Mineral Catalysts and Pre-biotic carbon fixation

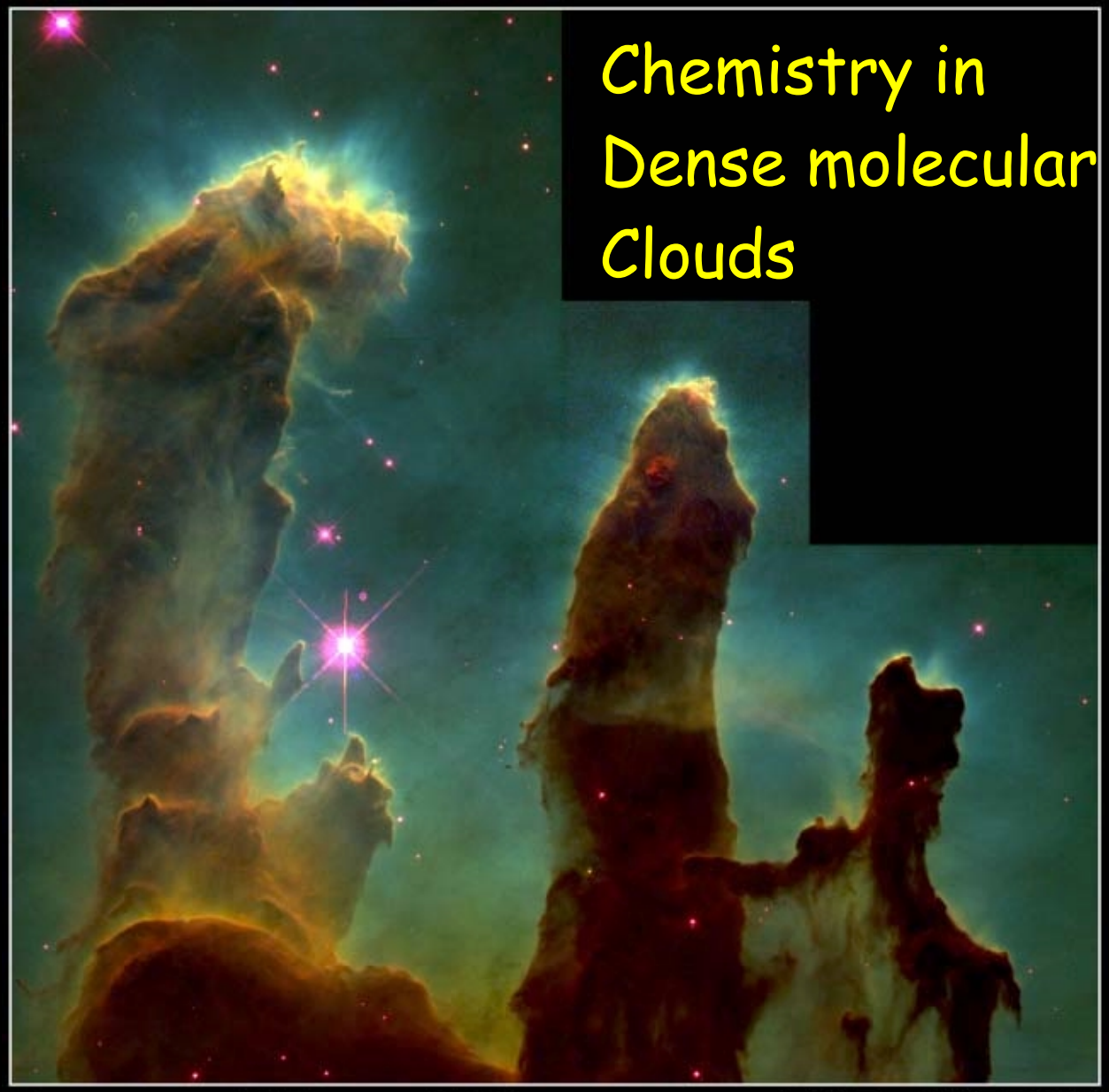
A component of
Astrobiological Research at CIW

George D. Cody
Carnegie Institution of Washington

Mineral - Organic reactions

- ubiquitous through out the galaxy
- organic matter detected in ISM
- organic molecules in Carbonaceous Chondrites
- perhaps critical to the prebiotic Origins of life

Chemistry in Dense molecular Clouds



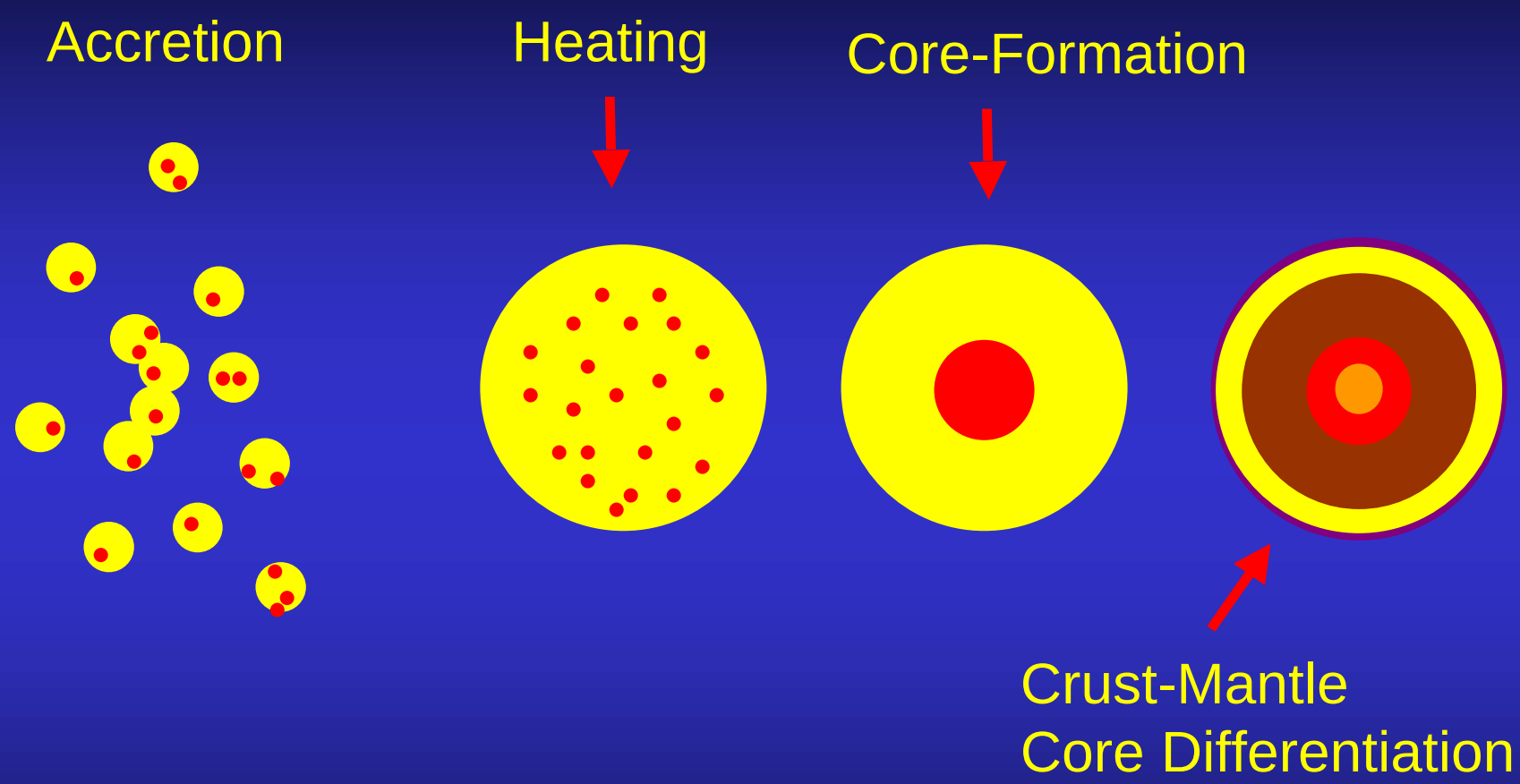
Gaseous Pillars · M16 HST · WFPC2

PRC95-44a · ST ScI OPO · November 2, 1995
J. Hester and P. Scowen (AZ State Univ.), NASA

Terrestrial Planet formation

Mineral-organic reactions occur within Planetisimals (hydrothermal and thermal)

The formation and Early Evolution of the Earth



Mineral catalyzed organic synthetic reactions may have initiated early In Earth's history

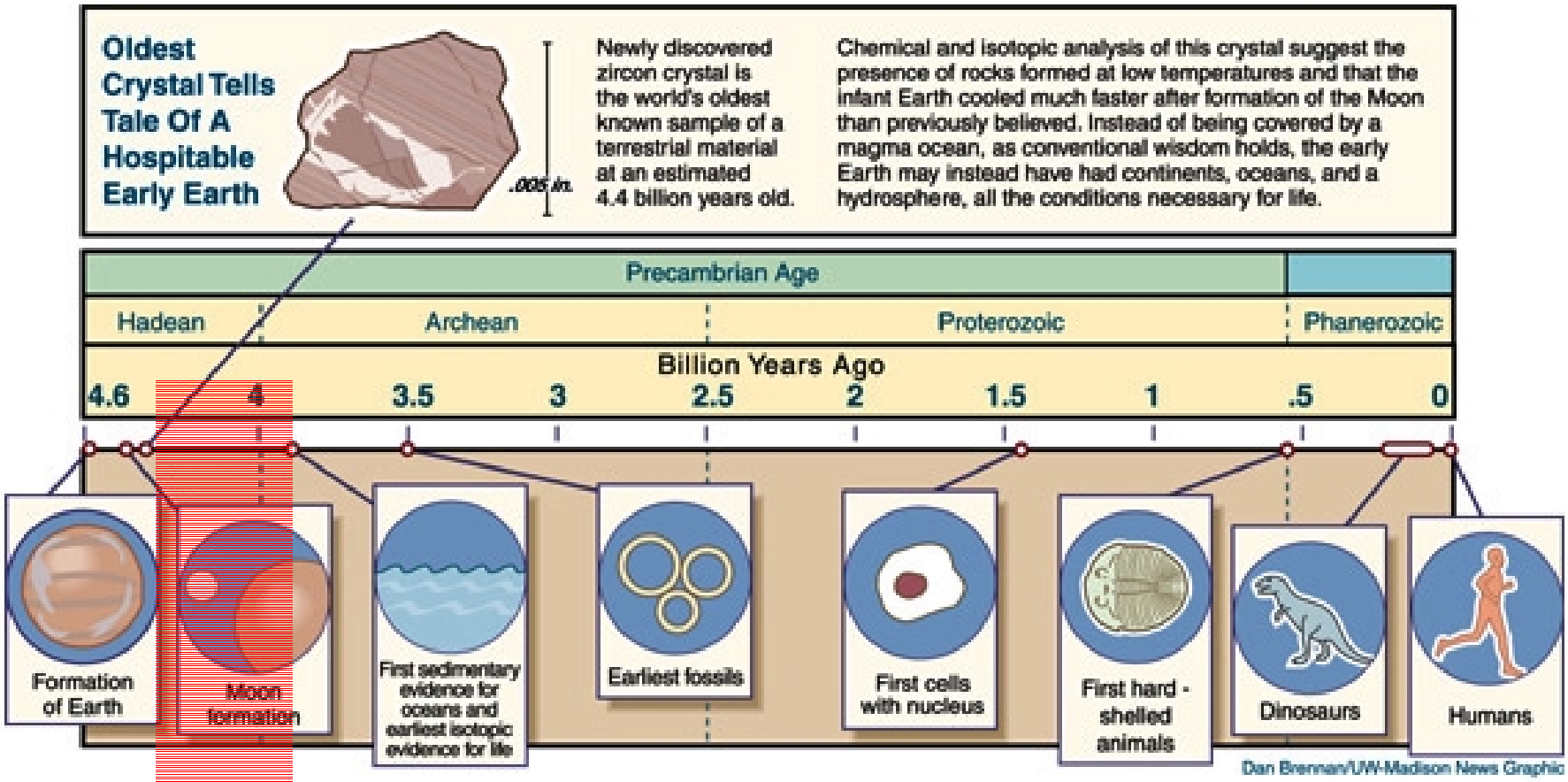
The origins of life and biosphere

Back ground:

When did life first arise?

Where did first life arise?

How did first life arise?



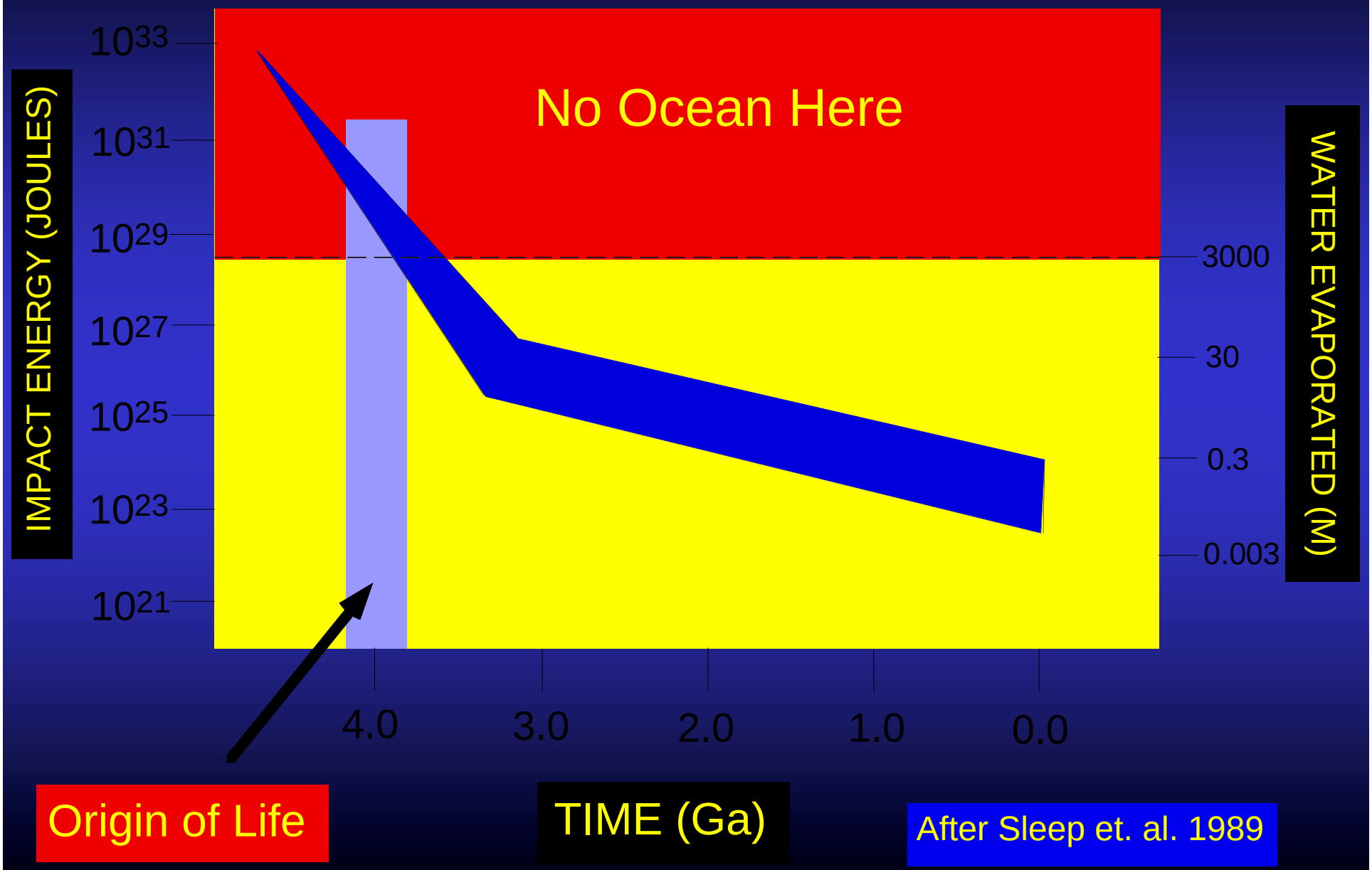
life established between 4,400 and 3,800 Million years ago

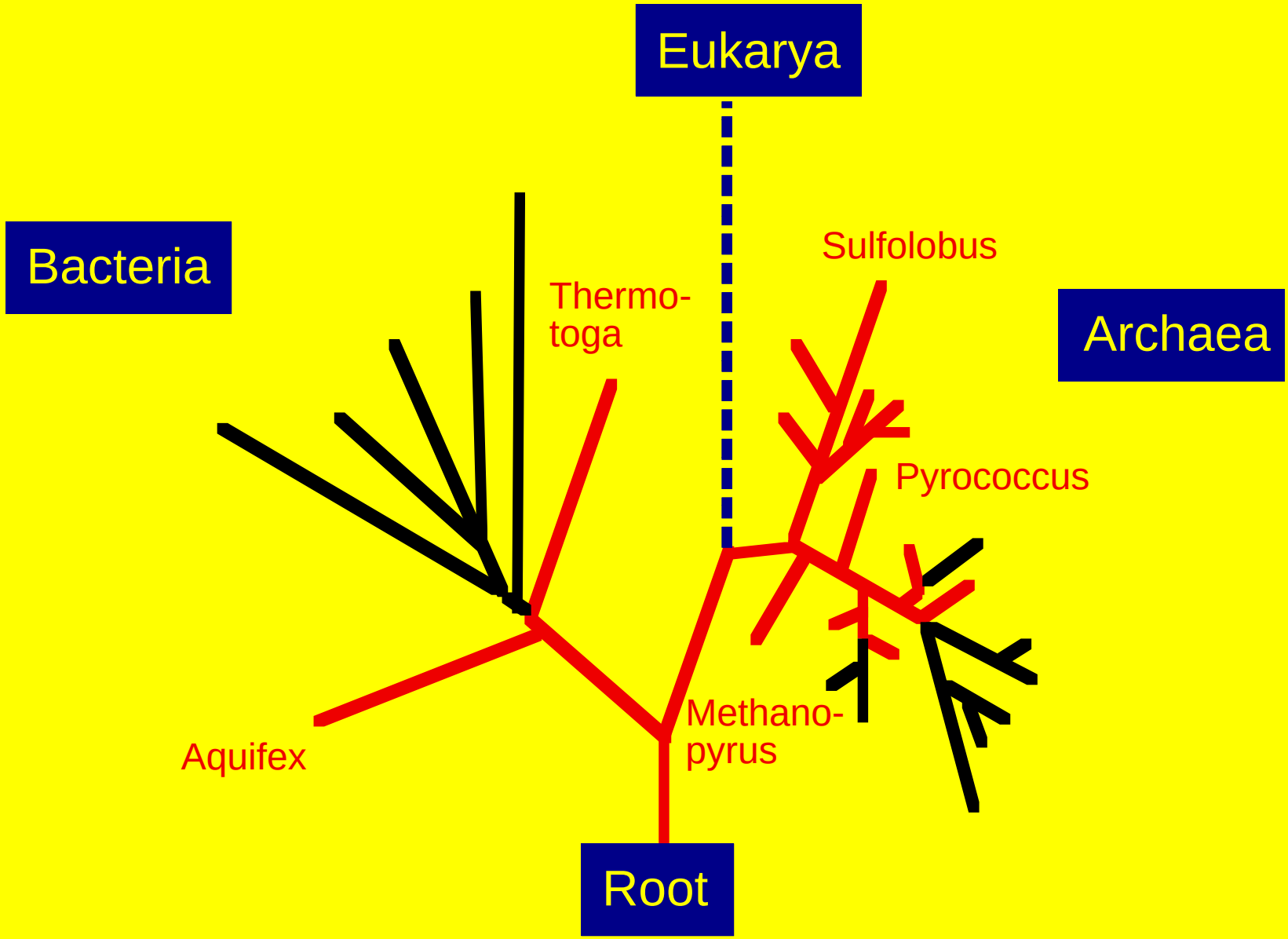
Where did first life arise?

