

# Laser Desorption/Ionization Time-of-Flight Mass Spectrometry for Future *In Situ* Planetary Missions



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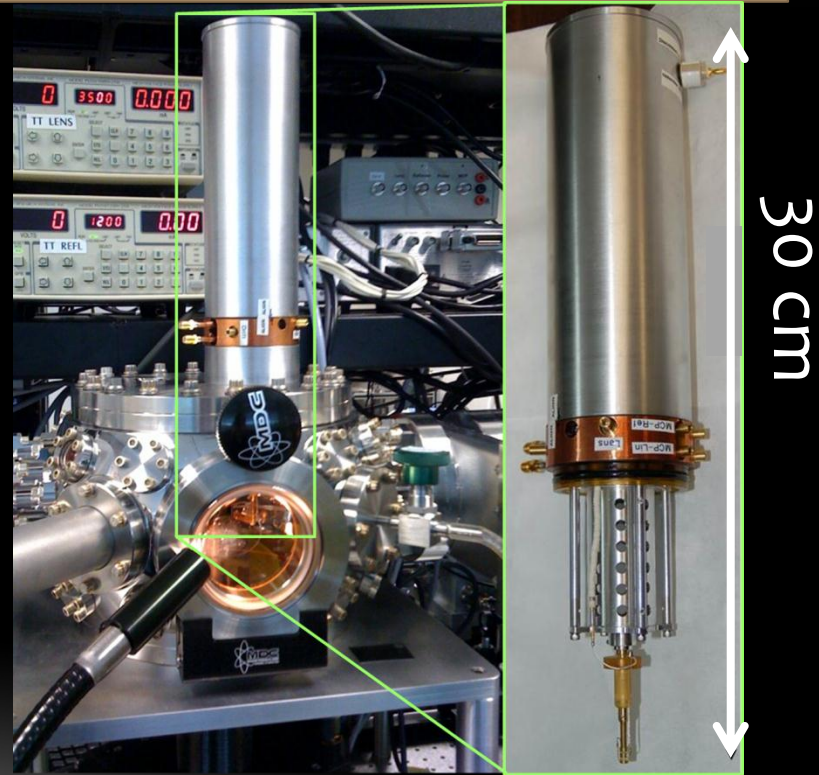
*New Mexico State University*

# IN SITU INSTRUMENT DEVELOPMENT: LD-TOF-MS IN A COMPACT INSTRUMENT



Commercial LD-TOF-MS is a gold-standard technique for the analysis of biomolecules

