5th Workshop of the Italian Astrobiology Society
«LIFE IN A COSMIC CONTEXT»

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K^+ *vs.* Na^+ Driving Force of Prebiotic Peptide Emergence

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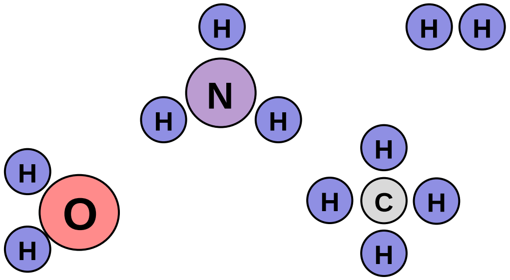
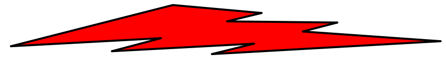
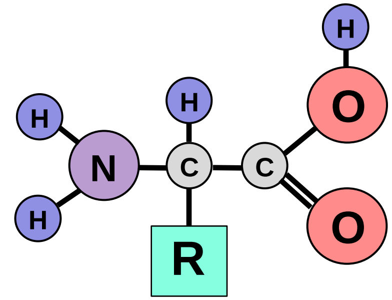
Russian Academy of Sciences

Inorganics→ Organic World





Discharge experiment
1953

