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Asymmetric synthesis of amino acid precursors in interstellar complex organics by circularly polarized light

Yoshinori Takano^{a,b,*}, Jun-ichi Takahashi^c, Takeo Kaneko^d,
Katsumi Marumo^b, Kensei Kobayashi^d

^a Department of Natural History Sciences, Graduate School of Science, Hokkaido University, N8W10, Kita-ku, Sapporo 060-0810, Japan

^b Institute of Geology and Geoinformation (IGG), National Institute of Advanced Industrial Science and Technology (AIST), AIST Central 7, 1-1-1 Higashi, Tsukuba, 305-8567, Japan

^c NTT Microsystem Integration Laboratories, 3-1 Wakamiya, Morinosato, Atsugi 243-0198, Japan

^d Department of Chemistry and Biotechnology, Yokohama National University, 79-5 Tokiwadai, Hodogaya-ku, Yokohama 240-8501, Japan

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Abstract

The asymmetric synthesis of amino acid precursors from complex organics have been performed. A gaseous mixture of carbon monoxide, ammonia and water (molecules which are among those identified in the interstellar medium) was irradiated with 3.0 MeV protons to obtain amino acid precursors within high-molecular-weight complex organics of up to 3000 Da. The amino acid precursor products synthesized were then irradiated with right (R-) or left (L-) ultraviolet circularly polarized light (UV-CPL) obtained from a synchrotron radiation (SR) source. Glycine was a predominant product, and number of chiral amino acids including alanine were identified following acid hydrolysis. R-UV-CPL preferentially produced D-alanine, while L-UV-CPL produced more L-alanine. Enantiomeric excesses (% D-% L) of +0.44% and -0.65% were obtained by R-UV-CPL and L-UV-CPL, respectively. These results imply that the origins of chirality in meteoritic amino acids could be accounted for by the formation of asymmetric amino acid precursors from extraterrestrial complex organics by CPL in space.

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Keywords: Asymmetric synthesis; Amino acid precursors; Complex organics; Carbonaceous meteorite; Circularly polarized light; Exogenous production

1. Introduction

Since the time of Pasteur, the development of specific chirality in terrestrial biomolecules has remained one of

the most important problems with regard to our knowledge concerning chemical evolution. The one-handedness of terrestrial amino acids and sugars is essential to the formation, structure, and function of biopolymers and is a defining molecular trait of life on the Earth. Numerous hypotheses regarding the origins of homochirality have been presented, from both biotic and abiotic viewpoints [1]; according to the former, life initially was based on achiral molecules and/or racemates and the use

* Corresponding author. Department of Natural History Sciences, Graduate School of Science, Hokkaido University, N8W10, Kita-ku, Sapporo 060-0810, Japan. Fax: +81 11 706 3683.

E-mail address: takano@nature.sci.hokudai.ac.jp (Y. Takano).

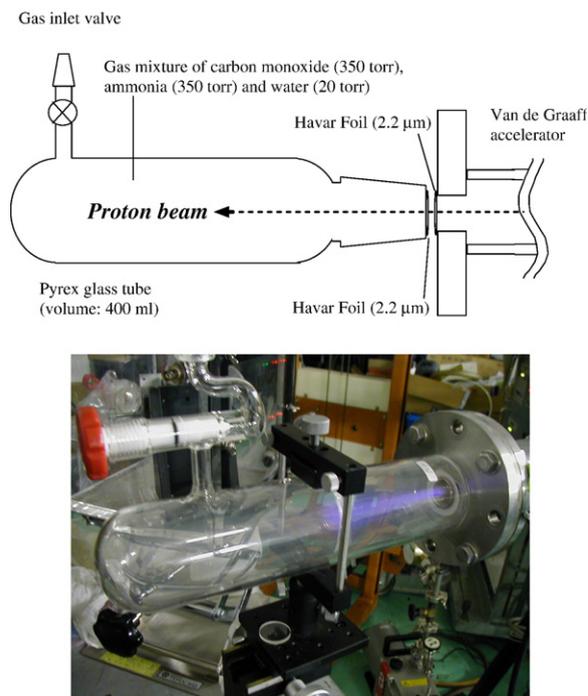


Fig. 1. Schematic diagram of the experimental setup for irradiating (3 MeV proton) the gas mixtures simulating interstellar media in the gas mixture. The irradiation was performed at ambient room temperature.

of specific enantiomers came about through evolution, whereas the latter theories propose that a tendency toward homochirality was inherent in prebiotic chemical evolution. Meteorites, specifically carbonaceous chondrites, carry abiotic records concerning the early organic chemical evolution of the solar system. The successful detection of amino acids in enantiomeric excess within the Murchison and Murray meteorites spawned a persuasive scenario for the exogenous origins of homochirality; so far, L-enantiomeric excesses of the amino acid were found to range from 0 to maxim 15.2% [2–4]. It was shown that the α -methyl- α -amino alkanolic acids could have been significant in the origin of terrestrial homochirality given their resistance to racemization and the possibility for amplification of their enantiomeric excesses suggested by the tendency of their polymers to form chiral secondary structure [3,4].