We have built a miniature LD-TOF-MS smaller by an order of magnitude

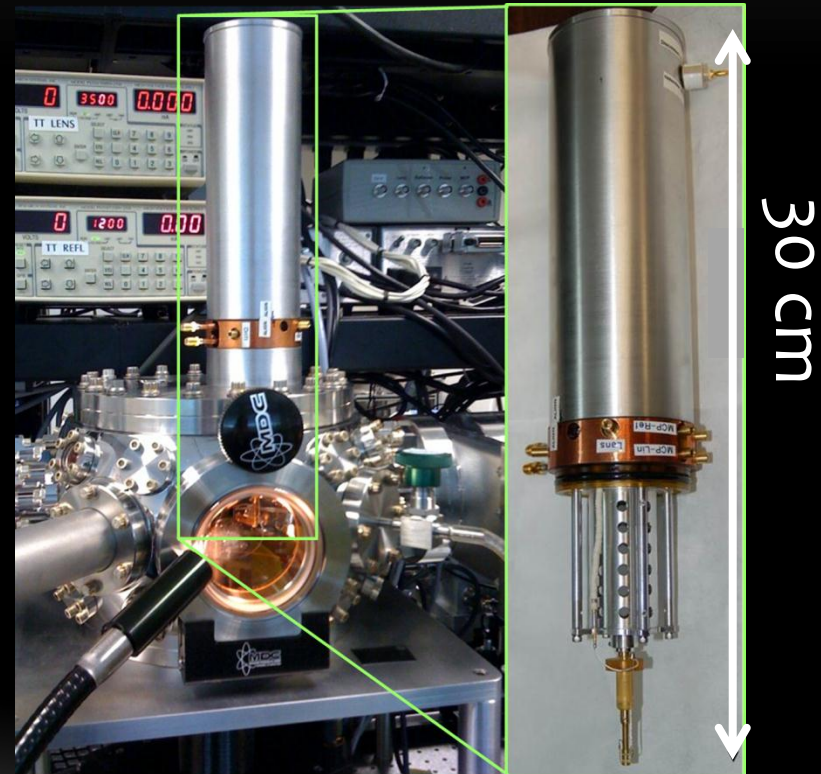


# IN SITU INSTRUMENT DEVELOPMENT: LD-TOF-MS FOR IN SITU COMPOSITION

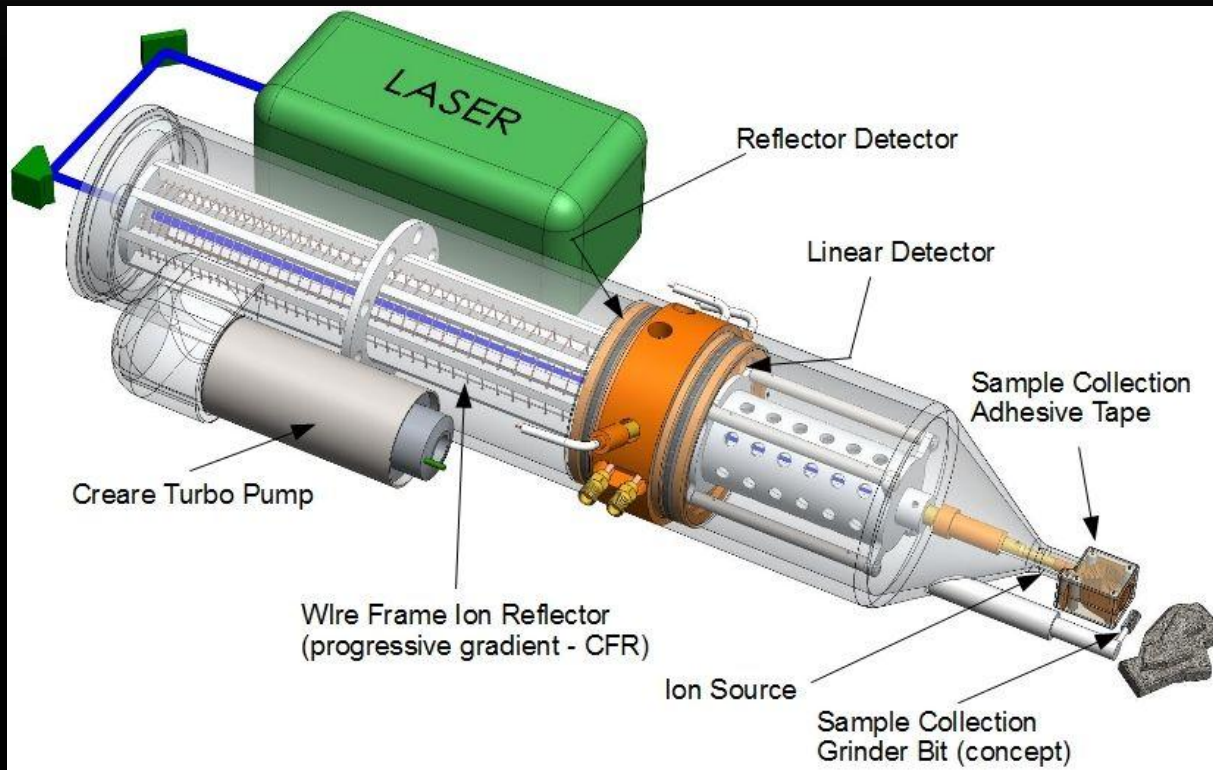
LD-TOF is more generally capable of broadband detection of inorganic and organic composition directly from a solid sample

- Mineral composition
- Small organics: amino acids, carboxylic acids, polycyclic aromatics, etc.
- Intermediate organics: molecular fossil precursors, conjugated polymers, etc.
- Large organics: peptides, biopolymers, etc.
- Can resolve elemental isotopes and  $^{12}\text{C}$ ,  $^{13}\text{C}$  isotope patterns in organics

We have demonstrated this broad detection capability using a diverse suite of standards, analogs, and simulants



# INSTRUMENT DESIGN: 5 KG-CLASS IN SITU ANALYZER



LD-TOF-MS Mass Estimate	
Subsystem	Mass/g
1. TOF-MS	700
1.1 Mass Analyzer	330
1.2 Housing	370
2. Laser	1693
3. Optical	380
4. Electronics	1826
4.1 Comm/Data	291
4.2 Power Supply	585
4.3 Pulsed HV	440
4.4 Detector	260
4.5 Harness	250
5. Turbo Pump	550
5.1 Pump, 200 krpm	200
5.2 Controller	350
TOTAL	5149
TOTAL + 30% Margin	6848

# COMPARISON: ADVANTAGES OF LD-TOF-MS

	GC-QMS (SAM)	LDI-ITMS (MOMA-MS)	LD-TOF-MS
Sample: Volatile vs Non-volatile	Volatile	Non-volatile (Volatile with GC- EI)	Non-volatile
Power Supply	RF	RF	Pulsed DC
Mass Range	2-535 Da	1-2,000 Da	1-150,000 Da
Ion Polarity	Positive ions	Positive ions	Positive and Negative
Instrument Mass [Estimates]	~15 kg	~7 kg	~5 kg

## EXAMPLE SPECTRA:

# STANDARDS AND ANALOG SAMPLES

### Positive Mode

- Inorganic (cation) Minerals •
  - Polycyclic Aromatics •
- High Molecular Weight Polymers and Biopolymers •

### Negative Mode

- Inorganic (anion) minerals •
- Amino Acids • Carboxylic Acids •
  - Analog Mixtures •

### Integrated *In Situ* Instrumentation

- Correlated IR and Mass Spectra •
- Advantages in Surface Operations, Confidence in Analyses •

### Advanced Mass Spectrometry

- Molecular Fingerprinting through Fragment Analysis •
- Specificity through Two-Step Laser Desorption/Ionization (L2MS) •

