Is life a cosmic imperative:

How would thermodynamics force life into existence?

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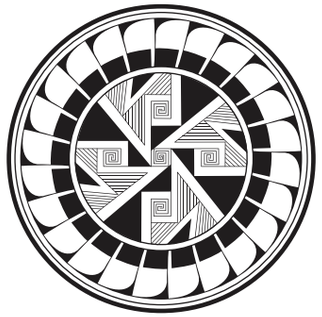

Searching for Life across Space and Time
Irvine, CA, 5-6 December 2016

Outline

- What does it mean for emergence of a biosphere to have been a “necessary” stage in planetary maturation?

- What detailed features of biochemistry and higher-level architecture can be invoked as having this interpretation?

- When does this move beyond being “essay” and become a theoretical claim? What conceptual systems do we have to support such questioning?

- Problems, opportunities, needed work, and cautions for exoplanet studies

The mathematical concept at issue: breakdown as a state of order in its own right

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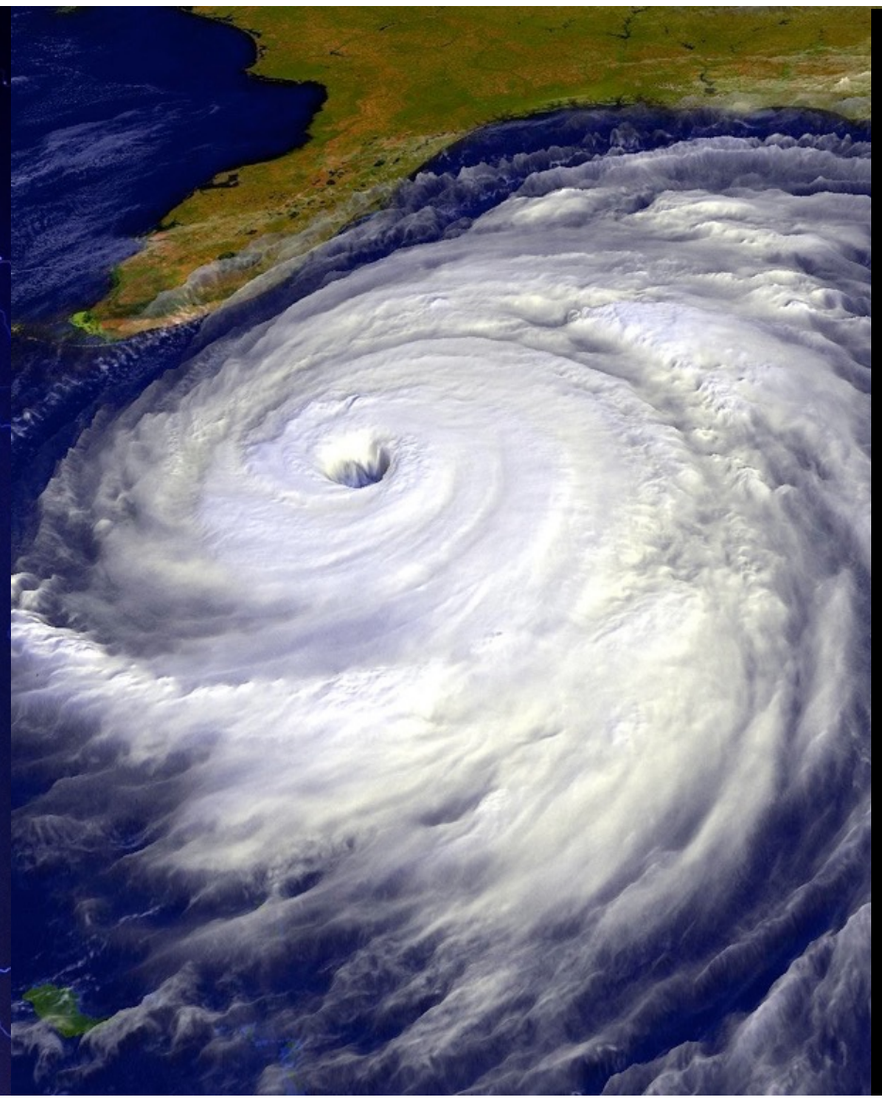
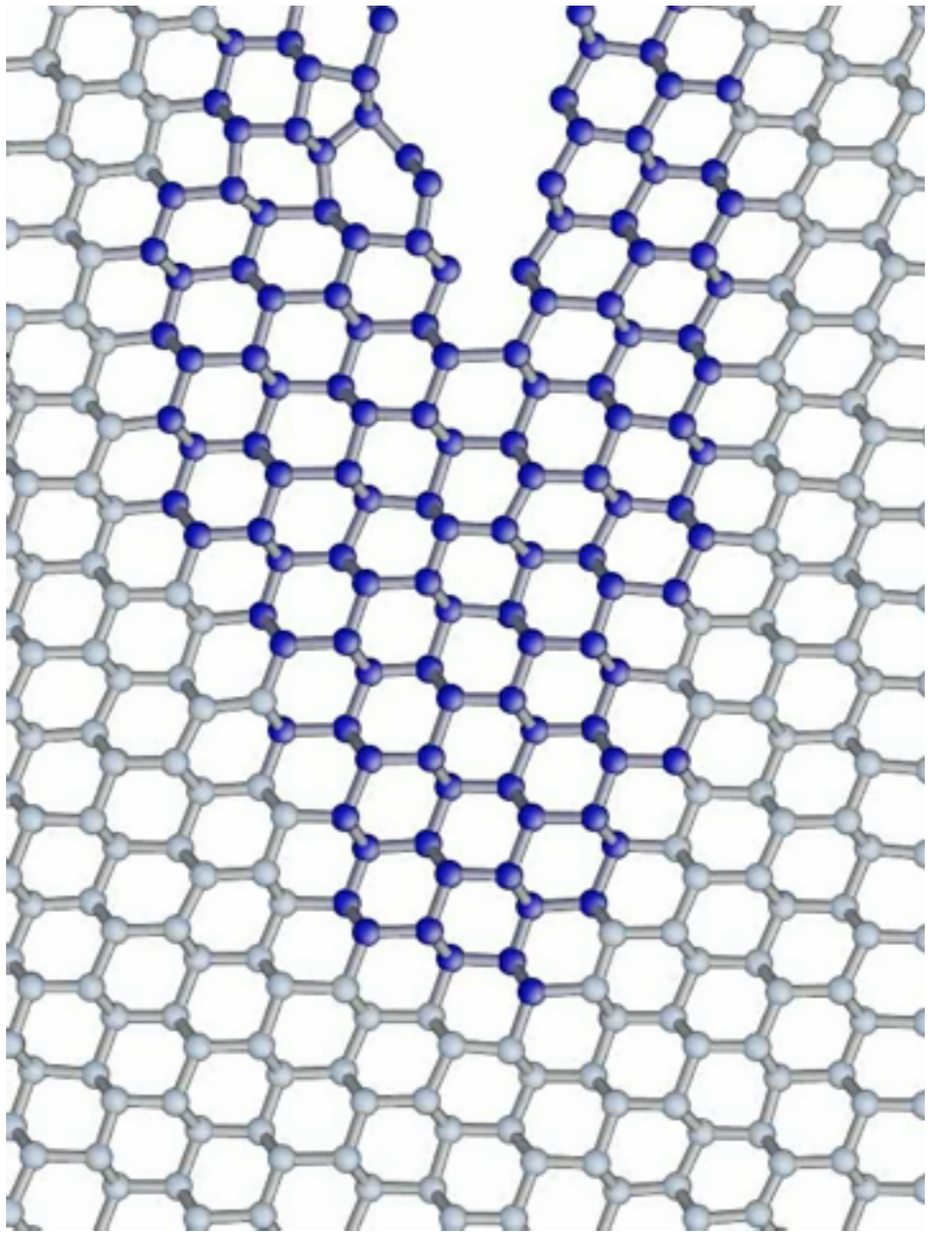
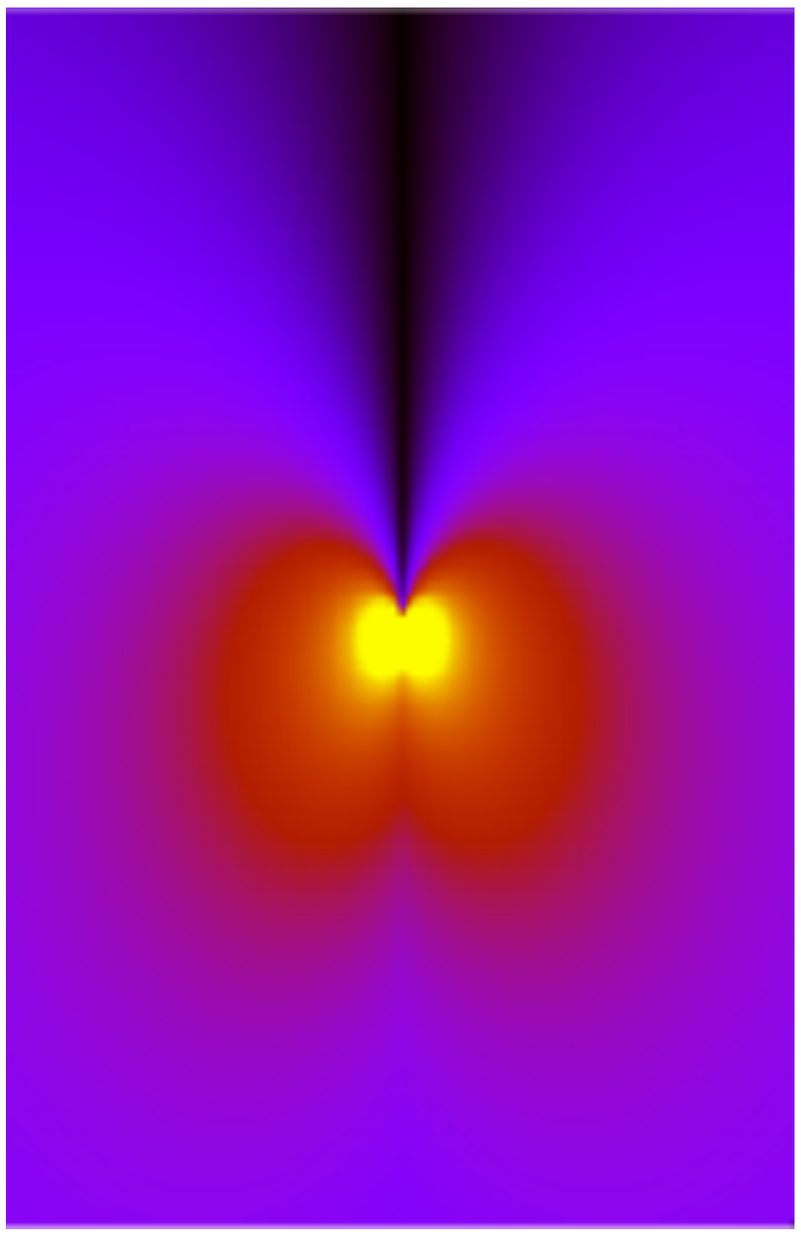
Breakdown processes are **robust states of dynamical order**



