

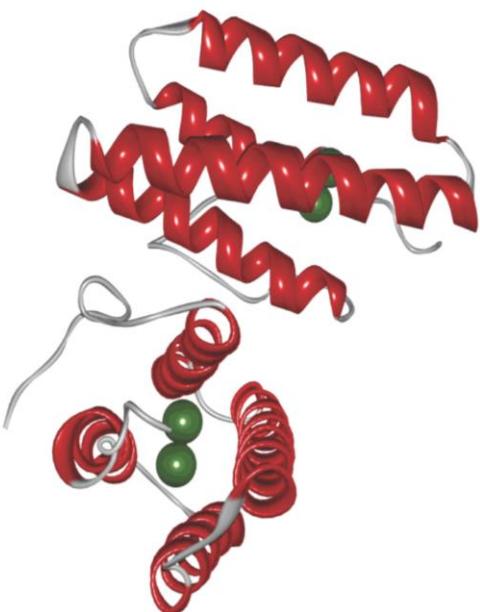
Proteine con Fe non-eme

1. proteine in cui il Fe è coordinato esclusivamente da amminoacidi (e/o H_2O , OH^- , O^{2-})
2. proteine che contengono centri Fe–S

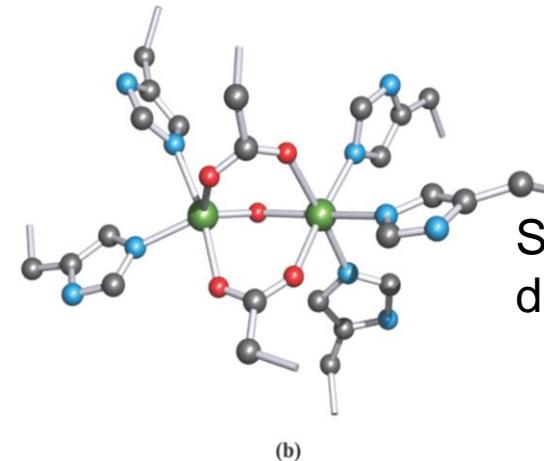
Emeritrina

trasporto O₂ in invertebrati marini, molluschi e ragni

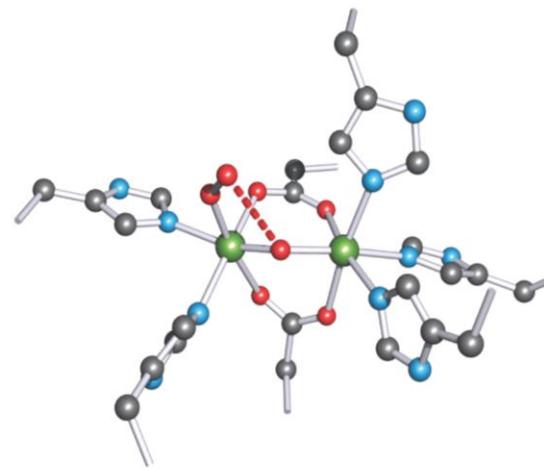
13,5 kDa
113 a.a.



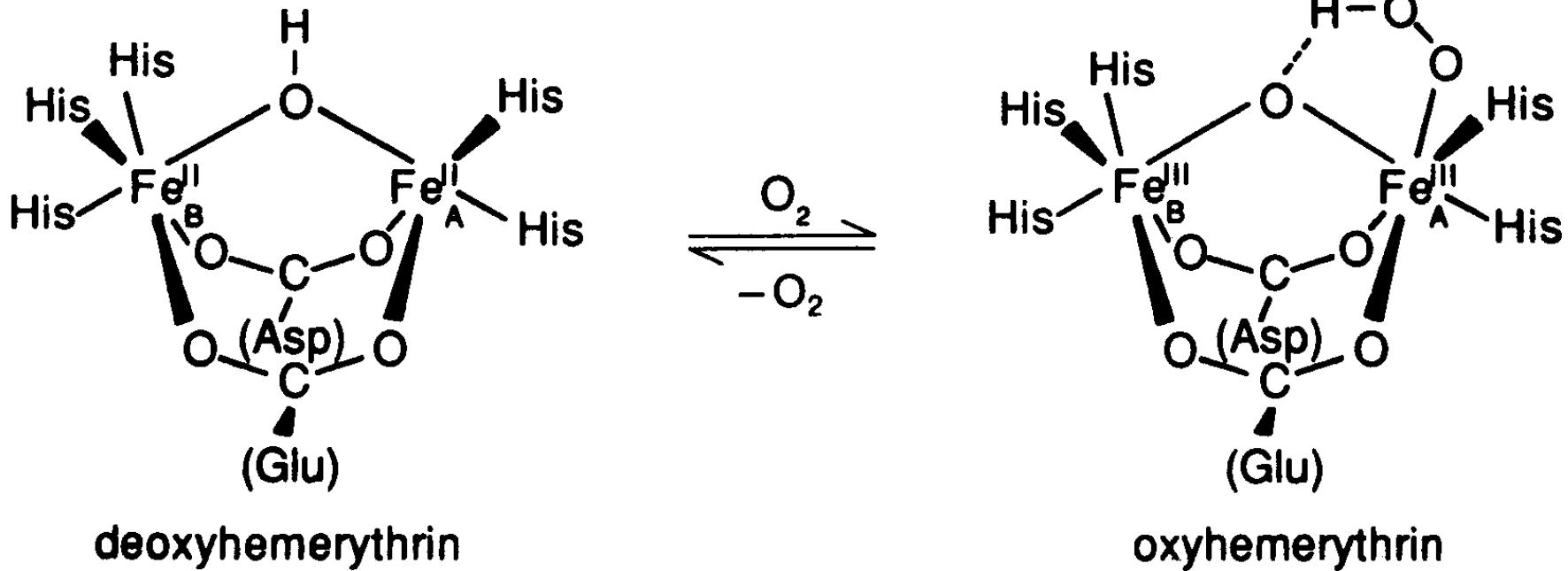
desossi-emeritrina
(2 di 8 sub-unità)



Sito attivo della
desossi-emeritrina



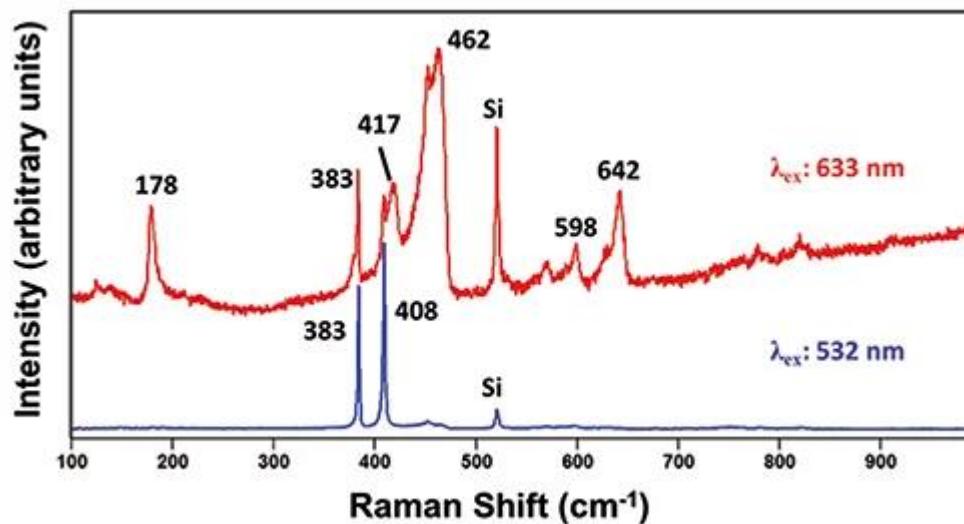
Sito attivo della
ossi-emeritrina



Incolore
2 Fe(II) h.s. ($S = 2$, debole acc. a.f.)
Mossbauer: 2 Fe(II) indistinguibili

Viola (LMCT, prob. da O_2^{2-} a Fe(III))
 1O_2
2 Fe(III) l.s. ($S = \frac{1}{2}$, forte acc. a.f.)
Raman risonante: 848 cm^{-1}
Mossbauer: 2 Fe(III) diversi

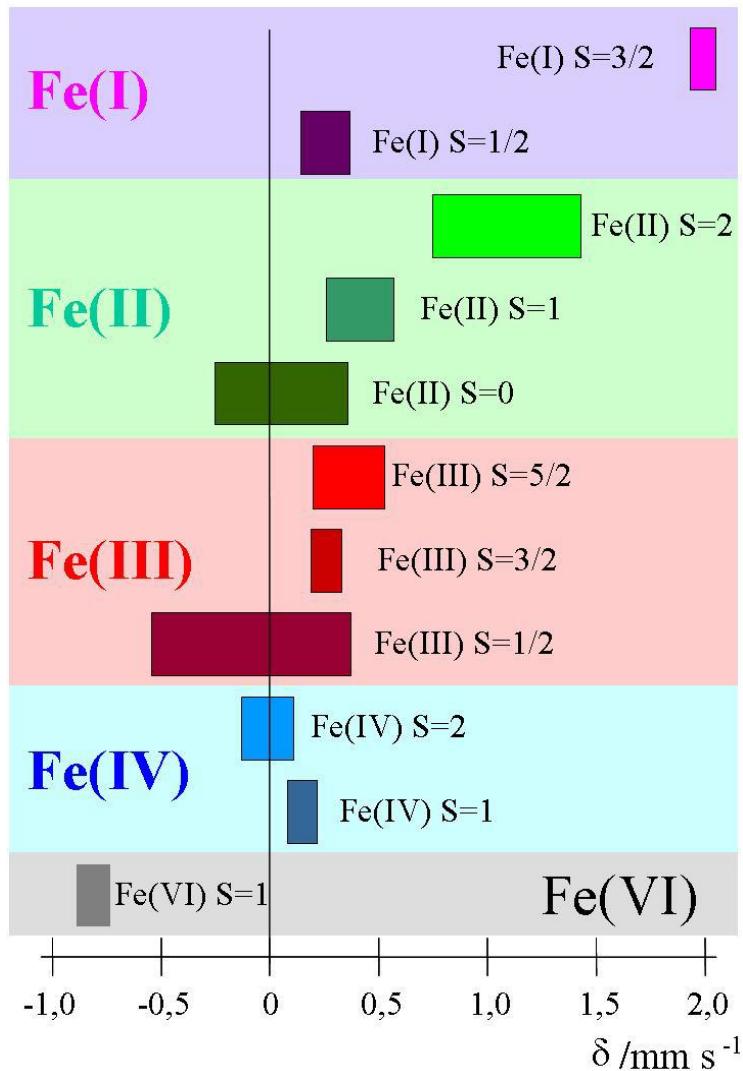
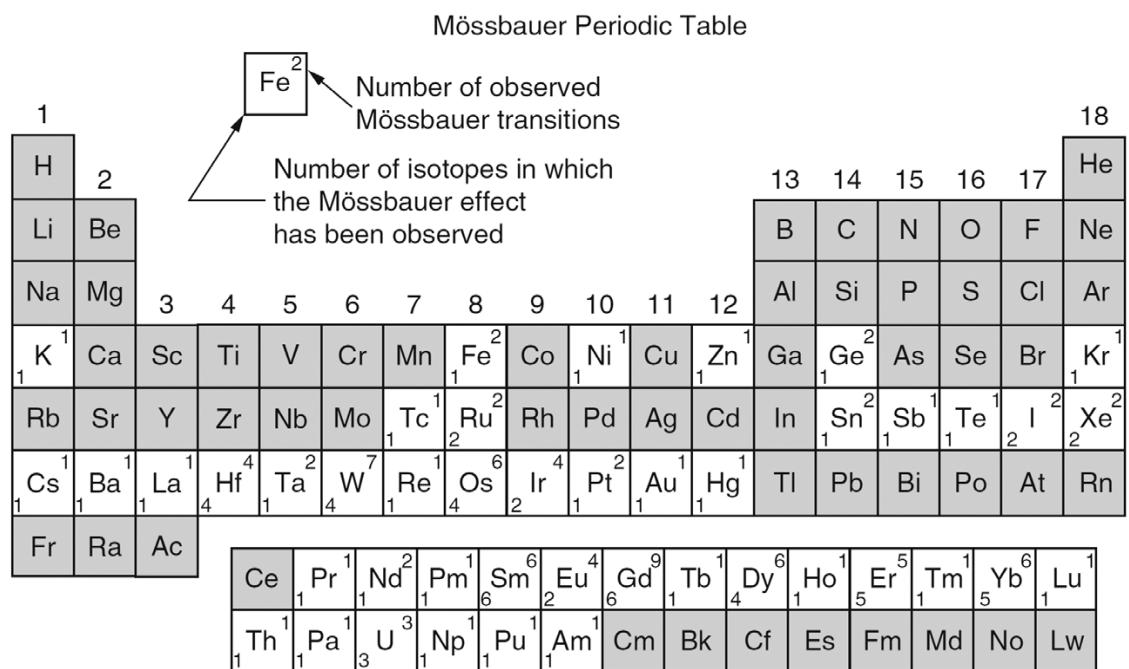
Resonance Raman



