Expanding the Inventory: Prebiotic Phosphate Minerals and Their Role in Phosphorylation

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Introduction: In biological systems phosphate imparts robust solubility to molecules while also providing stable phosphodiester bonds, a vital part in forming biopolymers and biochemical energy transfer. These properties of phosphate, so essential to modern life, would have been similarly valuable to primitive organic molecules which ultimately led to the origins of life on Earth. However, the availability of phosphate and its ability to be incorporated into organic molecules on an early Earth has been viewed as a major problem in the field of prebiotic chemistry. These issues arise from the conventional view that the vast majority of phosphate would have been sequestered in insoluble hydroxylapaptite ($Ca_5(PO_4)_3(OH)$) and there were not known chemical reactions to create organophosphates at reasonable temperatures and pH for a prebiotic Earth.

Results and Discussion: Our previous work directly addressed the chemistry of phosphorylation reactions by utilizing a urea-rich eutectic solvent which was able to phosphorylate organics at temperatures as low as 65 ^{o}C. Excitingly, this eutectic also showed the capability to corrode hydroxylapatite allowing it to be used as a phosphate source[1]. Additionally, in the presence of $MgSO_4$, hydroxylapatite was observed to transform into struvite ($MgNH_4PO_4$) and Newberyite ($MgHPO_4$), which were also demonstrated to be effective phosphorylating agents.

Our current work is focused upon exploring phosphate minerals which are formed from ferrous iron, a major ion present on a prebiotic Earth not found in our modern day oxygen-rich atmosphere. These synthetic minerals, in addition to hydroxylapatite, demonstrate a potentially large source of phosphate. When tested in the eutectic, these minerals also promote phosphorylation, showing enhanced availability when in the presence of NaCN. Overall, these results demonstrate that ferrous phosphate minerals were likely abundant on a prebiotic Earth and could be readily utilized as sources of phosphate.

[1] Burcar, B. T., et al. (2016) Angewandte Chemie Intl, **55**, 13249-13253.