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The Search for Chiral Asymmetry as a Potential Biosignature in Samples from Mars

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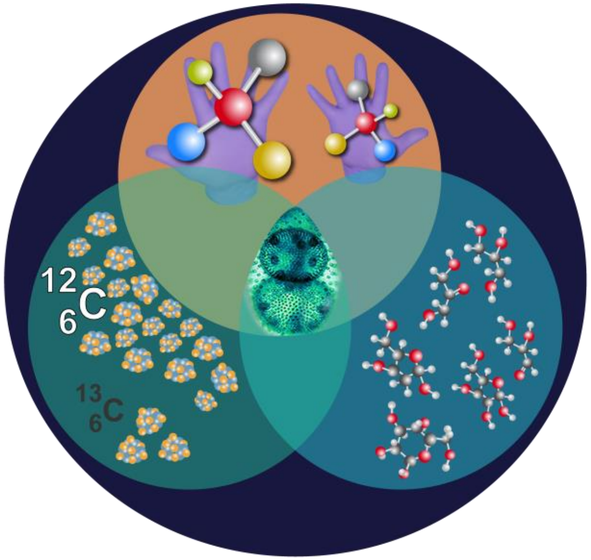

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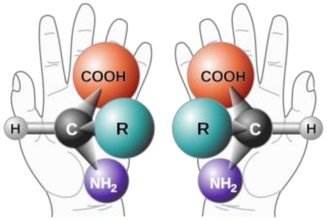
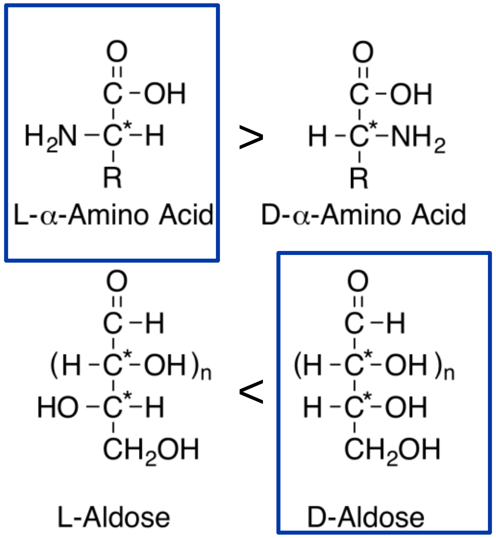
Motivation

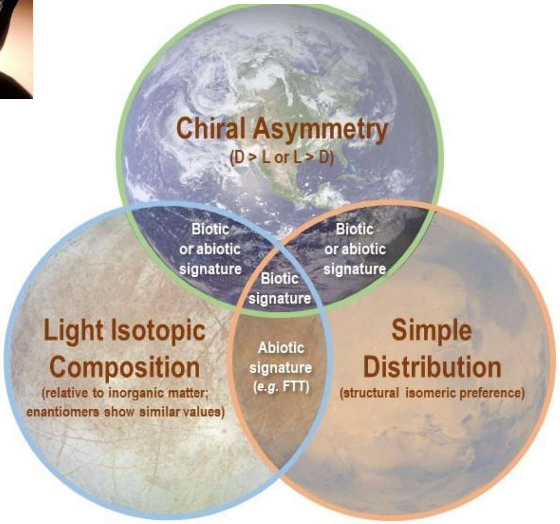
- **Homochirality** (L-amino acids in proteins and D-sugars in DNA and RNA) is thought to be a prerequisite for life and a powerful chemical biosignature.





- ***However***, some meteorites have large excesses of **L-amino acids (>60% *ee*) and D-sugar acids (up to 100% *ee*) produced by non-biological processes,** complicating use of chirality as a definitive biosignature

- **We propose a set of measurement criteria (chiral asymmetry, light isotopic composition, and simple distribution)** to be used to establish the origin (biotic or abiotic) of any amino acid or sugar enantiomeric excesses detected in future life detection experiments on Mars or elsewhere.



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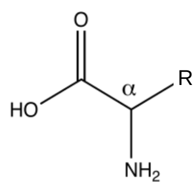
Biochemistry is Distinct from Abiotic Chemistry

Life (Biotic)

- **Simple distribution: 20 standard amino acids encoded in terrestrial proteins (all L)**

glycine (achiral)	L-glutamine
L-arginine	L-cysteine
L-histidine	**L-alanine**
L-lysine	**L-valine**
L-proline	**L-leucine**
L-aspartic acid	**L-isoleucine**
L-glutamic acid	L-methionine
L-serine	**L-phenylalanine**
L-threonine	**L-tyrosine**
L-asparagine	L-tryptophan

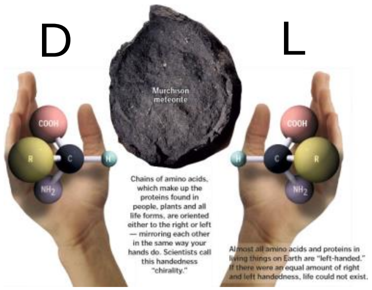
- **Isomer preference: only α-H amino acids found in protein**, although many other non-coded amino acids occur in biology.