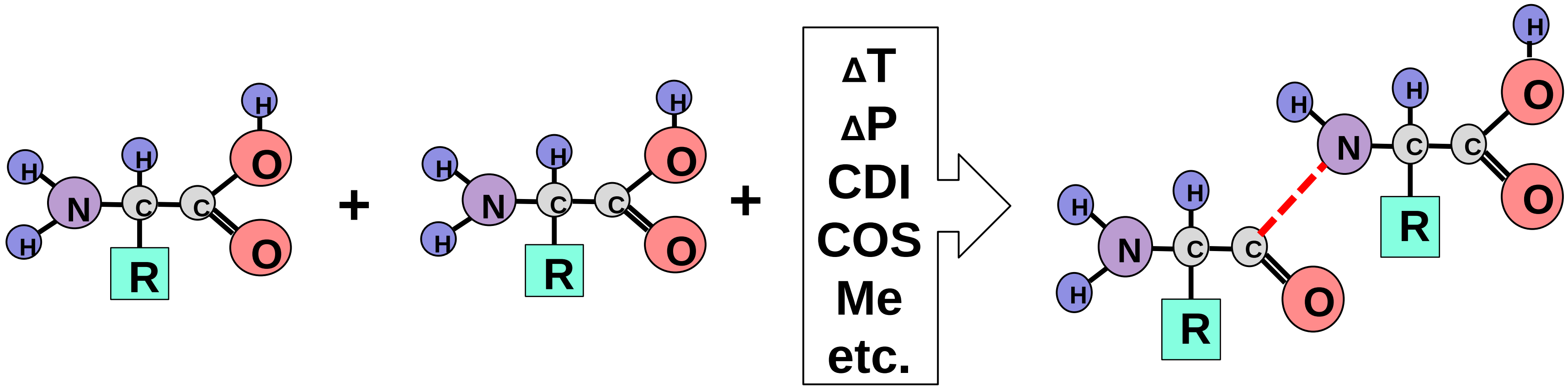


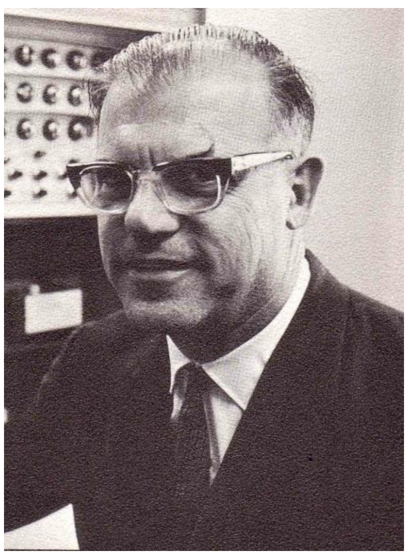
Alexander I. Oparin
1894 - 1980

Harold C. Urey
1893 - 1981

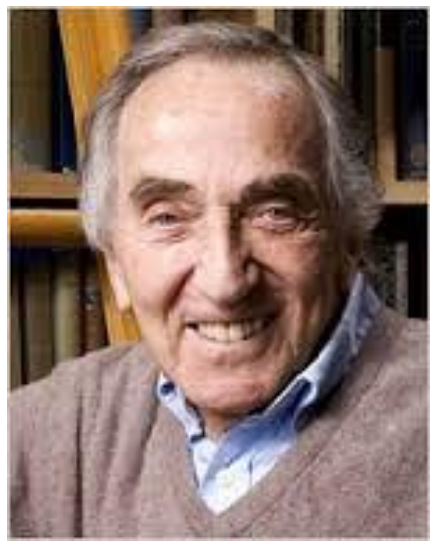
Stanley L. Miller
1930 -2007

Prebiotic Polymerization Problem





Sidney W. Fox
1912 - 1998



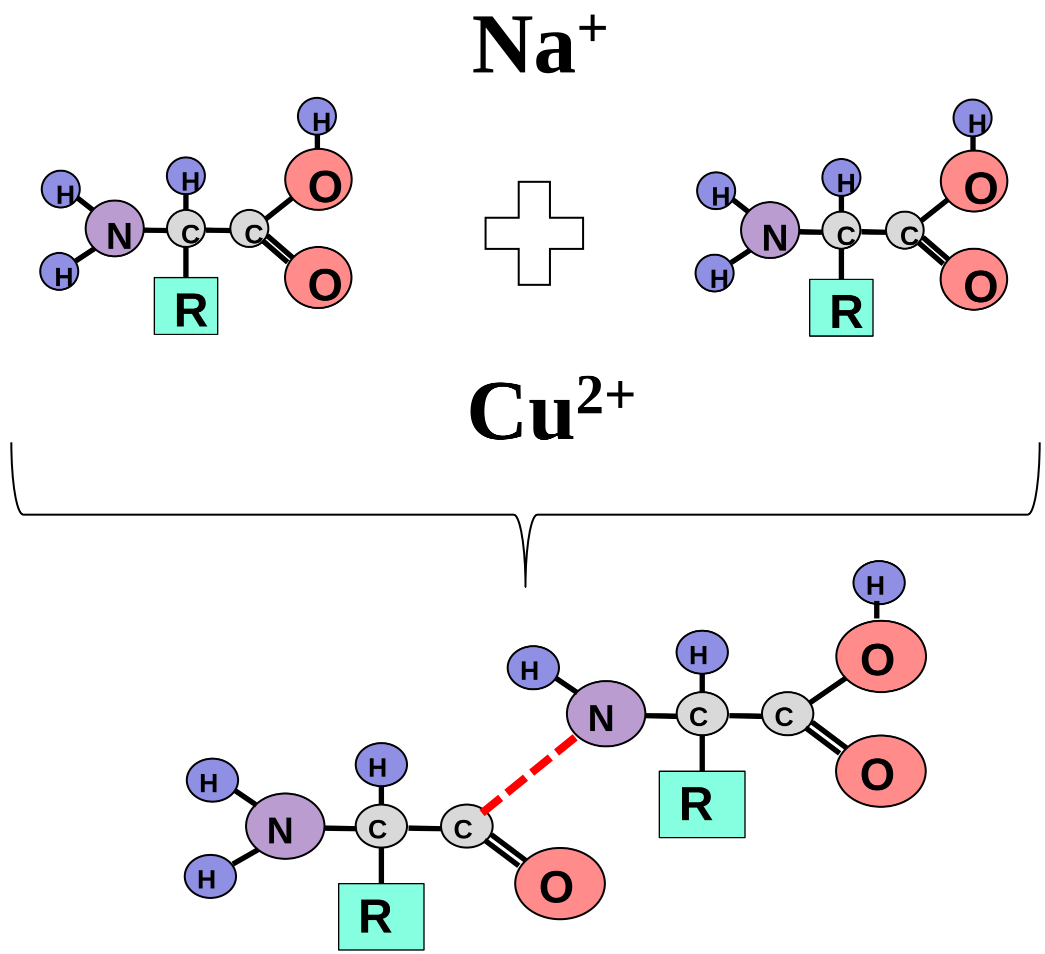
Leslie E. Orgel
1927 - 2007

Andre Brack
b. 1938

Salt-Induced Peptide Formation

Copper-Catalyzed

Bernd M. Rode
b. 1946



Analytical Sciences (1989)

