MOMA: Mars Organic Molecule Analyzer

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Harsh Environment Mass Spectrometry Workshop

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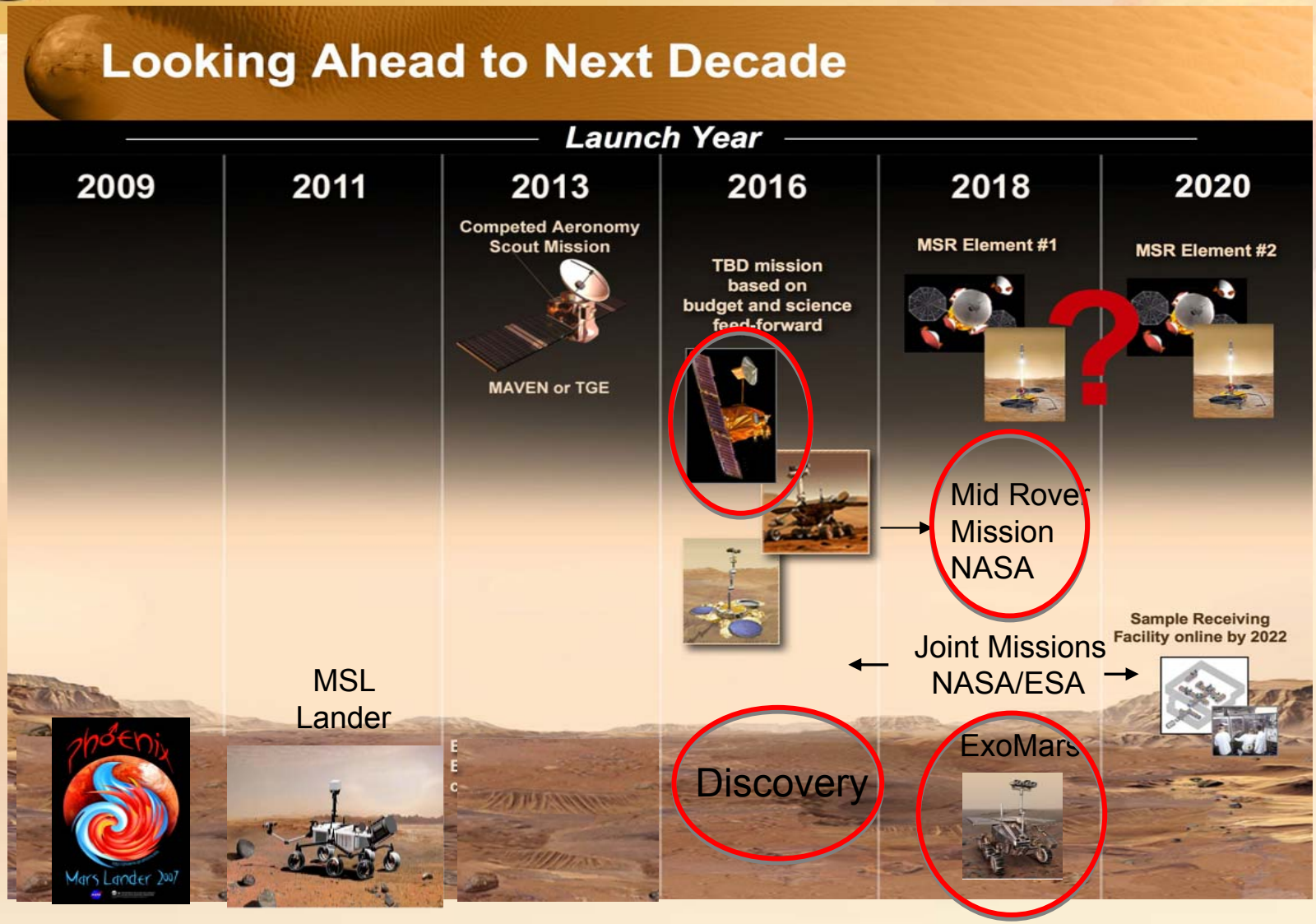
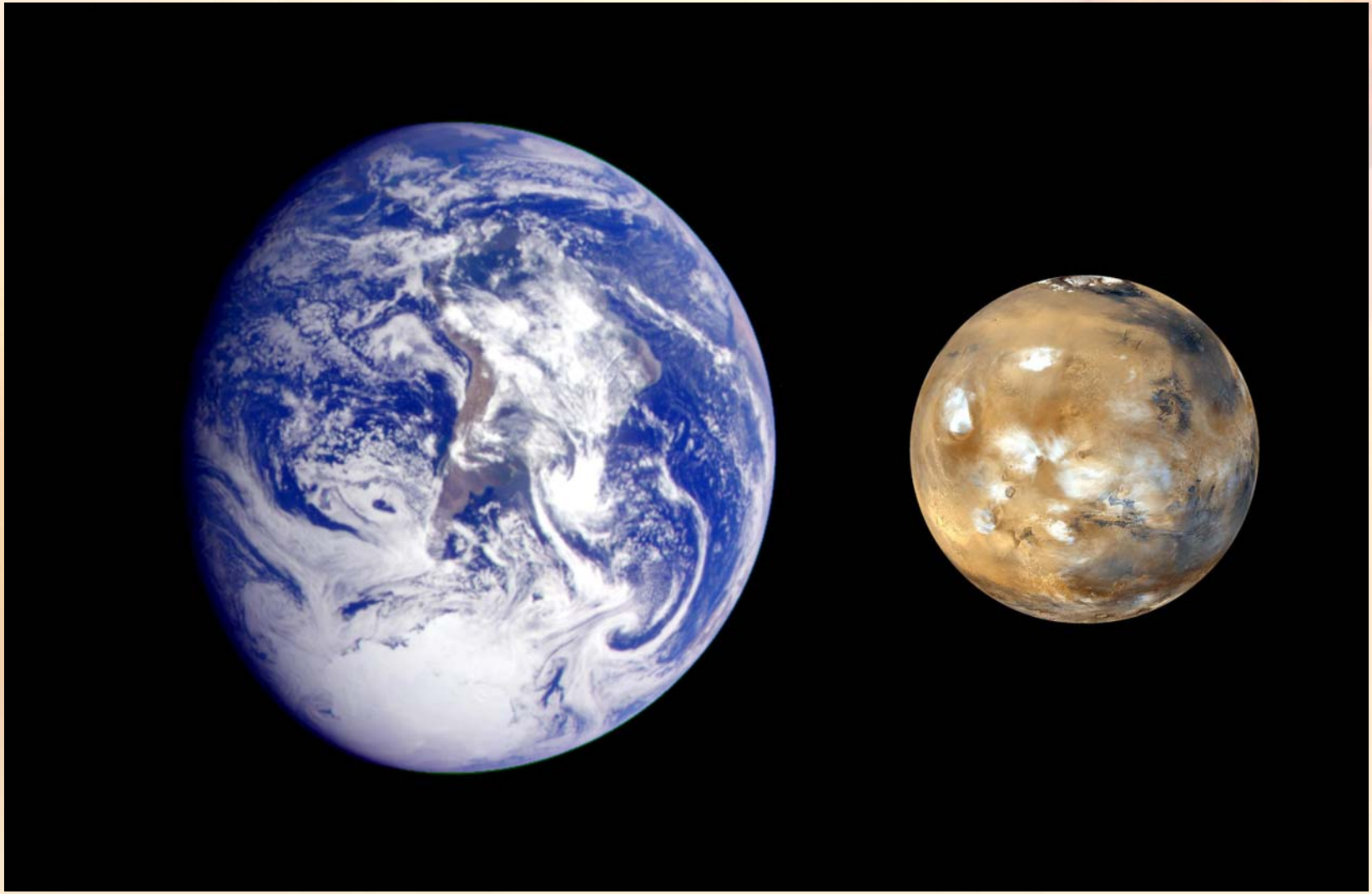
Strategy for Future Missions to Mars