Various indirect and debatable clues

- Planetary evolution models
- molecular phylogenetics
- bioinorganic chemistry

Bolide Impact on the Earth (Inferred) and Magnitude of Thermal Perturbation





Molecular Phylogenetic Tree (Ribosomal 16S rRNA)

Hyperthermophilic Organisms May be the Earliest Life Forms

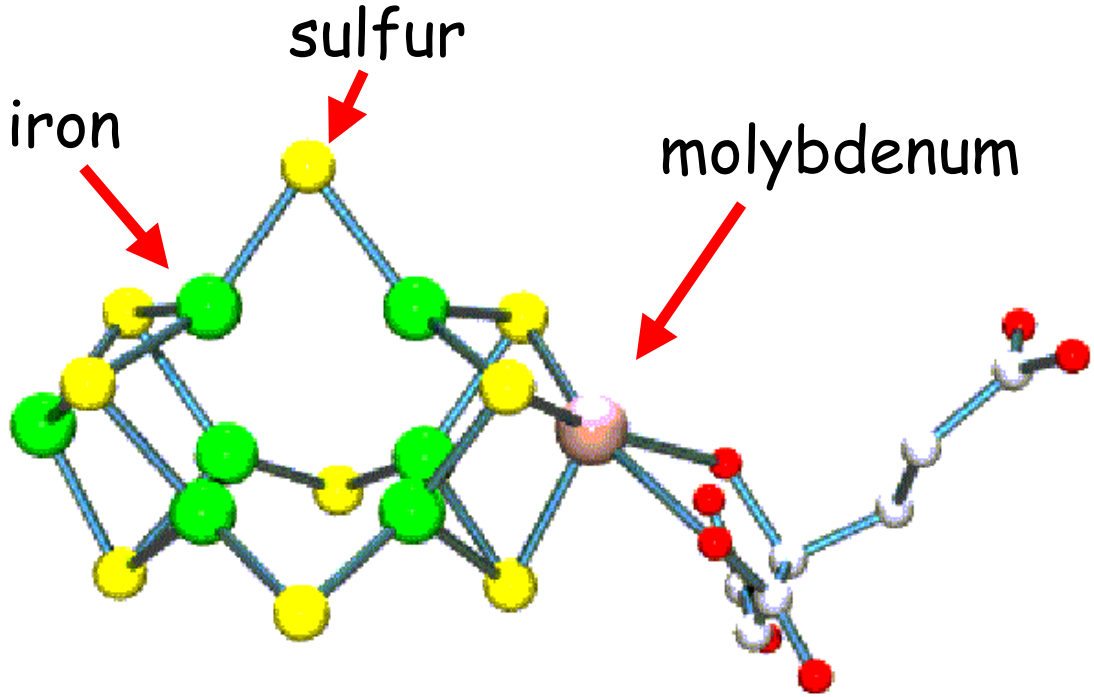
Clues from bioinorganic chemistry

"In the 'hidden world' of archaebacteria major catalysts remain Ni- and Co-based…but today in higher organisms these catalysts are lost or trivial in extent when compared with iron and copper Oxidases."

"… the early Earth provided large sources of H2S and various sulfide surfaces… The source of the unstable minerals and chemicals was and still is volcanoes and ocean vents"

Fraústo da Silva and Williams, The inorganic Chemistry of Life 1991

Clues to "where" from bio-inorganic chem.



Active Center of the enzyme - nitrogenase

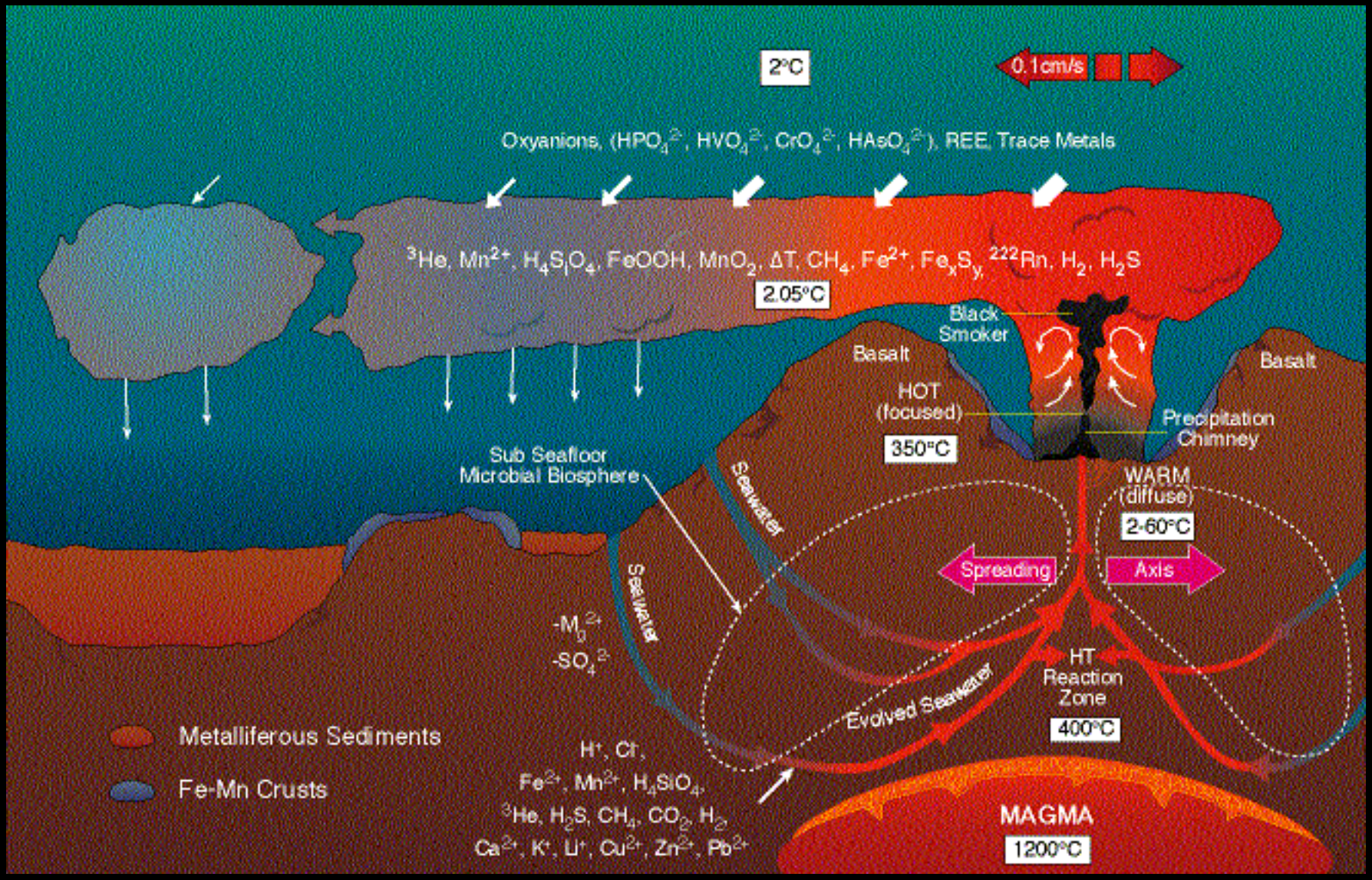
Function: Reduce N_2 to NH_3 (ammonia)

For nitrogen fixation

Deep Submarine Hydrothermal Vents

Life may have had Hydrothermal Origins

A Cartoon of a Hydrothermal Vent on the Ridge Crest



Globally significant chemical reactors

If life originated proximal to
Deep ocean hydrothermal vents
How did it begin?

Protometabolism

Geochemistry

RNA World

Synthesis of Polynucleotides

Development of RNA Replication

RNA-dependent Peptide Synthesis

Development of Translation

Emergence of protein enzymes

Metabolism

Biochemistry

After de Duve

Natural Sources of Reducing Power

Volcanic Exhalations: RedOx balanced by (FMQ)...

$3Fe_2SiO_4 + 2H_2O$ <-----> $2\ Fe_3O_4 + SiO_2 + \mathbf{2H_2}$

Hydrothermal Alteration of Sea Floor….

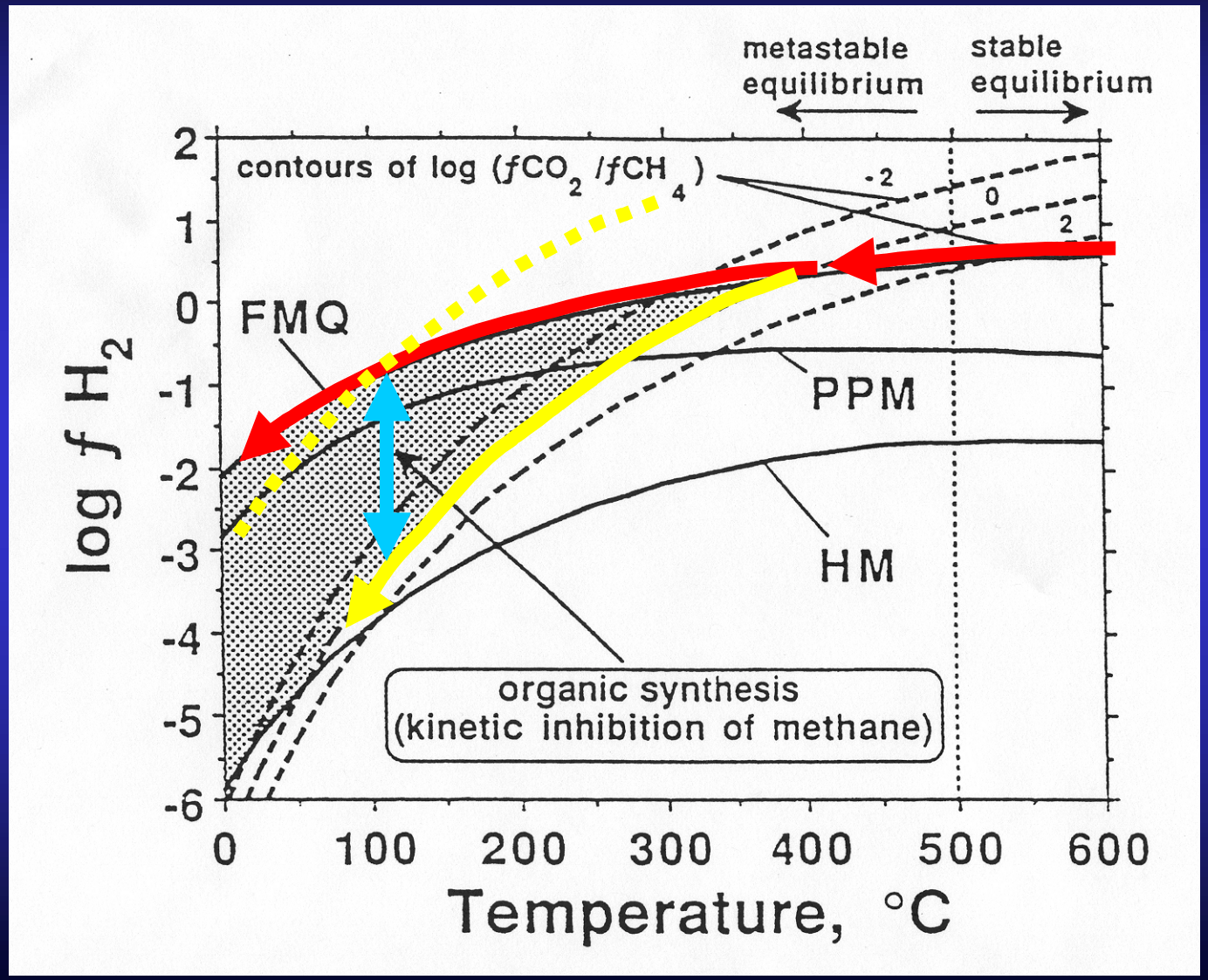
$6(Mg_{1.5}Fe_{0.5})SiO_4 + 7H_2O$ ------> $3[Mg_3Si_2O_5(OH)_4] +$

$Fe_3O_4 + \mathbf{H_2}$

The Possibility of Organosynthesis….

$CO_2 + 4H_2$ <-----> $CH_4 + 2H_2O$

$CO_2 + 4H_2$ <---> $CH_4 + 2H_2O$



From: Everett Shock OLEB 1990

Experiment: 300 °C 50 MPa

Hydrocarbon Generation Coupled with Serpentinization [*Bernd et. al. 1996*]

$CO_2 + H_2O + (Mg,Fe)_2SiO_4$ --->

CH_4 > C_2H_6 > C_3H_8 > ….

Source of Abiotic Lipid Formation

Pyrite pulled metabolism (Wächtershäuser, 1988)

$$FeS + H_2S \dashrightarrow FeS_2 + 2H^+ + 2e^-$$

and

$$CO_2 + 2H^+ + 2e^- \dashrightarrow H_2CO_2$$

then

$$FeS + CO_2 + H_2S \rightarrow FeS_2 + HCOOH \quad (\Delta G_r < 0)$$

The Synthesis of Methane thiol using the Reducing power of FeS-> FeS_2 (Heinen & Lauwers, 1996)

$FeS\text{-}FeS_2$

$$CO_2 + 3H_2 + H_2S \rightarrow CH_3SH + 2H_2O$$

The Synthesis of Acetic Acid from methane Thiol and M_xS_y (Hüber & Wächtershäuser, 1997)

(Fe,Ni)S

$$CO + CH_3SH + H_2O \rightarrow CH_3COOH + H_2S$$

Hydrothermal Mineralogy
An Abundance of Transition Metal Sulfides

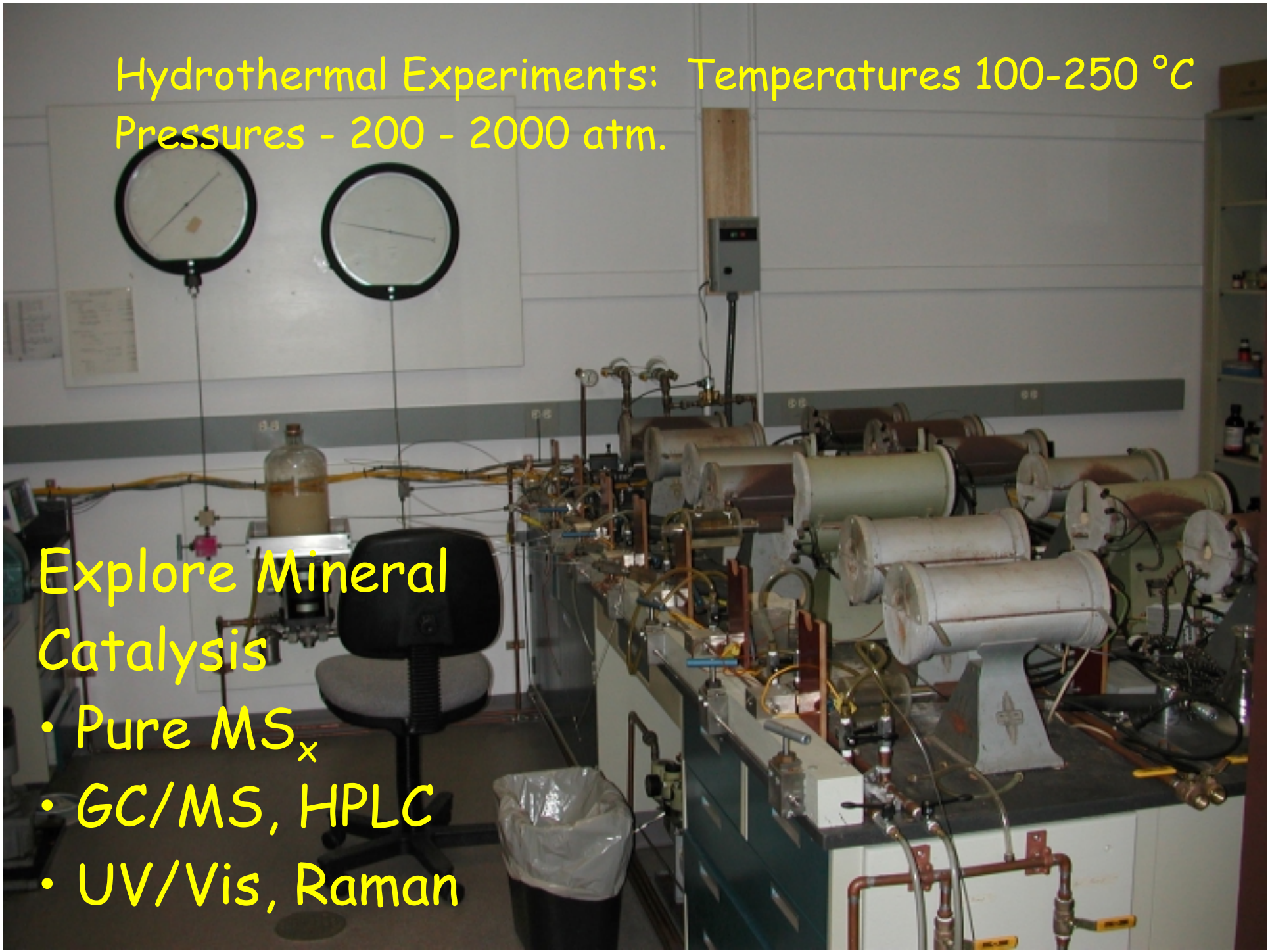
Pyrite (FeS_2), Pyrrhotite ($Fe_{1-x}S$), Chalcopyrite ($CuFeS_2$), Sphalerite (ZnS) And others.