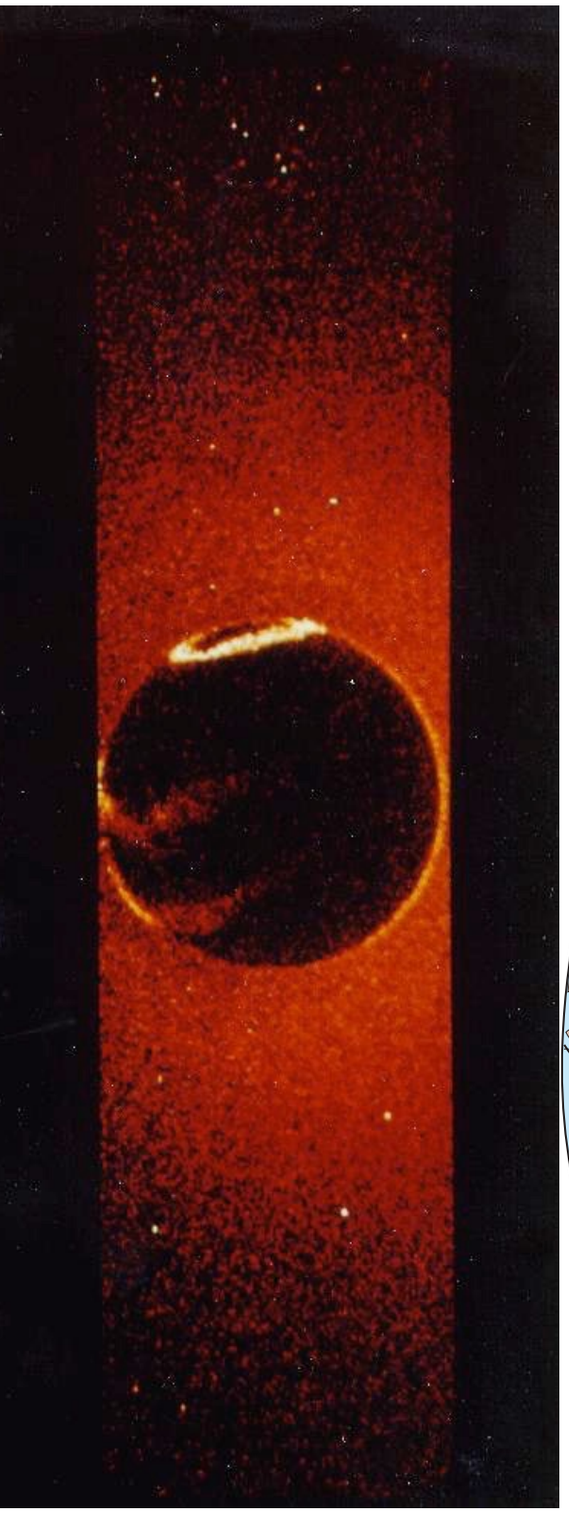
Q: Is the **emergence of a biosphere** a chemical version of this?

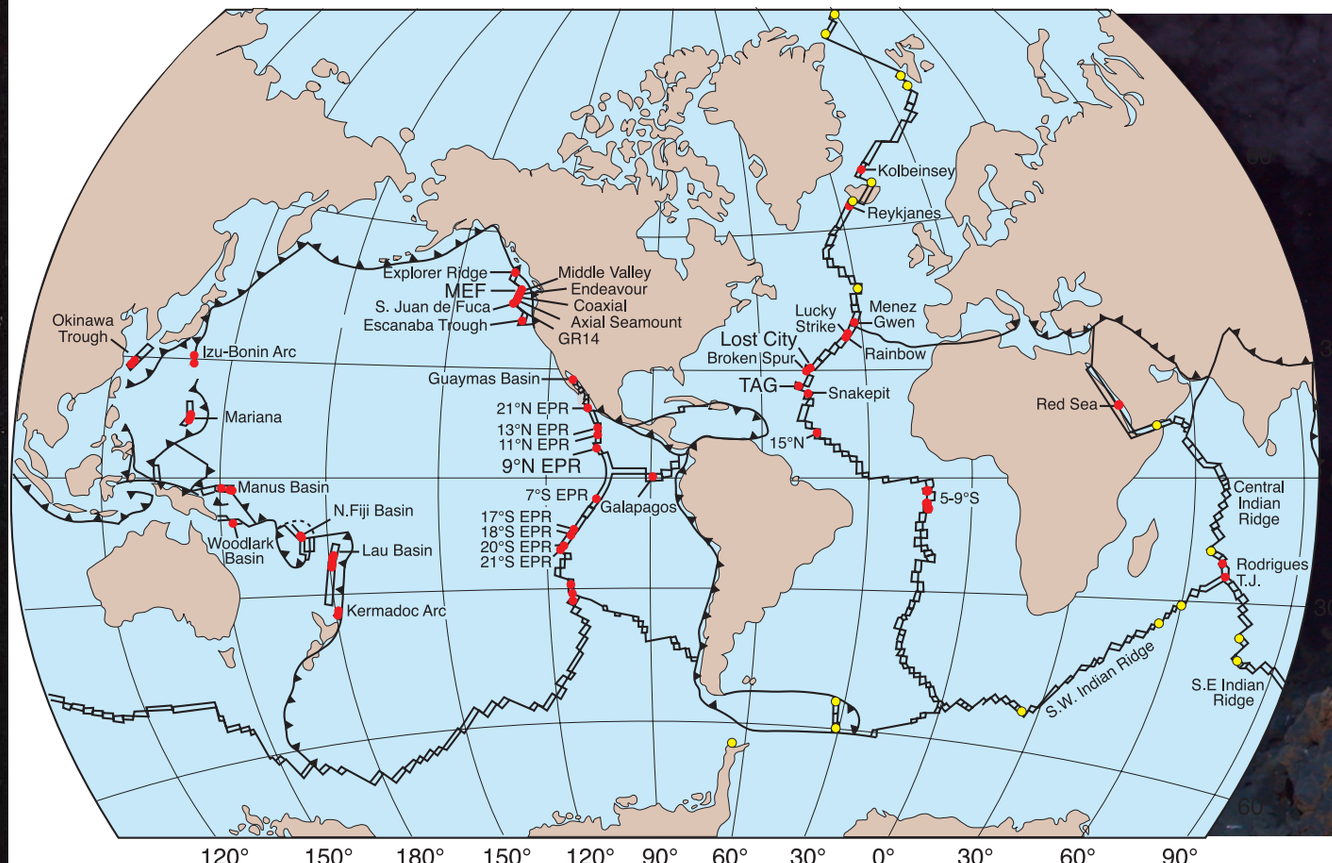
System characteristics that lead to breakdown states: self-amplifying positive feedbacks

