


Química Bioinorgánica del Hierro 2

A microscopic view of several red blood cells (erythrocytes) against a dark red background. The cells are biconcave discs, appearing as reddish, slightly flattened spheres with a darker center. They are scattered across the frame, with some in sharp focus and others blurred in the background.

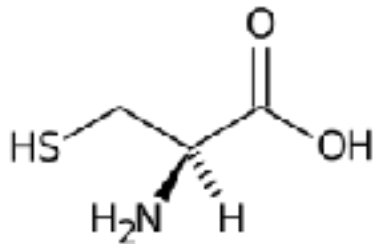
Curso de Introducción a la Química Bioinorgánica.
Dr. Manuel I. Azócar
Universidad de Santiago de Chile

Proteínas de Hierro Azufre:

Bacterias aeróbicas
Bacterias anaeróbicas y fotosintéticas
Algas

Hongos
Plantas superiores
Mamíferos

Azufre orgánico : (Cisteína)



Azufre Inorgánico



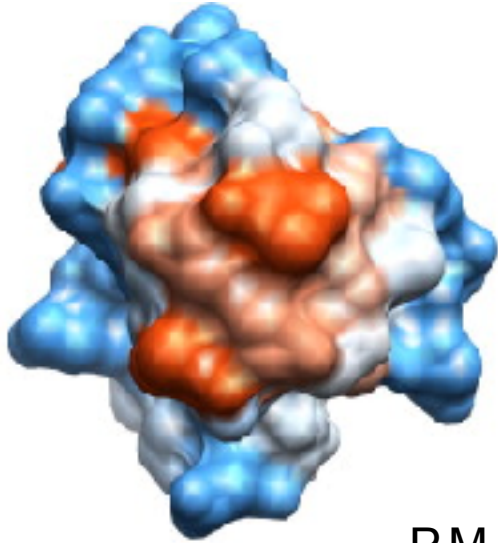
+350 mV / -600 mV

A large blue arrow points to the right, with a trail of smaller blue arrows and dots behind it, suggesting a transition or reaction. Below this arrow is a blue gradient oval.

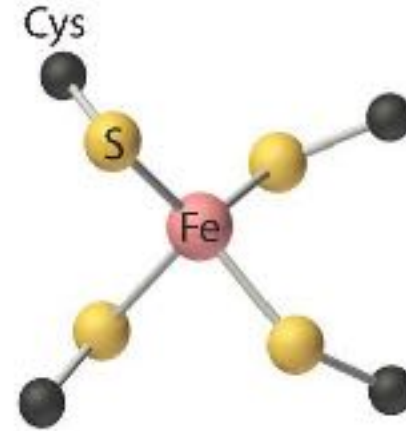
CUADRO 4.1
Propiedades de algunas proteínas hierro-azufre

PROTEÍNA	Composición Fe-S	Potencial redox mV (pH)	Masa molecular kDa (Subunidades)
• Rubredoxinas			
<i>Clostridium pasteurianum</i>	Fe	-53 (7,0)	6
<i>Pseudomonas oleovorans</i>	Fe		6
• Ferredoxinas [2Fe-2S]			
Equinatus	[2Fe-2S]	-420 (7,0)	11
Peripl	[2Fe-2S]		11
Euglena	[2Fe-2S]		11
Corteza suprarrenal (cerdo)	[2Fe-2S]	-270 (7,0)	16
<i>Pseudomonas putida</i>	[2Fe-2S]	-240 (7,0)	17,5
<i>Clostridium pasteurianum</i>	[2Fe-2S]	-300 (7,5)	25
Xantina oxidase	2 x [2Fe-2S] I	-343 (8,2)	280 (2)
	II	-303 (8,2)	
<i>Thermus thermophilus</i> (P. esko)	2 x [2Fe-2S]	+150 (7,8)	20
• Ferredoxinas [4Fe-4S]			
<i>Clostridium pasteurianum</i>	2 x [4Fe-4S]	-420 (8,2)	6
<i>Bacillus stearothermophilus</i>	[4Fe-4S]	-280 (8,0)	9,1
<i>Desulfotribria gigas</i> (Fd II)	[4Fe-4S]	-455 (8,0)	18 (3)
Aconitase (corazón bovino, activo)	[4Fe-4S]		81
<i>Chromatium vinosum</i> (-HIP)	[4Fe-4S]	+356 (7,0)	10
<i>Paracoccus</i> sp.	[4Fe-4S]	+262 (7,0)	10
<i>Azotobacter vinelandii</i> (Fd I)	[3Fe-4S]		14,5
	[4Fe-4S]	-645 (8,3)	
<i>Thermus aquaticus</i>	[3Fe-4S]		10,5
	[4Fe-4S]	-550 (9,0)	
• Ferredoxinas [3Fe-4S]			
<i>Desulfotribria gigas</i> (Fd II)	[3Fe-4S]	-130 (8,0)	6 (4)
<i>Azotobacter vinelandii</i> (Fd I)	[3Fe-4S]	-450 (8,3)	14,5
	[4Fe-4S]		
<i>Thermus aquaticus</i>	[3Fe-4S]	-260 (9,0)	10,5
	[4Fe-4S]		
Aconitase (corazón bovino, inactivo)	[3Fe-4S]		81