Pyrite
FeS_2

Chalco-
Pyrite
$CuFeS_2$

Sphalerite
ZnS

Nature's Catalysts ?


Hydrothermal Experiments: Temperatures 100-250 °C
Pressures - 200 - 2000 atm.
Explore Mineral Catalysis
• Pure MS_x
• GC/MS, HPLC
• UV/Vis, Raman

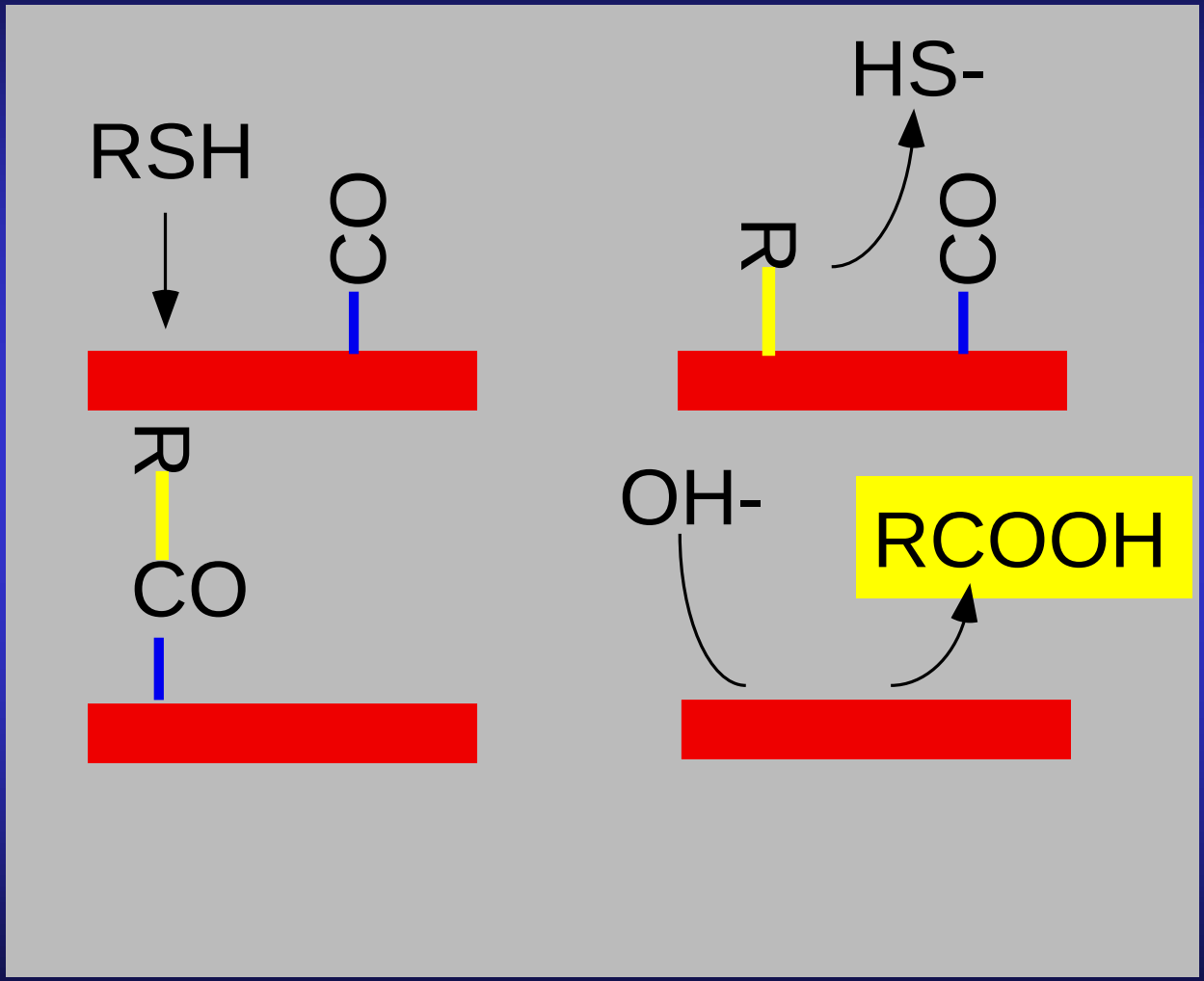
The Assay Reaction: Hydrocarboxylation aka the Koch reaction

$$R\text{-}SH + CO_2 + H_2 \longrightarrow R\text{-}COOH + H_2S$$

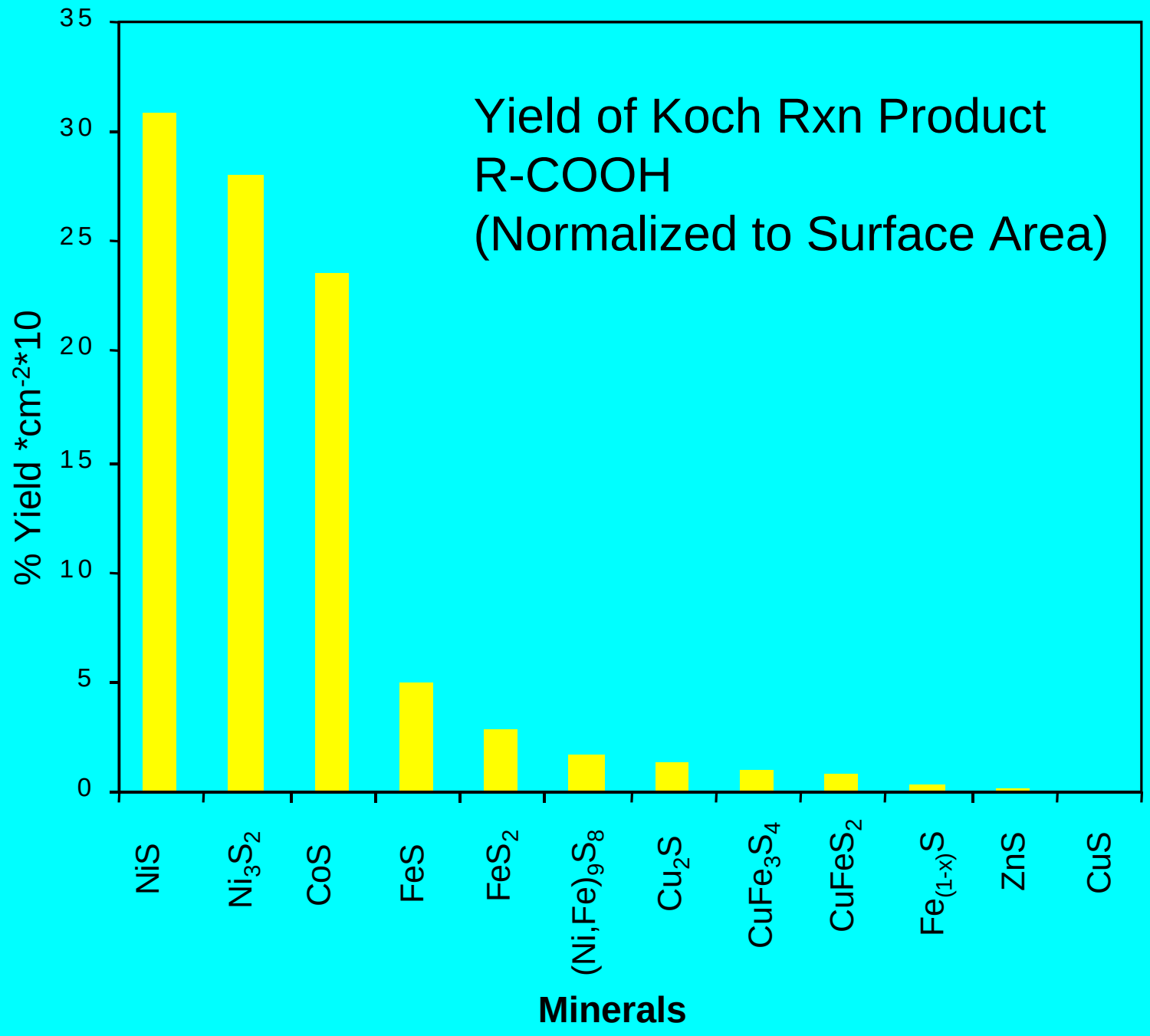
Where $R = CH_3(CH_2)_n$ in our case $n = 8$

Reaction conditions for optimum assay
i.e. total saturation of active sites

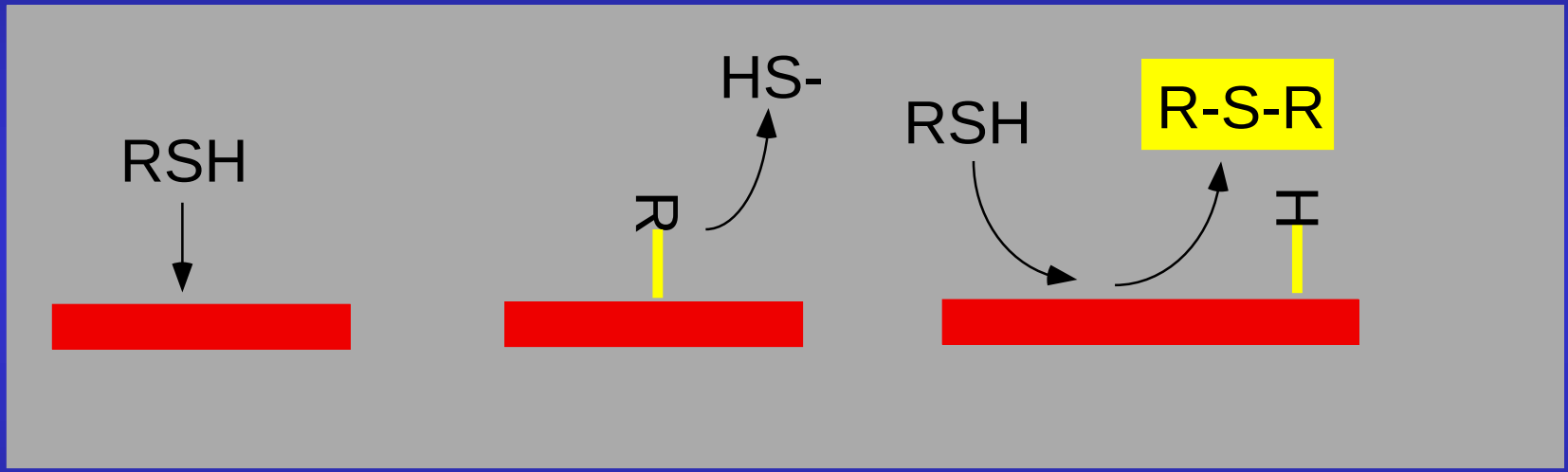
Carbonyl Insertion on Mineral Sulfide Surfaces



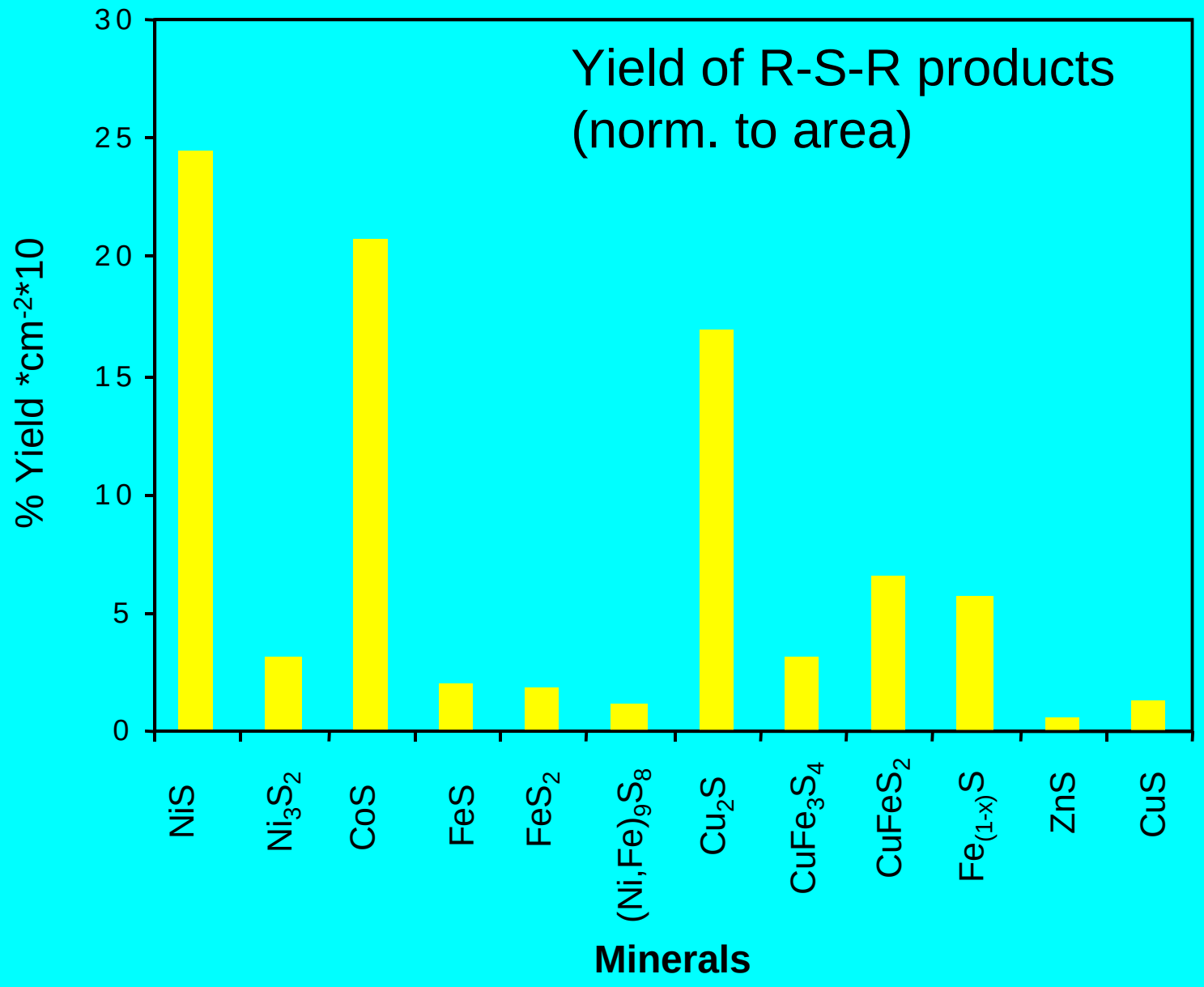
R = $CH_3(CH_2)_8$ [Nonyl group]


Yield of Koch Rxn Product
R-COOH
(Normalized to Surface Area)
% Yield *cm-2*10
35
30
25
20
15
10
5
0
NiS
Ni3S2
CoS
FeS
FeS2
(Ni,Fe)9S8
Cu2S
CuFe3S4
CuFeS2
Fe(1-x)S
ZnS
CuS
Minerals

