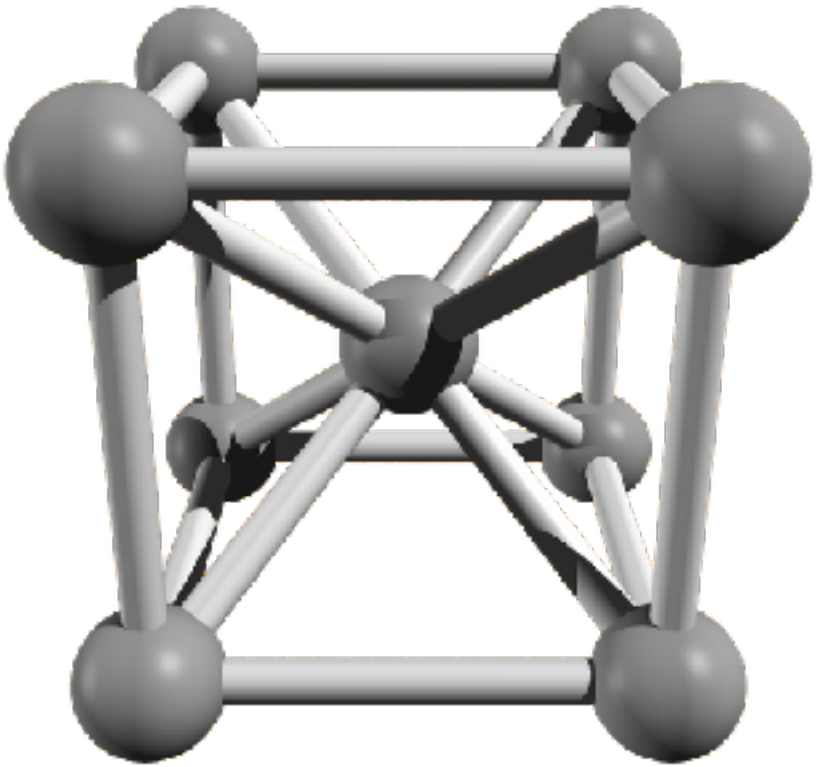
Química Bioinorgánica del Hierro I

Curso de Introducción a la Química Bioinorgánica.
Dr. Manuel I. Azócar
Universidad de Santiago de Chile

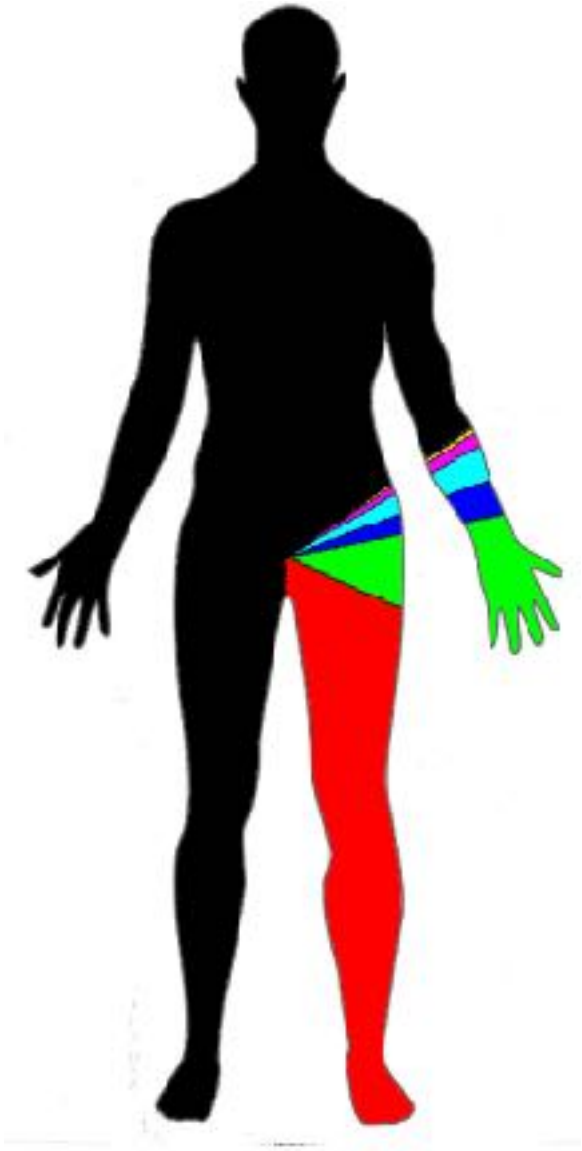
Generalidades del Hierro



Abundancia %	Elemento
46.71	O
27.69	Si
8.07	Al
5.05	Fe
3.65	Ca
2.75	Na
2.58	K
2.08	Mg

Numero atómico	26
Valencia	2,3
Estado de oxidación	+2, +3
Conf. Electrónica	$[Ar]3d^6 4s^2$
Masa atómica (g/mol)	55,847

Generalidades del Hierro: *Composición elemental en un humano de 70 Kgs.*



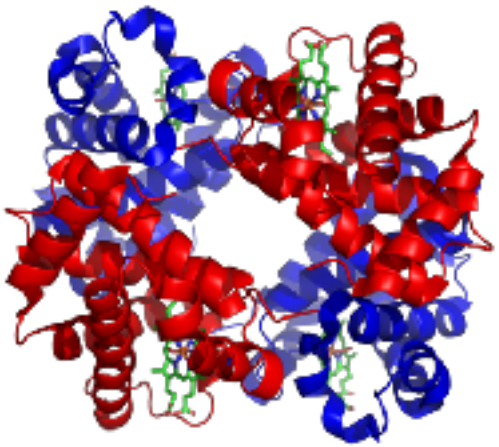
Masa de elementos e iones minerales			
Oxígeno	44 Kg	Fosforo	0,68 Kg
Carbono	12.6 Kg	Potasio	0,250 Kg
Hidrógeno	6.6 Kg	Cloro	0,115 Kg
Nitrógeno	1.8 Kg	Azufre	0,100 Kg
Calcio	1.7 Kg	Sodio	0,070 Kg
		Magnesio	0,042 Kg

Generalidades del Hierro: *Composición elemental en un humano de 70 Kgs.*

Elementos traza y ultra traza			
Fe	**5 g**	Pb	0,035 g
Si	3 g	Ba	0,021 g
Rb	0,36 g	Mo	0,014 g
Cu	0,28 g	B	0,014 g
Sr	0,28 g	As	0,003 g
Br	0,14 g	Co	0.003 g
Sn	0,14 g	Cr	0.003 g
Mn	0,070 g	Ni	0.003 g
I	0.070	Se	0.002 g
Al	0.035 g	Li / V	0.002 g

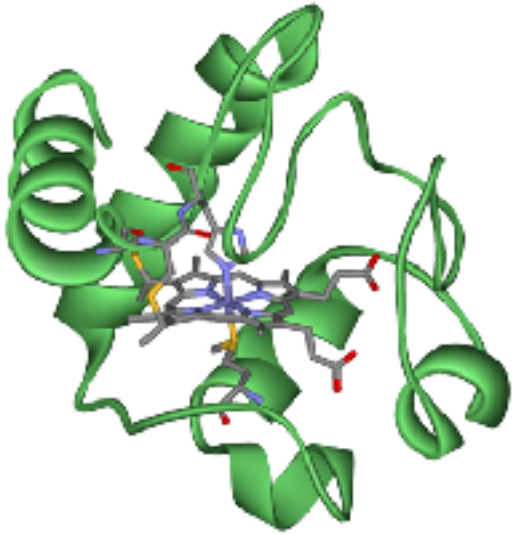
Hierro en el organismo

Transporte y almacenamiento de Oxígeno



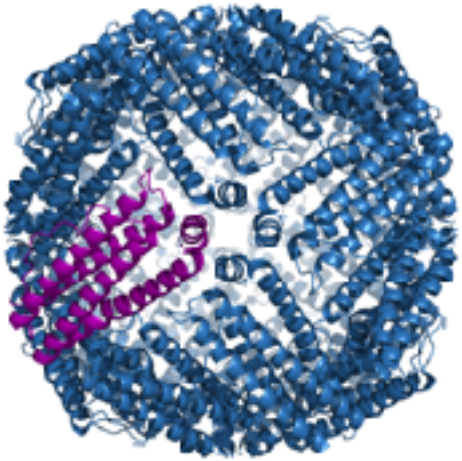
Hemoglobina: 65 % del Fe
Mioglobina: 10%

