



COLLÈGE
DE FRANCE
—1530—

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

Marc Fontecave

*Laboratoire de Chimie et Biologie des Métaux, Université Joseph Fourier, CNRS, CEA/DSV/iRTSV
CEA-Grenoble 17 rue des martyrs 38054 Grenoble cedex 9, France
mfontecave@cea.fr; Phone: (0033)438789103 ; Fax: (0033)438789124*

Collège de France, 11 Place Marcelin Berthelot, 75231 Paris Cedex 05

PERIODIC TABLE

Atomic Properties of the Elements

NIST

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

18
VIII A

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 ¹³³Cs

speed of light in vacuum	<i>c</i>	299 792 458 m s ⁻¹	(exact)
Planck constant	<i>h</i>	6.6261 × 10 ⁻³⁴ J s	(<i>h</i> = <i>h</i> /2π)
elementary charge	<i>e</i>	1.6022 × 10 ⁻¹⁹ C	
electron mass	<i>m_e</i>	9.1094 × 10 ⁻³¹ kg	
	<i>m_ec²</i>	0.5110 MeV	
proton mass	<i>m_p</i>	1.6726 × 10 ⁻²⁷ kg	
fine-structure constant	<i>α</i>	1/137.036	
Rydberg constant	<i>R_∞</i>	10 973 732 m ⁻¹	
	<i>R_∞c</i>	3.289 842 × 10 ¹⁵ Hz	
	<i>R_∞hc</i>	13.6057 eV	
Boltzmann constant	<i>k</i>	1.3807 × 10 ⁻²³ J K ⁻¹	

Solids
 Liquids
 Gases
 Artificially Prepared

Physics Laboratory physics.nist.gov		Standard Reference Data Group www.nist.gov/srd									
13 IIIA	14 IVA	15 VA	16 VIA	17 VIIA	18 VIII A	13 IIIA	14 IVA	15 VA	16 VIA	17 VIIA	18 VIII A
5 B Boron 10.811 1s ² 2s ² 2p 8.2980	6 C Carbon 12.0107 1s ² 2s ² 2p ² 11.2003	7 N Nitrogen 14.0067 1s ² 2s ² 2p ³ 14.5341	8 O Oxygen 15.9994 1s ² 2s ² 2p ⁴ 13.6181	9 F Fluorine 18.9984032 1s ² 2s ² 2p ⁵ 17.4228	10 Ne Neon 20.1797 1s ² 2s ² 2p ⁶ 21.5645	13 Al Aluminum 26.981538 [Ne]3s ² 3p 5.9858	14 Si Silicon 28.0855 [Ne]3s ² 3p ² 8.1517	15 P Phosphorus 30.9737316 [Ne]3s ² 3p ³ 10.4867	16 S Sulfur 32.065 [Ne]3s ² 3p ⁴ 10.3800	17 Cl Chlorine 35.453 [Ne]3s ² 3p ⁵ 12.9676	18 Ar Argon 39.948 [Ne]3s ² 3p ⁶ 15.7596
19 K Potassium 39.0983 [Ar]4s 4.3407	20 Ca Calcium 40.078 [Ar]4s 6.1132	21 Sc Scandium 44.955910 [Ar]3d ¹ 4s 6.5615	22 Ti Titanium 47.887 [Ar]3d ² 4s 6.8281	23 V Vanadium 50.9415 [Ar]3d ³ 4s 6.7462	24 Cr Chromium 51.9961 [Ar]3d ⁵ 4s 6.7695	25 Mn Manganese 54.938040 [Ar]3d ⁵ 4s 7.4340	26 Fe Iron 55.845 [Ar]3d ⁶ 4s 7.9024	27 Co Cobalt 58.933200 [Ar]3d ⁷ 4s 7.8810	28 Ni Nickel 58.6934 [Ar]3d ⁸ 4s 7.6398	29 Cu Copper 63.546 [Ar]3d ¹⁰ 4s 7.7264	30 Zn Zinc 65.409 [Ar]3d ¹⁰ 4s 9.3942
31 Ga Gallium 69.723 [Ar]3d ¹⁰ 4s ² 4p 5.9993	32 Ge Germanium 72.64 [Ar]3d ¹⁰ 4s ² 4p ² 7.8904	33 As Arsenic 74.92160 [Ar]3d ¹⁰ 4s ² 4p ³ 9.7886	34 Se Selenium 78.96 [Ar]3d ¹⁰ 4s ² 4p ⁴ 9.7524	35 Br Bromine 79.904 [Ar]3d ¹⁰ 4s ² 4p ⁵ 11.8138	36 Kr Krypton 83.798 [Ar]3d ¹⁰ 4s ² 4p ⁶ 13.9996	37 Rb Rubidium 85.4678 [Kr]5s 4.1771	38 Sr Strontium 87.62 [Kr]5s 5.6949	39 Y Yttrium 88.90585 [Kr]4d ¹ 5s 6.2173	40 Zr Zirconium 91.224 [Kr]4d ² 5s 6.6339	41 Nb Niobium 92.90638 [Kr]4d ⁴ 5s 6.7589	42 Mo Molybdenum 95.94 [Kr]4d ⁵ 5s 7.0924
55 Cs Cesium 132.90545 [Xe]6s 3.8939	56 Ba Barium 137.327 [Xe]6s 5.2117	72 Hf Hafnium 178.49 [Xe]4f ¹⁴ 5d ² 6s ² 8.8251	73 Ta Tantalum 180.9479 [Xe]4f ¹⁴ 5d ³ 6s ² 7.5496	74 W Tungsten 183.84 [Xe]4f ¹⁴ 5d ⁴ 6s ² 7.8640	75 Re Rhenium 186.207 [Xe]4f ¹⁴ 5d ⁵ 6s ² 7.8335	76 Os Osmium 190.23 [Xe]4f ¹⁴ 5d ⁶ 6s ² 8.4382	77 Ir Iridium 192.217 [Xe]4f ¹⁴ 5d ⁷ 6s ² 9.8670	78 Pt Platinum 195.078 [Xe]4f ¹⁴ 5d ⁹ 6s ¹ 9.6588	79 Au Gold 196.96655 [Xe]4f ¹⁴ 5d ¹⁰ 6s ¹ 9.2255	80 Hg Mercury 200.59 [Xe]4f ¹⁴ 5d ¹⁰ 6s ² 10.4375	81 Tl Thallium 204.3833 [Hg]6p 6.1082
87 Fr Francium (223) [Rn]7s 4.0727	88 Ra Radium (226) [Rn]7s 5.2784	104 Rf Rutherfordium (261) [Rn]5f ¹⁴ 6d ² 7s ² 6.0 ?	105 Db Dubnium (262)	106 Sg Seaborgium (266)	107 Bh Bohrium (264)	108 Hs Hassium (277)	109 Mt Meitnerium (268)	110 Uun Ununnilium (281)	111 Uuu Unununium (272)	112 Uub Unbibium (285)	114 Uuq Ununquadium (289)

Period

Atomic Number: 58
 Ground-state Level: ¹G₄
 Symbol: **Ce**
 Name: Cerium
 Atomic Weight: 140.116
 Ground-state Configuration: [Xe]4f5d6s²
 Ionization Energy (eV): 5.5387

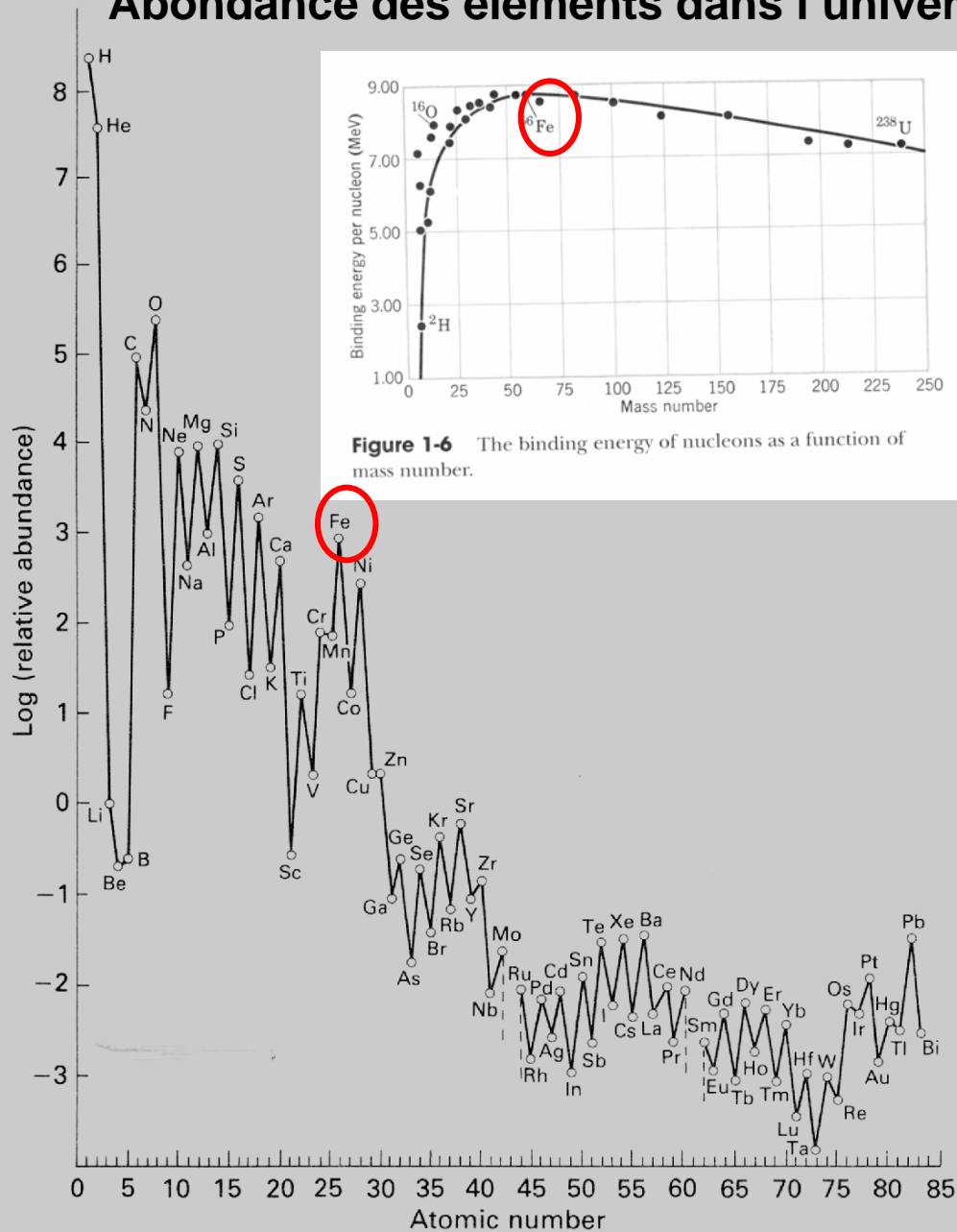
Lanthanides
Actinides

57 La Lanthanum 138.9055 [Xe]5d ¹ 6s ² 5.5769	58 Ce Cerium 140.116 [Xe]4f5d6s ² 5.5387	59 Pr Praseodymium 140.90765 [Xe]4f ³ 6s ² 5.473	60 Nd Neodymium 144.24 [Xe]4f ⁴ 6s ² 5.5250	61 Pm Promethium (145) [Xe]4f ⁵ 6s ² 5.582	62 Sm Samarium 150.36 [Xe]4f ⁶ 6s ² 5.6437	63 Eu Europium 151.964 [Xe]4f ⁷ 6s ² 5.6704	64 Gd Gadolinium 157.25 [Xe]4f ⁷ 5d ¹ 6s ² 5.8638	65 Tb Terbium 158.92534 [Xe]4f ⁹ 6s ² 5.9389	66 Dy Dysprosium 162.500 [Xe]4f ¹⁰ 6s ² 6.0215	67 Ho Holmium 164.93032 [Xe]4f ¹¹ 6s ² 6.0215	68 Er Erbium 167.259 [Xe]4f ¹² 6s ² 6.1077	69 Tm Thulium 168.93421 [Xe]4f ¹³ 6s ² 6.1843	70 Yb Ytterbium 173.04 [Xe]4f ¹⁴ 6s ² 6.2542	71 Lu Lutetium 174.967 [Xe]4f ¹⁴ 5d ¹ 6s ² 5.4259
89 Ac Actinium (227) [Rn]6d ¹ 7s ² 5.17	90 Th Thorium 232.0381 [Rn]6d ² 7s ² 6.3087	91 Pa Protactinium 231.03688 [Rn]5f ² 6d ¹ 7s ² 5.89	92 U Uranium 238.02891 [Rn]5f ³ 6d ¹ 7s ² 6.1941	93 Np Neptunium (237) [Rn]5f ⁴ 6d ¹ 7s ² 6.2657	94 Pu Plutonium (244) [Rn]5f ⁶ 7s ² 6.0260	95 Am Americium (247) [Rn]5f ⁷ 7s ² 5.9738	96 Cm Curium (247) [Rn]5f ⁸ 6d ¹ 7s ² 5.9914	97 Bk Berkelium (247) [Rn]5f ⁹ 7s ² 6.1979	98 Cf Californium (251) [Rn]5f ¹⁰ 7s ² 6.2817	99 Es Einsteinium (252) [Rn]5f ¹¹ 7s ² 6.42	100 Fm Fermium (257) [Rn]5f ¹² 7s ² 6.50	101 Md Mendelevium (258) [Rn]5f ¹³ 7s ² 6.58	102 No Nobelium (259) [Rn]5f ¹⁴ 7s ² 6.65	103 Lr Lawrencium (262) [Rn]5f ¹⁴ 7s ² 7p ¹ 4.9 ?

[†]Based upon ¹²C. () indicates the mass number of the most stable isotope.

