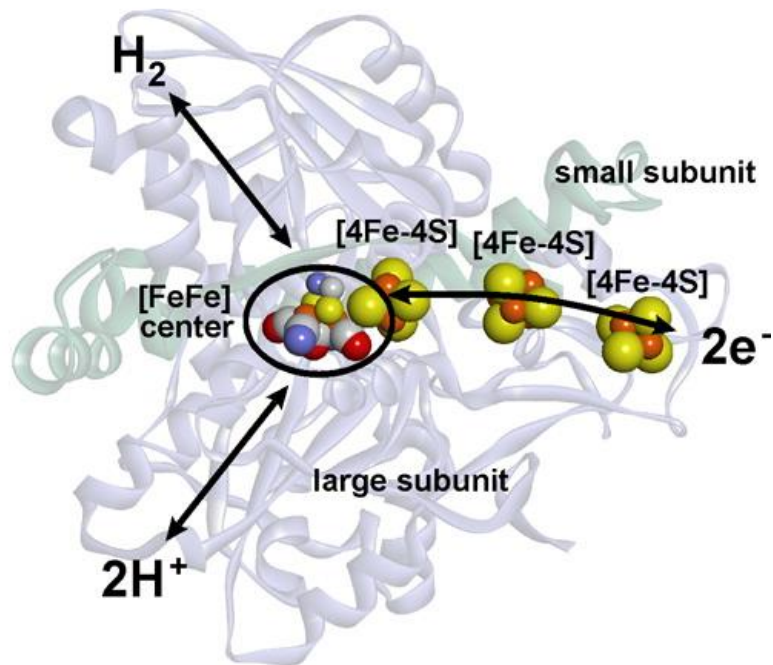
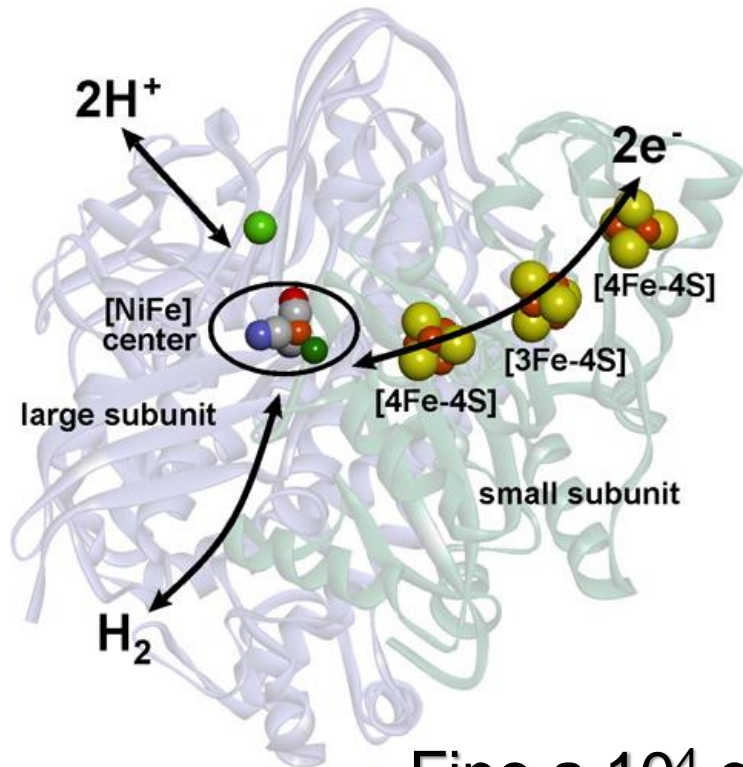
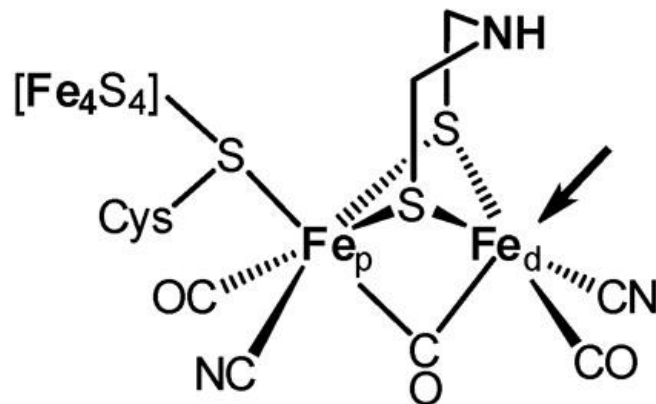
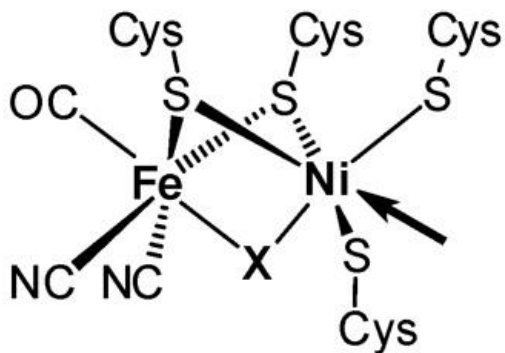


