Les métaux: des origines aux biocatalyseurs d'aujourd'hui

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PERIODIC TABLE

Atomic Properties of the Elements

NIST
National Institute of Standards and Technology
Technology Administration, U.S. Department of Commerce

Physics Laboratory
physics.nist.gov

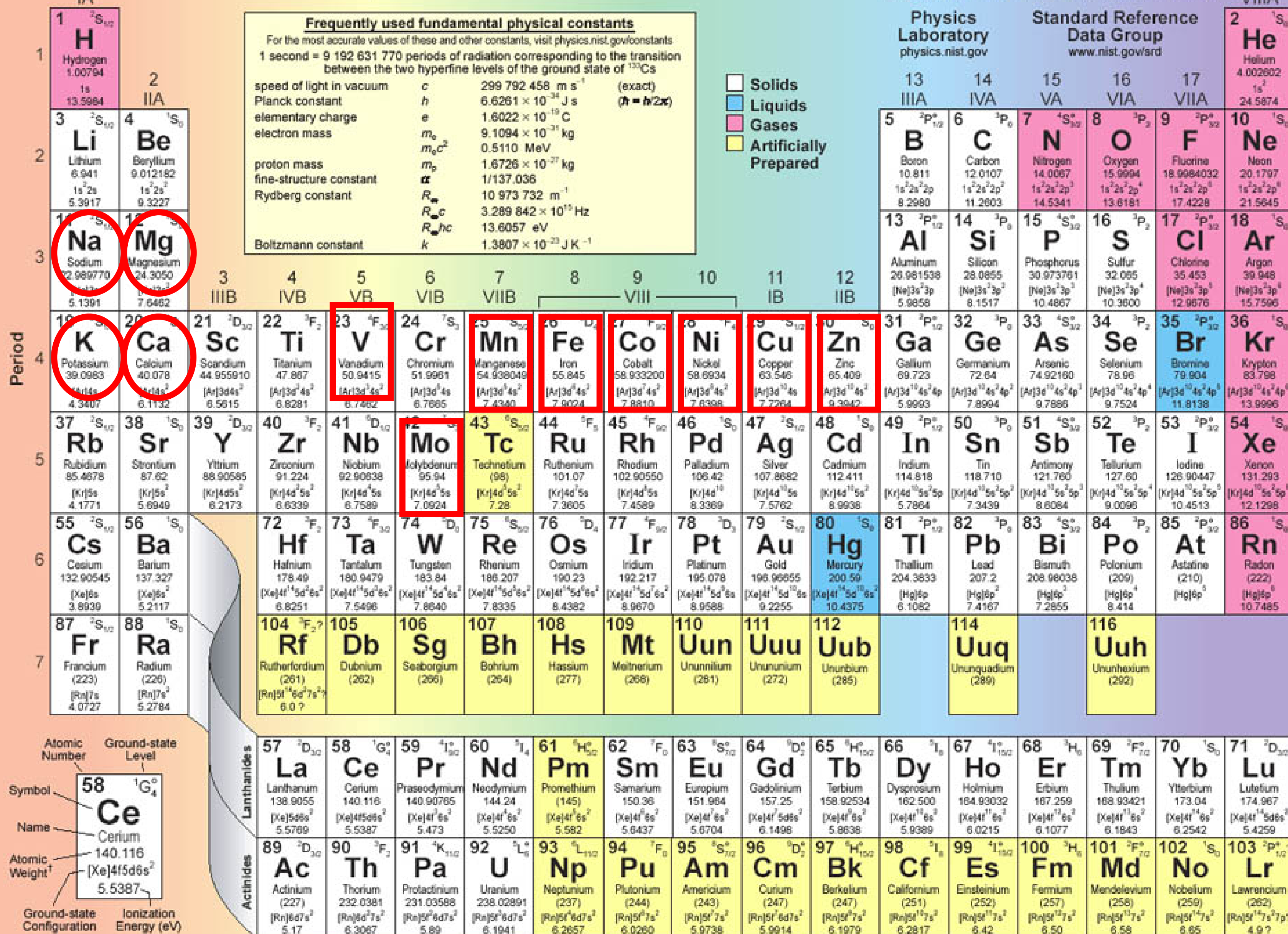
Standard Reference Data Group
www.nist.gov/srd

Frequently used fundamental physical constants

For the most accurate values of these and other constants, visit physics.nist.gov/constants

1 second = 9 192 631 770 periods of radiation corresponding to the transition between the two hyperfine levels of the ground state of ^{133}Cs

speed of light in vacuum	c	299 792 458 m s^{-1}	(exact)
Planck constant	h	6.6261×10^{-34} J s	($\hbar = h/2\pi$)
elementary charge	e	1.6022×10^{-19} C	
electron mass	m_e	9.1094×10^{-31} kg	
	$m_e c^2$	0.5110 MeV	
proton mass	m_p	1.6726×10^{-27} kg	
fine-structure constant	α	1/137.036	
Rydberg constant	R_∞	10 973 732 m^{-1}	
	$R_\infty c$	$3.289 842 \times 10^{15}$ Hz	
	$R_\infty hc$	13.6057 eV	
Boltzmann constant	k	1.3807×10^{-23} J K^{-1}	



†Based upon ^{12}C. () indicates the mass number of the most stable isotope.

For a description of the data, visit physics.nist.gov/data

NIST SP 966 (September 2003)

Abondance des éléments dans l'univers

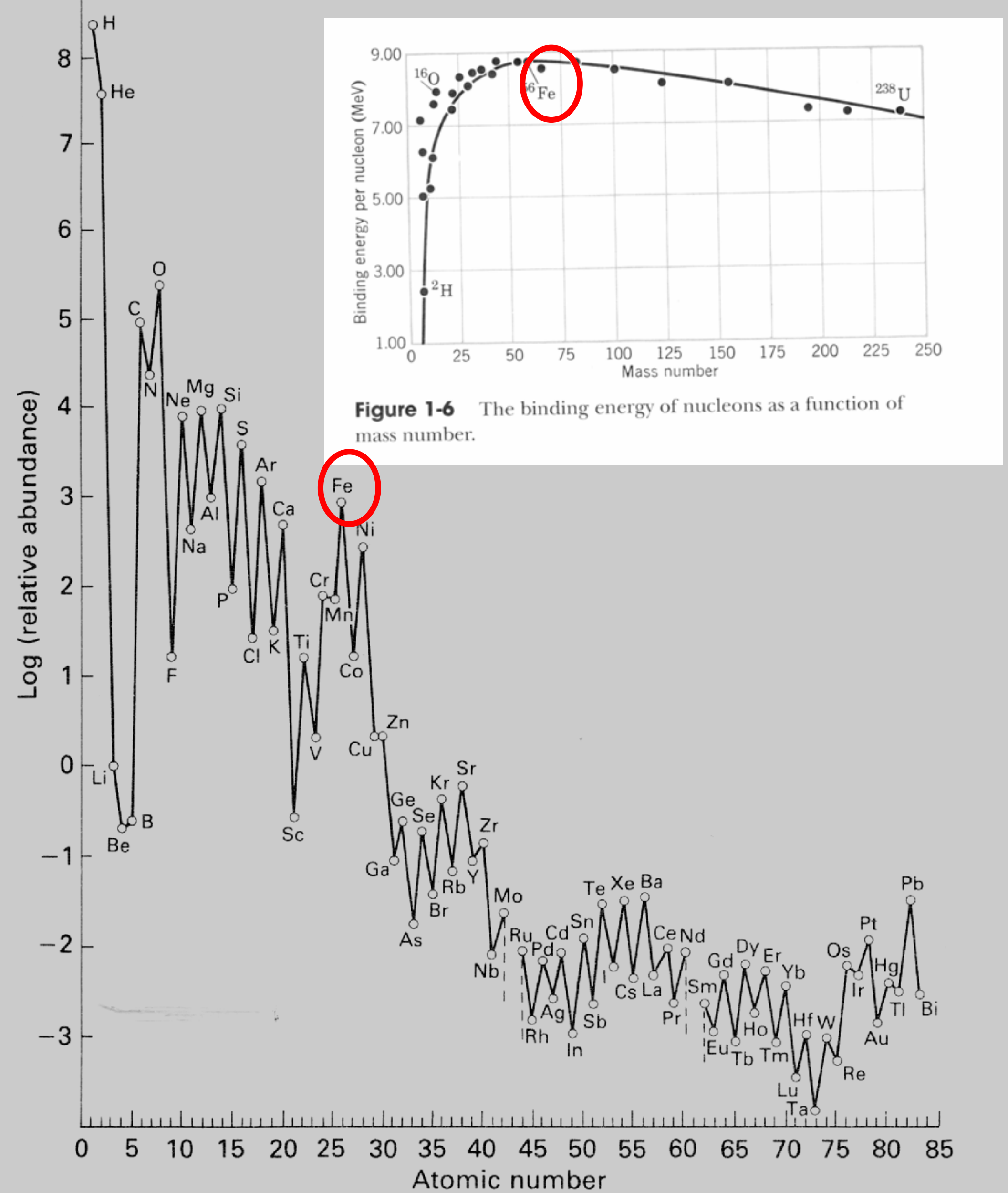
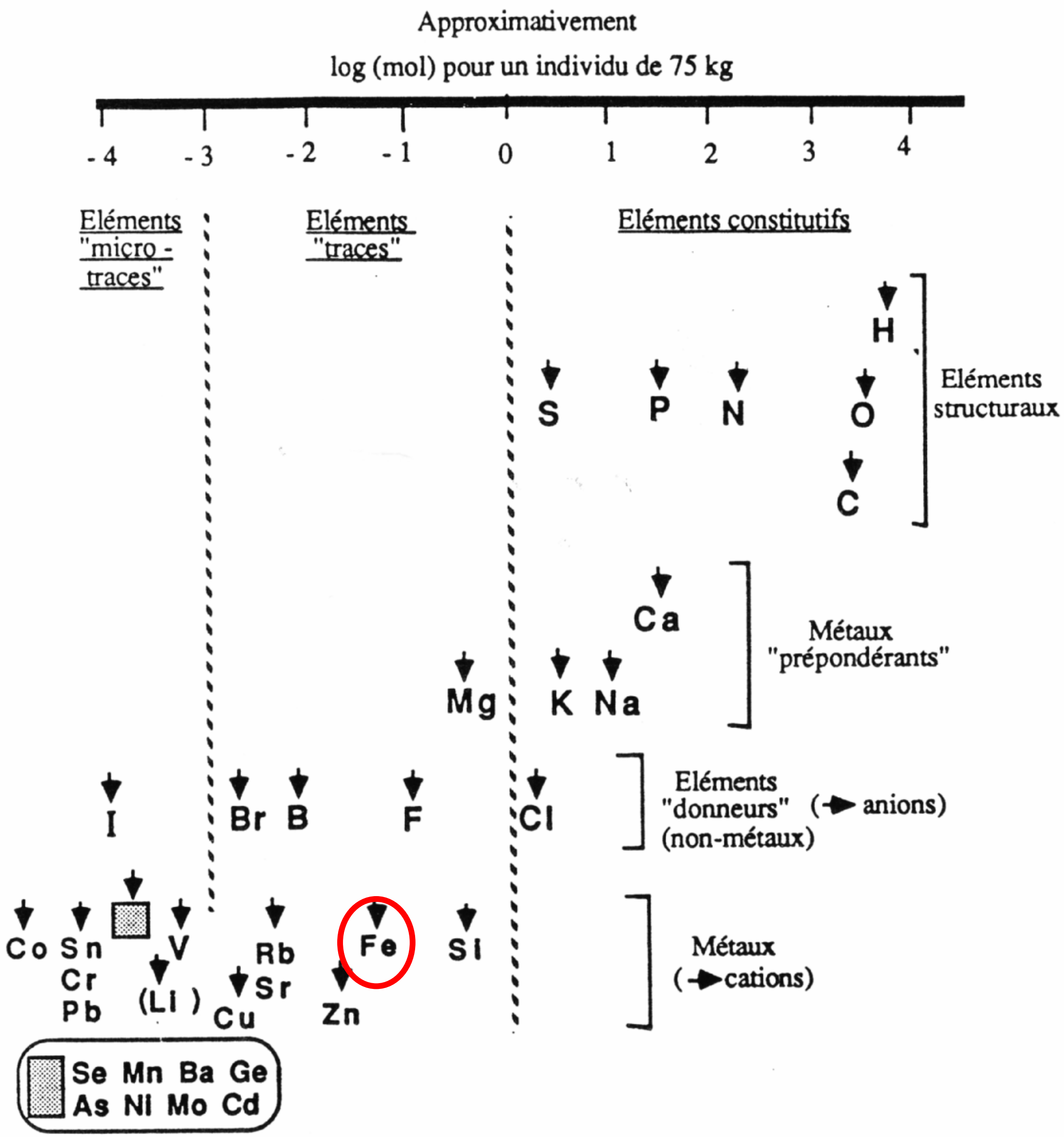


Figure 1-6 The binding energy of nucleons as a function of mass number.

