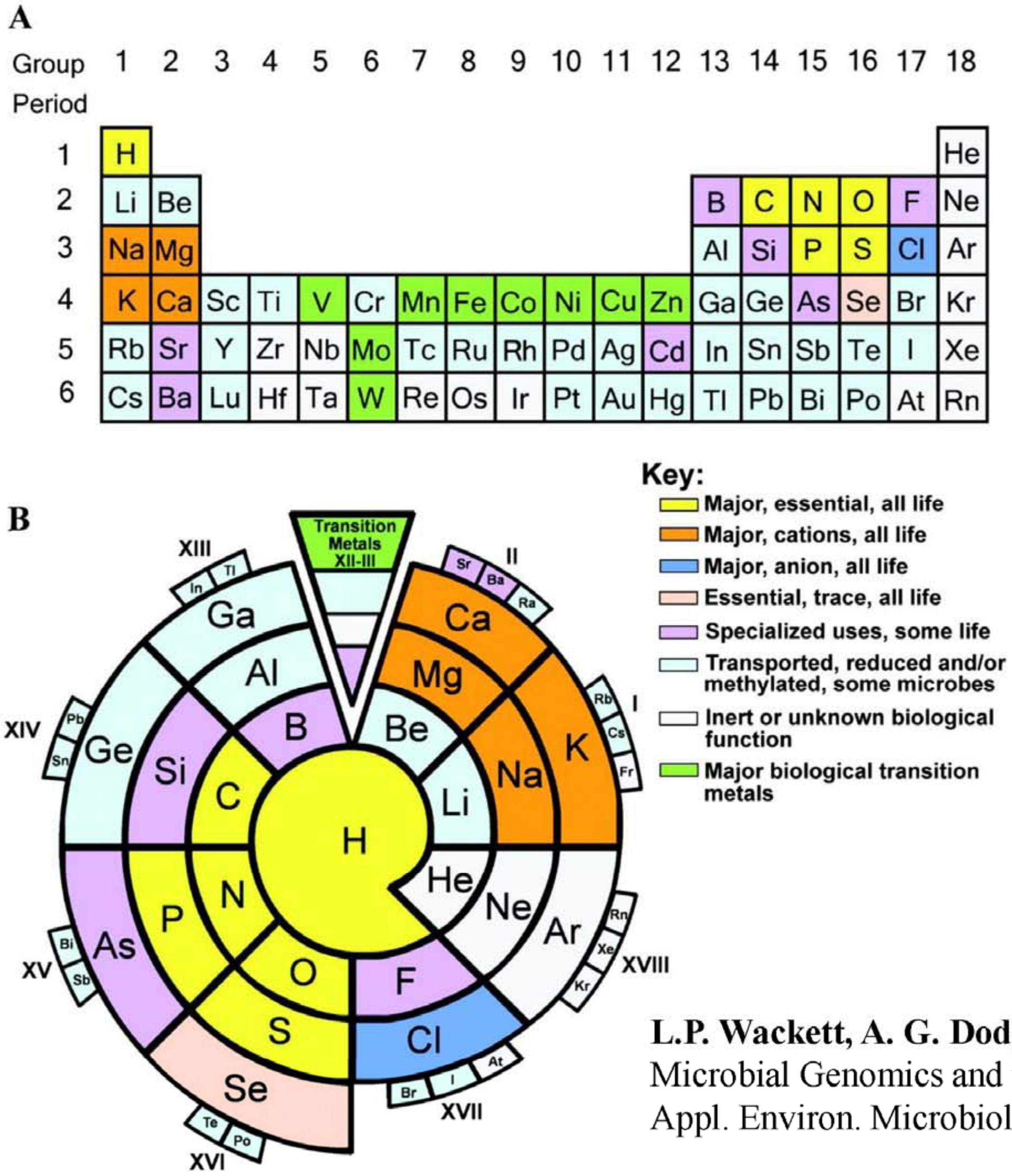
Biogeochemical Cycles

Hendrik Küpper, Advanced Course on Bioinorganic Chemistry & Biophysics of Plants, summer semester 2025

based on a lecture of Peter Kroneck, Universität Konstanz



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

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

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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

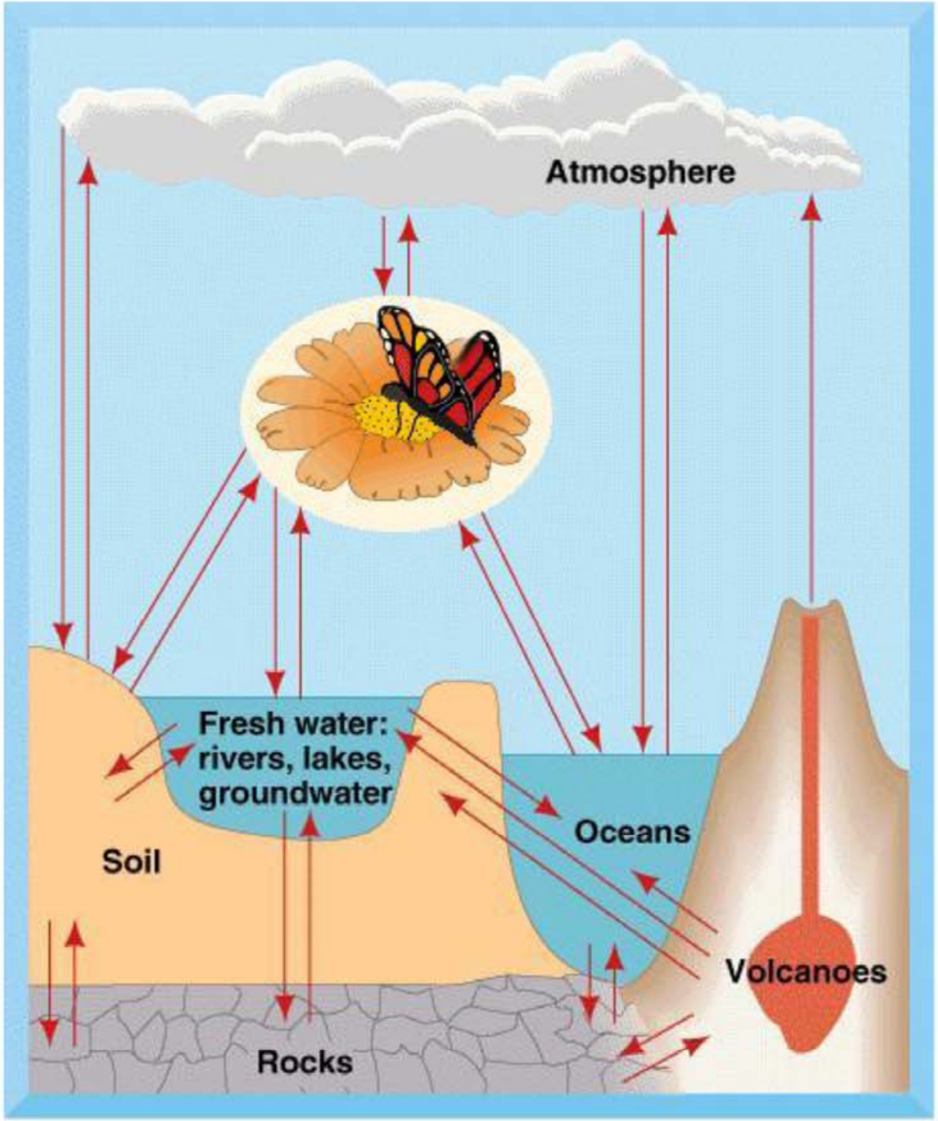
Oceanography 20, 117–123, The Sulfur Cycle

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.

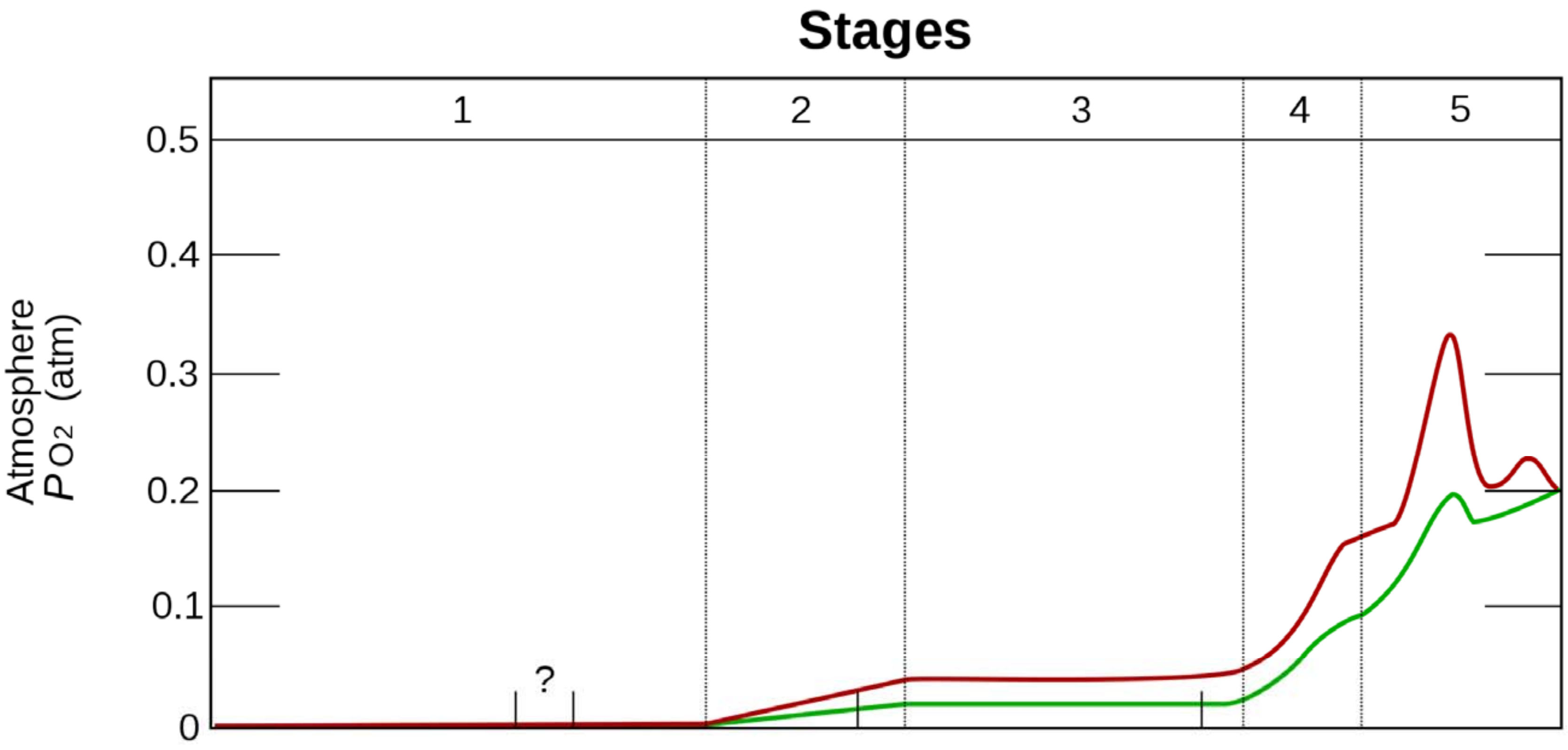
Citation

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



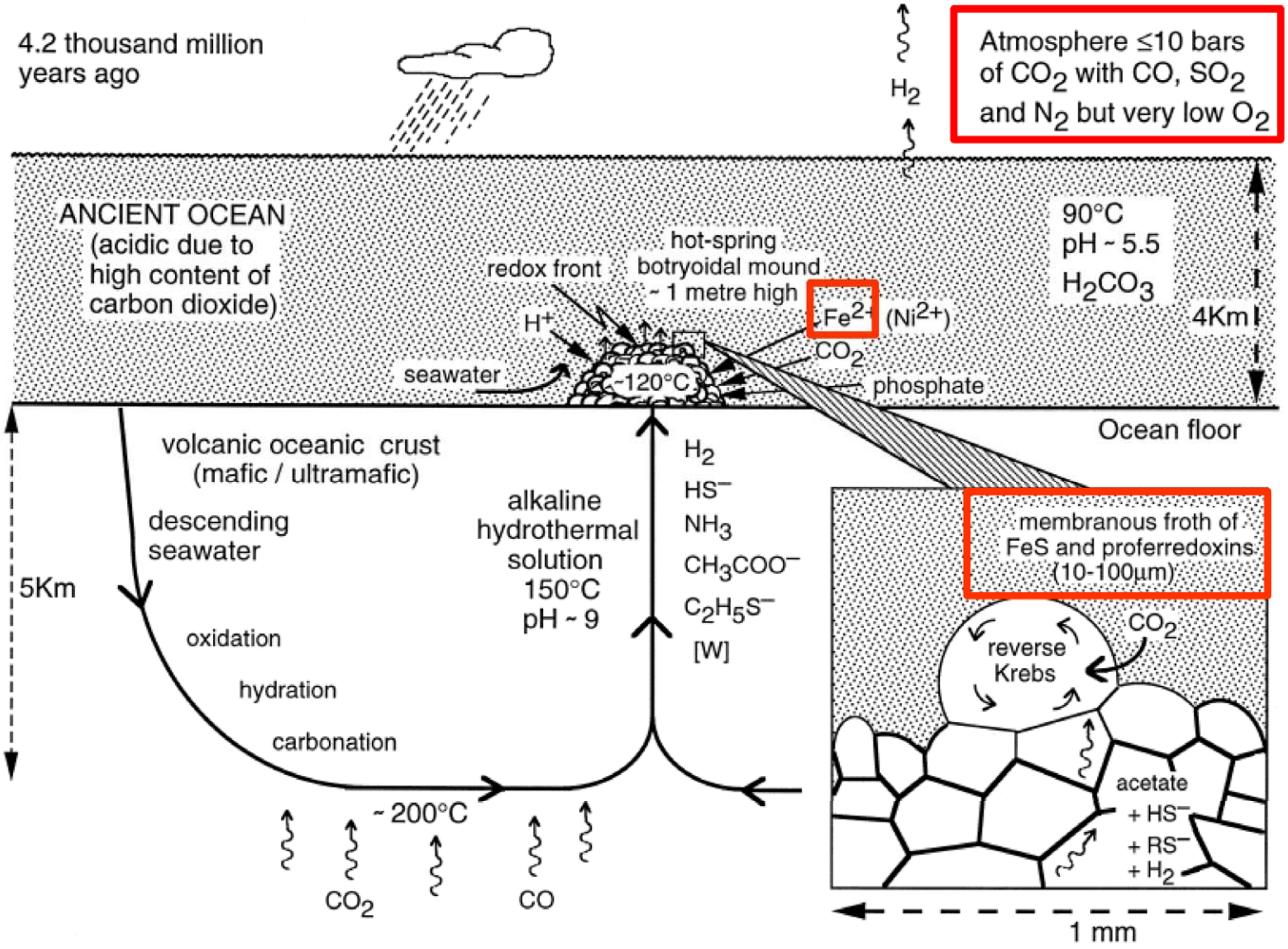
Estimated evolution of atmospheric O_2

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



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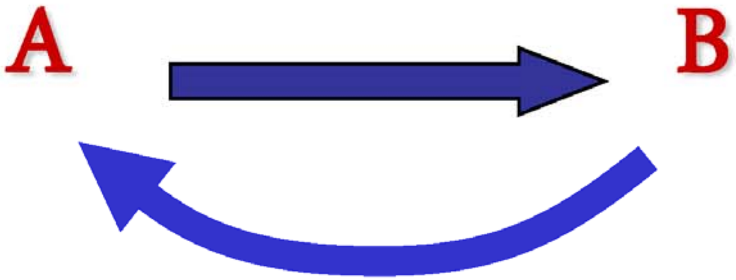
Biogeochemical Cycles

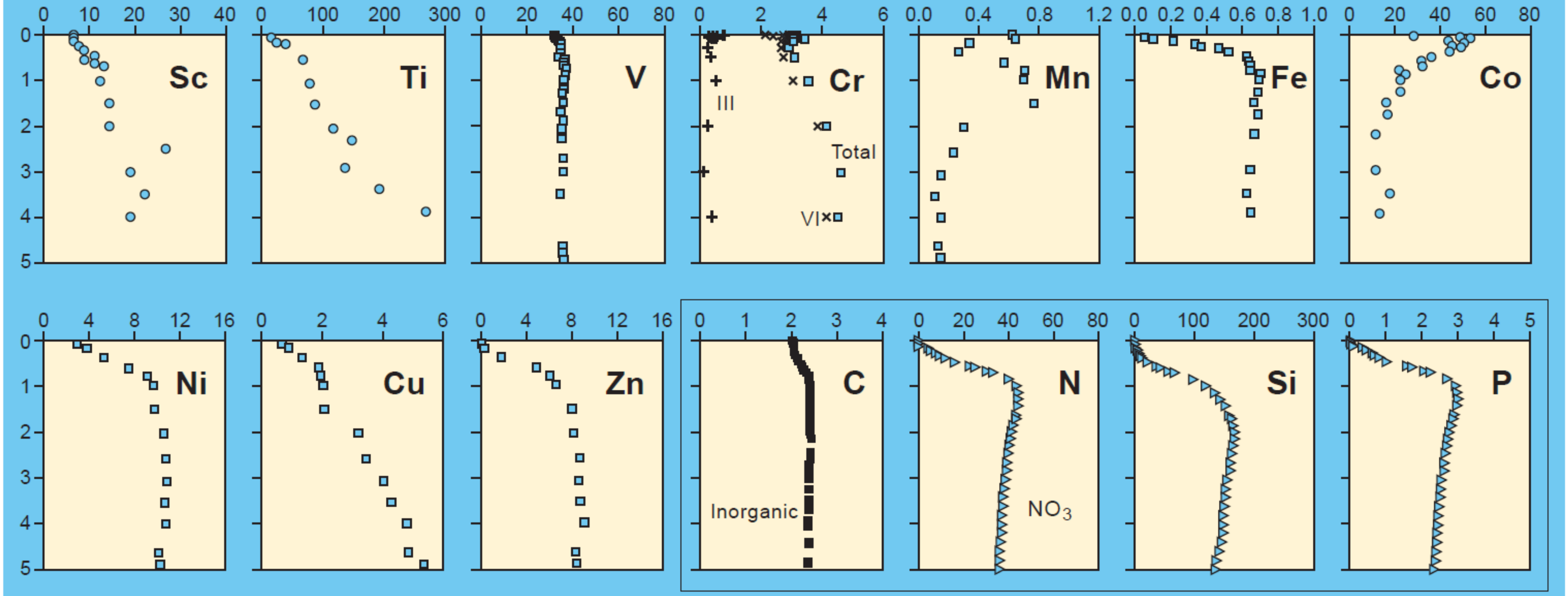
- **Metabolism: All organisms transform (different) compounds**



- **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



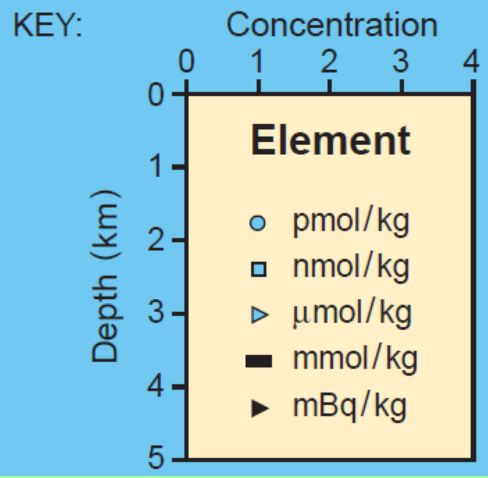
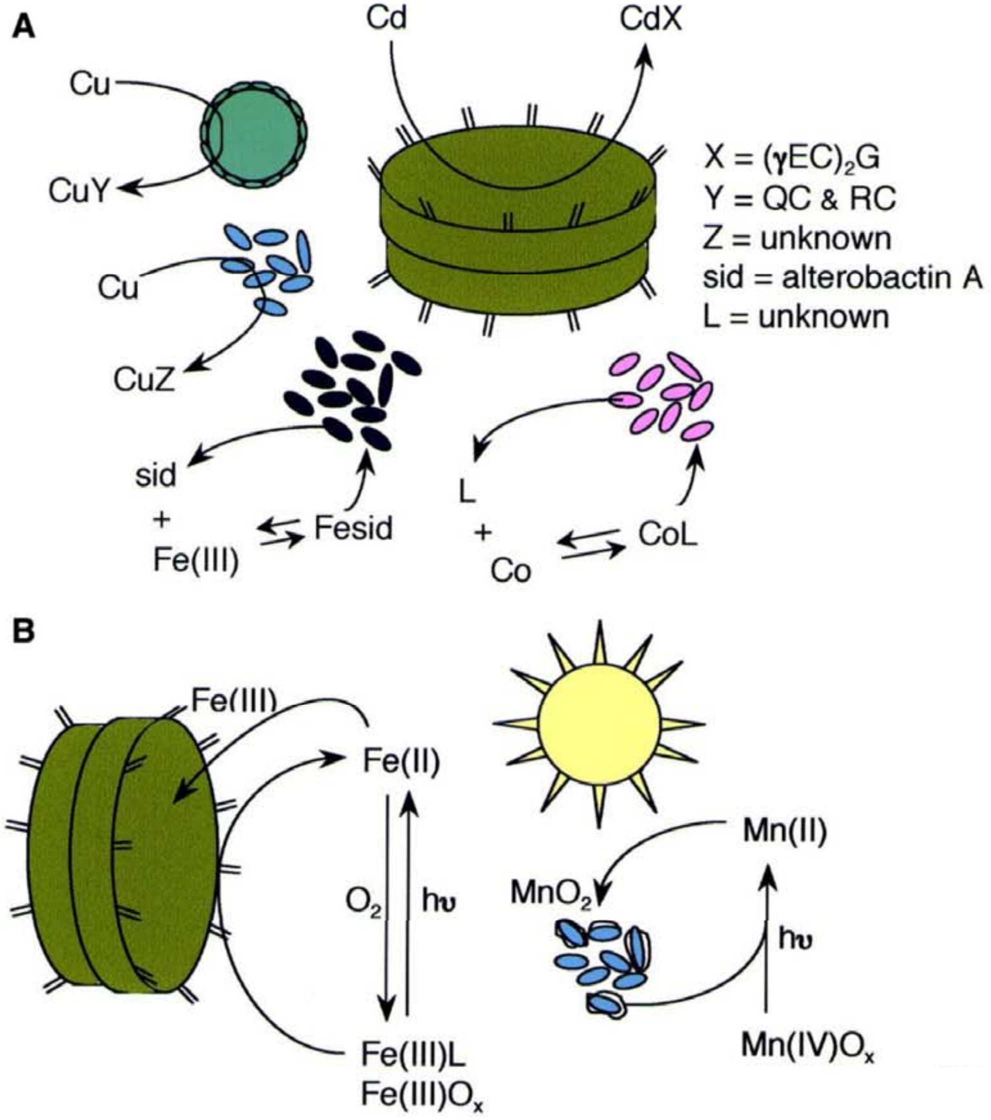


