Química de Coordinación

UNAM Mayo 25, 2017

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Iones metálicos en sistemas vivos - Metaloenzimas y metaloproteínas (Cobre)

Copper Types

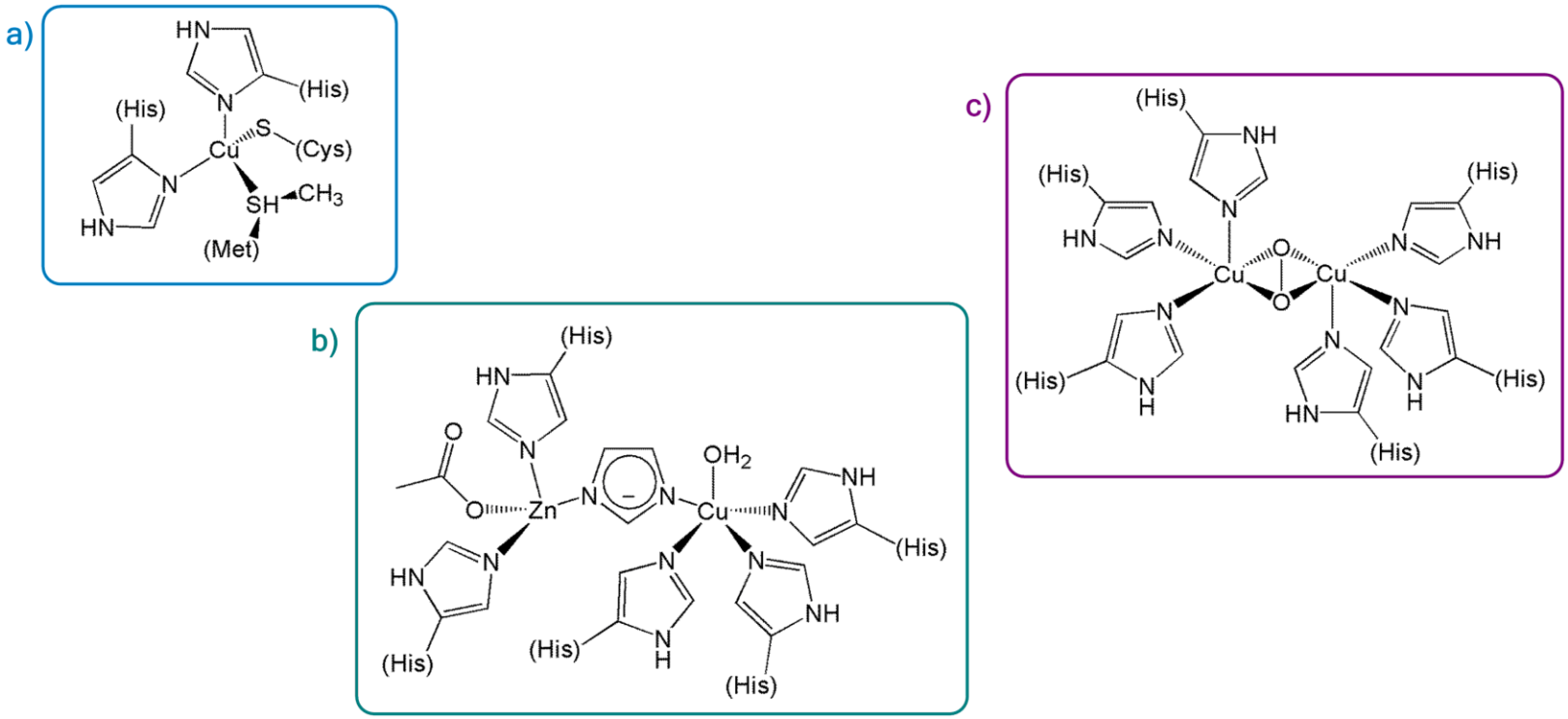
Concept of Malkin and Malmström (1971)
Advances in Enzymology, 33, 177-244

Classification of Cu sites according to UV/VIS and EPR Properties

Type 1 (blue; 1Cu), 2 (non-blue; 1Cu), 3 (EPR-silent; 2Cu)

CuA (mixed-valence, [Cu(1.5+)...Cu(1.5+)])

CuZ (4Cu-2S^{2-} Cluster)



Cu Types (Malkin and Malmström (1971))

a) Type 1 (blue; 1 Cu; Plastocyanin)
b) Type 2 (non-blue; 1 Cu; Superoxide Dismutase)
c) Type 3 (EPR-silent; 2 Cu; Hemocyanin)

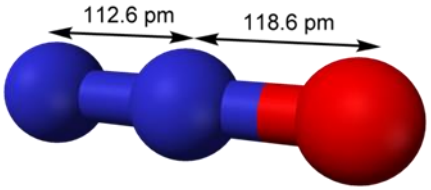
Nitrous Oxide Reductase is a purple Copper Enzyme

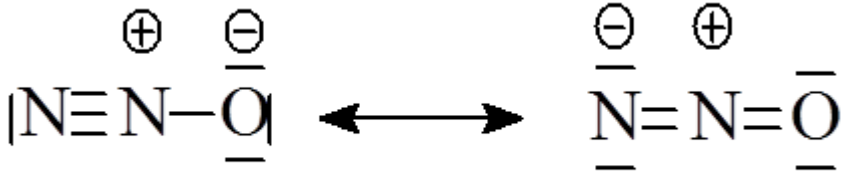
$$N_2O + 2H^+ + 2e^- \rightarrow N_2 + H_2O$$