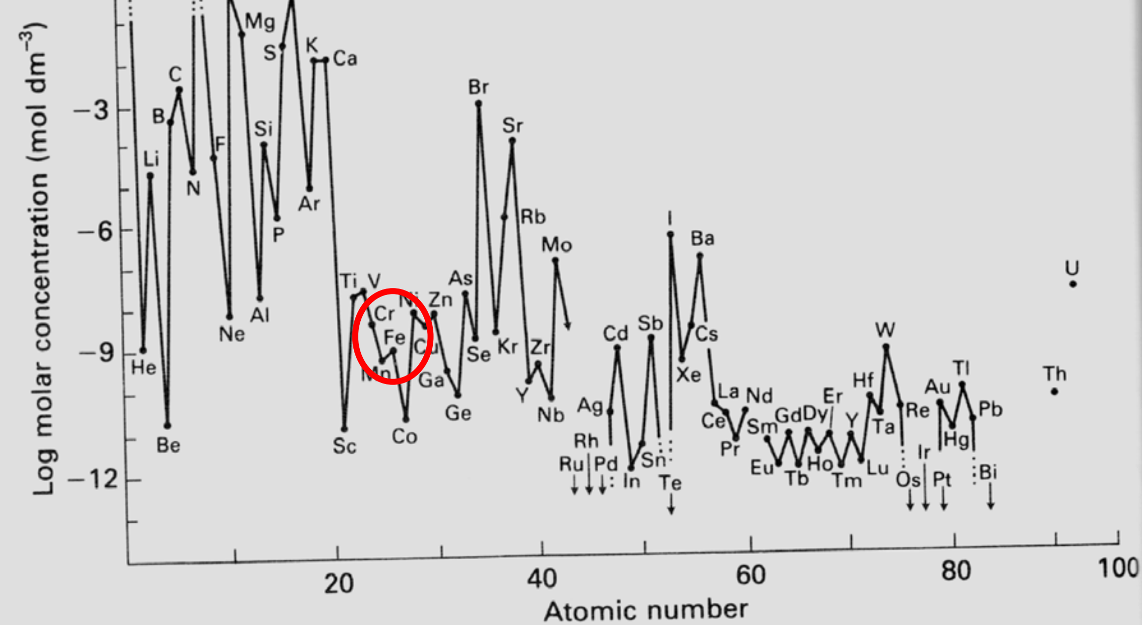
terre

O: 62,6 %
Si: 21,2
Al: 6,5
Fe: 1,9
Ca: 1,9
Na: 2,6
K: 1,4
Mg: 1,8
Autres: 0,1

Composition du corps humain adulte



Abondance des éléments dans l'eau de mer



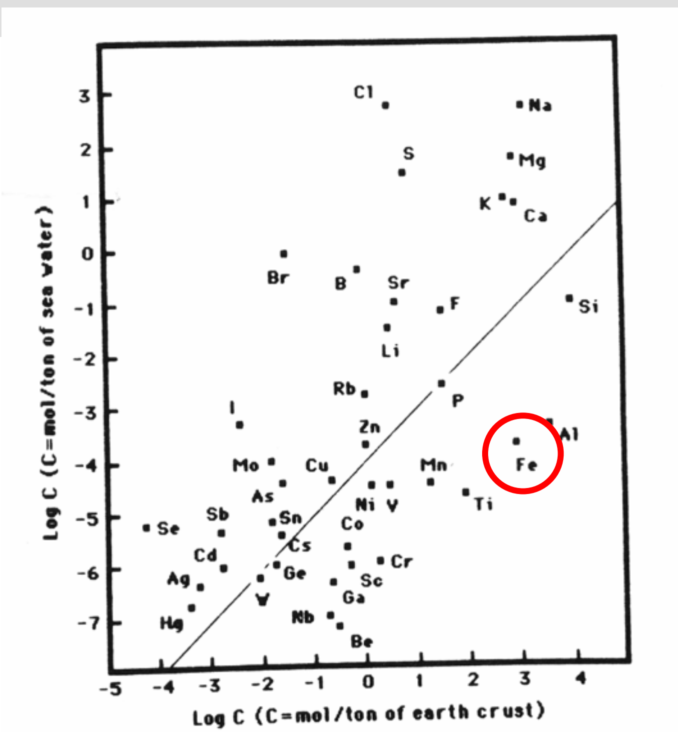
Un problème de solubilité

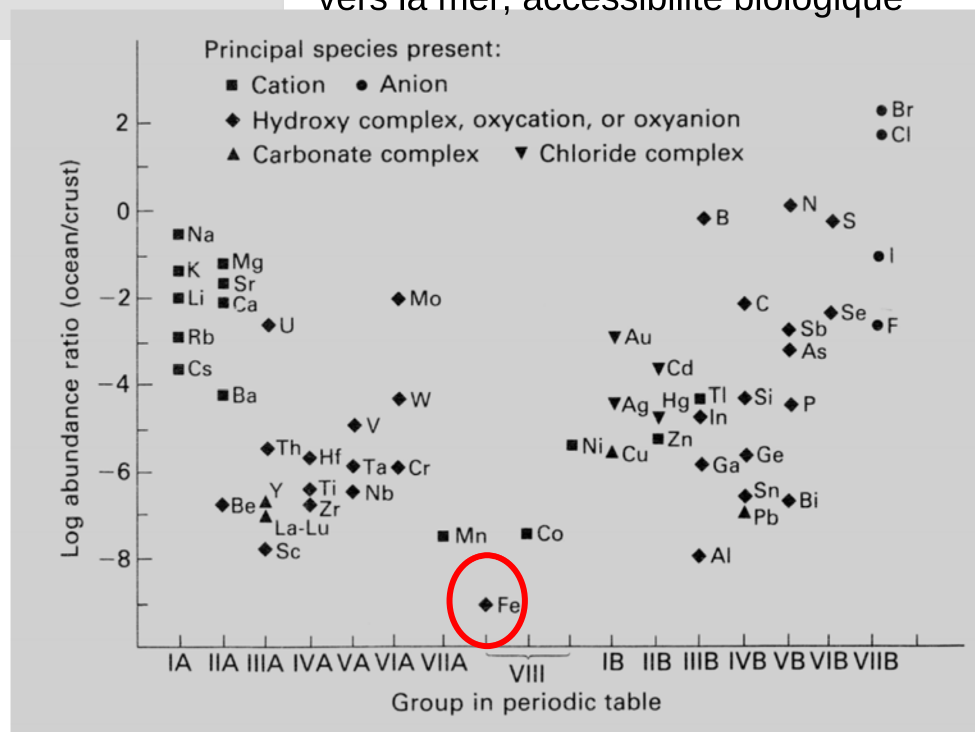
$$Fe^{3+} + 3\ OH^- \rightleftarrows Fe(OH)_3$$

$K_s = 10^{-39}$

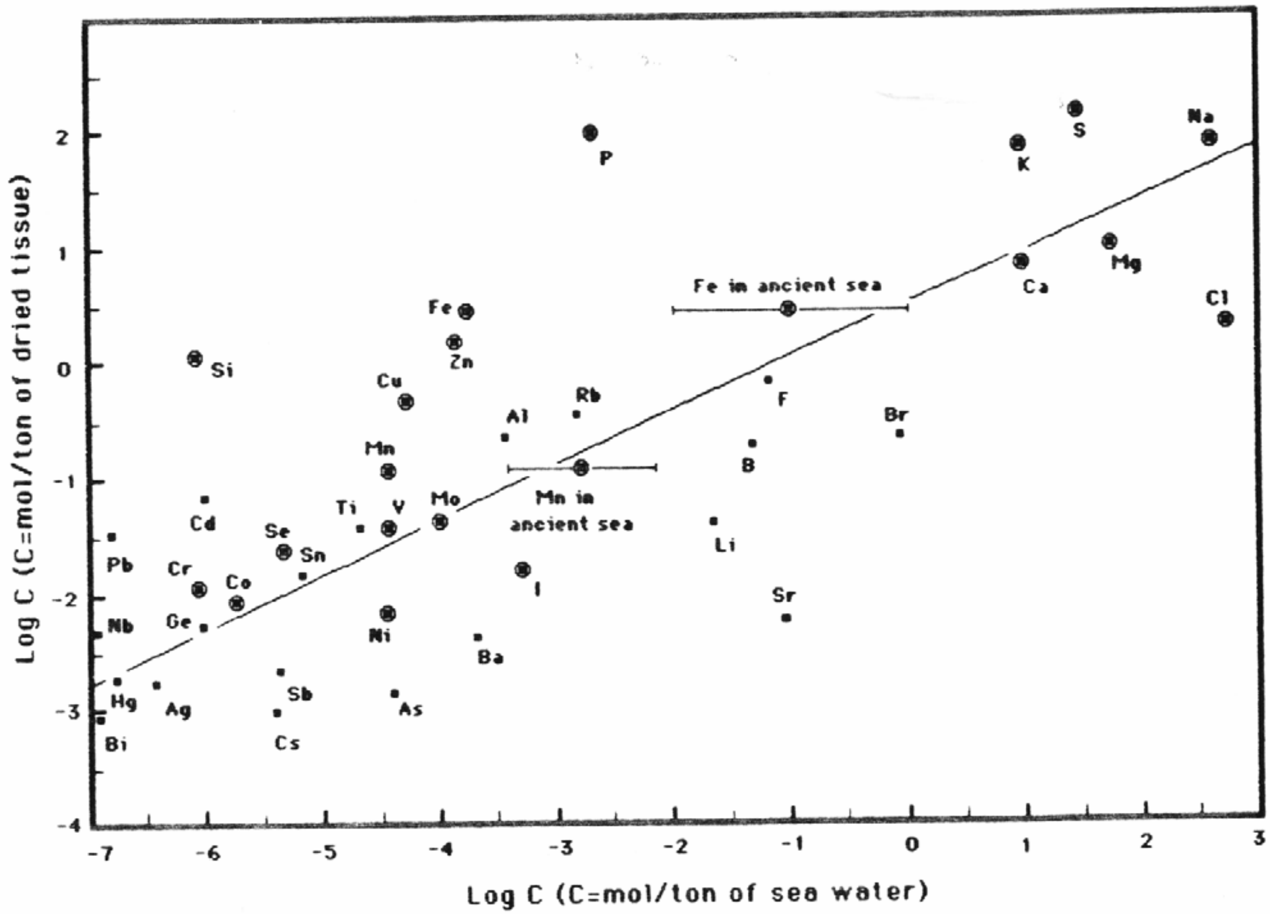
pH 7 $[Fe^{3+}] = 10^{-18}$M

Extractabilité des éléments de la terre vers la mer; accessibilité biologique



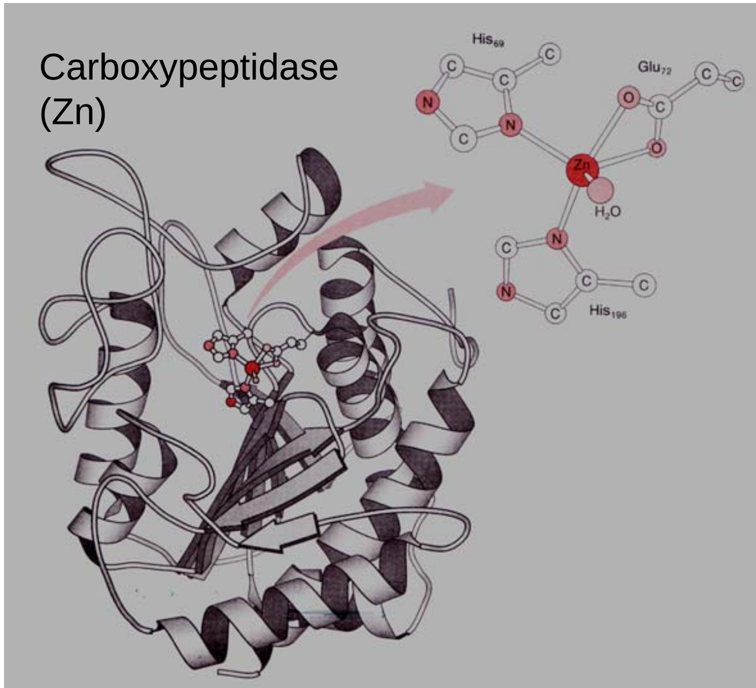


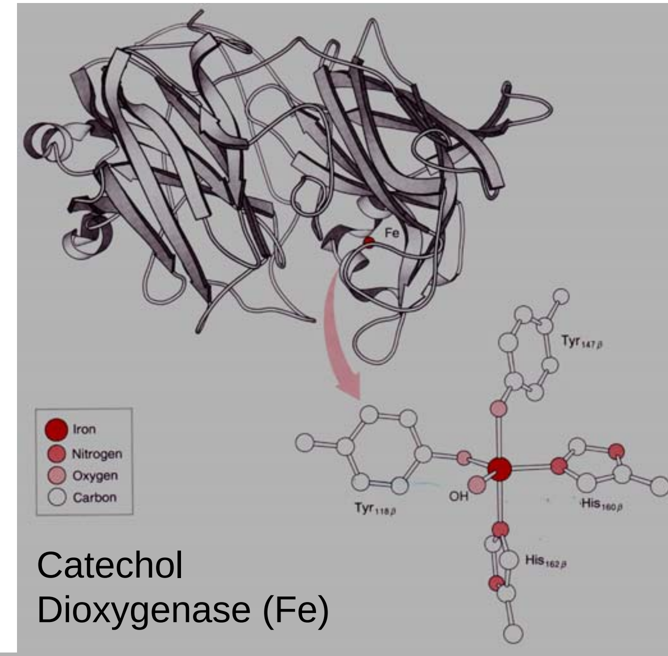
Corrélation: milieu vivant/eau de mer

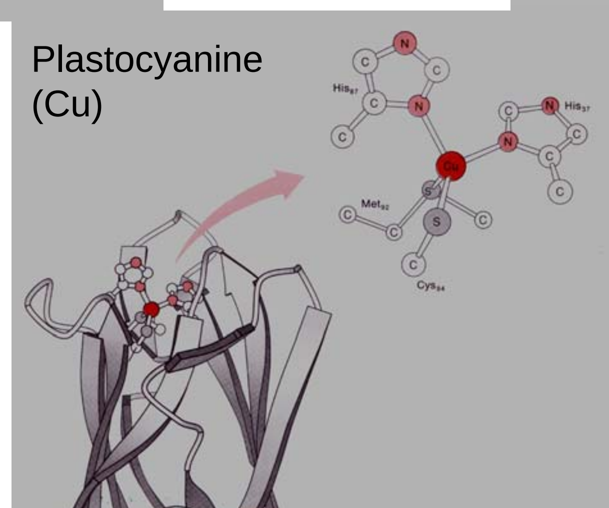


	eau de mer (mM)	plasma sanguin (mM)
Na^+	470	140
Mg^{2+}	50	2
Ca^{2+}	10	3
K^+	10	10
Cl^-	550	100
HPO_4^{2-}	0,001	1
SO_4^{2-}	28	1
Fe^{n+}	0.0001	0.02
Zn^{2+}	0.0001	0.02
Cu^{2+}	0.001	0.015
Co^{2+}	$10^{-5,5}$	0,002
Ni^{2+}	10^{-6}	0