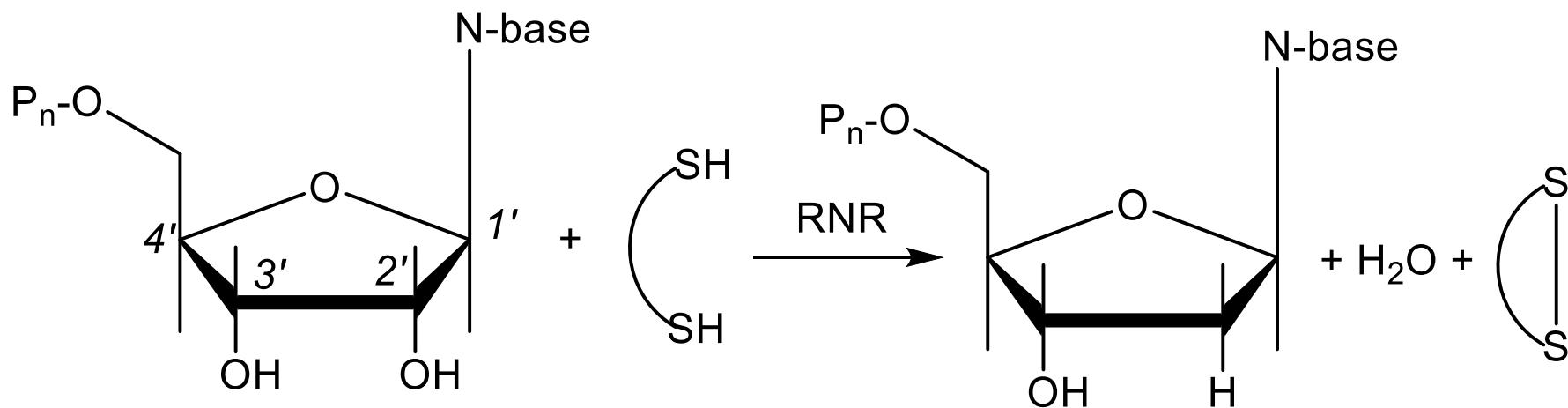
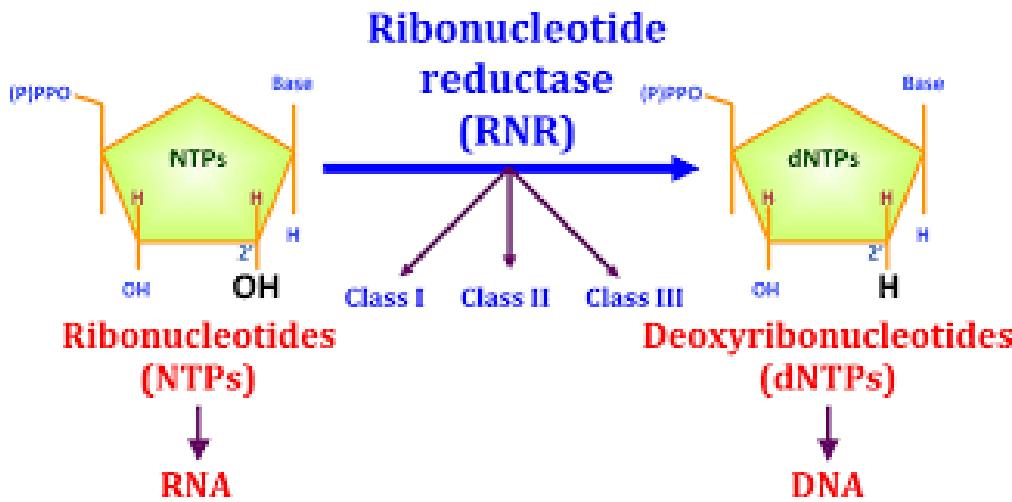
Resonance (top) and non-resonance (bottom) Raman spectra of MoS₂ on silicon. The excitation at 633 nm, near an electronic transition, causes appearance of bands that are too faint to be visible with excitation at 532 nm.

Mössbauer spectroscopy

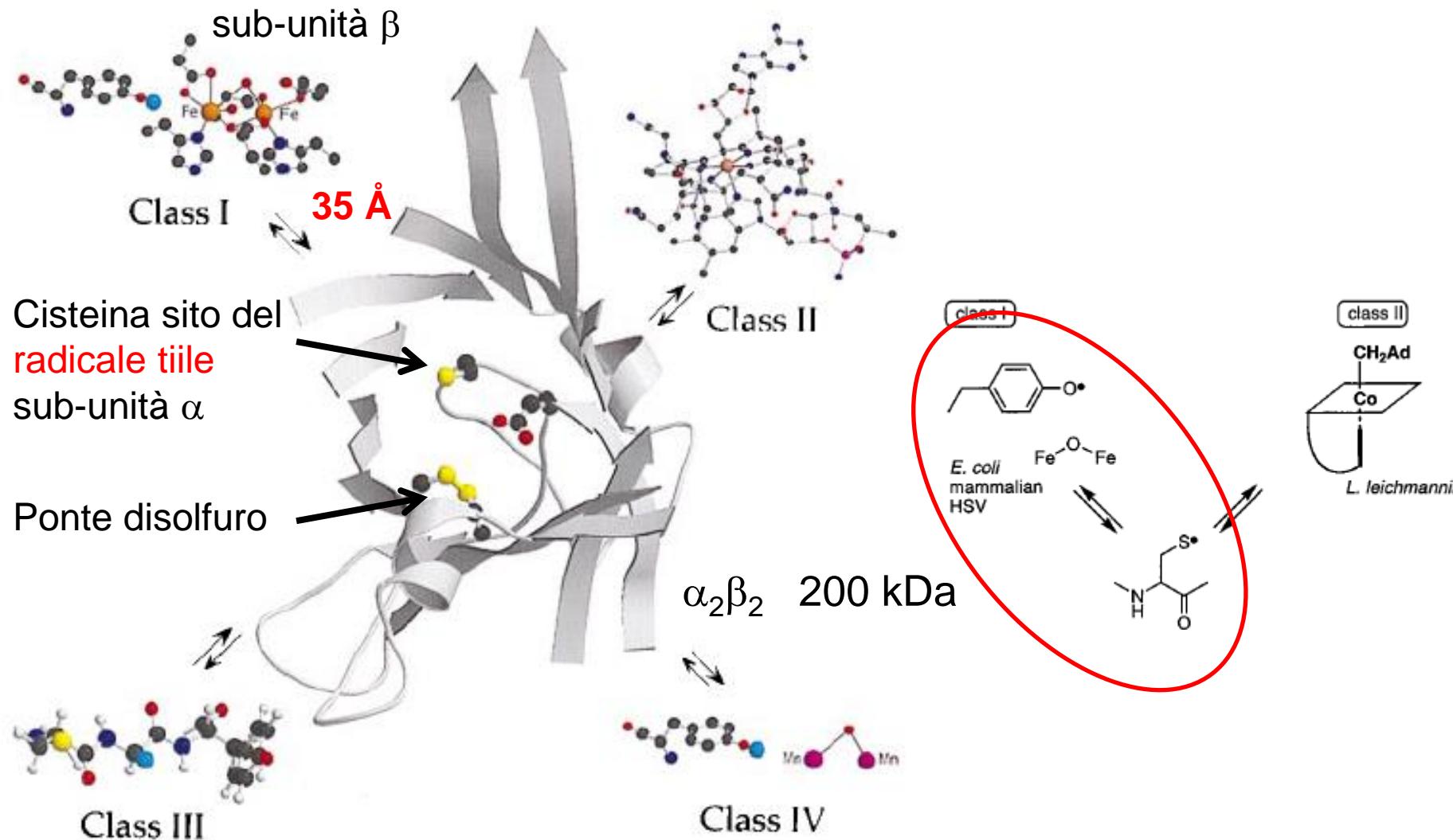
(Rudolf Mössbauer ,Nobel Prize for Physics in 1961)



