Hydroxy amino acids in carbonaceous chondrites and their formation mechanisms

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（炭素質コンドライト中のヒドロキシアミノ酸とその生成メカニズム）

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論　文　内　容　の　要　旨

Carbonaceous chondrites contain a variety of extraterrestrial amino acids, which were formed throughout the processes from the interstellar medium to the meteorite parent body. The abiotically synthesized amino acids can provide us information for understanding the chemical evolution of biological-related compounds and possibly the emergence of life on the early Earth. The molecular distributions and enantiomeric excesses of meteoritic amino acids have been thoroughly investigated in various types of carbonaceous chondrites over half a century. Recently, a family of C_3 and C_4 hydroxy amino acids (HAAs) was newly identified in the CM2 Murchison meteorite. However, the distributions and enantiomeric compositions of HAAs remained unknown in other carbonaceous chondrites.

This thesis consists of three chapters, as followed.

Chapter 1: The abundances, distributions, and enantiomeric ratios of C_3 and C_4 HAAs were investigated in five CM chondrites and four CR chondrites by gas chromatography/mass spectrometry (GC-MS) analyses. A new GC-MS analytical technique was developed to be capable of analyzing 13 different HAAs in a single run. The HAA analyses performed in this study revealed that 1) the petrographic type CR2 chondrites contained greater abundances of α-HAAs than CM chondrites and 2) the hot water and HCl extracts of CM and CR chondrites contained roughly similar ranges of abundances of β- and γ-HAAs. Application of the GC-MS method developed here resulted in the first successful chromatographic resolution of the enantiomers of an α-dialkyl HAA, D,L-α-methylserine, in carbonaceous chondrites. Meteoritic

α-methylserine was found to be mostly racemic within error and did not show L-enantiomeric excesses correlating with the degree of aqueous alteration, a phenomenon observed in meteoritic isovaline, another α-dialkyl amino acid. It is considered that HAAs in CM and CR chondrites could have been produced from the Strecker cyanohydrin reaction (for α-HAAs) and an ammonia-involved formose-like reaction (for β-, and γ-HAAs).

In Chapter 2, an amino acid synthesis experiment from glycolaldehyde and ammonia was performed to reveal the formation pathways of amino acids by the ammonia-involved formose-like reaction. This experiment was conducted under an air or a nitrogen atmosphere to evaluate the effects of free oxygen on the productions of amino acids and other organic compounds. The reaction products were analyzed by GC/MS to compare the distributions of synthesized organic compounds between the different conditions. As a result, oxygen in an air promoted the syntheses of amino acids and sugar acids, indicating oxidation was involved in their formation mechanisms. A precursor compound of glycine was identified as N-oxalylglycine that can be synthesized from ammonia and glyoxylic acid, which was produced by glycolaldehyde oxidation. The formation mechanism of glycine in this experiment could be generalized as the reaction of an oxoacid and ammonia; thus, it can be hypothesized that the reactions of α-, β-, and γ-oxo acids with ammonia could produce various structural isomers of amino acids, including α-, β-, and γ-HAAs.

In Chapter 3, the results and discussion obtained from the amino acid synthesis experiments were compared with the HAA distributions of the CM and CR chondrites and observations in the previous studies. This study suggests that the ammonia-involved formose-like reaction could complement previously proposed formation mechanisms such as the Strecker-cyanohydrin reaction to explain the distribution of meteoritic HAAs.