Métalloprotéines et sites métalliques





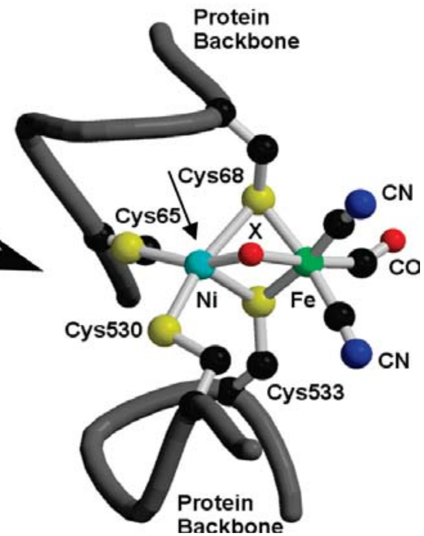


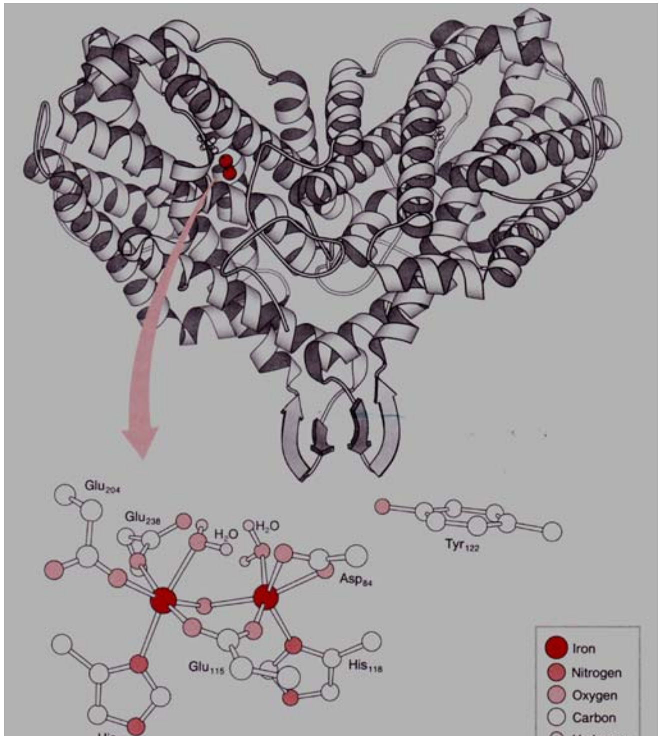
Bond Distances (Å)

	Cu(II)	Cu(I), pH = 7.0	Cu(I), pH = 3.8
Cu–S(Cys_{84})	2.13	2.17	2.13
Cu-S(Met_{92})	2.90	2.87	2.51
Cu–N(His_{37})	2.04	2.13	2.12
Cu–N(His_{87})	2.10	2.39	>4

Centres Binucléaires

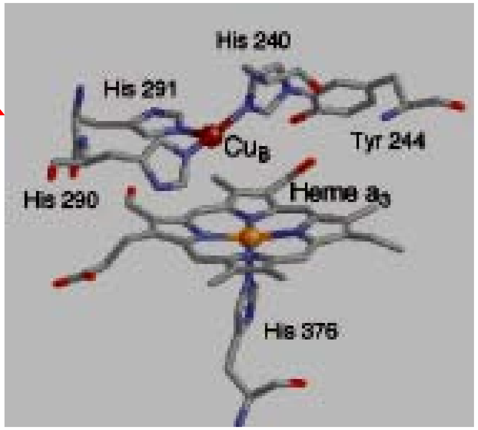
hydrogenase (Ni-Fe)

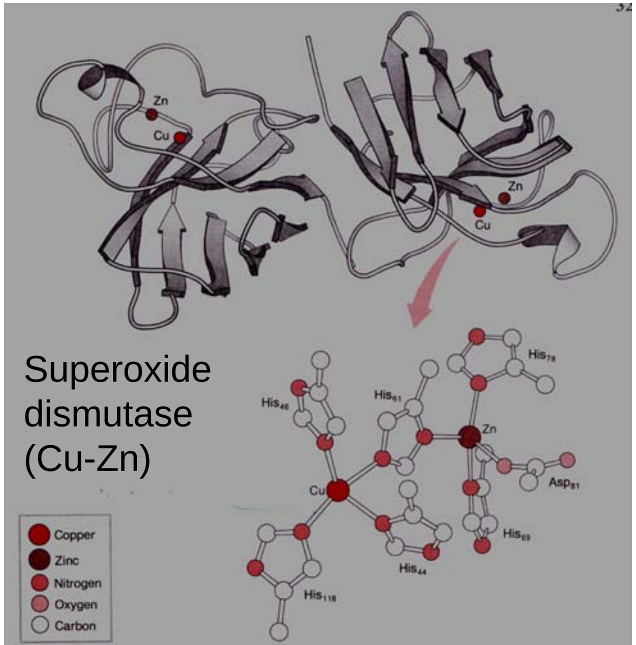




Ribonucleotide reductase (Fe_2)

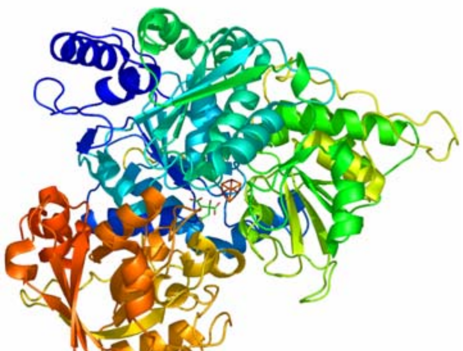
Cytochrome oxydase (Cu-Fe)



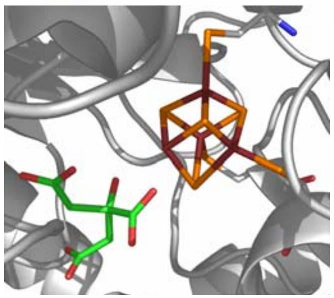


Superoxide dismutase (Cu-Zn)

