



A role for phosphorus redox in emerging and modern biochemistry

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Phosphorus is a major biogeochemical element controlling growth in many ecosystems. It has presumably been an important element since the onset of life. In most chemical and biochemical considerations, phosphorus is synonymous with phosphates, a pentavalent oxidation state that includes the phosphate backbone of DNA and RNA, as well as major metabolites such as ATP. However, redox processing of phosphates to phosphites and phosphonates, and to even lower oxidation states provides a work-around to many of the problems of prebiotic chemistry, including phosphorus's low solubility and poor reactivity. In addition, modern phosphorus cycling has increasingly identified reduced P compounds as playing a role, sometimes significant, in biogeochemical processes. This suggests that phosphorus is not redox-insensitive and reduced P compounds should be considered as part of the phosphorus biogeochemical cycle.

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Introduction

The element phosphorus is part of a suite of major biochemical elements, often termed 'CHONPS' for carbon, hydrogen, oxygen, nitrogen, phosphorus, and sulfur. Within this group, phosphorus is unique in that there exists no significant volatile P gas (although the gas phosphine, PH_3 , has been recognized as a potential player in the phosphorus cycle [1]), and terrestrial redox reactions of the element have historically been considered to be limited to the lab of the synthetic chemist [2^{**}], though the astrochemist is not similarly bound [3,4]. In contrast, redox chemistry drives the biogeochemical cycles of the other major elements, and volatile phases are the norm for

most of them (e.g. through photosynthesis and nitrogen fixation).

Within modern life, phosphorus is a key part of nucleic acids as it serves as the phosphate backbone of DNA and RNA, plays a critical role in metabolism as ATP and similar coenzymes and transfers chemical energy, and supports cellular structure as phospholipids [5]. These roles are conserved across all domains of life, and indicate a role for phosphorus in antiquity. Given the importance of phosphorus to biochemistry, it seems plausible that phosphorus played a role in the very earliest stages of life or even at life's onset.

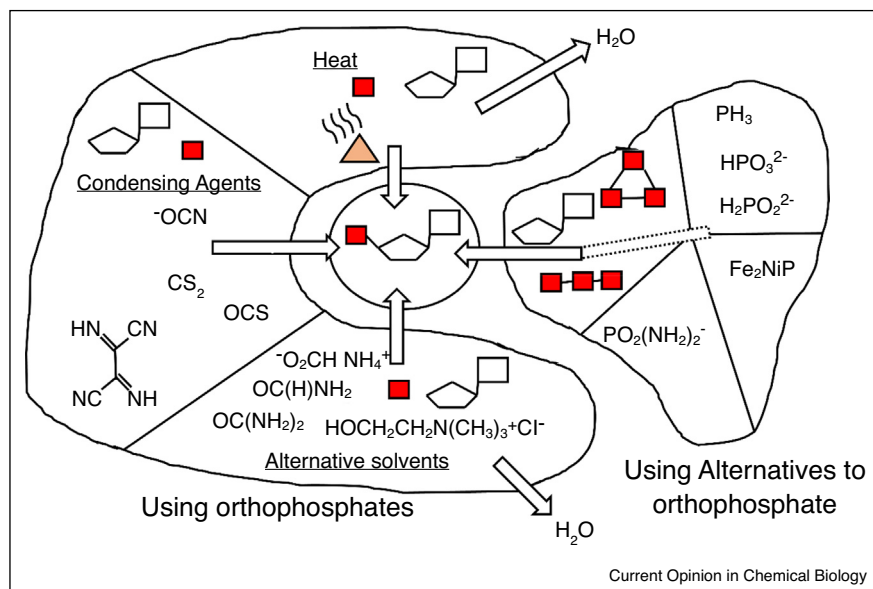
Phosphorus in the origin of life

Before the onset of modern enzymatic biochemistry, the first biomolecules had to arise from abiotic processes, such as the Miller-Urey process [6,7], formose chemistry [8], and HCN polymerization [9]. Phosphorylated molecules, were they present, would have had to have come ultimately through the reaction of a mineral of some sort—as effectively all phosphorus originates from minerals—with an organic substrate.