Fig. 2. Vertical profiles of the first-row transition metal ions and selected other elements in the North Pacific Ocean. Speciation is not included. Data compiled by Y. Nozaki (*2*). References for plotted data include: Sc (*40*), Ti (*41*), V (*3*), Cr (*42*), Mn (*43*), Fe (*44*), Co (*44*), Ni (*45*),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

From: A. Butler, 1998 Acquisition and Utilization of Transition Metal Ions by Marine Organisms, Science, 281, 207- 210

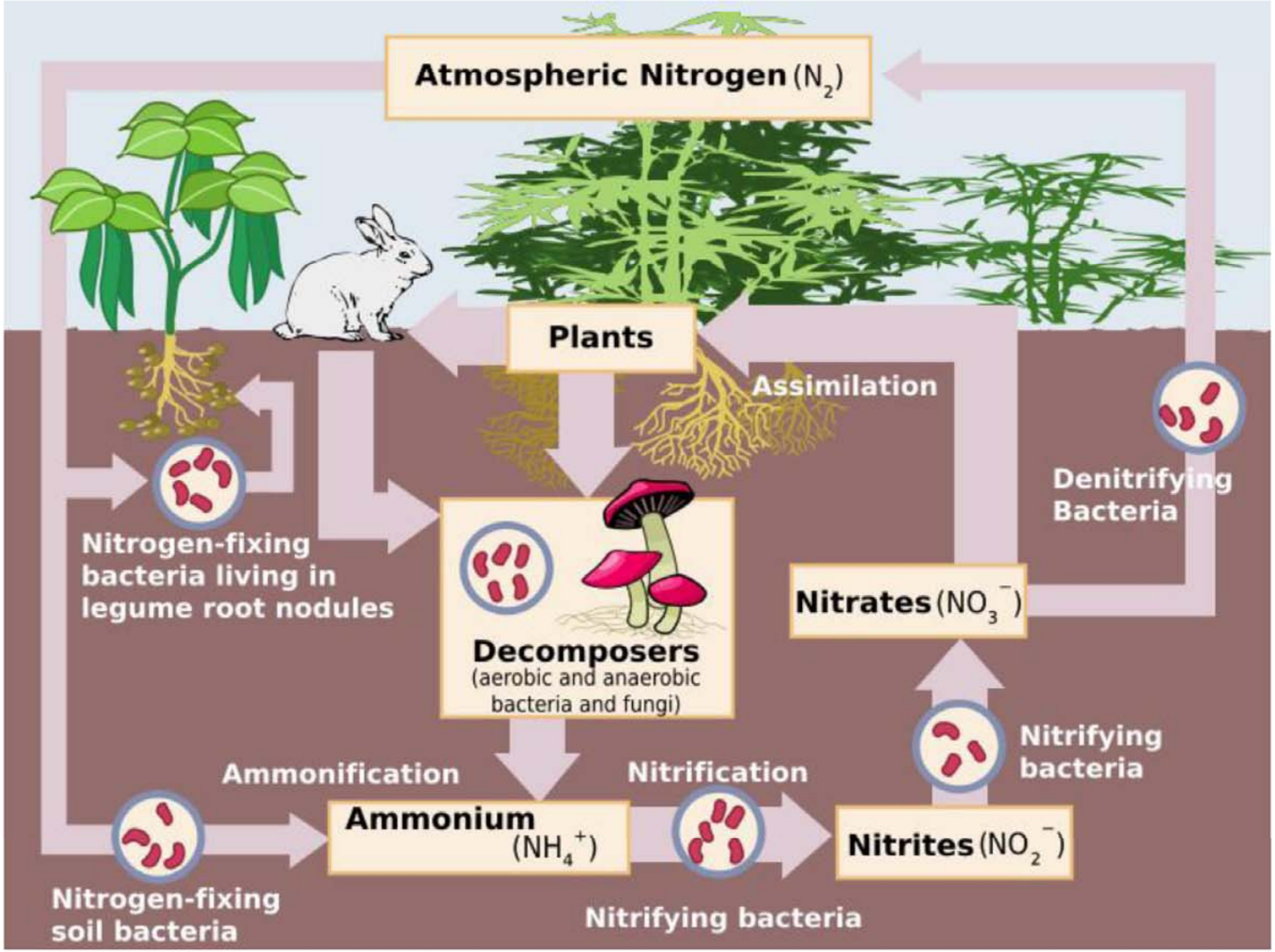
(A) Release of complexing agents and metal ligand complexes from marine plankton: CdX, phytochelatin-Cd complex released by diatoms; CuY, peptide complexes of Cu released by coccolithophorids; CuZ, unidentified Cu ligand complex released by Synechococcus; sid, siderophore released by heterotrophic bacteria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



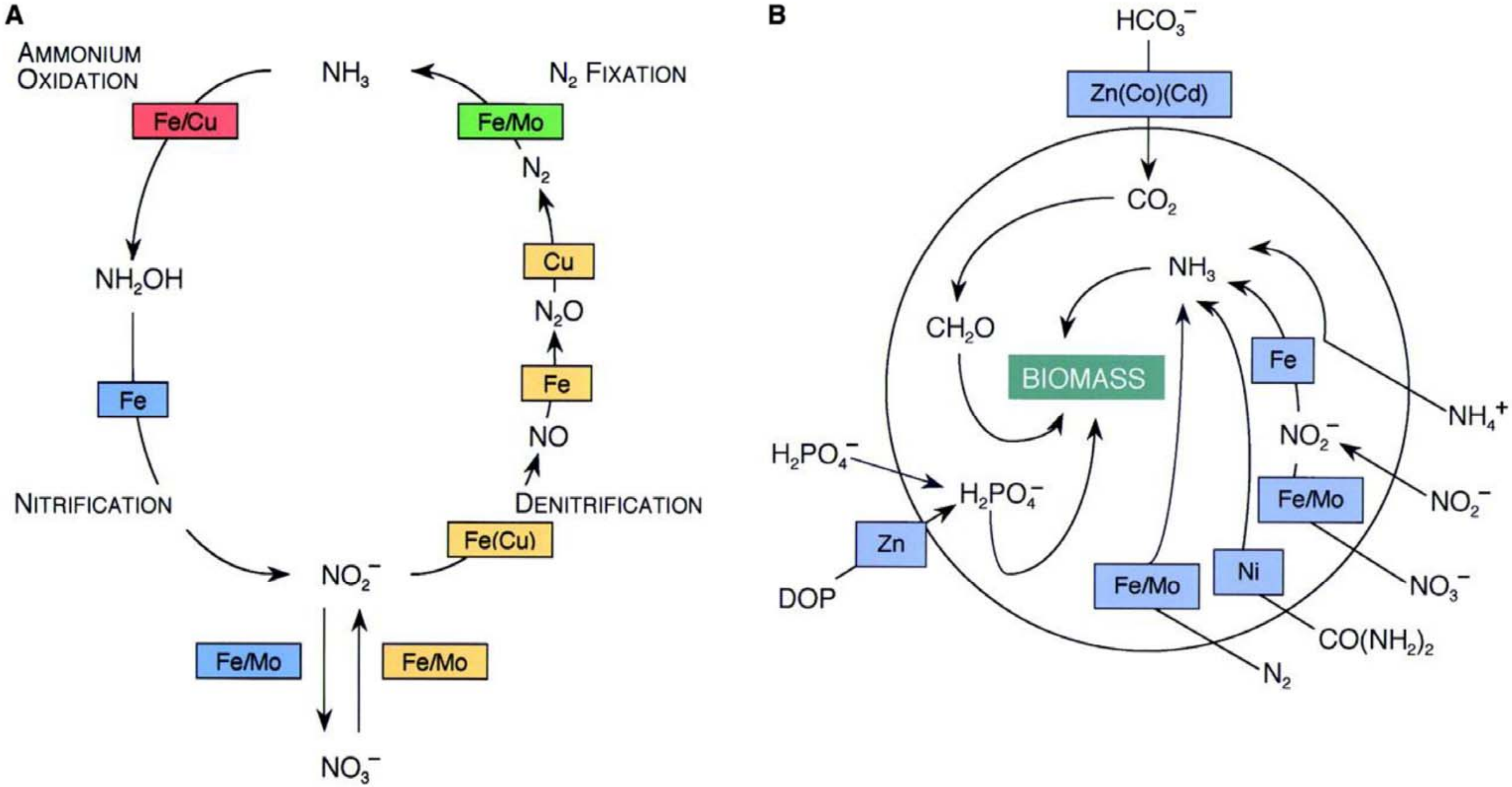
F M M Morel, N M Price Science 2003, 300,44-947

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, <u>300</u>, 944-947

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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	Cu	Mo/V
- Nitrate Reductase		- Nitrate Reductase
- Nitrite Reductase	- Nitrite Reductase	
- NO Reductase		
	- N_2O Reductase	
- Nitrogenase		- Nitrogenase
	- Ammonia Mono-oxygenase	
- Hydroxylamine Oxidoreductase		

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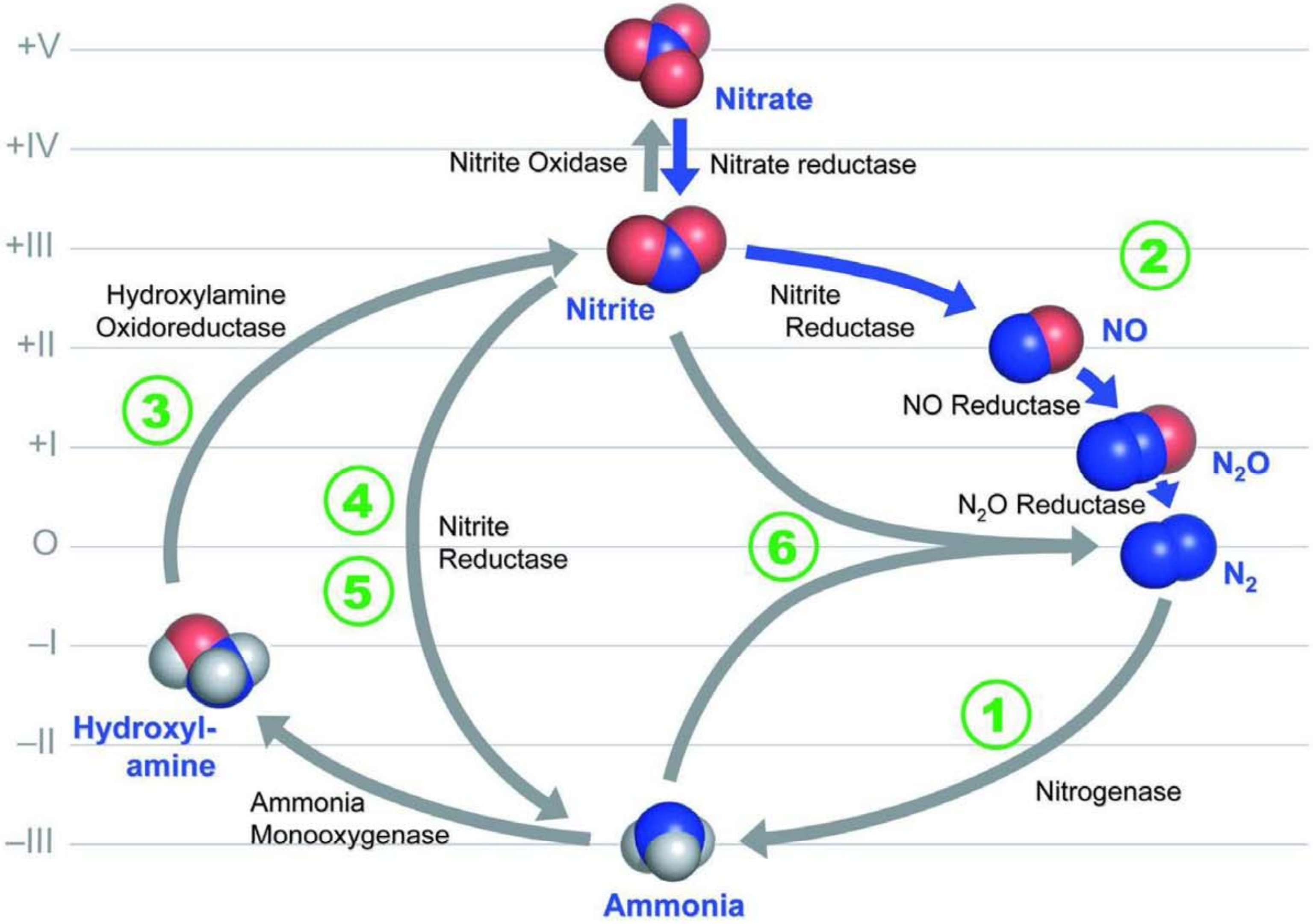
Important Reactions and Metal Enzymes of the Nitrogen Cycle



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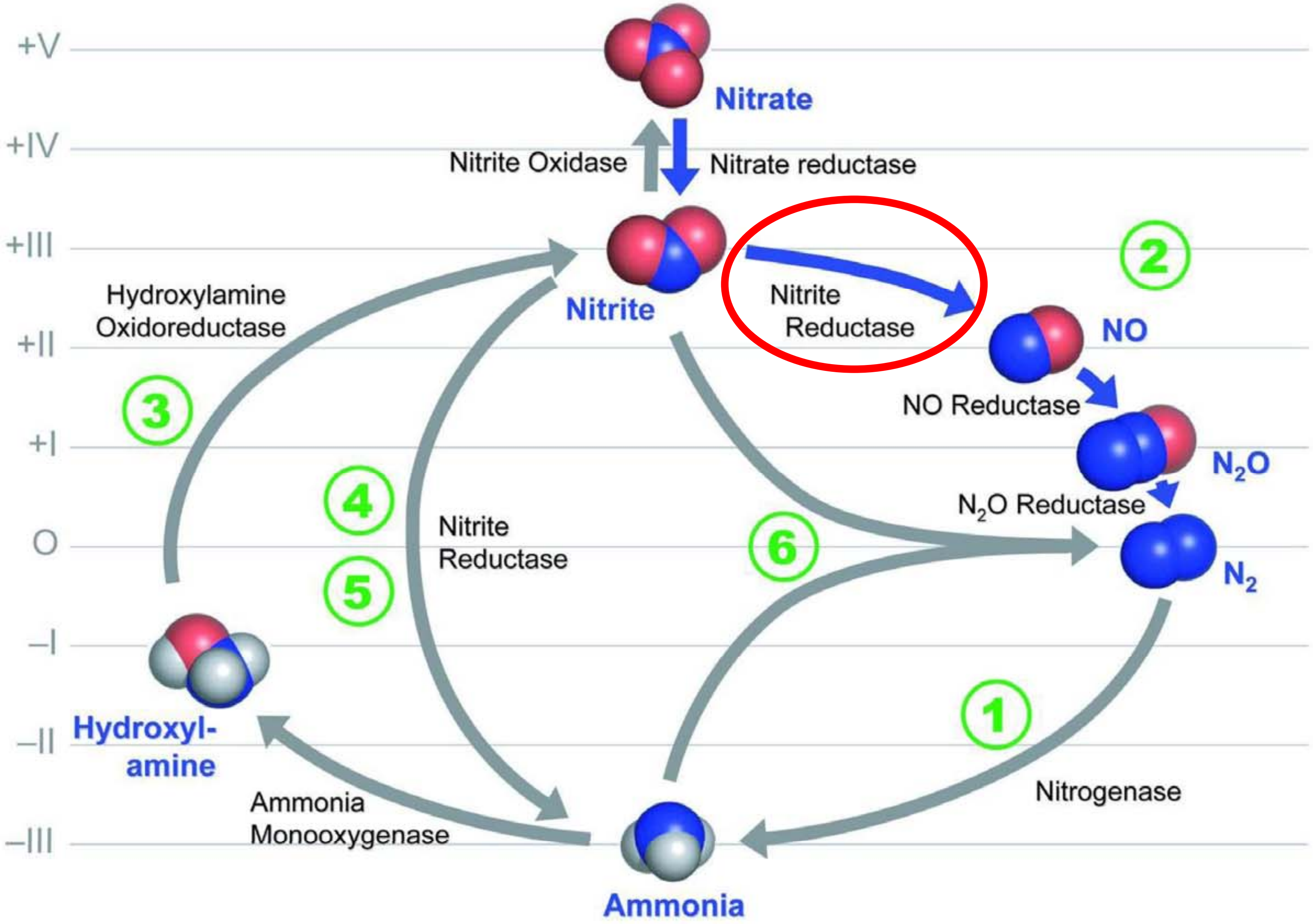
Important Reactions and Metal Enzymes of the Nitrogen Cycle



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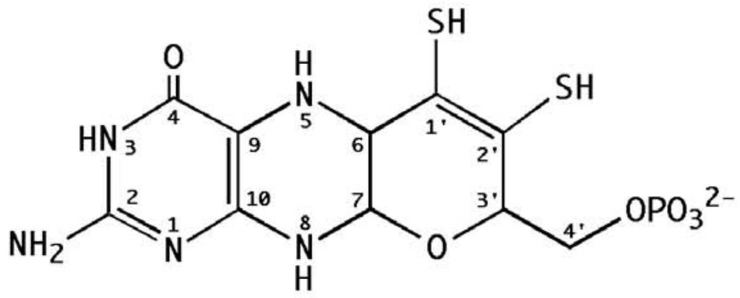
Nitrate Reductase

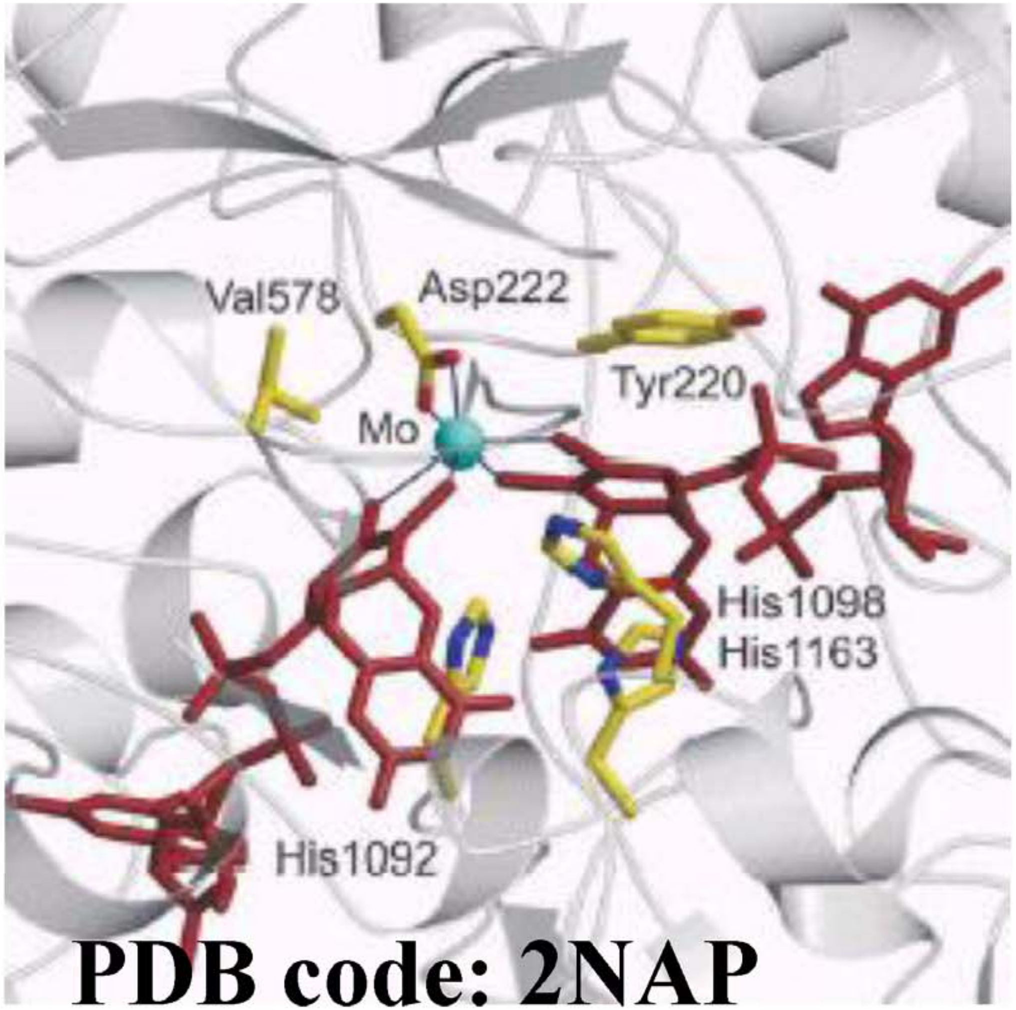
$$NO_3^- + 2H^+ + 2e^- \longrightarrow NO_2^- + H_2O$$