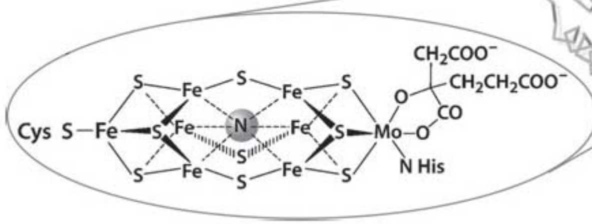
Clusters

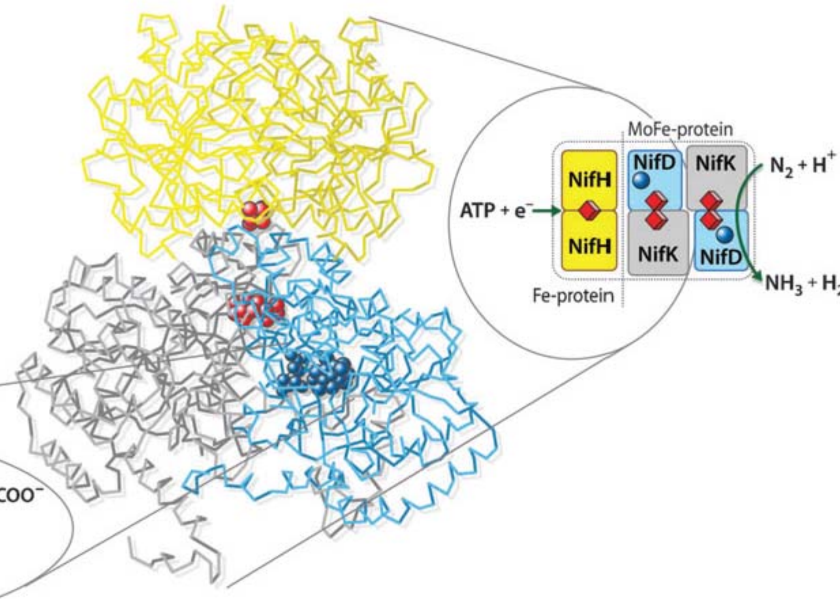


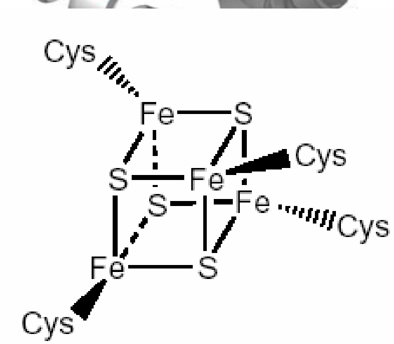
aconitase

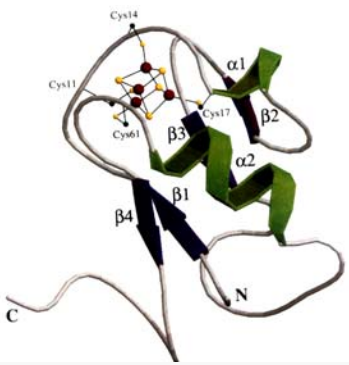


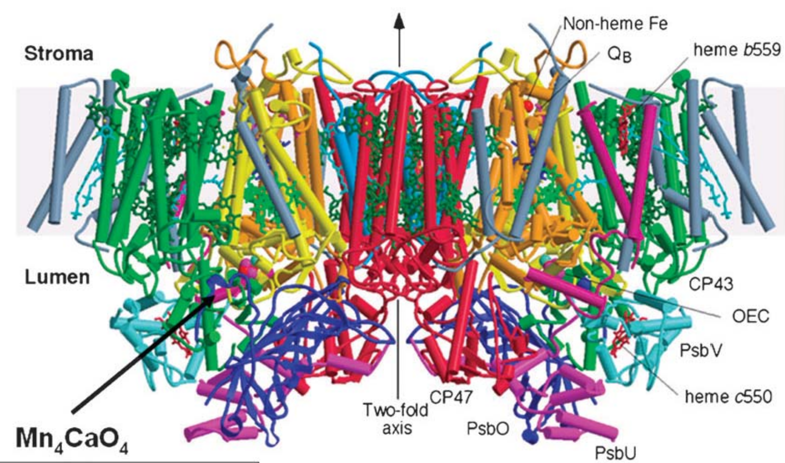
Nitrogenase

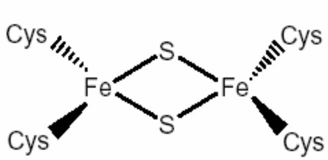




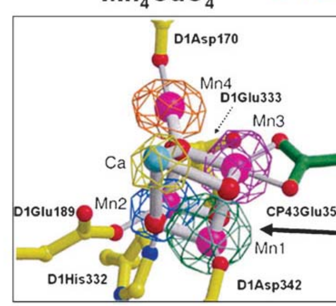








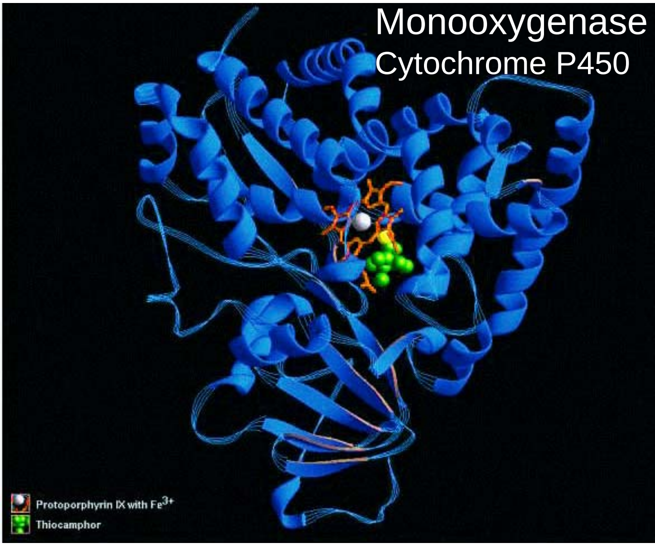
2Fe–2S

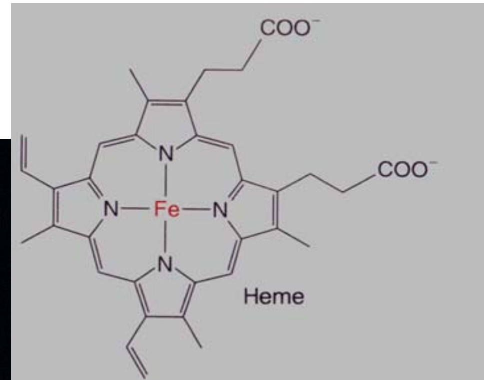


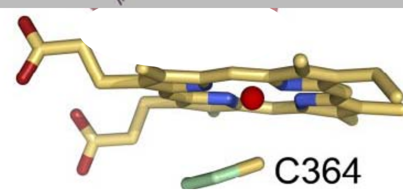
Photosystem Two

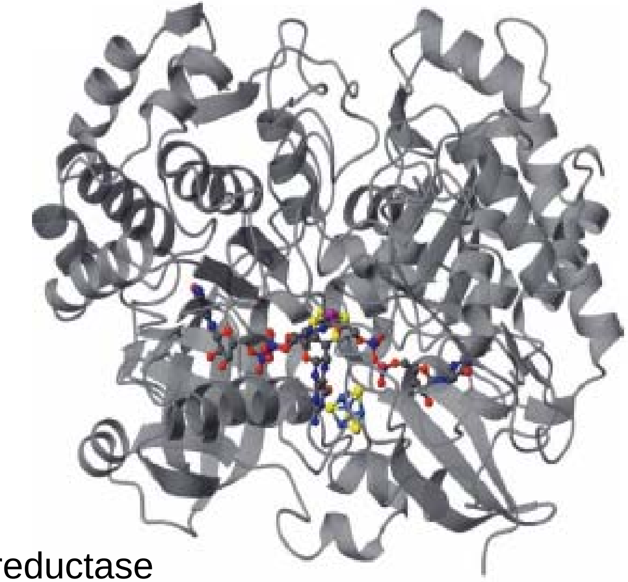
water splitting site

Métallocofacteurs

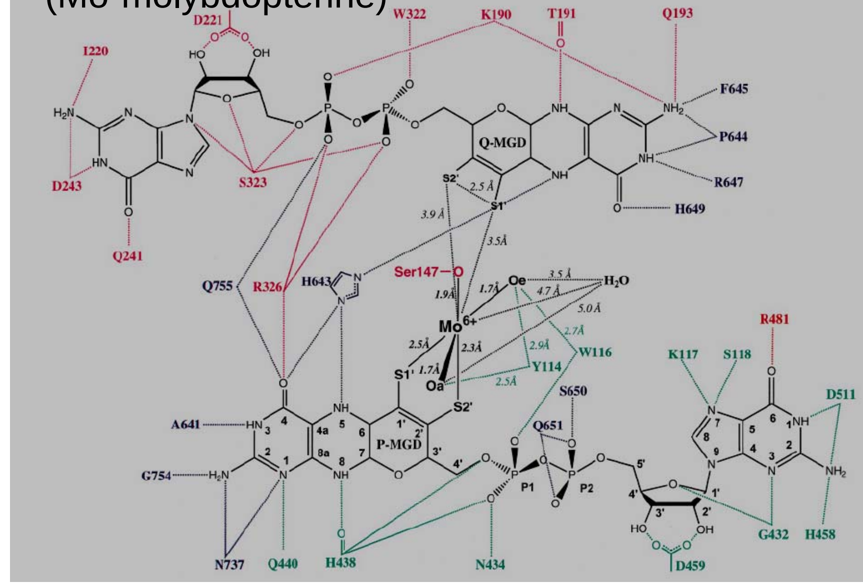




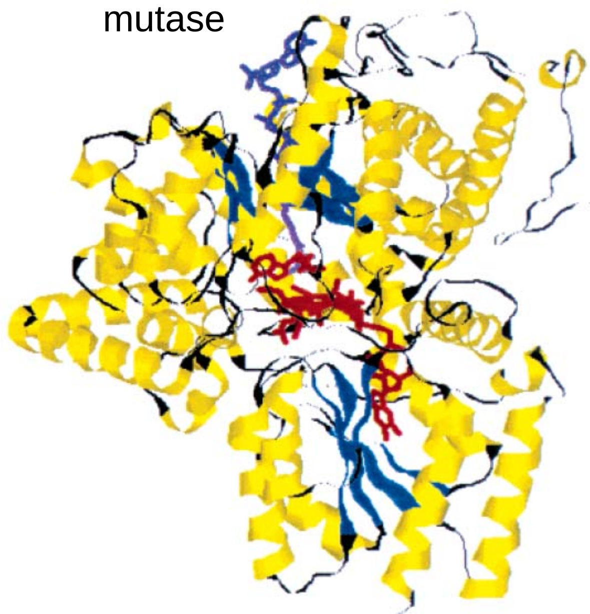


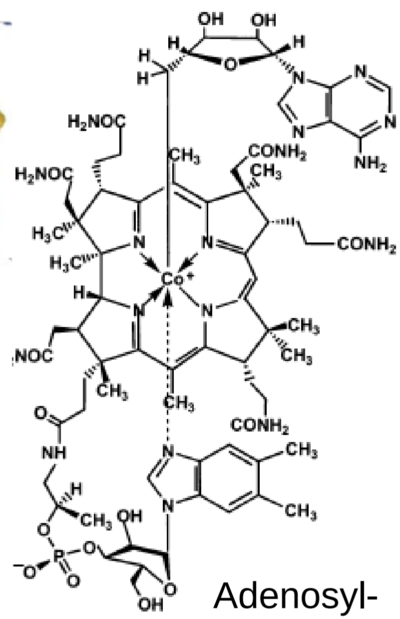


Nitrate reductase
(Mo-molybdopterine)



Methylmalonyl-CoA
mutase





Adenosyl-
cobalamine

Fer (Fe), Cuivre (Cu)

$Me^{(n+1)+}/Me^{n+}$ des ions à différents degrés d'oxydation
Réactions rédox: transfert d'électrons, transport et activation de l'oxygène (monooxygénases, dioxygénases, oxydases….), activation de peroxydes (peroxydases, catalase, cyclooxygénase,…), etc…
Réactions non rédox: déhydratases (Fe)
Régulation de l'expression des gènes: stress oxydant,…

Zinc (Zn)

Zn^{2+} un acide de Lewis
Réactions non rédox: hydrolyse (protéases, peptidases, phosphatases,…..)
Régulation de l'expression des gènes: doigts de Zn,…

Manganèse (Mn): photosystème
Nickel (Ni): hydrogénases, uréase
Cobalt (Co): vitamine B12, méthionine synthase
Molybdène (Mo): nitrogénase, formate déshydrogénase, réductases
Vanadium (V): péroxydases

Activation de petites molécules

H_2O

Zn, Ni (hydrolyse), Mn (photosystème),…

O_2

Fe, Cu (mono-,di-oxygénases),

N_2

Mo (nitrogénase)

H_2

Ni (hydrogénase)

CO, CO_2

Ni (CO dehydrogenase)

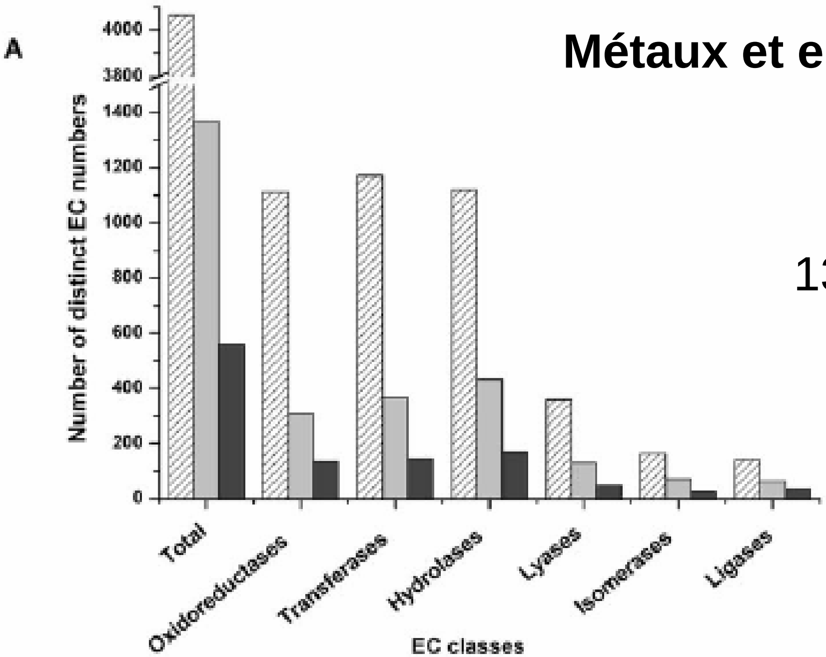
Polarisation de liaisons

Zn, Fe, Ca

Transferts d’électrons

Cu, Fe

Métaux et enzymes



>4000 EC

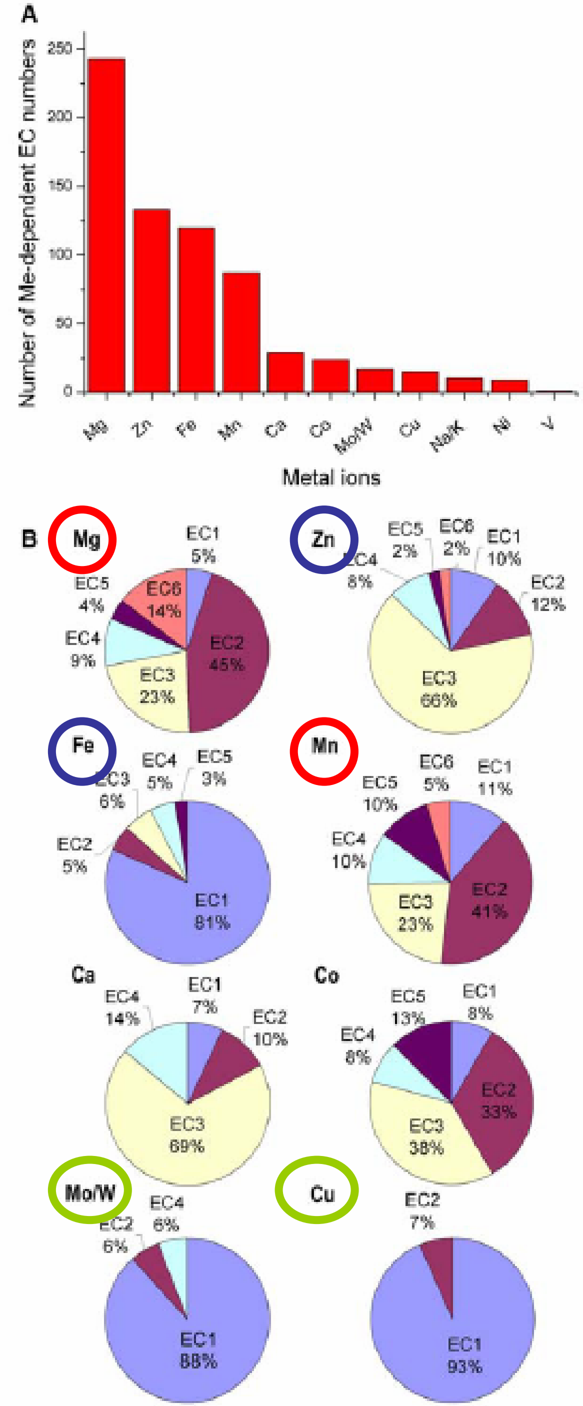
↓

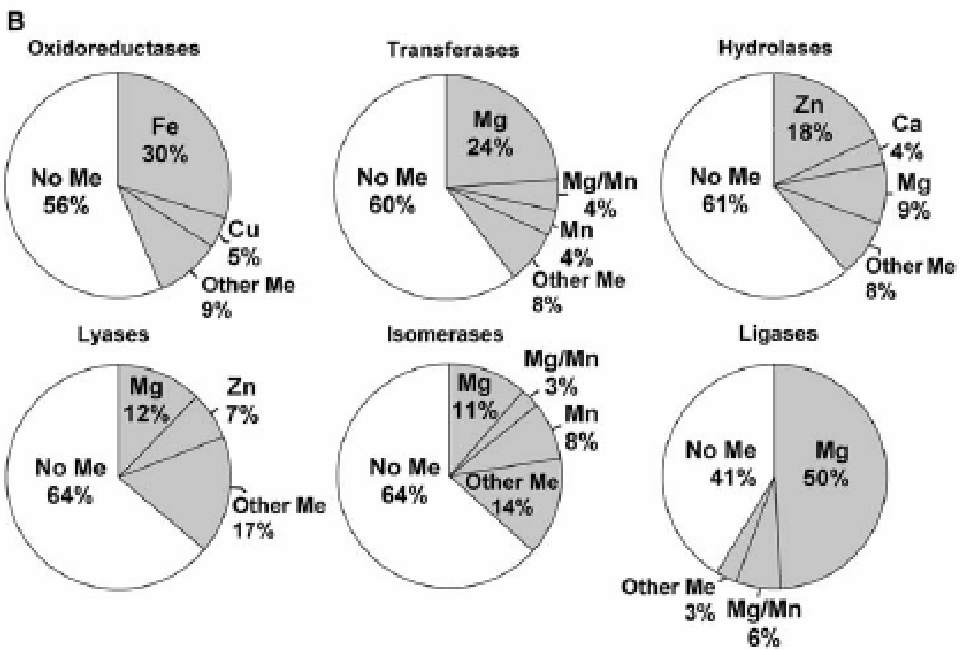
1371 (structure)

↓

558 (métal)

13 métaux différents





I. Bertini, *JBIC* 2008 13 1205

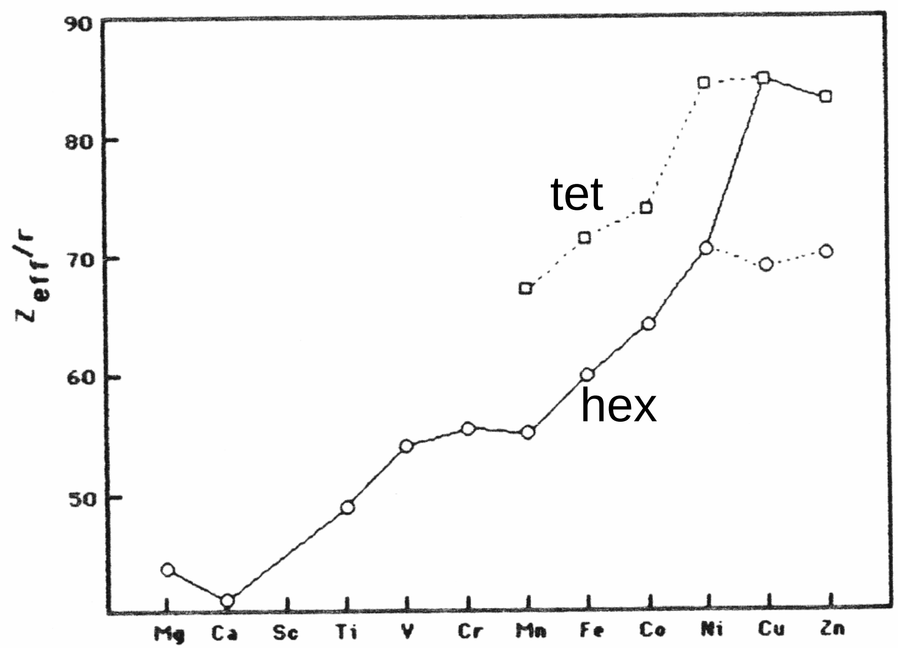
Quel métal pour quelle fonction ?

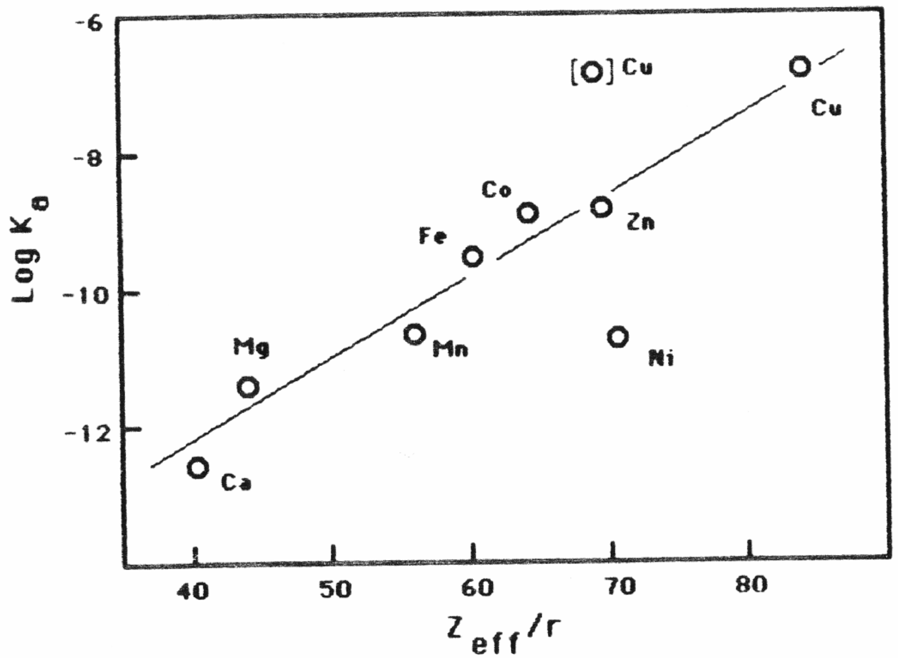
(1) Le critère d'abondance

(2) Le critère d'éfficacité chimique

Exemple 1: Zn^{2+}, le meilleur acide de Lewis

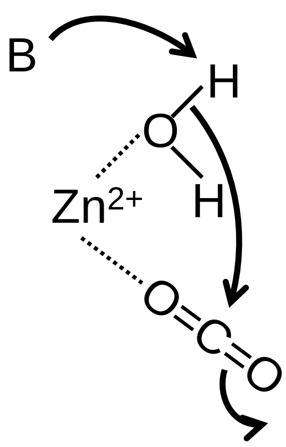
$$H_2O + M(H_2O)_q \rightleftharpoons H_3O^+ + M(OH^-)(H_2O)_{q-1}$$





Zeff charge électrique effective
r rayon ionique effectif

Co, Fe, Cu, Mn ??



