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

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Abstract

A novel method has been developed for compound-specific nitrogen isotope compositions with an achiral column which was previously shown to offer high precision for nitrogen isotopic analysis. We applied the method to determine the amino acid contents and stable nitrogen isotopic compositions of individual amino acids from the thermally metamorphosed (above 500 °C) Antarctic carbonaceous chondrites Ivuna-like (CI)1 (or CI-like) Yamato (Y) 980115 and Ornans-like (CO)3.5 Allan Hills (ALH) A77003 with the use of gas chromatography/combustion/isotope ratio mass spectrometry. ALHA77003 was deprived of amino acids due to its extended thermal alteration history. Amino acids were unambiguously identified in Y-980115, and the $\delta^{15}N$ values of selected amino acids (glycine +144.8 ‰; α-alanine +121.2 ‰) are clearly extraterrestrial. Y-980115 has experienced an extended period of aqueous alteration as indicated by the presence of hydrous mineral phases. It has also been exposed to at least one post-hydration short-lived thermal metamorphism. Glycine and alanine were possibly produced shortly after the accretion event of the asteroid parent body during the course of an extensive aqueous alteration event and have abstained from the short-term post-aqueous alteration heating due to the heterogeneity of the parent body composition and porosity. These carbonaceous chondrite samples are good analogs that offer important insights into the target asteroid Ryugu of the Hayabusa-2 mission, which is a C-type asteroid likely composed of heterogeneous materials including hydrated and dehydrated minerals.

Keywords: Carbonaceous chondrites, Meteorites, Astrochemistry, Compound-specific isotopic analysis, Nitrogen isotopes, Amino acids, Organic materials, Meteoritic composition, Gas chromatography/combustion/isotope ratio mass spectrometry

Introduction

Carbonaceous chondrites are primitive solar nebular aggregates that did not experience extensive planetary formation processes. They contain organic carbon materials that are soluble in common organic solvents. Carbonaceous chondrites may provide clues to the abiotic chemical evolution processes that predate and promote the onset of life and offer important insights into the target asteroids of the sample return missions Hayabusa-2 and OSIRIS-REx, which aim to collect and return to Earth samples from the surfaces of the C-type asteroids

Ryugu and Bennu. Through detailing the organic molecule inventory in the early solar system, and understanding the conditions and processes that occurred on the asteroid parent bodies, we may be able to develop testable hypotheses regarding pathways of abiotic developments of organic molecules.

Among the wealth of organic materials in carbonaceous chondrites, amino acids demonstrate a crucial significance on chemical evolution as they are also the monomers of protein and enzymes that are indispensable to life on Earth. Over 80 amino acids have been found in the Mighei-like (CM) chondrites Murchison and Murray, and a significant portion of these amino acids are rarely found to occur in biological context, such as α-aminoisobutyric acid (α-AIB) and isovaline

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(Botta and Bada 2002; Kvenvolden et al. 1970; Kvenvolden et al. 1971).

Since amino acids can be produced both biologically and non-biologically, the most fundamental task that is common to the study of meteoritic amino acids is to identify the amino acids that are indigenous to the meteorite, which were produced or obtained through processes prior to atmospheric entry, and to distinguish them from terrestrial contaminants. The Itokawa particles returned by the first Hayabusa mission, for example, were shown to be composed of proteic amino acids at blank levels only (Naraoka et al. 2012). Their results were supported by several other preliminary analyses of the Itokawa particles (e.g., Raman spectroscopy, X-ray absorption near edge structure (XANES) spectroscopy) (Kitajima et al. 2015; Uesugi et al. 2014; Yabuta et al. 2014), which suggested that although organic materials were present, it was difficult to ascertain their extraterrestrial origin. Other than identifying amino acids that have rare biological occurrence and determining the relative amino acid abundances and enantiomeric ratio, stable isotope ratio is a reliable and convenient tool used to tell apart terrestrial and extraterrestrial amino acids, as biology preferentially uses lighter isotopes, while amino acids formed by abiotic processes in cold environments are more enriched in heavier isotopes.

Compound-specific isotope analysis (CSIA) can be conducted with the use of gas chromatography/combustion/isotope ratio mass spectrometry (GC/C/IRMS) (Matthews and Hayes 1978). The common stable isotopes used for evaluating the synthetic origins of amino acids are carbon ($\delta^{13}C$), nitrogen ($\delta^{15}N$), and hydrogen (δD). Biologically synthesized materials on Earth are usually moderately to substantially depleted in the heavy stable isotopes ^{13}C, ^{15}N, and deuterium (D) relative to the interstellar values ($^{13}C < ^{15}N < D$) (Engel and Macko 1997; Engel et al. 1990; Epstein et al. 1987; Sephton and Gilmour 2001). Amino acids formed by abiotic processes are moderately to highly enriched in heavy isotopes. For example, amino acids in Murchison are enriched in ^{15}N (+60 to +200 ‰) relative to terrestrial organic matter (−20 to +30 ‰) (Burton et al. 2012b; Elsila et al. 2012; Engel and Macko 1997; Epstein et al. 1987; Ohkouchi and Takano 2014; Pizzarello et al. 1994; Pizzarello and Holmes 2009; Sephton and Gilmour 2001).

While there are more than two carbon and even more hydrogen atoms in the chemical structures of amino acid molecules, most amino acids contain only one nitrogen atom. Accordingly, amino acids required for nitrogen CSIA must be far more concentrated when compared to those used for carbon and hydrogen CSIA. Despite this shortfall for nitrogen CSIA, since amino acids must be structurally altered through chemical derivatization procedures involving laboratory hydrocarbon reagents prior to CSIA measurements, the derivatization process itself introduces extraneous carbon and hydrogen atoms that must be accounted for when determining isotopic ratios. Nevertheless, either carbon, nitrogen, or hydrogen CSIA offers valuable data, the targeted isotope is chosen depending on factors such as the compound being analyzed, sample abundance, and possible sources of contamination.

Over the past decades, amino acid contents of extraterrestrial objects have been extensively characterized to investigate the source of organic matter as well as to account for the effects of the alteration processes on the organic inventory on the parent body. However, CSIA of amino acids is limited to only a few numbers of studies, which include several nitrogen CSIA of amino acids (e.g., Brand et al. 1994; Elsila et al. 2012; Engel and Macko 1997; Merritt and Hayes 1994; Pizzarello et al. 1994; Pizzarello and Holmes 2009; Preston and Slater 1994). In these studies, CSIA has not only been used to interpret the origins of individual amino acids but also as a guide to their formation pathways, as the isotopic values are correlated to the precursors and formation mechanisms. The nitrogen isotopic values were also used to describe the chronology of the formation of individual amino acids, as lower $\delta^{15}N$ values of α-methyl amino acids, for example, indicate brief isotopic differentiation, and thus an earlier origin in the interstellar medium as opposed to α-H amino acids (Pizzarello and Holmes 2009).

