removed, and the solution added to an equal volume of 12 M HCl (Ultrex II ultrapure reagent, Baker) and heated for 16 h at 100 °C in an organic-free sealed glass ampoule. This material was dried *in vacuo* to remove water, HCl and any volatile organic acids, then analysed by GC-MS as above. GC-MS was performed on a Thermoquest-Finnigan GCQ with an injector temperature of 240 °C and a DB-17ms-60m (J&W Scientific) column at an initial temperature of 70 °C increasing at 5° per min to 240 °C.

Samples for HPLC were hydrolysed as above, and after drying, 100 μl of 10 mM pH 9.5 sodium borate was added to the tube which, after mixing, was re-dried *in vacuo* to remove volatile amines. The sample was analysed via the OPA/NAC fluorescent labelling and chromatography protocols of ref. 30 on a Hewlett Packard 1100 series HPLC with a Supelco Discovery C-18, 5 μm resin, 4.6 × 250 mm analytical column with a 5 μl sample loop. This chiral label reacts with chiral amines (such as alanine and serine), forming diastereomers which can be separated by HPLC. However, differing absorptivities of these labelled diastereomers results in pairs of peaks where the areas of diastereomers are different even though there are equal amounts of the D and L forms.

After a mild acid hydrolysis with the acid concentration diminished by a factor of 100 (0.06 M HCl), glycine and serine were measured at levels 3–4 times lower than for the standard hydrolysis procedure. Even hot water was adequate to release glycine, albeit an order of magnitude less than the standard hydrolysis.

Received 29 October 2001; accepted 1 February 2002.

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Acknowledgements

This work was supported by NASA grants from the Origins of Solar Systems, Exobiology, and Astrobiology programmes, as well as the NASA Ames Director's Discretionary Fund. We thank A. Weber, D. Glavin, O. Botta, J. Chambers and K. Nelson for discussions. We also acknowledge technical support from R. Walker.

Competing interests statement

The authors declare that they have no competing financial interests.

Correspondence and requests for materials should be addressed to M.P.B. (e-mail: mbernstein@mail.arc.nasa.gov).

Amino acids from ultraviolet irradiation of interstellar ice analogues

G. M. Muñoz Caro*, U. J. Meierhenrich†‡, W. A. Schutte*, B. Barbier†, A. Arcones Segovia*, H. Rosenbauer§, W. H.-P. Thiemann‡, A. Brack† & J. M. Greenberg*

* *Raymond and Beverly Sackler Laboratory for Astrophysics at Leiden Observatory, PO Box 9513, NL-2300 RA Leiden, The Netherlands*
† *Centre de Biophysique Moléculaire, Rue Charles Sadron, F-45160 Orléans, France*
‡ *Bremen University, Department of Physical Chemistry, FB 02, Leobener Straße, D-28359 Bremen, Germany*
§ *Max-Planck-Institut für Aeronomie, Max-Planck-Straße 2, D-37189 Katlenburg-Lindau, Germany*

Amino acids are the essential molecular components of living organisms on Earth, but the proposed mechanisms for their spontaneous generation have been unable to account for their presence in Earth's early history[1]. The delivery of extraterrestrial organic compounds has been proposed as an alternative to generation on Earth[2–5], and some amino acids have been found in several meteorites[6–9]. Here we report the detection of amino acids in the room-temperature residue of an interstellar ice analogue that was ultraviolet-irradiated in a high vacuum at 12 K. We identified 16 amino acids; the chiral ones showed enantiomeric separation. Some of the identified amino acids are also found in meteorites. Our results demonstrate that the spontaneous generation of amino acids in the interstellar medium is possible, supporting the suggestion that prebiotic molecules could have been delivered to the early Earth by cometary dust, meteorites or interplanetary dust particles.

Dense interstellar clouds are the birthplaces of stars and planetary systems. Here, dust particles accrete ice layers with H_2O, CO, CO_2, CH_3OH and NH_3 as the main molecular components[10]. This ice can undergo considerable processing by stellar ultraviolet (UV) photons and cosmic rays[11,12]. In star-forming regions it enters circumstellar disks where formation of planetary bodies as well as comets takes place. We simulated in the laboratory the processing going on in such regions.

