

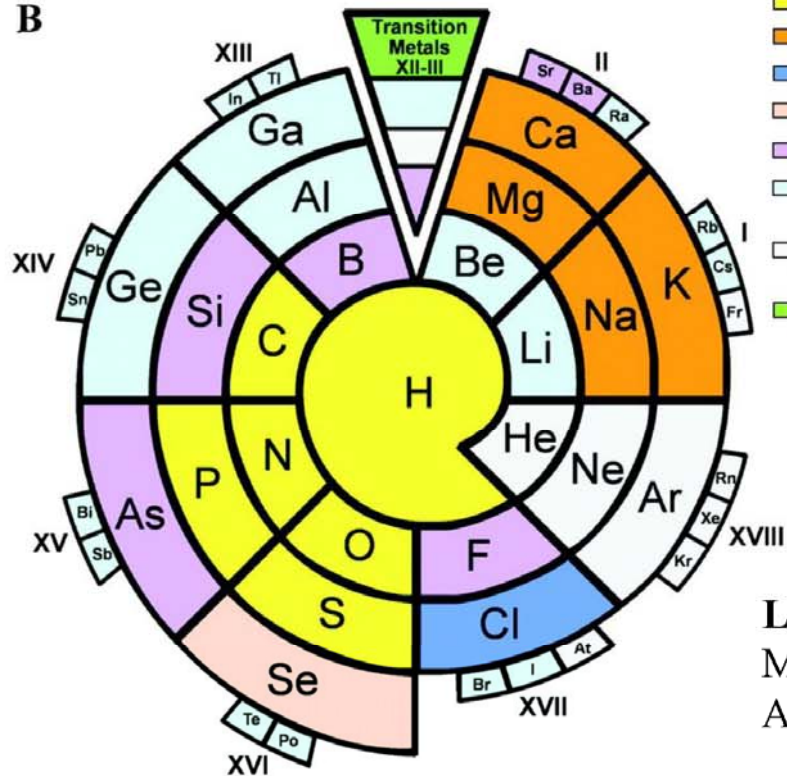
Biogeochemical Cycles

Hendrik Küpper, Advanced Course on Bioinorganic Chemistry & Biophysics of Plants, summer semester 2026
based on a lecture of Peter Kroneck, Universität Konstanz

A

Group	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
Period 1	H																	He
Period 2	Li	Be											B	C	N	O	F	Ne
Period 3	Na	Mg											Al	Si	P	S	Cl	Ar
Period 4	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Period 5	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Period 6	Cs	Ba	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn

B



Key:

- Major, essential, all life
- Major, cations, all life
- Major, anion, all life
- Essential, trace, all life
- Specialized uses, some life
- Transported, reduced and/or methylated, some microbes
- Inert or unknown biological function
- Major biological transition metals

Biogeochemical cycles of elements (nitrogen, sulfur, metals)

L.P. Wackett, A. G. Dodge, L. B. Ellis, 2004
Microbial Genomics and the Periodic Table,
Appl. Environ. Microbiol., 70, 647 - 655

References - Biogeochemical cycles of elements

A. Butler, 1998

Acquisition and Utilization of Transition Metal Ions by Marine Organisms, *Science*, 281, 207- 210

F. M. M. Morel and N. M. Price , 2003

Science , 300, 944-947, The Biogeochemical Cycles of Trace Metals in the Oceans

L.P. Wackett, A. G. Dodge, L. B. Ellis, 2004

Microbial Genomics and the Periodic Table, *Appl. Environ. Microbiol.*, 70, 647 - 655

M. Rudolf, P.M.H. Kroneck, 2005

The nitrogen cycle: Its biology. *Metal Ions in Biological Systems*, 43, 75-103

B.B. Ward, D.G. Capone, J.P. Zehr, 2007

Oceanography 20, 101–109, What's New in the Nitrogen Cycle ?

S.M. Sievert, R.P. Kiene, H.N. Schulz-Vogt, 2007

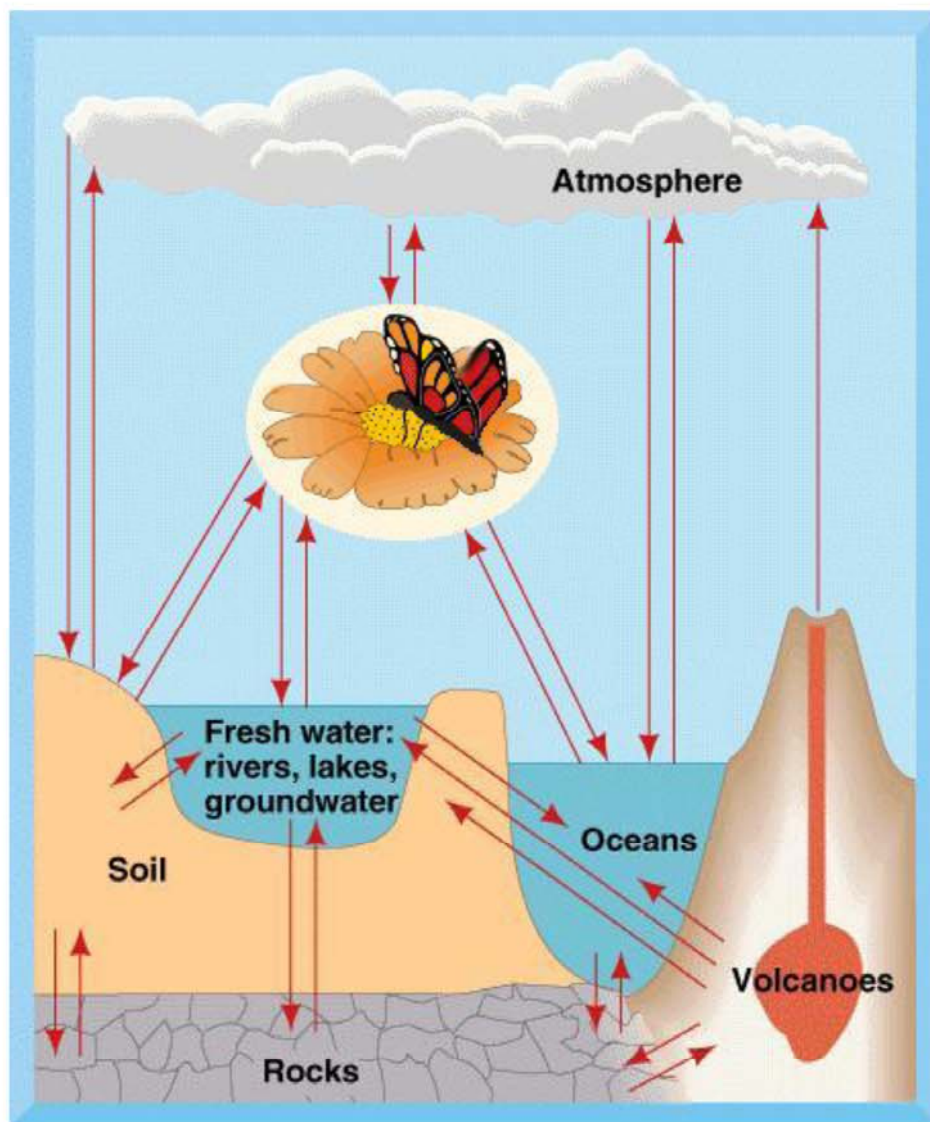
Oceanography 20, 117–123, The Sulfur Cycle

SCOR Working Group , 2007

GEOTRACES – An international study of the global marine biogeochemical cycles of trace elements and their isotopes, *Chemie der Erde*, 67, 85–131

G. M. Gadd, 2010

Metals, minerals and microbes: geomicrobiology, and bioremediation, *Microbiology*, 156, 609–643



Generalized biogeochemical cycle. The major parts of the biosphere are connected by the flow of chemical elements and compounds. In many of these cycles, the biota plays an important role. Matter from the Earth's interior is released by volcanoes. The atmosphere exchanges some compounds and elements rapidly with the biota and oceans. Exchanges of materials between rocks, soils, and the oceans are generally slower by comparison.

Citation

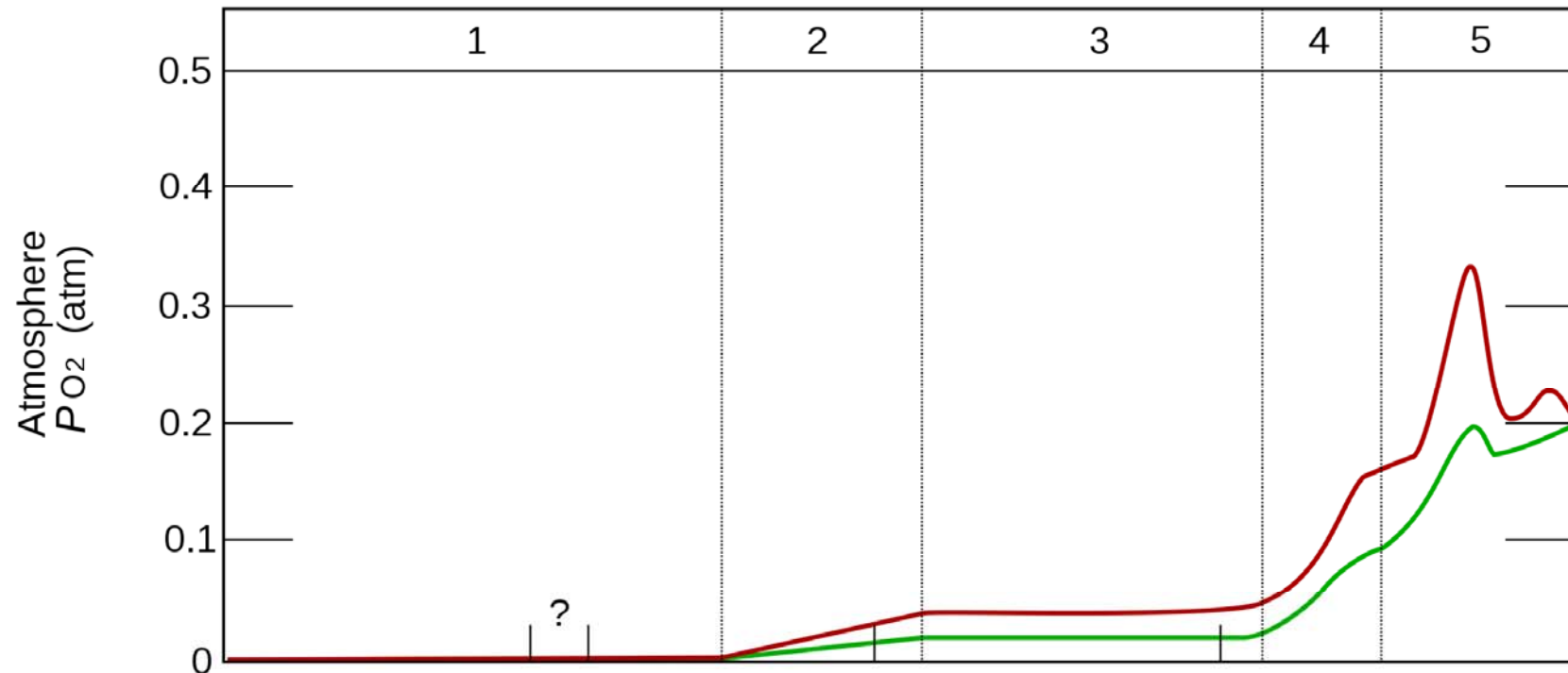
[Muhumuza Moses](#) (Lead Author); [C Michael Hogan](#) (Topic Editor) "Biogeochemical cycles". In: Encyclopedia of Earth. Eds. Cutler J. Cleveland (Washington, D.C.: Environmental Information Coalition, National Council for Science and the Environment). Last revised Date December 24, 2011. http://www.eoearth.org/article/Biogeochemical_cycles?topic=49553

As the Earth is essentially a closed system with respect to matter, we can say that *all matter on Earth cycles* .

Forms of Life – From *Anaerobic* to *Aerobic* anoxic conditions ($-O_2$) vs oxic conditions ($+O_2$)

H.D. Holland, Phil. Trans. R. Soc. B (2006) 361, 903-915

Stages



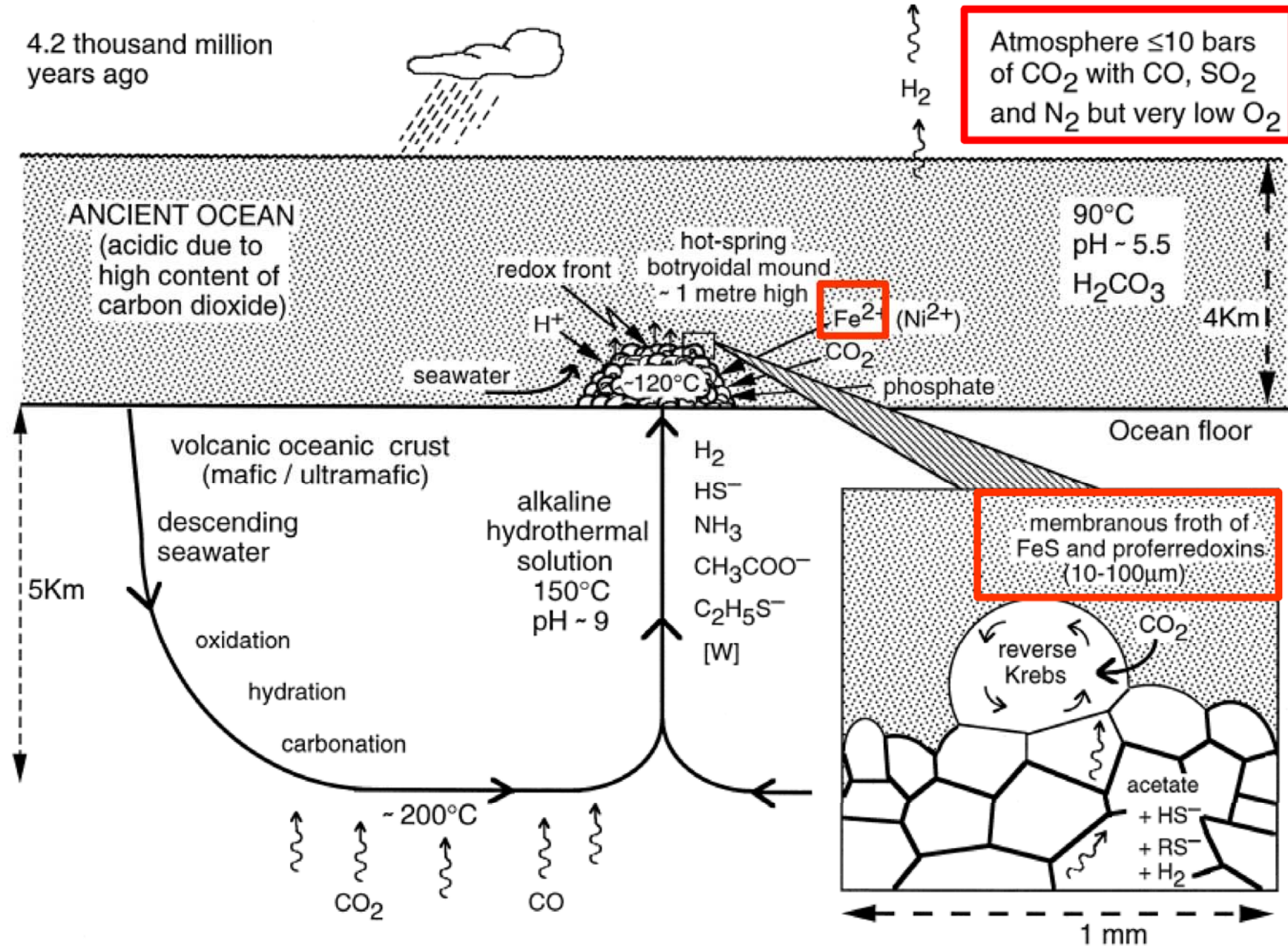
Estimated evolution of atmospheric O_2

The red and green lines represent the range of the estimates: stage1: 3.85–2.45 Gyr (Ga), stage2: 2.45–1.85Ga, stage3: 1.85–0.85Ga, stage4: 0.85–0.54Ga, stage5: 0.54Ga–present

www.globalchange.umich.edu/globalchange1/current/lectures/Perry_Samson_lectures/evolution_atm/index.html

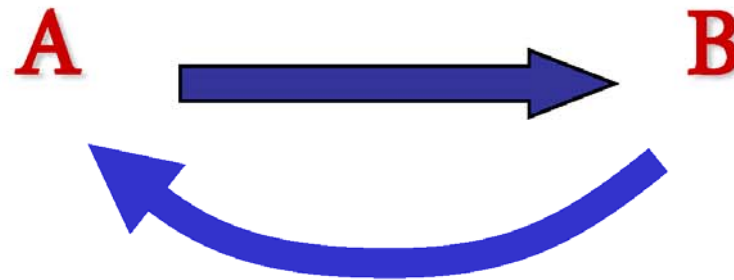
Emergence of life on the ocean floor

hydrothermal vent, Russel and Hall, 1997



Biogeochemical Cycles

- **Metabolism: All organisms transform (different) compounds**



- **Metabolic pathways** constitute closed global cycles, otherwise intermediates will accumulate. The larger the amount of the accumulated intermediate, the better substrate it will be for organisms. On a geological time scale, a new metabolic pathway will develop which will convert the intermediate.
- **Metabolic pathways** can be organized and classified according to different aspects, such as with regard to the **ELEMENTS**.

Elements in the Ocean

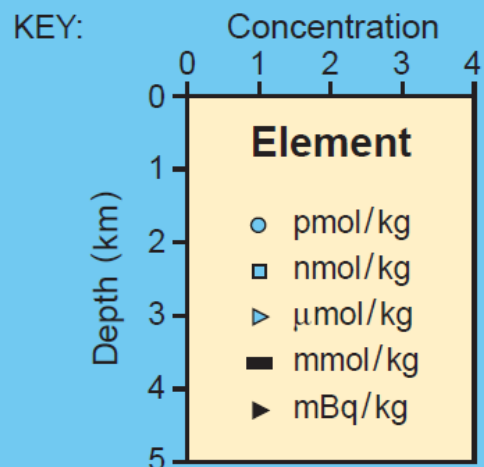
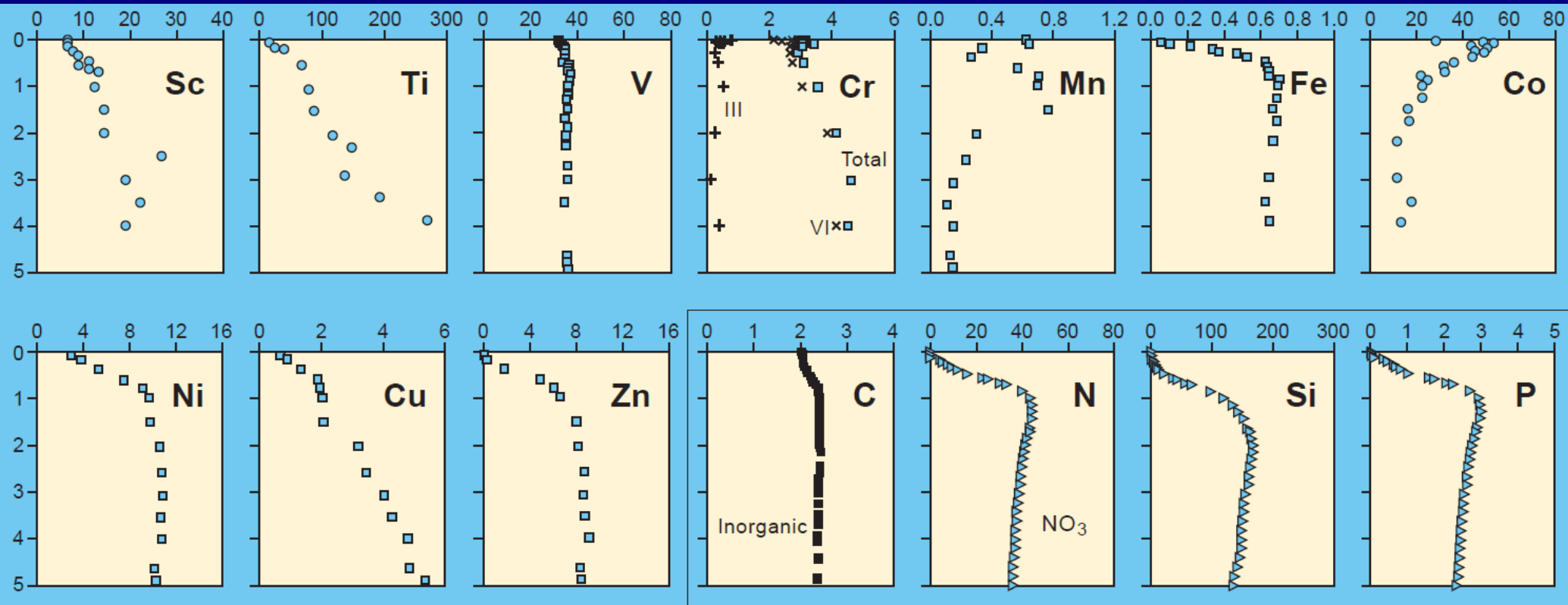
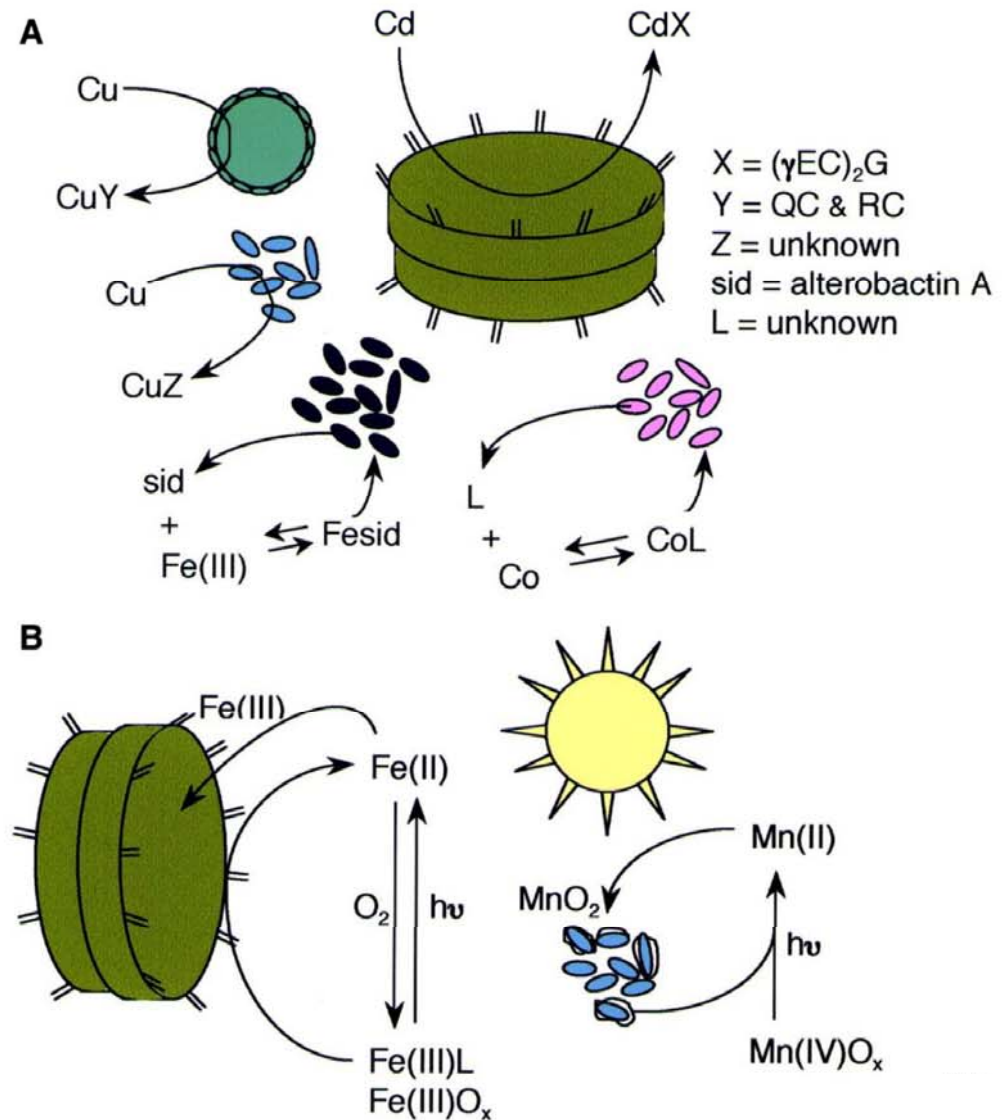


Fig. 2. Vertical profiles of the first-row transition metal ions and selected other elements in the North Pacific Ocean. Speciation is not included. Data compiled by Y. Nozaki (2). References for plotted data include: Sc (40), Ti (41), V (3), Cr (42), Mn (43), Fe (44), Co (44), Ni (45), Cu (45), and Zn (45). For a recent review, which includes speciation, see (1).

