A search for prebiotic signatures with the Mars 2020 rover

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+Tanja Bosak, Woody Fischer, John Grotzinger, Joel Hurowitz, Dimitar Sasselov, Roger Summons, John Sutherland, Jack Szostak, & the *Simons Collaboration on the Origins of Life*

= Group of organic chemists + biochemists + chemists + geoscientists + astronomers

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Overview

- **Motivation**
  - Even if Mars didn't evolve life (no black shales yet!) it can provide insight into prebiotic chemistry: Consider for 2020 & sample return
  - Can we find traces of prebiotic feedstocks or biomolecules from prebiotic chemistry? This seems like an under-studied issue.

Part 1) Environments for the origin of life

- Little time here to weigh pros & cons of all proposed environments
- We focus on an environment (lacustrine) that has the strongest experimental support of biomolecules made with specificity & yield

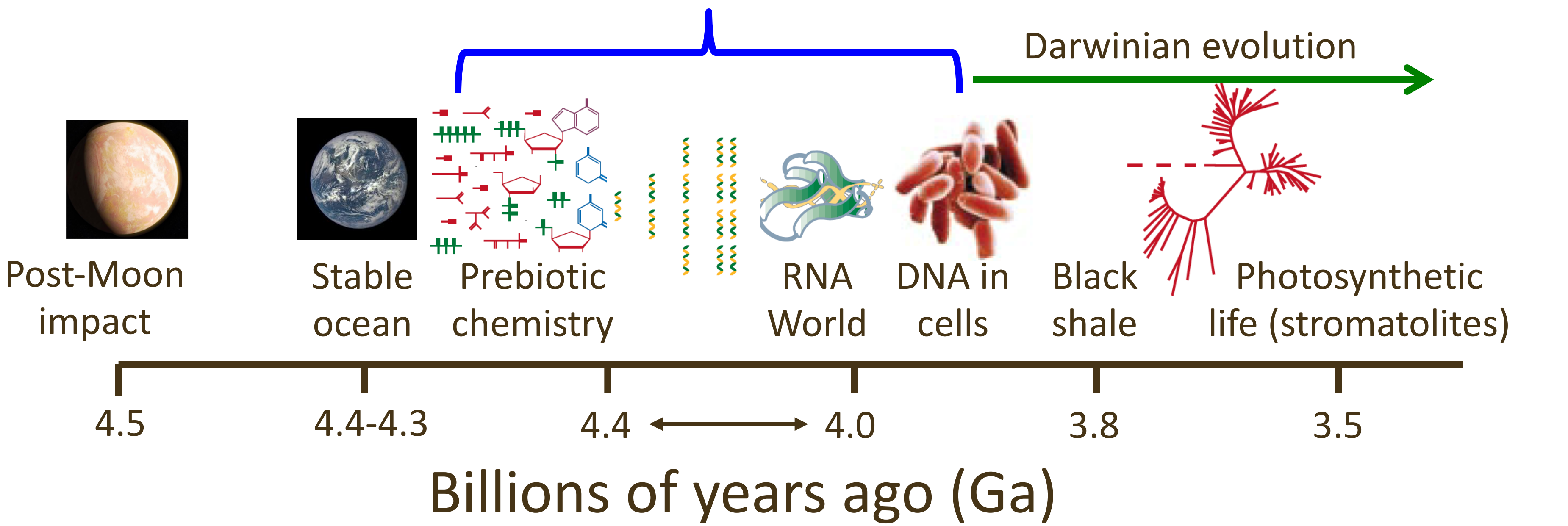
Part 2) What to look for? Will discuss traces of ingredients and products of prebiotic chemistry.

Part 3) Where to look? Lithologies of best preservation

Part 1: Environments for Origin of Life

The prebiotic is hidden on Hadean Earth from lack of rocks

Do prebiotic traces exist on Noachian (4.1 to ~3.7 Ga) Mars?



+ arguments that an origin of life anywhere would have similar organic molecules: e.g., Pace (2001) The universal nature of biochemistry. *P. Natl. Acad. Sci.*

Updated from Joyce (2002, *Nature*)

Many proposed environments for life's origin

Deep-sea vents? Surface vents/hot springs? Sea ice?

Lost City, mid-Atlantic carbonate chimney

Yellowstone

Evaporative lakes?

