



WHY NATURE NEVER MAKES CHIRAL TWINS ?

*Insights from cometary ice
analogues & extra-terrestrial
sample analysis*

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CENTRE NATIONAL D'ÉTUDES SPATIALES

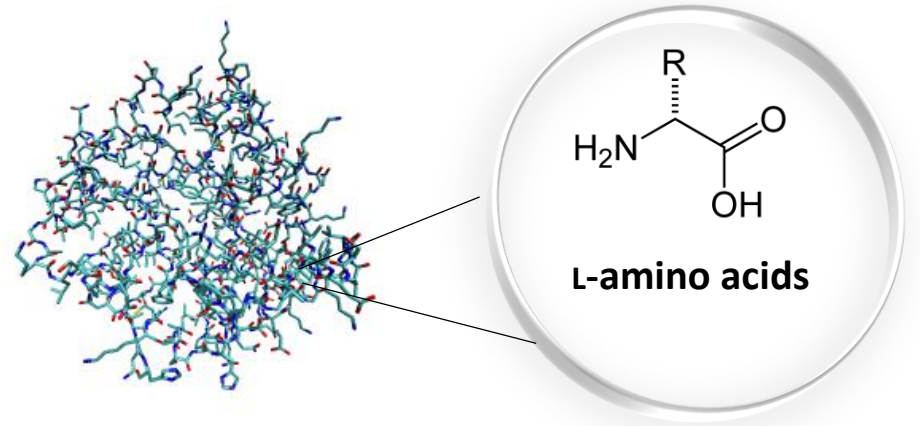
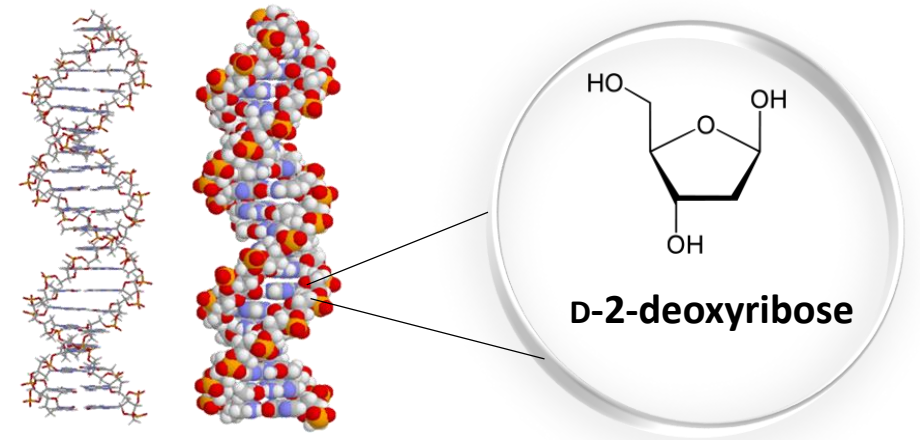
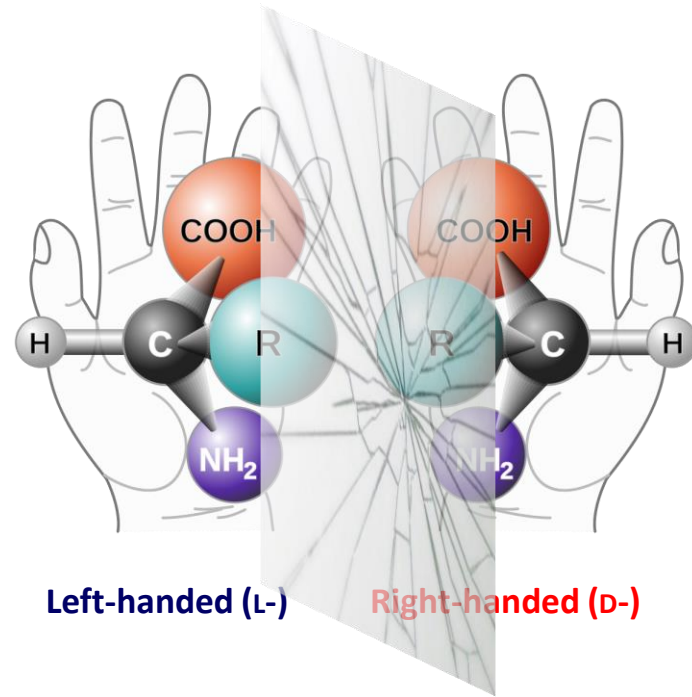
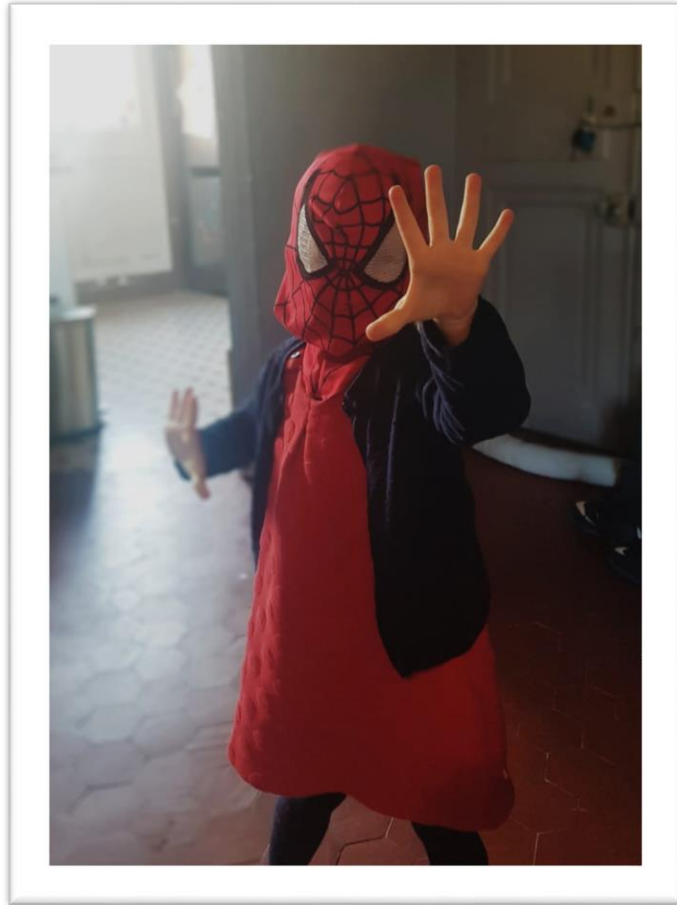


Institut de chimie



<https://www.mosbri.eu/>

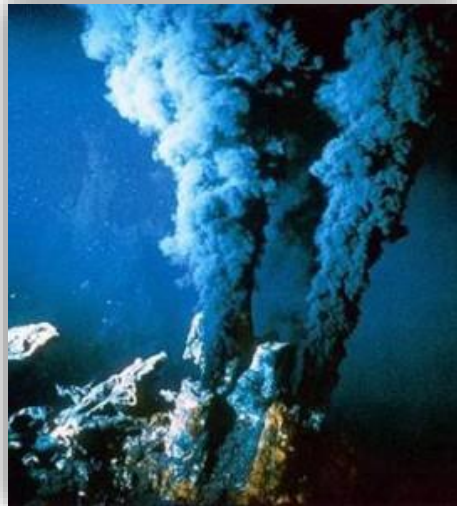
HOMOCHIRALITY OF LIFE



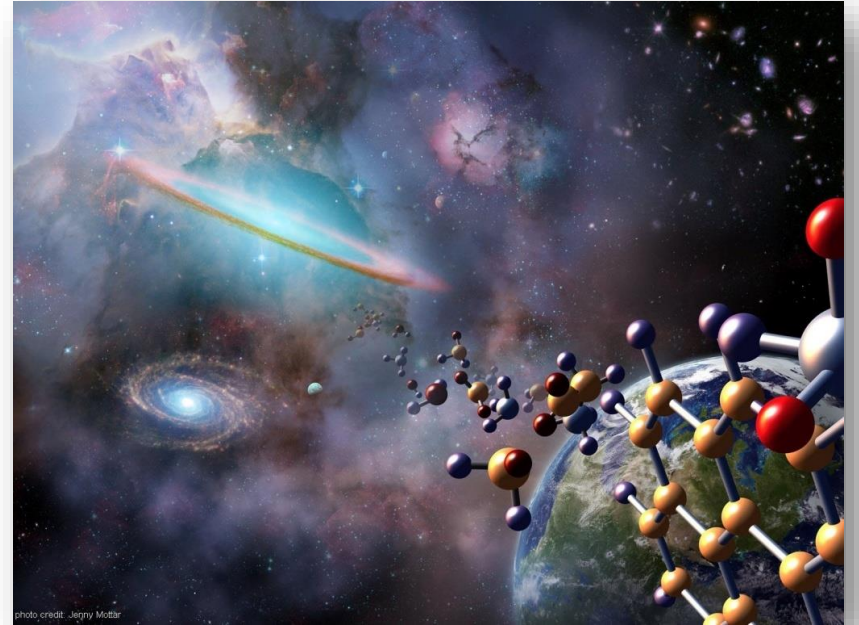
CHIRAL BUILDING BLOCKS OF LIFE: WHERE DO THEY COME FROM?



Primordial soup



Hydrothermal vents

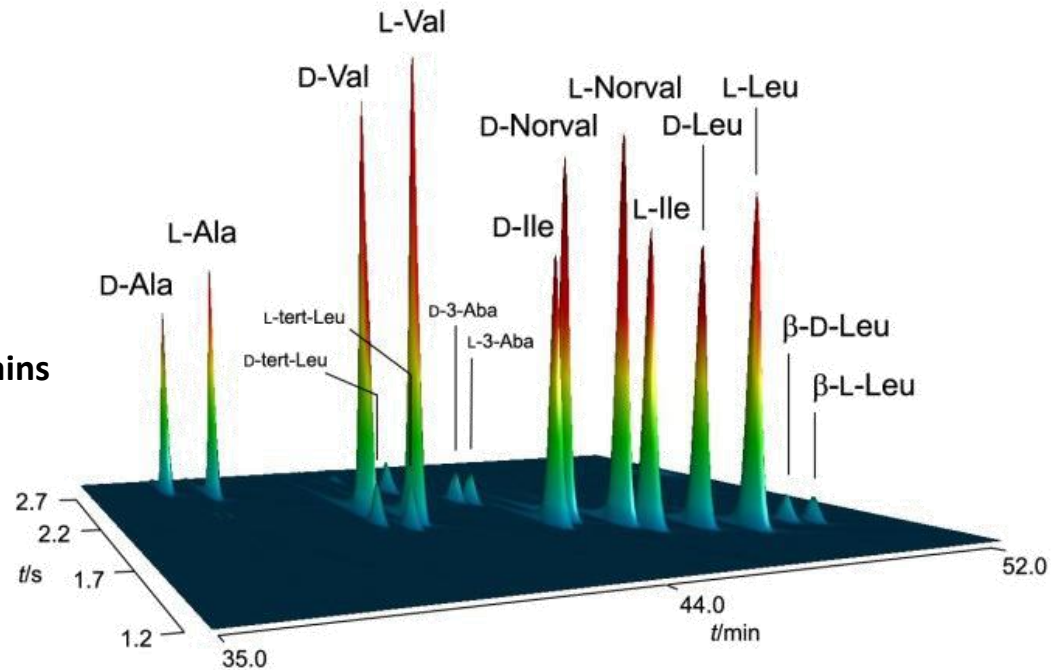


Cosmic Evolution of elements and organic molecules

INTERSTELLAR ORIGIN OF ORGANIC MOLECULES



Murchison meteorite contains over 500 organic molecules:

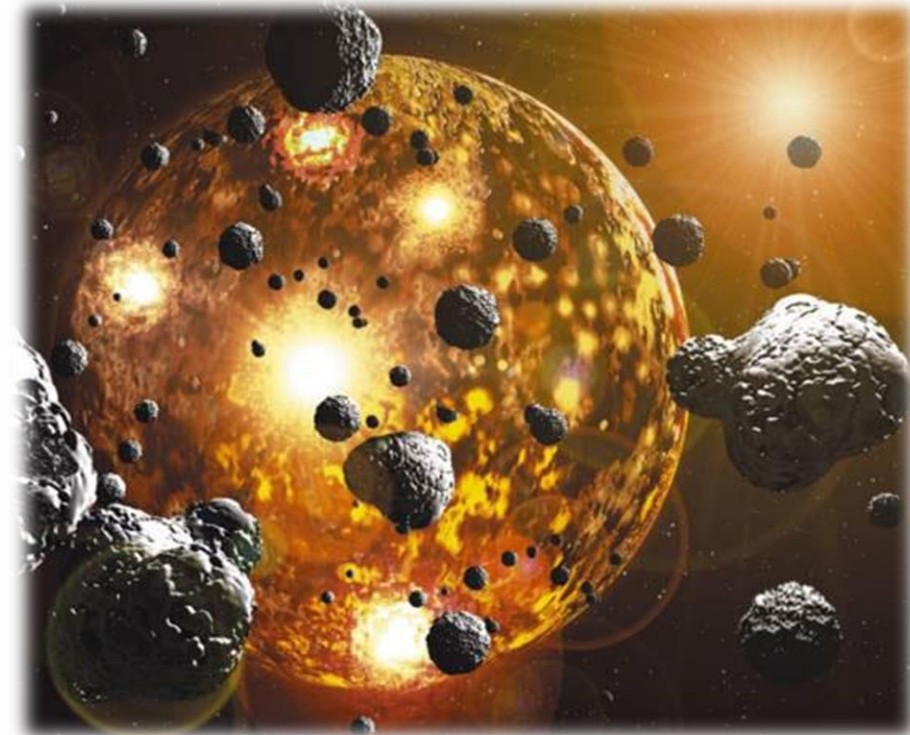


Resolution of amino acid enantiomers in a sample of Murchison using enantioselective GC×GC coupled to TOFMS.

Angew. Chem. Int. Ed. **54** (2015), 1402–1412.

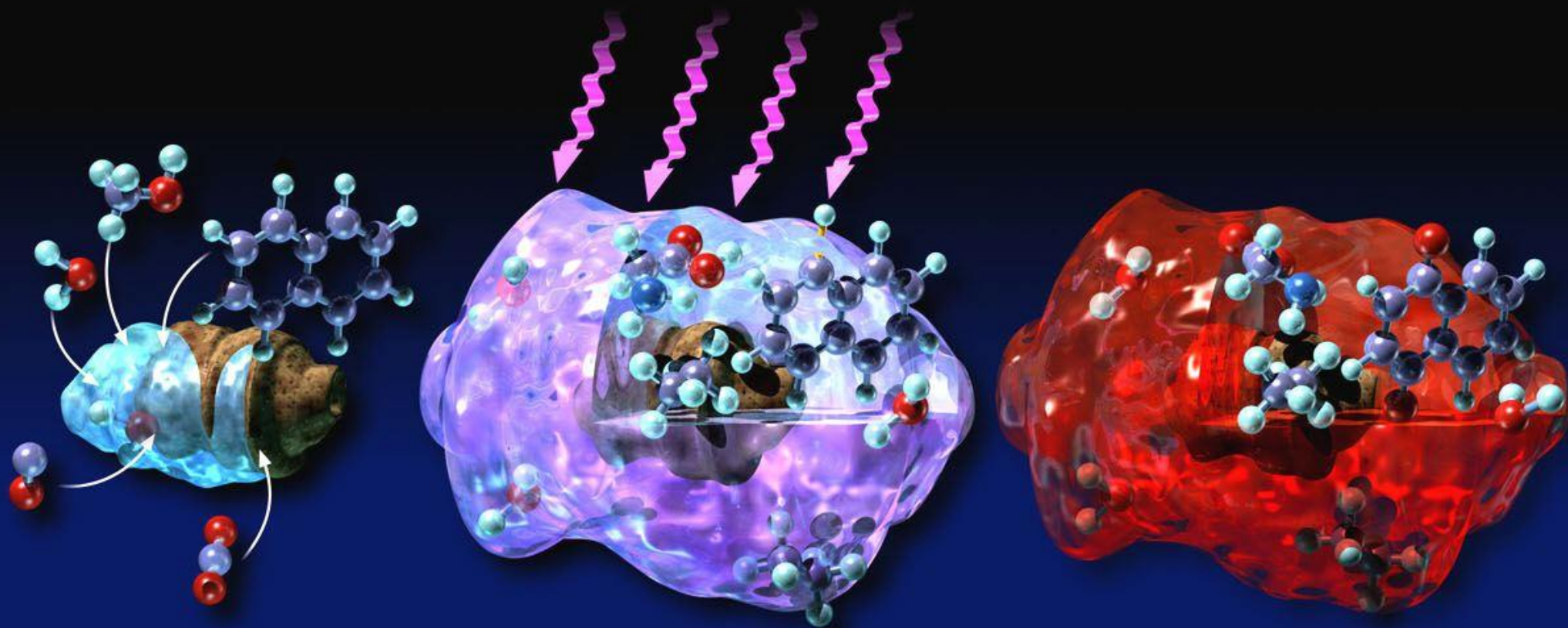
ChemPlusChem **79**, 781–785 (2014).

J. Chromatogr. A **1433**, 131–136 (2016).

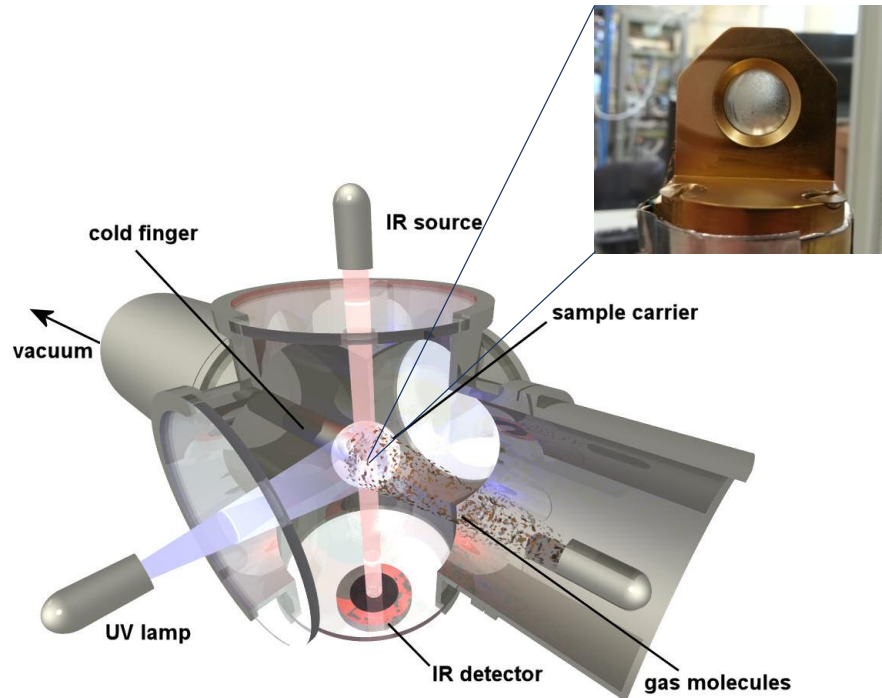


The seeding of organic molecules by meteorites

INTERSTELLAR SYNTHESIS OF CHIRAL MOLECULES

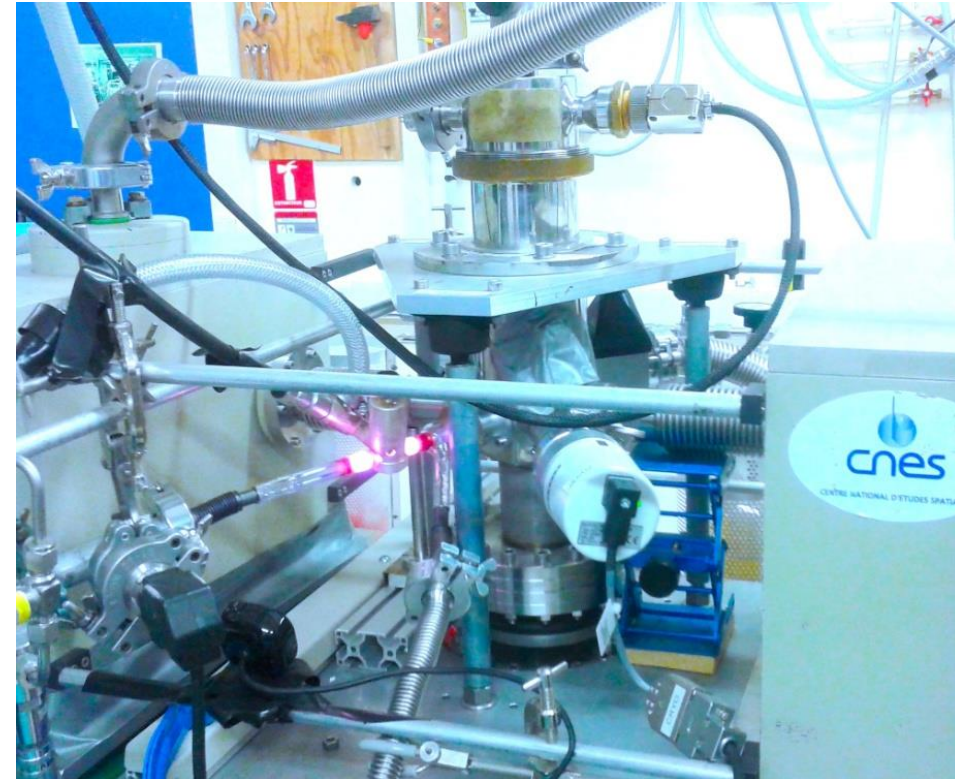


SPACE SIMULATOR: WHAT IS POSSIBLE UNDER SIMULATED INTERSTELLAR CONDITIONS?



