Eine Möglichkeit, Energie zu speichern: Biologische Methanbildung aus H_2 und CO_2

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20-11-2013

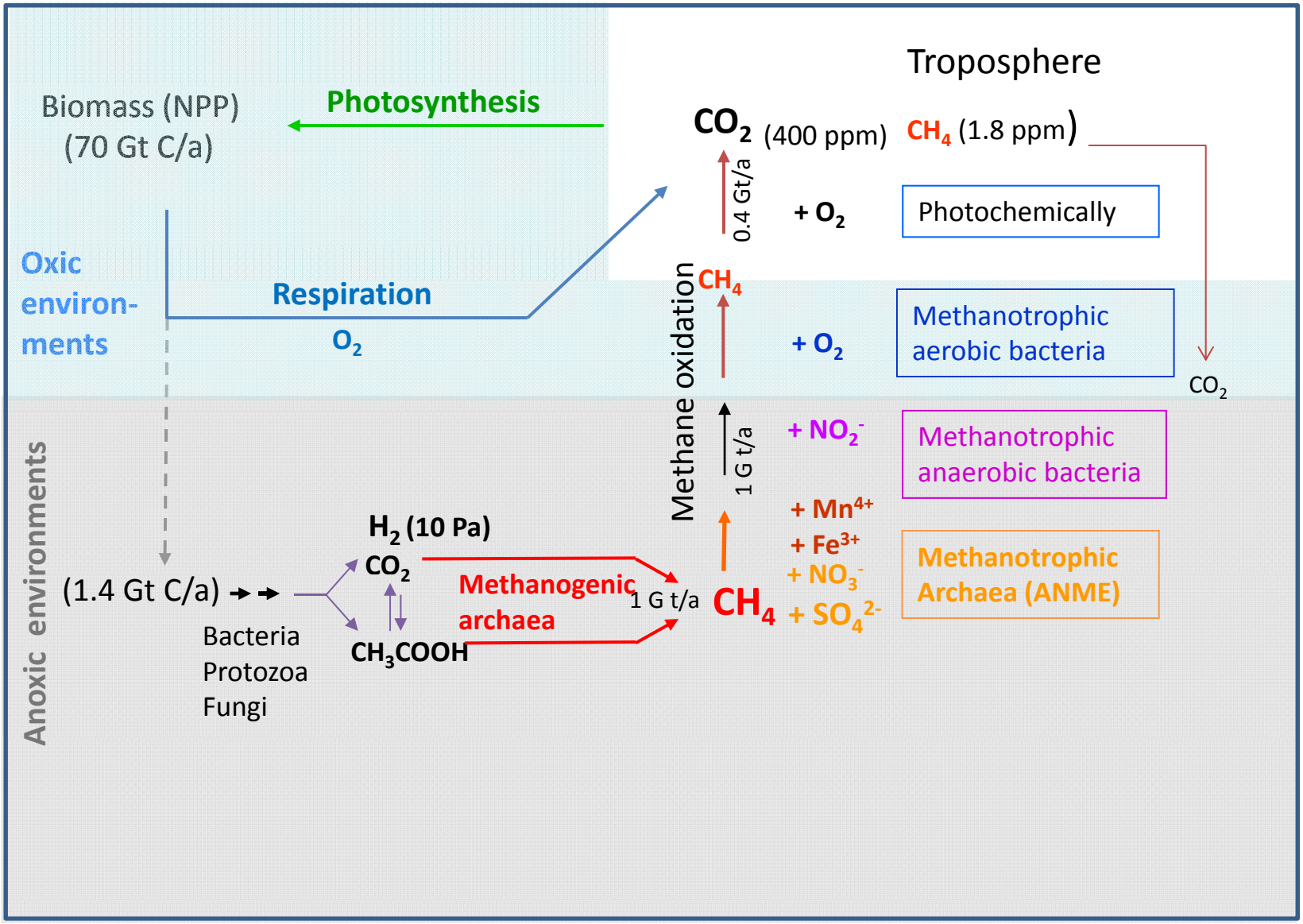
$4\ H_2 + 2\ O_2 = 4\ H_2O$ $\Delta H^o = -960$ kJ/mol

$4\ H_2 + CO_2 = CH_4 + 2\ H_2O$ $\Delta H^o = -160$ kJ/mol

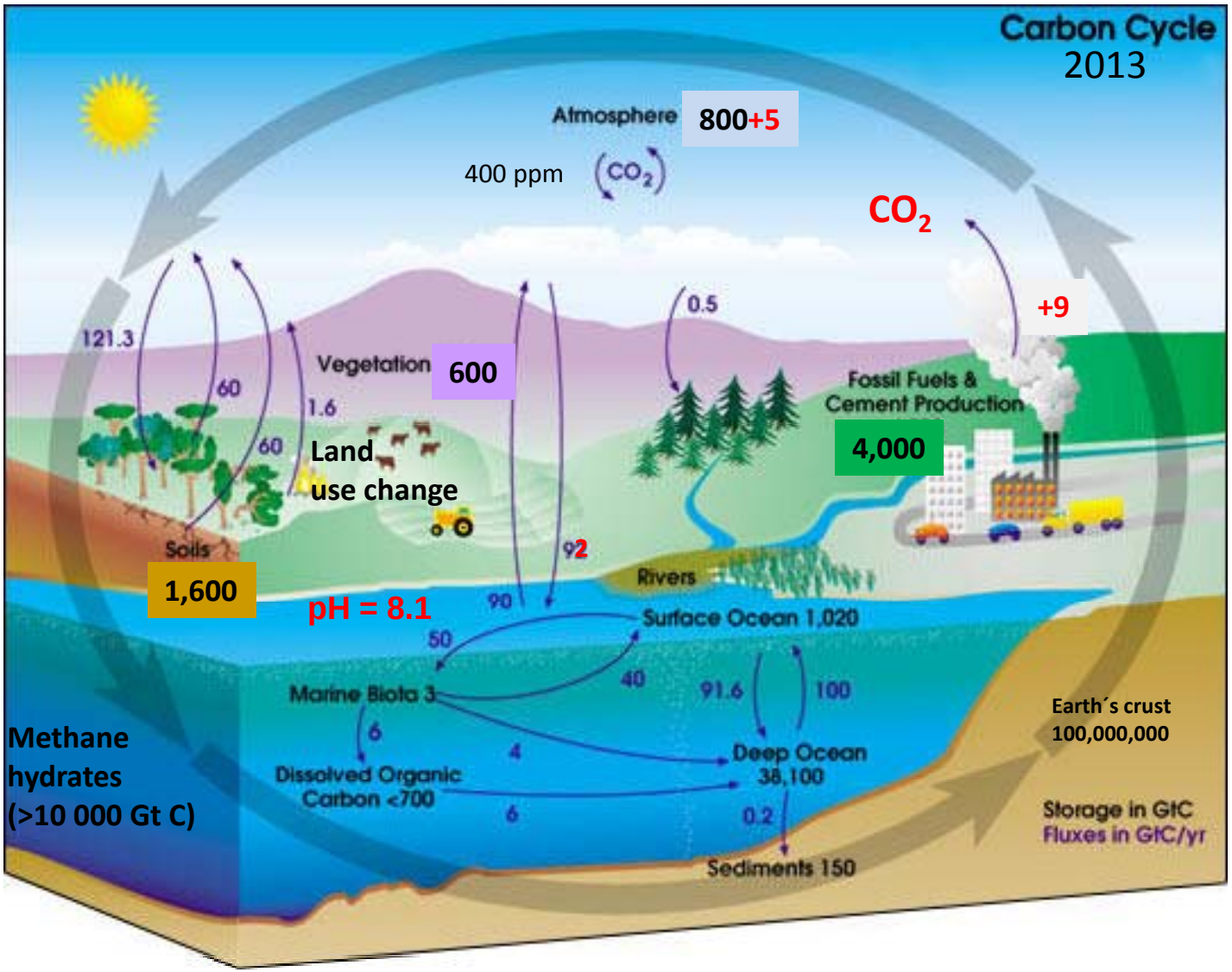
17% Verlust

$CH_4 + 2\ O_2 = 2\ H_2O + CO_2$ $\Delta H^o = -800$ kJ/mol

Methane cycle



Terrestrial NPP
= 60 GtC/yr



Marine NPP
= 10 GtC/yr

Storage in GtC Fluxes in GtC/yr Anthropogenic in GtC/yr

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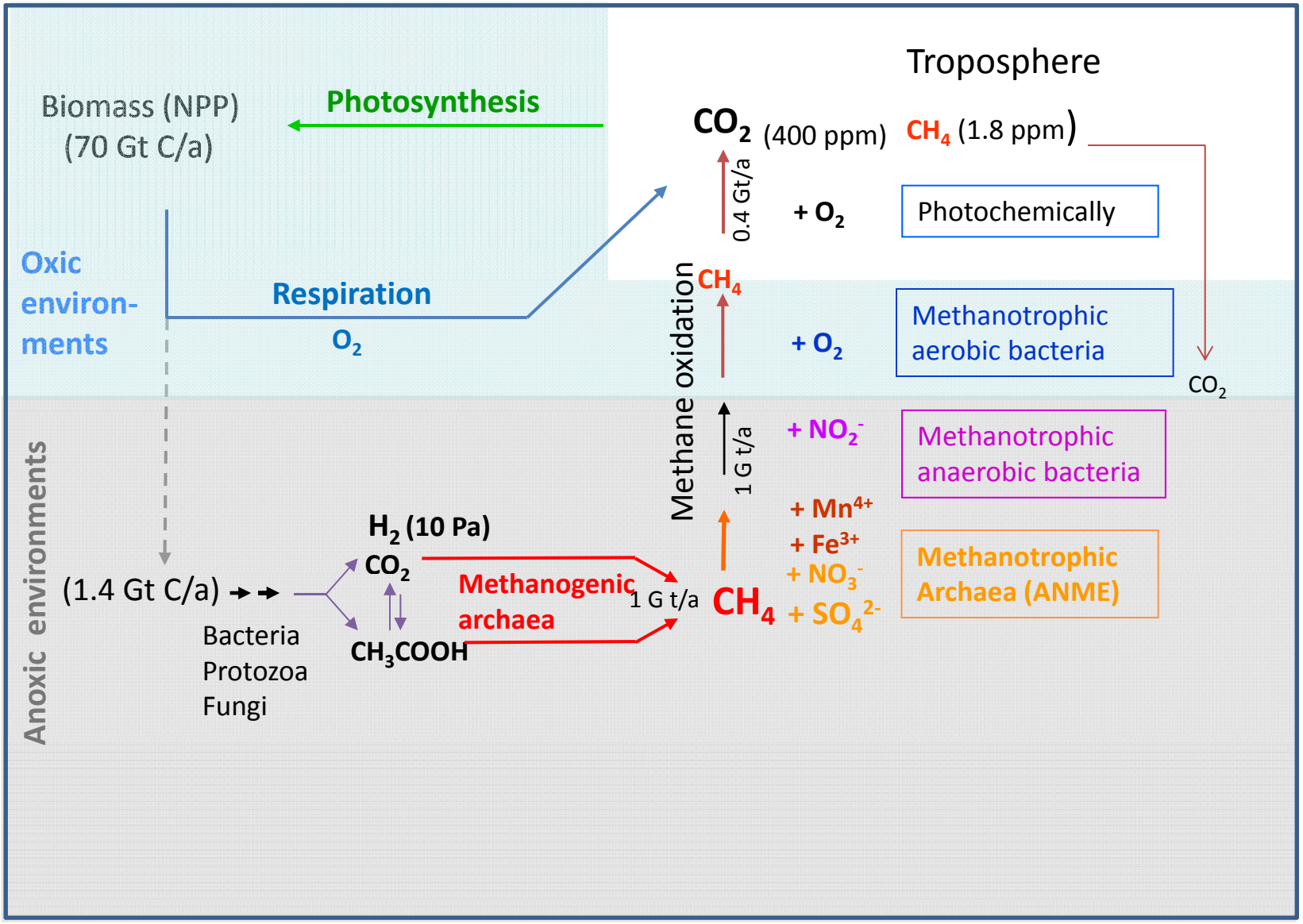
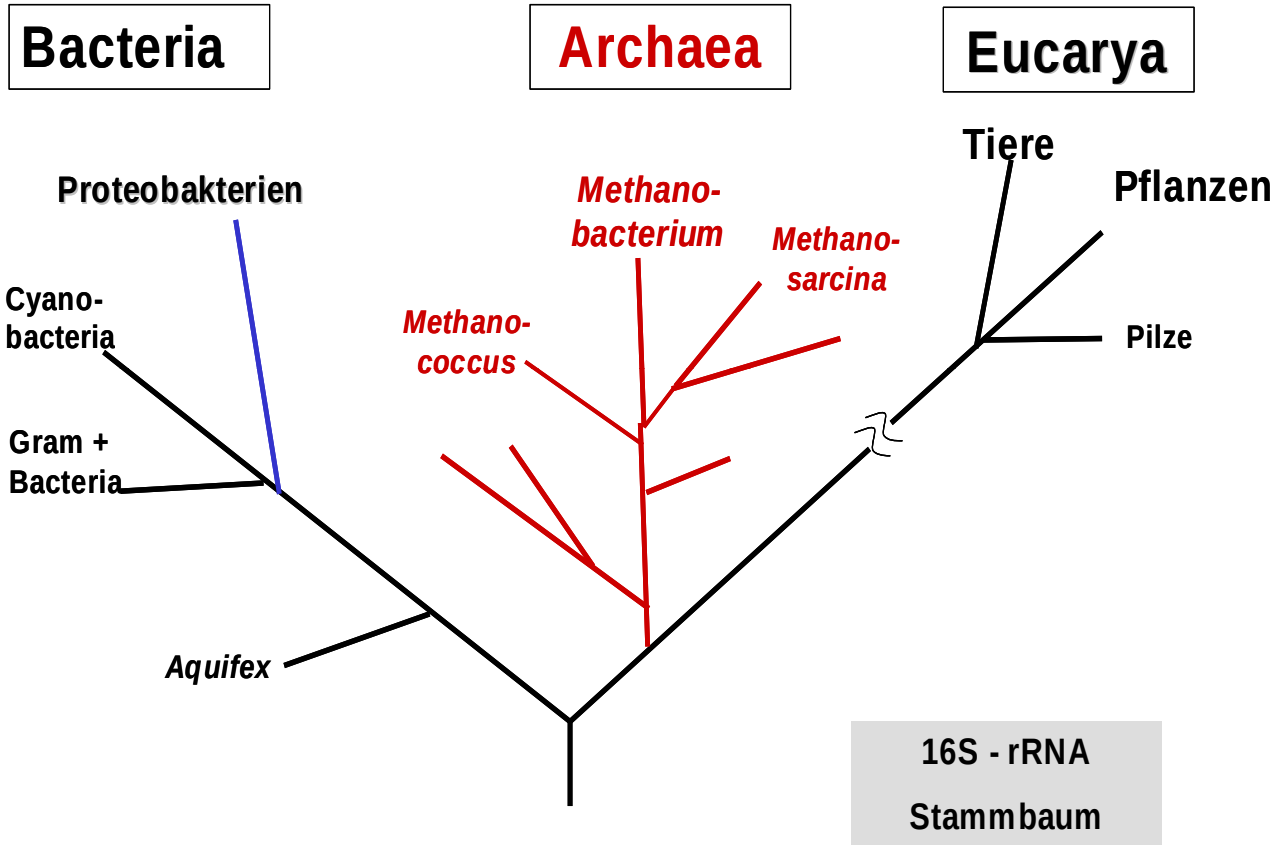
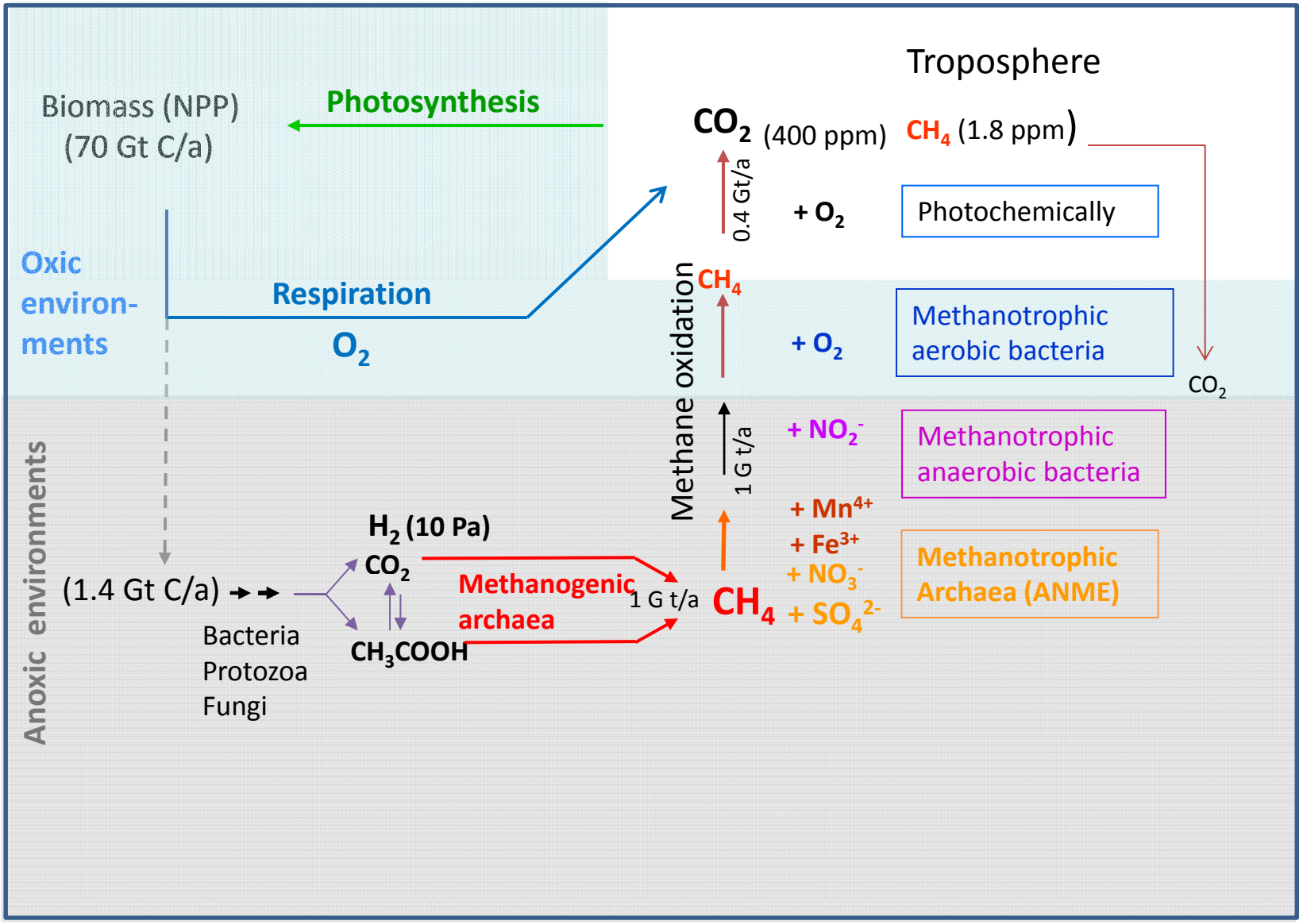
Methane cycle

