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Enantioselective three-dimensional high-performance liquid chromatographic determination of amino acids in the Hayabusa2 returned samples from the asteroid Ryugu

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ABSTRACT

The chirality of amino acids in extraterrestrial materials may provide an insight into the origin of the essential L-enantiopure amino acids in the terrestrial biosphere. In 2020, the Hayabusa2 mission succeeded in bringing back surface materials from the C-type asteroid (162173) Ryugu to the Earth. Amino acids were one of the targeted organic molecules to be studied in the Ryugu samples. To analyze the various structural isomers of amino acids, which were expected to be present, from the limited amount of the returned samples, the development of a highly-sensitive and selective analytical method was necessary. In the present study, a three-dimensional high-performance liquid chromatography (3D-HPLC) system has been developed for the enantioselective determination of five proteinogenic and three non-proteinogenic amino acids in the Ryugu samples, in which amino acids in the sample were separated by reversed-phase, anion-exchange and enantioselective columns after the fluorescence derivatization with 4-fluoro-7-nitro-2,1,3-benzoxadiozole. The applicability of the analytical system to the extraterrestrial samples was evaluated by analyzing several types of carbonaceous meteorites before applying the system to the Ryugu samples. In the analysis of the Ryugu samples, all of the target amino acids were successfully determined quantitatively. Non-proteinogenic amino acids including 2-amino-*n*-butyric acid, isovaline and norvaline, rarely present in the terrestrial environment, were found as almost racemic mixtures with 47.1 to 55.2%L.

1. Introduction

Extraterrestrial materials containing organic compounds provide clues to elucidate the origin and evolution of the Solar System, the surface environment of the early Earth and perhaps the origin of life on the Earth. Organic analyses of the Murchison carbonaceous meteorite, which fell in 1969, showed that the meteorite contained a variety of amino acids up to ~100 [1]. Their carbon isotopic ratios were different from those on the Earth [2,3], and many non-proteinogenic amino acids rarely present in the terrestrial environment were observed [4,5], suggesting an extraterrestrial origin. Excesses of L-enantiomers to their counterparts, the D-enantiomers, have been reported for some amino acids in the Murchison meteorite [6–12]. Similar L-enantiomeric excesses have also been found in other meteorites, such as Murray [8–10], Orgueil [13] and Tagish Lake [14]. The terrestrial biosphere is overwhelmingly dominated by the L-enantiomers of amino acids both as the components of proteins and biochemical intermediates with the D-enantiomers generally found in microbes [15,16]. Several hypotheses about the origin of the homochirality of terrestrial amino acids have been proposed; however, they are still under discussion [17,18]. Amino acids in meteorites, asteroids and comets are thought to be one of the possible source materials for the origin of life on the Earth, and the enantiomeric excesses of meteoritic organic compounds may have been responsible for breaking the chiral symmetry on the early Earth [19].

Since L-amino acids are rich in the present terrestrial environment, the contamination of L-amino acids is always a concern in the analyses of meteorites collected on the Earth. Thus, several sample return missions have been carried out to collect and bring back samples from primitive small bodies such as asteroids and comets. The National Aeronautics and Space Administration (NASA) obtained samples from comet Wild 2 by the Stardust spacecraft [20], and the Japan Aerospace Exploration Agency (JAXA) executed the Hayabusa mission to collect samples from the asteroid Itokawa [21]. These projects resulted in the finding of glycine (Gly) and several non-proteinogenic amino acids [22–24]. JAXA next launched the Hayabusa2 spacecraft to the asteroid Ryugu on December 3, 2014. After two touchdown samplings on February 21, 2019 (sample A) and July 11, 2019 (sample C), the Hayabusa2 spacecraft came back to the Earth with 5.4 g of Ryugu samples on December 6, 2020 [25]. Ryugu is categorized as a C_b-type asteroid, whose chemical and mineralogical characteristics are very similar to the primitive Ivuna-type (CI) carbonaceous meteorite, containing more organic carbon than the S-type asteroids like Itokawa [26]. Therefore, the Ryugu sample was expected to provide information especially about organic matters including amino acids in the primitive Solar System, which may be related to the origin of life on the Earth.

Though the return of 5.4 g of material from Ryugu is remarkable and far more than required for mission success, the sample is still rare and immensely valuable. Since the identification of specific amino acids is a destructive analytical process and the most similar class of meteorites (CI) shows a very complex distribution of organic compounds, an analytical technique with both high sensitivity and selectivity is required for the precise determination of amino acid enantiomers in the limited amount of the Ryugu samples. For the Ryugu samples, the detection of 23 proteinogenic and non-proteinogenic amino acids were reported by high-performance liquid chromatography (HPLC) using a HILIC column combined with mass spectrometry (MS), in which no chiral separation of the amino acids was achieved nor their concentrations determined [27].

Several methods using gas chromatography (GC) [28–31] and liquid chromatography (LC) [31–33] have so far been developed and utilized for the enantioselective analysis of amino acids in extraterrestrial samples. As for the GC method, an enantioselective capillary column including Chirasil-Val or Chirasil-Dex was utilized, and MS was frequently equipped to detect amino acids derivatized with non-chiral reagents such as trifluoroacetic anhydride/isopropanol [29,34,35]. A reversed-phase LC method has also been developed for extraterrestrial amino acids using chiral derivatization with *o*-phthaldialdehyde (OPA) plus *N*-acetyl-L-cysteine (NAC) [31,36]. By using these methods, a variety of amino acids has been found in meteorite samples, and their chiral properties have also been obtained. Most of these methods were designed to use one separation column equipped with fluorescence detection (FD) and/or MS. Such an LC method equipped with FD and MS detection have successfully been applied to the Ryugu samples to detect enantiomeric amino acids [37,38]. However, the chromatographic separations obtained by the one-dimensional methods were sometimes insufficient, and the interfering compounds disturbed the determination of trace amounts of the amino acid enantiomers, and the isobaric structural isomers were also usually difficult to be distinguished also by MS [13].

To achieve the highly-selective and sensitive determination of chiral amino acids, multi-dimensional HPLC is one of the most suitable approaches [39–45]. The three-dimensional (3D) HPLC system [43–45] is especially promising, in which amino acids in the sample are derivatized with a fluorescence reagent for the highly-sensitive detection followed by three different separation modes integrating reversed-phase, anion-exchange and enantioselective columns. In a previous study [37], we performed the initial analysis of Hayabusa 2 mission, and reported the occurrence of six amino acids in the Ryugu sample (A0106). In the initial analysis, the analyzed and found amino acids were alanine (Ala), glycine (Gly), valine (Val), 2-amino-*n*-butyric acid (α-ABA), isovaline (Iva) and norvaline (Nva). In the present study, we further improved our 3D-HPLC system for the determination of eight amino acids to reveal their stereochemistry in a variety of the Ryugu samples. Two proteinogenic amino acids, aspartic acid (Asp) and serine (Ser), were added to the previous targets in order to compare the enantiomeric ratios between proteinogenic and non-proteinogenic amino acids. The analytical conditions for all the target amino acids were investigated, and the applicability of the developed system was examined by the determination of amino acid enantiomers in four different carbonaceous meteorites (Murchison, Aguas Zarcas, Tarda and Jbilet Winselwan). As for the Ryugu sample, C0107 sample was used in addition to the A0106 sample (used for the initial analysis), and their hot-water extracts and hydrochloric acid (HCl) extracts were analyzed to determine the enantiomeric ratios of the amino acids.

2. Materials and methods

2.1. Materials

Racemic mixtures of Ala and α-ABA were obtained from FUJIFILM Wako Pure Chemical Corporation (Osaka, Japan). DL-Asp, DL-Ser and DL-Val were purchased from Nacalai Tesque (Kyoto, Japan). Gly and DL-Nva were obtained from Sigma-Aldrich (St. Louis, MO, USA). The enantiomers of Iva were products of AstaTech (Bristol, PA, USA). Acetonitrile (MeCN) of HPLC grade and the derivatization reagent for fluorescence detection, 4-fluoro-7-nitro-2,1,3-benzoxadiazole (NBD-F), were obtained from Nacalai Tesque and Tokyo Chemical Industry (Tokyo, Japan), respectively. Methanol (MeOH) of HPLC grade, boric acid, formic acid (FA), trifluoroacetic acid (TFA) and sodium hydroxide (NaOH) were purchased from FUJIFILM Wako Pure Chemical Corporation. Ultrapure water and ultrapure hydrochloric acid (HCl) for sample preparation were products from Tama Chemicals (Kawasaki, Japan). Water for the other experiments was purified using a Milli-Q Integral 3 system (Merck, Darmstadt, Germany). All other reagents were the highest grade and were used without further purification.

2.2. Sample extraction

Two aggregate Ryugu samples, A0106 (13.08 mg) and C0107 (10.73 mg), consisting of < 1 mm grains were used in this study. The A0106 sample was collected from the asteroid surface during the first touchdown. The C0107 sample was collected during the second touchdown after the small carry-on impactor experiment [46], possibly containing subsurface materials. The serpentine powder (16.21 mg), which was prebaked at 500 °C for 3 h, was prepared to check a procedural blank. The samples were extracted with hot water followed by aqueous HCl extraction in the clean bench (ISO 5) set inside the cleanroom (ISO 6) [37]. All of the glassware was baked at 500 °C for 3 h before use to remove any possible contamination by amino acids.

