New Techniques for Analytical Mass Spectrometry:

What can volatile composition tell us about the origin of the solar system and its intrinsic astrobiology

J. Hunter Waite, Jr.
Mark Libardoni
Greg Miller
Tim Brockwell
Ryan Blase

Presentation Outline

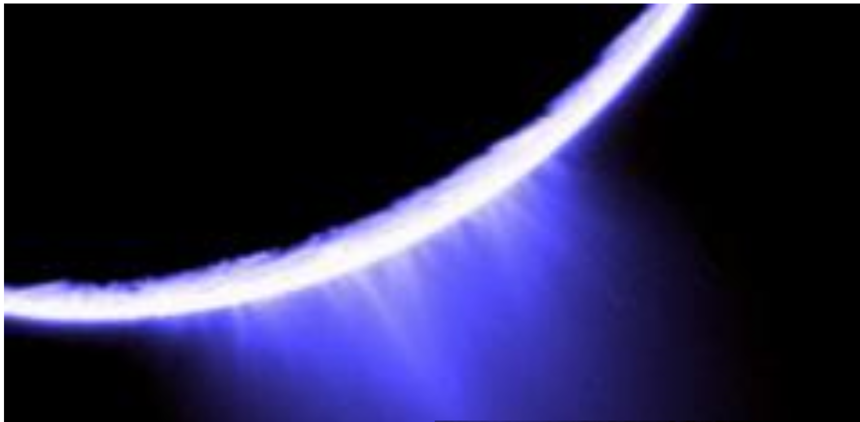
1. Motivation
    1. Enceladus plume composition
    2. Titan upper atmosphere composition

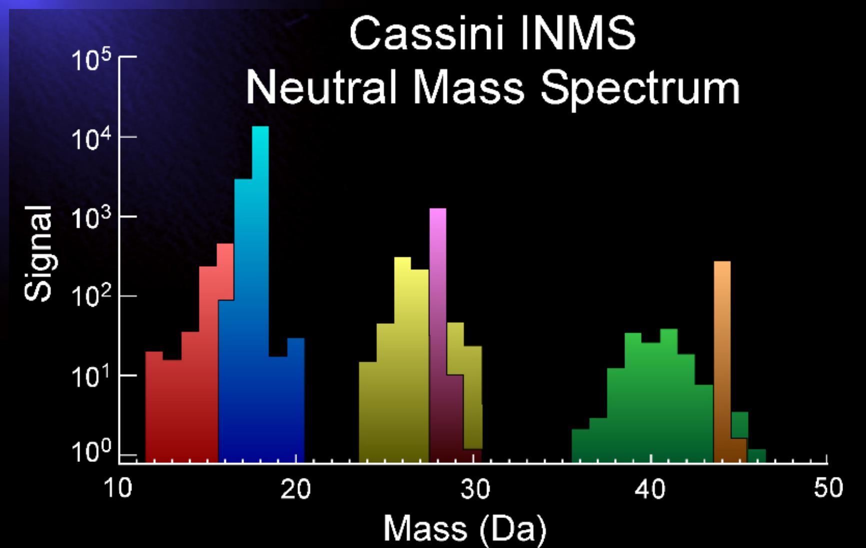
2. New Technologies: Center for Excellence in Analytical Mass Spectrometry
    1. Cryogenic volatile trapping
    2. Gas chromatography vs gas chromatography
    3. Isotope ratio mass spectrometry
    4. High resolution time-of-flight mass spectrometry

3. Mission opportunities
    1. Future missions to the Outer Solar System: Titan and Enceladus
    2. JUICE and Saturn Probe

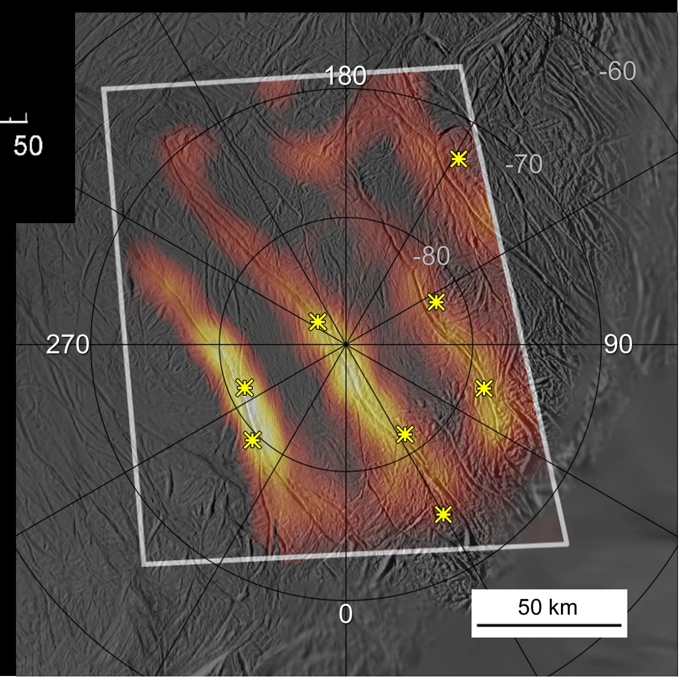
ENCELADUS AND TITAN: EXPLORING THE RICHNESS OF ORGANIC CHEMISTRY IN THE OUTER SOLAR SYSTEM