Chirasil-Val (chiral polysiloxanes [Chirasil-type] stationary phases with a valine diamide selector) is a popular optically active column selected for many studies. In order to enhance their detection, amino acids have to be derivatized prior to their injection into the instrument. Trifluoroacetyl/isopropyl (TFA/iPr) is commonly used as a derivatizing agent for GC analyses. Nevertheless, GC columns and amino acid derivatizing agents should be selected with caution for nitrogen isotopic analysis using GC/C/IRMS for several reasons. For instance, despite the proven advantages of using TFA/iPr as derivatizing agents for the detection of amino acids using GC, metal fluorides produced from fluorinated derivatives would rapidly degrade the combustion catalyst and oxidants in the GC/C/IRMS system (see Chikaraishi et al. 2010 and references therein). Also, isotopic fractionation on an electrophilic Chirasil-Val column and the contribution of nitrogen from the column's stationary phase may veil the analysis of nitrogen isotope ratio (Metges and Petzke 1999). Therefore, in this study, we selected an achiral DB-23 column for nitrogen CSIA of amino acids. DB-23 offers optimal baseline resolution of D and L enantiomers of amino acids during nitrogen CSIA. Although DB-23 also contains nitrogen in the stationary phase, it has been shown to offer high precision for nitrogen

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isotopic analysis as it is composed of a polymethylsilox-ane stationary phase that contains nucleophilic functionalities (Chikaraishi et al. 2010). Even with a 1–2 ‰ error introduced by column bleeding, the determined $\delta^{15}N$ values for amino acids using a DB-23 column are still more consistent than using other columns such as Chirasil-Val and DB-FFAP (as presented by the linearity on a GC/C/IRMS vs elemental analyzer (EA)/IRMS plot, a similar method of accessing data consistency is described in the "Results and discussion" section) (Chikaraishi et al. 2010). On the other hand, diastereomeric separation of amino acids can be optimized by using a DB-23 column as compared to other columns such as DB-35, HP-INNOWAX, and several Chirasil columns (Yoshito Chikaraishi, personal communication, March 2014). Similar results were presented by Takano et al. (2009) who separated chiral amino acids with a nonpolar achiral column and determined the nitrogen isotope compositions of individual amino acid enantiomers. Another merit of nonpolar achiral columns is the stability of the stationary phase over a wider range of temperatures, which span the range from 250 °C in the DB-23 column up to 310 °C in the HP-Ultra-2 column, as compared to the maximum temperature of only 220 °C in the Chirasil-Val.

In this study, we report the amino acid contents and nitrogen isotopic compositions of individual amino acids in two carbonaceous chondrites—Ivuna-like (CI) Yamato (Y) 980115 and Ornans-like (CO) Allan Hills (ALH) A77003, analyzed using a GC/C/IRMS. Our study provides the first nitrogen CSIA data for amino acids in CI and CO chondrites analyzed with a nonpolar achiral column in order to enhance amino acid detection under the GC/C/IRMS settings.

Methods
Samples, chemicals, and materials
The meteorite samples CI1 Y-980115 (sub no.: 68, 1.079 g) and CO3.5 (Greenwood and Franchi 2004) ALHA77003 (sub no.: 87, 1.015 g) were provided by the National Institute of Polar Research (NIPR) in Japan. Combusted quartz sand (heated to 500 °C for 3 h) was analyzed as a procedural blank for this work and was treated using the same experimental steps as the meteorite samples. Meteorites and the heated quartz sand were crushed into powder using a tungsten mortar and pestle pre-cleaned by three washes of 1 mL water (H_2O) and methanol. Sample crushing was performed in a clean booth with a HEPA-equipped ventilation system. All tools, glassware, and ceramics were cleaned of organics by baking at 500 °C for 3 h. We used amino acid standards purchased from Wako Pure Chemical Industries Ltd. (hereafter, Wako Chemical) and Sigma-Aldrich (purity of all amino acid standards is above 98 %). All

derivatization reagents, high-performance liquid chromatography (HPLC)-grade water, sodium hydroxide (NaOH) and hydrochloric acid (HCl) (37 %), dioxin analysis grade dichloromethane (DCM), and methanol were obtained from Wako Chemical. Analytical-grade cation-exchange resin (AG 50W-X8; 200-400 mesh, H^+ form) was from Bio-Rad Laboratories (Tokyo, Japan).

Sample extraction and desalting procedures
The amino acid extraction procedures employed in this study are based on the methods used in Chan et al. (2012) and Takano et al. (2009). The meteorites samples were powdered and homogenized. One hundred milligrams of each sample was transferred to individual vials for bulk analysis using EA/IRMS. The remaining samples were transferred to individual 5 mL reactor vials with polytetrafluoroethylene (PTFE)-lined caps for hot-water extraction. Two milliliters of HPLC water was added to each sample. The vials were then heated to 100 °C for 24 h in a heating block. After cooling to room temperature, the samples were centrifuged for 5 min. The water supernatant was transferred to a 1 mL reactor vial and dried under a stream of nitrogen. One milliliter of 12 M HCl was added, and the samples were then subjected to acid hydrolysis for 12 h at 110 °C.

After the hydrolysis procedure, the hydrolysate was filtered by centrifugation in a GHP nanosep (Pall Corp.) at 10,000 rpm for 10 s. The filtered samples were de-fatted by adding 0.5 mL of n-hexane/dichloromethane (3:2, *v/ v*), shaking for 10 s, and removing the upper organic solvent. This de-fat procedure was repeated three times. The remaining acidic solution was evaporated under stream of dry nitrogen to dryness with the addition of 0.2 mL methanol.

The samples were then treated with cation-exchange chromatography for further purification. Briefly, the samples were adjusted to pH 1 using 2 mL of 0.1 M HCl. The cation-exchange resin column was prepared by adding resin in H_2O into a glass pipette fitted with sterilized quartz wool. The resin was washed by running 3 bed volumes of 1 M HCl, H_2O, 1 M NaOH, and finally with H_2O. The resin was then conditioned by reactivating to the H^+ form using 3 bed volumes of 1 M HCl and rinsed with 3 bed volumes of H_2O. After conditioning the columns, samples were injected into separated columns and eluted with 3 bed volumes of 10 wt.% ammonia (NH_3) aqueous solution. The eluates were collected in 1 mL reactor vials and then evaporated to dryness.