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)





PDB code: 2NAP

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

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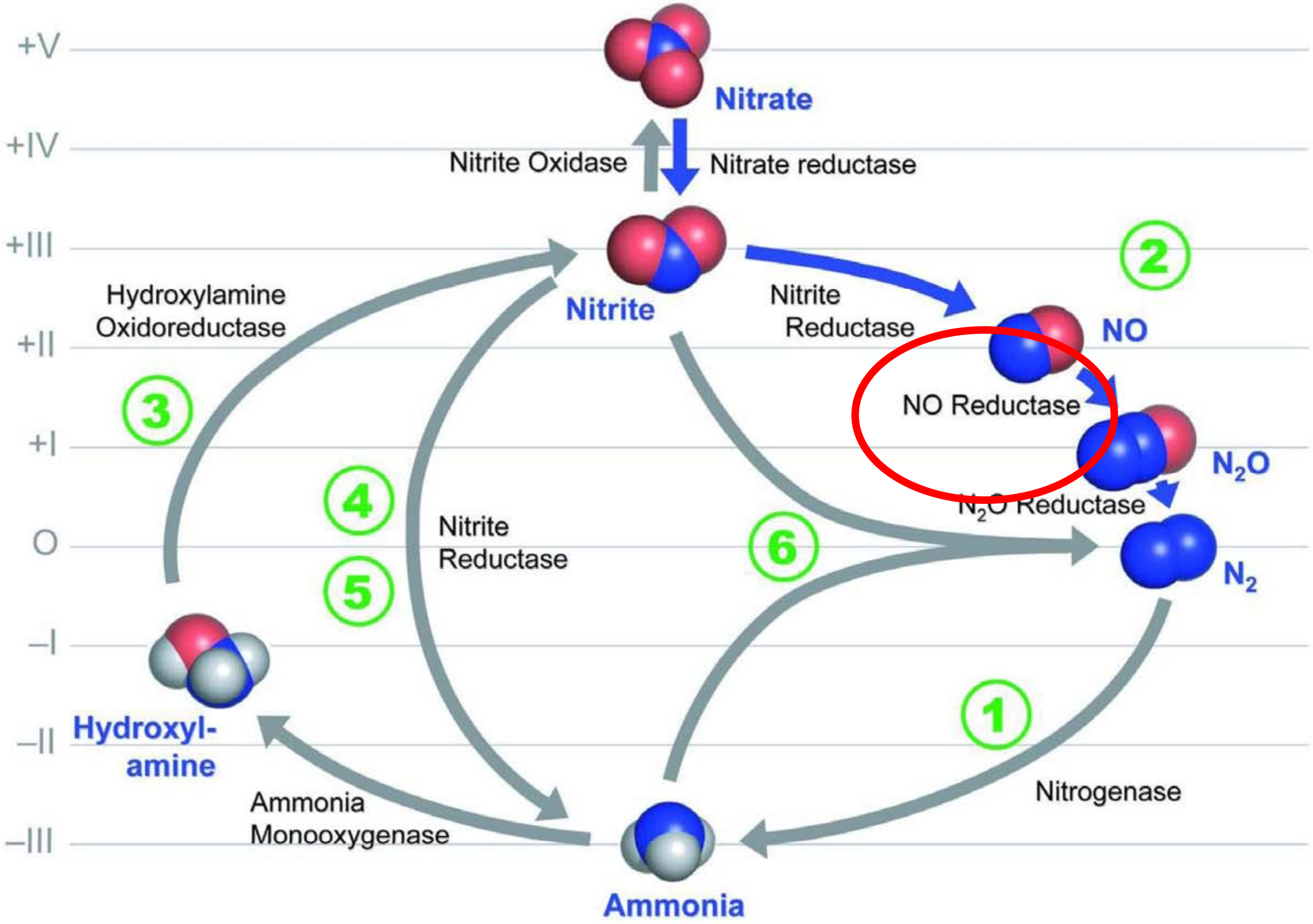
Important Reactions and Metal Enzymes of the Nitrogen Cycle



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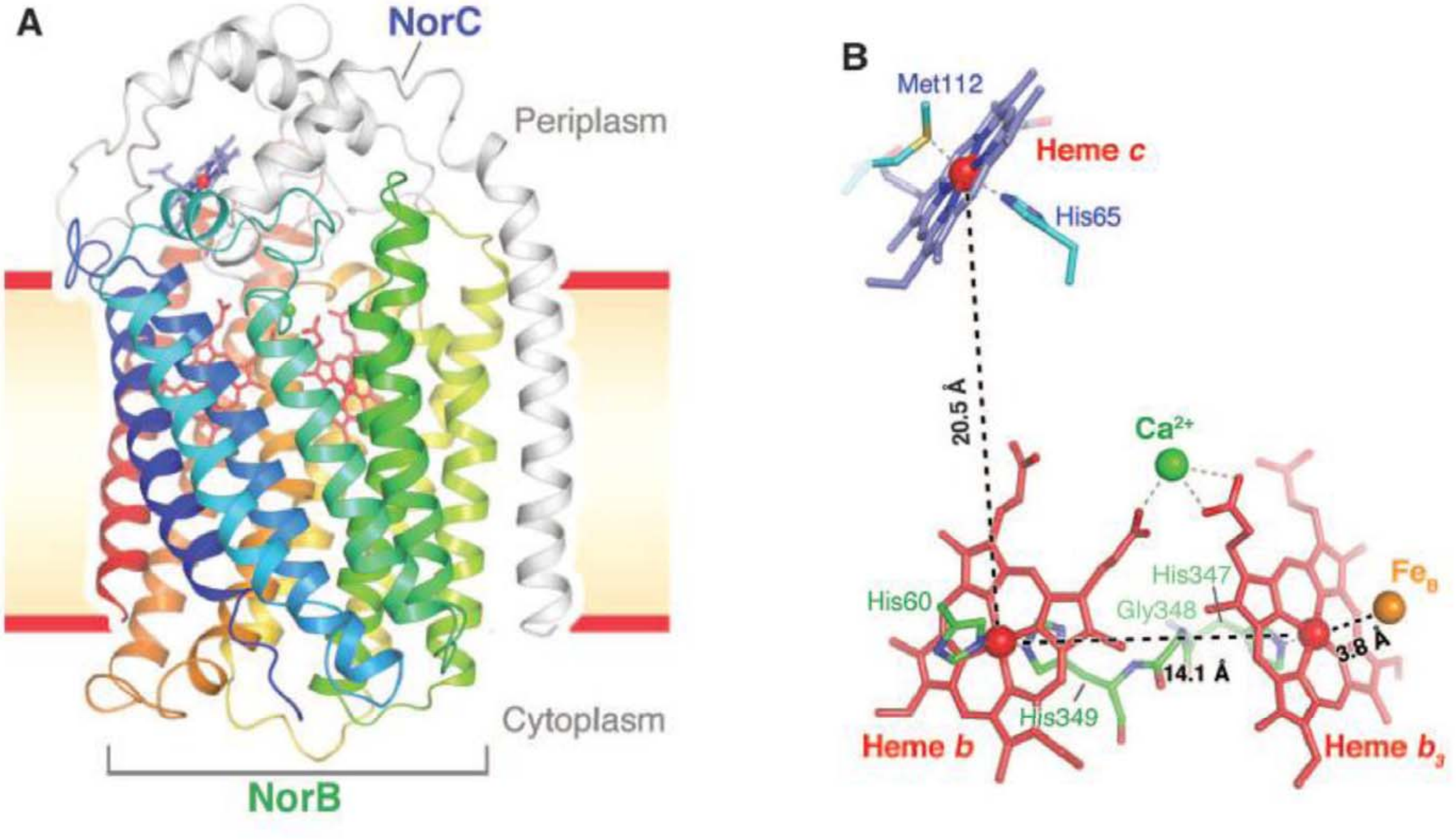
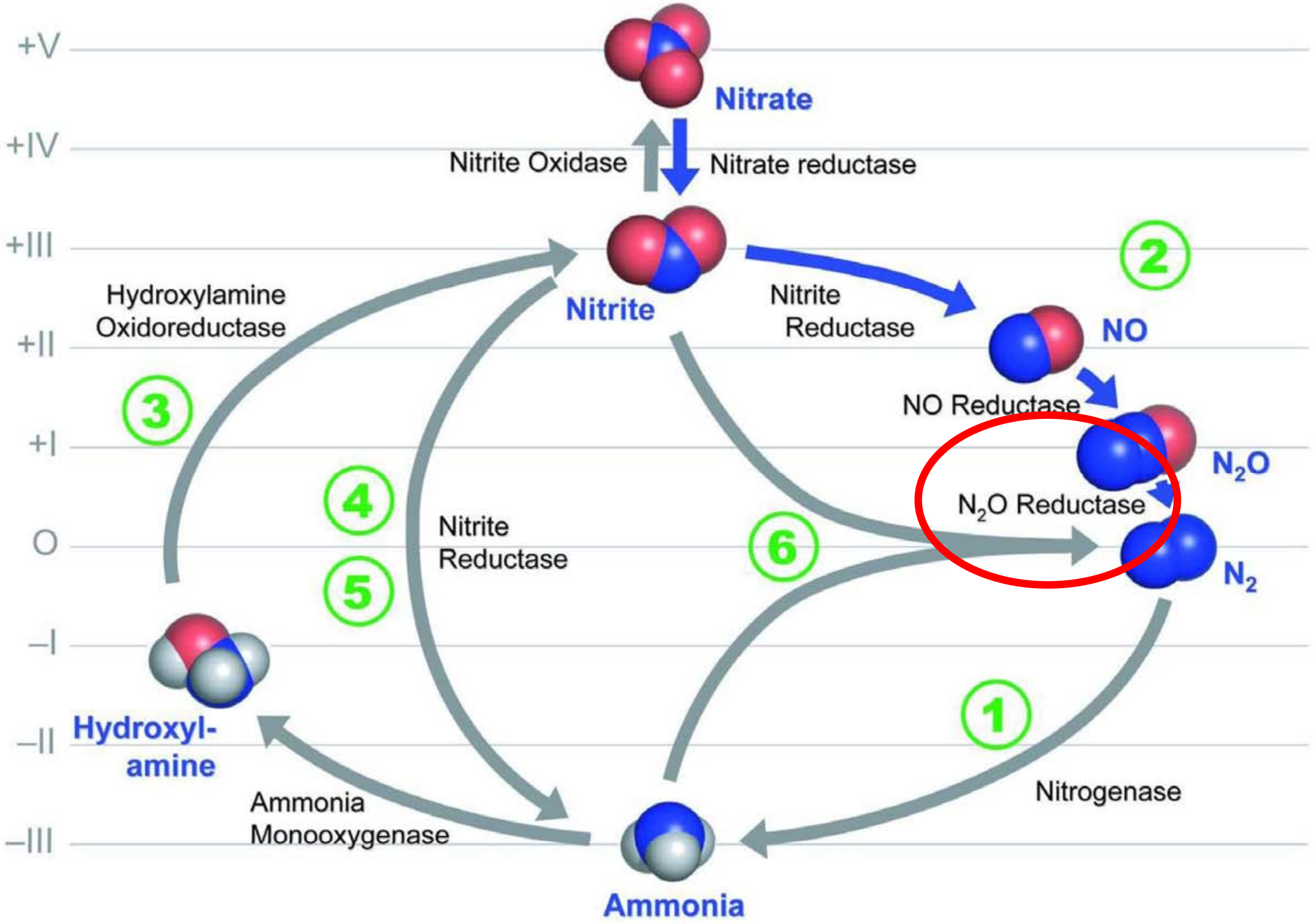
NO Reductase (NOR)

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



Important Reactions and Metal Enzymes of the Nitrogen Cycle



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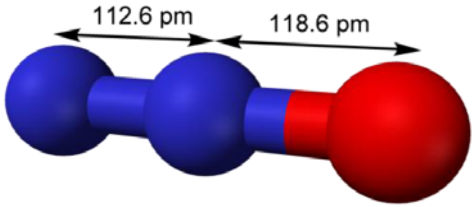
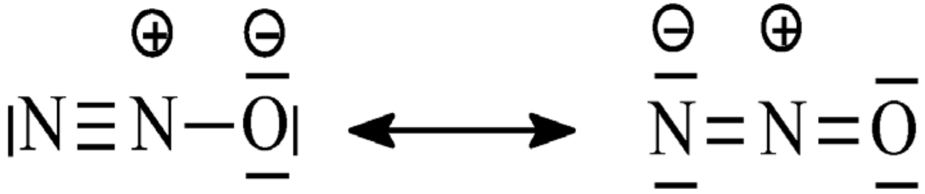
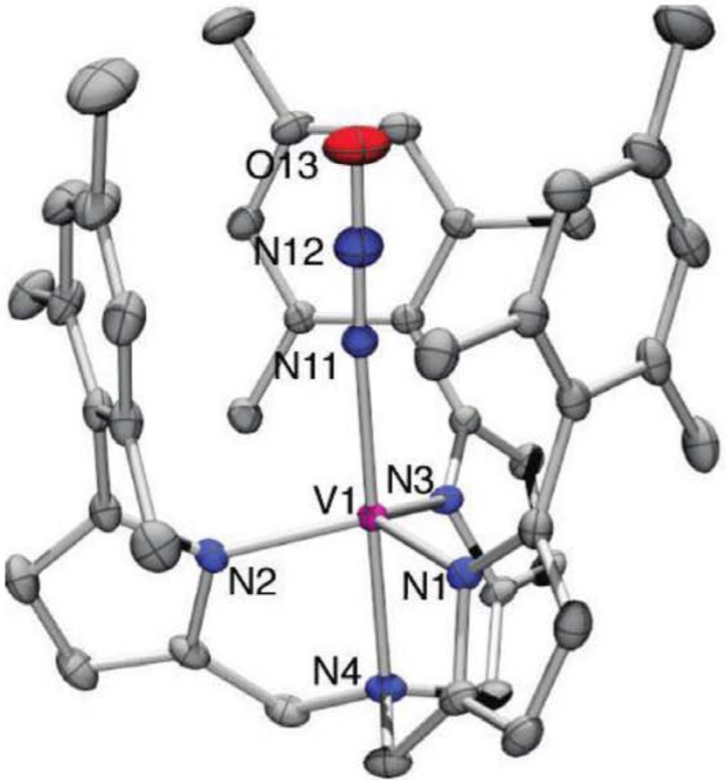
Nitrous Oxide – Dinitrogen Monoxide
Laughing Gas – Sweet Air





$$|N\equiv\overset{\oplus}{N}-\overset{\ominus}{\underline{\overline{O}}}| \longleftrightarrow \overset{\ominus}{\underline{\overline{N}}}=\overset{\oplus}{N}=\underline{\overline{O}}$$

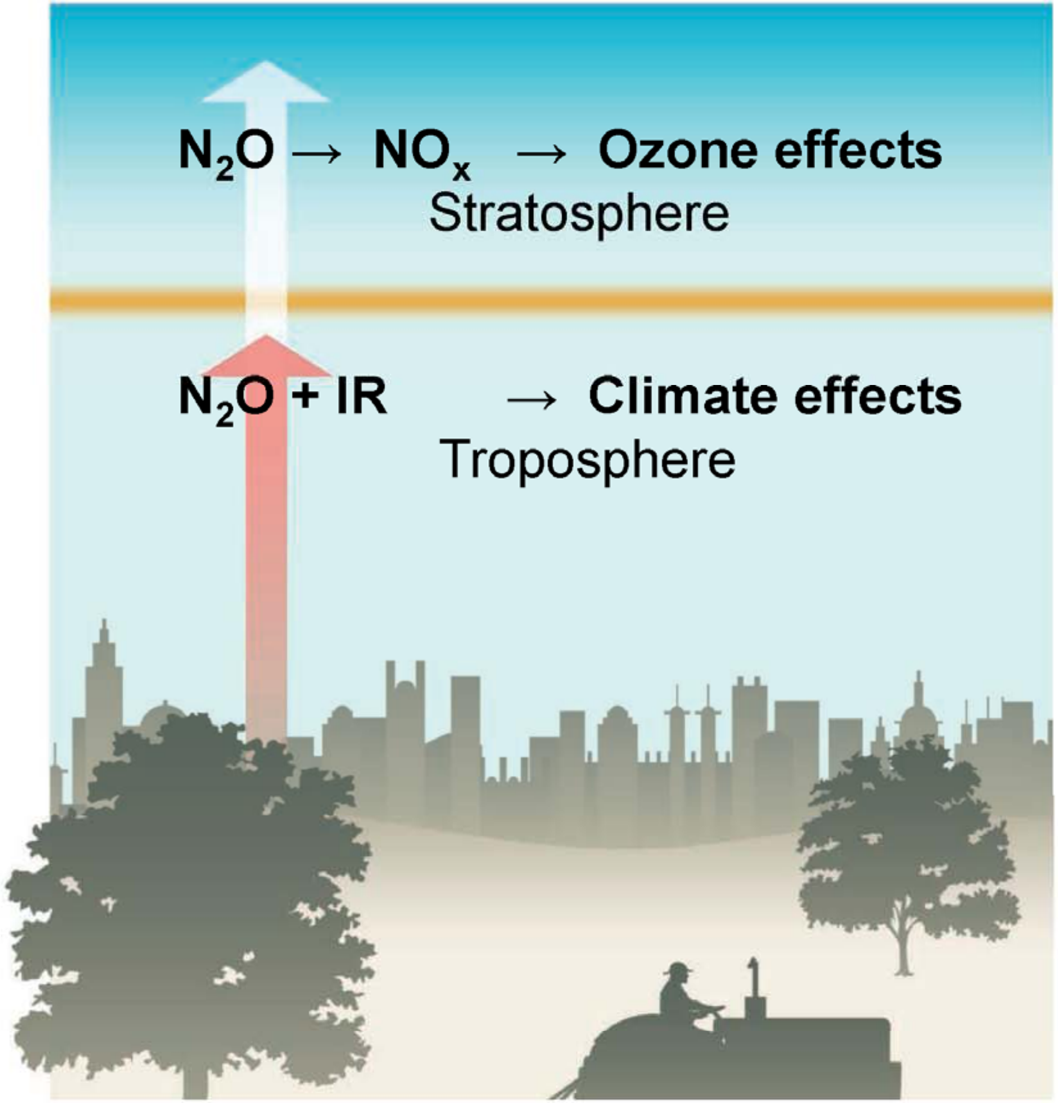


A Structurally Characterized Nitrous Oxide Complex of Vanadium

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

N_2O – A Potent Greenhouse Gas

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



$N_2O \rightarrow NO_x \rightarrow$ Ozone effects

Stratosphere

N_2O + IR $\rightarrow$ Climate effects

Troposphere

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

MENACING GAS

Agriculture is the primary source of N_2O emissions worldwide

THOUSANDS OF METRIC TONS	**N_2O 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

