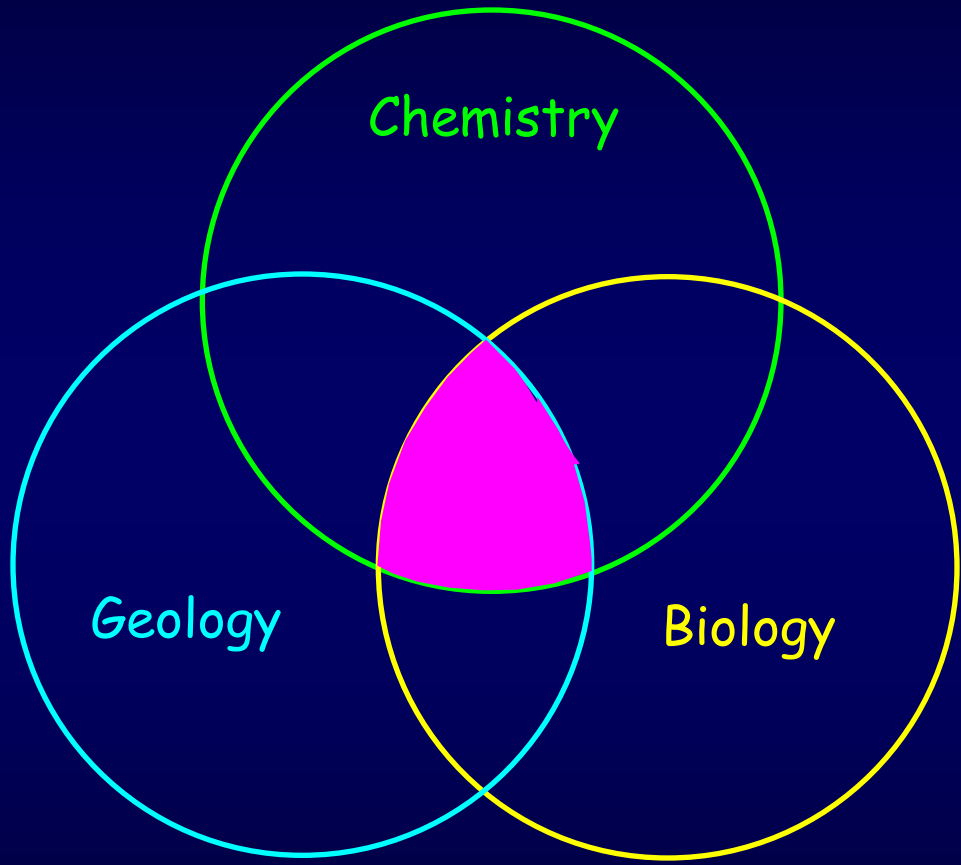


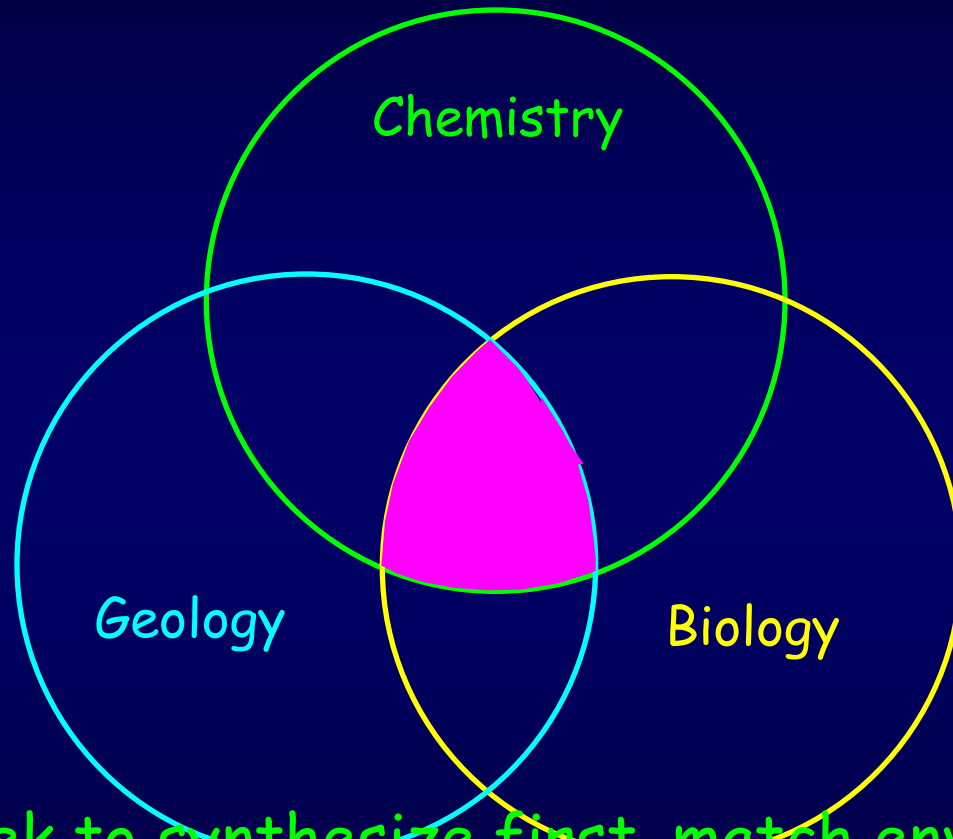
Abiotic Organic Synthesis Catalyzed by metals at High Temperatures and Pressures



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The origins of life problem: How to link viable chemistry
With biological utility to geologically reasonable environments



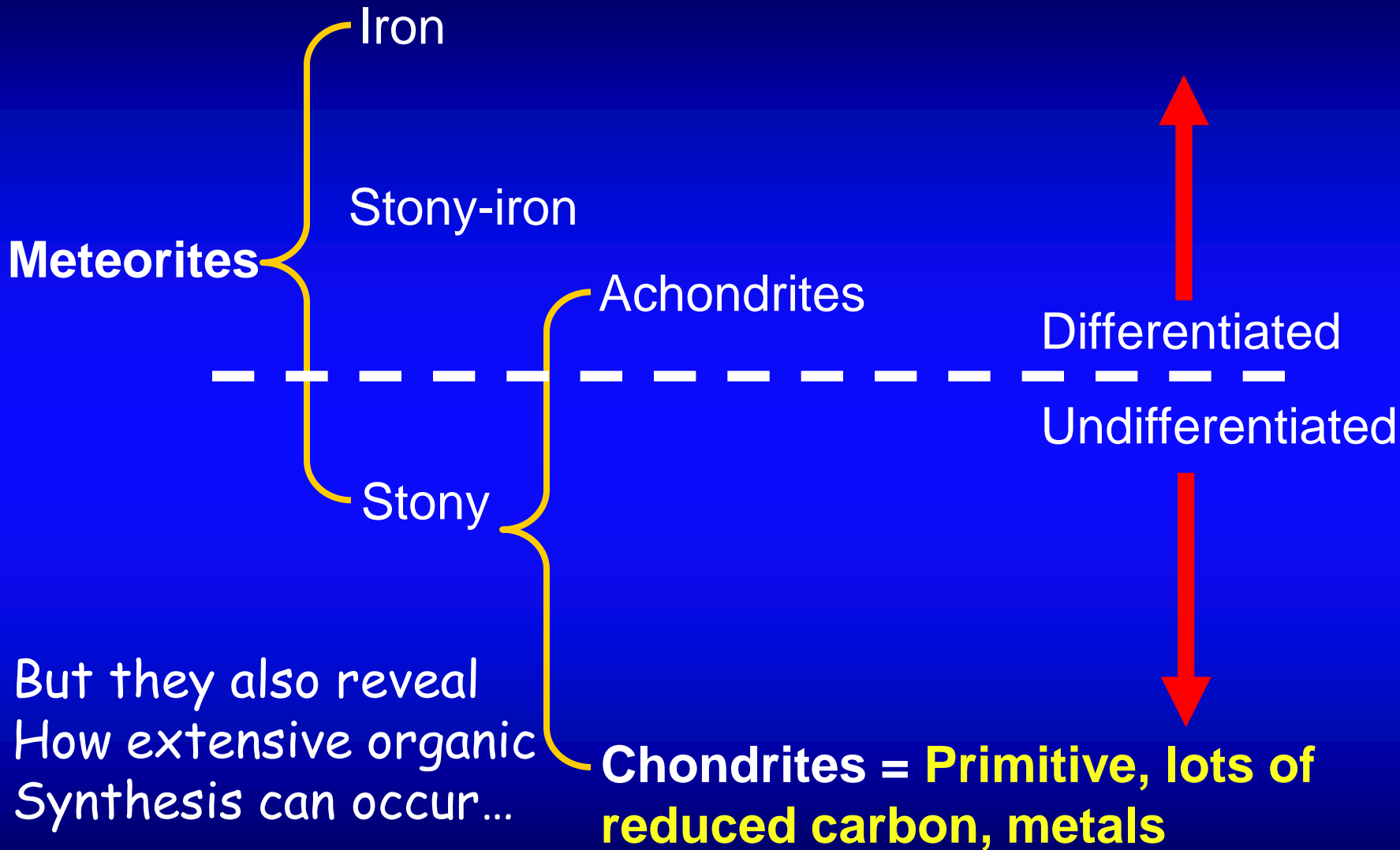
The Problem
Is...

Chemists- seek to synthesize first, match environment second

Biologists- seek links to the familiar

Geologists- worry whether any chemistry can actually be done

Meteorites are remnants of planetesimals and provide information on how planets evolve



Carbonaceous chondrite parent body interiors- an environment where abiotic organosynthesis plausibility is known fact

Environment:

Warm (not hot)

Wet

Initially far from equilibrium (interstellar ice, metals, anhydrous silicates, organics)

Relatively rich in reduced carbon

Catalytic phases FeNi metal + FeS

Potentially millions of years of mild hydrothermal reaction

The rich abiotic organic inventory of Chondrites

Total Carbon ~ 2.0 %

Interstellar Grains

Diamond	400 ppm
SiC	7 ppm
Graphite	<2 ppm

Carbonates 2 - 10 % total C

Macromolecular (aka IOM) 70 - 99 % Total C

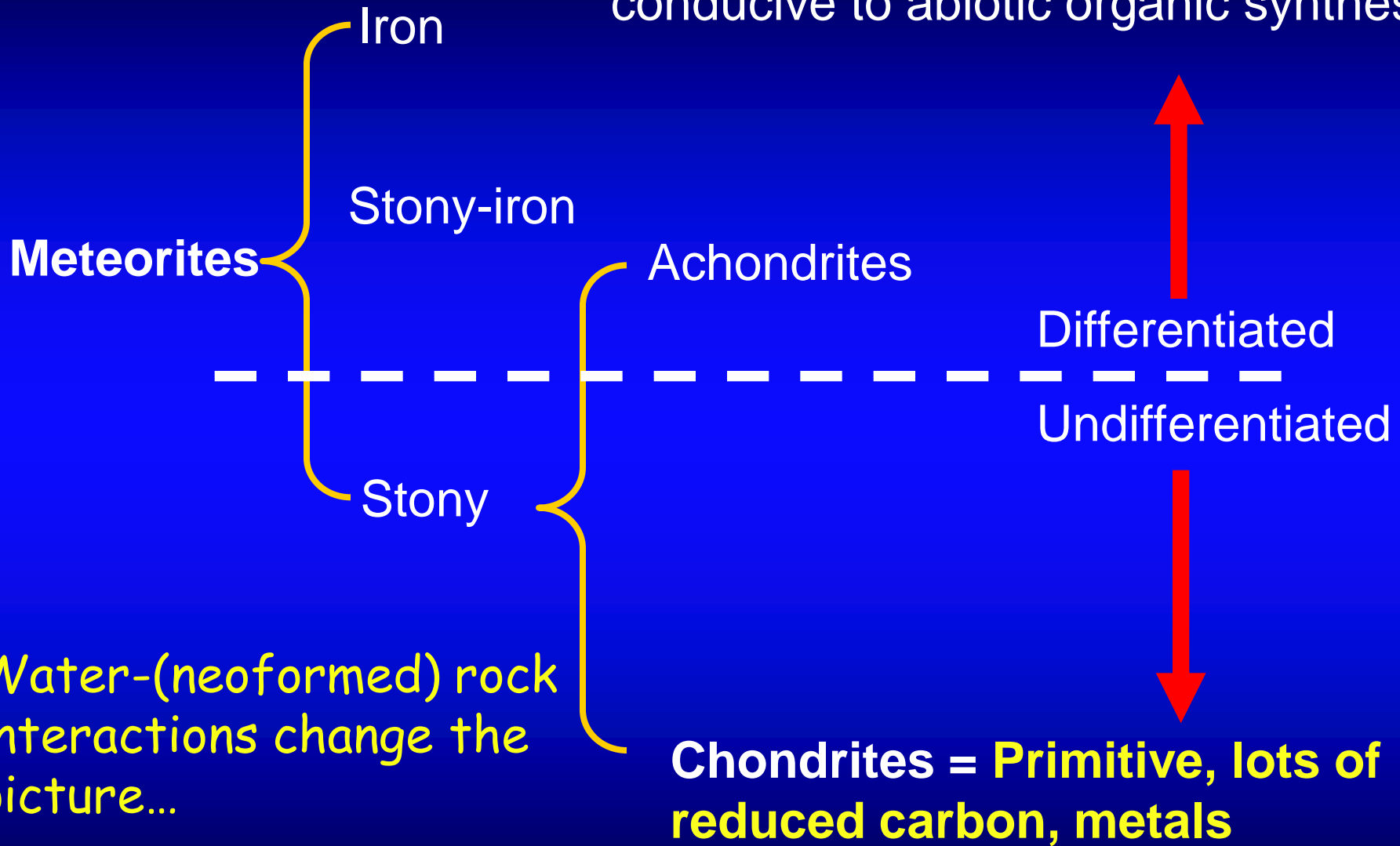
Organic Compounds 30 - 0 % Total C

Aliphatic HC's	++	Dicarbox. Acids	++
Aromatic HC's	++	Sulfonic Acids	+++
Polar HC's	+++	Phosphonic Acids	+
Volatile HC's	+	N-Heterocycles	+
Aldehyde/Ketone	++	Purine/Pyrimidine	+
Alcohols	++	Carboxamides	++
Amines	+	Hydroxyacids	++
Fatty Acids	+++	Amino Acids	++
Sugars and sugar derivatives	+++		

