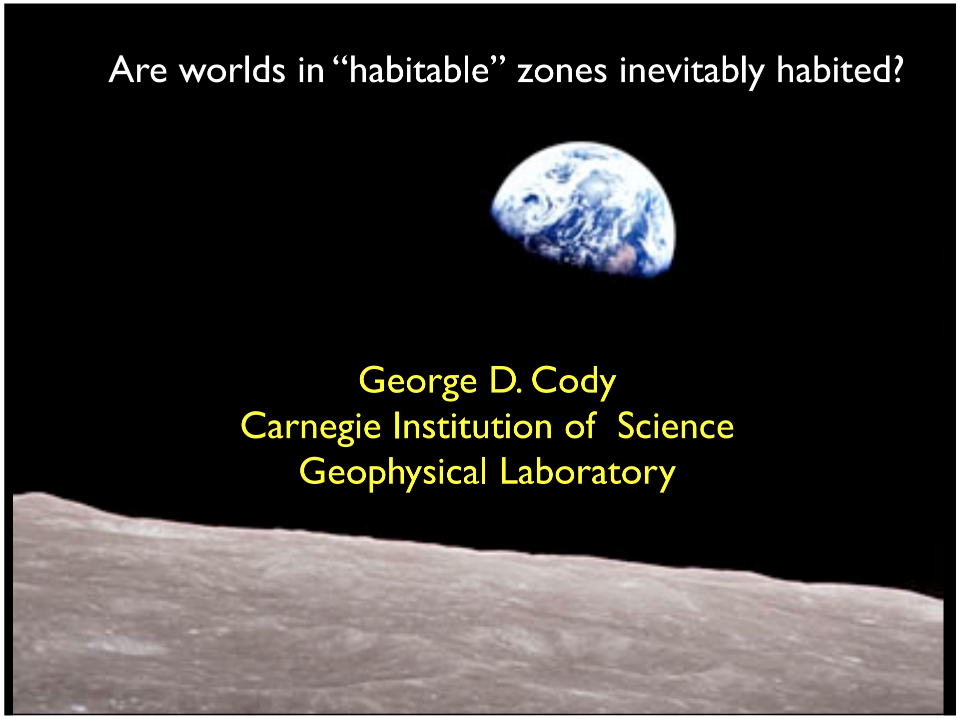
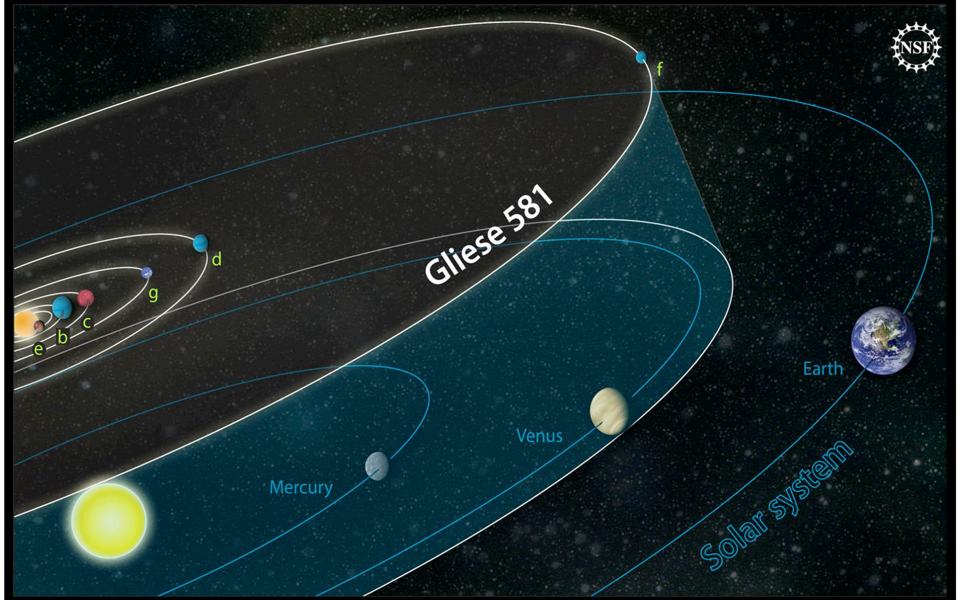


Are worlds in “habitable” zones inevitably habited?

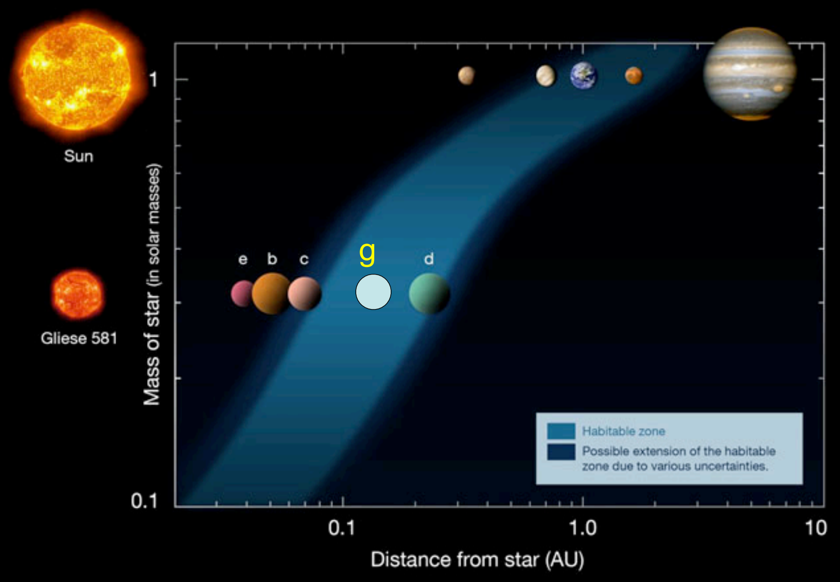
George D. Cody
Carnegie Institution of Science
Geophysical Laboratory

In the fall of 2010 a remarkable announcement…



A potential fifth world around Gliese ("Gle'za") 581

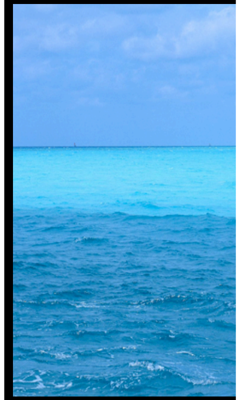
Planets in the "Habitable Zone"

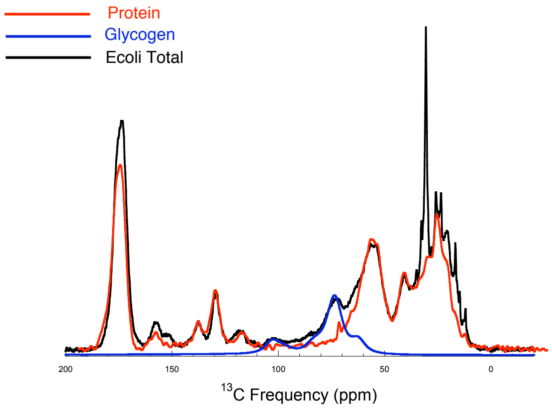


Habitable Zone = Liquid water possible on Planet surface

Liquid water may imply life, but an abiotic carbon cycle is also “required” for the emergence of life...

Biochemistry does not actually “like” water- The “Robert Shapiro Conundrum”





^{13}C NMR showing you bacteria as a molecular spectroscopist observes them...

60-70 protein, ~ 15 % glycogen, ~ 11 % lipids, ~ 5 % RNA/DNA

Life Works to get rid of water

60 - 70 % protein...
$AA + AA = (AA)_2 + H_2O$

~ 15 % glycogen...
glu + glu -> glycogen + H_2O

~ 11 % lipid
acetyl-CoA + malonyl-CoA = Lipid + H_2O

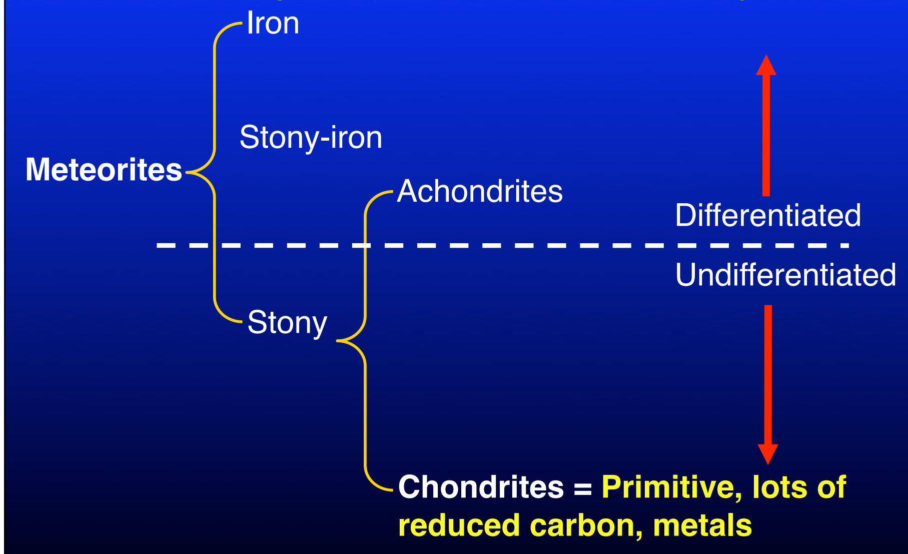
~ 5 % RNA/DNA
aminoacyl nucleotide X 2-> dinucleotide + H_2O

all of this takes ATP; where ADP + Pi -> ATP + H_2O

Life excretes H_2O, H_2O is actually harmful to life...

