UV-Driven Monte Carlo Chemistry: COMs Formation on Icy Grains

Presentation on “Organic Chemistry on Planets”

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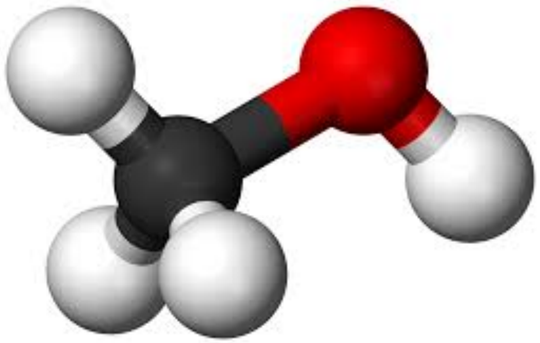
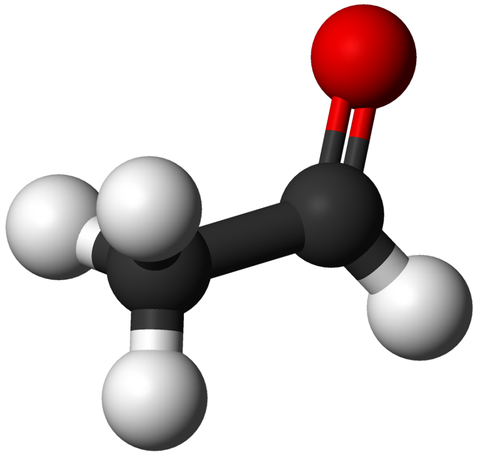
Complex Organic Molecules(COMs)

Definition & Brief Introduction

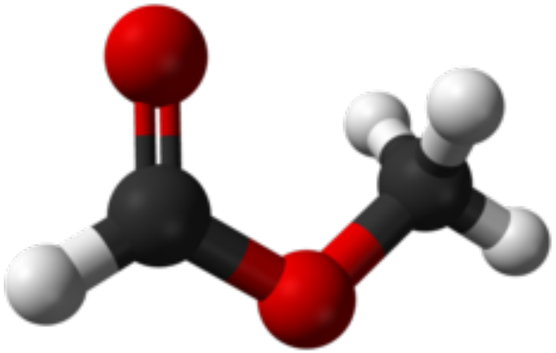
- COMs: Molecules with ≥6 atoms, including C, H, O and/or N.



Methanol(甲醇)



Acetaldehyde(乙醛)



Methyl formate(甲酸甲酯)

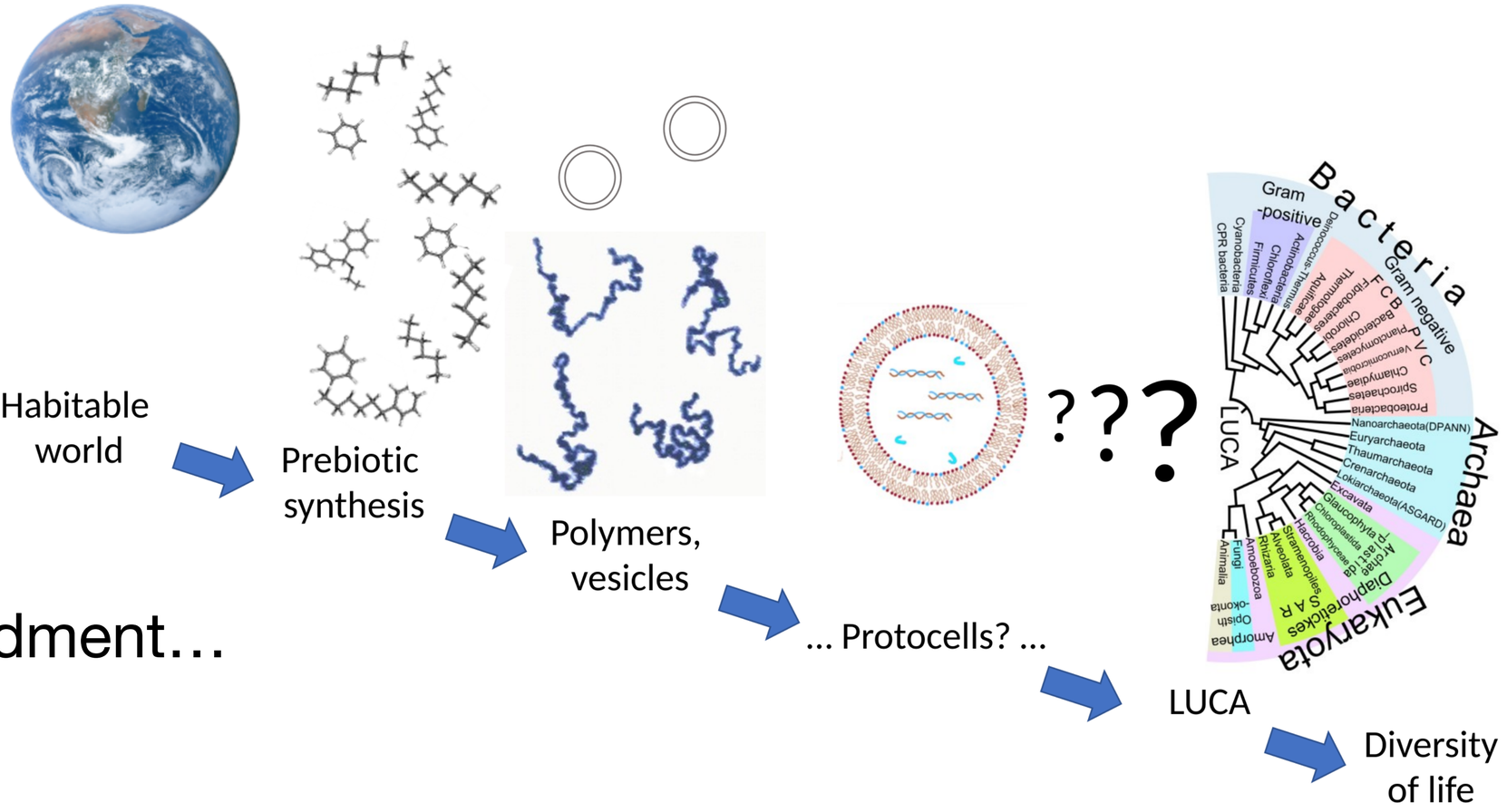
- On Earth, most organics are related to life…

Complex Organic Molecules(COMs)

Building Blocks for Life

- In Space, COMs are thought to be “building blocks for life”.