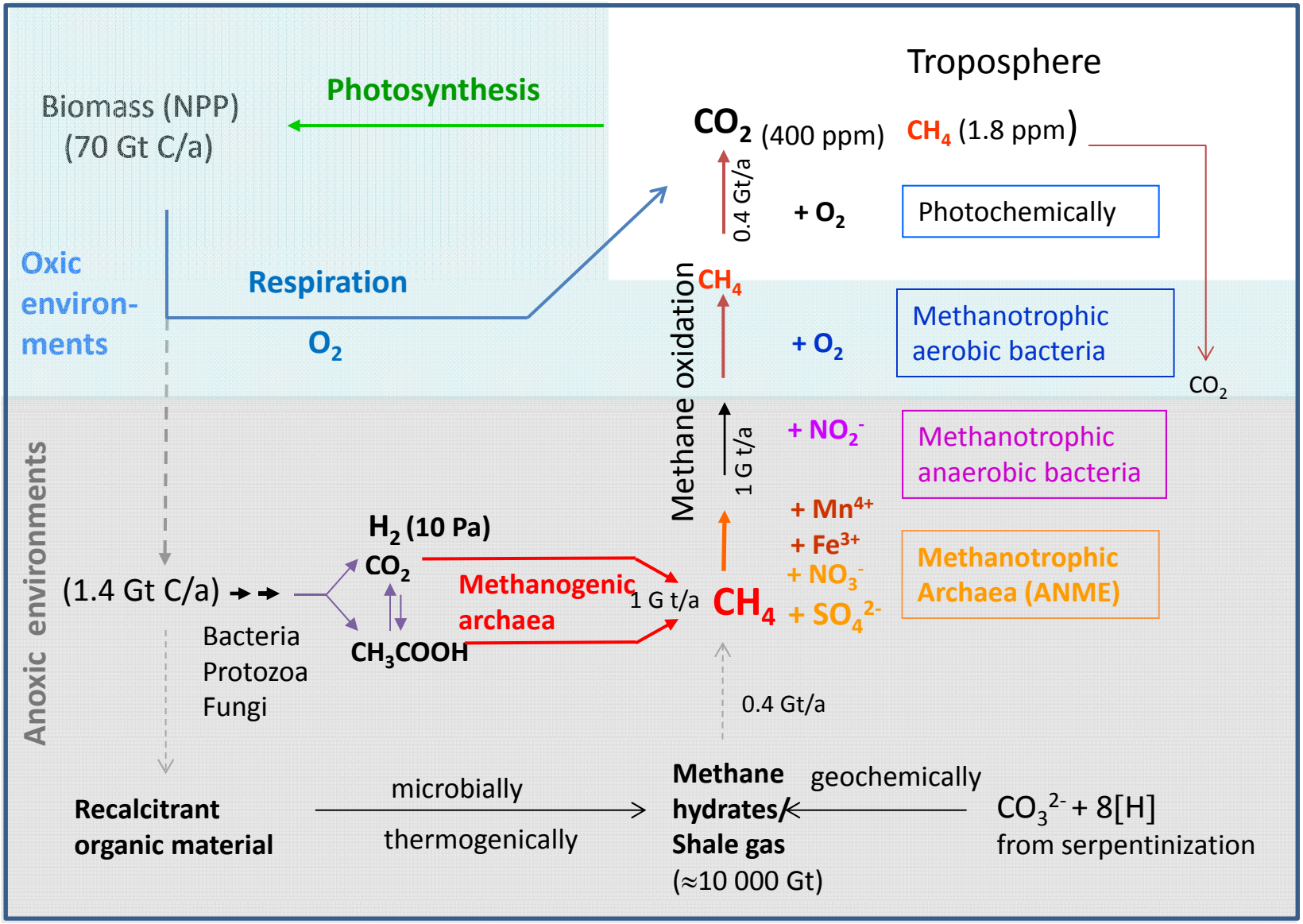



Bacteria
Archaea
Eucarya
Tiere
Pflanzen
Proteobakterien
Methano-
bacterium
Methano-
sarcina
Cyano-
bacteria
Methano-
coccus
Pilze
Gram +
Bacteria
Aquifex
16S - rRNA
Stammbaum

