

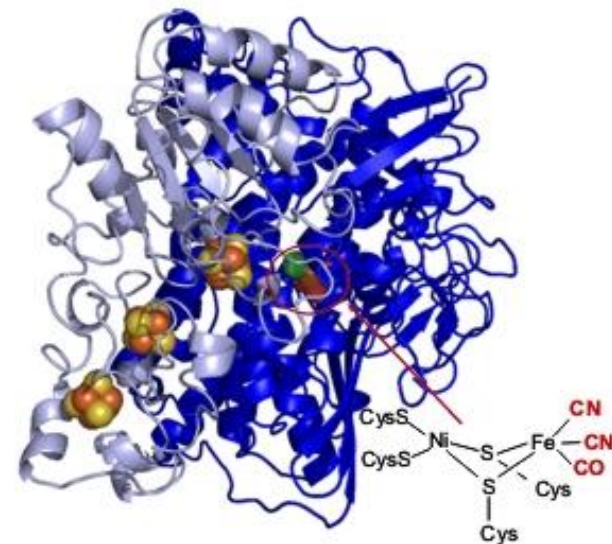
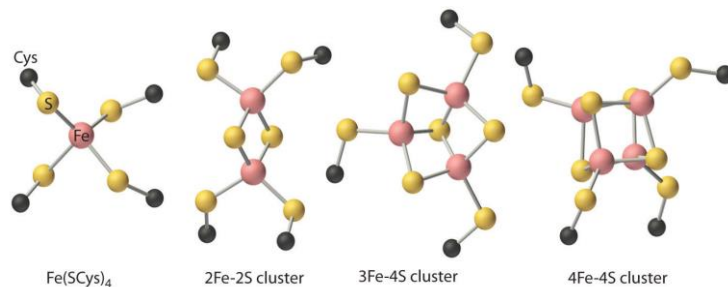
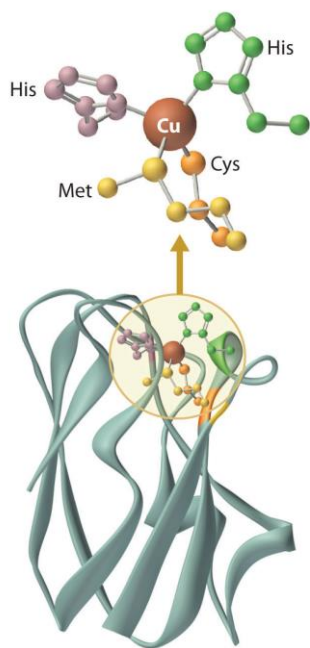
Química de Coordinación (2)

UNAM 2023

peter.kroneck@uni-konstanz.de

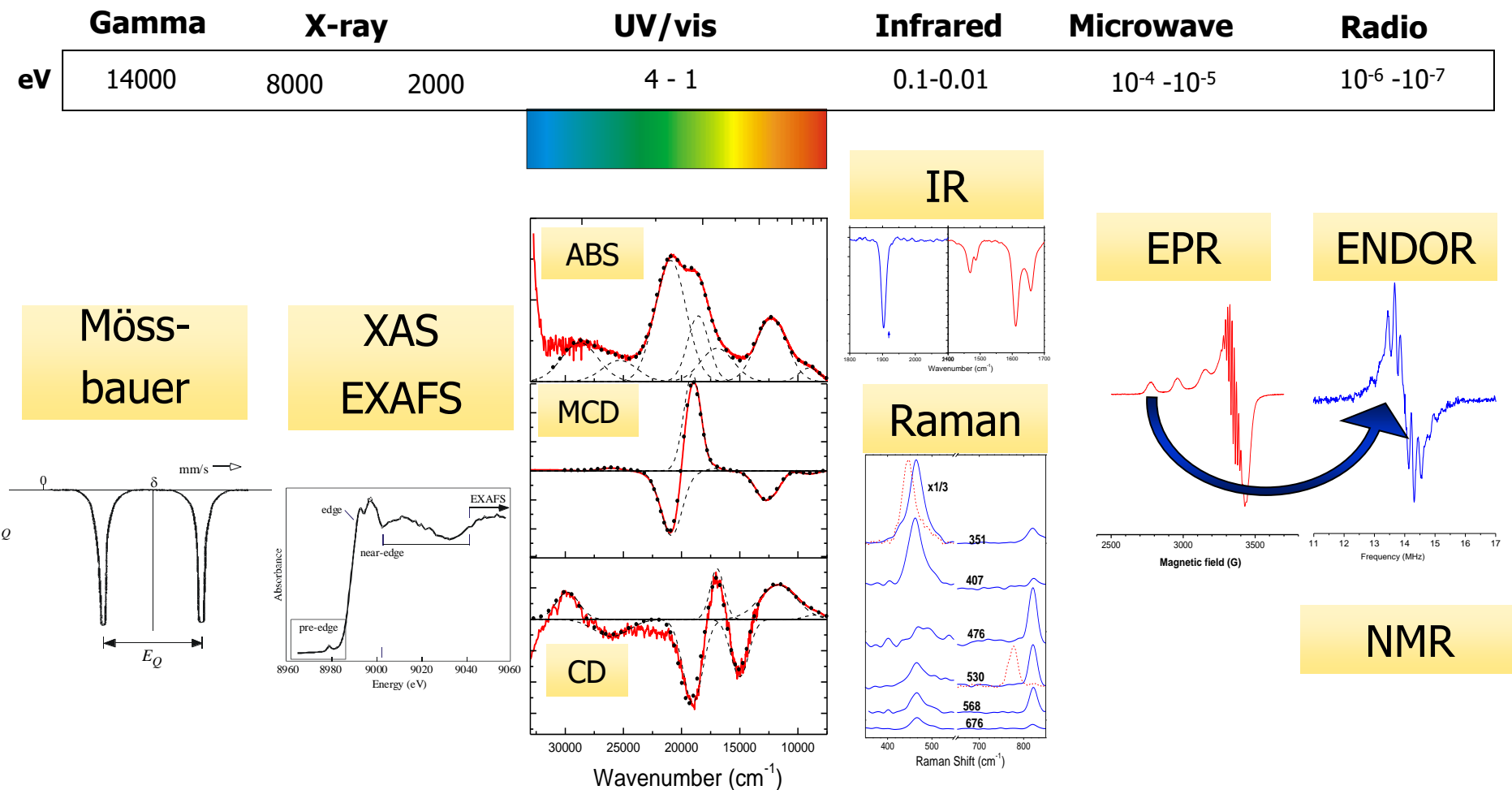
<https://www.researchgate.net/profile/Peter-Kroneck>

Iones metálicos en sistemas vivos Metaloenzimas y Metaloproteínas



La espectroscopia es importante

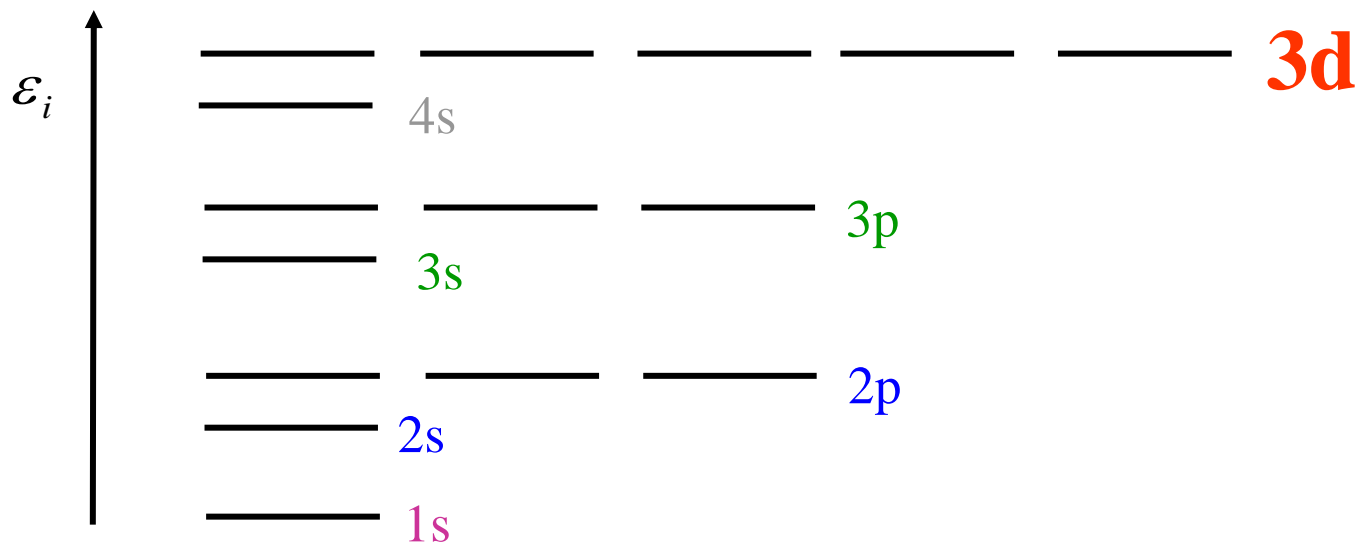
Practical Approaches to Biological Inorganic Chemistry, 2nd Edition,
R.R. Crichton, R. Louro, Elsevier, 2020



(Bio)Metals – Periodic Table - Electrons

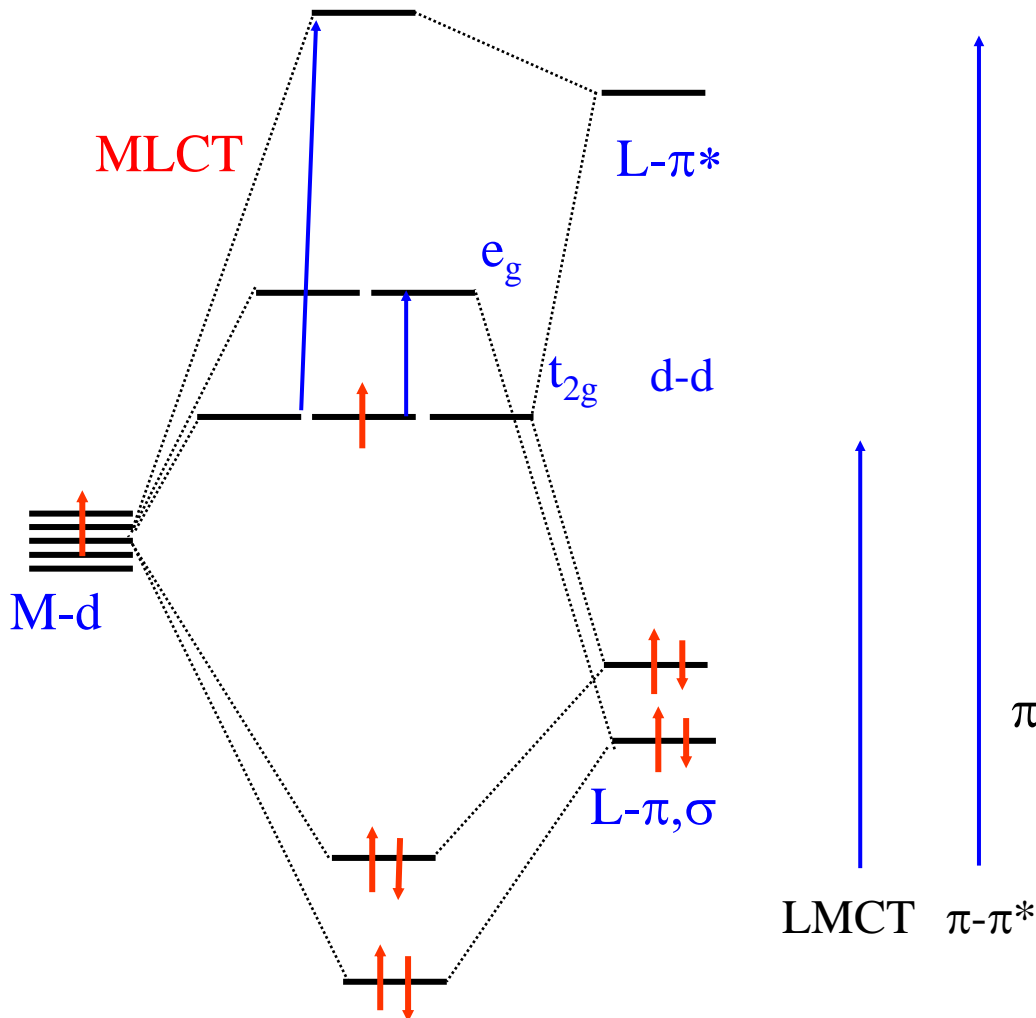
www.webelements.com

H	www.webelements.com																He
Li	Be											B	C	N	O	F	Ne
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
					Mo												
					W												



Propiedades ópticas

Spin y Laporte permitieron transiciones electrónicas



Typical Intensities

d-d : $\epsilon \sim 0-500 \text{ M}^{-1} \text{ cm}^{-1}$

LMCT: $\epsilon \sim 500-15,000 \text{ M}^{-1} \text{ cm}^{-1}$

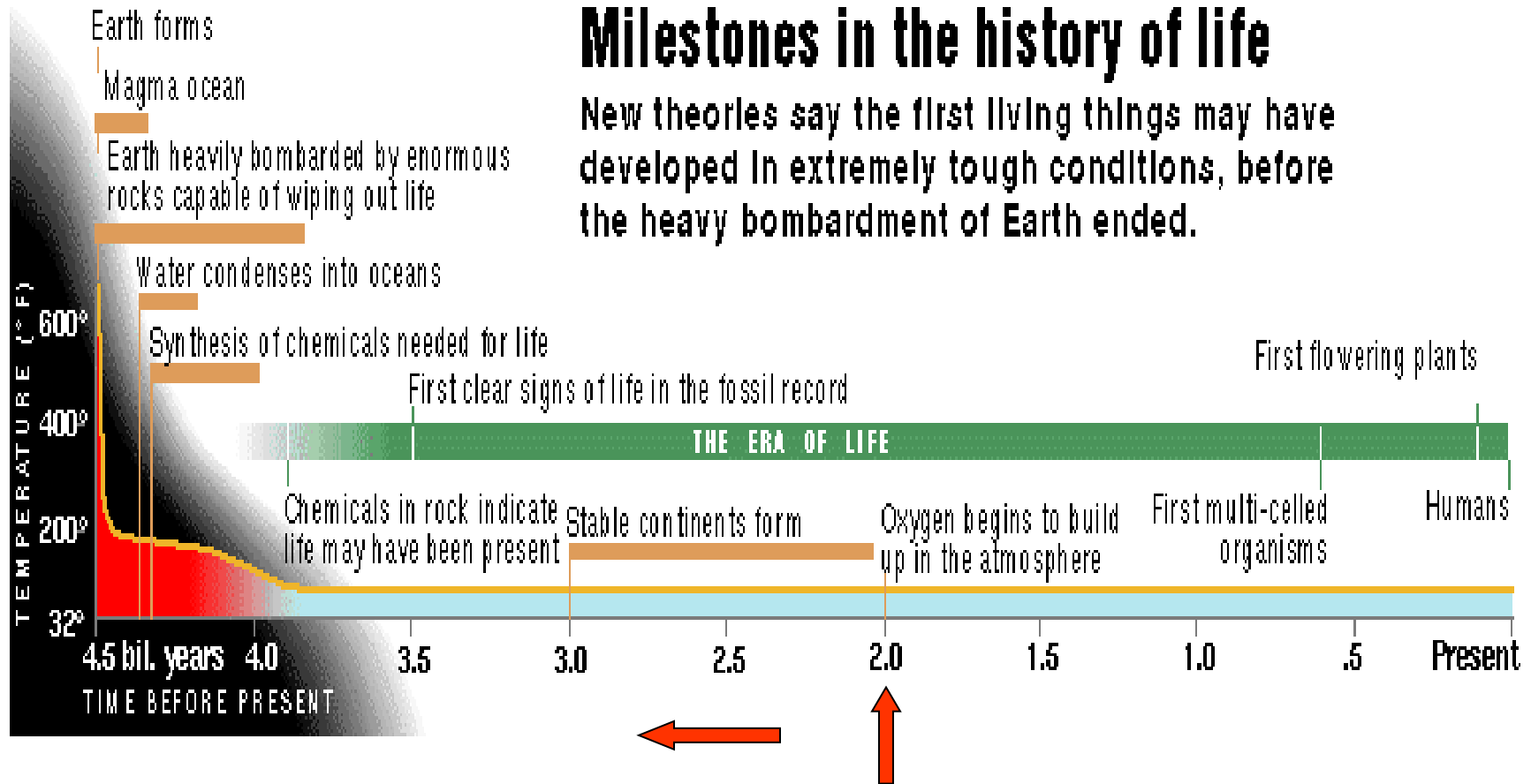
MLCT: $\epsilon \sim 500-15,000 \text{ M}^{-1} \text{ cm}^{-1}$