Meteorites provide information on how planets evolve

Prolific Abiotic Organic synthesis is required for origins of life



Iron

Stony-iron

Meteorites

Achondrites

Differentiated

Undifferentiated

Stony

Chondrites = Primitive, lots of reduced carbon, metals

Carbonaceous chondrite parent body interiors- an environment where prebiotic synthesis plausibility is known fact

Environment:

Warm (not hot)

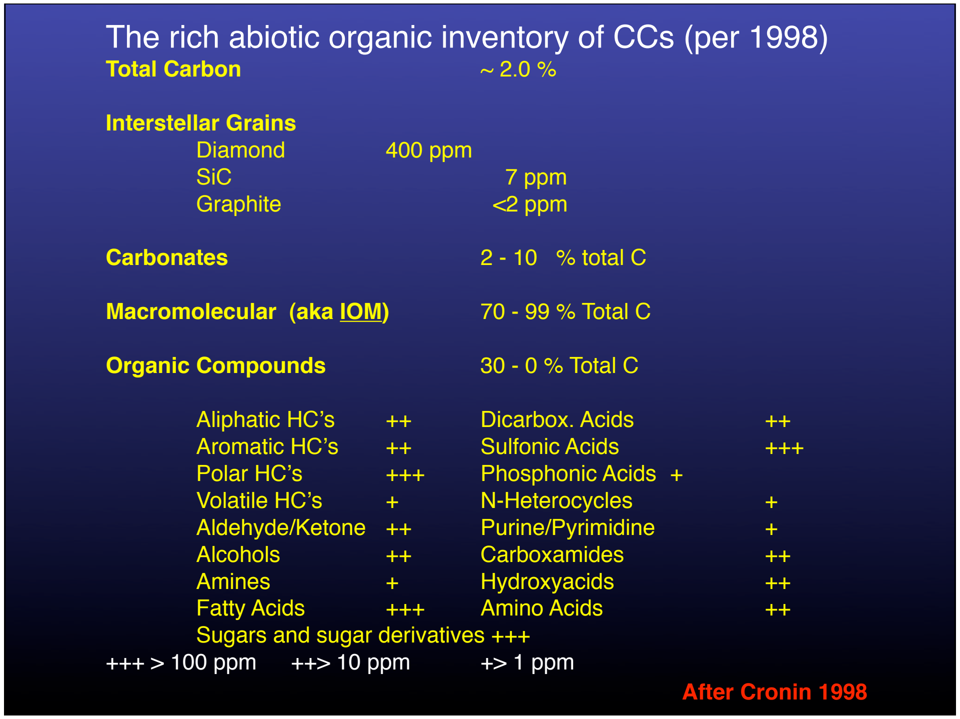
Wet- not soaked

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 CCs (per 1998)

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

Over 50,000 isomers detected, > 10^6 individual molecules

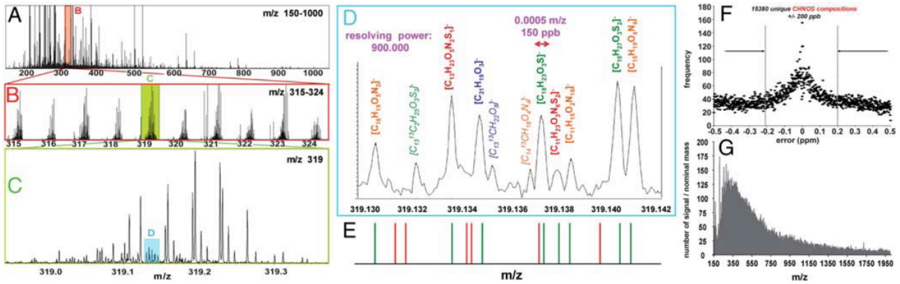
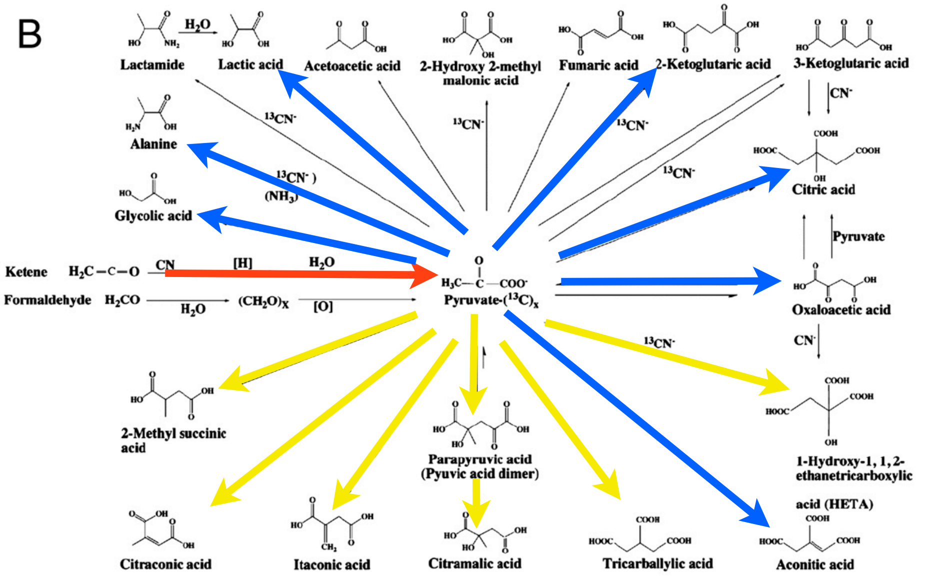


Table 1. Counts of elemental compositions as a function of extraction solvents and calculation procedures

Solvent	Number of signals, S/N 2 (S/N 1)	Sum all C, H, O, N (≤3), S (≤3) elemental compositions (200 ppb, N-rule)	Sum all C, H, O, N (≤3), S (≤3) elemental compositions (DBE > 0, H/C < 2.5, O/C < 0)	CHO	CHOS	CHNO	CHNOS
Water	17,784	6,145	4,170	1,333	470	1,759	608
Methanol	31,554 (113,493)	15,380 (29,498)	10,299 (12,313)	1,526			
2,311 (2,680)	3,051 (3,473)	3,411 (4,455)					
Methanol	24,347	8,627	4,540	1,008	598	1,681	1,253
Ethanol	27,835	11,951	7,852	1,097	2,168	1,969	2,618
Acetonitril	17,306	3,757	1,720	144	693	217	666
DMSO	12,741	1,619	264	57	55	48	104
Chloroform	18,986	4,589	2,236	926	369	815	126
Toluene	15,532	3,255	994	550	198	129	117
Total	141,738	46,696	27,535	5,633	6,264	7,988	7,650
Unique	100,687	26,530	14,197	2,022	3,340	4,021	4,814

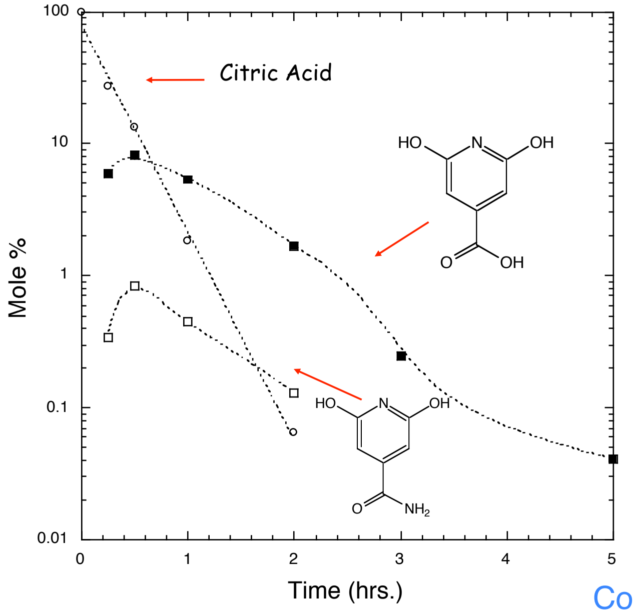
Schmitt-Kopplin et al (2010) PNAS

Common metabolic intermediates present in Murchison...



And some non-metabolic "intermediates..." Cooper et al. (2011) PNAS

Cooper concluded that all of these formed immediately after planetesimal accretion, but... most are unstable in water over time



~ fast decomposition in pure water to low molecular weight product.

Note that Citric acid is more robust than any alpha keto acid!

