Analytical Techniques for Extraterrestrial Organics

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September 15th, 2026

GSFC ASTROBIOLOGY ANALYTICAL LAB http://science.gsfc.nasa.gov/691/analytical/

Extraterrestrial Organic Compounds

Understand the abiotic origins of the organic compounds

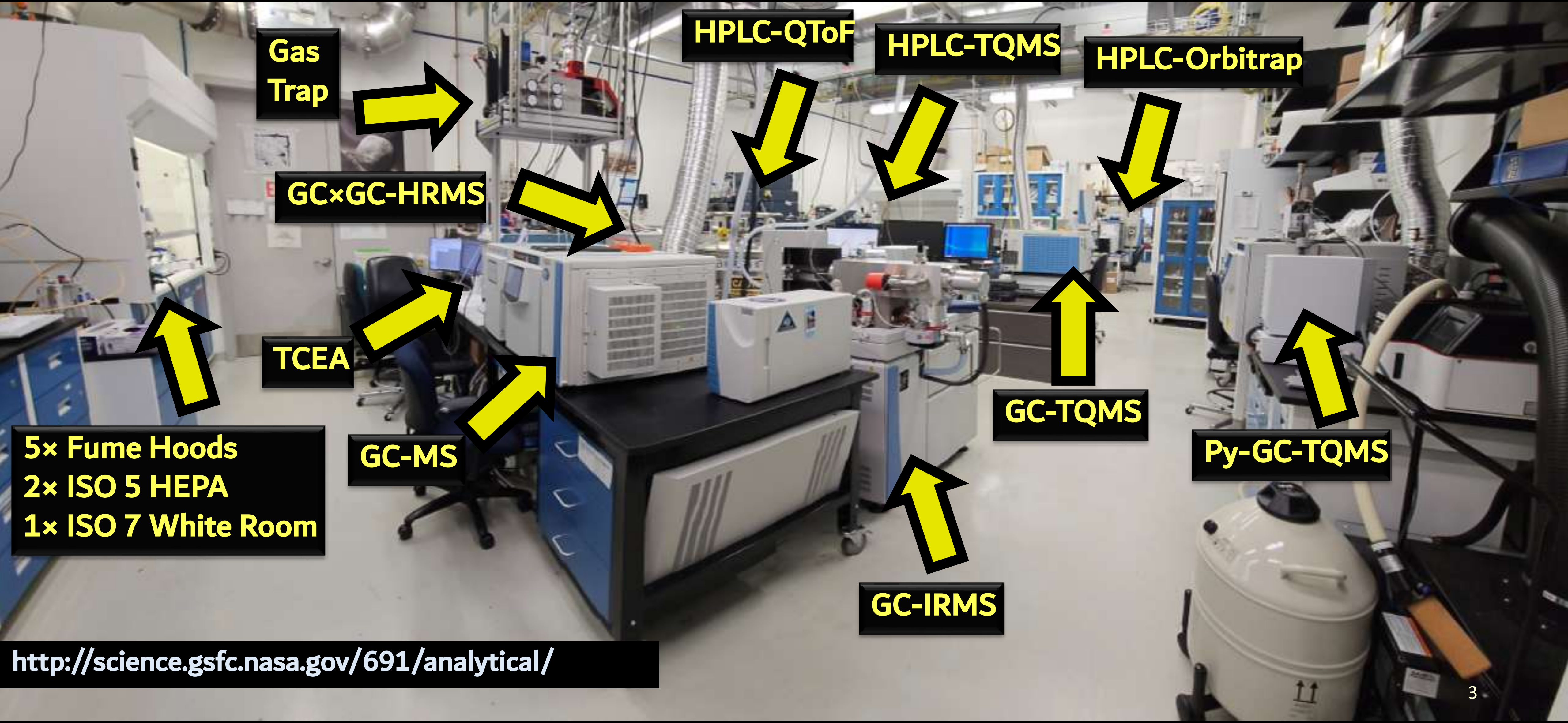
Soluble organic compounds → Distribution, Isotopic values, Chirality

Organics in carbonaceous chondrites (meteorites)

Solar system formation

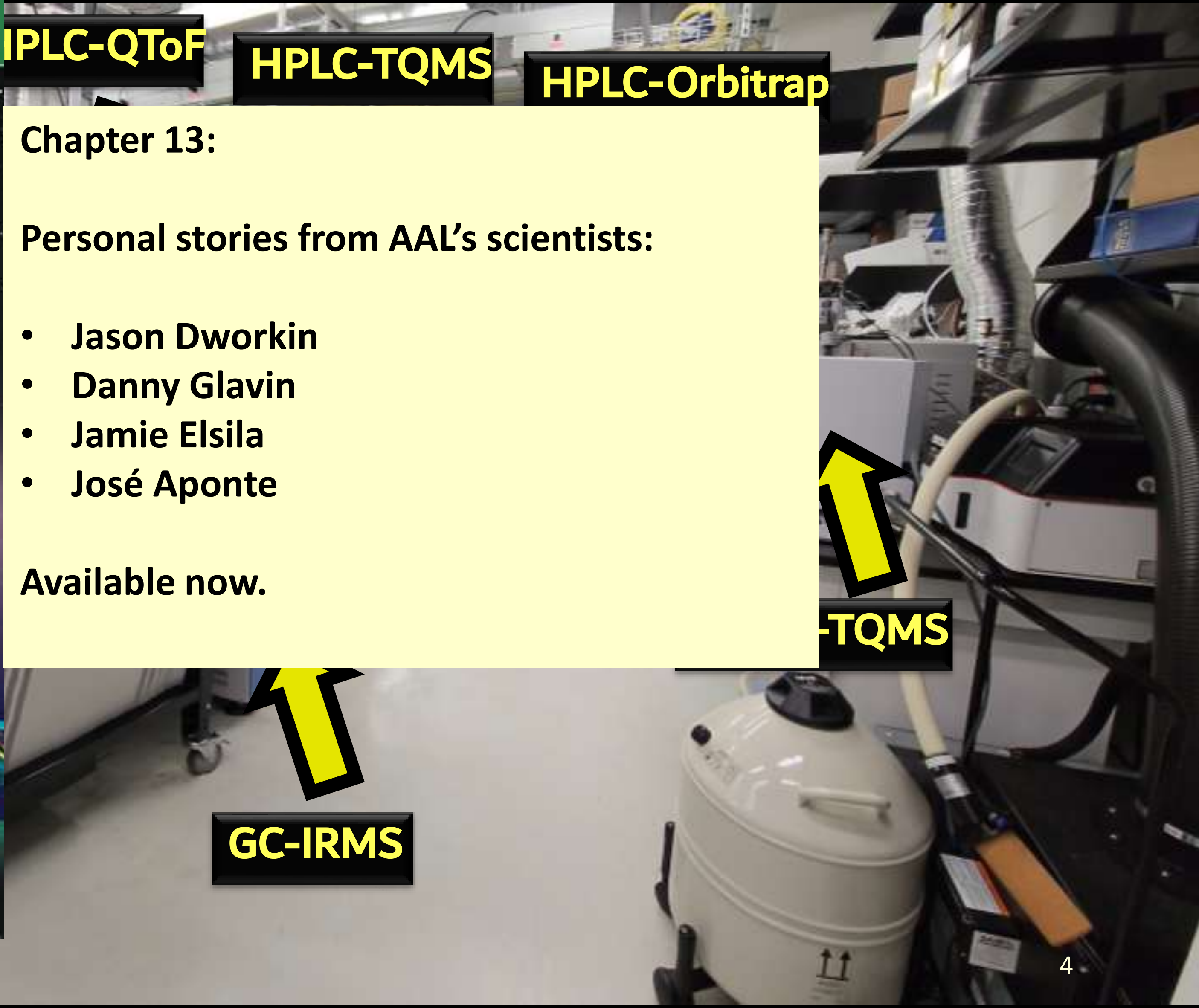
Processes in parent body

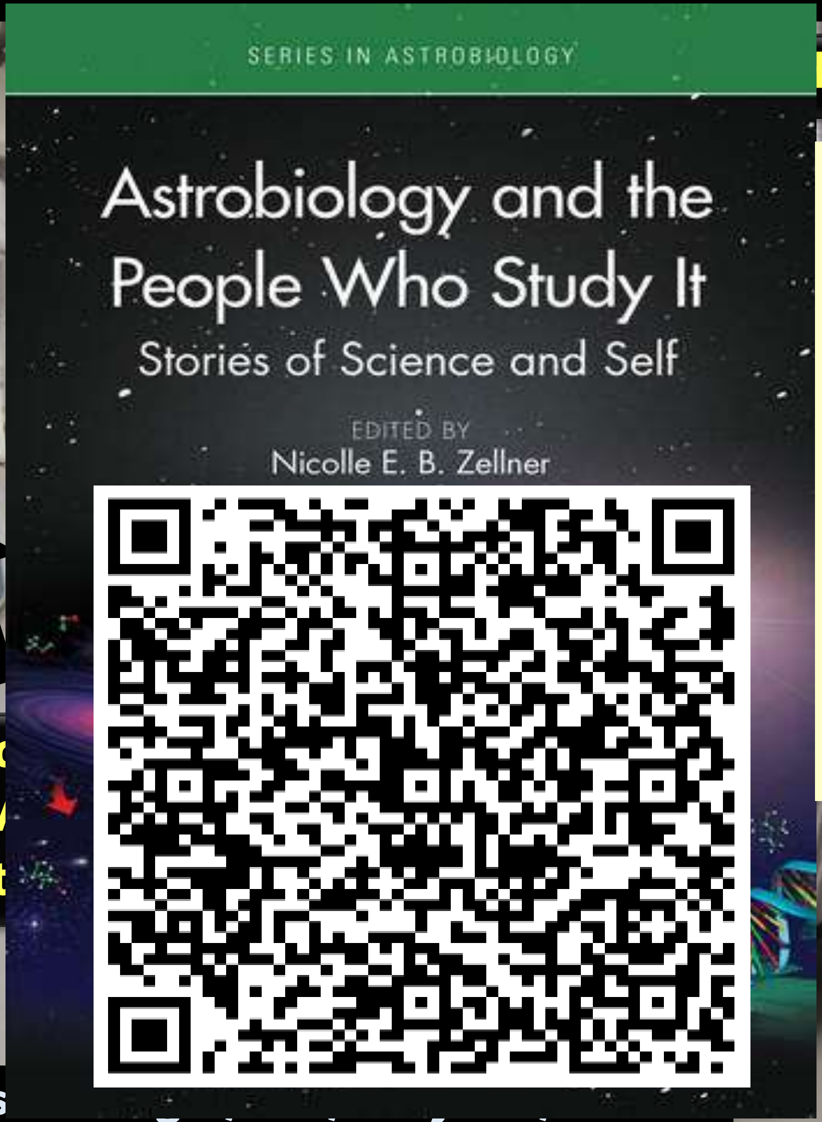
Our laboratory at NASA Goddard



http://science.gsfc.nasa.gov/691/analytical/

Our laboratory at NASA Goddard





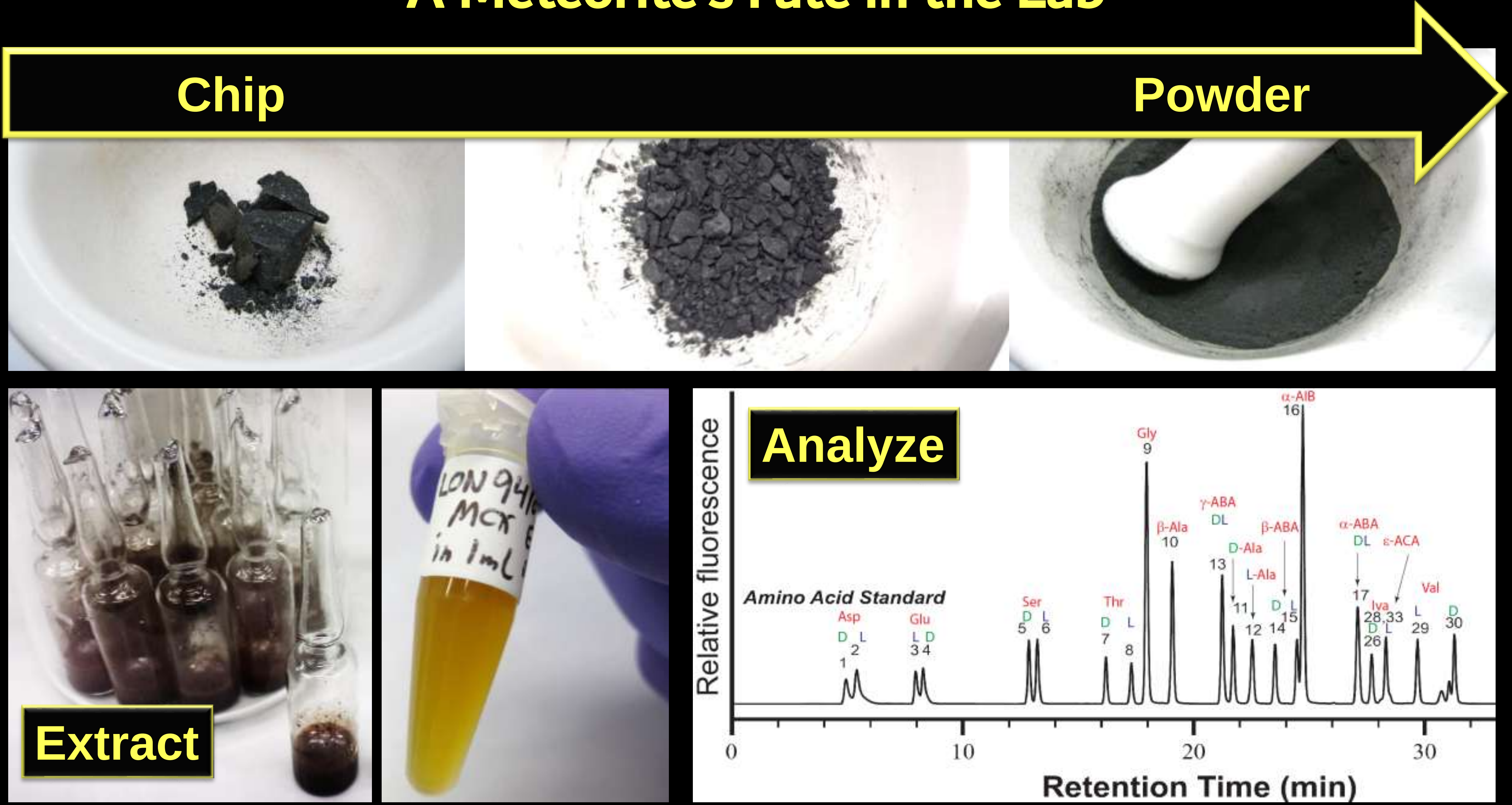
Chapter 13:

Personal stories from AAL's scientists:

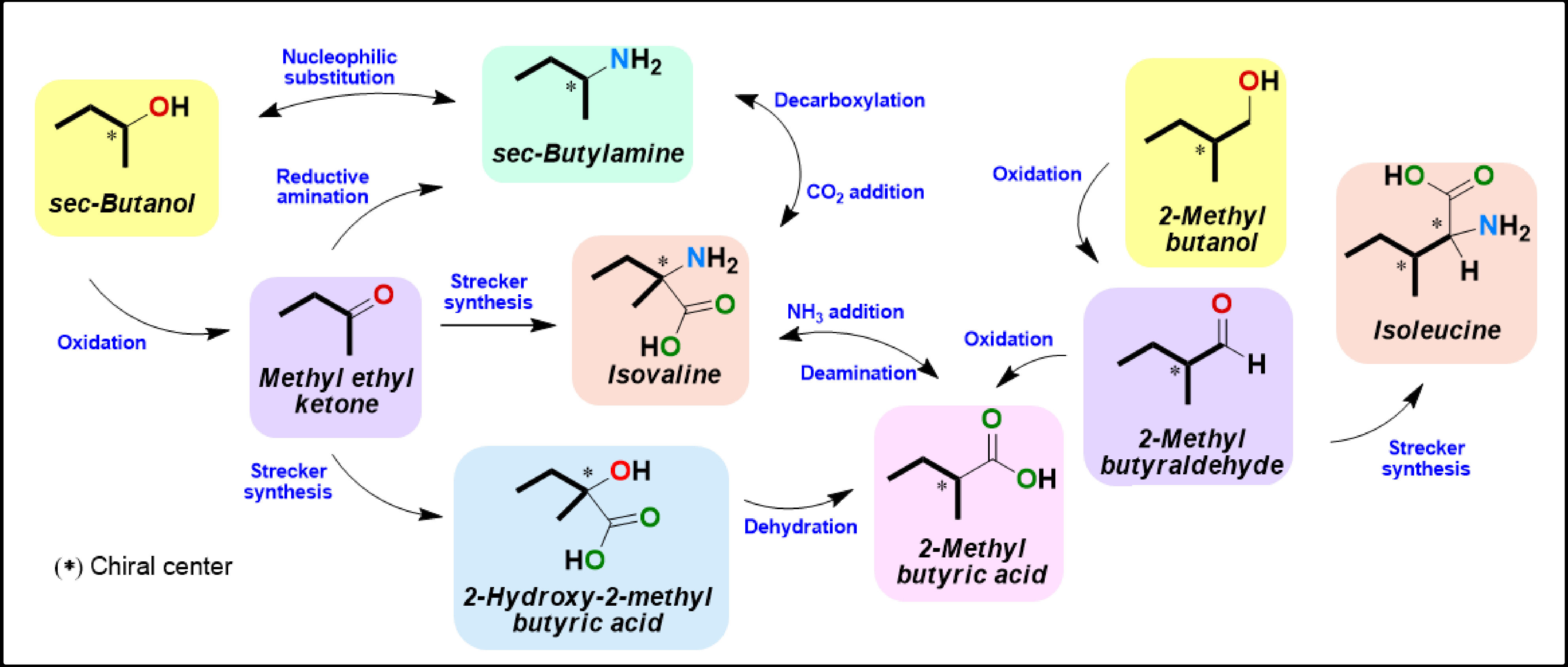
- Jason Dworkin
- Danny Glavin
- Jamie Elsila
- José Aponte

Available now.

