

Formation of Diastereoisomeric Piperazine-2,5-dione from DL-Alanine in the Presence of Olivine and Water

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Abstract DL-Alanine (Ala) was heated with/without powdered olivine and water at 120 °C for 8 days to investigate the formation of the diastereoisomers of piperazine-2,5-dione (diketopiperazine, DKP). When only DL-Ala was heated with a small amount of water, 3.0 % of DL-Ala changed to *cis*- and *trans*-DKP after 8 days. DKPs were not detected after heating when no water was added. The presence of a small amount of water is important factor controlling peptide production rates under thermal conditions. When DL-Ala was heated with olivine powder for 8 days, the yields of *cis*- and *trans*-DKP were 6.8 and 4.9 %, respectively. The high yield of *cis*-DKP compared with *trans*-DKP was attributed to greater thermal stability of *cis*-DKP. After heating for 8 days, the diastereoisomeric excess of *cis*-DKP without olivine was 7.3 %, whereas a much higher value of 16.3 % was obtained in the presence of olivine. Taken together, these results show that olivine is not only an efficient catalyst for the formation of DKPs but that it also play a significant role in determining the diastereoisomer selectivity of these cyclic dipeptides.

Keywords Diketopiperazine · Alanine · Olivine · Diastereoisomeric excess · Chemical evolution

Introduction

The formation of organic polymers is an essential process to produce the life precursors that lead to the production of proteins, polysaccharides, complex lipids, DNA, and RNA. The

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primary production of peptides and proteins is believed one of the possible scenarios of origin of life on primitive Earth (Fitz et al. 2007; Ikehara 2009; Marshall-Bowman et al. 2010). Abiotic peptide formation [i.e., n amino acids \rightarrow peptide + $(n - 1) \text{H}_2\text{O}$] was likely an important process to build up the protein precursors. However, the peptide formation reaction is thermodynamically and kinetically unfavorable on present day Earth (Fox et al. 2015).

High temperature conditions are thermodynamically favorable for the abiotic peptide formation because the reaction is endothermic (Shock 1992; Lemke et al. 2009). Some researchers observed the self-polymerization of tri-functional amino acids (e.g., aspartic acid, glutamic acid, and lysine) at high temperature anhydrous conditions (120–210 °C) (Harada 1959; Fox and Nakashima 1967; Melius and Srisomsap 1997). Many hydrothermal experiments have found that short-chain peptides can be synthesized by heating a solution containing highly concentrated amino acids for a short period of time (Zamaraev et al. 1997; Imai et al. 1999; Alargov et al. 2002; Bujdak and Rode 2004; Cleaves et al. 2009; Lemke et al. 2009; Sakata et al. 2010). However, the yields of these reactions are typically very low (<1 %) and the resulting peptides are rapidly hydrolyzed to amino acid monomers, indicating that peptides rarely survive under hydrothermal conditions for long periods of time (Qian et al. 1993; Bada et al. 1995; Fuchida et al. 2014a, 2015).

Several studies have reported that relatively large amounts of peptides can be formed when amino acids are heated in the absence of water. Napier and Yin (2006) reported that >10 % of alanine (Ala) changed into dipeptides when it was heated at 80 °C for 600 h with copper reagents. Kitadai et al. (2011) investigated the effects of anhydrous salts (MgSO_4 , SrCl_2 , BaCl_2 and Li_2SO_4) on the peptide formation at 140 °C, and reported that 6.92 % of glycine (Gly) formed peptides when heated for 20 days with MgSO_4 . Fuchida et al. (2014b) found that 13.9 % of Gly became peptides after heating at 150 °C for 336 h with montmorillonite. However, these studies reported that no peptides were formed without those materials. Anhydrous thermal conditions and in the presence of catalysts may therefore produce more peptides than hydrothermal conditions do.