Bacterial Nitrous Oxide Reductase is a purple Copper Enzyme

$$N_2O + 2H^+ + 2e^- \rightarrow N_2 + H_2O$$

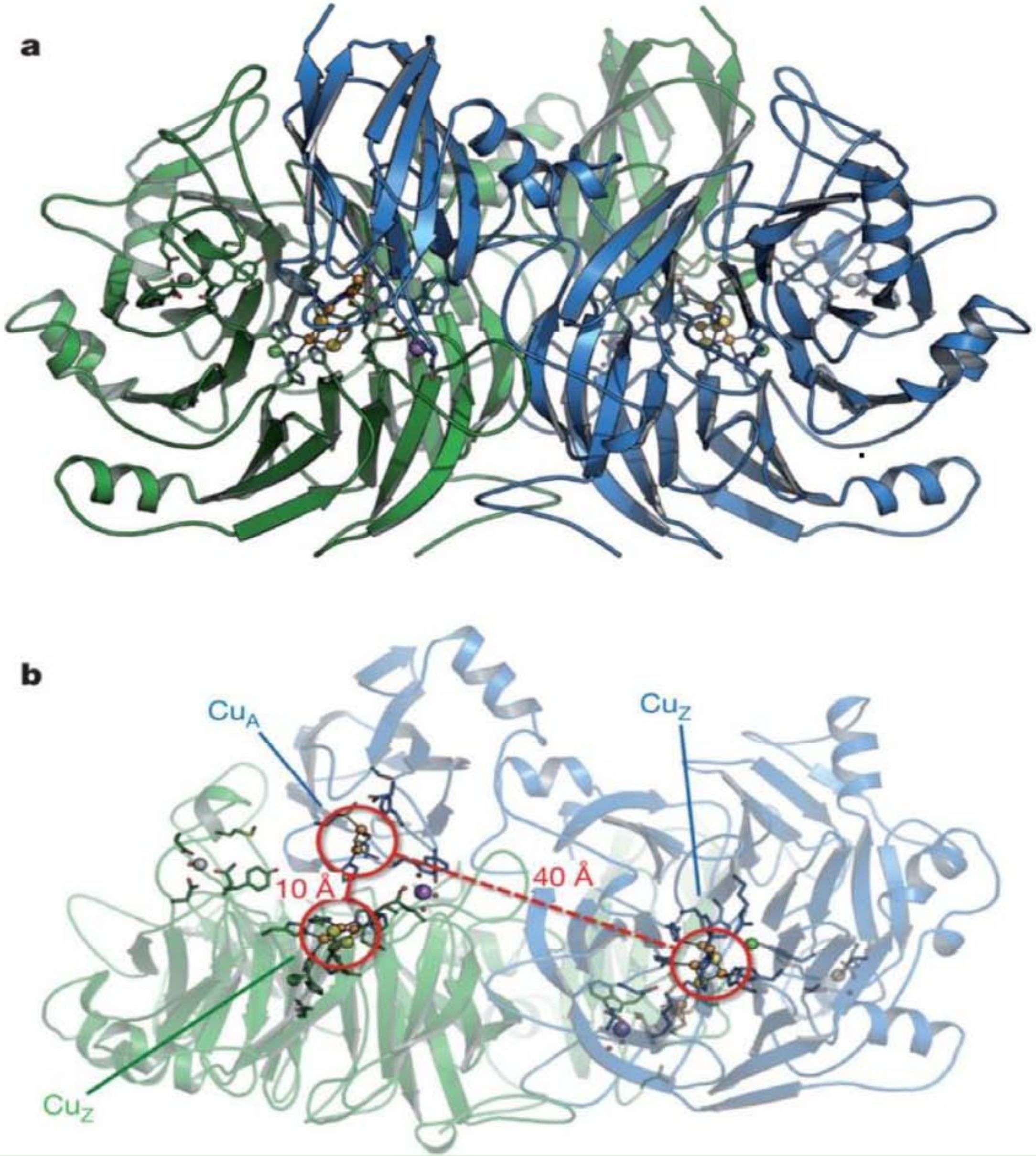
$$E'_o = +1.35\ V$$

kinetically inert molecule

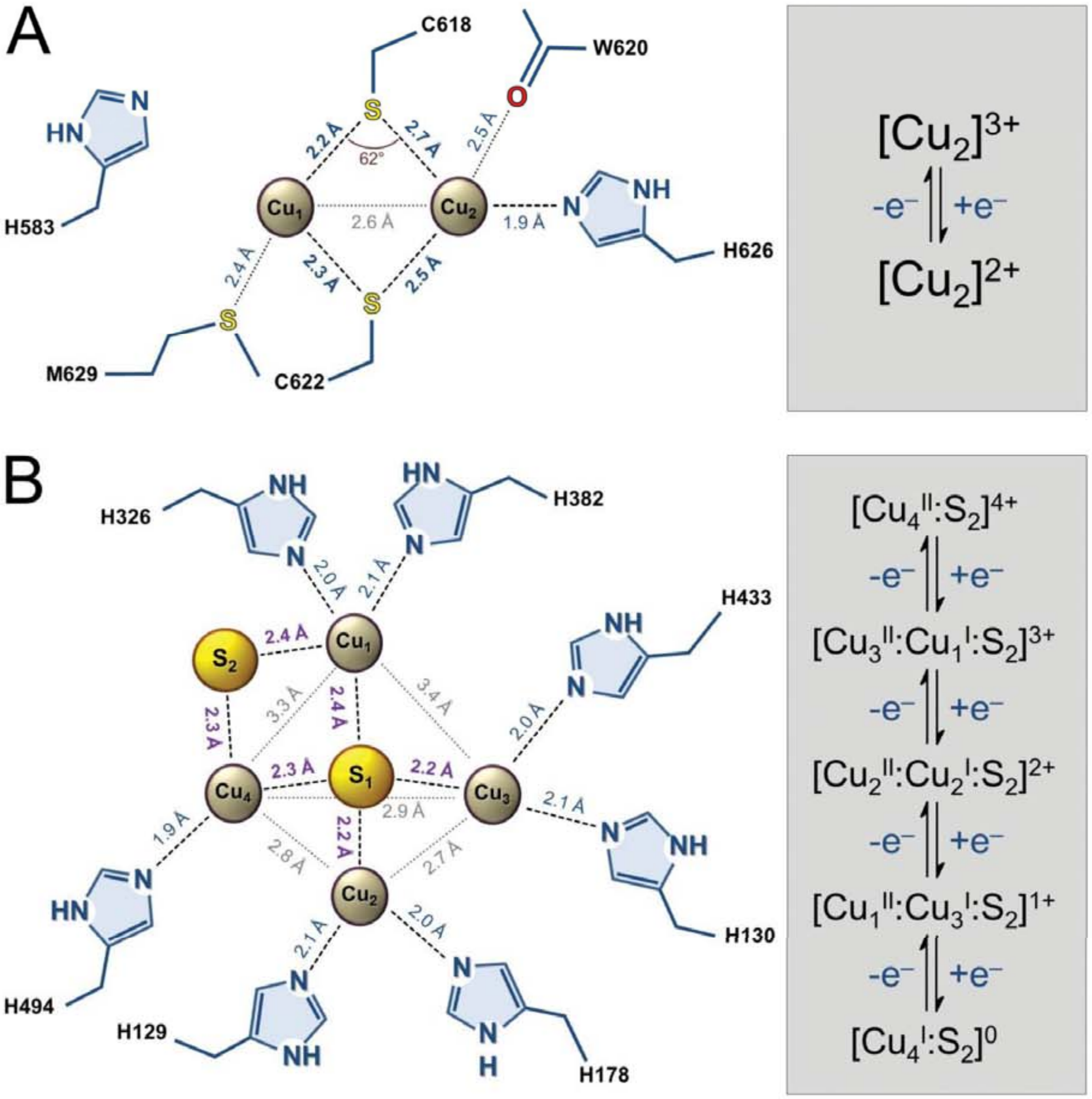
~ 59 kcal/mol activation barrier

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



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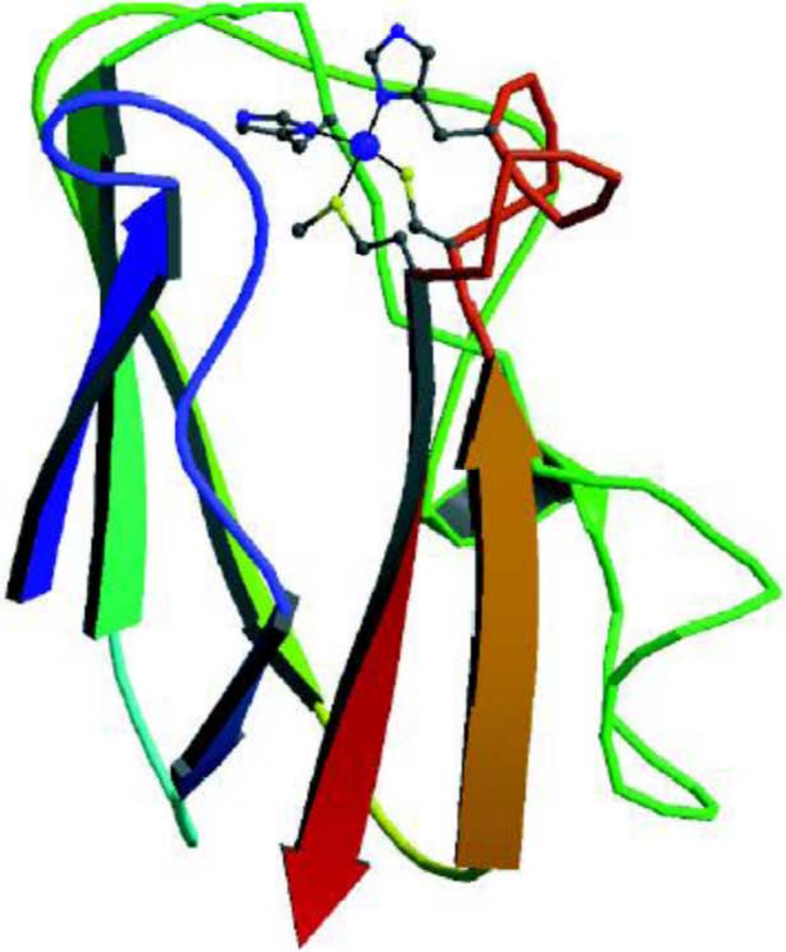
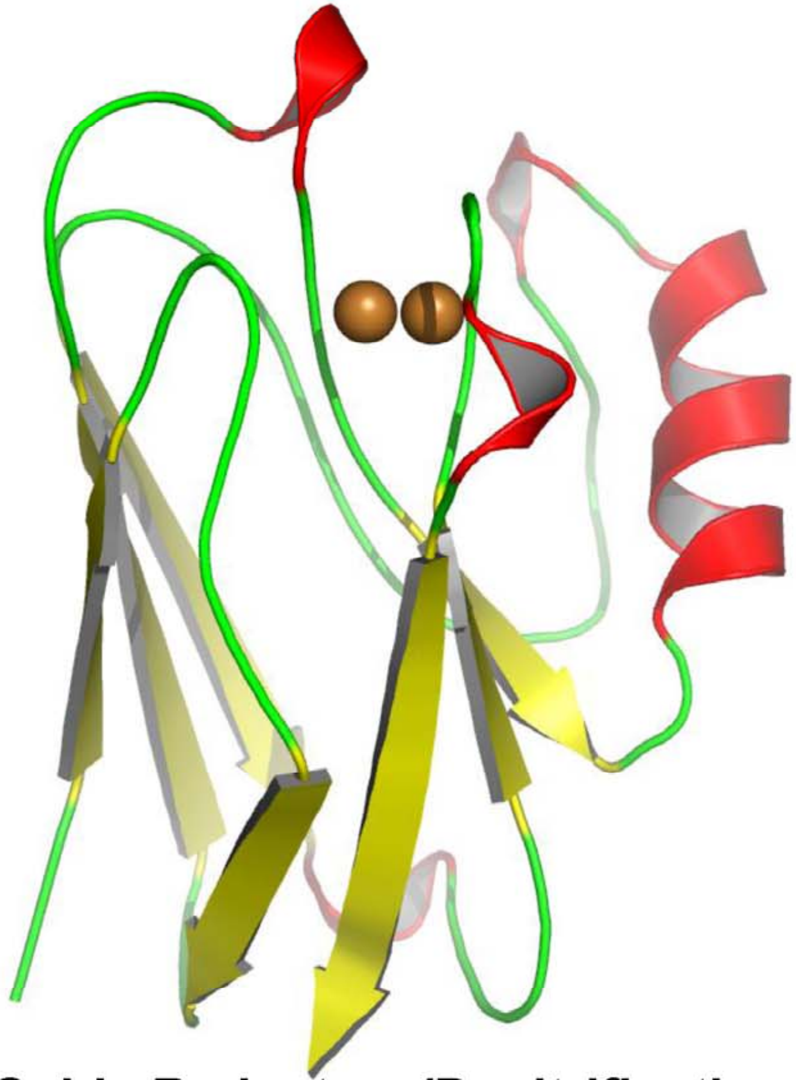
Evolution and Bioengineering through Loop directed Mutagenesis From a Blue Mononuclear Cu to a Purple Dinuclear CuA

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

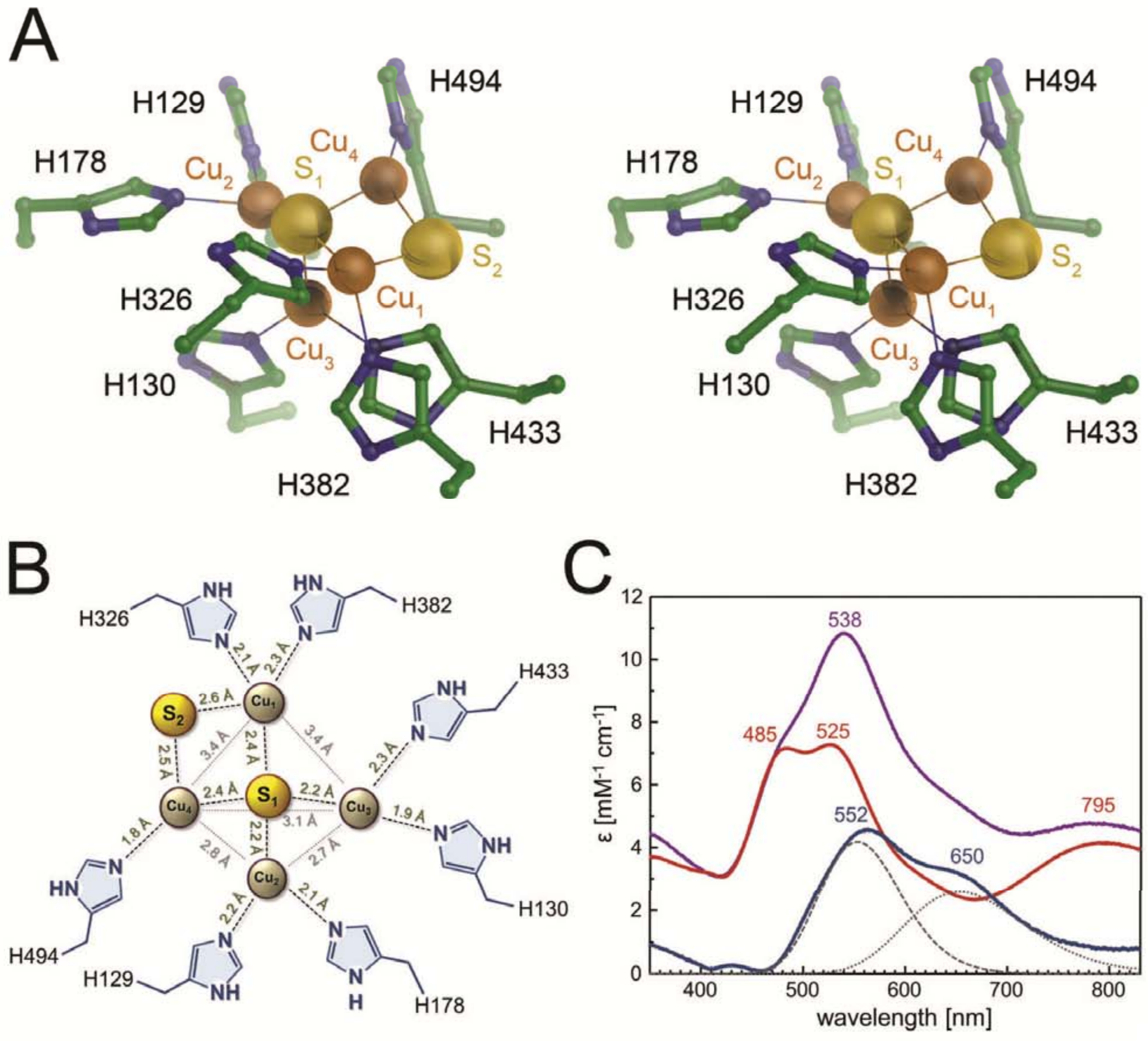


Plastocyanin/Photosynthesis

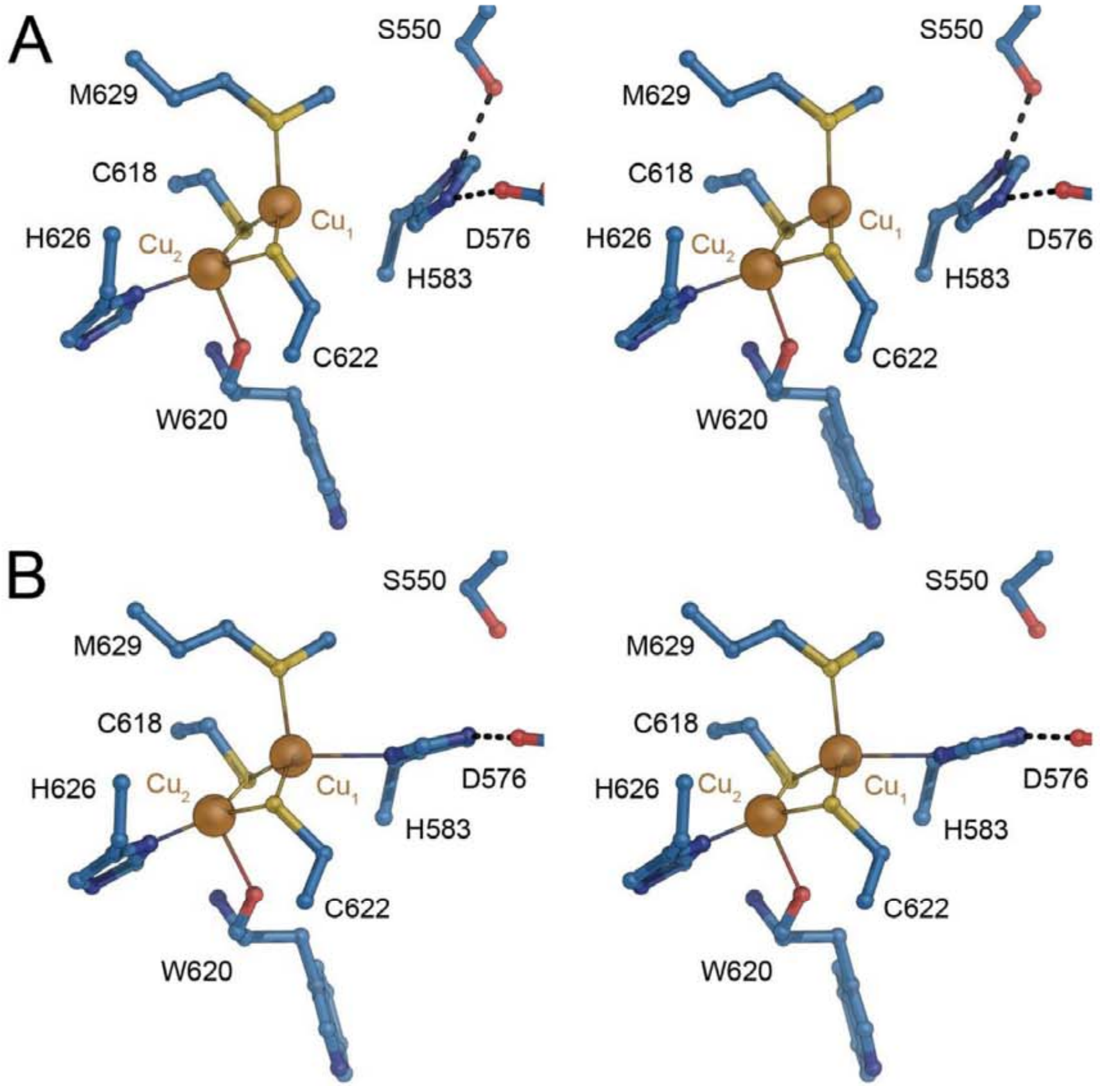


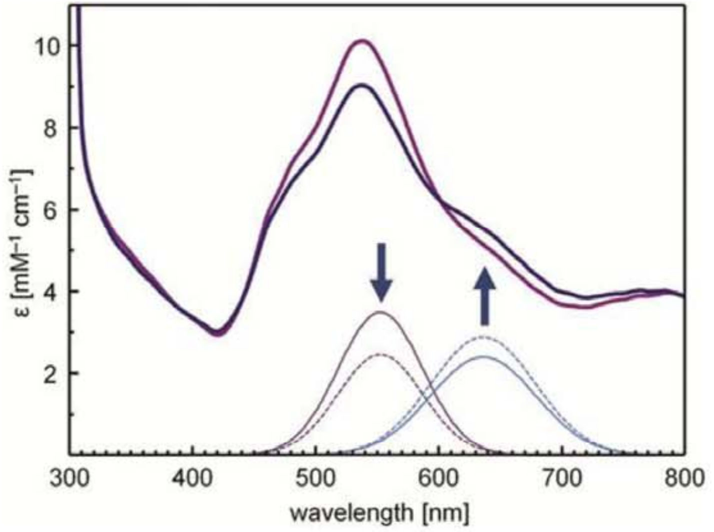
Nitrous Oxide Reductase/Denitrification
Cytochrome *c* Oxidase/Respiration