Transferencia de electrones



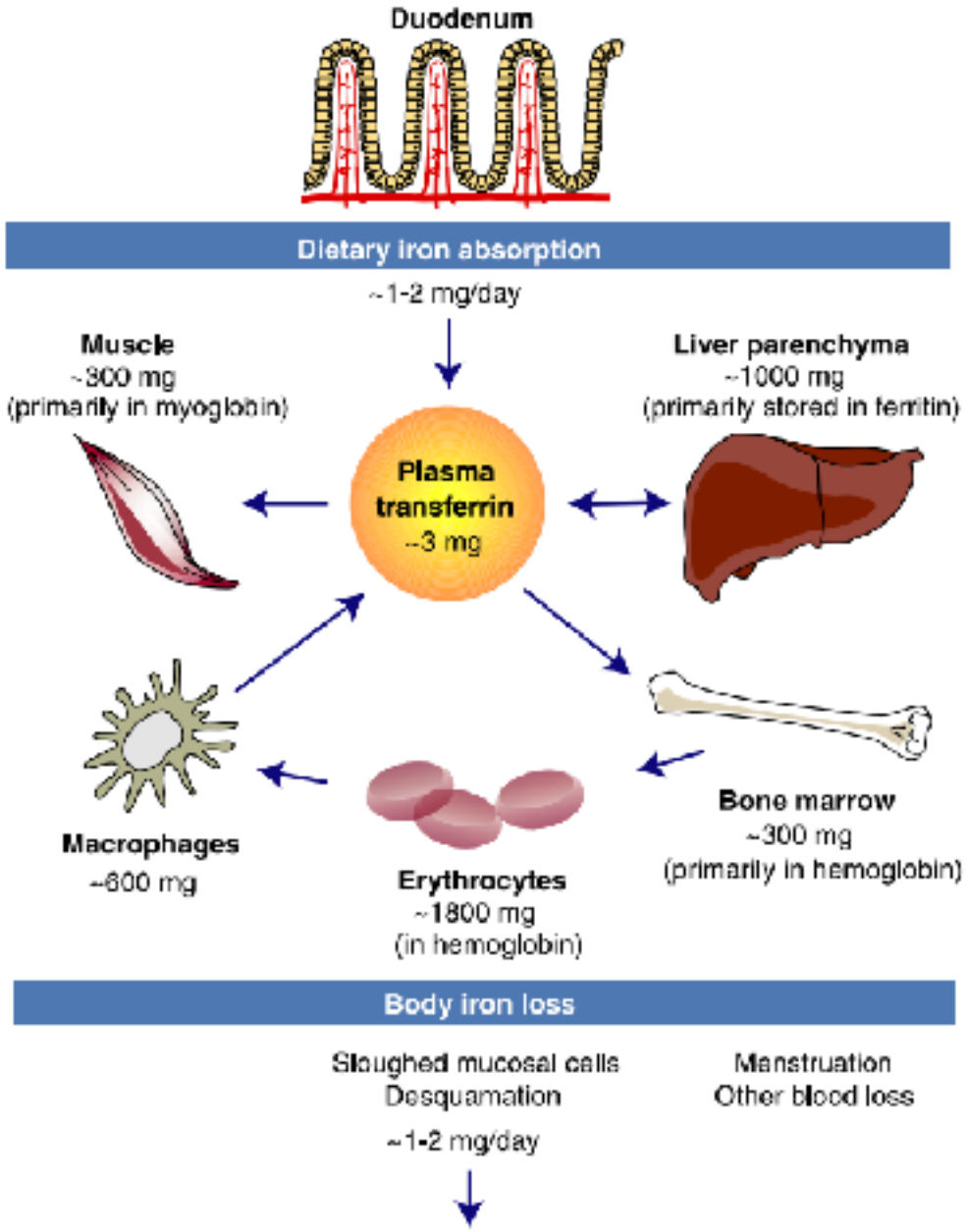
3%
Citocromos
Enzimas

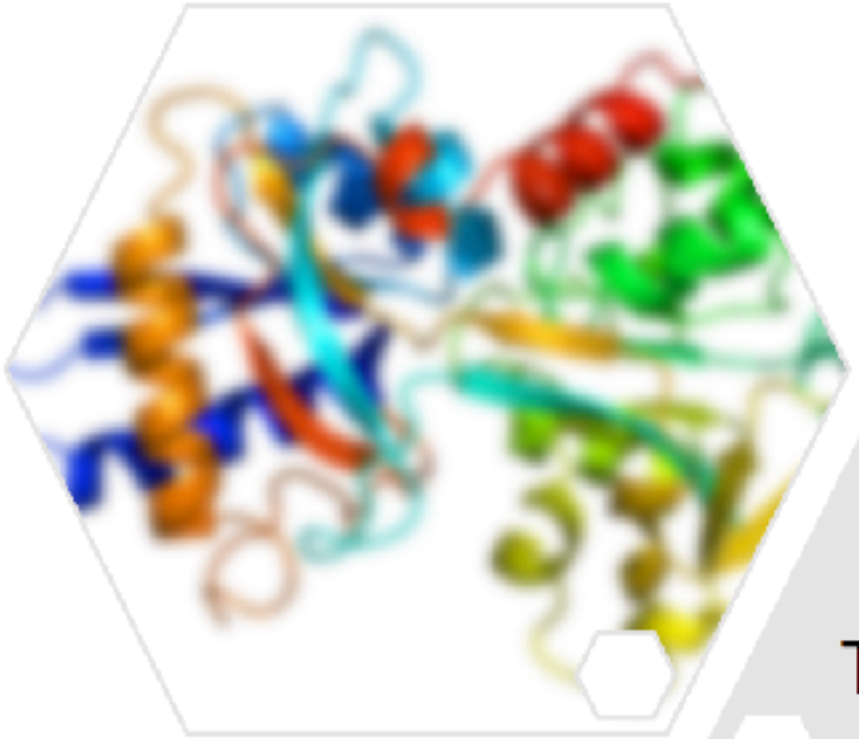
Retención o acumulación



22% del Fe
Ferritina

Hierro en el organismo





Transportadores de Hierro en el organismo

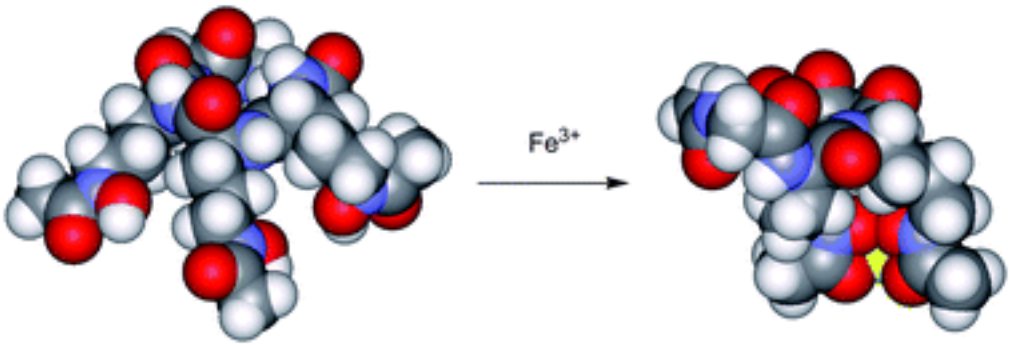
Sideróforos: Quelantes transportadores de Fe

Sideros phoros "portadores de hierro"

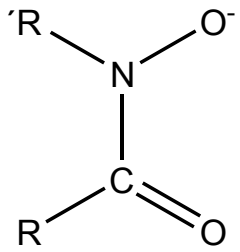
Secretado por bacterias, levaduras y hongos

Agentes quelantes específicos para el Fe^{3+}

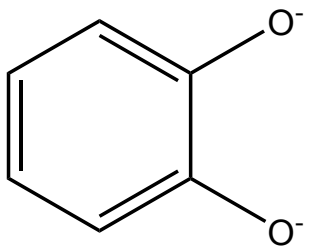
$1.1x10^{-36} = Fe(OH)_3$ $1 \times 10^{-19} = FeS$



Sideróforos: Quelantes transportadores de Fe



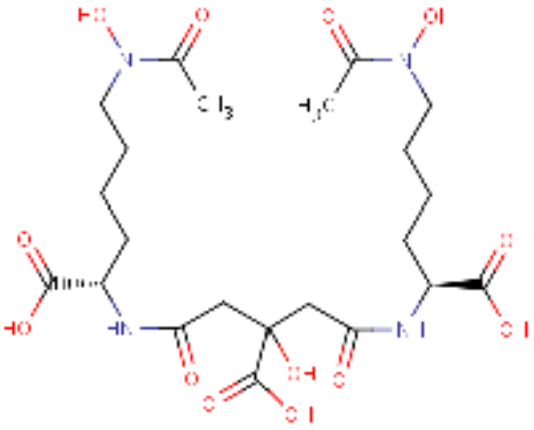
Hidroxamatos
(secretados por hongos)



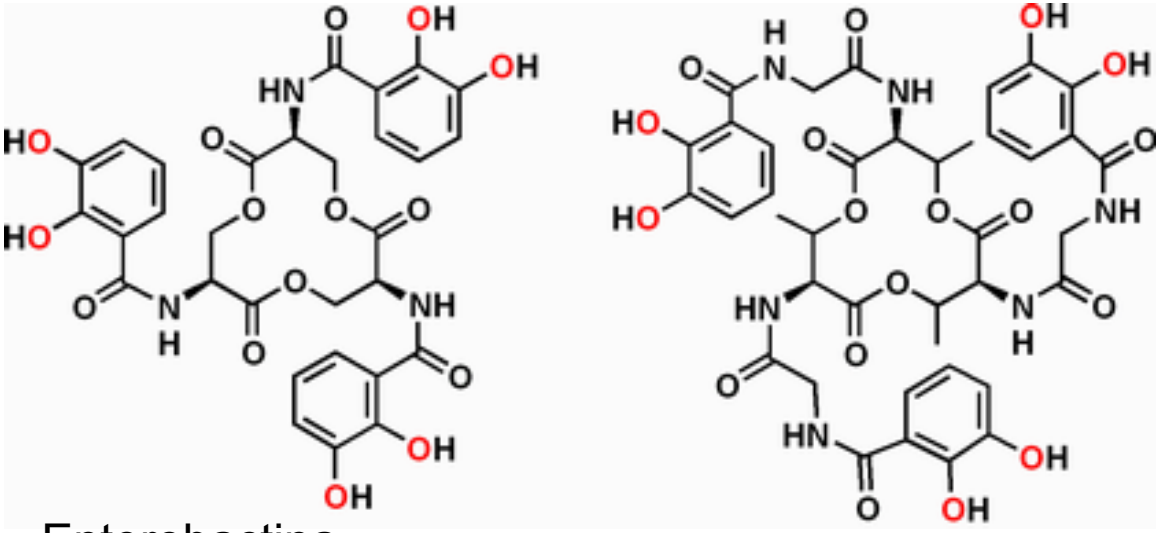
Catecolatos
(bacterias)

$K = 10^{30}$

$K = 10^{45\text{-}52}$



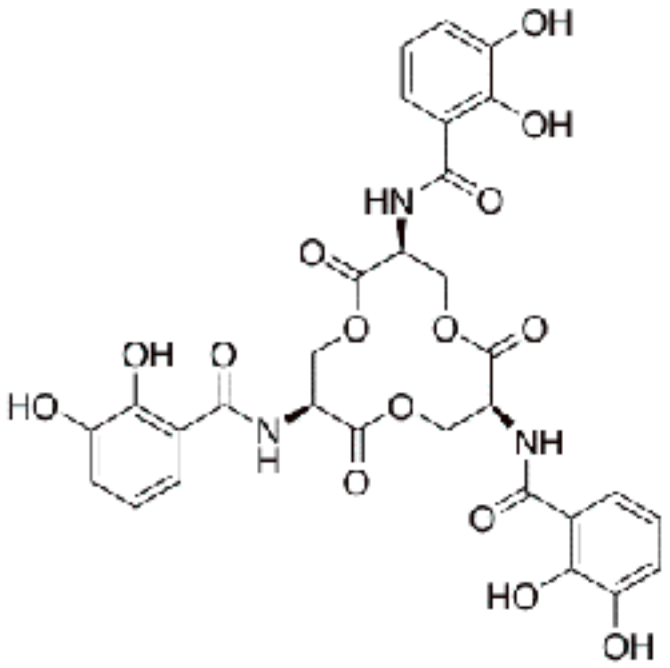
Aerobactina
E.coli



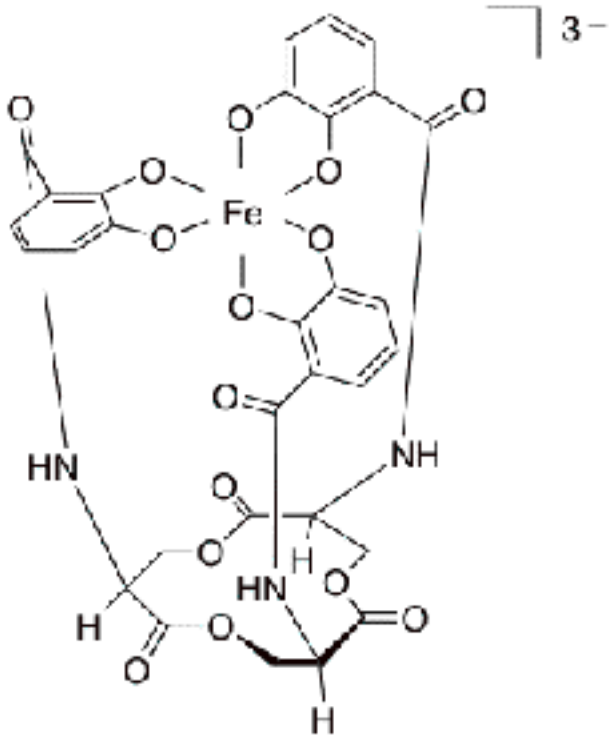
Enterobactina
Bacillibactina
El agente mas fuerte
Para Hierro(III)