- Lessons learned from ‘Past’ Rover/Lander Missions: Emphasis on Life Detection
- ‘Present’ Missions: Looking Ahead to the Next Decade
- New Instrument Concepts in Search for Life: MOMA

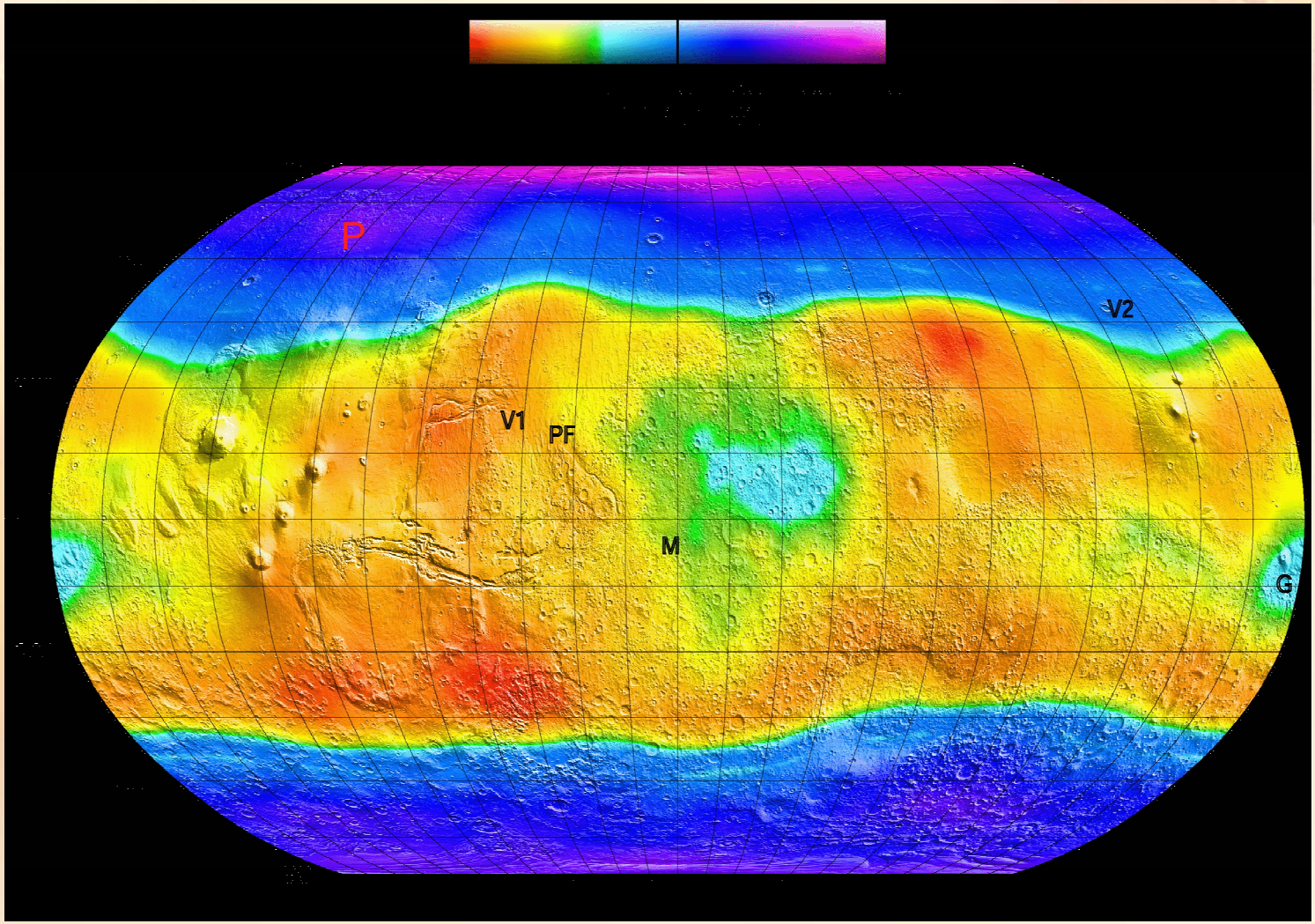
Mission Timeline



Earth and Mars Today



Map of Mars showing H_2O and Landing Sites



Previous Mass Spectrometry Concepts

Mission	Year	Planet	Name	Sample Acquisition	Sampling Depth	Volatilization	Ionization	Analyzer	MS Modes	Number of samples	Max Mass (Da)
Viking	1976	Mars	GCMS	Scoop fines; oven; atmosphere	~20 cm	Pyr (500 C)	EI	Sector	GC-MS	3	215
Cassini	2004	Titan	GCMS	Atmosphere	n/a	Direct samping; Pyr 600 C (ACP)	EI	QMS	GC-MS	n/a	141
Phoenix	2008	Mars	TEGA/MS	Cut/scoop ice, fines; oven	50 cm	Pyr (1000 C)	EI	Sector	Pyr-MS	8	140
MSL	2010	Mars	SAM	Core/crush rock; sample cups; atmosphere	10 cm	Pyr (1100 C)	EI	QMS	Pyr/GC-MS; Derivatization	Baseline 74; Unlimited with reuse	535
Rosetta	2014	Comet	Ptolemy	Drill	25 cm	Pyr (600 C)	EI	ITMS	Pyr/GC-MS	4	140
Rosetta	2014	Comet	COSAC	Drill	25 cm	Pyr (600 C)	EI	TOF-MS	Pyr/GC-MS	12	330 (5000 possible)
ExoMars	**2013**	**Mars**	**MOMA**	**Drill/grind cores; scoop; UREY extracts**	**2 m**	**Laser Desorption; Pyr (1000 C)**	**LDI; EI**	**ITMS**	**LDI-MS; LD-EI-MS; Pyr/GC-MS; Derivatization**	**Baseline 20; Unlimited with reuse**	**2000**