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.

ChemPlusChem **77** (2012), 186–191;
Nature **416** (2002), 403–406.

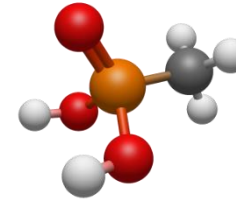
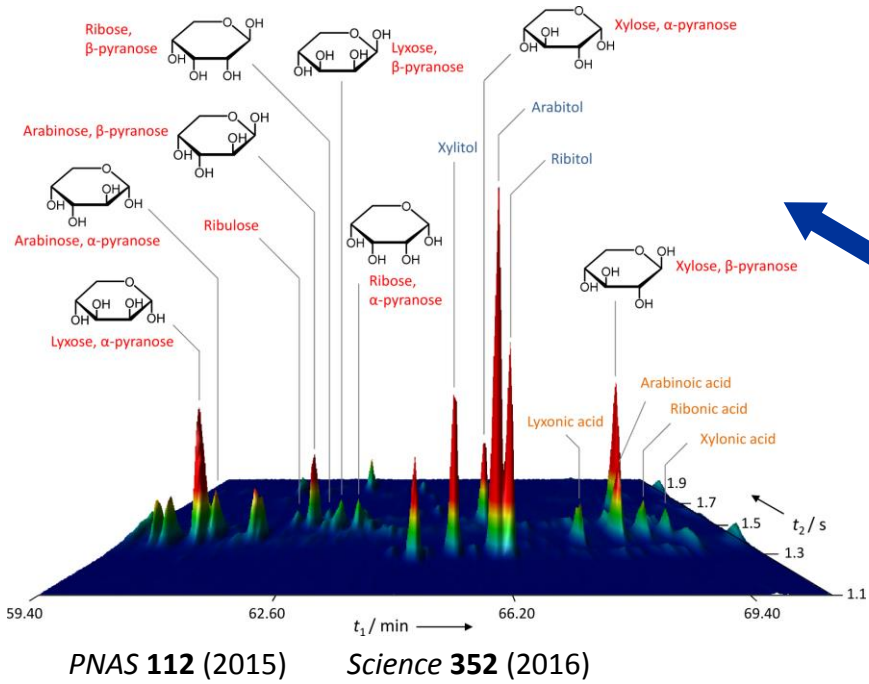


Space simulation chamber

@PIIM, Aix-Marseille Université, Marseille

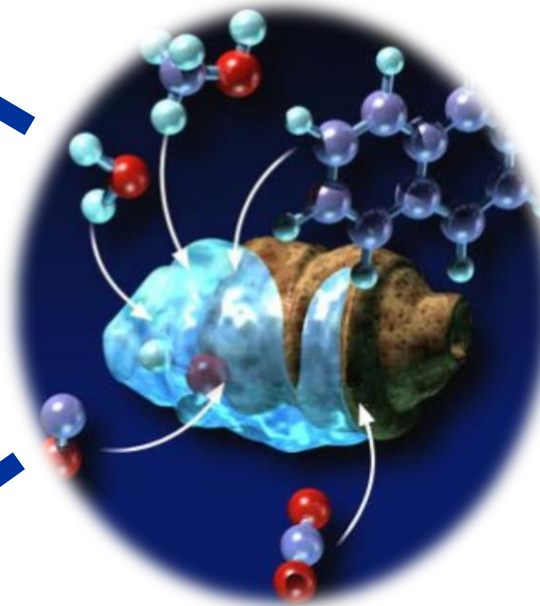
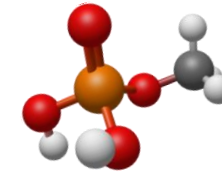


SUGARS, SUGAR ACIDS, SUGAR ALCOHOLS



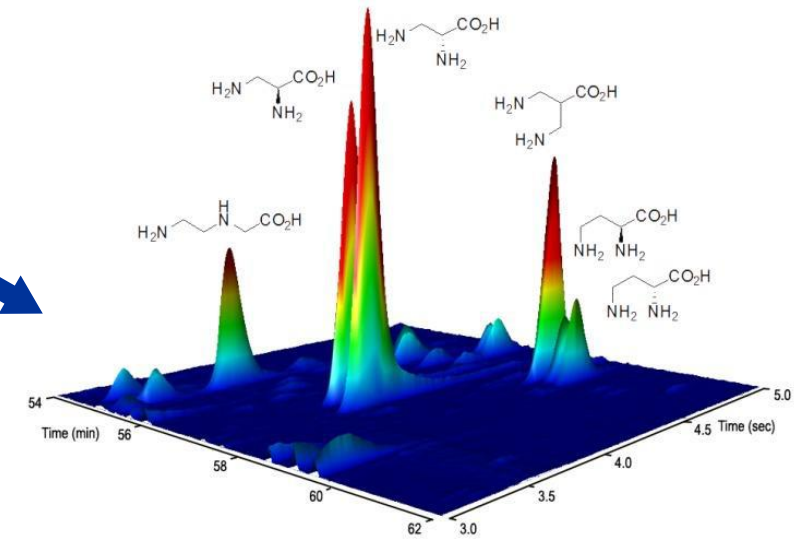
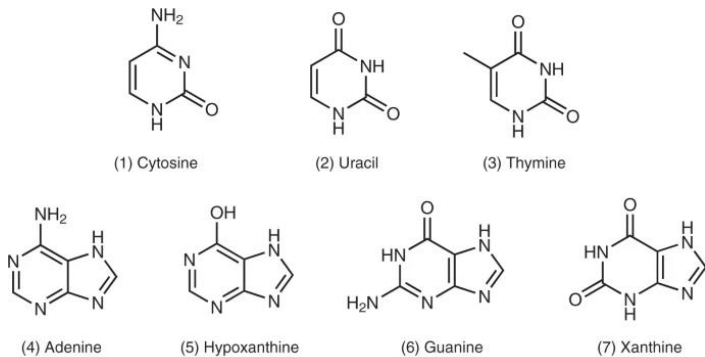
ATP & LIPID PRECURSOR, GLUE IN DNA

Nature Com. **9**: 3851 (2018)
Science Advances **5**, eaaw4307 (2019).



NUCLEOBASES

Oba et al. Nature Comm. **10** (2019)

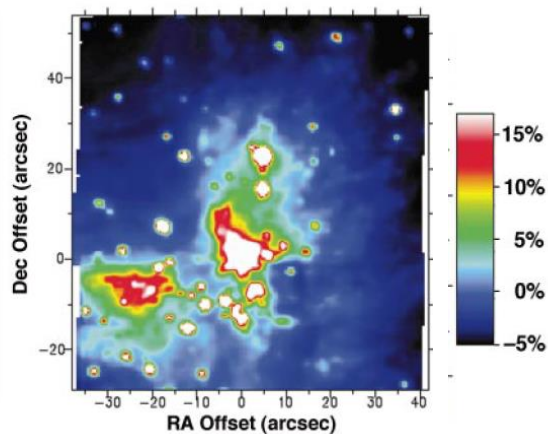
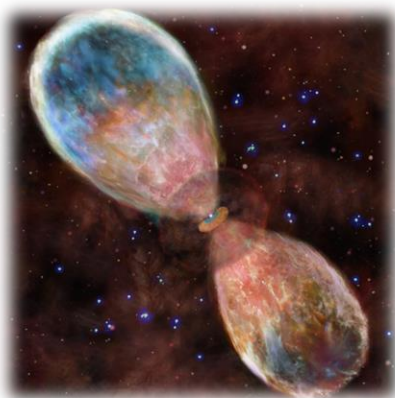


>30 AMINO ACIDS
ChemPlusChem **77** (2012)

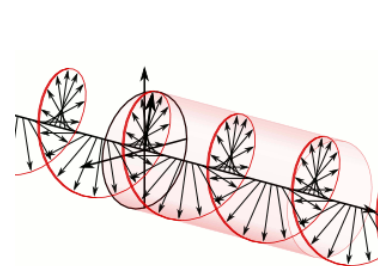
SELECTION OF HANDEDNESS AT THE DAWN OF MOLECULAR EVOLUTION



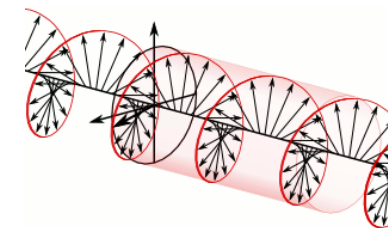
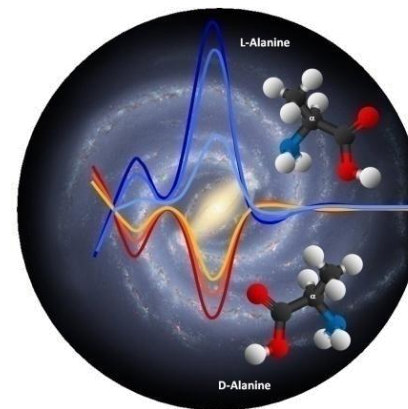
L-excess of amino acids in meteorites