[NiFe] Hydrogenase

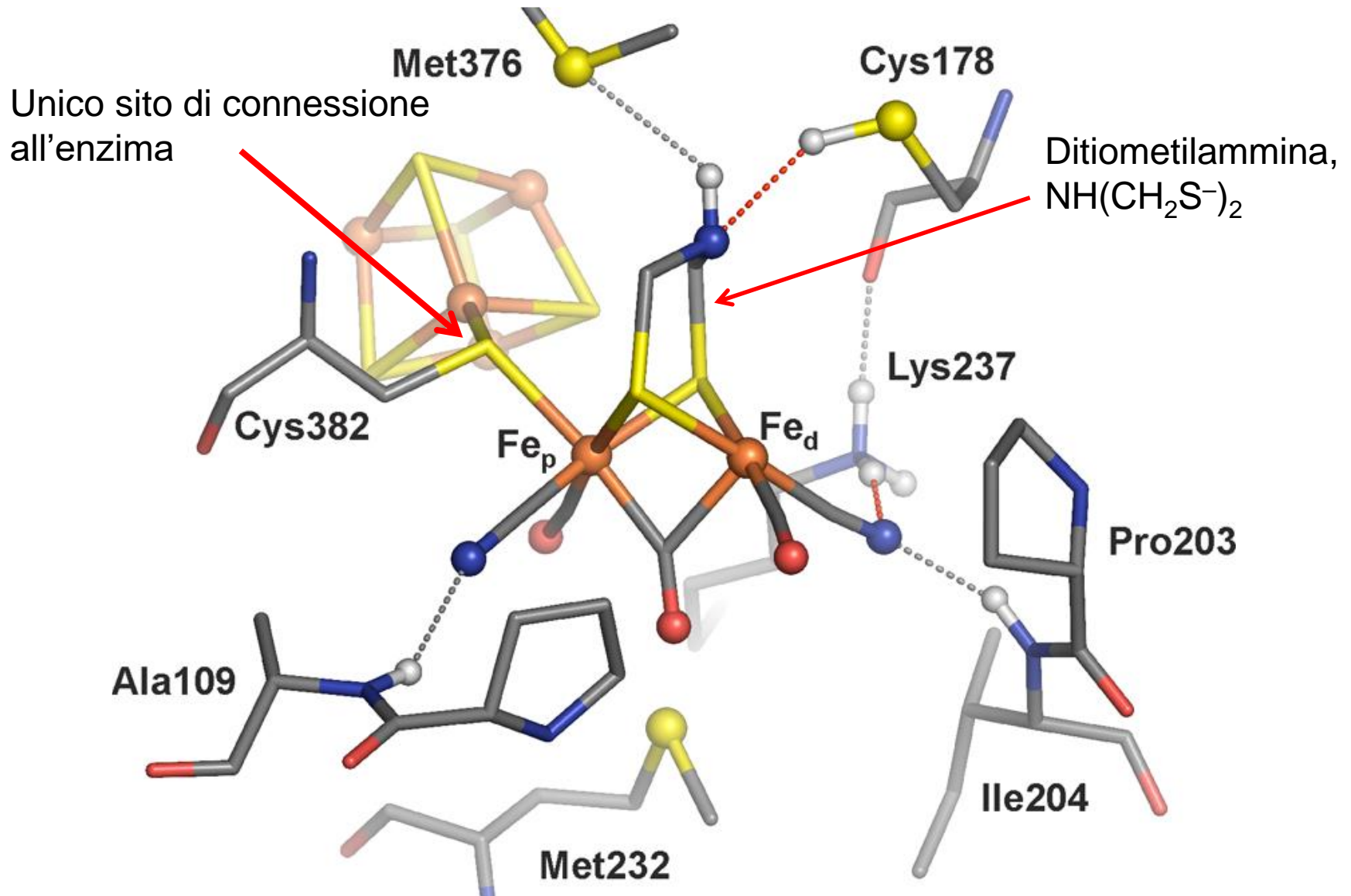
[FeFe] Hydrogenase

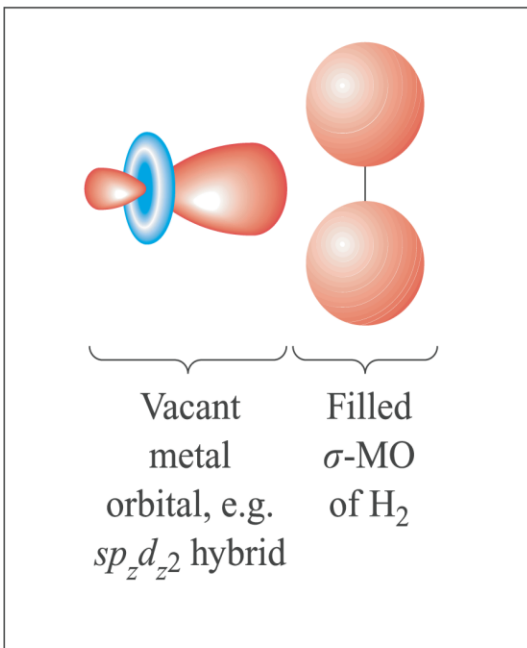
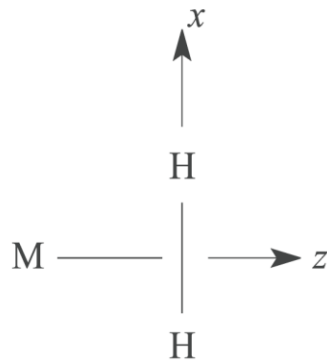


Fino a 10⁴ cicli/secondo

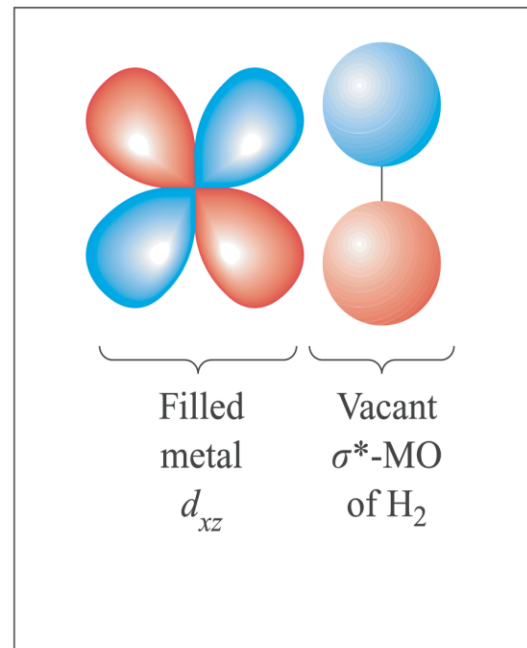


[FeFe] Idrogenasi



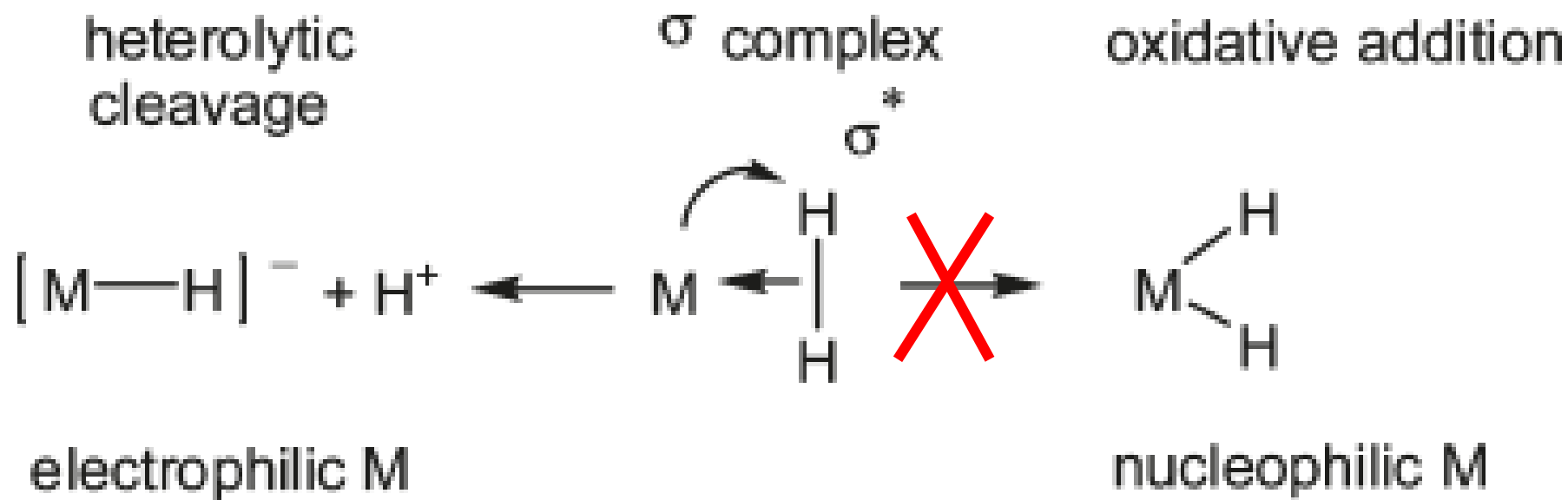


H_2 -to-M donation
(a)