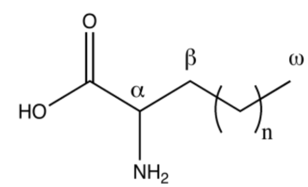
- **Isotopically depleted (biological fractionation):**
  - **δ^{13}C** ~ -70 to +11 ‰ VPDB
  - **δ^{15}N** ~ -20 to +30 ‰ AIR
  - **δD** ~ -270 to +66 ‰ VSMOW

Meteorites (Abiotic)

- **Complex distribution: 96 amino acids *named* in the Murchison meteorite, 12 protein amino acids**, many non-existent in biology; most racemic (D = L), but some can have L-excesses up to ~60%.



- **Amino acids often exhibit complete structural diversity** (all possible isomers, α-, β-, γ-, δ-amino acids, etc.)



- **Isotopically enriched (cold formation):**
  - **δ^{13}C** ~ -18 to +52 ‰ VPDB
  - **δ^{15}N** ~ +37 to +184 ‰ AIR
  - **δD** ~ +180 to +7245 ‰ VSMOW

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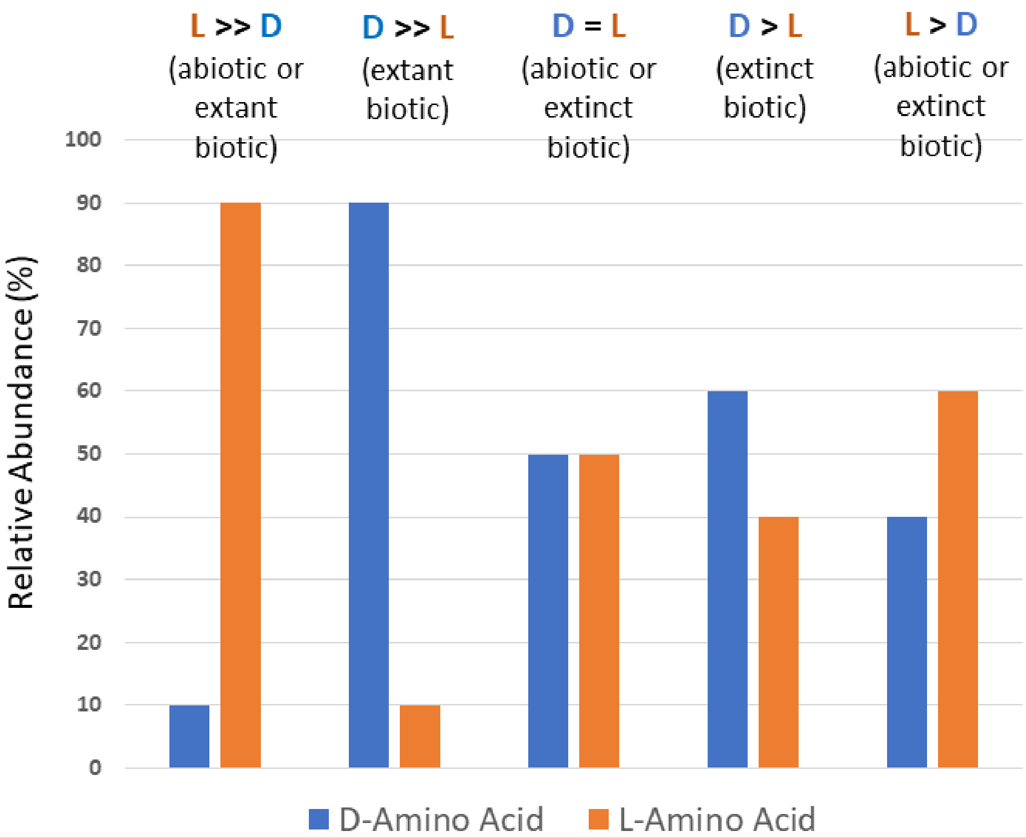
Hypothetical Chiral Distributions and Possible Origins



How can we make it easier to distinguish between abiotic and biotic origins in more likely cases with L > D?

