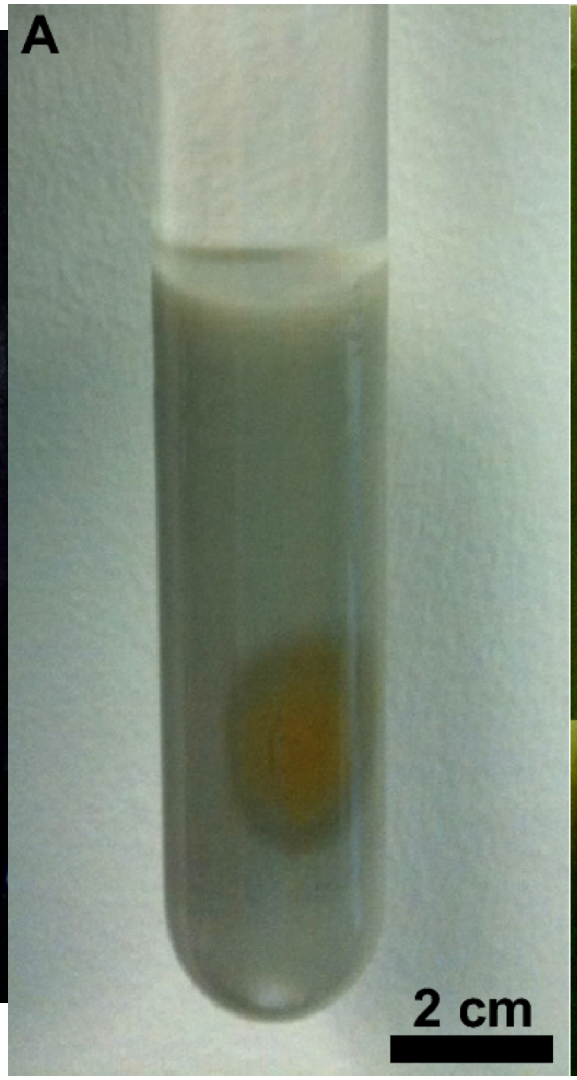
Evolution of Nanomachines In Geospheres and Microbial Ancestors

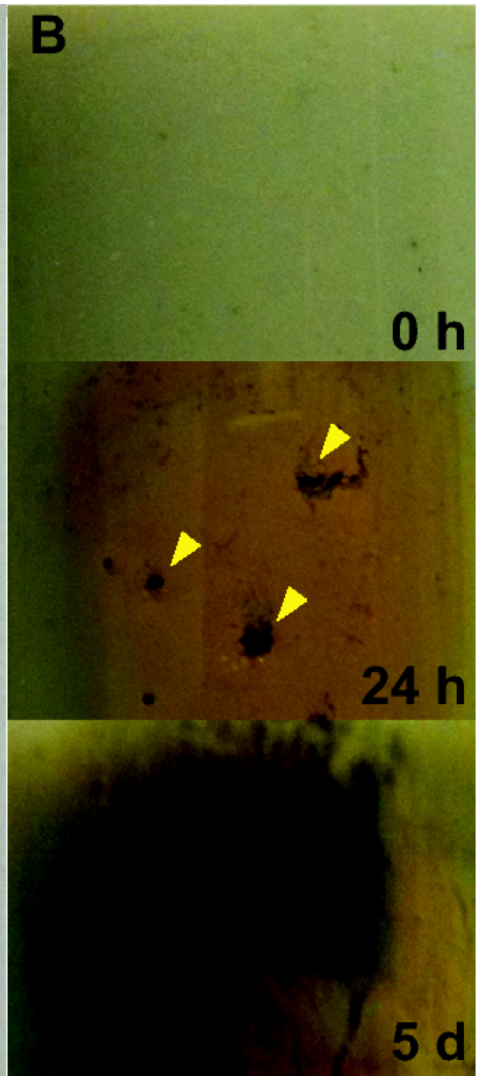
https://enigma.rutgers.edu

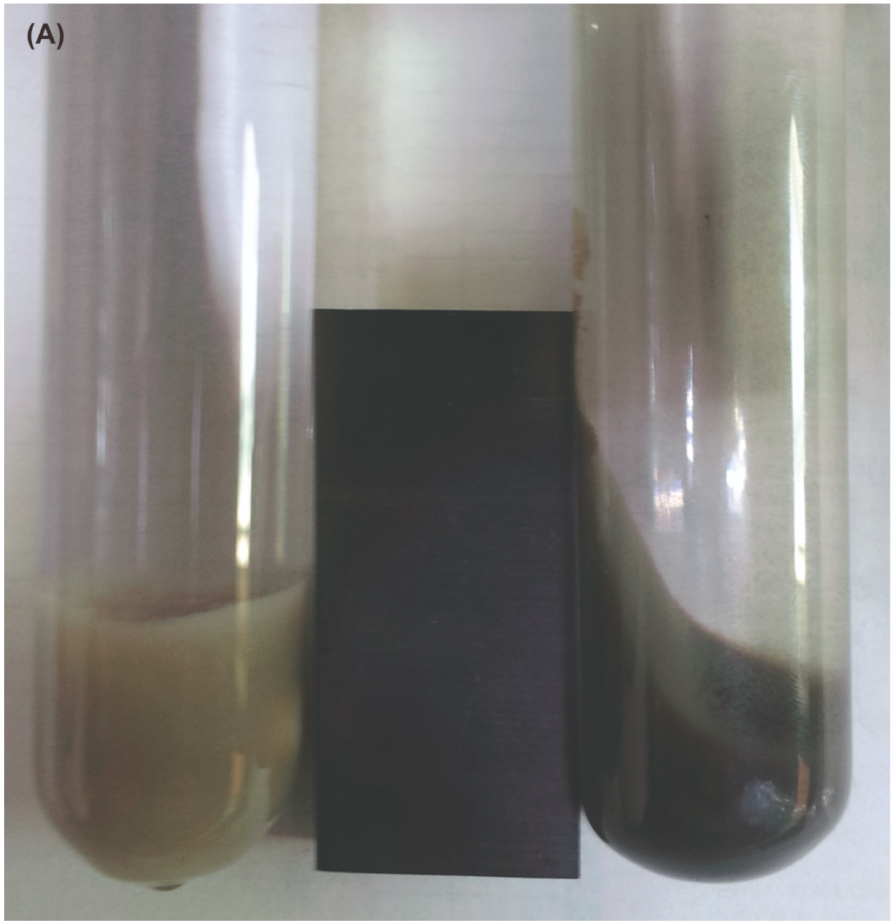
The Enigma research team is part of
the NASA Astrobiology Institute (NAI)

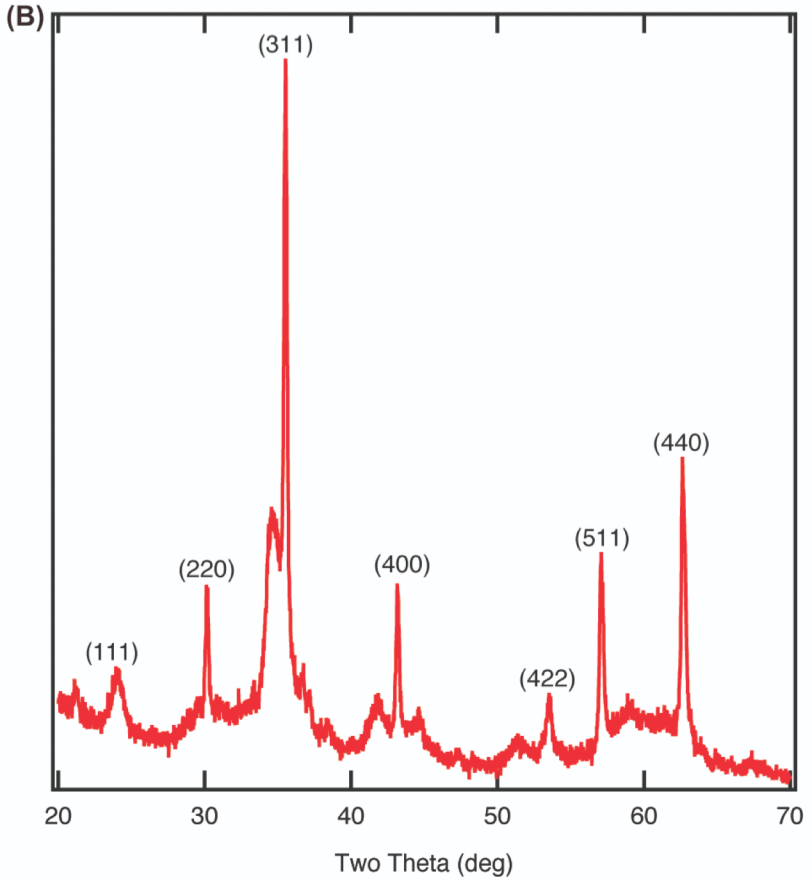

Top of Atmosphere
At Surface
10 m Below
Ocean Surface
Irradiance (W m-2 nm-1)
Wavelength (nm)
0.0
0.5
1.0
1.5
2.0
500
1000
1500
2000