Chiral photons observed in the molecular cloud



Left circularly polarized light

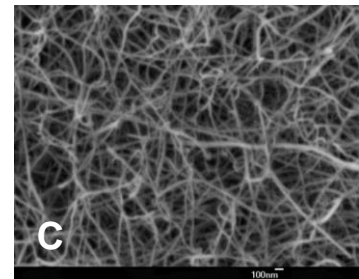
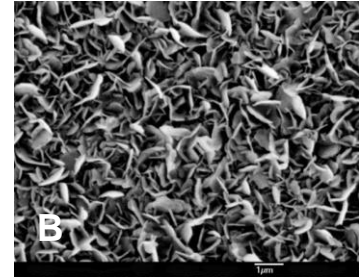
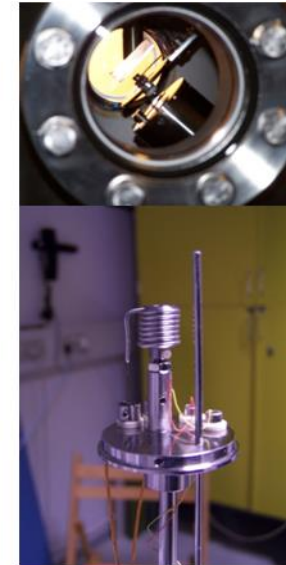
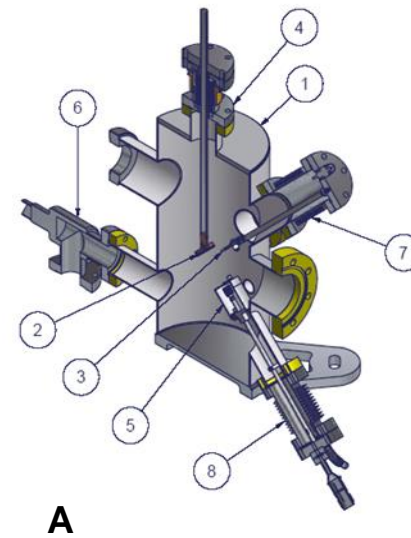
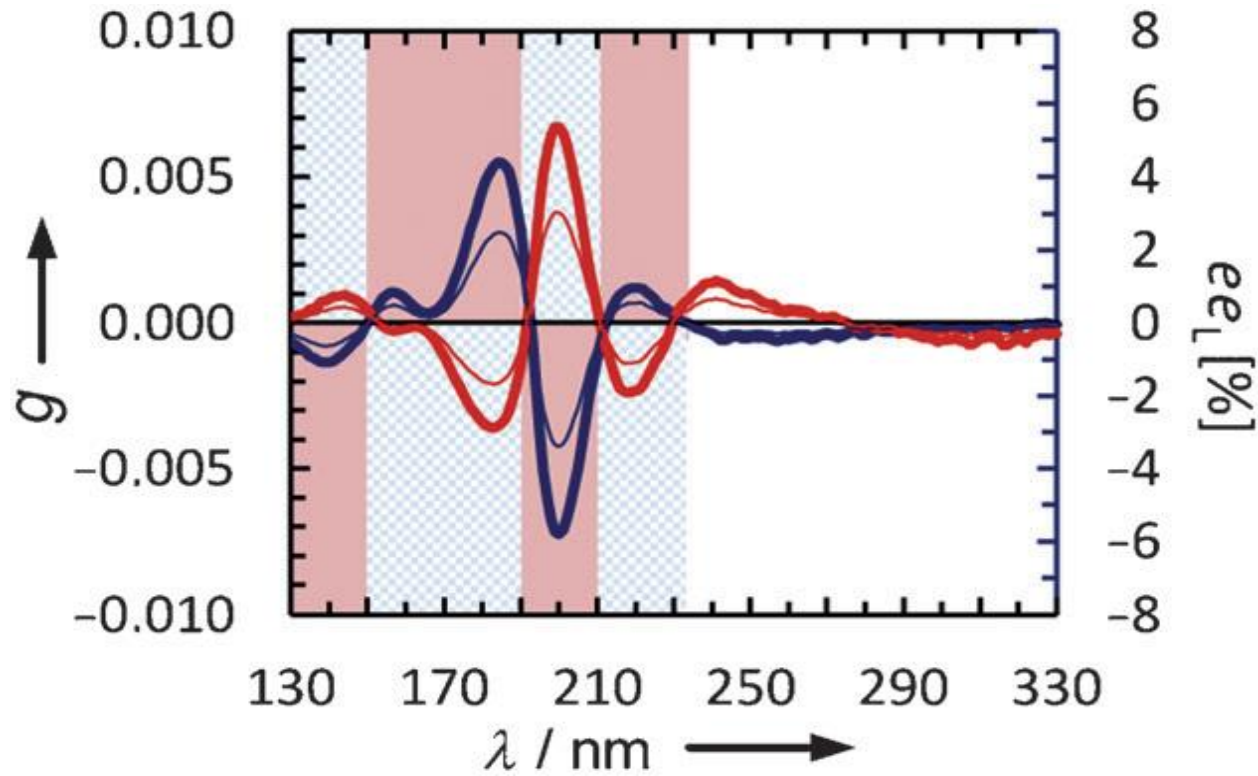


Right circularly polarized light

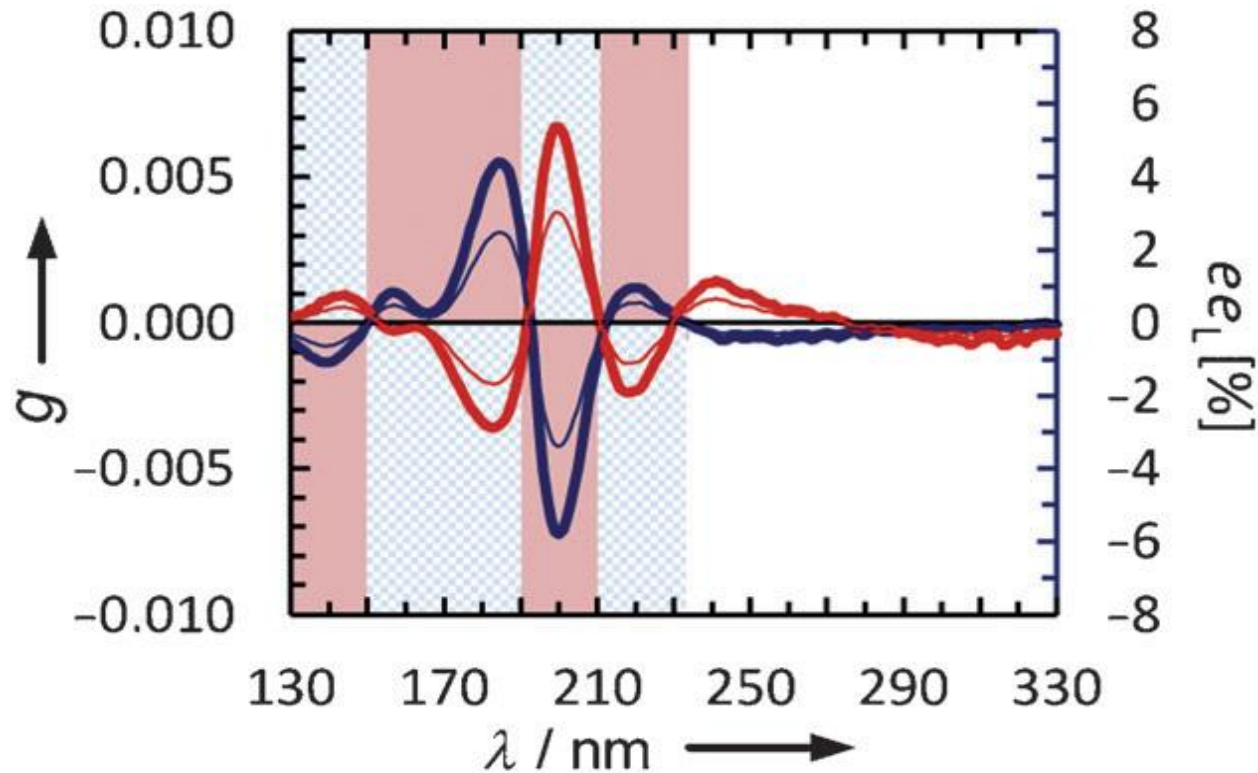
Enantiospecific photochemistry depends on: $\Delta\epsilon = \epsilon_L - \epsilon_R$

Chem. Soc. Rev. **41** (2012), 5447–5458; *Phys. Life Rev.* **8** (2011), 307–330; *Symmetry* **2** (2010), 1055–1080.

