THE IMPORTANCE OF MASS SPECTROMETRY IN THE 2061 PROGRAM

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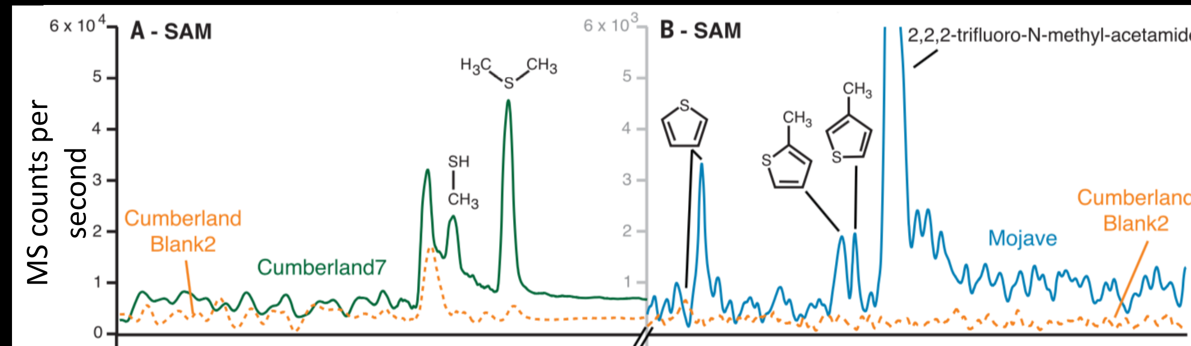
Some Recent History of MS in Space

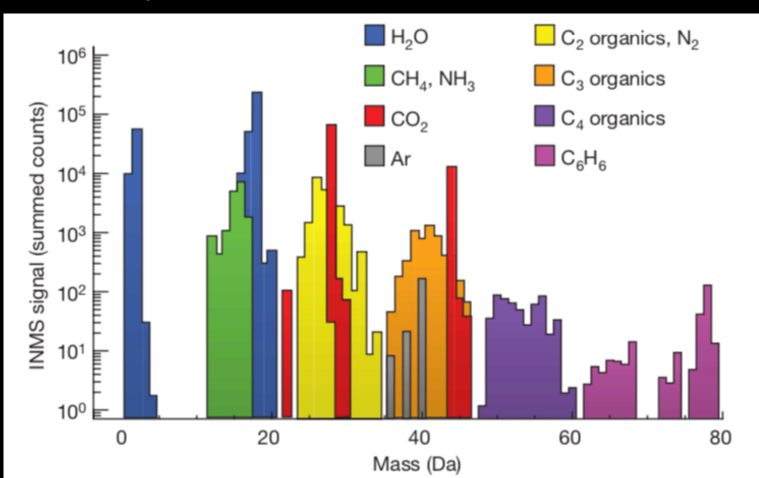
Right: Martian organics from Eigenbrode+, 2018



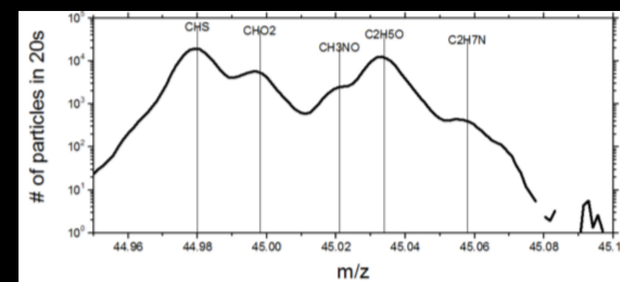
Curiosity's SAM
Target: Mars
Results: Identification of Martian organics
Interpretation Challenges: sample handling, resolution of 0.1 Da, low abundances

Cassini's INMS
Target: Saturnian system
Results: composition of Enceladus plume, Titan atmosphere, Saturn ring rain
Interpretation Challenges: unit mass resolution

Below: Enceladus spectrum from Waite+, 2009

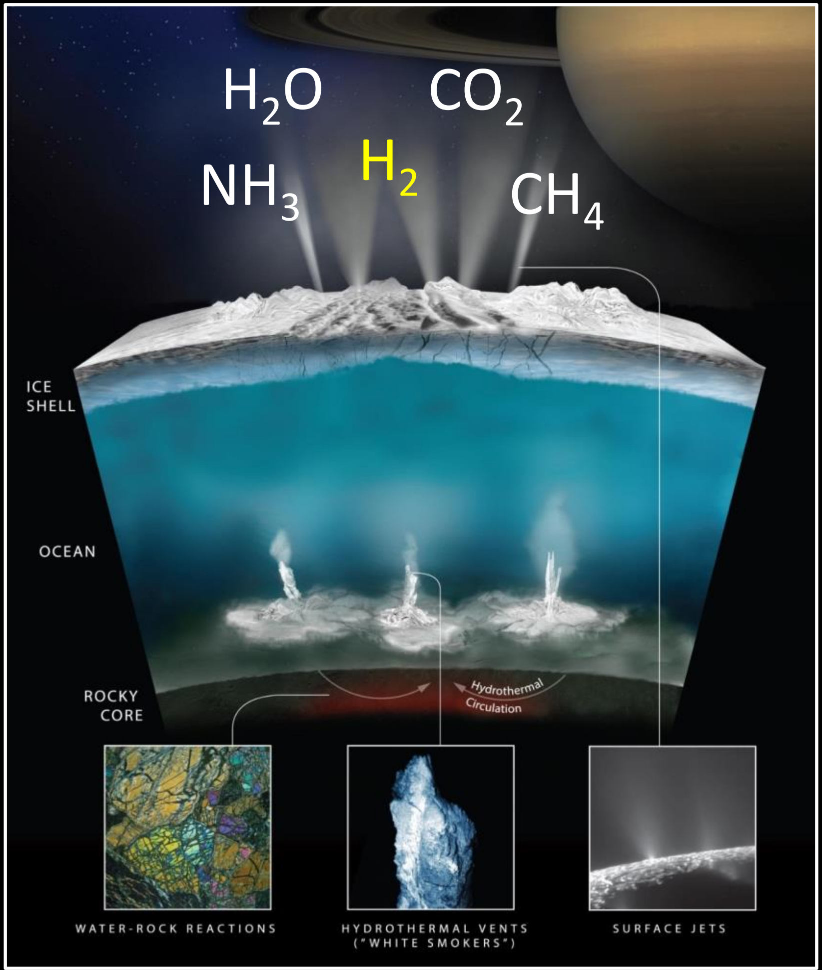


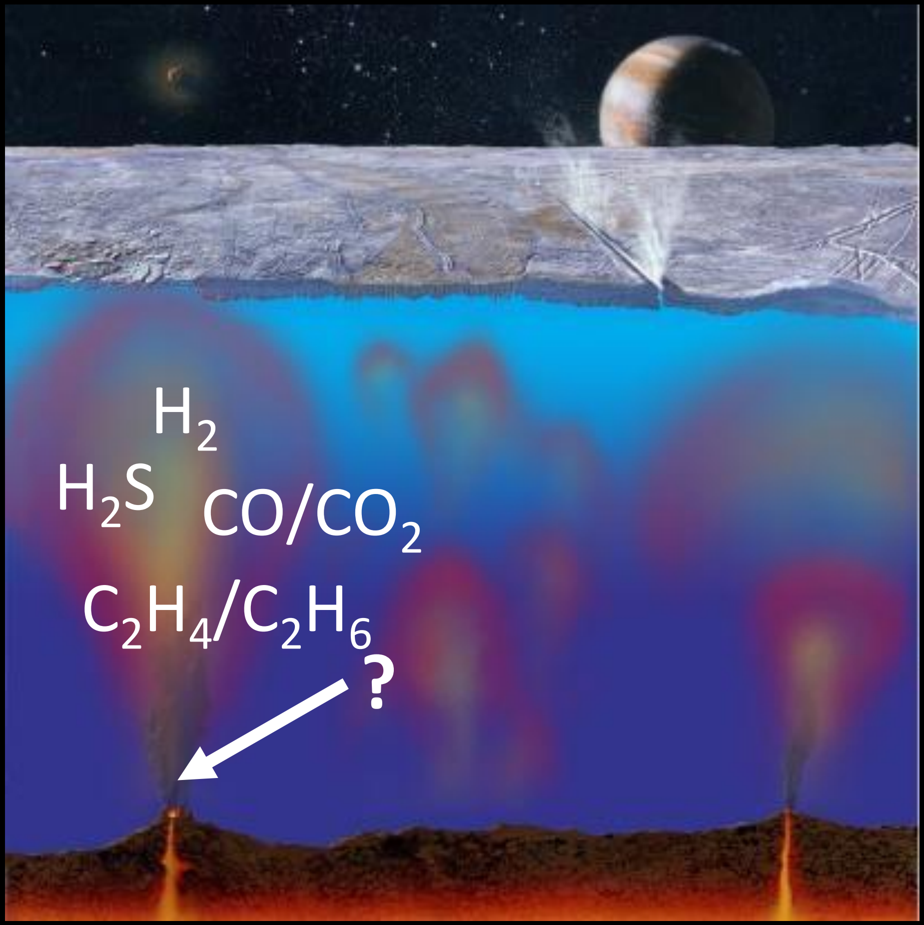
Rosetta's ROSINA
Target: Comet 67P/Churyumov-Gerasimenko
Results: cometary noble gas budgets, ID of organics
Interpretation Challenges: calibration



Above: Resolution of 45 u fragments at Comet 67P from Altwegg+, 2017

Searching for Life in Ocean Worlds





Enceladus

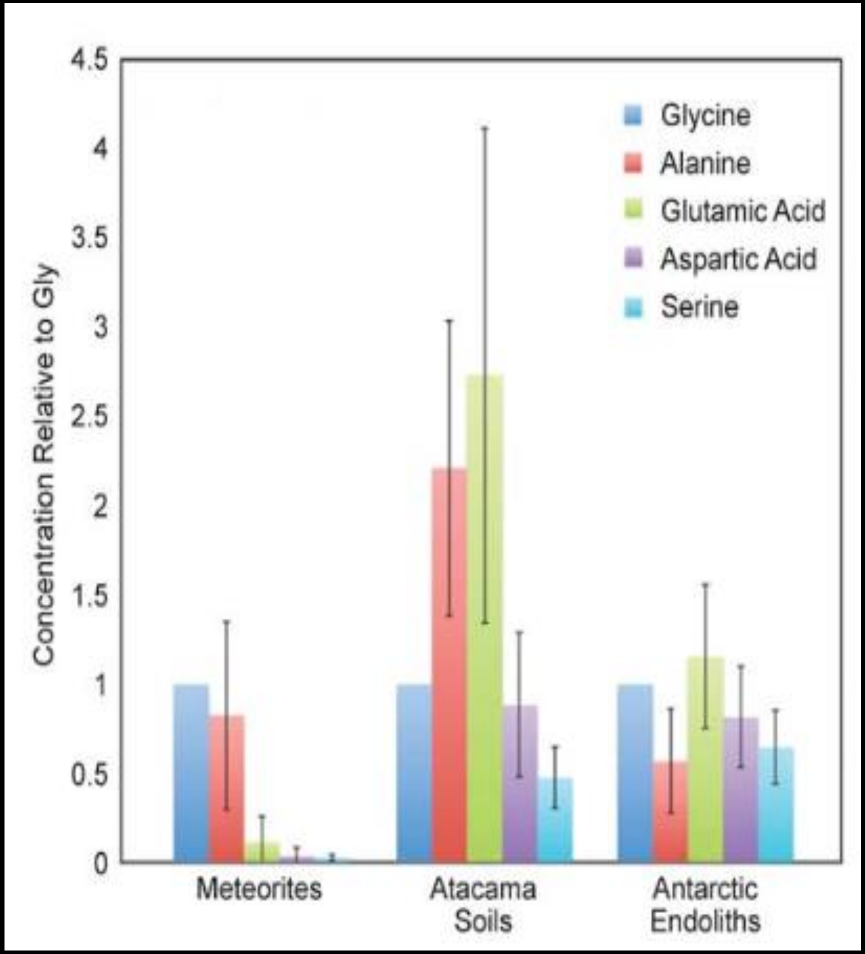
Europa

Three Tests for Biological Processes

1. Amino acid pattern different for abiotic and biological sources

LEGO principle: life chooses a small number of building blocks out of the wide spectrum of available organic molecules.