- High mass range à complex organic analysis
- Drill to 2m; depth profiling
- Multiple sampling modes

Viking Missions: What Happened?

Viking (1976)

- GCMS: Surface soil
- No organics found by GCMS
- Nutrient Experiment
  Inconclusive

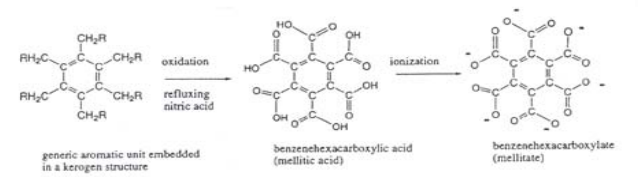
Conclusions:

Highly oxidizing soil, low pH (acidic), ionizing radiation produce non-volatile organic salts resulting in more refractory 'labile' organic material

1

Expected Metastable Products from Organic Substances in the Murchison meteorite

Substance	Concentration (parts per million)	Metastable Products
Acid insoluble kerogen	14500	Benzenecarboxylic acids
Aliphatic hydrocarbons	12–35	Acetate
Aromatic hydrocarbons	15–28	Benzenecarboxylic acids
Monocarboxylic acids	~330	Acetate/oxalate
2-Hydroxycarboxylic acids	14.6	Acetate/carbonate
Alcohols (primary)	11	Acetate
Aldehydes	11	Acetate
Ketones	16	Acetate, benzenecarboxylic acids
Amines	10.7	Acetate
Urea	25	Carbonate
Heterocycles	12	Carbonate, other products