Sodium vs. Potassium Contradictions

Yuri Natochin
b. 1932

A commonly believed thoughts:

First protocell could have emerged in salty seawater

Seawater:

K^+ ~ **0.01** mol/L Na^+ ~ **0.46** mol/L

Cell cytoplasm (all "modern" living cells):

K^+ ~ **0.10** mol/L Na^+ ~ **0.01** mol/L

Natochin's hypothesis:

First protocell could not emerge in NaCl solutions, but in KCl

Paleontological Journal (2005)

Sodium vs. Potassium Contradictions

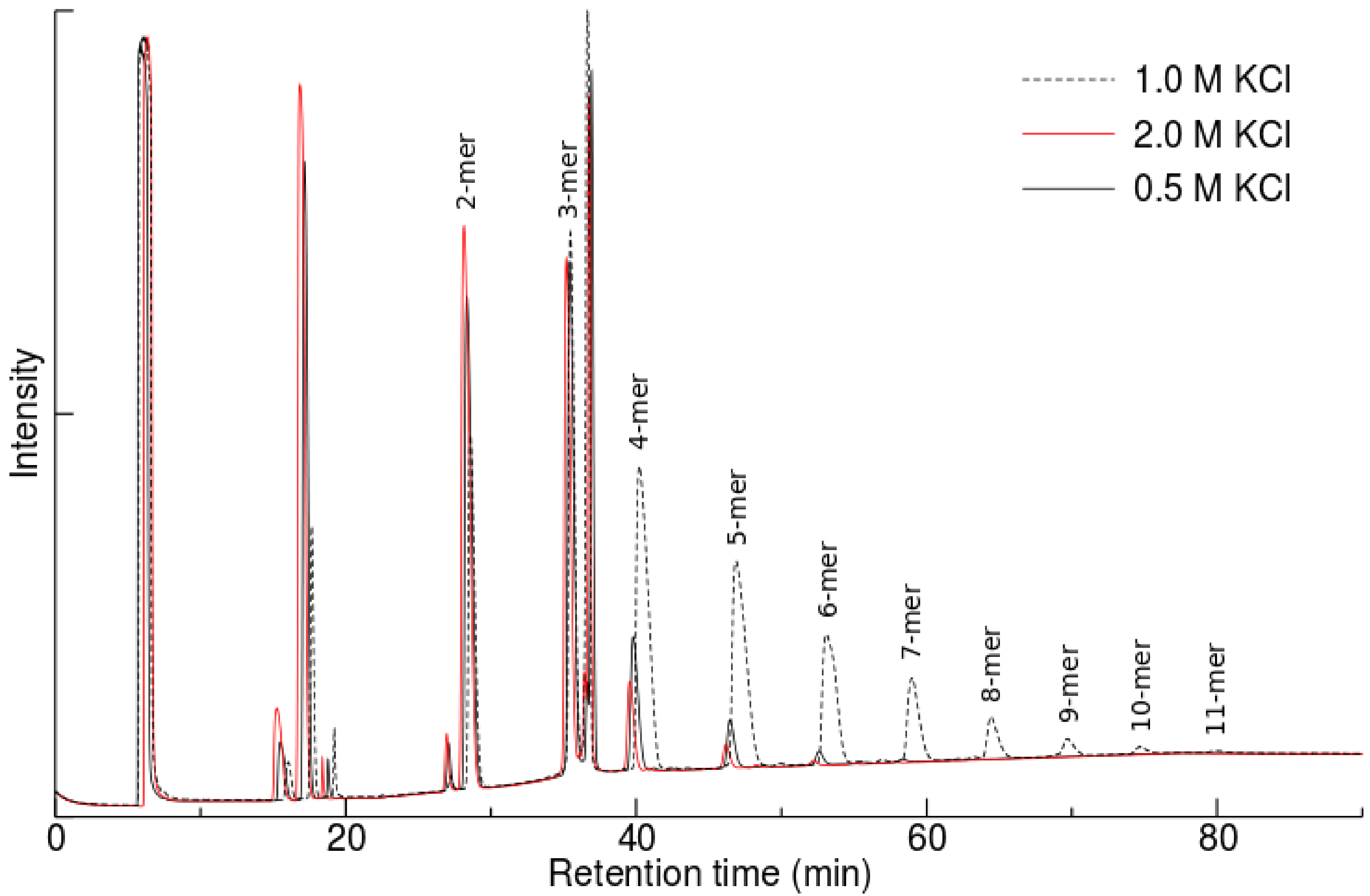
Physical-chemical properties

	Atomic weight	Ionization Energy, eV	Ionic radius, Å	Diffusion coefficient, $\times 10^{-5}$ cm^2/sec
Na^+	22.9897	5.1391	0.95	1.334
K^+	39.0983	4.3407	1.33	1.957