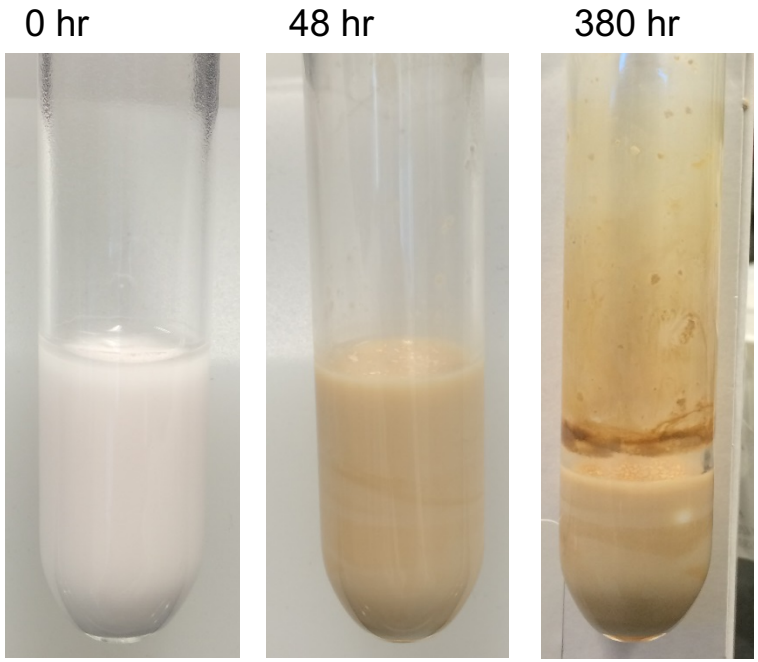

A
2 cm

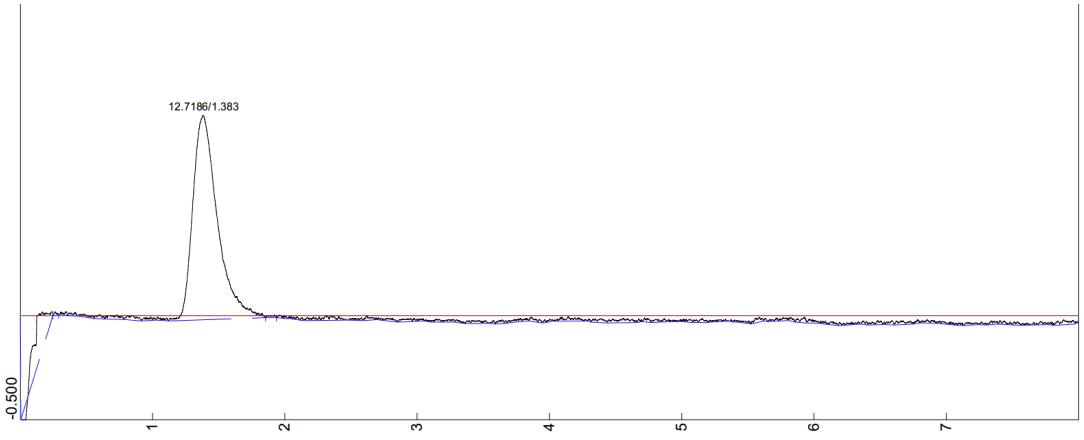

B
0 h
24 h
5 d

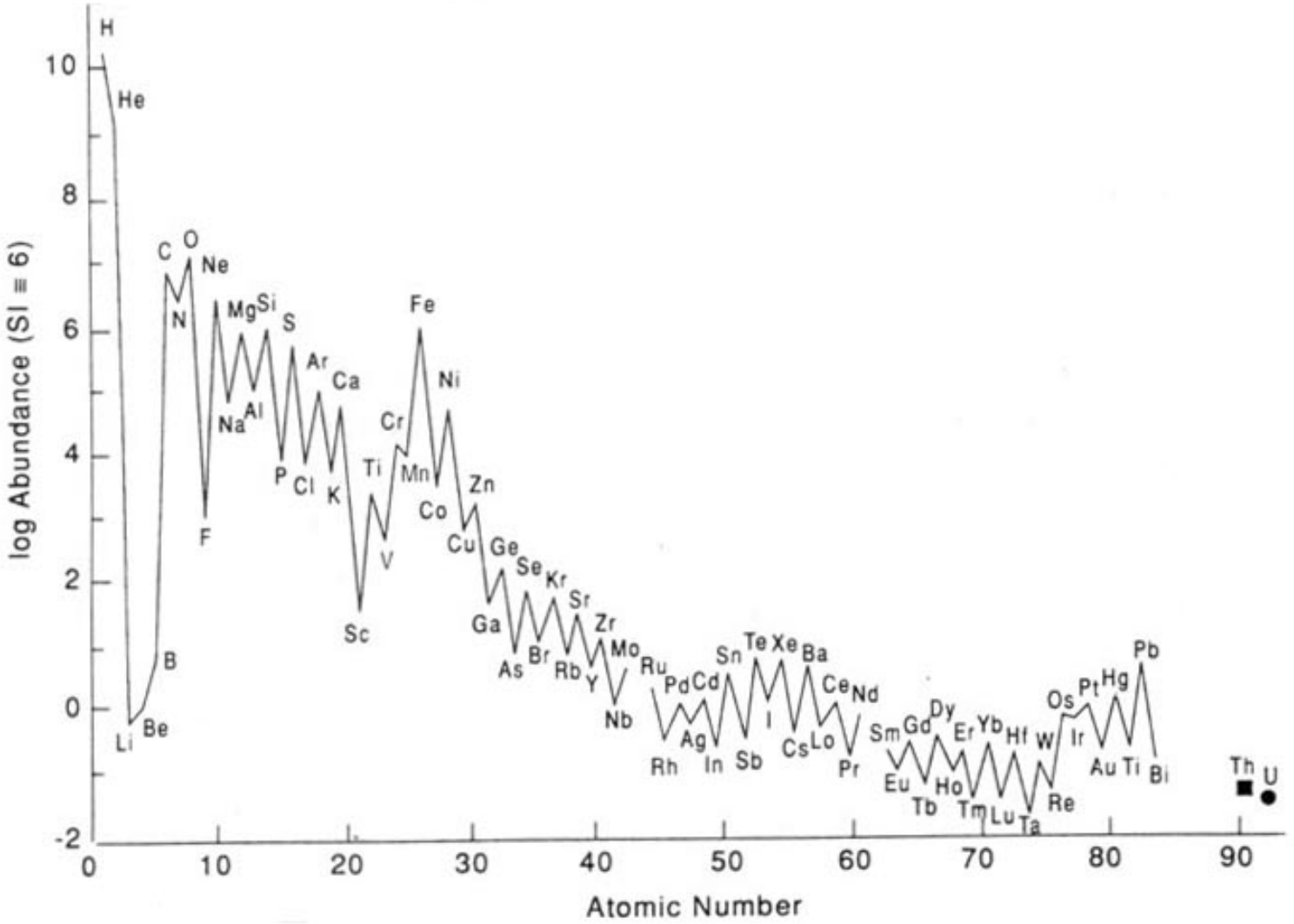

(A)


(B)
(311)
(440)
(511)
(220)
(400)
(111)
(422)
20
30
40
50
60
70
Two Theta (deg)

Production of H_2 from the irradiation of $MnCO_3$ with UV light






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
Lo
Pr
Ce
Nd
Sm
Eu
Gd
Tb
Dy
Ho
Er
Tm
Yb
Lu
Hf
Ta
W
Re
Os
Ir
Pt
Au
Hg
Ti
Pb
Bi
Th
U

The origin of life is the invention 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"

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)

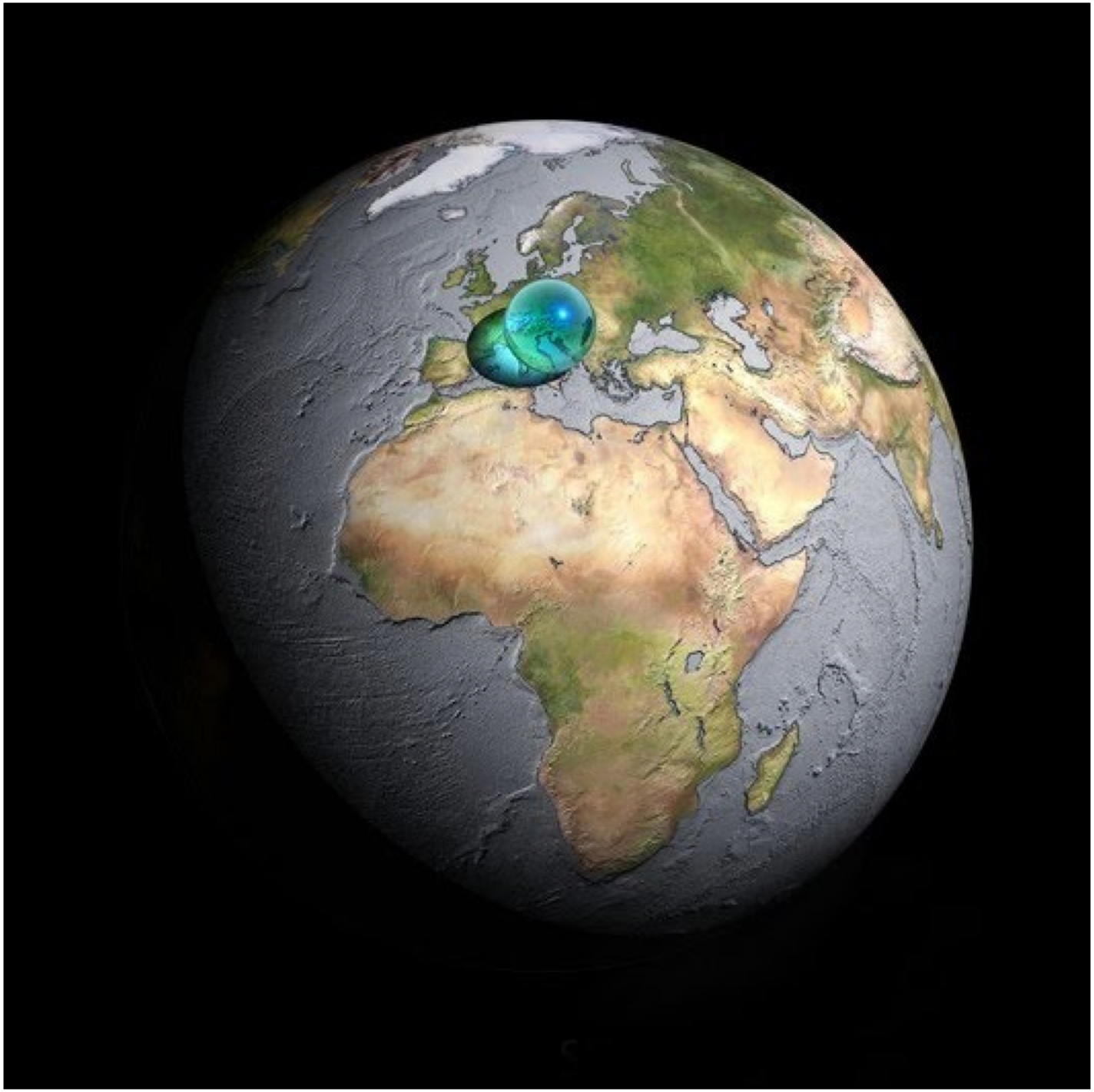
In the Archean Oceans the primary sources of electrons were…

H_2, Fe(II), H_2S and CH_2O

The major source of electrons today is

LIQUID WATER

(H_2O)



as per Vernadsky

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

Many of the core metabolic processes are related to gas exchange processes.

The ensemble of redox reactions are coupled on a Planetary SCALE

Oxygenic Photosynthesis

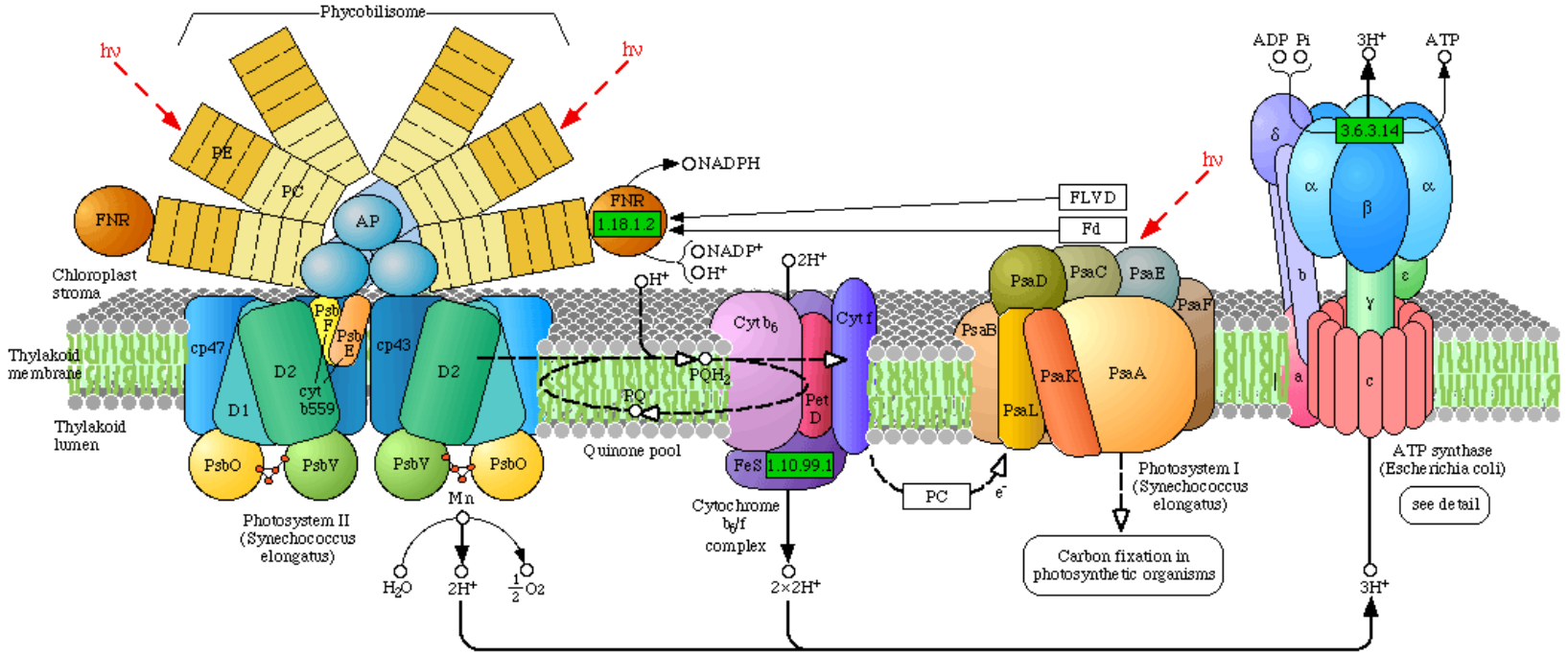
$$H_2O + CO_2 \longrightarrow (CH_2O)_n + O_2$$

Aerobic Respiration:

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

The evolution of nannomachines
–
selection of biological catalysis

PHOTOSYNTHESIS



Photosystem II

D1	D2	cp43	cp47	cyt b559			
PsbA	PsbD	PsbC	PsbB	PsbE	PsbF		
PsbL	PsbJ	PsbK	PsbM	PsbN	PsbH	PsbT	PsbI
PsbO	PsbP	PsbU	PsbV	PsbW	PsbX	PsbY	PsbZ