The hot-water extraction was performed by adding 200 μL of water to the sample powder (A0106, C0107 and serpentine) and heated at 105 °C for 20 h in a nitrogen-purged close glass ampoule. After the extraction, the content including the residue and solution was transferred to a glass vial. The glass vial was centrifuged at 14,000 rpm for 8 min, and the supernatant was transferred to another glass vial. The ampoule used for the extraction was rinsed with water (200 μL), and the water was transferred to the glass vial containing the residue. After shaking and centrifuging at 14,000 rpm for 8 min, the supernatant was transferred to the vial containing the first supernatant. This rinse step was performed twice, and the obtained supernatant (total 600 μL) was well mixed (hot-water extract solution). To 250 μL of the solution (each hot-water extract was equivalent to 5.45 mg of A0106, 4.47 mg of C0107 and 6.75 mg of the serpentine blank), 250 μL of aqueous HCl (ca. 6 mol/L) was added and heated at 105 °C for 20 h. The reaction mixture was evaporated to dryness under reduced pressure and used for the amino acid analysis by 3D-HPLC. The same volumes of the hot-water extracts were sent for a parallel amino acid analysis with somewhat different hydrolysis conditions [38].

As for the HCl extraction, half of the residue obtained after the hot-water extraction was mixed with 200 μL of 3 mol/L aqueous HCl in a nitrogen-purged glass ampoule. The glass ampoule was closed and heated at 105 °C for 20 h, and the supernatant was transferred to a glass vial. To the glass ampoule containing the residue, 200 μL of water was added, and the glass ampoule was ultrasonicated for 15 min. After centrifugation, the supernatant was transferred to the same glass vial. This process was performed twice, and a total of 600 μL of the supernatant was obtained (HCl extract solution). An aliquot (200 μL) of the solution was evaporated to dryness and utilized for the 3D-HPLC analysis (each HCl extract equivalent to 2.18 mg of A0106, 1.79 mg of C0107 and 2.70 mg of the serpentine blank). Again, the same volumes of the fractions were sent for a parallel amino acid analysis [38].

Four meteorite samples, including three CM-type (Murchison, Aguas Zarcas and Jbilet Winselwan) and one C-ungrouped (Tarda) carbonaceous chondrites, were used in this study. While the Murchison meteorite fell in 1969, the Aguas Zarcas and Tarda meteorites were recent falls in 2019 and 2020, respectively. The Jbilet Winselwan meteorite was found from the Sahara desert in 2013. The inner fragments of the meteorites were powdered using an alumina mortar and pestle. The meteorite powders were extracted with hot water in the same manner as the Ryugu samples. The sample amounts were 22.0 mg for Murchison, 3.9 mg for Aguas Zarcas, 3.7 mg for Jbilet Winselwan and 3.9 mg for Tarda.

2.3. Derivatization of the amino acids

The dried Ryugu extract was dissolved in 100 μL of water. The neutralization of the sample solution was performed with aqueous NaOH and was confirmed by a pH test paper. Two hundred μL of water was added to each of the Aguas Zarcas, Tarda and Jbilet Winselwan samples, and 150 μL of the solution was neutralized. For the Murchison meteorite, after 200 μL of water was added, 50 μL of the solution was diluted five times by water and neutralized. An aliquot (20 μL) of the neutralized solution was mixed with 400 mM sodium borate buffer (pH 8.0, 20 μL) and 100 mM NBD-F in MeCN (5 μL) in a light-shielded glass vial. The mixed solution was heated at 60 °C for 6 min. After adding an aqueous 2 % (v/v) TFA solution (55 μL), 10 μL of the reaction mixture was injected into the 3D-HPLC system.

2.4. 3D-HPLC conditions

The HPLC instruments were developed using the NANOSPACE SI-2 series produced by Shiseido (Tokyo, Japan) and Singularity series designed by collaboration with KAGAMI (Ibaraki, Osaka, Japan). The system consisted of the NANOSPACE 3101 and 3201 pumps, a 3202 degasser, a 3033 auto-sampler, 3004 and 3014 column ovens and a Singularity LED-3 fluorescence detector with three detection cells. NANOSPACE high-pressure valves (3011 and 3012) and a 9986 multi-loop valve (having 8 loops of 300 μL) were operated by a Singularity valve-controlling system to perform the multi-dimensional analysis. An EZChrom Elite system was used for data processing. Fig. 1 represents the flow diagram of the system. A Singularity RP18 column (C18 bonded silica particle-packed column, 3-μm particle size, 1.0 × 250 mm) was used at 45 °C in the first dimension for the reversed-phase separation. The mobile phase A was a mixed solution of TFA/MeCN/water (0.025/5/95, v/v/v) and B was a mixed solution of TFA/MeCN/water (0.025/25/75). The gradient elution was carried out as follows: 100 % A for 45 min, linear gradient elution of 100 % A to 100 % B for 75 min and 100 % B for 30 min. The flow rate was 50 μL/min. After the reversed-phase separation, the target amino acids were separately trapped in the loops of the multi-loop valve, and the collected fractions were sequentially introduced into the second separation column.

In the second dimension, an anion-exchange column, Singularity AX (aminopropylsilica particle packed column, 5-μm particle size, 1.0 × 150 mm) was equipped at 25 °C for the further separation of the target amino acids from interferences. The mobile phases were mixed solutions of MeOH and MeCN (50/50) containing FA (0.04 % for Ala, α-ABA, Val and Nva, 0.07 % for Ser, Gly and Iva, 0.30 % for Asp) at the flow rate of 100 μL/min. The target amino acids were again fractionated in the loops of the multi-loop valve (having two loops of 450 μL), and the fractions were transferred to an enantioselective column representing the third dimension. The enantioselective column was a tandemly connected Singularity CSP-001S column (*N*-(3,5-dinitrophenylaminocarbonyl)-L-leucine bonded aminopropylsilica particle packed column, 5-μm particle size, 1.5 × 250 mm, total length was 500 mm) maintained at 25 °C. The mobile phases were mixed solutions of MeOH and MeCN (50/50) containing FA (0.15 % for Ala, α-ABA, Val and Nva, 0.30 % for Ser and Gly, 0.70 % for Asp). For the enantiomer separation of Iva, a mixed solution of MeOH and MeCN (90/10) containing 0.14 % FA was used as the mobile phase. The flow rate was 200 μL/min. The NBD-amino acids were quantified by their fluorescence detection ($\lambda_{ex} = 470$ nm, $\lambda_{em} = 530$ nm) in all dimensions.

3. Results and discussion

3.1. Development and evaluation of an enantioselective 3D-HPLC system for extraterrestrial amino acids

Eight α-amino acids (α-ABA, Ala, Asp, Gly, Ser, Val, Iva and Nva) were selected as the target molecules for the Ryugu samples because the number of analytes for the 3D-HPLC system was limited. Concerning Asp and Ser, they are abundantly present in the terrestrial environment, and the large excesses of their L-forms are well known. They were additionally chosen in the present study from the initial analysis to compare the chiral property between proteinogenic and non-proteinogenic amino acids and evaluate the terrestrial contamination. All the selected amino acids have already been found in several carbonaceous chondrites [5,12,14,32], though some studies have not distinguished the enantiomers. The chromatograms obtained for the standard amino acids with the present 3D-HPLC system are shown in Fig. S1. In the first dimension (1D), all of the target amino acids were separated within 150 min by a gradient elution of 5–25 % MeCN 0.025 % TFA in H_2O at the flow rate of 50 μL/min. The target amino acids were individually trapped in the multi-loops at the time periods indicated by the black bars below the baseline of the 1D chromatogram in Fig. S1. The collected fractions were sequentially introduced into the second dimension (2D). The fraction volumes were 162.5 μL (195 s) for Ser, 200 μL (240 s) for Asp, 150 μL (180 s) for Gly, Iva, Val and Nva, 125 μL (150 s) for Ala and 100 μL (120 s) for α-ABA. The target amino acids in the fractions were then separated from interferences by an anion-exchange column. The FA concentrations in mobile phases (MeOH-MeCN, 90/10. v/v) were investigated in order to obtain the appropriate retention times of the target amino acids. The selected FA concentrations were 0.07 % for Ser, Gly and Iva, 0.30 % for Asp, 0.04 % for Ala, α-ABA, Val and Nva. With these mobile phases, all the amino acids eluted within 20 min and were fractionated into the second multi-loops at the time periods as indicated by black bars below the baseline of 2D chromatogram in Fig. S1. The fraction volumes were 300 μL (180 s) for Ser, 275 μL (165 s) for Asp, 200 μL (120 s) for Gly and Nva, 225 μL (135 s) for Ala, α-ABA, Iva and Val. The collected fractions were then transferred to an enantioselective column in the third dimension (3D). Both in the first and second dimensions, relatively large volumes of the fractions (over 100 μL) were collected and transferred/introduced into the next dimension. However, the target amino acids were appropriately retained to the columns, and their peak shapes remained sharp enough to be fractionated and quantified. These results indicated that the mobile phase compatibility issues between first-second and second-third dimensions were acceptable and sufficient for the quantitative analyses. Since the enantiomer separation of Iva was difficult, two Singularity CSP-001S columns (1.5 × 250 mm) were tandemly connected (total length was 500 mm) as described above to obtain a sufficient separation. After the thorough mobile phase investigation, the Iva enantiomers were separated within 60 min by using

