Cometary amino acids from NASA's STARDUST mission

Jamie Elsila

December 4, 2009

http://astrobiology.gsfc.nasa.gov/analytical

Thanks to the following for contributing to this work:

Jason Dworkin, Daniel Glavin, Jennifer Stern, Millie Martin

The Stardust Sample Allocation Team

This research is supported by:

The NASA Astrobiology Institute, the Goddard Center for Astrobiology, and the STARDUST Sample Analysis Program

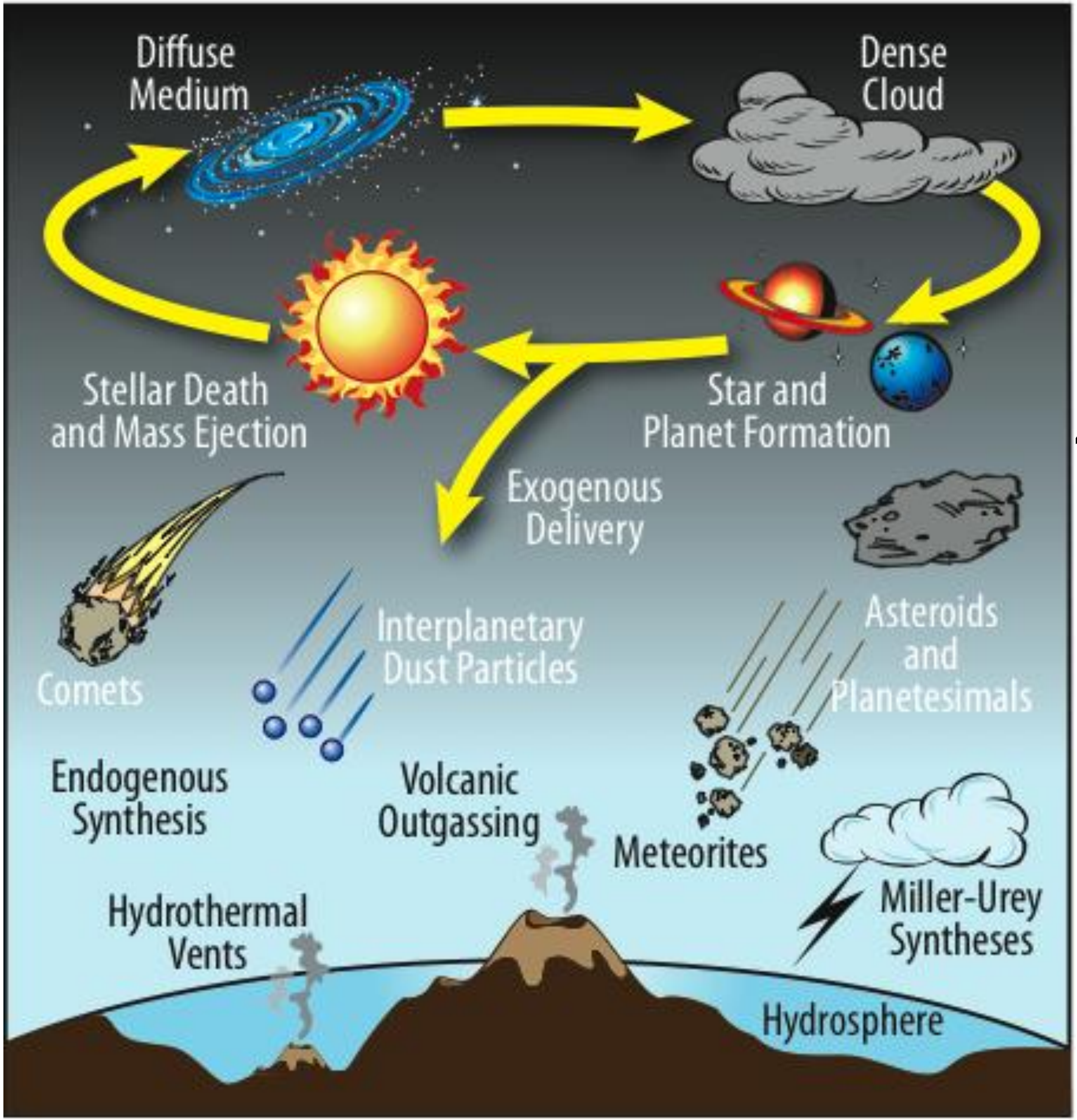
For a detailed discussion, see:

Elsila, Glavin, and Dworkin, *Meteoritics and Planetary Science* (2009) **44**(9), 1323-1330.

Outline

- Prebiotic organic chemistry (what, why, and how)
- NASA’s STARDUST mission
- New results on cometary amino acids