Photosystem I

PsaA	PsaB	PsaC	PsaD	PsaE	PsaF	PsaH	PsaI
PsaJ	PsaK	PsaL	PsaM	PsaN	PsaX		

Cytochrome b6/f complex

PetB	PetD	PetA	PetC	PetL	PetM	PetN	PetG	PetE	PetF	PetH

Allophycocyanin (AP)

ApcA	ApcB	ApcC	ApcD	ApcE	ApcF

Phycocyanine (PC)

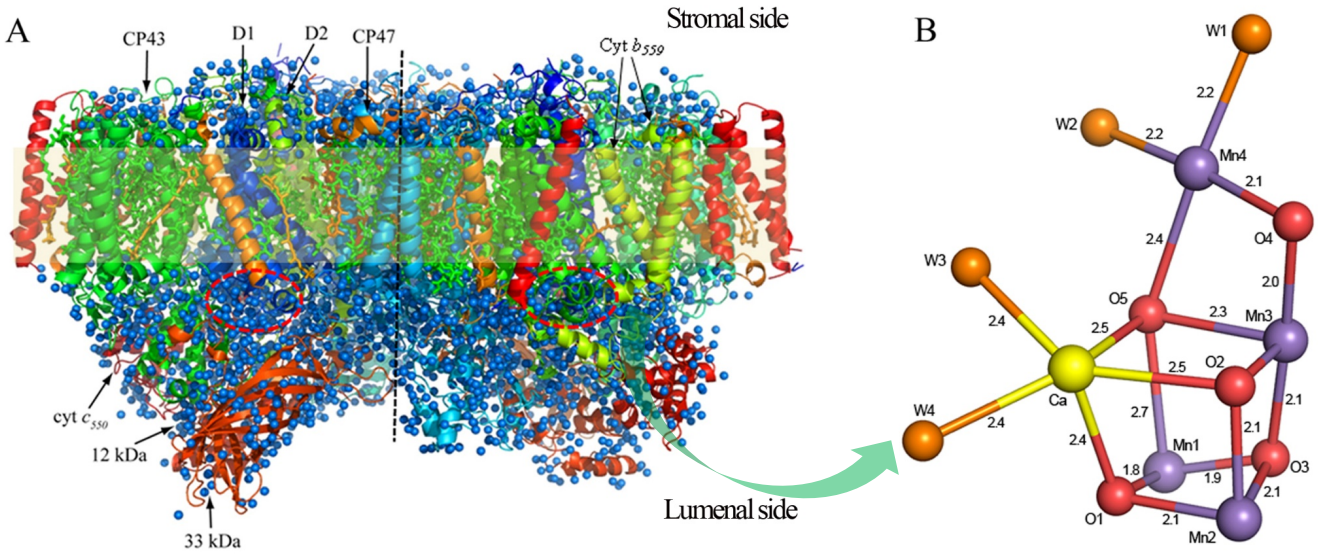
CpcA	CpcB	CpcC	CpcD	CpcE	CpcF	CpcG

Phycoerythrin (PE)

PecA	PecB	PecC	PecE	PecF

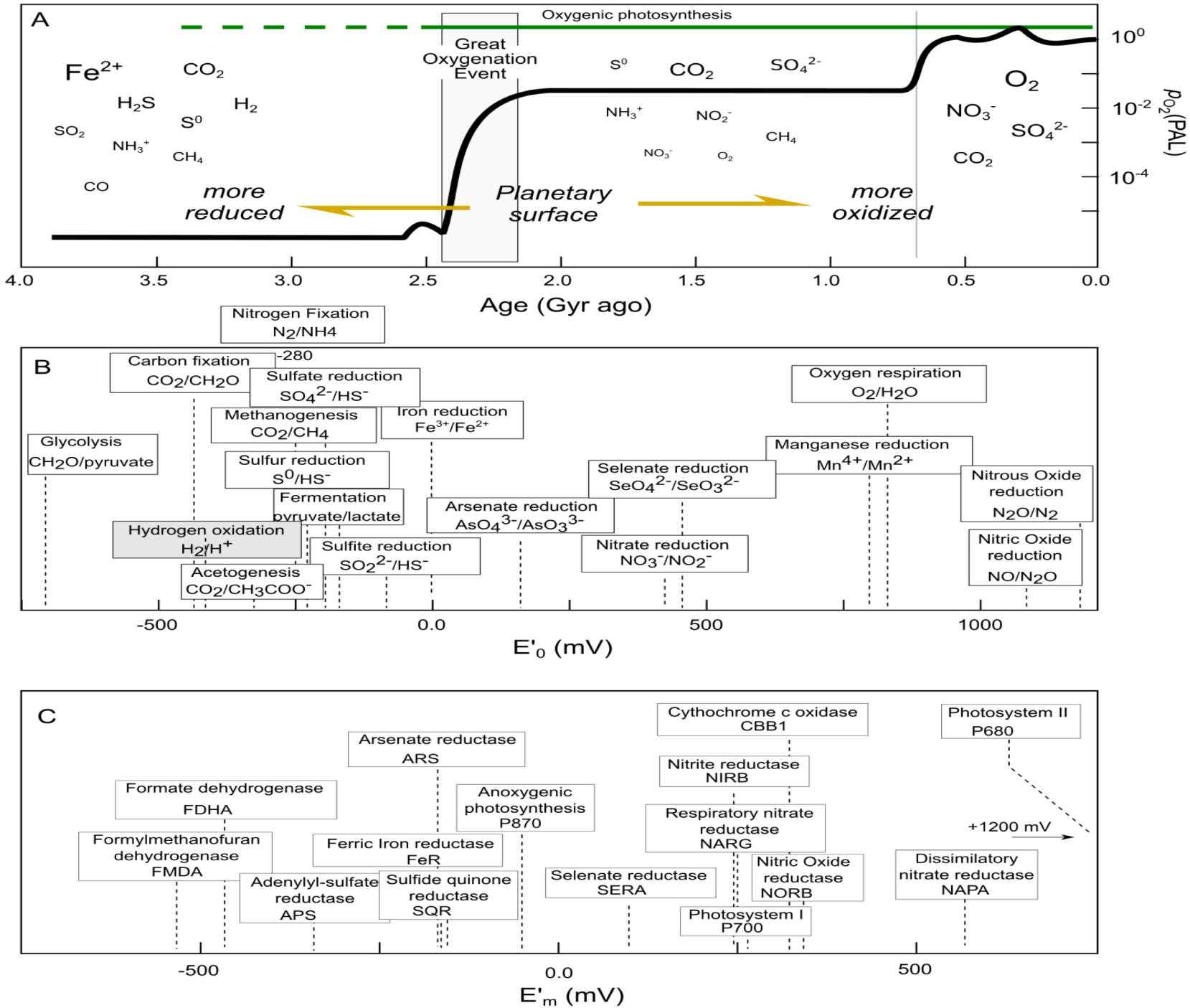
00195 7/16/03

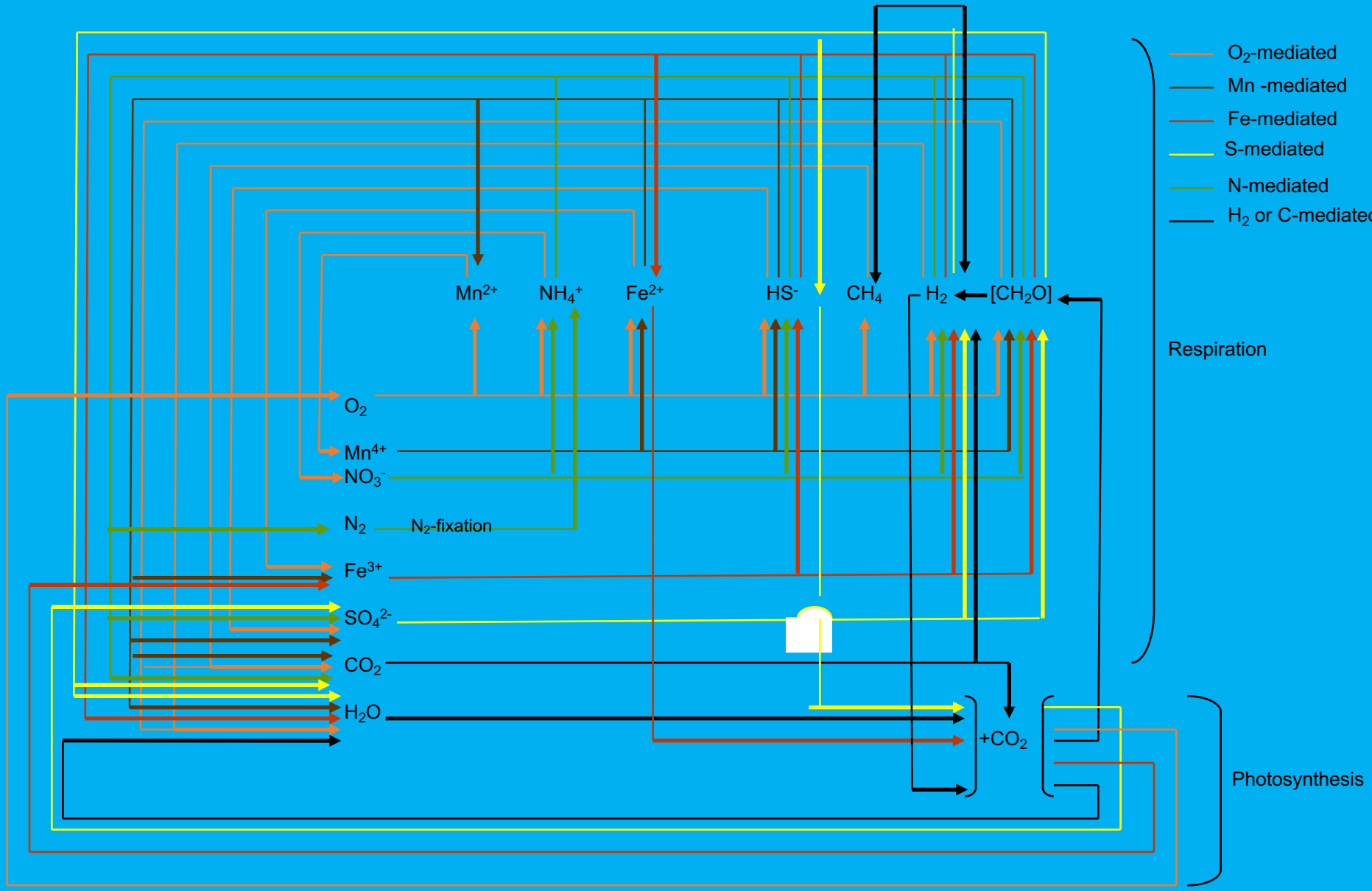
1.9 Å resolution structure of PSII dimer