Exemple 2: $Fe^{3+/2+}$, le meilleur couple rédox

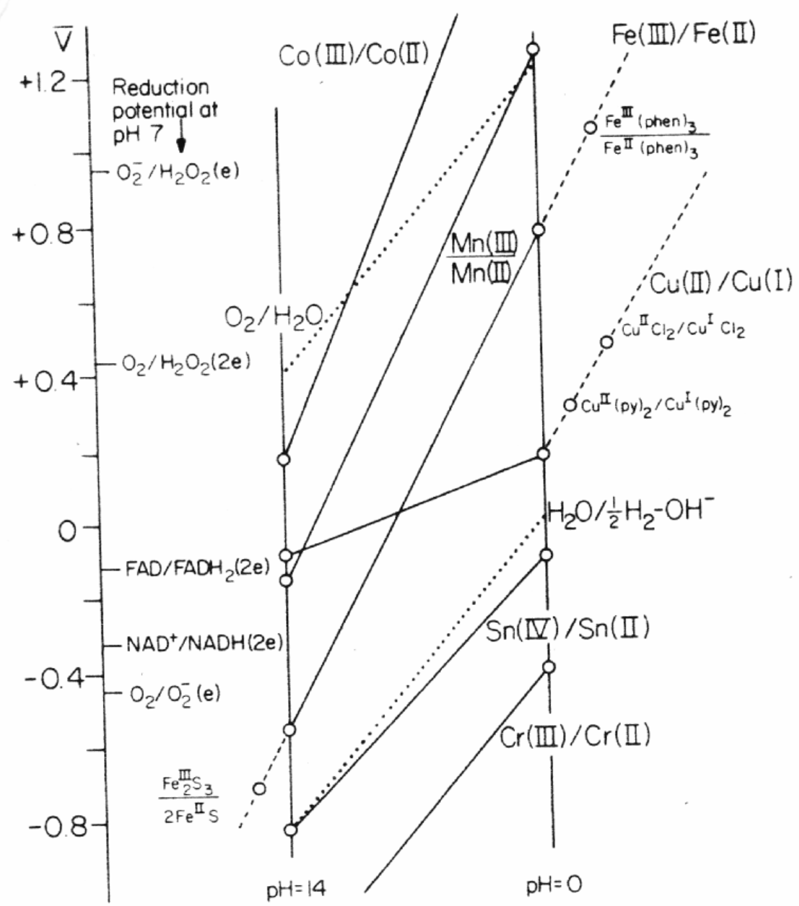


Figure 1. The reduction potentials of some important metal ions and other redox systems. O represents the reduction potential of a metal ion in an aqueous medium either at pH = 0 or at pH = 14, or the reduction potential of a simple metal complex. See the text for a more detailed explanation.

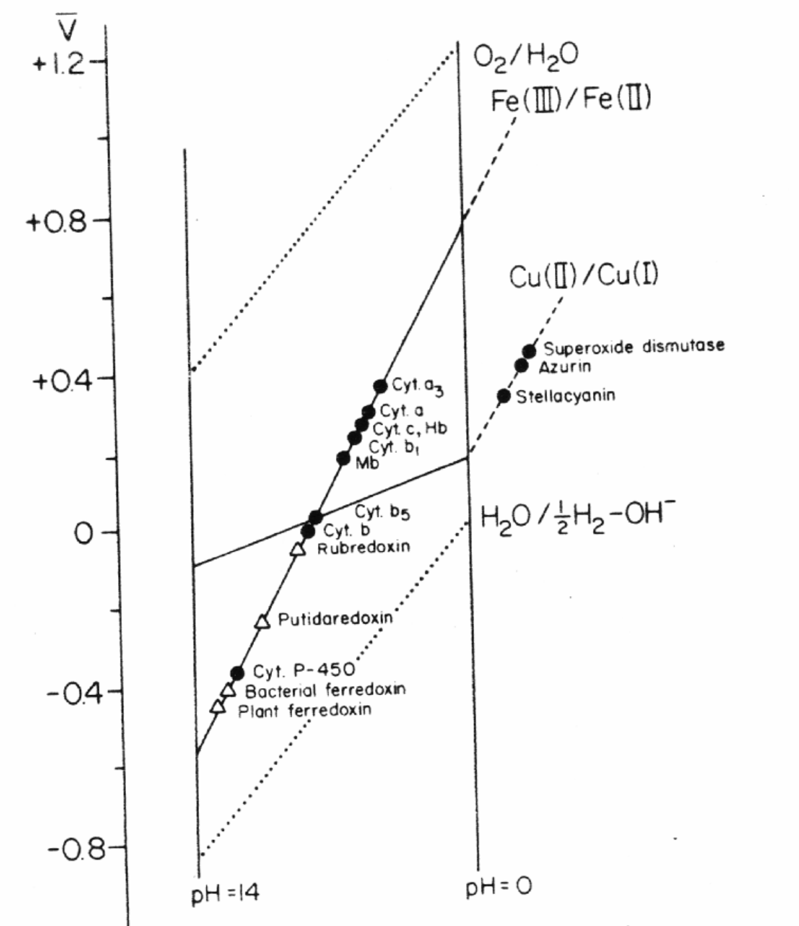


Figure 2. The reduction potentials of iron- and copper-enzymes and proteins at pH 7. The point represents merely the reduction potential value; the position on the pH axis has no meaning. See Figure 1 for the explanation of the dotted lines and the straight solid or broken lines.

Exemple 3: Fe^{2+} et Cu^{+} pour le transport d'O_2

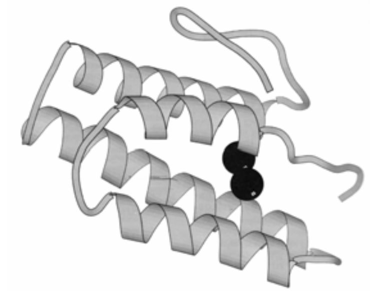
Hemocyanine

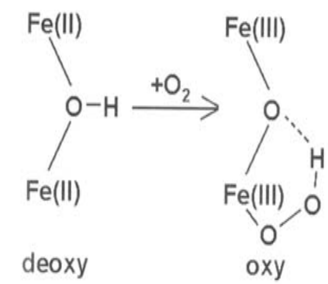
$$M^{n+} + O_2 \rightleftharpoons [M^{n+1+}O_2^{-}]:\ \Delta G_a$$

$$2M^{n+} + O_2 \rightleftharpoons [M^{n+1+}O_2^{2-}M^{n+1+}]:\ \Delta G_b$$

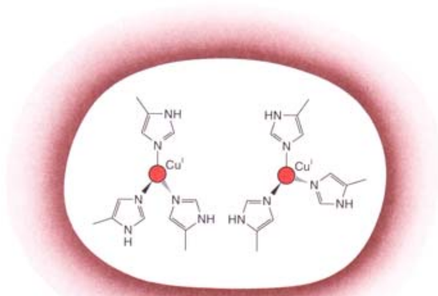
Rough Estimates of ΔG_a (kcal/mole) and ΔG_b (kcal/mole)

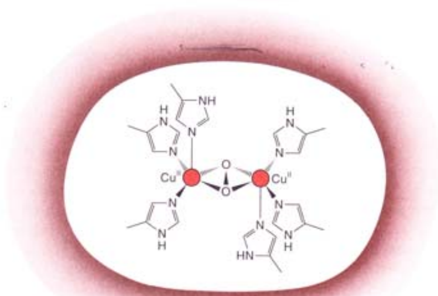
M^{n+}	ΔG_a	ΔG_b
Ti(II)aq	+1.7	−29.2
Ti(III) (in 5 *F* H_3PO_4)	+6.9	−19.0
V(II)aq	+4.4	−24.0
Cr(II)aq	+0.9	−31.0
Mn(II) (in 8 *F* H_2SO_4)	+47.7	+62.6
Mn(II)/CN^-	+5.2	−22.4
Fe(II) (pH $\lesssim$ 2)	+28.0	+23.2
Fe(II) (pH ~ 6)	+10.0	−11.8
$Fe(OH)_2$	−2.6	−38.0
Fe(II)/CN^-	+18.6	−4.4
Co(II)aq	+52.7	+72.6
Co(II)NH_3	+12.6	−7.6
Co(II)/CN^-	−9.0	−50.8
Cu(I)/aq	+13.8	−4.8
Cu(I)/NH_3	+10.1	−12.6

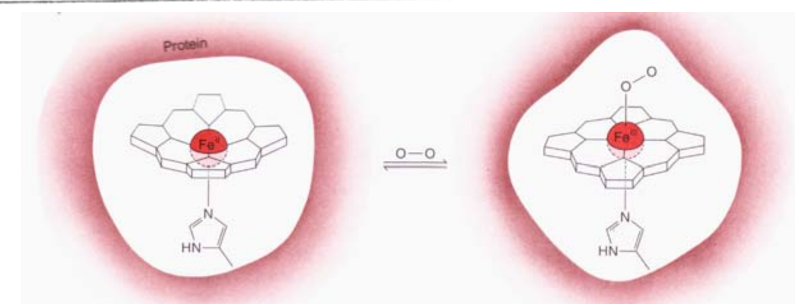




hemerythrine


(a) Deoxyhemocyanin

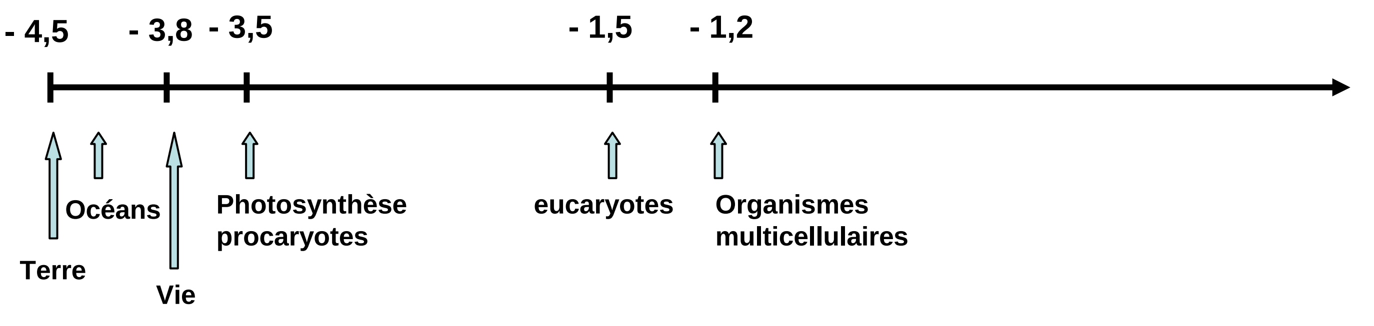

(b) Oxyhemocyanin



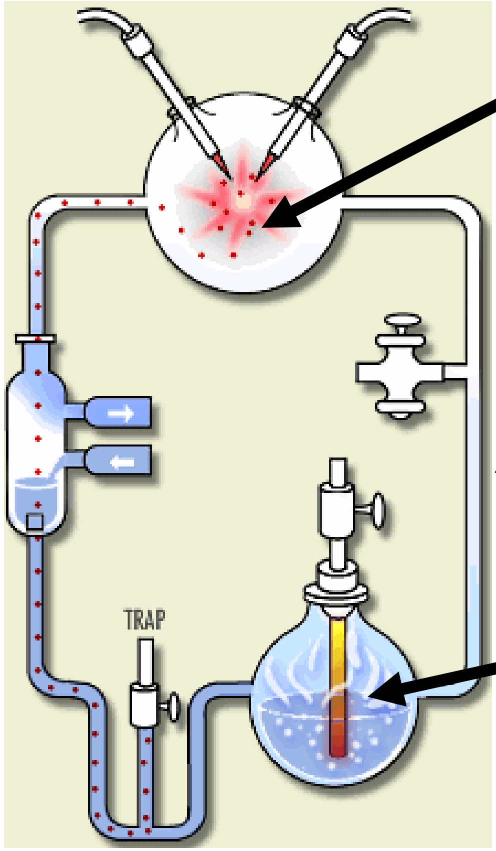
Hemoglobine
myoglobine

Les métaux à l’origine de la vie ?

- Contre cations: Na^+, K^+, Ca^{2+}, Mg^{2+}
- Activation de petites molécules (H_2O, O_2, N_2, CO_2, H_2…): Fe^{2+}, Zn^{2+}, Mn^{2+}, Cu^{2+}, Ni^{2+}



Fondement de la chimie prébiotique
L'expérience de Miller (1953)



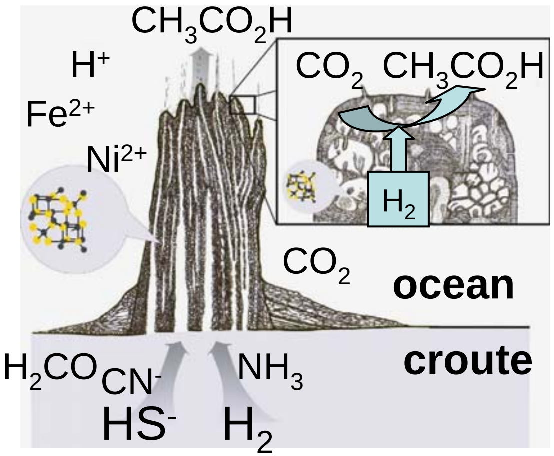
« Atmosphère irradiée »
H_2O, CH_4
NH_3, H_2
…

« Océan chaud »

Acides,
Acides aminés,
Sucres,…

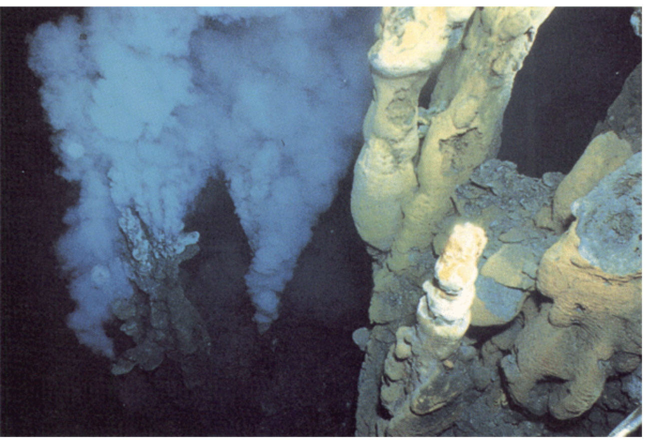
Stanley Miller
(1930-2007)

⇨ Origine hétérotrophe de la vie

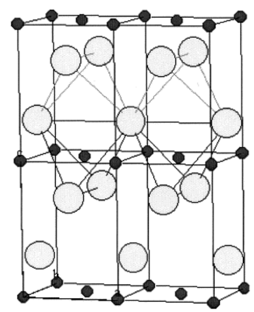


Origine autotrophe de la vie ?