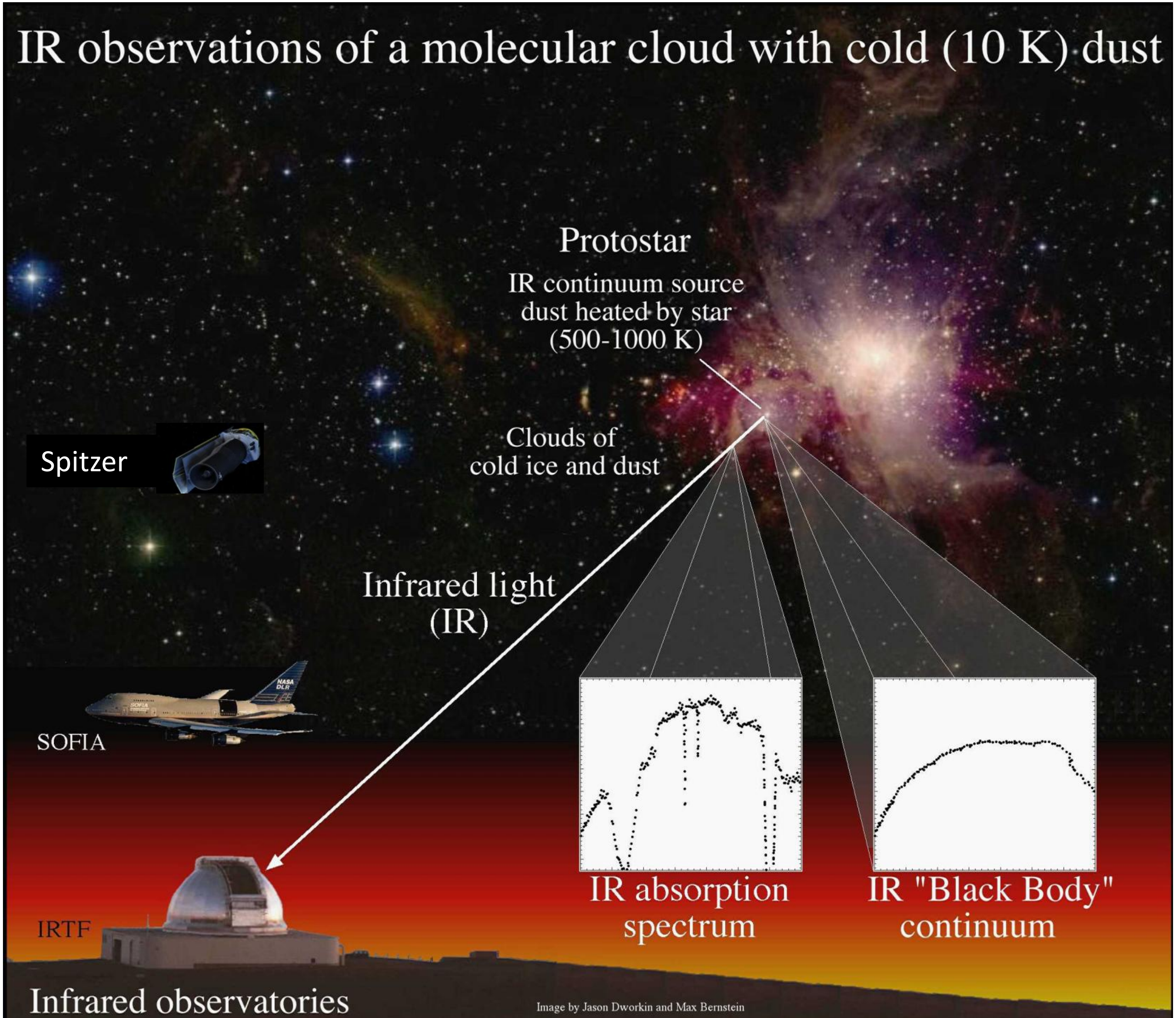
Prebiotic Chemistry



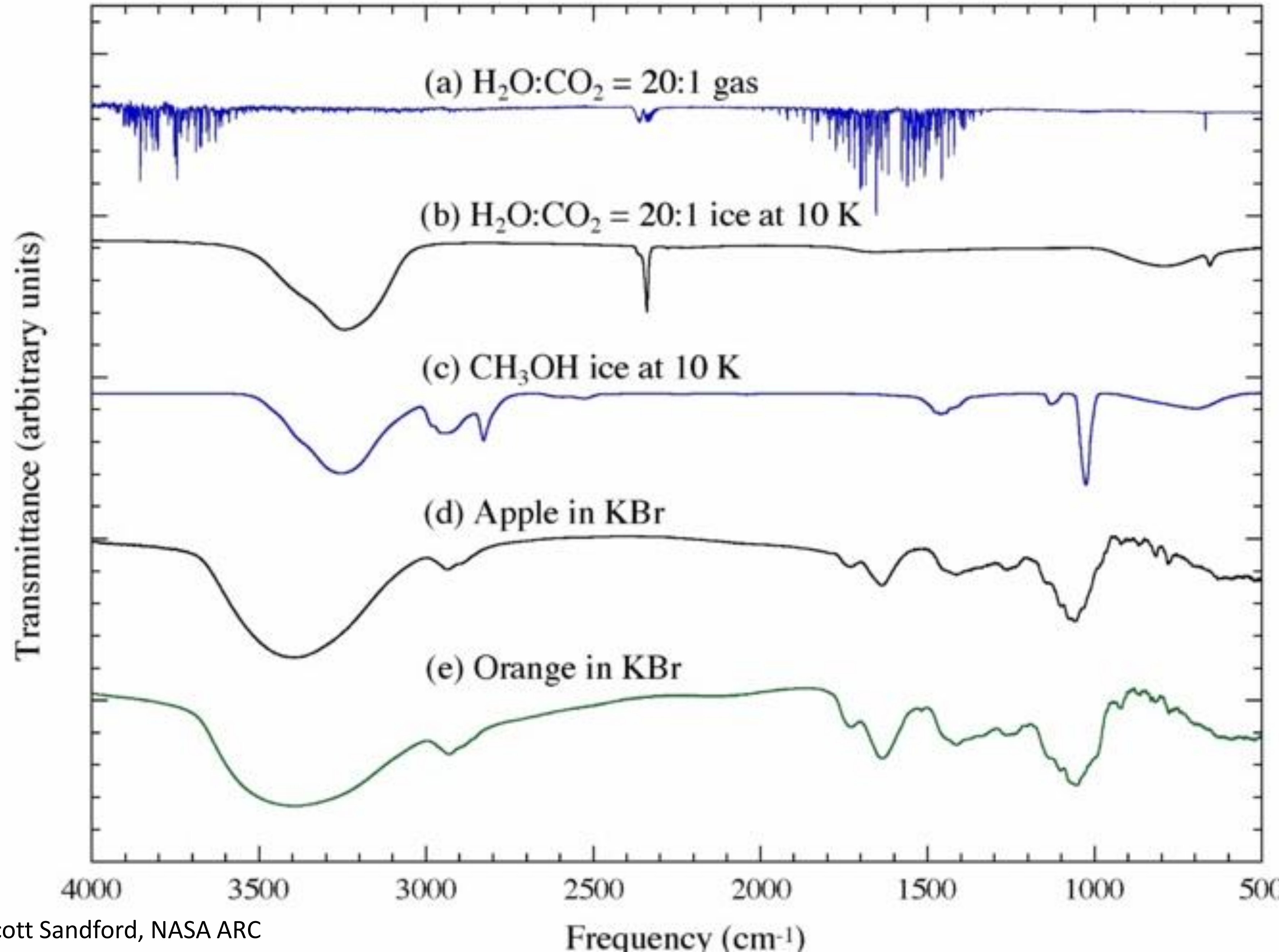
Observations & Simulations

Lab Analysis

Simulations

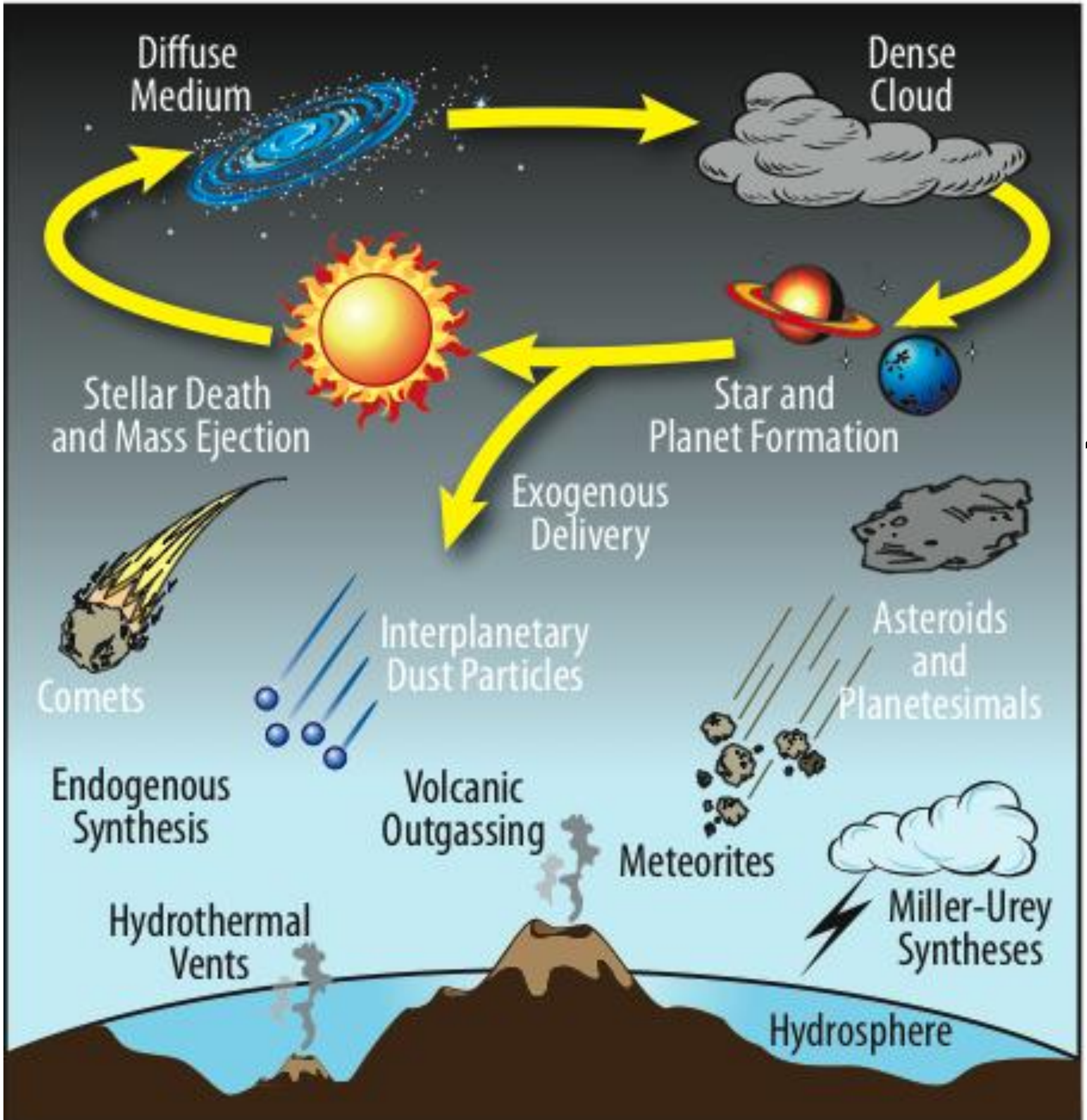

IR observations of a molecular cloud with cold (10 K) dust
Protostar
IR continuum source
dust heated by star
(500-1000 K)
Clouds of
cold ice and dust
Spitzer
Infrared light
(IR)
SOFIA
IRTF
IR absorption
spectrum
IR "Black Body"
continuum
Infrared observatories
Image by Jason Dworkin and Max Bernstein

Spectroscopy (e.g. IR) Is Used for Remote Observations



Scott Sandford, NASA ARC

Prebiotic Chemistry



Observations & Simulations

Lab Analysis

Simulations

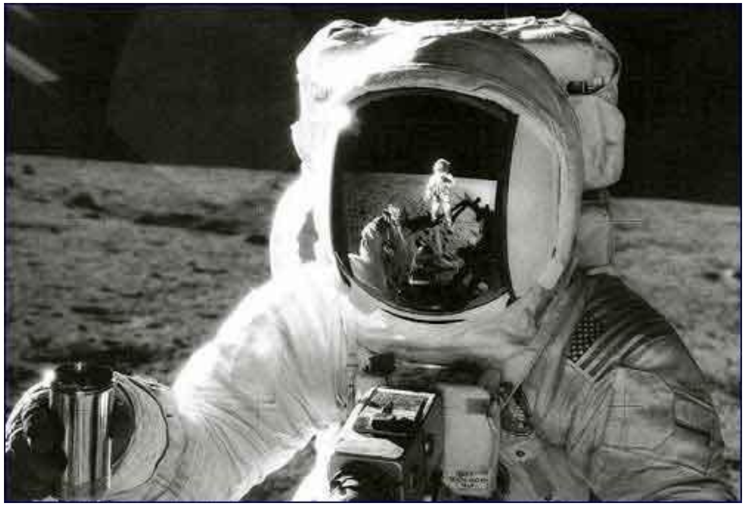
Extraterrestrial Origin of (the ingredients of) Life?

Extraterrestrial Samples

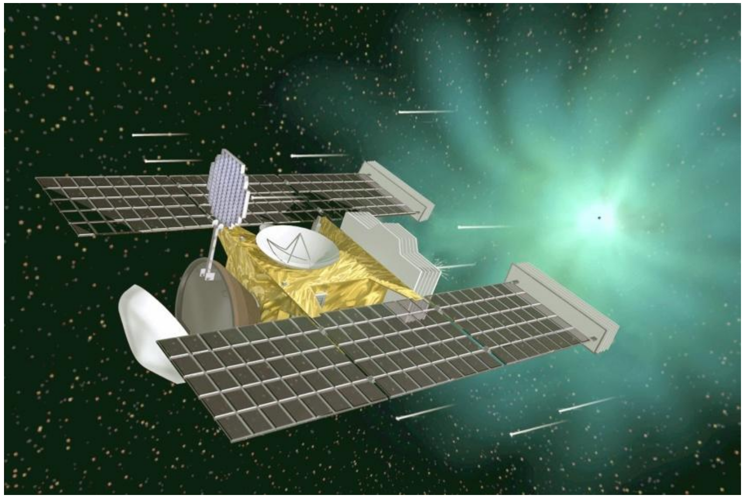
Meteorites:
Falls

and Finds

Extraterrestrial Samples



Sample Return: Apollo and STARDUST



The Advantages of Sample Return Missions

- **Allows for use of state-of-the-art analytical techniques and equipment, providing for the ultimate current precision, sensitivity, resolution, and reliability**

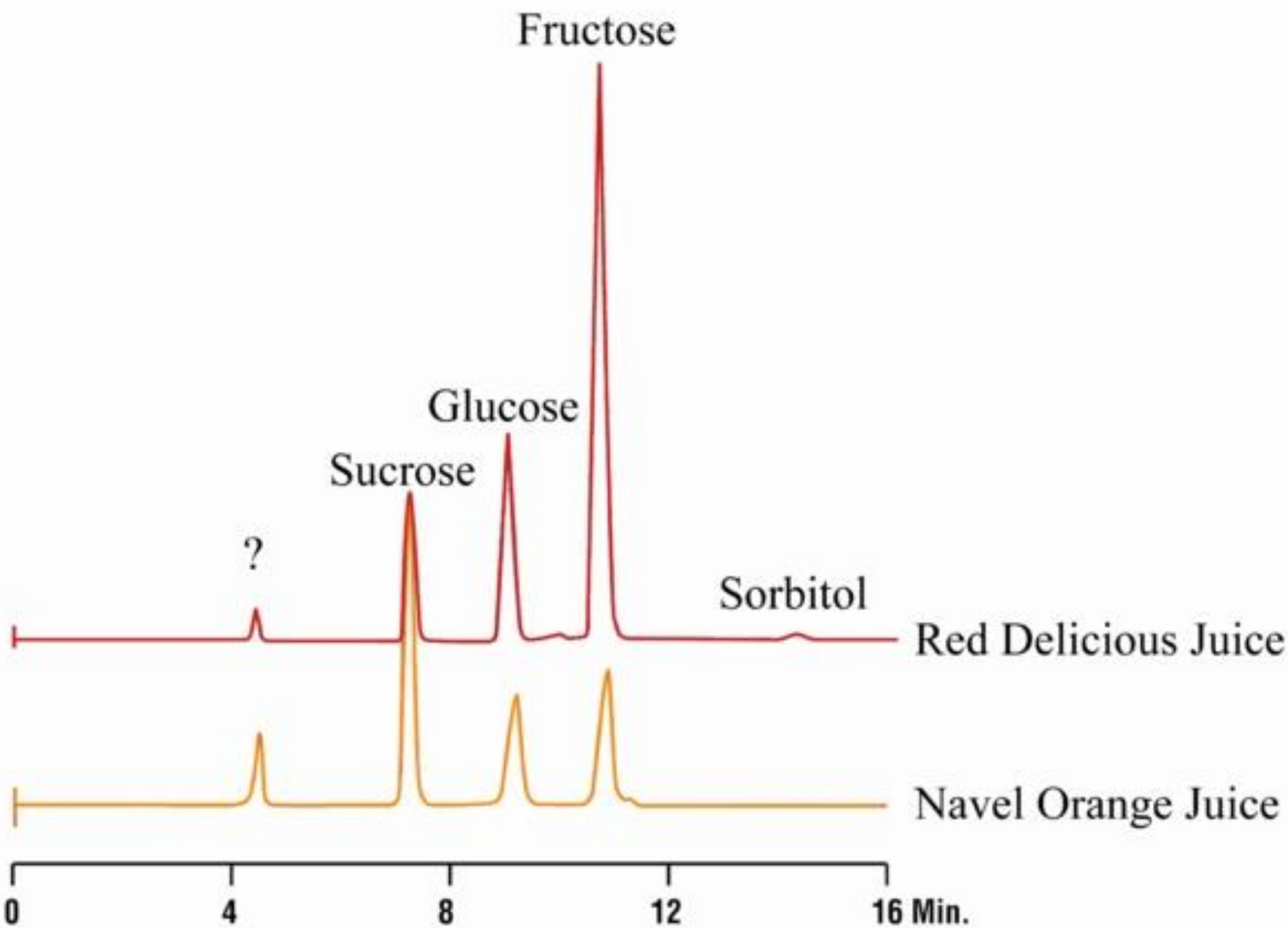
- **The returned samples are a resource for current and *future* studies by a broad international community**

- **Analyses are iterative and fully adaptive - results are not limited by "instrument' design or current ideas**

- **Avoids limitations associated with cost, power, mass, and reliability**

- **Analyses can be replicated, verified, done with multiple techniques and instruments, fully calibrated, and contamination can be fully evaluated**

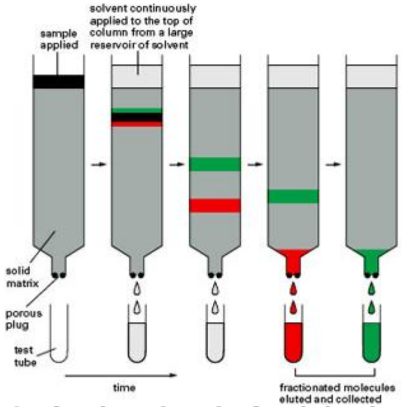
Laboratory Analysis of Organic Compounds



Chudy & Young (1999) Carbohydrate profiles of orange juice and apple juice by HPLC and evaporative light scattering detection.