$\pi-\pi^*$: $\epsilon \sim 1000-100,000 \text{ M}^{-1} \text{ cm}^{-1}$

LMCT $\pi-\pi^*$

Formas de vida: anaeróbica → aeróbica

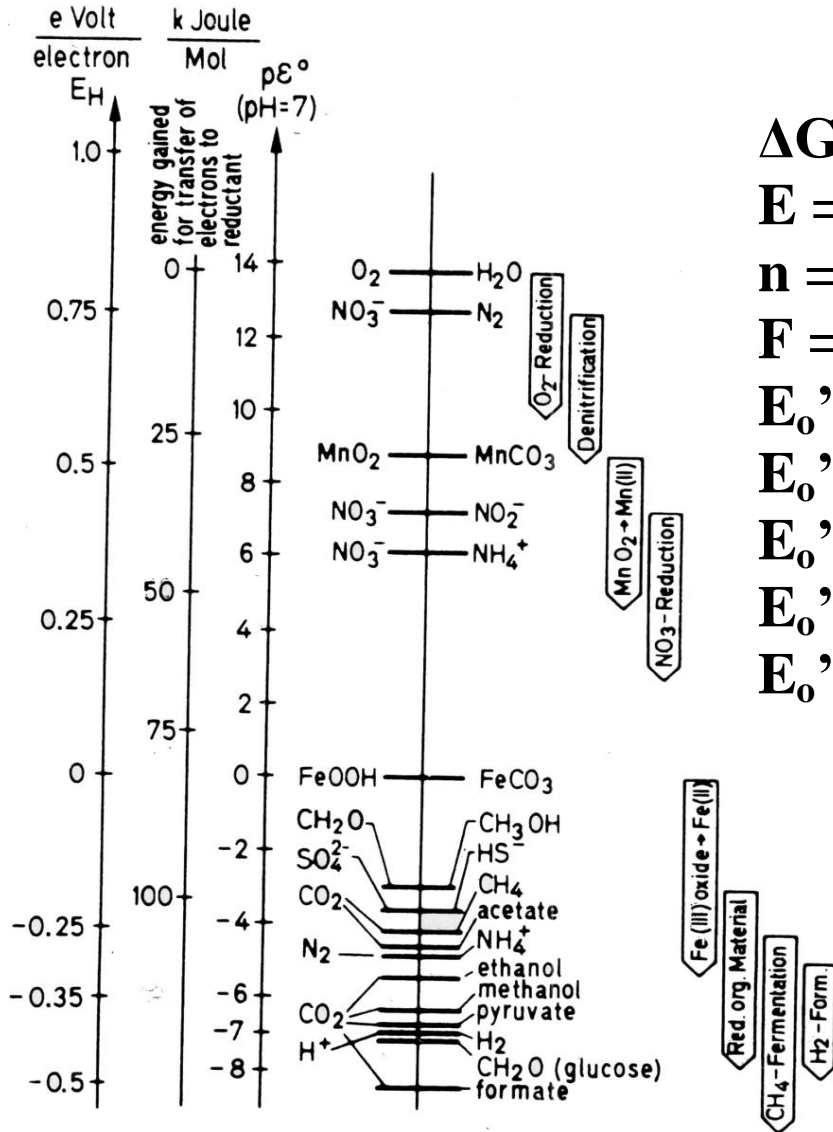
Condiciones anóxicas (-O₂) vs Condiciones óxicas (+O₂)



Metals, Microbes, Minerals: The Biogeochemistry of Life, P.M.H. Kroneck, M.E. Sosa Torres, Metal Ions in Life Sciences, Vol. 21, 2021

REDOX: Conservación de energía

Thauer et al., Bacteriol. Rev., 41, 100-180 (1977)



$$\Delta G_o' = - n \cdot F \cdot \Delta E_o'$$

$$E = E_o + 2.3 RT/nF \log_{10} ([OX]/[RED])$$

n = number of electrons transferred

F = Faraday constant, **R** = Gas constant)

E_o' H⁺/1/2H₂ = - 420 mV (H₂ 1.0 atm)

E_o' NAD⁺/NADH = - 320 mV

E_o' Cit. *c* ox/red + 220 mV

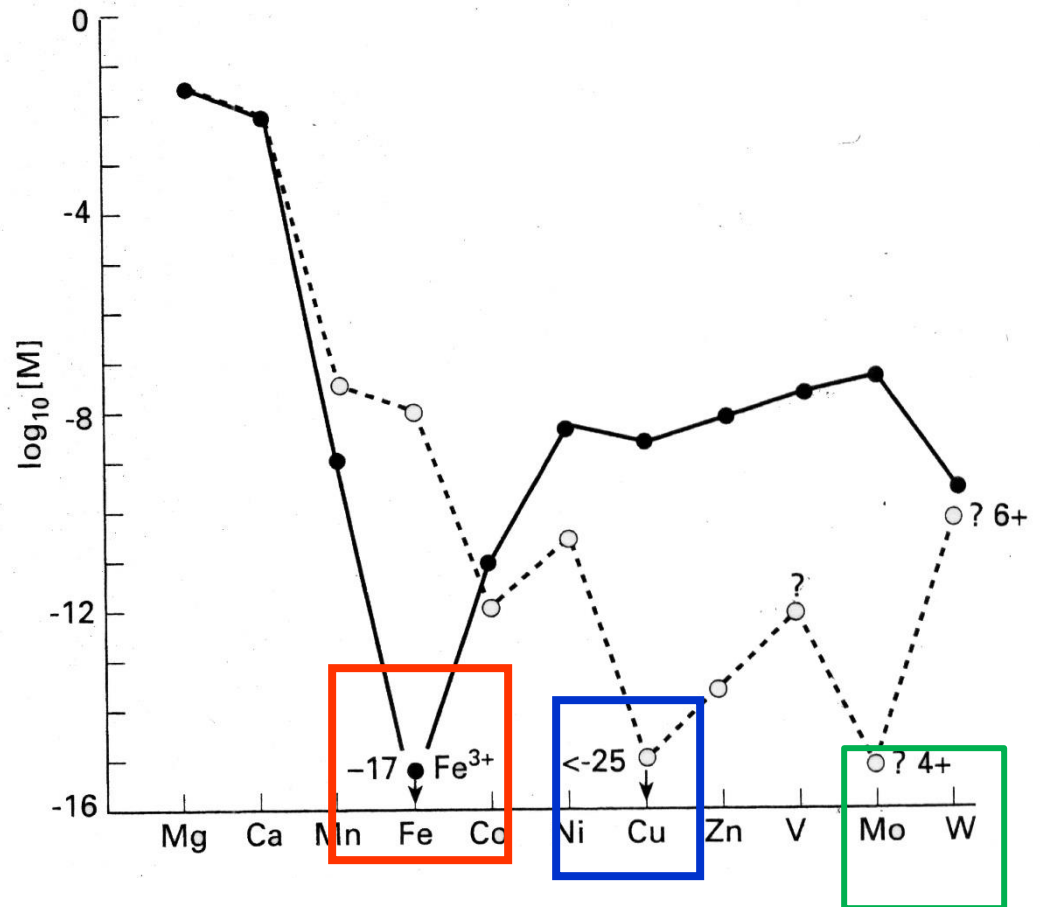
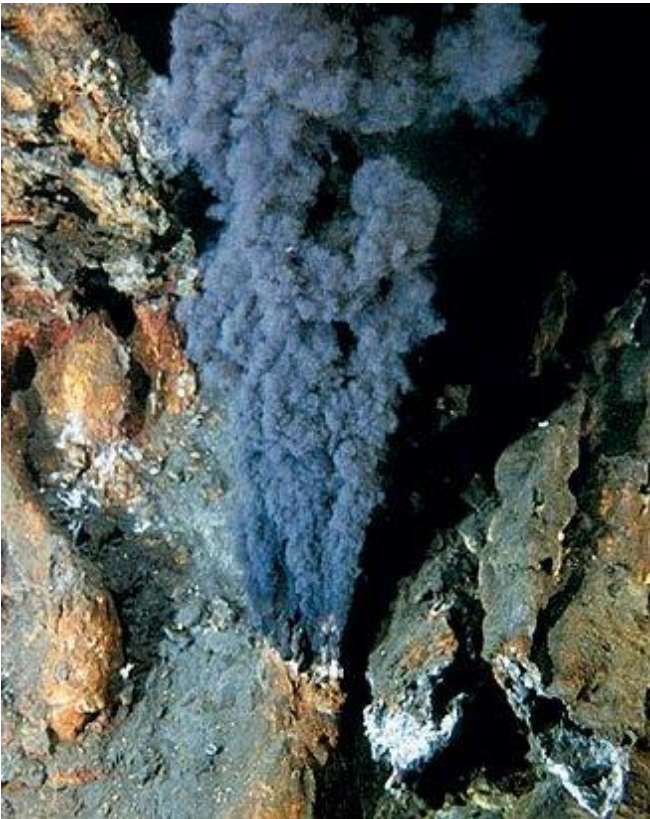
E_o' S^o/H₂S = - 240 mV

E_o' O₂(1.0 atm)/2H₂O (55 M) = + 820 mV

Biodisponibilidad de metales esenciales Fe, Cu, Mo, W

Solubilidad

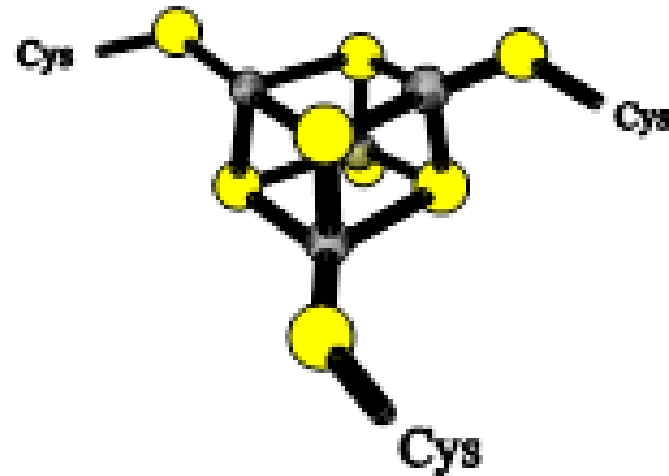
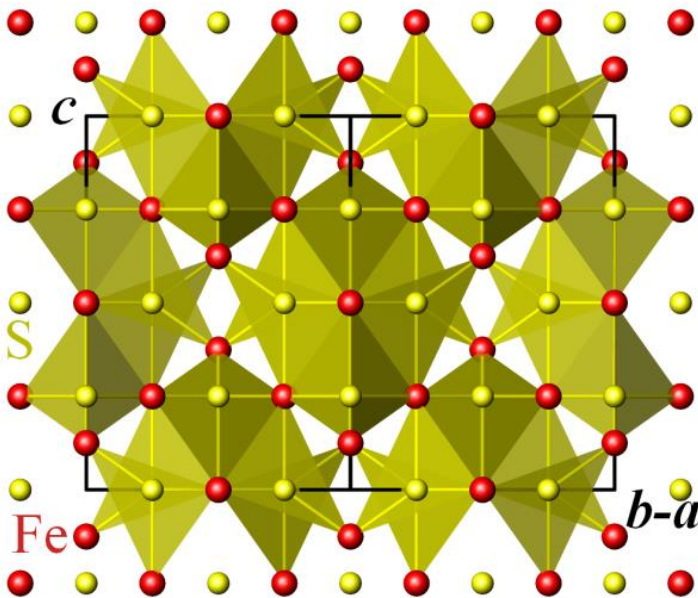
(free elements, in aerated - vs sulfidic sea --)



Catalizadores de vida temprana

Candidato para un catalizador: el mineral
Greigite $[\text{Fe}_3\text{S}_4]$ (Fe(II)Fe(III)₂ mineral)

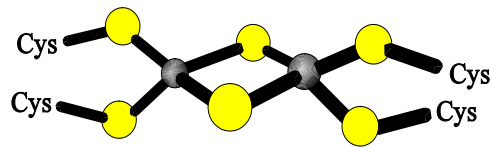
Nota: su estructura molecular es muy similar a la de la
unidad $[4\text{Fe}-4\text{S}]$ que se encuentra en las proteínas FeS