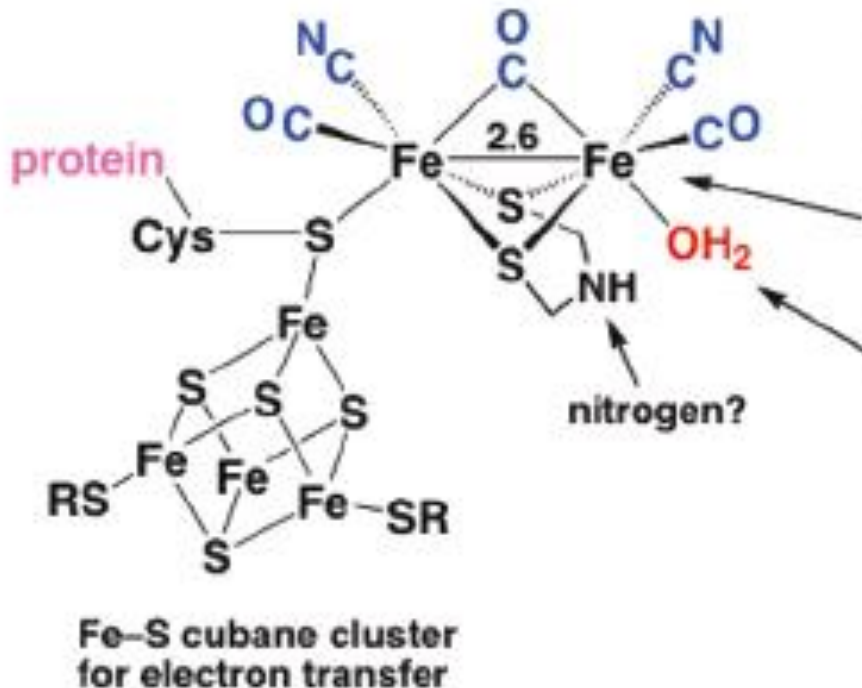


M-to- H_2 back-donation
(b)

Il CO coordinato favorisce la rottura eterolitica di H₂



Fe-Fe Hydrogenase

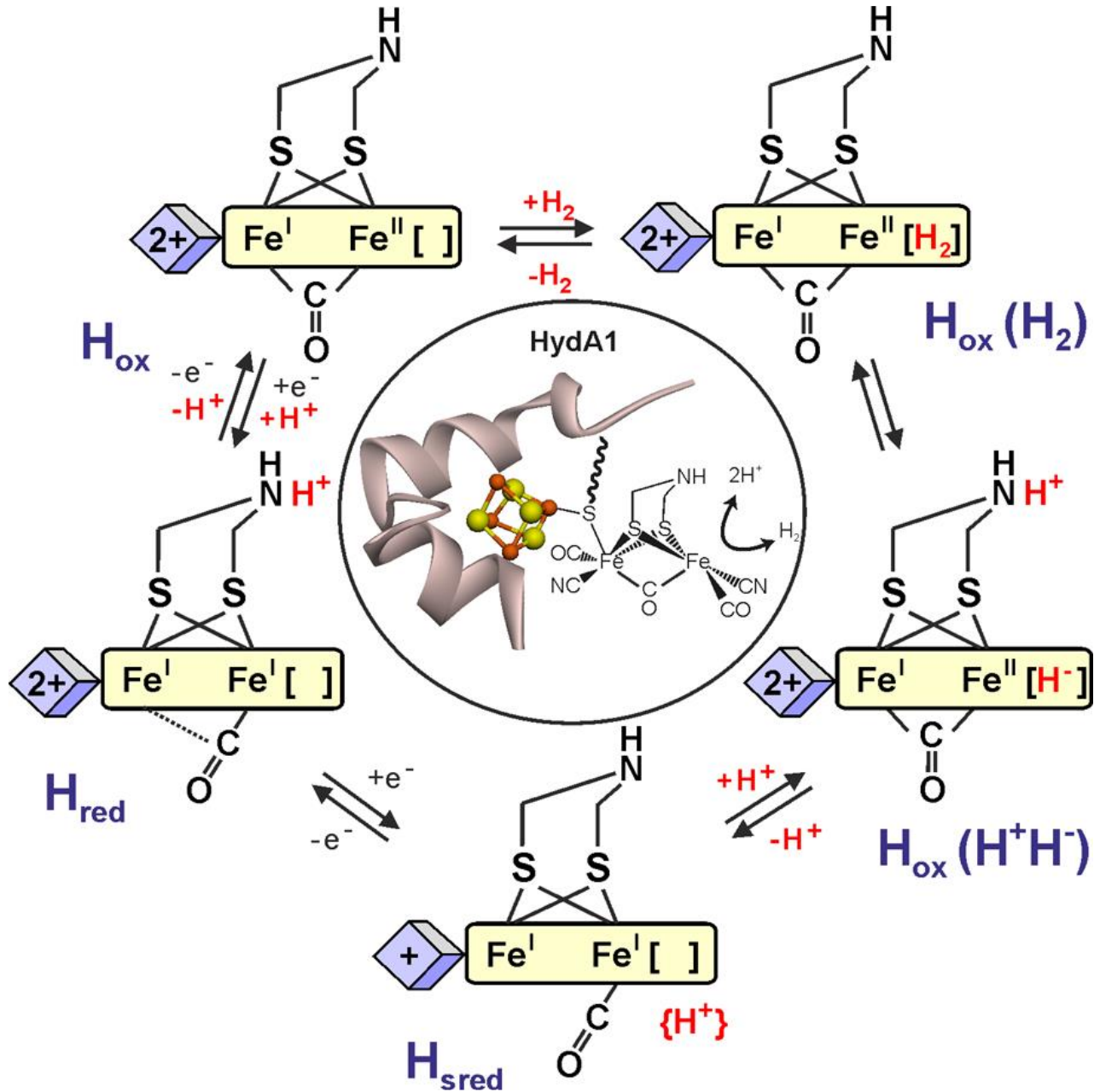


- Active site attached at only **one point**
- **CO** and **CN** ligands on low-spin Fe^{II}
- Metal-metal bonds
- Intramolecular heterolysis of **H₂** ostensibly at this site
CO can displace **H₂O**; can **H₂**?
H₂ is slightly stronger ligand than **H₂O** on W(CO)₃(PR₃)₂