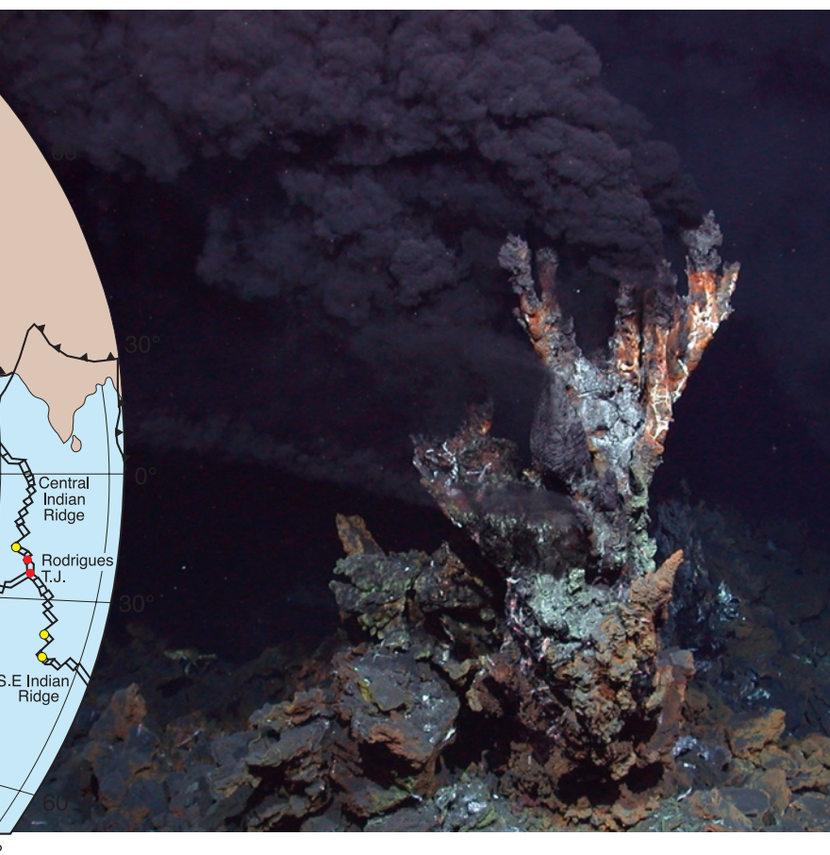




Earth's redox battery is the most obviously-coupled disequilibrium to autotrophy and core biochemistry





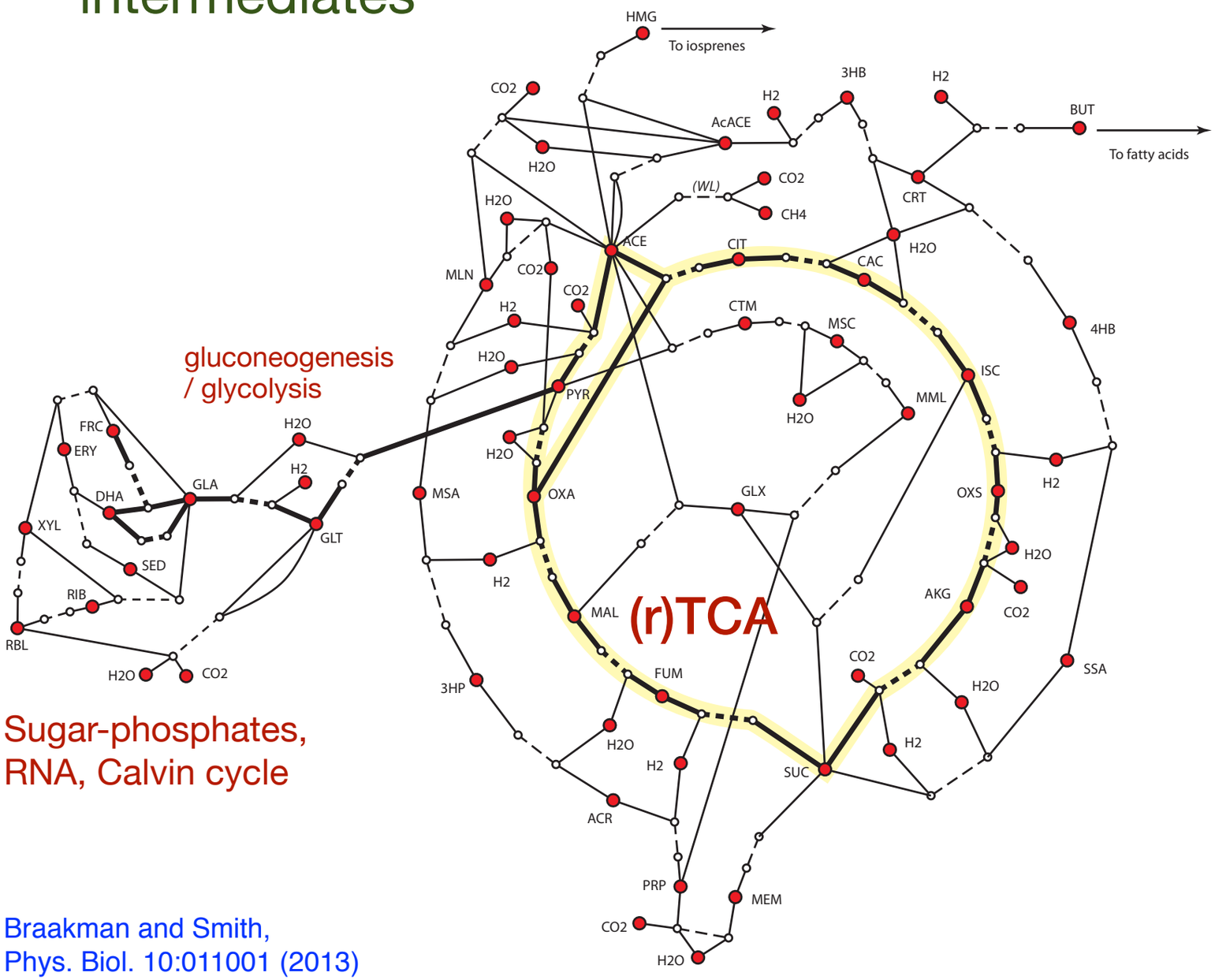


Where would this show up? Evidence for biochemistry as an outgrowth of geochemistry

- Continuity of **ancient and universal biochemistry** with selective organic geochemistry
    - Could happen by “lock-in” or as shared reflection of paths of least resistance
        - Infer phylogenetically from evolution’s “dogs that didn’t bark” -- Small-molecule chemistry unchanged even with modern enzymes
- **“Upward causation”**: metabolic patterns imprinted at higher levels where Central Dogma reasoning would argue it doesn’t belong

Universality and recapitulation in autotrophic Carbon Fixation and core anabolic pathways