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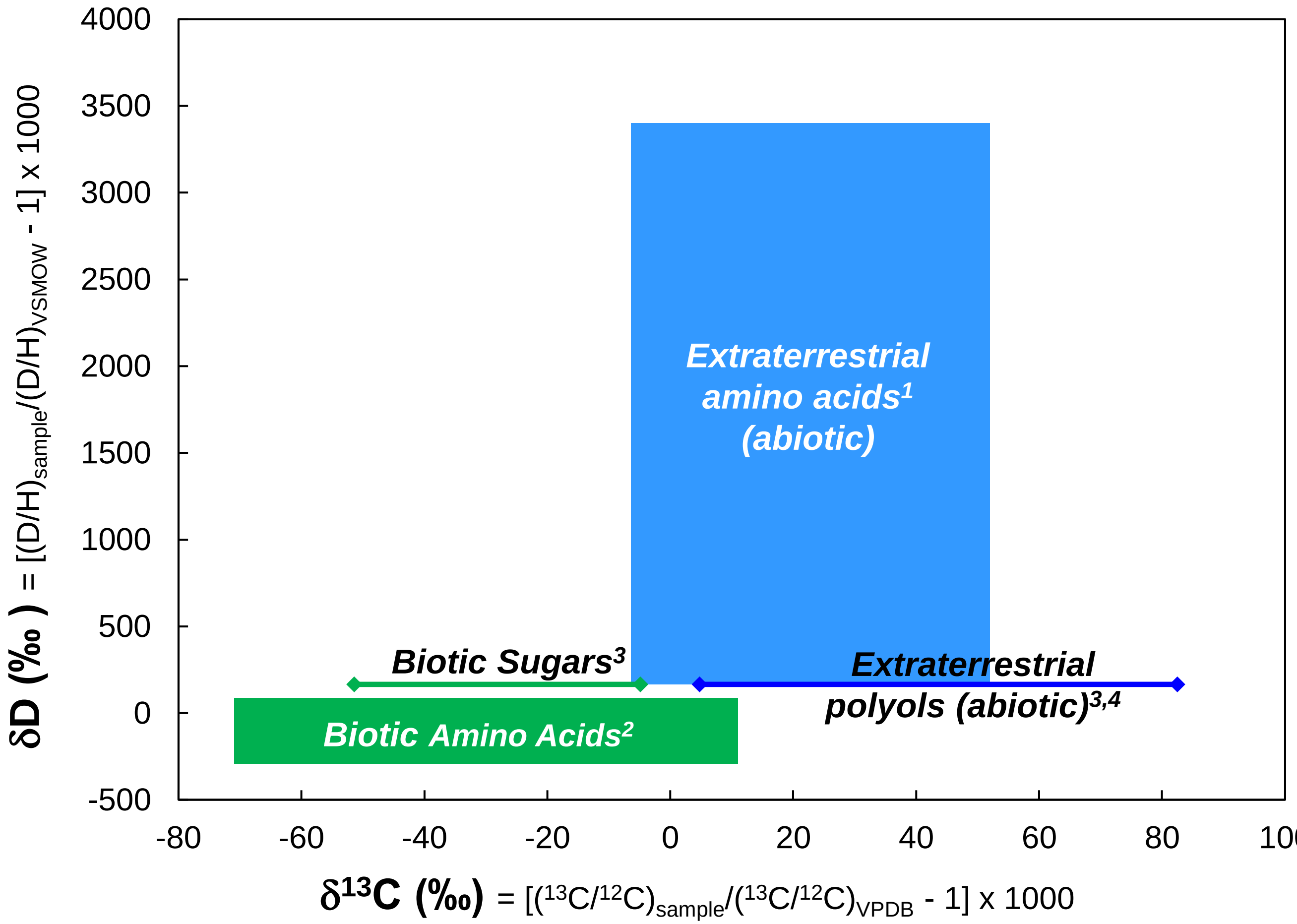
Isotopic Measurements – Strong Preference in Terrestrial Biology for Light Isotopes (^{12}C, ^{14}N, and ^{1}H)



[1]Elsila *et al.* (2012) *MAPS* **47**: 1517-1536
[2]Scott *et al.* (2006) *Astrobiology* **6**: 867-880
[3]Furukawa *et al.* (2019) *PNAS* **116**: 24440-24445
[4]Cooper and Rios (2016) *PNAS* **113**: E3322-E3331

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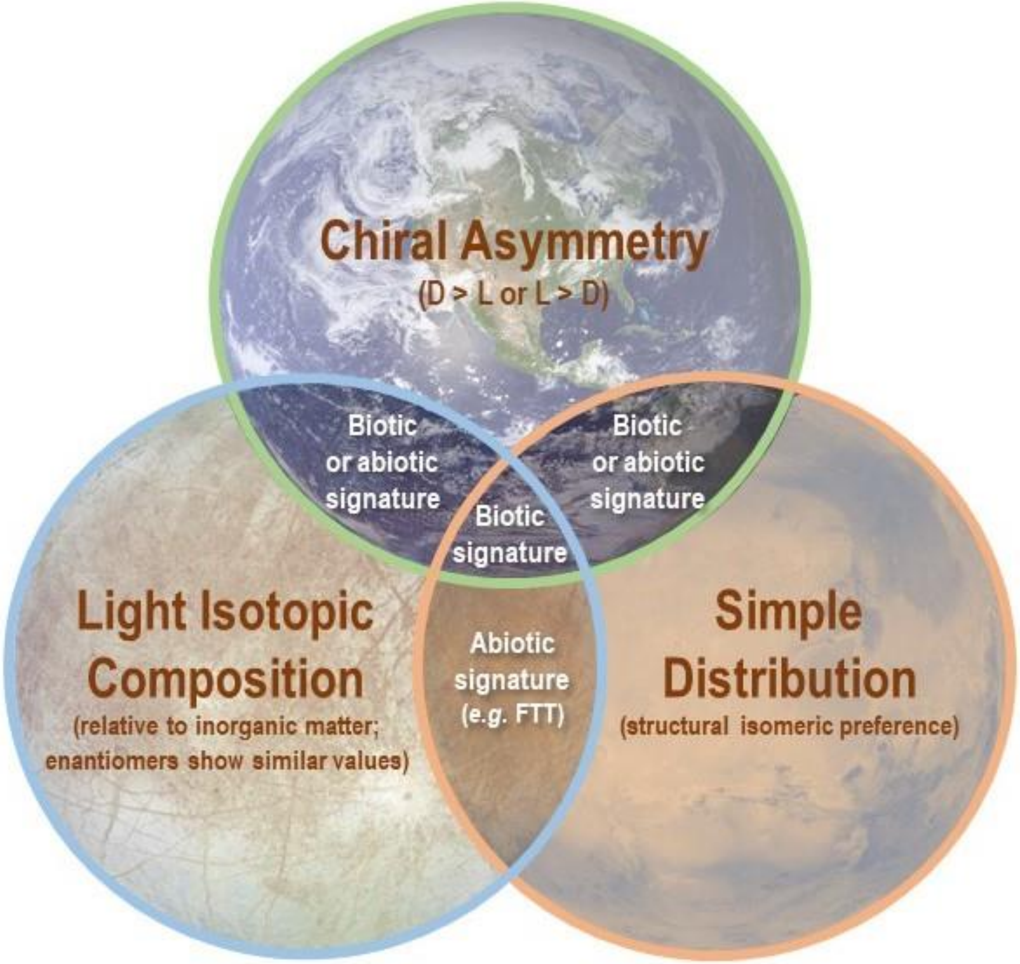
Proposed Criteria to Establish Origin of Chiral Asymmetry