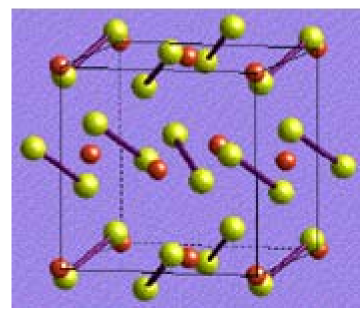
- Eau liquide
- Absence d'O_2
- Atmosphère « oxydante »: CO_2, CO, N_2,..
- **Fe**, Ni et soufre: pyrite FeS_2, greigite (FeNi)S, mackinawite,…Catalyse hétérogène
- Hyperthermophile ? (source hydrothermale)



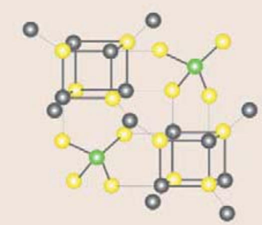
mackinawite

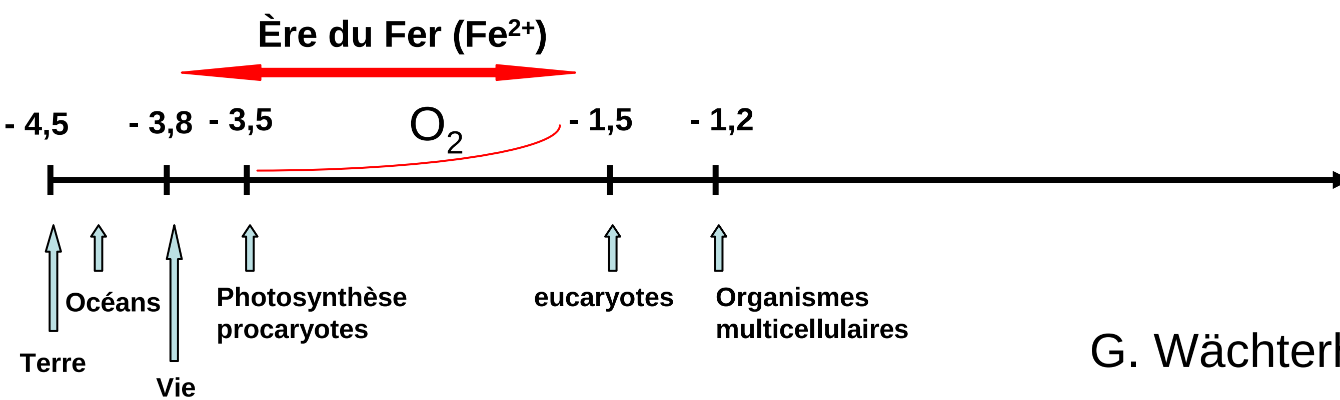


pyrite



greigite





G. Wächterhäuser

Réactions chimiques

Fe(Ni)-sulfures: une source de pouvoir réducteur et un catalyseur

$FeS + H_2S \longrightarrow FeS_2 + H_2\ (2H^+ + 2e^-)$ $\Delta G° = -9.2$ kcal/mol (Nature 1990)

CO_2/CO: une source de carbone; H_2S: une source de soufre

Réductions

$4H_2S + 3FeS + CO_2 \longrightarrow CH_3SH + 3FeS_2 + 2H_2O$ (Orig. Life Evol. Biosph. 1996)

$3H_2S + 3FeS + N_2 \longrightarrow 3FeS_2 + 2NH_3$ (Angew. Chem. 2003)

Formation de liaisons C-C

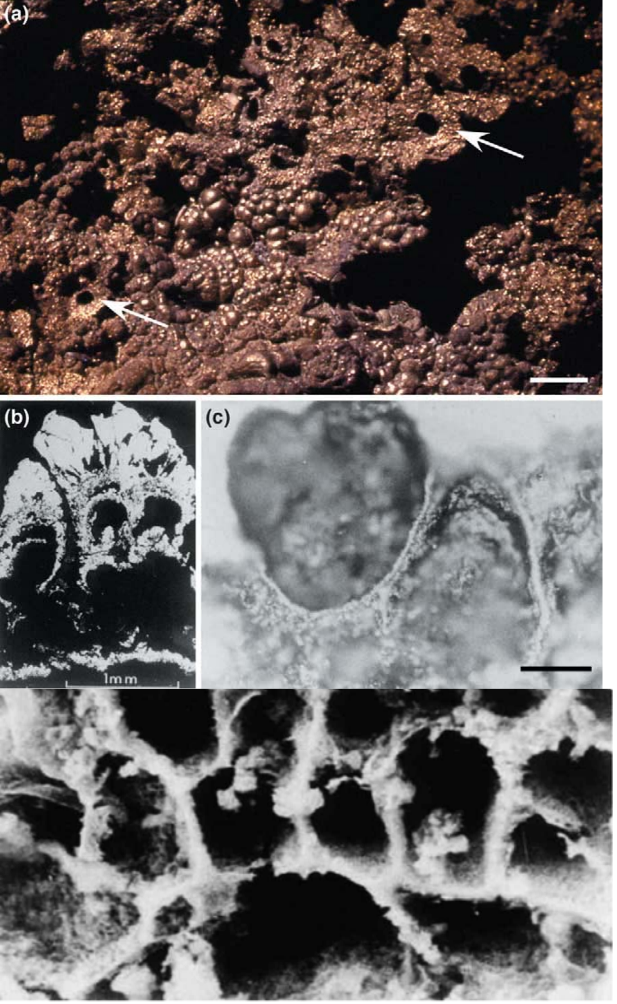
Acide acétique /thioester $CH_3SH + H_2O + CO \longrightarrow CH_3CO\text{-}OH + H_2S$

$CH_3CO\text{-}OH + CH_3SH \longrightarrow CH_3CO\text{-}SCH_3$ (Science 1997)

Acides aminés $CH_3SNa + Na_2S + KCN + CO \xrightarrow{\text{Fe(Ni) sulfates}} R\text{-}CH(NH_2)COOH$ (Science 2006)

Pyruvate $2FeS + 2H_2S + 3CO \longrightarrow CH_3\text{-}CO\text{-}COOH + 2FeS_2$ (Science 2000)

Peptide amino acid $\xrightarrow[\text{CO}]{\text{Fe(Ni)S}}$ dipeptide (Science 1998)



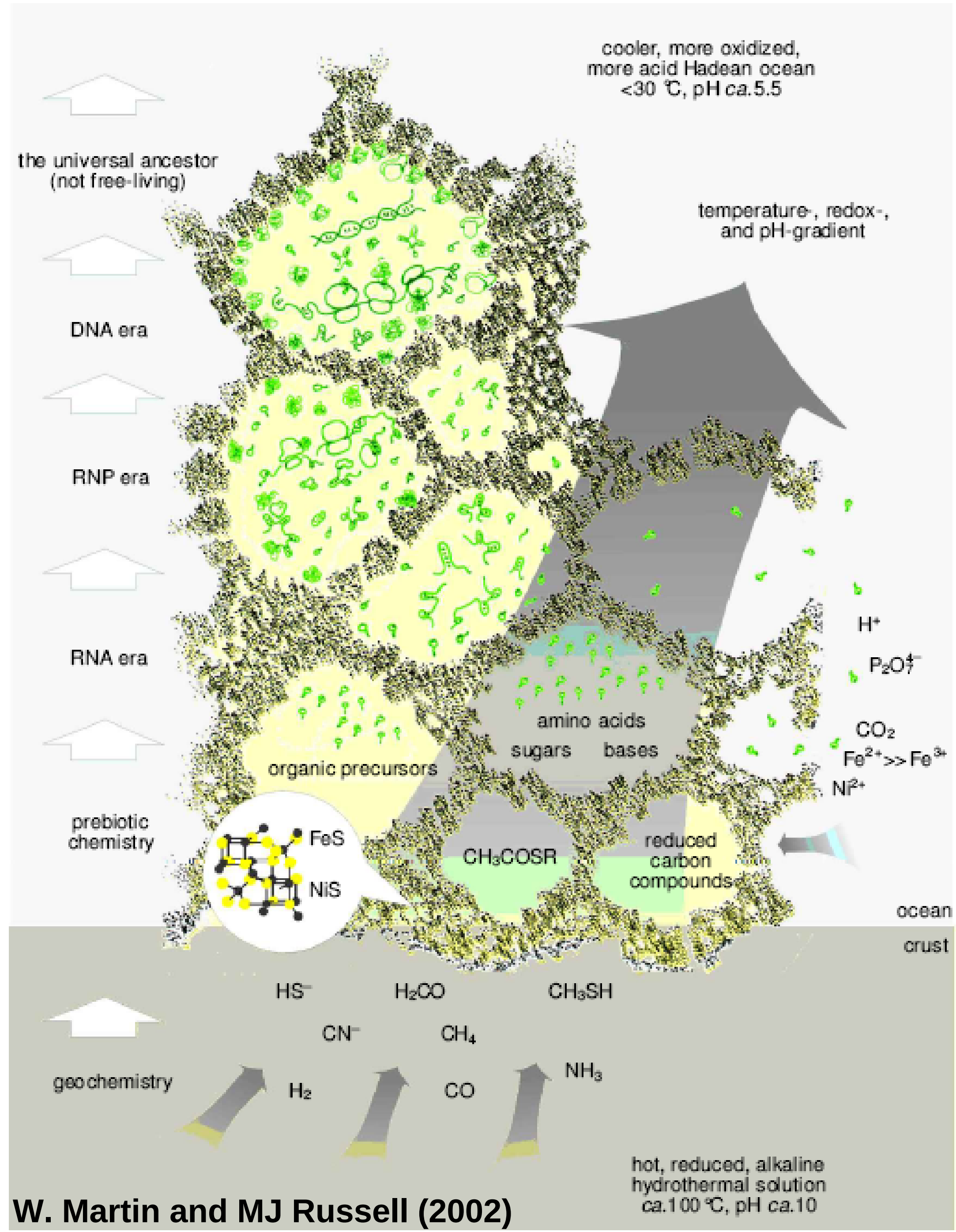
$$HS^{-} + Fe^{2+} \rightleftharpoons FeS + H^{+}$$

Fe(Ni)-sulfures

« membranes »

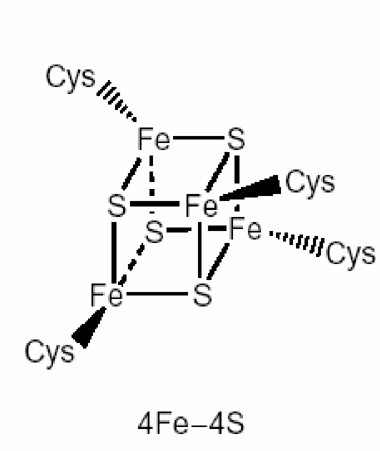
et « catalyseurs »

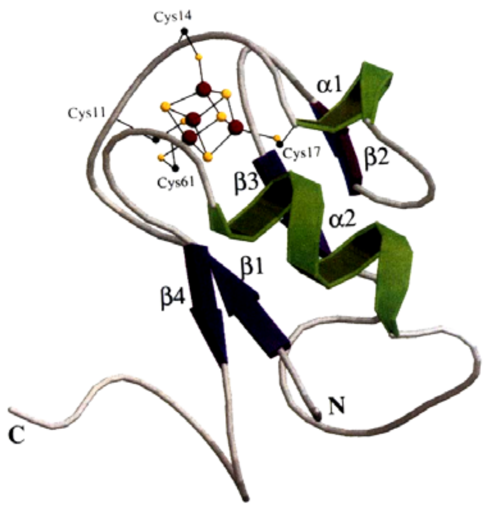
de cellules « prebiotiques »

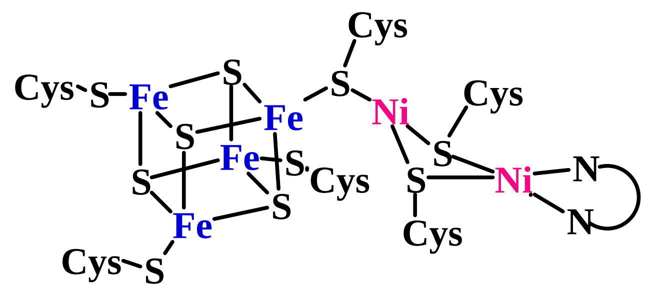


W. Martin and MJ Russell (2002)

Centres Fe(M)S de protéines: inventions du monde biologique ou mimes d'ancêtres minéraux capables d'activité catalytique ?