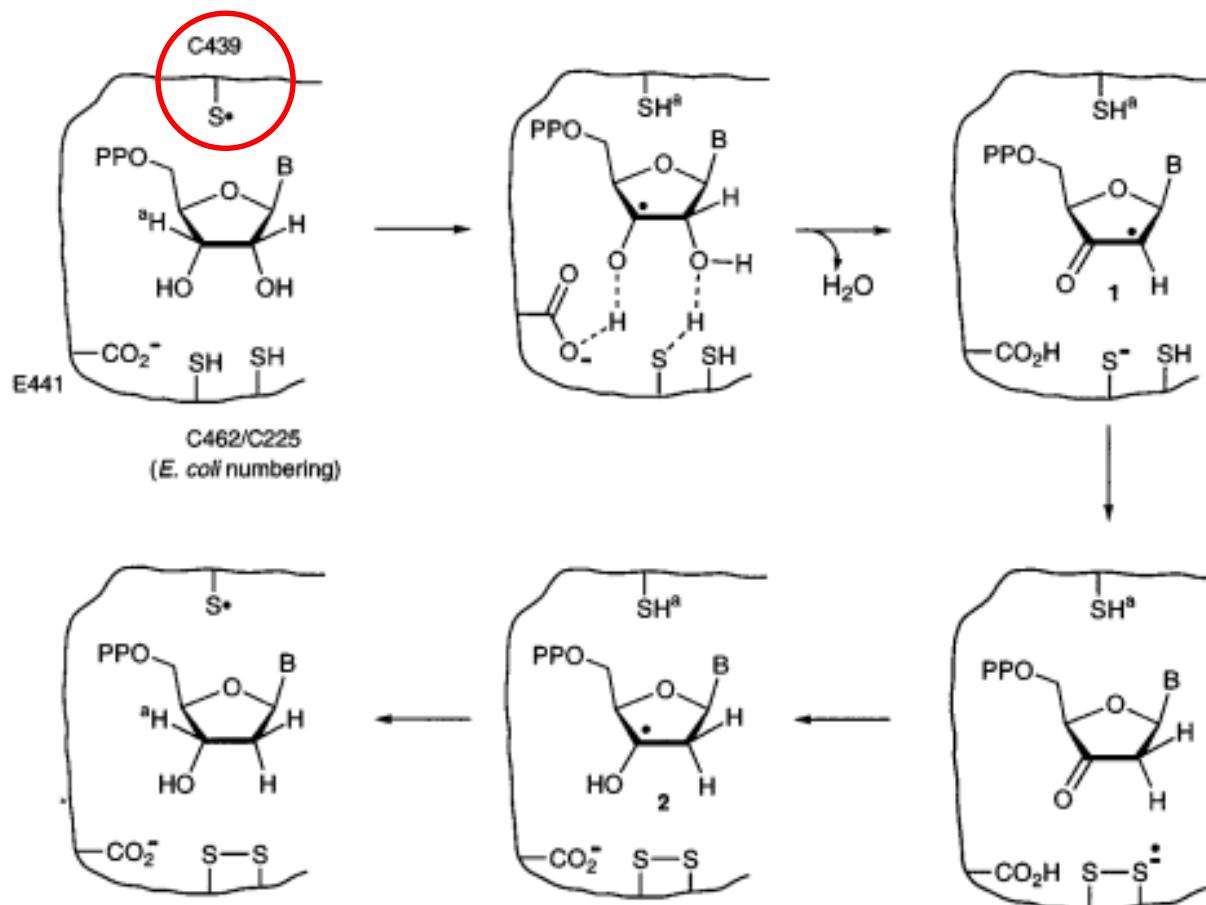
Ribonucleotide Riduttasi (RNR)

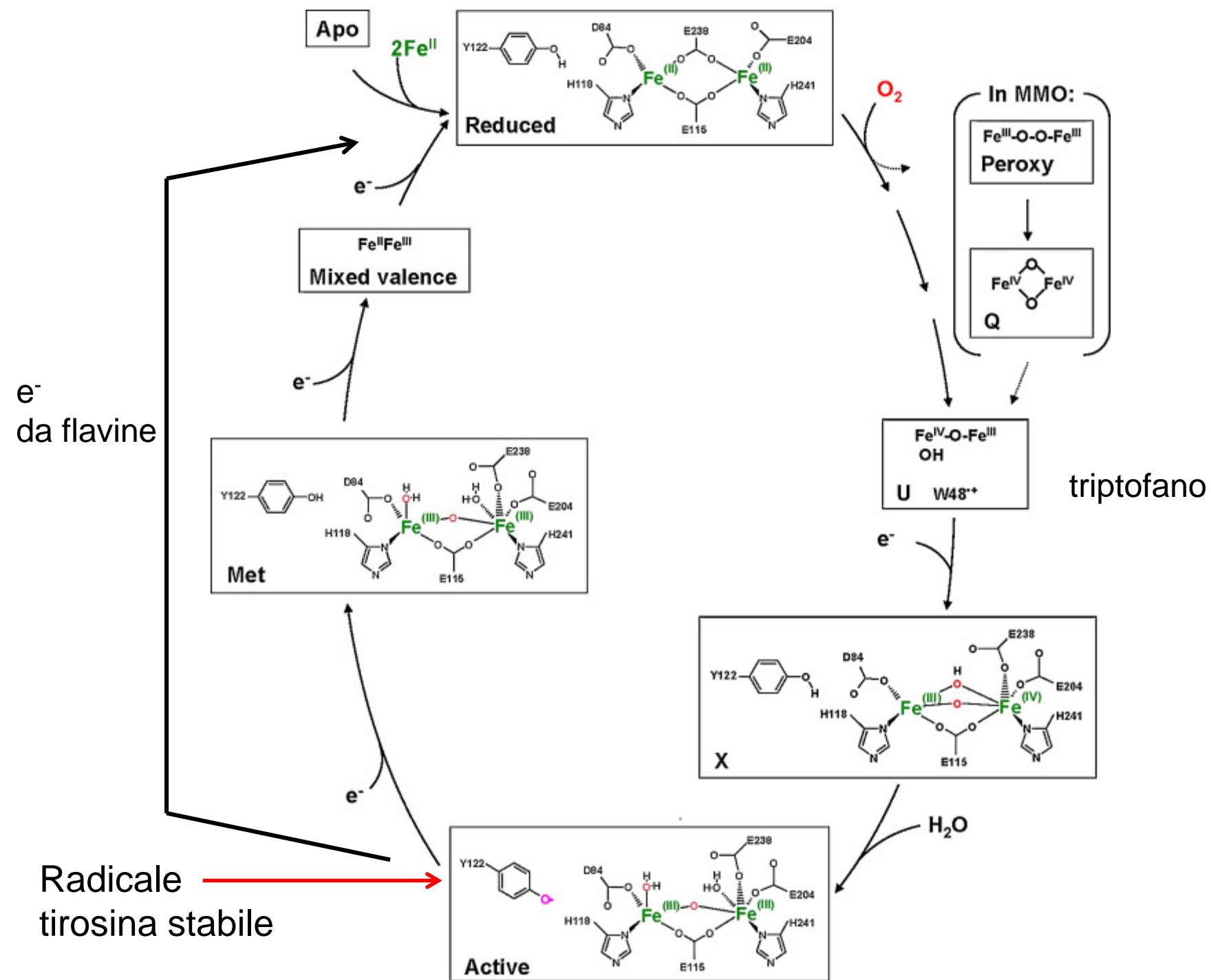


Sito attivo e cofattori metallici delle varie classi di Ribonucleotide Riduttasi



Meccanismo radicalico della RR



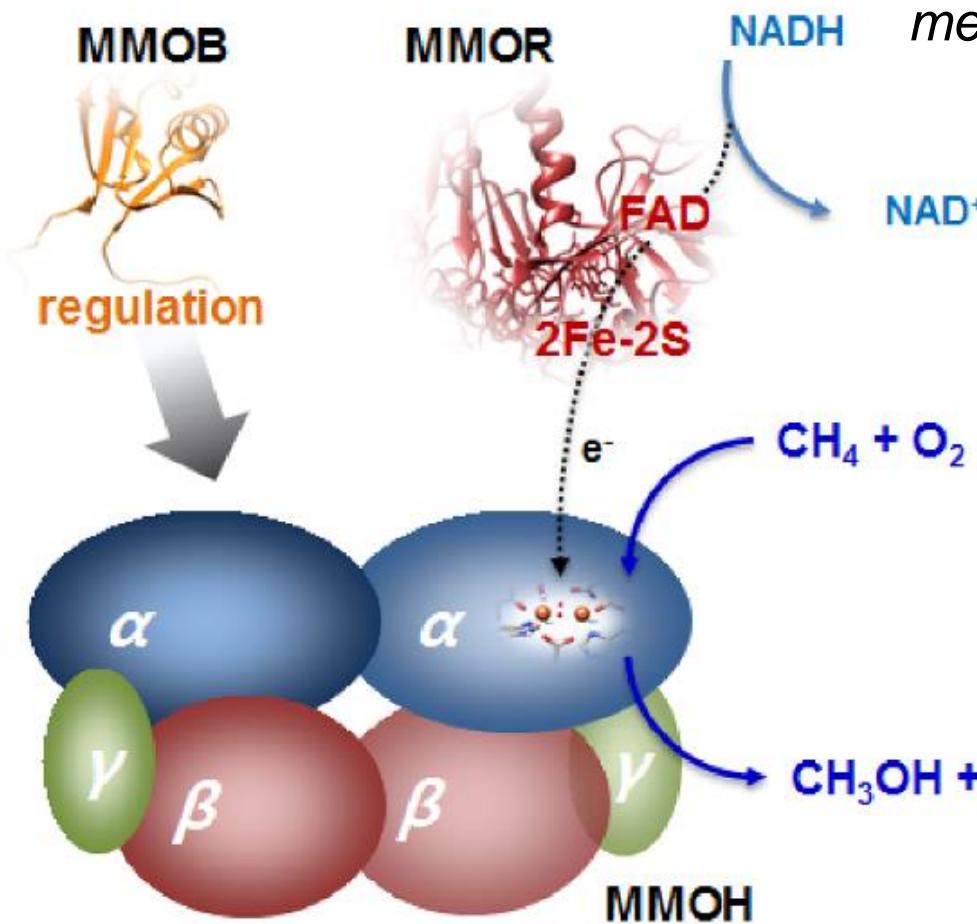


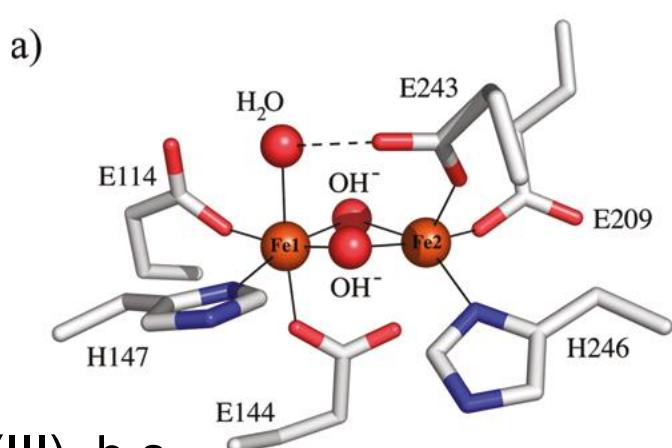
Metano monoossigenasi solubile (sMMO)