+++ > 100 ppm ++ > 10 ppm + > 1 ppm

After Cronin 1998

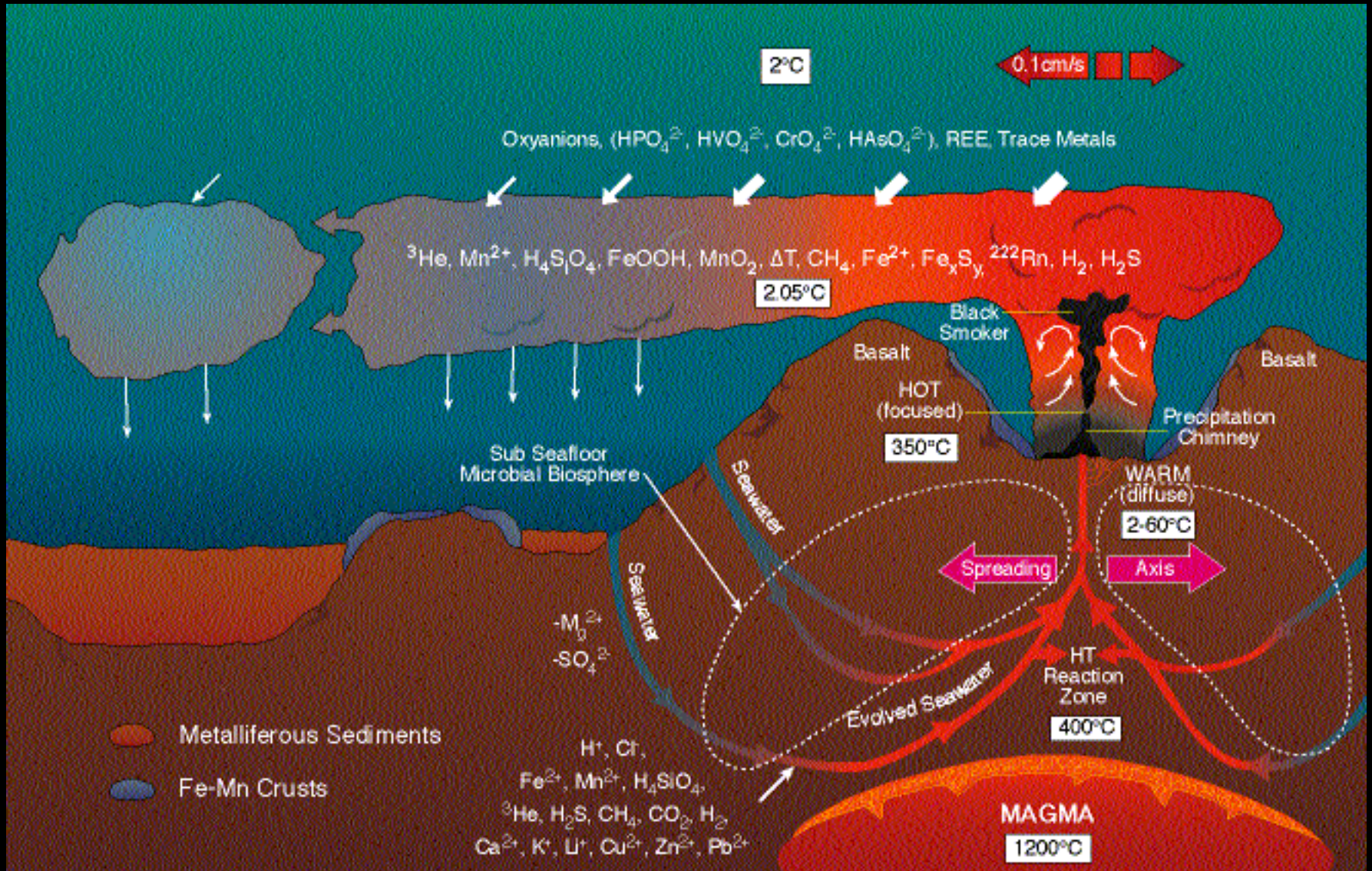
Terrestrial planets: largely oxidized silicate crust and mantle, not generally conducive to abiotic organic synthesis



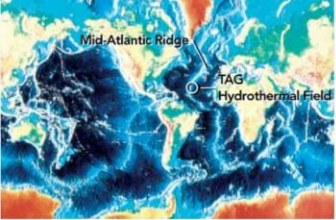
Water-(neoformed) rock interactions change the picture...

Oceans meet tectonics

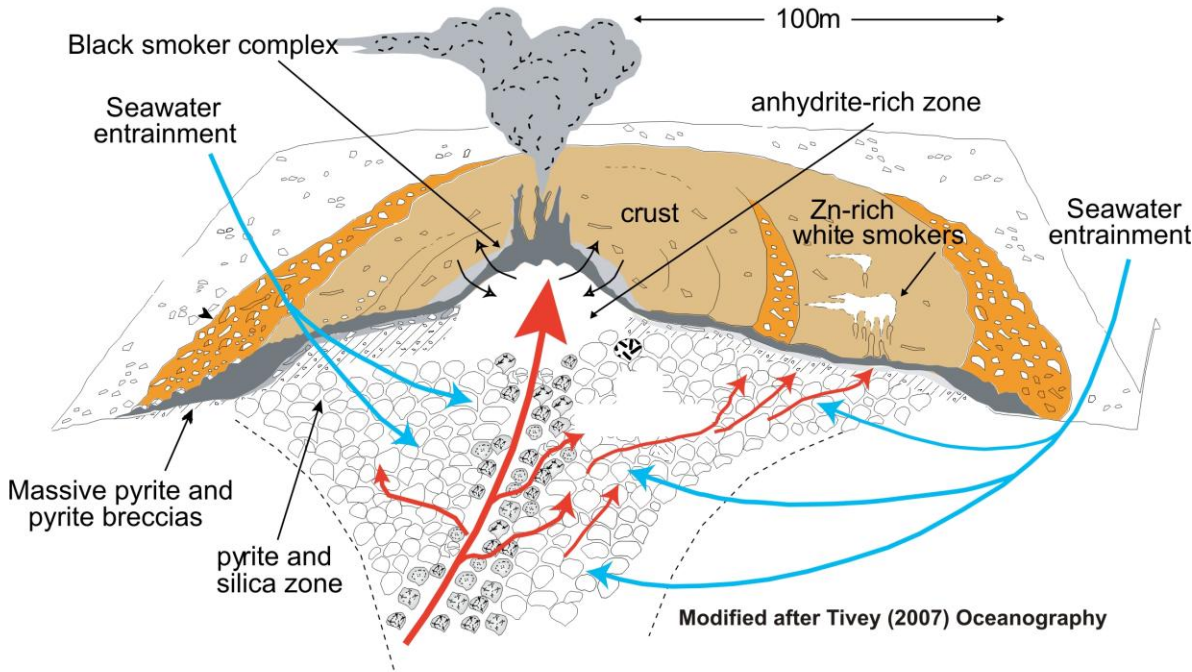
Extensive water/rock interaction yield ore rich in transition metals



Formation of fresh sea floor provides an environment far from equilibrium
 And where abiotic organic reactions can occur



TAG Hydrothermal Mound



For example:

1.4 x 10⁸ m³ of basalt required to yield the Cu content at the TAG ore deposit

Basalt is hardly a highly permeable material

Transition metal aqueous extraction not efficient

Extensive H₂O-rock interaction required

	Cu	Fe	Zn	Sulfur
Concentration in black smoker fluids (μM)	120-150	5590	46	2500-3500 (H ₂ S)
Concentration in fresh basalt (ppm)	73	76000	90	500-1000
Mass of element in the TAG deposit (x10 ⁶ kg)	~45	1100	15	1600
Total mass of element in reaction zone required to form the deposit (x10 ⁶ kg)	43-85	3800	20-30	2300

ppm

10⁶ kg



Pyrite
 FeS_2



Chalco-
Pyrite
 CuFeS_2



Sphalerite
 ZnS

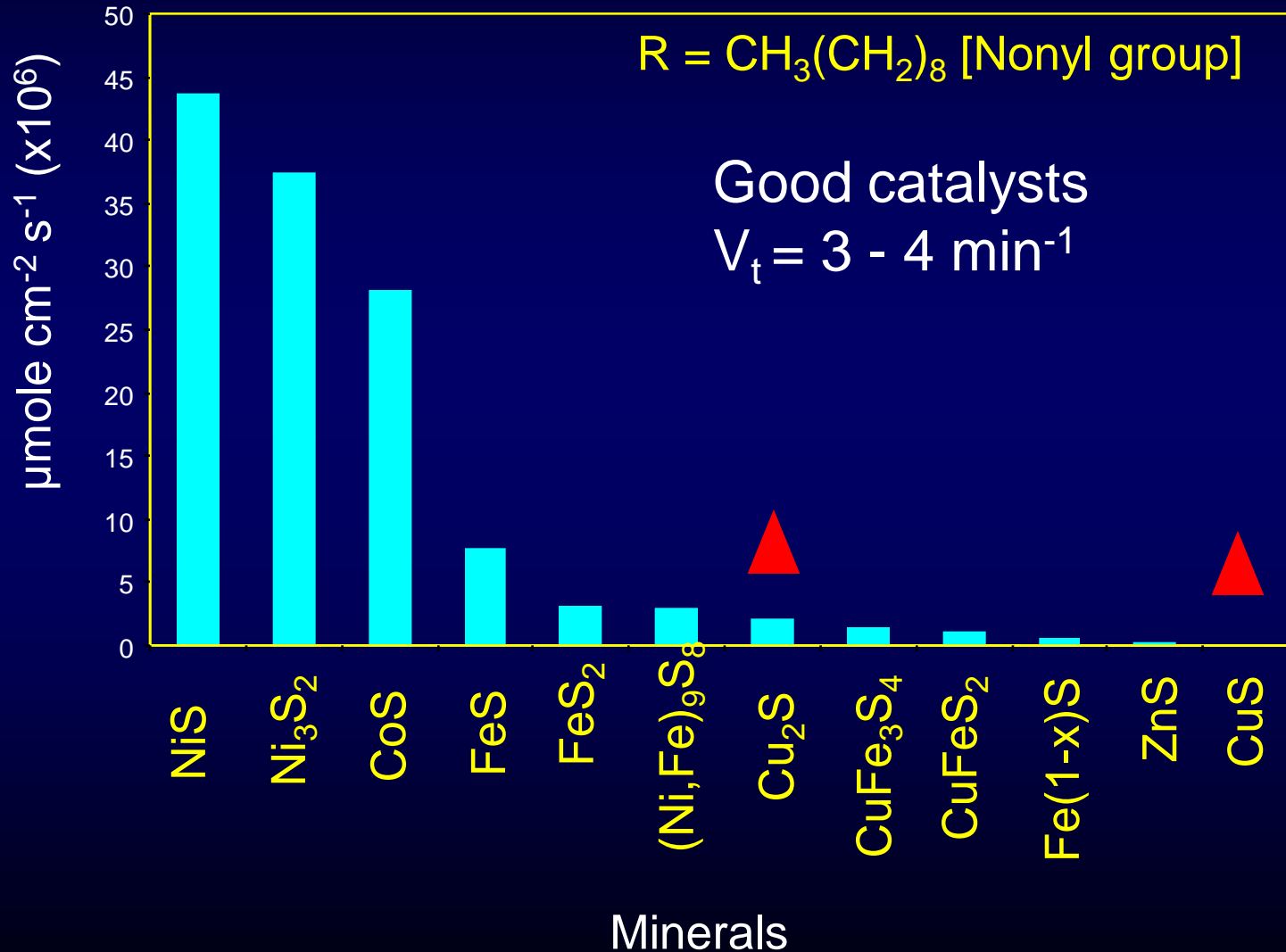


Catalysts formed via
water-rock interaction

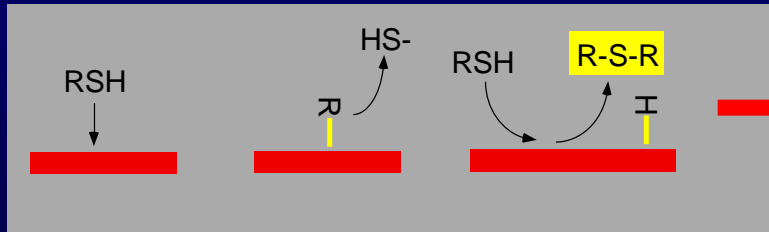
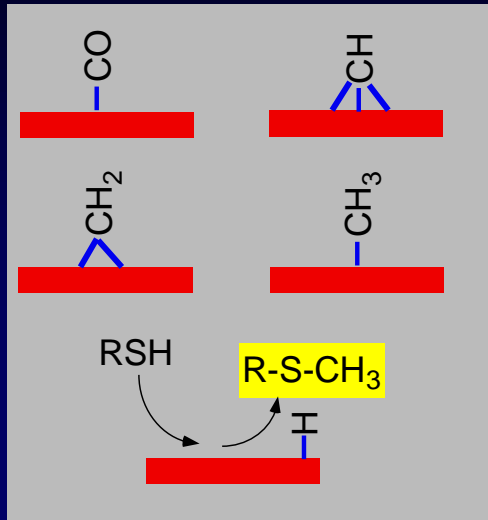
Assaying transition metal sulfide minerals for C-fixation..



