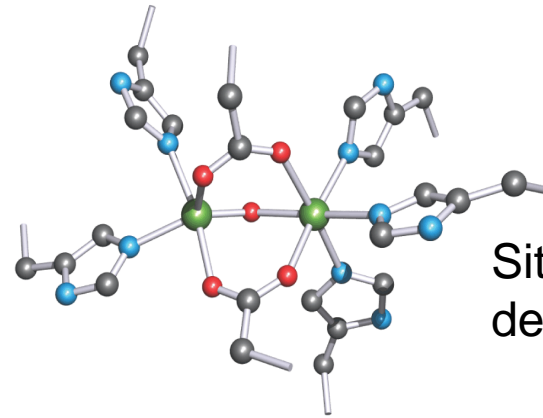
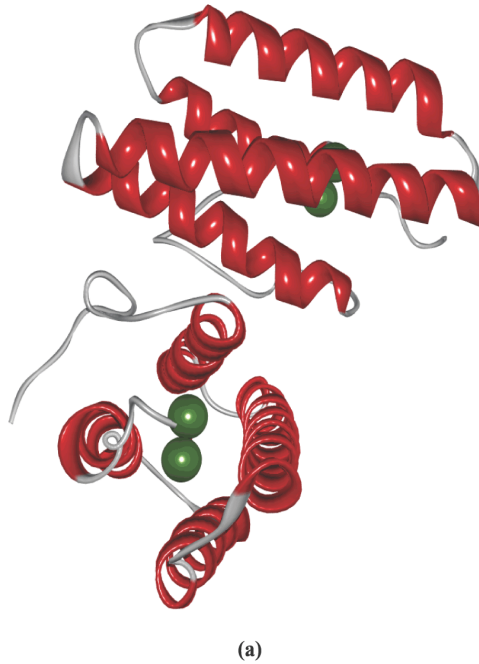


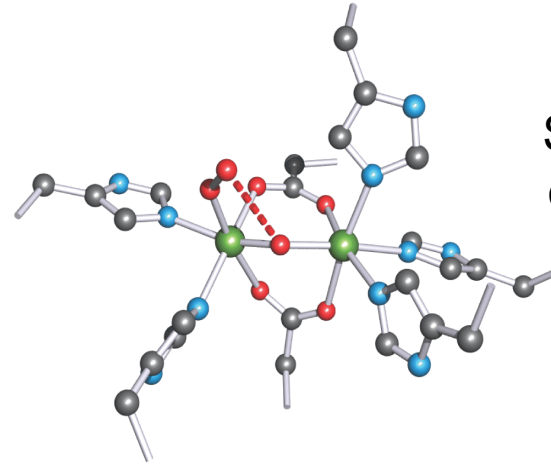
Desossi-emeritrina

(2 di 8 sub-unità)

13,5 kDa
113 a.a.

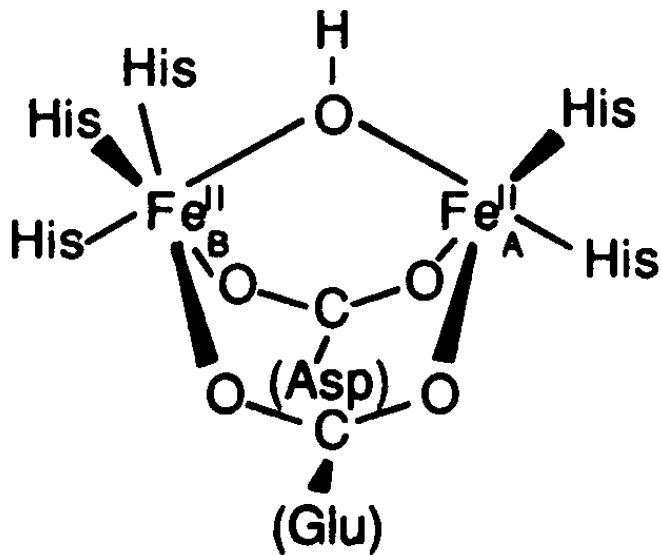


Sito attivo della
desossi-emeritrina



Sito attivo della
ossi-emeritrina

Trasporto O₂ in invertebrati marini, molluschi e ragni

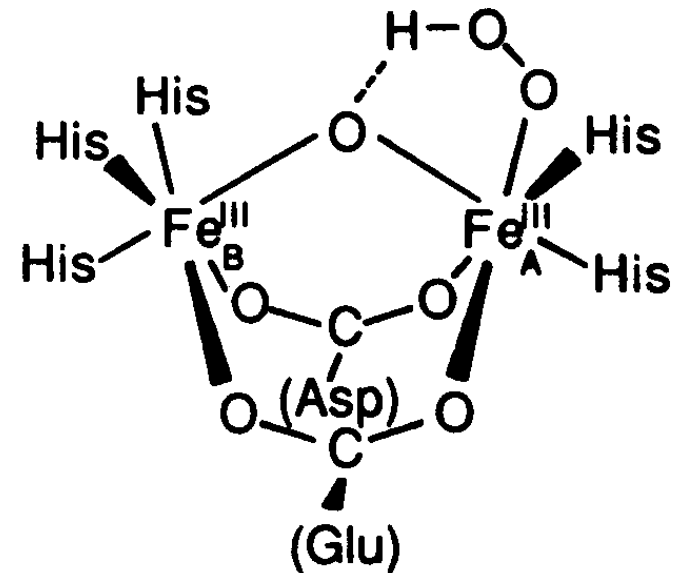
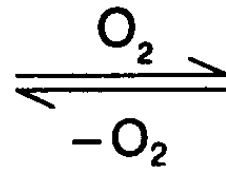


deoxyhemerythrin

Incolore

Fe(II) h.s. ($S = 2$, debole acc. antiferro)

Mossbauer: 2 Fe(II) indistinguibili



oxyhemerythrin

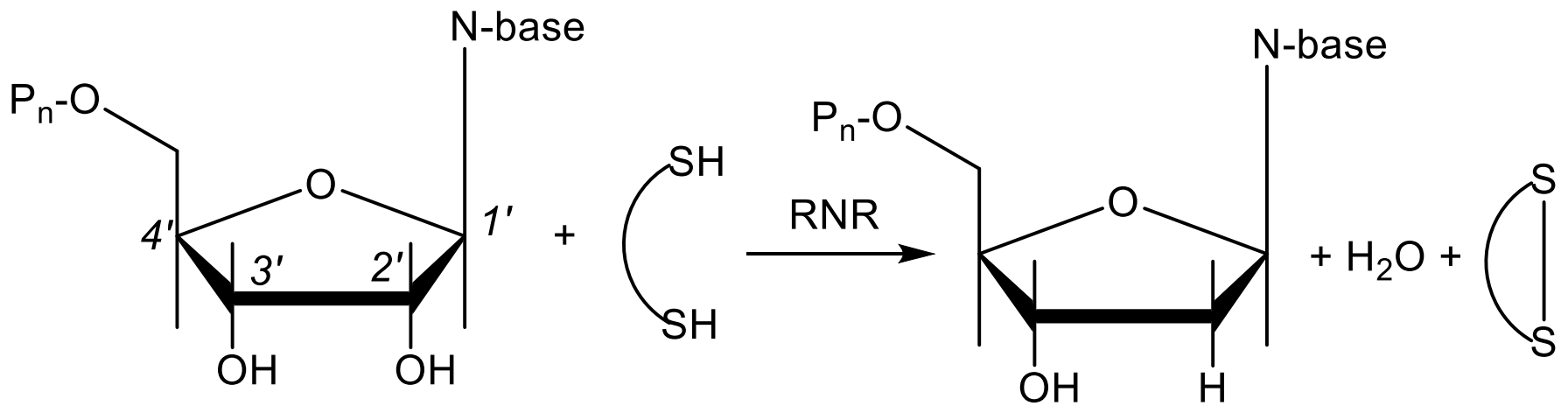
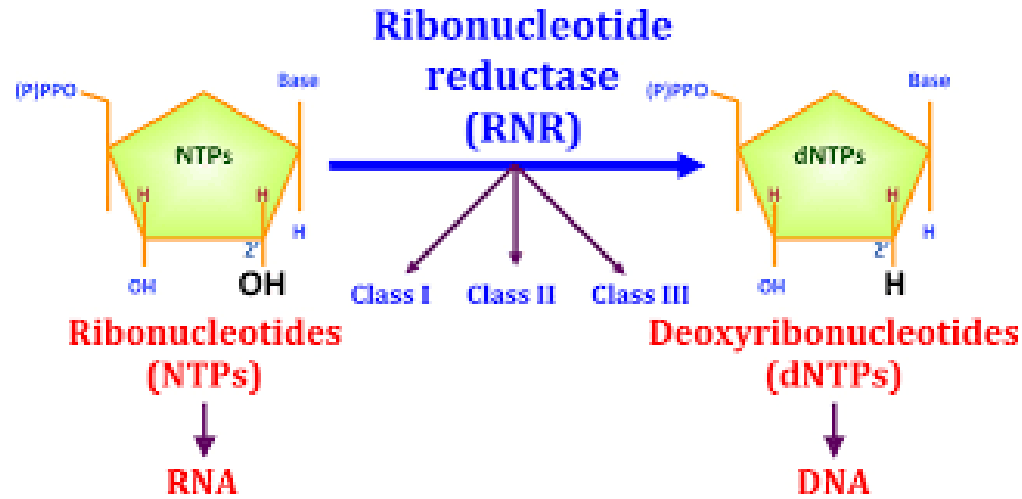
Viola (LMCT)

Fe(III) l.s. ($S = \frac{1}{2}$, forte acc. antiferro)