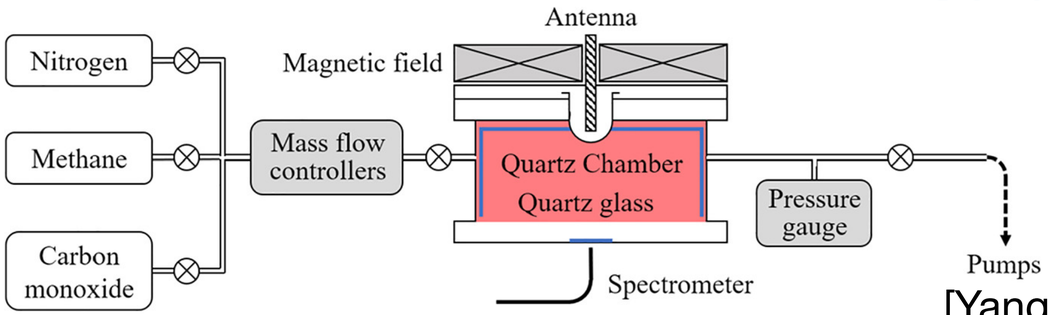
- Abiotic processes:
  - Ice thermal processing
  - **UV irradiation**
  - Cosmic ray
  - Electron & ion bombardment…



Limitations of Approaches to COMs Synthesis

- **Lab experiment**

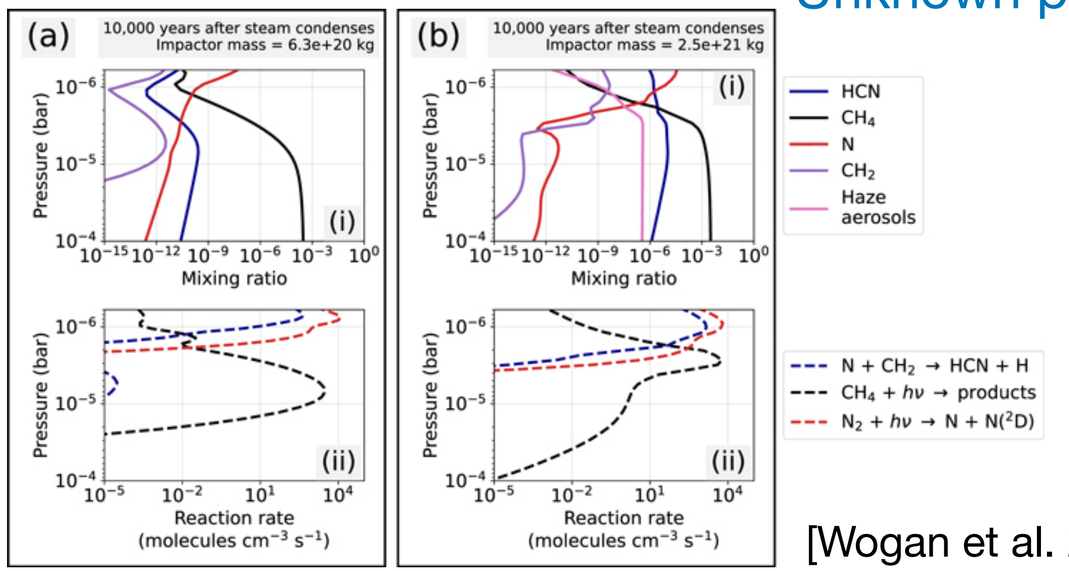
Conditions?



[Yang et al. 2025]

- **Photochemical model**

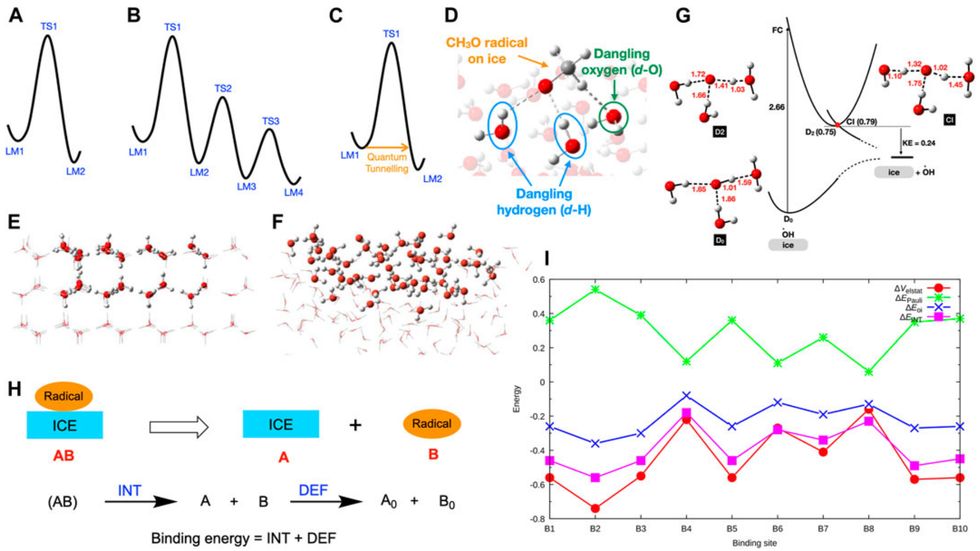
Unknown product?