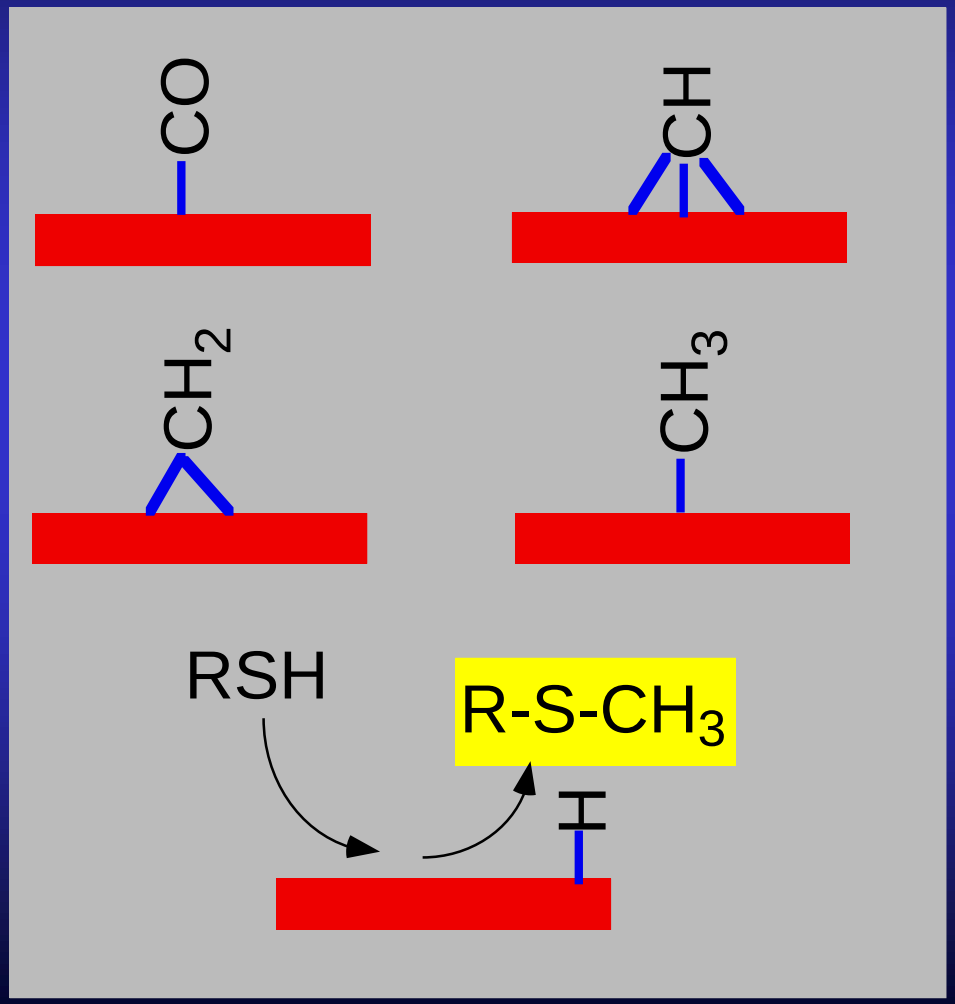
Alkyl Cation Transfer: Dialkyl sulfide



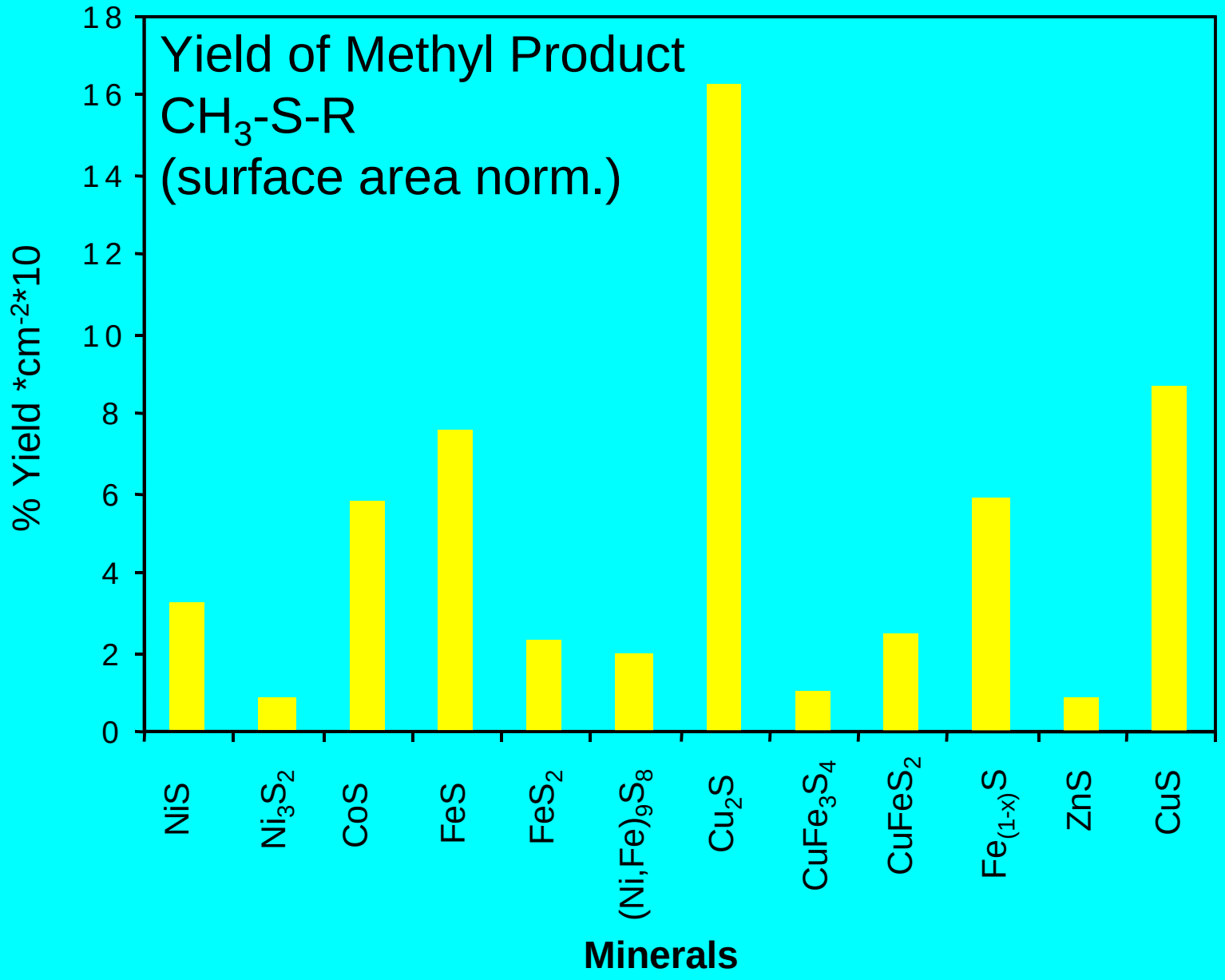
R = $CH_3(CH_2)_8$ [Nonyl group]


Yield of R-S-R products
(norm. to area)
% Yield *cm-2*10
30
25
20
15
10
5
0
NiS
Ni3S2
CoS
FeS
FeS2
(Ni,Fe)9S8
Cu2S
CuFe3S4
CuFeS2
Fe(1-x)S
ZnS
CuS
Minerals

Formation of CH_3 From CO Reduction



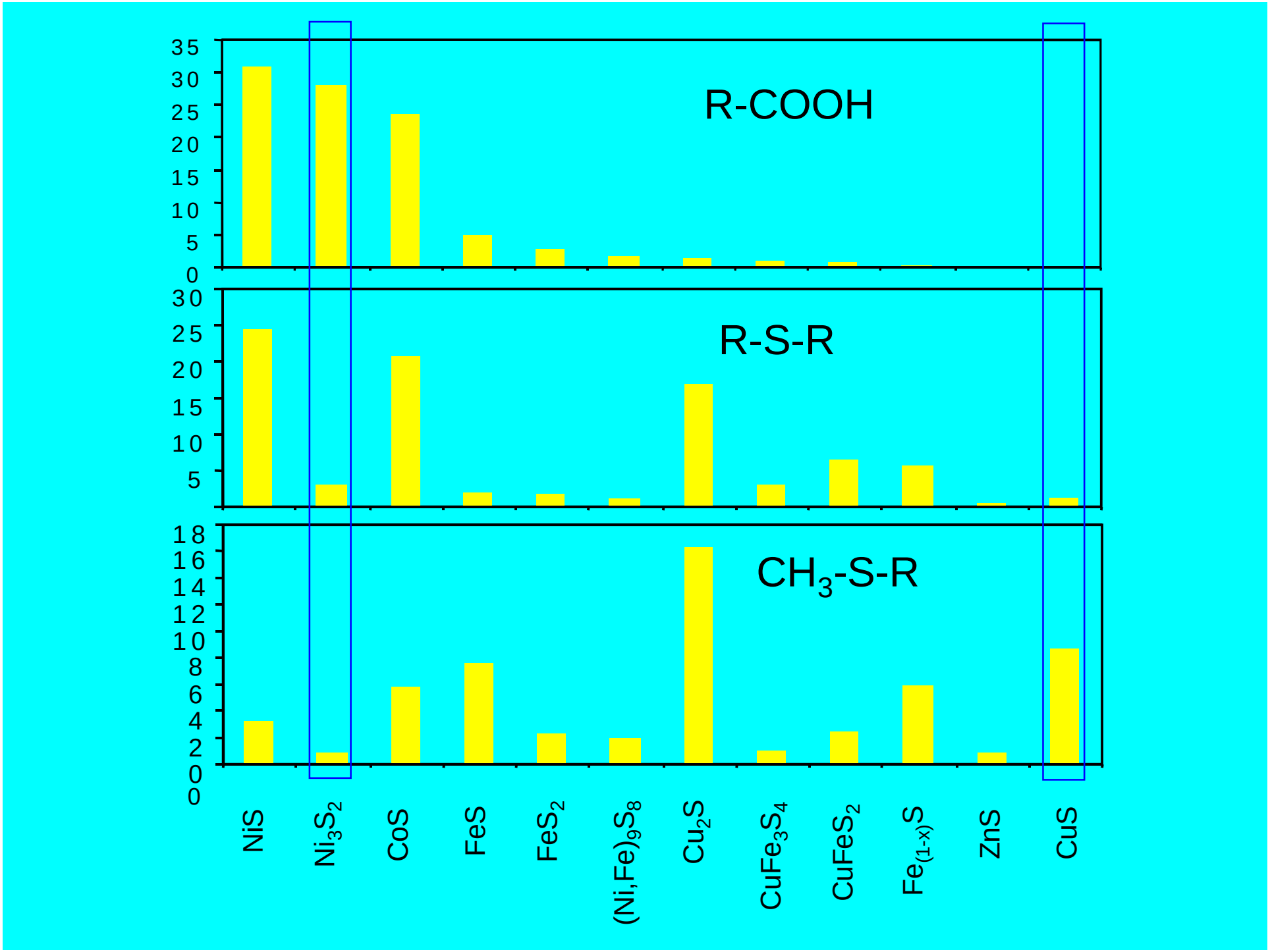
R = $CH_3(CH_2)_8$ [Nonyl group]

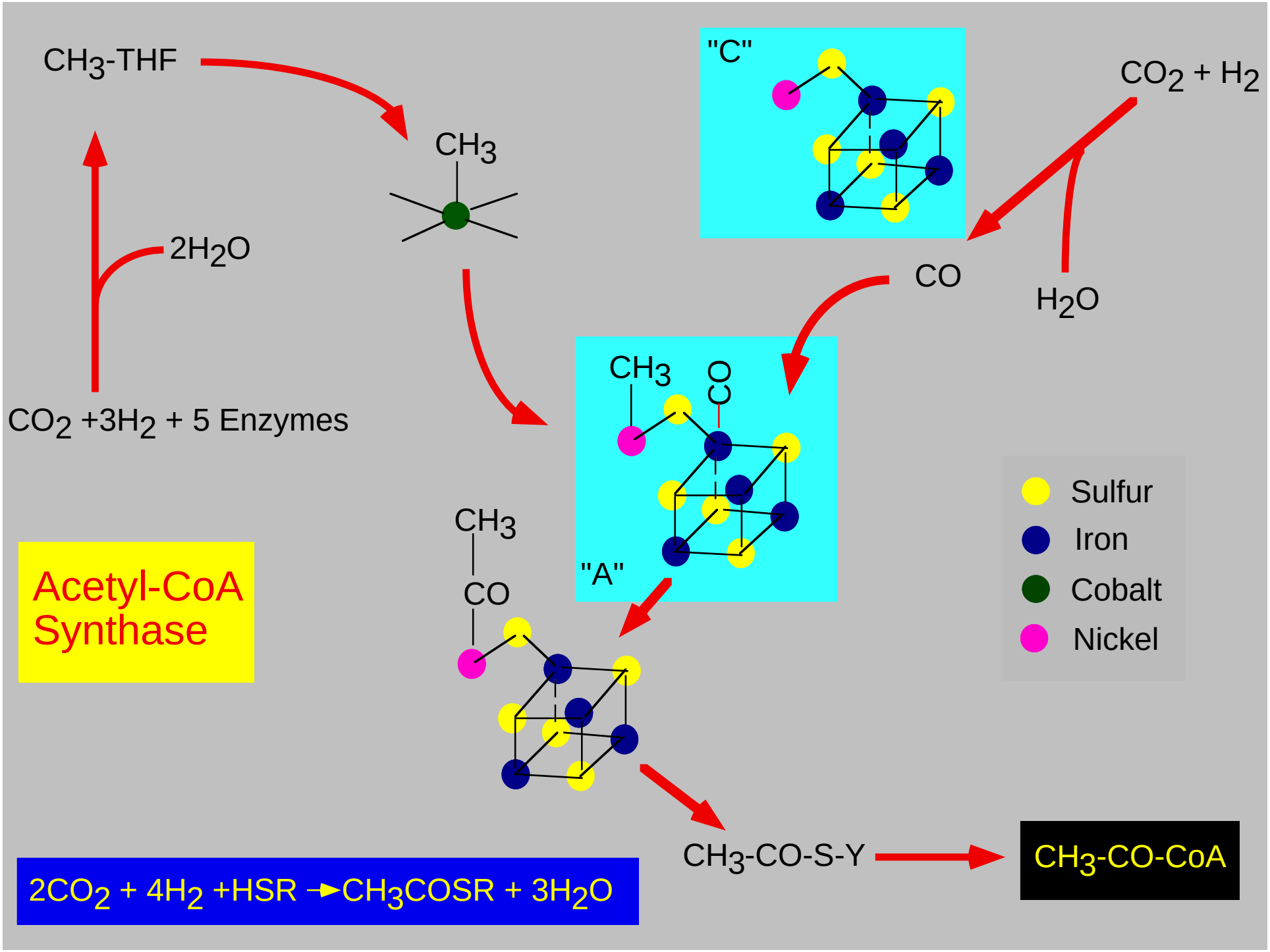

Yield of Methyl Product
CH3-S-R
(surface area norm.)
% Yield *cm-2*10
0
2
4
6
8
10
12
14
16
18
NiS
Ni3S2
CoS
FeS
FeS2
(Ni,Fe)9S8
Cu2S
CuFe3S4
CuFeS2
Fe(1-x)S
ZnS
CuS
Minerals

Different transition metal sulfides exhibit variations in Reaction selectivity

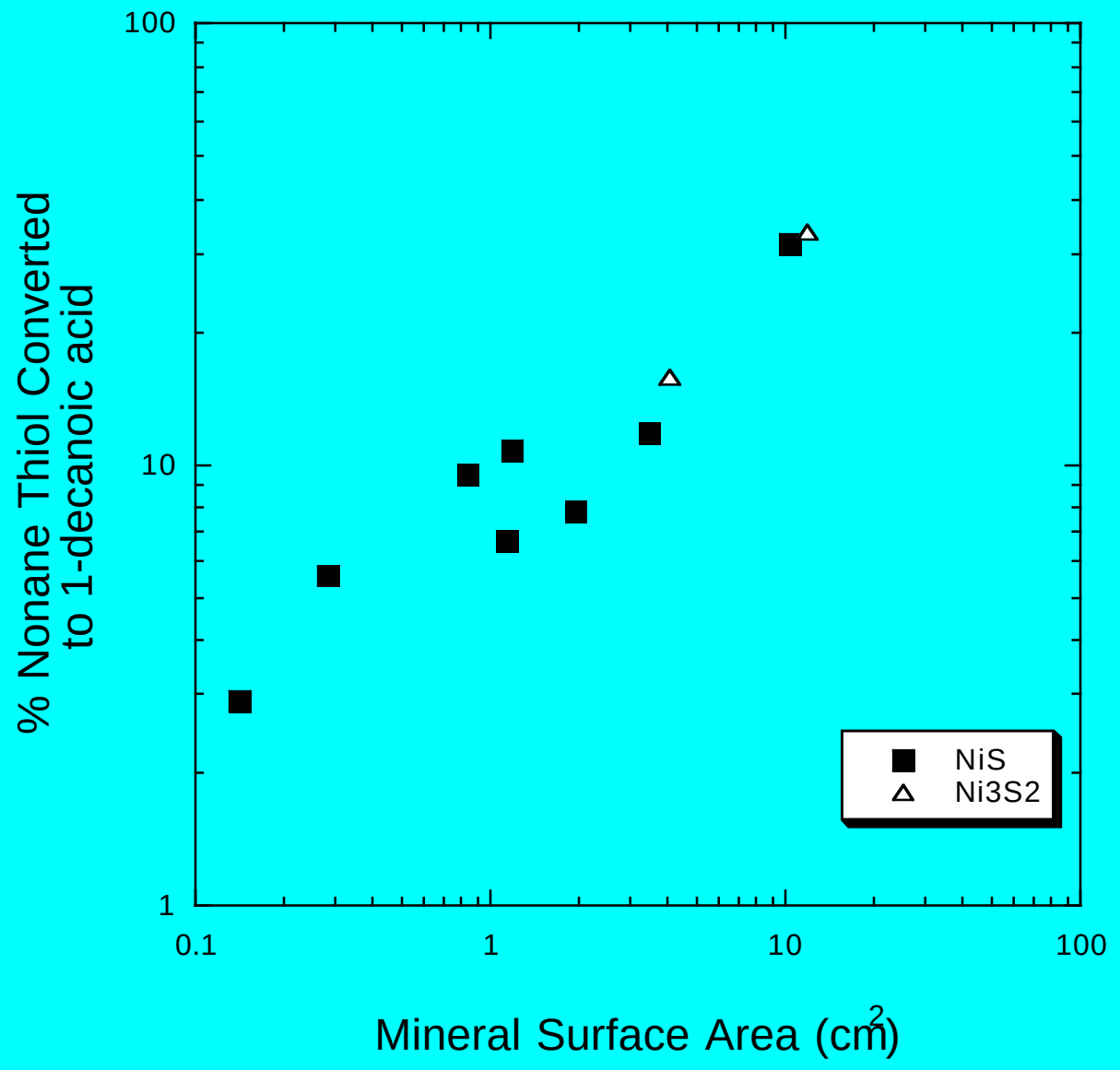
This suggests that fine admixtures of 2, 3, … might Work synergistically

Similarly, doping of pure phases with other metals May be expected to produce interesting possibly Synergistic effects


R-COOH
R-S-R
CH3-S-R
35
30
25
20
15
10
5
0
30
25
20
15
10
5
18
16
14
12
10
8
6
4
2
0
0
NiS
Ni3S2
CoS
FeS
FeS2
(Ni,Fe)9S8
Cu2S
CuFe3S4
CuFeS2
Fe(1-x)S
ZnS
CuS

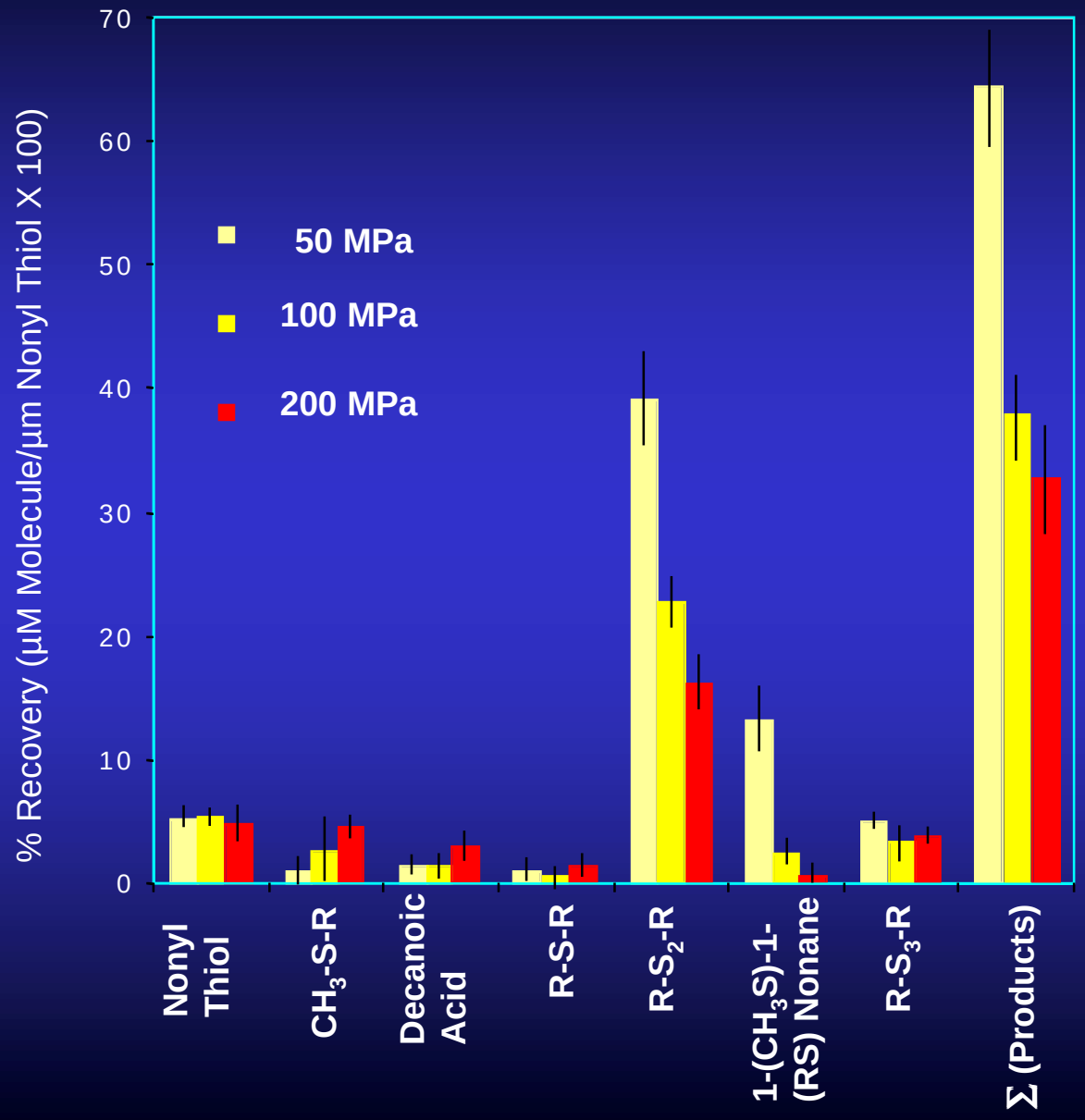

CH3-THF
CH3
2H2O
CO2 +3H2 + 5 Enzymes
"C"
CO2 + H2
CO
H2O
CH3
CO
"A"
CH3
CO
Acetyl-CoA Synthase
Sulfur
Iron
Cobalt
Nickel
CH3-CO-S-Y
CH3-CO-CoA
2CO2 + 4H2 +HSR → CH3COSR + 3H2O

Are these rxns surface catalyzed?