A Meteorite's Fate in the Lab



Interrelation of the Molecules of Life

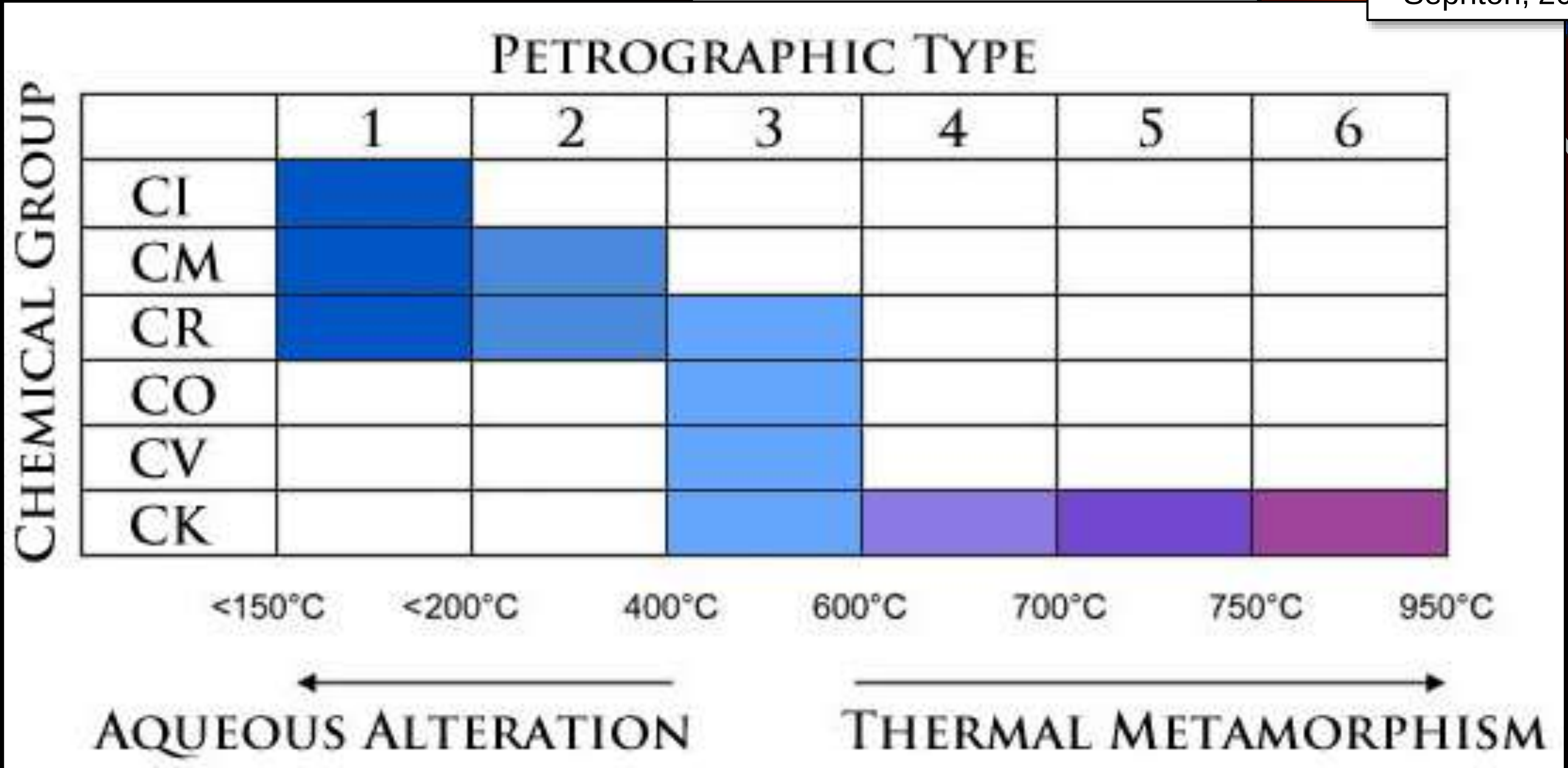


Simplified synthetic scheme of soluble meteoritic organics

Simkus et al. 2019

NC meteorites:
Metallic, organic-poor, thermally altered

Sephton, 2002

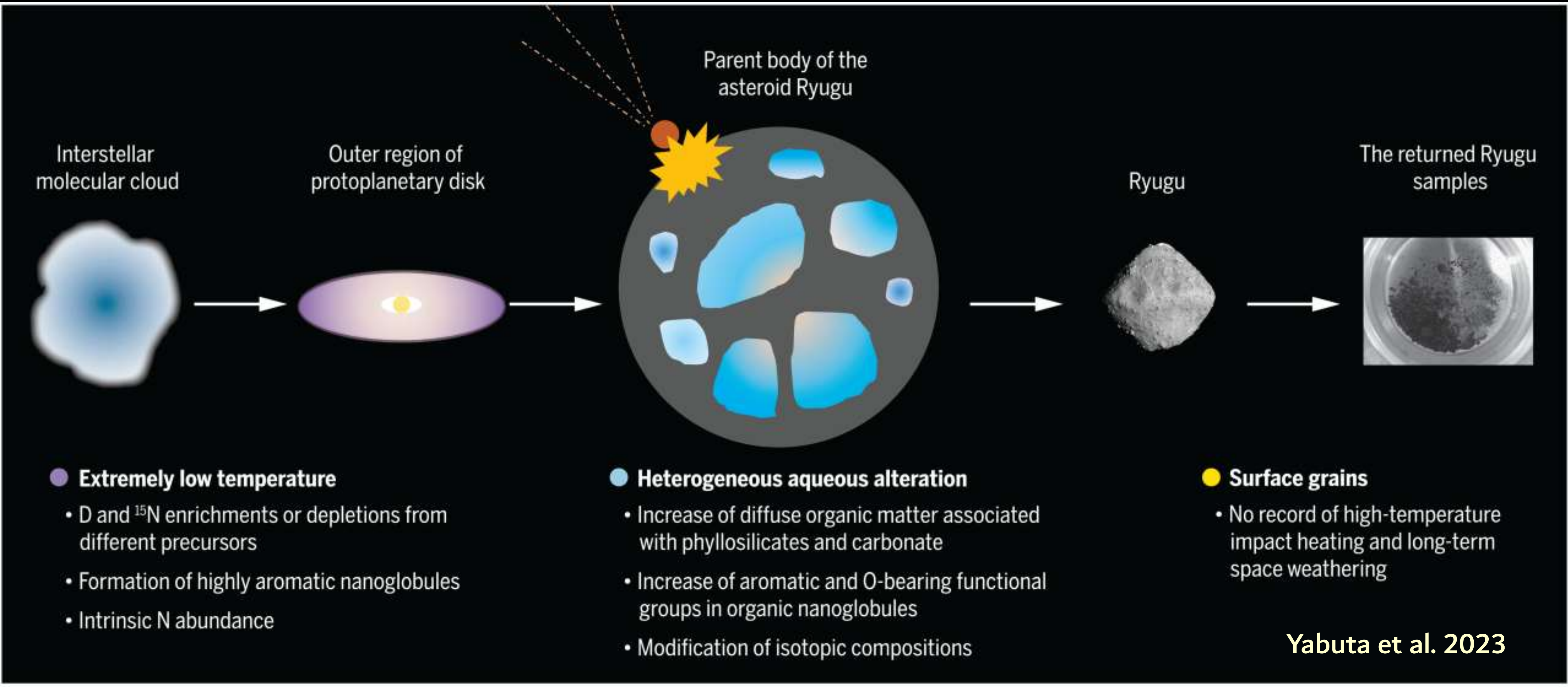


CI meteorites: highly aqueously altered, low temperature, likely cometary fragments.

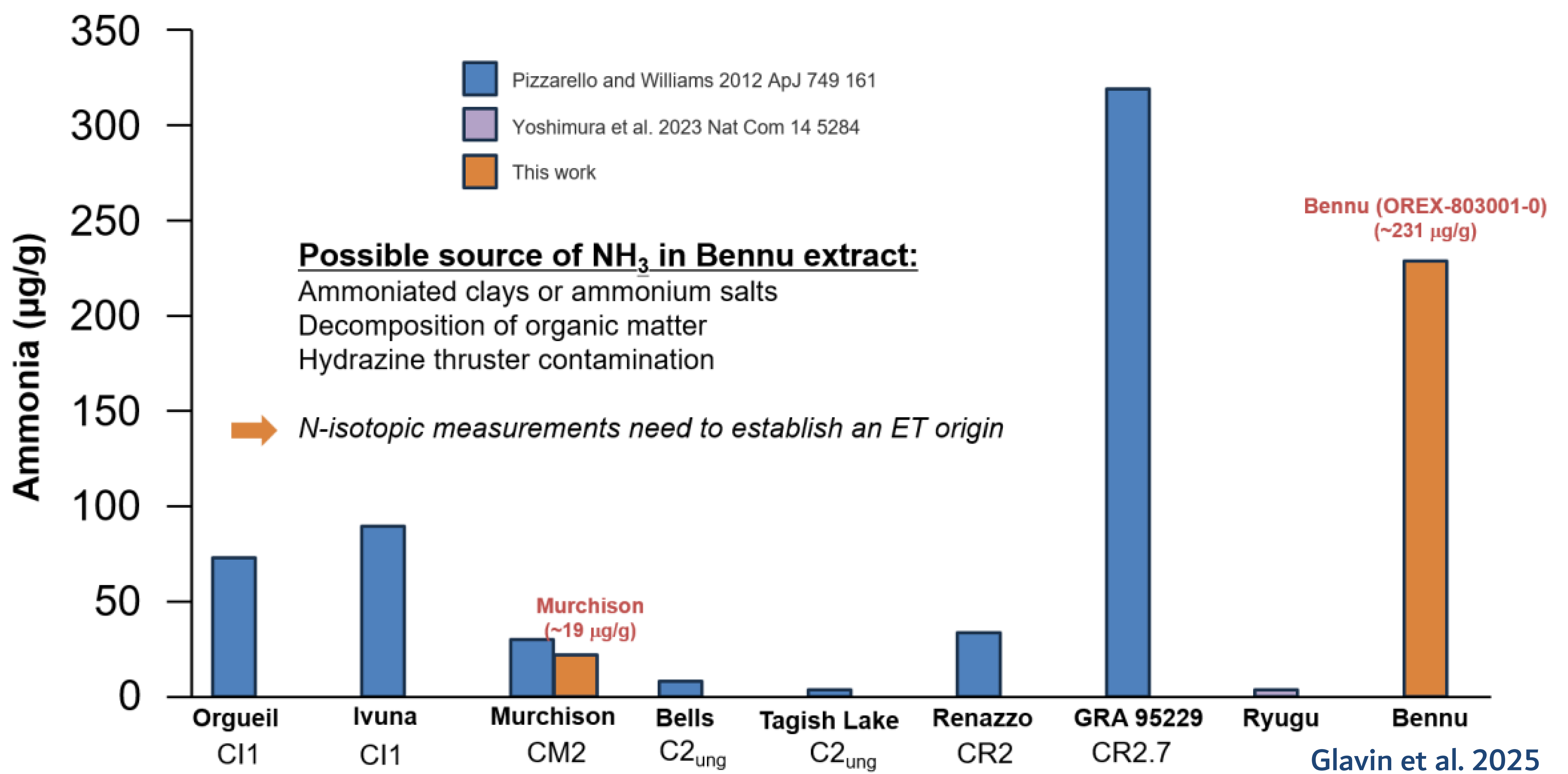
NC: Non-carbonaceous
CC: Carbonaceous chondrite
CI: Ivuna-type CC

HL Tauri (Atacama Large Millimeter Array)

What is a Parent Body?



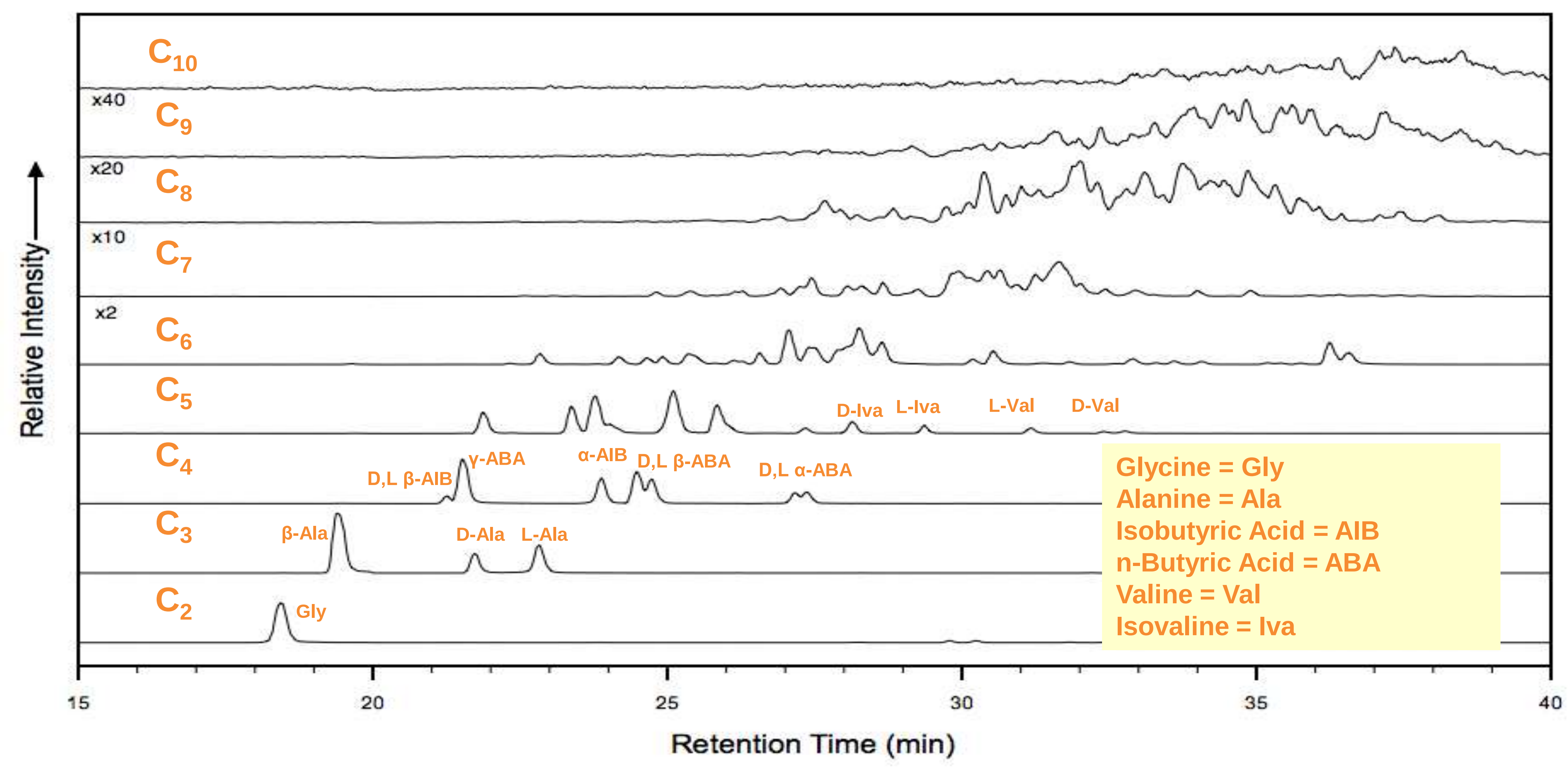
Relationship Between Chondrite Type and Abundances



