AMINO ACIDS IN CARBONACEOUS CHONDRITES YAMATO 980115 AND ALLAN HILLS A77003. H.-S. Chan[1,2], Y. Chikaraishi[1], Y. Takano[1], N. O. Ogawa[1], and N. Ohkouchi[1], [1]Japan Agency for Marine-Earth Science and Technology, Japan, [2]NASA Johnson Space Center, Houston, Texas 77058, USA.

Introduction: Carbonaceous chondrites (CCs) are primitive solar nebular aggregates that have evaded extensive planetary formation processes. CCs have been under the research spotlight because they may provide clues to the processes that predate and promote the onset of life. Among the wealth of organic materials in CCs, soluble compounds such as amino acids demonstrate a crucial significance on biochemical evolution as they are also the monomers of protein and enzymes that are indispensable to life on Earth. The most fundamental task that is common to studies of extraterrestrial materials is to identify amino acids that are indigenous to the meteorite. One of the methods is isotopic composition analysis of individual molecule within complex organic mixtures, also known as compound specific isotope analysis (CSIA).

Nitrogen isotope analysis of amino acids was first demonstrated by several laboratories in 1994 [1-3] . The method was then revised with the use of *N*-pivaloyl, *O*-isopropyl (Pv/iPr) esters to enhance chromatographic resolution [4]. Isotope analyses of amino acids esters derivatized using *N*-trifluoroacetyl, *O*-isopropyl (TFA/iPr) on optically active GC capillary column has also been employed. Nevertheless, metal fluorides produced from fluorinated derivatives would rapidly degrade the combustion catalyst and oxidants [5], while isotopic fractionation through the electrophilic column and nitrogen contributed from its stationary phase may veil the analysis of nitrogen isotope ratio [6]. Therefore, in this study we report the amino acid contents and nitrogen isotopic compositions for Pv/iPr amino acid derivatives of two CCs – CI (Ivuna) Yamato (Y) 980115 and CO (Ornans) Allan Hills (ALH) A77003, using gas chromatography/mass spectrometry (GC/MS) and gas chromatography/combustion/isotope ratio mass spectrometry (GC/C/IRMS).

Samples and Experimental Procedures: The meteorite samples Y-980115 (1.079 g) and ALHA77003 (1.015 g) were provided from the National Institute of Polar Research (NIPR) in Japan. These meteorites were collected in Antarctica in 1998 and 1977 respectively. The powdered, Pv/iPr derivatized 12 M HCl-hydrolysed meteorite hot-water extracts, procedural blank, and a mixture of amino acid standards were analysed for their amino acid contents using a GC/MS, and nitrogen CSIA measurements using a GC/C/IRMS. Total organic carbon (TOC), total nitrogen (TN), carbon and nitrogen isotopic compositions of the samples were determined with an improved isotope ratio mass spectrometer (IRMS; ThermoFinnigan Delta Plus XP) coupled to a Flash elemental analyzer (EA; ThermoFinnigan EA1112) via a Conflo III interface. Detailed experimental procedures have been described in the literature [7-10].

Results and Discussion: The GC/MS chromatograms and the individual/total amino acid abundances of the samples are described in further details in [11]. We have compared the $\delta^{15}N$ values for amino acid standards determined by GC/C/IRMS to EA/IRMS independently (Figure 1). The linearity on the observed $\delta^{15}N$ values indicates the precision and repeatability of the isotopic analysis we present in this study.

Amino acid contents. The CCs are shown to be depleted in amino acids. The total amino acid (free plus bound) abundances of Y-980115 and ALHA77003 are 374 ppb and 824 ppb respectively. Only amino acids that are common in biological context, such as aspartic acid, glutamic acid, glycine, leucine, and serine, were detected in the samples. No extraterrestrial amino acid were identified in the samples, presumably due to the small concentration of bulk organic carbon (0.33 wt%) and nitrogen (0.005 wt%) in ALHA77003.

Nitrogen isotopic compositions. The GC/C/IRMS chromatograms for the amino acid derivatives of the meteorite samples are shown in Figure 2. The meteorite samples were devoid of laboratory contamination as advised by the contrasting amino acid contents and the absence of peaks representing other biotic amino acids such as aspartic acid and glutamic acid.

As shown in Figure 2, in CI1 Y-980115, only glycine and α-alanine were identifiable above detection limit of the GC/C/IRMS. The $\delta^{15}N$ values of the glycine and α-alanine are +144.8‰ (S/N=16, ±0.5‰) and +121.2‰ (S/N=3, ±5−10‰) respectively, strongly suggesting extraterrestrial signatures. Although glycine is a very common terrestrial amino acid, this exceptionally high stable isotope value indicates that glycine is indigenous to Y-980115, or possibly an interstellar source for its precursors. The amino acid abundance of ALHA77003, on the other hand, is well below the detection limit of the instrument and thus we were not able to observe any peak of known amino acid on the GC/C/IRMS chromatogram for this meteorite.