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

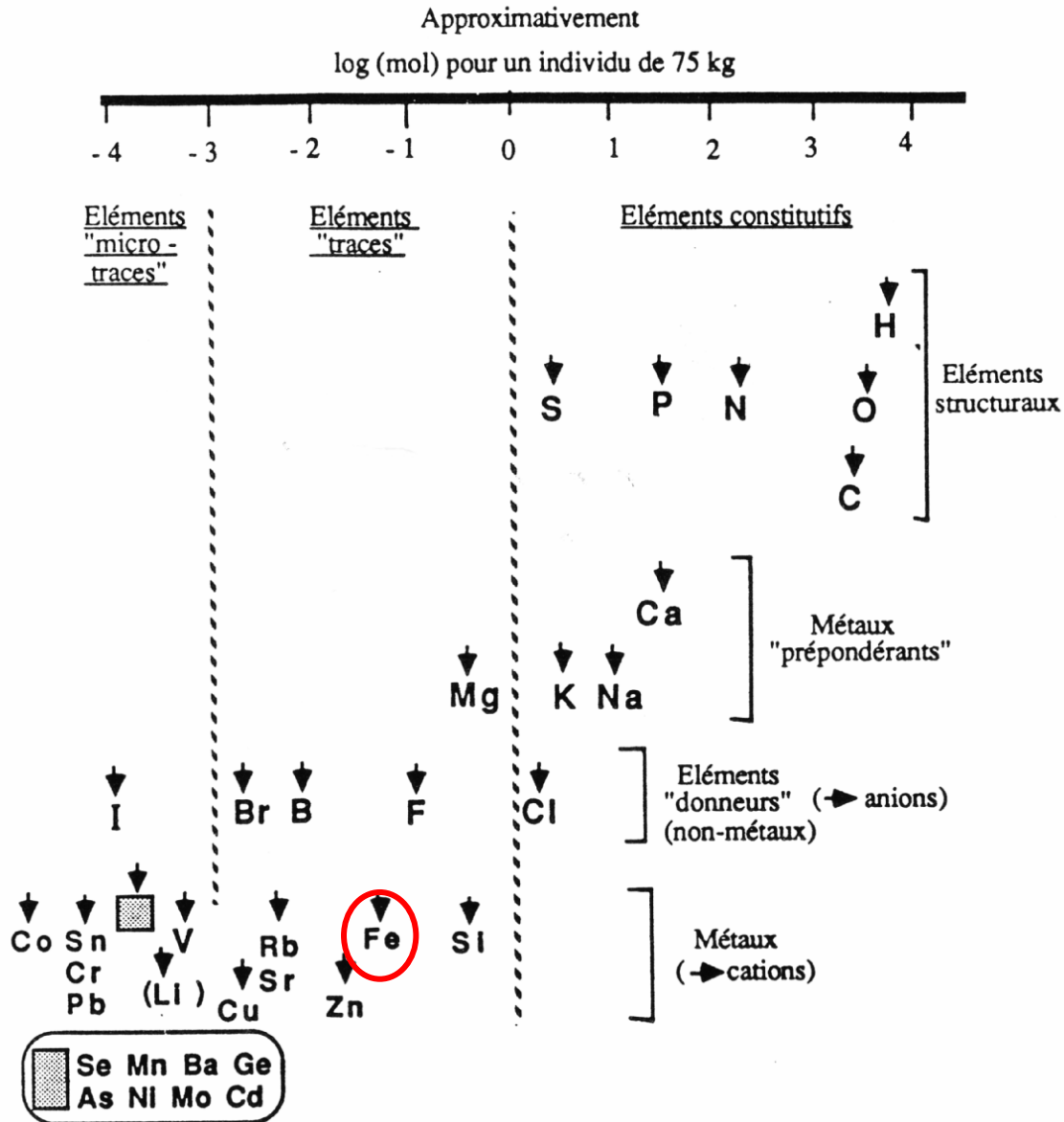
Abondance des éléments dans l'univers



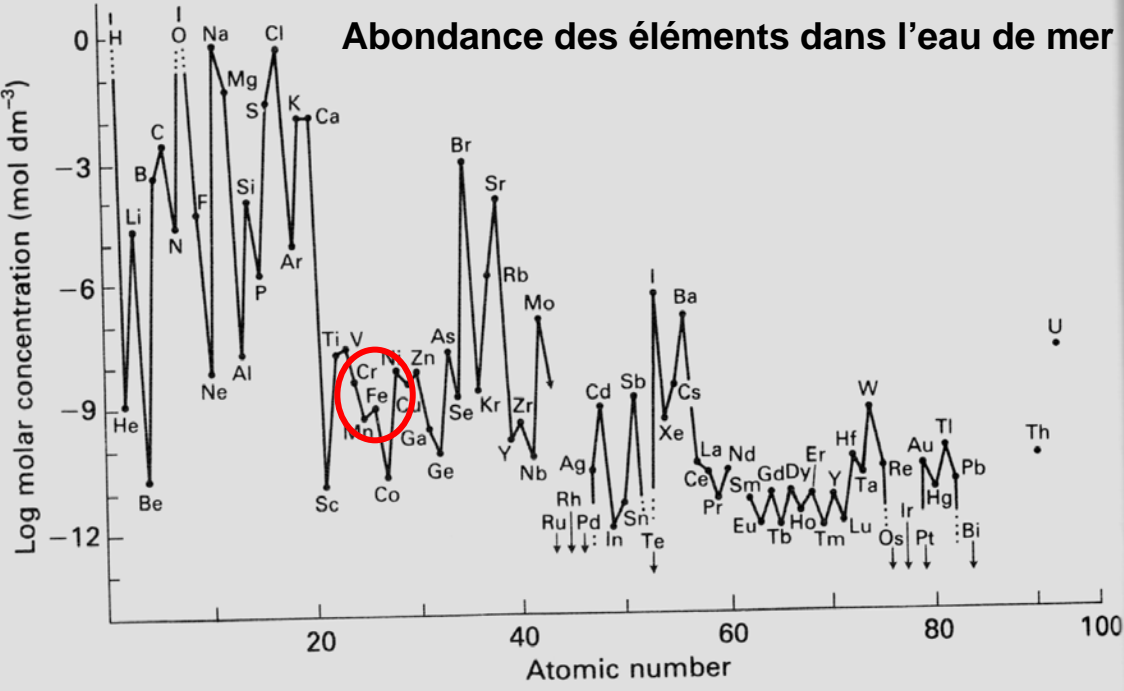
terre

- 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

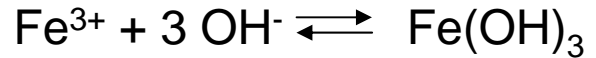
Composition du corps humain adulte



Abundance des éléments dans l'eau de mer



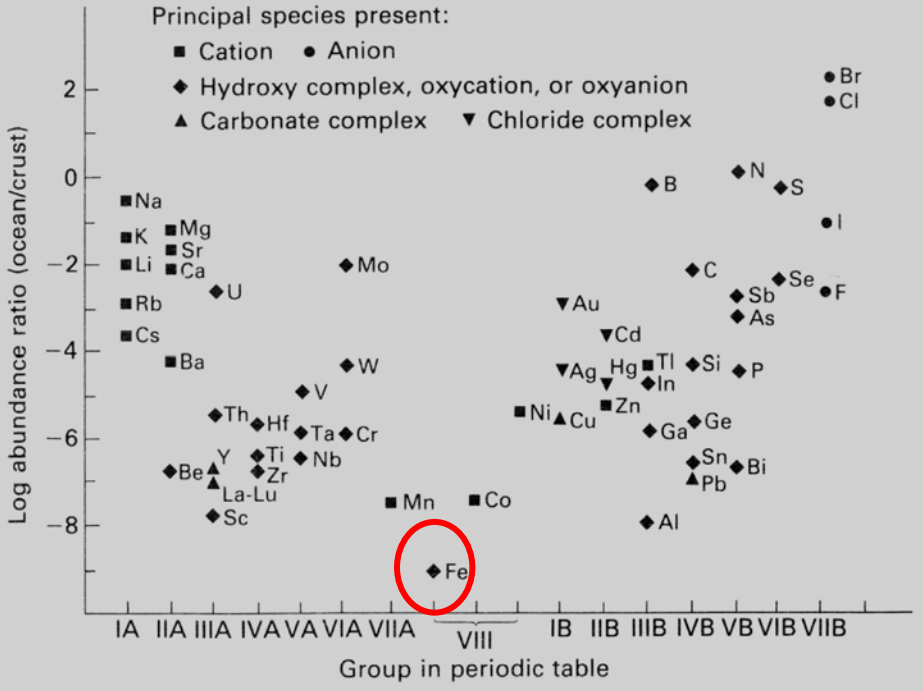
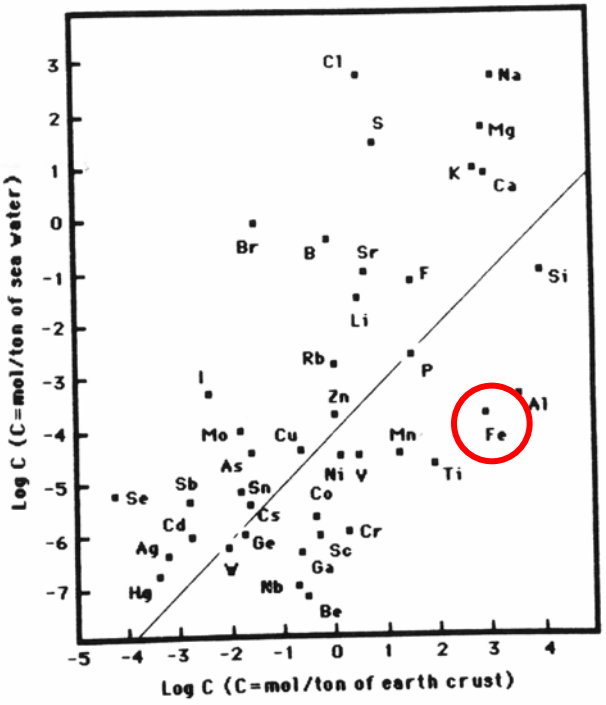
Un problème de solubilité