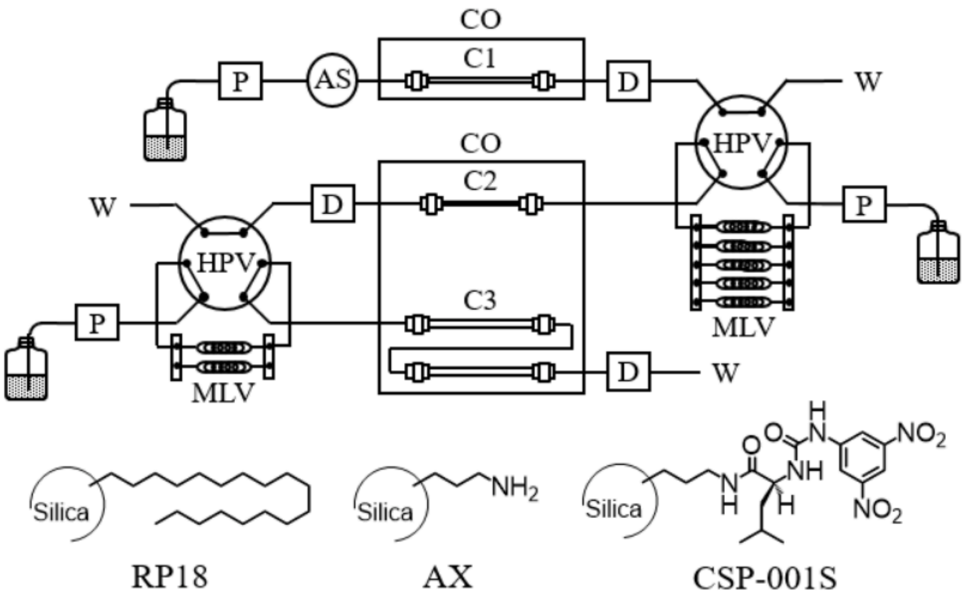

Fig. 1. Flow diagram of the 3D-HPLC system. C1, Singularity RP18 (1.0 × 250 mm); C2, Singularity AX (1.0 × 150 mm); C3, Singularity CSP-001S (1.5 × 500 mm). AS, auto sampler; CO, column oven; D, detector; HPV, high pressure valve; MLV, multi-loop valve; P, pump; W, waste.

0.14 % FA in a mixed solution of the MeOH-MeCN (90/10, v/v). Enantioselective separations of the other amino acids were achieved within 50 min by the mobile phases of MeOH-MeCN (50/50, v/v) solutions containing FA; 0.30 % for Ser, 0.70 % for Asp and 0.15 % for Ala, α-ABA, Val and Nva. The obtained resolution factors (*Rs*) were 6.32 for Ser, 1.77 for Asp, 4.76 for Ala, 4.10 for α-ABA, 1.13 for Iva, 2.65 for Val and 4.15 for Nva. Although the Iva enantiomers were not completely separated ($Rs<1.5$), their separation was practically sufficient to quantify the enantiomeric ratio.

The developed 3D-HPLC system was validated using standard solutions. Because the contamination of the proteinogenic L-amino acids and D-Ala from reagents, water and laboratory wares was not negligible, the calibration curves of these amino acid enantiomers were constructed in the range from 5 to 100 fmol to 10 pmol depending on their environmental levels. The range of Gly was from 200 fmol to 20 pmol because its concentration in the extraterrestrial samples is usually higher than the other amino acids. For the other amino acid enantiomers, except for Iva, the calibration curves were constructed in the range from 1 fmol to 10 pmol. As for the Iva enantiomers, the calibration range was set from 4 fmol to 40 pmol. All of the calibration curves showed good linearities with a coefficient of determination (r^2) higher than 0.9989 (Table 1). The lowest points of the calibration curves were adopted as the lower limit of quantification (LLOQ; 1 fmol for D-Ser, D-Asp, D,L-α-ABA, D-Val and D,L-Nva, 4 fmol for D,L-Iva, 5 fmol for D-Ala and L-Val, 10 fmol for L-Ser, L-Asp and L-Ala, and 200 fmol for Gly). For the precision, the results of five continuous analyses were evaluated as the between-run precision using low and high concentrations of the standard amino acid solutions. Since the total analysis time for the full 3D-HPLC determination was more than six hours, the intra-day precision could not be checked. The obtained relative standard deviation (RSD) values of the between-run precision were 2.15–6.56 % for the low concentration and 0.33–8.38 % for the high concentration of the standard amino acids. The system validation was also made with the Murchison carbonaceous chondrite. The analytical results of the hot-water extract of the Murchison meteorite are summarized in Table 1. The amino acids in the Murchison meteorite were determined, and the RSD values were 4.37–7.40 % ($n = 5$). As for the recovery of the amino acids, two concentrations of the standard amino acids were added to the hot-water extract of Murchison, and the obtained accuracy values for the low and high concentrations were 89.4–104.6 % and 89.0–107.8 %, respectively.

Several multi-dimensional GC or LC methods have been developed by combining more than two separation modes to obtain the higher selectivity for enantiomeric separation of the amino acids [39,44,47]. The 2D-GC-MS method consisted of a polyethylene glycol-based column and an enantioselective column, and 19 chiral amino acids in the Murchison meteorite sample were separated and determined [47]. Concerning multi-dimensional LC, even though several 2D- and 3D-HPLC methods have been developed for the determination of trace amounts of amino acids in the Murchison and Antarctic carbonaceous meteorites [39,44], the present 3D-HPLC system was improved for the enantioselective analysis of trace levels of the extraterrestrial amino acids. The current 3D-HPLC system enables the separation of the Ala, α-ABA, Iva, Val and Nva enantiomers (with *Rs* values of 1.13–4.76) equal to or greater than the previous study (*Rs* values from 1.04 to 4.65) [44], and Ser and Asp enantiomers were also separated with sufficient *Rs* values (6.32 for Ser and 1.77 for Asp). The ranges of the calibration curves were expanded from those of the previous methods, especially for the non-proteinogenic amino acid enantiomers (0.004–40 pmol for Iva, 0.001–10 pmol for α-ABA and Nva), and the validation of the developed method was successfully performed with good linearities of the calibration curves, practically low RSD values of the precision and a sufficient accuracy. These results showed that the present 3D-HPLC system is highly-selective, sensitive and quantitative for the determination of chiral amino acids in the extraterrestrial samples.

The current 3D-HPLC system can precisely quantify the 8 target amino acids, while the OPA/NAC method (also used for the analysis of Ryugu sample) can detect most amino acids using one separation column [38]. Although the non-targeted amino acid analysis was performed in a relatively short analytical time using the OPA/NAC method, the most effective use of the 3D-HPLC system is to precisely quantify each enantiomer of the amino acids due to its high selectivity. The three-dimensional separation results in a significant decrease of the unknown interfering peaks for the detection of trace levels of the amino acids.

3.2. Chiral amino acids in carbonaceous meteorites

The validated 3D-HPLC system was applied to the determination of amino acids in the carbonaceous meteorites (Murchison, Aguas Zarcas, Tarda and Jbilet Winselwan) as rehearsal analyses of the Ryugu sample.

Table 1
Method validation for the enantioselective determination of 8 target amino acids.