$K = 10^{52}$

Sideróforos: Quelantes transportadores de Fe



Enterobactin

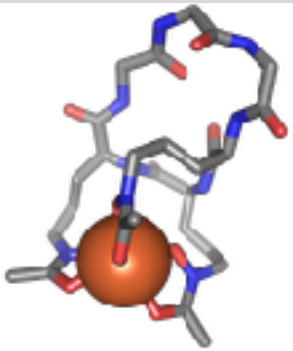


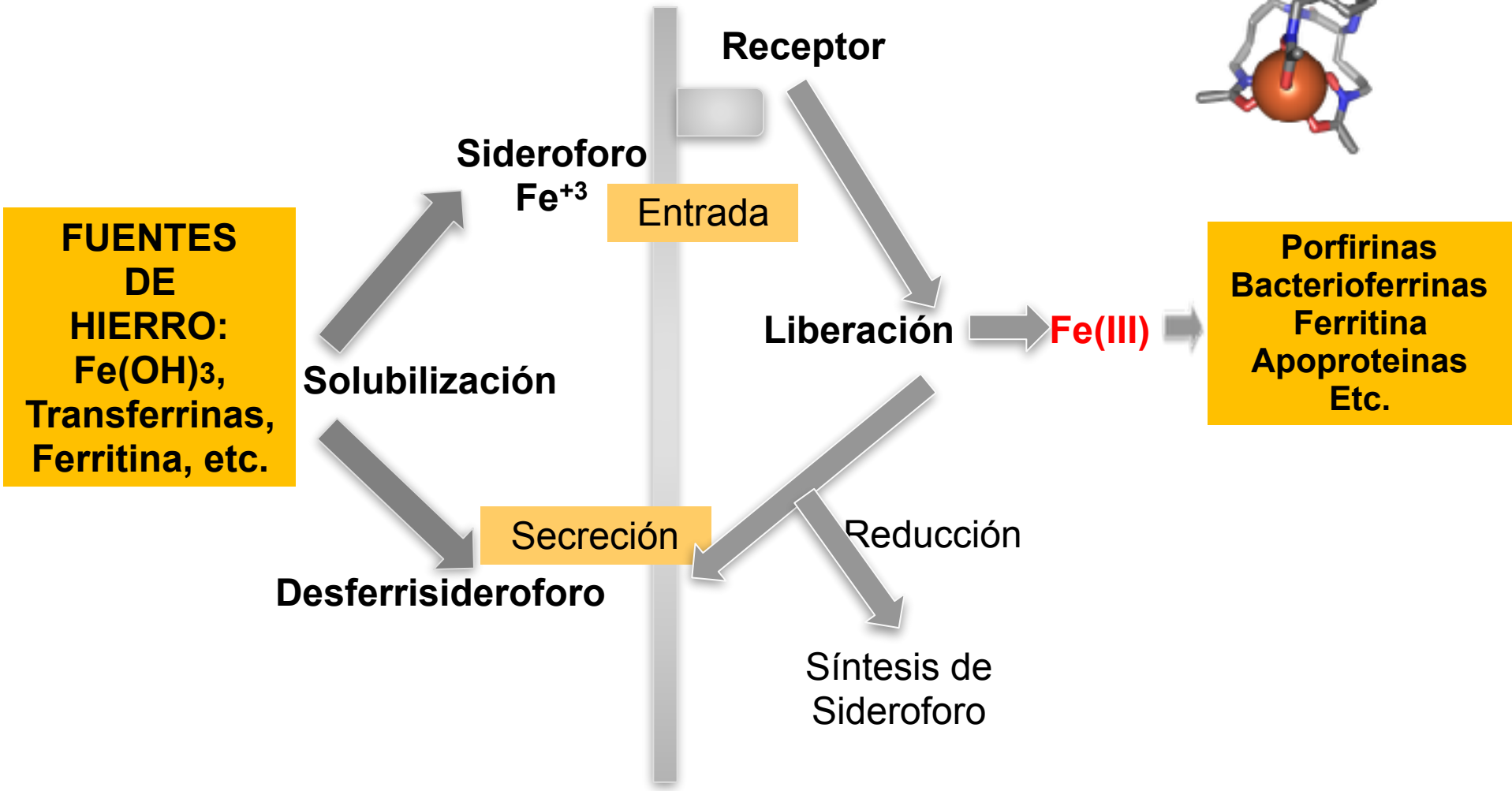
Fe(III)-Enterobactin

$$K_f = 1x10^{51}$$

Carrano, Carl J., and Kenneth N. Raymond (1979). «Ferric Ion Sequestering Agents. 2. Kinetics and Mechanism of Iron Removal From Transferrin by Enterobactin and Synthetic Tricatechols». J. Am. Chem. Soc. 101: pp. 5401–5404. doi:10.1021/ja00512a047.

Ferricromo(sideroforo del hongo *Ustilago sphaerogena*): mecanismo



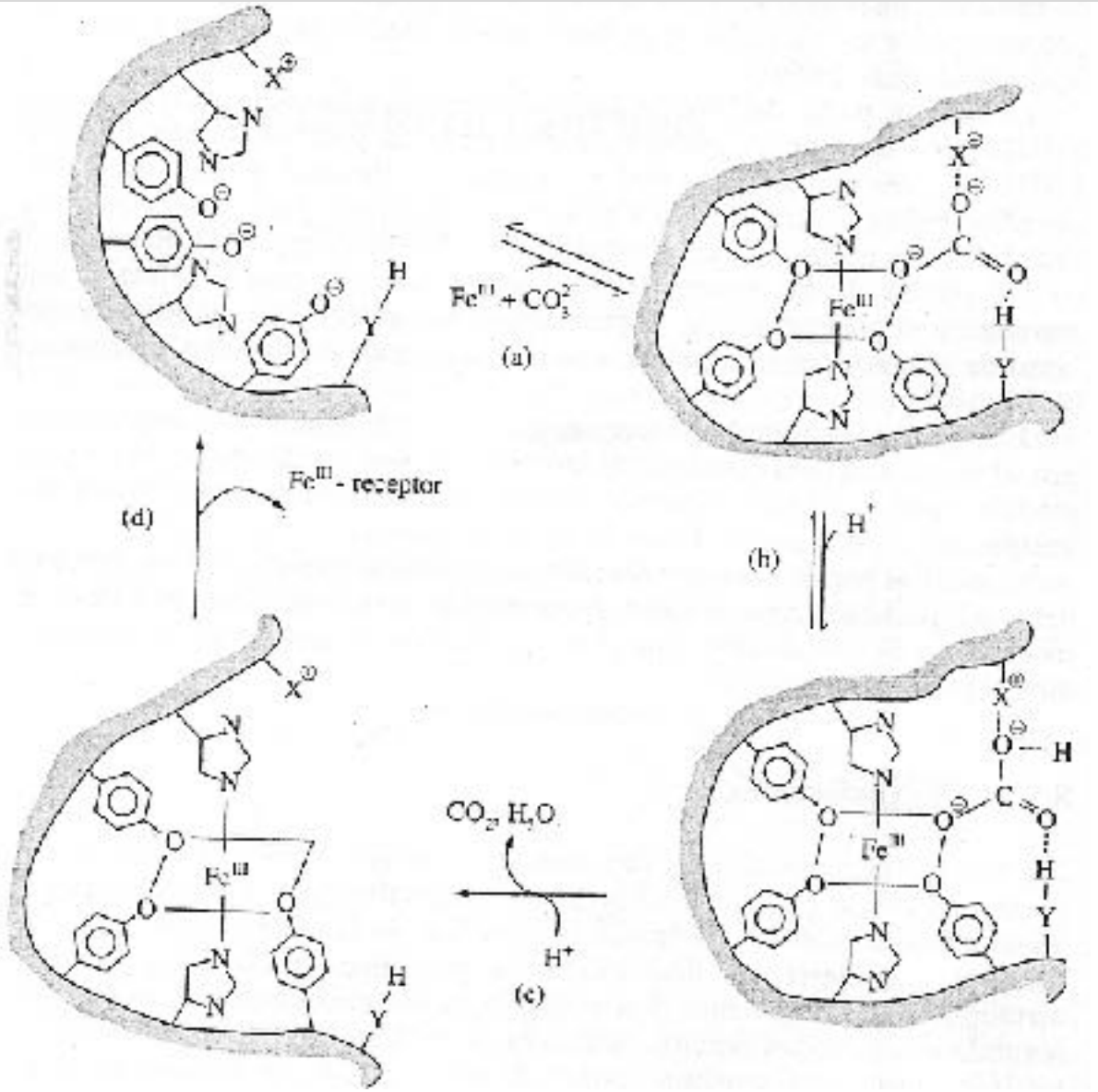


Transferrina: Transportador de Fe en la sangre para su posterior almacenamiento

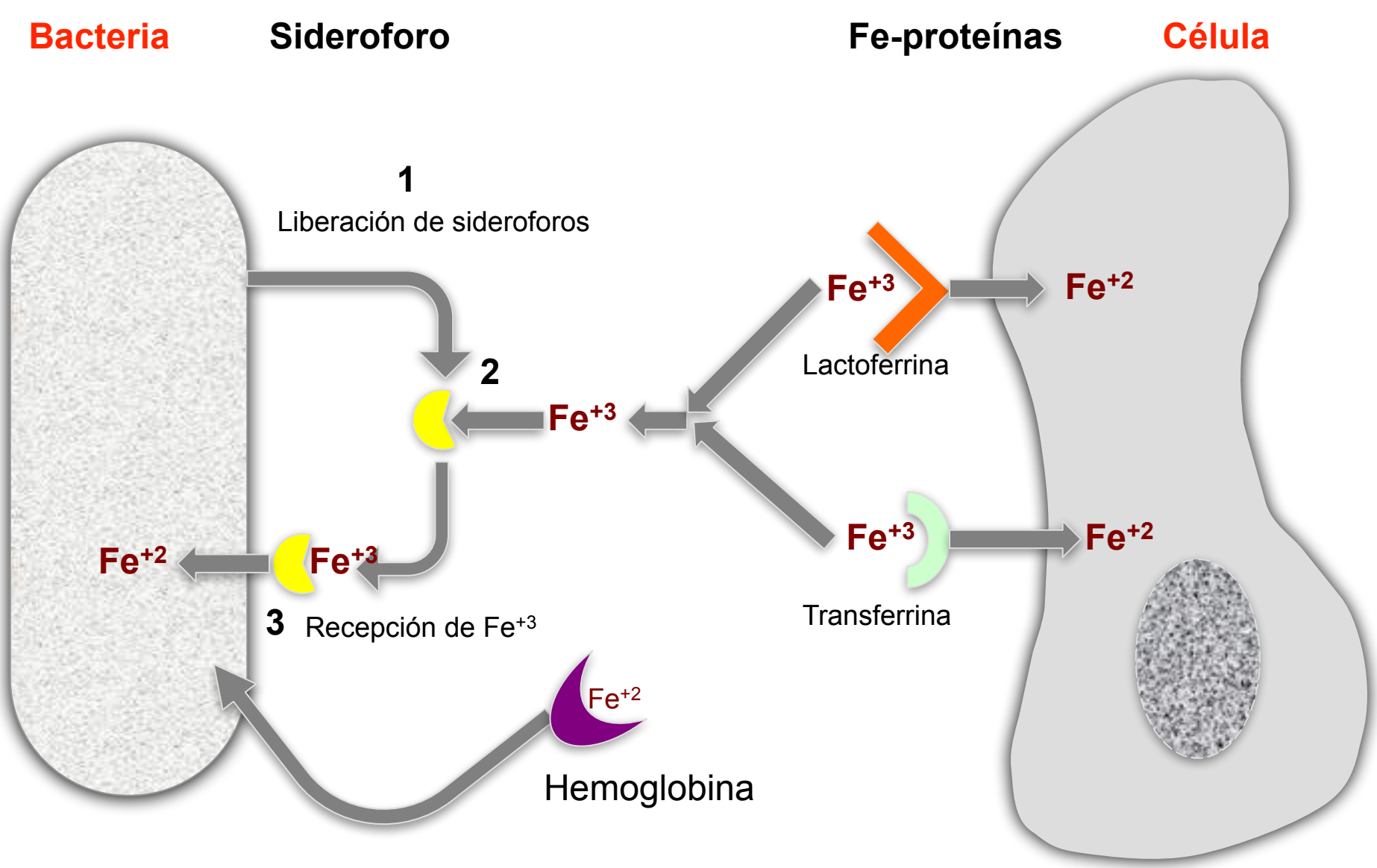
Sangre

Fe: Kf = 10^{24}

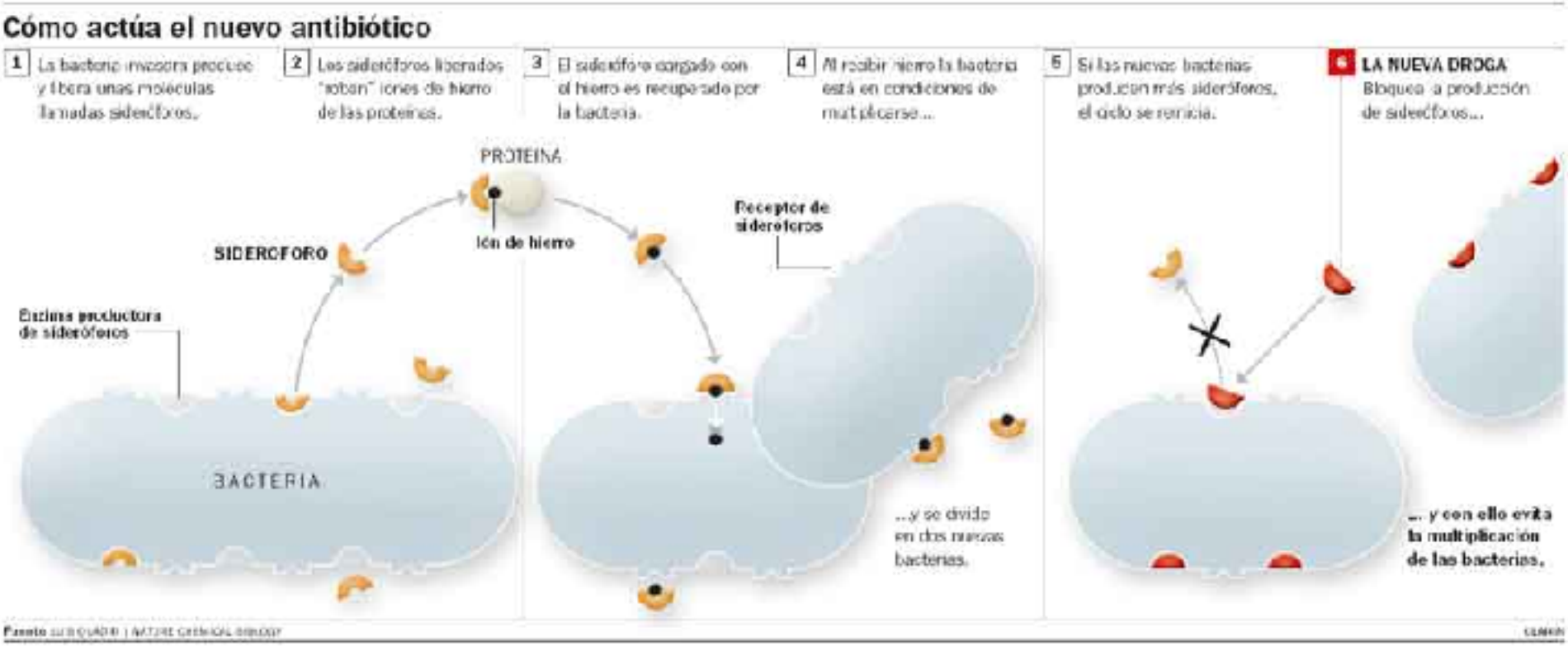
Cr^{+3}
Al^{+3}
Cu^{+2}
Co^{+2}
VO^{+2}
Cd^{+2} …