When prepared/crystallized under the strict exclusion of O_2, CuZ is a Cu_4S_2 Cluster



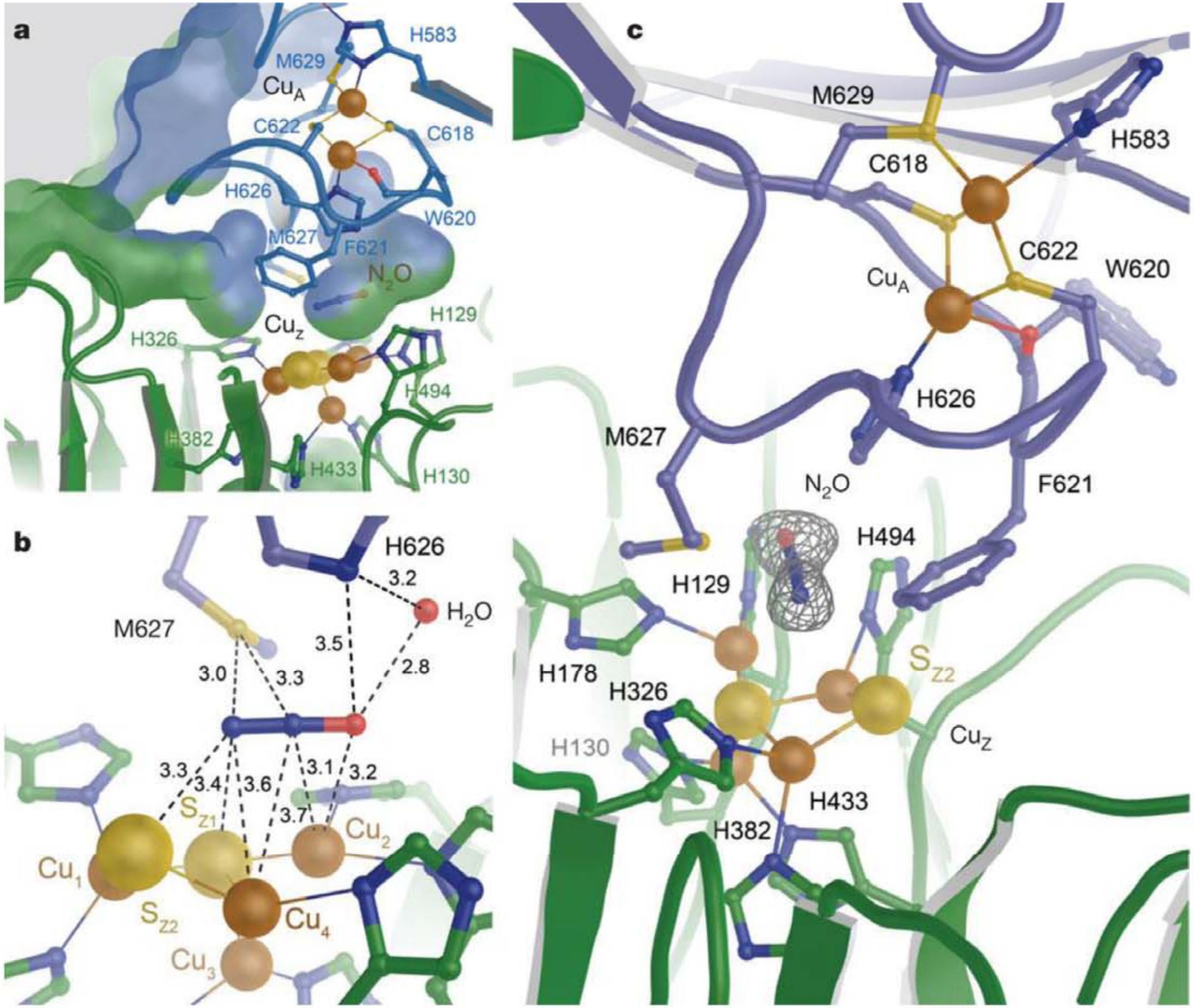
Upon binding of N_2O (Xtal under N_2O pressure) the ligands of CuA rearrange and His 583 flips to ligate Cu1 of CuA



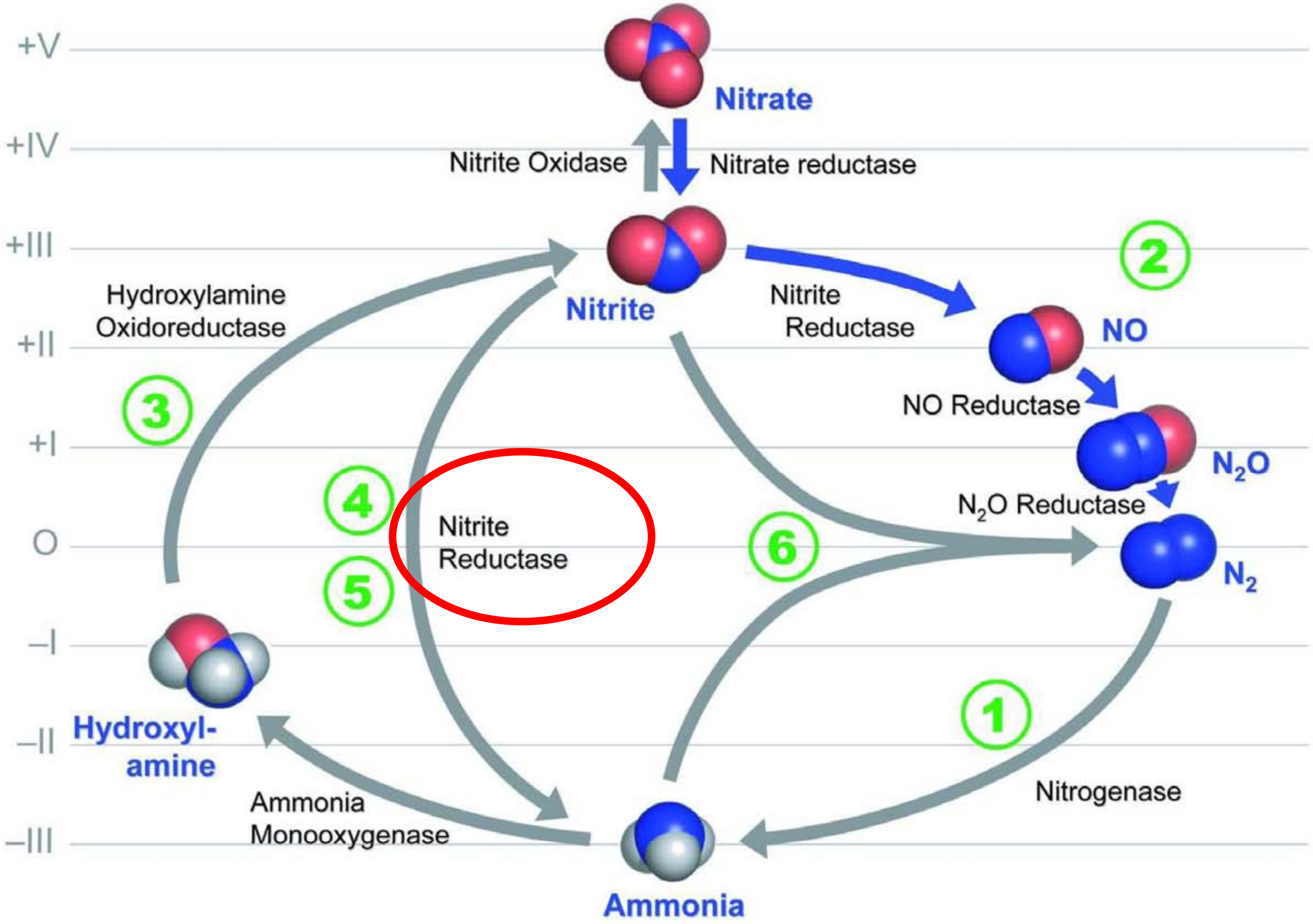


Catalysis: CuA and CuZ operate *in concert*

Xtal under N_2O pressure



Important Reactions and Metal Enzymes of the Nitrogen Cycle



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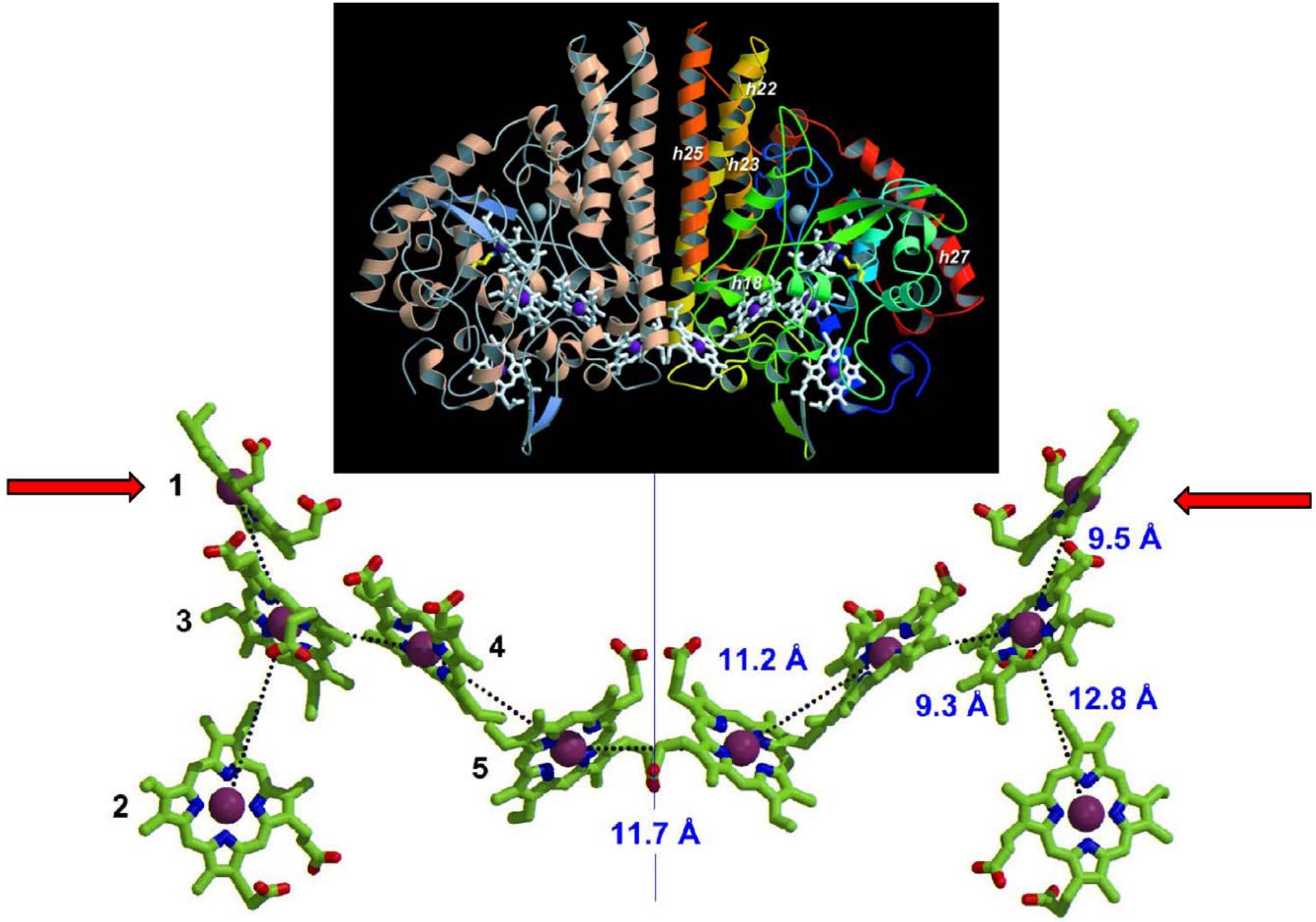
Dissimilatory Nitrite Reductase

$$NO_2^- + 8H^+ + 6e^- \longrightarrow NH_4^+ + 2H_2O$$

Cytochrome *c* Nitrite Reductase

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



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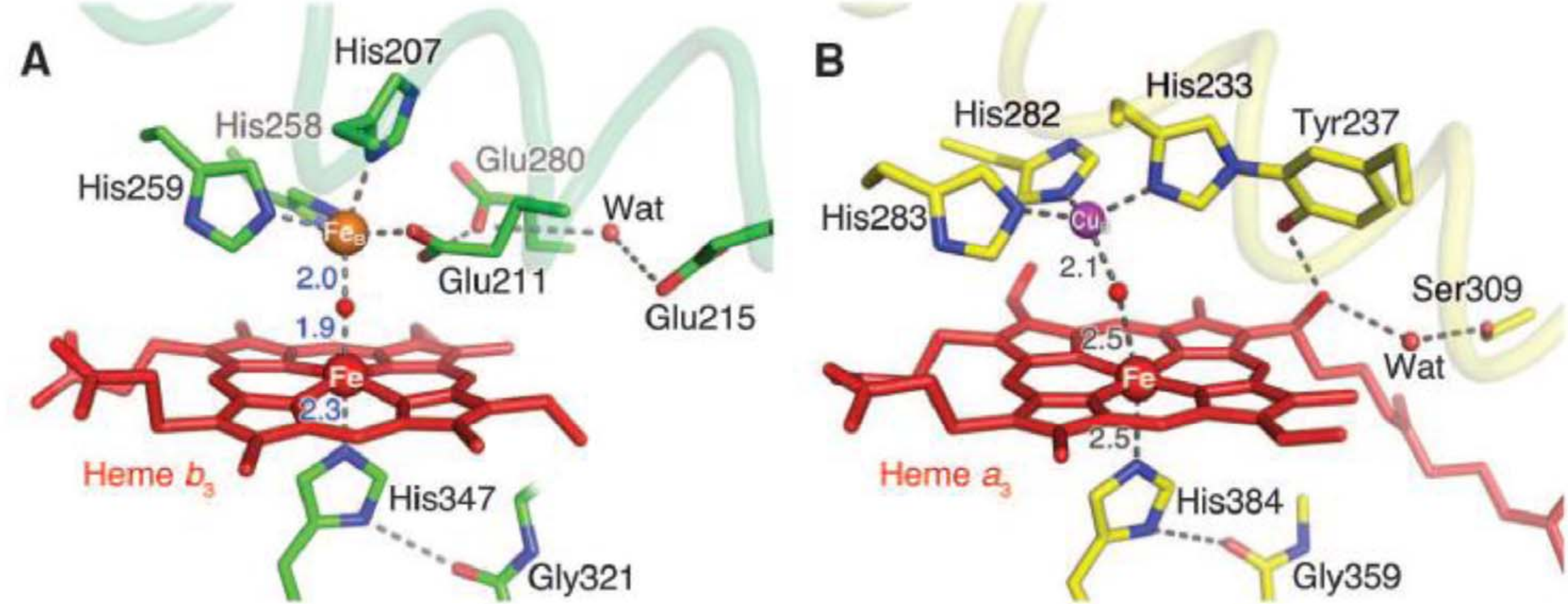
Active Sites of NOR (A) and COX (B)



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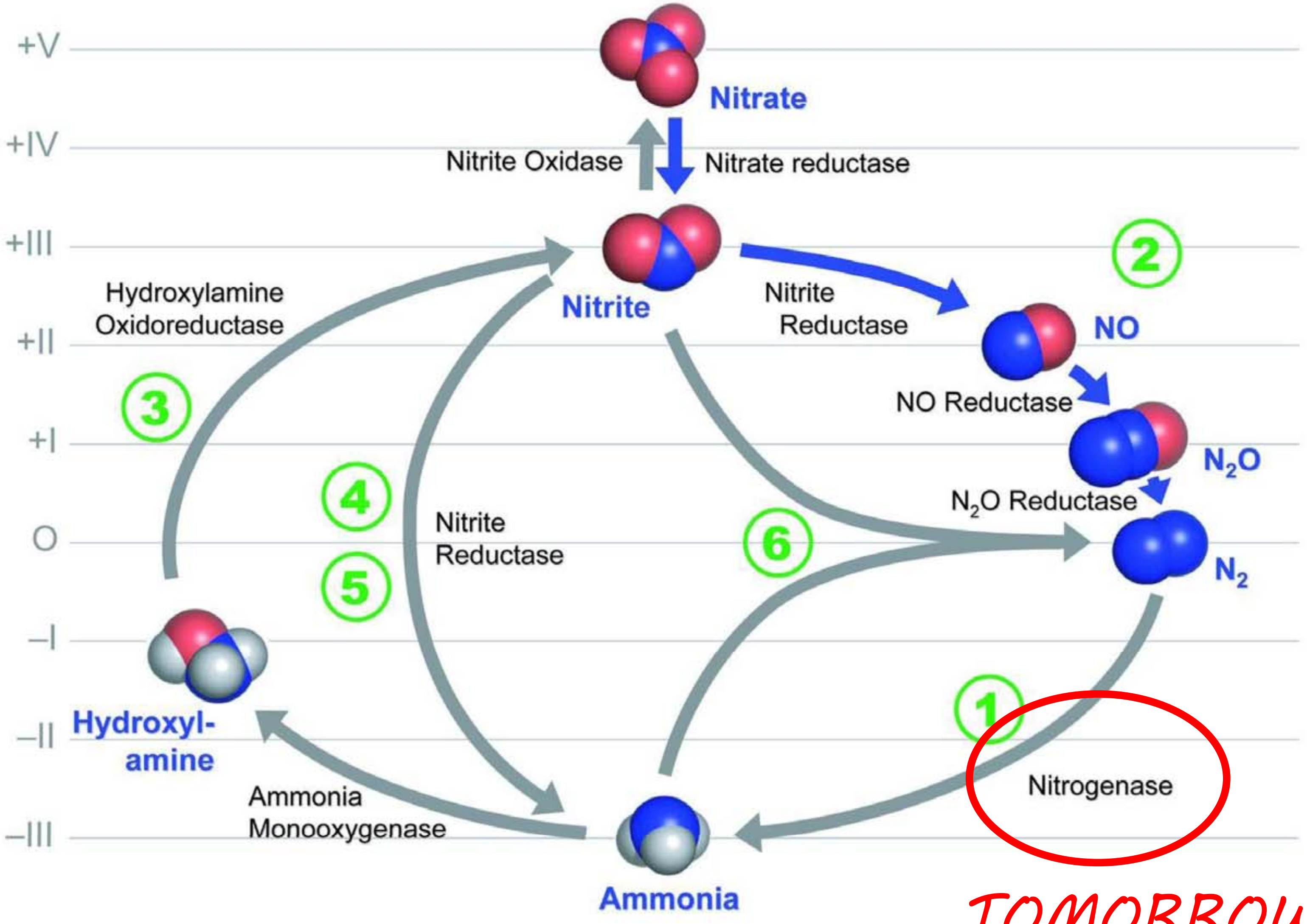
Important Reactions and Metal Enzymes of the Nitrogen Cycle



TOMORROW…

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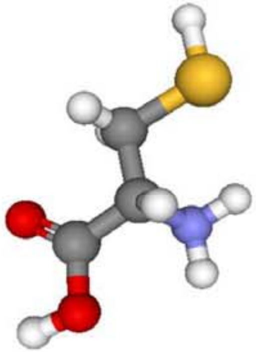
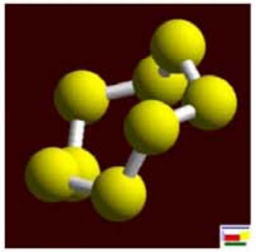
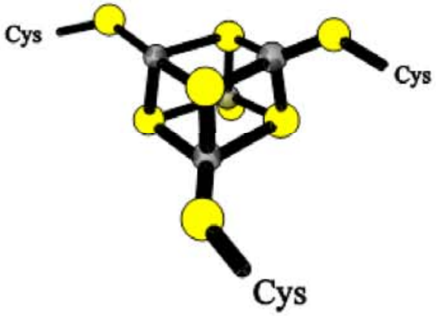
The Biogeochemical Cycle of Sulfur

