From quantum computational physics to the origins of life

A. Marco Saitta

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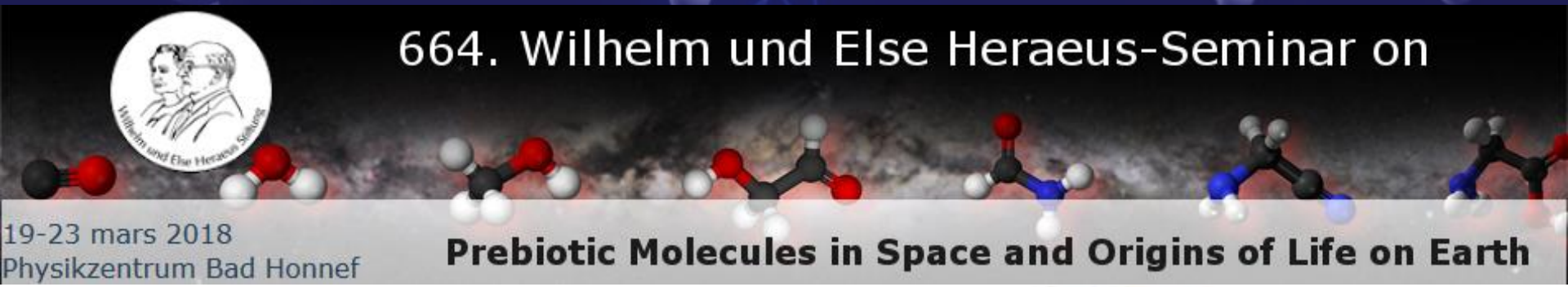

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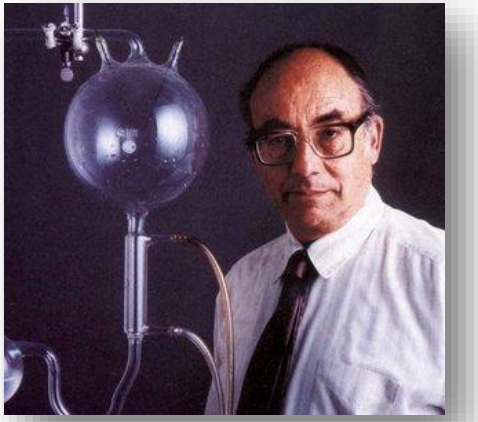
MUSÉUM NATIONAL D'HISTOIRE NATURELLE

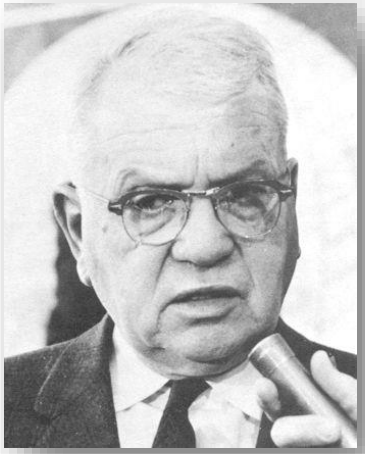
Outline

- ❑ *Ab initio* prebiotic chemistry and *in silico* Miller experiments
- ❑ Topology-based method for transformations in matter
- ❑ Full *ab initio* DFT free-energy surfaces (FES) of amino-acids in parent-body meteoritic conditions
- ❑ Full *ab initio* DFT free-energy surfaces (FES) of RNA nucleotides in hydrothermal conditions
- ❑ Perspectives and conclusions

Miller(-Urey) experiment(s)

- 1950's: hypotheses on early Earth atmosphere and conditions
- Strong volcanic activities, lightning
- Reducing chemical composition: H_2O, NH_3, CH_4, H_2

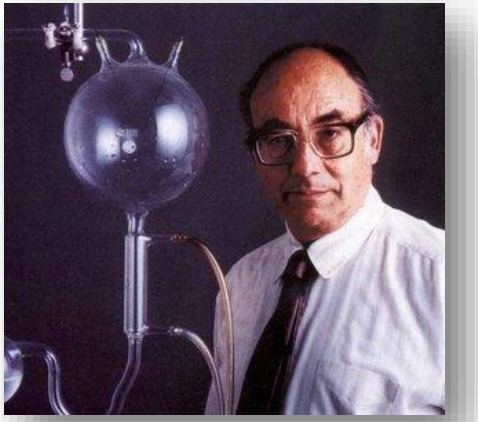


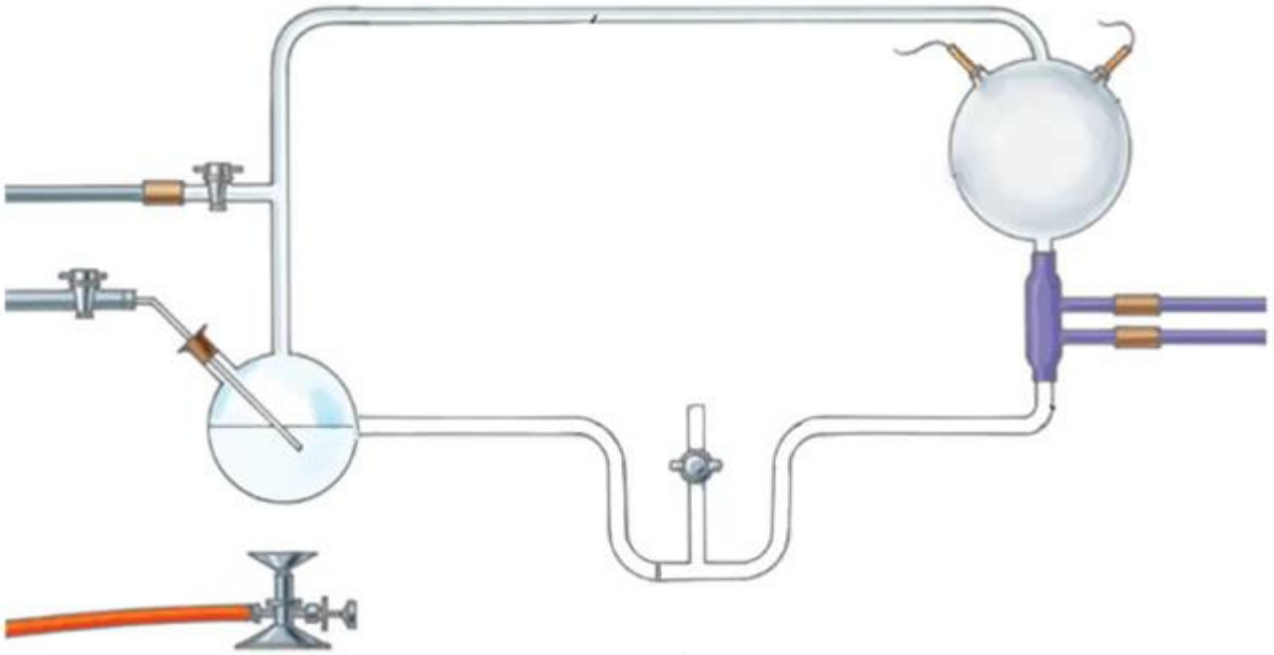


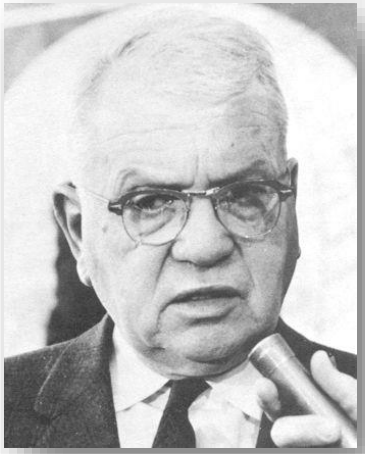
Ancient & Middle Ages	1600's	1700's	1862	1871	1920's	Post-WWII	1953

Miller(-Urey) experiment(s)

- 1953: Milestone lab simulation of lightning in primordial atmosphere







Ancient & Middle Ages	1600's	1700's	1862	1871	1920's	Post-WWII	1953

Ab initio Miller experiment?

