**STRUVITE (NH₄MgPO₄ • 6H₂O) AS A PREBIOTIC MINERAL AND SOURCE OF AVAILABLE PHOSPHATE.** C. Menor-Salvan¹, B. Burcar¹, M. Pasek² and N.V. Hud¹, ¹School of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, GA 30033 (USA), cesar.menor@chemistry.gatech.edu. ²School of Geosciences, University of South Florida, Tampa, FL (USA).

**Introduction:** The natural occurrence of struvite is uncommon and associated with the decay of putrescent organic matter ever since its first description [1]. Struvite is also formed as a biomineral in microbial ecosystems and in the kidneys of fish and mammal. The mineral was first discovered in the subsoil of the St. Nicholas church in Hamburg, built over an ancient deposit of manure. Struvite is unstable when exposed to our oxygenated atmosphere, a fact that limits its natural occurrence. Struvite gained interest among prebiotic chemists due to its ability to efficiently transfer phosphate in a potential prebiotic formation of nucleotides [2]. However, concerns regarding the prebiotic availability of struvite [3] and the fixation of inorganic phosphate in the form of highly insoluble minerals, the so-called ‘phosphate problem’ [4], led researchers to consider other alternatives in the prebiotic formation of organophosphates [5]. If Earth had an active prebiotic organic chemistry, including in situ synthesis and/or delivery of organic precursors from meteorites or comets, it is reasonable to propose the existence of pools containing water-soluble organics on the prebiotic Earth that would have been concentrated by water evaporation. One of the organics enriched in the pools would likely have been urea, an abundant product of model prebiotic reactions [6]. Living matter is not a prerequisite for the formation of struvite, just organic matter in anoxic conditions. One of the best places for the formation of struvite are the manure ponds associated with agriculture, where the decomposition of urea into ammonia and CO₂ is the driving reaction for the struvite formation. Interestingly, struvite is the dominant phosphate mineral in these environments, and the calcium phosphates (such as brushite) are less common, with negligible apatite formation. We hypothesized that fresh water ponds on prebiotic Earth would have had organic matter in common with modern manure ponds (without the enzymatic decomposition of organics by bacteria), so we investigated struvite formation in these model prebiotic environments, a process that could make phosphate available for the prebiotic formation of nucleotides [7].

**Results and Discussion:** To test the formation of struvite as a potential solution to the ‘phosphate problem’, we used hydroxylapatite as primary phosphate and epsomite as magnesium source. Hydroxyapatite was treated with a magnesium sulfate and an aqueous urea solution at 65 °C, pH 5.5 to 8, in a glass vial. The solutions were left drying and diluted with a magnesium sulfate solution. The wet-dry cycles were repeated over the course of two weeks. The solid material (Fig.1) was analyzed by Raman spectroscopy and X-ray diffraction.

![Gypsum and Newberyite formed by hydroxylapatite alteration.](image)

As a proof of concept, we performed the synthesis of struvite in model prebiotic conditions using free phosphate, demonstrating that the rate of non-enzymatic urea decomposition is sufficient for the efficient crystallization of struvite. We also observed the fast transformation of struvite into newberyite (Mg(PO₄)OH)·3H₂O, a mineral that maintains the phosphorylation ability of struvite.

We found the thermodynamically favorable (K=10⁻⁵⁹ at 298 K) reaction:

$$H^+ + 1.5(NH₂)₂CO + 3H₂O + 4.5Mg^{2+} + 5SO₄^{2-} + Ca₂(PO₄)₂OH \rightarrow 3MgNH₂PO₄·6H₂O + 5CaSO₄·2H₂O + 1.5MgCO₃$$

for the secondary formation of struvite from hydroxyapatite. This phosphate mobilization reaction induced by urea is directly connected with the phosphorylation of nucleosides, linking the geochemistry of phosphate with the prebiotic formation of nucleotides and other organophosphates in a one-pot, evaporating water pool scenario [6].

**References:**