Free energy corollary: Relative abundances of biomolecules are not determined by the thermodynamic gradients (free energies of formation) or kinetics of the system.

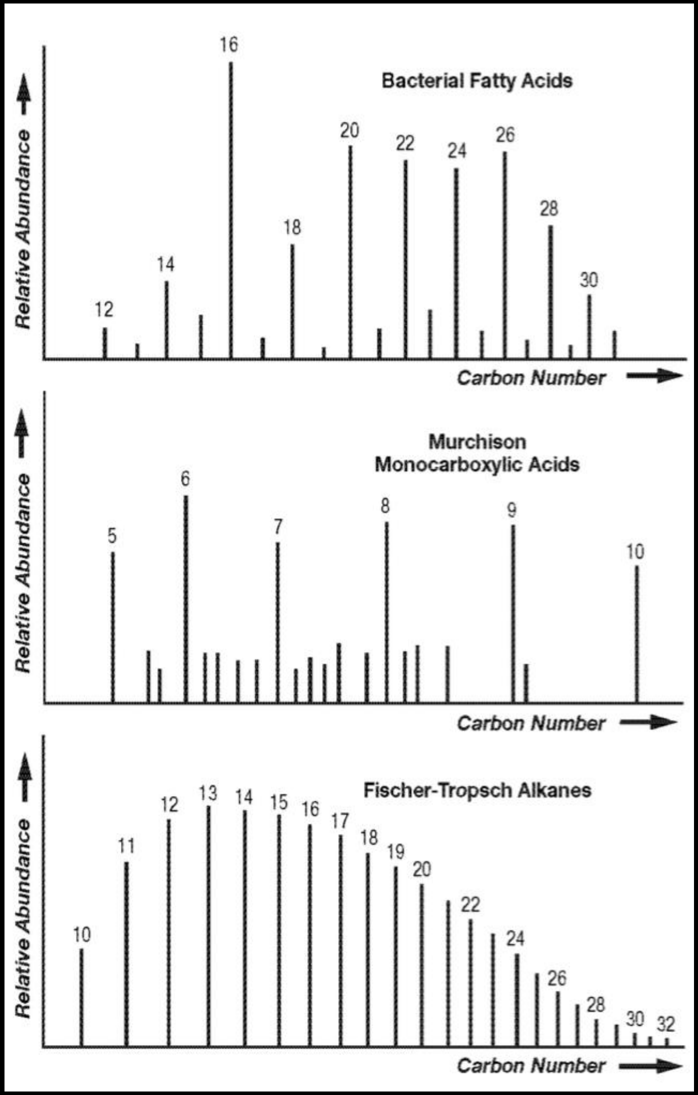


Three Tests for Biological Processes

2. Repeating subunits and clustering in membrane-building molecules

LEGO principle: life chooses a small number of building blocks out of the wide spectrum of available organic molecules.

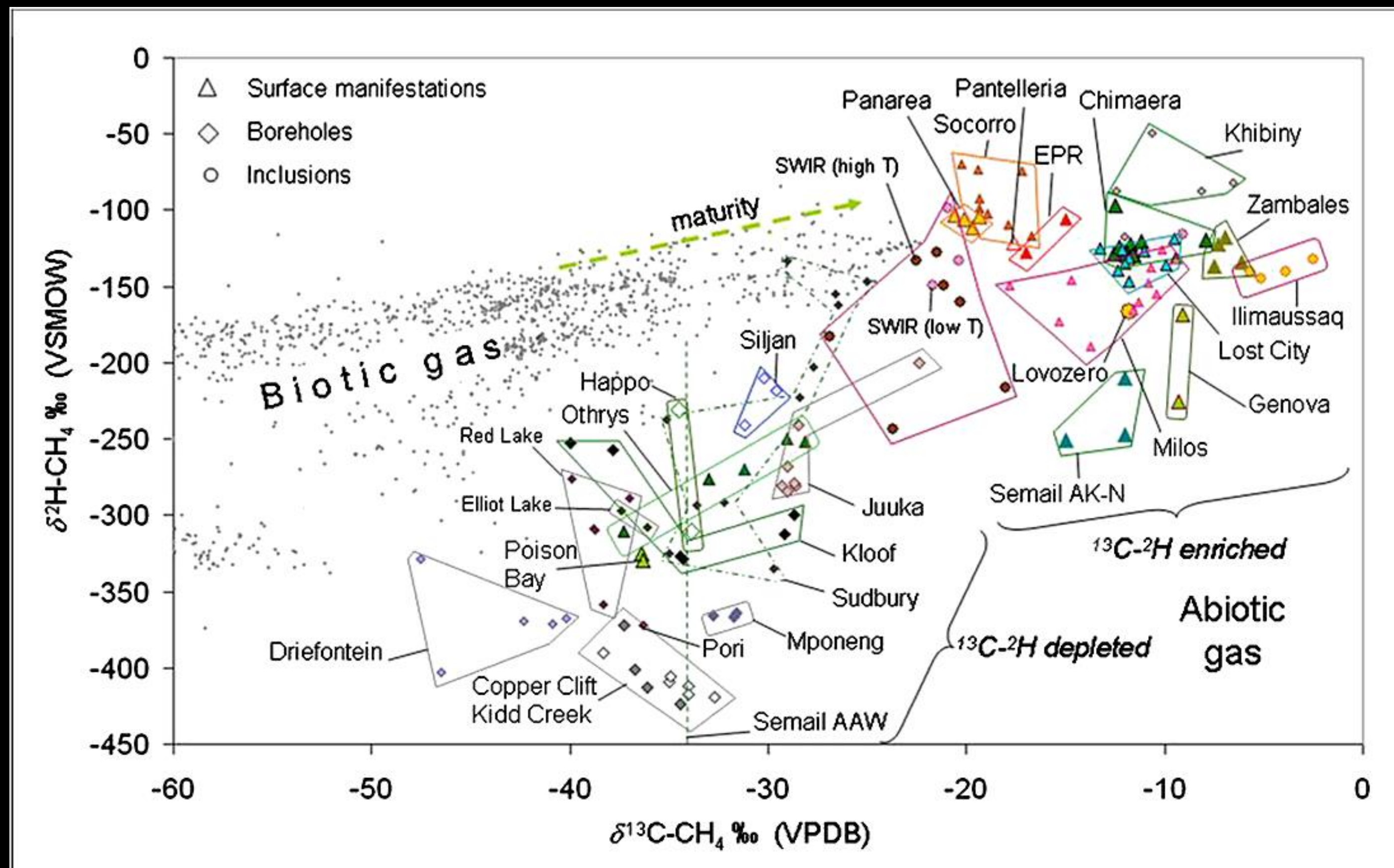
Pattern recognition ordering in large organic compounds can be used to search for signs of life.



Three Tests for Biological Processes

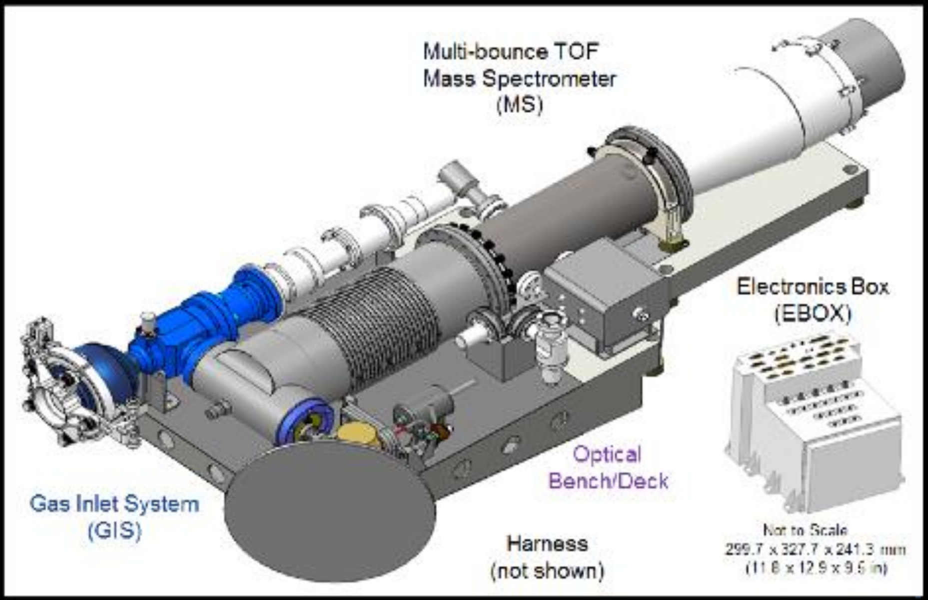
3. Combined isotopic and compositional trends

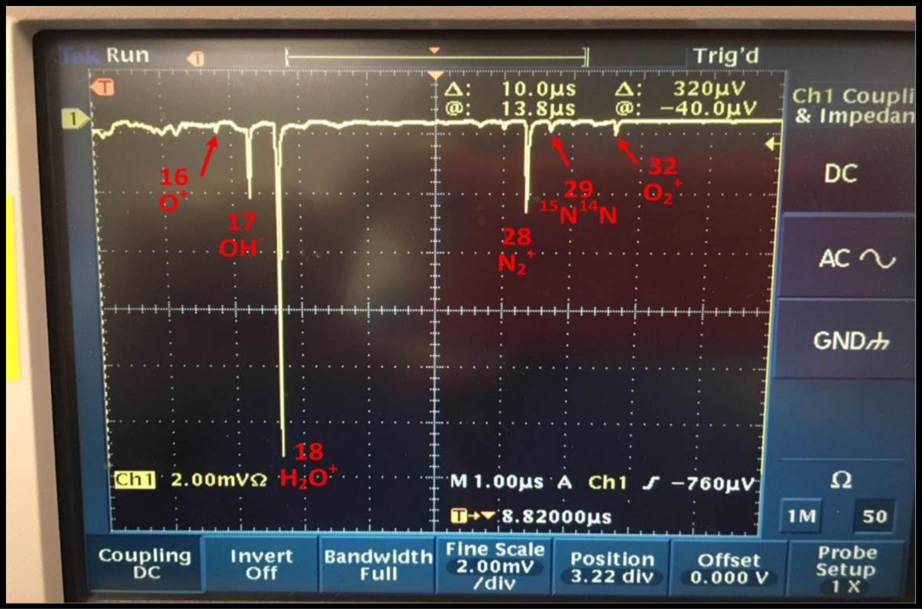
In addition to specific patterns and ratios of organic compounds, biological activity leads to isotopic patterns, such as the biotic versus abiotic regions for methane isotopes.