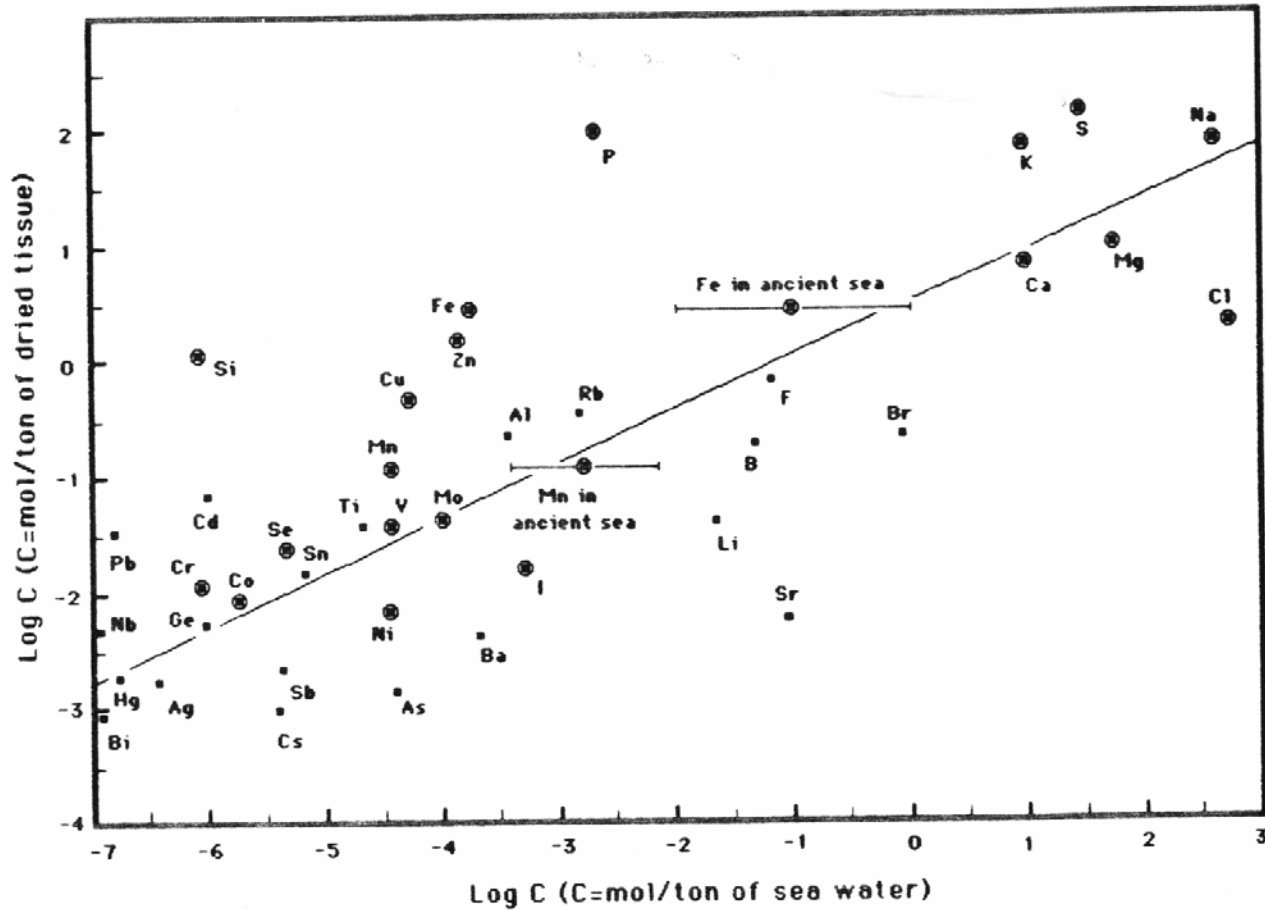
$$K_s = 10^{-39}$$

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

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

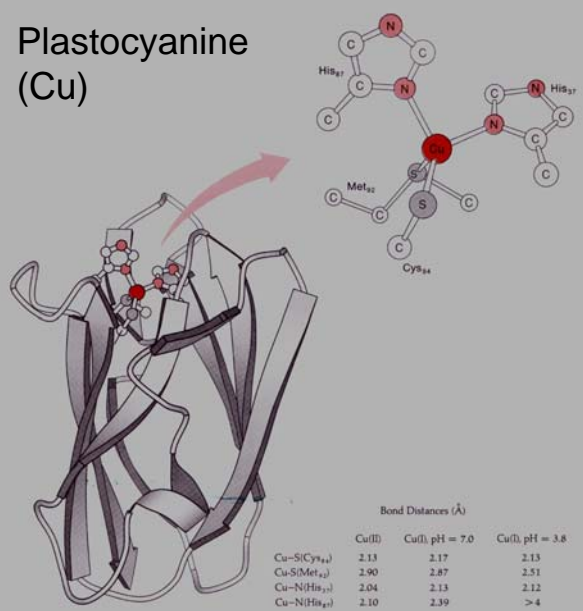
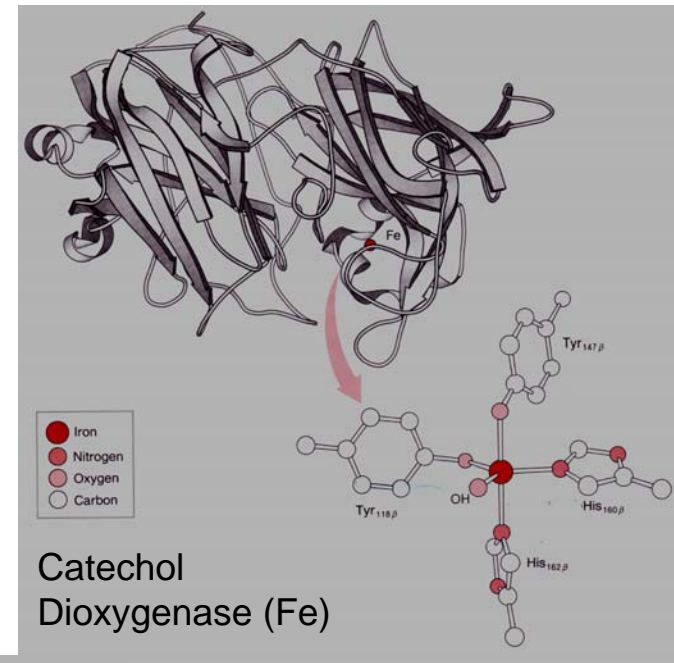
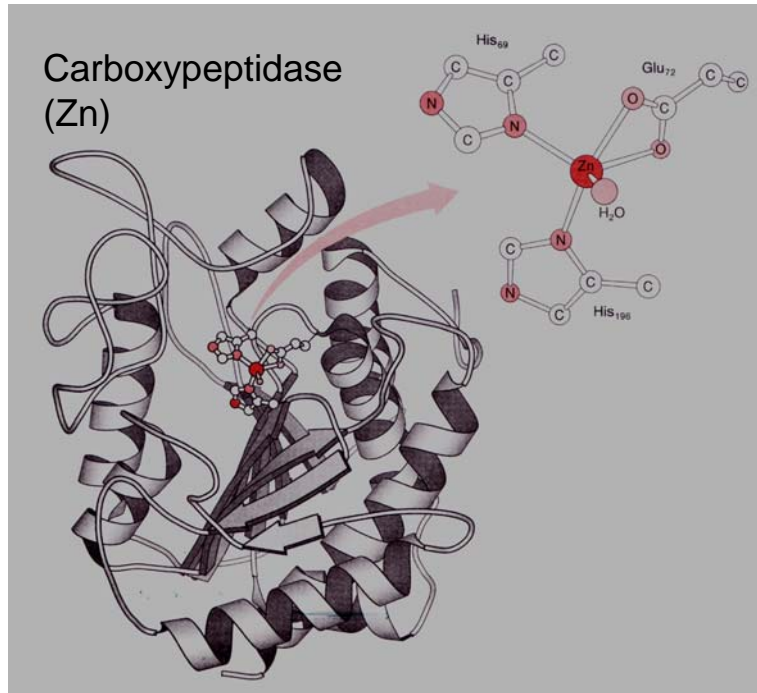


Corrélation: milieu vivant/eau de mer

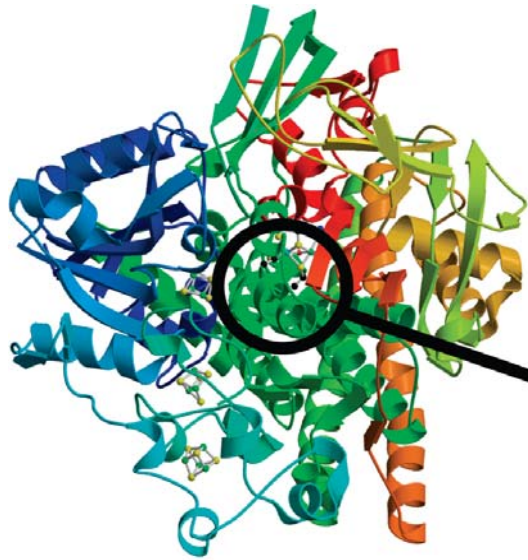


	eau de mer (mM)	plasma sanguin (mM)
Na ⁺	470	140
Mg ²⁺	50	2
Ca ²⁺	10	3
K ⁺	10	10
Cl ⁻	550	100
HPO ₄ ²⁻	0,001	1
SO ₄ ²⁻	28	1
Fe ⁿ⁺	0.0001	0.02
Zn ²⁺	0.0001	0.02
Cu ²⁺	0.001	0.015
Co ²⁺	10 ^{-5,5}	0,002
Ni ²⁺	10 ⁻⁶	0

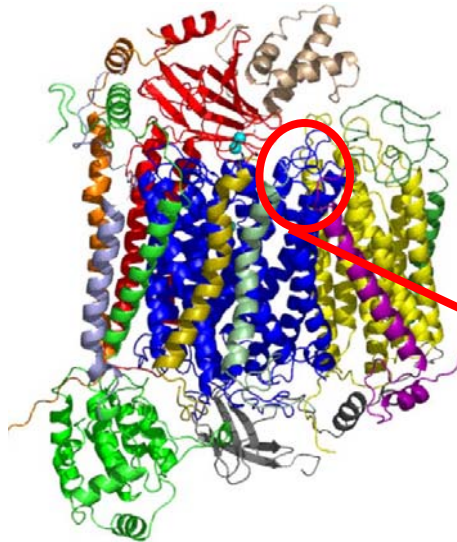
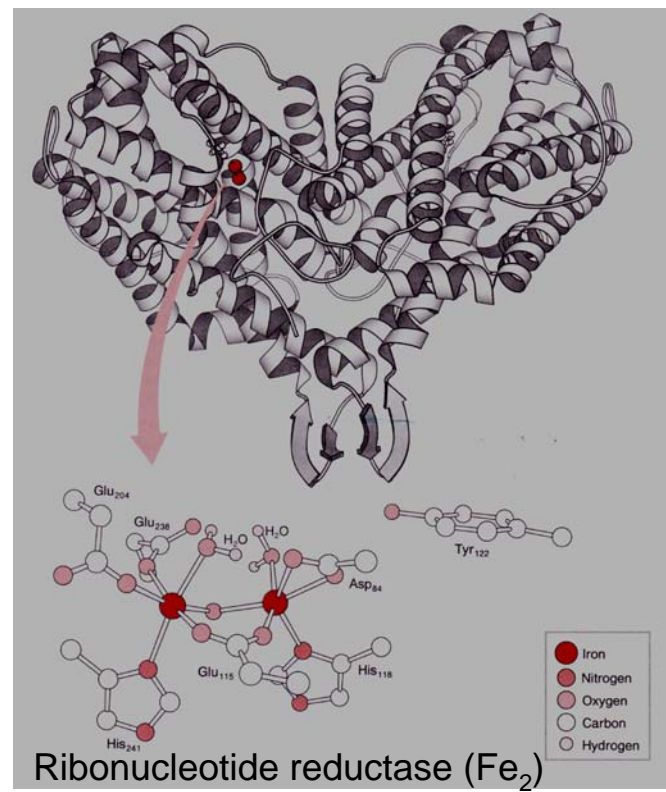
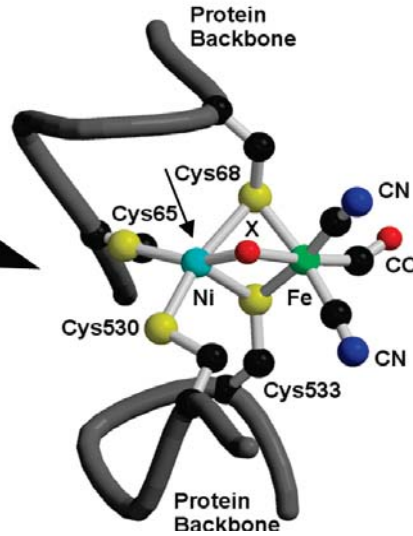
Métalloprotéines et sites métalliques



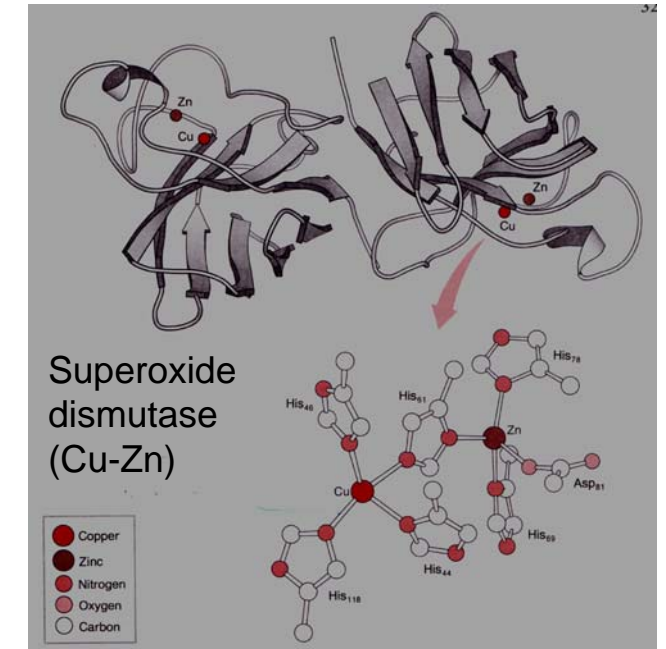
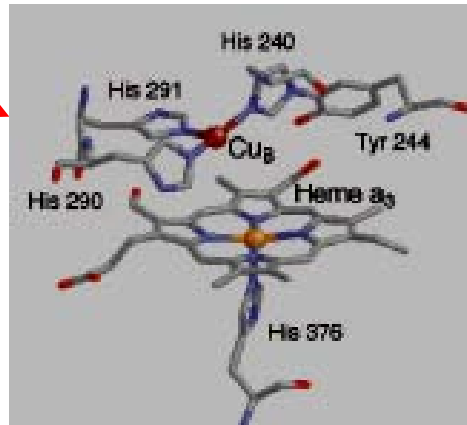
hydrogenase (Ni-Fe)

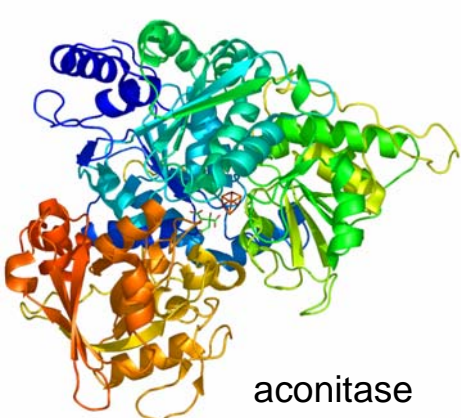


Centres Binucléaires



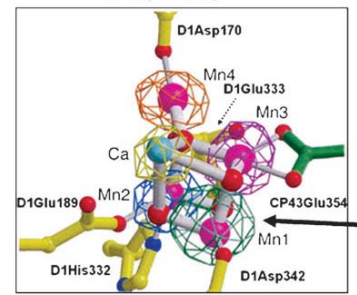
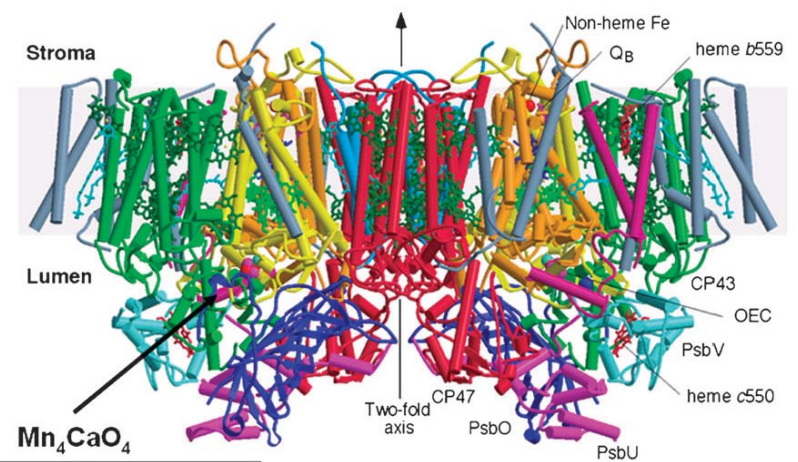
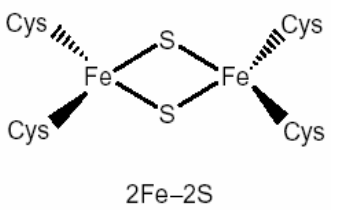
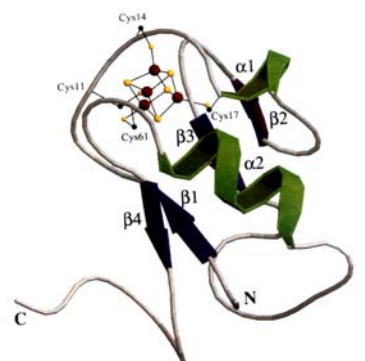
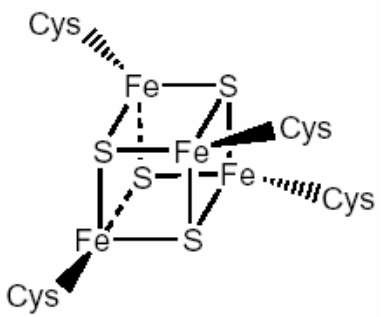
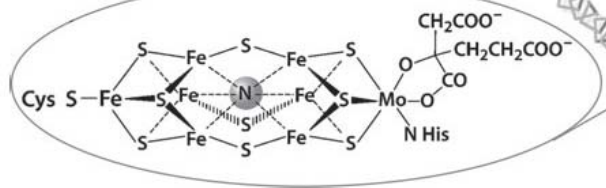
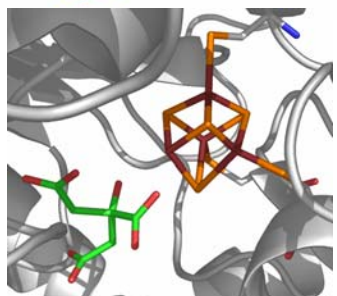
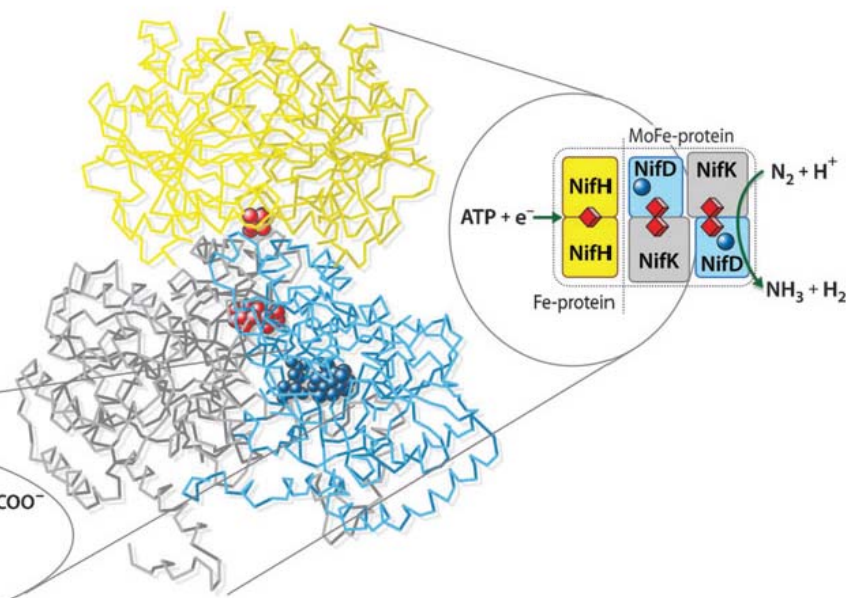
Cytochrome oxidase (Cu-Fe)