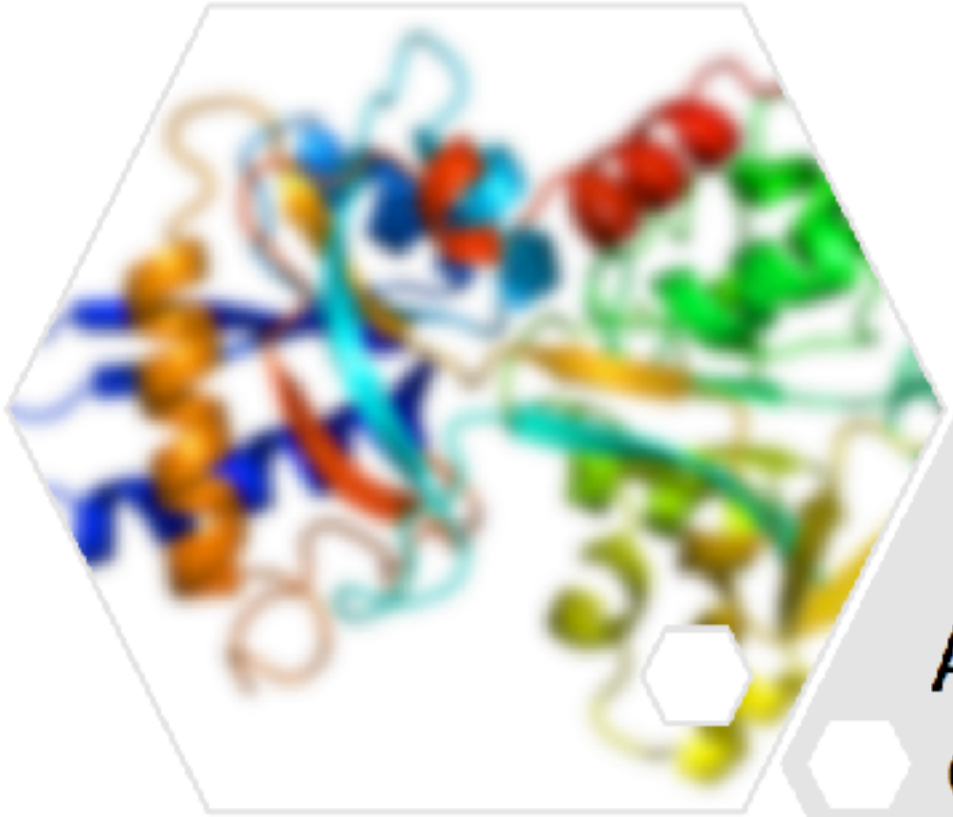


Transportadores de Fe: mecanismos de adquisición



Transportadores de Fe: mecanismos de adquisición





Almacenadores de Hierro en el organismo

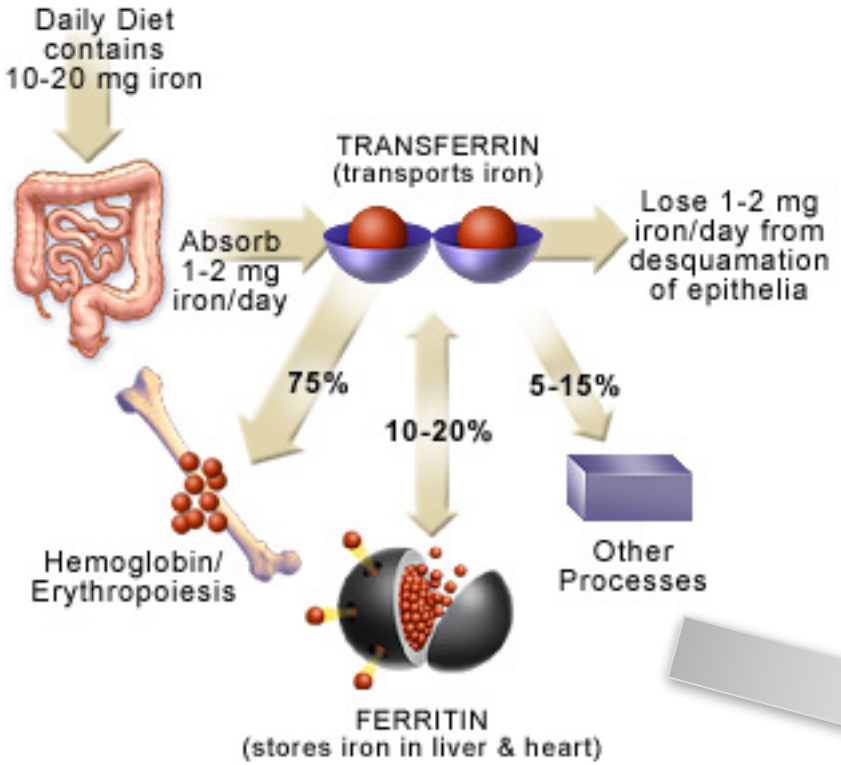
Almacenamiento de hierro: Requerimientos

1. El **Fe** debe encontrarse estable y no susceptible al ataque de la enorme cantidad de potenciales agentes complejantes.
2. El **Fe** debe ser fácil y rápidamente disponible, según sea el requerimiento del organismo.
3. Las moléculas de ligando deben ser estables y sometidas a fácil y estricto control biológico.
4. Máxima asociación de una cantidad de hierro por molécula de almacenamiento.

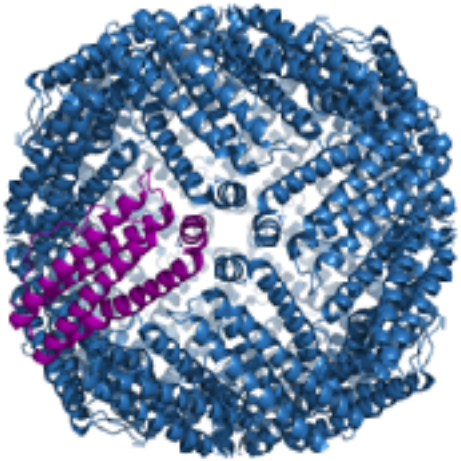
Transferrina: 1g de hierro → 500 g de proteína X

Serotransferrinas: suero sanguineo - **Ovotransferrinas**: clara de huevo – **Lactotrasnferrinas**: leche, leucocitos y lagrimas

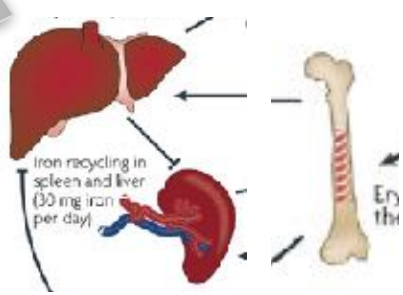
Almacenamiento de hierro



Ferritina y Hemosiderina(1867)

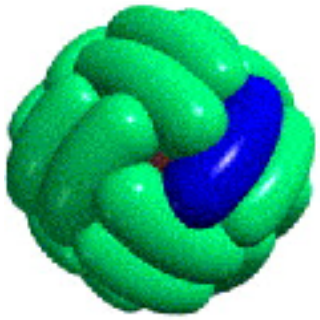


Ubicación

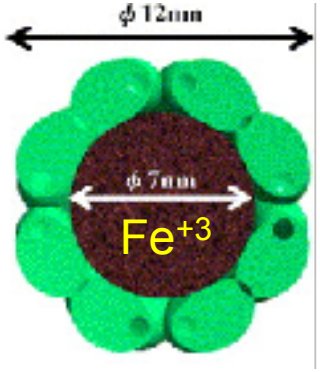


Almacenamiento de hierro

Apoferritina
Ferritina



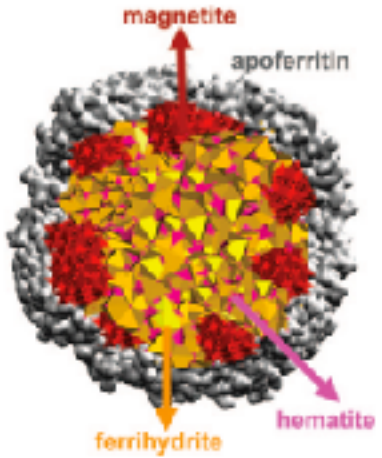
Fe^{+2}



PM: 444.000

PM: 900.000

$(FeO^*OH)_8(FeO^*OPO_3H_2)$: Ferrihidrita
$FeO^*Fe_2O_3$: Magnetita
Fe_2O_3: Hematita
4.500 atomos de hierro



Schematic core–shelled ferritin iron core structure.

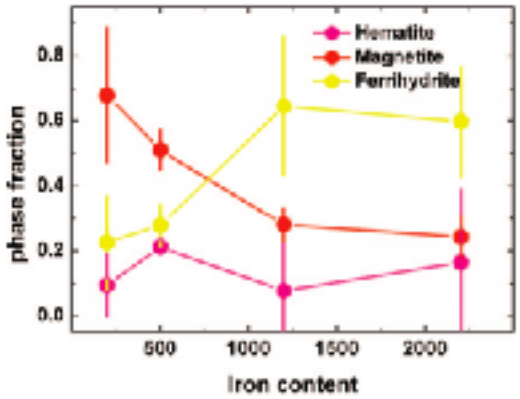
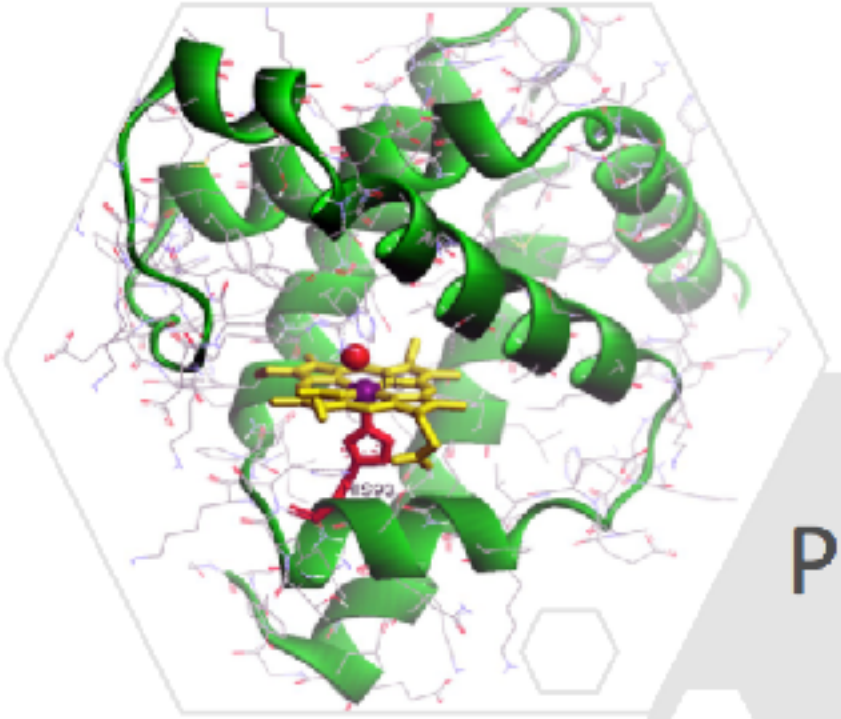


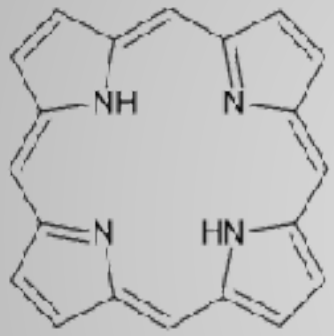
Figure 4. Phase distribution for ferritin samples with different iron content (200–2220 atoms) obtained from XANES experiments (see text). Purple (hematite), red (magnetite), and yellow (ferrihydrite).