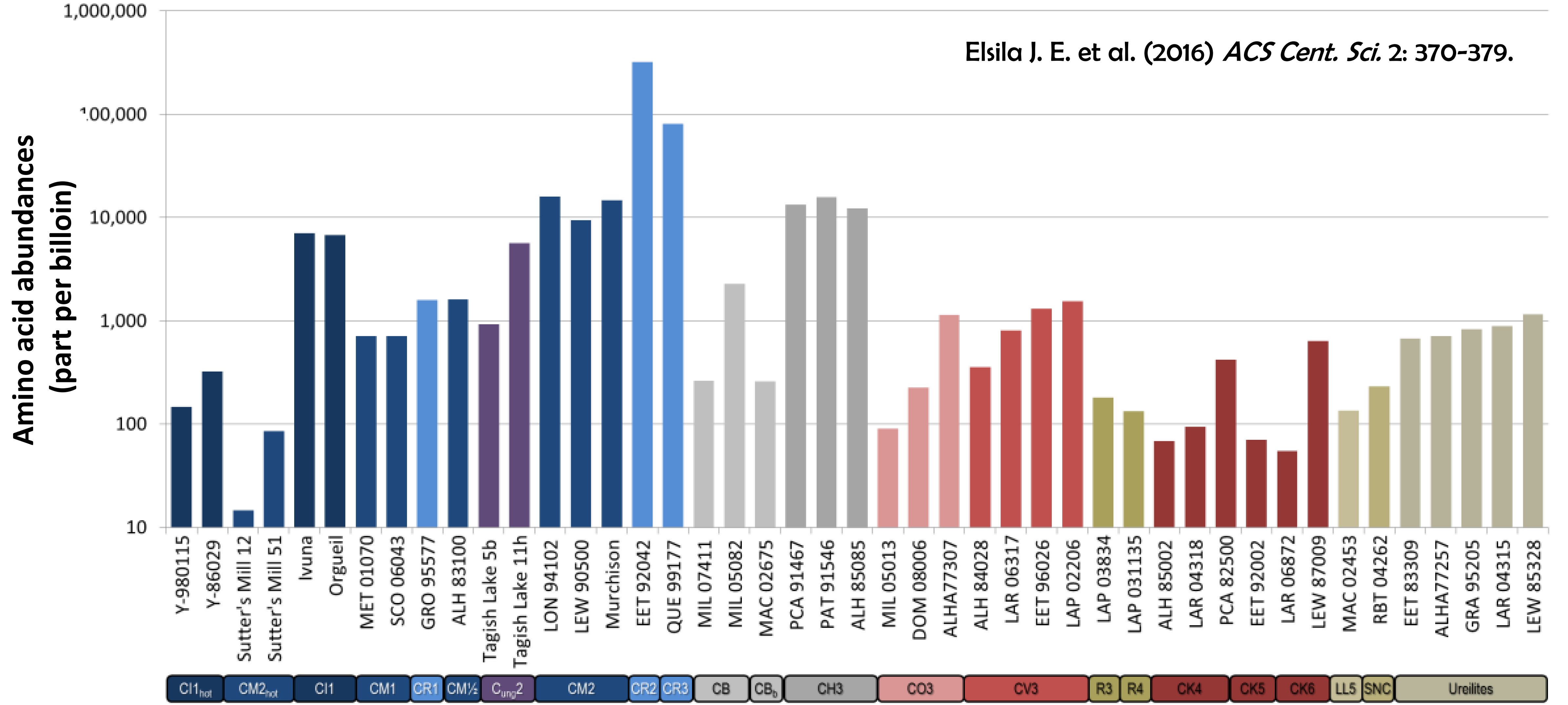
Glavin et al. 2025

Analyses of Molecular Distributions

Amino acids in the Murchison (CM2) meteorite

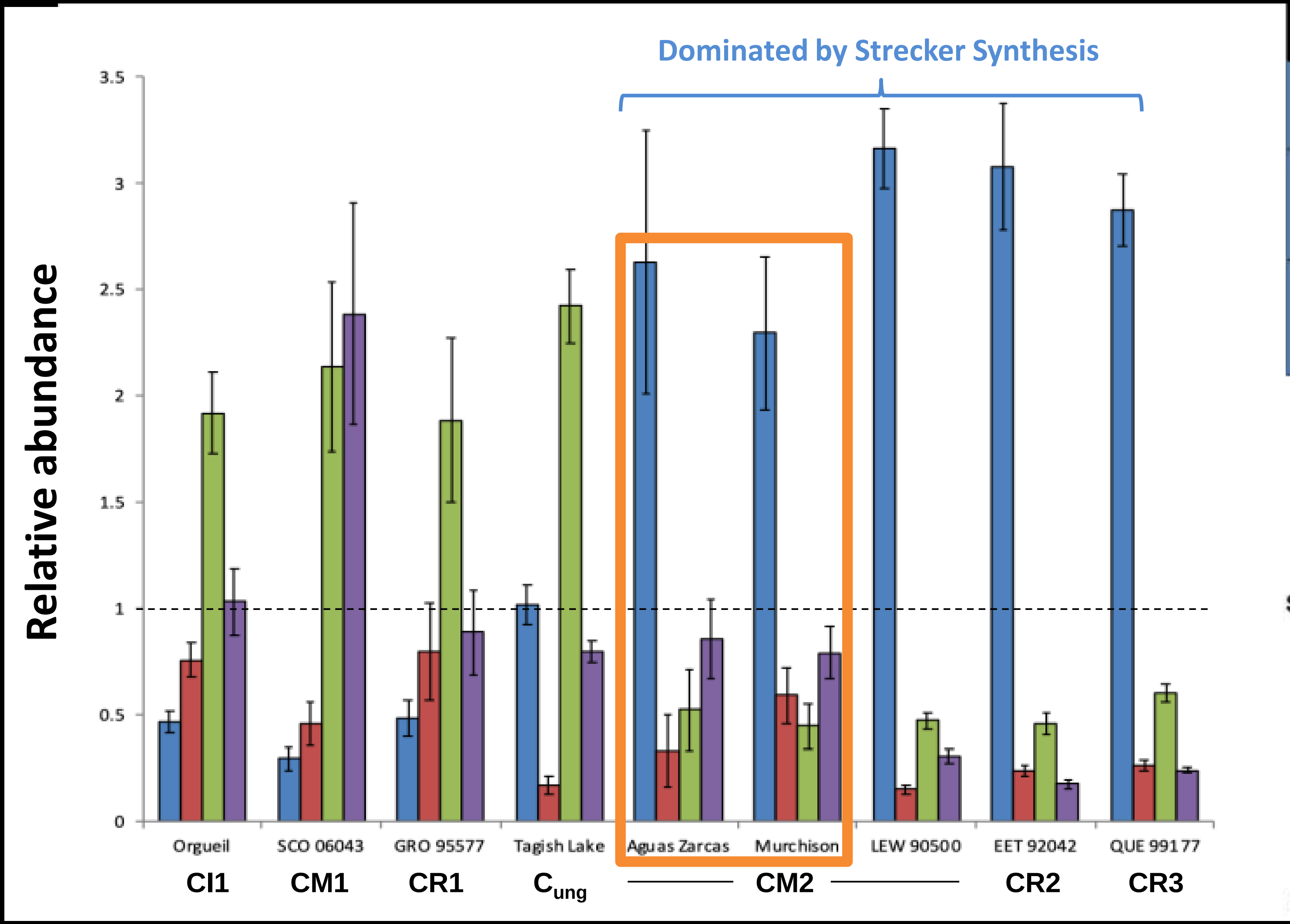


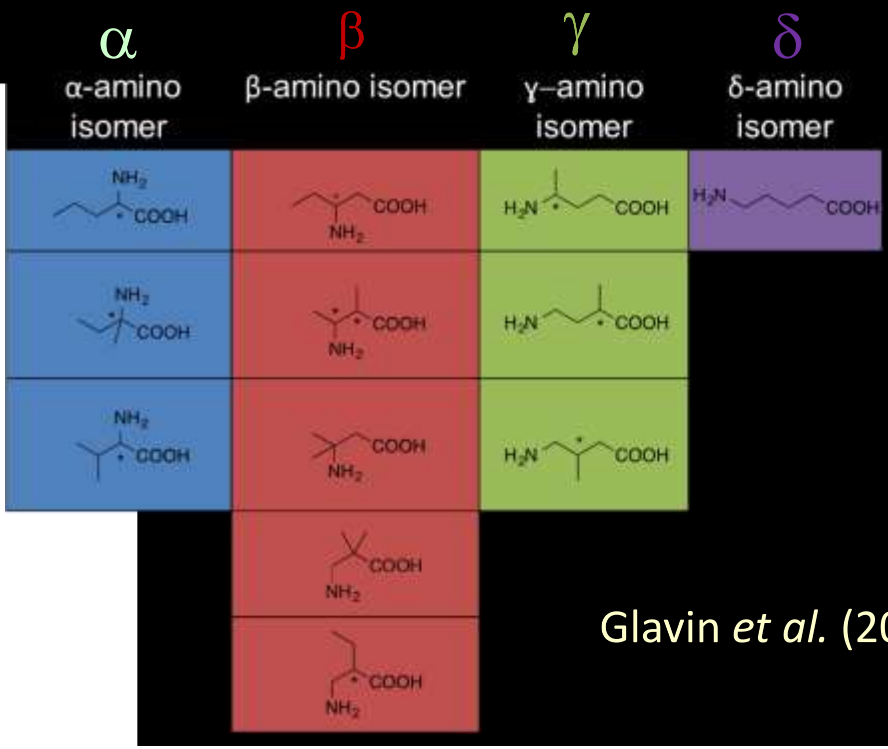
Amino acid abundances vary by more than three orders of magnitude



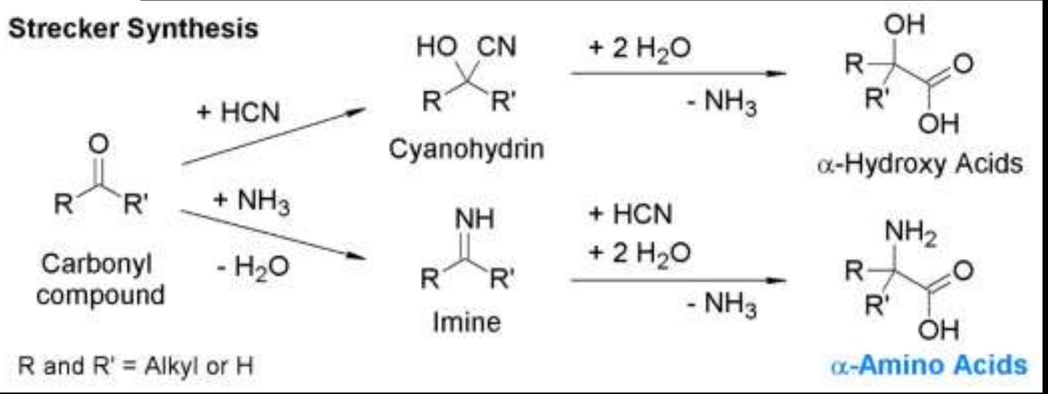
*In all plots, meteorites are arranged roughly in order of petrographic high aqueous alteration on the left to high thermal alteration on the right

Abundances of C5 Amino Acids Reveal Formation Mechanisms and Asteroid Conditions

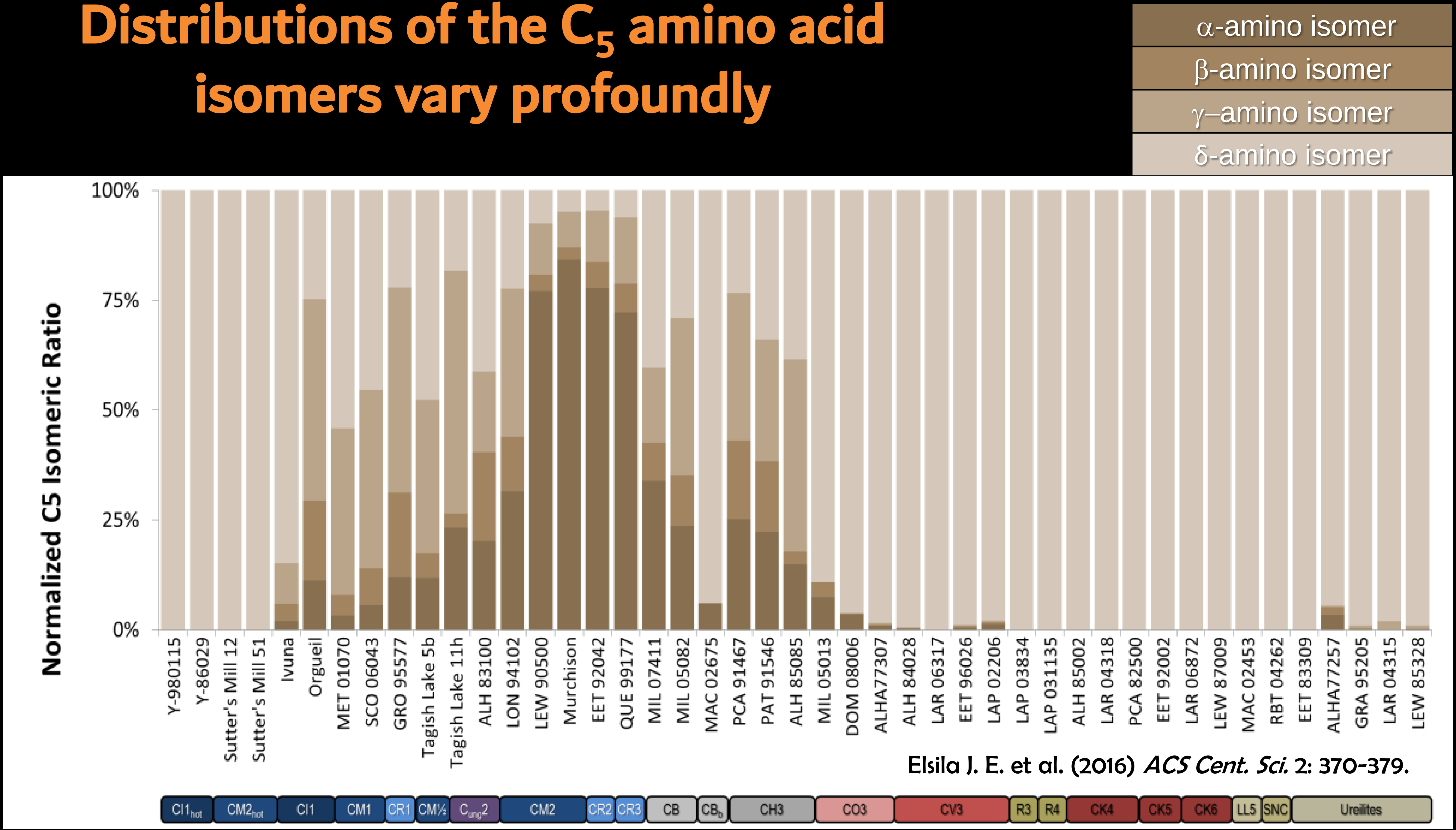




Glavin *et al.* (2020)

