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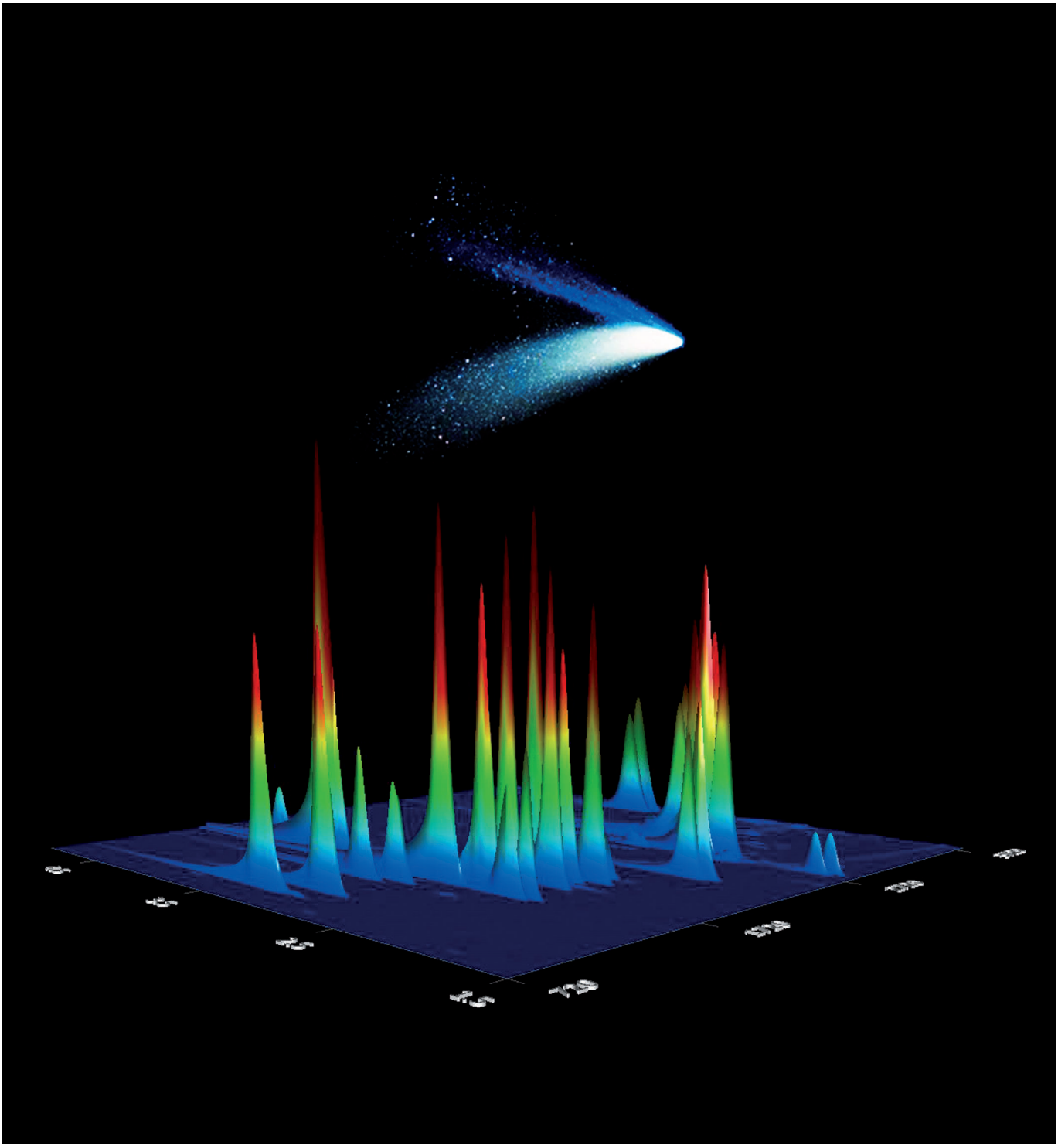
N-(2-Aminoethyl)glycine and Amino Acids from Interstellar Ice Analogues

Cornelia Meinert,*[a] Jean-Jacques Filippi,[a] Pierre de Marcellus,[b] Louis Le Sergeant d'Hendecourt,[b] and Uwe J. Meierhenrich*[a]

In memory of Benoît Mandelbrot (1924–2010)