- Solve DFT equations, calculate ab initio enthalpies and forces (at T = 0 K)

$$E[n] = T_s[n] + \int d^3r\, V_{\rm ext}(\vec{r})\, n(\vec{r}) + E_{\rm H}[n] + E_{\rm xc}[n]$$

- Finite temperature: move atoms, explore (chemical) phase space

$$\mathbf{f}_i = \mathrm{m}\,\ddot{\mathbf{r}}_i \qquad \mathbf{f}_i = -\frac{\partial \mathrm{U}(\mathbf{r}^N)}{\partial \mathbf{r}_i} = -\vec{\nabla}_{\mathbf{r}_i}\mathrm{U}(\mathbf{r}^N)$$

- Add an electric field

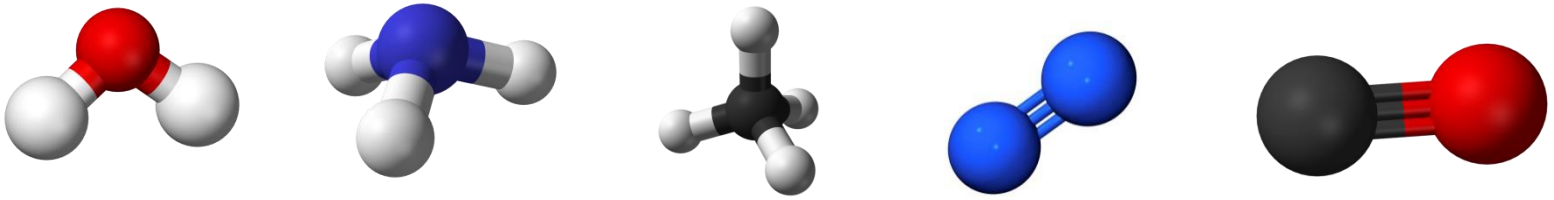
VOLUME 89, NUMBER 15 PHYSICAL REVIEW LETTERS 7 OCTOBER 2002

***Ab initio* Molecular Dynamics in a Finite Homogeneous Electric Field**

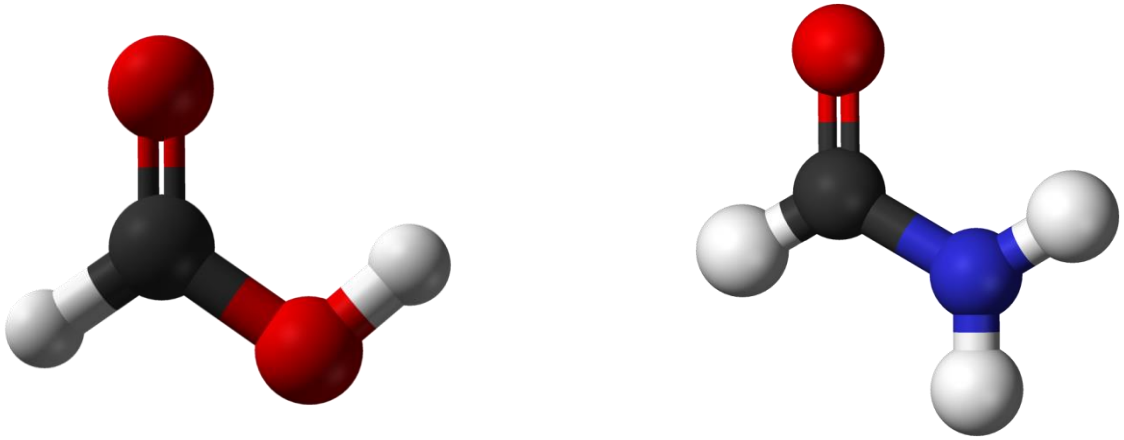
P. Umari and Alfredo Pasquarello

In silico Miller experiments

- Start: Miller molecules in strong fields



- Spontaneous formation of formic acid and formamide!

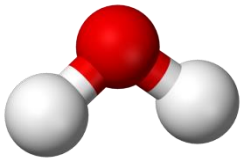
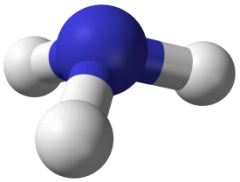
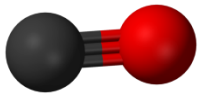
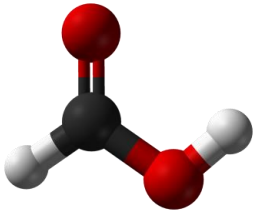
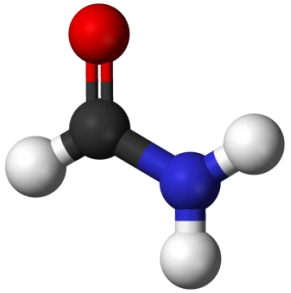


AMS and F. Saija, PNAS 111, 13768 (2014)

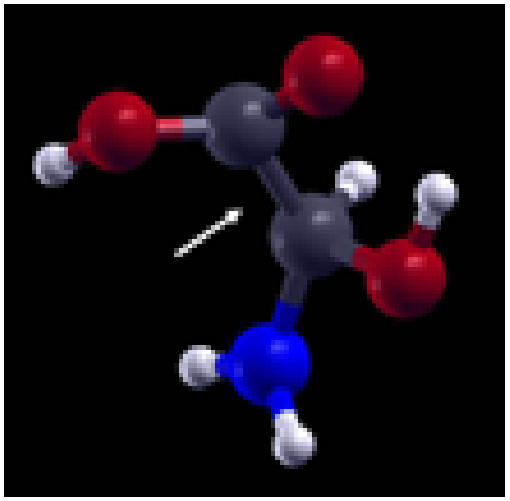
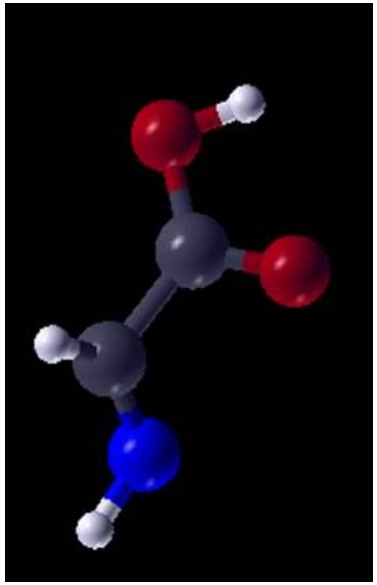
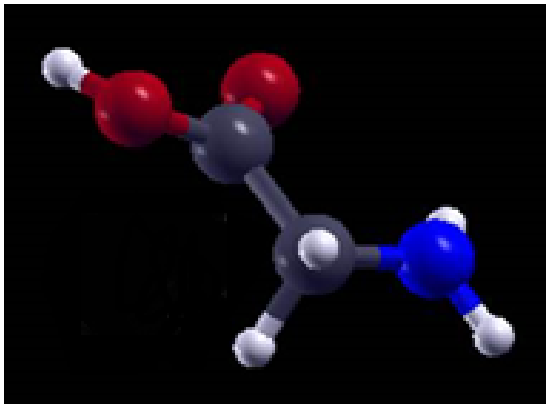
In silico Miller experiments

From formamide and formic acid to amino-acids

- Start: new molecules in strong fields

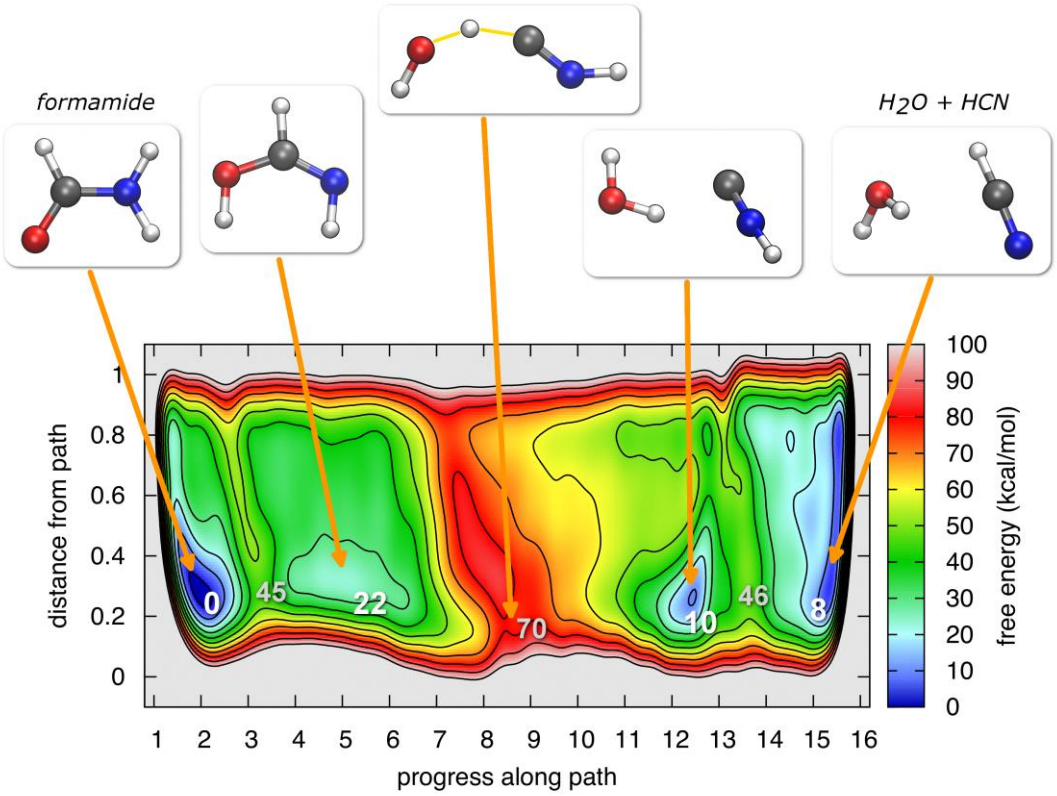
- … and finally glycine !!