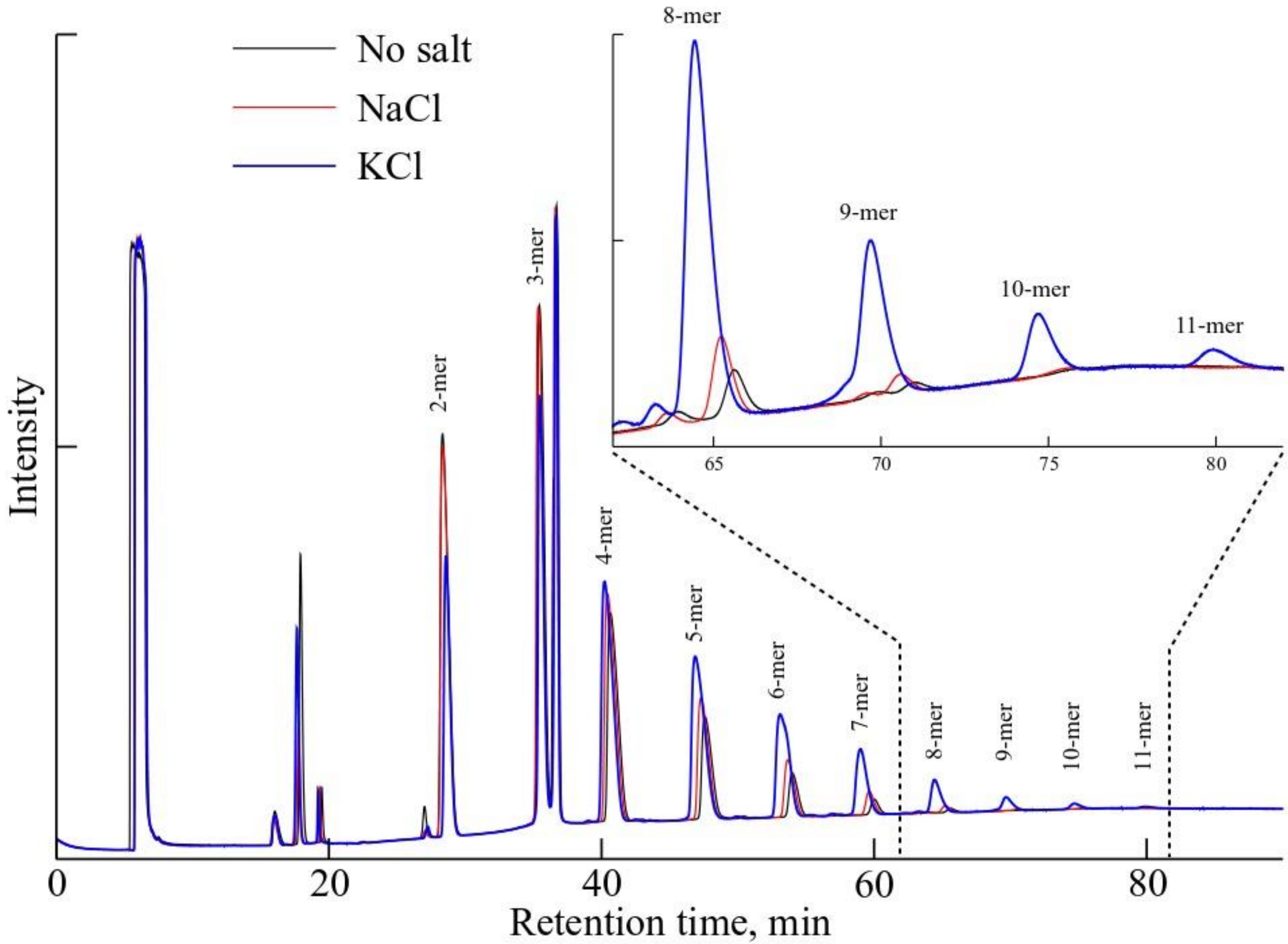
Biological properties

	DNA amplification	Ribosomal peptide synthesis	Active transport across cell membrane
Na^+	inhibition	decreasing	outside
K^+	facilitation	increasing	inside

Na^+- or K^+-mediated (0.5M, 1M, 2M) CDI-induced L-Glu oligopeptide formation



K$^+$ and Na$^+$ in the CDI-induced L-Glu oligopeptide formation: *chromatograms*



Dubina M. et al. OLEB (2013)

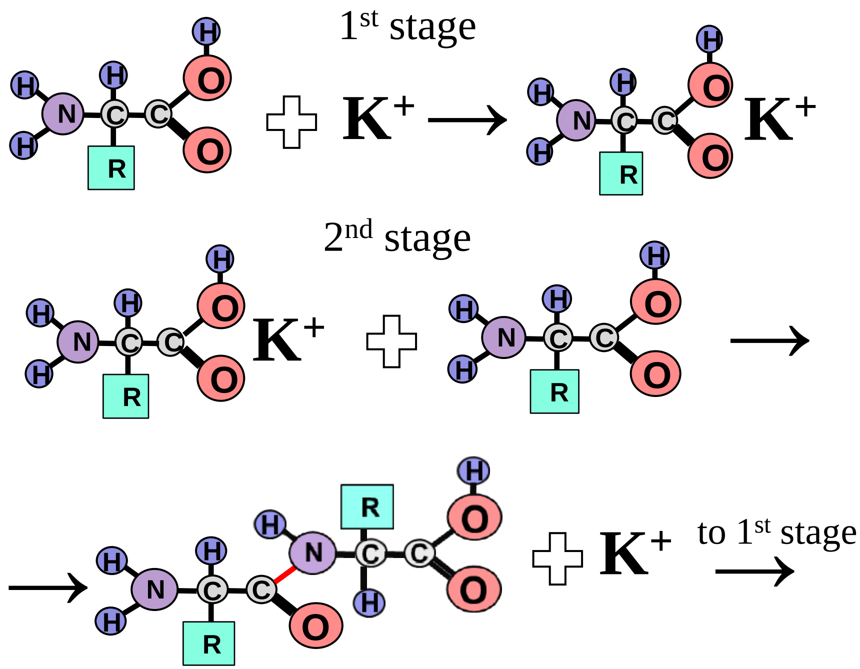
K^+ predominates over Na^+ in the CDI-induced L-Glu oligopeptide formation: *HPLC-MS/MS*

N_{res}	L-Glu oligs + 1.0 M NaCl			L-Glu oligos + 1.0 M KCl		
	MS $[M+H]^+$ ($[M+Na]^+$)	HPLC		MS $[M+H]^+$ ($[M+K]^+$)	HPLC	
	Found, Da	Peak area	Relative area, %	Found, Da	Peak area	Relative area, %
2	277.101 (299.085)	963	**100.0**	277.103 (315.089)	534	**100.0**
3	406.146 (428.127)	1060	**110.1**	406.146 (444.101)	709	**132.8**
4	535.187 (557.172)	770	**80.0**	535.187 (573.145)	833	**156.0**
5	664.230 (686.212)	408	**42.4**	664.231 (702.187)	651	**121.9**
6	793.272 (815.252)	174	**18.1**	793.272 (831.229)	411	**77.0**
7	922.315 (944.285)	61	**6.3**	922.315 (960.273)	223	**41.8**
8	1051.352	18	**1.9**	1051.352 (1089.311)	99	**18.5**
9	–	4	**0.4**	1180.394	45	**8.4**
10	–	–	–	–	17	**3.2**
11	–	–	–	–	6	**1.1**