The abiotic synthesis of peptides from amino acid monomers under anhydrous conditions can lead to the rapid formation of cyclic dipeptides, such as piperazine-2,5-dione (diketopiperazine, DKP), through dehydration reactions as shown by Fig. 1. The formation of DKPs can be promoted the surface of specific minerals (Bujdak and Rode 1996; Lambert 2008; Lambert et al. 2013). For example, Meng et al. (2004) used spectroscopic analysis to show that when Gly adsorbed on silica surface was heated at 150–200 °C under anhydrous conditions, it condensed to DKP. Furthermore, Fuchida et al. (2014b) found that 86 % of the

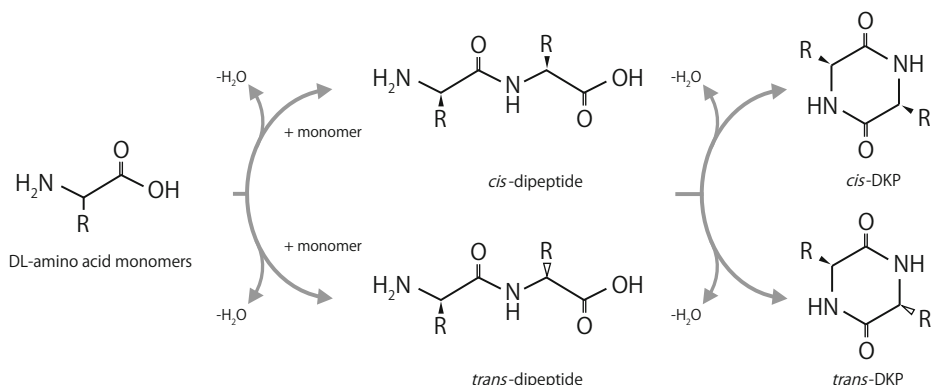


Fig. 1 Model of the formation of diastereoisomeric DKPs from chiral amino acids

peptides formed on the surface of montmorillonite when they were heated at 150 °C for 336 h under anhydrous conditions existed in the form of DKPs.

DKPs are regarded as an obstacle to the elongation of peptides (Steinberg and Bada 1981; Basiuk et al. 1990). On the other hand, Nagayama et al. (1990) observed that yield of GlyGlyGly increased with heating time when DKP heated with Gly monomer under hydrothermal conditions. Based on these results, they suggested that liner peptides were elongated via the opening of the DKP ring and subsequent bonding to another amino group, and that DKPs can be effective intermediates to provide the necessary internal free energy to facilitate the formation of additional peptide bonds. Once the peptide bonds in DKPs are formed, they can be rearranged to elongate liner peptides at almost no free enthalpy cost (Lambert et al. 2013). If DKPs can act as intermediates, then their formation could be an important first step in the chemical evolution of the peptides responsible for life of the Earth.

In general, two types of diastereoisomeric DKPs [i.e., cis (LL and DD) and trans (LD) isomers] may be formed from LD-amino acids (Naraoka and Harada 1986). The formation of diastereoisomeric DKPs is important to consider the enantiomeric excess problem of L-amino acids in biological proteins (Bujdak et al. 2006). However, previous studies concerning the formation of DKPs have not discussed diastereomeric DKPs because they generally used Gly ($\text{H}_2\text{N}-\text{CH}_2-\text{COOH}$), which is the simplest amino acid, and is achiral. In this study, we have investigated the formation of diastereoisomeric DKPs from Ala [$\text{H}_2\text{N}-\text{CH}(\text{CH}_3)-\text{COOH}$] at 120 °C for up to 8 days. Ala is the simplest chiral amino acid and has been abundantly synthesized in experiments simulating primitive Earth environments (e.g., Miller 1953; Aubrey et al. 2009; Zaia et al. 2008).

Futhermore, we have investigated the use of olivine [$(\text{Fe}, \text{Mg})_2\text{SiO}_4$] as a catalyst for the formation of these peptides. Olivine is the most common silicate mineral in the upper mantle of the Earth's crust and the main component of mafic igneous rocks. The hydration of olivine is thermodynamically favorable (Berndt et al. 1996; Neubeck et al. 2011), suggesting that its surface would favor the formation of DKPs via the dehydration of the corresponding amino acid monomers.

Experimental

Materials

DL-alanine (DL-Ala, pure grade, 98 %), 3,6-dimethylpiperazine-2,5-dione (pure grade, 97 %), and other chemicals (analytical grade) used for high-performance liquid chromatographic (HPLC) analysis were obtained from Wako Pure Chemical Industries, Ltd. (Osaka, Japan). The olivine (San Carlos, AZ, USA) was manually powdered with an aluminum mortar and pestle sieved with a 1/4 mm mesh.