AMS and F. Saija, PNAS 111, 13768 (2014)

The formamide controversy

- Formamide not detected in Miller experiments (gas phase)
- Gas-phase free-energy surface: comparable/favored

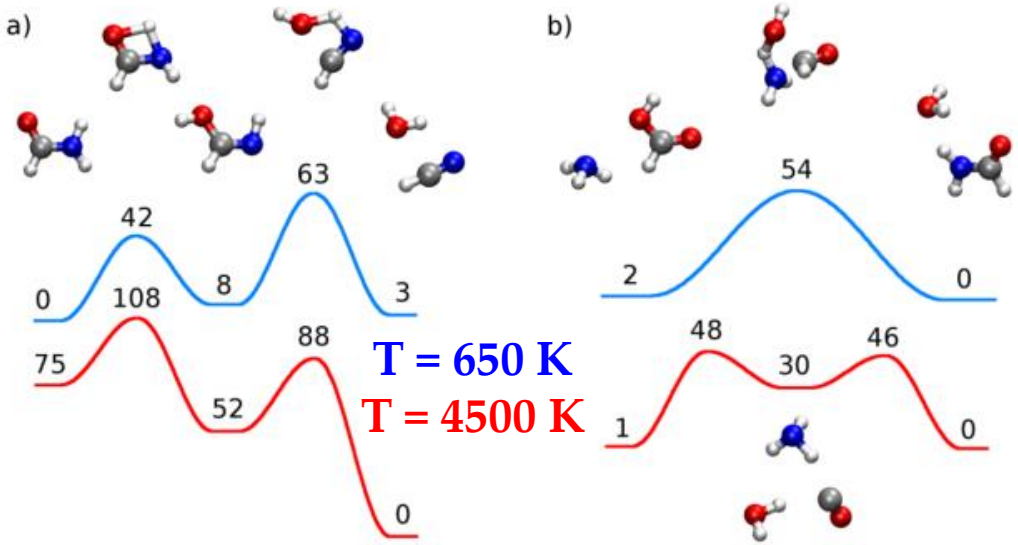


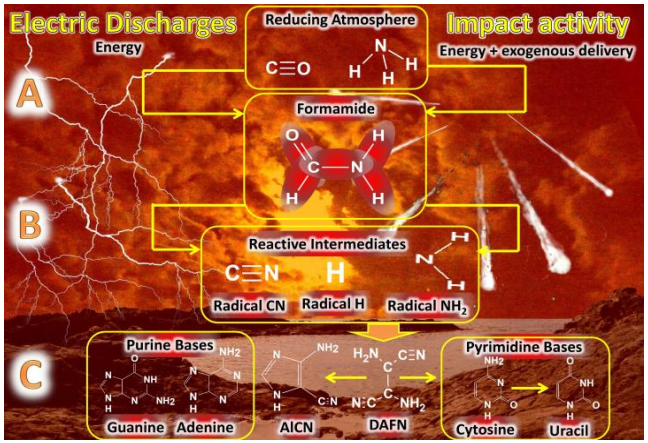
Bada and Cleaves, PNAS 112, E342 (2015)

A.M. Saitta, F. Saija, F. Pietrucci, F. Guyot, PNAS 112, E343 (2015)

Formamide gas chemistry

- Formamide not detected in Miller experiments (gas phase)
- Gas-phase free-energy surface: comparable/favored
- Favorable comparison to high-energy gas phase experiments

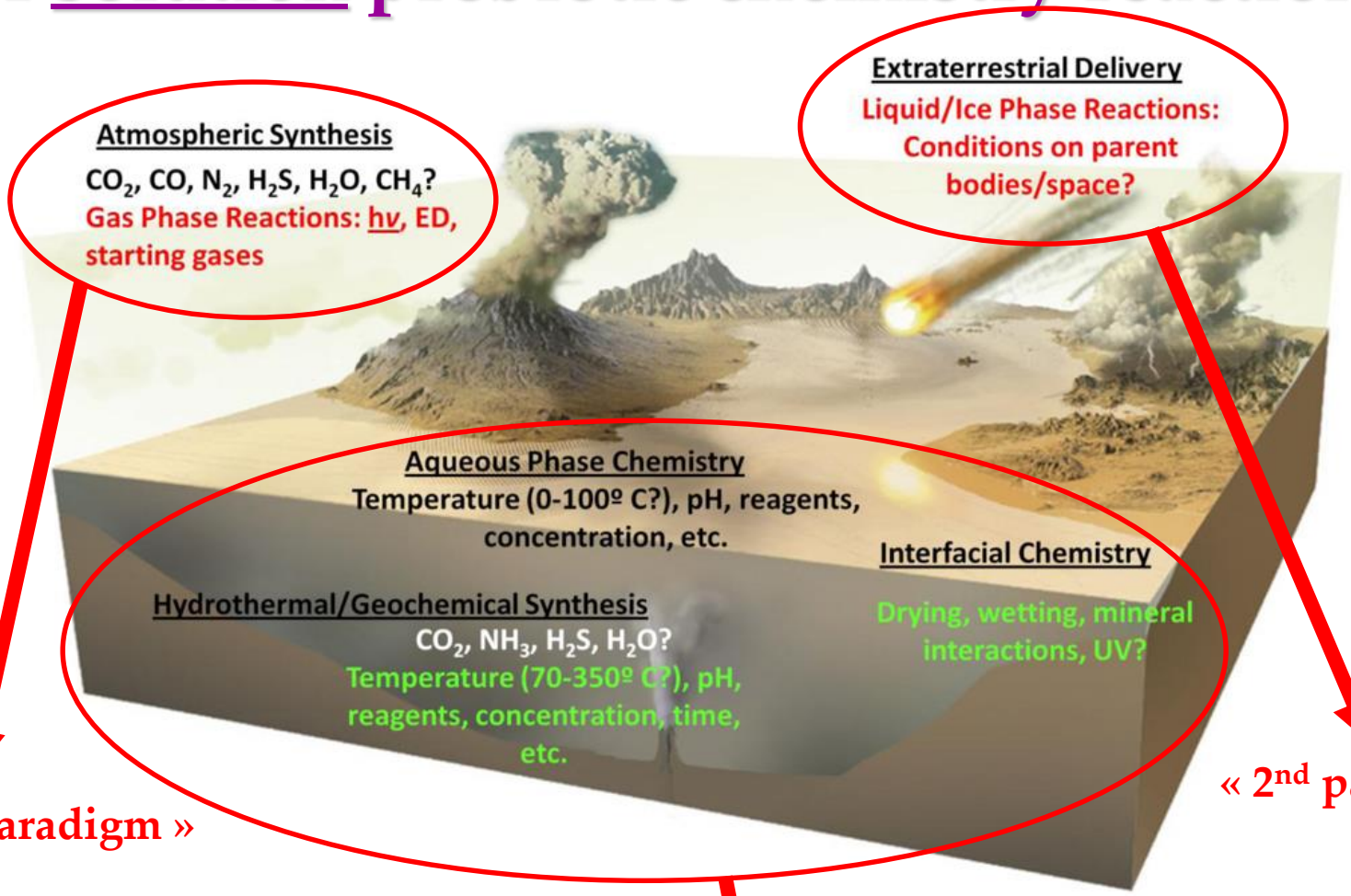




AMS, F. Saija, F. Pietrucci, F. Guyot, PNAS 112, E343 (2015)