How could any of these survive 10^6 years of aqueous alteration? **Can’t**

Cody et al. Unpublished

Cooper et al. (2011) envisions an immediate explosion of molecular complexity

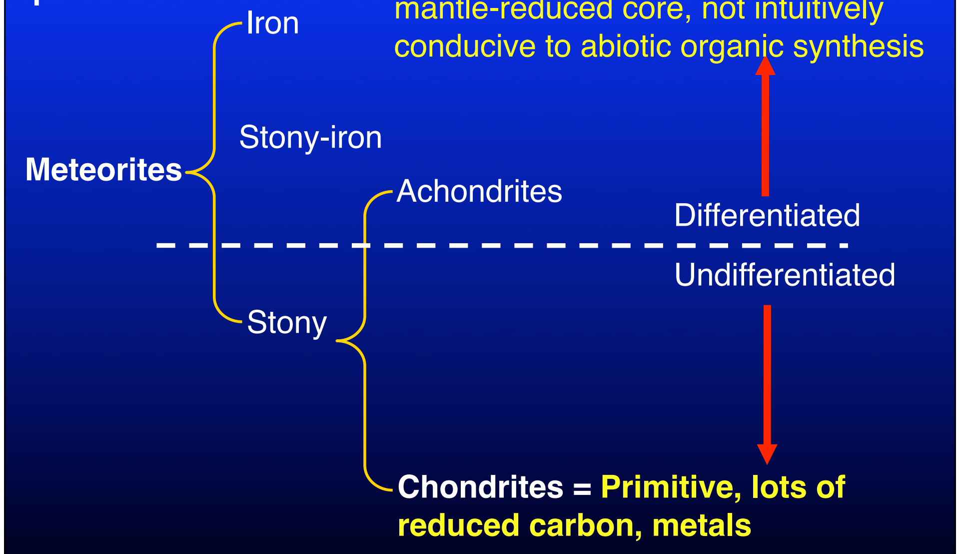
- But, aqueous alteration of Murchison Parent body lasted upwards of 10's of millions of years.

- Most of compounds detected are unstable in warm water short 1/2 lives ...virtually ***none*** of these compounds would be expected to survive 100's to 10,000 years. Oxalacetate would not survive days...

- This requires that these compounds represent a continuous, replenishing, dynamic organic reaction network: the *"holy grail"* of abiotic organic chemistry.

But…Where we find life is on a highly differentiated planet

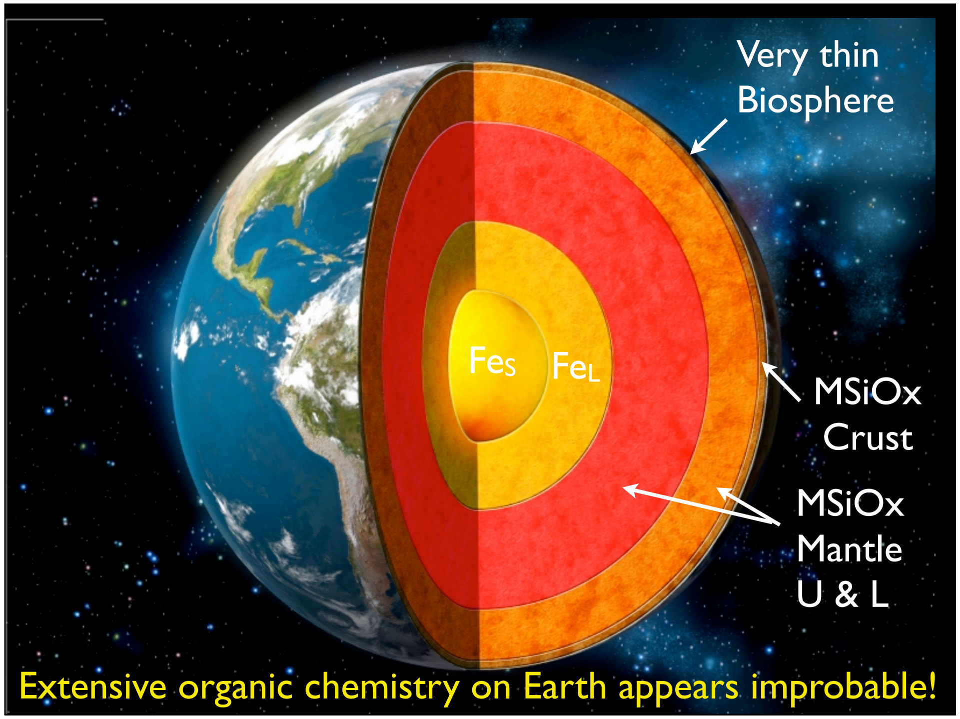
Terrestrial planets: Highly differentiated oxidized silicate crust and mantle-reduced core, not intuitively conducive to abiotic organic synthesis



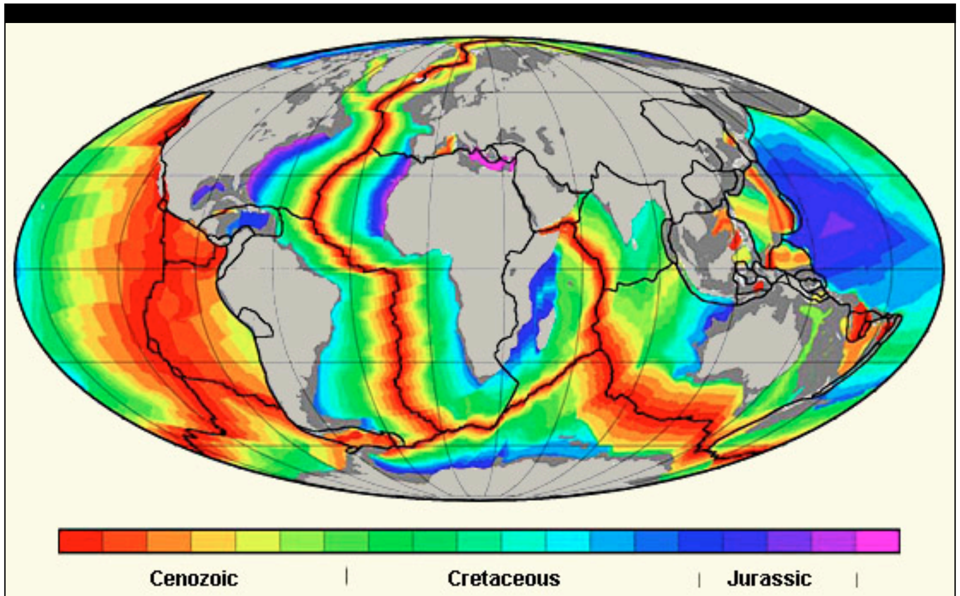
Meteorites
- Iron
- Stony-iron
- Stony
  - Achondrites
  - **Chondrites = Primitive, lots of reduced carbon, metals**

Differentiated

Undifferentiated



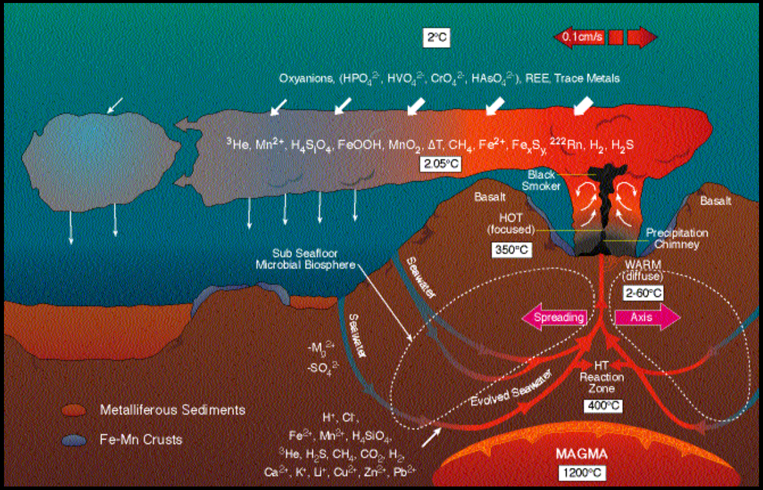
Extensive organic chemistry on Earth appears improbable!



Modern ocean floors colour-coded by geological age

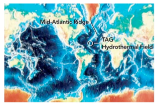
The crust either side of the spreading centres becomes progressively older. Note how the floor of the Pacific Ocean has been subducting eastwards under North and South America.

Deep Sea Hydrothermal vents exist where new sea floor forms: This is a site where tectonics regenerates the disequilibrium conditions similar to that of a CC parent body

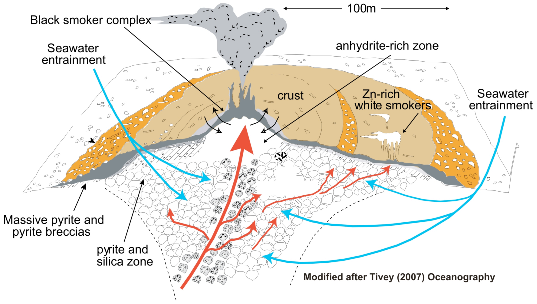


Formation of fresh sea floor provides an environment far from equilibrium
And where abiotic organic reactions can occur

Deep sea hydrothermal vents yield organosynthetic catalysts…



TAG Hydrothermal Mound



Modified after Tivey (2007) Oceanography

	Cu	Fe	Zn	Sulfur
Concentration in black smoker fluids (μM)	120-150	5590	46	2500-3500 (H_2S)
Concentration in fresh basalt (ppm)	73	76000	90	500-1000
Mass of element in the TAG deposit (x10^6 kg)	30-60	1100	15	1600
Total mass of element in reaction zone required to form the deposit (x10^6 kg)	43-85	3800	20-30	2300

