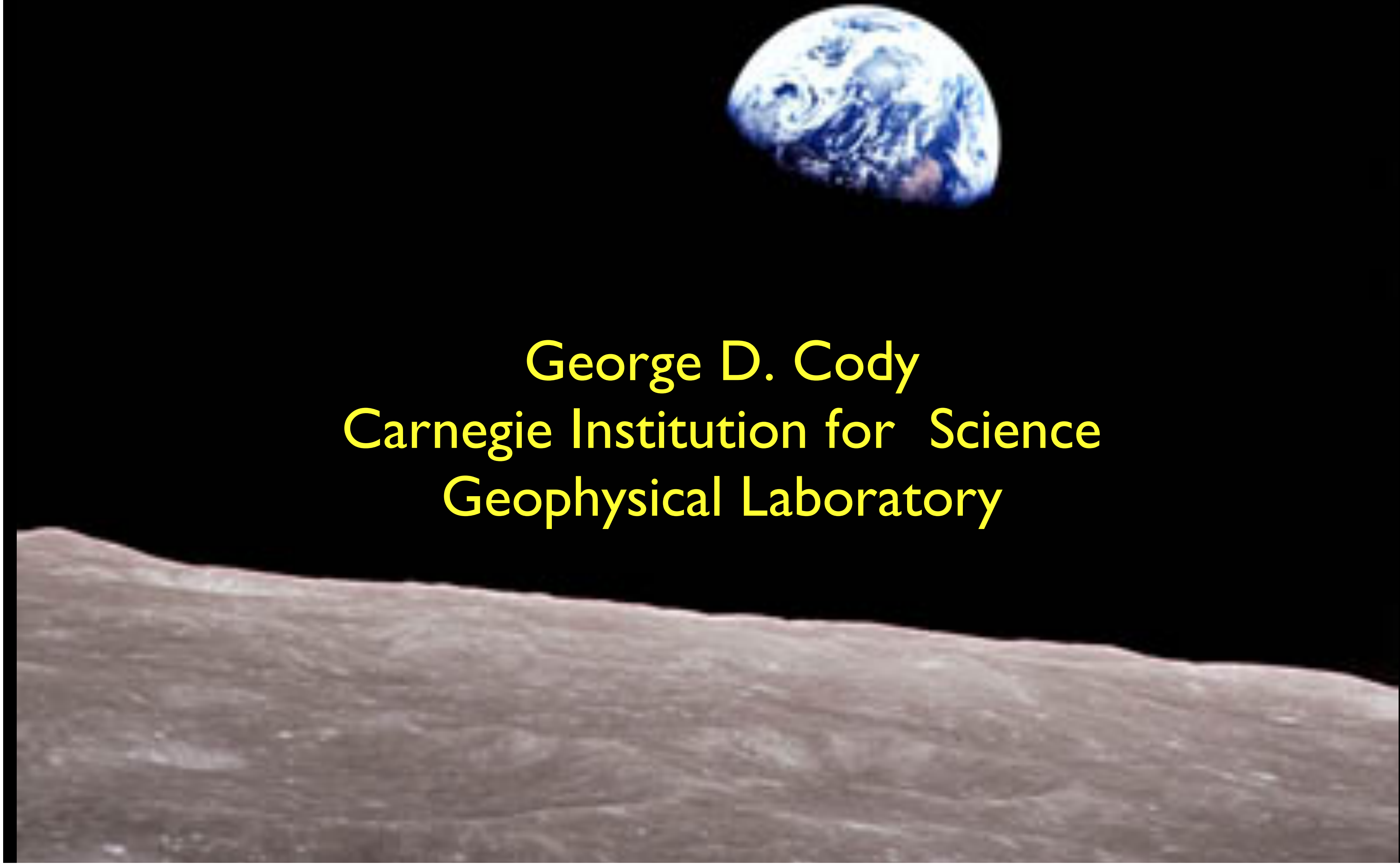
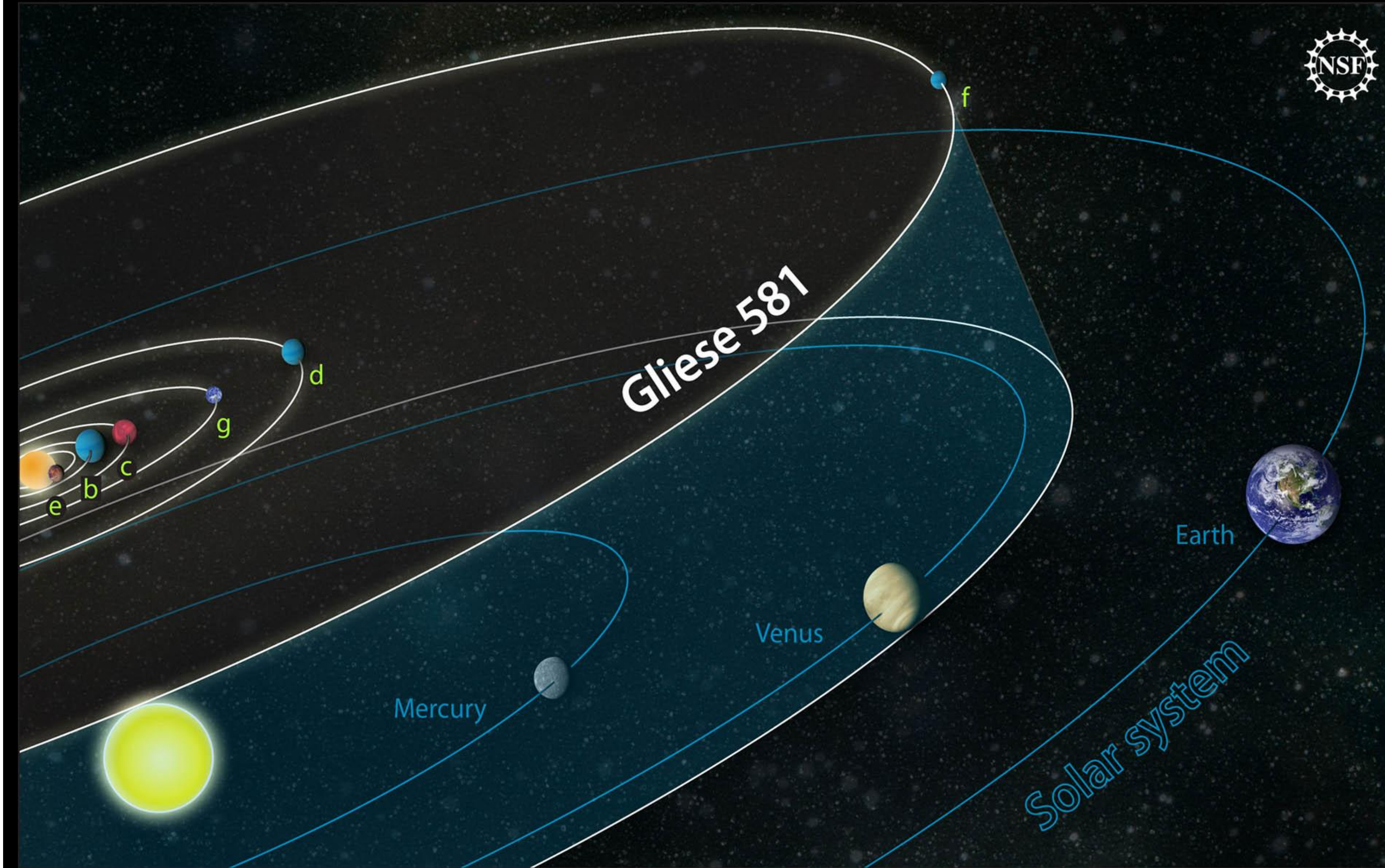
# Are worlds in "habitable" zones inevitably habited?