Derivatization
The desalted, acid-hydrolyzed amino acid extracts were derivatized according to the methods described in Chikaraishi et al. (2007) and Takano et al. (2009). The samples were equally divided into two portions, which

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were derivatized to yield N-pivaloyl, O-isopropyl (Piv/iPr) and N-pivaloyl, O-(S)-2-butyl (Piv/2-Bu) derivatives, respectively (Fig. 1). Piv/iPr has been shown to improve the chromatographic resolution of amino acid nitrogen CSIA by GC/C/IRMS (Metges et al. 1996). Chromatographic chiral separation without the use of chiral stationary-phase columns can be achieved through derivatization of amino acid diastereomers by optically active reagents like (S)-(+)-2-butanol (Takano et al. 2009). Esterification was performed with thionyl chloride/2-propanol (TC/iPr, 1/4, v/v), or thionyl chloride/ (S)-(+)-2-butanol mixture (TC/2Bu, 1/4, v/v) at 110 °C for 2 h, and acylation was performed with pivaloyl chloride/dichloromethane (PC/DCM, 1/4, v/v) at 110 °C for 2 h. Detailed procedures are described in the following.

Derivatization was carried out in 1 mL reactor vials. Two hundred microliters of TC/iPr or TC/2Bu was added to each of the samples. The vials were tightly capped, and the samples were esterified in a heating block set at 110 °C for 2 h. After that, the samples were cooled to room temperature and dried under a gentle stream of dry nitrogen at about 80 °C. Two hundred microliters of DCM was added to the sample and dried twice to help removing the derivative agent completely. Acylation was carried out by adding 200 μL of PC/DCM to the dried sample and heated at 110 °C for another 2 h. The samples were then cooled to room temperature, and the excess reagent was removed under a slow stream of dry nitrogen. DCM was added to aid the evaporation process.

The samples were then further purified by adding 200 μL of H$_2$O and 500 μL of n-hexane/dichloromethane (~3/2, v/v) into the sample vial, mixed by shaking for 10 s, and the upper layer (i.e., amino acid derivatives in organic solvent) was filtered using a GHP Nanosep with MgSO$_4$ powder for dehydration. This dehydration process was repeated twice. The samples were then brought up in 200 μL of degassed DCM and stored at −20 °C until further analysis.

Nitrogen CSIA by GC/C/IRMS

The samples were analyzed by GC/C/IRMS to determine the stable isotopic ratios of the most abundant amino acids. Nitrogen isotope analysis of the amino acid derivatives was carried out by a GC/C/IRMS using an Agilent Technologies 6890N GC with a programmable temperature vaporization (PTV) injector coupled to a Thermo Fisher Scientific DELTAplusXP IRMS via a GC/C/TC III interface. Through the GC/C/TC III interface, amino acid derivatives were combusted to CO$_2$, N$_2$, NOx, and H$_2$O in a microvolume ceramic tube (length 32 cm; internal diameter 0.6 mm) with CuO, NiO, and Pt wires at 1000 °C, and the NOx was reduced to N$_2$ in a microvolume ceramic tube (length 32 cm; internal diameter 0.5 mm) with reduced Cu wires at 550 °C. A counter current dryer (Permeable membrane, Nafion™) and a liquid nitrogen trap were installed between the reduction furnaces and the IRMS instrument for removing CO$_2$ and H$_2$O generated during amino acid combustion, as well as CO generated by the decomposition of CO$_2$ (which will impose a major problem for nitrogen isotopic analysis due to the same mass-to-charge ratio as nitrogen gas, m/z 28). All the connections were carefully tightened to prevent contamination of the GC/C/IRMS system by atmospheric N$_2$. The carrier gas flow rate was 1.4 mL min^{-1}. The amino acid derivatives were injected into a J&W DB-23 column
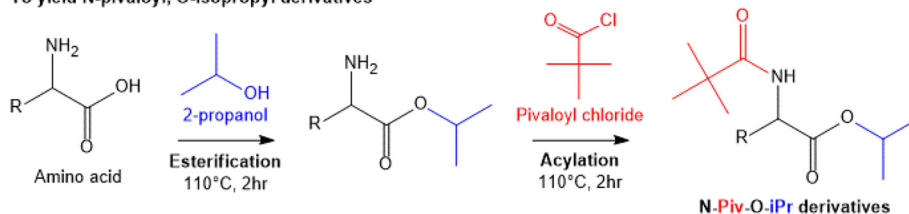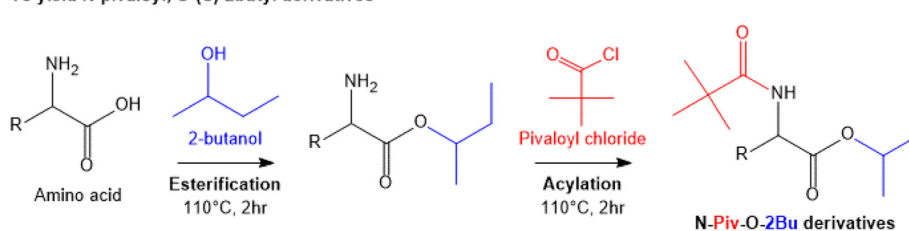
Fig. 1 The chemical derivatization pathways to produce Piv/iPr and Piv/2Bu amino acid derivatives

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(60 m × 0.32 mm i.d., 0.52 μm film thickness, Agilent Technologies) using the PTV injector in solvent vent mode. The PTV temperature was programmed as follows: 50 °C (initial temperature) for 0.2 min, heating from 50 to 260 °C at the rate of 600 °C min^{-1}, and isothermal hold at 260 °C for 10 min. The GC oven temperature was set as follows: 40 °C (initial temperature) for 2 min, heating from 40 to 120 °C at the rate of 30 °C min^{-1}, heating to 240 °C at the rate of 7 °C min^{-1}, and isothermal hold at 240 °C for 14 min.

Results and discussion

Accuracy and precision of the GC/C/IRMS analysis

The total carbon, total nitrogen, carbon, and nitrogen isotopic compositions of the samples were determined with an improved IRMS (Thermo Finnigan DELTAplusXP) coupled to a FLASH EA (Thermo Finnigan EA1112) via a Conflo III interface (Ogawa et al. 2010). The standard material for the EA/IRMS was Ni-chelated octaethylporphyrin (Ni OEP) in this study (Ogawa et al. 2010).

Figure 2a shows the signal-to-noise (S/N) ratios and $\Delta^{15}N$ values (i.e., the difference between $\delta^{15}N_{EAIRMS}$ and $\delta^{15}N_{GCCIRMS}$) for four amino acid standards (alanine, valine, glutamic acid, and phenylalanine) to demonstrate the accuracy and precision of the observed $\delta^{15}N$ values. In order to ensure a high accuracy and precision analysis, we minimized the background noise level through optimization of the instrumental conditions. We determined empirically that $\delta^{15}N$ analyses were optimal at S/N ratio above 10 (Fig. 2a), implying that the peaks should preferentially be above 30 mV at a noise level of 3 mV. We have also compared the $\delta^{15}N$ values for amino acid standards determined by GC/C/IRMS to EA/IRMS independently (Fig. 2b). The linearity of the observed $\delta^{15}N$ values supports a high precision and repeatability of the isotopic analysis we present in this study ($R^2 = 0.9995$).