A universal biosynthetic core exists, Organized around TCA intermediates

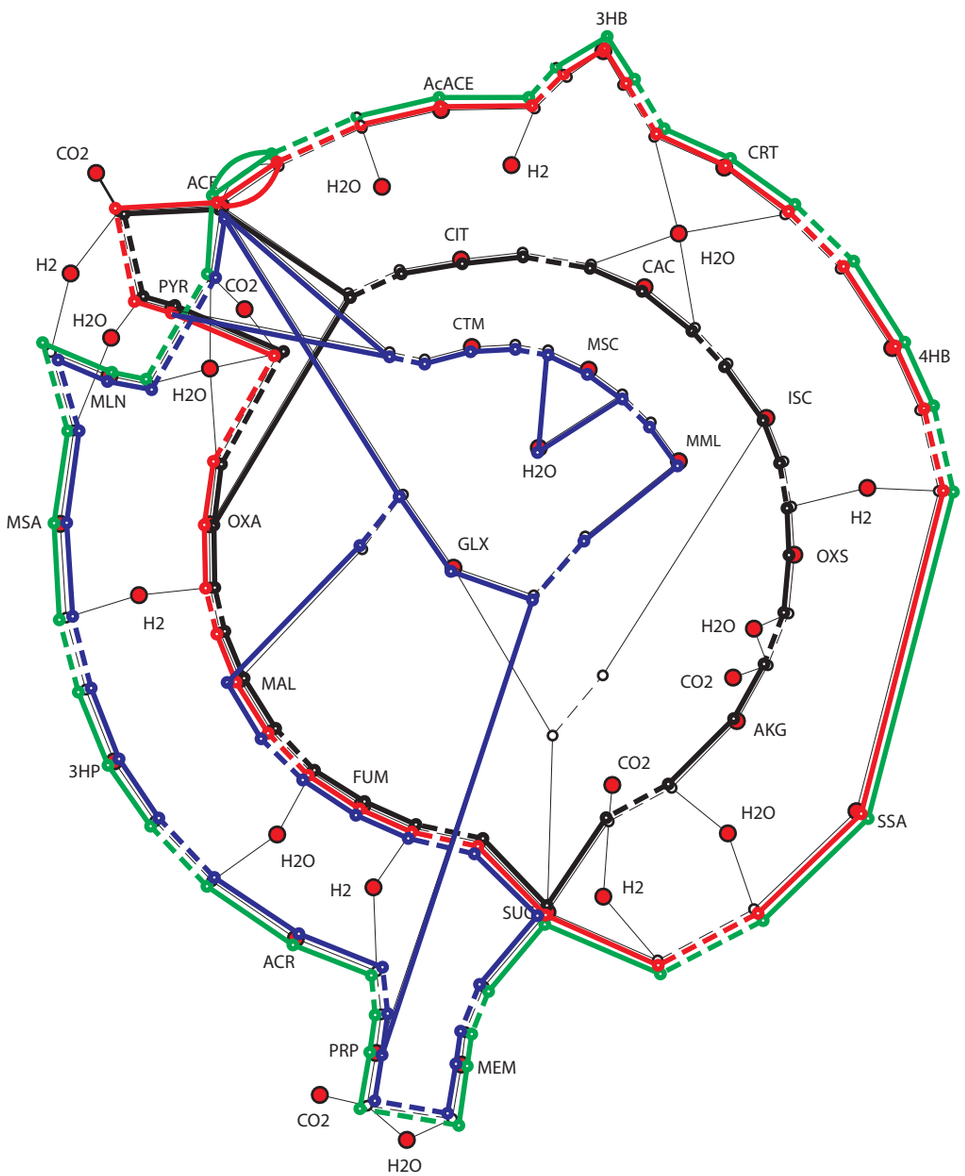


gluconeogenesis / glycolysis

Sugar-phosphates, RNA, Calvin cycle

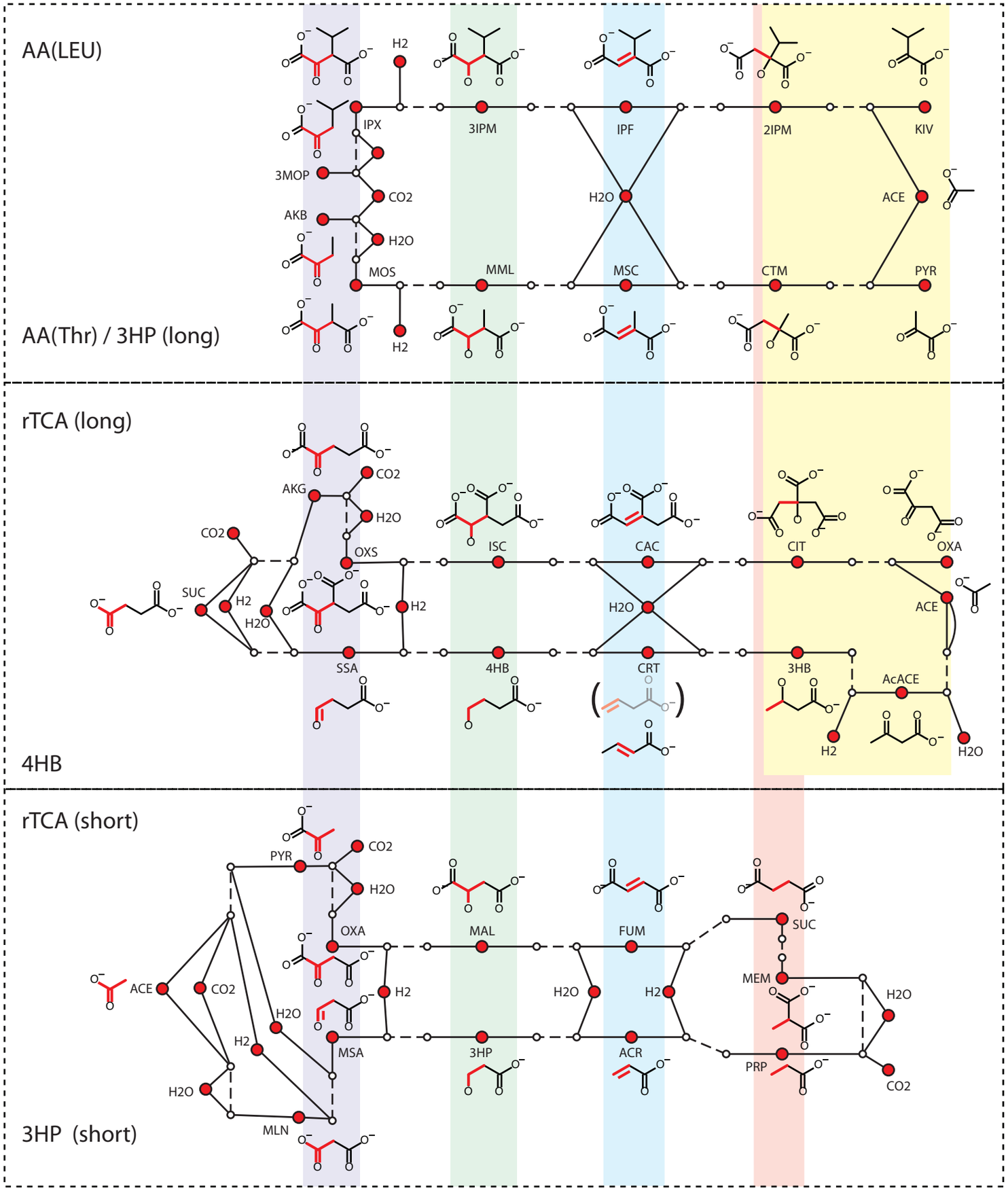
Braakman and Smith, Phys. Biol. 10:011001 (2013)

All innovation in Carbon Fixation has remained close to a TCA template

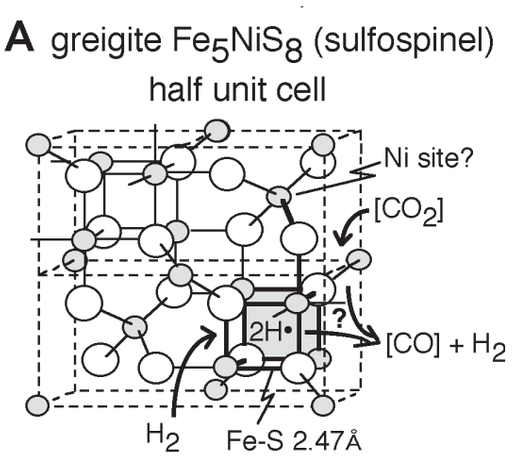


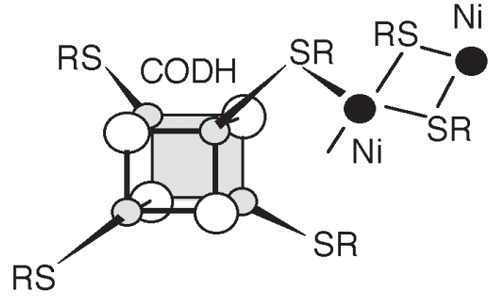
Pathway innovations concentrate in ~single Carbon-addition steps;

Associated with conserved protein families and metal centers



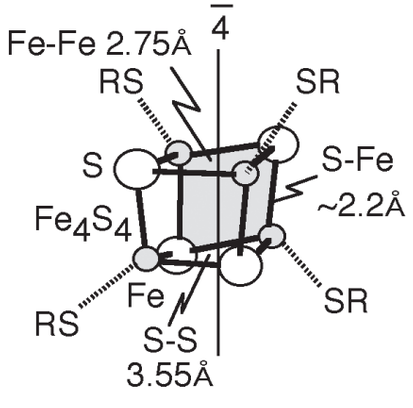
Braakman and Smith, Phys. Biol. 10:011001 (2013)

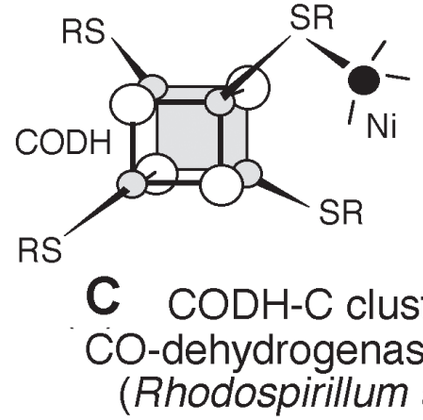




E CODH-A cluster
CO-dehydrogenase

B thiocubane (in ferredoxin)