Comets are accretions of frozen volatiles and rocky debris left over from the interstellar molecular cloud that formed the Solar System.[1] The chemical composition of comets is of key importance to understand chemical properties and molecular interactions during planetary system formation and may further hold molecular information on the first steps of the prebiotic chemical evolution in the primitive Earth environment. However, a true cometary nucleus sample return mission has not yet been realized.[2] The NASA Stardust cometary tail sample return mission provided encouraging data on the presence of organics of prebiotic interest.[3] Cometary nucleus analyses by GC-MS are envisaged starting in 2015 by the Rosetta mission.[4] Herein, we report on the formation of interstellar ices reproduced stepwise in the laboratory and under controlled and comprehensive astrophysical conditions. Representative interstellar molecules such as H_2O, CH_3OH, and NH_3 were condensed on a cooled surface at $T=80$ K in a high vacuum chamber while being irradiated with ultraviolet (UV) photons. The obtained simulated interstellar ices were warmed up to room temperature, thus leaving an organic residue which was extracted with water, hydrolyzed, and analyzed by comprehensive two-dimensional gas chromatography coupled to a time-of-flight mass spectrometer (GC×GC-TOFMS). Twenty amino acids and six diamino acids including *N*-(2-aminoethyl)glycine were identified in the simulated interstellar ice residue. Contamination with biological amino acids could be excluded due to isotopic ^{13}C-labeling of the condensed $^{13}CH_3OH$ reactant and the identification of exclusive ^{13}C- labeled mass spectrometric fingerprints in the analytes. The molecular composition of the residue is found to be similar, but not identical, to the amino acids and diamino acids identified in meteorites.[5–8] The results support the assumption that potentially prebiotic organic molecules do form in inter/protostellar environments from where they could have been delivered by comets to the early Earth,[9] where they may have been important for triggering prebiotic chemistry in a favorable environment up to the appearance of life.[10,11]

Comets are the most pristine objects in the Solar System. They form out of dense interstellar clouds that enter circumstellar disks. During cometary formation, interstellar dust particles aggregate while being subjected to UV photons and cosmic ray irradiation. Interstellar dust particles are composed of silicate grains surrounded by defined layers of condensed ice mantles of H_2O, CH_3OH, NH_3, and other volatile components.[12] We simulated this process in the laboratory under plausible astrophysical conditions.

[a] *Dr. C. Meinert, Dr. J.-J. Filippi, Prof. Dr. U. J. Meierhenrich*
Institut de Chimie de Nice
UMR 7272 CNRS UNSA, Université de Nice-Sophia Antipolis
Faculté des Sciences, Parc Valrose, 06108 Nice (France)
E-mail: Cornelia.Meinert@unice.fr
Uwe.Meierhenrich@unice.fr

[b] *Dr. P. de Marcellus, Dr. L. Le Sergeant d'Hendecourt*
Institut d'Astrophysique Spatiale, Astrochimie et Origines
UMR 8617 CNRS, Université Paris-Sud, Orsay (France)

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We condensed the volatile molecules H_2O, $^{13}CH_3OH$, and NH_3 in a high vacuum chamber on a solid surface while irradiating with UV photons at $T=80$ K. These physicochemical parameters were selected to represent the conditions of interstellar ice evolution. A temperature of $T=80$ K was selected because of its experimental accessibility by cooling with liquid nitrogen. The use of liquid helium for obtaining temperatures down to $T=4$ K has shown in former experiments not to alter the formation of interstellar ice analogues.[13] Besides, a temperature of 80 K does favor diffusion of reactants within the matrix, thus allowing a higher chemical reactivity of the system so, compared to interstellar processes, a relative enhancement of the efficiency of the photochemistry is favored, albeit not a different one. After a total of ten days of ice deposition and simultaneous irradiation, the obtained residue at room temperature was extracted with water, hydrolyzed, derivatized, and analyzed by enantioselective GC×GC-TOFMS. The analytical instrumentation allowed for high chromatographic resolution of the analytes from interfering coelution mainly composed of solvent tailing and column bleeding. High signal-to-noise ratios resulting from the applied peak modulation combined with a deconvolution technique referring to the mass spectrometric data let us achieve low detection limits. Figure 1 and Figure S1 in the Supporting Information show the multidimensional gas chromatograms of the simulated interstellar ice residue, in which 20 amino acids and 6 diamino acids including glycine, alanine, serine, aspartic acid, proline, and *N*-(2-aminoethyl)glycine were identified. We highlight that each point in the chromatographic 3D space is accompanied by its individual mass spectrum.