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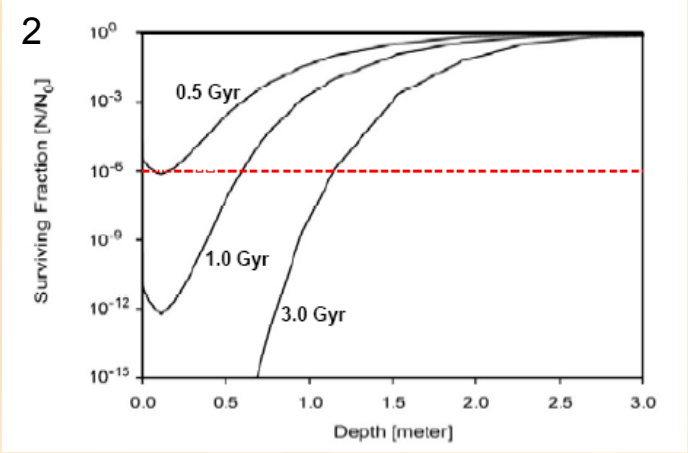
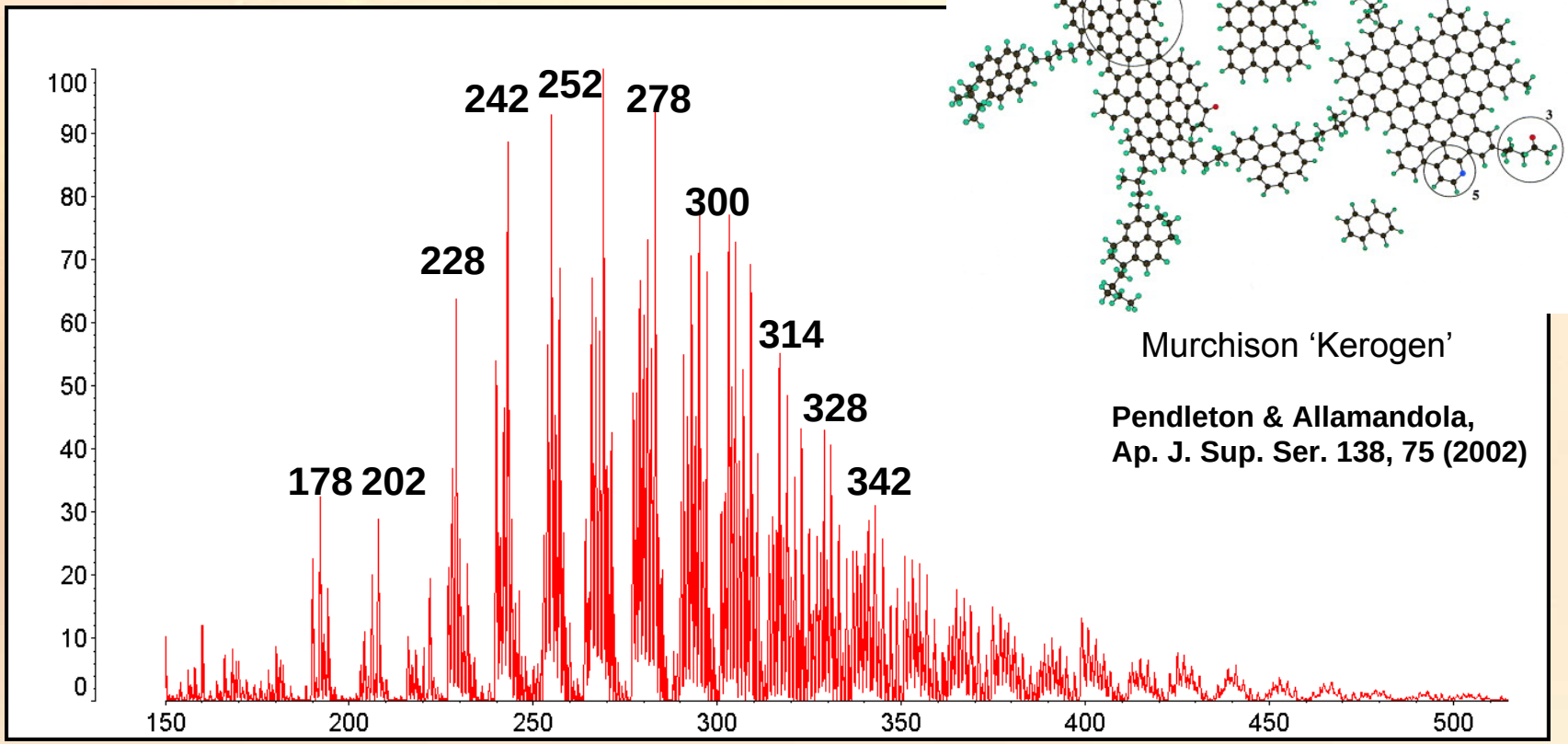
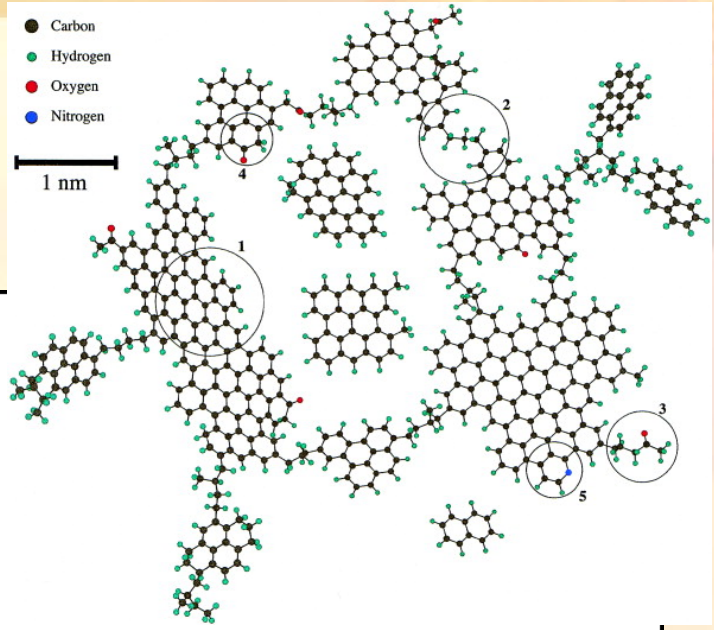


[1]Benner et al., (2000) The Missing Organic Molecules on Mars? *PNAS* 2425-2430.
[2]Kminek G and Bada JL (2006). The effect of ionizing radiation on the preservation of amino acids on Mars. *Earth Planet. Sci. Lett., 245*, 1−5.