Proteínas de Hierro Azufre transportadora de e⁻: Rubredoxina



P.M. 6.000
Fe (III) Roja
Fe(II) Incolora
Alto spin

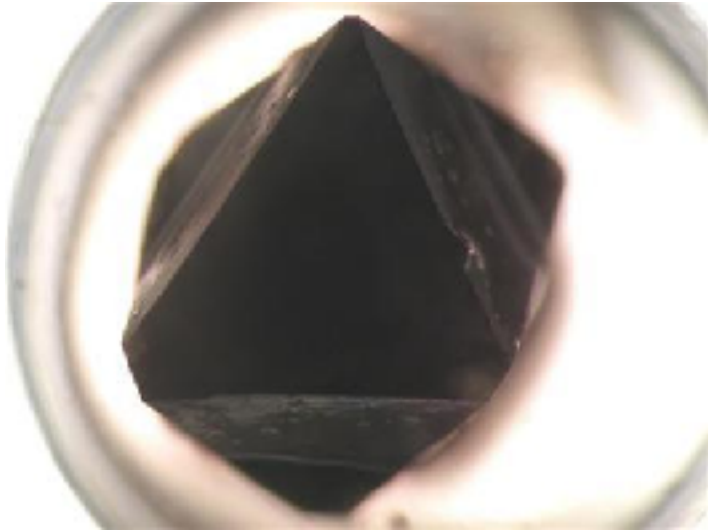


Fe(SCys)₄

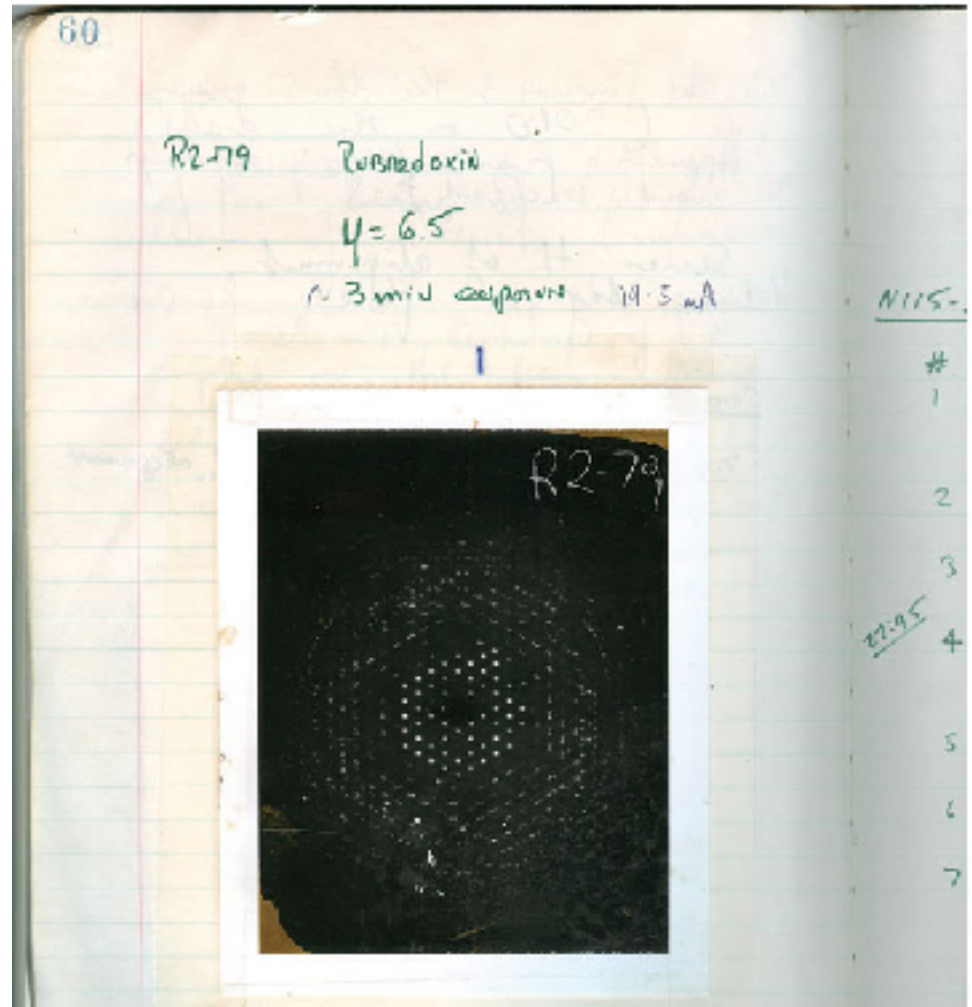
Hidroxilación de ácidos grasos



Proteínas de Hierro Azufre transportadora de e⁻: Rubredoxina



Crystal of *Pyrococcus furiosus* rubredoxin. The strong red colour of the crystal comes from the Fe-4S cluster in the protein (Fe III). The crystal is a 3mm wide square bipyramid. Dr. Maxime Cuypers Keele University , Institut Laue Langevin (ILL), Grenoble, France

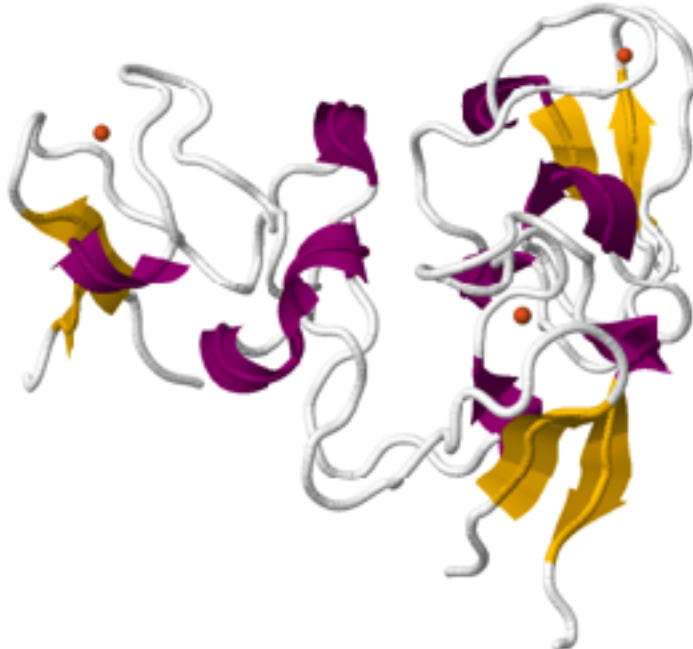


In **1975**, X-rays called rubredoxin.

Proteínas de Hierro Azufre transportadora de e⁻: Rubredoxina

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NOTE: Use your mouse to drag, rotate, and zoom in and out of the structure. [Help](#)



Biological assembly 1 assigned by authors

Select a Viewer

JSmol (JavaScript) ▾

Structure Details

Structure: Biological Assembly 1 ▾

Symmetry Type: Global Symmetry ▾

Symmetry: C3

Stoichiometry: A3

Select Orientation

◀ Side face-centered ▶

Select Display Mode

Secondary Structure Subunit Symmetry

Display Options

Style: Cartoon ▾

Color: Secondary Structure ▾

Surface: None ▾

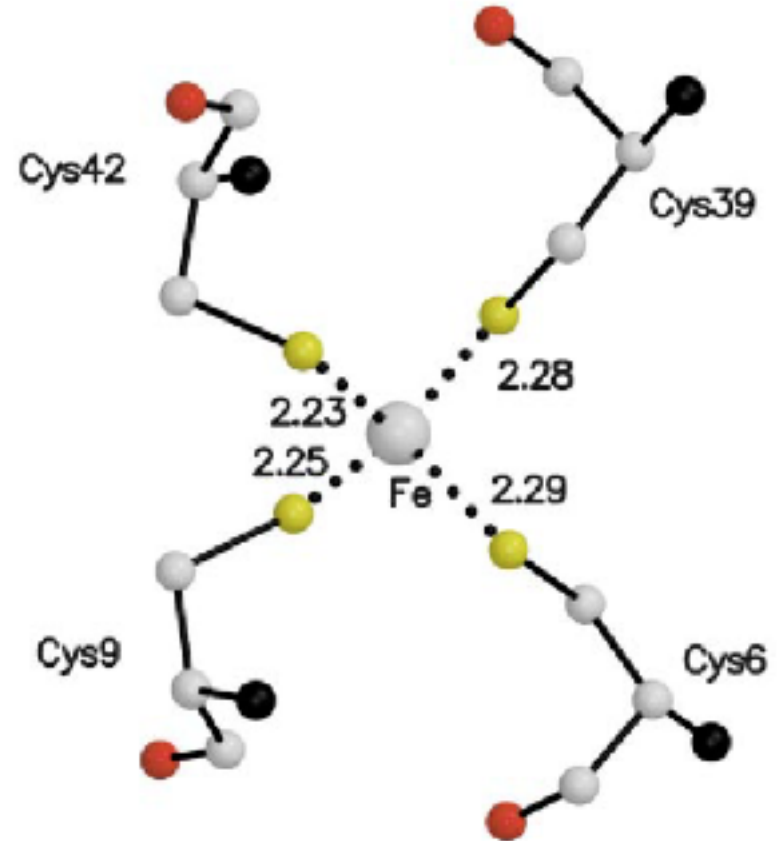
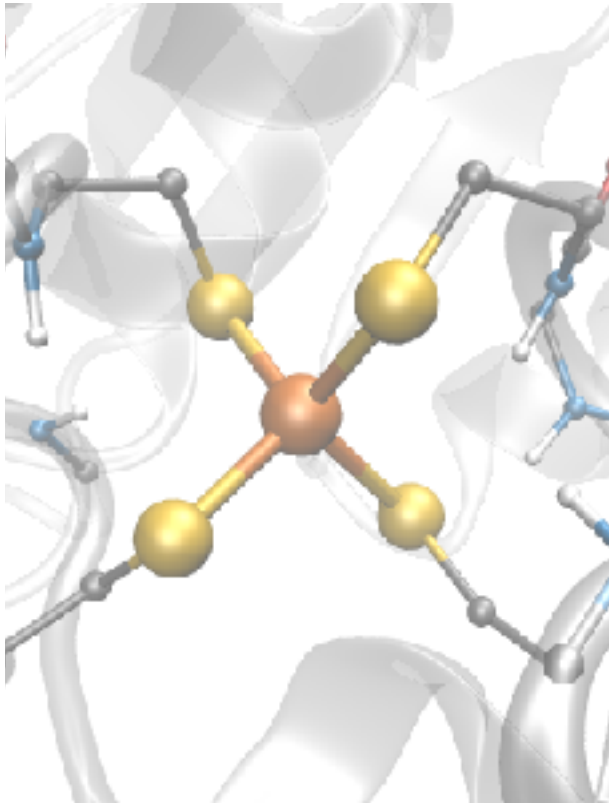
H-Bonds SS Bonds

Rotation Black Background

Polyhedron Axes

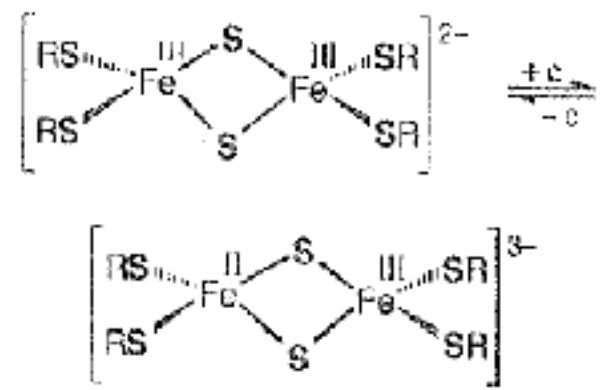
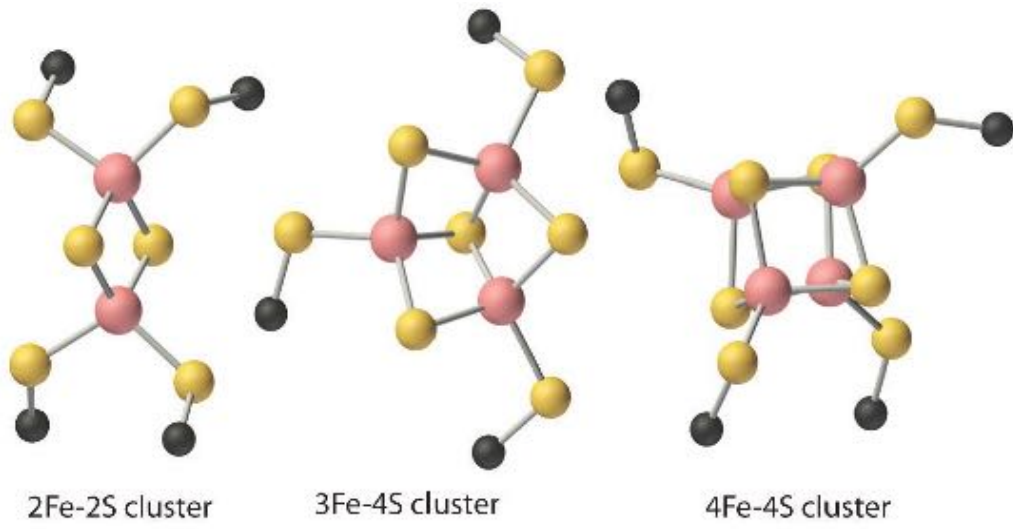
JSmol