~ 2 billion kg

<u>For example:</u>

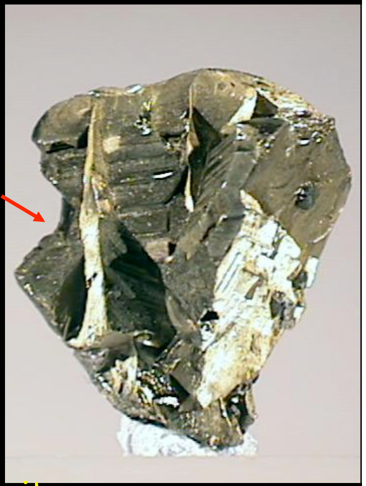
1.4 x 10^8 m^3 of basalt required to yield the Cu content at the TAG ore deposit

Basalt is hardly a highly permeable material

Transition metal aqueous extraction not efficient

Extensive H_2O-rock interaction required

Pyrite
FeS_2



Chalco-
Pyrite
$CuFeS_2$

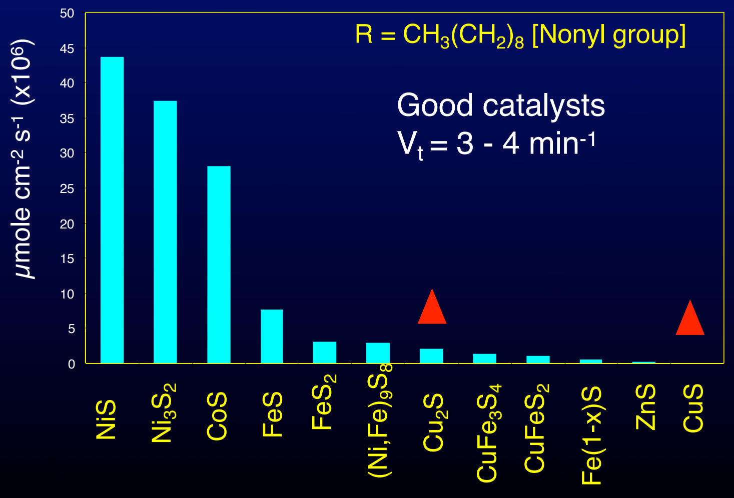
Sphalerite
ZnS

Catalysts formed via water-rock interaction

Assaying transition metal sulfide minerals for C-fixation…

$$\text{R-SH} + \text{CO} + H_2O \dashrightarrow \text{R(COOH)}$$

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



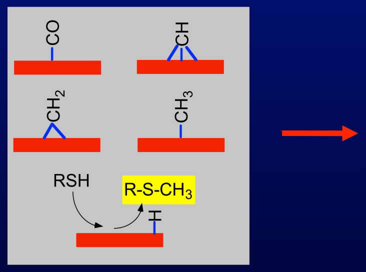
R = $CH_3(CH_2)_8$ [Nonyl group]

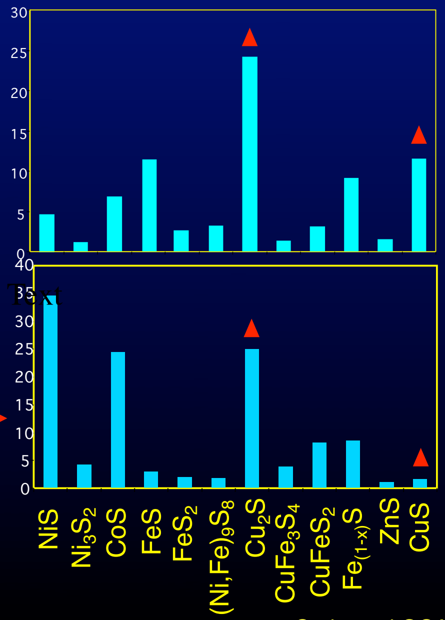
Good catalysts
V_t = 3 - 4 min^{-1}

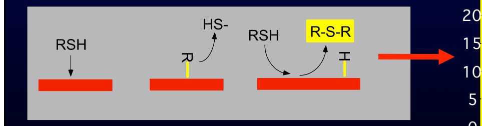
Minerals

Cody et al GCA 2004

CO reduction to CH_3 facile with metal sulfides…

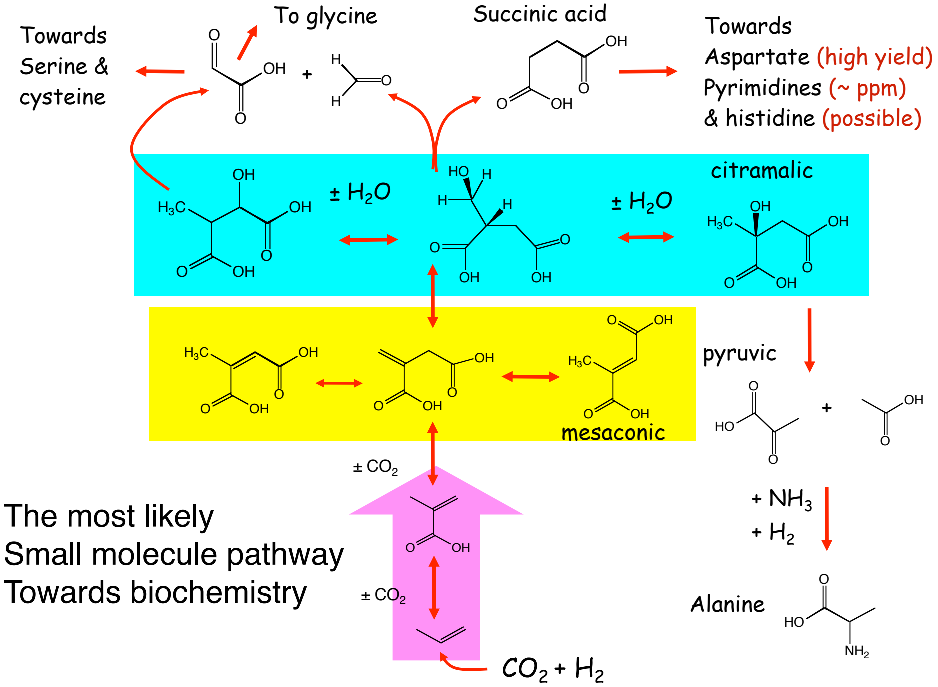






Note: that activity for carbonyl
Insertion different that activity
For CO reduction to CH_3

Cody et al GCA 2004



Towards Serine & cysteine

To glycine

Succinic acid

Towards
Aspartate (high yield)
Pyrimidines (~ ppm)
& histidine (possible)

± H_2O

± H_2O

citramalic

pyruvic

mesaconic

± CO_2

± CO_2

$CO_2 + H_2$

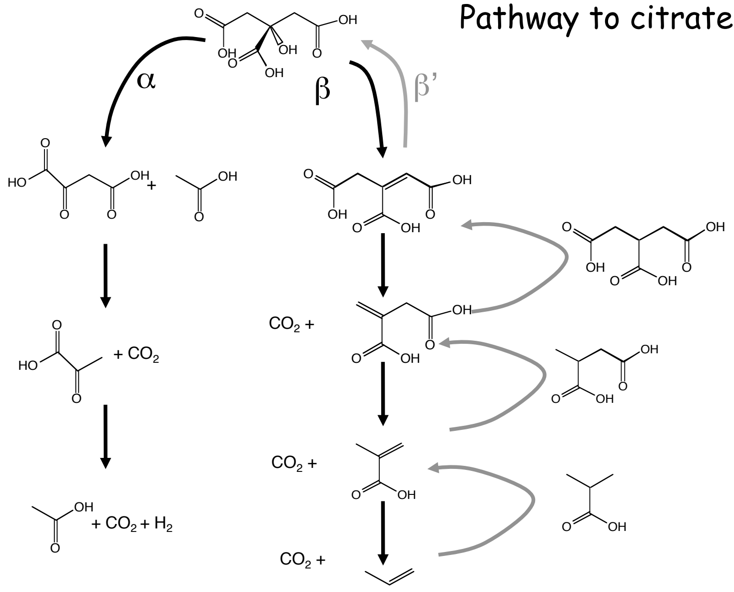
+ NH_3
+ H_2

Alanine

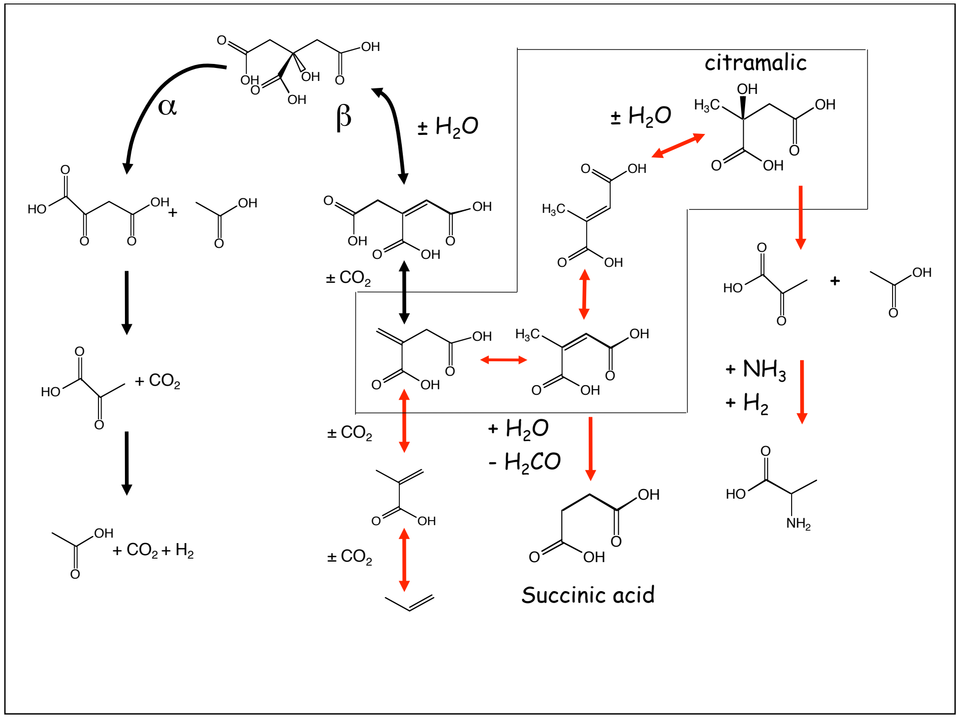
The most likely
Small molecule pathway
Towards biochemistry