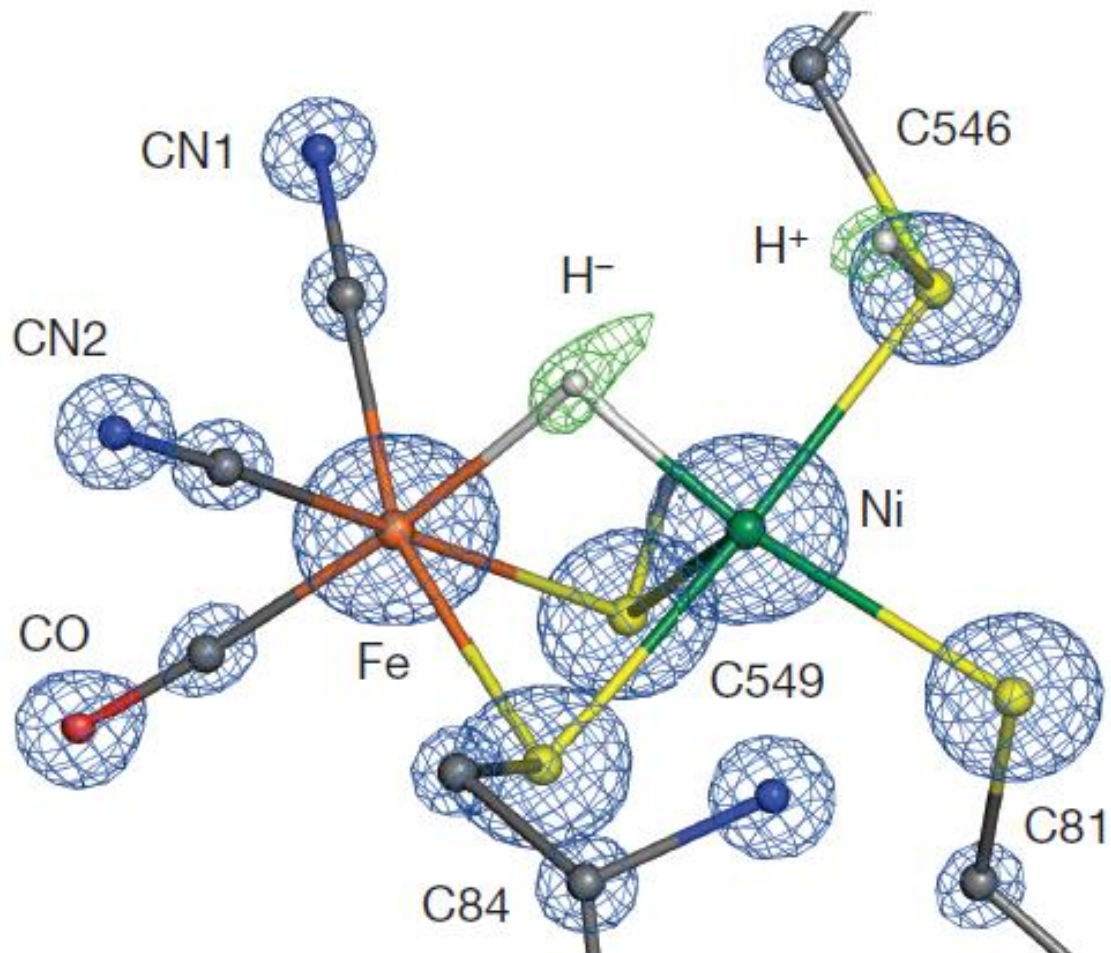
Trans **CO** ligand favors H₂ coordination and heterolysis