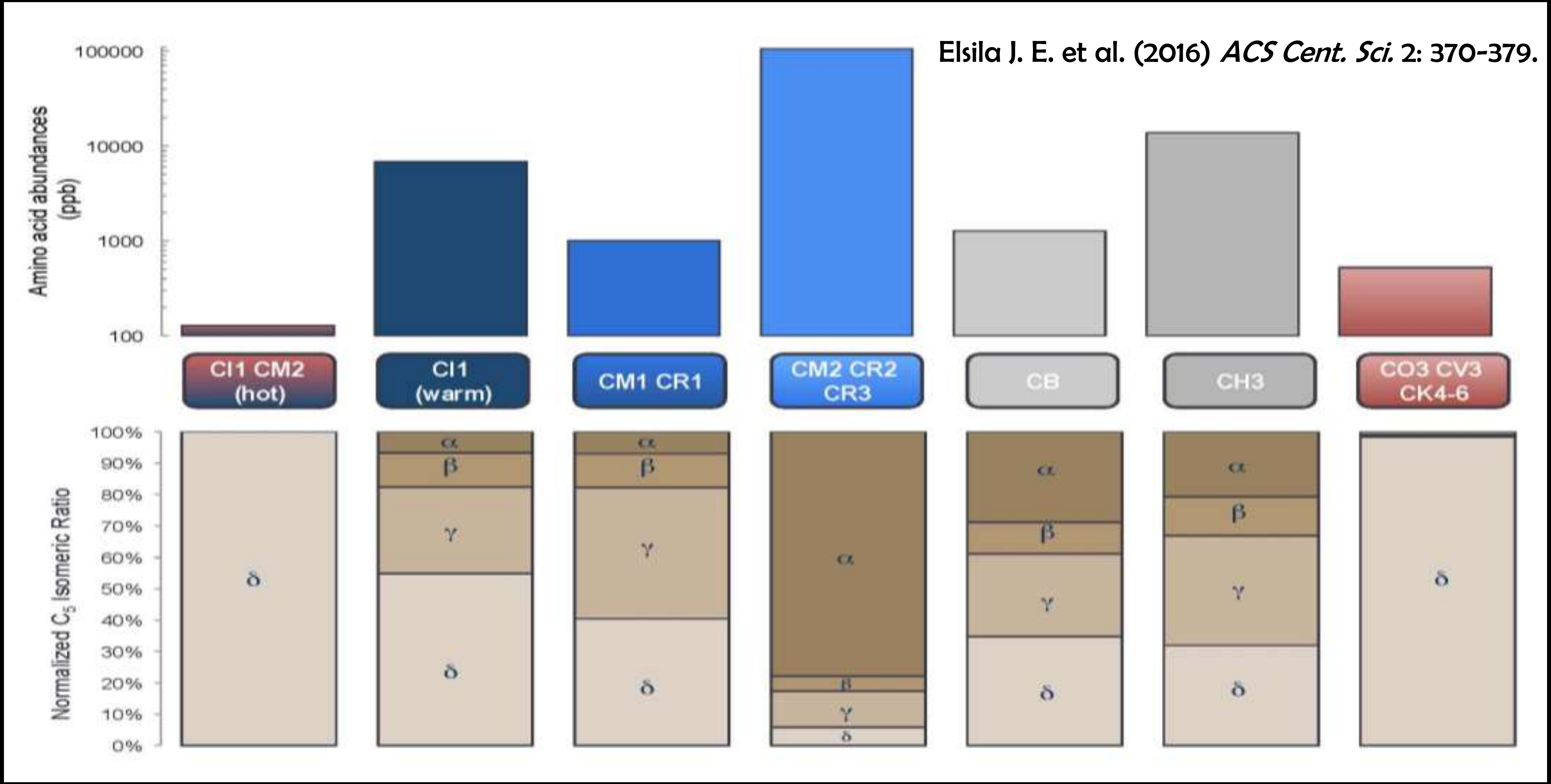


Distributions of the C_5 amino acid isomers vary profoundly

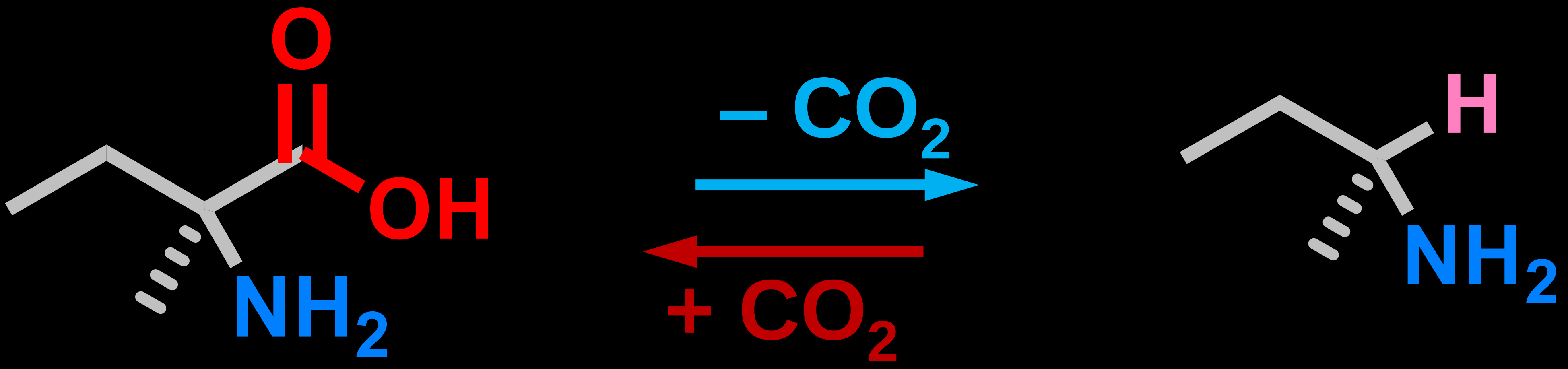


Elsila J. E. et al. (2016) *ACS Cent. Sci.* 2: 370-379.

"Sweet spot" of high abundance of primarily α-amino acids



Amino Acids and Amines



L-Isovaline

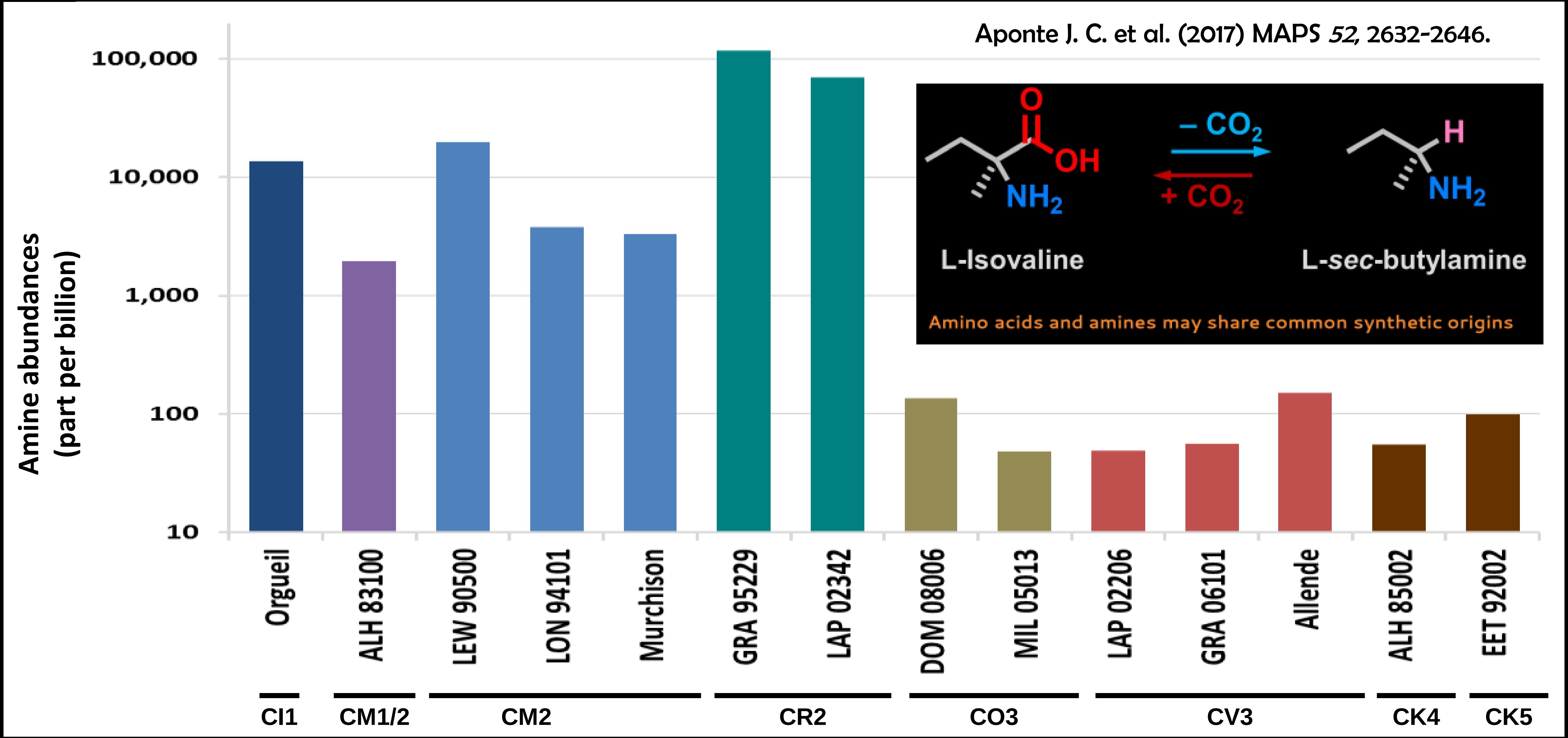
L-*sec*-butylamine

Amino acids and amines may share common synthetic origins

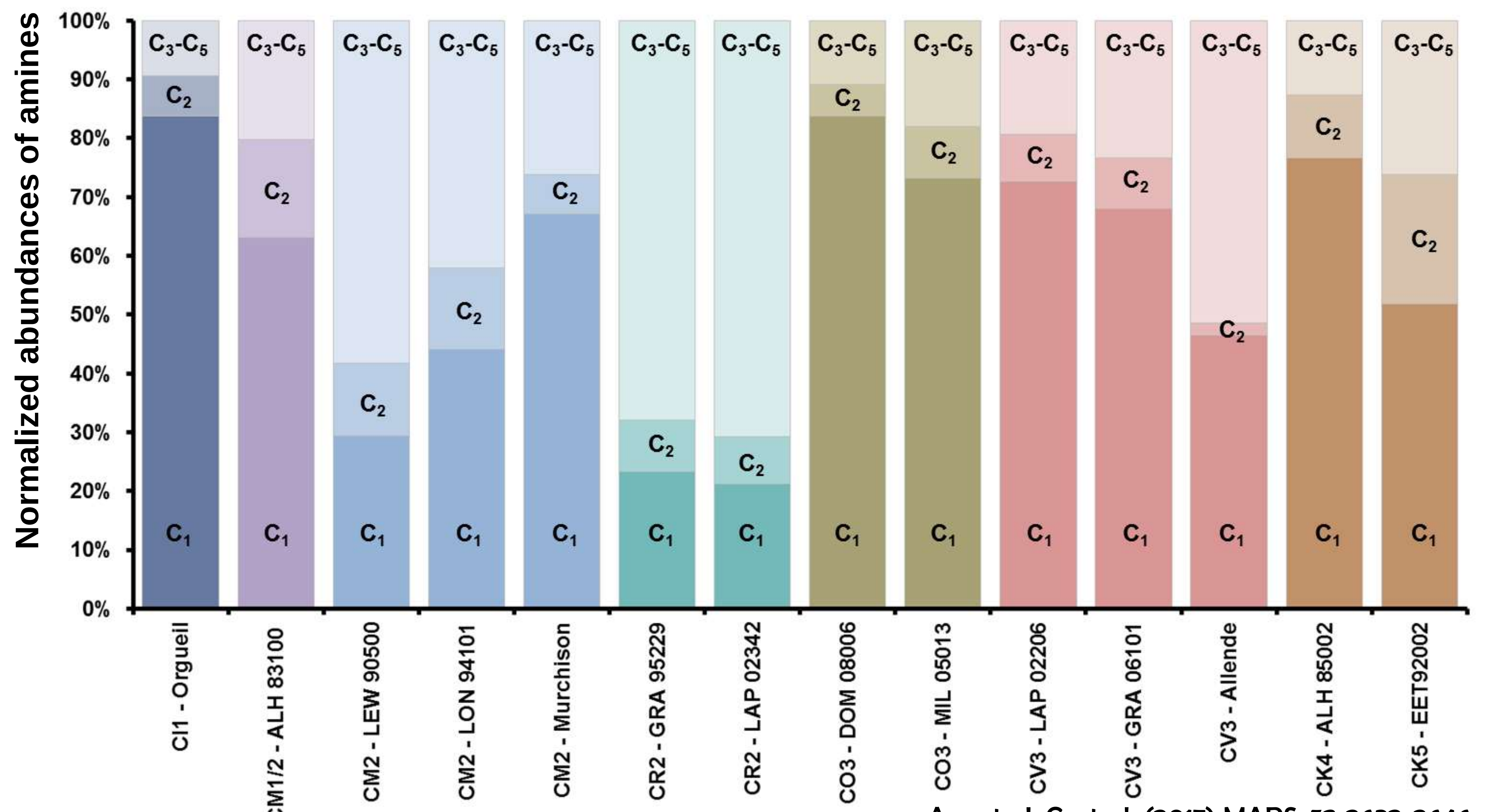
† For simplicity in this presentation, I'm equating L with S and D with R.

Aponte J. C., Dworkin J. P., Elsila J. E. (2014) *Geomchim. Cosmochim. Acta* 141:331.