Our experimental set-up consists of a high-vacuum chamber where a gas mixture is deposited on a cold 'finger' (an aluminium block at 12 K) and irradiated by UV (ref. 13). An ice mixture containing $H_2O{:}CH_3OH{:}NH_3{:}CO{:}CO_2 = 2{:}1{:}1{:}1{:}1$ (molar composition) was selected as representative of the interstellar medium. This composition resembles the ice found close to protostellar sources[10,14,15]. After warming the system to room temperature a small amount of material remained. The dominant components of

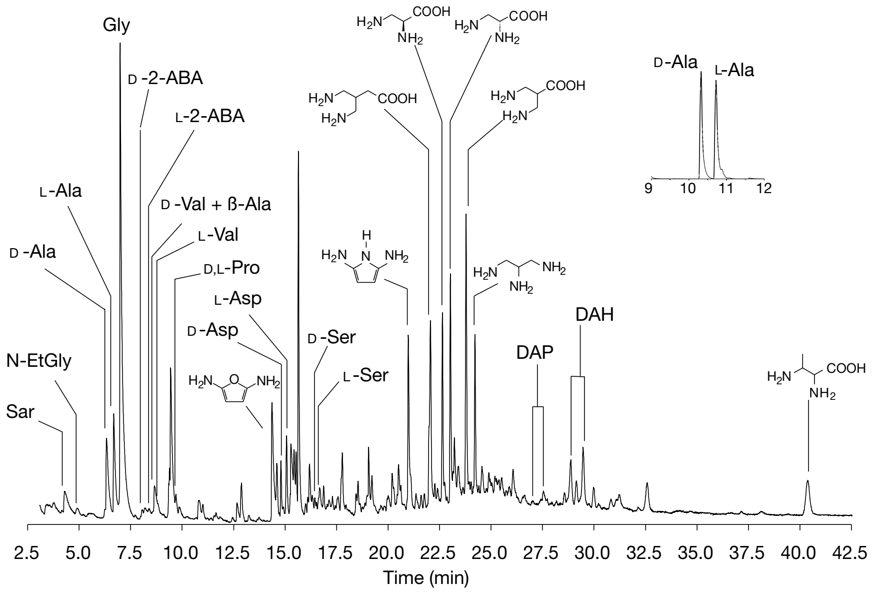

Figure 1 Gas chromatogram showing the amino acids and other compounds generated under simulated interstellar pre-cometary conditions. Data were obtained from analysis of the room temperature residue of photoprocessed interstellar medium ice analogue taken after 6 M HCl hydrolysis and derivatization (ECEE derivatives, Varian-Chrompack Chirasil-L-Val capillary column 12 m × 0.25 mm inner diameter, layer thickness 0.12 μm; splitless injection, 1.5 ml min^{-1} constant flow of He carrier gas; oven temperature programmed for 3 min at 70 °C, 5 °C min^{-1}, and 17.5 min at 180 °C; detection of total ion current with GC–MSD system Agilent 6890/5973). The inset shows the determination of alanine enantiomers in the above sample (Chirasil-L-Val 25 m, single ion monitoring for Ala-ECEE base peak at 116 a.m.u.). DAP, diaminopentanoic acid; DAH, diaminohexanoic acid; a.m.u., atomic mass units.

this residue were saturated organic compounds containing carboxylic groups and hexamethylenetetramine[16–18]. Previous work claimed the detection of trace amounts of a limited number of amino acids in photolysed interstellar ice analogues[17,19]. Except for glycine, however, these analytical results were not confirmed by isotopic labelling, a necessary verification to exclude contamination with trace organic components.