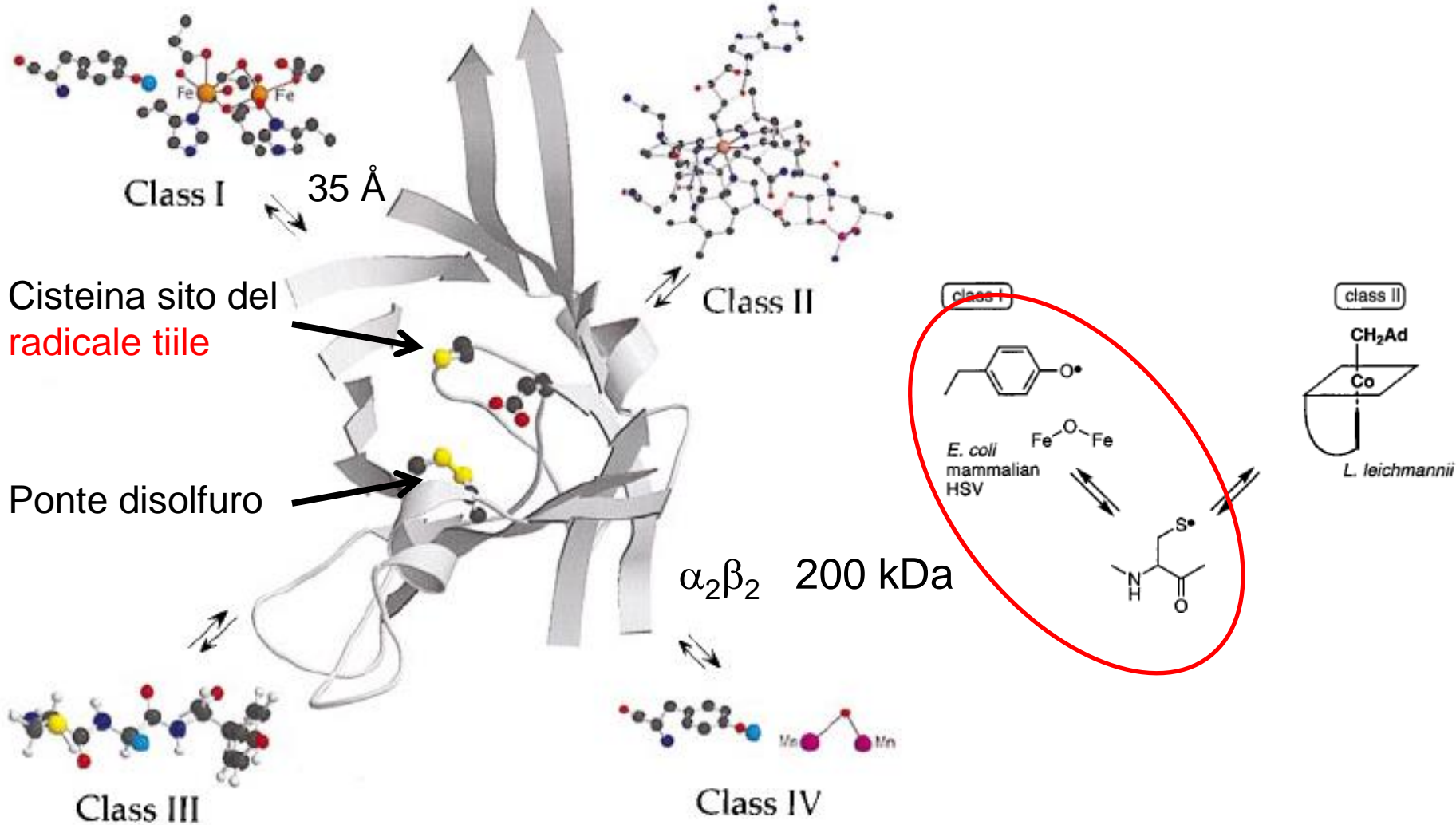
Raman risonante: 848 cm^{-1}

Mossbauer: 2 Fe(III) diversi

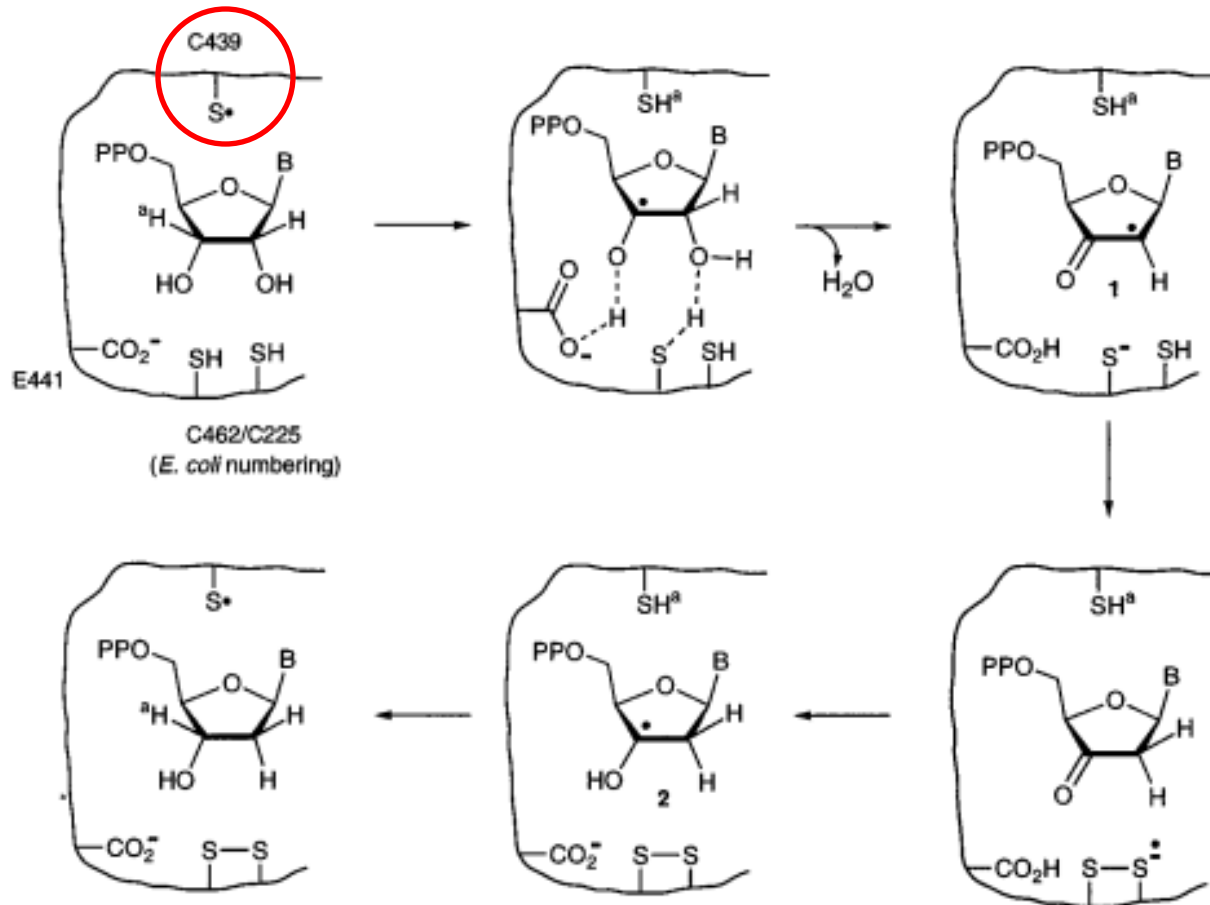
Ribonucleotide Riduttasi (RNR)

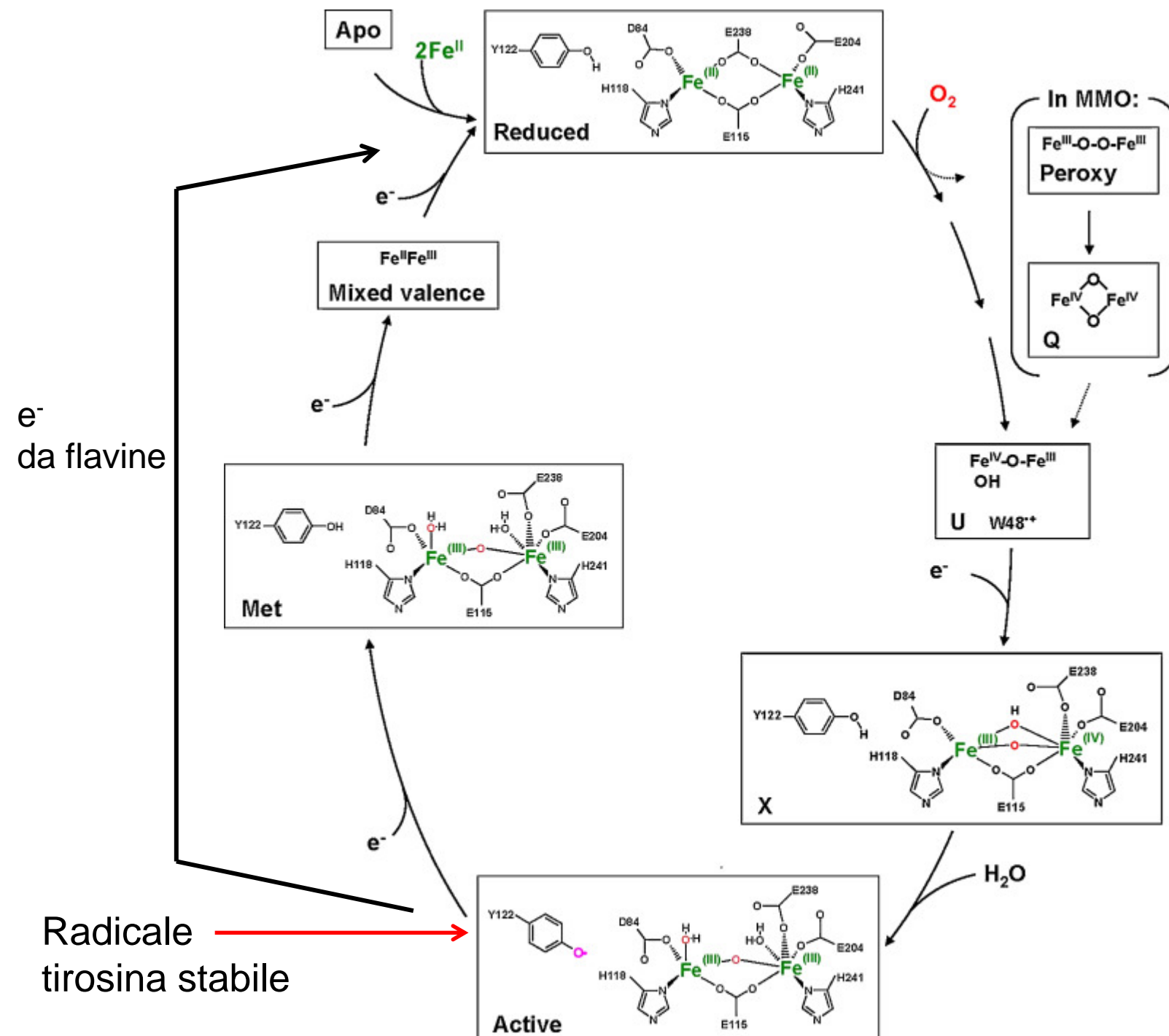


Sito attivo e coenzimi metallici delle varie classi di Ribonucleotide Riduttasi

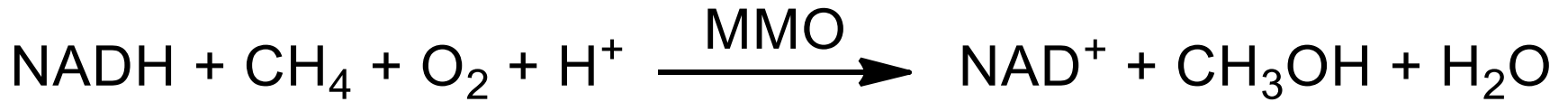


Meccanismo radicalico della *RR*

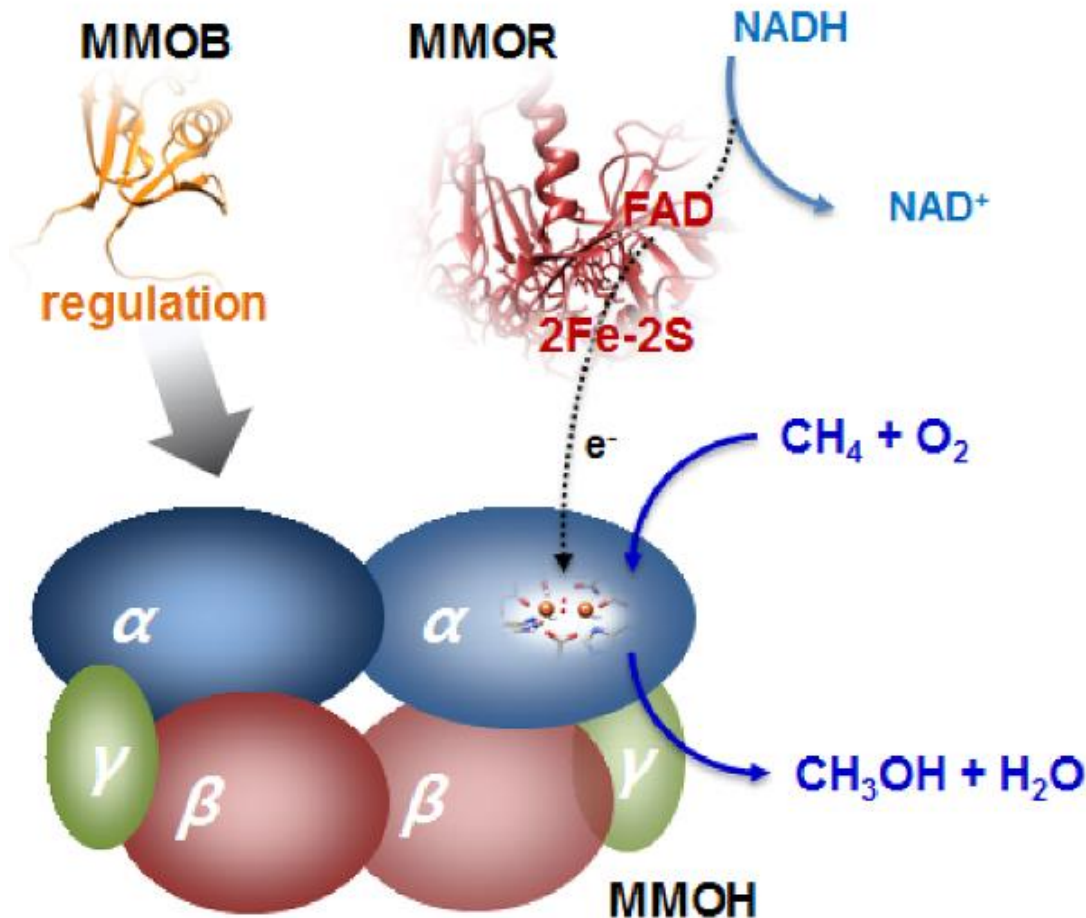




Metano monoossigenasi solubile (sMMO)

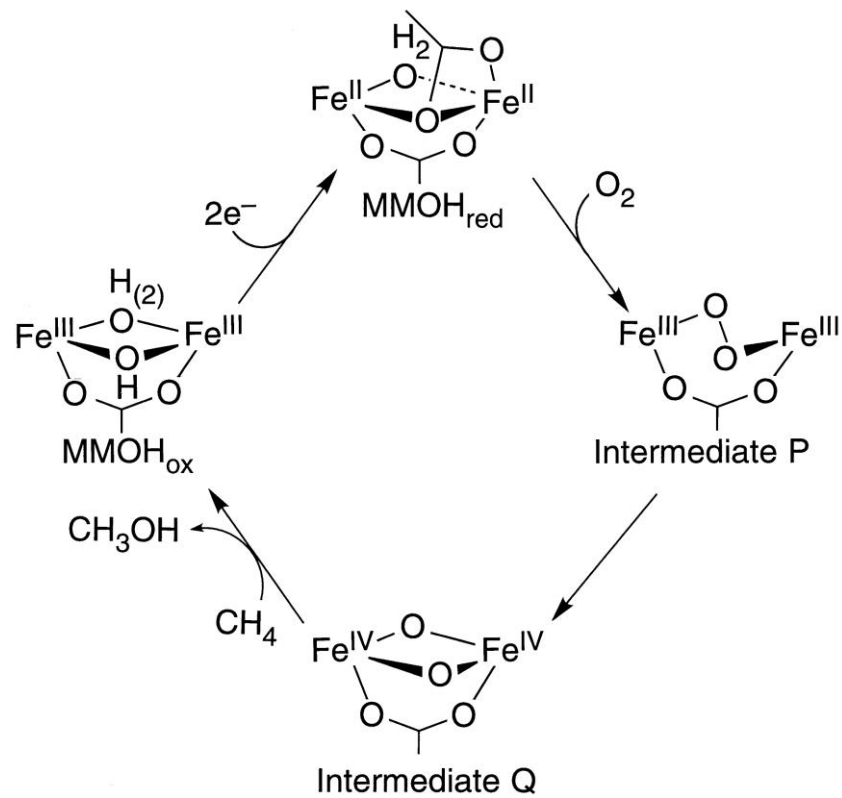
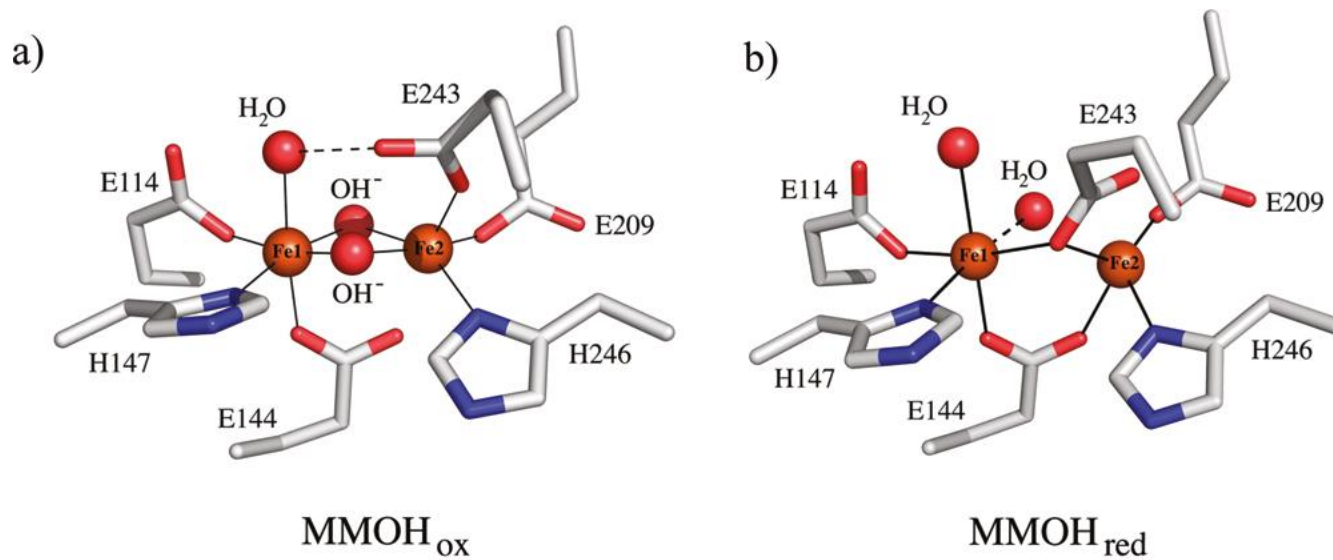