Low amino acid abundances of Y-980115 and ALHA77003

Carbonaceous chondrites are valuable meteorites that only comprise about 5 % of observed falls; therefore, sample abundance is a common concern for meteoritic analyses. Among the NIPR Antarctic Meteorite Collection, for example, only a handful of the meteorite finds are carbonaceous chondrites that weigh over 100 g (Yamaguchi et al. 2014). CSIA typically requires a large amount of samples. Several grams of meteorite sample are usually required for isotopic analyses using GC/C/IRMS. With a total amino acid abundance of around 15 ppm, more than 7 g of CM Murchison sample was analyzed (Engel and Macko 1997). With a total amino acid abundance ten times higher than Murchison, the amount of LaPaz Icefield (LAP) 02342 used for nitrogen CSIA can be reduced to around 300 mg (Pizzarello and

Holmes 2009). In this study, we have demonstrated amino acid CSIA analysis of meteorites with a small sample amount (<1 g) and low amino acid abundances (ppb level). Based on the calculated amino acid abundance of Y-980115 given by Burton et al. (2014b), the limit of quantification for individual amino acids by the method used in this study was at picomole (pmol) level. The typical instrumental sensitivity for GC/C/IRMS is 0.1–10 nmol (Sessions 2006). With the combustion/reduction furnaces and liquid nitrogen trap in the GC/C/IRMS system, the gas introduced to the IRMS ion source was much cleaner without any excess compounds but N_2. This particular advantage combines with the novel analytical method (pmol level) (Metges et al. 1996) with good chromatographic resolution to offer a high instrumental sensitivity in this study. We have also conducted an initial GC/MS scan (Additional file 1: Figure S1) which clearly shows that no coeluting compound was present to interfere the IRMS analyses of the meteorite samples.

We have determined the amino acid contents and nitrogen isotope values for Y-980115 and ALHA77003 (Fig. 3). Due to the low amino acid abundances, independent $\delta^{15}N$ measurement for D and L amino acids was difficult, and we could not identify any peak in the Piv/2-Bu derivatized portions. Despite the featureless ALHA77003 chromatogram, this blank-level result alternatively reflects the cleanliness of the sample preparation procedures of this work and indicates that minimal terrestrial contamination (as possible coelution compounds) would interfere with the interpretation of the GC/C/IRMS results we obtained for Y-980115 described below. As shown in Fig. 3, in Y-980115, only glycine and α-alanine were identifiable above the detection limit of the GC/C/IRMS. A previous amino acid analysis of Y-980115 conducted by Burton et al. (2014a) 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 CI chondrites such as Orgueil and Ivuna (total amino acid abundance >4000 ppb), which accounts for its alternative nomenclature as "CI-like chondrite," commonly named for a range of chondrites with isotopic and petrographic characteristics that differ remarkably from typical CI chondrites (Tonui et al. 2014). Modal mineralogy of Y-980115 indicates that it has experienced short-lived thermal metamorphism above 500 °C (King et al. 2015b), which is notably lower than the estimated peak temperature (<220 °C) for Orgueil insoluble organic matter (IOM) obtained from micro-Raman spectroscopy (Busemann et al. 2007) (although micro-Raman spectroscopy is not sensitive to weaker thermal events such as flash-heating or impact (Quirico et al. 2005)) and inferred from its

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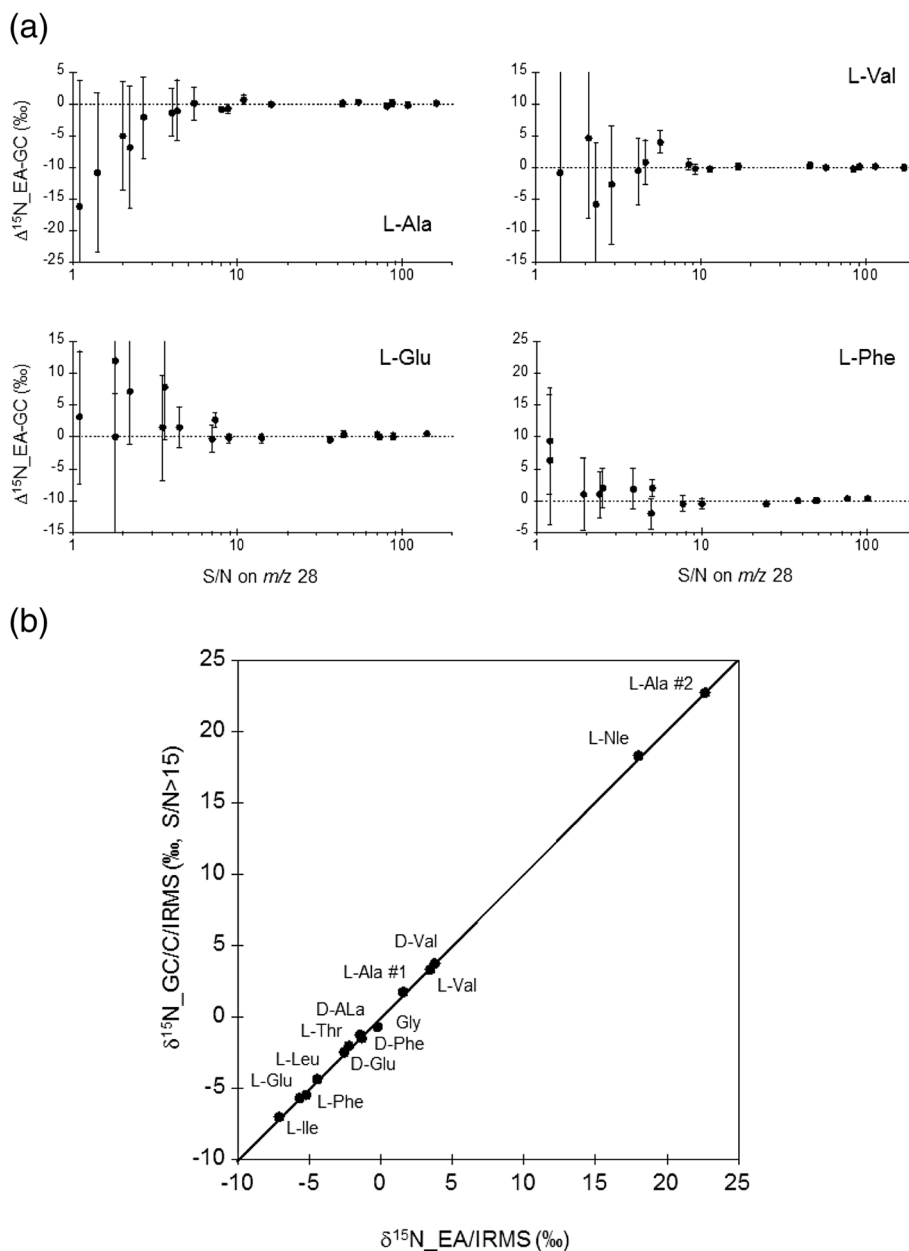
Fig. 2 The precision and repeatability of the nitrogen isotopic values determined by GC/C/IRMS and EA/IRMS. **a** The analytical relationship between S/N ratio (signal-to-noise ratio) and $\Delta^{15}N$ (defined as difference between $\delta^{15}N_{EAIRMS}$ and $\delta^{15}N_{GCCIRMS}$) for alanine (*Ala*, C_3 neutral amino acid), valine (*Val*, C_5 neutral AA), glutamic acid (*Glu*, C_5 acidic AA), and phenylalanine (*Phe*, C_9 aromatic AA). **b** Comparison of nitrogen isotopic compositions of amino acid standards (as Piv/iPr ester derivatives) determined by EA/IRMS (before derivatization) and GC/C/IRMS (after derivatization). The isotopic composition of each amino acid was expressed as the per mil (‰) deviation from a standard (AIR), as defined by: $\delta^{15}N = [(^{15}N/^{14}N)_{sample}/(^{15}N/^{14}N)_{standard} - 1] \times 1000$ (‰)

