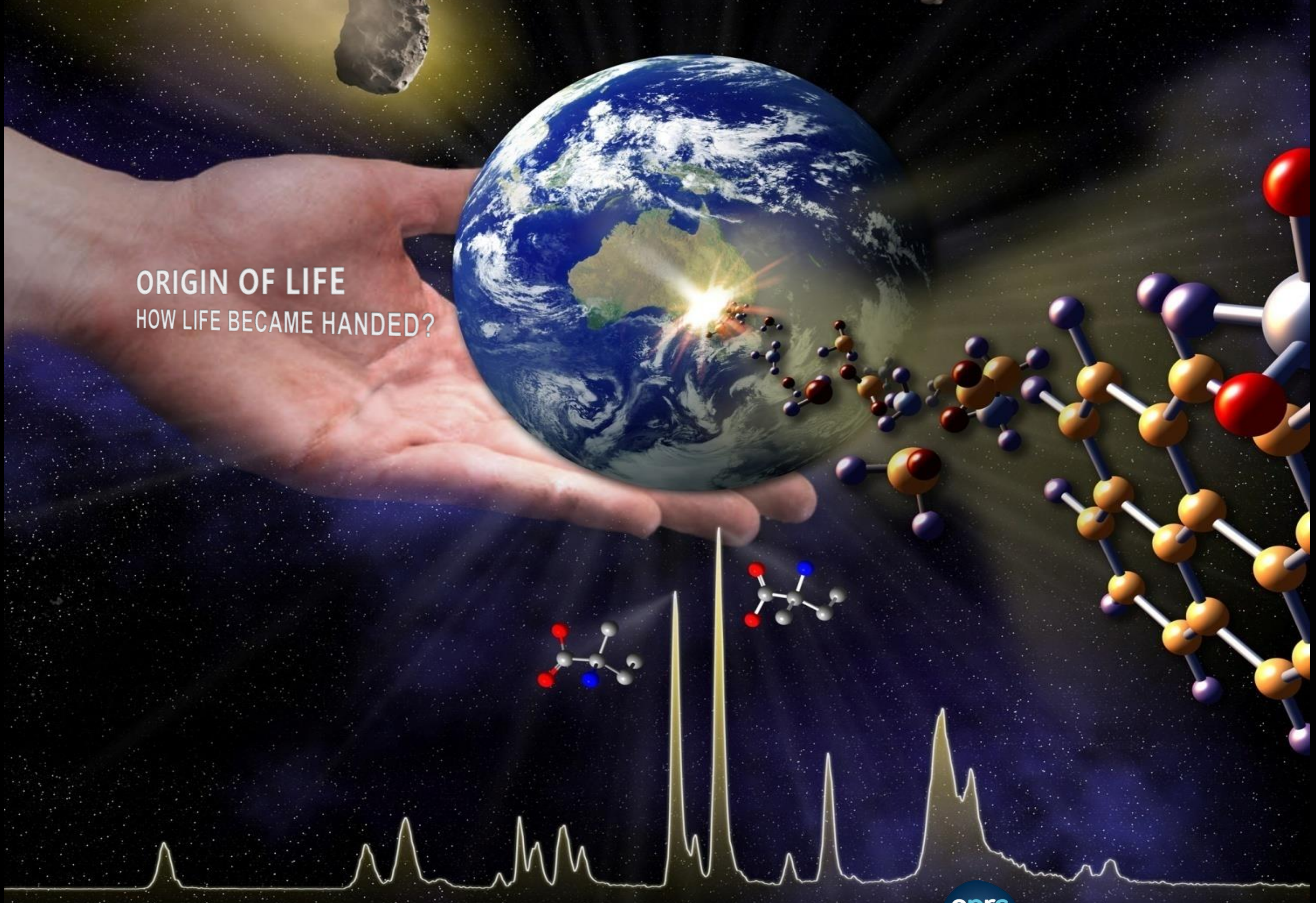
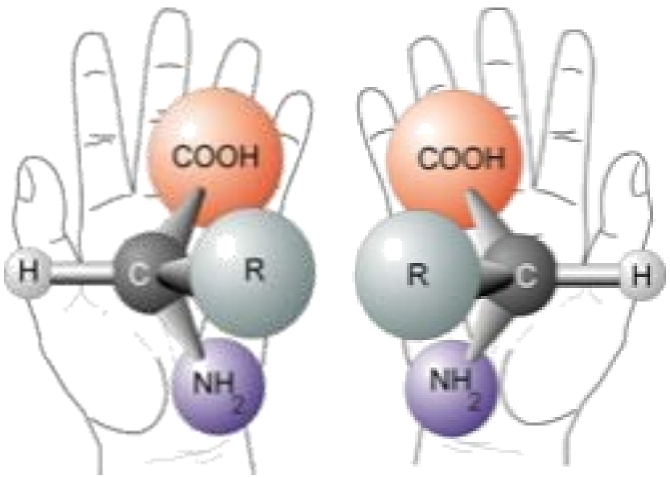
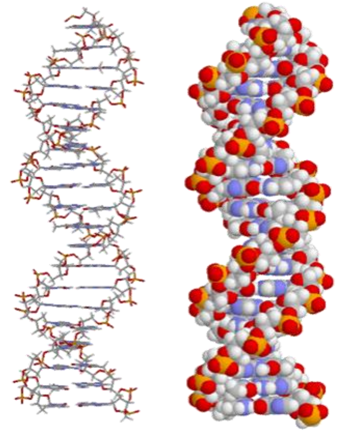


Cornelia MEINERT, *Institut de Chimie de Nice,* Université Côte d'Azur
Rencontres SFE 2018 à l'Observatoire de Haut Provence, October 16th, 2018

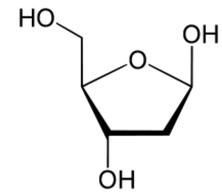
HOMOCHIRALITY OF LIFE





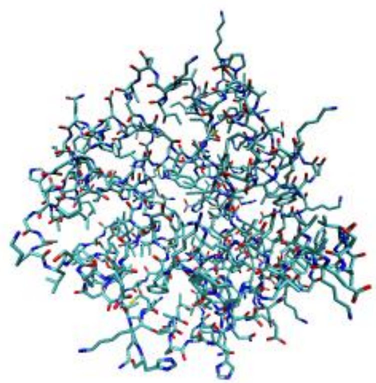
DNA

chiral monomer



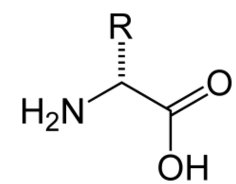
D-2-deoxyribose

carbohydrates



Proteins

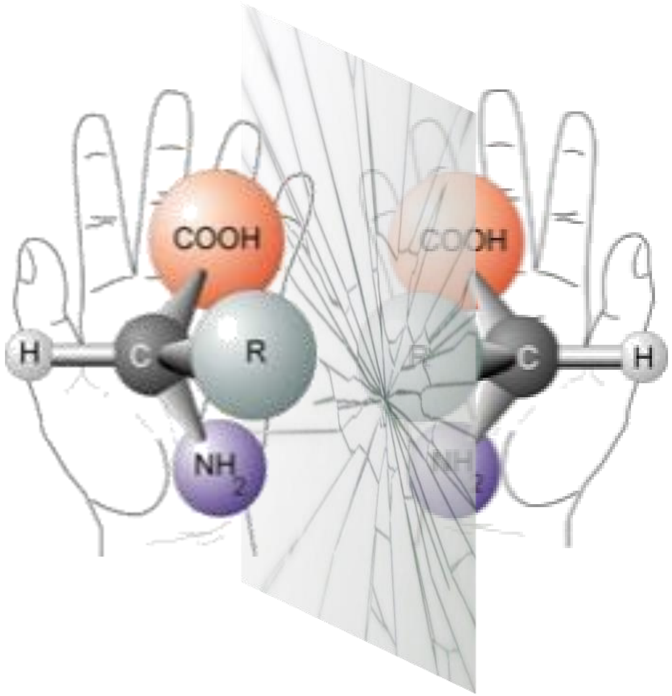
chiral monomer

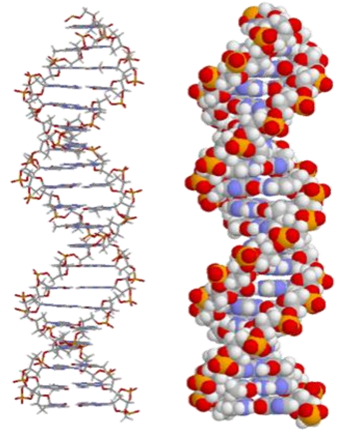


α-L-amino acids

Amino acids

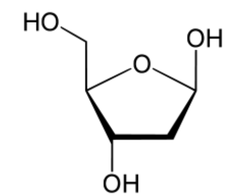
Homochirality of Life





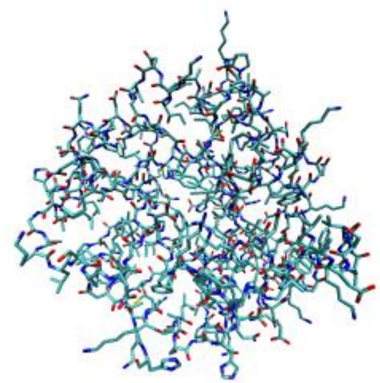
DNA

chiral monomer



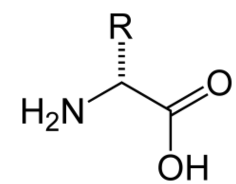
D-2-deoxyribose

carbohydrates



Proteins

chiral monomer



α-L-amino acids

Amino acids

How did life originate ?

And why were left-handed amino acids & right-handed sugars selected for its architecture ?