J. AM. CHEM. SOC. 2008, 130, 8062–8068

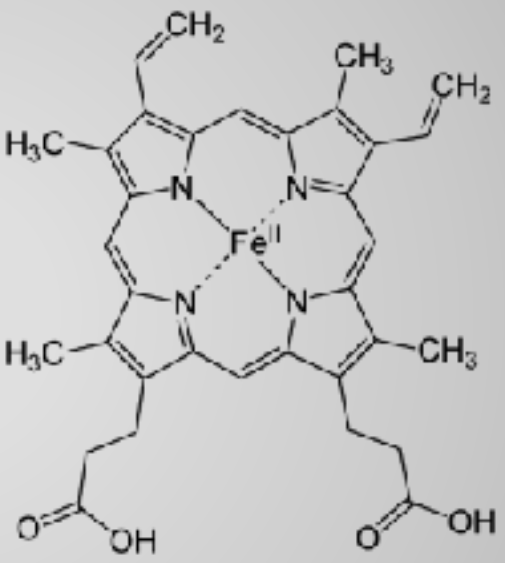


Proteinas de hierro con grupos hemo

Hierro con grupos hemo

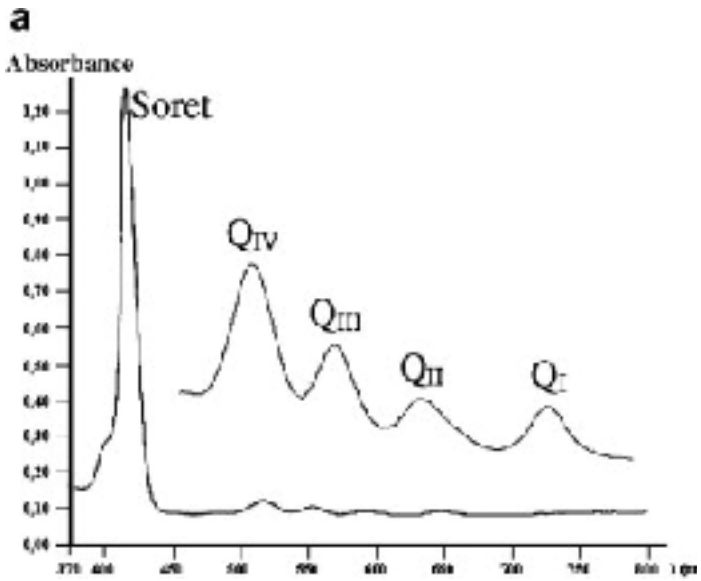


Anillo porfirinico

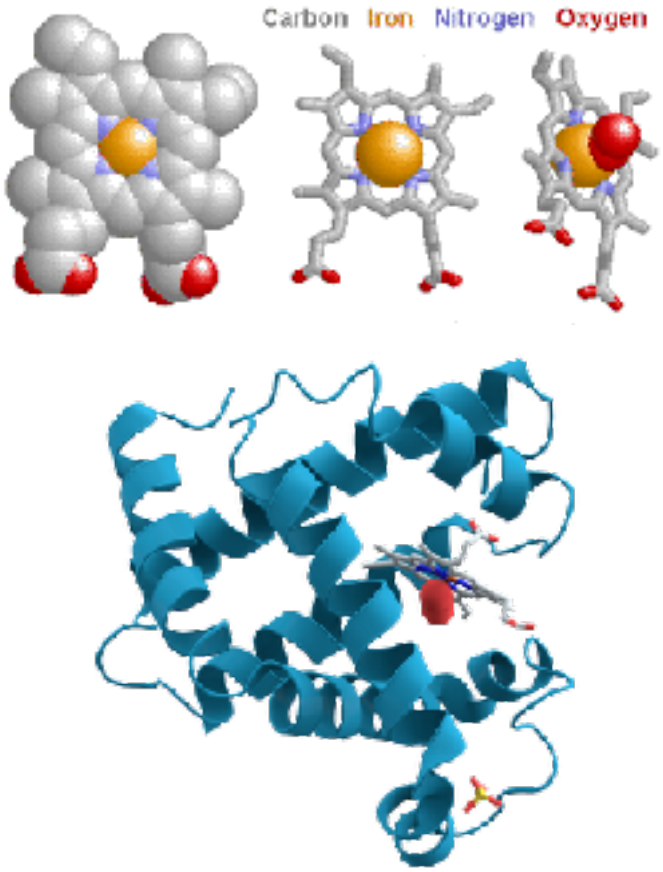


Protoporfirina IX

Hemoglobina,
Mioglobina,
Citocromos,
Catalasas y
Peroxidasas

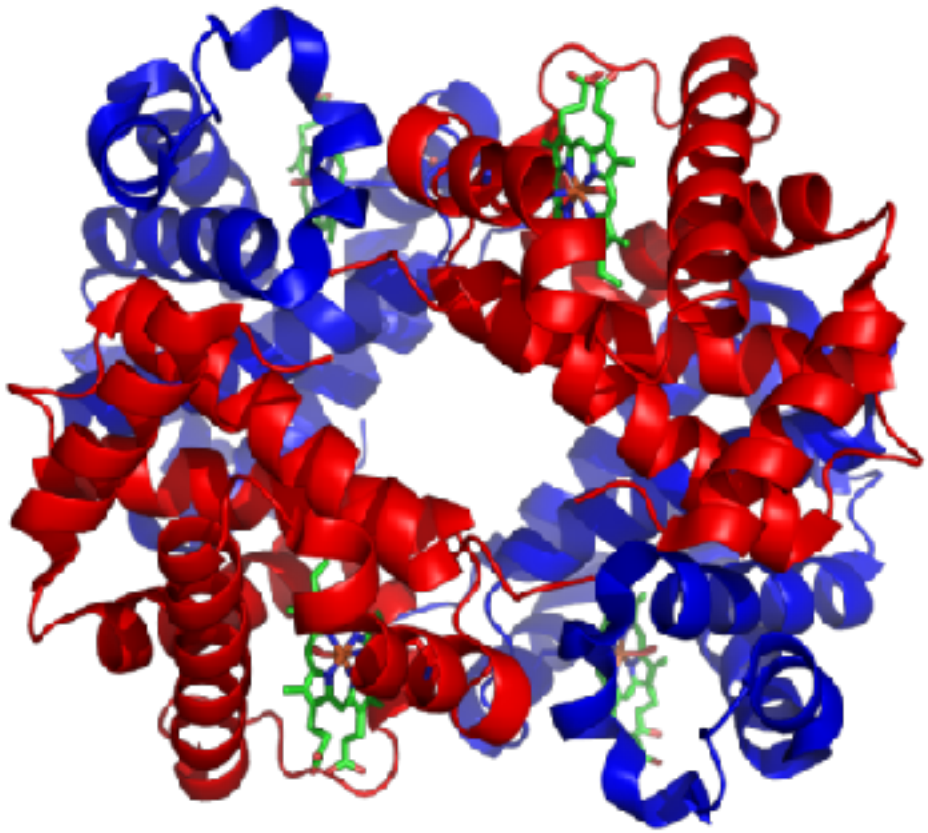


Hierro con grupos hemo



Mioglobina
PM: 17.800

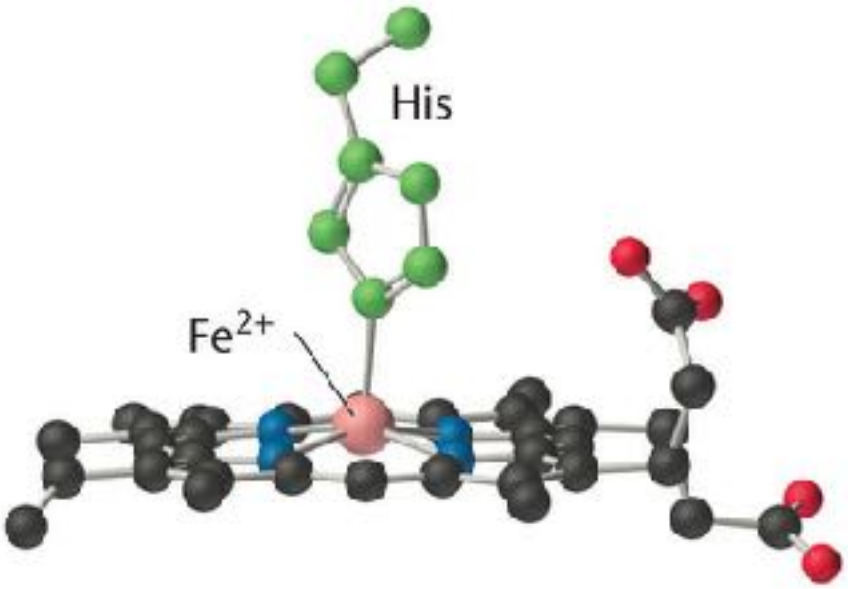
Acumulación y trans. Oxígeno



Hemoglobina
PM: 64.500

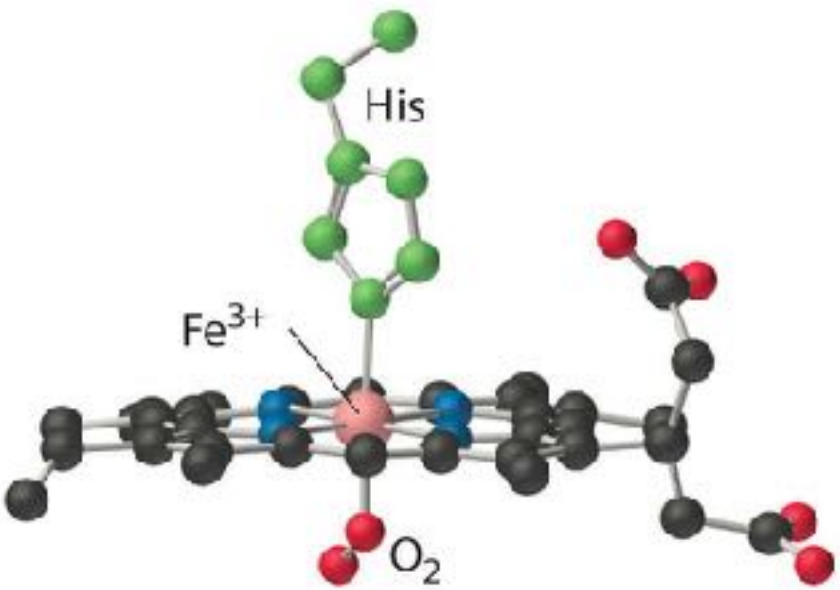
Transporte de oxígeno

Hierro con grupos hemo



(a) Deoxymyoglobin

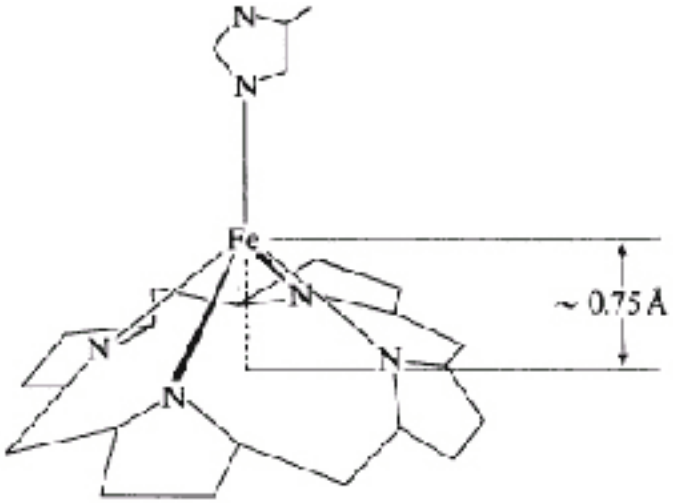
Hierro alto spin



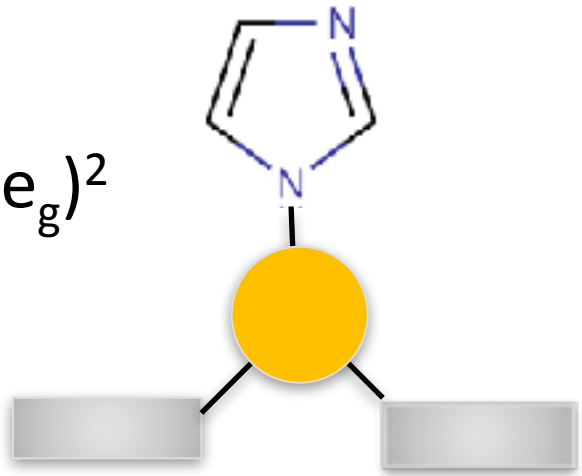
(b) Oxymyoglobin

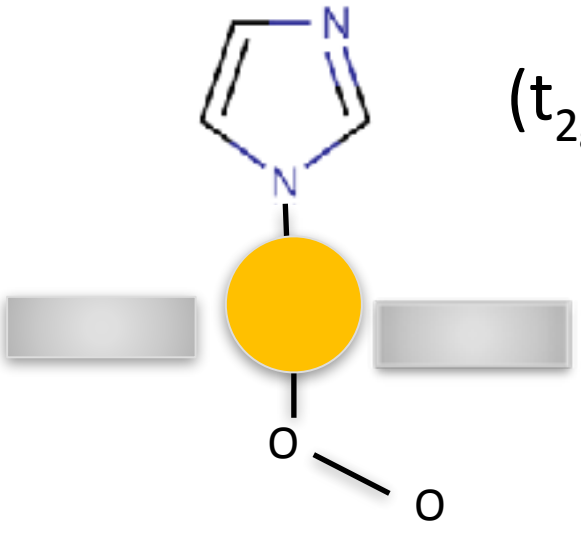
Hierro bajo spin

