Can interstellar asymmetric photochemistry explain the origins of biomolecular homochirality on Earth?

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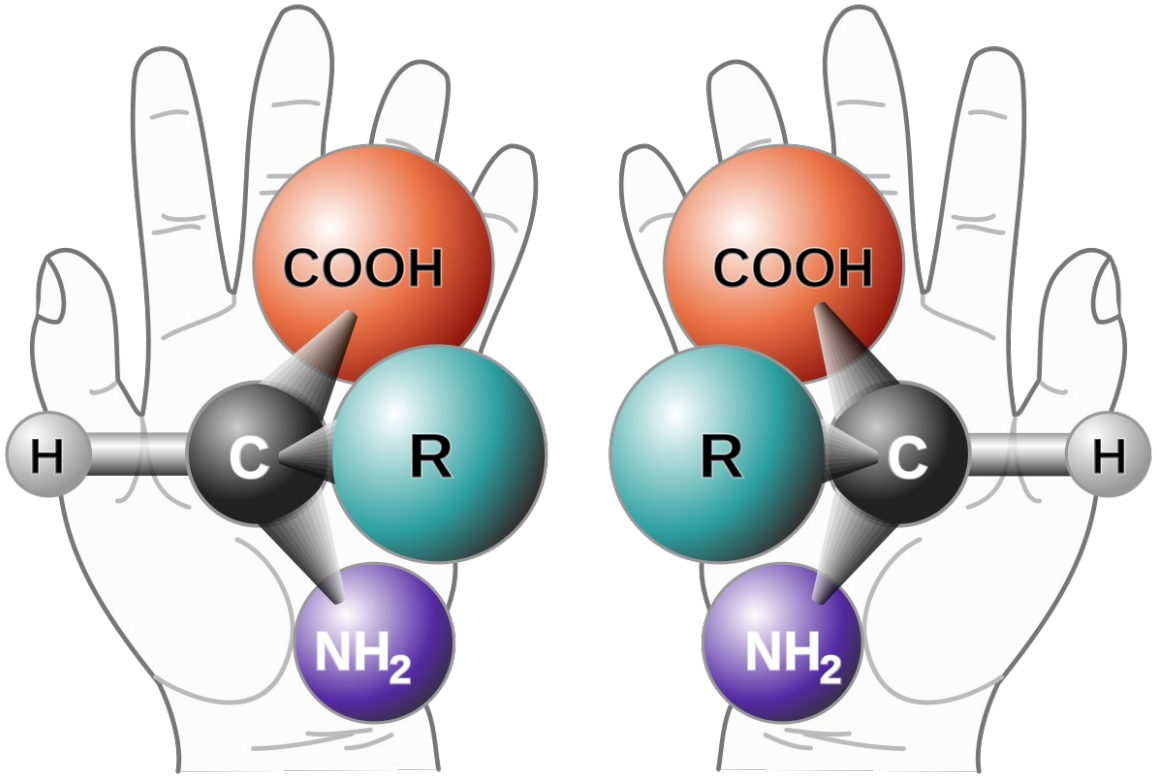
ASTRID2, Department of Physics and Astronomy, Aarhus University, Denmark

29th February 2024

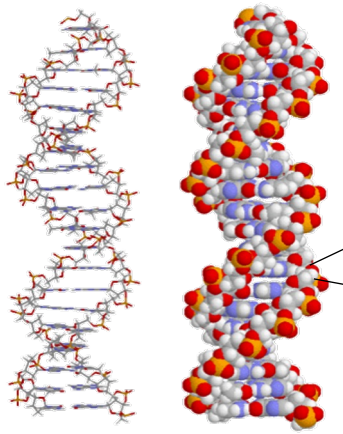
Homochirality of amino acids and sugars

Enantiomers of chiral molecules

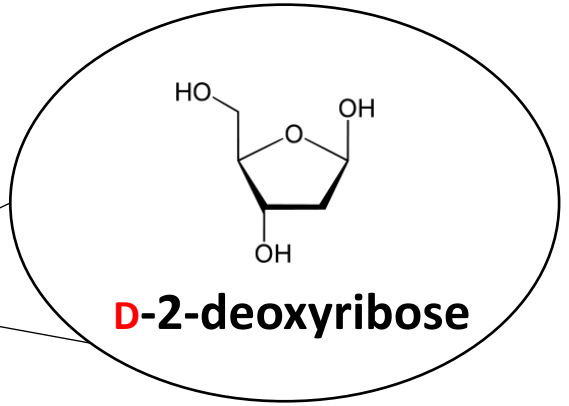


Left-handed (L-) **Right-handed (D-)**

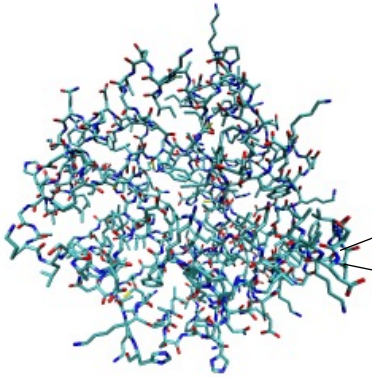
Biopolymers on Earth



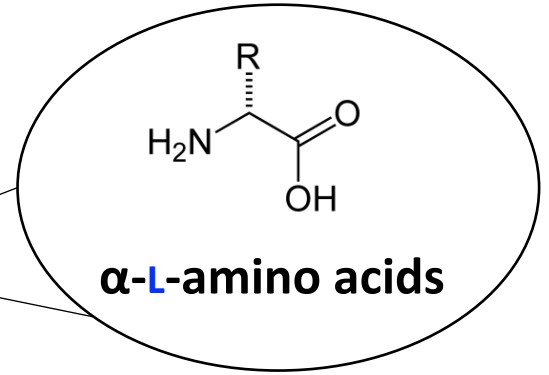
DNA



D-2-deoxyribose



Proteins

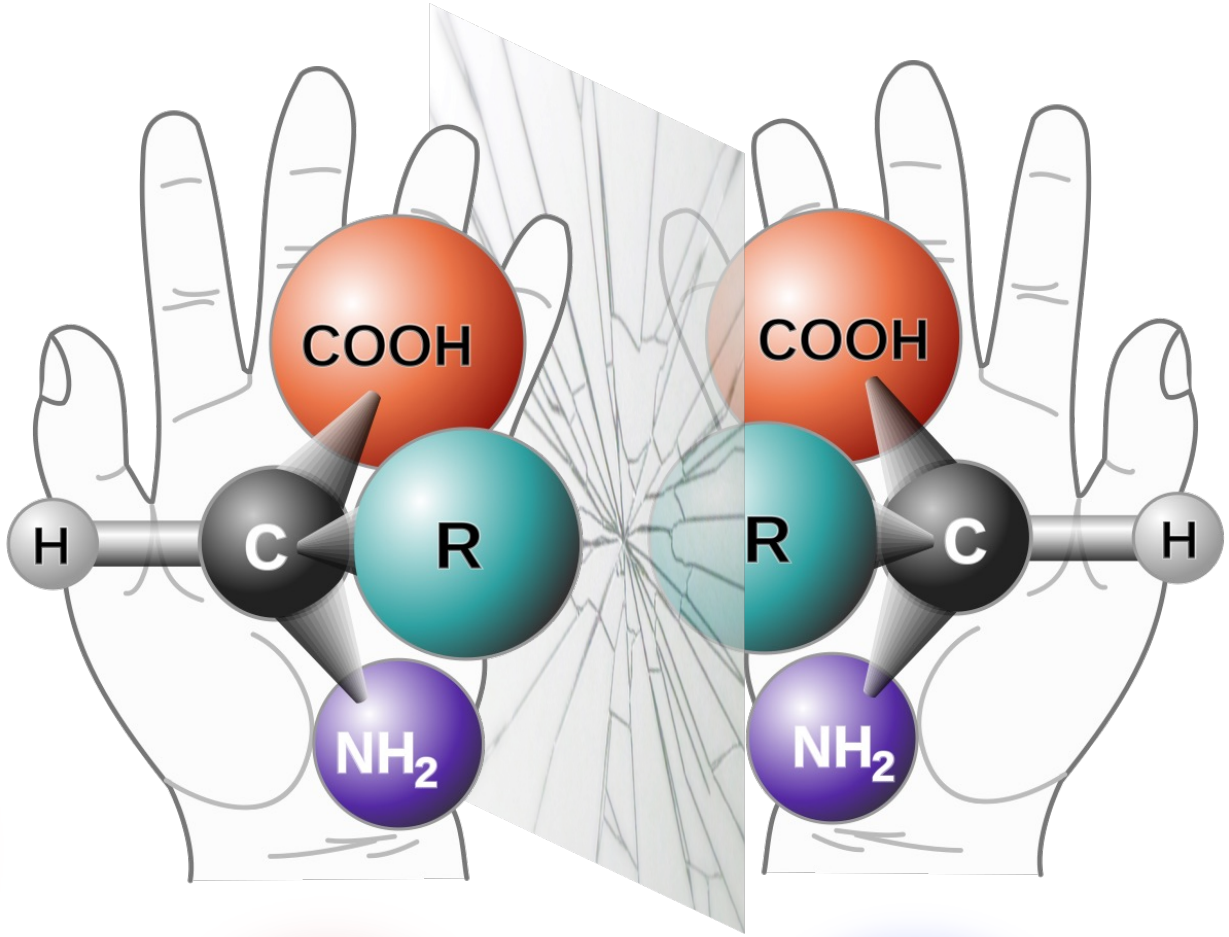


α-L-amino acids

Crystallisation

Enantioselective synthesis on chiral quartz

Adsorption on chiral crystals



Spin-polarized electrons

Inherent energy difference between enantiomers

Circularly polarized electromagnetic radiation

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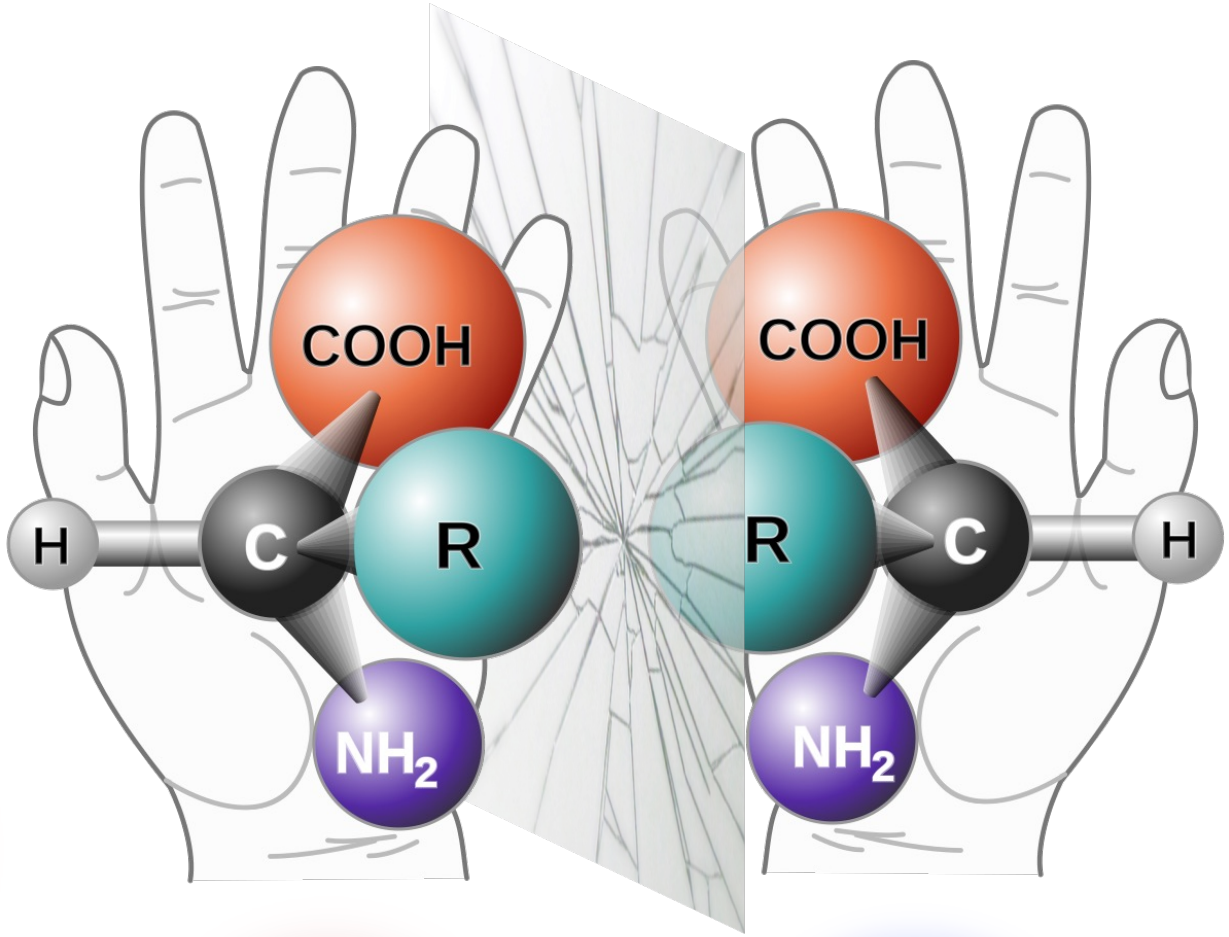

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Circularly polarized electromagnetic radiation

Astrophysical circularly polarized light (CPL) scenario

Credit: NASA/Jenny Mottar

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1. L-excess of amino acids in meteorites

Glavin et al. Chem. Rev. **120** (2020)

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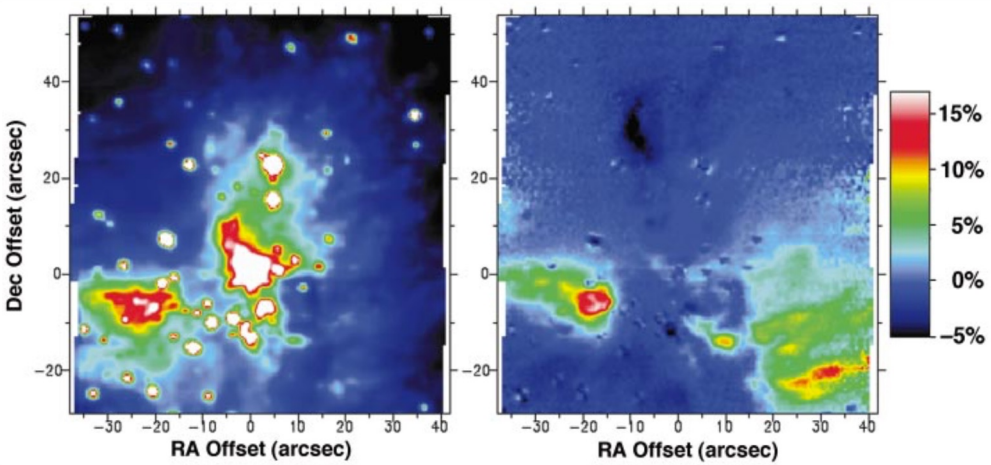
2. IR-CPL detected in space



Bailey et al. *Science* **281** (1998)

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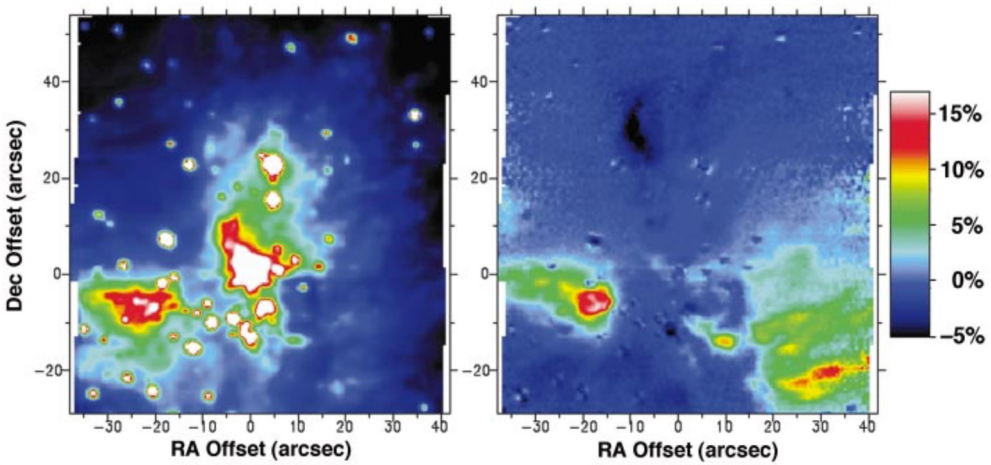