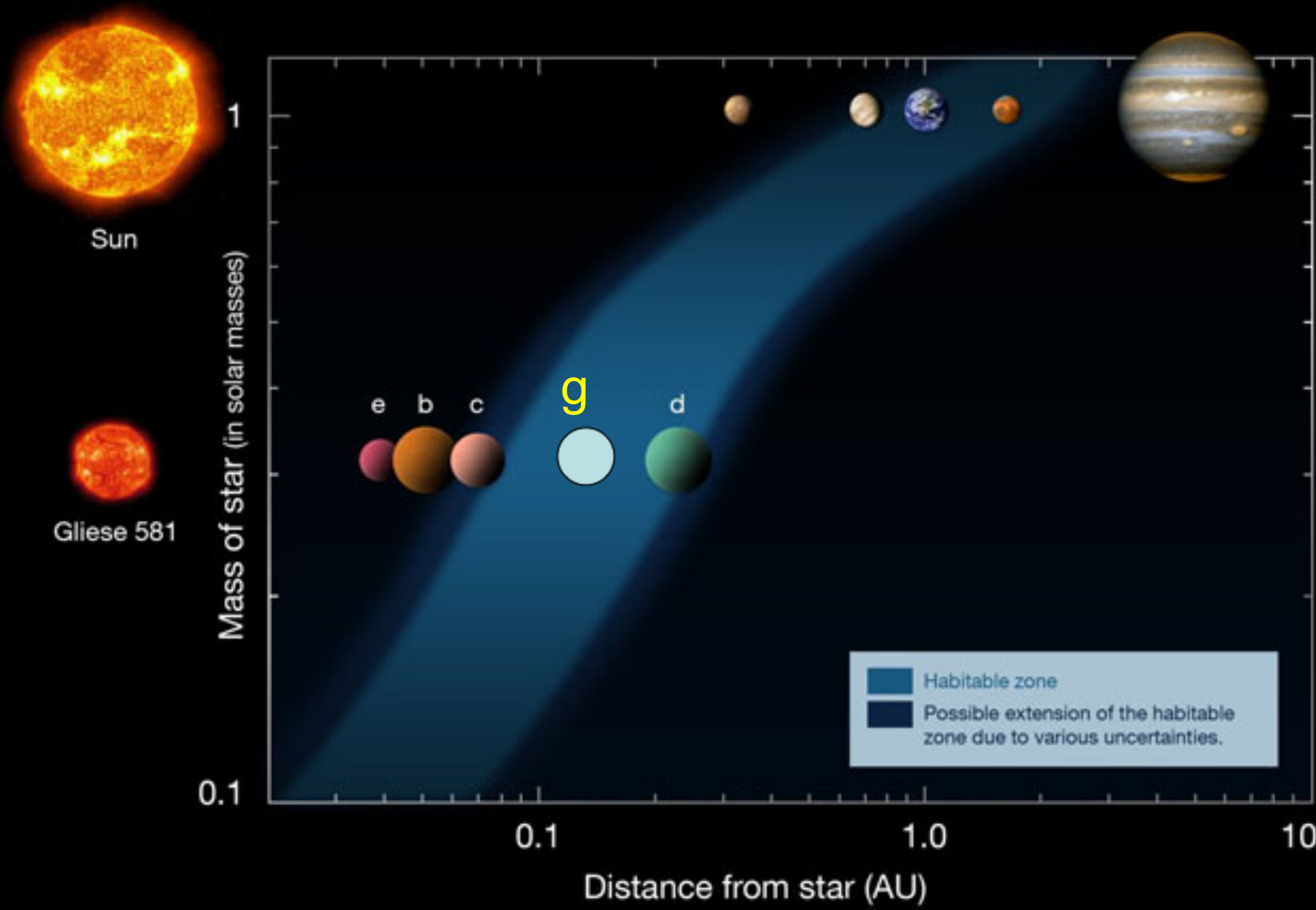
George D. Cody
Carnegie Institution for Science
Geophysical Laboratory

In the fall of 2010 a remarkable announcement…




A potential fifth world around Gliese (“Gle’za”) 581

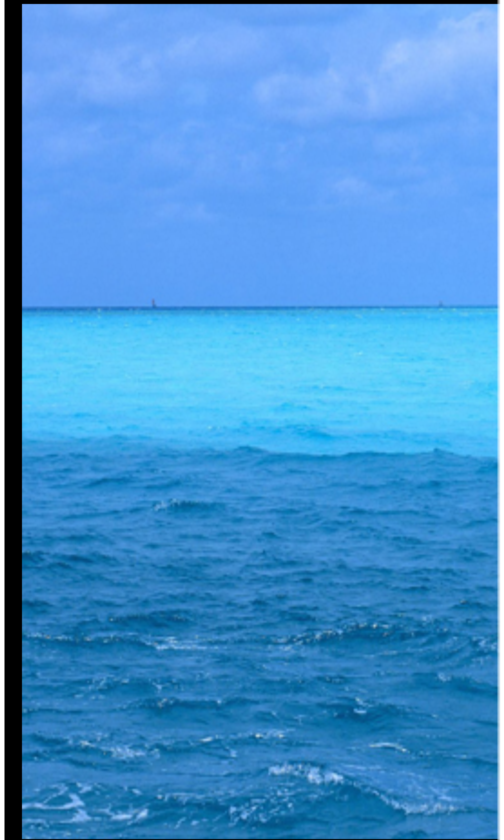
# Planets in the “Habitable Zone”

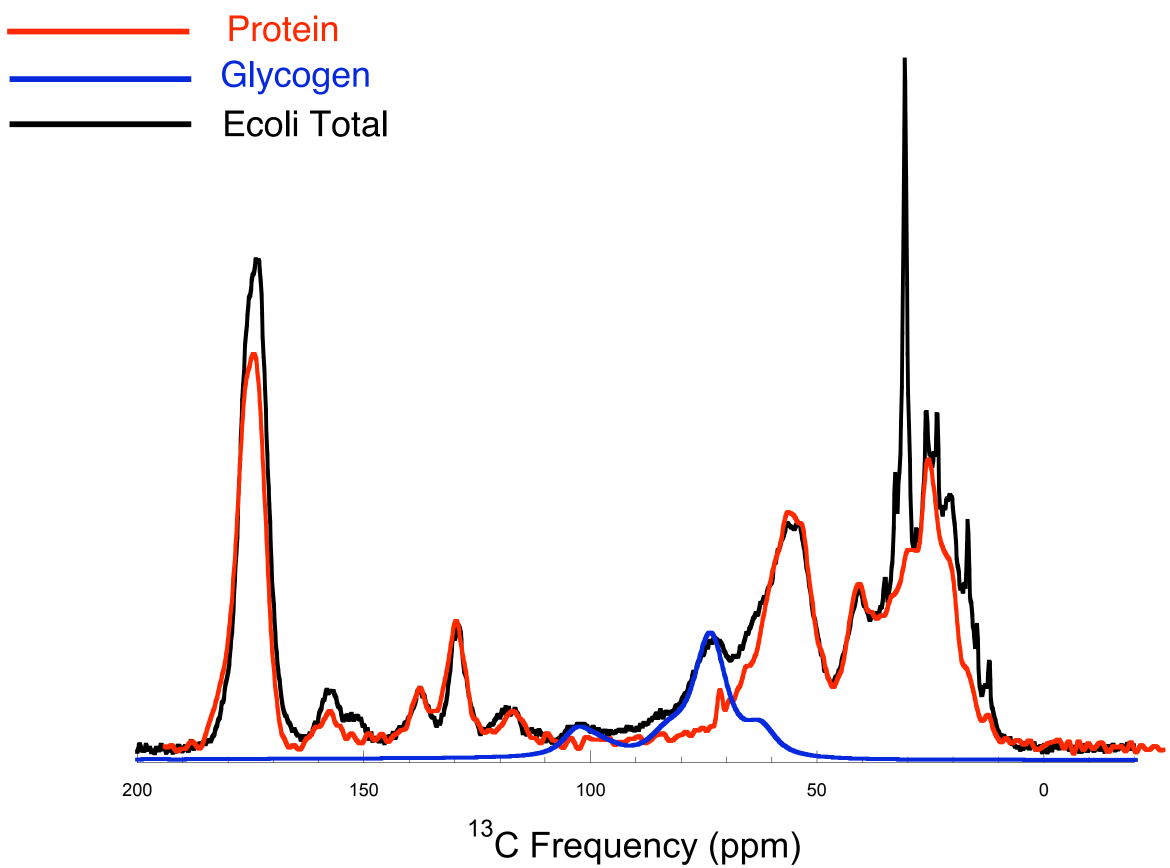


Habitable Zone = Liquid water possible on Planet surface

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 + $H_2O$

## Meteorites provide information on how planets evolve

Prolific Abiotic Organic synthesis is required for origins of life

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

Differentiated

Undifferentiated

**Carbonaceous chondrite parent body interiors**- an environment where prebiotic synthesis plausibility is known fact (*scientists not involved!*)