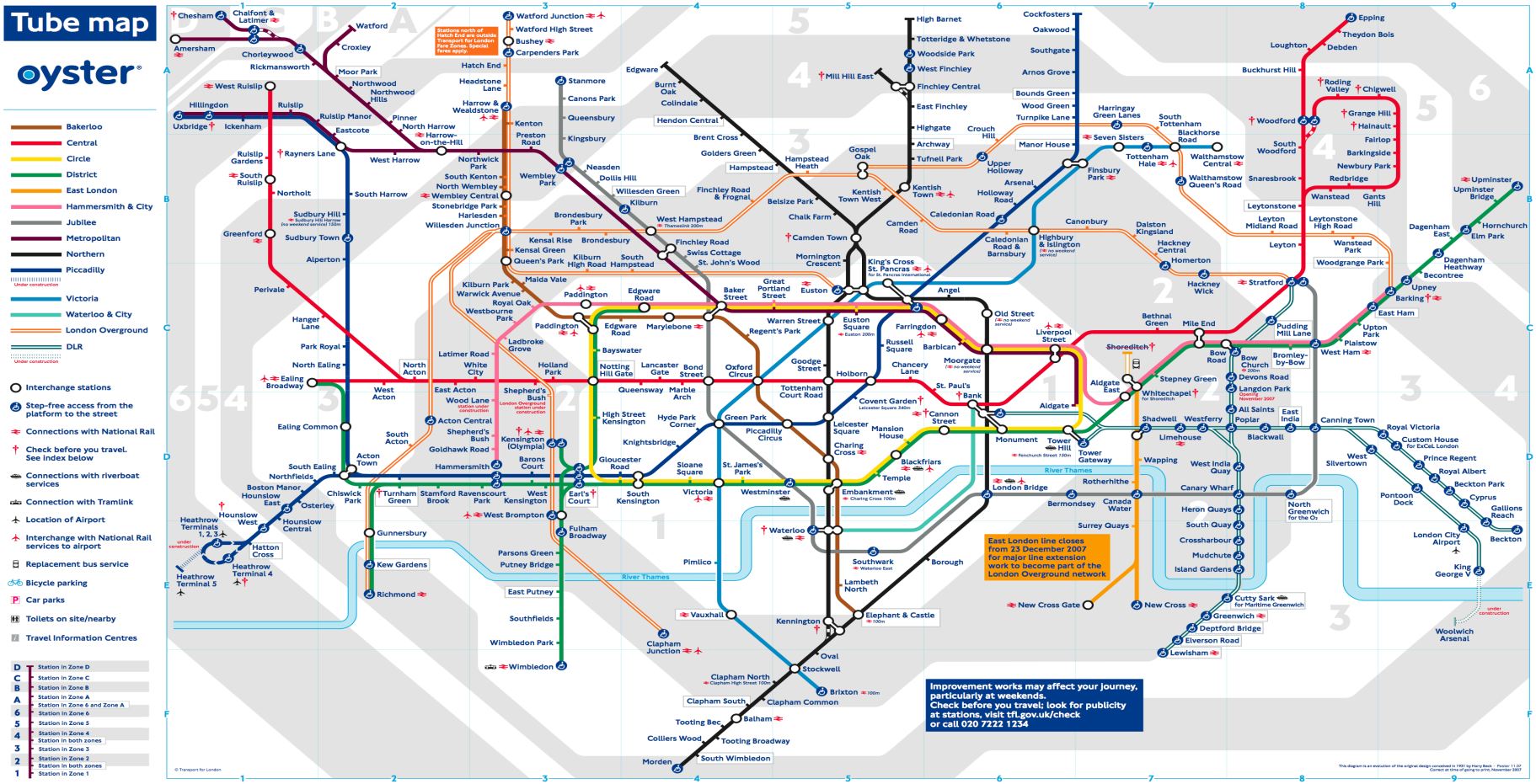
Nature (2011, 2015, 2017)

Total subunits : 40
Overall MW : 700 kDa
The largest membrane protein complex whose structure has been solved beyond 2.0 Å


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
Selenate reductase SERA
Adenylyl-sulfate reductase APS
Sulfide quinone reductase SQR
Photosystem I P700
-500
0.0
500
E'm (mV)



Falkowski, Fenchel and Delong, Science, 2008



MAYOR OF LONDON

24 hour travel information 020 7222 1234

Website tfl.gov.uk

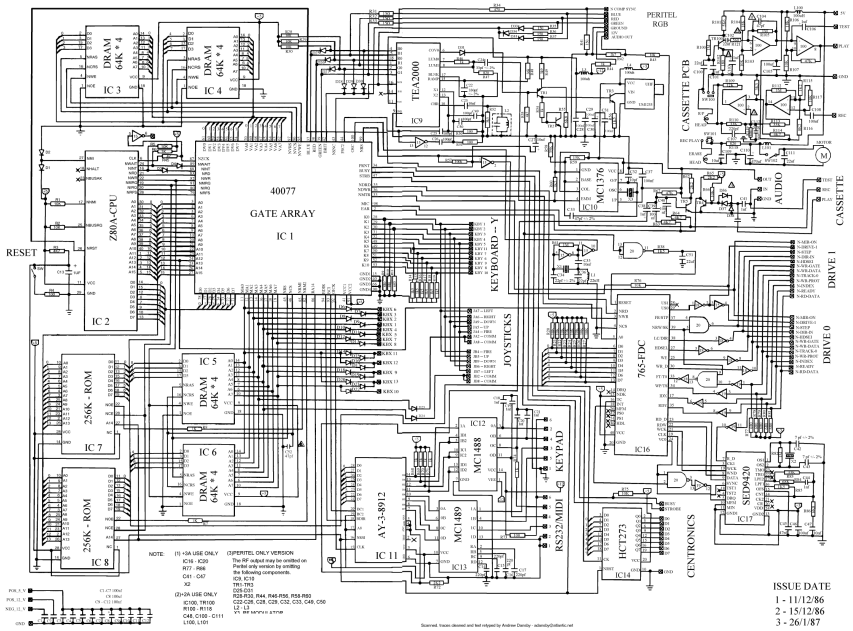
Transport for London

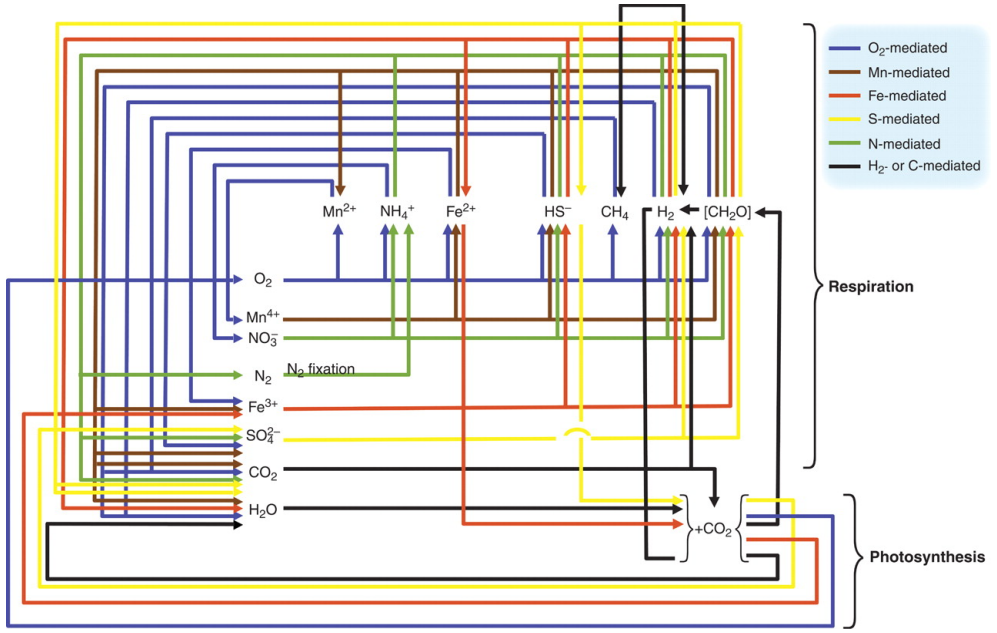
TM Quad 3d 11.07 4 Colour Process

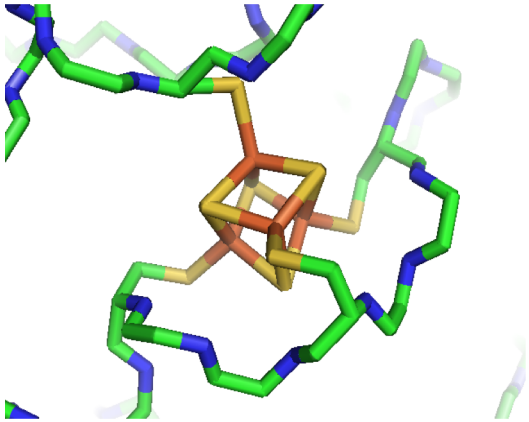
This annotation of this metabolic map reveals there are only about **400** core genes responsible for all electron transport reactions on the planet!

How are the electrons connected?

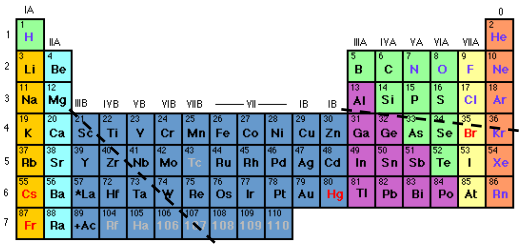
Metals in protein “transistors”







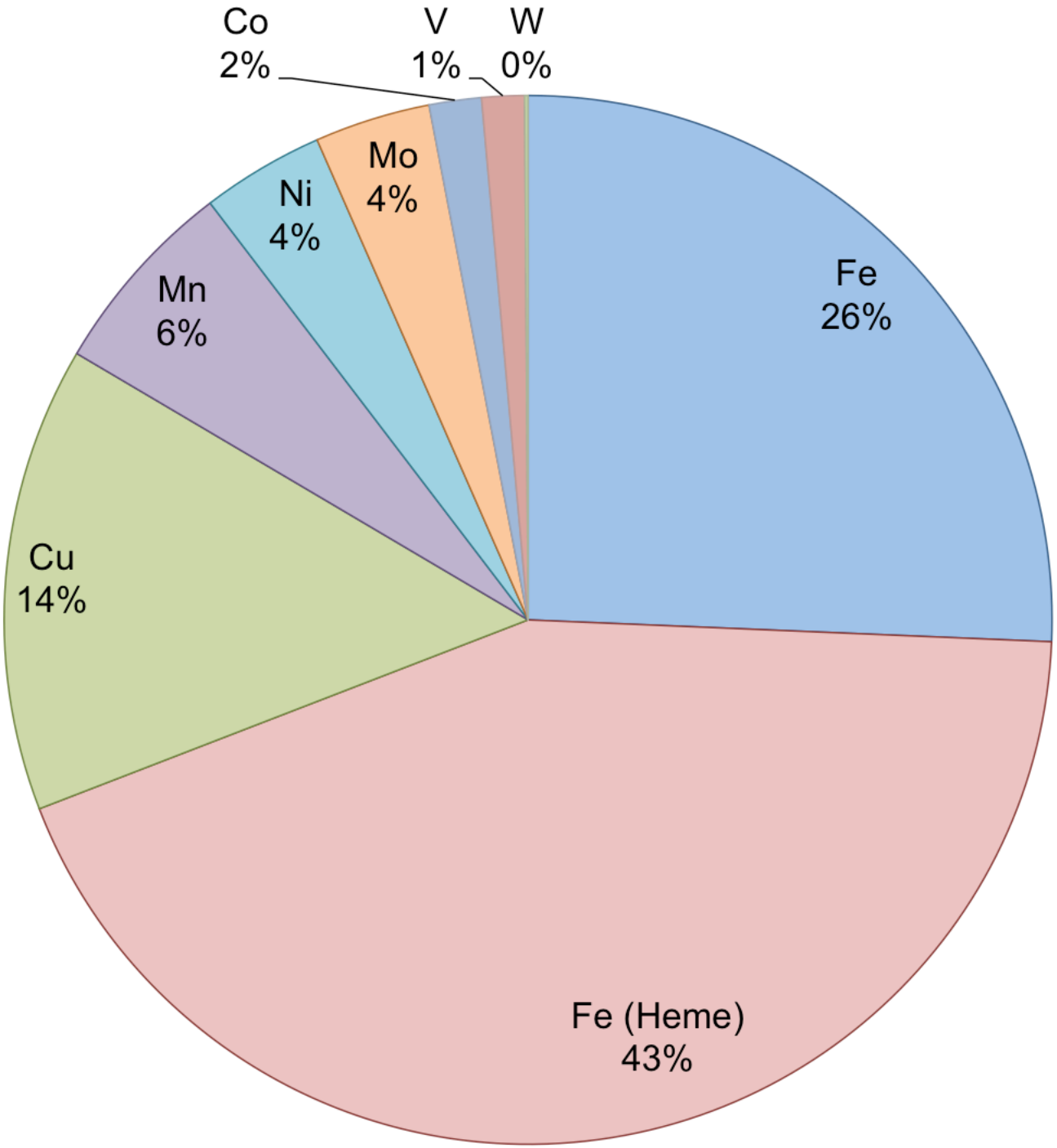
“Periodic Table” of Transition Metal Binding Proteins