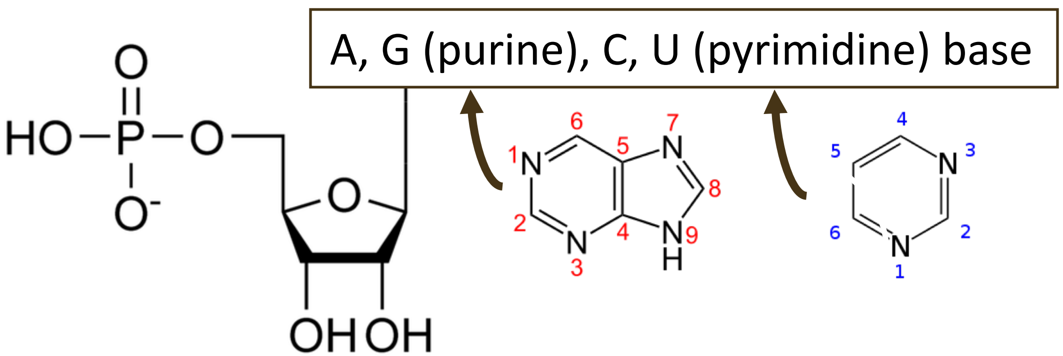
What does the most successful lab prebiotic chemistry imply about the geochemical environment?

Prebiotic chemistry to geochemical scenario

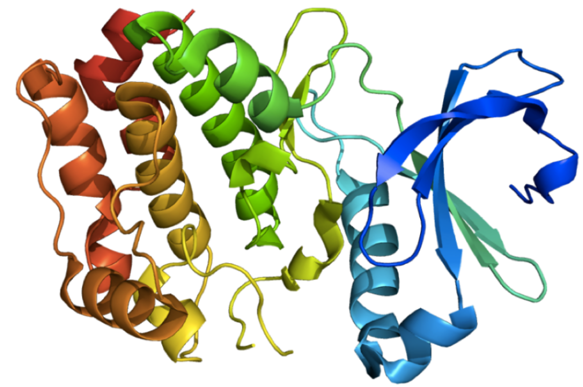
The problem: How (geo)chemistry transitioned into biology

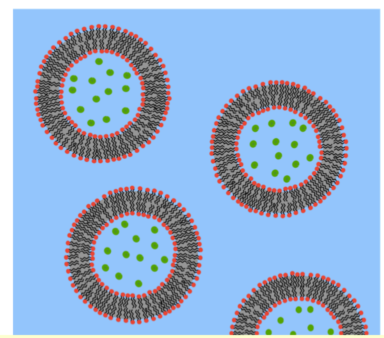
Work backwards: How necessary prebiotic chemistry informs geochemistry

ribonucleotide



proteins
(amino acids)





lipids

Systems Chemistry approach (pioneered by John Sutherland, Univ. of Cambridge)

1) Examine subsystem synthesis separately
2) Merge common chemistry
3) Thus make all pieces in one go (ribonucleotides, amino acids, lipids)
4) Infer a geological scenario that accommodates this chemistry

