Polymerization of glycine under hydrothermal conditions

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The abiotic formation of oligopeptides is mandatory to the emergence of enzymatic activity and the first metabolic pathways of life. As a dehydration reaction, polymerization is unfavorable in water but is favoured by hydrothermal conditions, *i.e.* under lower water activity [1-3]. However, high temperature also tends to degrade amino acids and often leads to the dominant formation of the cyclic dimer diketopiperazine, *i.e.* a dead-end product for the synthesis of longer linear peptides. Hence it is crucial to understand the parameters that control the stability of amino acids and the yield of the polymerization reaction. The latter can be evaluated as the ratio of linear to cyclic dimers. This study focused on the evolution of a glycine solution under high pressure and high temperature, up to 300°C and 3 GPa. Experiments were conducted in an externally heated diamond anvil cell and analysed *in situ* using high resolution Raman spectroscopy. Four experiments were carried out at 200°C and between 100 and 400 MPa, for 7 to 20 hours. Upon heating, the pressurized samples produced up to 10 mol% of linear diglycine against 1 mol% of cyclic dimer. Those products remained stable afterwards, even after quenching. Thermal degradation was small or negligible. To our knowledge, such a high ratio in favour of the linear polymer has not yet been described. Further exploration of the pressure-temperature landscape showed that below 400 MPa, temperature activated polymerization but also significantly enhanced the degradation of the monomers whilst pressure in excess of 1 GPa stabilized the starting glycine and inhibited further reactions. This experimental work supports the hypothesis that primitive deep hydrothermal environments in the fractured bedrock could have witnessed the formation of polypeptides and contributed to the emergence of life.

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