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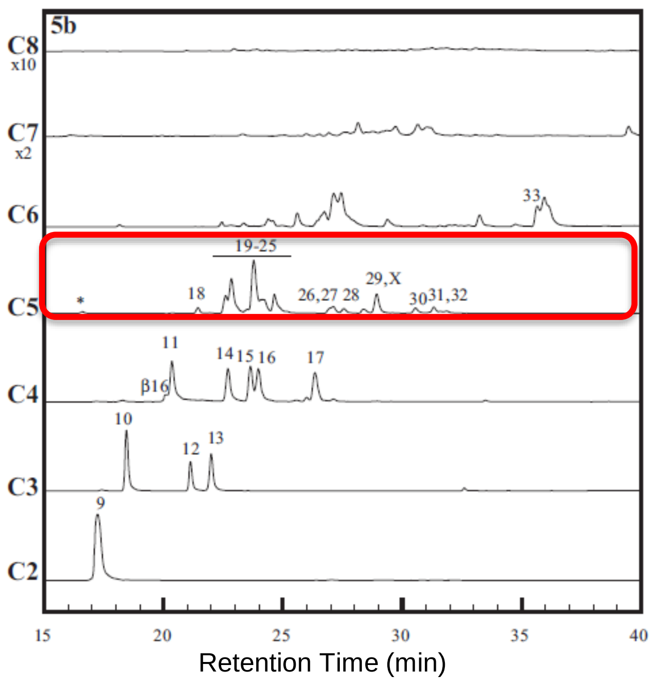
Tagish Lake Meteorite - Abiotic

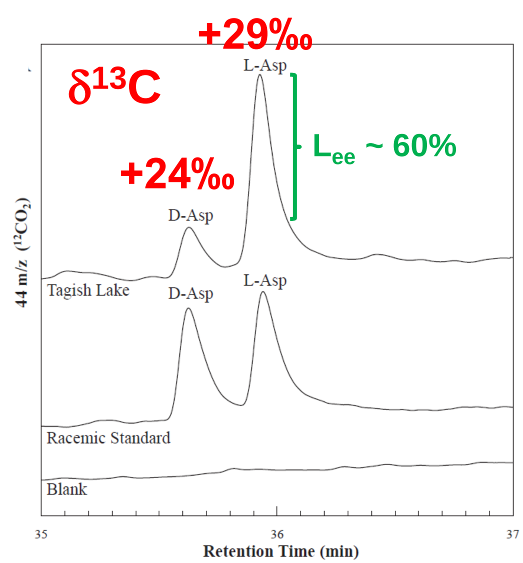
Fell in Northern British Columbia, Canada on Jan. 18, 2000

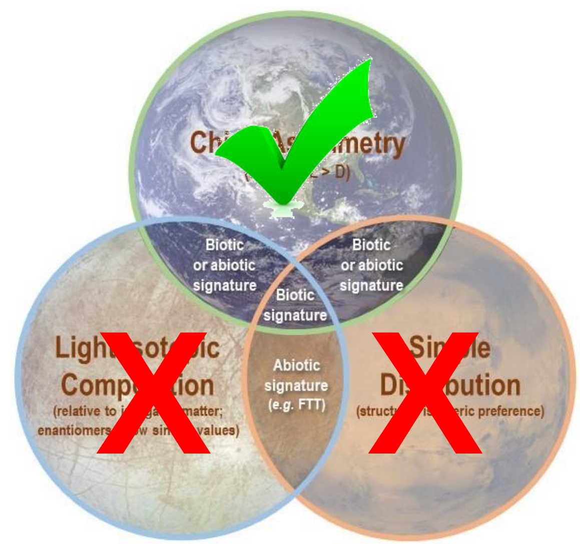
Chiral asymmetry for a few amino acids (L > D); others (*e.g.* alanine) racemic

Complex distribution: Near complete structural diversity of C_2 to C_8 amino acids including all possible five carbon α-, β-, γ-, and δ-isomers.