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

kinetically inert molecule

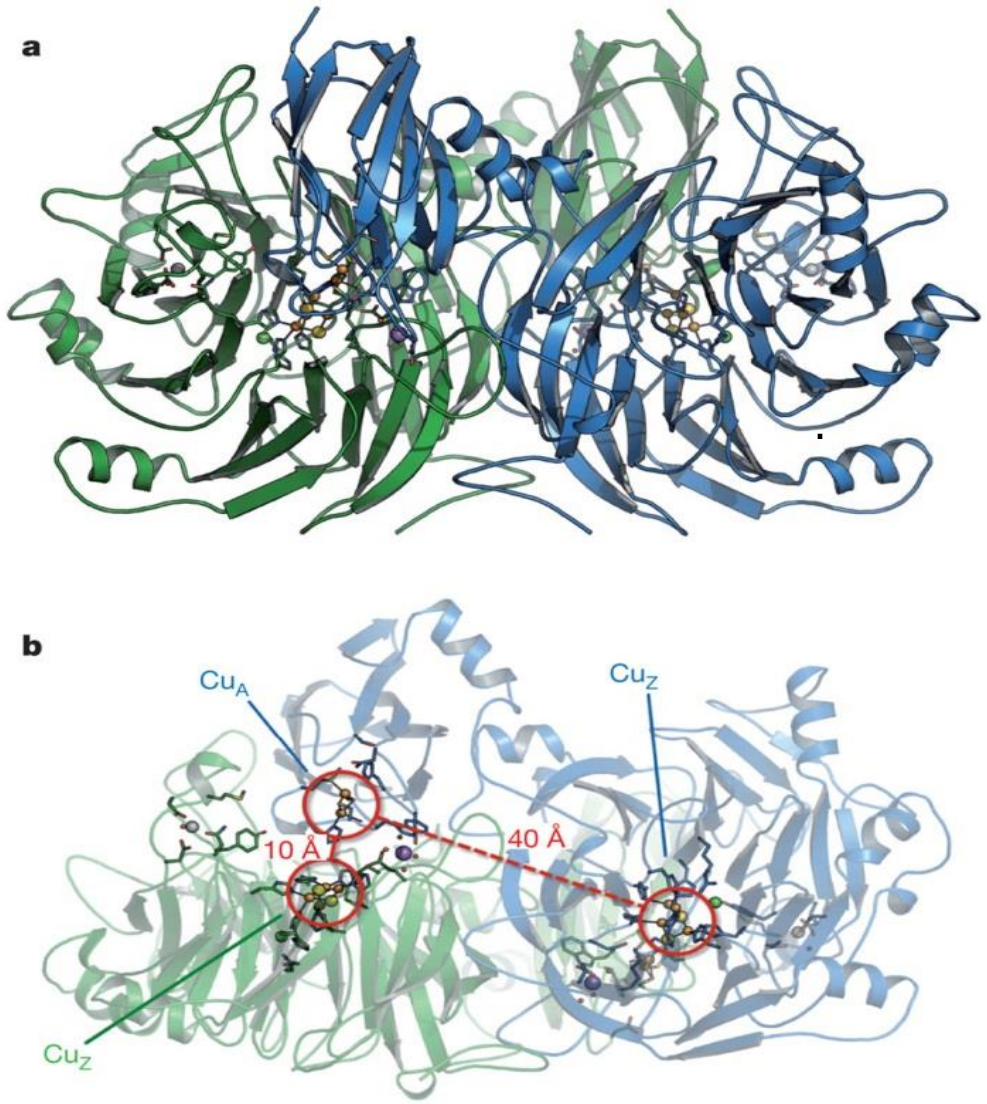
~ 59 kcal/mol activation barrier



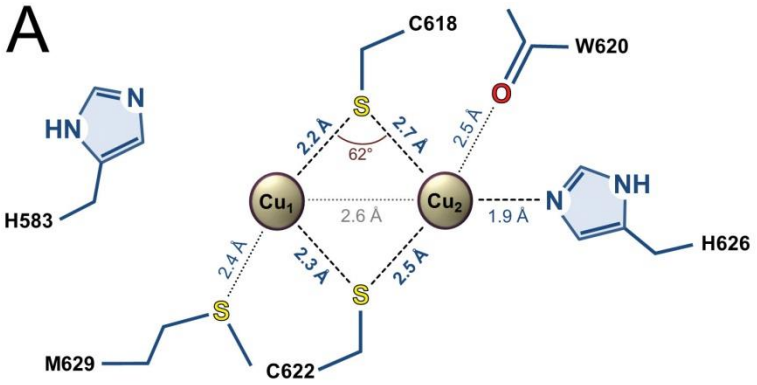


Bacterial Nitrous Oxide Reductase is a head-to-tail homodimer, with 6 Cu/monomer

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



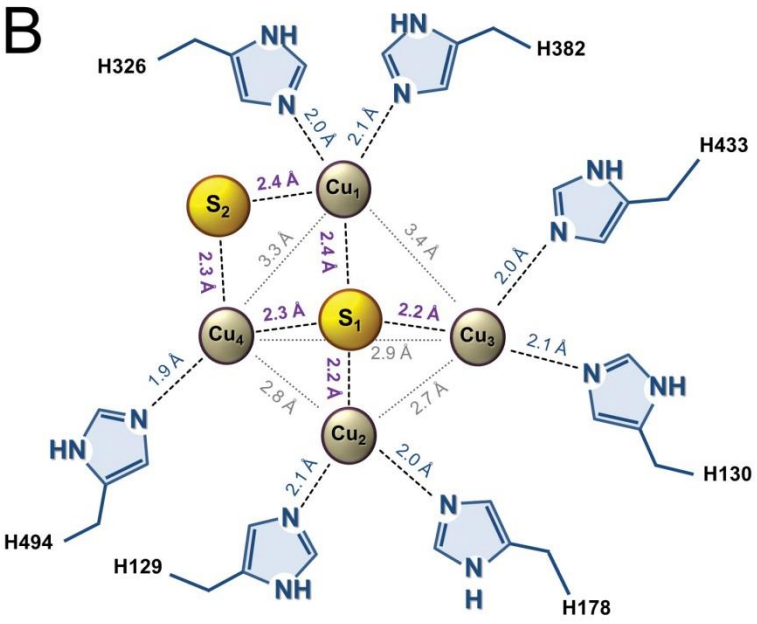
There are two novel Copper-Sulfur sites (A) the dinuclear CuA, (B) the tetranuclear CuZ