Testing extraterrestrial environments for these features requires (1) **higher resolution** to separate similar masses and improve identification and (2) **higher**

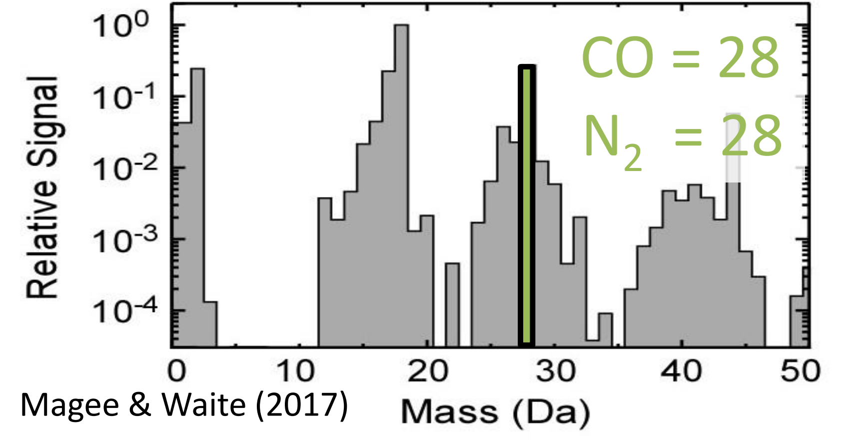
MASPEX Investigation Overview





- **Science Team**
  - PI: Waite, SwRI
  - Sci Co-I's:
    - SwRI: Bolton, Teolis, Wyrick, Brockwell, Glein
    - Wash-U: McKinnon
    - ASU: Shock, Zolotov
    - SETI: McGrath
    - CNRS: Mousis
    - Imperial College: Sephton
  - Instrument optical design: G. Miller, SwRI

- **Instrument Architecture**
  - Multi-bounce, time of flight (MBTOF) mass spectrometer
  - Instrument control and telemetry collection electronics in vault (microprocessor based)
  - HV distribution and science data collection at instrument
- **Instrument Heritage**
  - Rosetta ROSINA: TOF and HV
  - Cassini INMS – S/C Operations
  - Flight Software - MMS and CYGNSS

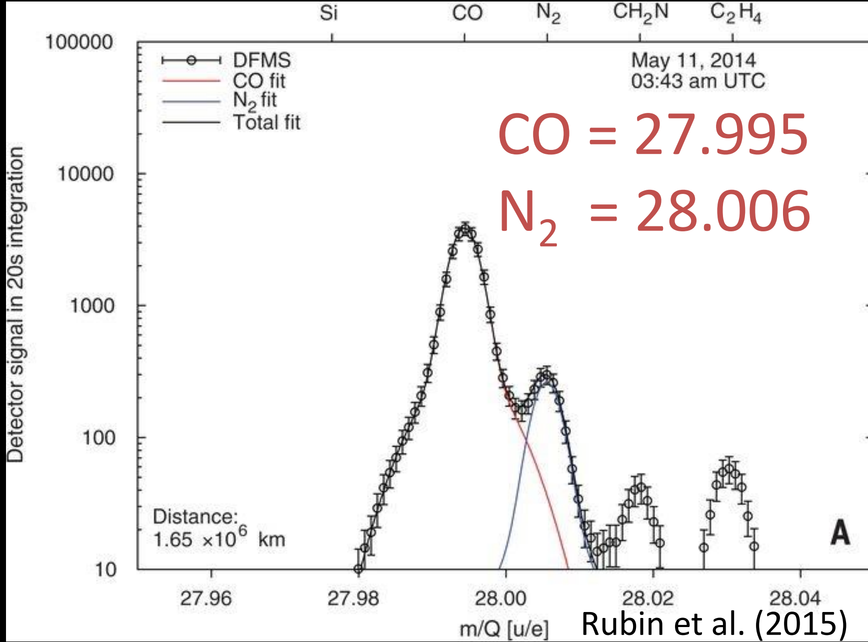


Magee & Waite (2017)

Cassini at Enceladus

Resolution

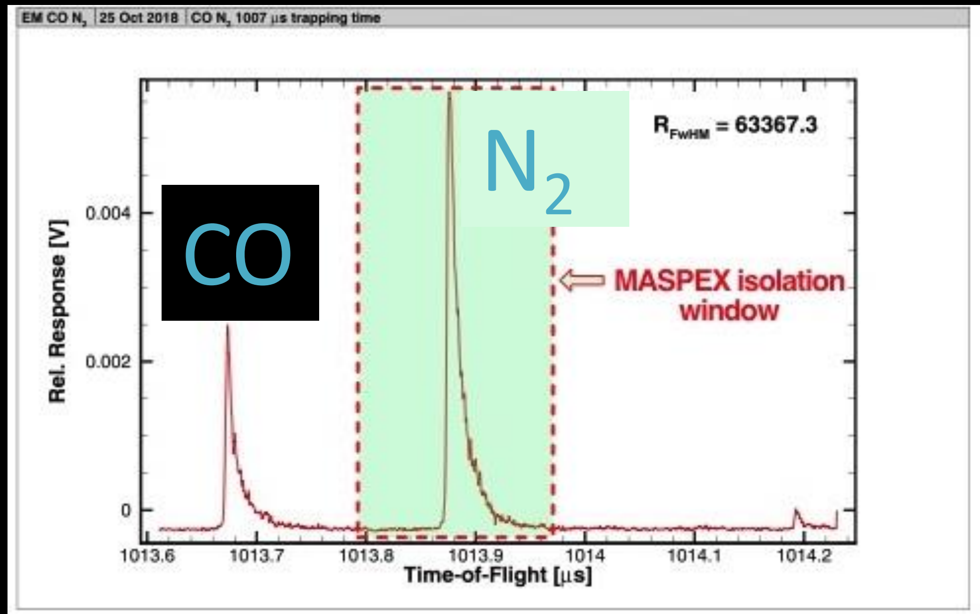
- Defines the ability of the mass spectrometer to separate adjacent masses
- Two main definitions; Full-width half-maximum, and 10% valley
- Without peak separation errors in quantitation increase
- The resolution required for separation is affected by peak intensity as well as mass difference



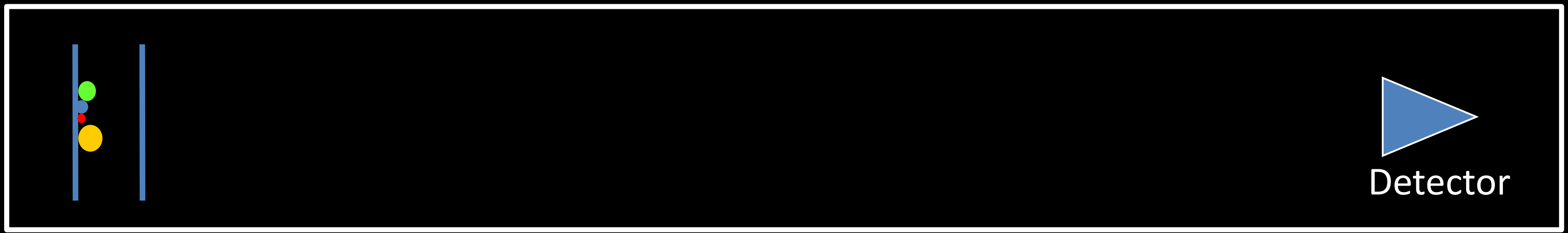
Rubin et al. (2015)

Rosetta at comet 67P

Europa Clipper MASPEX

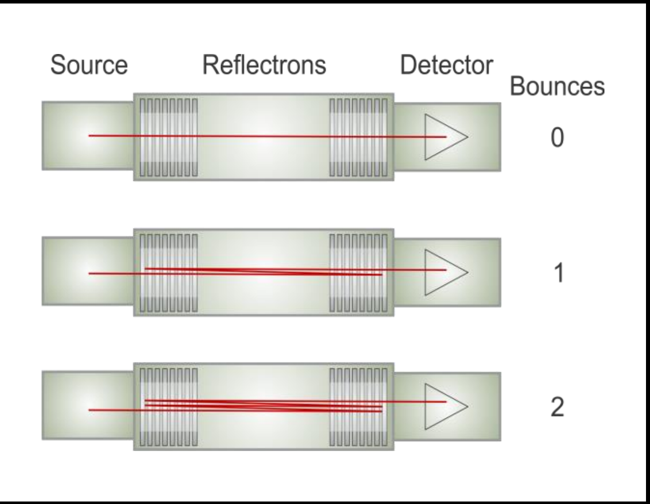


MB-TOF Concept for Resolution



Simple time-of-flight design

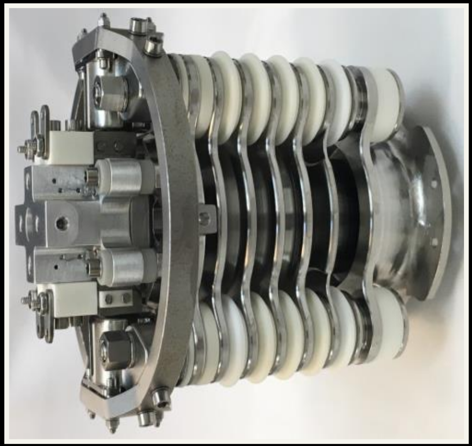
Reflectron time-of-flight design



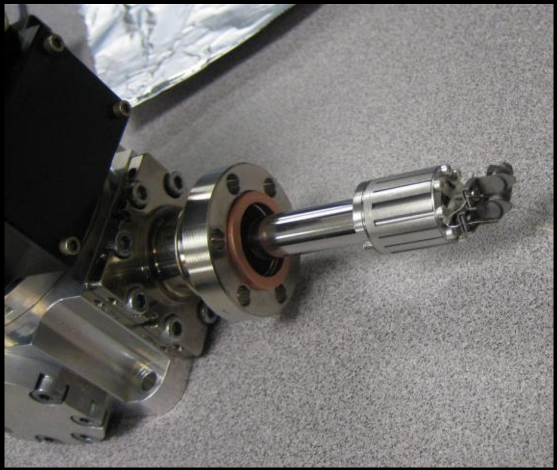
- A packet of ions is accelerated to a defined kinetic energy and the time required to move through a fixed distance is measured
- As KE = $mv^2/2$ then lighter ions travel faster than heavier ones → mass separation
- The greater the distance between source and detector the smaller the mass difference that can be seen (resolution)

Technologies for Improving Sensitivity

- Ion storage source
  - 0.02
    counts s^{-1} per molecule
    cm^{-3}

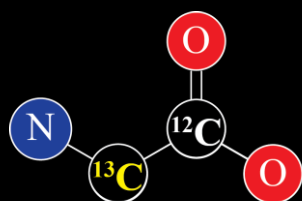


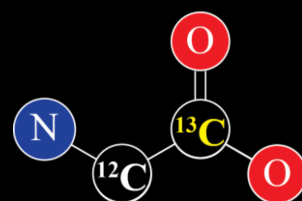
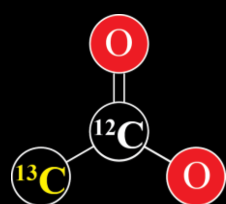
- Cryotrap
  - 2000
    counts s^{-1} per molecule
    cm^{-3}
  - 10^5 sensitivity
    improvement

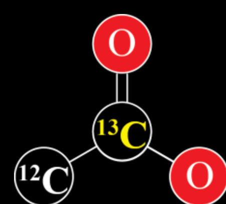


Advancements for the Future of MS

Chirality on Steroids:
Position Specific Isotopic Analyses (PSIA)

<table>
<tr><th>Compound</th><th>Possible Arrangements</th><th>Compound Isotopic Ratio ($^{13}C/C_{total}$)</th></tr>
<tr><td>Propane</td><td>^{12}C-^{12}C-^{13}C
^{12}C-^{13}C-^{12}C</td><td>1/3</td></tr>
<tr><td>Glycine</td><td>


