Analysis of Organics in Solar System Samples

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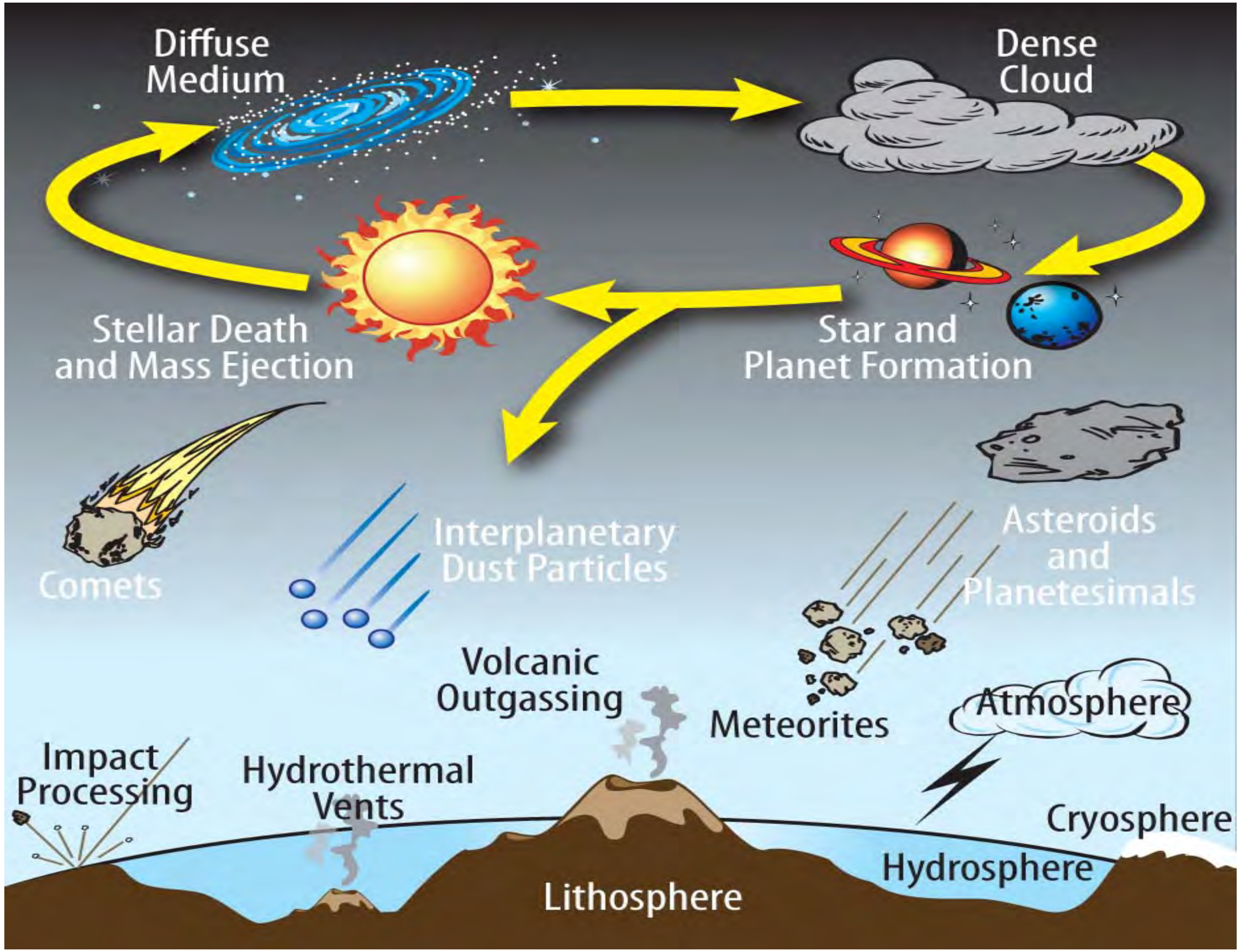
Organic Delivery and the Ancient Earth

- Earth was bombarded during and shortly after accretion by impactors, **delivering water and organic material**.
    - 30,000 tons of cosmic dust (meteorites, micrometeorites, interplanetary dust particles) fall to Earth each year today
    - During heavy bombardment period, more than 1000 times this amount may have fallen to Earth
- Extraterrestrial material could have been a major **source of prebiotic organic ingredients** needed for the origin of life
- Studying this material can **help us understand the origin of life** on Earth and **understand the chemistry of the solar system**

Organic Formation Processes and Locations



Remote Observations & Simulations

***In Situ* Detection**

Sample Return

Lab Analyses

Simulations

After Deamer et al., (2002)
Astrobiology **2**:371-381

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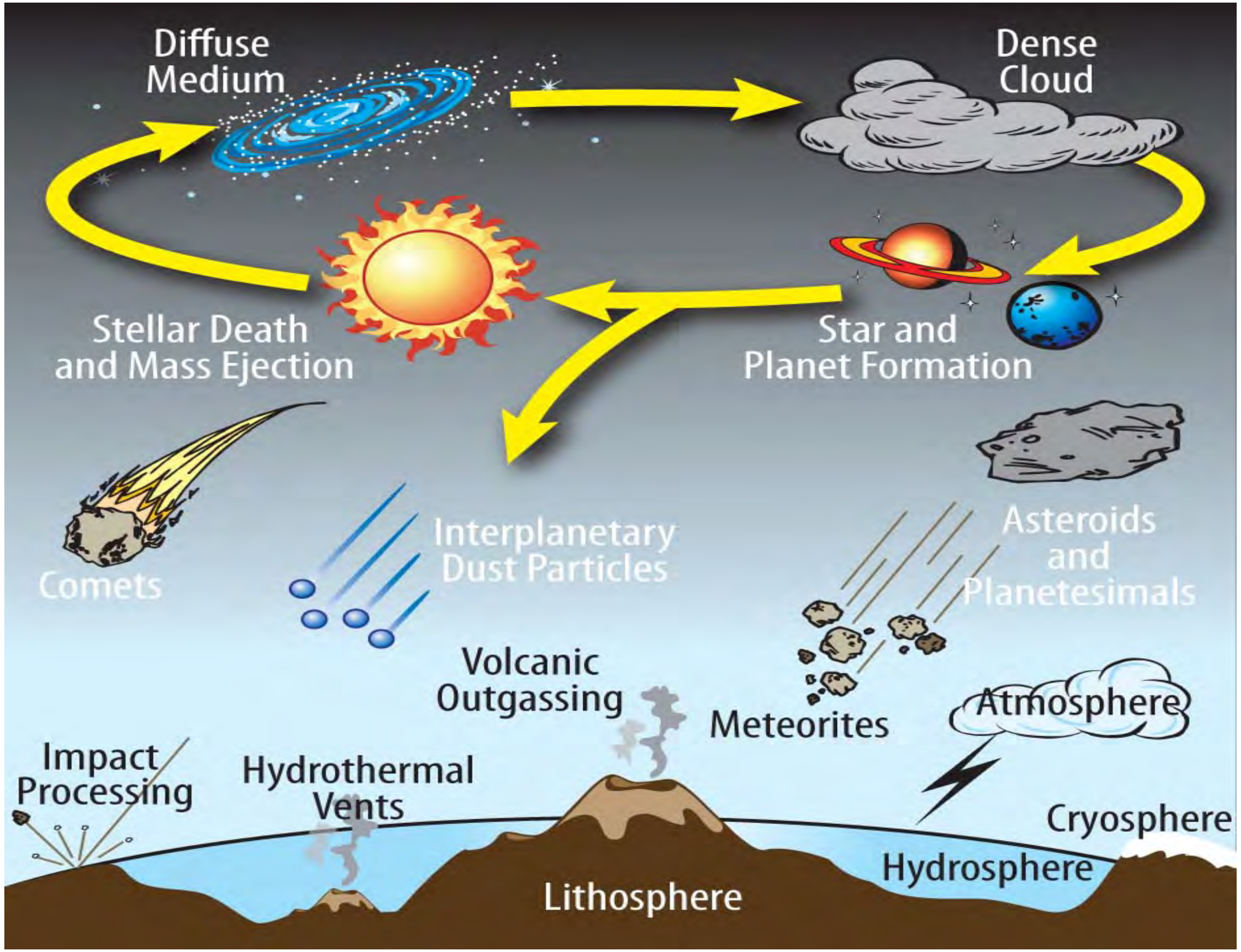

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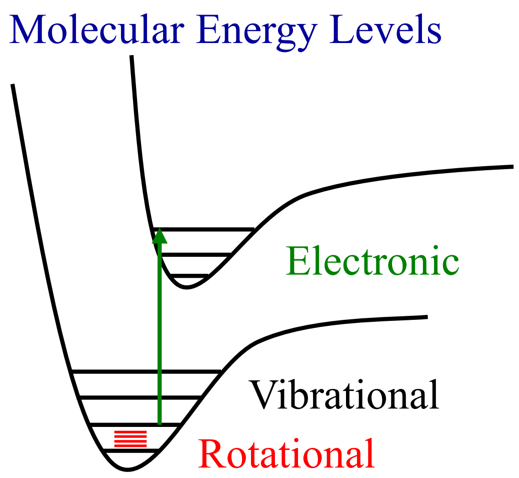
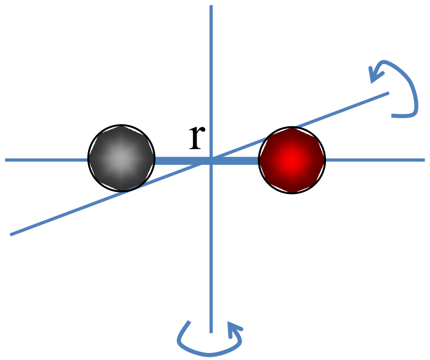
Rotational Spectroscopy

- Interstellar and circumstellar gas is cold (T ~ 50 K)
- Rotational energy levels of molecules primarily filled by collisional excitation.
- Identification by “Finger Print” Pattern.
  - Unique to a Given Chemical Compound
- Requires lab spectrum of standard
- Only gas phase small molecules





$$I = \mu r^2$$

$$B = \hbar^2/2I$$

$$\nu = 2B(J + 1)$$

Courtesy of Stefanie Milam

Some Known Interstellar Molecules

2

H_2, OH, SO, SO^+, SiO, SiS, NO, NS, HCl, $NaCl$, KCl, $AlCl$, AlF, PN, SiN, NH, CH

CH^+, CN, CO, CS, C_2, SiC, CP, CO^+, HF, SiH, HO^+, PO, HD, AlO

3

H_2O, H_2S, SO_2, NNH^+, HNO, CCS, NH_2, H_3^+, NNO, HCO, HCO^+, OCS, CCH, HCS^+, c-$SiCC$, CCO, $AlOH$

C_3, HNC, HCN, CH_2, NH_2, HOC^+, $NaCN$, $MgNC$, $AlNC$, $SiCN$, $SiNC$, H_2D^+, KCN, $MgCN$, HCP, H_2O^+, CCP

4

NH_3, H_3O^+, H_2CO, H_2CS, $HNCO$, $HNCS$, $CCCN$, HCO_2^+, $CCCH$, c-C_3H, $CCCO$, C_3S, $HCCH$, $HCNH^+$, $HCCN$, H_2CN, c-SiC_3, C_3N^-, $HSCN$

5

SiH_4, CH_4, $CHOOH$, $HC{\equiv}CCN$, CH_2NH, NH_2CN, H_2CCO, C_4H, c-C_3H_2, CH_2CN, C_5, SiC_4, H_2C_3, $HCCNC$, $HNCCC$, H_2COH^+, $HC(O)CN$

6

CH_3OH, NH_2CHO, CH_3CN, CH_3NC, CH_3SH, C_5H, HC_2CHO, $CH_2{=}CH_2$, H_2C_4, HC_3NH^+, C_5N, c-H_2C_3O

7

CH_3CHO, CH_3NH_2, CH_3CCH, CH_2CHCN, $H(C{\equiv}C)_2CN$, C_6H, c-CH_2OCH_2, $H_2CC(OH)H$

8

CH_3CO_2H, HCO_2CH_3, CH_3C_2CN, C_7H, H_2C_6, CH_2OHCHO, NH_2CH_2CN

9

CH_3CH_2OH, $(CH_3)_2O$, CH_3CH_2CN, $H(C{\equiv}C)_3CN$, $H(C{\equiv}C)_2CH_3$, C_8H

10

$CH_3(C{\equiv}C)_2CN$, $(CH_2OH)_2$, CH_3COCH_3

11

$H(C{\equiv}C)_4CN$

12

n-C_3H_7CN

13

$H(C{\equiv}C)_5CN$

>15 ions
6 rings
>100 Carbon Molecules
11 Silicon Species
9 Metal Containing Molecules