We analysed the residue by gas chromatography–mass spectrometry (GC–MS) using a chiral capillary column. Using new, more sensitive detection methods, we report here the identification of 16 amino acids in the residue, 6 of which are protein constituents. Figure 1 shows the chromatogram corresponding to the residue obtained from the photoprocessed interstellar ice analogue mixture. Most of the observed peaks were due to amino acids, but three exceptions were identified as 2,5-diaminopyrrole, 2,5-diaminofuran, and 1,2,3-triaminopropane. The calculated signal-to-noise ratio was $S/N \geqslant 10$, even for the least abundant amino acids identified. A similar chromatogram was obtained for the isotopically labelled sample (molar concentration H_2O:$^{13}CH_3OH$:NH_3:^{13}CO:$^{13}CO_2 = 2:1:1:1:1$), with the exceptions of valine and proline, which were below the detection limit. Proline was found in the ^{13}C-labelled residue of a test sample, which did not contain CH_3OH in the starting ice composition, and therefore could not be a contaminant. The abundance was obtained by integrating the peak area of a given amino acid calibrated with the corresponding standard. The quantum yield (Φ) was obtained by dividing the abundance by the number of photons. For the total amount of residue, $\Phi(\text{residue}) \approx 8.0 \times 10^{-3}$ (ref. 20). Glycine, the simplest amino acid, with $\Phi(\text{Gly}) \approx 3.6 \times 10^{-5}$, was the most abundant. The total amino-acid quantum yield was $\Phi \approx 1.0 \times 10^{-4}$. Table 1 lists the detected molecules, and their corresponding abundances relative to glycine. The mass fragments of the elutants in the ^{12}C and ^{13}C samples are given along with their retention times (R_t). The main mass fragments are shown in boldface in Table 1. For amino acids bearing only one amino group, species with higher molecular mass were less abundant. We were surprised to find that species with two amino groups showed relatively high abundances. Aspartic acid was the only dicarboxylic compound found in the residues. Decarboxylation is known as the main photodamage of UV-exposed amino acids and probably competes with photoproduction[21]. Decarboxylation should give rise to the formation of radicals that could react with NH_3 to favour the formation of diamino-compounds.

In the case of reported analyses of meteoritic material, the absolute abundances of the detected amino acids are enhanced by acid hydrolysis[6]. Similarly in our case, amino acids in the residue are detected at considerable amounts only after acid hydrolysis, which probably indicates that these products are originally formed as peptidic molecules, and released as free amino acids after hydrolysis at room temperature. It has been suggested that hydrolysis of hexamethylenetetramine, an abundant product of photolysis for the selected ice mixture, leads to formation of amino acids[18]. In order to test this possibility, an external standard of hexamethylenetetramine was analysed using the same protocol as for the residues and no amino acids were detected. No evidence for contamination was found after comparison with the samples produced from ^{13}C-labelled reactants. We used the mass spectrometric data on amino-acid ECEE (N-ethoxycarbonyl ethyl ester) derivatives reported in the literature[22] for identification.

The selected starting ice composition here reported is only indicative, because the composition of the ice can vary significantly for different sources. The NH_3 ice abundance used was enhanced with respect to that derived from astronomical observations to obtain a larger amount of residue, but it is also based on the fact that NH_3 photo-dissociates very readily, leading to other species, so that the original budget of NH_3 was probably larger than what is observed. Additional irradiation experiments involving a ten times higher H_2O ice concentration or deposition at 80 K, monitored by infrared spectroscopy, showed that the residue production was equally efficient, although the relative abundances of the main components, hexamethylenetetramine and carboxylic acids, varied somewhat[23].