Heating Procedure

DL-Ala powder (12 mg) was mixed with 20 μL or 1 mL of ultrapure water and without water in the presence or absence of the olivine powder (200 mg) in a 2 cm^3 glass ampoule, followed by sealing under Ar atmosphere. The ampoules were heated in a drying oven at 120 °C for 1–8 days. After cooling to room temperature, the reaction mixture was extracted with 5 mL ultrapure water by sonication and the dissolved diastereoisomers of DKPs were quantified by HPLC.

Quantification of Diastereoisomeric DKPs

cis- and *trans*- DKP were separated using an InertSustain C18 column (4.6 mm inner diameter \times 250 mm length, GL Science Inc., Tokyo, Japan), and analyzed using UV detector (GL-7450, GL Science) at 195 nm. The eluent was CH₃OH/H₂O (96/4, v/v), and the flow rate of the mobile phase was 1.0 mL/min at 40 °C. Figure 2a and b show examples of the chromatograms of the standard and the sample with olivine heated at 120 °C for 8 days, respectively.

Results and Discussion

Effects of Olivine and Water on DKP Formation

Figure 3 shows the change in the yield of total DKPs (ratio of produced DKPs/initial DL-Ala in mol %) as a function of heating time. When no water was added, DKPs were not detected even after heating with olivine for 8 days (Table 1). Fuchida et al. (2014b) reported that 99 % of the Gly remained and no peptides formed when Gly powder was heated at 150 °C for 336 h in the absence of water. Kitadai et al. (2011) also reported that peptides hardly formed from Gly powder after heating at 140 °C for 20 days. Based on Le Chatelier' principle, peptide formation rates increase with decreasing amounts of water because the reaction is dehydration (Lambert 2008; Georgelin et al. 2013), therefore the peptide formation may be theoretically favored in bulk solids under high temperature and anhydrous conditions. However, the reaction is significantly slow and kinetically unfavorable without an activation process (Rodriguez-Garcia et al. 2015). Free amino acids are zwitterions (i.e., intramolecular salts) under neutral conditions, and crystalline amino acids have strong intermolecular ionic bonds between the protonated amino groups and deprotonated carboxyl groups, which are very stable under high temperature and anhydrous conditions (Rosado et al. 1997; Reva et al. 1994; Fujimoto et al. 2015; Rodriguez-Garcia et al. 2015). The stable ionic bonds in crystalline amino acids would become a kinetic barrier to form peptides under anhydrous conditions.

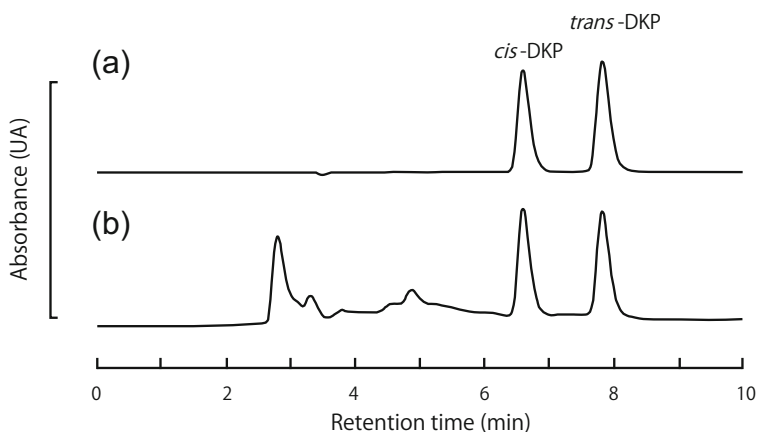
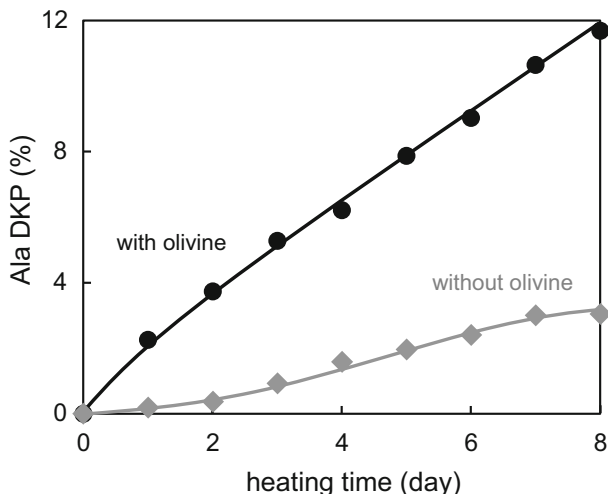