The $\delta^{13}C$ and $\delta^{15}N$ values for bulk rock composition are −11.6‰ and −2.8‰ for Y-980115, and −12.7‰ and −10.5‰ for ALHA77003. The observed values are far lower than the CSIA measurements for amino acids, accounting for a source of lighter isotopes contributed by other compounds in the meteorites, stressing that CSIA offers a more precise window for determining the synthetic origin of a compound in the sample, and underscoring the advantage of CSIA over the traditional bulk isotopic analysis. The nitrogen and carbon isotope values for bulk Y-980115 is within the zone of chondrites, and is comparable to the values obtained for carbonaceous and ordinary chondrites.

Amino acids formation pathways. Plausible extraterrestrial synthetic pathways for amino acids as well as processes of isotopic fractionation have undergone heated debate. It has been suggested that glycine and alanine in CI chondrites could have been produced through HCN polymerization if the parent body had been exposed to elevated temperatures (up to 100℃) [12]. Heat source on asteroids are available from radioactive decay, as well as minor contribution from the episodic impact heating. Aqueous alteration was proposed to have taken place on the CI parent body under water abundant conditions at higher temperatures (>100℃) shortly after accretion [13], in this connection, we consider HCN polymerization could have formed glycine in CI chondrites when both asteroidal liquid water and heat source were available on the parent body.

Summary: The CI1 chondrite Y-980115 belongs to the most aqueously altered members of carbonaceous meteorites, and we have identified glycine at high $\delta^{15}N$ value (up to +144.8‰) which accounts for an extraterrestrial origin. With reference to previous petrologic studies, we have also established an understanding that this meteorite has exposed to a certain degree of thermal alteration in the early history of the parent body shortly after its accretion. This may have supported the theory that glycine and alanine, the life important biomolecules, could have been formed on the parent body during a very early phase of the span of our Solar System.

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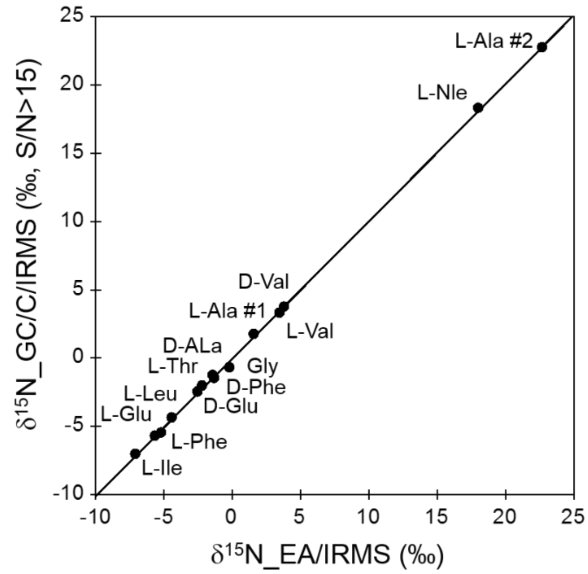

Figure 1. Comparison of nitrogen isotopic compositions of amino acid standards (as Pv/iPr ester derivatives) determined by EA/IRMS (before derivatization) and GC/C/IRMS (after derivatization). The carbon and nitrogen isotopic composition of each amino acid was expressed as the per mil (‰) deviation from a standard (Air).

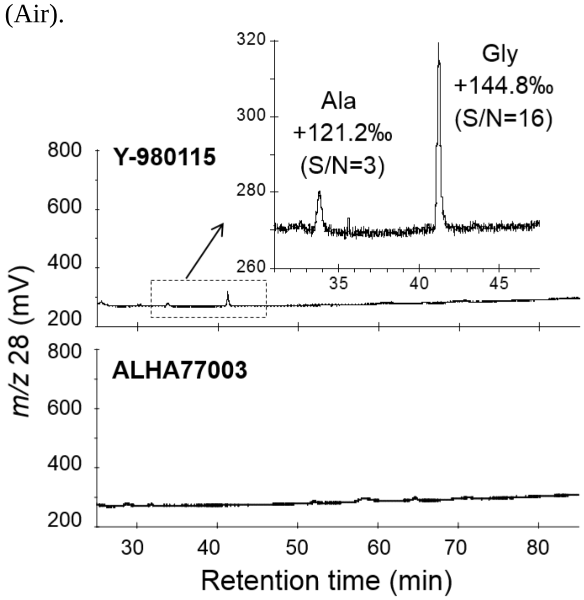

Figure 2. GC/C/IRMS chromatograms of the 12 M HCl-hydrolysed hot-water extracts of Pv/iPr amino acid esters in Y-980115 and ALHA77003. The peaks were identified by comparing the retention time to peaks of the amino acid standard mixture. The $\delta^{15}N$ values are indicated on the chromatograms with the corresponding peak heights (mV) shown in brackets. Abbreviations; Gly, Glycine; Ala, Alanine.