[Wogan et al. 2023]

- **Quantum Chemical Model**

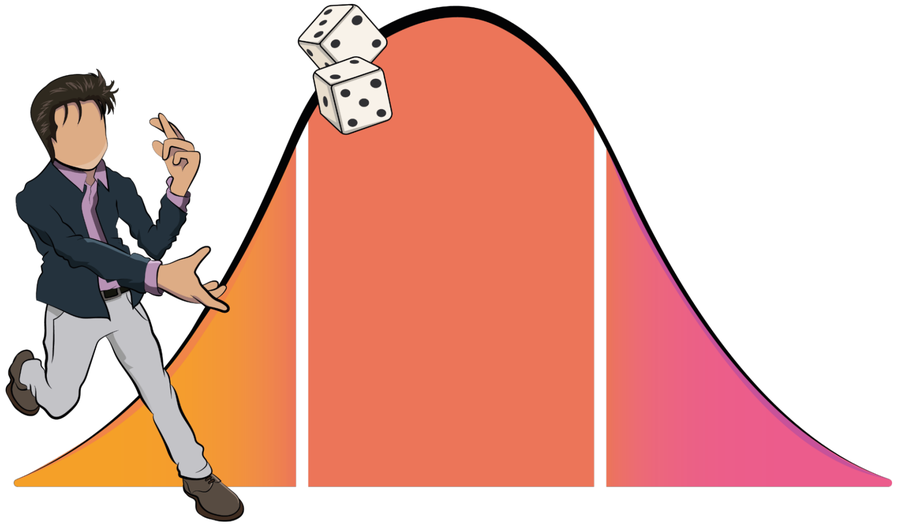
Computing resources!

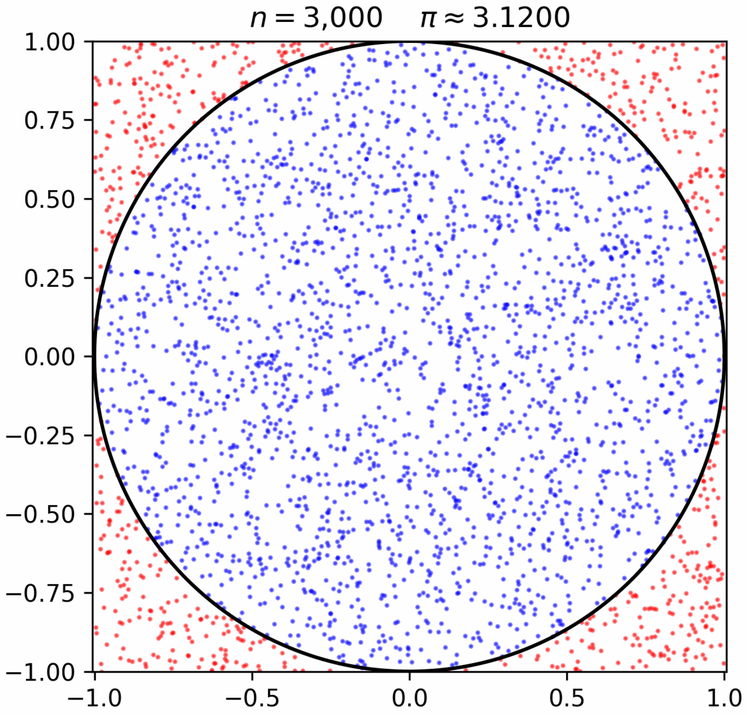


[Sameera et al. 2022]

What is Monte Carlo(MC) Simulation?

- Monte Carlo simulation is a stochastic(random) numerical method that samples possible system evolutions using random numbers, guided by physically motivated probabilities.





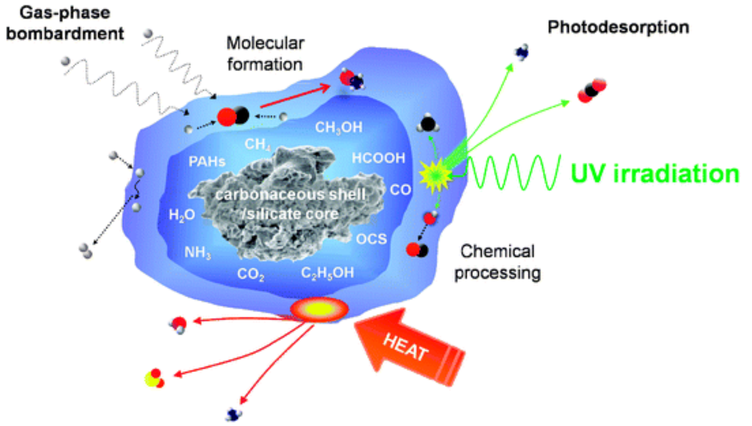
Monte Carlo Simulation of COMs Synthesis

- Takehara, H., Shoji, D., & Ida, S. (2022). Monte Carlo simulation of sugar synthesis on icy dust particles intermittently irradiated by UV in a protoplanetary disk. Astronomy & Astrophysics, 662, A76.
- Ochiai, Y., Ida, S., & Shoji, D. (2022). Monte Carlo simulation of amino acid synthesis driven by UV irradiation in protoplanetary disks and primitive Earth atmosphere. Meteoritics & Planetary Science, 57.
- **Ochiai, Y., Ida, S., & Shoji, D. (2024). Monte Carlo simulation of UV-driven synthesis of complex organic molecules on icy grain surfaces. Astronomy & Astrophysics, 687, A232.**
- Ochiai, Y., Ida, S., & Shoji, D. (2025). Exploring impact vapor plume reactions from asteroidal impacts: Monte Carlo simulations and implications for biomolecules synthesis. Icarus, 116736.

Physical Picture & Key Assumptions

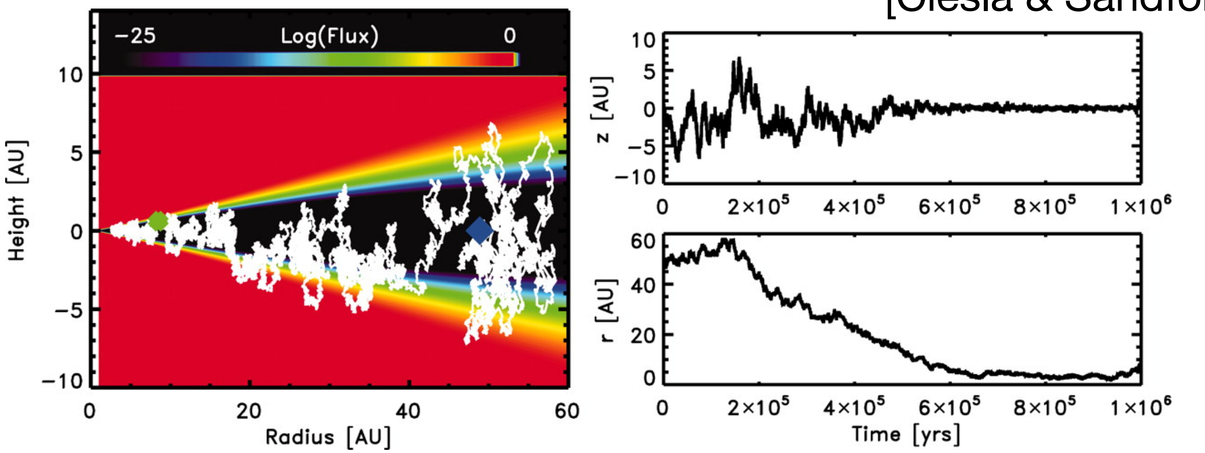
Ochiai et al. 2024

[Bruke & Brown 2010]