Enceladus
The Cryo-Geyser



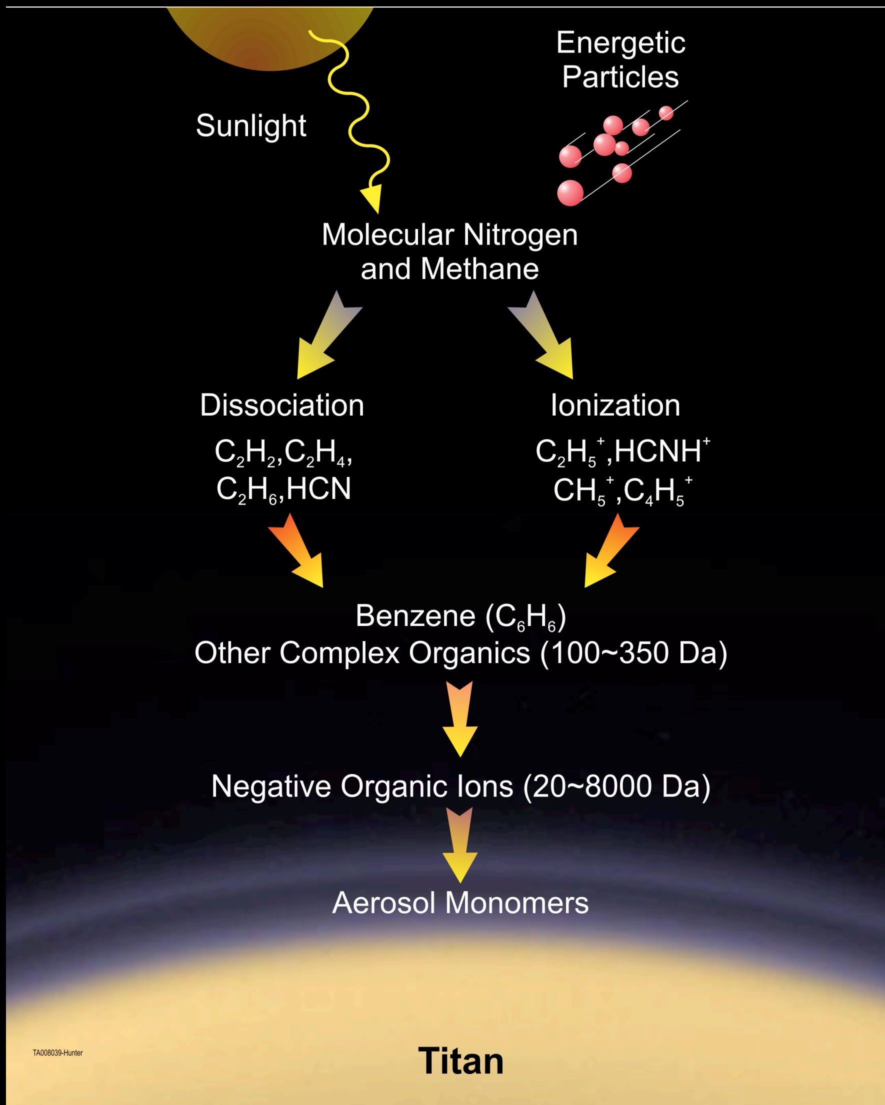


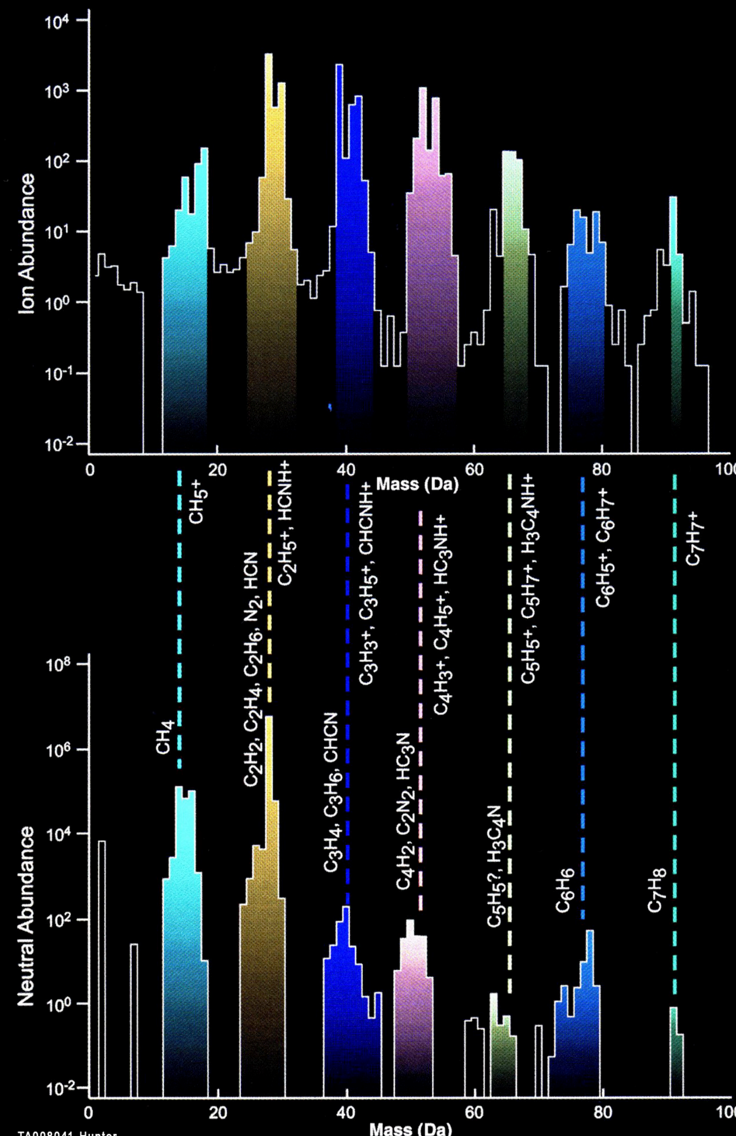
Composition like a comet?



Tidal heating of the icy interior

Titan's Upper Atmosphere





After Waite et al, Science, **316** p. 870 (2007)

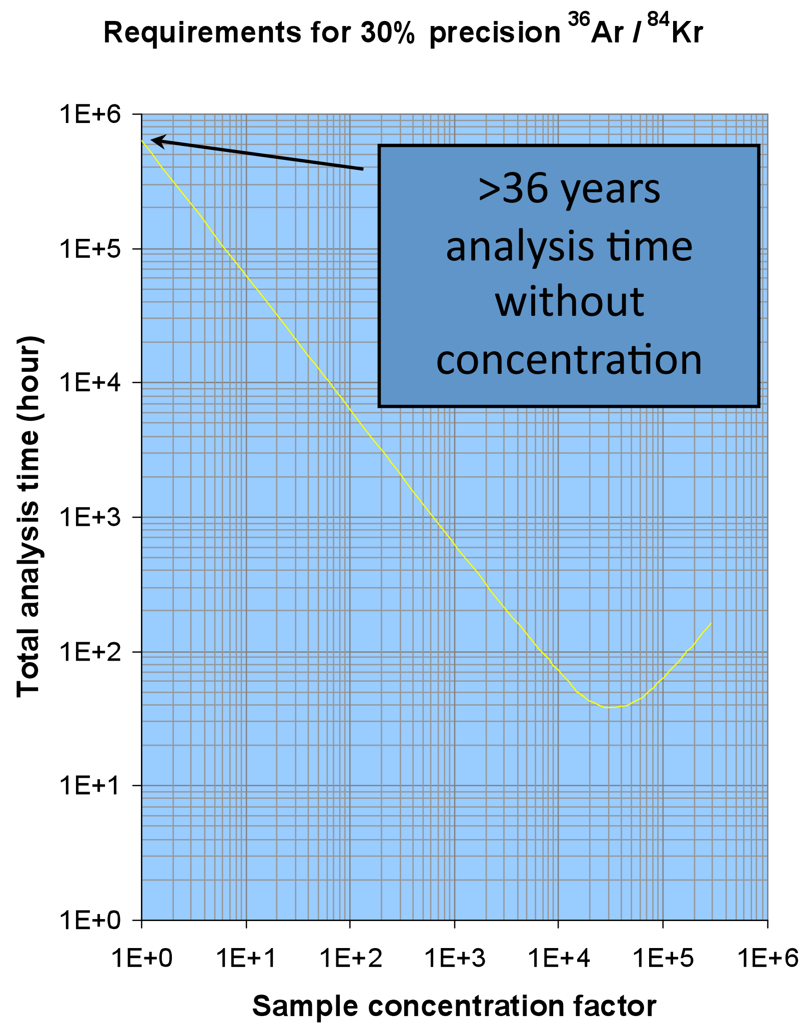
Lessons learned from Cassini

1. Extended mass range is required to survey the complexity of volatile organics.
2. Mass resolution or GC separation is needed to provide identify of compounds or measure isotopic ratios in volatiles, i.e. hydrocarbons from nitriles and H/D in water.
3. High sensitivity is needed to measure trace volatiles that track origin and evolutionary processes, such as noble gases.