Amine abundances are like those of meteoritic amino acids

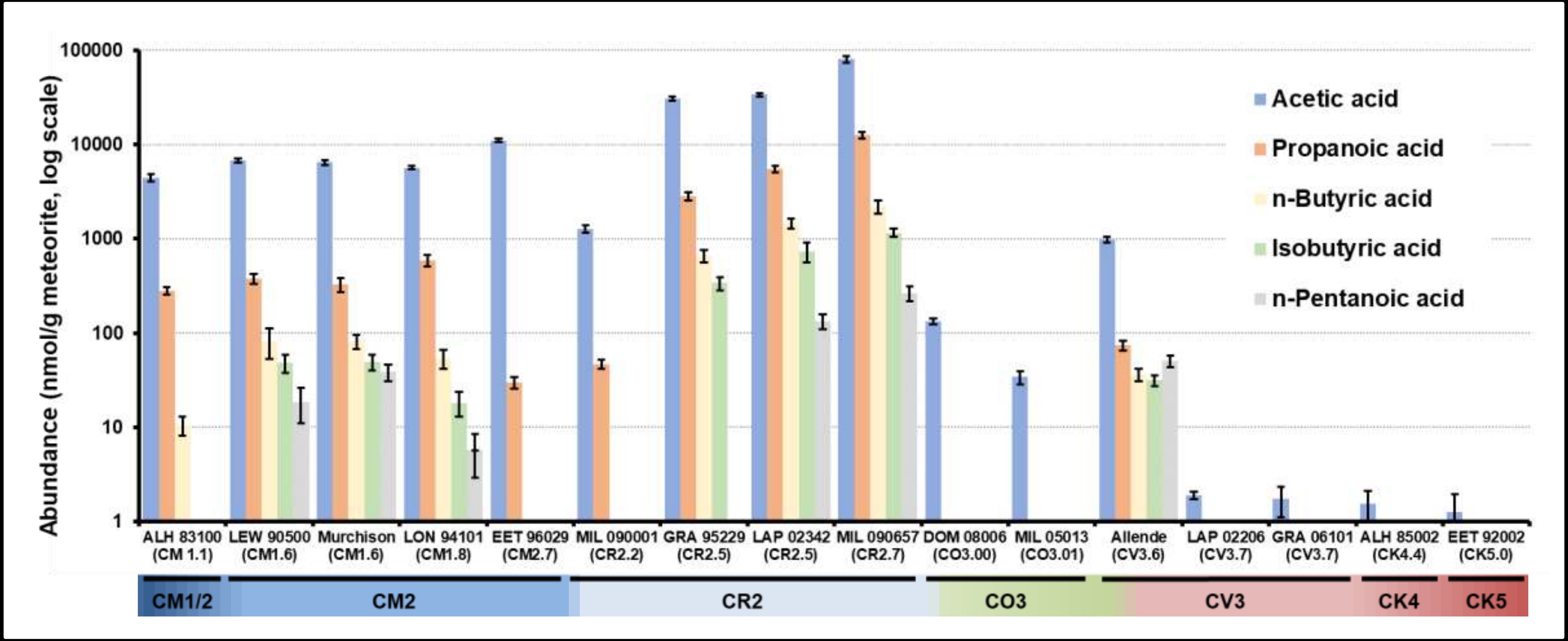


Methylamine is abundant, but not in CR2

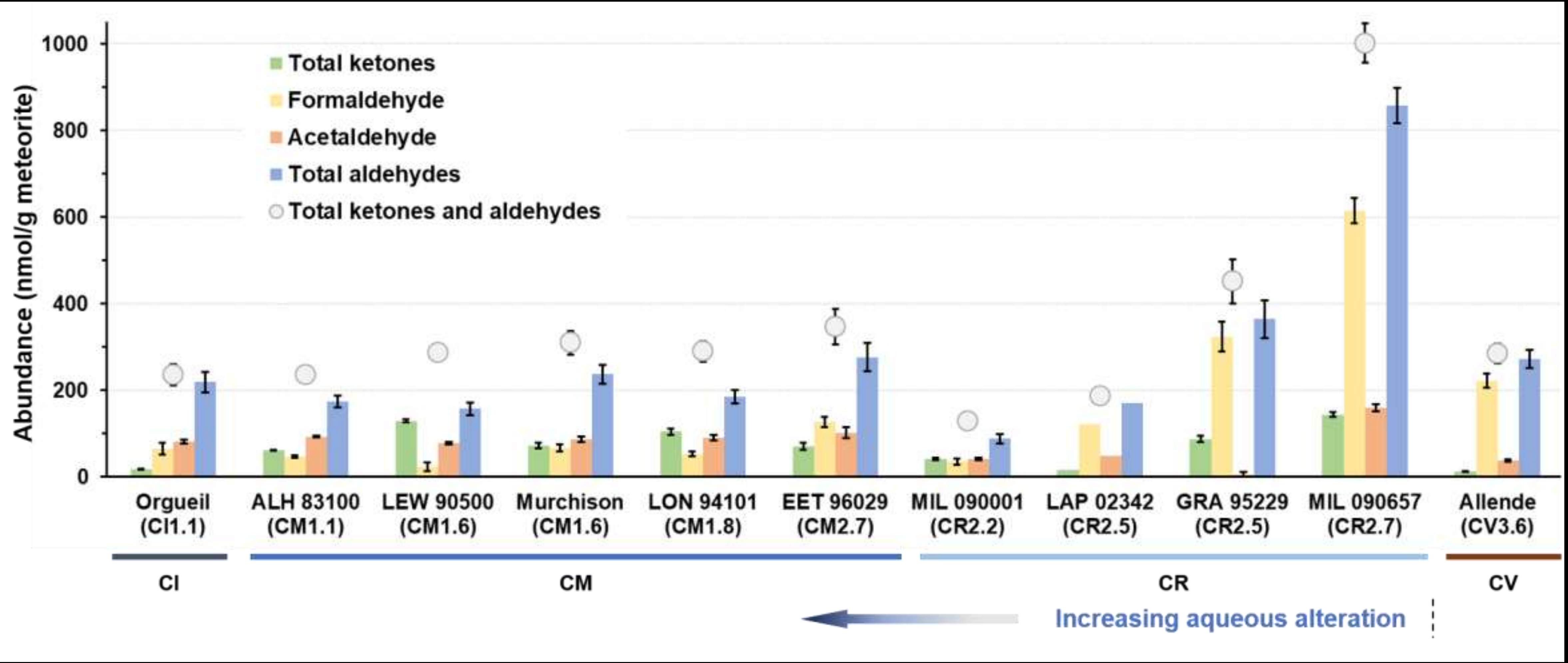


Aponte J. C. et al. (2017) MAPS *52*, 2632-2646.

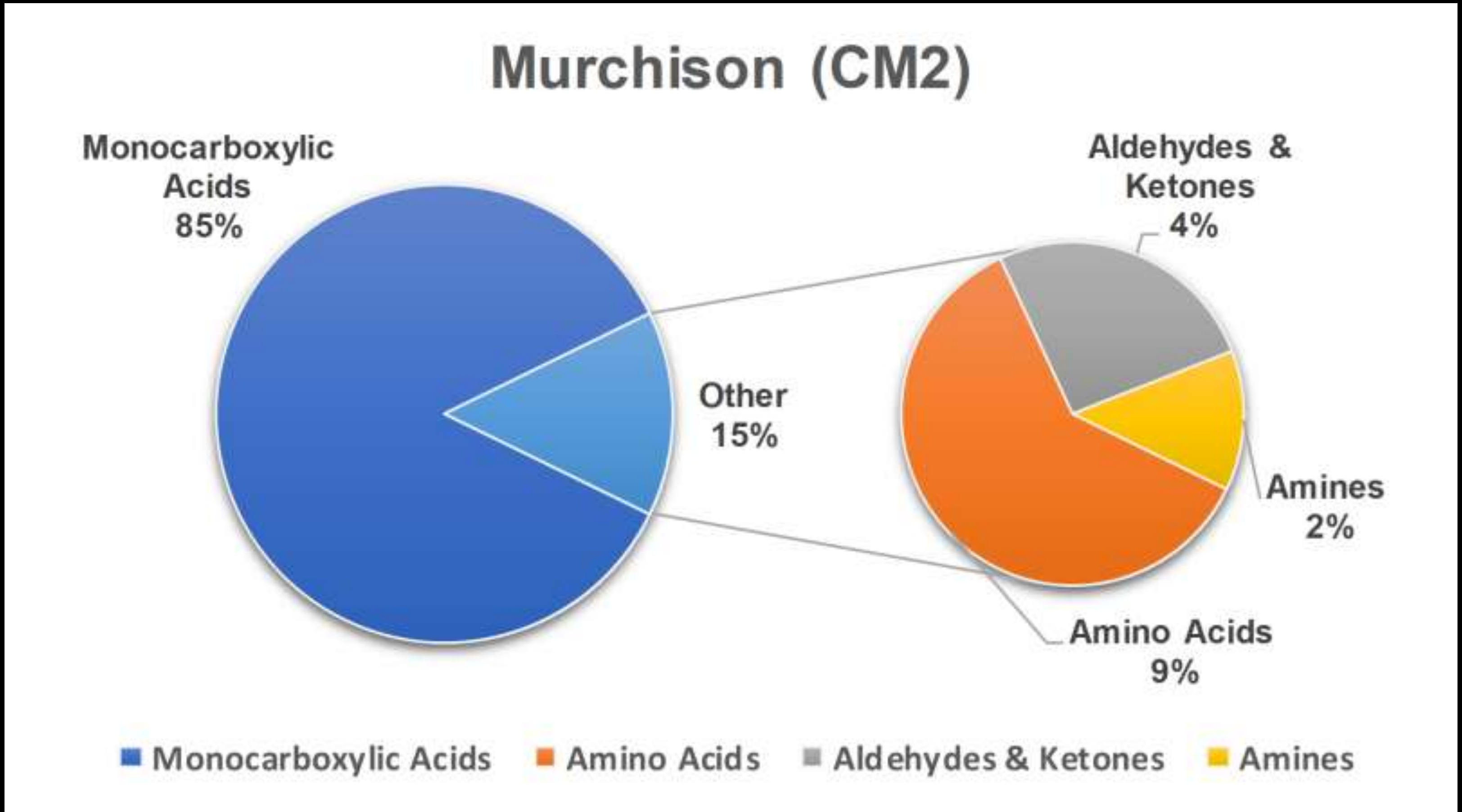
Carboxylic Acids Abundances



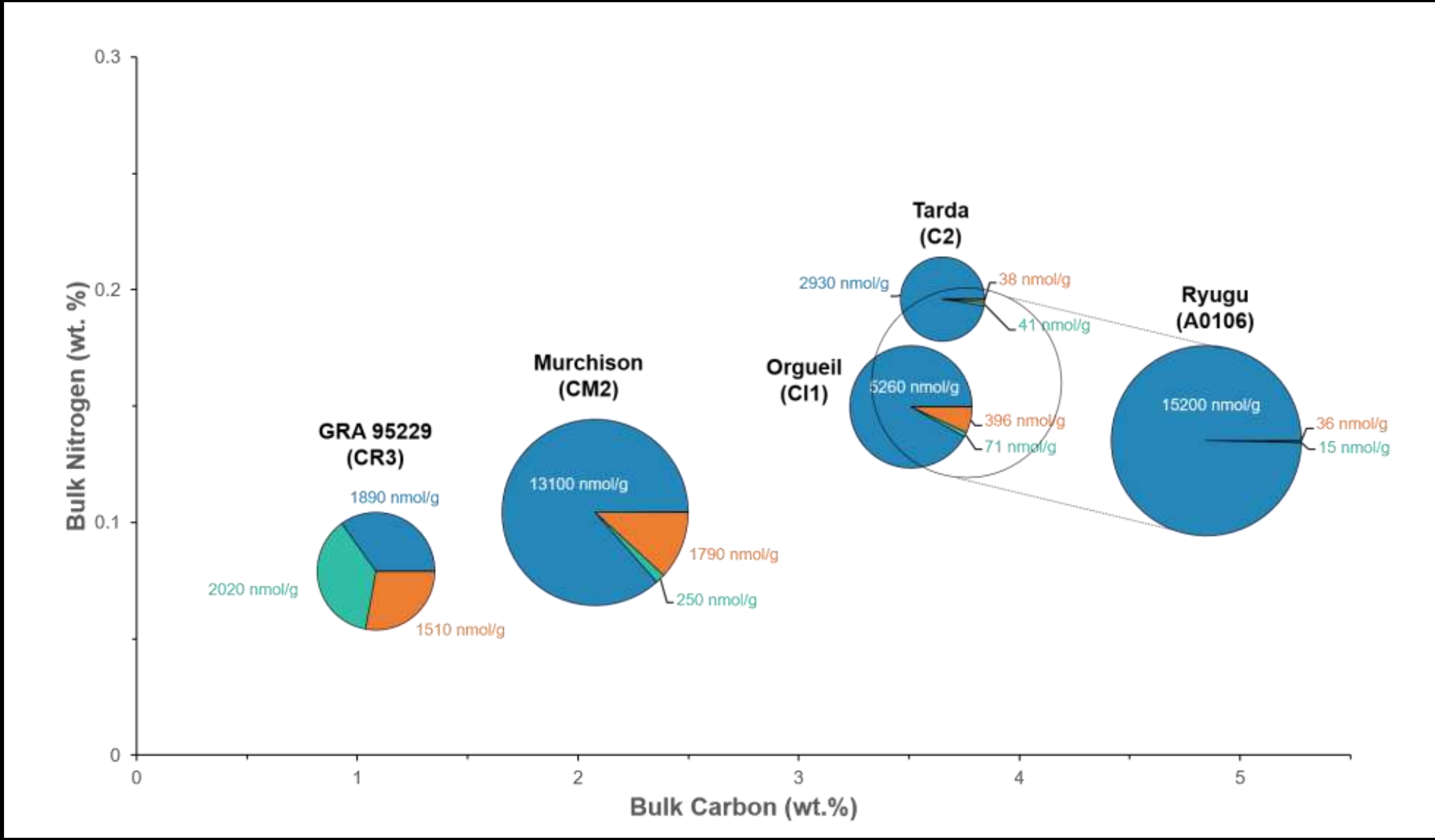
Formaldehyde and Acetaldehyde



Which the Most Abundant Soluble Organic?



Which the Most Abundant Soluble Organic?

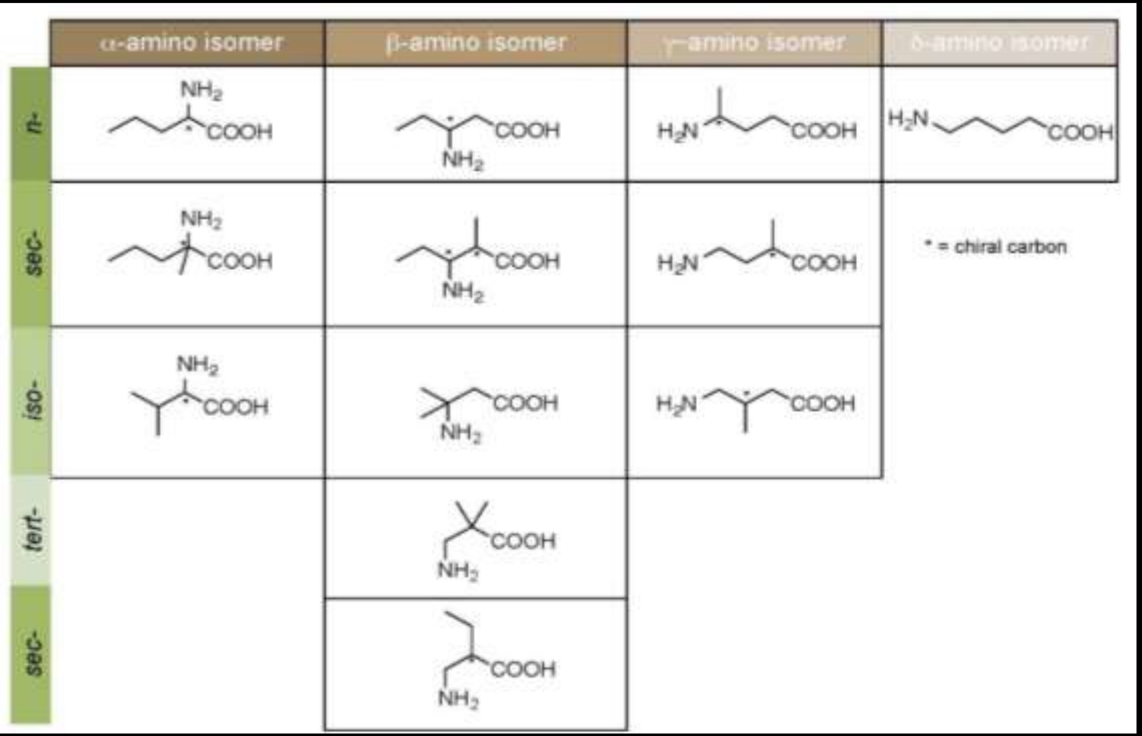


Chiral Analyses

Life on Earth is Homochiral

19 of the 20 standard α-hydrogen protein amino acids are chiral

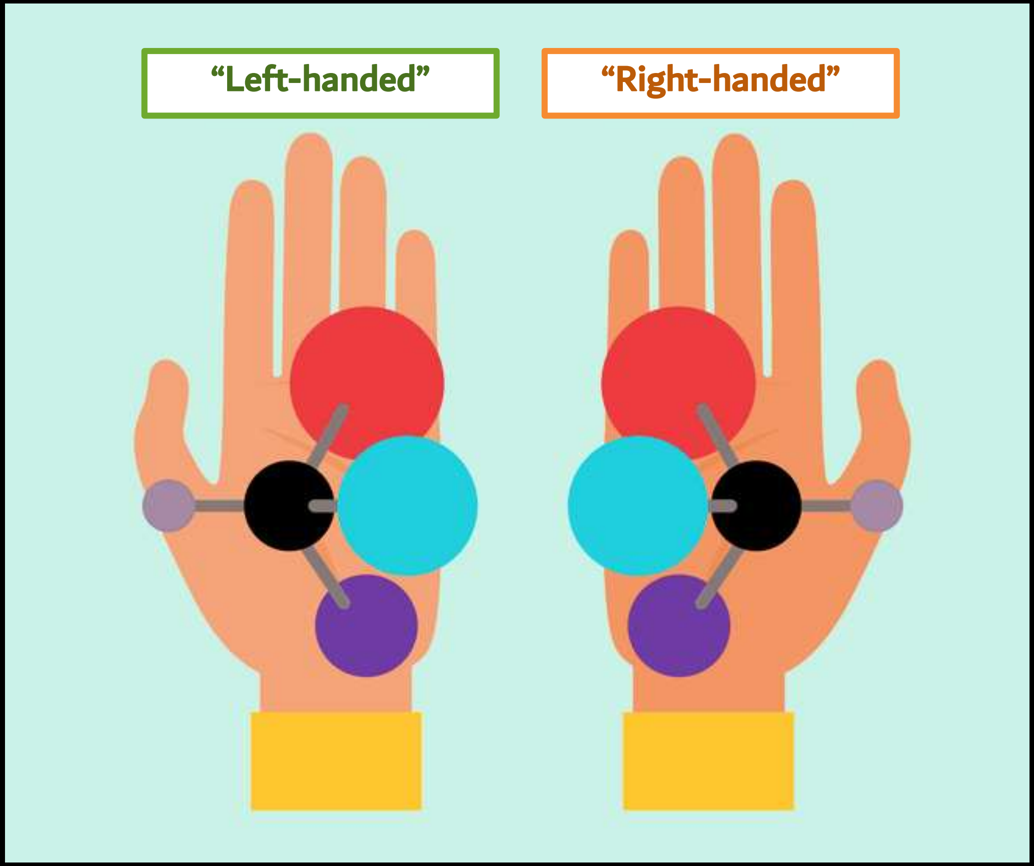
Life on Earth uses L-amino acids



Meteoritic amino acids are highly diverse &
Show L-enantiomeric excesses

Chirality

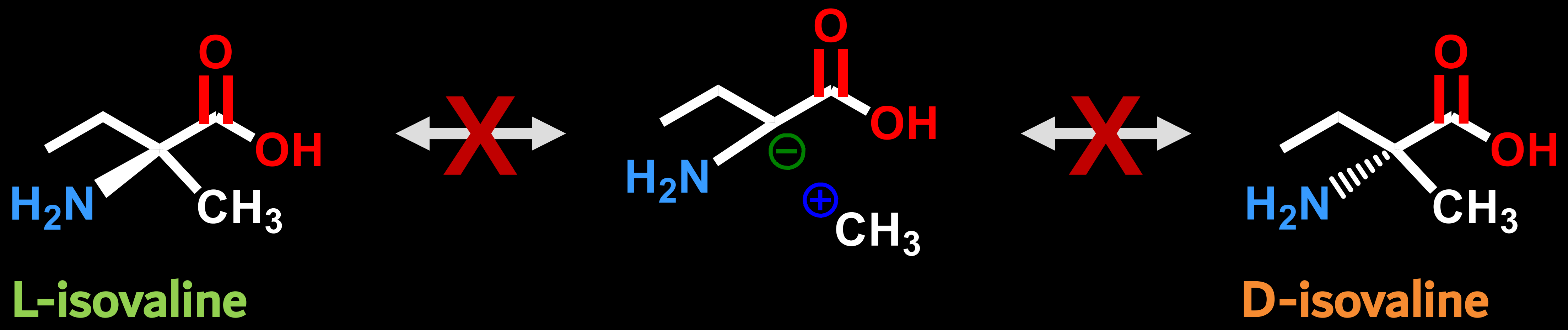
LEFT (L) and RIGHT (D) hands of an amino acid