*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

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

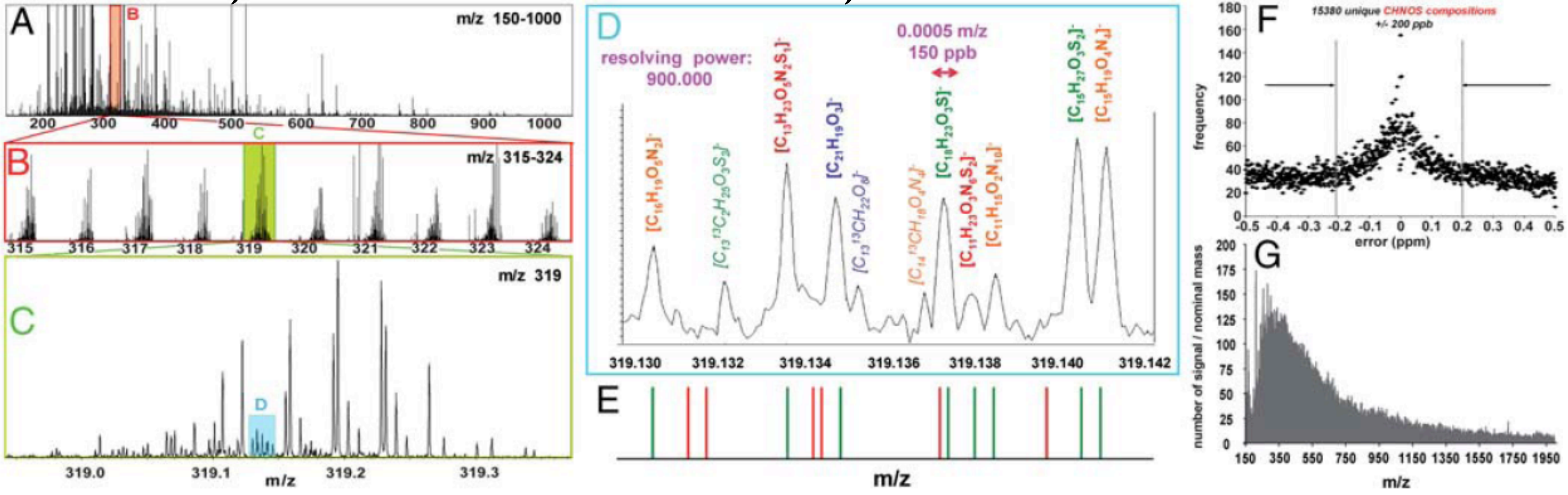
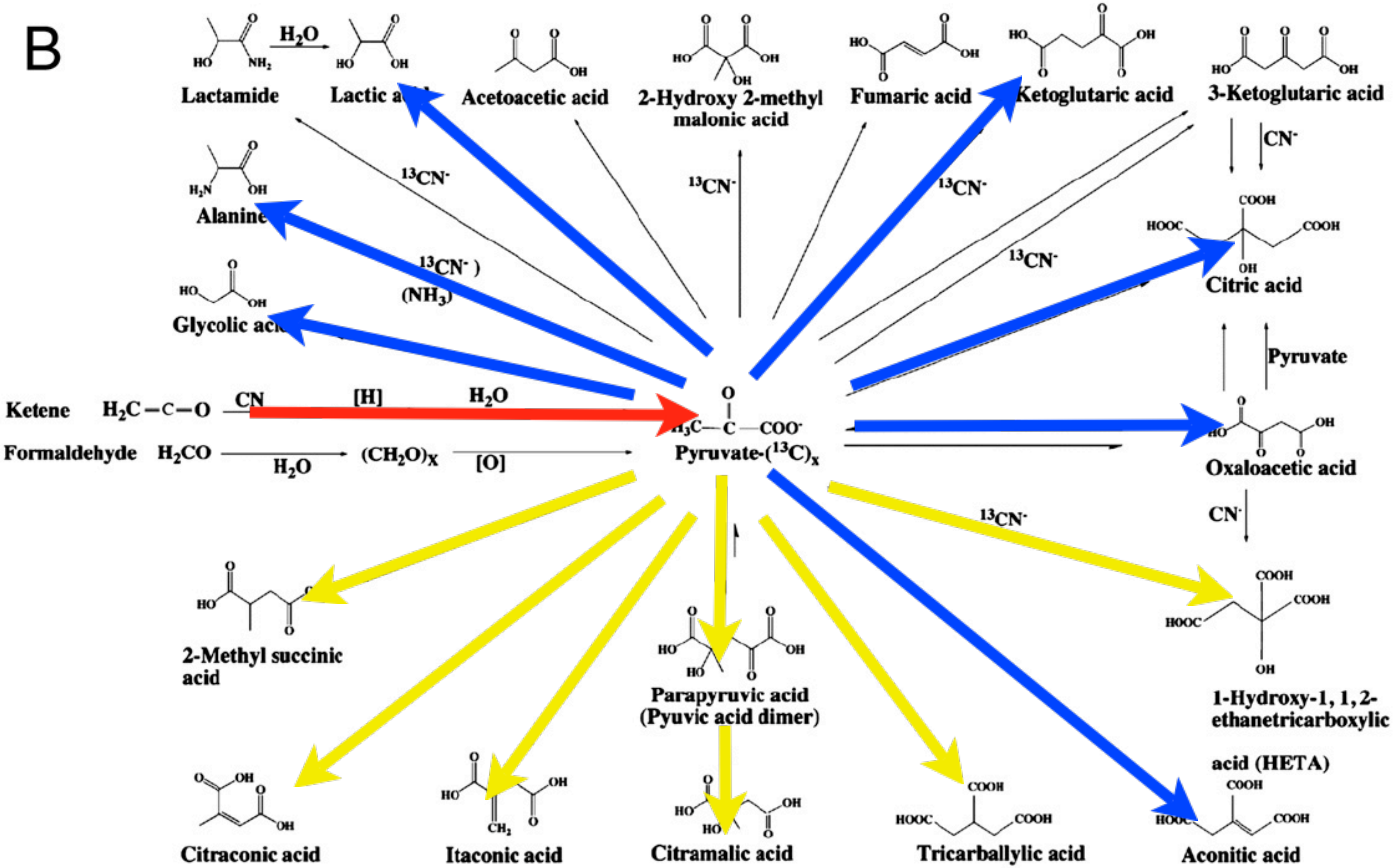