Cody et al. Science 2000; Cody et al. GCA 2001, 2004

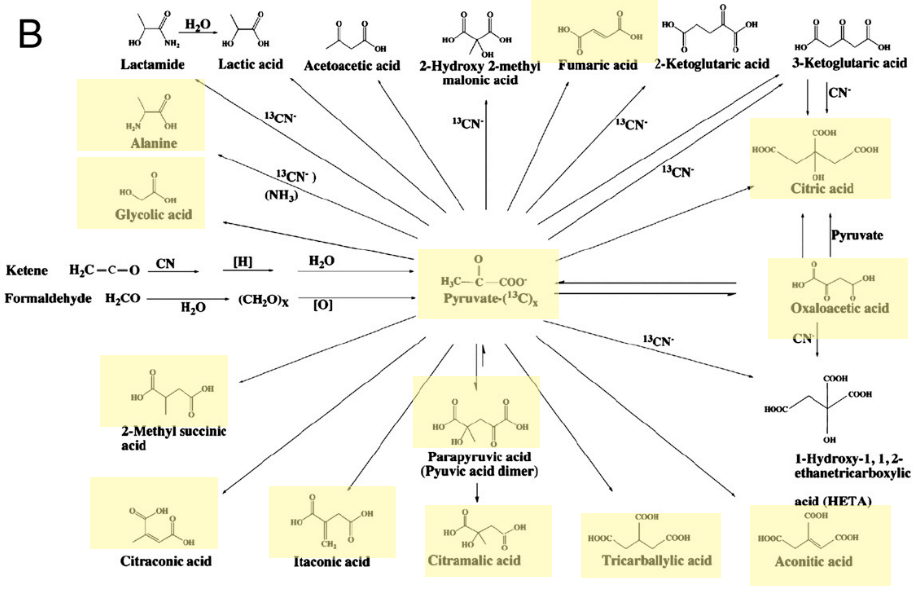
An alternative abiotic Pathway to citrate?



Cody et al GCA 2001


α
β
± H2O
± CO2
+ CO2
+ CO2 + H2
citramalic
± H2O
± CO2
± CO2
+ H2O
- H2CO
+ NH3
+ H2
Succinic acid

Many of the Cooper et al molecules observed 2011



Were are found **via exp.** by Cody et al 2001, 2004

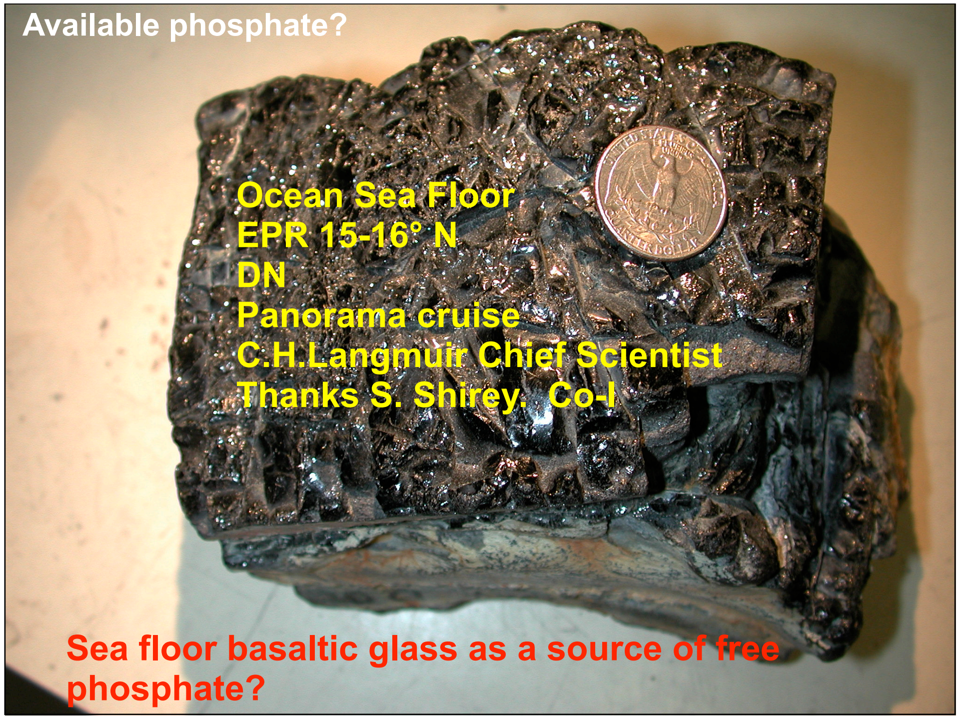
The “Chris Chyba Question” (~ 2001)

Carbonaceous chondrite parent bodies clearly had all that was necessary for wide ranging abiotic organosynthesis.... nucleobases, amino acids, sugars, central metabolic intermediates ... all of the molecules we recognize as essential to life...

But as far as we can tell* no evidence that life emerged in these bodies. What does this tell us?

*Are we missing something here? Life as we do not know it? Proto-life? Unknown...

Available phosphate?



Ocean Sea Floor
EPR 15-16° N
DN
Panorama cruise
C.H.Langmuir Chief Scientist
Thanks S. Shirey. Co-I

Sea floor basaltic glass as a source of free phosphate?

Basalt Composition (GERM reservioir data base)

Oxides	Basalt 1(wt %)	Basalt 2(wt%)
SiO_2	50.5	49.2
Al_2O_3	15.3	15.7
FeO	10.2	10.5
CaO	10.0	9.5
MgO	9.4	6.7
Na_2O	2.4	2.9
K_2O	1.1	1.1
P_2O_5	0.3	0.1
Other	0.8	4.3

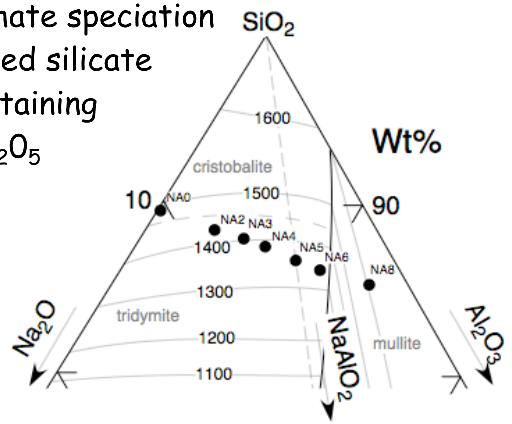
Not much phosphate, but lets put this in context…

Volumetrically ~ 5 mM in basalt
vs ~ 0.2 μM in Archean sea water (Bjerrum and Canfield 2002)

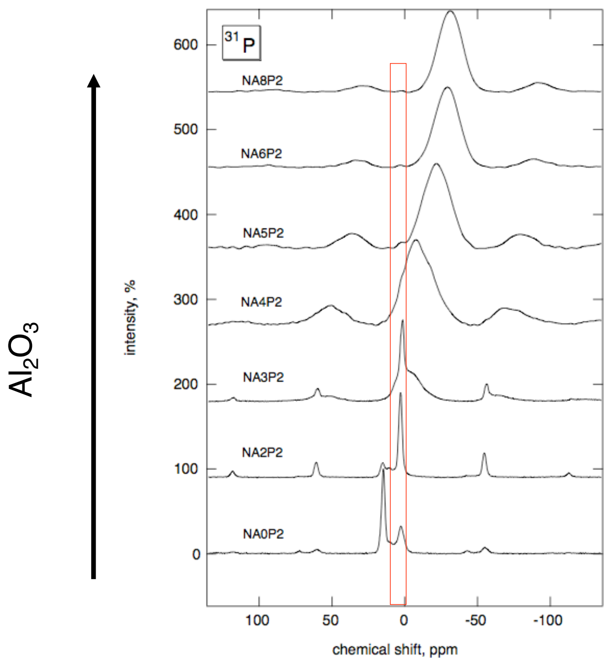
$P_{basalt} \sim 25000 \times P_{seawater}$

What is the speciation of P in basaltic glass?