~200 molecules

https://cdms.astro.uni-koeln.de/

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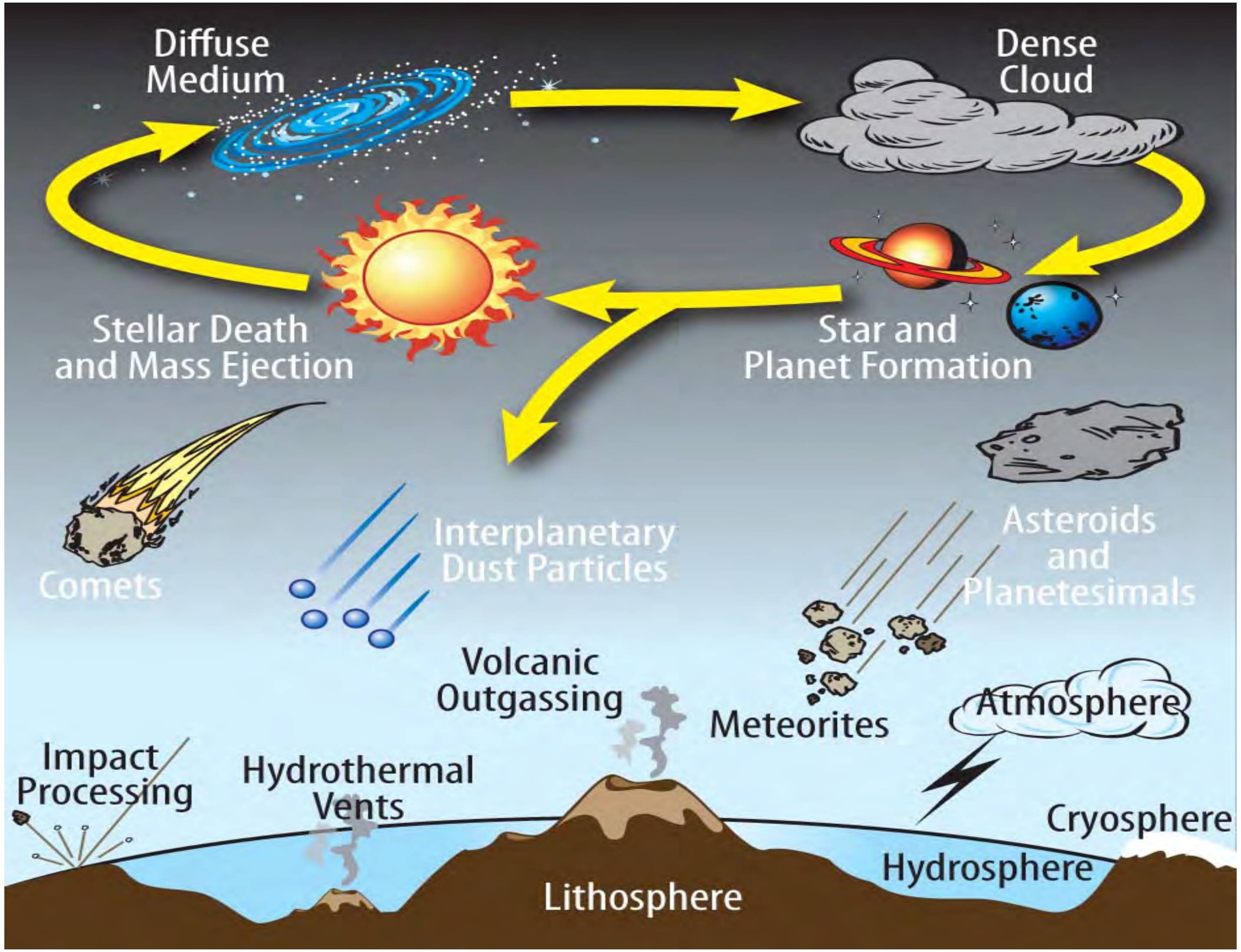

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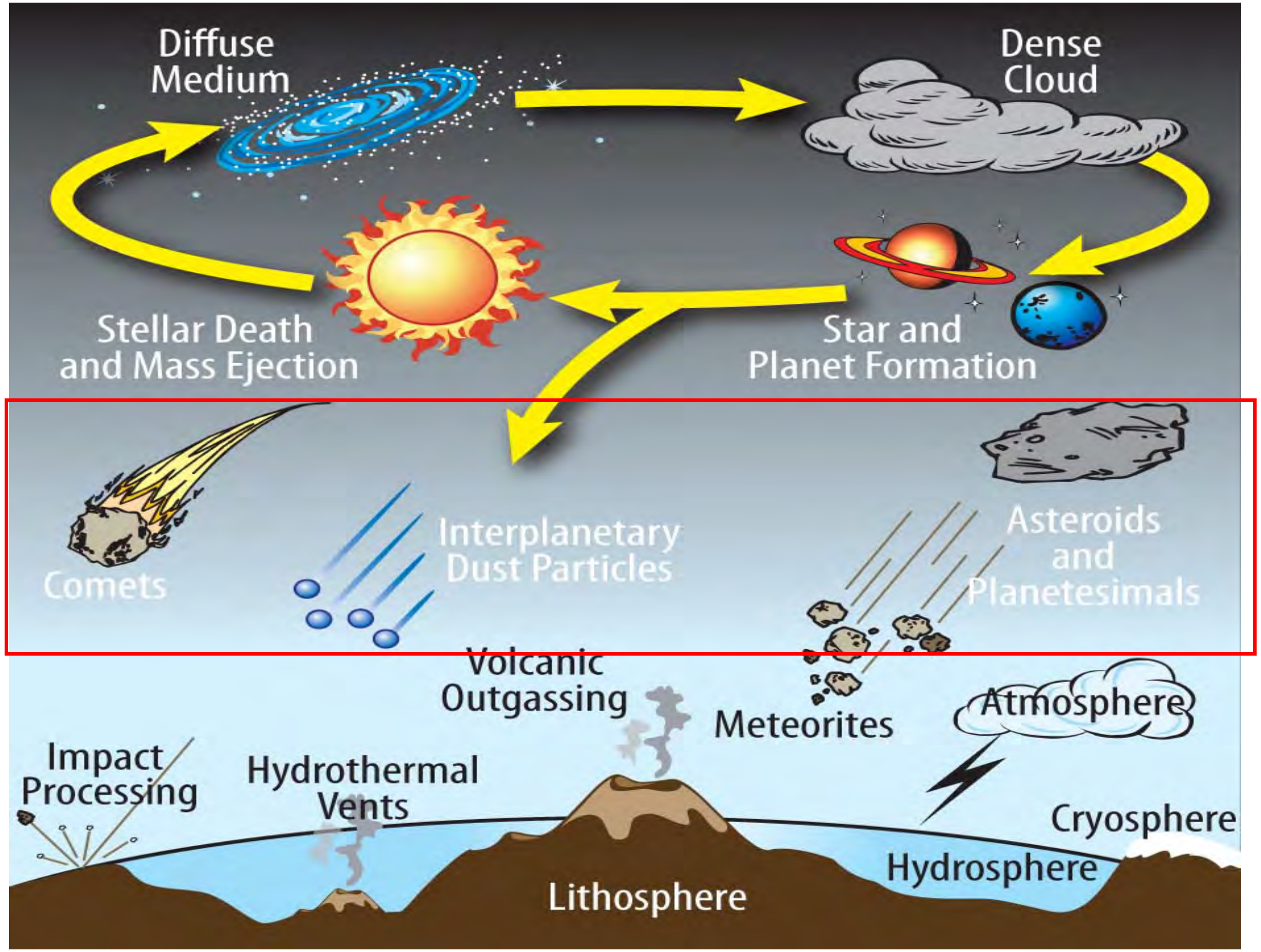

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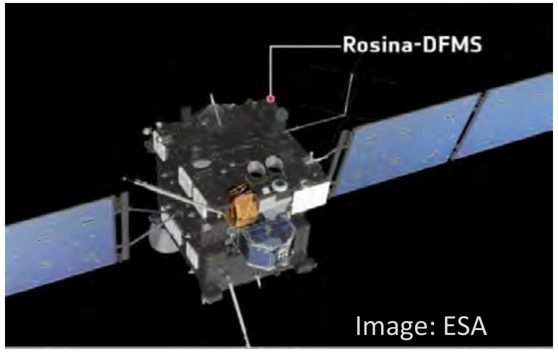
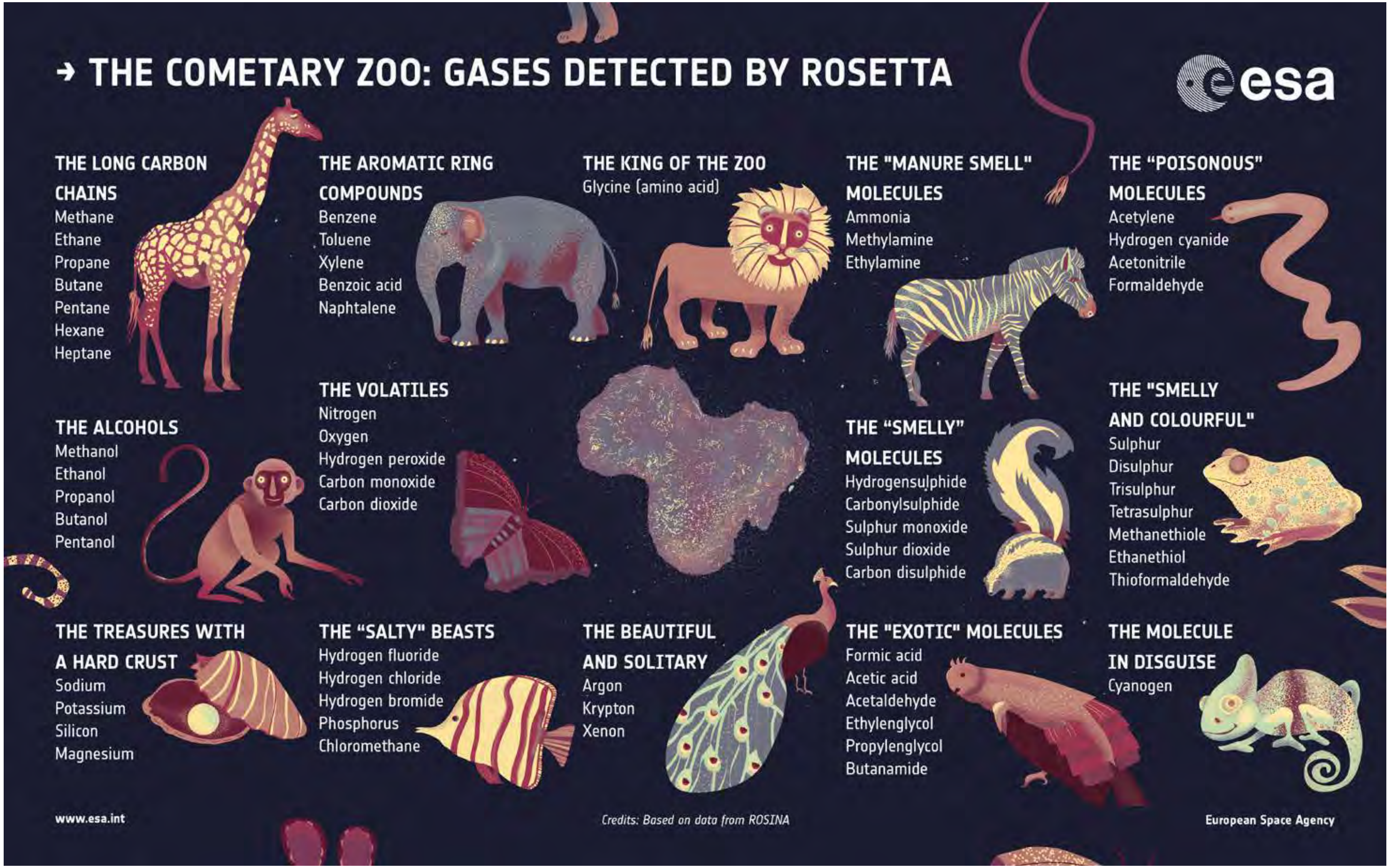
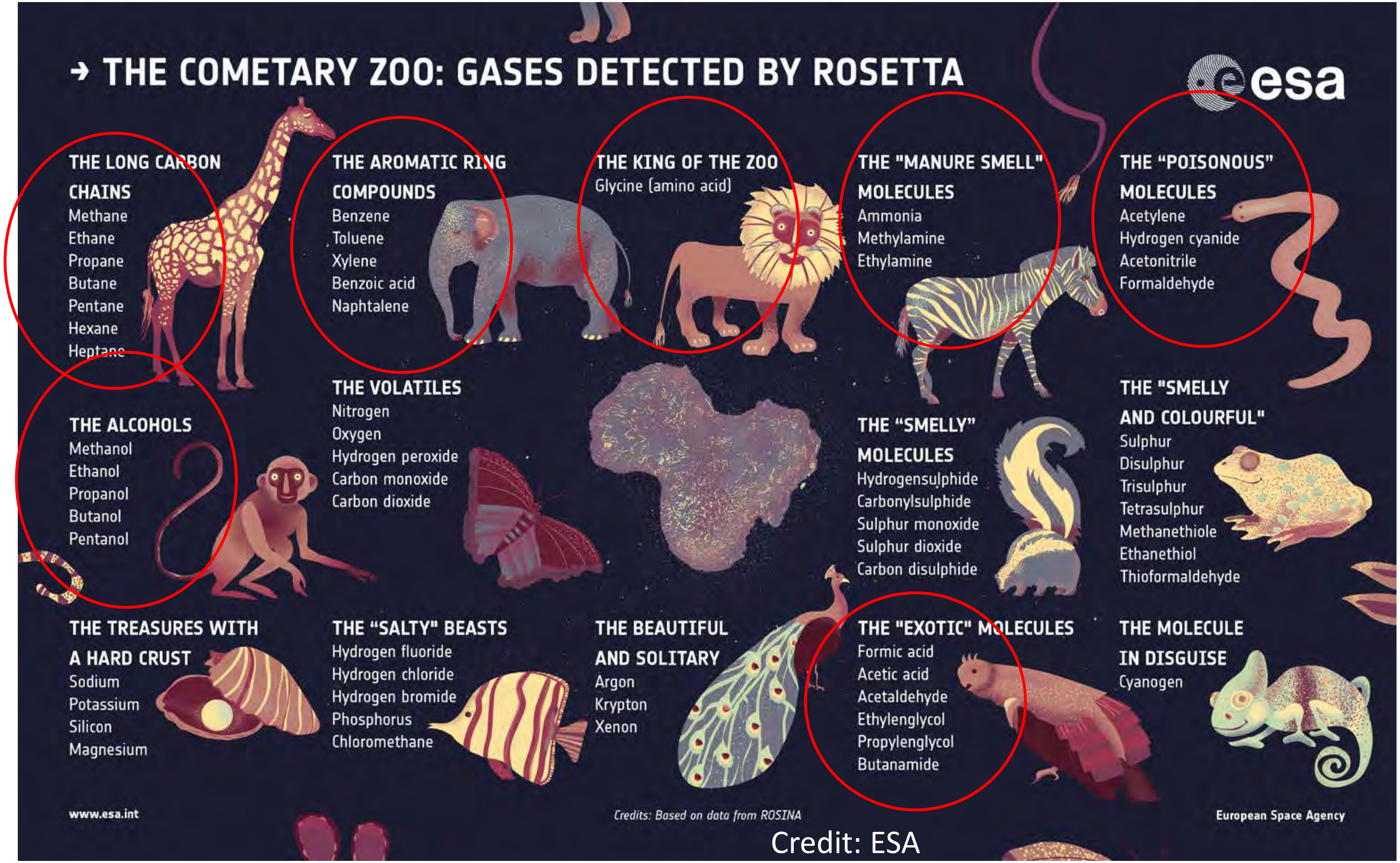
Rosetta Cometary Observations

The ROSINA mass spectrometer observed a wide variety of molecules at Comet 67P/Churyumov-Gerasimenko