Amino acids	Standard					Murchison meteorite		
	Calibration curves			Precision (RSD,%)		Precision (RSD,%)	Accuracy (%)	
	Calibration range (pmol)	Equation	r^2	Low	High		Low	High
D-Ser	0.001–10	$y = 19.8\,x + 0.06$	0.9999	2.29	1.56	4.92	95.9	91.9
L-Ser	0.01–10	$y = 12.9\,x + 0.19$	0.9999	2.24	1.55	5.03	89.4	89.0
D-Asp	0.001–10	$y = 15.5$ x - 0.46	0.9993	2.38	1.29	7.40	94.2	95.3
L-Asp	0.01–10	$y = 12.2$ x - 0.64	0.9989	2.15	1.10	7.36	93.6	94.6
Gly	0.2–20	$y = 25.7\,x + 1.29$	0.9998	2.85	1.02	5.71	94.0	91.5
D-Ala	0.005–10	$y = 20.8$ x - 0.52	0.9997	2.97	0.33	6.33	94.3	97.0
L-Ala	0.01–10	$y = 15.4$ x - 0.60	0.9995	2.36	0.45	6.38	94.2	96.6
D-α-ABA	0.001–10	$y = 24.7$ x - 0.60	0.9997	3.09	1.06	4.99	94.9	96.7
L-α-ABA	0.001–10	$y = 19.2$ x - 0.48	0.9997	3.02	0.90	5.10	95.0	97.2
D-Iva	0.004–40	$y = 2.9\,x + 0.55$	0.9992	4.90	8.38	6.38	103.9	95.8
L-Iva	0.004–40	$y = 2.8\,x + 0.54$	0.9993	5.03	8.31	6.49	104.6	96.1
D-Val	0.001–10	$y = 25.0$ x - 0.32	1.0000	2.32	2.11	4.39	97.5	100.0
L-Val	0.005–10	$y = 21.2$ x - 0.33	1.0000	2.34	1.97	4.37	97.8	99.7
D-Nva	0.001–10	$y = 23.8$ x - 0.65	0.9997	6.56	3.53	6.98	95.5	107.6
L-Nva	0.001–10	$y = 18.4$ x - 0.56	0.9996	6.41	3.49	6.84	92.1	107.8

Equations were made where x was the injection amount of the amino acids (pmol) and y was the peak height (mV). Injection amounts of D-Ser, D-Asp, D,L-α-ABA, D-Val and D,L-Nva were 0.001, 0.005, 0.01, 0.1, 1, 5 and 10 pmol. Those of L-Ser, L-Asp and L-Ala were 0.01, 0.1, 1, 5 and 10 pmol. Those of Gly were 0.2, 2, 10 and 20 pmol. Those of D-Ala and L-Val were 0.005, 0.01, 0.1, 1, 5 and 10 pmol. Those of D- and L-Iva were 0.004, 0.02, 0.04, 0.4, 4, 20 and 40 pmol. For the precision of the standard ($n = 5$), 0.2 and 5 pmol of racemic amino acids and Gly were injected (0.8 and 20 pmol were used for DL-Iva). For the precision of the carbonaceous meteorite ($n = 5$), the intrinsic amino acids in the Murchison meteorite were determined. For the accuracy, 1 or 2.5 pmol of DL-Ser, DL-Asp, DL-Val and DL-Nva, 2 or 5 pmol of Gly and DL-Ala, 0.4 or 1 pmol of DL-α-ABA and 0.1 or 0.25 pmol of DL-Iva were added to the Murchison meteorite.

The obtained 3D-HPLC chromatograms of the Murchison meteorite are shown in Fig. 2. In the first dimension, there were many peaks derived from the meteorite. Fractions of the target amino acids were collected at the time decided by the analysis of the standard amino acids, then they were transferred to the next separation column. Although the fractions included unknown interferences which eluted with the target amino acids in the first dimension, the target amino acids were purified from these interfering compounds by a Singularity AX column in the second dimension (Fig. 2, 2D). Many peaks were observed in the magnified chromatograms, and they are possibly disturbing the precise determination when the fractions from the first dimension are directly injected into the final enantioselective and quantifying dimension (representing a 2D-HPLC system). In the present 3D-HPLC system, the fractions separated in the second dimension were collected in the loop at the same time as the standard and were introduced into the third dimension. The enantiomer separations of all the target amino acids were sufficiently achieved by a tandemly connected Singularity CSP-001S column (Fig. 2, 3D). The other meteorites were also analyzed by the 3D-HPLC system, and the target amino acid concentrations in the meteorite samples were successfully determined. The quantified amounts (nmol/g) in the tested meteorites are summarized in Table 2. In the Murchison meteorite, the %L values (L/(D + L) × 100) of the proteinogenic amino acids (Ser, Asp, Ala and Val) were higher than 60 %, which could be attributed to contamination from the L-amino acid-rich terrestrial environment. On the other hand, the non-proteinogenic amino acids (α-ABA, Iva and Nva) were present as almost racemic mixtures (50.0 ≤ %L ≤ 52.0). The amino acids in the Aguas Zarcas meteorite showed the same tendency, and the %L values of the proteinogenic amino acids were 53.2–80.0. These values were lower than those of the Murchison meteorite, indicating less contamination of the terrestrial amino acids. In the Tarda meteorite, Ala was present as an almost racemic mixture (%L = 50.5) in addition to the non-proteinogenic amino acids, and Ser, Asp and Val presented %L values (52.3–68.3 %) lower than those of the Murchison and Aguas Zarcas meteorites. The most recent fall, Tarda, may receive the least terrestrial contamination. The Jbilet Winselwan meteorite contained the lowest amounts of amino acids among the analyzed meteorites, so the observed excessive proteinogenic L-amino acids (%L ≥ 79.0) could be mostly derived from the terrestrial contamination. Concerning the non-proteinogenic amino acids in the Jbilet Winselwan meteorite, the amounts of the α-ABA and Nva enantiomers were below the LLOQ, and the Iva enantiomers were not observed. Because the sample preparation procedure contains severe steps for severe HCl extraction, the amino

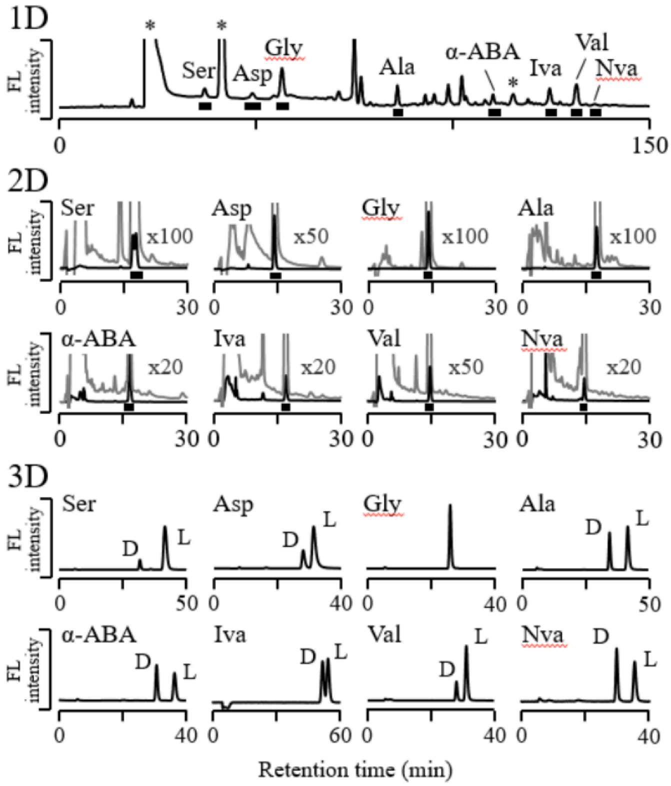

Fig. 2. 3D-HPLC determination of the amino acid enantiomers in the Murchison meteorite. The reagent peaks are indicated by asterisks (*). The collected peaks are indicated by the black bar below the baseline. In 2D, the magnified chromatograms were shown as gray lines.

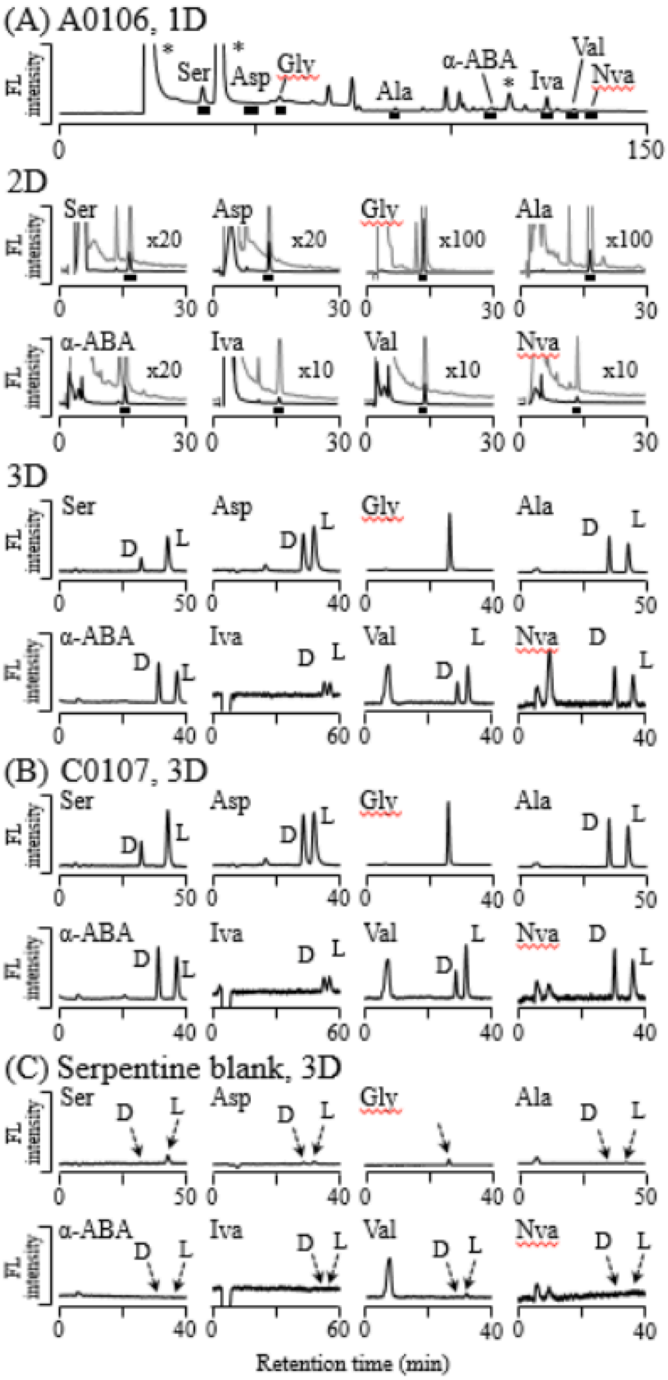

Fig. 3. Enantioselective determination of the amino acids in the hot water extracts of the A0106 (A), C0107 (B) and serpentine blank (C) samples. In 2D of the A0106 sample, the magnified chromatograms were shown as gray lines. The chromatograms of 3D for Gly, Ala, α-ABA, Iva, Val and Nva in A0106 and serpentine blank samples are shown in the previous report [37].