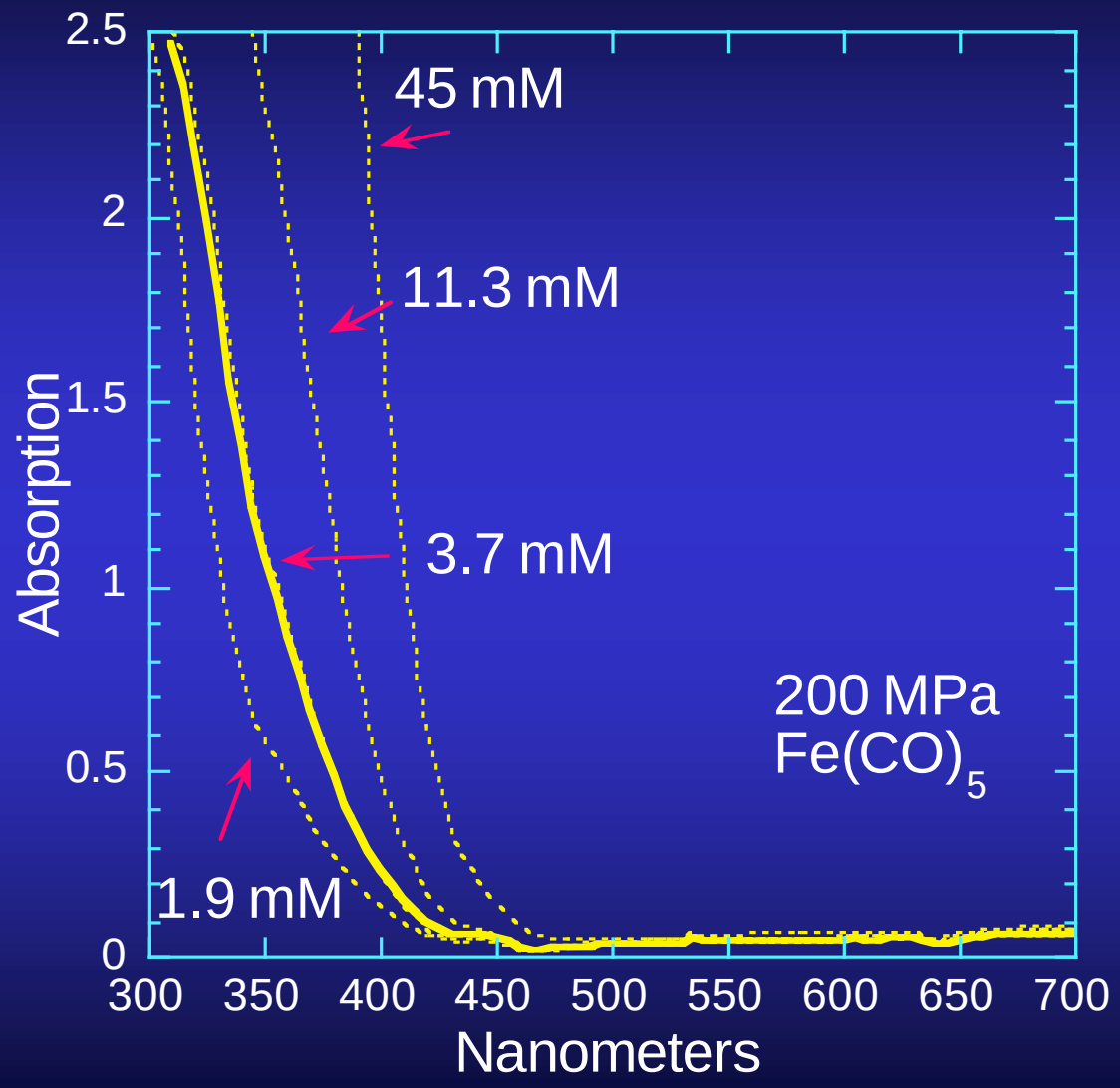
Yield of Acid vs. Mineral Surface Area: 250°C 200 MPa 6 h.s

FeS Formic - Thiol Reactions Variable P



250 °C
6 h

Reaction: Aqueous Formic Acid - FeS 250°C 200 MPa 6h



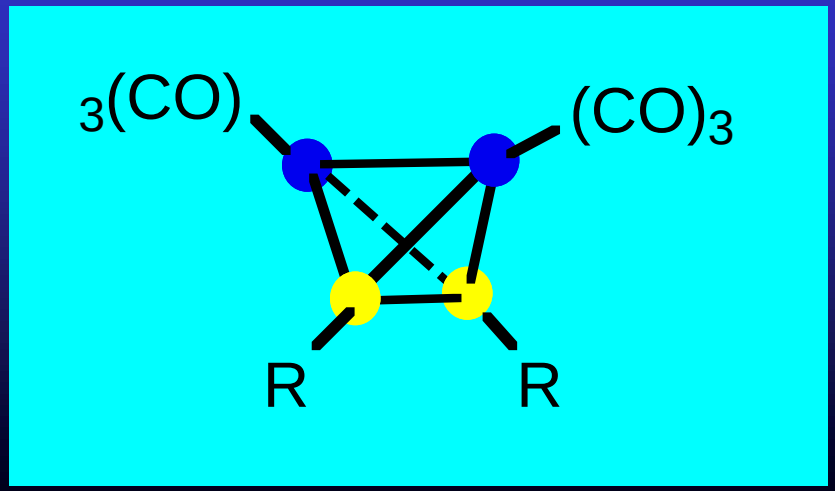
Yield of Iron Carbonyl: 2 % of Fe and 17 % of C_1

Additional Reactions Involving FeS, CO, and Alkyl Thiols

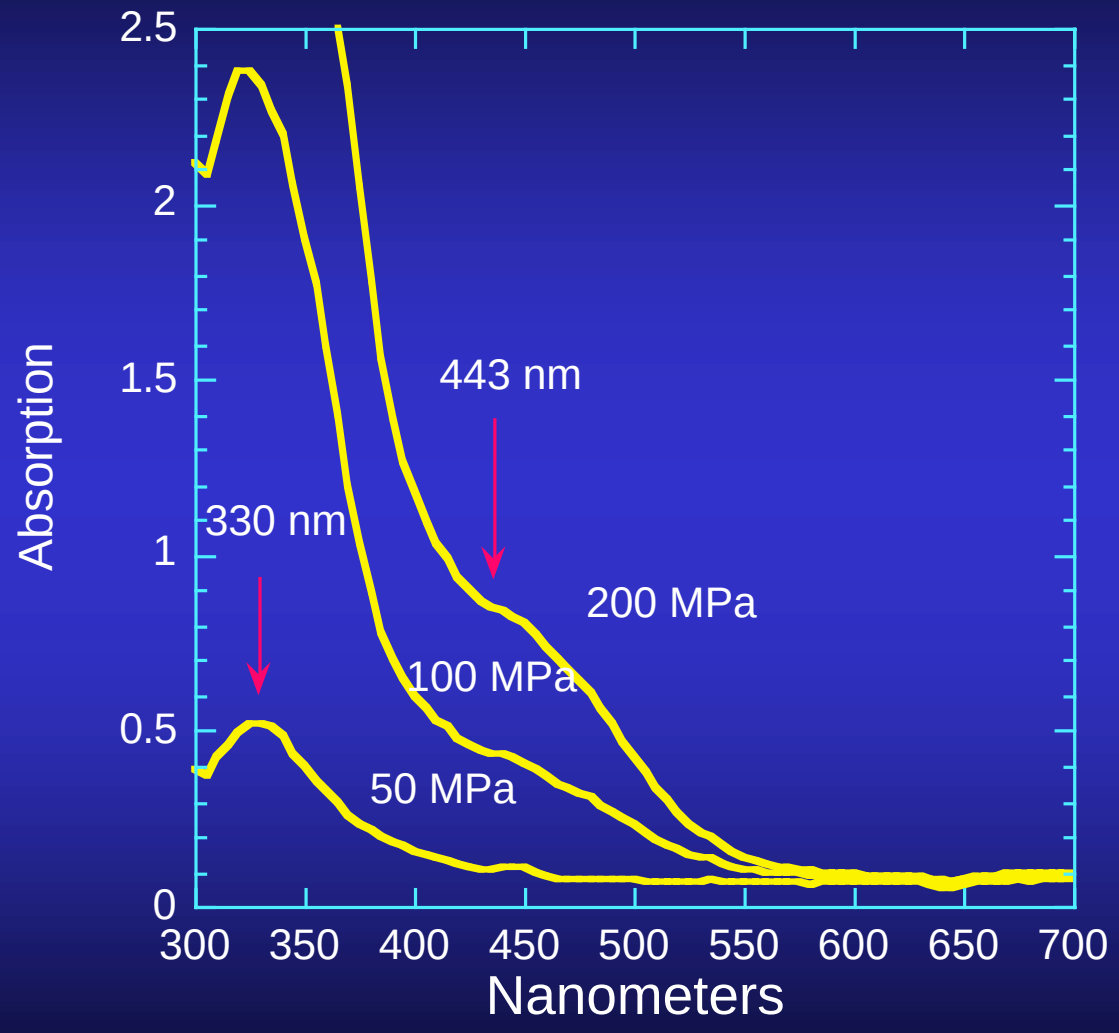
$FeS + 5CO \leftrightarrow Fe(CO)_5 + S^0$

$2\ R\text{-}SH + S^0 \leftrightarrow R\text{-}S\text{-}S\text{-}S\text{-}R + H_2$

$2\ R\text{-}SH + 2\ Fe(CO)5 \leftrightarrow Fe_2(RS)_2(CO)_6 + 4CO + H_2$

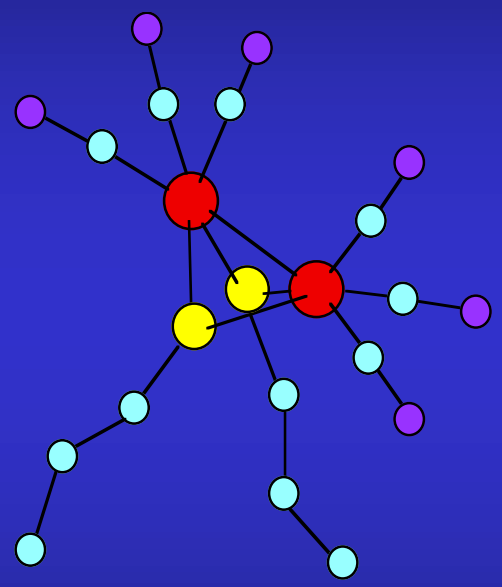


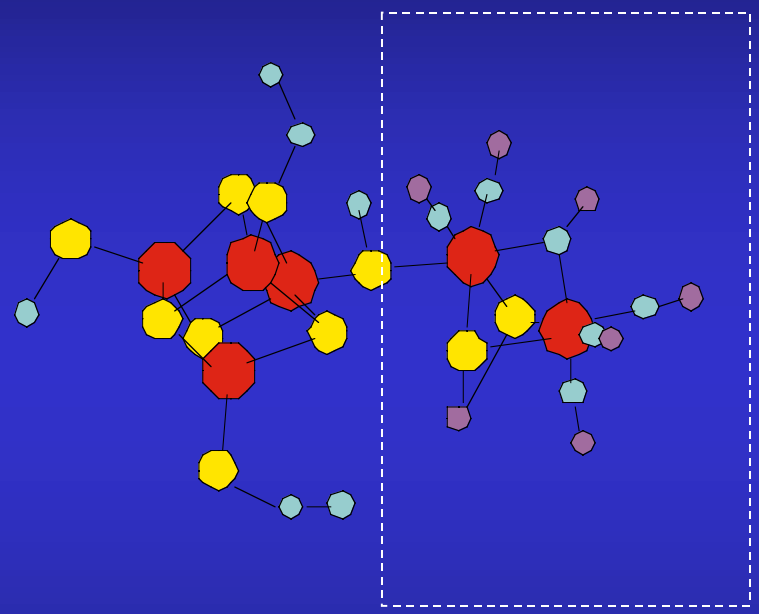
Reaction: Aqueous Formic Acid - FeS - Nonylthiol
250°C 200 MPa 6h



Iron-sulfur Carbonyls + 20-50% Dissolution of FeS

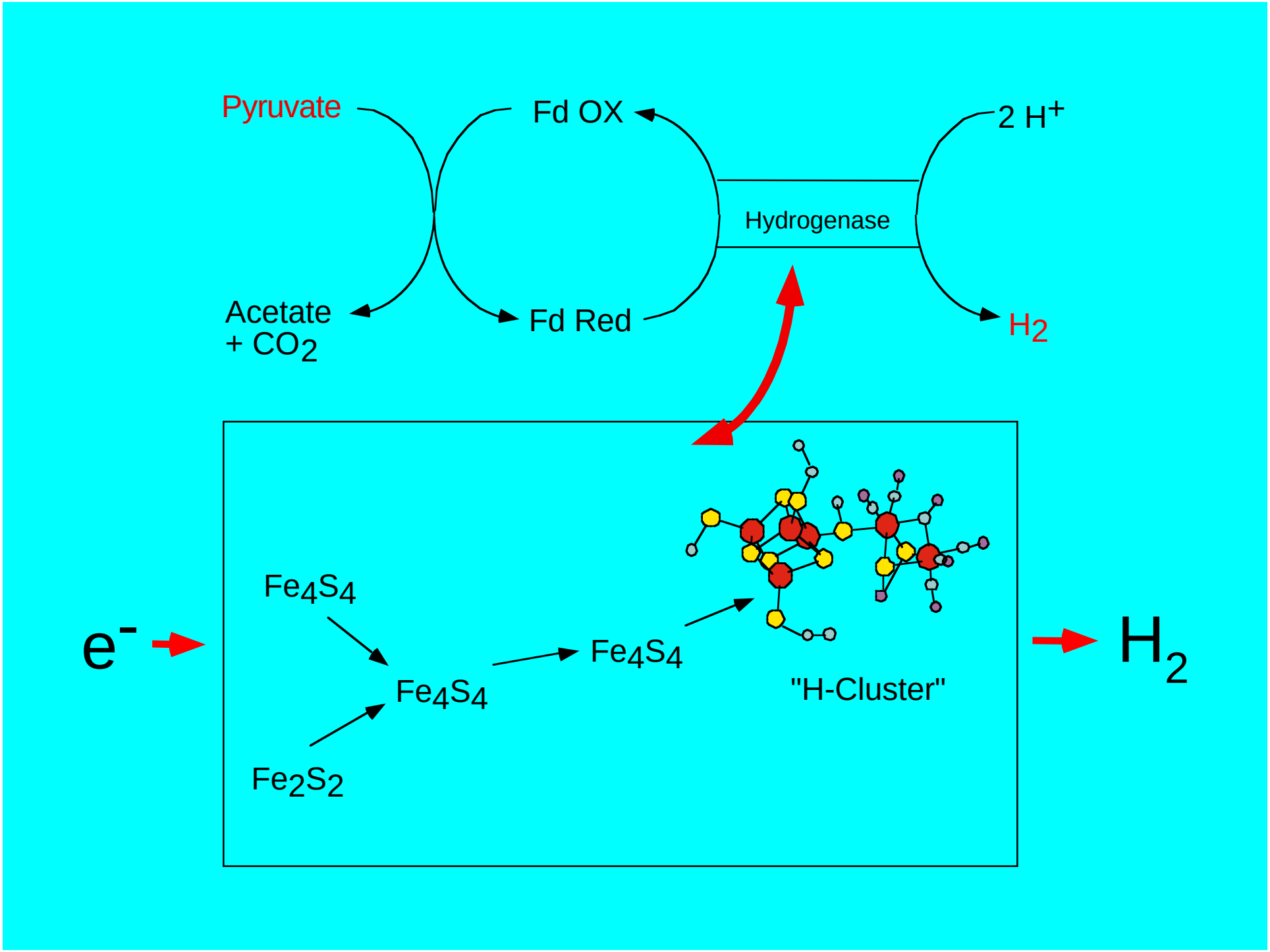
Carbonylated Fe-S Clusters & Biochemical Connections





Product of FeS Rxn's With Formic Acid and Nonyl-thiol @ Hi P and T

'H-Cluster' in Hydrogenase 2-Fe domain with CO or CN ligands


Pyruvate
Fd OX
2 H+
Hydrogenase
Acetate
+ CO2
Fd Red
H2
e-
Fe4S4
Fe4S4
Fe4S4
Fe2S2
"H-Cluster"
H2

