

Caught in the Act of Formation: Amino Acids and the Asymmetry of Life

Prof. Dr. Uwe Meierhenrich

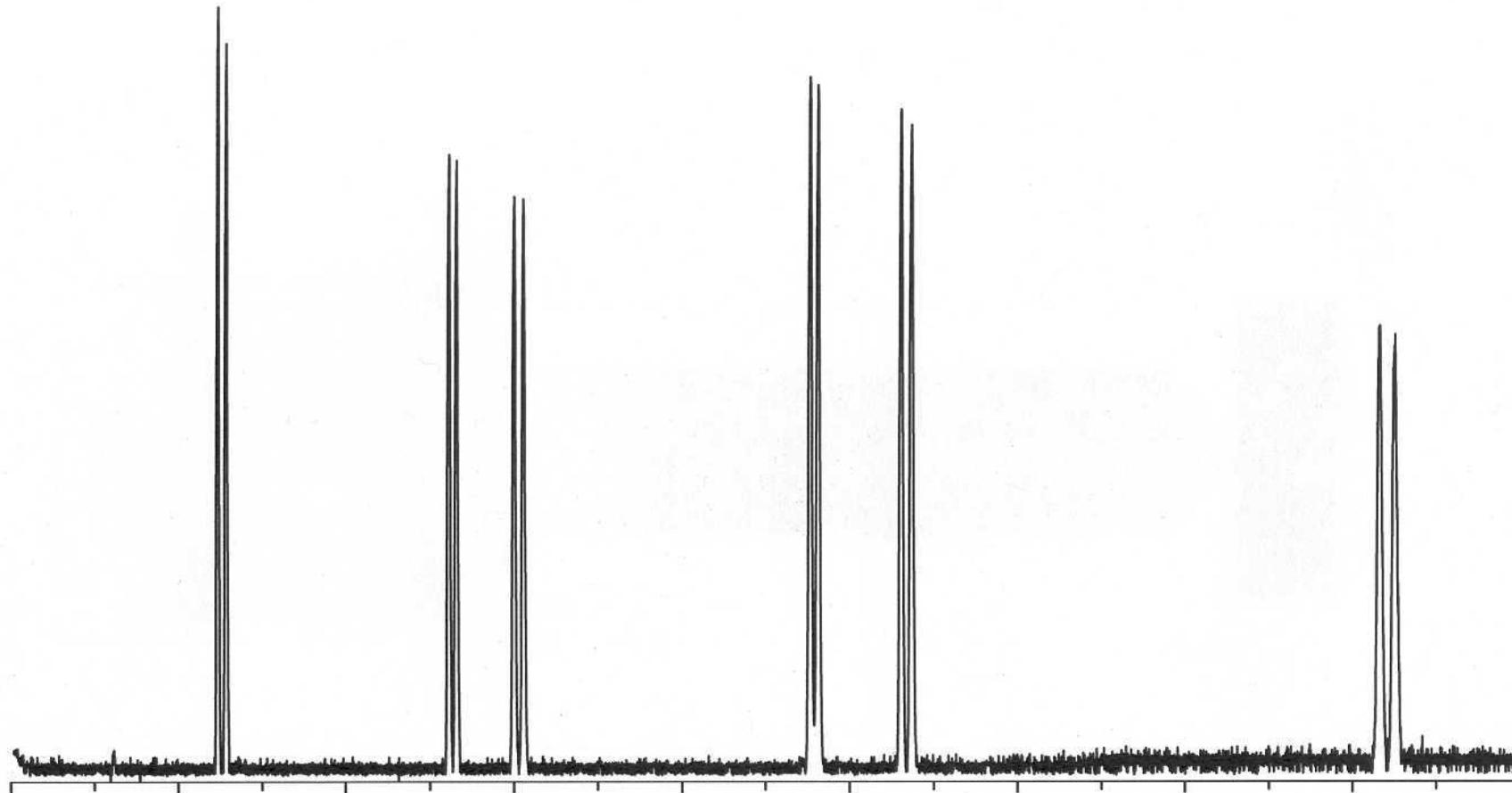
Université de Nice-Sophia Antipolis, France
UMR 6001 CNRS, LCMBA

NIS Colloquium
First chemical steps towards the origin of life
Torino, Italy, 16–17 September 2010



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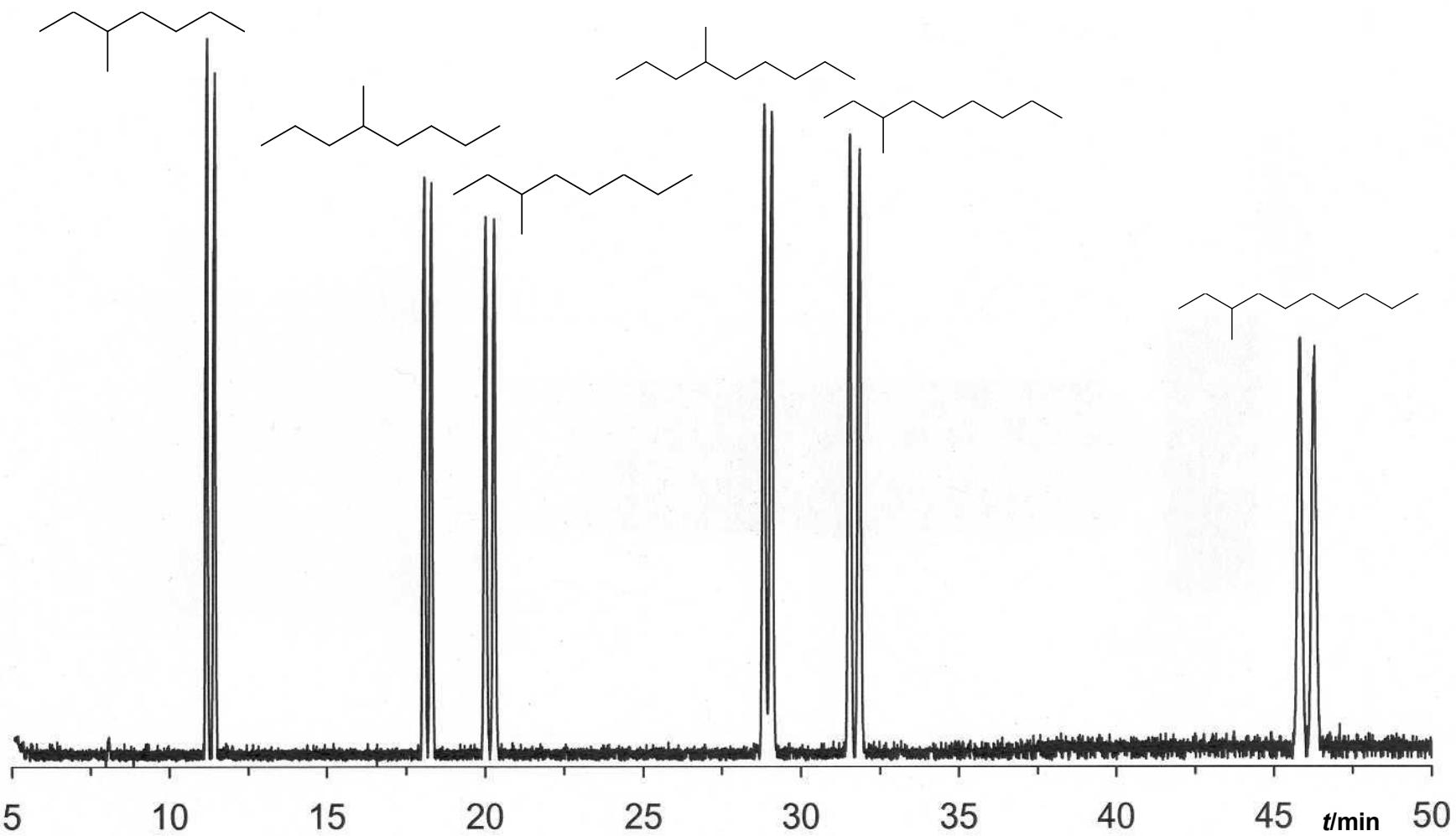


Fig. 1. Gas chromatogram of resolved hydrocarbon enantiomers 3-methylheptane, 4-methyloctane, 3-methyloctane, 4-methyl-nonane, 3-methylnonane, and 3-methyldecane separated on a capillary column coated with permethylated β -cyclodextrin (Chirasil-Dex CB, 25 m, 0.25 mm inner diameter, layer thickness 0.25 μ m, Varian-Chrompack). Meierhenrich U.J. et al.: *Chirality* **15** (2003), S13-S16.

***H*ow did life originate ?**

***A*nd why were left-handed amino acids selected for its architecture ?**

- 1) Formation of amino acids in interstellar space**
- 2) Diamino acids in interstellar space and in meteorites**
- 3) Chirality: The enantiomeric excess of interstellar amino acids**
- 4) Cometary mission Rosetta**



Fig.5: Knots of gas in the Dumbbell Nebula. Dense knots of gas and dust seem to be a natural part of the evolution of planetary nebulae. They form in the early stages, and their shape changes as the nebula expands. Image taken by Hubble's Wide Field Planetary Camera 2 in November 2001. The filters used to create this color image show oxygen in blue, hydrogen in green and a combination of sulfur and nitrogen emission in red.

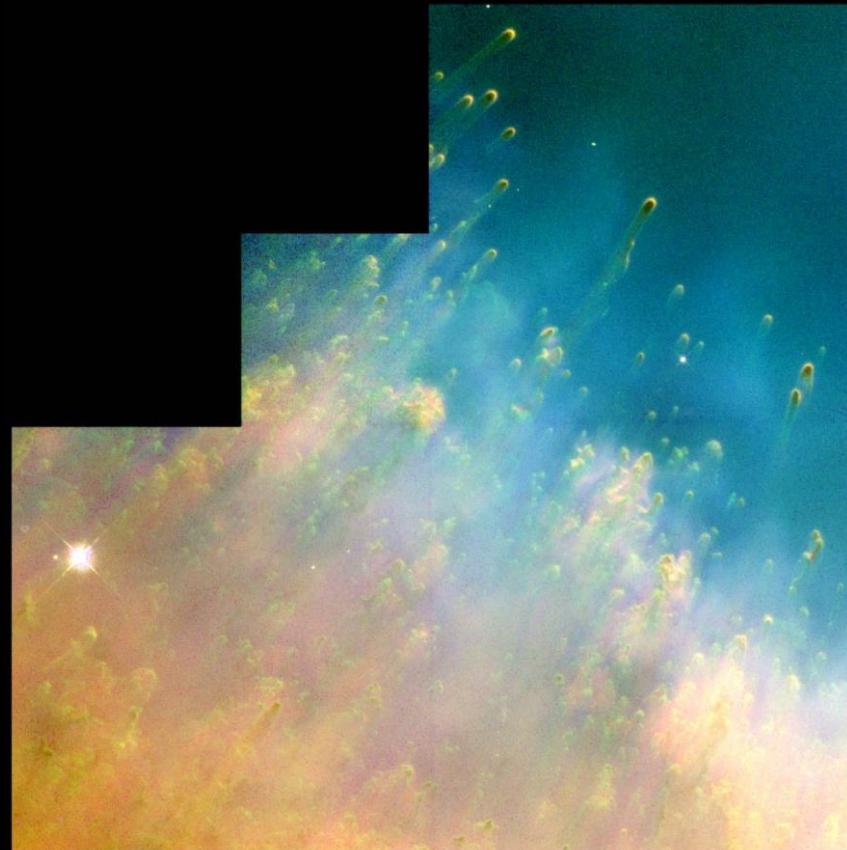
Image courtesy of C.R. O'Dell (Vanderbilt University), Image STScI-PRC2003-06



Fig.4a: A dark interstellar molecular cloud by the passage of a star cluster in the Pleiades. Reflection nebulosity.

Image courtesy of NASA and the Hubble Heritage Team

STScI-PRC2000-36



Helix Nebula · NGC 7293

Hubble Space Telescope · WFPC2

PRC96-13a · April 15, 1996 · ST Scl OPO · C.R. O'Dell (Rice Univ.), NASA



Fig.4b: Gas collision in the Helix nebula. Image taken by Hubble's Wide Field Planetary Camera 2. Red light depicts nitrogen emission ([NII] 6584 Å); green, hydrogen ([H-alpha], 6563 Å); blue, oxygen (5007 Å).

Image courtesy of C. Robert O'Dell and Kerry P. Handron, Rice University, NASA

Image STScI-PRC1996-13a

Brownlee-particles

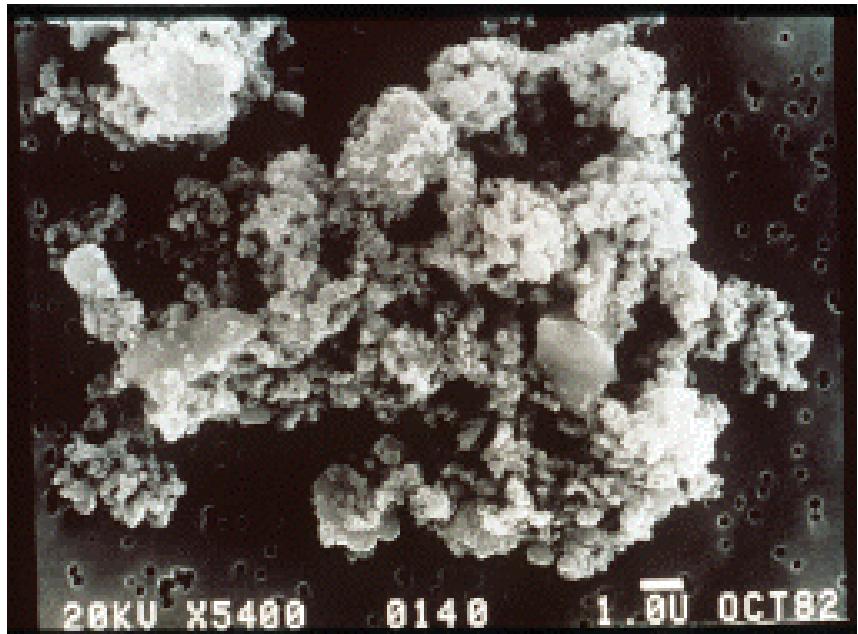


Fig.5a: A Brownlee particle is composed of Interstellar Dust is composed of rocky material that are assumed to make comets. The grains themselves seem to be made of smaller grains. There are many holes, or pores. In a comet, these holes would be filled with ice. This example of Interstellar Dust is called a Brownlee Particle. Dr. Brownlee first detected these particles in the Earth's atmosphere

Image courtesy of JPL

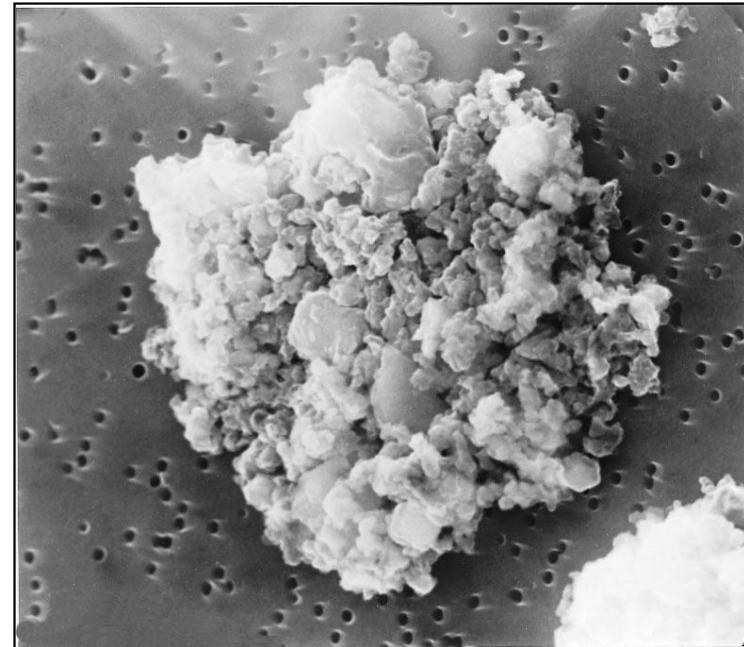


Fig.5b: An aggregate of interstellar dust particles. Larger silicate and Fe, Ni-sulfide grains are embedded in a porous matrix. The open spaces in the matrix are believed to have contained ice when the particle resided in a comet nucleus. Secondary electron image, 20 µm across.

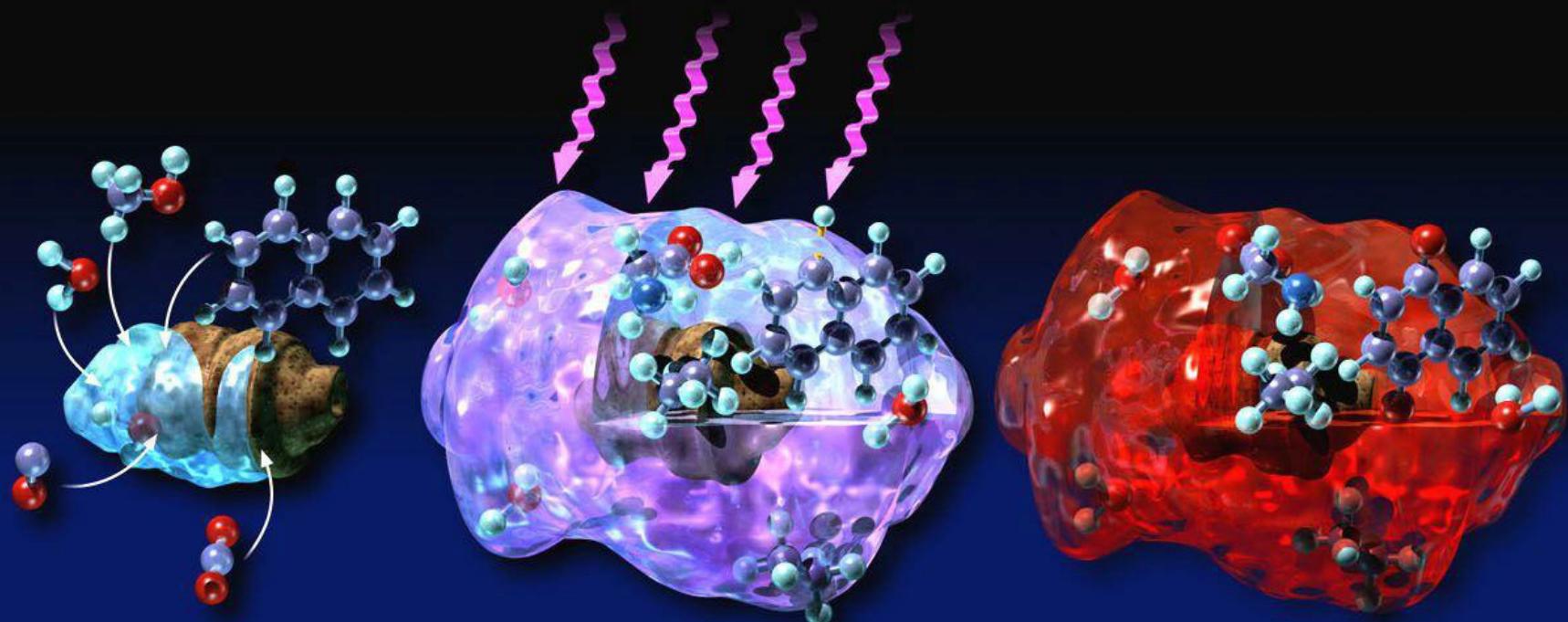
Image courtesy of NASA

Interstellar dust particle (IDP) in diffuse and dense interstellar medium

Fig.1a: IDP with thin ice layer containing molecules such as H₂O, CO₂, CO, CH₃OH, and NH₃.