Batteri metanotropici

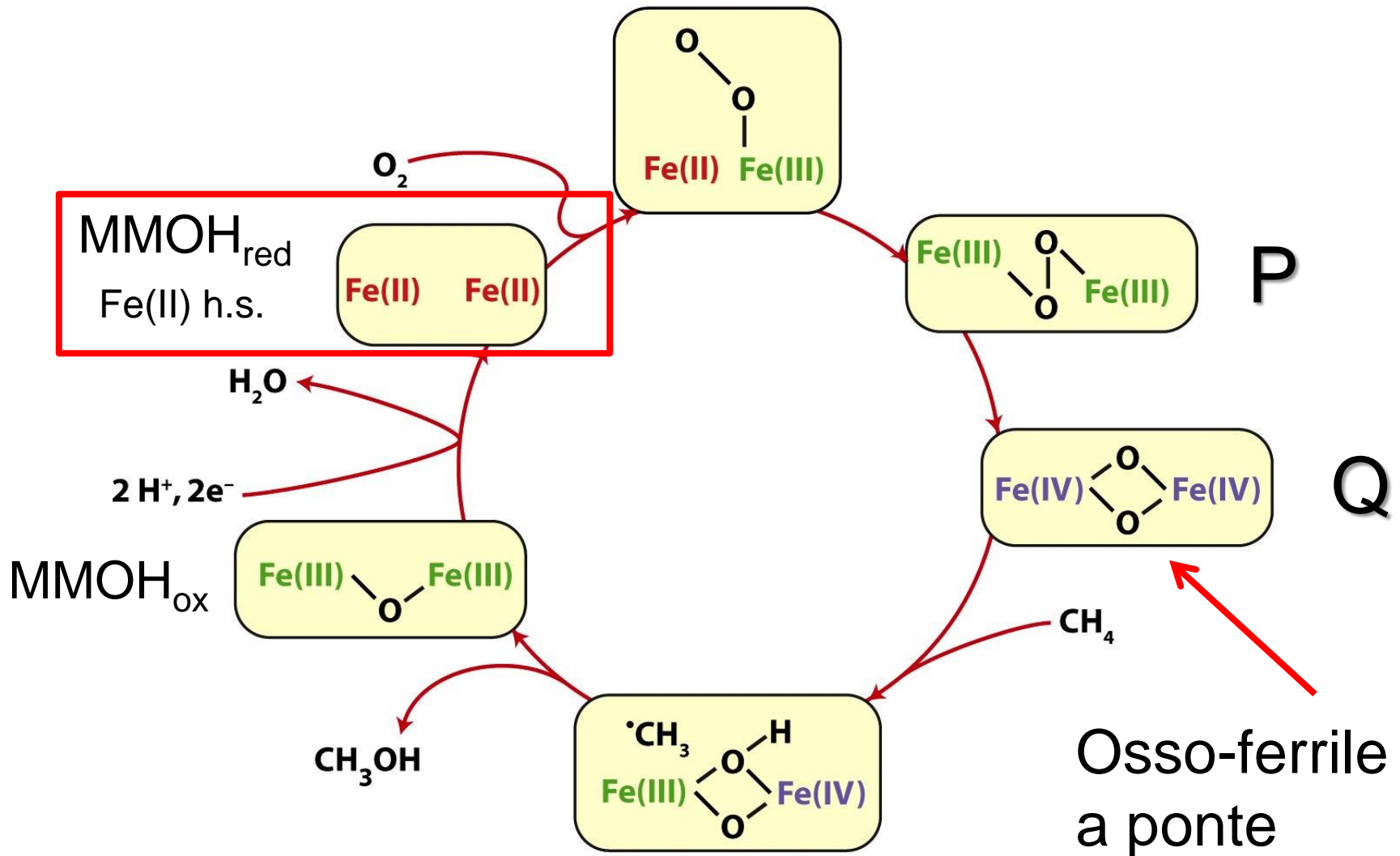


Fe(III)/Fe(III), incolore

300 kDa

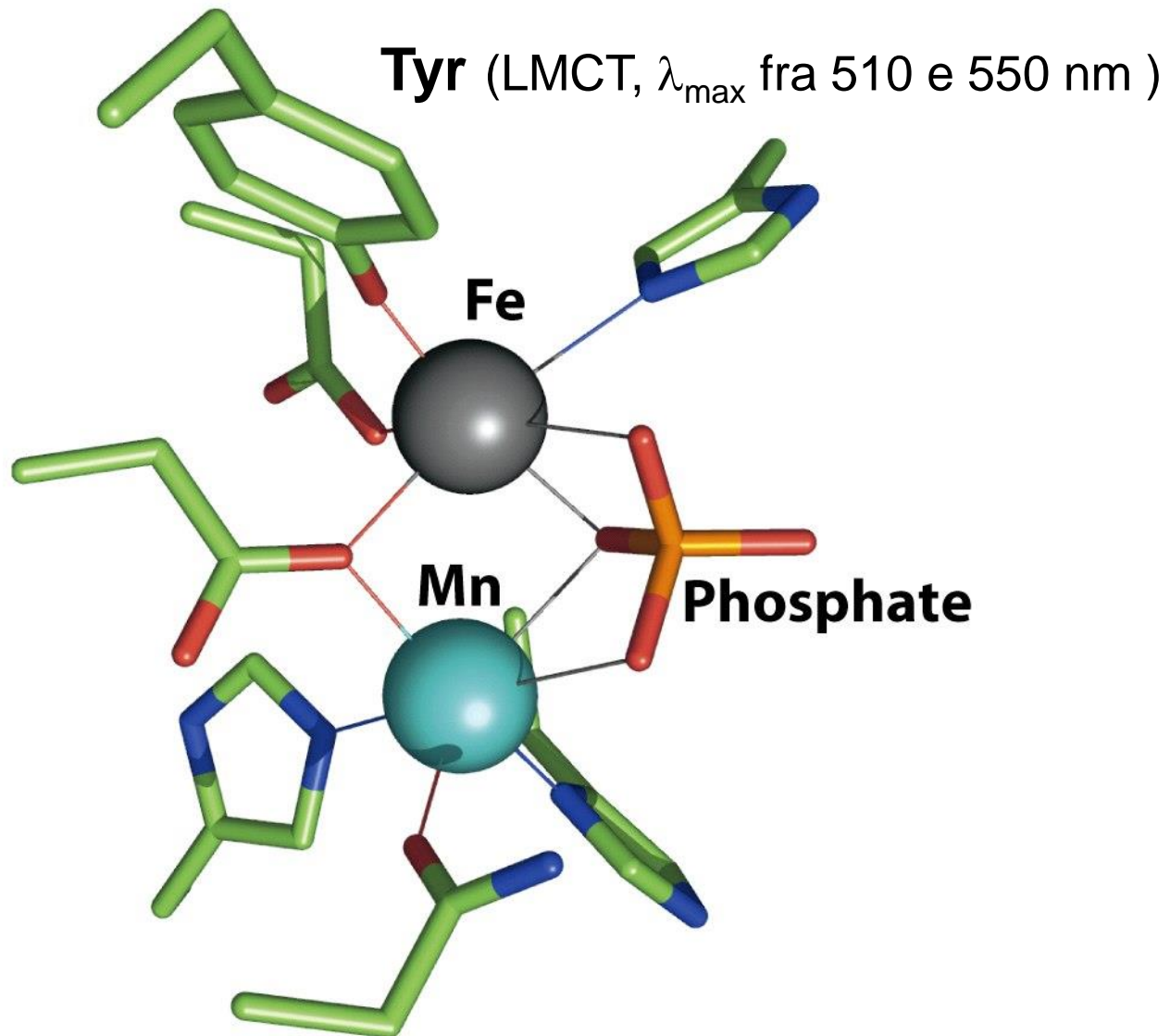


Ipotesi di ciclo catalitico della MMO

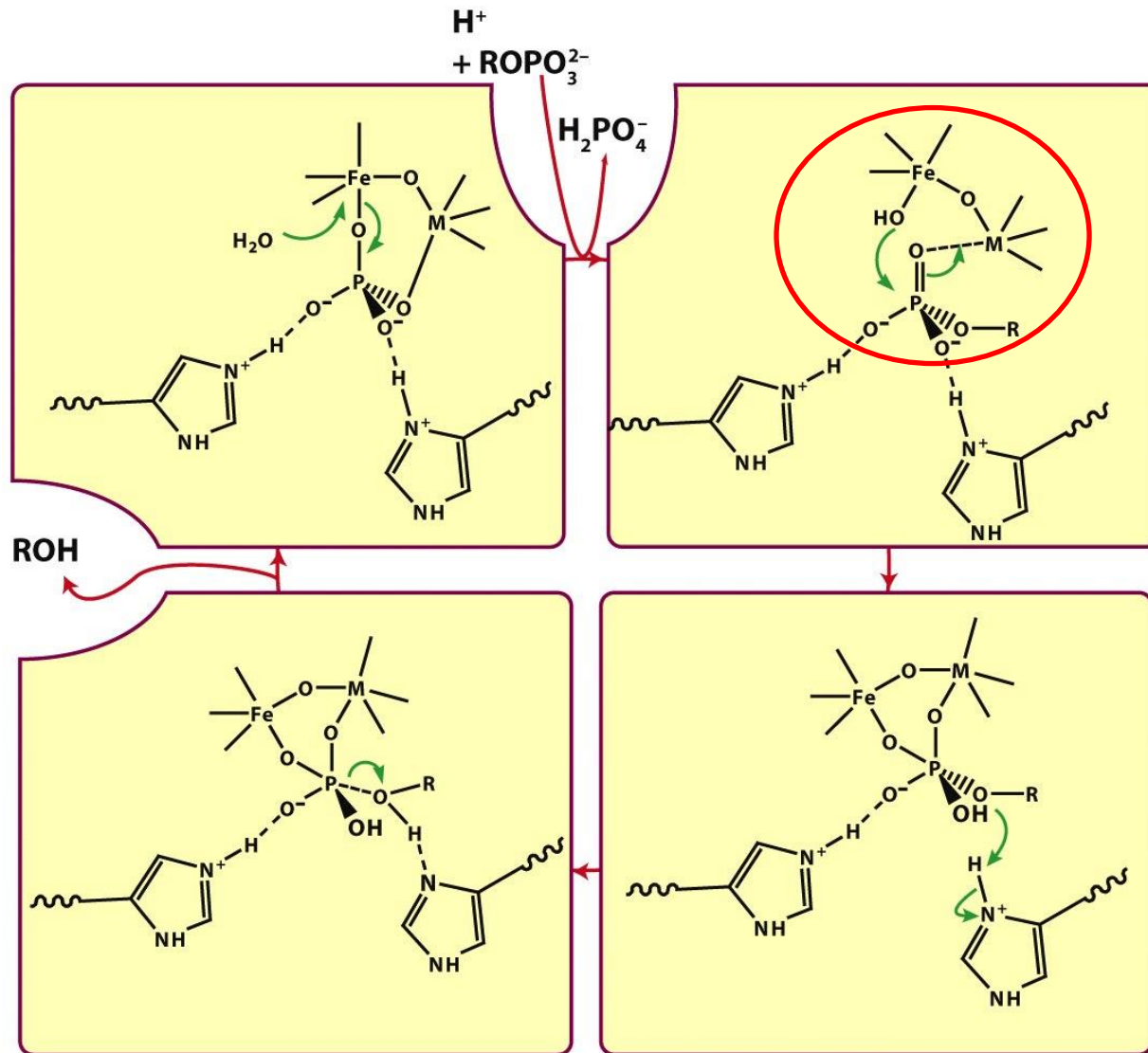


P e Q sono intermedi caratterizzati spettroscopicamente