Table 2
Amounts of target amino acids in the meteorites.

Amino acids		Murchison		Aguas Zarcas		Tarda		Jbilet Winselwan	
		nmol/g	%L	nmol/g	%L	nmol/g	%L	nmol/g	%L
Ser	D	1.28	87.2	0.14	80.0	0.14	68.3	0.86	79.0
	L	8.71		0.58		0.30		3.24	
Asp	D	3.39	75.1	0.22	66.6	0.48	52.3	0.47	82.6
	L	10.22		0.44		0.53		2.23	
Gly		66.10	–	12.26	–	24.96	–	4.88	–
Ala	D	9.29	61.6	2.49	53.2	4.45	50.5	0.73	84.3
	L	14.92		2.83		4.54		3.94	
α-ABA	D	2.94	50.4	0.74	49.8	0.64	50.2	trace	–
	L	2.99		0.73		0.64		trace	
Iva	D	6.21	52.0	1.70	53.2	0.31	50.0	n.d.	–
	L	6.73		1.93		0.31		n.d.	
Val	D	1.82	77.6	0.44	60.0	0.10	56.5	0.04	98.2
	L	6.30		0.66		0.13		2.31	
Nva	D	0.53	50.0	0.14	50.0	0.08	50.4	trace	–
	L	0.53		0.14		0.08		trace	

trace = under the lower limit of quantification.
n.d. = not detected.

acids in the samples may partly be racemized. However, considering that %L values of several amino acids are high in some of the meteorites (for example, %L Val of Jubilet Winselwan meteorite is 98.2 %), the results especially for non-proteinogenic amino acids indicating that they are present as almost racemates in the meteorites.

Among the tested meteorites, the Murchison meteorite has been extensively studied because it has been a long time since its impact on the Earth in 1969, and also because the Murchison meteorite contains abundant amino acids. In the previous papers [6,9,11–13,32,35,44,47,48], amino acids in the Murchison meteorites have been determined by GC-MS, LC-FL/MS, and multi-dimensional GC/LC methods. The amounts (nmol/g) of the present target amino acids in the Murchison meteorites were measured as 1.0–8.2 for Ser, 2.5–8.2 for Asp, 24.5–77.5 for Gly, 5.2–31.5 for Ala, 2.0–6.2 for α-ABA, 10.5–43.2 for Iva, 1.6–10.4 for Val and 0.2–1.4 for Nva. Concerning the enantiomer excess, the reported %L values of the target amino acids were 60.0–96.4 for Ser, 52.2–83.6 for Asp, 49.7–64.0 for Ala, 50.0–54.1 for α-ABA, 50.1–59.3 for Iva, 51.1–83.6 for Val and 33.3–67.9 for Nva. As for the Aguas Zarcus meteorite, amino acid amounts (nmol/g) were reported to be 1.8–21.4 for Ser, 0.7–42.1 for Asp, 20.0–158.0 for Gly, 5.1–55.0 for Ala, 1.4–2.9 for α-ABA, 5.9–9.0 for Iva, 1.6–30.6 for Val and 0.3–1.0 for Nva. Few studies have been reported for chiral amino acids in the Tarda and Jbilet Winselwan meteorites. In the present study, four types of meteorites were analyzed, and the obtained amino acid amounts and %L values in the Murchison and Aguas Zarcus meteorites were in good agreement with those previously reported. In addition, the present 3D-HPLC method successfully determined trace amounts of non-proteinogenic amino acids (α-ABA, Iva and Nva) in the Tarda meteorite because the system has sufficient LLOQ values. These results indicated that the present analytical method is one of the most suitable tools for the determination of chiral amino acids in extraterrestrial materials including the Ryugu grains.

3.3. Amino acids in the Ryugu samples

The hot-water extracts and HCl extracts of the Ryugu A0106 and C0107 samples, collected at the first and second touchdown sites, respectively [25], were analyzed by the developed 3D-HPLC system. The prebaked serpentine powder was also analyzed as a procedural blank. The chromatograms obtained for the hot-water extract of the A0106, C0107 and serpentine blank samples are shown in Fig. 3. In the first and second dimensions in analyzing the A0106 grain (Fig. 3A), a variety of interfering substances were detected, and their profiles were different from those in the other extraterrestrial samples including Murchison meteorite shown in Fig. 2. These interfering substances were successfully separated from the target amino acids in all tested samples, showing the high selectivity of the present 3D-HPLC method. In the serpentine blank, trace amounts of the proteinogenic amino acids were observed, whereas the non-proteinogenic amino acids were not found. As for the hot-water extracts of the A0106 and C0107 samples, the peaks of all the target amino acids were clearly observed and were obviously higher than those of the serpentine blank. The determined amounts of the target amino acids in the hot-water and HCl extracts of the A0106 and C0107 samples are summarized in Table 3. Among the results, the data of Gly, Ala, α-ABA, Iva, Val and Nva in the hot water extract from the A0106 sample have been already shown in the previous reports [37]. The C0107 sample contained slightly higher levels of amino acids than the A0106 sample, and the profiles of the amino acids were similar between the two samples, indicating that the chiral amino acid amounts in Ryugu are mostly uniform. Comparing the amounts of Ala, α-ABA and valine isomers (Val, Nva and Iva), their amounts tended to decrease as the carbon number increased. Though the amounts of the valine isomers in the Ryugu samples were extremely low, the present method gave clear peaks and enabled the quantification in most of the samples.

The L-enantiomer excesses of Ser, Asp and Val were observed in almost all the samples including the carbonaceous chondrites and the Ryugu samples. L-Proteinogenic amino acids were frequently observed in terrestrial environments (also observed in the serpentine blank). On the other hand, the %L values of Ala (also a protein amino acid and abundant on the Earth) were less than 55 % in the Ryugu samples except for the HCl extract of the C0107. The amounts of the Ala enantiomers in the Ryugu samples were much higher than those of the serpentine blank (over ×20) and also higher than those of the other proteinogenic amino acids. Thus, intrinsic Ala in the Ryugu samples could be evaluated with less effect by contamination from the terrestrial environment, and the Ala enantiomers were likely to be present in nearly equal amounts. As for the non-proteinogenic amino acids, the α-ABA, Iva and Nva enantiomers were observed as almost racemates with the %L values of 47.1–55.2.

All the Ryugu samples and blank were also analyzed by OPA/NAC and LC-fluorescence orbitrap-MS at the NASA Goddard Space Flight Center (GSFC) [37,38]. The reported amounts of D-amino acids (minor

Table 3
Amounts of target amino acids in the Ryugu samples.

Amino acids		A0106				C0107			
		Hot water extract		HCl extract		Hot water extract		HCl extract	
		nmol/g	%L	nmol/g	%L	nmol/g	%L	nmol/g	%L
Ser	D	0.033	79.9	trace	–	0.076	77.7	0.072	86.8
	L	0.13		trace		0.26		0.47	
Asp	D	0.13	61.0	trace	–	0.23	57.9	trace	–
	L	0.21		trace		0.31		trace	
Gly		5.61*	–	trace	–	7.61	–	4.87	–
Ala	D	0.72*	52.7	1.15	54.4	1.18	54.0	1.73	61.0
	L	0.80*		1.37		1.39		2.70	
α-ABA	D	0.11*	50.8	0.19	51.4	0.17	51.8	0.26	55.2
	L	0.11*		0.20		0.18		0.32	
Iva	D	0.053*	47.1	n.d.	–	0.062	51.3	n.d.	–
	L	0.047*		n.d.		0.065		n.d.	
Val	D	0.026*	67.9	trace	–	0.041	70.1	0.077	82.0
	L	0.056*		trace		0.10		0.35	
Nva	D	0.017*	50.9	0.043	48.4	0.027	51.1	0.059	48.2
	L	0.017*		0.040		0.028		0.055	

trace = under the lower limit of quantification.
n.d. = not detected.
* : data shown in the previous report [37].

forms in the terrestrial biosphere) in Ryugu grains were 0.03–0.10 nmol/g for Ser, 0.03–0.52 nmol/g for Asp and 0.025–2.2 nmol/g for Ala, and that of Gly was 0.46–15.8 nmol/g. Their amounts (nmol/g) in the present study were 0.033–0.076 for Ser, 0.13–0.23 for Asp, 0.72–1.73 for Ala and 4.87–7.61 for Gly, and these values were in consistent with those reported by NASA team. The amino acid amounts in the C0107 sample tended to be higher than those in the A0106 sample in the report by NASA team, and Ala and a non-proteinogenic amino acid, β-aminoisobutyric acid, were reported to be nearly racemic. In the present study, Ala and non-proteinogenic amino acids were also observed to be racemic, suggesting that they are present as almost racemates in Ryugu. As for the other amino acids, α-ABA were not separated by the LC-FL/HRMS method, and Val isomers were below the limit of quantification. Because the developed 3D-HPLC system in the present study has a high sensitivity and selectivity, α-ABA enantiomers were completely separated, and extremely trace amounts of amino acids, especially for the Val isomers, could be determined. These results indicated that the present system is one of the most suitable tools for the enantioselective determination of trace levels of amino acids in extraterrestrial samples.