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

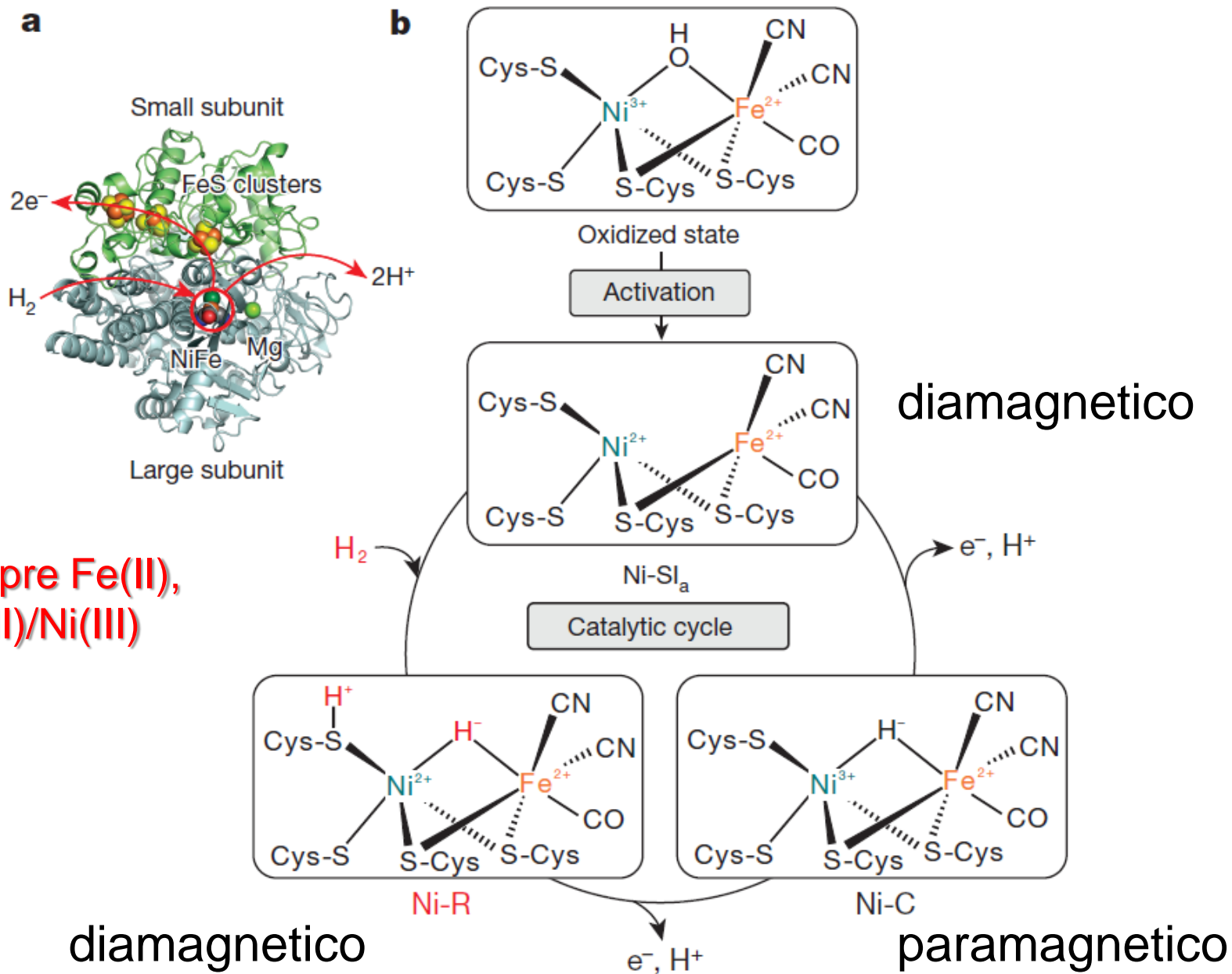


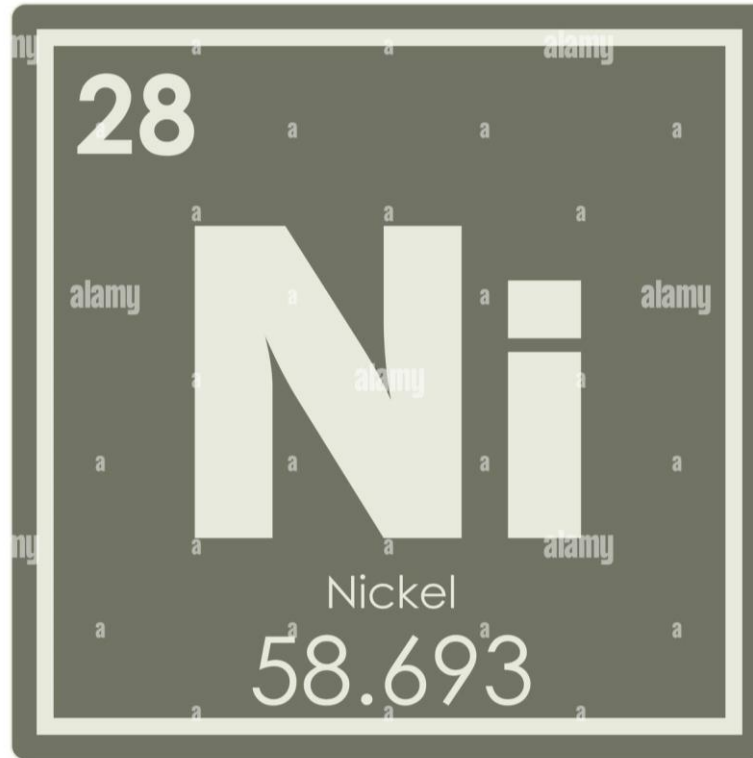
Fe–Ni Hidrogenasi



Nature, 2015

Ipotesi di meccanismo





Enzimi al nichel svolgono ruoli cruciali in batteri, *archei*, funghi, alghe e piante. Al momento non sono noti Ni-enzimi nei mammiferi, e il nichel è classificato come “elemento possibilmente essenziale” per animali e uomini.

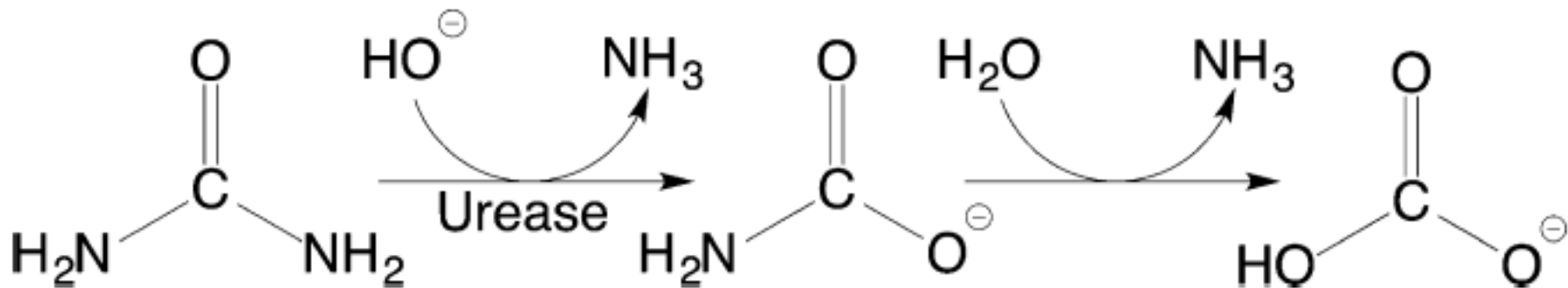
Enzimi redox

- Leganti anionici allo zolfo (Cys⁻ e S²⁻)
- Coppia redox Ni(II)/Ni(III)
- Insaturazione coordinativa
- Basso spin

