NASA SCIENCE PLANETS

NASA ASTROBIOLOGY INSTITUTE

SIMONS FOUNDATION

Extreme Synthesis of Extreme Organics in Extreme Meteorites

Jason P. Dworkin

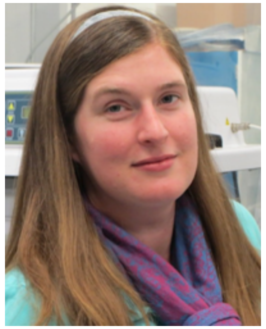
NASA Goddard Space Flight Center

51st ESLAB Symposium Extreme Habitable Worlds

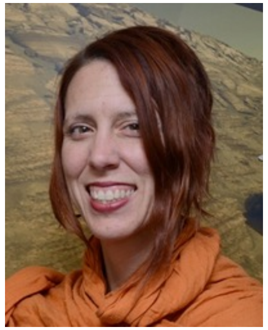
DANNY GLAVIN

JAMIE ELSILA

JOSÉ APONTE



HANNAH MCLAIN

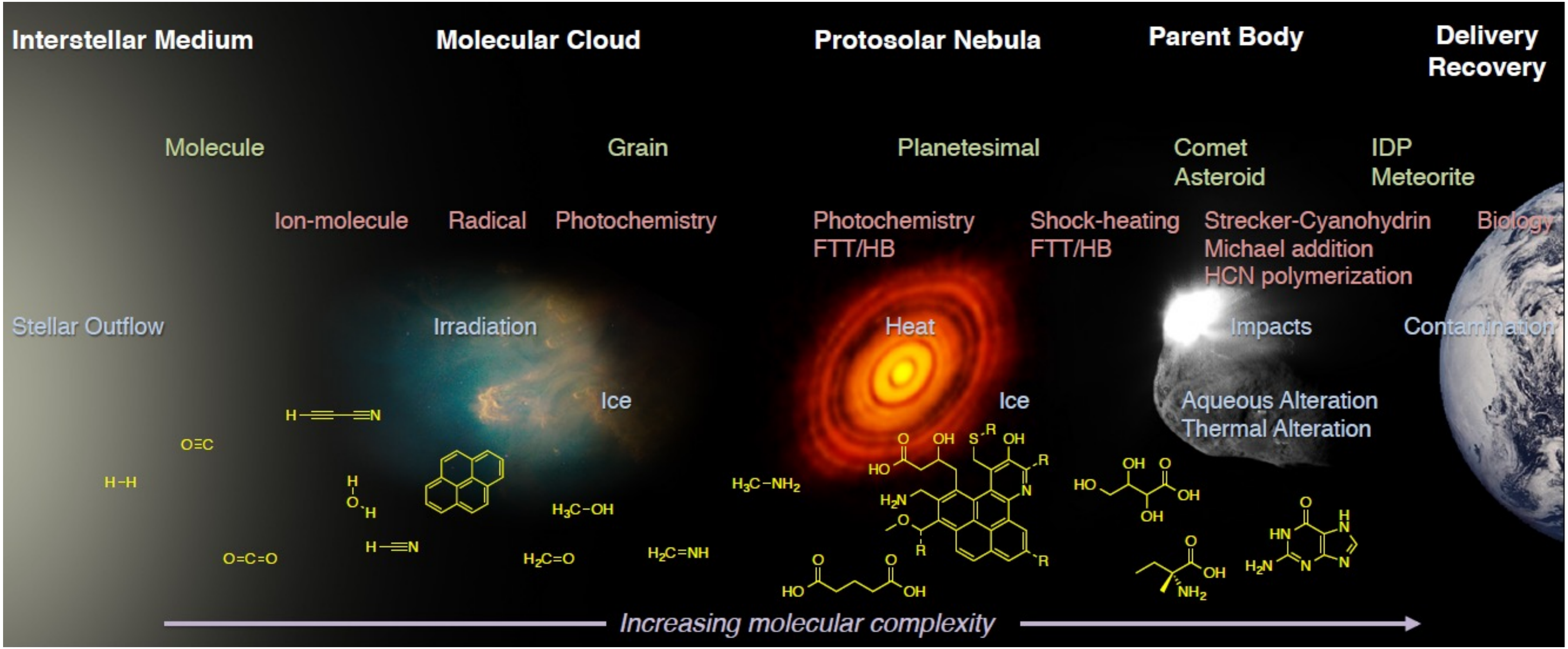


HEATHER GRAHAM

ERIC PARKER

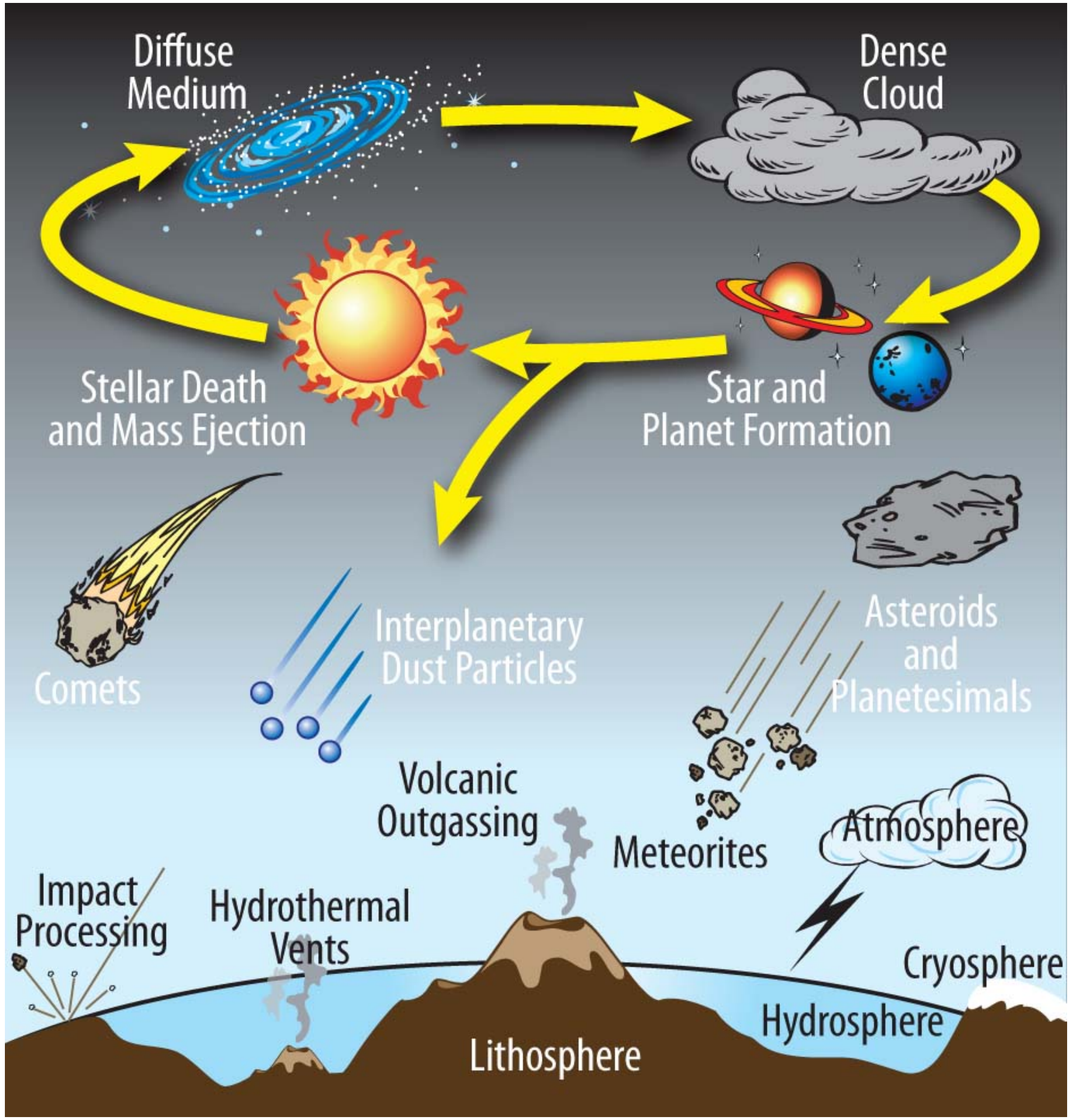
GSFC ASTROBIOLOGY ANALYTICAL LAB

Astrochemical Processes



Glavin et al. in *Primitive Meteorites and Asteroids*, ed. Neyda Abreu, in press.