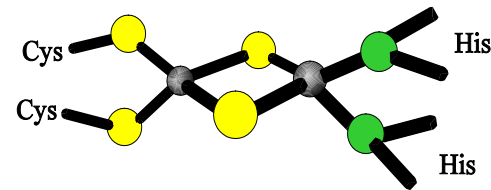
Basic [2Fe-2S] Centers

2 Types:

[2Fe-2S]-Cluster



**Plant type [2Fe-2S]
(Ferredoxin)**



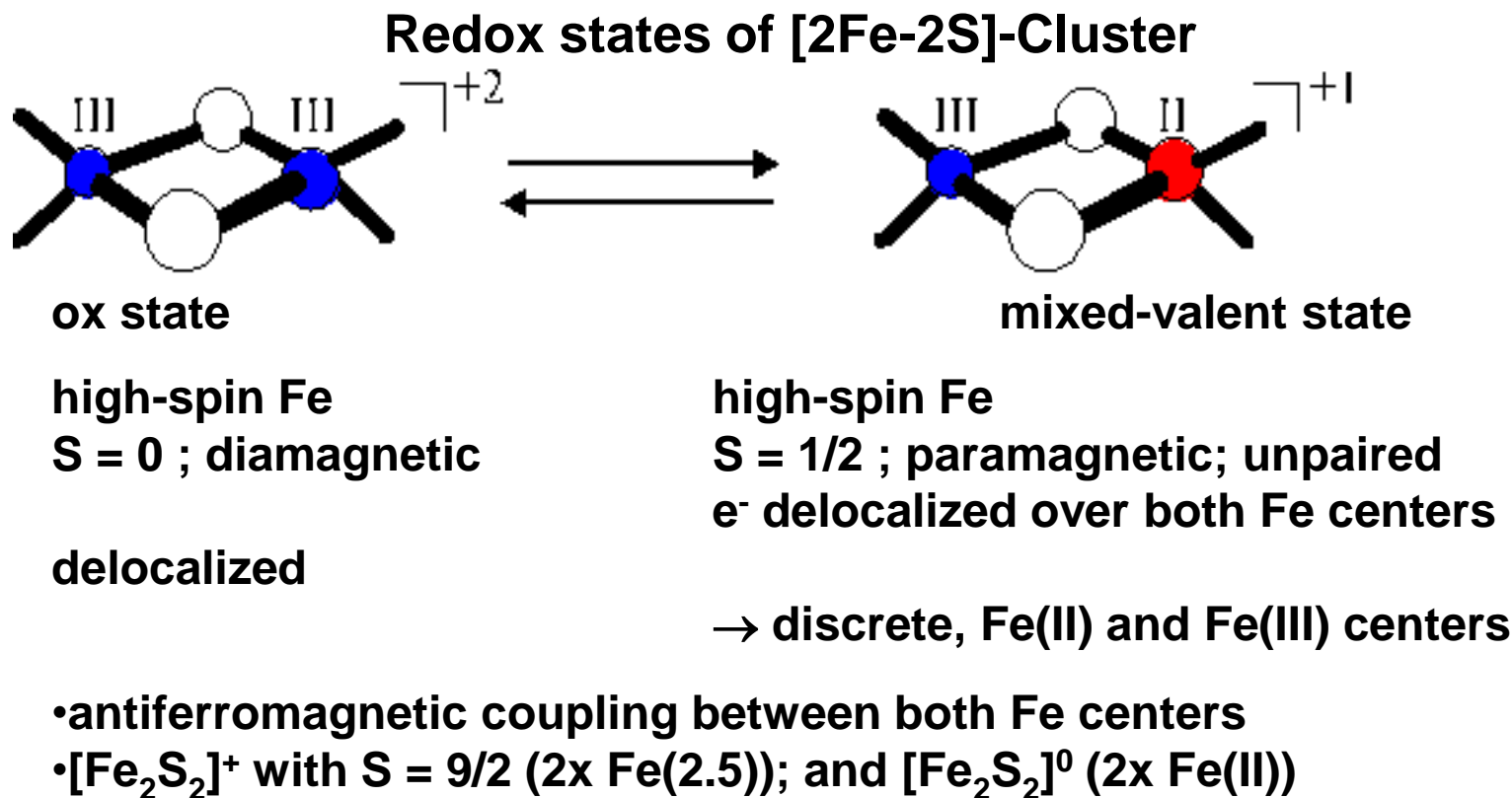
Rieske type [2Fe-2S]

2 tetrahedrally coordinated Fe-Atoms, bridged via 2 acid-labile, inorganic sulfur (S^{2-})

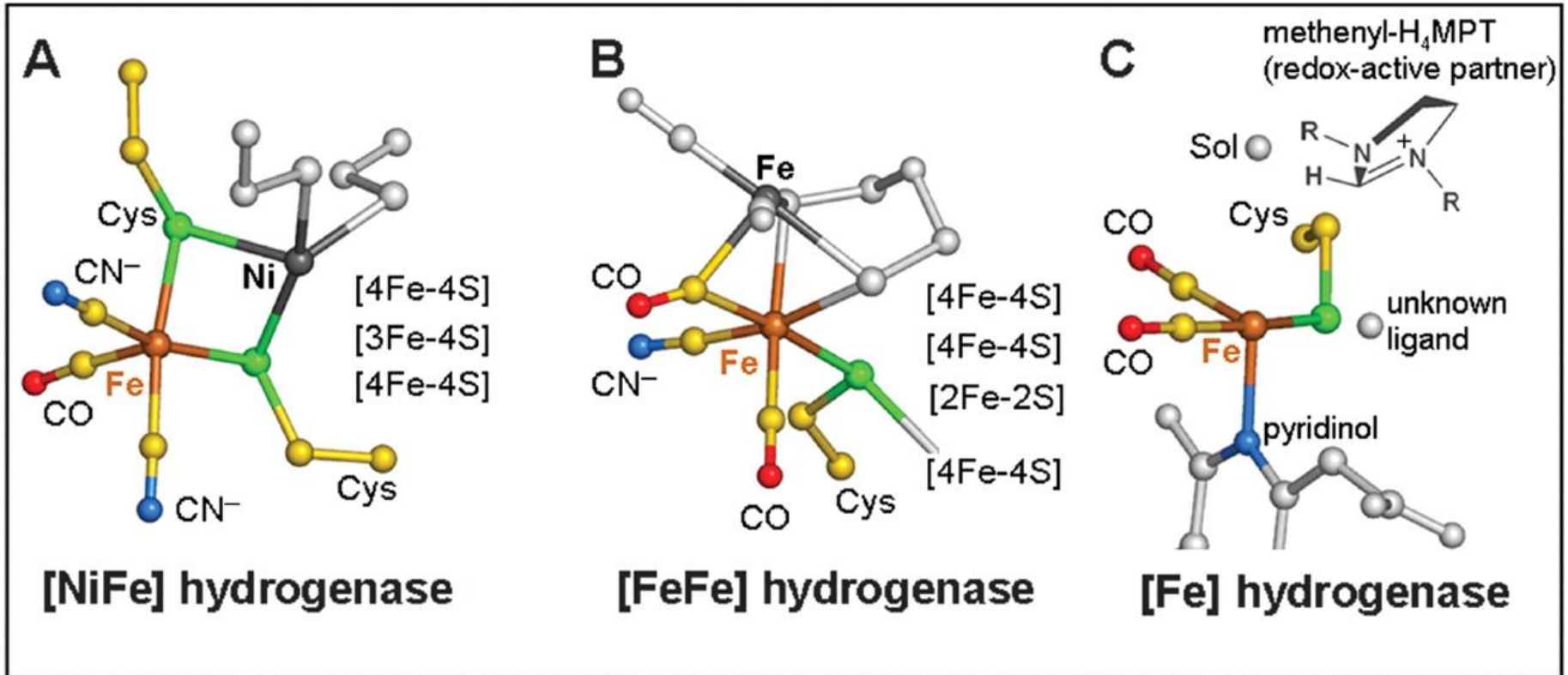
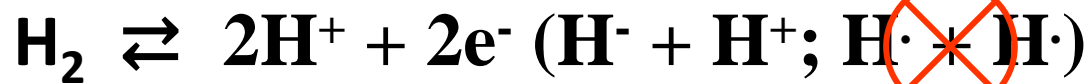
Xtal structures known

Redox potentials: -420 to 0 mV (Plant type), +150 to +350 mV (Rieske)

[2Fe-2S] FeS center

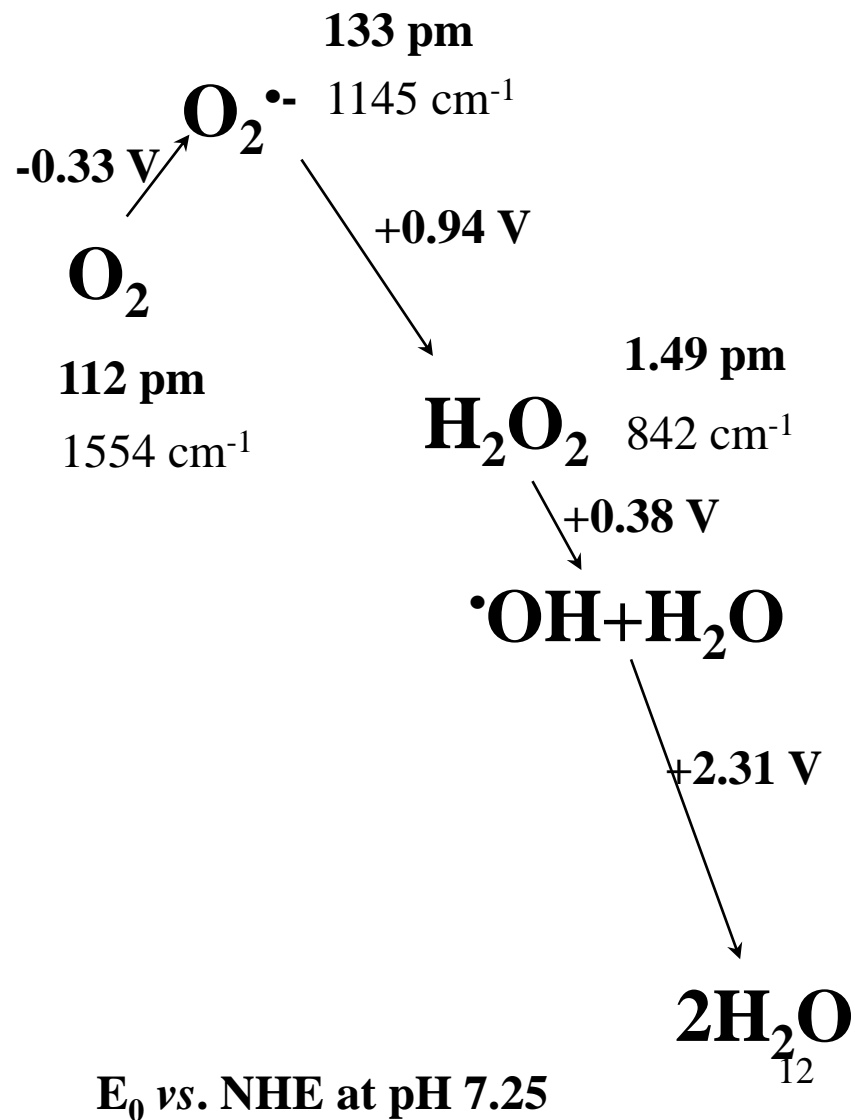
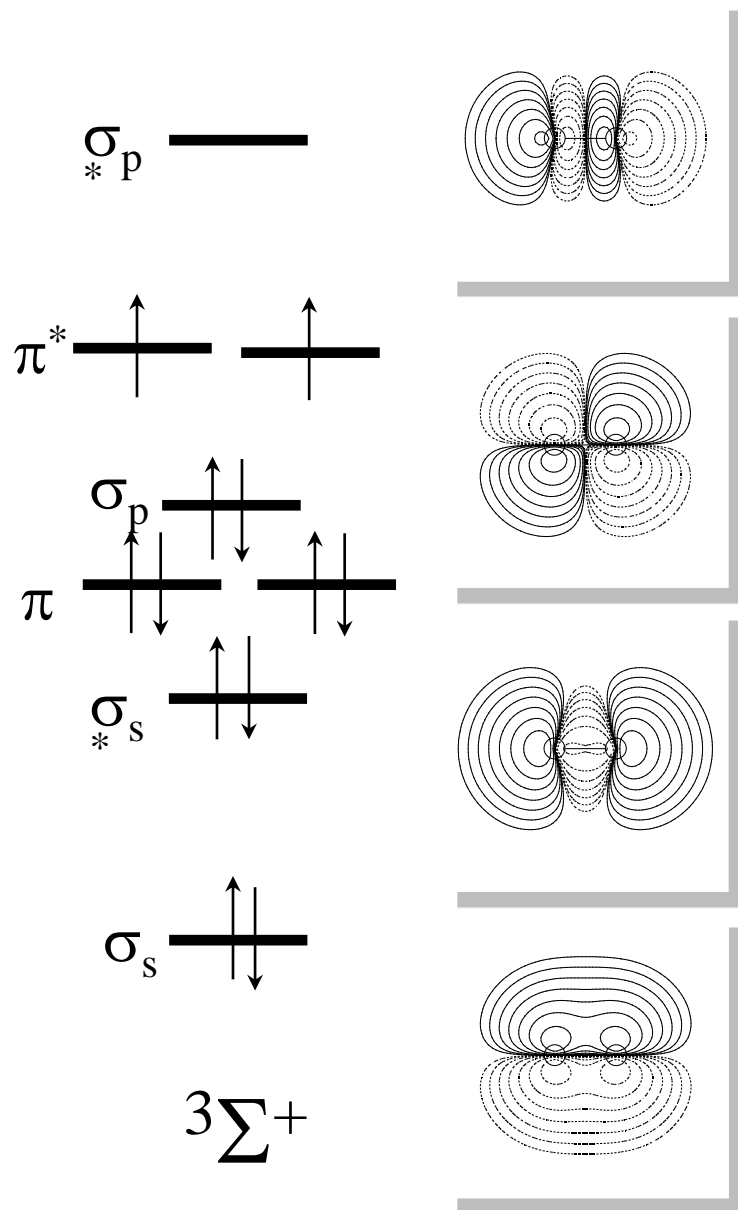


Dihidrógeno = combustible más simple



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

Activación de O₂



Proteínas Cu y Fe

Activación y transformación de O₂



Otto Heinrich Warburg (1883–1970), fue un fisiólogo, médico y premio Nobel alemán. Obtuvo dos doctorados en química y medicina, y ganó el Premio Nobel en 1931, por su investigación sobre la respiración celular, mostrando que el cáncer prospera en condiciones anaeróbicas (sin oxígeno) o ácidas. Fue uno de los principales bioquímicos del siglo XX. Fue nominado tres veces sin precedentes para el premio Nobel por tres logros separados.

"El cáncer, por encima de todas las demás enfermedades, tiene innumerables causas secundarias. Pero, incluso para el cáncer, solo hay una causa principal. Resumido en pocas palabras, la causa principal del cáncer es el reemplazo de la respiración de oxígeno en las células normales del cuerpo por una fermentación de azúcar.