Laboratory Analysis of Organic Compounds

- Often involves solvent extraction, chromatography, and compound detection



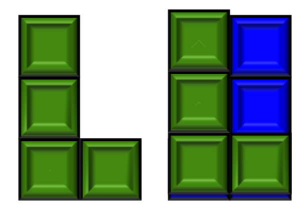
- A variety of organic compounds have been identified in meteorite samples, including over 80 **amino acids**

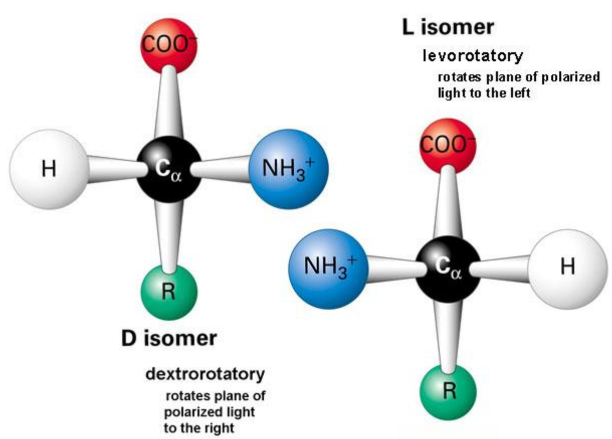
Amino Acids

- Building blocks of proteins
  - 20 proteinogenic amino acids
- Essential to life on Earth
- Possess chirality (handedness)

Amino Acids

- Building blocks of proteins
  - 20 proteinogenic amino acids
- Essential to life on Earth
- Possess chirality (handedness)





Extraterrestrial or Contamination?

- How can we be sure these compounds are indigenous?
  - Controls: procedures, equipment, soil, etc.
  - Molecular distribution
  - Chirality
    - Most non-biological processes produce equal handedness, whereas life on Earth is based on L-amino acids
  - Isotopic measurements

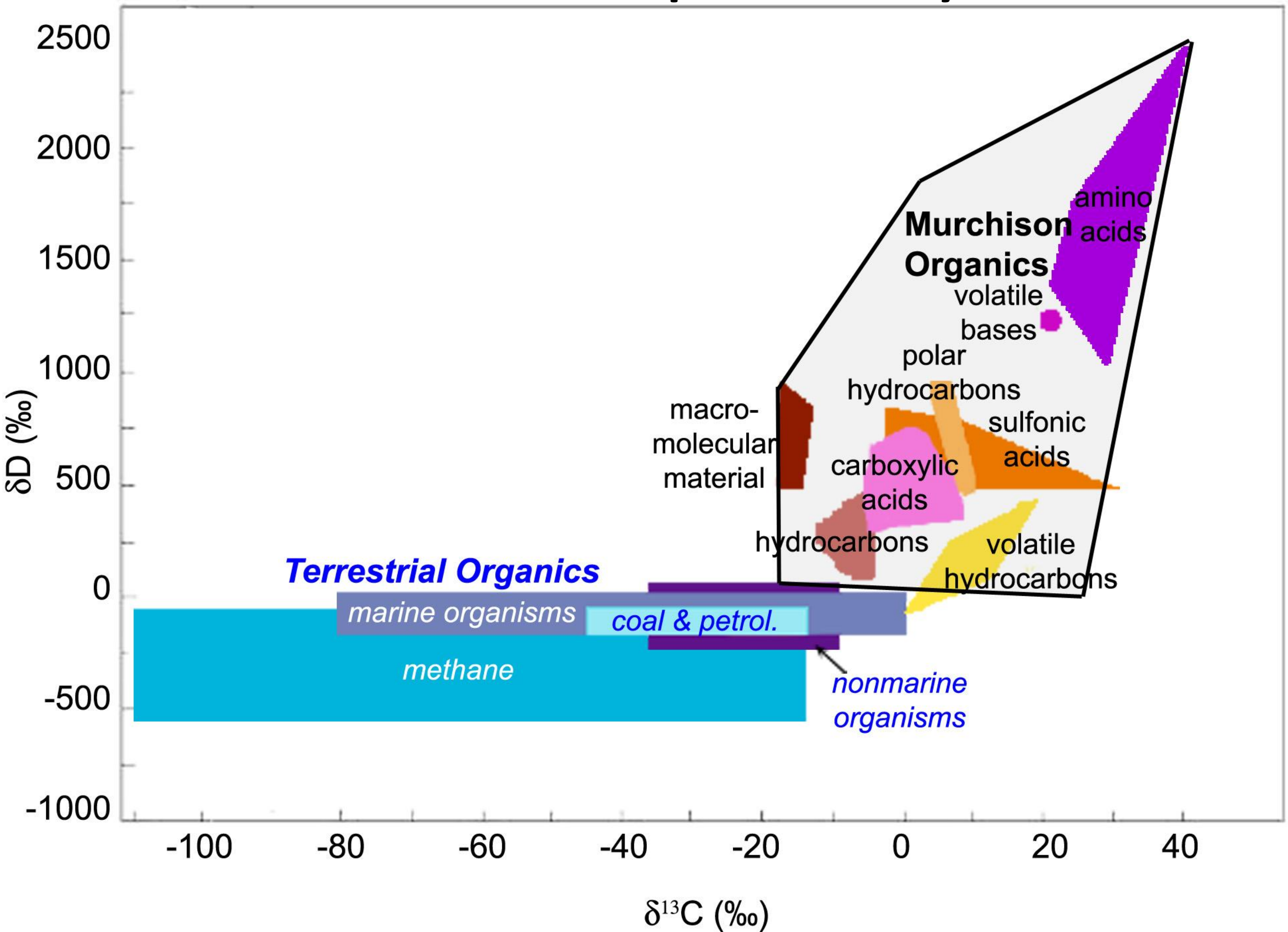
Stable Isotope Ratios

- Isotope ratios of interest in prebiotic organic chemistry: $^{13}C/^{12}C$, $^{15}N/^{14}N$, D/H
- Provide clues to chemical, physical, and biological processes.
- Expressed in delta notation:

$$\delta^{13}C = \frac{[(^{13}C/^{12}C)_{sample} - (^{13}C/^{12}C)_{std}]}{(^{13}C/^{12}C)_{std}} \times 1000$$

- “Enriched” = heavier (more positive)
- “Depleted” = lighter (more negative)

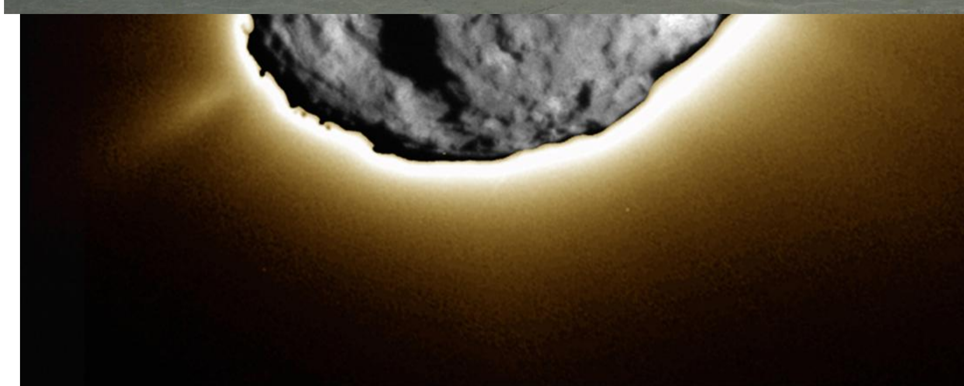
Stable Isotope Analysis



Prebiotic Chemistry Summary

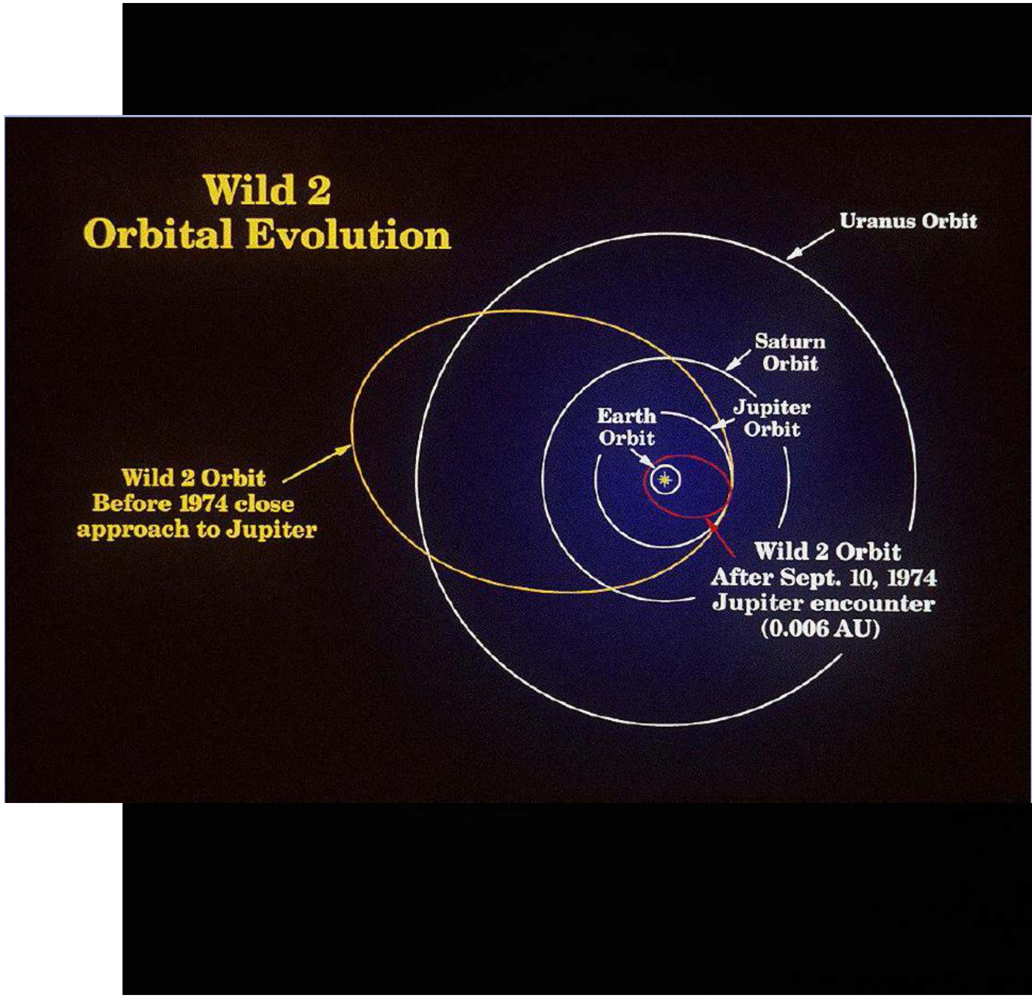
- Exogenous delivery of organic compounds may have provided the **ingredients for life**
- Laboratory analysis of extraterrestrial samples determines the **inventory of these compounds**
- Chirality and isotopes are tools that help determine the **origin of these compounds**

- NASA's first sample return mission launched since Apollo
- Spacecraft launched 1999
- Comet Wild-2 encounter January 2004
- Returned to Earth January 2006
- Total distance traveled – 2.88 billion miles
- Average cost = 7¢ per mile)