</td><td>1/2</td></tr>
<tr><td>Acetic acid</td><td>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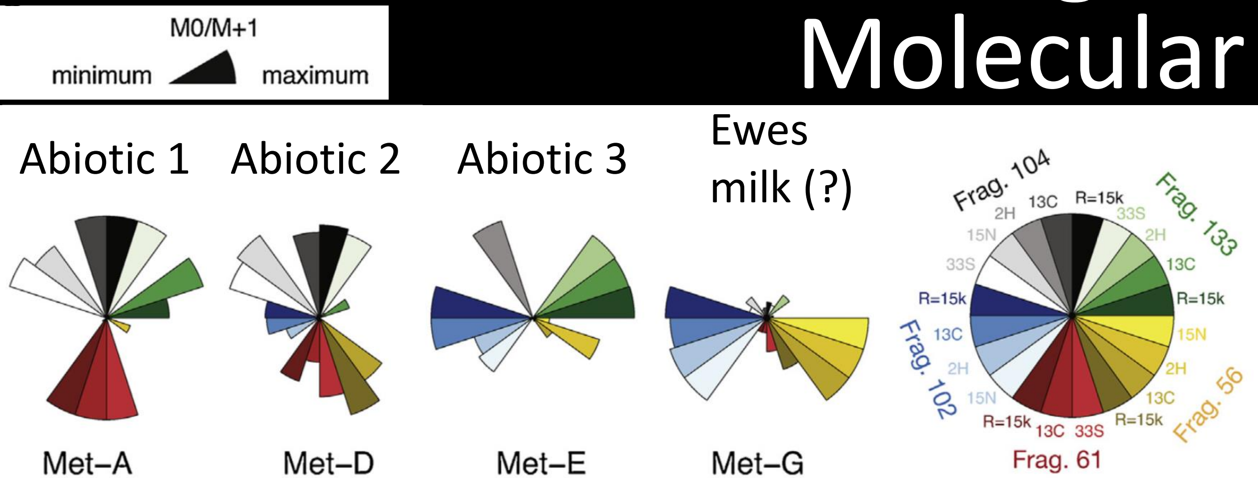
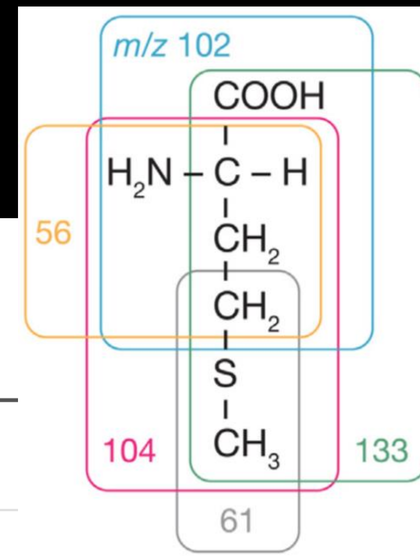
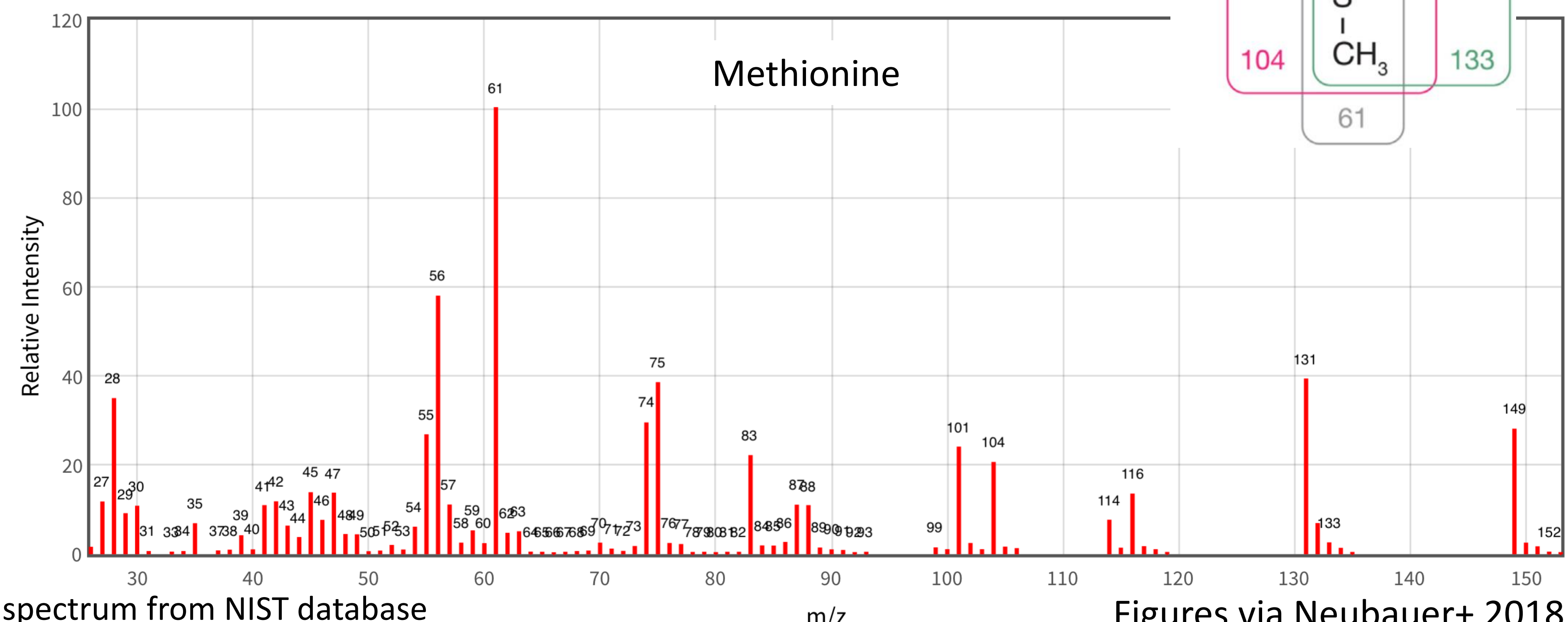
Determining Biotic vs Abiotic Molecular Origins



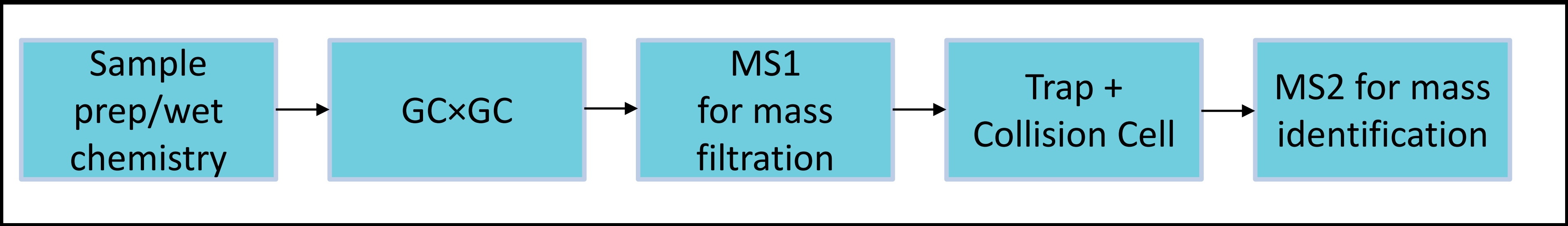




spectrum from NIST database

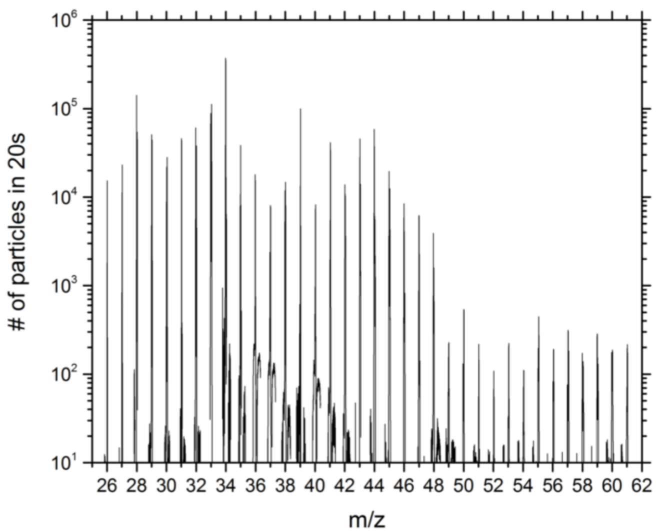
Figures via Neubauer+ 2018

Sample MS Configuration

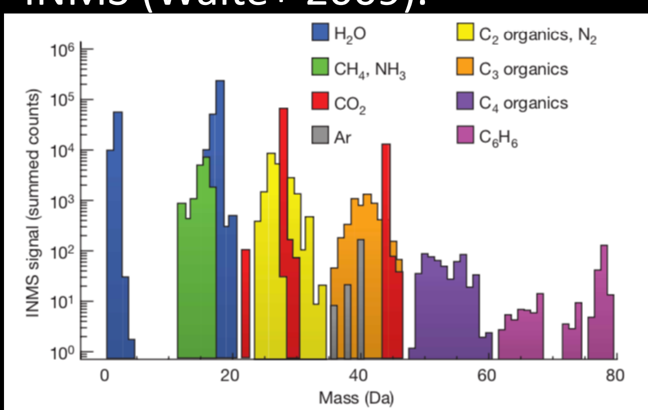


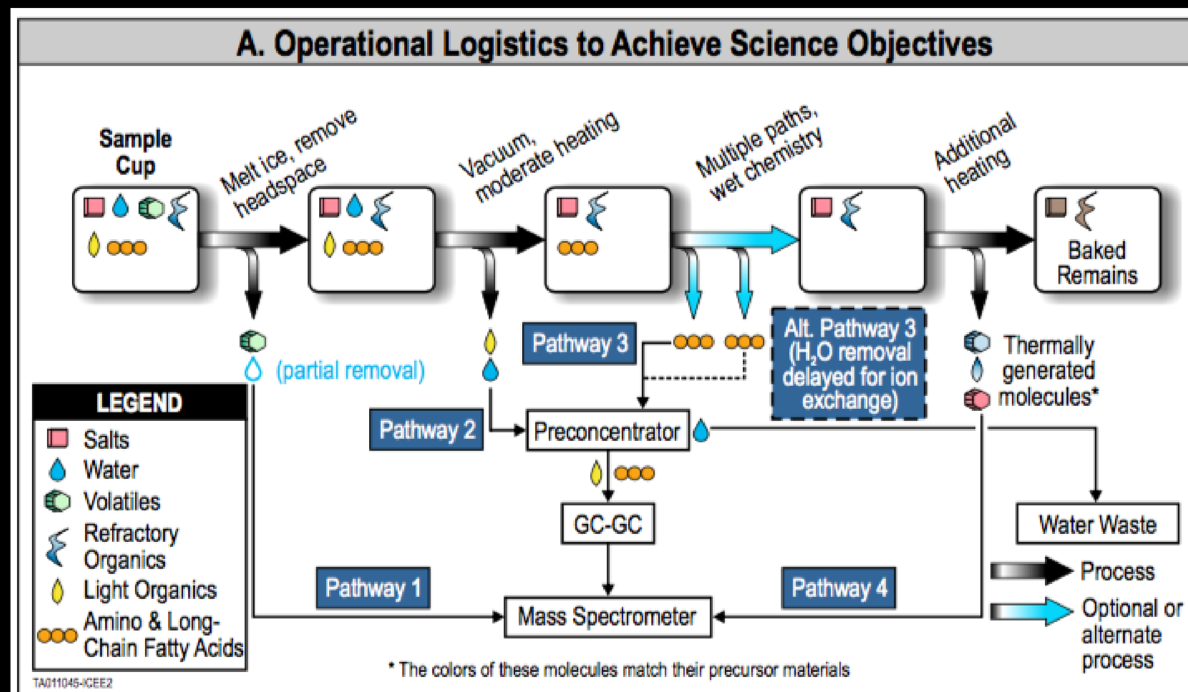
- 4 layers of separation: high signal to noise from coincident signals
- Key considerations:
  - Sample prep and GC × GC separation facilitates analysis of complex natural mixture
  - Front-end mass filter required to separate peaks of interest, increase signal/noise, control for space charging effects; high resolution and high through-put desirable
  - Fragmentation required to distinguish between positions
  - High resolution mass analyzer needed at detection to separate peaks of interest

MASPEX development for future ocean world landers



Volatile-rich natural environments result in complex spectra. Separation + sample prep aids identification. Above: Comet 67P as seen by ROSINA (Altwegg+ 2017). Below: Enceladus plume as observed by INMS (Waite+ 2009).