Non-superimposable mirror images

Isovaline

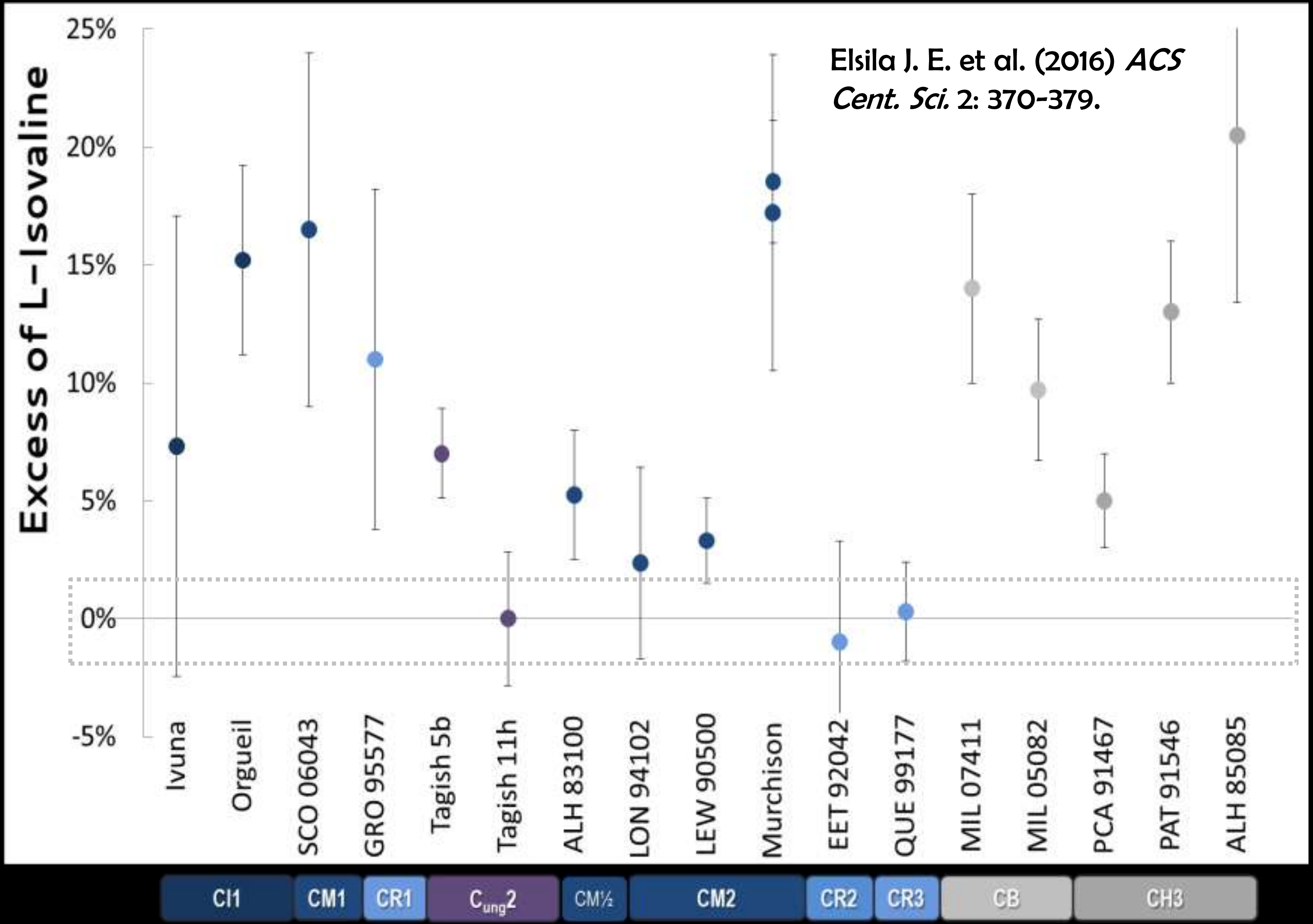
Isovaline is rare in biology, abundant in many carbonaceous meteorites, and very resistant to racemization



L-isovaline excesses of up to 18% in Murchison measured

L-isovaline excess now found in 14 meteorites of different classes

Meteoritic Enantiomeric Excesses of Isovaline

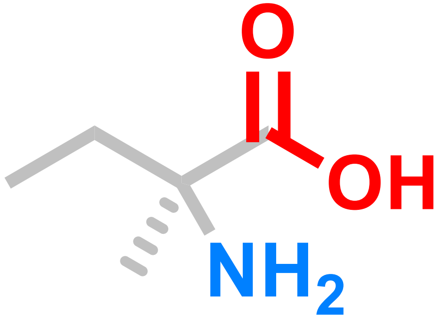


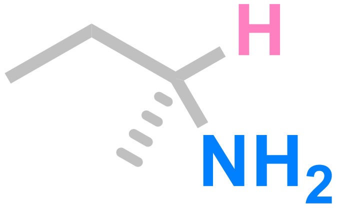
Higher amino acid enantiomeric excesses found in meteorites that have been aqueously altered

Much lower excesses of L-isovaline (0-3%) detected in least aqueously altered meteorites

No D-excesses have been found in any meteorite

Meteoritic Enantiomeric Excesses of Isovaline





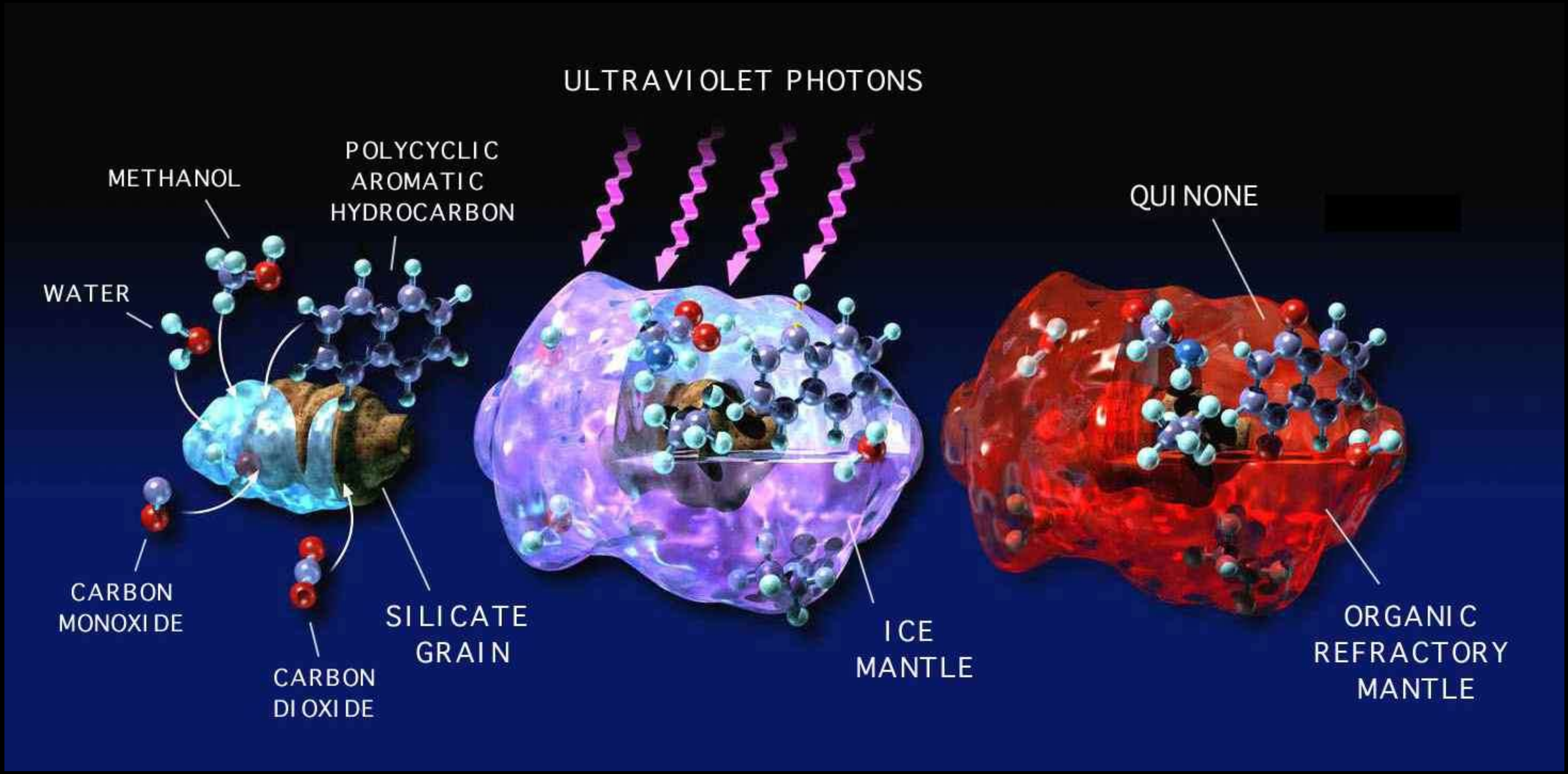
More water ↑ Less water

Meteorite	Isovaline (D/L)[a]	*Sec*-butylamine (*R*/*S*)
Orgueil (CI1)	0.73 ± 0.07[a]	0.95 ± 0.06
ALH 83100 (CM1/2)	n.a.	0.99 ± 0.02[c]
Murchison (CM2)	0.83 ± 0.01[b]	1.00 ± 0.01[b]
LON 94101 (CM2)	0.95 ± 0.08[a]	0.99 ± 0.02[c]
LEW 90500 (CM2)	0.94 ± 0.03[a]	0.98 ± 0.03[c]
LAP 02342 (CR2)	n.a.	0.99 ± 0.01[c]
GRA 95229 (CR2)	n.a.	1.00 ± 0.01[c]

[a]Glavin et al. (2011) *Meteorit. Planet. Sci.* 45:1948-1972. [b]Aponte et al. (2014) *Geochim. Cosmochim. Acta* 141:331-345. Aponte et al. (2016) *Geochim. Cosmochim. Acta* 189:296-311.

Why is there an enantiomeric excess?

1- Origin

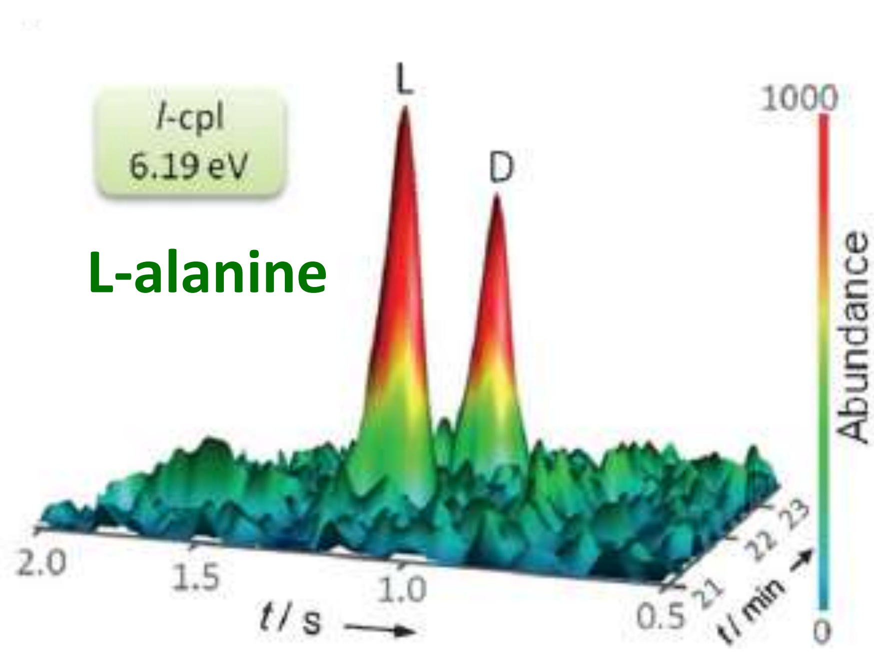


Meinert et al. (2014) *Angew. Chem. Int. Ed.* 53:210-214.

Why is there an enantiomeric excess?

1- Origin

Selective asymmetric decomposition or synthesis of amino acids using ultra-violet circularly polarized light



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2-Amplification

Why is there an enantiomeric excess?