All the chiral amino acids detected showed enantiomeric separa-

Table 1 Peak identification for Fig. 1

Amino acid	Quantum yield of ISM sample, $\Phi \times 100/\Phi$ (Gly)	MS-fragmentation		R_t of analyte (min)	Biological occurrence
		^{12}C-sample (a.m.u.)	^{13}C-sample (a.m.u.)		
Glycine	100	175, 130, **102**	177, 132, **103**	6.99	Yes
α-D-alanine	19.3	189, 144, **116**, 88	147, **118**, 90	6.33	No
α-L-alanine	20.0	189, 144, **116**, 88	147, **118**, 90	6.68	Yes
β-alanine	4.29	189, 160, 144, 116, **115**, 102, 98	192, 147, 119, **117**, 103, 101	8.66	No
Sarcosine (N-methylglycine)	5.71	189, 144, **116**, 88	192, 147, **118**, 90	4.29	No
D-2-aminobutyric acid	0.46	130	133	8.05	No
L-2-aminobutyric acid	0.48	130	133	8.37	No
N-ethylglycine	1.91	**130**, 84, 58	**133**, 207	4.90	No
D-valine	0.61	**144**	≤d.l.	8.66	No
L-valine	0.61	**144**	≤d.l.	8.80	Yes
D,L-proline	0.06	142	≤d.l.	9.59	No, Yes
D-serine	3.29	175 (McLafferty), 160, **132**, 114	116, 134	16.45	No
L-serine	3.86	204, 187, 175 (McLafferty), 160, **132**, 114	116, 134	16.67	Yes
D-aspartic acid	1.14	**188**, 142	**191**, 145	14.90	No
L-aspartic acid	1.07	**188**, 142	**191**	15.05	Yes
D-2,3-diaminopropanoic acid	20.0	231, 203, 188, **175**, 157, 129, 102	234, 205, 190, **177**, 159, 131, 103	22.64	No
L-2,3-diaminopropanoic acid	20.0	231, 203, 188, **175**, 157, 129, 102	234, 205 190, **177**, 159, 131, 103	23.03	No
2,3-diaminobutyric acid	14.1	**203**, 157, 115, 85	**205**	40.38	No
3,3′-diaminoisobutyric acid	32.9	290, 245, 238, 216, 188, 167, 156, **142**, 128, 115, 102	249, 219, 191, **145**, 132, 103	23.79	No
4,4′-diaminoneopentanoic acid	22.4	304, 259, 230, 202, 188, 182, 166, 156, 142, **116**	264, 206, 191, 187, 171, 160, 145, **118**	22.05	No
A-diaminopentanoic acid*	1.72	**142**(c.i.i.), 129, 70	≤d.l.	27.05	No
B-diaminopentanoic acid*	1.92	**142**(c.i.i.)	≤d.l.	27.54	No
A-diaminohexanoic acid†	33.1	272, **156**(c.i.i.), 128, 102, 84	272(cyclic ion), **160**	28.86	No
B-diaminohexanoic acid†	35.4	272, **156**(c.i.i.), 128, 102, 84	272(cyclic ion), **160**	29.48	No
2,5-diaminofurane	23.1	242, 169, 153, 125, **97**, 81, 69, 53	246, 173, 157, 129, **101**, 85, 72, 56	14.36	
2,5-diaminopyrrole	20.0	241, 213, 212, 196, **168**, 140, 124, 109, **96**, 81, 69, 54, 53	245, 217, 216, 200, **172**, 144, 128, 113, 100, 85, 72, 57	20.98	
1,2,3-triaminopropane	16.3	232, 187, 159, 144, 130, 115, **102**	189, 162, 147, 132, 117, **103**	24.22	
Unidentified	36.5	233, 188, 160, 129, 114, **102**	237, 192, 163, 131, 117, **103**	15.64	

For glycine, $\Phi(\mathrm{Gly}) \approx 3.6 \times 10^{-5}$. Numbers designated in boldface are the main mass fragments. A designates the first eluting enantiomer, and B the second eluting enantiomer. c.i.i., cyclic immonium ion. R_t, retention time. ISM, interstellar medium. MS, mass spectrometry. d.l., detection limit; McLafferty indicates that a McLafferty rearrangement has occurred.

* Exact molecular structure not yet known. Ornithine or its constitutional isomer.

† Exact molecular structure not yet known. Lysine or its constitutional isomer.

tion, with the exception of proline, which could not be separated by the selected protocol[24]. As expected for photosynthesis using non-polarized light, the amino acids produced appeared to be racemic, with enantiomeric excesses fluctuating within experimental errors.