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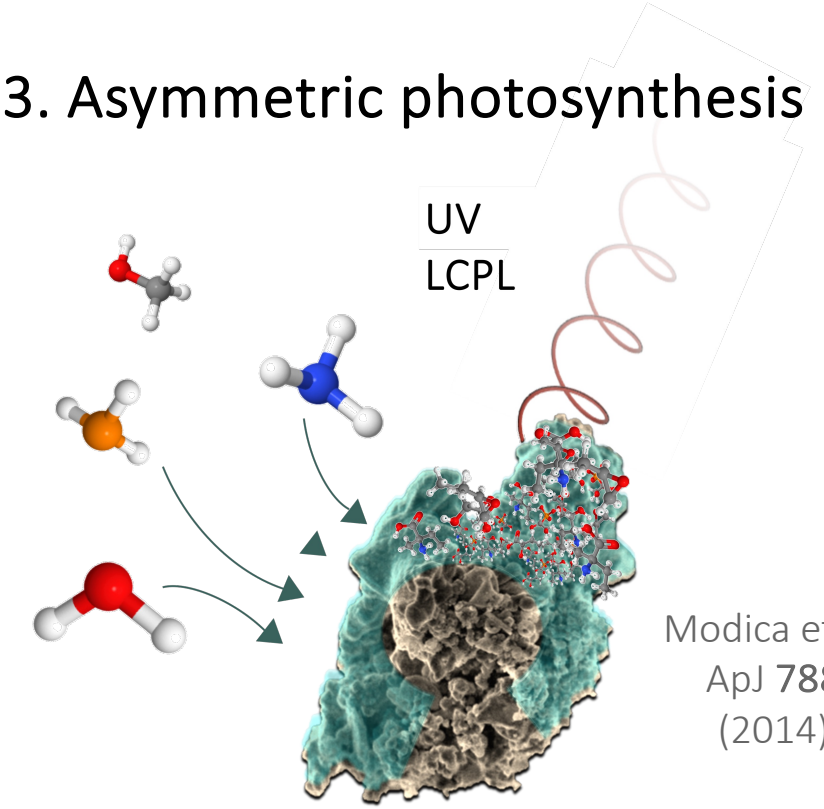
3. Asymmetric photosynthesis



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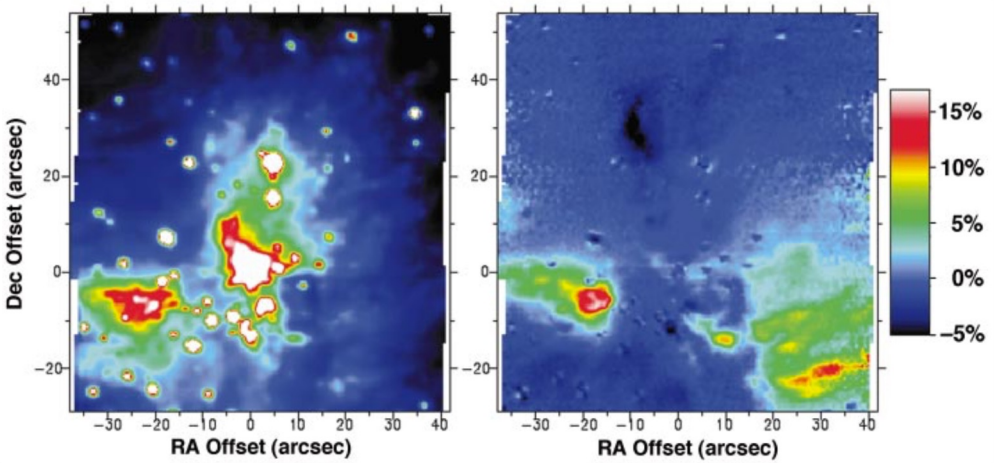

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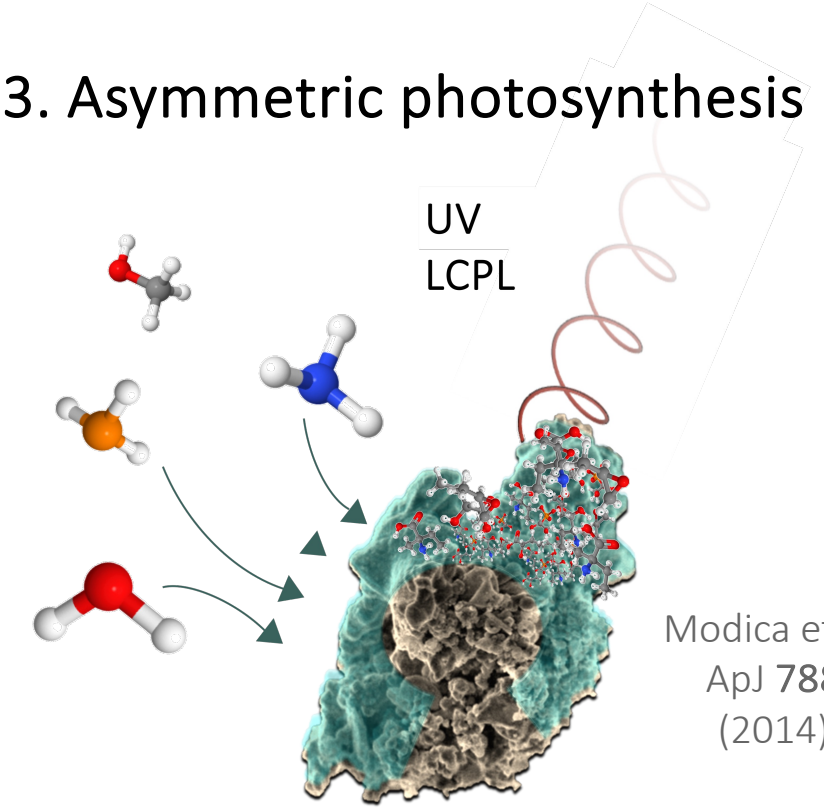

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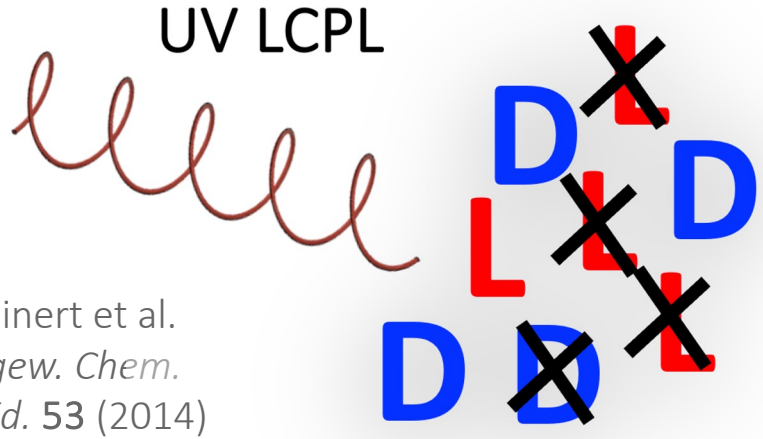


Meinert et al. *Angew. Chem. Int. Ed.* **53** (2014)

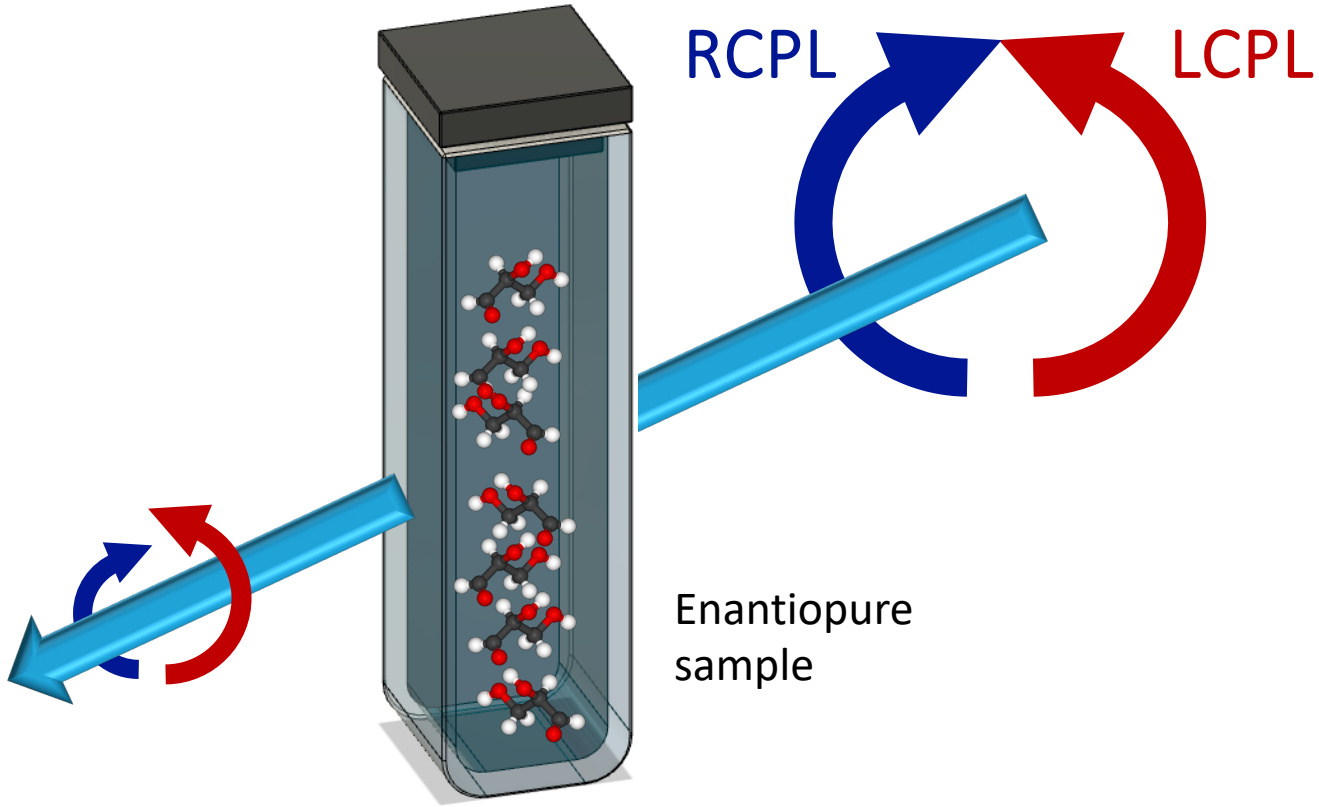
CD and anisotropy spectroscopy experiments at ISA in Aarhus

$CD = A_{LCPL} - A_{RCPL}$

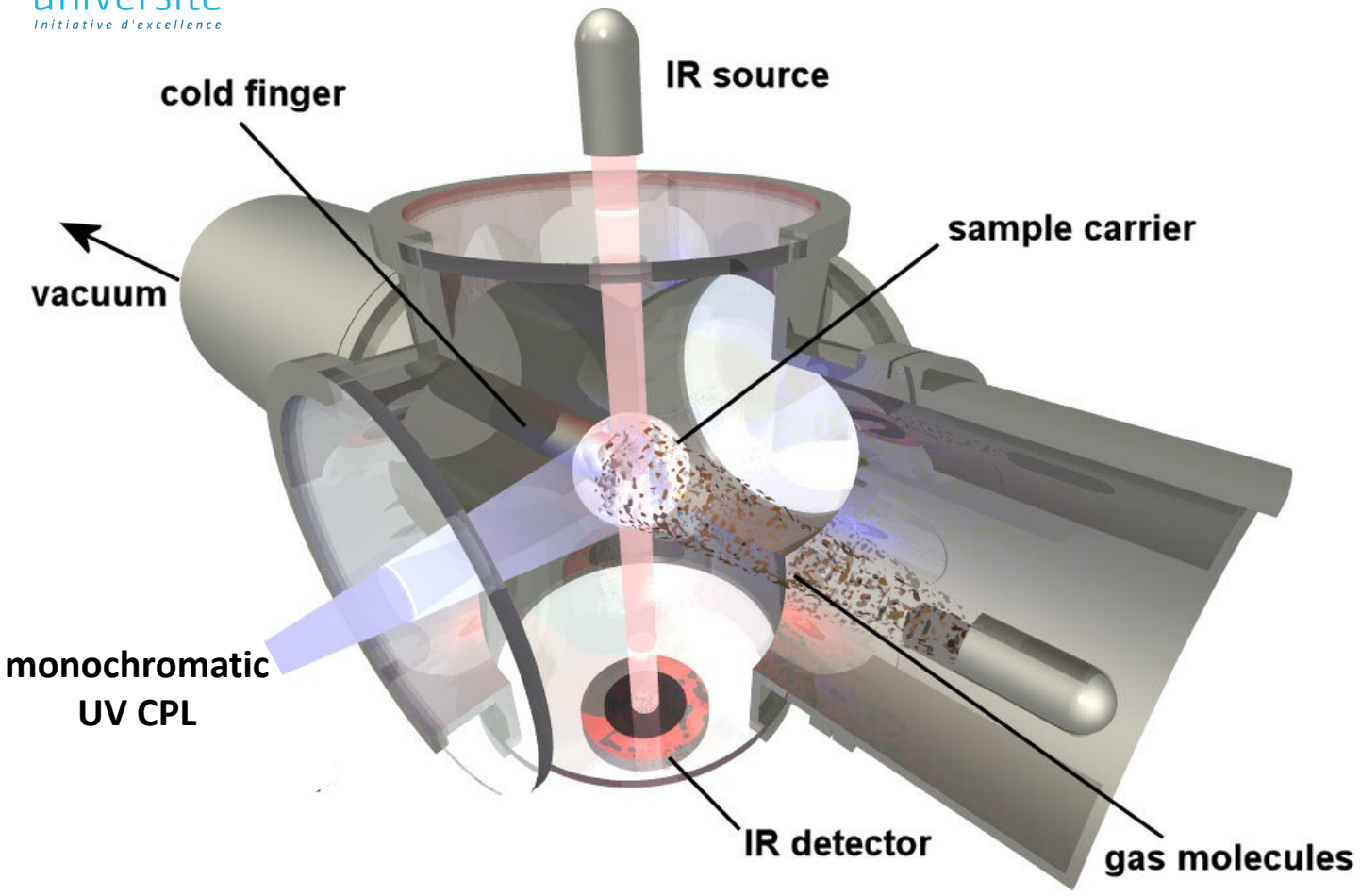
$$g(\lambda) = (A_{LCPL} - A_{RCPL})/A = \Delta\varepsilon/\varepsilon$$

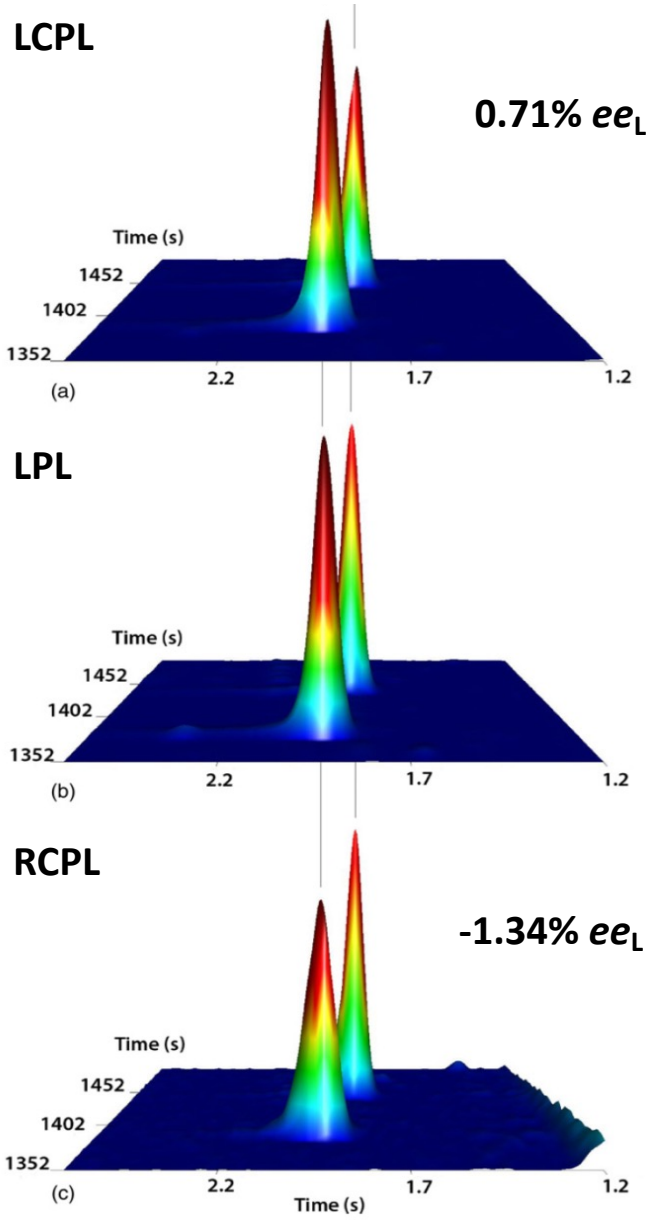
$$|\%ee| \geq (1 - (1 - \xi)^{|g|/2}) \times 100\%$$