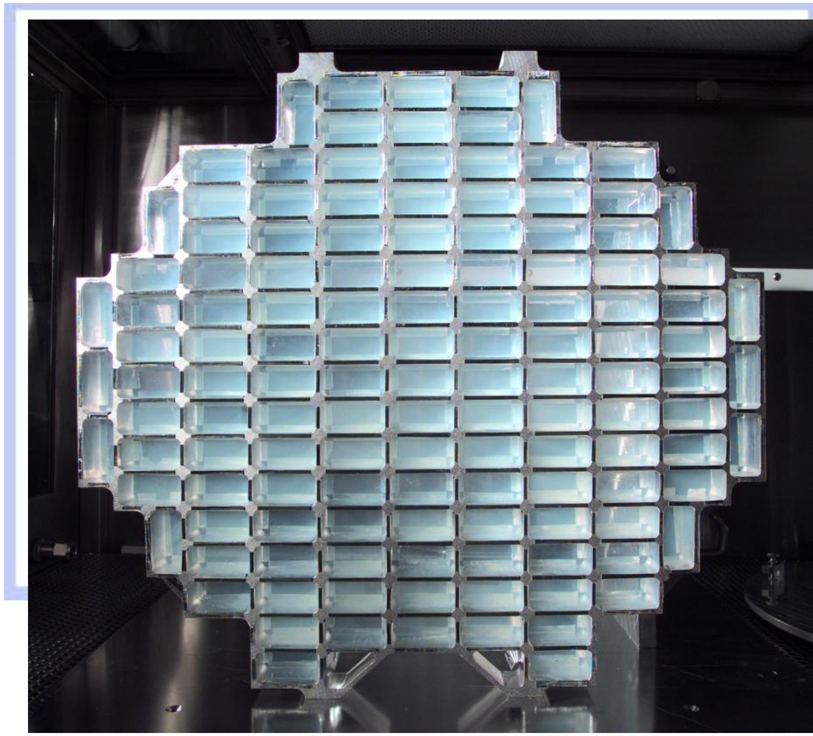
Comet Wild-2

- Wild-2 is relatively pristine, having only passed the sun 5 times
- Orbit changed in 1974, bringing it into the inner solar system

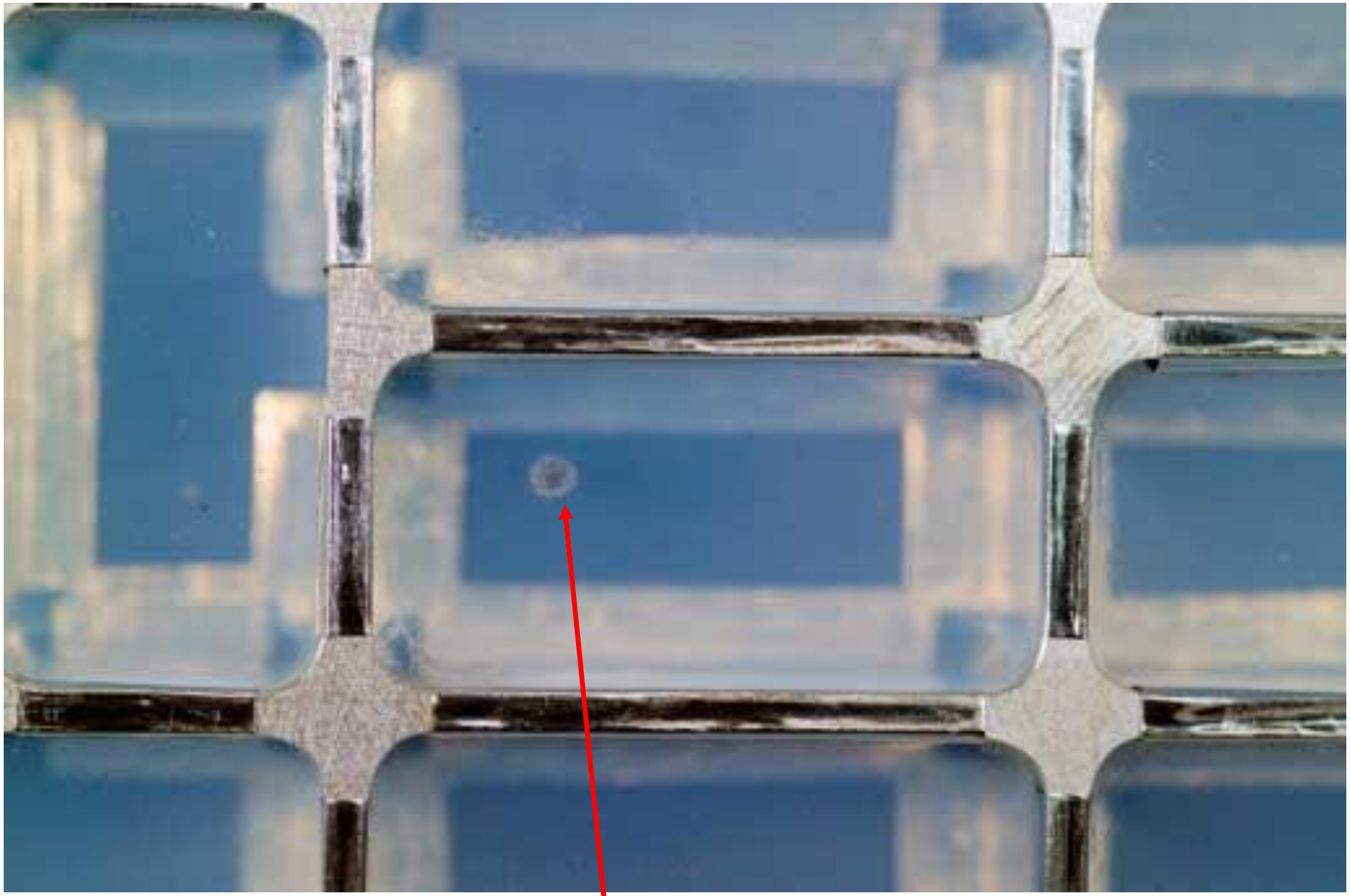


STARDUST Collector

- The STARDUST spacecraft deployed a dust collector to capture cometary particles
- The collector was made of aerogel, a glassy sponge that slowed and trapped the particles

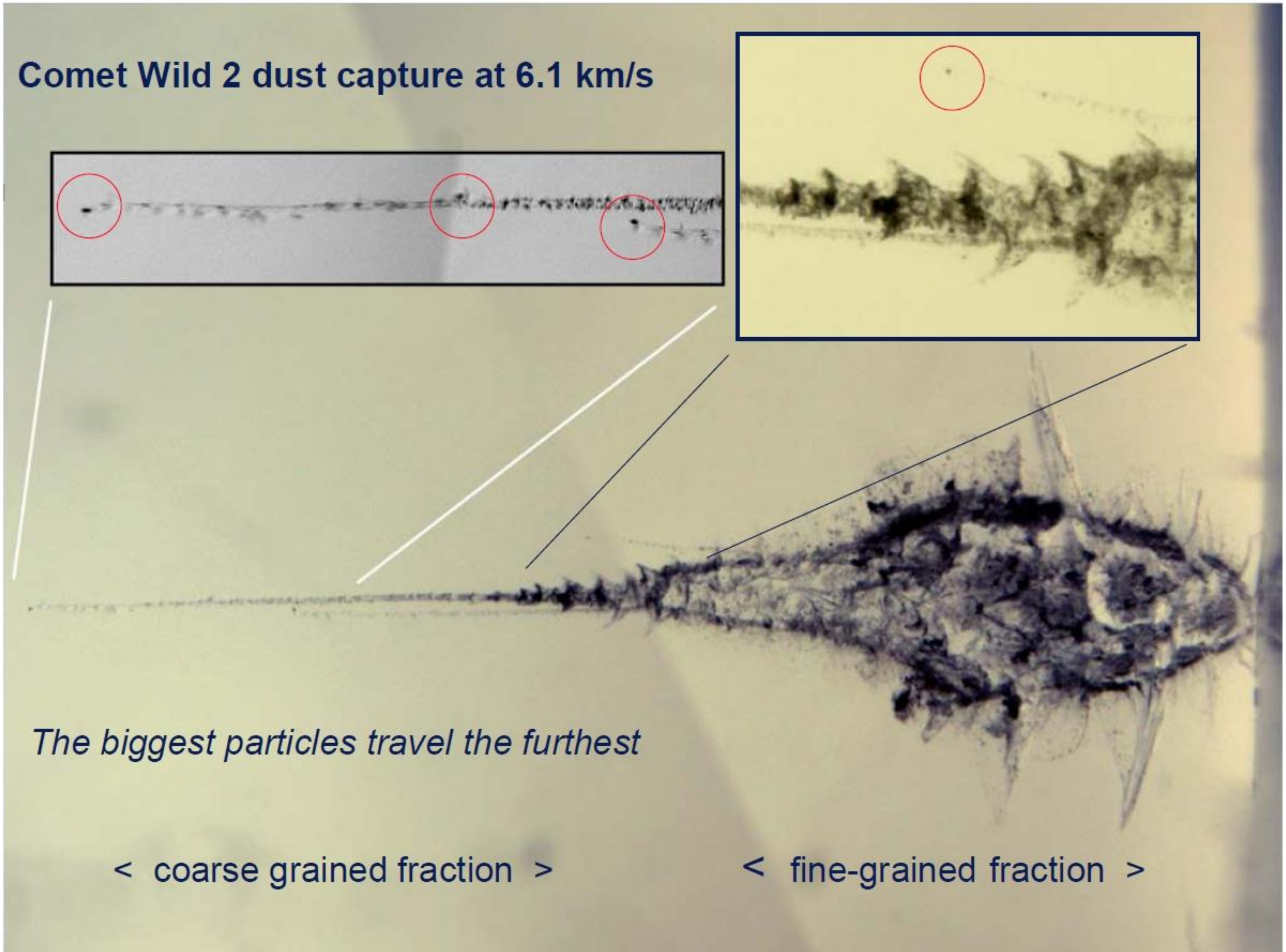


Aerogel Impacts



Impact of Cometary Particle

Particle capture



Preliminary Stardust analysis

- The Preliminary Examination Team initially analyzed the returned samples (now available to all investigators)
- Micro-analytical techniques included:
  - Scanning and Transmission Electron Microscopy (structure, mineralogy, elemental composition, imaging)
  - IR, Raman, and XANES spectroscopy (molecular bonds)
  - SIMS and TOF-SIMS (elemental, isotopic, molecular abundances)
  - μL2MS (molecular identities)
  - X-ray diffraction (crystal structure)
  - X-ray absorption spectroscopy (elemental abundances)
  - Scanning Transmission X-ray Microscopy (imaging)
  - Electron Energy Loss Spectroscopy (light element abundances)
  - **Liquid Chromatography with Fluorescence Detection and Mass Spectrometry (organic compounds)**