Batteri metanotropici

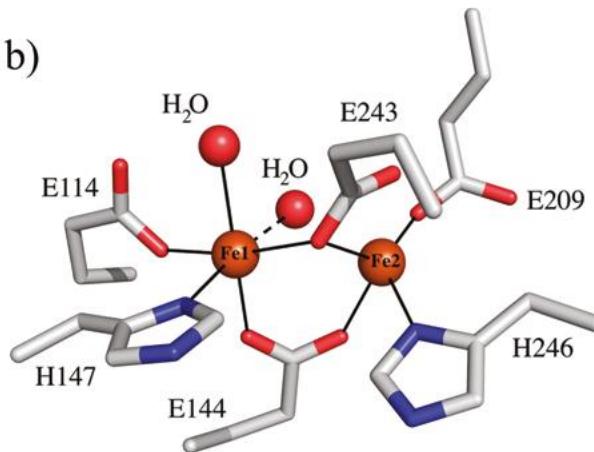
metano come fonte di C e di energia





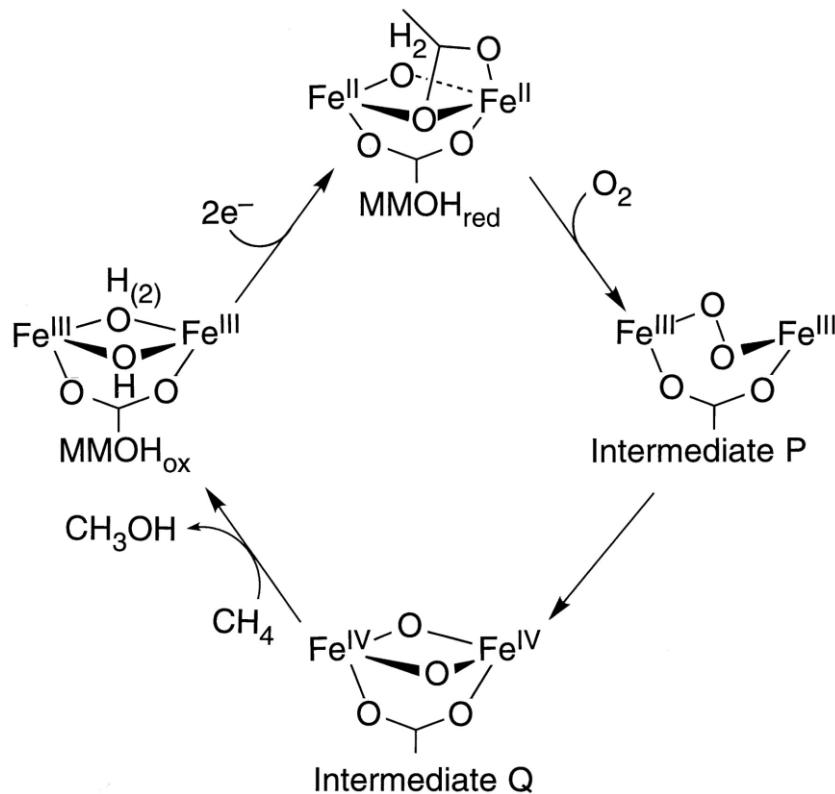
**Fe(III), h.s.
incolore
diamagnetico
(forte acc. a.f.)**