The Ubiquity of Hydrogenase

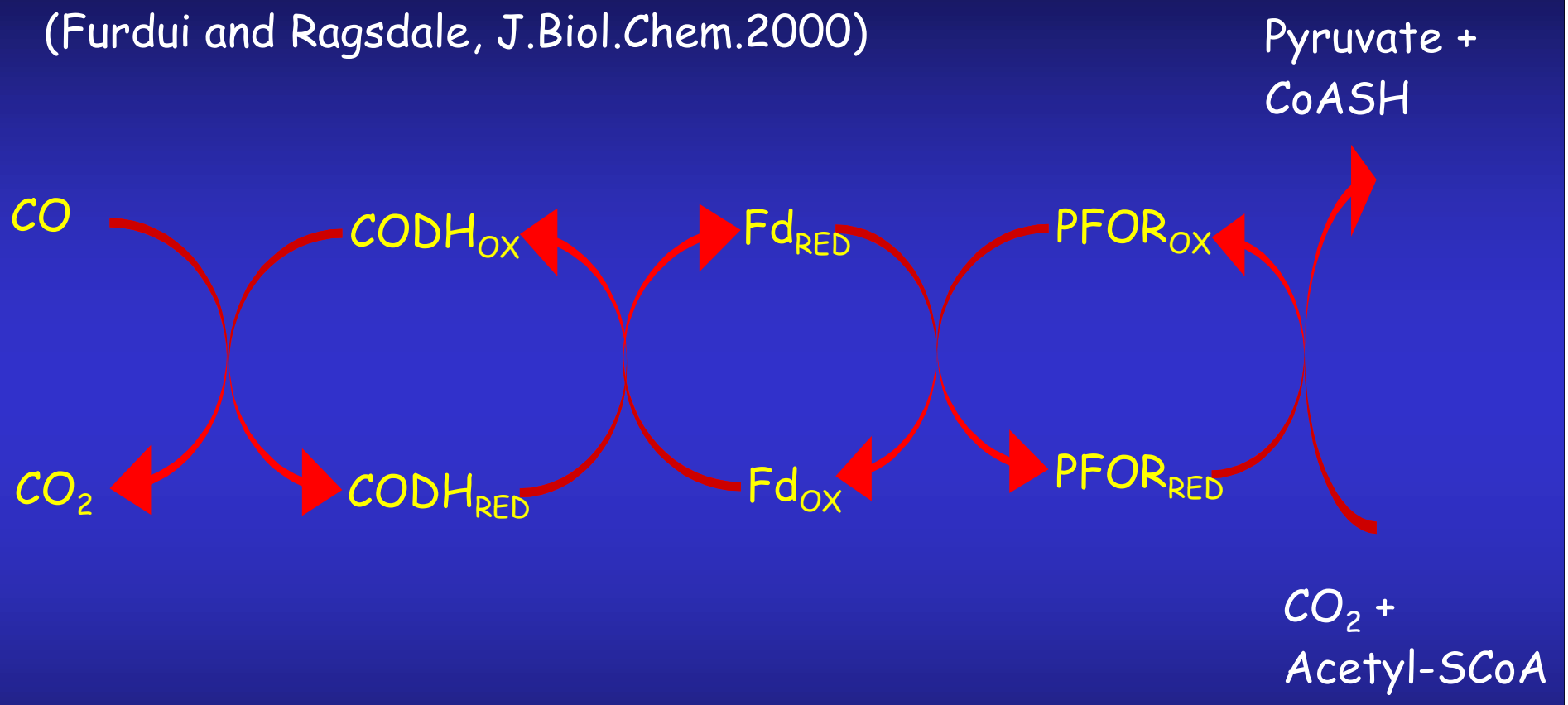
H_2 →

CO_2	Methanogens →	CH_4
CO_2	Acetogens →	Acetate
SO_4^{-2}	Sulfur Reducers →	H_2S
Fe^{3+}	Iron Reducers →	Fe^{2+}
NO^{3-}	Denitrification →	N_2
N_2	Nitrogen fixation →	NH_2^-
CO_2	Photosynthesis →	Sugars

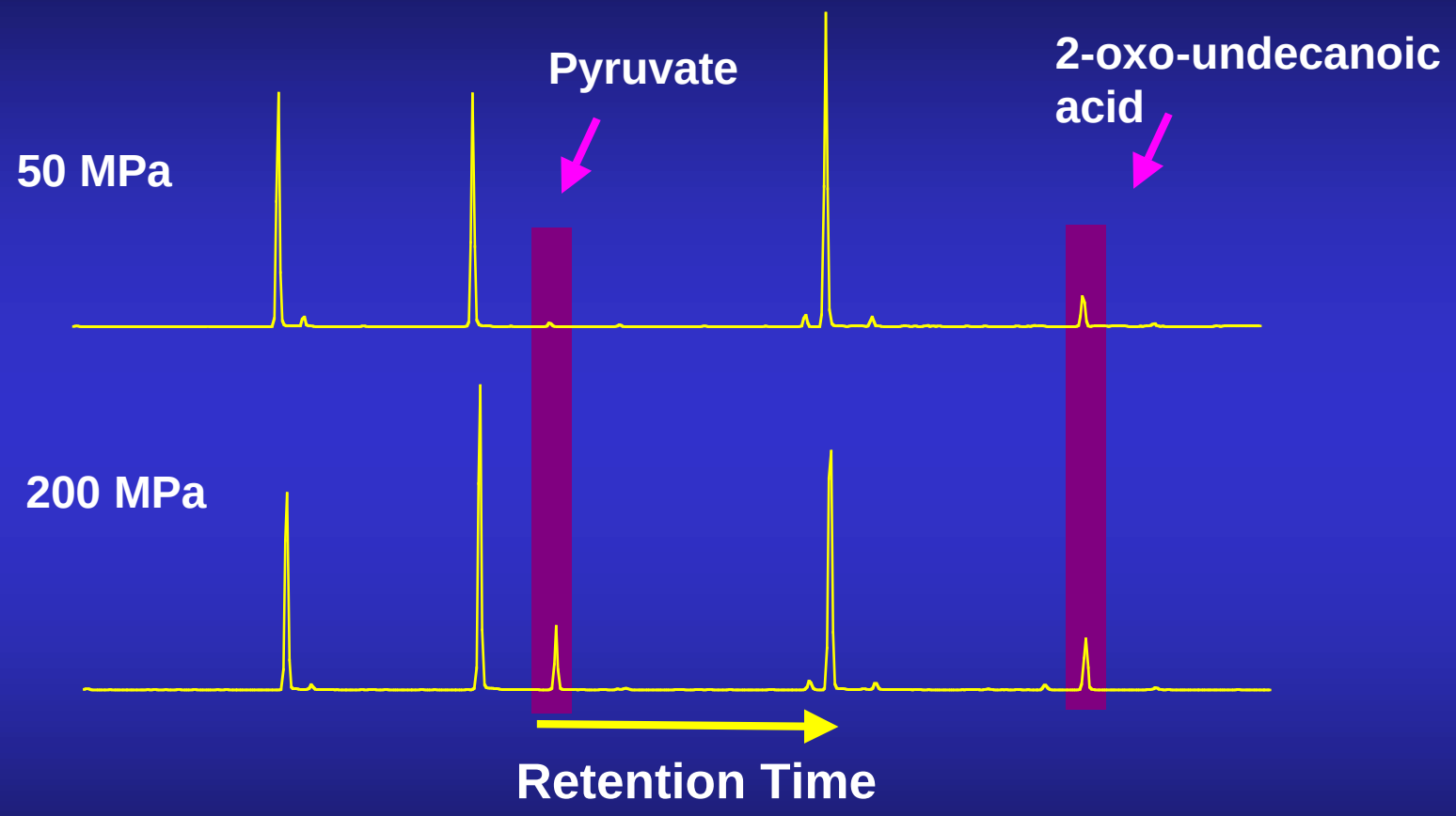
Chemautotrophy

Pyruvate Ferrodoxin Oxidoreductase (PFOR) can Operate in reverse to synthesize pyruvate

(Furdui and Ragsdale, J.Biol.Chem.2000)



Carbonylated Fe-S Clusters May Promote double Carbonyl Insertion Reactions



Low Yields (< 1%) revealed via SIM Detection

In Primordial Hydrothermal Systems

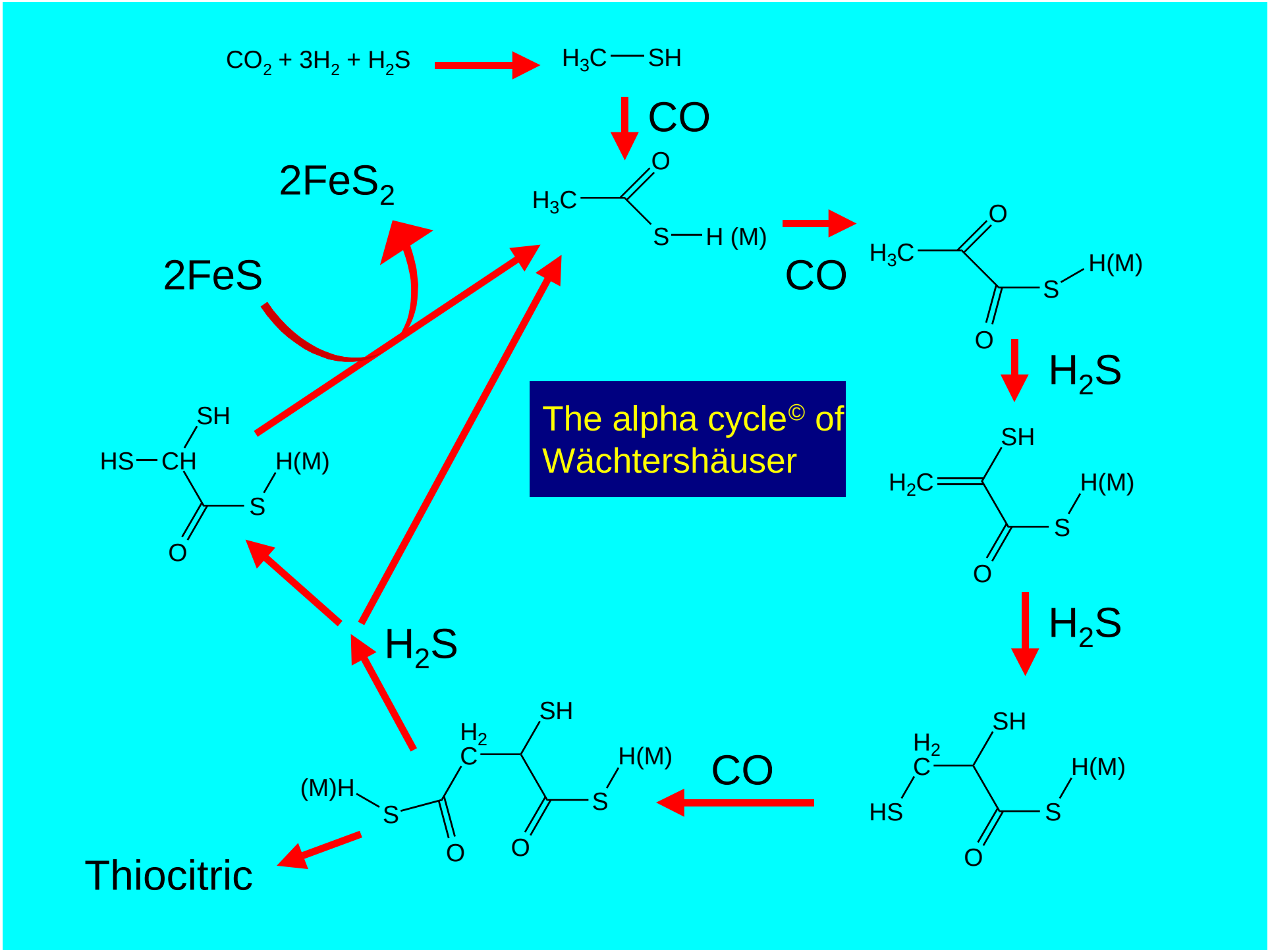
No Adenosine triphosphate
No NADH

3.2 Ga (Archean Rocks)

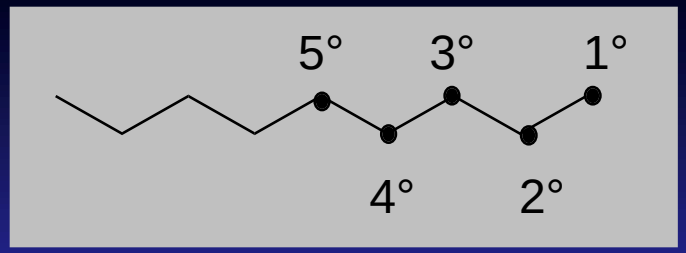
[ancient sea floor: de Ronde et al.1997]

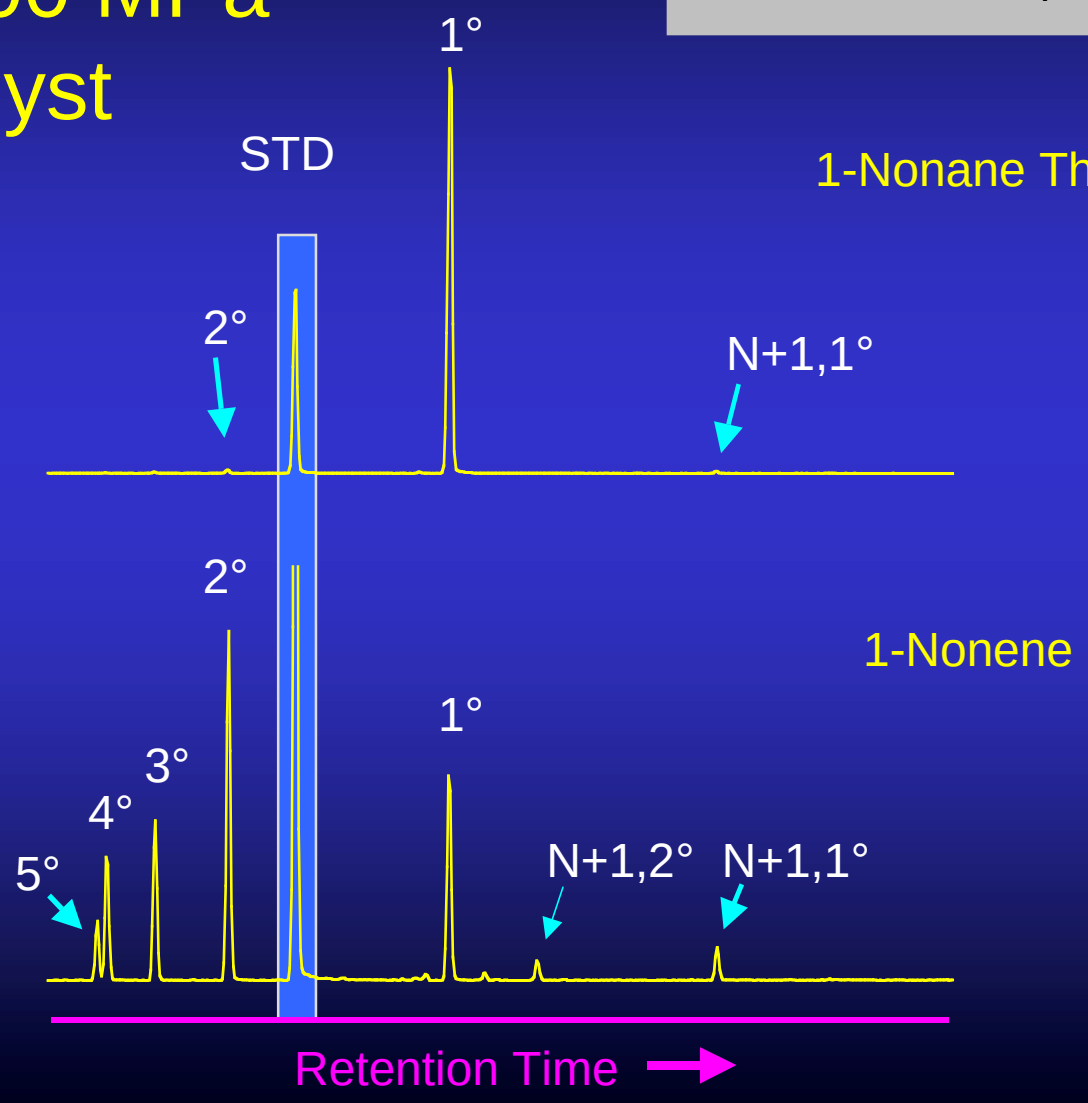
CO_2, H_2, Transition Metal Sulfides, COS, H_2S,

+ Alkenes- *e.g.* Ethylene, **Propene**, butene

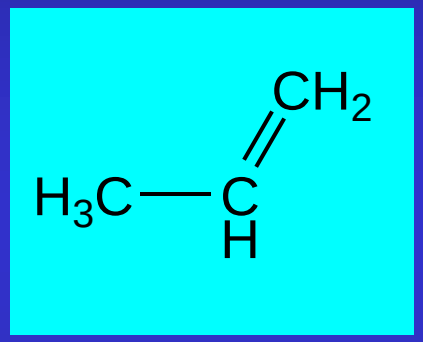

CO2 + 3H2 + H2S
H3C—SH
CO
H3C
O
S—H (M)
CO
H3C
O
S
H(M)
O
H2S
H2C
SH
H(M)
S
O
H2S
SH
H2
C
HS
H(M)
S
O
CO
SH
H2
C
H(M)
(M)H
S
S
O
O
Thiocitric
2FeS2
2FeS
HS—CH
SH
H(M)
S
O
H2S
The alpha cycle© of
Wächtershäuser