Rosetta Cometary Observations: Organics



Credit: ESA

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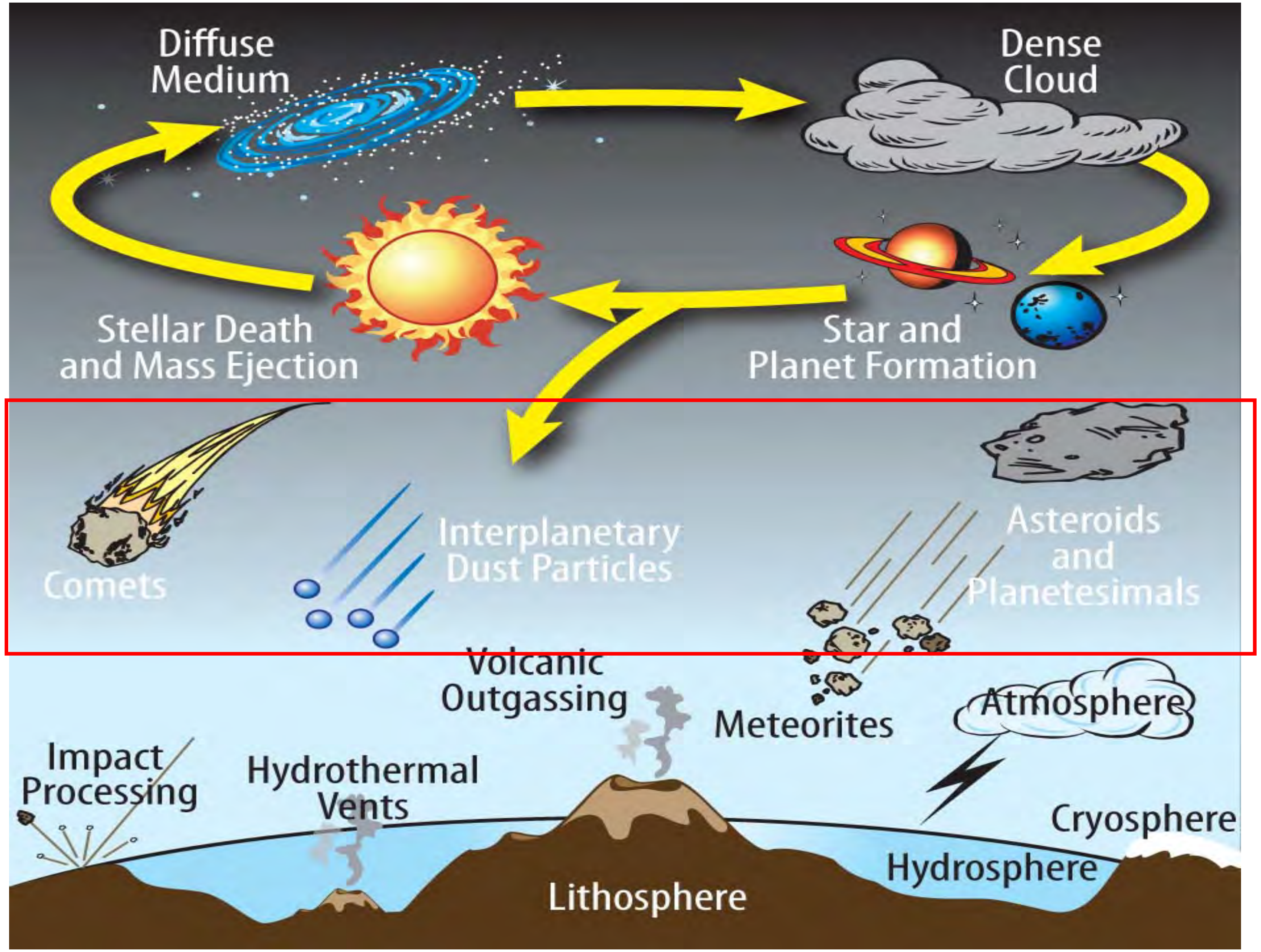

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Laboratory Analysis

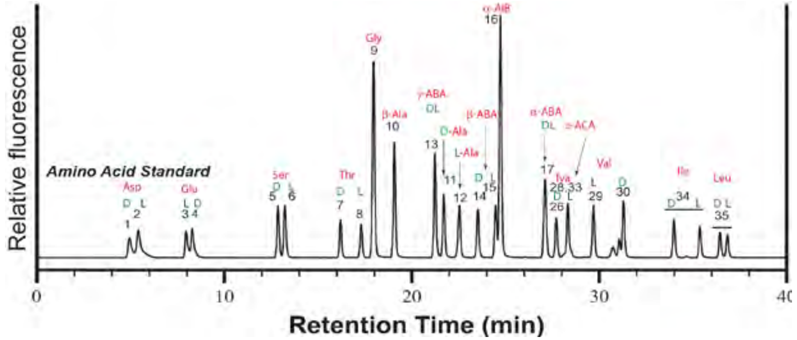
Crush Sample →

Solvent Extraction and Hydrolysis →

Desalting

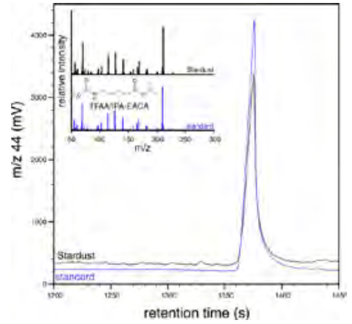
Derivatization of Purified Extract

Liquid chromatography with fluorescence detection and time-of-flight mass spectrometry →



Quantitation of Detected Compounds

Gas chromatography with mass spectrometry and isotope ratio mass spectrometry →



Compound-specific isotope ratios

Solar System Materials for Lab Analyses

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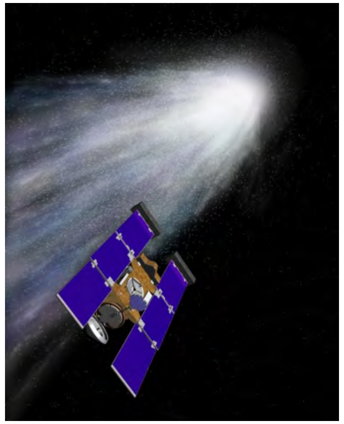
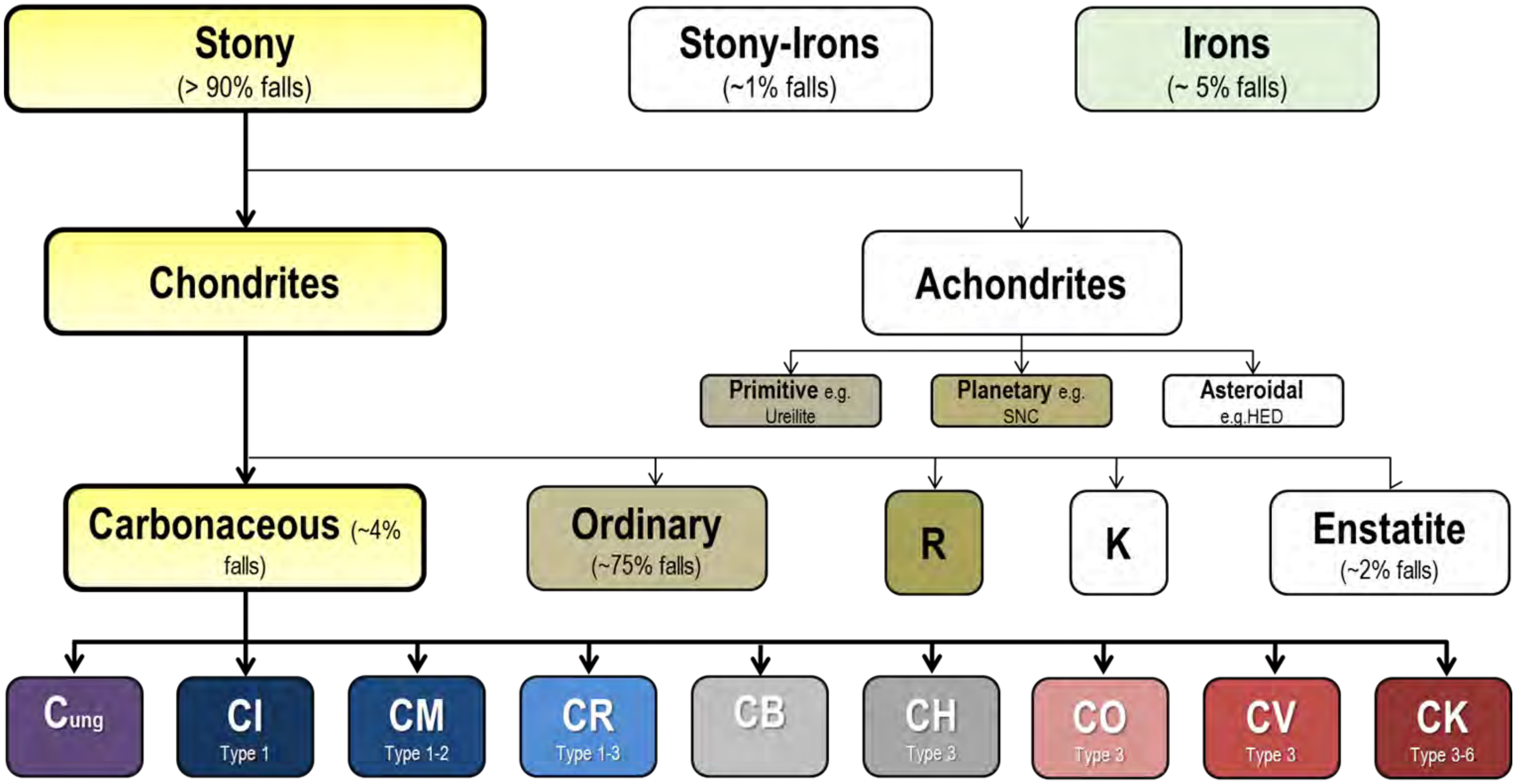


Meteorites: Sampling Different Parent Bodies



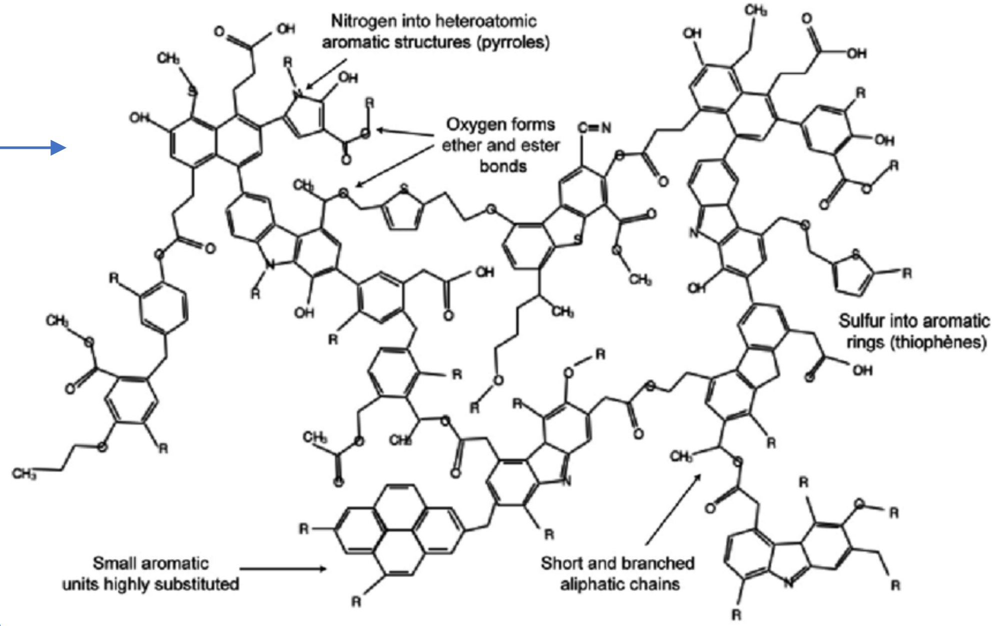
Cometary?

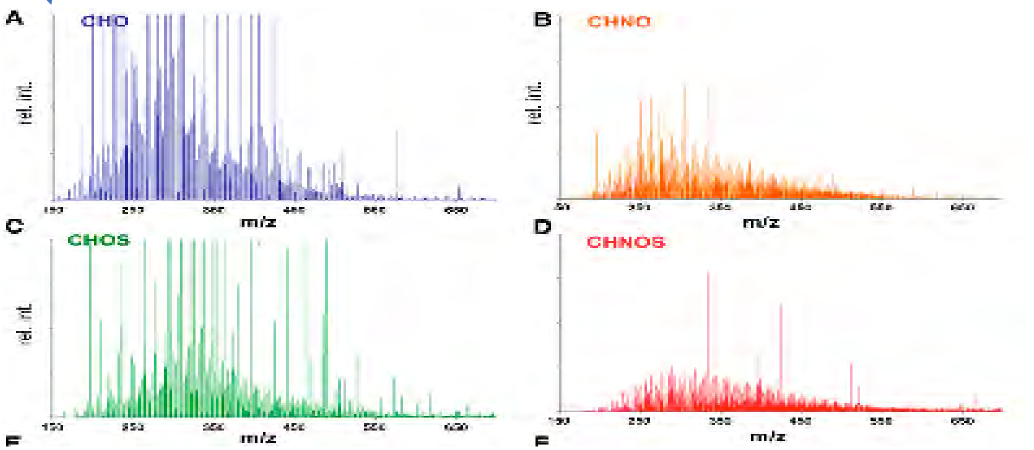
Murchison (CM Type 2) is Rich in Organics

Insoluble Organic Matter (IOM)	Abundance
Macromolecular material ($C_{100}H_{70}N_3O_{12}S_2$)	70-99% total organic C

Soluble Organic Matter (SOM)	Concentration (ppm)
Carboxylic acids	>300
Polar hydrocarbons	<120
Sulfonic acids	67
Amino acids (>90 named)	60
Dicarboxyimides	>50
Aliphatic hydrocarbons	>35
Dicarboxylic acids	>30
Polyols	30
Aromatic hydrocarbons	15-28
Hydroxy acids	15
Aldehydes and Ketones	>14
Amines	13
Alcohols	11
N-heterocycles	7
Phosphonic acids	2
Purines and pyrimidines	1

After *Meteorites and the Early Solar System II,* (2006) and *Primitive Meteorites and Asteroids (2018)*