Fig.1b: IDP with thick ice layer from the dense interstellar medium; in the diffuse medium this ice layer becomes irradiated by energetic UV-irradiation

Fig.1c: In the ice mantle of the IDP photoreactions occur that from radicals and organic molecules.



Greenberg-model of a cometissimal



Image courtesy of the Leiden Observatory, The Netherlands

Fig.8: A model of a piece of a comet. The agglomerated interstellar dust particles consist of a rocky core coated with a mantle of yellow organic material, that is surrounded by an ice mantle consisting of condensed gases (water, carbon monoxide, carbon dioxide, methanol, ammonia). Refractory yellow material is formed when the ices are irradiated by energetic ultraviolet light, emitted by young stars.
Nature **321** (1986), 385

Irradiation set-up for simulating interstellar ices

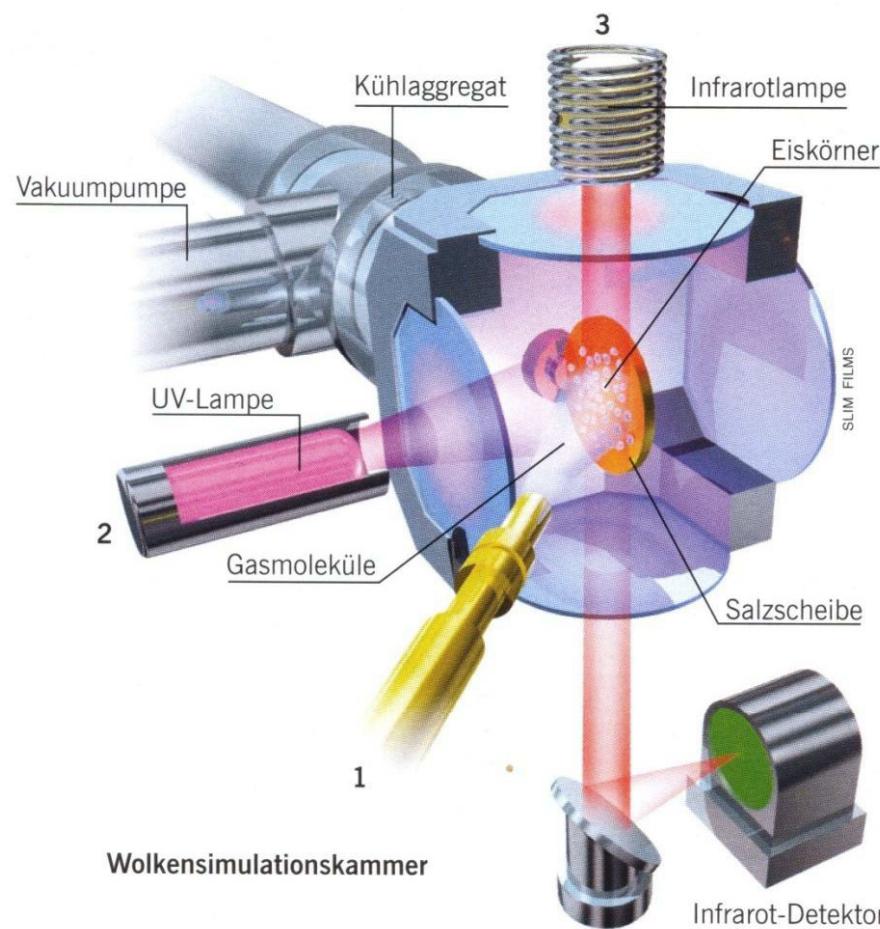


Fig.2a: Principle of a simulation chamber for interstellar particles. The ice sample composed of H_2O , CO , CO_2 , NH_3 , and CH_3OH is deposited 1 in the center on a MgF_2 -window at a temperature of -261°C and irradiated by lamp producing energetic UV photons 2. *n situ* IR-spectra can be taken 3.

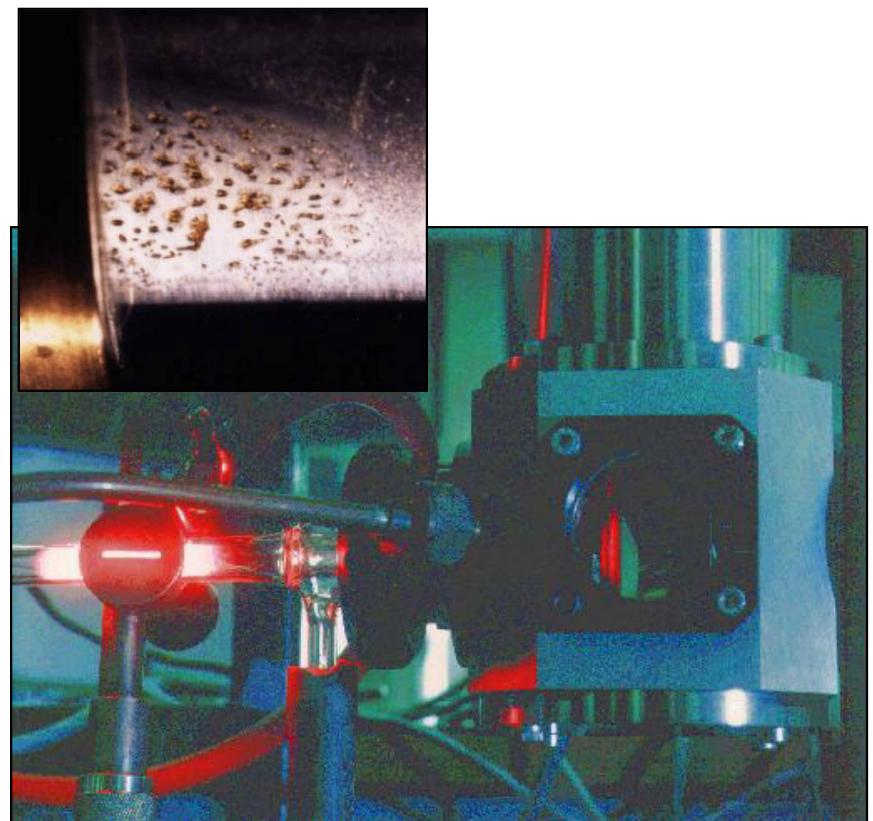


Fig.2b: Space simulation chamber at the Leiden Observatory. The ice sample (inset) is located inside the vacuum chamber on an aluminum block at a temperature of -261°C is irradiated by a lamp producing energetic UV photons. Matter remains after irradiation.

Amino acids in interstellar ice analogues

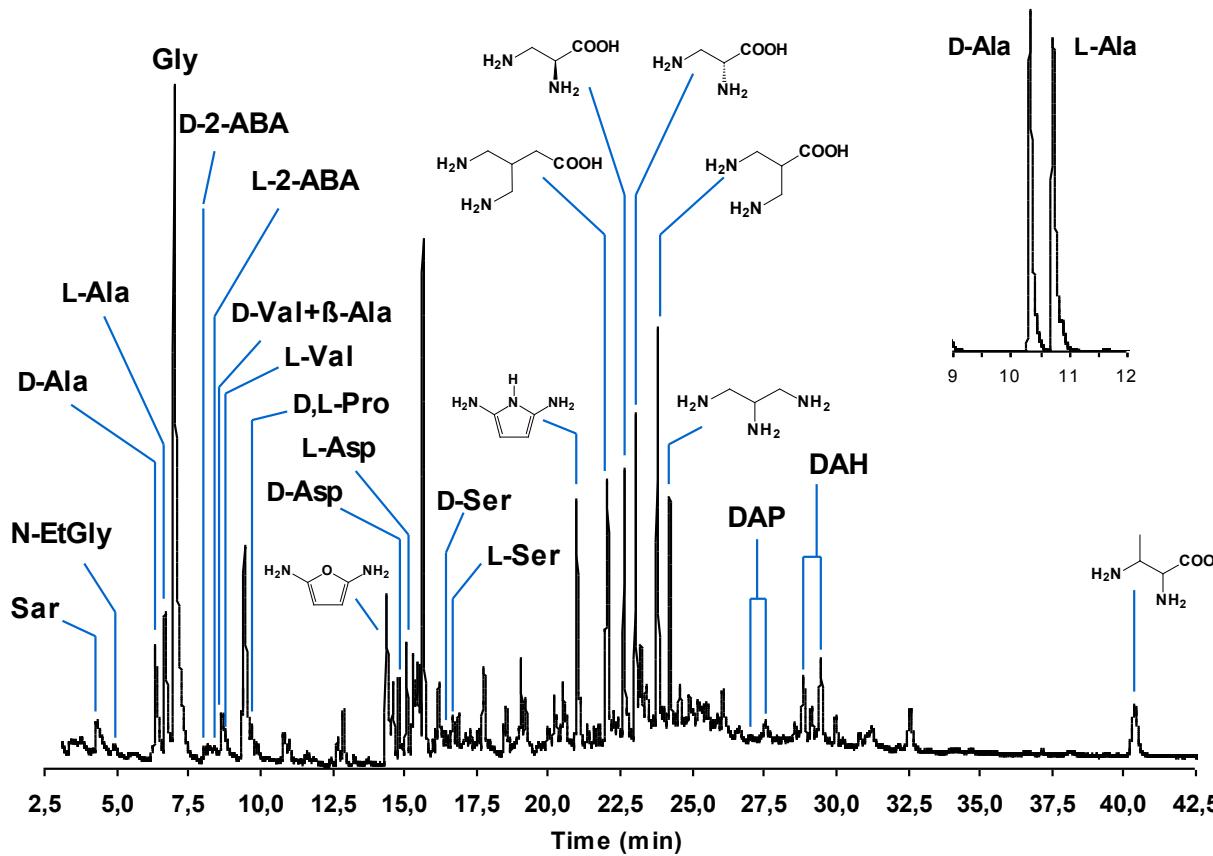


Figure 3. Gas chromatogram showing the amino acids and other compounds generated under simulated interstellar pre-cometary conditions. Data were obtained from analysis of the room temperature residue of photoprocessed interstellar medium ice analogue taken after 6 M HCl hydrolysis and derivatization (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.

Mass fragmentation of amino acids in interstellar ice analogues

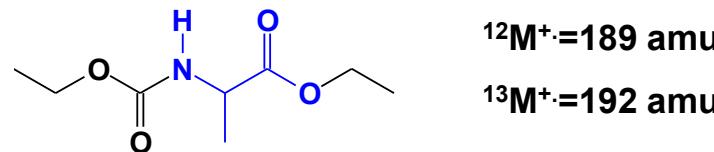


Table 1 Mass spectroscopic peak Identification for amino acids in simulated interstellar ices

Amino acid	Quantum yield of ISM sample, $\phi \times 100/\phi(\text{Gly})$	MS-fragmentation ^{12}C sample (a.m.u.)	^{13}C sample (a.m.u.)	R_t analyte (min)	Biological occurrence
Glycine	100	175, 130, 102		6.99	Yes
α -D-alanine	19.29	189, 144, 116 , 88		6.33	No
α -L-alanine	20.00	189, 144, 116 , 88		6.68	Yes
β -alanine	4.29	189, 160, 144, 116, 115 , 102, 98		8.66	No
Sarcosine (N-methylglycine)	5.71	189, 144, 116 , 88		4.29	No
D-2-aminobutyric acid	0.46	130		8.05	No
L-2-aminobutyric acid	0.48	130		8.37	No
N-ethylglycine	1.91	130 , 84, 58		4.90	No
D-valine	0.61	144		8.66	No
L-valine	0.61	144		8.80	Yes
D,L-proline	0.06	142		9.59	No, Yes
D-serine	3.29	175 (McLafferty), 160, 132 , 114		16.45	No
L-serine	3.86	204, 187, 175 (McLafferty), 160, 132 , 114		16.67	Yes
D-aspartic acid	1.14	188 , 142		14.90	No
L-aspartic acid	1.07	188 , 142		15.05	Yes

For glycine, $\phi(\text{Gly}) = 3.6 \times 10^{-5}$. Numbers designated in boldface are the main mass fragments. R_t retention time, ISM interstellar medium, MS mass spectrometry, d.l. detection limit.

Public outreach

Washington Post “Elements of life may have been delivered to Earth from space ...”

Die Süddeutsche Zeitung „Kometen sollen als „Biofähren“ durchs Universum reisen und bei ihrem Absturz Planeten befruchten ...“

New Scientist “Life’s building blocks created in space simulator ...”

Der Spiegel „Das Leben erhielt außerirdische Nachhilfe ...“

Astronomy “This not only suggests that the seeds of life on Earth might have come from space, but that prebiotic ingredients could be everywhere ...”

Le Monde „Des briques du vivant dans un cosmos artificiel ...“

BBC News “Life’s origin among the stars ...”

ZDF „Mit Bruchstücken von Kometen sind möglicherweise die ersten Lebensbausteine auf die Erde gekommen. Für diese schon recht alte Theorie glauben Bremer Forscher nun Beweise gefunden zu haben...“

ARD „Bremer Forscher stießen auf etwas, was eine der meistgestellten Fragen in den Naturwissenschaften beantworten könnte ...“

etc.

Les réactions de la télé et la presse

ARD télévision 27.3.2002, ZDF heute télévision 27.3.2002, BBC News télévision 21h14, 27.3.2002, ORF télévision 28.3.2002, NDR télévision 11h00, 28.3.2002, SAT 1 Nachrichten télévision 11.4.2002, Deutsche Welle TV 1.1.2003, N-24 TV 2h50 29.1.2003, N-24 TV 10.2.2004, ARD télévision 26.2.2004, SAT 1 27.2.2004, NDR télévision 27.2.2004, SAT 1 2.3.2004, ZDF heute télévision 21.6.2004, ARD télévision 21.6.2004, ORF 22.6.2004, 3sat 22.6.2004, NDR télévision 22.6.2004, Der Spiegel online 28.3.2002, Frankfurter Rundschau 28.3.2002, Süddeutsche Zeitung 28.3.2002, Die Tageszeitung taz 28.3.2002, Die Welt 28.3.2002, New Scientist 28.3.2002, The Guardian 28.3.2002, The Alchemist 28.3.2002, Der Standard, Vienne 28.3.2002, de Volkskrant, Pays-Bas 28.3.2002, Süddeutsche Zeitung 28.3.2002, Max-Planck-Gesellschaft, communiqué de presse 28.3.2002, Universität Bremen communiqué de presse 28.3.2002, CNRS communiqué de presse anglais, version française 28.3.2002, Informationsdienst Wissenschaft 28.3.2002, Nature Highlights allemand 28.3.2002, Nature Highlights 28.3.2002, Hessischer Rundfunk HR1, 8h50 Interview life 28.3.2002, Nord-West-Radio 28.3.2002, Radio Bremen 1, 28.3.2002, Radio Bremen 4, 28.3.2002, Radio Wir von Hier 12h05, 28.3.2002, WDR5 16h00-17h00 Leonardo Interview life 28.3.2002, Deutschlandfunk (107.1 MHz) 16h35-17h00, 28.3.2002, de Volkskrant, Pays-Bas 28.3.2002, Scienctimes Chine 29.3.2002, Vietnam Express 29.3.2002, Die Welt 30.3.2002, Astronomy 31.3.2002, NDR 4 (95.0 MHz) 15h00-16h00, 31.3.2002, Washington Post 1.4.2002, FAZ Radio (93.6 MHz) 14h30 Interview life 2.4.2002, Libération, France 2.4.2002, Focus 8.4.2002, Süddeutsche Zeitung 9.4.2002, Daily Telegraph London 10.4.2002, Le Monde 13.4.2002, Folha, Brésil 29.4.2002, ESA Focus 28.5.2002, Bild der Wissenschaft Juin 2002, Max-Planck-Forschung 2/2002, Highlights Université de Brême 7/2002, New Scientist 28.9.2002, Die Tageszeitung taz 24.1.2003, Frankfurter Rundschau 16.4.2003, Nord-West-Radio 2.6.2003, Weser-Kurier 9.2.2004, Informationsdienst Wissenschaft 18.2.2004, Frankfurter Allgemeine Zeitung FAZ 3.3.2004, Chemical & Engineering News 14.6.2004, Spiegel online 21.6.2004, Informationsdienst Wissenschaft 21.6.2004, communiqué de presse Université Brême 21.6.2004, Radio Brême 21.6.2004, Bayrischer Rundfunk, 21.6.2004, Die Welt 21.6.2004, Berliner Zeitung 22.6.2004, Nordwest Zeitung 22.6.2004, Hamburger Abendblatt 22.6.2004, Bild Zeitung 22.6.2004, Stern 22.6.2004, Frankfurter Allgemeine Zeitung FAZ 22.6.2004, Der Standard, Wien, 22.6.2004, Spiegel online 22.6.2004, Radio Brême 22.6.2004, Nachrichten aus der Chemie 52 (2004) 412, Jornal da Ciência, Brésil, 22.6.2004, Jornal a Página, Portugal, 22.6.2004, Beijing Evening News 23.6.2004, Nachrichten aus der Chemie 52 (2004), 894; Le Journal du CNRS Octobre 2004, Science & Vie Octobre 2004, St. Galler Tagblatt, Suisse, 21.7.05, Gallileus, 21.7.05, Paca Informations Economique, 21.7.05, Le Monde, 22.7.05, Le Figaro, 22.7.05, Jornal do Commercio, Brésil, 23.7.05, La Toile de Sherbrooke, 24.7.05, Stern, Allemagne, 24.7.05, Jornal a Página, Portugal, 25.7.05, Radio France, 26.7.05, Analytik News, 28.7.05, Nice-Matin, 30.7.05, Der Tagesspiegel, Berlin, 8.8.05, New Scientist, 24.8.05, Kennislink, Pays-Bas, 25.8.05, El Universal, Mexico, 25.8.05, La Chronica, 25.8.05, Der Spiegel, Allemagne, 27.8.05, Magyar Orvosi Kamara, Hongrie, 29.08.05, Origo, 30.8.05, Spectroscopy Now, September 2005, Sciences et Avenir, Septembre 2005, Pour la Science, Septembre 2005, La Recherche, Octobre 2005, Banque des Savoirs, Novembre 2005, Deutschlandfunk Radio 16.11.2005. Vous pouvez trouver tout les rapportes online www.unice.fr/lasi.