Insight from a study
Of phosphate speciation
In quenched silicate
Melts containing
2 mol % P_2O_5



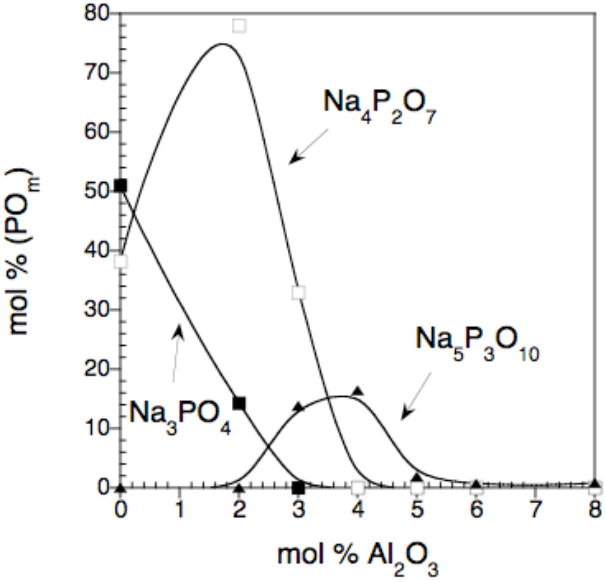
Cody et al. 2001



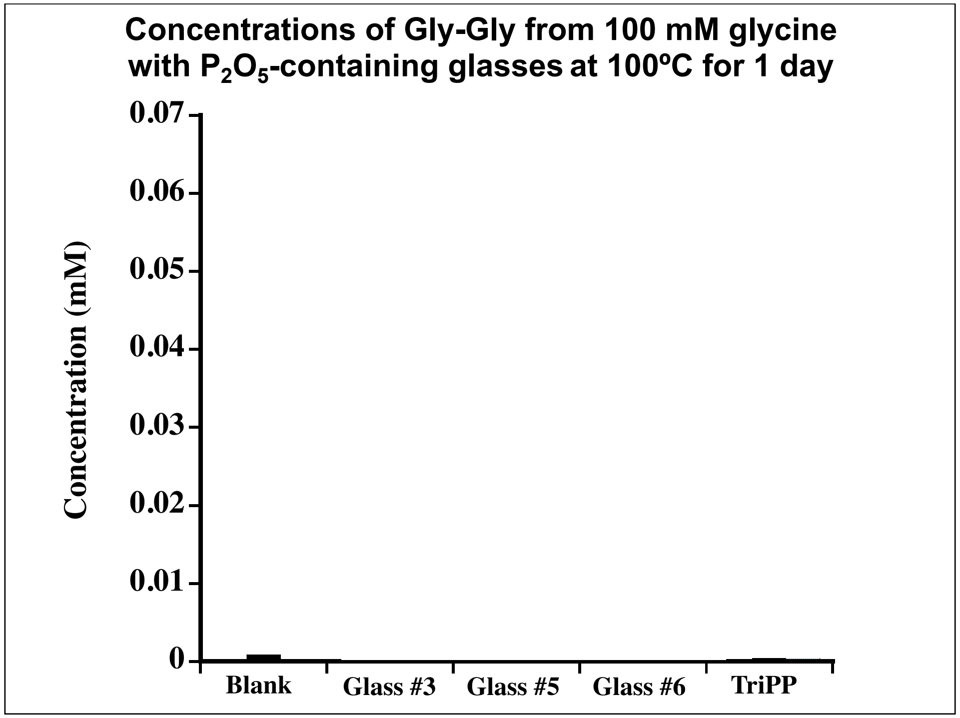
Pyrophosphate
Favored with
Increased mode
Aluminum
content

Cody et al. 2001

Volcanic glasses provide a source of PP_i and PPP_i Can model glasses drive condensation reactions?



Cody et al. 2001



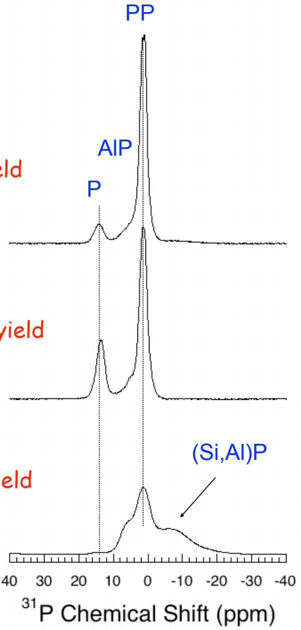
Concentrations of Gly-Gly from 100 mM glycine with P_2O_5-containing glasses at 100ºC for 1 day
Concentration (mM)
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0
Blank
Glass #3
Glass #5
Glass #6
TriPP

Yield drops with increasing Al_2O_3: Al-O-P increases

$2Na_2O{\cdot}1/2Al_2O3{\cdot}8SiO_2$ + 5 mol % P_2O_5: 25 x yield

$2Na_2O{\cdot}1/4Al_2O3{\cdot}8SiO_2$ + 5 mol % P_2O_5 : 46 x yield

$2Na_2O{\cdot}1Al_2O3{\cdot}8SiO_2$ + 5 mol % P_2O_5 : 23 x yield



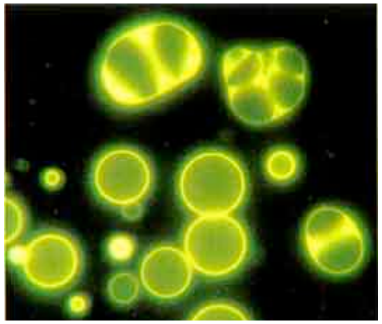
Sea Floor glass is far from equilibrium with sea water and is potentially a useful condensation reagent

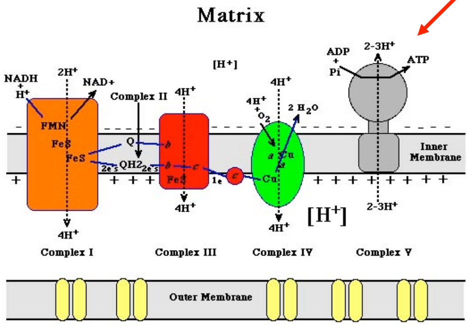
In a world largely devoid of available P_i, basaltic glass is relatively concentrated.

Preliminary work looks promising,but considerable exploration is required (e.g. pH) - solution chemistry will evolve considerably over reaction time.

Polyphosphatic sea floor glass promoted reactions could intersect with the transition metal sulfide catalyzed small molecule reactions in a single environment

Compartmentalization?





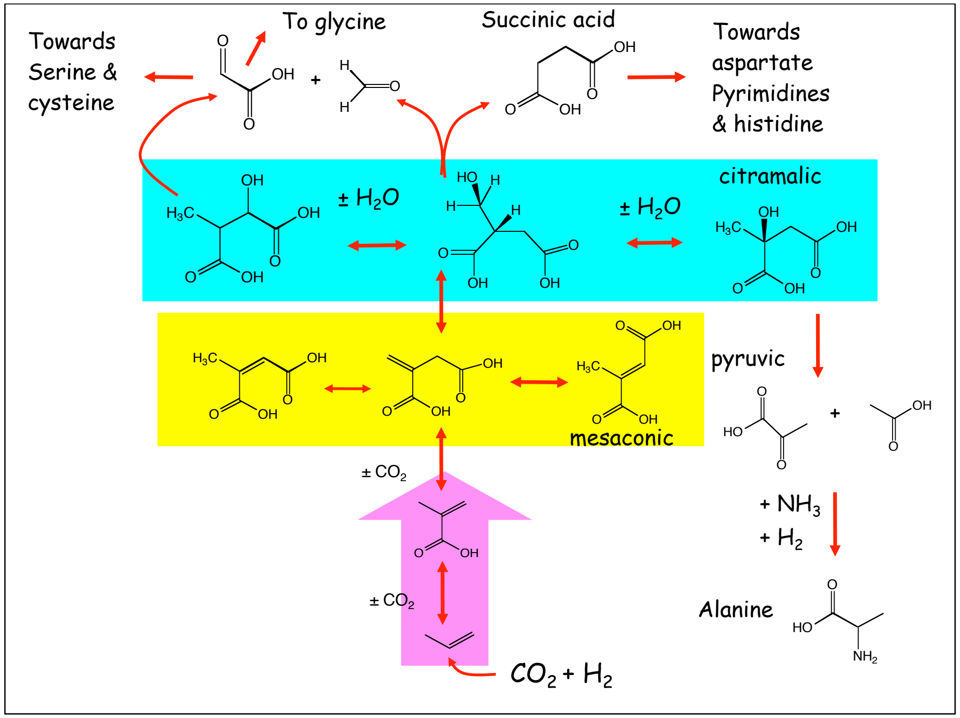
Necessary to support heredity and genetic evolution

Presumably required for electron transport phosphorylation (ETP)

But… Substrate level phosphorylation surely came first

& ETP <u>very</u>, <u>very</u>, complex certainly a later development

Need to develop electron transport chains - HOW?



