

Diastereoisomeric excess of Ala-DKP during condensation of racemic-Ala on olivine under hydrothermal condition

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<Introduction>

When peptides are abiotically formed from amino acid monomers under thermal condition, cyclic dipeptides, diketopiperazine (DKP), are intensely dominant. DKP was defined as an obstacle for peptide elongation (Basiuk et al., 1990), while, Nagayama et al. (1990) supposed that the DKP was an effective intermediate phase to provide internal free energy necessary to form additional peptide bond. If DKP play as an intermediate phase, DKP formation must be important as the first step of chemical evolution of peptides continuing to life. Minerals promote the DKP formation under laboratory thermally condition (e.g., Bujdak and Rode, 1996; Meng et al., 2004); e.g., DKP formation would be promoted on olivine surface, where amino acid monomers are dehydrated and the olivine is hydrated (serpentinization). Diastereoisomeric DKPs (*cis/trans*) are formed, when chiral amino acids are dimerized. In this study, the diastereoisomeric excess (*de*) of DKP formed from the simplest chiral amino acid, alanine (Ala), was observed on the surface of olivine (during aqueous reaction with olivine) at 120 degree C for 8 days.

<Experiment>

DL-Ala powder was reacted with/without powdered olivine and a small amount of ultrapure water in sealed glass ampoules under Ar atmosphere. The ampoules were heated in a drying oven at 120 degree C for 1-8 days. After cooling at room temperature, the reacted product was suspended in 5 mL ultrapure water and the dissolved diastereoisomers of DKP were quantified using a high performance liquid chromatograph with UV detection.

<Result and Discussion>

When the DL-Ala was heated without olivine, 3.0 % DL-Ala transformed into DKPs. On the other hand, 12.2 % of Ala changed to DKPs when the olivine coexisted. Olivine would be a good catalyst for DKPs formation. The DKPs were not detected even if the olivine coexisted after heating for 8 days, when a small amount of water was not added. A small amount of water would play a role to break the strong bonds of Ala crystals and promote the DKP formation reaction.

When $de = \frac{[cis\ DKP] - [trans\ DKP]}{[cis\ DKP] + [trans\ DKP]}$ is defined, positive *de* means *cis* DKP excess. The *de* of DKP formed from the reaction without olivine heating for 8 days was +7.3 %. On the contrast, it was +16.3 % when reacted with olivine. It was reported that *trans* DKP is preferentially formed relative to *cis* DKP during racemic amino acid condensation, then the *de* gradually decreased with increasing reaction time (Naraoka and Harada, 1986). In this study, the *de* of DKP considerably increased when reacted with olivine. Olivine would be not only an efficient catalyst to promote the DKPs formation but also a determining factor on the selectivity of diastereoisomeric DKPs. Thus, serpentinization of ultramafic rock would have connection to DKP formation with regulation of peptide stereoisomers in the primitive ocean on planets.

Keywords: diketopiperazine, diastereoisomeric excess, olivine, alanine