Recent studies have documented the optical counterpart of an isolated neutron star [5] and strong IR polarization from the Orion molecular cloud [6,7]. From a photochemical point of view, continuous circularly polarized light (CPL) from supernovae, which are elliptically and ultimately circularly polarized, may have contributed to the origin of biomolecular asymmetry [8,9]. In the first achievement of laboratory experiments, UV–CPL photolysis (212.8 nm) has been

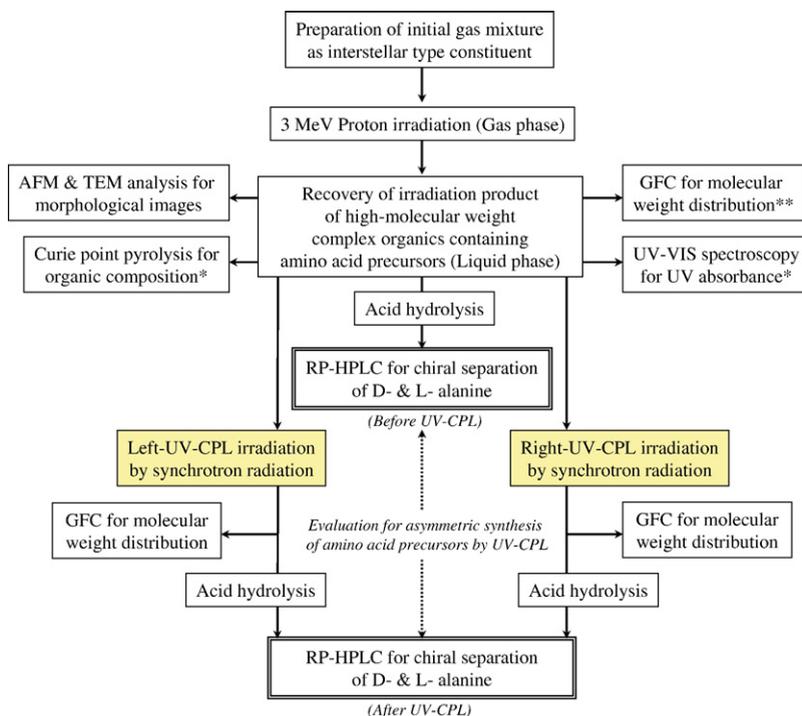


Fig. 2. Experimental procedures of asymmetric synthesis of amino acid precursors from interstellar type complex organics. The asterisk mark of single (*) and double (**) stands for our previous result of [17] and [18], respectively.

shown to give rise to enantiomeric excesses in racemic leucine of 1.98% (right handed) and 2.50% (left handed) with 59% and 75% overall decomposition, respectively [10]. Several other investigations have attempted to examine the possible asymmetric photolysis of free amino acids in strong acidic solution [10–12] or in ice film [9,13]. The verification of asymmetric amino acids behavior as a chiral catalysts has been performed by using threose and erythrose from glycolaldehyde [14].

Simulation experiments have suggested, however, that not free amino acids but complex organic compounds containing amino acid precursors are formed in interstellar environments. Only trace amounts of amino acids were detected among the products of simulation experiments prior to hydrolysis [15,16]. Additionally, we preliminary reported that the irradiation products included amino acid precursors in the high-molecular-weight complex organics [17,18]. The molecular weight distribution ranged from several hundreds to a maximum of 3000, and wide variety of amino acids were detected after acid-hydrolysis [18]. Thus, the primary irradiation products were not free amino acids having high-molecular-weight distribution. Here, we report novel possible pathway of chiral amino acid precursors via asymmetric synthesis using UV-CPL. These results imply that the chirality in meteoritic amino acids could be accounted for by the formation of asymmetric amino acid precursors from extraterrestrial complex organics by CPL in space.

