New formation mechanisms of meteoritic amino acids based on the discovery of hydroxy amino acids identified in the Murchison meteorite

*Toshiki Koga¹, Hiroshi Naraoka¹

1. Department of Earth and Planetary Sciences Kyushu University

ntroduction: Carbonaceous chondrites contain a diverse suite of extraterrestrial amino acids, which have various structures such as α , β , γ or δ amino-group [1], while terrestrial life use only α -amino acids. The distribution of meteoritic amino acids had been influenced by aqueous alteration on the meteorite parent body (e.g. α -aminoisobutyric acid versus β -alanine [2], and L-enantiomeric excess of isovaline [3]). However, a comprehensive formation mechanism, which could explain the diversity of meteoritic amino acids, remains unclear. In our previous study, nine new hydroxy amino acids and one β -aminodicarboxylic acid were identified in the extract of the Murchison for the first time (Koga and Naraoka, under revision). In this study, the simulation experiments of amino acid synthesis were performed under plausible conditions of the meteorite parent body in order to pursue their formation mechanisms.

Materials and Methods: The aqueous solutions containing ammonia/formaldehyde/acetaldehyde and/or glycolaldehyde (100/10/1/1 by mol) with NH_3/H_2O (1/100 by mol) were heated at 60 °C for 6 days in a N $_2$ -purged glass ampoule with or without olivine or quartz powder with the water/mineral ratio of 1/9 (by weight). The reaction mixtures were extracted with hot water at 100 °C for 20 h. The supernatants were divided into three fractions: one hydrolyzed with 6M HCl for analysis of amino acid distribution, and two non-hydrolyzed for investigation of their precursors. The hydrolyzed and one non-hydrolyzed fractions were analyzed by GC/MS with a Chirasil-L-Val capillary column. The other non-hydrolyzed fraction was analyzed by GC/MS with a DB-5 capillary column.

Results and Discussion: The simulation experiments gave totally 20 amino acids including the nine new amino acids identified in the Murchison extract by our previous study (Koga and Naraoka, under revision). Glycine was the most abundant (approximately 0.1 % relative to the total initial carbon concentration of aldehydes), which is the similar occurrence as observed by the previous study. The amount and variety of amino acids increased in the presence of olivine compared to those in the absence of olivine and the presence of quartz. When glycolaldehyde was used in addition to formaldehyde, acetaldehyde and ammonia, the yield of hydroxy amino acids increased 1.4 times, but β -aminodicarboxylic acid decreased by one-fifth relative to the experiment in the absence of glycolaldehyde. These results indicate that formose reaction with ammonia in the presence of mineral is an important formation pathway to produce meteoritic amino acids during aqueous alteration on the meteorite parent body. In addition, the identification of a hydroxy amino acid precursor (3-Hydroxy-2-pyrrolidinone) is suggestive of a possible formation pathway using the formose reaction products with ammonia.

References: [1] Burton A. S. et al. (2012) Chem. Soc. Rev., 41, 5459-5472. [2] Glavin D.P. et al. (2006) Meteor. Planet. Sci., 41, 889-902. [3] Glavin D. P. and Dworkin J. P. (2009) Proc. Natl. Acad. Sci. USA, 106, 5487-5492.

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