ANISOTROPY SPECTRA OF SOLID-STATE AMINO ACIDS



ANISOTROPY SPECTRA OF SOLID-STATE AMINO ACIDS

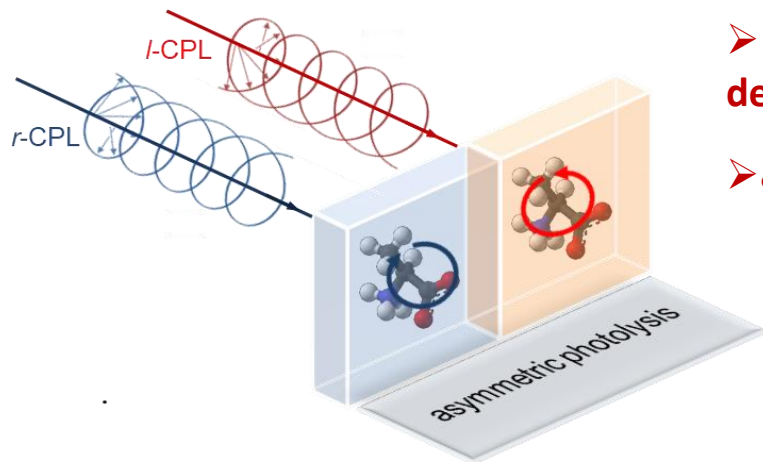


$$g(\lambda) = 4R/D = \Delta\varepsilon/\varepsilon$$

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

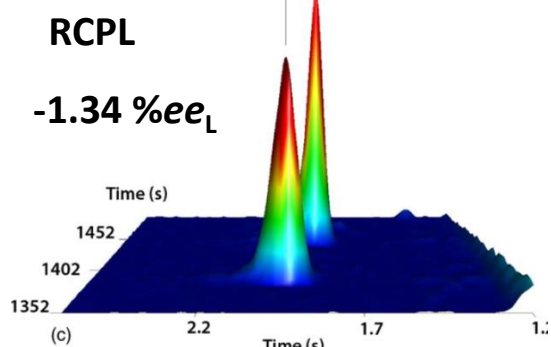
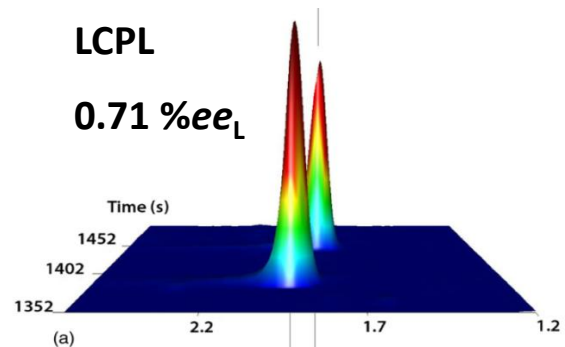
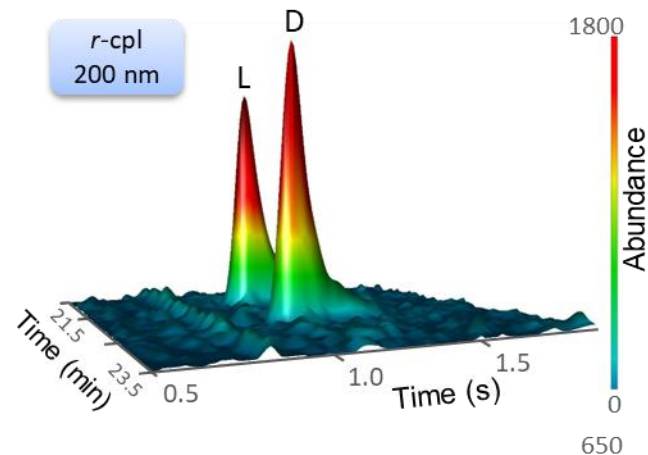
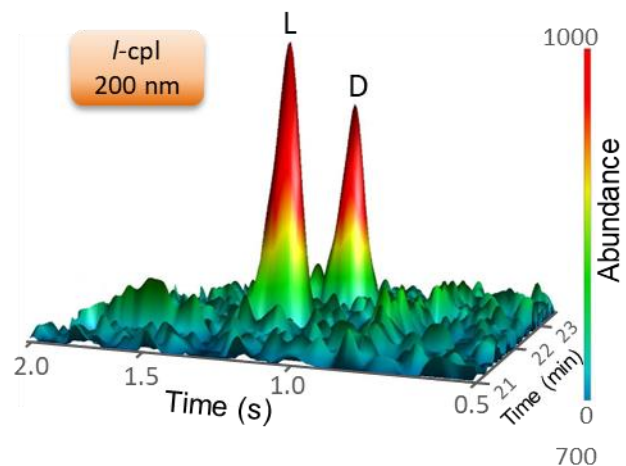
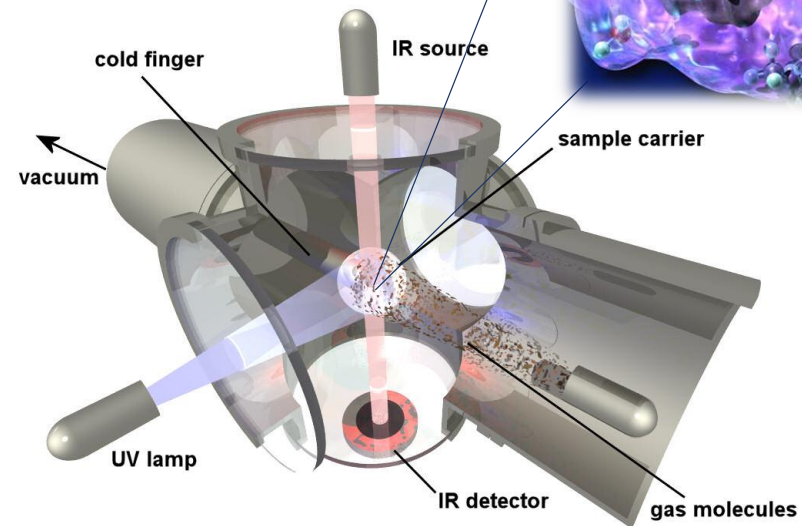
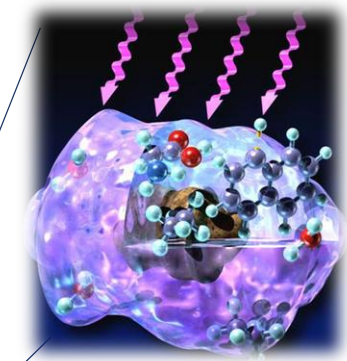
- prediction of the sign of the induced ee ,
- determination of ees by enantioselective photolysis,
- the selection of the CPL wavelength best suited for inducing ee .

ASYMMETRIC PHOTOCHEMISTRY USING CHIRAL PHOTONS



➤ sign of induced ee depends upon helicity of CPL

➤ & energy



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

Astroph. J. L **788** (2014) 79.

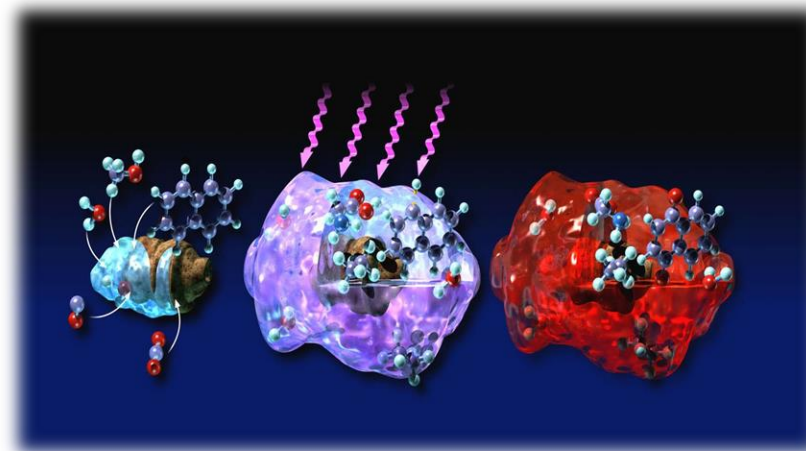
INTERSTELLAR ENVIRONMENTS TO FAVOR ASYMMETRIC PHOTOSYNTHESIS



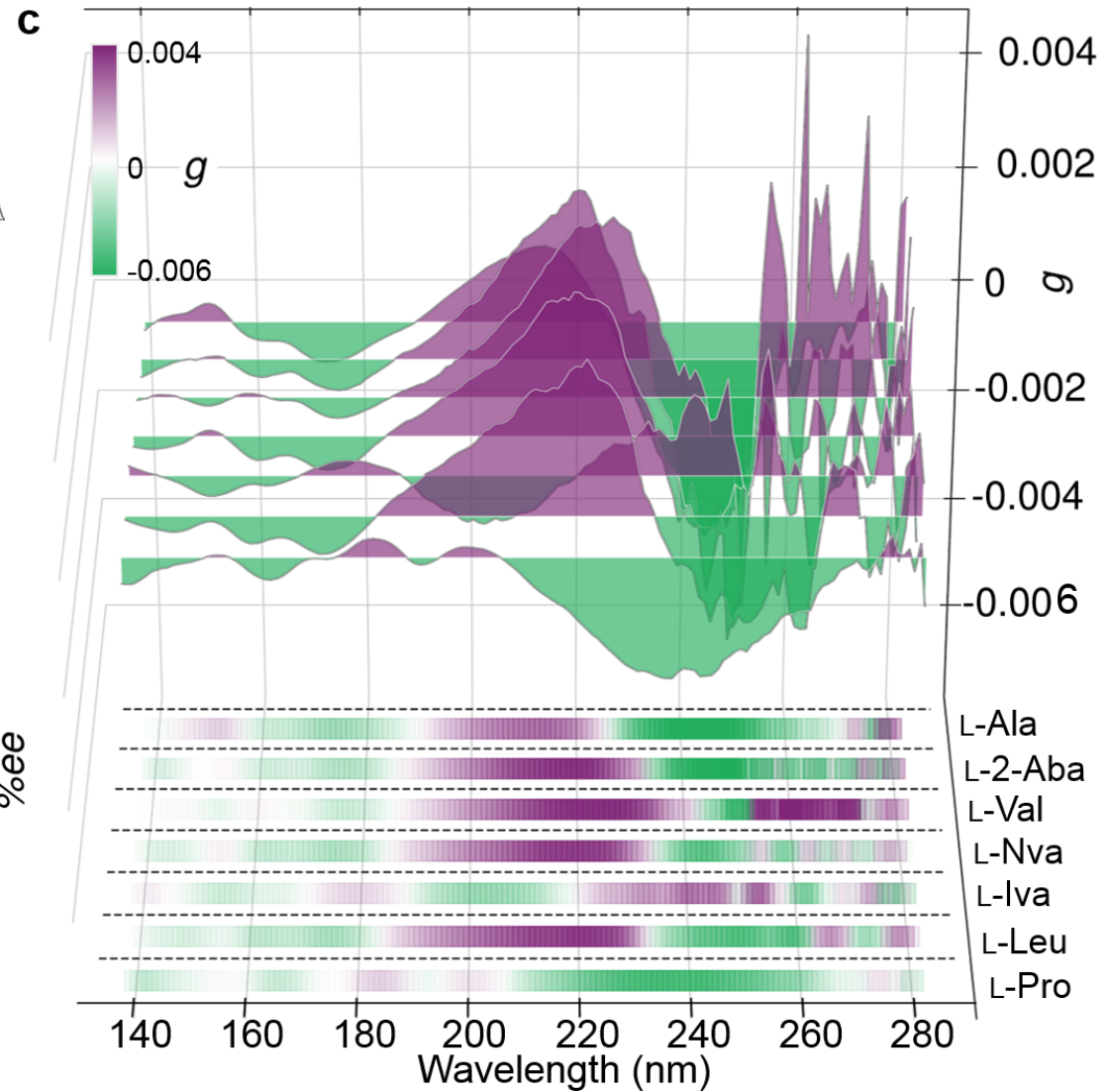
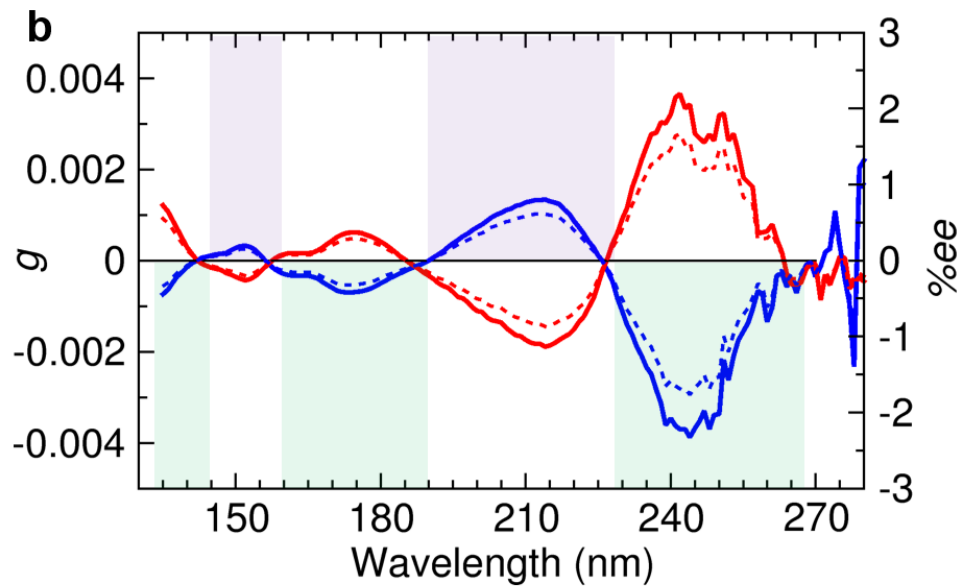
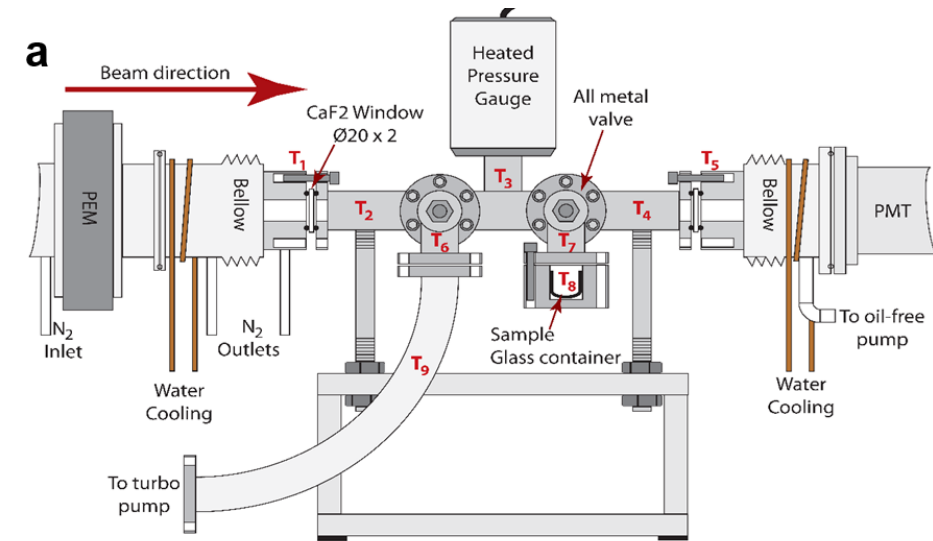
Glycine in the coma of
67P/Churyumov-Gerasimenko