MMOH_{ox}

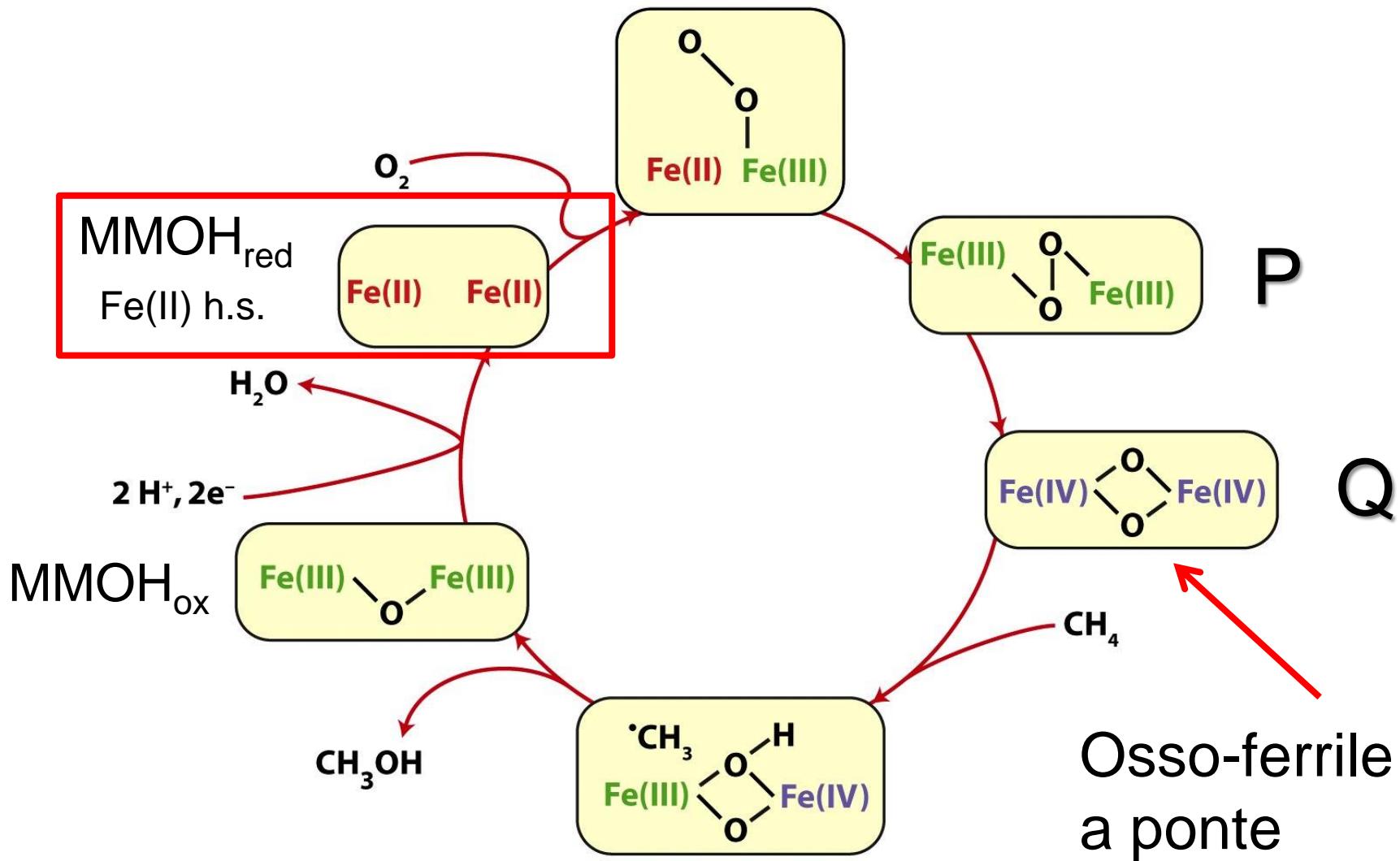


MMOH_{red}

**Fe(II), h.s.
(debole acc. a.f.)**

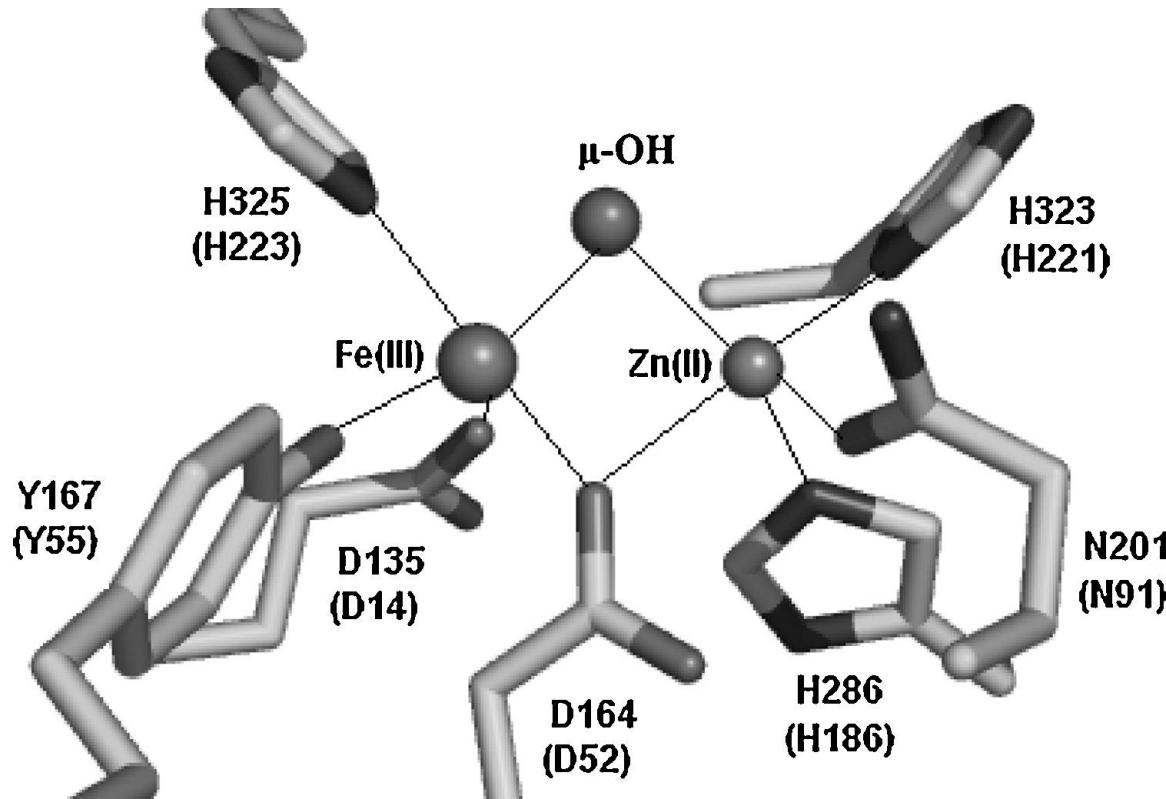


Ipotesi di ciclo catalitico della MMO



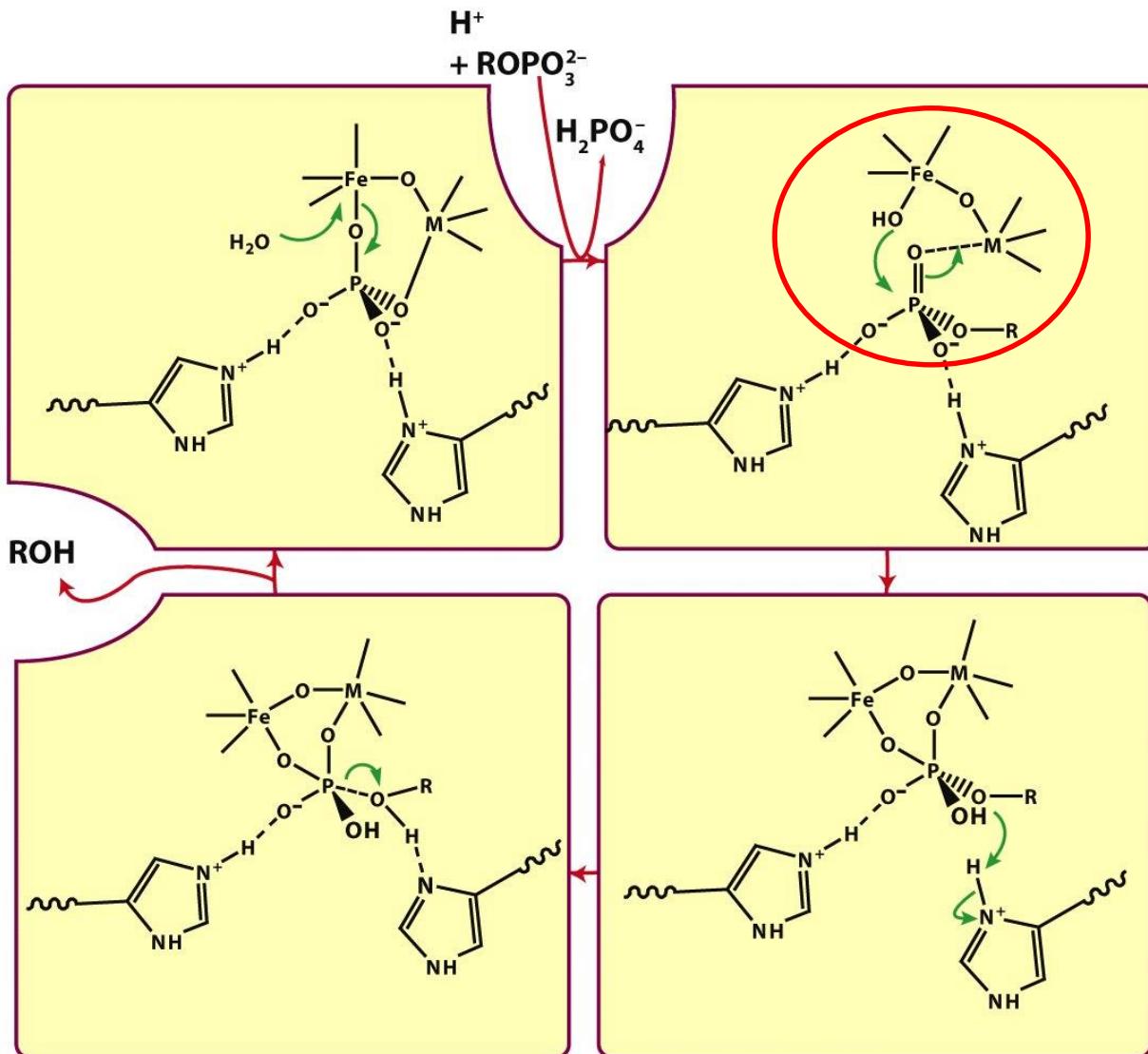
P e Q sono intermedi caratterizzati spettroscopicamente

Sito attivo di una fosfatasi acida



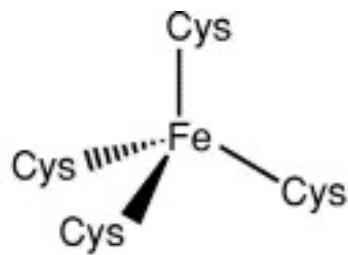
Tyr (LMCT, λ_{\max} fra 510 e 550 nm),
responsabile del colore da rosa da violetto