Sito attivo di una fosfatasi acida

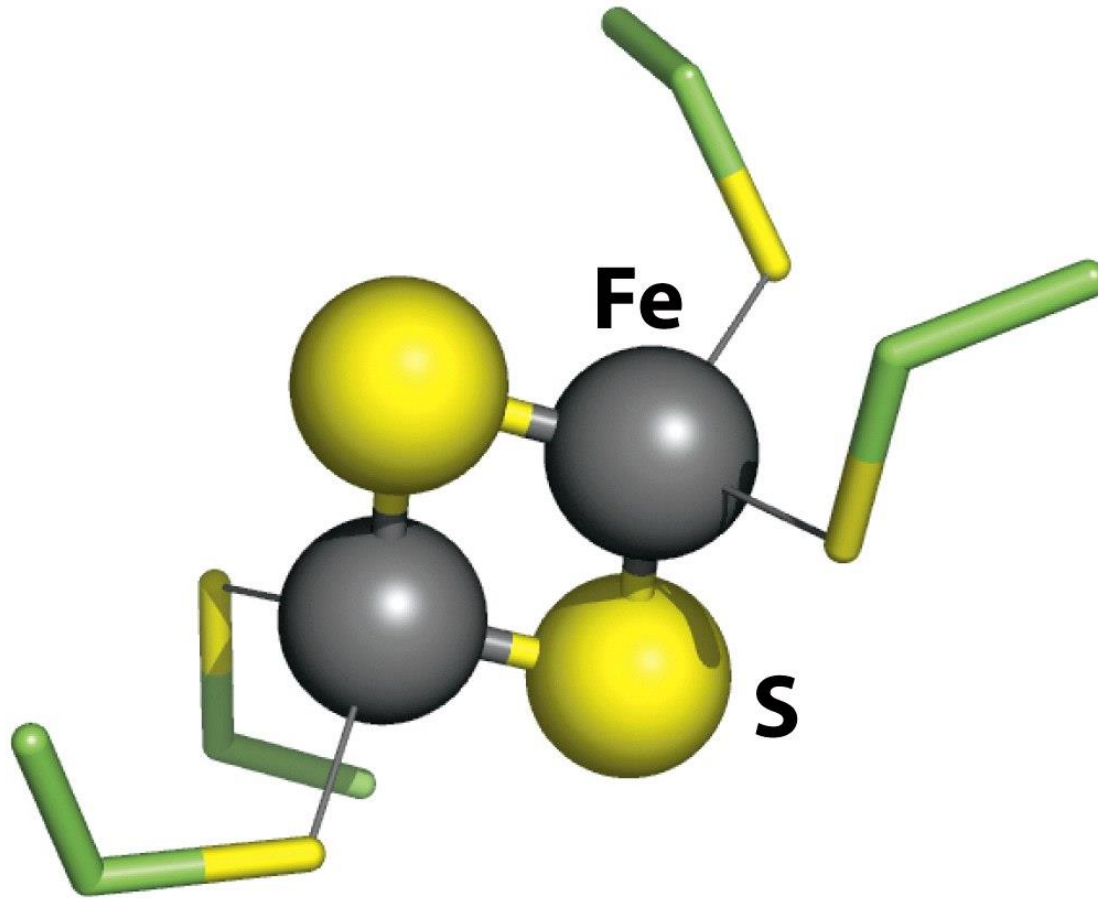


Ciclo catalitico di una fosfatasi acida

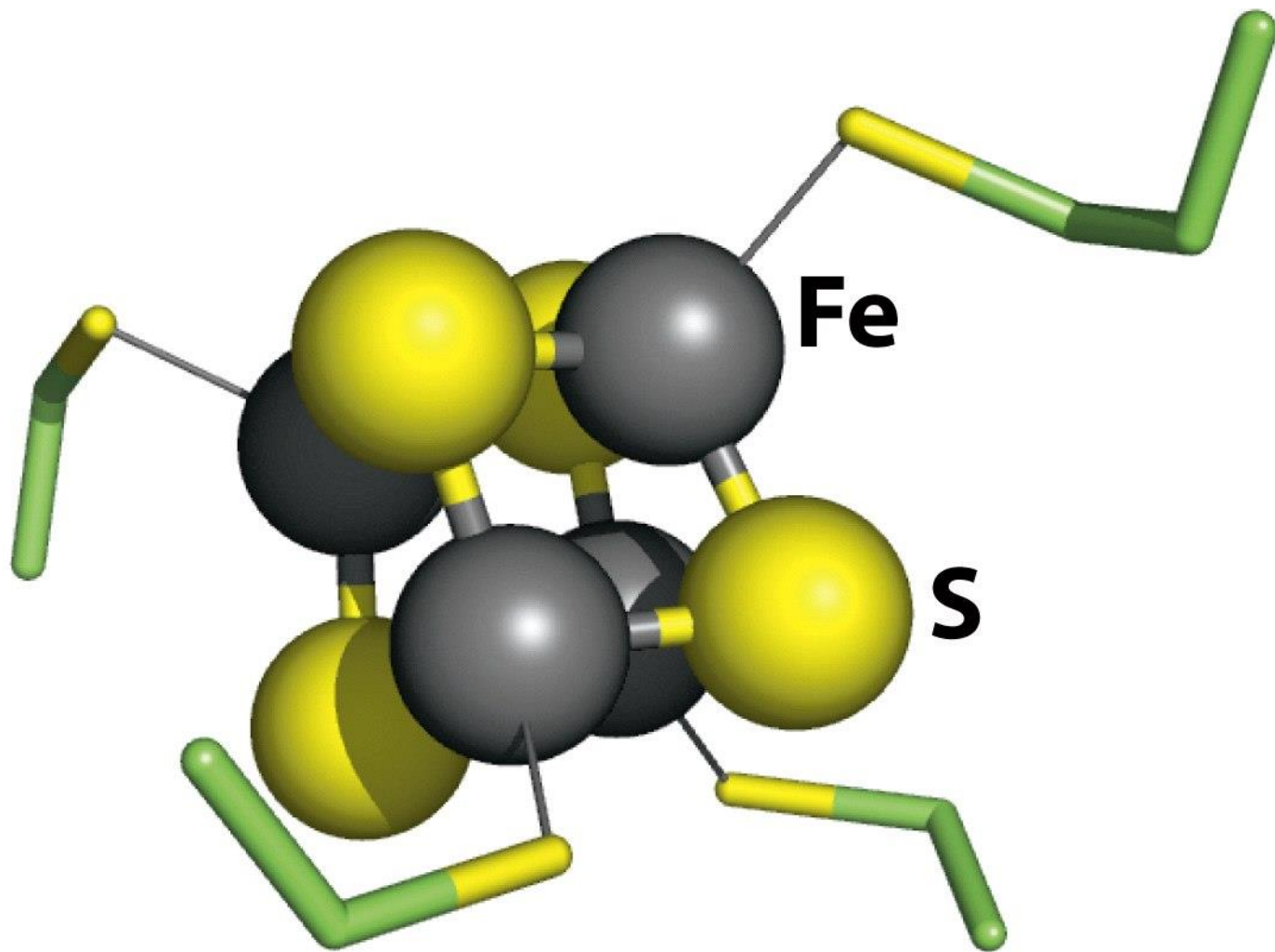


Sito attivo: Fe(III)-Fe(II)

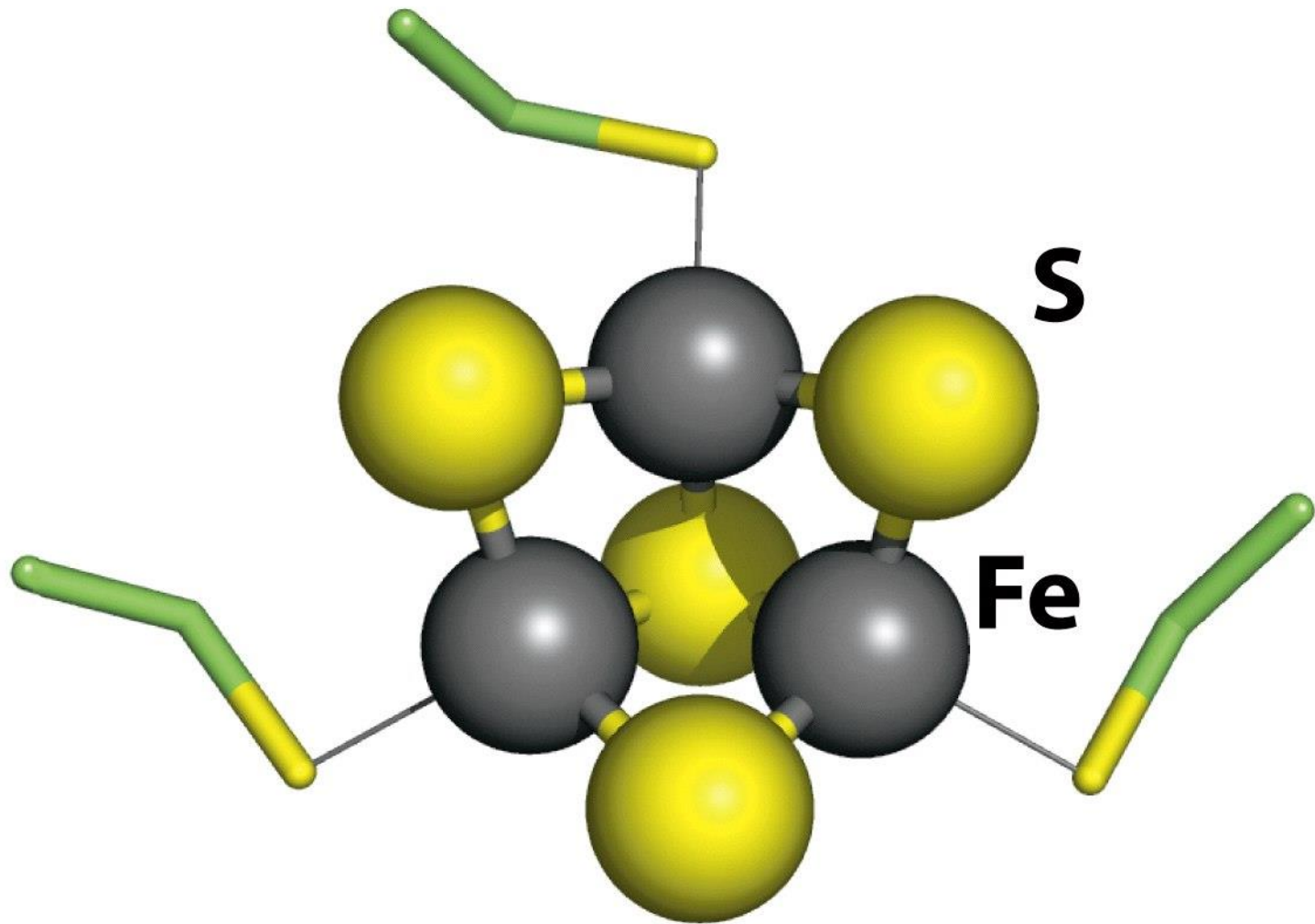
Proteine Fe-S



2Fe-2S]

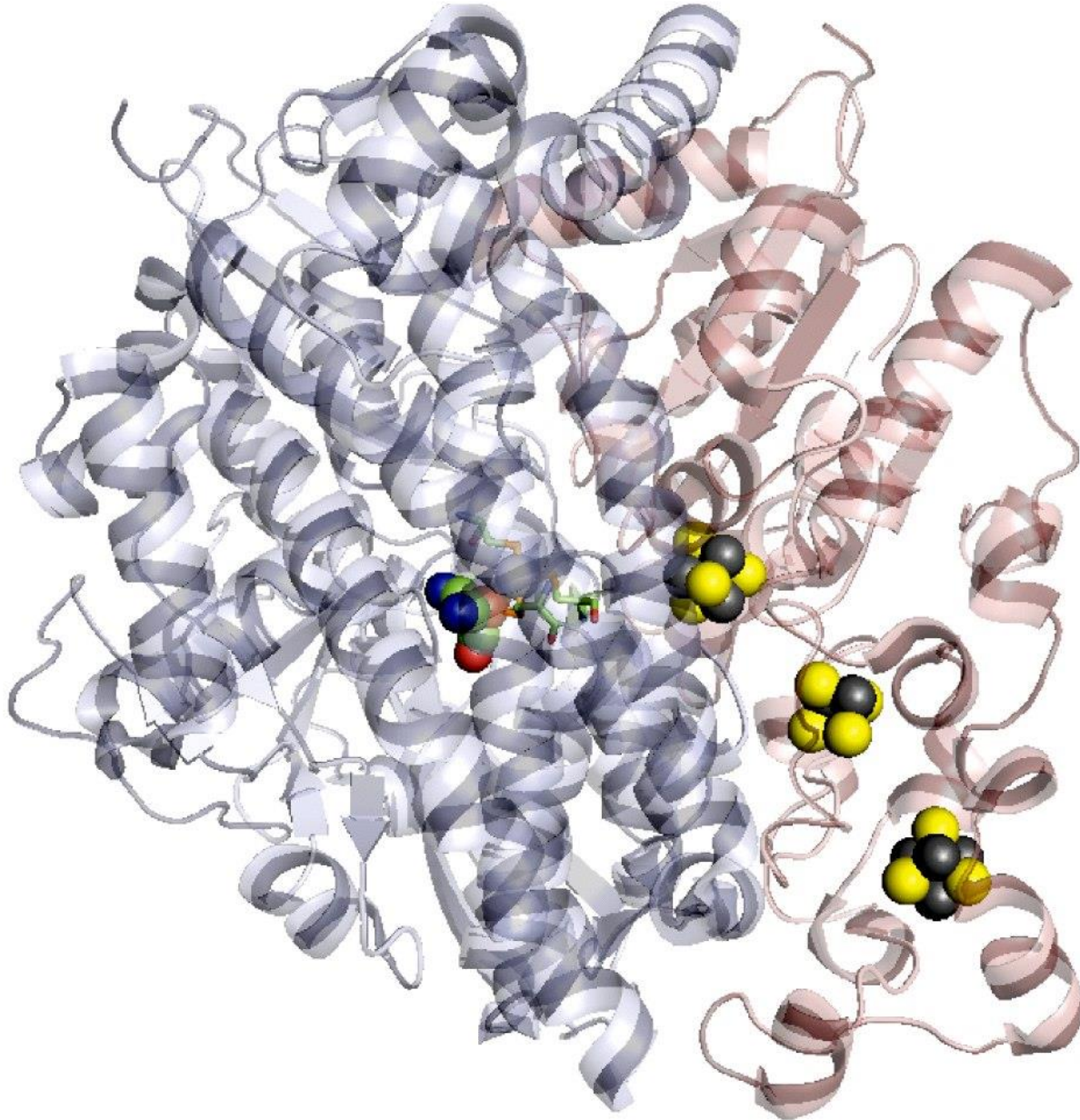


[4Fe-4S]