Proteínas de Hierro Azufre transportadora de e⁻: Rubredoxina



Interacciones cortas: **Fe-S**

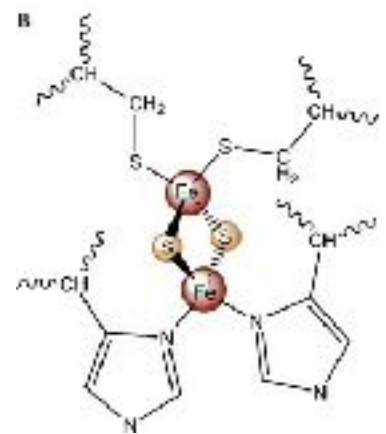
Proteínas de Hierro Azufre transportadora de e⁻: Ferredoxinas



E.O = 2.5 ~~X~~

Procesos fotosintéticos

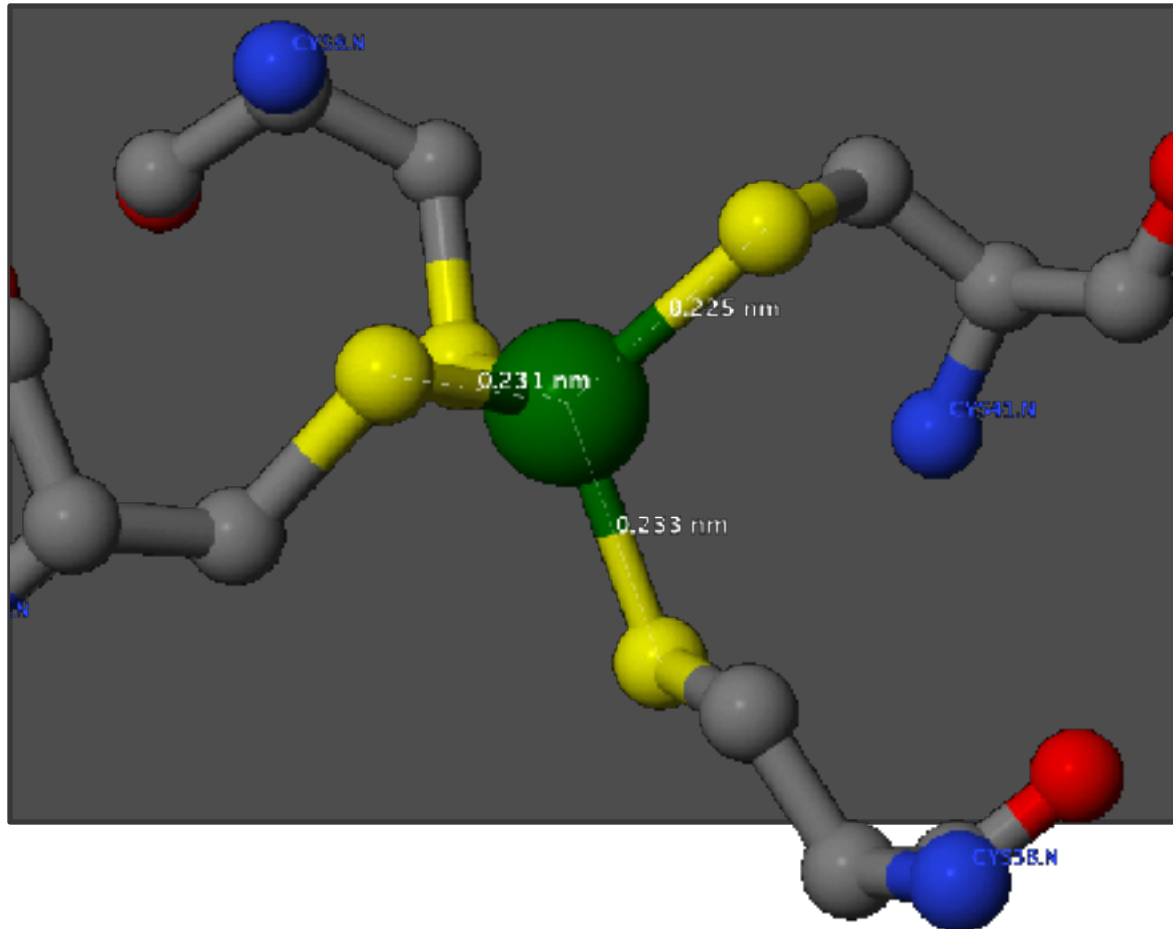
Ferredoxina → Adrenodoxina → Catálisis de hidroxilación de esteroides



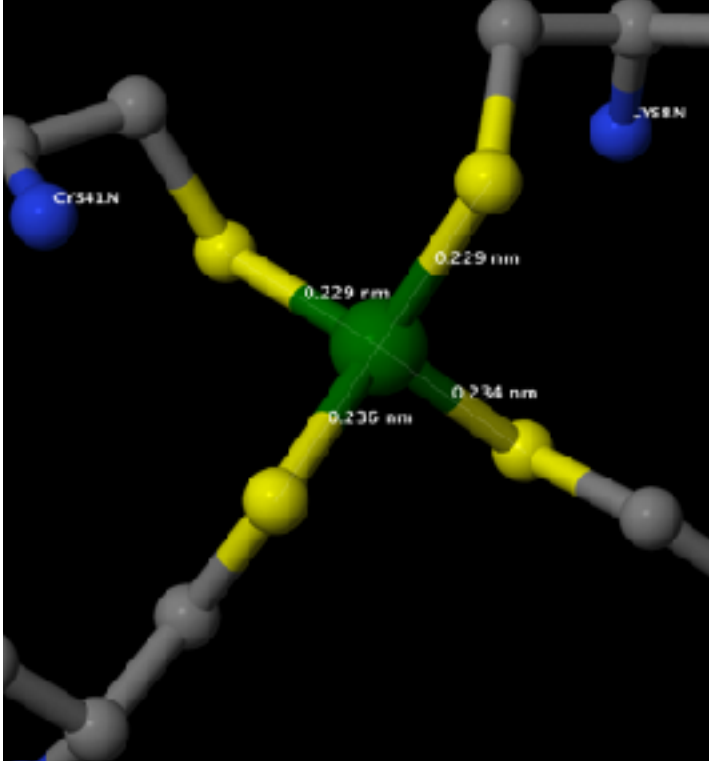
Rieske: +150 mV

Fe(III)-Fe(III) : Alto spin, forma oxidada // Fe(III)-Fe(II): Alto spin → Moossbauer, EPR

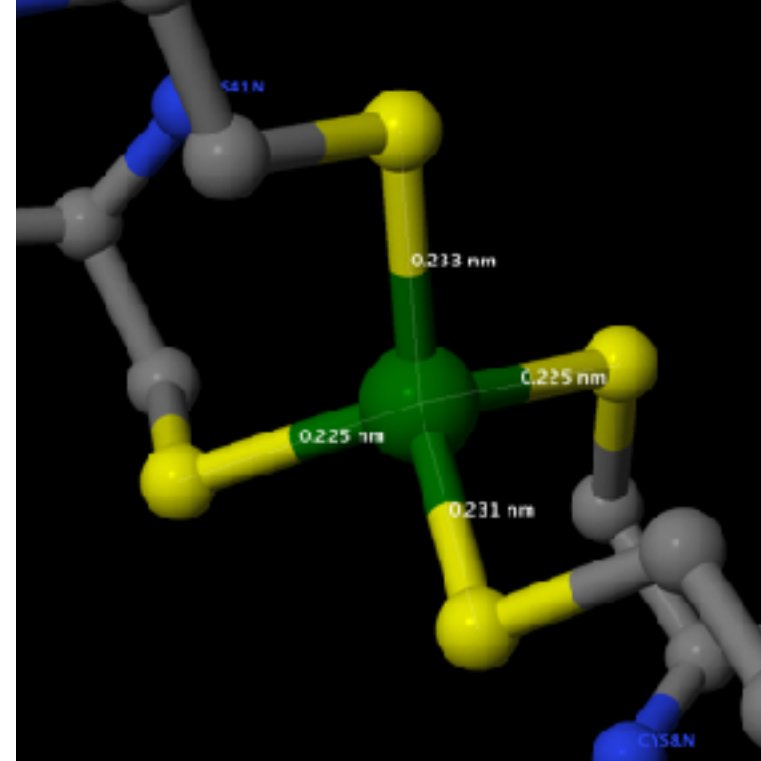
Proteínas de Hierro Azufre transportadora de e⁻: Ferredoxinas