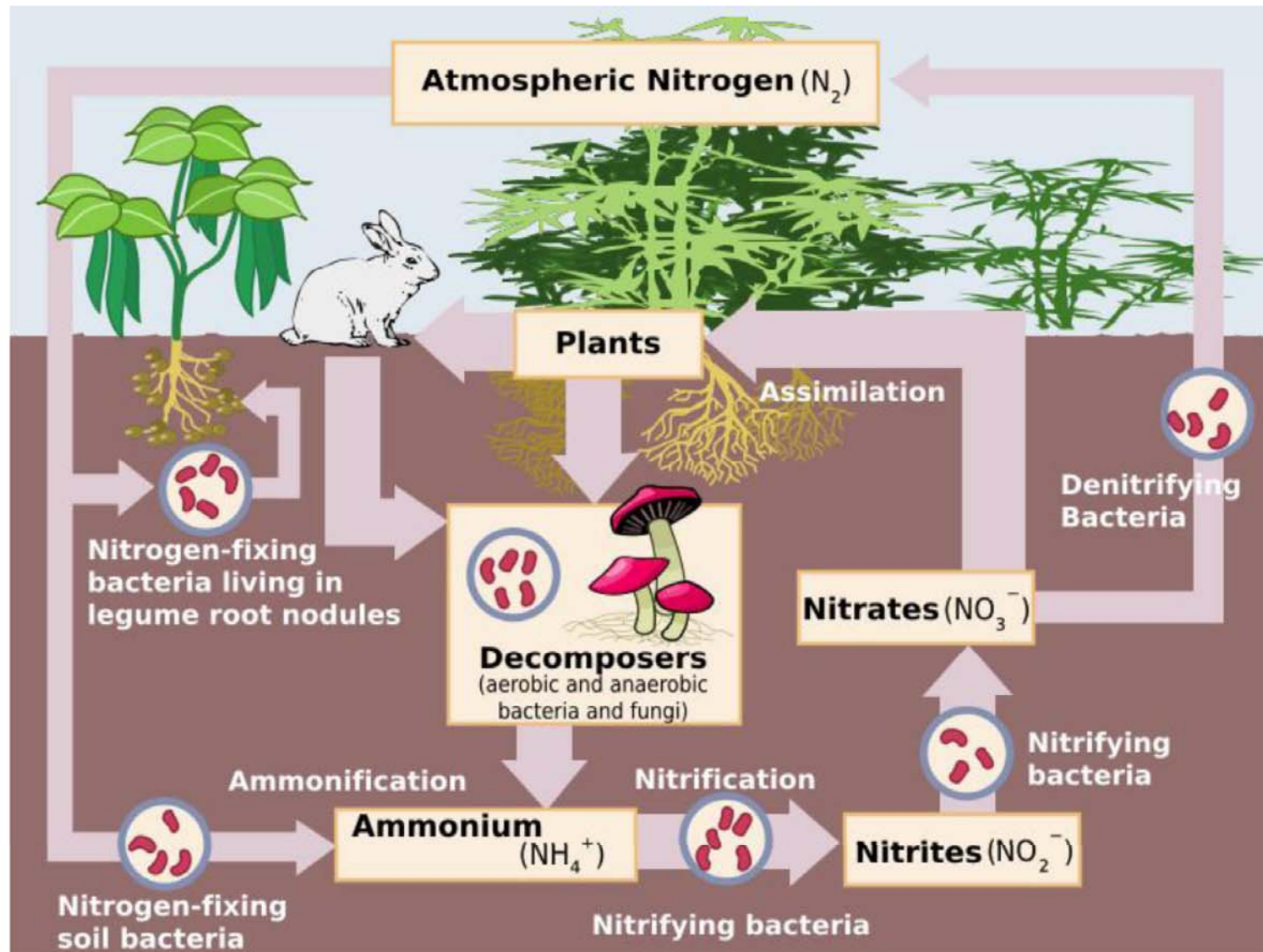
(A) Release of complexing agents and metal ligand complexes from marine plankton: CdX, phytochelatin-Cd complex released by diatoms; CuY, peptide complexes of Cu released by coccolithophorids; CuZ, unidentified Cu ligand complex released by *Synechococcus*; sid, siderophore released by heterotrophic bacteria and cyanobacteria; L, unidentified Co complexing agent released by *Prochlorococcus*; C, Cys; E, Glu; G, Gly; Q, Gln; and R, Arg.



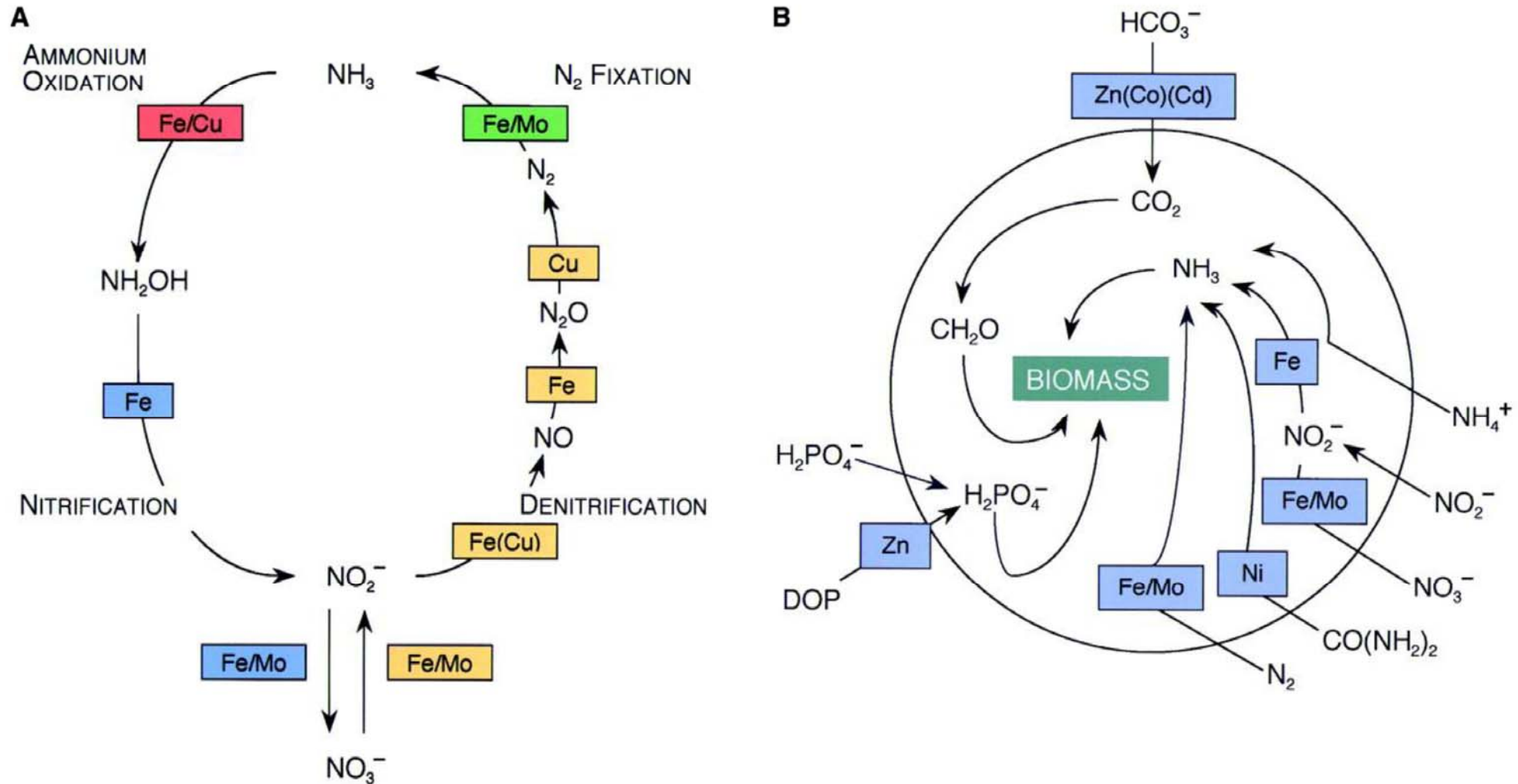
F M M Morel, N M Price Science 2003,
300,44-947

The nitrogen cycle – plants depend on bacteria

http://en.wikipedia.org/wiki/Nitrogen_cycle



The N cycle, illustrating the metal cofactors in each enzymatically catalyzed step. (B) Primary metal requirements for C, N, and P acquisition and assimilation by phytoplankton



F M M Morel, N M Price Science 2003,
300, 944-947

Oxidation states of N

+5	+3	+2	+1	± 0	-1	-3
NO_3^-	NO_2^-	NO	N_2O	N_2	H_2NOH	NH_3

New intermediate: hydrazine, H_2NNH_2

Kuypers et al. (2003) „Anaerobic ammonium oxidation by anammox bacteria in the Black Sea”,
Nature 422, 608-611

Essential Metals of the N Cycle

Fe

- Nitrate Reductase
- Nitrite Reductase
- NO Reductase
- Nitrogenase
- Hydroxylamine Oxidoreductase

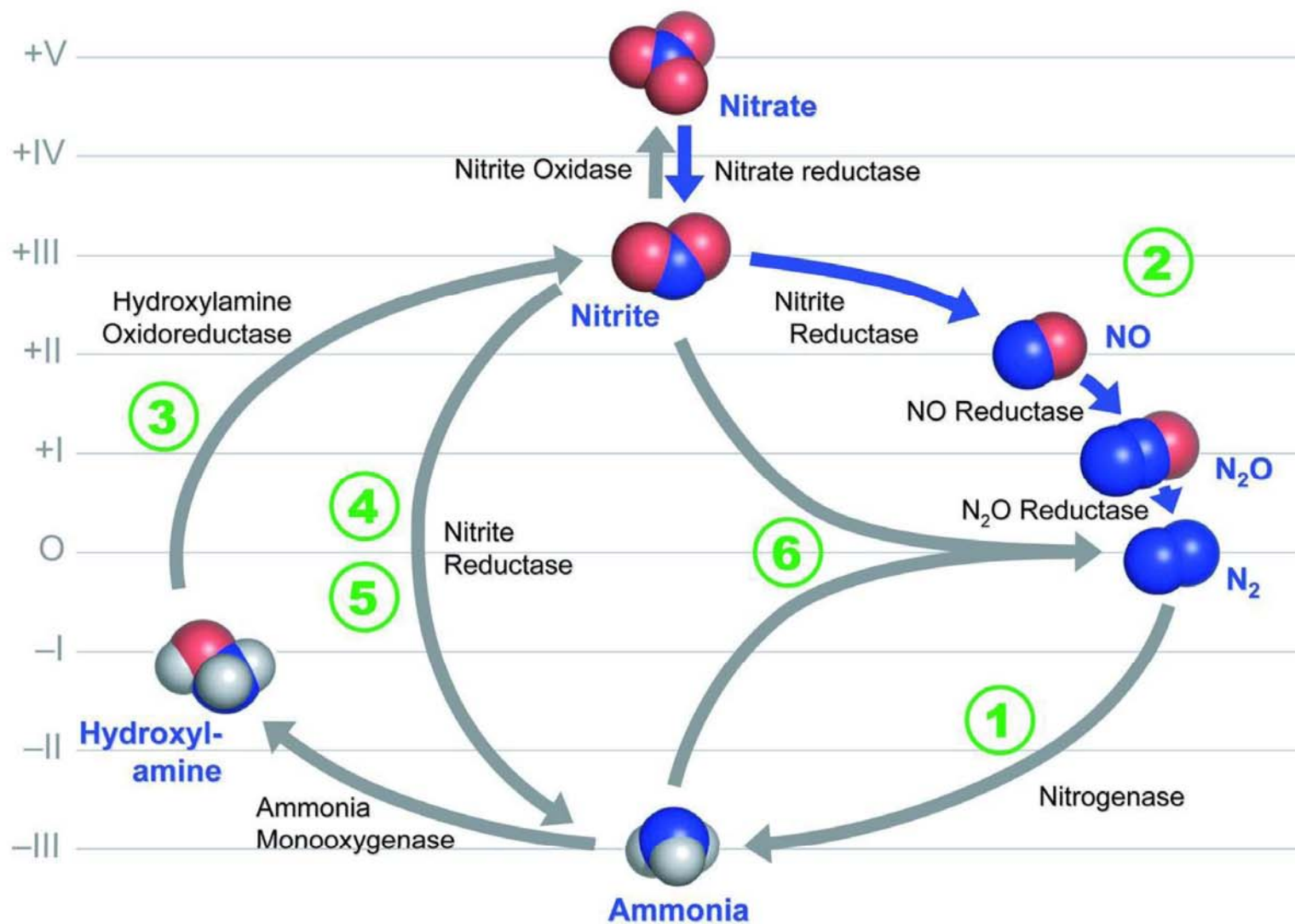
Cu

- Nitrite Reductase
- N₂O Reductase
- Ammonia Mono-oxygenase

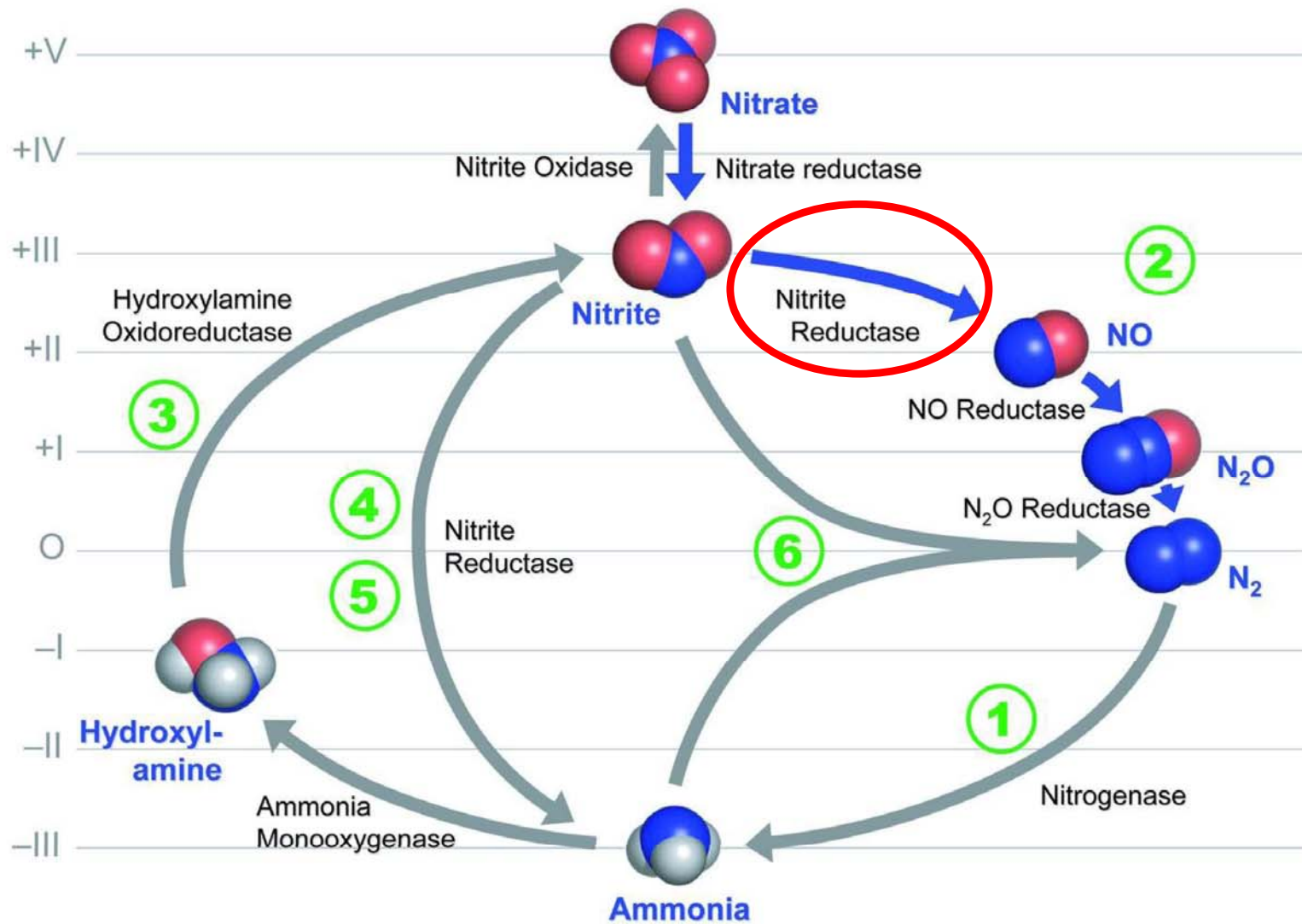
Mo/V

- Nitrate Reductase
- Nitrogenase

Important Reactions and Metal Enzymes of the Nitrogen Cycle



Important Reactions and Metal Enzymes of the Nitrogen Cycle



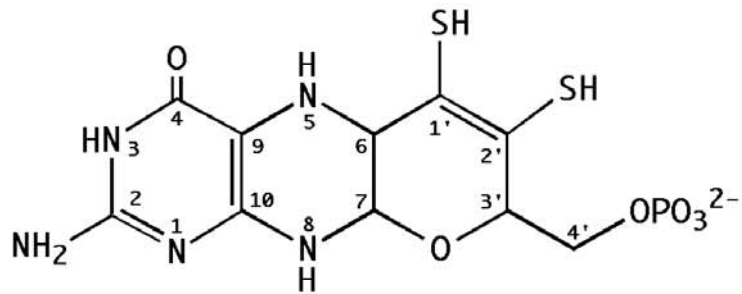
Nitrate Reductase



Mo bound to Molybdopterin

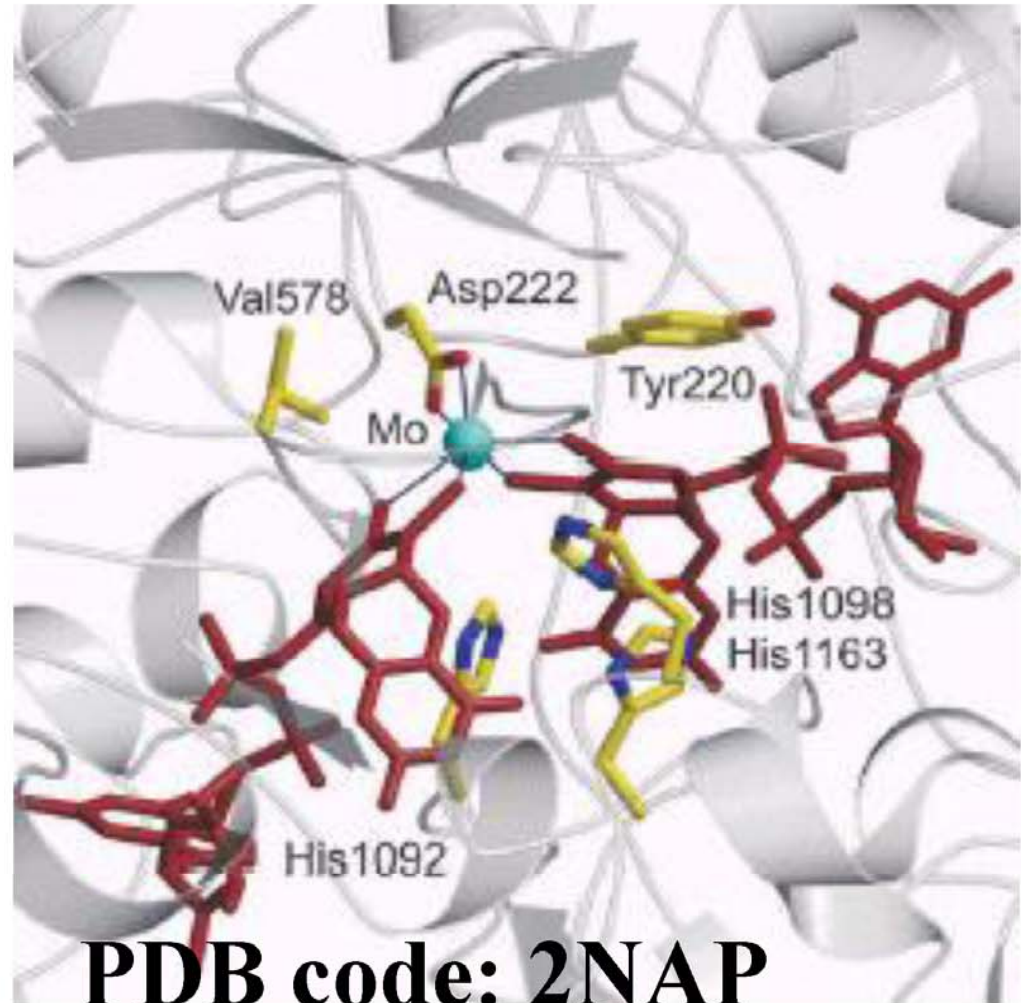
(a dithiolene – coordinates both Mo and W)