[3Fe-4S]

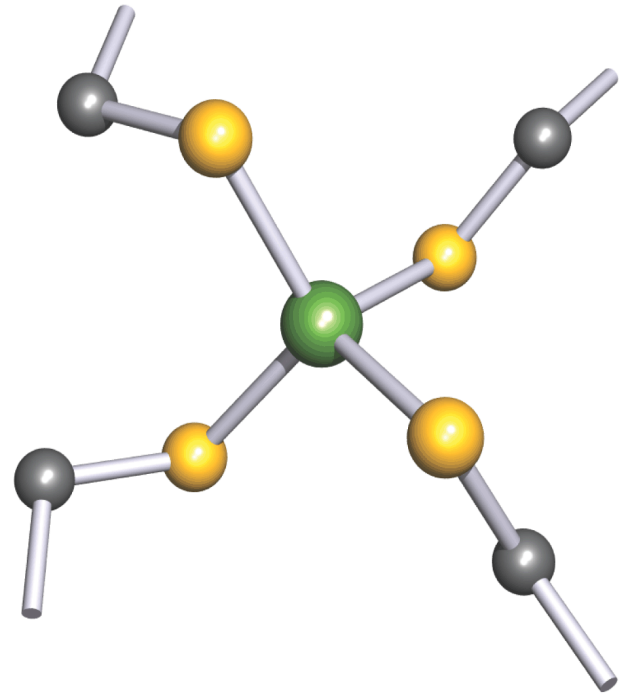
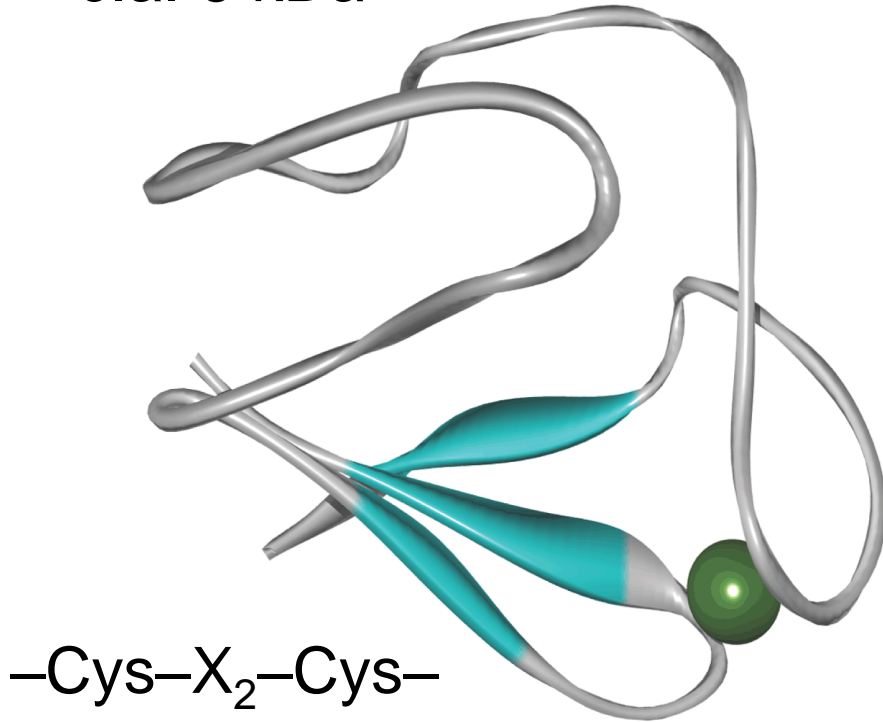
[Ni-Fe]-idrogenasi



Rubredossina da *clostridium pasteurianum*

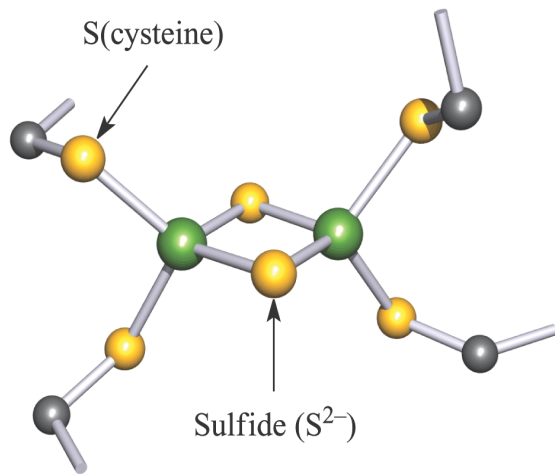
c.a. 6 kDa

$E^\circ \approx 0 \text{ V}$



Unità ferro-zolfo da ferridossine

E° fra -250 e -450 mV

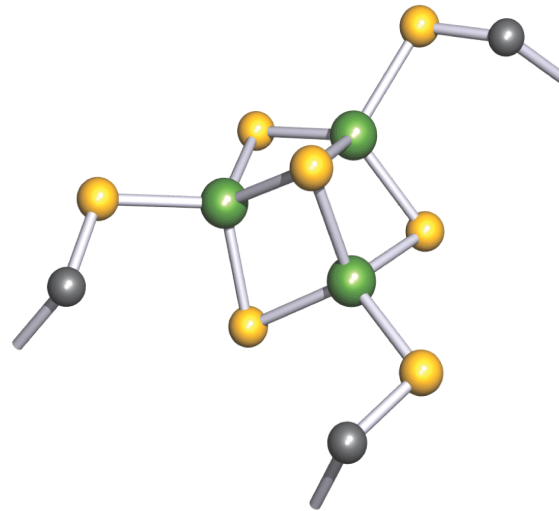


[2Fe-2S]

da spinaci

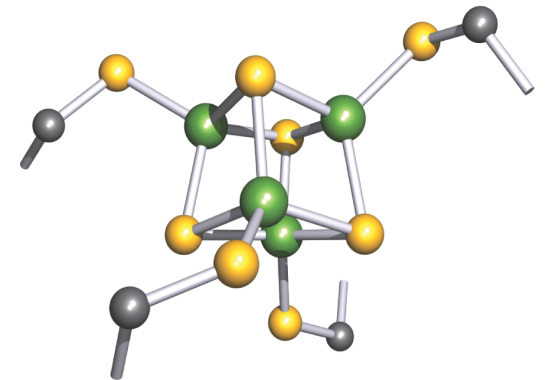
$E^\circ = -420$ mV

Fe(III)/Fe(III) – Fe(II)/Fe(III)



[3Fe-4S]

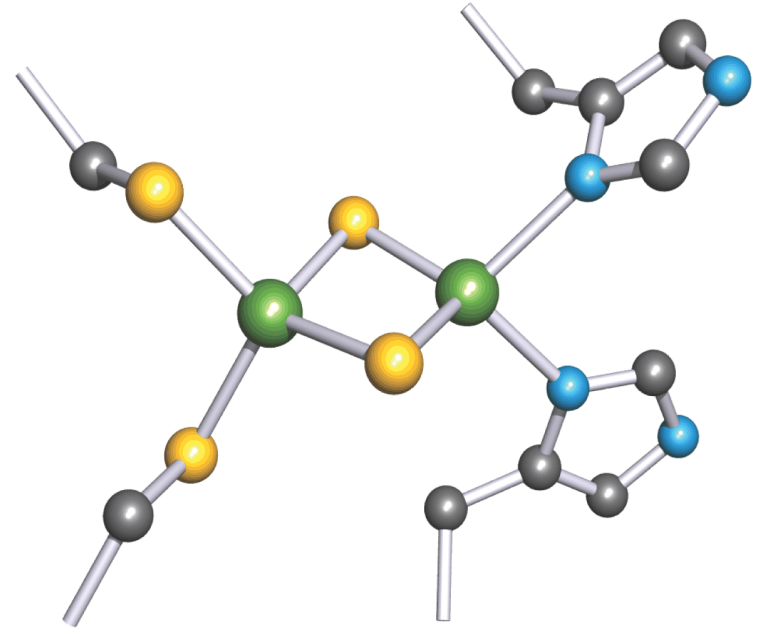
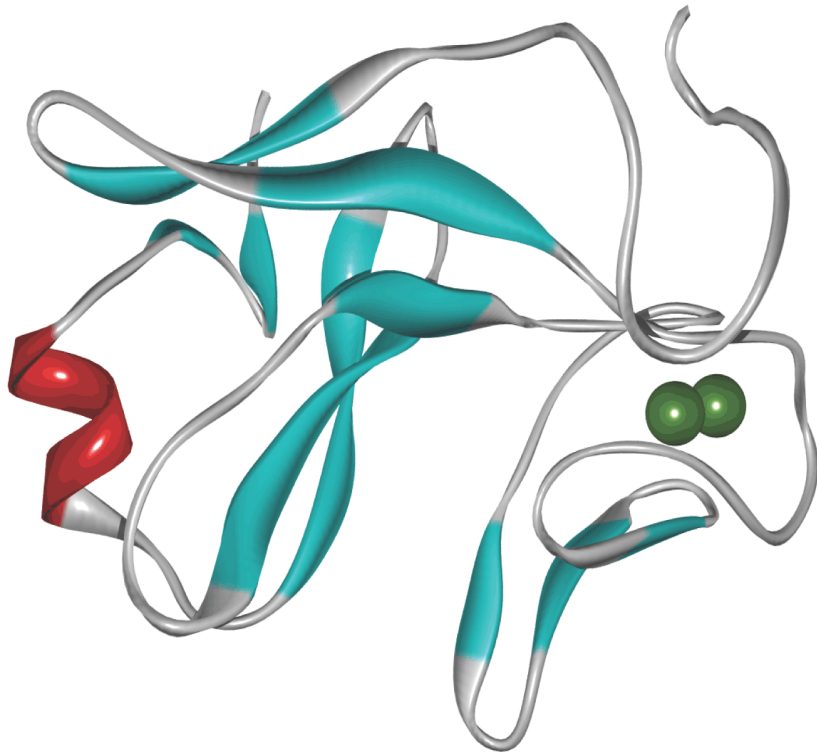
azotobacter vinelandii



[4Fe-4S]