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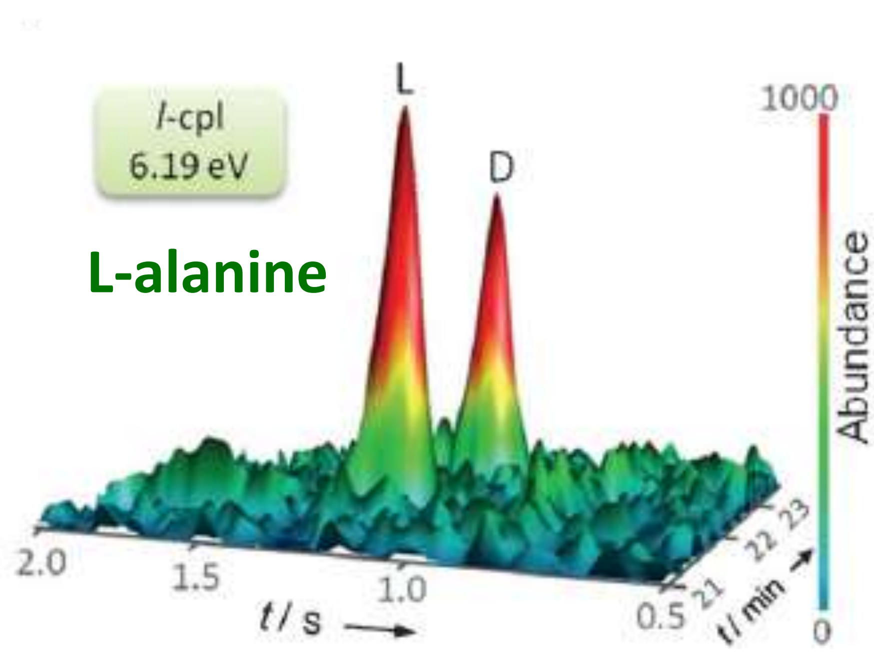
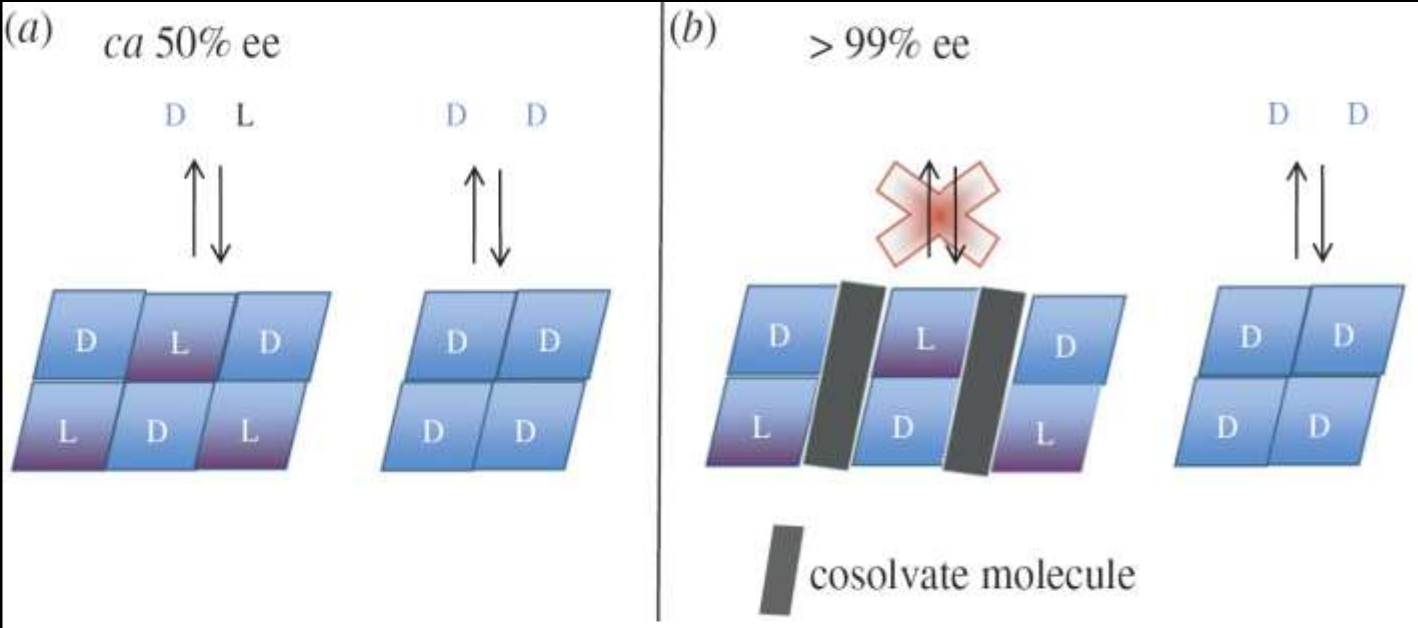


Meinert et al. (2014) *Angew. Chem. Int. Ed.* 53:210-214.

2-Amplification

Differences in solubility between pure and racemic crystals may amplify the initial small excess



Blackmond D. G. (2011) *Phil. Trans. R. Soc. B* 366:2878-2884.

Why is *sec*-butylamine racemic?

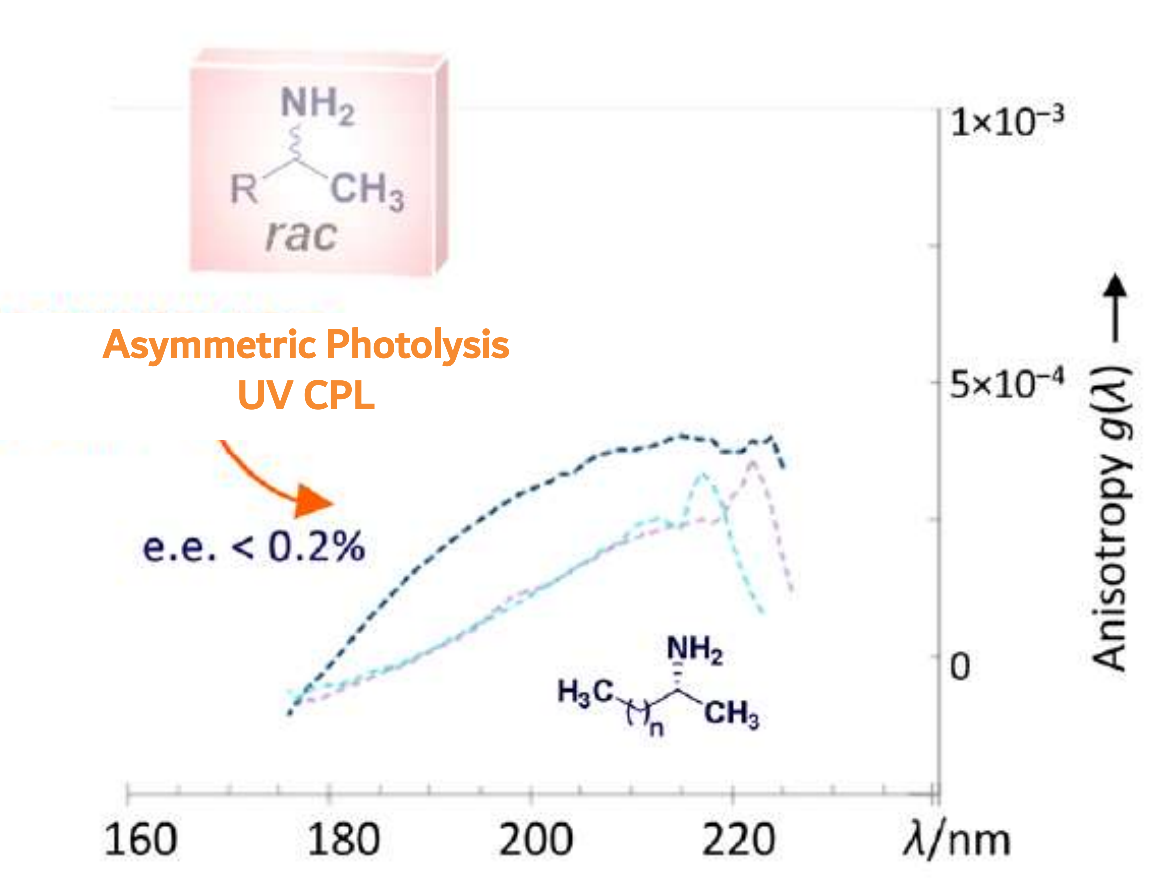
Meteoritic isovaline shows L-ee

but

sec-butylamine is racemic

Opposite to amino acids, amines show low anisotropies which may explain their racemic composition in meteoritic samples

Anisotropy is a direct measure of the effectiveness of asymmetric photochemical reactions



Meinert et al. (2016) *J. Photochem. Photobiol. A: Chem.* 331:130-137.

Isotopic
Analyses

Stable Isotope Analysis

Stable Isotopes

$^{12}_{6}C$ $^{13}_{6}C$ $^{14}_{6}C$

fferent mass numbers

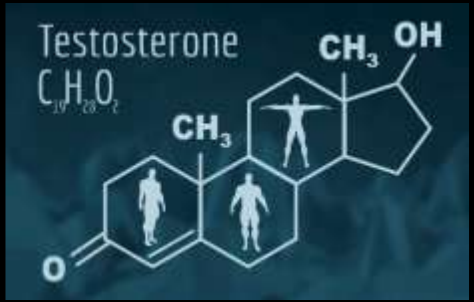
Same atomic number

$^{1}_{1}H$ (hydrogen) $^{2}_{1}H$ (deuterium) $^{3}_{1}H$ (tritium)

Doping in sports

Not in human body

In human body



Meteoritic Stable Isotope Analysis

Stable Isotopes

$^{12}_{6}C$ $^{13}_{6}C$ $^{14}_{6}C$

fferent mass numbe

Same atomic number

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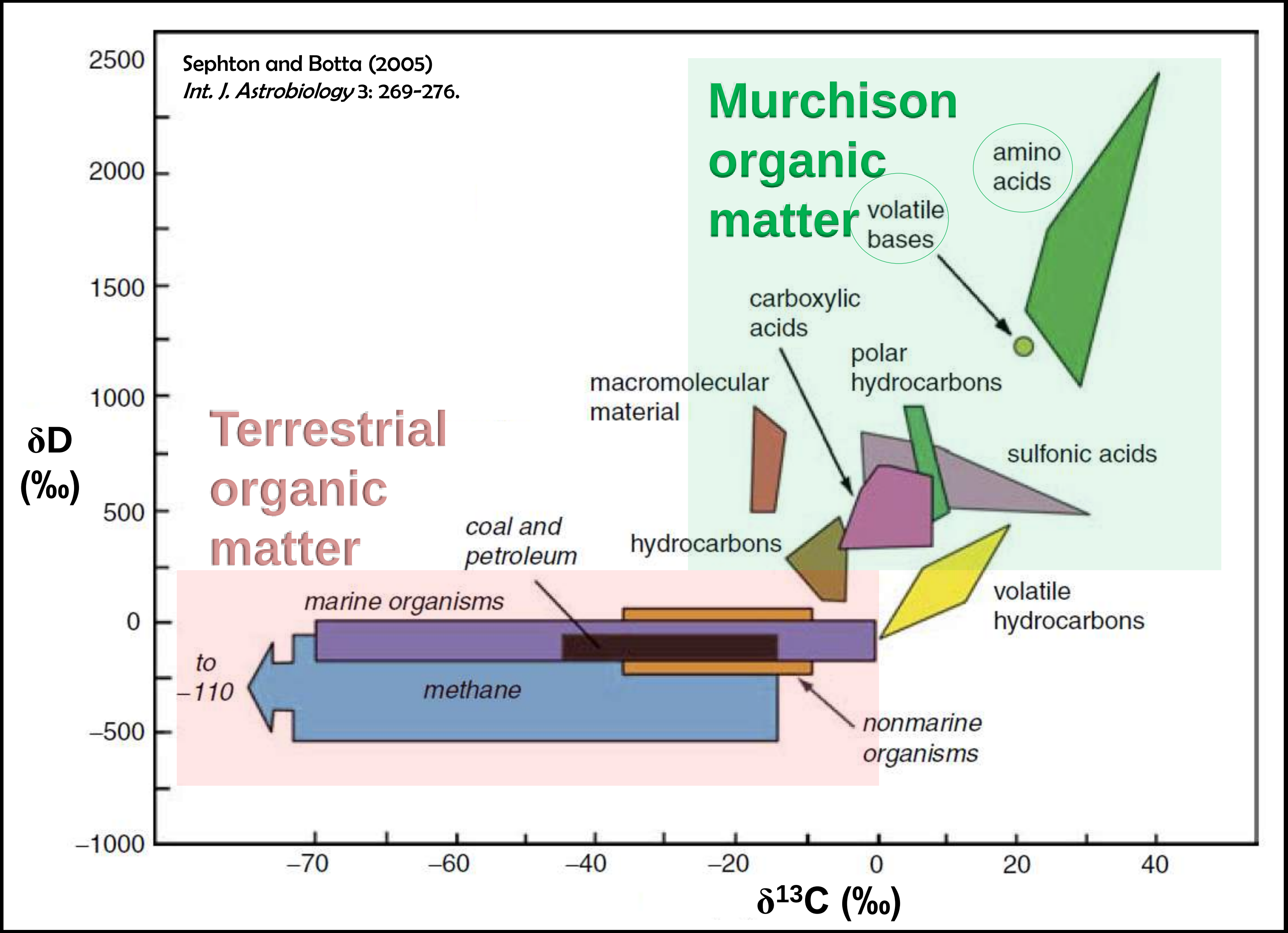
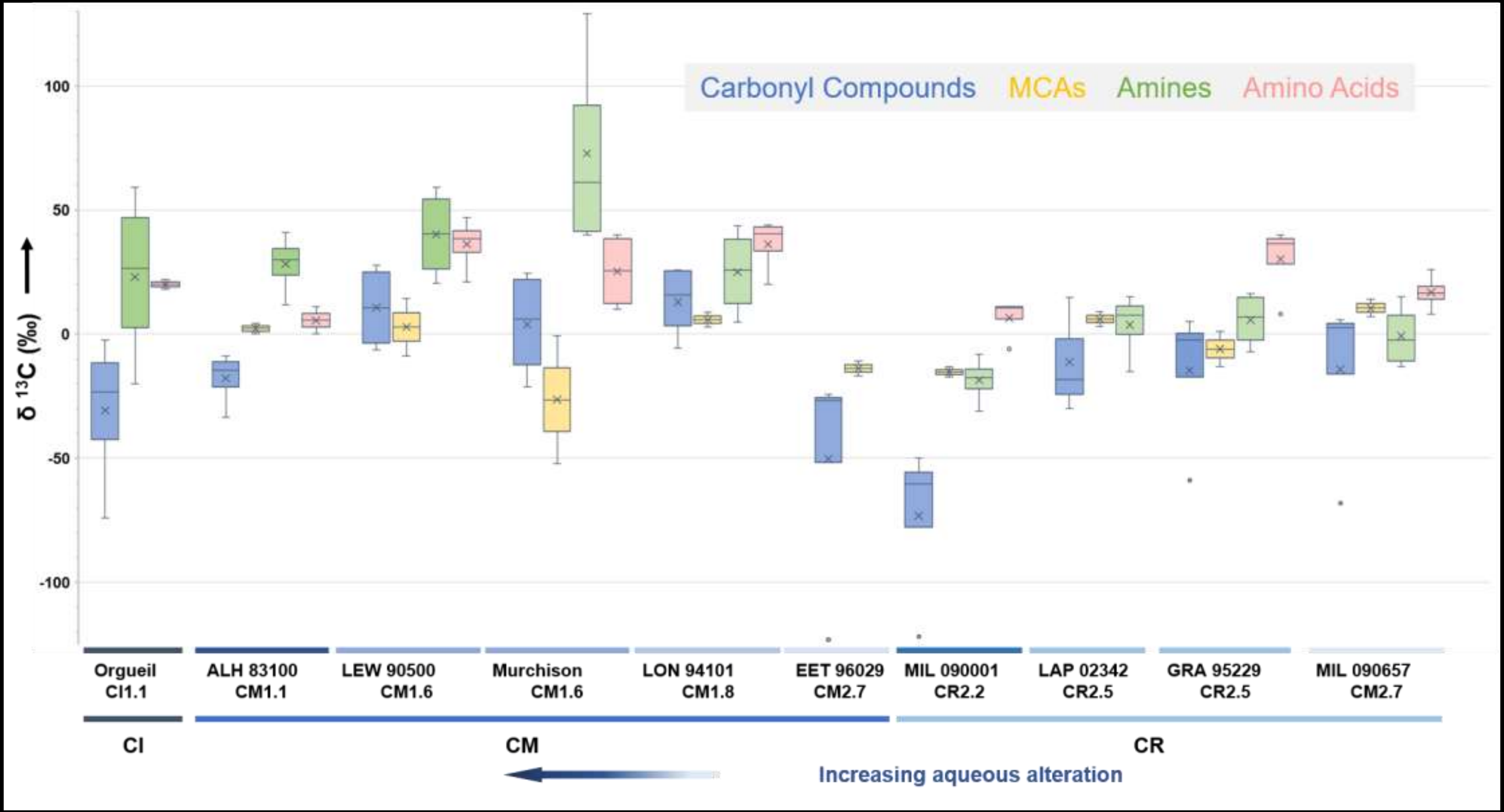
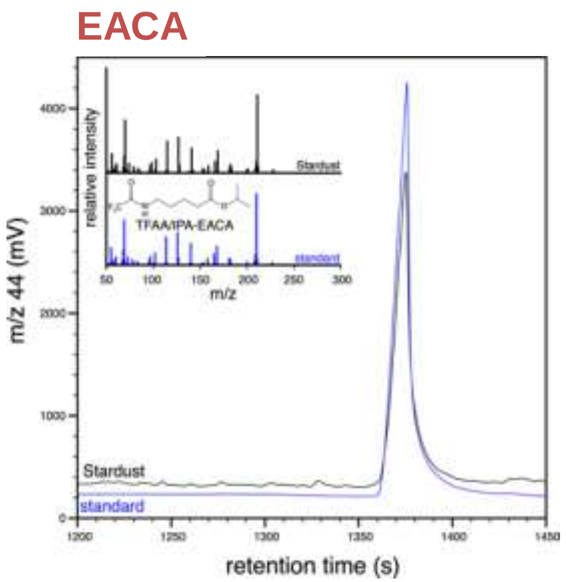
(hydrogen) (deuterium) (tritium)