Clusters

Nitrogenase



Photosystem Two

water splitting site

➡ **Fer (Fe), Cuivre (Cu)**

Me⁽ⁿ⁺¹⁾⁺/Meⁿ⁺ 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)**

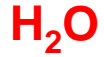
Zn²⁺ un acide de Lewis

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): peroxydases

 **Activation de petites molécules**



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



Fe, Cu (mono-,di-oxygénases),



Mo (nitrogénase)



Ni (hydrogénase)



Ni (CO dehydrogenase)

 **Polarisation de liaisons**

Zn, Fe, Ca

 **Transferts d'électrons**

Cu, Fe

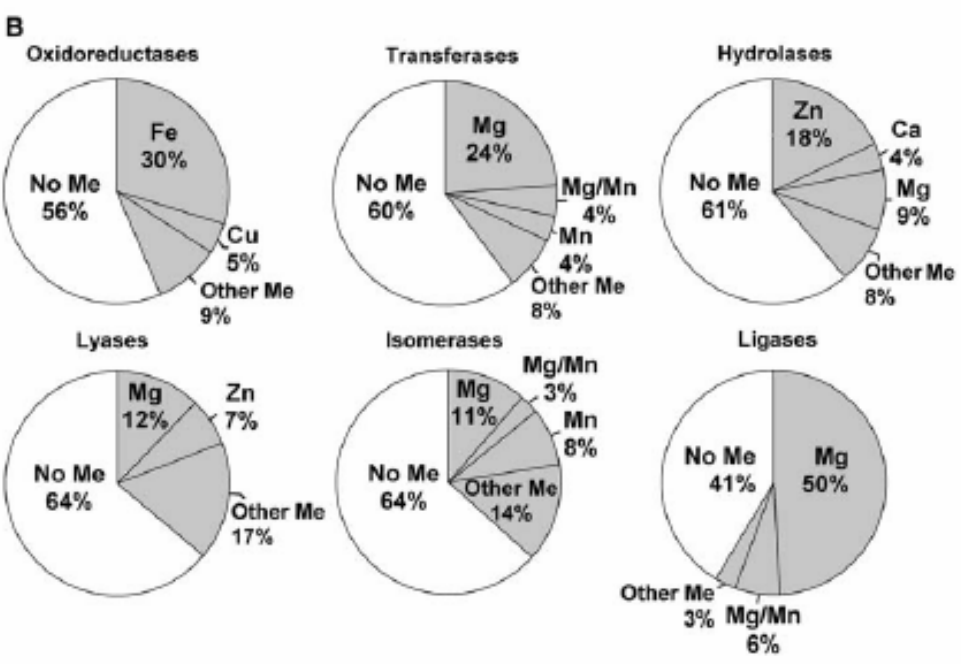
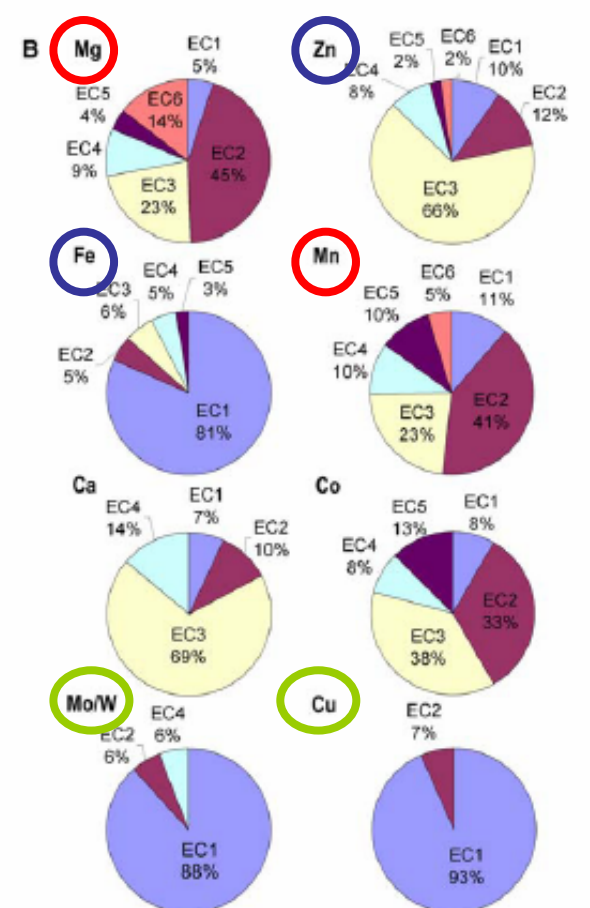
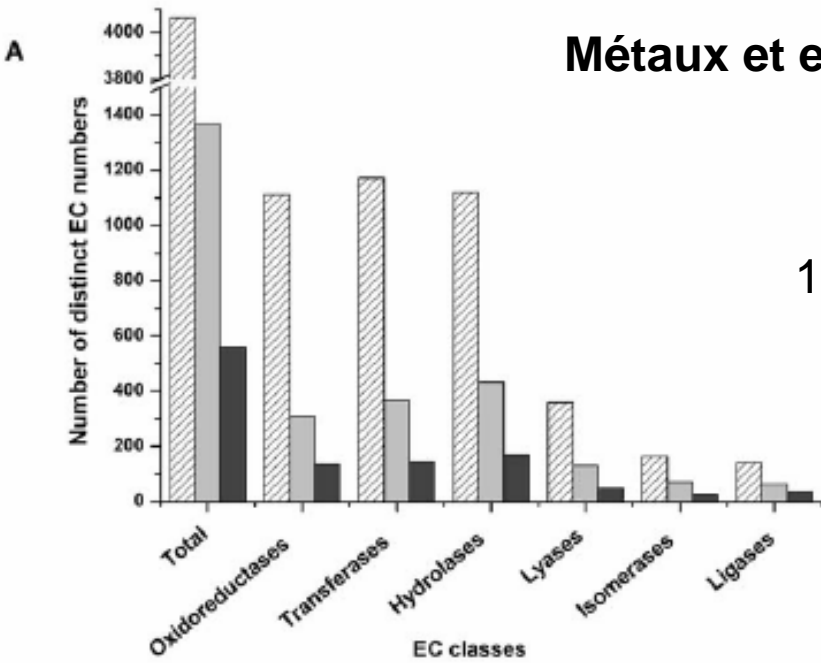
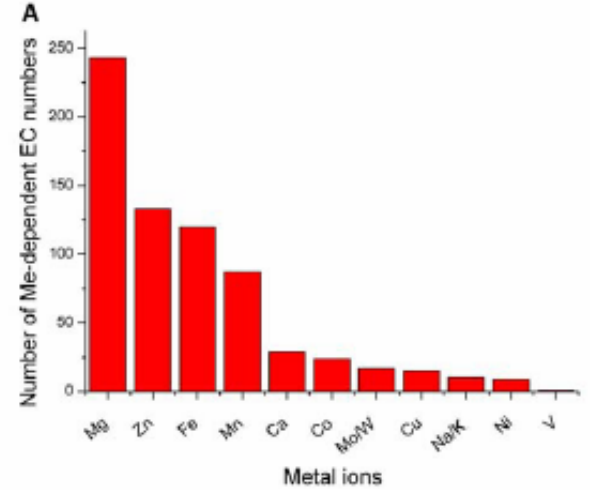
Métaux et enzymes

>4000 EC

1371 (structure)

558 (métal)

13 métaux différents

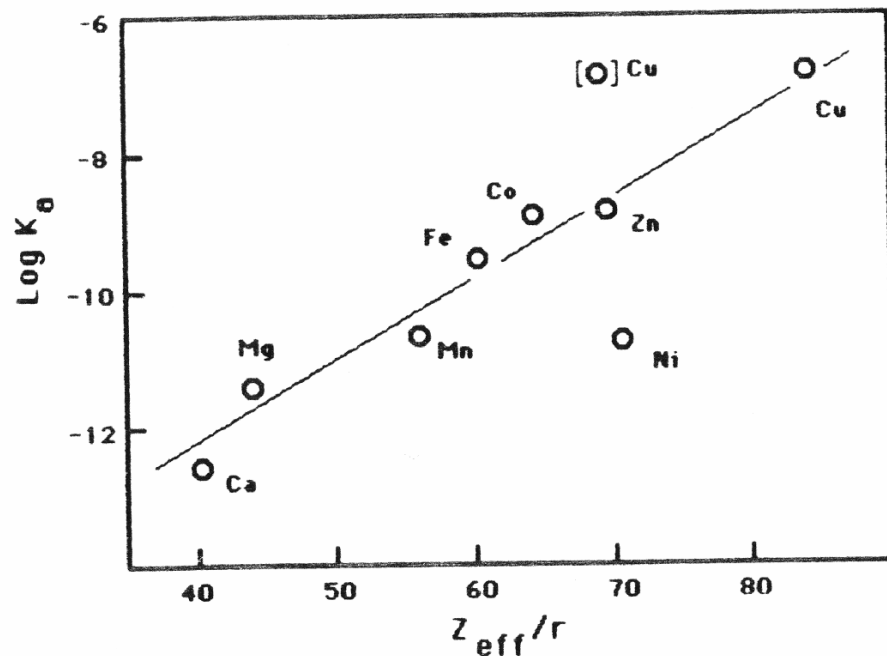
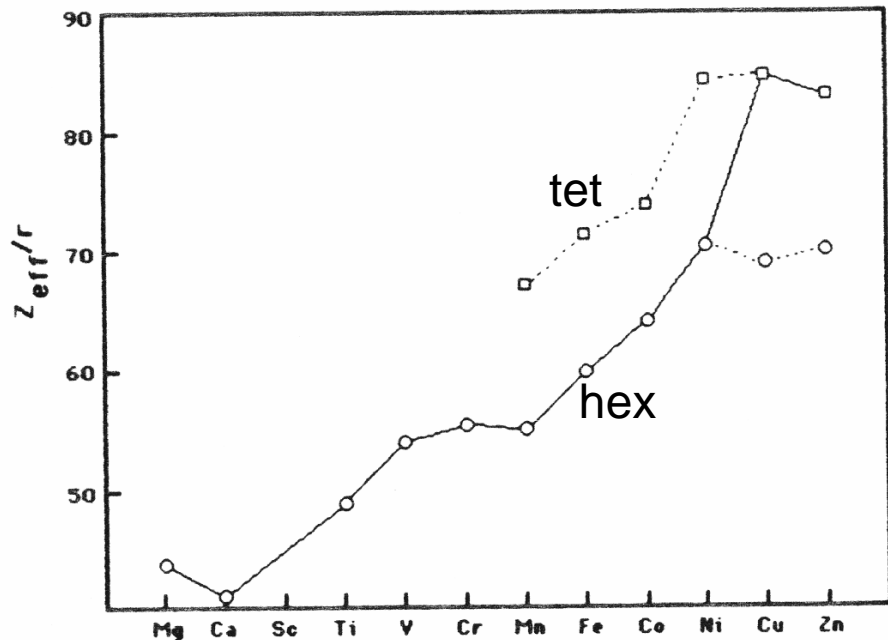
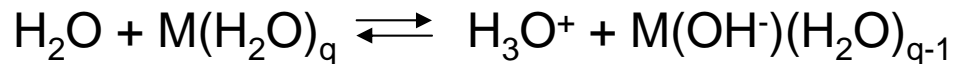


Quel métal pour quelle fonction ?

(1) Le critère d'abondance

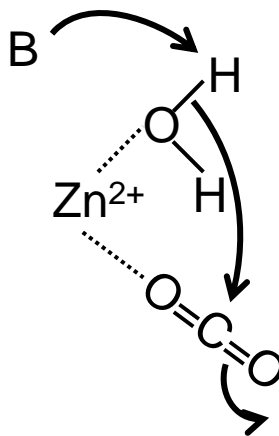
(2) Le critère d'efficacité chimique

Exemple 1: Zn²⁺, le meilleur acide de Lewis



Z_{eff} charge électrique effective
r rayon ionique effectif

Co, Fe, Cu, Mn ??



