

# Layered double hydroxides as nanoreactors for prebiotic chemistry

B. Grégoire (1,2), C. Carteret (1), V. Erastova (3), H.C. Greenwell (3) and D. Fraser (2)

(1) Laboratoire de Chimie, Physique et Microbiologie pour l'Environnement, UMR CNRS-Université de Lorraine, 405 rue de Vandoeuvre, 54601 Villers-lès-Nancy, France

(2) Department of Earth Sciences, University of Oxford, South Parks Road, Oxford, OX1 3AN, United Kingdom

(3) Department of Chemistry, University of Durham, South Road, Durham, DL1 3LE, United Kingdom

## Abstract

The conversion of simple organic molecules to macromolecules, possessing functional activities is one of the key hurdles limiting our understanding on how life began on Earth in the Hadean period. Here, we aim to report new data showing the potential of anionic lamellar compounds to concentrate, protect, and catalyze the condensation reactions of amino-acids to form oligopeptides.

## 1. Introduction

One of the most enigmatic steps in Earth's ancient transition from a lifeless planet to a living world was the process or processes by which prebiotic organic molecules were selected, concentrated, and organised into the essential macromolecules of life. More than half a century of theory and experimental investigation points to the critical role of mineral surfaces in the formation of proteins [1]. Since the formation of peptide bonds requires dehydration, the reaction is thermodynamically unfavourable in aqueous solution. However, clay mineral suspensions in alternating drying-wetting cycles have been found to promote the oligomerisation of amino acids [2]. The possible roles of mineral surfaces in protecting, selecting, concentrating, templating and catalysing reactions of prebiotic organic molecules are recurrent themes in discussions of the origins of life [3].

Here, we propose that layered double hydroxides (LDHs), which could have been present in the Early Earth in alkaline pH hydrothermal vents, played a major role in prebiotic chemistry. LDH systems consist of layers of inorganic sheets, whose structure is analogous to brucite,  $Mg(OH)_2$ . They carry a net positive charge because of the substitution of divalent cations by trivalent ions. Electro-neutrality is achieved by the presence of anions along with water molecules intercalated between the two sheets, i.e. in the interlayer domain. Due to the presence of

high charge-density on the layers, these materials may concentrate amino acids in the interlayer domain to a greater extent than do the surfaces on three-dimensional minerals. The presence of a nano-scale "gallery" may also act as a sheltering environment, thus enhancing the stability of the intercalated amino acid.

## 2. Objectives

Several objectives were defined and investigated:

- (i) Aspartate (our model amino-acid) can be intercalated and concentrated into the interlayer domain of LDHs.
- (ii) The presence of the lamellar structure act as a sheltering environment, enhancing the stability of the intercalated amino-acids.
- (iii) Amino-acids can be polymerised to form oligopeptides within the interlayer domain.

## 3. Results

To correlate the structure of the interlayer domain with its reactivity, well-crystallised materials with only aspartate molecules in the interlayer galleries was a prerequisite. The synthesis of this material can only be obtained by exchange reactions. Solid-state analysis performed on these samples indicated the successful intercalation of the target molecules, and no trace of other anions was detected. Interestingly, by varying the layer charge density of the LDH or the water content of the interlayer gallery, the aspartate is accommodated in different orientations. Since the driving force of the formation of peptides is dehydration, the LDH materials were heated to 250 °C and changes in the structure were monitored by *in-situ* infrared, *in-situ* Raman and *in-situ* X-ray diffraction. Combining these techniques is particularly interesting in elucidating the structure and the chemistry of the interlayer domain. Similar

experiments were performed on the aspartate salt, serving as a reference sample. It has been shown that the interlayer domain of the LDH enhances the thermal stability of the amino-acid since its degradation takes place at 100 °C higher than the pristine aspartate salt. At around 250 °C, chemical reactions take place both in the aspartate salt and in the aspartate-LDH. Interestingly, the nature of the products formed was found to be completely different. Upon heating, the salt formed exclusively polysuccinimide species, while the presence of amide bonds was detected in the interlayer domain of the LDH.

## 4. Conclusions

Though these experiments were not carried out under geochemical conditions representative of the Hadean, the data demonstrate that lamellar species such as LDH are an ideal environment to protect and promote the condensation of amino-acids to form peptides. In addition, as emphasized by Greenwell et al., these materials provide a high coding environment and have the theoretical capability of self-replication with a high degree of fidelity [4].

## References

- [1] Cleaves, H. J., Michalkova, A., Hill, F., Leszczynski, J., Sahai, N. and Hazen, R., Mineral-organic interfacial processes: potential roles in the origins of life, *Chemical Society Reviews*, Vol. 41, pp. 5502-5525, **2012**.
- [2] Saetia, S., Liedl, K. R., Eder, A. H. and Rode, B. M., Evaporation cycle experiments — A simulation of salt-induced peptide synthesis under possible prebiotic conditions, *Origins of Life and Evolution of Biospheres*, Vol. 23, pp. 167-176, **1993**.
- [3] Lambert, J.-F., Adsorption and Polymerization of Amino Acids on Mineral Surfaces: A Review, *Origins of Life and Evolution of Biospheres*, Vol. 38, pp. 211-242, **2008**.
- [4] Greenwell, H. and Coveney, P., Layered Double Hydroxide Minerals as Possible Prebiotic Information Storage and Transfer Compounds, *Origins of Life and Evolution of Biospheres*, Vol. 36, pp. 13-37, **2006**.