Hemoglobina y Mioglobina



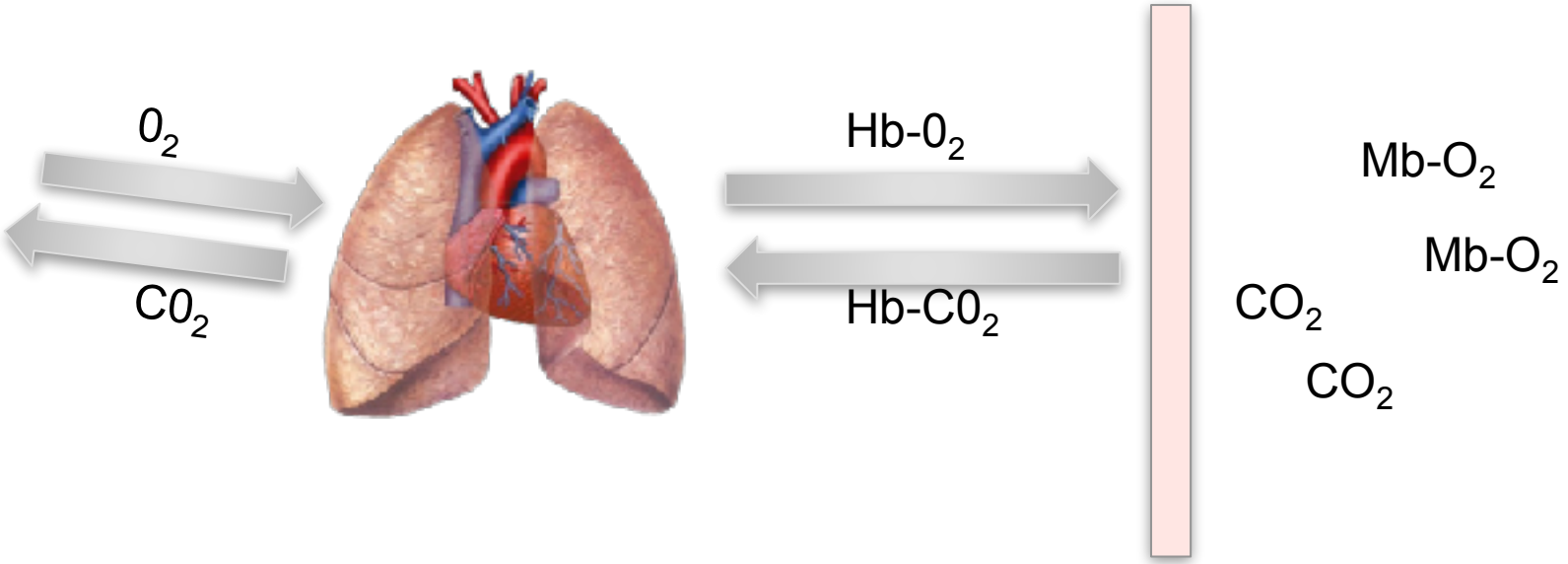
$(t_{2g})^4(e_g)^2$



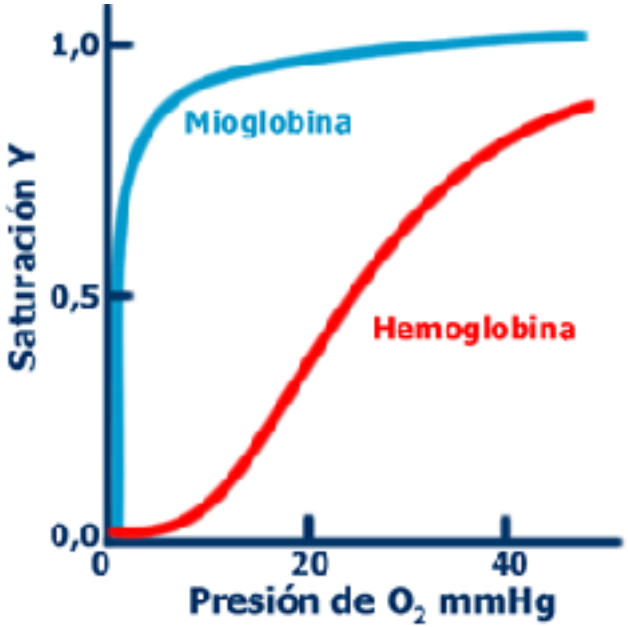


$(t_{2g})^6(e_g)^0$

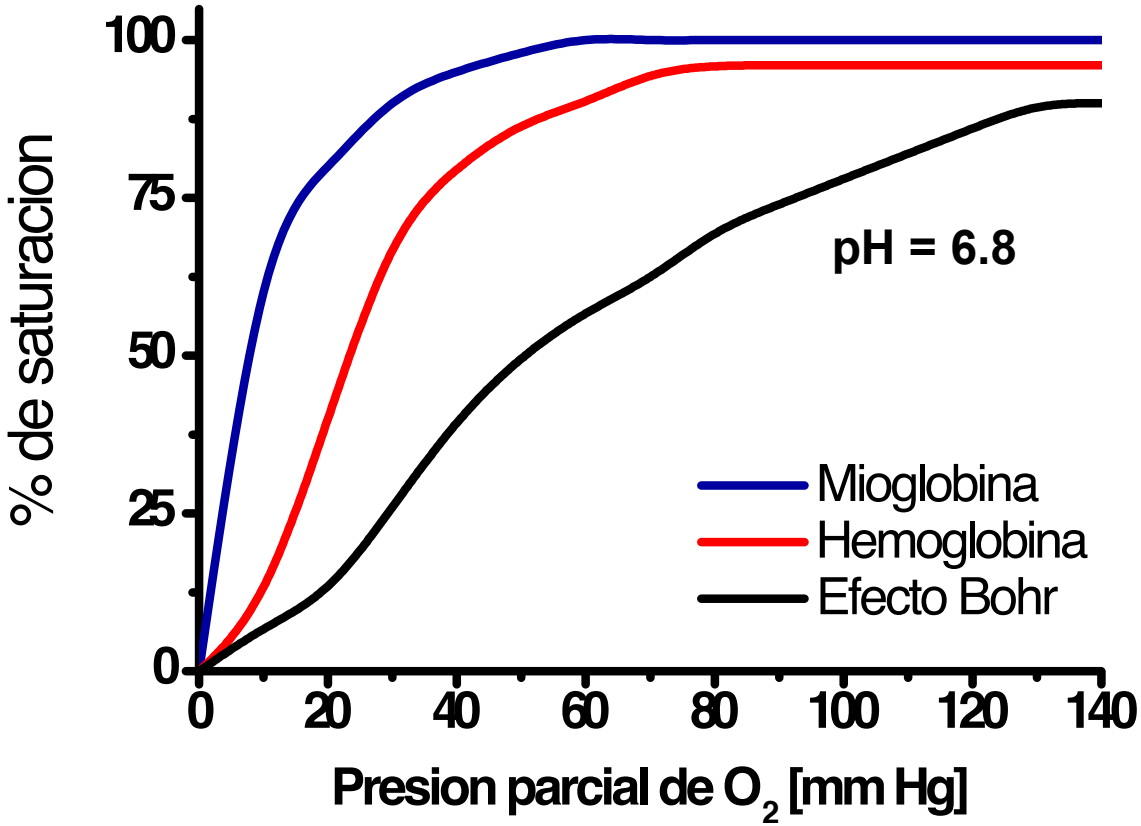
Hemoglobina y Mioglobina

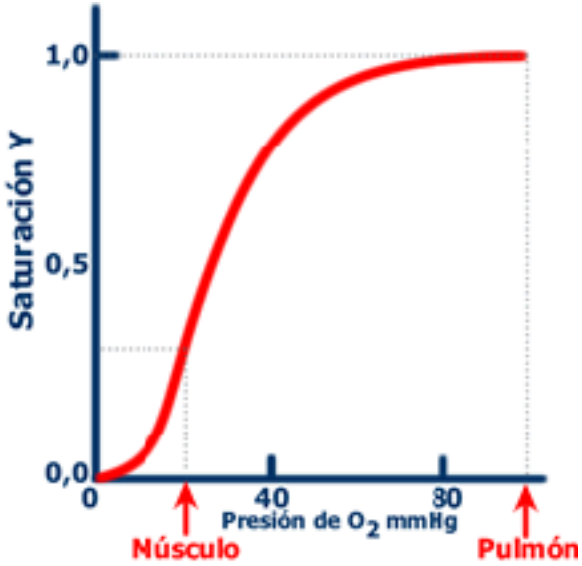


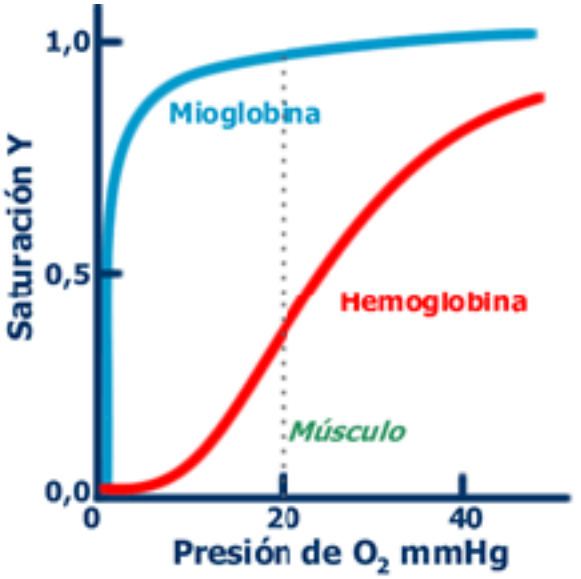
$$K_{Mb/O} = \frac{[MbO]}{[Mb][O_2]}$$



Hemoglobina y Mioglobina

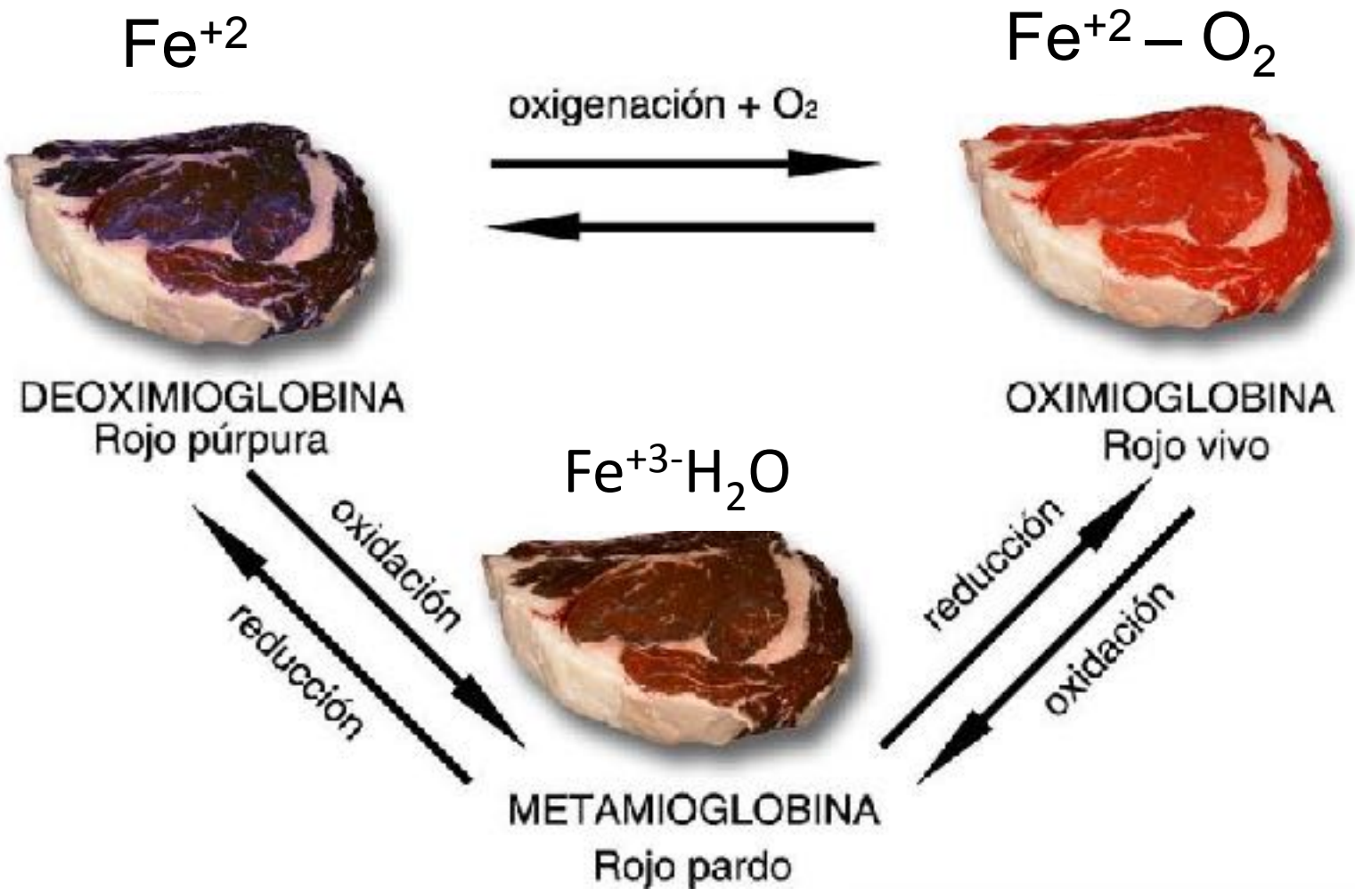






$$CO_2 + H_2O \rightleftharpoons HCO_3^- + H^+$$

Hemoglobina y Mioglobina

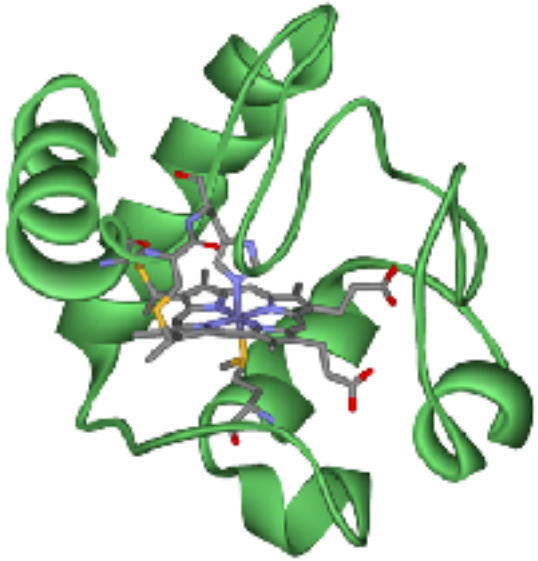


Hemoglobina y Mioglobina

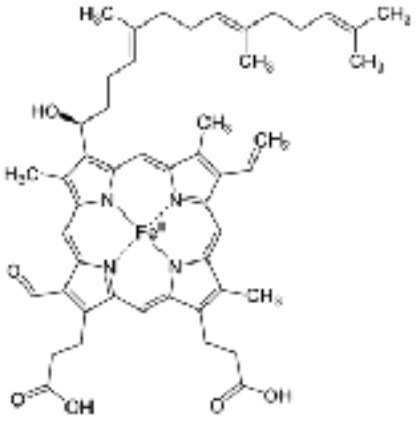
Sin Mioglobina

Mioglobina

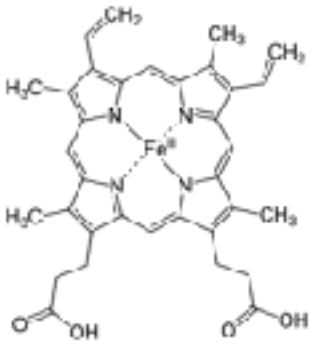
Citocromos: Transferencia de electrones



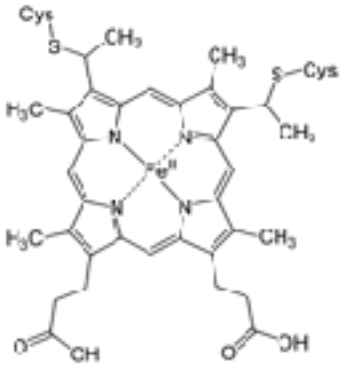
PM: 12.000
Fe(II) / Fe(III)
Fijacion de Nitrogeno
Fotosintesis