Altwegg et al. Sci. Adv. 2016, 2

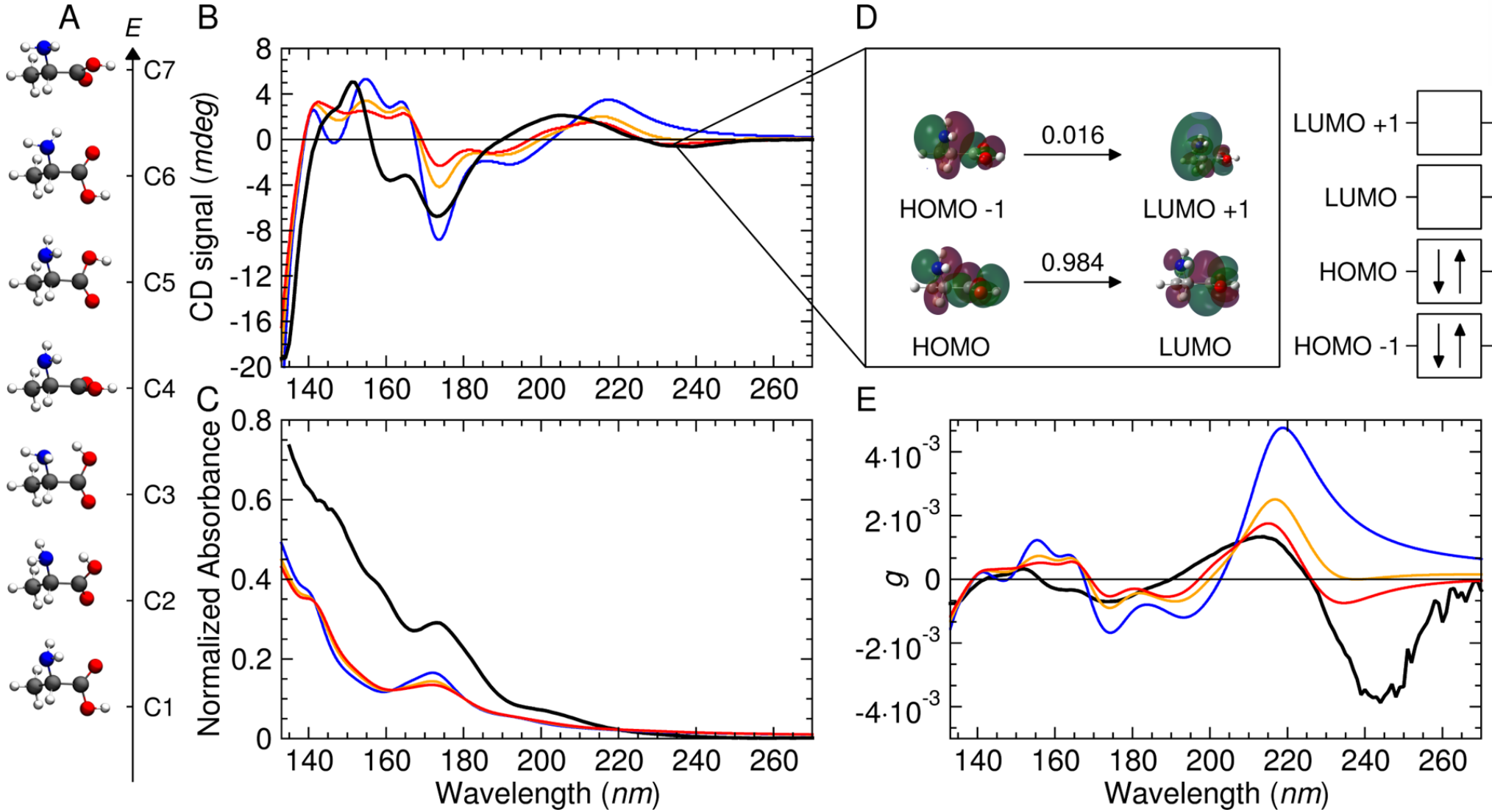
Potential precursors of amino
acids and sugars partitioned
between *solid* and *gas phase*



INTERSTELLAR ENVIRONMENTS TO FAVOR ASYMMETRIC PHOTOSYNTHESIS



AMINO ACIDS – GAS PHASE ASYMMETRIC PHOTOCHEMISTRY



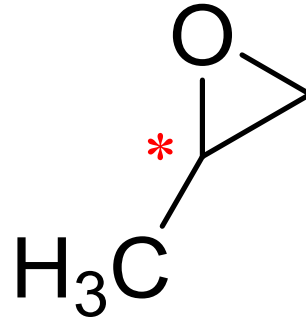
❖ largest g band @ 240 nm caused by conformer 4

PROPYLENE OXIDE – GAS PHASE ASYMMETRIC PHOTOCHEMISTRY



First chiral molecule observed in the interstellar medium

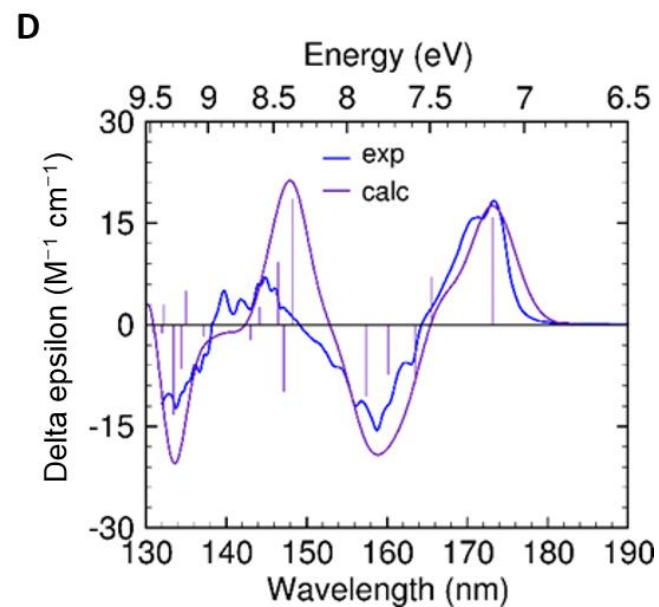
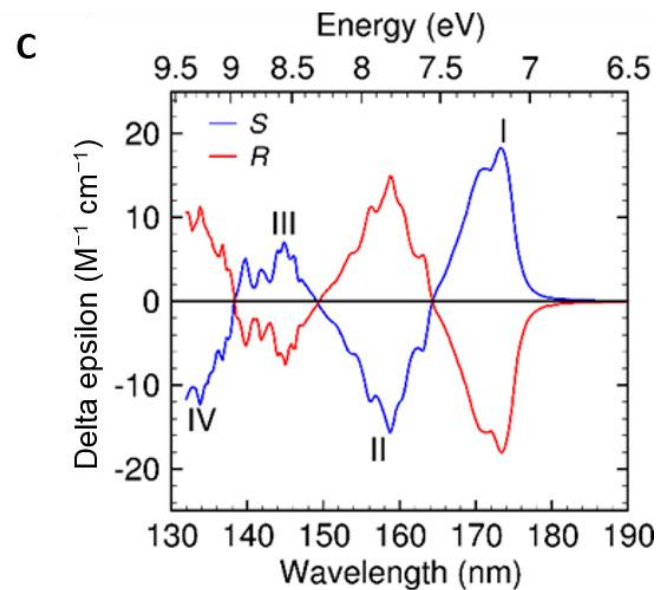
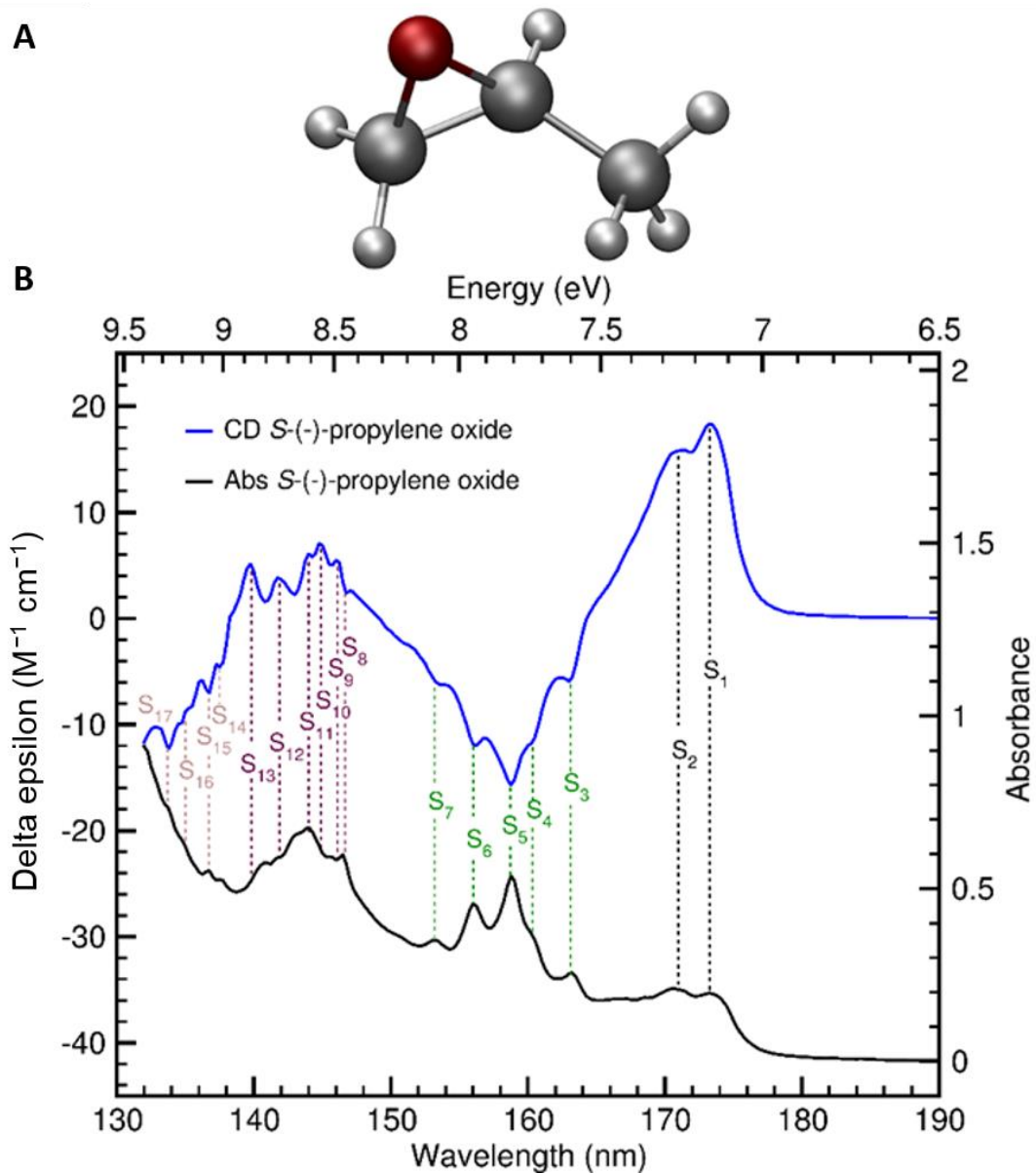
McGuire *et al.* *Science*, **2016**, 352