Using the above efficient derivatization and sensitive GC-MS technique we were able to identify a total of 16 different amino acids in the residue. Hence, we show that photochemical processing of interstellar ice analogues leads to a large variety of products, which can only be identified by very specific detection techniques. We recently found evidence for the presence of a number of new organic components in the residues[23].

In addition to amino acids, 1,2,3-triaminopropane, 2,5-diaminofurane and 2,5-diaminopyrrole were identified as shown in Fig. 1. This is the first detection of pyrroles and furanes in photolysed interstellar ice analogues. Such cyclic molecules were tentatively identified in the mass spectra of comet Halley[25]. All the products reported in Table 1 were also found in the residue of a sample containing only CO as the carbon carrier (starting ice molar composition H_2O:NH_3:CO = 2:1:1). We also obtained results from experiments involving different ice mixtures[23].

Glycine has so far not been detected in the interstellar medium. Some of the amino acids reported here were also found in carbonaceous chondrites[6–9]. However, no amino acids with more than one amino group were detected in these objects. Our work suggests that these species might also be present in meteorites.

How life originated is one of the earliest and most intriguing questions for humanity. Early experiments on the processing of a gas mixture simulating the primitive Earth conditions assumed a reducing atmosphere with CH_4 as the carbon-containing molecule[26]. Several amino acids were formed under these conditions as products of spark discharge, photoprocessing or heat. It is now believed, however, that the Earth's early atmosphere was rather non-reducing, with CO_2 as the main carbon carrier. Processing of these alternative gas mixtures under experimental conditions leads to the formation of, at most, traces of amino acids[1].

The results reported in this paper support the concept of extraterrestrial delivery of prebiotic molecules triggering the appearance of life on Earth[2–5]. We show that, at least to some extent, amino acids and other prebiotic molecules such as pyrroles and furanes could be of extraterrestrial origin. Earlier analysis of the residues of photochemically processed interstellar ice analogues revealed other components of prebiotic interest such as quinones and aromatic alcohols[27]. It is probable that comets, to a large extent, consist of pristine interstellar materials[28,29]. Such species could, therefore, have been delivered to the early Earth by comet dust, as well as asteroids and interplanetary dust particles during the epoch of heavy bombardment[30]. Similar experiments using circularly polarized ultraviolet light could result in the formation of non-racemic amino acids, such as those found in the proteins of living organisms, which are exclusively of L-configuration.

Several parameters still need to be better constrained (such as UV exposure, particle fluxes, and number of collisions) before a reliable estimation on the extraterrestrial delivery of amino acids to the early Earth can be made. To this end, *in situ* analysis of cometary material will be performed in the near future by space probes such as Rosetta and Stardust. ☐

Methods

Simulation of the interstellar medium

The high-vacuum system for UV-irradiation of the ice was powered by a turbo pump (Pfeiffer Balzers TSH 280H) backed up by a diaphragm pump (Vacuubrand MD4T). The system pressure at room temperature was $P_s \approx 10^{-7}$ mbar. A temperature of 12 K, typical of dust in dense clouds, was achieved by means of a closed-cycle helium cryostat (Air Products Displex DE-202). CO_2 was kept in a separate bulb in order to prevent it from reacting with the ammonia, NH_3. Simultaneous deposition of CO_2 and the other components was achieved via two separate deposition tubes, one for each bulb. The gas molecules were condensed on an aluminium block mounted on the tip of the cryostat.

During the deposition, the accreting ice layer was irradiated by UV from a microwave-stimulated hydrogen flow discharge lamp (output, $F \approx 1.5 \times 10^{15}$ photons s^{-1} (ref. 31); photon energy, $E_{\text{photon}} = 7.3$–10.5 eV, with main emission at Lyman-α (10.2 eV)). The lamp spectrum roughly resembles the UV emission from early-type stars, which dominates the interstellar radiation field between 0.09 and 0.25 μm (ref. 20). The UV-irradiation/deposition typically lasted 24 hours. The total gas flow was $F \approx 1 \times 10^{16}$ molecules s^{-1}, implying an average UV dose of 0.15 photons per molecule. Subsequently, the system was warmed at 1 K min^{-1} to $T = 40$ K using a temperature controller (Scientific Instruments 9600-1), and then at about 4 K min^{-1} up to room temperature. The aluminium block with the residue was removed from the system and stored inside a capsule in a nitrogen atmosphere.