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

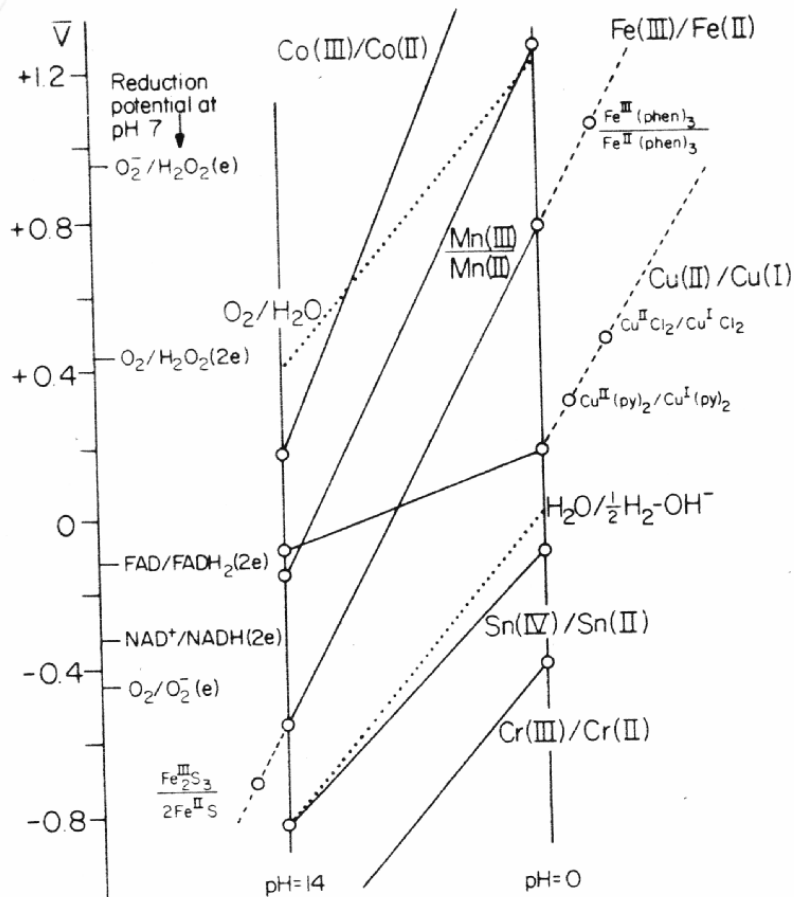


Figure 1. The reduction potentials of some important metal ions and other redox systems. O represents the reduction potential of a metal ion in an aqueous medium either at pH = 0 or at pH = 14, or the reduction potential of a simple metal complex. See the text for a more detailed explanation.

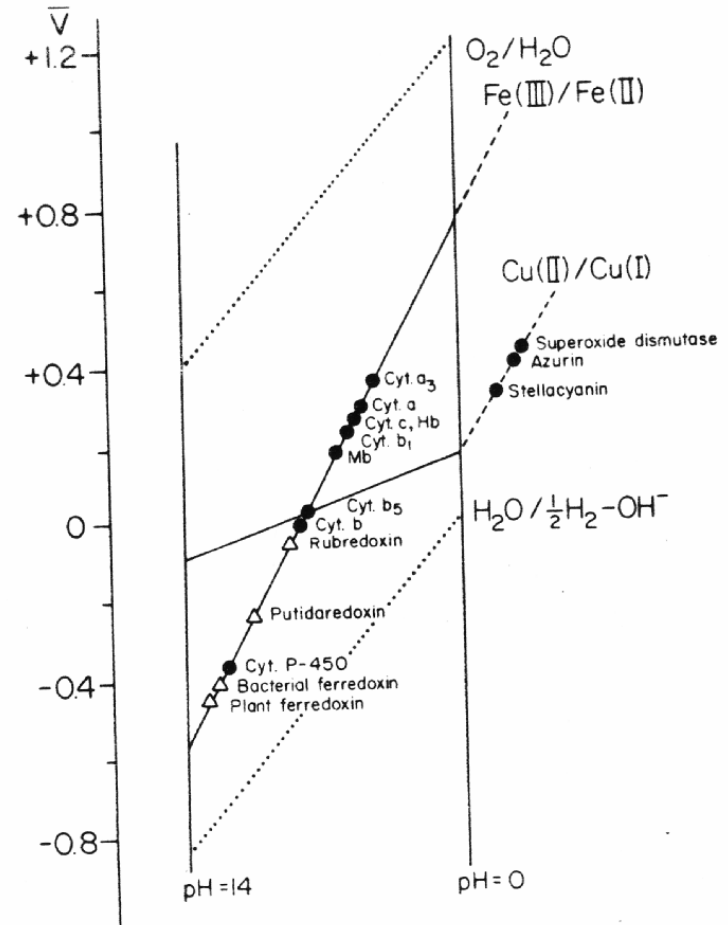
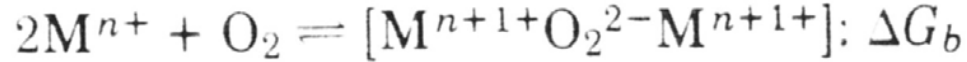


Figure 2. The reduction potentials of iron- and copper-enzymes and proteins at pH 7. The point represents merely the reduction potential value; the position on the pH axis has no meaning. See Figure 1 for the explanation of the dotted lines and the straight solid or broken lines.

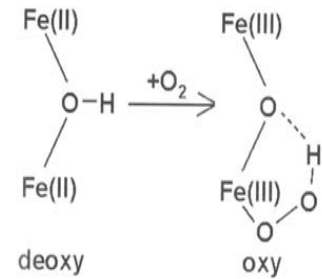
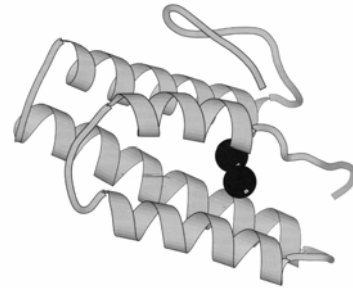
Exemple 3: Fe²⁺ et Cu⁺ pour le transport d'O₂

Hemocyanine

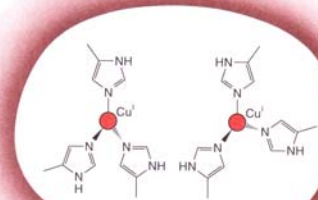


Rough Estimates of ΔG_a (kcal/mole) and ΔG_b (kcal/mole)

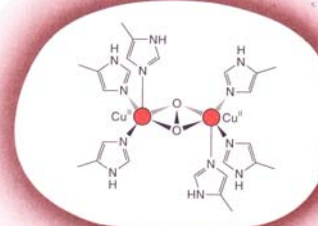
M ⁿ⁺	ΔG_a	ΔG_b
Ti(II)aq	+1.7	-29.2
Ti(III) (in 5 F H ₃ PO ₄)	+6.9	-19.0
V(II)aq	+4.4	-24.0
Cr(II)aq	+0.9	-31.0
Mn(II) (in 8 F H ₂ SO ₄)	+47.7	+62.6
Mn(II)/CN ⁻	+5.2	-22.4
Fe(II) (pH \lesssim 2)	+28.0	+23.2
Fe(II) (pH \sim 6)	+10.0	-11.8
Fe(OH)₂	-2.6	-38.0
Fe(II)/CN⁻	+18.6	-4.4
Co(II)aq	+52.7	+72.6
Co(II)NH 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



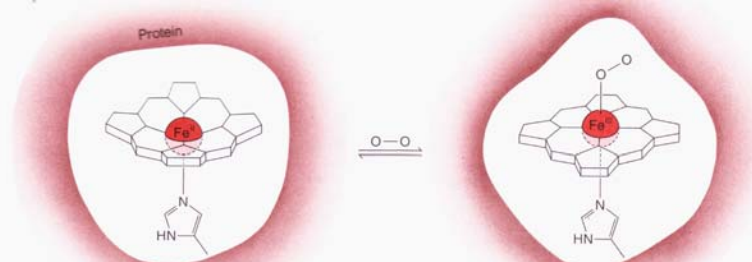
hemerythrin



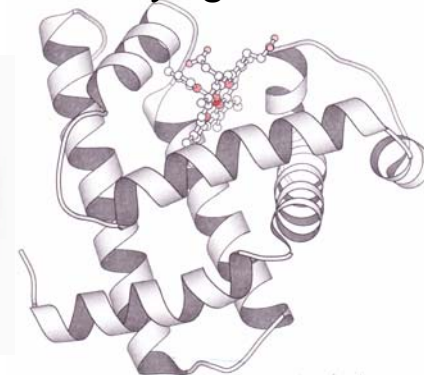
(a) Deoxyhemocyanin



(b) Oxyhemocyanin



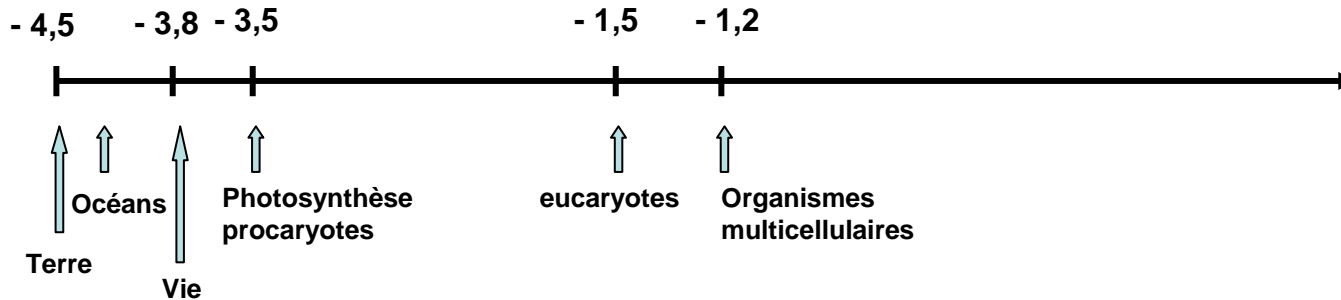
Hemoglobine
myoglobine



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 , $\text{H}_2\dots$):
 Fe^{2+} , Zn^{2+} , Mn^{2+} , Cu^{2+} , Ni^{2+}

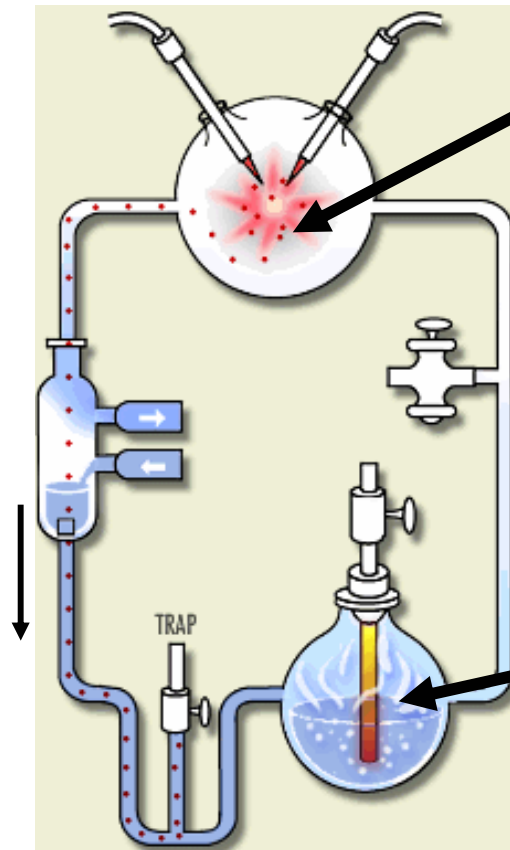


Fondement de la chimie prébiotique

L'expérience de Miller (1953)



Stanley Miller
(1930-2007)



« Atmosphère irradiée »
H₂O, CH₄
NH₃, H₂
...

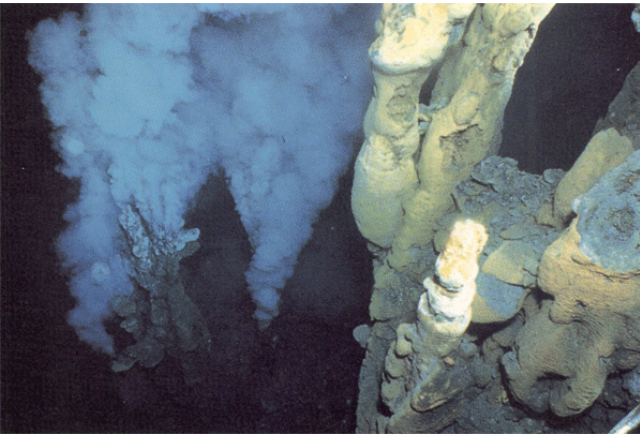
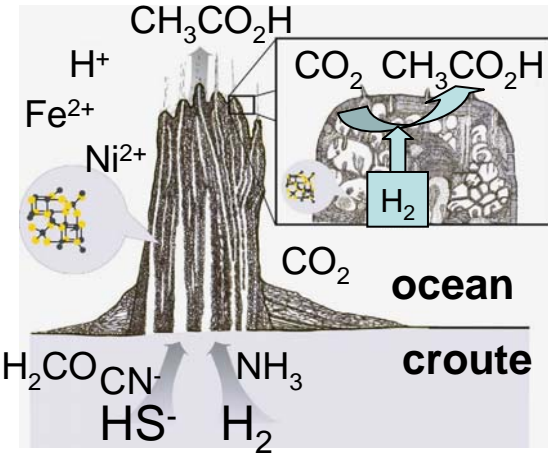
« Océan chaud »
Acides,
Acides aminés,
Sucres,...



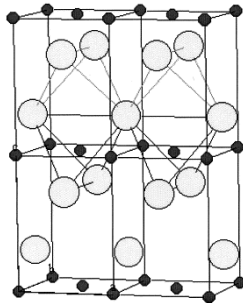
Origine hétérotrophe de la vie

Origine autotrophe de la vie ?