Astrochemical Processes



Remote Observations & Simulations

***In Situ* Detection**

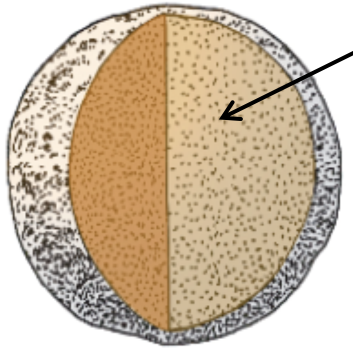
Sample Return

Lab Analyses

Simulations

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

Meteorites Sample Different Environments

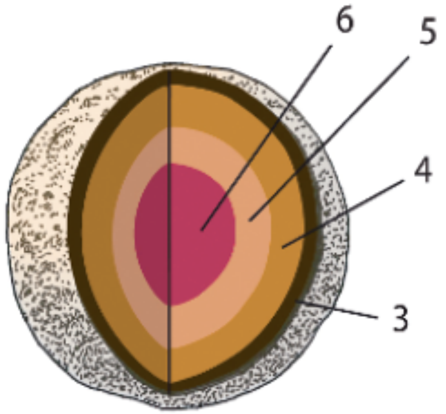


Icy regolith

Internal heating

Short-lived radioisotopes (e.g. ^{27}Al, ^{60}Fe)

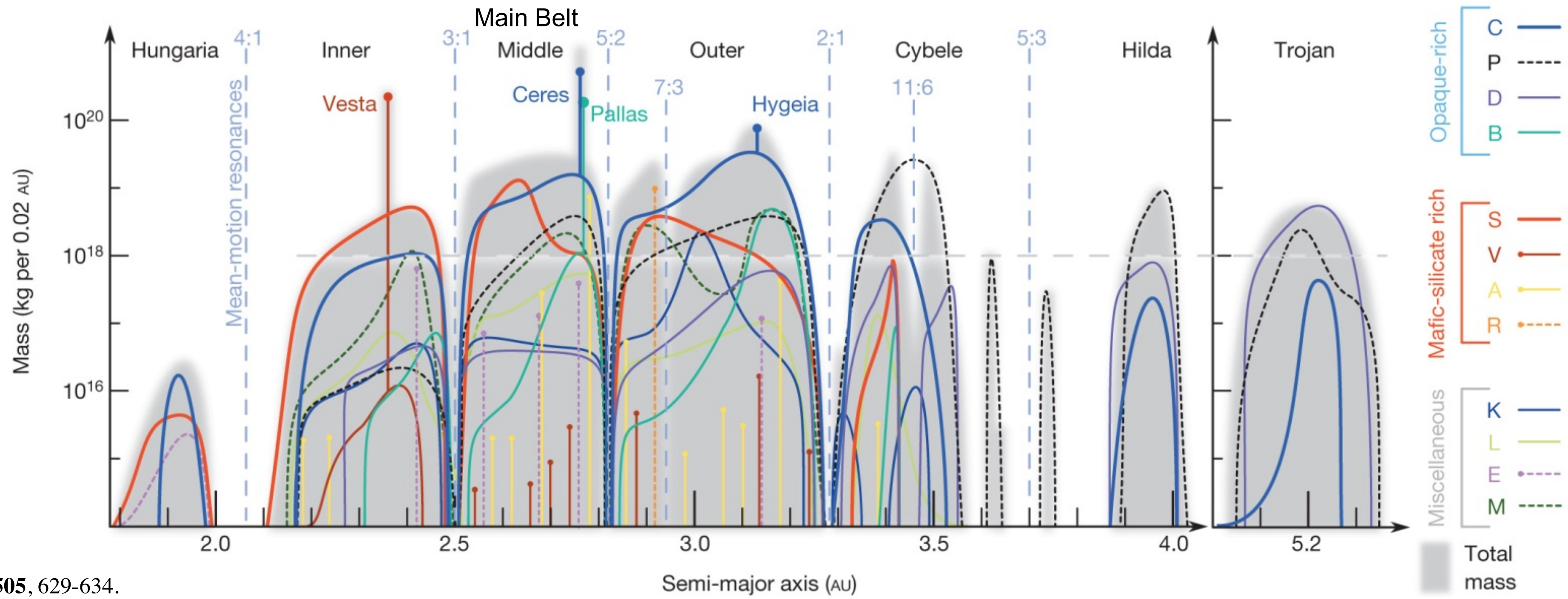
Thermal metamorphism + Aqueous alteration



Chondritic parent body

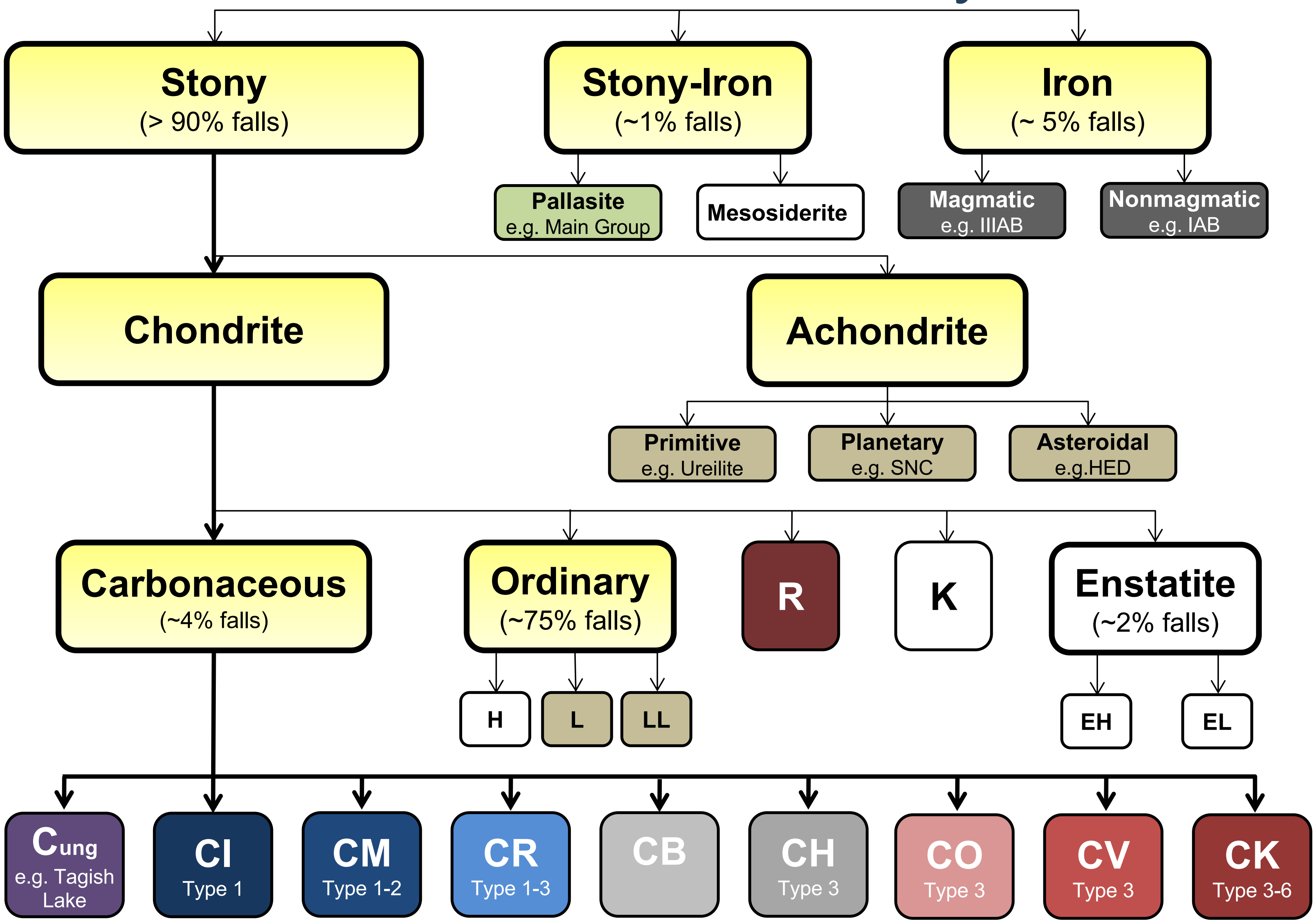
Onion shell model

After: Field Guide to Meteors and Meteorites, eds. Norton & Chitwood

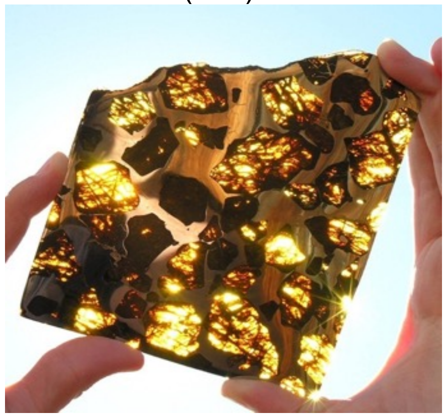


DeMeo and Carry *Nature* (2014) **505**, 629-634.