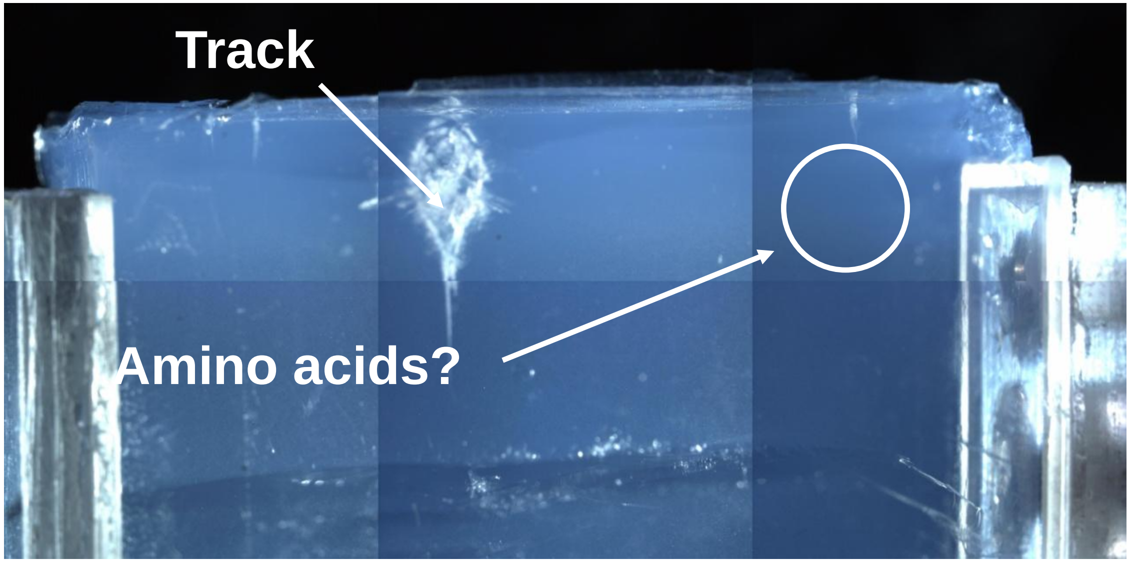
Science, Dec. 15, 2006, and Meteoritics and Planetary Science (2008) v. 43 issue 1-2

Interesting STARDUST results

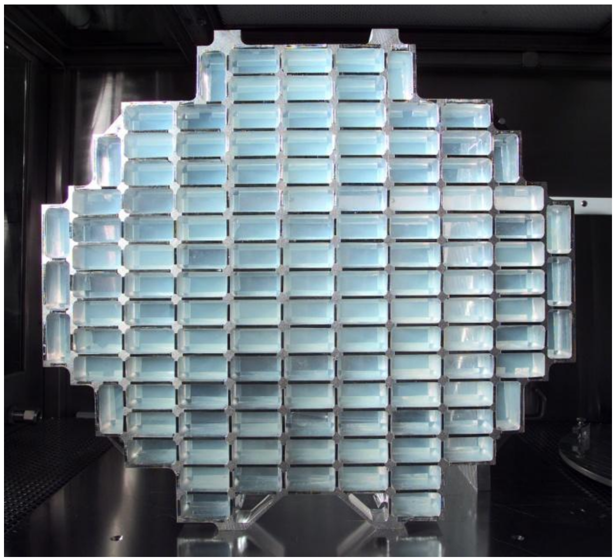
- The expectation was that comets contain mostly pre-solar material, but:
  - “High temperature” minerals seen
  - Some presolar grains observed
  - This suggests mixing in the early solar nebula
- Most grains were weakly bound aggregates
- The comet is a repository of relatively unprocessed early Solar System materials
- Organics present in a greater compositional diversity than in primitive carbonaceous meteorites and appear to be “primitive”/presolar

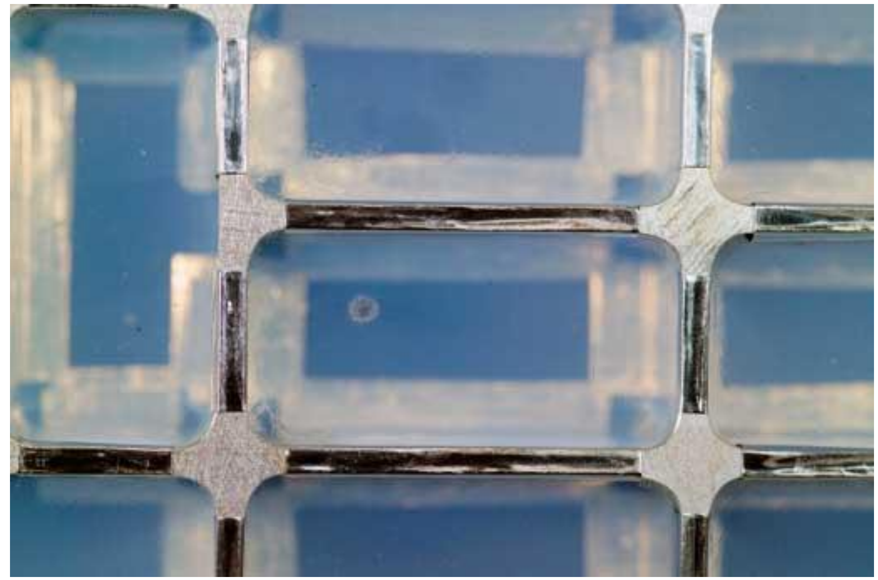
GSFC Organic Analysis

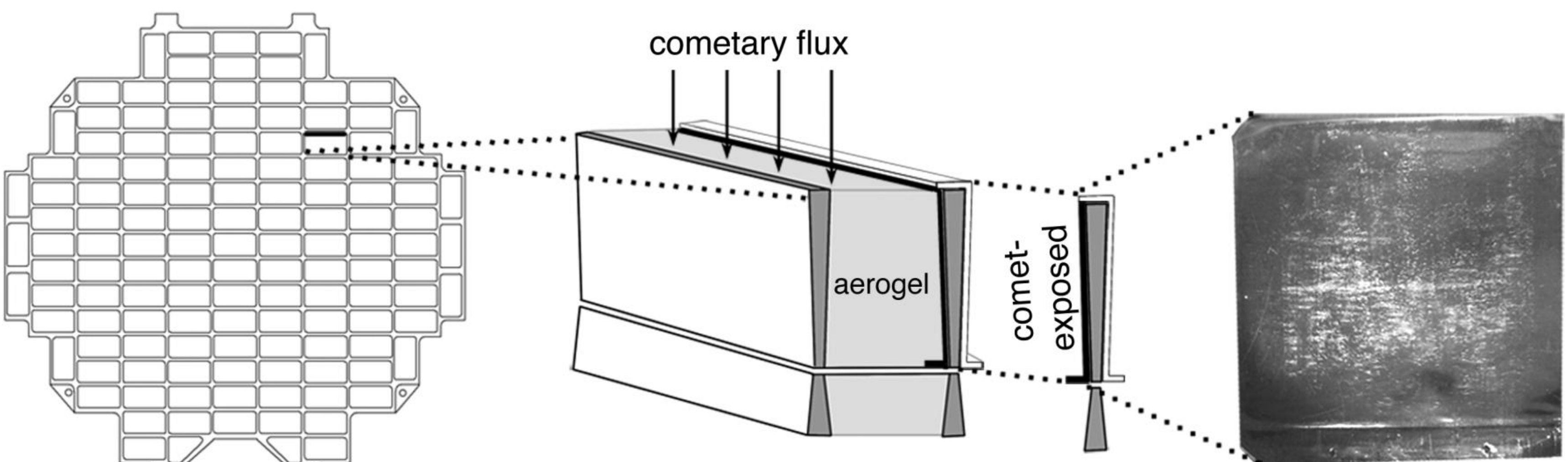
- Most groups focused on particles, what about bulk materials?
- Cometary organics outside of track?
- Terrestrial contamination?
- These questions can be addressed by studying **amino acids/amines**



Bulk Samples





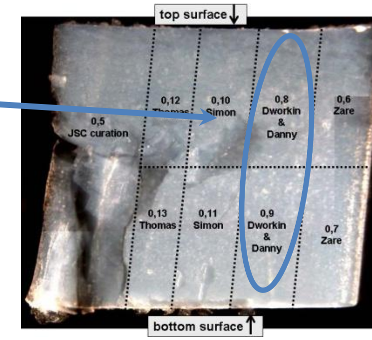


Contamination Control Samples

Air samples from cleanroom and UTTR

Synlube 100
(aerogel mold release)

Flight Aerogel Witness Coupon

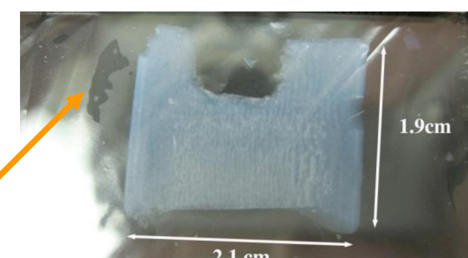


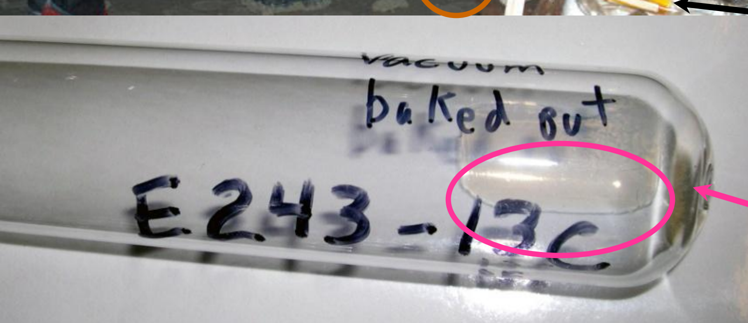
SRC backshell, heatshield, and filters

UTTR mud samples

Kapton tape

Nylon bag (curation)



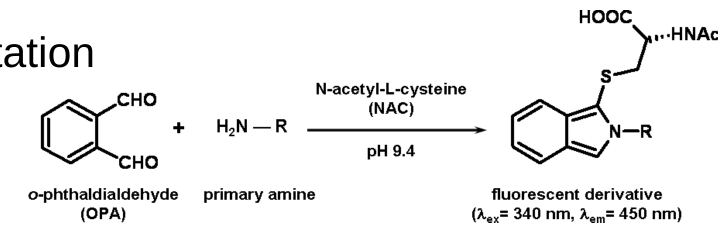


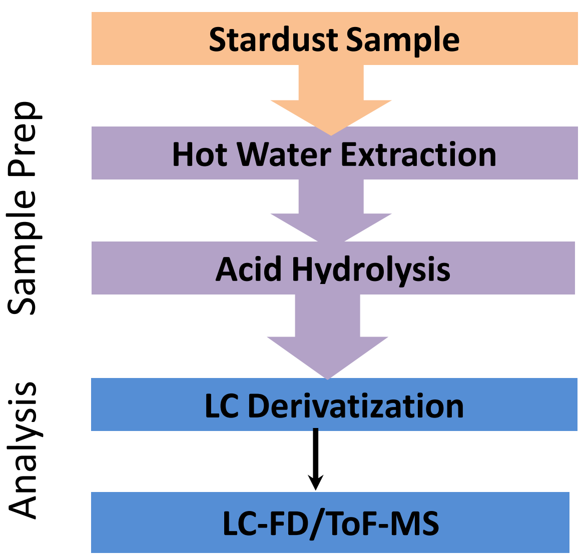
Preflight aerogel

Protocol for Amino Acid Detection

Liquid Chromatography with Fluorescence and Electrospray Time of Flight Mass Spectrometric Detection (LC-FD/ToF-MS)

- Exact molecular mass of parent ion without fragmentation
- UV fluorescence confirmation of functional group
- >1000x more sensitive than GC-MS ($<10^{-15}$ moles)