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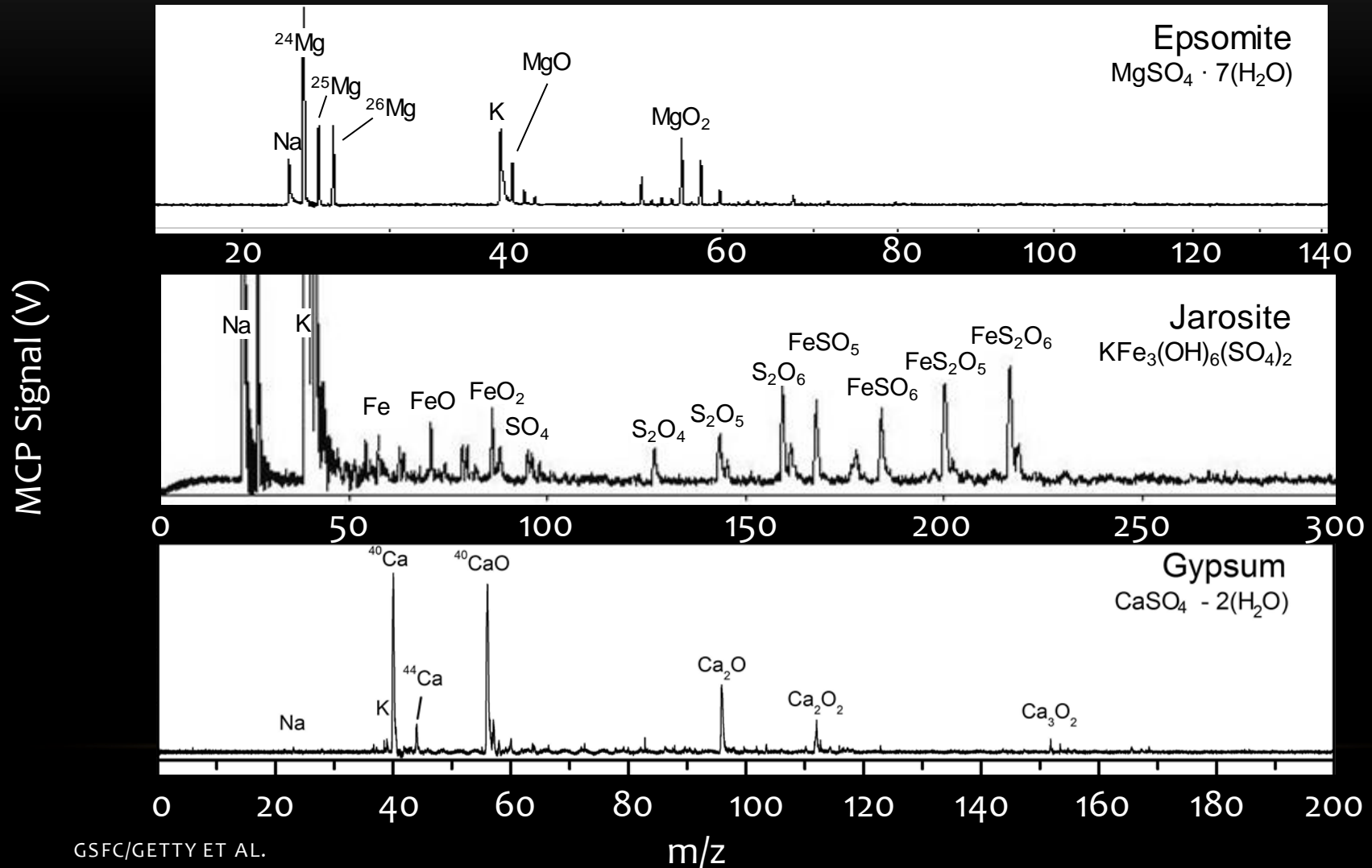
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## POSITIVE ION MODE:

# INORGANIC (CATION) COMPOSITION

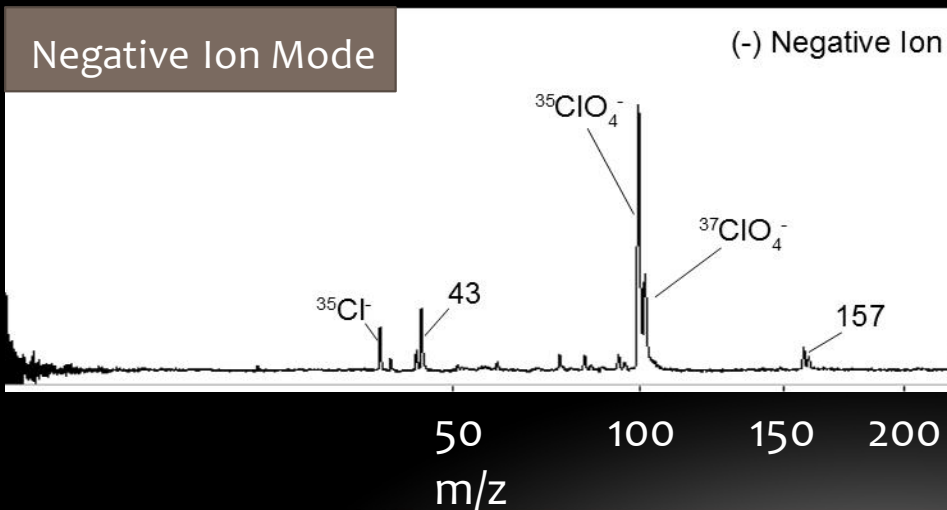
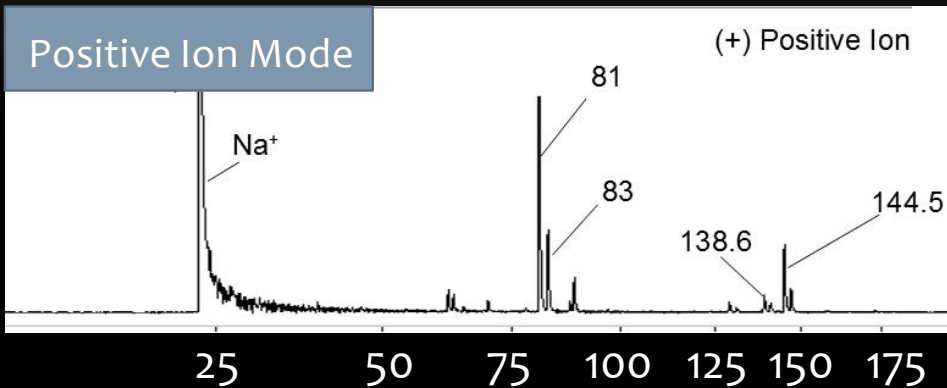
Sedimentary and Aqueously Altered Minerals,  
e.g., Sulfates, Carbonates, Iron Oxides, etc.