$$\%ee = \frac{L-D}{L+D} \times 100\%$$



Asymmetric photosynthesis of amino acids



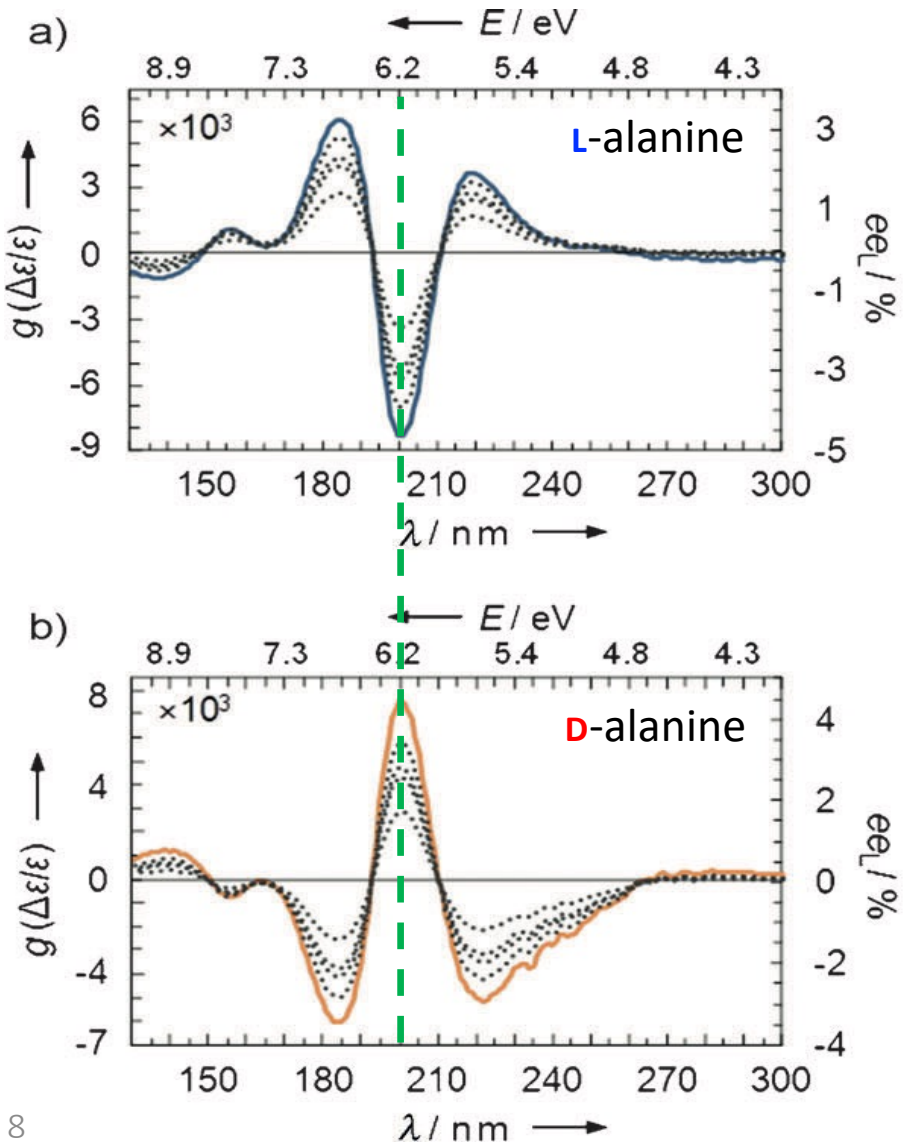


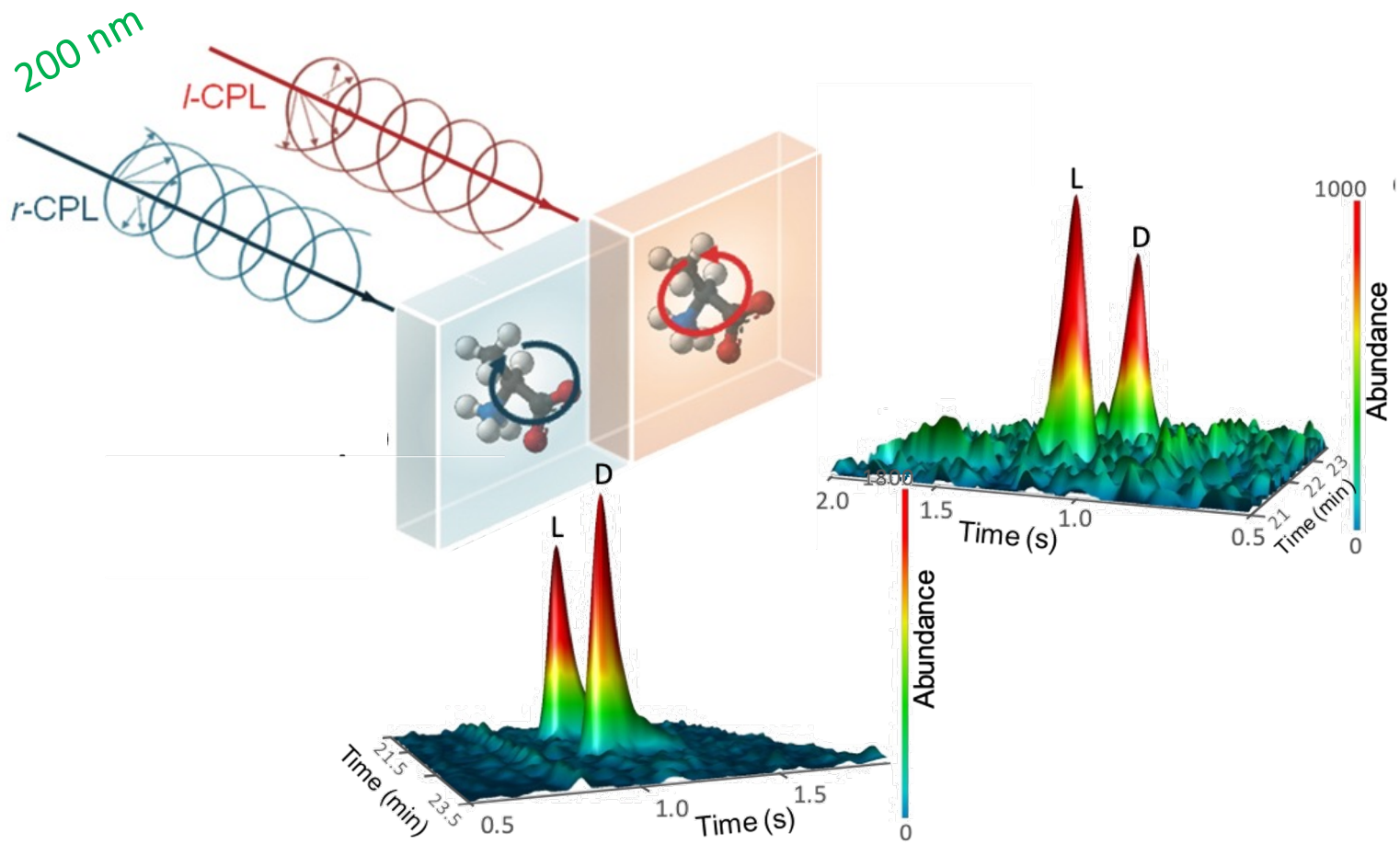
de Marcellus et al. *Astroph. J. Letters* **727** (2011), L27

Modica et al. *Astroph. J. Letters* **727** (2014) L27.

Asymmetric photolysis of racemic solid-state alanine

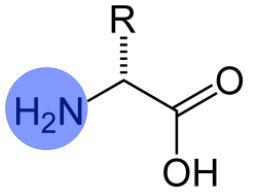
$CD = A_{LCPL} - A_{RCPL}$



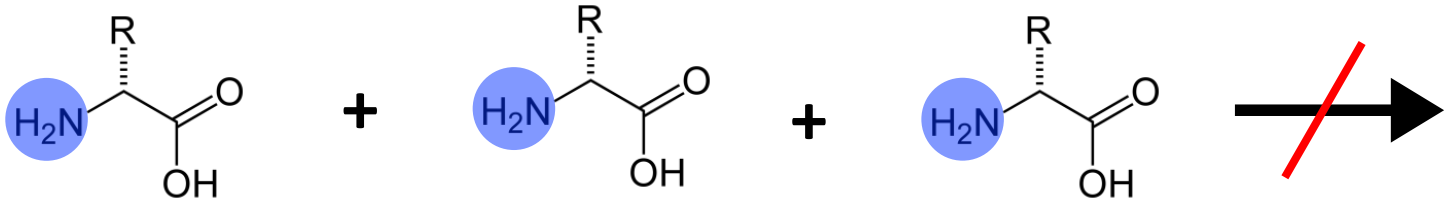


Meinert et al. *Angew. Chem. Int. Ed.* **51** (2012) & **53** (2014)

Depsipeptides as proto-peptides



amino acid



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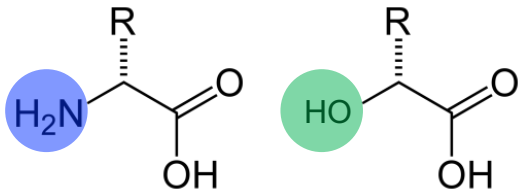
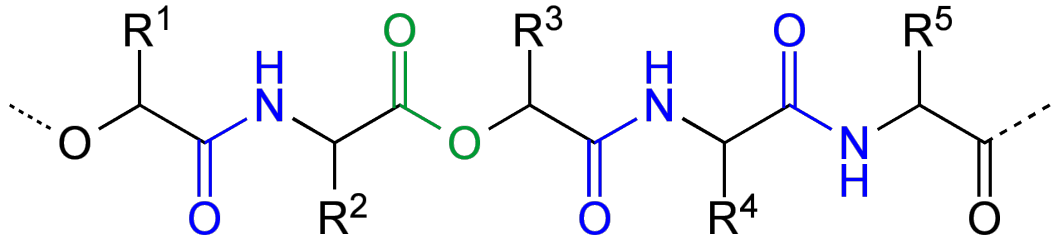


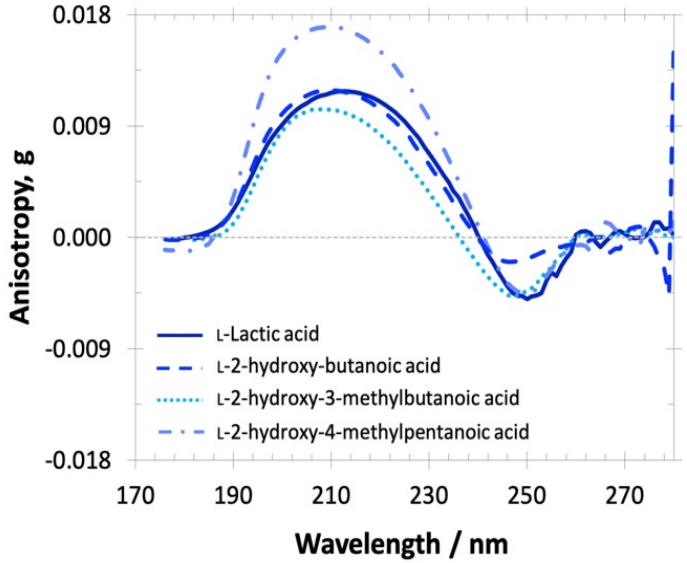
amino acid **HCA**

Forsythe et al. *Angew. Chem. Int Ed.* **54** (2015)

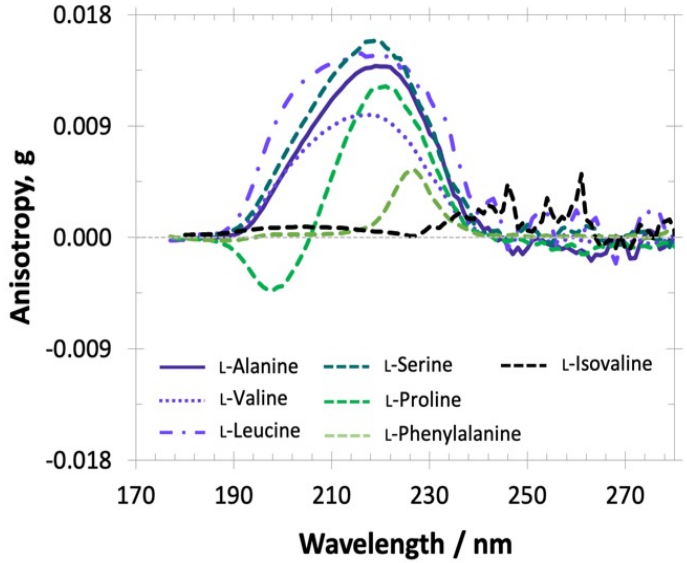


Anisotropy spectroscopy

L-Hydroxycarboxylic acids

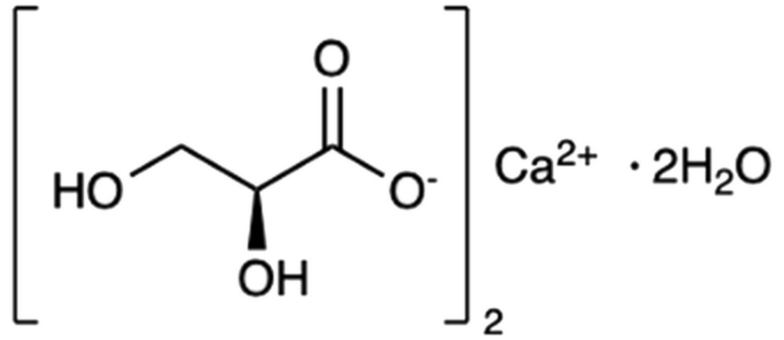


L-Amino acids

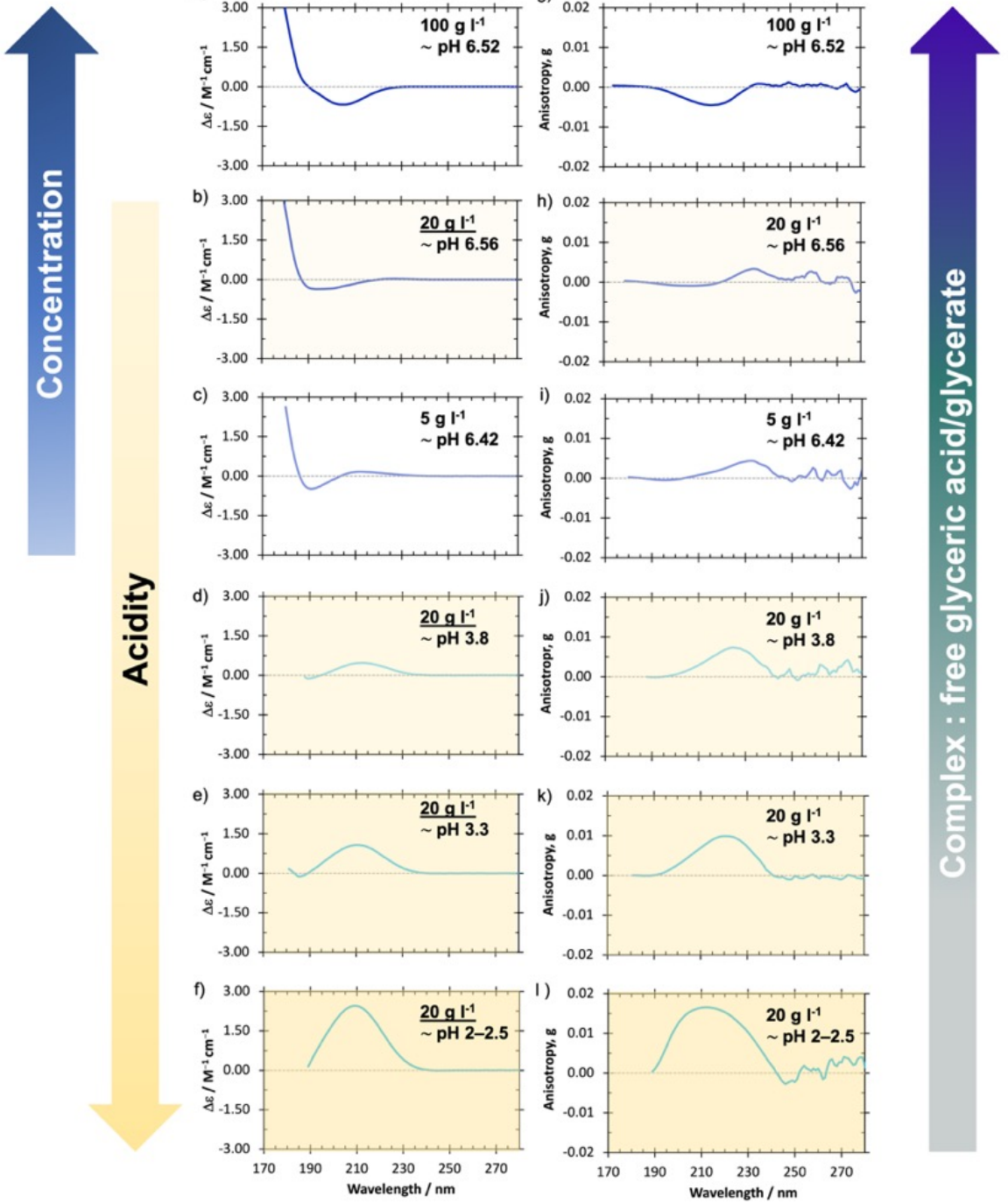


Bocková* et al. *Commun. Chem.* **4** (2021). Bocková et al. *Chirality* **34** (2022).