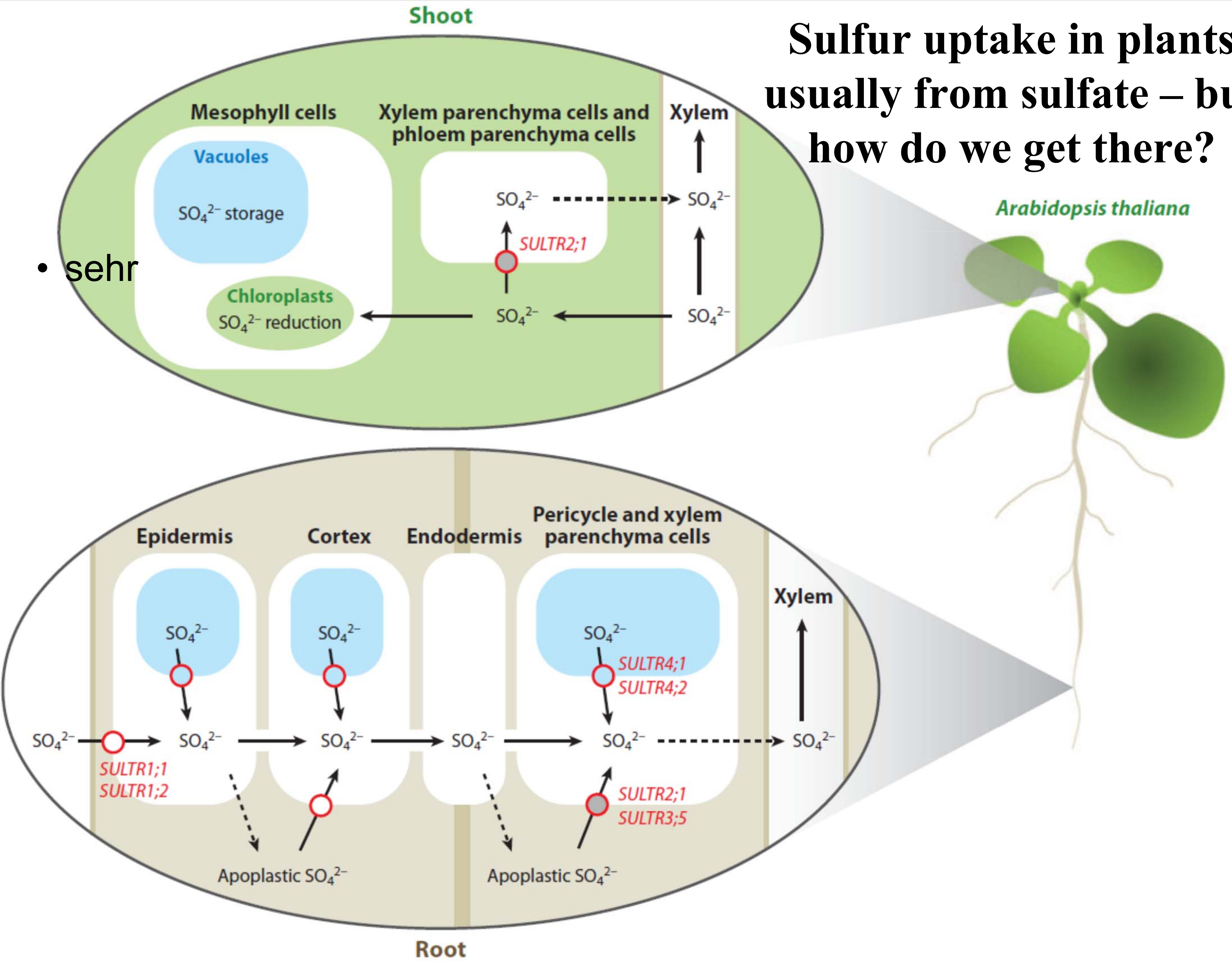






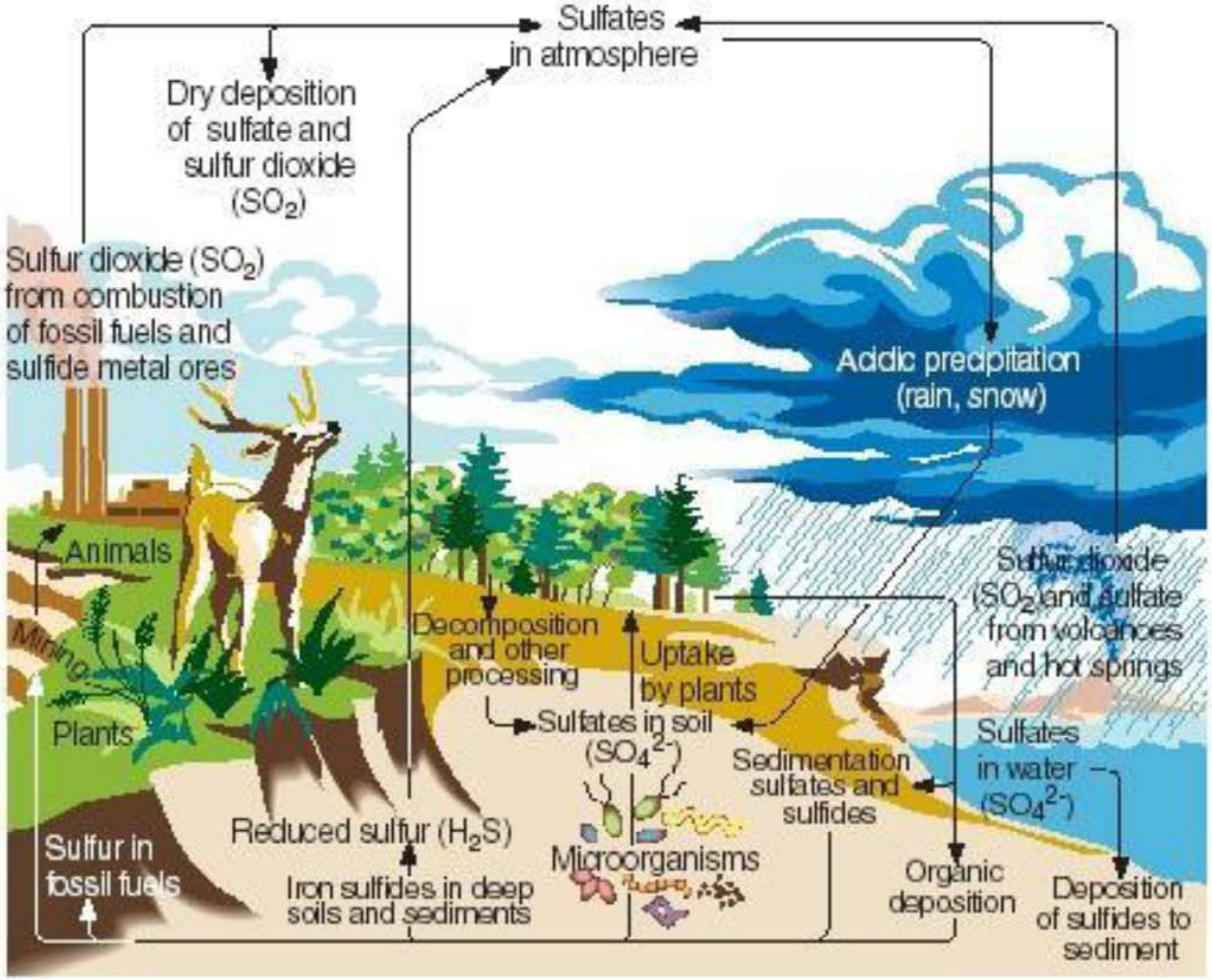
Sulfur uptake in plants usually from sulfate – but how do we get there?

- sehr



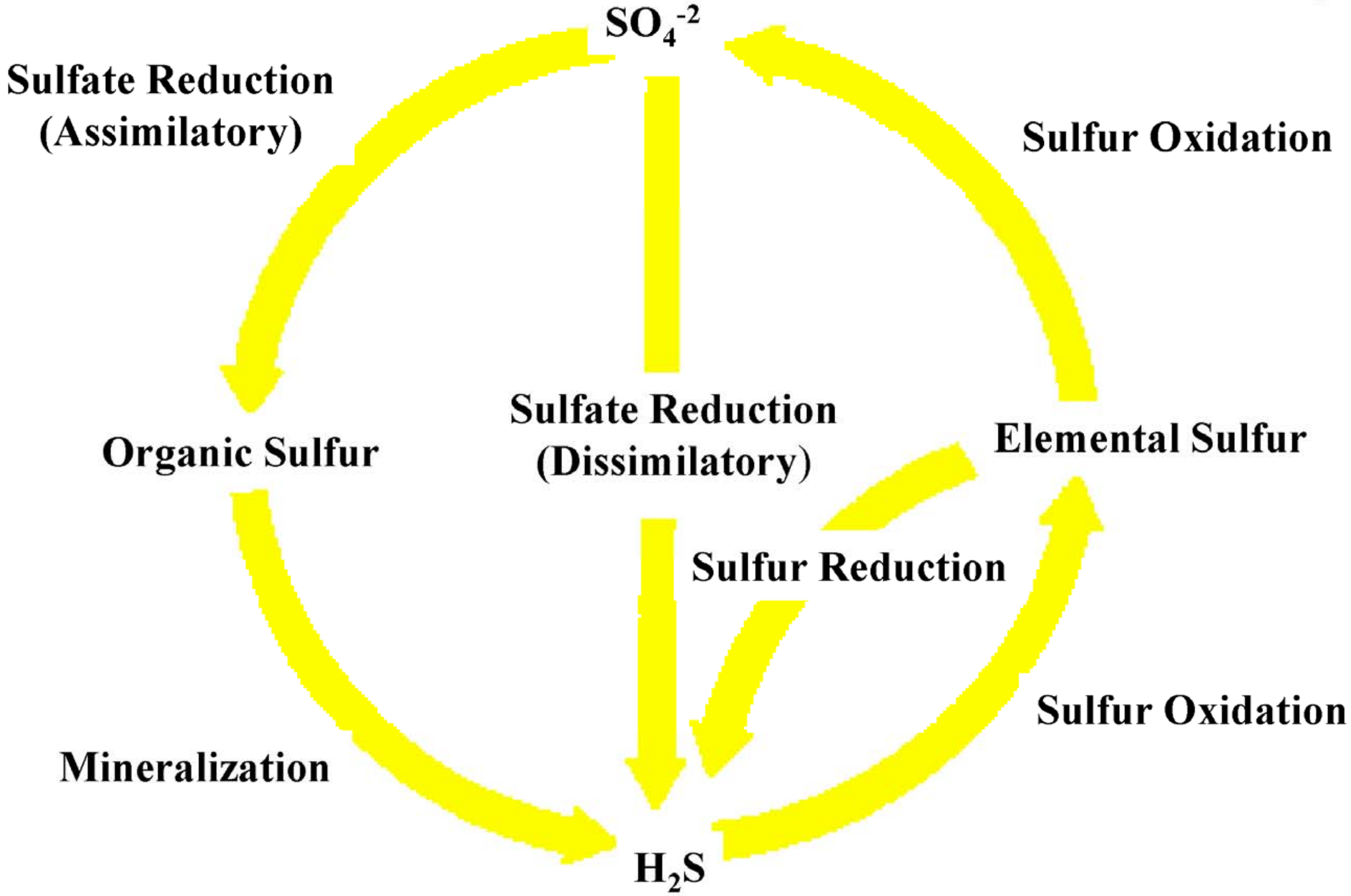
Takahashi H, et al. (2011) AnnuRevPlantBiol 62, 157-84

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



SO_4^{-2}

Sulfate Reduction
(Assimilatory)

Sulfur Oxidation

Organic Sulfur

Sulfate Reduction
(Dissimilatory)

Elemental Sulfur

Sulfur Reduction

Sulfur Oxidation

Mineralization

H_2S

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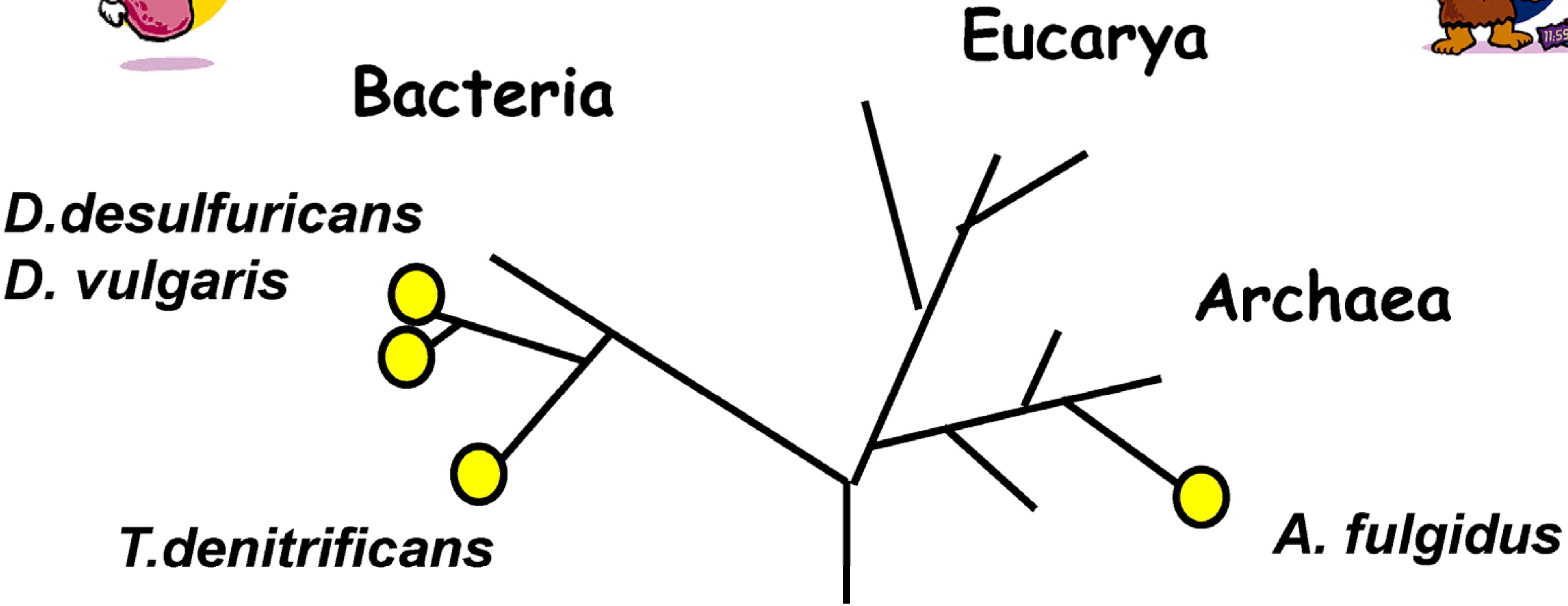
Oxidation/Reduction of Sulfur Compounds Coupled to Energy Conservation Evolved Early in Prokaryotic Evolution



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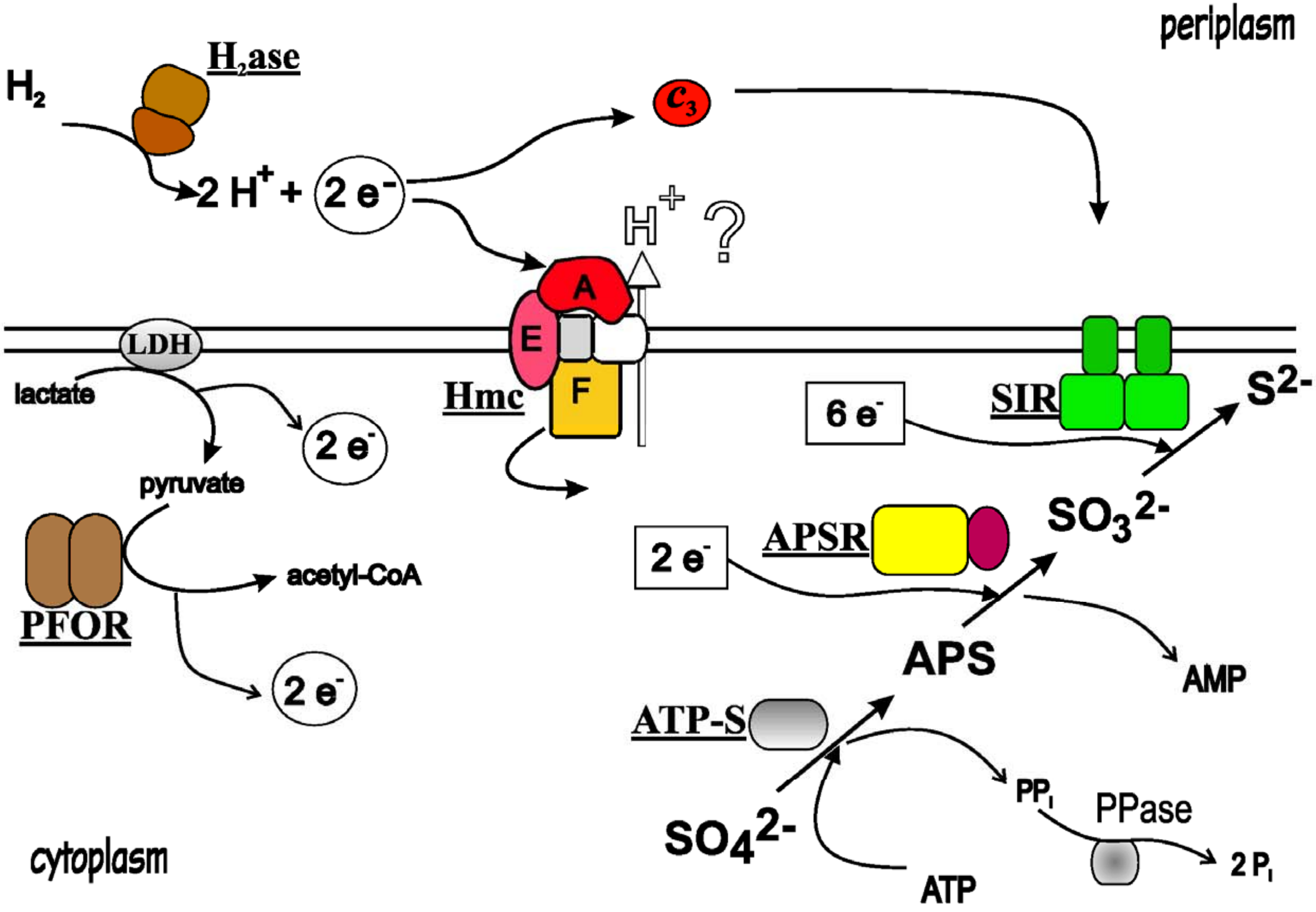
Life without O_2 - Sulfur Respiration

Reduction of SO_4^{2-} to H_2S, a multi-electron, multi-proton transfer process coupled to energy conservation



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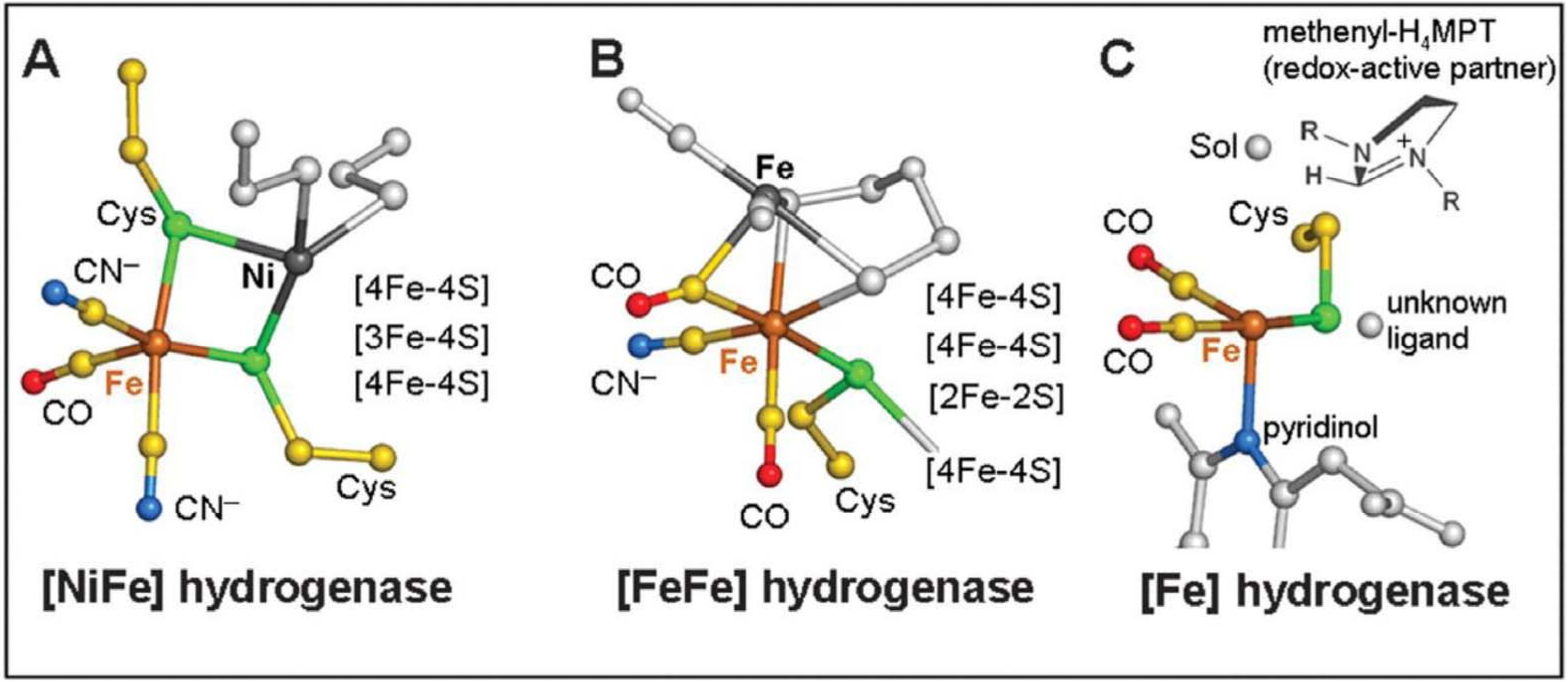
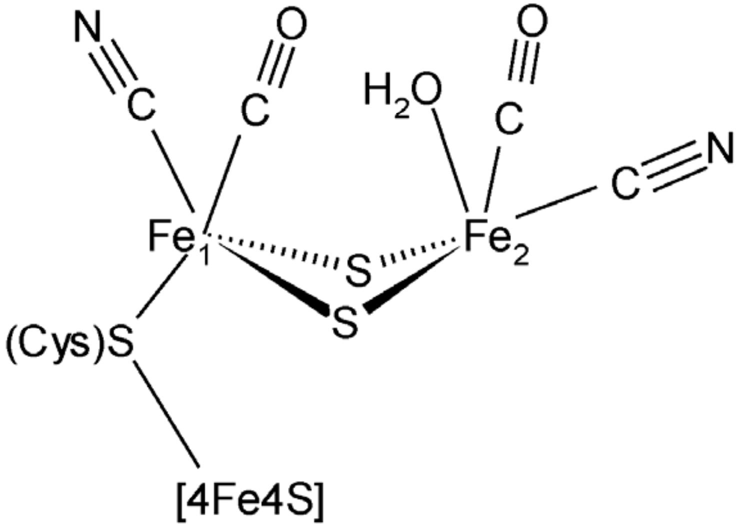
Tracking Footprints of Early Life
Nature's Toolbox to handle Dihydrogen