M. Ferus, F. Pietrucci, AMS, et al. PNAS 114, 4306 (2017)

Thermodynamics (and kinetics) of solution prebiotic chemistry reactions



« 1st paradigm »

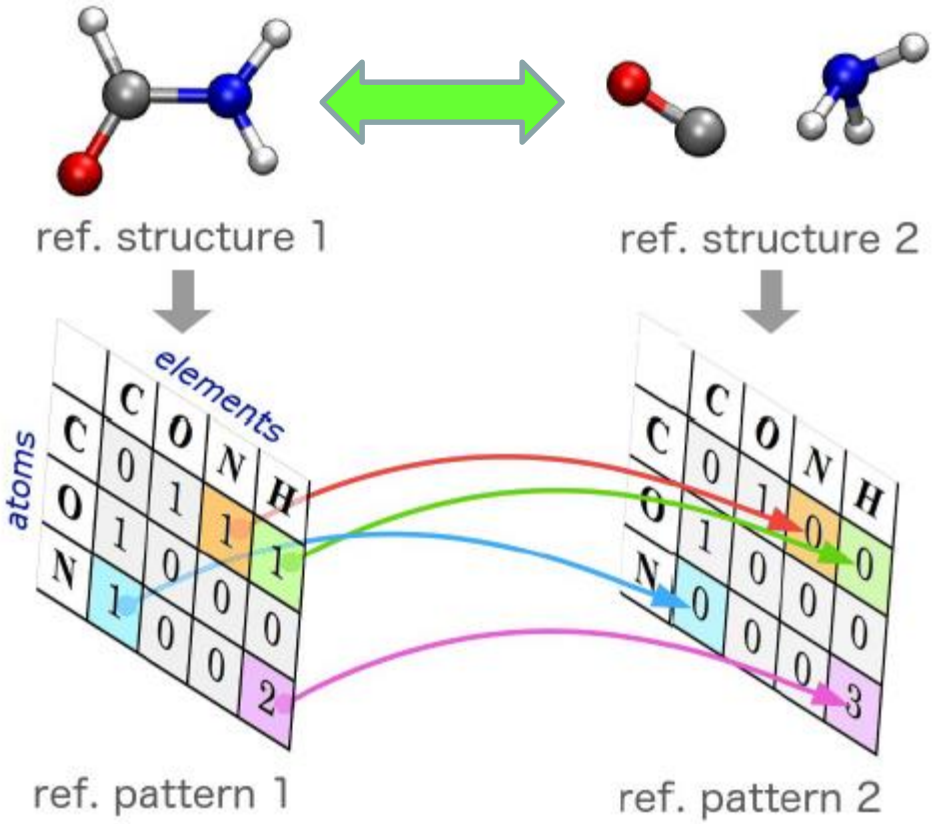
« 2nd paradigm »

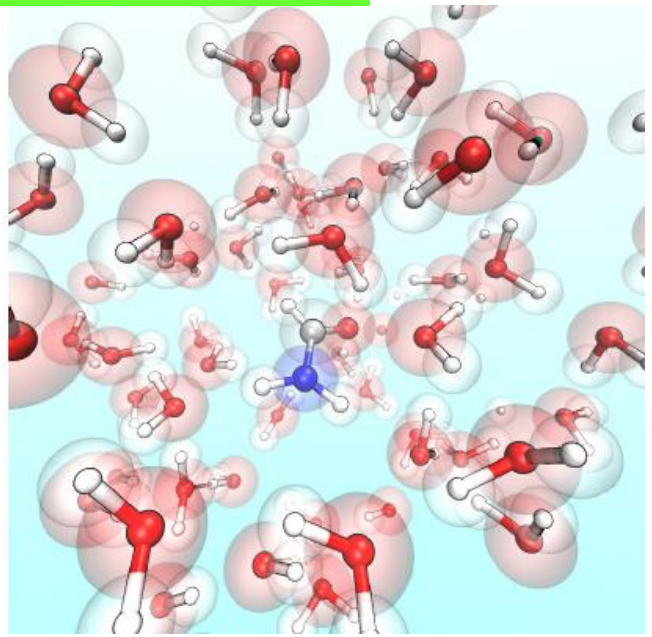
« 3rd paradigm »

New topology-based approach for *any-phase* transformation

- Topological amphibian definition of reaction coordinates

N atoms: 3N-dimensional configurational space!!

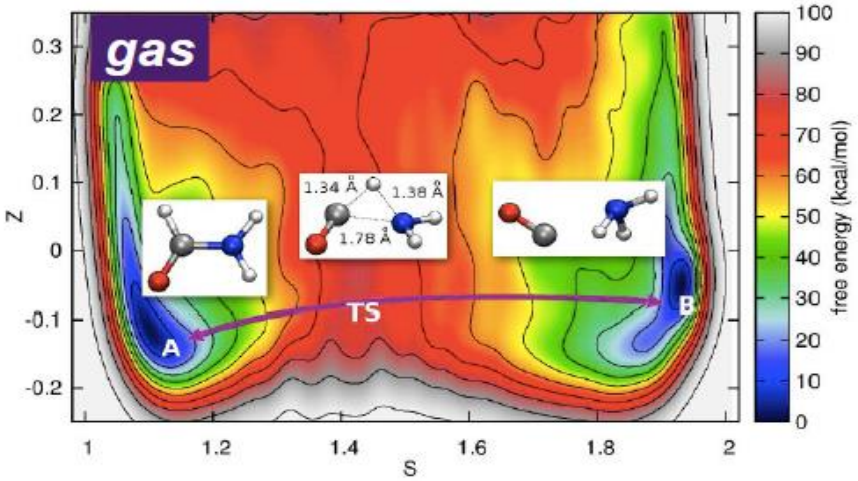




F. Pietrucci & A.M. Saitta, PNAS 112, 15030 (2015)

New topology-based approach for *any-phase* transformation

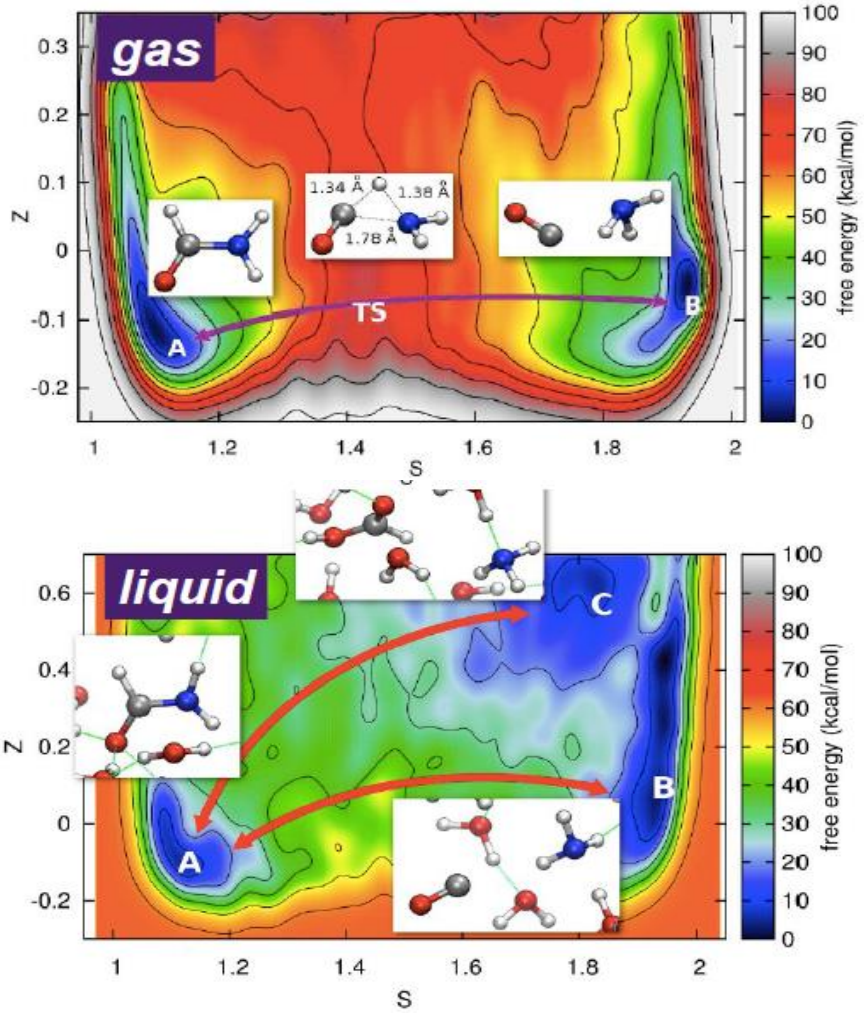
- Amphibian reaction coordinate space: gas phase