4. Conclusions

In the present study, a 3D-HPLC system combining reversed-phase, anion-exchange and enantioselective columns was developed for the enantioselective determination of Ser, Asp, Gly, Ala, α-ABA, Iva, Val and Nva in the Hayabusa2 returned samples from the surface of the carbonaceous asteroid Ryugu. The system was applied to the chiral amino acid analyses of two Ryugu samples, A0106 and C0107, and all the target amino acids were successfully determined without interferences. In both the A0106 and C0107 samples, similar amino acid profiles were observed, and the aliphatic amino acids tended to have lower contents as the carbon number increased. Concerning the chirality of amino acids, non-proteinogenic amino acids (α-ABA, Iva and Nva) and Ala were nearly racemates in the Ryugu samples. The developed 3D-HPLC system enables the highly-sensitive and selective analyses of chiral amino acids in extraterrestrial samples, and further applications to various meteorite and asteroid samples are expected.

CRediT authorship contribution statement

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.jcoa.2024.100134.

References

[1] D.P. Glavin, C.M.O'D. Alexander, J.C. Aponte, J.P. Dworkin, J.E. Elsila, H. Yabuta, Chapter 3 - the origin and evolution of organic matter in carbonaceous chondrites and links to their parent bodies, in: N. Abreu (Ed.), Primitive Meteorites and Asteroids, Elsevier Inc., Amsterdam, 2018, pp. 205–271.

[2] M.H. Engel, S.A. Macko, J.A. Silfer, Carbon isotope composition of individual amino acids in the Murchison meteorite, Nature 348 (1990) 47–49, https://doi.org/10.1038/348047a0.

[3] S. Pizzarello, Y. Huang, M. Fuller, The carbon isotopic distribution of Murchison amino acids, Geochim. Cosmochim. Acta 68 (2004) 4963–4969, https://doi.org/10.1016/j.gca.2004.05.024.

[4] K.A. Kvenvolden, J.G. Lawless, C. Ponnamperuma, Nonprotein amino acids in the Murchison meteorite, Proc. Natl. Acad. Sci. USA 68 (1971) 486–490, https://doi.org/10.1073/pnas.68.2.486.

[5] T. Koga, H. Naraoka, A new family of extraterrestrial amino acids in the Murchison meteorite, Sci. Rep. 7 (2017) 636, https://doi.org/10.1038/s41598-017-00693-9.

[6] J.R. Cronin, S. Pizzarello, Enantiomeric excesses in meteoritic amino acids, Science 275 (1997) 951–955, https://doi.org/10.1126/science.275.5302.951.

[7] M.H. Engel, S.A. Macko, Isotopic evidence for extraterrestrial non-racemic amino acids in the Murchison meteorite, Nature 389 (1997) 265–268, https://doi.org/10.1038/38460.

[8] J.R. Cronin, S. Pizzarello, Amino acid enantiomer excesses in meteorites: origin and significance, Adv. Space Res. 23 (1999) 293–299, https://doi.org/10.1016/S0273-1177(99)00050-2.

[9] S. Pizzarello, J.R. Cronin, Non-racemic amino acids in the Murray and Murchison meteorites, Geochim. Cosmochim. Acta 64 (2000) 329–338, https://doi.org/10.1016/S0016-7037(99)00280-X.

[10] S. Pizzarello, G.W. Cooper, Molecular and chiral analyses of some protein amino acid derivatives in the Murchison and Murray meteorites, Meteorit. Planet. Sci. 36 (2001) 897–909, https://doi.org/10.1111/j.1945-5100.2001.tb01929.x.

[11] S. Pizzarello, M. Zolensky, K.A. Turk, Nonracemic isovaline in the Murchison meteorite: chiral distribution and mineral association, Geochim. Cosmochim. Acta 67 (2003) 1589–1595, https://doi.org/10.1016/S0016-7037(02)01283-8.

[12] D.P. Glavin, J.E. Elsila, H.L. Mclain, J.C. Aponte, E.T. Parker, J.P. Dworkin, D. H. Hill, H.C. Connolly Jr., D.S. Lauretta, Extraterrestrial amino acids and L-enantiomeric excesses in the CM2 carbonaceous chondrites Aguas Zarcas and Murchison, Meteorit. Planet. Sci. 56 (2021) 148–173, https://doi.org/10.1111/maps.13451.

[13] D.P. Glavin, J.P. Dworkin, Enrichment of the amino acid L-isovaline by aqueous alteration on CI and CM meteorite parent bodies, Proc. Natl. Acad. Sci. USA 106 (2009) 5487–5492, https://doi.org/10.1073/pnas.0811618106.

[14] D.P. Glavin, J.E. Elsila, A.S. Burton, M.P. Callahan, J.P. Dworkin, R.W. Hilts, C.D. K. Herd, Unusual nonterrestrial L-proteinogenic amino acid excesses in the Tagish Lake meteorite, Meteorit. Planet. Sci. 47 (2012) 1347–1364, https://doi.org/10.1111/j.1945-5100.2012.01400.x.

[15] F. Cava, H. Lam, M.A. de Pedro, M.K. Waldor, Emerging knowledge of regulatory roles of D-amino acids in bacteria, Cell. Mol. Life Sci. 68 (2011) 817–831, https://doi.org/10.1007/s00018-010-0571-8.

[16] A.D. Radkov, L.A. Moe, Bacterial synthesis of D-amino acids, Appl. Microbiol. Biotechnol. 98 (2014) 5363–5374, https://doi.org/10.1007/s00253-014-5726-3.

[17] K. Tamura, Perspectives on the origin of biological homochirality on Earth, J. Mol. Evol. 87 (2019) 143–146, https://doi.org/10.1007/s00239-019-09897-1.

[18] D.G. Blackmond, The origin of biological homochirality, Cold Spring Harb. Perspect. Biol. 11 (2019) a032540, https://doi.org/10.1101/cshperspect.a002147.

[19] D.P. Glavin, A.S. Burton, J.E. Elsila, J.C. Aponte, J.P. Dworkin, The search for chiral asymmetry as a potential biosignature in our Solar System, Chem. Rev. 120 (2020) 4660–4689, https://doi.org/10.1021/acs.chemrev.9b00474.

[20] D.E. Brownlee, P. Tsou, J.D. Anderson, M.S. Hanner, R.L. Newburn, Z. Sekanina, B. C. Clark, F. Hörz, M.E. Zolensky, J. Kissel, J.A.M. McDonnell, S.A. Sandford, A. J. Tuzzolino, Stardust: comet and interstellar dust sample return mission, J. Geophys. Res. 108 (2003) 8111, https://doi.org/10.1029/2003JE002087.

[21] J. Kawaguchi, A. Fujiwara, T. Uesugi, Hayabusa—Its technology and science accomplishment summary and Hayabusa-2, Acta Astronaut 62 (2008) 639–647, https://doi.org/10.1016/j.actaastro.2008.01.028.

[22] J.E. Elsila, D.P. Glavin, J.P. Dworkin, Cometary glycine detected in samples returned by Stardust, Meteorit. Planet. Sci. 44 (2009) 1323–1330, https://doi.org/10.1111/j.1945-5100.2009.tb01224.x.

[23] H. Naraoka, H. Mita, K. Hamase, M. Mita, H. Yabuta, K. Saito, K. Fukushima, F. Kitajima, S.A. Sandford, T. Nakamura, T. Noguchi, R. Okazaki, K. Nagao, M. Ebihara, H. Yurimoto, A. Tsuchiyama, M. Abe, K. Shirai, M. Ueno, T. Yada, Y. Ishibashi, T. Okada, A. Fujimura, T. Mukai, M. Yoshikawa, J. Kawaguchi, Preliminary organic compound analysis of microparticles returned from Asteroid 25143 Itokawa by the Hayabusa mission, Geochem. J. 46 (2012) 61–72, https://doi.org/10.2343/geochemj.1.0134.

[24] E.T. Parker, Q.H.S. Chan, D.P. Glavin, J.P. Dworkin, Non-protein amino acids identified in carbon-rich Hayabusa particles, Meteorit. Planet. Sci. 57 (2022) 776–793, https://doi.org/10.1111/maps.13794.