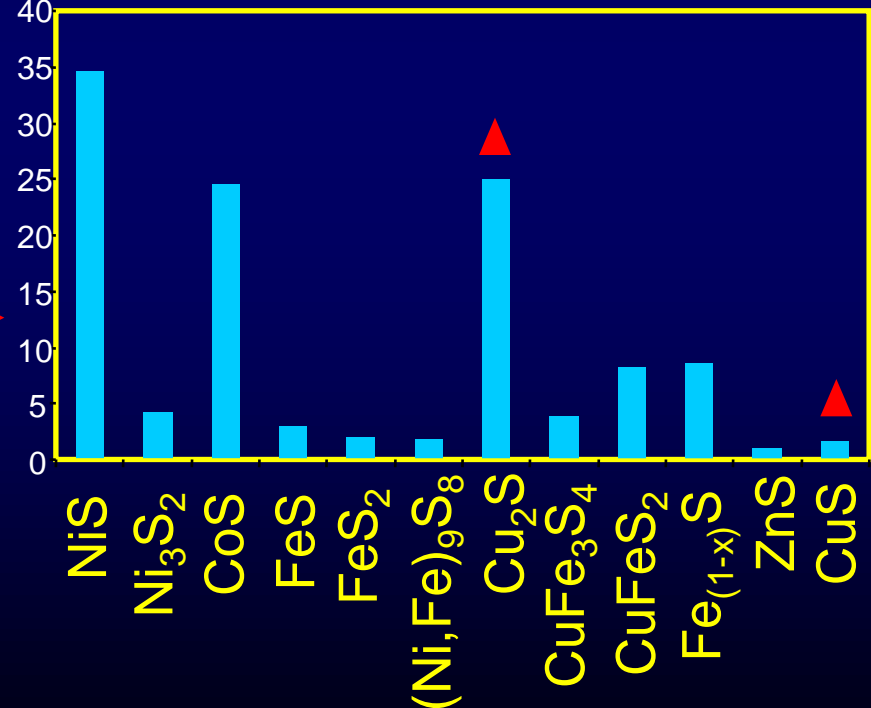
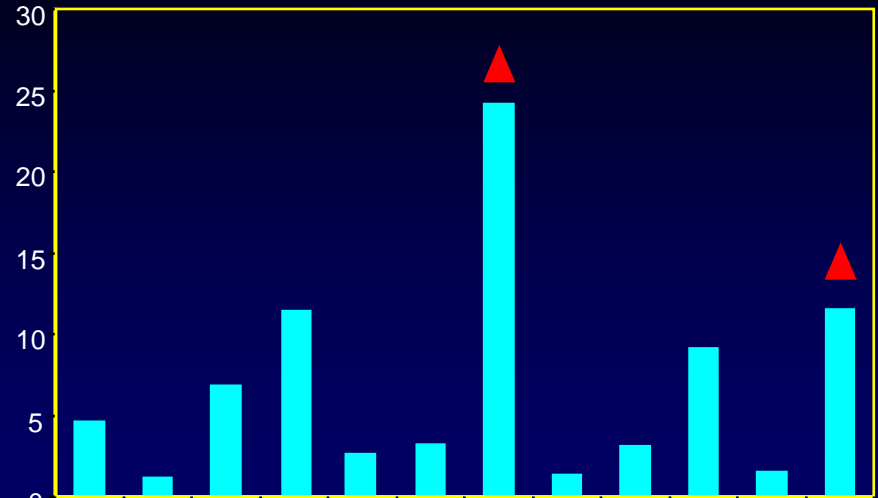
Yield Decanoic Acid 250°C , 200 MPa, 6 hrs.

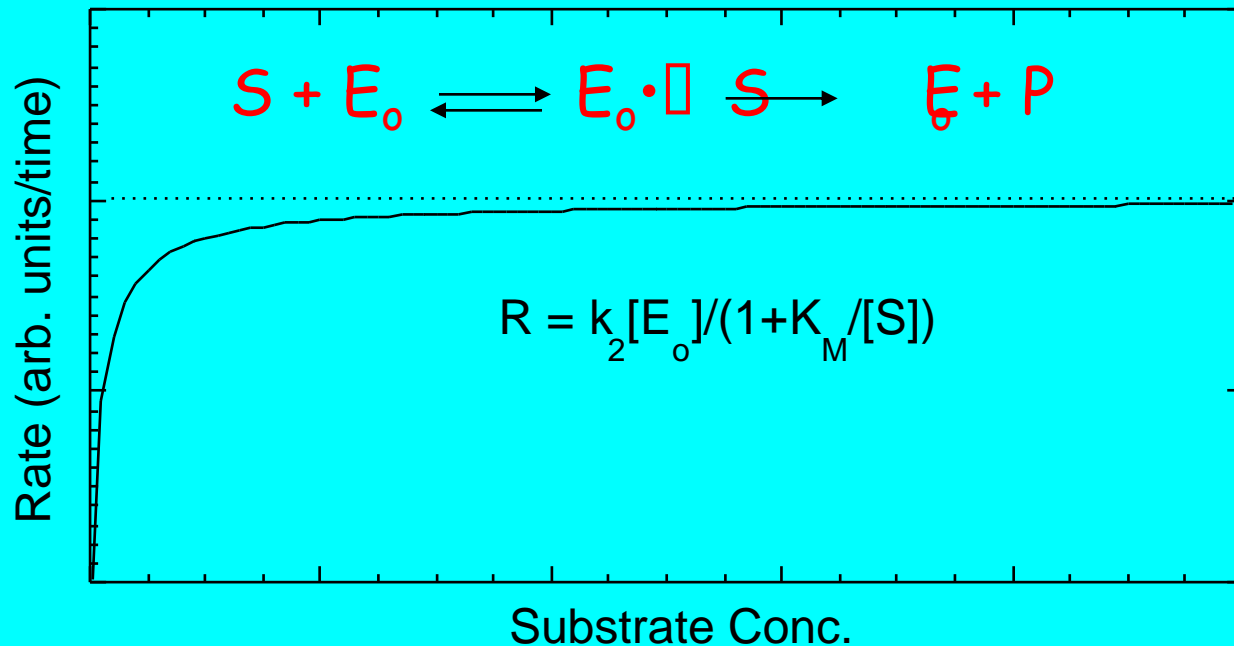


CO reduction to CH_3 facile with metal sulfides...

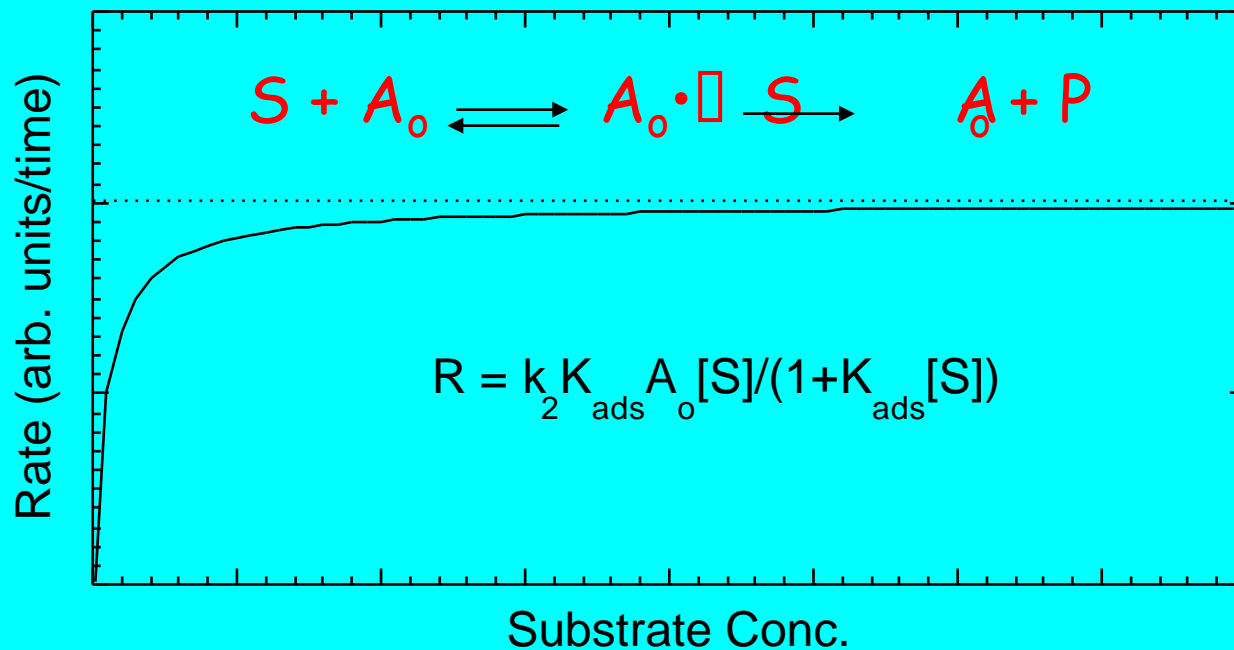


Note: that activity for carbonyl Insertion different that activity For CO reduction to CH_3





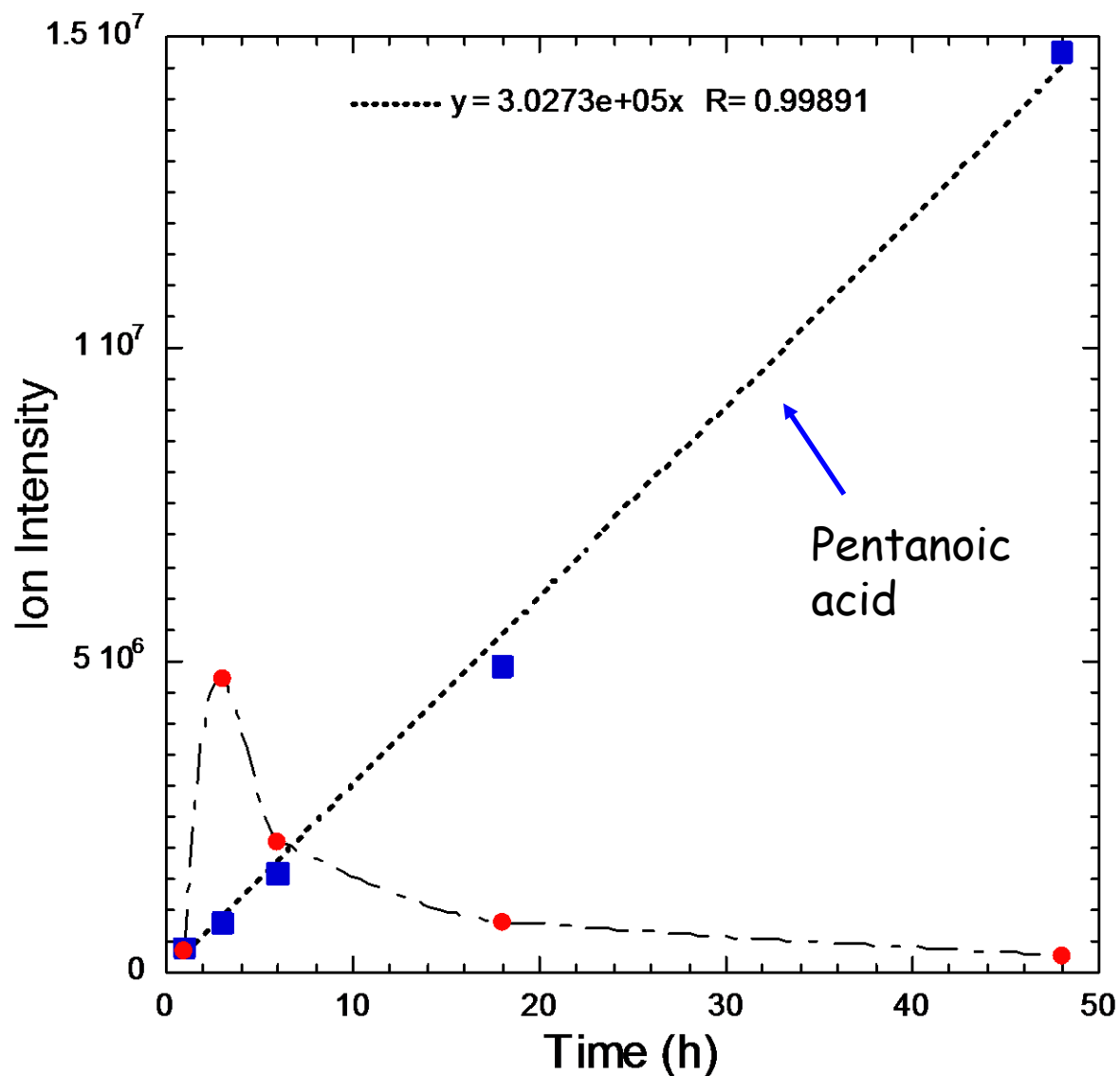
$R = k_2 [E_o]$
 Enzyme



$R = k_2 [A_o]$
 Mineral Surface

More interesting chemistry: Butane thiol- $\text{CO}_2 + \text{H}_2$ w NiS 250 ° C 200 MPa

Note: Zeroth order kinetics with regard to Butane thiol!