Demonstrated in lab: Simple "feedstock" molecules to biomolecules

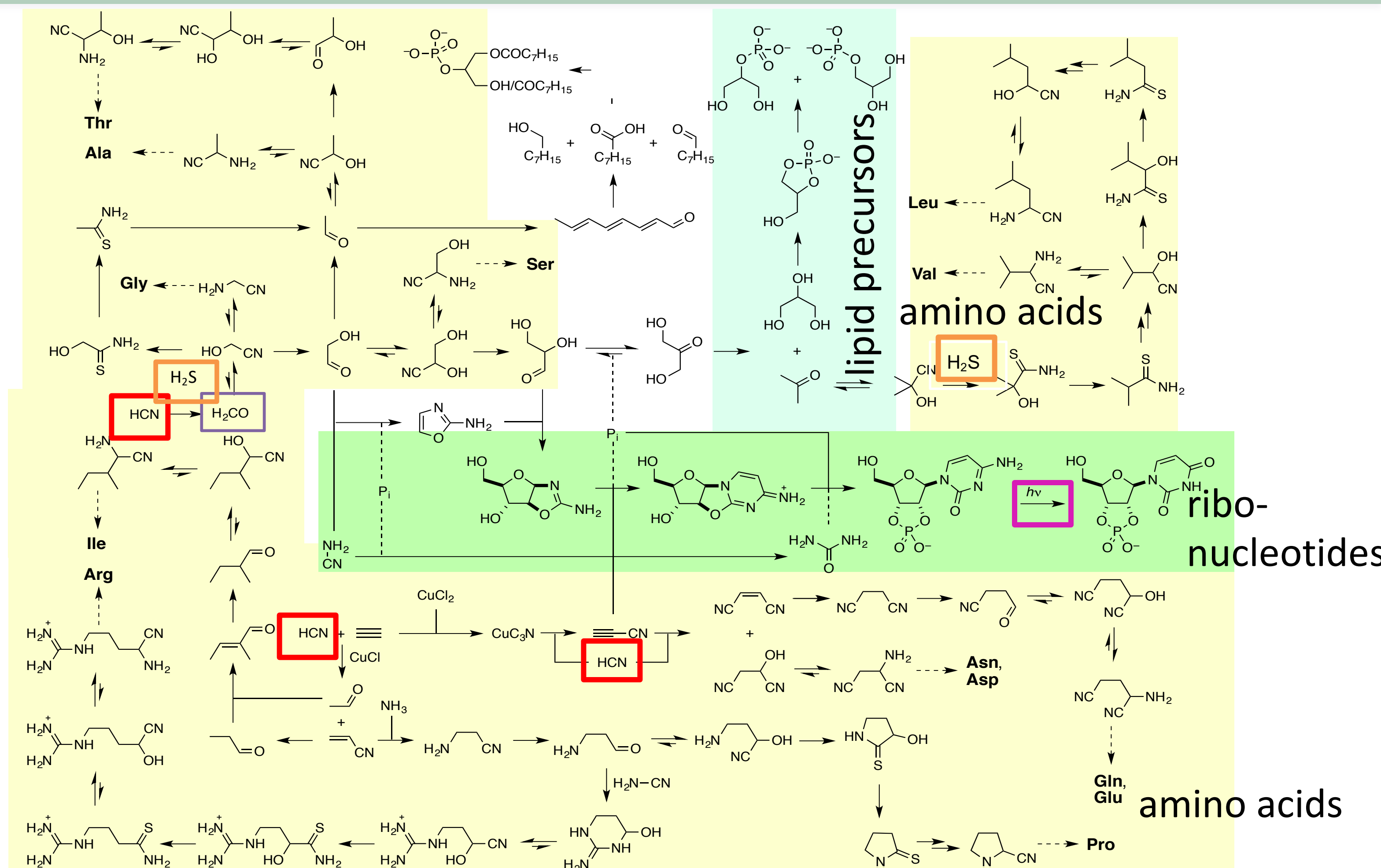
Last decade: A series of papers shows that ribonucleotides, lipid precursors, and amino acids form from simple, common ingredients in cyanosulfidic photoredox chemistry:

HCN | reductant H_2S, | phosphate groups (PO_4^{3-}), | UV (200-300 nm)