Amino acids in interstellar ice analogues

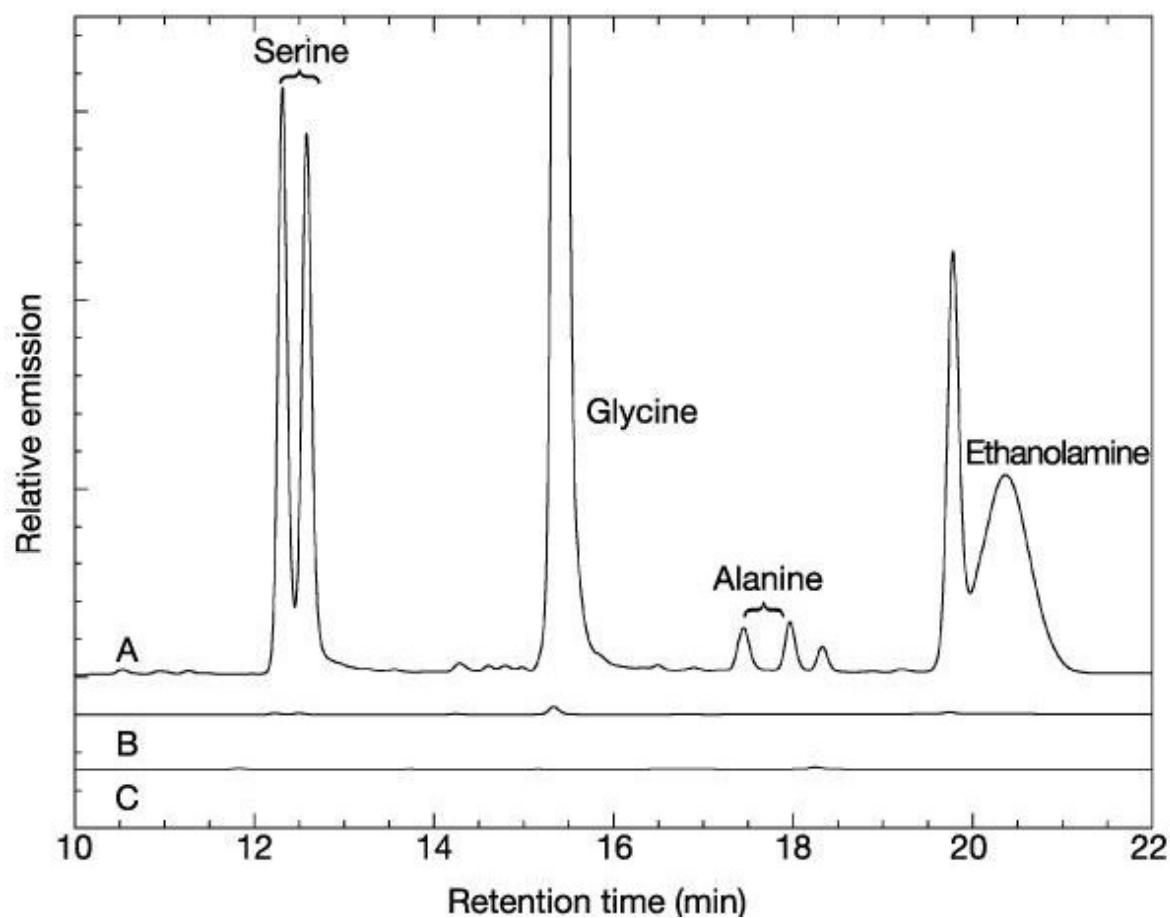


Figure 4 Amino acids are formed by the UV photolysis of a realistic interstellar ice analogue. This is demonstrated by the comparison of HPLC traces of derivatized amines resulting from: trace A, the UV photolysis of an $\text{H}_2\text{O}:\text{CH}_3\text{OH}:\text{NH}_3:\text{HCN} = 20:2:1:1$ ice showing that the amino acids serine, glycine and alanine, as well as other molecules, are produced; trace B, a control of the same ice with no UV photolysis; and trace C, a procedural blank. In trace A, a single peak indicates the presence of the amino acid glycine but the chiral fluorescent tag, which separates enantiomeric amines, causes the racemic serine and alanine to appear as pairs of peaks. Differing molar absorptivities of the labelled D,L serine and alanine diastereomers account for asymmetry in the peak pairs. The unlabelled peaks are unidentified amines. The racemic nature of the serine and alanine and the absence of prominent peaks in traces B and C indicate that contamination is not significant.

Amino acid identification in simulated interstellar ices

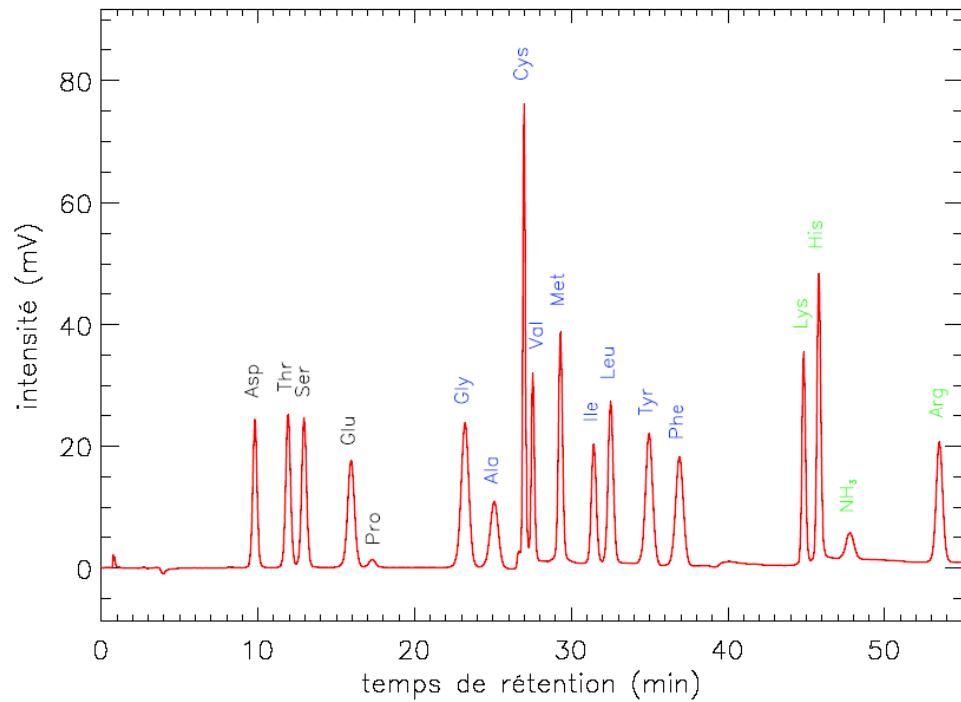


Figure 4, Amino acid standard for the identification of 17 amino acids and ammonia with a Hitachi analyser. Each amino acid is of 2 nmol, proline is of 4 nmol concentration.

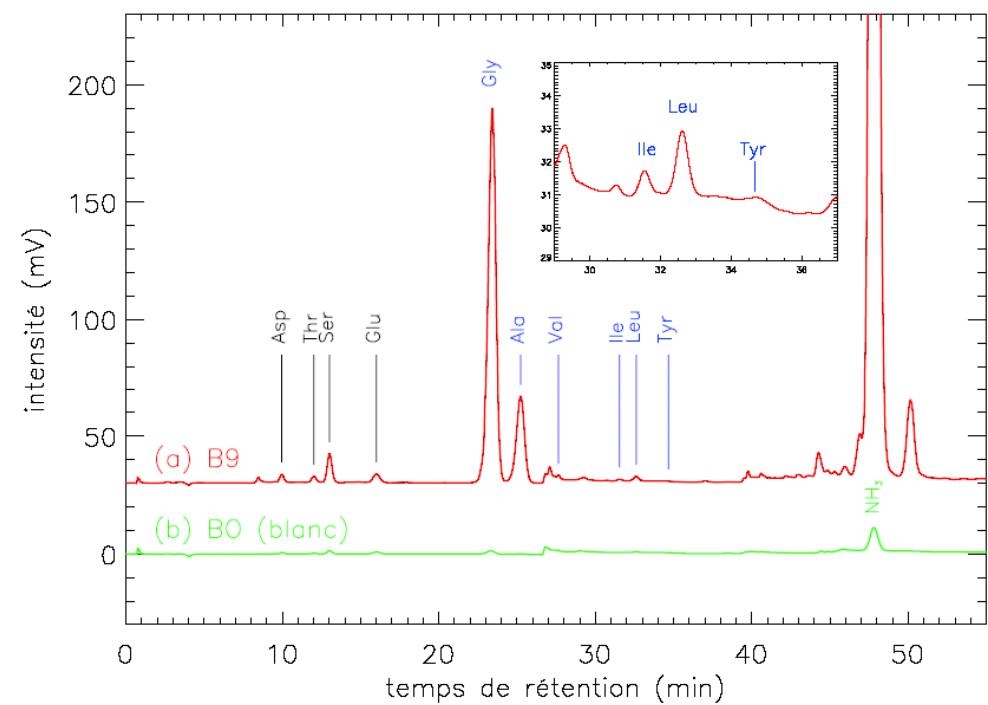


Figure 4, Chromatogram of a $\text{CH}_3\text{OH}:\text{NH}_3$ sample (1:1) irradiated at $T = 81$ K after water extraction and acid hydrolysis.

Evolutionary gain and loss of amino acids

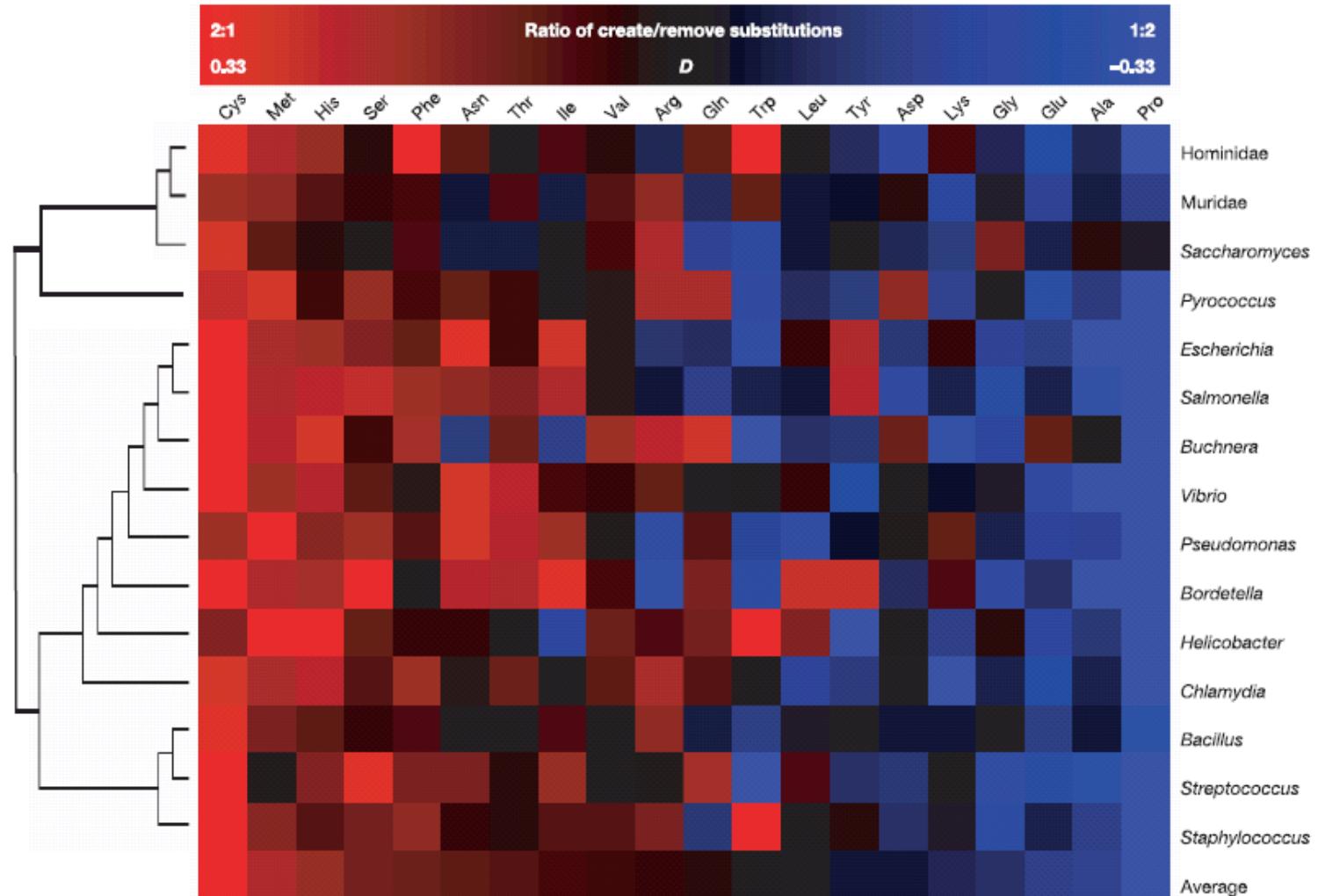


Figure 1 Normalized differences (D) between the number of substitutions creating (C) and removing (R) each amino acid ($D = (C - R)/(C + R)$) in 15 genome triplets.

$|D| = 0.33$ corresponds to a twofold difference between C and R . A tentative phylogenetic tree of the analysed taxa is shown to the left of the matrix.

***H*ow did life originate ?**

***A*nd why were left-handed molecules
selected for its architecture ?**

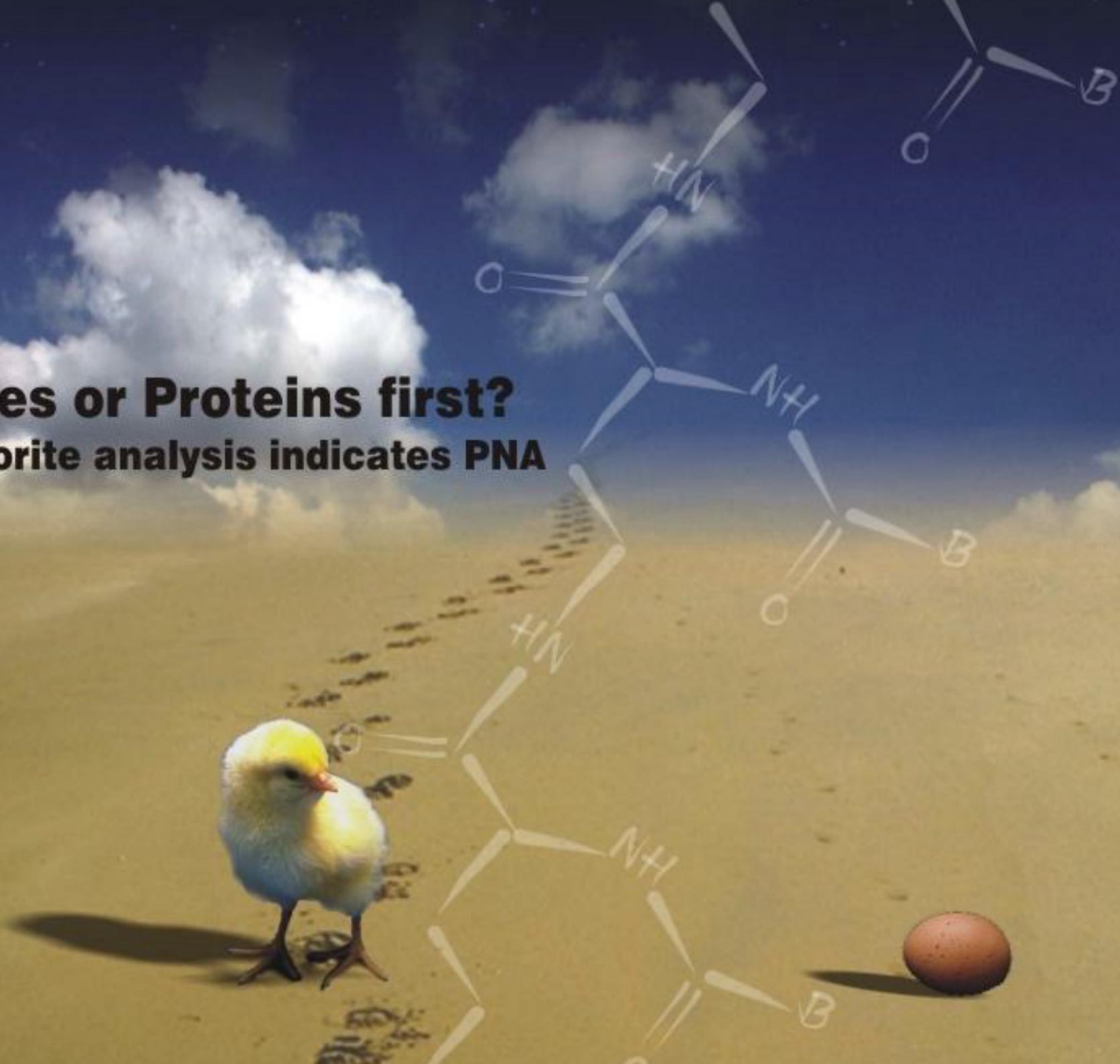
1) Amino acids form in interstellar space

***H*ow did life originate ?**

***A*nd why were left-handed molecules
selected for its architecture ?**

- 1) Amino acids form in interstellar space***
- 2) Diamino acids in interstellar space and in meteorites***

Genes or Proteins first? Meteorite analysis indicates PNA



Meteorites contain organic molecules

Total carbon 2 %

Organic compounds

Aliphatic hydrocarbons	> 10 ppm
Aromatic hydrocarbons	> 10 ppm
Polar hydrocarbons	> 100 ppm
Volatile hydrocarbons	> 1 ppm
Aldehydes and ketones	> 10 ppm
Alcohols	> 10 ppm
Amines	> 1 ppm
Monocarboxylic acids	> 100 ppm
Dicarboxylic acids	> 10 ppm
Sulfonic acids	> 100 ppm
Phosphonic acids	> 1 ppm
N-heterocycles	> 1 ppm
Purines & Pyrimidines	> 1 ppm
Carboxamides	> 10 ppm
Hydroxy acids	> 10 ppm
Amino acids	> 10 ppm

Cronin J.R.: Clues from the origin of the Solar System:
meteorites. In: Brack, A., The Molecular Origins of Life.
Cambridge University Press 1998, pp. 119-146.