2. Experimental

2.1. Sample preparation

A Pyrex glass tube (400 ml) was filled with the following components: 350 Torr of carbon monoxide,

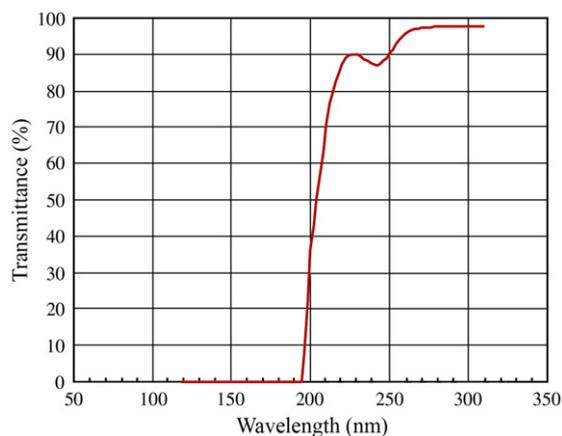


Fig. 3. Transmittance (%) curve of fused quartz window versus wavelength (nm) [37].

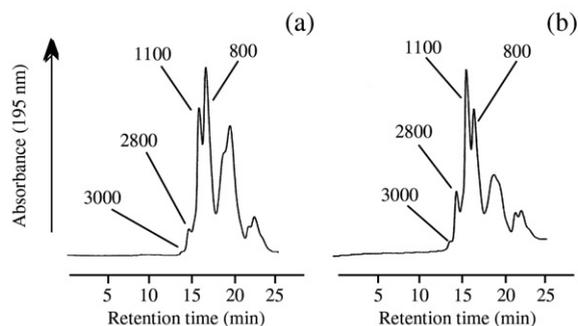


Fig. 4. Gel filtration chromatograms of proton irradiation products from the gas mixture consisting of carbon monoxide (350 Torr), ammonia (350 Torr) and water (20 Torr). Each peak is labeled with the molecular weight, which was estimated by calibration with polyethylene glycols and human serum albumin. (a) Proton irradiation product [18], (b) Proton and UV-CPL irradiation product (this study). The same analytical condition and injection volume were applied to (a) and (b).

350 Torr of ammonia over liquid water (5 ml), which provided 20 Torr of water vapor at room temperature [17,18], as shown in Fig. 1. The whole experimental procedures to evaluate asymmetric synthesis of amino acid precursors from interstellar type complex organics are shown in Fig. 2. Ultra-pure grade carbon monoxide and ammonia gases were purchased from Nihon Sanso Co. Initially, gas mixtures were irradiated with high energy protons (4.0 MeV) generated using a van de Graaff accelerator (Tokyo Institute of Technology) in an effort to synthesize complex organic compounds [17,18,20]. Energy of protons were decreased to ca. 3 MeV after passing through Havar foil, a concave window, and the air gap between them (Fig. 1). The total energy deposited to the gas mixture was 4.4 kJ, which was given as the product of the number of the particles

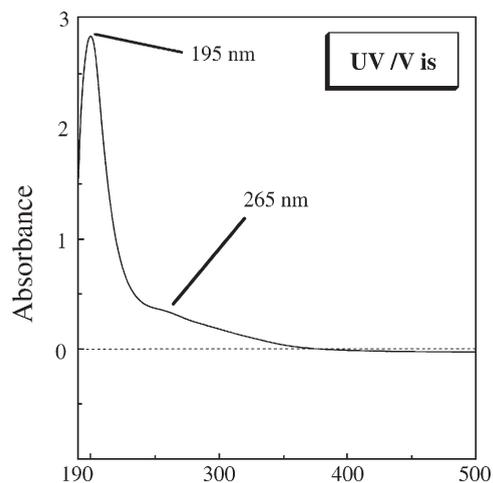


Fig. 5. Ultraviolet absorbance of proton irradiation products. Peaks of at 195 nm and 265 nm were observed [17].