[25] S. Tachibana, H. Sawada, R. Okazaki, Y. Takano, K. Sakamoto, Y.N. Miura, C. Okamoto, H. Yano, S. Yamanouchi, P. Michel, Y. Zhang, S. Schwartz, F. Thuillet, H. Yurimoto, T. Nakamura, T. Noguchi, H. Yabuta, H. Naraoka, A. Tsuchiyama, N. Imae, K. Kurosawa, A.M. Nakamura, K. Ogawa, S. Sugita, T. Morota, R. Honda, S. Kameda, E. Tatsumi, Y. Cho, K. Yoshioka, Y. Yokota, M. Hayakawa, M. Matsuoka, N. Sakatani, M. Yamada, T. Kouyama, H. Suzuki, C. Honda, T. Yoshimitsu, T. Kubota, H. Demura, T. Yada, M. Nishimura, K. Yogata, A. Nakato, M. Yoshitake, A.I. Suzuki, S. Furuya, K. Hatakeda, A. Miyazaki, K. Kumagai, T. Okada, M. Abe, T. Usui, T.R. Ireland, M. Fujimoto, T. Yamada, M. Arakawa, H. C. Connolly Jr., A. Fujii, S. Hasegawa, N. Hirata, N. Hirata, C. Hirose, S. Hosoda, Y. Iijima, H. Ikeda, M. Ishiguro, Y. Ishihara, T. Iwata, S. Kikuchi, K. Kitazato, D. S. Lauretta, G. Libourel, B. Marty, K. Matsumoto, T. Michikami, Y. Mimasu, A. Miura, O. Mori, K. Nakamura-Messenger, N. Namiki, A.N. Nguyen, L.R. Nittler, H. Noda, R. Noguchi, N. Ogawa, G. Ono, M. Ozaki, H. Senshu, T. Shimada, Y. Shimaki, K. Shirai, S. Soldini, T. Takahashi, Y. Takei, H. Takeuchi, R. Tsukizaki, K. Wada, Y. Yamamoto, K. Yoshikawa, K. Yumoto, M.E. Zolensky, S. Nakazawa, F. Terui, S. Tanaka, T. Saiki, M. Yoshikawa, S. Watanabe, Y. Tsuda, Pebbles and sand on asteroid (162173) Ryugu: in situ observation and particles returned to Earth, Science 375 (2022) 1011–1016, https://doi.org/10.1126/science.abj8624.

[26] T. Yokoyama, K. Nagashima, I. Nakai, E.D. Young, Y. Abe, J. Aléon, C.M. O'D. Alexander, S. Amari, Y. Amelin, K. Bajo, M. Bizzarro, A. Bouvier, R. W. Carlson, M. Chaussidon, B.G. Choi, N. Dauphas, A.M. Davis, T. Di Rocco, W. Fujiya, R. Fukai, I. Gautam, M.K. Haba, Y. Hibiya, H. Hidaka, H. Homma, P. Hoppe, G.R. Huss, K. Ichida, T. Iizuka, T.R. Ireland, A. Ishikawa, M. Ito, S. Itoh, N. Kawasaki, N.T. Kita, K. Kitajima, T. Kleine, S. Komatani, A.N. Krot, M.C. Liu, Y. Masuda, K.D. McKeegan, M. Morita, K. Motomura, F. Moynier, A. Nguyen, L. Nittler, M. Onose, A. Pack, C. Park, L. Piani, L. Qin, S.S. Russell, N. Sakamoto, M. Schönbächler, L. Tafla, H. Tang, K. Terada, Y. Terada, T. Usui, S. Wada, M. Wadhwa, R.J. Walker, K. Yamashita, Q.Z. Yin, S. Yoneda, H. Yui, A.C. Zhang, H. C. Connolly Jr., D.S. Lauretta, T. Nakamura, H. Naraoka, T. Noguchi, R. Okazaki, K. Sakamoto, H. Yabuta, M. Abe, M. Arakawa, A. Fujii, M. Hayakawa, N. Hirata, N. Hirata, R. Honda, C. Honda, S. Hosoda, Y. Iijima, H. Ikeda, M. Ishiguro, Y. Ishihara, T. Iwata, K. Kawahara, S. Kikuchi, K. Kitazato, K. Matsumoto, M. Matsuoka, T. Michikami, Y. Mimasu, A. Miura, T. Morota, S. Nakazawa, N. Namiki, H. Noda, R. Noguchi, N. Ogawa, K. Ogawa, T. Okada, C. Okamoto, G. Ono, M. Ozaki, T. Saiki, N. Sakatani, H. Sawada, H. Senshu, Y. Shimaki, K. Shirai, S. Sugita, Y. Takei, H. Takeuchi, S. Tanaka, E. Tatsumi, F. Terui, Y. Tsuda, R. Tsukizaki, K. Wada, S. Watanabe, M. Yamada, T. Yamada, Y. Yamamoto, H. Yano, Y. Yokota, K. Yoshihara, M. Yoshikawa, K. Yoshikawa, S. Furuya, K. Hatakeda, T. Hayashi, Y. Hitomi, K. Kumagai, A. Miyazaki, A. Nakato, M. Nishimura, H. Soejima, A. Suzuki, T. Yada, D. Yamamoto, K. Yogata, M. Yoshitake, S. Tachibana, H. Yurimoto, Samples returned from the asteroid Ryugu are similar to Ivuna-type carbonaceous meteorites, Science 379 (2023) eabn7850, https://doi.org/10.1126/science.abn7850.

[27] E. Nakamura, K. Kobayashi, R. Tanaka, T. Kunihiro, H. Kitagawa, C. Potiszil, T. Ota, C. Sakaguchi, M. Yamanaka, D.M. Ratnayake, H. Tripathi, R. Kumar, M. L. Avramescu, H. Tsuchida, Y. Yachi, H. Miura, M. Abe, R. Fukai, S. Furuya, K. Hatakeda, T. Hayashi, Y. Hitomi, K. Kumagai, A. Miyazaki, A. Nakato, M. Nishimura, T. Okada, H. Soejima, S. Sugita, A. Suzuki, T. Usui, T. Yada, D. Yamamoto, K. Yogata, M. Yoshitake, M. Arakawa, A. Fujii, M. Hayakawa, N. Hirata, N. Hirata, R. Honda, C. Honda, S. Hosoda, Y. Iijima, H. Ikeda, M. Ishiguro, Y. Ishihara, T. Iwata, K. Kawahara, S. Kikuchi, K. Kitazato, K. Matsumoto, M. Matsuoka, T. Michikami, Y. Mimasu, A. Miura, T. Morota, S. Nakazawa, N. Namiki, H. Noda, R. Noguchi, N. Ogawa, K. Ogawa, C. Okamoto, G. Ono, M. Ozaki, T. Saiki, N. Sakatani, H. Sawada, H. Senshu, Y. Shimaki, K. Shirai, Y. Takei, H. Takeuchi, S. Tanaka, E. Tatsumi, F. Terui, R. Tsukizaki, K. Wada, M. Yamada, T. Yamada, Y. Yamamoto, H. Yano, Y. Yokota, K. Yoshihara, M. Yoshikawa, K. Yoshikawa, M. Fujimoto, S. Watanabe, Y. Tsuda, On the origin and evolution of the asteroid Ryugu: a comprehensive geochemical perspective, Proc. Jpn. Acad., Ser. B 98 (2022) 227–282, https://doi.org/10.2183/pjab.98.015.

[28] K. Kvenvolden, J. Lawless, K. Pering, E. Peterson, J. Flores, C. Ponnamperuma, I. R. Kaplan, C. Moore, Evidence for extraterrestrial amino-acids and hydrocarbons in the Murchison meteorite, Nature 228 (1970) 923–926, https://doi.org/10.1038/228923a0.

[29] J.G. Lawless, K.A. Kvenvolden, E. Peterson, C. Ponnamperuma, C. Moore, Amino acids indigenous to the Murray meteorite, Science 173 (1971) 626–627, https://doi.org/10.1126/science.173.3997.626.

[30] S. Pizzarello, Y. Huang, M.R. Alexandre, Molecular asymmetry in extraterrestrial chemistry: insights from a pristine meteorite, Proc. Natl. Acad. Sci. USA 105 (2008) 3700–3704, https://doi.org/10.1073/pnas.0709909105.

[31] O. Botta, Z. Martins, P. Ehrenfreund, Amino acids in Antarctic CM1 meteorites and their relationship to other carbonaceous chondrites, Meteorit. Planet. Sci. 42 (2007) 81–92, https://doi.org/10.1111/j.1945-5100.2007.tb00219.x.

[32] O. Botta, D.P. Glavin, G. Kminek, J.L. Bada, Relative amino acid concentrations as a signature for parent body processes of carbonaceous chondrites, Orig. Life Evol. Biosph. 32 (2002) 143–163, https://doi.org/10.1023/a:1016019425995.