$[Cu_2]^{3+}$

$-e^- \rightleftharpoons +e^-$

$[Cu_2]^{2+}$



$[Cu_4^{II}:S_2]^{4+}$

$-e^- \rightleftharpoons +e^-$

$[Cu_3^{II}:Cu_1^{I}:S_2]^{3+}$

$-e^- \rightleftharpoons +e^-$

$[Cu_2^{II}:Cu_2^{I}:S_2]^{2+}$

$-e^- \rightleftharpoons +e^-$

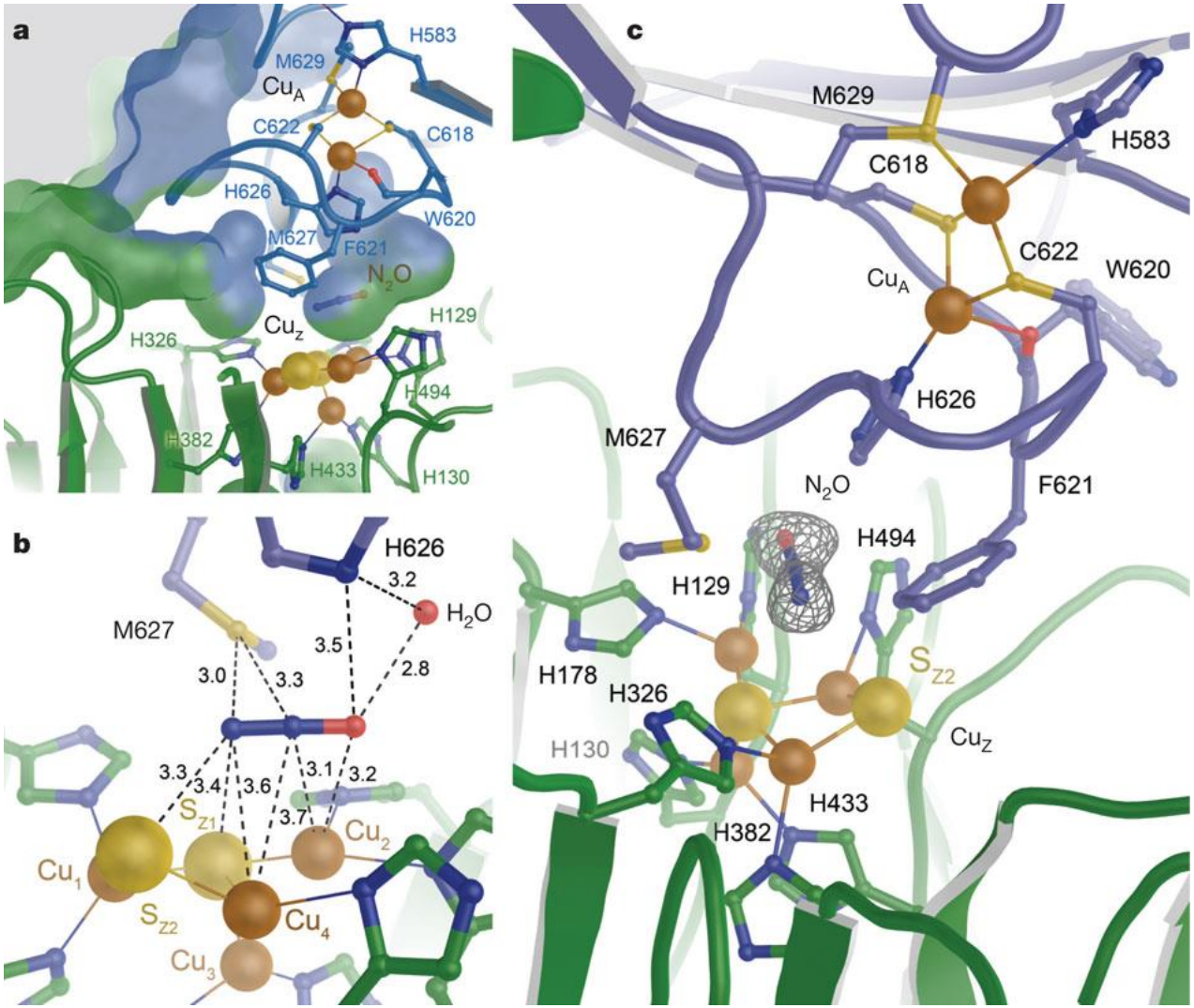
$[Cu_1^{II}:Cu_3^{I}:S_2]^{1+}$

$-e^- \rightleftharpoons +e^-$

$[Cu_4^{I}:S_2]^{0}$

Catalysis: CuA and CuZ operate *in concert*

Xtal under N_2O pressure

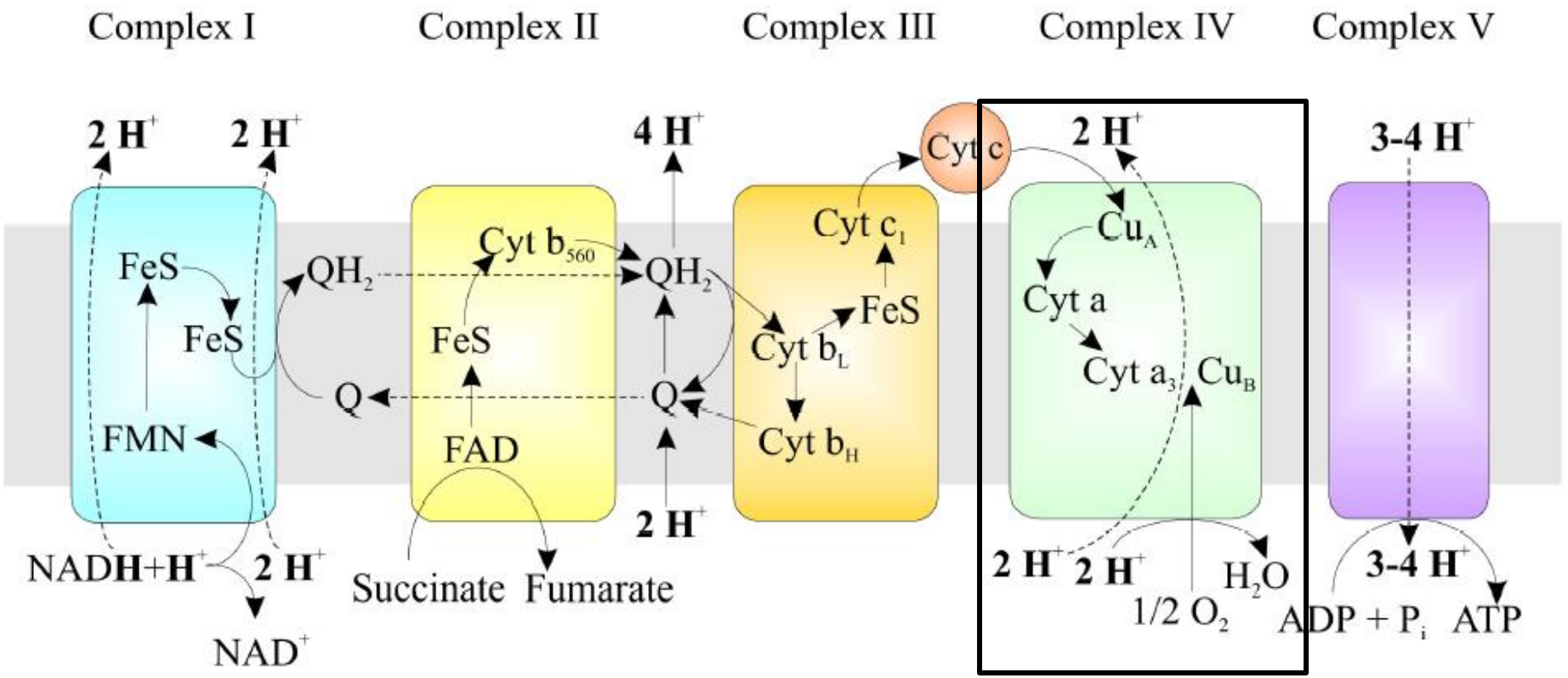


Cytochrome *c* oxidase (COX), a redox-driven proton pump

Proton-Coupled Electron Transfer in COX

Kaila, Verkhovsky, Wikstroem, Chemical Reviews (2010) 110, 7062–7081

$$4\,\text{cyt}\ c^{2+} + 8\,H_i^+ + O_2 \rightarrow 4\,\text{cyt}\ c^{3+} + 4\,H_o^+ + 2\,H_2O$$



Cytochrome *c* oxidase oxidase (COX)

S. Yoshikawa, K. Muramoto, K. Shinzawa-Itoh Annu. Rev. Biophys. (2011) 40, 205–23
Tomoya Hino, et al. SCIENCE (2010) 330, 1666-1670

$O_2 + 4H^+ + 4H_i^+ + 4e^- \rightarrow H_2O + H_2O + 4H_o^+$ (+ 818 mV)(COX)

$N_2O + 2H^+ 2e^- \rightarrow N_2 + H_2O$ (+1355 mV) (N2OR)
$2NO + 2H^+ + 2e^- \rightarrow N_2O + H_2O$ (+1175 mV) (NOR)

metals (Cu, Fe-heme, Mg, Zn)