« La lumière a donné un sens à la vie »
Le Monde: 08-01-2011

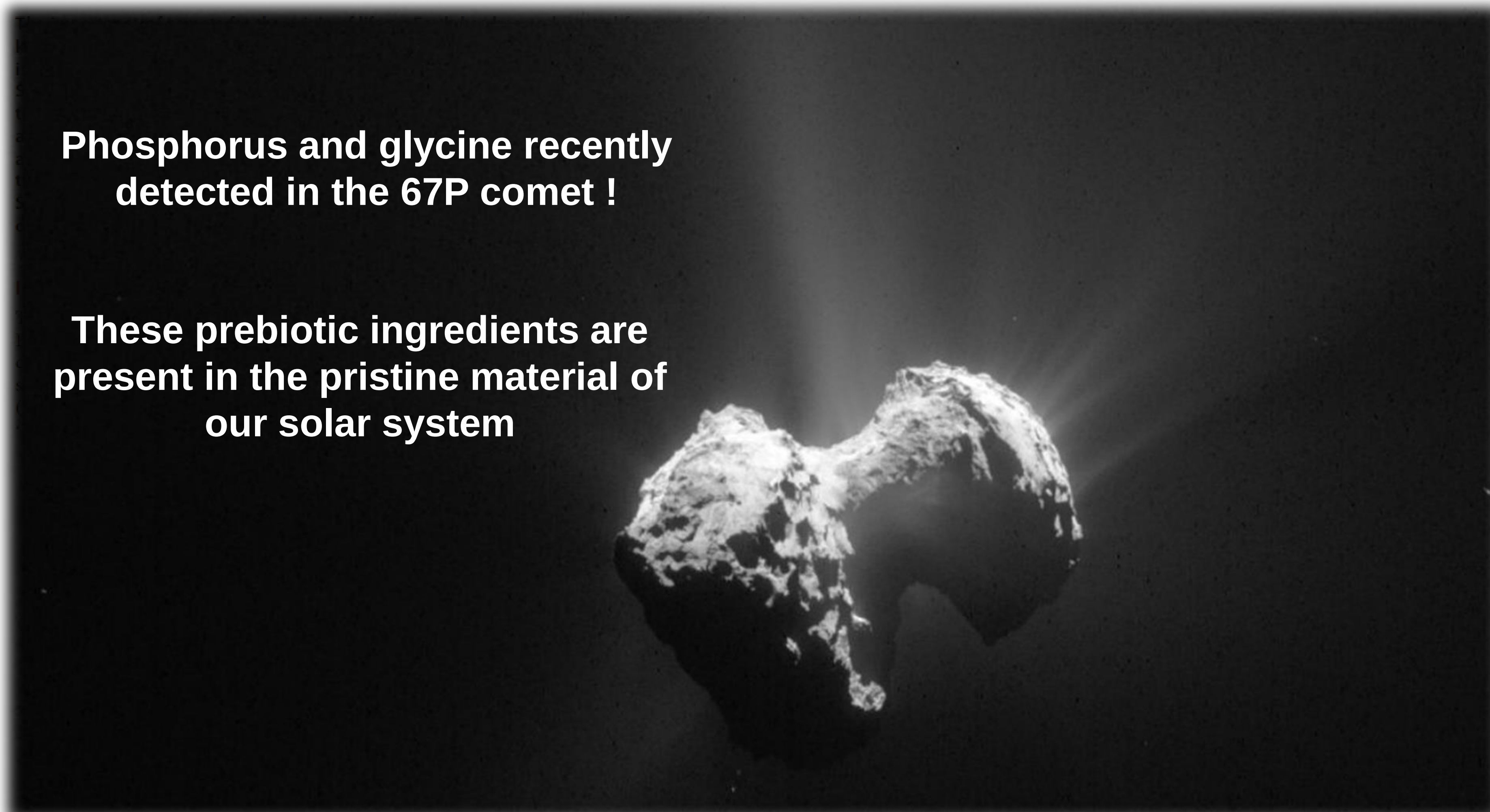
RESEARCH ARTICLE

SPACE SCIENCES

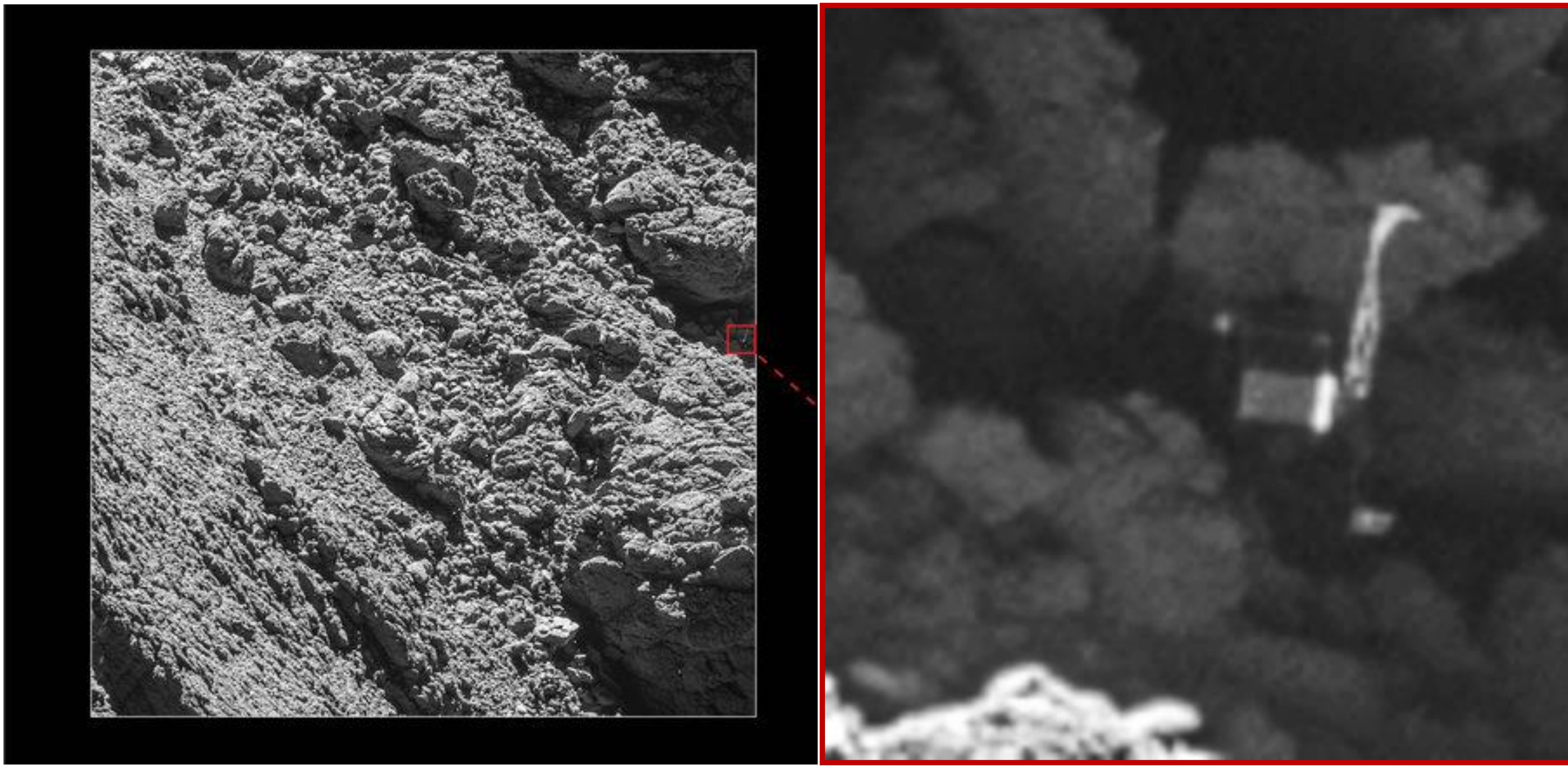
Prebiotic chemicals—amino acid and phosphorus—in the coma of comet 67P/Churyumov-Gerasimenko

10.1126/sciadv.1600285

Kathrin Altwegg,[1,2]* Hans Balsiger,[1] Akiva Bar-Nun,[3] Jean-Jacques Berthelier,[4] Andre Bieler,[1,5] Peter Bochsler,[1] Christelle Briois,[6] Ursina Calmonte,[1] Michael R. Combi,[5] Hervé Cottin,[7] Johan De Keyser,[8] Frederik Dhooghe,[8] Bjorn Fiethe,[9] Stephen A. Fuselier,[10] Sébastien Gasc,[1] Tamas I. Gombosi,[5] Kenneth C. Hansen,[5] Myrtha Haessig,[1,10] Annette Jäckel,[1] Ernest Kopp,[1] Axel Korth,[11] Lena Le Roy,[2] Urs Mall,[11] Bernard Marty,[12] Olivier Mousis,[13] Tobias Owen,[14] Henri Rème,[15,16] Martin Rubin,[1] Thierry Sémon,[1] Chia-Yu Tzou,[1] James Hunter Waite,[10] Peter Wurz[1]



PHILAE FOUND!



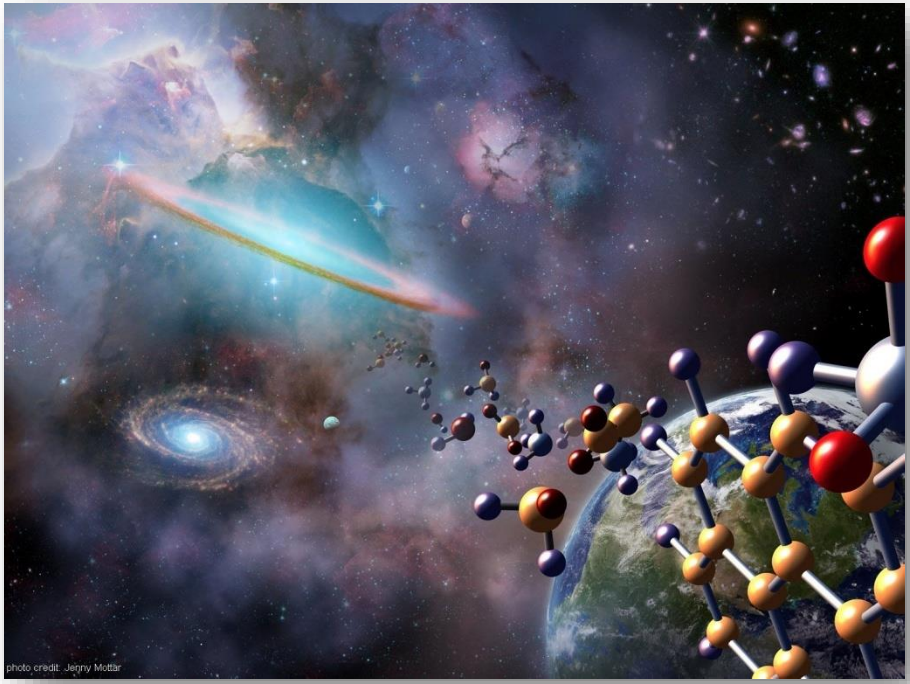
The images were taken **on 2 September 2016** by the OSIRIS narrow-angle camera as the orbiter came within 2.7 km of the surface.

Building blocks of life: Where do they come from?

Murchison meteorite contains over 500 organic molecules:

Hydrocarbons	> 20 ppm
Aldehydes and ketones	> 10 ppm
Alcohols	> 10 ppm
Amines	> 1 ppm
Carboxylic acids	> 100 ppm
Sulfonic acids	> 100 ppm
Phosphonic acids	> 1 ppm
Purines & Pyrimidines	> 1 ppm
Amino acids	**> 10 ppm**

Cronin J.R.: In: Brack, A., The Molecular Origins of Life. Cambridge University Press 1998, pp. 119-146.