Table 1 lists the molecules detected and the mass fragments of the corresponding *N*-ethoxycarbonyl heptafluorobutyl amino acid ester (ECHFBE) derivatives. The mass fragmentation reveals that the formed amino acids are entirely composed of ^{13}C-isotopes which confirm that the amino acids exclusively formed out of the $^{13}CH_3OH$ reactant. Biological amino acid contaminants would have shown their ^{12}C-isotopic signature and can thus be excluded.

The multidimensional gas chromatographic retention times R_{t1} and R_{t2} of the analytes are given in the first and second dimension. Corresponding quantum yields, Φ, and detailed mass spectrometric information are given in Table S1. Some of the amino acids have already been identified in residues from simulated interstellar ice analogues.[14,15] These ices were prepared under different astrophysical conditions and different derivatization and detection techniques were applied.

Some of the identified amino acids have been detected in carbonaceous chondrites,[5–8] thus showing the relevance of these simulations in an astrophysical context. The in-depth comparison of cometary and interstellar ices is known to be straightforward.[16] However, comparison between the simulated cometary matter from laboratory experiments and carbonaceous chondrites is not necessarily straightforward because carbonaceous chondrites experienced a different experienced on their parent body a different history and underwent—possibly frequent—alterations through aqueous processing, thermal effects, or shocks, which all may have affected their original

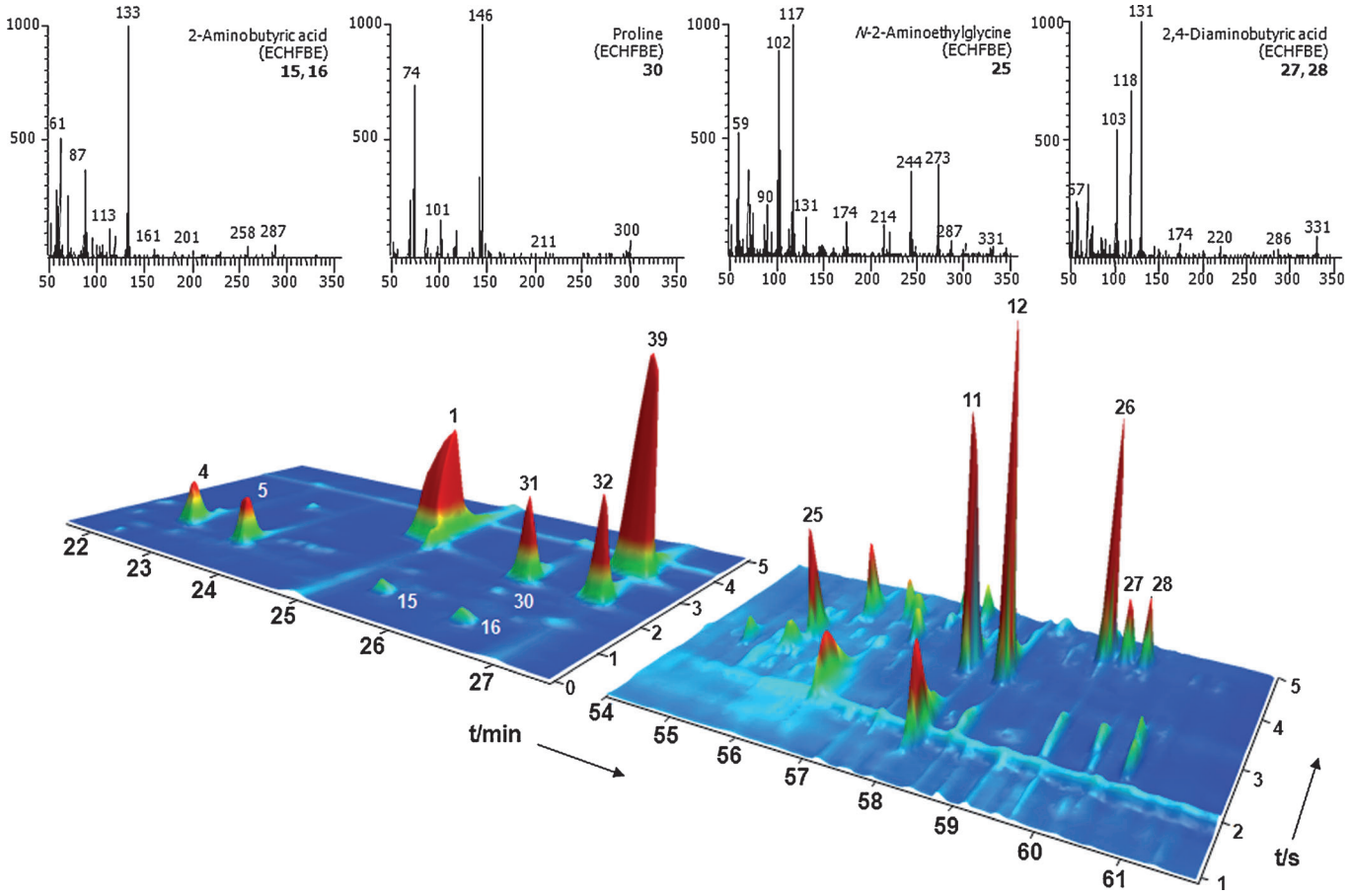
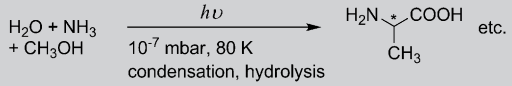