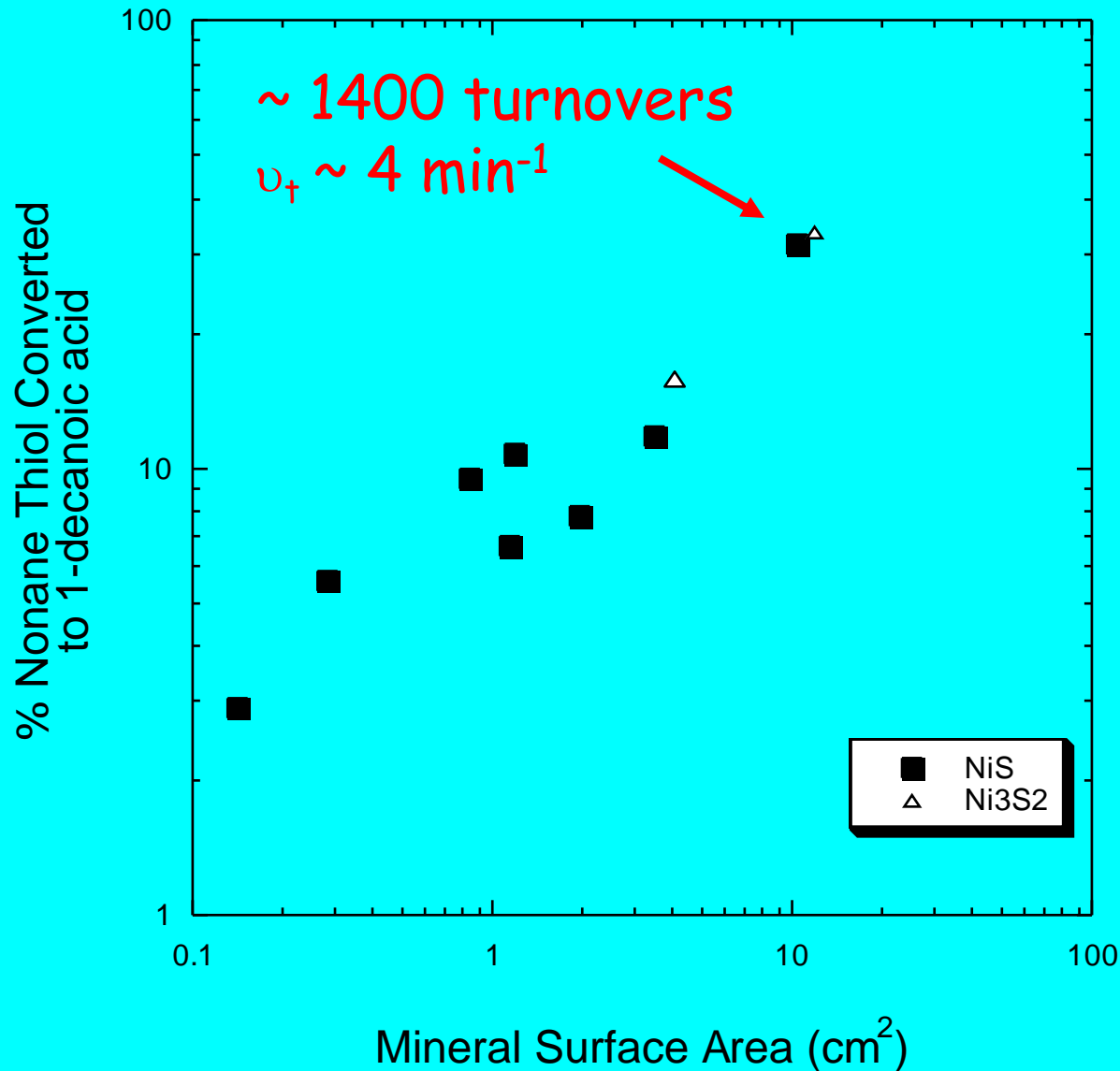
~ 50 % yield

~8,400
turnovers in
48 hours

Turnover
frequency (ν_t)

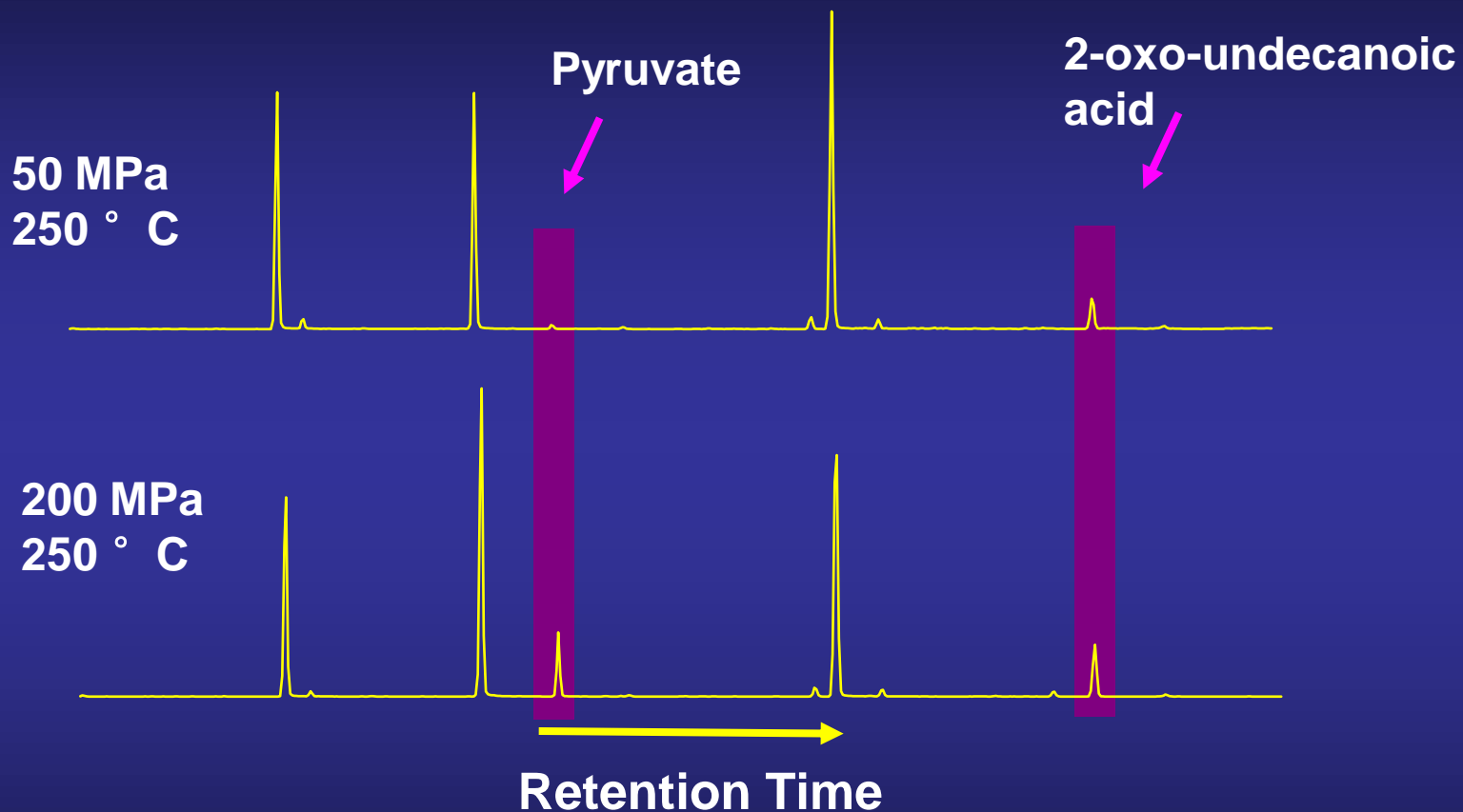
~ 2.9 min^{-1}

Nonane thiol reactions



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

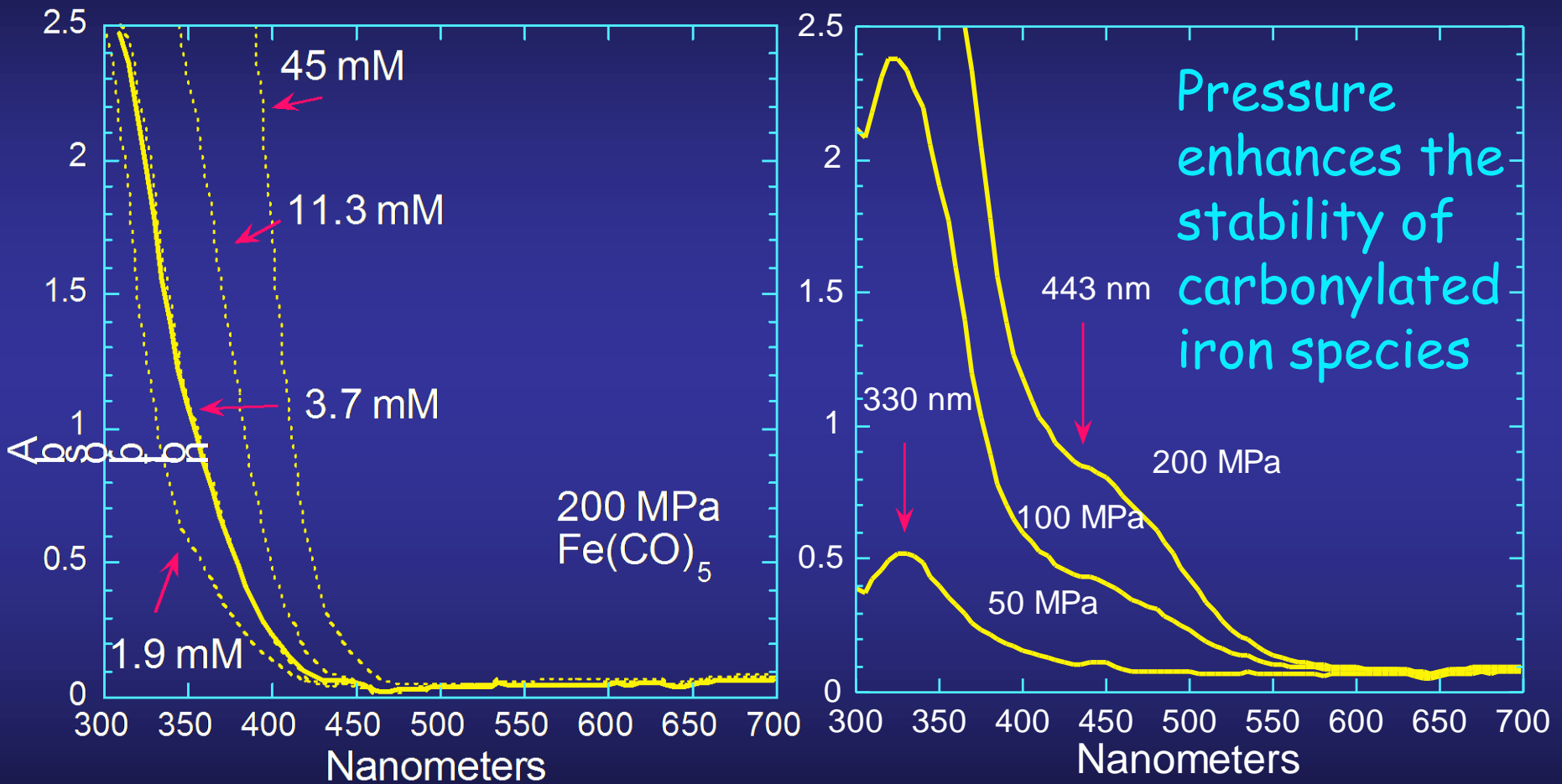
The synthesis of alpha keto acids in the presence of FeS



Low Yields (< 1%) revealed via SIM Detection
(Cody et al. Science, 2000)

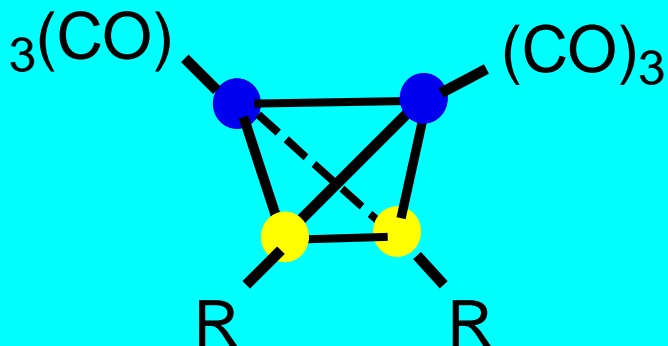
FeS exhibits unique behavior

Aqueous Formic Acid + FeS + Nonane thiol 250° C 200 MPa 6h



Iron sulfur Carbonyls + 20-50% Dissolution of FeS

Additional Reactions Involving FeS, CO, and Alkyl Thiols



It is these highly carbonylated Species that we believe lead to the synthesis of alpha-keto acids

