July 16-21, 2017 at UC San Diego, CA, USA

A molecular vestige of the origin of life on minerals : phosphorybosyl-disphosphate

M. Akouche[1], M. Jaber[2], M.-C. Maurel[3], J.-F. Lambert[1], T. Georgelin*[1], [1]Sorbonne Universités, UPMC Paris 06, CNRS UMR 7197, Laboratoire de Réactivité de Surface 4 place Jussieu, F-75005 Paris-France, [2]Sorbonne Universités, UPMC Paris06, CNRS UMR 8220, Laboratoire d'Archéologie Moléculaire et Structurale 4 place Jussieu, F-75005 Paris-France, [3]UMR 7205-ISyEB, CNRS-MNHN- UPMC Univ Paris 06, F - 75005, Paris, France
* thomas.georgelin@upmc.fr

In the "RNA world" prebiotic scenario, ribonucleotide polymers are considered as the first biochemical species to have emerged. These play a fundamental role in metabolism but their formation involves a particular problem since their synthesis is thermodynamically unfavorable.This is a significant question in the frame of the "RNA world", which explains later stages of evolution, but requires the previous existence of nucleosides and nucleotides. In solution, synthesis routes of nucleotides have been described [1] that involve unstable chemical intermediates or noncanonical nucleobases. Another possible pathway to nucleotides involves mineral surfaces, which have been considered in prebiotic processes at least since the work of Bernal in 1951 [2]. Mineral surface scenarii have been tested for several prebiotic reactions[3], such as phosphorylations, phosphate polymerization or nucleotide oligomerization[4]. No matter how interesting these studies may be, they do not solve the thermodynamical problem because they do not start from "naked" monomers, but from activated nucleotides whose polymerisation is already thermodynamically favored. Thus, the assembly of the individual elements of the nucleotide, as well as its later polymerization to RNA on a mineral surface are a great prebiotic challenge. Our current research focuses on the synthesis of nucleotides and oligonucleotides from their elementary components : α-D-ribofuranose, canonical nucleobases (adenine) and the inorganic monophosphate on amorphous silica surface. In our experiments, reaction products were analyzed by in situ infrared spectroscopy, solid state NMR spectroscopy and mass spectrometry. When adenine, ribose and phosphate were adsorbed on minerals, the one pot formation of adenosine monophosphates was observed after activation at moderate temperatures (70 °C). A key intermediate was observed : phosphoribosylpyrophosphate (PRPP). In our proposition, the main reaction (the endergonic step)[5] in the nucleotides formation mechanism is the PRPP synthesis. Minerals act as metabolic support for the formation of PRPP and then the formation of nucleotides can occur. For the first time, a metabolic intermediate was analyzed in prebiotic way. The PRPP is probably a molecular relic of the origin of life. Our results have also shown, in a second pot reaction, the formation of dimer of nucleotide on mineral surfaces.

[1] a. H. D. Bean, Y. Sheng, J. P. Collins, F. A. L. Anet, J. Leszczynski, N. V. Hud, *Journal of the American Chemical Society* 2007, *129*, 9556-+; b. M. W. Powner, C. Anastasi, M. A. Crowe, A. L. Parkes, J. Raftery, J. D. Sutherland, *Chembiochem* 2007, *8*, 1170-1179; c. M. W. Powner, B. Gerland, J. D. Sutherland, *Nature* 2009, *459*, 239-242; d. J. D. Sutherland, *Cold Spring Harbor Persp. Biol.* 2010, *2*, article #005439; e. M. W. Powner, J. D. Sutherland, *Angewandte Chemie-International Edition* 2010, *49*, 4641-4643.

[2] J. Bernal, *The Physical Basis of Life*, Routledge and Kegan London, 1951.

[3] a. J.-F. Lambert, *Origins of Life and Evolution of Biospheres* 2008, *38*, 211-242; b. T. Georgelin, M. Jaber, H. Bazzi, J.-F. Lambert, *Origins of Life and Evolution of Biospheres* 2013, *43*, 429-443;

[4] J. P. Ferris, A. R. Hill, R. Liu, L. E. Orgel, *Nature* 1996, *381*, 59-61.

[5] J. E. Sponer, J. Sponer, M. Fuentes-Cabrera, *Chemistry-a European Journal* 2011, *17*, 847-854.