SWRI TECHNOLOGY DEVELOPMENT

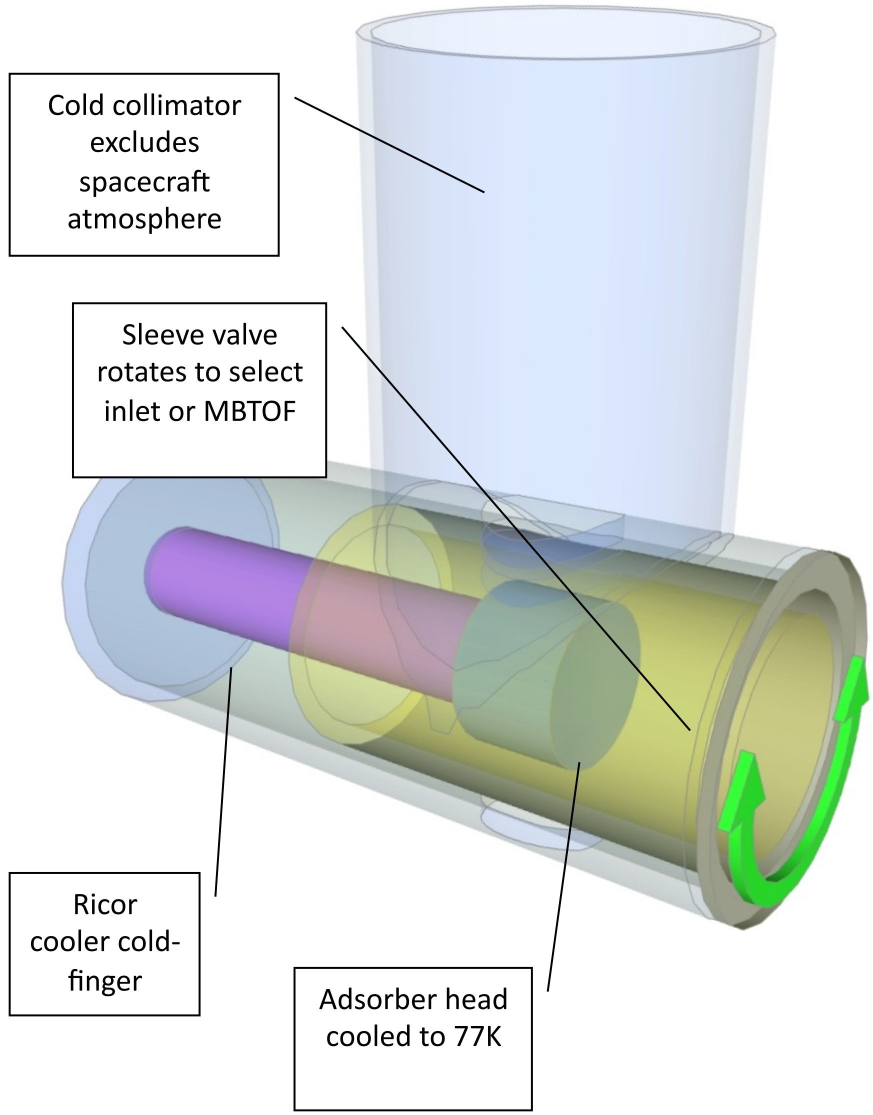
Motivation: Cryo-trapping

- Sample concentration
  - Even though MBTOF is over 1000 times more sensitive than Cassini INMS (10x from ion source strength and 100x from better duty cycle), calculations show that it would take thirty six years to reach the desired precision through direct sampling.
  - Cryo-trapping increases the signal and reduces the required analysis intervals for the most difficult components – the noble gases - to ~40 hours.
  - The cryo-trapping also increases ion source pressures to ~10^{-6} Torr, well above the anticipated chemical background seen on Cassini INMS, improving signal to noise for the analysis.



Cryo-trap Implementation

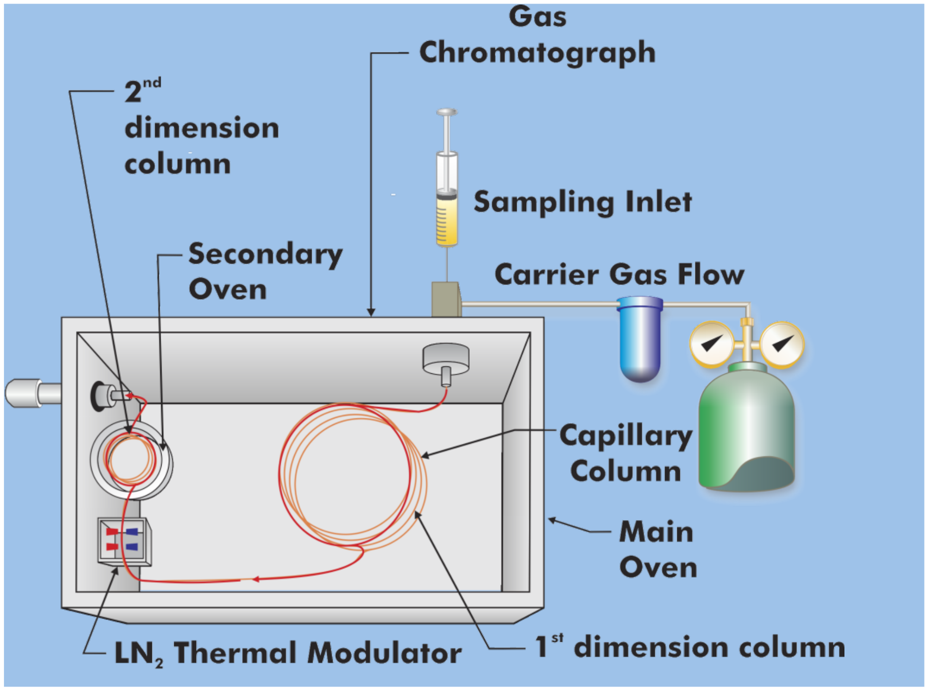
- Cryo-trapping
  - Long established vacuum technique
  - Freeze gas onto adsorber at 77K
  - Uses space heritage Ricor cooler (used on CRISM, VIRTIS (Venus Express, Rosetta), VIR (Dawn), and Messenger
- Operation cycle
  - Cool adsorber to 77K
  - Open adsorber to gas
  - Trap for required time
  - Open adsorber to MBTOF
  - Warm to release gas
- Near term development plan
  - SwRI is in the midst of a very similar development program for space applications of cryo-trapping that will result in a TRL for the proposed cryo-trap before the due date of the MBC Discovery proposal.
  - The cryo-trap has been shown in the previous viewgraph to be necessary to reach the sensitivity levels for the noble gas requirements from the RFI.