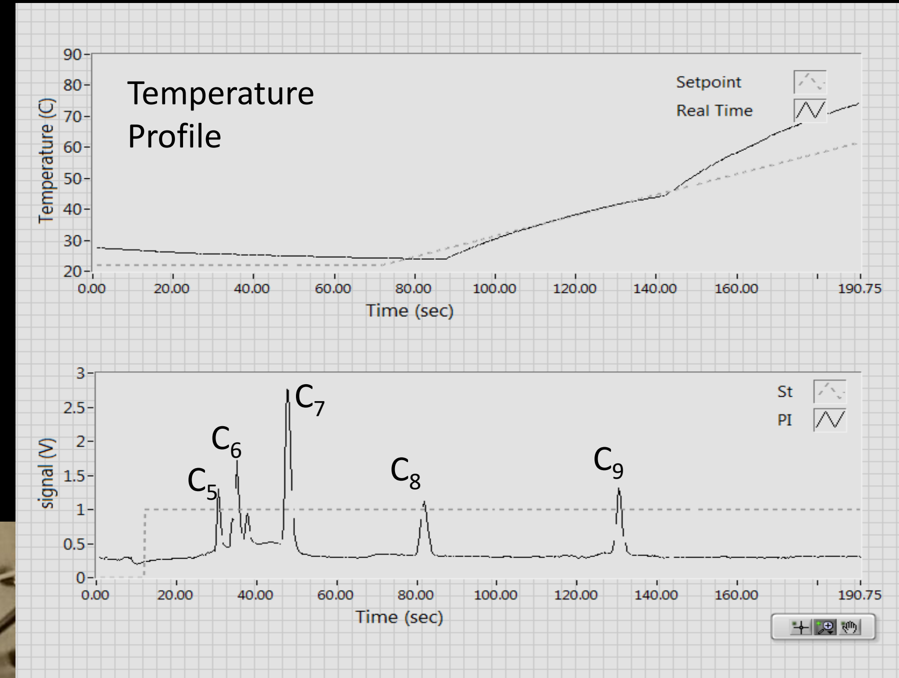


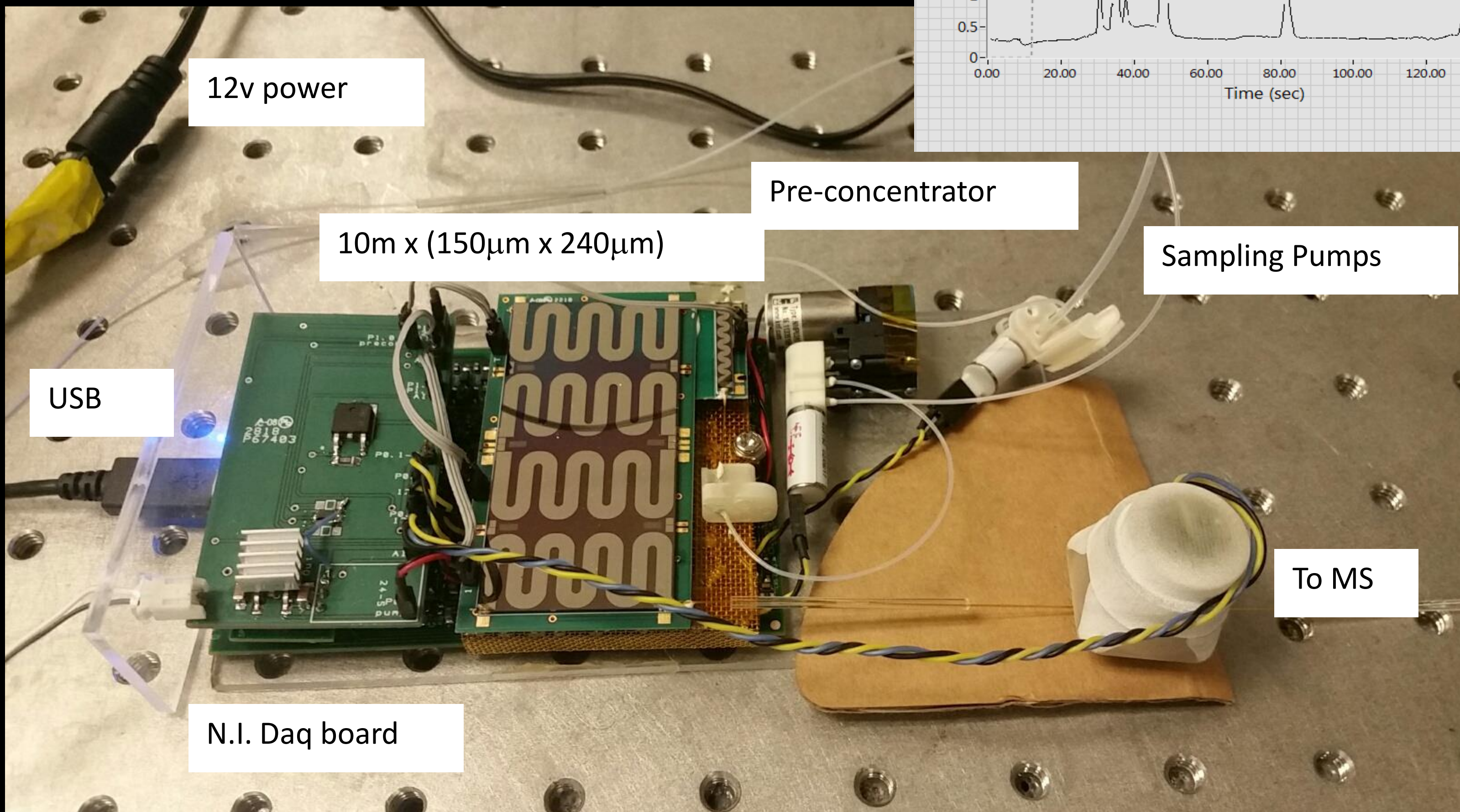


Analysis plan for MASPEX-ORCA for Europa Lander, PI Glein

A Step Towards the Future: Microfluidic Gas Chromatography

Data credit: M. Libardoni, R. Blase, K. Kurabayashi and the MASPEX-ORCA team



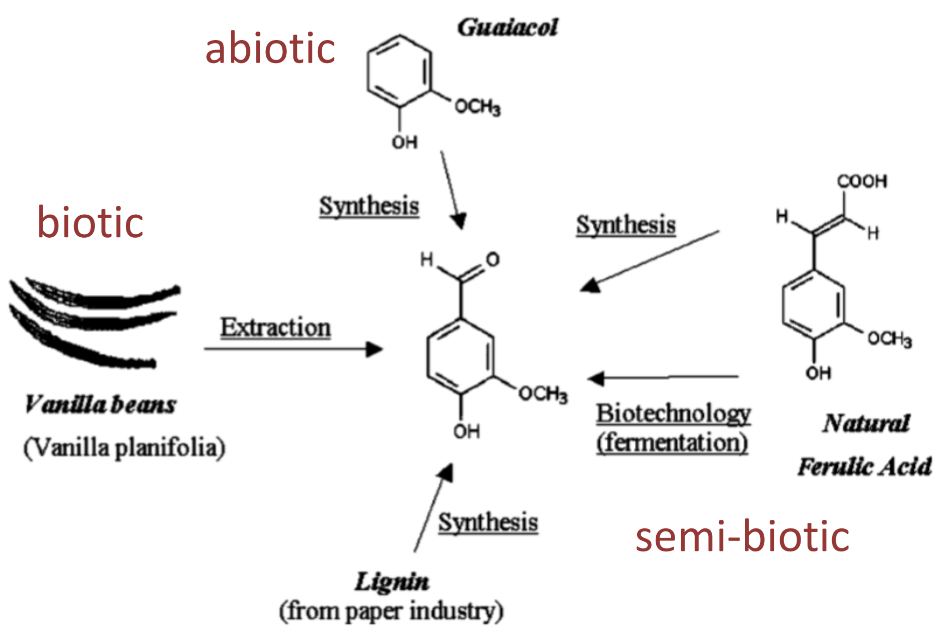


Summary

- MS has made valuable scientific contributions in both inner and outer solar system; lots of heritage to build from
- Deeper quantitative understanding of planetary origins, evolution, and tests for life require advanced analytical tools
  - High resolution + high sensitivity
  - Precise isotopic characterization
- MASPEX will address these goals and increase heritage at Europa
- Future advancements include more sophisticated sample preparation, separation techniques, position specific isotopic analyses (PSIA)

