STRUVITE ($NH_4MgPO_4 \bullet 6H_2O$) AS A PREBIOTIC MINERAL AND SOURCE OF AVAILABLE PHOSPHATE

C. Menor-Salvan[1], B.T. Burcar[1], M. Pasek[2], N.V. Hud[1].*

[1]NSF/NASA Center for Chemical Evolution, Georgia Institute of Technology, Atlanta, Georgia; [2]School of Geosciences, University of South Florida, Tampa, Florida.

Introduction

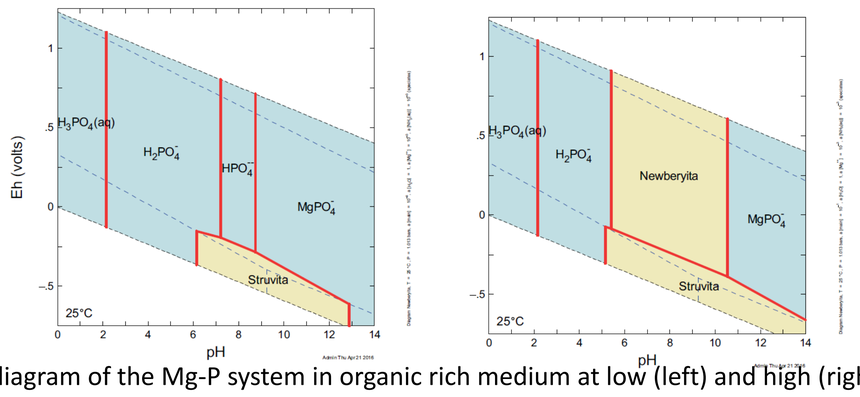
• The so called "**phosphate problem**" was a classic question in chemical evolution: what was the origin of organophosphate, if the inorganic phosphate is fixed in highly insoluble minerals?.

•Struvite [1] 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] led researchers to consider other alternatives in the prebiotic formation of organophosphates [5].

• We hypothesized that water ponds on prebiotic Earth would have had organic matter in common with modern environments where struvite is formed, so we investigated struvite formation in these model prebiotic environments, a process that could make phosphate available for the prebiotic formation of nucleotides [7]

•[1] Ulex G.L. (1846) *Philosophical Magazine Series, 3, 29:192,* 124-128. [2] Gull M., Pasek M.A. (2013) *Life 3,* 321-330. [3] Handschuh G.J. and Orgel L.E. (1973) Science 179, 483-484. [4] Schwartz, A.W. (2006) *Phil. Trans. R. Soc. B, 361,* 1743-1749. [5] Benner. [6] Förstel M. *et al.* (2015) *Chem. Comm. 52,* 741-744. [7] Burcar, B. *et al.* (2016) *Angew. Chem. Int. Ed. 55*, 13249-13253.

Thermodynamic predictions



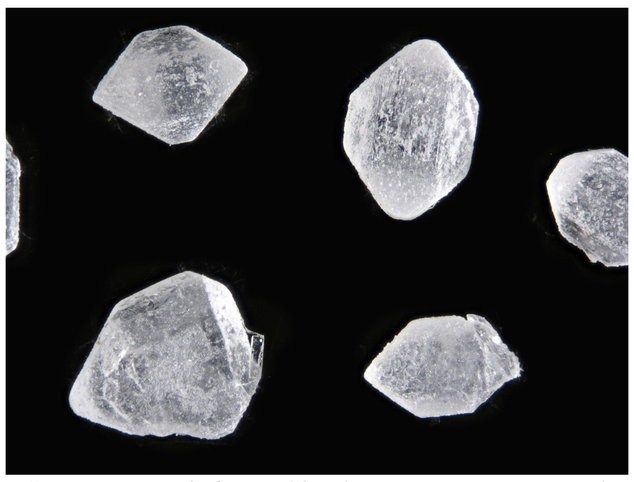
•Eh-pH diagram of the Mg-P system in organic rich medium at low (left) and high (right) phosphate concentration. The Eh (redox potential) of urea solutions are in the range 0.0 tp -0.28.

•The reaction:

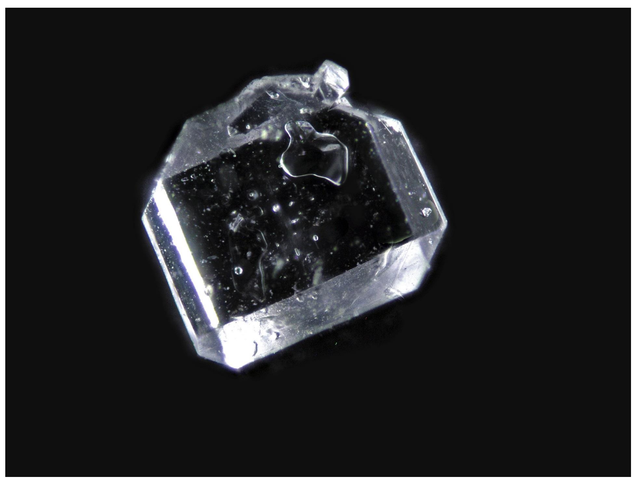
$H^+ + 1.5(NH_2)_2CO$ (**urea**) $+ 30H_2O + 4.5Mg^{2+} + 5SO_4^{2-}$ (**epsomite**) $+ Ca_5(PO_4)_3OH$ (**hydroxylapatite**) → $3MgNH_4PO_4{\cdot}6H_2O$ (**struvite**) $+ 5CaSO_4{\cdot}2H_2O$ (**gypsum**) $+ 1.5MgCO_3$

Is thermodynamically favorable with a $K=10^{59}$ at 298 K.