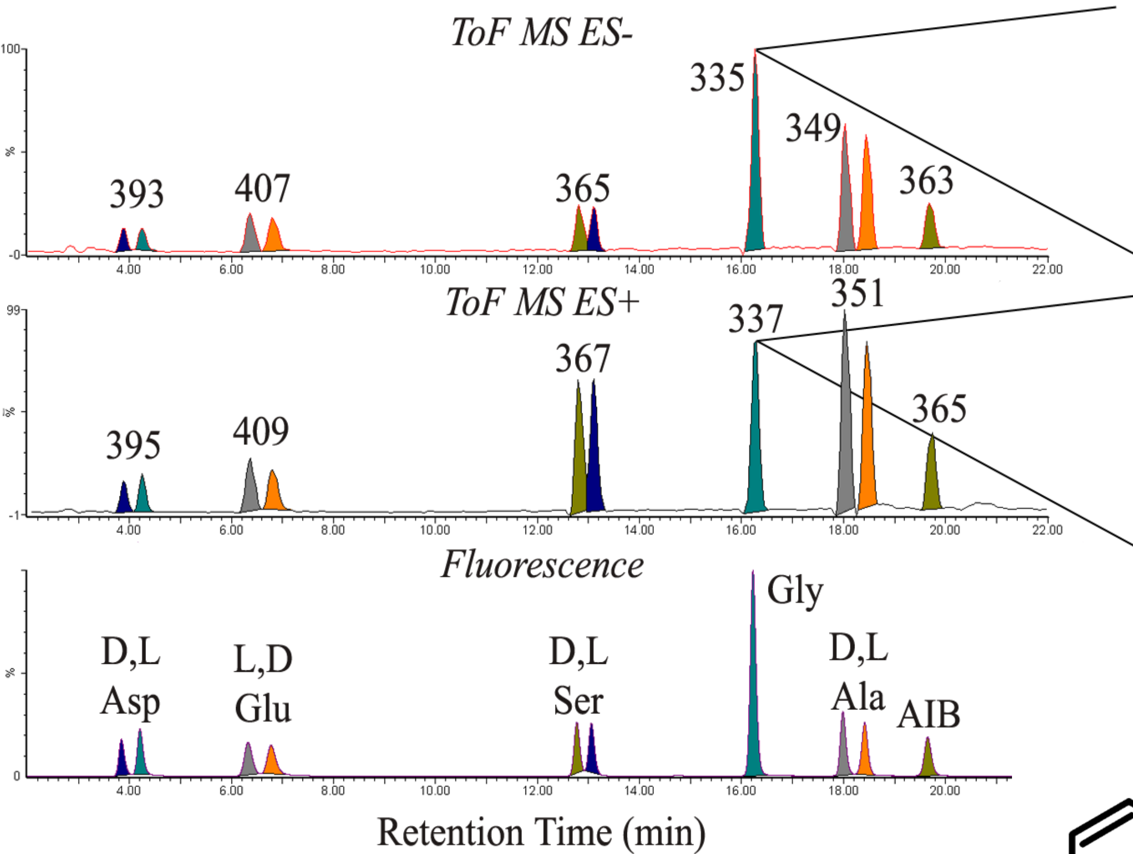


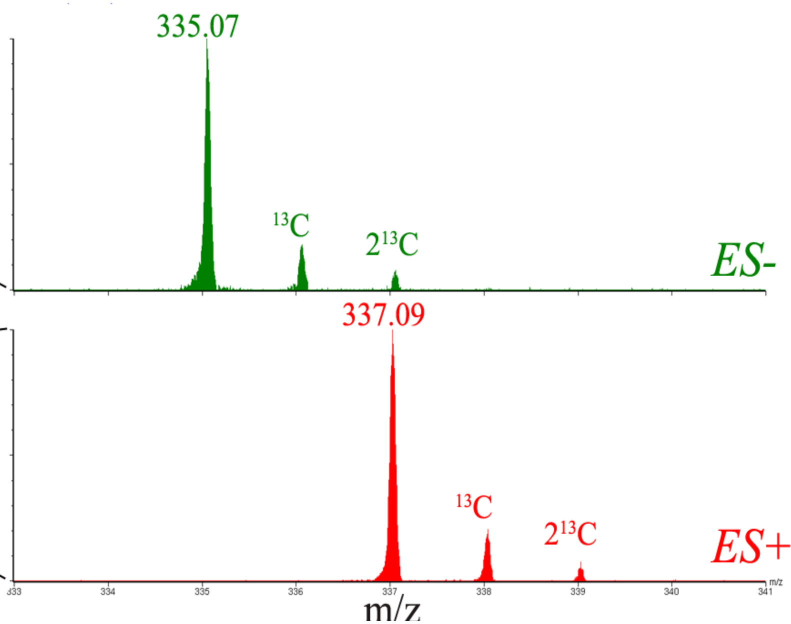


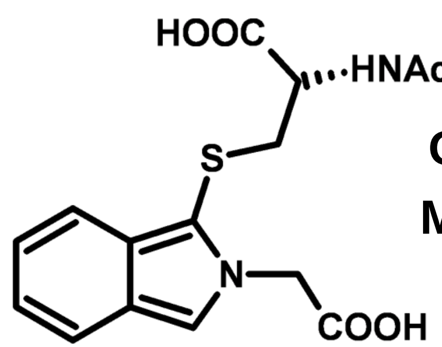
LC - FD / ESI ToF-MS

Amine Identification

Simultaneous UV fluorescence and ToF-MS detection



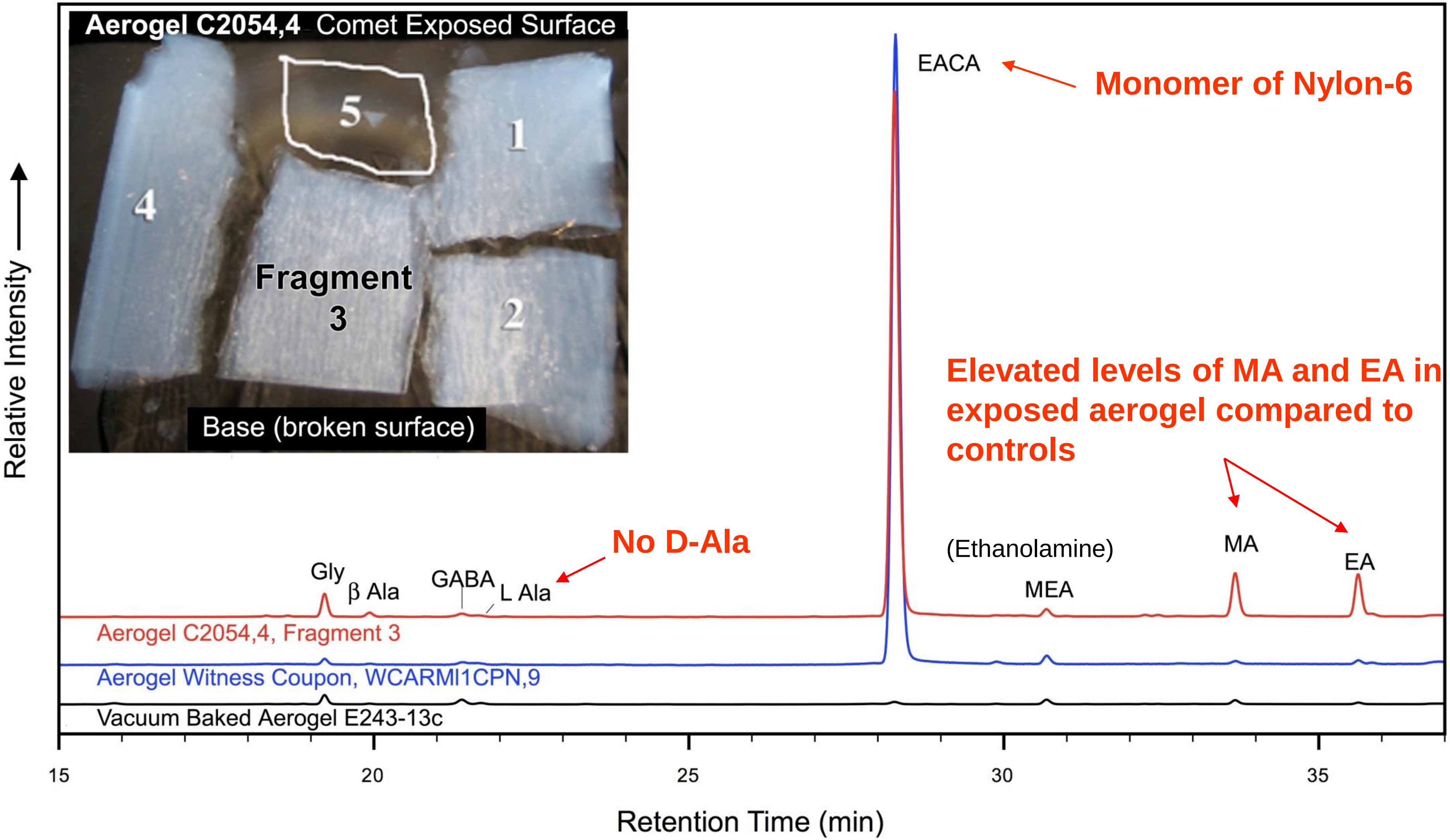




OPA/NAC-glycine

MW = 336.0780 Da

LC-FD/ToF-MS Results



Glycine

- Glycine is the simplest amino acid
- It is achiral (no possibility of chirality), so no information is learned from handedness

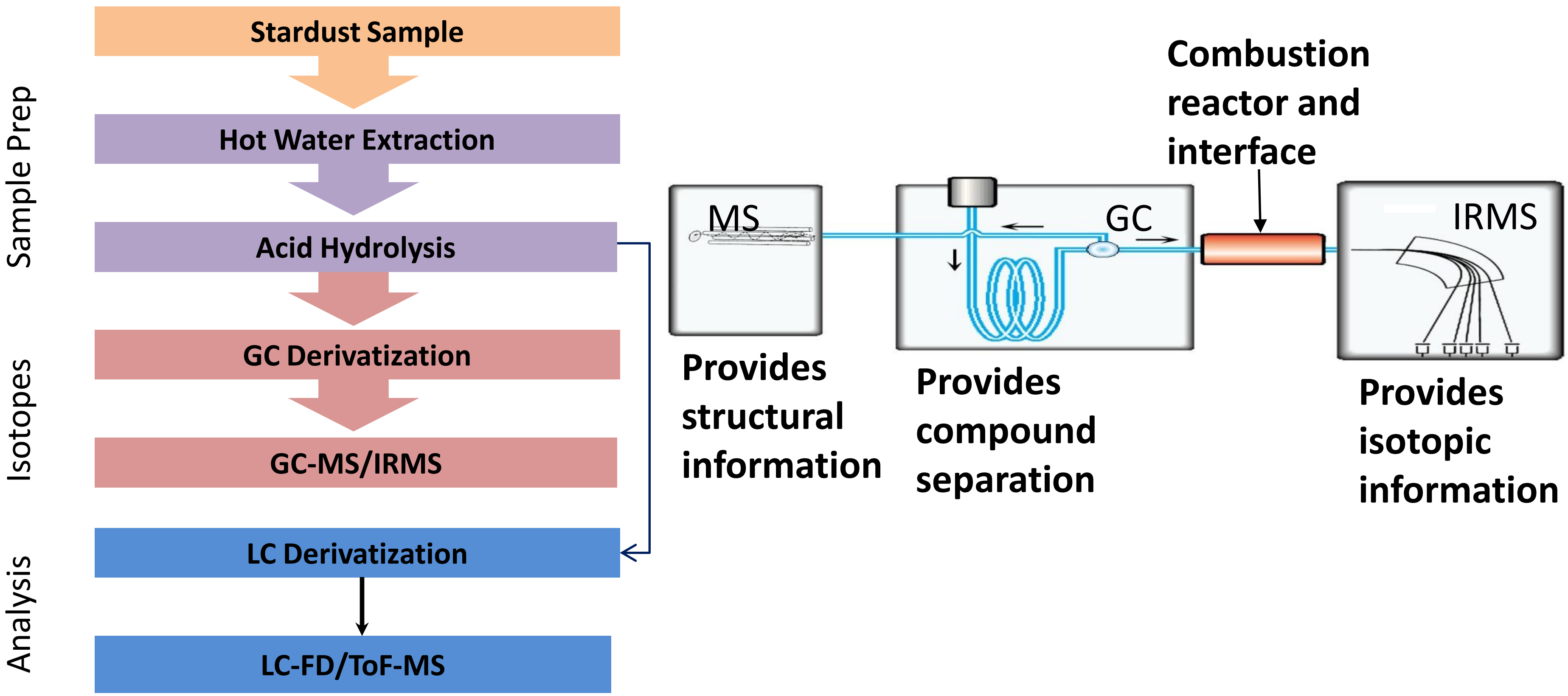
LC-FD/ToF-MS Results

Compound	Probable Source
Gly	Aerogel, Wild 2?
β-Ala	Aerogel, Wild 2?
L-Ala	Aerogel
GABA	Aerogel (partial bakeout)
EACA	Aerogel (Nylon-6)
MEA	Aerogel (Synlube 100)
MA	Wild 2, Aerogel?
EA	Wild 2