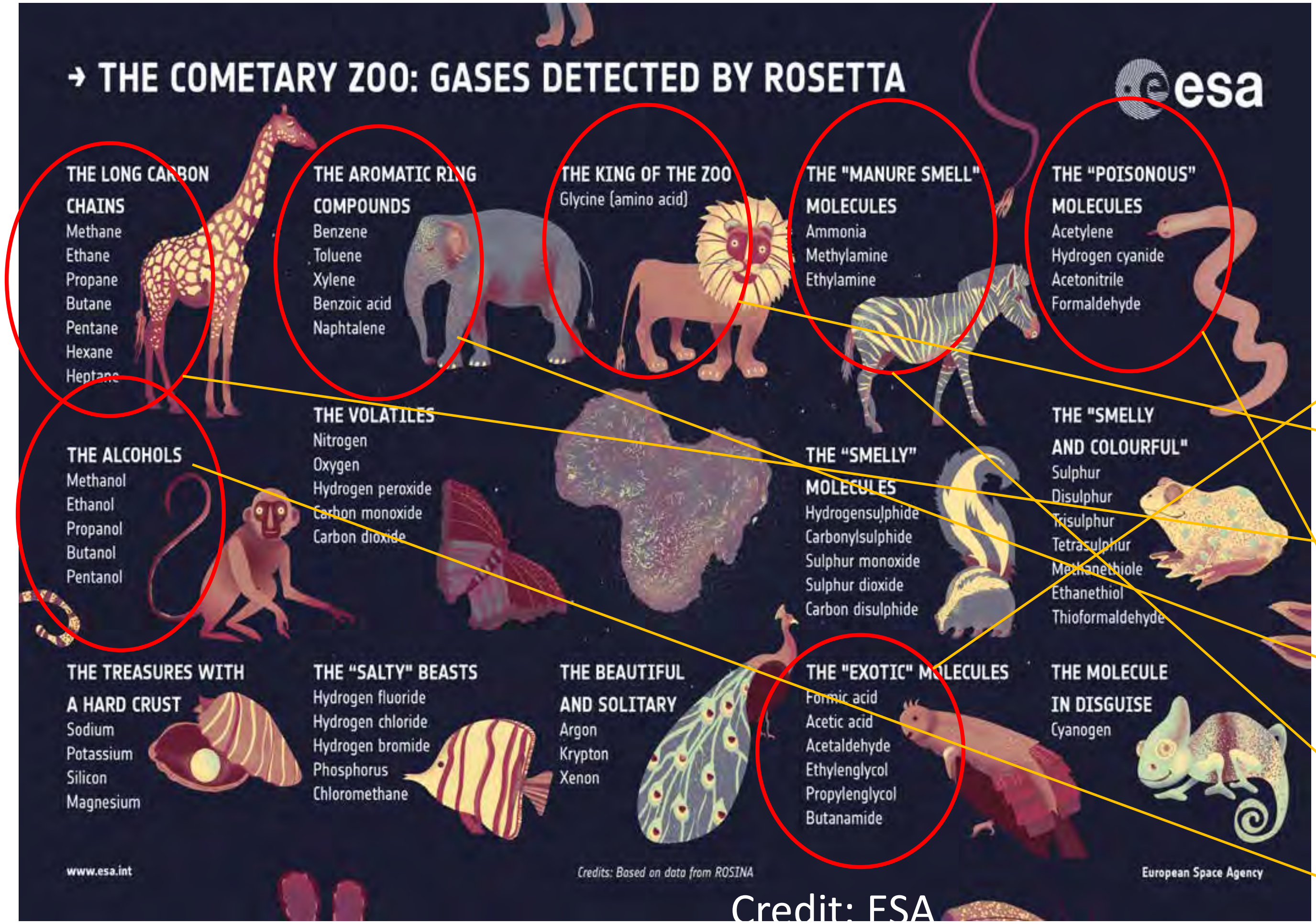




High resolution mass spectrometry analysis suggests millions of chemical structures

(Schmitt-Kopplin *et al.* 2010)

Rosetta Observations vs. Lab Measurements



Credit: ESA

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Amino Acids

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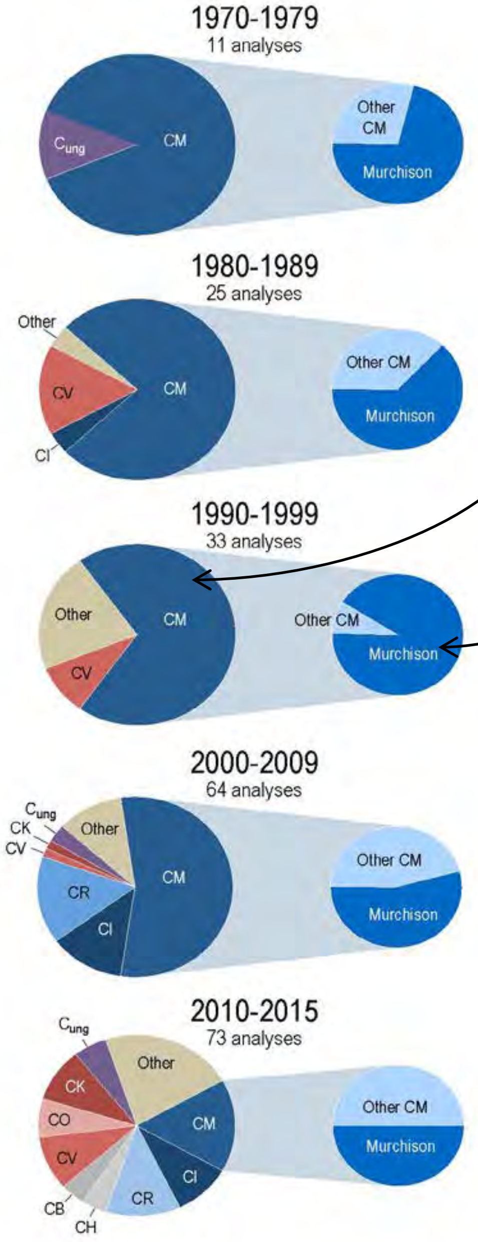
Amino acids (>90 named)	60

- **Amino acids** are of particular interest because they are relevant to life, often chiral, and comprise a constrained yet structurally diverse group
- **Glycine** is the simplest amino acid

Meteoritic Amino Acid Analyses



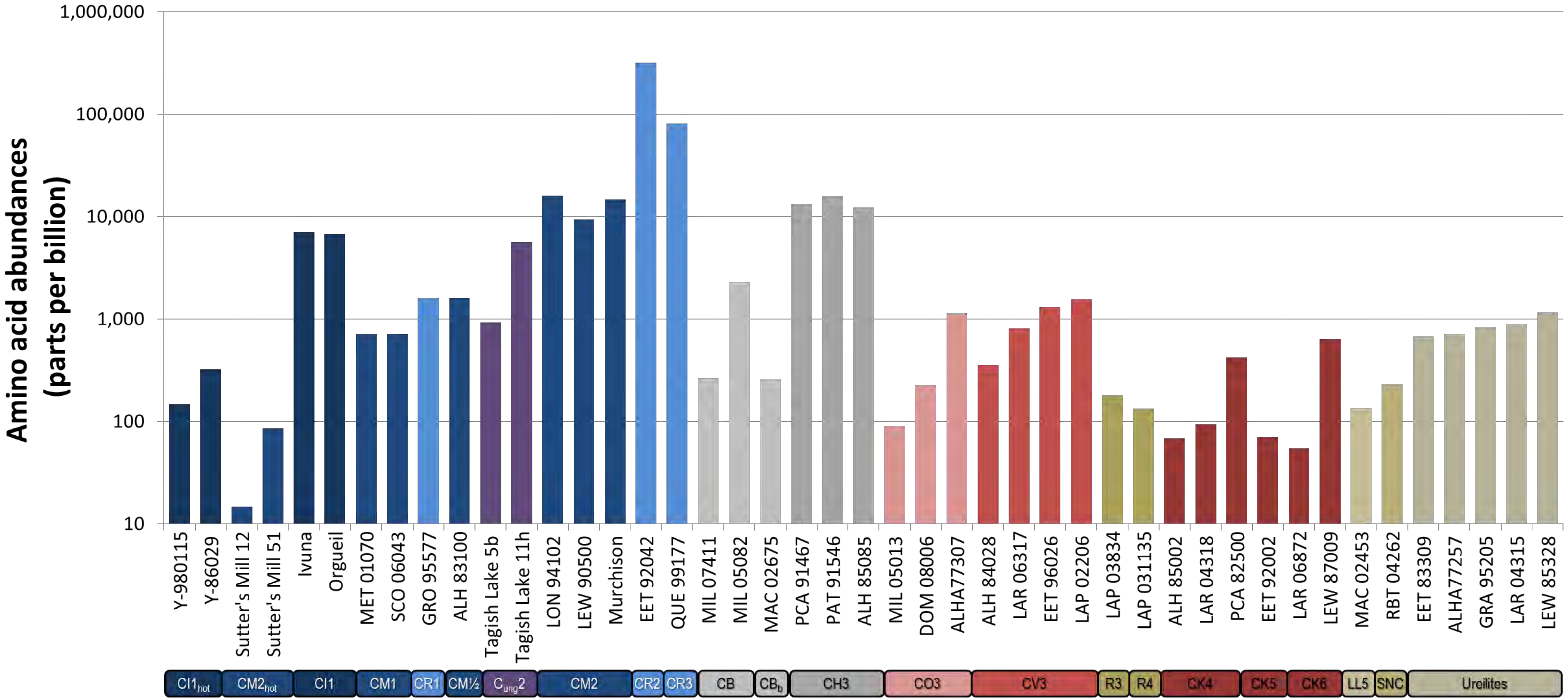
Publications with CM2 and especially Murchison amino acid data has dominated the literature until recently.

This CM2 carbonaceous chondrite is viewed as the archetype of organic-rich meteorites.

Murchison meteorite photo.
Drake Building, U. Arizona

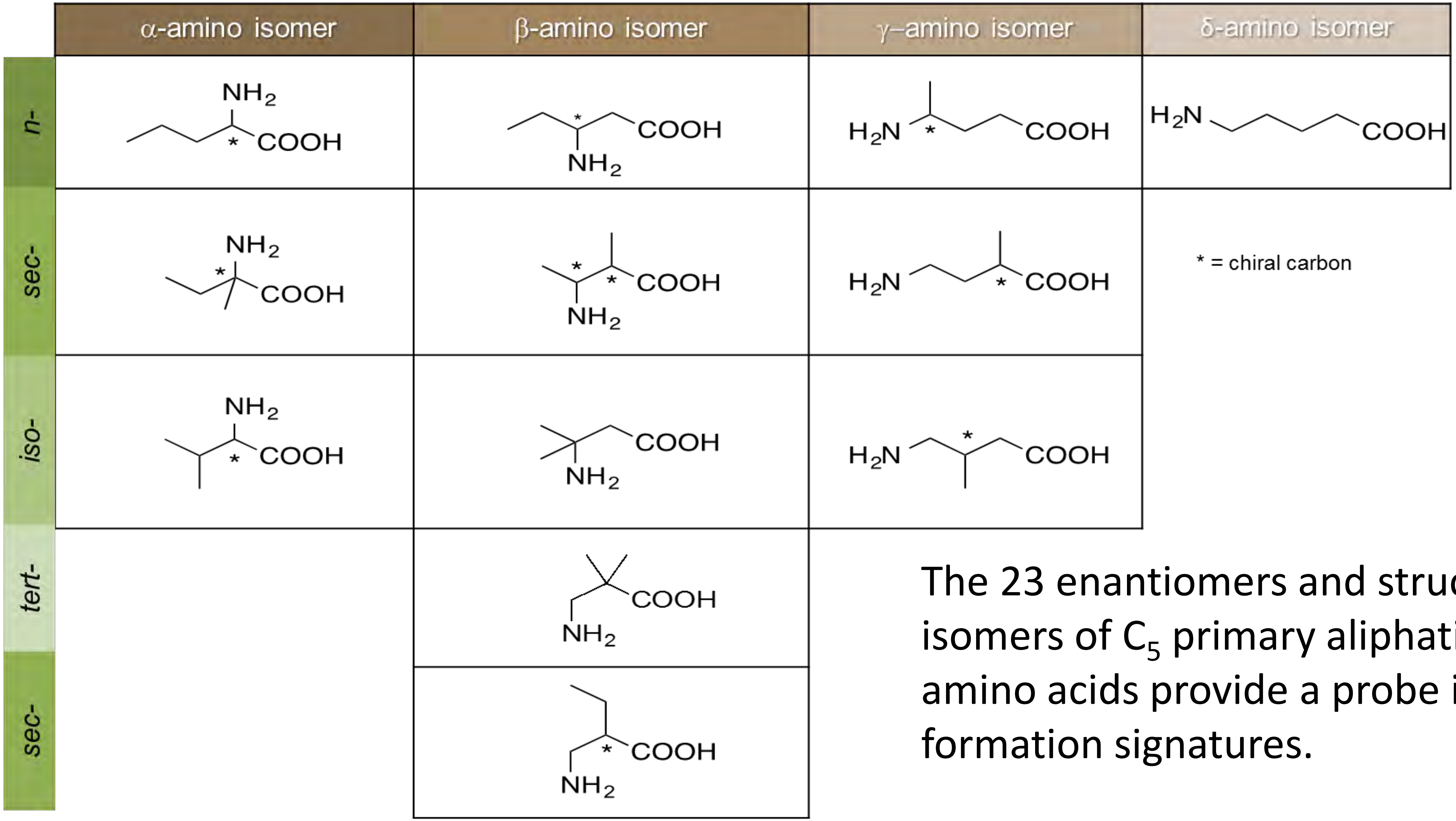
Elsila et al., (2016) *ACS Central Science* 2, 370-379.