Fig.14: Fragment of the
Murchison Meteorite.

Meteorites contain organic molecules

Total carbon 2 %

Organic compounds

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Volatile hydrocarbons	> 1 ppm
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Alcohols	> 10 ppm
Amines	> 1 ppm
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Dicarboxylic acids	> 10 ppm
Sulfonic acids	> 100 ppm
Phosphonic acids	> 1 ppm
N-heterocycles	> 1 ppm
Purines & Pyrimidines	> 1 ppm
Carboxamides	> 10 ppm
Hydroxy acids	> 10 ppm
Amino acids	> 10 ppm



Video: Sample preparation of 1 g of the Murchison Meteorite in clean room.

Cronin J.R.: Clues from the origin of the Solar System:
meteorites. In: Brack, A., The Molecular Origins of Life.
Cambridge University Press 1998, pp. 119-146.

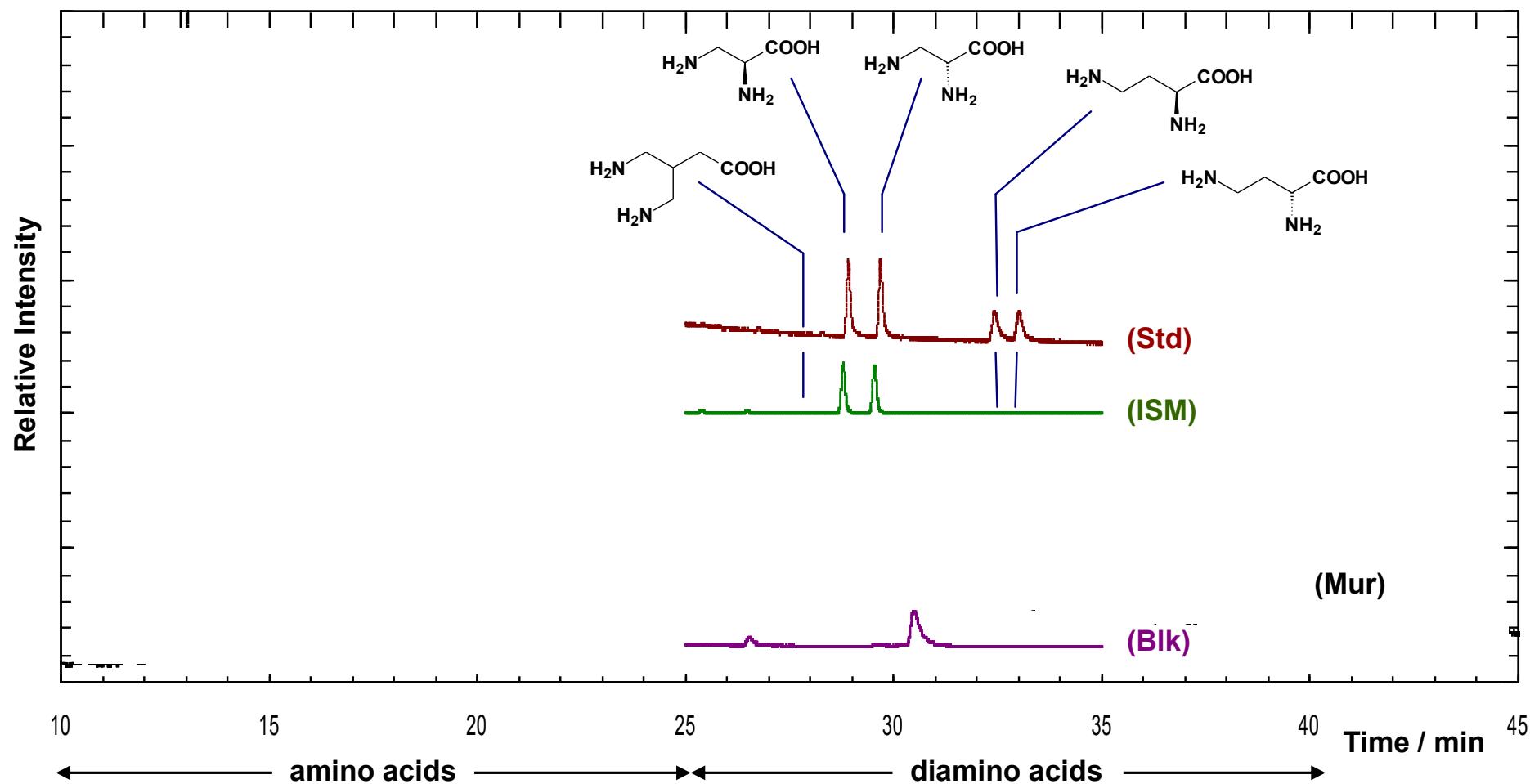


Fig. 13: Gas chromatograms showing (**Mur**) diamino acids identified in a sample of the Murchison meteorite. Data were obtained after hot water extraction, 6 M HCl hydrolysis, and ECEE derivatisation. Detection in the single ion monitoring mode of mass trace 175 a.m.u. typical for ECEE diamino acid derivatives. The insets show the external standard of the enantiomer separated diamino acids D,L-2,3-DAP and D,L-2,4-DAB (**Std**) detected in the total ion current; a laboratory sample produced by UV-irradiation of circumstellar/interstellar ice analogues (**ISM**) detected in the single ion monitoring of mass trace 175 a.m.u.; and a serpentinite blank (**Blk**) at mass trace 175 a.m.u. that had been heated before extraction for 4 h at 500°C and passed through the analytical protocol.

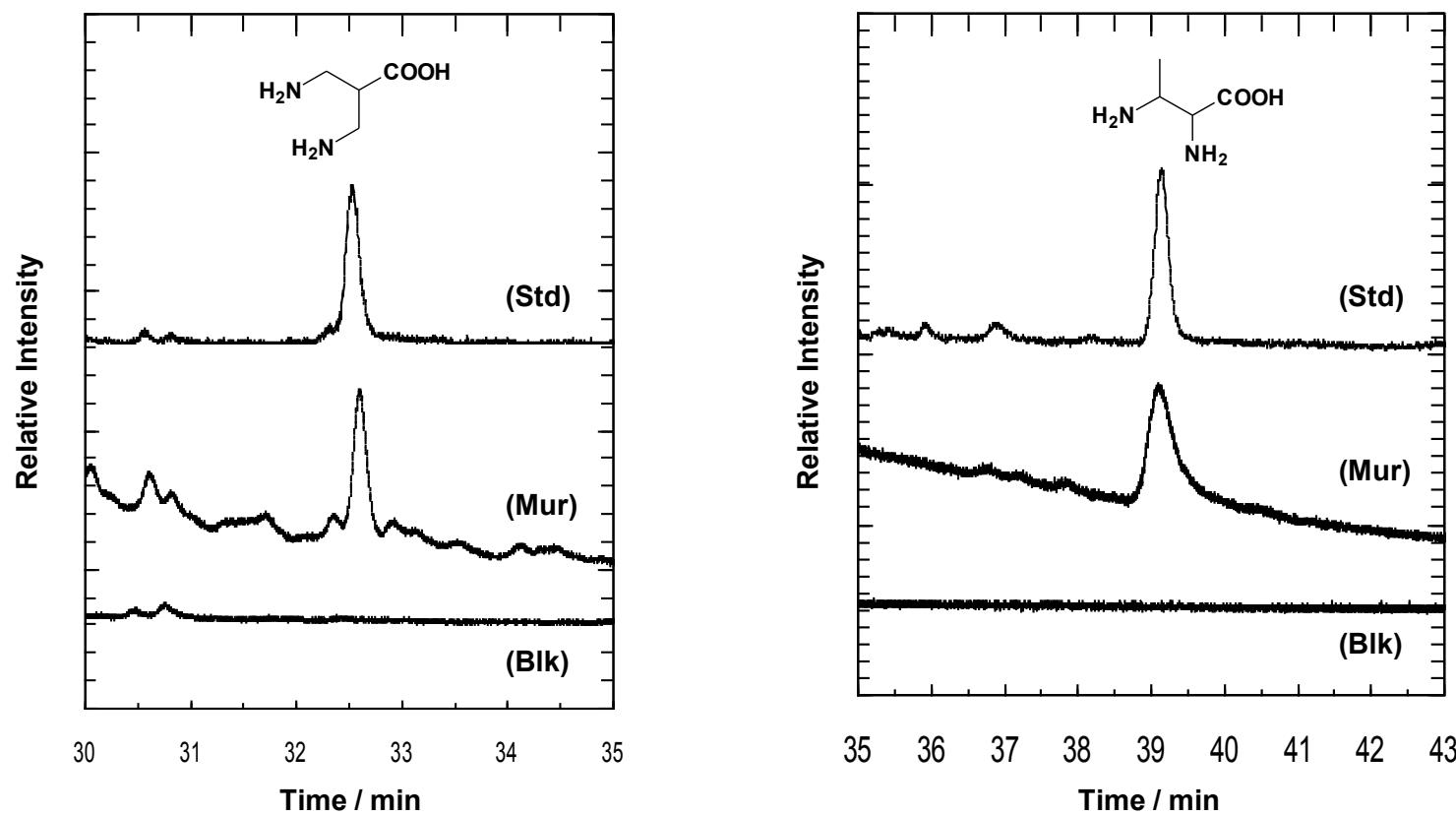


Fig. 14: Gas chromatogram (**Mur**) showing the diamino acid 3,3'-diaminoisobutyric acid (left) and 2,3-diaminobutyric acid (right) identified in a sample of the Murchison meteorite. Data were obtained after hot water extraction, 6 M HCl hydrolysis, and ECEE derivatisation by application of the standard GC-MS protocol (left) and on 12 m Chirasil-L-Val stationary phase, with oven temperature programmed for 3 min at 70 °C, 5 °C min⁻¹, and 17.5 min at 180 °C (right). Detection in the single ion monitoring mode of mass trace 142 a.m.u. (left) and 203 a.m.u. (right). For comparison, the chromatogram of a sample produced experimentally by photoprocessing of circumstellar ice analogues was used as external standard (**Std**) in the extract ion mode at $m/z = 142$. The blank sample chromatogram (**Blk**) was obtained from a serpentine sample (left) resp. from a solvent sample that had passed the whole analytical protocol and was detected in the single ion monitoring mode of mass trace 203 a.m.u. (right).

Development of genetic material during Chemical Evolution

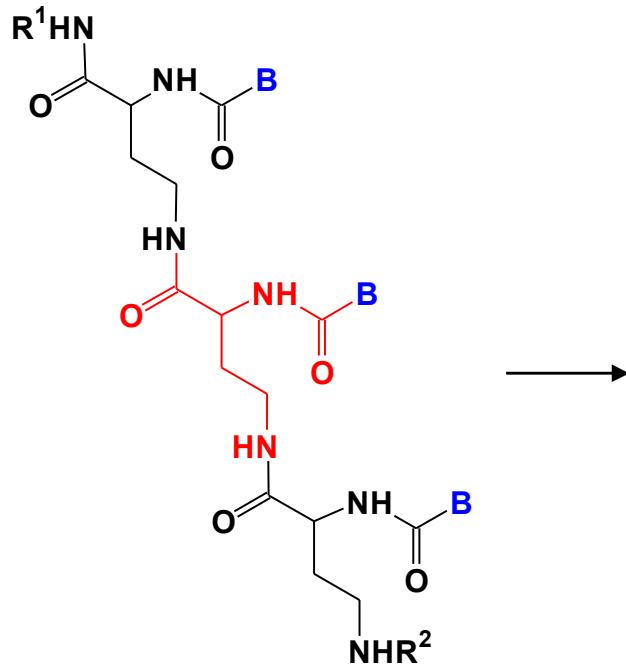
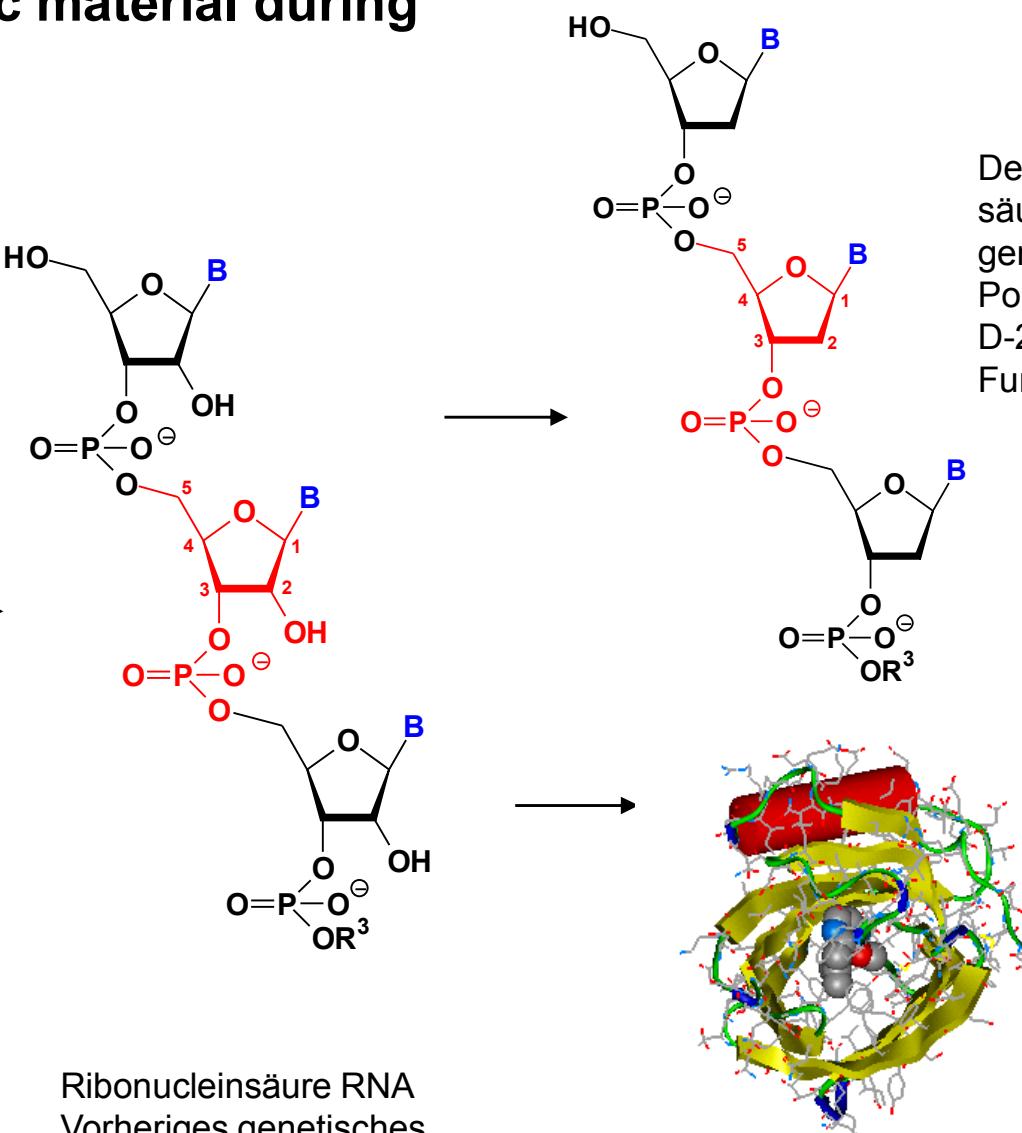
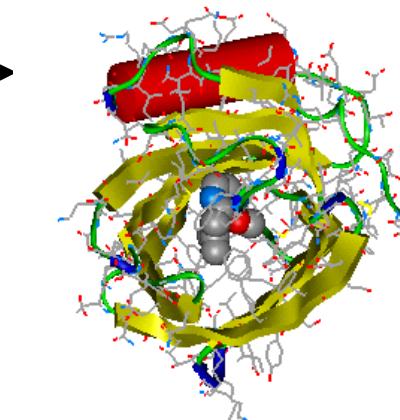


Fig. 11a: Peptid
Nucleinsäure PNA
Ursprüngliches genetisches
Material, Nielsen et al.:
Science **254** (1991), 1497
Polyamid-Kette



Ribonucleinsäure RNA
Vorheriges genetisches
Material „RNA-Welt“
Gilbert: *Nature* **319** (1986),
618, D-Ribose in Furanose-
Form

Desoxyribonucleinsäure DNA, Heutiges genetisches Material, Polyester-Kette
D-2-Desoxyribose in Furanose-Form



Odorant binding (OB) protein
including α -helix and β -sheet (and an
odorant molecule in its center)