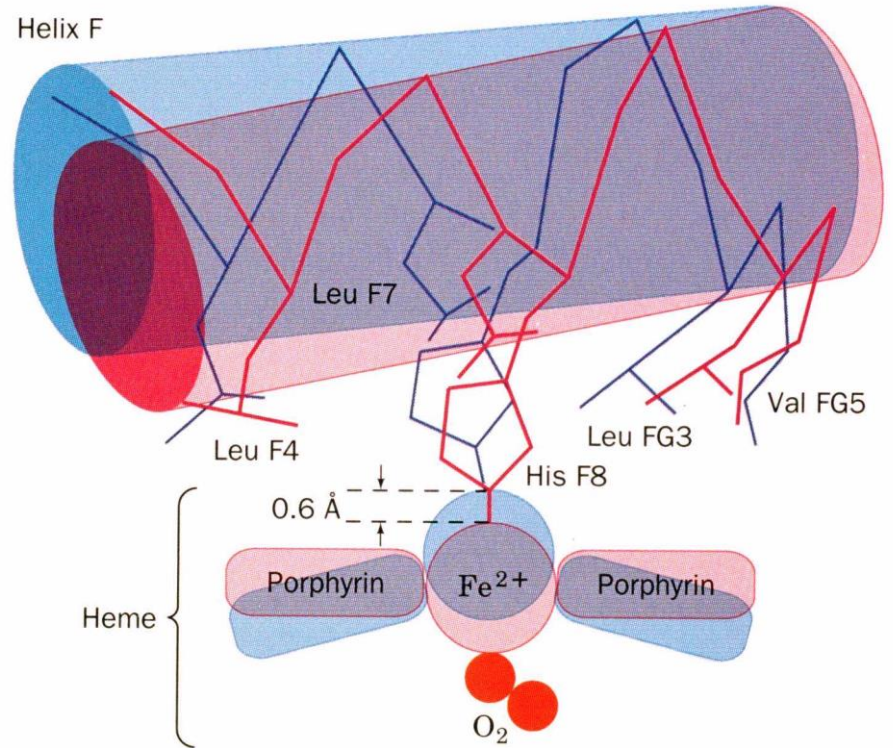
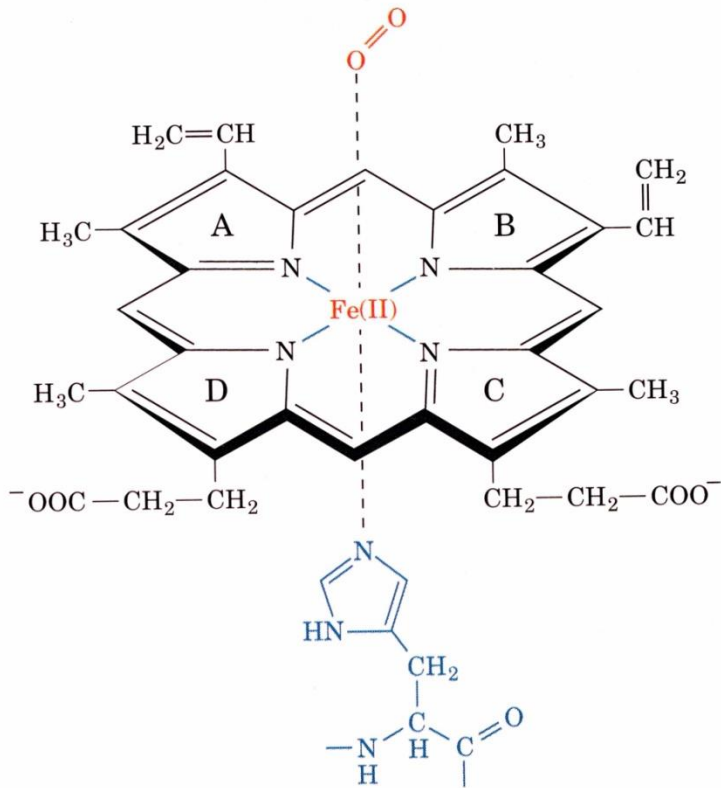
O. Warburg (1956), "On the origin of cancer cells", *Science* 123, 309–14

Otto H. Warburg
Nature Reviews (2011)
11, 325

Activación de O₂ – Tipos de reacción

- **Reversible binding of O₂ – Myoglobin, Hemoglobin (Fe), Hemocyanin (Cu-Cu)**
- **O₂^{•-} dismutation – Superoxide Dismutase (Mn, Fe, Ni, Cu, Zn)**
$$\text{O}_2^{\cdot-} + \text{O}_2^{\cdot-} + 2\text{H}^+ \rightarrow \text{O}_2 + \text{H}_2\text{O}_2$$
- **H₂O₂ decomposition – Catalase (Mn, heme-Fe)**
$$2 \text{H}_2\text{O}_2 \rightarrow 2 \text{H}_2\text{O} + \text{O}_2$$
- **Oxygenases R-H + O₂ + NADPH + H⁺ → R-OH + H₂O + NADP⁺**
- **Oxidases (2-electron reduction to H₂O₂; Fe, Cu)**
$$\text{O}_2 + 2\text{e}^- + 2\text{H}^+ \rightarrow \text{H}_2\text{O}_2$$
- **Oxidases (4-electron reduction to H₂O; heme-Fe, Cu)**
$$\text{O}_2 + 4\text{e}^- + 4\text{H}^+ \rightarrow 2 \text{H}_2\text{O}$$
 (focus on Cu enzyme Ascorbic Acid Oxidase and Fe,Cu enzyme Cytochrome *c* Oxidase)

Unión reversible de O₂ Mioglobina y Hemoglobina



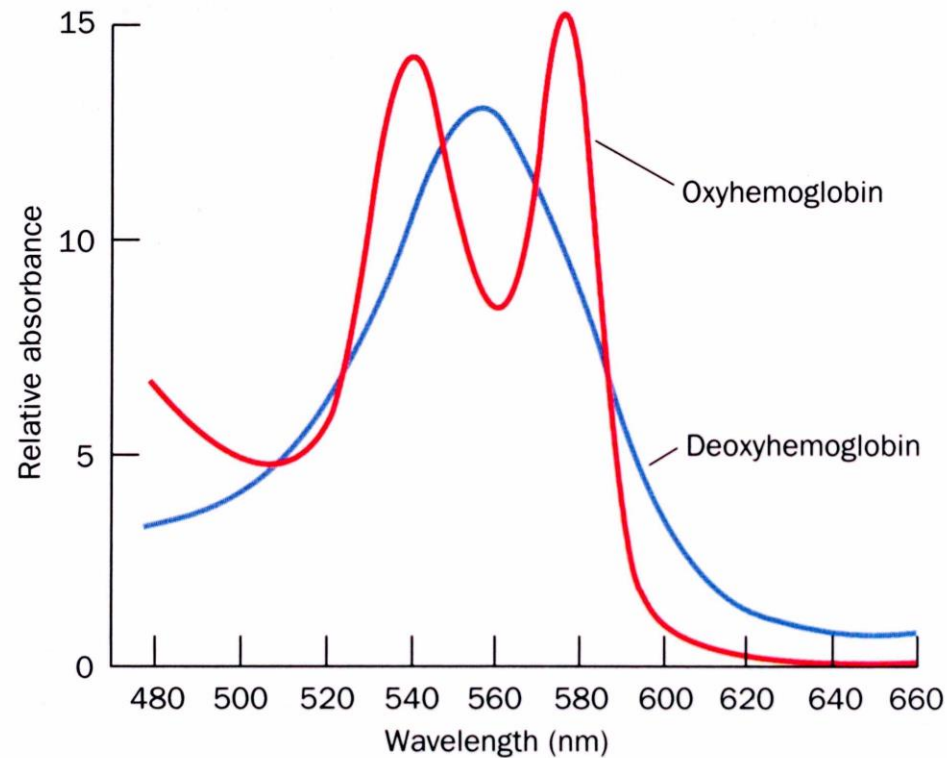
The Fe must be in the Fe(II) (ferrous oxidation) state

La unión de O₂ reorganiza la distribución electrónica y altera la energía orbital d.

Esto causa una diferencia en los espectros de absorción:

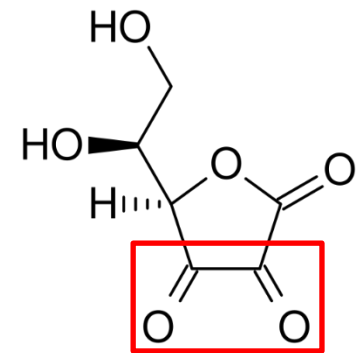
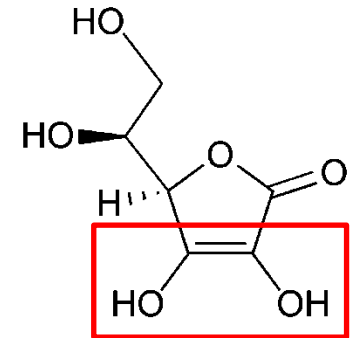
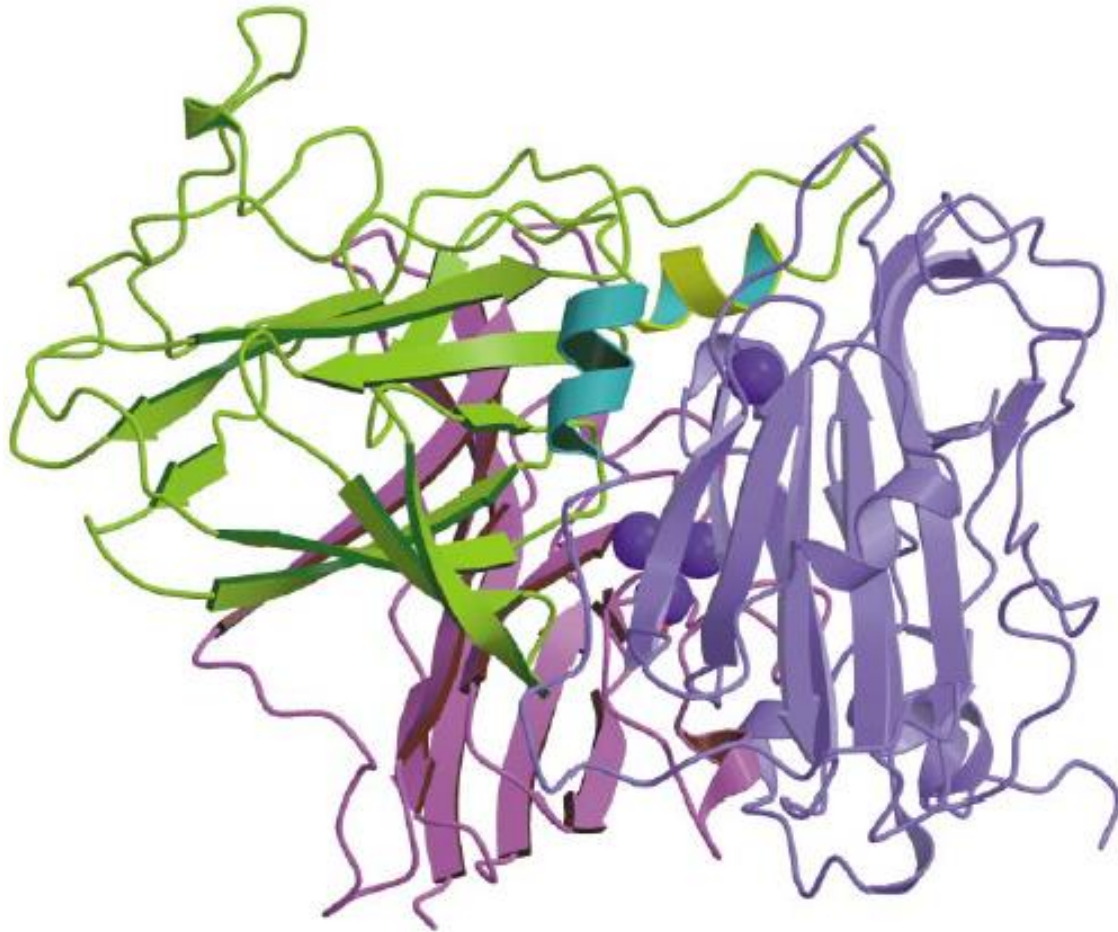
Deoxy Hb, Oxy Hb

La medición de la absorción a 578 nm permite un método fácil para determinar el porcentaje de O₂ unido a la hemoglobina.



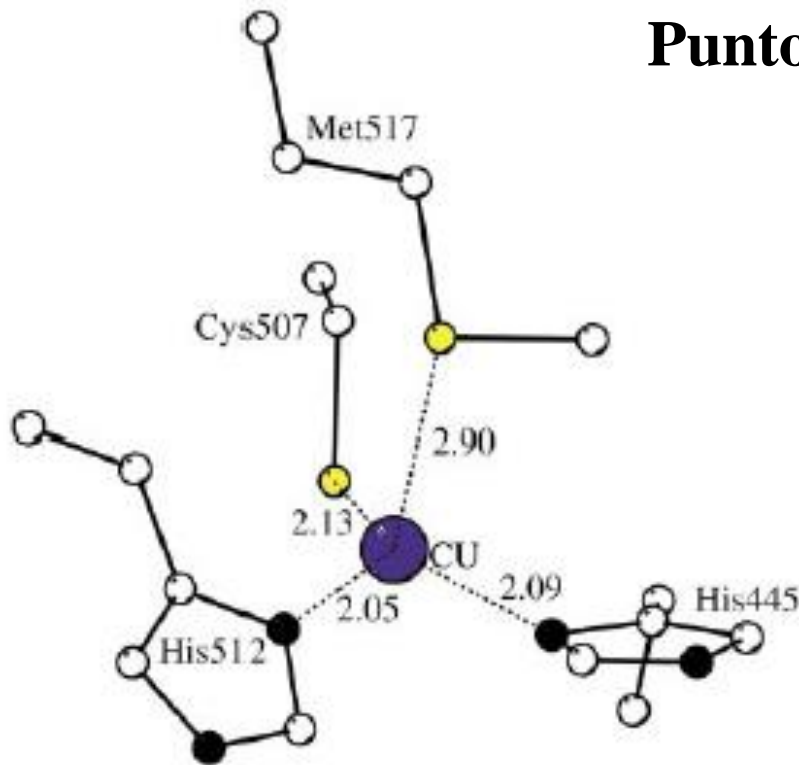
Ácido ascórbico (Vitamina c) Oxidasa

Multi-Copper oxidase (8Cu/homodimer) PDB code 1AOZ

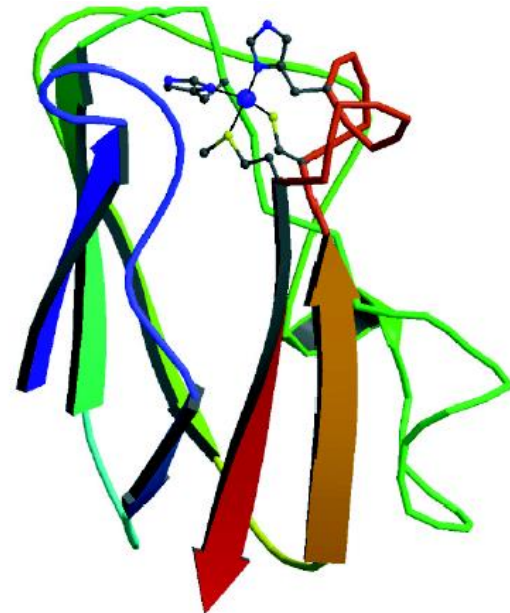


Type 1 Cu ET center (como en Plastocyanin) T.