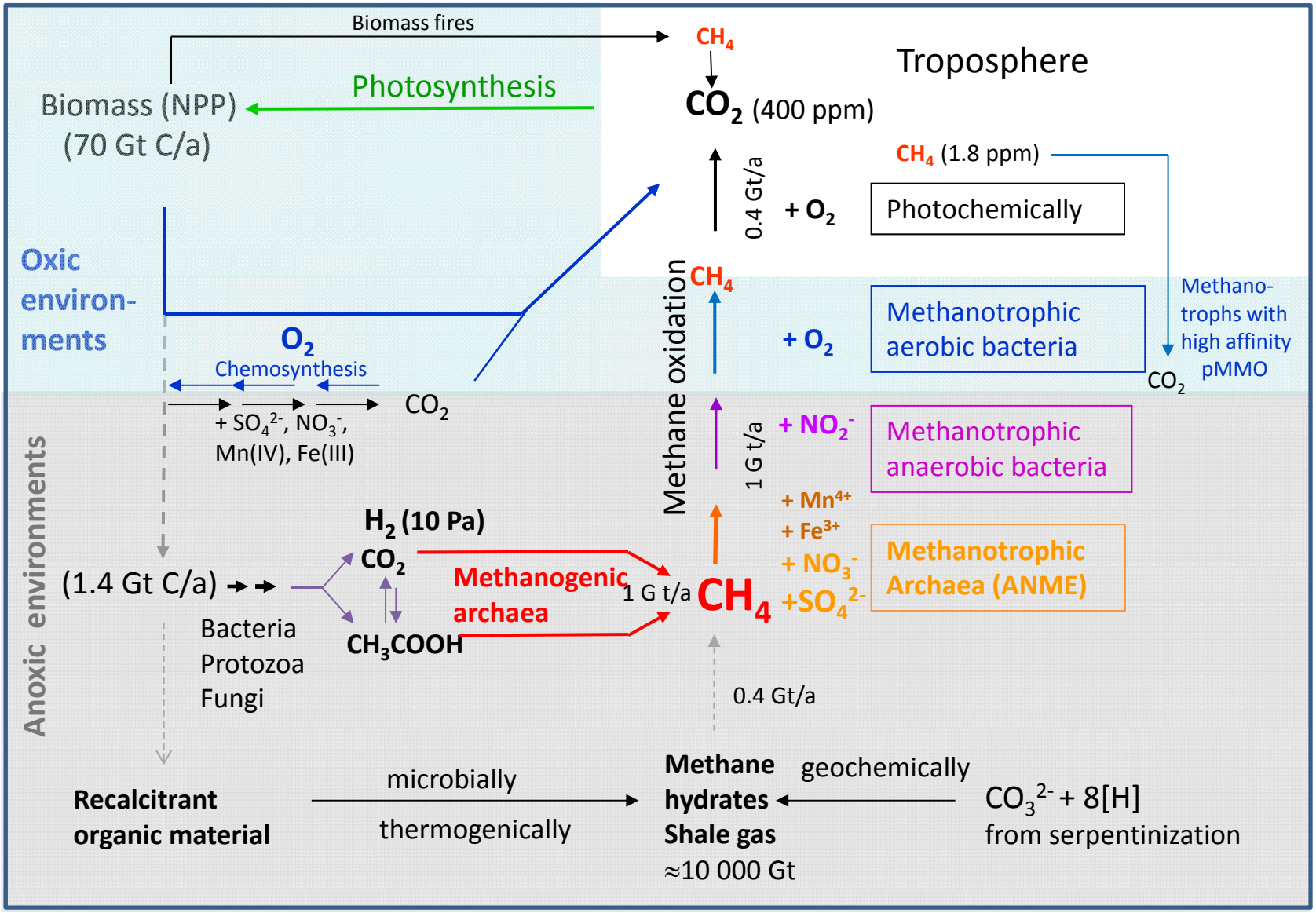
Methane cycle



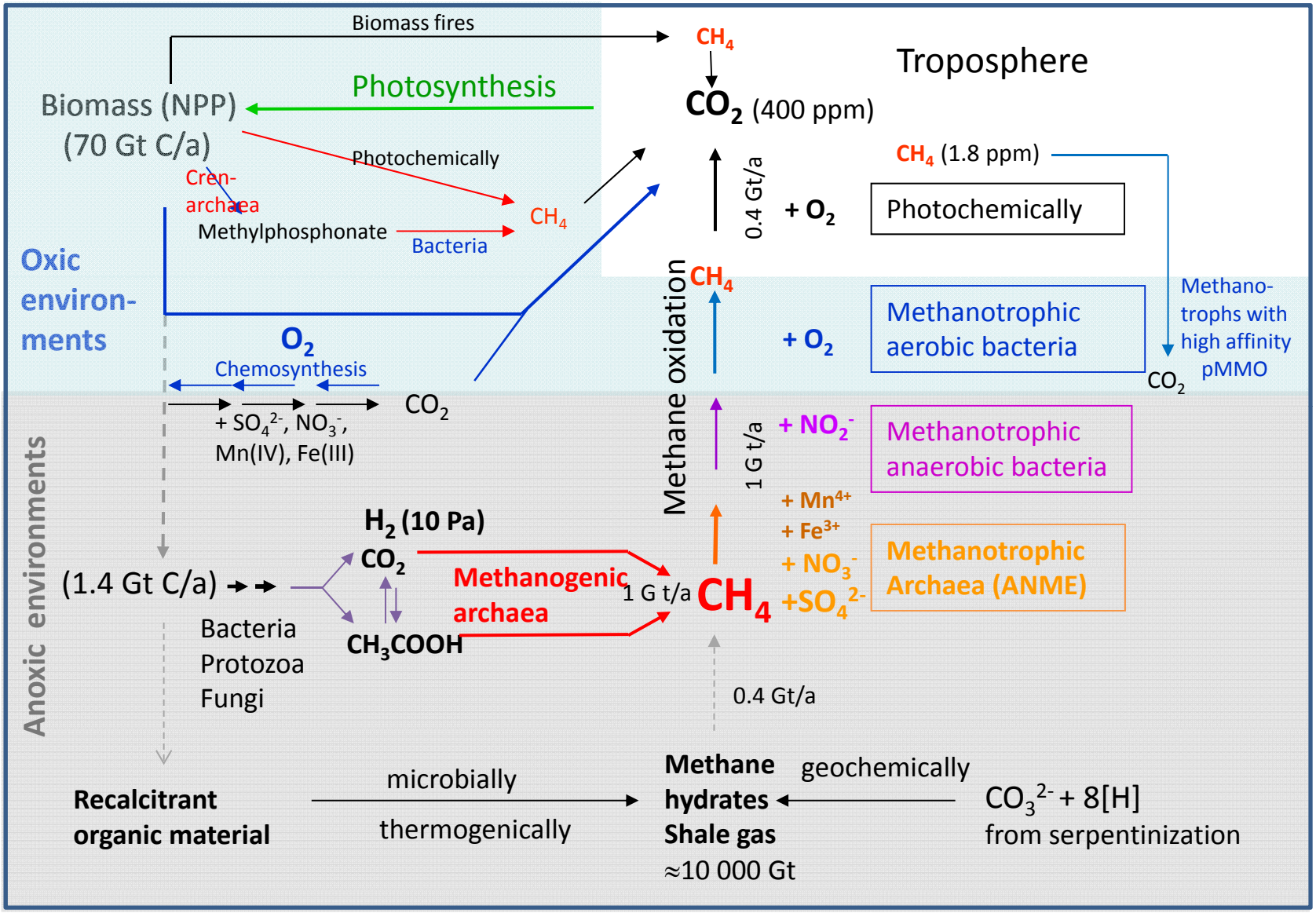
Methane cycle

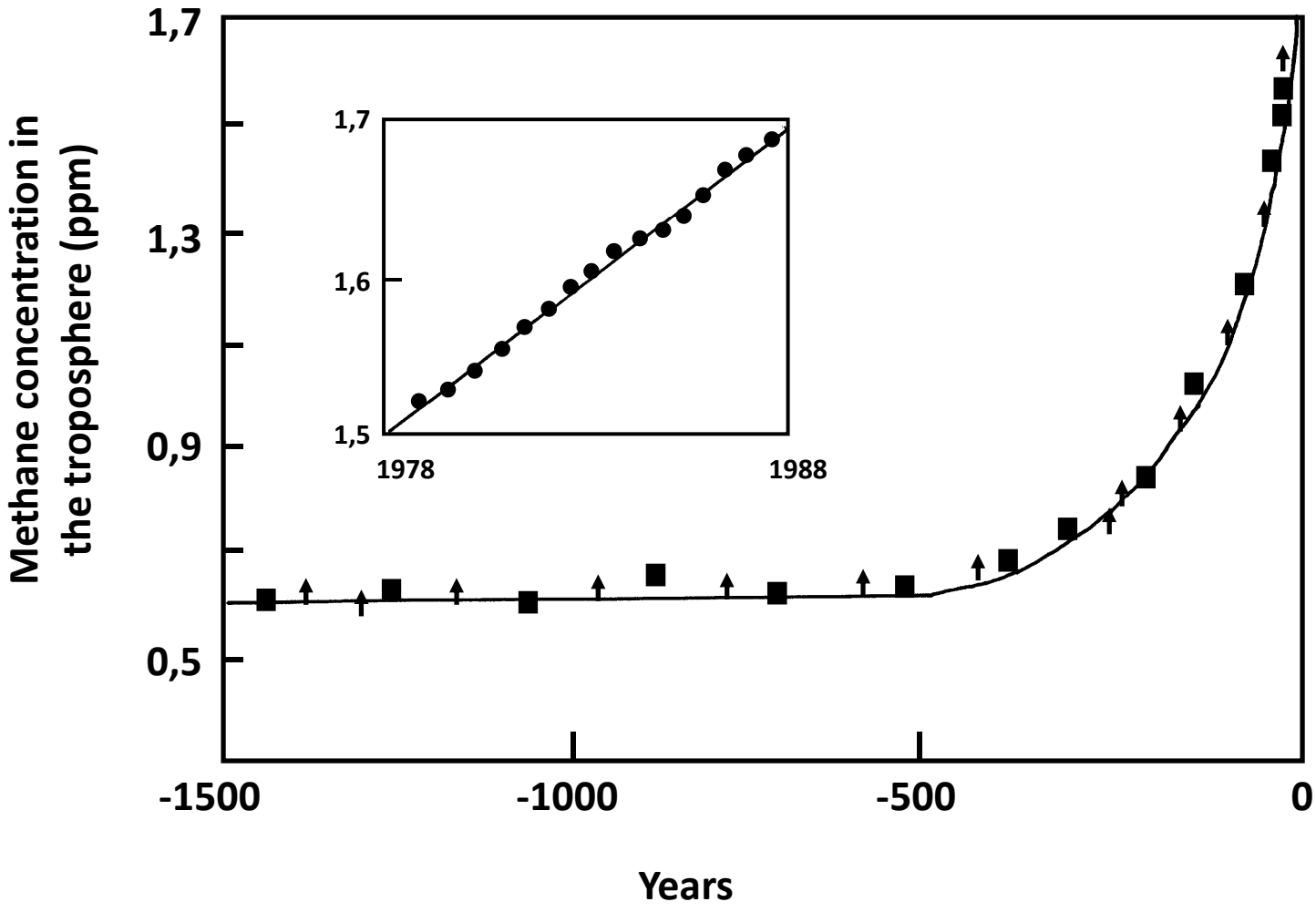


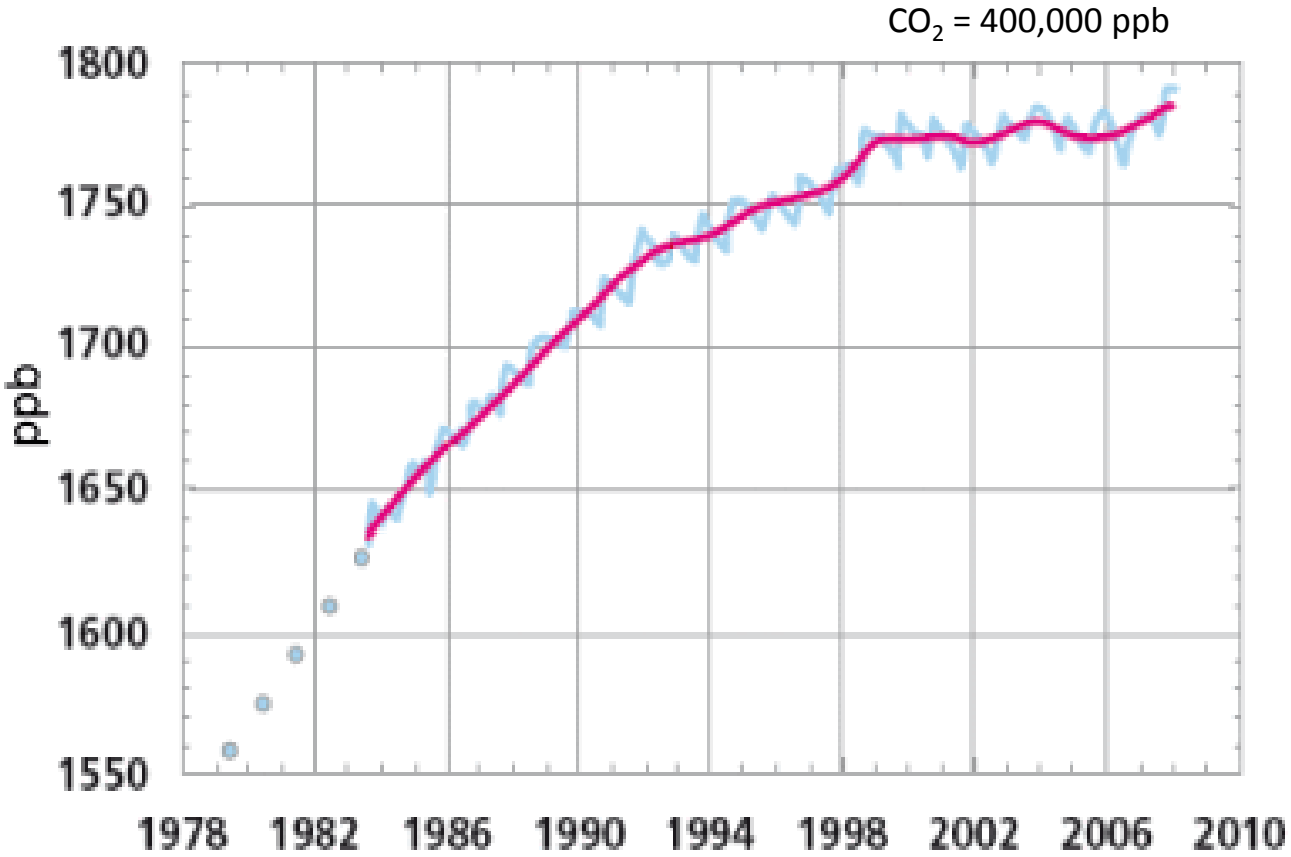
Methane cycle



Methane cycle




Methane concentration in the troposphere (ppm)
1,7
1,3
0,9
0,5
-1500
-1000
-500
0
Years
1,7
1,6
1,5
1978
1988

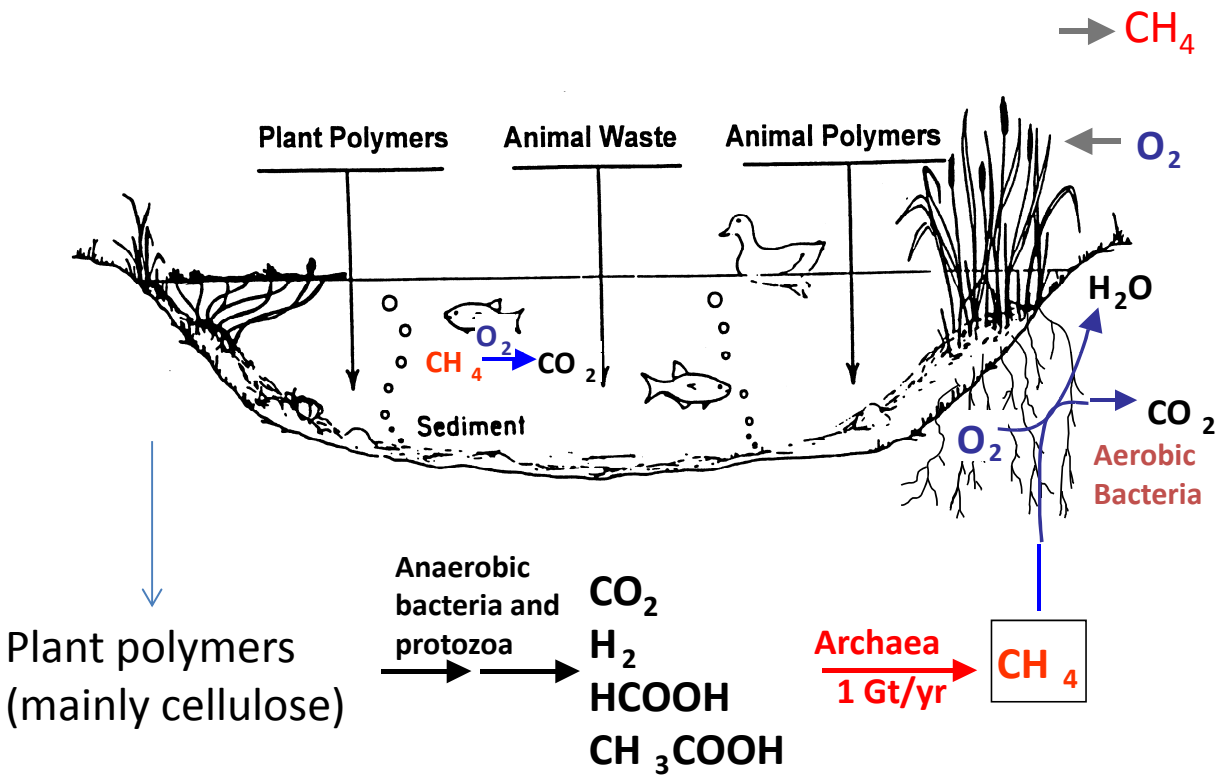


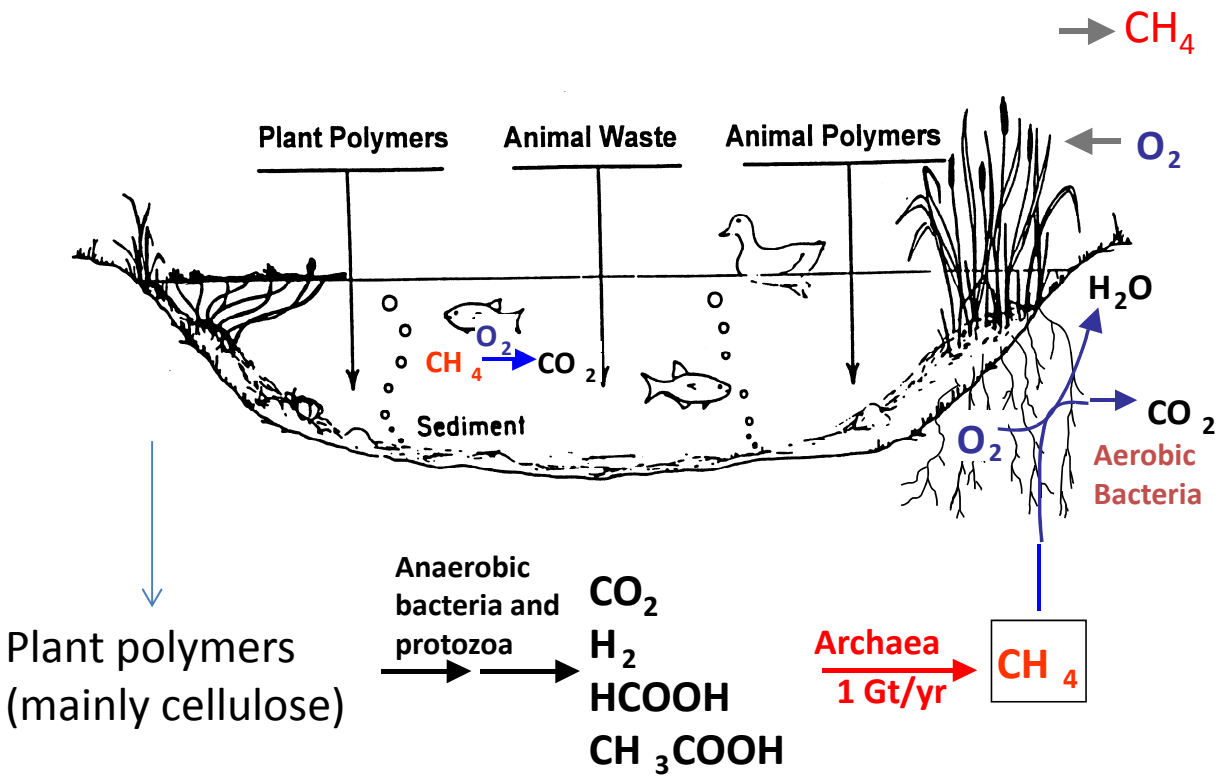
CH_4 has 25 fold higher GHG potential than CO_2

About 50% of European CH_4 emissions are from agriculture

Increase of the methane concentration in in the atmosphere since 1979.
Synthesis Report Climate Change: Global Risks, Challenges & Decisions. Copenhagen 2009, 10-12 March.

MPI


CH4
Plant Polymers
Animal Waste
Animal Polymers
O2
H2O
O2
CH 4
CO 2
CO 2
Sediment
O2
Aerobic
Bacteria
Plant polymers
(mainly cellulose)
Anaerobic
bacteria and
protozoa
CO2
H2
HCOOH
CH 3COOH
Archaea
1 Gt/yr
CH 4

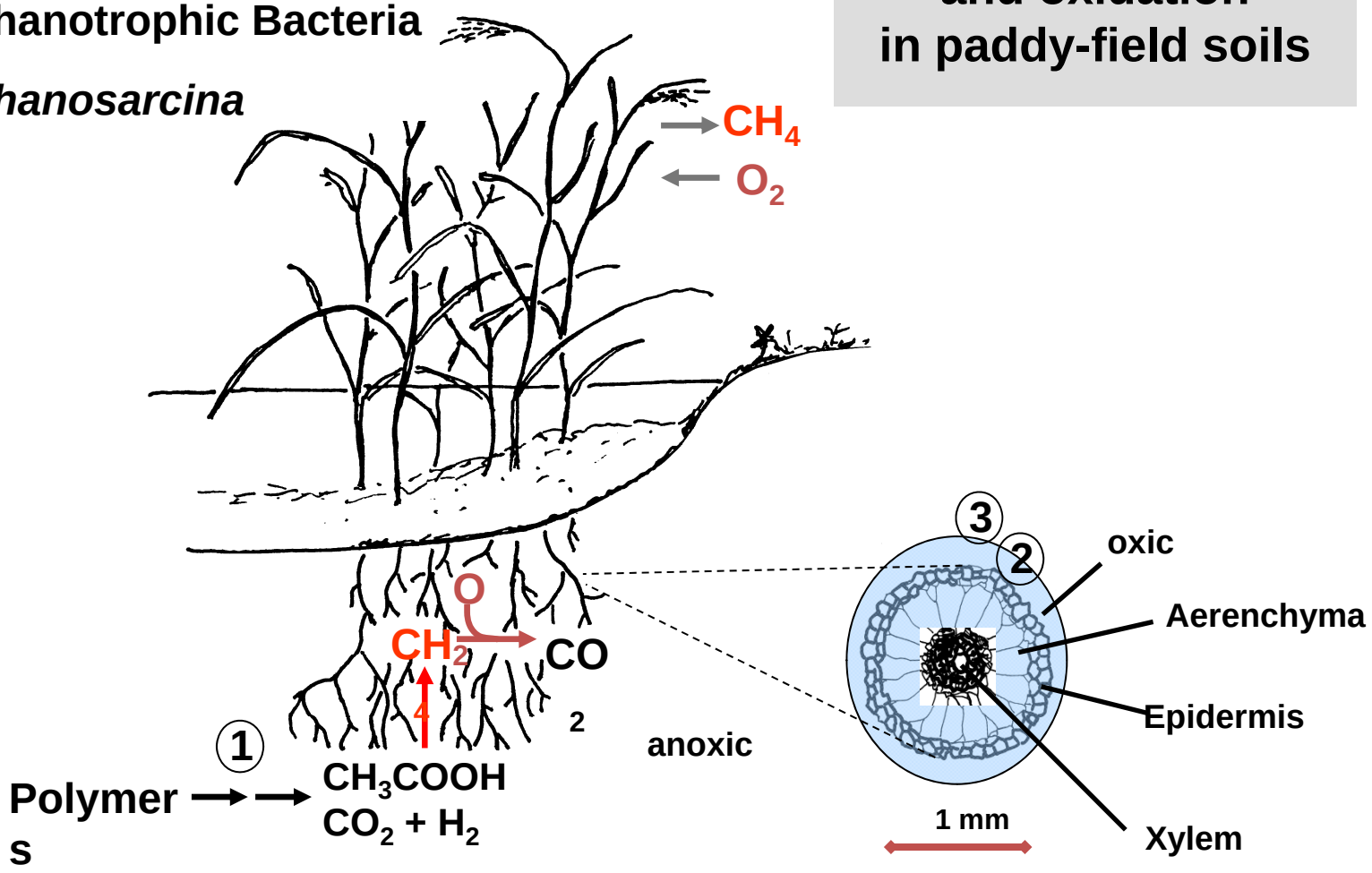

CH4
Plant Polymers
Animal Waste
Animal Polymers
O2
H2O
O2
CH 4
CO 2
CO 2
Sediment
O2
Aerobic
Bacteria
Plant polymers
(mainly cellulose)
Anaerobic
bacteria and
protozoa
CO2
H2
HCOOH
CH 3COOH
Archaea
1 Gt/yr
CH 4