CN^- nucleophile: donates e^- pair to make C-C chains into big molecules with N

H_2CO → **sugars**

e^- release, photoexcitation drives reactions



Powner+ (2009) *Nature*

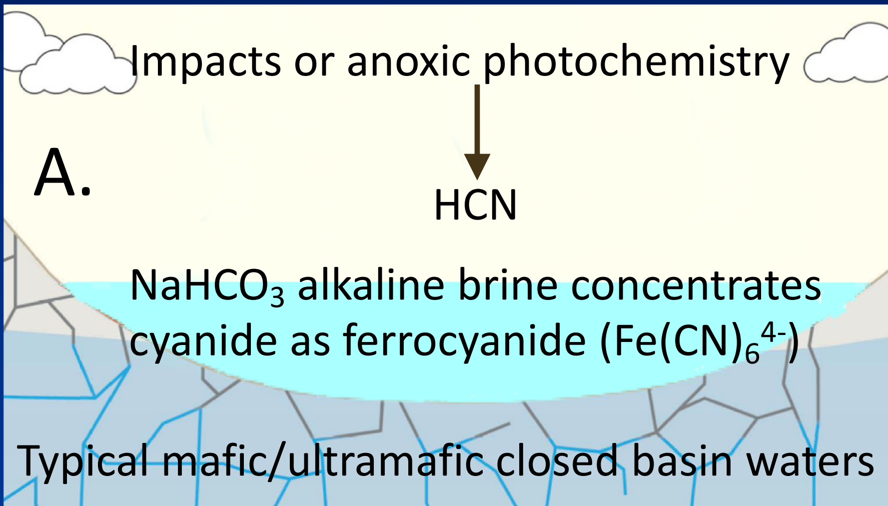
Patel+ (2015) *Nature Chem.*

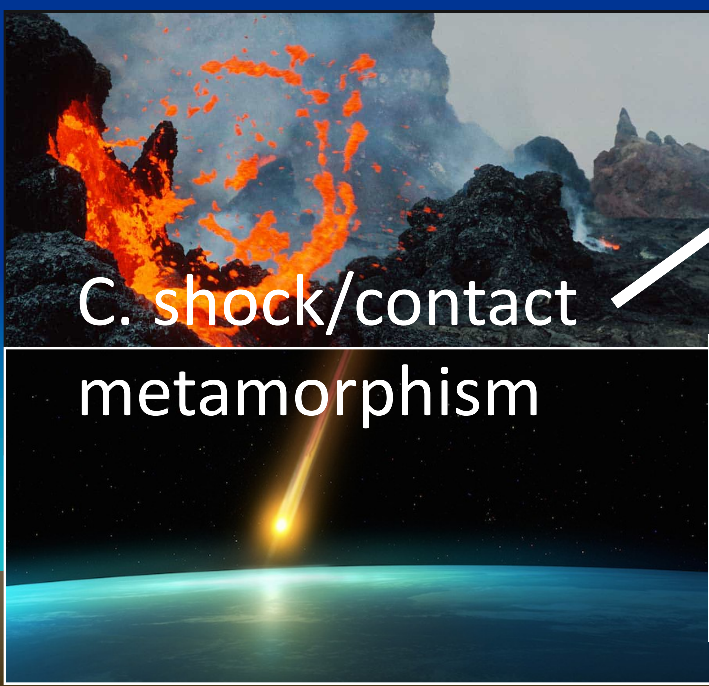
Ritson+ (2018) *Nature Comm.*

Implied geochemistry

A key need: concentrated cyanide

Toner & Catling (2018), in review





NaCN
CaO, MgO, FeO
NaCl, KCl, Na_2CO_3, FeC_3, C

+ water →

Aqueous: Na^+, CN^-, Cl^-, carbonate (high pH)

Solids: $Ca(OH)_2$, $Mg(OH)_2$, $Fe(OH)_2$ FeC_3, C

Pyrite + cyanide → HS^- + ferrocyanide

Fe-phosphate + cyanide → PO_4^{3-} + ferrocyanide

Part 2: What to look for: (a) minerals

1) Generally: Sedimentary minerals in evaporite environments that concentrate prebiotic precursors.
   - Are they in your spectral library?

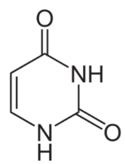
2) Specific minerals:
- Ferrocyanide ($Fe(CN)_6^{4-}$) salts (Na-, Cu-, Fe-)
- Associated with Fe/Ca/Mg carbonates, halite, sulfates
- Associated impact shock products: Iron carbide, elemental carbon

3) Signs of anoxic environments:
- Elemental sulfur (S_8) could indicate a reducing atmosphere
- Anoxia: Detrital sulfide, authigenic Fe^{2+}-clays, siderite, magnetite

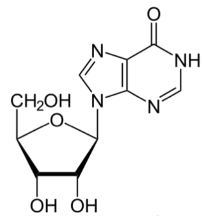
4) Aside: Has cyanide already been detected on Mars?
   Eigenbrode+ (2018) MSL data has mass = 27 (HCN)

Part 2: What to look for: (b) organics

The 2020 payload limits *in situ* analysis, but what if samples for return had signs of 3 prebiotic subsystems: Nucleic acids, peptides & lipids? It could revolutionize our understanding of origin of life. E.g.:

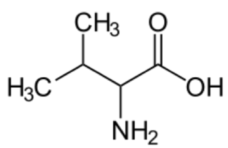


Uracil base



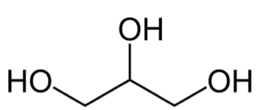
inosine nucleoside

RNA precursors (steps to RNA World)



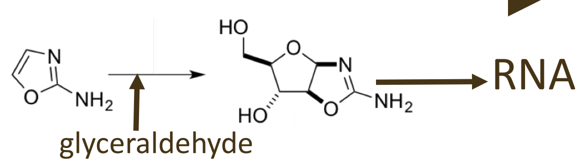
hydrolytically stable **amino acids**, e.g. valine

peptide & protein precursors

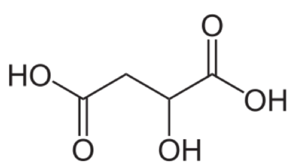


Glycerol (C_3)

e.g.,



Indicative of C_3 glyceraldehyde precursor of amino acids, lipids, and ribonucleotides



malic acid

C_4 acid related to amino acid aspartate & used in the (reverse) citric acid cycle