**Table 1. Counts of elemental compositions as a function of extraction solvents and calculation procedures**

| 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

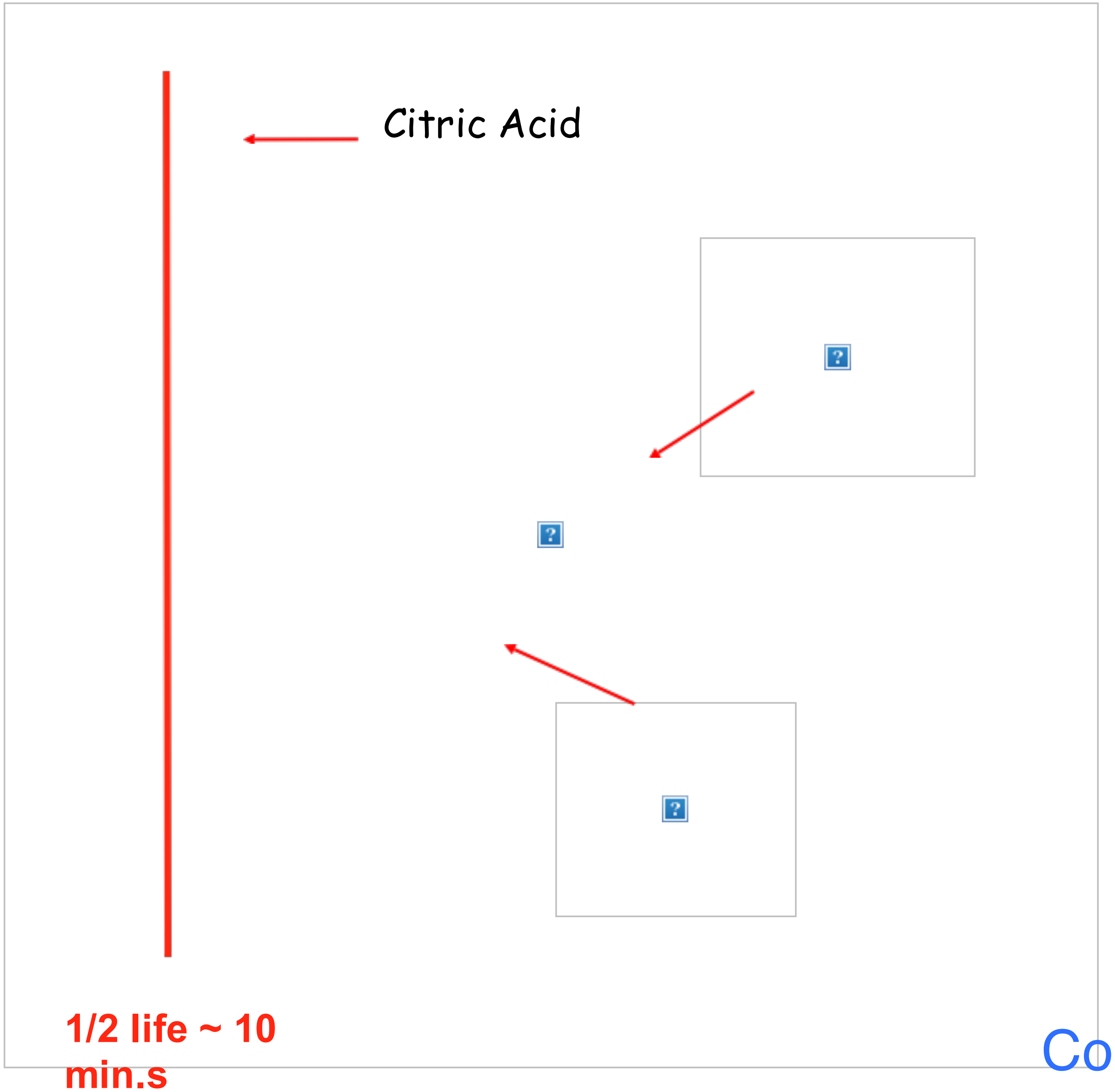
# Common metabolic intermediates present in Murchison...




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




1/2 life at 200 °C 10 minutes

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

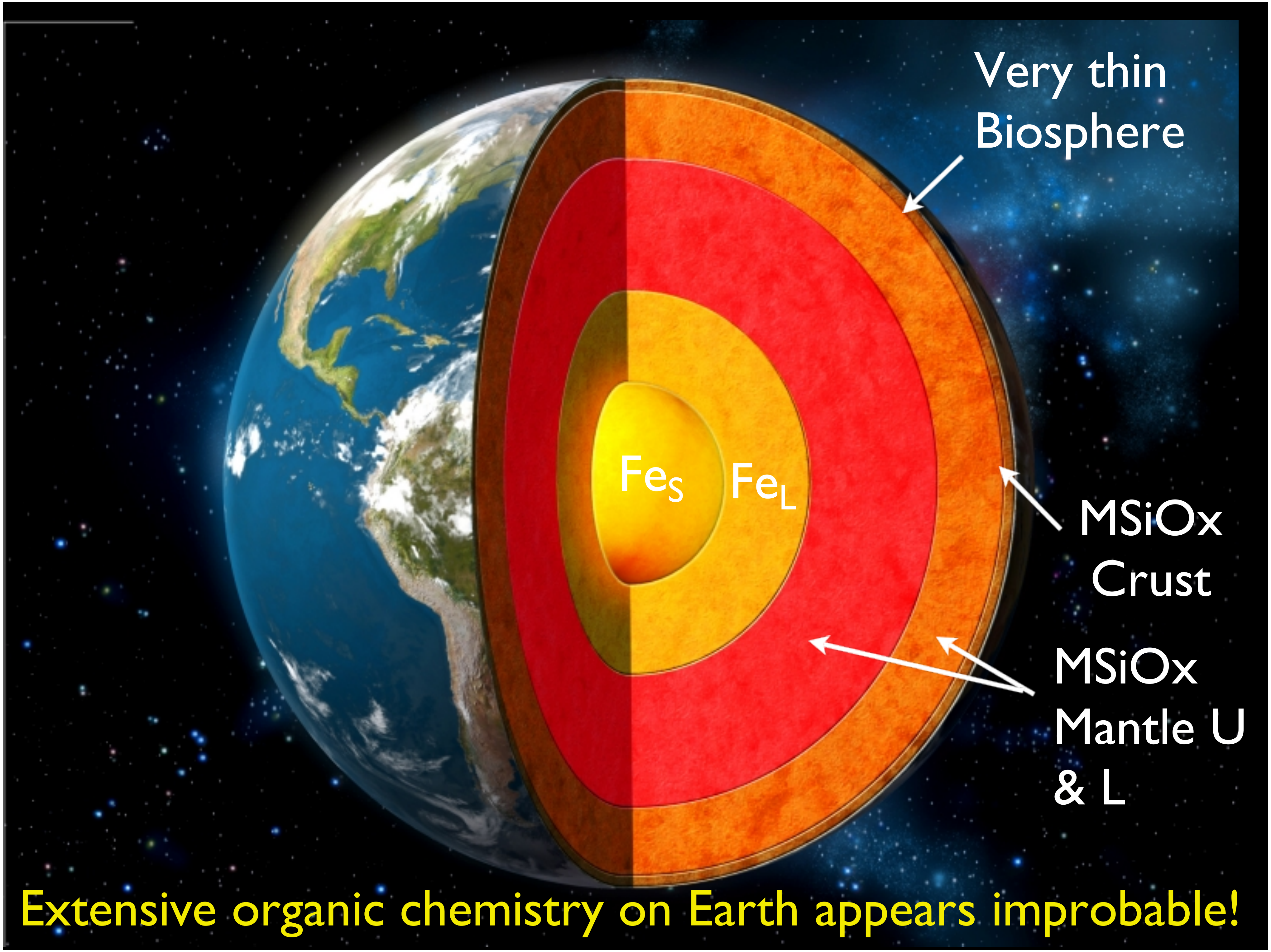
**Terrestrial planets**: Highly differentiated oxidized silicate crust and mantle-reduced core, not intuitively conducive to abiotic organic synthesis