JOURNAL of BIOLOGICAL CHEMISTRY (2009) 284, p. e10, N Kresge, R D Simoni, R L Hill:
(The Discovery and Characterization of Molybdopterin - the Work of K. V. Rajagopalan)



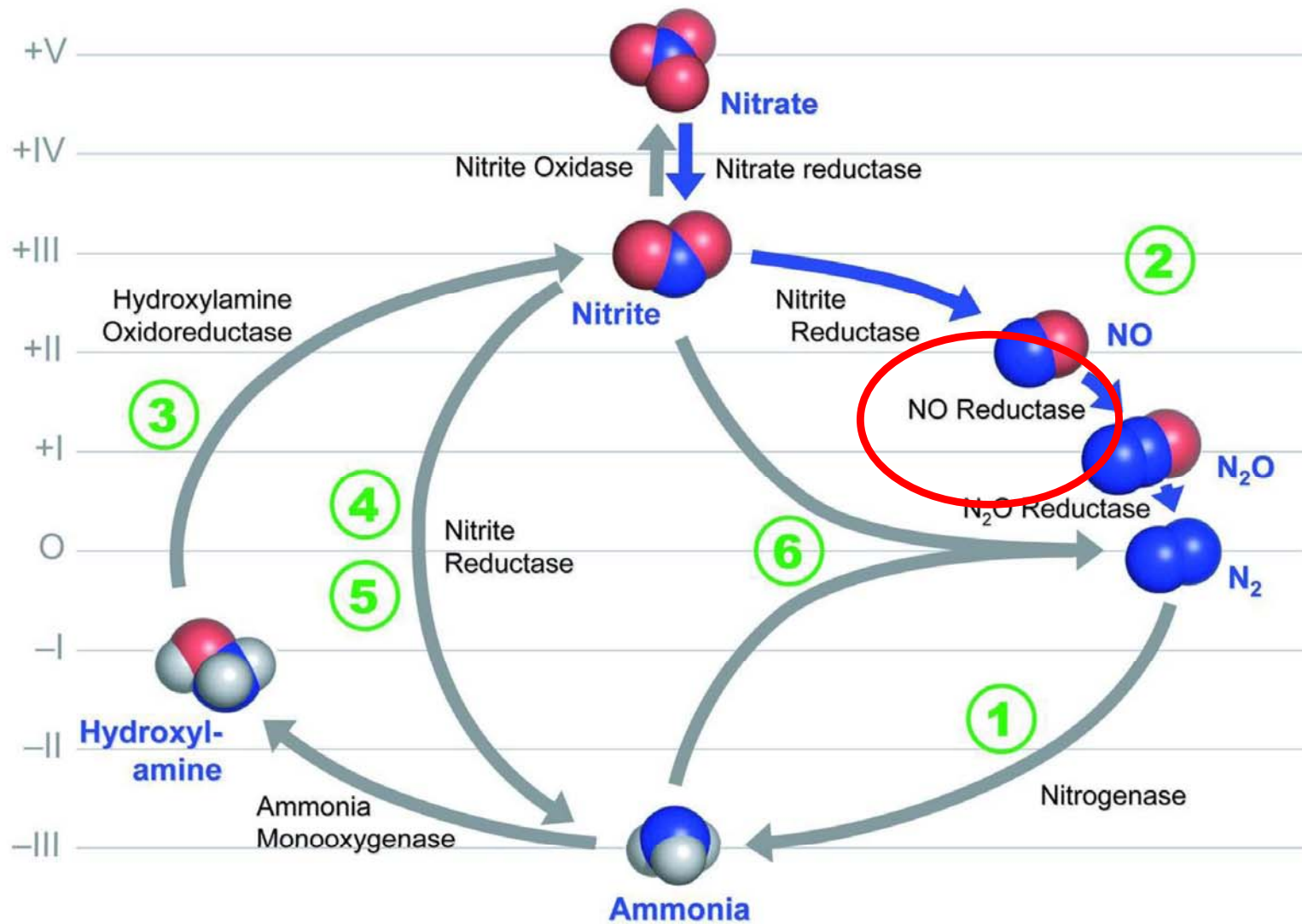
Numerous different forms of nitrate reductase depending on the organism

http://www.ebi.ac.uk/thornton-srv/databases/cgi-bin/enzymes/GetPage.pl?ec_number=1.7.99.4



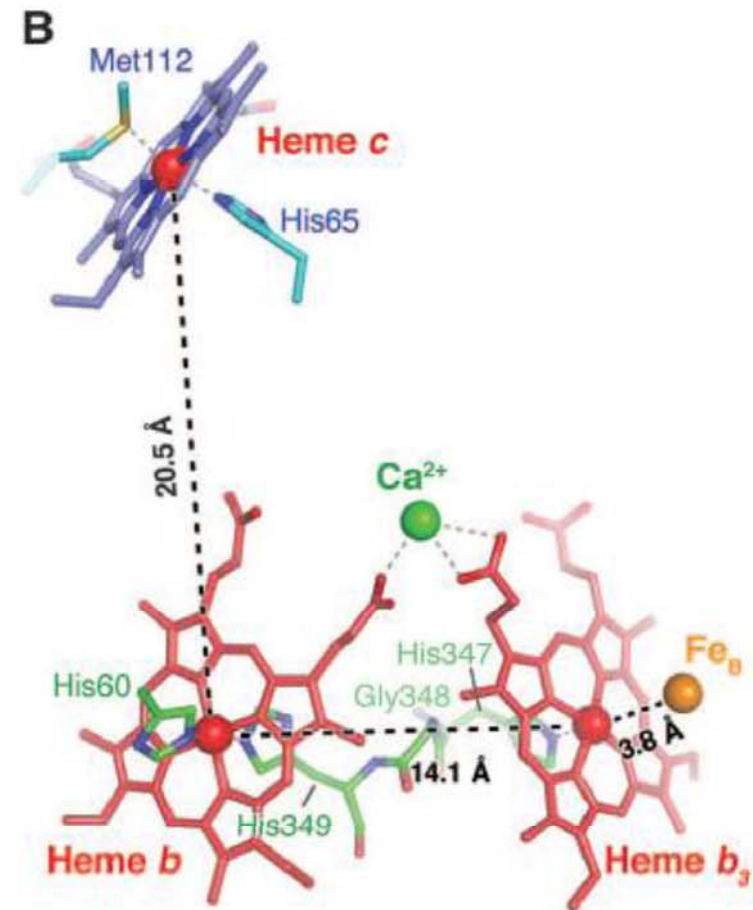
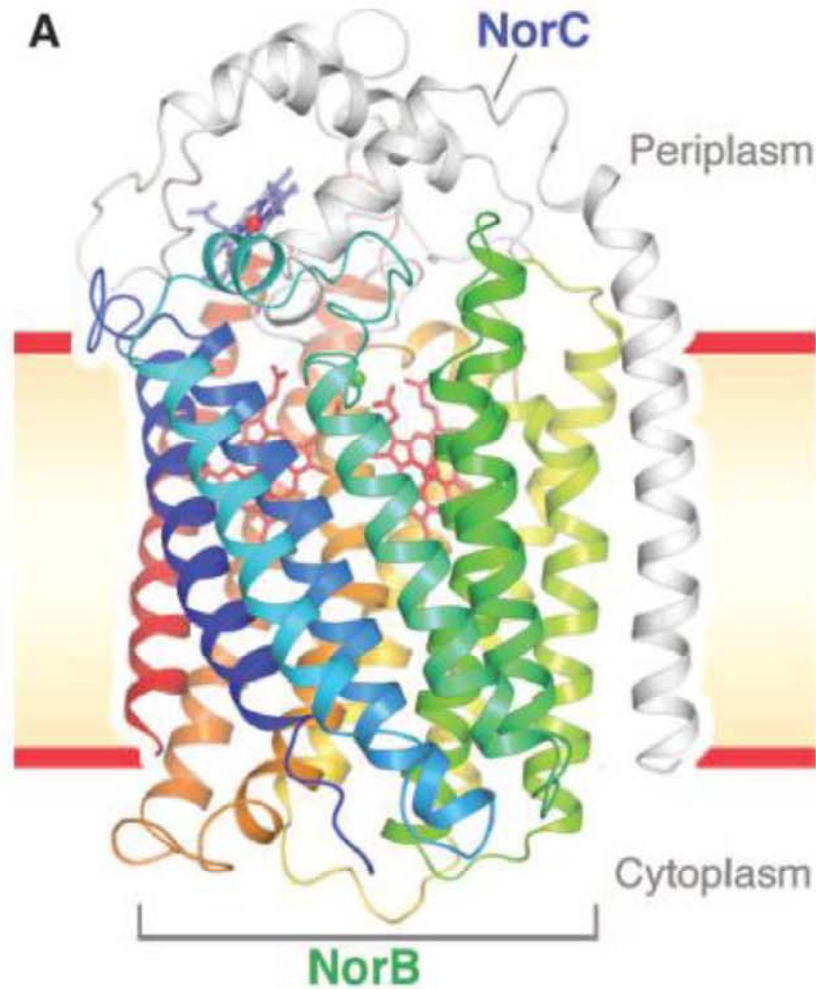
PDB code: 2NAP

Important Reactions and Metal Enzymes of the Nitrogen Cycle

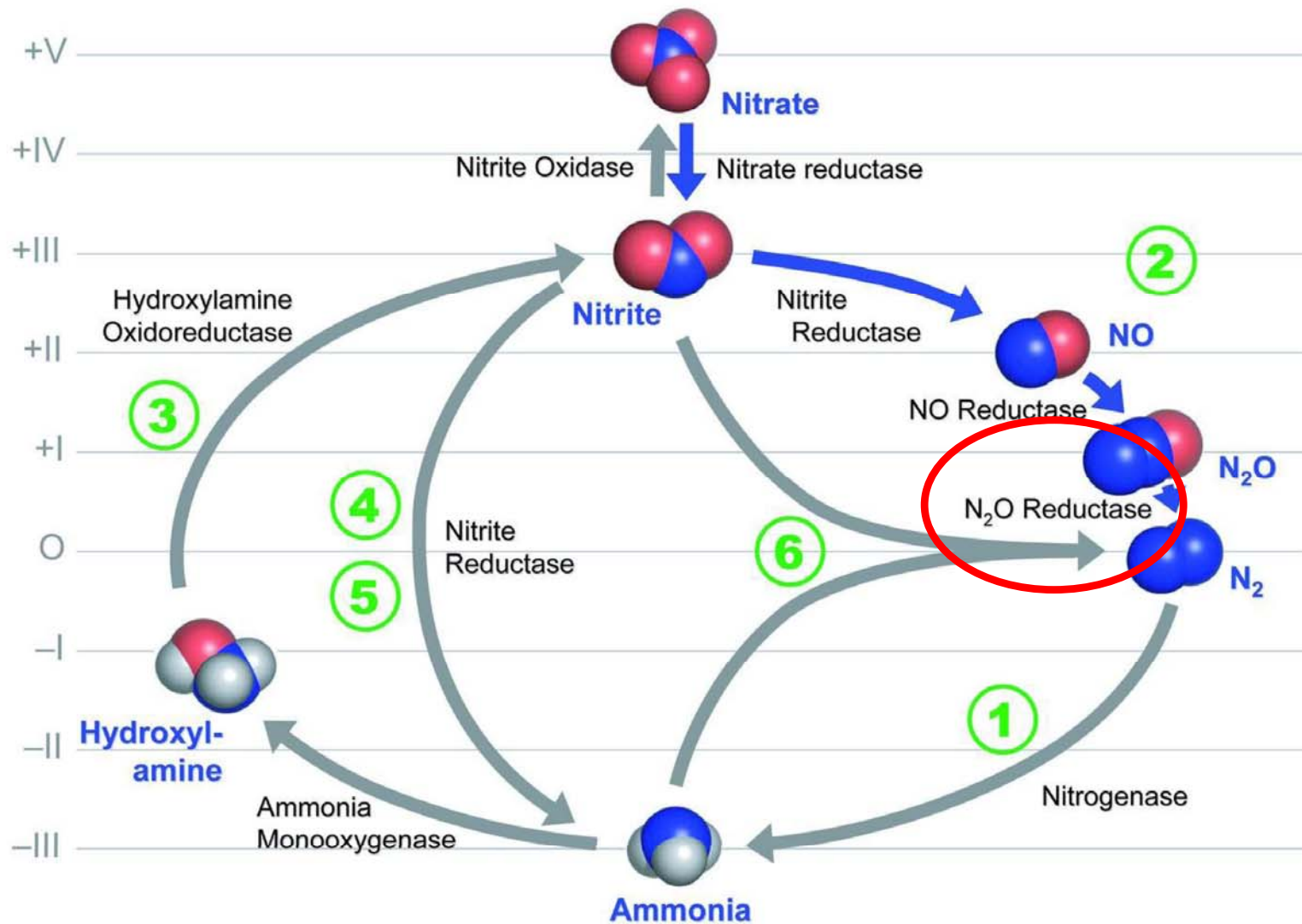


NO Reductase (NOR)

T. Hino, et al. SCIENCE (2010) 330, 1666-1670

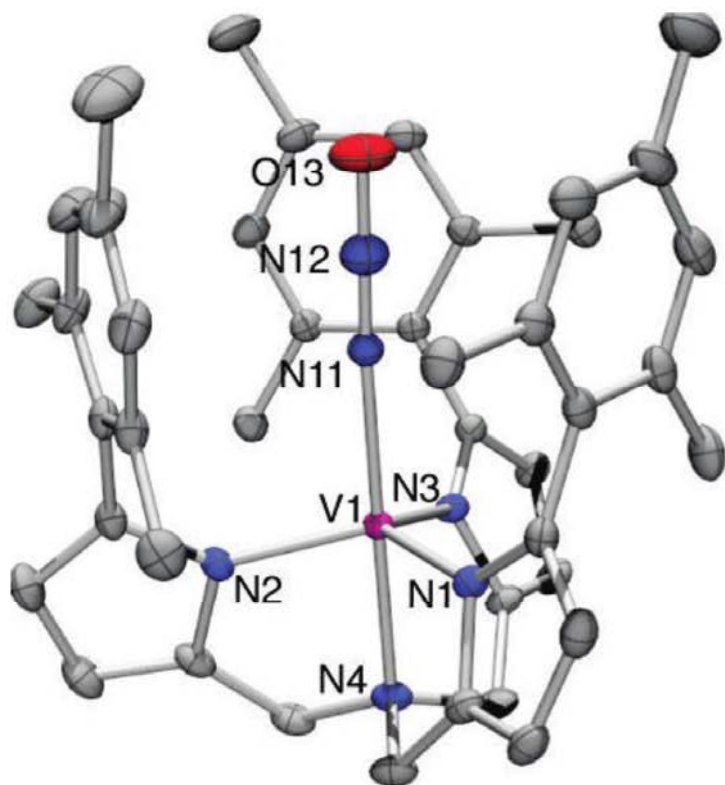
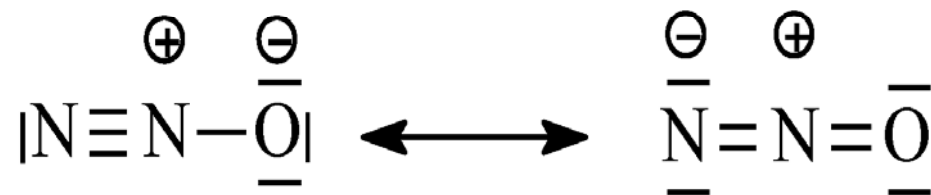
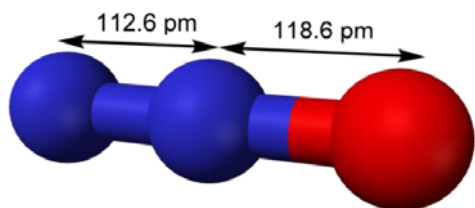


Important Reactions and Metal Enzymes of the Nitrogen Cycle



Nitrous Oxide – Dinitrogen Monoxide

Laughing Gas – Sweet Air

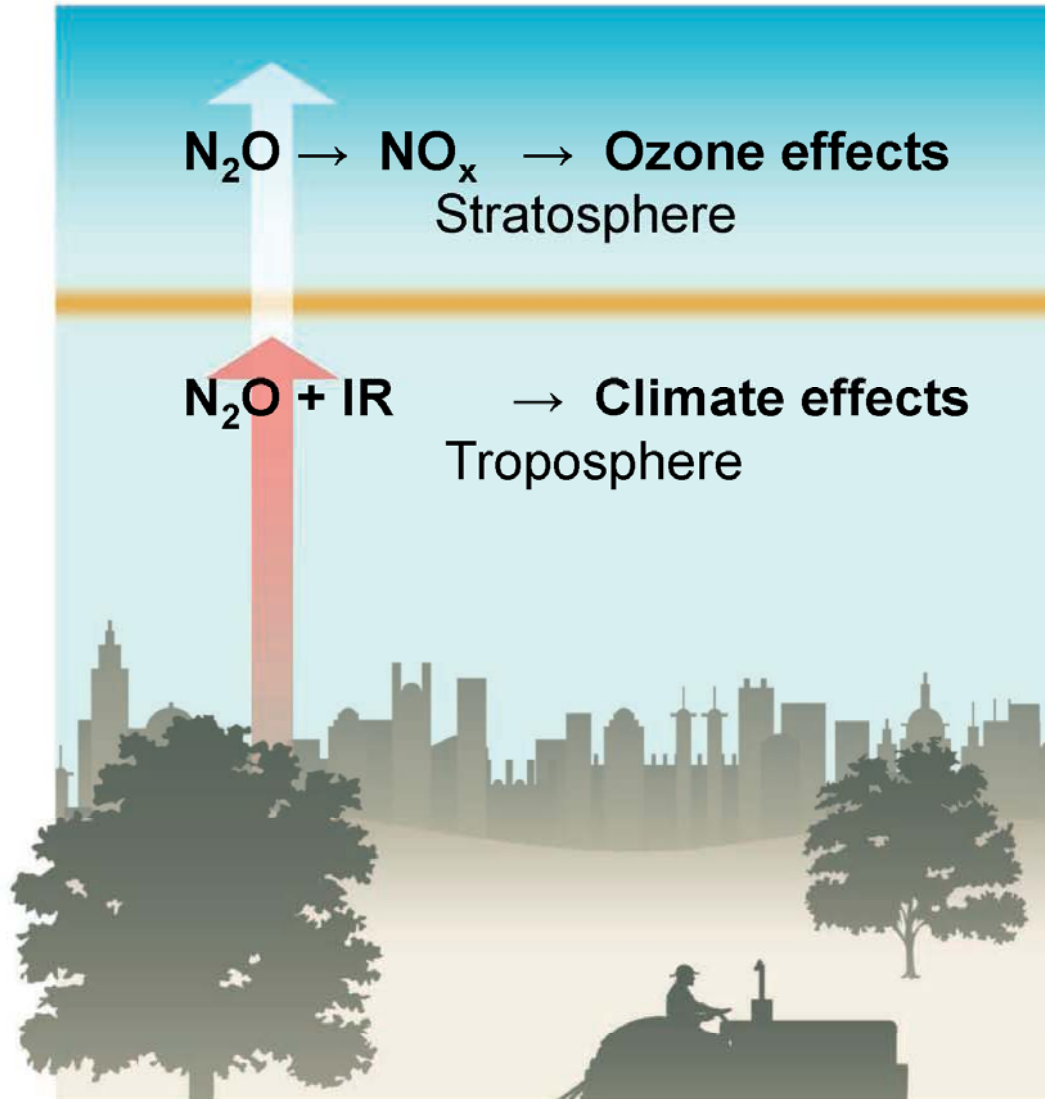


A Structurally Characterized Nitrous Oxide Complex of Vanadium

Piro et al., J. Am. Chem. Soc. (2011) 133, 2108–2111

N₂O – A Potent Greenhouse Gas

Wuebbles, Science (2009), 326, 56-57



<http://epa.gov/climatechange/emissions/usinventoryreport.html>

MENACING GAS

Agriculture is the primary source of N₂O emissions worldwide

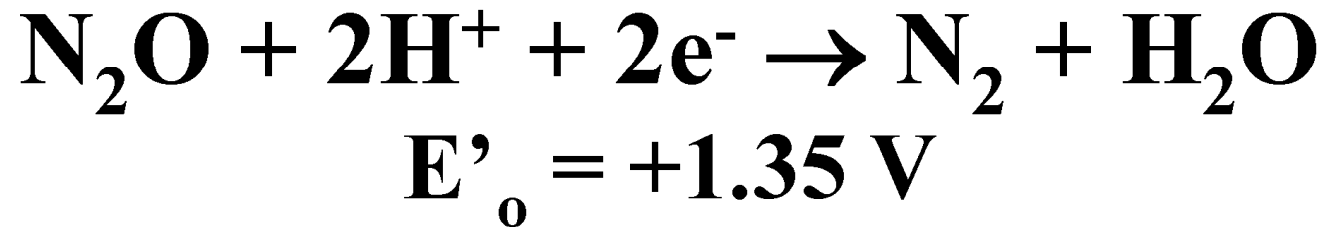
THOUSANDS OF METRIC TONS	N ₂ O EMISSIONS
Agricultural soils	8,005
Other agricultural activities	885
Manure management	728
Fossil fuel combustion	703
Production of adipic & nitric acids	531
Biomass combustion	108
Other nonagricultural activities	60