F. Pietrucci & A.M. Saitta, PNAS 112, 15030 (2015)

New topology-based approach for *any-phase* transformation

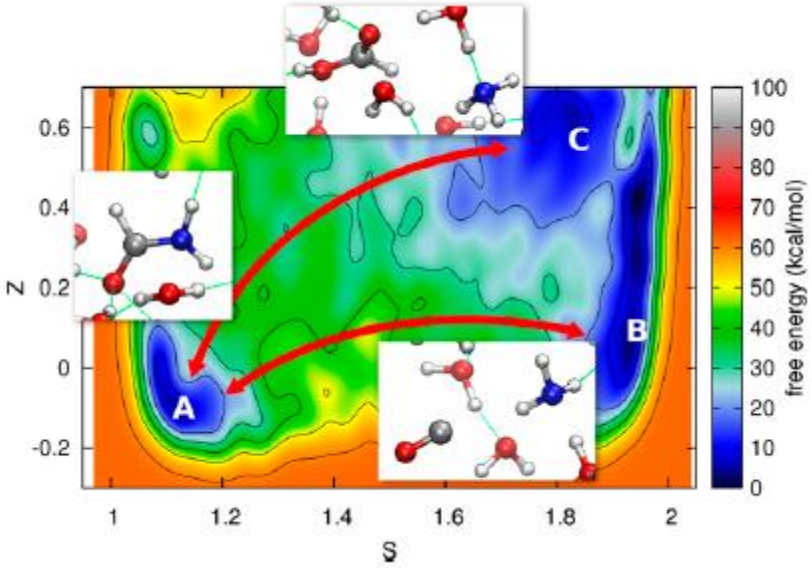
- Amphibian reaction coordinate space: condensed phase

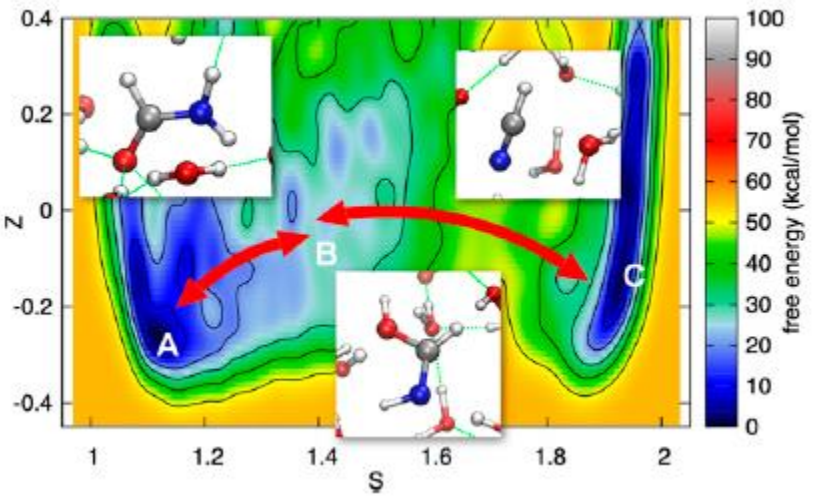


F. Pietrucci & A.M. Saitta, PNAS 112, 15030 (2015)

New method: formamide reaction networks and prebiotic scenarios

- Unbiased exploration of reaction pathways, quantitative determination of free energy landscapes





- Formamide in bulk prebiotic conditions slightly more stable than HCN: reconciling different scenarios?

- Identification of transition states, hints on kinetics

F. Pietrucci & A.M. Saitta, PNAS 112, 15030 (2015)

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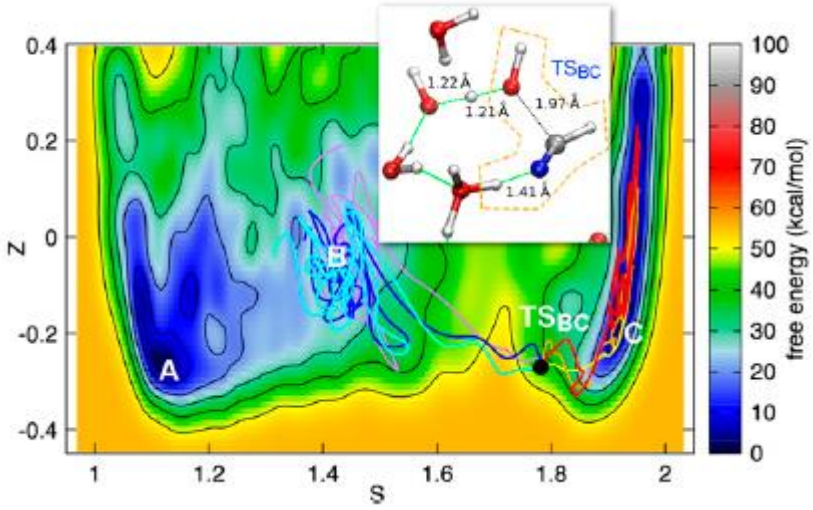
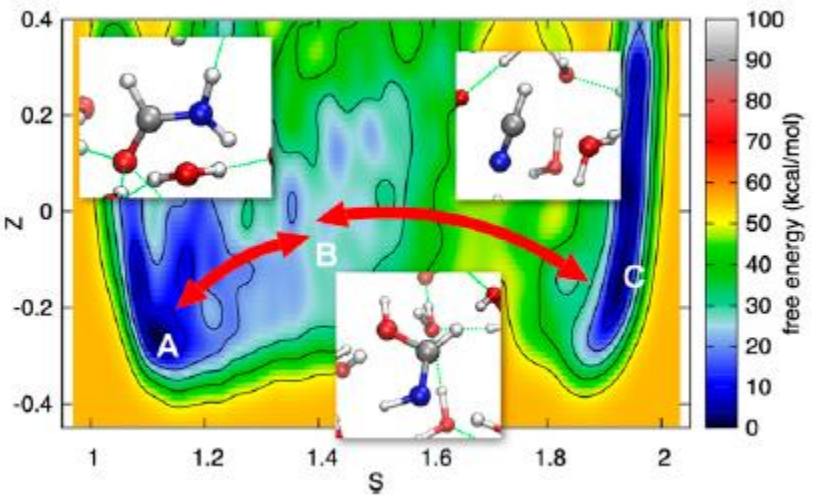




- Formamide in bulk prebiotic conditions slightly more stable than HCN: reconciling different scenarios?

- Identification of transition states, hints on kinetics

F. Pietrucci & A.M. Saitta, PNAS 112, 15030 (2015)

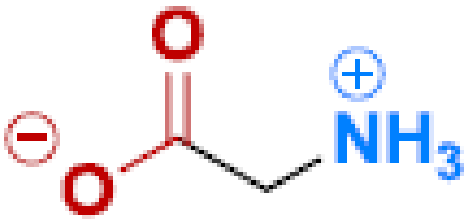
Beyond formamide: more complex prebiotic chemistry

- Amino acids

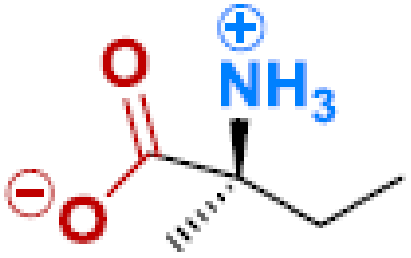
- (RNA) nucleotides

Amino acid meteoritic solution chemistry

- Deamination/decarboxylation of glycine (achiral) and isovaline (exhibiting the most enantiomeric excess)



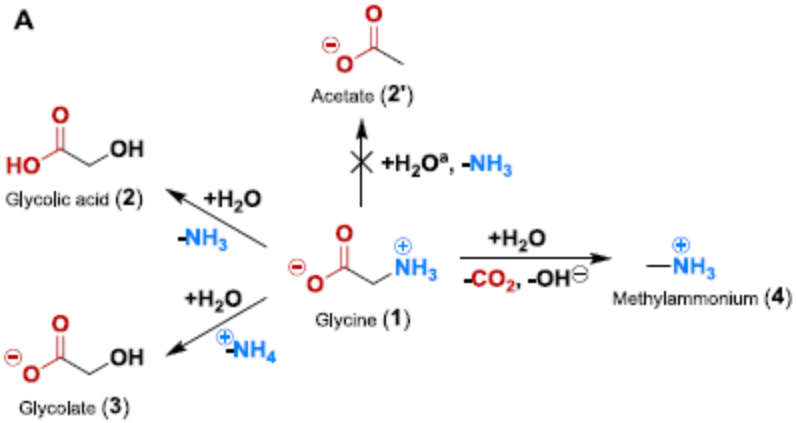
Glycine (**1**)