Proteínas de Hierro Azufre transportadora de e⁻: Ferredoxinas



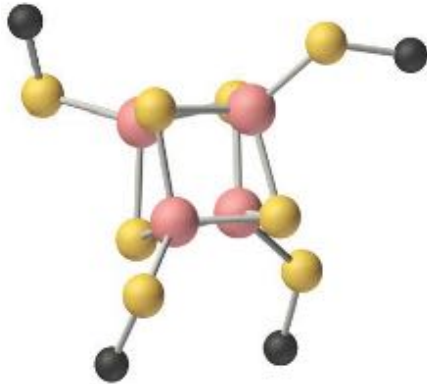
Forma Reducida



Forma Oxidada

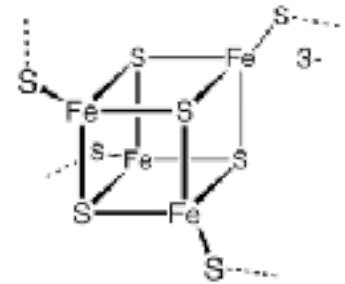
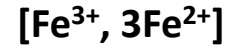
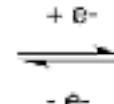
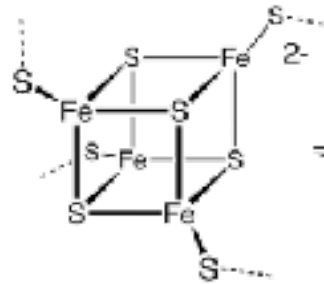
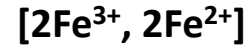
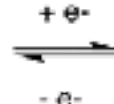
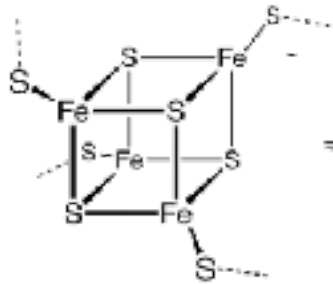
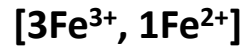
ferredoxinas oxidadas son rojizas, y se decoloran en la forma reducida

Proteínas de Hierro Azufre transportadora de e⁻: Ferredoxinas bacterianas



4Fe-4S cluster

Diamag



Proteínas y enzimas de hierro sin grupos hemo

189

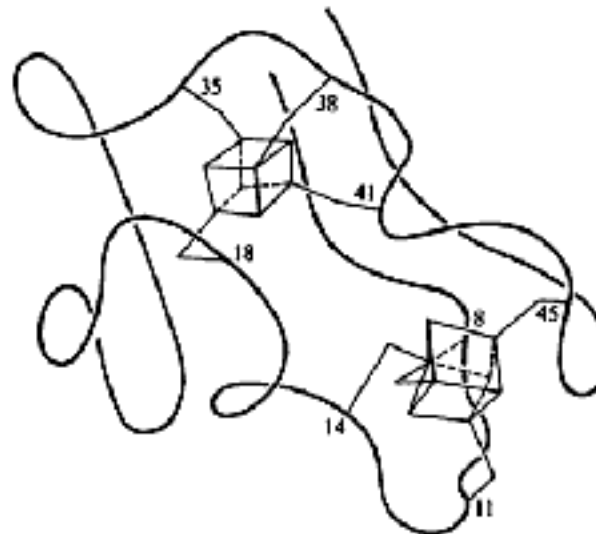
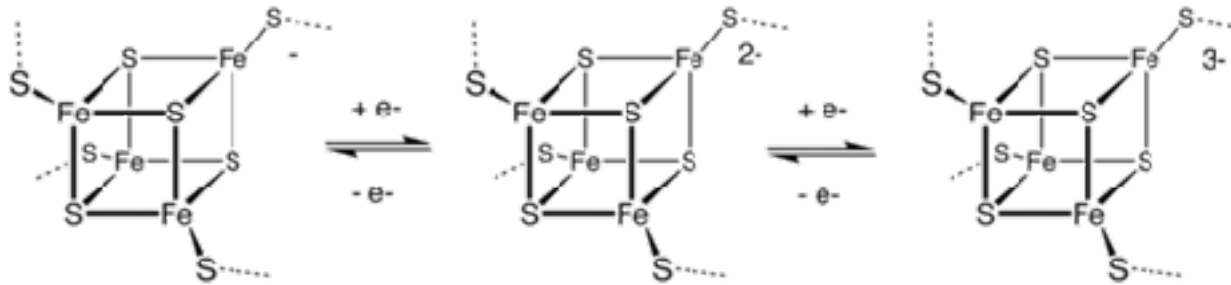


Figura 8.15 Estructura de la ferredoxina del *Micrococcus aerogenes*. [Según Jensa y col., Biochem. Soc. Trans., 1, (1973), p. 29.]

Proteínas de Hierro Azufre transportadora de e⁻: Ferredoxinas bacterianas



400-500 nm : Fe(III)-Fe(III)
??: : Fe(III)-Fe(II)

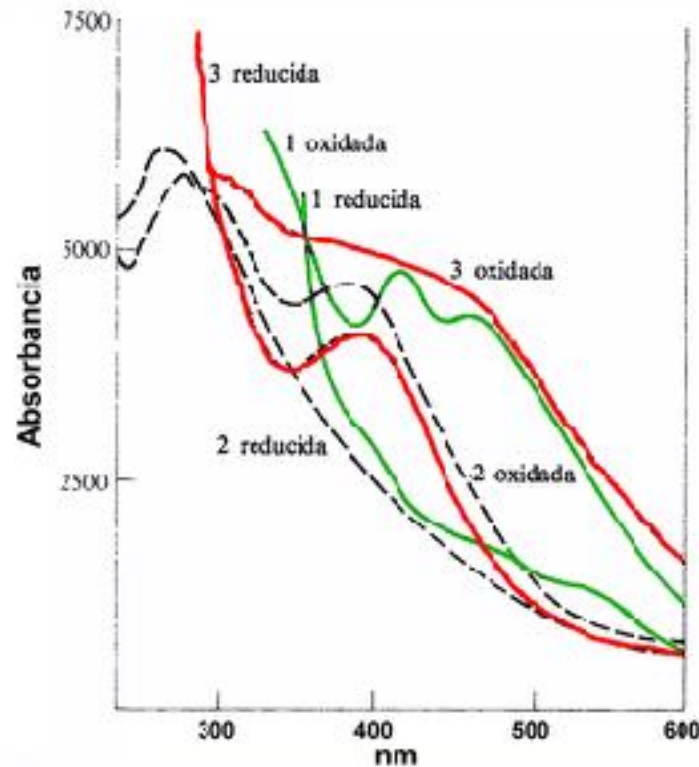


Figura 8.3 Espectro de absorción de (1) ferredoxina de espinacas, (2) ferredoxina de *Clostridium pasteurianum*, y (3) HIPIP (ox = estado oxidado, red = estado reducido). [Según Palmer y Brintzinger, en «Electron