NOTE: Projected values for 2010. **SOURCE:** EPA



46

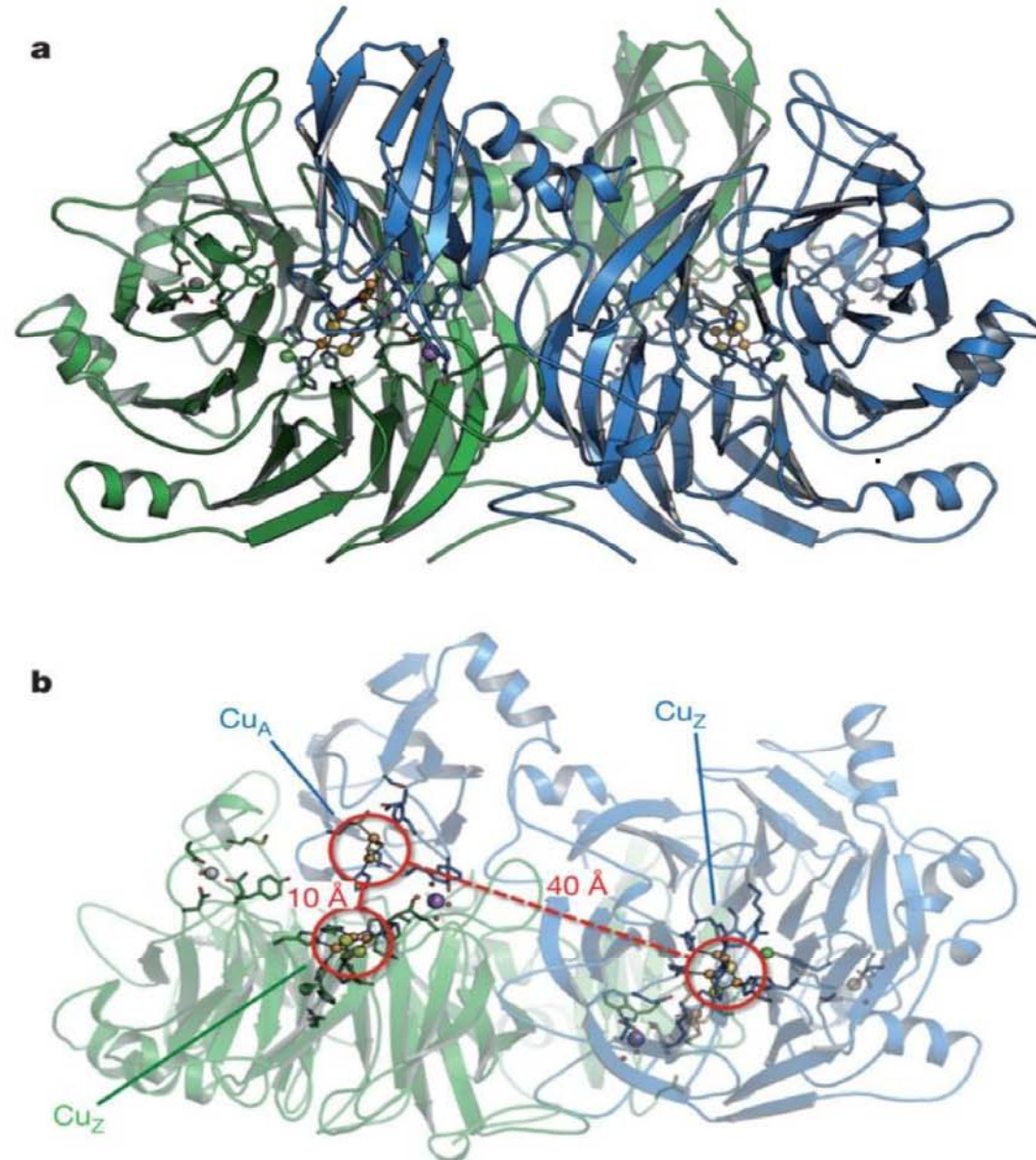
Bacterial Nitrous Oxide Reductase is a purple Copper Enzyme



kinetically inert molecule
~ 59 kcal/mol activation barrier

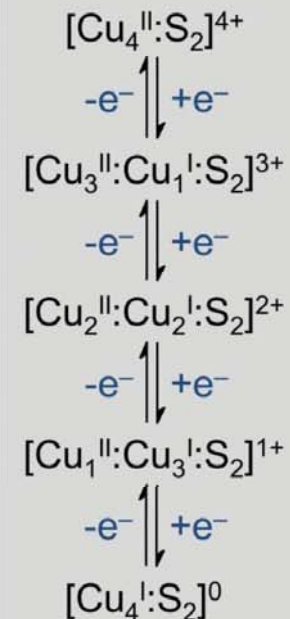
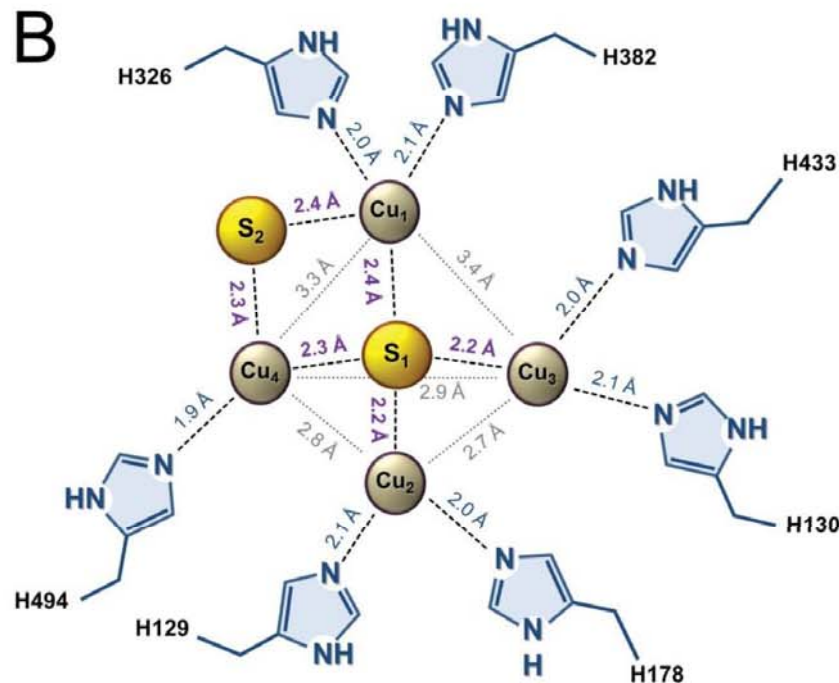
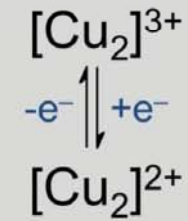
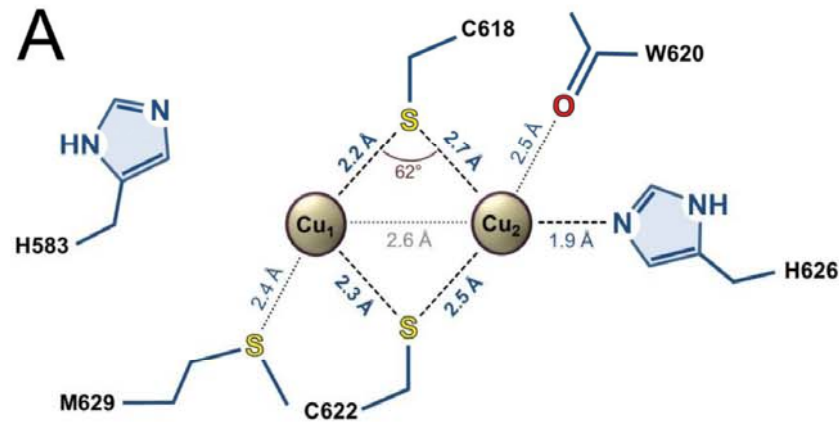
Bacterial Nitrous Oxide Reductase is a head-to-tail homodimer, with 6 Cu/monomer

A. Pomowski, W.G. Zumft, P.M.H. Kroneck, O. Einsle (2011) *Nature* 477, 234-237



There are two novel Copper-Sulfur sites

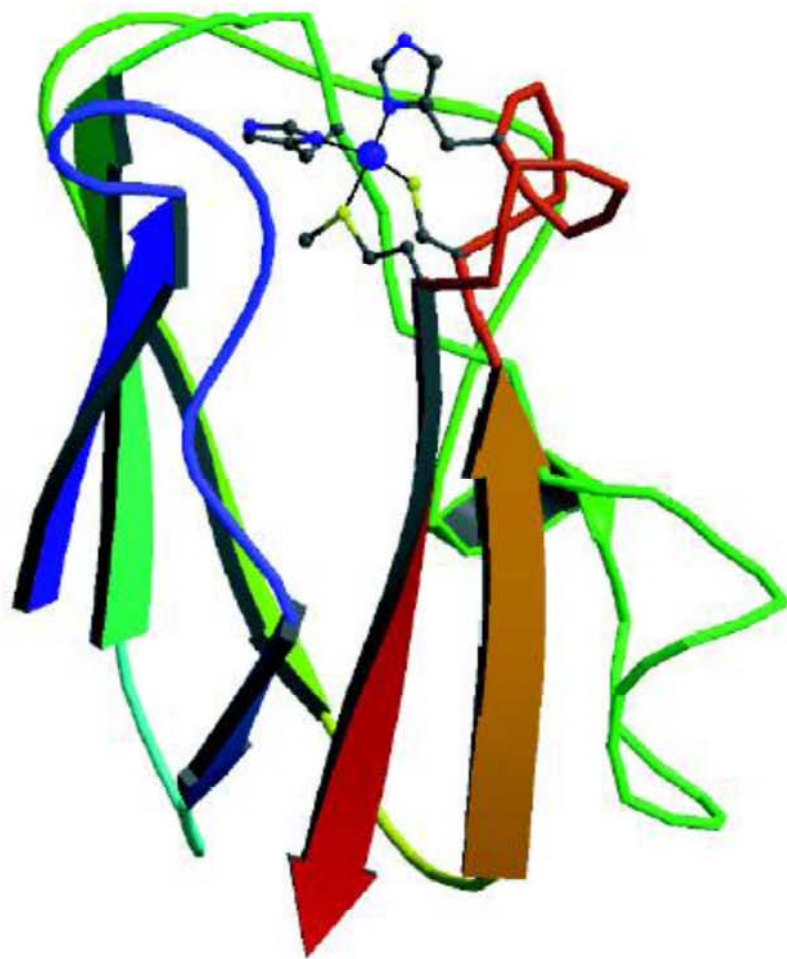
(A) the dinuclear CuA, (B) the tetranuclear CuZ



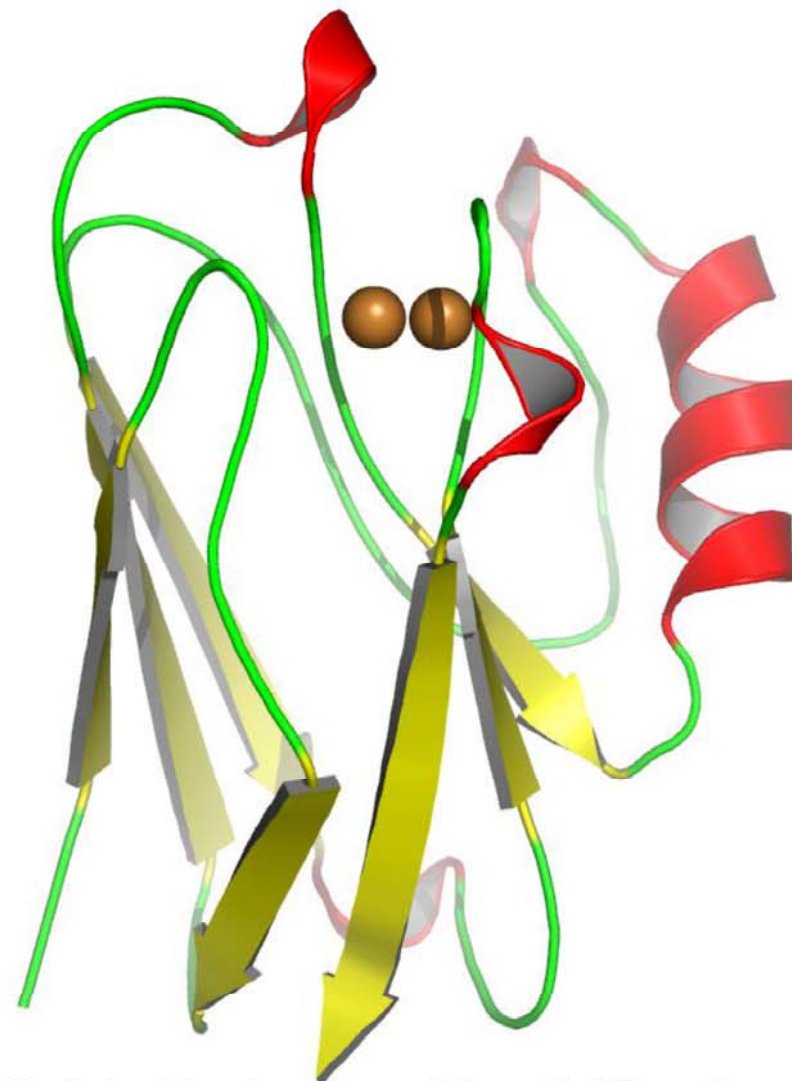
Evolution and Bioengineering through Loop directed Mutagenesis

From a Blue Mononuclear Cu to a Purple Dinuclear Cu₂

MG Savelieff, Y Lu, J Biol Inorg Chem, 15, 967-976 (2010)

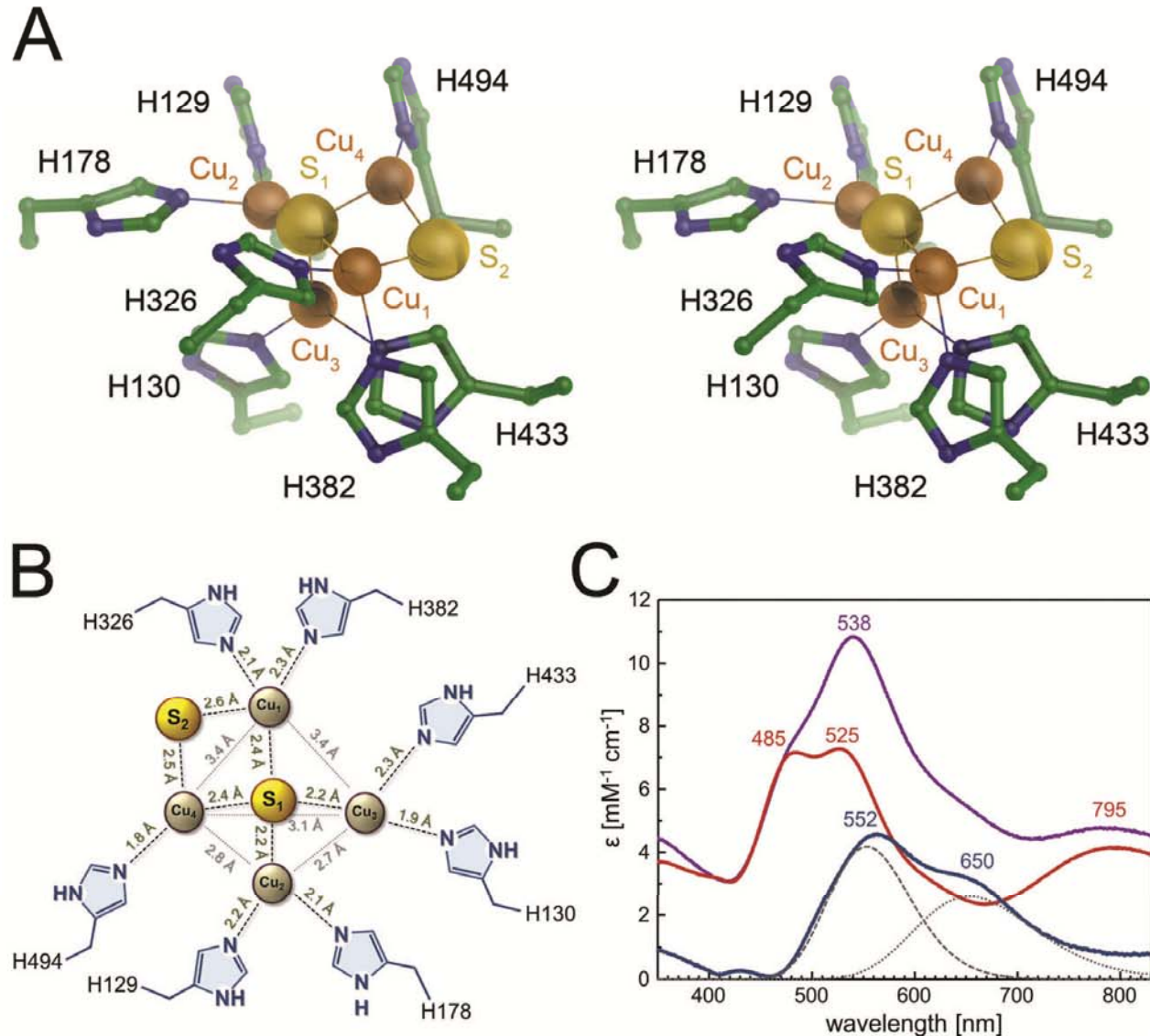


Plastocyanin/Photosynthesis

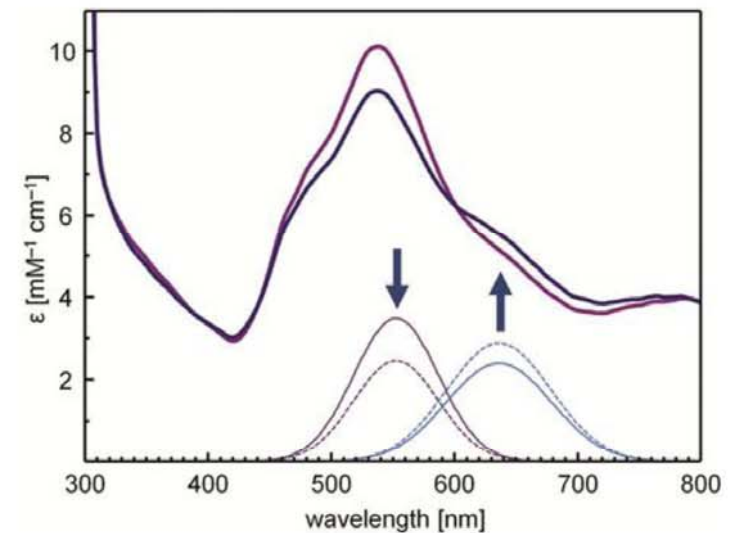
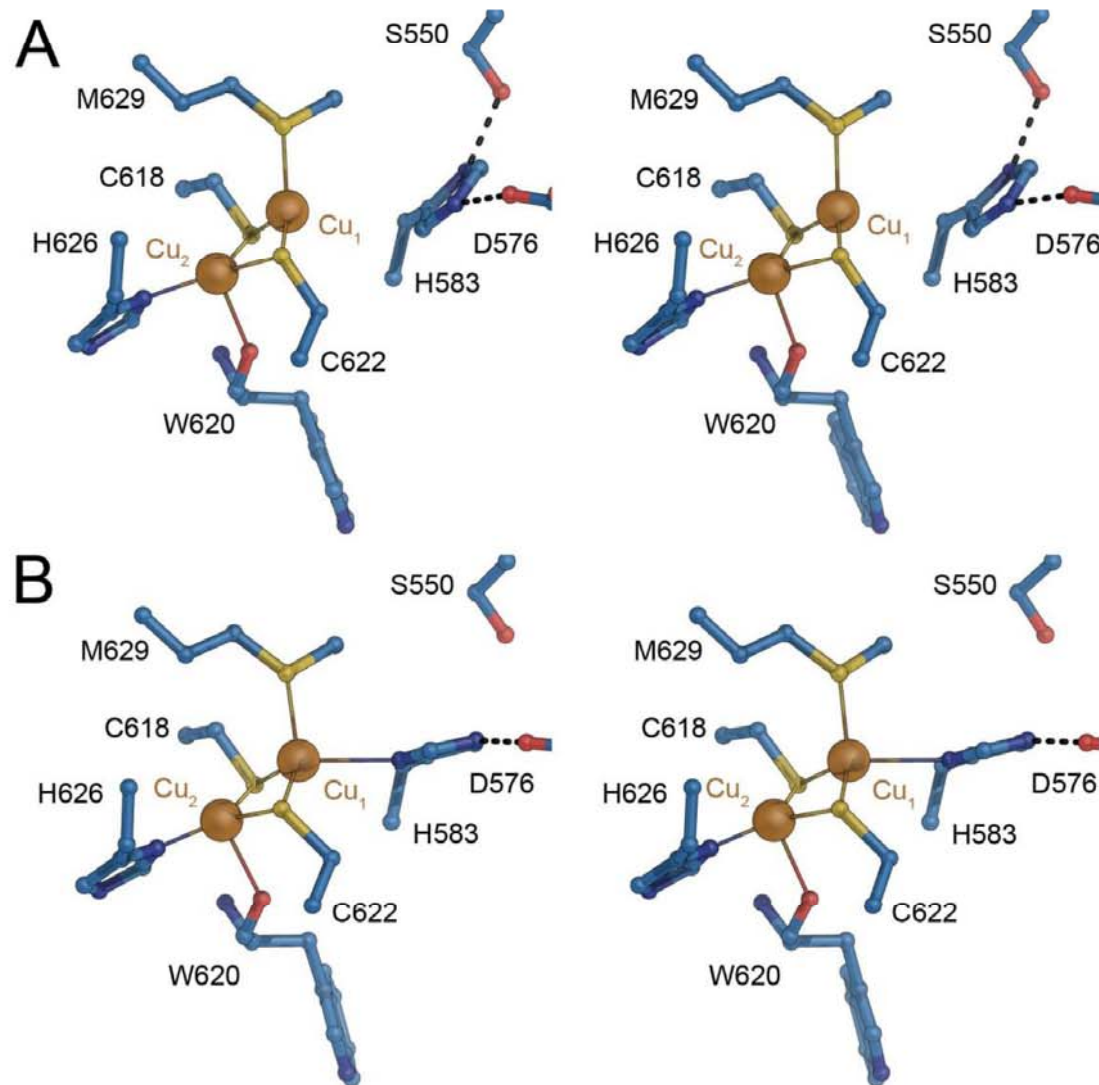