Analytical procedure

A 100-μl water extract of the above produced residue was hydrolysed in 6 M HCl at 110 °C for 24 h under argon atmosphere. This is a standard procedure for hydrolysis of peptides and has been used for the detection of amino acids in meteorites[7]. After evaporation of 6 M HCl, the residues were dissolved in 0.1 M HCl and derivatized using the procedure of ref. 24, leading to amino acid ECEE derivatives. The identities of the amino acid peaks were verified by comparing the retention times and the mass spectra with external standards, purchased from Fluka. By using the single ion monitoring mode, it was possible to select a given ion mass, characteristic of the target amino acid in order to increase both chromatographic resolution and sensitivity. The determination of the signal-to-noise ratio for each amino acid was performed in the extract ion mode.

Received 16 November 2001; accepted 17 January 2002.

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Acknowledgements

We thank A. MacDermott, F. Goesmann and R. Roll for discussions and K. Getliffe for suggestions. Our collaboration was originally supported by the Max-Planck-Institut für Aeronomie at Katlenburg-Lindau with grants for G.M.M.C. and U.J.M., as preparatory work for the Rosetta mission. The work was performed at the Sackler Laboratory for Astrophysics at Leiden Observatory and the Centre Biophysique Moléculaire at Orléans, where it was funded by the European Union and by French sponsors: CNES, FNAD, Région Centre, and Département du Cher. In Orléans U.J.M. was supported by a Le Studium grant. U.J.M. is grateful for a habilitation grant by the Deutsche Forschungsgemeinschaft, and G.M.M.C. for an AIO allowance by Leiden University. This paper is dedicated to the memory of J.M.G., who died on 29 November 2001.

Competing interests statement

The authors declare that they have no competing financial interests.

Correspondence and requests for materials should be addressed to U.J.M.
(e-mail: mhenrich@uni-bremen.de).

Exchange-biased quantum tunnelling in a supramolecular dimer of single-molecule magnets

Wolfgang Wernsdorfer[*], **Núria Aliaga-Alcalde**[†], **David N. Hendrickson**[‡] **& George Christou**[†]

[*] *Laboratoire Louis Néel-CNRS, BP166, 25 Avenue des Martyrs, 38042 Grenoble, Cedex 9, France*
[†] *Department of Chemistry, University of Florida, Gainesville, Florida 32611-7200, USA*
[‡] *Department of Chemistry, University of California at San Diego, La Jolla, California 92093-0358, USA*

Various present and future specialized applications of magnets require monodisperse, small magnetic particles, and the discovery of molecules that can function as nanoscale magnets was an important development in this regard[1–3]. These molecules act as single-domain magnetic particles that, below their blocking temperature, exhibit magnetization hysteresis, a classical property of macroscopic magnets. Such 'single-molecule magnets' (SMMs)[4] straddle the interface between classical and quantum mechanical behaviour because they also display quantum tunnelling of magnetization[5,6] and quantum phase interference[7]. Quantum tunnelling of magnetization can be advantageous for some potential applications of SMMs, for example, in providing the quantum superposition of states required for quantum computing[8]. However, it is a disadvantage in other applications, such as information storage, where it would lead to information loss. Thus it is important to both understand and control the quantum properties of SMMs. Here we report a supramolecular SMM dimer in which antiferromagnetic coupling between the two components results in quantum behaviour different from that of the individual SMMs. Our experimental observations and theoretical analysis suggest a means of tuning the quantum tunnelling of magnetization in SMMs. This system may also prove useful for studying quantum tunnelling of relevance to mesoscopic antiferromagnets.

The compound $[Mn_4O_3Cl_4(O_2CEt)_3(py)_3]$ (hereafter Mn4) con-