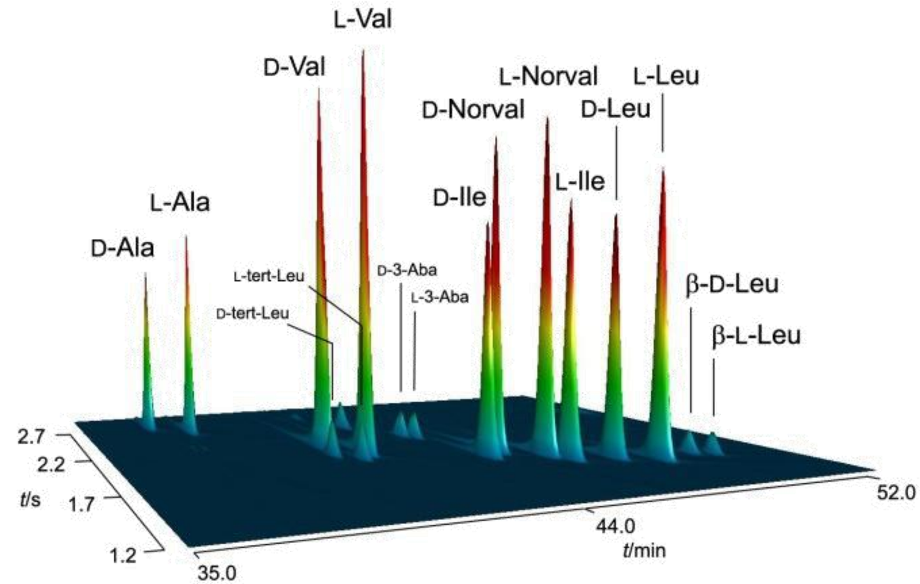


Cosmic Evolution of elements and organic molecules.

ENANTIOMER-ENRICHED AMINO ACIDS IN METEORITES

Table 1| Enantiomeric excesses ee_L in the Murchison meteorite.

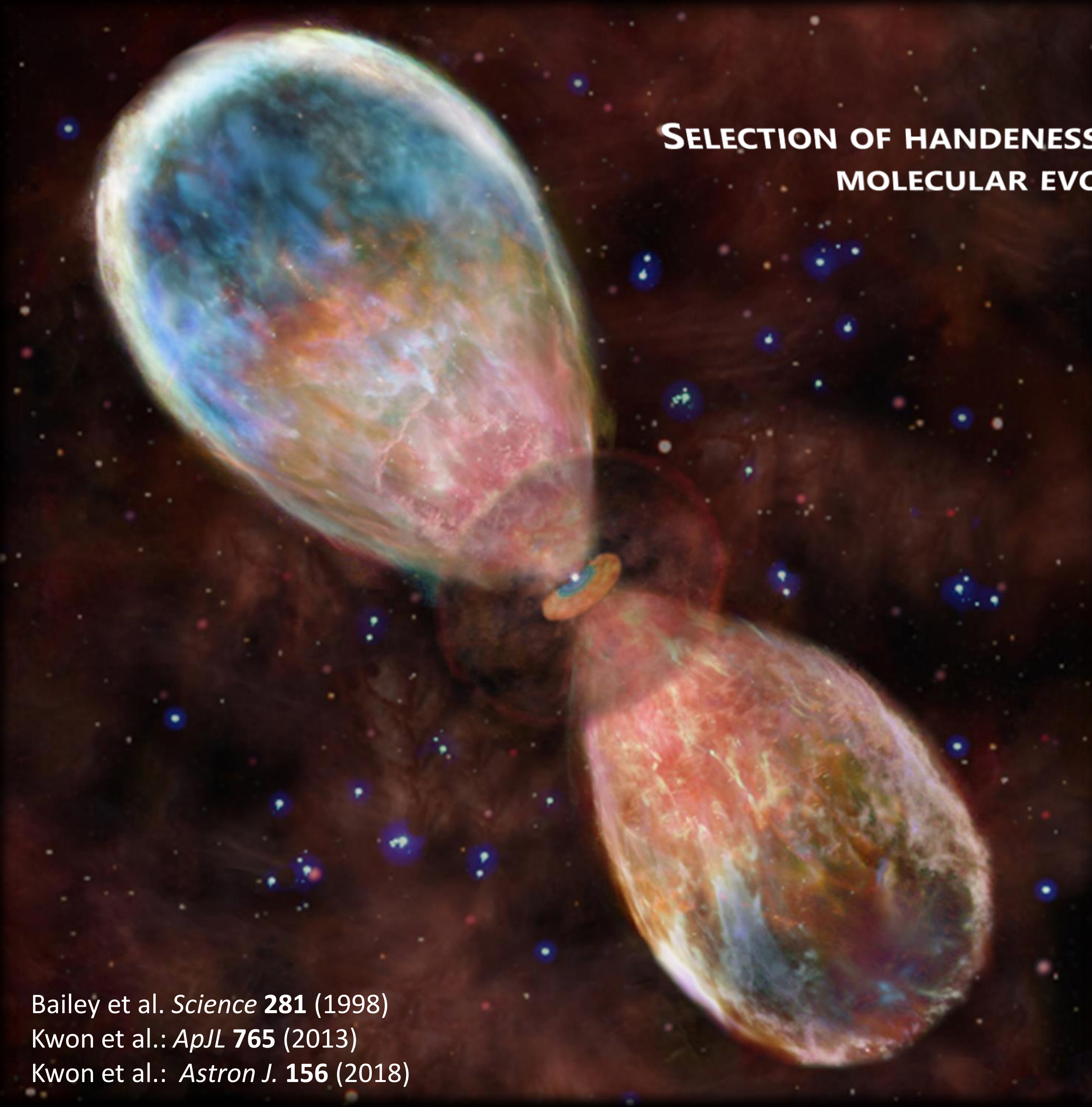
Amino acid	**ee_L (%) ± 3σ**	**R_S**
Proteinogenic amino acids		
Alanine	3.16 ± 0.80	4.00
Aspartic acid	4.31 ± 0.59	2.25
Valine	4.88 ± 0.73	3.20
Glutamic acid	3.79 ± 1.07	3.67
Isoleucine	9.49 ± 1.16	9.00
Leucine	26.33 ± 0.76	4.75
non-proteinogenic amino acids		
2-Aminobutyric acid	2.04 ± 0.86	3.80
3-Aminobutyric acid	5.95 ± 0.62	1.43
Norvaline	0.55 ± 0.21	4.50
Pyroglutamic acid	3.85 ± 0.78	3.20
non-proteinogenic α-dialkyl amino acids		
Isovaline	4.61 ± 0.83	1.67
Methylpyroglutamic acid	0.61 ± 0.03	3.60
Methylleucine	6.16 ± 0.26	2.00

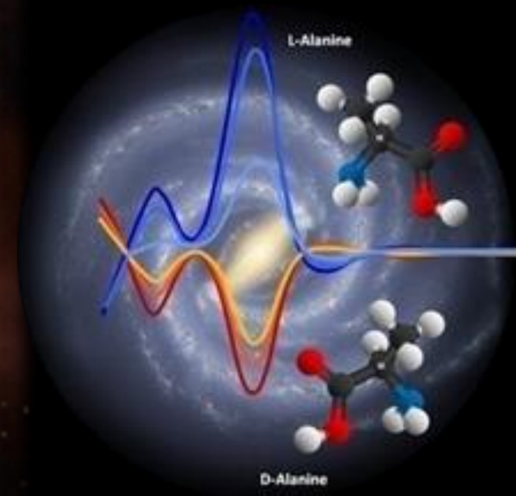


Resolution of amino acid enantiomers in a sample of Murchison using ***GC×GC-TOFMS****.*

Angew. Chem. Int. Ed. **54** (2015), 1402–1412.
ChemPlusChem **79**, 781–785 (2014).
J. Chromatogr. A **1433**, 131–136 (2016).

SELECTION OF HANDENESS AT THE DAWN OF MOLECULAR EVOLUTION

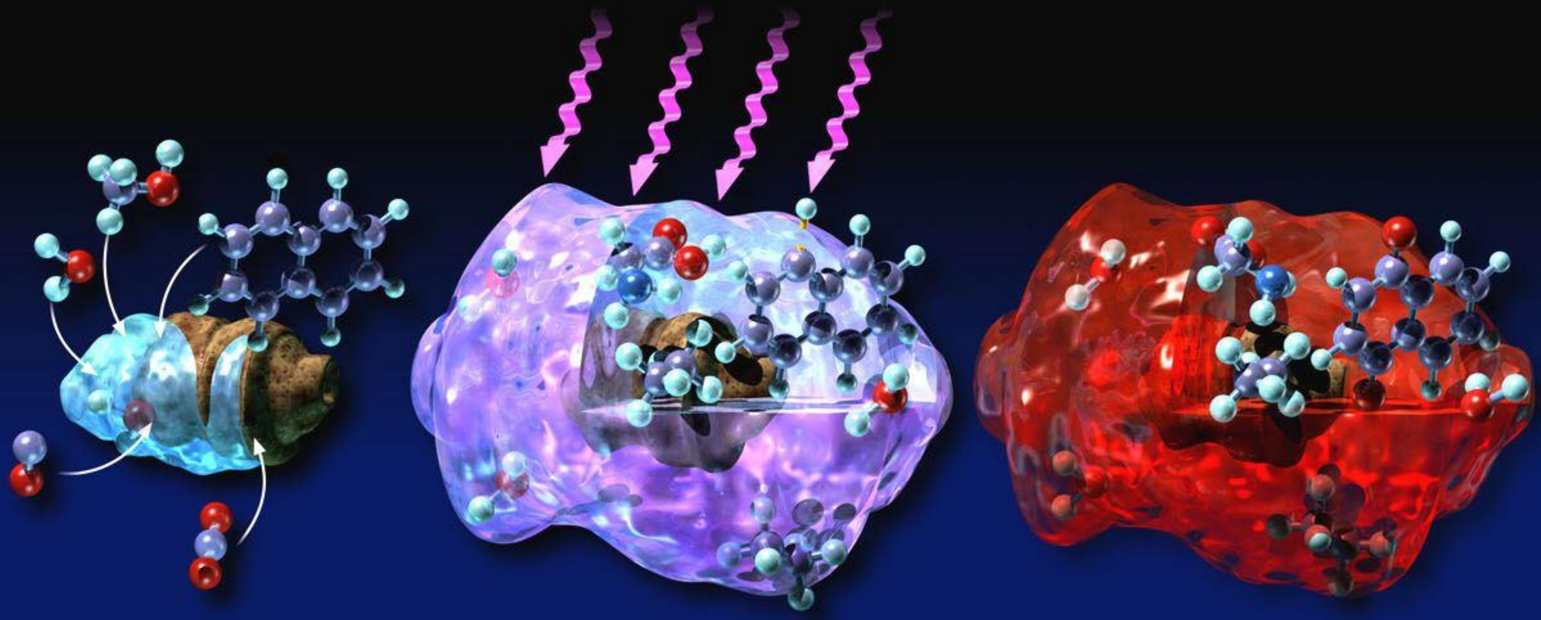




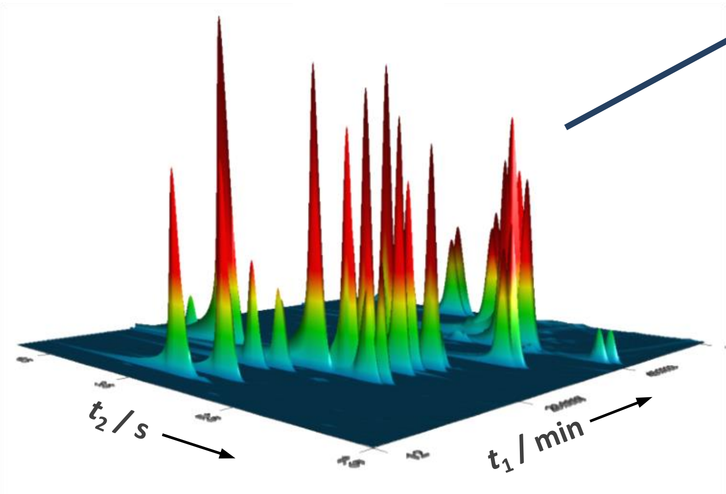
Chem. Soc. Rev. 2012

Bailey et al. *Science* **281** (1998)
Kwon et al.: *ApJL* **765** (2013)
Kwon et al.: *Astron J.* **156** (2018)