Motivation: GCxGC separation

- Good separation systems and high mass resolution mass spectrometers are needed to disentangle the ambiguities of the rich organic spectra found in Titan, Enceladus, comets and other bodies in the outer solar system.
- Current space instrumentation has low mass resolution.
- An instrument must also be capable of high resolution operation, be light, compact, and low power.
- Requires a long flight path time-of-flight instrument

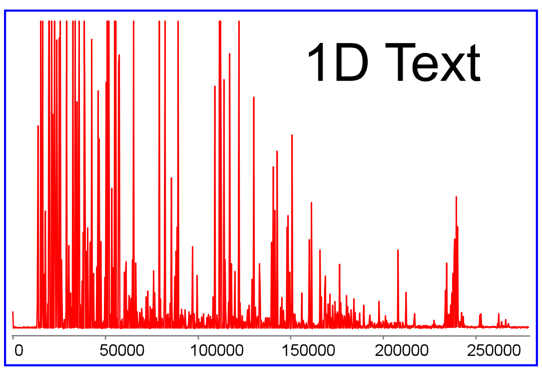
Gas Chromatography by Gas Chromatography (GCxGC)

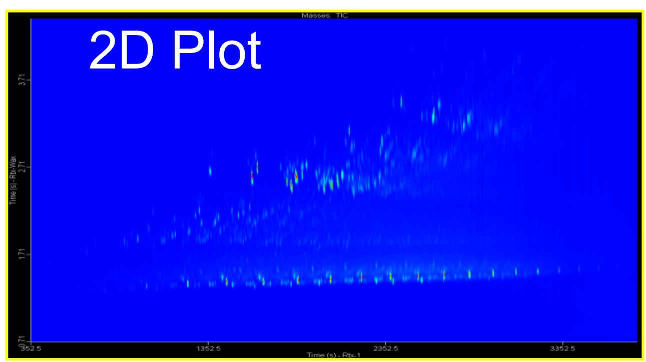


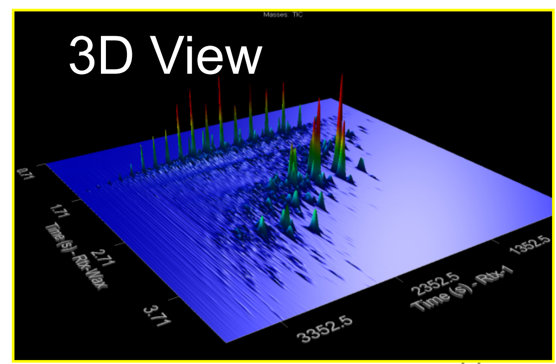
- 1st Dimension Column-Long (non-polar)
- 2nd Dimension Column - Short (polar)
- Connected via a Modulator

Benefits

- Large available peak capacity
- Increased detectibility
- Structured chromatograms



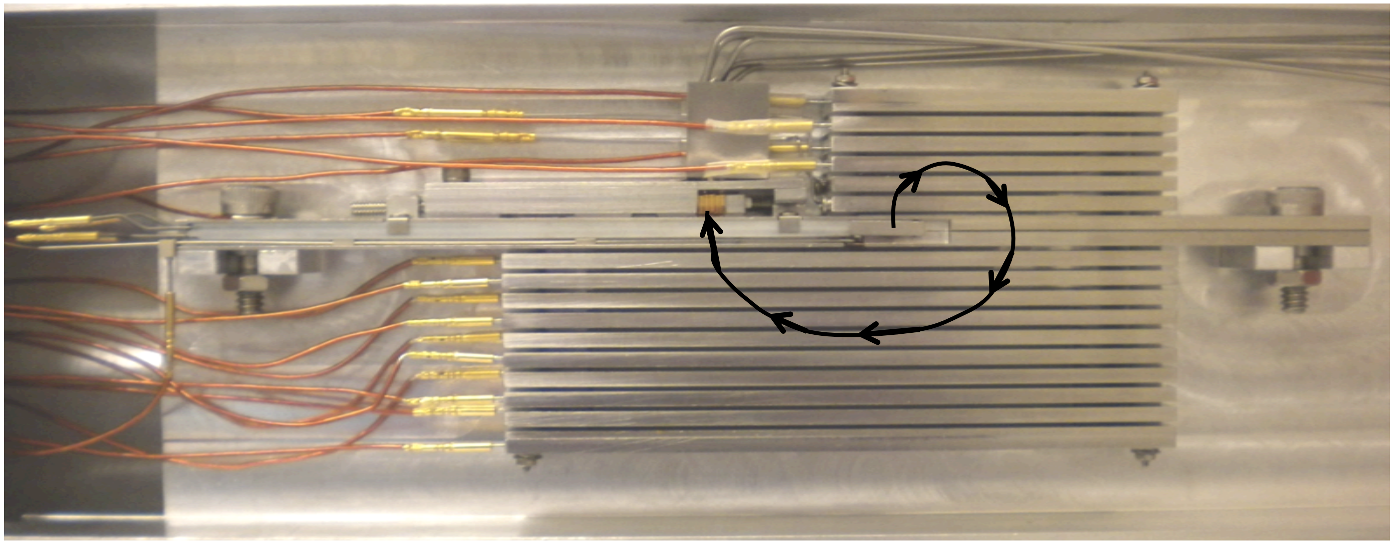




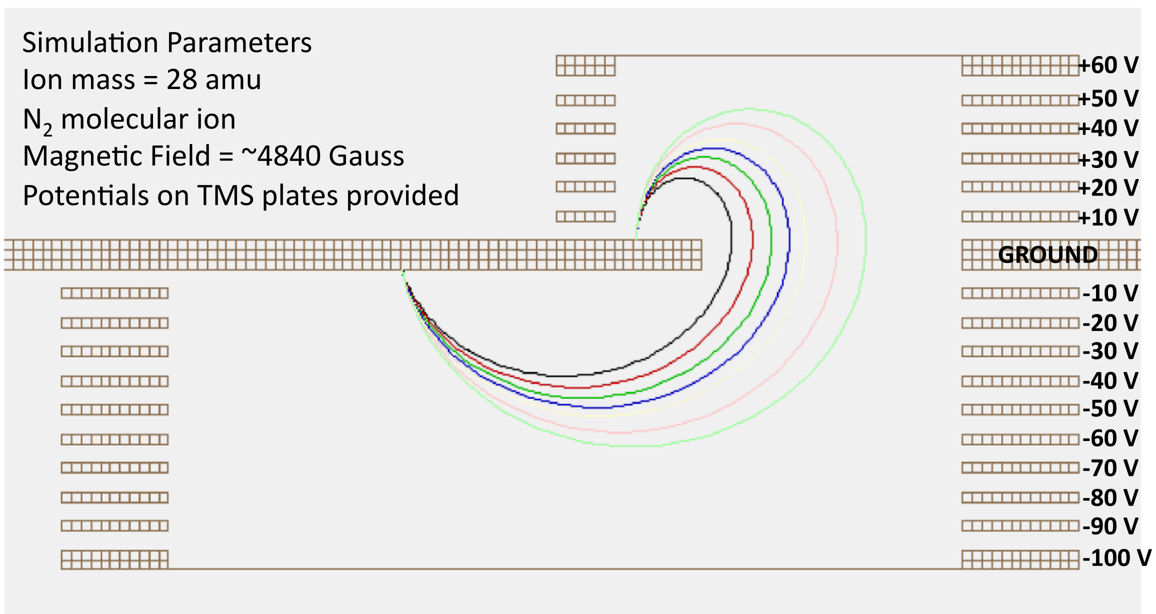
Motivation: Isotopic ratio MS

- Isotope ratios provide important information about origin and evolution.
- Current space instrumentation has unproven precision.
- Improving precisions means moving towards laboratory measurement procedures.
- Requires a dispersive instrument with a large focal plane.
- Instrument must also be capable of high resolution operation, be light, compact, and low power.
- A trochoidal mass spectrometer (TMS) meets these requirements.