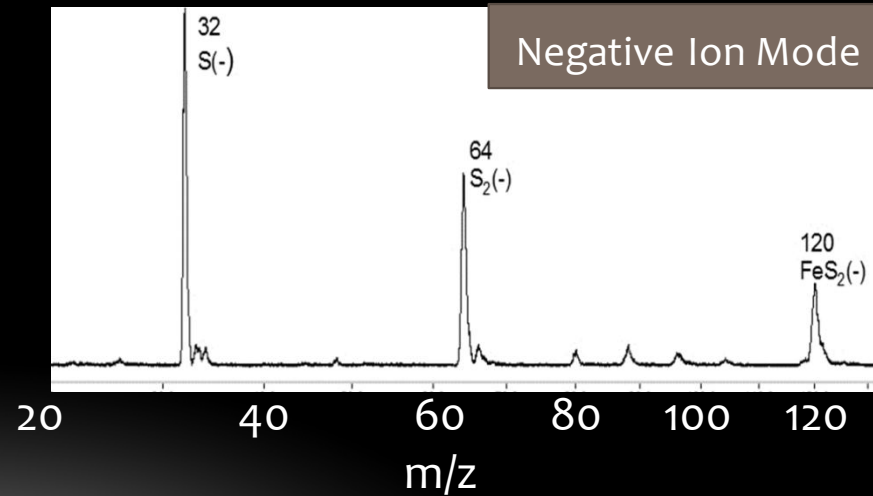
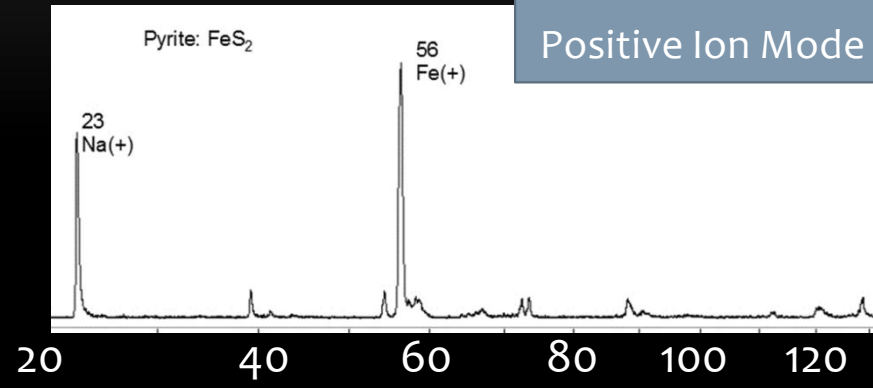


# COMPLEMENTARY POSITIVE AND NEGATIVE ION DETECTION: E.G., PERCHLORATES AND SULFIDES

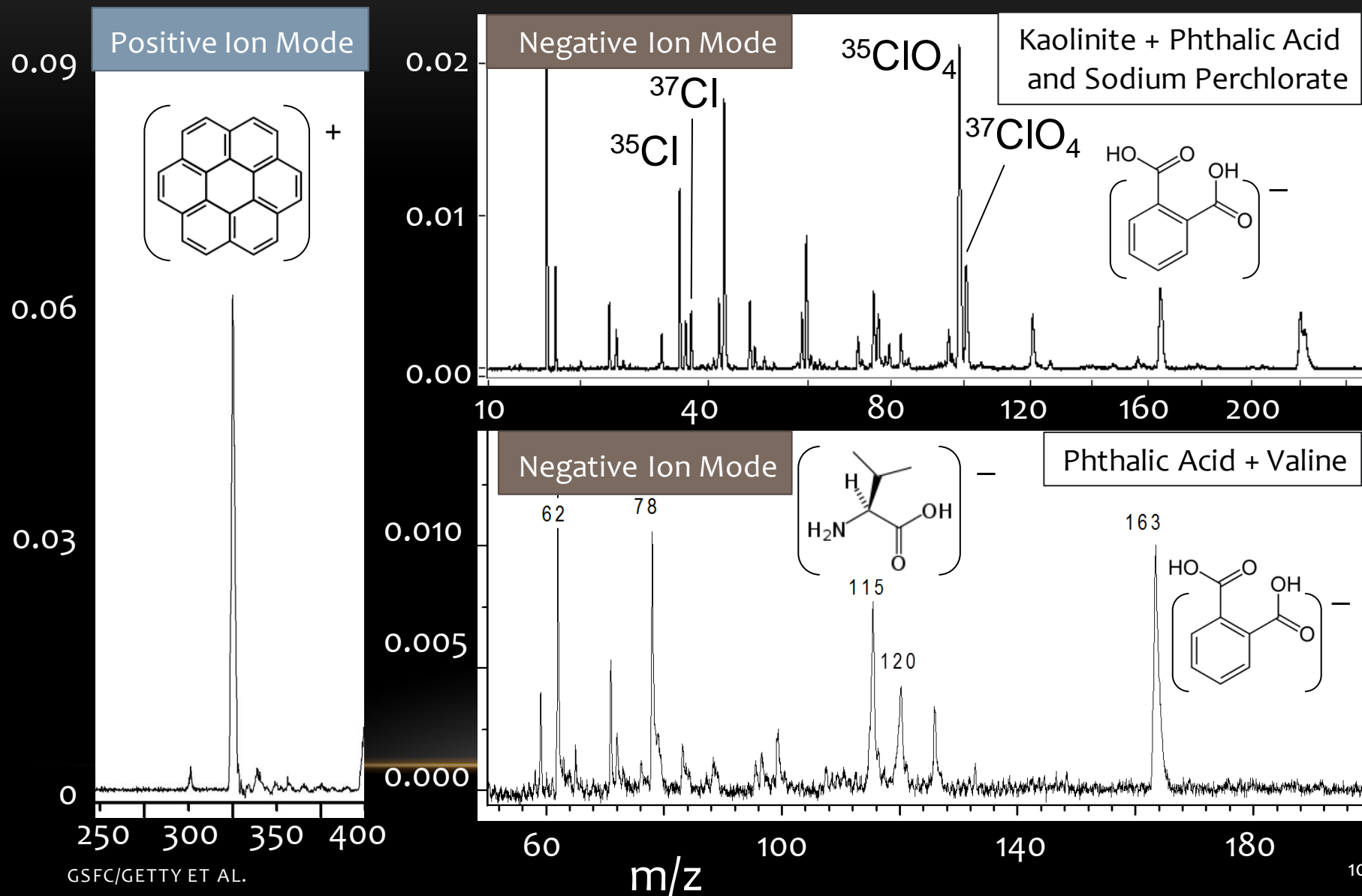
## Sodium Perchlorate ( $\text{NaClO}_4$ )