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

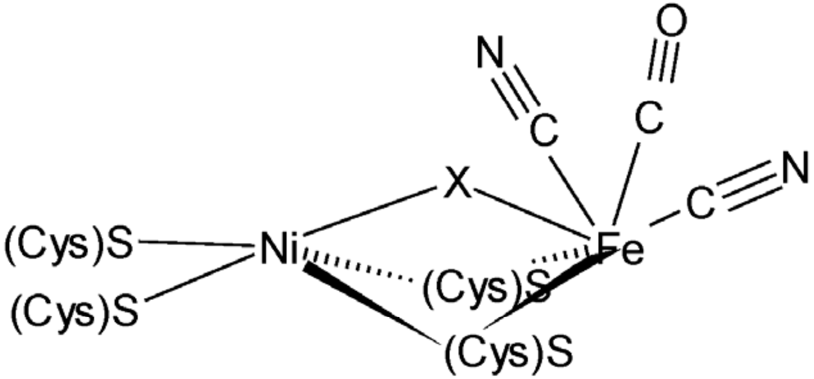


S. Shima et al., Science (2008), 321, 572 - 575

Fe-only *vs* Ni,Fe Hydrogenase

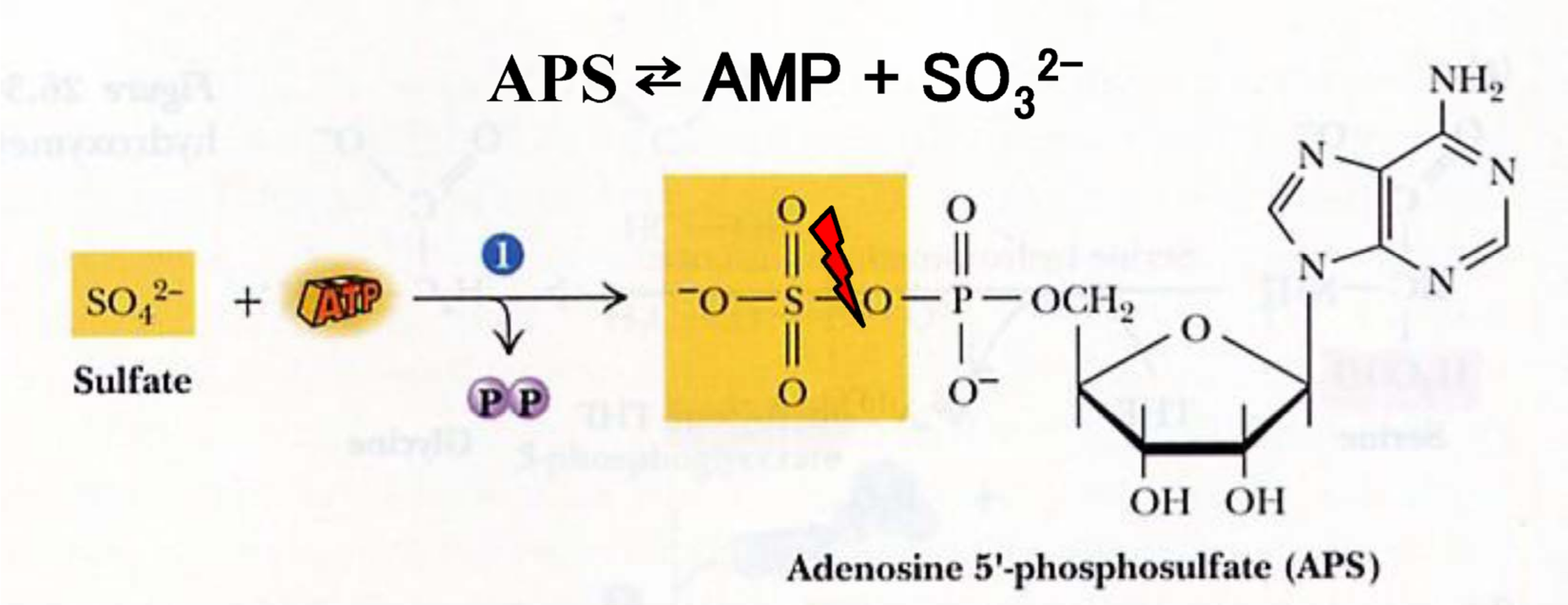


H-Cluster der
Fe-only Hydrogenase



[NiFe] Cluster der
Ni,Fe Hydrogenase

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



$$APS \rightleftarrows AMP + SO_3^{2-}$$

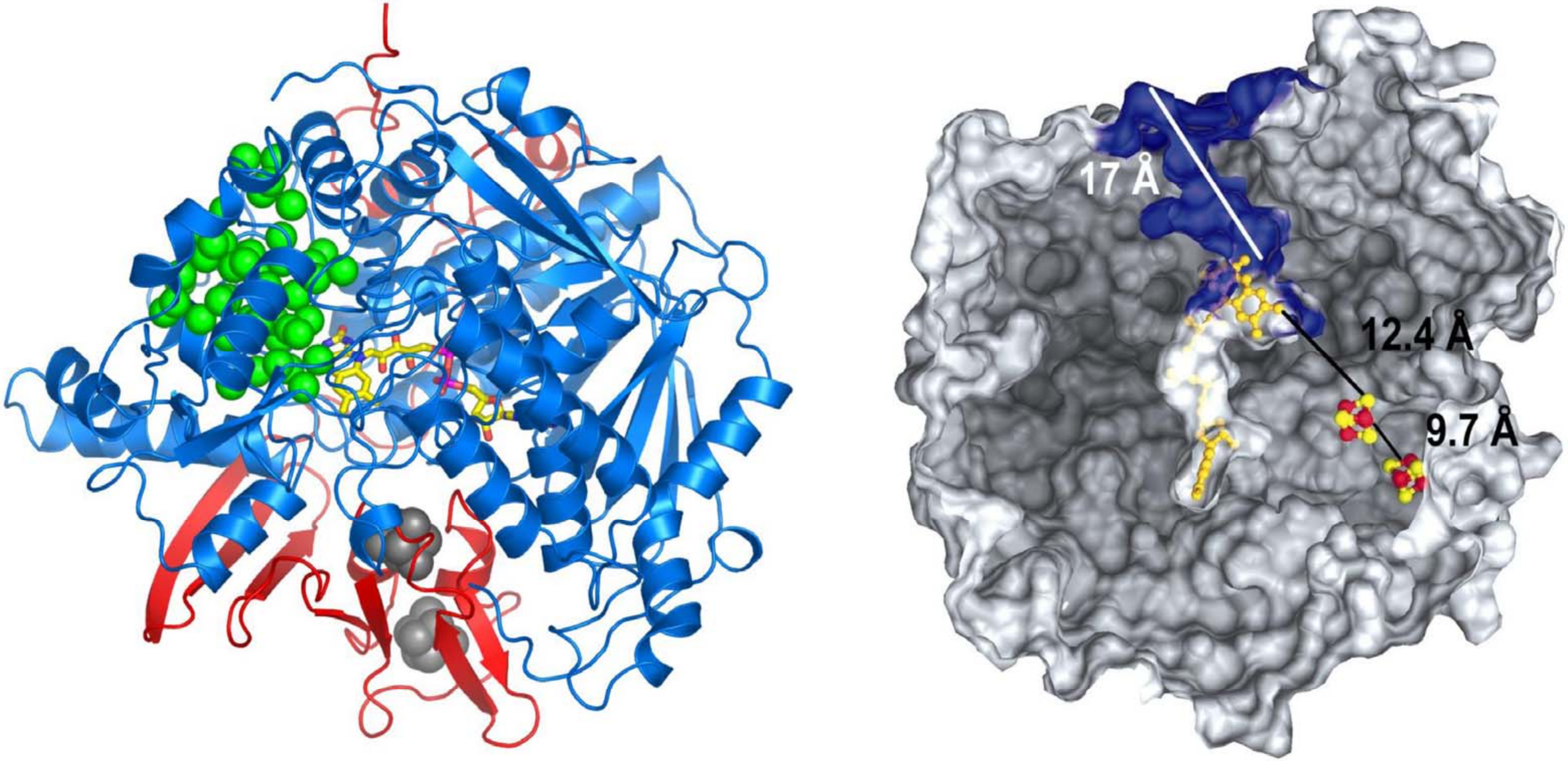
Adenosine 5'-phosphosulfate (APS)

Activation of sulfate (E°’ = -516 mV) to

adenosine-5’-phosphosulfate = APS (E°’ = -60 mV)

APS Reductase from thermophilic *Archaeoglobus fulgidus*

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



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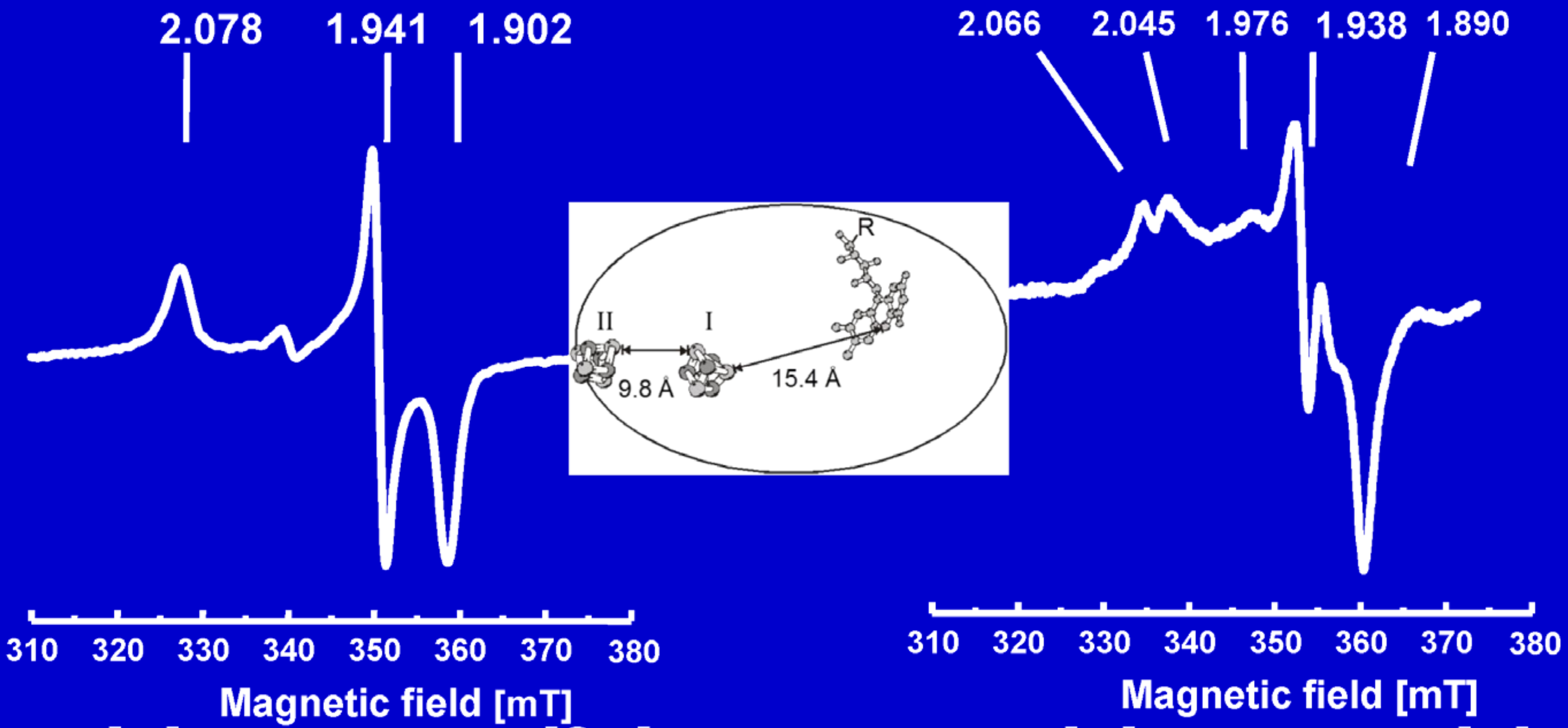
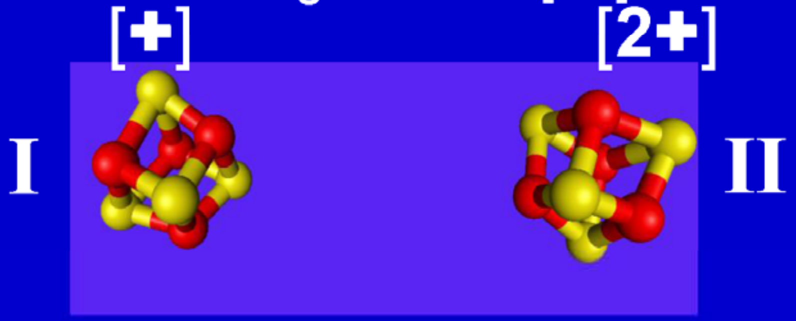
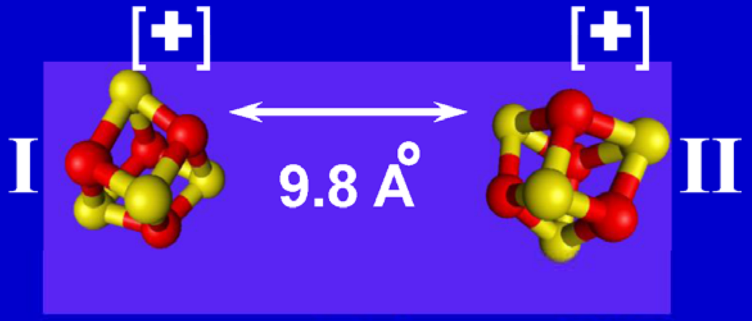
APSR has two [4Fe-4S] – Clusters which interact



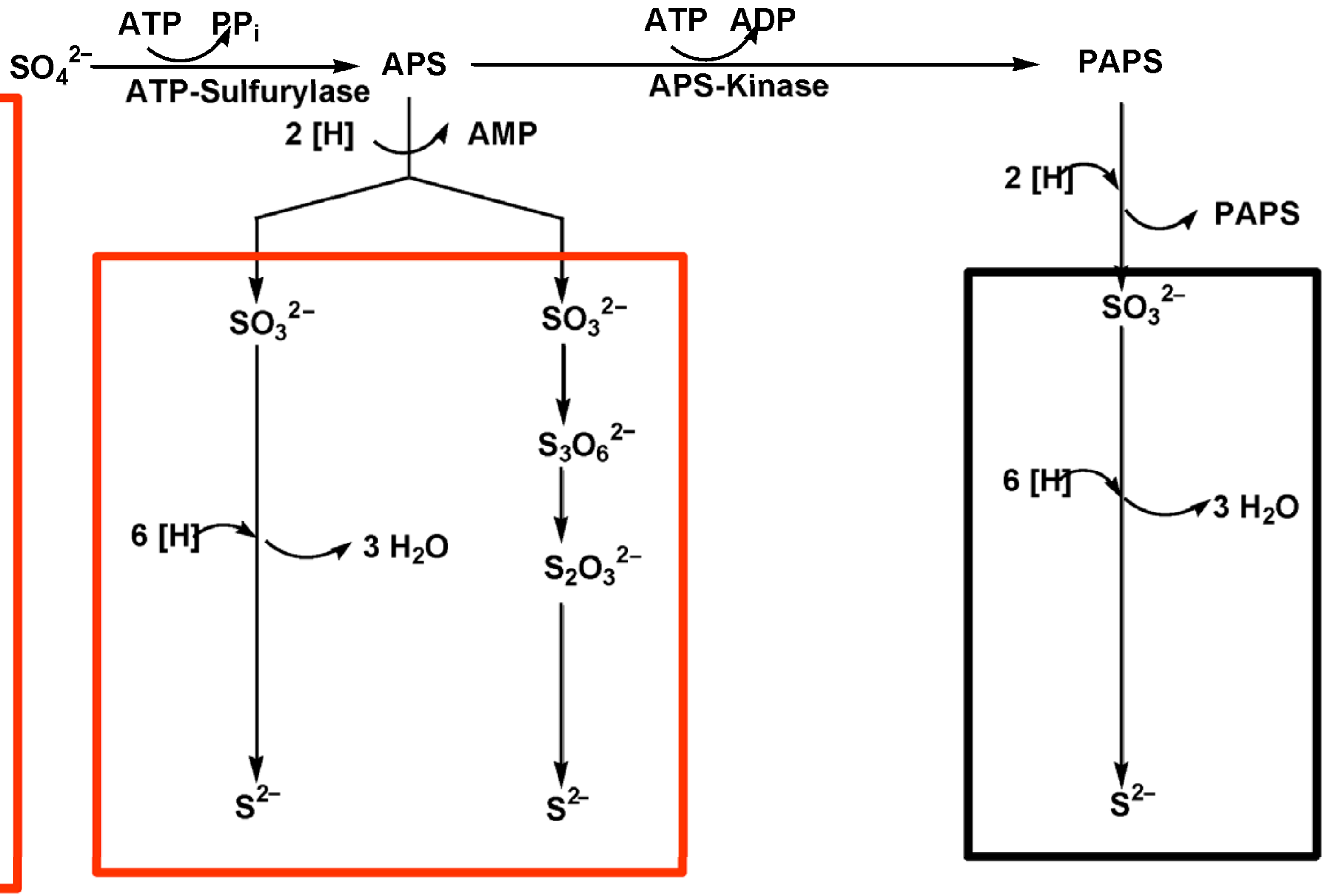




$E_o' = -60$ mV >>> $E_o' = -520$ mV

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

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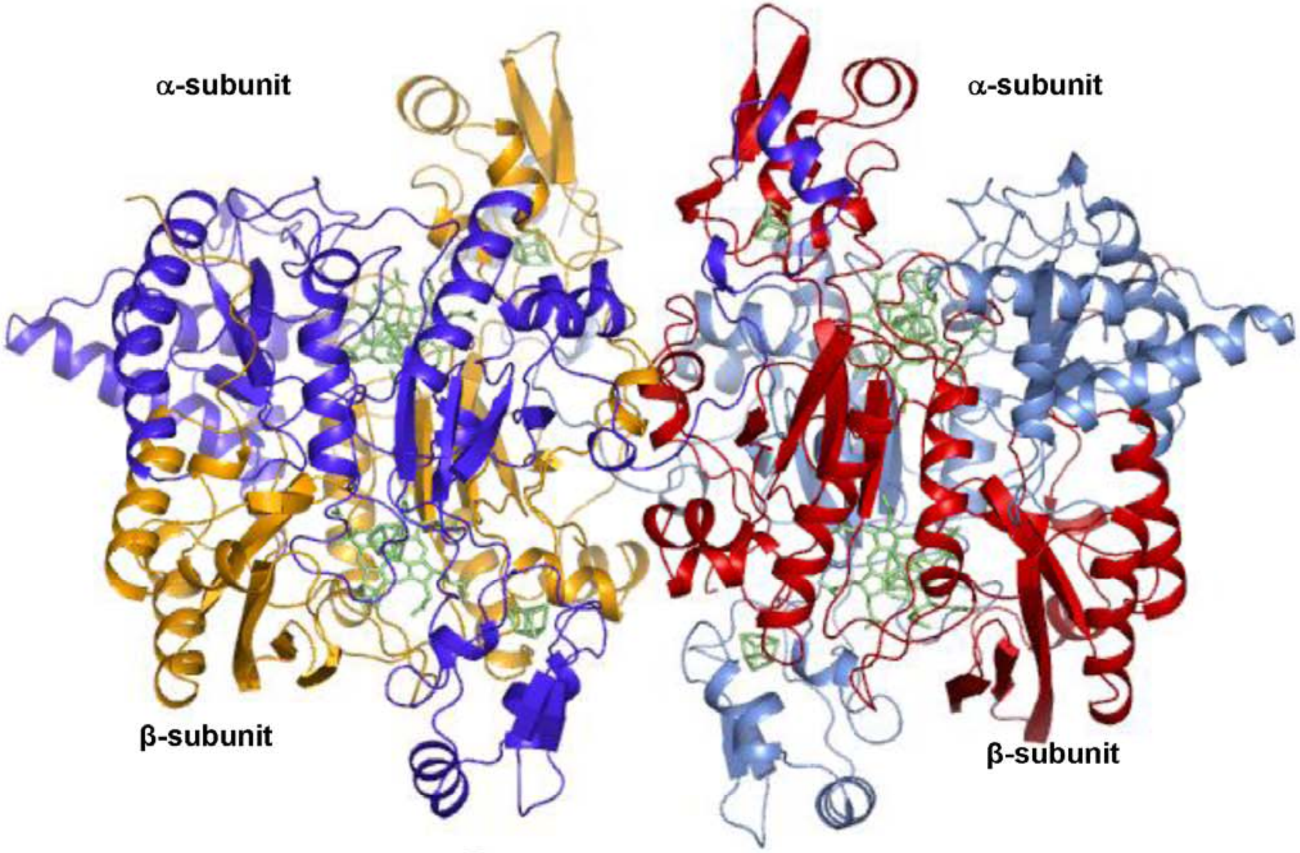
Overall structure of *A. fulgidus* dSIR $\alpha_2\beta_2$ complex