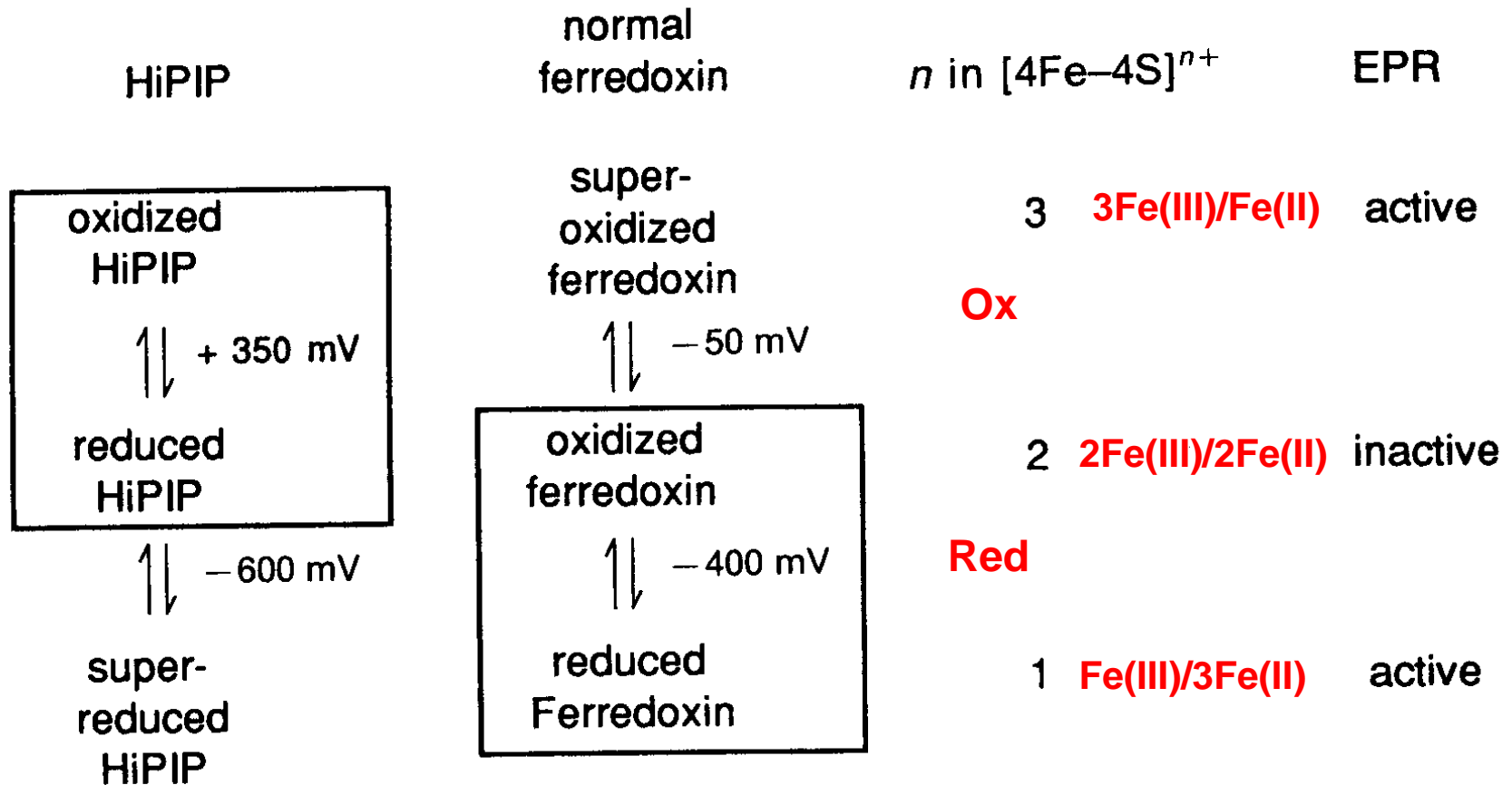
chromatium vinosum

Proteina Rieske da cloroplasti di spinaci



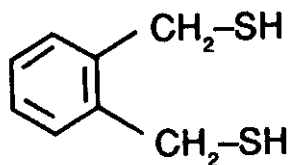
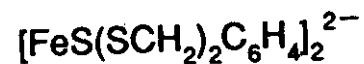
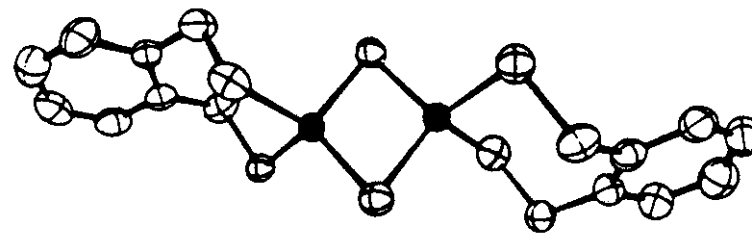
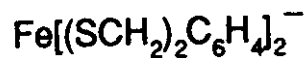
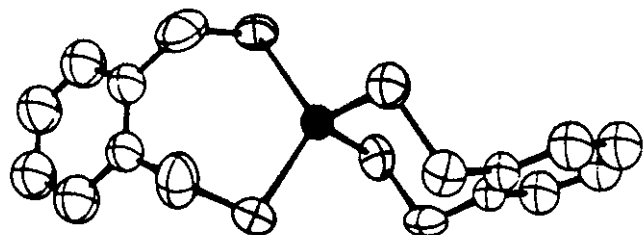
$$E^{\circ} = +290 \text{ mV}$$

High Potential Iron-sulfur Proteins (HiPIP)

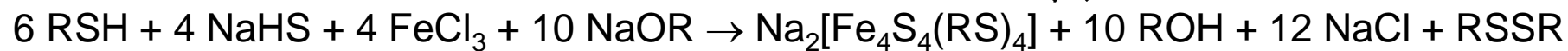
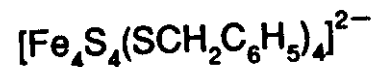
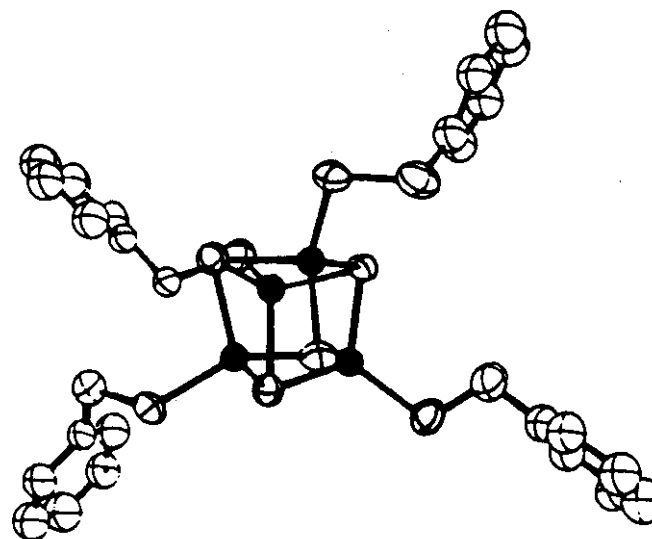


[Rd]:	-Cys-X ₂ -Cys-X _n -Cys-X ₂ -Cys-
[2Fe-2S]:	-Cys-X ₄ -Cys-X ₂ -Cys-X ₂₉ -Cys-
[4Fe-4S]:	-Cys-X ₂ -Cys-X ₂ -Cys-X _n -Cys-
HiPIP:	-Cys-X ₂ -Cys-X ₁₆ -Cys-X ₁₃ -Cys-
[3Fe-4S]:	-Cys-X _{5,7} -Cys-X _n -Cys-

