

Phosphorylation of prebiotic precursors on the early Earth

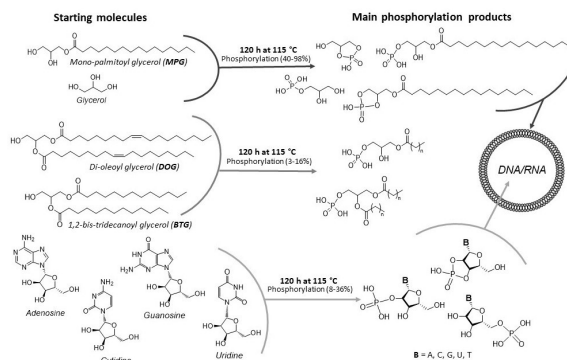
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Organic phosphate esters are central to the functioning and regulation of nucleic acids, the energy-carrying molecule ATP, and phospholipids as the main precursors of cell membranes. The conventional wisdom is that phosphorylation of alcohols occurred on the early Earth during wet-dry cycles in the presence of non-volatile reduced nitrogen compounds [1]. Intense impact bombardment was the main source of phosphorus in minerals that would have subsequently oxidized at the early Earth surface [2].

Although phosphorus has been known to be essential for life, there is not yet a conclusive answer about its implication in prebiotic enzyme-free reactions on the early Earth. How does phosphorylation that is thermodynamically unfavourable in water [3] result in the spontaneous formation and polymerization of prebiotic precursors? The key is using a "condensing" agent that takes away water and becomes the driving force for phosphorylation [4]. Another challenge is involving naturally phosphorous-containing minerals that are characterized by low water solubility and difficulty of using prebiotically plausible early Earth's material [3].

We conducted experiments varying starting molecules – glycerol and its derivatives, nucleosides; condensing agents – urea, cyanamide and carboxamides; and phosphorus sources – inorganic model phosphates – orthophosphate with different protonation states, thiophosphate, and cyclic trimetaphosphate; and natural prebiotically plausible minerals including vivianite, struvite.

We conclude that phosphorylation of prebiotic precursors occurs with relatively high yields even under the harsh and dry conditions of early Earth (scheme 1). The presence of a condensing agent is mandatory in reactions with single-long carbon-chain glycerol derivatives such as mono palmitoyl glycerol (MPG) or nucleosides, and an excess of the condensing agent increases reaction yields. The next step is the investigation of the studied reactions under hydrothermal conditions that could have prevailed on the early Earth and ultimately the search of favourable conditions for the spontaneous polymerization of abiotic phosphorylated prebiotic precursors, such as those obtained in the present study.

[1] M. Pasek et al, (2017), *Chemical Geology*, 475.

[2] S. J. Mojzsis et al, (2001), *Nature*, 409, 178.

[3] J. Hao et al, (2020), *Geochimica et Cosmochimica Acta*, 280.

[4] M. Fiore et al, (2016), *Life* 6, 17