Structural changes due to the complexation with Ca^{2+} reflected in the ECD/anisotropy spectra of **glyceric acid.**



L-glyceric acid calcium salt dihydrate



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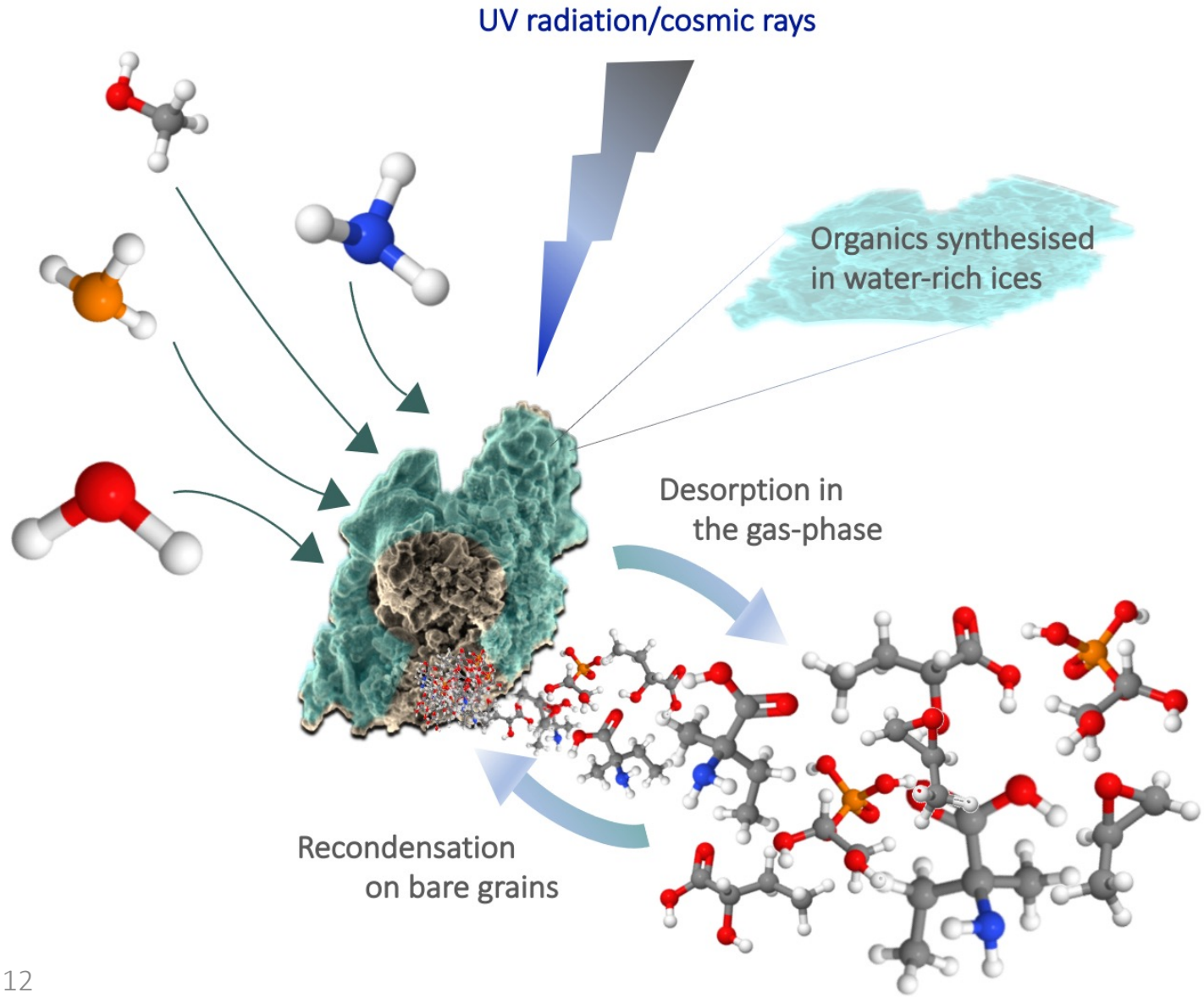
Different surrounding environments in space



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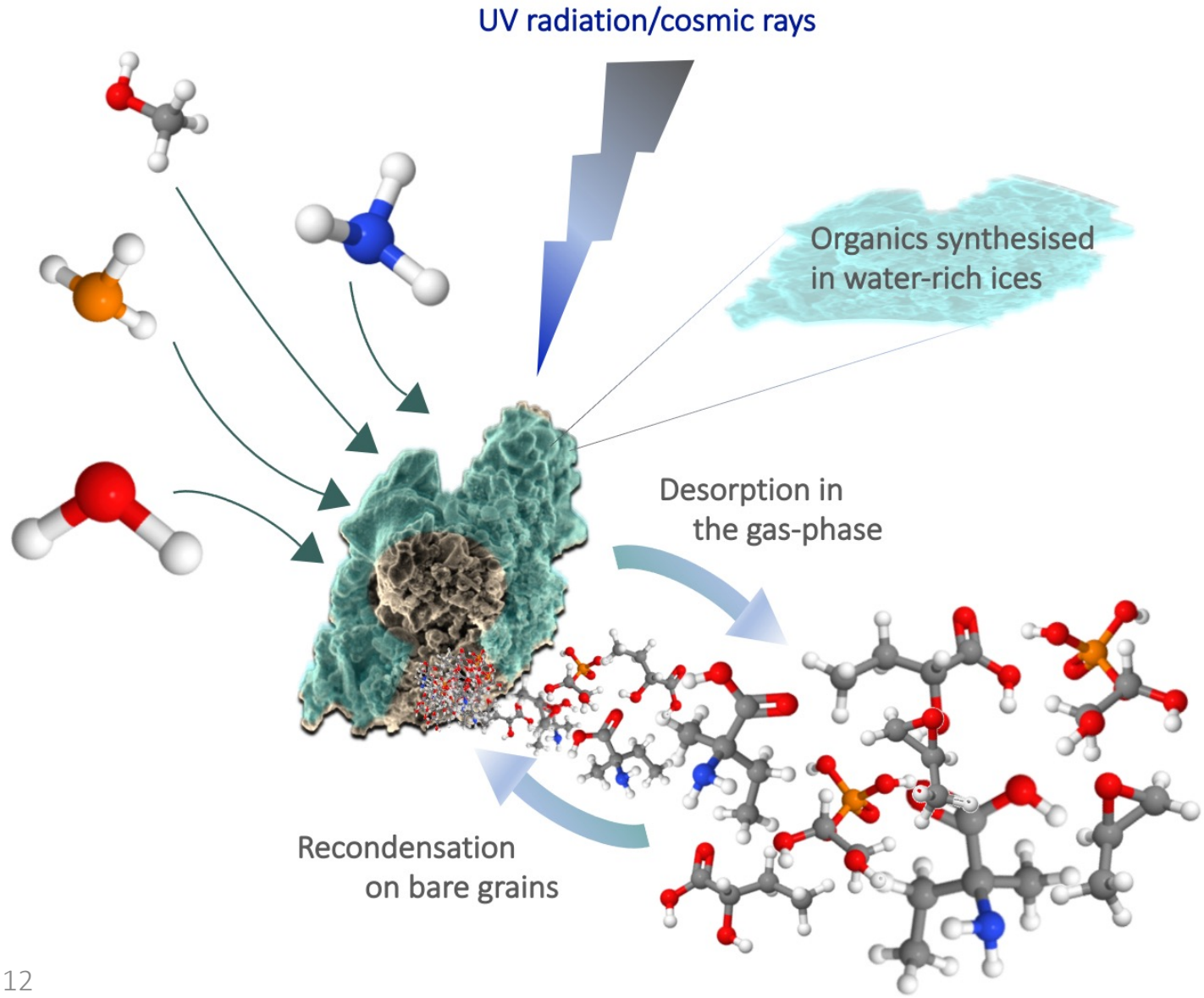
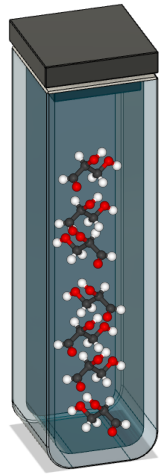
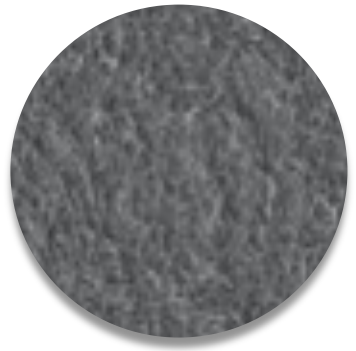


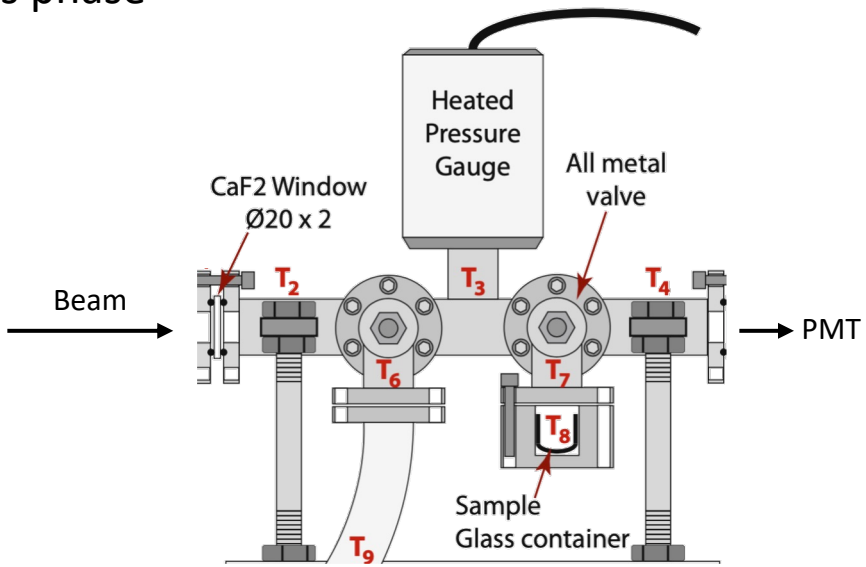
Aqueous solution



Isotropic amorphous solid films

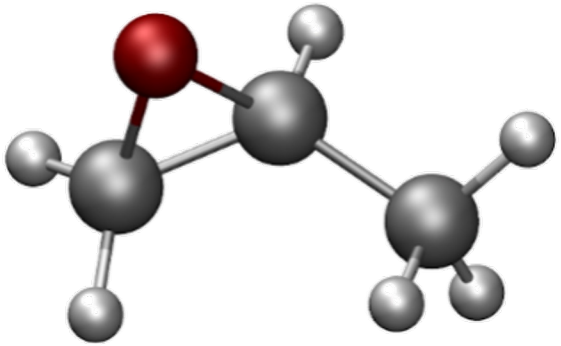


Gas phase



Meinert et al. *Nat. Commun.* **13** (2022).

Propylene oxide: the 1st chiral molecule detected in space



Murchison: $ee_R \approx 10\%$

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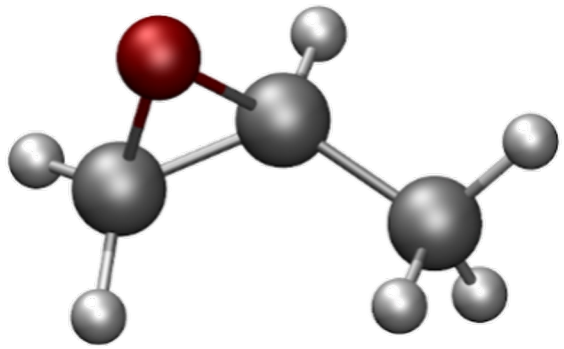

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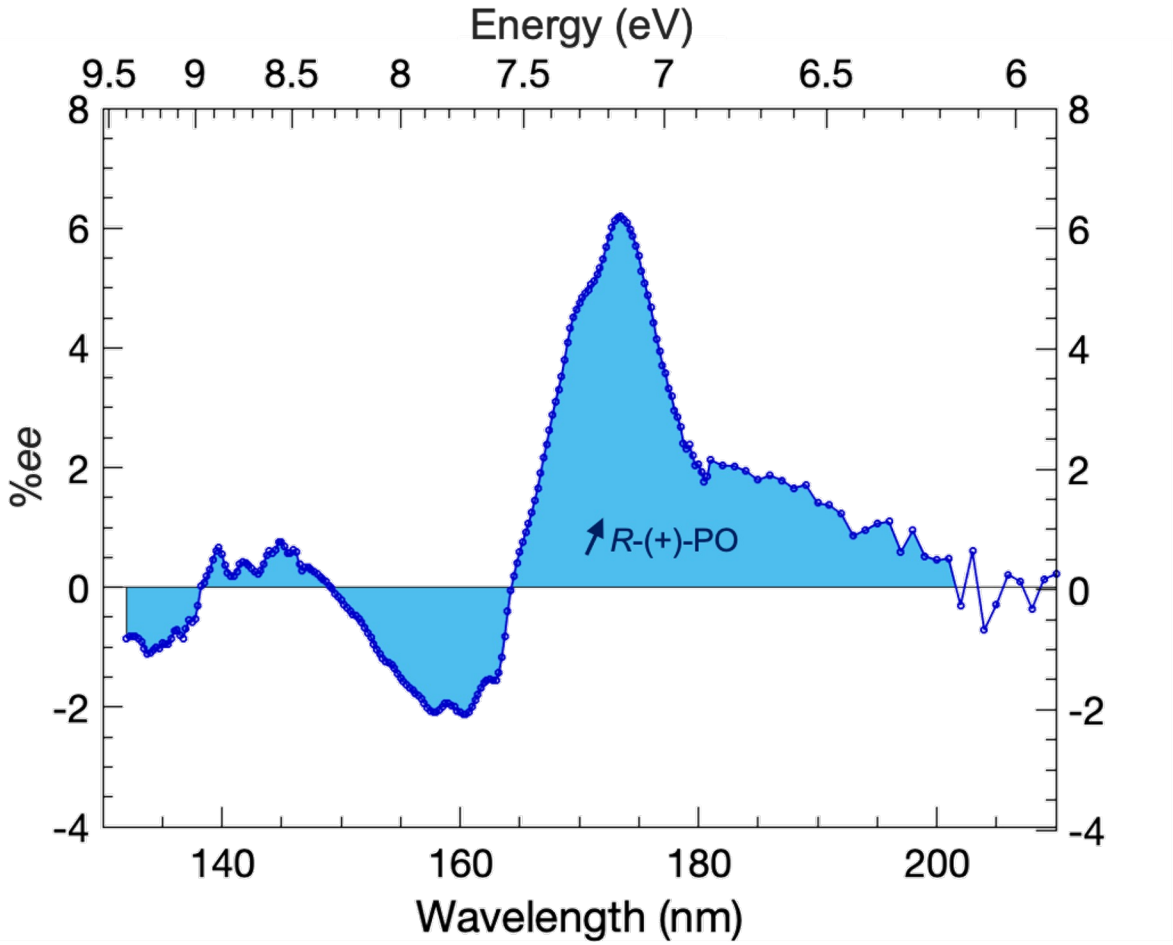

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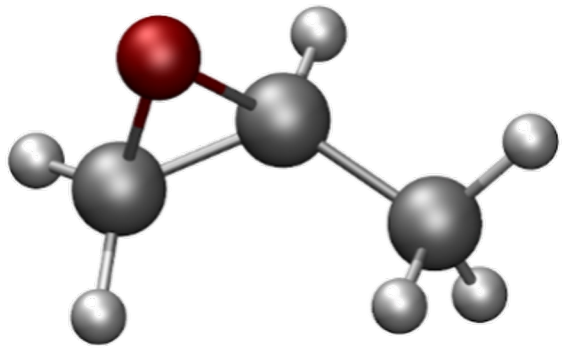

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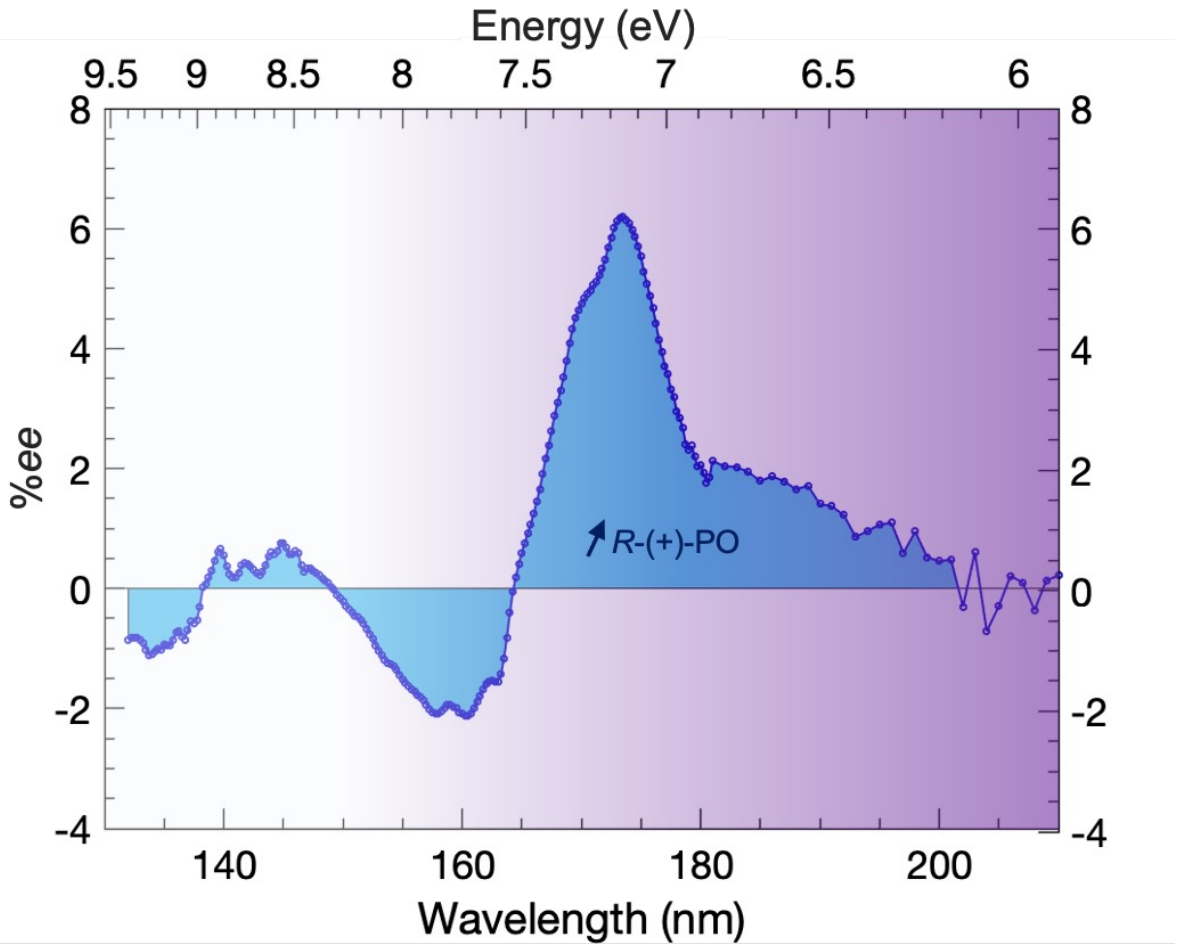
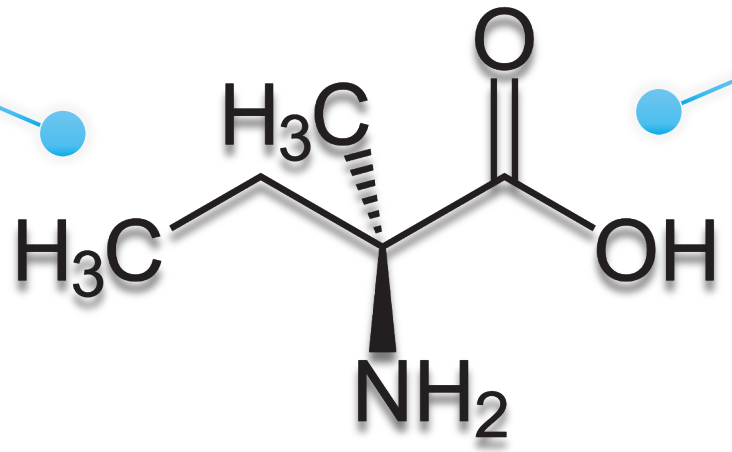


Garcia et al. *Sci. Adv.* **8** (2022).

