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CATALYTIC PEPTIDE HYDROLYSIS BY MINERAL SURFACE: IMPLICATIONS FOR THE ORIGIN
OF LIFE ON PLANETARY SURFACES**Abstract**

The abiotic polymerization of amino acids may have been important for the origin of life, as peptides may have been components of the first self-replicating systems. Although amino acid concentrations in the primitive oceans may have been too dilute for significant oligomerization to occur, mineral surface adsorption may have provided a concentration mechanism. As unactivated amino acid polymerization is thermodynamically unfavorable and kinetically slow in aqueous solution, we studied mainly the reverse reaction of polymer degradation to measure the impact of mineral surface catalysis on peptide bonds. Aqueous glycine (G), diglycine (GG), diketopiperazine (DKP), and triglycine (GGG) were reacted with minerals (calcite, hematite, montmorillonite, pyrite, rutile, or amorphous silica) in the presence of 0.05 M, pH 8.1, KHCO₃ buffer and 0.1 M NaCl as background electrolyte in a thermostatted oven at 25, 50 or 70 C. Below 70 C, reaction kinetics were too sluggish to detect catalytic activity over amenable laboratory time-scales. Minerals were not found to have measurable effects on the degradation or elongation of G, GG or DKP at 70 C in solution. At 70 C pyrite was the most catalytic mineral with detectible effects on the degradation of GGG, although several others also displayed catalytic behavior. GGG degraded 1.5–4 times faster in the presence of pyrite than in control reactions, depending on the ratio of solution concentration to mineral surface area. The rate of pyrite catalysis of GGG hydrolysis was found to be saturable, suggesting the presence of discrete catalytic sites on the mineral surface. The mineral-catalyzed degradation of GGG appears to occur via a GGG to DKP + G mechanism, rather than via GGG to GG + G, as in solution-phase reactions. These results are compatible with many previous findings and suggest that minerals may have assisted in peptide synthesis in certain geological settings, specifically by speeding the approach to equilibrium in environments where amino acids were already highly concentrated, but that minerals may not significantly alter the expected solution-phase equilibria. Thus the abiotic synthesis of long peptides may have required activating agents, dry heating at higher temperatures, or some form of phase separation.