Towards Serine & cysteine

To glycine

Succinic acid

Towards aspartate Pyrimidines & histidine

± H_2O

± H_2O

citramalic

pyruvic

mesaconic

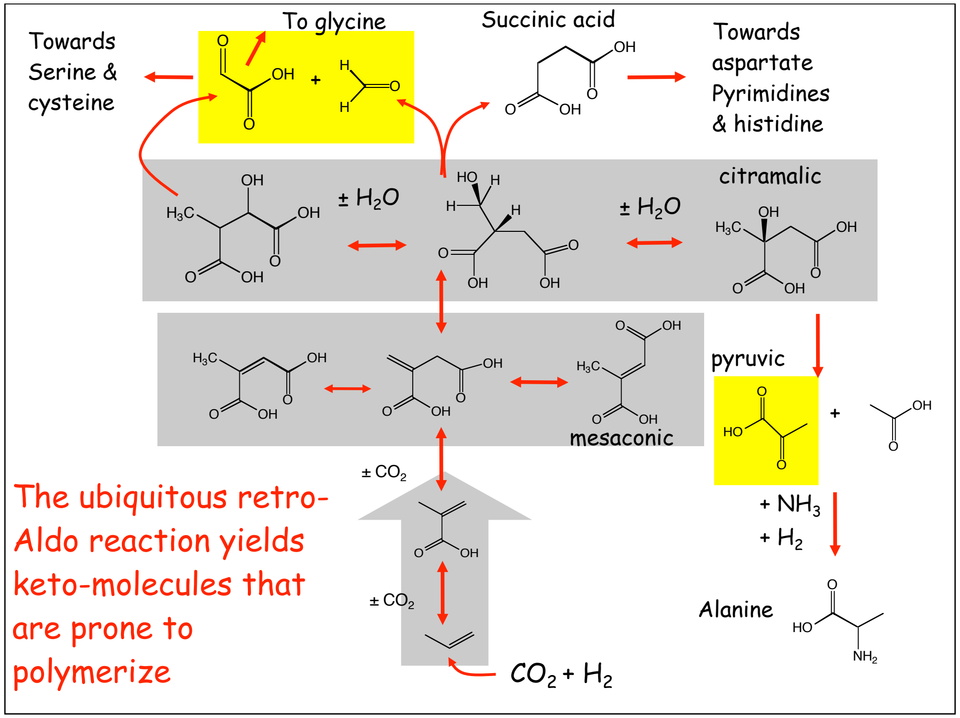
± CO_2

± CO_2

+ NH_3
+ H_2

Alanine

$CO_2 + H_2$



Towards Serine & cysteine

To glycine

Succinic acid

Towards aspartate Pyrimidines & histidine

± H_2O

± H_2O

citramalic

pyruvic

mesaconic

± CO_2

± CO_2

+ NH_3

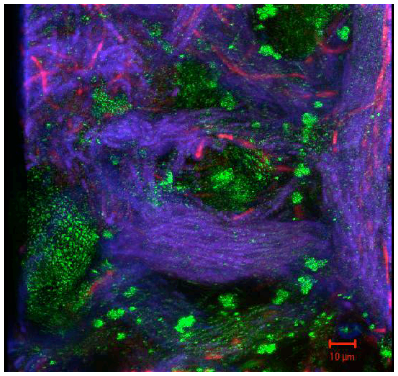
+ H_2

Alanine

$CO_2 + H_2$

The ubiquitous retro-Aldo reaction yields keto-molecules that are prone to polymerize

Are poly-Aldol polymers interesting?



Hi-mag image of a biofilm,
EPS - Blue
Bacteria - Red & green

Polyelectrolyte gels can support similar osmotic function of cell membrane, but with considerably greater structural simplicity.

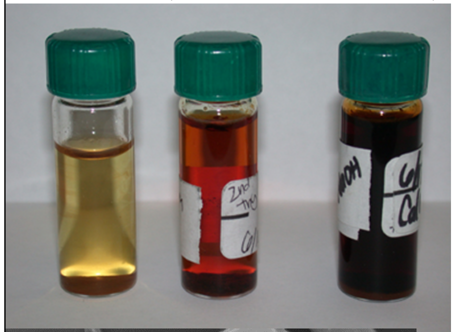
Currently,

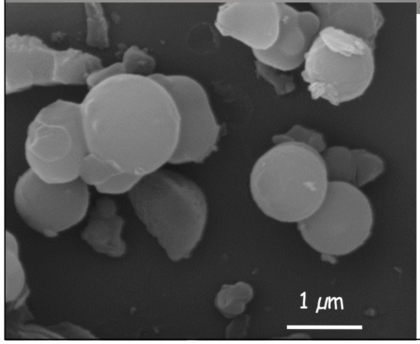
Microbes ---> biofilms (EPS)

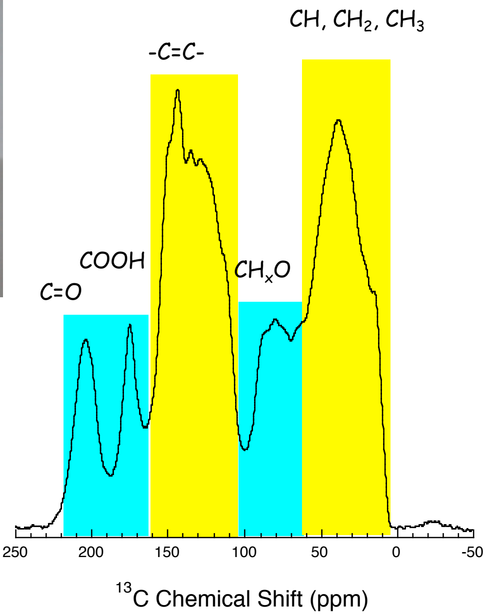
What if originally,

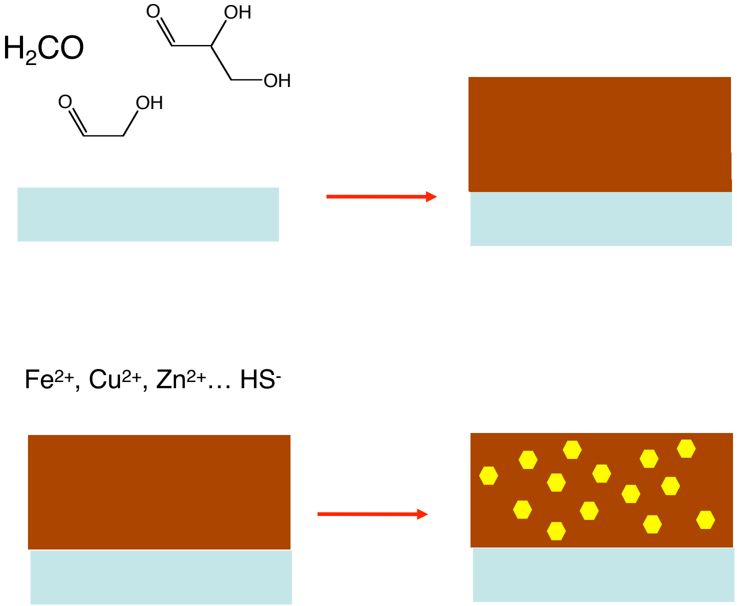
Biofilms (EPS) ----> first cells

Formaldehyde condensation yields: formose polymer









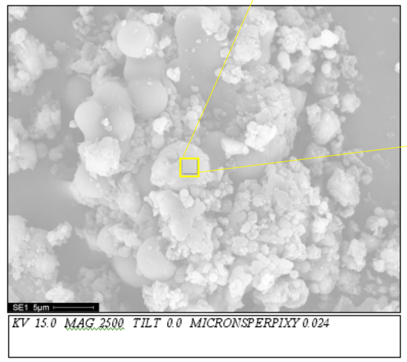
H_2CO

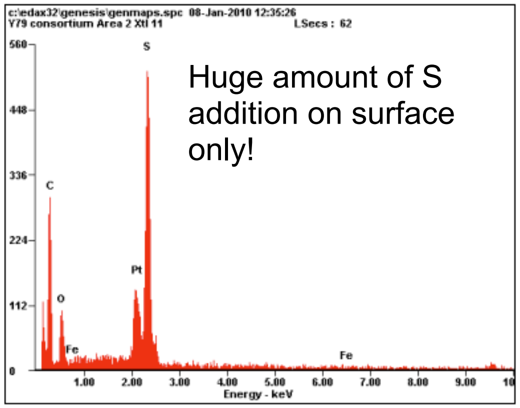
Fe^{2+}, Cu^{2+}, Zn^{2+}… HS^-

Transition metal sulfide/polymer nano-composites could be interesting as catalysts and primitive electron transport systems

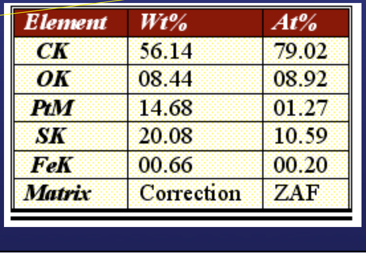
FeS$_{AQ}$ addition in F-polymer via aqueous chemistry

Failure: F-polymer hydrophobic, only surface is sulfurized.