Meteorite Variety



Canyon Diablo Iron
(IAB)



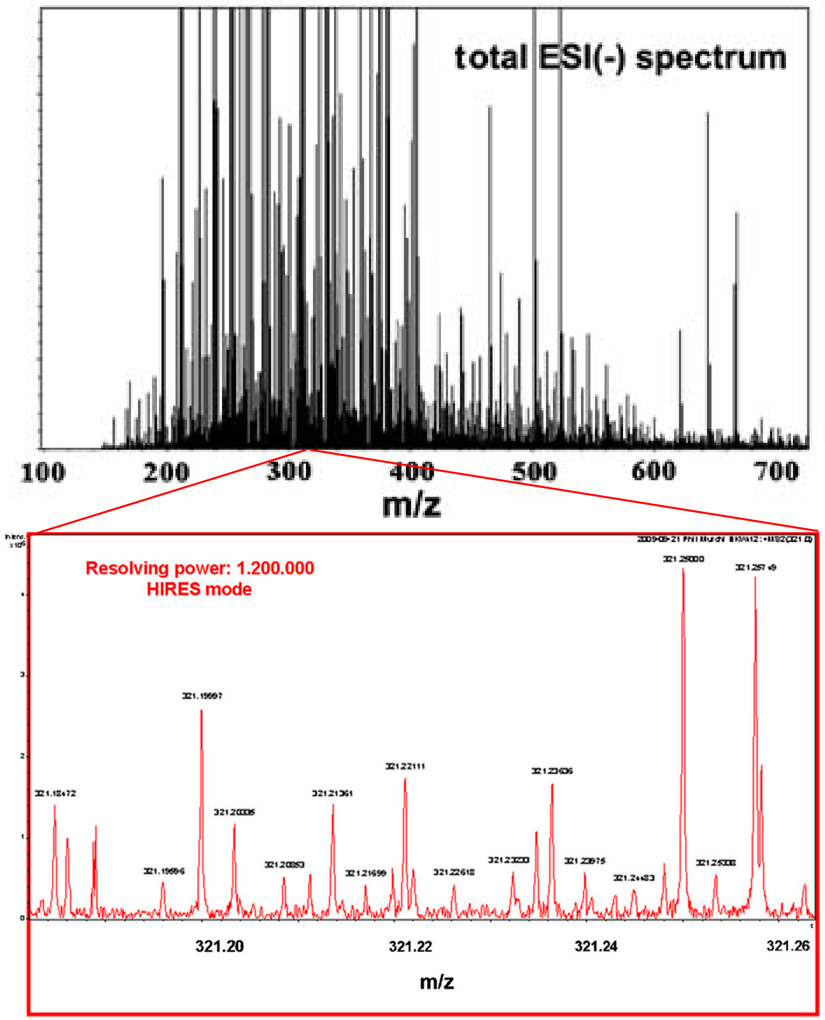
Fukang Pallasite
(Main Group)

Allende
Carbonaceous Chondrite
(CV3)

CM
Type 2

Murchison is Rich and Well Studied

Fell on September 28, 1969 in Murchison, Australia

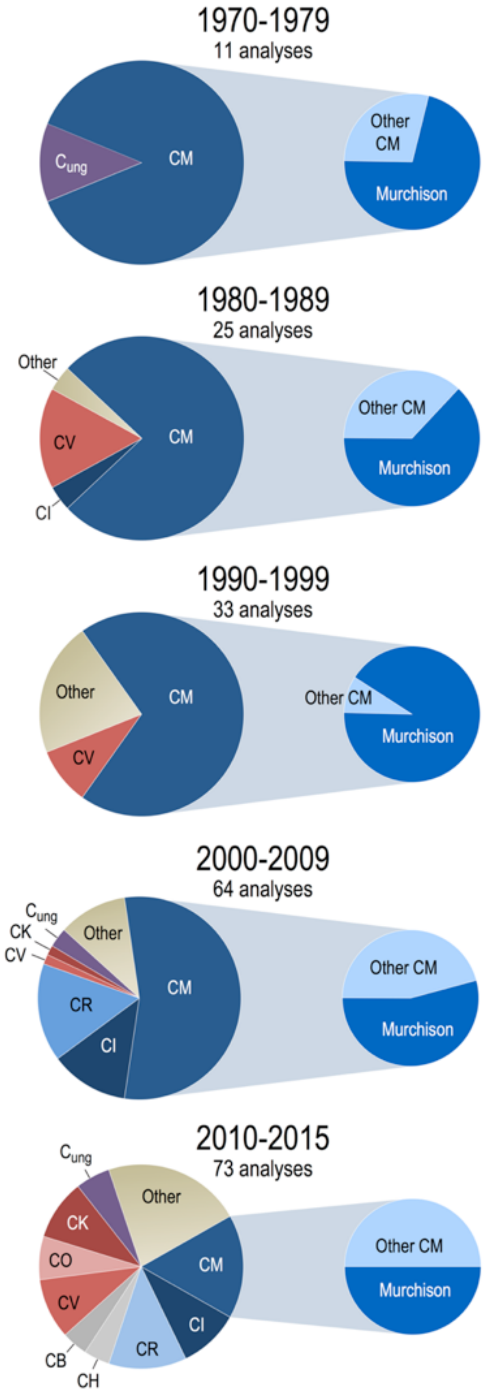


“likely millions of diverse structures”

Schmitt-Kopplin et al., *PNAS* **107**:2763–2768.

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
Amines	13
Pyridine carboxylic acids	>7
N-heterocycles	7
Phosphonic acids	2
Purines and pyrimidines	1

After Pizzarello, S., Cooper, G. W., and Flynn, G. J., (2006) *Meteorites and the Early Solar System II*, pp. 625-651, eds. D. S. Lauretta and H. Y. McSween

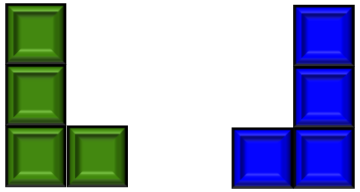


Elsila et al. (2016), ACS Cent Sci, **2**:370–379.

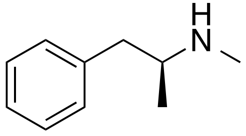
Why Study Amino Acids?

- **Astrobiology**
  - Molecules of life
  - But contamination is a concern
  - There's more to life than amino acids
- **Structural diversity**
  - Enough to probe chemistry and stable isotopes
  - But meteorites are heterogeneous
- **Chirality**
  - Meteorite amino acids can have abiotic chiral excesses
  - But contamination is a concern
- **Technology**
  - Commercial instrumentation exists
  - But it is not designed for complex low abundance samples
  - Sample workup is still an art

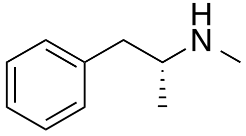
Origin of Homochirality is a Mystery



Homochirality – the presence of only L or only D enantiomers
Racemic – a 50/50 mix of L and D enantiomers



D-methamphetamine



L-methamphetamine

Life on Earth is (essentially) **homochiral:**

- L-amino acids (proteins)
- D-sugars (DNA and RNA)

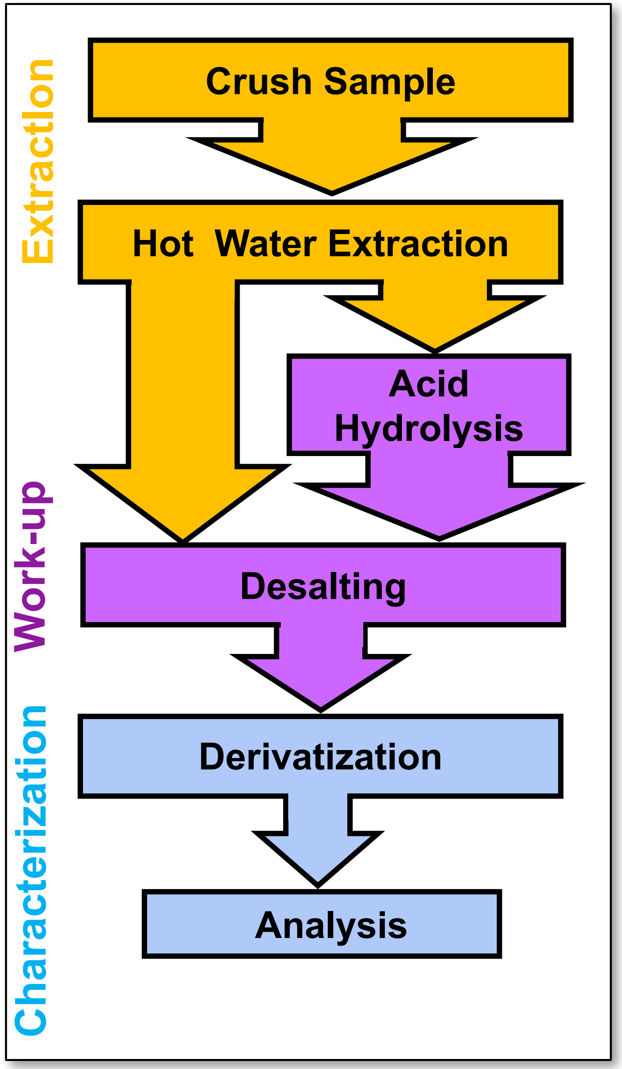
It takes chirality to make chirality

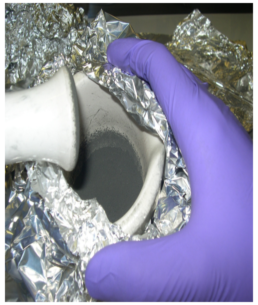
- Without a chiral driving force, syntheses produce **racemic** mixtures

How did the transition from racemic to homochiral occur on the ancient Earth?

Is it a sensor for habitable or inhabited worlds?

