

# The role of liquid-liquid immiscibility of sulfate fluids in concentrating and preserving amino acids in prebiotic hydrothermal environments

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Polymerization of life's building blocks (e.g., amino acid) to form biopolymers (e.g., peptide) is a critical step towards the formation of life. The relevant polymerization reactions, however, are suppressed in prebiotic hydrothermal environments because they generally are dehydration reactions and hence are kinetically unfavored in aqueous fluids [1]. To overcome this kinetic barrier, life's building blocks need to be concentrated in low-water-activity aqueous phases [2].

In the present study, by combining a suit of *in-situ* experimental methods and quantitative Raman spectroscopic analysis, behavior of glycine in sulfate ( $\text{MgSO}_4$ ,  $\text{ZnSO}_4$ ,  $\text{CdSO}_4$ ) fluids was investigated at 25-300 °C, vapor-saturated pressure. All sulfate-glycine fluids investigated exhibited liquid-liquid immiscibility (LLI) in the temperature range of 222-304 °C, consistent with previous studies on pure sulfate fluids [3]. During LLI sulfate-glycine fluids split into a sulfate-rich liquid (L1) and a sulfate-poor liquid (L2). Noteworthily, *in-situ* Raman spectroscopic analyses revealed that glycine is strongly enriched into the L1 liquid after LLI. This observation is qualitatively indicated by the much higher Raman peak intensity of glycine in the L1 liquid. To quantitatively evaluate the enrichment effect, concentrations of glycine in the L1 liquid were estimated via their  $\text{H}_2\text{O}$ -normalized Raman peak areas ( $A(\text{Gly})/A(\text{H}_2\text{O})$ ). Results show that concentrations of glycine in the L1 liquid are 4-18 times higher than glycine concentrations in the starting sulfate-glycine fluids before LLI. Additionally, Raman spectra were recorded continuously from the L1 liquid of a 1 *m*  $\text{MgSO}_4$ -0.25 *m* glycine solution at 300 °C over 12 hours. Concentration of glycine in the L1 liquid gradually decreased with time, suggesting thermolysis of glycine. Through concentration-time profile obtained, decomposition rate constant of glycine in the L1 liquid at 300 °C was derived. We found that glycine has particularly high thermostability in the L1 liquid. In summary, our experimental results indicate that liquid-liquid immiscibility is a promising mechanism to concentrate and preserve life's building blocks in prebiotic hydrothermal environments.

[1] Marshall (2020), *Nature* 588, 210-213. [2] Kitadai et al. (2023), *Geochim. Cosmochim. Acta* 349, 55-63. [3] Wang et al. (2013), *Geochim. Cosmochim. Acta* 103, 1-10.