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## Could mineral surfaces have oriented amino acid polymerization towards useful products?

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While it has been shown for a long time that mineral surfaces can promote the formation of oligopeptides from amino acids,<sup>[1]</sup> little is known on the potential selectivity of this prebiotic pathway: can order emerge through the appearance of non-random amino acids sequences from mixtures of the monomers? Our work is devoted to identifying (biomolecules/minerals) systems that show promising selectivity for condensation reactions.

In a first step toward taking into account the complexity of the “prebiotic soup”, we have selected four amino acids in the “short list” of prebiotic chemistry, namely G, A, L, V, D and E<sup>[2]</sup>. Two couples have been identified that seem to give rise to selective adsorption and/or cooperative adsorption on silicic materials: (V + D) and (L + E) (valine + aspartic acid and leucine + glutamic acid), raising the possibility that they form adducts with a well-defined structure on these minerals. Their thermal reactivity has then been followed upon drying at moderate temperatures, using thermogravimetric analysis, in situ IR and solid-state NMR spectroscopies, and ex situ analysis of organic molecules after desorption (by HPLC and ESI-MS). We observed the formation of several oligomers in conditions where single amino acids only give rise to cyclic dimers. Depending on the heating conditions, and specifically on the water activity, peptides up to hexamers could be formed in a single step. Furthermore, for each chain length, a limited amount of peptides compositions were observed, showing the non-randomness of the process.

In a further step, we compared the reactivity of the selected amino acid couples on different silicic materials. We studied the effect on polymerization of porosity<sup>[3]</sup>, surface defects such as strained cycles and silanols<sup>[4]</sup>, and the presence of transition metal with variable oxidation states (Fe<sup>3+/2+</sup>). To achieve this, we selected silicic materials with well-defined properties, such as pyrogenic and precipitated silicas, mesoporous silica, and clay minerals including montmorillonite and nontronite. Even within this limited set of related materials, very different amino acid reactivities are observed, underlining the importance of a “surface science” approach to questions of prebiotic chemistry.

Our results may provide the missing link between prebiotic syntheses of small molecules such as amino acids, and self-organization phenomena that may come into play once complexity reaches the level of oligopeptides assemblies.

### References:

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