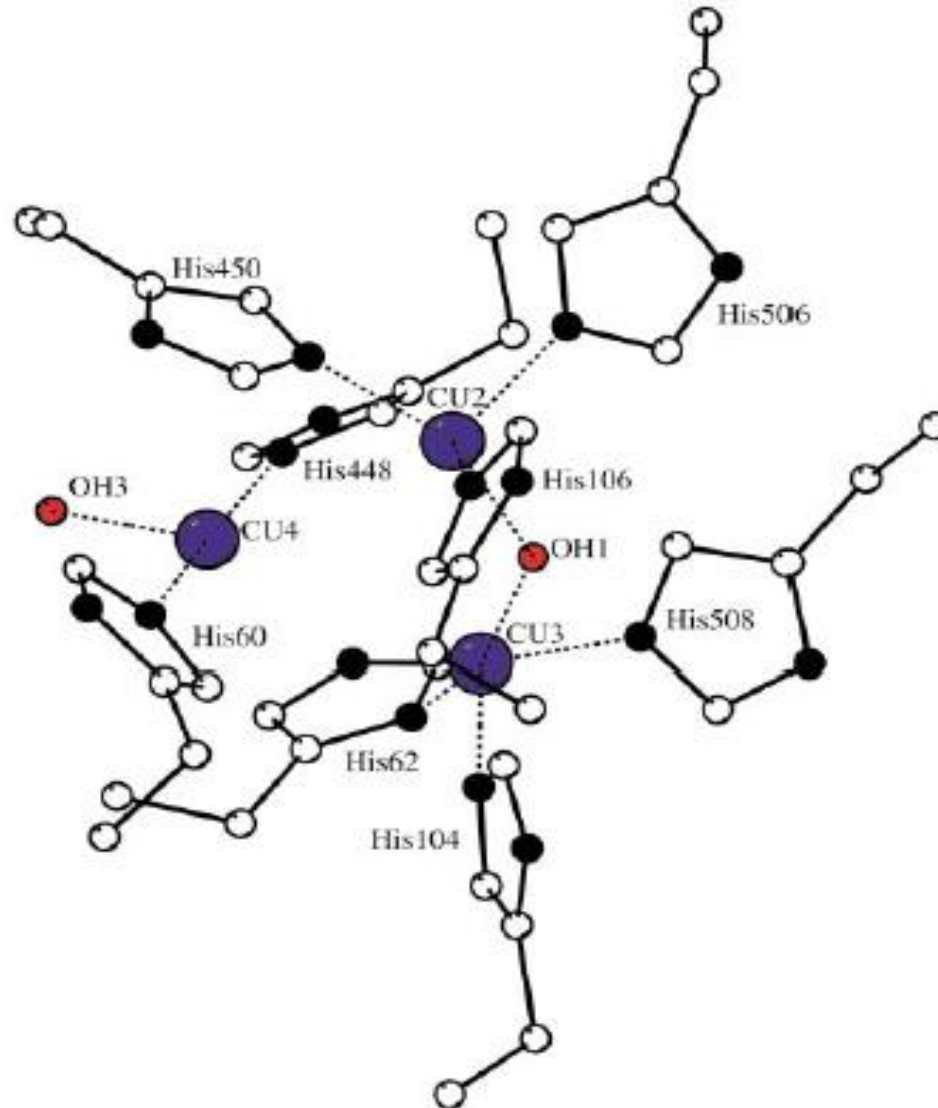
Arcos-Lopez, N. Schuth, L. Quintanar, in Transition Metals and Sulfur: A Strong Relationship For Life, M.E. Sosa Torres, P.M.H. Kroneck, METAL IONS IN LIFE SCIENCES, Vol. 20, 2020



Punto de entrada para electrones



Trinuclear Cu center - Sitio de reducción de O₂ a H₂O



Cytochrome *c* oxidase

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

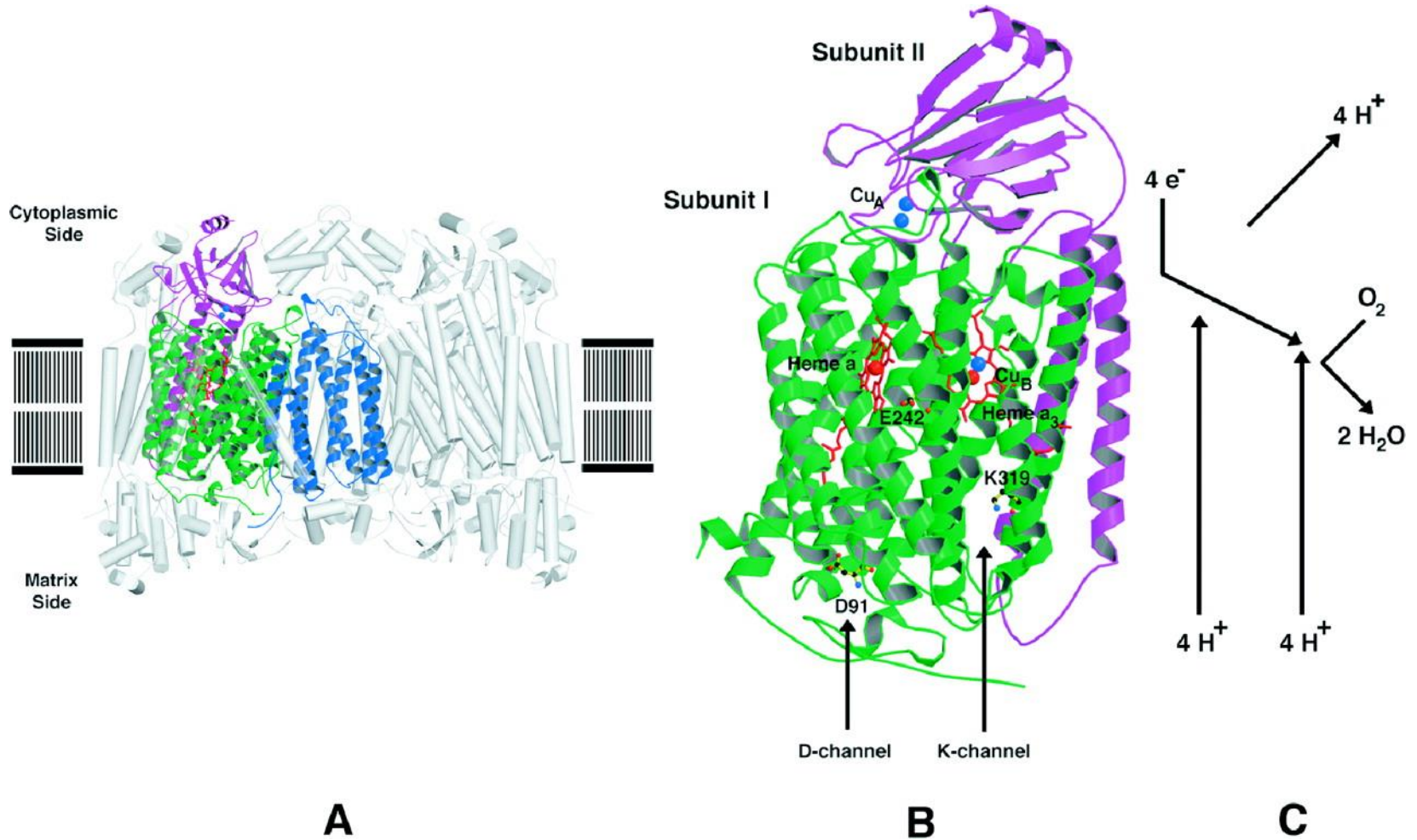
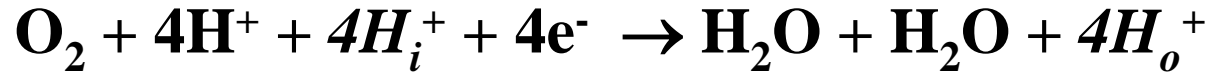


metals (CuA, Fe-heme, Mg, Zn)

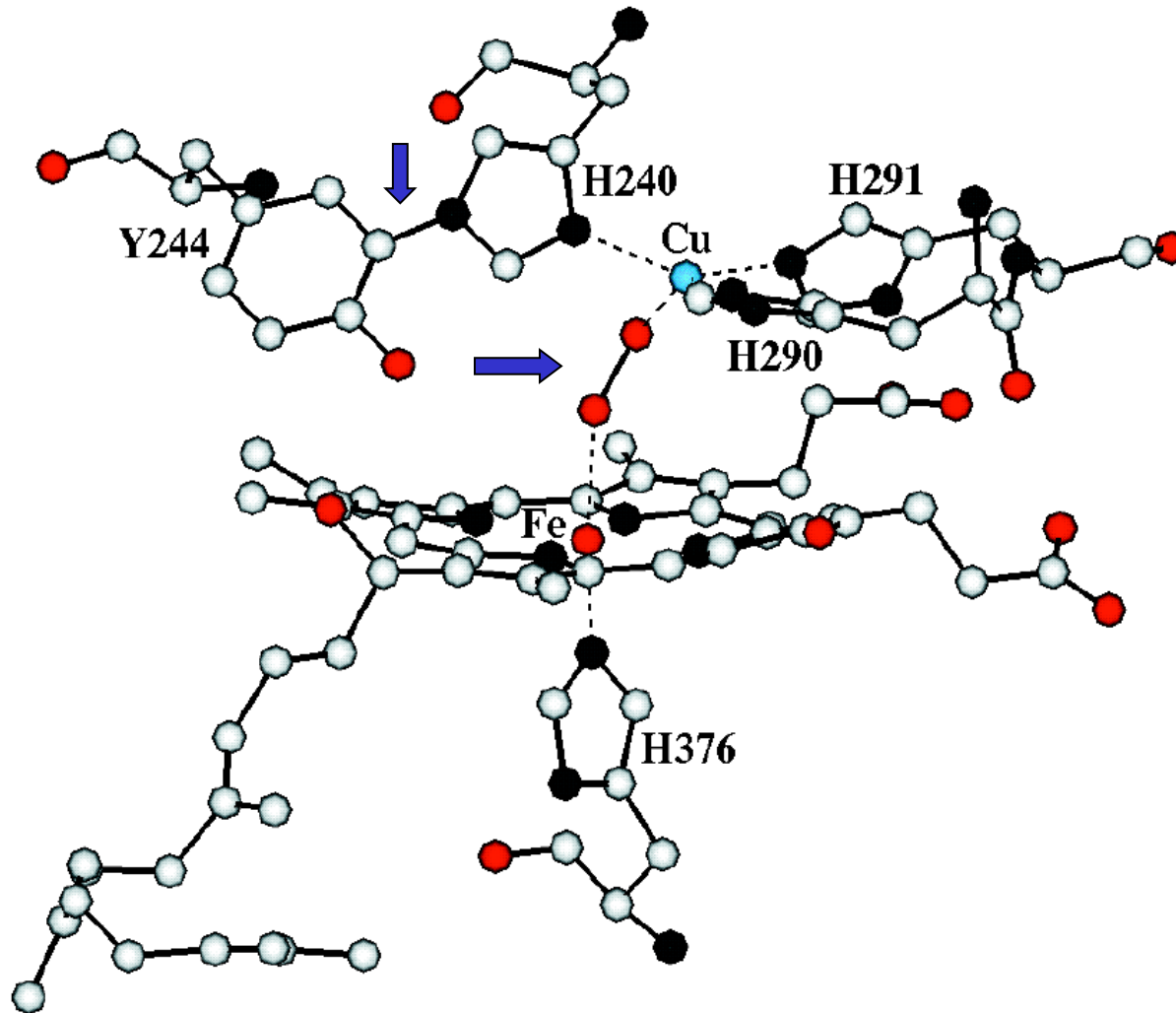
e^- transfer (redox; tyrosyl radical ?), H^+ transfer (pump)

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

Cytochrome *c* oxidase



Sitio de reducción de O_2 (Fe(III)-Cu(II) State – covalent link Tyr-His)



Catálisis heterogénea

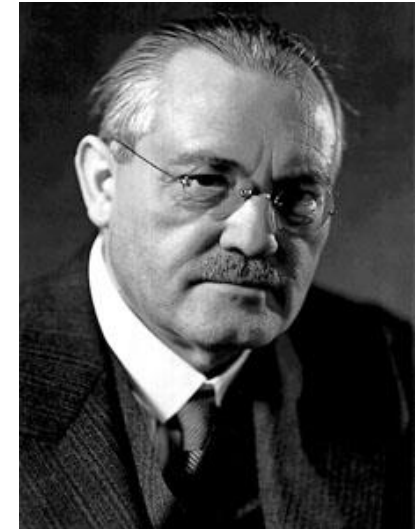
Cómo escindir compuestos cinéticamente estables



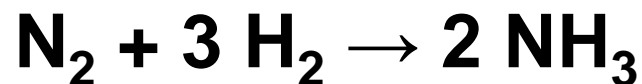
Fritz Haber
1868 - 1934
Nobel Prize 1918



Gerhard Ertl, Fritz-Haber Institute Berlin
(Nobel Laureate/Chemistry/2007)

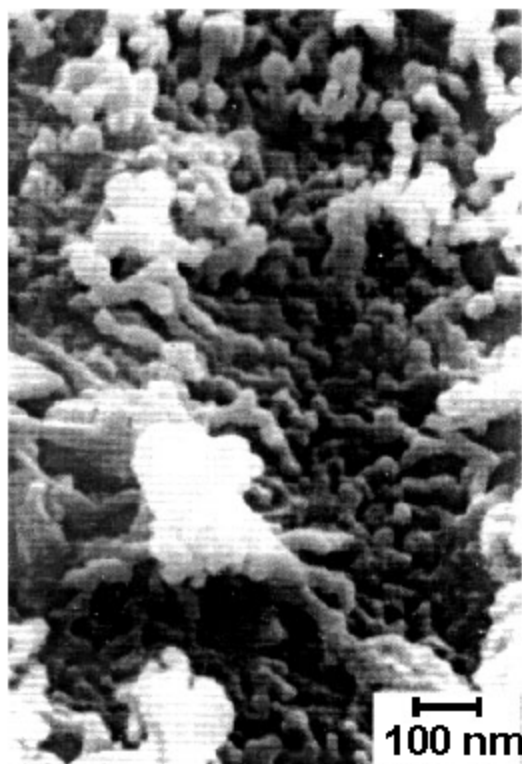


Carl Bosch
1874 - 1940
Nobel Prize 1931



Catalytic synthesis of ammonia

(Haber- Bosch process)



Technical conditions: $T \approx 400^\circ\text{C}$, $p \approx 300$ bar
promoted iron catalyst

BASF S6-10 catalyst (at. %)

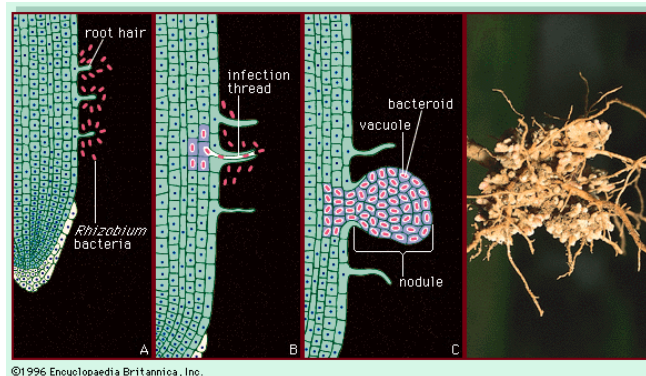
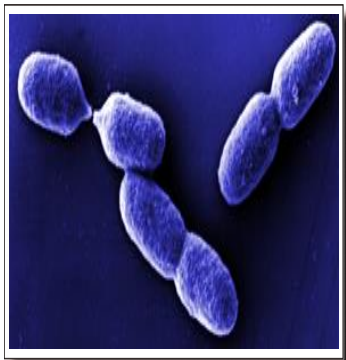
	Fe	K	Al	Ca	O
Bulk composition	40.5	0.35	2.0	1.7	53.2
Surface –					
unreduced	8.6	36.2	10.7	4.7	40.0
reduced	11.0	27.0	17.0	4.0	41.0
cat. active spot	30.1	29.0	6.7	1.0	33.2

Fijación biológica N₂

Los microorganismos pueden hacer el trabajo en "condiciones normales" (T, P)

- free living soil bacteria, e.g. *Azotobacter vinelandii*
- Cyanobacteria with specialized cells, e.g. *Anabaena sp.*, *Nostoc sp.*)
- *Rhizobia* which live in special plant organelles (root noudles)

The process, however, is costly. Plants have to deliver up to 25% of their photosynthetically produced ATP to N₂ fixing bacteria in the root nodules.