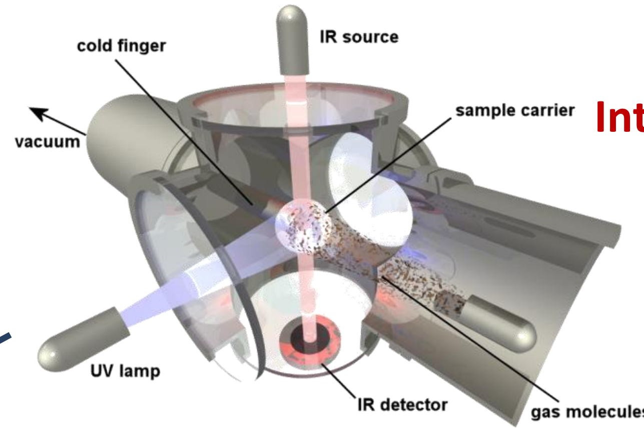
INTERSTELLAR SYNTHESIS OF CHIRAL MOLECULES



Enantioselective multidimensional gas chromatography



Angew. Chem. 2012



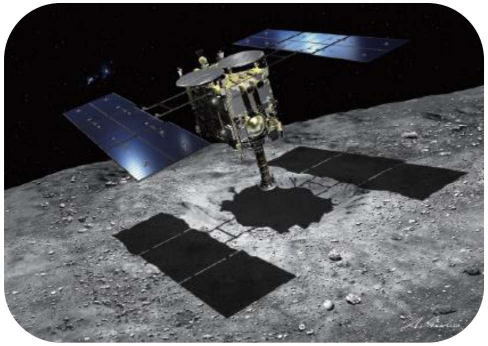
Interstellar ice simulations

PNAS 2015
Science 2016

ee ≠ 0

Meteorites

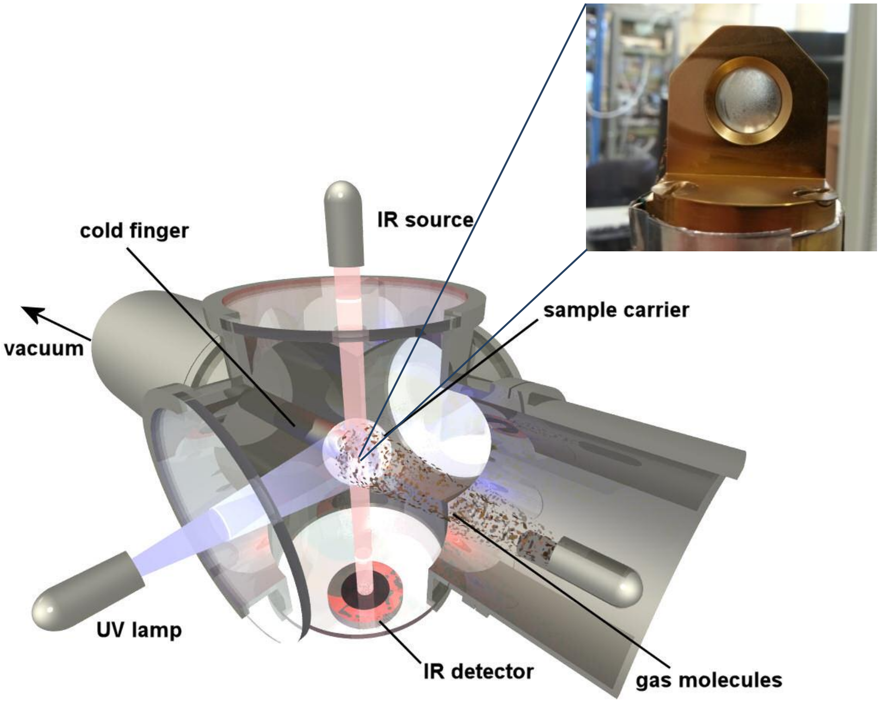
Angew. Chem. 2015



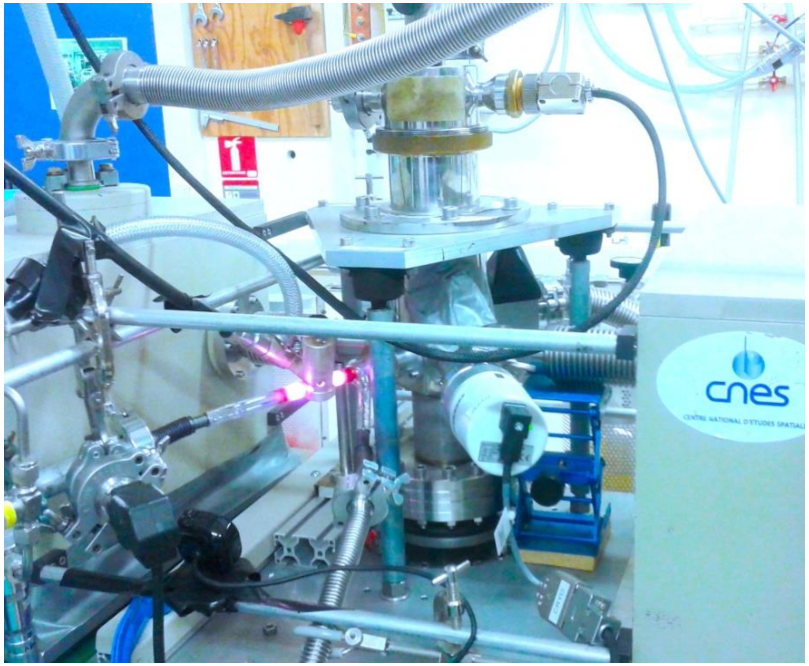
Asteroid sample return missions

Hayabusa2 (JAXA), OsirisRex (NASA)

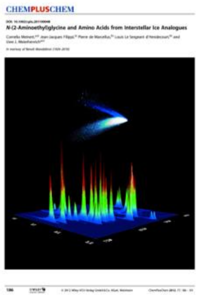
PRIMITIVE CHEMICAL SYNTHESIS: WHAT IS POSSIBLE UNDER SIMULATED INTERSTELLAR CONDITIONS?



Principle of a simulation chamber for interstellar photochemistry: *the ice sample composed of H_2O, NH_3, and $^{13}CH_3OH$ is deposited in the center on a MgF_2-window at a temperature of 80 K and irradiated by vacuum UV light.*



Space simulation chamber *@Institut d'Astrophysique Spatiale (IAS), CNRS Université Paris-Sud, Orsay.*

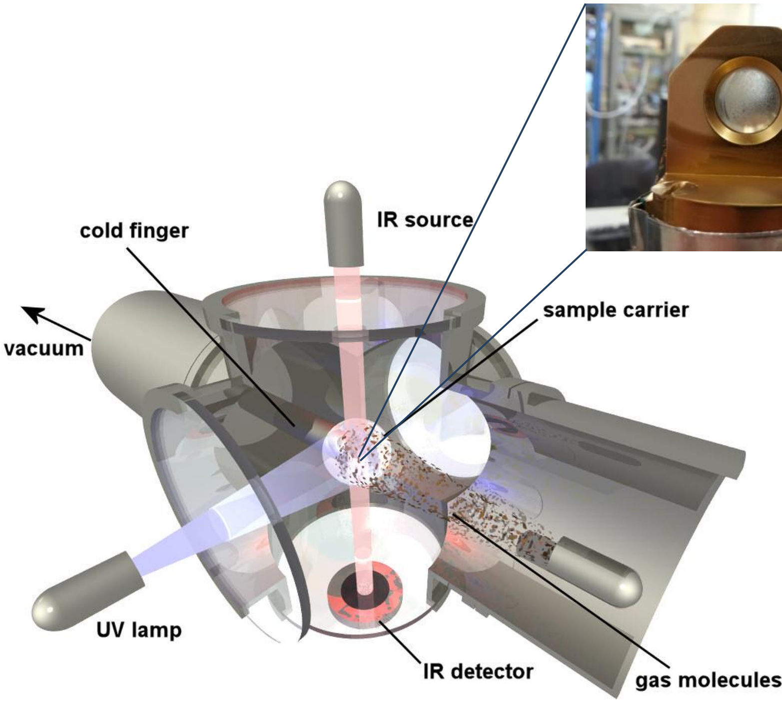

CHEMPLUSCHEM

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

ChemPlusChem **77** (2012), 186–191;

Nature **416** (2002), 403–406.

AMINO & DIAMINO ACIDS DETECTED IN COMETARY ANALOGUES



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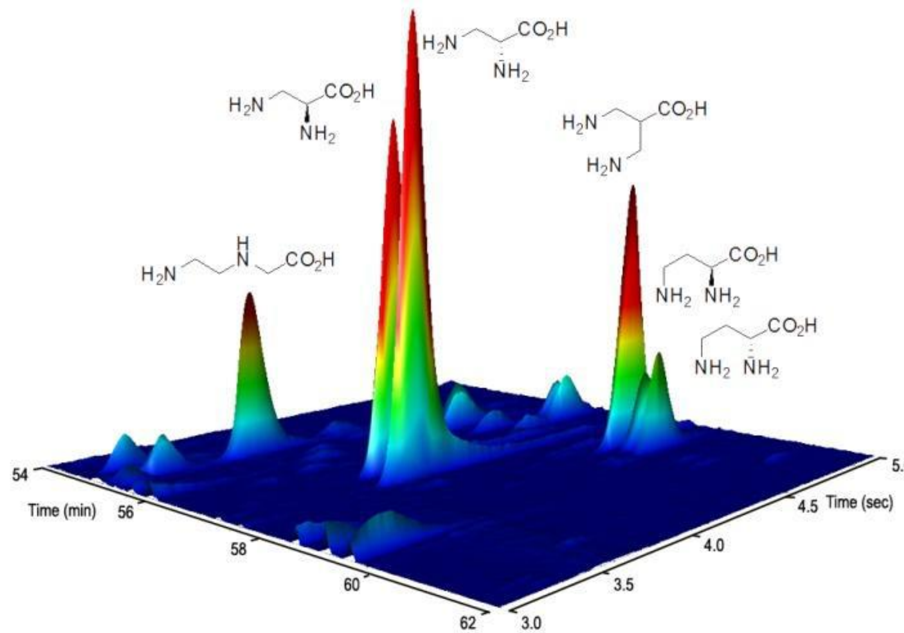
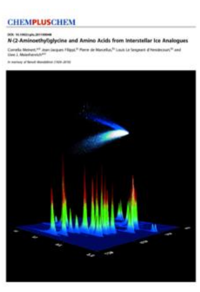