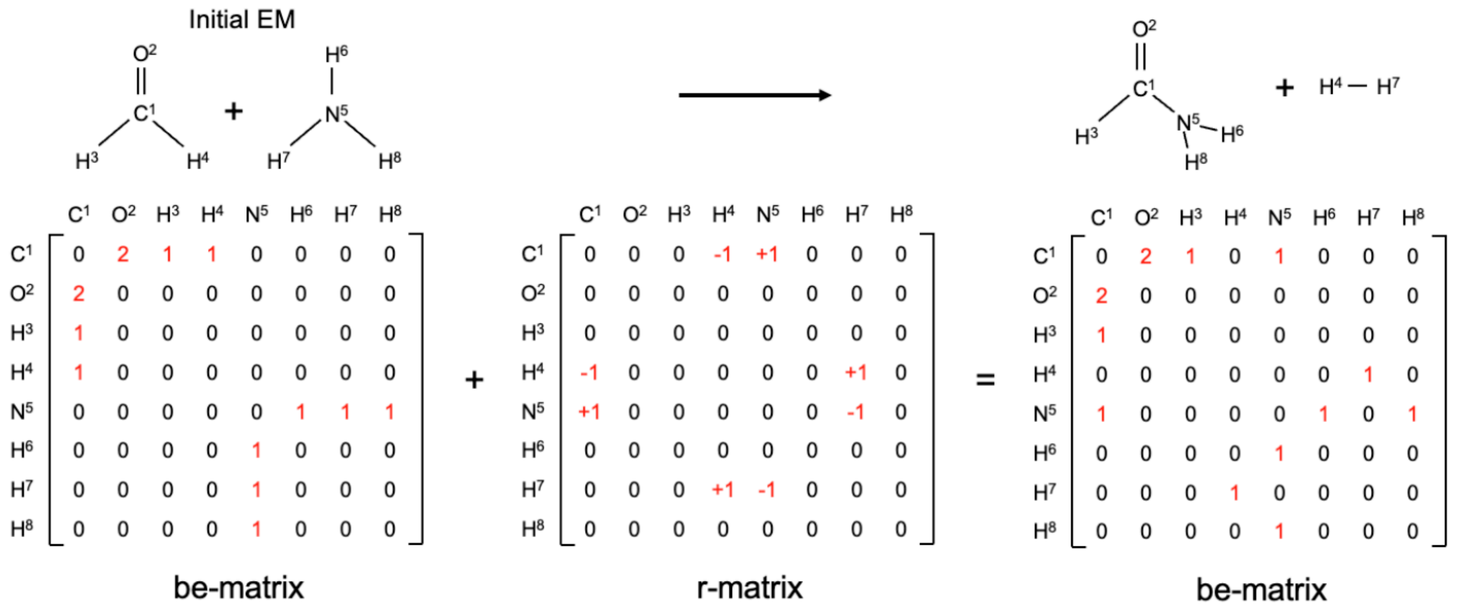
- Site of synthesis:
  - Surface of icy dust grains in *warm regions* of protoplanetary disks
  - Typical temperatures: 50-100 K (Jupiter to Neptune orbits)
    - (warm ice allows efficient diffusion, enhances random collisions)
- Grains are temporarily exposed to UV radiation at disk upper layers (lifted by turbulence)
- Two phases chemical evolution
  - UV phase
  - Post-UV phase

[Ciesla & Sandford 2012]



Dugundji-Ugi Model

Dugundji & Ugi 1973, a Graph-theoretical Matrix-type Model



[Ochiai et al. 2024]

- Describe chemical rxns. in graph-theory adjacency matrix (邻接矩阵)
- be-matrix (bond & electron), r-matrix (rxn)
- In the simulation, the r-matrix only have two elements of -1 / 1
  - Double bonds / triple bonds are treated as isolated

Reaction Rate Theory: Arrhenius Equation & BEP Principle

- After candidate runs are listed.
- From the Arrhenius rate law: $k = A\exp(-\frac{E_a}{RT})$
  - Weight: $W = \exp(-\frac{E_a}{RT})$
    - E_a: activation energy of run
    - $RT \simeq 0.83(\frac{T}{100\mathrm{K}})\mathrm{kJ\ mol^{-1}}$
- Evaluation of E_a: Bell-Evans-Polanyi (BEP)
- Enthalpy change (焓变, ΔH): bond energy change
  - (difference under conditions are neglected)
- $E_a = \max(0,\ \alpha\Delta H + \beta)$
  - $\alpha = 1,\ \beta = 100\ \mathrm{kJ\ mol^{-1}}$ are used

Newly Incorporated “Bonds”

UV & Radical(自由基)

- Type1: Photodissociation $\mathrm{AB} + \mathrm{h}\nu \rightarrow \mathrm{A} + \mathrm{B}$ $(\mathrm{A\text{-}B} + \mathrm{X\text{-}X} \rightarrow \mathrm{A\text{-}X} + \mathrm{B\text{-}X})$
- Type2: Radical-radical rxn $\mathrm{A} + \mathrm{B} \rightarrow \mathrm{AB}$ $(\mathrm{A\text{-}X} + \mathrm{B\text{-}X} \rightarrow \mathrm{A\text{-}B} + \mathrm{X\text{-}X})$
- Type3: Radical-nonradical rxn $\mathrm{A} + \mathrm{BC} \rightarrow \mathrm{AB} + \mathrm{C}$ $(\mathrm{A\text{-}X} + \mathrm{B\text{-}C} \rightarrow \mathrm{A\text{-}B} + \mathrm{C\text{-}X})$
- Type4: Nonradical-nonradical rxn $\mathrm{AB} + \mathrm{CD} \rightarrow \mathrm{AC} + \mathrm{BD}$ $(\mathrm{A\text{-}B} + \mathrm{C\text{-}D} \rightarrow \mathrm{A\text{-}C} + \mathrm{B\text{-}D})$
- Type5: No change