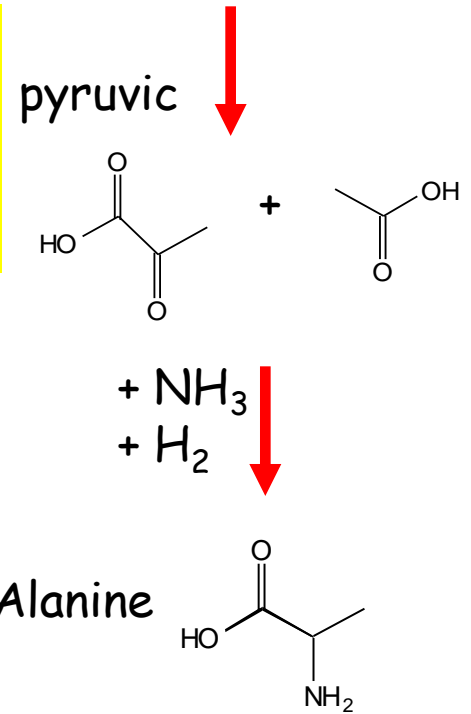
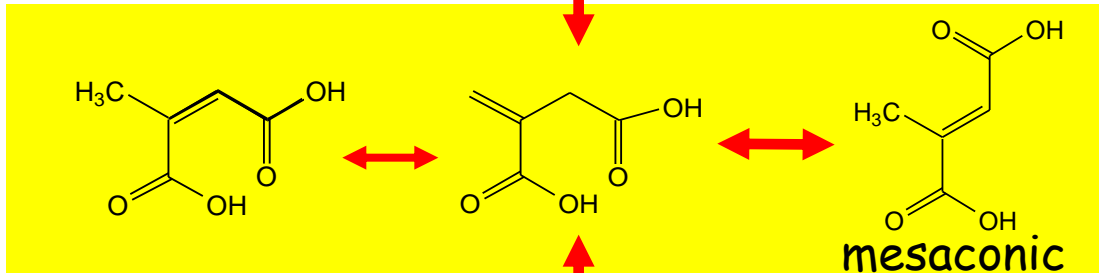
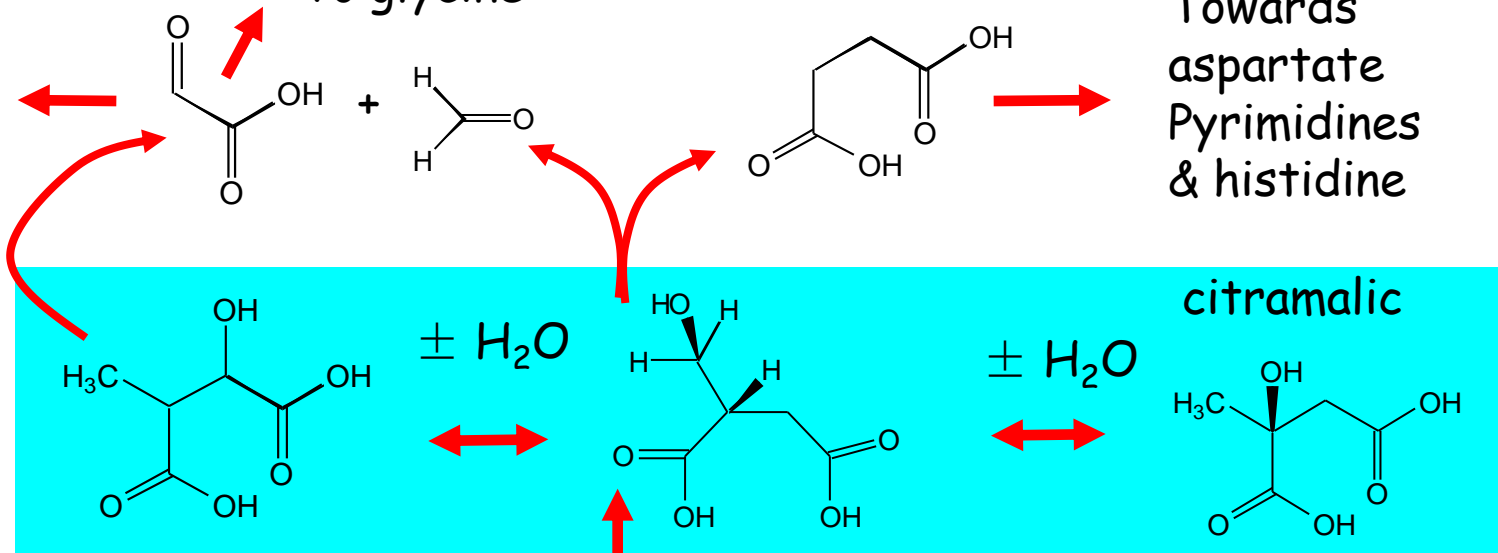
Which is strongly favored at higher pressures

Towards
Serine &
cysteine

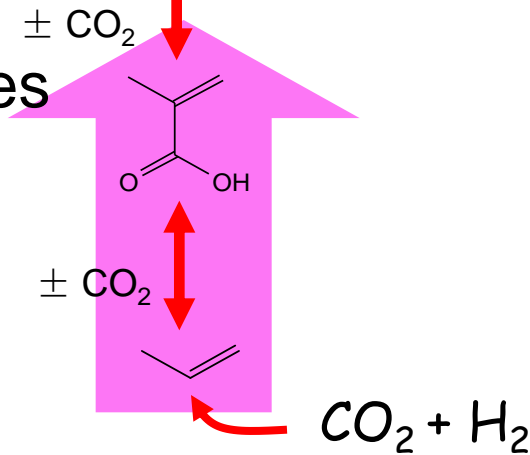
To glycine

Succinic acid

Towards
aspartate
Pyrimidines
& histidine

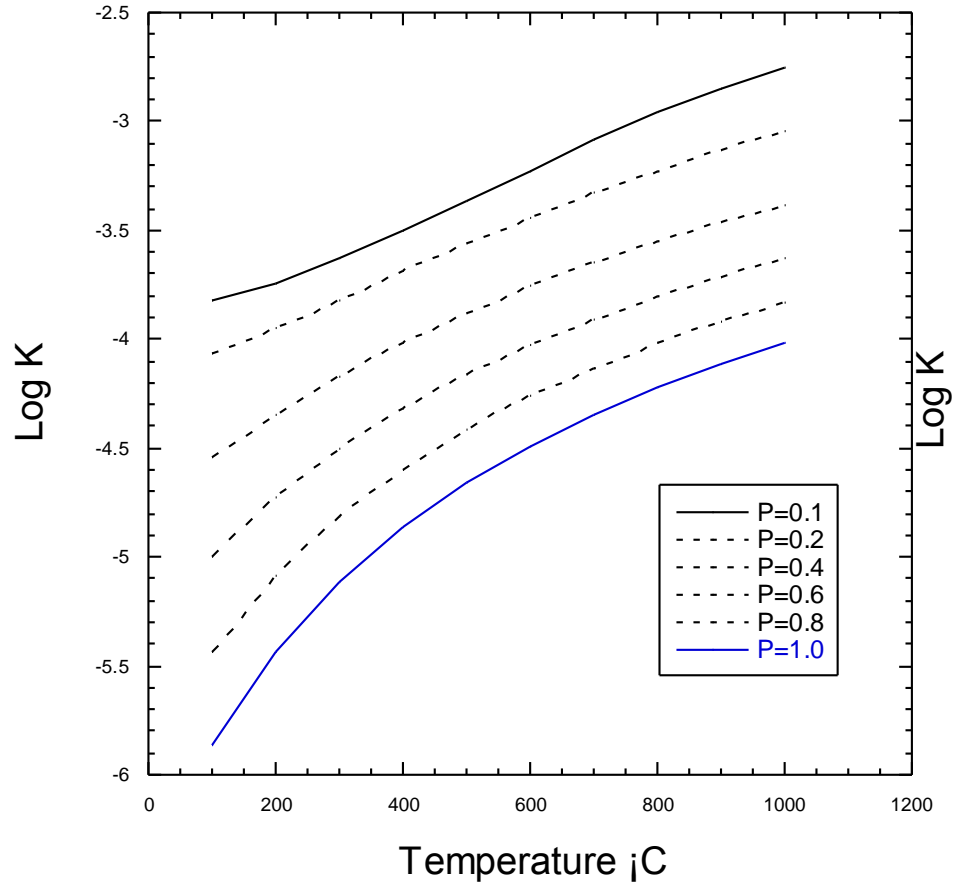


Transition metal catalyzes
Small molecule abiotic
Pathway towards
Chemistry that is similar
To biological

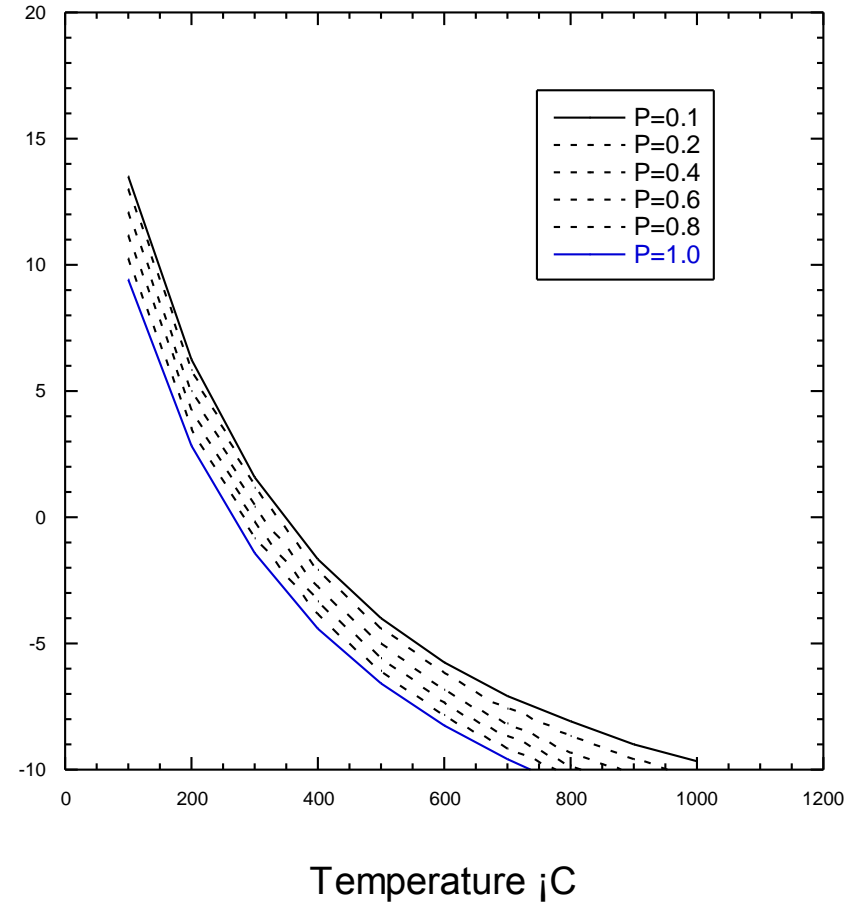


The bottom line starts with CO_2 reduction. $\text{CO}_2 + \text{H}_2$ can do two things... CH_x formation or the WGR rxn

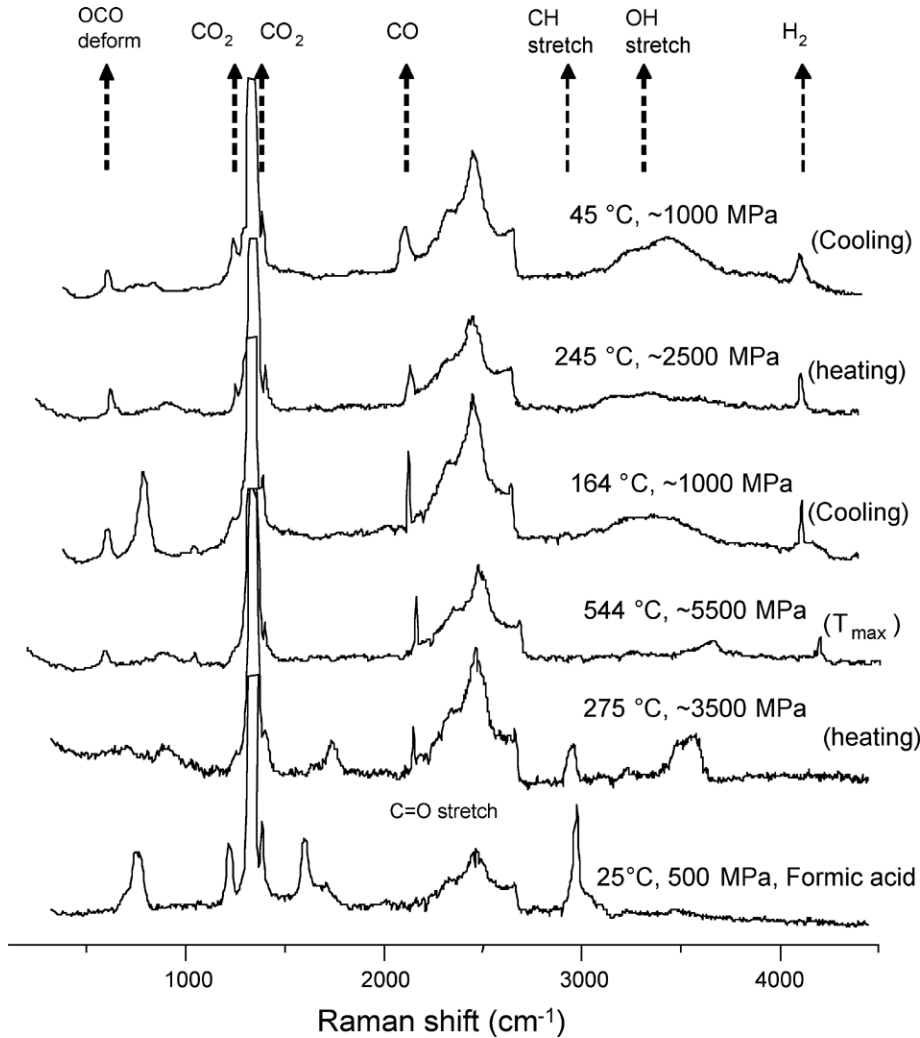
Water Gas Shift Rxn
 $\text{CO}_2 + \text{H}_2 \leftrightarrow \text{CO} + \text{H}_2\text{O}$



