

Formation and stability of amides in hydrothermal systems

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Hydrothermal synthesis and transformation of organic C and N compounds can play important roles in a wide range of geochemical settings and the deep subsurface biosphere. Amides represent an important organic functional group in hydrothermal environments because of their linkage to peptide bonds, which possibly, relating to the origin or evolution of life on early Earth. However, the chemistry of amides under hydrothermal conditions is poorly studied, and their formation pathway and stability are not well understood. In this study we describe a feasible abiotic pathway for amide synthesis in hydrothermal water at 250 °C and 40 bar (P_{sat}), with high selectivity and yield (up to 90%). Hydrothermal experiments with a suite of substituted organic substrates were conducted to obtain both kinetics and mechanistic information for the reaction. The stability of amides was also examined and found to be pH dependent under the hydrothermal condition. In addition, we observed some dramatic effects of copper salts on the amide synthesis, which suggests a significant role of metal ions in the hydrothermal formation of peptide bonds. This study not only highlights an overlooked pathway for amide hydrothermal synthesis, but also emphasizes the geochemical constraints on organic C and N transformations in submarine hydrothermal systems.