Nitrous Oxide Reductase/Denitrification
Cytochrome c Oxidase/Respiration

When prepared/crystallized under the strict exclusion of O₂, CuZ is a Cu₄S₂ Cluster

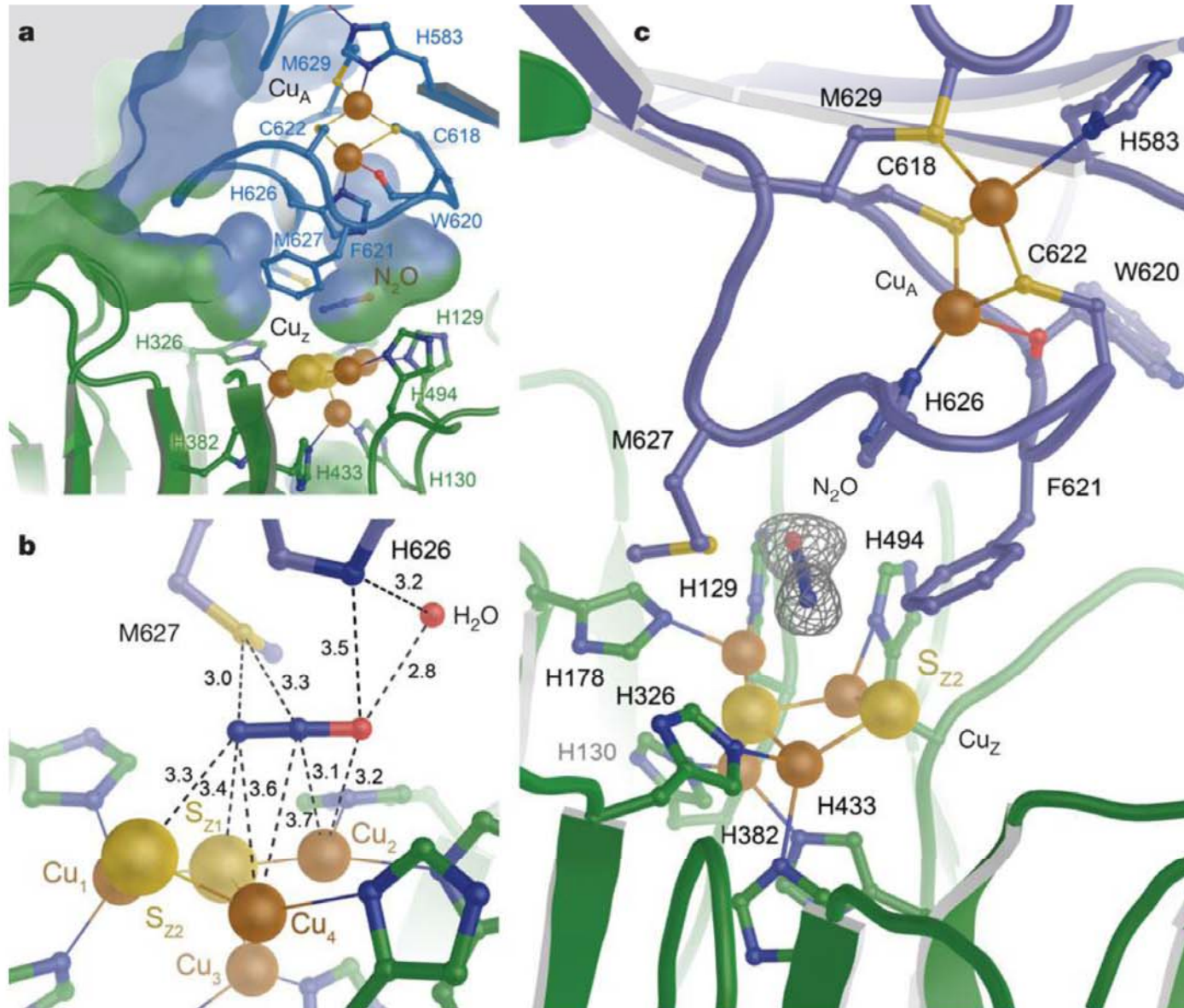


Upon binding of N₂O (Xtal under N₂O pressure) the ligands of CuA rearrange and His 583 flips to ligate Cu1 of CuA

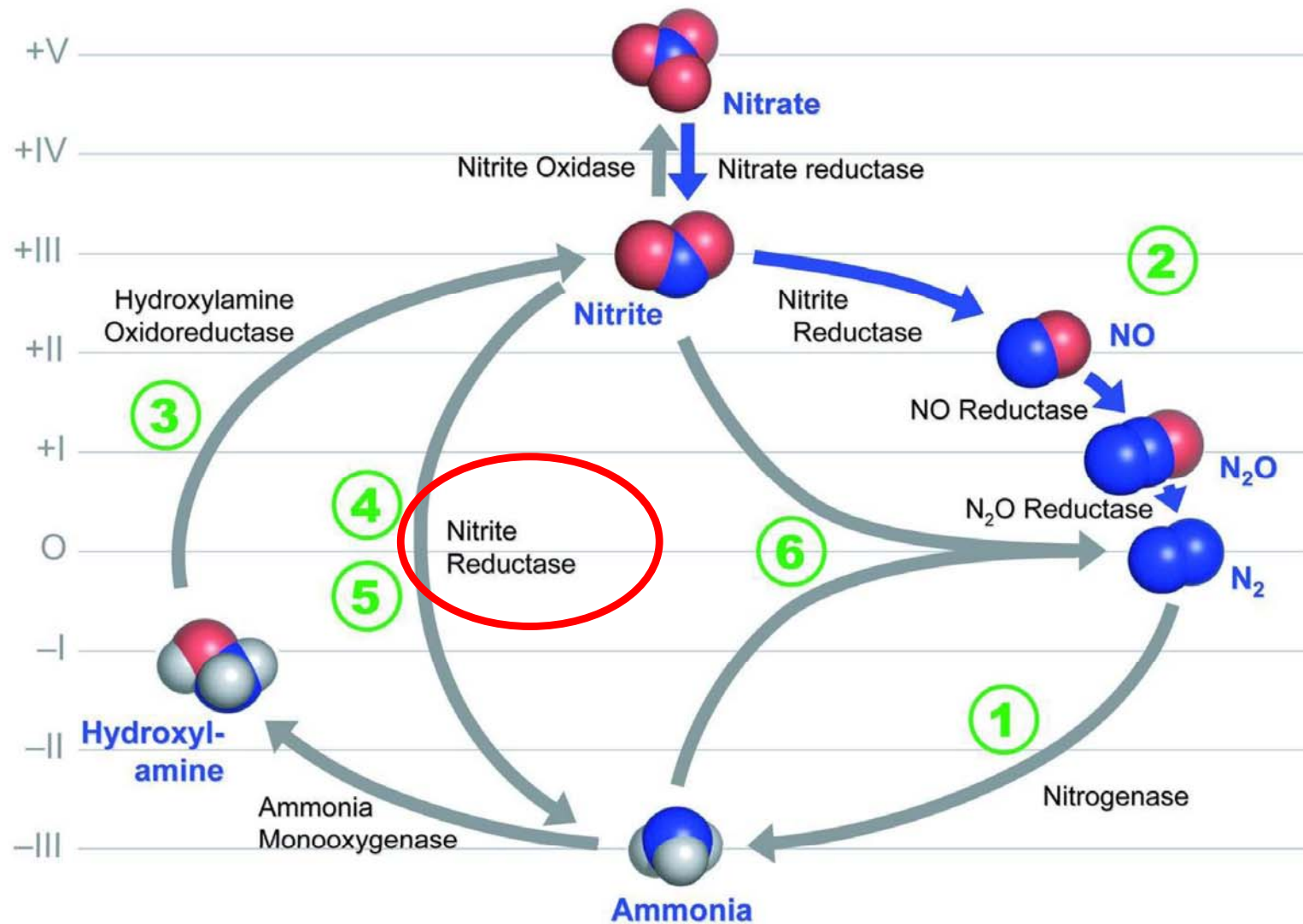


Catalysis: CuA and CuZ operate *in concert*

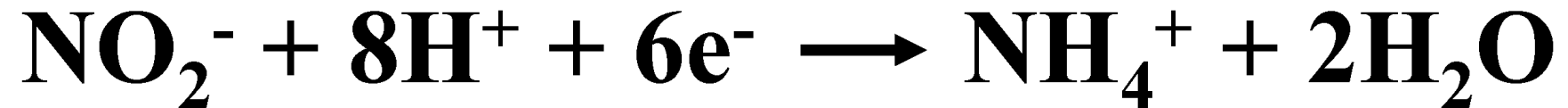
Xtal under N₂O pressure



Important Reactions and Metal Enzymes of the Nitrogen Cycle

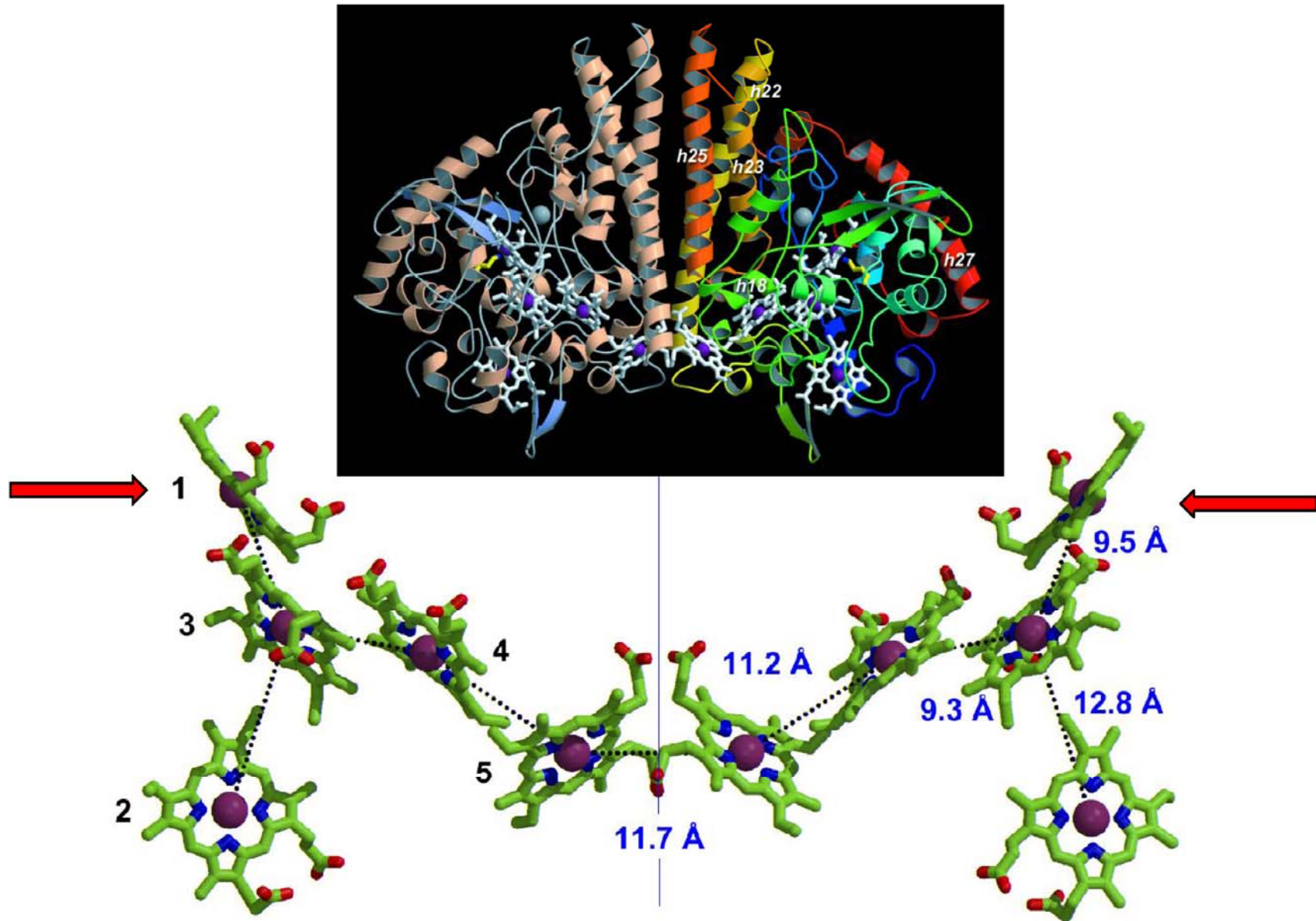


Dissimilatory Nitrite Reductase

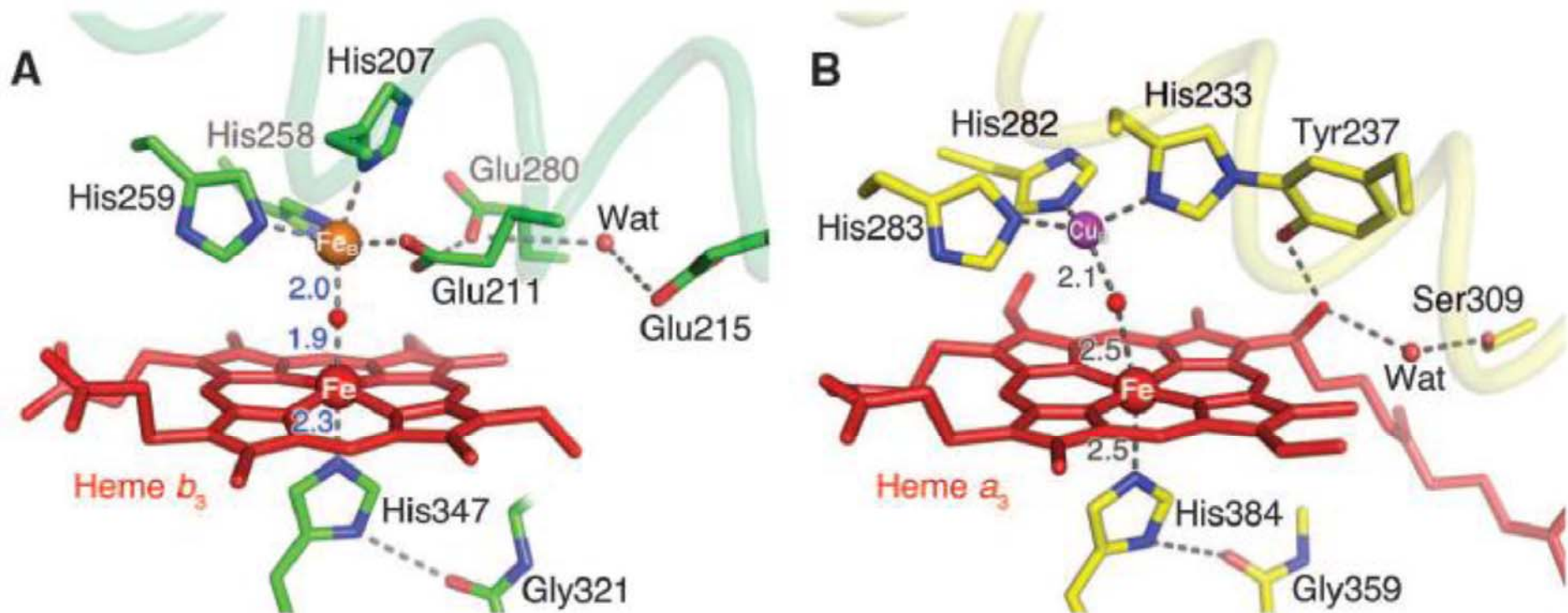


Cytochrome *c* Nitrite Reductase

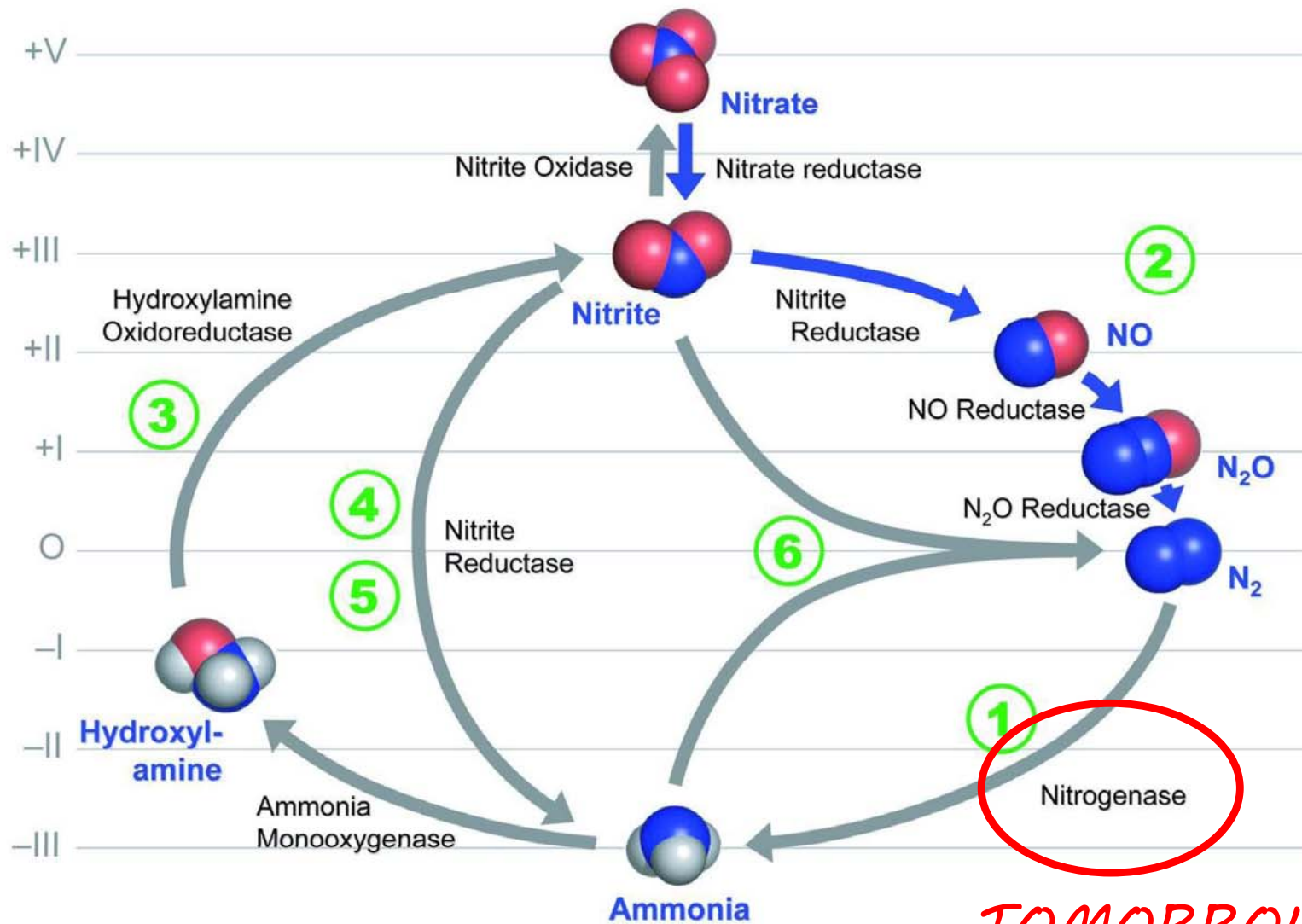
Einsle O, Messerschmidt A, Stach P, Bourenkov GP, Bartunik HD, Huber R, Kroneck
PMH (1999) *Nature*, 400 , 476–80



Active Sites of NOR (A) and COX (B)

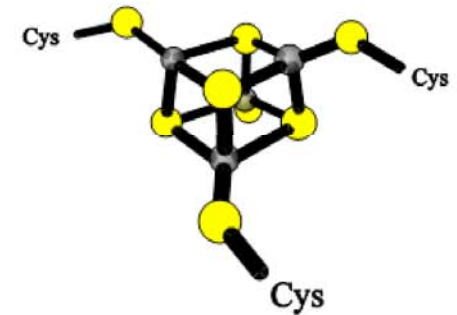
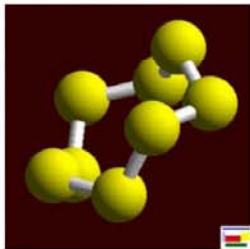
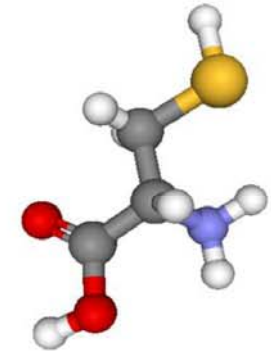


Important Reactions and Metal Enzymes of the Nitrogen Cycle



TOMORROW...