## Pyrite ( $\text{FeS}_2$ )

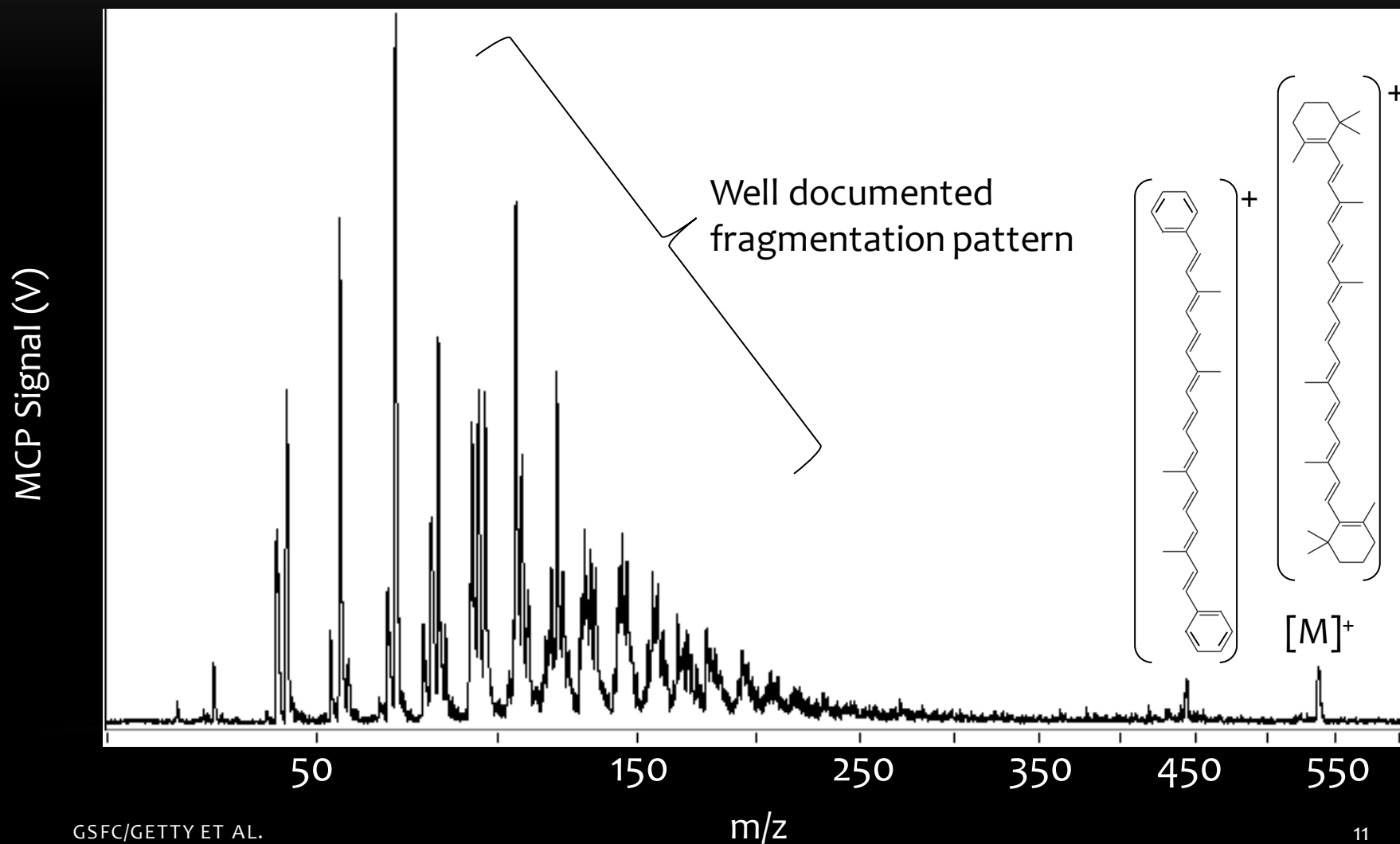


# COMPLEMENTARY POSITIVE AND NEGATIVE ION DETECTION: DETECTING ORGANICS ACROSS CLASSES



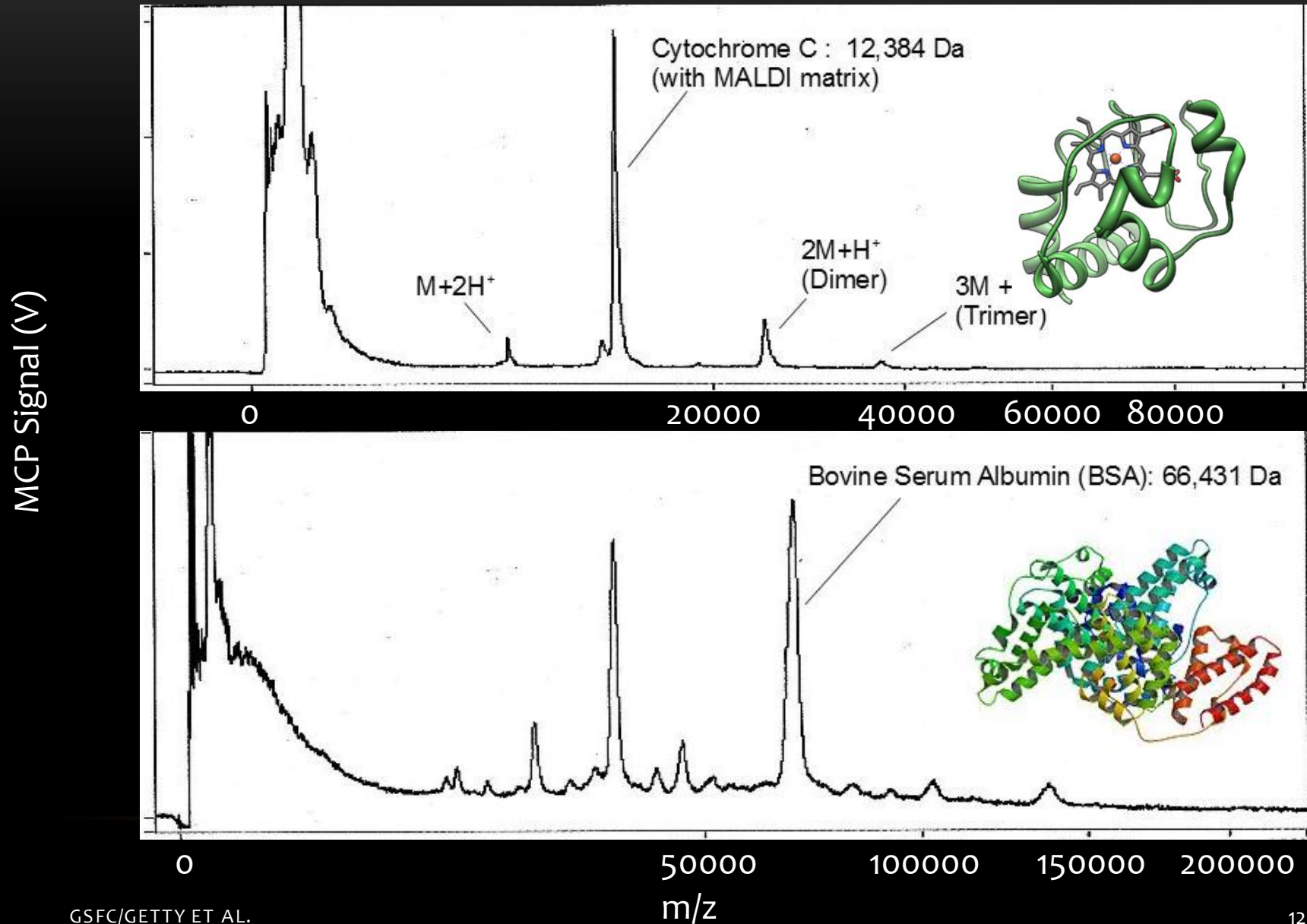
# POSITIVE ION MODE: ORGANIC COMPOSITION

Beta-Carotene: relevant compound to molecular fossil precursors,  
polyacetylene synthesis in interstellar clouds



# EXAMPLE MEASUREMENTS:

## BIOMOLECULES NEXT GENERATION *IN