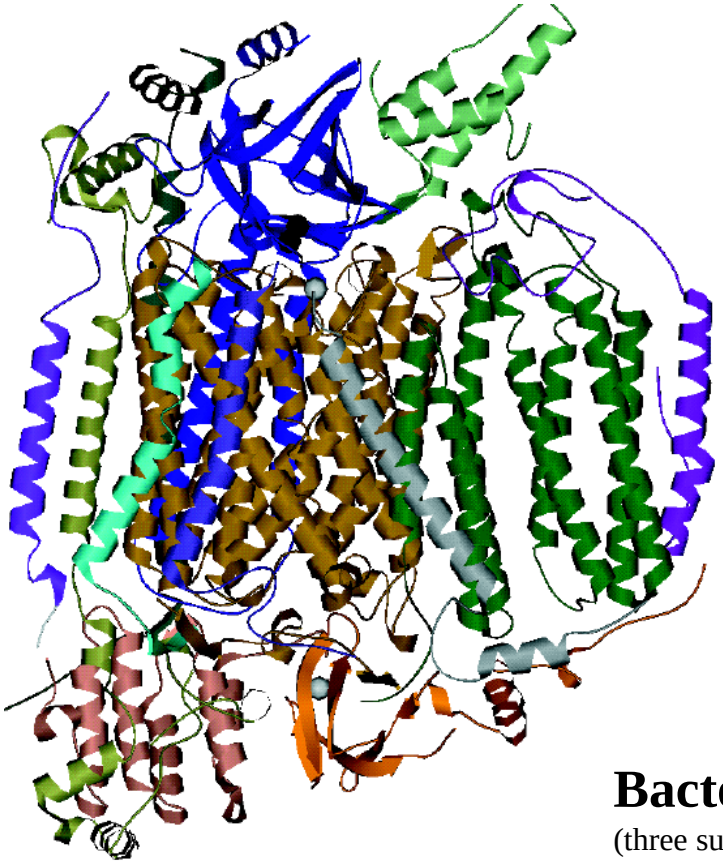
e^- transfer (redox; tyrosyl radical ?), H^+transfer (pump)

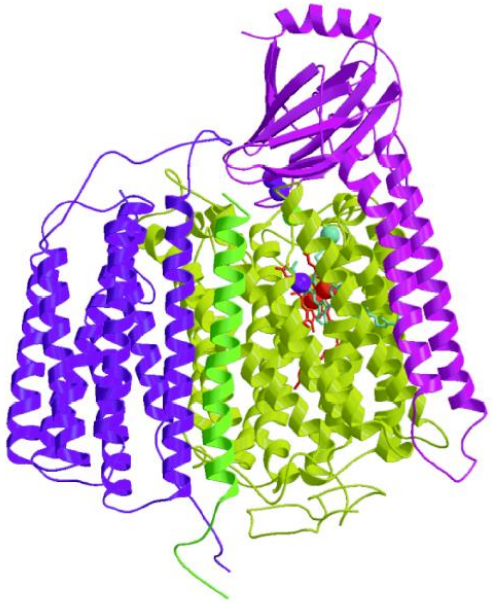
metal centers: CuA $\rightarrow$ ET; Fe-CuB $\rightarrow$ O_2 reduction

Mitochondrial Cytochrome *c* oxidase (COX)

(representation of the monomer from bovine heart/13 subunits)

Tsukihara et al., SCIENCE 1995, *269*, 1069; Yoshikawa et al., SCIENCE 1998, *280*, 1723; S. Yoshikawa et al., Annu. Rev. Biophys. 2011, *40*, 205–223; S. Yoshikawa et al., Biochim. Biophys. Acta 4 2012, *1817*, 579–589.