The Trochoidal isotope Ratio Mass Spectrometer



SIMION simulation of PTMS



**Drawing omitted source slit, exit slits and Faraday cups for simplification.

Legend for accelerating potential of ions

- 40 eV
- 50 eV
- 60 eV
- 70 eV
- 80 eV
- 100 eV
- 120 eV

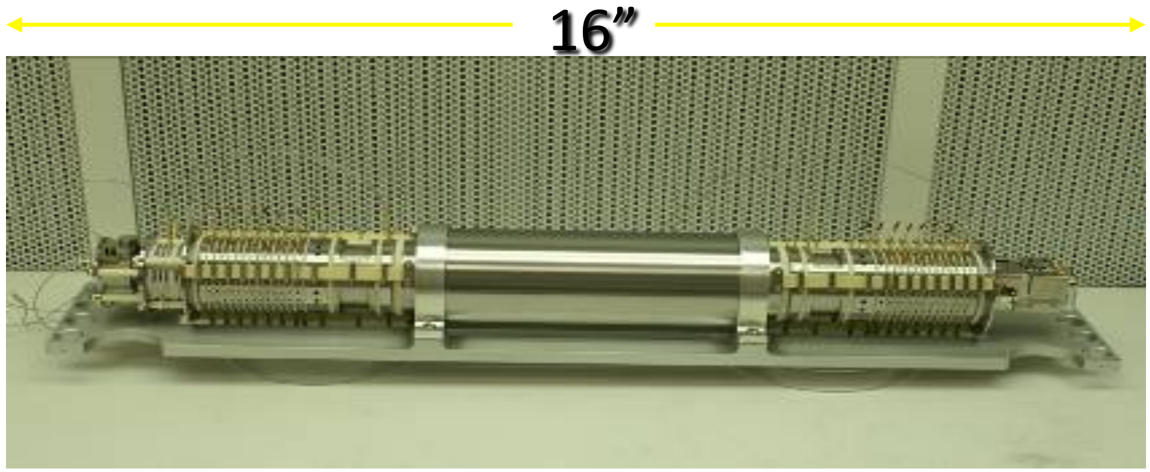
**Simulation for N_2 shows varying ion accelerating potential (ion injection energy) over a 120 eV range results in only a 1.86 percent variation in the pitch of the trochoid at the focal plane.

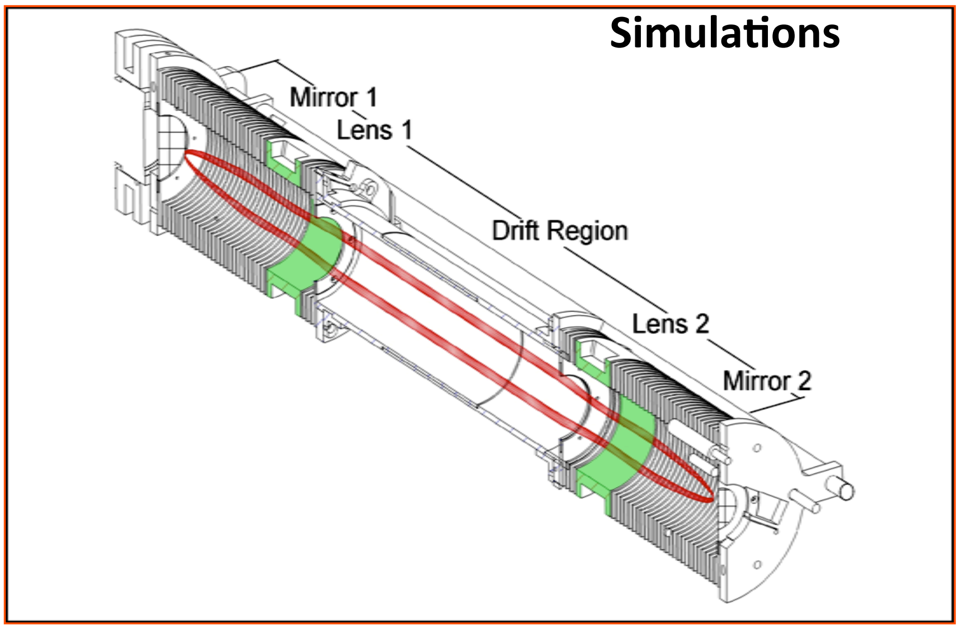
Motivation: MBTOF

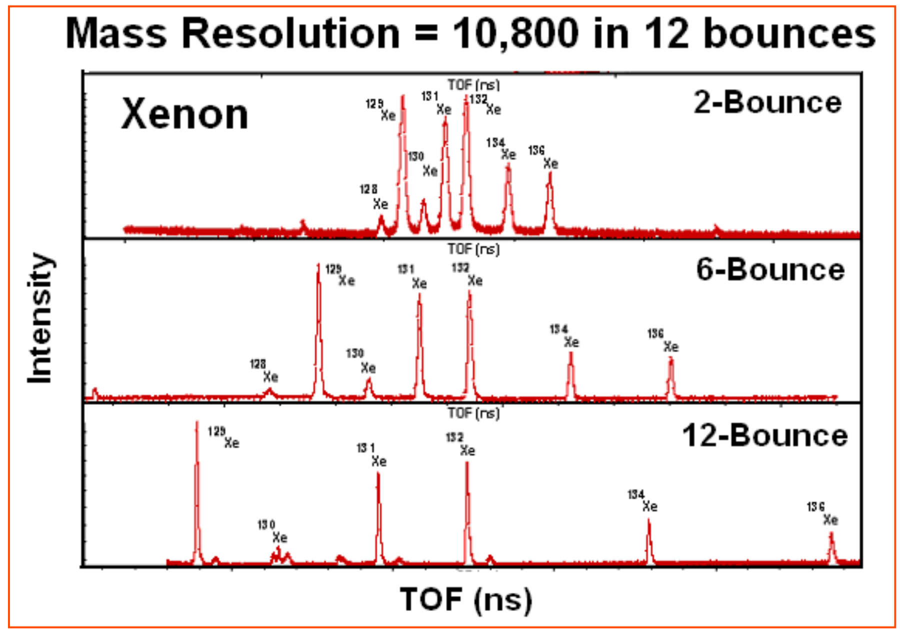
- Low resolution mass spectrometry leads to ambiguities in molecular identification, especially in separating nitriles from hydrocarbons and identifying isotopes of H, C, N, and O that overlap in a complex organic environment.
- Current space instrumentation is low mass resolution.
- Using Time-Of-Flight (TOF) mass spectrometry also leads to a factor of greater than 100 sensitivity increase relative to present day quadrupoles, which is extremely important for measurement of trace species such as noble gases.
- Instrument must also be capable of high resolution operation, be light, compact, and low power.
- The Multi-Bounce TOF (MBTOF) meets these requirements.