SITU* ASTROBIOLOGY



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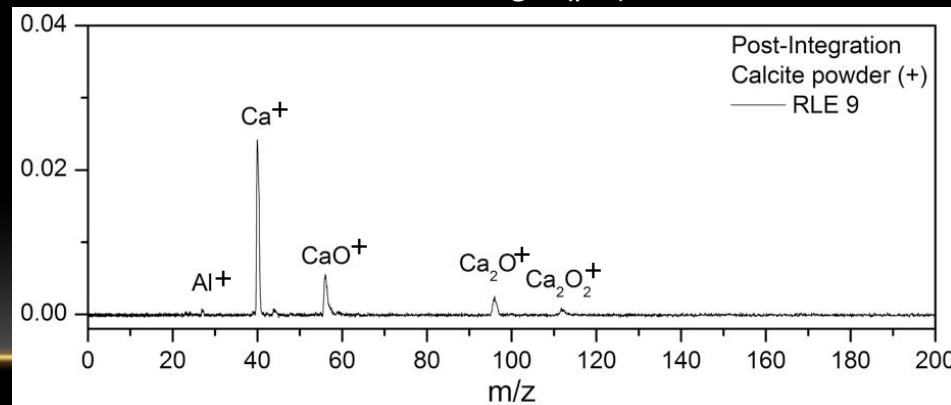
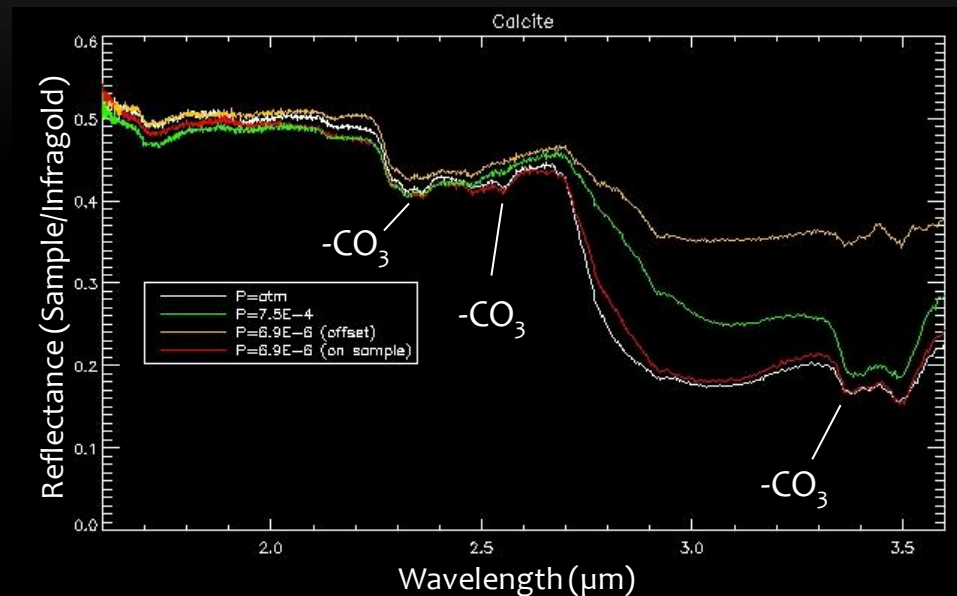
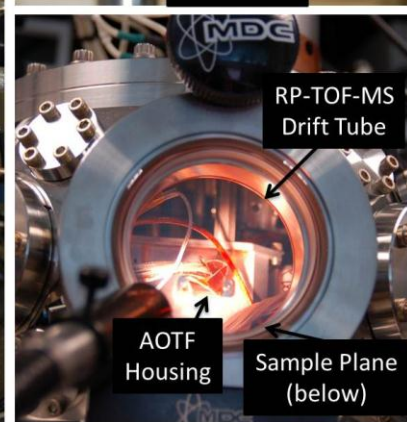
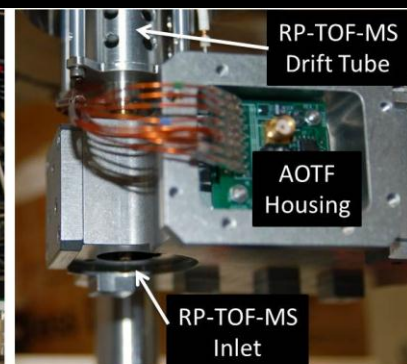
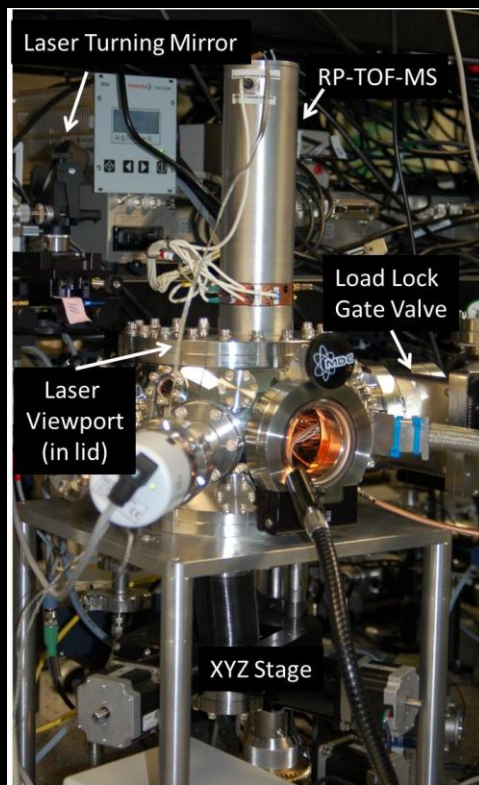
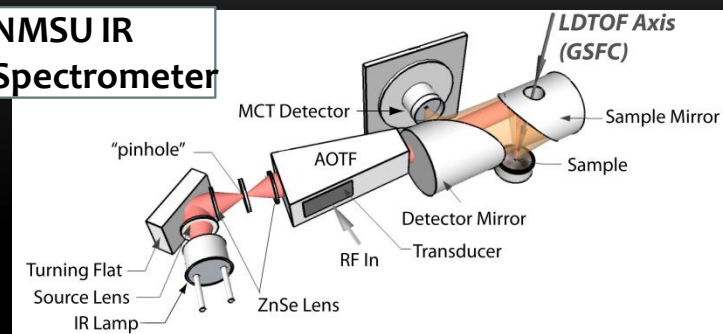
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# COMPLEMENTARY IN SITU ANALYSES: COINCIDENT IR AND MASS SPECTRA