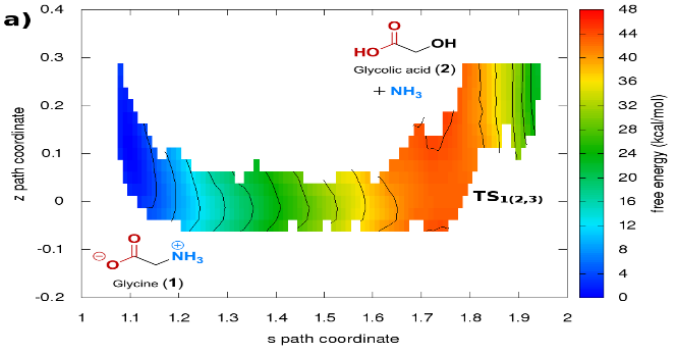


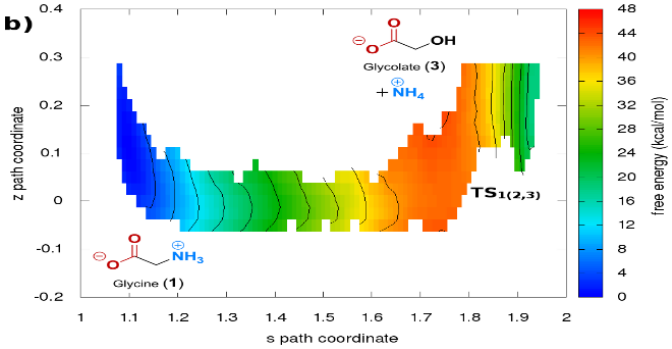
L-Isovaline (**5**)[b]

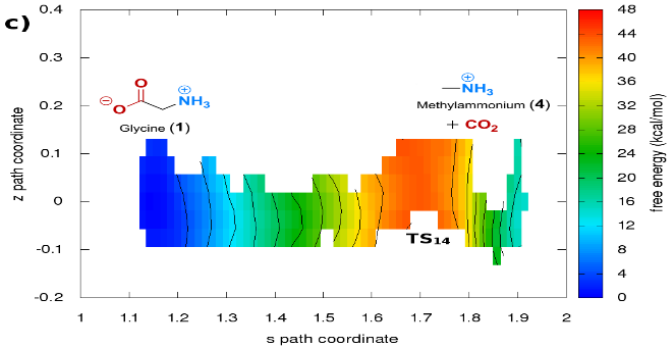
Amino acid meteoritic solution chemistry

❑ Deamination/decarboxylation of glycine (achiral) and isovaline (exhibiting the most enantiomeric excess)









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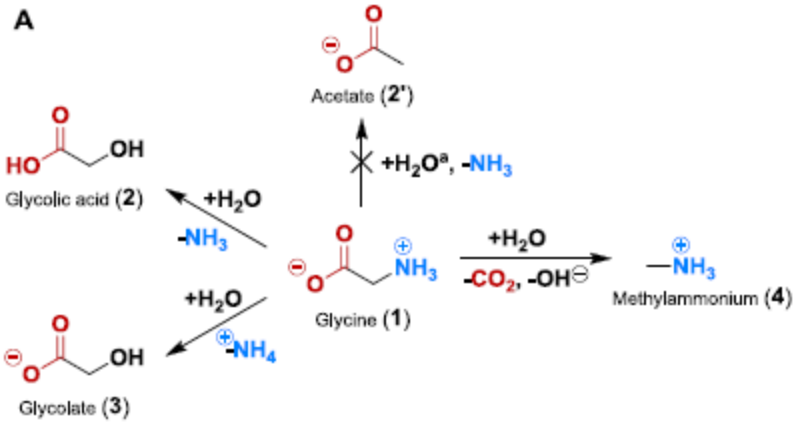
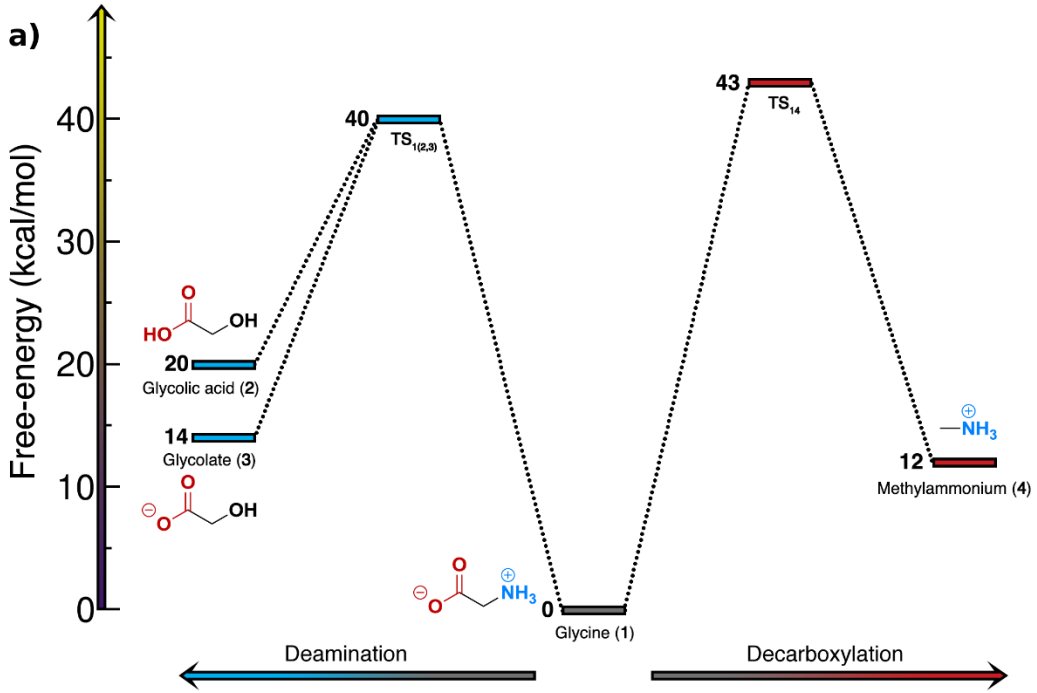
Amino acid meteoritic solution chemistry

❑ Deamination/decarboxylation of glycine (achiral) and isovaline (exhibiting the most enantiomeric excess)





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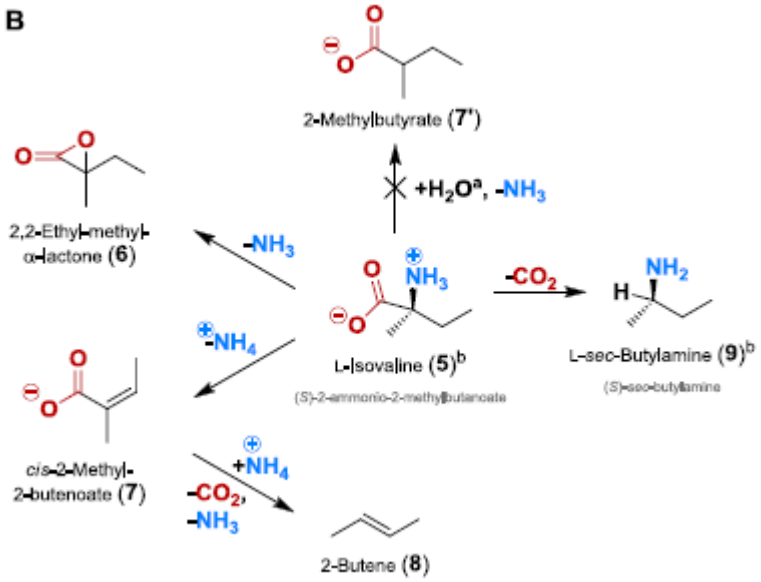

