

PHOSPHORYLATION IN THE RNA FIRST MODEL FOR ORIGIN OF LIFE. LÜNEBERGITE AND OTHER EXOTIC MINERALS. H.-J. Kim¹, Y. Furukawa², T. Kakegawa², A. Bitá³, R. Scorei⁴ and S. A. Benner¹
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Two classes of hypotheses describe how life might have originated on Earth. The first considers deep-sea hydrothermal vents, with an environment rich in transition metals but constrained by the need to have product organics stable enough to survive high temperatures. This stability problem is quite challenging for genetic polymers such as RNA and DNA, and is worsened by the abundance of water, which is corrosive for many bonds in these molecules. The second class models the emergence of Darwinian biopolymers in surface environments having variable access to water, with aqueous input coming from serpentinizing rocks. It also has intermittent access to high temperatures in the form of hydrothermal pools on land.

This talk will present new data discussing the second class of hypotheses under the "Discontinuous Synthesis Model" (DSM) for the prebiotic synthesis of RNA. Each step of the DSM has laboratory experimental support. It begins from formaldehyde, hydrogen cyanide, and cyanamide arising from electrical discharge and ultraviolet light passing through a prebiotic atmosphere containing CO₂, N₂, and H₂O, as well as smaller amounts of more reduced species. These compounds rain onto serpentinizing basalts that have borate-containing tourmalines, molybdate, igneous (and possibly meteoritic) phosphates, and other minerals. The effluent runs into a dry basin beneath a pH neutralizing atmosphere. There, secondary products accumulate, such as formamide (from HCN), urea (from NCNH₂), and borate-complexed carbohydrates (from HCHO).

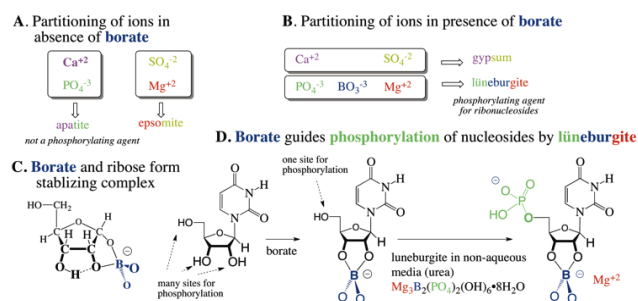
Laboratory work has found examples of each of these products, and now seeks more examples of the conversion of these secondary products to give nucleobases, nucleosides, nucleoside phosphates, and short oligonucleotides, all with increasing degrees of continuity. Here, the dry environment, together with the "exotic" solvents urea and formamide, are essential to manage the thermodynamic instability of phosphate esters with respect to hydrolysis.

The DSM has taken on new relevance due to recent discoveries by the Curiosity rover now exploring Gale Crater on Mars. These explorations offer for the first time the potential to match laboratory research, which merely *simulates* prebiotic mineral ensembles, with field research on Mars that allows us to study (if only remotely) the very evaporate basins that the DSM re-

quires, basins that arose at least 3.5 billion years. Especially important has been the discovery on Mars of co-occurring calcium sulfate (gypsum) and borate. Experimental laboratory results show how this combination allows nucleoside building blocks to be selectively converted to nucleoside phosphates (**Figure**). Also found on Gale Crater are the mineral substrates of serpentinization and their products, as well as a range of oxidation states conducive to prebiotic chemistry.

The concordance between laboratory work guided by geological hypotheses and the discoveries made on Mars is remarkable, and will be the focus of this talk. It will report experimental results showing how these guide the movement of organic carbon from prebiotic precursors (such as formaldehyde) towards nucleoside building blocks, as well as recent work showing the possibility that sugars other than ribose might productively participate in prebiotic pathways. Undiscovered so far in Gale Crater is molybdate, and we will present evidence showing how molybdenum might be present at this oxidation level, as well as experimental results showing how molybdate allows the tar-free in a conversion of carbohydrates, the most delicate of all the prebiotic species.

This presentation may encourage specific new explorations on Mars to seek additional specific mineral species (like molybdate), in a process where lab chemistry directs the exploration towards interesting mineral species, and the results of this exploration guide future lab work. This process that has already worked well to guide the discovery of borate on Mars.



References: Kim, H.-J. Furukawa, Y., Kakegawa, T., Bitá, A., Scorei, R., Benner, S.A. (2016) *Angew. Chem.* **55**, 15816-15820.
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