Isovaline

Non-proteinogenic amino acid

NOT ubiquitous on Earth (racemic/D)



ee_L of up to ~20% in carbonaceous chondrites

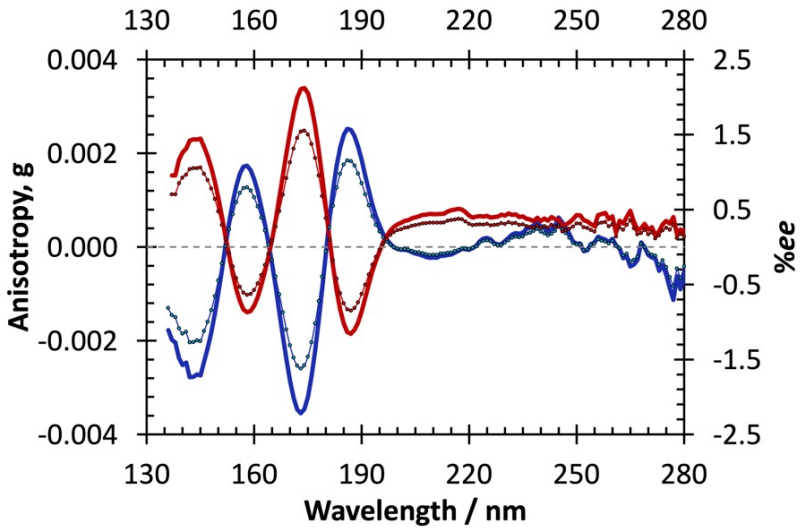
Not prone to rapid racemisation

Magnitude of ee_L ~ the extent of aqueous alteration (CI, CR, CM)

Asymmetric photochemistry of isovaline

Bocková et al. *Nat. Commun.* **14** (2023).

1. CD/anisotropy spectroscopy



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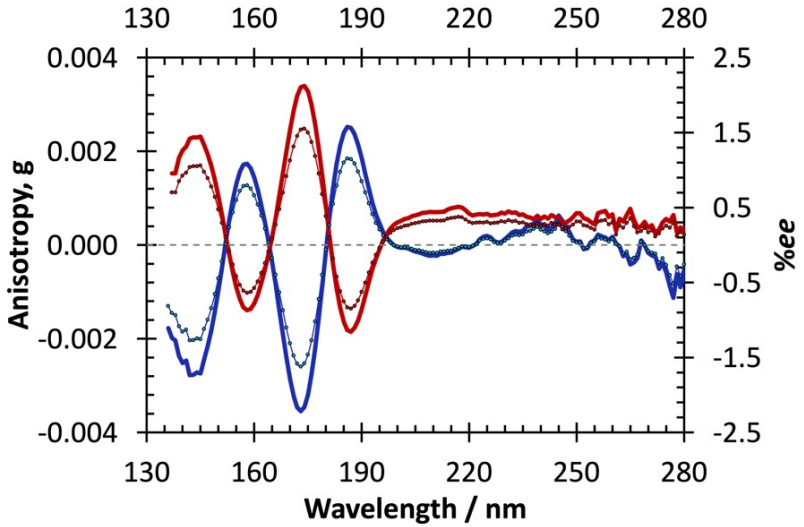

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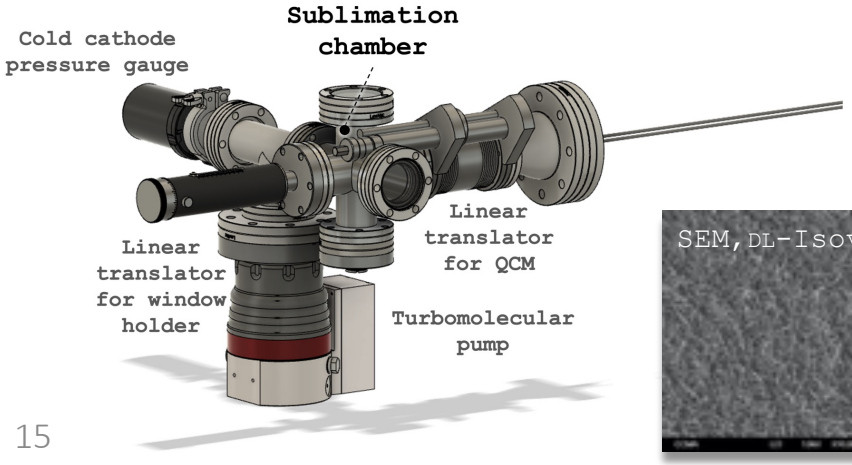

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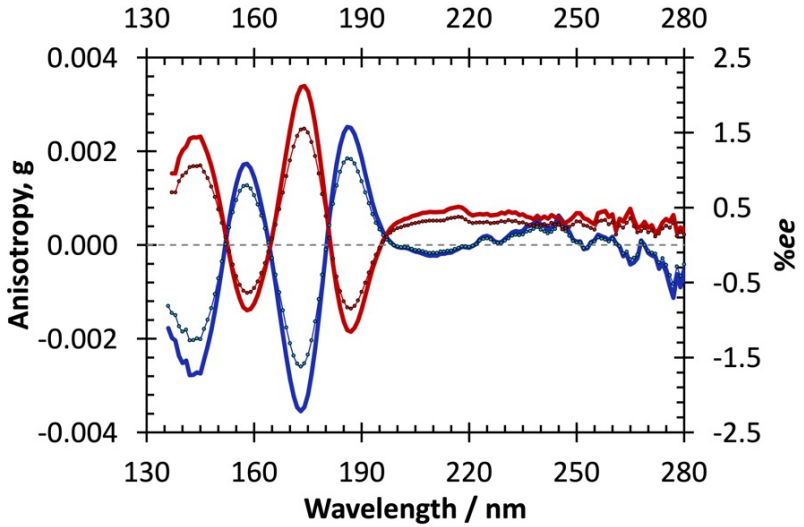

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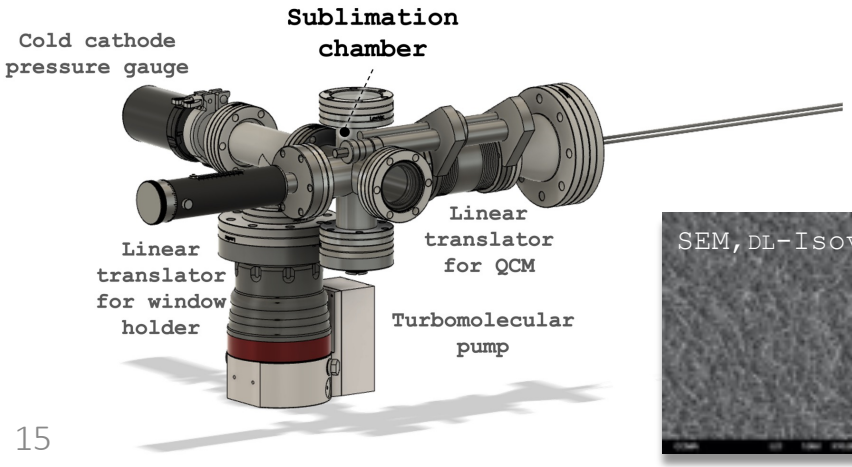
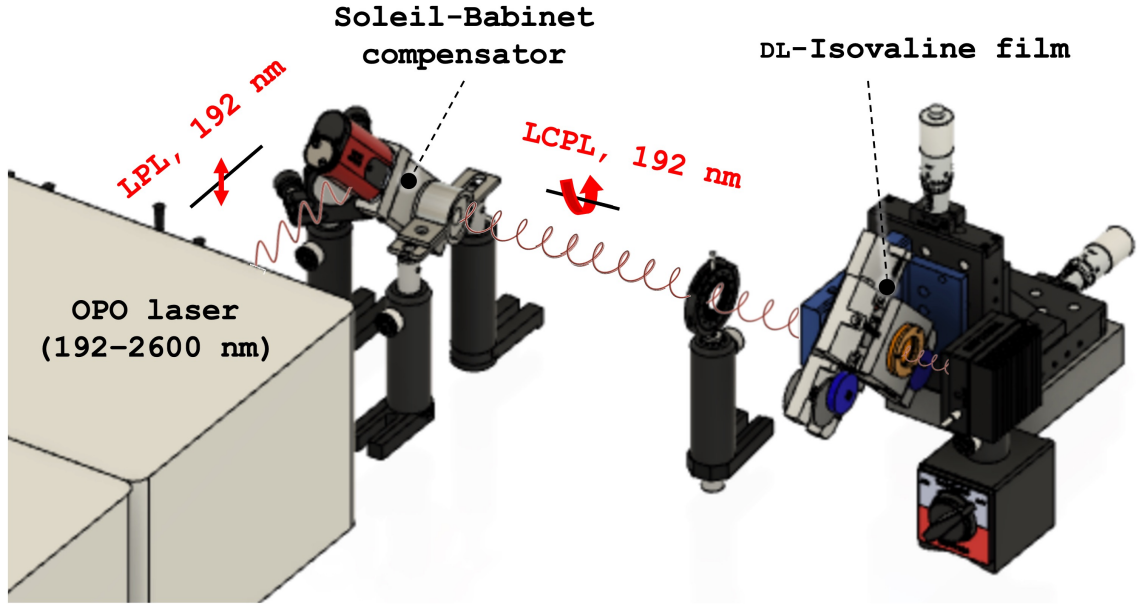


3. UV CPL irradiation

Bocková et al. *Nat. Commun.* **14** (2023).



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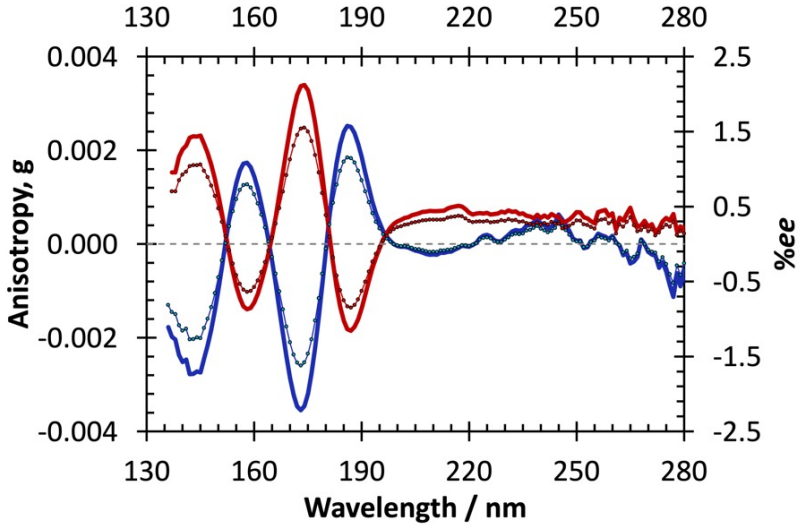

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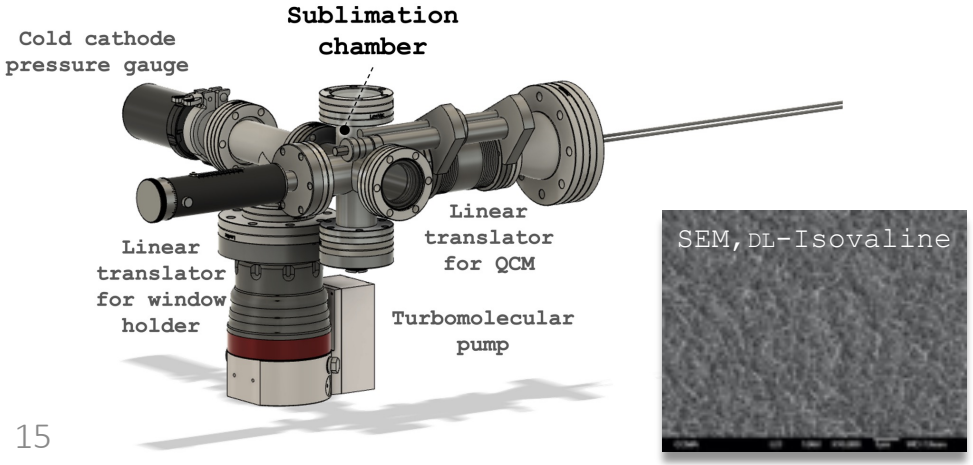

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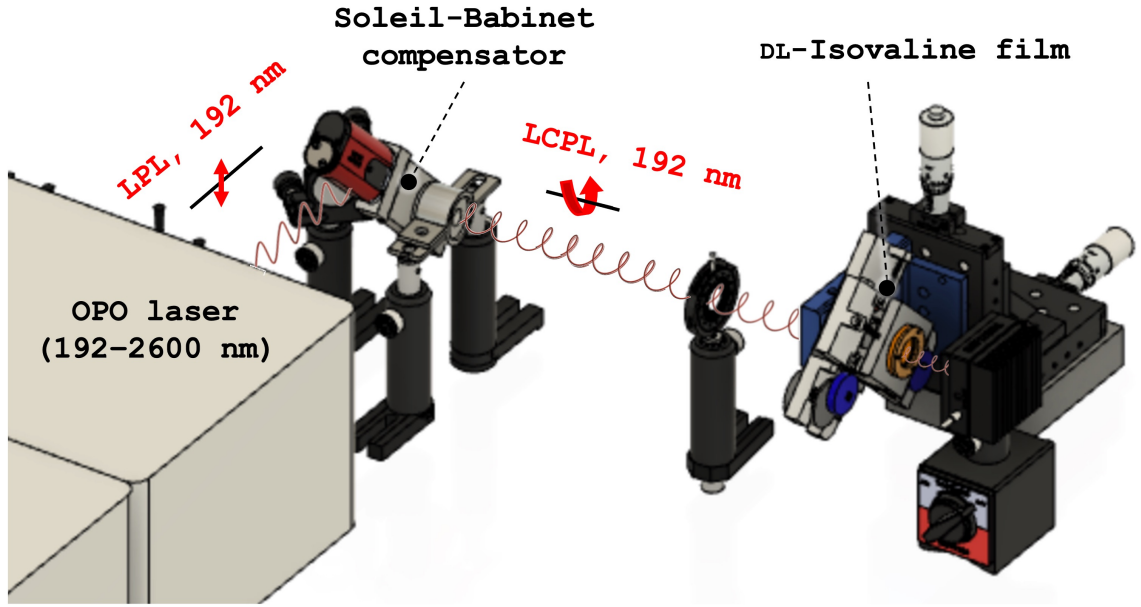
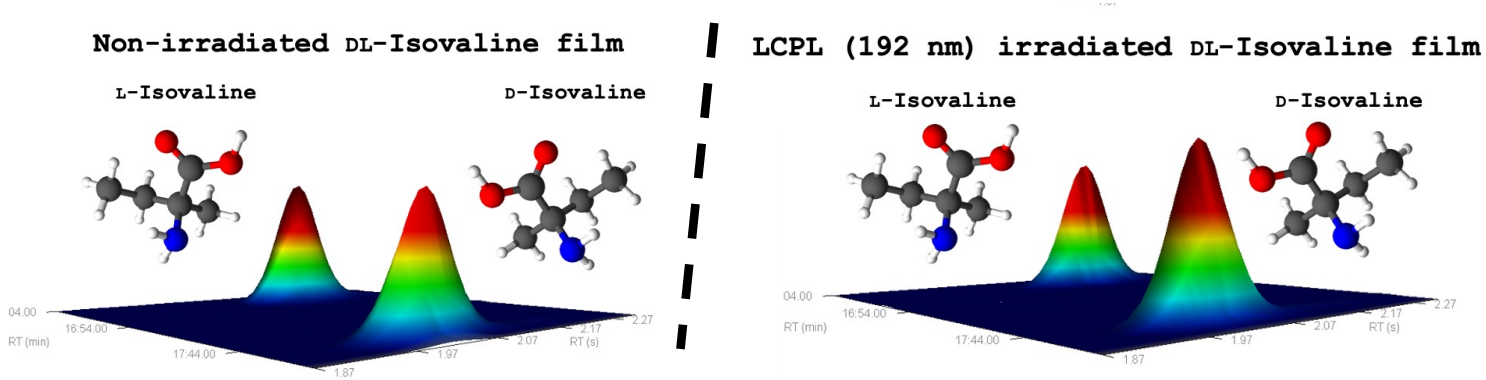
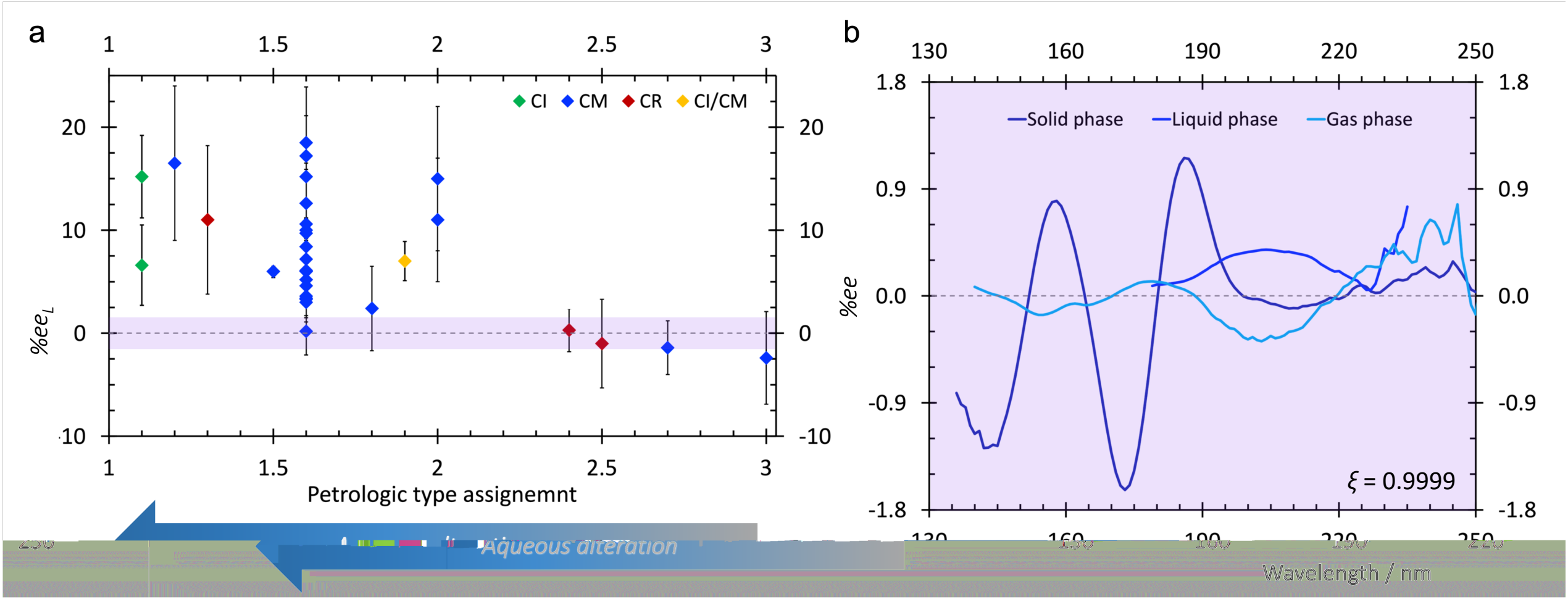