**Meteorites**

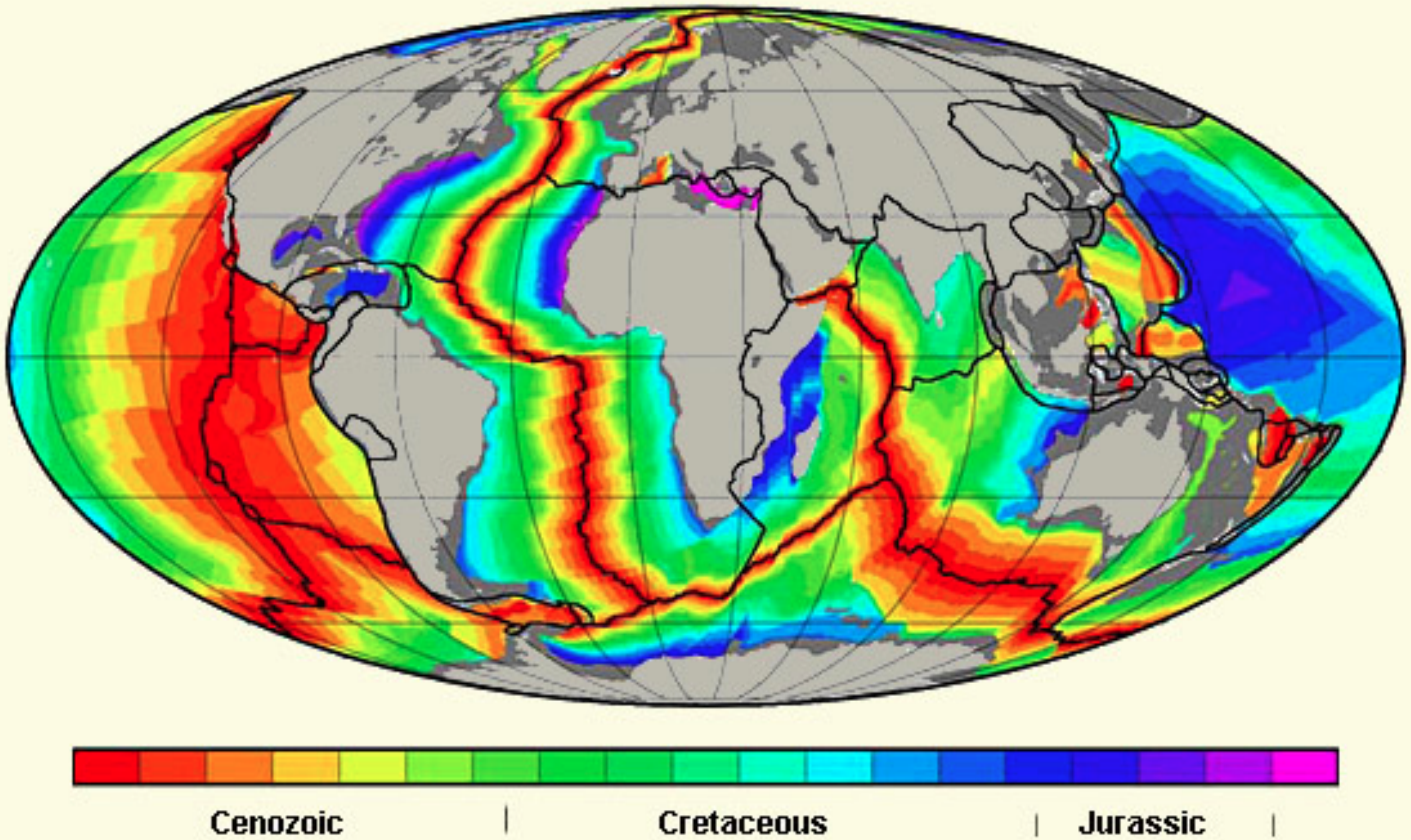
- Iron
- Stony-iron
- Stony
  - Achondrites
  - **Chondrites** = **Primitive, lots of reduced carbon, metals**

Differentiated

Undifferentiated

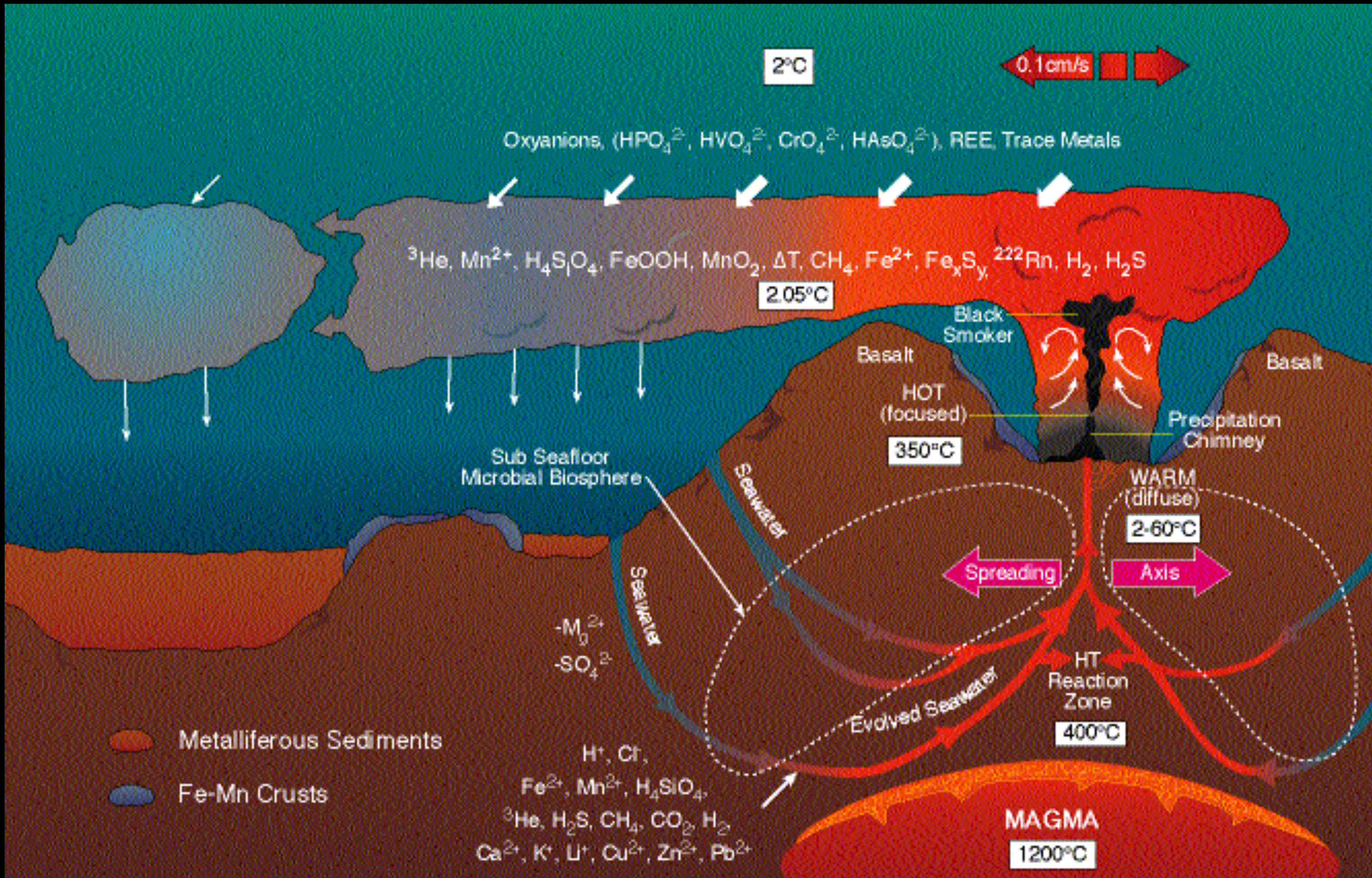

Very thin
Biosphere
$Fe_S$
$Fe_L$
MSiOx
Crust
MSiOx
Mantle U
& L
Extensive organic chemistry on Earth appears improbable!