Candidate precursor molecules to RNA

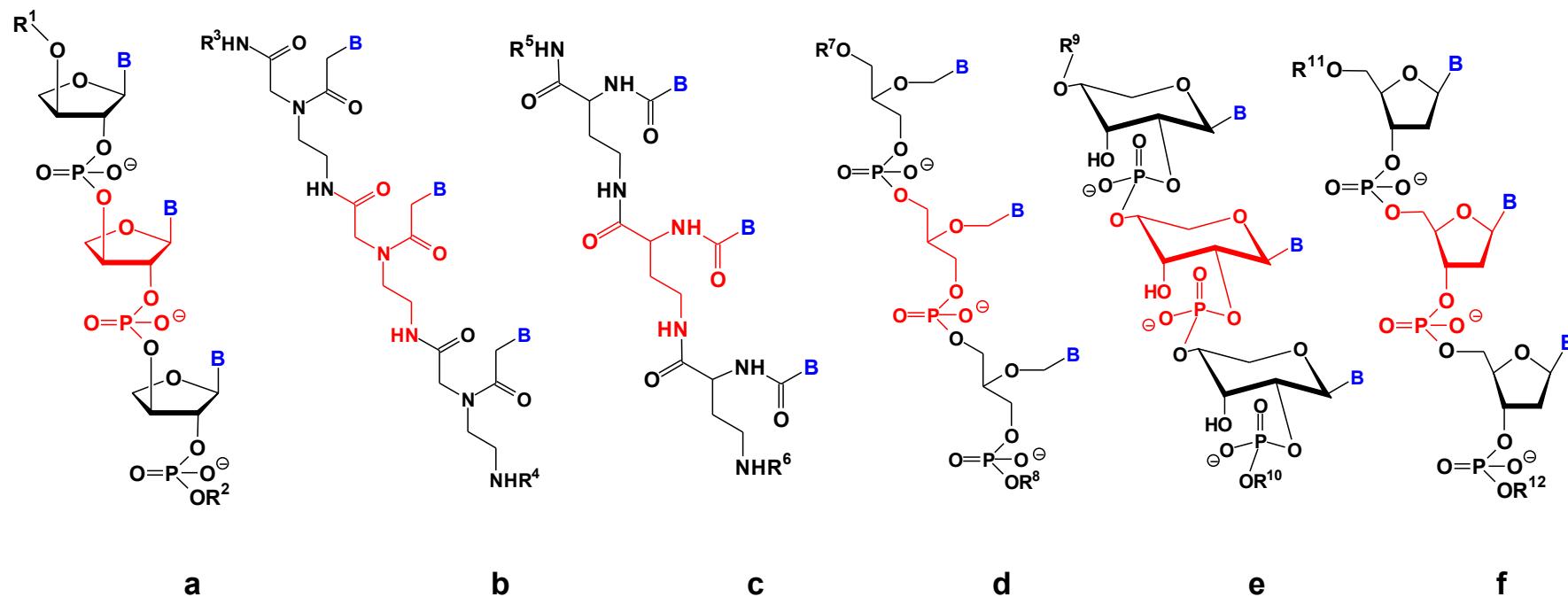


Fig. 12: Chemical structures of candidate precursors to RNA during the early history of life on Earth. **a**, Threose nucleic acid (TNA); **b**, peptide nucleic acid based on *N*-(2-aminoethyl)glycine monomers (PNA); **c**, peptide nucleic acid based on 2,4-diaminobutanoic acid monomers; **d**, glycerol-derived nucleic acid analogue; **e**, (D)- β -ribo-pyranosyl-(2'→4') oligonucleotide (p-RNA); **f**, ribonucleic acid (RNA). **B**, Nucleotide base. Monomers are depicted in red colour.

The Origin of Life

On the Origin of Primitive Cells—From Nutrient Intake to Elongation of Encapsulated Nucleotides

Uwe J. Meierhenrich,* Jean-Jacques Filippi, Cornelia Meinert, Pierre Vierling, and Jason P. Dworkin

Keywords:
amphiphiles · liposomes · micelles ·
nucleotides · vesicles

Dedicated to Professor Wolfram H.-P.
Thiemann

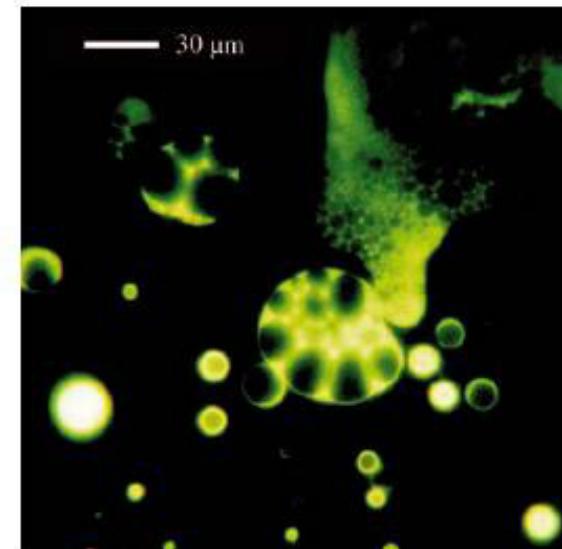
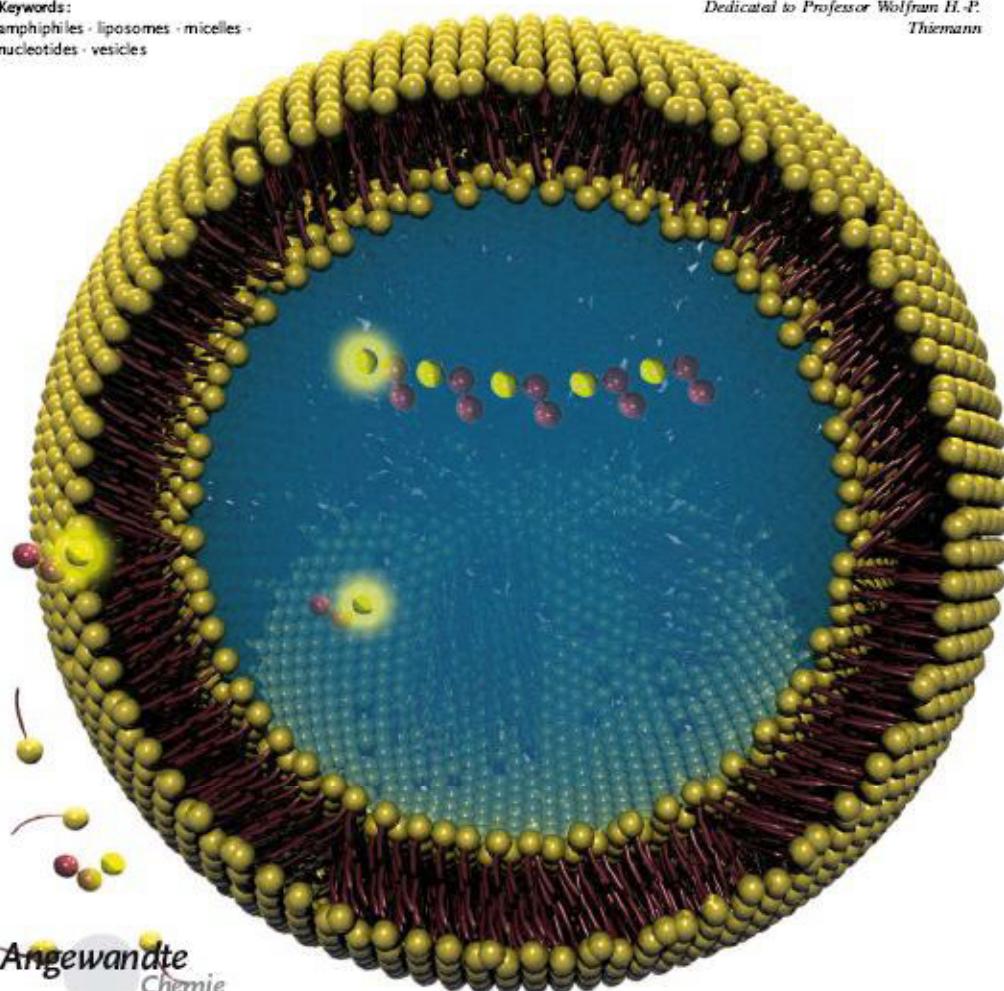


Figure 2. Compounds from meteorites seen in a new light: pyranine dye encapsulated in vesicles made from an extract of the Murchison meteorite. Vesicles show interior spaces with sizes in the micrometer range; oil droplets and inverse emulsions are also visible.^[15] Copyright (2001) National Academy of Sciences, USA.

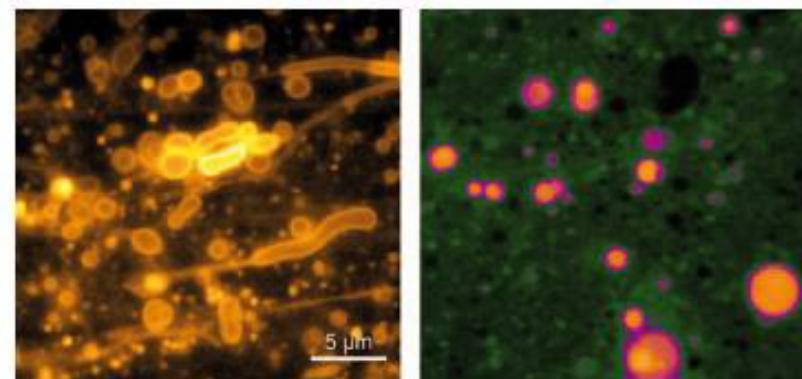


Figure 4. Left: Decanoic acid/decanol vesicles stained with fluorescent rhodamine; right: 600 mers of DNA encapsulated in vesicles of decanoic acid alone by the dehydration/rehydration method. The DNA was stained with 3,6-dimethylaminoacridine (acridine orange), a nucleic acid selective stain used to enhance the contrast in the microscopic image. Reprinted with permission from David Deamer, UC Santa Cruz.

The Origin of Life

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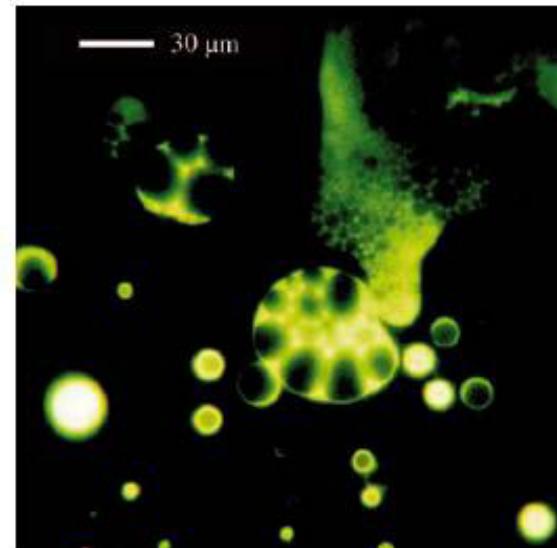
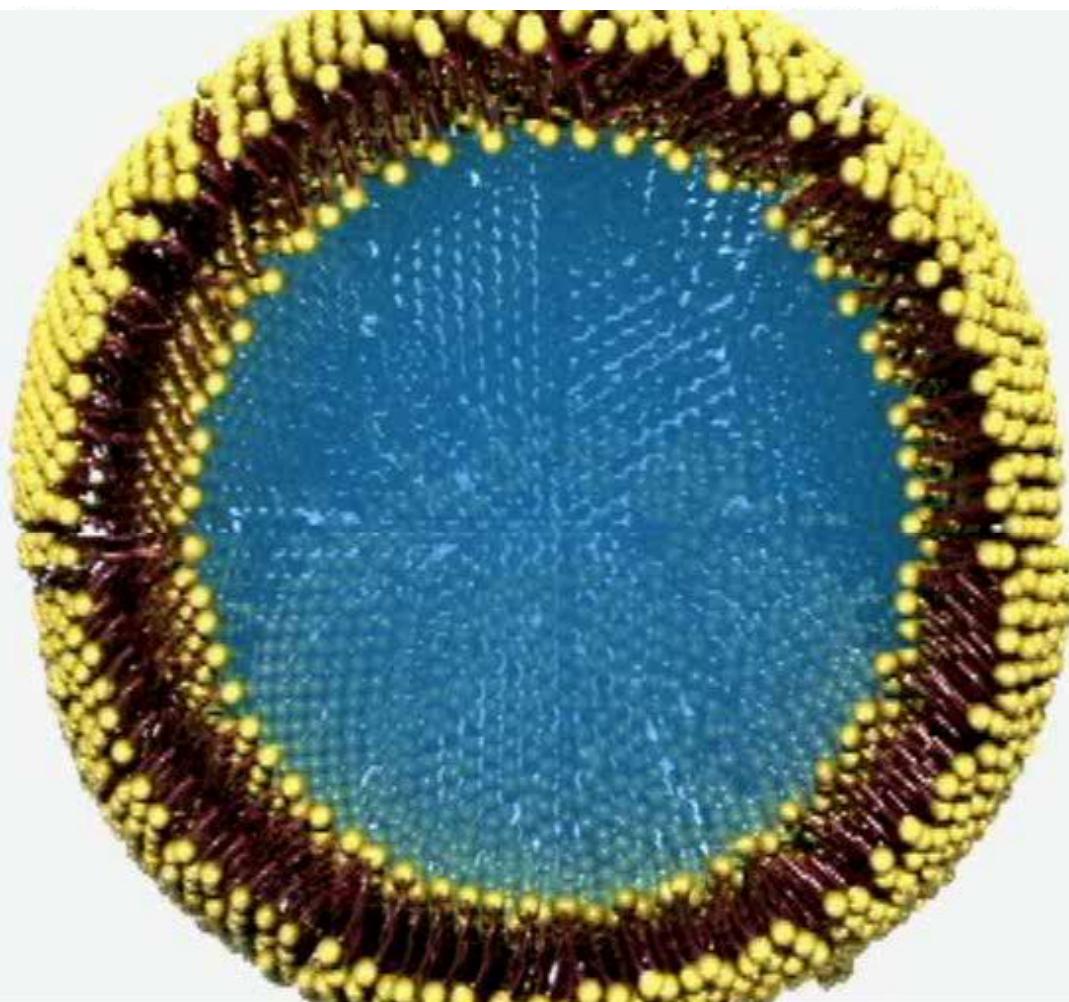


Figure 2. Compounds from meteorites seen in a new light: pyranine dye encapsulated in vesicles made from an extract of the Murchison meteorite. Vesicles show interior spaces with sizes in the micrometer range; oil droplets and inverse emulsions are also visible.^[15] Copyright (2001) National Academy of Sciences, USA.

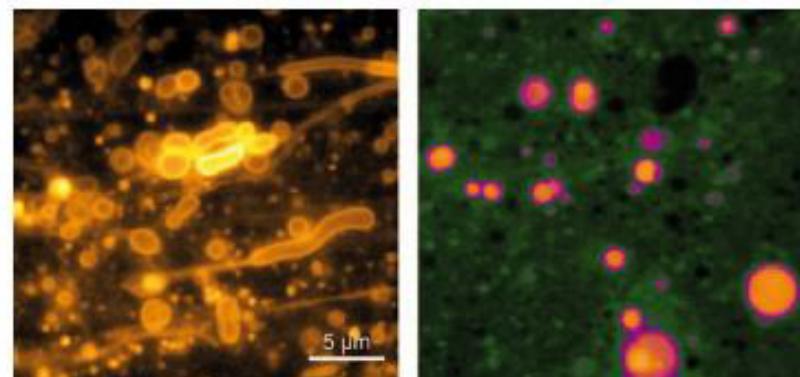


Figure 4. Left: Decanoic acid/decanol vesicles stained with fluorescent rhodamine; right: 600 mers of DNA encapsulated in vesicles of decanoic acid alone by the dehydration/rehydration method. The DNA was stained with 3,6-dimethylaminoacridine (acridine orange), a nucleic acid selective stain used to enhance the contrast in the microscopic image. Reprinted with permission from David Deamer, UC Santa Cruz.

***H*ow did life originate ?**

***A*nd why were left-handed molecules
selected for its architecture ?**

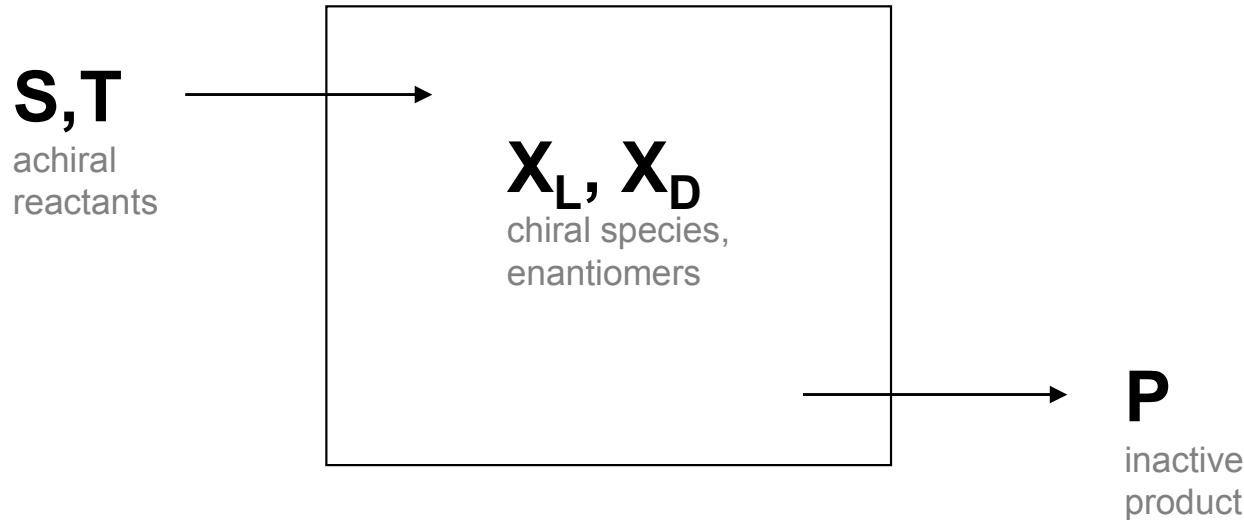
- 1) Amino acids form in interstellar space***
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- 1) Amino acids form in interstellar space***
- 2) Diamino acids form in interstellar space and in meteorites***
- 3) Chirality: The enantiomeric excess of interstellar amino acids***

Amplification of enantiomeric excesses calculated with *Mathematica*[®]

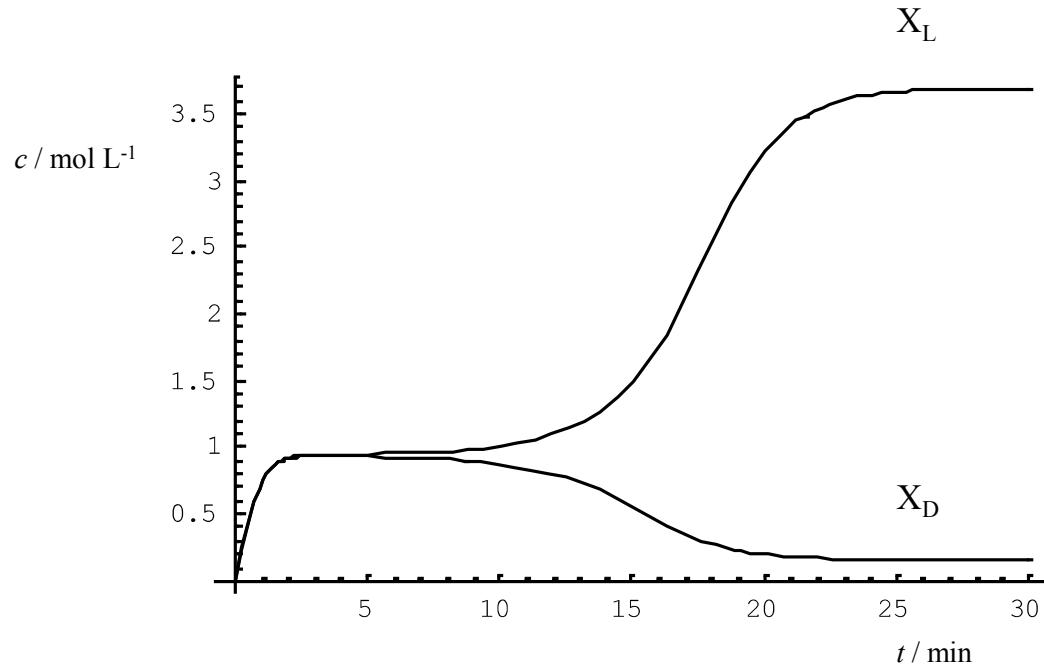


$$\frac{d[X_L]}{dt} = k_{1f}[S][T] - k_{1r}[X_L] + k_{2f}[S][T][X_L] - k_{2r}[X_L]^2 - k_3[X_L][X_D]$$

$$\frac{d[X_D]}{dt} = k_{1f}[S][T] - k_{1r}[X_D] + k_{2f}[S][T][X_D] - k_{2r}[X_D]^2 - k_3[X_L][X_D]$$

Figure: Kondepudi-Prigogine model assumed an open system into which the achiral reactants **S** and **T** are introduced, forming chiral species **X_L** and **X_D**. The achiral product **P** is to be taken out of the system.
Kondepudi D.: *Modern Thermodynamics*, Wiley, New York, 1998.