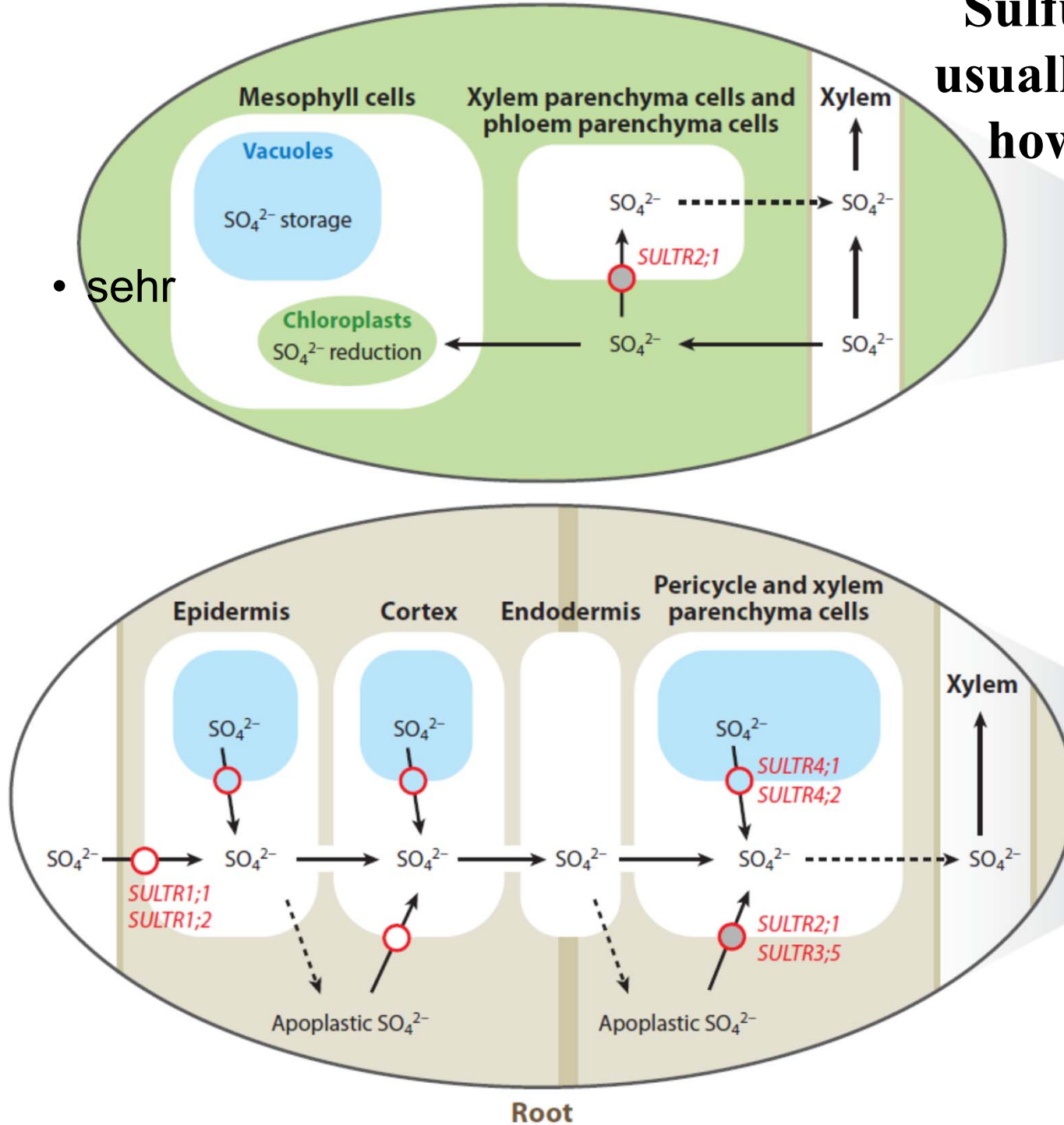
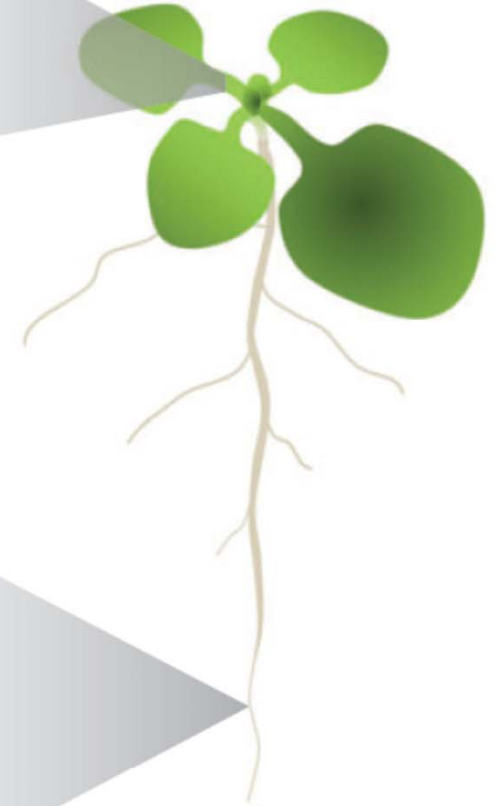
The Biogeochemical Cycle of Sulfur



Sulfur uptake in plants usually from sulfate – but how do we get there?

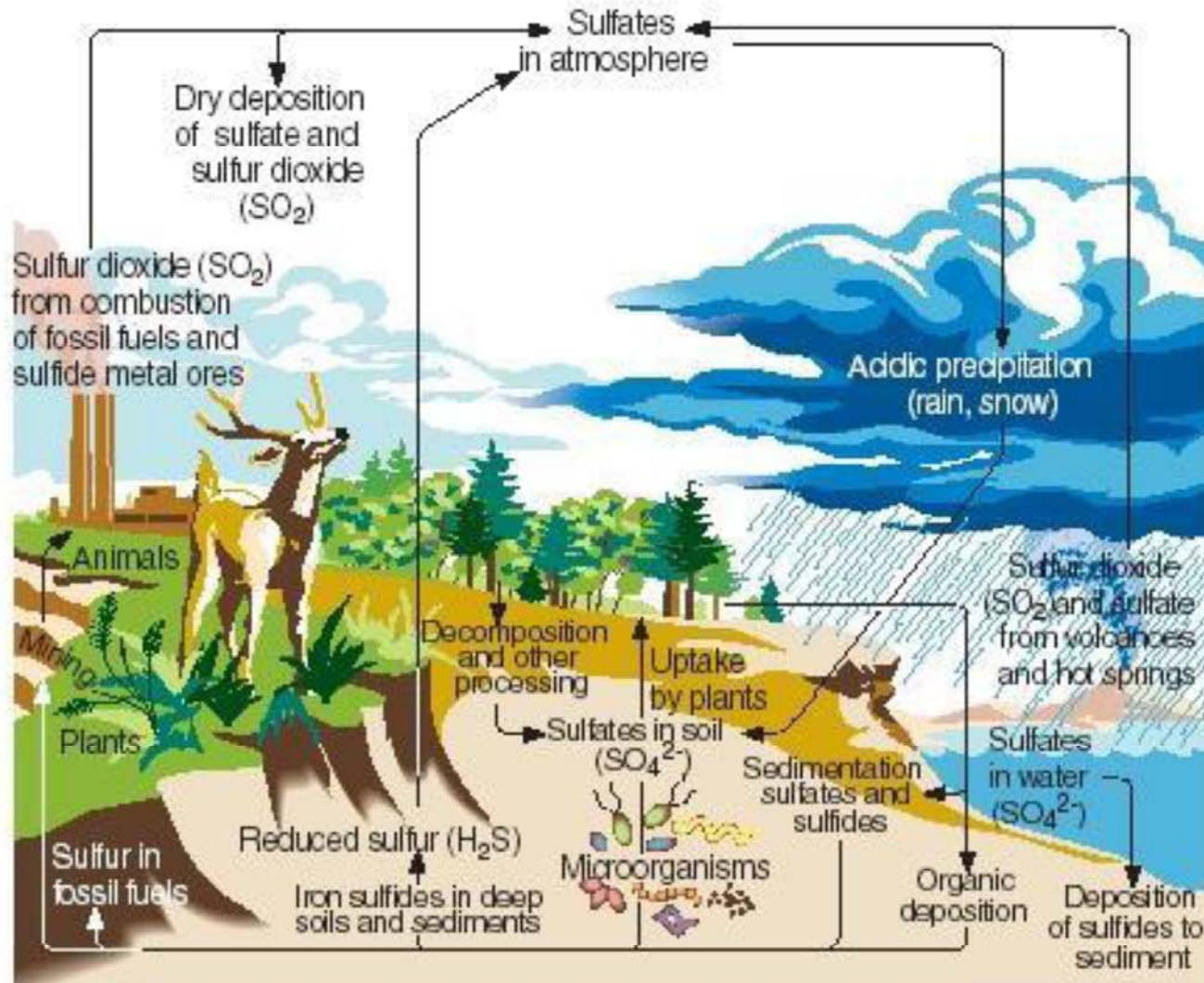
• sehr

Arabidopsis thaliana



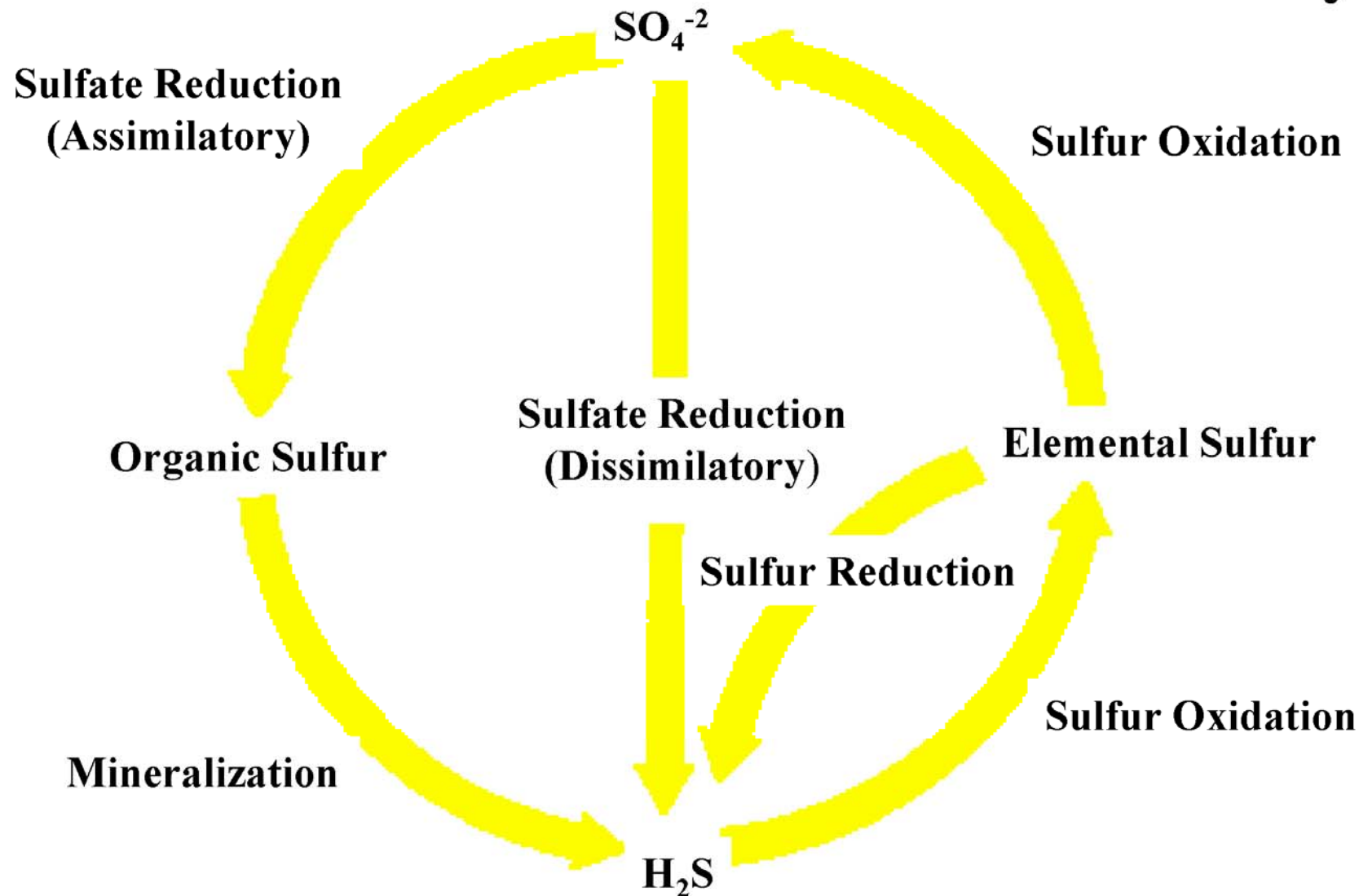
Life without Dioxygen – Respiration with S-Oxides

Reduction of SO_4^{2-} to H_2S

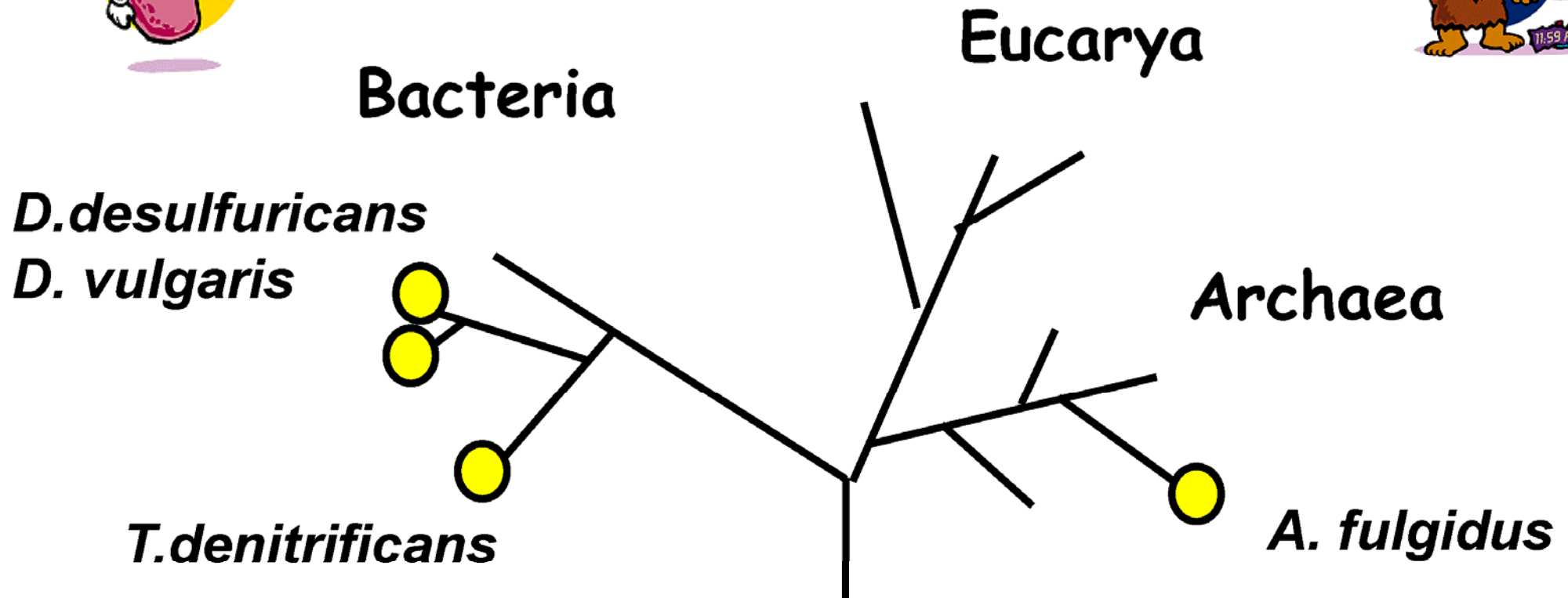


<http://www.scienceclarified.com/Oi-Ph/Oxygen-Family.html>

Reactions of the Biogeochemical Sulfur Cycle

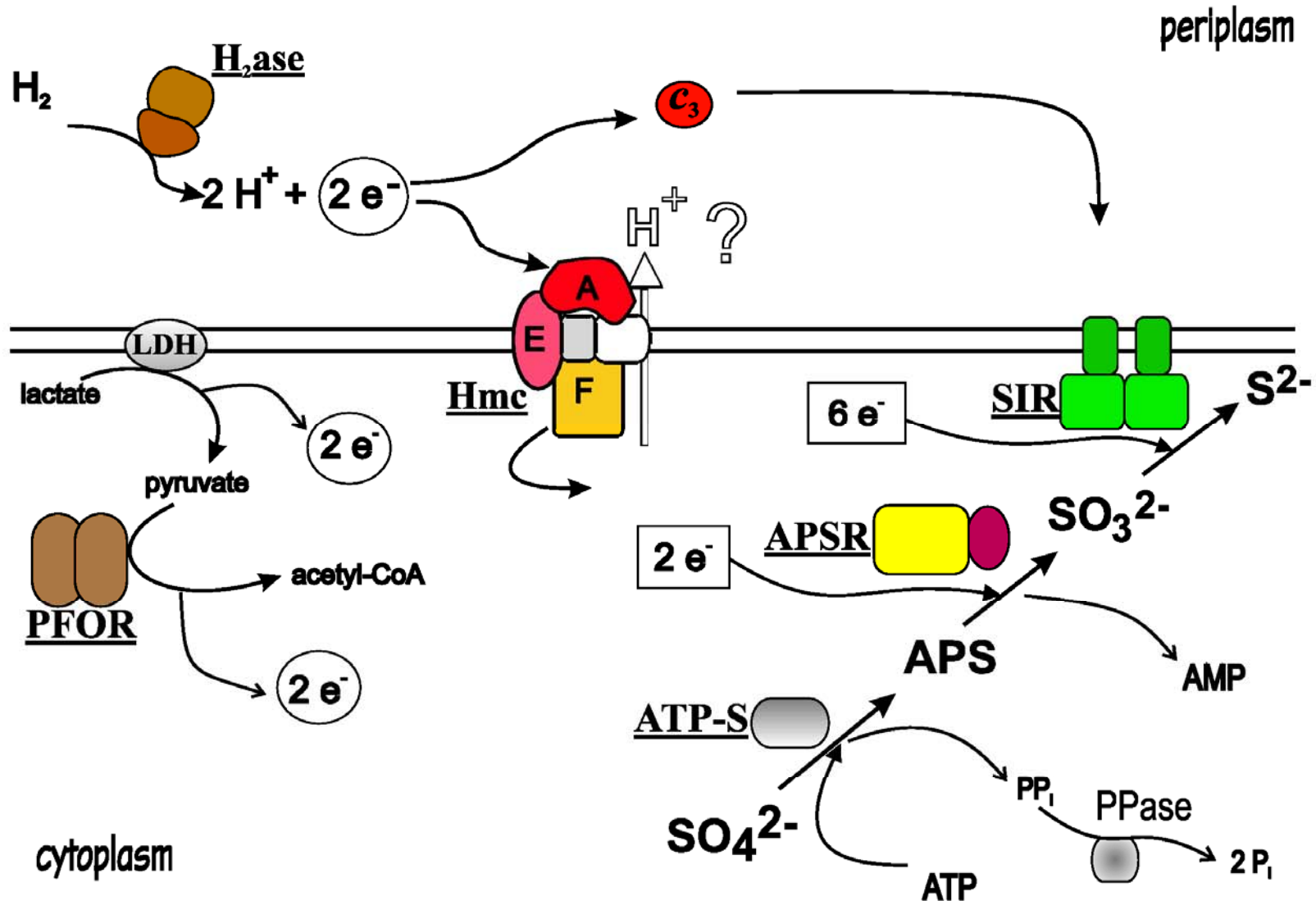


Oxidation/Reduction of Sulfur Compounds Coupled to Energy Conservation Evolved Early in Prokaryotic Evolution



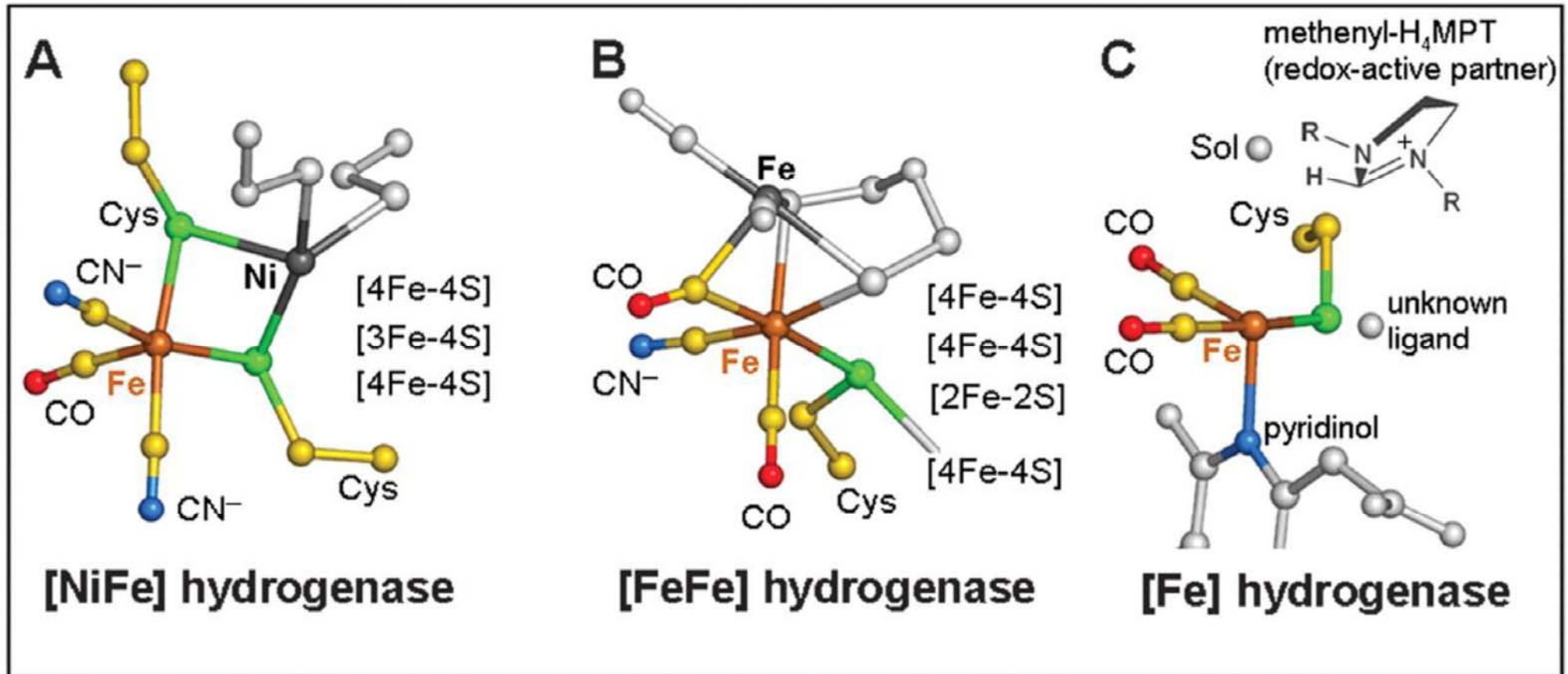
Life without O₂ - Sulfur Respiration

Reduction of SO₄²⁻ to H₂S, a multi-electron, multi-proton transfer process coupled to energy conservation