Methane formation and oxidation in paddy-field soils

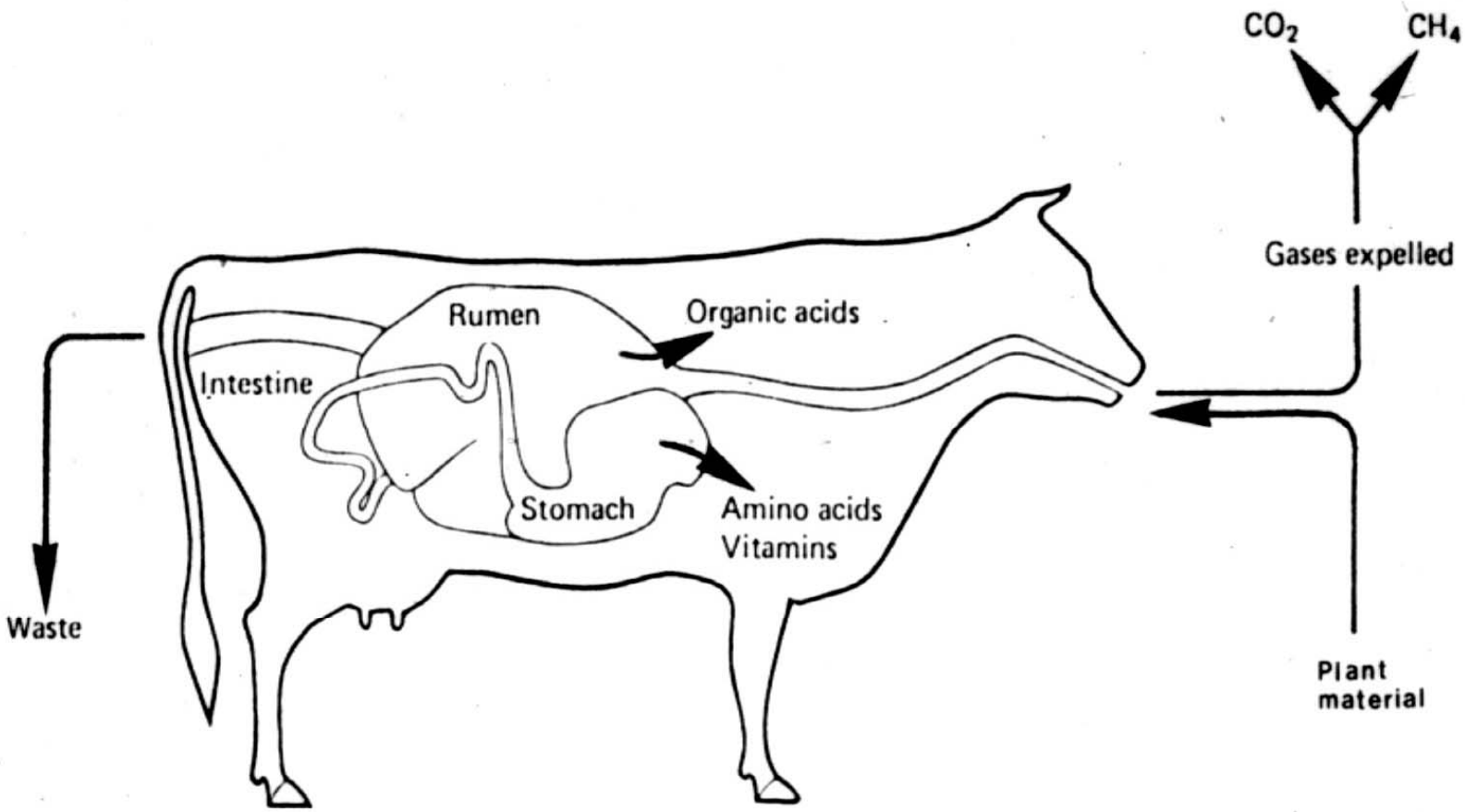
① Anaerobic Bacteria and Protozoa

② Methanotrophic Bacteria

③ *Methanosarcina*

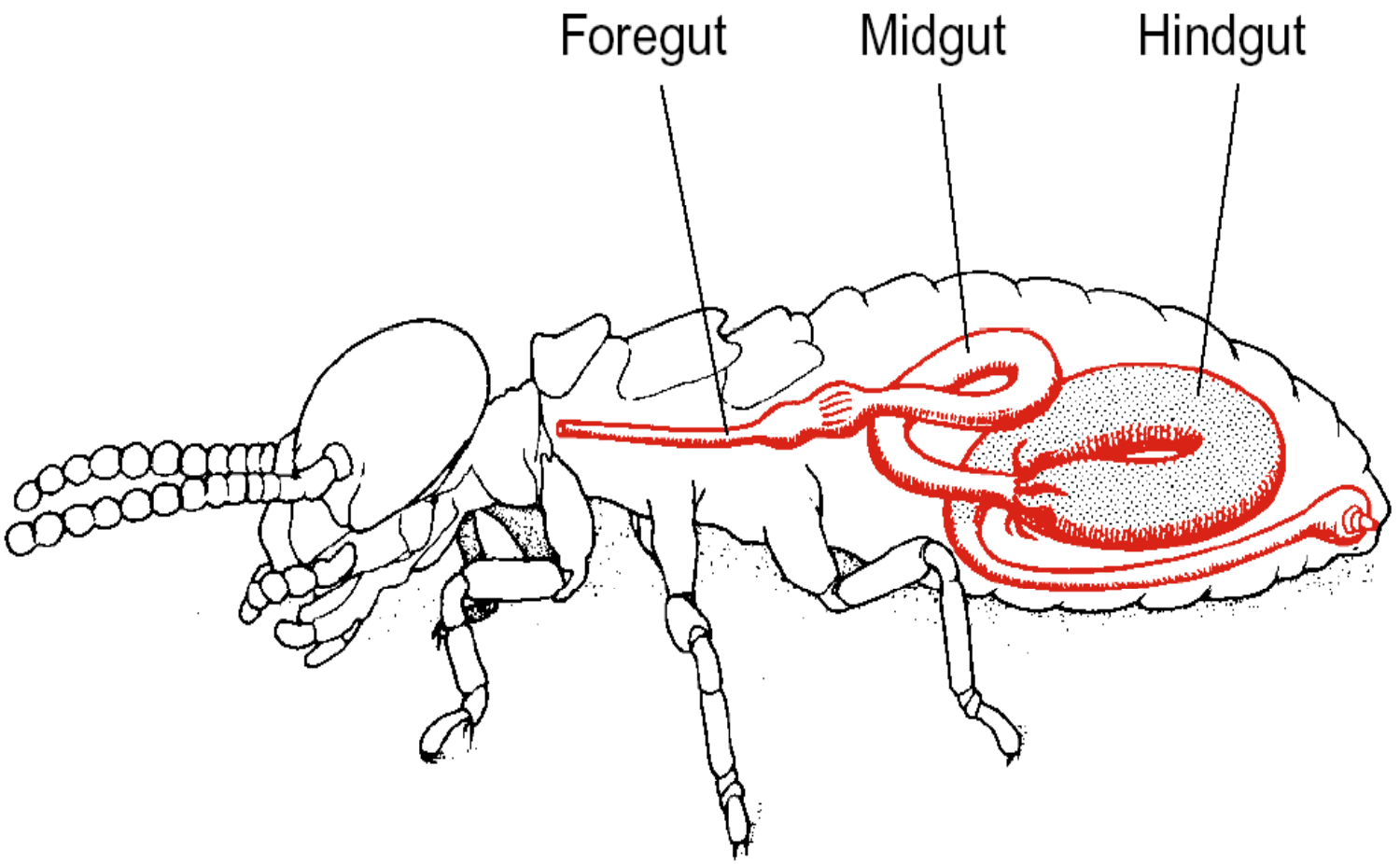


300 l pro Tag

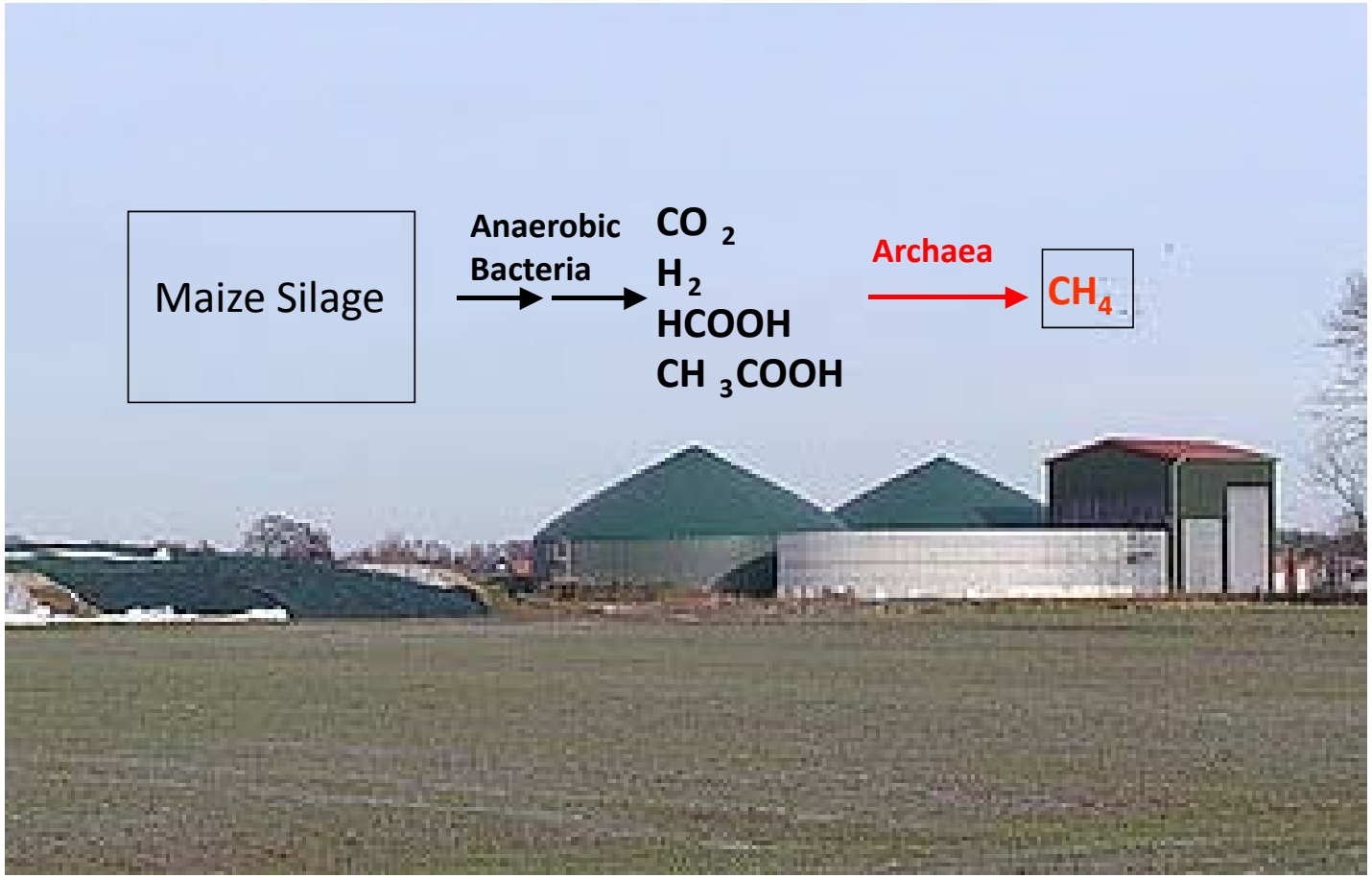


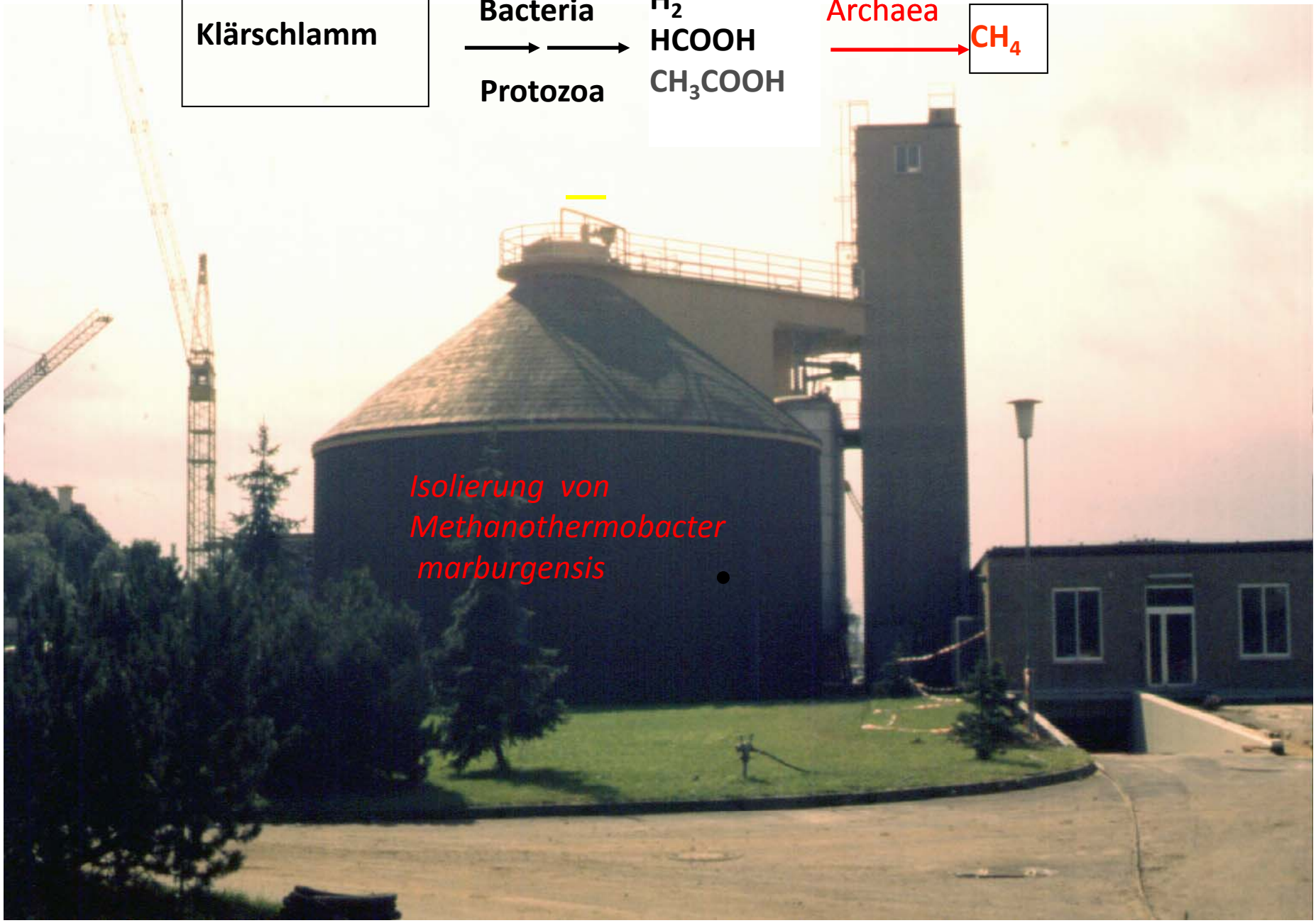
From Brock 1978

MPI


Foregut
Midgut
Hindgut

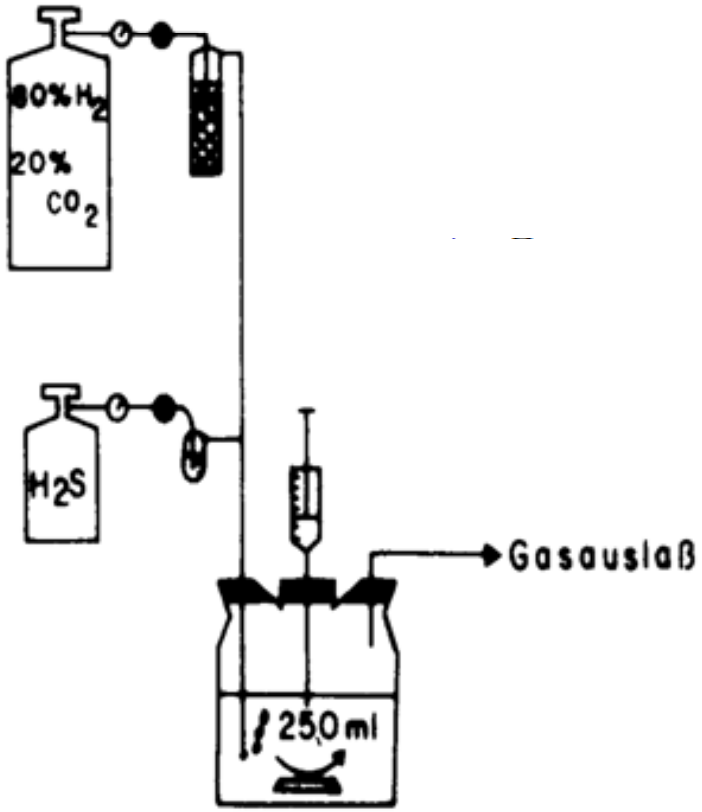
Glucose → 3 CH_4 + 3 CO_2




Klärschlamm
Bacteria
Protozoa
CO_2
H_2
HCOOH
CH_3COOH
Archaea
CH_4
Isolierung von Methanothermobacter marburgensis