Terterov I. et al. Rapid Communications in Mass Spectrometry (2014)

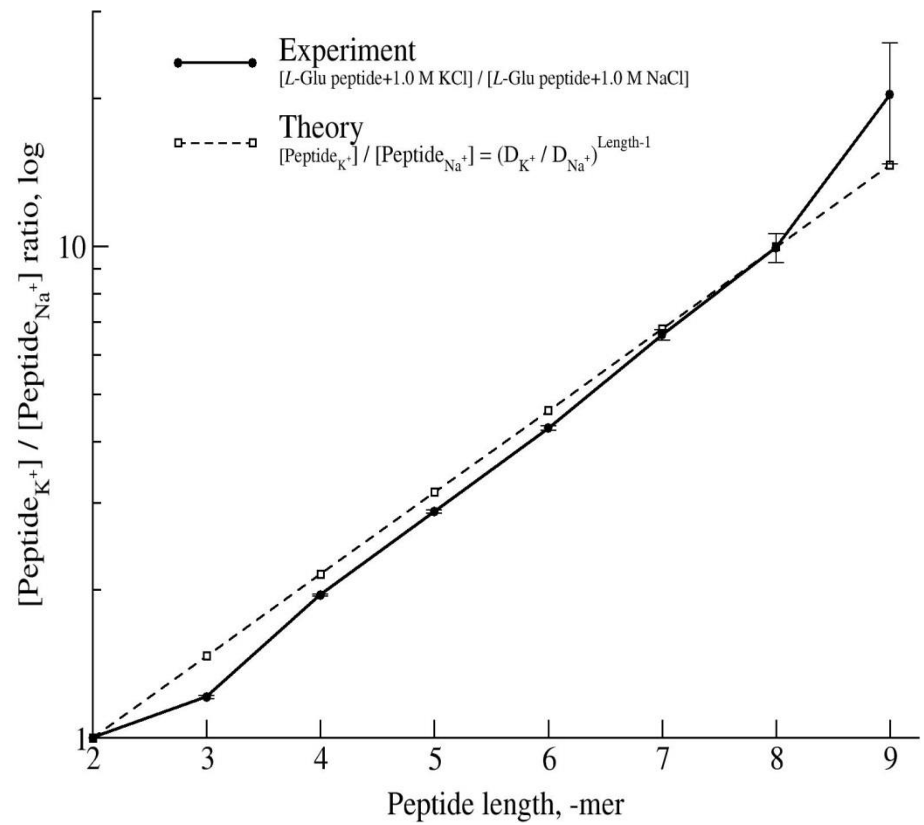
Physical-chemical model of K⁺ vs. Na⁺ mediated oligopeptide formation