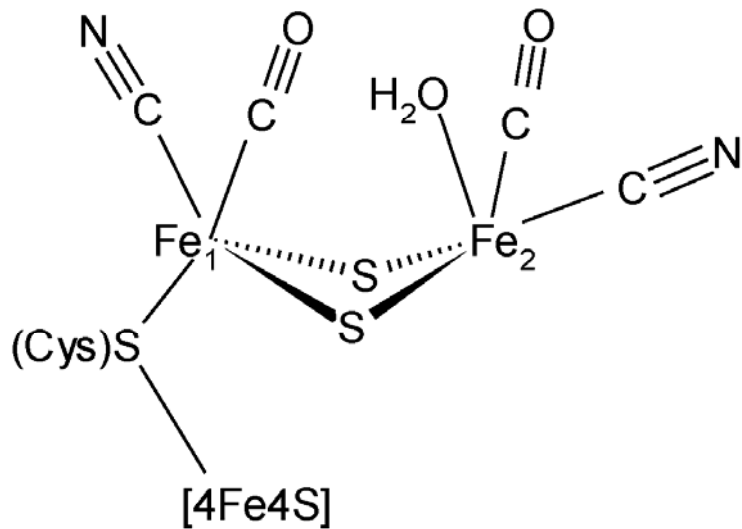
Tracking Footprints of Early Life

Nature's Toolbox to handle Dihydrogen

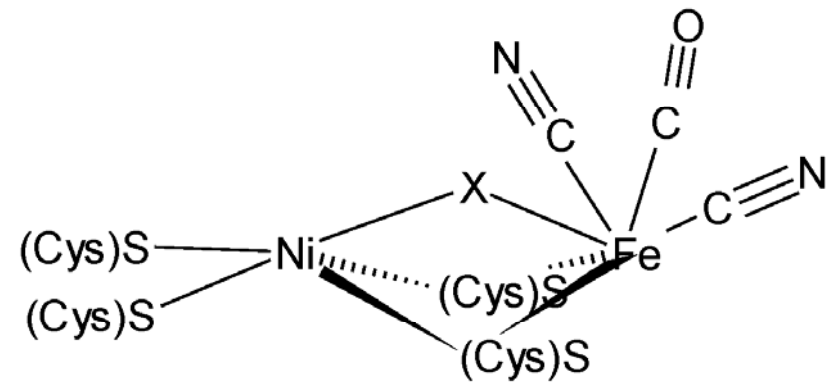


S. Shima et al., Science (2008), 321, 572 - 575

Fe-only vs Ni,Fe Hydrogenase

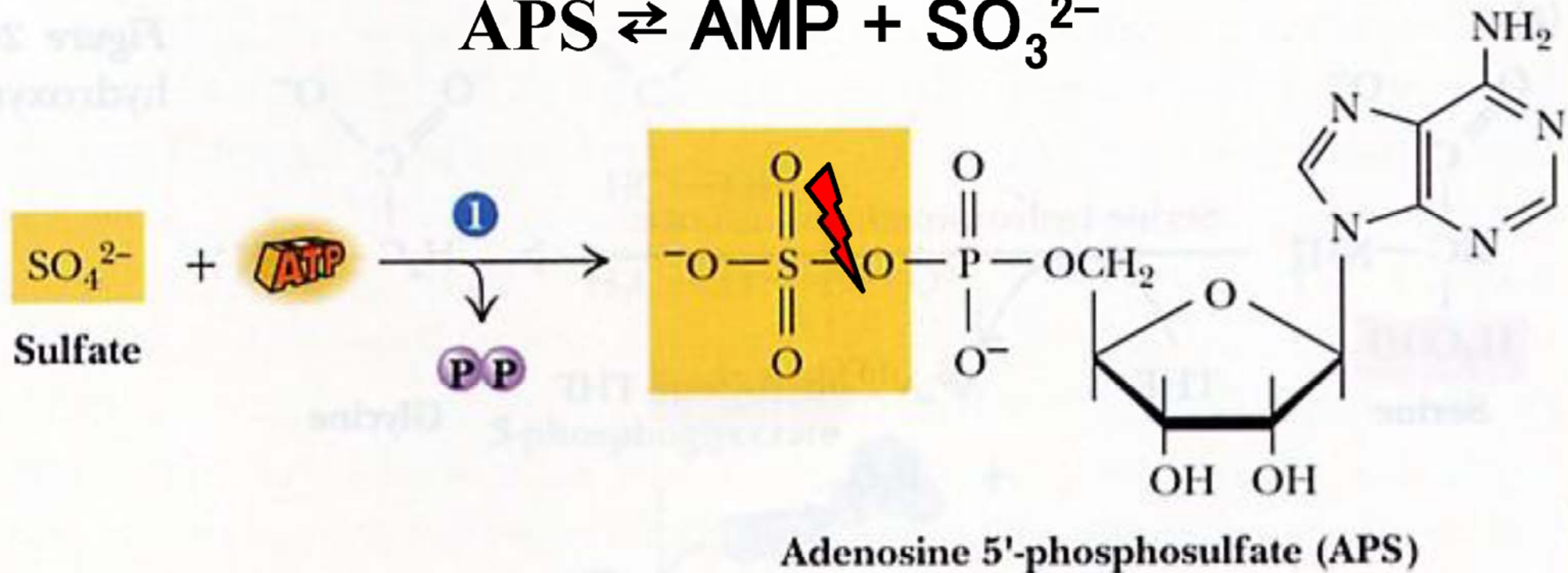


H-Cluster der
Fe-only Hydrogenase



[NiFe] Cluster der
Ni,Fe Hydrogenase

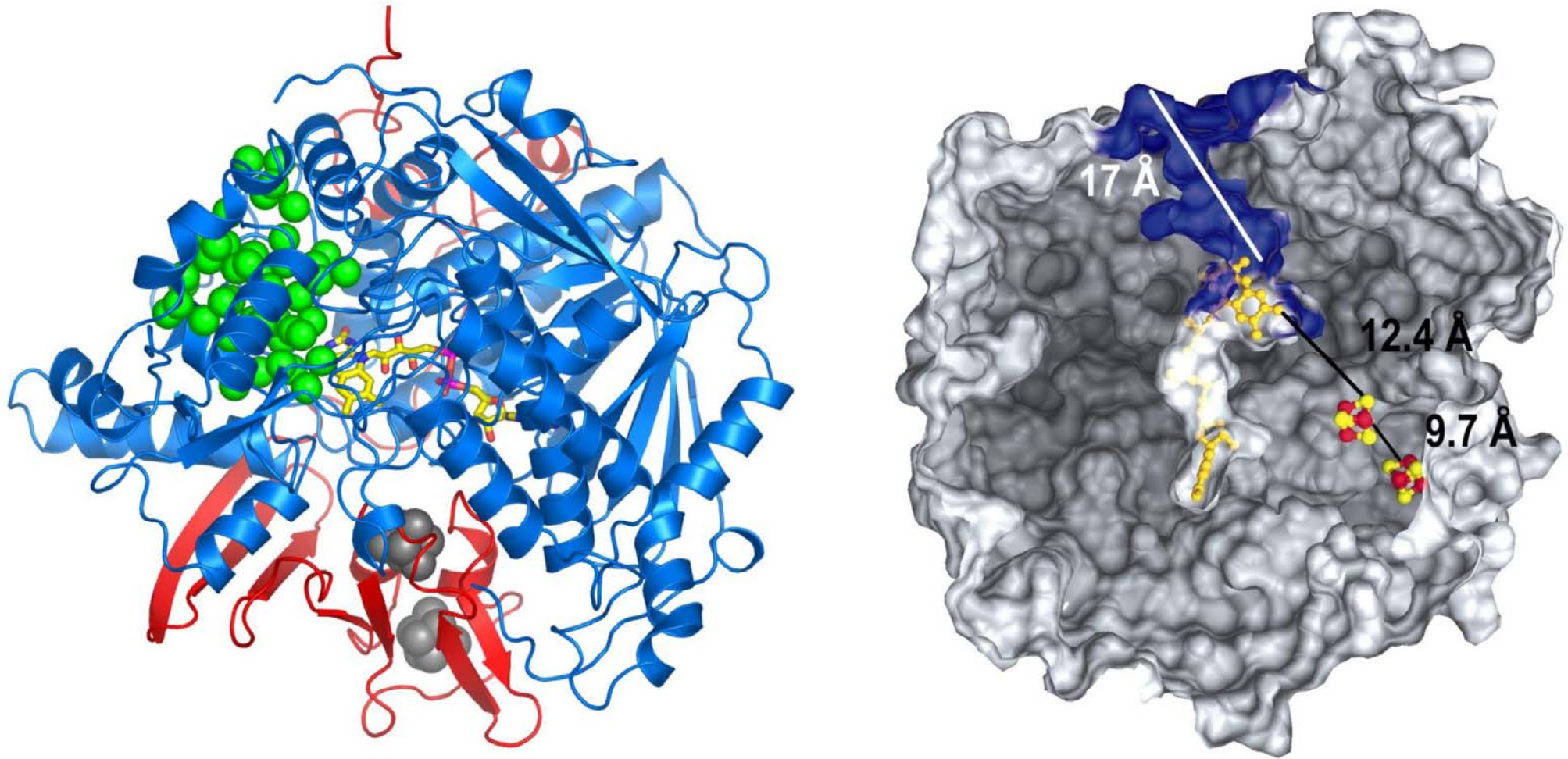
**SO_4^{2-} must be first activated,
then microorganisms *can eat* it**



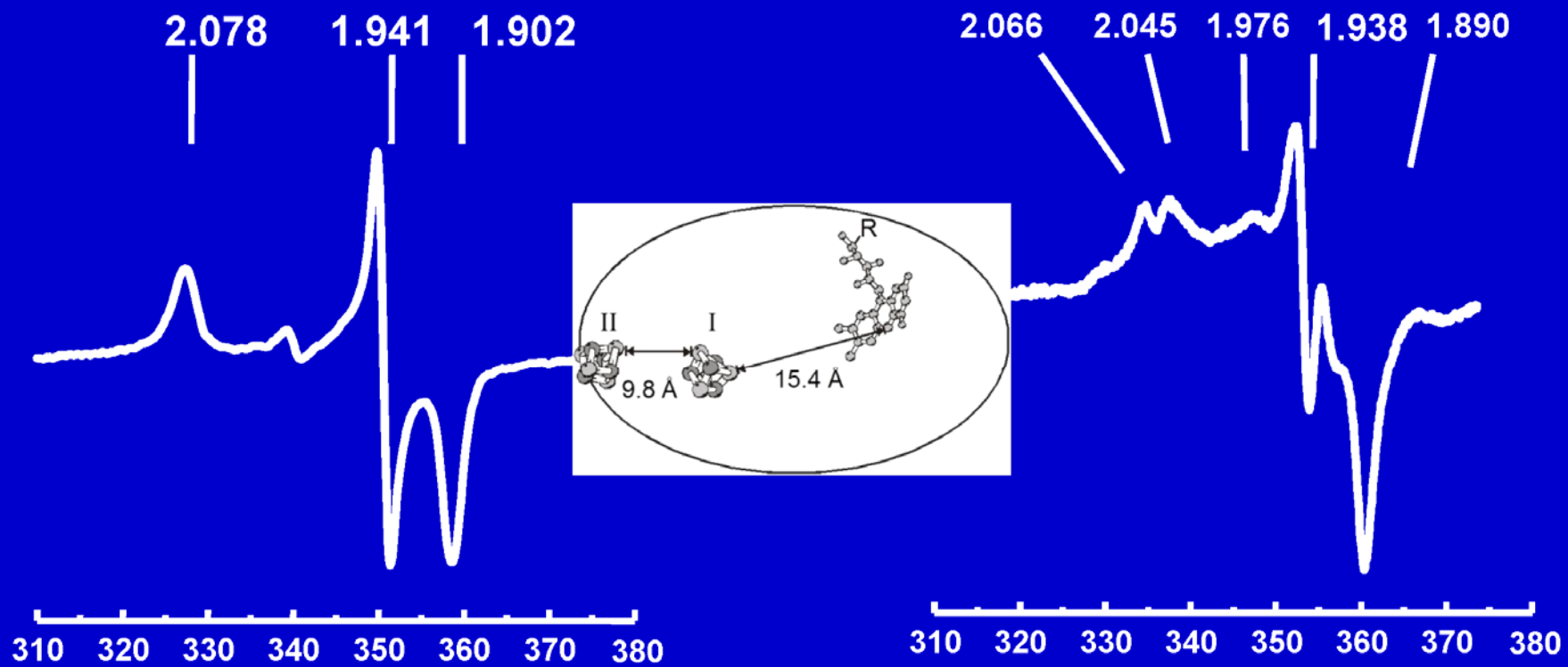
**Activation of sulfate ($E^{\circ\prime} = -516 \text{ mV}$) to
adenosine-5'-phosphosulfate = APS ($E^{\circ\prime} = -60 \text{ mV}$)**

APS Reductase from thermophilic *Archaeoglobus fulgidus*

Fritz et al., PNAS (2002), 99, 1836-41; Schiffer et al., Biochemistry (2006), 45, 2960-67

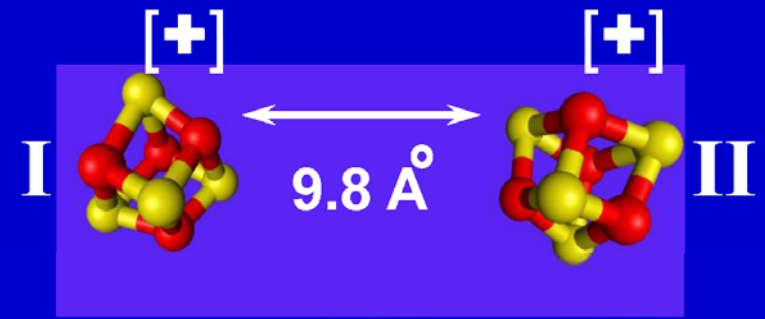
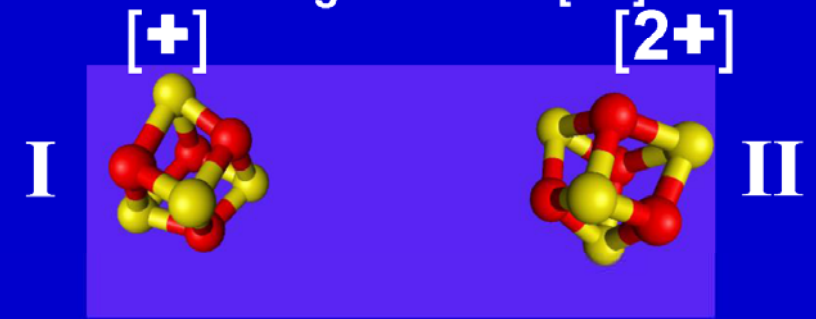


APSR has two [4Fe-4S] – Clusters which interact



Magnetic field [mT]

Magnetic field [mT]

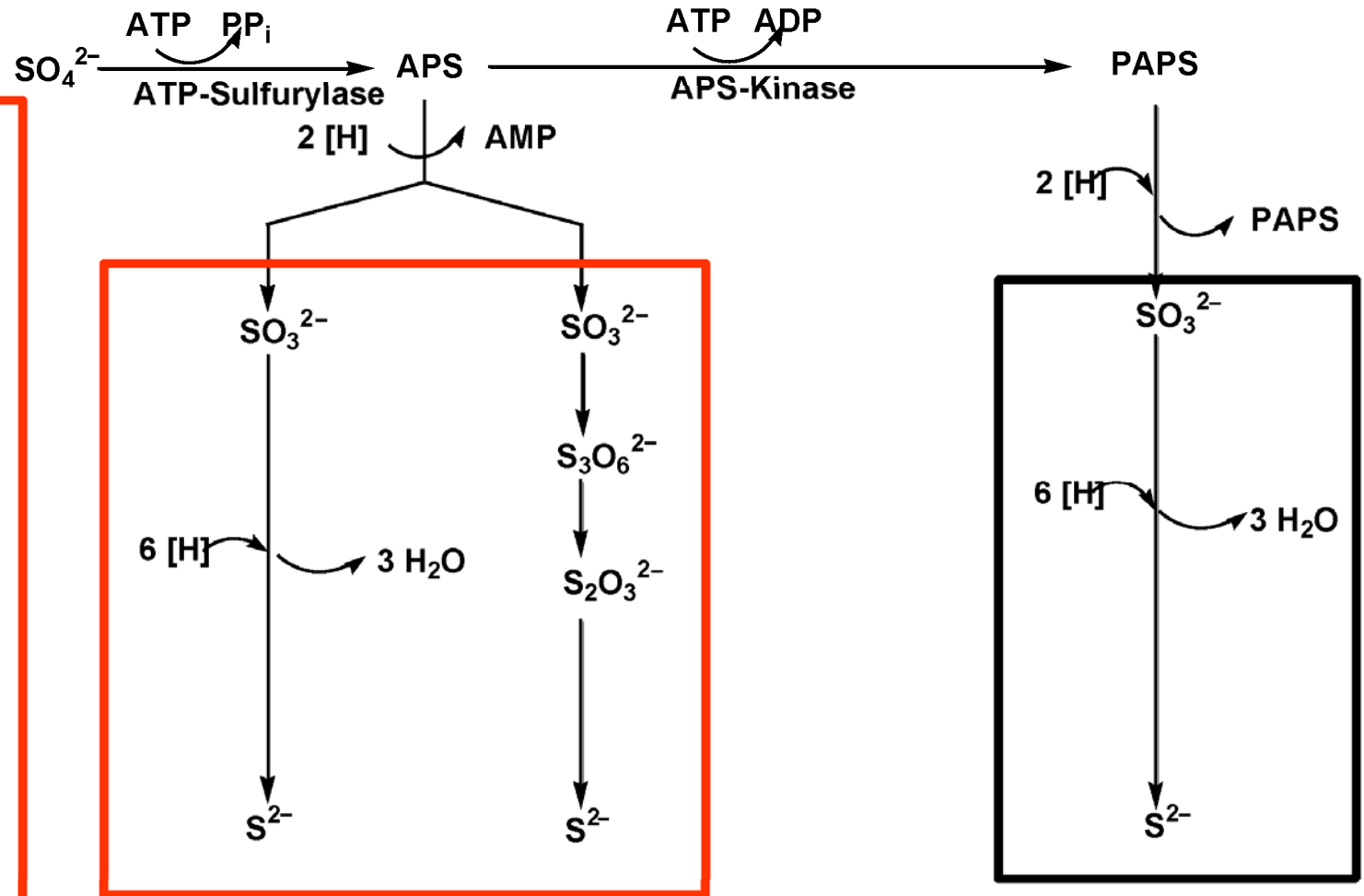


$E_o' = -60 \text{ mV}$

$\gg \gg$

$E_o' = -520 \text{ mV}$

Chemistry of Sulfite Reduction

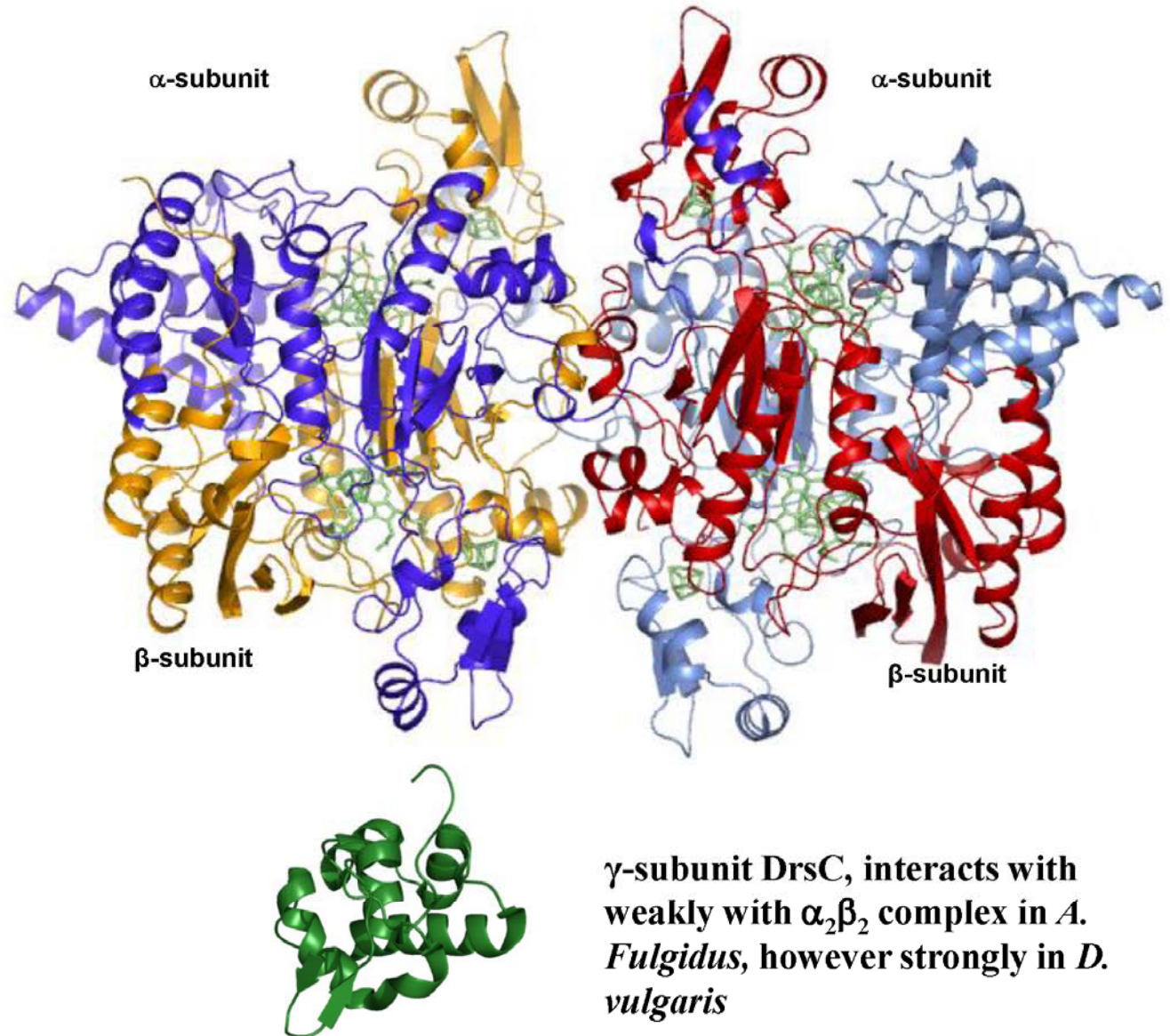


Sulfite reduced to sulfide (directly or via trithionate/thiosulfate) by sulfite reductase in a six-electron transfer process