Versuchsanlage zur Züchtung von
***M. marburgensis* auf H_2 und CO_2**

$4\ H_2 + CO_2 = CH_4 + 2\ H_2O$



1978

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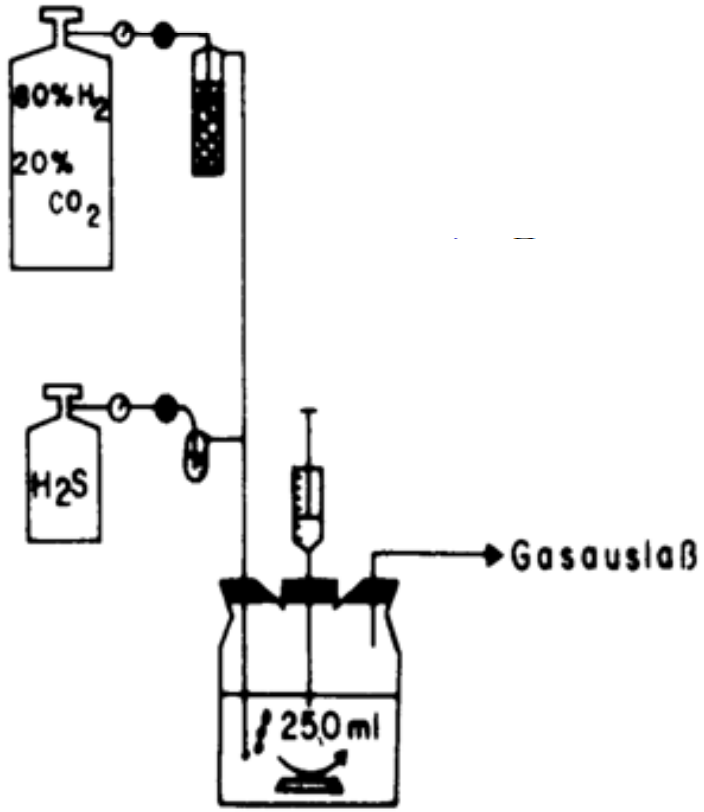
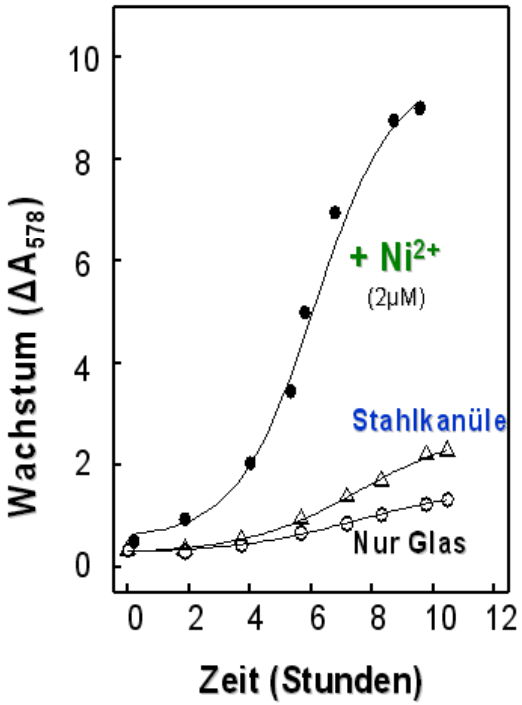
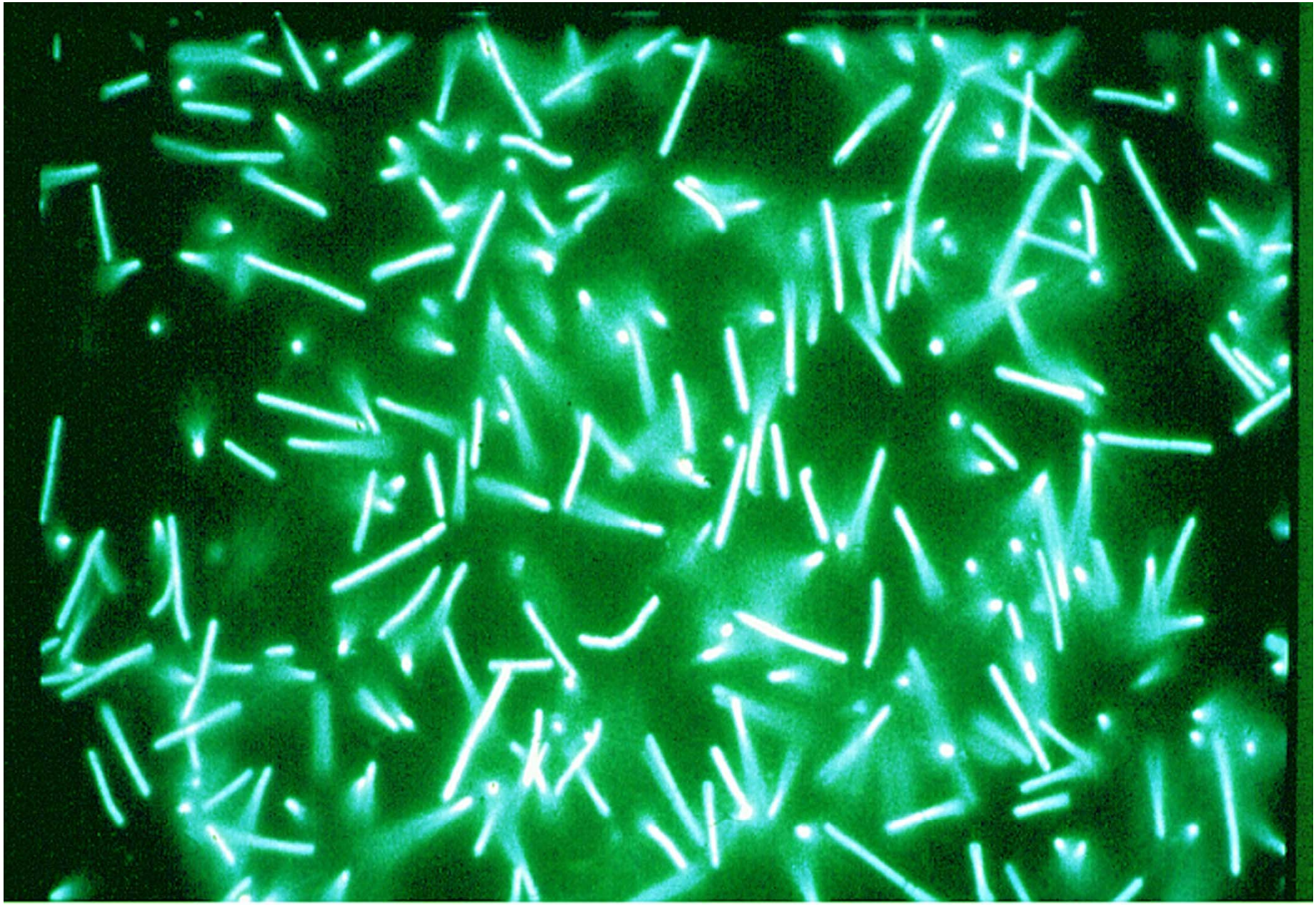
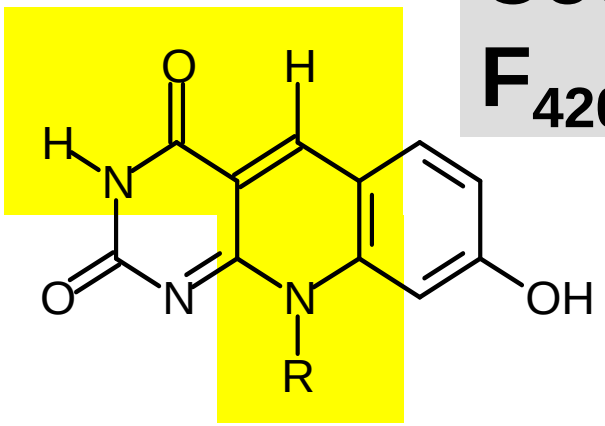




1978

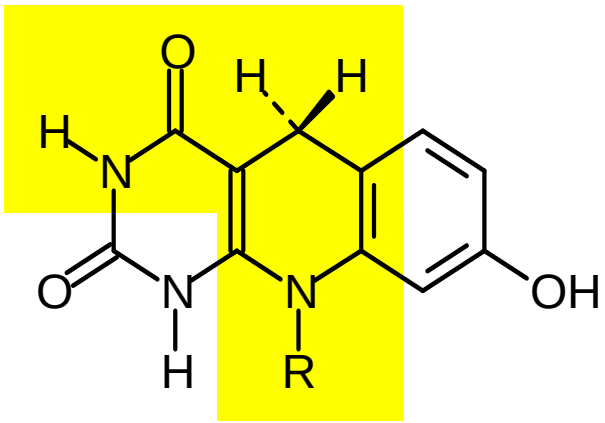


Coenzyme F_{420}



Oxidized form

$E^{0'}$ = - 360 mV



Reduced form

L. Eirich, E. Vogels, R. Wolfe (1978)

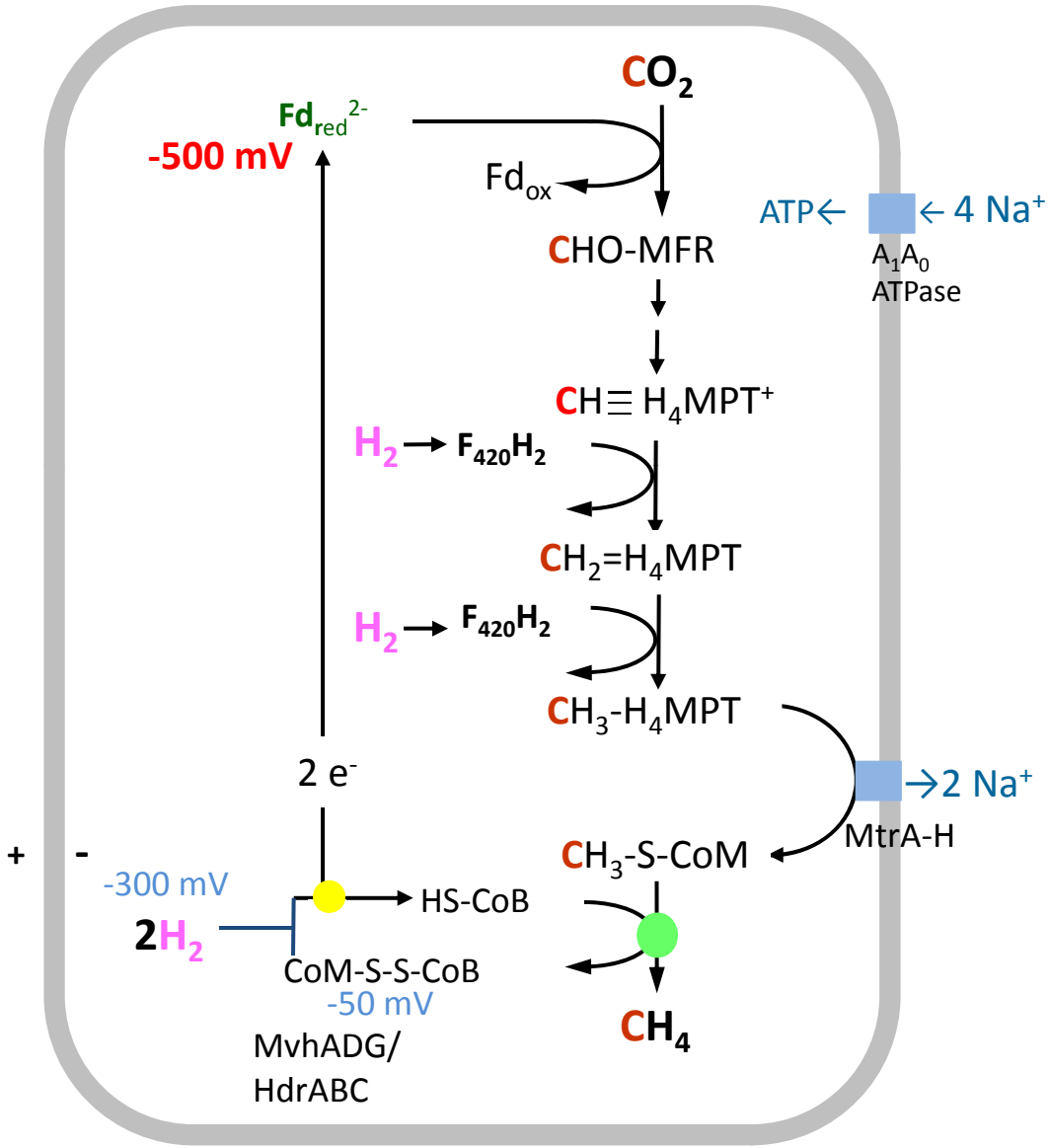
Methanopyrus kandleri
Methanobacteriales
Methanococcales
Methanomicrobiales
Methanocellales

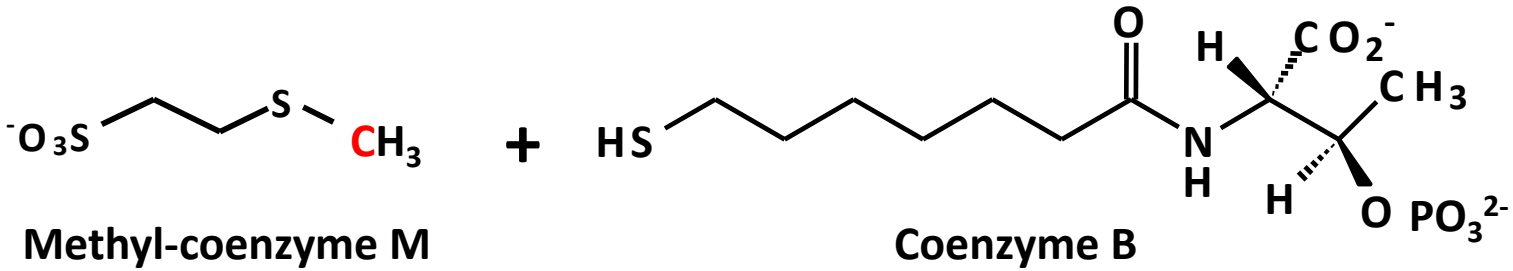
$4\ H_2 + CO_2 \rightarrow CH_4 + 2\ H_2O$
ΔG^o = - 131 kJ/mol
ΔG = - 40 kJ/mol
at pH_2 = 10 Pa

0.5 ATP/CH_4

Methane forming step is catalyzed by methyl-coenzyme M reductase

(Kaster, Thauer et al. 2011, PNAS)





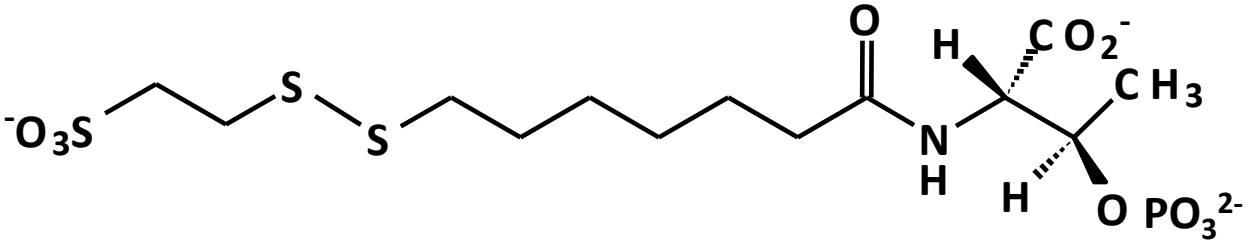
Methyl-CoM Reductase

$\alpha_2\beta_2\gamma_2$

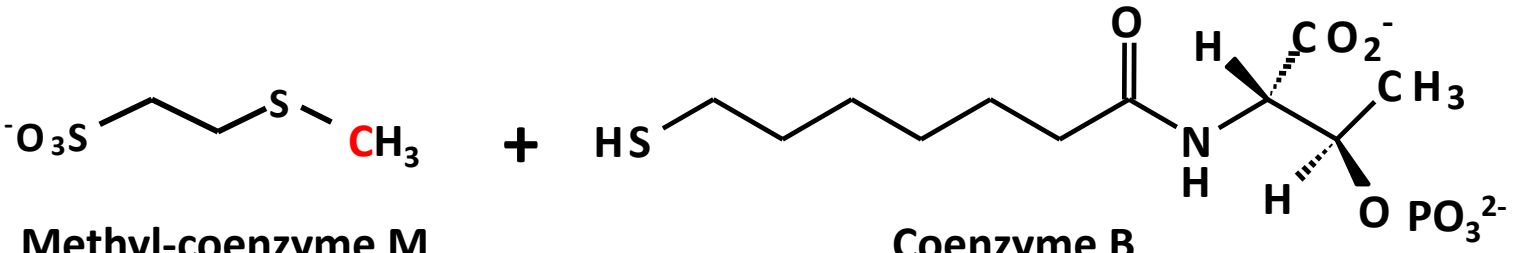
$\Delta G^{o'}$ = -30 kJ/mol

100 µmol/min/mg

CH_4



Ellermann,Thauer et al. (1986)



Methyl-coenzyme M **Coenzyme B**

Specific rate ≈12 nmol/min/mg at 1 bar CH_4

Apparent K_M ≈ 10 bar)