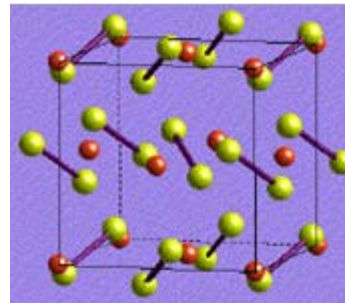
- Eau liquide
- Absence d'O₂
- Atmosphère « oxydante »: CO₂, CO, N₂,...
- **Fe**, Ni et soufre: pyrite FeS₂, greigite (FeNi)S, mackinawite, ... Catalyse hétérogène
- Hyperthermophile ? (source hydrothermale)



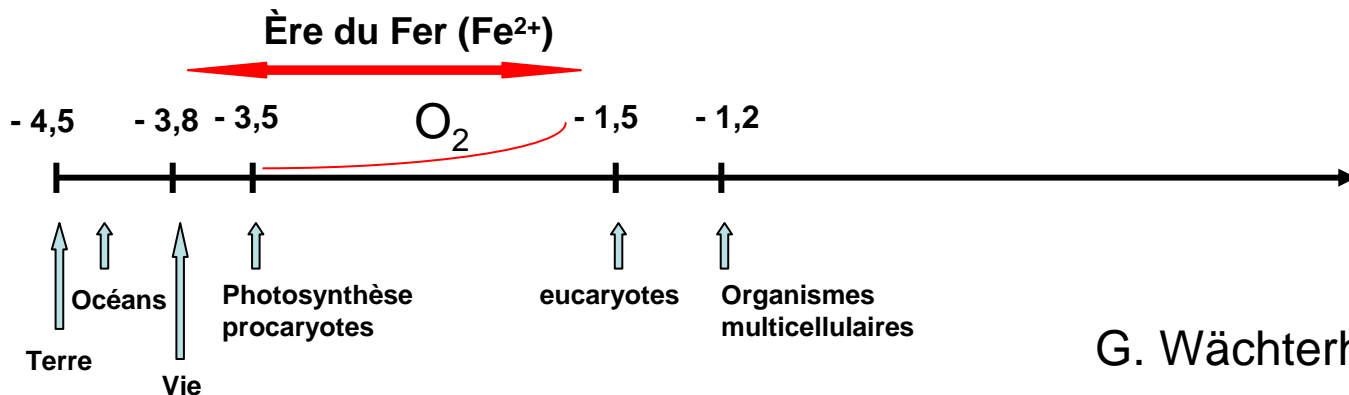
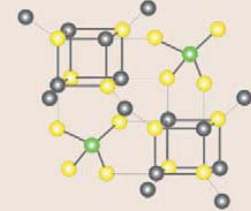
mackinawite



pyrite

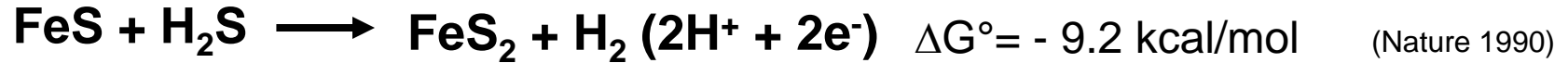


greigite

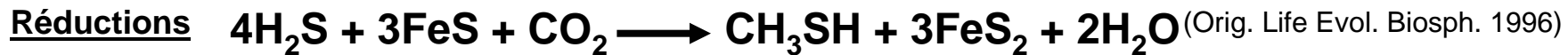


Réactions chimiques

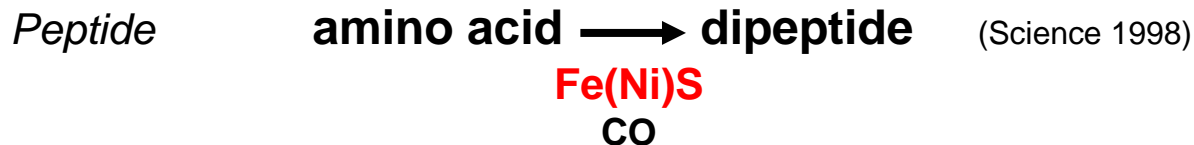
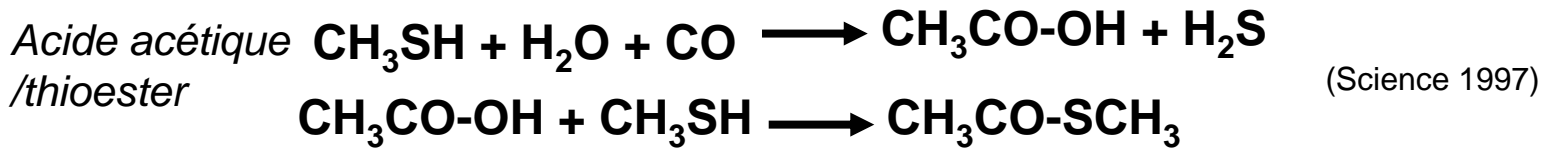
Fe(Ni)-sulfures: une source de pouvoir réducteur et un catalyseur

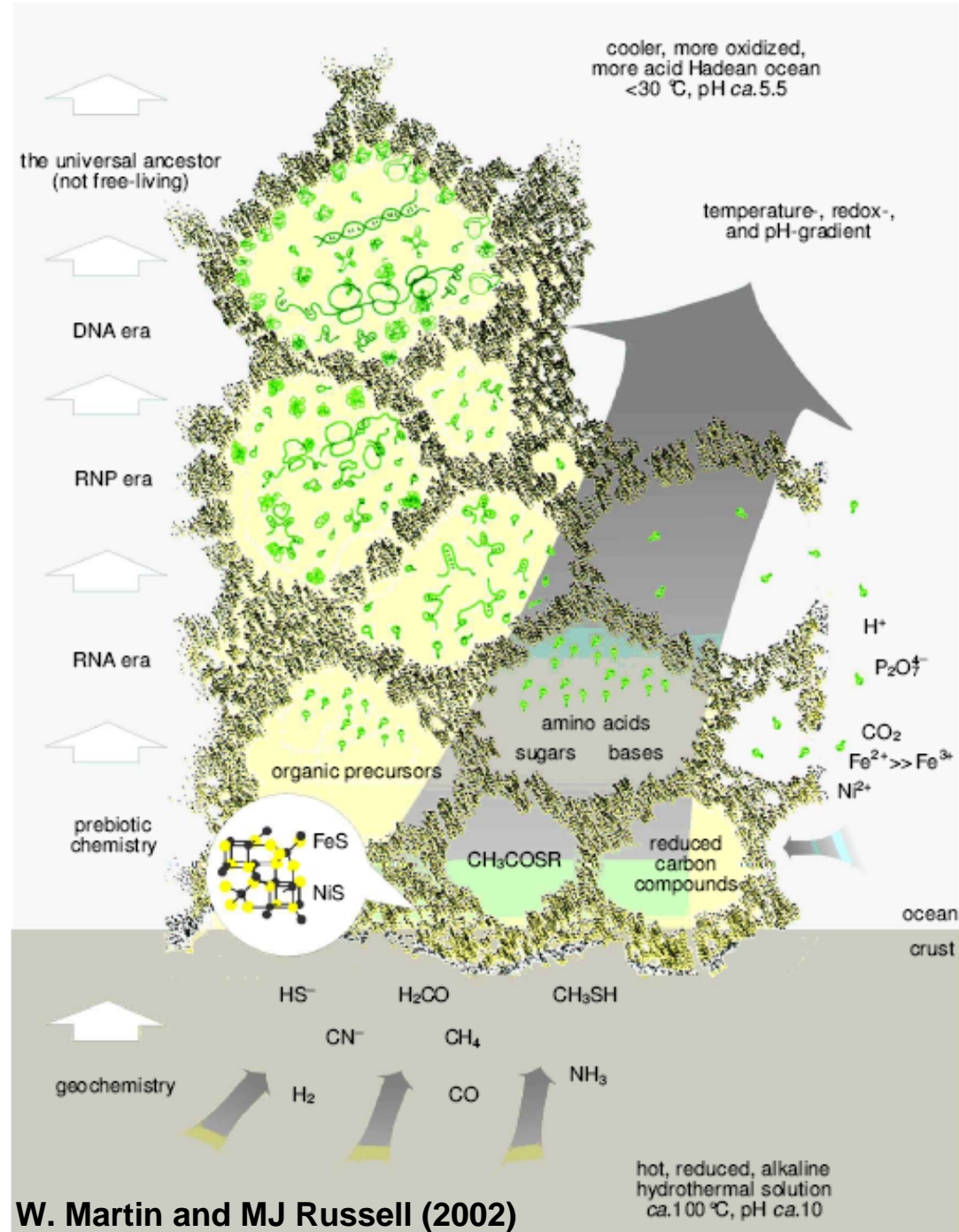
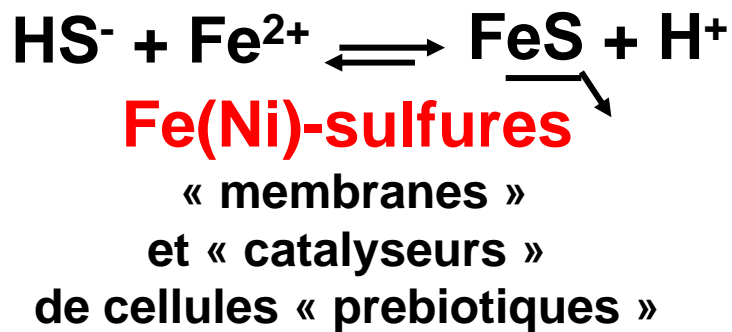
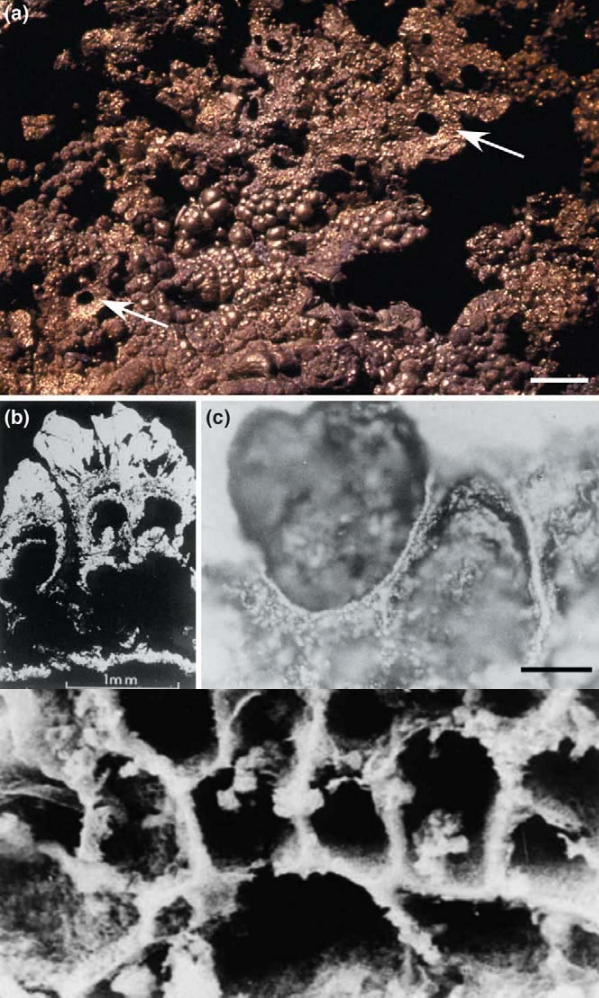


CO₂/CO: une source de carbone; **H₂S**: une source de soufre

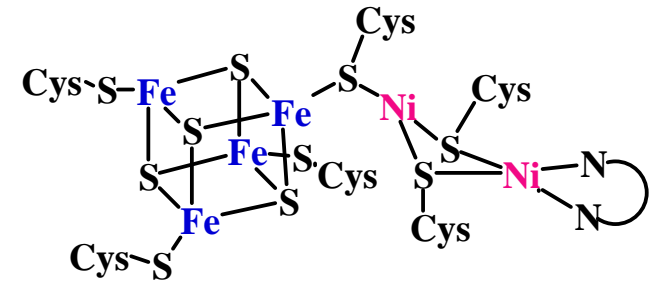
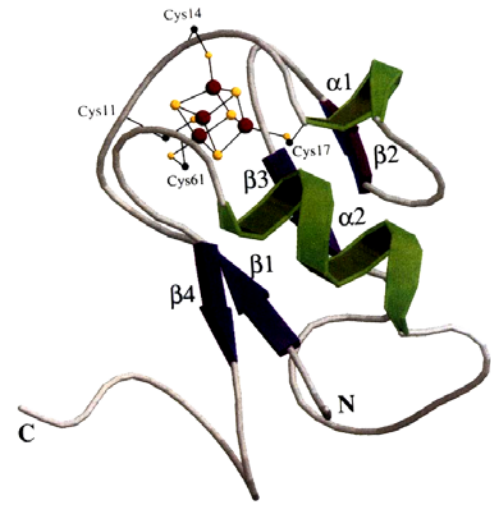
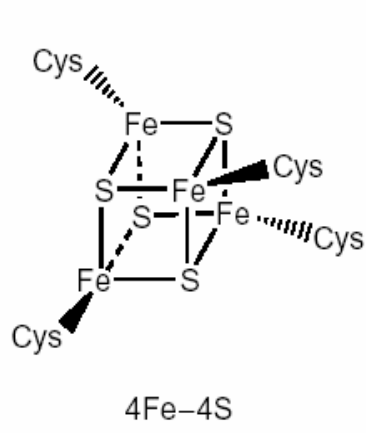