# Plate tectonics saves the day?  Maybe... but why?




**Modern ocean floors colour-coded by geological age**

**Where new Sea floor is formed... one has a continous new environment that provides lots of free energy. A successful situtation for 4.5 Ga!**




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

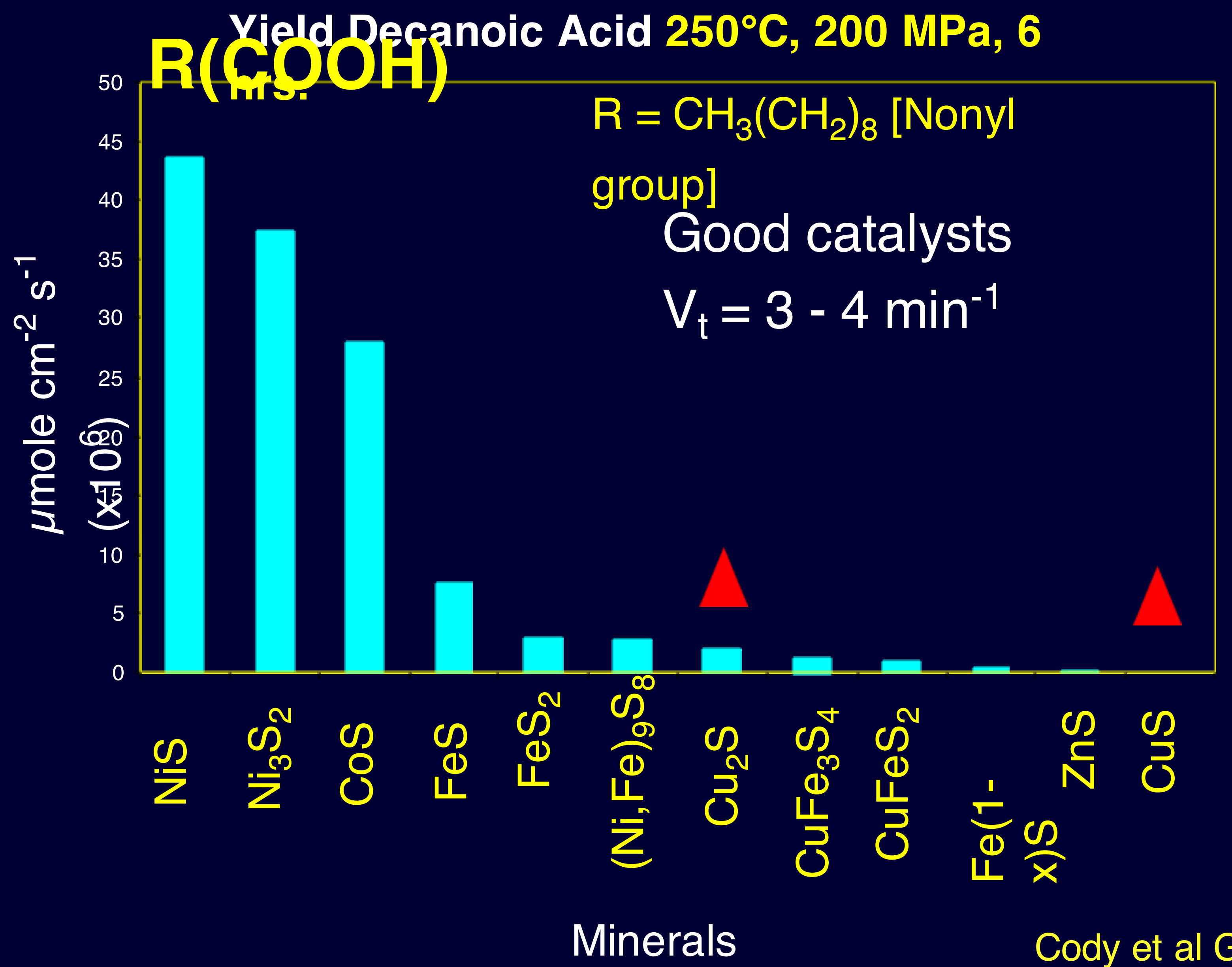



# Water-Rock interaction

leads to ore bodies which provide excellent catalysts

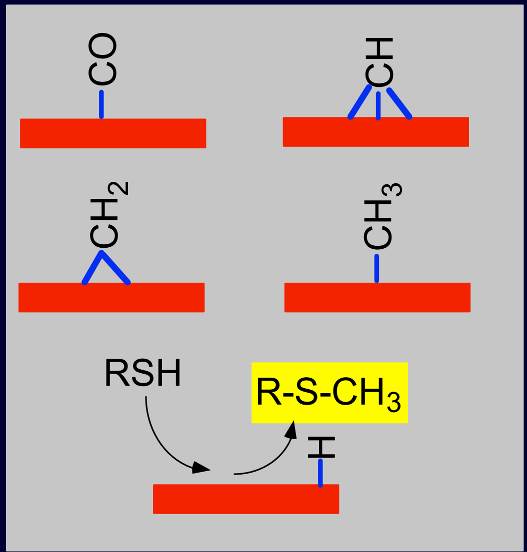
# Assaying transition metal sulfide minerals for C-fixation…

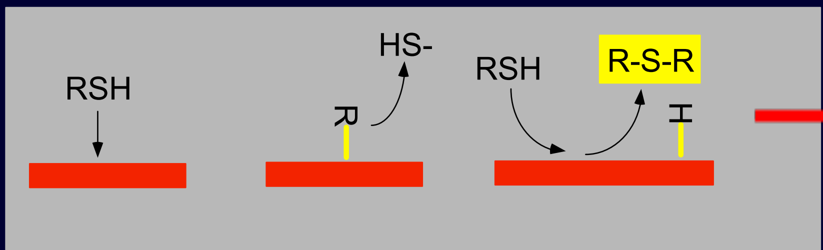
**$R\text{-}SH + CO + H_2O \rightarrow R(COOH)$**