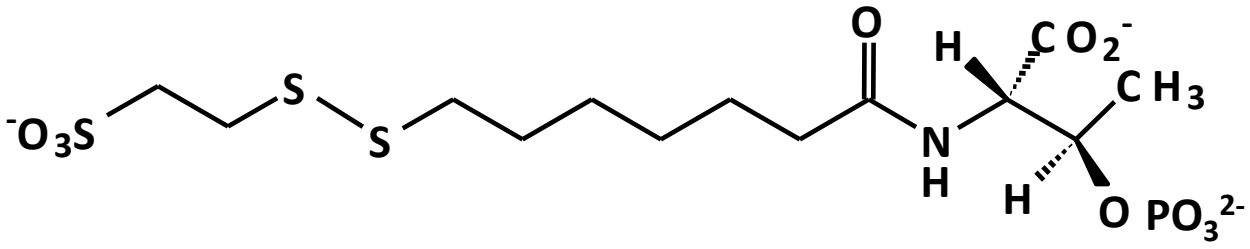
Methyl-CoM Reductase

$\alpha_2\beta_2\gamma_2$

$\Delta G^{o'}$ = -30 kJ/mol

100 µmol/min/mg

CH_4

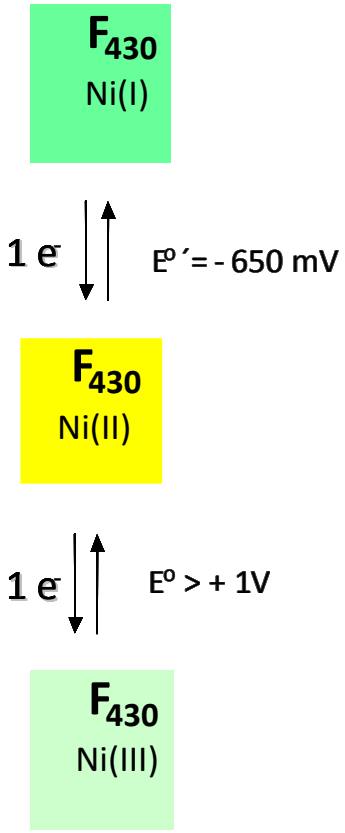


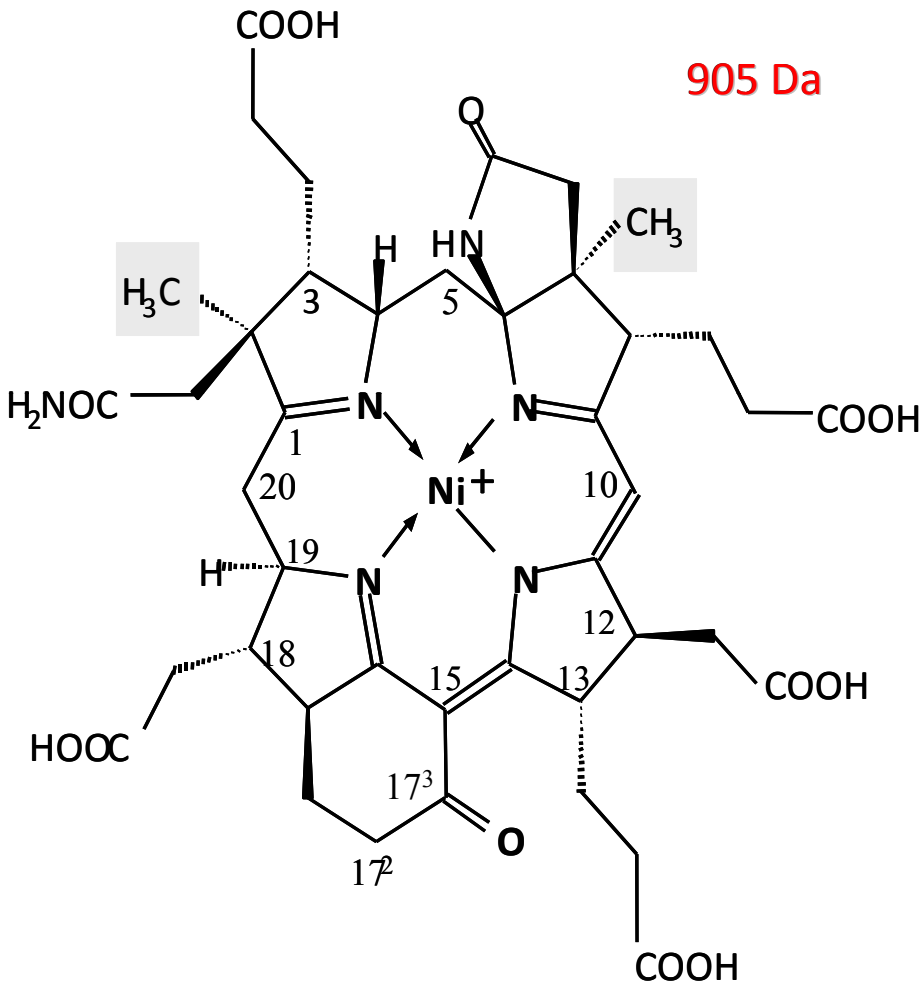
Heterodisulfide

Scheller, Thauer, Jaun et al. (2010)
Nature

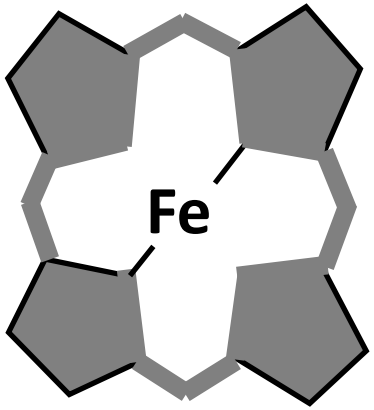
MPI

Prosthetic group of methyl-coenzyme M reductase

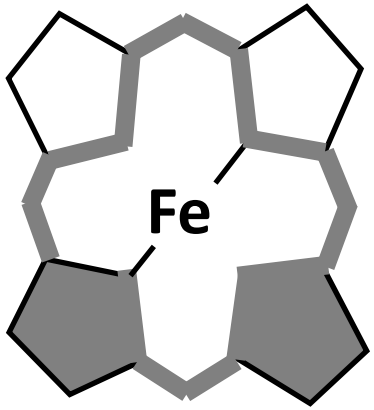




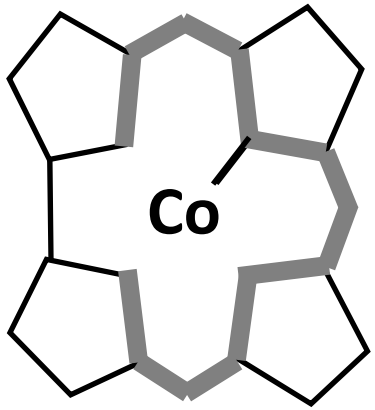
Pfalz, Jaun, Thauer, Eschenmoser et al. (1983)



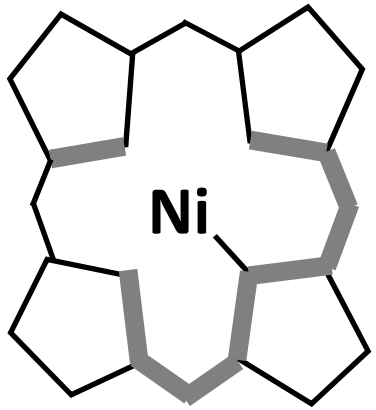
Häm



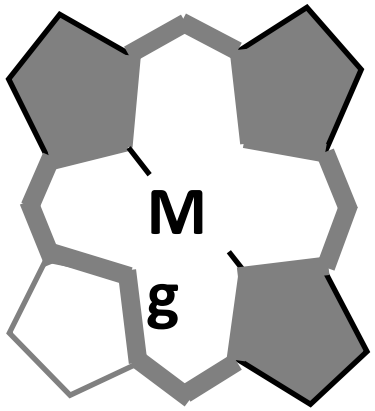
Sirohäm



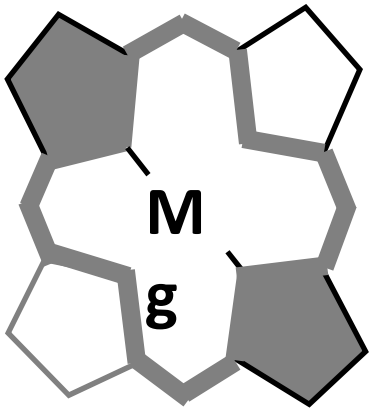
B_{12}



F_{430}

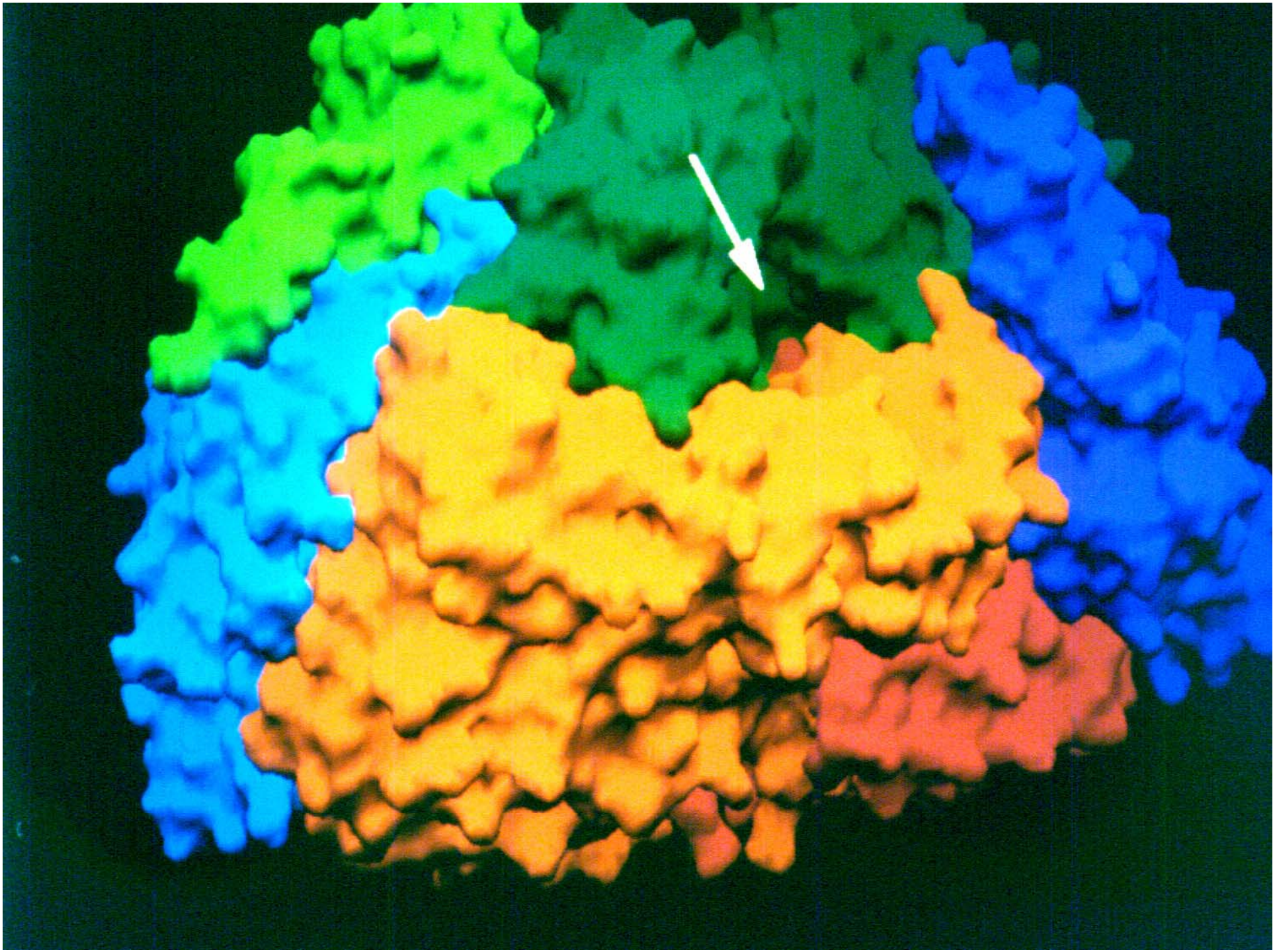


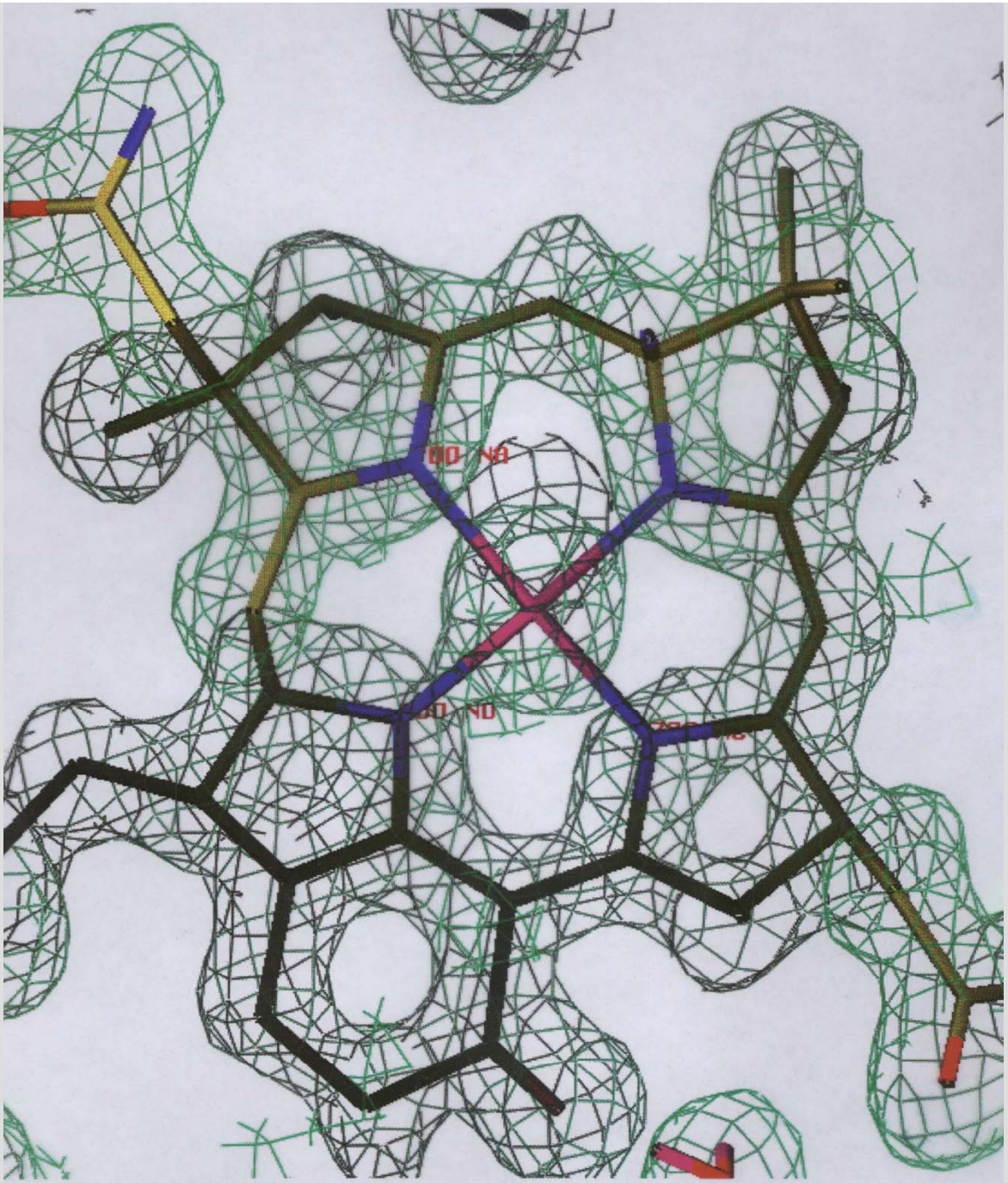
Chlorophyll



Bakteriochrorophyll

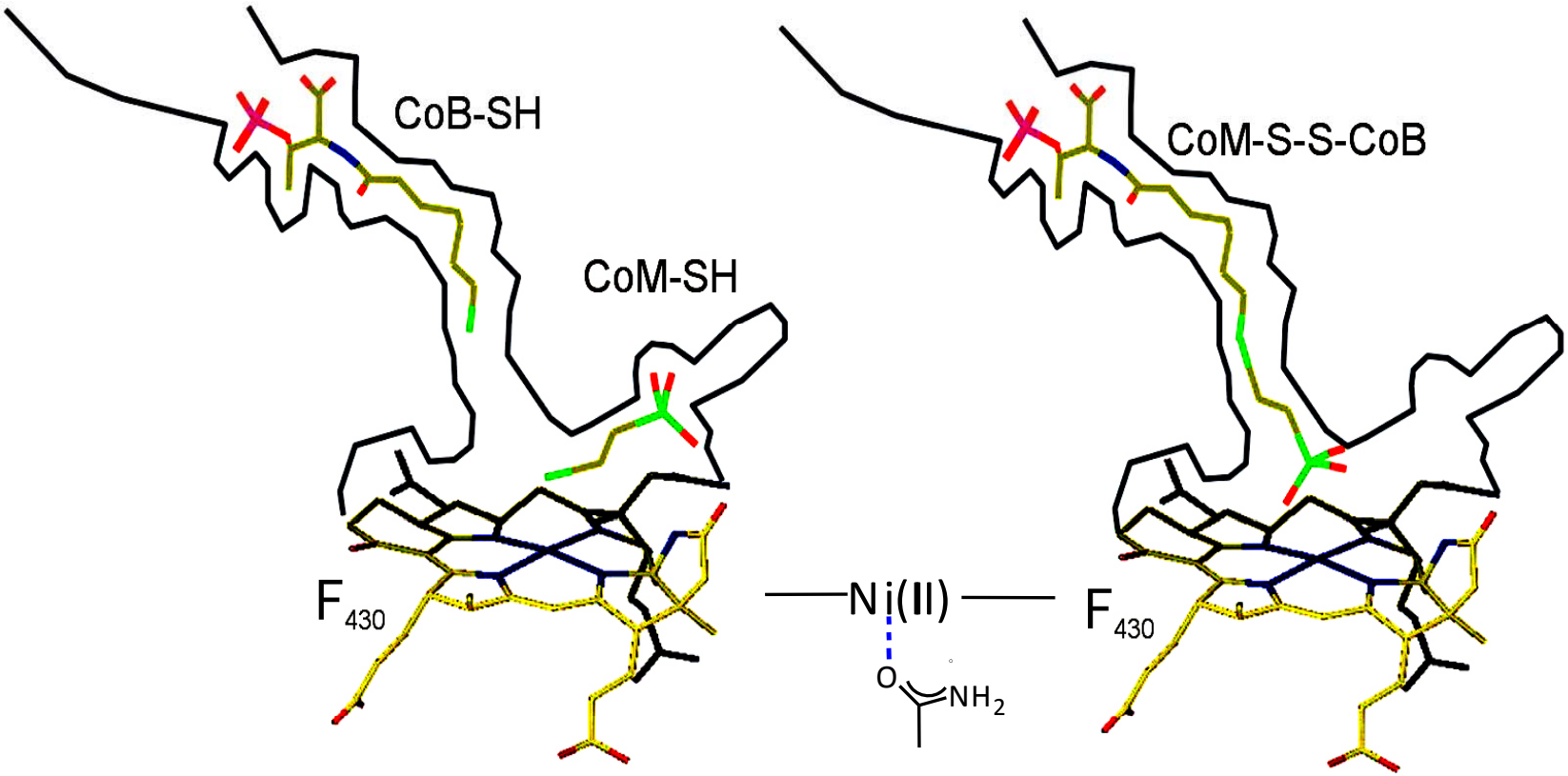
Eschenmoser (1988)