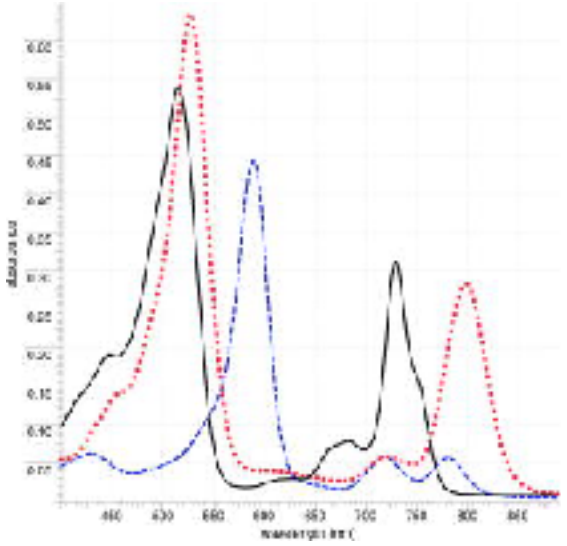
600 nm



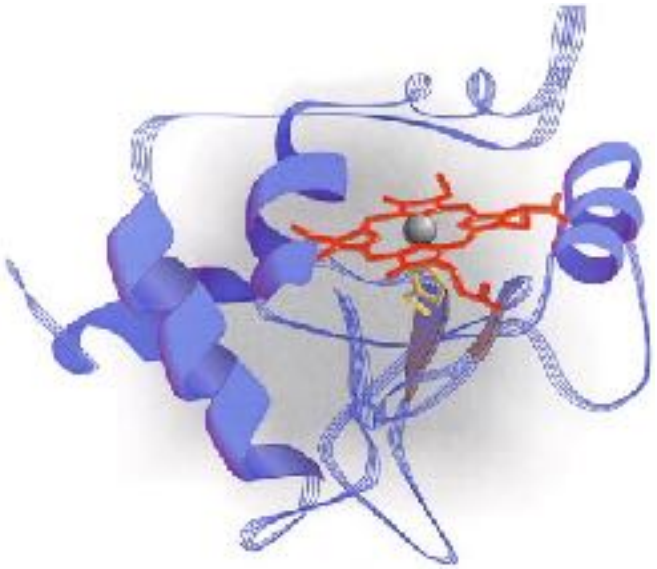
560 nm

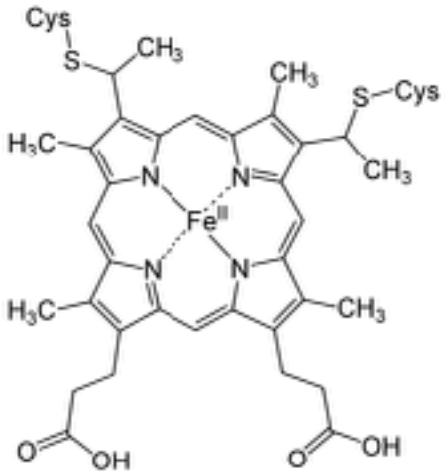


550 nm

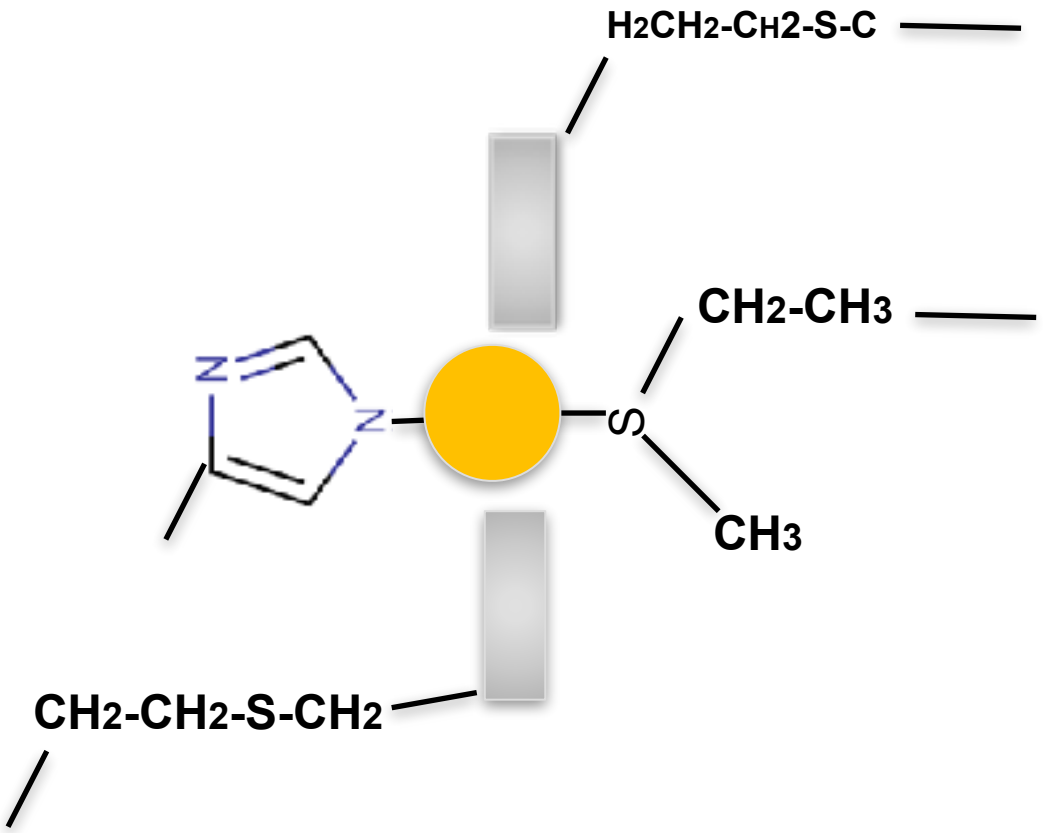


Citocromo C: Transferencia de electrones





550 nm



Fe(II) / Fe(III)
Bajo spin

Citocromo C: Transferencia de electrones

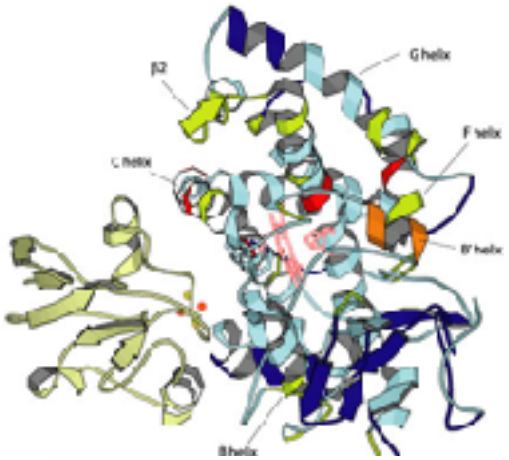
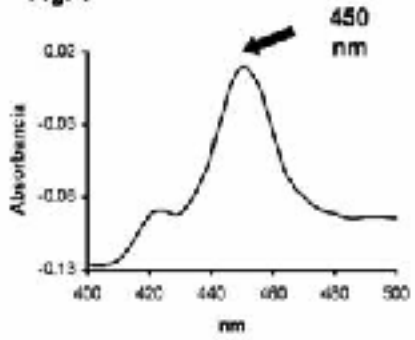
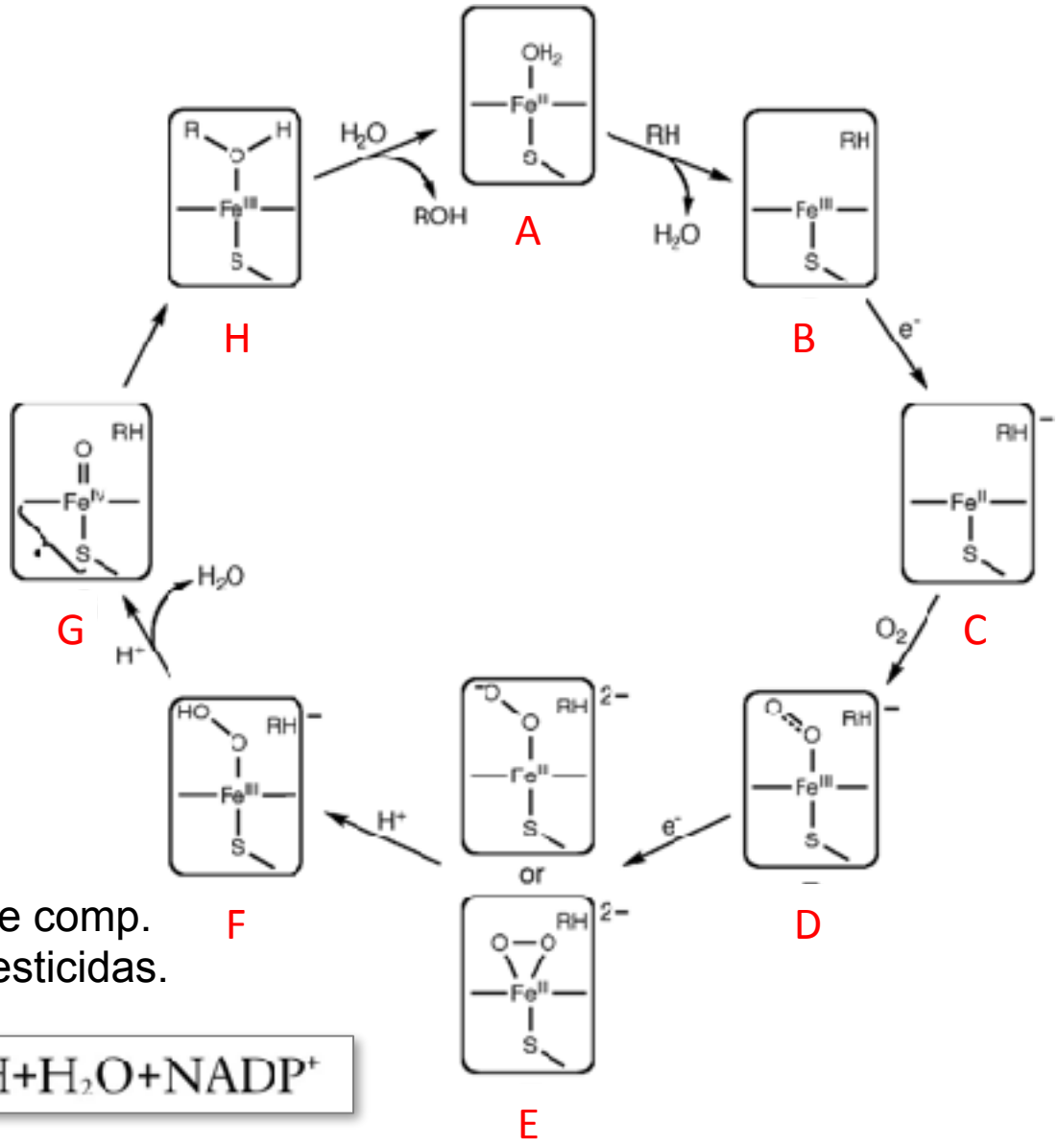


Fig. 1





Insercion de Oxigeno: proteccion de comp. Hidrofobicos: esteroides, drogas y pesticidas.

$$S\text{-}H + O_2 + NADPH, H^+ \rightarrow S\text{-}OH + H_2O + NADP^+$$

Hemoproteinas: Peroxidasas y Catalasas