Decanoic Acid Synthesis
250° C 200 MPa
NiS Catalyst

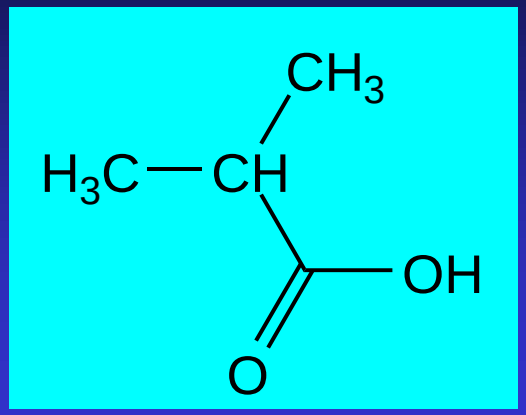


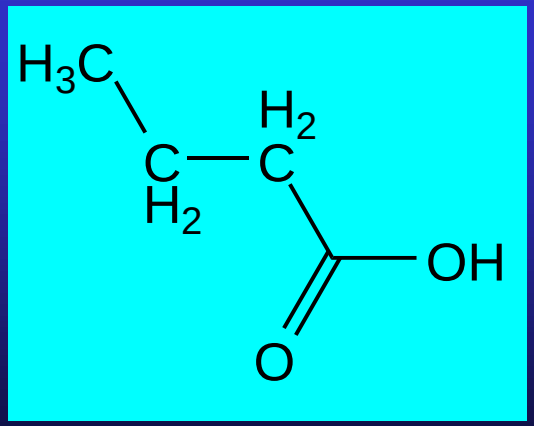


Propene

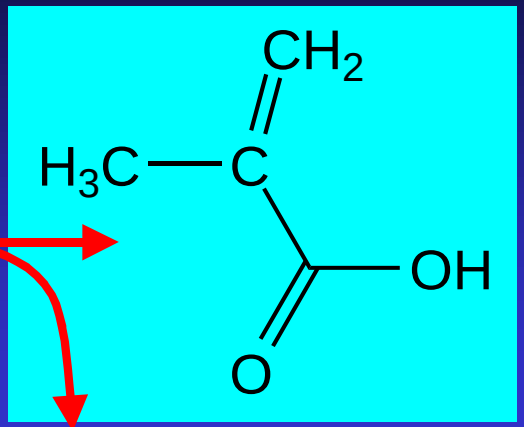


$CO_2 + H_2$





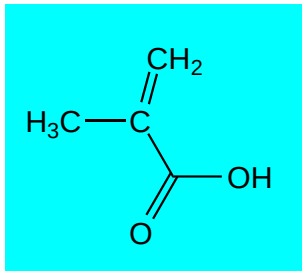
Methacrylic Acid



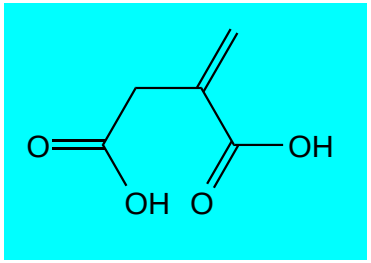
$2\ H^+ + 2\ e^-$

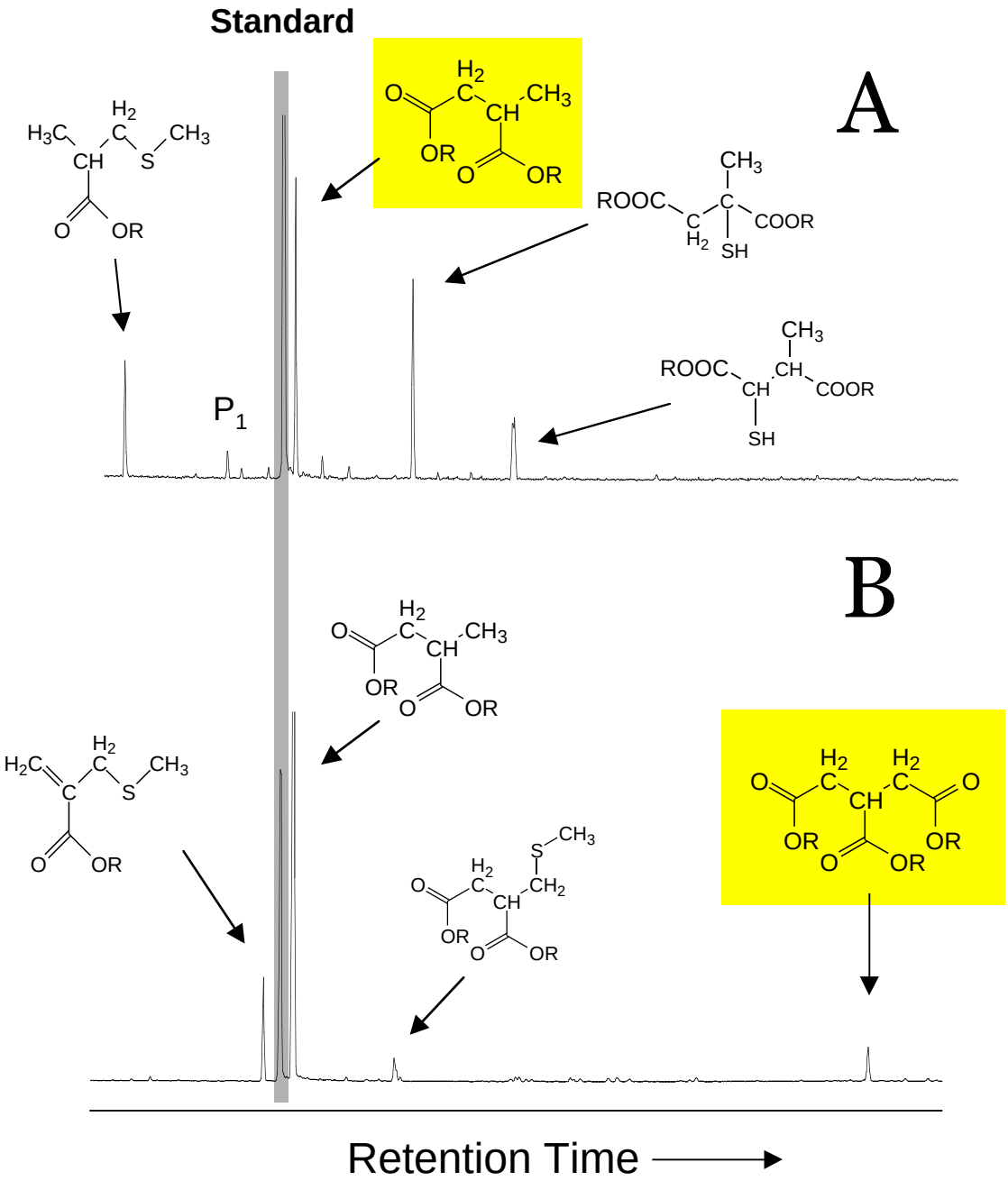
$\Delta Gr > 0$

Methacrylic Acid + HCOOH + NiS

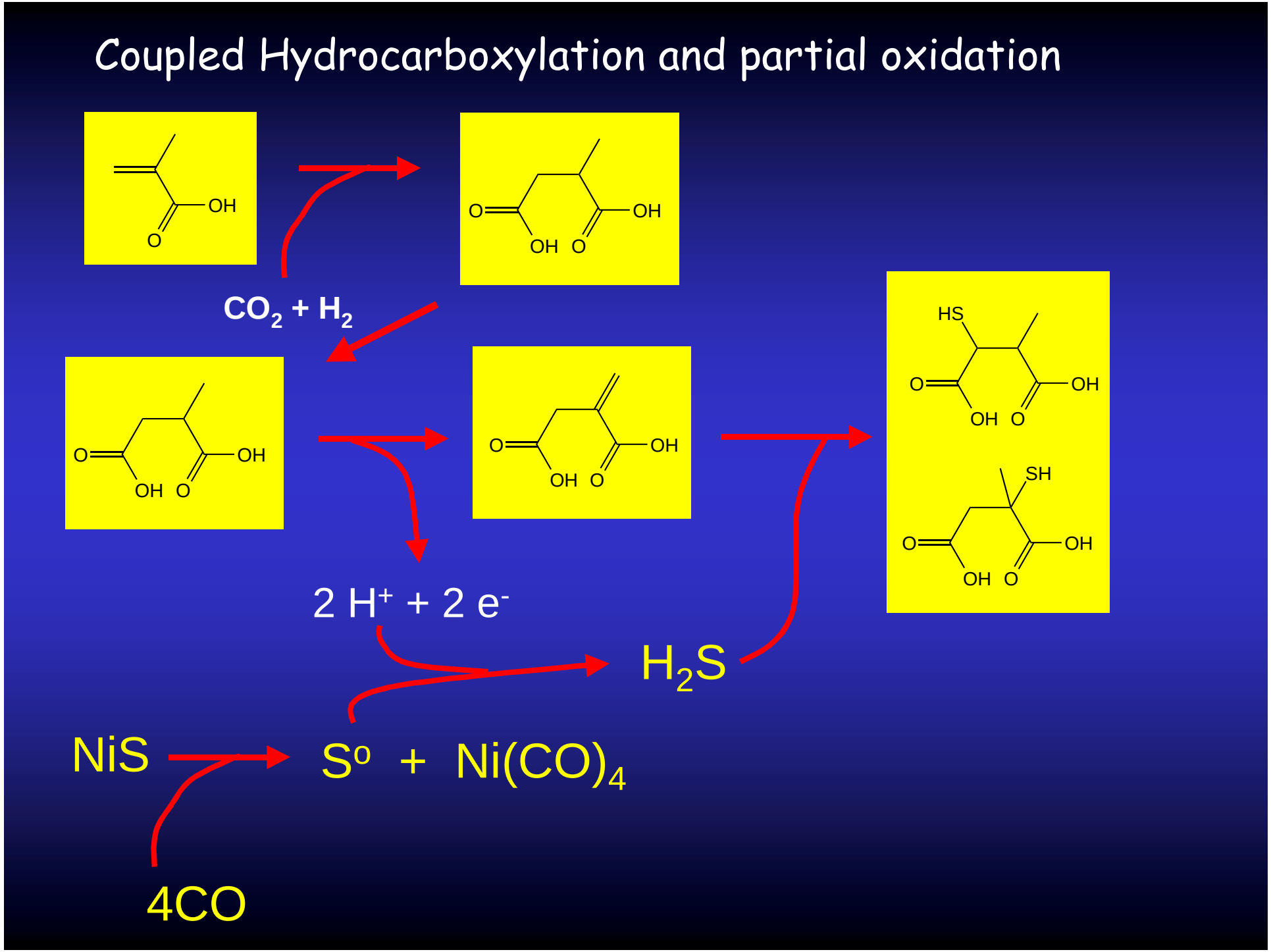


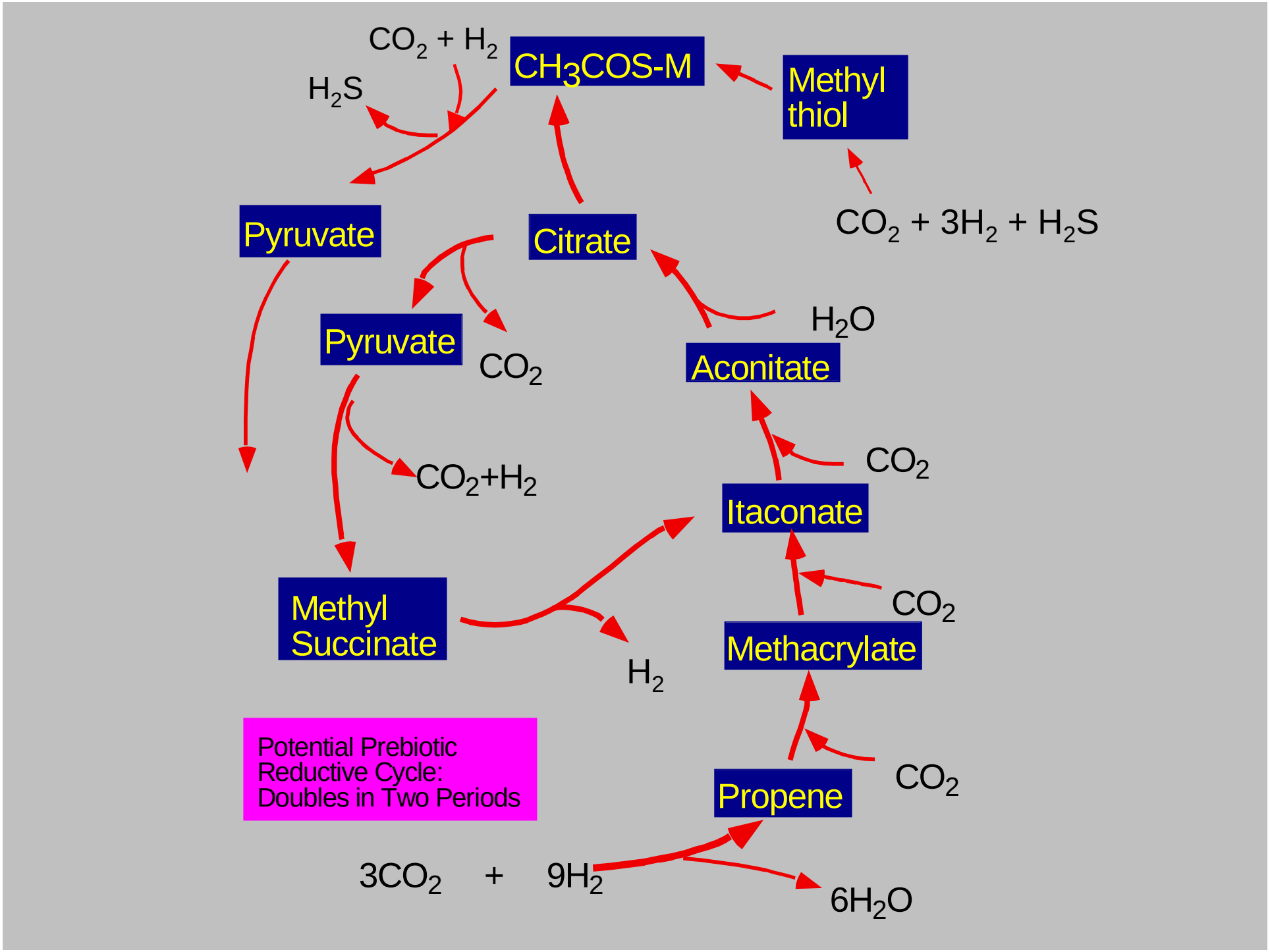
Itaconic Acid + HCOOH + NiS

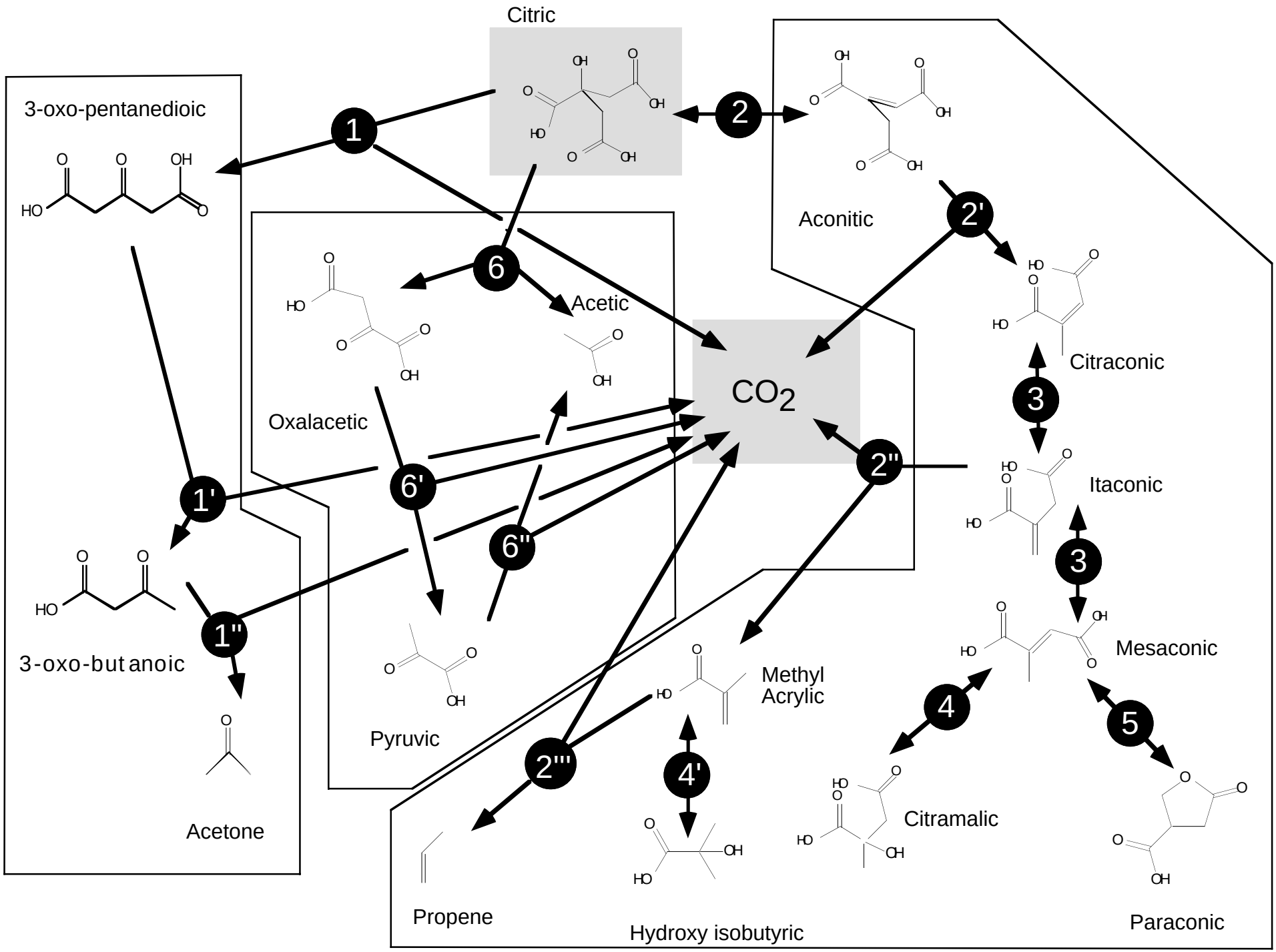


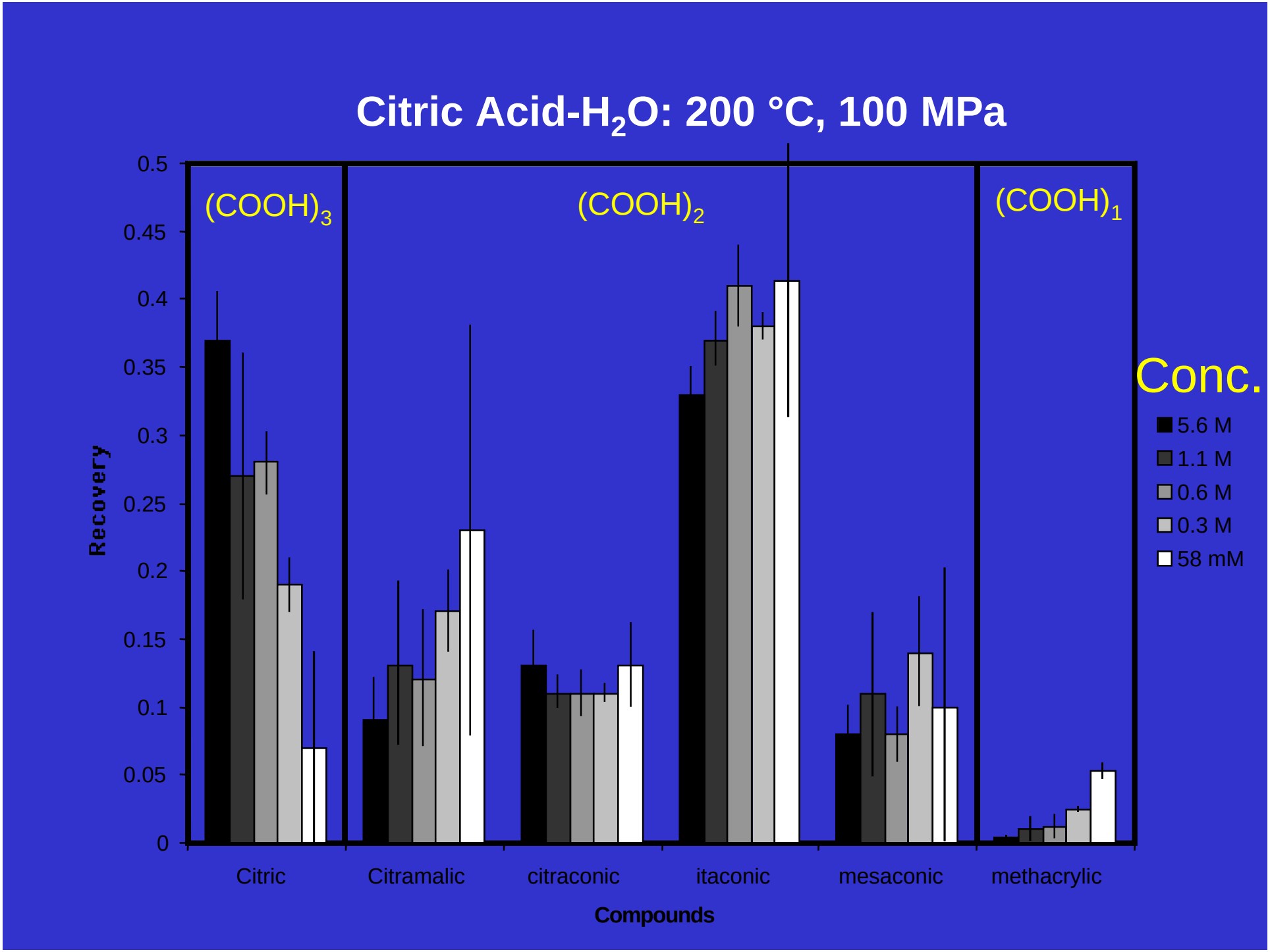


Coupled Hydrocarboxylation and partial oxidation

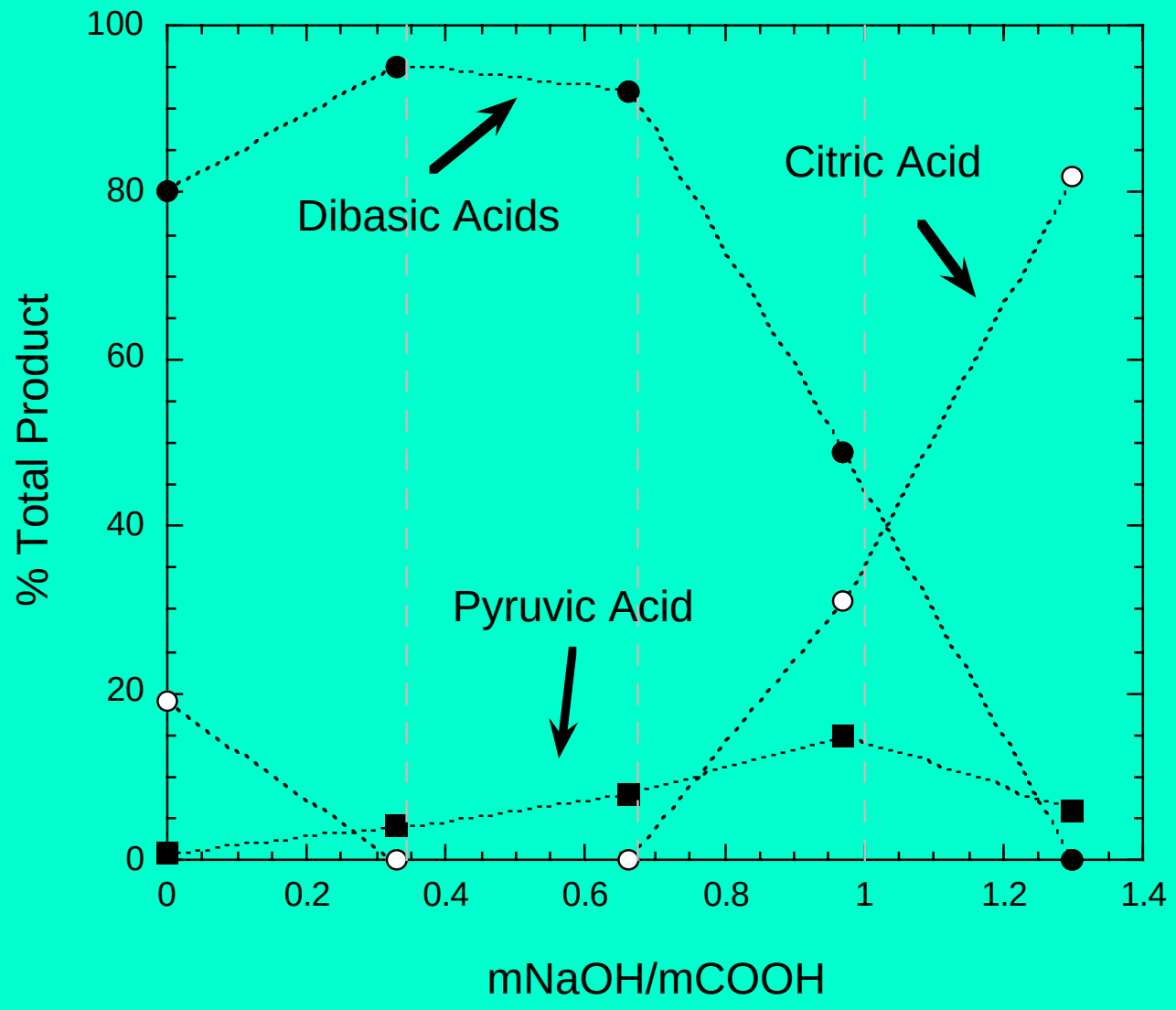



$CO_2 + H_2$
CH_3COS-M
Methyl thiol
H_2S
Pyruvate
Citrate
$CO_2 + 3H_2 + H_2S$
Pyruvate
CO_2
H_2O
Aconitate
CO_2
CO_2+H_2
Itaconate
CO_2
Methyl Succinate
Methacrylate
H_2
Potential Prebiotic Reductive Cycle: Doubles in Two Periods
Propene
CO_2
$3CO_2$ + $9H_2$
$6H_2O$


Citric
3-oxo-pentanedioic
Aconitic
Acetic
Oxalacetic
CO_2
Citraconic
Itaconic
Mesaconic
3-oxo-butanoic
Pyruvic
Methyl Acrylic
Acetone
Citramalic
Propene
Hydroxy isobutyric
Paraconic
1
2
2'
3
3
1'
1"
6
6'
6"
2"
2'''
4
4'
5


Citric Acid-H2O: 200 °C, 100 MPa
(COOH)3
(COOH)2
(COOH)1
Recovery
0.5
0.45
0.4
0.35
0.3
0.25
0.2
0.15
0.1
0.05
0
Citric
Citramalic
citraconic
itaconic
mesaconic
methacrylic
Compounds
Conc.
5.6 M
1.1 M
0.6 M
0.3 M
58 mM

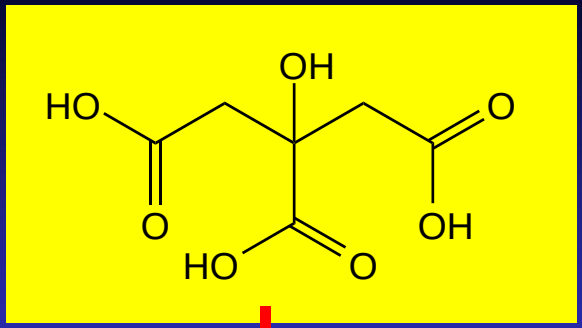
Citric acid decomposition progresses even up to high pH's
Citric acid + nNaOH + H_2O: 100 mM 200°C 200 MPa, 2 hr.s



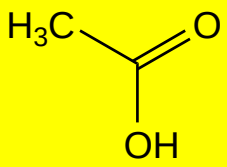
Hydrothermal Amino Acids