Amplification of enantiomeric excesses calculated with *Mathematica*[®]



```
k1f=0.5; k1r=0.01; k2f=0.5; k2r=0.2; k3=1.5;
S=1.25; T=S;
Soln1=NDSolve[
{XL'[t]==k1f*S*T-k1r*XL[t]+k2f*S*T*XL[t]-
k2r*(XL[t])^2-k3*XL[t]*XD[t],
XD'[t]==k1f*S*T-k1r*XD[t]+k2f*S*T*XD[t]-
k2r*(XD[t])^2-k3*XL[t]*XD[t],
XL[0]==0.002, XD[0]==0.0},{XL,XD},{t,0,30},
MaxSteps->500];
Plot[Evaluate[{XL[t],XD[t]} /. Soln1],{t,0,30}]
```

Figure: Numerische *Mathematica*[®] Berechnung eines Systems von Differentialgleichungen, die eine autokatalytische Funktion beinhalten. Für die Konzentration des Enantiomers X_L wurde für den Zeitpunkt $t = 0$ der Wert $X_L(0) = 0,002 \text{ mol L}^{-1}$ eingesetzt; das Enantiomer D erhielt demgegenüber den Startwert $X_D(0) = 0,000 \text{ mol L}^{-1}$. Derart kleine Asymmetrien lassen sich mithilfe autokatalytischer Reaktionsschritte wie abgebildet in geeigneten Reaktionsmechanismen amplifizieren.

CPL in Orion star formation region

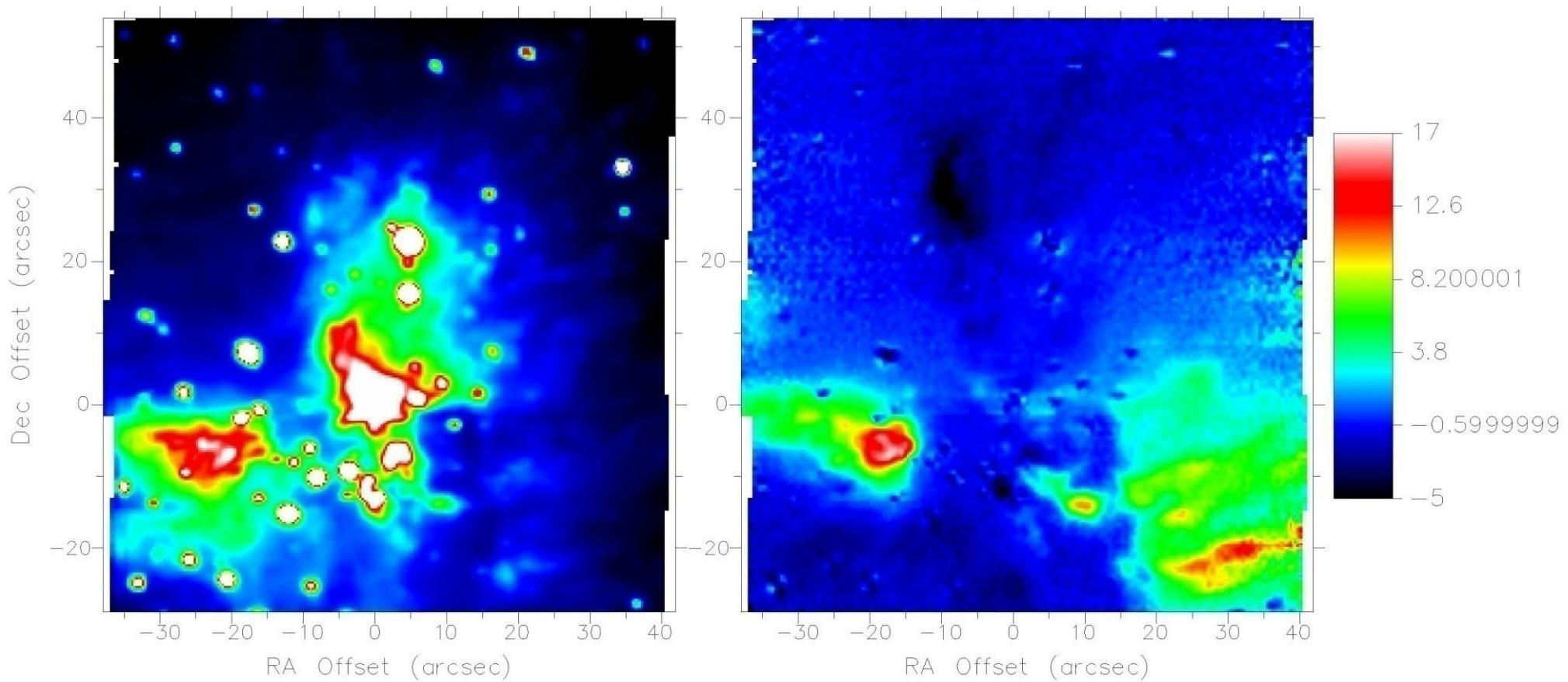


Fig.6: Circular polarization image of the OMC-1 star formation region in Orion at 2.2 μm . (Right) Percentage circular polarization ranging from – 5 % (black) to +17 % (white). Polarization accuracy ranges from about 0.1 % in the brighter regions to 1 % in the fainter regions. By convention, positive polarization means that the electric vector is seen to rotate counterclockwise in a fixed plane by an observer looking at the source. (Left) The total IR intensity. The bright source at coordinates (0,0) is the Becklin-Neugebauer object. The size of a typical protostellar disk (100 astronomical units) is less than 1 arc sec at the 450 pc distance of OMC-1 and therefore much smaller than the observed polarization structure.

UHV sublimation chamber with amino acid reservoir

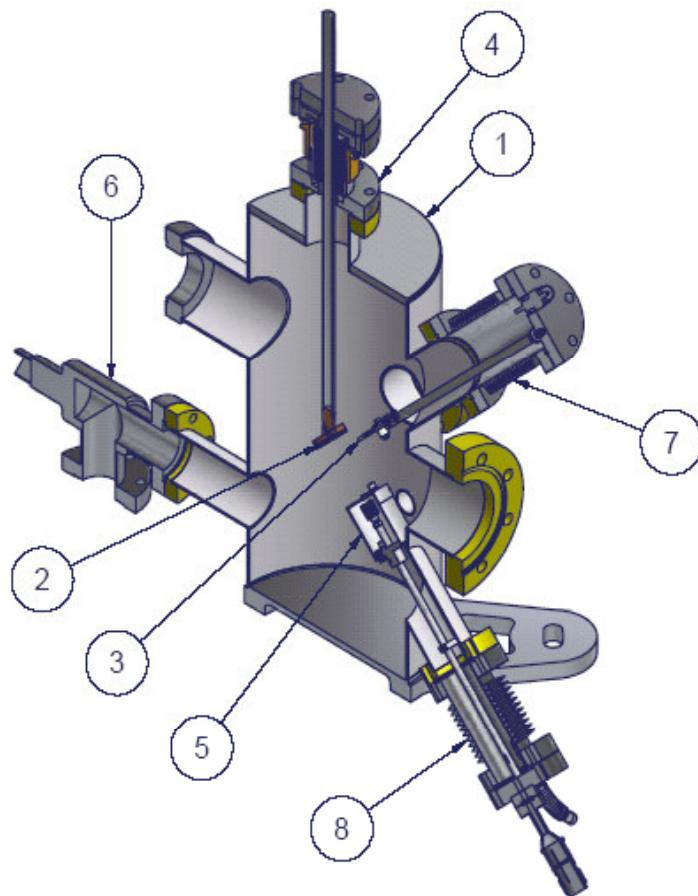
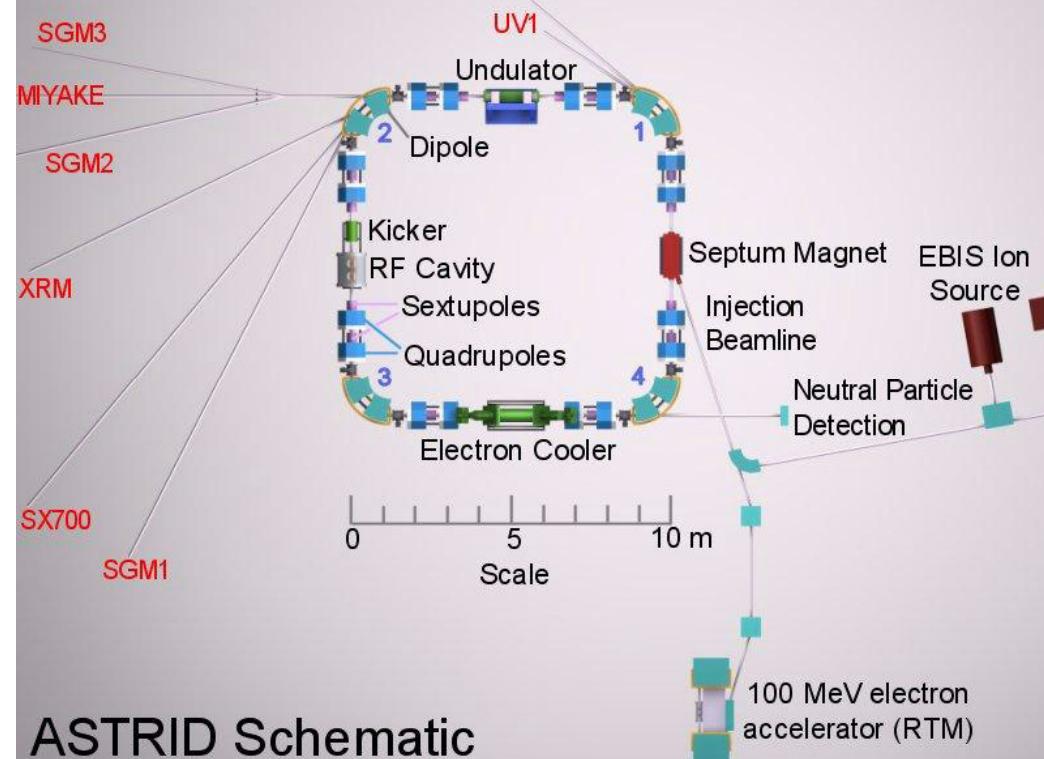


Fig. 8. Temperature and pressure controlled UHV chamber for controlled sublimation of amino acids. 1 UHV chamber, 2 MgF₂ crystal holder, 3 QCM, 4 Manipulator, 5 reservoir of analyte, 6 UHV pump, 7 QCM support, 8 reservoir support.





ASTRID Schematic

Property of ISA, (2005)



VUV CD spectra of alanine enantiomers

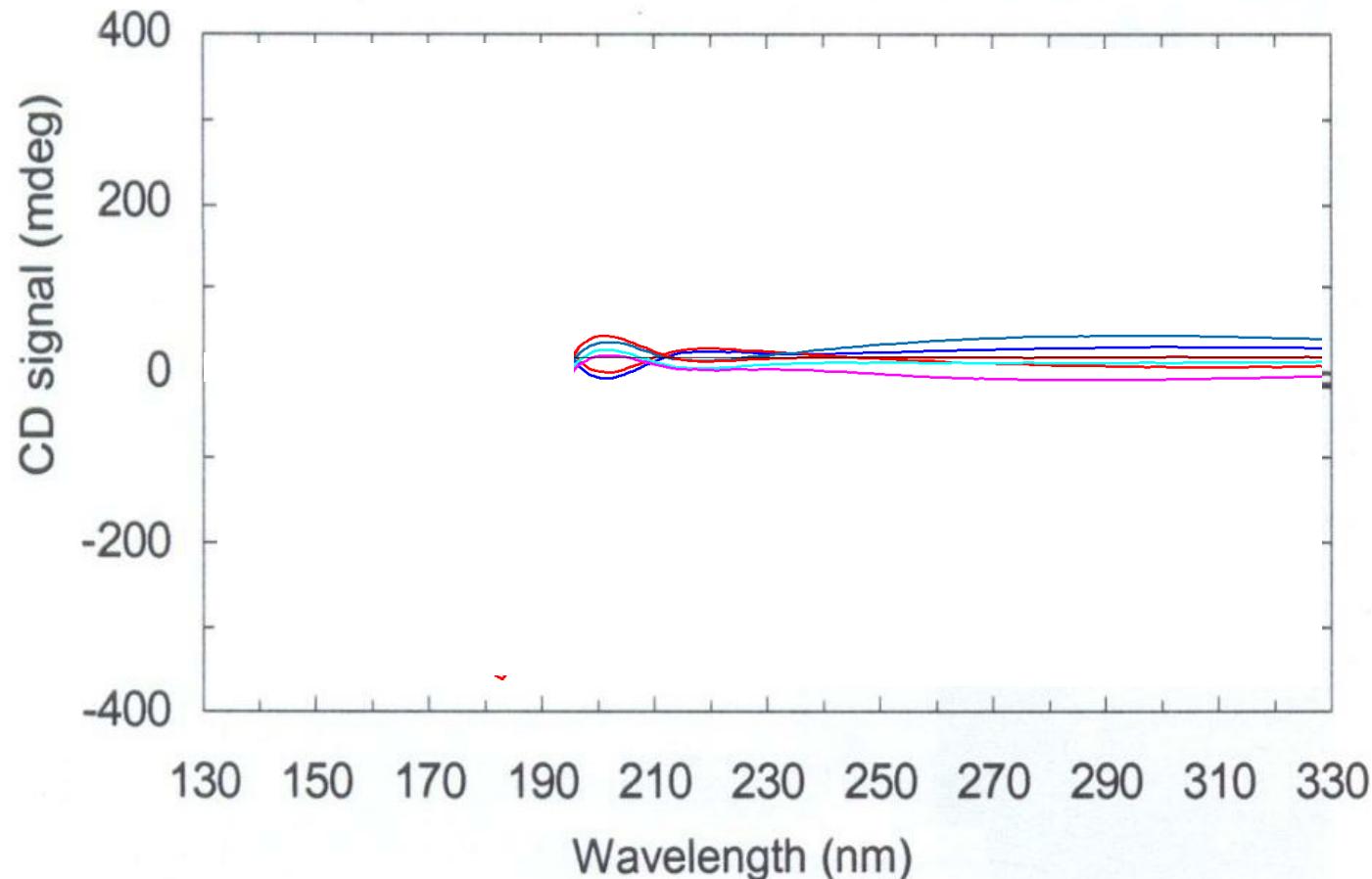


Fig. 8. Vacuum ultra violet circular dichroism spectrum of amorphous solid-state alanine enantiomers. *Blue and red lines:* L-alanine. *Rose, green, turkish and bright red lines:* D-alanine.