Figure 1. Multidimensional enantioselective gas chromatograms depicting amino acids identified in simulated interstellar ice residues. Each point in the 3D chromatogram is accompanied by its individual mass spectrum. The chromatogram was recorded in the total ion current using a temperature program of 40 °C for 1 min, 10 °C min^{-1}, 80 °C for 3 min, 2 °C min^{-1}, and 190 °C for 22 min in the first dimension and 70 °C for 1 min, 10 °C min^{-1}, 110 °C for 3 min, 2 °C min^{-1} to 160 °C, 4 °C min^{-1}, and 220 °C for 37 min in the second dimension coupled by a modulation time of $P_m = 5$ s.

composition.[17] We observed that the abundances of amino acids in simulated interstellar matter decrease roughly logarithmically with increasing carbon number. Similar observations have been reported for the abundance of amino acids in carbonaceous meteorites[8] and residues of interstellar ice analogues.[14] The decline in concentration with increasing carbon number suggests a kinetically controlled chain elongation mechanism in which higher homologues are progressively build-up by the addition of one-carbon species. The precise mechanism of the formation of amino acids in interstellar ices and in meteorites is unknown. Owing to a variety of systematic experiments performed in our laboratory and other studies[18] we assume that vacuum ultraviolet photons create radicals in the ice. The formation of radicals is assumed neither to depend on the energy of the photons nor on temperature or the nature of the support material. These radicals are assumed to react with neighboring molecules in subsequent reactions allowing for the formation of macromolecules, the precise structure of which is still unknown. Hydrolysis of the macromolecule favors the release of free amino acids. In the reported analyses of meteoritic material, the absolute abundance of amino acids is generally enhanced by antecedent 6 M HCl hydrolysis.[19] Acid hydrolysis increased the amount of free diamino acids by factors between 1.7 and 6.0 relative to the extraction with hot water at 100 °C.[8] This also applies to our case, where amino acids and diamino acids in the simulated interstellar matter sample are detected in higher amounts after acid hydrolysis, as compared to without acid hydrolysis. The data suggest that these products have originally been part of molecules of higher molecular mass,[20] and released as free amino acids and diamino acids after hydrolysis. As an alternative pathway nitrile groups of aminonitriles can be hydrolyzed to form amino acids.

These results underline that monomer subunits of proteins such as glycine, α-L-alanine, L-serine, L-aspartic acid, and L-proline do form in simulated interstellar matter. We note that during early stages of life's evolution on Earth these particular amino acids are considered to be incorporated first into proteins.[21] We also identified diamino acids including the achiral *N*-(2-aminoethyl)glycine and the two enantiomers of D,L-2,4-diaminobutyric acid in the simulated interstellar matter. These diamino acids might have been involved in the development of a primitive genetic material. An attractive model suggests that DNA and RNA might have been preceded by peptide nucleic

Table 1. Amino acids and organic compounds identified in a sample of an interstellar ice analogue as illustrated in Figure 1.