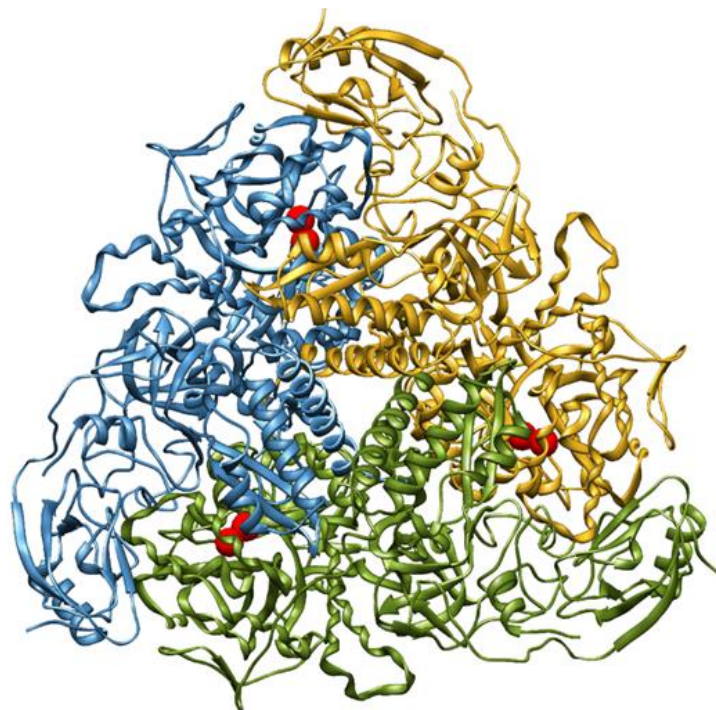
Enzimi non-redox

- Sempre Ni(II), acido di Lewis
- Leganti O/N
- Esacoordinato
- Alto spin

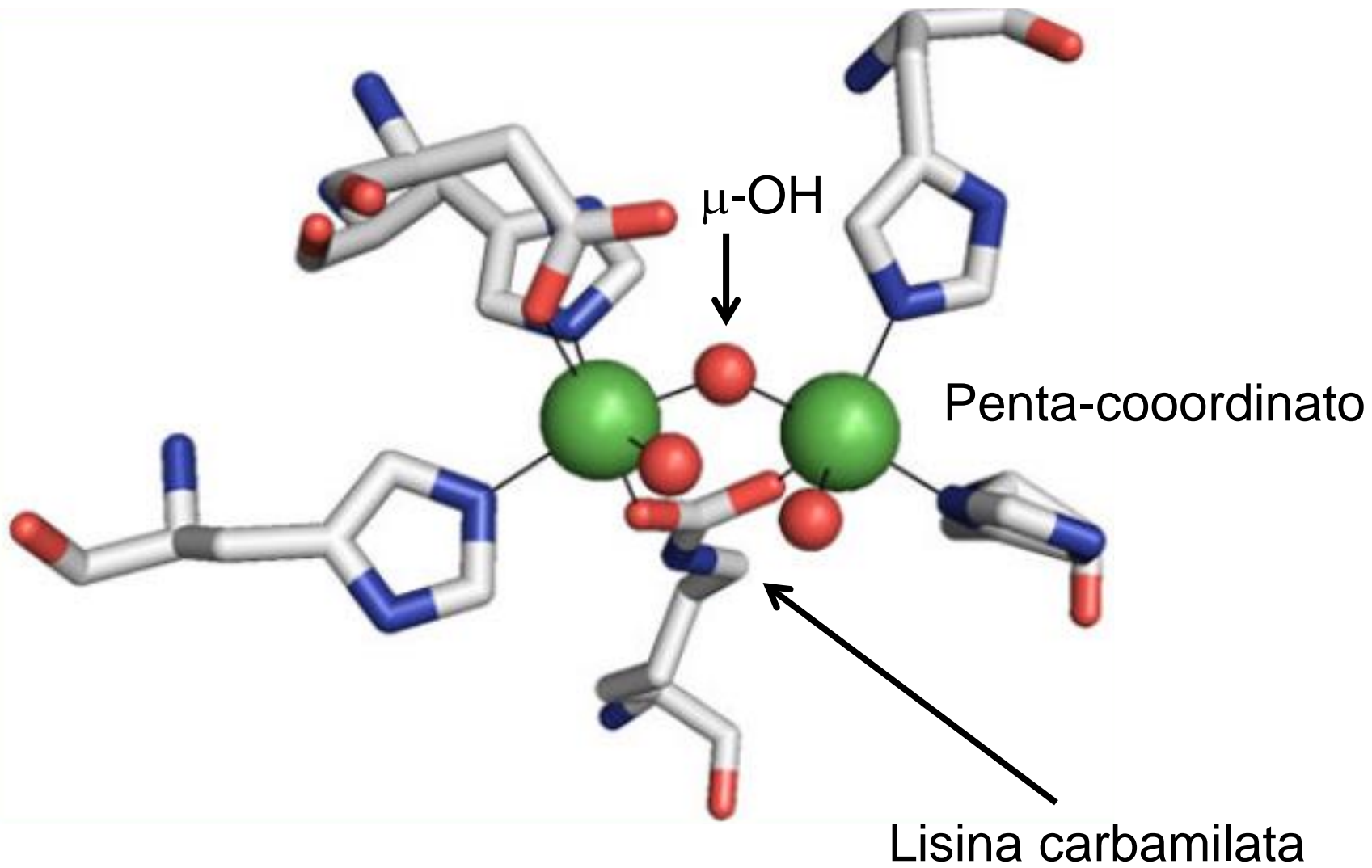
Ureasi (enzima non-redox)



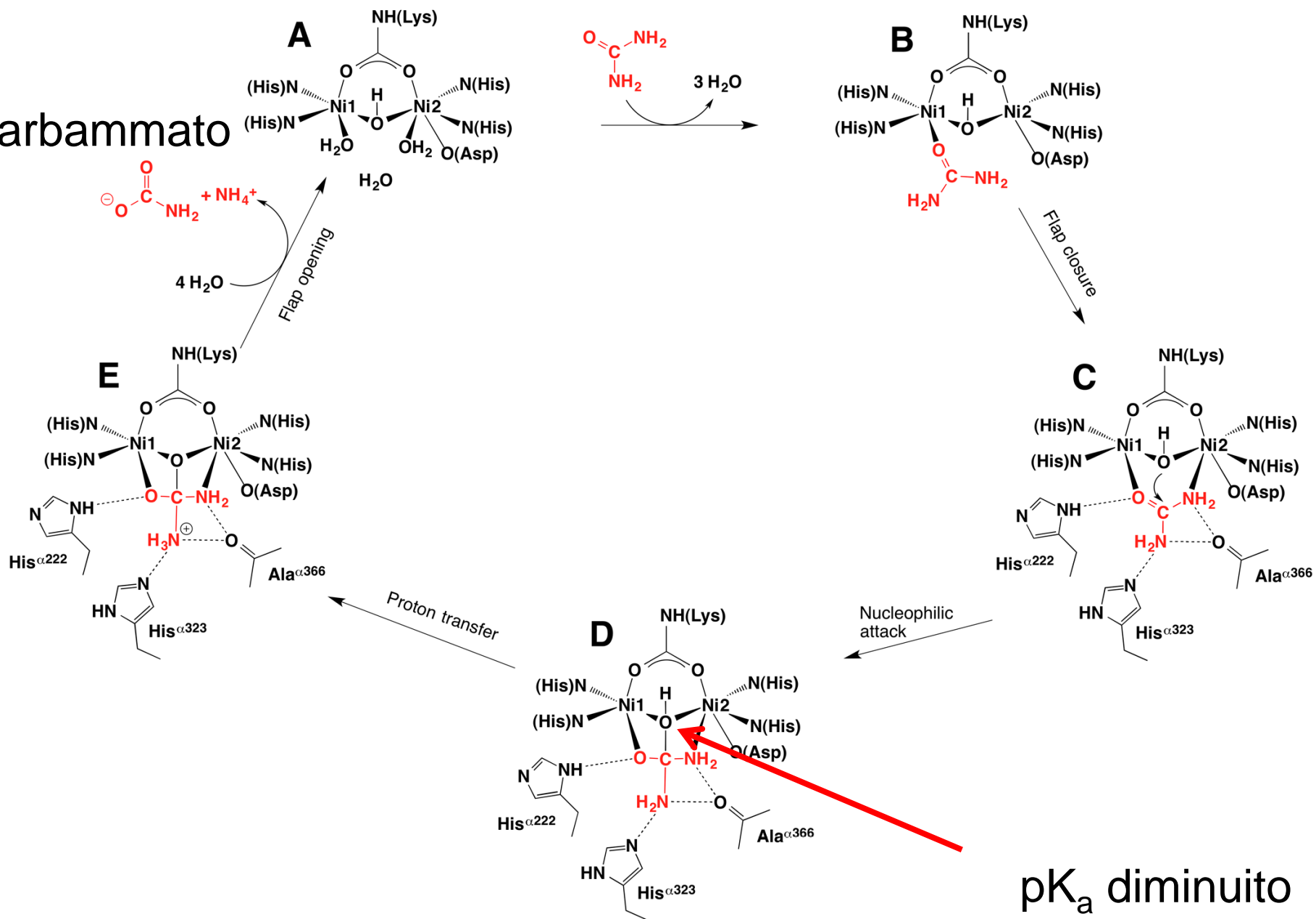
l'ureasi è la più efficiente tra le idrolasi note, induce un aumento di velocità rispetto alla reazione non catalizzata di 3×10^{15} volte (da centinaia di anni a microsecondi)