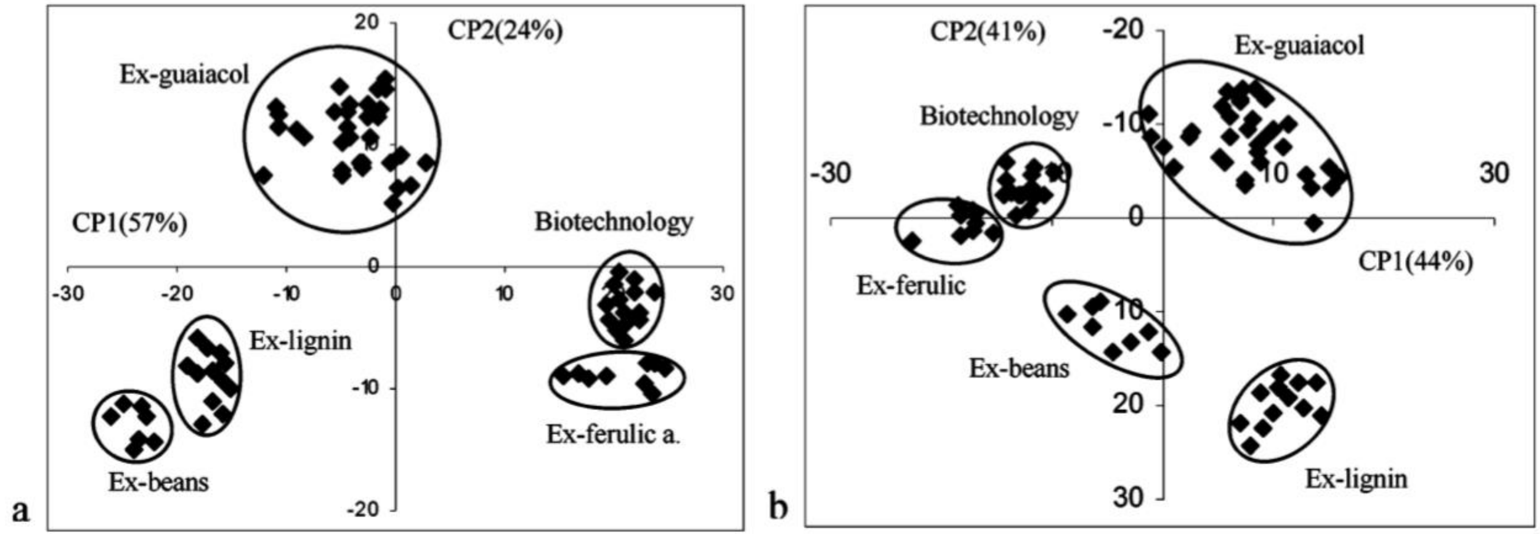
Back-up slides

Determining Biotic vs Abiotic

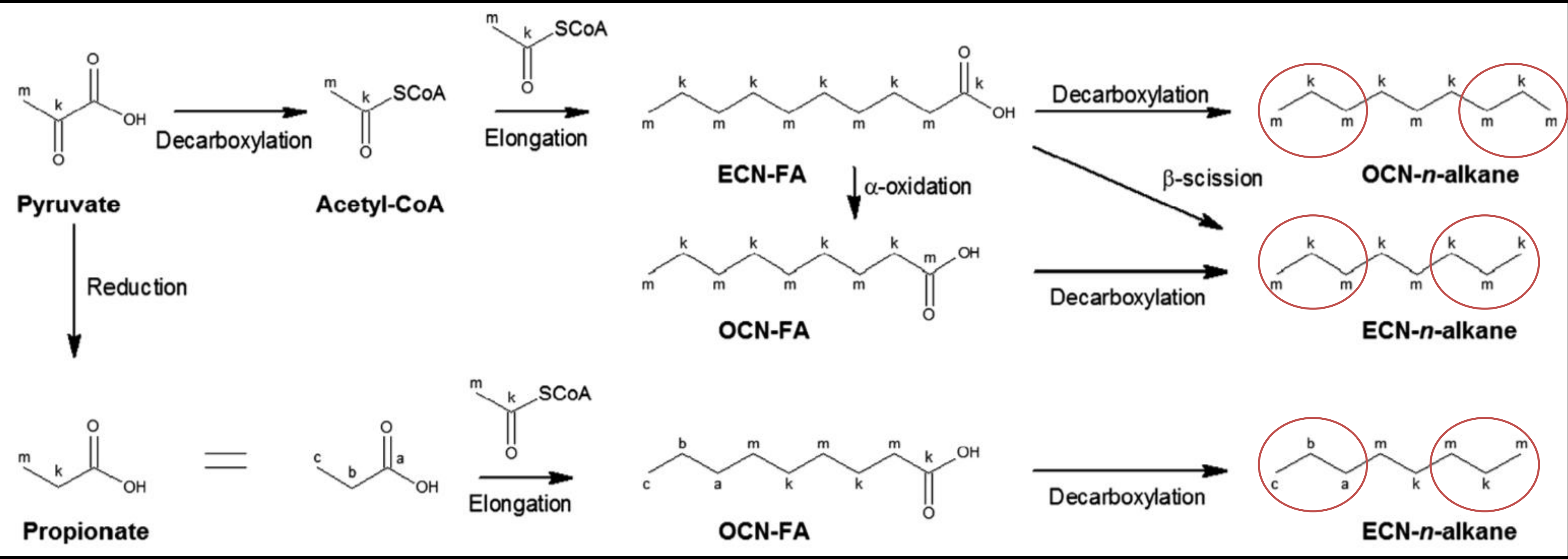


- NMR analyses already in use for molecular forensics, including medical synthesis pathways, drug and food provenance, and natural gas sources
- PSIA offers:
  - Strong discrimination between biotic and abiotic processes
  - Insight into process
  - Broadband/agnostic method

Identification of vanillin origins via NMR (Tenailleau+, 2004)



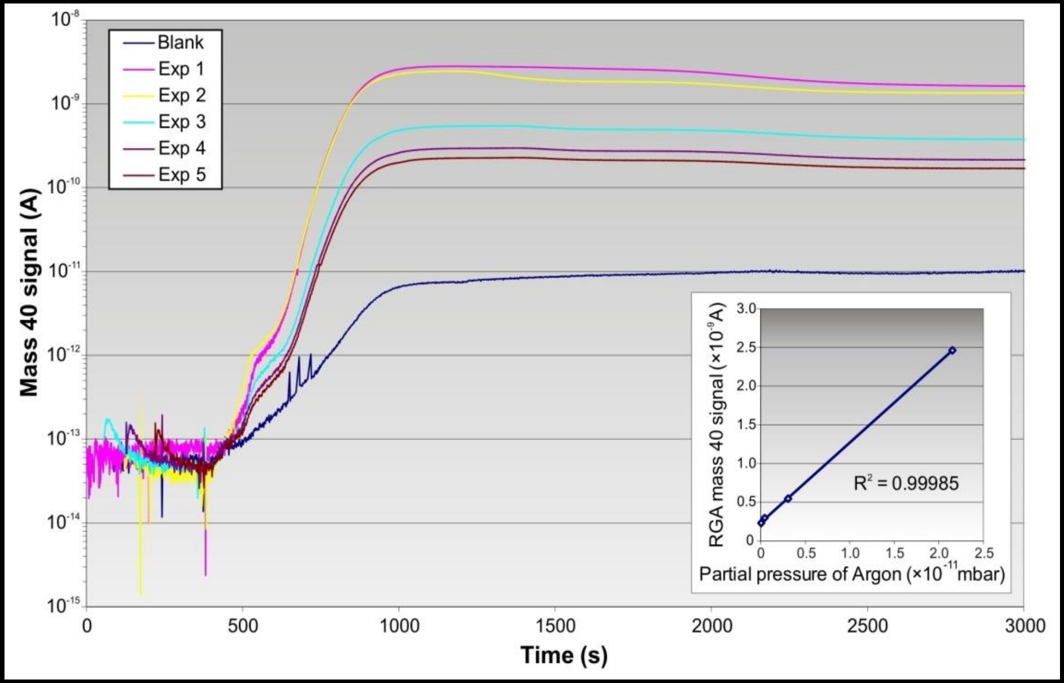
Why are PSI Ratios Different?



Mechanisms for Isotopic Patterns in Alkanes
(Gilbert+, 2013)

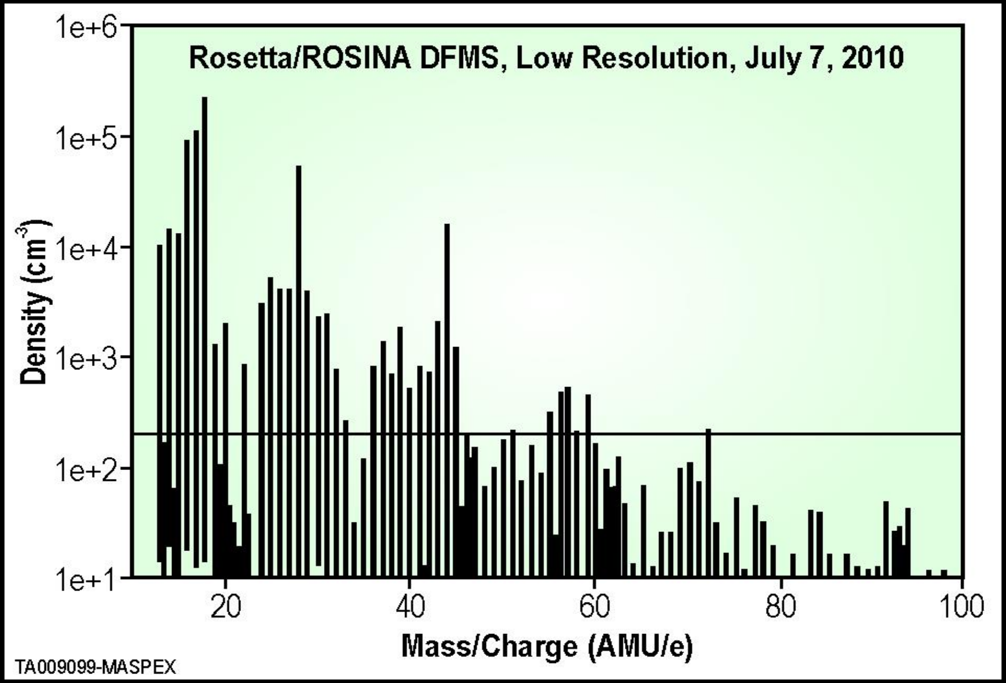
Cryotrap

- The cryotrap simply retains a sample of the gas from the flyby
- By sealing the volume of MASPEX releasing the trapped gases into the confined space it raises the density higher than the ambient gas
- Higher density leads to greater ion counts so trace species can be measured in less time than in ambient
- Unlike the flyby where the sample is changing all the time, the sample is static enabling co-addition to measure the trace components



Why is contamination control so important?

Spacecraft Contamination



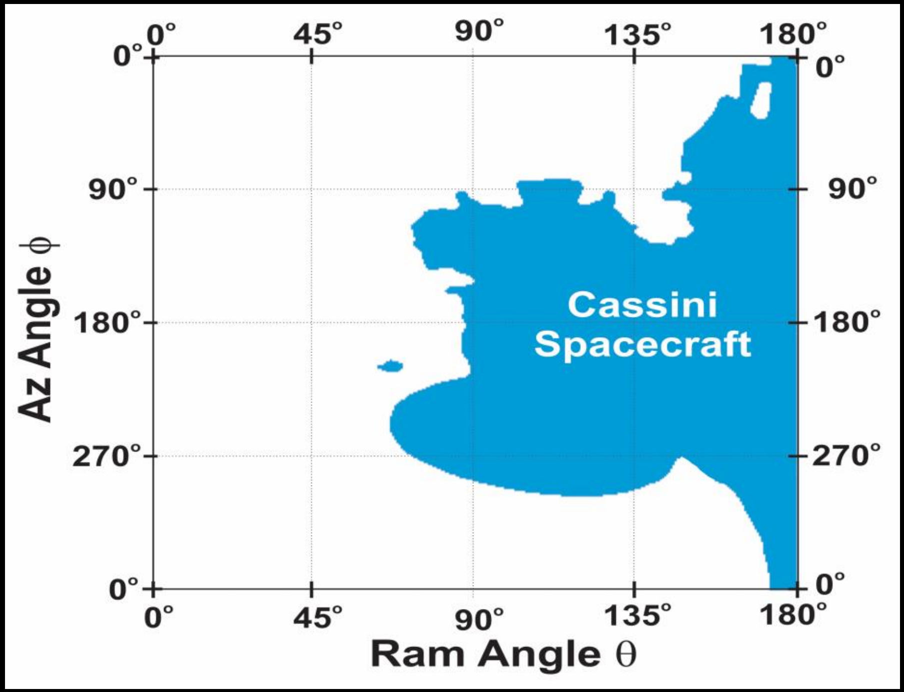
Plot of spacecraft contamination seen by ROSINA aboard the Rosetta spacecraft. {From Schlappi et al., 2011}.

The black horizontal line is the limit of detection of Cassini INMS as determined from the dark counts attributed to radiation and cosmic rays. From this comparison, we suggest that although the Cassini INMS is less sensitive than the ROSINA Double Focusing Mass Spectrometer (DFMS), the INMS data do not show the same level of contamination as seen by ROSINA. ***The differences between Rosetta and Cassini-Huygens are due to both spacecraft accommodation issues.***

Origins of SMOG

- Desorption
  - All surfaces have a covering of material that will outgas
- Decomposition
  - Breakdown of solids to produce more volatile molecules
- Diffusion
  - Gas dissolved in solids diffuses to the surface
- Permeation
  - Trapped gas permeates through solids to the surface
- Thrusters
  - Designed to ‘outgas’ material rapidly

Accommodation



Blue shaded region: Cassini INMS FOV directions shadowed by the Cassini spacecraft.
Adapted from Teolis et al., A Revised Sensitivity Model for Cassini INMS: Results at Titan, Space Science Reviews, submitted 2014.