Vacuum UV circular dichroism spectra of solid state amino acids

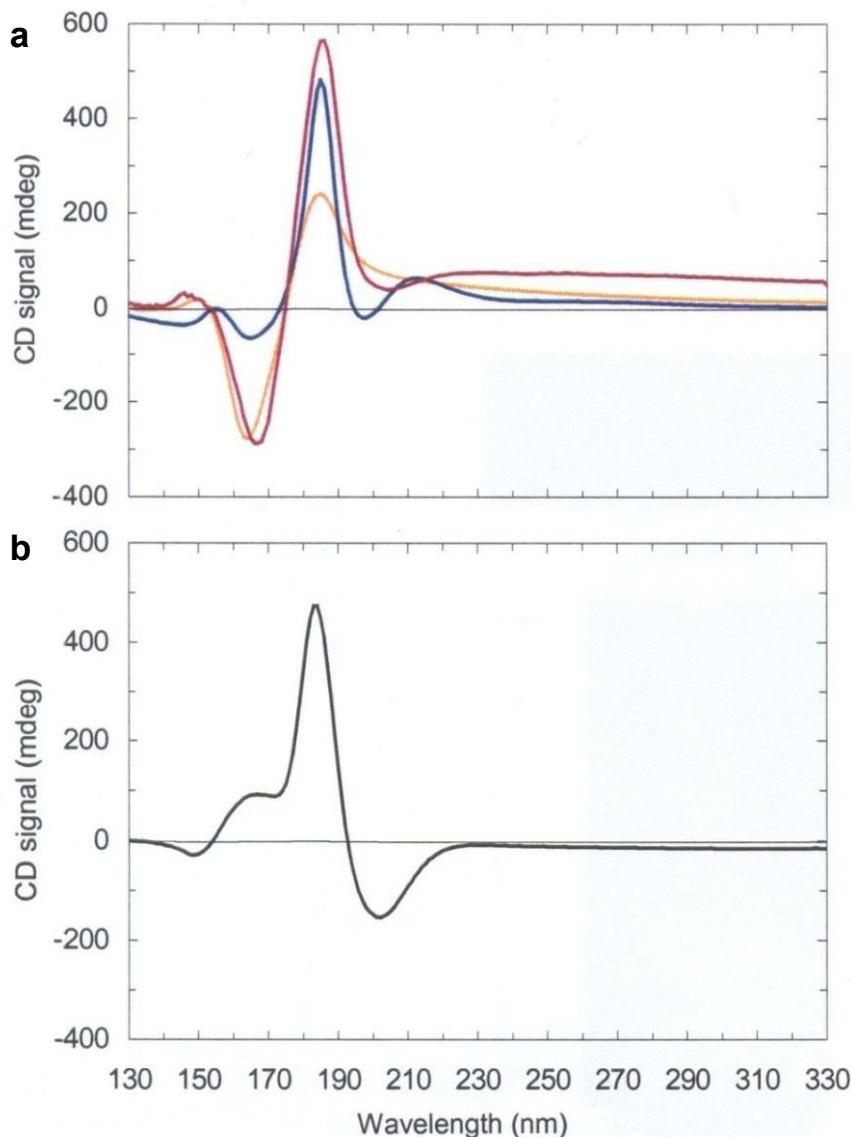


Fig. 7: Vacuum ultraviolet circular dichroism spectra of solid-state amino acids.

a, CD spectra between 130 and 330 nm of solid amorphous L-valine sublimate (red line), L-alanine sublimate (blue line), and L-leucine sublimate (yellow line) immobilized on MgF_2 .

b, L-proline sublimate. A CSA standard was used for instrument calibration purposes; D-enantiomers gave CD spectra of opposite sign. The band of L-proline matched the band of L-alanine, L-valine, and L-leucine.

Beamline SU-5 at Synchrotron Center LURE, Paris-Orsay

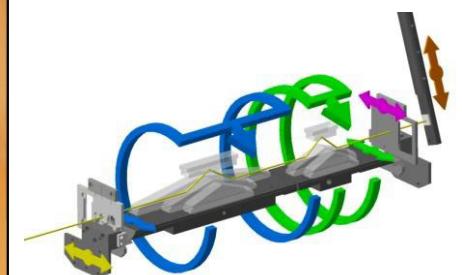
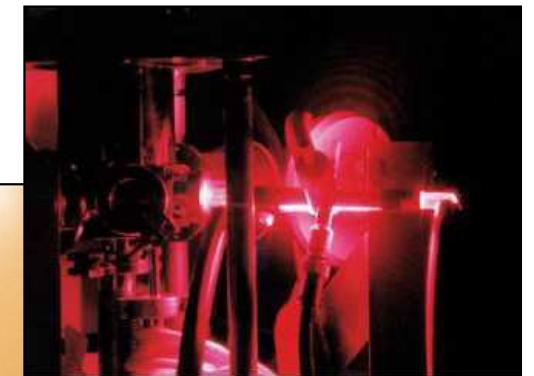
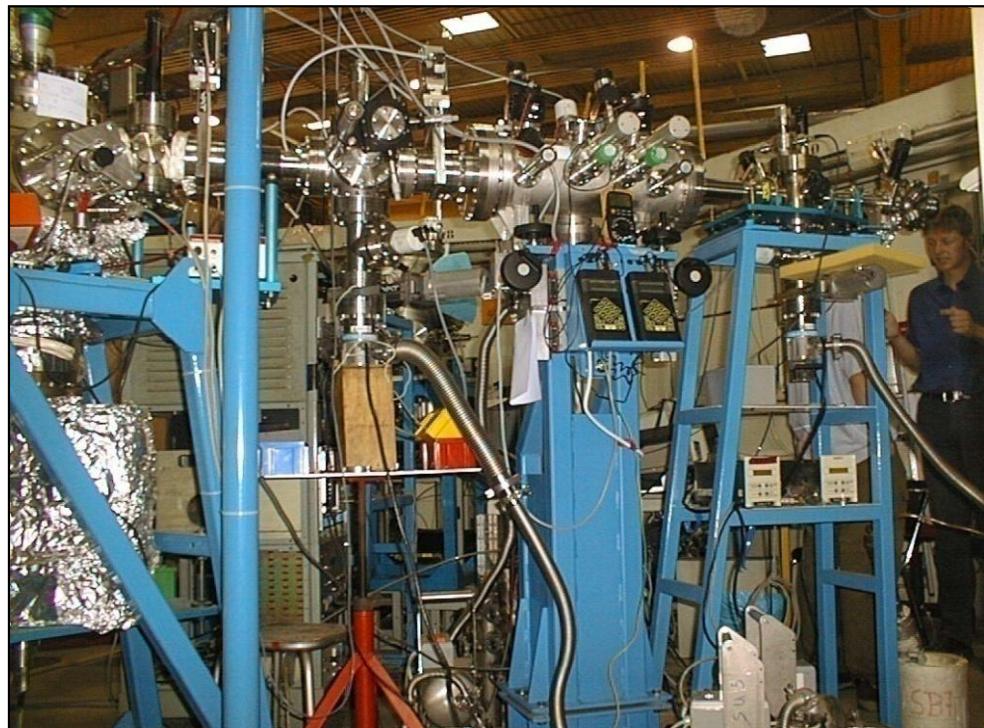


Fig.7: Beamline SU-5, part of the Laboratoire pour l'Utilisation du Rayonnement Electromagnétique LURE, Centre Universitaire Paris-Sud, in France, is constructed to produce circular polarized synchrotron radiation. Right: Onuki-type polarimeter for detection of the four Stokes parameters in the vacuum ultra-violett. L. Nahon *et al.*: *Applied Optics* **43** (2004), 1024-1037. Right top: Chamber for reproduction of the interstellar medium at IAS/SOLEIL.

Synchrotron Center SOLEIL, Gif-sur-Yvette, France



Fig.7: The synchrotron SOLEIL (Source Optimisée de Lumière d'Energie Intermédiaire du LURE) is a third generation synchrotron optimized for intense photon fluxes. It started its activities with the inauguration by President Jacques Chirac in December 2006.

Asymmetric VUV photolysis of leucine in the solid state

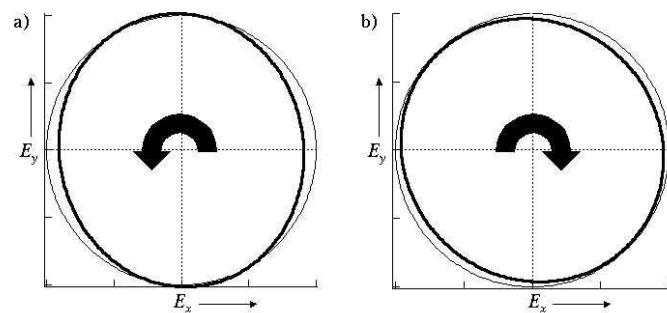


Fig. 29: Measured polarization ellipses (thick lines) at the sample location. They were measured for a SR centered at 6.8 eV (182 nm), for a) *l*-CPSR and b) *r*-CPSR, as produced by the Ophelie undulator of the SU-5 beamline. Absolute circular polarization rates are of 91 % for *r*-CPSR and 94 % for *l*-CPSR.

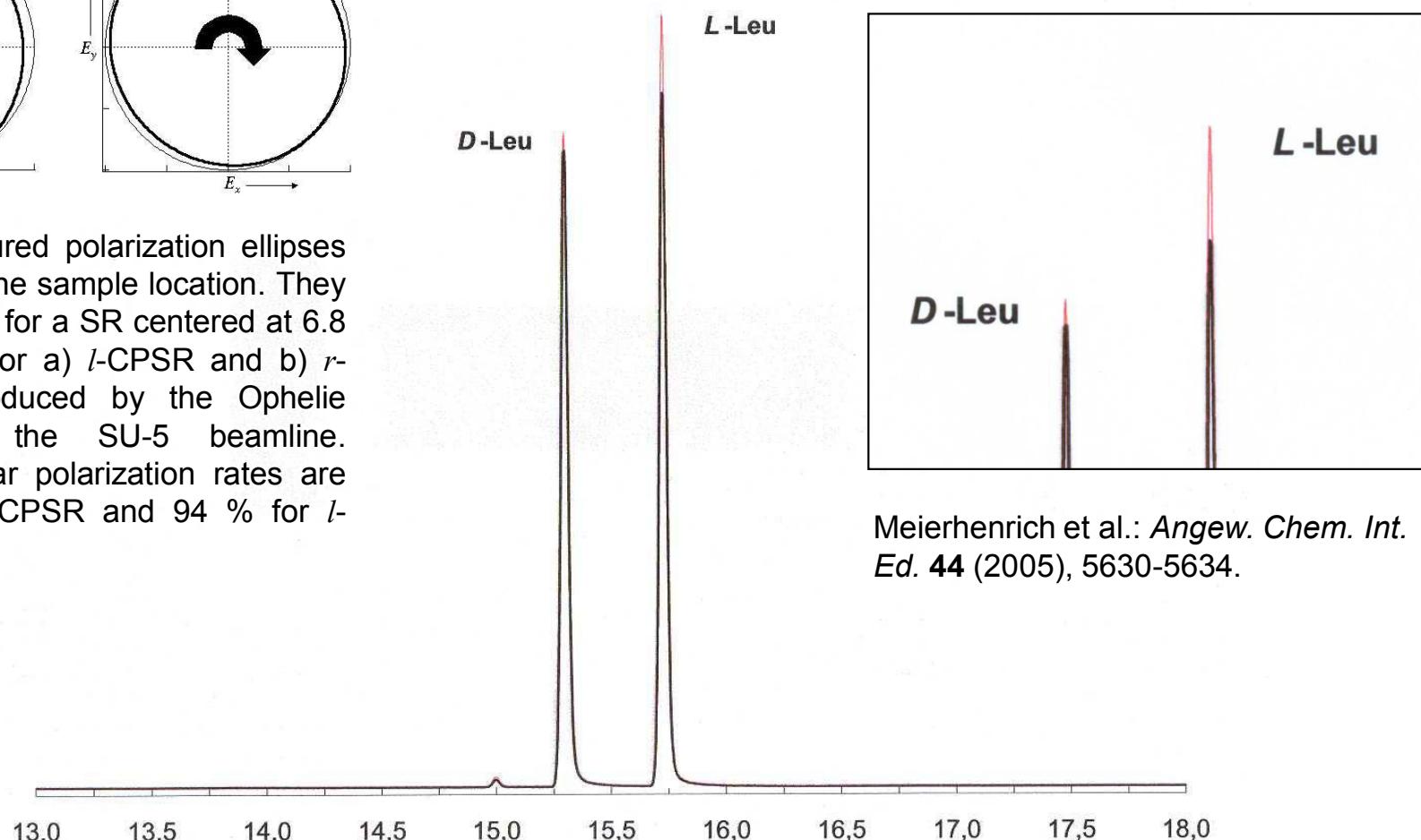


Fig. 29: Gas chromatographic enantiomer separation of the ECEE derivatives of the amino acid leucine. One sample (black line) was irradiated with *r*-CPL, the other (red line) with *l*-CPL at 6.9 eV.

Asymmetric VUV photolysis of leucine in the solid state

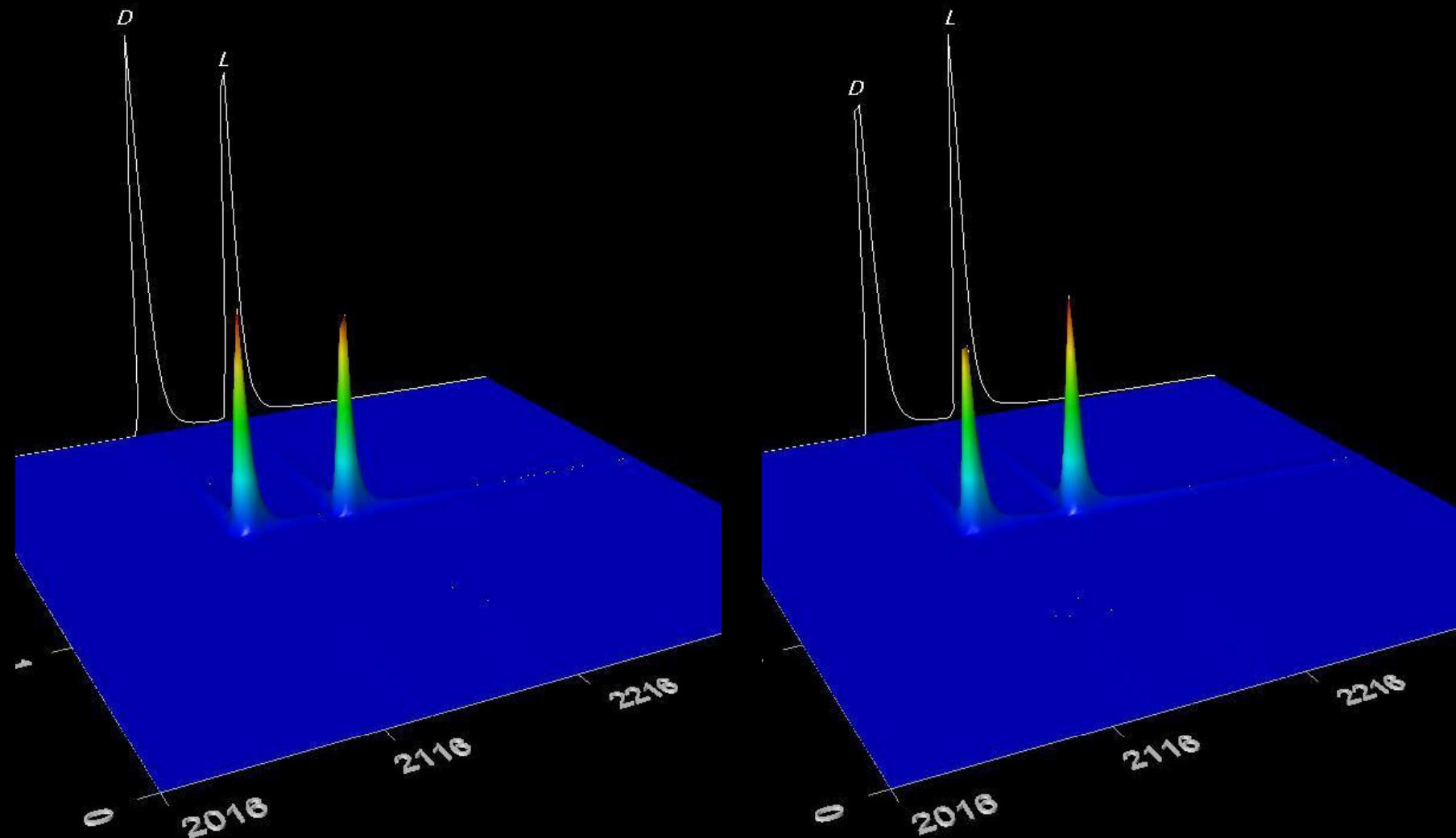


Fig. 30: Multidimensional gas chromatographic enantiomer separation of the ECEE derivatives of the amino acid leucine. Sample (left) was irradiated with *r*-CPL, sample (right) with *i*-CPL at 6.9 eV.

Multidimensional gas chromatogram

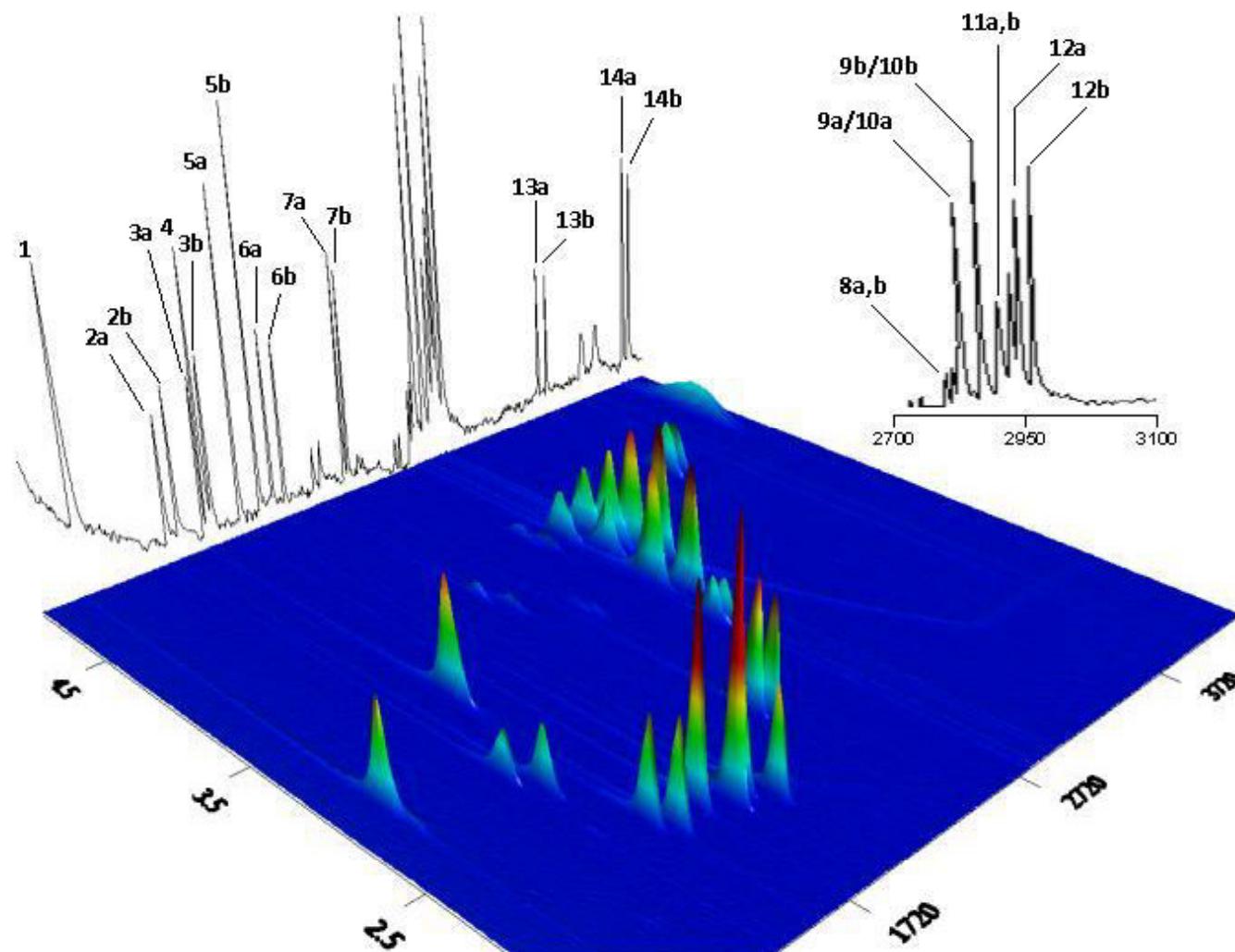


Fig. 30 : Nouveau chromatogramme multidimensionnel et énantiomélectif en phase gazeuse d' un standard externe de 14 acides aminés obtenu au LCMBa de l'UNS. Avant la séparation les acides aminés ont été transformés en dérivés N-ethoxycarbonyl heptafluoro-butanol ester (ECHFE). Sarcosine, 2a d-Alanine, 2b l-Alanine, 3a d-Valine, 4 d,l-Proline, 3b l-Valine, 5a d-Iso-leucine, 5b l-Iso-leucine, 6a d-Leucine, 6b l-Leucine, 7a d-Acidé aspartique, 7b l-Acidé aspar-tique, 8a d-Threonine, 8b l-Threonine, 9a d-Glutamine, 10a d-Méthionine, 9b l-Glutamine, 10b l-Méthionine, 11a d-Serine, 11b l-Serine, 12a d-Phényl-alanine, 12b l-Phénylalanine, 13a d-DAP, 13b l-DAP, 14a d-Histidine, 14b l-Histidine.