Dissimilatory (dSIR) Assimilatory (aSIR) Sulfite Reduction

Overall structure of *A. fulgidus* dSIR $\alpha_2\beta_2$ complex

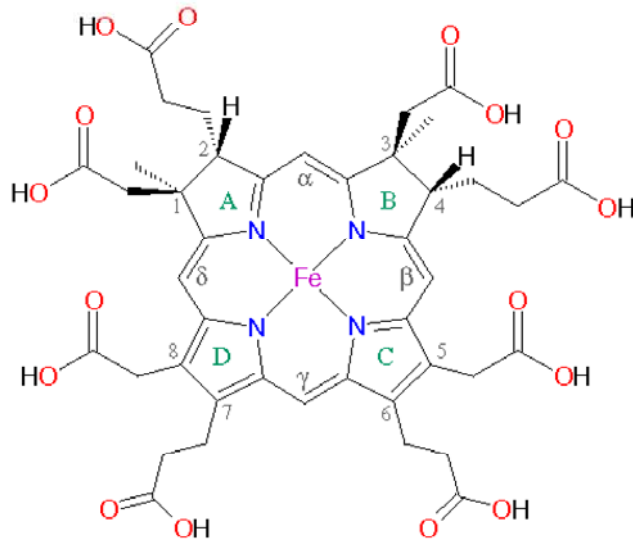
- Final model contains four siroheme and eight [4Fe-4S] centers = 36 Fe
- N- and C-terminal ends involved in intradimer and interdimer formation
- Tetrameric state may help to survive in hot environments
- One $\alpha\beta$ -unit contains the catalytic siroheme center



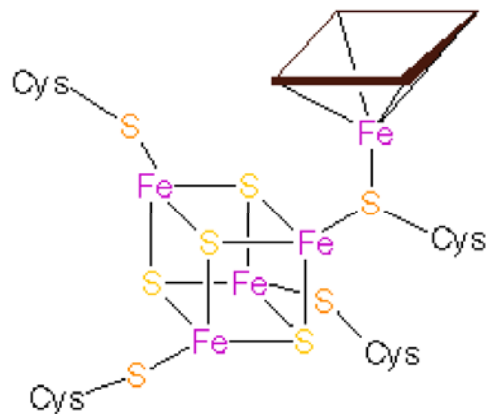
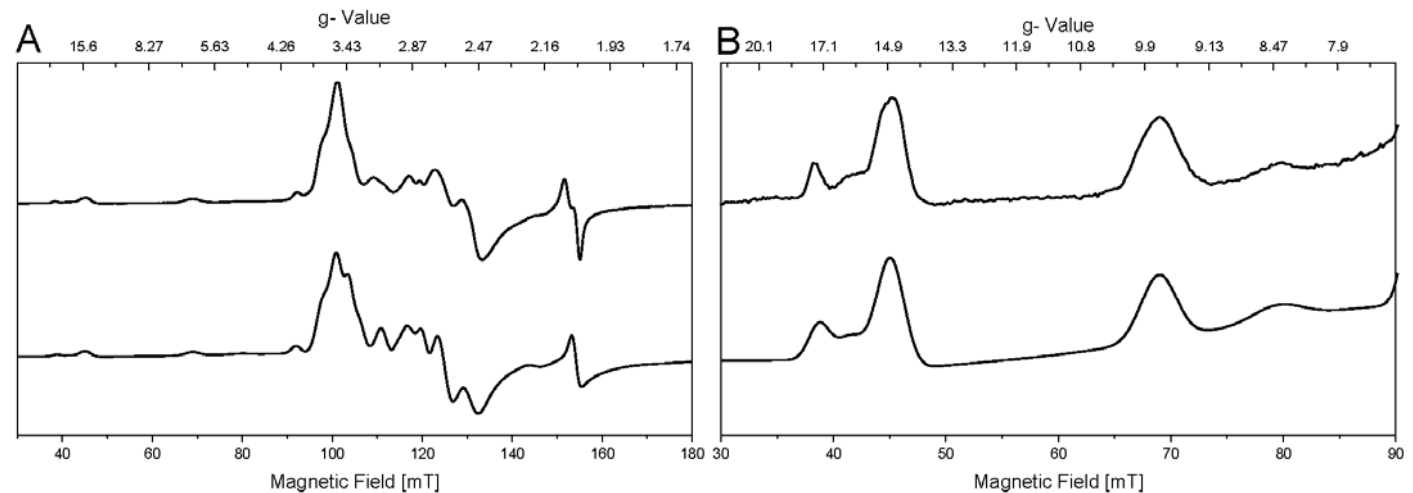
Sulfite Reductase (36 Fe) from *Archaeoglobus fulgidus*



Schiffer et al. (2008) *J. Mol. Biol.*, 379, 1063-74; Parey et al. (2010) *Biochemistry*, 49, 8912-21

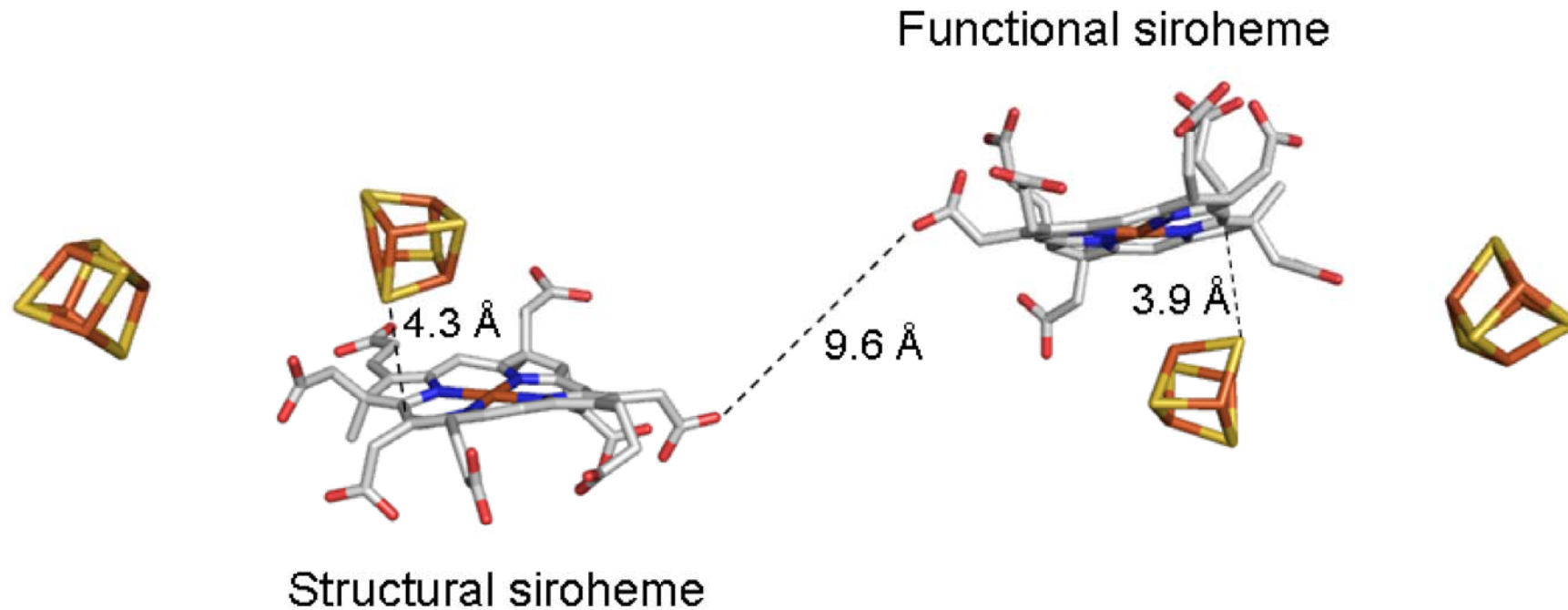


EPR (X-Band), resonances between g 18 and g 1.9



Unique cofactor: Siroheme coupled to [4Fe-4S]

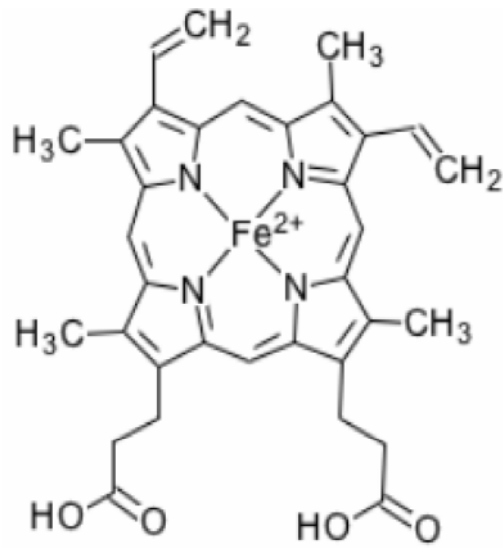
Cofactors of *A. fulgidus* dSIR



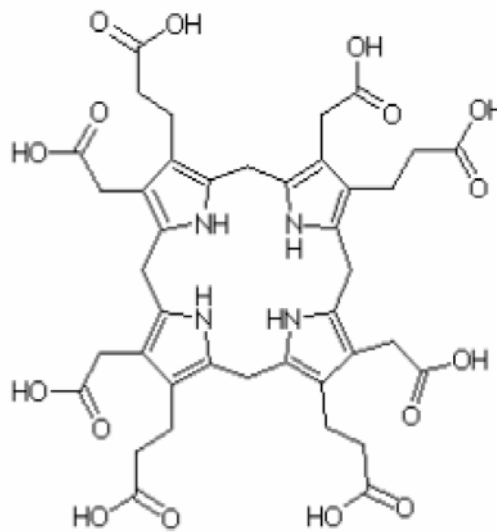
Functional and structural siroheme-[4Fe-4S] centers in one $\alpha\beta$ dimer; both sirohemes are arranged towards each other.

Minimal distance between the acetate carboxylates 9.6 Å; distance 3.9-4.3 Å from the siroheme to next [4Fe-4S] cluster.

SIR contains Siroheme



Heme b
(red)

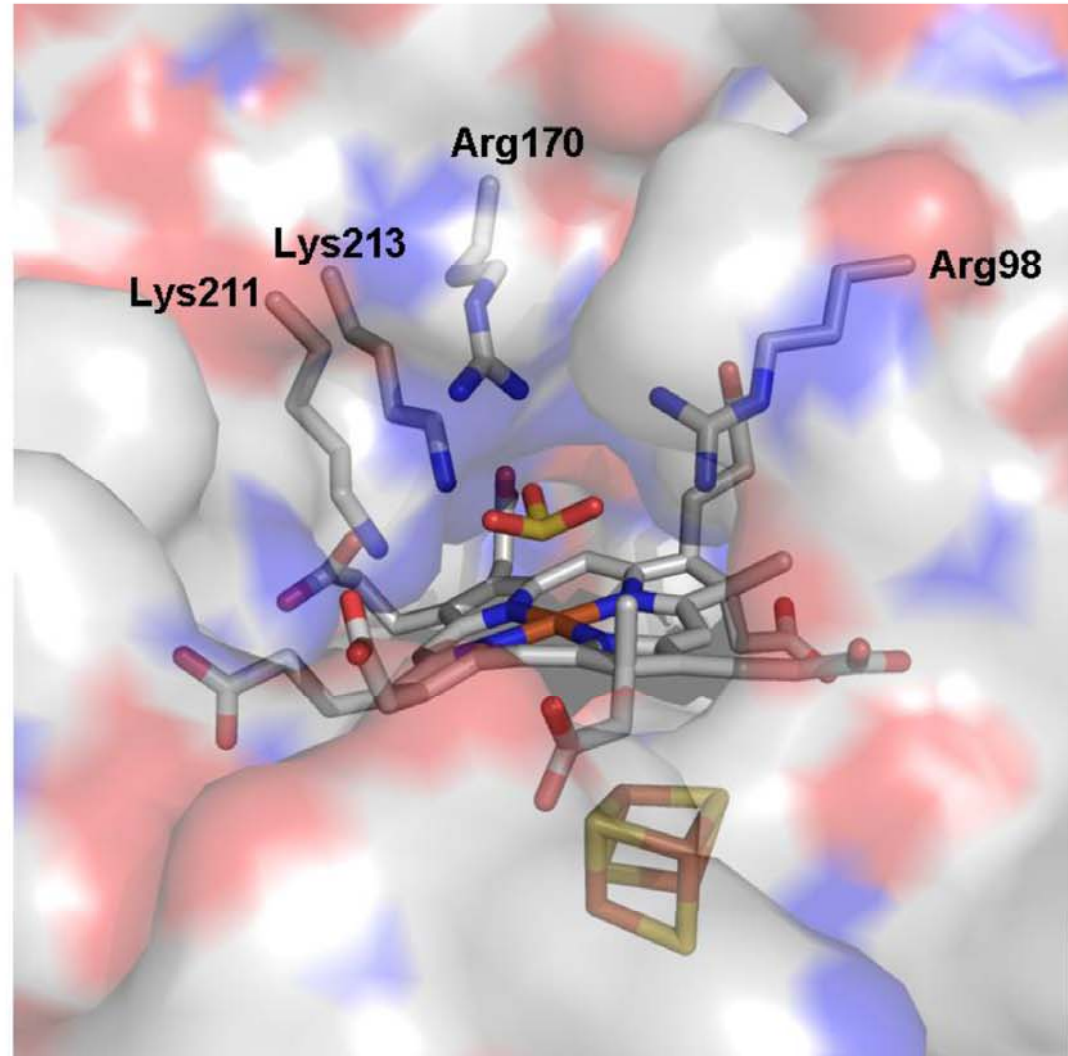
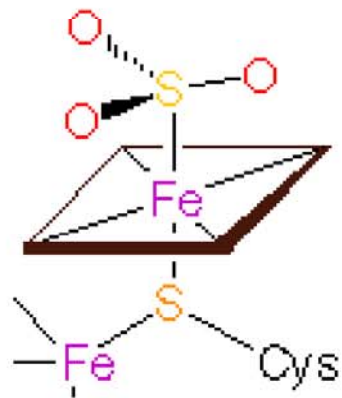
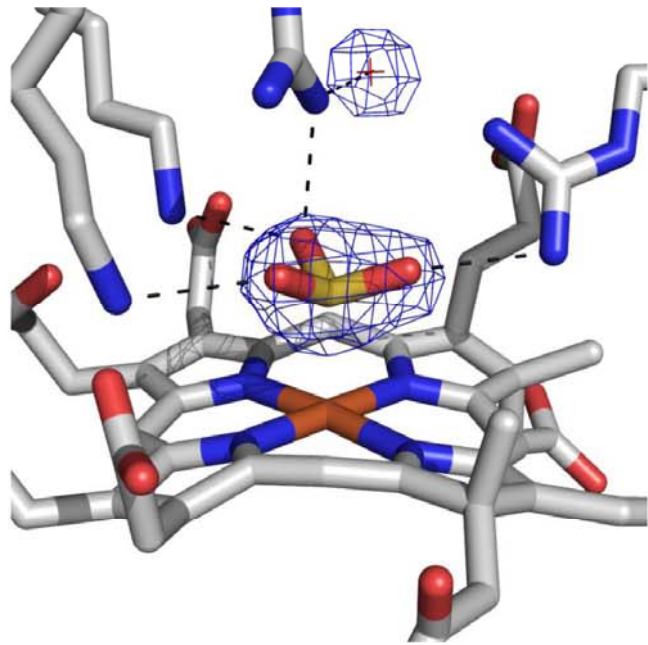


Siroheme
(green)

- Siroheme = heme-type prosthetic group
- catalyzes the six-electron reduction of sulfite to sulfide, and of nitrite to ammonia
- formed by methylation, oxidation, and Fe insertion into uroporphyrinogen III

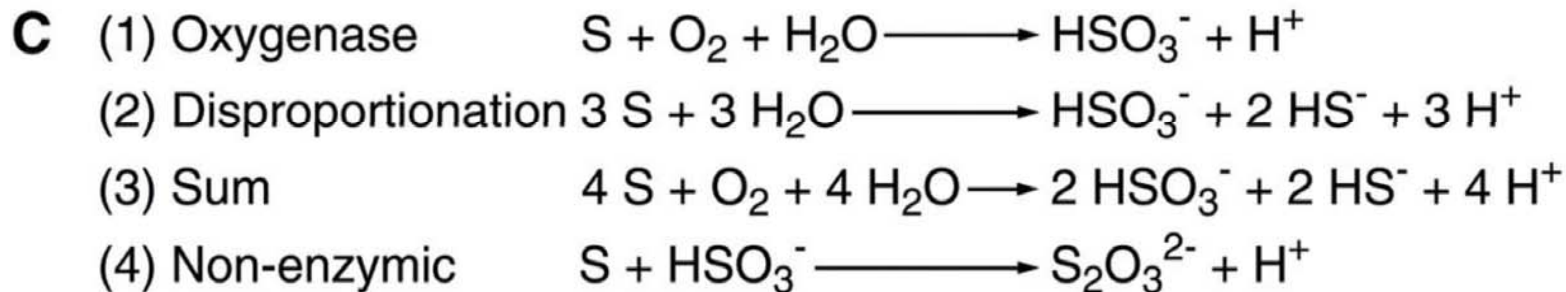
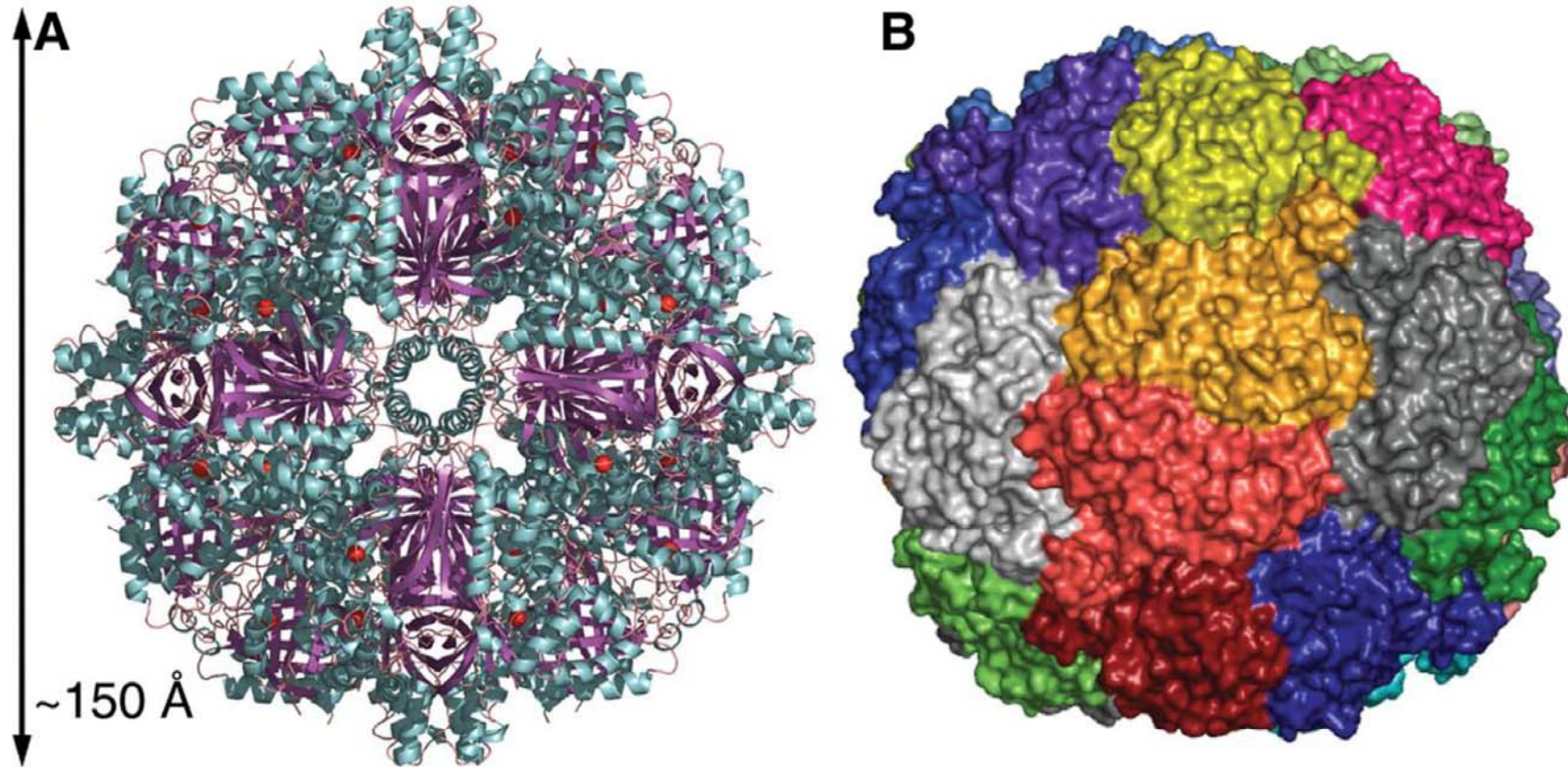
SO_3^{2-} Adduct and the Substrate Channel

Positively charged residues guide the substrate Parey et al. (2010) *Biochemistry* **49**, 8912-21



Structure of a Self-Compartmentalizing Sulfur Cycle

T. Urich et al. (2006) *Science* 311, 996 – 999



Take Home Message

*“Dear Lord, I fall upon my knees
and pray that all my syntheses
may cease to be inferior
to those conducted by bacteria”*

Leslie D. Pettit, X. International Symposium on
Bioinorganic Chemistry, Szklarska Poreba, Poland
(2005)

Bacteria are outstanding Chemists

**All slides of my lectures can be downloaded
from my workgroup homepage**

Biology Centre CAS → Institute of Plant Molecular Biology → Departments
→ Department of Plant Biophysics and Biochemistry,
or directly

http://webserver.umbr.cas.cz/~kupper/AG_Kuepper_Homepage.html