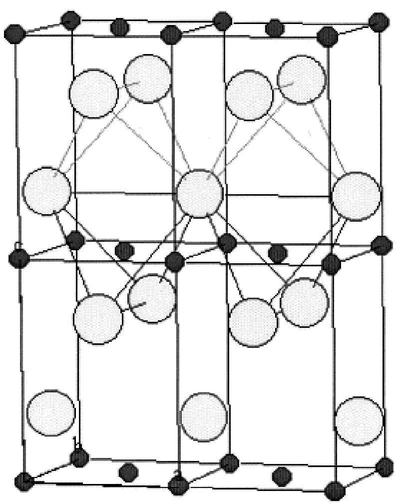




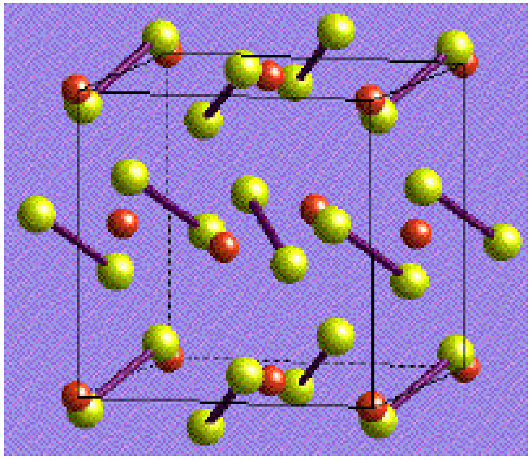


Cluster A de l'ACS (acetyl-CoA synthase)

mackinawite



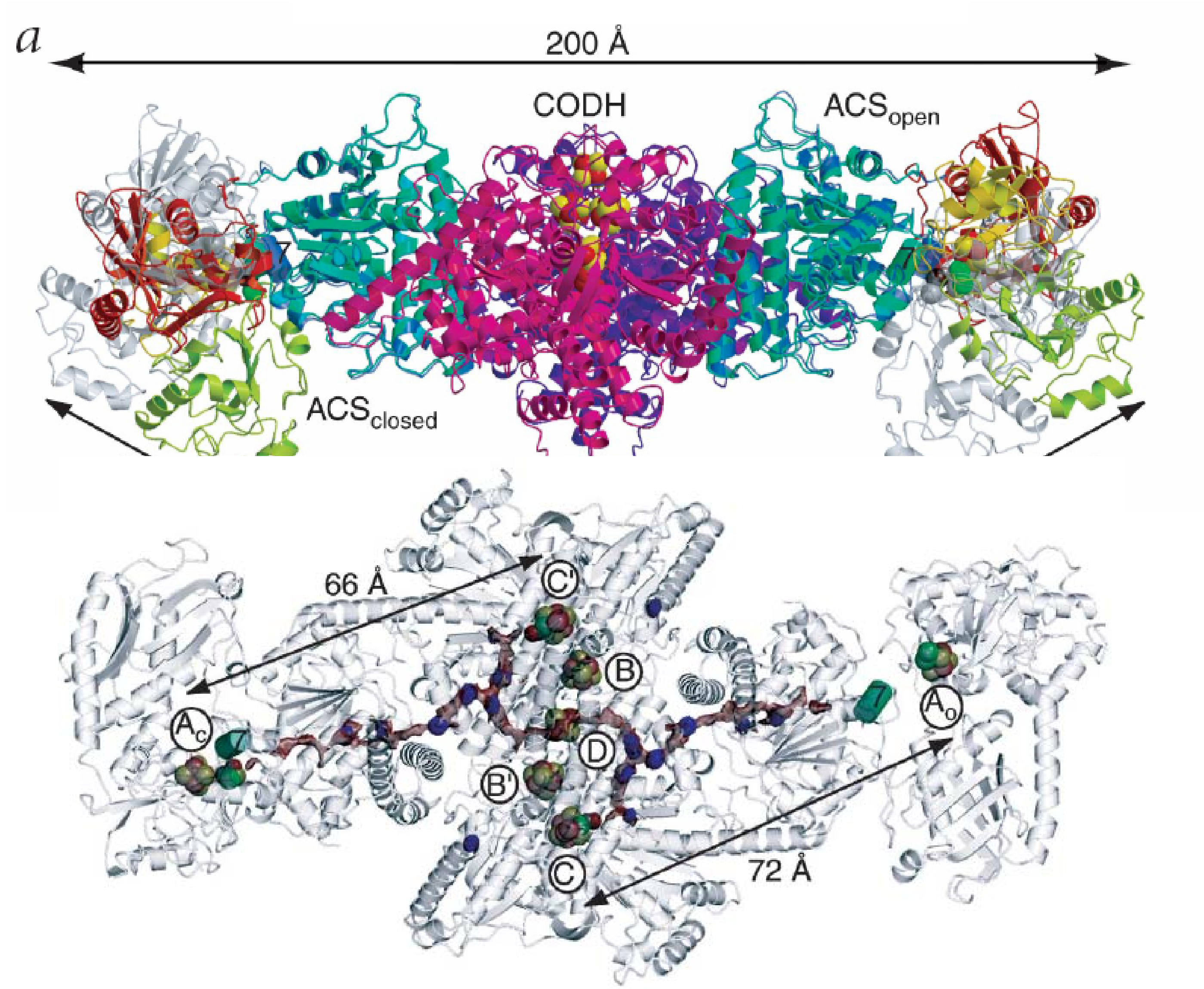
pyrite



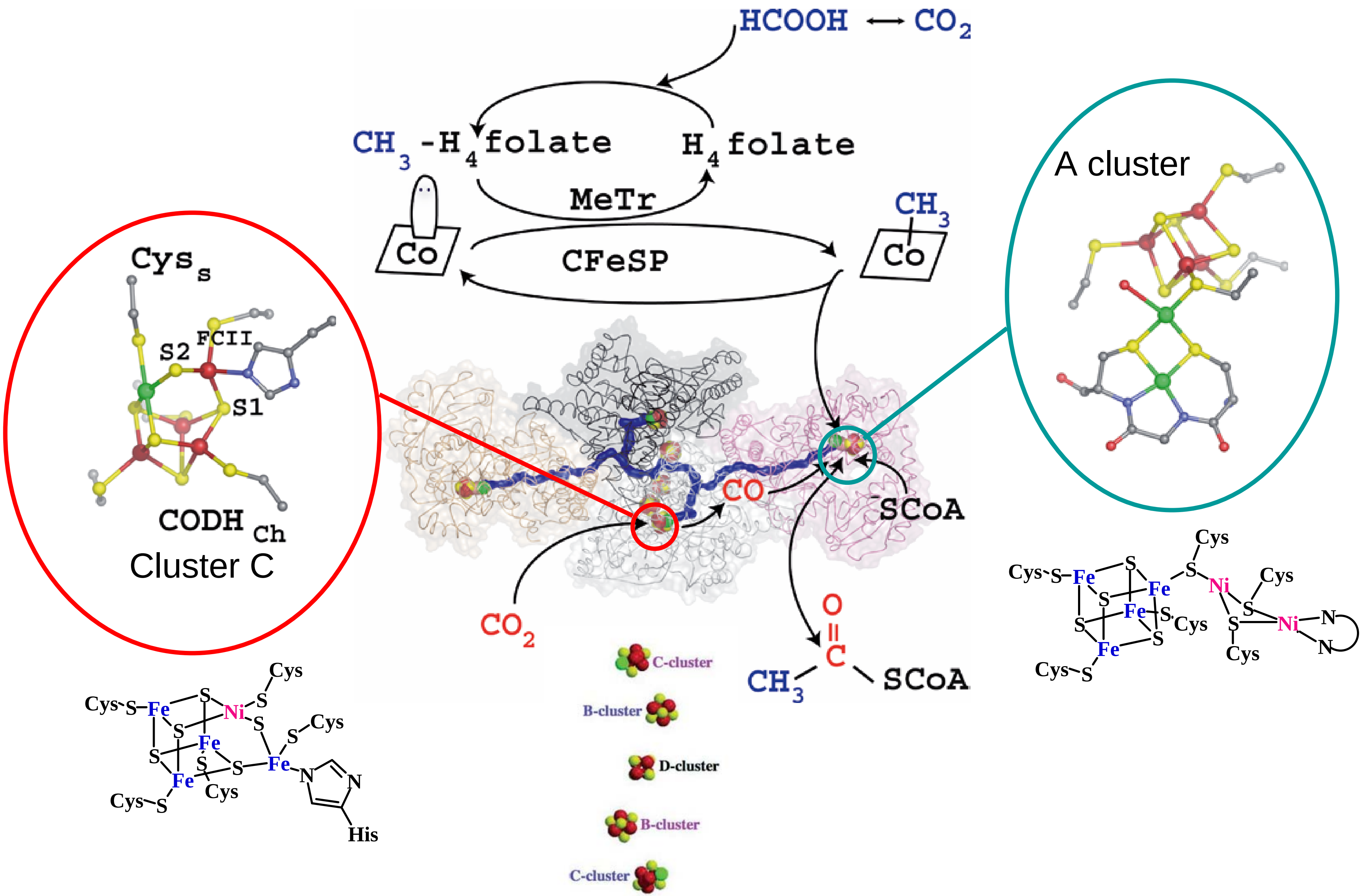
greigite

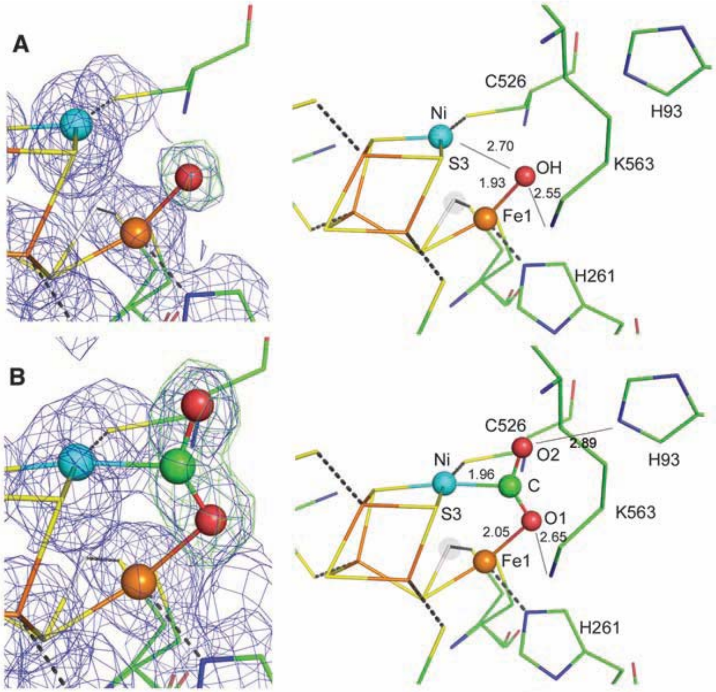
Fe(Ni)-sulfures: CO-dehydrogenase/acetyl-CoA synthase

Acetyl-CoA ⟵ $CO + H_2O \rightleftharpoons CO_2 + 2e^- + 2H^+$ ⟶ **H_2**



Fe(Ni)-sulfures: CO-dehydrogenase/acetyl-CoA synthase

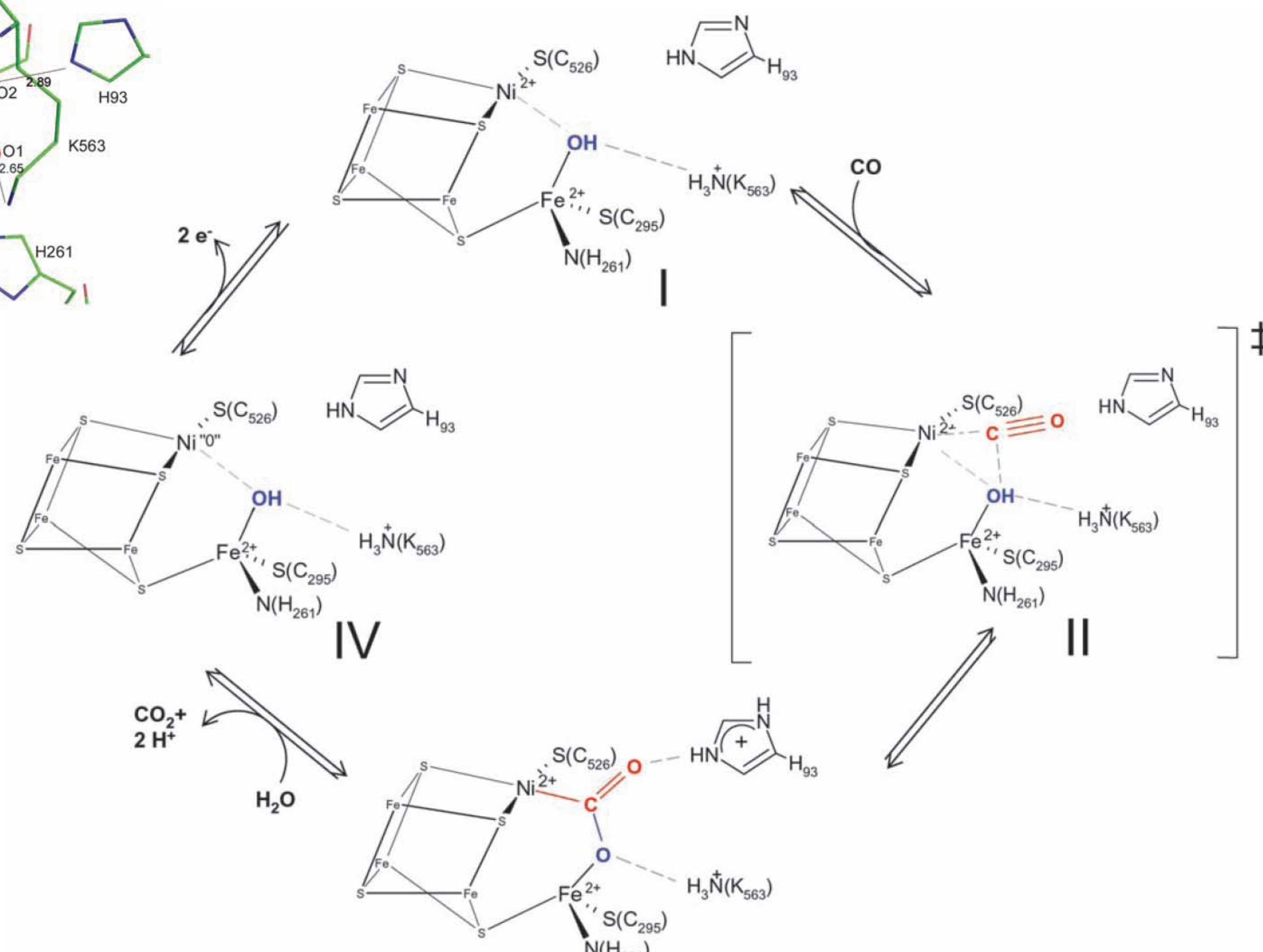




Carbon Dioxide Activation at the Ni,Fe-Cluster of Anaerobic Carbon Monoxide Dehydrogenase