organic content (Nagy et al. 1963). Textural and mineralogical observations and oxygen isotopic compositions of major mineral phases in CI chondrites suggest even lower alteration temperatures of <150 °C (Clayton and Mayeda 1984; Zolensky et al. 1993). Amino acids are irreversibly decomposed at temperatures as low as 240 °C (Bada et al. 1995), therefore, metamorphism above 500 °C could destroy any preexisting amino acids

in the CI-like parent body. These explain the disparities between the amino acid content of Y-980115 and other CI chondrites.

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.%) (Table 1). Liquid chromatography analysis of Y-980115 indicates that the most abundant

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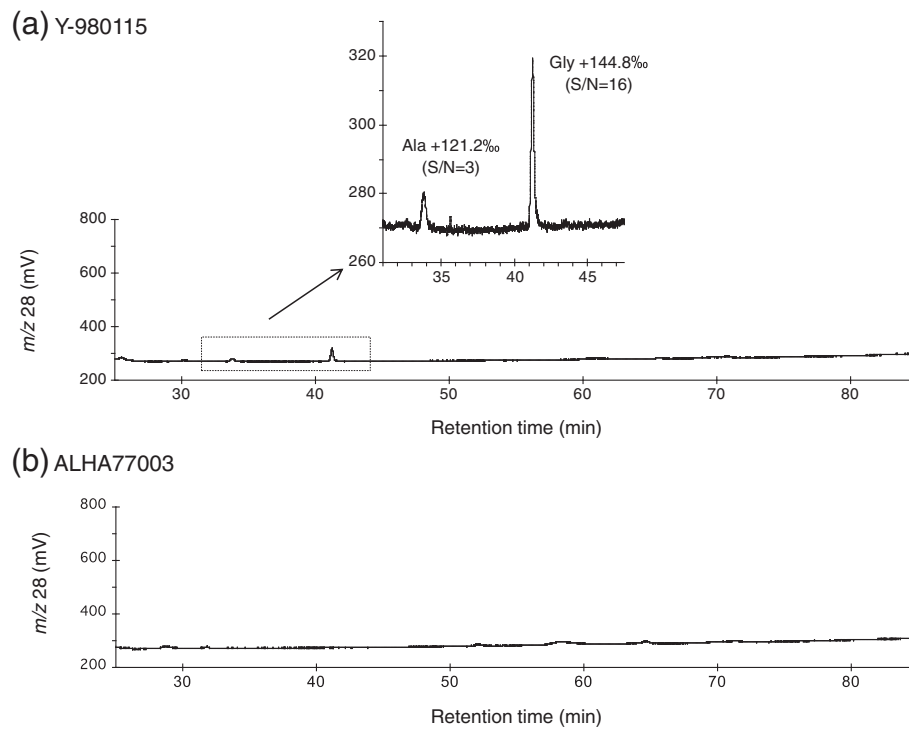
Fig. 3 GC/C/IRMS chromatograms of CI1 Y-980115 and CO3 ALHA77003. GC/C/IRMS chromatograms of the 12 M HCl-hydrolyzed hot-water extracts of the Piv/iPr amino acid esters in **a** CI1 Y-980115 and **b** CO3 ALHA77003. The peaks were identified by comparing the retention time to peaks of the amino acid standard mixture. The $\delta^{15}N$ values are indicated on the chromatograms with the corresponding peak heights (mV) shown *in parentheses*. Abbreviations: Gly - glycine, Ala - alanine

amino acids were ε-aminocaproic acid (EACA), serine, α-alanine, and glycine (Burton et al. 2014b). EACA and serine are unlikely indigenous, since EACA is a common terrestrial contaminant derived from nylon sample bags (Glavin et al. 2010), while serine is present with low enantiomeric ratio (D/L≈0.01) (Burton et al. 2014b) and is another common contaminant found in human fingerprints (Hamilton 1965). Nevertheless, the higher D/L ratios for several proteinogenic amino acids (aspartic acid≈0.67; glutamic acid≈0.74) indicate that they are possibly indigenous. The D/L ratio for alanine is low (~0.29) suggesting sources of terrestrial contaminations in their

analysis, which was observable as a major L-alanine peak in the blank sample (Burton et al. 2014b).

The amino acid abundance of ALHA77003, conversely, is below the detection limit of the instrument (0.1–10 nmol), 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 of the asteroid parent body. Since no prior amino acid analysis was provided for ALHA77003,

Table 1 The total carbon, total nitrogen, and isotopic compositions of CI and CO carbonaceous chondrites

Meteorite	Group	TC (wt.%)	TN (wt.%)	C/N (wt ratio)	$\delta^{13}C$ (‰, vs. PDB)	$\delta^{15}N$ (‰, vs. air)	Reference
Y-980115	CI1	3.8	0.09	41.0	−11.6	−2.8	This study
Orgueil	CI1	3.75	0.15	25.4	−15.6	+46	Kerridge (1985)[b]
Ivuna	CI1	3.7	0.19	19.5	−9.4	+52	Kerridge (1985)[b]
ALHA77003	CO3	0.33	0.005[a]	85.3	−12.7	−10.5[a]	This study
Ornans	CO3	0.12	0.0012	100	−16.0	−13	Kerridge (1985)[b]

The profiles of CI and CO chondrites for total carbon, total nitrogen, and bulk isotopic compositions. The isotopic compositions of Y-980115 and ALHA77003 were obtained using EA/IRMS in this study
[a]Data from this study were the average of duplicate analyses (*n* = 2)
[b]Data were previously reported by Kerridge (1985) and references therein

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here, we compare its low amino acid abundance to other CO3 chondrites. Likewise, CO3 chondrites generally present low amino acid concentrations as compared to other chondritic types, and the range of amino acid concentrations is present in large variability (total amino acid abundance 260–2400 ppb) (Burton et al. 2012a; Chan et al. 2012; Glavin et al. 2010). Petrologic type 3 meteorites often represent the most pristine materials. Although ALHA77003 is a type 3 CO chondrite, the parent body has likely experienced extensive thermal alteration, similar to other amino acid-depleted CO3 type meteorites. It also contains evidence of a minor extent of shock metamorphism, which indicates that the asteroid has been exposed to elevated temperatures during the accretion process (Scott et al. 1992). Studies of geochemical features such as FeO enrichment in olivine equilibration of ALHA77003 have revealed a peak metamorphic temperature of about 500 °C (Rubin 1998), which agrees with spectroscopic studies of the chondritic IOM (Kebukawa et al. 2011). The high peak metamorphic temperature leads to the subtype 3.5 given to this meteorite.