Methanogenesis
 $\text{CO}_2 + 4\text{H}_2 \leftrightarrow \text{CH}_4 + 2\text{H}_2\text{O}$

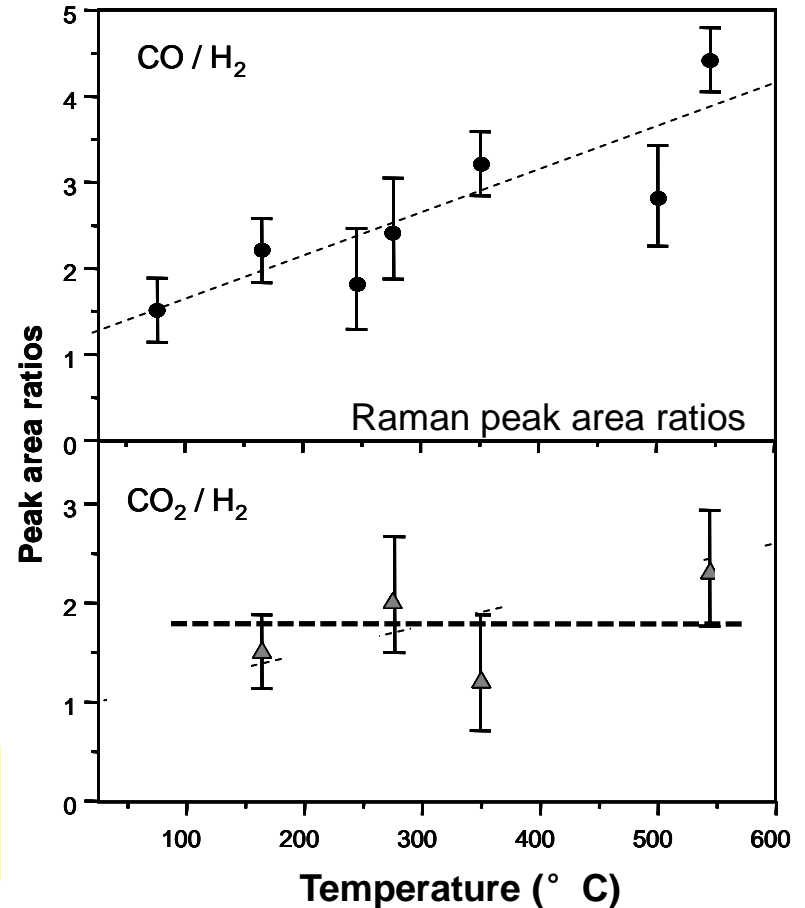


Formic acid ($\text{CO}_2 + \text{H}_2$, no catalyst)



NO Methane detected, even as thermodynamics are extremely favorable

In-situ Raman spectra reveals the expected water-gas shift (WGS) reaction enhancing CO at higher temperature.

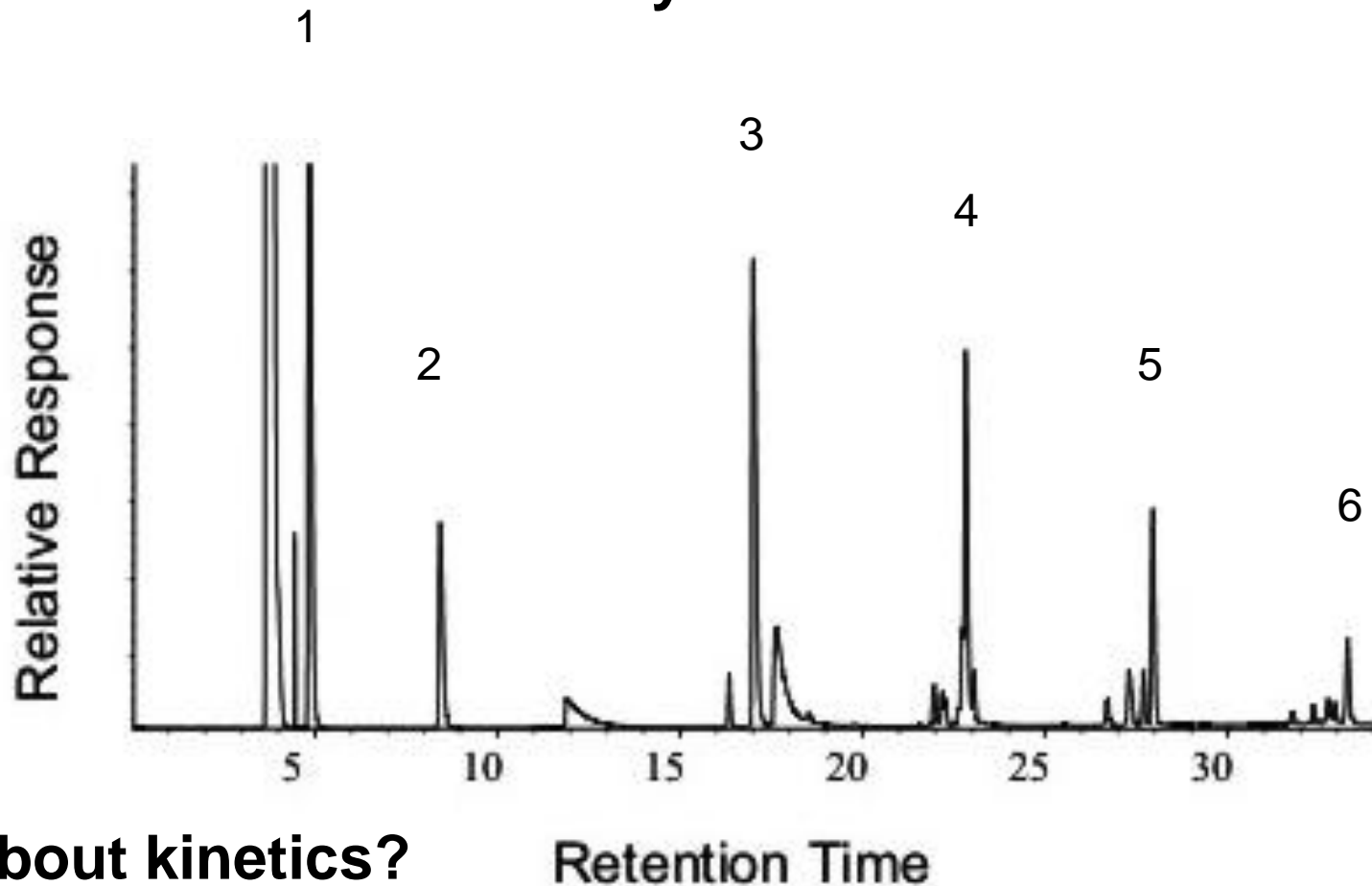


Inhibition of methane formation has been observed many times

Cold Seal Reactor Experiments 250 ° C, 200 MPa (w and w/o) Fe metal + aqueous Formic acid (Penny Morril, Cody, Fogel, Sherwood-Lollar, Weinburger submitted)

W/O Fe-metal no methane is formed

W Fe metal Methane and HC synthesis extensive

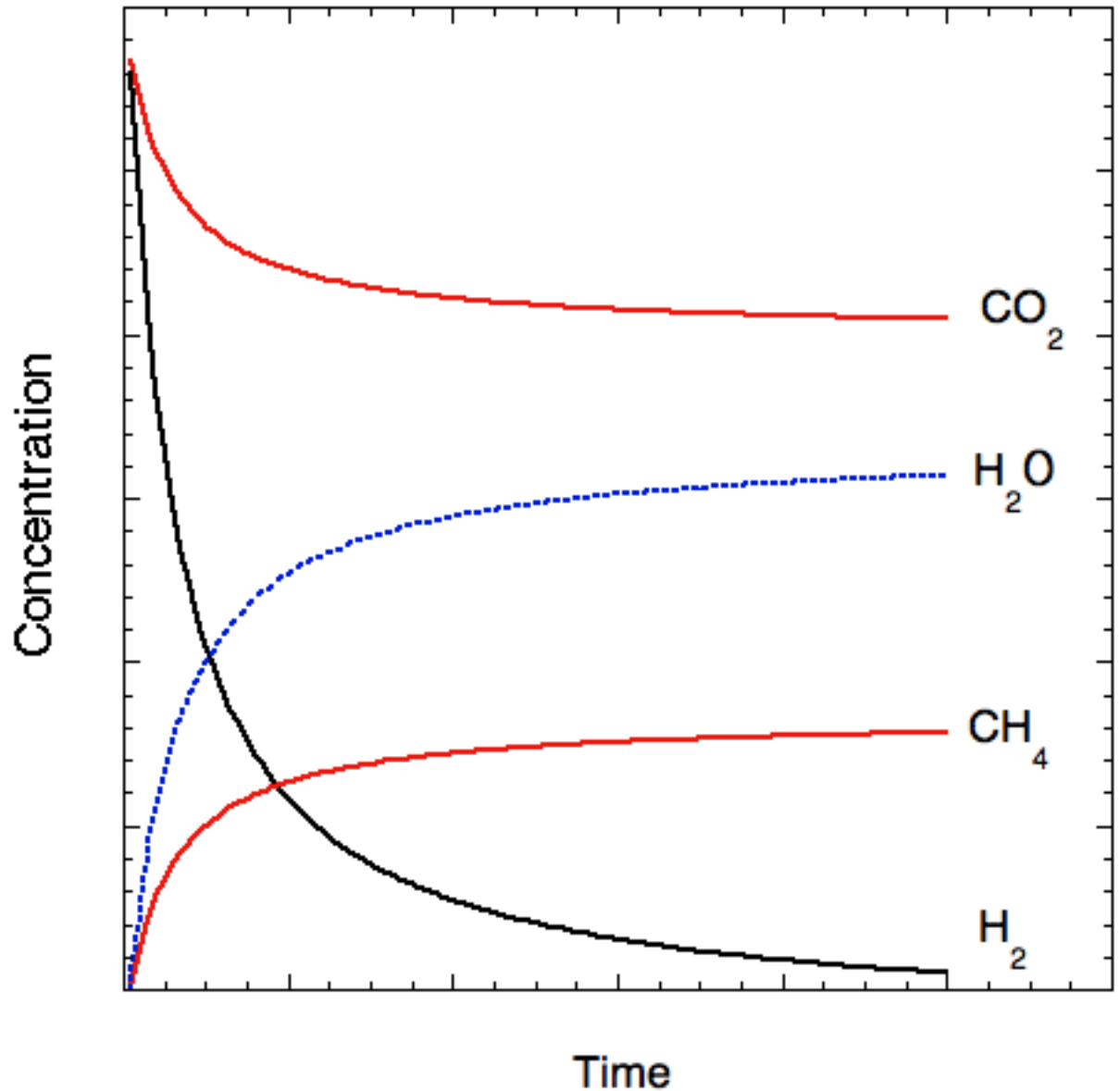


How about kinetics?