Fig. 2 Chromatograms of (a) the standard solution containing *cis*- and *trans*-DKP (500 μM) and (b) the sample solution with olivine after heating at 120 °C for 8 days

Fig. 3 Evolution of the yield of Ala-DKPs as a function of heating time at 120 °C



On the other hand, a total of 3.0 % of the DL-Ala transformed into DKPs after heating for 8 days, when the DL-Ala was heated with a small amount of water (20 μ L) in the absence of olivine. These results suggest that a small amount of water would break the strong ionic bonds in the Ala crystals, activate Ala molecules, and promote the peptide bond formation. The addition of a small amount of water is kinetically favor to form peptide bonds. Thus, the presence of a small amount of water must be important factor controlling stability of amino acids and peptide production rates under thermal conditions.

When a large amount of water (1 mL) was added to the system, the yield of total DKPs was <0.1 % after heating for 8 days (Table 1). As mentioned above, a small amount of short peptides (<1 %) can form under simulated hydrothermal conditions without catalysts. Based on thermodynamic calculations, Shock (1992) suggest that the hydrothermal stability of peptide bonds increases with increasing temperature. Lemke et al. (2009) showed that the Gibbs free energy for the reaction of Gly to GlyGly (i.e., $2\text{Gly} \rightarrow \text{GlyGly} + \text{H}_2\text{O}$) decreases to 16.0, 7.9 and 2.9 kJ/mol at temperatures of 160, 220 and 260 °C, respectively, while the free energy is 14.2 kJ/mol at 25 °C. These thermodynamic calculations explain that the peptide formation reactions are likely favored by hydrothermal conditions. However, these calculations assumed no degradation of amino acid monomers during the heating experiments, although it gradually decomposes via deamination and decarboxylation under hydrothermal conditions, therefore equilibrium state would never be reached under these conditions (Qian

Table 1 DKP yield (%) after heating at 120 °C for 8 days

Olivine	Water	DKPs		
		cis	trans	Total
+	+	6.8	4.9	11.7
+	-	n.d.*	n.d.	n.d.
-	+	1.6	1.4	3.0
-	-	n.d.	n.d.	n.d.
-	++	<0.1	<0.1	<0.1

* n.d. = not detectable

1993; Marshall-Bowman et al. 2010). In the presence of excess water conditions, the hydrolysis of peptides and the decomposition of amino acid monomers is the main reaction, and the peptide formation rates are controlled by high reactivity of water (Fuchida et al. 2014b). In addition, kinetics calculation by Qian et al. (1993) suggested that peptides are hydrothermally unstable and rapidly hydrolyzed according to a first-order reaction, and the stability decrease exponentially with increasing temperature. Therefore, peptide production would be kinetically and thermodynamically limited in the presence of excessive water.

When DL-Ala was heated with olivine powder, 11.7 % of the DL-Ala formed DKPs after heating for 8 days. The DKP formation was remarkably promoted by heating with olivine, indicating that olivine is a good catalyst under thermal conditions. Peptide formation (DKP formation) can be promoted by the adsorption of amino acid monomers on mineral surfaces (Lahav et al. 1978; Bujdak and Rode 1996; Lambert 2008; Fuchida et al. 2014b). For example, clay minerals are good candidates for the production of peptides because of the strong affinity between amino acids and the surfaces, and the high specific surface area (Greenland et al. 1964; Hedges and Hare 1987; Benetoli et al. 2007). It is commonly recognized that olivine is unstable more than all other rock-forming silicate minerals, especially in the presence of hot water, and serpentines, Fe oxides, Mg hydroxides, and other hydrous silicate minerals are formed by the hydrothermal alteration (Delvigne 1979; Wilson 2004; Velbel 2009). Organic acids such as amino acids also promote the alteration of olivine (Barman et al. 1992; Neubeck et al. 2011). Varadachari et al. (1994) investigated the alteration products of olivine in the presence of amino acids and other organic acids, and determined that cations (Mg^{2+} and Fe^{2+}) in olivine are released and change into insoluble oxalates (MgC_2O_4 and FeC_2O_4), and structural silica (SiO_4^{4-}) remains during the alteration of olivine, based on spectroscopic analysis. The residual structural silica (silanol group) would be important as adsorption sites of amino acids because it has high reactivities (Zaia 2004; Stievano et al. 2007).