Although Y-980115 and ALHA77003 have both exposed to peak metamorphic temperatures >500 °C, a small amount of amino acids was still detectable in Y-980115, while ALHA77003 was deprive of amino acids or has a much lower amino acid concentration that fell below the detection limit of GC/C/IRMS. Different parent body processes can offer to explain this disparity: (1) Y-980115 has only experienced short-lived thermal metamorphism likely caused by minor impact shock. Due to the heterogeneity of the parent body composition and porosity, the effects of shock and heating were localized, allowing some local benign regions that are heated to a lesser degree. Contrarily, CO parent body was exposed to a prolonged heating during or post accretion with heat sources derived from in situ decay of radionuclides and hydration reactions. The duration of the thermal alteration is a function of the size of the asteroid body (Fujiya et al. 2013) but can generally last 10^6–10^8 years (Rubin 1998). While half-lives for gas-phase thermal decarboxylation reactions of amino acids are on the order of 1–100 years at 500 °C, the reactions will take 10^6–10^9 years at 300 °C (see Burton et al. 2012a and references therein). Therefore, amino acids will likely survive a short-lived heating event as experienced by Y-980115 as opposed to an enduring metamorphism experienced by ALHA77003, although the peak metamorphic temperatures of both parent bodies were ~500 °C. The presence of slightly higher phyllosilicate abundance in Y-980115 as compared to other CI-like chondrites also suggested that the thermal metamorphism was short-lived and/or occurred at lower temperatures (King et al. 2015a; King et al. 2015b). (2) Aqueous

alteration was detrimental to the preservation of amino acids or their precursors in meteorites as low-temperature chemical oxidation can remove the aliphatic moieties (e.g., Cody and Alexander 2005; Glavin and Dworkin 2009). This however contradicts with our observation that the comparatively more aqueously altered Y-980115 (as evident by the presence of hydrated mineral phases (King et al. 2015a; King et al. 2015b)) has a higher amino acid abundance than ALHA77003 which exhibits thermal alteration without the aid of fluids (Chizmadia et al. 2002) and suggests that heating processes or a combination effect of the two could be more influential towards the decomposition of amino acids. (3) Finally, the abundances of amino acid precursor molecules could be different in the two parent bodies.

Nitrogen isotopic compositions

As seen in Fig. 3, the $\delta^{15}N$ values of glycine and alanine in Y-980115 are +144.8 (S/N = 16, 1σ = 0.5 ‰) and +121.2 ‰ (S/N = 3, 1σ = 10–20 ‰), respectively. Although glycine and alanine are common terrestrial amino acids, the exceptionally high $\delta^{15}N$ values indicate that they are indigenous to Y-980115 or possibly an interstellar source for their precursors.

In the literature, nitrogen CSIA has been conducted chiefly on CM and Renazzo-like (CR) chondrites ($^{15}N \approx +60$ to +200 ‰) (e.g., Burton et al. 2012b; Elsila et al. 2012; Engel and Macko 1997; Epstein et al. 1987; Ohkouchi and Takano 2014; Pizzarello et al. 1994; Pizzarello and Holmes 2009; Sephton and Gilmour 2001), considering their high amino acid abundances (the total amino acid concentration of the CR Graves Nunataks (GRA) 95229 was shown to be as high as 249 ppm (Martins et al. 2007)). This study provides the first nitrogen CSIA data for amino acids in CI (CI-like) and CO chondrites. 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 of the amino acids in CR chondrites (Fig. 4). The similarity between the isotopic distributions of the CI-like and CR amino acids suggests that their nitrogen-bearing precursors or formation mechanisms/environments are similar. This hypothesis requires further information such as $\delta^{13}C$ and δD values to validate.

The $\delta^{15}N$ values of meteoritic amino acids are characterized by the high values and large variation. As noted by Rodgers and Charnley (2004), the range of $\delta^{15}N$ values in meteorites is higher than the values calculated by Terzieva and Herbst (2000) based on ion molecule reactions in interstellar medium (ISM) molecular clouds. They described a mechanism for nitrogen fractionations through the formation of gas-phase atomic nitrogen as CO was frozen out from the gas phase in pre-stellar cores, which subsequently leads to ^{15}N enhancements in nitrogen-containing molecules. A large variation has been observed

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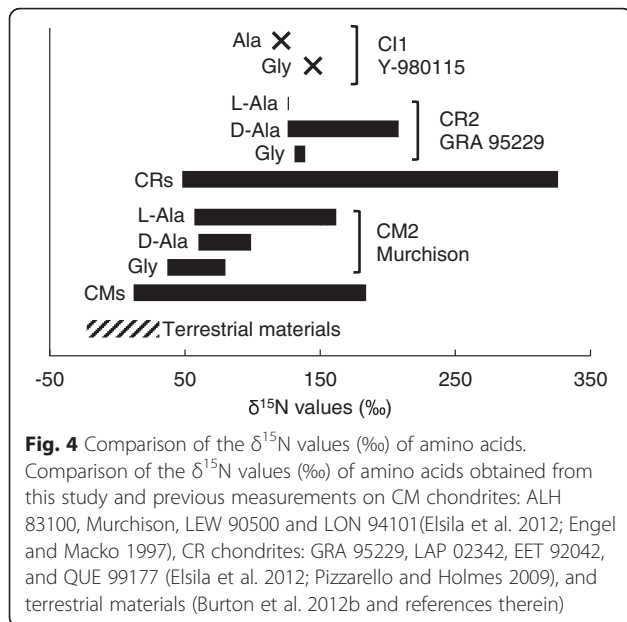
Fig. 4 Comparison of the $\delta^{15}N$ values (‰) of amino acids. Comparison of the $\delta^{15}N$ values (‰) of amino acids obtained from this study and previous measurements on CM chondrites: ALH 83100, Murchison, LEW 90500 and LON 94101(Elsila et al. 2012; Engel and Macko 1997), CR chondrites: GRA 95229, LAP 02342, EET 92042, and QUE 99177 (Elsila et al. 2012; Pizzarello and Holmes 2009), and terrestrial materials (Burton et al. 2012b and references therein)