Proteínas de Hierro Azufre transportadora de e⁻: Ferredoxinas bacterianas

Estado oxidado:
Menos favorable

Estado reducido:
Mas favorable

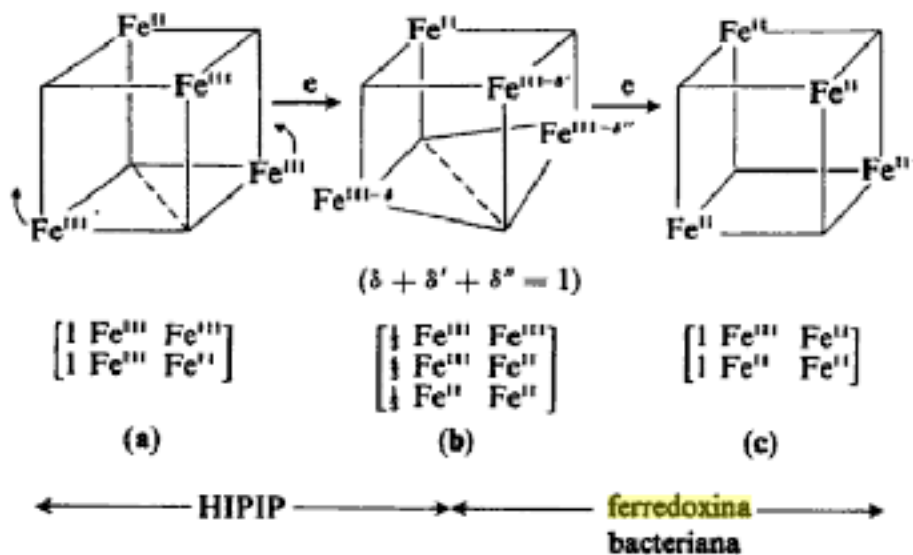
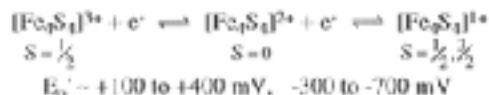
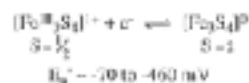
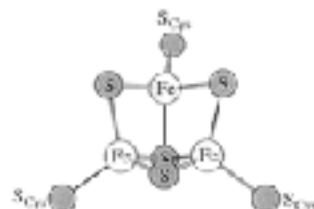
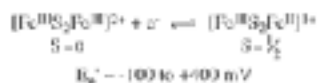
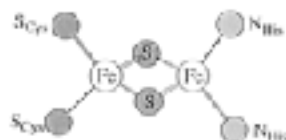
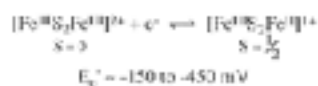
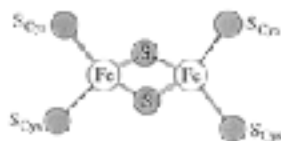
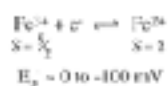
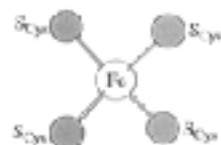


Figura 8.16 Representación esquemática de los tres estados de oxidación de un agregado Fe₄S₄. [Las formas de (a) y (b) están basadas en los datos de Carter y col., *J. Biol. Chem.*, 249, 6339 (1974).]





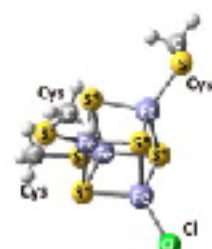
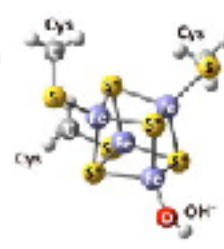
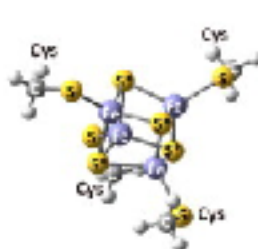
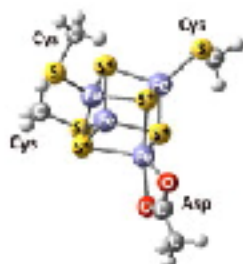
NB cluster model

D36C model

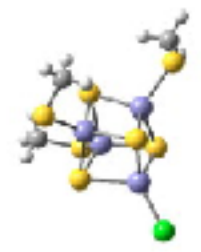
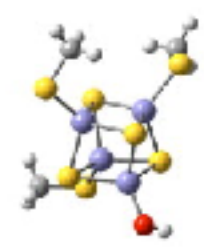
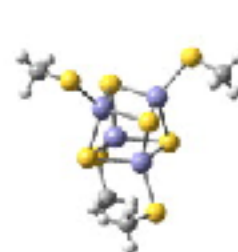
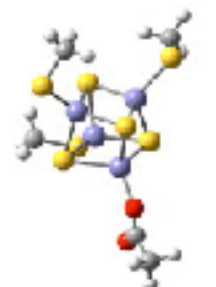
D36A_OH model

D36A_Cl model

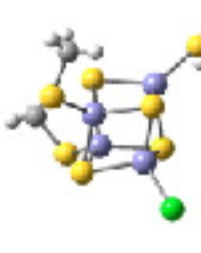
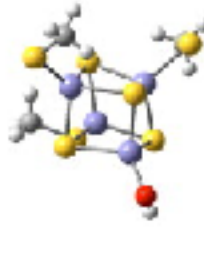
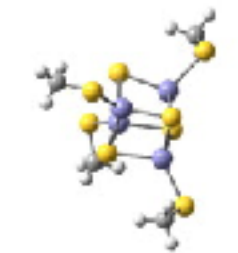
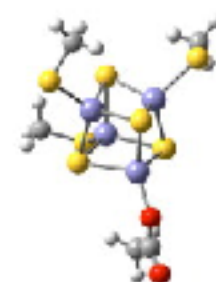
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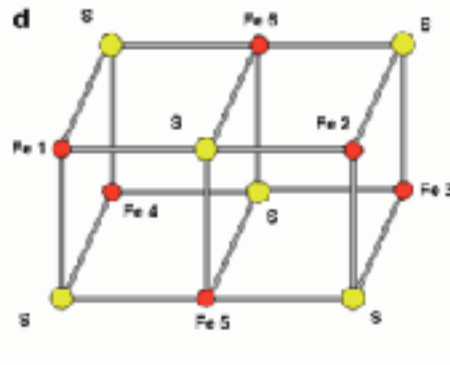
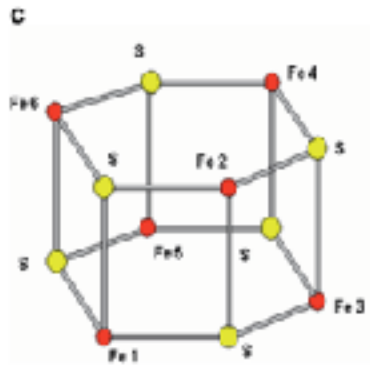
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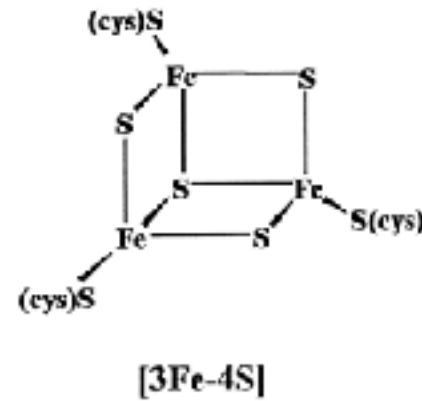
3-



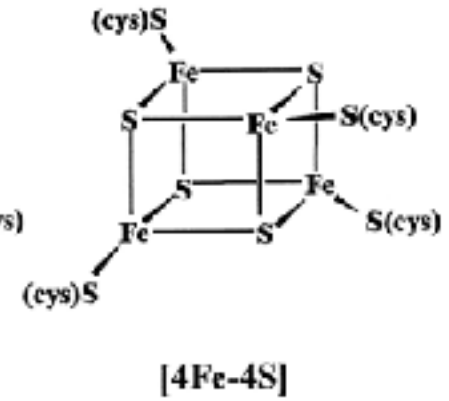
6FeS6 : Transportador de electrones



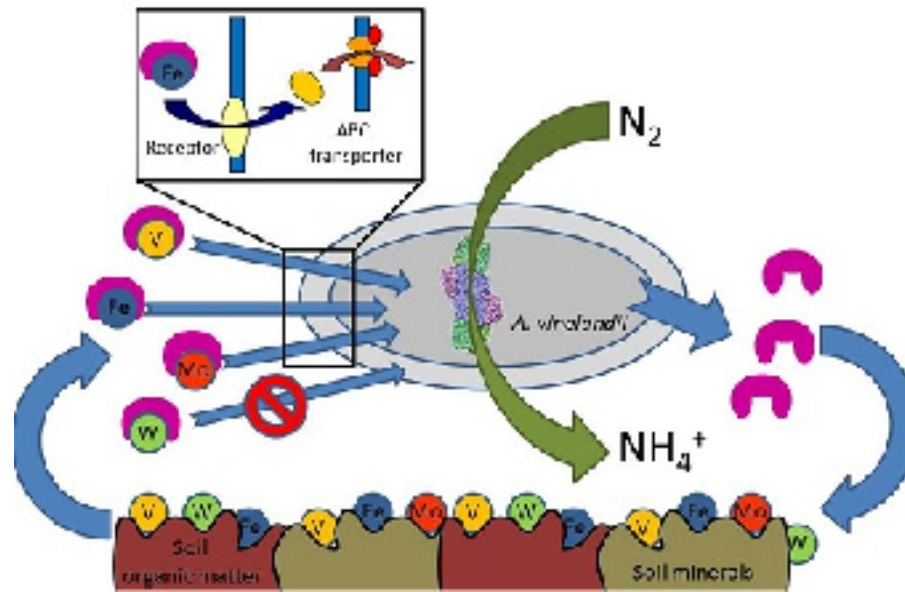
?