## NMSU IR Spectrometer



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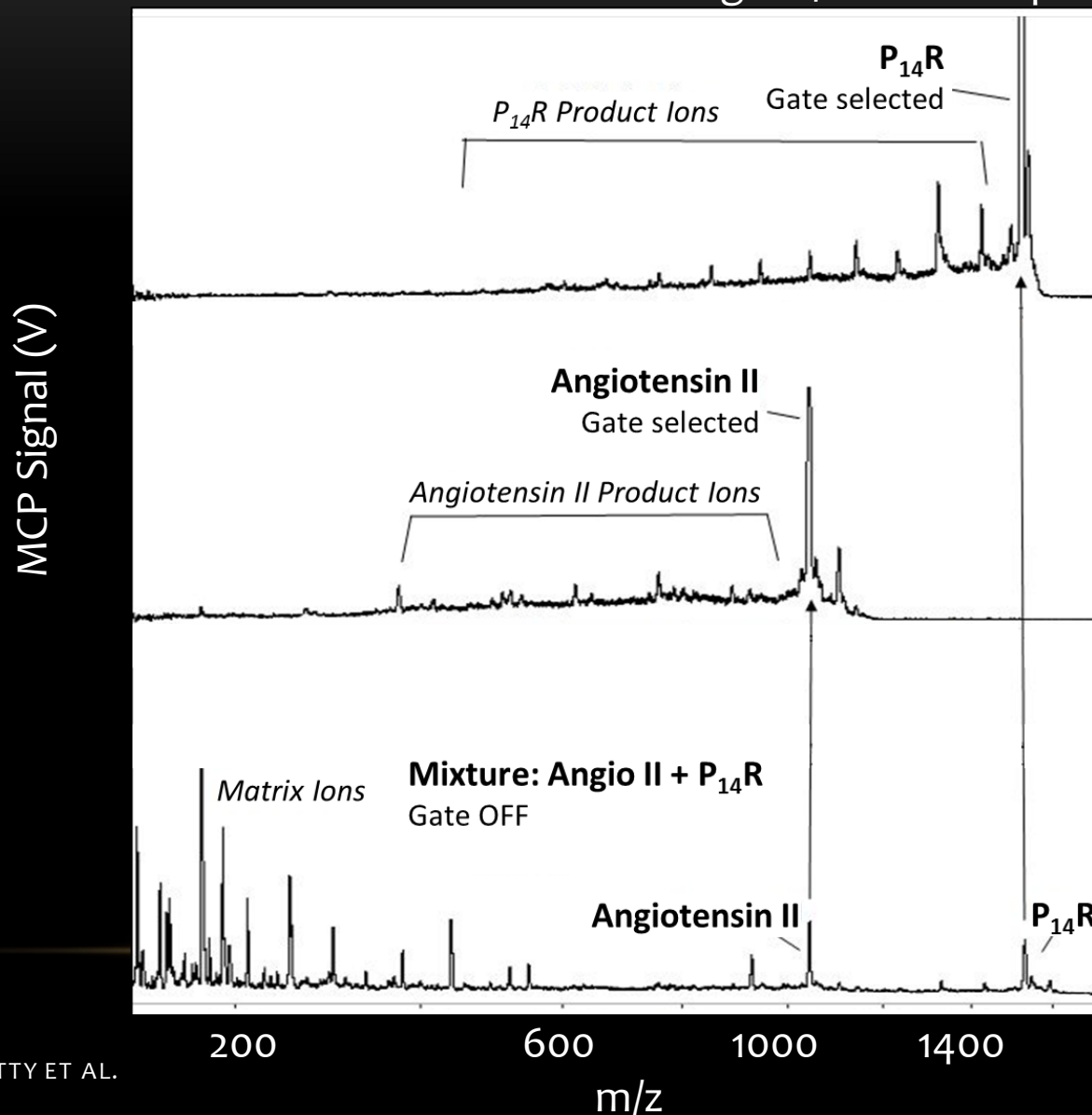
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# PRECISION ION GATING AND TANDEM MS