Swiss-Prot+Gene Ontology

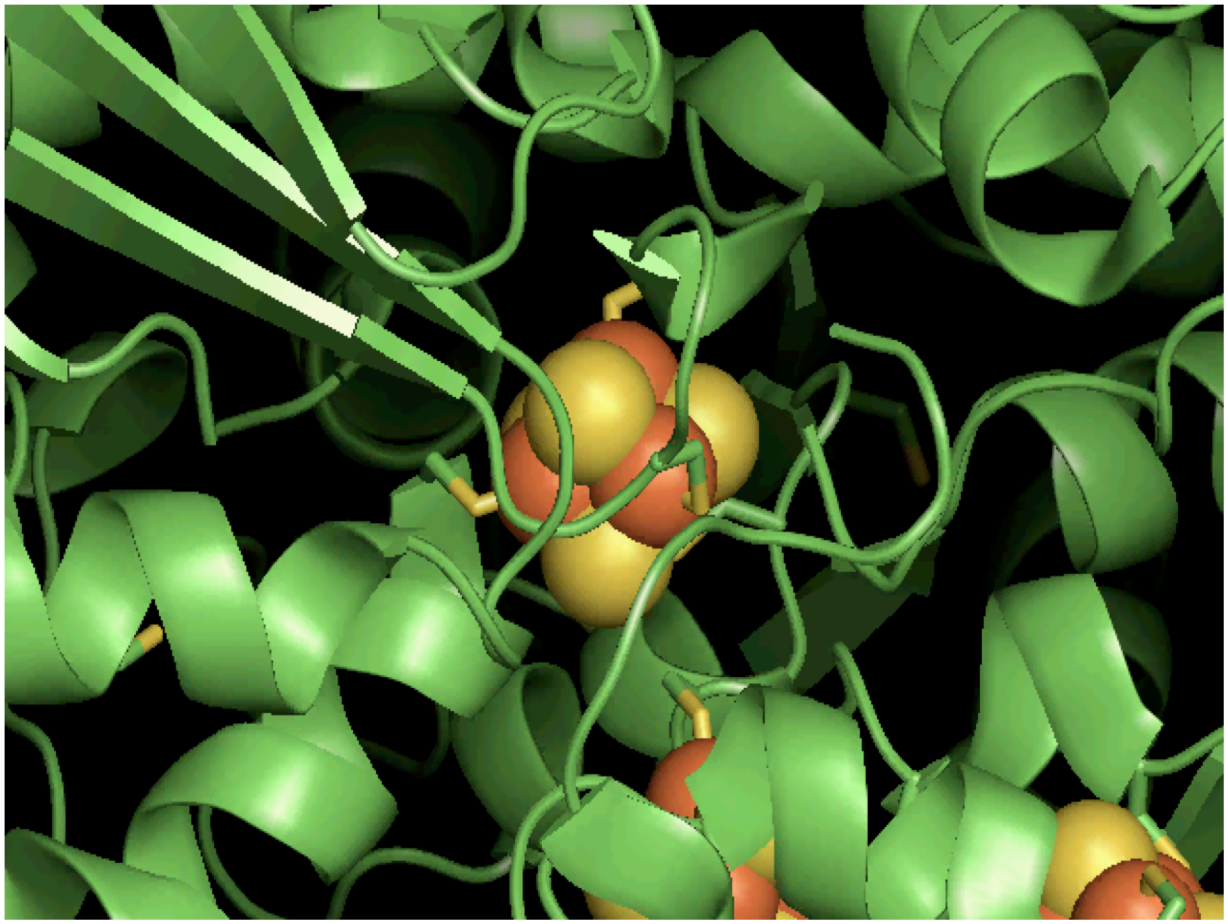
								47	77
		7 1		647 23	8248 360	86	247 75	1299	2090
21 **Sc** Scandium 44.955910	22 **Ti** Titanium 47.867	23 **V** 7	24 **Cr** Chromium 51.9961	25 **Mn** 7039	26 **Fe** 25006	27 **Co** 914	28 **Ni** 2829	29 **Cu** 2730	30 **Zn** 37263
39 **Y** Yttrium 88.90585	40 **Zr** Zirconium 91.224	41 **Nb** Niobium 92.90638	452 16 42 **Mo** 554	43 **Tc** Technetium (98)	44 **Ru** Ruthenium 101.07	45 **Rh** Rhodium 102.90550	46 **Pd** Palladium 106.42	47 **Ag** Silver 107.8682	4 48 **Cd** 39
57 **La** Lanthanum 138.9055	72 **Hf** Hafnium 178.49	73 **Ta** Tantalum 180.9479	1 1 74 **W** 1	75 **Re** Rhenium 186.207	76 **Os** Osmium 190.23	77 **Ir** Iridium 192.217	78 **Pt** Platinum 195.078	79 **Au** Gold 196.96655	26 1 80 **Hg** 78
89 **Ac** Actinium (227)	104 **Rf** Rutherfordium (261)	105 **Db** Dubnium (262)	106 **Sg** Seaborgium (263)	107 **Bh** Bohrium (262)	108 **Hs** Hassium (265)	109 **Mt** Meitnerium (266)	110 (269)	111 (272)	112 (277)

Number of SwissProt proteins associated with transition metals: All, EC1, and experimentally validated EC1