Amino Acid Analysis





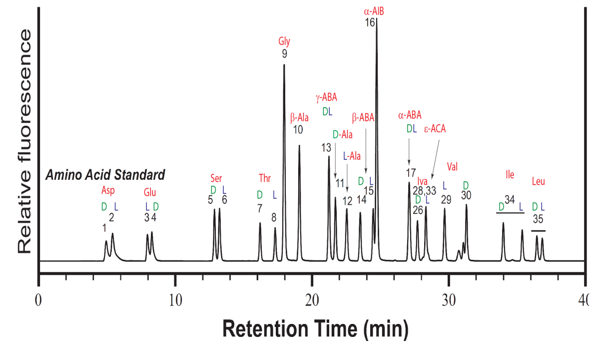
Crush Sample

Solvent Extraction and Optional Hydrolysis

Desalting

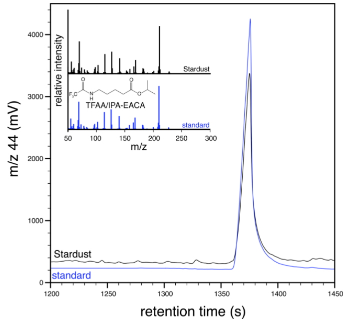
Derivatization of Purified Extract

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



Quantitation

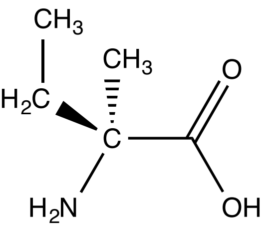
Gas chromatography with mass spectrometry and isotope ratio mass spectrometry



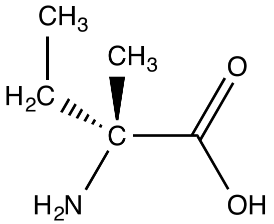
Compound-specific isotope ratios

Burton, et al. (2012) *Chem. Soc. Rev.*, **41**, 5459-5472.