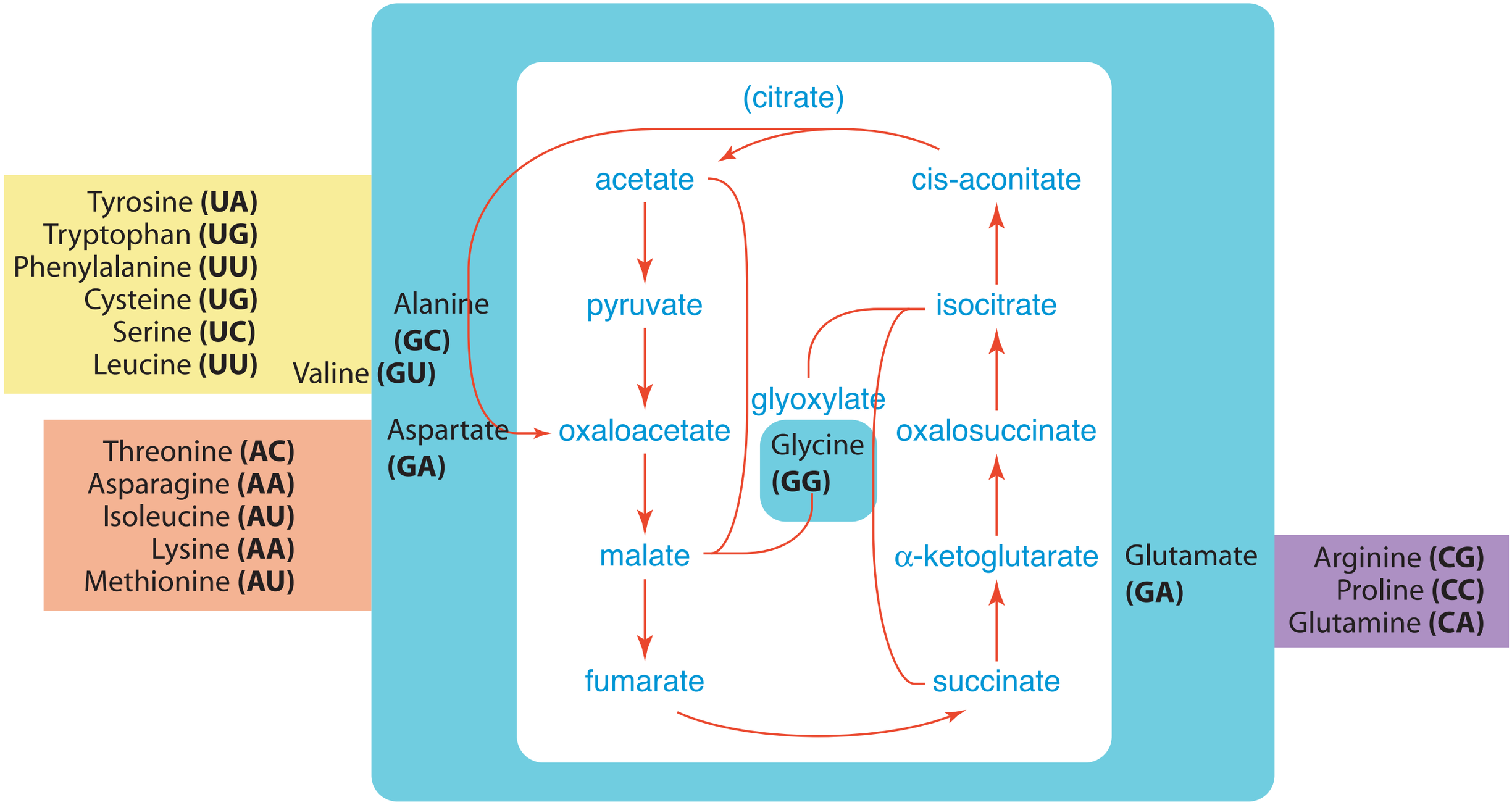
C CODH-C cluster
CO-dehydrogenase
(*Rhodospirillum sp.*)

From Russell et al. Econ Geol. 100:419 (2005)

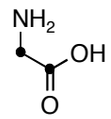
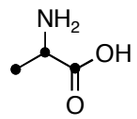
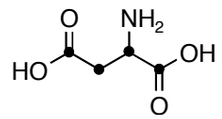
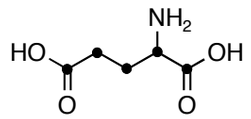
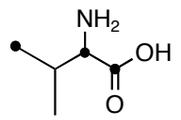
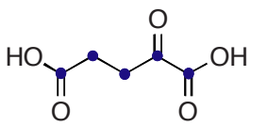
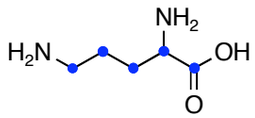
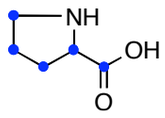
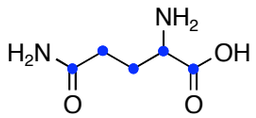
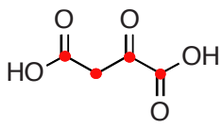
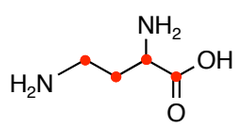
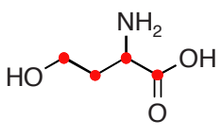
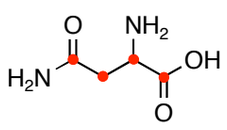
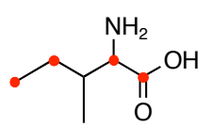
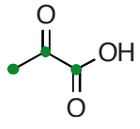
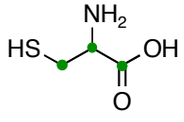
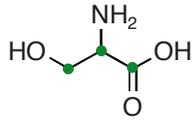
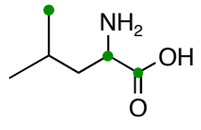
Upward causation: suggestions that the genetic code was entrained on biosynthetic regularities

- Ideal code should be a “firewall”
- Central Dogma suggests arbitrary assignments (Crick’s “adapter” argument)
- Error buffering (polar requirement etc.) departs from naive “adapters”, but still only applies to properties of the full amino-acids *as used*
- *Yet:* the code is most “compressible” in terms of early-biosynthetic pathway regularities

Code First Base: Organized according to backbone starting point in the Citric Acid Cycle



Code Second Base: physical properties reflect re-used modifications to TCA backbones

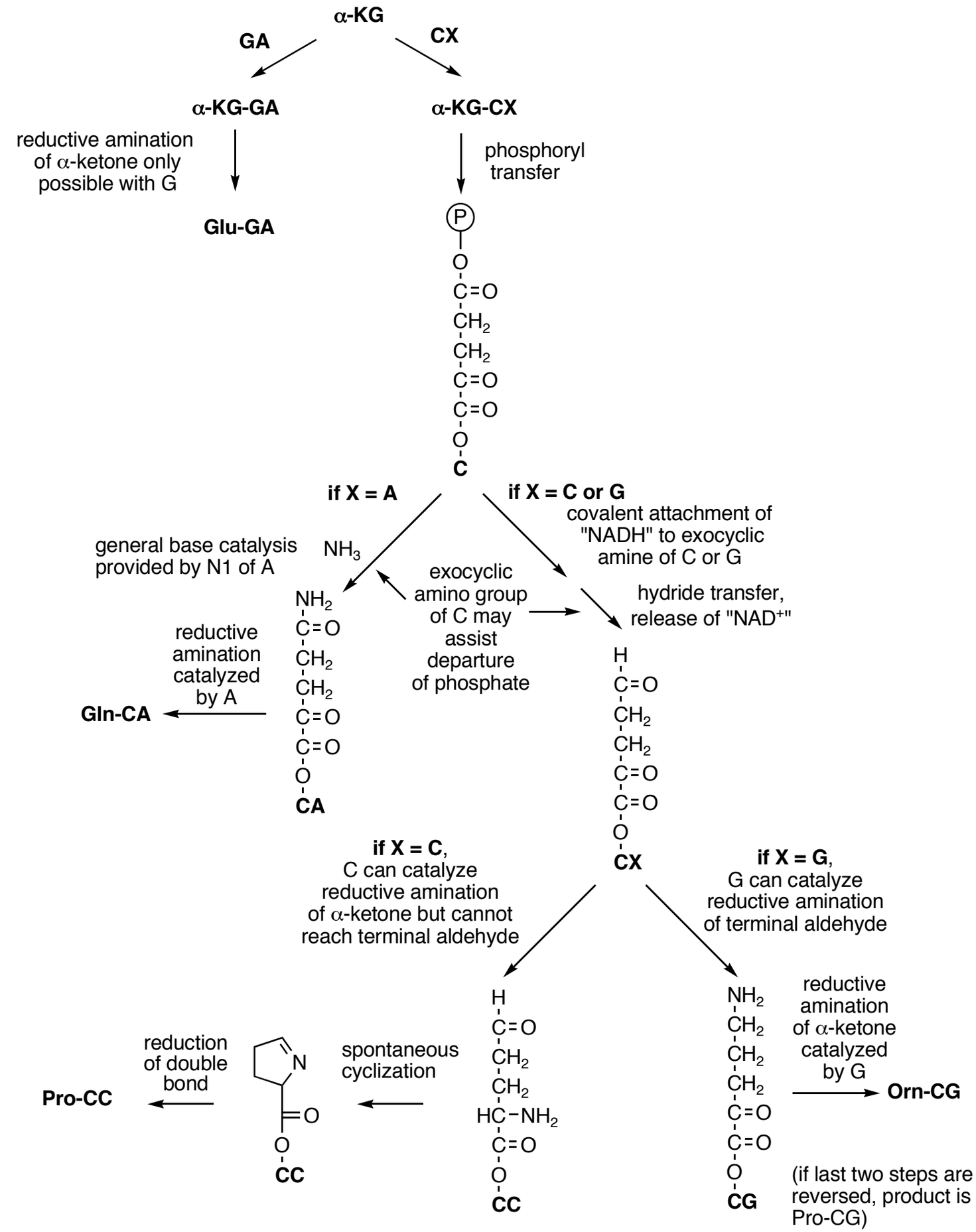
first position	second position			
	G	C	A	U
G	**Gly**	**Ala**	**Asp/Glu**	**Val**
	Gly	**Ala**	**Asp/Glu**	**Val**
			 	