***H*ow did life originate ?**

***A*nd why were left-handed molecules
selected for its architecture ?**

- 1) Amino acids form in interstellar space***
- 2) Diamino acids form in interstellar space and in meteorites***
- 3) 2.6 % ee were induced in leucine under interstellar conditions***

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- 4) *Cometary mission Rosetta*

ROSETTA

ROSETTA



SUN

SCALE
134.2
km

DISTANCE
200 000
km



The COSAC experiment onboard Rosetta/Philae

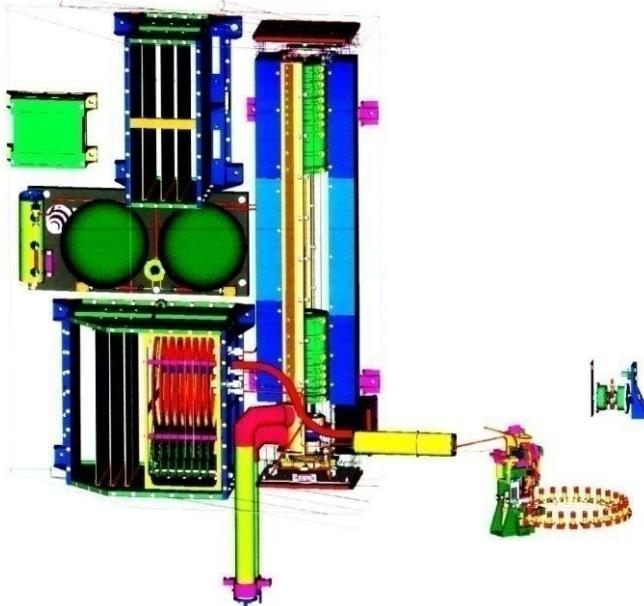


Fig.17: Schematic view of the GC-TCD-MS instrumentation for the COSAC experiment onboard RoLand.

Photos: Max-Planck-Institut für Aeronomie, Katlenburg-Lindau, Germany



Fig.16: COSAC, das Cometary Sampling and Composition Experiment, soll komplexe organische Moleküle auf dem Kometen Tschuryumow-Gerasimenko aufspüren und identifizieren. Das Instrument besteht aus einer Kombination von einem multi-column Gaschromatographen und einem reflectron time-of-flight rTOF Massenspektrometer.

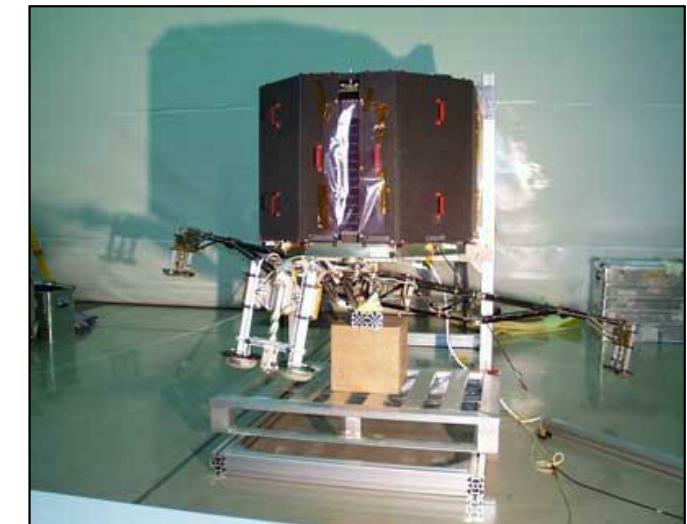


Fig.15: Der "Rosetta Lander", verkleidet mit Schutzpanelen. Zu erkennen sind die Landebeine mit ihren "Füßen" und den Eisschrauben, mit denen sich der Lander in der Kometenoberfläche verankert.



Figure 19: Simulation of the Rosetta spacecraft approaching comet Churyumov-Gerassimenko.
The launch has taken place successfully on 2 March 2004 with an Ariane 5-plus rocket.

Meierhenrich U.J.: *Nachr. Chem.* **50** (2002), 1338-1341.

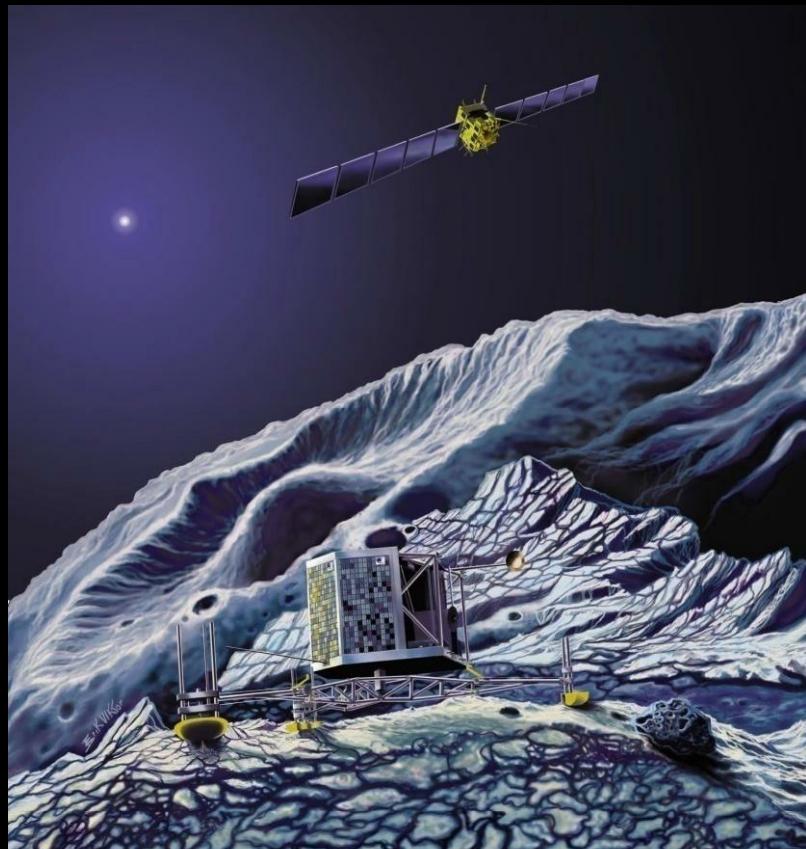


Figure 20: Simulation of the Rosetta Lander Philae close before the landing maneuver on the nucleus of comet Churyumov-Gerassimenko.



**ROSETTA
ON ITS WAY TO 67/P**

ESA ExoMars Mission

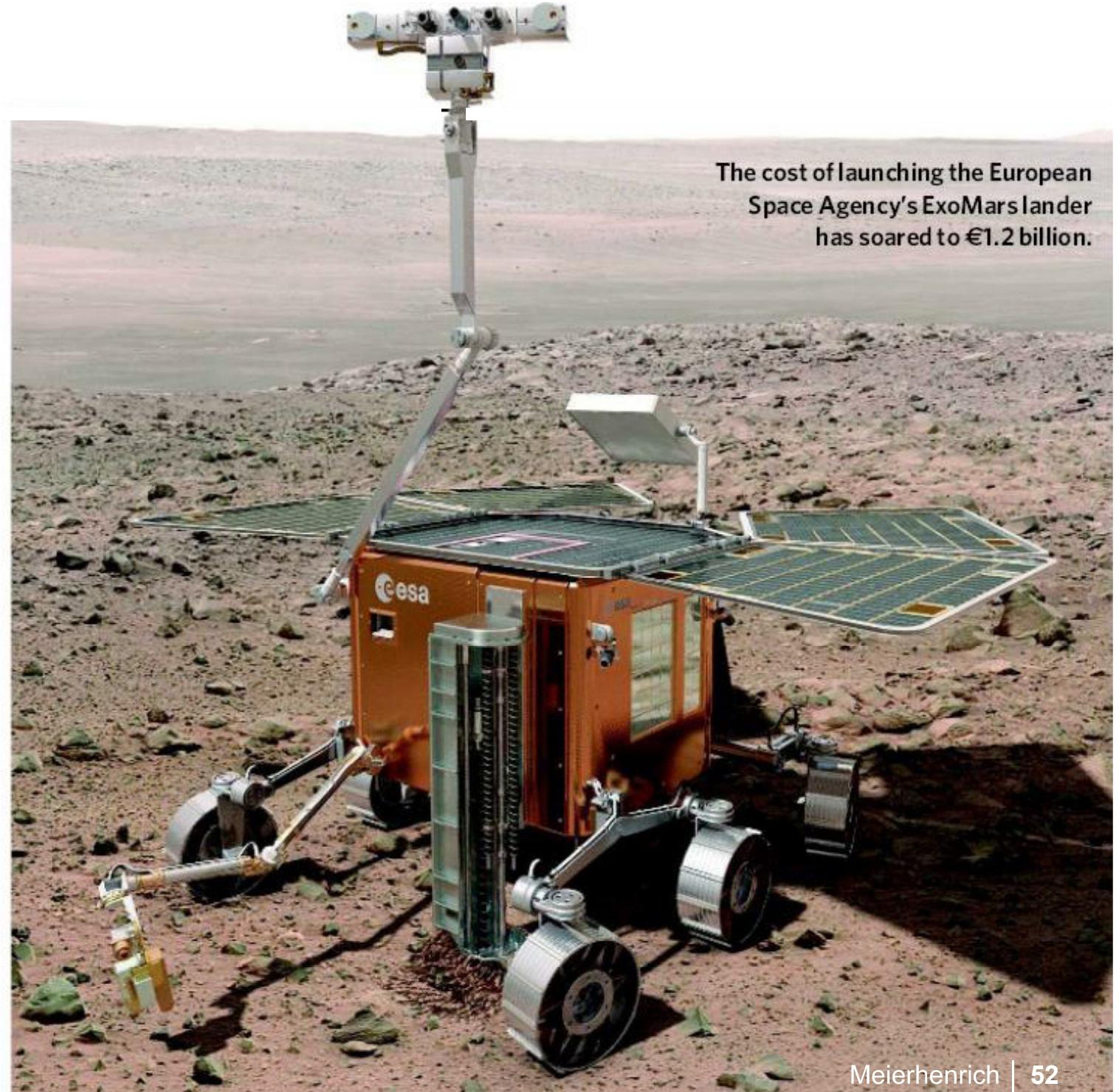
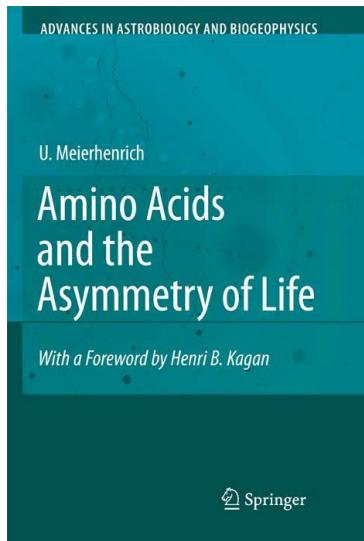


Fig. 9.10. Artist's impression of the ExoMars Rover drilling into the Martian surface. Nature 455 (2008), 840. Credits: ESA

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*A*nd why were left-handed molecules selected for its architecture ?

- 1) *Amino acids form in interstellar space*
- 2) *Diamino acids form in interstellar space and in meteorites*
- 3) *2.6 % ee were induced in leucine under interstellar conditions*
- 4) *The design of cometary mission Rosetta includes chirality*



U. Meierhenrich, Université Nice-Sophia Antipolis, France

Amino Acids and the Asymmetry of Life

Caught in the Act of Formation

"How did life originate and why were left-handed molecules selected for its architecture?" This question of high public and interdisciplinary scientific interest is the central theme of this book. It is widely known that in processes triggering the origin of life on Earth, the equal occurrence, the parity between left-handed amino acids and their right-handed mirror images, was violated. The balance was inevitably tipped to the left – as a result of which life's proteins today exclusively implement the left form of amino acids. Written in an engaging style, this book describes how the basic building blocks of life, the amino acids, formed. After a comprehensible introduction to stereochemistry, the author addresses the inherent property of amino acids in living organisms, namely the preference for left-handedness. What was the cause for the violation of parity of amino acids in the emergence of life on Earth? All the fascinating models proposed by physicists, chemists and biologist are vividly [...]

- A thrilling story built around the question, "How did life originate and why were left-handed molecules selected for its architecture?"
- Topic of high public and interdisciplinary interest
- Strong coverage in the press
- With a foreword by Henri B. Kagan

2008. XX, 242 p. 127 illus., 12 in color. (Advances in Astrobiology and Biogeophysics) Hardcover



Fig. 2.1 *Escherichia coli* bacterial cultures. Luria-Burk-Bauer is a routine medium to culture bacteria with the loss of stereoselectivity. It is usually verified that 50% of the chiral amino acids are converted to the left-handed form. The figure shows a petri dish with a colony of a standard spore 1 bacterial species randomly and very evenly distributed.

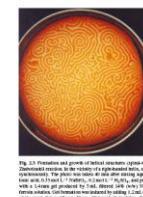


Fig. 2.2 *Escherichia coli* bacterial cultures. Luria-Burk-Bauer is a routine medium to culture bacteria with the loss of stereoselectivity. It is usually verified that 50% of the chiral amino acids are converted to the left-handed form. The figure shows a petri dish with a colony of a standard spore 1 bacterial species randomly and very evenly distributed.

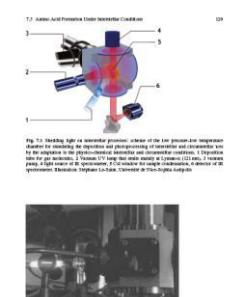


Fig. 7.1 *Light intensity*. In the laboratory, the intensity of the light source is important. The intensity of the light source is measured by the detector. The figure shows a schematic diagram of the experimental setup used to measure the intensity of the light source. The light source is a blue rectangle, and the detector is a small circle at the end of the optical fiber.



Fig. 8.1 *The protein effect on the light source*. The protein effect on the light source is measured by the detector. The figure shows a schematic diagram of the experimental setup used to measure the protein effect on the light source. The light source is a blue rectangle, and the detector is a small circle at the end of the optical fiber.

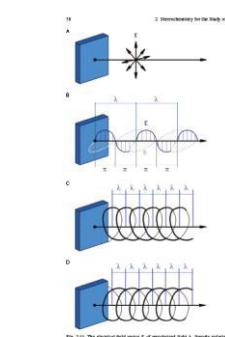


Fig. 9.1 *The electric field effect of the segmented light*. In the present type II, the segmented light source is used to measure the intensity of the light source. The figure shows a schematic diagram of the experimental setup used to measure the intensity of the light source. The light source is a blue rectangle, and the detector is a small circle at the end of the optical fiber.



Fig. 10.1 *The light source*. The light source is used to measure the intensity of the light source. The figure shows a schematic diagram of the experimental setup used to measure the intensity of the light source. The light source is a blue rectangle, and the detector is a small circle at the end of the optical fiber.



Fig. 11.1 *The Rosetta Comet landing site*. The lander Philae successfully lands on the surface of comet 67P/Churyumov-Gerasimenko. The landing is scheduled for November 12, 2014. The lander will explore the surface of the comet to study its composition and history. The lander is shown in its deployed state, with its solar panels extended.



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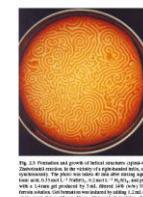


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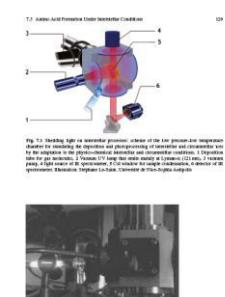


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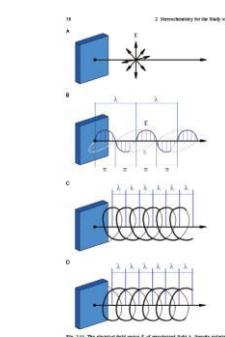


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Amino Acids and the Asymmetric Origin of Life

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Dr. L. d'Hendecourt **Institut d'Astrophysique Spatiale**

Dr. J. P. Dworkin **Goddard**



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