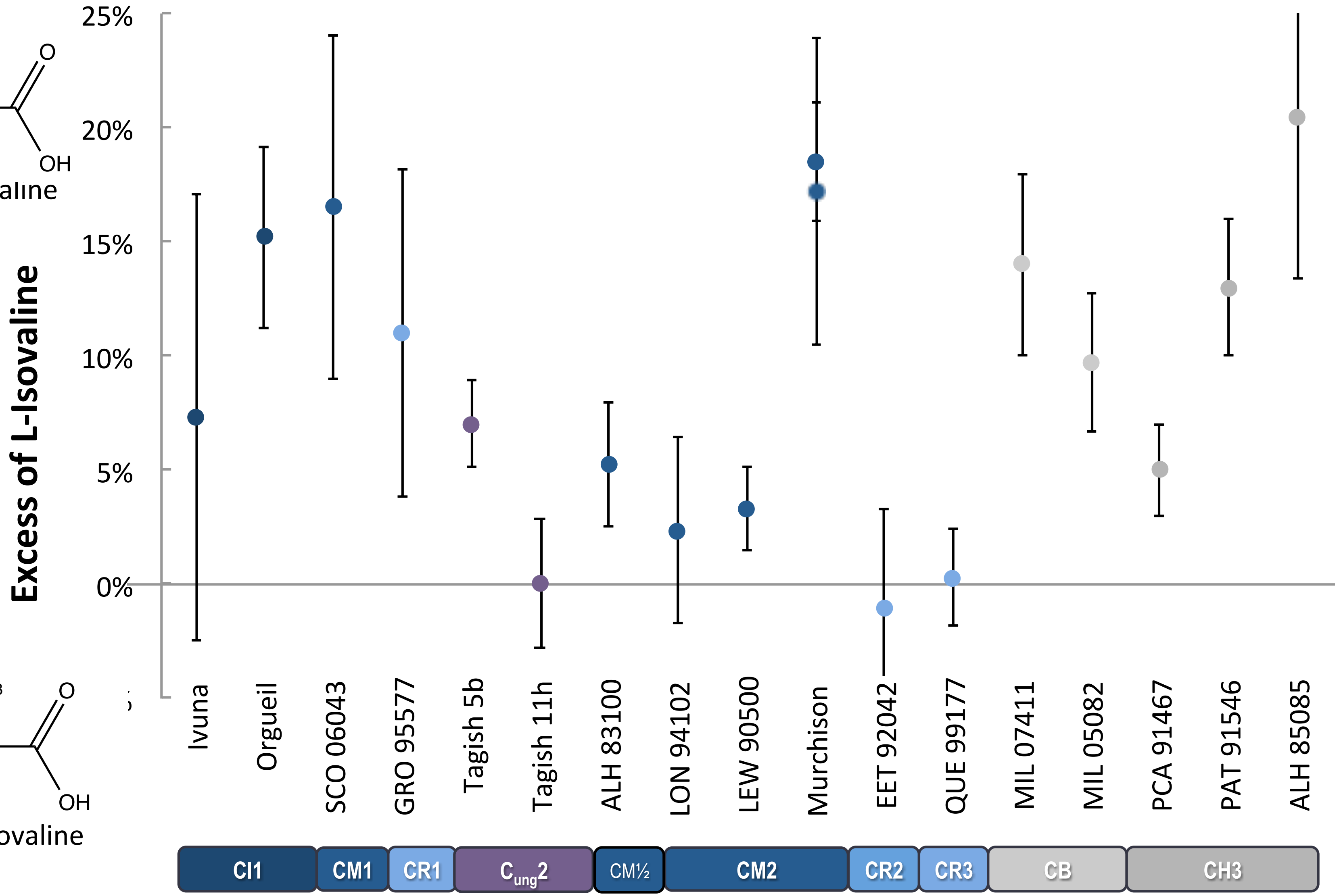
Excess L-Isovaline

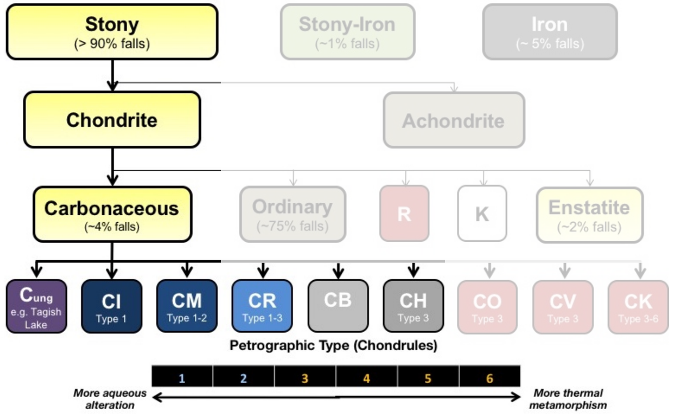


L-isovaline



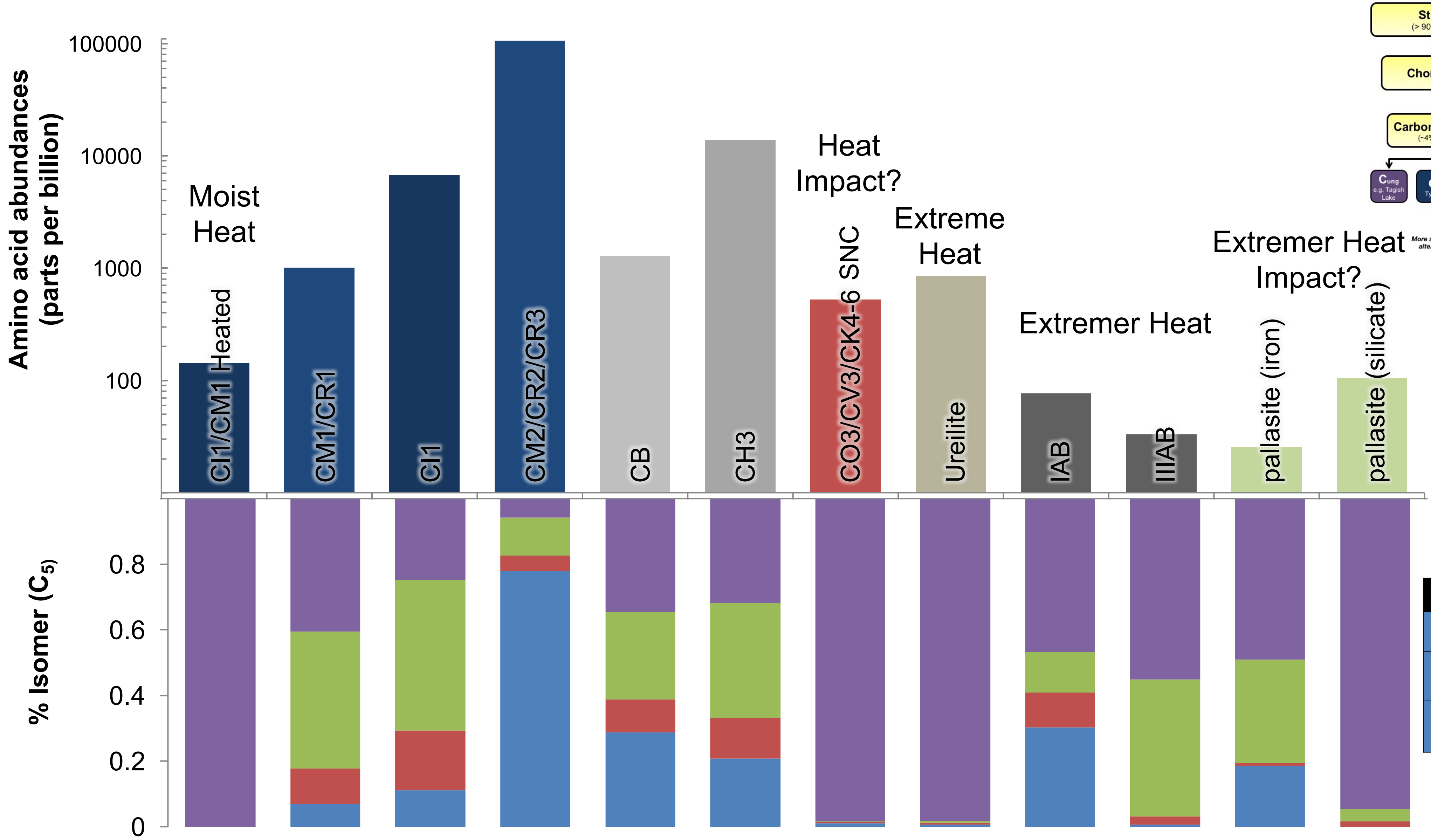
D-isovaline

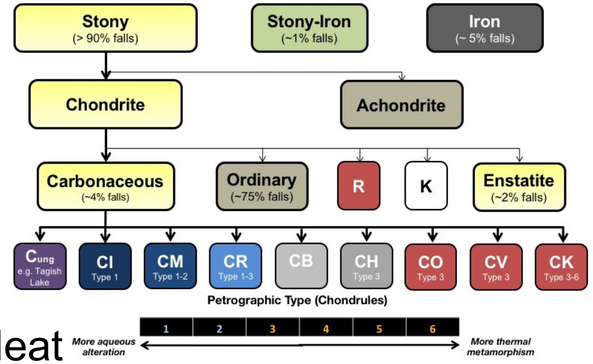


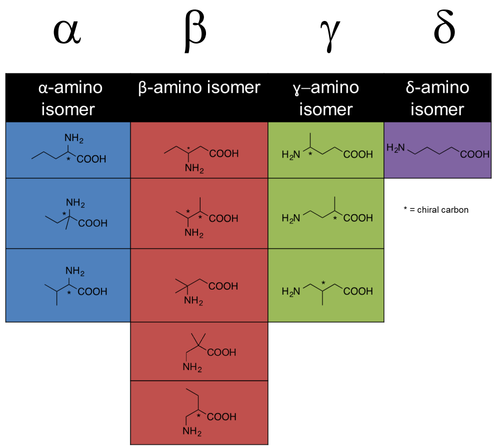


Elsila et al. (2016), ACS Cent Sci, **2**:370–379 and references therein.

Meteorites Vary in Amino Acid Abundance and Distribution







Amino Acid Synthetic Routes

CI Type 1

CM Type 1½ -2

CR Type 2-3

CO Type 3

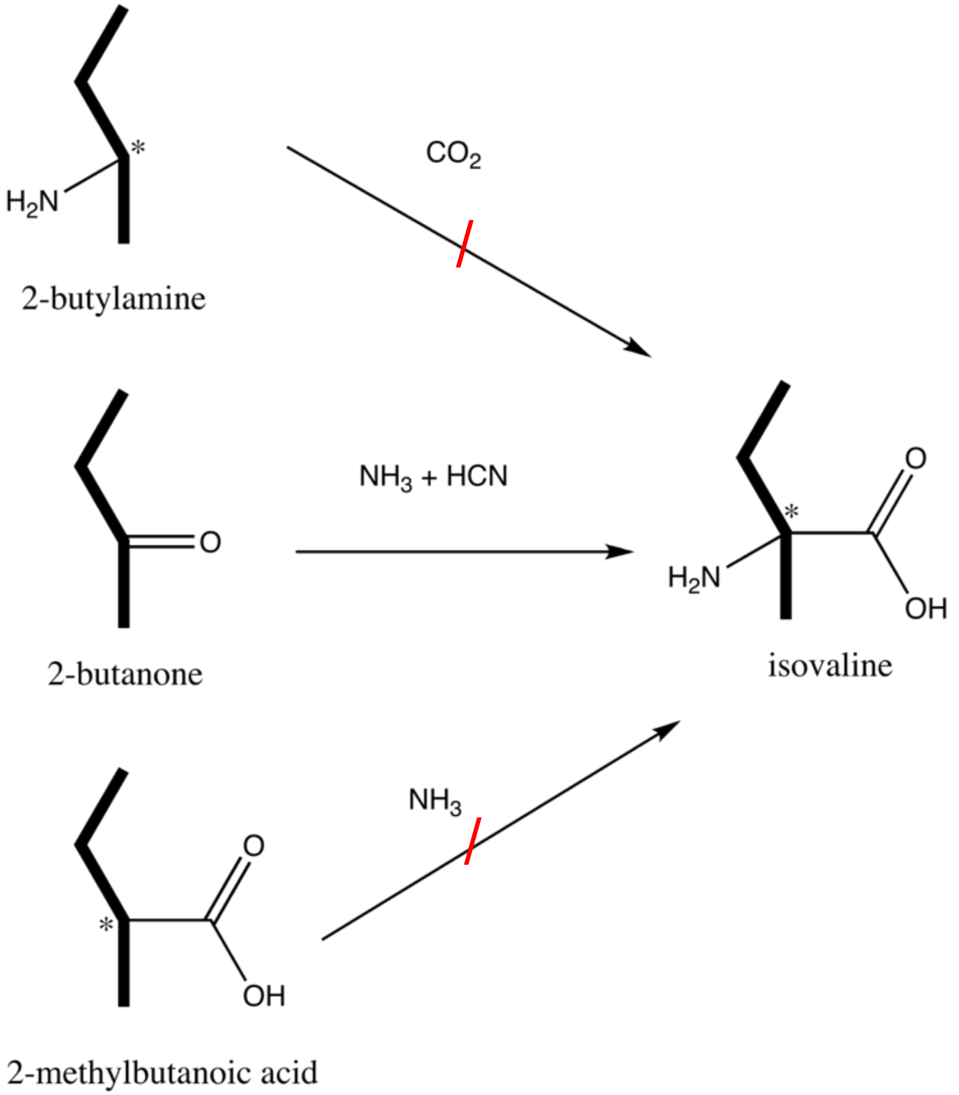
CV Type 3

CK Type 4-5

Similar ^{13}C to isovaline but Racemic (CI, CM, CR, CV, CO, CK)

Achiral

Racemic (CI, CM, CR)



L-Excess in some CM CI
Racemic in CR
Absent in CV, CO, CK

Aponte et al. (2017) *MAPS* **52**: 2632–2646
Aponte et al. (2016) *GCA* **189**: 296-311.
Aponte et al. (2015) *MAPS* **50**:1733-1749.
Aponte et al. (2014) *GCA* **141**:331-345.

Protein Amino Acid Excesses?

- Reports of protein amino acids with enantiomeric excesses of up to **60%** have been seen.
  - Glavin et al. 2012 (aspartic acid in C_{ung})
  - Pizzarello et al. 2012 (isoleucine in CR2)
- **Even greater caution** must be taken in analyzing these due to the constant specter of biologic contamination
- Complete analysis of potential interfering compounds and stable isotopic analysis is necessary