4. GC×GC analysis



Isovaline's *ee* below detection limits in pristine chondrites

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

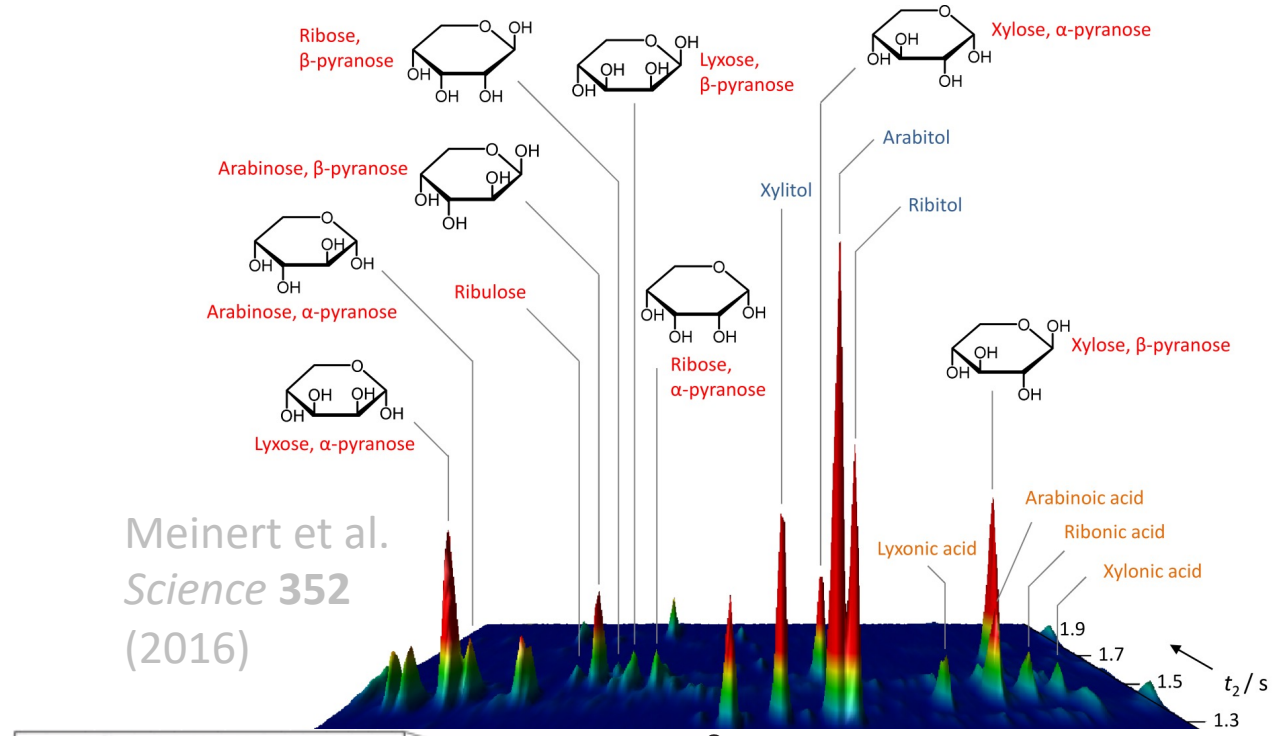


Bocková et al. *Nat. Commun.* **14** (2023).

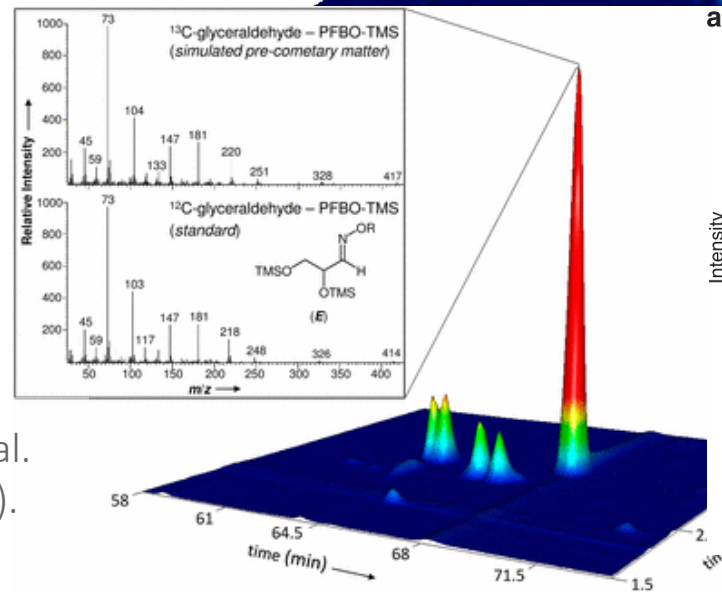
What about sugars…?

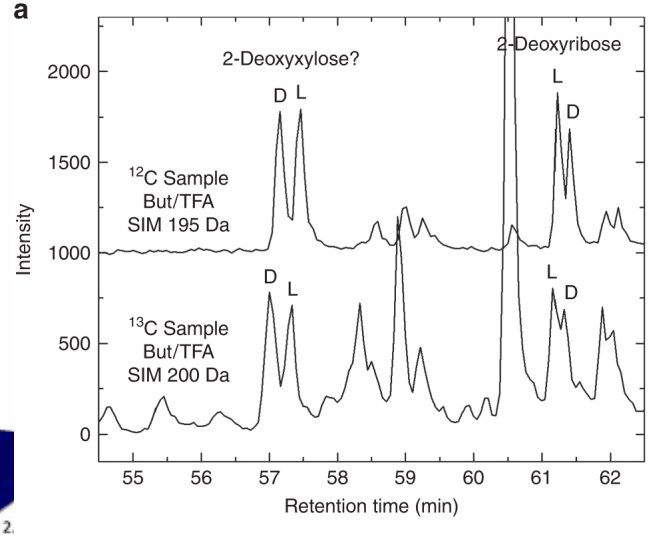
Furukawa et al. *PNAS* **116** (2019).

Meinert et al. *Science* **352** (2016)



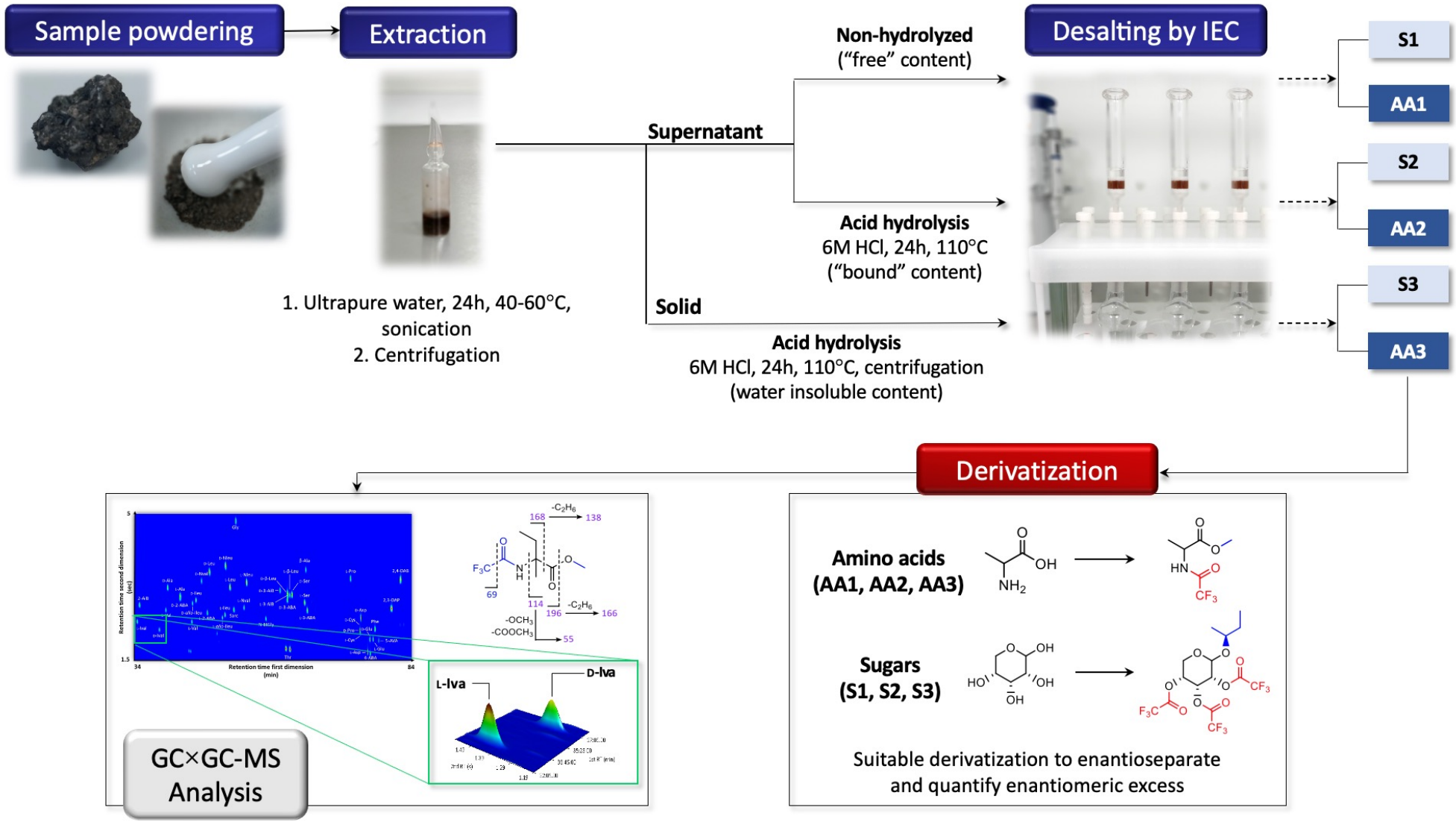
de Marcellus et al. *PNAS* **112** (2015).