Multi-Bounce Time-of-Flight

THIRD GENERATION Prototype







MISSION OPPORTUNITIES

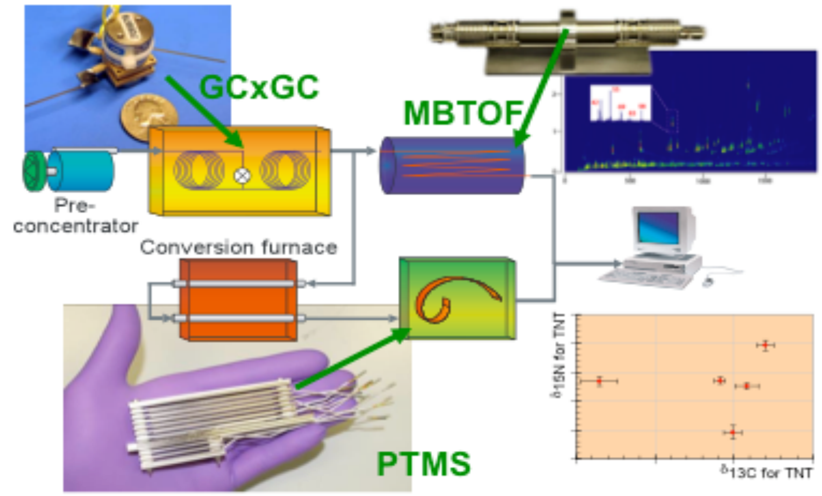
MASS SPECTROMETRY ON LANDED ASSETS: OTGINS, EVOLUTION, AND ASTROBIOLOGY

Robotic In Situ Life Detector

Description and Objectives

Robotic detection of life elsewhere in the solar system with an accurate and broad-based analytical methodology.

System Level Diagram



Resources: Size: 28" L x 16" W x 16" H; Mass:50kg; Power:150W

Approach

A cryogenic pre-concentrator will concentrate volatiles from a sample. These will then be separated using GC-GCxGC to provide highly selective compound isolation. A high resolution mass spectrometer will provide positive chemical identification of each organic component with synchronous isotopic analysis, which will provide highly-specific biological versus abiotic compound identification.

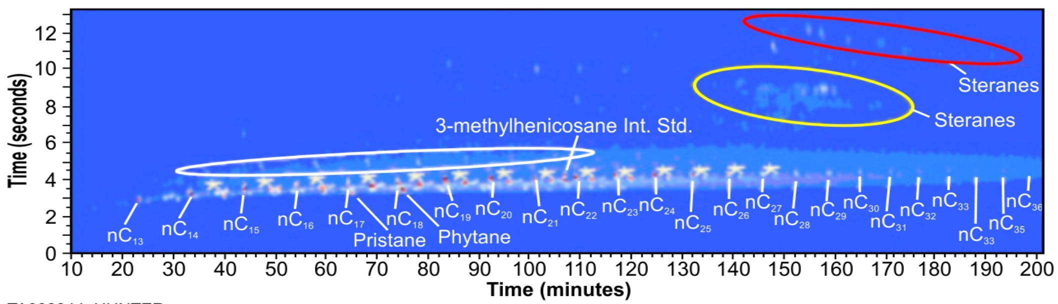
Mutiple coincidence

Coincidence dimensions

1. Organic pattern recognition – abiotic vs biotic
2. Chirality of individual compounds
3. Carbon and nitrogen isotopic ratios of individual compounds

Triple coincidence is the key to high probability of identification of biological from abiotic organic compounds – low number of false positives.

Pattern recognition coupled with isotopic and chiral correlation analysis



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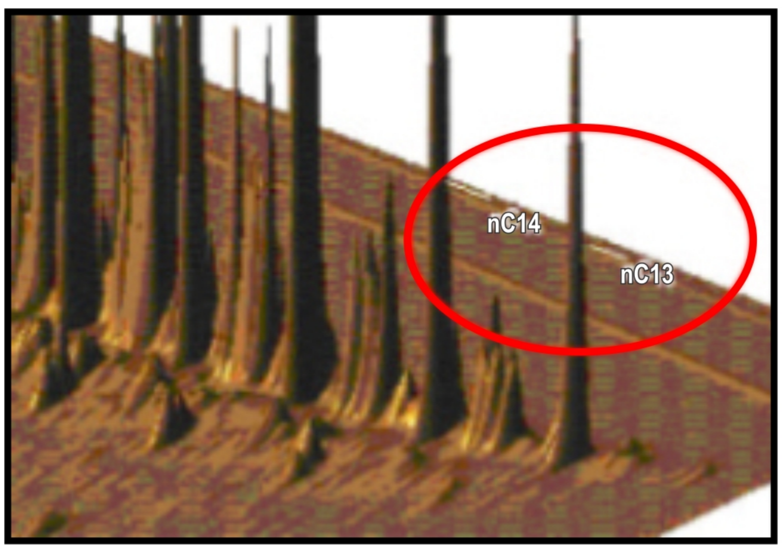