[3Fe-4S]



[4Fe-4S]



Azotobacter vinelandii

Actúan como cofactores en procesos Redox

Prot. Fe-S + Flavoproteínas : Succinato deshidrogenasa, NADH deshidrogenasa, dihidroorotato deshidrogenasa

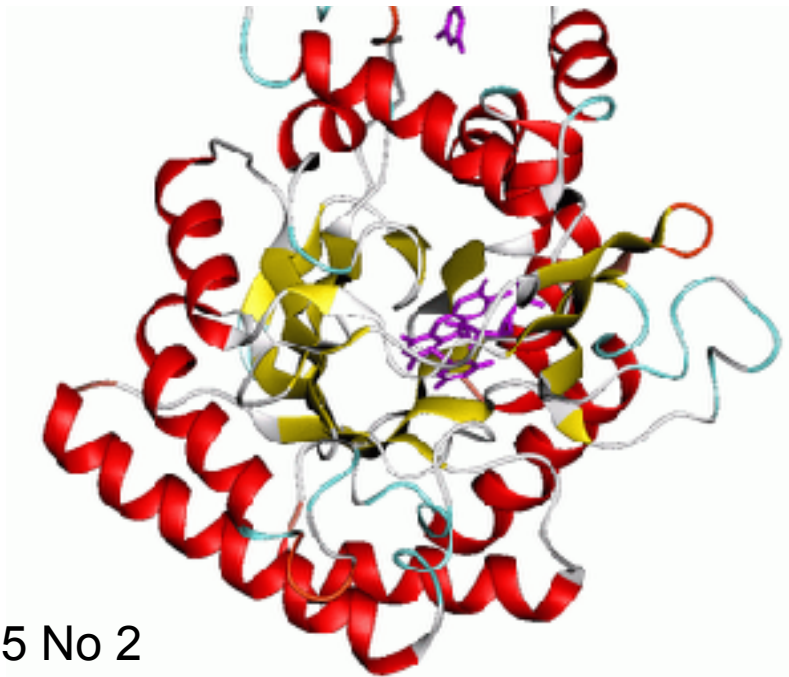
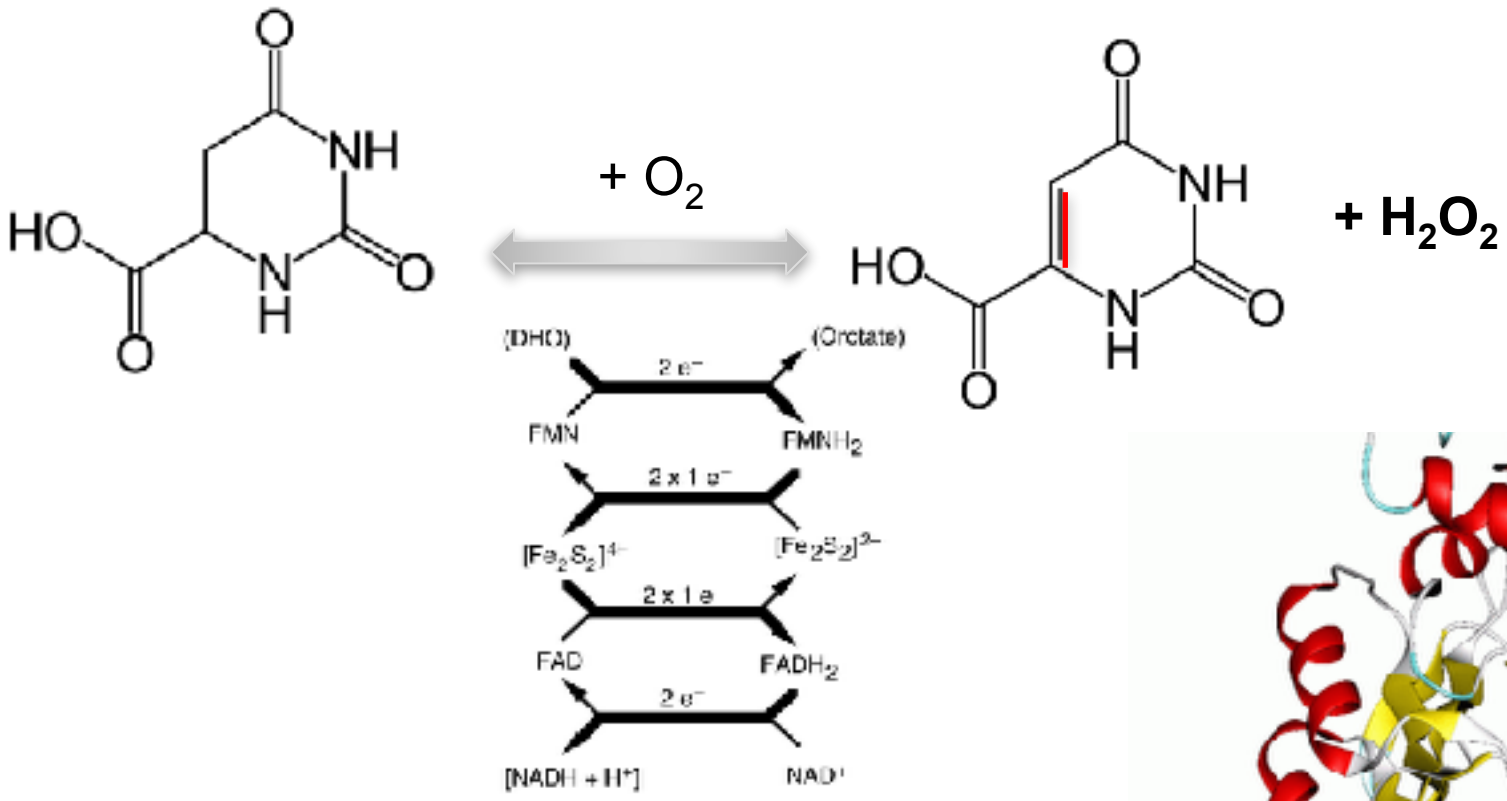
Prot. Fe-S + Molibdeno + Flavoproteína: Xantina oxidasa, aldehído deshidrogenasa, nitrogenasa

Prot. Fe-S

Enzima	P. Molecular	Flavina	Fe	S. Inorg
Succinato deshidrogenasa	550.000	2FMN	32-36	42
NADH deshidrogenasa	175.000	2FAD	8	8
Dihidroorotato deshidrogenasa	124.000	2FAD 2FMN	4	4 Fe ₂ S ₂

Dihidroorotato deshidrogenasa

Enzima que cataliza en 4 etapas la biosíntesis de pirimidina. Convierte dihidroorotato a orotato(pirimidina):

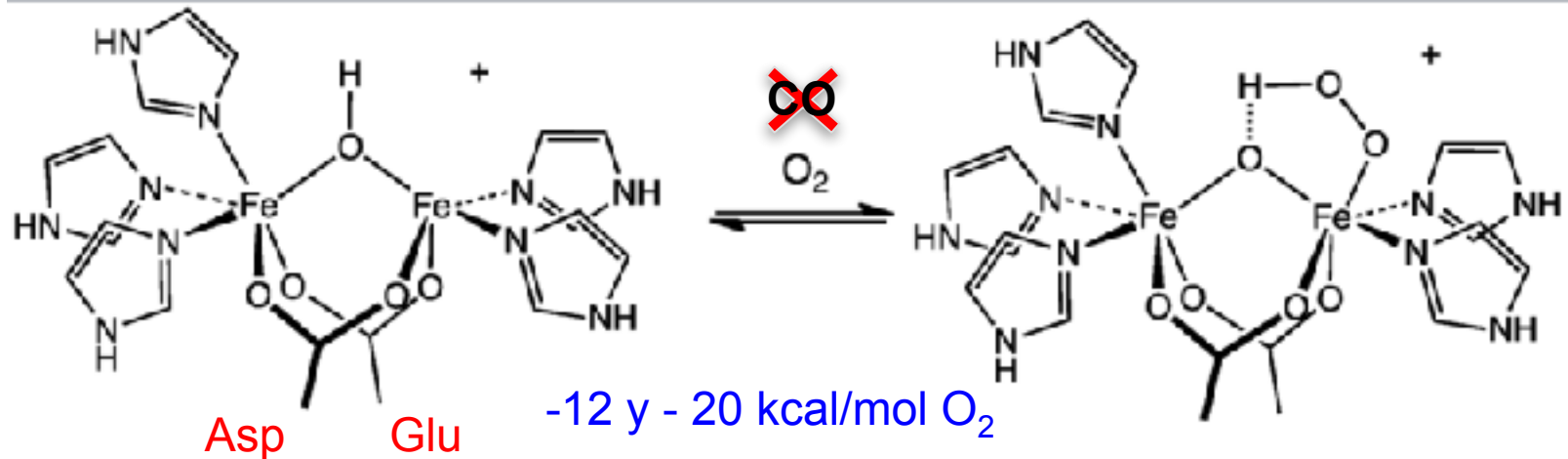


Hemeritrina: transporte de oxígeno en invertebrados marinos



Golfingia gouldii

El único compuesto de hierro no hemo natural que funciona como transportador de oxígeno