^{13}C enriched D- and L-aspartic acids are outside of terrestrial biotic aspartic acid range ($\delta^{13}C$ = -4 to -48‰)







Glavin *et al.* (2012) *MAPS* **47**: 1347-1364

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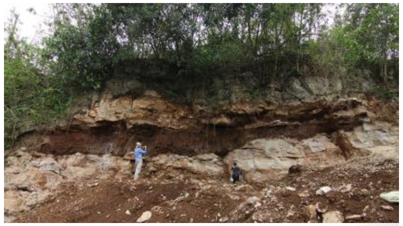
Terrestrial Soil - Biotic

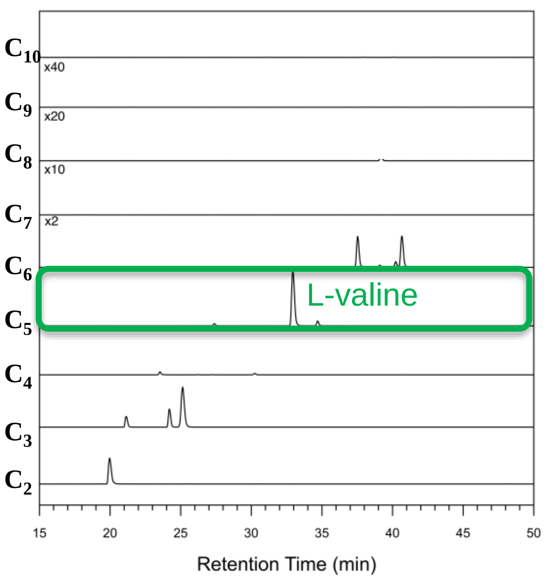


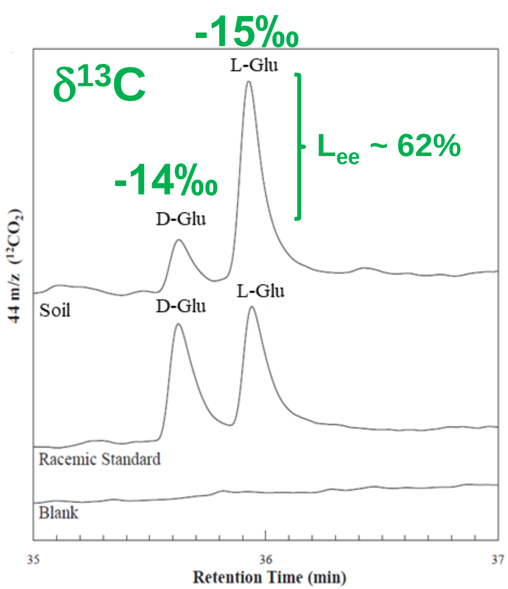
Soil from the Aguas Zarcas meteorite strewn field in Costa Rica

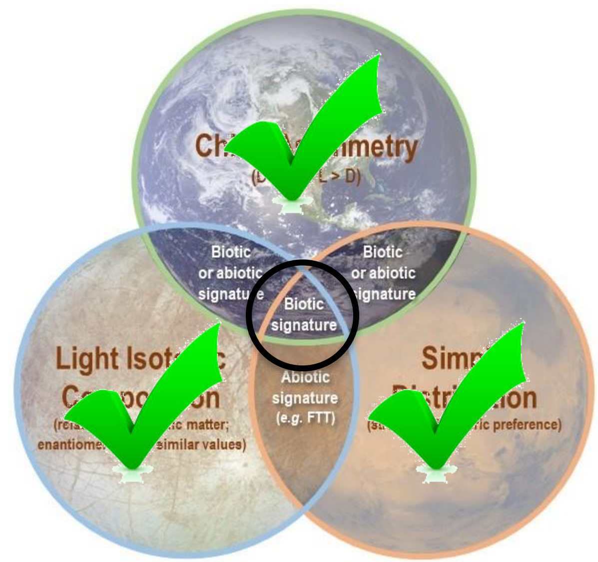
Chiral asymmetry (L > D): for all chiral amino acids

Simple distribution: C_2 to C_6 amino acids with only one C_5 amino acid valine (dominated by α-H amino acids)

^{13}C depleted D- and L-glutamic acid and other protein amino acids in soil ($\delta^{13}C$ ~ +5 to -22‰) all fall within biological range







Glavin *et al.* (2020) *MAPS* **in press**, doi: 10.1111/maps.13451

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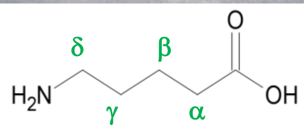
Martian Meteorite - Abiotic

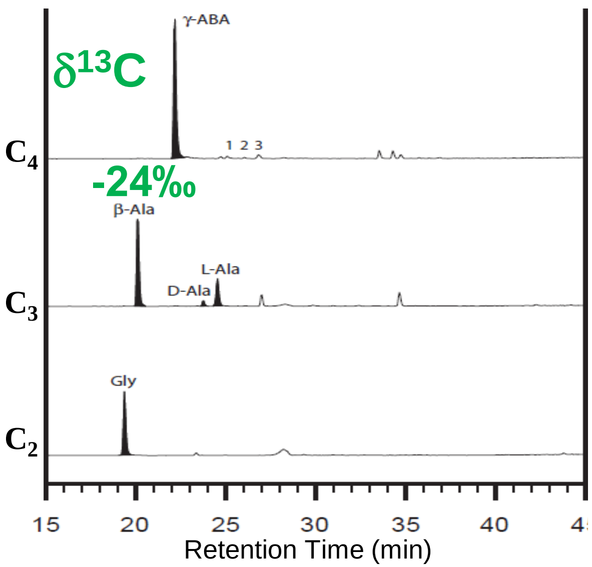
Roberts Massif (RBT) 04262 is a martian shergottite. Ejected from Mars ~3 Mya and recovered in Antarctica in 2004.