Amino acid abundances vary by more than three orders of magnitude across meteorite groups



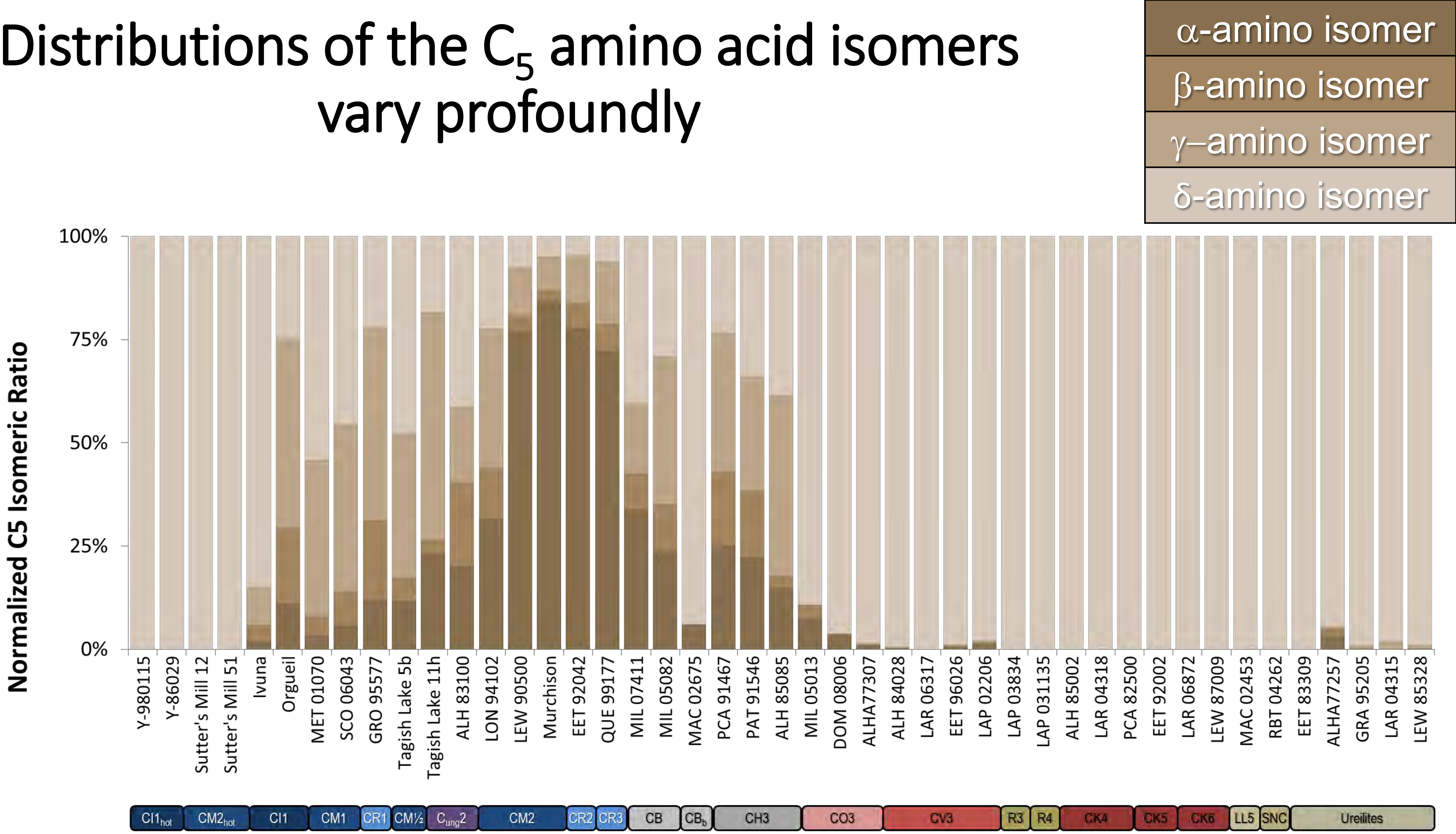
In all plots, meteorites are arranged roughly in order of petrographic high aqueous alteration on the left to high thermal alteration on the right

Amino Acid Structural Diversity

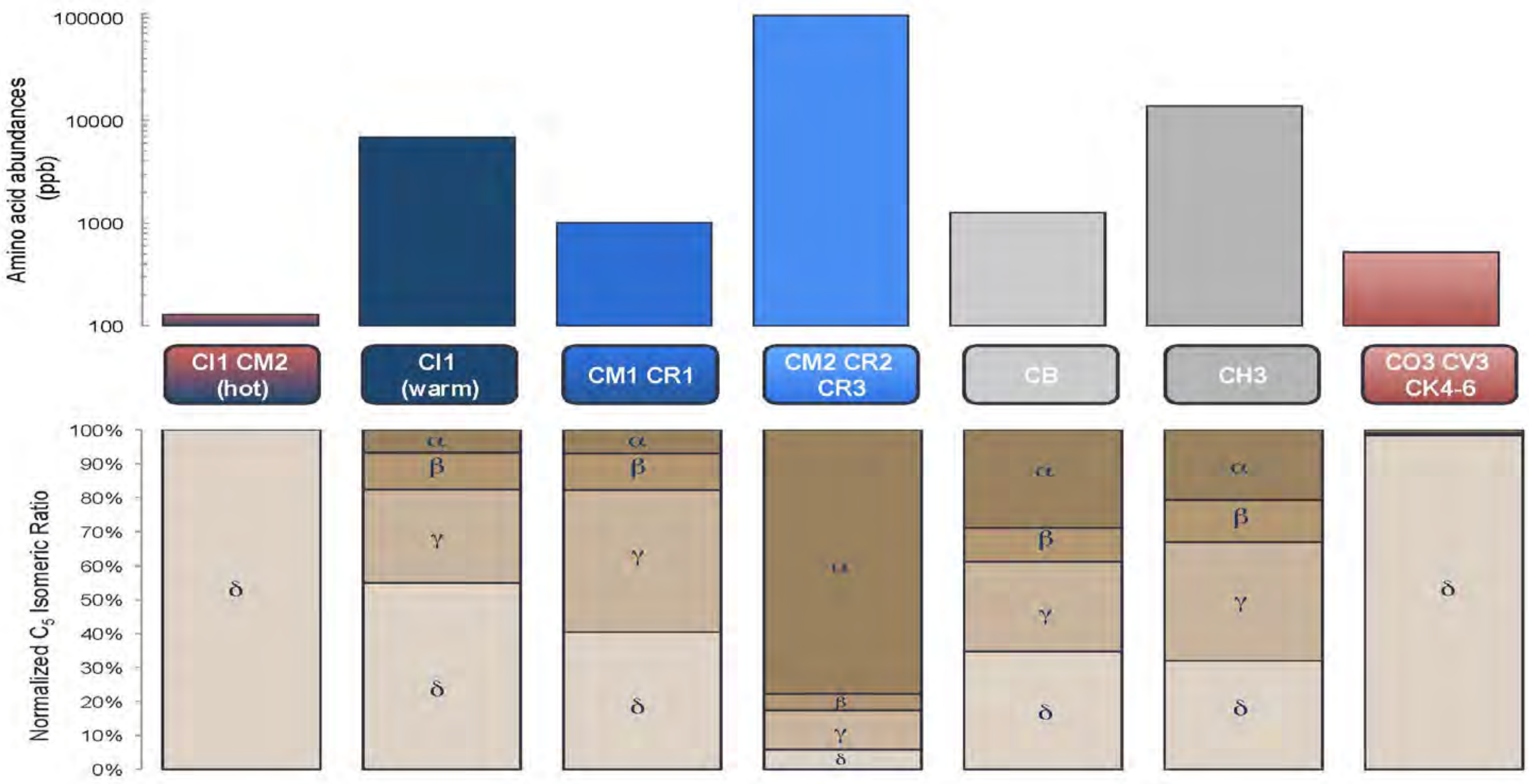


The 23 enantiomers and structural isomers of C_5 primary aliphatic amino acids provide a probe into formation signatures.

Distributions of the C_5 amino acid isomers vary profoundly



Meteoritic variations may reflect different formation pathways and histories

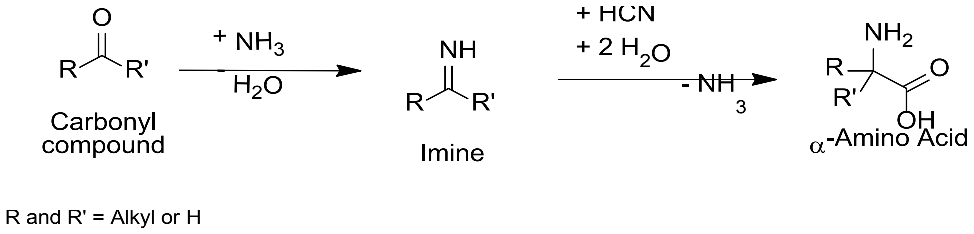


Elsila et al., (2016) *ACS Central Science* 2, 370-379.

Diversity of Formation Reactions Required

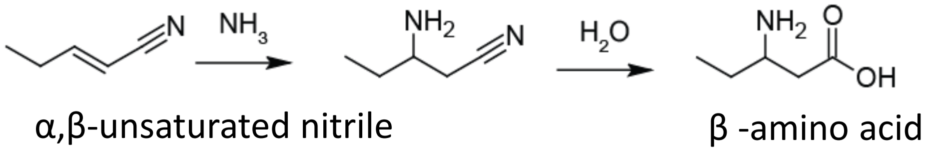
<u>α-amino acids:</u>

- Aqueous Strecker/cyanohydrin synthesis
- Presolar ice chemistry



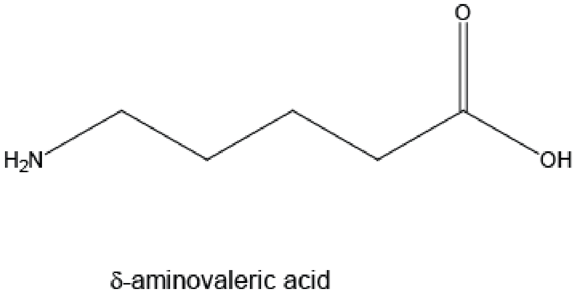
<u>β-amino acids:</u>

- Michael addition



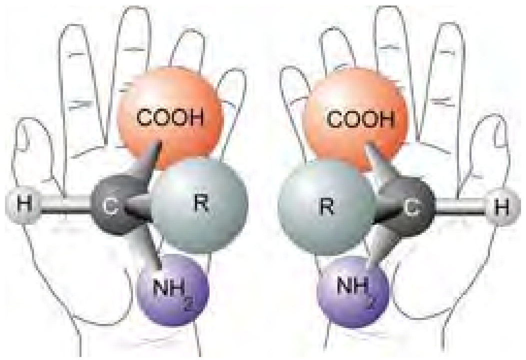
<u>Straight-chain, amino-terminal amino acids (*n*-ω-amino acids)</u>

- Fischer-Tropsch-Type (surface catalyzed) $CO + H_2 + N_2 \rightarrow$ amino acids

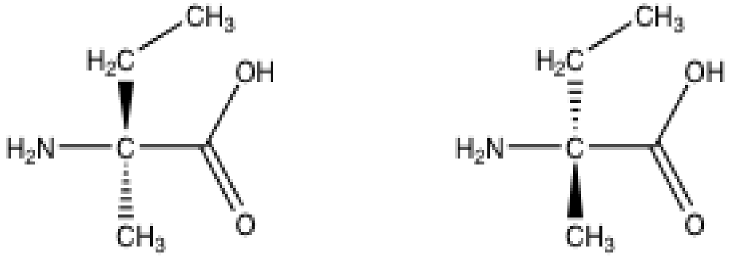


Preaccretion vs. Parent Body Alteration?

Amino Acid Chiral Excesses

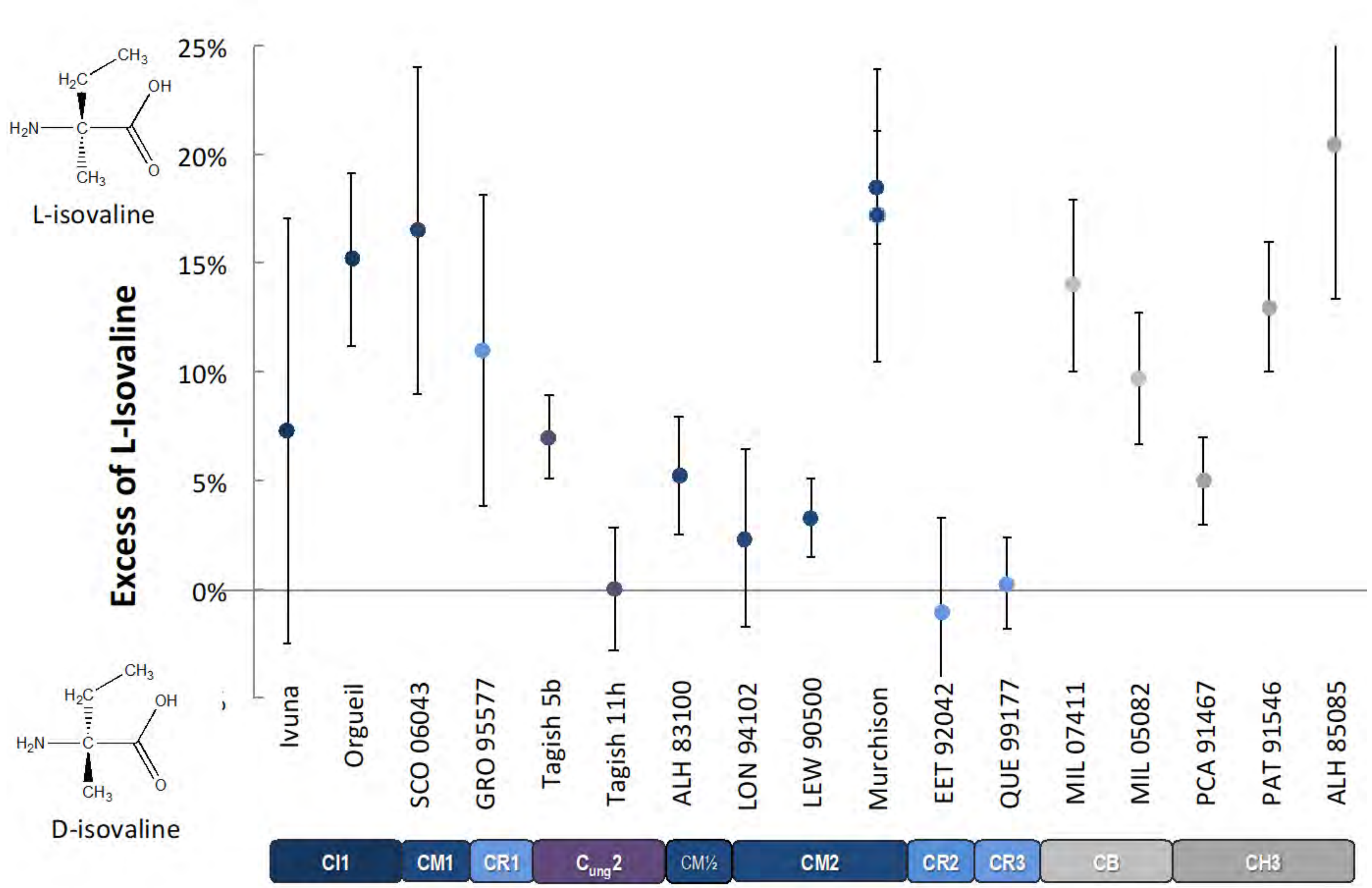


- Many amino acids are chiral, existing in nonsuperimposable mirror-image forms
- Abiotic chemistry should produce equal amounts of these two forms
- Biology on Earth uses primarily the “left-handed” (L) form
- Meteorite analyses show enantiomeric excesses in the amino acid isovaline