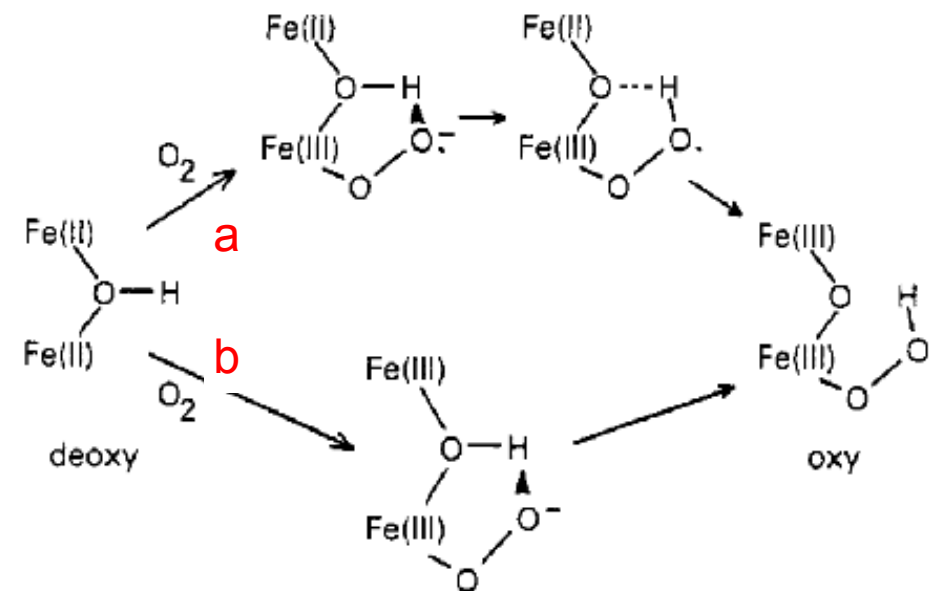
Fe²⁺—OH—Fe²⁺ deoxy (reduced)

Fe²⁺—OH—Fe³⁺ metemeritrina

Fe³⁺—O—Fe³⁺—OOH⁻ oxy (oxidized)

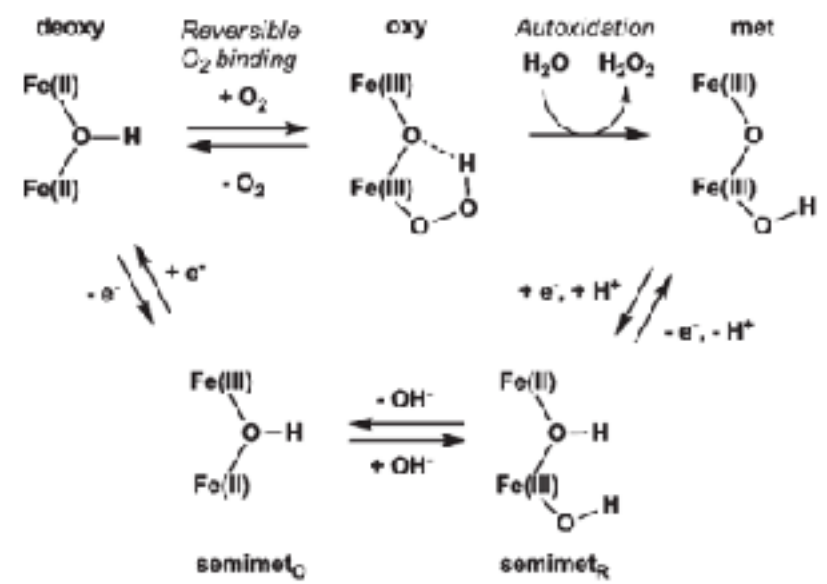
Fe³⁺—OH—Fe³⁺— (any other ligand) met (oxidized)

Hemerritina: transporte de oxígeno en invertebrados marinos



Chemical Reviews, 1994, Vol. 94, No. 3

Scheme 1. Plausible Reaction Mechanism of the Diiron Site [Fe1 (upper) and Fe2 (bottom)] in the Hr Family of Proteins^a



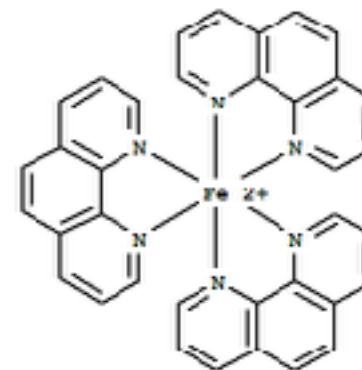
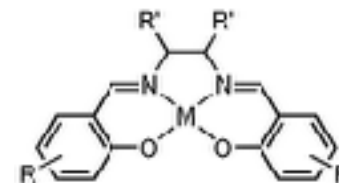
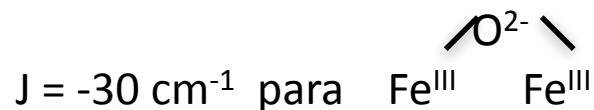
^a OH⁻ ligand binds to Fe2. In the case of the DcrH-Hr protein, the semimet_O form is undetectable.

Modelos de estudio:

	$-J(\text{cm}^{-1})$
$(\text{Fe}(\text{salen}))_2\text{O}$	-95
$(\text{Fe}(\text{phen})_2)_2\text{O}^{4+}$	95-105
$(\text{Fe}(\text{HEDTA}))_2\text{O}^{2-}$	95
$(\text{Fe}(\text{TPP}))_2\text{O}$	100



Lineal



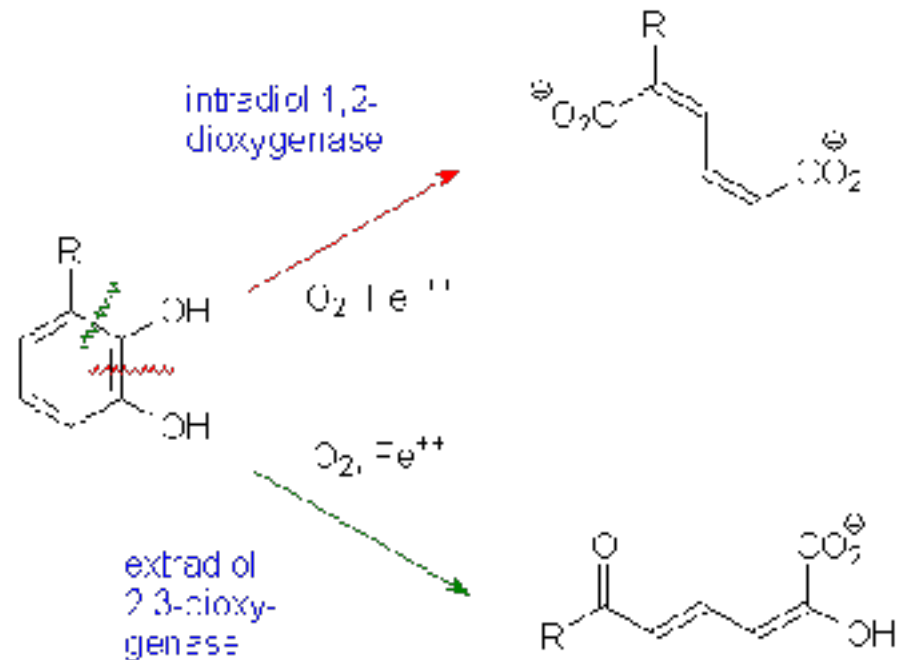
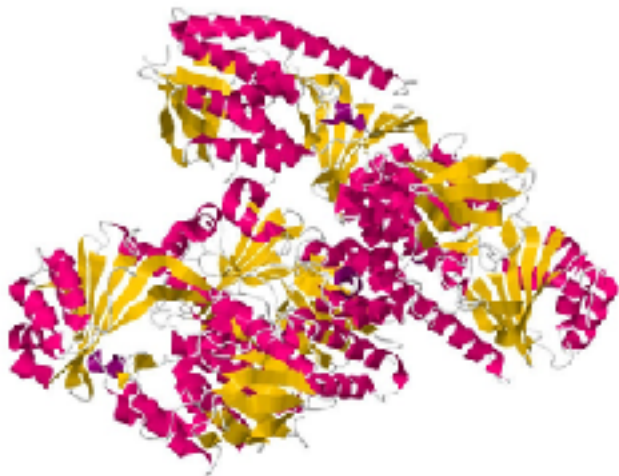
Oxigenasas y Dioxigenasas:

Una oxigenasa es cualquier enzima que oxida un sustrato mediante la transferencia de oxígeno presente en el oxígeno molecular (O_2 , como en el aire).