CR
Type 2

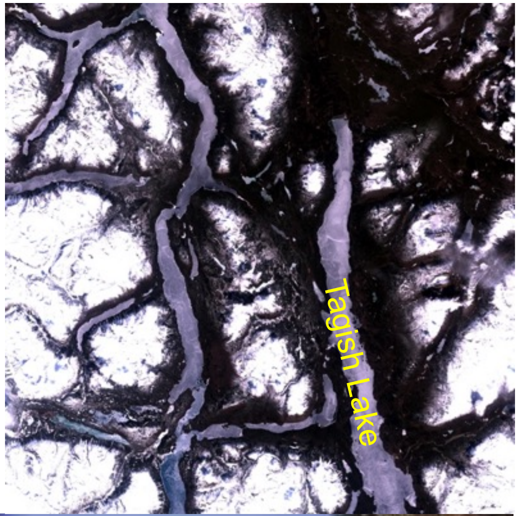
MET 00426

Tagish Lake

C_{ung}

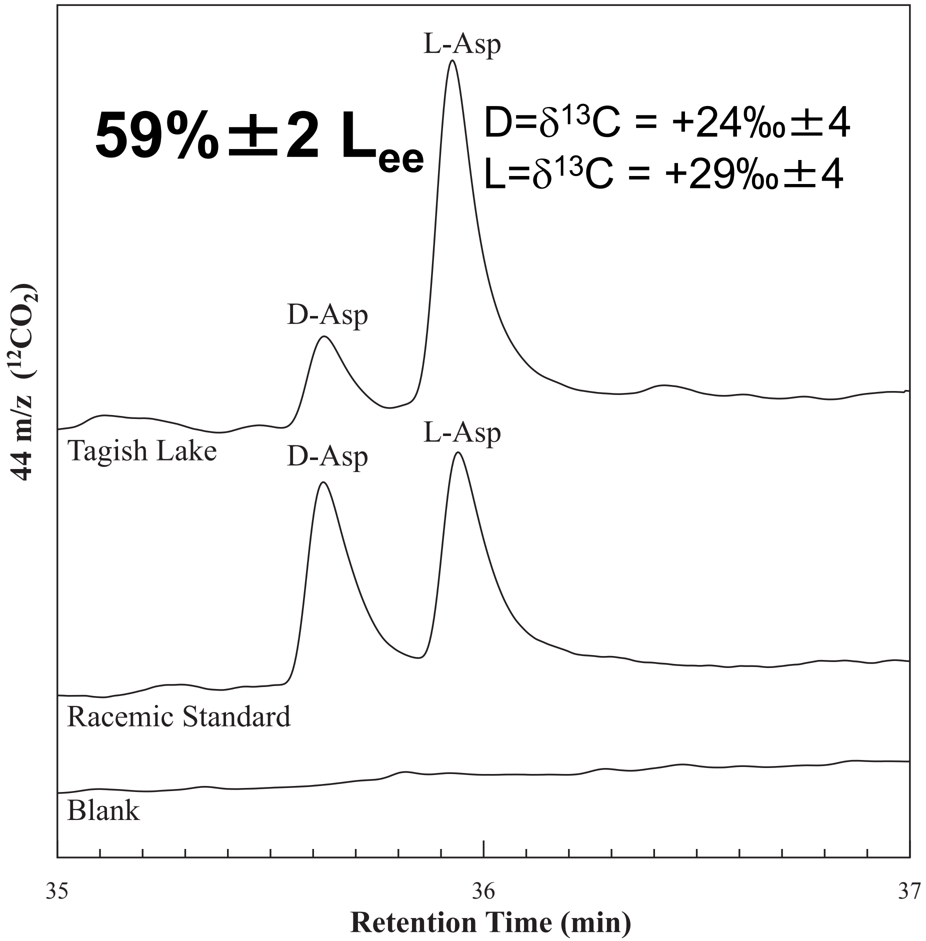
Cung

Greater Caution

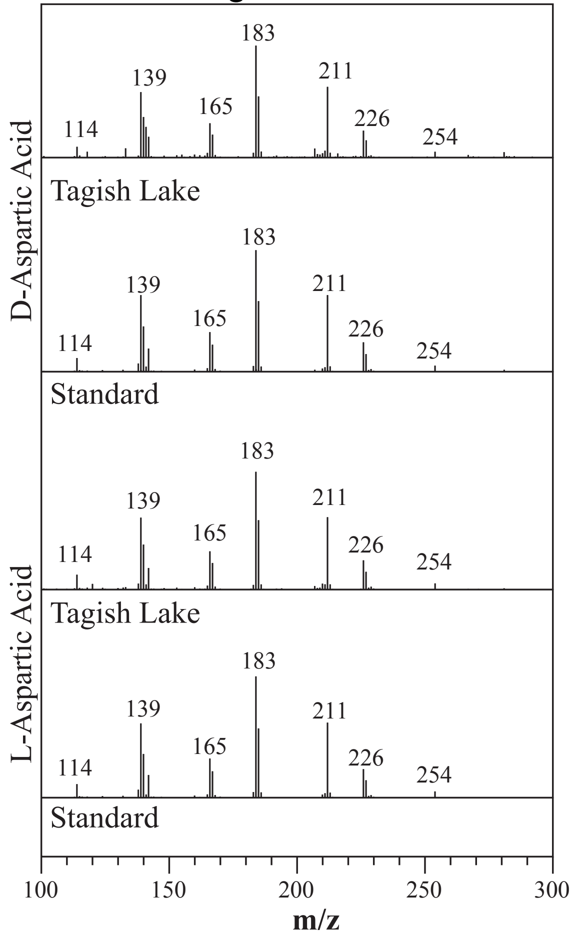


Glavin et al. (2012), MAPS, **47**:1347-1364.

GC-C-IRMS Chromatograms



GC-MS Fragmentation Patterns



No interfering compounds are possible based on mass and properties.

L_{ee}=55-99% L-Glu, L-Ser, and L-Thr suggested but unconfirmed, but isotopic measurements not possible due to low abundances or co-elution.

Racemic Ala, Nva, Iva (though fragment 5b shows Iva 7% excess, but no isotopes).

Extraterrestrial Samples

Geoff Notkin and Steve Arnold

"Alpha" Kansas, USA Brenham Strewn Field

Muawia Shaddad, Peter Jenniskens, and U. Khartoum students

Nubian Desert, Sudan. Almahata Sitta Fall

Scott Messenger and Danny Glavin with Dante Lauretta (background)

MacAlpine Hills, Antarctica ANSMET

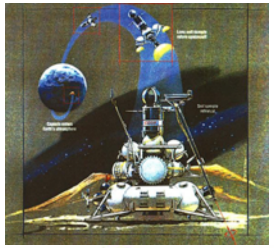
NASA's OSIRIS-REx mission to collect 60-2000g of

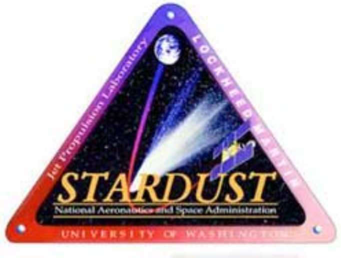
asteroid Bennu surface and return to Earth

More contaminated ⟷ Less contaminated

Sample Return Missions:
The gift that keeps on giving

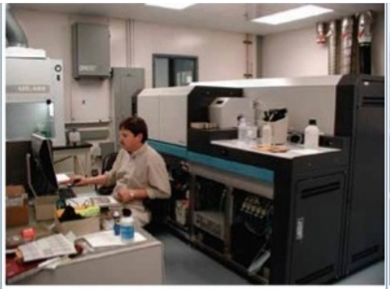
- Moon (1969-72, 1976)
  - NASA Apollo 11, 12, 14, 15, 16, and 17
  - Soviet Luna 16, 20, and 24
- Solar wind (returned 2004)
  - NASA Genesis
- Comet tail (returned 2006)
  - NASA Stardust
- Stony Asteroid (returned 2010)
  - JAXA Hayabusa
- Carbonaceous Asteroid
  - JAXA Hayabusa2 (launch 12/14, return 12/20)
  - NASA OSIRIS-REx (launch 9/16, return 9/23)



