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Solubilization and Activation of Phosphorus on the Early Earth

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Introduction: The formation of phosphorylated biomolecules has long been a challenge in prebiotic chemistry due to the poor solubility of phosphate minerals and their minimal reactivity towards organic substrates [1]. In recent times, several new routes have been proposed to overcome these phosphorylation problems, including newly demonstrated phosphorylation by the meteoritic mineral schreibersite in water [2] and phosphorylation promoted by mineral transformation and solubilization within non-aqueous [3] and semi-aqueous [4] solvents. While efficient, these routes require either specific meteoritic minerals, or pools of organic-rich solvents to promote reactions. We report here a new route to enhancing phosphorus reactivity that we propose was active on a wide scale on the the early earth.

Phosphorus Reduction and Solubilization: Phosphate reacts with ferrous iron to form phosphite with a concomitant oxidation of iron. The reaction quotient K is about 0.001 to 0.01, at temperatures less than 200°C. Additionally, with the comparatively high solubility of phosphite relative to phosphate, if water flows through rock where this reaction is occurring, phosphite will be preferentially extracted, promoting further reduction of phosphate.

This reaction is confirmed by experiments demonstrating reduction of phosphate when heated with ferrous iron. Additionally, analyses of rocks of early Archean age demonstrate a persistent presence of phosphite as a major P constituent. While previously this phosphite was attributed to meteoritic sources [5], a source from oxidation of ferrous iron is also feasible for many of these rocks.

Additionally, we have measured the oxidation rate of phosphite ions, and find the principal route to its oxidation is by reaction of oxygen radicals (OH or OOH) or by biological mediation. Given neither were likely present in abundance on the early earth, phosphite was thus likely a major phosphorus-bearing constituent of Hadean and Archean oceans.

Phosphorus Activation by Oxidation: Phosphite, though kinetically stable, is oxidized by OH and OOH radicals. Both are formed by reaction of peroxide with ferrous iron, via the Fenton reaction. We have demonstrated previously that phosphite is oxidized by these ions and forms phosphate, pyrophosphate, triphosphate, and trimetaphosphate [6]. To this end, the large-scale reduction of phosphate by iron, followed by the iron-mediated oxidation of phosphite, provide a large, steady-state abundance of polyphosphates present at high (disequilibrium) concentrations, ready to promote phosphorylation and setting the stage for the formation of phosphorylated prebiotic compounds.

[1] Pasek MA (2017) *Geoscience Frontiers* 8:329-335. [2] Gull M et al. (2015) *Scientific Reports* 5:17198. [3] Gull M et al. (2014) *Journal of Molecular Evolution* 78:109-117. [4] Burcar B et al. (2016) *Angewandte Chemie International Edition* 55:13249-13253. [5] Pasek MA et al. (2013) *Proceedings of the National Academy of Science USA* 110:10089-10094. [6] Pasek MA et al. (2008) *Angewandte Chemie International Edition* 47:7918-7920.