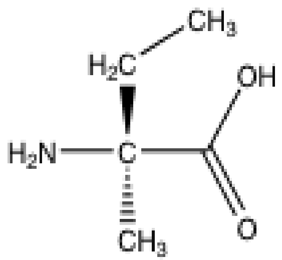
L-isovaline D-isovaline

Meteoritic Enantiomeric Excesses of Isovaline

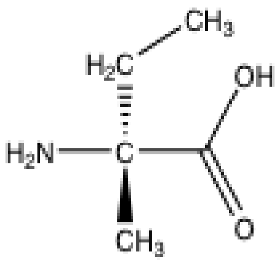


Amino Acid Chiral Excesses

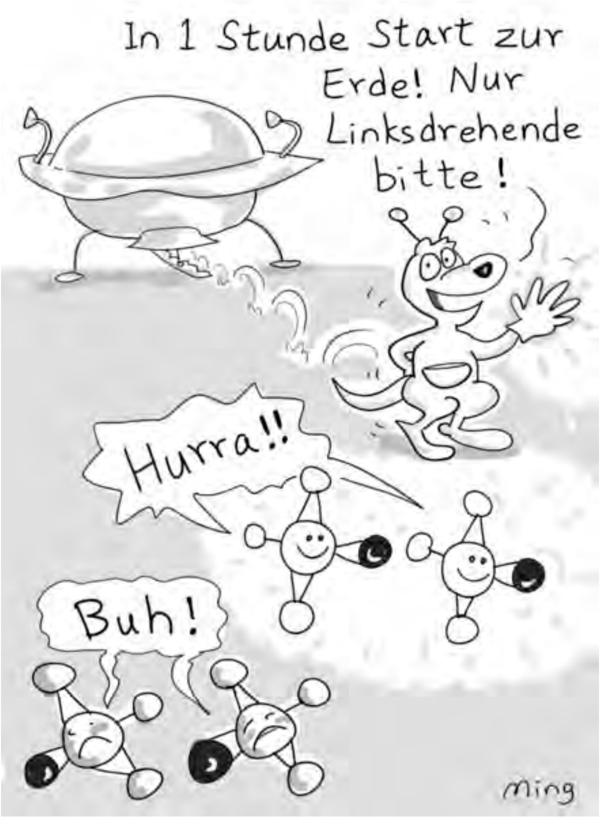
- Could the Earth or the entire Solar System have been biased towards L from an early stage?
- This may influence how we search for or interpret signs of life on other planets



L-isovaline



D-isovaline



Leaving for Earth in one hour! Only left handed, please!

http://www.neues-deutschland.de/artikel/146710.linker-start-fuers-leben.html

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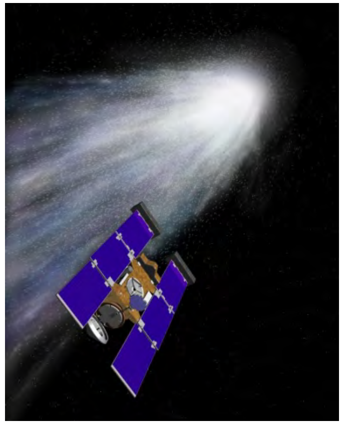


Sample Return Missions:
The gift that keeps on giving

Moon (1969-72, 1976)
- NASA Apollo 11, 12, 14, 15, 16, and 17
- Soviet Luna 16, 20, and 24

Solar wind (returned 2004)
- NASA Genesis

Comet tail (returned 2006)
- **NASA Stardust**

Stony Asteroid (returned 2010)
- JAXA Hayabusa

Carbonaceous Asteroid
- JAXA Hayabusa2 (launch 12/14, return 12/20)
- **NASA OSIRIS-REx** (launch 9/16, return 9/23)

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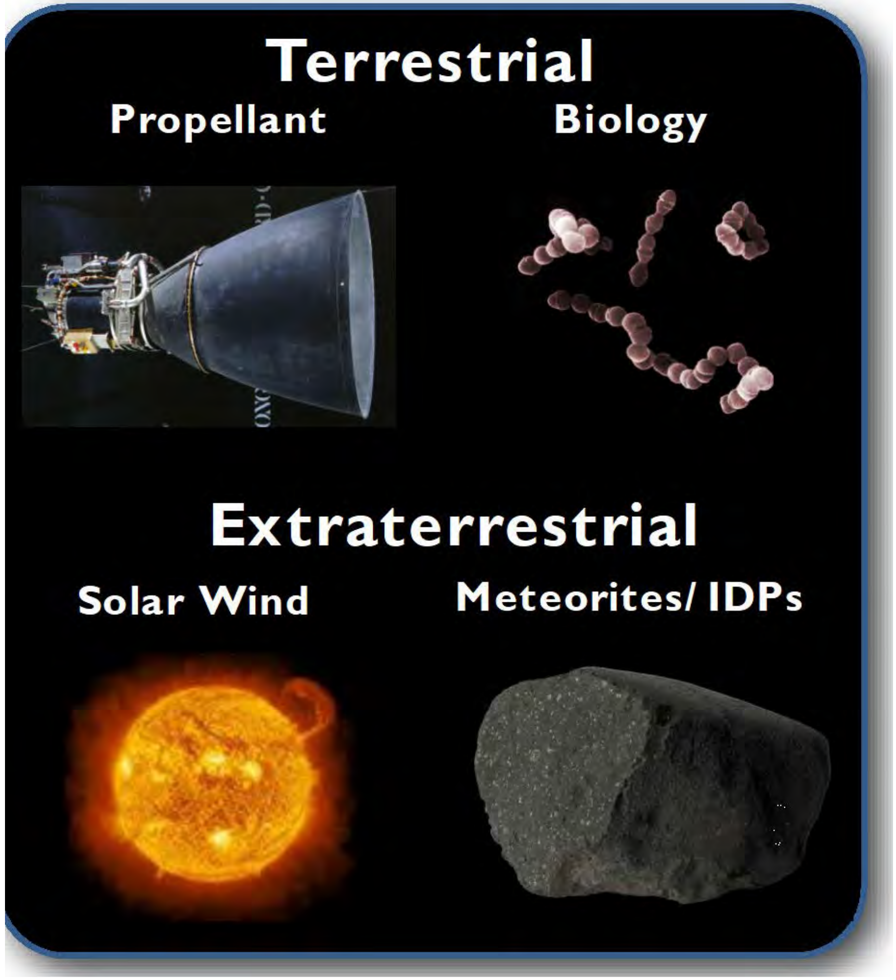
Lunar amino acids and potential sources

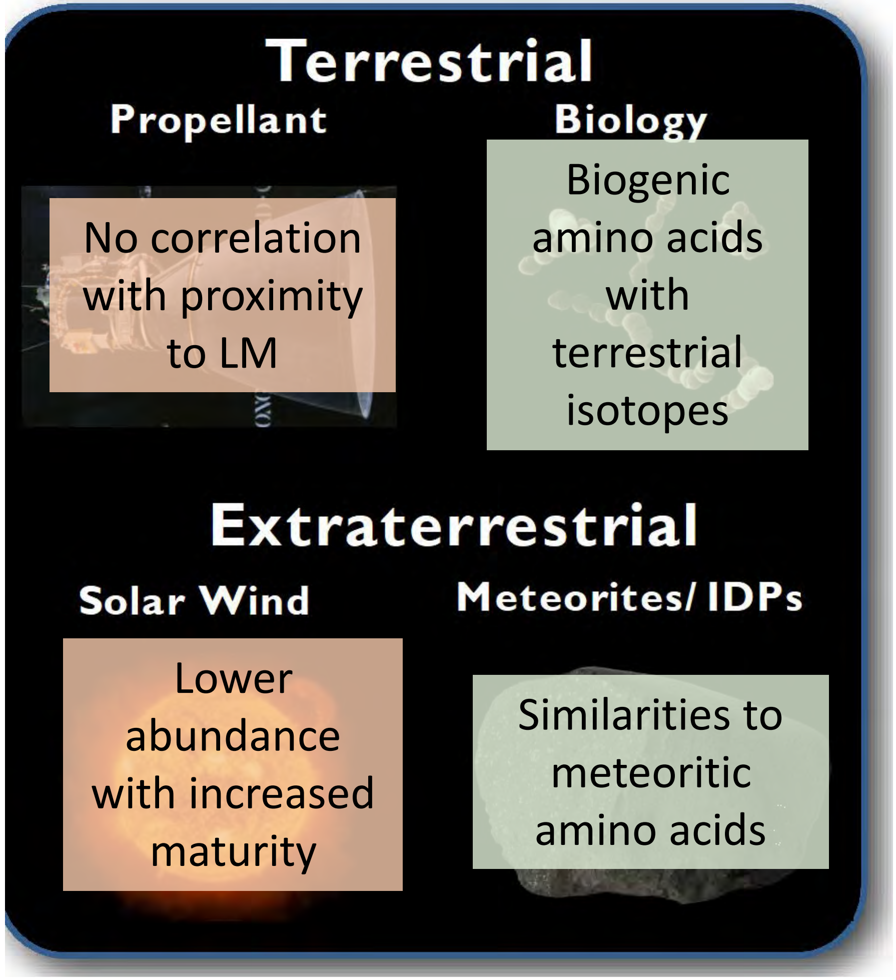
- Amino acids were detected in Apollo samples during 1970s, but no consensus on their origins
- Four potential sources
- Distinguishable by:
  - structural distribution
  - variations between samples
  - isotopic signature

- **Re-examination possible because of sample return**



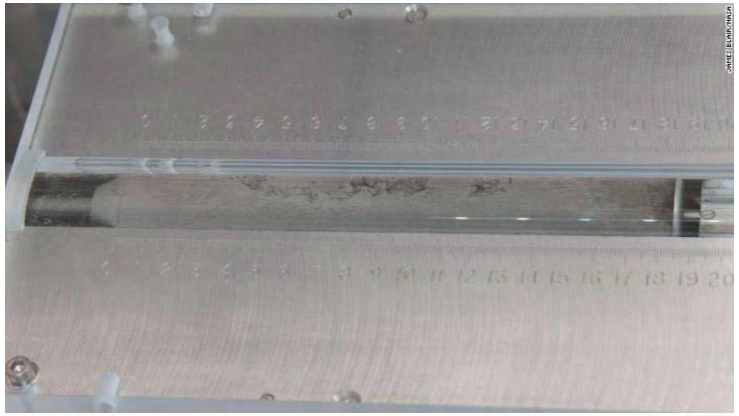
Lunar amino acids and potential sources

- Re-analysis of Apollo 16 and 17 samples
  - No correlation with location
  - Least mature samples had highest abundances
  - Majority of amino acids came from bound precursors, consistent with biology; some samples consistent with meteoritic bound abundances
  - Measurable carbon isotopes in terrestrial range
  - Non-proteinogenic amino acids observed
- Conclusions: amino acids detected in lunar samples primarily from terrestrial contamination, with some contribution possible from meteoritic infall



Elsila et al. (2016) *Geochim. Cosmochim. Acta* **172**, 357-369 *linking generations of lunar explorers from Apollo to Artemis*

Apollo Next Generation Sample Analysis (ANGSA)



- Previously unexamined Apollo samples that have been specially curated are being opened and studied:
  - Apollo 17 double drive tube sample, with the bottom half sealed under lunar vacuum
  - Apollo 17 samples placed in freezer within 1 month of arrival
  - Apollo 15 samples stored under helium
- Nine teams with over 50 scientists and engineers (including my lab) are studying these samples
- Stay tuned for results from our analysis of volatile organic compounds…

https://www.lpi.usra.edu/ANGSA/

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Cometary Glycine

- Before Rosetta, Stardust analyses were first detection of a cometary amino acid
- Cometary particles collected by Stardust are too small for amino acid identification by existing laboratory methods
- Bulk comet-exposed material from the collector was analyzed instead
- Aerogel witness coupon used to understand background amino acid signal