Complex Lab Instruments Cannot Be Flown on Spacecraft


NanoSIMS


LA-ICP-MS


LC-FT-MS


FE-STEM


FT-IR


Electron Microprobes


GC-MS/c-IRMS


LC-TOF-MS


SEM


FIB


TOF-SIMS


GC-MS


IR Microscope

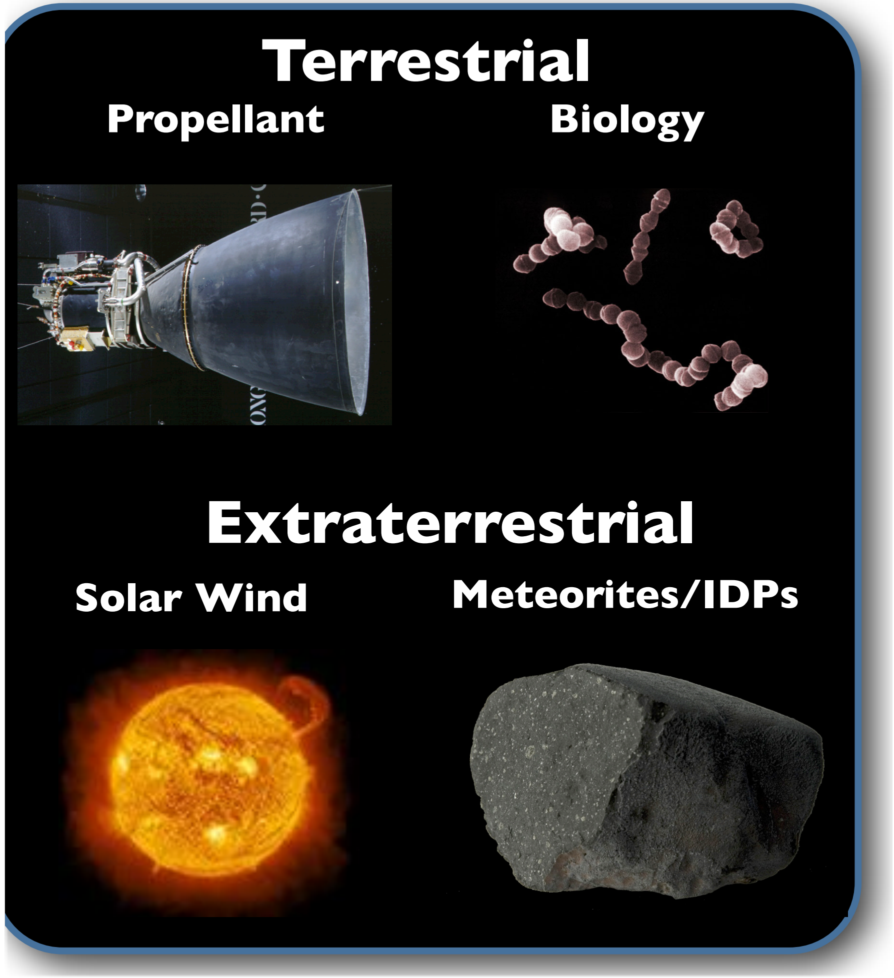

Accelerator Mass Spectrometer


ALS Synchrotron Beamline for XANES


Future Scientists will Invent New Instruments

Lunar amino acids and potential sources

- Amino acids 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**

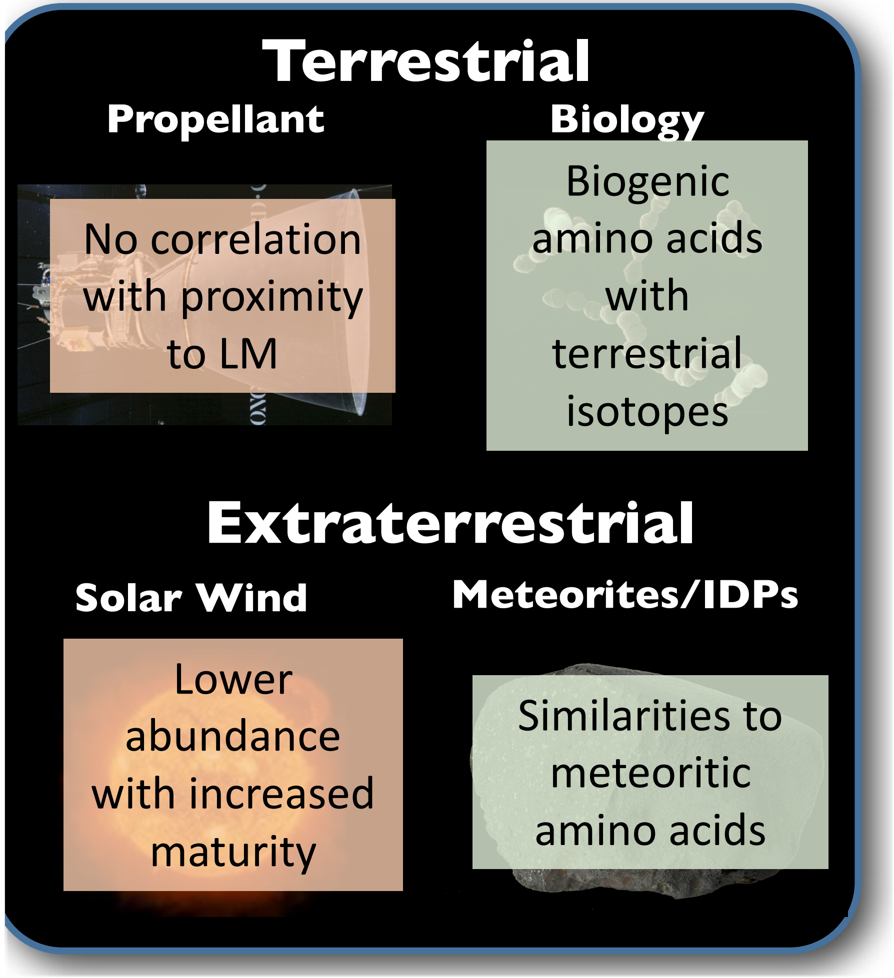


Elsila et al. (2016) *Geochim. Cosmochim. Acta* **172**, 357-369

Lunar amino acids and potential sources

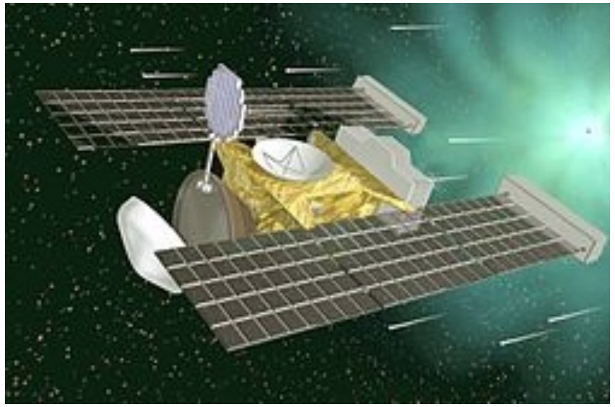
- Re-analysis of Apollo 16 and 17 samples
  - No correlation with location
  - Least mature samples had highest abundances
  - Majority of amino acids came from bound precursors, consistent with biology; some samples consistent with meteoritic bound abundances
  - Measurable carbon isotopes in terrestrial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

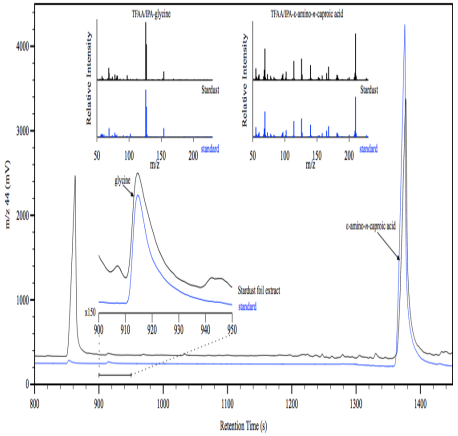
- Amino acids detected in lunar samples primarily from **terrestrial contamination with** some contribution possible from **meteoritic infall**



Cometary Amino Acid

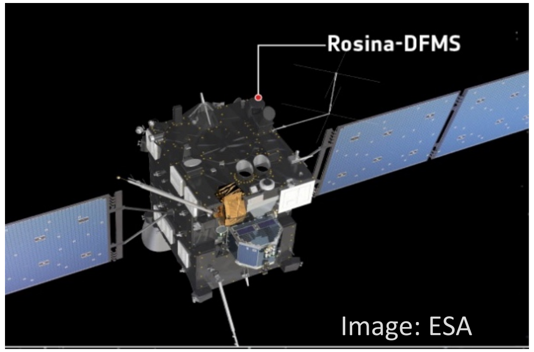
- Stardust first detection of cometary **glycine** in 81P/Wild 2
  - Glycine confirmed cometary, $\delta^{13}C = +29‰ \pm 6‰$
  - Cometary methylamine and ethylamine likely, β-Alanine possible
  - Witness material from Stardust spacecraft and curation essential to determining contamination vs. cometary origin

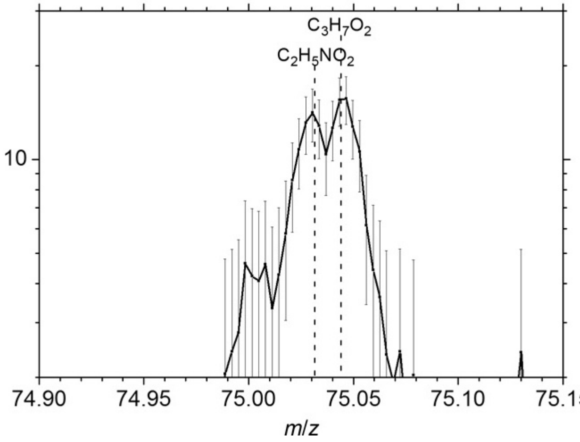




Sandford et al., (2006) *Science* **314**, 720-724.
Glavin et al., (2008) *Meteorit. Planet. Sci.* **43**, 399-413.
Elsila, et al. (2009) *Meteorit. Planet. Sci.* **44**, 1323-1330.

- Rosetta first detection of *in situ* **glycine** at Comet 67P/Churyumov-Gerasimenko
  - ROSINA mass spectrometer observed glycine, methylamine, and ethylamine in multiple observations





Altwegg et al. (2016) Sci Adv **2**:e1600285

Comet nucleus sample return needed to detect less-abundant compounds

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

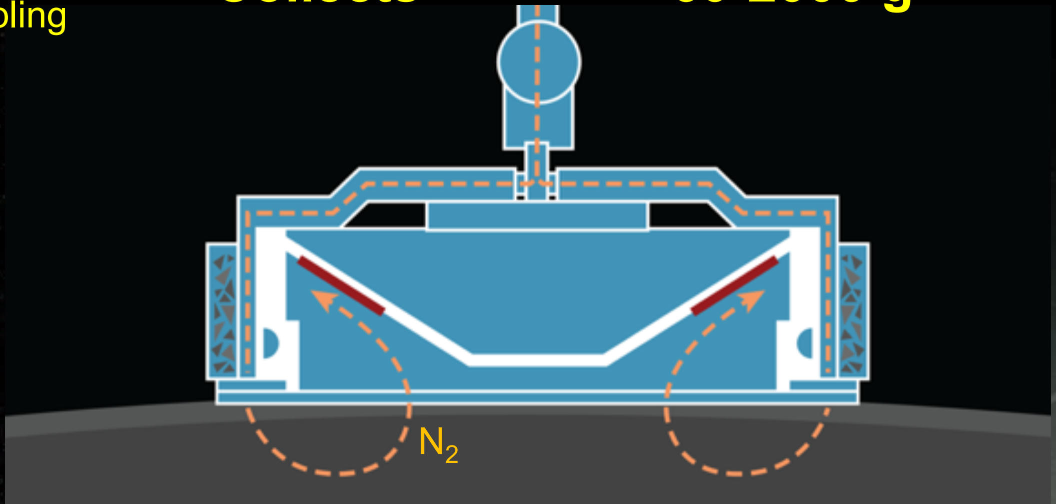
Resource Identification: Map the chemistry and mineralogy of a primitive carbonaceous asteroid