for the $\delta^{15}N$ values of individual amino acids in the carbonaceous chondrites (Fig. 4). The large isotopic anomalies in meteorites were suggested to be related to the nitrogen-bearing functional groups (nitriles and amines), which were influenced by spin-state-dependent chemistry of the potential interstellar precursors (e.g., hydrogen cyanide (HCN), NH_3) that were formed in the protosolar nebula (Wirström et al. 2012). Pizzarello and Holmes (2009) described a prominent variation in the $\delta^{15}N$ values of amino acids in CR chondrites, with 2-H amino acids having higher $\delta^{15}N$ than 2-methyl amino acids and suggested that the nitrogen isotope fractionation indicated that the two amino acid groups or their direct precursors were produced at different ISM stages of star formation. High $\delta^{15}N$ values for 2-H amino acids in GRA 95229 ($\delta^{15}N$ value of glycine≈+130 ‰; alanine≈+125 ‰) indicate that they were formed at a later stage in pre-stellar cores, possibly with higher temperatures and the presence of liquid water, as opposed to amino acids with lower $\delta^{15}N$ values, which were likely formed in an earlier cold ISM environment that precede star formation (Pizzarello and Holmes 2009). The $\delta^{15}N$ values of glycine and alanine in Y-980115 (+144.8 and +121.2 ‰, respectively) fall in the higher range of the $\delta^{15}N$ span, which agree with the results and interpretation given by Pizzarello and Holmes (2009) for meteoritic 2-H amino acids.

The amino acid inventory and alteration history of Y-980115

CI chondrites are extremely rare, possibly due to the brecciated nature of the meteorites so most of them disintegrated when impacted onto the Earth's surface. Only nine CI meteorites (Alais, Orgueil, Tonk, Ivuna,

Revelstoke, Y-86029, Y-86737, Y-980115, and Y-980134) have been found on Earth among the 45,000 or more meteorites ever recovered. CI chondrites are considered to be the most primitive solar system material that match best the chemistry of the Sun and are used to estimate the abundances of elements in the solar system (Anders and Ebihara 1982). However, they are also known to be the most hydrated of all chondrite groups, which are supported by their fine-grained phyllosilicate matrix with magnetite, sulfides, carbonates, and sulfates (Brearley 2006). Therefore, CI chondrites may provide crucial information about the nature of water in the solar system, aqueous processes experienced by the parent body, and the associated organic formation pathways. Y-980115 is depleted in chondrules that are typical to chondritic meteorites. It is considered to be a "CI-like" chondrite, which usually indicates an extensive aqueous alteration as suggested by the lack of chondrules and a large proportion of fine-grained matrix (Tonui et al. 2003).

Y-980115 contains abundant dolomite grains that were formed as secondary replacement materials during aqueous alteration on the parent body. The $^{55}Mn/^{52}Cr$ ratios of carbonates in Y-980115 suggest an age of 4.56 Ga for the aqueous alteration event of this meteorite (Fujiya et al. 2013). After the accretion of the CI parent body, decay energy of short-lived radionuclides provided sufficient heat source for aqueous alteration to occur on the parent body for more than 9 Myr. Hydration reactions can liberate large amounts of heat that can reach temperatures up to 150 °C, and thus post-hydration low-to-medium temperature heating, which is also known to be common in CI chondrites. The post-aqueous alteration thermal metamorphism in the CI-like parent body of Y-980115 was suggested to be short-lived which likely caused by impacts, as opposed to long-duration heating derived from the decay energy of short-lived radionuclides which could last for millions of years. Thermal metamorphism can generate heat which can result in dehydration of phyllosilicates and formation of small olivine of low crystallinity, leading to the occurrence of contrasting features indicating both low-temperature hydration and high-temperature heating in meteorites (Nakamura 2005). Modal mineralogy of Y-980115 indicates that it has been exposed to thermal metamorphism at temperatures between 500 and 600 °C (Harries and Langenhorst 2011; King et al. 2015b). The matrix olivine is not primary to the meteorite, which suggests its formation through partial dehydration of the phyllosilicate, and therefore indicates that thermal metamorphism was subsequent to a preceding aqueous alteration phase. We are not aware of any studies about the precise timing of the

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thermal alteration on Y-980115, but chronologically, thermal alteration should occur at a later stage as suggested by the association between olivine and phyllosilicate.

Due to the low amino acid concentration and limited information regarding the precursor inventory, it is premature to conclude the synthetic origin of the amino acids in Y-980115 but we can offer a brief account here. Ehrenfreund et al. (2001) suggested that glycine and alanine (glycine/alanine ratio of 3) in CI chondrites were produced through HCN polymerization if the parent body had been exposed to elevated temperatures (up to 100 °C). Y-980115 is aqueously altered as well as heated to >100 °C shortly after accretion through hydration reactions (Fujiya et al. 2013), and the relative abundance between glycine and alanine in Y-980115 is also roughly 3:1 (Fig. 3), making HCN polymerization a likely mechanism. However, the high abundance of β-alanine for CI chondrites is not observed for Y-980115, indicating that the amino acid synthetic pathway of Y-980115 deviates from CI chondrites. Amino acids can also be produced by Fischer-Tropsch type (FTT) reactions at 200° to 700 °C in the presence of CO, H_2, NH_3, and catalysts (Yoshino et al. 1971). Despite the evidences of thermal metamorphism exhibited by Y-980115, its amino acid content is dissimilar to the previously analyzed thermally altered CV and CO chondrites, which were dominated by straight-chain amino acids (Burton et al. 2012a). Nevertheless, glycine and alanine can also be synthesized by FTT reactions (Pizzarello 2012; Yoshino et al. 1971); thus, the dissimilarity between the amino acid contents of Y-980115 to CV/CO chondrites does not necessarily rule out FTT reactions as the possible amino acid formation pathway for this meteorite. In this circumstance, simple organic precursors could have been produced during the aqueous alteration regime of the parent body, which then became the feedstocks for FTT reactions during thermal metamorphism postdating the aqueous event. The duration and temperatures of the FTT reactions used in laboratory were set to simulate short-term shock events (Hayatsu and Anders 1981), but whether the kinetics are applicable to shock should be further explored. Alternatively, Strecker-cyanohydrin synthesis could have taken place to form α-amino acids with a trend of decreasing α-amino acid abundances with increasing chain length (e.g., glycine >alanine >α-aminobutyric acid (α-ABA)). This trend is similar to the observed amino acid content of Y-980115, while α-ABA was not detected in this study either because it was absent or present at very low abundance (e.g., Cronin and Chang 1993). In any case, glycine and/or alanine can be effectively produced through various mechanisms; it leads a significant role in abiotic chemical evolution as an intermediate molecule which could further react to yield other amino acids (e.g., α-ABA, glutamic acid, aspartic acid) (Yoshino et al. 1971).