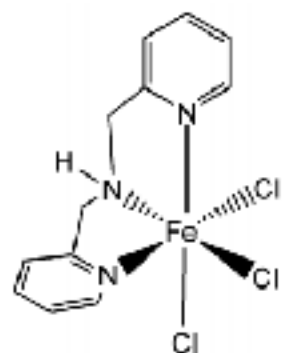
Se distinguen dos tipos de oxigenasas:

Monooxigenasas, que transfieren un átomo de oxígeno al sustrato, y reducen el otro oxígeno a agua.

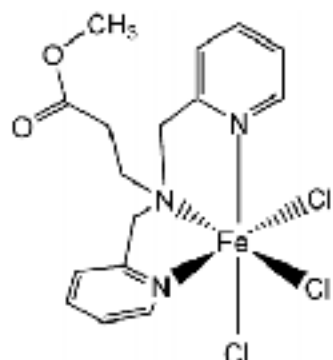
Dioxigenasas, u oxígeno transferasas, que transfieren al sustrato ambos átomos de oxígeno de la molécula.



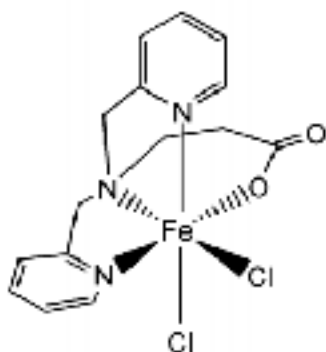
Oxigenasas y Dioxigenasas:



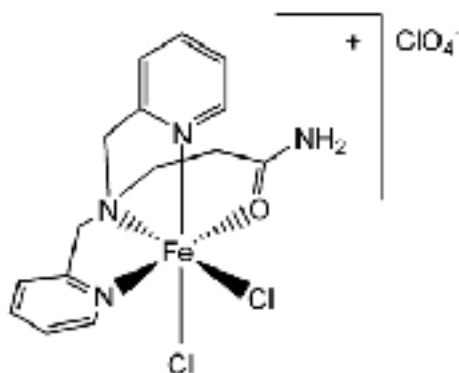
[Fe (BMPA)Cl₃] 1



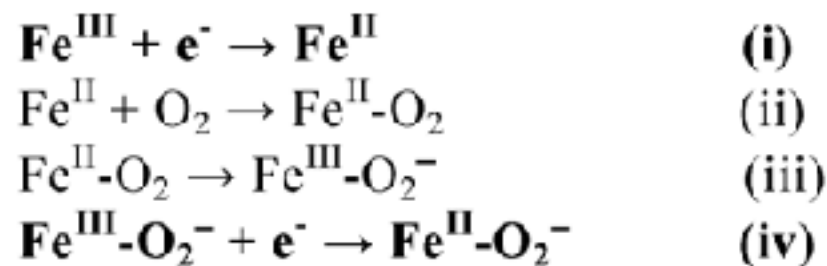
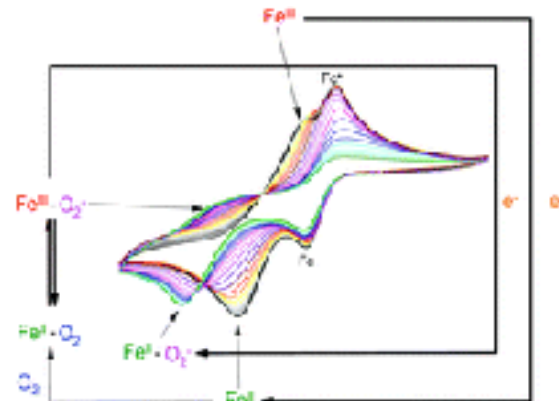
[Fe (MPBMPA)Cl₃] 2



[Fe (PBMPA)Cl₂] 3



[Fe (PABMPA)Cl₂](ClO₄) 4

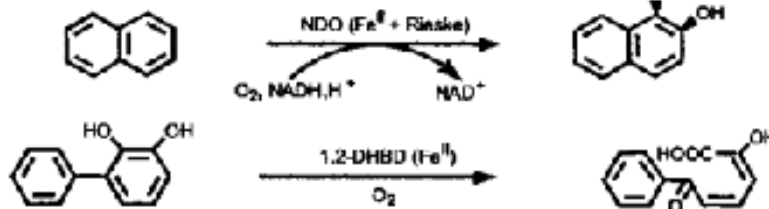


Enzimas-Fe^{II} y Enzimas Fe^{III}:

Fe^{II}/O₂ Activation

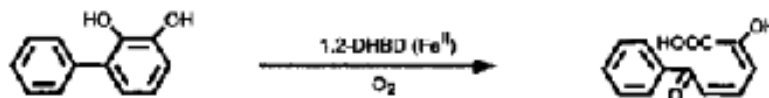
cis-hydroxylation

naphthalene 1,2-dioxygenase (7)



extradiol dioxygenation

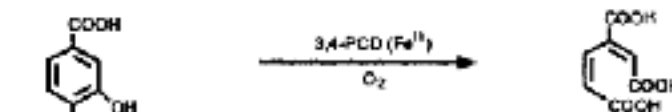
dihydroxybiphenyl dioxygenase (9)



Fe^{III}/Substrate Activation

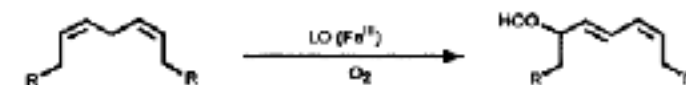
intradiol dioxygenation

protocatechuete 3,4-dioxygenase (10)



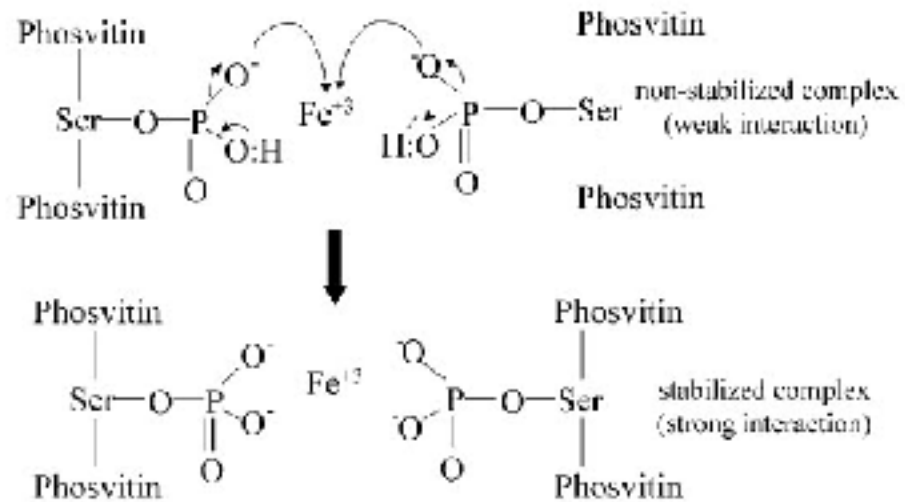
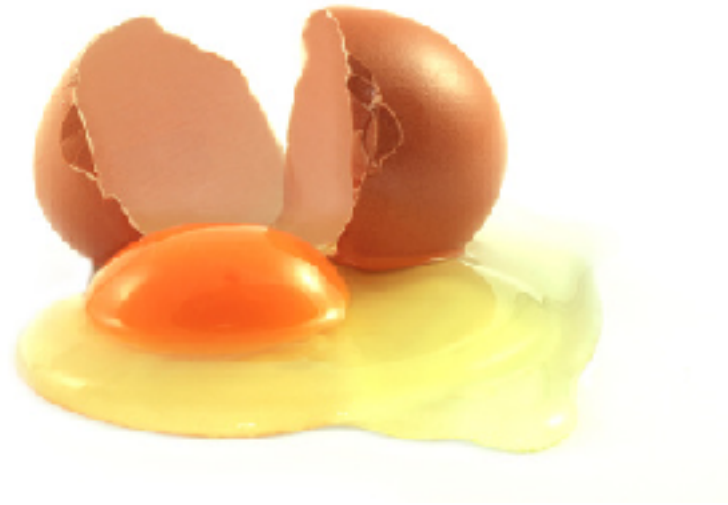
hydroperoxidation

lipoxygenases (8)



Fosvitina :

1mol de Fosvitina--- 47 g de Fe



Fin clase
2016