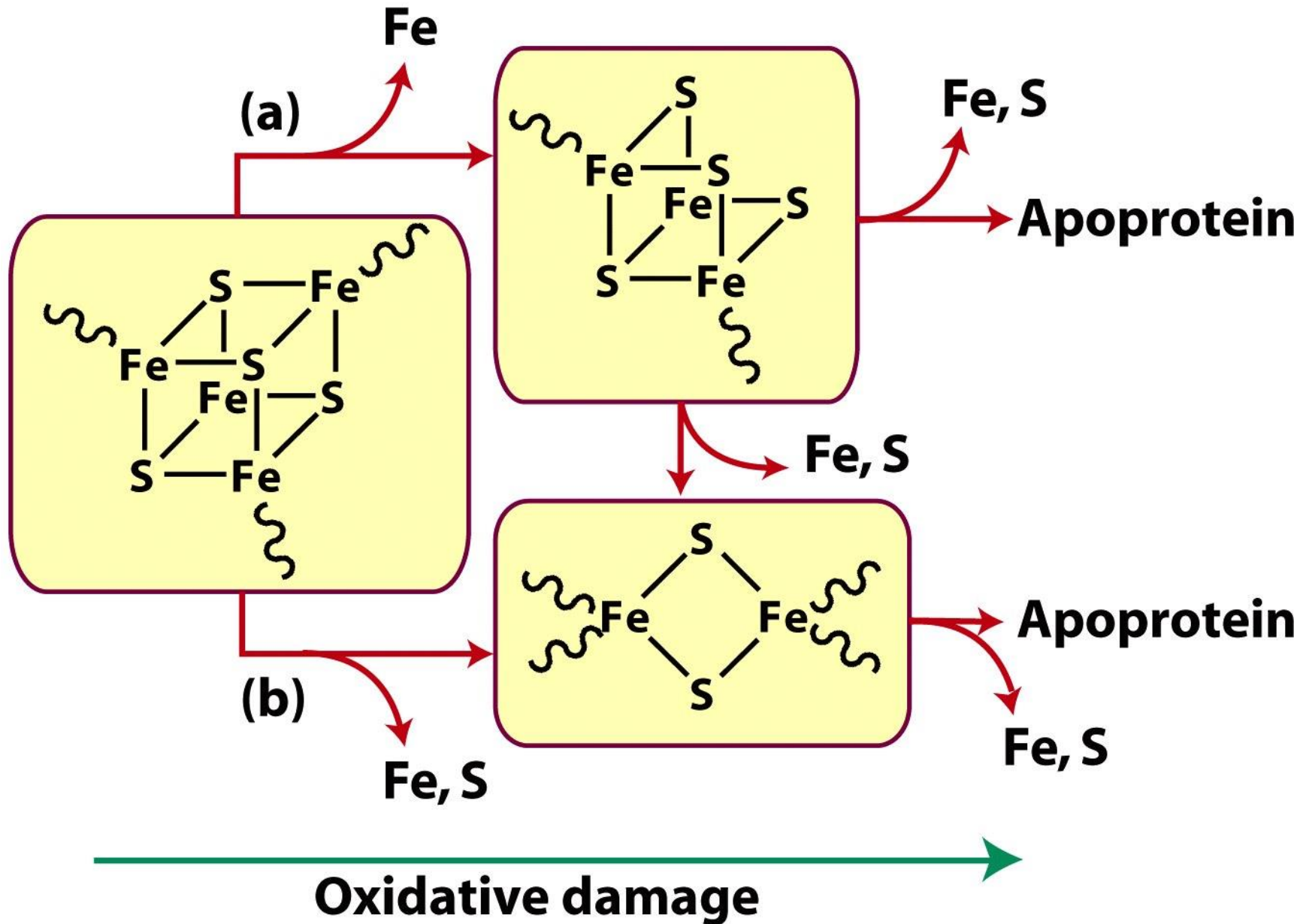
Complessi modello



o-xylene- α, α' -dithiol, $(\text{HSCH}_2)_2\text{C}_6\text{H}_4$

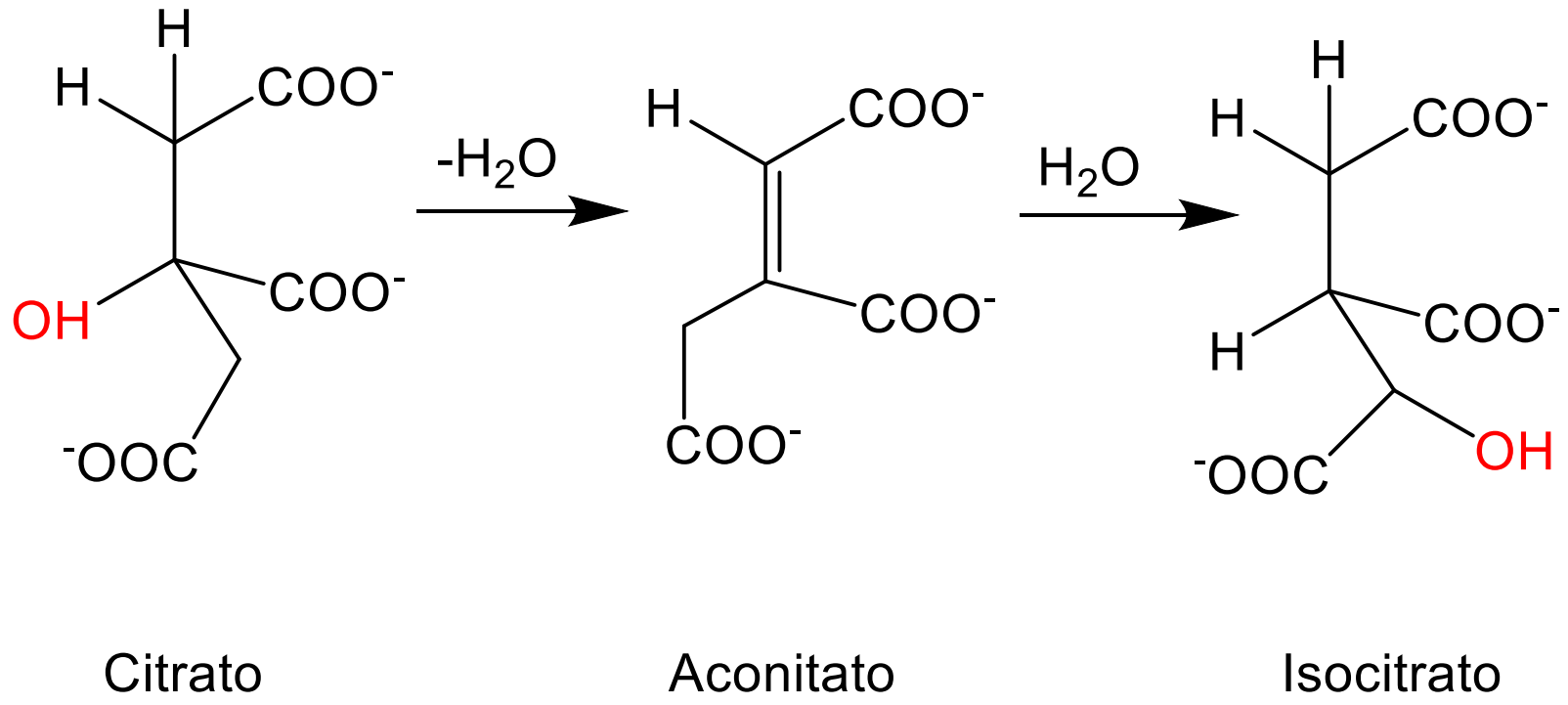


Proteine Fe-S come sensori di O₂

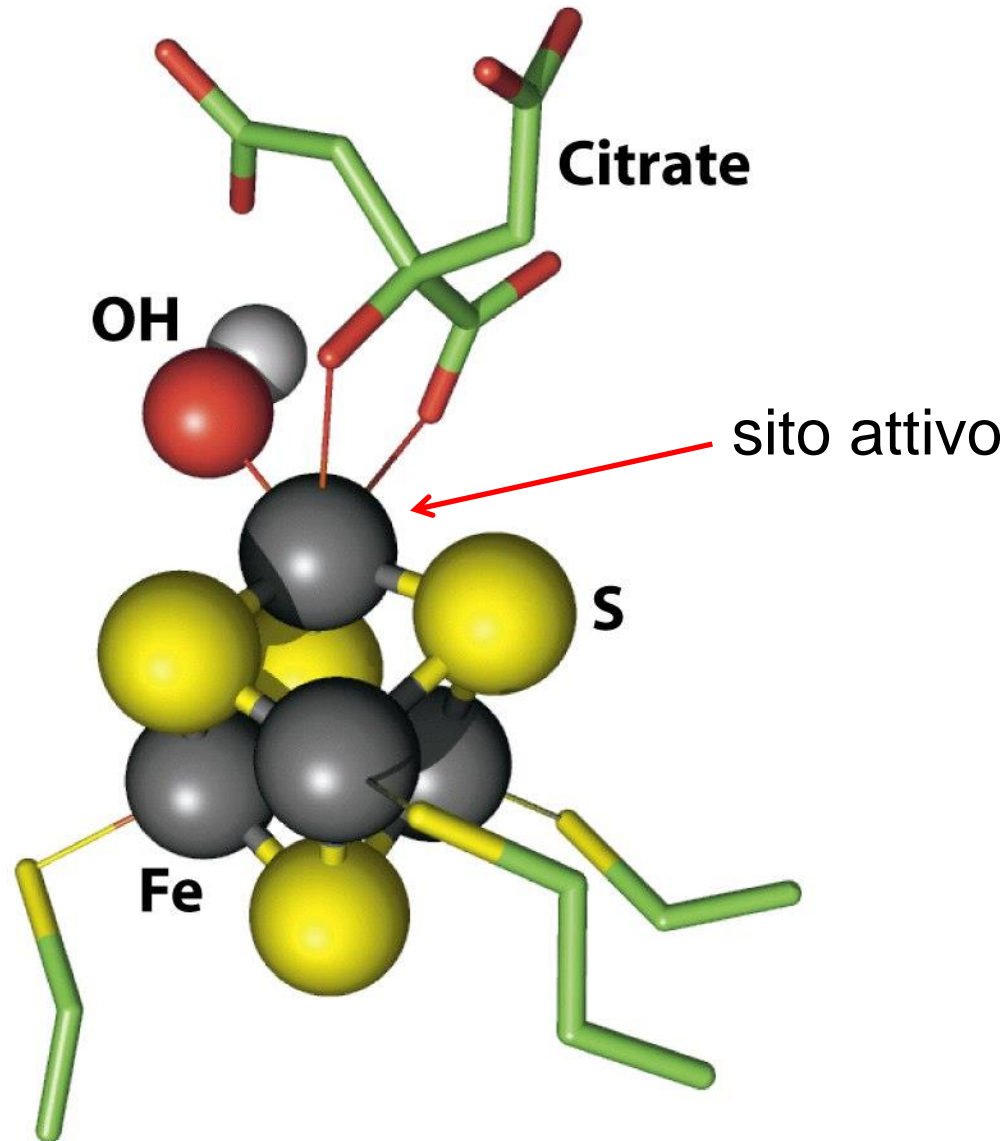


Enzima Aconitasi

catalizza interconversione del citrato in isocitrato



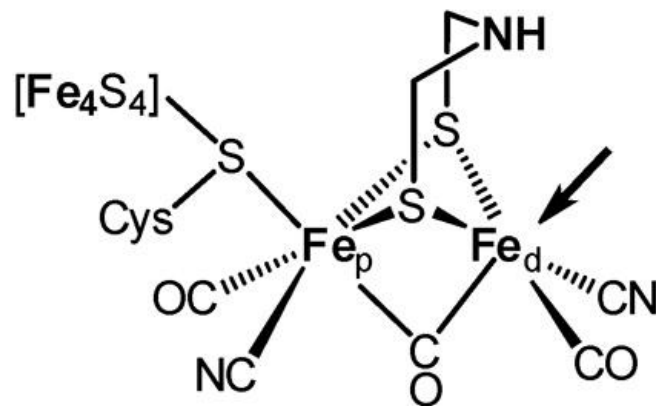
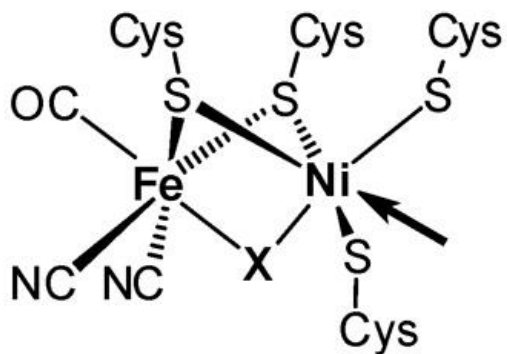
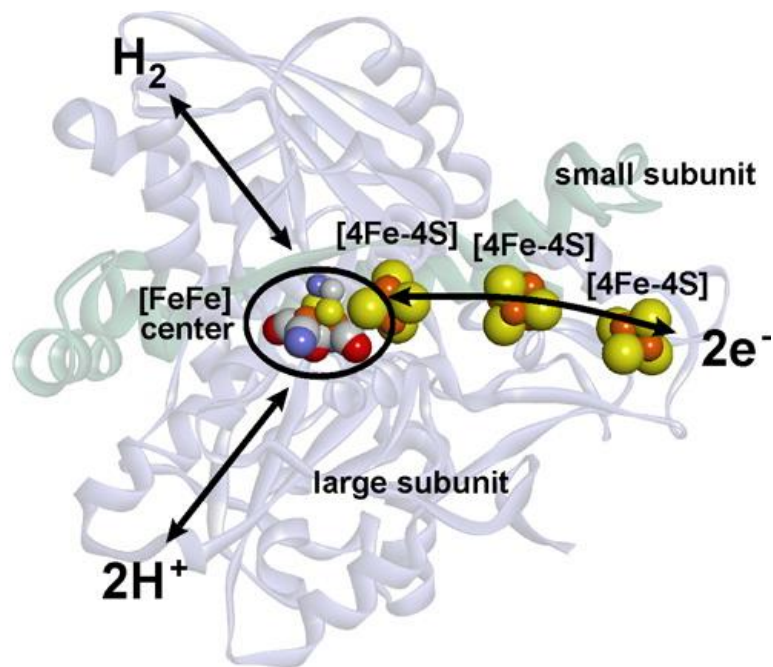
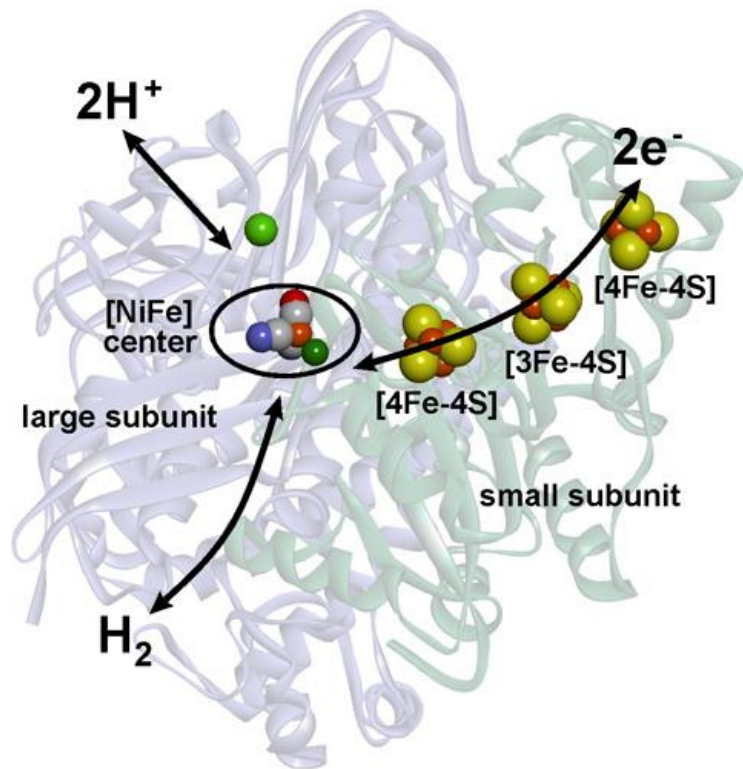
Sito catalitico dell'aconitasi