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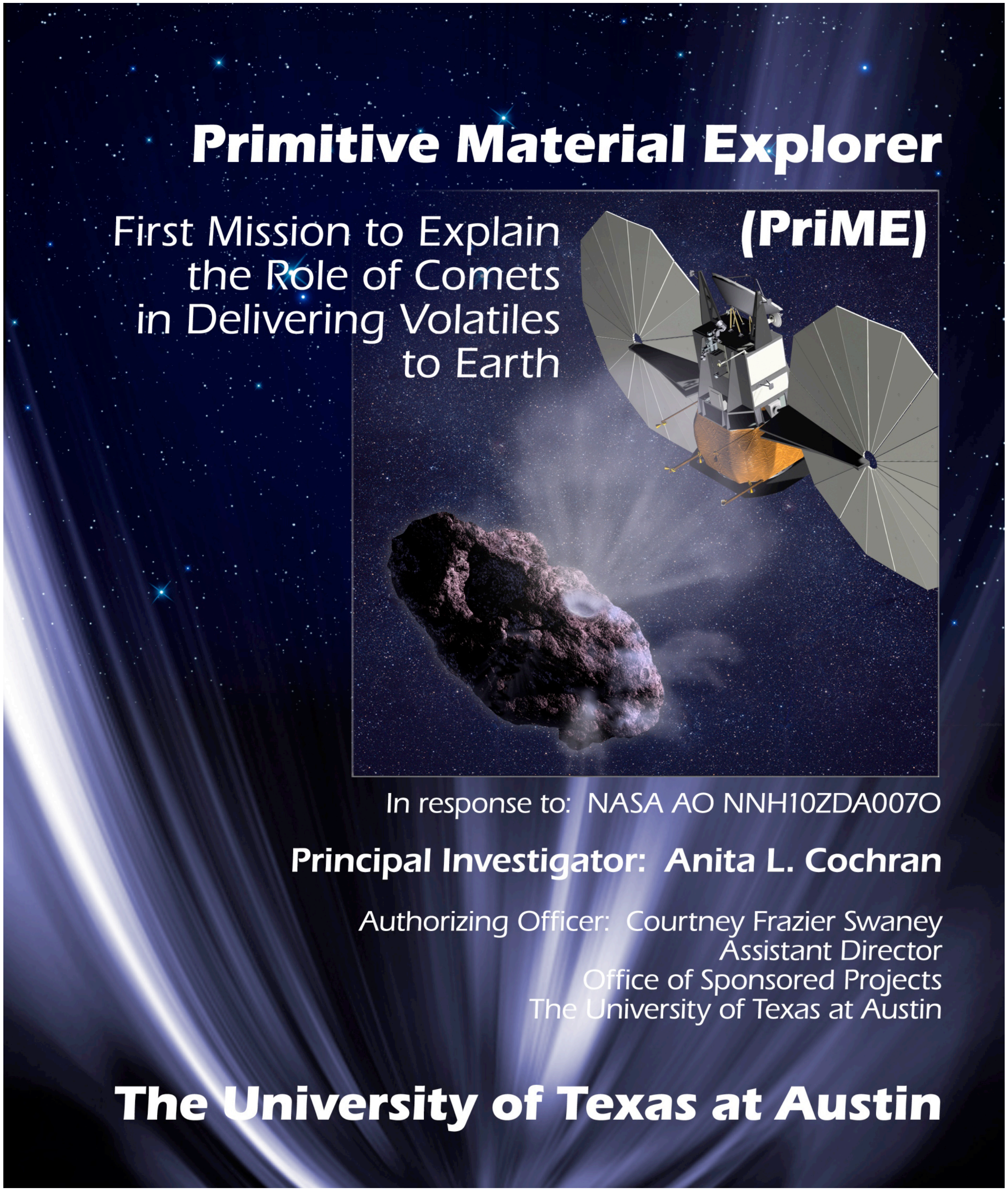
Contrast the abiotic meteroritic sample of the last slide with this Oman sediment sample. Note the even/odd alkane pattern over a range of ten carbon numbers. If we select this pattern and perform a compound by compound isotopic and chiral analysis, which repeats the same pattern we can deduce a high probability (<1 in 10^{-8}) that the occurrence occurred by random independent processes. However, the correct probability must be determined based on the proposed chemical kinetic mechanism.

COMETS AND OUTER PLANET SATELLITES



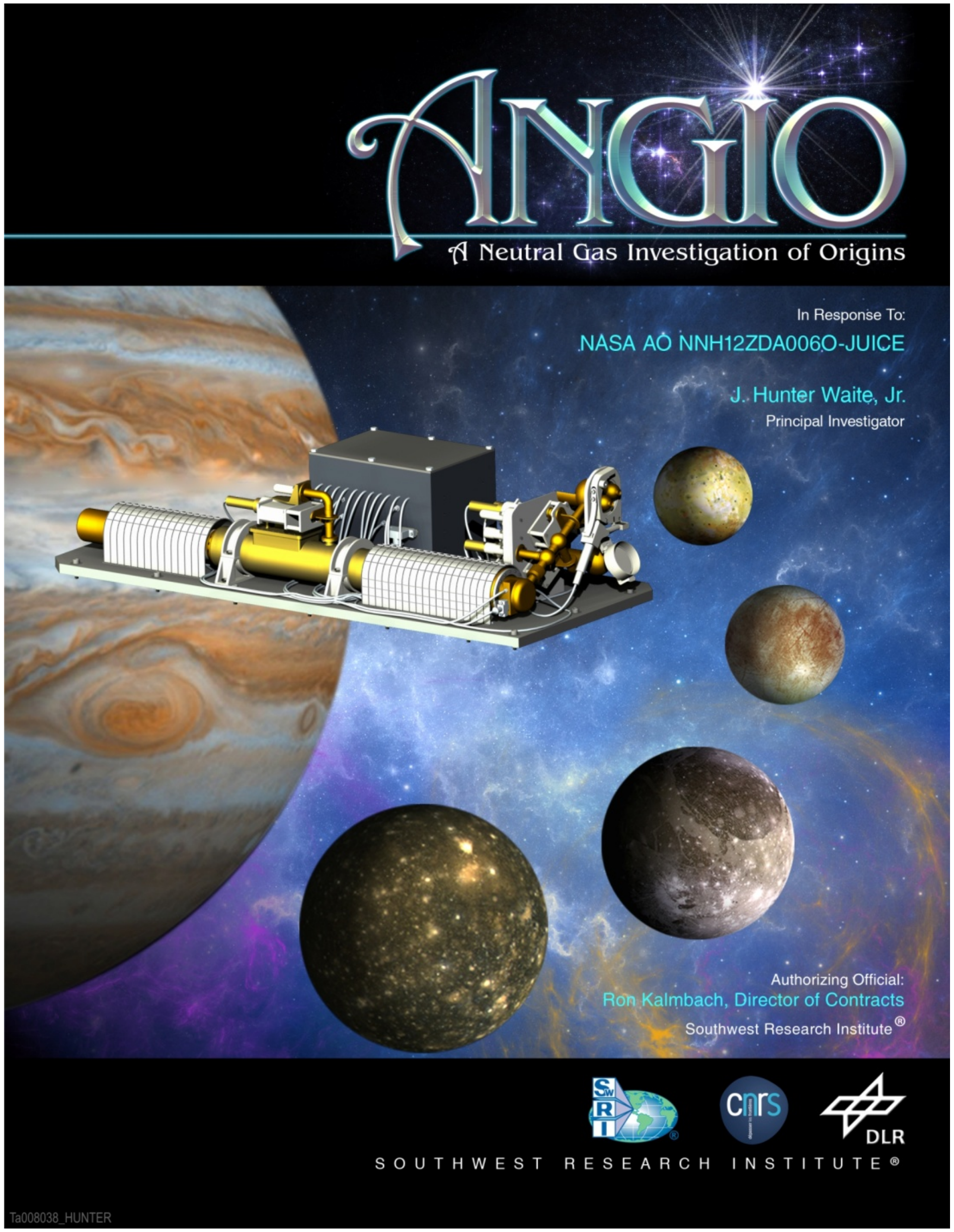
PriME is a

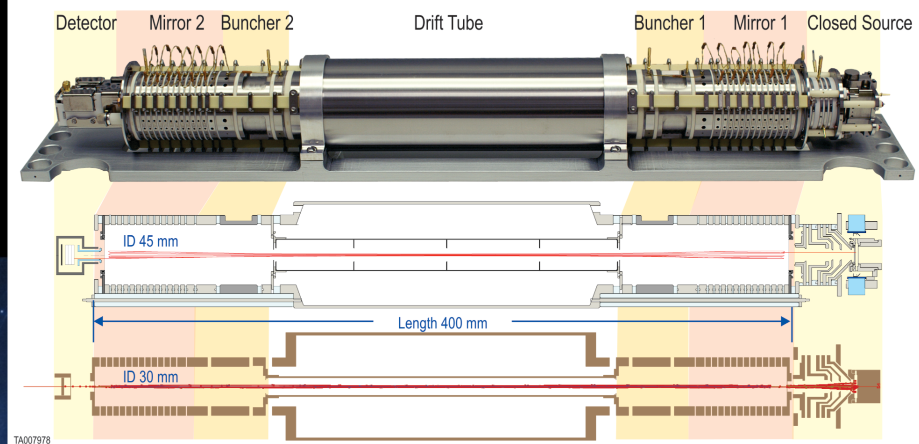
Proposed **NASA Discovery** Mission

The proposal was selected in the last round of Discovery in Category 3, which provides technology funding for the mass spectrometer.