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

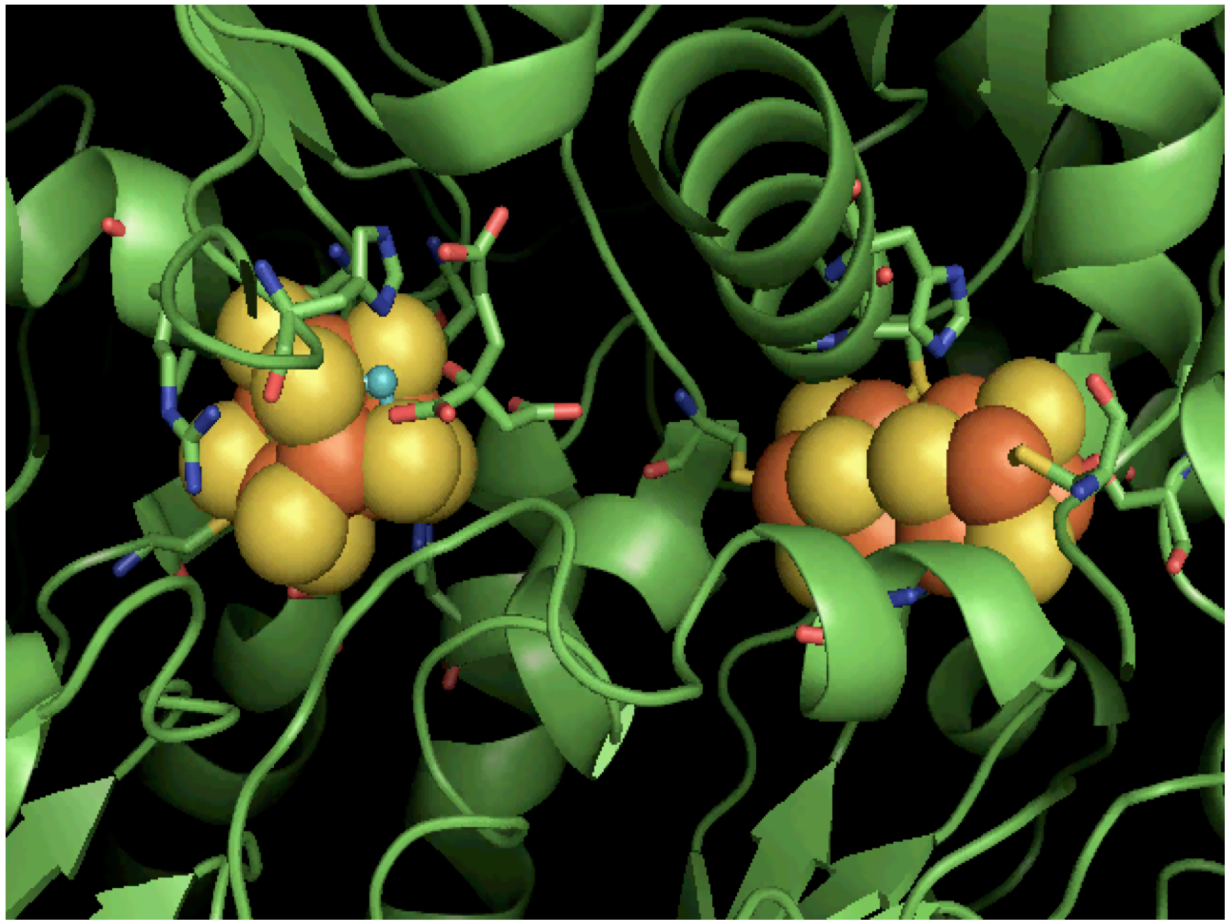
ferredoxin

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



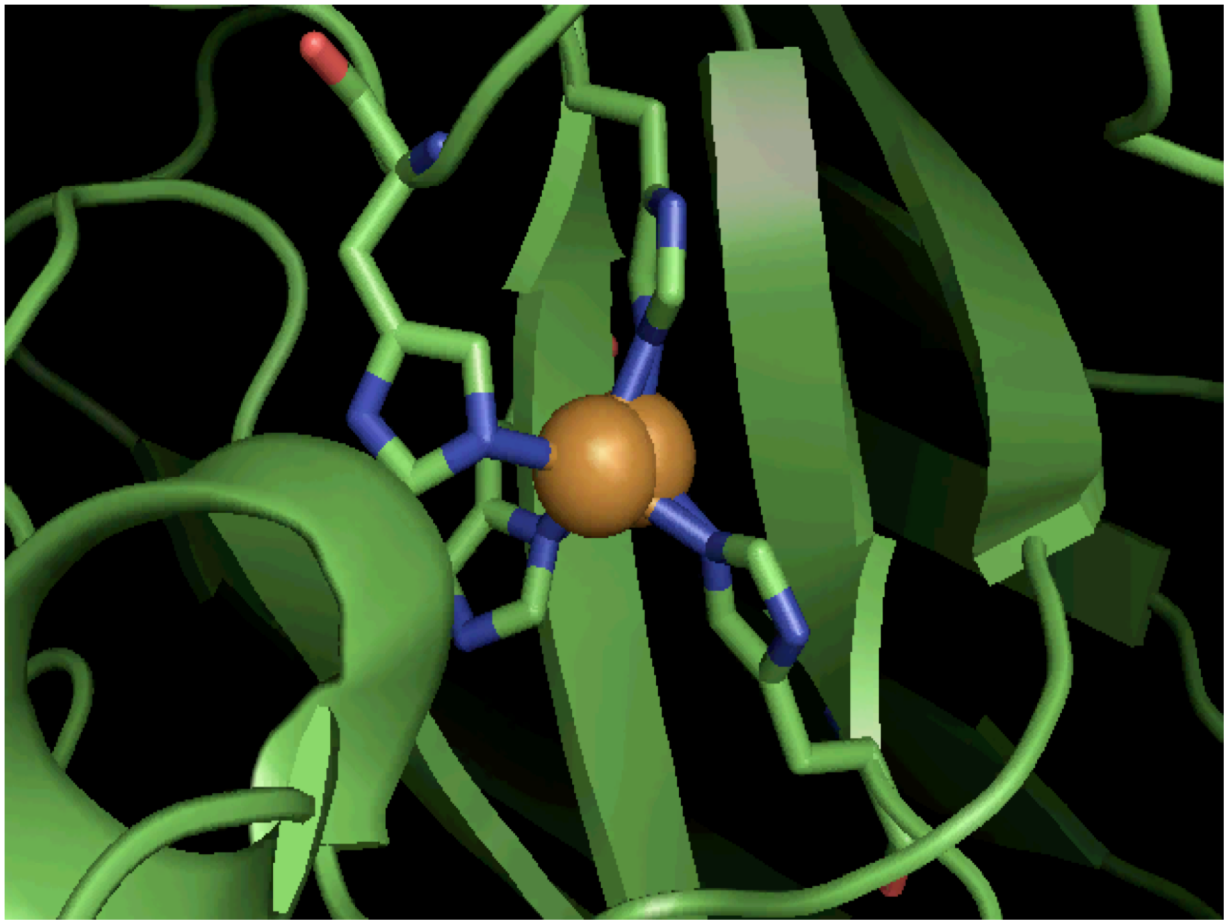
nitrogenase

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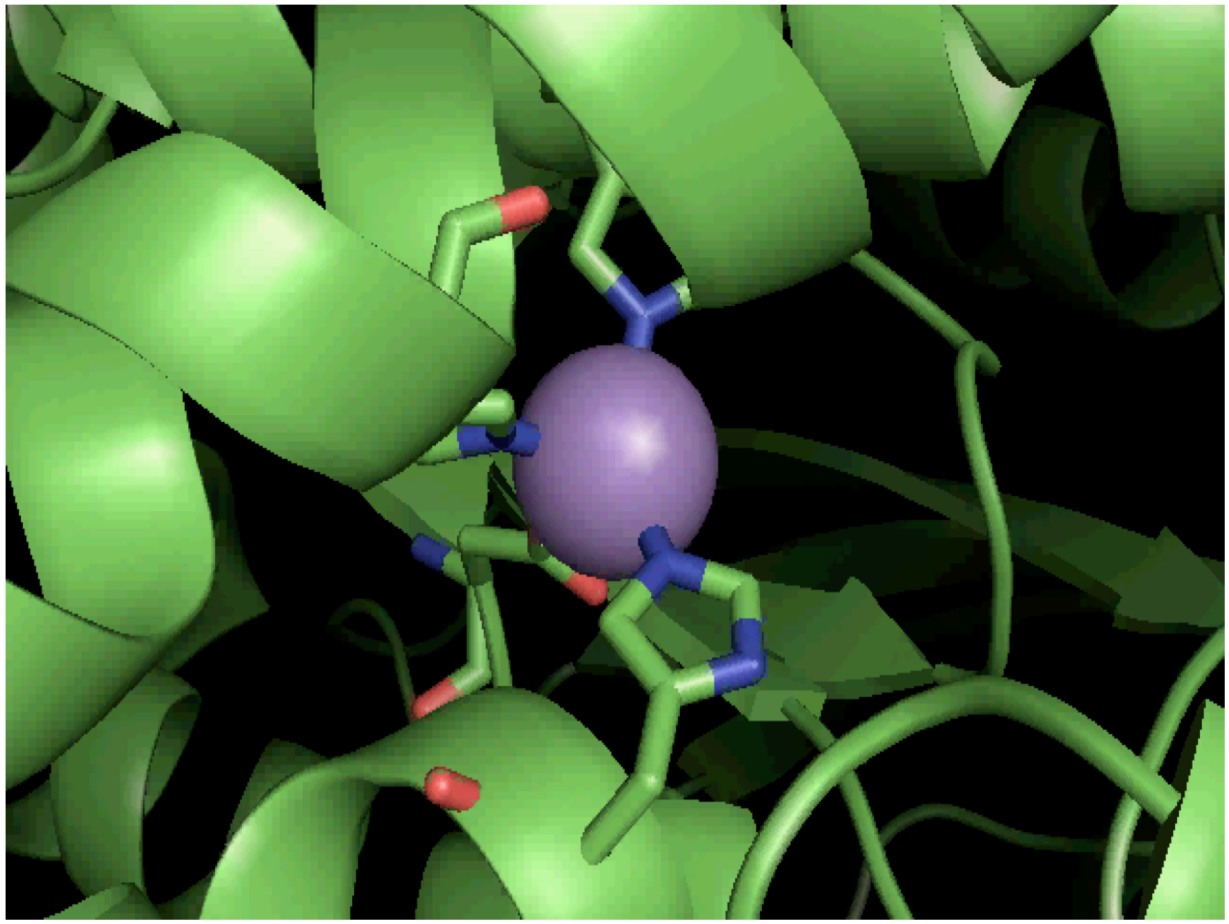
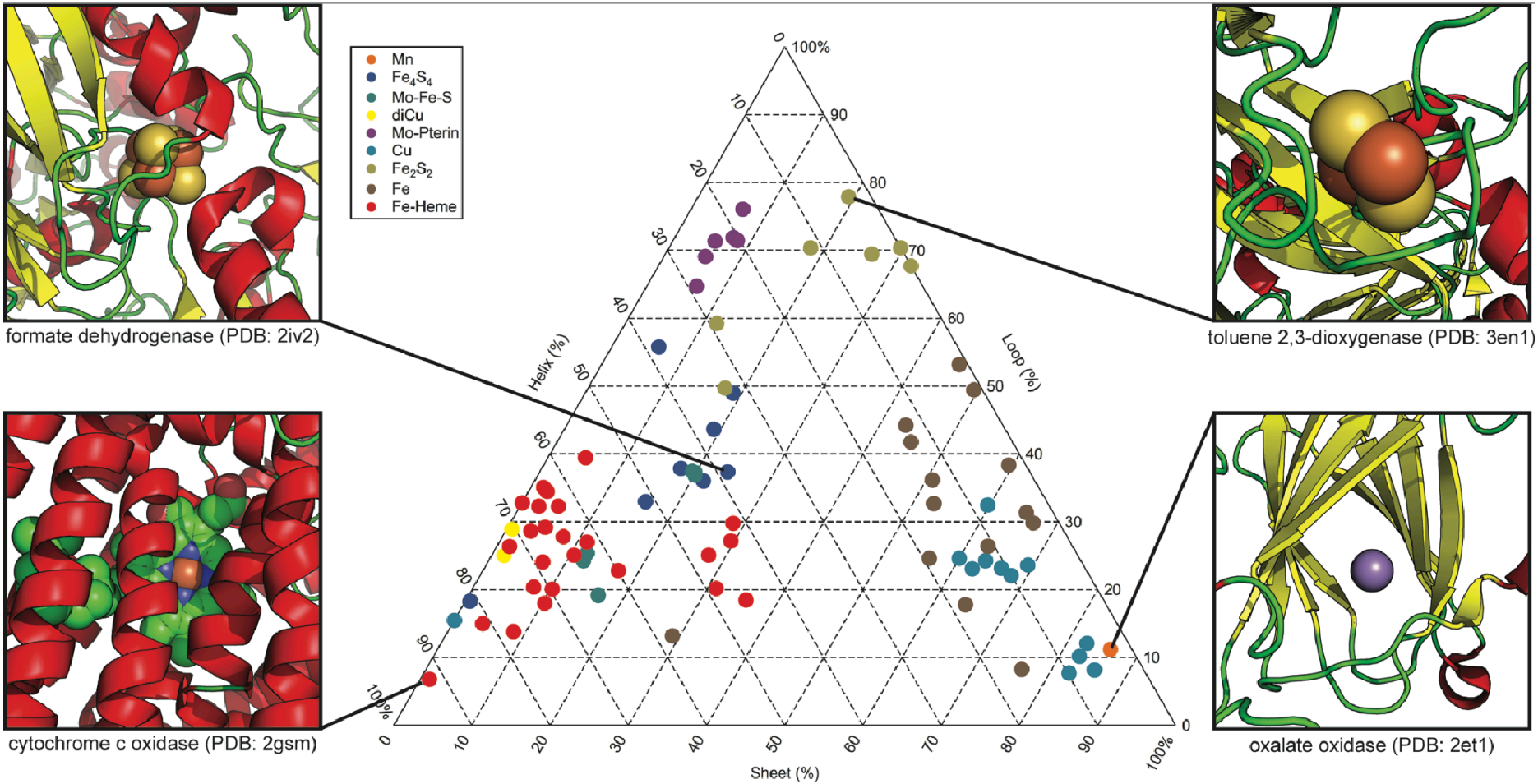
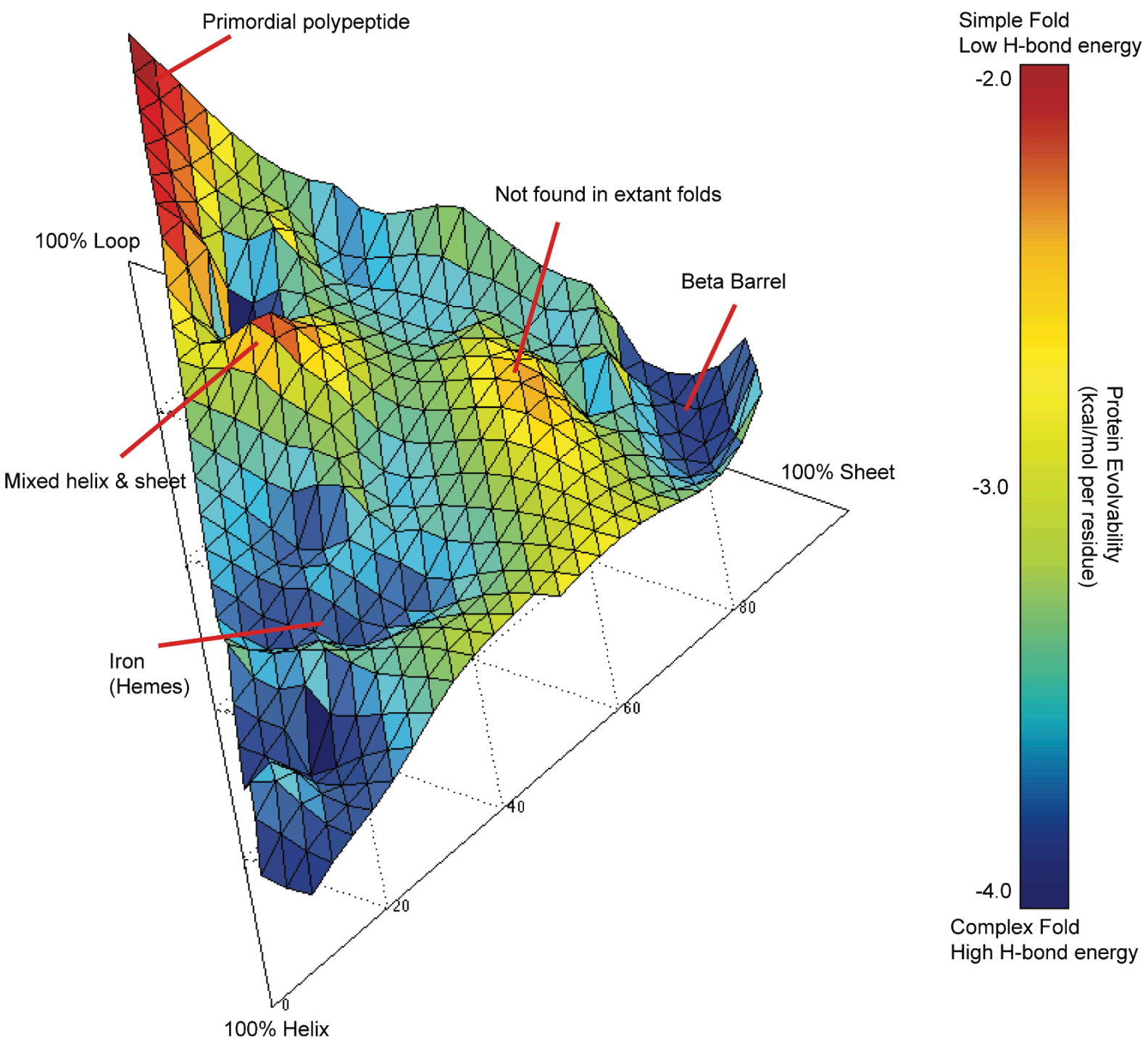
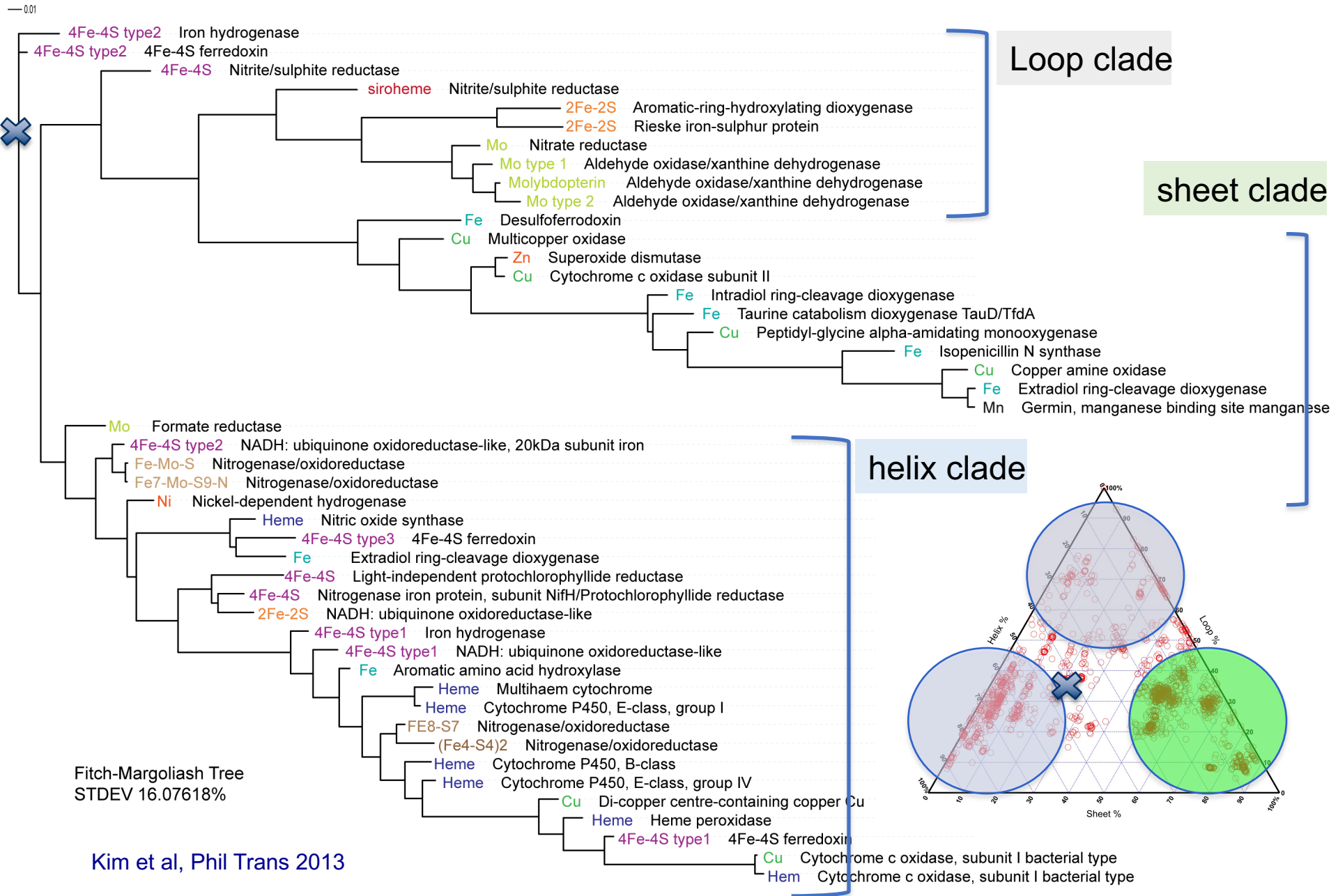
yttrium	zirconium	niobium	molybdenum	technetium	ruthenium	rhodium	palladium	silver	cadmium
39	40	41	42	43	44	45	46	47	48
Y	**Zr**	**Nb**	**Mo**	**Tc**	**Ru**	**Rh**	**Pd**	**Ag**	**Cd**
88.906	91.224	92.906	95.94	[98]	101.07	102.91	106.42	107.87	112.41
lutetium	hafnium	tantalum	tungsten	rhenium	osmium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