	Compound[a]	MS fragmentation[b]	R_{t1} [min][c]	R_{t2} [sec][d]
1	Glycine	257, 132, **103**, 57	25.5	2.73
2	Sarcosine	272, 228, **118**, 90	16.0	2.42
3	*N*-Methyl-D,L-alanine	287, **133**, 105, 61	16.8	1.97
4	α-L-Alanine	272, **118**, 72	23.0	2.04
5	α-D-Alanine	272, **118**, 72	24.0	1.98
6	β-Alanine	147, 117,[e] **103**, **101**, 73	27.4	2.11
7	L-Serine[f]	258, 206, **116**, 103, 88	44.6	2.64
8	D-Serine[f]	258, 206, **116**, 103, 88	45.1	2.61
9	D,L-Amino (methylamino) acetic acid	330, 258, 132, **103**, 57	42.1	2.79
10	*N*-Aminomethyl glycine	244, 214, 132, **103**, 57	43.3	3.63
11	L-2,3-Diaminopropanoic acid	258, 205, 159, **103**, 87	60.0	5.02
12	D-2,3-Diamino-propanoic acid	258, 205, 159, **103**, 87	60.9	5.02
13	Triaminopropane	189, 132, 117, **103**, 75	70.9	2.13
14	*N*-Ethylglycine	285, 133, **131**, 103, 59	18.2	2.01
15	L-2-Aminobutyric acid	287, 258, **133**, 87, 61	26.0	1.68
16	D-2-Aminobutyric acid	287, 258, **133**, 87, 61	27.0	1.60
17	D,L-3-Aminoisobutyric acid	162, 132, 116, **103**, 87	27.9	1.82
18	L-3-Aminobutyric acid	288, 272, 244, 161, **118**	29.0	1.72
19	D-3-Aminobutyric acid	288, 272, 244, 161, **118**	29.3	1.70
20	4-Aminobutyric acid	288, 244,[e] 104, **88**, 58	36.6	1.56
21	L-Aspartic acid	345,[g] 273, 255, **73**, 57	39.5	1.57
22	D-Aspartic acid	345,[g] 273, 255, **73**, 57	39.9	1.56
23	L-Pyroglutamic acid[h]	88	46.6	2.88
24	D-Pyroglutamic acid[h]	88	47.4	2.85
25	*N*-(2-aminoethyl) glycine	273, 244,[e] **117**, 102, 59	56.6	4.45
26	3-Amino-2-(aminomethyl) propionic acid[i]	160, 145, 117, **104**, 75	63.0	6.60
27	L-2,4-Diaminobutyric acid[i]	220,[j] **131**, **118**, 103, 85	63.6	6.72
28	D-2,4-Diaminobutyric acid[i]	220[j],**131**, **118**, 103, 85	64.1	6.72
29	Glycine-glycine[i]	258, 132, **103**, 75, 57	69.2	0.22
30	D,L-Proline	300, **146**,[j] 101, 74	26.8	1.97
31	L-Norvaline	287, 258, **148**, 103, 75	27.0	2.04
32	D-Norvaline	287, 258, **148**, 103, 75	27.6	2.15
33	Aminomethyl butanoic acid[k]	274, 258, 229, **148**, 58	30.7	1.82
34	5-Aminovaleric acid	**104**, 75, 58	38.0	1.57
35	D,L-Hydroxyproline	301, 218, 100,[j] **72**	49.8	3.18
36	L-Aminomethyl pentanoic acid[l]	259, 163, 148, 134, **62**	30.3	1.87
37	D-Aminomethyl pentanoic acid[l]	259, 163, 148, 134, **62**	30.9	1.84
38	Aminomethyl pentanoic acid[l]	244, 229,163, 134, **62**	32.2	2.12
39	Unidentified	258, 214, **133**, **105**, 60	27.5	2.46

[a] Compound number. [b] Numbers in boldface are the main mass fragments. [c] GC×GC retention time of 1st dimension and [d] GC×GC retention time of 2nd dimension recorded under chromatographic conditions given with Figure S1. [e] McLafferty rearrangement. [f] Bis-acylated compound. [g] Cyclic oxonium ion. [h] Dehydration product of glutamic acid. [i] Wrap around. [j] Cyclic iminium ion. [k] and [l] Exact molecular structure not yet known. Constitutional isomers of leucine and valine, respectively.

acid (PNA) molecules. PNA is an uncharged analogue of a standard nucleic acid, in which the sugar-phosphate backbone is replaced by a diamino acid backbone held together by amide bonds. Nucleic bases are attached by spacers to the PNA structure. The backbone can either be composed of *N*-(2-aminoethyl)glycine (aeg) leading to aegPNA molecules or of 2,4-diaminobutyric acid (da) leading to daPNA structures. PNA forms stable double helices with complementary molecules of RNA or DNA.[22]

The detection of different well-defined isomers of aminobutyric acid (**15**–**20**) in the simulated interstellar matter does not yet allow for deciphering the reason for the nonexpression of any aminobutyric acid in proteins by anabolic pathways in contemporary life. α-Methyl amino acids such as isovaline, as detected in carbonaceous chondrites in enantioenriched form, were so far not identified in the artificial cometary/interstellar matrix. The reason of which is not yet entirely clear, probably this is due to steric hindrance and limited accessibility of the Cα atom to bind a nonhydrogen ligand and due to a reduced reactivity of the intermediate tertiary radical. α-Methyl amino acids might be formed by an alternative Strecker mechanism.