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$$

$$O_2 \rightarrow O_2^- \rightarrow O^{-2}{}_2 \rightarrow 2O^{2-}$$

$$H_2O_2 + RH \xrightarrow{\text{Peroxidasas}} 2H_2O + R$$

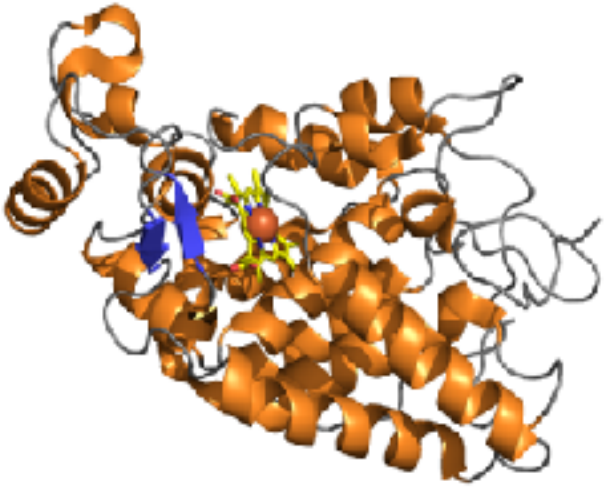
$$H_2O_2 + H_2O_2 \xrightarrow{\text{Catalasas}} 2H_2O + O_2$$

Fe (IV)

Ácidos grasos, aminas y fenoles

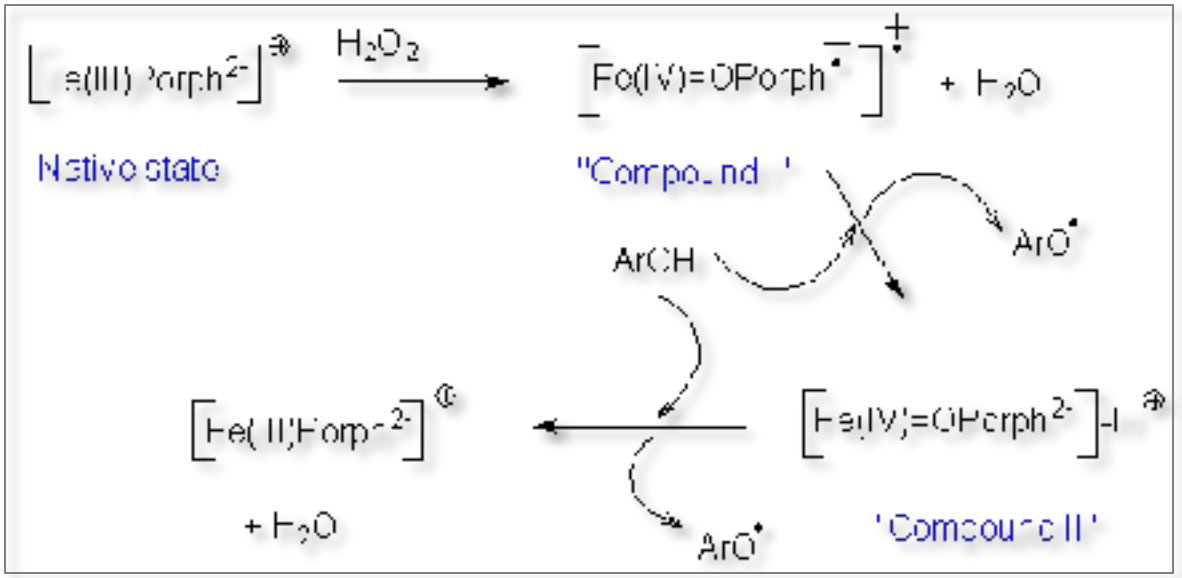
Hemoproteinas: Peroxidasas

Vegetales: Protoporfirina IX + Fe(III)



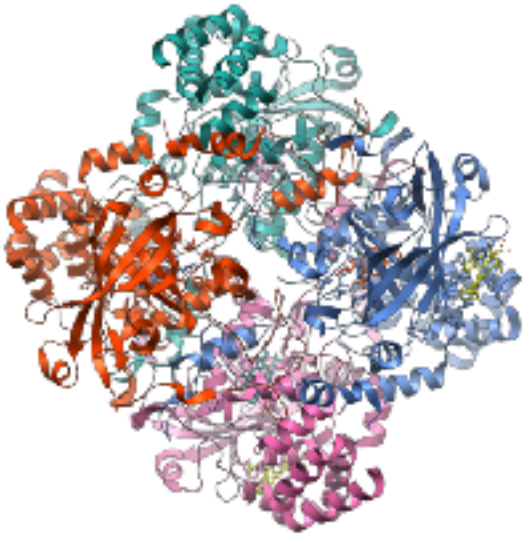
Peroxidasa de rábano

PM 40.000



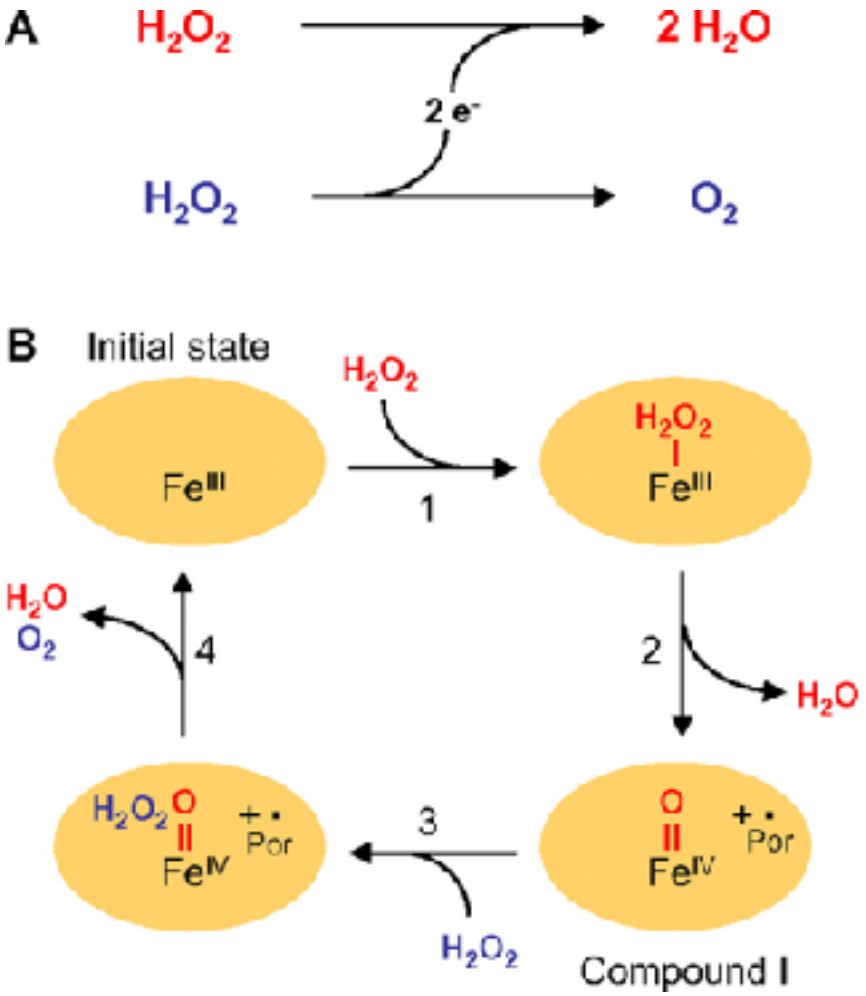
Haloperoxidasas: R-H + H_2O_2 + X^- + H^+ → R-X + $2H_2O$

Hemoproteinas: Catalasa



Catalasa

PM 240.000



Fin clase
2016