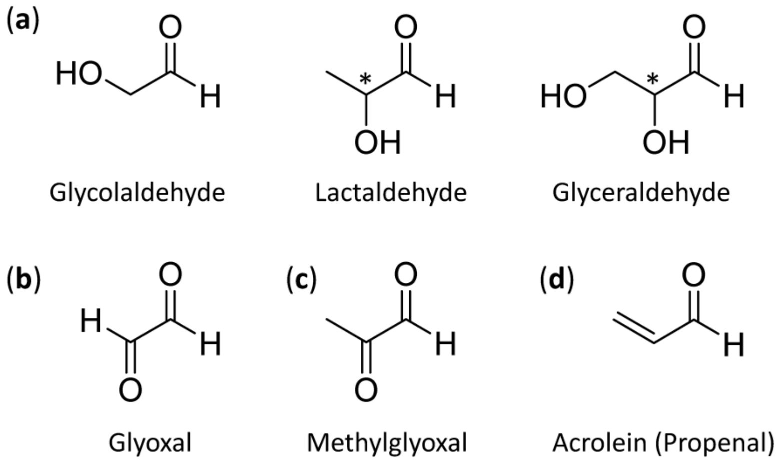
Close-up view of the ***2D enantioselective gas chromatogram depicting ECHFBE derivatives of*** ^{13}***C-labelled diamino acids****.*



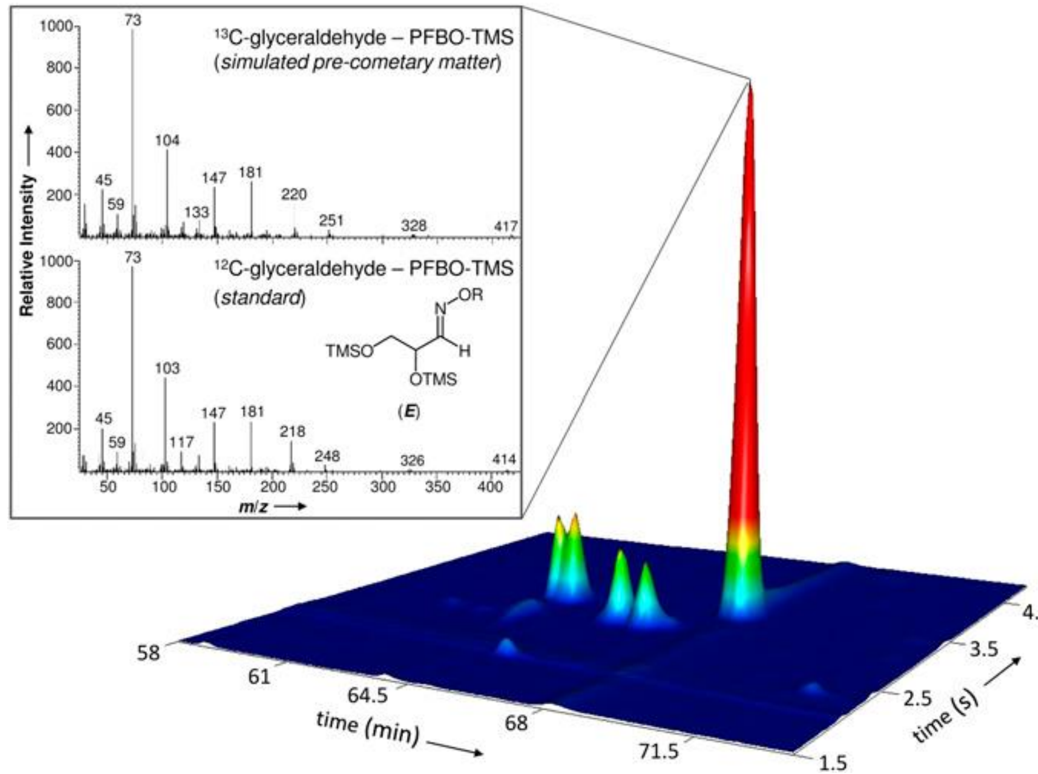
ChemPlusChem **77** (2012), 186–191;

Nature **416** (2002), 403–406.

ALDEHYDES DETECTED IN COMETARY ANALOGUES

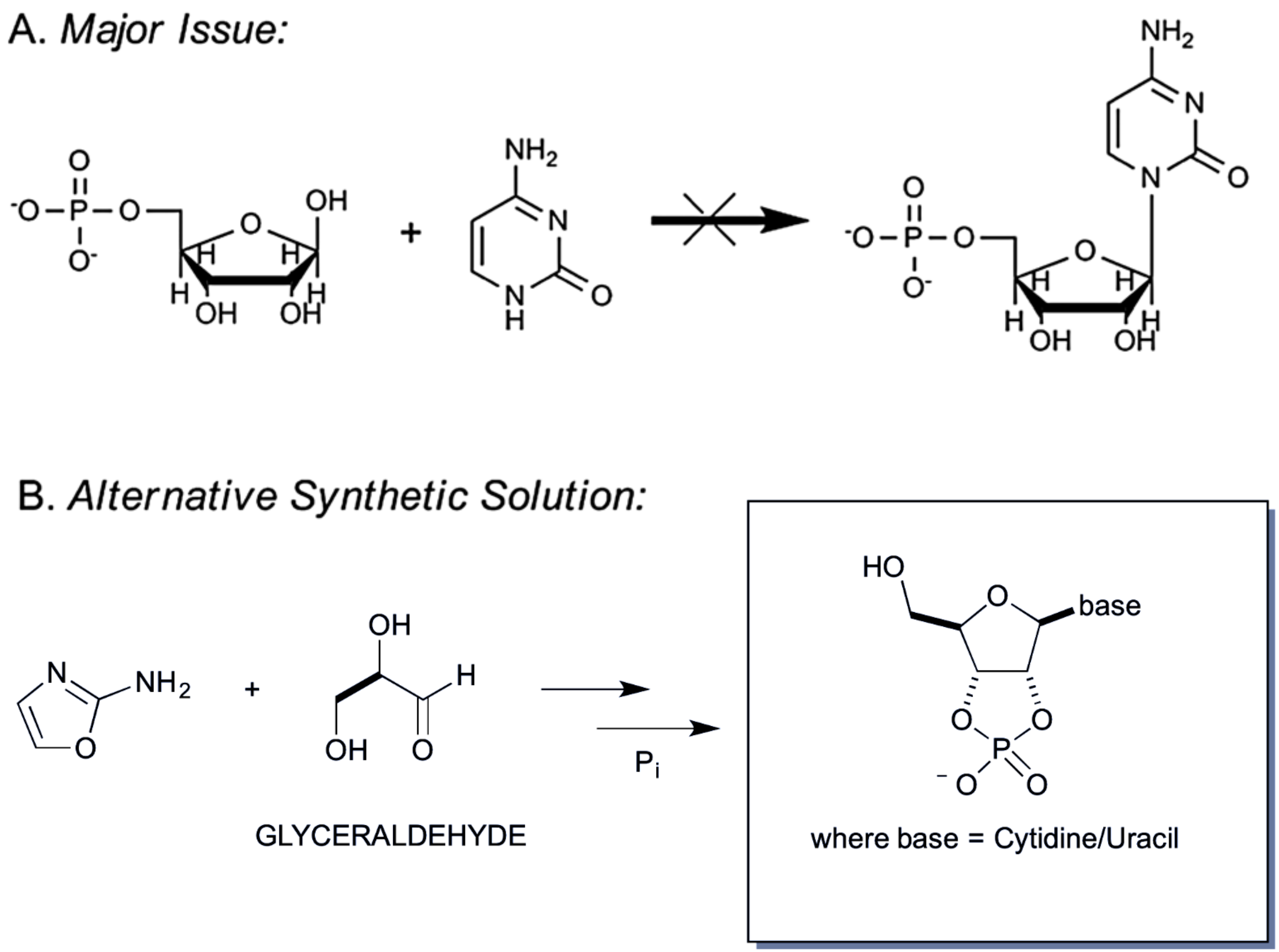


Selected aldehydes identified at room temperature in simulated pre-cometary organic residues.



Close-up view of the ***2D enantioselective gas chromatogram depicting ECHFBE derivatives of*** ^{13}***C-labelled diamino acids****.*

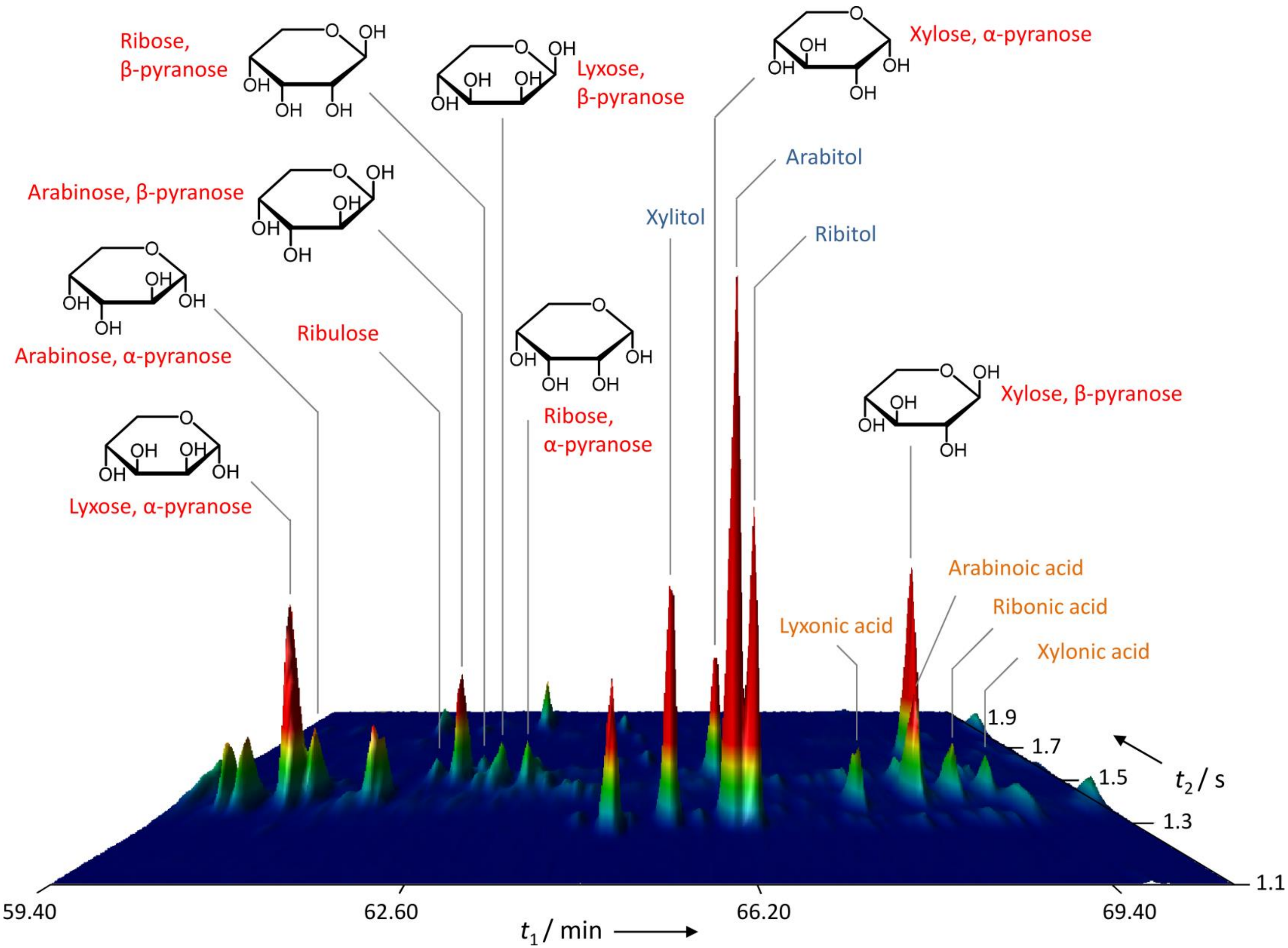
PNAS **112** (2015), 965–970.