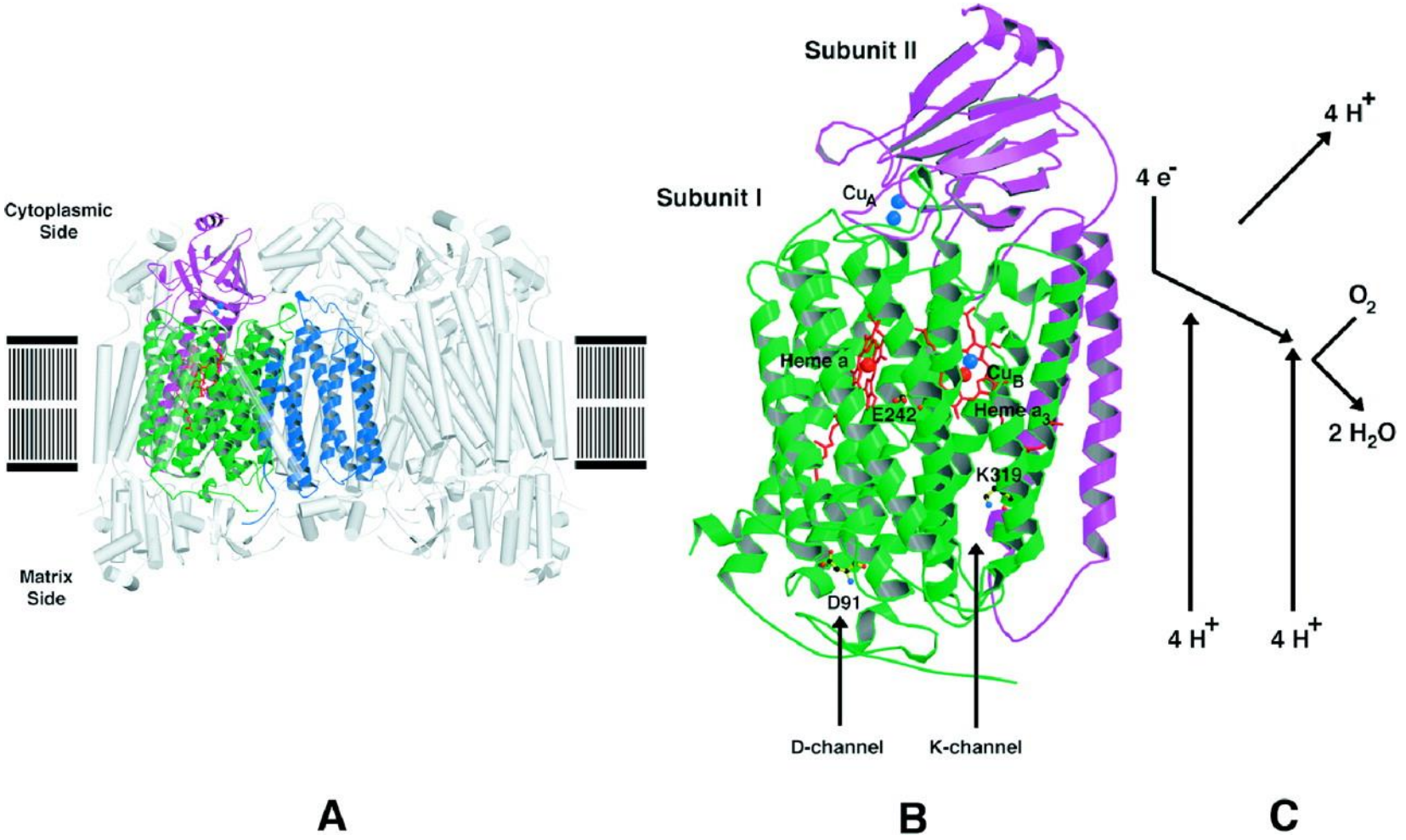


Bacterial COX from *Pseudomonas denitrificans*

(three subunits; Iwata et al., NATURE, 1995, *376*, 660)