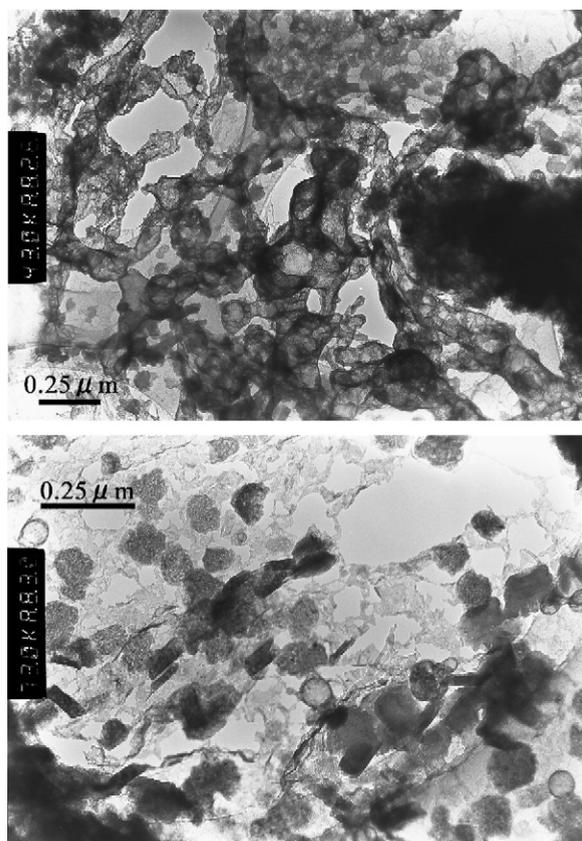


Fig. 6. Two-dimensional transmission electron microscopy (TEM) images of aggregated high-molecular-weight complex organic materials synthesized by proton irradiation. The elemental composition of the complex organics was also investigated using a Parkin Elmer Series II CHNS/O analyzer with the following results: C, 28.9%; H, 8.1%; N, 30.9%; O, 28.2%. The number of racemic proteinous and non-proteinous amino acids (50.0:50.0 mixtures of D- and L-amino acids) found in the proton-irradiated product following acid hydrolysis is shown in Table 1.

delivered and the ionization energy loss of a single particle in the gas mixture. The irradiation was performed at ambient room temperature for 2 h.

Deionized water was further purified with a Millipore Milli-Q LaboSystem™ and a Millipore Simpli Lab-UV (Japan Millipore Ltd., Tokyo, Japan) in order to remove both inorganic ions and organic contaminants. Prior to use, all glassware was newly purchased and heated in a high temperature oven (Yamato DR-22) at 500 °C for 2 h in order to eliminate any possible contaminants.

2.2. Asymmetric synthesis of amino acid precursors

After recovery of proton-irradiated sample by twice time extraction with 5 ml of pure ion-exchanged water, a liquid portion of the whole proton-irradiated 5 sample was subjected to irradiation with right (R-) or left

(L-) continuum ultraviolet circularly polarized light (UV-CPL) obtained from a synchrotron radiation (SR) source. The volume of the all quartz container used was 14 ml, and the thickness of the liquid layer was 10 mm. In order to make no headspace, the liquid completely filled the container. The UV-CPL used was generated from the ABL-6A beam line of a normal conducting accelerator ring (NAR) at NTT's SR facility [19]. The SR is an electromagnetic wave with a wide range of wavelengths, and can be used to simulate a variety of radiation, such as that emitted by a neutron star. A fused quartz window mounted at the beam exit from a vacuum chamber ($<10^{-9}$ Torr) passed the ultraviolet component ($\lambda > 200$ nm) of the SR beam as shown in Fig. 3. A portion of the UV-CPL sample was injected into a gel filtration chromatograph (GFC) system [17] in an effort to estimate the molecular weight of the irradiation products. The GFC Systems was composed of a High Performance Liquid Chromatography (HPLC) pump (TOSOH DP-8020) and a UV detector (TOSOH UV-8020). The columns used were TSKgel G2000 SW \times L (7.8 mm i.d. \times 300 mm) for gel filtration, and Inertsil ODS-3 (4.6 mm i.d. \times 250 mm) for reversed-phase partition chromatography. The mobile phase was a mixture of 25 mM acetonitrile (25%) and 0.1% trifluoroacetic acid (75%). Molecular weights were calibrated using several molecular weights of polyethylene glycol (PEG) and human serum albumin.