It is not an actual

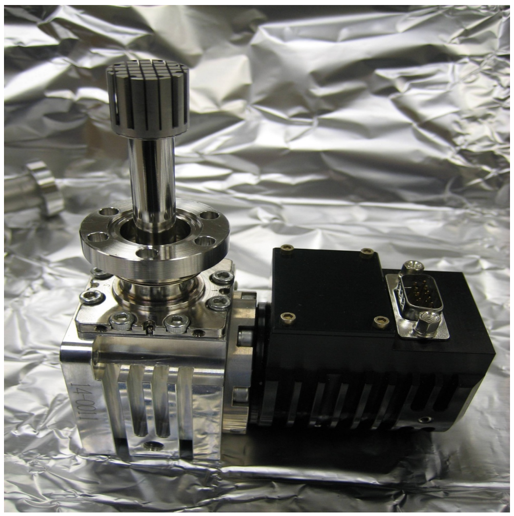
JUICE MISSION

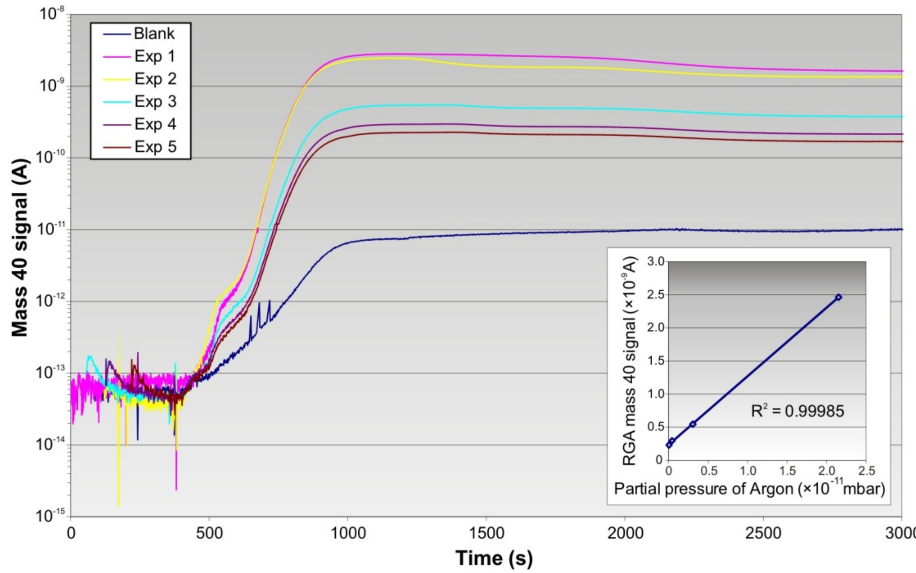




Sensitivity and mass resolution allow ANGIO to study the origin and evolution of the Galilean satellites by measuring H and O isotopic ratios in water, N isotopic ratios in ammonia, and noble gas abundances.

High Sensitivity: Cryo-trapping



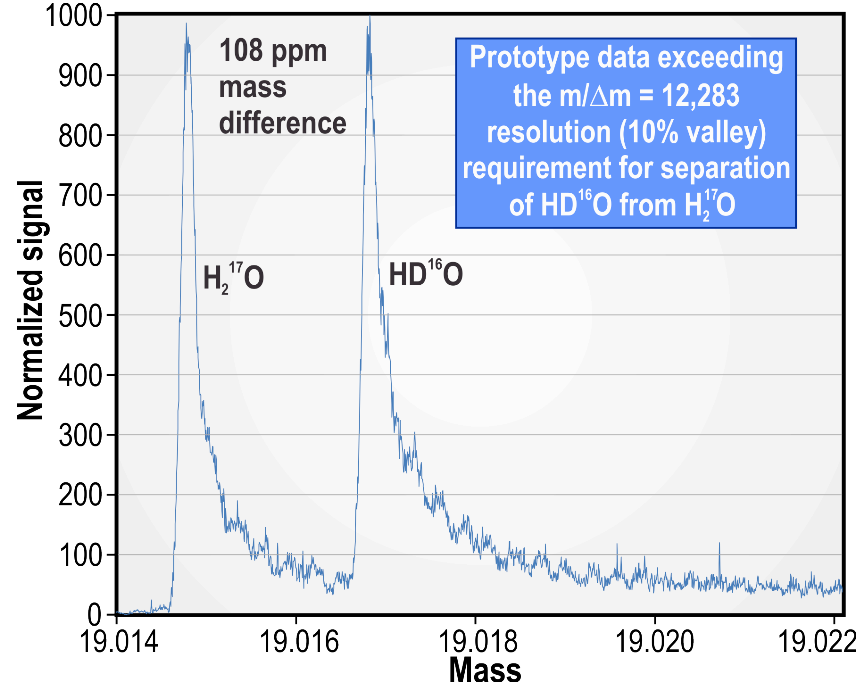


The results for Argon over 5 sample sizes and a blank. The data up to ~450 seconds is when the sample is held on the adsorber; during this period the ion pump is opened and a dip in the line would indicate that some of the sample remains unadsorbed. The noisy trace seen here is because the RGA is at the limit of its sensitivity. The ion pump is then closed and the adsorber allowed to warm to room temperature, during which period the trapped sample is evolved. The results from sample 1 are anomalous, but after deducting the blank contribution the remaining four samples fit the calibration curve with an R^2 value of 0.99985 and indicate that the adsorber is quantitative.

High Mass Resolution:

Isotopic determination in complex volatile mixtures

High mass resolution mass spectrometry is essential for H, C, N, and O isotope determination in complex mixtures containing water, ammonia, methane, and organic volatiles. Shown here is the determination of the H/D ratio in water requiring a resolution of 12,300, which takes 30 bounces on the MBTOF.



ATMOSPHERIC PROBES

MAss Spectrometer for Planetary EXploration (MASPEX)

- MASPEX has been proven by test and simulation to meet or exceed AO science requirements
- Multi-bounce time-of-flight (MBTOF) mass spectrometry is the most straightforward and accurate method for sampling a column of Saturn's atmosphere from 0.5 to 20 bar.
- Gas from column is collected, concentrated, and analyzed at high speed and resolution to give breakthrough measurements of Saturn's atmosphere.
- MASPEX resources are commensurate with performance.
- New technologies are at or approaching TRL6.