200 °C, 200 MPa, pH_{25}=5.4

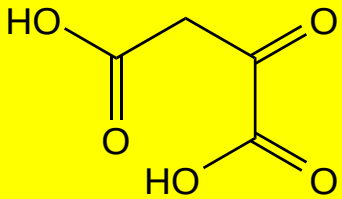
Citrate



Acetate

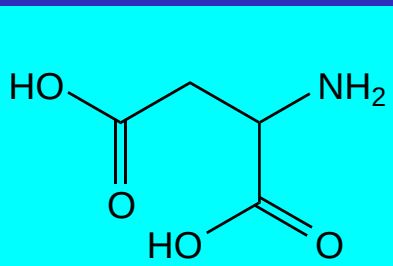


Oxaloacetic

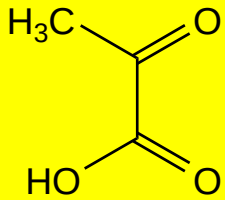


NH_4^+

Aspartic acid



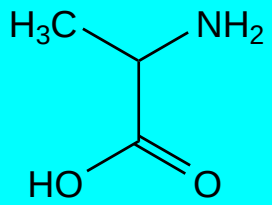
Pyruvate



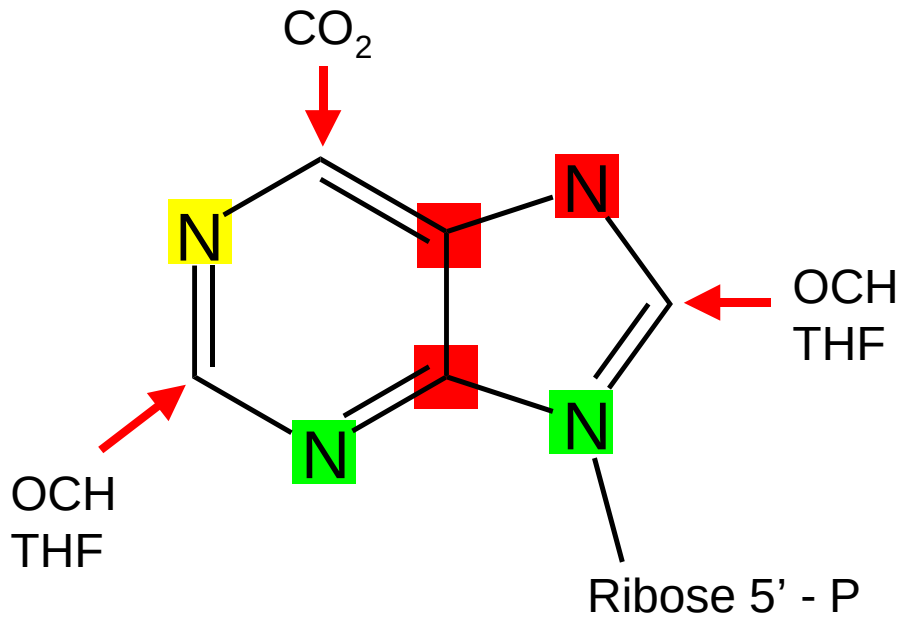
CO_2

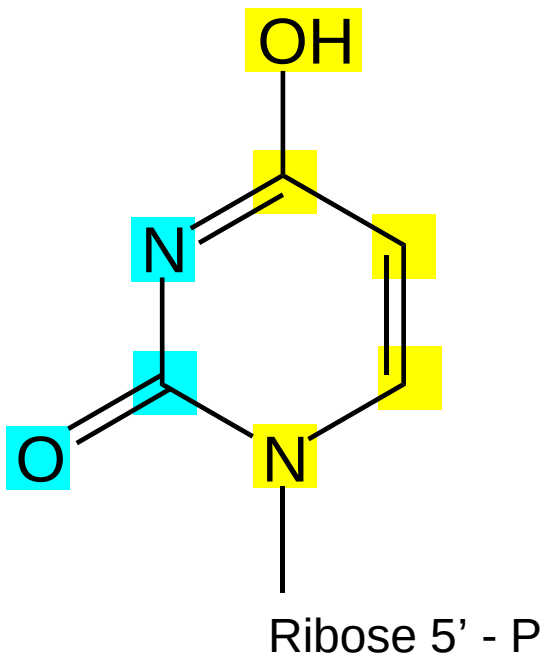
Pyr/For

Alanine



Sources of Carbon and Nitrogen for the synthesis of purine (IMP) and pyrimidine (UMP)





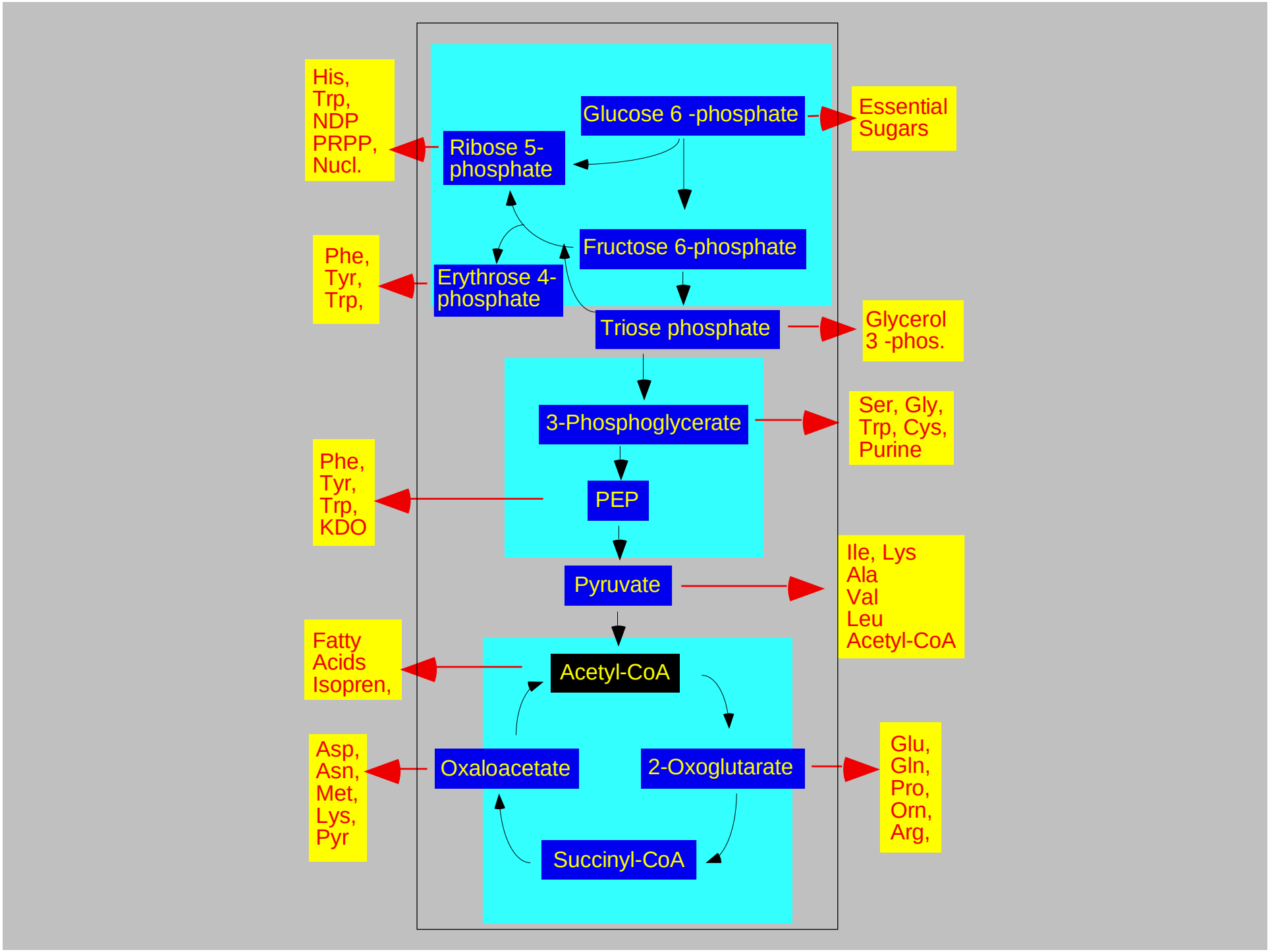
Gln

Asp

Gly

CAP

Synthesis of Simple nucleosides not yet Realized, but ...


His,
Trp,
NDP
PRPP,
Nucl.
Glucose 6 -phosphate
Essential
Sugars
Ribose 5-
phosphate
Fructose 6-phosphate
Phe,
Tyr,
Trp,
Erythrose 4-
phosphate
Triose phosphate
Glycerol
3 -phos.
3-Phosphoglycerate
Ser, Gly,
Trp, Cys,
Purine
Phe,
Tyr,
Trp,
KDO
PEP
Pyruvate
Ile, Lys
Ala
Val
Leu
Acetyl-CoA
Fatty
Acids
Isopren,
Acetyl-CoA
Asp,
Asn,
Met,
Lys,
Pyr
Oxaloacetate
2-Oxoglutarate
Glu,
Gln,
Pro,
Orn,
Arg,
Succinyl-CoA

Chemistry Under What Circumstances ?

Systems with periodic influxes of H_2 into a Catalytically lined hydrothermal reservoir

- **Fracture Networks in Flank Regions of Spreading Centers**
- **Hot Springs/Geyser Systems**

Possibilities and Consequences:

Under plausible conditions synthesis of useful bioorganic compounds

Detection of organic molecules that Appear to be derived from biological Sources may be misleading life indicators

The facile synthesis of recognizable "bio"molecules suggest that Hydrothermal systems may be useful To the origins of life

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NASA Astrobiology Institute