The Cassini INMS experience has taught us two accommodation issues :

1) a FOV for the instrument clear of spacecraft obstructions, and
2) placement of the thrusters.

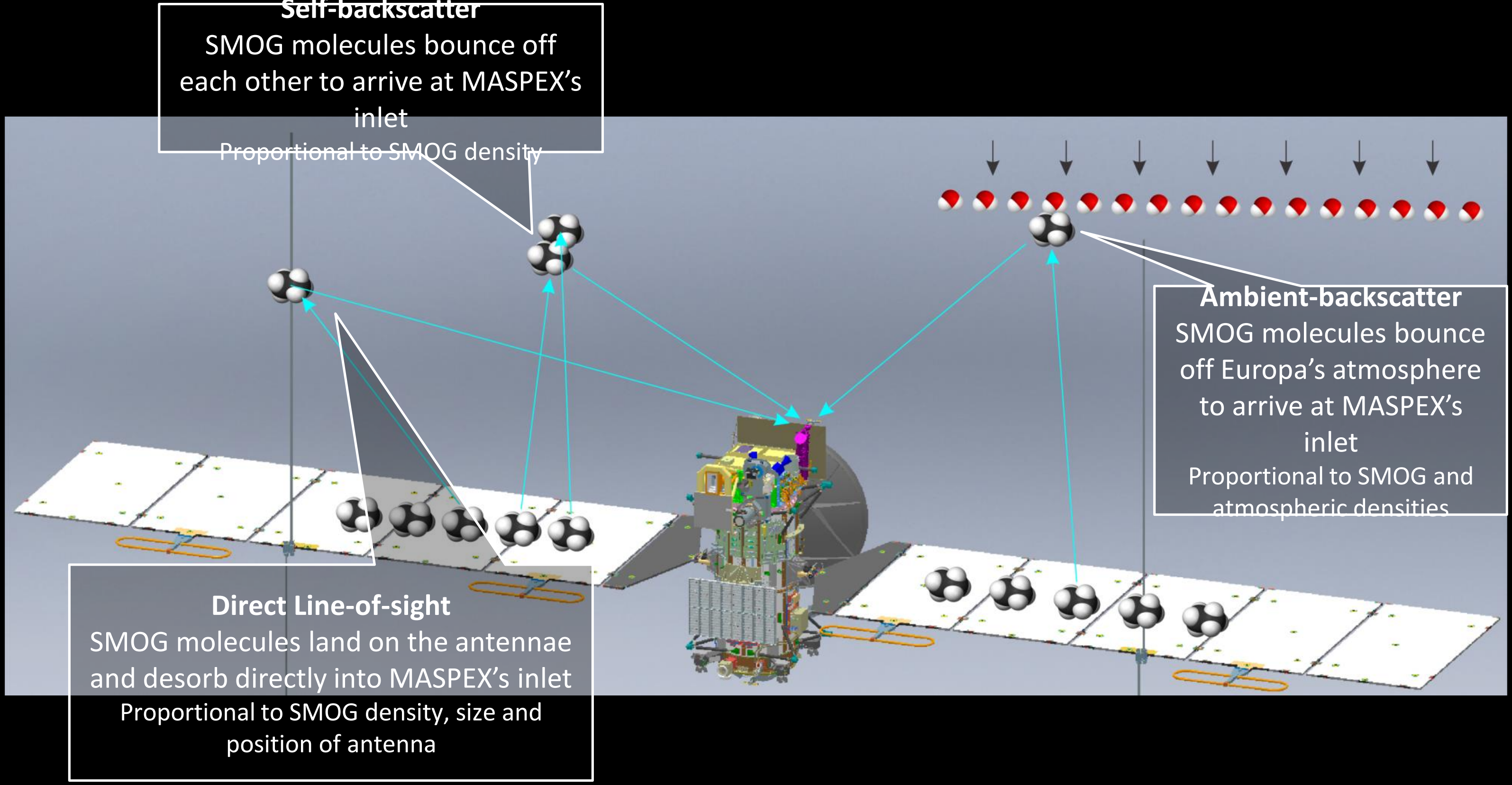
2.1% of the incoming flux to the closed source is derived from spacecraft surfaces.

Estimated flux of volatiles;

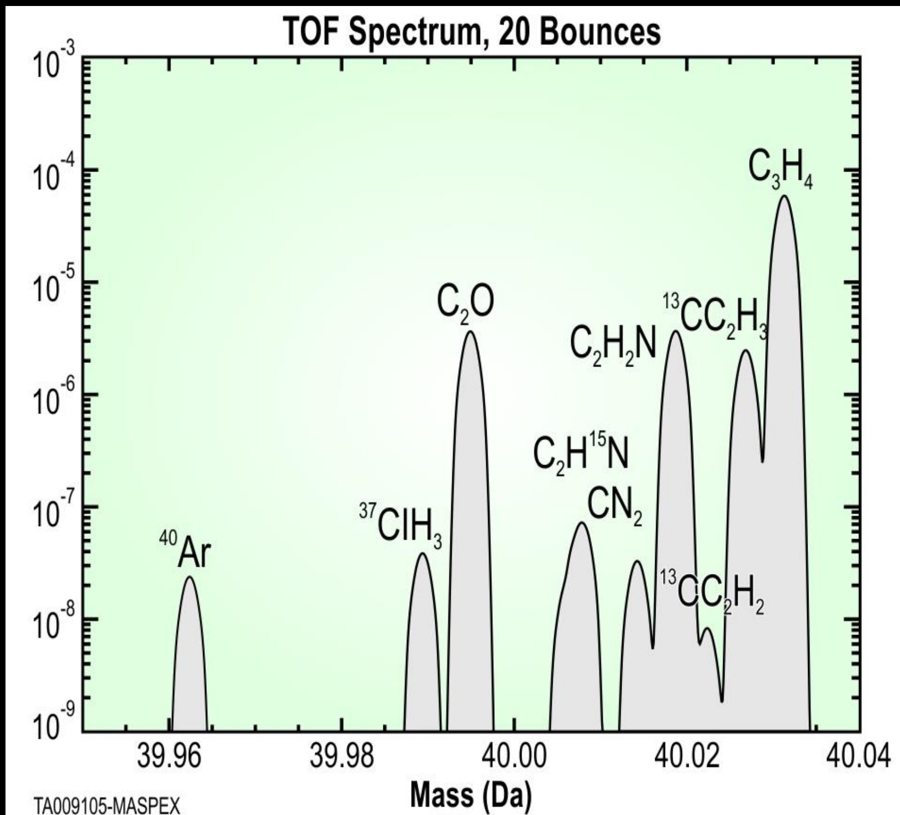
- From S/C surfaces: 4.0×10^8 cm^{-2} s^{-1}
- SMOG backscatter: 1.7×10^2 cm^{-2} s^{-1}

PROVIDING a FOV *clear* of spacecraft surfaces is the most important contamination mitigation step.

Sources of Contamination

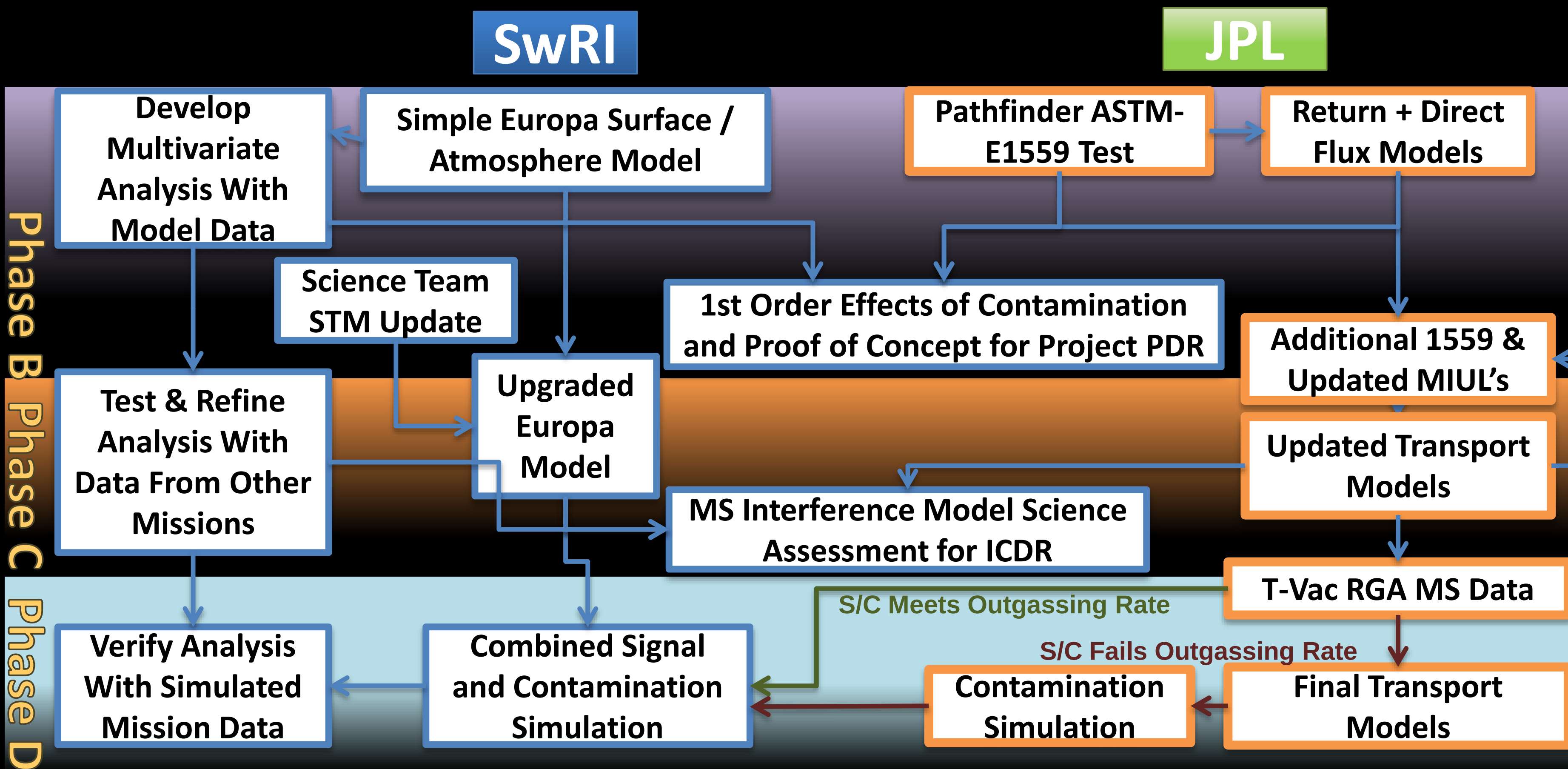


Mitigation Measures



- An example spectrum, with a random sample of organic compounds that produce fragment ions near mass 40 (a proxy for worst-case spacecraft contamination)
- Using a resolution of ~11,000 m/Δm @10% of peak height
- ^{40}Ar can be easily separated from contaminants.
- ➔**High mass resolution can separate contamination from signal**