Electron density of F_{430} contoured at 1 σ level

Structures of MCR in two inactive (Ni^{2+})MCR forms at 1.16 Å resolution

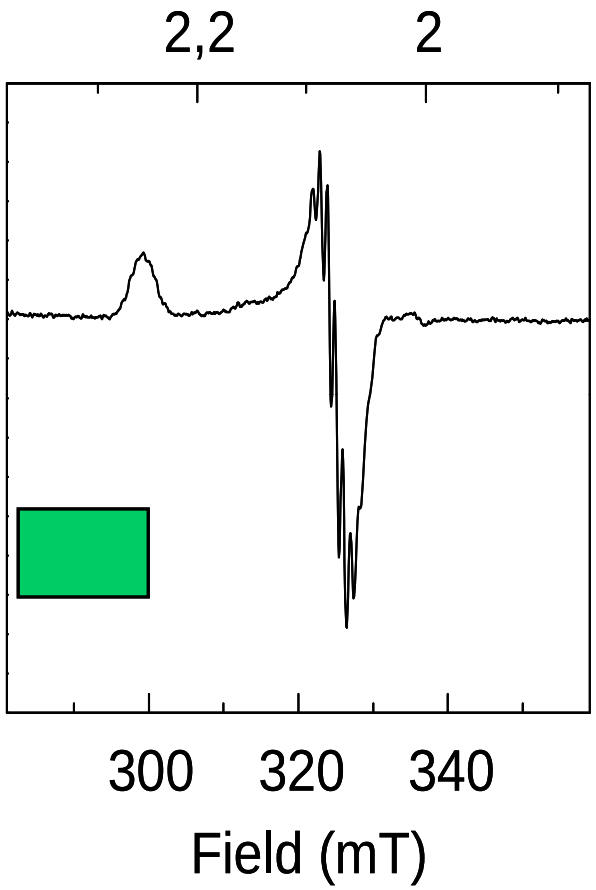


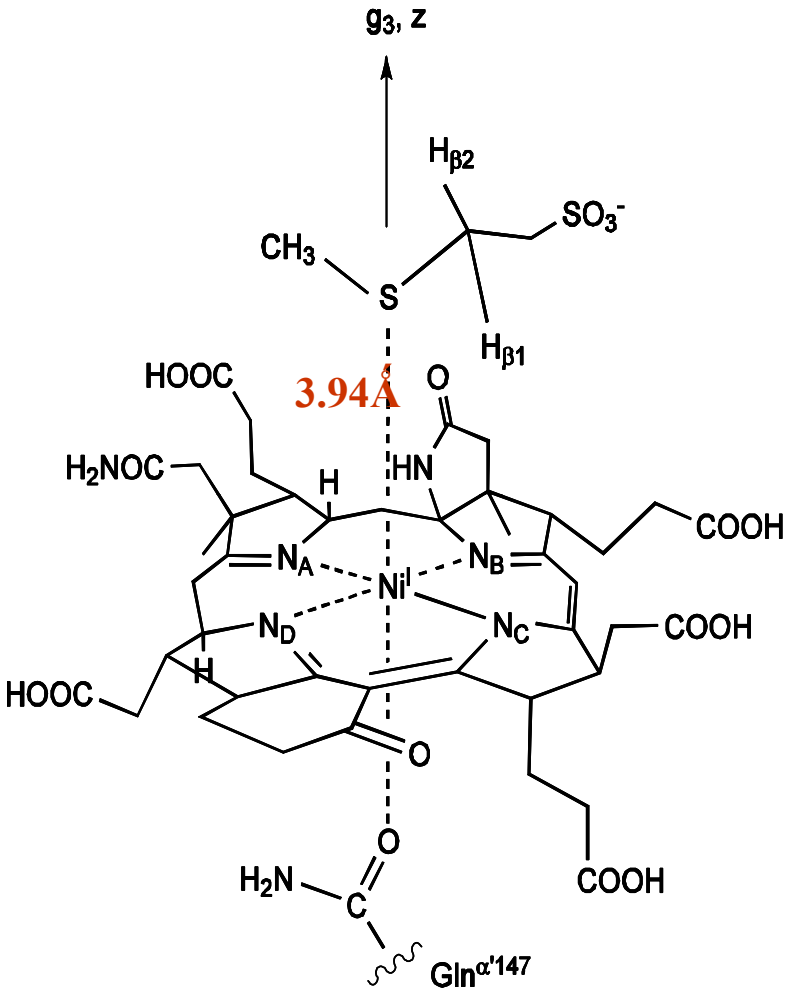
The active site is completely hydrophobic;
Five postranslational modifications

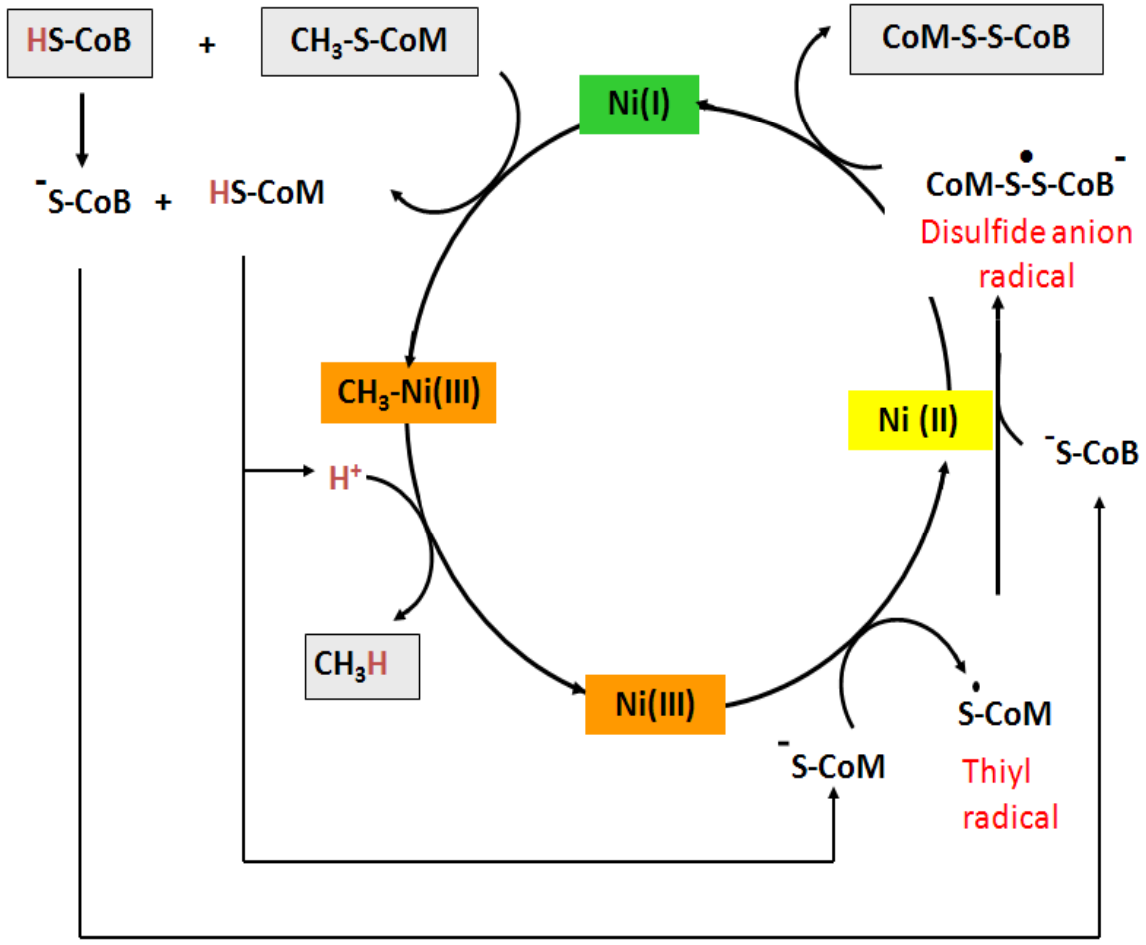
Ermler, Shima, Thauer et al. 1996

MPI

MCRred1 + CH_3-S-CoM

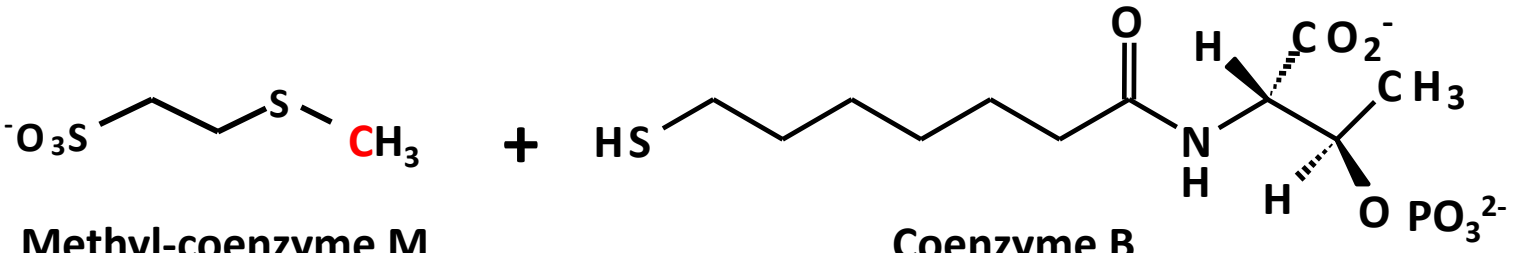






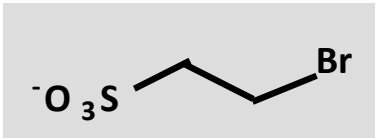
Scheller, Thauer, Jaun et al. (2013 a and b) JACS

Mechanism 1



Methyl-coenzyme M **Coenzyme B**

MCR is inactivated by BES



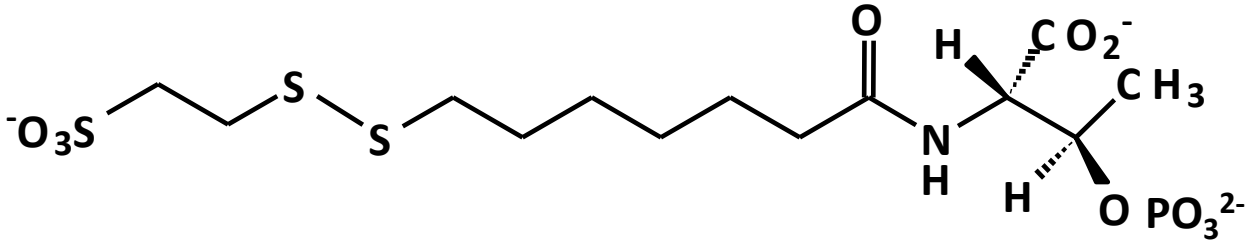
Methyl-CoM Reductase

$\alpha_2\beta_2\gamma_2$

100 µmol/min/mg

$\Delta G^{o'}$ = -30 kJ/mol

CH_4



Heterodisulfide

Methanopyrus kandleri
Methanobacteriales
Methanococcales
Methanomicrobiales
Methanocellales