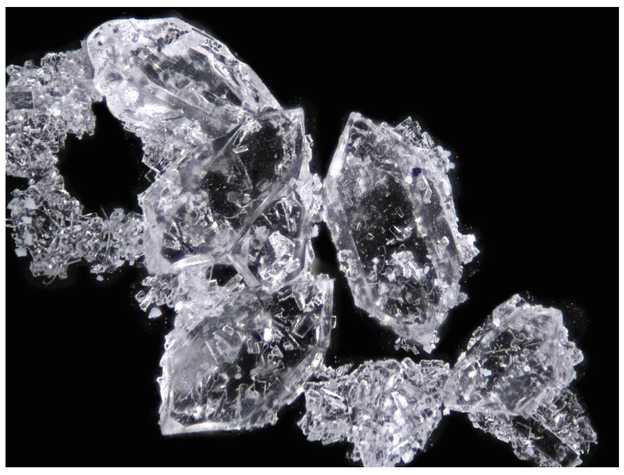
Results



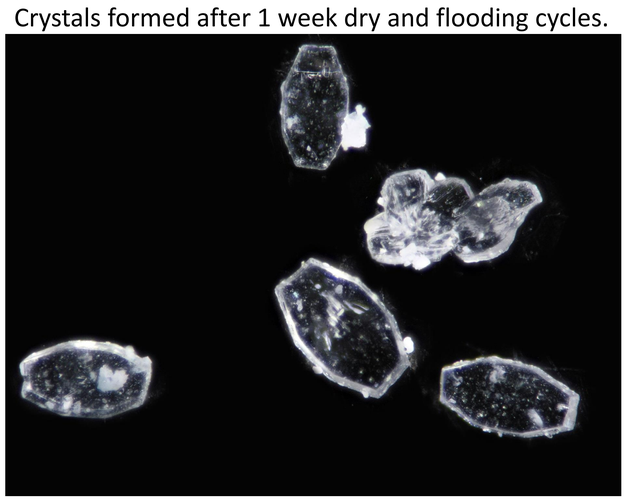
•Struvite crystals formed by dry-wetting an urea and epsomite solution at pH 7.5, with gradual enrichment in phosphate by simulation of contribution of hydrothermal fluid with geochemically plausible phosphate content (10 µM) to the pond. Crystals formed after 1 week dry and flooding cycles.



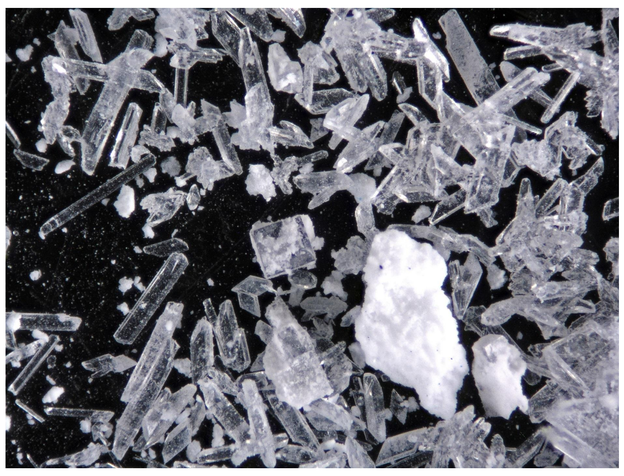
•Newberyite crystals formed by dry-wetting an urea and epsomite solution at pH 6, with gradual enrichment in phosphate by simulation of contribution of hydrothermal fluid with geochemically plausible phosphate content (10 µM) to the pond. Crystals formed after 1 week dry and flooding cycles.



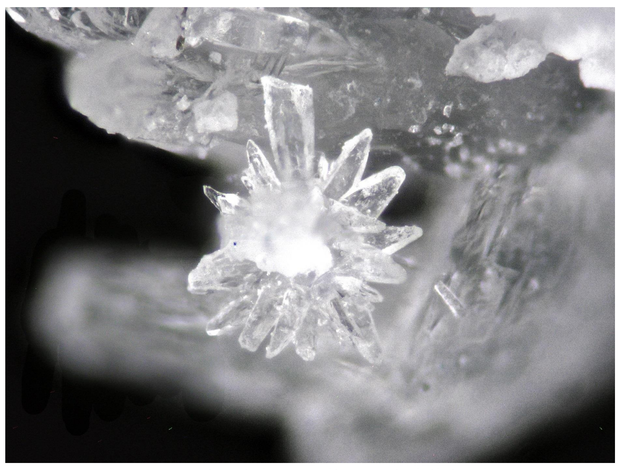
•Struvite is unstable and the transformation on or coexistence with Newberyite is common. In the image, Struvite crystals covered by newberyite during the prebiotic small warm pond simulation.