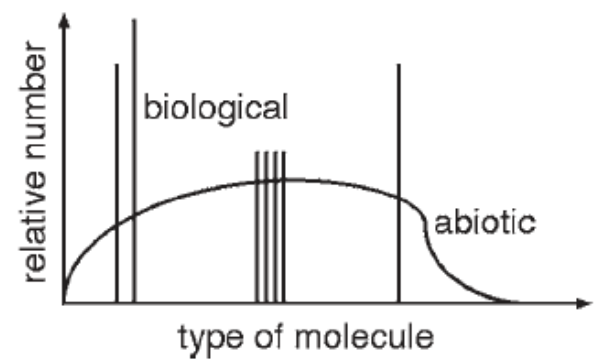
Part 2: What to look for: (b) organics

Organic-preserving (returned) samples may allow us to distinguish:

1. meteorite organics: kerogen pyrolysis dominated by 1-3-ring aromatics with less aliphatic substitution than 4-5 rings in biology; amino acids ^{13}C- ^{15}N-rich vs. depleted in biology (Engel & Macko, '90,'97)

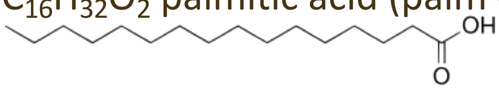
2. cyanosulfidic prebiotic: limited assemblage of small organics (Patel+ 2015)

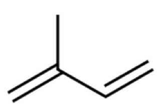
3. Fischer-Tropsch-type (FTT): isomeric mixtures vs. favored isomers of molecular series in biology (Mißbach+ 2018). Exponential drop off with C_{number} modified by loss of C_{low} volatiles.



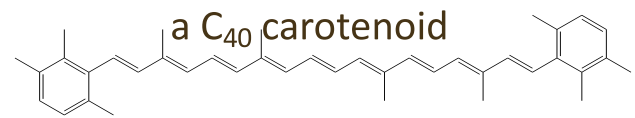
4. biology is selective with a Lego principle of tail-head repeat units: lipids of
1) acetyl (C_2) polymers

$C_{16}H_{32}O_2$ palmitic acid (palm oil)



2) isoprene (C_5H_8)  polymers.

a C_{40} carotenoid



Part 3: Where to look?

Silica

Fine-grained, ideally opaline SiO_2 deposited under reducing, non-acidic conditions

- Adsorbs proteins, RNA (Biondi+ 2016), lipids, nucleotides
- Can adsorb intermediates of prebiotic chemistry
- Stabilizes C_5 sugars in the formose reaction (sugar formation from formaldehyde) (Lambert+ 2010)

Clays

Fine-grained sediments rich in clay minerals

- Smectites can protect organics from degradation (e.g., Ogawa and Kuroda, 1997)
- Can adsorb nucleobases, nucleotides (Ferris, 1989; Feuillie+ 2013; Pedreira-Segade+ 2016), proteins, amino acids (Aufdenkamp+ 2001), organoammonium (Ogawa & Kuroda, 1997)

Evaporites: Carbonates, halite, sulfates

Pros

- Carbonates & sulfates in marine environments and playas incorporate & protect organics (O'Reilly+ 2016; Cabestrero+ 2018)
- Carbonates can preserve microbial textures
- Ancient halite can preserve nucleic acids (Jaakkola+ 2016).
- Borate proposed prebiotic chemistry (Ricardo+ 2004; Kim & Benner, 2017).

Cons

- If minerals later dissolve, loss of organic matter is possible

Look for sedimentary. If hydrothermal, may have less or no prebiotic organics

Summary

- In the last decade, common feedstock prebiotic chemistry has generated ribonucleotides, lipid precursors & amino acids
  - CN^-, sulfide, and UV are key to this successful scheme
  - Could have happened on Mars. Even if life didn't evolve, we might learn much about life's origins from prebiotic chemical traces on Mars.