2.3. Chiral separation of amino acid enantiomers

After UV-CPL irradiation, an aliquot of the aqueous irradiated solution containing amino acid precursors was hydrolyzed with 6 M HCl at 110 °C for 24 h. Following acid hydrolysis and evaporation to dryness, the hydrolyzed fraction were dissolved in 0.1 M HCl and subsequently applied to a Bio-Rad AG-50W-X8 cation exchange resin column (200–400 mesh) for desalting. The amino acid fraction was eluted from the column with 10% NH_3 aqueous solution, evaporated to dryness and then re-dissolved in 0.1 M HCl. Amino acid enantiomers were separated by Reversed-Phase High Performance Liquid Chromatography (RP-HPLC) following derivatization with *o*-phthalaldehyde and *N*-acetyl-L-cysteine in sodium acetic acid buffer. RP-HPLC was composed of high performance liquid chromatograph pumps (TOSOH CCPM II) attached with a reversed phase column (YMC-pack Pro C18 4.6 mm i.d. \times 250 mm) and TOSOH FS 8020 detector (excited wavelength: 355 nm and emission wavelength: 435 nm). An aliquot of the pretreated sample was mixed well with *o*-phthalaldehyde and *N*-Acetyl-L-cysteine in a

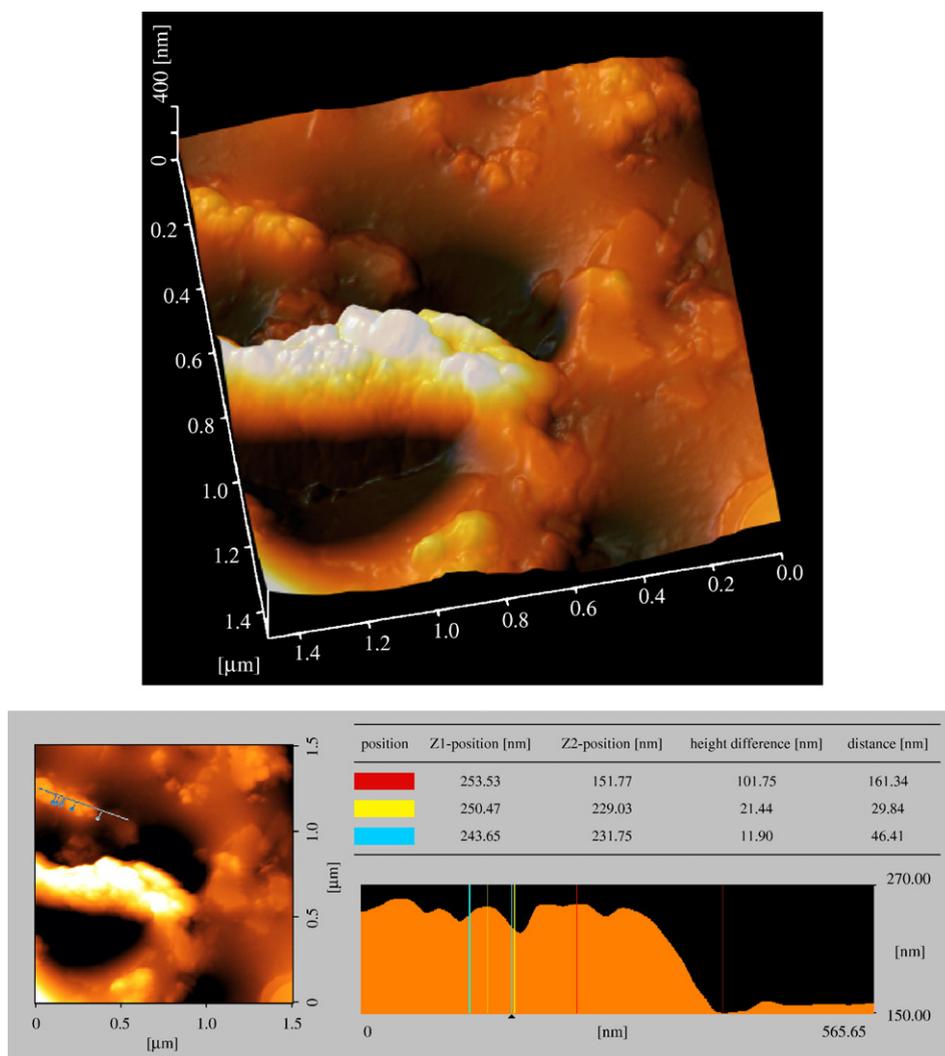


Fig. 7. Three-dimensional atomic force microscopy (AFM) images of aggregated high-molecular-weight complex organic materials synthesized by proton irradiation.

glass vial and injected into the HPLC column. Gradient elution was applied using the following eluents; A: 40 mM sodium acetic acid buffer (pH 6.5), B: 100% methanol (ultra-pure HPLC grade). The gradient program was as follows: 10 min (Eluent B: 0%) – 25 min (Eluent B: 10%) – 65 min (Eluent B: 20%) – 80 min (Eluent B: 20%) – 85 min (Eluent B: 40%) – 115 min (Eluent B: 60%) – 120 min (Eluent B: 80%) – 135 min (Eluent B: 0%). Multiple experimental runs were performed (7 times for each, and 21 times in total).