Note: N₂ Fixation is done by anaerobes.

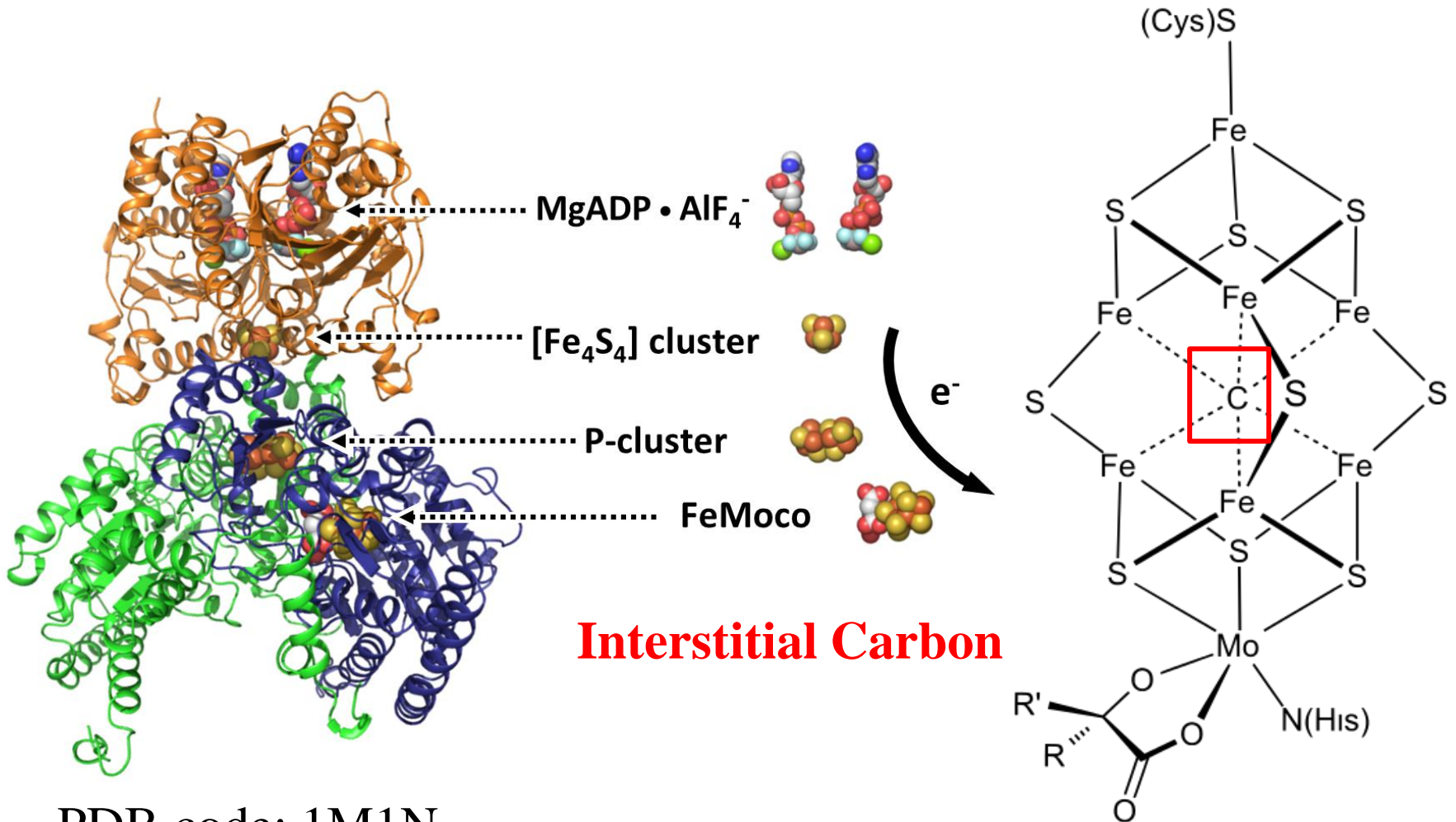
N₂ Fixation

<http://en.wikipedia.org/wiki/Nitrogenase>



Elementos estructurales básicos de la nitrogenasa

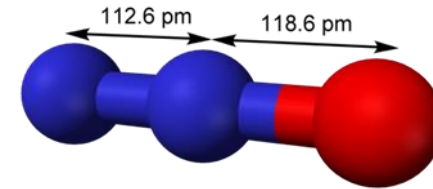
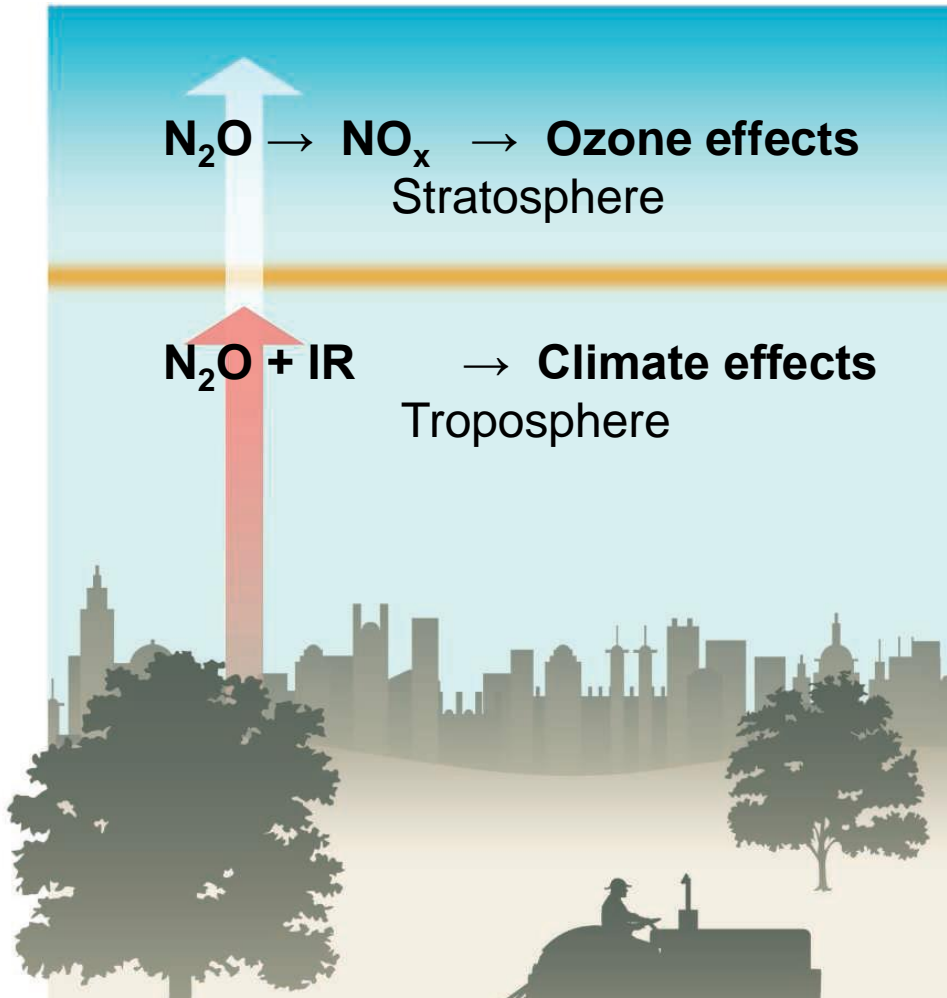
Hu, Ribbe, Acc. Chem. Res. (2010), 43, 475-484; Ramaswamy, Science (2011), 334, 914-915



PDB code: 1M1N

N₂O – Potente gas de efecto invernadero

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



Steady increase in the atmosphere

3rd only to CO₂ and CH₄

N₂O is isoelectronic to CO₂

green-house effect of N₂O/CO₂ ~ 200

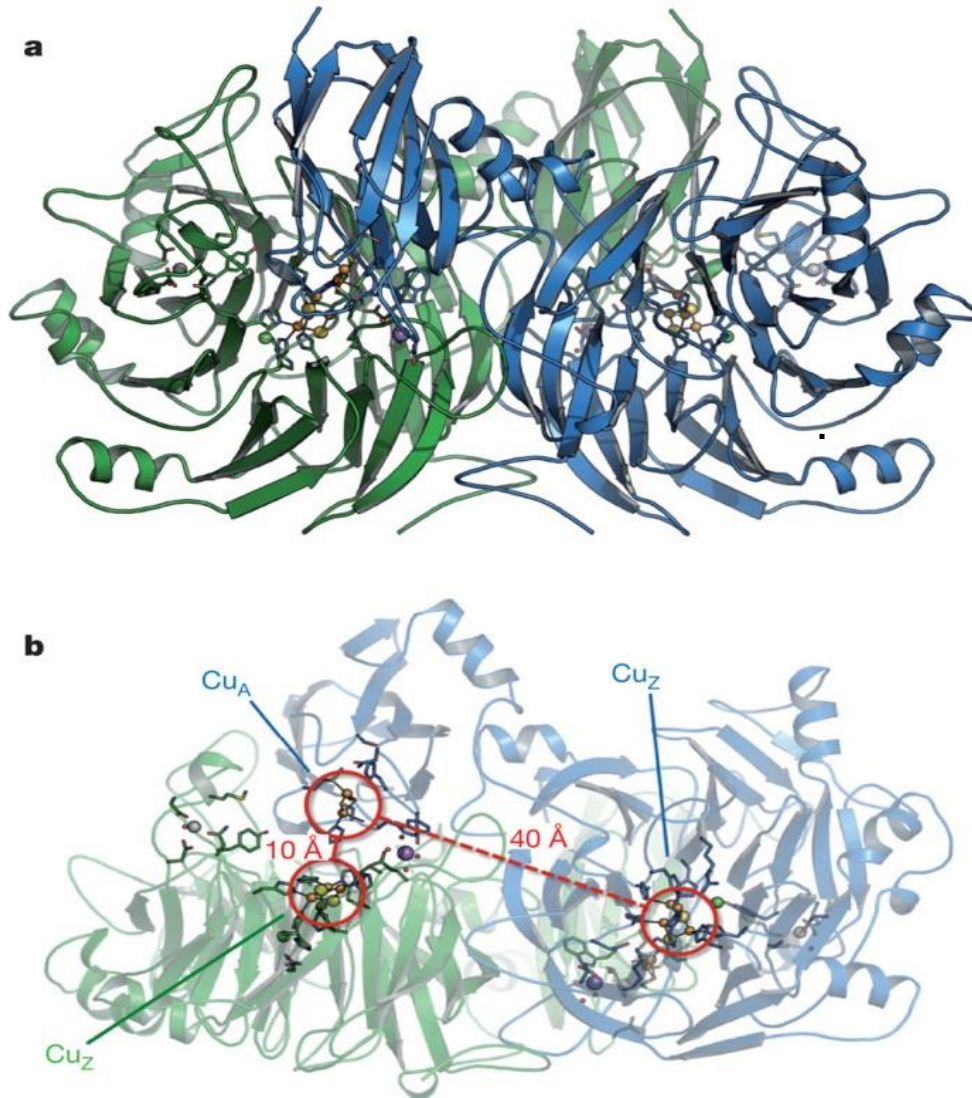


<http://epa.gov/climatechange/emissions/usinventoryreport.html>

Nitrous Oxide Reductase es un *head-to-tail* homodímero

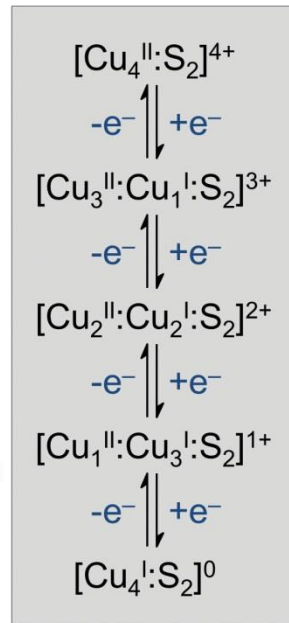
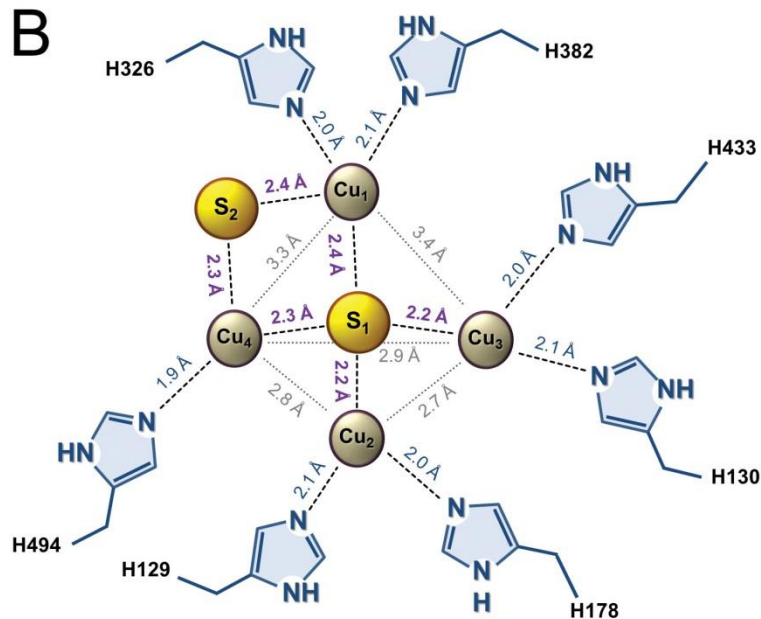
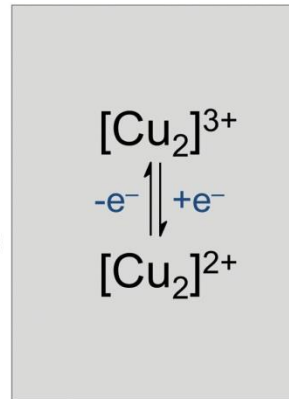
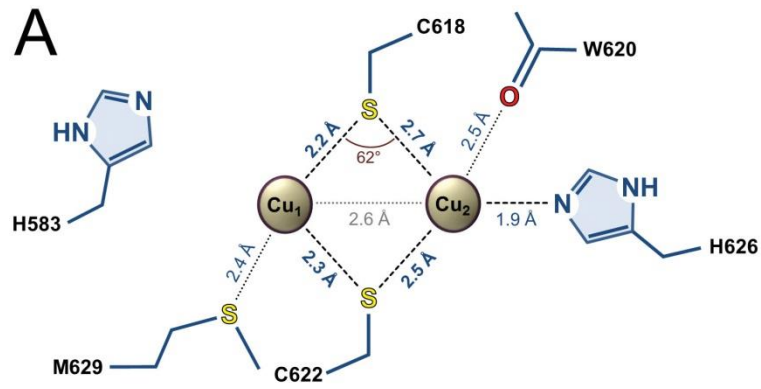
6 Cu/monómero