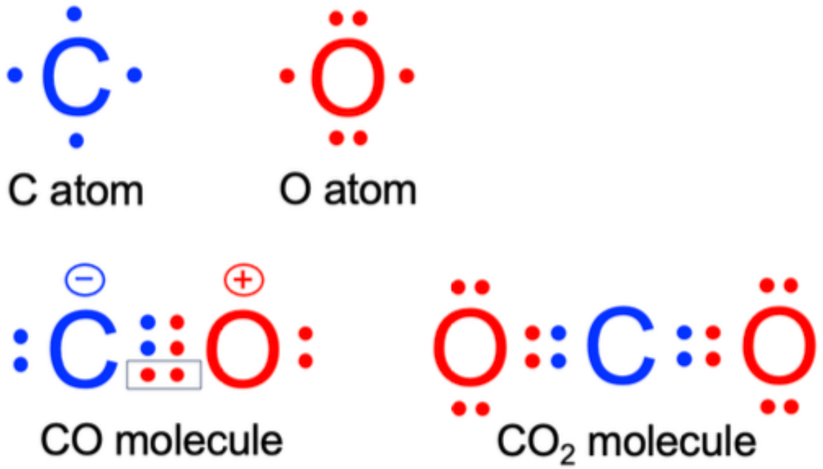
- Photodissociation $\Delta H_{\mathrm{pd}} = BE_{\mathrm{broken}} - 1000 \left(\frac{E_{\mathrm{UV}}}{10\ \mathrm{eV}} \right)\ \mathrm{kJ\,mol^{-1}}$ $W = \exp(-\frac{\max(\Delta H_{\mathrm{pd}}, 0)}{RT})$
- Radical bond $(\mathrm{A\text{-}X})$: zero bond energy

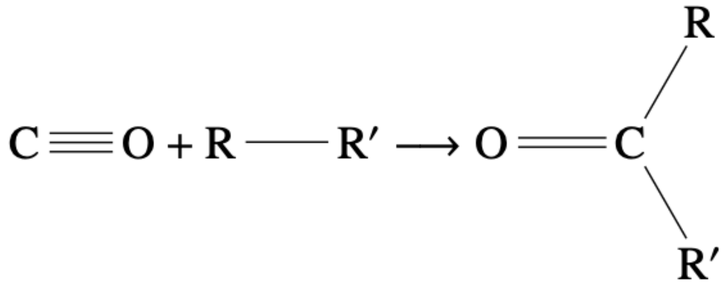
Environmental Timescale Constraint

- Monte Carlo sampling based on relative probabilities
  - (Select a rxn, even if all rxns are slow in absolute terms)
- Eyring eq.: $k = \frac{\kappa k_B T}{h} \exp\left(-\frac{\Delta G^{\ddagger}}{RT}\right) \approx \frac{k_B T}{h} \exp\left(-\frac{E_a}{RT}\right)$
- Rxn half-life: $t_{1/2} = \frac{\ln 2}{k}$
- For a given environmental timescale $t_{1/2}$, this defines a critical activation barrier $E_{a,\mathrm{crit}}$
  - $t_{1/2}(E_{a,\mathrm{crit}}) = t_{\mathrm{env}}$= 1000 yr (vertical mixing timescale of dust grains)
  - Rxns with $E_a > E_{a,\mathrm{crit}}$ are statically suppressed

Treatment of CO Bond

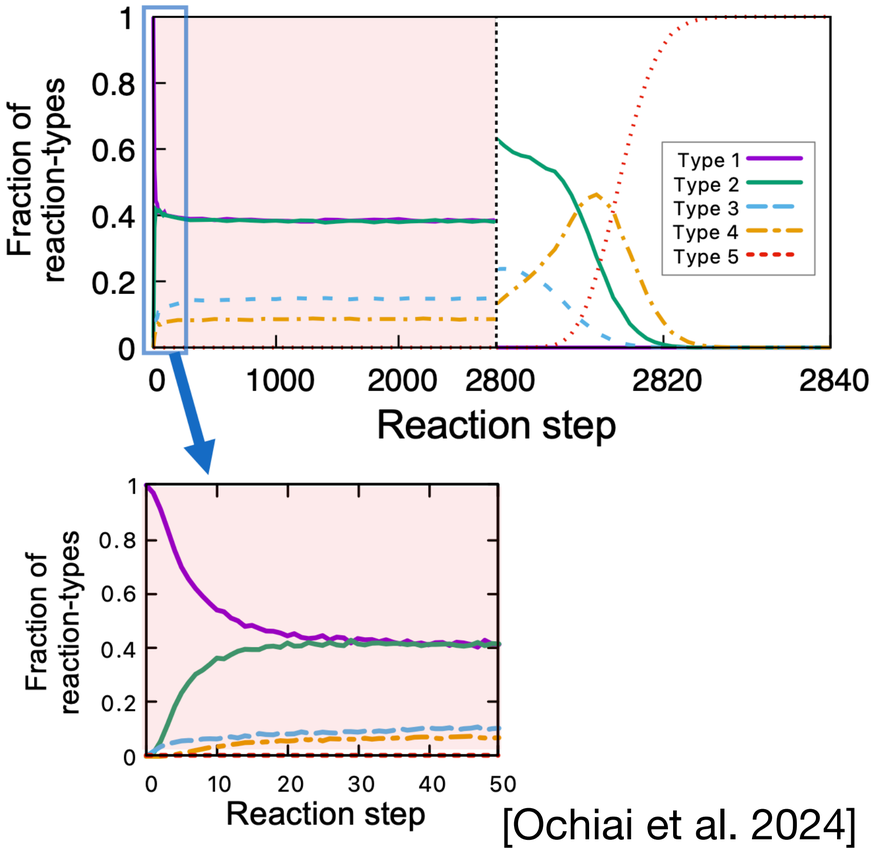
- CO's triple bond consists of two shared electrons and one donated lone pair.
- CO rxs only via radical pathways(eg. $CO + OH \rightarrow CO_2 + H$), treated as barrier less rxns with $E_a = 0$
  - (Rxn between two CO, photodissociation of CO is prohibited)