2.4. Microscopic study of complex organics

After proton irradiation, an aliquot of the radiation products was dried at ambient temperature and ambient

pressure in clean bench. Application of transmission electron microscopy (TEM, Philips CM-12, USA) and atomic force microscopy (AFM, Seico Instruments Inc., SII SPA 400 unit, Japan) were also performed to the yellow colored residue of proton irradiation product.

3. Results and discussion

3.1. Synthesis of interstellar type complex organics

Complex organics resembling those found in interstellar dust containing amino acid precursors were synthesized by proton irradiation of interstellar components in the gas phase at room temperature. The molecular weight distribution ranged between several hundreds and 3000 Da, with peaks corresponding to

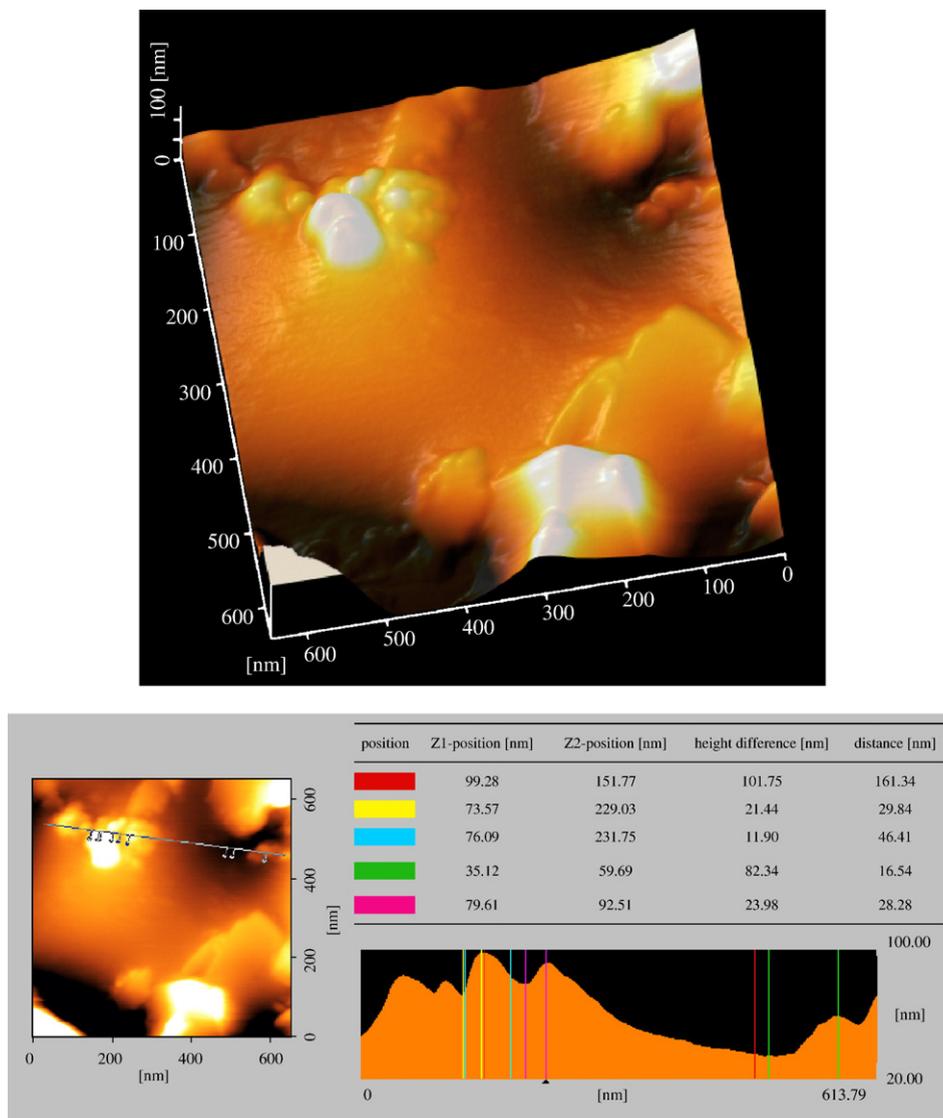


Fig. 7 (continued).