Excess of the *R*-enantiomer (10%) found in a meteoritic propylene oxide derivative

Pizzarello *et al.* *Earth Planet. Sci. Lett.* **2018**, 496, 198

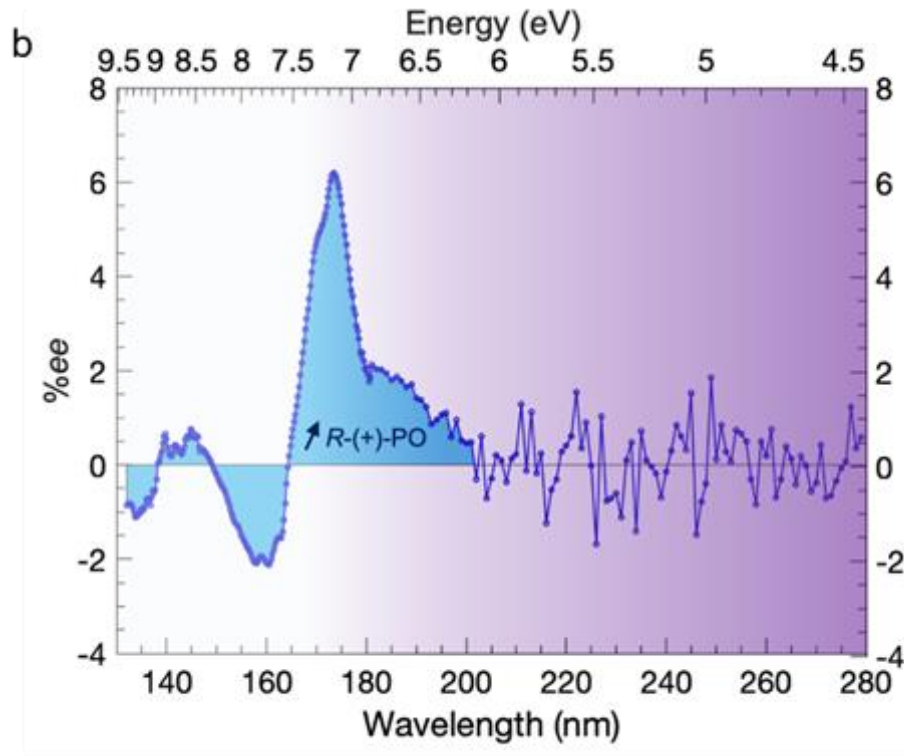
PROPYLENE OXIDE – GAS PHASE ASYMMETRIC PHOTOCHEMISTRY



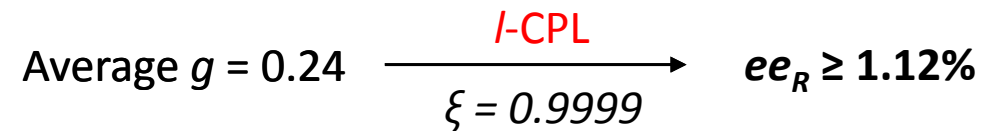
$g_{max} = 0.014 @ 175 \text{ nm}$,
with $\xi = 0.9999$

→ ee ≥ 6.2 %

PROPYLENE OXIDE – GAS PHASE ASYMMETRIC PHOTOCHEMISTRY

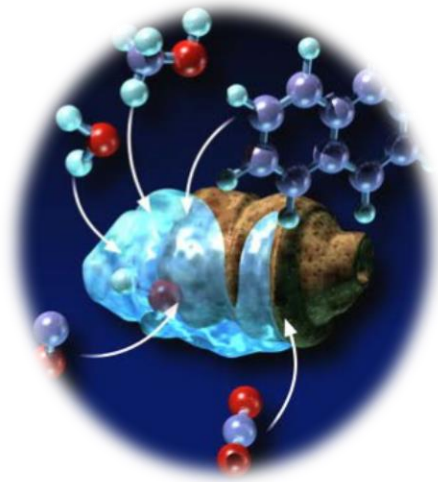


Excess of the R-PO (10%) found in Murchison meteorite

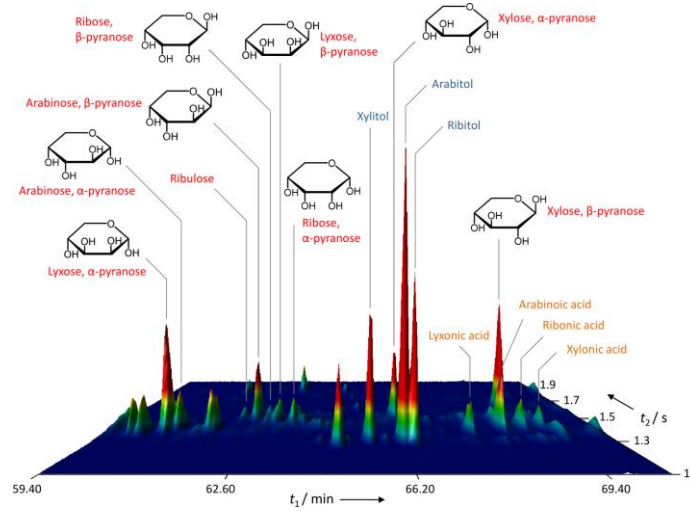


The R-excess in propylene oxide could be a clue to predict the polarization of CPL that illuminated our protoplanetary disk

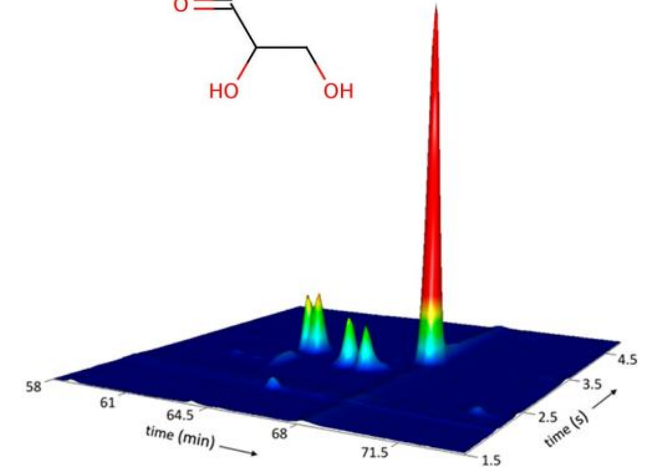
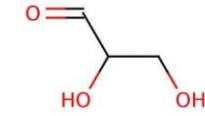
WHAT ABOUT SUGARS?



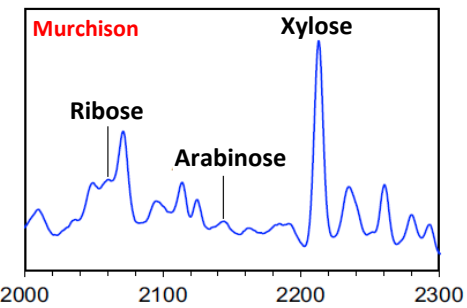
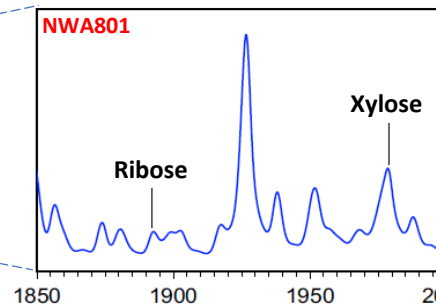
Interstellar ice analog^{1,2}



Glyceraldehyde



Meteorite³



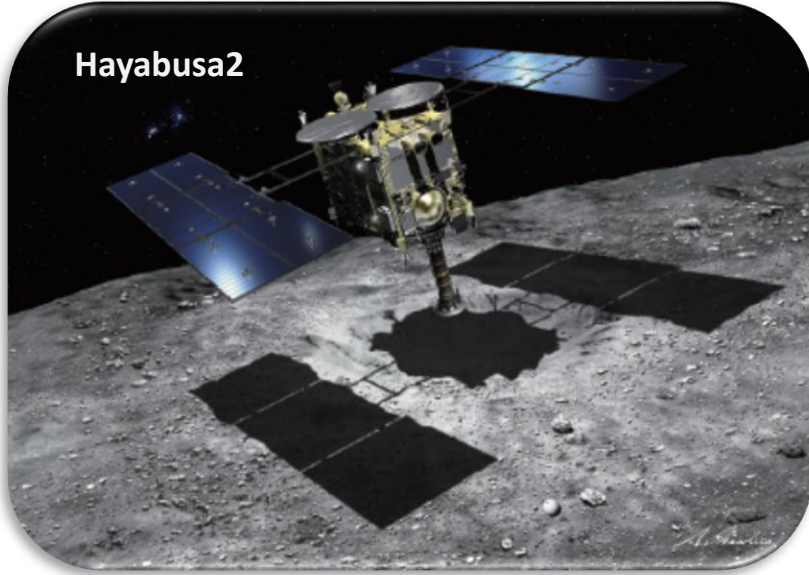
¹ Meinert *et al. Science*, 2016, 352

² De Marcellus *et al. Proc. Natl. Acad. Sci. USA*, 2015, 112

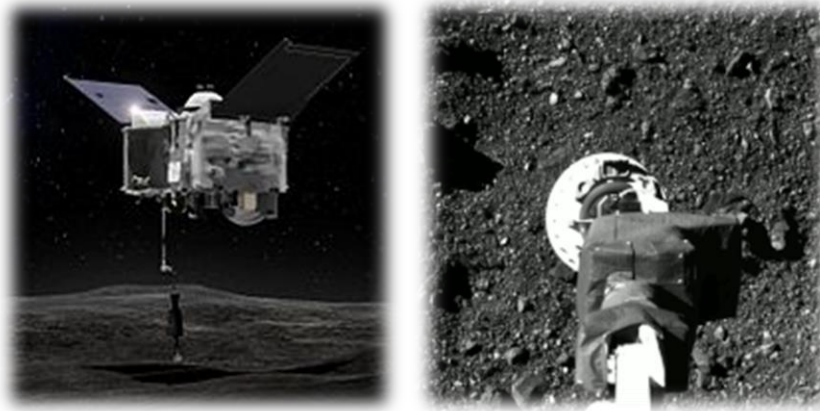
³ Furukawa *et al. Proc. Natl. Acad. Sci. USA*, 2019, 116