Peak volume quantification of individual enantiomers of chiral amino acids such as **4** and **5**, but also **11** and **12** shows a racemic ratio. This racemic state is expected because an achiral environment was used for the preparation of the interstellar samples. Experiments on the irradiation of chiral organic mole-

cules including amino acids using circularly polarized electromagnetic radiation have been performed to study enantioselective photolysis[23] which may be at the origin of biomolecular homochirality.[24] Circularly polarized light of the same helicity over large distance scales has been detected in interstellar molecular clouds,[25] and recently the first promising experiments simulating amino acid formation under interstellar conditions induced a significant enantiomeric excess of 1.3% into the amino acid α-alanine.[26]

The obtained results let us conclude that the formation of organic compounds of prebiotic interest in interstellar/protostellar environments[27] followed by their delivery by meteorites, interplanetary dust particles, or by comets[9] to the early Earth represents a plausible astro-physicochemical scenario for the appearance of life on Earth.[28] We found a molecular reservoir of amino acid species which, together with complementary sources, might have preceded and triggered the formation of proto-proteins and peptide-based nucleic acid analogues on the early Earth, and which we explicitly interpret as an intermediate state of the evolution of life. The reported identification of 20 amino acids and six diamino acids in a sample of an interstellar ice analogue is of importance for all scenarios describing the appearance of life on Earth on the molecular level.

Moreover the scientific objectives of the cometary Rosetta Lander Philae will benefit from these data. Philae includes the Cometary Sampling and Composition (COSAC) instrument, which is an enantioselective GC-TOFMS designed to identify organic molecules including chiral amino acids in cometary ices after landing on a cometary nucleus in 2015.[4,15]

Experimental Section

Simulated interstellar matter (organic residue) was produced by repetitive condensing over ten days of H_2O, $^{13}CH_3OH$, and NH_3 (molecular composition 2:1:1) on a liquid-nitrogen-cooled MgF_2 window at $T=80$ K during photoprocessing at 121 nm using a microwave-stimulated hydrogen flow discharge lamp. The photon/molecule ratio was 1:1. The selected gas composition slightly differs from previous experiments, in which CO and CO_2 had been included.[14] According to former experiments this gas composition has no influence on the formation of the organic residue and is easier to handle in the laboratory. Amino acids were identified in the water extract of the room-temperature residue of the interstellar ice analogue after hydrolysis with 6 M HCl at 110 °C for 24 h and transformation into *N*-ethoxycarbonyl heptafluorobutyl esters (ECHFBE) followed by GC×GC/TOF-MS analyses by using the LECO's Pegasus 4D instrument equipped with ChromaTOF software. Aliquots of 1 μL, injected in splitless mode, were separated on a Chirasil-D-Val as first stationary phase (25 m, 0.25 mm, 0.08 μm) coupled to Carbowax (1.4 m, 0.1 mm, 0.1 μm) in the second dimension with a constant He flow of 1.2 mL min^{-1}. The temperature program is 40 °C for 1 min, 10 °C min^{-1}, 80 °C for 3 min, 2 °C min^{-1}, 180 °C for 25 min in the first dimension and 70 °C for 1 min, 10 °C min^{-1}, 110 °C for 3 min, 4 °C min^{-1}, 210 °C for 50 min in the second dimension coupled by a modulation time of $P_m=6$ s, if not indicated otherwise. The presence of amino acids in the interstellar ice analogue was confirmed by comparison with external standards of amino acids that have identical retention times and shifted mass spectra according to ^{12}C composition. We selected $m/z=146$, 148, 133, 257, and 272 for Figure 1 (left) and 117 and 131 for Figure 1 (right). A blank sample consisted of an MgF_2 window, on which the $H_2O/^{13}CH_3OH/NH_3$ gas mixture was deposited at 80 K, while not irradiating with UV light. The blank sample was submitted to the entire analytical protocol, in which no amino acids and diamino acids were detected (Figure S3). The quantum yields obtained are very similar to previous experiments.[14]

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Keywords: amino acids · chirality · comets · gas chromatography · origins of life

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