(A) The RNA World is thermodynamically unfavorable if originating from ribose sugar plus nucleobase; (B) an alternative route to an RNA World.

Powner, Gerland, Sutherland. *Nature* **459** (2009), 239–242

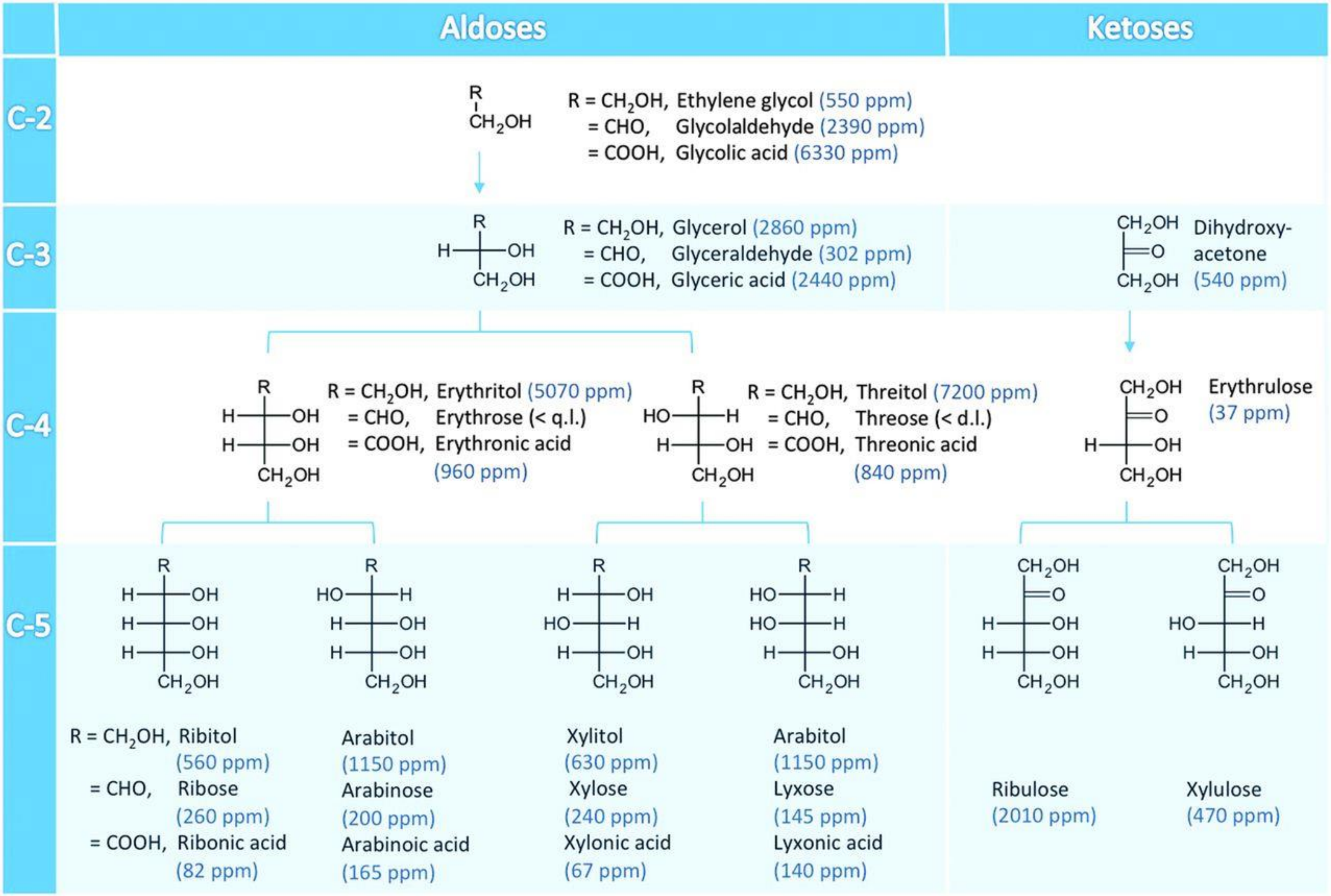
RIBOSE DETECTED IN COMETARY ANALOGUES



RIBOSE - A key sugar found in RNA has been created in the laboratory under conditions similar to those around comets.

Science **352** (2016), 208–212.

RIBOSE & ITS SISTER ALDOPENTOSES DETECTED IN COMETARY ANALOGUES

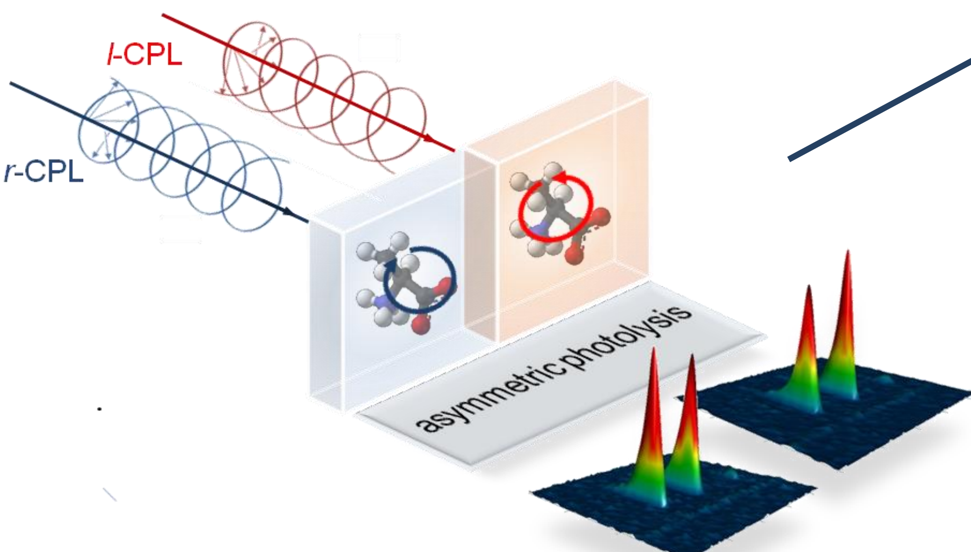


Science **352** (2016), 208–212.

II – CHIRAL PHOTON-INDUCED ASYMMETRY

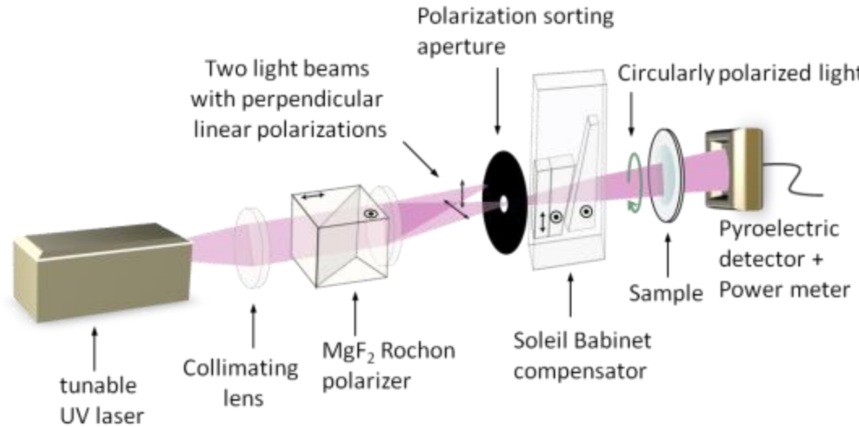
SOLEIL SYNCHROTRON

Asymmetric photolysis / photosynthesis



in-house **energy-tunable laser**

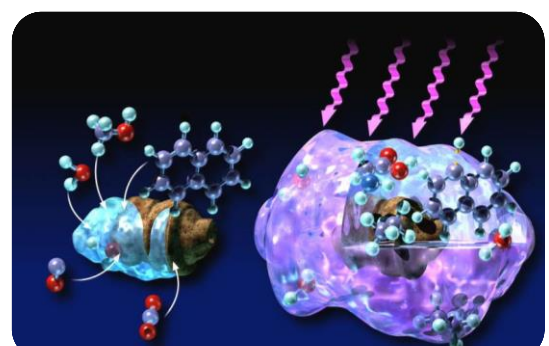
CPL-irradiation experiments….coming soon



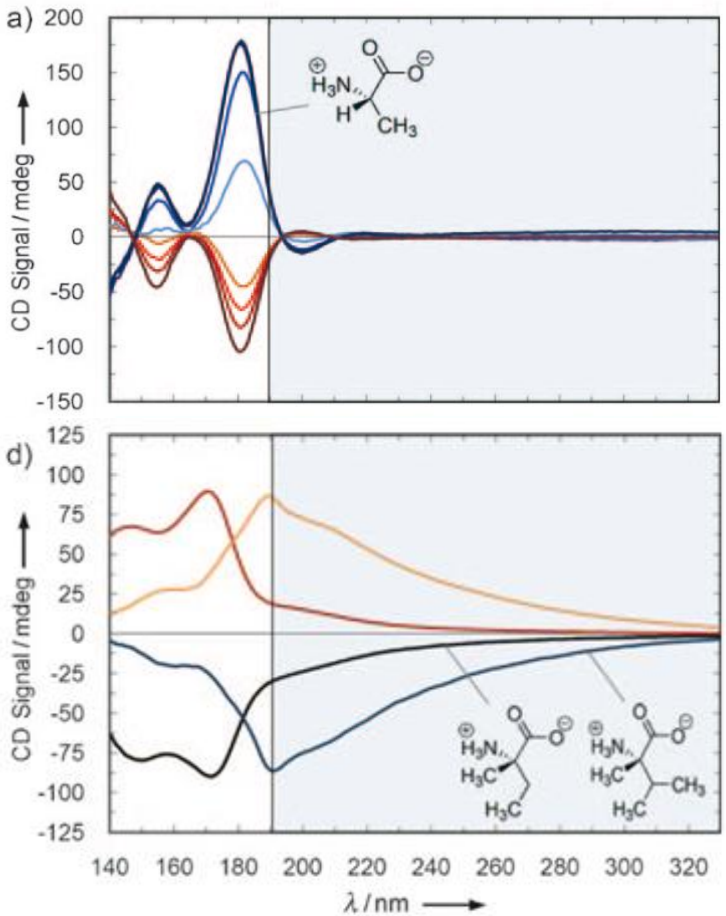
Enantiospecific photochemistry depends on:

$\Delta\varepsilon = \varepsilon_R - \varepsilon_L$

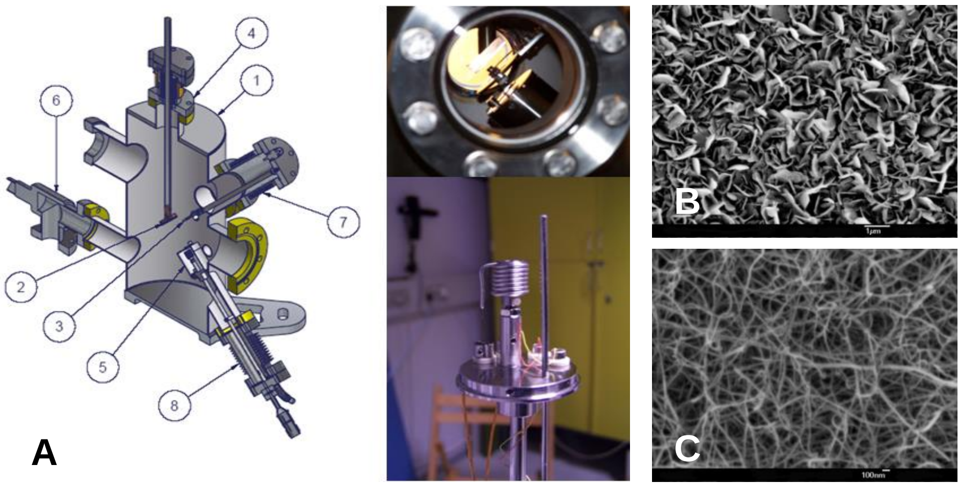
Absolute asymmetric *photo*-synthesis of chiral genome & proteome precursors



VUV CIRCULAR DICHROISM SPECTRA OF SOLID STATE AMINO ACIDS



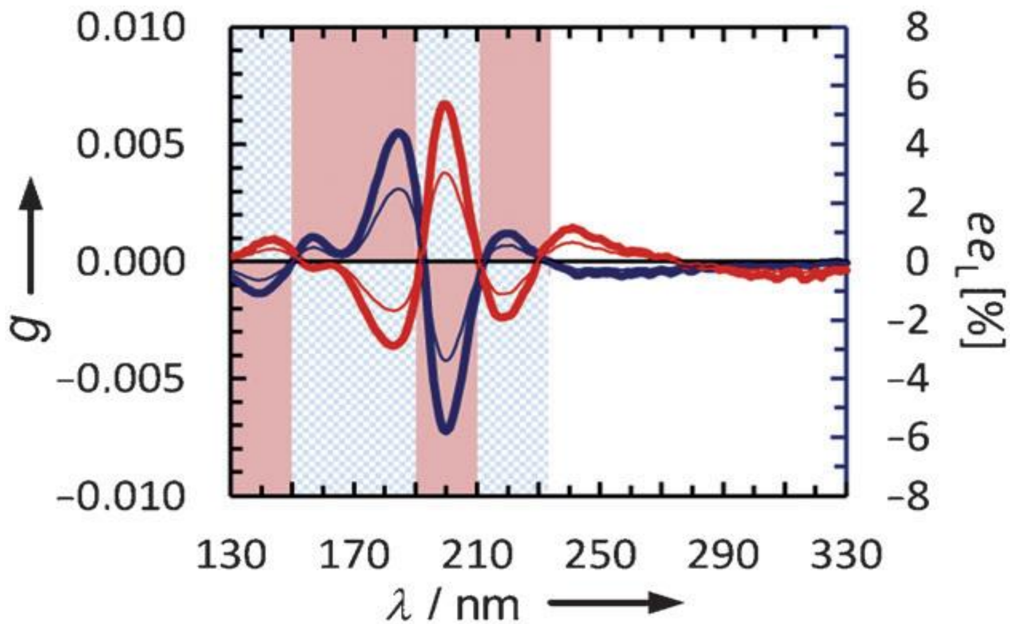
CD spectra of isotropic amorphous amino acid films *between 140 and 190 nm. a) Blue lines: L-alanine; red lines: D-alanine. b) L-isovaline (black), D-isovaline (red), L-α-methyl valine (blue), D-α-methyl valine (orange).*



Temperature- and pressure-controlled UHV chamber *for controlled sublimation of amino acids (**A**).* ***Scanning electron microscope (SEM) images*** *of isotropic amorphous L-valine and (**B**) D-α-methyl valine (**C**). The non-crystalline **isotropic amorphous films** show no long-range order.*

Angew. Chem. Int. Ed. **49** (2010), 7799–7802.

ANISOTROPY SPECTRA OF SOLID STATE AMINO ACIDS



Anisotropy spectra of isotropic amorphous D-alanine (red) and L-alanine (blue) in the vacuum UV and UV spectral region. *Thin lines represent the L-enantiomeric excess (ee_L) inducible by either left- or right-cpl into alanine at a given photolysis rate of 99.99 %.*

Angew. Chem. Int. Ed. **51** (2012), 4484–4487

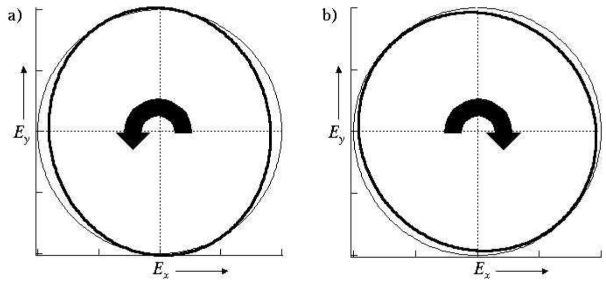
$$g(\lambda) = 4R/D = \Delta\varepsilon/\varepsilon$$

$$\boldsymbol{ee \geq (1 - (1 - \xi)^{g/2}) \times 100\ \%}$$

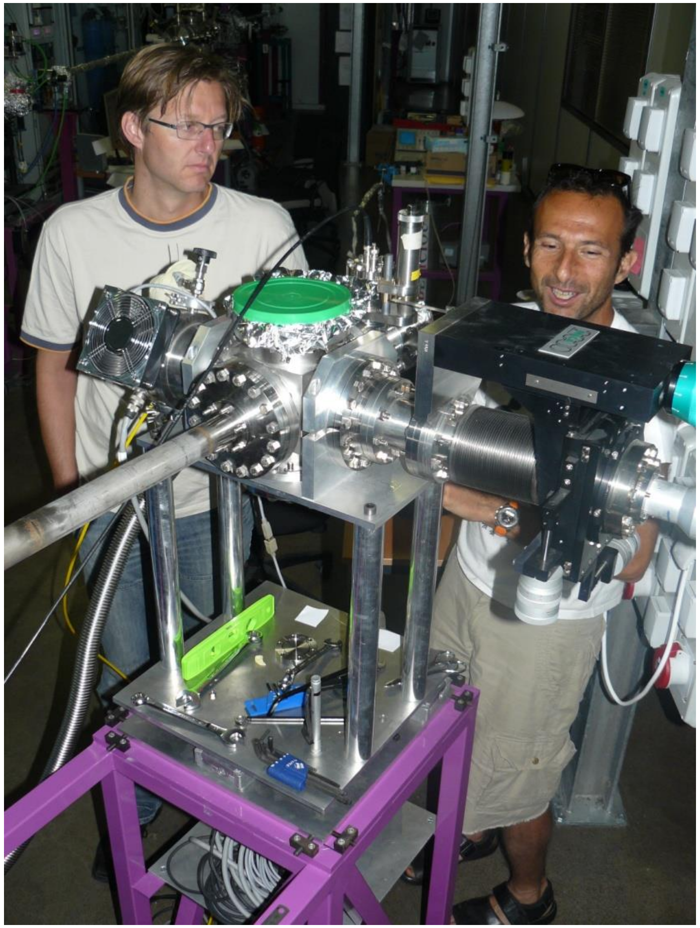
a) prediction of the sign of the induced *ee*,

b) determination of kinetics and *ee*s of enantioselective photolysis,

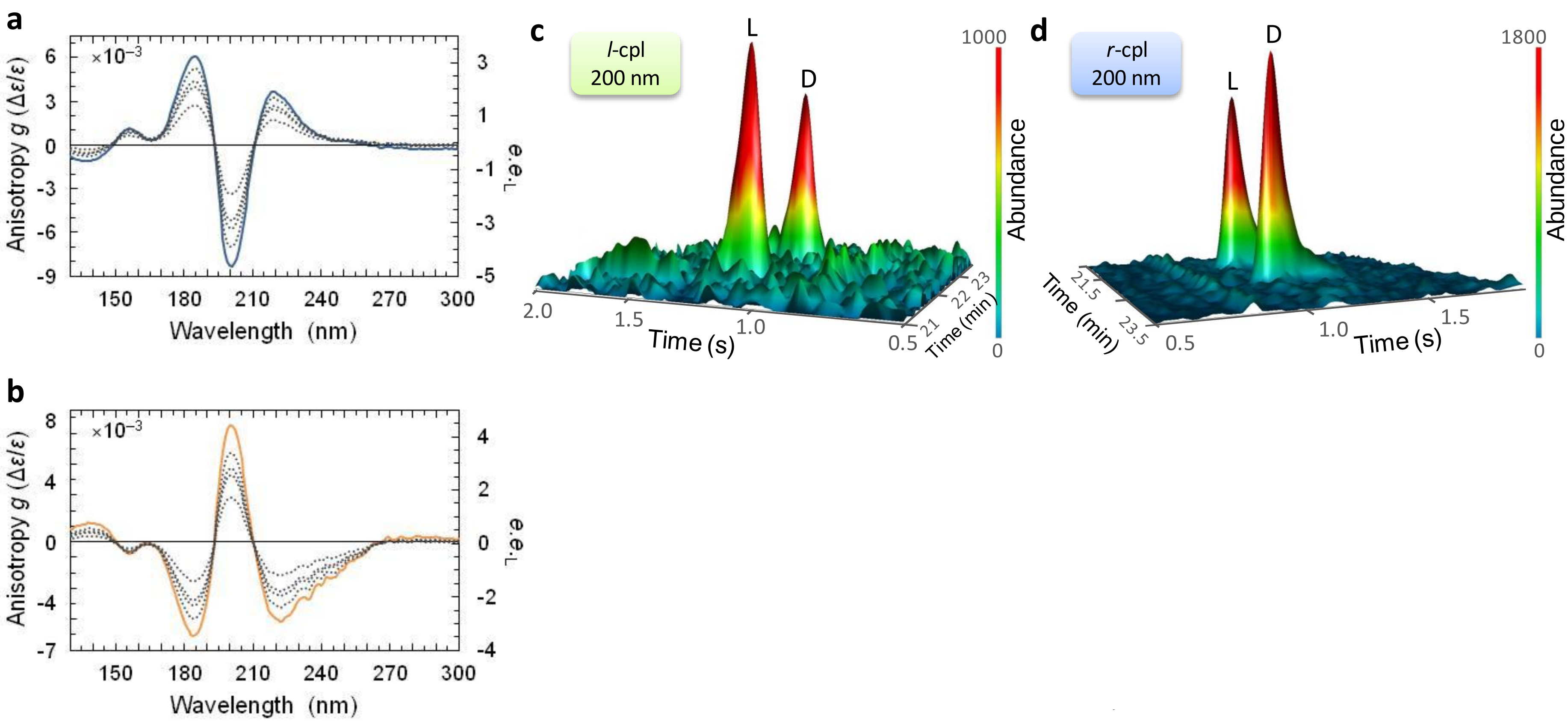
c) the selection of the CPL wavelength best suited for inducing *ee.*



Measured polarization ellipses (thick lines) at the sample location as produced by the OPHELIE2, HU640 type undulator. Absolute circular polarization rates are of 91 % for r-CPSR (b) and 94 % for l-CPSR (a).