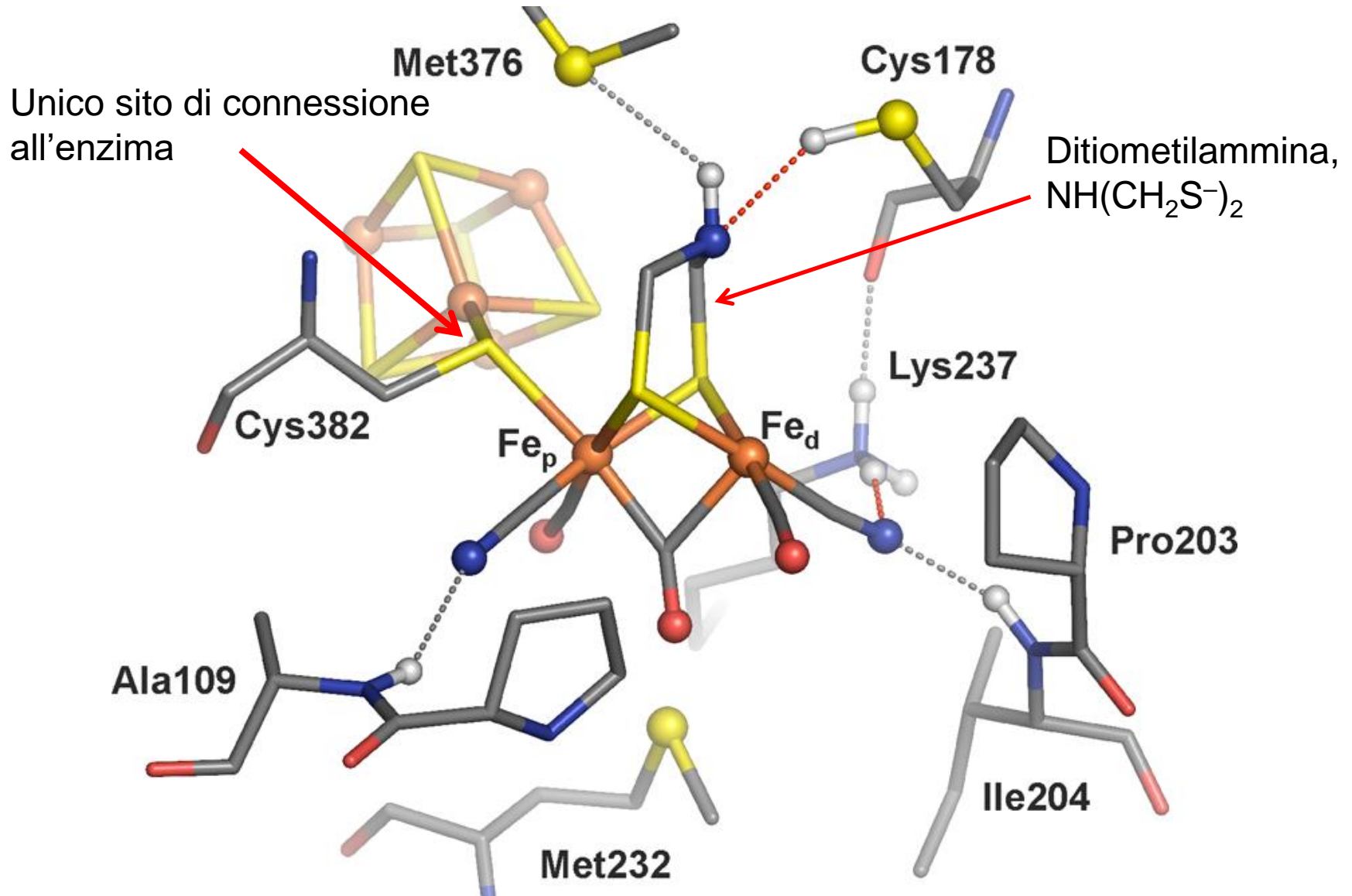


[NiFe] Hydrogenase

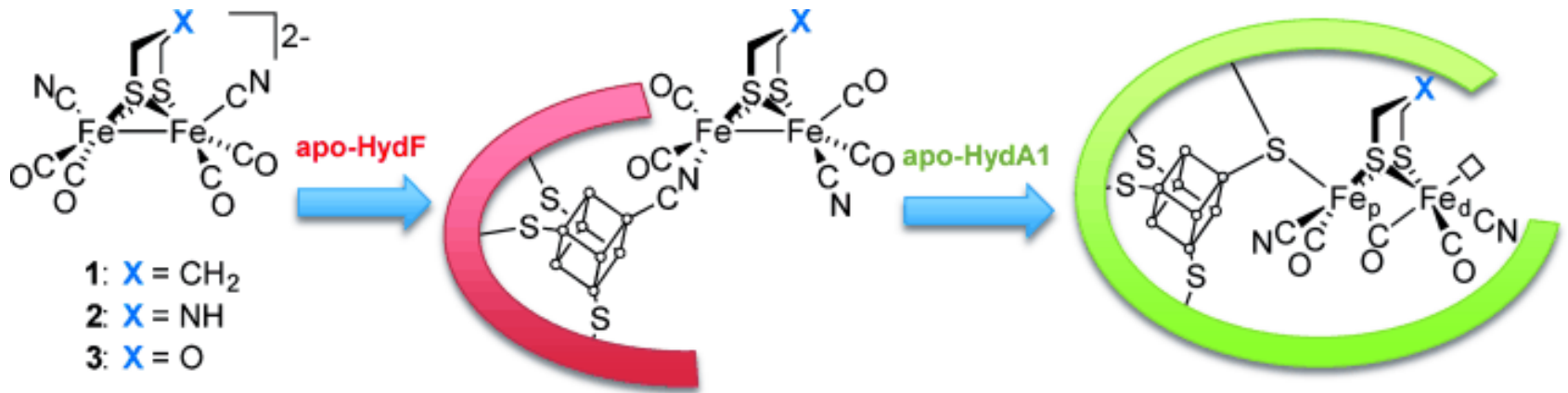
[FeFe] Hydrogenase



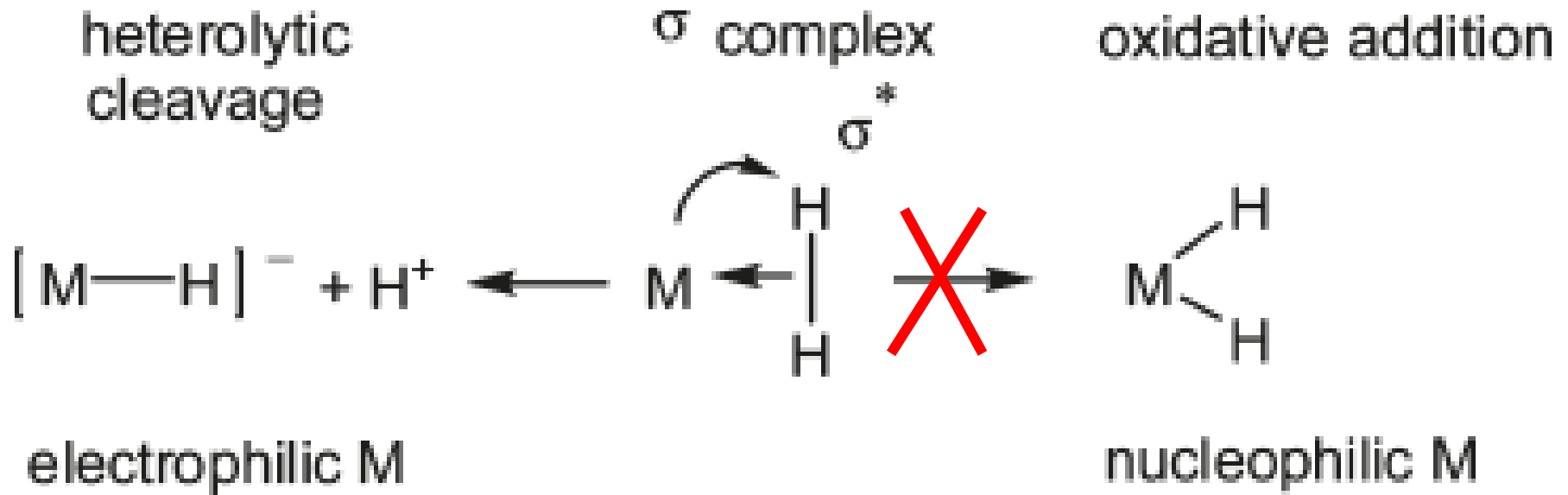
[FeFe] Idrogenasi



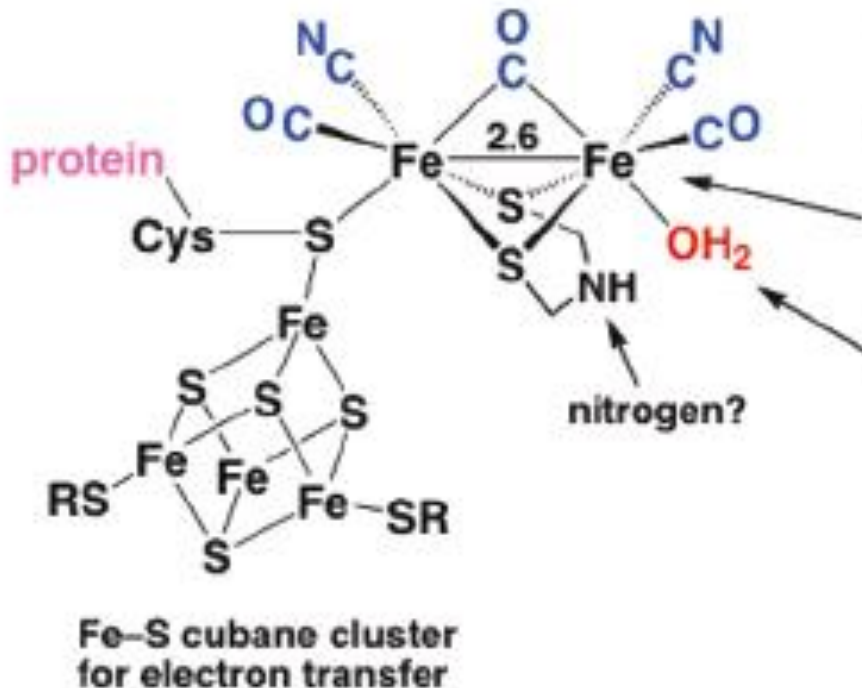
Soltanto l'enzima con X = NH è cataliticamente attivo



Il CO coordinato favorisce la rottura eterolitica di H₂



Fe-Fe Hydrogenase

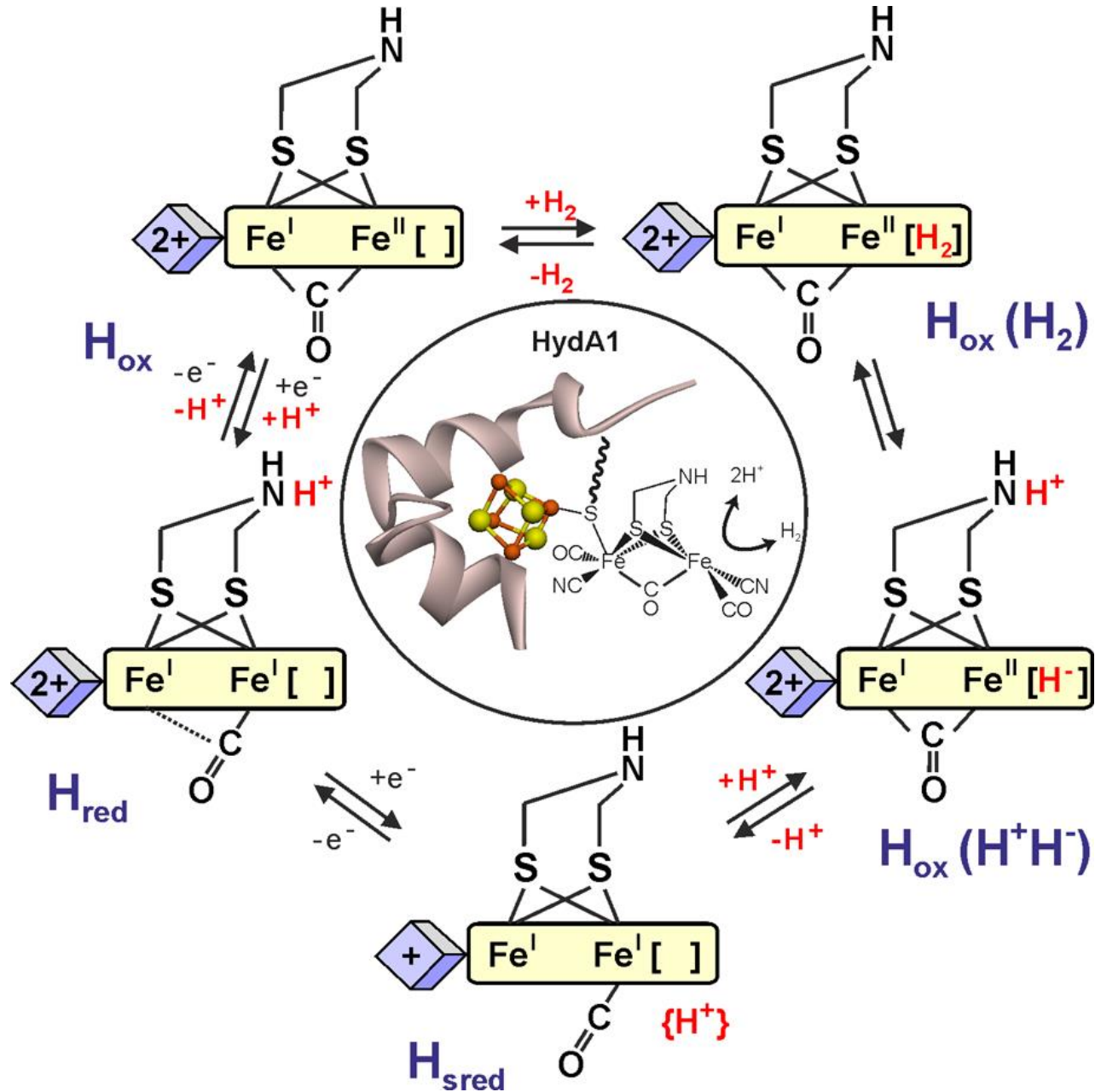


- Active site attached at only **one point**
- **CO** and **CN** ligands on low-spin Fe^{II}
- Metal-metal bonds
- Intramolecular heterolysis of **H₂** ostensibly at this site
CO can displace **H₂O**; can **H₂**?
H₂ is slightly stronger ligand than **H₂O** on W(CO)₃(PR₃)₂

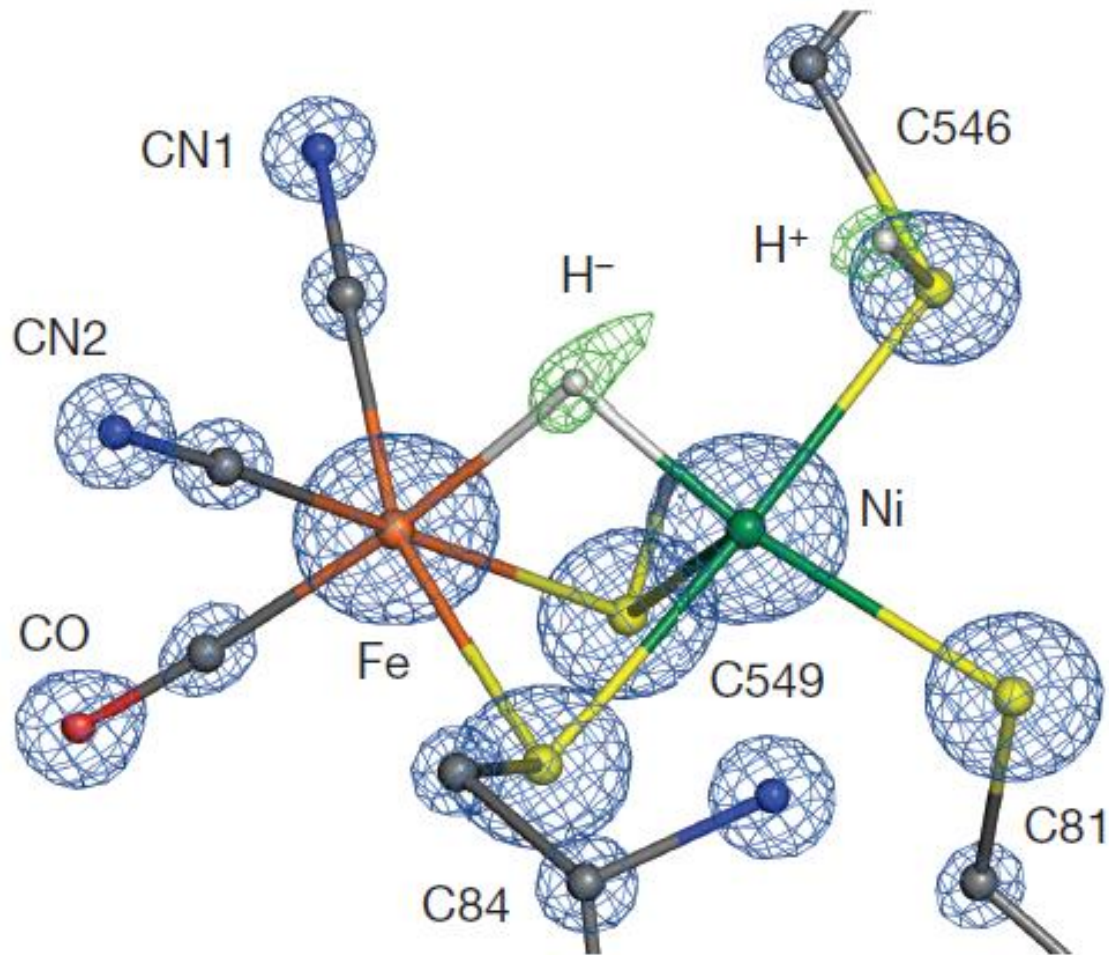
Trans **CO** ligand favors H₂ coordination and heterolysis

High ligand-field strength of **CN** may be needed to help maintain a *low-spin state* for Fe that is critical for strong CO binding. High-spin Fe^{II}-CO complexes are rare

Ipotesi di meccanismo



Fe–Ni Hidrogenasi



Nature, 2015

Ipotesi di meccanismo