UV Phase Rxns

- Type1 dominates at the beginning, converts initial molecules into radicals
- As radicals accumulate, Type1(source) & Type2(sink) reach a balance
- With 10 eV photons
  - Type1 can cleave any $\mathrm{C/N/O/H}$ bond
  - Type2 $E_a = 0$ (barrierless)
- Keeps reshuffling bonds!
- Enable growth to complex molecules

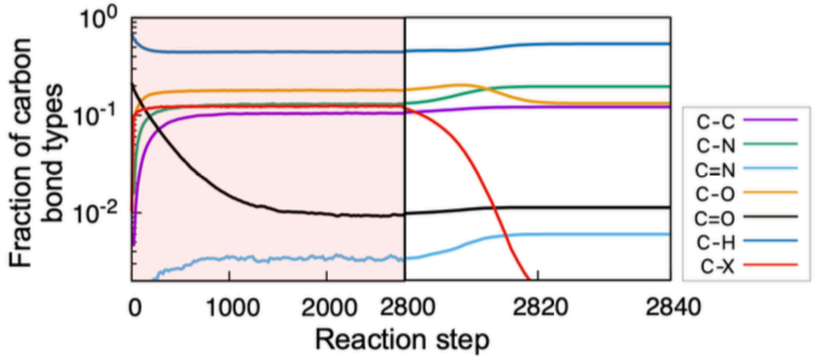


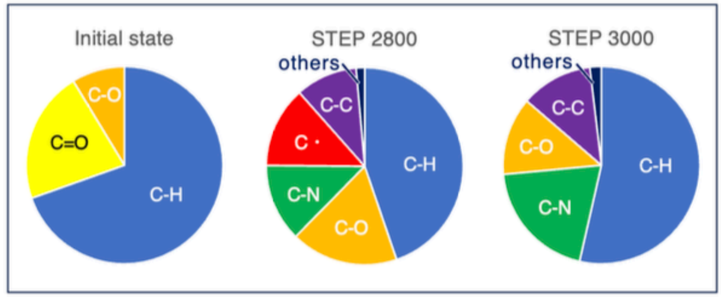
[Ochiai et al. 2024]

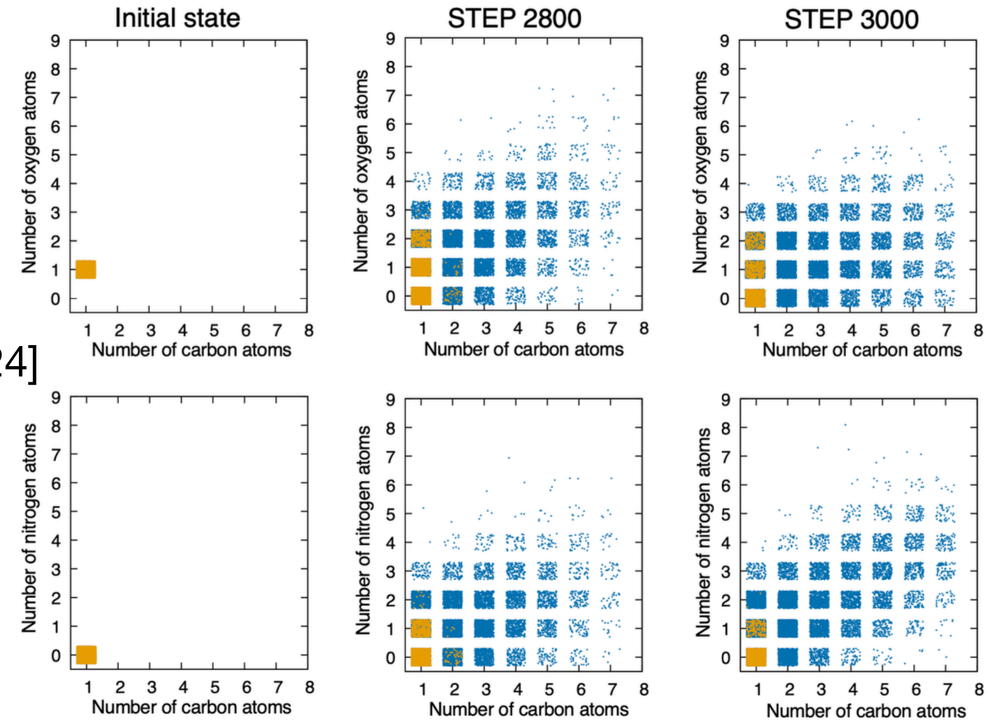
Post-UV Phase Rxns

- UV off ⇒ Type1 halts ⇒ Type2 dominate ⇒ most radicals are consumed
- UV off made unstable bonds cleanup ⇒ slightly increase $\mathrm{C\text{-}N}$ & $\mathrm{C\text{-}O}$
- Barriered rxns emerge:
  - $\mathrm{C\text{-}O + H\text{-}H \rightarrow C\text{-}H + O\text{-}H}$
  - Reduce $\mathrm{O/N}$ substitution on carbon
  - Competes with Type2
- Rxn timescale 10^3 yr, $E_a < E_{a,\mathrm{crit}}$, chemistry stops

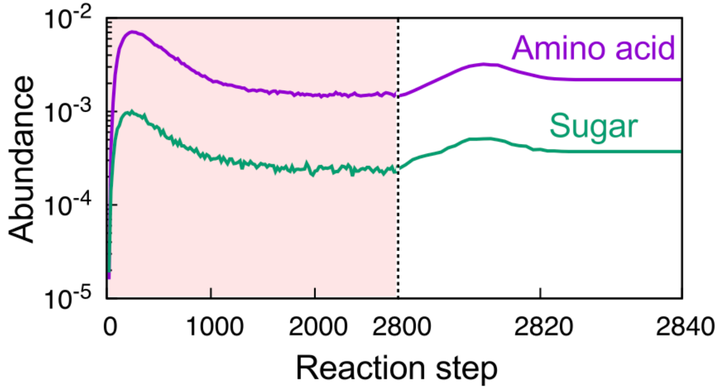
[Ochiai et al. 2024]