2800, 1100 and 800 Da being observed, as shown in Fig. 4(a). The yellow-colored proton-irradiated product was soluble in water, suggesting that the high-molecular-weight complex organics contained hydrophilic functional groups such as $-\text{OH}$ and $-\text{NH}_2$ bonds. In our previous study [17], the maximum UV absorbance was observed at 195 nm with a slight shoulder peak on 265 nm (Fig. 5). The peak at 195 nm is typical of organic compounds. The peak around 265 nm might suggest the presence of cyclic compounds, such as aromatic or heterocyclic compounds. Two-dimensional and three-dimensional images of aggregated high-molecular-weight complex organics were performed by transmission electron microscopy (TEM,

Philips CM-12 unit, USA) and atomic force microscopy (AFM, Seico Instruments Inc., SII SPA 400 unit, Japan) as shown in Figs. 6 and 7, respectively. These TEM and AFM images of irradiated samples show amorphous particulate cottony images of high-molecular-weight complex organics.

Glycine was predominant among the hydrolyzed amino acids with G -values (number of molecules per deposited energy of 100 eV) in the order of 10^{-2} [17]. Since glycine is achiral, the enantiomeric excess (% D –% L) of alanine, which is the predominant chiral amino acid, was precisely determined instead. When a portion of an unhydrolyzed fraction was subjected to RP-HPLC analysis, only trace amounts of glycine were

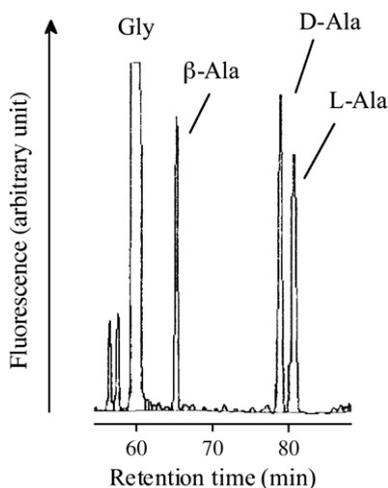


Fig. 8. RP-HPLC separation of D- and L-alanine enantiomers obtained from Right-UV-CPL irradiation of putative interstellar components. In order to determine the statistical significance, multiple experimental runs were performed (7 times for each, and 21 times in total). Abbreviations: Gly, glycine; D-Ala, D-alanine; L-Ala, L-alanine; β-Ala, β-alanine.

detected. D- and L-alanine, together with glycine and various other amino acids, were detected following acid hydrolysis, which indicated that combined amino acid analogs (rather than free amino acids) were present in the UV-CPL-irradiated samples.

3.2. Asymmetric formation of chiral amino acids from complex organics

Fig. 8 shows a typical RP-HPLC chromatogram for the R-CPL-irradiated mixture following hydrolysis, where D- and L-alanine were clearly separated. The results of multiple analyses relating to the enantiomeric excess of D, L-alanine are shown in Table 1. Enantiomeric excesses (%D–%L) of +0.44% and –0.65% were convincingly obtained by Right-UV-CPL (R-CPL) and

Table 1

Enantiomeric excess of D, L-alanine in the complex organics formed by ultraviolet circularly polarized lights (UV-CPL) obtained from a synchrotron radiation (SR) source

UV-CPL	Energy deposit	Enantiomer ratio		Enantiomeric Excess	
Beam	eV	%D	%L	%D–%L	σ
None	None	50.00	50.00	0.00	± 0.35
RCPL	1.57×10^{10}	50.22	49.78	+0.44	± 0.31
LCPL	1.57×10^{10}	49.68	50.34	–0.65	± 0.23

“None” indicates the proton irradiation product defined as the standard of racemic alanine. Enantiomer ratios were compared to a standard solution corrected to D-/L- to 50.00/50.00. Plus-minus (\pm) represents standard deviation (σ) of multiple analyses.