Formation de liaisons C-C

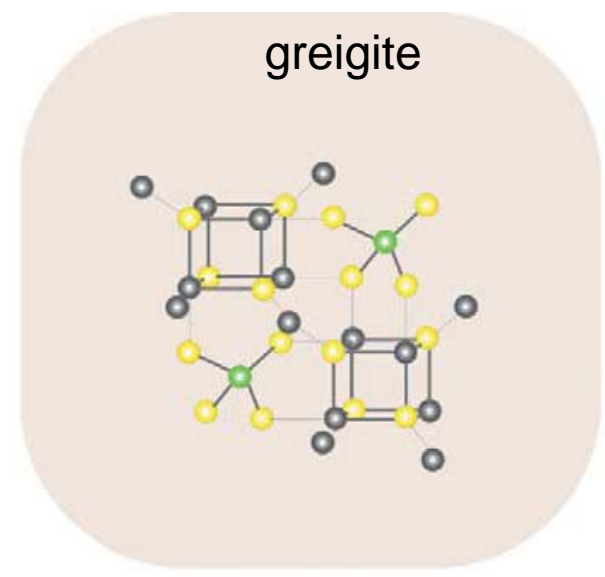
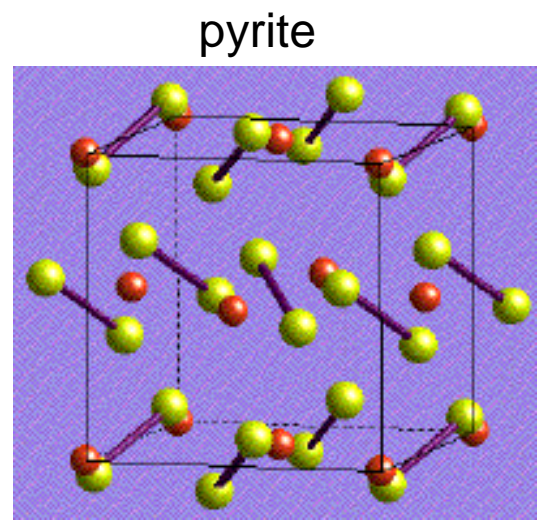
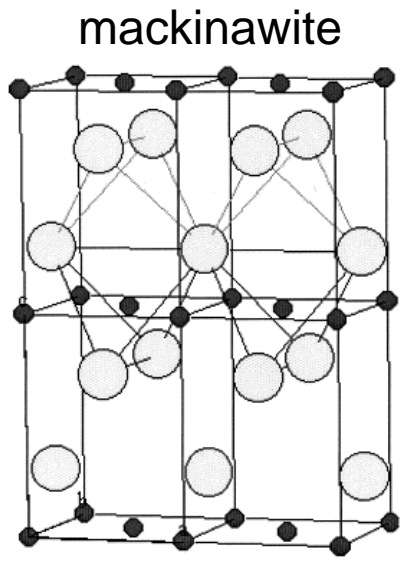




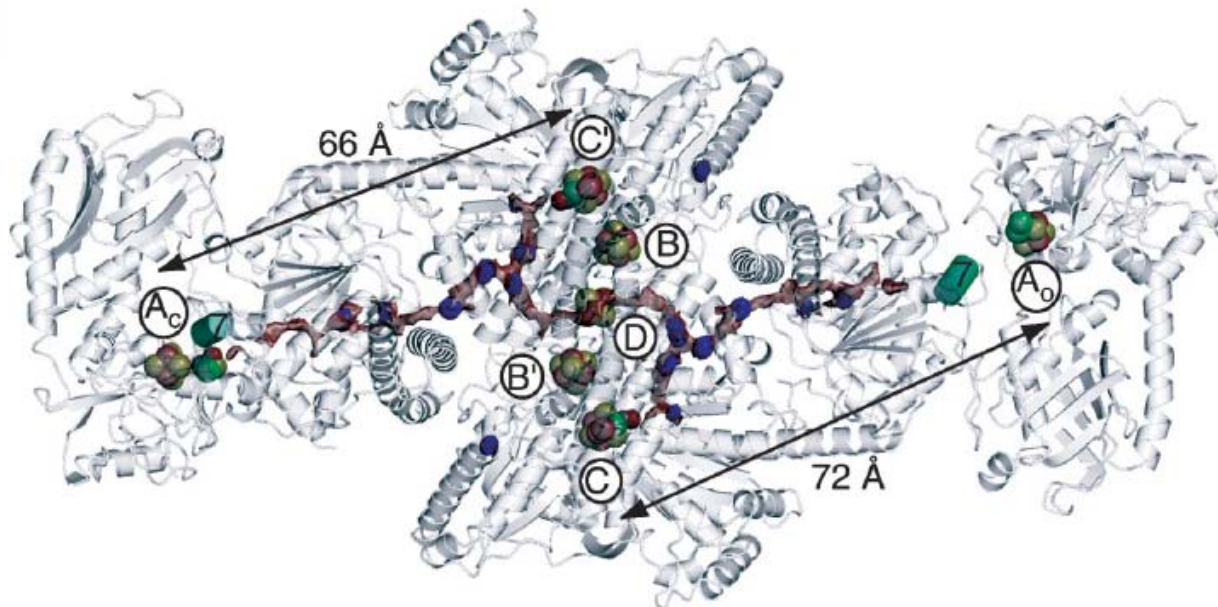
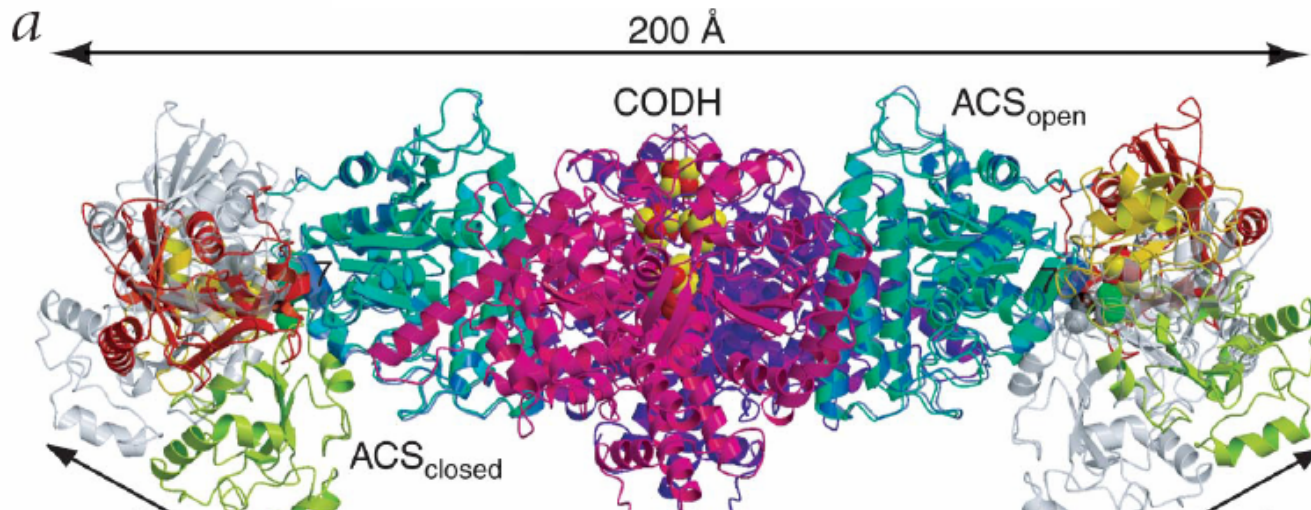
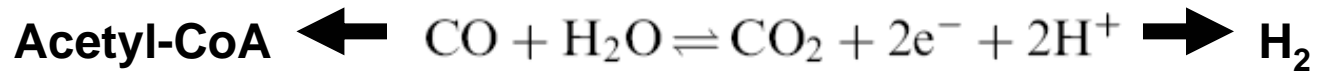
Centres Fe(M)S de protéines: inventions du monde biologique ou mimes d'ancêtres minéraux capables d'activité catalytique ?



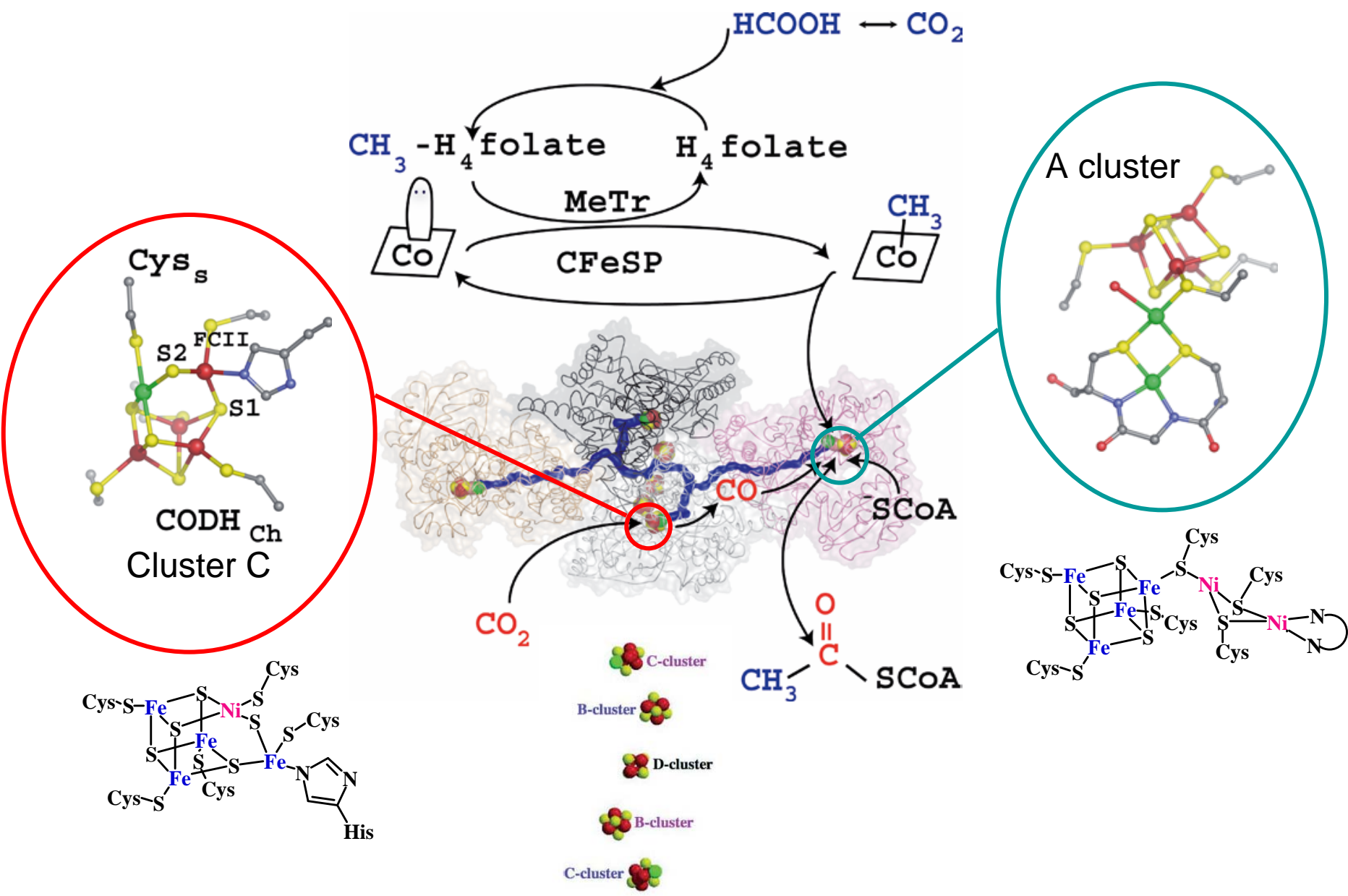
**Cluster A de l'ACS
(acetyl-CoA synthase)**



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



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);