As amino acids are irreversibly decomposed at temperatures as low as 240 °C (Bada et al. 1995), heating at pyrolytic temperatures of over 500 °C could destroy most of the amino acids that were synthesized earlier on the parent body. Since aqueous alteration on the parent body of Y-980115 was followed by thermal metamorphism at more than 500 °C, any preexisting amino acids would have been destroyed through thermal decarboxylation, and yet, we detected indigenous glycine and alanine. Thus, a major question to their presence is how they survived the heating.

The structure of glycine makes it more resilient to high temperatures when compared to other amino acids (Rodante et al. 1992). We suspect that if glycine and alanine were produced on the parent body during the aqueous alteration regime, they should have survived the asteroidal heating by sublimation and dissipation through cracks or connected voids into zones where the temperature was more benign. Low intensity impacts could have caused transient shock heating on localized areas on Y-980115's parent body, and the heterogeneity in the parent body composition could have impeded the impact effects and thus created regions with very different thermal histories and minimal post-shock thermal metamorphism (Bland et al. 2014). Thus, the petrologically more pristine zones might have provided a temporary site for organics to sublime and survive heating. Since thermal metamorphism preferentially destroys amino acids that are susceptible to heating, it is also possible that other amino acids could have been produced prior to the heating episode but did not survive the late-stage metamorphism, which then resulted in the amino acid content currently observed for the meteorite sample.

Synthesis and preservation of amino acids on the asteroid parent body are influenced by the sequence and relative timing of the alteration events. For instance, if the aqueous alteration occurred concurrently with thermal alteration, the combination of heating and hydrous conditions would have a prominent destructive effect on the organic inventory on the asteroid, which was discussed in Burton et al. (2014b) to account for the absence of amino acids in the CI-like chondrites. If thermal metamorphism is followed by aqueous alteration, the heat-recycled molecules could subsequently develop into ammonia and precursor carbonyl molecules, which can produce α-amino acids through Strecker synthesis, resulting in an amino acid content similar to that of Murchison which is dominated by α-amino acids such as α-AIB

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(Cronin and Moore 1971; Peltzer et al. 1984). Conversely, if amino acid synthesis is followed by another heating episode where FTT reactions are feasible, the final amino acid inventory would comprise chiefly straight-chain amino acids like β-alanine and γ-ABA, similar to the result reported for the thermally altered meteorites (Burton et al. 2012a). Lastly, if the asteroidal body had experienced an extensive heating regime, the heat would only serve to decompose any preexisting molecules, which likely describes what might have happened on ALHA77003.

Conclusions

Carbonaceous chondrites have become the focus of the study of origin of life in light of their high organic contents which have made subtle analyses plausible. However, the organic contents vary among different chondritic classes, and some meteorites are shown to contain only a trace amount of detectable organics, which sometimes make their analyses challenging. This study provides important implications for the upcoming sample return missions such as Hayabusa-2 and OSIRIS-REx that target to visit C-type asteroids. C-type asteroids have likely experienced parent body aqueous and thermal processing which are commonly associated with equivalent meteorite samples of low organic contents, and thus a well-planned analytical protocol is crucial for the effective study of these valuable returned samples. In this study, we utilized a new analytical technique that involves the use of an achiral GC column to obtain the nitrogen isotopic values for individual amino acids in spite of the low amino acid concentrations and small sample amount. This method offers high precision for nitrogen CSIA by minimizing the effect of isotopic fractionation that might occur to other techniques. ALHA77003 was thermally altered, and no amino acid was detected. With reference to previous petrologic studies, we understand that Y-980115 has been exposed to aqueous alteration shortly after the accretion of its parent body and subsequent thermal metamorphism at 500 °C or higher. We detected glycine and alanine in Y-980115 with high $\delta^{15}N$ values which indicated that they are unlikely terrestrial contaminants. While glycine and alanine are crucial amino acids in biological systems, they also occur ubiquitously in extraterrestrial materials. These structurally simple and thermally resilient amino acids might have been synthesized on the asteroid parent body in the early prebiotic world, which could have catalyzed or provided an intermediate organic feedstock for subsequent chemical evolution into complex polymeric materials.

Additional file

Additional file 1: Figure S1. GC/C/IRMS chromatogram of the 12 M HCl-hydrolyzed hot-water extracts of the Piv/iPr amino acid esters in Y-980115. The subgraph (a) shows the magnified region with the alanine and glycine peaks. The single-ion traces GC/MS chromatograms of (b) Y-980115 and (c) amino acid standard mixture of the same region as shown in (a) indicate that no coeluting compounds were present that could have interfered the IRMS analysis of Y-980115 and that only alanine and glycine are the main nitrogen-bearing compounds in the region.

Abbreviations

2-Bu: 2-butyl (esters) or 2-butanol (as derivatization reagent); ABA: aminobutyric acid; AIB: aminoisobutyric acid; ALH: Allan Hills; C: carbon; CI: Ivuna-like; CM: Mighei-like; CO: Ornans-like; CR: Renazzo-like; CSIA: compound-specific isotope analysis; D: deuterium; D/L ratio: enantiomeric ratio; DCM: dichloromethane; EA: elemental analyzer; FTT: Fischer-Tropsch type; GC/C/IRMS: gas chromatography/combustion/ isotope ratio mass spectrometry; GRA: Graves Nunataks; H_2O: water; HCl: hydrochloric acid; HCN: hydrogen cyanide; HPLC: high-performance liquid chromatography; IOM: insoluble organic matter; iPr: isopropyl; ISM: interstellar medium; LAP: LaPaz Icefield; $MgSO_4$: magnesium sulfate; N: nitrogen; NaOH: sodium hydroxide; NH_3: ammonia; Ni OEP: Ni-chelated octaethylporphyrin; NIPR: National Institute of Polar Research; PC: pivaloyl chloride; Piv: pivaloyl; PTFE: polytetrafluoroethylene; PTV: programmable temperature vaporization; R^2: correlation coefficient; S/N: signal-to-noise; TC: thionyl chloride; TFA: trifluoroacetyl; TN: total nitrogen; Y: Yamato.

Authors' contributions
QHSC conducted all sample preparation procedures, carried out the chromatography studies and interpretation of data, and drafted the manuscript. YC carried out the GC/C/IRMS analysis and interpretation of data and drafted the manuscript. YT participated in the design of the study, sample preparation, and interpretation of data and drafted the manuscript. NOO carried out the EA/IRMS analysis and drafted the manuscript. NO participated in the design of the study and interpretation of data and drafted the manuscript. All authors read and approved the final manuscript.

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