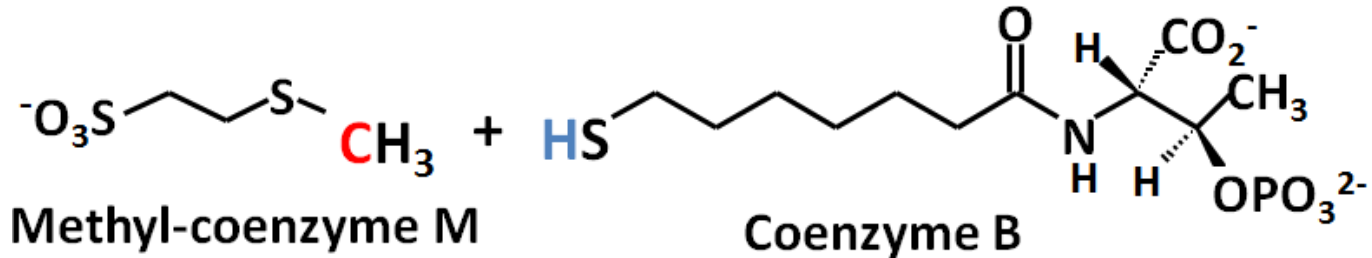
trimero di trimeri del tipo $(\alpha\beta\gamma)_3$



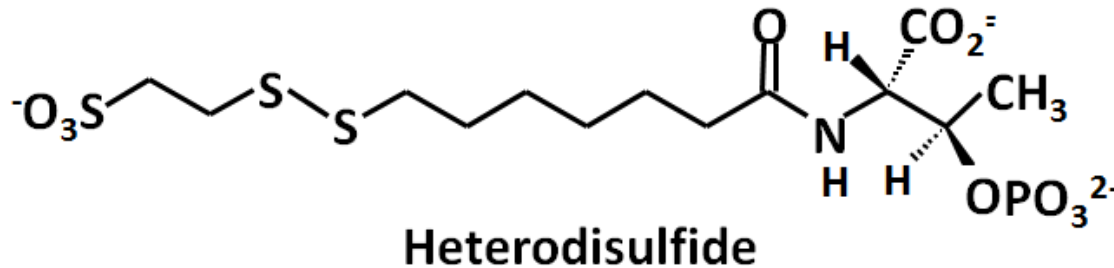
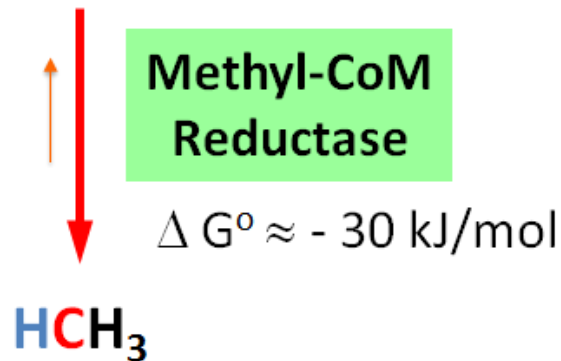
carbammato



metil-coenzima M riduttasi (MCR) enzima redox (*archei* metanogenici)

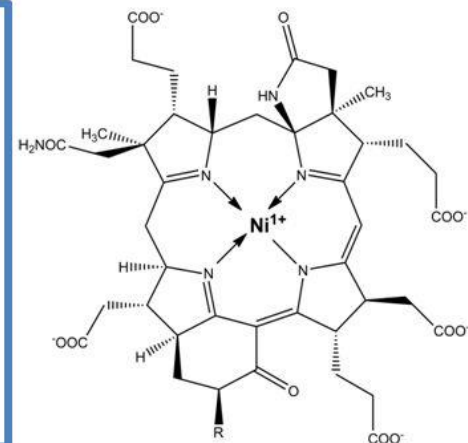
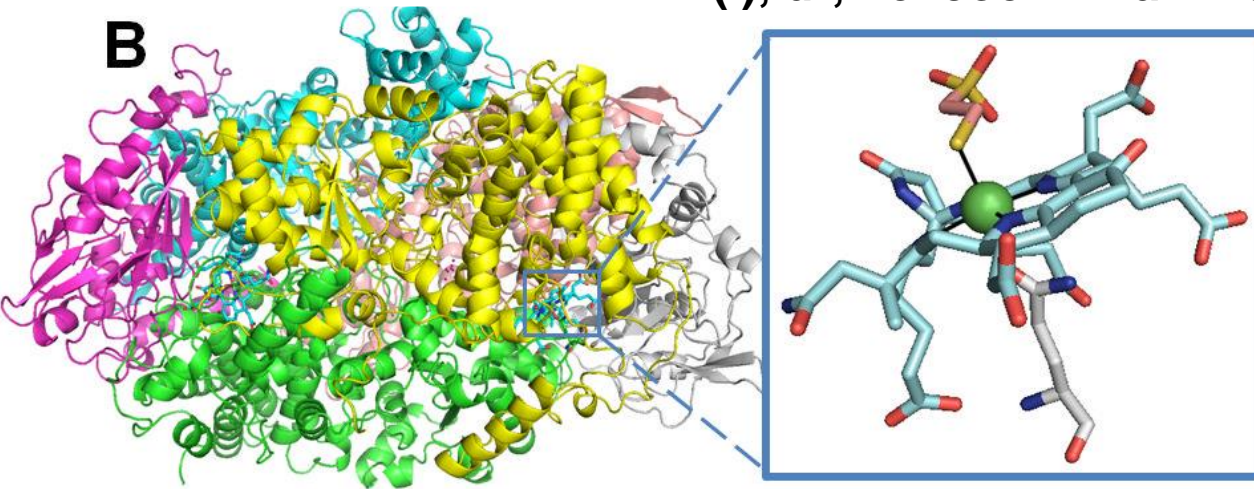