Theoretically: At modest T & P, using formic acid as source of equiv. Conc. $\text{CO}_2 + \text{H}_2$, reaction stoich predicts 25 % CH_4

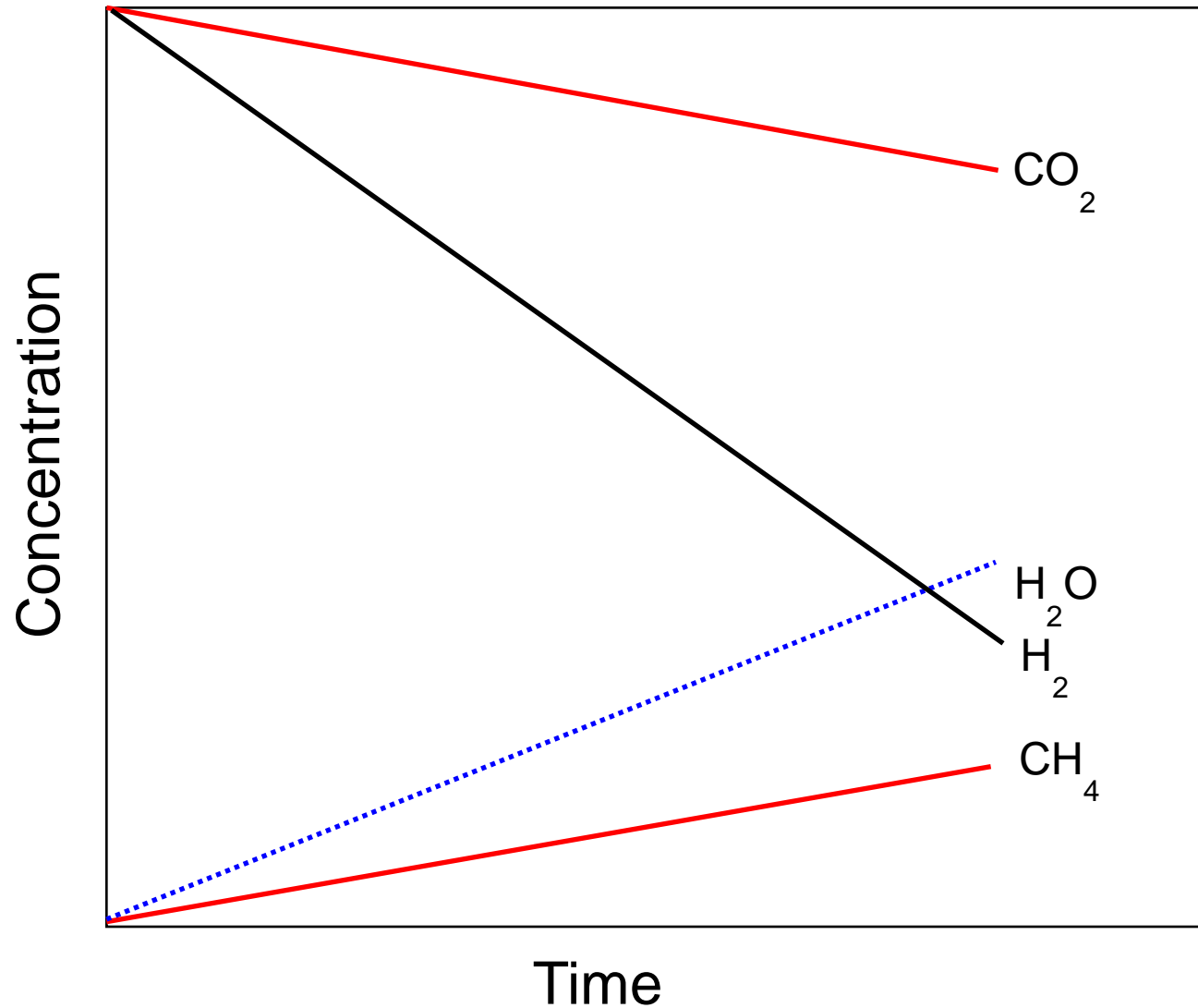
Homogeneous
Kinetics expected
to look like this...

Classic 2nd order
kinetics



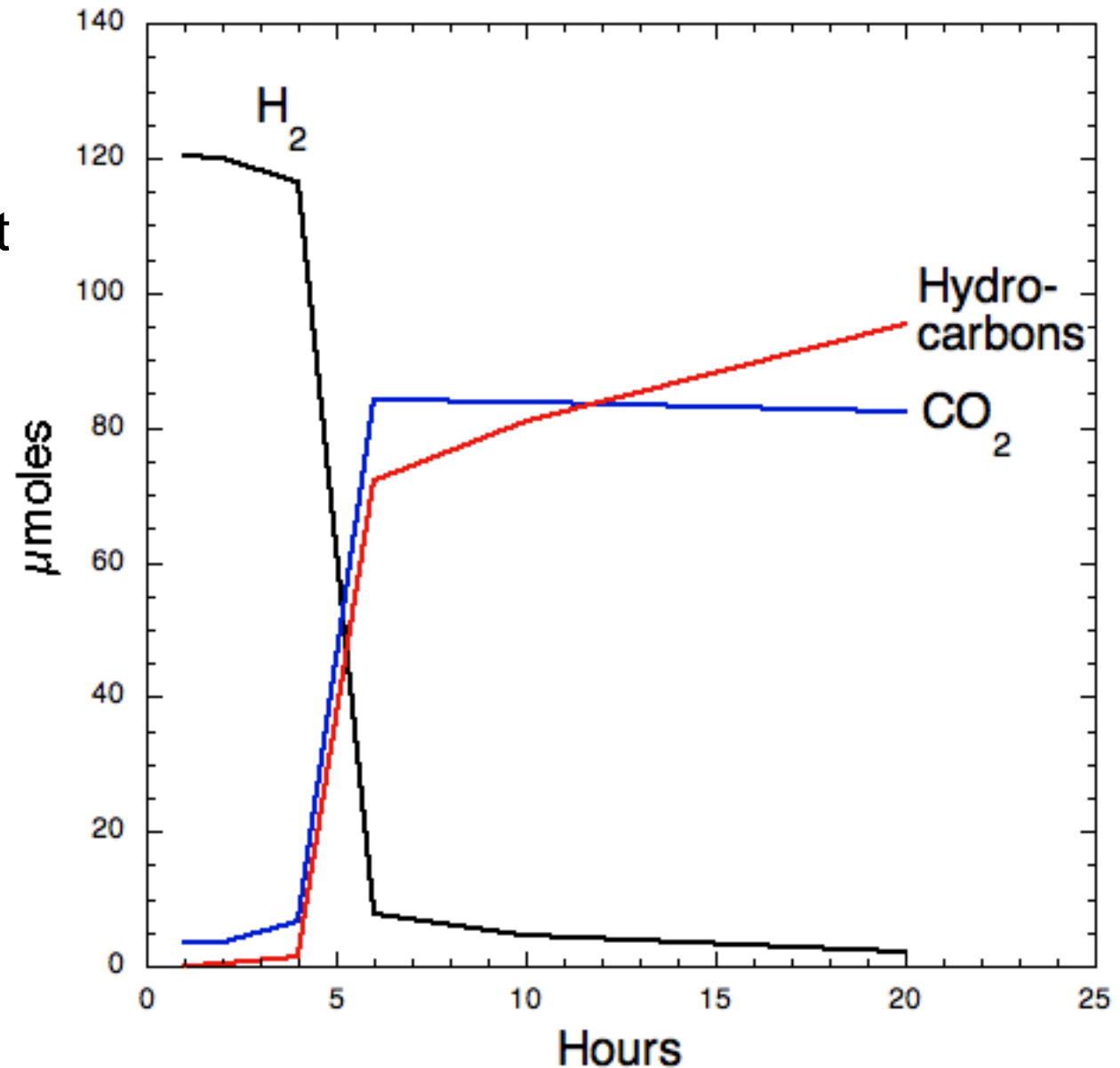
Heterogeneous (surface catalyzed) Kinetics
expected to look something like this...

Substrate
saturated
heterogeneous
rxns exhibit 0th
order kinetics

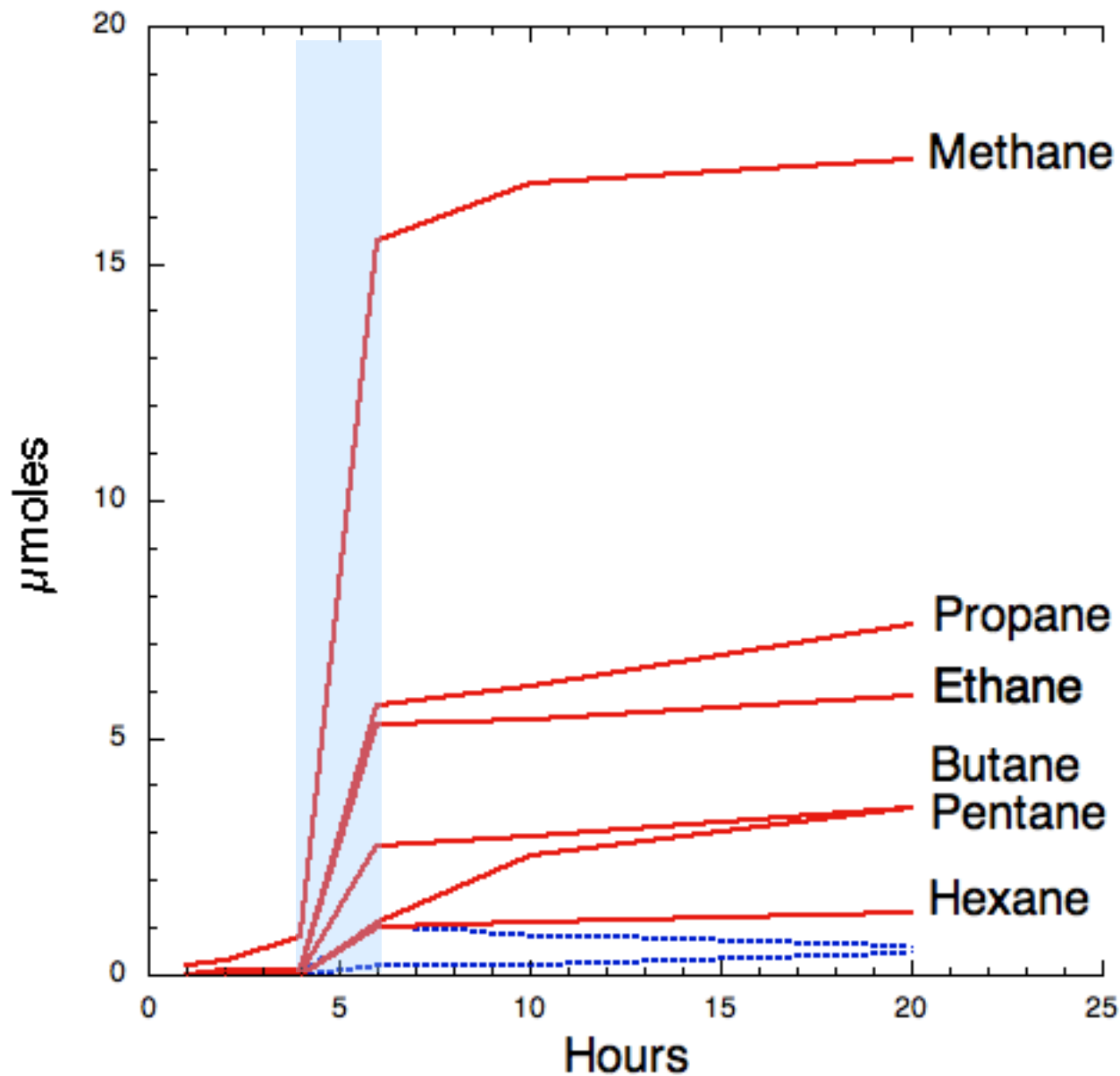


What we observe is unexpected kinetic behavior...

- minimal CO₂ observed for first 4 hours.
- abrupt transition at 4-6 hours
- slow rxn at 6 to 20 hours.
- What is going on?