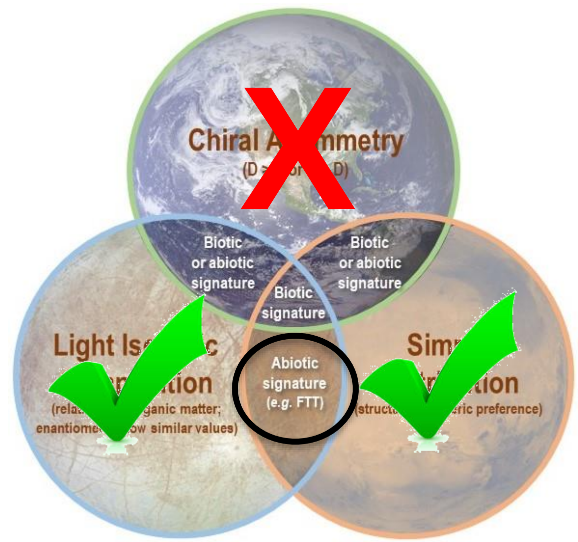
Simple distribution: strong preference for straight-chain, *n*-ω-amino acids (glycine, β-alanine, γ-amino-*n*-butyric acid)



^{13}C depleted β-alanine: similar to C-isotopic composition of reduced igneous carbon in SNCs, thermally altered carbonaceous meteorites, FTT reactions, biology

No chiral asymmetry: martian amino acids are all achiral





Callahan *et al.* (2013) *MAPS* **48**: 786-795

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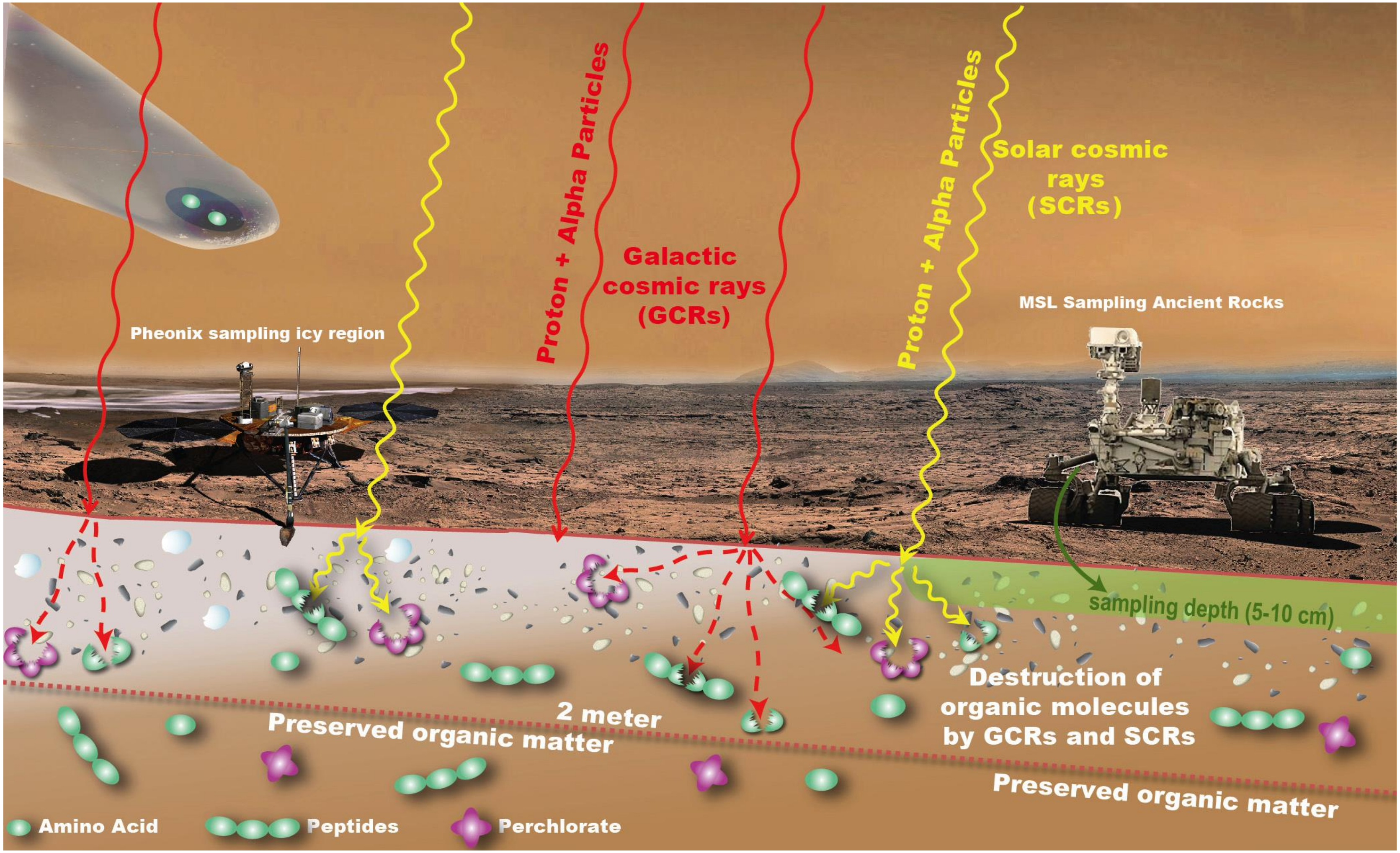
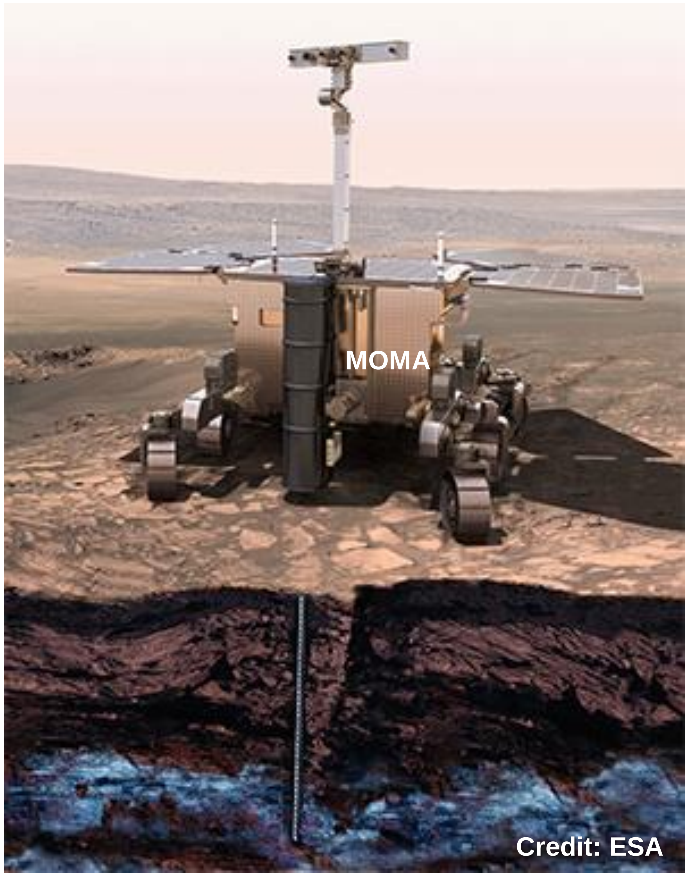
Challenge - Amino Acid Preservation