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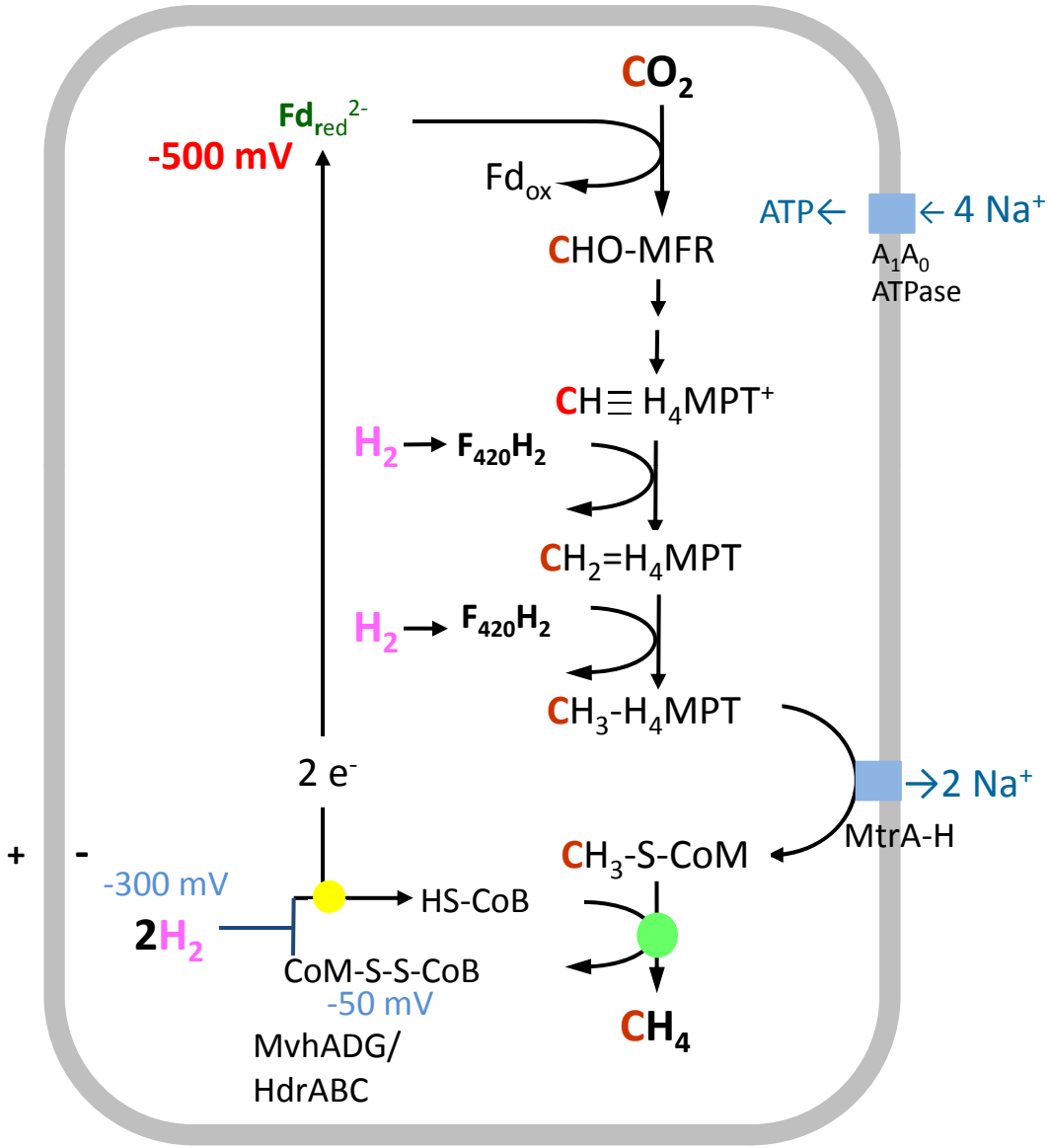
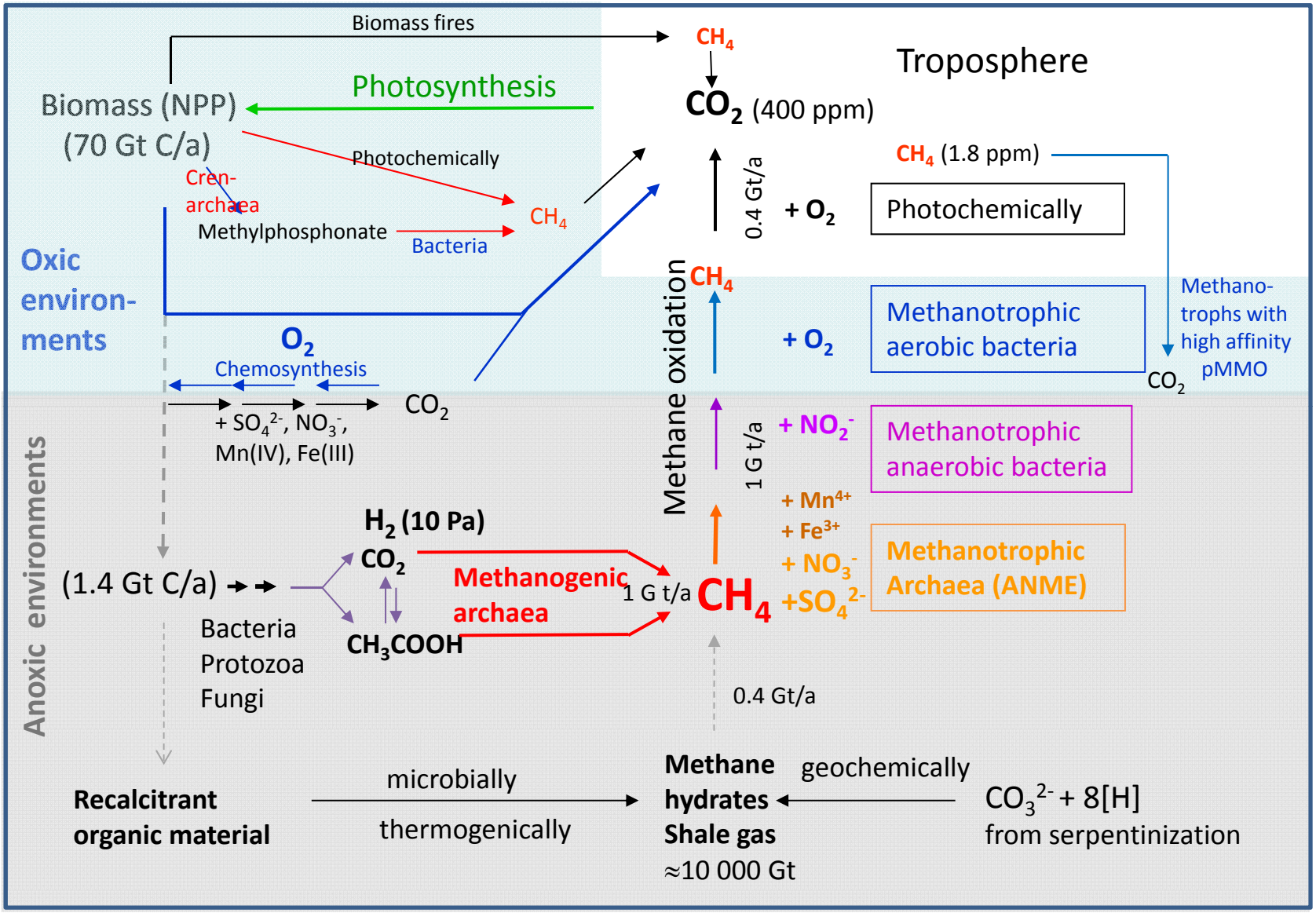
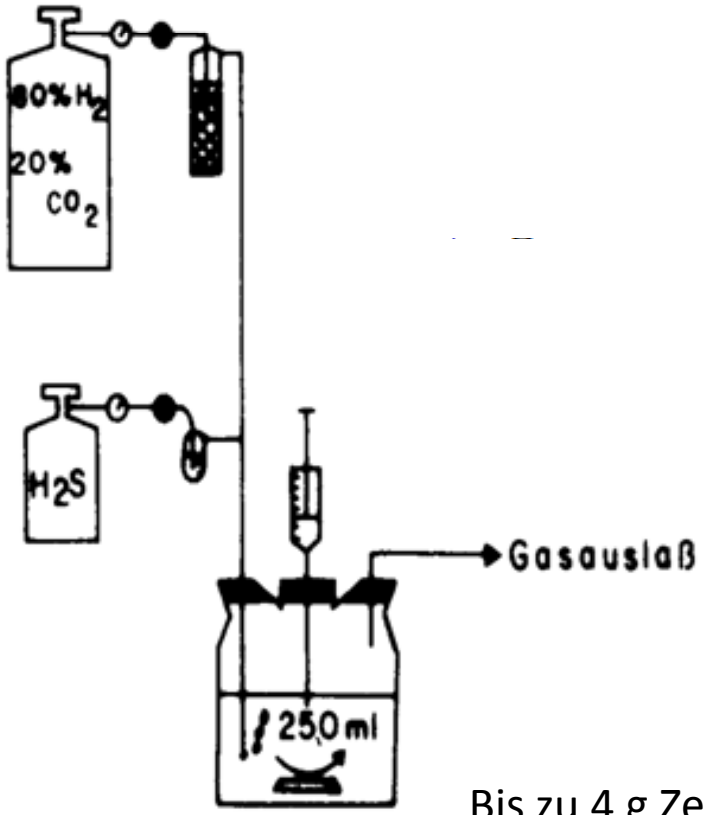


Methane cycle



Versuchsanlage zur Züchtung von
M. marburgensis **auf H_2 und CO_2**

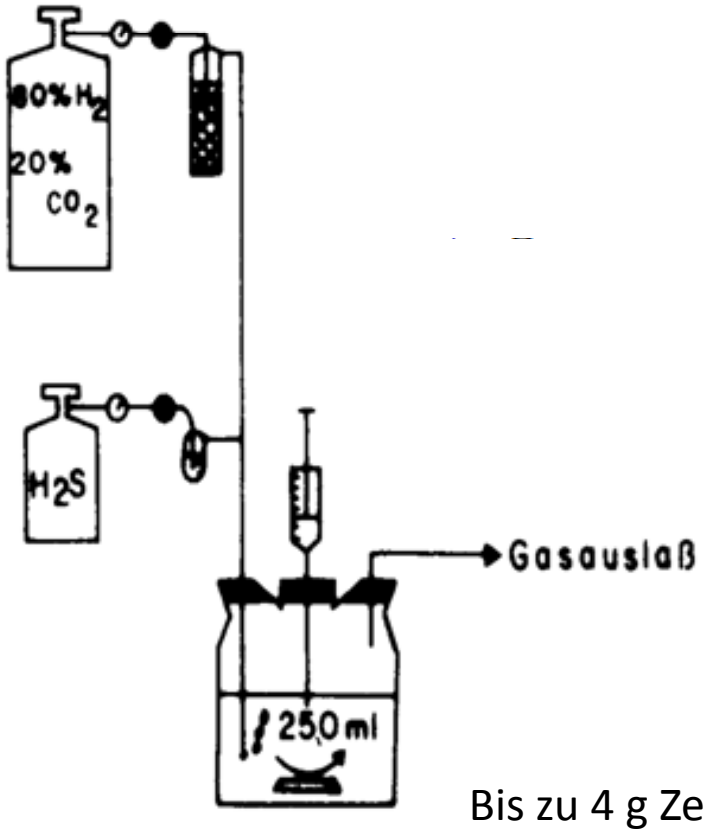
$4\ H_2 + CO_2 = CH_4 + 2\ H_2O$



Bis zu 4 g Zellen pro l, die bis zu 2.5 µmol CH_4 pro min und mg Zellen bilden können

Versuchsanlage zur Züchtung von *M. marburgensis* auf H_2 und CO_2

$4\ H_2 + CO_2 = CH_4 + 2\ H_2O$

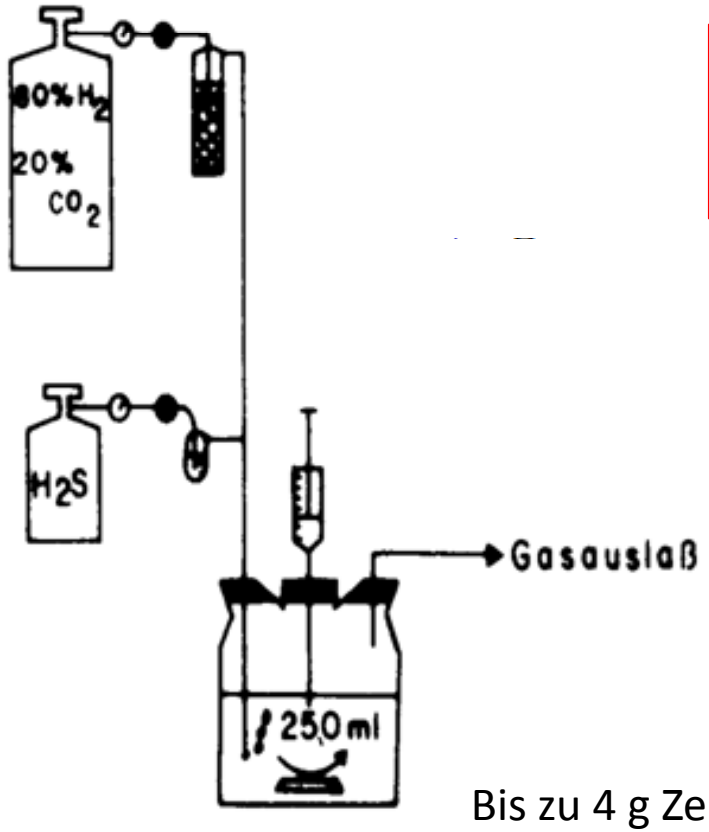


Maximal 56 ml CH_4 pro min
oder
322.5 l CH_4 pro l und Tag

Bis zu 4 g Zellen pro l, die bis zu 2.5 µmol CH_4 pro min und mg Zellen bilden können

Versuchsanlage zur Züchtung von *M. marburgensis* auf H_2 und CO_2

$4\ H_2 + CO_2 = CH_4 + 2\ H_2O$



Professor
Dr. Christoph Herwig
Technische Universität Wien

Maximal 56 ml CH_4 pro min
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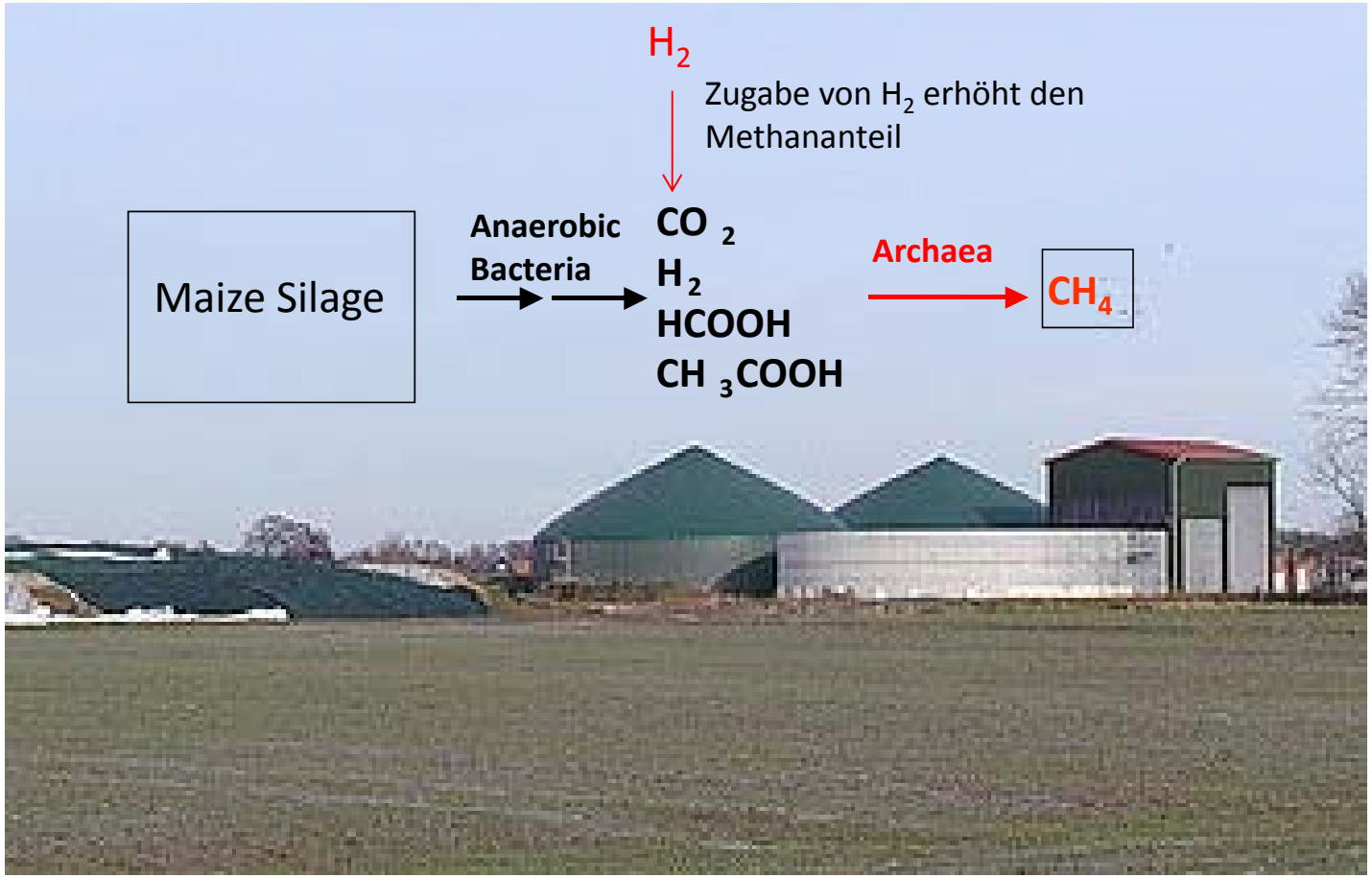
Glucose + 4 H_2 → 4 CH_4 + 2 CO_2 + 2 H_2O



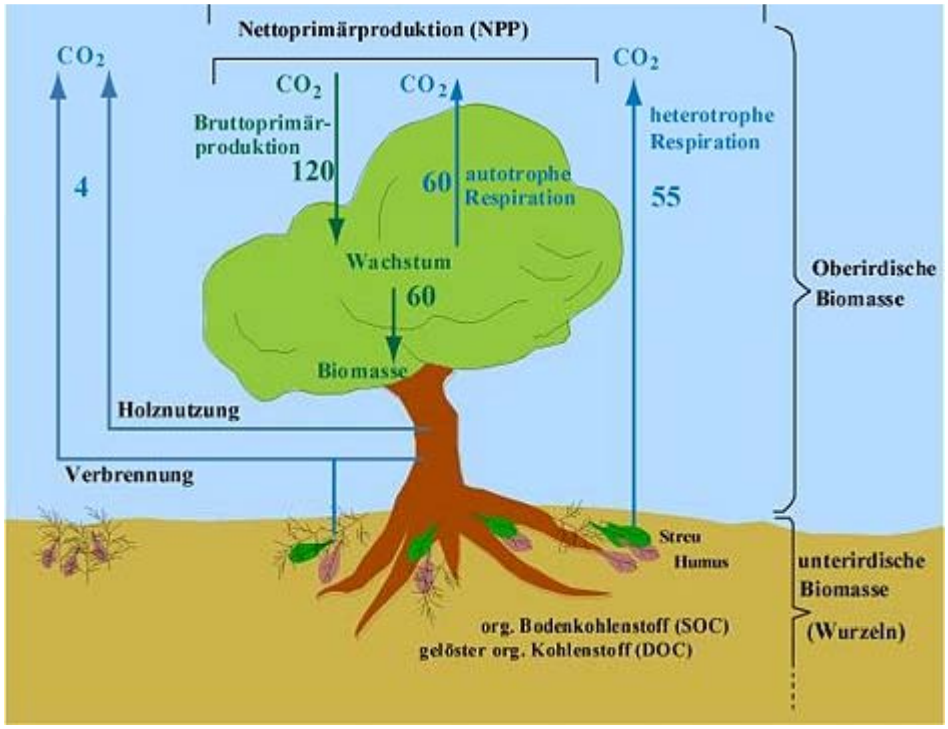
Electron bifurcation
Anne Kaster

Methyl-coenzyme M reductase
Meike Brefort
Reinhard Boecher
Seigo Shima

ETH Zürich
Bernhard Jaun
Stefan Mayr
Silvan Scheller

MPI für Biophysik Frankfurt
Ulrich Ermler

MPI Bremen
Fritz Widdel
Jana Milucka


Nettoprimärproduktion (NPP)
CO_2
CO_2
CO_2
CO_2
Bruttoprimär-
produktion
120
60
autotrophe
Respiration
heterotrophe
Respiration
55
4
Wachstum
60
Biomasse
Holznutzung
Verbrennung
Oberirdische
Biomasse
Streu
Humus
unterirdische
Biomasse
(Wurzeln)
org. Bodenkohlenstoff (SOC)
gelöster org. Kohlenstoff (DOC)