Left-UV-CPL (L-CPL), respectively. R-UV-CPL preferentially produced D-alanine, while L-UV-CPL produced more L-alanine. The standard deviation (σ) of enantiomeric excesses reflected the high precision of the present RP-HPLC technique, and the standard deviation (σ) of the sample without UV-CPL irradiation, and for R- and L-CPL-irradiated samples were ± 0.35 , ± 0.31 and ± 0.23 , respectively. Analytical bias was eliminated by multiple analysis (each seven times) and parallel running of the non-irradiated sample along with the UV-CPL-irradiated samples. As shown in Fig. 4(b), the distribution in molecular weight of the complex organics following CPL-irradiation was similar to that prior to UV-CPL irradiation, with peaks corresponding to 2800, 1100 and 800 Da being observed after UV-CPL irradiation. The peak corresponding to 1100 Da remained predominant, while that corresponding to 800 Da decreased slightly following UV-CPL irradiation. Thus, the proton-irradiated product consisted of a mixture of complex organics with high-molecular-weight and was quite resistant to photolysis. Table 2 shows molar ratio of hydrolyzed amino acids versus total hydrolyzed amino acids. The molar ratio distribution was also similar to that prior to UV-CPL irradiation while about 10% of determined overall amino acids were quantitatively newly yielded by UV-CPL irradiation. Consequently, the present study is essentially different from previous photolysis experiment using monomer amino acid components [9–13].

Table 2

Molar ratio of hydrolyzed amino acids (mol%) versus total hydrolyzed amino acids by before UV-CPL irradiation (only proton irradiation) and after UV-CPL irradiation

Amino acid (mol%)	Before UV-CPL		After UV-CPL	
	None		RCPL	LCPL
Asp	1.13		1.43	1.10
Thr	0.02		0.04	tr.
Ser	1.14		1.04	1.13
Glu	0.06		0.15	0.07
α-AAA	0.10		0.41	0.07
Gly	88.88		88.25	89.55
Ala	4.73		3.79	4.76
α-ABA	3.16		2.98	2.71
Val	0.15		0.19	tr.
β-Ala	0.60		1.68	0.59
γ-ABA	0.03		0.03	0.03
Total	100.00		100.00	100.00

Abbreviations. Asp, aspartic acid; Thr, Threonine; Ser, serine; Glu, glutamic acid; α-AAA, α-amino adipic acid; Gly, glycine; Ala, alanine; α-ABA, α-aminobutyric acid; Val, valine; β-Ala, β-alanine; γ-ABA, γ-aminobutyric acid. The same analytical conditions were quantitatively applied to the both portion of before and after UV-CPL irradiation.

The organic component of the proton-irradiated product was preliminarily examined by employment of a curie-point pyrolysis gas chromatographic-mass spectral analysis technique (Pyr-GC-MS). A wide variety of organic compounds, including a number of alkyl amide and cyclic compounds, were detected by the pyrolysis of complex organics [17]. In brief, the detection of biologically interesting compounds, such as glycolamide ($\text{HOCH}_2\text{CONH}_2$) [17] in organic matter is also cosmochemically interesting as these may have acted as possible precursors of amino acids and/or sugars [21]. Polycyclic aromatic hydrocarbons (PAHs), naphthalene (C_{10}H_8), phenanthrene ($\text{C}_{14}\text{H}_{10}$) and phenanthrene ($\text{C}_{14}\text{H}_{10}$) were also detected using select ion monitoring (SIM) mode. The chemistry of PAHs is of particular interest, since PAHs represent one of the most abundant forms of carbon in the interstellar medium, and many variations of these molecules have been detected in meteorites [22–25]. When exposed to ultraviolet irradiation, monomeric PAHs are converted into secondary products consisting of alcohols, quinones and ethers [23].

4. Conclusions

The present enantiomeric excesses were less than 1.0%, respectively. It has been reported, however, that there are possible amplification pathways that yield high enantiomeric enrichment. In typical experiments using auto-catalytic reactions, an initial small enantiomeric excess was successfully enlarged to high enantiomeric excess of the products [26,27]. Thus, even a very small enantiomeric excess generated from extraterrestrial environments may act as a seed of homochirality in terrestrial environments, and is followed by the emergence of life on the Earth. Cometary organics are considered to be a possible source of the terrestrial biosphere [28]. Although complex organic compounds were discovered in the coma of Comet Halley, the presence of free amino acids was not confirmed [29]. Recent simulation experiments have shown that not free amino acids but complex organics containing amino acid precursors were formed by proton irradiation [5,18], UV irradiation [30–32] and gamma-rays irradiation [33,34] under simulated interstellar environments. It has also been shown that bound amino acid analogs were photochemically much more stable under gamma-rays and UV irradiation environment than free amino acid analogs [35].

Our work has implications and suggests that the large amount of exogenous organic carbon [36], including complex precursors of asymmetric amino acids deliv-

ered by comets and meteorites, may have played a significant catalytic role [14] in the origin of biomolecular chirality in the early stages of chemical evolution on the Earth.

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