Ciclo catalitico di una fosfatasi acida

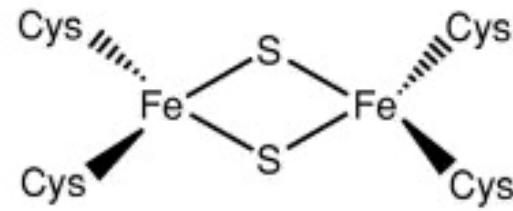


Sito attivo: Fe(III)-Fe(II)
Entrambi alto-spin

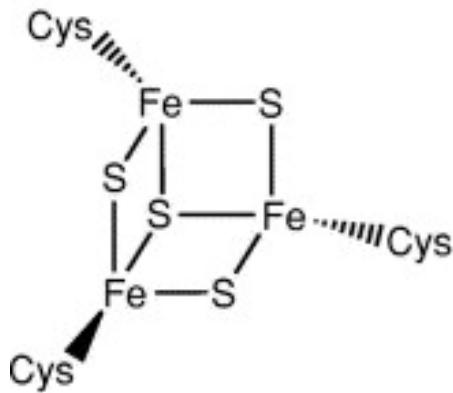
Proteine Fe-S



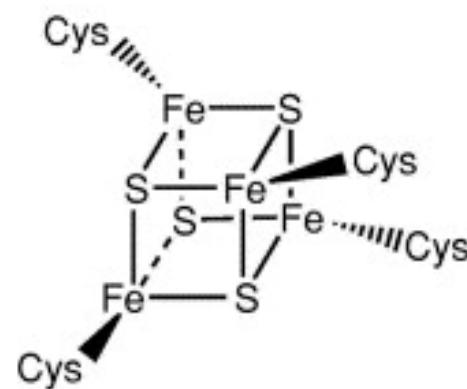
Rubredoxin type



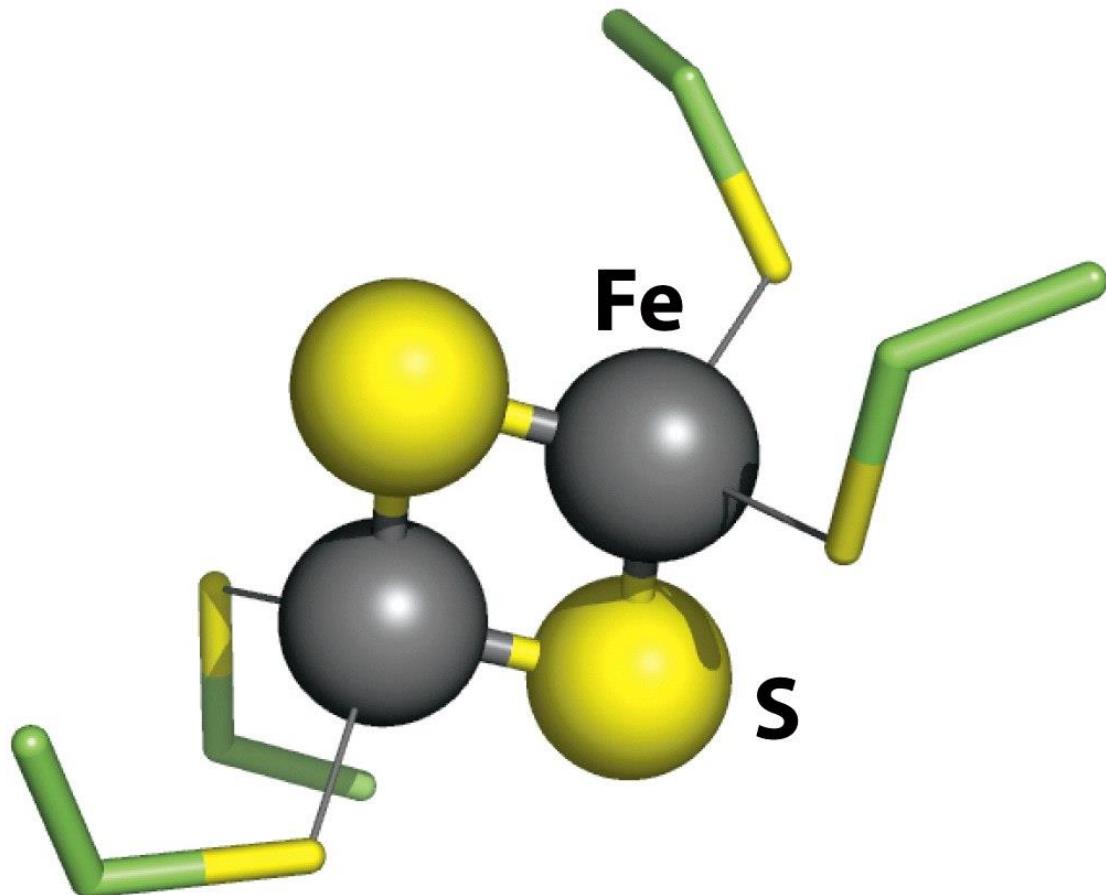
2Fe-2S



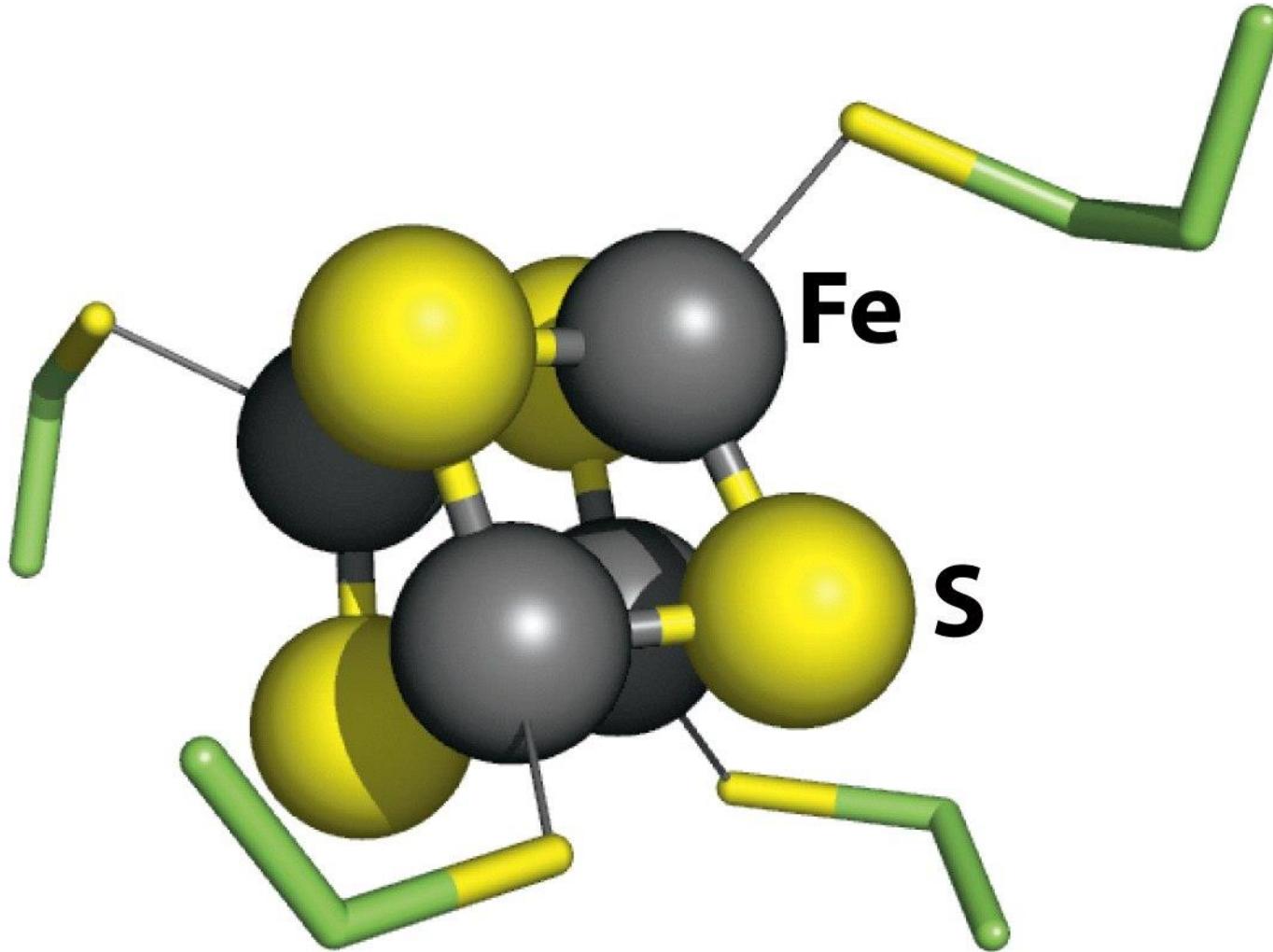
3Fe-4S



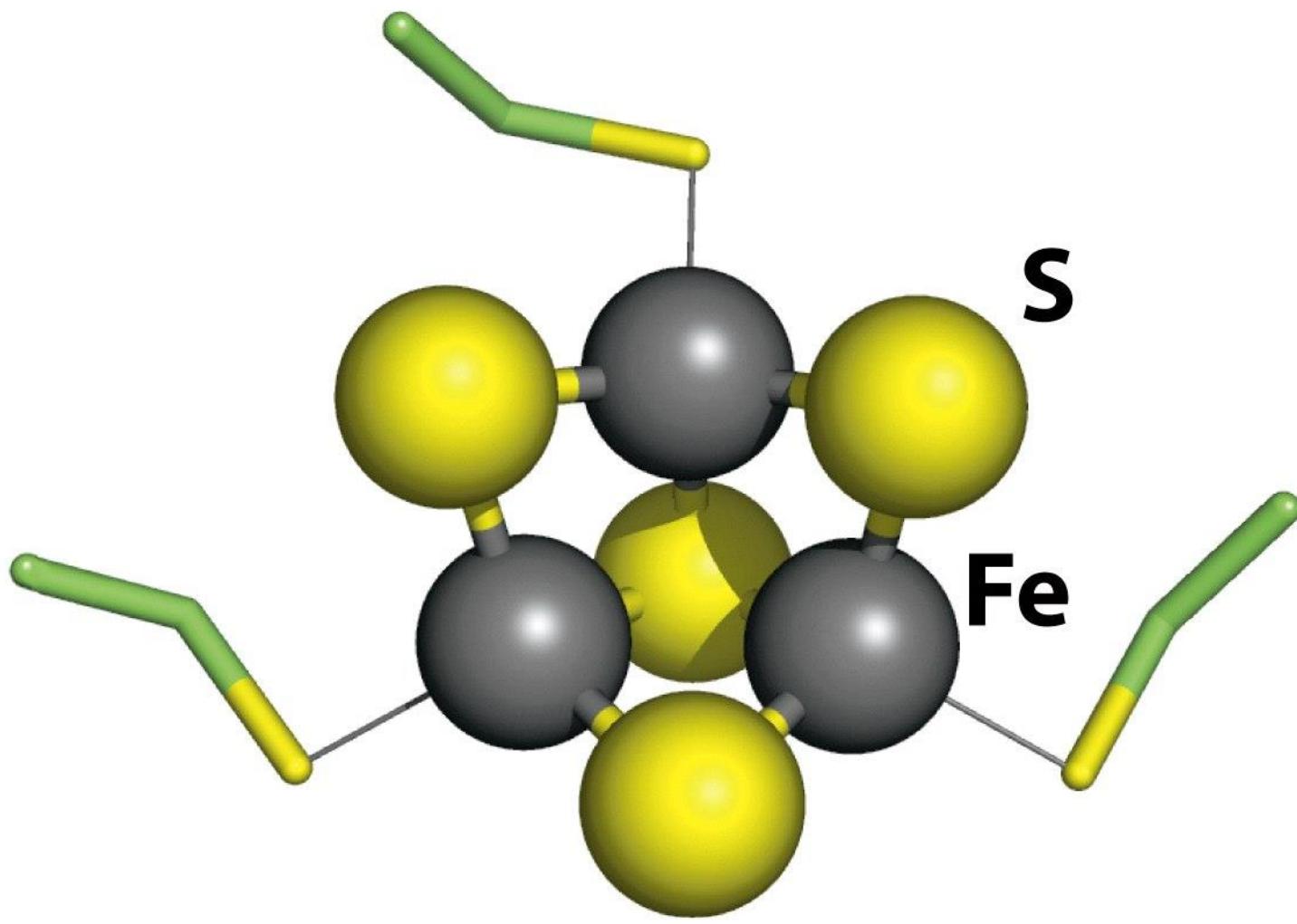
4Fe-4S



2Fe-2S]

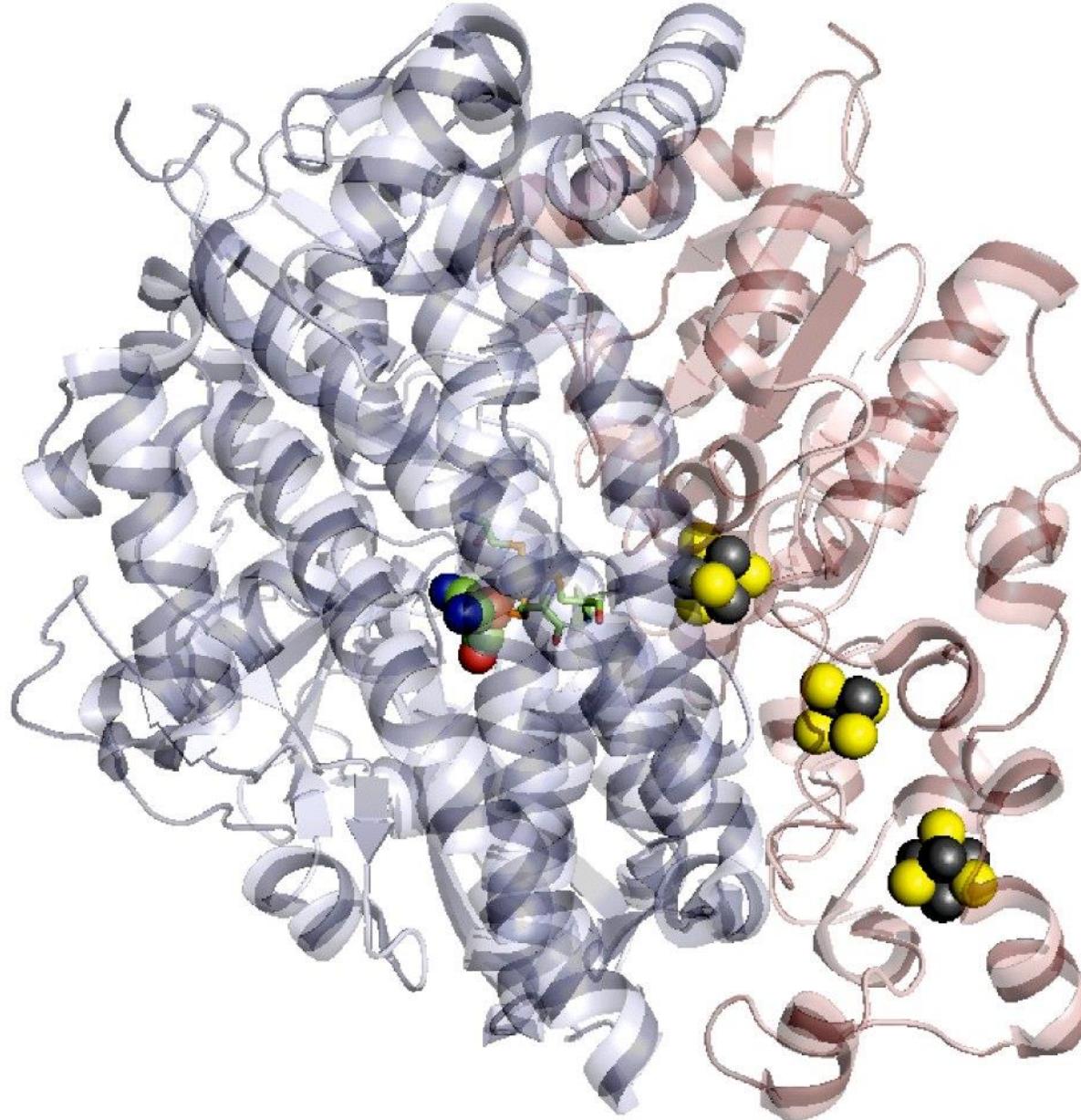


[4Fe–4S]



[3Fe-4S]

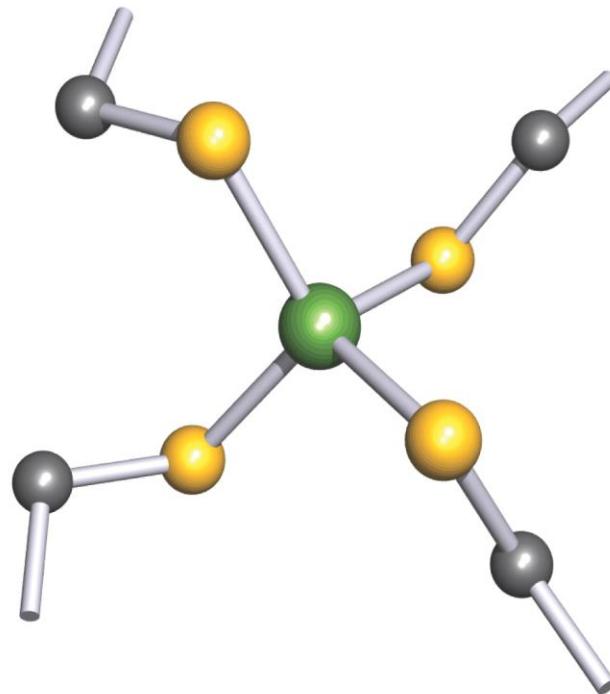
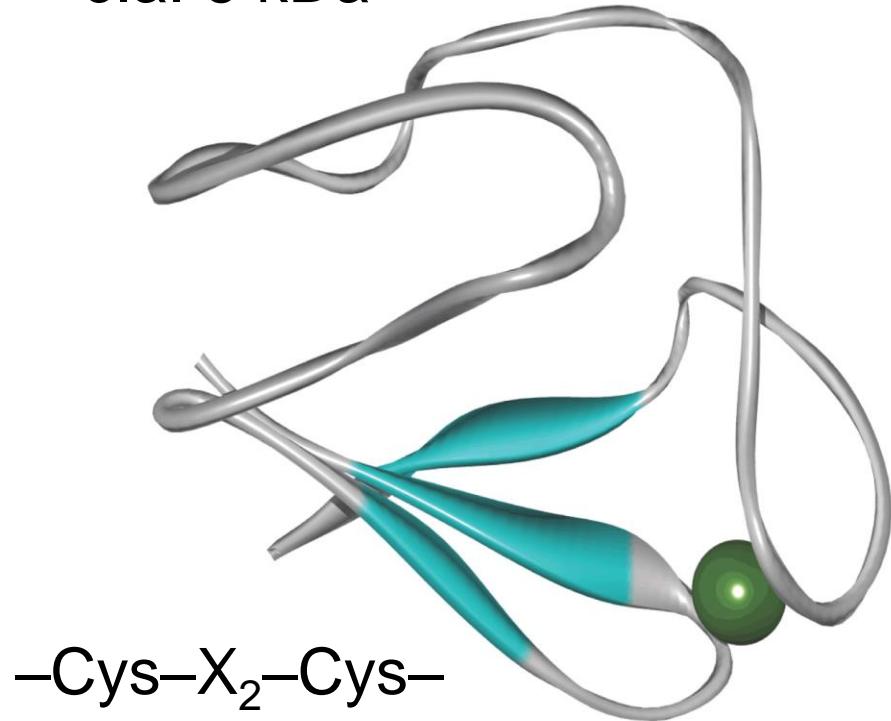
[Ni–Fe]-idrogenasi: percorso redox