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



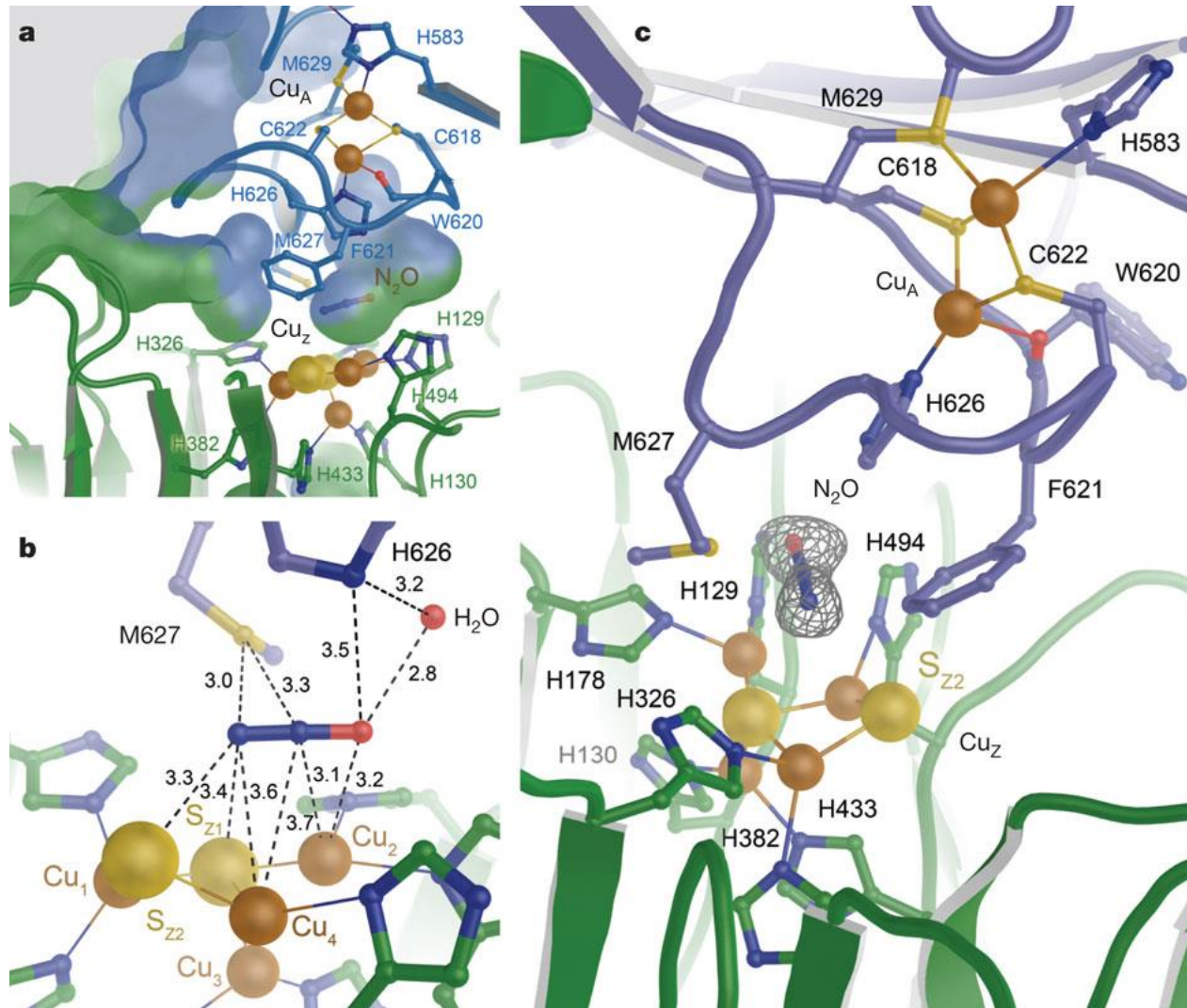
Dos nuevos sitios de cobre-azufre

(A) dinuclear CuA, (B) tetranuclear CuZ

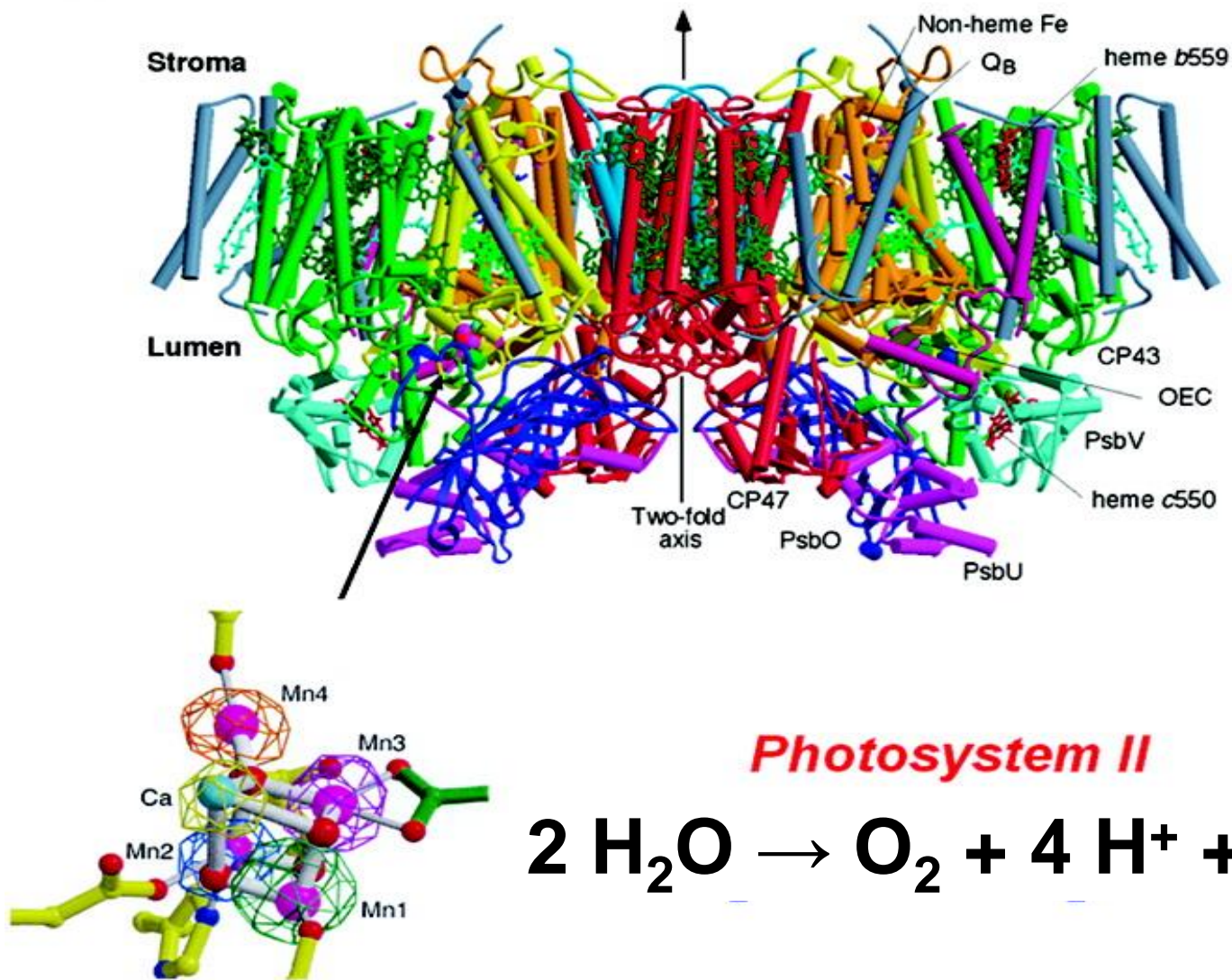


Catálisis: CuA y CuZ operan en concierto

Xtal under N₂O pressure



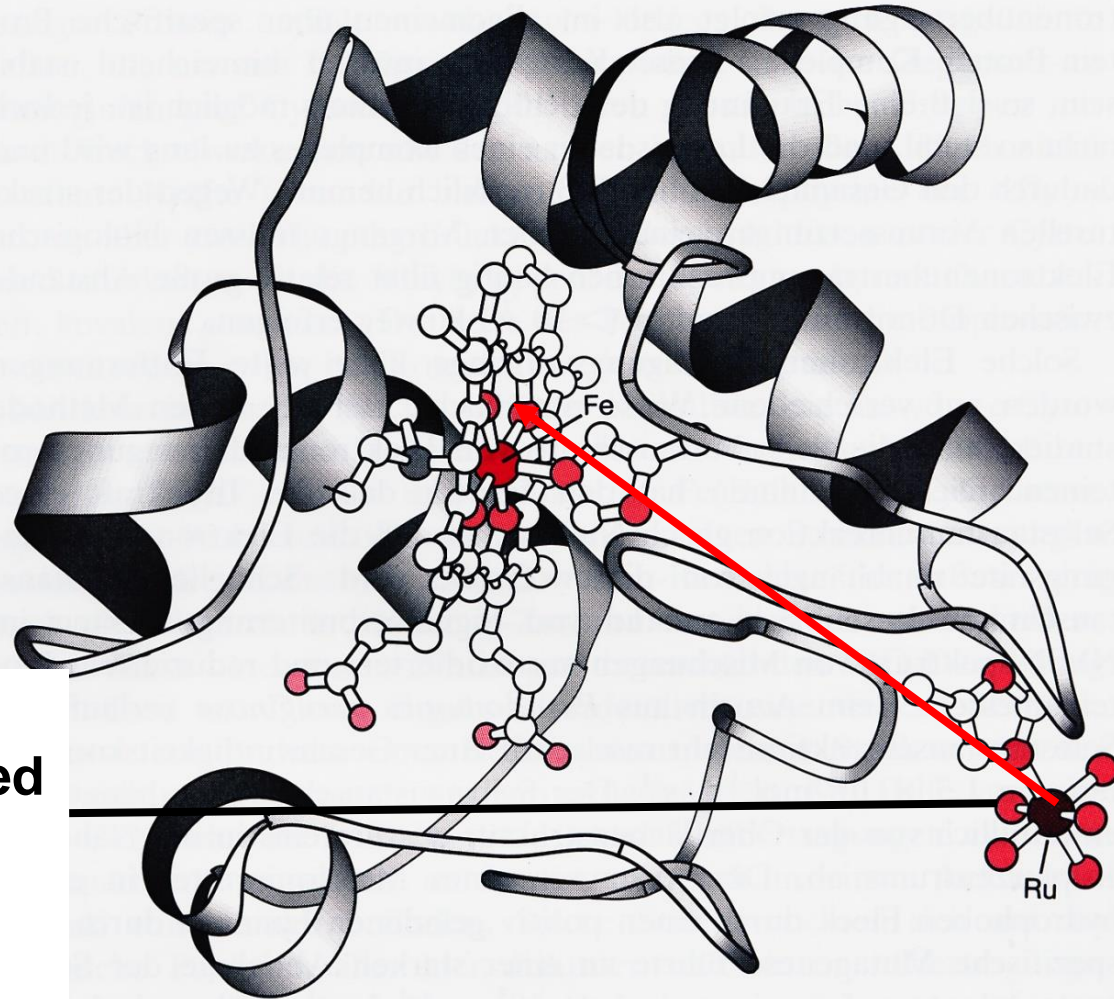
El complejo evolutivo de O₂ – División de H₂O en un centro catalítico de CaMn₄O₅



Transferencia de electrones a través de la matriz de proteínas

Nature of biological electron transfer, Moser, Keske, Warncke, Farid, Dutton,
NATURE (1992), 355, 796-802