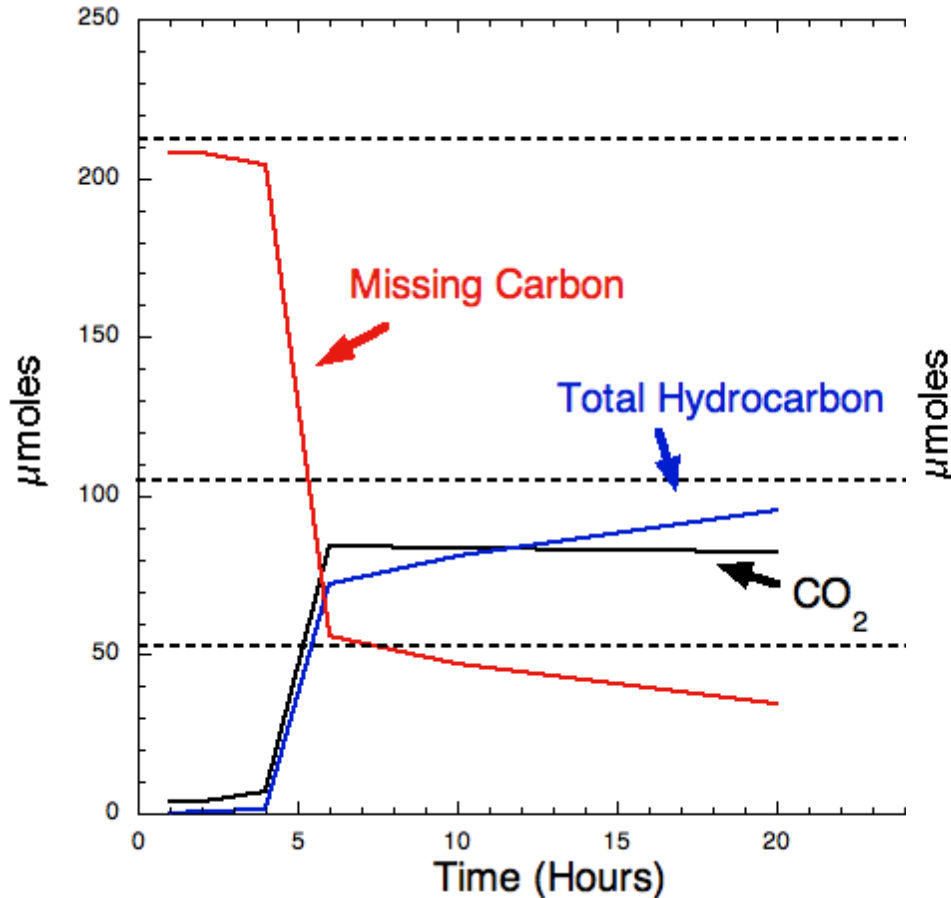


HC products look classically FTT-like: note both normal and branched HC's



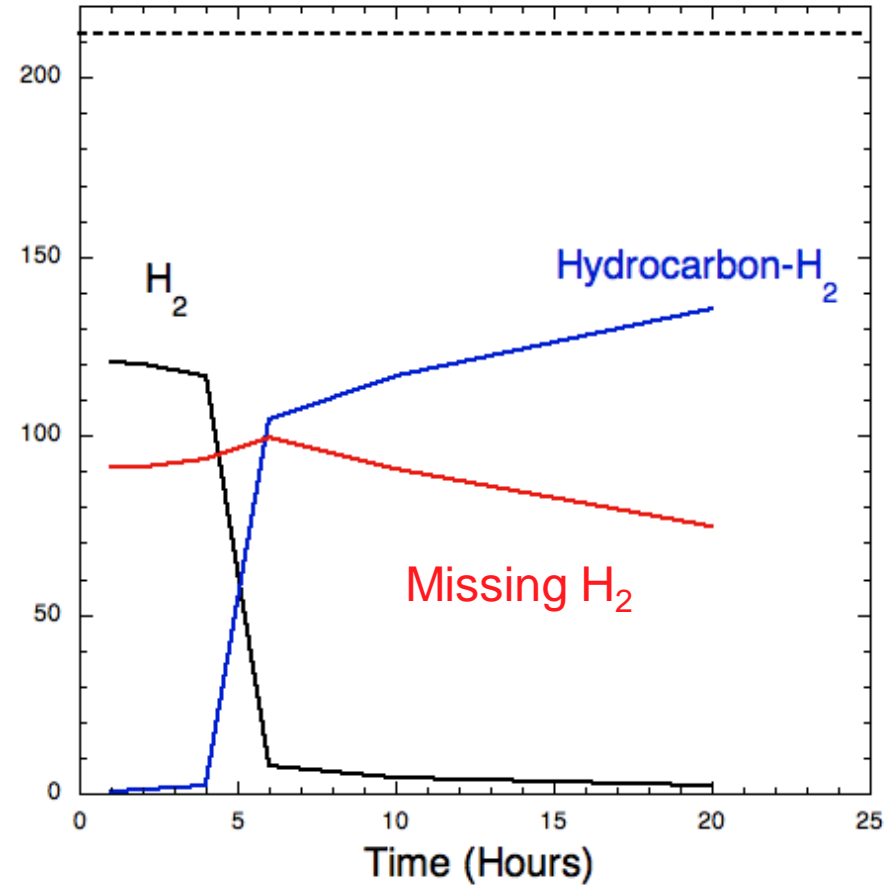
We start with 212 μmoles CO_2 and H_2 , each

Carbon budget



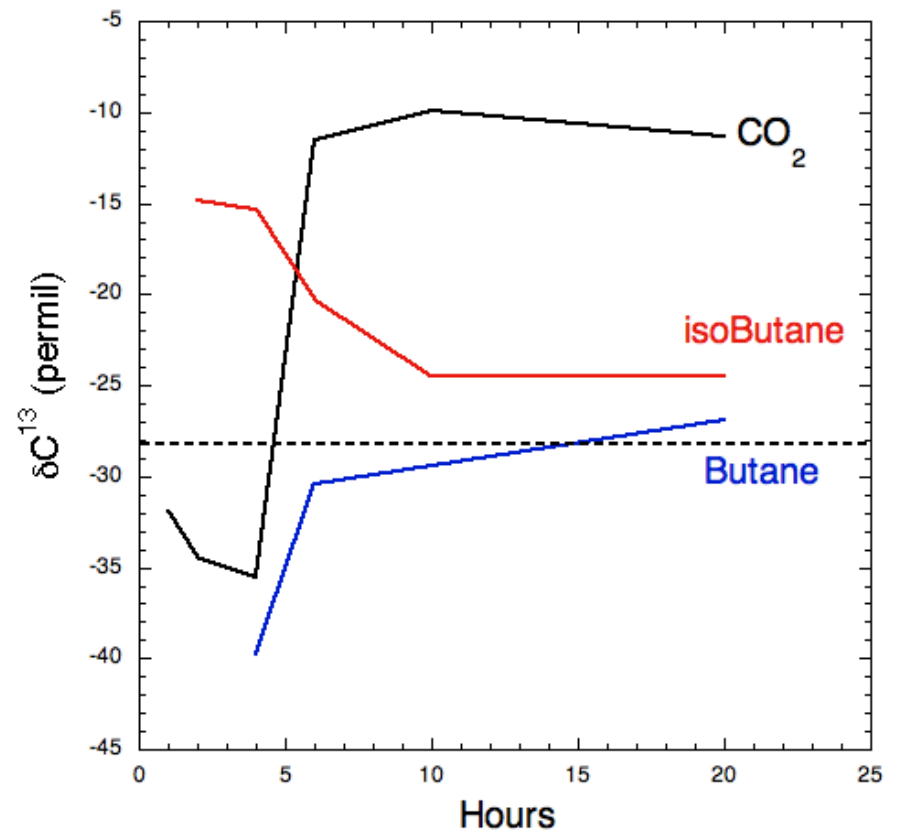
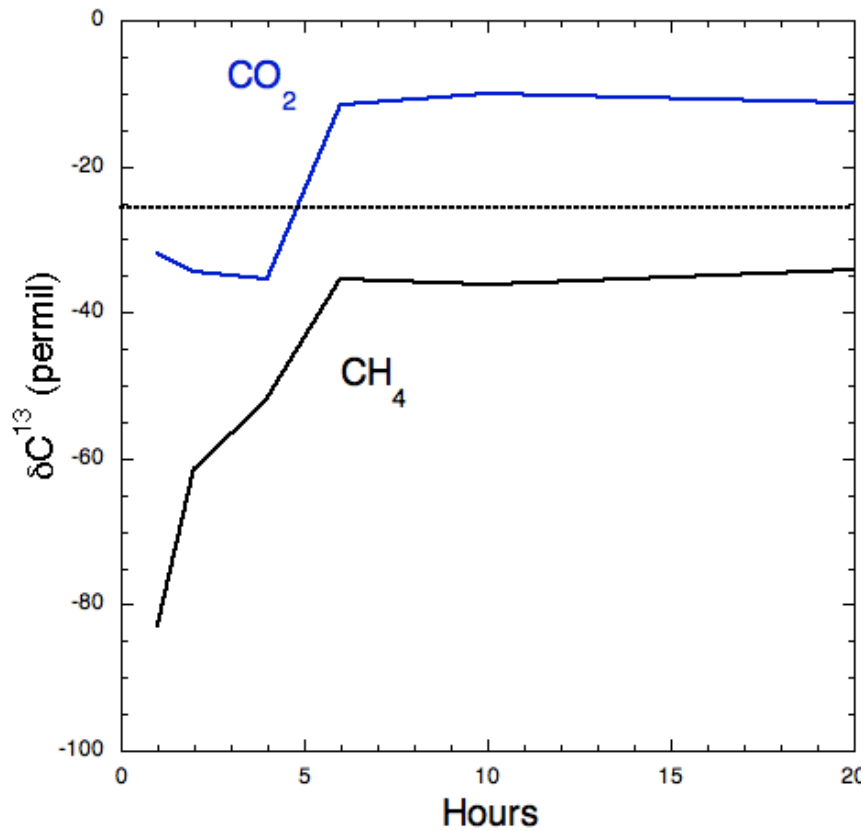
During first 4 hours, ~ 100 % of carbon is unaccounted for.

Hydrogen budget



Throughout the experiment only ~ 50 % of the H_2 is accounted for.

Stable isotopes reveal hidden complexities; two carbon reservoirs



- As methane gets heavier, CO_2 gets lighter- **C reservoir # 1**
- early isobutane heavy, gets lighter- **C reservoir # 2**

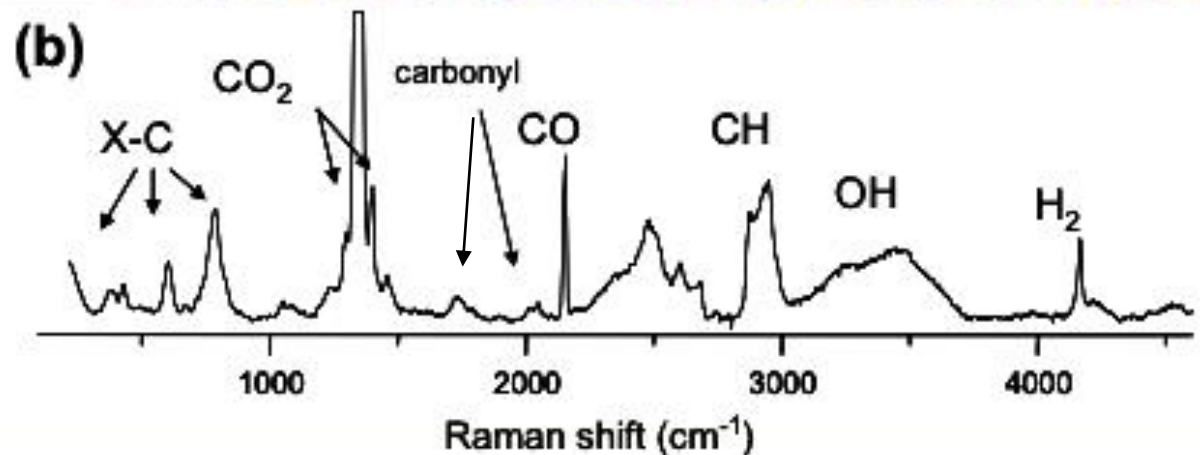
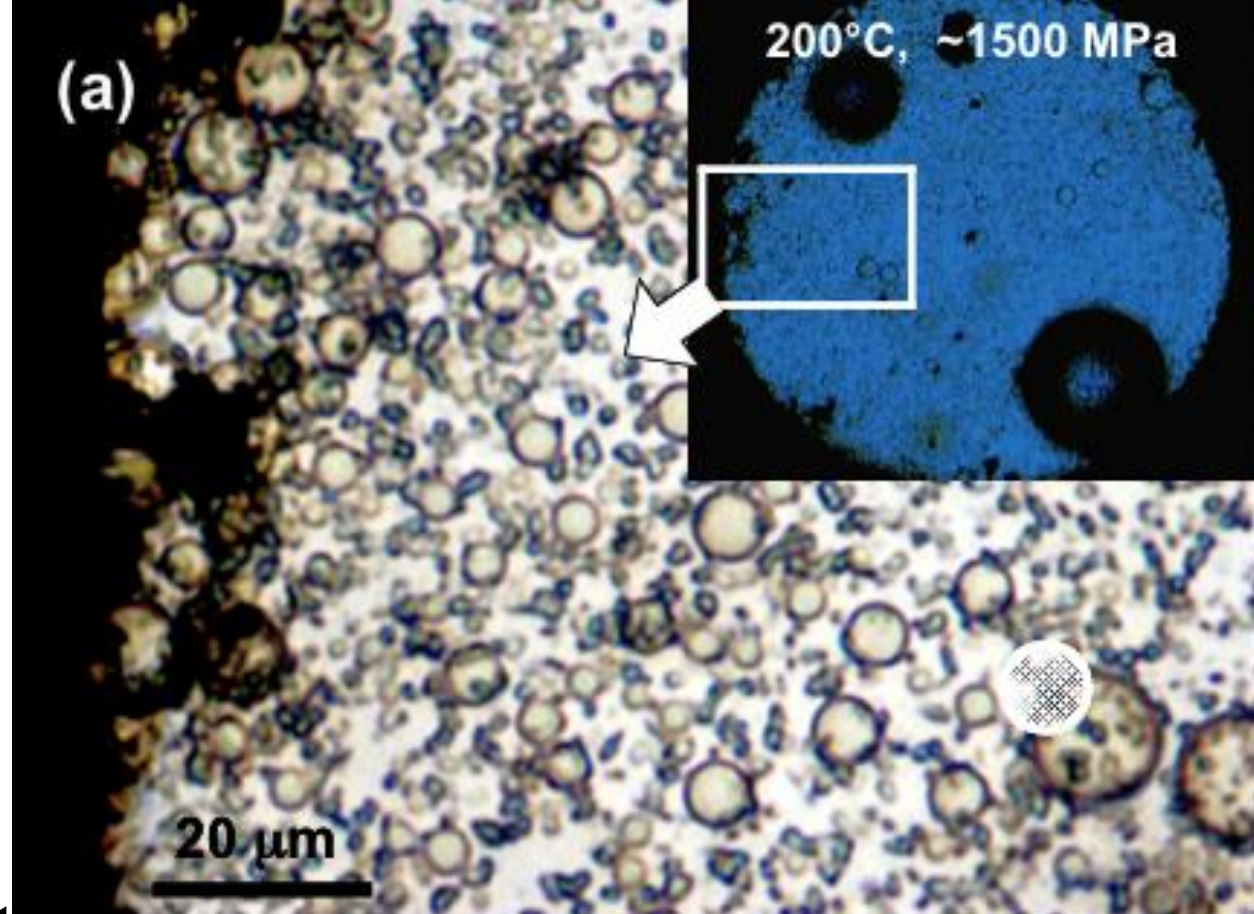
What one observes via hydrothermal diamond anvil cell

Three phases clearly evident

1 crystalline
2 fluids-immiscible

Transition metal
carbonyls abundant

HC's and CO
abundant



Conclusions:

In the Hadean/Archean Deep carbon fluxes likely were essential to the emergence of life

Organometallic complexes, e.g. transition metal carbonyls might have play a significant role in organosynthesis given favorable geochemistry

Even simple experiments are rarely simple...the hidden mineral chemistry drive the system towards rapid HC synthesis.

Unusual kinetics; our best het-catalyst 10 %/hr, this system yields ~ 80 %/hr (not likely heterogeneous catalysis).

With thanks:

NASA Astrobiology, NSF FIBR, The organizers of this remarkable meeting.