Rubredossina da *Clostridium pasteurianum*

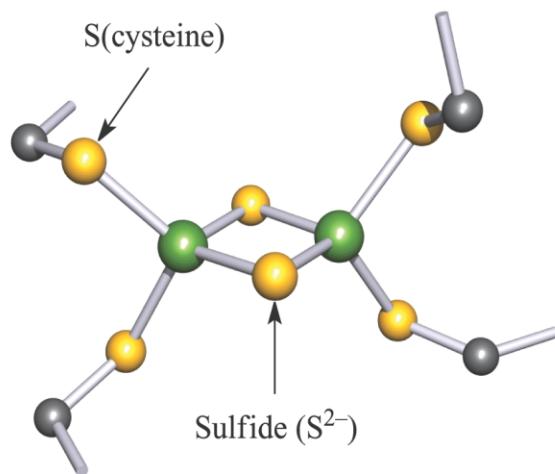
c.a. 6 kDa

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

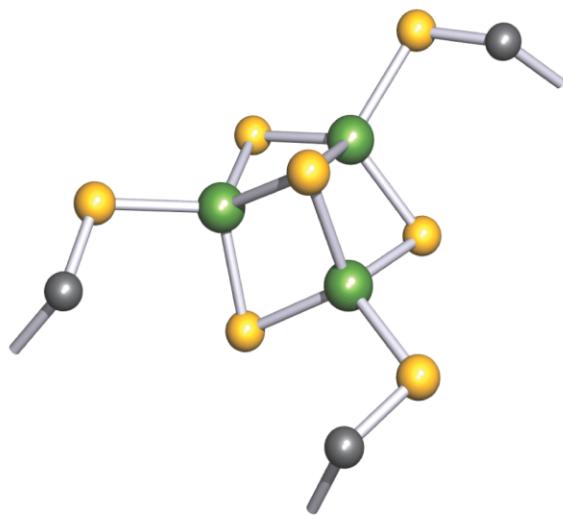


Unità ferro-zolfo da ferridossine

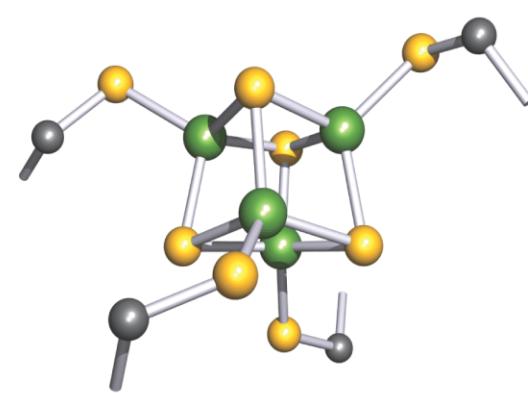
E° fra -250 e -450 mV



[2Fe–2S]
da spinaci



[3Fe–4S]
azotobacter vinelandii

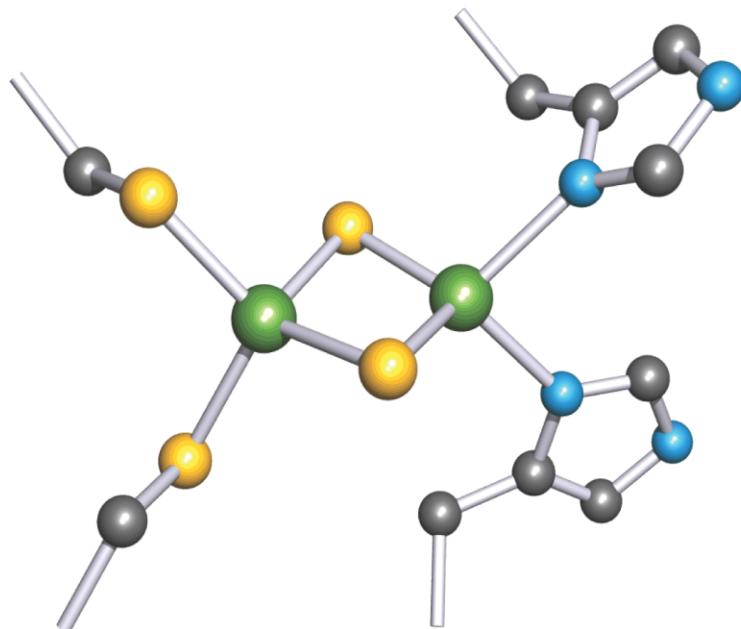
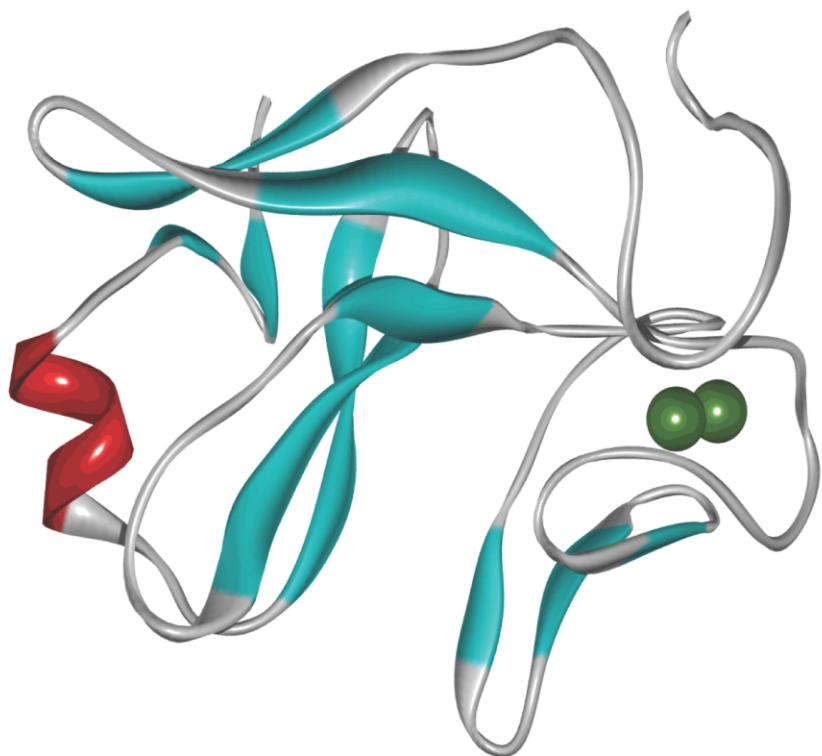


[4Fe–4S]
chromatium vinosum

$E^\circ = -420$ mV

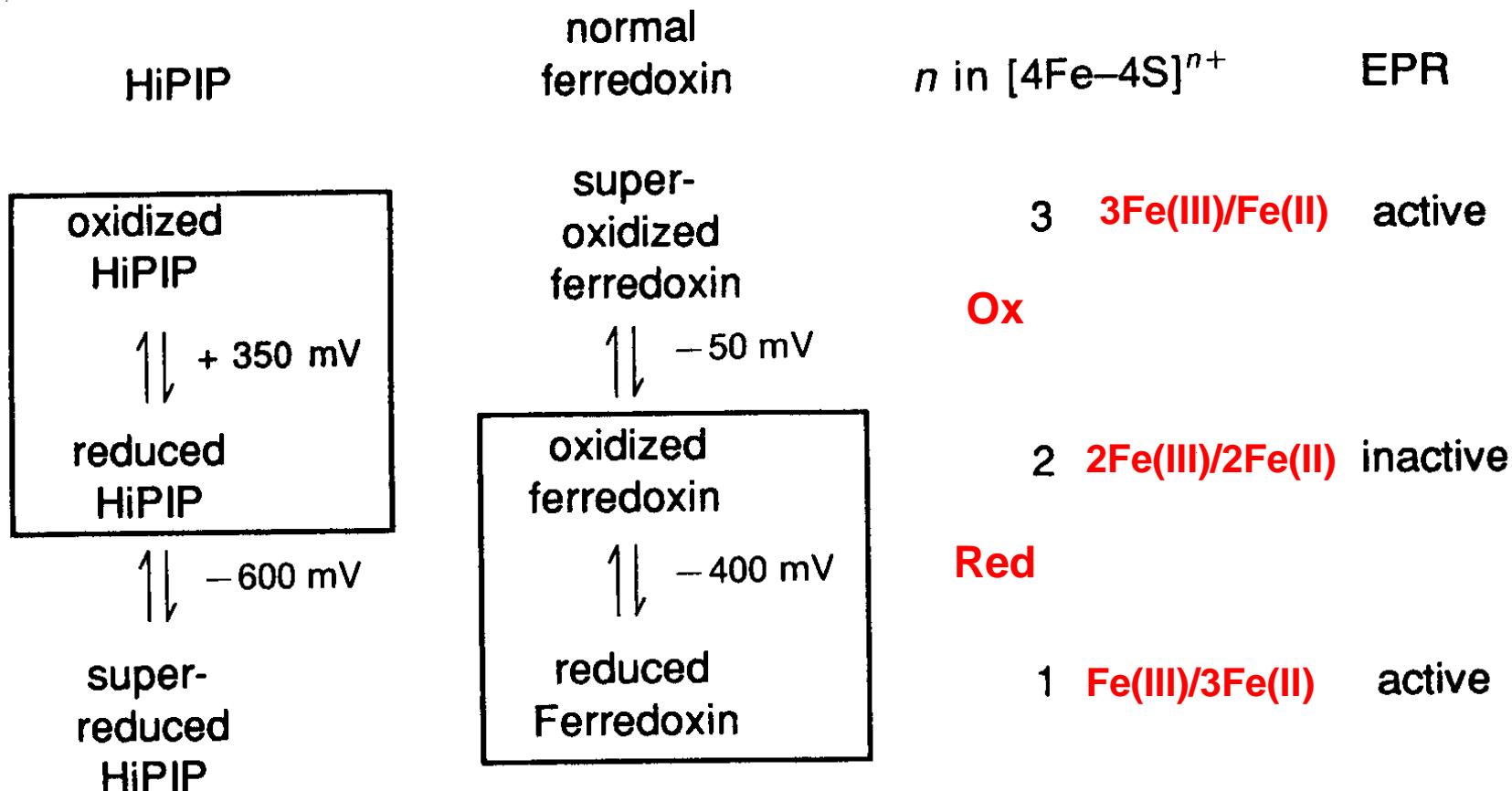
Fe(III)/Fe(II) – Fe(II)/Fe(III)

