Pressure-induced formation of alanine oligopeptides at 25 °C

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Introduction

Oligomerization of amino acids can provide a clue to the origin of life because it is a fundamental step of protein synthesis. Under high pressure, increases of intermolecular interactions result in chemical reaction which cannot proceed under ambient condition. Oligomerization of amino acids was reported from experiments under high pressure and high temperature conditions simulating impact of comets, hydrothermal vents, diagenesis in sub-seafloor sedimentary environments (e.g., Sugahara and Mimura, 2015; Imai and Honda, 2010; Otake et al., 2011). In these experiments, both high pressure and high temperature are the important factors for amino acids oligomerization. However, it is unknown which factor is more efficient for forming oligomers. In this study, we focus on exclusive effect of high pressure on oligomerization reaction. We tested oligomerization of L-alanine under a room temperature and high-pressure condition. Fujimoto et al. (2015) reported pressure-induced oligomerization of L-alanine up to the trimer using GC-MS analysis (Fig 1). In the present study, we used LC-MSMS to detect higher oligomers.

Experimental procedures

All high-pressure experiments were carried out at 25 °C. Starting material was loaded in a high-pressure cell with three different conditions: wet, dry and solution (wet: L-Alanine powder with its saturated aqueous solution. dry: L-alanine powder. solution: saturated L-alanine aqueous solution.). Sample was compressed using a large-volume opposed-anvil apparatus or a “Kawai-type” multi-anvil apparatus. Experimental runs were conducted at pressures of approximately 5 GPa, 7 GPa, 9 GPa, 11 GPa, and 16 GPa using an opposed-anvil apparatus and 18 GPa and 23 GPa using a multi-anvil apparatus. After decompression to ambient pressure, run products were dissolved in pure water and analyzed using LC-MSMS.

Results and discussion

Alanine dimer was detected from all the run products. With increasing pressure, the yields of alanylalanine increased for each experimental condition (wet, dry, and solution). At pressures higher than 9 GPa, formation of alanine trimer was detected and the yield increased with pressure. These results are consistent with the results of Fujimoto et al. (2015). It is noteworthy that oligomerization of alanine occurred under water-coexisting conditions. In the pressure and temperature conditions applied in this study, water in the samples existed as ice VII, the oligomerization observed here was a solid-phase reaction. Higher oligomers were detected from the samples recovered from high pressure. Under the wet condition, the formed oligomers decreased with increasing the oligomer size and the largest oligomer detected was 8-mer.

This study revealed that oligomerization of amino acids occurs under high pressure at room temperature with existence of water as ice VII which is known to exist in the interiors of icy planets. This study proposes an interior of an icy planet as a new abiotic condition for oligomerization of amino acids.

Keywords: amino acids, high pressure, oligomerization

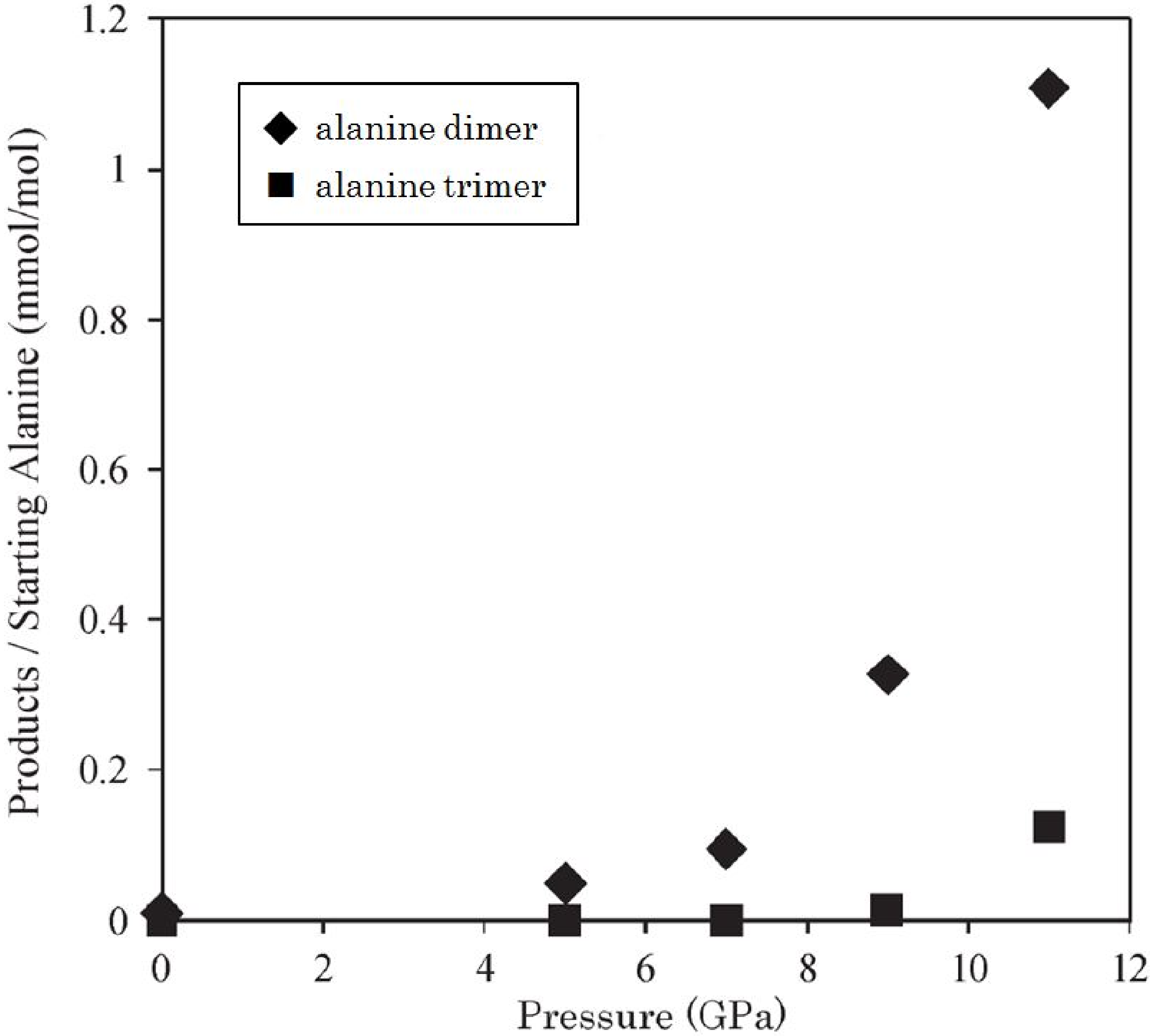

Fig. 1 Molar ratios of alanine dimer and trimer to starting alanine vs. pressure. (Fujimoto et al., 2015)