10^9 t/y di metano biologico

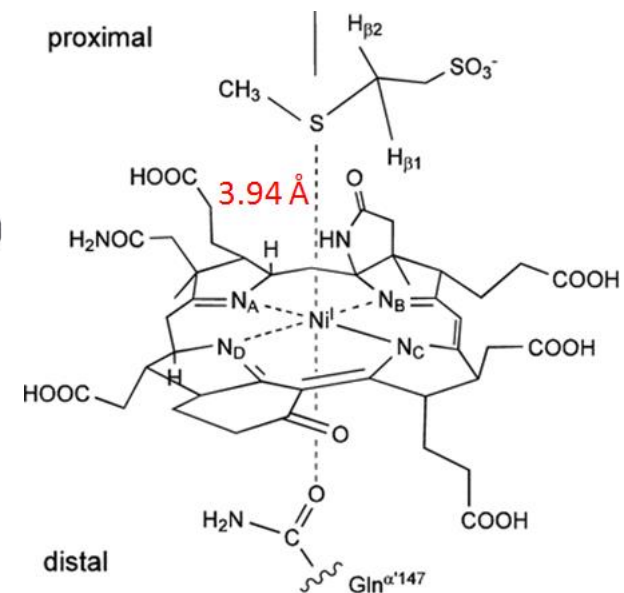
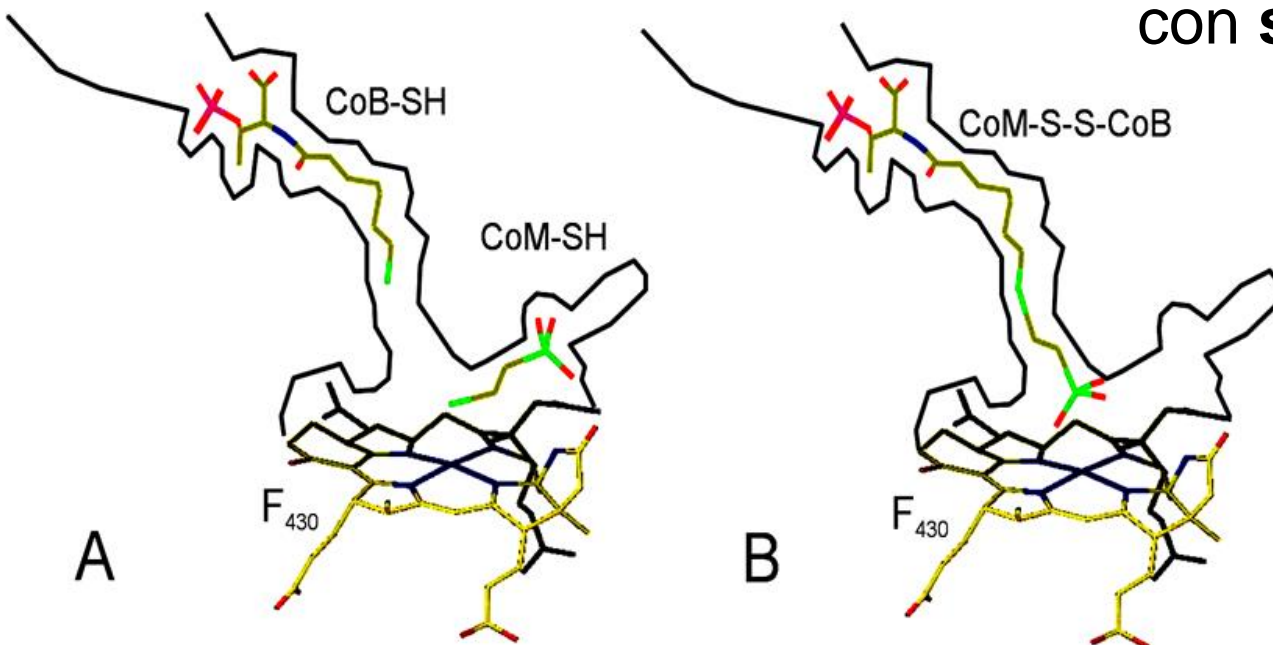


Gli *archei* metanogenici utilizzano H_2 e CO_2 come uniche fonti di energia e di carbonio

Ni(I), d^9 , nel coenzima F-430

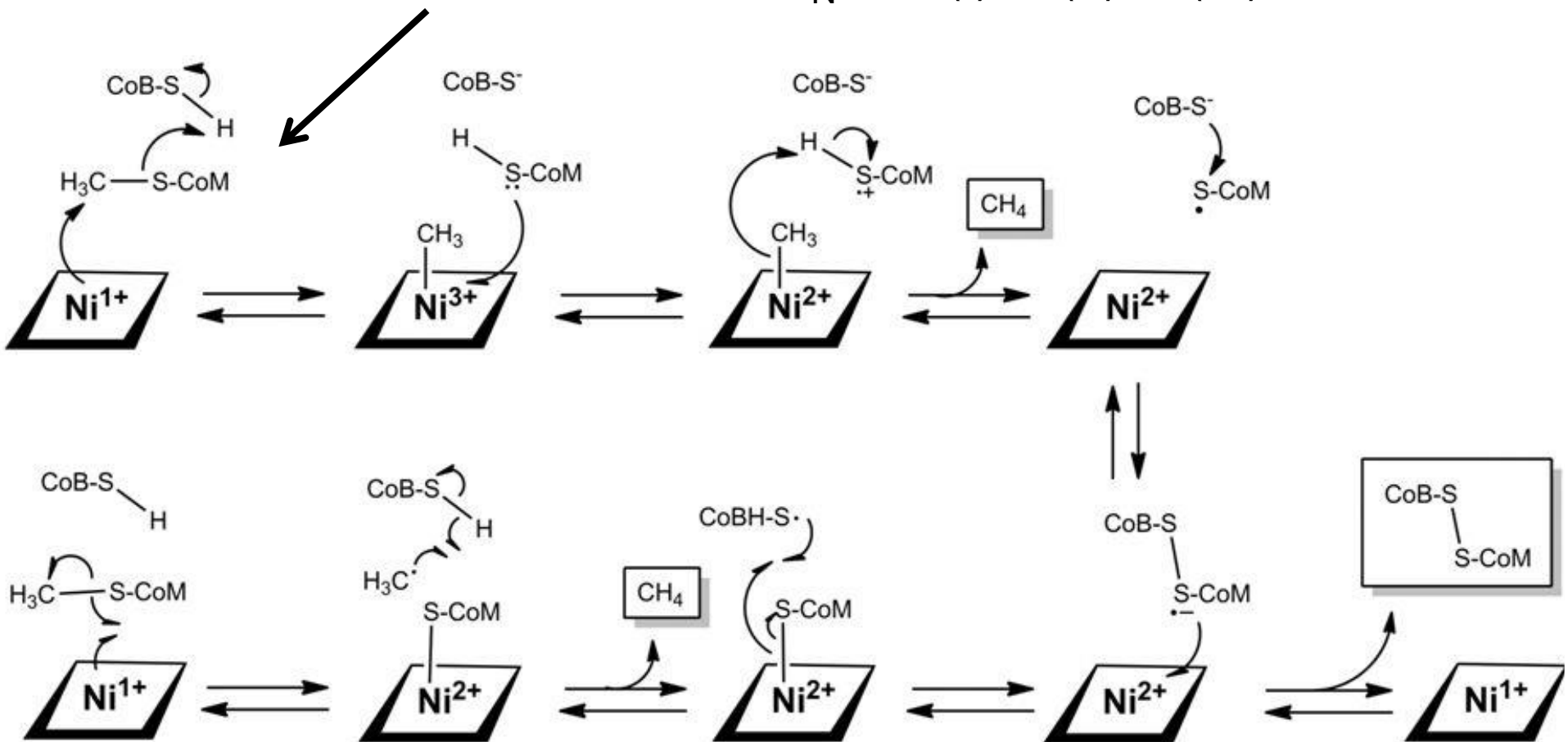


Macrociclo tetrapirrolico
con **solo 5 doppi legami**



glutamina

Meccanismo S_N2 , Ni(I)/Ni(II)/Ni(III)



Meccanismo radicalico, Ni(I)/Ni(II)