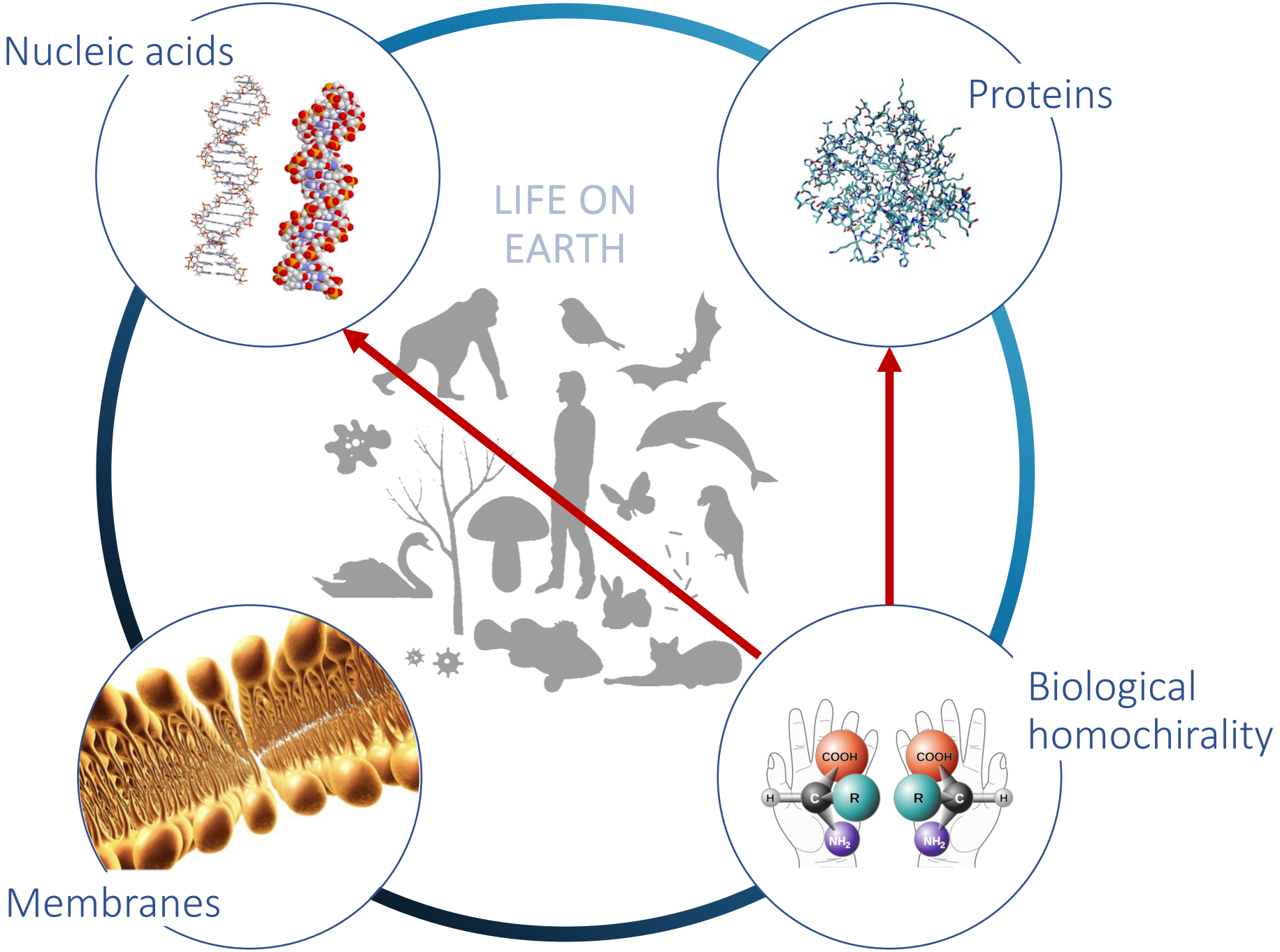


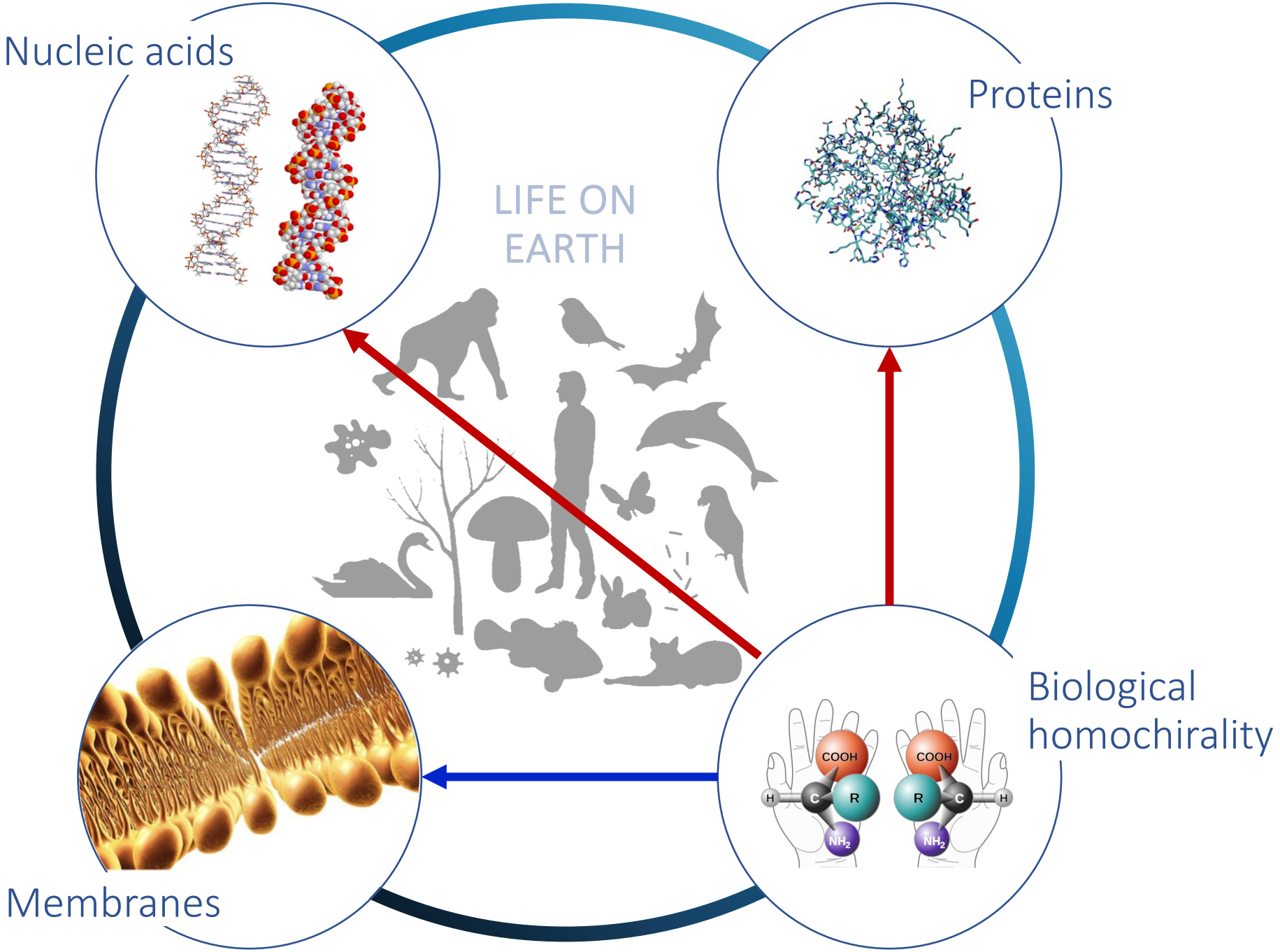
Nuevo et al. Nat. Commun. **9** (2018)

Development of a protocol for simultaneous enantioselective analysis of sugars and amino acids in extra-terrestrial samples.

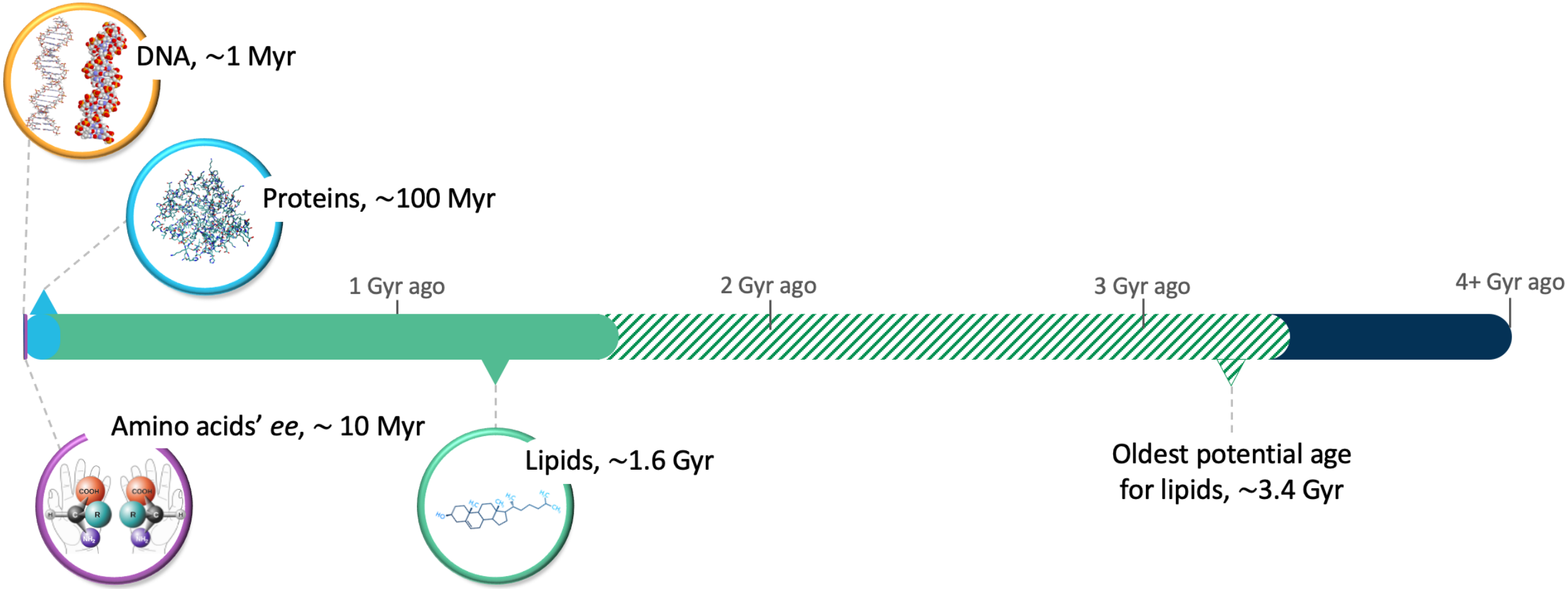


Pepino et al. *J. Sep. Sci.* ***45*** (2022). Garcia, Leyva et al. *Talanta* ***271*** (2024).


Nucleic acids
Proteins
LIFE ON EARTH
Biological homochirality
COOH
H
C
R
NH2
Membranes


Nucleic acids
Proteins
LIFE ON EARTH
Biological homochirality
COOH
H
C
R
NH2
Membranes

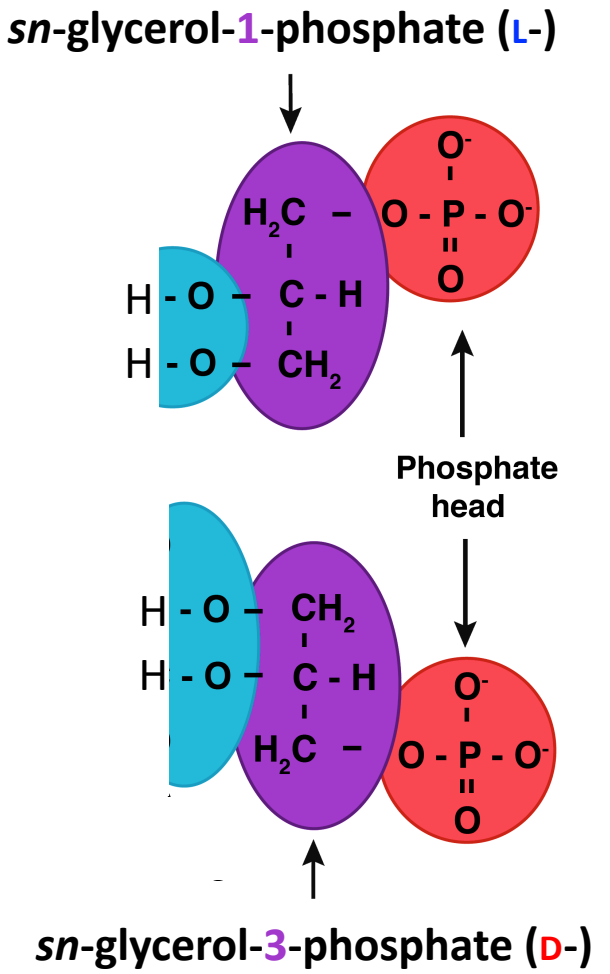
Longevity of lipids



Wilhelm et al. *52nd Lunar Planet. Sci. Conf.* **2634** (2021).

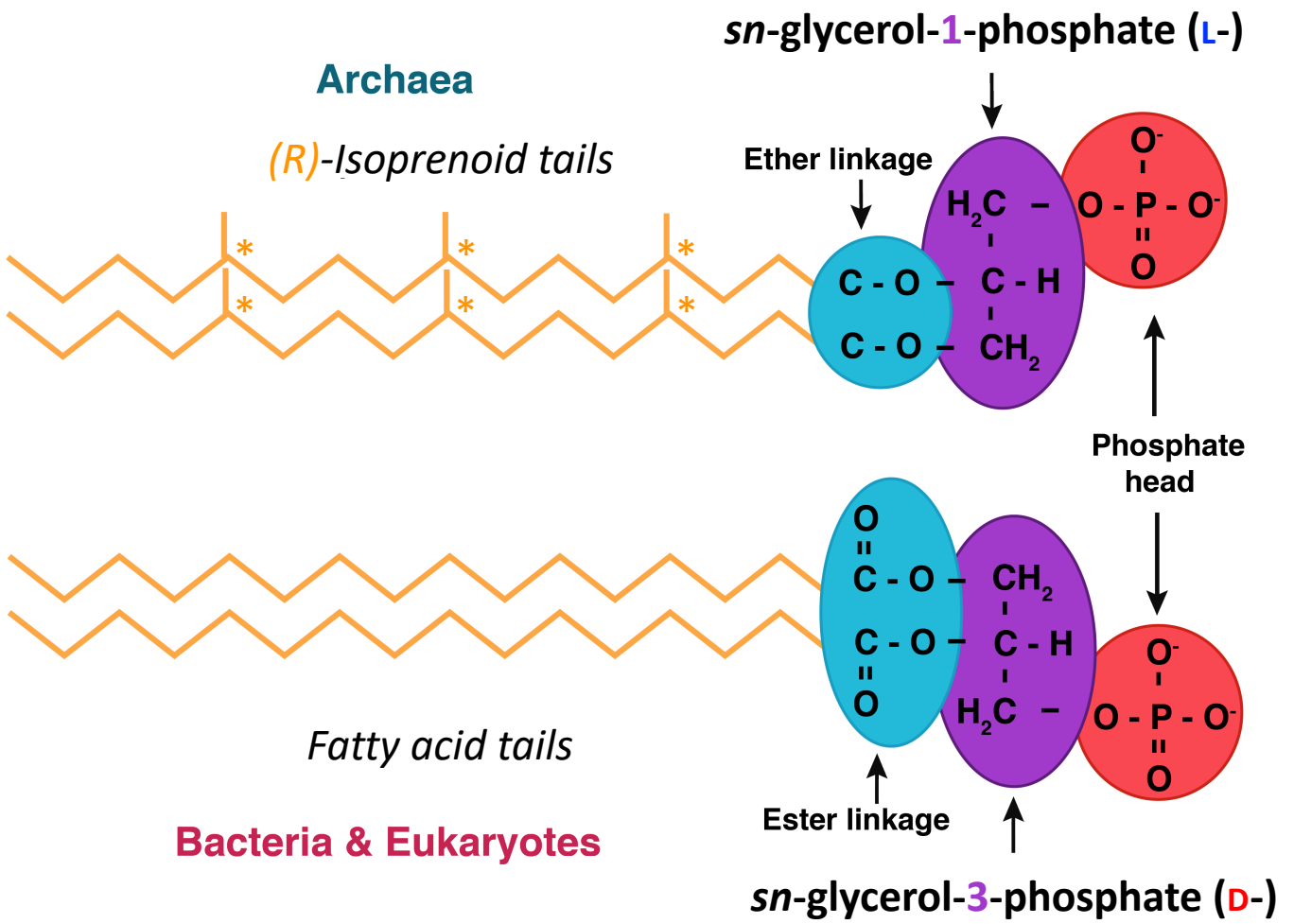
Contemporary membrane phospholipids

Archaea

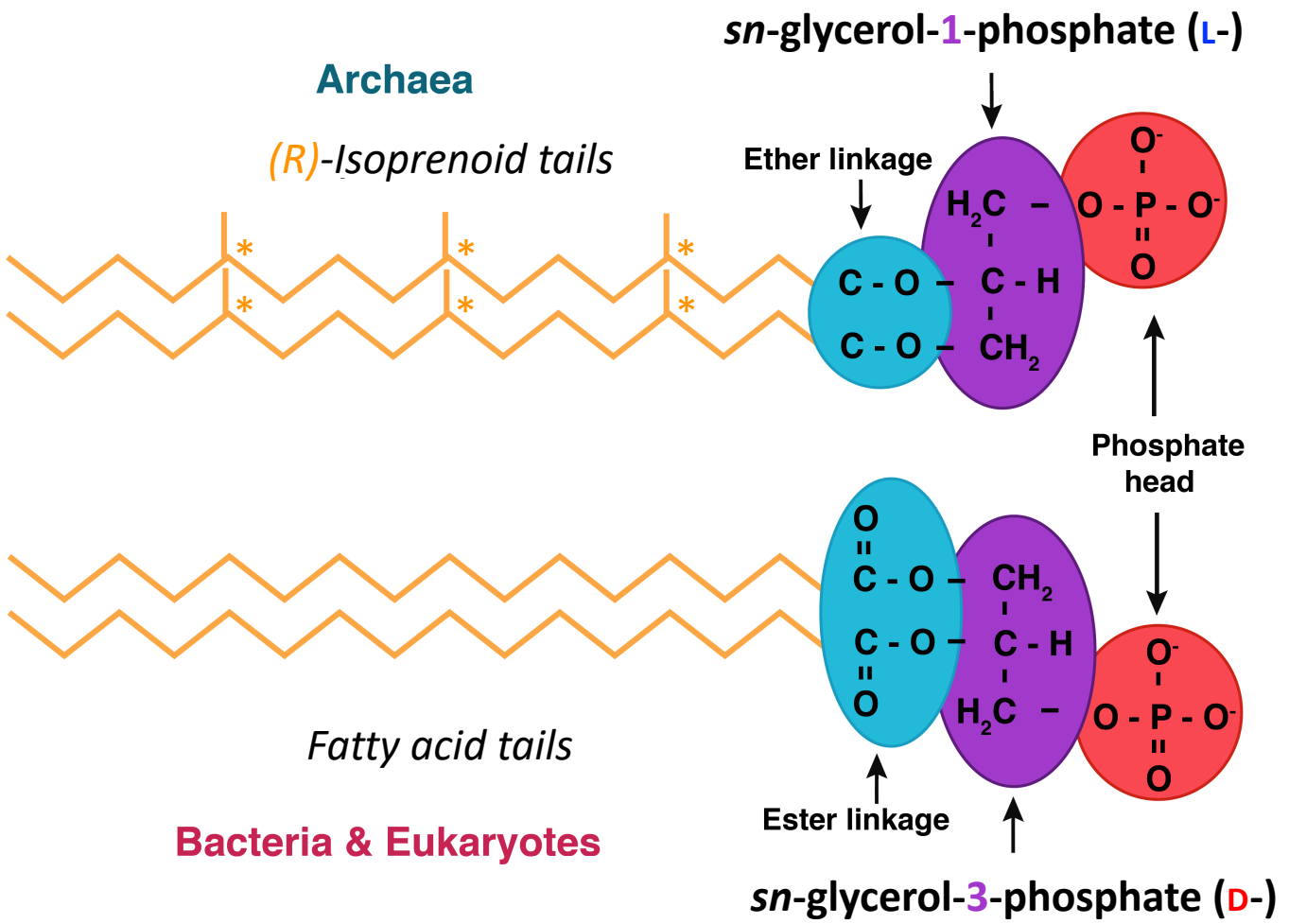


Bacteria & Eukaryotes

Contemporary membrane phospholipids



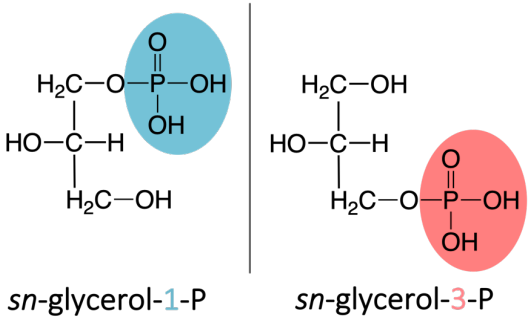
Contemporary membrane phospholipids



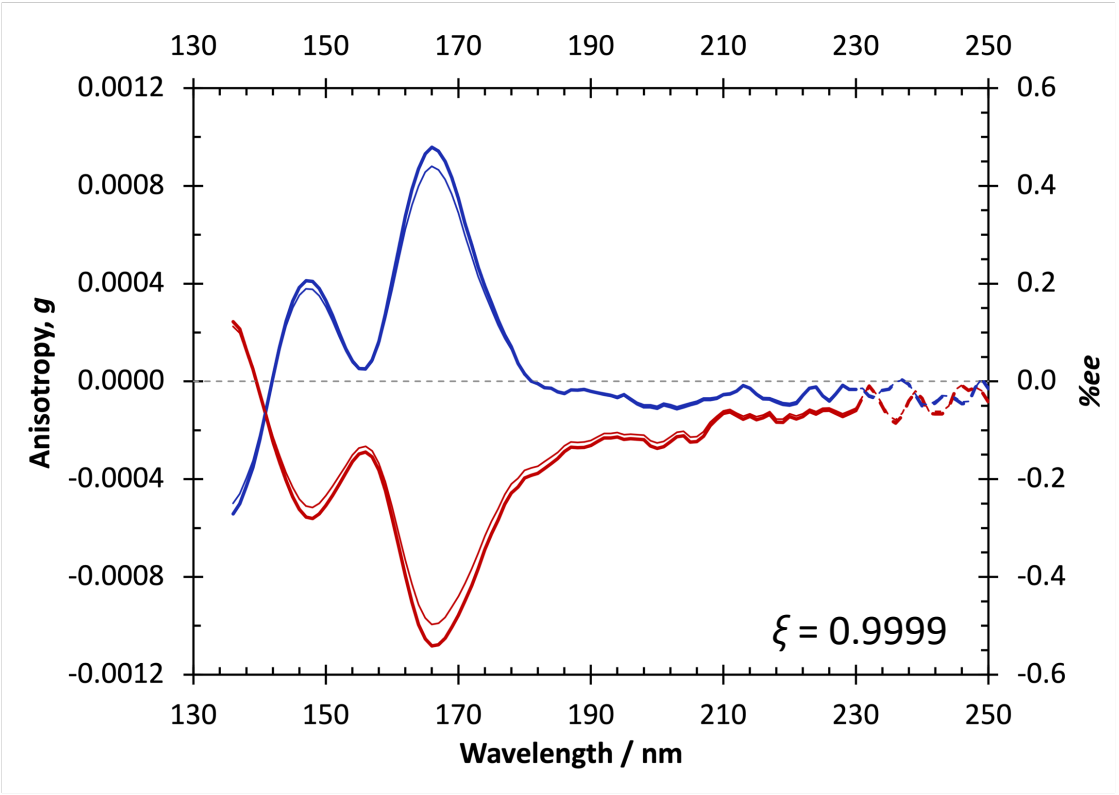
Backbones & side chains detected in simulated ices, e.g.:

Zhu et al. *ApJL* **899** (2020).
Zhu et al. ApJS **234** (2018).