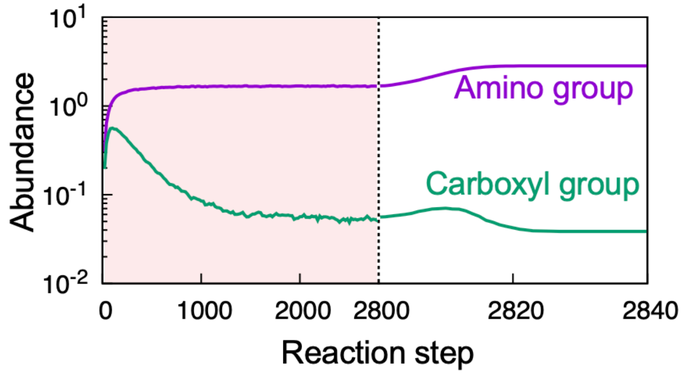




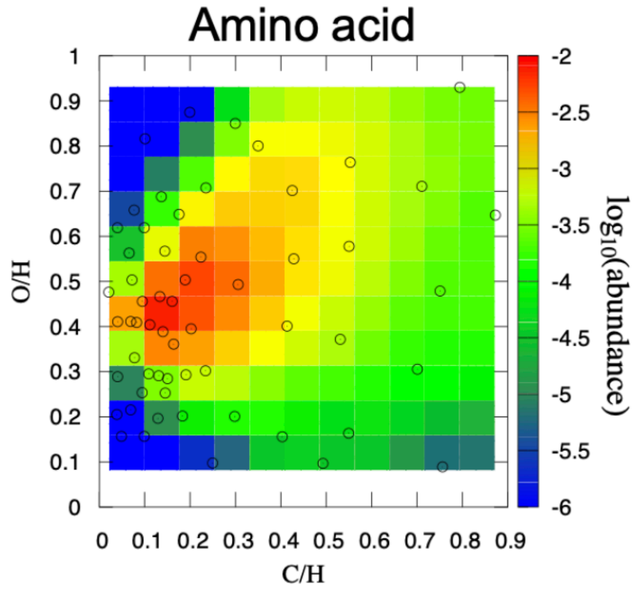


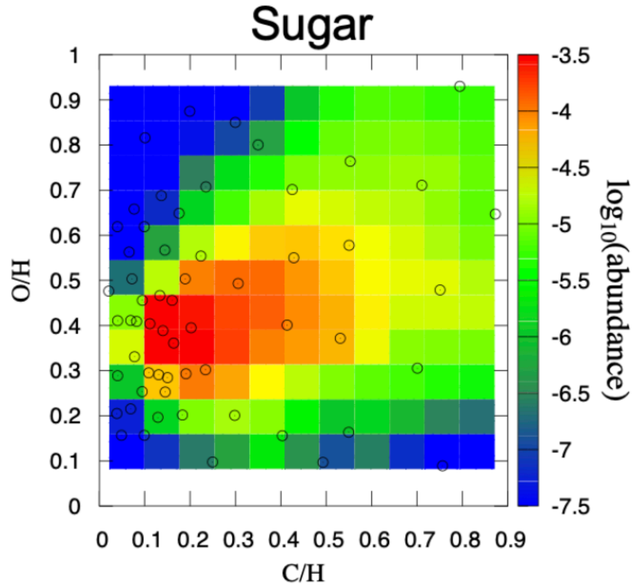
Amino Acids & Sugars Synthesis





[Ochiai et al. 2024]



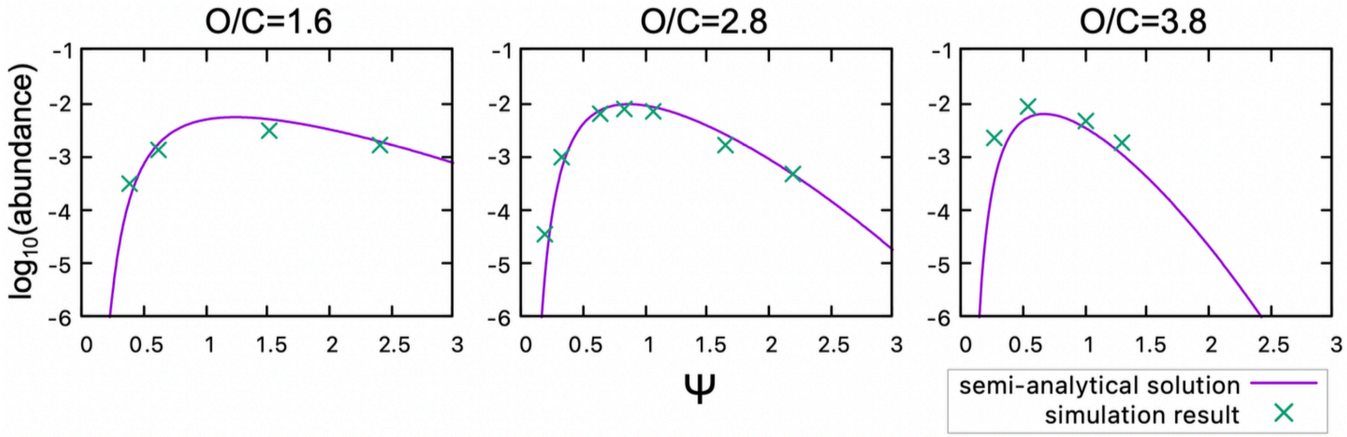


- Key bottleneck: $\mathrm{C{=}O}$ formation
  - Amino group > Carboxyl(羧基) group
  - Sugar (no carboxyl) still track amino acids closely: $\mathrm{C{=}O}$
- Extremely sensitive to $\mathrm{C/H}$ & $\mathrm{O/H}$
  - Peak locations:
    - Amino acids: $\mathrm{C/H} \approx 0.15, \mathrm{O/H} \approx 0.4 - 0.5$
    - Sugars: $\mathrm{C/H} \approx 0.15, \mathrm{O/H} \approx 0.3 - 0.4$