^{13}C-Isotope of Meteoritic Organics



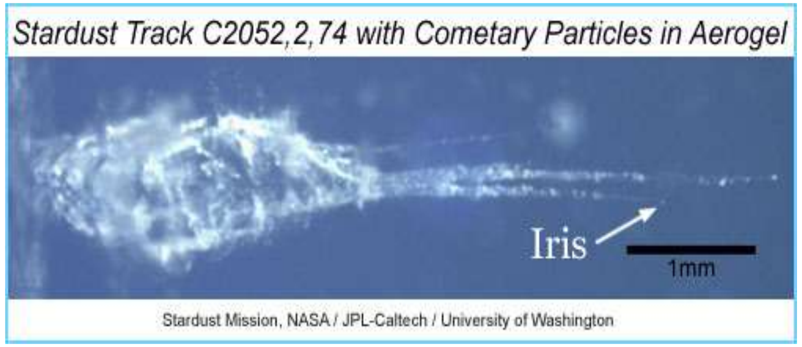
Stardust Foil Isotopic Results

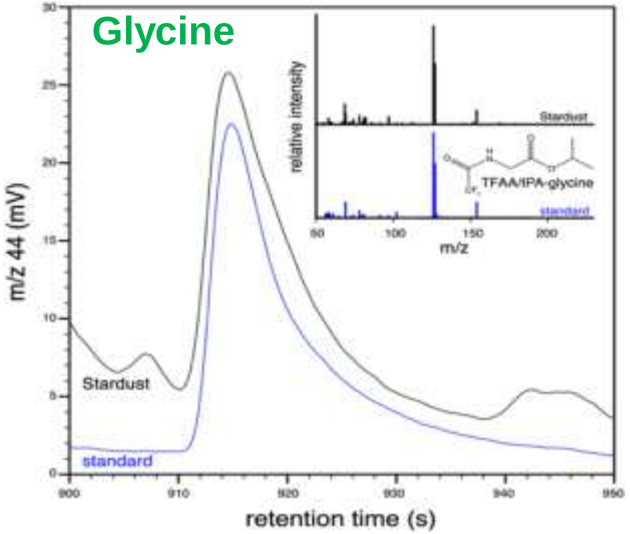


EACA from Stardust: **δ^{13}C = –25±2‰**

EACA from Nylon shipping bag: δ^{13}C = –26.8±0.2‰

EACA is terrestrial





Glycine from Stardust: **δ^{13}C = +29‰ ± 6‰**

Meteoritic glycine: δ^{13}C ≈ +20‰ to +40‰
Terrestrial carbon ranges from –6 to –40 ‰

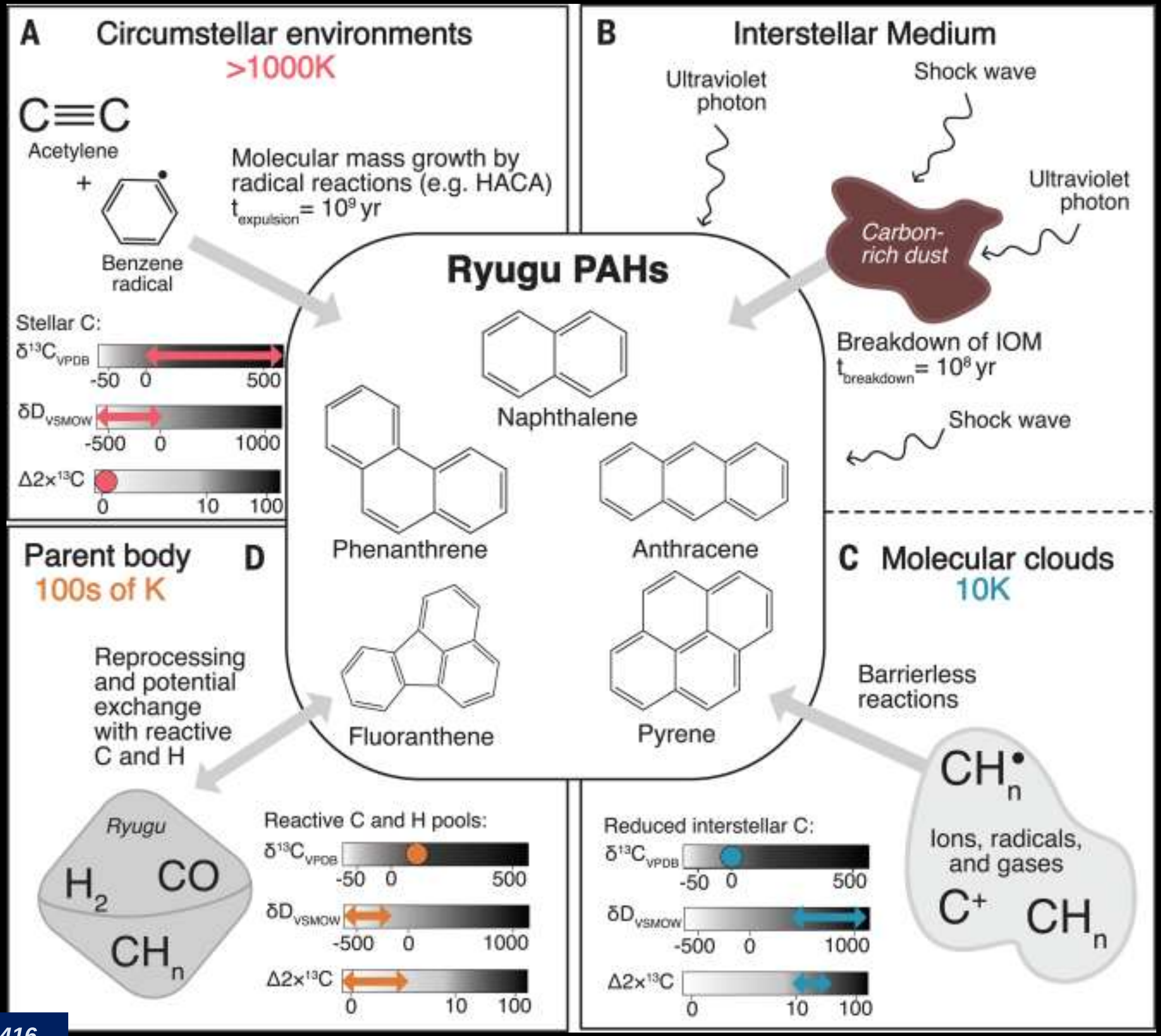
Glycine is extraterrestrial

Elsila et al., 2009

Compound- and Site-Specific Stable Isotope Analysis

HOT env.
Mid-Hi ^{13}C
Low D

WARM env.
Mid ^{13}C
Low D



COLD env.
Mid ^{13}C
High D

COLD env.
Low ^{13}C
High D

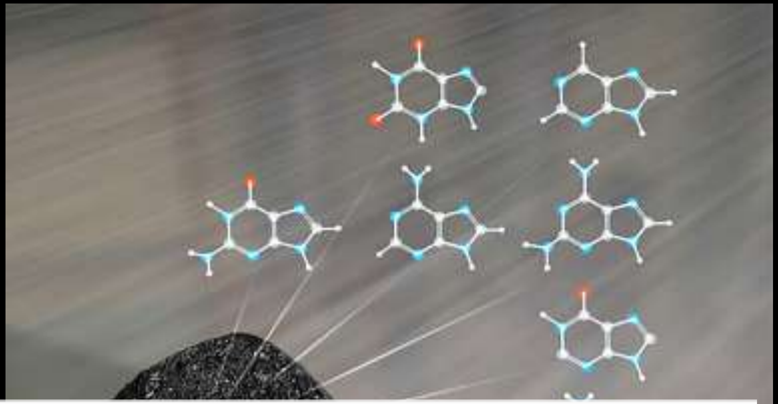
Zeichner et al. (2023) *Science 382, 1411-1416.*

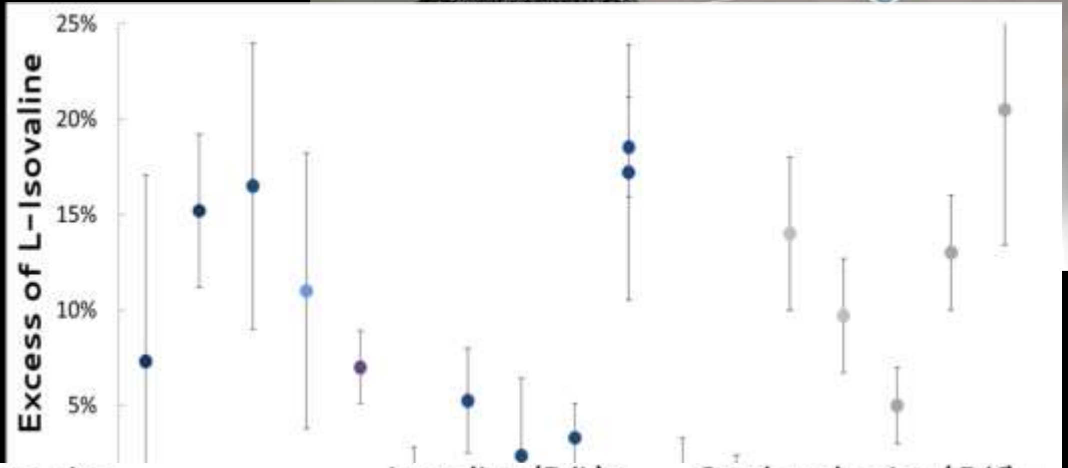
Rewinding

Meteoritic compounds can tell us about the origins of organic matter in the Solar System, and may have been an important source of prebiotic organics,

The origin of homochirality on Earth may have been influenced by extraterrestrial delivery,

Isotope analysis provide information about the origins and synthetic formation pathways of organic compounds.





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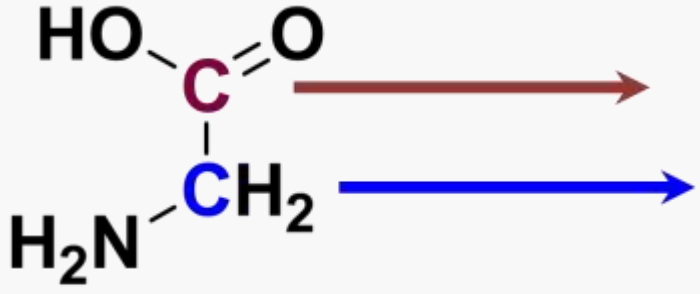
The BIG Caveats

Meteoritic Organics and their Precursors

Meteorite	Type	δ^{13}C (‰)						
		CO	CO_2	CO_3^{2-} (carbonate)	HCN	CH_3CO_2H (acetic acid)	CH_3NH_2 (methylamine)	$NH_2CH_2CO_2H$ (glycine)
Orgueil	CI1	–	–	+60 ± 3[2], +59.2 ± 0.2[3], +68.8 ± 0.2[3]	–	–	+43 ± 10[6]	+22[10]
ALH 83100	CM1/2	–	–	+44.5 ± 0.2[3]	–	–	+41 ± 6[7]	+11[11], +53 ± 3[7]
Murchison	CM2	–32 ± 2[1]	+29.1 ± 0.2[1]	+37 ± 3[2], +43.9 ± 0.2[3]	+5 ± 2[4]	+22.7 ± 0.2[1], –7.7 ± 0.2[5]	+129 ± 7[8]	+22[12], +41 ± 2[13], +13 ± 3[11]
LEW 90500	CM2	–	–	+41.3 ± 0.2[3]	–	–	+59 ± 8[7]	+47 ± 10[11], +47 ± 1[7]
LON 94101	CM2	–	–	+41.3 ± 0.2[3]	–	–	+44 ± 6[7]	+38 ± 3[11], +36 ± 4[7]
LAP 02342	CR2	–	–	+36.2 ± 0.2[3]	–	–	+64.6 ± 1.6[9], +10 ± 13[7]	+20.1 ± 0.1[14]
GRA 95229	CR2	–	–	+42.0 ± 0.2[3]	–	–	+64.0 ± 2.1[9], –1 ± 9[7]	+33.8 ± 1.6[15], +35 ± 9[11]

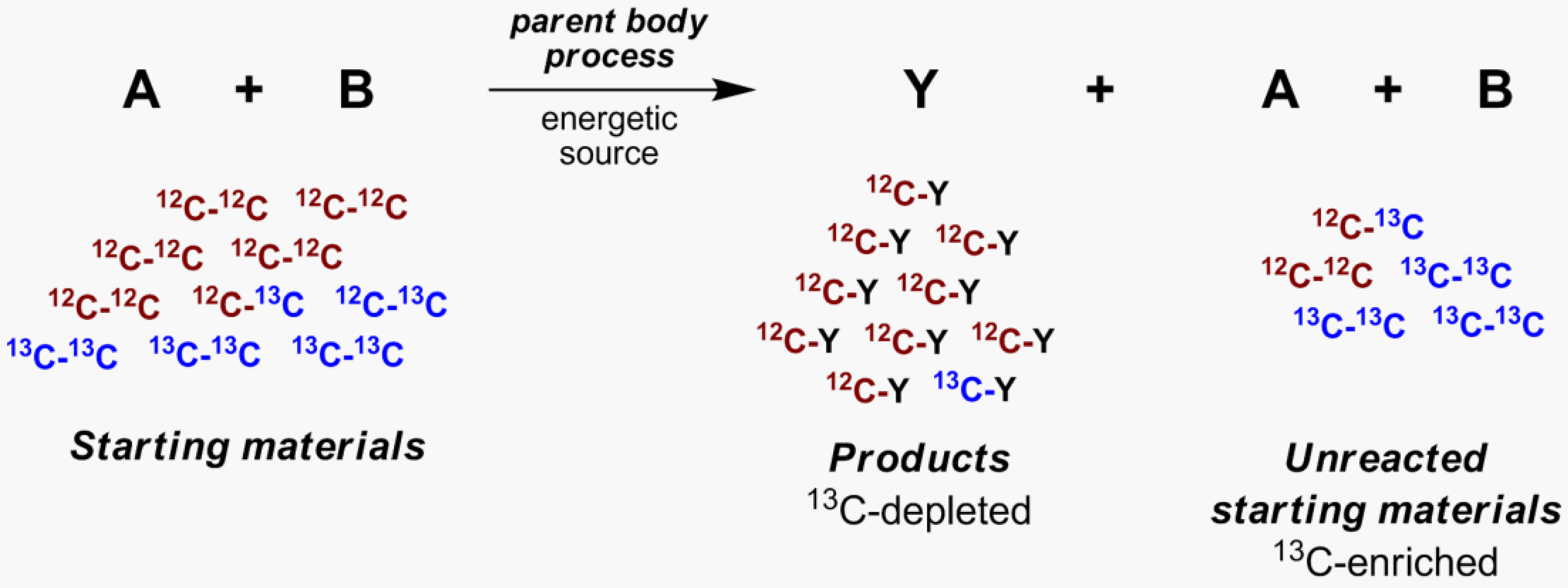


Murchison has a range of δ^{13}C values (+13 to +41)

Are carbon atoms coming from CO_2, CO, HCN, other?

Aponte et al. (**2017**) *ACS Earth Space Chem.* **1**, 3-13.

Isotopic Fractionation*



*The extent of fractionation in each reaction is still <u>insufficiently understood</u>

Aponte et al. (2017) *ACS Earth Space Chem.* 1, 3-13.

Two Main Challenges

To understand the molecular distribution of soluble meteoritic organics we have to fight/accept two main challenges:

1. the unknown molecular abundance of the precursor molecules and end products,

2. the unknown level of fractionation (synthesis/destruction) experienced over different periods of time and physicochemical conditions inside the parent body.

Aponte et al. (**2017**) *ACS Earth Space Chem.* **1**, 3-13.

We Need Synergistic Approaches

How can we constrain the various chemical routes associated with the formation of meteoritic organics to a common set of molecular precursors?

- We need to **combine** astronomical searches, theoretical modeling, experimental work on reactions in the gas-phase and in interstellar ice analogs, together with the isolation and isotopic analysis of meteoritic species, and...

- Greater effort should be placed on **quantitative** analysis focused on measuring reaction rates, as well as the inherent molecular stability, abundance, isomeric distribution, and isotope effect of organic products in the gas phase and interstellar ice analogs.

Aponte et al. (**2017**) *ACS Earth Space Chem.* **1**, 3-13.