

## Prebiotic amino acid chemistry on the early Earth

H. Strasdeit

Department of Bioinorganic Chemistry, University of Hohenheim, Stuttgart, Germany (h-strasd@uni-hohenheim.de / Fax: +49-711-45923950)

### Introduction

In organisms, amino acids mainly occur as building blocks of proteins. As the proteins form one of the chemical pillars of today's life, it has long been hypothesized that amino acids were already involved in the chemical evolution that preceded life. In recent years, the results of new simulation experiments and analyses of extraterrestrial materials changed our view on the prebiotic chemistry of this class of compounds. In the present contribution some of these results are reviewed and their implications are discussed.

### Prebiotic Sources of Amino Acids

There is one prebiotic source of amino acids that is undisputed, namely the exogenous delivery by carbonaceous chondrites. These meteorites contain a large number of abiotically formed amino acids of which the most abundant, such as glycine (**1**), alanine (**2**),  $\alpha$ -aminoisobutyric acid (**3**), isovaline (**4**) and  $\beta$ -alanine (**5**), often have individual concentrations in the ppm range.

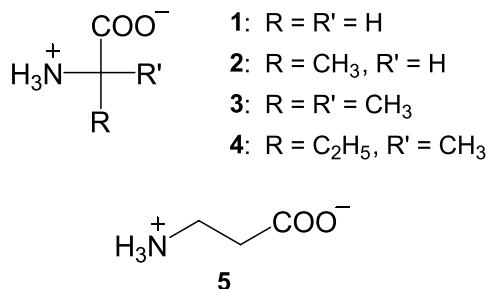


Figure 1: Structures of some amino acids that are abundant in carbonaceous meteorites

Another probable source is electric discharges in the bulk atmosphere and in volcanic ash-gas clouds ("volcanic lightning") [1]. It is mostly assumed that Earth's atmosphere four billion years

ago was redox-neutral. It has been thought that under such conditions an efficient amino acid synthesis is not possible. But this view has been challenged by the results of recent laboratory experiments [2, 3]. The hydrolysis of HCN polymers might have been a further abiotic route to amino acids. It is not yet clear whether submarine hydrothermal vents could have been net producers of prebiotic amino acids (see below).

### Prebiotic Sinks for Amino Acids

On the Hadean Earth (and possibly on the Noachian Mars), amino acids could have been photochemically destroyed, provided that sufficiently intense UVC radiation reached the ground. Due to the lack of an ozone layer this might have been in fact the case. Another probable sink for amino acids is decomposition by heat. Main heat sources on Earth and Mars were volcanoes and impacts of asteroids, meteorites and comets. If submarine hydrothermal vents existed they possibly acted more efficiently as sinks than as sources [4]. The thermal decomposition of amino acids depends on several factors besides temperature. For example, the heating time, presence or absence of water, and the chemical bonding state and type of the amino acid are important. Among the different thermal reactions of amino acids (see below), decarboxylation and deamination are the prebiotically least productive ones. Some amino acids show a surprisingly high thermal stability. **3**, for example, sublimes without decomposition when heated to 350 °C in an open system under a nitrogen atmosphere. In contrast, **1** decomposes already around 180 °C to form a black water-insoluble residue. In the case of **1** it has been demonstrated that the coordination to metal ions and the intercalation into layer silicates such as montmorillonite can drastically change the thermal behaviour of an amino acid [5, 6].

### Productive Reactions of Prebiotic Amino Acids

A steady-state amino acid concentration of 0.3 mM has been estimated for the primordial ocean [7]. In drying lagoons and rock pools, much higher concentrations and therefore more favorable conditions for peptide formation might have existed. In the laboratory, thermal peptide formation has, for example, been observed in highly saline copper(II)-containing solutions [8]. At the coasts of primordial volcanic islands, the evaporation of seawater by streams of lava must have resulted in amino acid-containing salt crusts. Simulation experiments revealed that further heating of these crusts can produce the chemical building blocks of potential photoreceptor and electron-transfer molecules [9]. Some  $\alpha,\alpha$ -dialkyl amino acids in carbonaceous chondrites show significant L-enantiomeric excesses which are definitely not caused by terrestrial contaminations. In this respect, the amino acid 4, for which L-ee values up to 18.5 % have been reported, is probably most interesting [10]. There is no satisfactory explanation for the origin of such large enantiomeric excesses. However, the enantioselective photodecomposition of the amino acid or a precursor molecule by circularly polarized UV radiation in combination with other still unknown mechanisms is conceivable. It has been demonstrated that L-4 acts as an enantioselective catalyst in the prebiotically plausible aldol reaction of glycolaldehyde [11]. These findings support the idea that non-racemic meteoritic amino acids could have triggered the biological homochirality.

The scenarios described above are not necessarily confined to the Hadean/early Archaen Earth but may frequently emerge on terrestrial planets in certain stages of their development. For example, the requirements for a rich amino acid chemistry – active volcanoes, meteorite impacts, layer silicates, liquid water, and soluble salts – existed in Martian history, too.

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