Mn
Fe_4S_4
Mo-Fe-S
diCu
Mo-Pterin
Cu
Fe_2S_2
Fe
Fe-Heme
Helix (%)
Loop (%)
Sheet (%)
formate dehydrogenase (PDB: 2iv2)
toluene 2,3-dioxygenase (PDB: 3en1)
cytochrome c oxidase (PDB: 2gsm)
oxalate oxidase (PDB: 2et1)


Primordial polypeptide
Not found in extant folds
100% Loop
Beta Barrel
Mixed helix & sheet
100% Sheet
Iron
(Hemes)
0
20
40
60
80
100% Helix
Simple Fold
Low H-bond energy
-2.0
-3.0
-4.0
Protein Evolvability
(kcal/mol per residue)
Complex Fold
High H-bond energy

A secondary structural tree of EC1 proteins



Kim et al, Phil Trans 2013

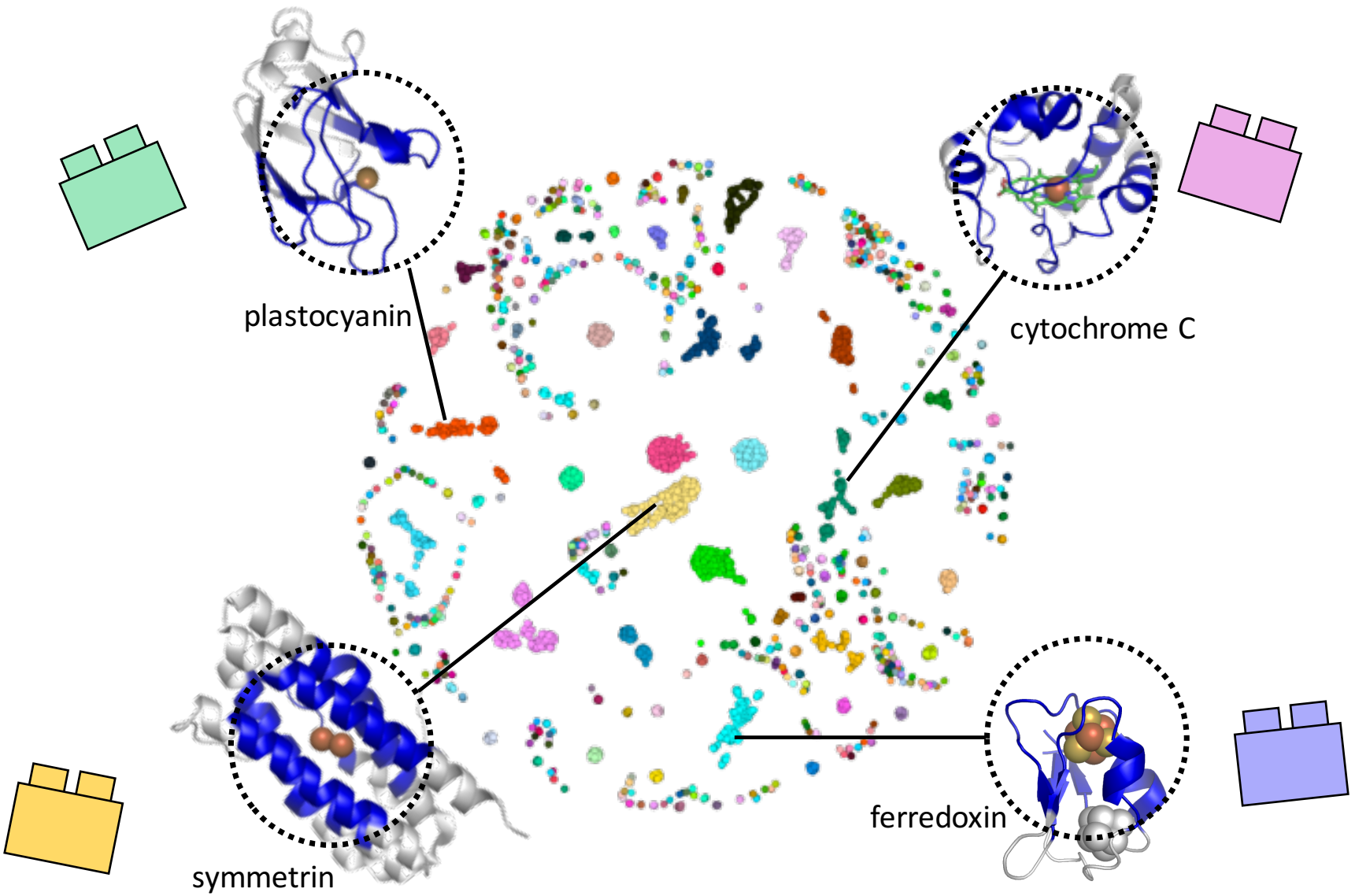
Evolution of Sequences and Folds

- Evolution of core structural motifs
- The paradox of structure/sequence divergence
- ***The processes of natural selection severely inhibit any change a well-adapted system on which several other essential components depend. (***Eck RV, Dayhoff MO, 1966)

Motifs (i.e., folds)

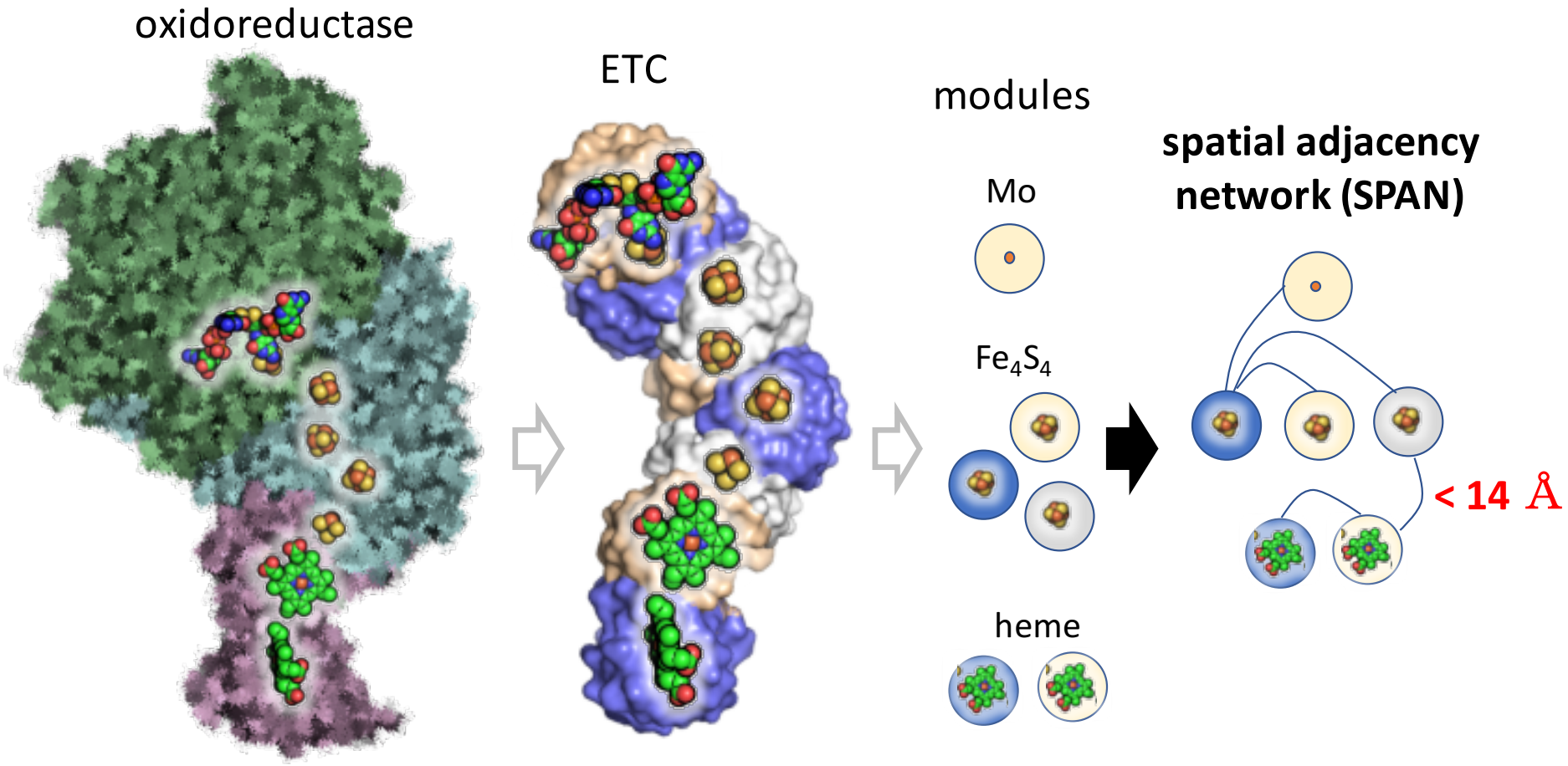
- There appear to be only **35** motifs in all of the extant electron transfer reactions in nature.
- Decifering the evolutionary history of these motifs is one of the grand challenges of science.

