Solid state peptide formation from valine under high P and T conditions:Implications for the chemical evolution in the crust

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It has been debated as to how and where the single amino acids polymerized to peptides on the primitive Earth. Previous studies indicated that alanine and glycine can polymerize effectively in high temperature and pressure conditions simulating environments in deep seafloor sediments. However, it is not certain for other bio-essential amino acids, including valine.

High-temperature and pressure experiments for valine were performed in this study using an autoclave. As we support dehydration reaction of the deep seafloor sediments, all experiments were performed in non-aqueous conditions, without mixing valine powder with water. Experiments were performed under various pressures of 0.5-150 MPa at 150-200^{o}C for 1-32 days, simulating deep seafloor sediments of the primitive Earth. In addition to the simple valine system, a mixture of valine and Na-montmorillonite was also examined. Total of 33 experimental runs were performed during the course of this thesis study. Running products were carefully analyzed using a high performance liquid chromatograph and that connected to a mass spectrometer (LC/MS).

The results of current study show the following four points: (1) With the elapsed time, polymerization of valine was promoted resulting in di-peptide formation at 150^{o}C, also promoted to tri-peptide at 175^{o}C and tetra-peptide at 200^{o}C, respectively. At 200^{o}C, peptides were rapidly formed, and the reaction was equilibrated at 1 day. With more elapsed time, once-formed peptides were converted into other products, which are difficult to identify. (2) valine is stable at 150^{o}C and 100 MPa for 32 days and also at 175^{o}C and 100 MPa for 16 days. On the other hand, valine was converted into other products rapidly at 200^{o}C and 100 MPa. (3) The optimum pressure was found for the polymerization reaction of valine through the series of experiments, although it is obviously that high-pressure condition is more favorable to promote the polymerization compared to normal pressure. (4) Na-montmorillonite is a good catalyst in the reaction that valine is converted into di-peptide and tri-peptide and tetra-peptide under high-pressure and high-temperature conditions. Note that these findings were only possible by analyzing products with LC/MS and this is the first study to adapt LC/MS for analyses of polymerized valine. The above results suggest that chemical evolution could have happened in deep seafloor sediments of the primitive Earth in where pressure, temperature, and clay minerals were available.