[33] D.P. Glavin, J.P. Dworkin, A. Aubrey, O. Botta, J.H. Doty III, Z. Martins, J.L. Bada, Amino acid analyses of Antarctic CM2 meteorites using liquid chromatography–time of flight–mass spectrometry, Meteorit. Planet. Sci. 41 (2006) 889–902, https://doi.org/10.1111/j.1945-5100.2006.tb00493.x.

[34] Z. Martins, P. Modica, B. Zanda, L.Le Sergeant d'Hendecourt, The amino acid and hydrocarbon contents of the Paris meteorite: insights into the most primitive CM chondrite, Meteorit. Planet. Sci. 50 (2015) 926–943, https://doi.org/10.1111/maps.12442.

[35] A. Shimoyama, R. Ogasawara, Dipeptides and diketopiperazines in the Yamato-791198 and Murchison carbonaceous chondrites, Orig. Life Evol. Biosph. 32 (2002) 165–179, https://doi.org/10.1023/a:1016015319112.

[36] J.L. Bada, D.P. Glavin, G.D. McDonald, L. Becker, A search for endogenous amino acids in Martian meteorite ALH84001, Science 279 (1998) 362–365, https://doi.org/10.1126/science.279.5349.362.

[37] H. Naraoka, Y. Takano, J.P. Dworkin, Y. Oba, K. Hamase, A. Furusho, N.O. Ogawa, M. Hashiguchi, K. Fukushima, D. Aoki, P. Schmitt-Kopplin, J.C. Aponte, E. T. Parker, D.P. Glavin, H.L. McLain, J.E. Elsila, H.V. Graham, J.M. Eiler, F. R. Orthous-Daunay, C. Wolters, J. Isa, V. Vuitton, R. Thissen, S. Sakai, T. Yoshimura, T. Koga, N. Ohkouchi, Y. Chikaraishi, H. Sugahara, H. Mita, Y. Furukawa, N. Hertkorn, A. Ruf, H. Yurimoto, T. Nakamura, T. Noguchi, R. Okazaki, H. Yabuta, K. Sakamoto, S. Tachibana, H.C. Connolly Jr., D.S. Lauretta, M. Abe, T. Yada, M. Nishimura, K. Yogata, A. Nakato, M. Yoshitake, A. Suzuki, A. Miyazaki, S. Furuya, K. Hatakeda, H. Soejima, Y. Hitomi, K. Kumagai, T. Usui, T. Hayashi, D. Yamamoto, R. Fukai, K. Kitazato, S. Sugita, N. Namiki, M. Arakawa, H. Ikeda, M. Ishiguro, N. Hirata, K. Wada, Y. Ishihara, R. Noguchi, T. Morota, N. Sakatani, K. Matsumoto, H. Senshu, R. Honda, E. Tatsumi, Y. Yokota, C. Honda, T. Michikami, M. Matsuoka, A. Miura, H. Noda, T. Yamada, K. Yoshihara, K. Kawahara, M. Ozaki, Y. Iijima, H. Yano, M. Hayakawa, T. Iwata, R. Tsukizaki, H. Sawada, S. Hosoda, K. Ogawa, C. Okamoto, N. Hirata, K. Shirai, Y. Shimaki, M. Yamada, T. Okada, Y. Yamamoto, H. Takeuchi, A. Fujii, Y. Takei, K. Yoshikawa, Y. Mimasu, G. Ono, N. Ogawa, S. Kikuchi, S. Nakazawa, F. Terui, S. Tanaka, T. Saiki, M. Yoshikawa, S. Watanabe, Y. Tsuda, Soluble organic molecules in samples of the carbonaceous asteroid (162173) Ryugu, Science 379 (2023) eabn9033, https://doi.org/10.1126/science.abn9033.

[38] E.T. Parker, H.L. McLain, D.P. Glavin, J.P. Dworkin, J.E. Elsila, J.C. Aponte, H. Naraoka, Y. Takano, S. Tachibana, H. Yabuta, H. Yurimoto, K. Sakamoto, T. Yada, M. Nishimura, A. Nakato, A. Miyazaki, K. Yogata, M. Abe, T. Okada, T. Usui, M. Yoshikawa, T. Saiki, S. Tanaka, S. Nakazawa, Y. Tsuda, F. Terui, T. Noguchi, R. Okazaki, S. Watanabe, T. Nakamura, Extraterrestrial amino acids and amines identified in asteroid Ryugu samples returned by the Hayabusa2 mission, Geochim. Cosmochim. Acta 347 (2023) 42–57, https://doi.org/10.1016/j.gca.2023.02.017.

[39] K. Hamase, Y. Nakauchi, Y. Miyoshi, R. Koga, N. Kusano, H. Onigahara, H. Naraoka, H. Mita, Y. Kadota, Y. Nishio, M. Mita, W. Lindner, Enantioselective determination of extraterrestrial amino acids using a two-dimensional chiral high-performance liquid chromatographic system, Chromatography 35 (2014) 103–110, https://doi.org/10.15583/jpchrom.2014.014.

[40] C. Ishii, A. Furusho, C.L. Hsieh, K. Hamase, Multi-dimensional high-performance liquid chromatographic determination of chiral amino acids and related compounds in real world samples, Chromatography 41 (2020) 1–17, https://doi.org/10.15583/jpchrom.2020.004.

[41] R. Karongo, J. Horak, M. Lämmerhofer, Comprehensive online reversed-phase × chiral two-dimensional liquid chromatography-mass spectrometry with data-independent sequential window acquisition of all theoretical fragment-ion spectra-acquisition for untargeted enantioselective amino acid analysis, Anal. Chem. 94 (2022) 17063–17072, https://doi.org/10.1021/acs.analchem.2c03042.

[42] M. Oyaide, C. Ishii, A. Fujii, A. Takeyuki, M. Mita, M. Nagano, K. Hamase, Enantioselective determination of hydroxy amino acids in Japanese traditional amber rice vinegars, Chromatography 43 (2022) 59–65, https://doi.org/10.15583/jpchrom.2022.006.

[43] A. Furusho, R. Koga, T. Akita, M. Mita, T. Kimura, K. Hamase, Three-dimensional high-performance liquid chromatographic determination of Asn, Ser, Ala, and Pro enantiomers in the plasma of patients with chronic kidney disease, Anal. Chem. 91 (2019) 11569–11575, https://doi.org/10.1021/acs.analchem.9b01615.

[44] A. Furusho, T. Akita, M. Mita, H. Naraoka, K. Hamase, Three-dimensional high-performance liquid chromatographic analysis of chiral amino acids in carbonaceous chondrites, J. Chromatogr. A 1625 (2020) 461255, https://doi.org/10.1016/j.chroma.2020.461255.

[45] C. Ishii, R. Morinaga, M. Takahashi, M. Mita, T. Akita, K. Hamase, Development of a three-dimensional HPLC system for acidic amino acid enantiomers and determination of their amounts in mice lacking D-aspartic acid oxidase activity, J. Pharm. Biomed. Anal. Open 1 (2023) 100004, https://doi.org/10.1016/j.jpbao.2023.100004.

[46] M. Arakawa, T. Saiki, K. Wada, K. Ogawa, T. Kadono, K. Shirai, H. Sawada, K. Ishibashi, R. Honda, N. Sakatani, Y. Iijima, C. Okamoto, H. Yano, Y. Takagi, M. Hayakawa, P. Michel, M. Jutzi, Y. Shimaki, S. Kimura, Y. Mimasu, T. Toda, H. Imamura, S. Nakazawa, H. Hayakawa, S. Sugita, T. Morota, S. Kameda, E. Tatsumi, Y. Cho, K. Yoshioka, Y. Yokota, M. Matsuoka, M. Yamada, T. Kouyama, C. Honda, Y. Tsuda, S. Watanabe, M. Yoshikawa, S. Tanaka, F. Terui, S. Kikuchi, T. Yamaguchi, N. Ogawa, G. Ono, K. Yoshikawa, T. Takahashi, Y. Takei, A. Fujii, H. Takeuchi, Y. Yamamoto, T. Okada, C. Hirose, S. Hosoda, O. Mori, T. Shimada, S. Soldini, R. Tsukizaki, T. Iwata, M. Ozaki, M. Abe, N. Namiki, K. Kitazato, S. Tachibana, H. Ikeda, N. Hirata, N. Hirata, R. Noguchi, A. Miura, An artificial impact on the asteroid (162173) Ryugu formed a crater in the gravity-dominated regime, Science 368 (2020) 67–71, https://doi.org/10.1126/science.aaz1701.

[47] I. Myrgorodska, C. Meinert, Z. Martins, L. Le Sergeant d'Hendecourt, U. J, Meierhenrich Quantitative enantioseparation of amino acids by comprehensive two-dimensional gas chromatography applied to non-terrestrial samples, J. Chromatogr. A 1433 (2016) 131–136, https://doi.org/10.1016/j.chroma.2016.01.014.

[48] J.M. Friedrich, H.L. McLain, J.P. Dworkin, D.P. Glavin, W.H. Towbin, M. Hill, D. S. Ebel, Effect of polychromatic X-ray microtomography imaging on the amino acid content of the Murchison CM chondrite, Meteorit. Planet. Sci. 54 (2019) 220–228, https://doi.org/10.1111/maps.13188.