Therein lies the most significant problem with prebiotic phosphorylation: unlike the other biogenic elements, there is no major volatile form (limiting gas-phase reactions such as those suggested by Miller and Urey [7]), and redox reactions are considered rare for phosphorus. Hence phosphates are generally poorly reactive, and because most phosphorylation reactions release water in an aqueous solvent, phosphorylation is thermodynamically unfavored. This coupled with the poor solubility of phosphate minerals has led origins of life researchers to propose that prebiotic chemistry is confounded by a 'Phosphorus Problem' [2^{**},10,11]. Phosphorylation of organics ultimately must take place via a dehydration reaction, and in most cases necessitate higher concentrations of phosphate than would be possible compared with phosphate from early phosphate mineral dissolution. It is hence hard to envision such conditions in an early ocean.

This problem has been addressed through four main routes (Figure 1) in the literature: by heating, use of condensing agents, condensed phosphates, and alternative solvents [2^{**}]. Each of these has its advantages, and some have significant problems. Heating [12,13] can cause degradation of organics [14], and most must be heated above 100 °C to promote condensation. Condensing agents [15] are those compounds that promote the

Figure 1



Prebiotic phosphorylation routes explored in prior work. The goal molecule shown here is a nucleotide, with phosphate shown as the red rectangle. Most phosphorylation routes utilize phosphate as the monomer (PO_4^{3-} , or its protonated forms). Both heating and use of alternative solvents drive off water, which either evaporates (heating) or has a sparingly low activity (alternative solvents). Use of alternatives to phosphates include condensed phosphates, reduced phosphorus compounds, amidophosphates, and phosphide minerals. Many of these overcome some of the difficulties of prebiotic phosphorylation but require geochemical justification of their starting material.

condensation of phosphate and an organic and include cyanate [16], but most aren't phosphate-specific, and few have been shown to work adequately in water. Condensed phosphates overcome the phosphate-specific problem [17], but there are few known polyphosphate minerals [18], suggesting they may be sparse. Recent work has shown amidophosphates as excellent phosphorylating agents, but again, a geologic source is unknown [19[•],20]. Alternative solvents such as formamide work quite well for promoting condensation as the production of water is no longer thermodynamically uphill [21–23], but the prevalence of alternative solvents compared to water is unknown [24].

Because of the broad issues of phosphorylation in prebiotic chemistry, some researchers have suggested alternatives to phosphate at the onset of the origin of life [25[•]]. Alternatives that have been investigated include arsenate [26] and glyoxylate [27]. From the perspective of geochemistry phosphate is generally superior, as phosphate tends to be more common than arsenate and does not induce further chirality, unlike glyoxylate. However, recently there have been suggestions that phosphate may have altogether not even been present at the origin of life [28^{••}], though that begs the question of when modern biochemistry arose.

Phosphorus redox in prebiotic chemistry

A novel route to phosphorylation may lie in the rather unexplored natural redox chemistry of phosphorus. Although most geochemists consider phosphate and phosphorus to be synonyms, new evidence suggests lower redox states of phosphorus may both be ubiquitous and biogeochemically important (see subsequent section).

The transformation of phosphate to a lower redox state of phosphorus such as phosphite or hypophosphite results in a few positive effects. Firstly, the lower redox states of phosphorus are much more soluble under similar conditions than the equivalent phosphates. For instance, calcium phosphite is $1000\times$ as soluble as calcium phosphate, and calcium hypophosphite is about $10^6\times$ as soluble. In addition, since reduced P compounds are thermodynamically unstable, they might be more reactive towards some organic reagents than phosphate. These arguments were made over half a century ago by Addison Gulick [29].

The reduced phosphorus argument was quickly stymied by the experimentalist leaders in the field [7]. Gulick's hypothesis neglected the essentials of geochemistry: under the redox conditions where water is present, no reduced P species should be possible (assuming equilibrium chemistry, see Figure 2).

With the denunciation of reduced P [7], little was done to explore reduced P in nature over the next few decades.

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