**Ru-Complex
covalently attached
to Fe protein
cytochrome c**

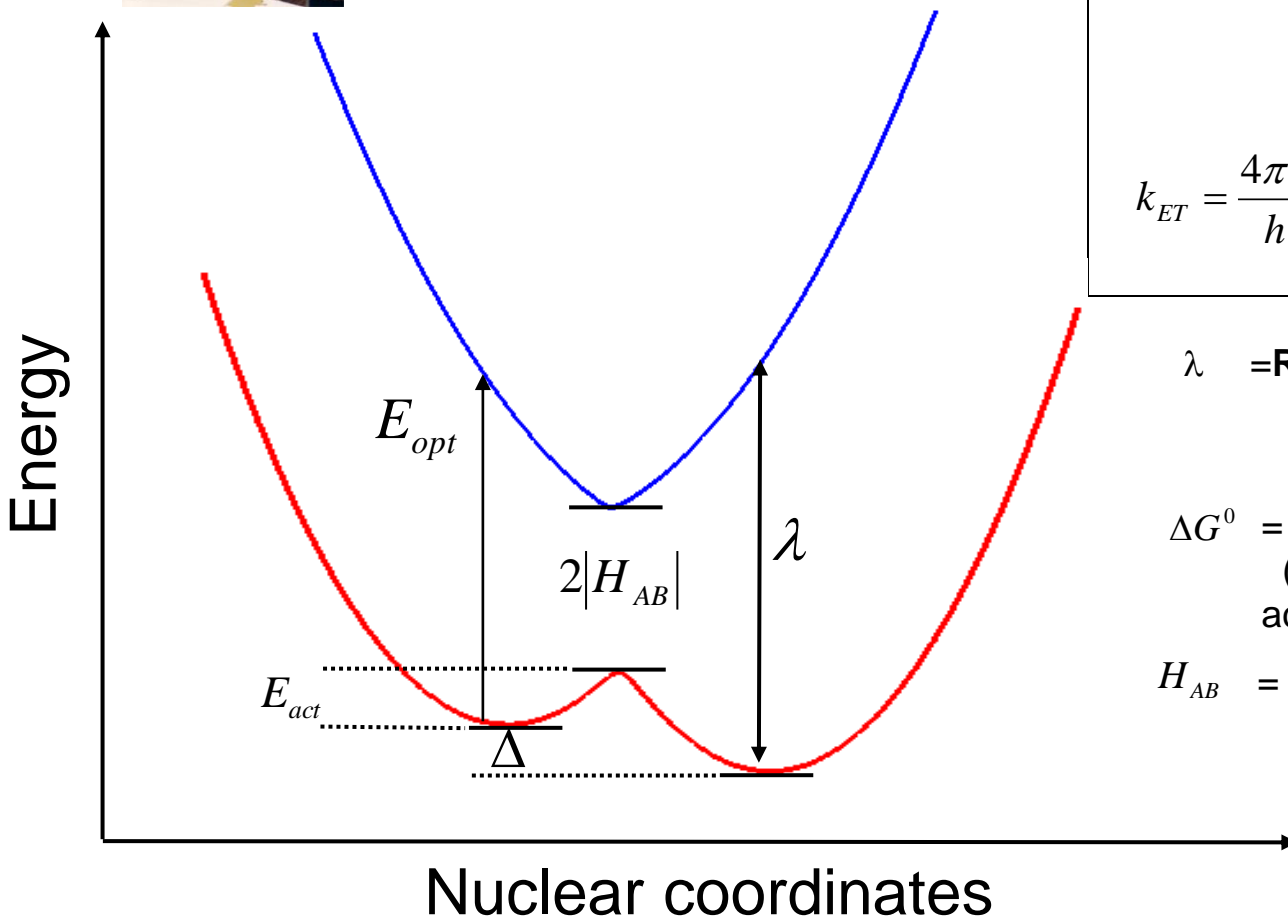


Transferencia de electrones: Teoría de Marcus



RA Marcus Nobel Prize Chemistry 1992

<https://www.nobelprize.org/prizes/chemistry/1992/marcus/lecture/>



$$A_{ox} + B_{red} \rightarrow A_{red} + B_{ox}$$

$$k_{ET} = \frac{4\pi^2}{h} \underbrace{(4\pi\lambda kT)^{-1/2} e^{-\left(\frac{(\Delta G^0 - \lambda)^2}{4\lambda kT}\right)}}_{\text{"Franck-Condon Factor"}} \underbrace{H_{AB}^2}_{\text{"Electronic Factor"}}$$

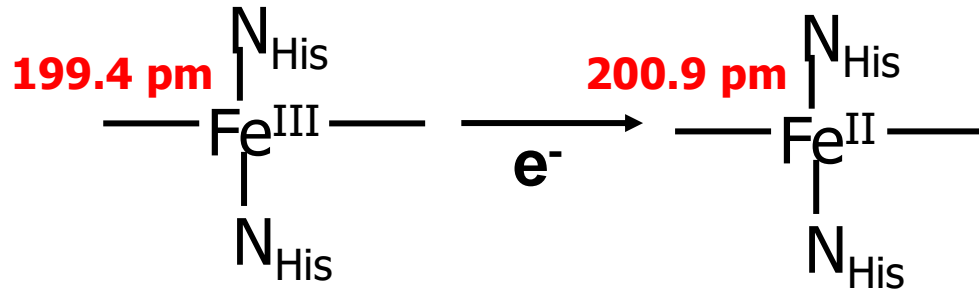
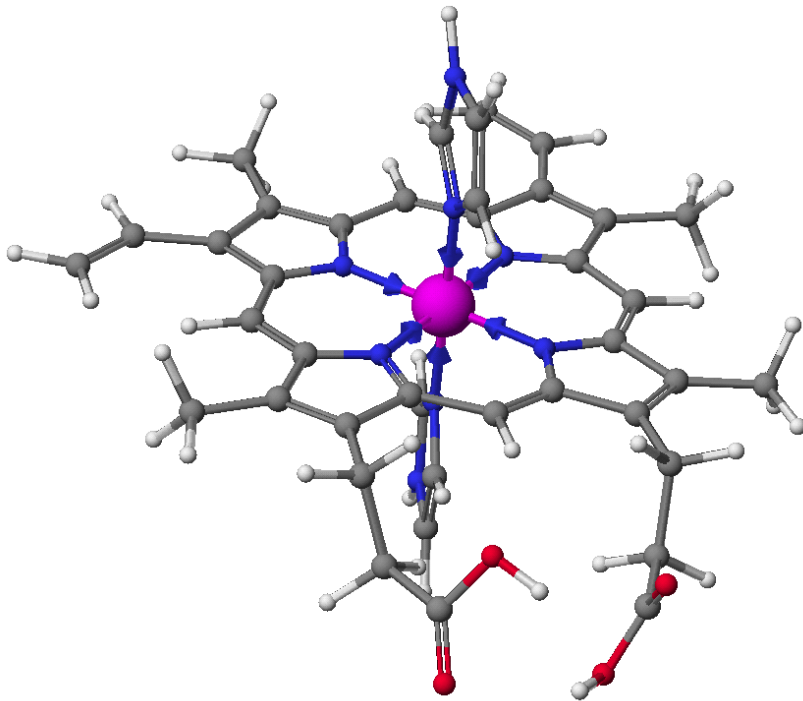
λ = **Reorganization energy**
(\propto structural change upon ET)

ΔG^0 = **Driving force**
(\propto difference of potentials donor vs acceptor)

H_{AB} = **Electronic Coupling**
("overlap of orbitals")

Baja (cero) Energía de reorganización

Low-Spin Heme center

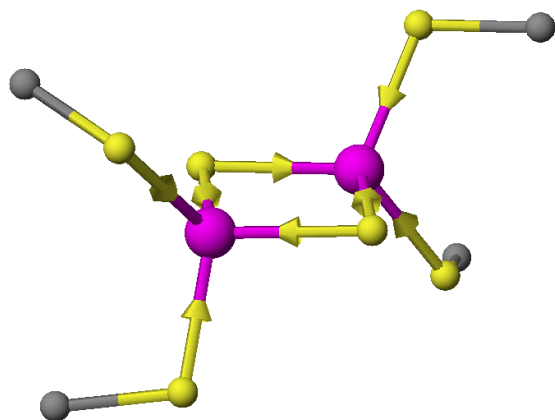


Reorganization Energy

in Cytochromes $\leq 4\text{-}5$ kcal/mol

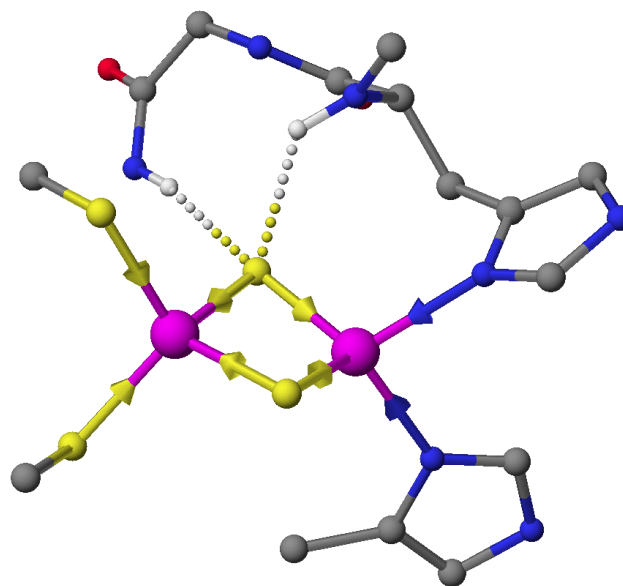
Modulación de Redox potentials (H bridges)

2Fe-2S Ferredoxin



$E^{0'} \sim -400 \text{ mV}$

2Fe-2S Rieske



$E^{0'} \sim +280 \text{ mV}$

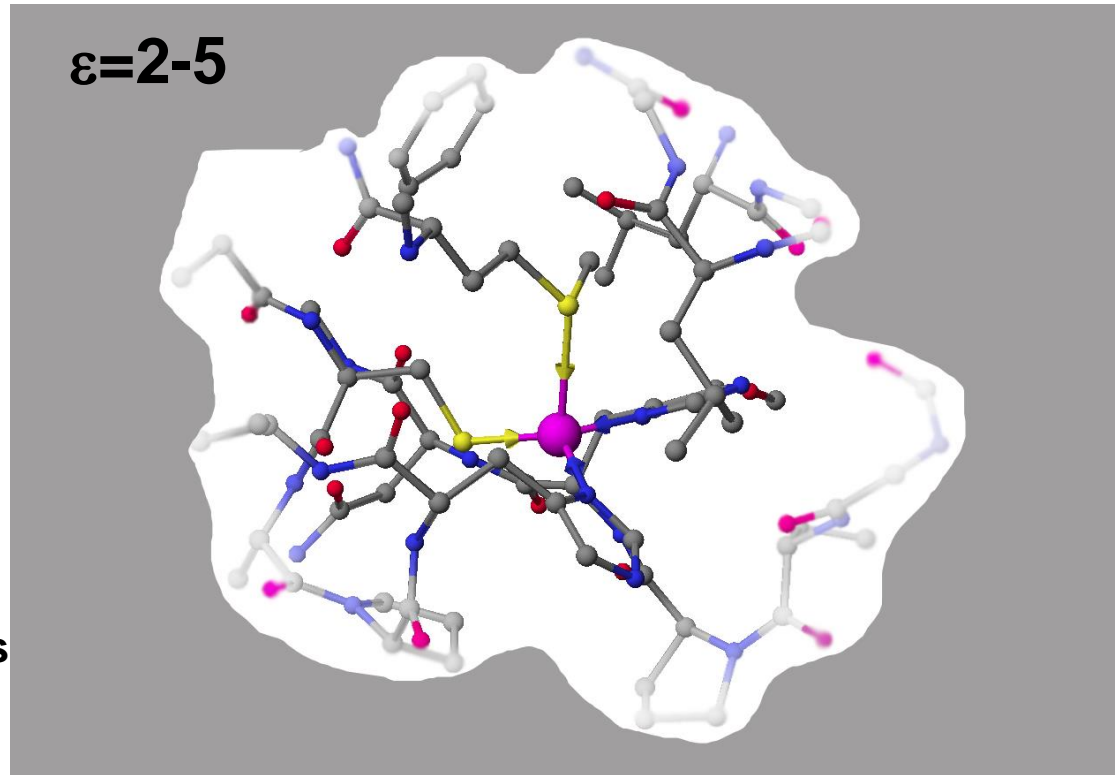
(+150 mV without H bridges)

- (a) Stephens, P.J.; Jollie, D.R.; Warshel, A. (1996) *Chem. Rev.*, 96, 2491
(b) Link, T.A. (1999) *Adv. Inorg. Chem.*, 47, 83

Bio-ET/Catalysis

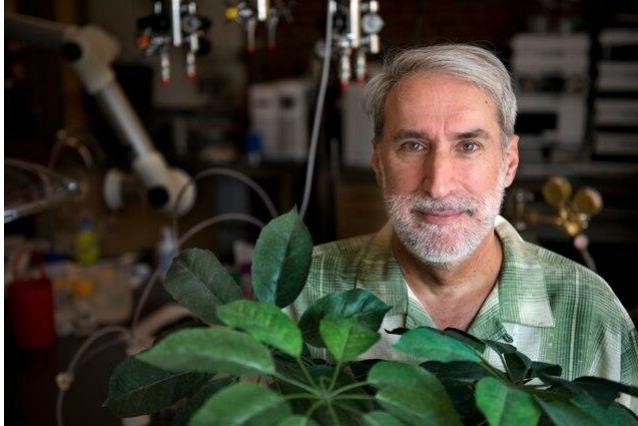
Influence of the protein environment

- Stabilization of unfavorable metal-ligand combinations
- Low polarity
 - Hydrophobic chemistry
- Preformed sites
 - ‚Entatic State‘
- Substrate specific channels and bindings sites
- Fine-tuned acid/base chemistry
- Local production of intermediates – transition states



Cambio climático - Energía

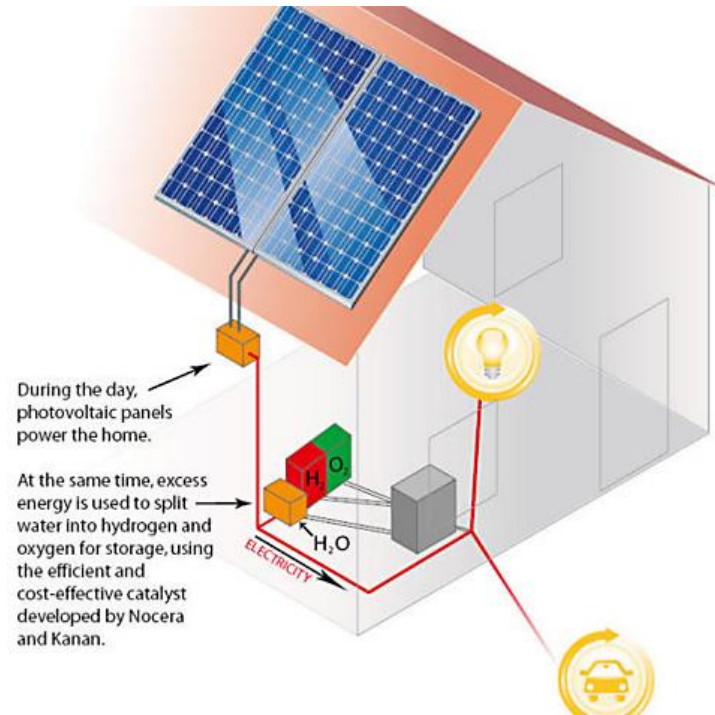
Fotosíntesis – El Sol



D. Nocera – Artificial Leaf

Acc. Chem. Res. 2012, 45, 767-776

SCI AMERICAN 2017, J. Garcia Martinez



El futuro ? Fotosíntesis y vivienda moderna



**Microalgas
fotosintéticas**

Conclusión

Las propiedades estructurales y funcionales de los iones metálicos en los sistemas biológicos se pueden entender combinando los principios de la química de coordinación con el conocimiento del entorno único creado por las biomoléculas.



Bo G. Malmström, Göteborg, 1927-2000