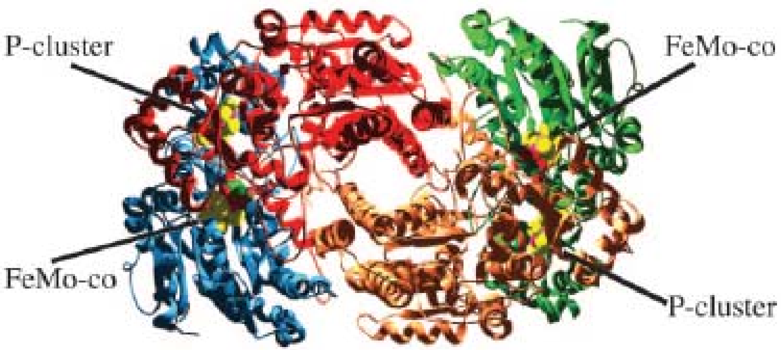
Jae-Hun Jeoung, *et al.*

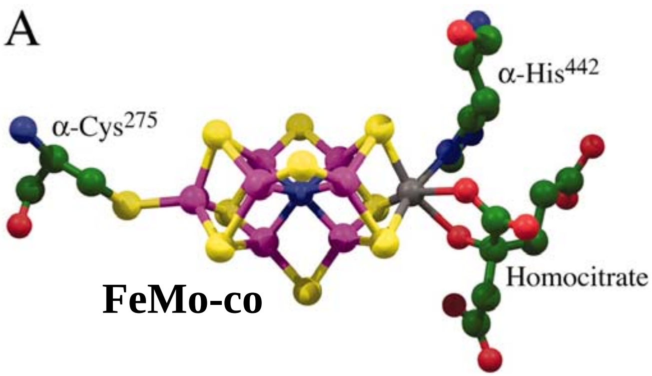
Science **318**, 1461 (2007);



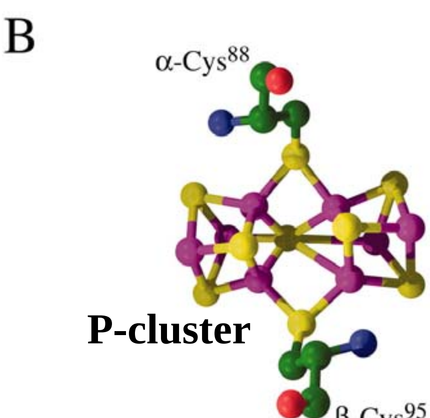
Nitrogenase

$$N_2 + 6H^+ + 6e^- \rightleftharpoons 2NH_3$$



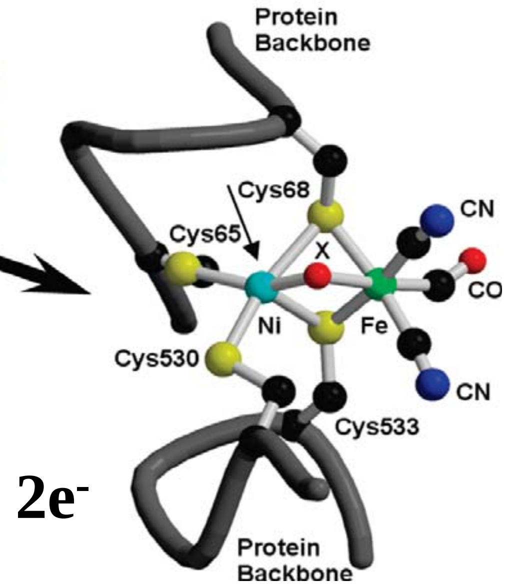


FeMo-co

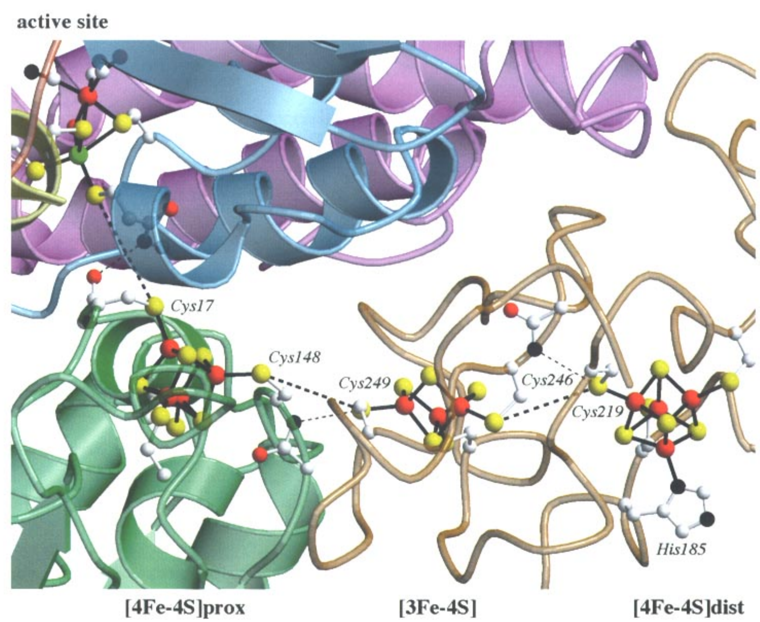


P-cluster

Hydrogenase

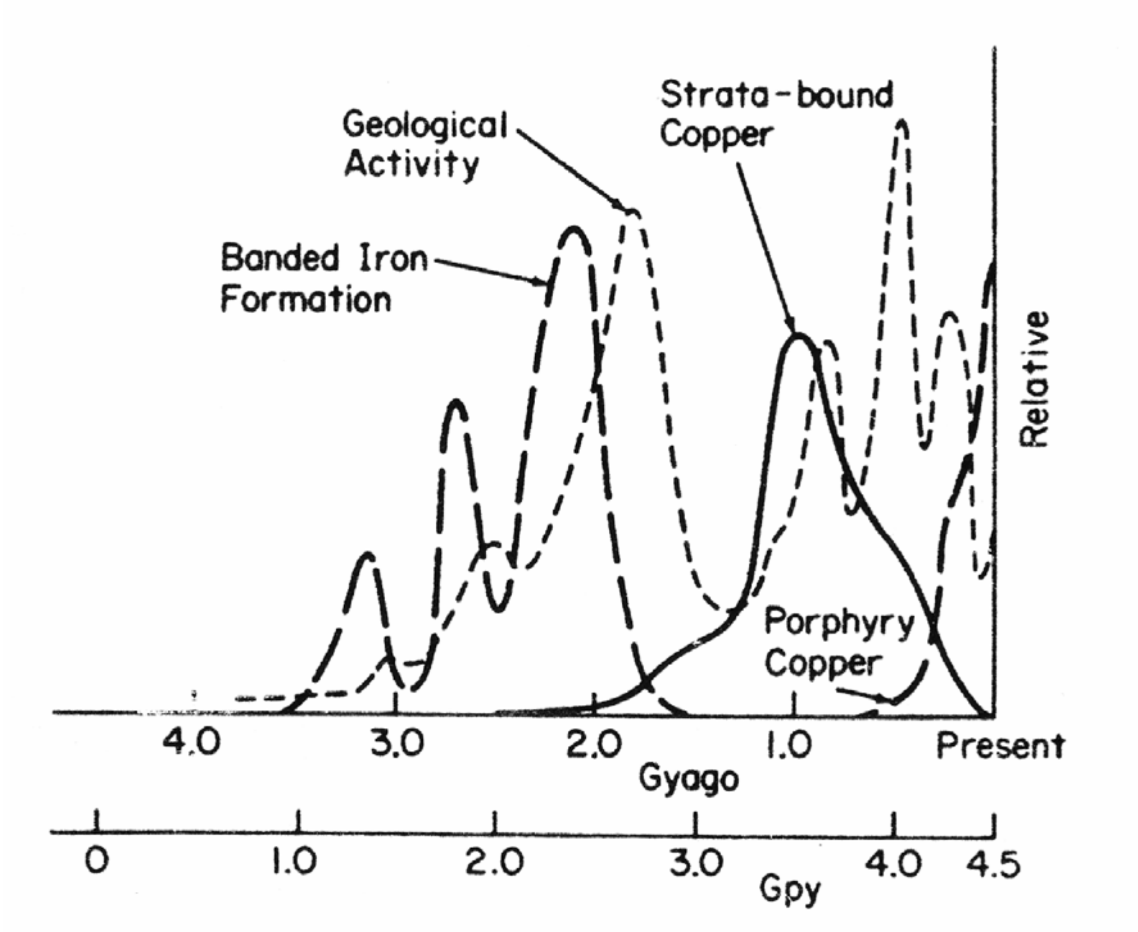


$$H_2 \rightleftharpoons 2H^+ + 2e^-$$

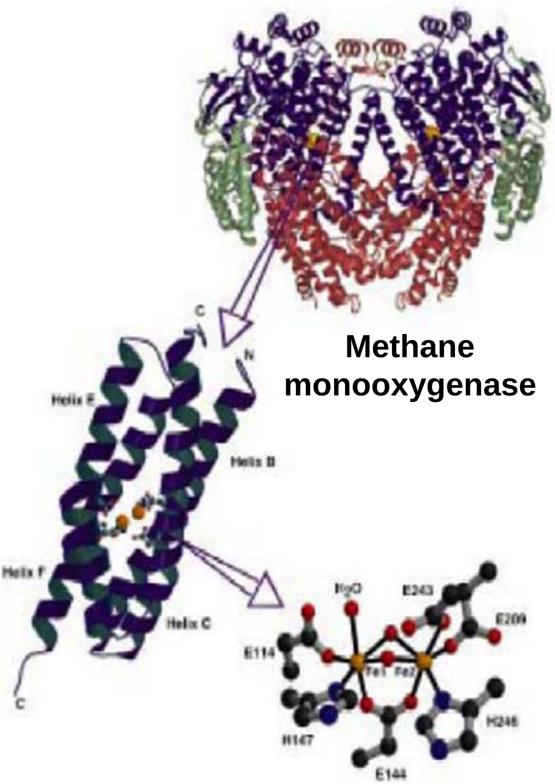


La vie à l'oxygène ?

- Oxydation et précipitation du fer
- Réduction massive du carbone
- Disparition massive d'organismes vivants

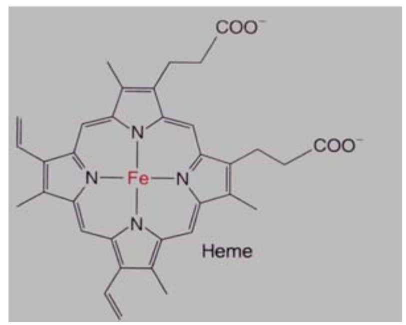


La vie à l'oxygène: conséquences



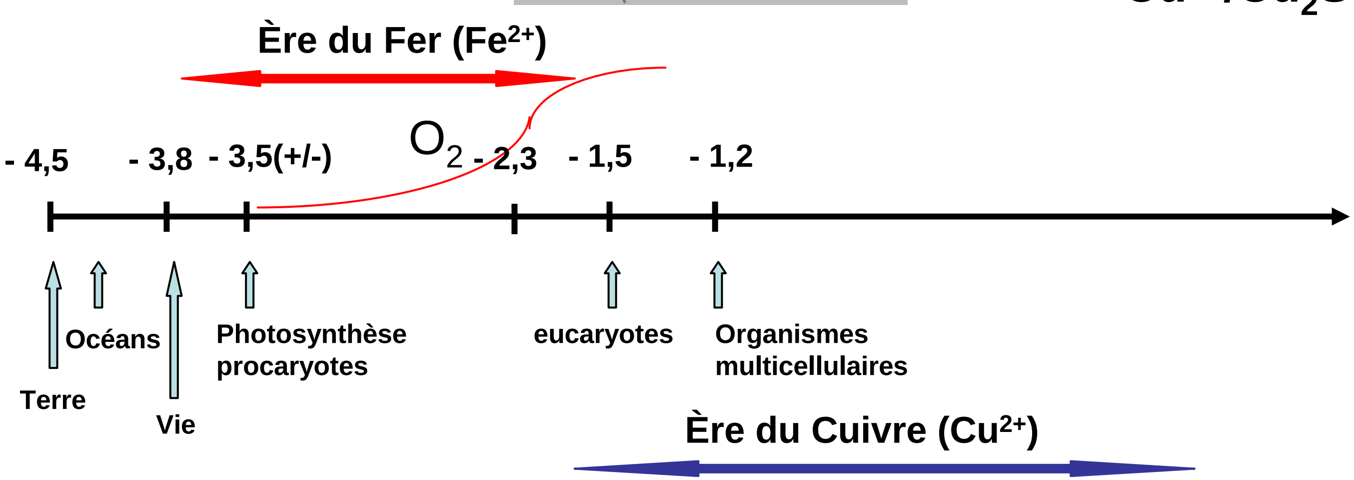
Methane monooxygenase

- Adaptation: systèmes antioxydants (métalloenzymes)
- Stratégies moléculaires de solubilisation des oxydes de fer et de réduction à l'état Fe^{2+}
- Nouveaux cofacteurs enzymatiques: **Cu^{2+}**, heme, Fe-O-Fe,..
- Disparition des centres fer-soufre



Fe_2O_3/Fe^{2+}: - 0,2V
Fe^{2+}/Fe: - 0,44V

Cu^{2+}/Cu: + 0,34V
Cu^{2+}/Cu_2S: + 0,2V



La vie à l'oxygène: conséquences

→ Disparition des centres fer-soufre

Correlation motif $CX_2CX_2CX_3C$ (120 génomes) avec:

-**Méthanogénèse**
-**Archaea**
-**Anaérobiose**
-***hyperthermophilie***

Numbers of the 4Fe–4S iron–sulfur motif $CX_2CX_2CX_3C$ within the genomes of various prokaryotic groups

Physiological and phylogenetic groups	No. of genomes[a]	Avg. no. of motifs perf 1000 ORFs[a]
ARCHAEA, all	22	14.8
Non-methanogens	11	7.4
aerobes	6	6.4
faculatative anaerobes	2	8.6
anaerobes	3	8.6
non-methanogens, non-hyperthermophiles	4	6.2
Methanogens (+*Archaeoglobus fulgidus*[b])	11	22.2
hydrogenotrophs	6	25.3
methylotrophs	4	16.4
HYPERTHERMOPHILES, all	12	12.2
archaea	10	12.5
non-methanogenic archaea	7	8.1
bacteria	2	10.6
BACTERIA, all	98	3.7
aerobes	49	2.8
facultative anaerobes	38	3.7
anaerobes	11	7.4
mesophiles	93	3.6
thermophiles	3	2.6
photosynthetic	10	4.7
pathogens	66	3.1
proteobacteria	50	4.3