•The low reduction potential is essential In the prebiotic formation of Struvite. Here, Struvite crystals formed by dry-wetting an urea and epsomite solution supplemented with potassium cyanide.

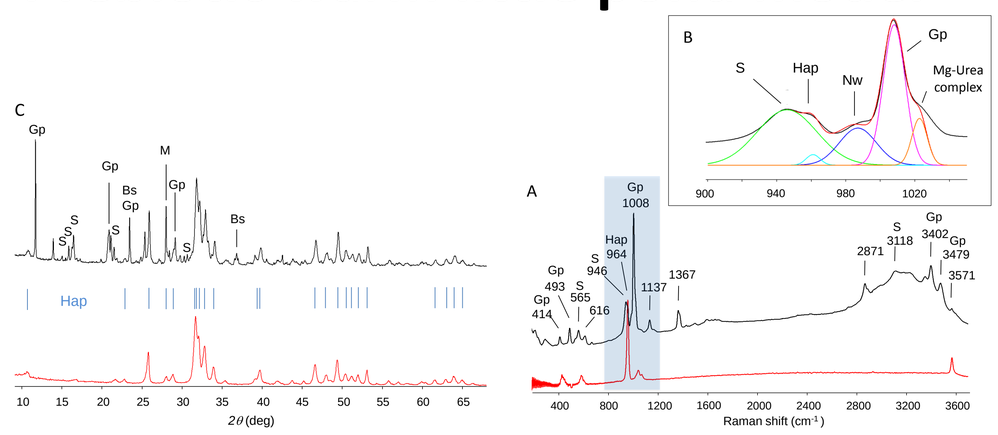


•**Key result**: alteration of Hydroxylapatite to form gypsum crystals and Newberyite in urea-rich solution.



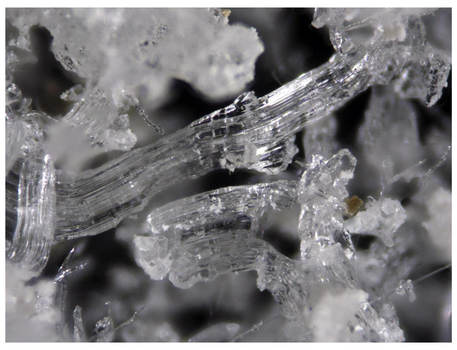
•**Key result**: Organic-rich mediums inhibit the precipitation of highly insoluble apatites and form Brushite, the Ca analog of Newberyite and a good phosphorylating agent..

Prebiotic warm little pond model

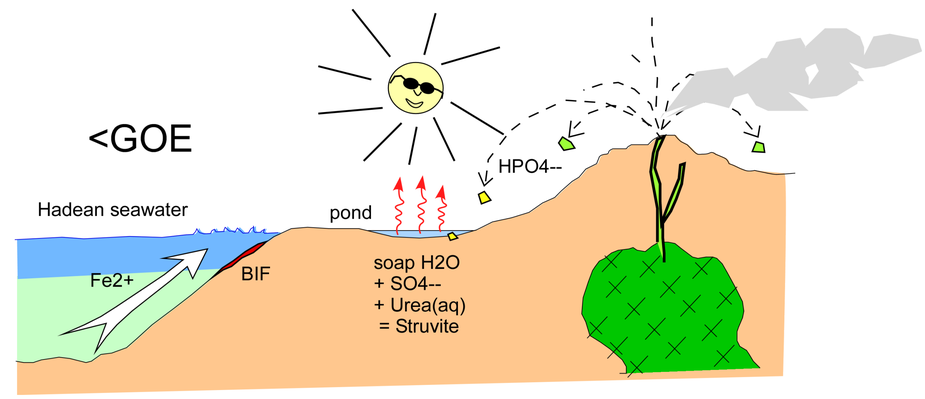


•Analysis (XRD and Raman spectroscopies) of the formation of secondary phosphate minerals by alteration of hydroxylapatite in urea-rich solutions.

•Natural struvite formed in an urea-rich deposit



•Epsomite (magnesium sulfate). A common mineral in evaporitic environments. Unexpected co-protagonist in prebiotic phosphorylation.



apatites + urea + Mg^{2+} + SO_4^{2-} ⟶ Gypsum + struvite/newberyite + carbonates

urea + H_3PO_4 + Mg^{2+} + Ca^{2+} + SO_4^{2-} ⟶ Gypsum + newberyite + carbonates+ brushite

Acknowledgements

•This work was jointly supported by NSF and the NASA Astrobiology Program, under the NSF Center for Chemical Evolution, CHE-1004570