C (α-ketoglutarate)	**Arg**	**Pro**	**Gln**	**Leu**
	Orn	**Pro**	**Gln**	**?**
				?
A (oxaloacetate)	**Ser / Arg**	**Thr**	**Asn**	**Ile**
	Dab	**Hsr**	**Asn**	**Ile**
				
U (Pyruvate)	**Cys**	**Ser**	**Tyr/stop**	**Leu**
	Cys	**Ser**	**X**	**Leu**
			**X**	

Copley et al.
PNAS 201:4442 (2005)

A Decision Tree:

Dependence on early biosynthetic pathway steps is even stronger than properties of the terminal amino acids:

Requires some imprint of history, beyond a simple version of error-buffering



Copley et al. PNAS 201:4442 (2005)

Main premises of the usual “metabolism-first” interpretation

- **Continuity premise:** some network selectively organized around these pathways was already a Hadean geochemical feature

- “The rest” of metabolism was what could be most easily built from these precursors, which were present in excess abundance

- As organic control systems came to be found among this inventory, fitness was pre-disposed by the system contexts already in place

- **Consequence:** evolution refined and re-invented catalysts, but many of the pathways were locked in place

- In some cases they were the best solutions anyway; no fitness advantage for deviating from them, even with refined genes and enzymes (evolutionary constraint and convergence tend to exist along a continuum)

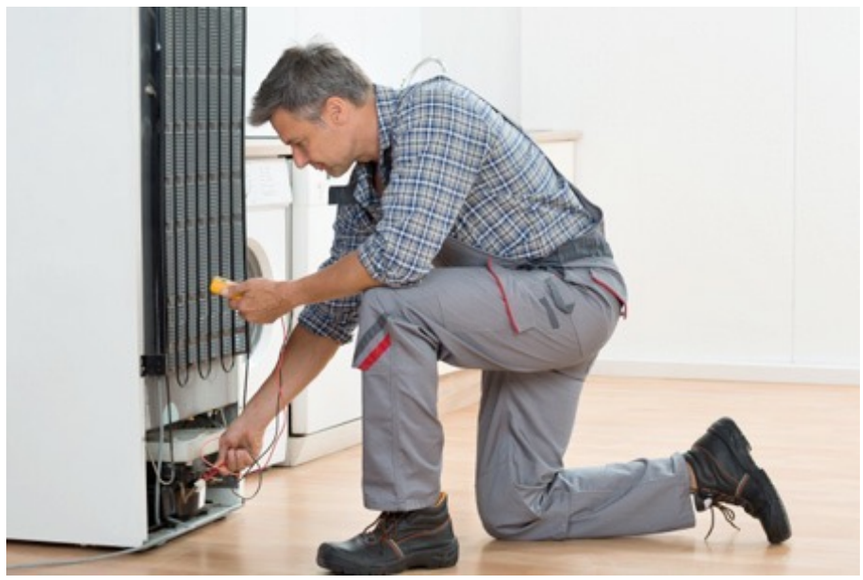
When does this “essay” become a theory?

Rehearsing Boltzmann is a start, but not enough

Second law?
No problem!

The problem:
When does repair of things that constantly fall apart become a robust and generic outcome?

This is fundamentally a question about ***kinetics*** and ***trajectories***



Thermodynamics neither ~~must~~ nor ~~should~~ mean *equilibrium*: need a theory of *process* and *history*

- Concept behind ordered macro-phases:
  — convergence on exponential families
  — scale separates from structure

scale structure

$$P_{\text{fluct}} = e^{-N\hat{S}}$$

Touchette. Phys. Rep 478:1—69 (2009)

- Dynamic context: Equilibrium Free Energy -> Effective Action

- Dynamic phase transitions <-> shifts of central tendencies of macrostates

- **Connection to the concept of "repair":** Optimal error correction is a *thermodynamic* theory in this sense

- Consequence for evolution:
  3-way trade-off between **robustness**, capacity for **complexity**, and **cost**

Robustness, Correlation length, Capacity, Complexity (Rate)

$$P_{\text{error}} \sim e^{-D(\mathcal{C}-\mathcal{R})}$$

scale structure

Universal metabolism through the lens of dynamical phase transition theory

- Abiotic Earth becomes a dynamically *metastable* condition

- Maximum-path-entropy condition has the most ways to fluctuate into it and the fewest ways to fluctuate out: definition of **“path of least resistance”**

- Contributions from familiar equilibrium thermodynamics and chemical kinetics
  1) “Easy” chemistry is water-based pair/group transfer, duplicated widely
  2) “Hard” chemistry is all metal-center, suggesting mineral or MLC origin (?)

- Contributions from network-level of fluctuation/control statistics
  3) Self-amplifying positive feedbacks concentrate matter and energy flows
  4) Feedbacks on shortest-possible (?) loops; less to diffuse/less to control

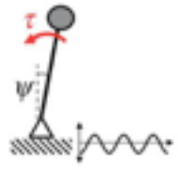
Current problems: connecting the biological story to convincing synthetic and geo-organic chemistry

- The pathways that seem ***necessary and specific*** biologically do not seem either ***inevitable or special*** geologically

- **Reactivity is self-defeating:** e.g. C_1 reduction

Energetic control

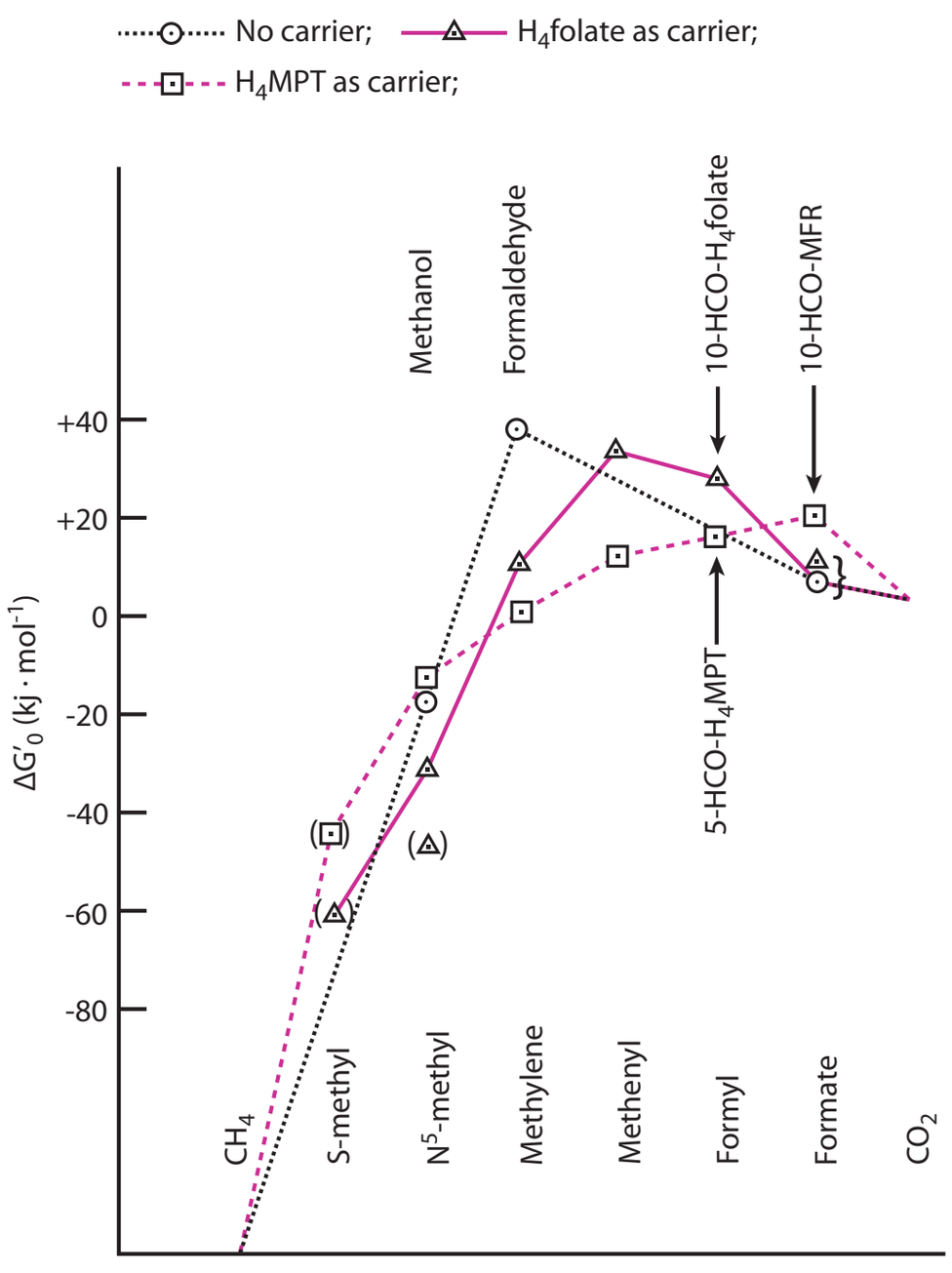
Kinetic control



Corollary: formose reaction is in a qualitatively different class from reductive carboxylation