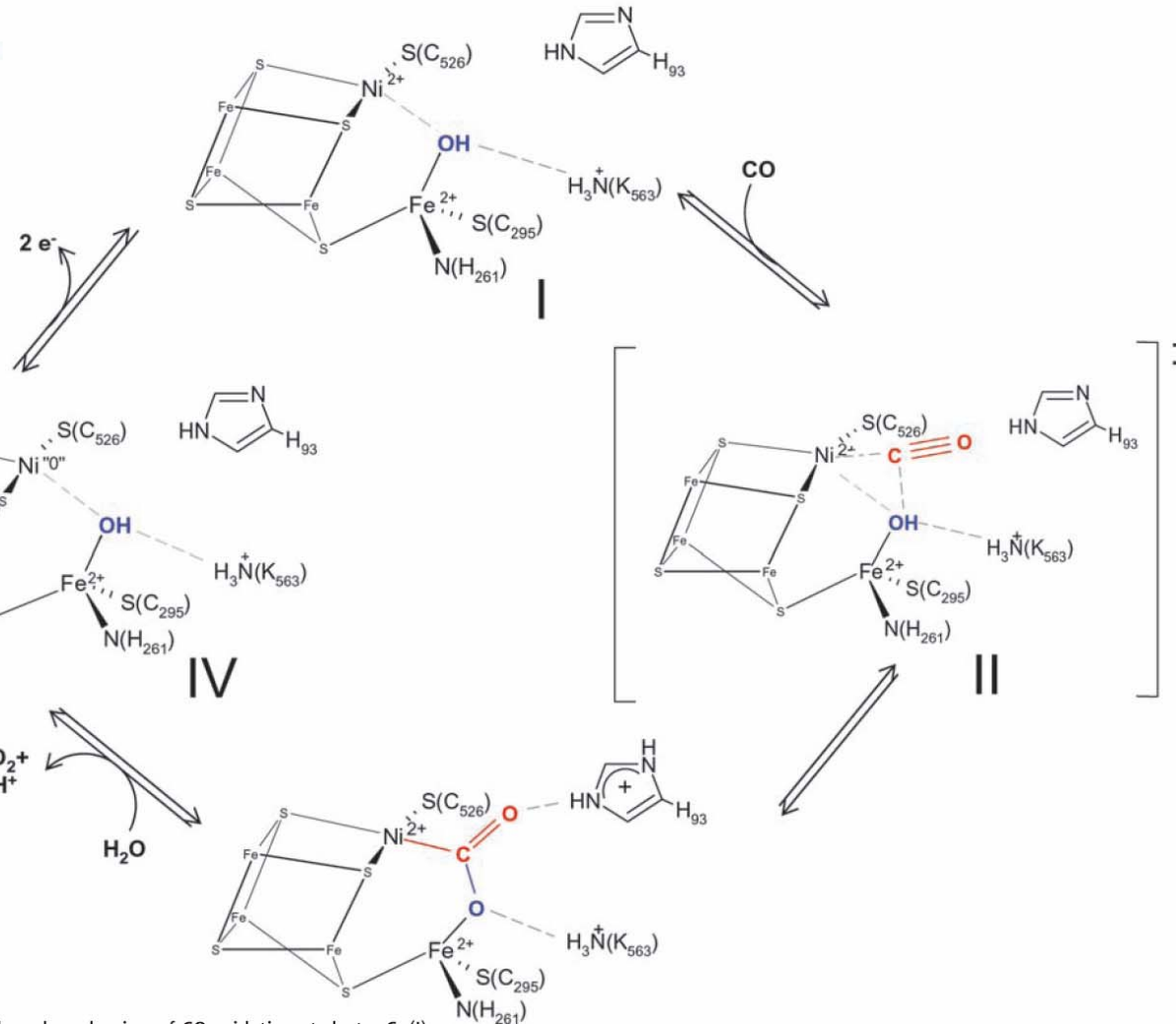
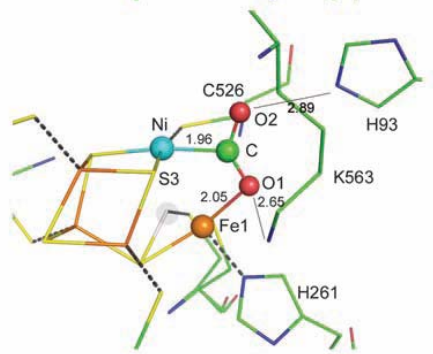
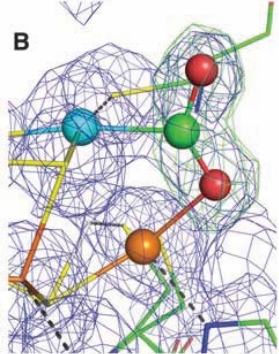
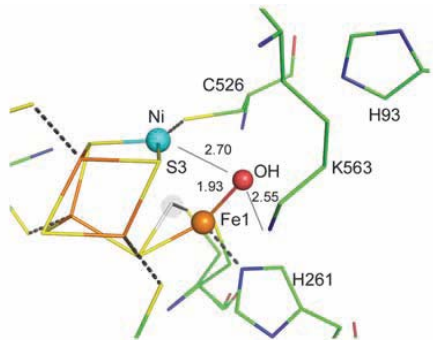
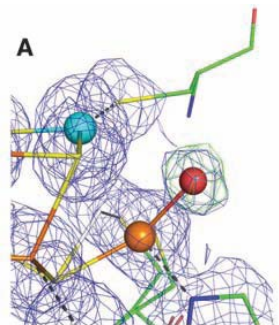
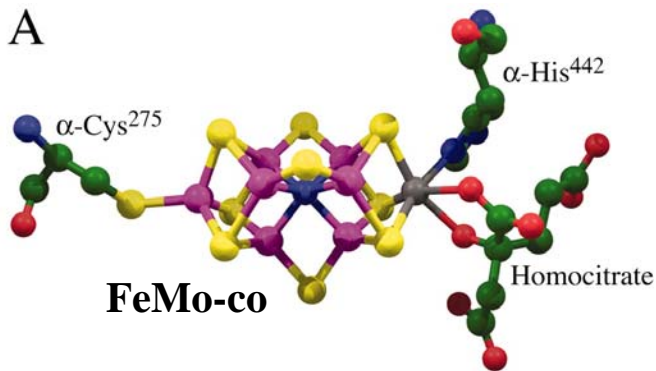


Fig. 2. Structural analysis of CO activation at C(4)

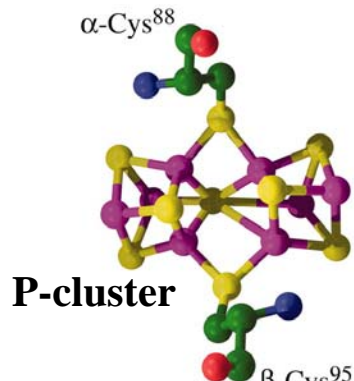
Nitrogenase



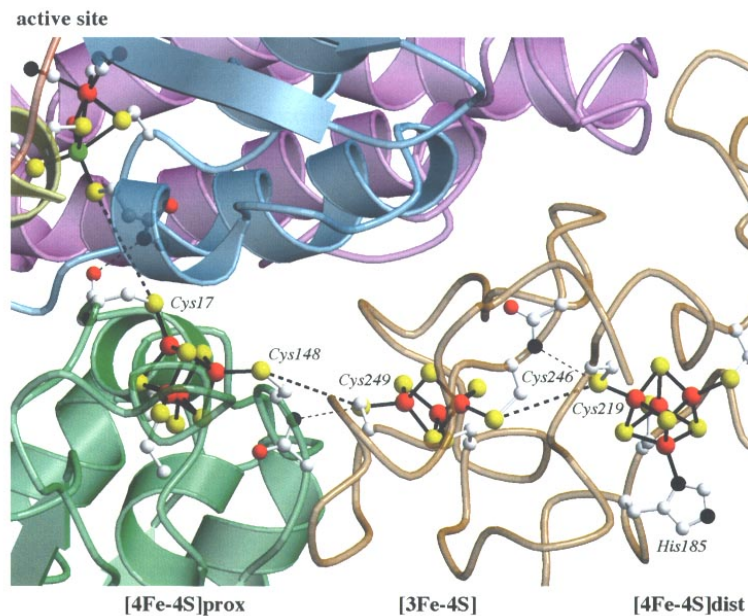
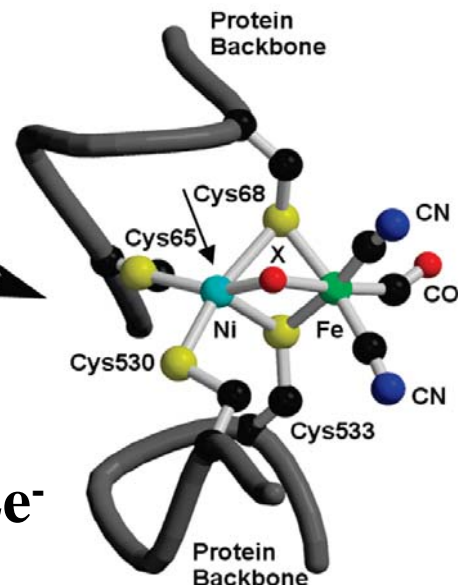
A



B

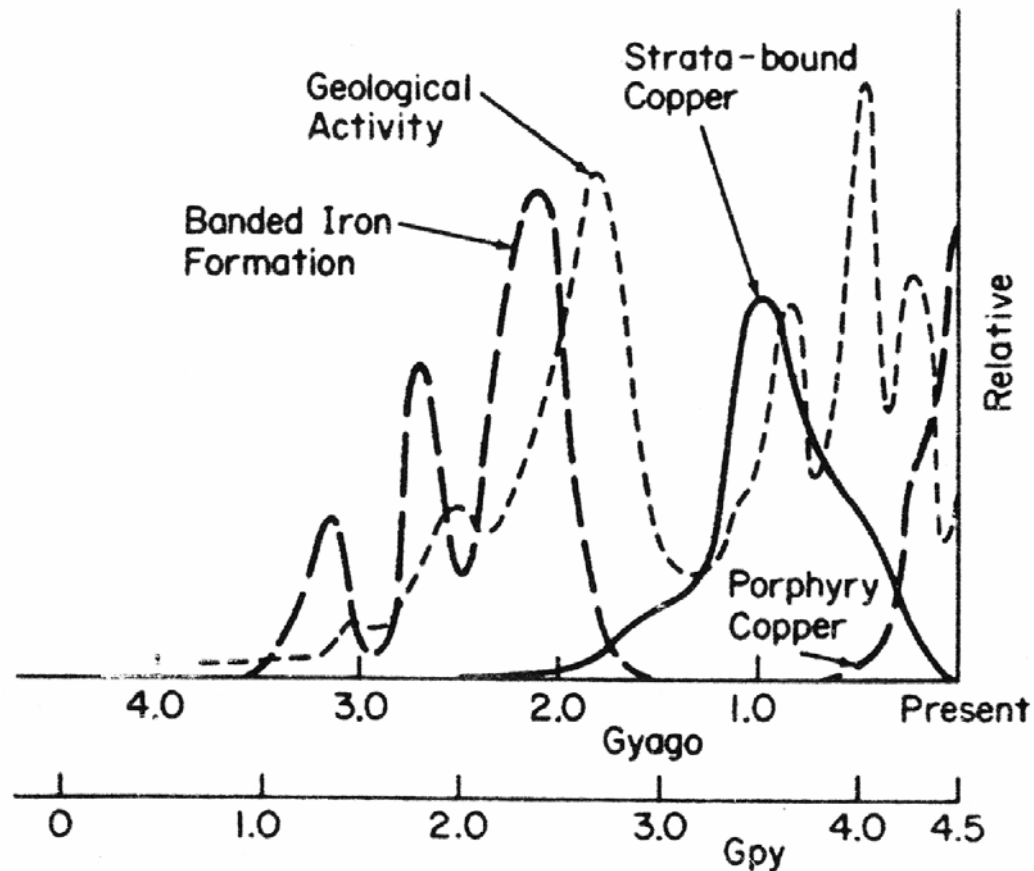


Hydrogenase

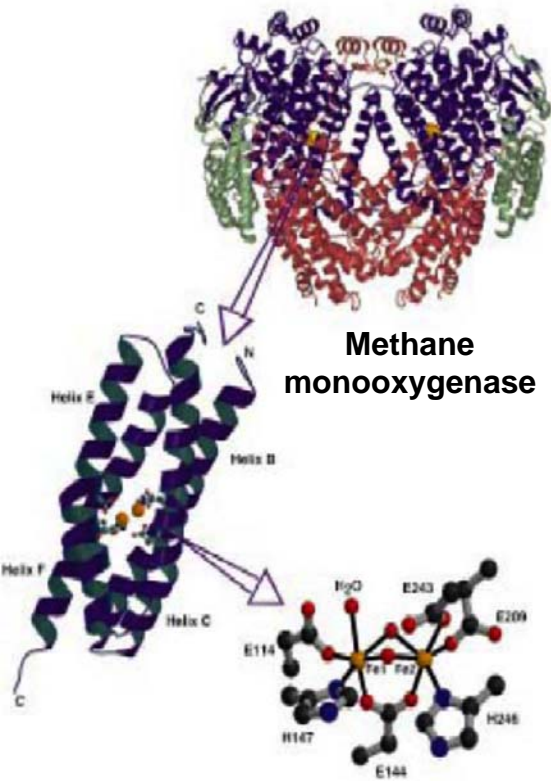


La vie à l'oxygène ?

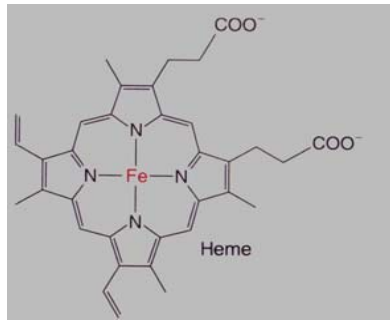
- Oxydation et précipitation du fer
- Réduction massive du carbone
- Disparition massive d'organismes vivants



La vie à l'oxygène: conséquences



- ⇒ 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

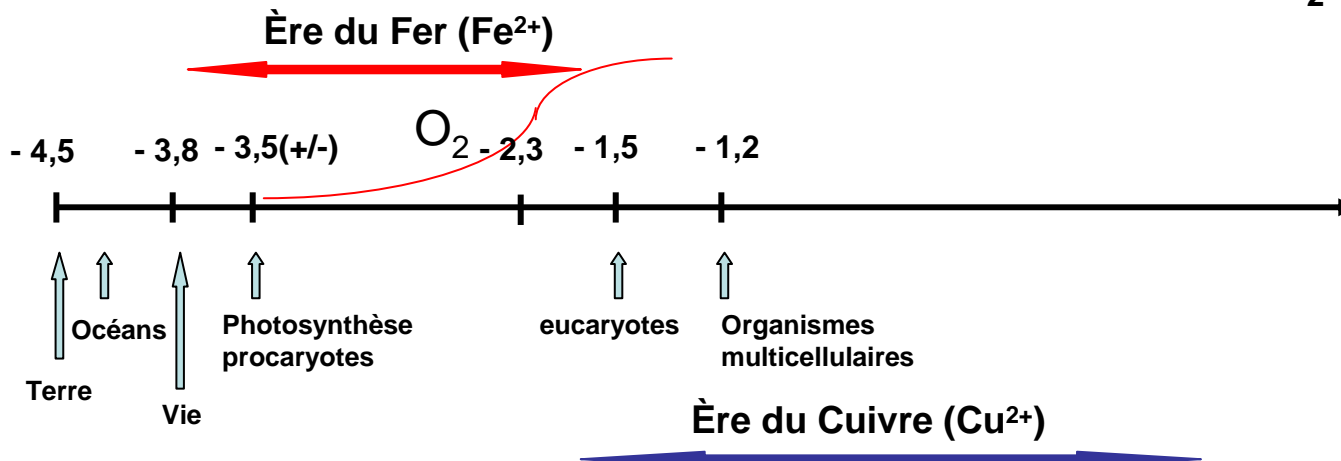


$$Fe_2O_3/Fe^{2+}: - 0,2V$$

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

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

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



La vie à l'oxygène: conséquences

→ Disparition des centres fer-soufre

Correlation motif CX₂CX₂CX₃C (120 génomes) avec:

-Méthanogénèse

-Archaea

-Anaérobiose

-*hyperthermophilie*

Numbers of the 4Fe-4S iron-sulfur motif CX₂CX₂CX₃C 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
facultative anaerobes	2	8.6
anaerobes	3	8.6
non-methanogens, non-hyperthermophiles	4	6.2
Methanogens (+ <i>Archaeoglobus fulgidus</i> ^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