Amino acid compositions in heated carbonaceous chondrites and their compound-specific nitrogen isotopic ratios. Q. 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).

In this study we determined the amino acid contents and nitrogen isotopic compositions for CI1 (or CI-like) Yamato (Y) 980115 and CO3.5 Allan Hills (ALH) A77003. The two meteorites were shown to be thermally metamorphosed (above 500°C) caused by minor impact shock or heating during the accretion process [1, 2].

Samples and Methods:

The meteorite samples CI1 Y-980115 (Sub no.: 68, 1.079 g) and CO3.5 [3] ALHA77003 (Sub no.: 87, 1.015 g) were provided by the National Institute of Polar Research (NIPR) in Japan.

The powdered meteorite samples and a procedural blank were subjected to hot-water extraction, acid-hydrolysis, and derivatization, and were then analyzed for their nitrogen isotopic values using a gas chromatography/combustion/ isotope ratio mass spectrometry (GC/C/IRMS). Nitrogen isotope analysis of amino acids has been revised with the use of *N*-pivaloyl, *O*-isopropyl (Pv/iPr) esters to enhance chromatographic resolution [4]. 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 [5-8].

Results and Discussion:

Figure 1 shows the comparison of the ^{15}N values of amino acid standards determined by EA/IRMS (before derivatization) and GC/C/IRMS (after derivatization) to demonstrate the accuracy and precision of the observed $\delta^{15}N$ values. The linearity on the observed $\delta^{15}N$ values indicates the precision and repeatability of the isotopic analysis we present in this study ($R^2 = 0.9995$).

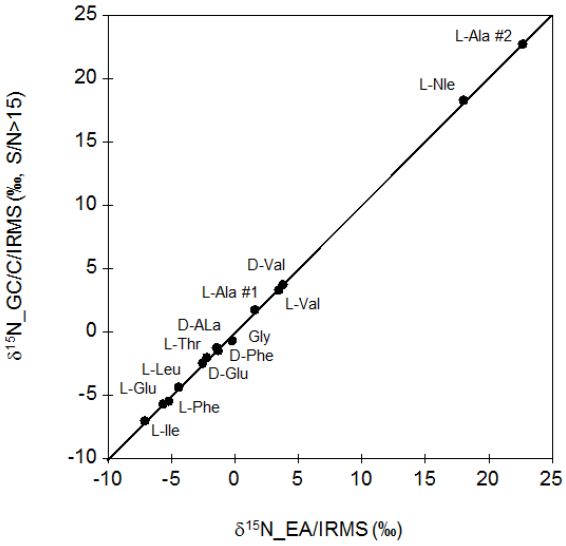

Figure 1. Comparison of nitrogen isotopic compositions of amino acid standards determined by EA/IRMS and GC/C/IRMS.

Amino acid contents. The samples are depleted in amino acids. Only glycine and α-alanine were identifiable above the detection limit of the GC/C/IRMS in Y-980115. A previous amino acid analysis of Y-980115 conducted by Burton and co-workers [9] showed that Y-980115 had a low total amino acid abundance ~3 nmol/g (which translates to ~300 ppb, with a molar mass of ~100 g/mol). This low amino acid abundance makes Y-980115 distinct from other CIs such as Orgueil and Ivuna (total amino acid abundance >4,000 ppb), which accounts for its alternative nomenclature as 'CI-like chondrite', commonly named for a range of CIs with isotopic and petrographic characteristics that differ remarkably from typical CIs [10]. The lower amino acid abundance in Y-980115 is also reflected by its low bulk nitrogen content (0.09 wt%) as compared to Ivuna and Orgueil (Ivuna: 0.19 wt%; Orgueil: 0.15 wt%).

The amino acid abundance of ALHA77003, conversely, is 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 low amino acid abundance is reflected by the small concentrations of

bulk organic carbon (0.33 wt%) and nitrogen (0.005 wt%; Table 1), and can be correlated to the extensive metamorphic history (>500 ℃, [11]) of the asteroid parent body.

Nitrogen isotopic compositions. In the literature, nitrogen CSIA has been conducted chiefly on CM and CR chondrites ($^{15}N \approx +60$ to $+200‰$) [e.g., 12, 13], considering their high amino acid abundances. This study provides the first nitrogen CSIA data for amino acids in CI (CI-like) and CO chondrites. The GC/C/IRMS chromatograms for the amino acid derivatives of the meteorite samples are shown in Figure 2. The $\delta^{15}N$ values of the glycine and α-alanine in Y-980115 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. 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.

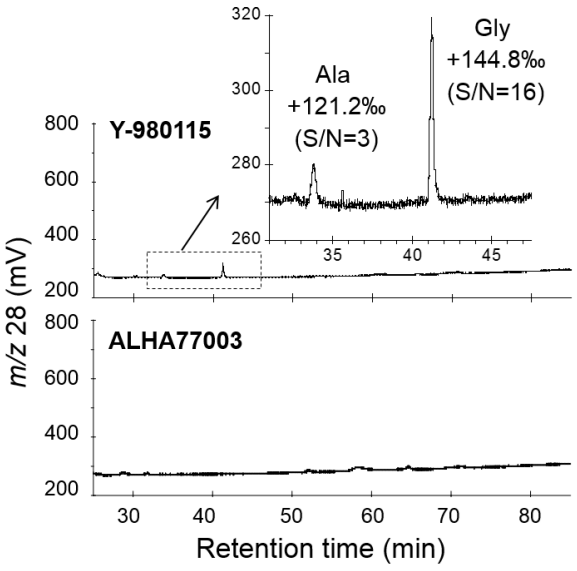

Figure 2. GC/C/IRMS chromatograms of the acid-hydrolyzed hot-water extracts of Pv/iPr amino acid esters in Y-980115 and ALHA77003.

The $\delta^{15}N$ values of the amino acids in Y-980115 are comparable to the data obtained for meteoritic amino acids, and are closer to the values for the amino acids in CRs. The similarity between the isotopic distributions of the CI-like and CR amino acids suggests that their precursors or formation mechanisms/environments are similar. This hypothesis requires further information such as $\delta^{13}C$ and δD values to validate.

Summary:

The CI1 chondrite Y-980115 belongs to the most aqueously altered members of carbonaceous meteorites, and we have identified glycine and alanine at high $\delta^{15}N$ values which suggest an extraterrestrial origin. With reference to previous petrologic studies, we have also established an understanding that the aqueous event, which likely account for the formation of these amino acids, occurred 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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