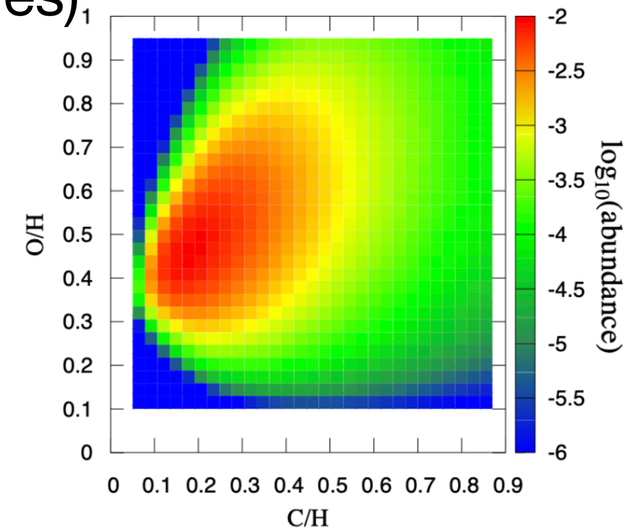
Semi-analytic Yield Predictor

Amino acids & Sugars

- A “potential complexity” index:
  - $$\Psi = \frac{4\mathrm{C} + 3\mathrm{N} + 2\mathrm{O} - \mathrm{H}}{\mathrm{H}}$$



- Highest amino acid/sugar yields occur at intermediate Ψ
  - (Too large will shift products to complex C-C/C-O macromolecules)
- $$A_{\mathrm{final}} = c_1\left(\frac{O}{H}\right)\left(\frac{O}{C}\right)^2 \exp\left[-c_2\frac{1}{\Psi}\frac{H}{O} - c_3\Psi - c_4\left(\frac{O}{H}\right)^2\left(\frac{O}{C}\right)^2\right]$$

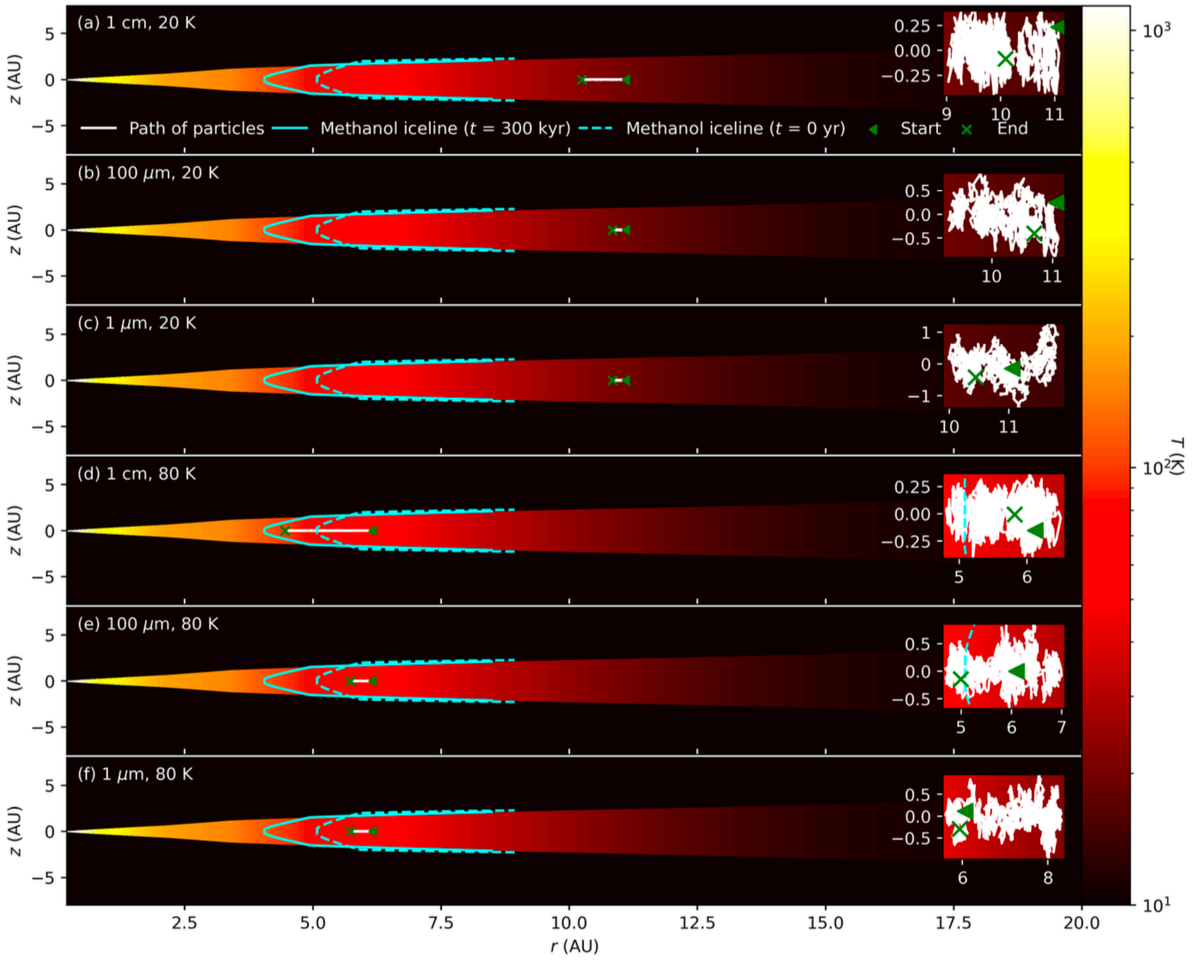


Future Applications

Couzinou et al. 2024

- Particle transport model tracks the evolution of pebbles during the lifetime of the protosolar nebula.
- Only **methanol ice** was considered as the parent species for COMs formation.
  - (UV threshold for methanol ice to form COMs from exps)
- Molecules other than methanol?
- Chemical photorxn model like **Ochiai et al. 2024**!

[Couzinou et al. 2024]



Summary

- **Goal:** Model how complex organic molecules (COMs) form on warm icy grains under intermittent UV irradiation.
- **Method:** A Monte Carlo chemical evolution using the Dugundji–Ugi graph/matrix representation to sample huge reaction networks.
- **Physics constraints:** Reaction weights from Arrhenius with BEP-estimated barriers, plus an environmental timescale cutoff to exclude “too-slow” reactions.
- **Two-phase chemistry:** UV phase generates radicals; post-UV consumes radicals and reorganizes products until freeze-out.
- **Main results:** $\mathrm{C{=}O}$ formation is a key bottleneck; amino-acid and sugar yields are highly sensitive to $\mathrm{C/H}$ and $\mathrm{O/H}$ and peak at intermediate complexity (measured by Ψ).

Reference

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