- **What is the right concept of disequilibrium?**
  "Chasing equilibrium?" *(hot/cold or wet/dry cycling)*

  Biochemistry uses **group-transfer cascades** and **"compartmented quasi-equilibrium"**
  (acknowledge Y. Oono)



From Maden Biochem J. 350:609 (2000)

Proposed useful next steps

- Rudolf Thauer *et al.,* Everett Shock *et al.* (*et al. et al.*) have for decades assembled essential databases of thermodynamic landscapes for biochemically relevant organic reactions

- **We need a similar encyclopedia for kinetics:**
  -- Mineral metal-center catalytic selectivity and activity
  Edge/vertex effects
  Impurities and mineral/mineral interfaces in complexes
  -- Metal-ligand complex catalysis in solution phase
  Element, redox state, ligand-field geometry and orbital properties

- Much of the progress in my generation (microbiology, geo-energetics) has come from decades of painstaking (*non-flashy*) highly professional work; **How best to organize and support such work in the above topics?**

Need to connect Hadean atmosphere/ocean calibration to main controlling reaction classes

Kharecha, Kasting, Seifert, Geobiology 3:53 (2005)

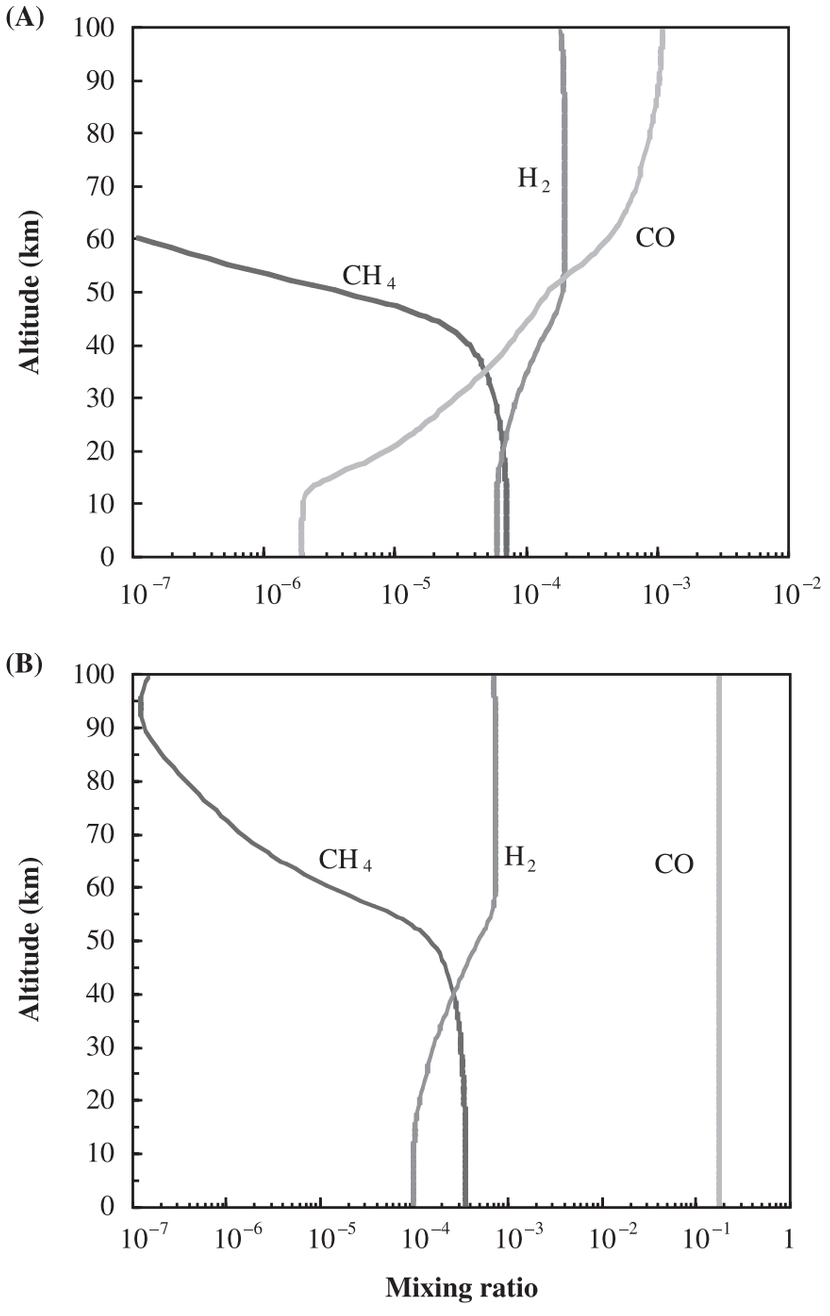
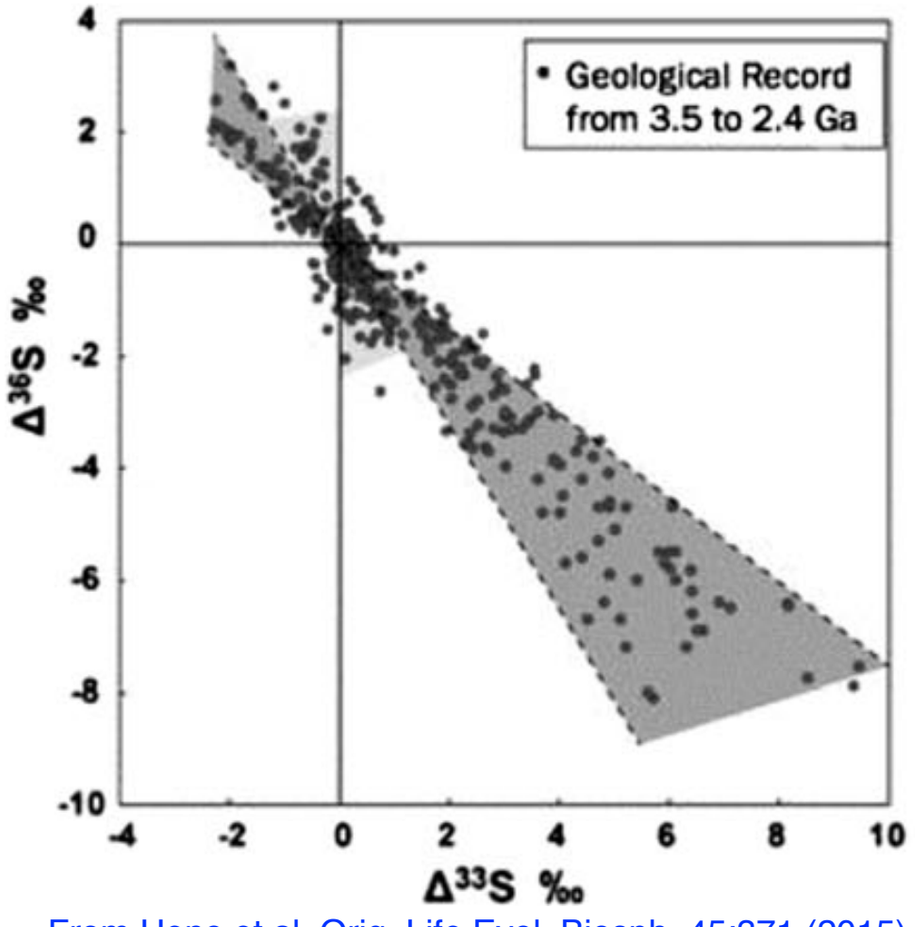


Fig. 5 Vertical mixing ratio profiles of H_2, CH_4, and CO in our Case 1 ecosystem for $f_{tot}(H_2)$ = (a) 200 ppmv and (b) 800 ppmv. The CO_2 mixing ratio was fixed at 2500 ppmv for both cases. In the absence of a biotic sink, CO can quickly accumulate to very high levels in a methanogenic ecosystem.