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

Approaches Bennu July 2018
Map & Rehearse until July 2020 Sampling

Collects **60-2000 g**



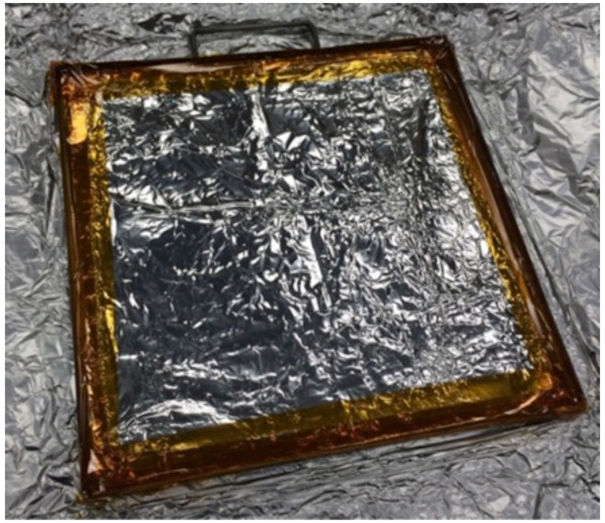
Earth return, Utah, USA
8:53 am UTC-6, 24 September 2023

Conclusions

- **Amino acids are present in many extreme extraterrestrial environments**
  - Meteorites of different groups from modest to molten
  - Lunar samples
  - Cometary material
- **Diversity in structures and distributions may reflect different formation histories**
- **Chiral excess is not a guaranteed measure of life**
  - Necessary, but insufficient for life
- **Amino acid analysis is also valuable in determining contamination in returned samples**
  - Witness materials are essential as “controls”

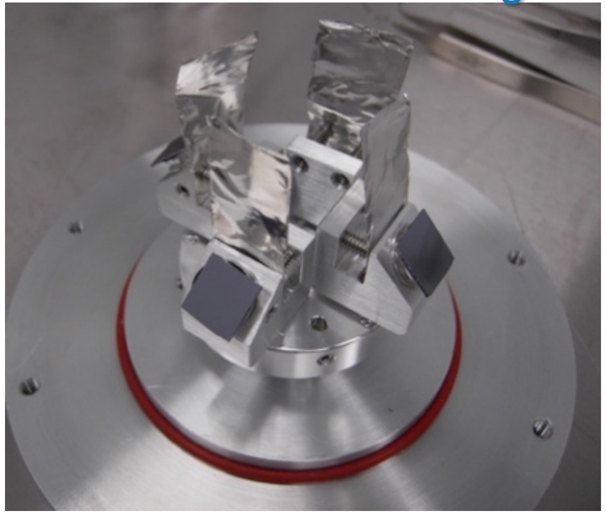
Preparing for OSIRIS-REx Sample Return:
Documenting Contamination Before Flight

- OSIRIS-REx contamination control requirements: <180 ng/cm^2 of amino acids on sampler head surface (0.96 ng/cm^2 achieved)
- Level 100 A/2 particles and films
- Monitored during assembly via witness plates
- Analysis and archiving of materials for comparison with future sample analyses

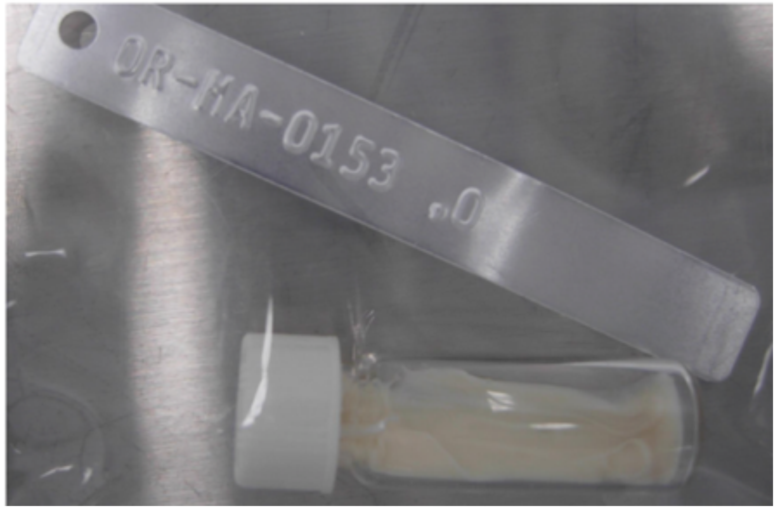


Contamination Monitoring Plates

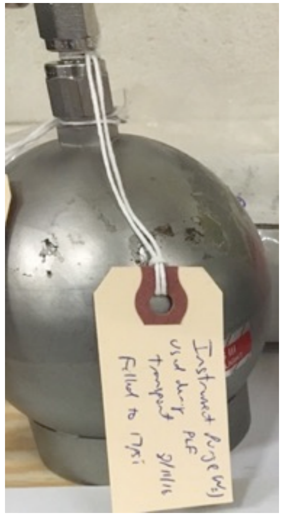
Monopropellant



Contamination Knowledge Plates



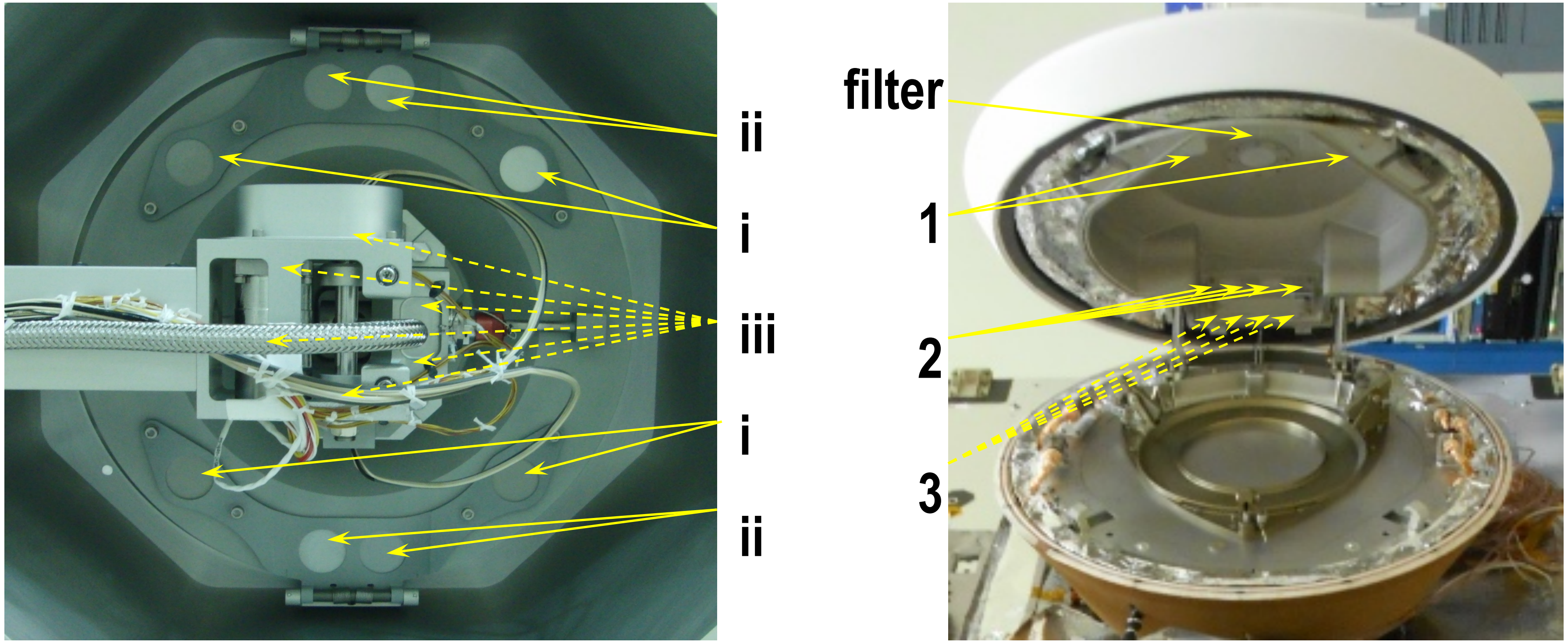
Material Archive



Gases

Dworkin et al. *Space Science Reviews* (in press)
https://arxiv.org/abs/1704.02517

Preparing for OSIRIS-REx Sample Return:
Documenting Contamination During Flight



2014	5/2016	9/2016	9/2023	9/2023	10/2023 -
Assembly & Test	**Launch Operations**	**Space**	**Recovery**	**Curation**	
Sampler Assembly	Launch	Bennu Arrival; Sampling	Earth Return; Recovery; Opening SRC	Disassembly of Sampler; Curation	

- Pre-Collection Witnesses (TAGSAM) ii
- Post-Collection Witnesses (TAGSAM) iii
- Pre-Stow Witnesses (SRC) 2
- Post-Stow Witnesses (SRC) 3
- Always Open Witnesses (TAGSAM& SRC) i & 1

Dworkin et al. *Space Science Reviews* (in press); https://arxiv.org/abs/1704.02517