Quasi-chemical nucleation model



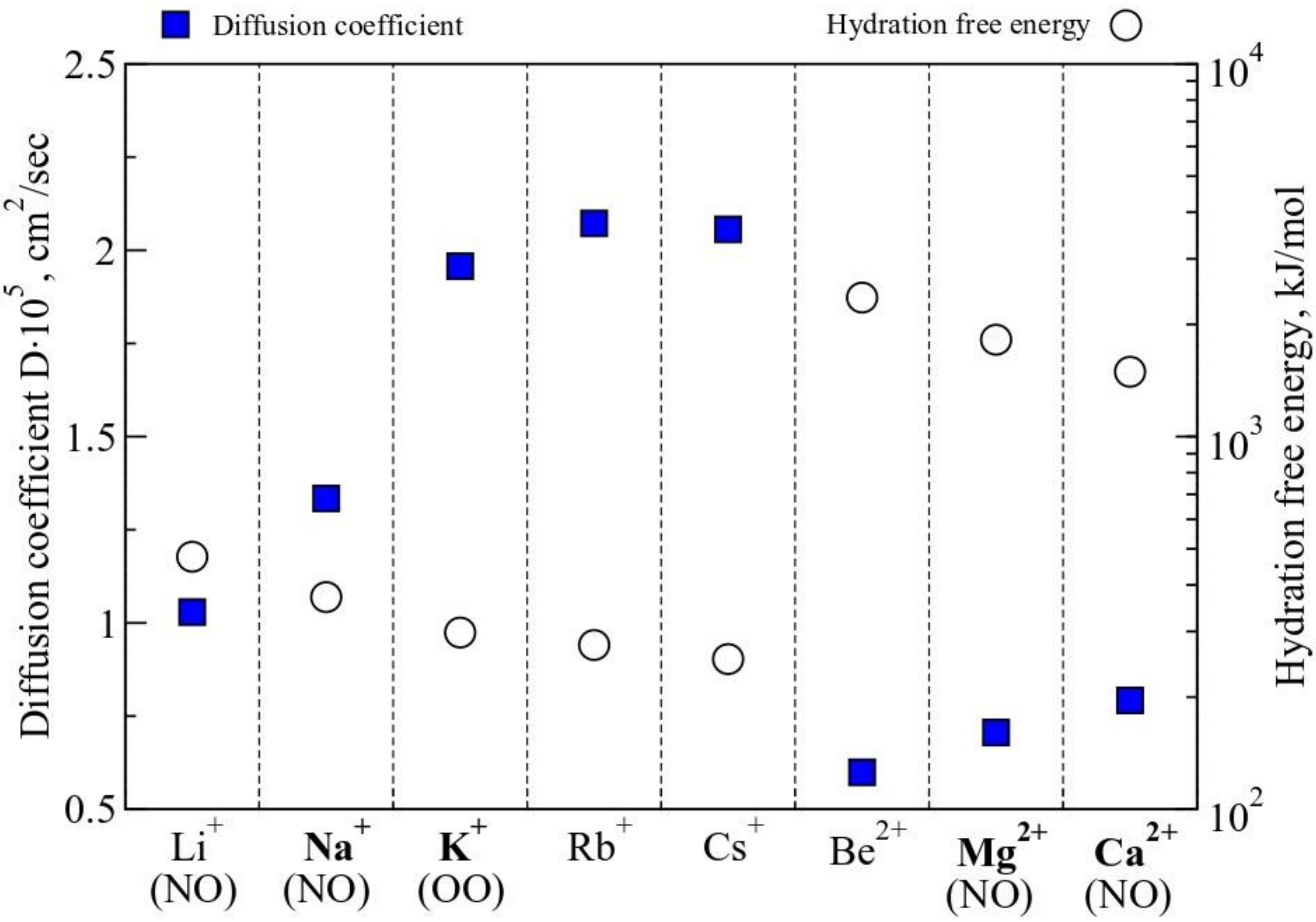
Equilibrium solution

$$\frac{[Peptide_K]}{[Peptide_{Na}]} = \left(\frac{D_K}{D_{Na}}\right)^{LENGTH-1}$$



Dubrovskii V. et al. Journal of Chemical Physics (2013)

Metal ion diffusion, hydration and coordination to amino acids



Conclusion

K^+ predominates over Na^+ in the prebiotic formation of peptides

The following conditions could have enforced the first step in the chemical evolution of self-assembling organic molecules:

(1) aqueous media contained the building blocks of organic matter and positive inorganic ions, which are *geochemically abundant*

(2) binding reversibility to amino acids and the moderate hydration energy of the ions in liquid phase at 0-100 ˚C

(3) high diffusion and *specific ion coordination* to oxygen atoms of amino acids in zwitterion form, which enhances the ion-dependent yields of oligomerization

K^+ complies with all the above-listed requirements, which is unique in contrast to other mono- and divalent metallic ions

Thanks to the project team!

Sergey Vyazmin
Chemistry

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Chemistry

Ivan Terterov
Mathematics

Yuri Natochin
Physiology

Yuri Trushin
Physics

Maxim Lubov
Physics

Vladimir Dubrovskii
Physics

Igor Eliseev
Physics

Thoughts and on-going research

The emergence of the ancient metabolic and information systems of the protocells could have occurred in potassium-rich habitats.

Thus it seems evident that all the living cells would have evolved to preserve the initial ion gradients by using energy-dependent membrane pumps in sodium aqueous media (seawater).

If the same predominance of K^+ over Na^+ in CDI-induced polymerization of all amino acids?

Is SIPF without Cu^{2+} (with K^+ only) possible?

What were terrestrial or extra-terrestrial sources of potassium-rich water reservoirs on prebiotic Earth?