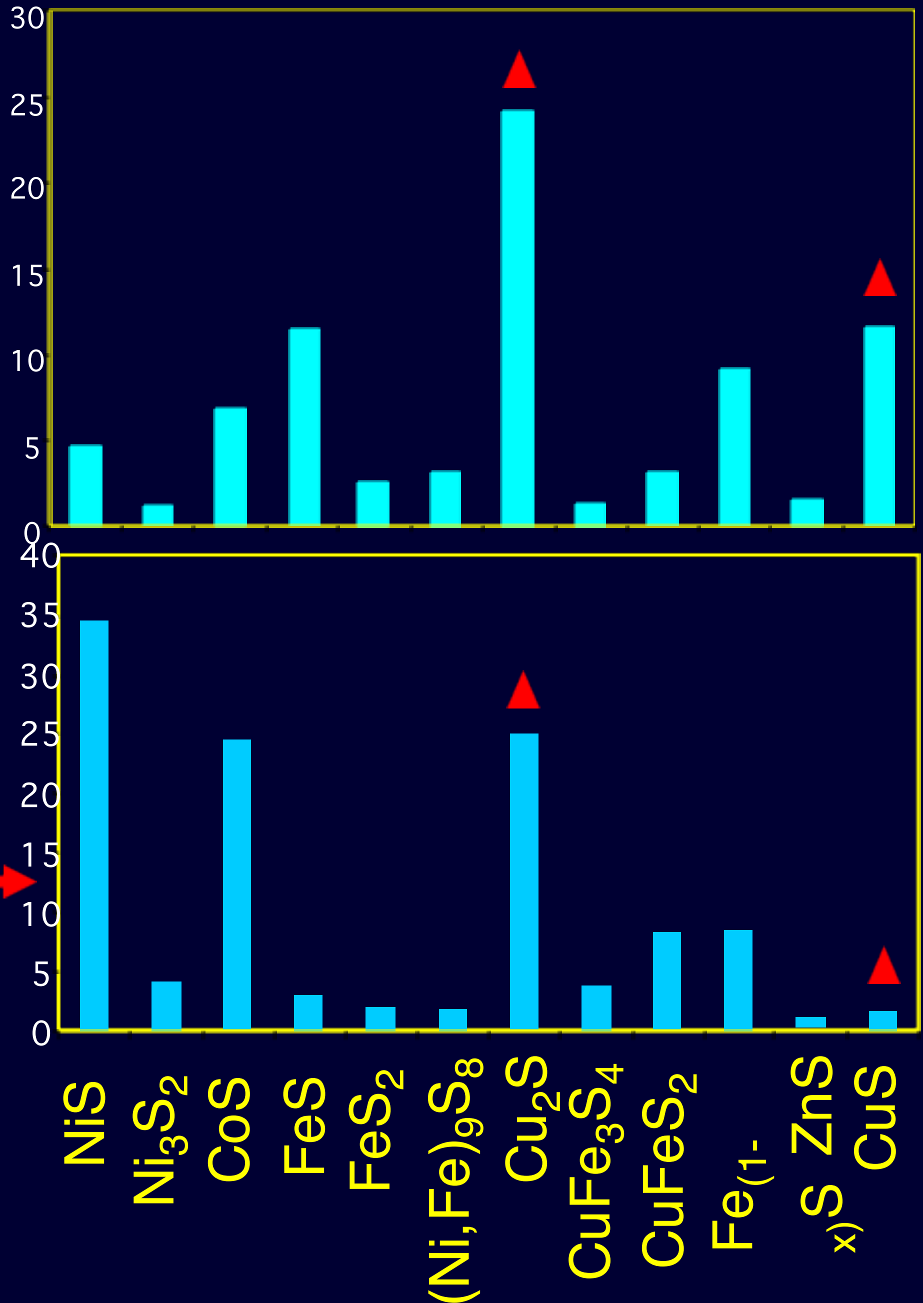



Cody et al GCA 2004

# Transition metal sulfides catalyze other reactions...

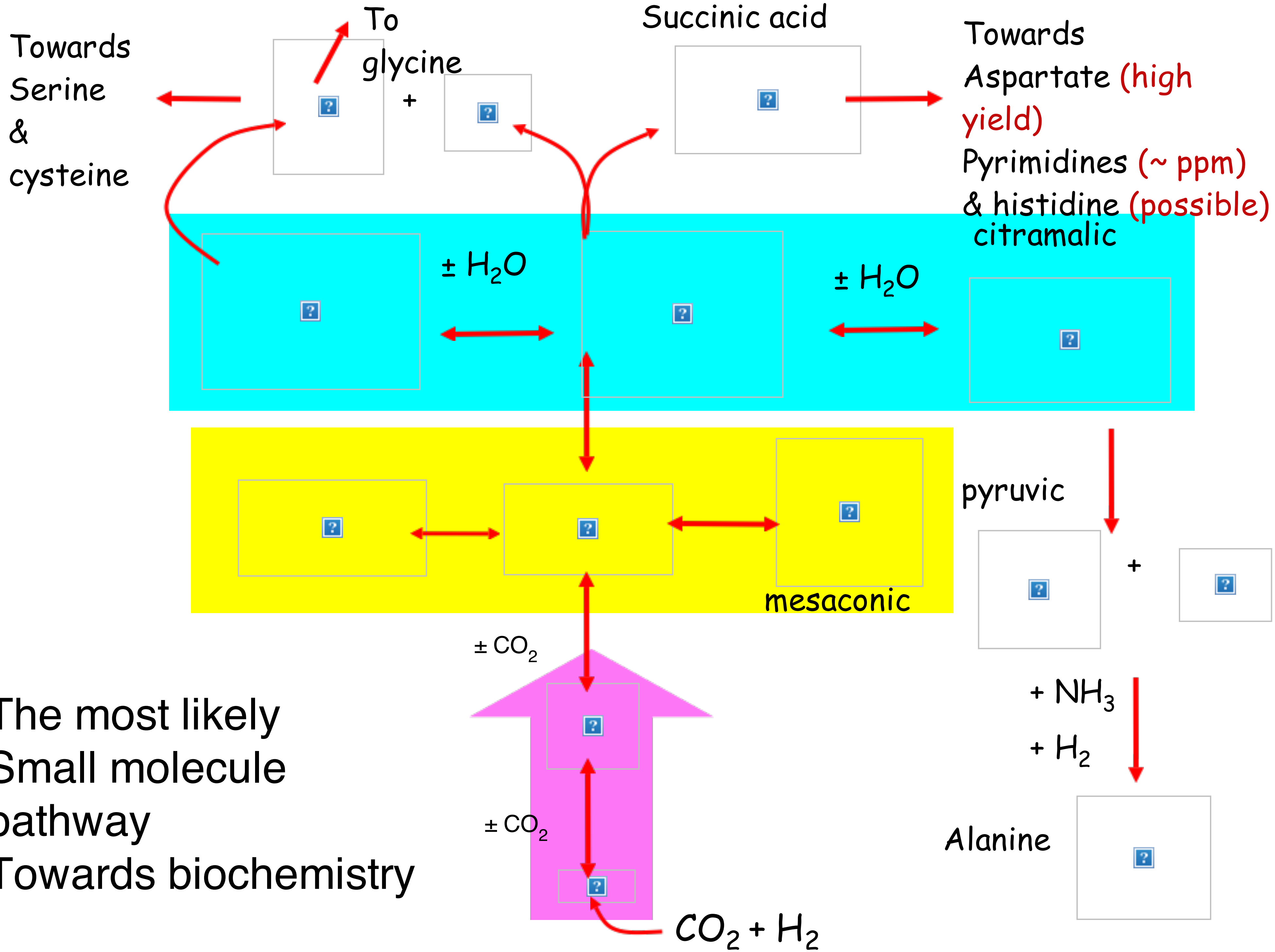



Note: that activity for carbonyl
Insertion different that activity
For CO reduction to $CH_3$

Cody et al GCA 2004




The most likely
Small molecule
pathway
Towards biochemistry

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

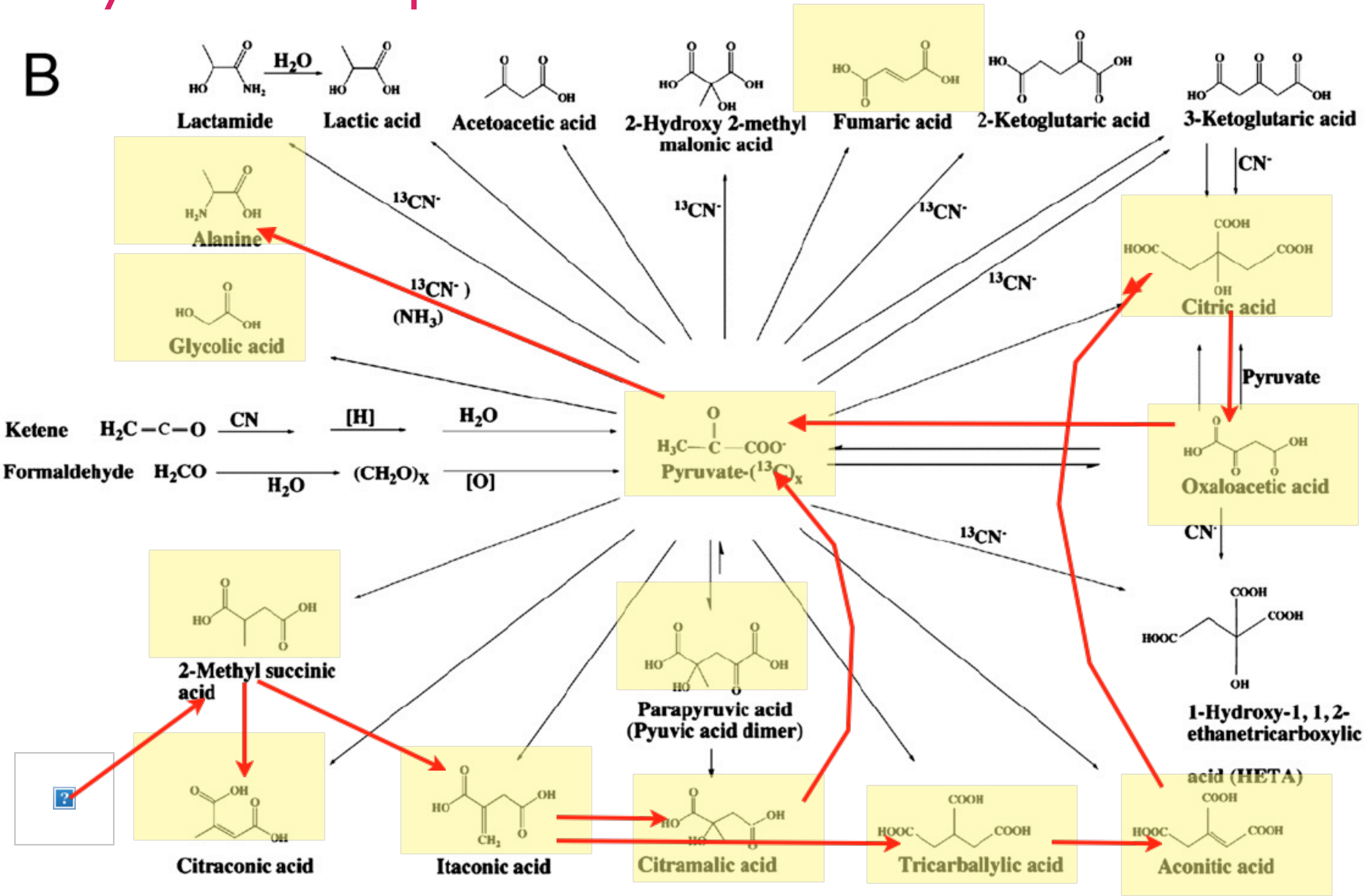
A lot can form from a little...