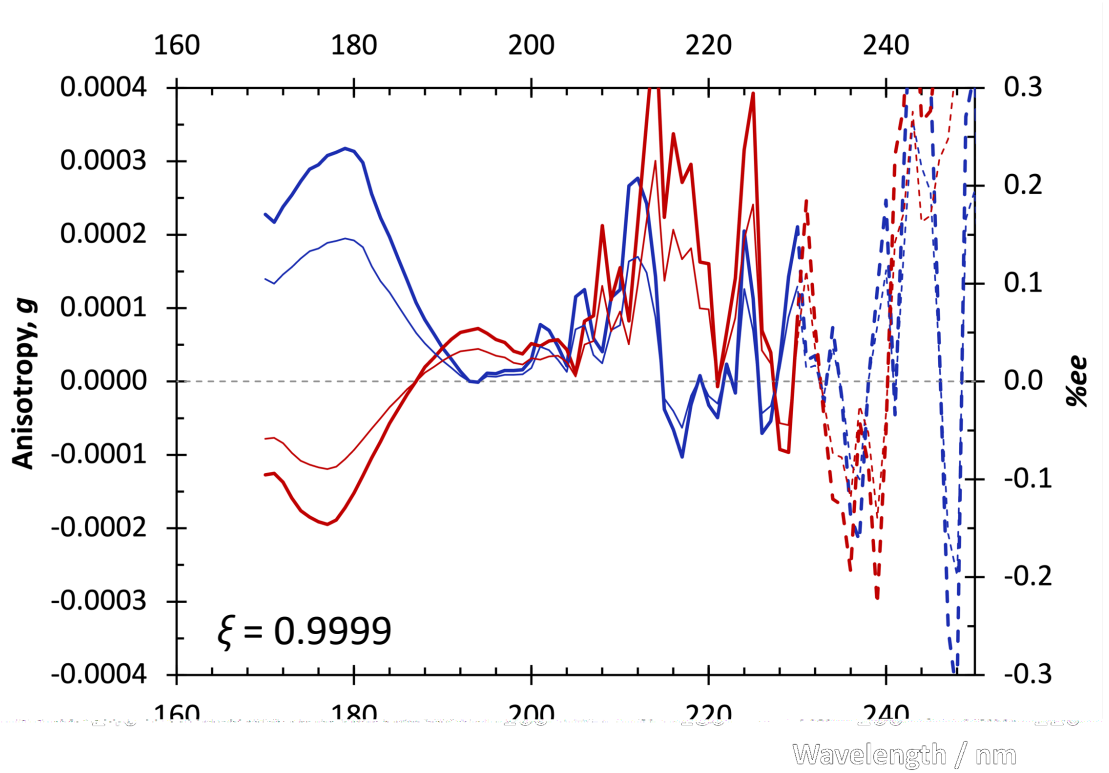
Chiral backbones of phospholipids



Solid phase

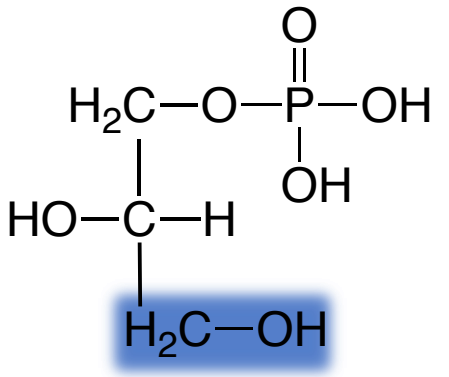


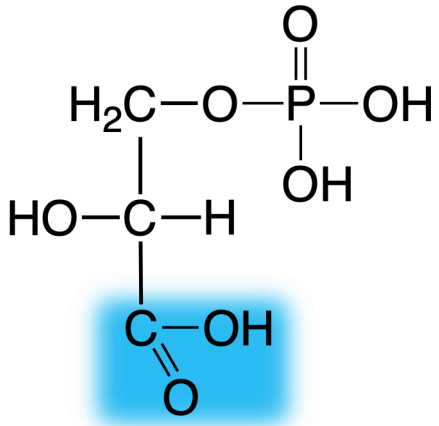
Liquid phase

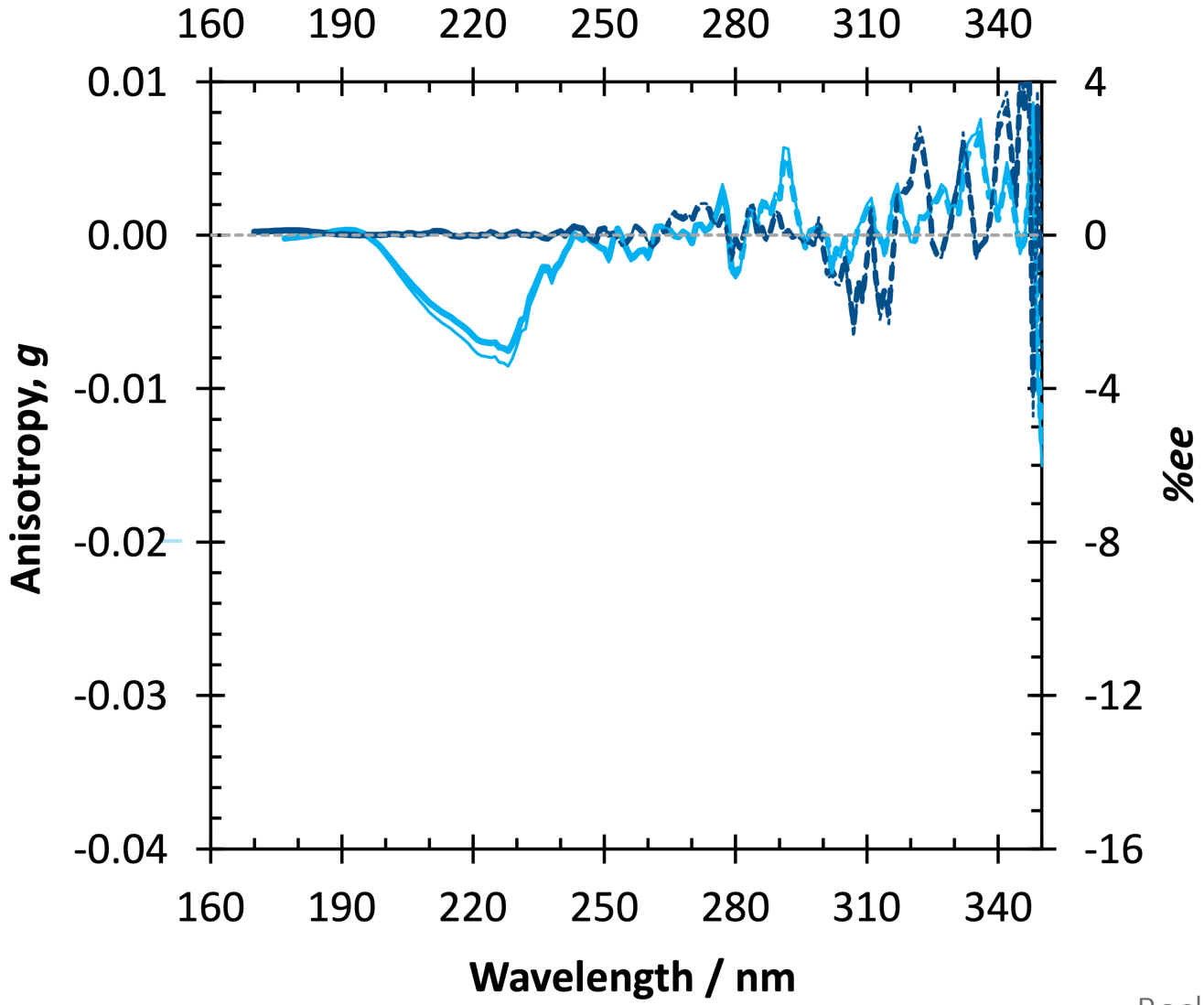


Bocková et al. *Chirality* **accepted** (2024).

Alternative backbone precursors

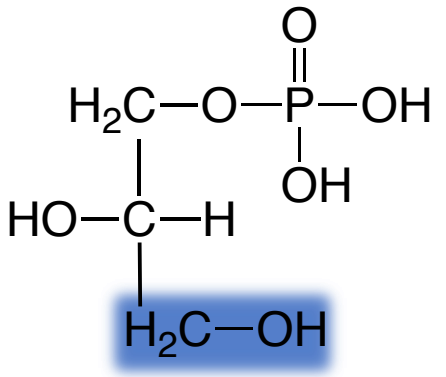


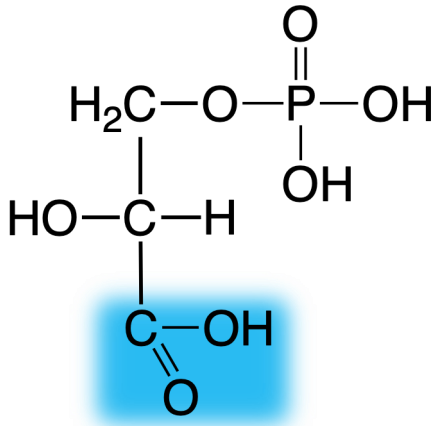


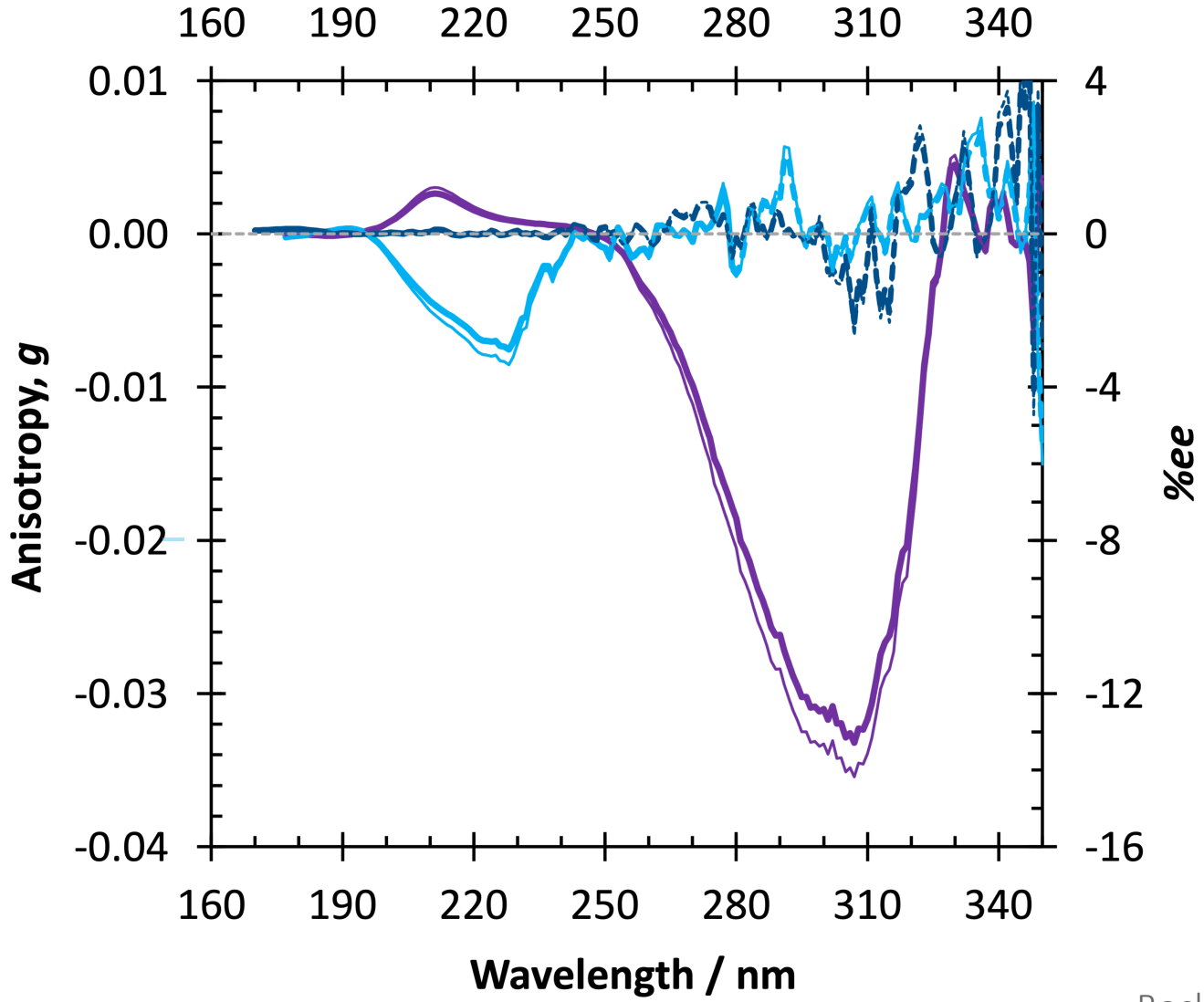


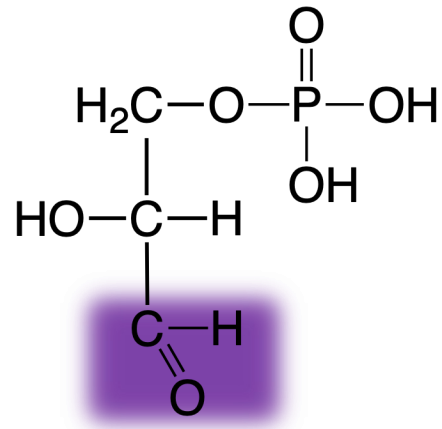
Bocková et al. *Chirality* **accepted** (2024).

Alternative backbone precursors



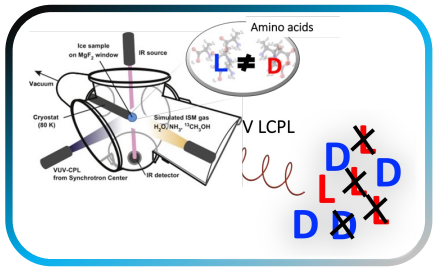




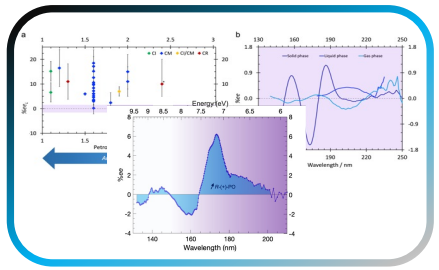


Bocková et al. *Chirality* **accepted** (2024).

To sum up...



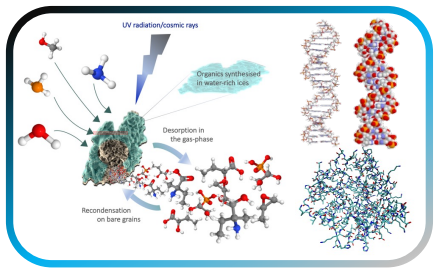
Asymmetric photo-lysis/-synthesis of amino acids by monochromatic CPL is capable of inducing **chiral bias.**



Different environments & **broad wavelength range**

Explanation of non-detections of isovaline's *ee* in meteorites.

Propyleneoxide: 1st prediction of the handedness of polarization in our pre-solar nebula.



Studying the **net effect of broadband CPL across different molecular families and environments**…

The asymmetry team

Vanessa Leyva (PhD student)

Dr. Raphaël L. Pepino

Dr. Adrien D. Garcia

Dr. Cornelia Meinert (PI)

Dr. Søren V. Hoffmann

Dr. Nykola C. Jones

Thank you for your attention!

Soleil-Babinet compensator