PDB:1OCC,1QLE

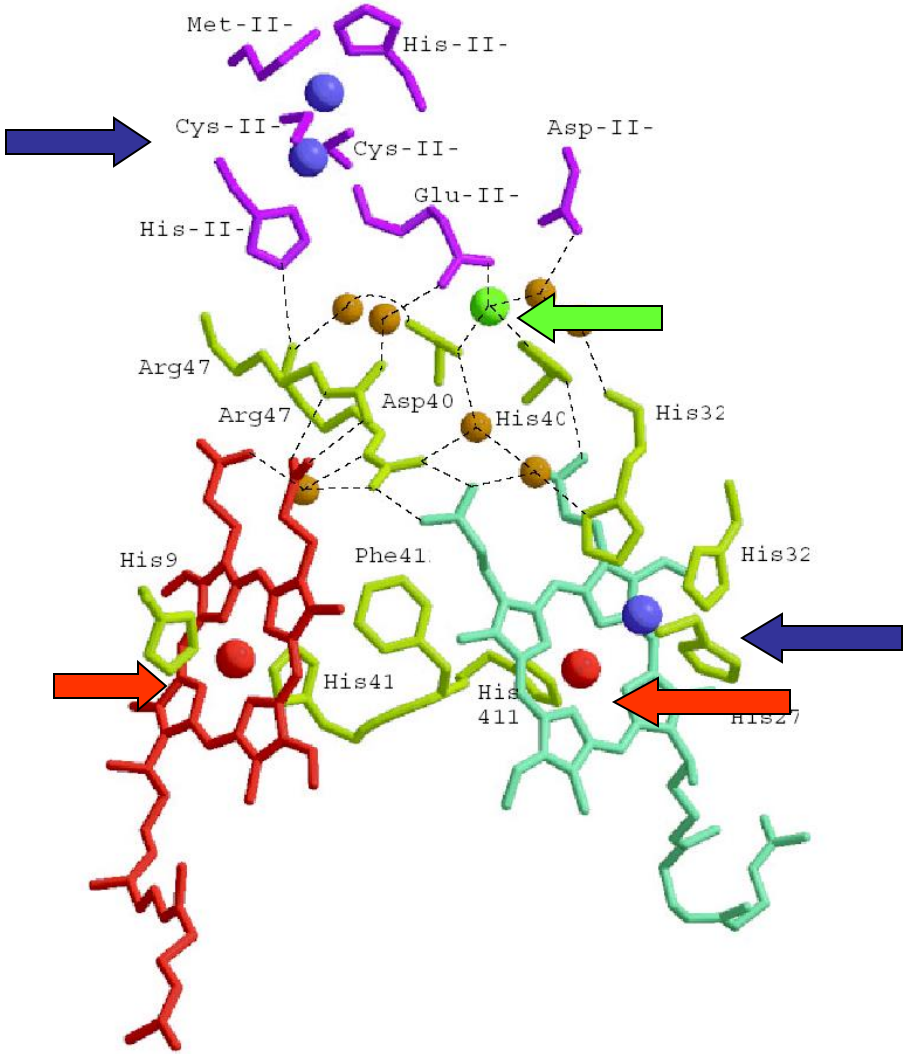
Cytochrome *c* oxidase



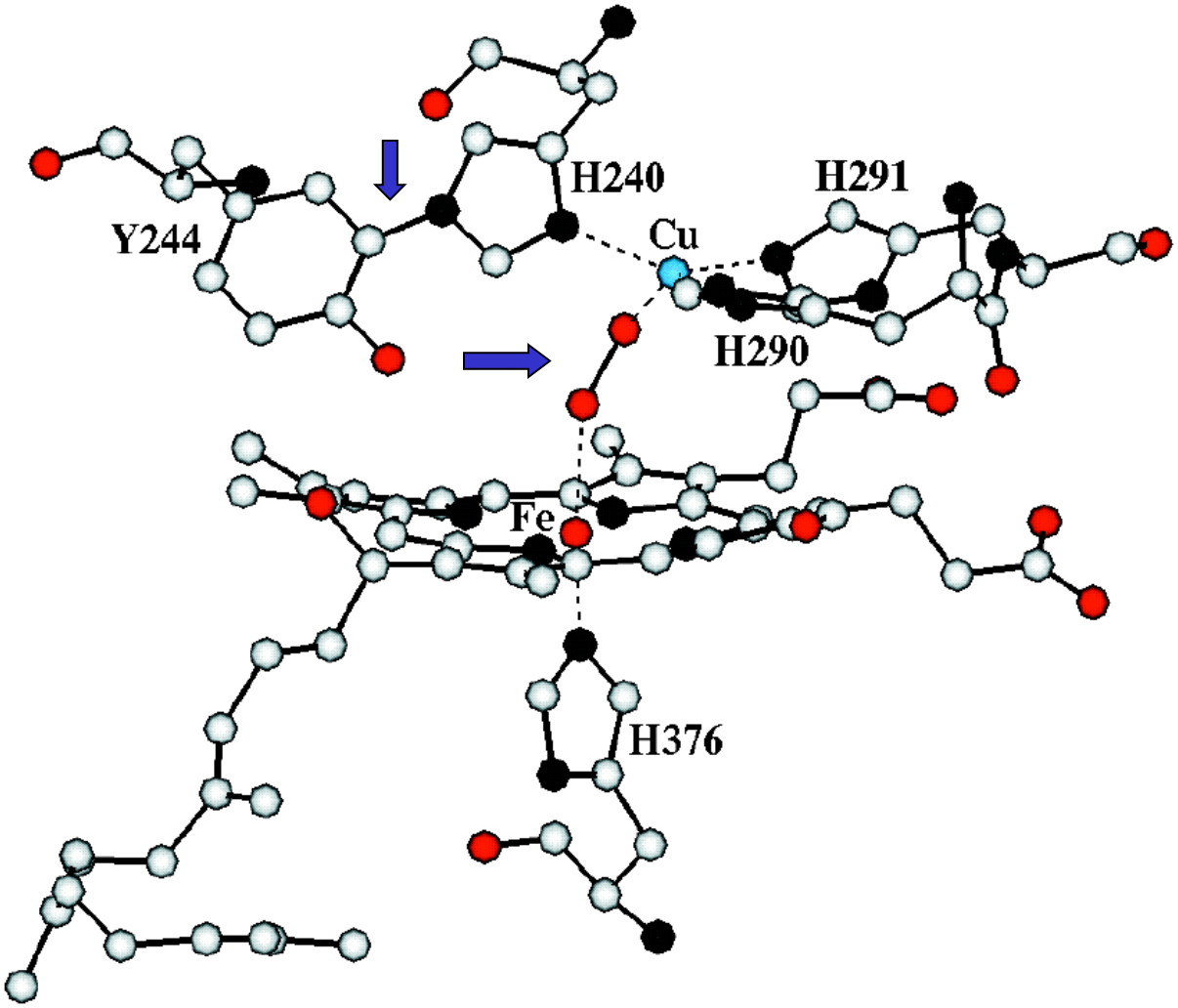
M Saraste Science (1999) 283,1488-1493

Metal Centers in bacterial COX

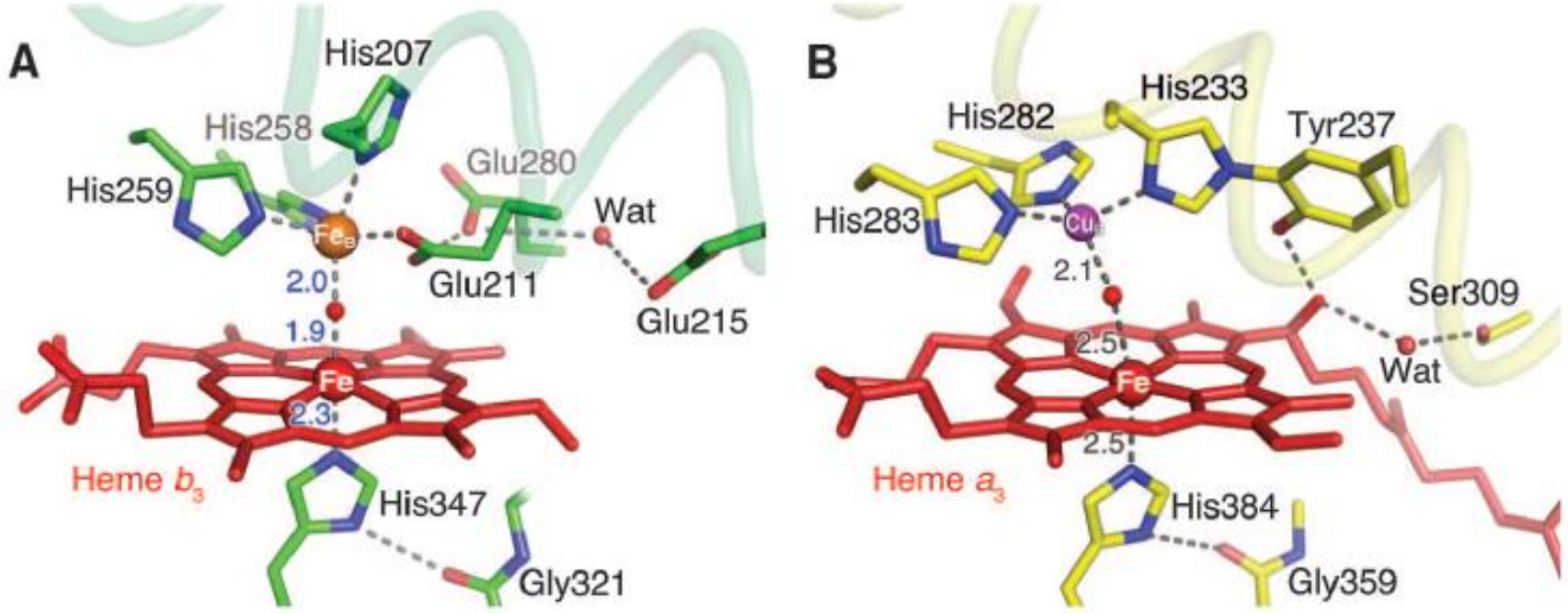
Cu Fe Mg