Synchrotron SOLEIL is a third generation synchrotron optimized for intense photon fluxes.

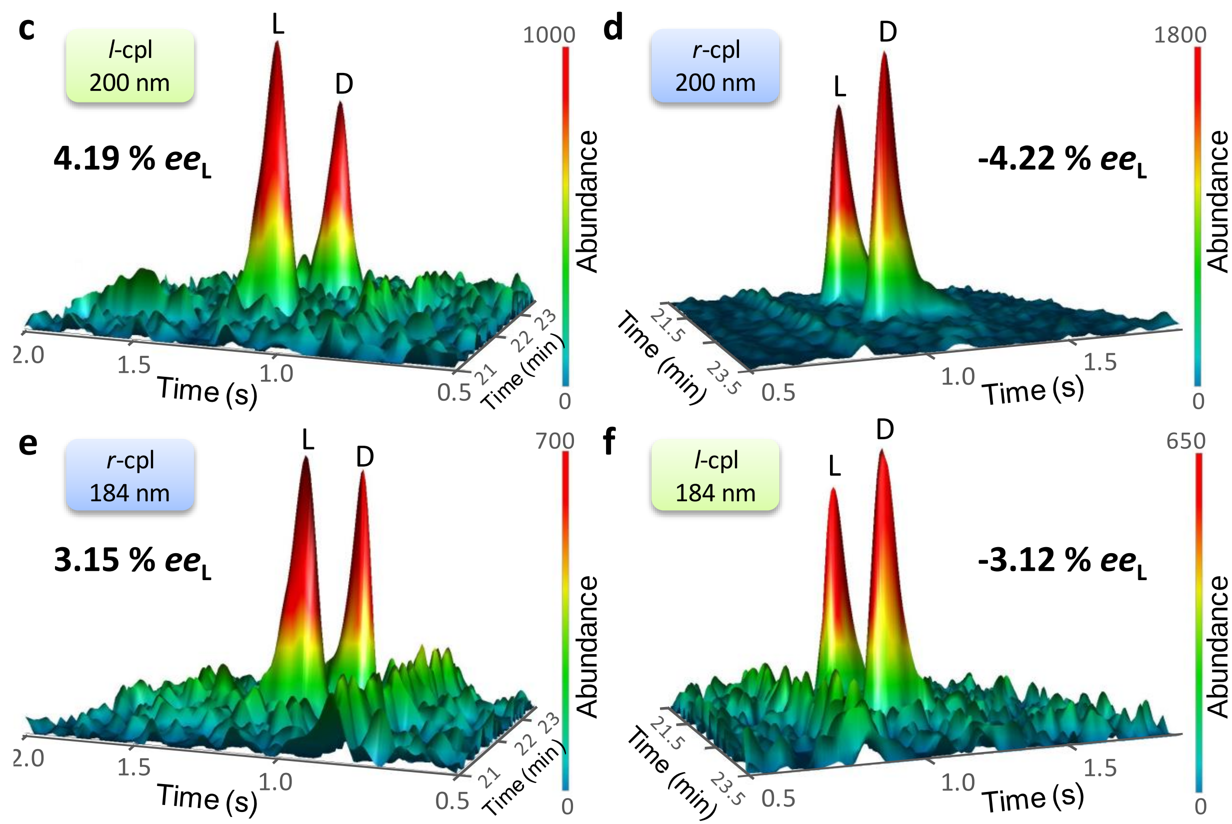


Energy- and polarization-dependent CPL-induced symmetry breaking. *(**a, b**) Anisotropy spectra g(λ) and inducible* ee_L *of L-Ala & D-Ala. (**c–d**) Enantioselective GC×GC of* ^{13}*C-Ala after irradiation with different CPL-polarization and at different photon energies for 5h.*

Angew. Chem. Int. Ed. **53** (2014), 210–214

PHOTON-ENERGY-CONTROLLED SYMMETRY BREAKING

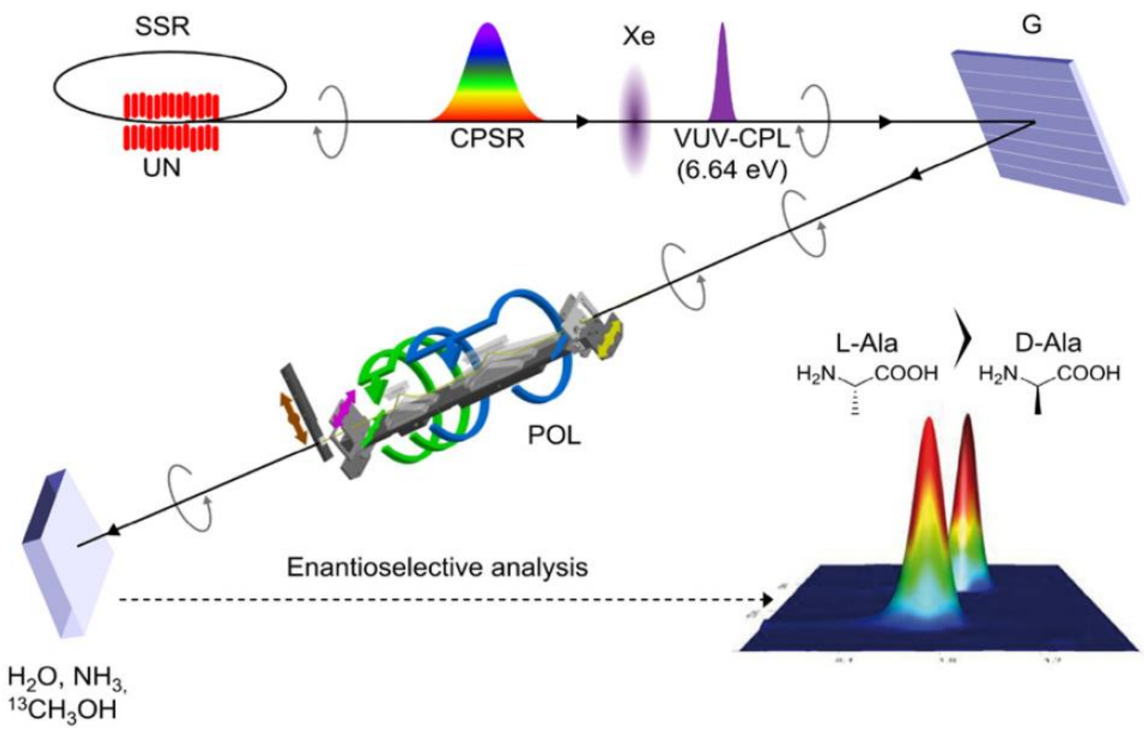
- sign of induced *ee* depends upon helicity of CPL
- sign of induced *ee* depends upon the energy of *l*-CPL and *r*-CPL

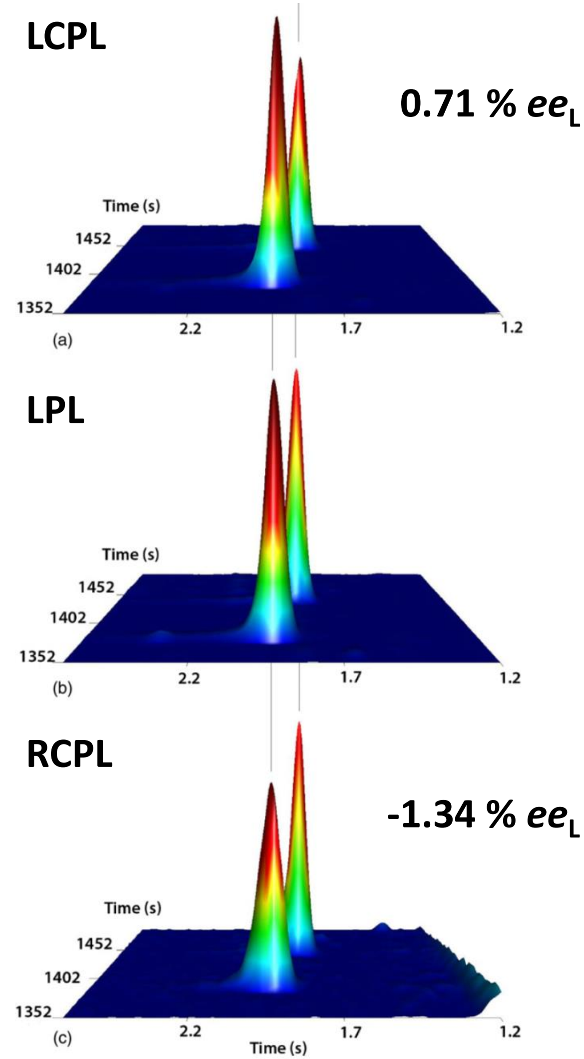


Energy- and polarization-dependent CPL-induced symmetry breaking. *(**a, b**) Anisotropy spectra g(λ) and inducible* ee_L *of* L*-Ala &* D*-Ala. (**c–d**) Enantioselective GC×GC of* ^{13}*C-Ala after irradiation with different CPL-polarization and at different photon energies for 5h.*

Angew. Chem. Int. Ed. **53** (2014), 210–214

Absolute Asymmetric Amino Acid Synthesis





Set-up of asymmertic VUV photolysis at the sychrotron radiation facility SOLEIL *(left).* ***Multidimensional gas chromatograms of*** ^{13}***C-alanine enantiomers for the three polarization regimes*** *(right).*

Astroph. J. Letters **727** (2011), L27

Follow-up study: asymmetric synthesis of five amino acids

Astroph. J. Letters **727** (2014) L27.

The Asymmetry Team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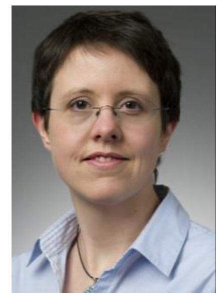
Université Paris Sud
Orsay, France




Dr. N. C. JONES
Dr. S. V. HOFFMANN

Department of Physics & Astronomy,
ISA - Institute for Storage Ring Facilities, Aarhus University
Aarhus, Denmark

Dr. L. NAHON

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Chirality as a trigger of selection, interaction & feedback in the evolution of the first biopolymers

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