Several studies explained that amino acid monomers was activated and oligomerized through the formation of an ester bond ($Si-O-C(=O)-R$) between the carboxyl group of the amino acid (COO^-) and the silanol group ($Si-OH$) on the mineral surface under anhydrous thermal conditions (Basiuk et al. 1990; Bujdak and Rode 1996, 1999; Basiuk and Gromovoy 1993). However, the ester bond cannot be easily formed at <100 °C, because this temperature is thermodynamically unfavorable for the formation reaction (Rimola et al. 2006). Meng et al. (2004) explained that more reasonable adsorption mechanism is hydrogen bond formation between the positively charged amino groups (NH_3^+) and negatively charged silanol ($Si-O^-$) on mineral surface. Using Fourier transform infrared spectroscopy, Fuchida et al. (2014b) observed the adsorption of Gly by the hydrogen bonding on clay surface, and estimated that it activated and promoted the oligomerization of Gly under anhydrous thermal conditions. Therefore, DL-Ala would adsorb on the structural silica by the hydrogen bonding, activate and change into DKPs. In that case, the alteration of olivine and its resolvents must be important for an efficient first step of the DKP formation.

Stereochemistry of Ala-DKPs

Two type of diastereoisomeric DKPs (i.e., *cis*- and *trans*-DKP) formed from DL-Ala in this study. Figure 4 shows the changes in the yields of *cis*- and *trans*-DKP as a function of heating time. The yields of *cis*-DKP and *trans*-DKP after heating for 8 day were similar: 1.6 and 1.4 %, respectively (Fig. 4a). When DL-Ala was heated with olivine, the amounts of *cis*-DKP and *trans*-DKP after heating for 8 days was 6.8 and 4.9 %, respectively, while the amount of

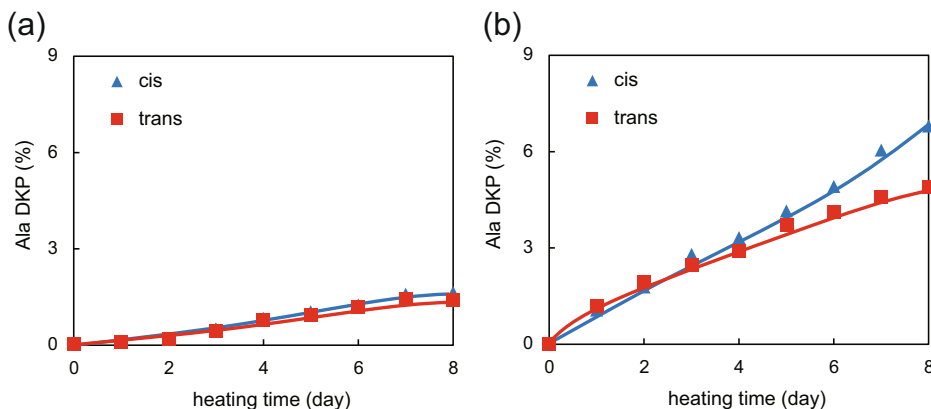


Fig. 4 Change in the yield of diastereoisomers of DKP (a) without and (b) with olivine after heating at 120 °C for 8 days

trans-DKP (2.0 %) was higher than that of *cis*-DKP (1.8 %) after 2 days' heating (Fig. 4b). The value of the diastereoisomeric excess (*de*) of DKP is defined as follows:

$$de = (\text{cis} - \text{trans}) / (\text{cis} + \text{trans}) \times 100\%$$

A positive *de* means an excess of *cis*-DKP. The *de* value of the DKPs formed without olivine was 7.3 % after 8 days of heating. In contrast, the *de* value increased to 16.3 % when the reaction was conducted in the presence of olivine, indicating that the olivine led to a considerable increase in the *de* value of those DKPs. These results therefore indicate that olivine is not only an efficient catalyst for the formation of DKP but that it also plays a significant role in determining the selectivity of diastereoisomeric DKPs. It has been reported that the formation of *cis*-DKP is kinetically favored over *trans*-DKP, and that the *de* value of these products gradually decreases with increasing reaction time (Naraoka and Harada 1986). NMR analysis suggests that *cis*-DKP exists as a boat-type ring, whereas *trans*-DKP exists as a planar-type ring (Fig. 5, Eguchi and Kakuta 1974). Planar-type DKP is more labile than boat-type DKP because the amide bonds in planar DKP are strained (Eguchi and Kakuta 1974). Bujdak et al. (2006) found that when a mixture of linear *cis*-Ala₂ and *trans*-Ala₂ was heated with montmorillonite for 5 days at 85 °C, the yield of *cis*-DKP was two times higher than that of *trans*-DKP. However, the yield of DKP decreased significantly, and a similar trend was observed when the mixture was heated without montmorillonite. They estimated that the configuration of the molecules of linear *cis*-Ala₂ would favor intramolecular interactions between nucleophilic amino groups and electrophilic carboxyl groups (i.e., peptide bond

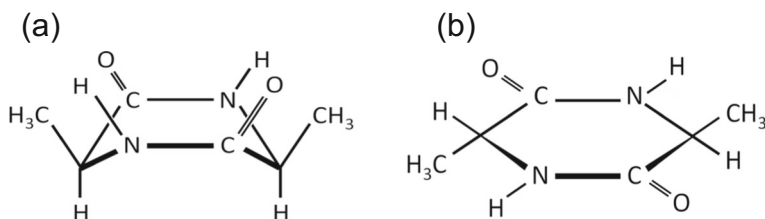


Fig. 5 Conformations of (a) *cis*-DKP and (b) *trans*-DKP (Egami and Kakuta 1974)

formation). In other words, *cis* dipeptides are more rapidly cyclized to DKP than their *trans* counterparts because they experience less steric hindrance during their cyclization to *cis*-DKP (Naraoka and Harada 1986). Several other studies have also observed reported the formation of *cis*-DKP (Saetia et al. 1993; Plasson et al. 2011), suggesting that *cis*-DKP and peptides could accumulate during thermal abiotic peptide formation.

cis-DKP has a homogeneous conformation: L and L, or D and D. The emergence of homogeneous peptides is still a matter of debate in the origin of life. In this study, *cis*-DKP (i.e., a homogeneous dipeptide) selectively accumulated on the olivine surface when DKPs were synthesized from a mixture of racemic amino acids under thermal conditions in the presence of olivine. Several studies reported the chiral amplification of amino acids on mineral surfaces. Bonner et al. (1974) found the asymmetric adsorption of Ala on quartz surface; L-Ala and D-Ala were selectively adsorbed on *l*-quartz and *d*-quartz surfaces, respectively. Fraser et al. (2011) observed that L-amino acids were selectively adsorbed on vermiculite surface. Thus, mineral surface would have the ability to amplify the stereoselectivity. In this study, olivine surface would amplify the stereoselectivity of *cis*-DKP, although the mechanism is not clear.

As discussed above, if DKPs are important intermediates for the elongation of peptides, the selective accumulation of *cis*-DKP would be important as the first step in the formation of homogeneous peptide (i.e., homochirality) and the subsequent formation of proteins on primitive Earth.

Conclusions

We found that the formation of DKP from DL-Ala was promoted on the surface of olivine when these materials were heated with a small amount of water, and that *cis*-DKP (LL and DD) was more stable than *trans*-DKP because of the greater stability of its geometric conformation. These results therefore not only demonstrate that olivine is an efficient catalyst for the formation of DKP, but that it also plays an important role in determining the stereoselectivity of the cyclic peptide products. Taken together, these results indicate that olivine may have been involved in the abiotic formation of organic compounds and their homochiral distribution on primitive Earth and other planets.

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