Site of O_2 Reduction
(Fe(III)-Cu(II) State – covalent link Tyr-His)

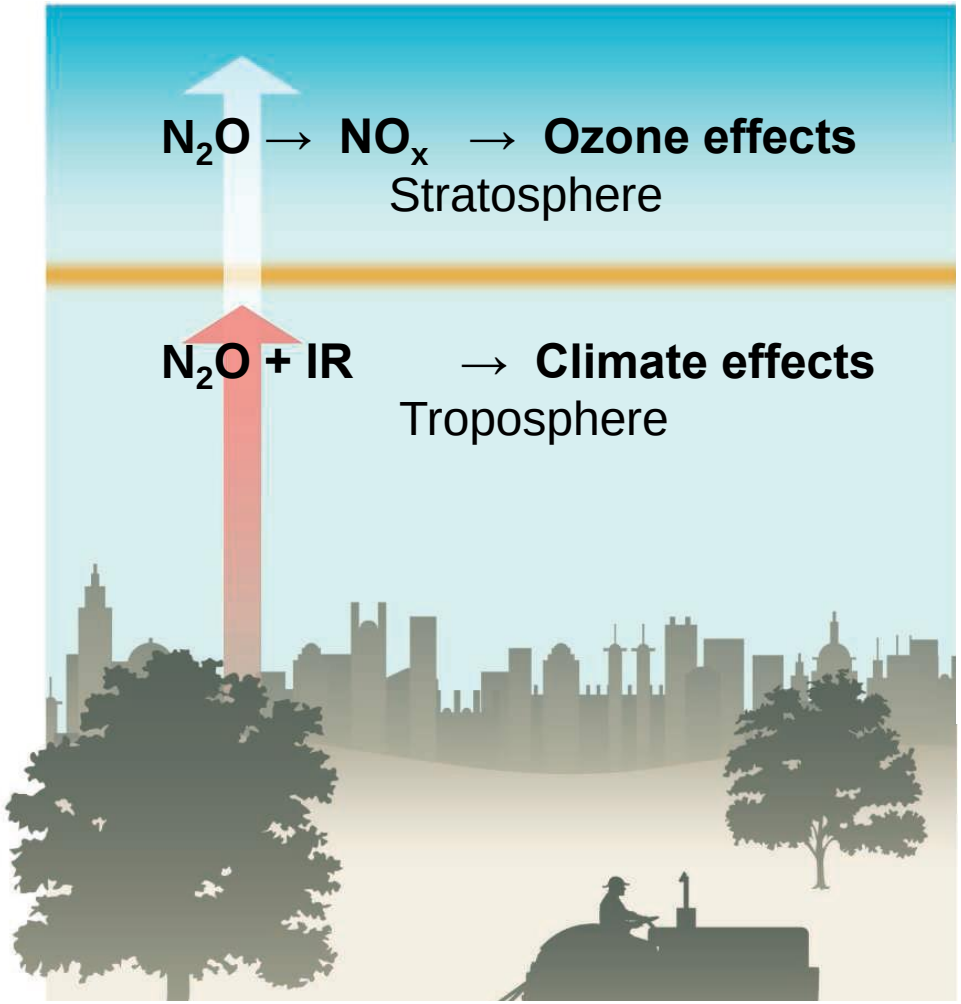


Active Sites of NOR (A) and COX (B)



N_2O – 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 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