Proteina Rieske da cloroplasti di spinaci



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

High Potential Iron-sulfur Proteins (HiPIP)



[Rd]:

—Cys—X₂—Cys—X_n—Cys—X₂—Cys—

[2Fe–2S]:

—Cys—X₄—Cys—X₂—Cys—X₂₉—Cys—

[4Fe–4S]:

—Cys—X₂—Cys—X₂—Cys—X_n—Cys—

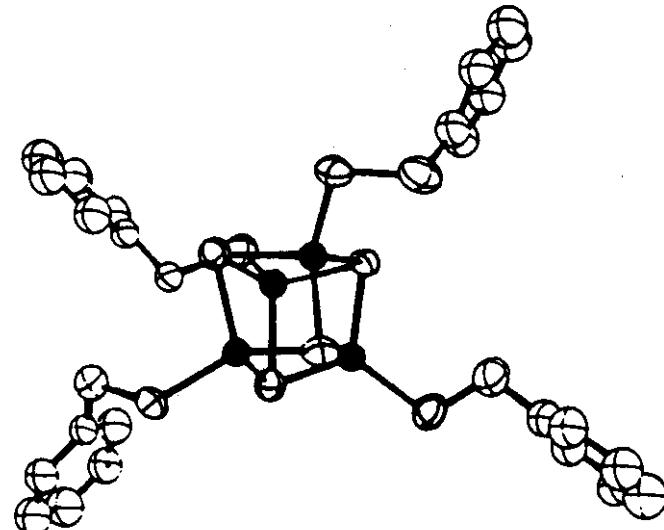
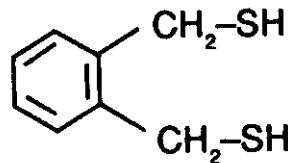
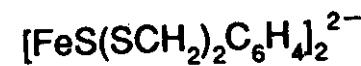
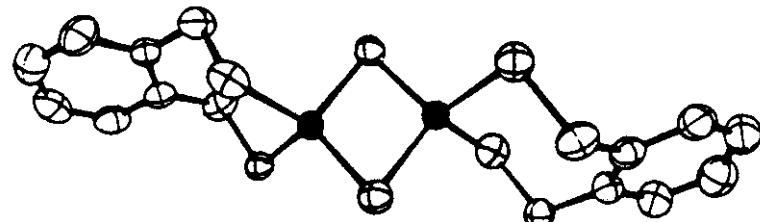
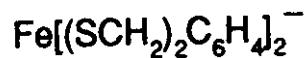
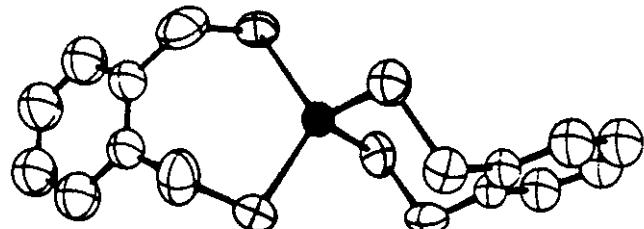
HiPIP:

—Cys—X₂—Cys—X₁₆—Cys—X₁₃—Cys—

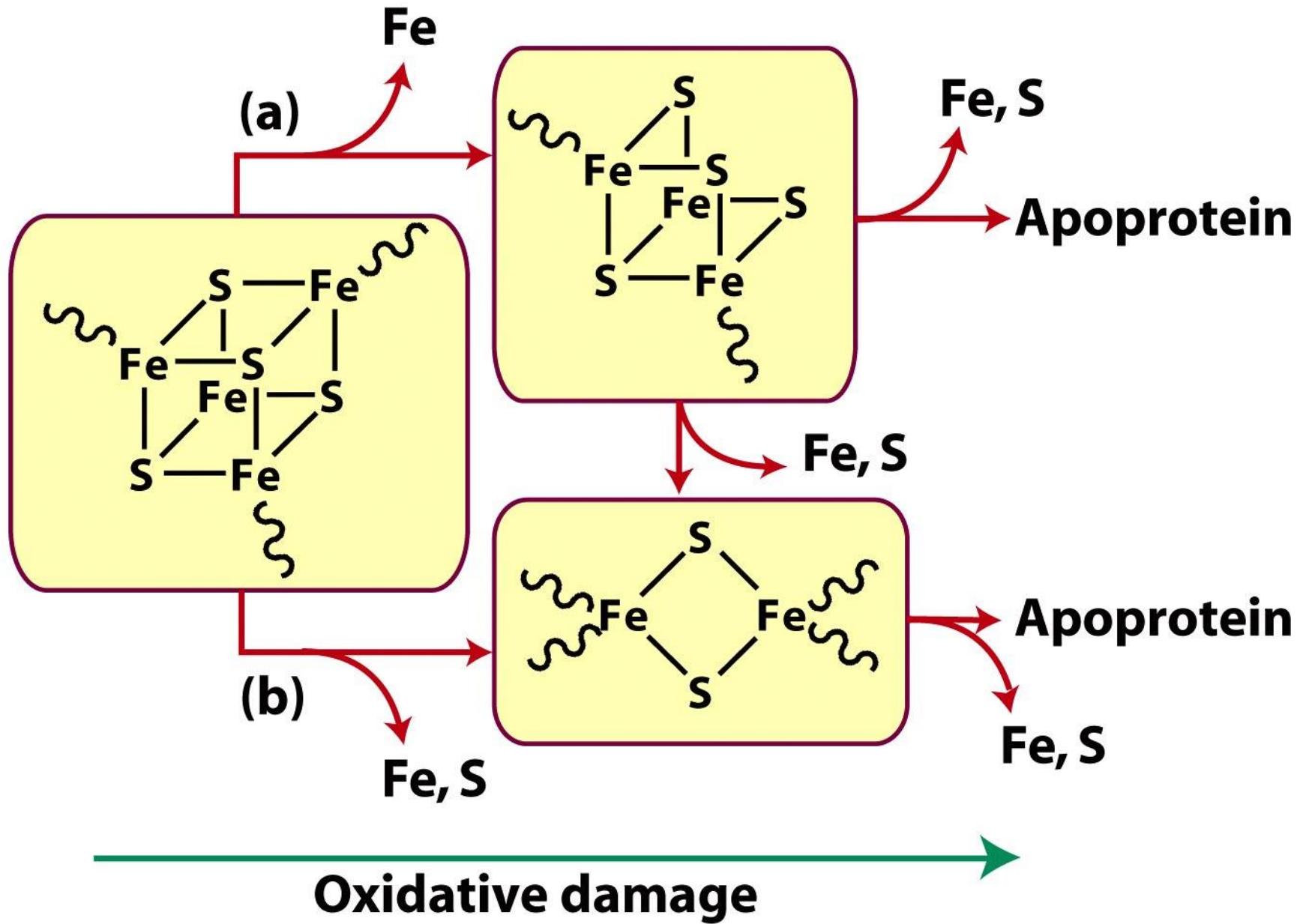
[3Fe–4S]:

—Cys—X_{5,7}—Cys—X_n—Cys—

Complessi modello

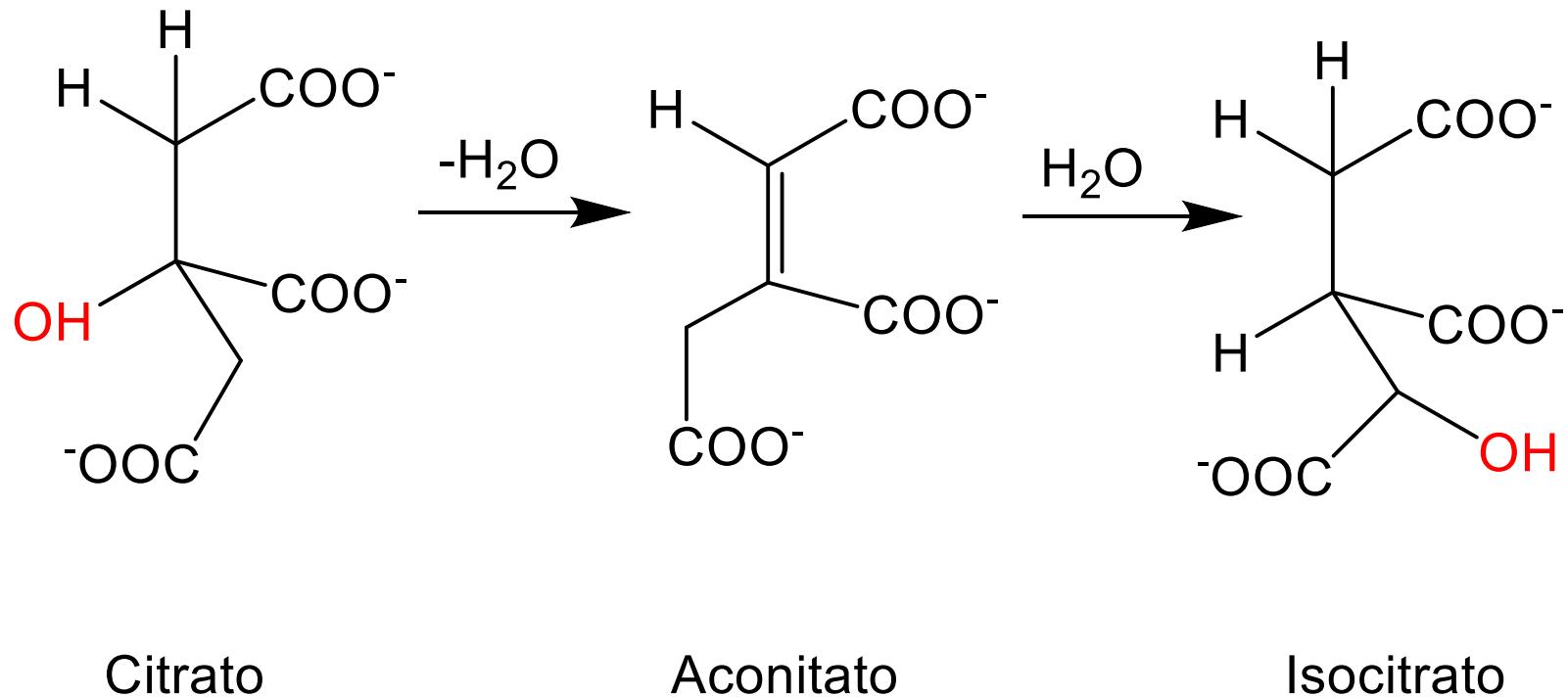


Proteine Fe–S come sensori di O₂



Enzima Aconitasi

catalizza interconversione del citrato in isocitrato



Sito catalitico dell'aconitasi