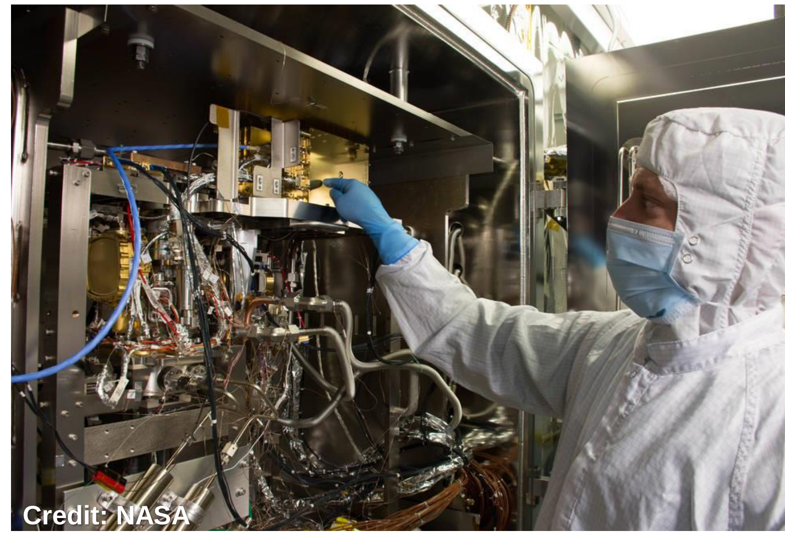
Credit: J. Friedlander, NASA

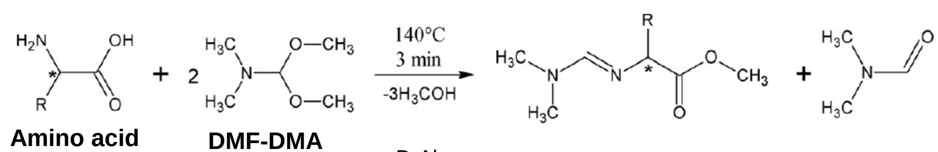
ExoMars Rover and MOMA

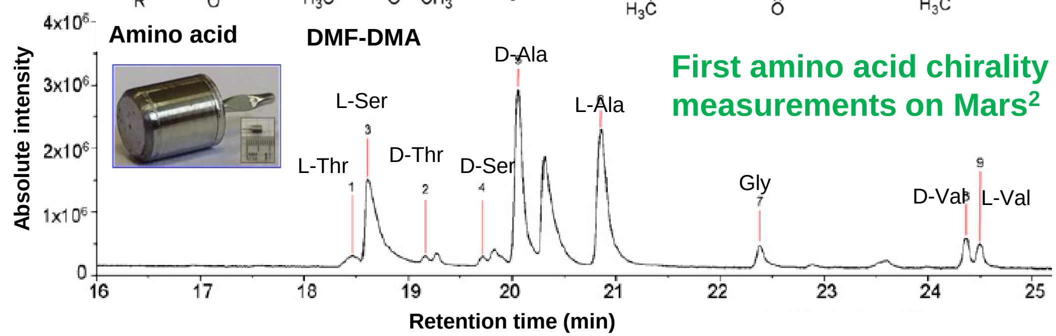


ExoMars rover will acquire subsurface samples down to ~2 m

Mars Organic Molecule Analyzer (MOMA)
GCMS and LDMS capability[1]