- Ueno et al. suggest, from quadruple S-isotope fingerprints, more reducing atmosphere with significant CO
- CO as an addition reagent rather than CO_2 is intriguing, but much is left to do to tell a full story



From Ueno et al. Orig. Life Evol. Biosph. 45:371 (2015)

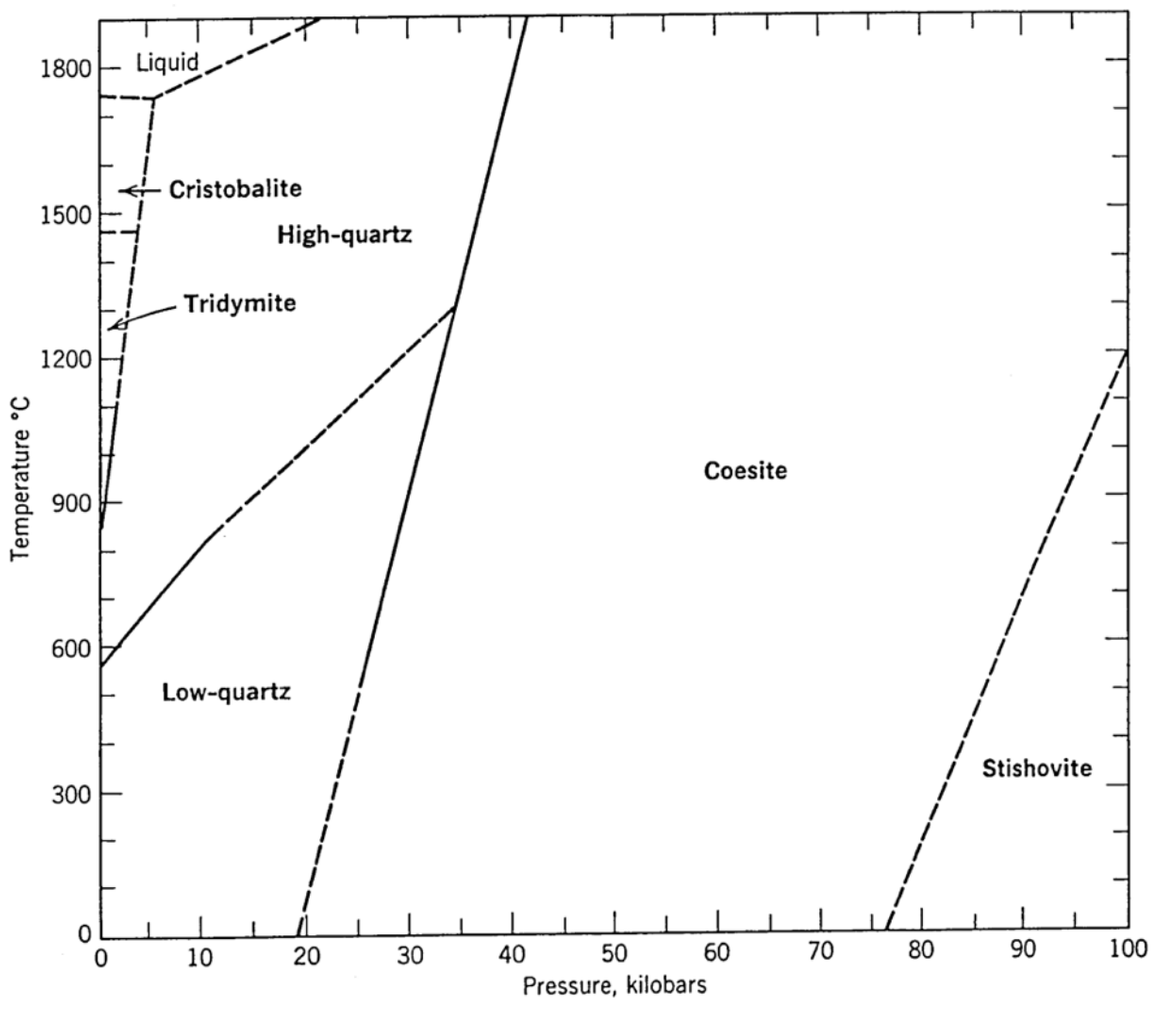
Closing thoughts: Even if this is somehow right…. Cautions for exoplanet studies

- We need to move beyond the mentality of “getting to a material”
  Many conversations are already shifting well in that direction
  - Not “organics” per se, but organics out of equilibrium with the context
  - Big-and-random (tar) is not “complex” -- complex implies elements of selectivity. How much of the selection of metabolism was geochemical?
    Gell-Mann and Lloyd, Complexity 2:44—52 (1996)
- Not all disequilibria are equivalent, w.r.t. problems of biological origin
  Redox $\neq$ radioactivity $\neq$ thermal activation $\neq$ dehydration

Inevitable does not mean generic: Complex Order is often Context Sensitive

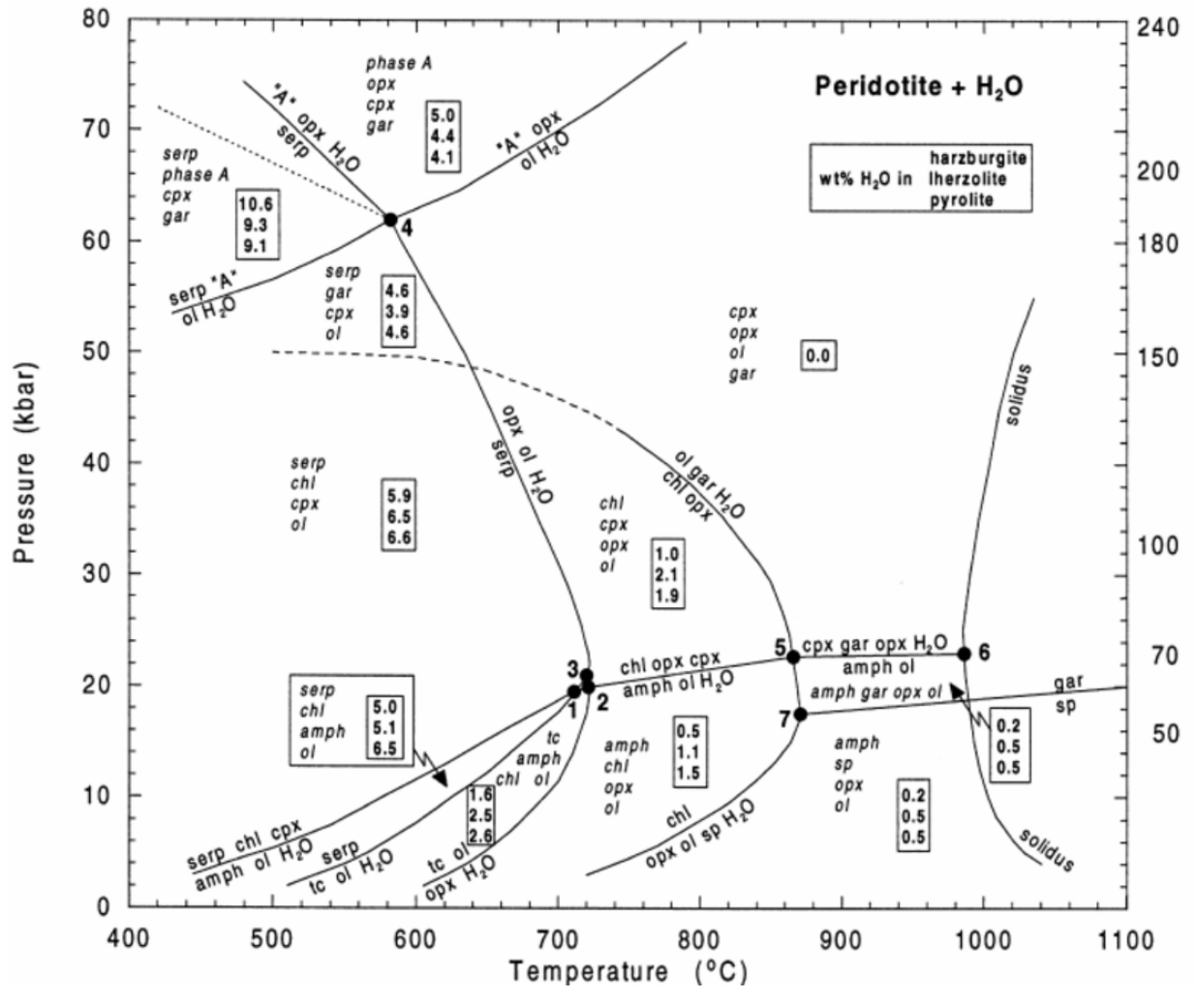
Remember: crystallography only has to solve constraints of matching representations of the rotation group to spatial lattices

http://www.geo.arizona.edu/xtal/geos306/fall13-16.htm



(P, T)

https://www.researchgate.net/publication/222451682_Experimentally_based_water_budgets_for_dehydrating_slabs_and_consequences_for_arc_magma_generation



(P, T, composition)

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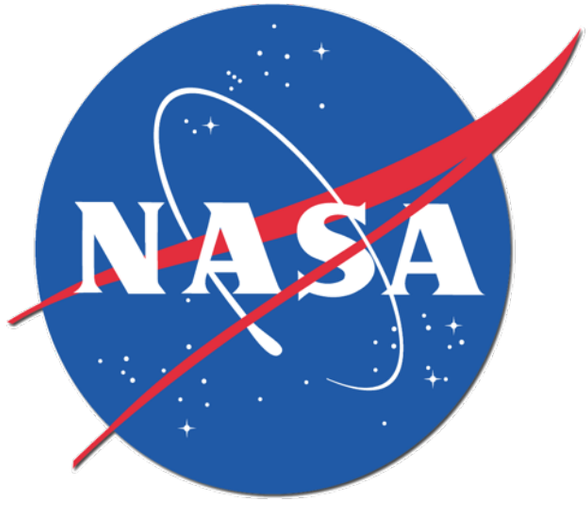

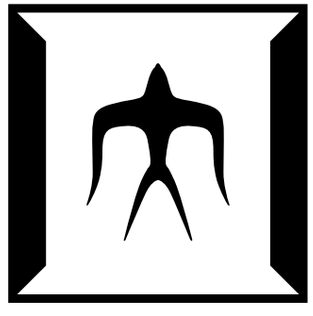

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