

In situ synthesis of nucleotides on silica surface.M. Akouche¹, M. Jaber², M.-C. Maurel³, J.-F. Lambert¹, T. Georgelin^{1*}

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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 implies mineral surfaces, which have been considered in prebiotic processes at least since the work of Bernal in 1951.^[2] Mineral surface scenarios have been tested for several prebiotic reactions^[3], as phosphorylations, phosphate polymerization or nucleotide oligomerizations. In particular, a series of publications by Ferris, Orgel et al.^[4] have mentioned that ribonucleotides can form rather long polymers (up to 55 monomers) in the presence of clay minerals. 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 thermodynamically favorable - but whose presence in prebiotic conditions is rather dubious. Thus, the assembly of the individual elements of the nucleotide, as well as its later polymerization to RNA on mineral surface are a great prebiotic challenge.

Our current research focuses on the synthesis of nucleotides from their elementary components : α -D-ribofuranose, canonical nucleobases and the inorganic monophosphate on amorphous silica surface (used as a model for cherts or silicates). In our experiments, thermal treatments were carried out and reaction products were analyzed by *in situ* infrared spectroscopy and solid state NMR spectroscopy, evidencing several condensation reactions. We have focused our attention on ribose phosphorylation and glycosylation with canonical nucleobases on silica surface. These experiments have first allowed to describe the stability and the chemical reactivity of ribose and nucleobases on acidic mineral surfaces. For example, it was shown that ribose is stable on silica surfaces

from room temperature to 150 °C. At higher temperature, the cyclic ribose becomes linear and ribonolactone appears around 200 °C. The reactivity of ribose however was modified by the presence of some divalent cations. Phosphorylation of ribose was demonstrated after co-adsorption of sugar and monophosphate whereas glycosylation could be observed following co-adsorption of sugar and nucleobases, both with and without phosphate. Thus the main steps of nucleotide buildup from simpler components can occur on the surface of a common oxide mineral, without the need for carrying out elaborate chemistry.

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