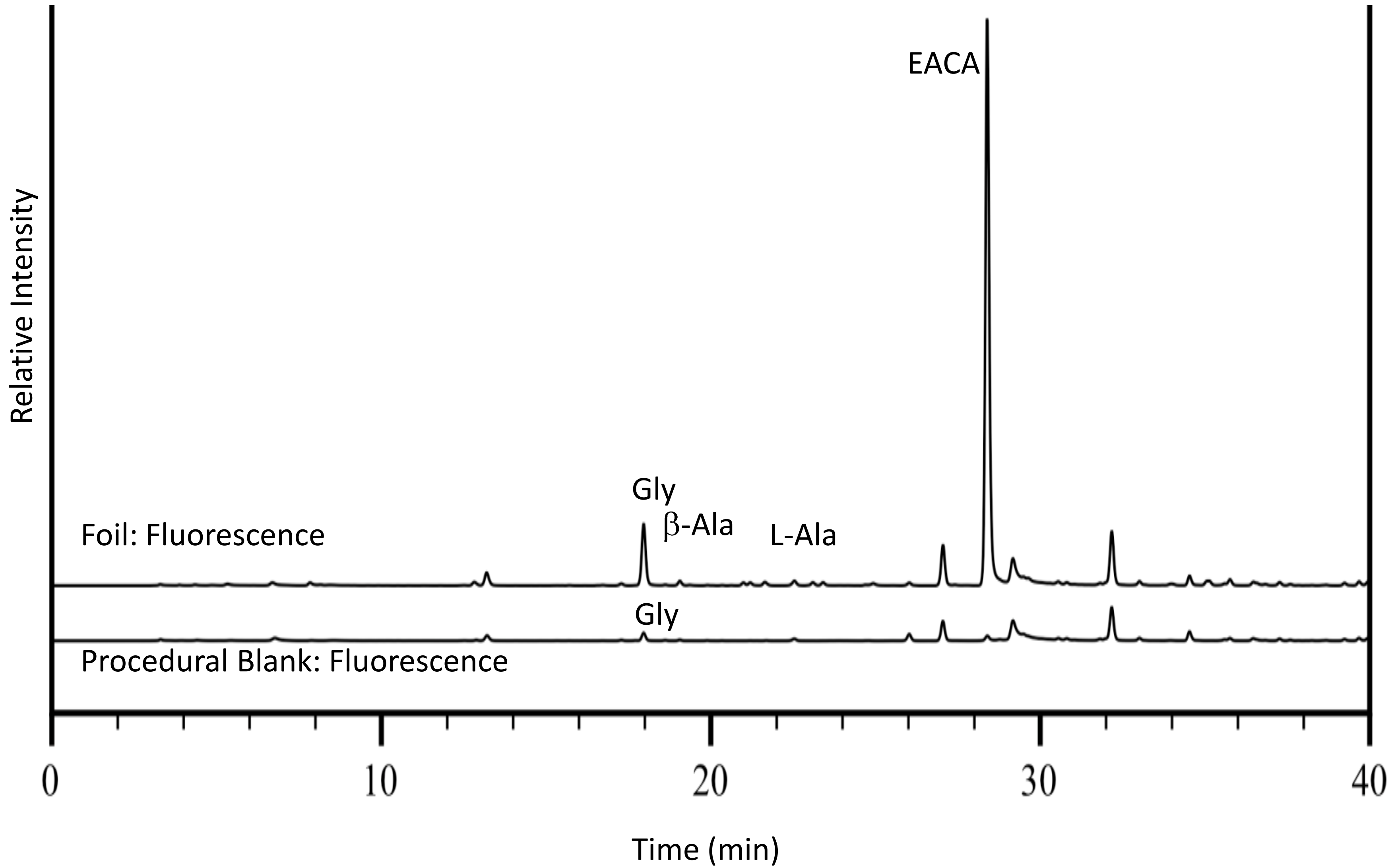
Protocol for Stable Isotope Analysis

Gas Chromatography with Mass Spectrometry and Isotope Ratio Mass Spectrometry (GC-MS/IRMS)

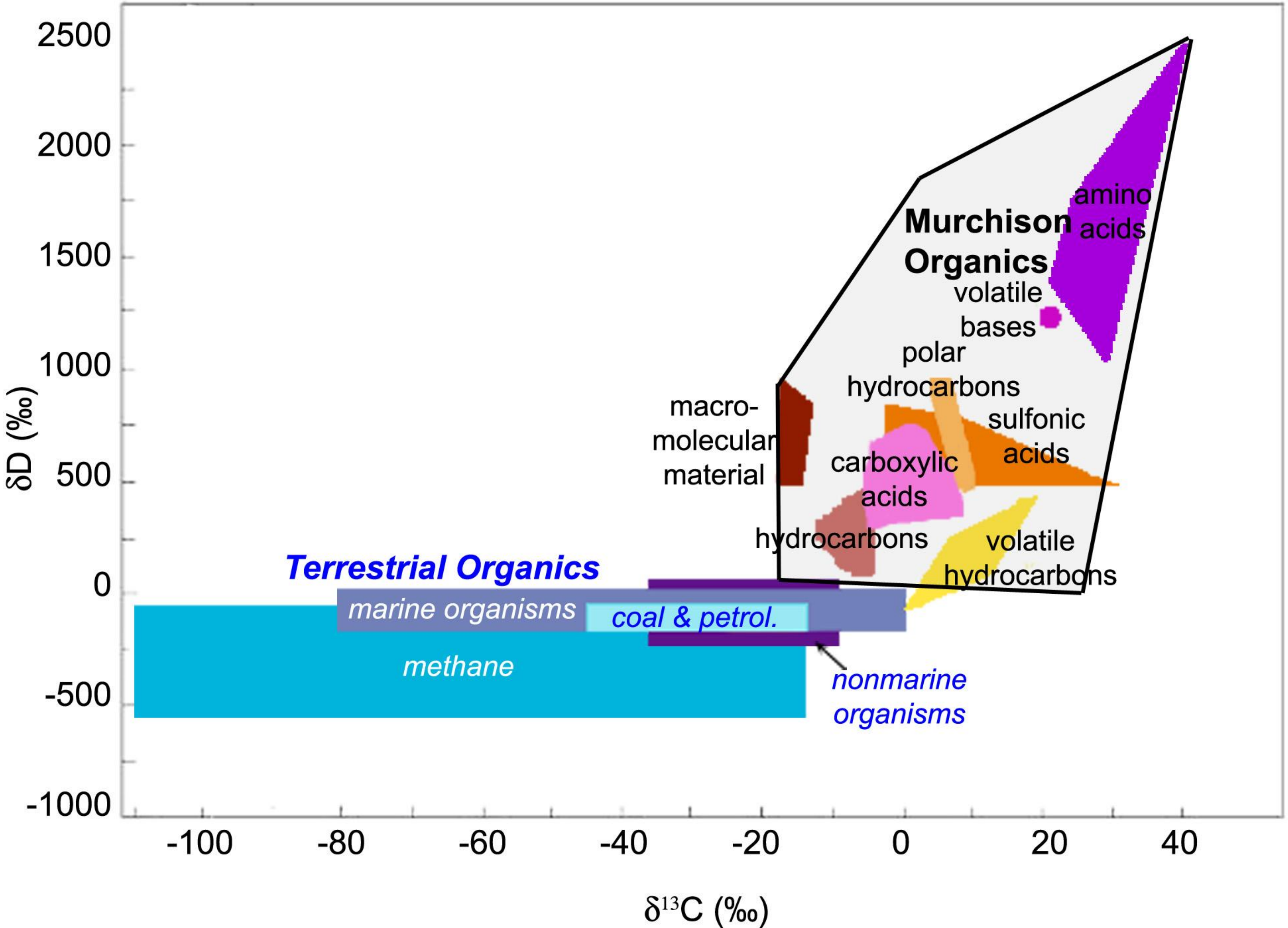
- Compound-specific carbon isotope ratios
- Mass spectral confirmation of compound identity



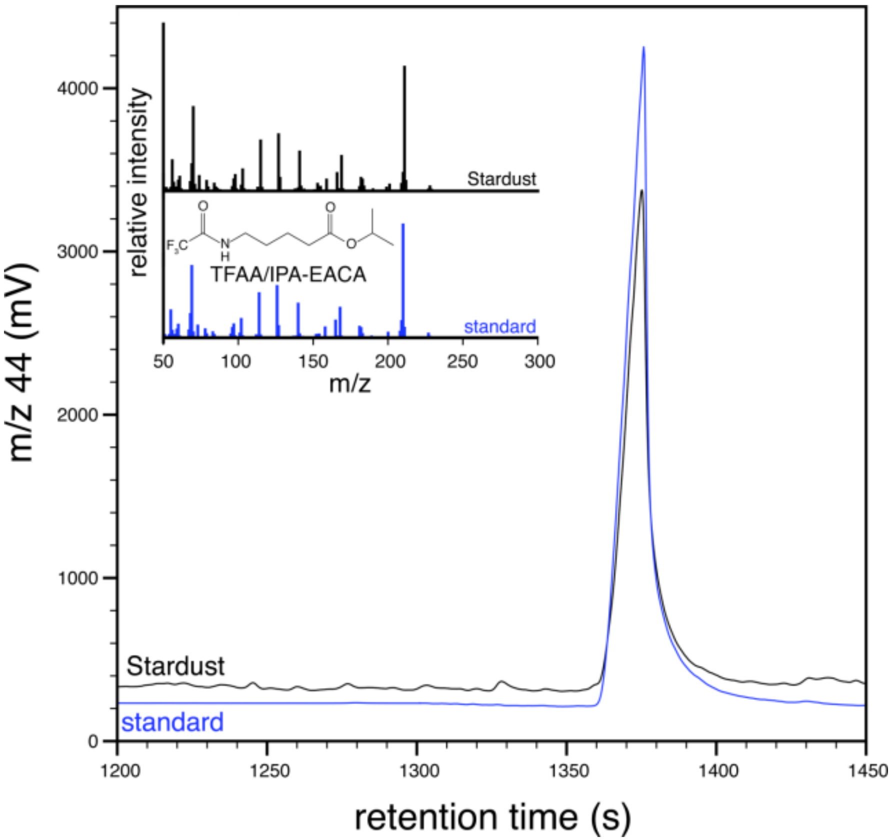
LC-FD/ToF-MS Results



Stable Isotope Analysis



STARDUST EACA



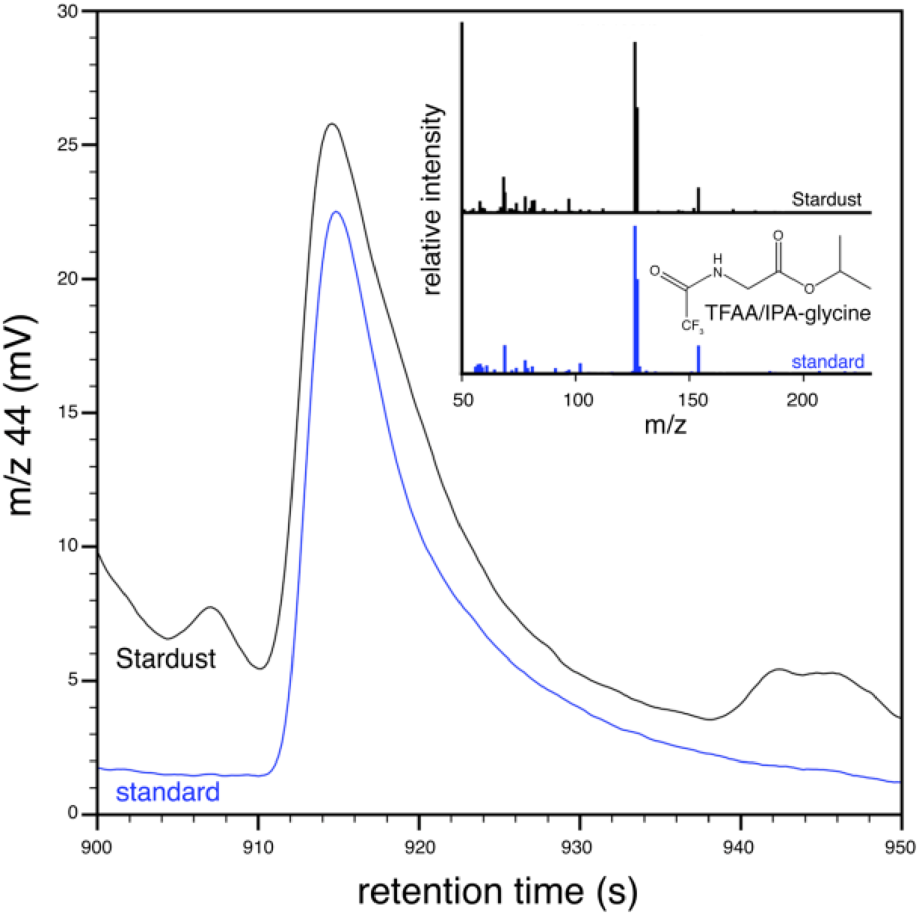
$\delta^{13}C = -25‰ \pm 2‰$

EACA from a Nylon shipping bag used by curators at Johnson Space Center:

$\delta^{13}C = -26.8‰ \pm 0.2‰$

EACA is terrestrial

STARDUST Glycine



$\delta^{13}C$ = +29‰ ± 6‰

Terrestrial carbon usually ranges from -6 to -40 ‰

Meteoritic glycine:
$\delta^{13}C$ ≈ +20‰ to +40‰

Glycine is extraterrestrial

Glycine Sources?

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

Significance and Summary

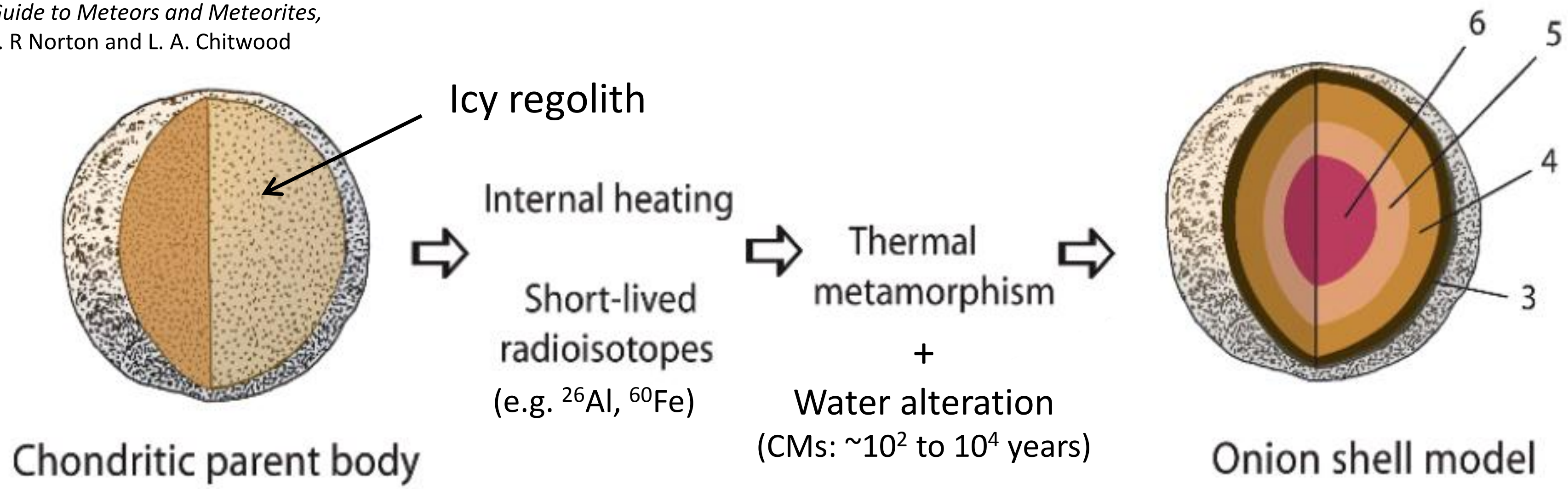
- The extraterrestrial glycine found is the first reported detection of a cometary amino acid
- EACA was a terrestrial contaminant from curation; may affect future curation techniques
- Comets could have delivered amino acids to the early Earth

Potential Future Work

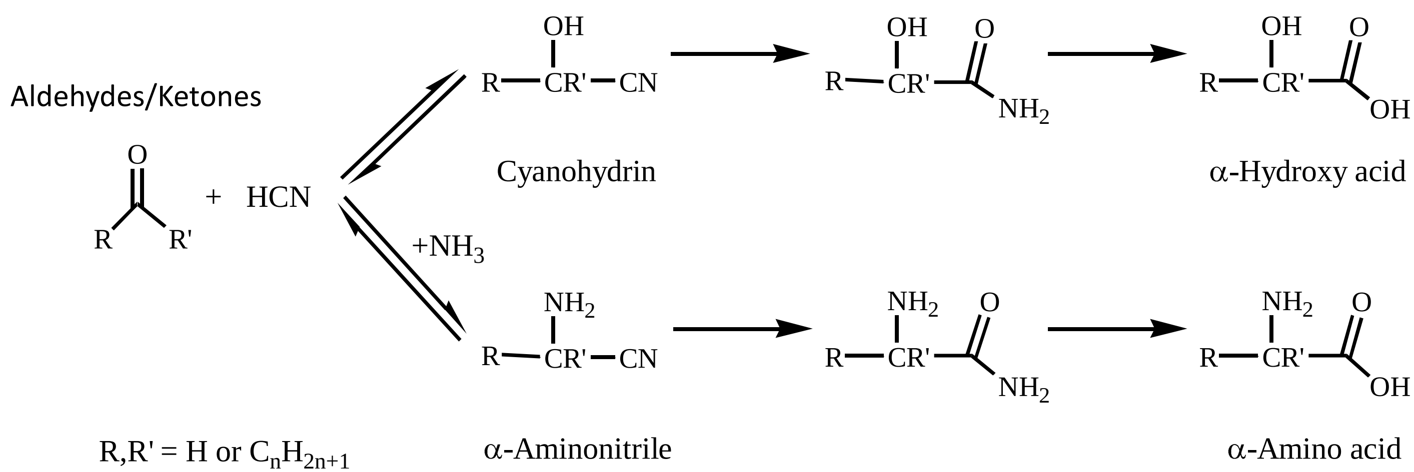
- Determine the amount of “free” vs. “bound” glycine, although more sample will be needed
- Correlation of glycine abundance with collector map and impacts
- The foils sampled primarily the volatile component of the comet; the comet may contain a more complex organic mixture (**comet nucleus sample return mission)**

Amino Acid Formation on Parent Body

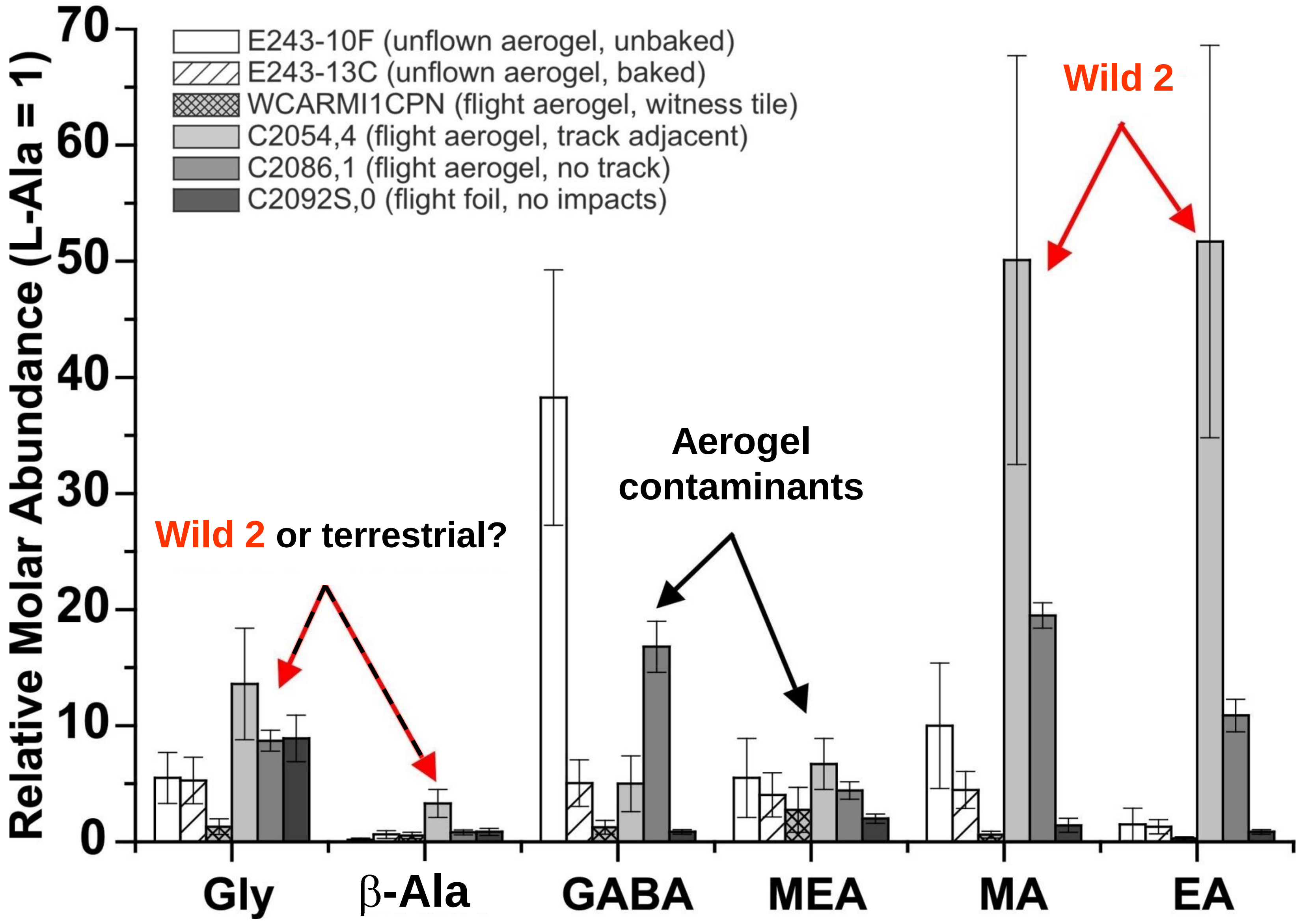
Modified from:
Field Guide to Meteors and Meteorites,
eds. O. R Norton and L. A. Chitwood



Aqueous alteration will drive Strecker synthesis:



Relative Amine Abundances



Amino Acid	**Stardust Flight Foils**[a]					
	C2103N,0	***C2016N,2***	***C2017N,0***	***C2078N,0***	***C2125N,2***†	
	Both sides				*Aerogel side*	*Metal side*
Glycine	34	2	13	19	21	< 3
β-Alanine	2	1	1	3	< 2	< 2
D-Alanine	< 3	< 3	< 3	< 3	< 3	< 3
L-Alanine	2	< 1	1	1	1	< 3
EACA[b]	327	51	66	327	186	126

[a]All values are reported in 10^{-12} mol per cm^2 extracted foil surface area ($pmol/cm^2$). The uncertainty in the values reported is ± 10%.

[b]Hydrolysis product of Nylon-6

†Data from Glavin *et al.* (2008) *Met. Plan. Sci.*, **43**, 399-413