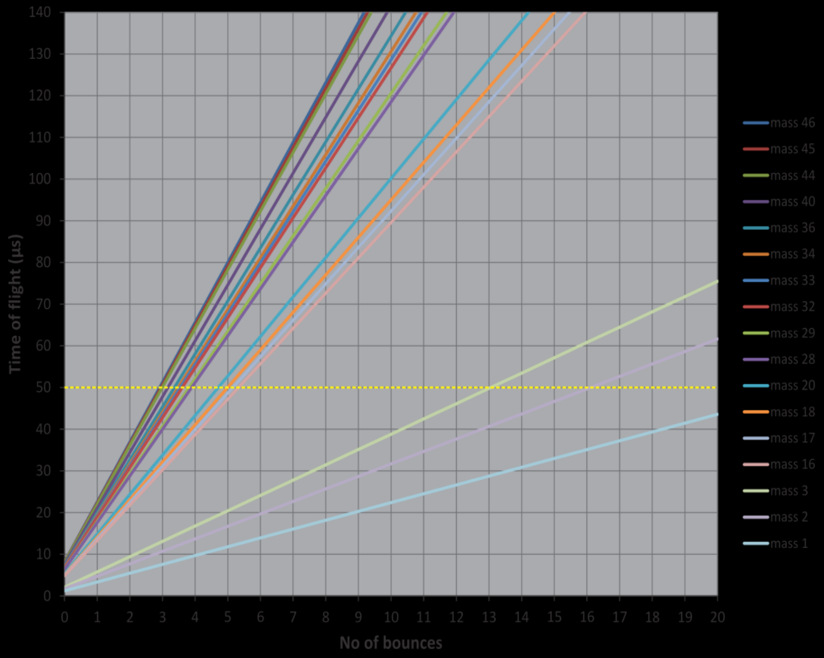
Contamination Control Approach



Racetracking and Regions of Interests (ROIs)

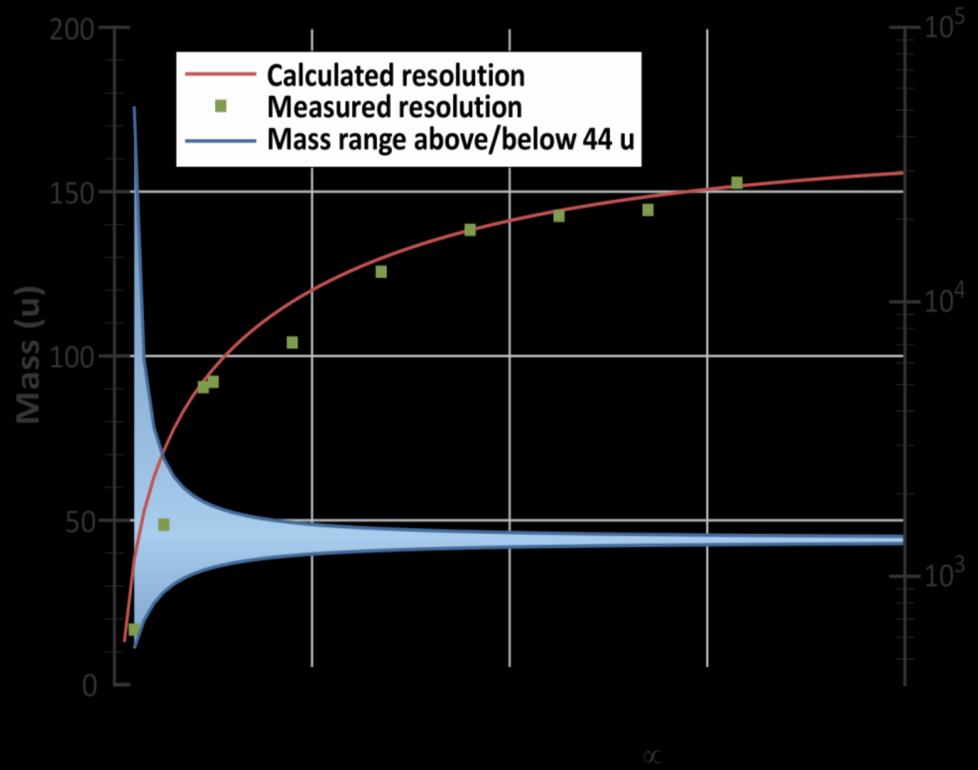
MASPEX Features: Racetracking

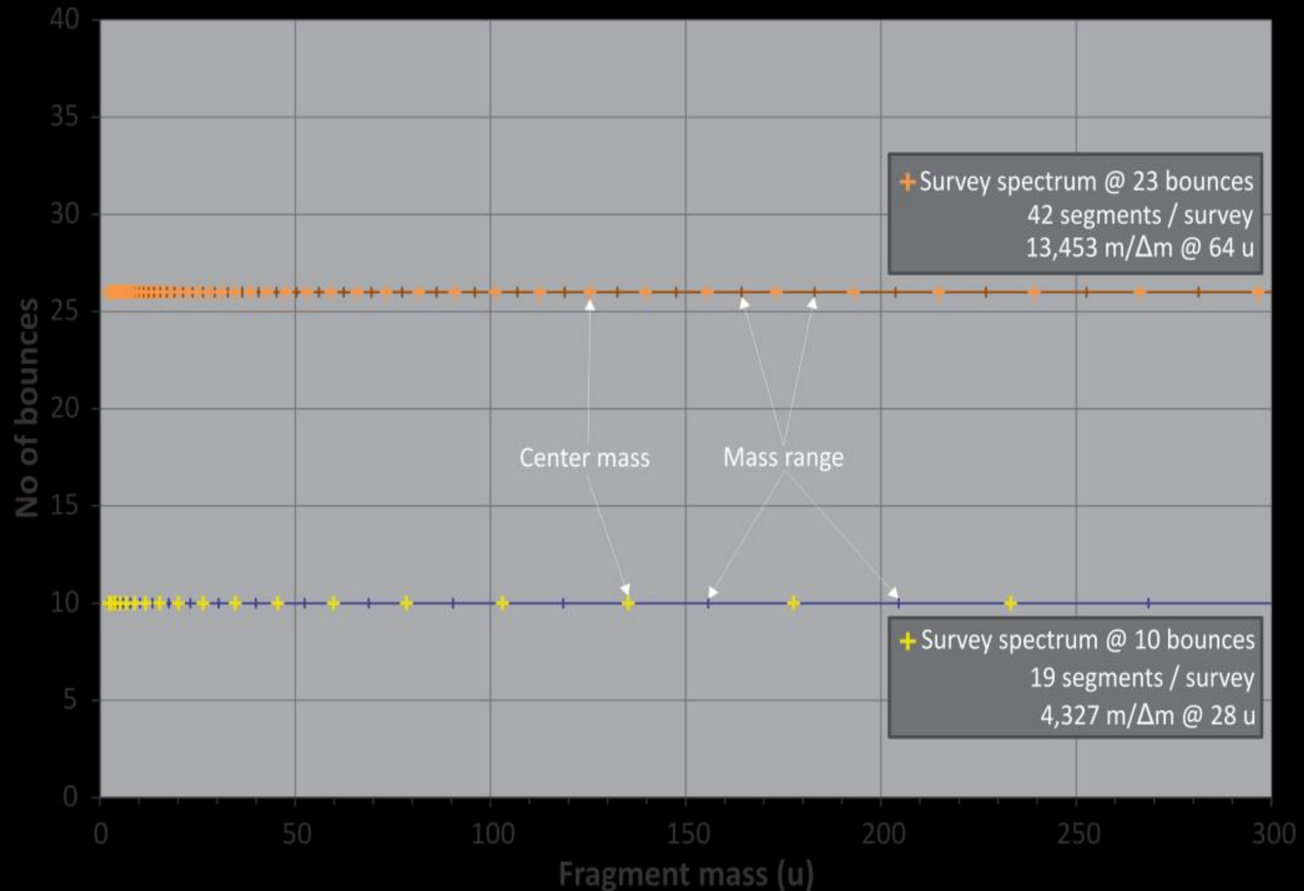
- Folding the ion flight path results in faster ions lapping the slower ones
- Gives spectra with peaks on different bounces
- Complicates the mass scale
- Can overlap other peaks



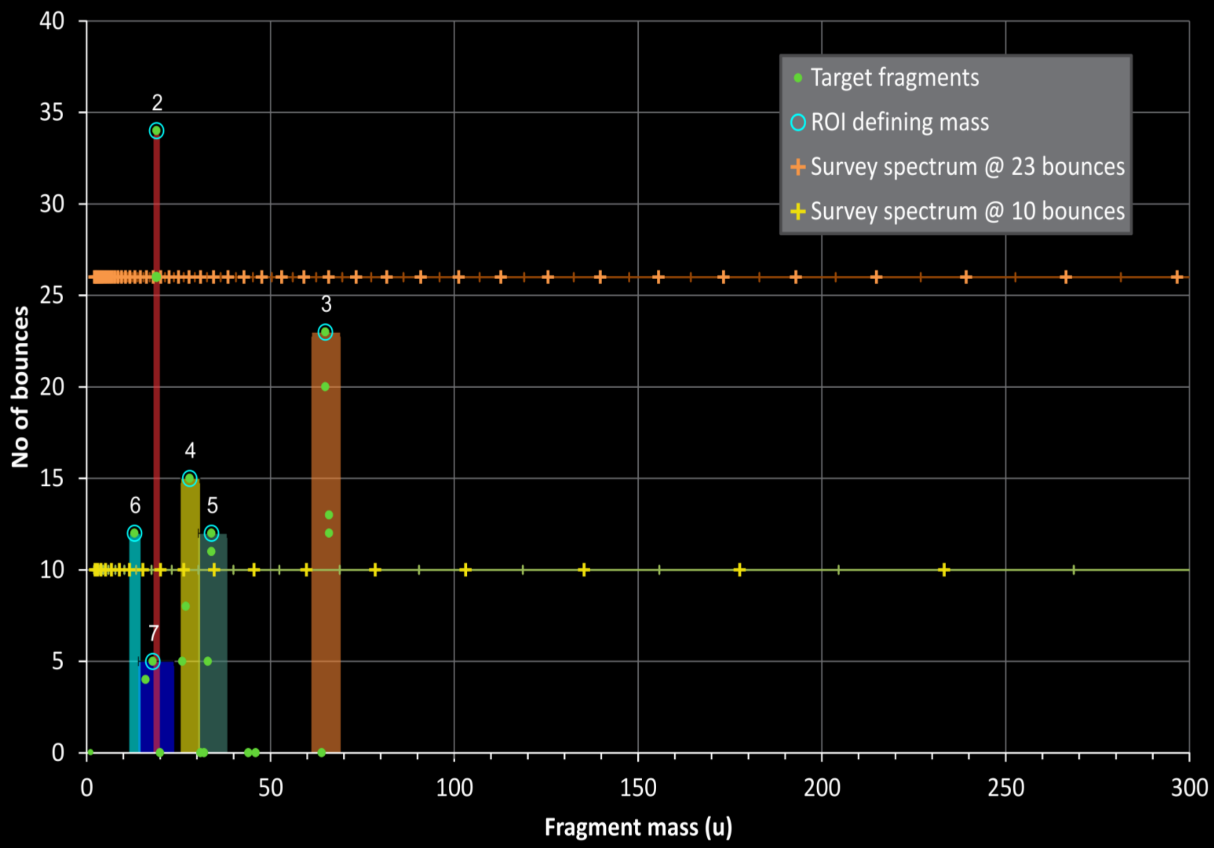
Operational Characteristics

- Controlling race-tracking limits the mass range





40
35
30
25
20
15
10
5
0
No of bounces
0
50
100
150
200
250
300
Fragment mass (u)
Survey spectrum @ 23 bounces
42 segments / survey
13,453 m/Δm @ 64 u
Center mass
Mass range
Survey spectrum @ 10 bounces
19 segments / survey
4,327 m/Δm @ 28 u



- The science investigation generally has specific targets
- Region-of-interest operation reduces the amount / time / volume of data acquisition
- Only the specific mass ranges and resolutions are measured