“redox protein construction kit” ~ 1000 domains

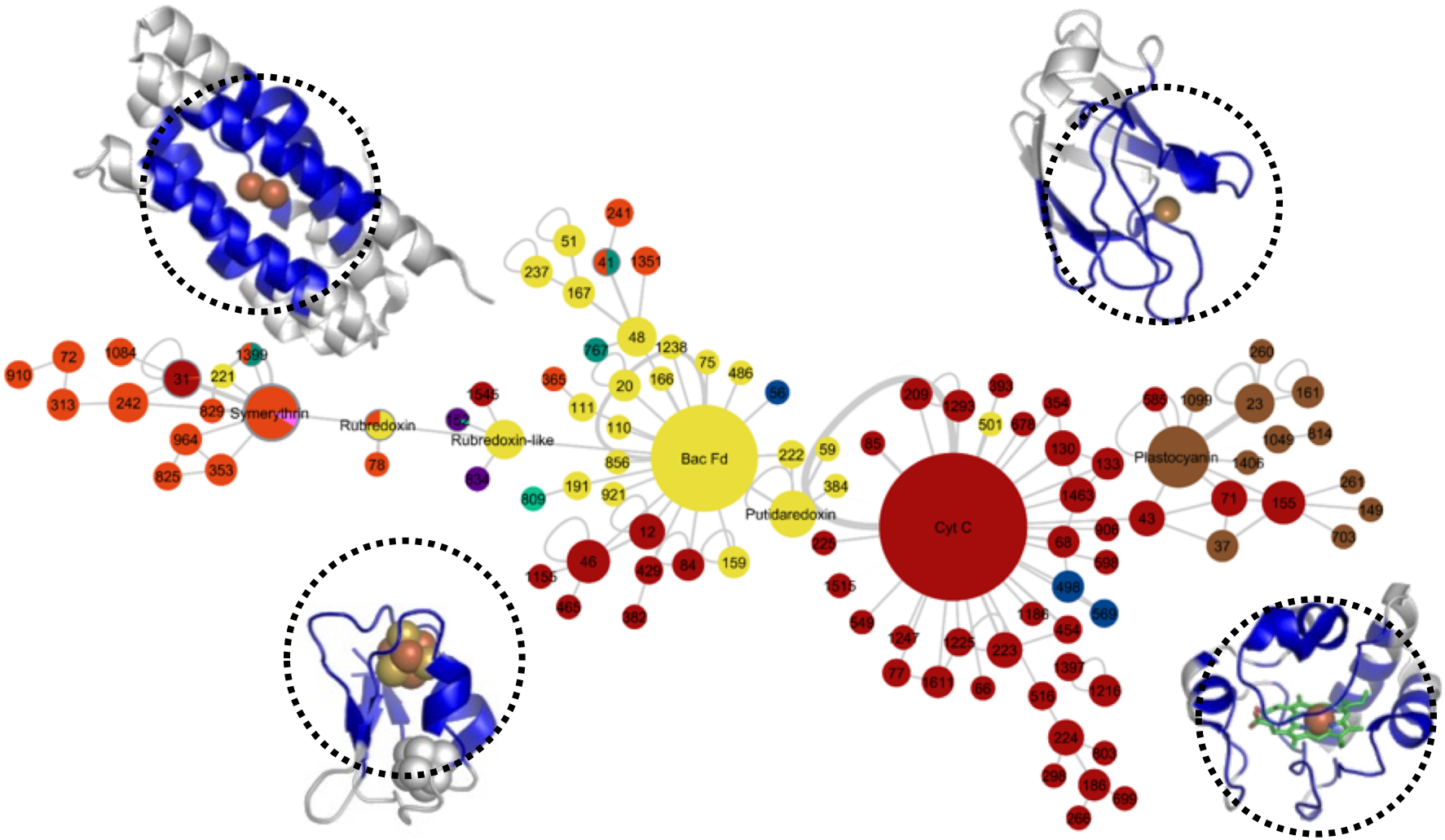


Ranaan et. al. *PNAS* (2018)

construct a SPAN for oxidoreductases



oxidoreductase SPAN composed of ~100 modules

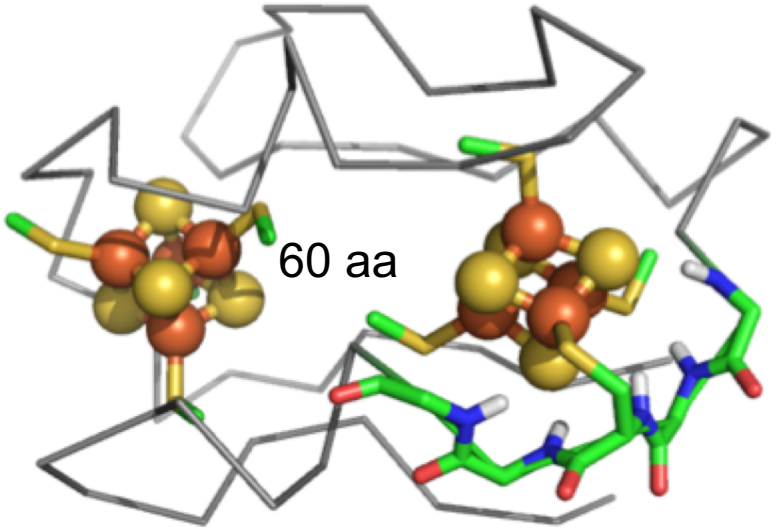


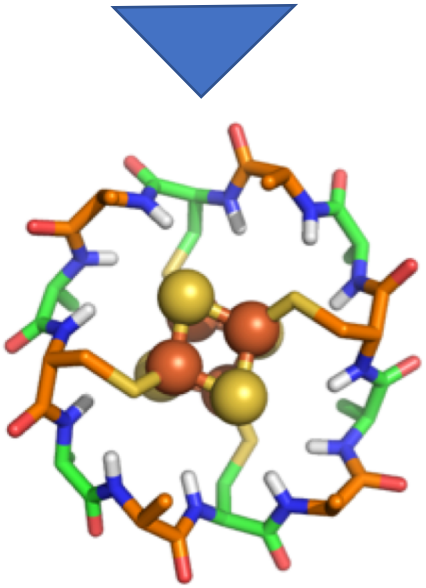
node = module; size = number of edges to other modules

edge = co-occurance in structure (m-m distance < 14Å);
thickness = number of instances

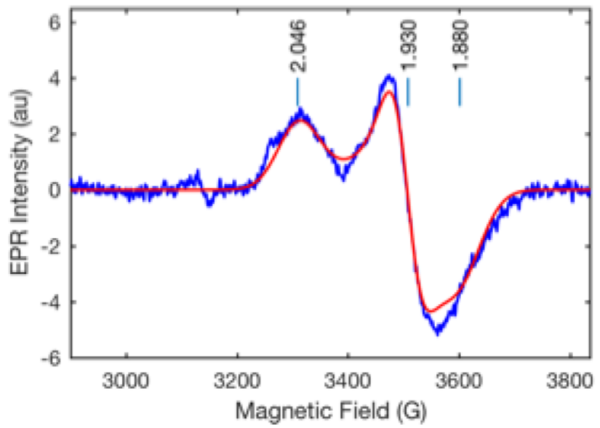
Ranaan et. al. *PNAS* (2018)

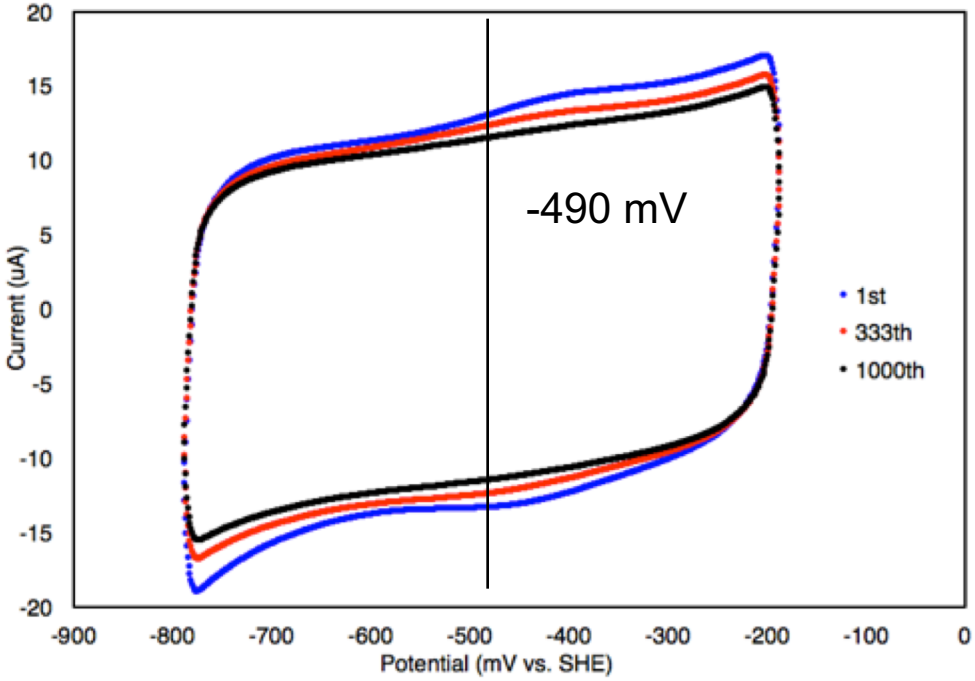
design of a primordial ferredoxin



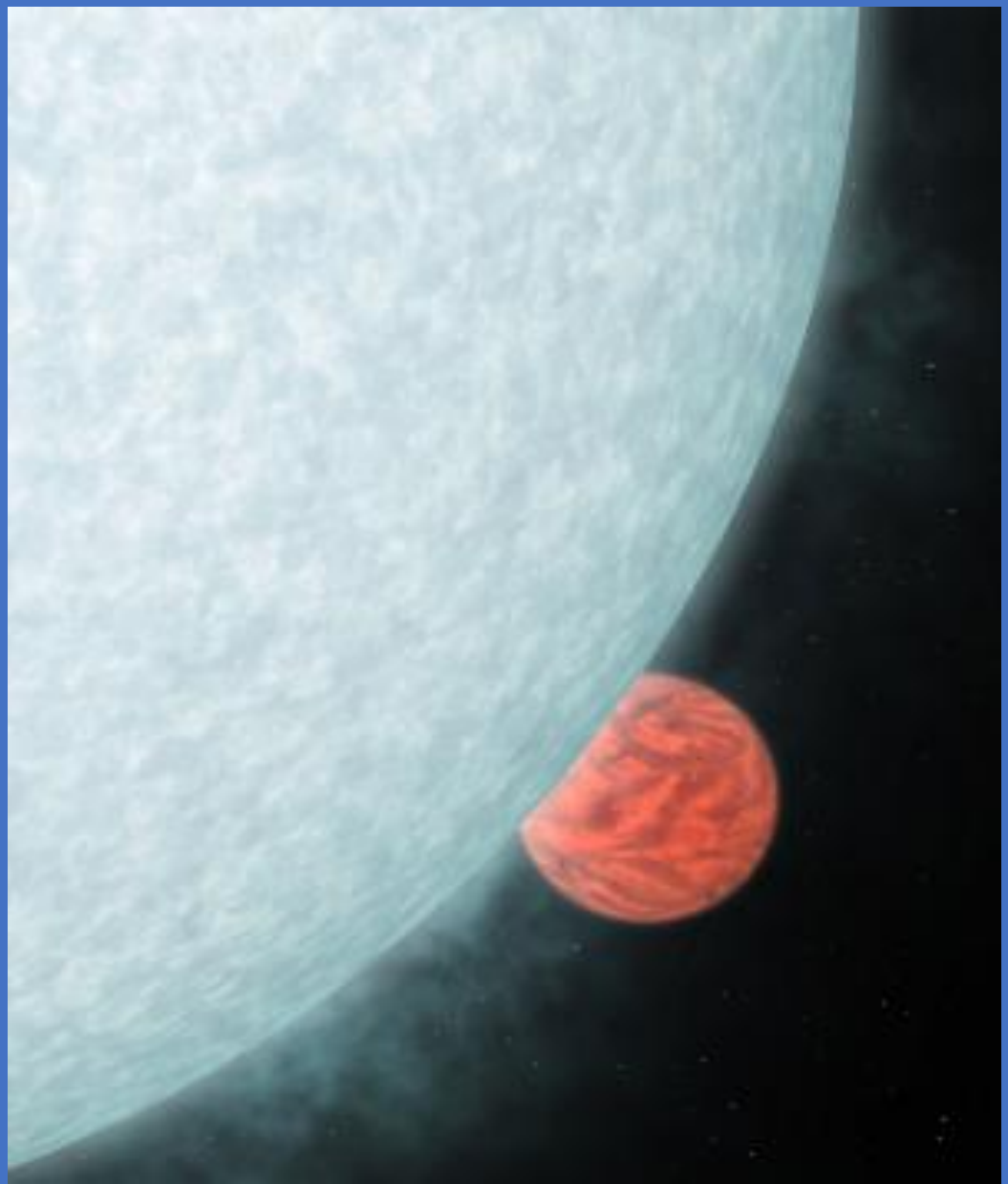


12 aa





Glows from other planets



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 electons 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**

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Thank you!