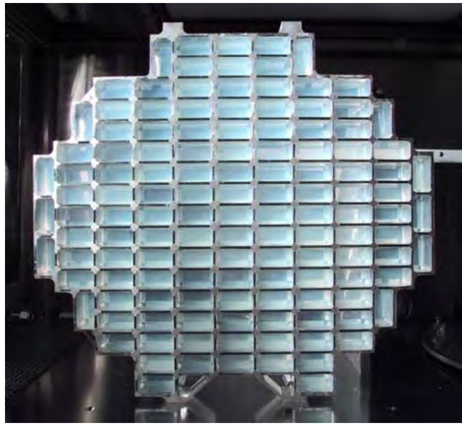
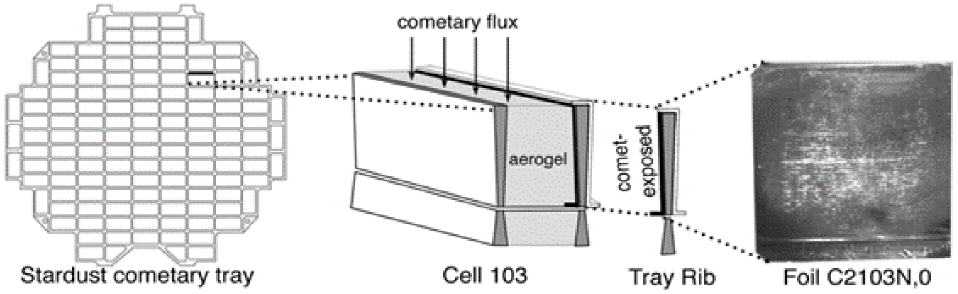
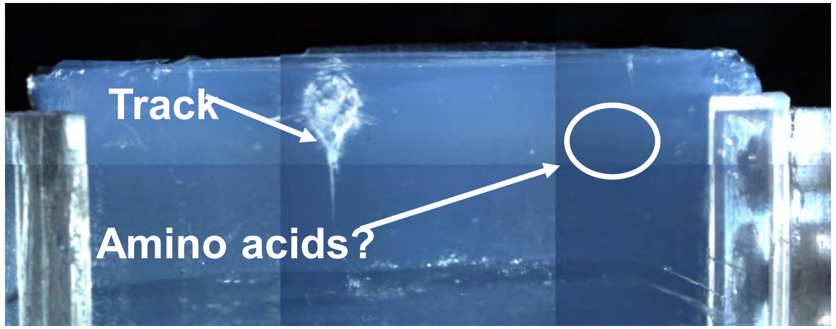
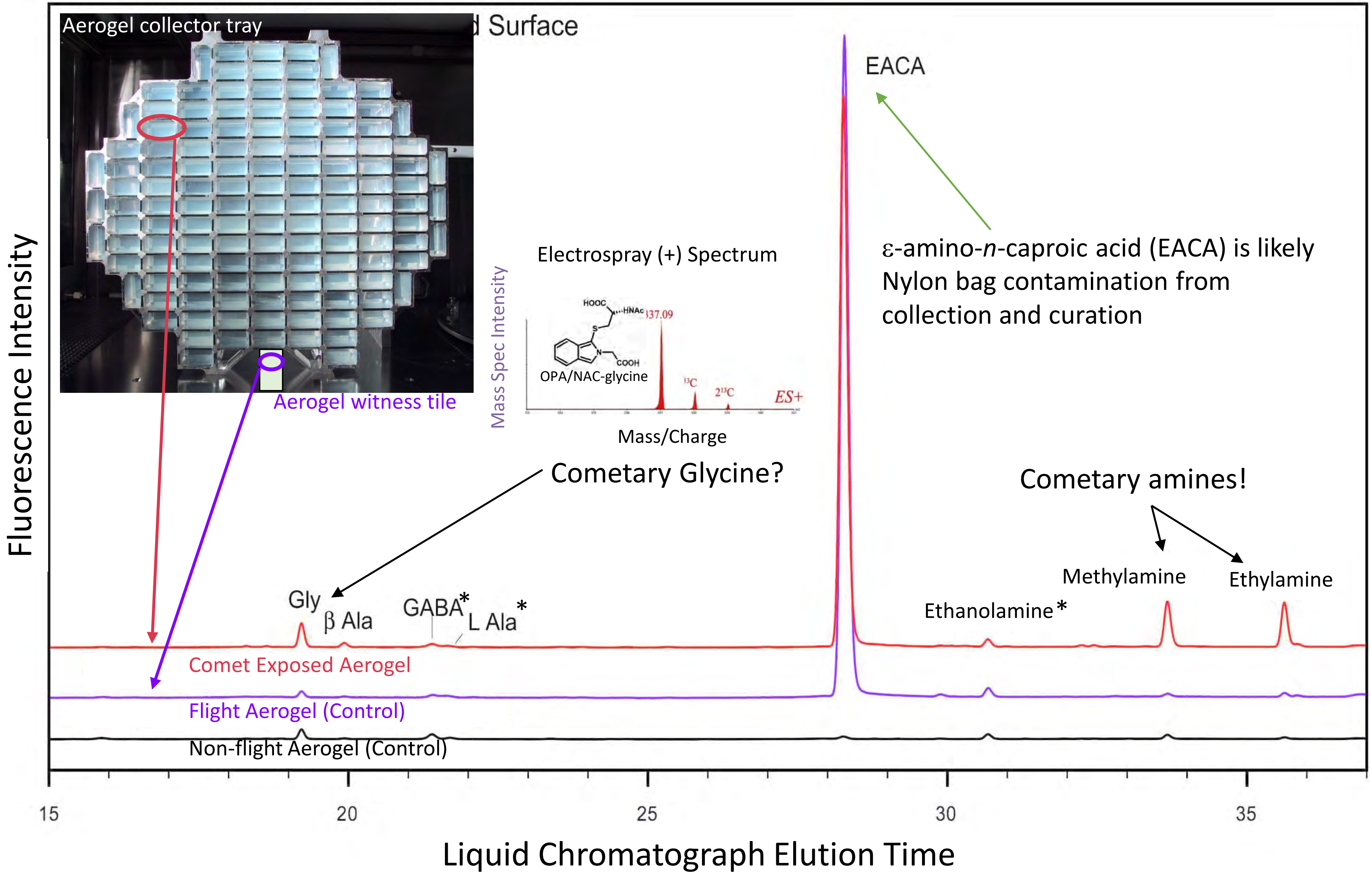


Image from psrd.Hawaii.*edu*





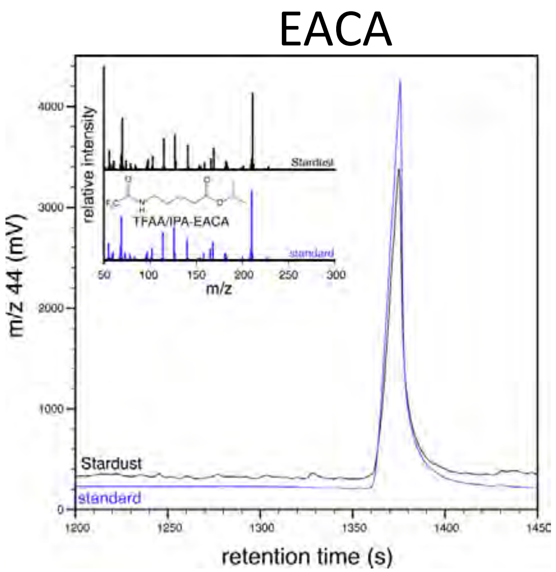
Amines in Stardust Aerogel



* Aerogel contamination

Sandford et al., 2006, Glavin et al., 2008

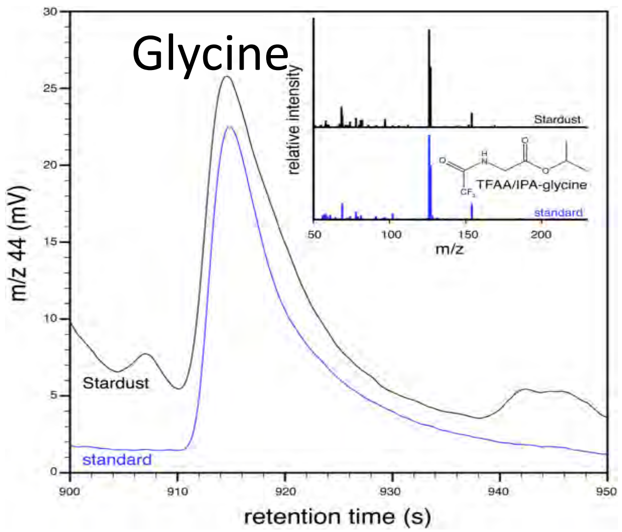
Stardust Foil Compound-Specific Isotopic Results



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‰

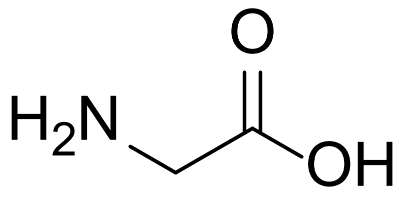
Terrestrial carbon ranges from -6 to -40 ‰

Glycine is extraterrestrial

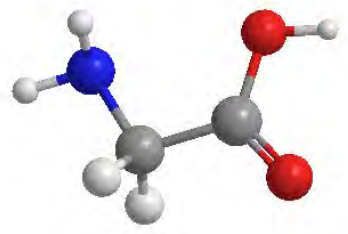
Elsila, et al. (2009) *Meteorit. Planet. Sci.* **44**, 1323-1330.

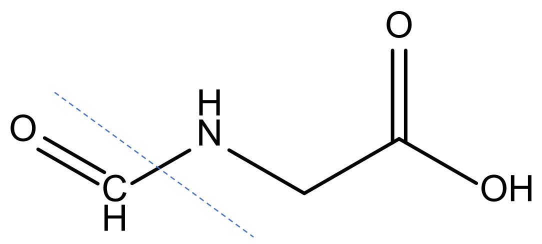
Stardust Glycine Sources?

- Detected glycine contains extraterrestrial carbon
- Possibilities:
  - “Free” glycine molecules from cometary gas (as seen by Rosetta)
  - “Bound” glycine liberated during acid hydrolysis
  - Precursors (e.g. HCN polymer) that release glycine upon hydrolysis

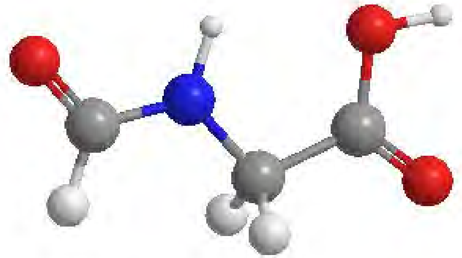


Free glycine

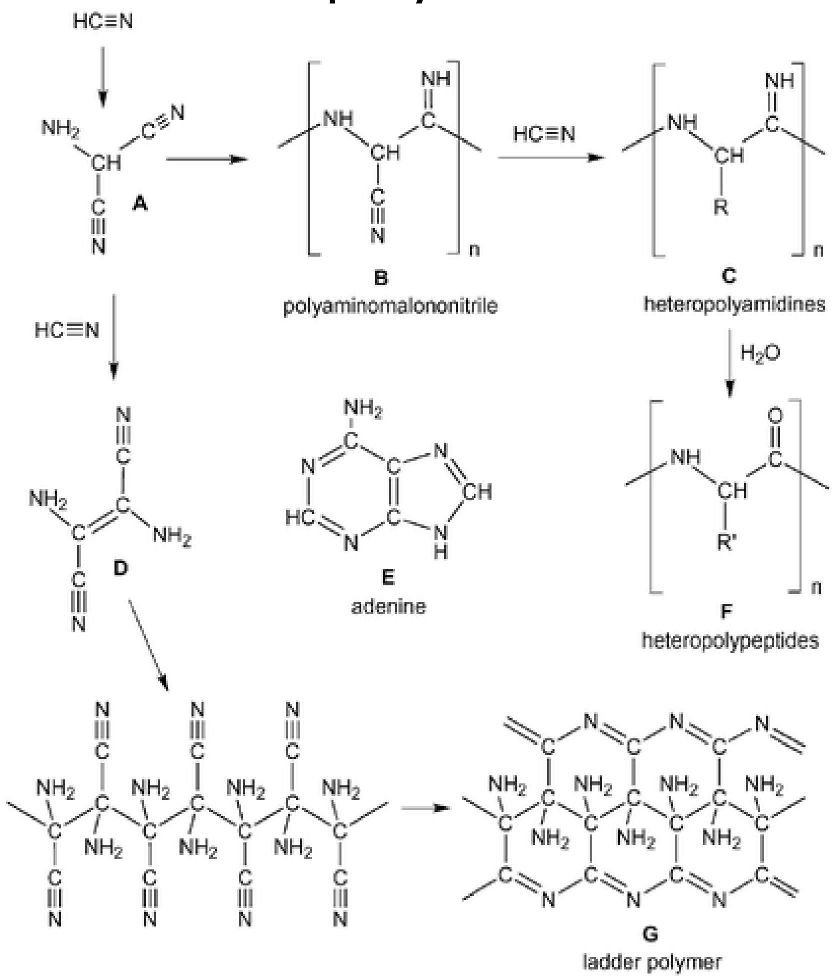




Bound glycine



HCN polymer



From Matthews and Minard, 2006

Sample Return Missions:
The gift that keeps on giving

Moon (1969-72, 1976)
- NASA Apollo 11, 12, 14, 15, 16, and 17
- Soviet Luna 16, 20, and 24

Solar wind (returned 2004)
- NASA Genesis

Comet tail (returned 2006)
- **NASA Stardust**

Stony Asteroid (returned 2010)
- JAXA Hayabusa

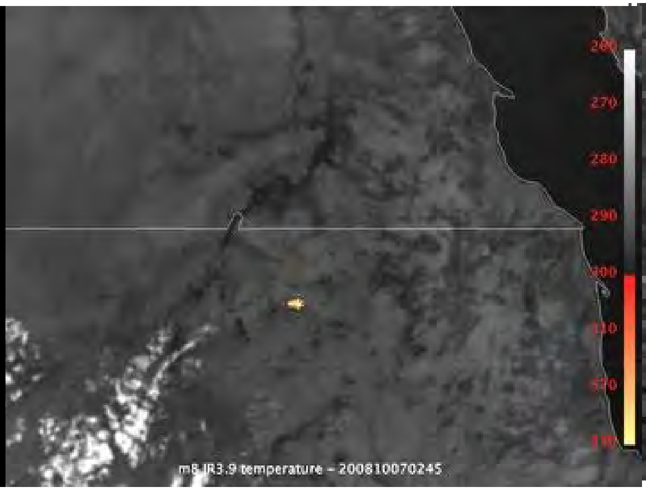
Carbonaceous Asteroid
- JAXA Hayabusa2 (launch 12/14, return 12/20)
- **NASA OSIRIS-REx** (launch 9/16, return 9/23)

The Few Parent Body-Meteorite Connections

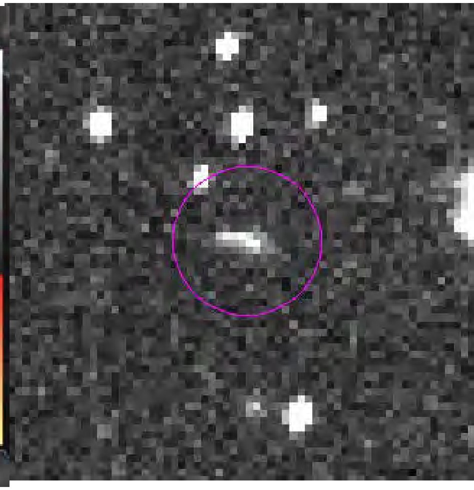
Mars
Numerous (SNC)

Moon
Numerous

Asteroid Vesta
Numerous (HED)



Asteroid 2008 TC3
Almahata Sitta, Sudan



Asteroid 2018 LA
Unnamed Botswana

Asteroid sample return missions provide pristine samples with context

OSIRIS-REx

Origins

Return and analyze a sample of pristine carbonaceous asteroid regolith

Spectral Interpretation

Provide ground truth for telescopic data of the entire asteroid population

Resource Identification

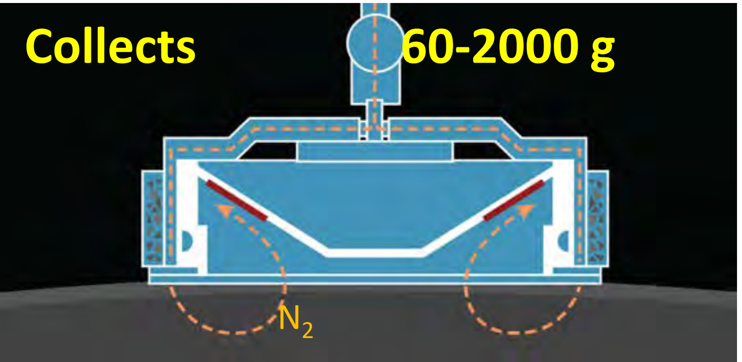
Map the chemistry and mineralogy of a primitive carbonaceous asteroid