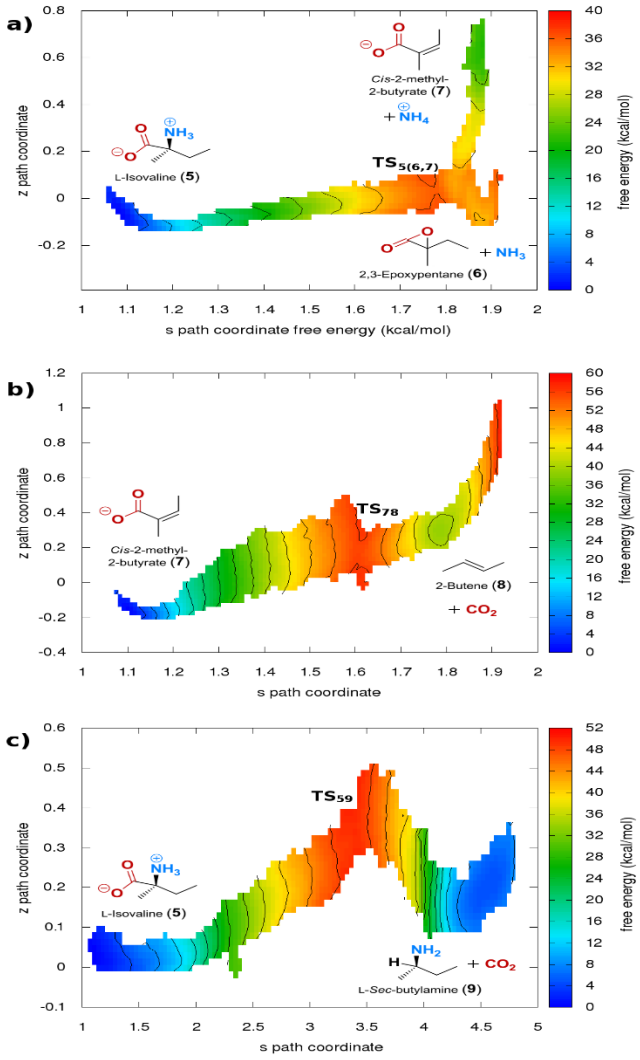

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NASA Goddard

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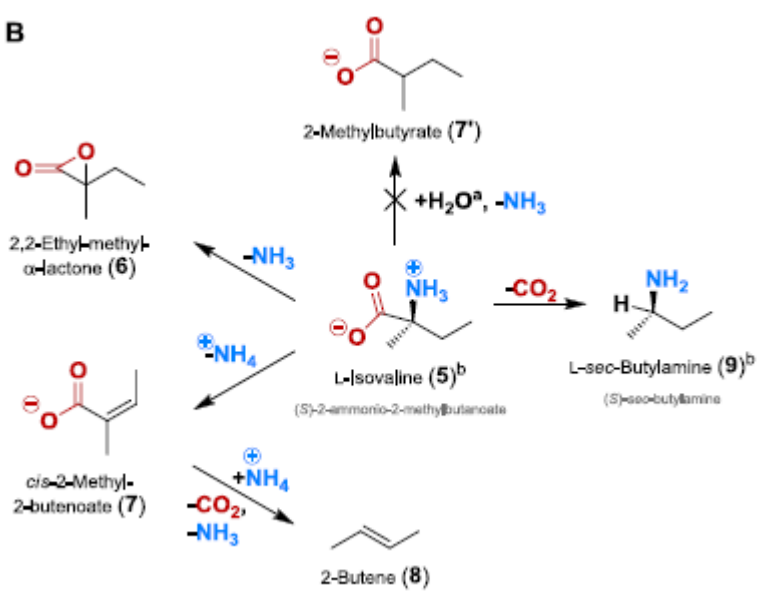
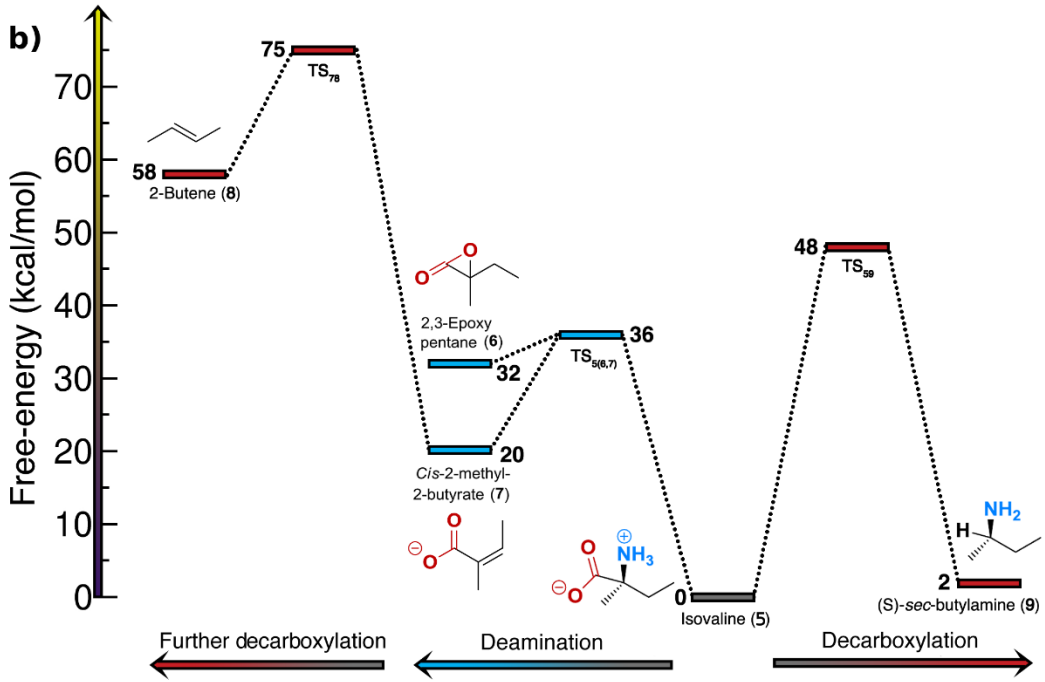