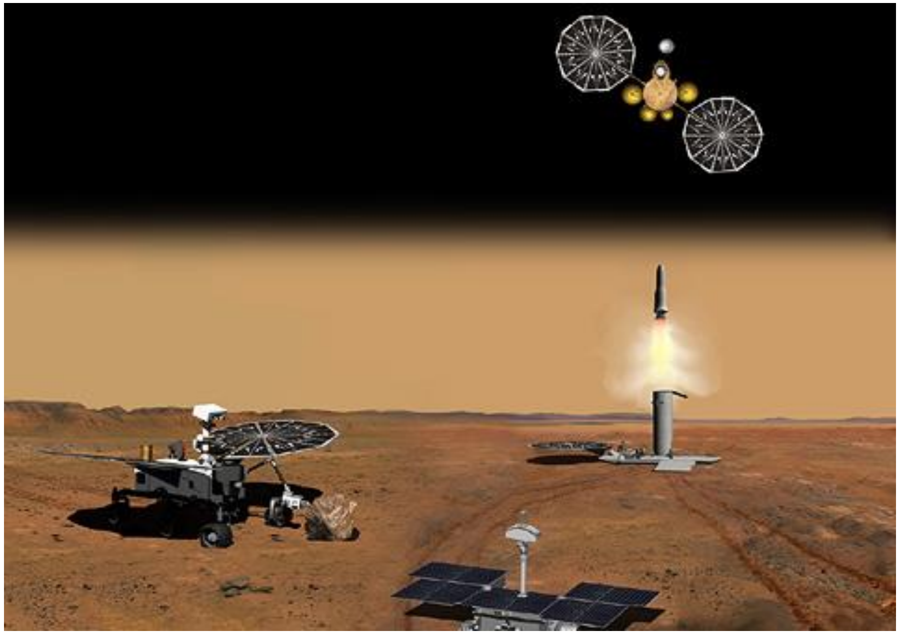


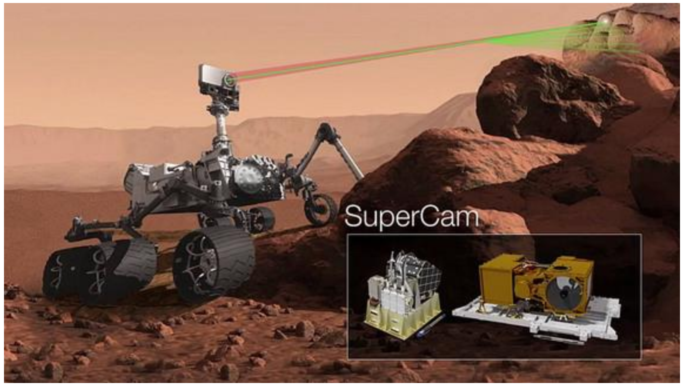
[1]Goesmann *et al.* (2017) *Astrobiology* **17**: 655-685
[2]Freissinet *et al.* (2010) *J. Chromat. A* **1217**: 731-740

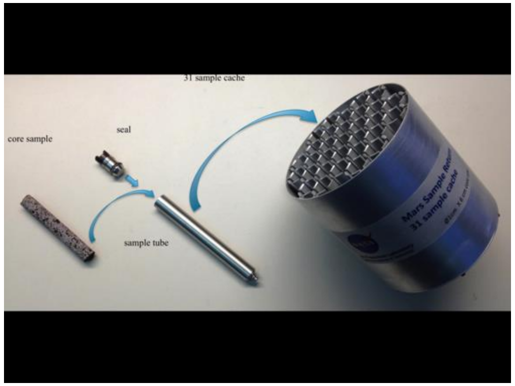
Mars 2020 and Sample Return

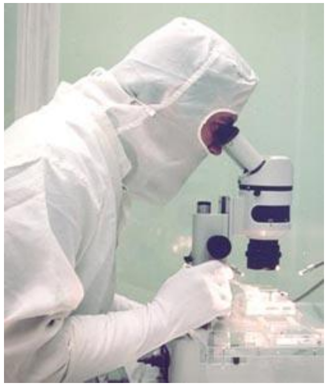
Mars 2020 Perseverance rover has sample caching capability. First step for joint NASA-ESA Mars sample return campaign.

Ultimately, Earth-based laboratory analyses of a carefully selected set of samples from Mars may be our best chance of unambiguous biosignature detection.









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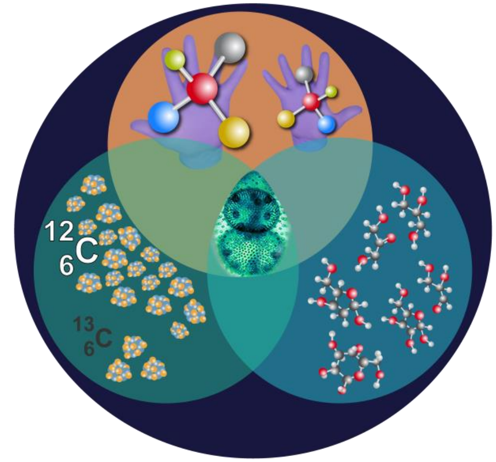
Conclusions

- The detection of chiral asymmetry will need to be carefully interpreted in the context of other key observations including the molecular distribution and isotopic compositions.

- One compelling biosignature would be the detection of chiral molecules with the opposite handedness as life on Earth (i.e., D-amino acids and L-sugars); however, this is unlikely given the evidence from meteorites.

- Enantiomeric excesses detected in chiral molecules that display structural isomeric preference with light isotopic compositions would provide a strong biosignature.

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