Security

Measure the Yarkovsky effect on a potentially hazardous asteroid

Regolith Explorer

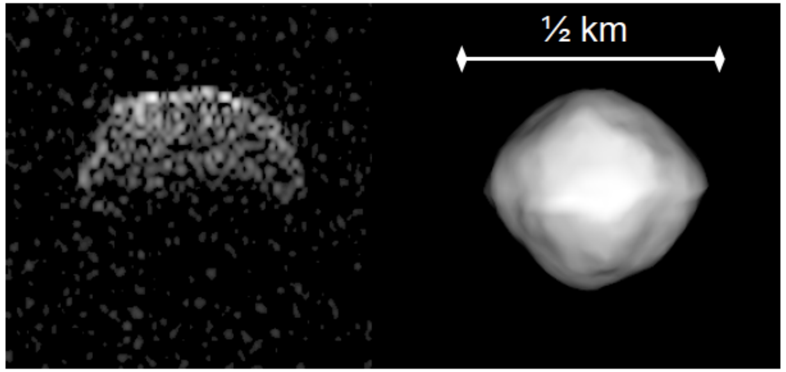
Document the regolith at the sampling site at scales down to the sub-cm

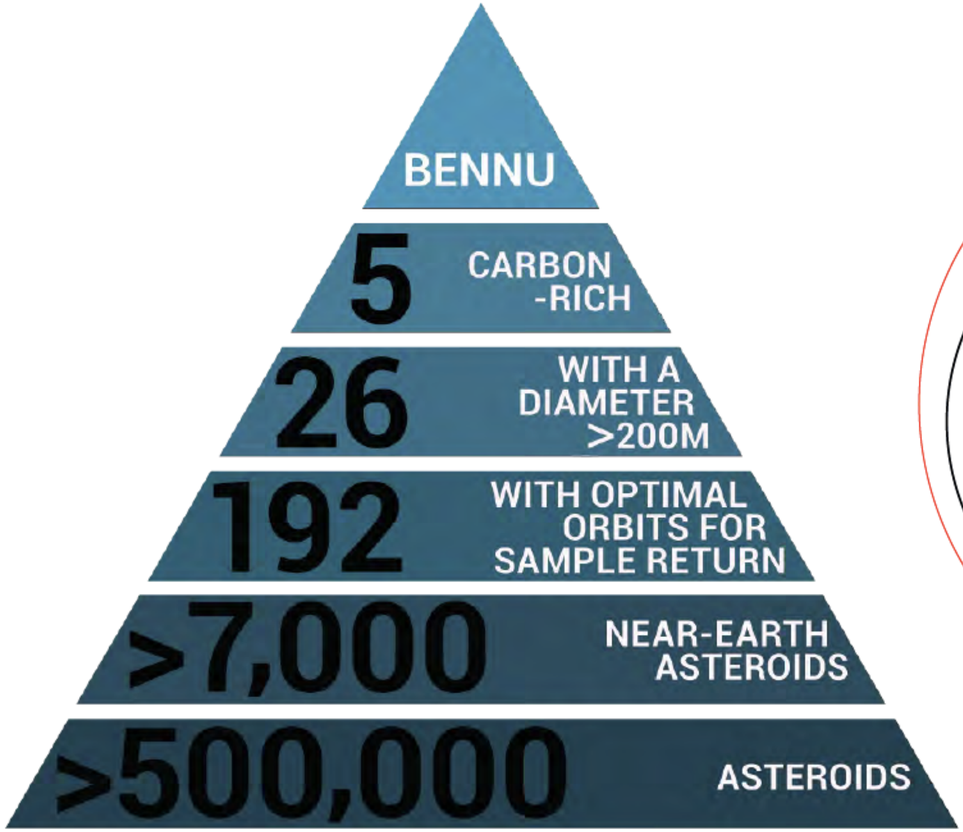


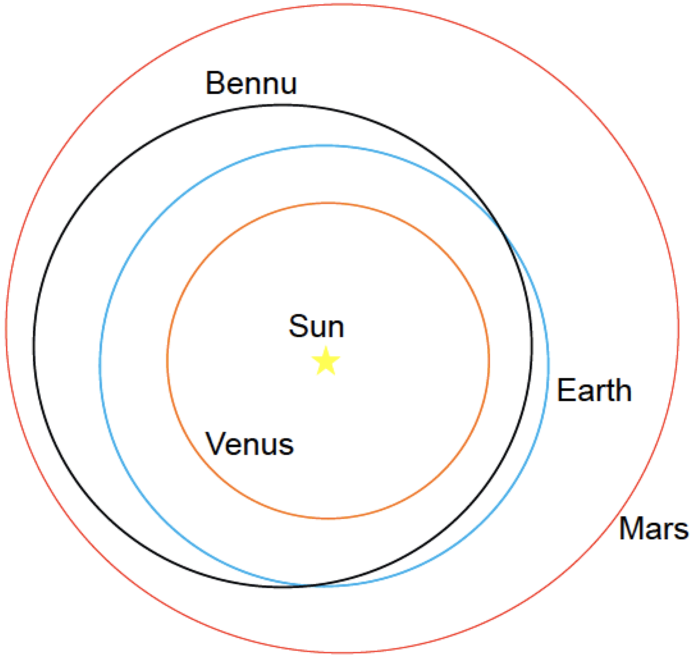
Overview of the OSIRIS-REx Mission

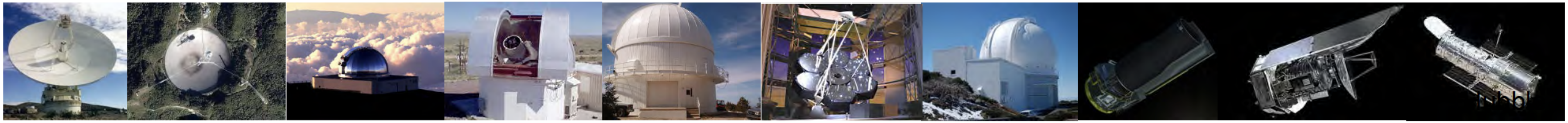
- ✓ 2004 – Initial concept
- ✓ 2011 – May 25: Mission Selection
- ✓ 2013 – June 1: Mission Confirmation
- ✓ 2014 – April 10: Complete Critical Design Review
- ✓ 2016 – September 8: Launch
- ❖ 2018 – 2021: Bennu encounter
  - ✓ 2018 – August: Approach Phase – Astronomical properties and environment
  - ✓ 2018 – December: Survey Phase – Bulk properties, shape and spectroscopy
  - ✓ 2019 – January: Orbital Phase – Topography, gravity, and preliminary site characterization
  - ✓ 2019 – September: Recon Phase – Detailed sample-site characterization
  - ✓ 2019 – December: Sampling site selection
  - o 2020 - Rehearsal Phase – Rehearse sampling maneuvers
  - o 2020– August: **Collect 60-2000 grams** of asteroid regolith
    - o (schedule and s/c allows for 2 additional attempts)
  - o 2021 – March: Leave vicinity of asteroid
- o 2023 – September 24: **Return Sample to Earth**
- o 2025 – September 30: End of Sample Analysis and End of Mission

Bennu is Well Characterized





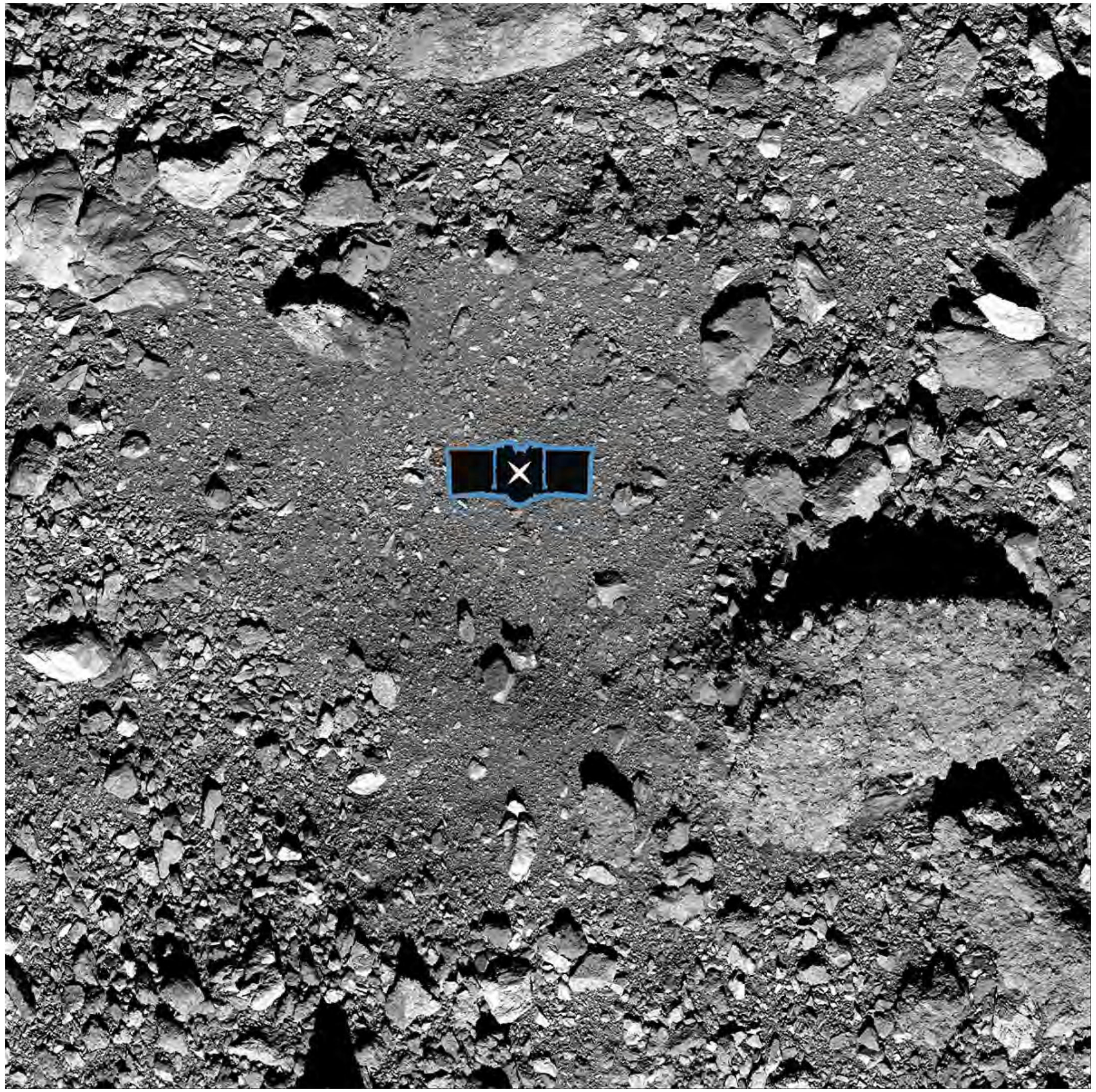




Goldstone Arecibo IRTF LINEAR Kuiper Magellan WHT Spitzer Herschel Hubble

OSIRIS-Rex Sampling Site: Nightingale

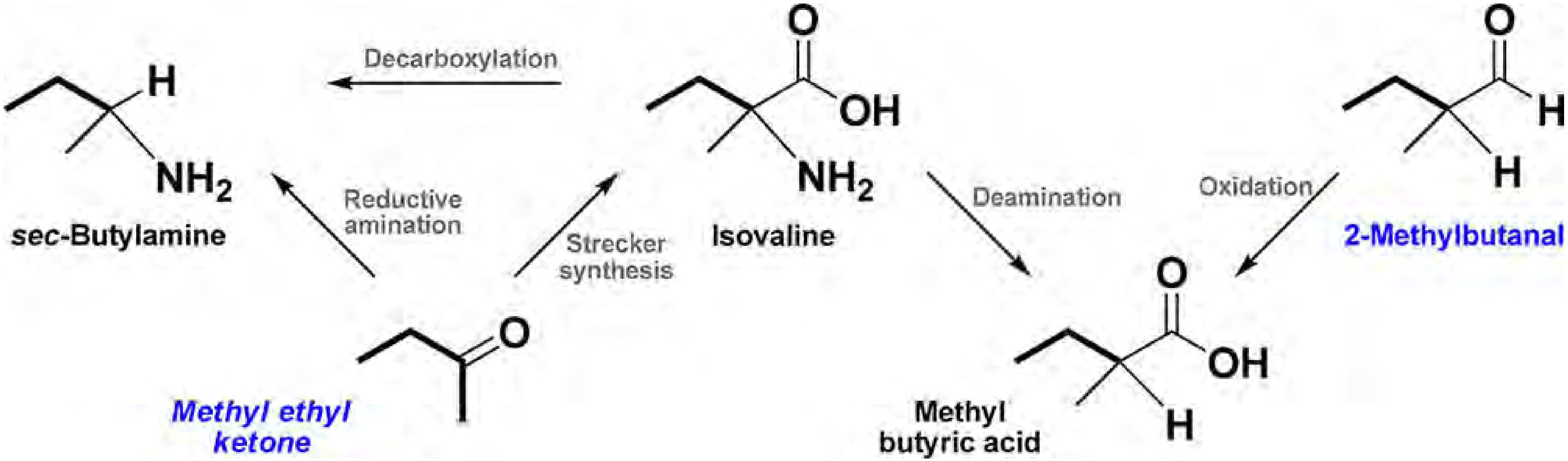
- Bennu's surface is more rugged than originally expected
- Months of reconnaissance allowed the selection of a sampling site
- Nightingale is located in a northern crater 460 ft wide.
- The area safe for the spacecraft to land is 52 ft in diameter.
- Nightingale's regolith is dark, and images show that the crater is relatively smooth



https://www.asteroidmission.org/

Beyond Amino Acids

- Amino acids are only one of the organic compound classes being studied in solar system materials
- Analysis of diverse molecular species can reveal chemical formation pathways
- Studies include structural abundances, isotopic ratios, and enantiomeric compositions



Summary

- Impactors may have delivered a rich organic chemistry to the early Earth
- Remote, *in situ*, and laboratory studies can identify organic compounds
- Meteorites sample a diverse range of parent bodies and contain a multitude of organic compounds
- Sample return missions can provide pristine samples with context
- Comparison of organic distributions, enantiomeric ratios, and isotopic compositions can aid in understanding astrochemical formation pathways

For more information, visit our website:
https://science.gsfc.nasa.gov/691/analytical/
Astrobiology Analytical Lab at NASA Goddard