For example: If you start with *butanoic acid* and *isobutanoic acid* and allow for following reactions...

carbonyl insertion
partial oxidation
Retro-Aldol cleavage
Aldol condensation
Amination and reductive amination

One easily generates in excess of 350 molecules including saturated and olefinic polycarboxylic acids, amino-acids, keto acids, alcohol acids

# Many of the Cooper et al molecules observed 2011




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

## 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...

similar environmental parameters...

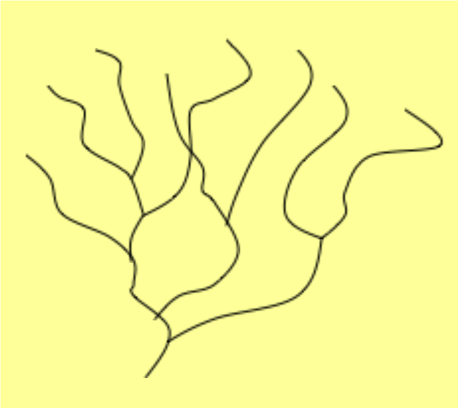
So why did life emerge on Earth and “apparently” not on chondritic parent bodies?

Easy answer: Don’t know

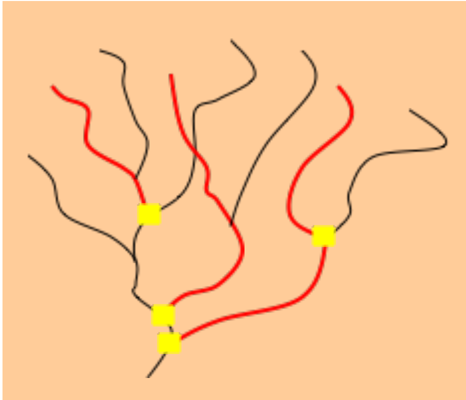
Reality there are some differences...

Tectonics created a novel environment....

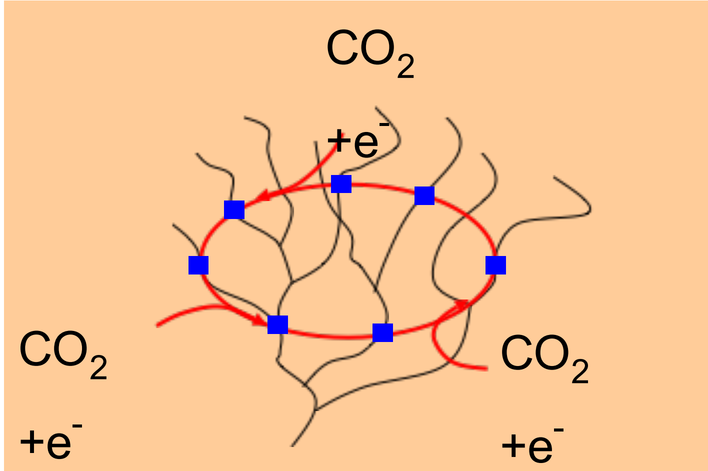
And a ***recursive*** environment (consistent for 4.5 Ga)



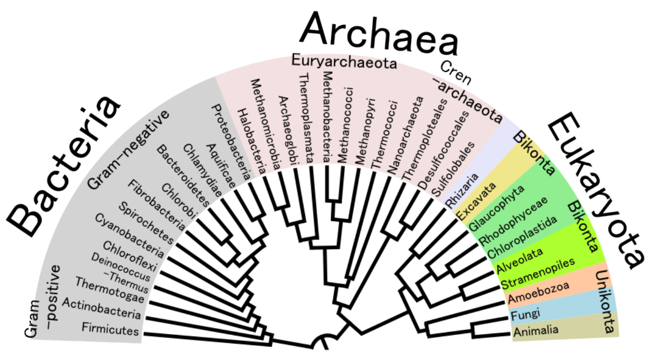
$CO_2$, $H_2$, $NH_4^+$, Simple Abiotic Chemistry



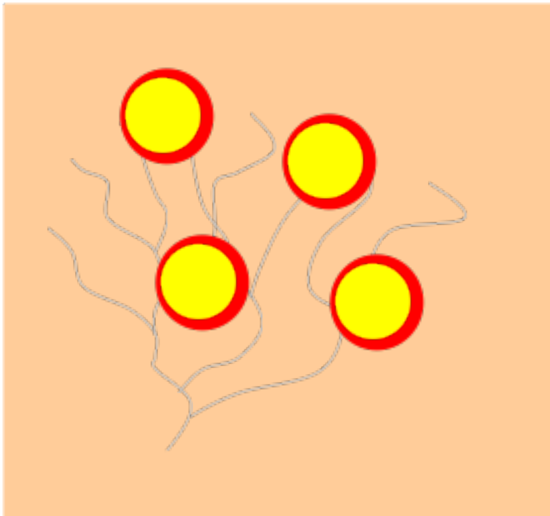
Enhanced Abiotic Chemistry-



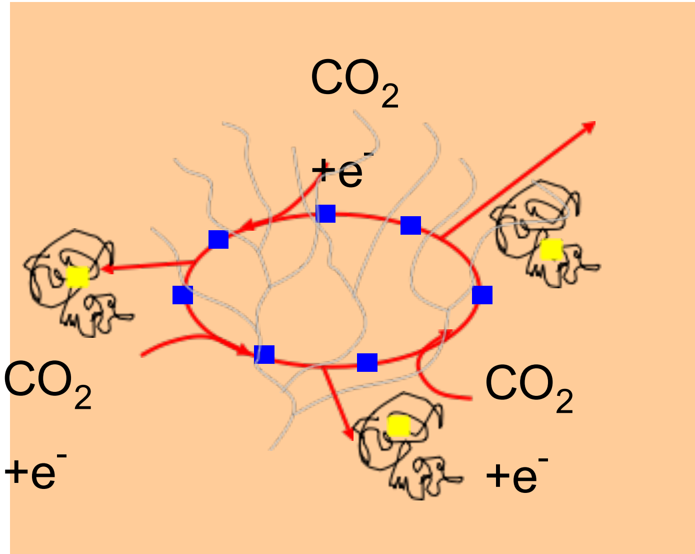

Systems Chemistry: auto-catalysis




Phylogenetics begins



Innovation of DNA, cellularlization emergence of individuality-mixotrophy




Embedded RNA/peptide catalysis: a complex “eco-system” but not an individual

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 Darwinian Landscape... maybe

Plate Tectonics Key... a question of volatiles?

This Research was funded by NASA's Astrobiology Program.

Special thanks to:

Dr. Shohei Ohara
Dr. Yoko Kebukawa
Dr. Hikaru Yabuta
Dr. Chris Glein
Dr. Dionysis Foustoukos
Dr. Bjorn Mysen