- Prebiotic chemistry implies the plausible geochemistry
  - Alkaline, $NaHCO_3$-rich evaporite lakes best concentrate CN^- as ferrocyanide "storage" that can be released later
  - Such lakes commonly form in (ultra)mafic closed basins
  - Arid, low-temperature (≤ 25ºC) places are favored

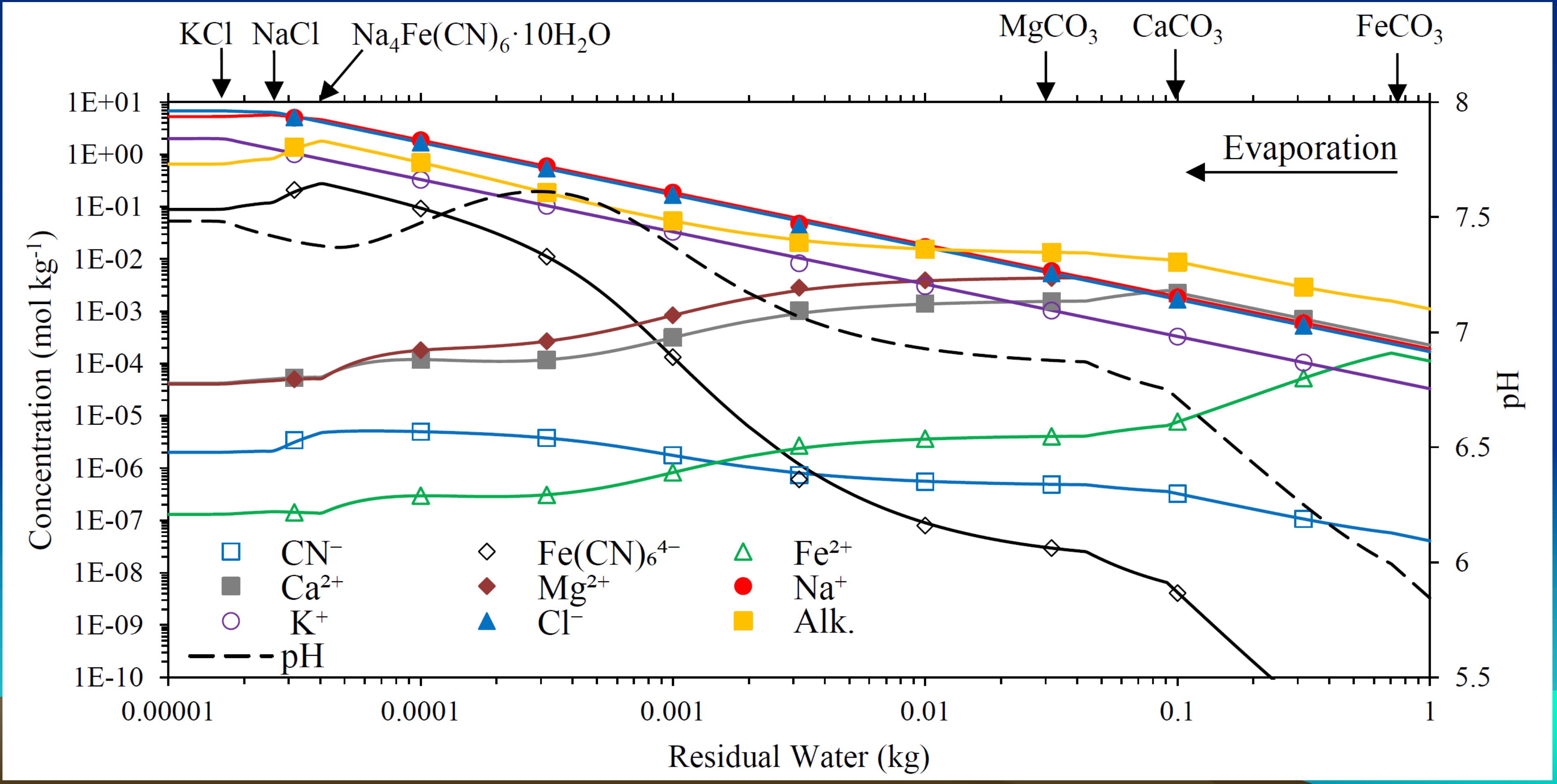
  } Mars

- What to look for:
  - Sedimentary minerals: Ferrocyanides in carbonate & Cl^- evaporites
  - Organics: Meteorite vs. cyanosulfidic vs. Fischer-Tropsch vs. biology
- Where to look:
  - Preserved in fine grained sedimentary silica or clays or evaporites

Back-up slides follow

Aqueous model results

- Concentration of cyanide by closed-basin lake water (Toner & Catling, in review)



C–C bond formation and C_1 feedstocks