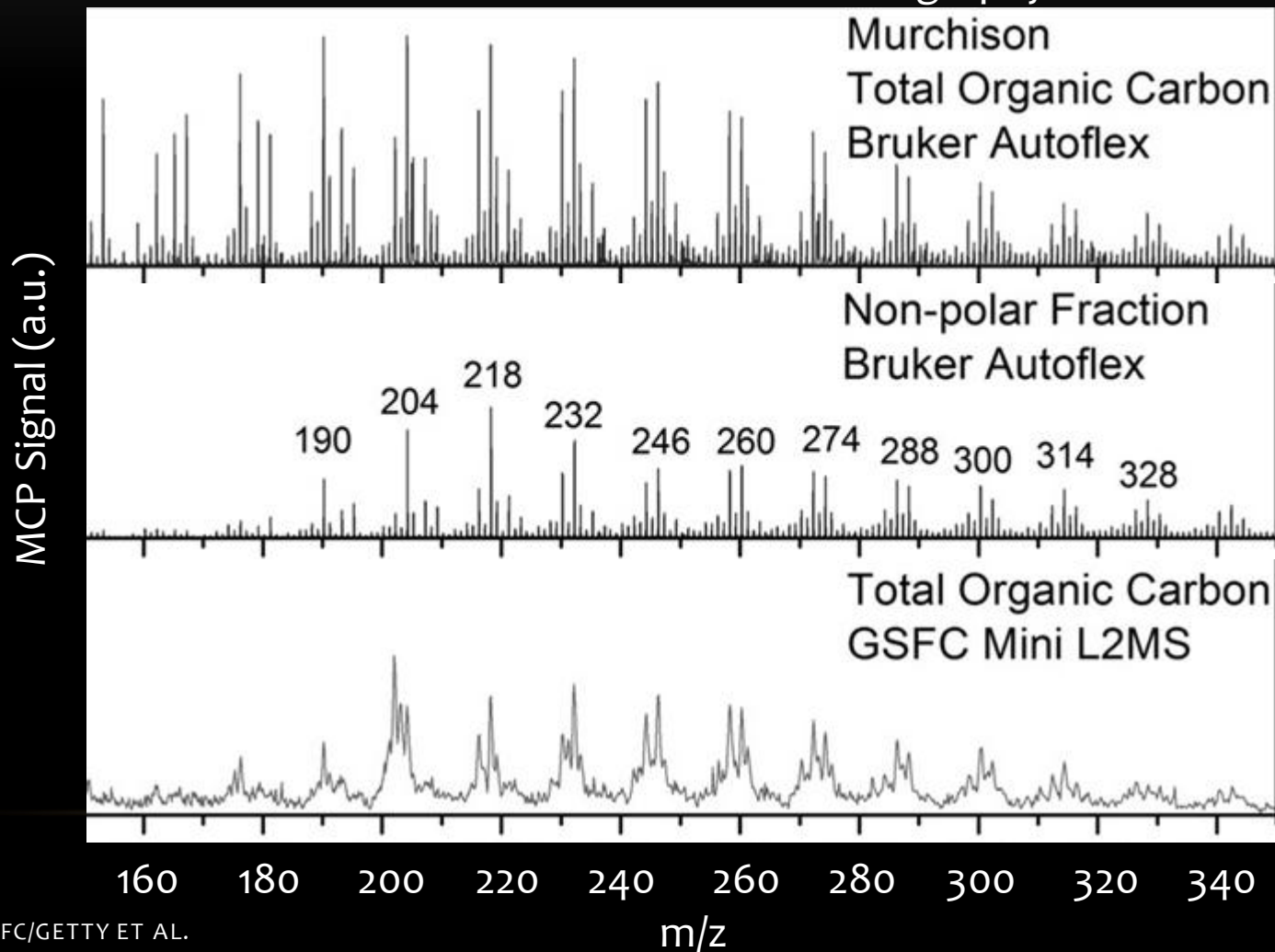
Structural determination using MS/MS techniques





# ADVANCED MASS SPECTROMETRY: TWO-STEP LASER IONIZATION FOR SPECIES SELECTIVITY IN A COMPLEX MIXTURE

Isolate the non-polar, aromatic fraction of complex sample  
*without* front-end chromatography



LD-TOF-MS offers a compelling *in situ* capability for exploration of high priority planetary surface materials: Sediments – Regolith – Ices  
Contextual Mineralogy • Organic Building Blocks • Biological Polymers

**Planetary Evolution:**

Evidence for extinct/extant life  
Preserved organics  
Sample selection  
Mineralogical context

**Primitive Materials:**

Prebiotic chemistry  
Organics available to early Earth  
Sample selection  
Mineralogical context