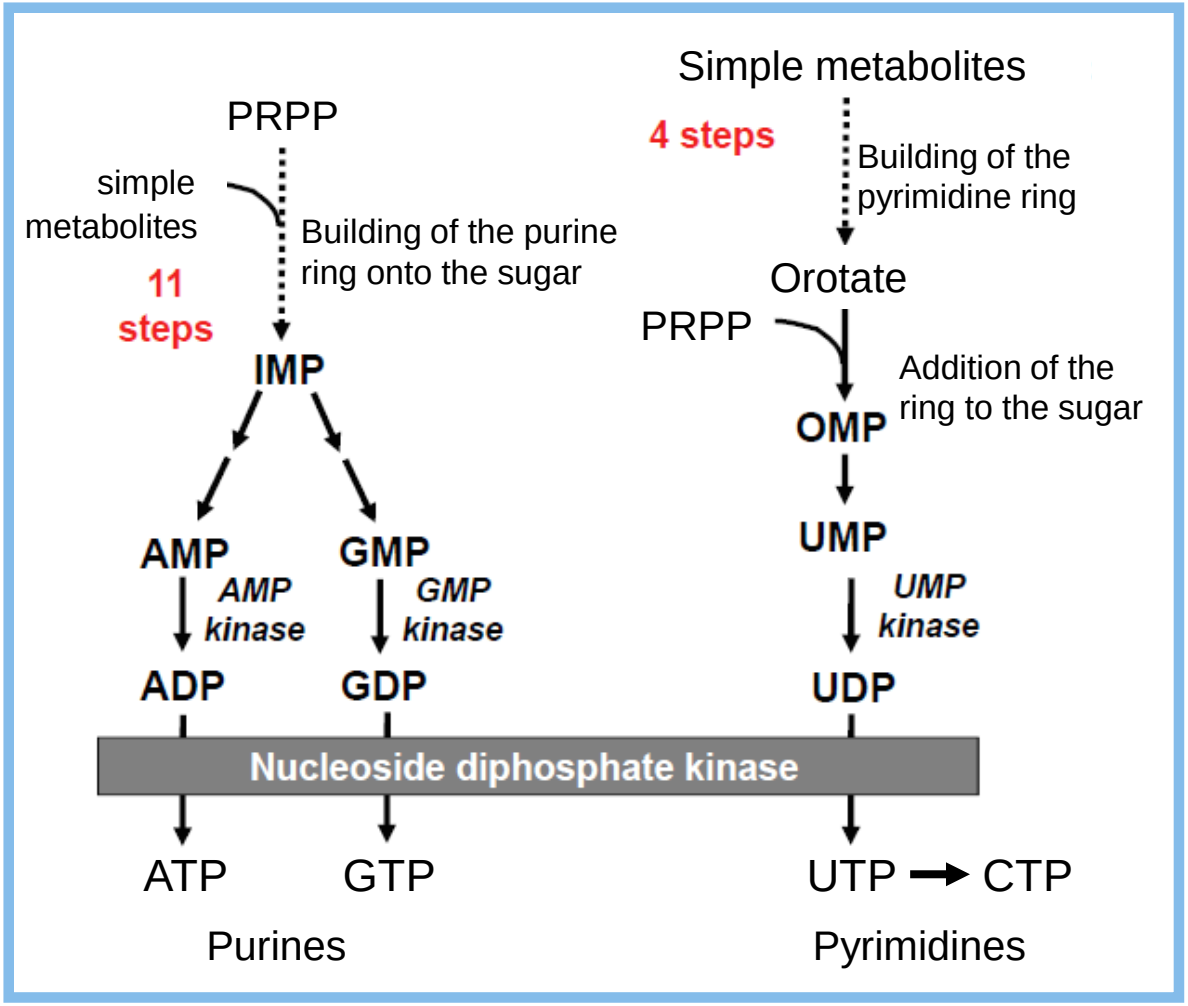


F. Pietrucci, J.C. Aponte, A. Perez-Villa, R. Starrr, J.E. Elsila, J.P. Dworkin & AMS, under review (2018)

RNA nucleotide chemistry

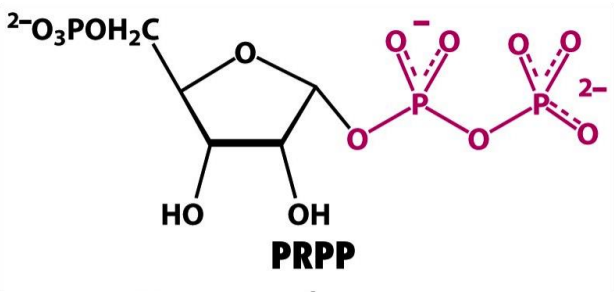
- "How do you make these bonds?"

de novo Nucleotide Synthesis



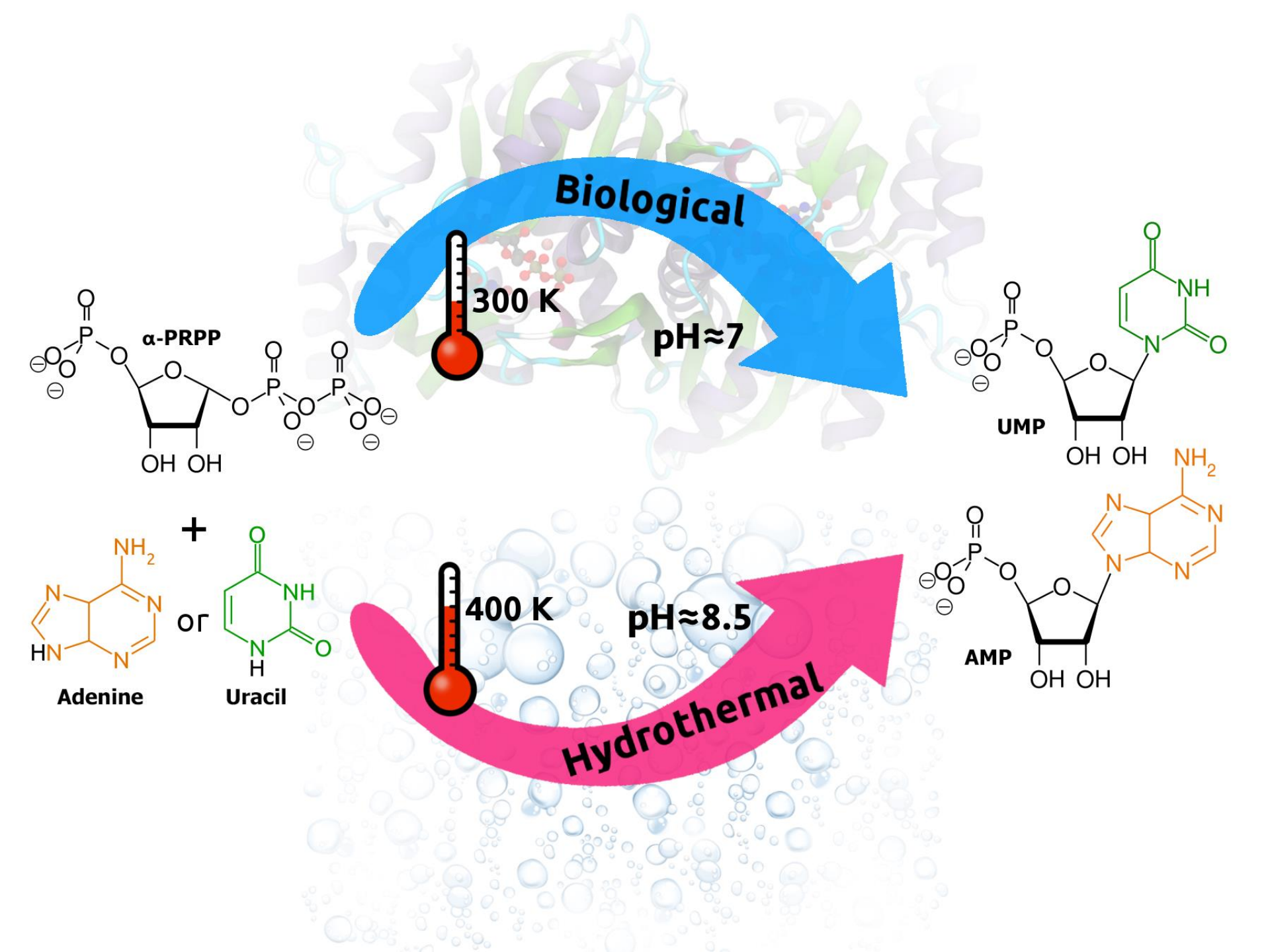
★Current living systems:

PRPP+N.base → Nucleotide



PRPP was also important in the abiotic environments?

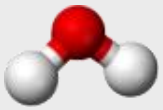
Georgelin et al. Angew Chem (2017)

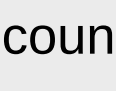

Biological
300 K
pH≈7
α-PRPP
UMP
+
or
Adenine
Uracil
400 K
pH≈8.5
Hydrothermal
AMP

Nucleotide in prebiotic conditions

Simulation box:

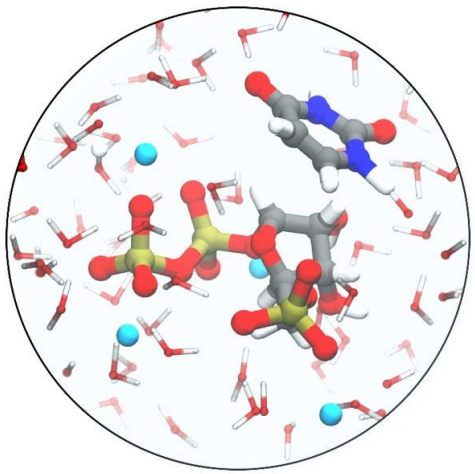
- About 380 atoms
  - ~110 explicit water molecules
  - 5 Na+ counter ions

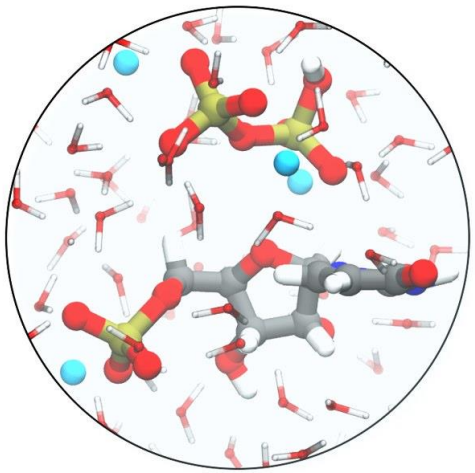




- 400 K, pH≈7

All explicit *and* ab initio





Conclusions

- ❑ Ab initio Miller experiments and ab initio prebiotic chemistry
- ❑ Formamide identified (again) as an important prebiotic chemistry precursor
- ❑ A topology-based description of reaction coordinates is a promising tool to study **thermodynamic plausibility** of prebiotic (or any other) reactions
- ❑ Free-energy surfaces and mechanisms of key **amino acids degradation and synthesis reactions** in plausible parent-body meteoritic conditions
- ❑ Free-energy surfaces and mechanisms of **RNA nucleotide spontaneous synthesis** in plausible early-Earth prebiotic conditions

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