SEARCH FOR **CHIRAL BIOSIGNATURES** IN CELESTIAL BODIES AND ON PLANETARY SURFACES

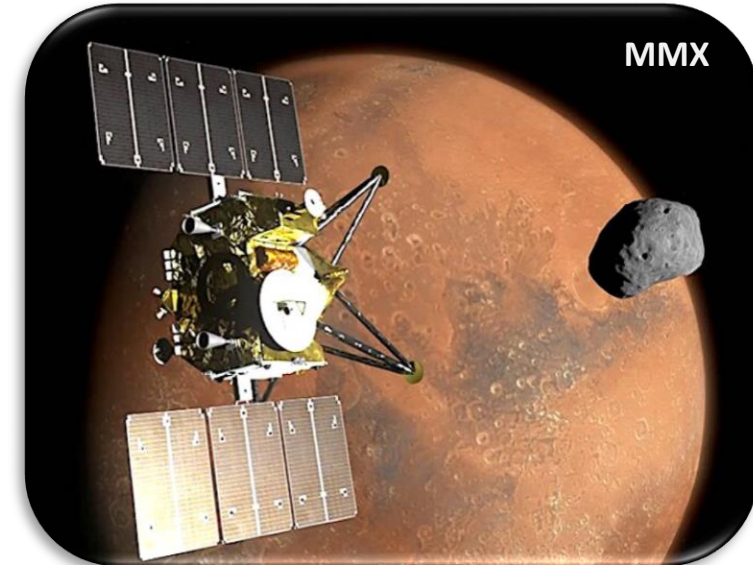
Hayabusa2



OSIRIS-REx

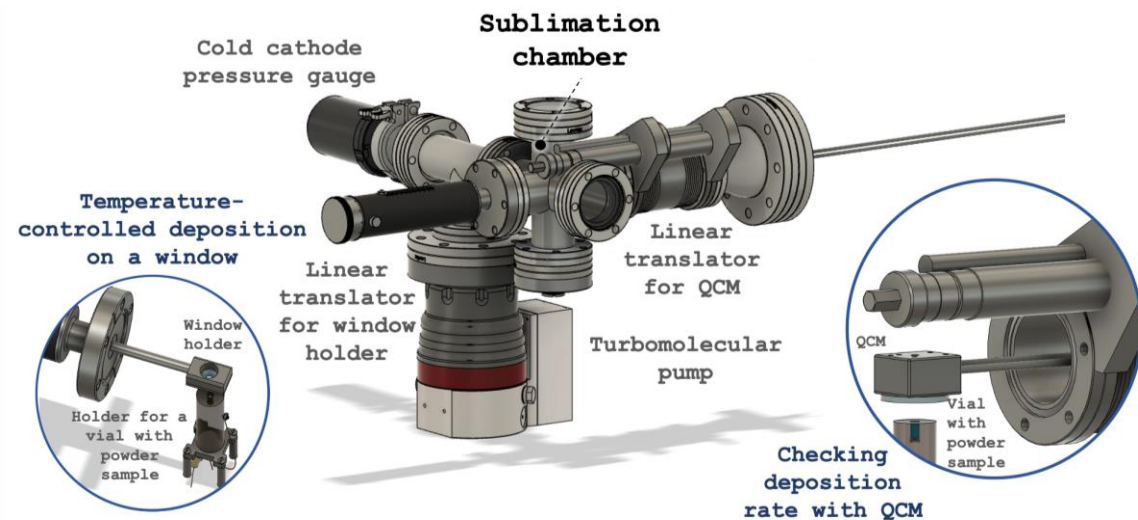


MMX

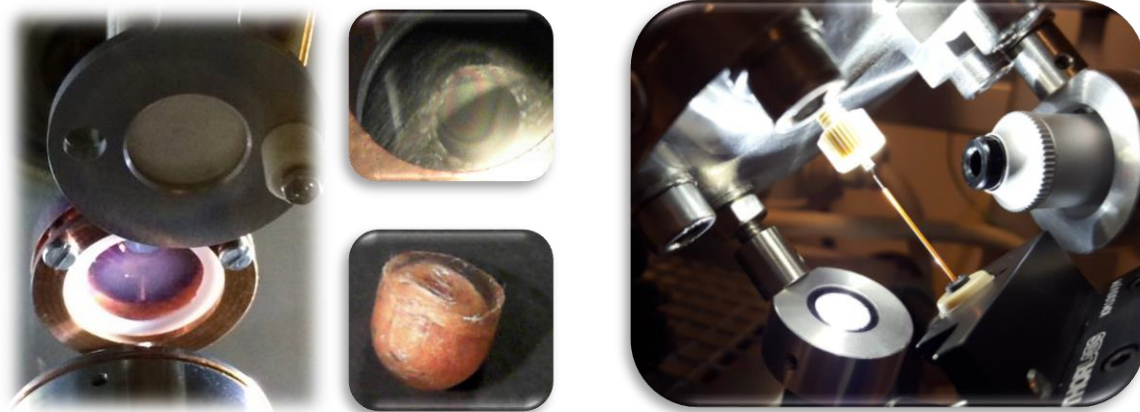
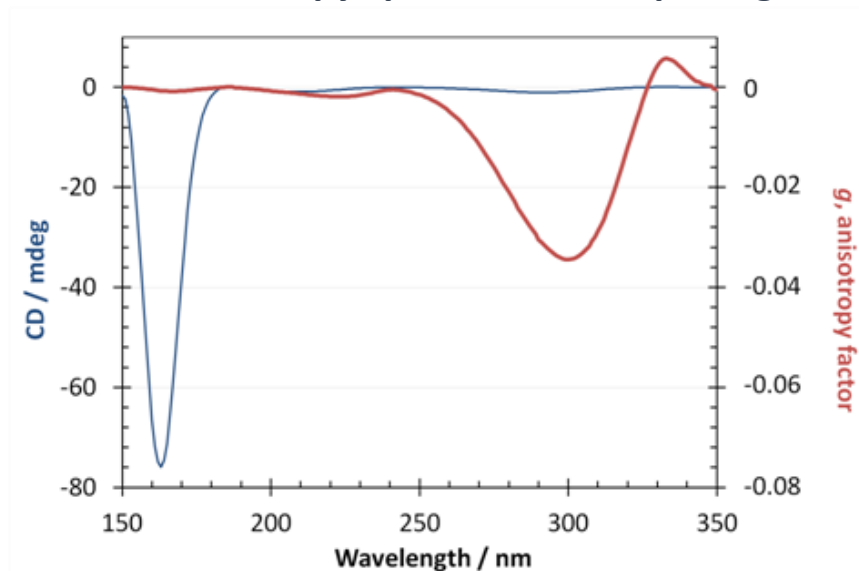


ASYMMETRIC PHOTOLYSIS EXPERIMENTS OF AMINO ACIDS & SUGARS

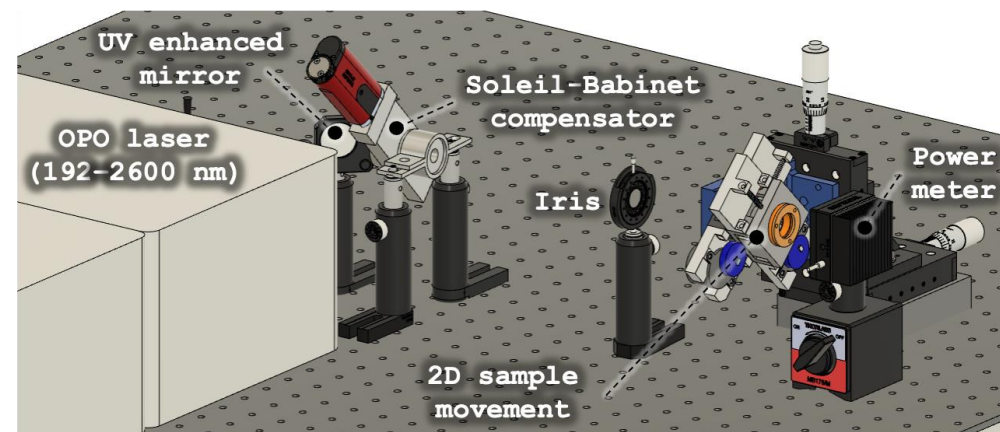
1. Thin film production



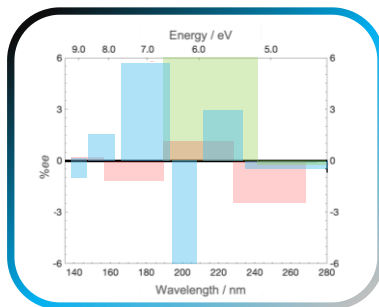
2. Anisotropy spectra of isotropic sugar films



3. UV/VUV CPL irradiation set-up



Future Trends...



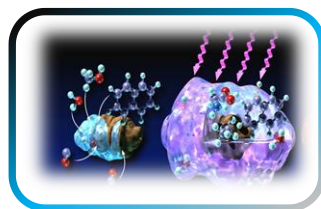
Studying the net effect of **polychromatic CPL** across **molecular families and environments...**

Assess conditions in which CPL would have acted



Search for chiral **biosignatures** (?) in **meteorites and samples returned from asteroids.**

Correlate any *ee* with anisotropy spectra



Chiral amplification of small *ee* under early Earth conditions & the emergence of **homochiral pre-biopolymers.**

Alternative origins of biomolecular homochirality...

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Société Française d'Exobiologie

Société Française d'Exobiologie

Conférence Nationale d'Exobiologie: Grenoble 2023



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IAU Astrobiology

The International Society for the Study of the Origin of Life – The International Astrobiology Society

Topics

Chemistry in Giant Molecular Clouds, Nebular Chemistry, Formation of Planetary Systems, Habitability at all scales, The Early Earth, When (and How) Does Life Arise?, Evolution of Life in Our Solar System and Beyond.