- **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 αβ-unit contains the catalytic siroheme center**

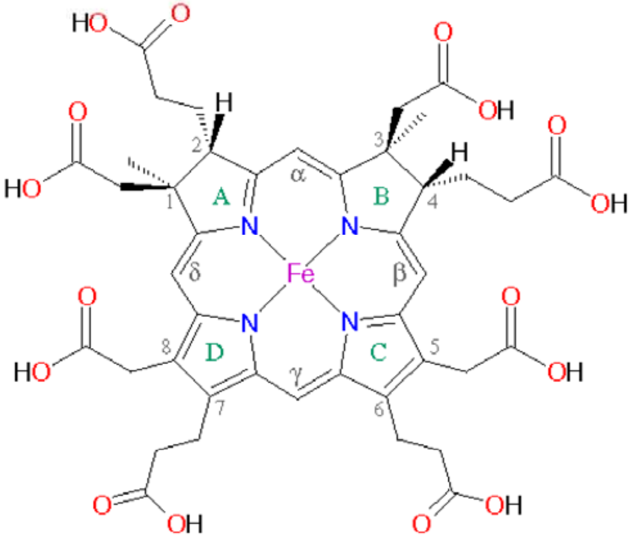


γ-subunit DrsC, interacts with weakly with $\alpha_2\beta_2$ complex in *A. Fulgidus*, however strongly in *D. vulgaris*

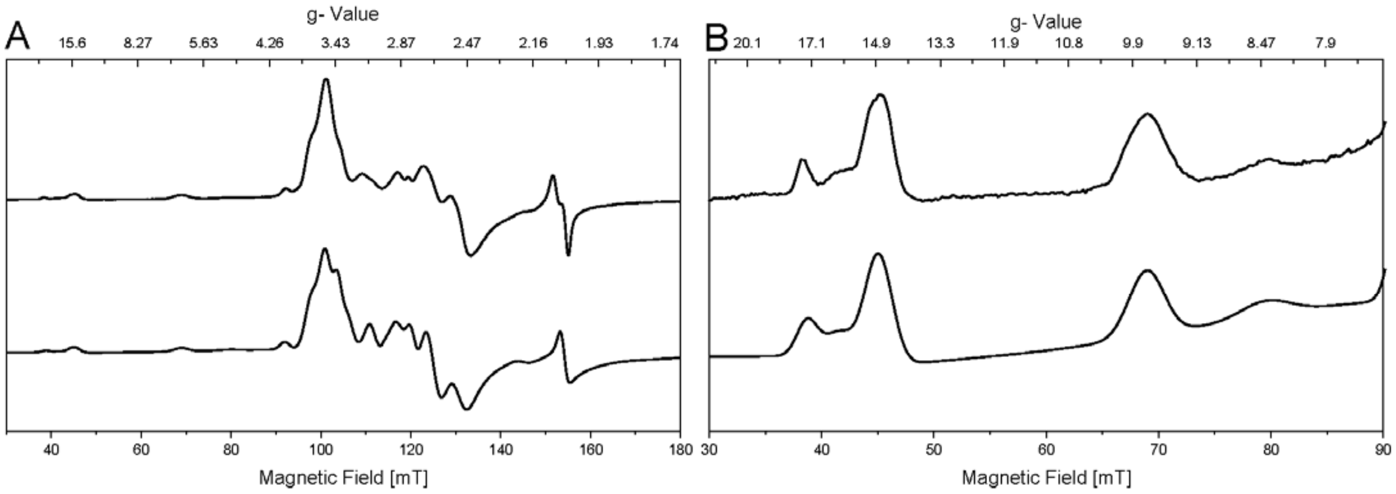
Sulfite Reductase (36 Fe) from *Archaeoglobus fulgidus*

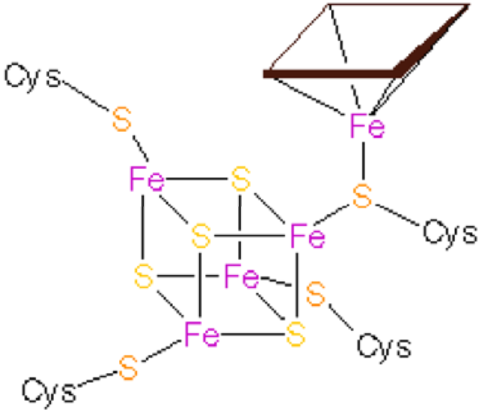
$$SO_3^{2-} + 6e^- + 8H^+ \rightarrow H_2S + 3\ H_2O$$

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



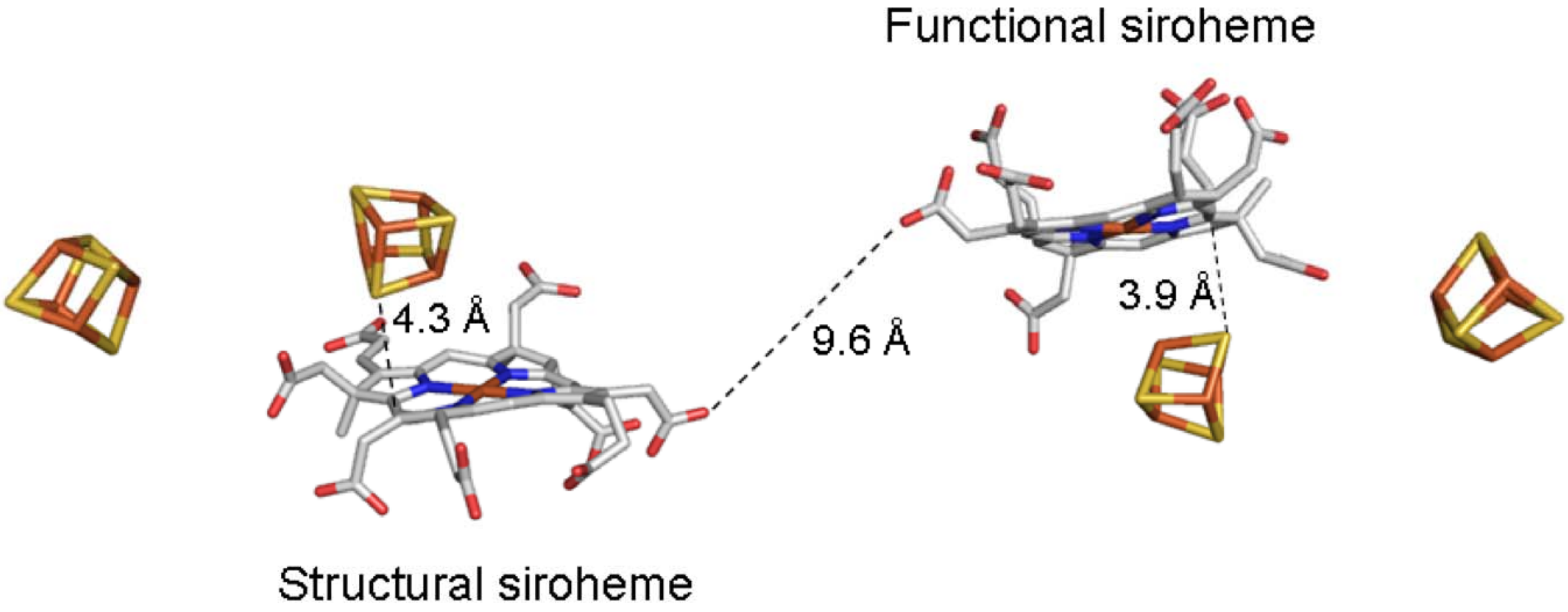
EPR (X-Band), resonances between *g* 18 and *g* 1.9





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

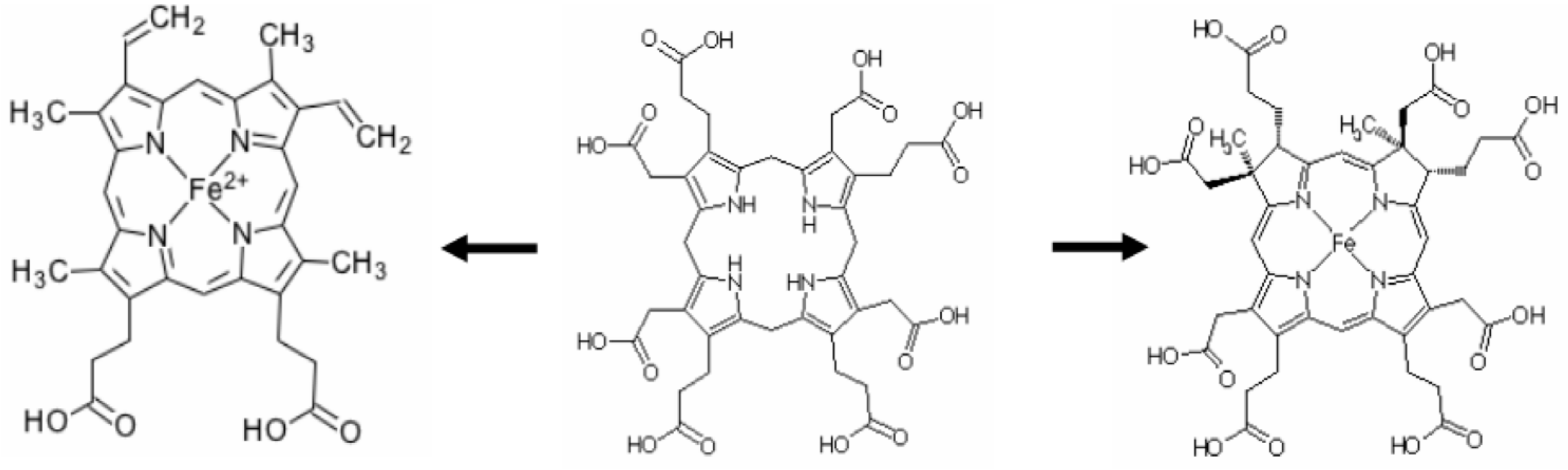
Cofactors of *A. fulgidus* dSIR



Functional and structural siroheme-[4Fe-4S] centers in one αβ 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



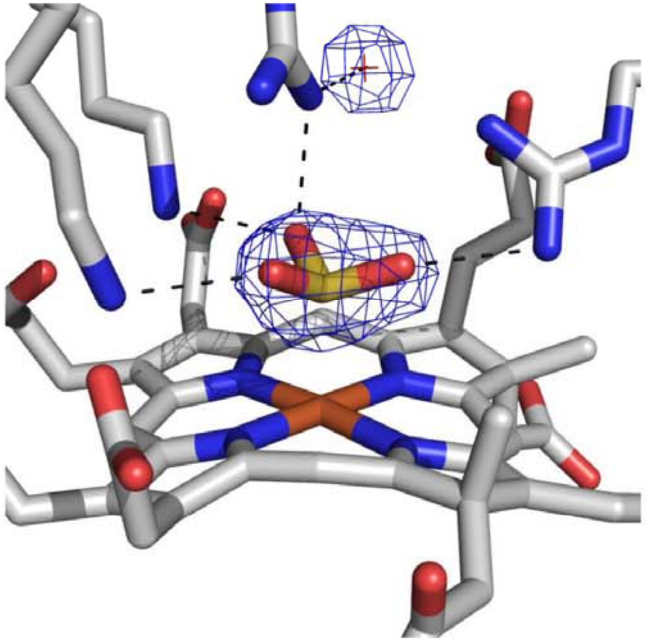
Heme *b*
(red)

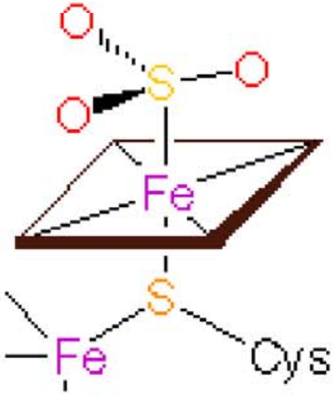
Siroheme
(green)

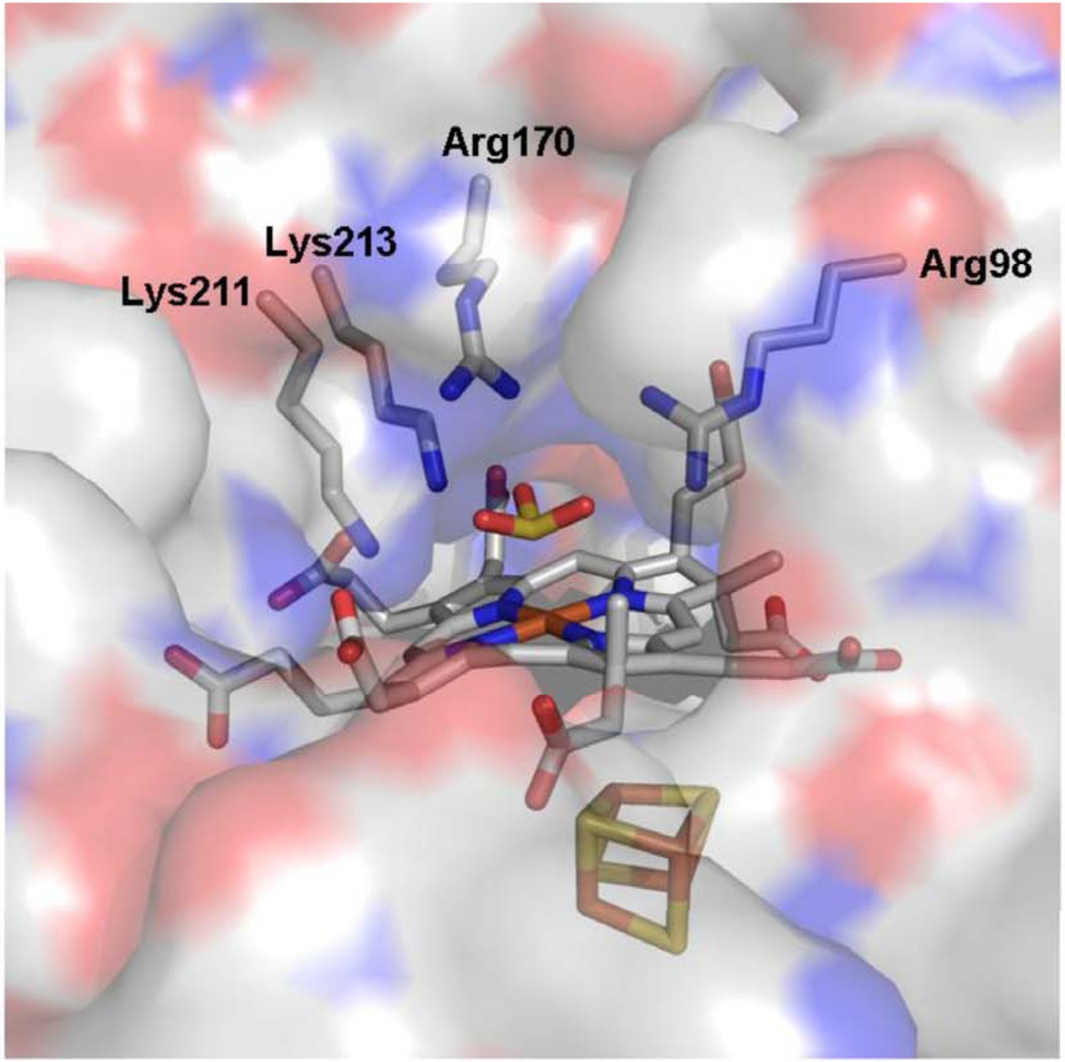
- Siroheme = heme-type prosthetic group
- catalyzes the six-electron reduction of sulfite to sulfide, and of nitrite to ammonia
- formed by methylation, oxidation, and Fe insertion into uroporphyrinogen III

SO_3^{2-} Adduct and the Substrate Channel

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







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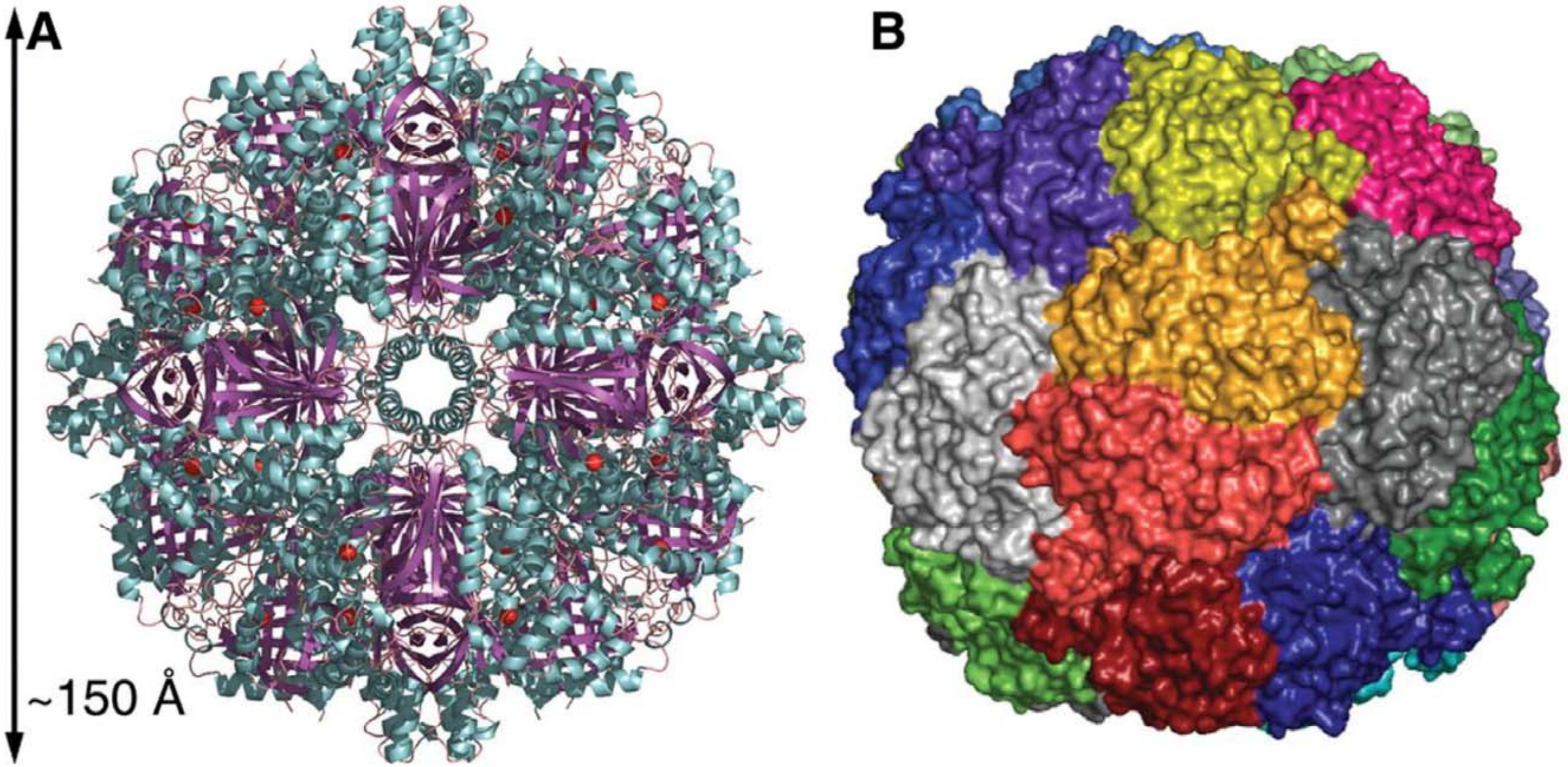
Structure of a Self-Compartmentalizing Sulfur Cycle

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



C (1) Oxygenase $S + O_2 + H_2O \longrightarrow HSO_3^- + H^+$

(2) Disproportionation $3\ S + 3\ H_2O \longrightarrow HSO_3^- + 2\ HS^- + 3\ H^+$

(3) Sum $4\ S + O_2 + 4\ H_2O \longrightarrow 2\ HSO_3^- + 2\ HS^- + 4\ H^+$

(4) Non-enzymic $S + HSO_3^- \longrightarrow S_2O_3^{2-} + H^+$

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