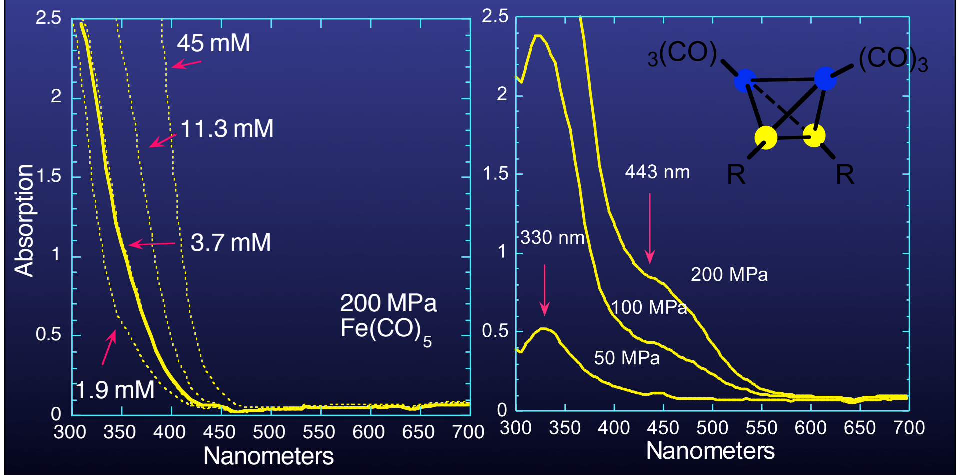
Huge amount of S addition on surface only!



Element	*Wt%*	*At%*
CK	56.14	79.02
OK	08.44	08.92
PtM	14.68	01.27
SK	20.08	10.59
FeK	00.66	00.20
Matrix	Correction	ZAF

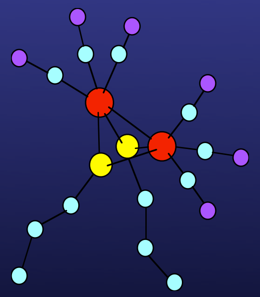
How about lipophilic FeS species?

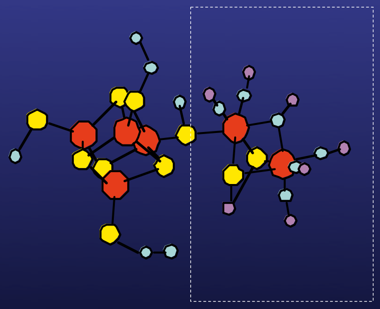
CO + FeS + Nonane thiol 250°C 200 MPa 6h



Iron sulfur Carbonyls + 20-50% Dissolution of FeS

Carbonylated Fe-S Clusters & Biochemical Connections





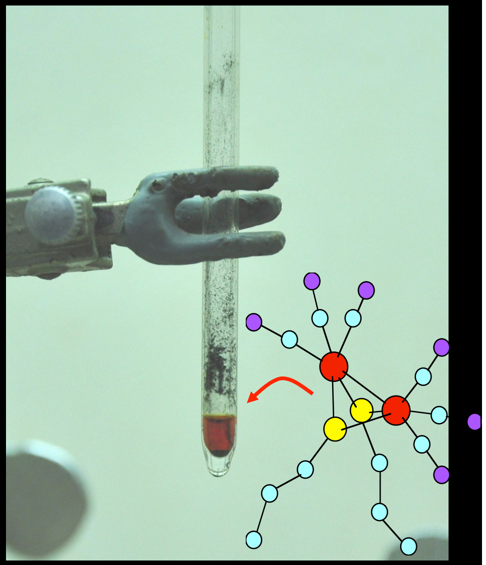
Product of FeS Rxn’s
With Formic Acid and
Nonyl-thiol @ Hi P and T

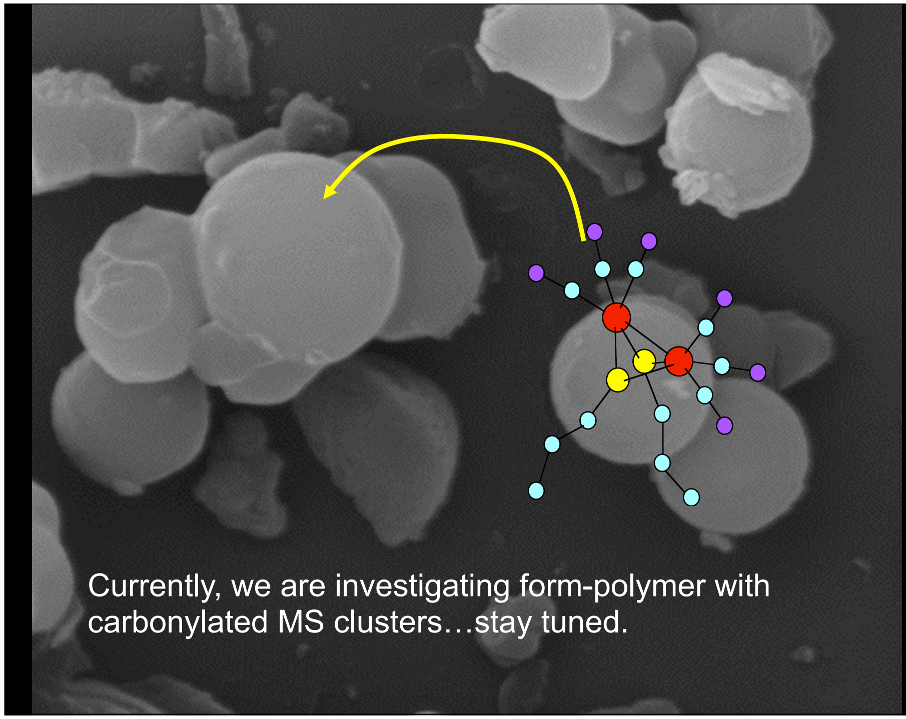
‘H-Cluster’ in Hydrogenase
2-Fe domain with CO or CN
Ligands (John Peters and
colleagues)

But high pressures are required if high temperatures are used in order stabilized the carbonylated MSs

It turns out one can achieve a high yield at room temperature

Lower temperatures are always more attractive





Currently, we are investigating form-polymer with carbonylated MS clusters…stay tuned.

So why did life emerge on Earth and “apparently” not on chondritic parent bodies?

Easy answer: Don’t know

Reality there are some differences…

Tectonics created a novel environment….

And a ***recursive*** environment (consistent for 4.5 Ga)

The abiotic organic chemistry on Earth was localized and temporal- *Key: Water-rock interaction via tectonics continuously generated disequilibrium*

"Emergent chemistry on a treadmill"

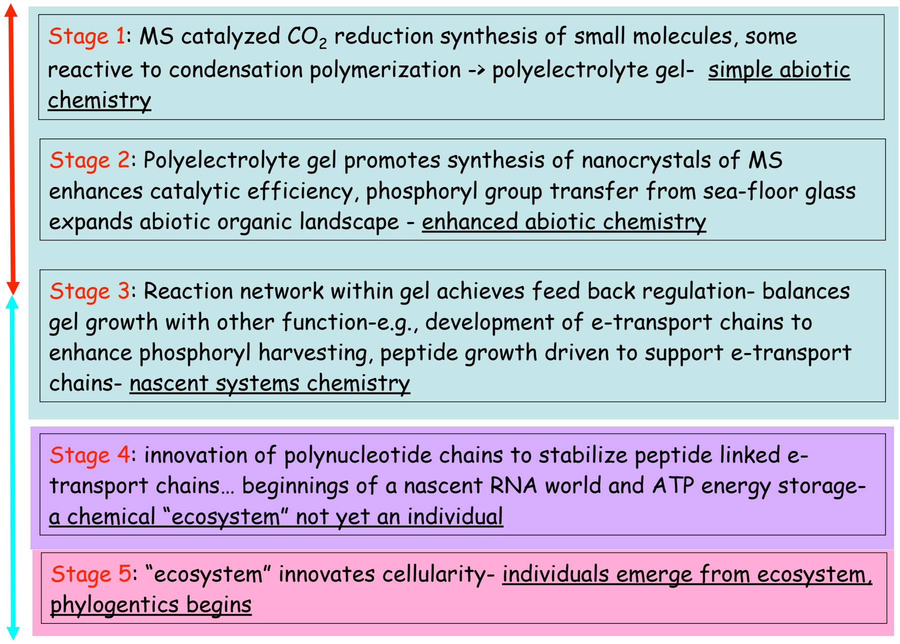
That which did not succeed was carried off to the abyssal wasteland. Innovation against progressive alteration was awarded with fresh substrate.

Continuous opportunities to "invent"- fail and you die

A strange but familiar Darwian Landscape... maybe

Plate Tectonics Key... a question of volatiles?

A Proposal for life's origins in the vicinity of deep sea ore bodies…



Stage 1: MS catalyzed CO_2 reduction synthesis of small molecules, some reactive to condensation polymerization -> polyelectrolyte gel- simple abiotic chemistry

Stage 2: Polyelectrolyte gel promotes synthesis of nanocrystals of MS enhances catalytic efficiency, phosphoryl group transfer from sea-floor glass expands abiotic organic landscape - enhanced abiotic chemistry

Stage 3: Reaction network within gel achieves feed back regulation- balances gel growth with other function-e.g., development of e-transport chains to enhance phosphoryl harvesting, peptide growth driven to support e-transport chains- nascent systems chemistry

Stage 4: innovation of polynucleotide chains to stabilize peptide linked e-transport chains… beginnings of a nascent RNA world and ATP energy storage- a chemical "ecosystem" not yet an individual

Stage 5: "ecosystem" innovates cellularity- individuals emerge from ecosystem, phylogentics begins