Organics in Murchison Meteorite

Murchison Meteorite LDMS-TOF



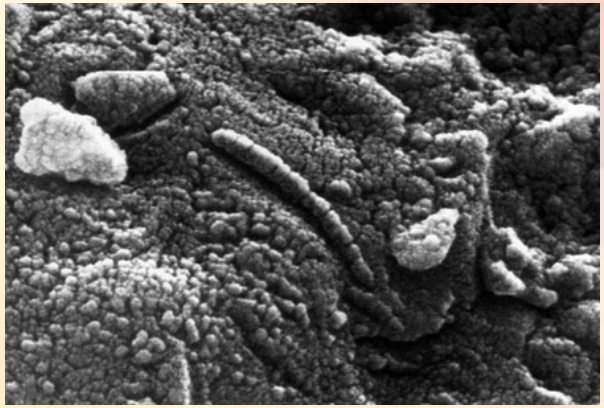


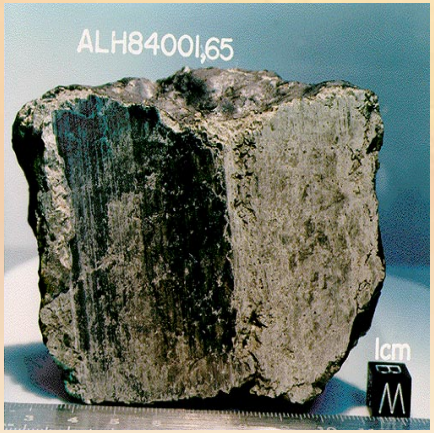
Murchison 'Kerogen'

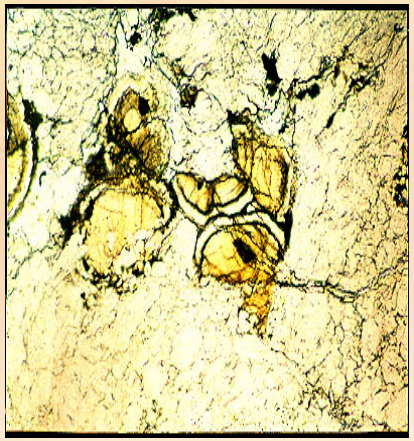
Pendleton & Allamandola, Ap. J. Sup. Ser. 138, 75 (2002)

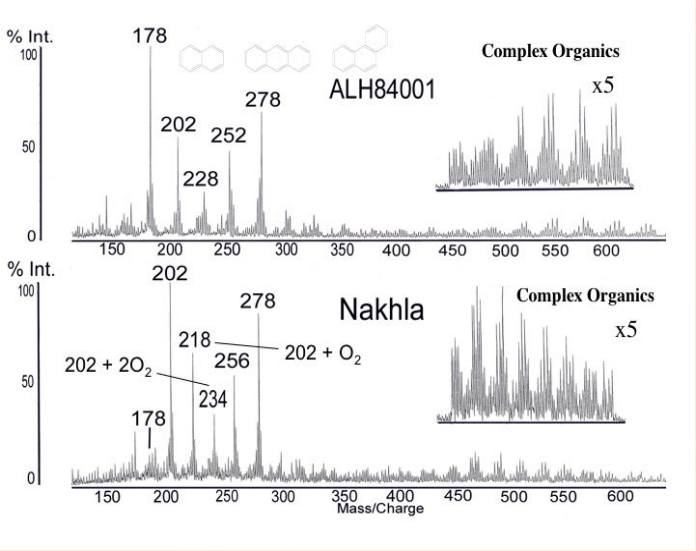
Is there, or was there, life on Mars?

- ALH84001
  - Martian meteorite
  - Antarctica
  - 1996: nanobacteria fossils; amino acids, PAHs found









[1] Becker, L., Popp, B., Rust, T., Bada, EPSL., *167*, 71-79 (1999); Becker, L. NRC Signs of Life Workshop, 161-173 (2000) .
[2] Becker, L., Popp, B., Rust, T., Bada, J. *Adv. Space Res., 24*, **4**, 477 (1999).

What is MOMA?

- AP MALDI = Atmospheric Pressure Matrix Assisted Laser Desorption/Ionization (ASTEP)
  - a pulsed laser is focused onto a solid sample in ambient environment (Mars P = 5-10 Torr CO_2; IR or UV laser Nd:YAG 266 nm)
  - neutral and ionized molecules are produced
  - molecules are drawn into a mass spectrometer for analysis
- ITMS = Ion Trap Mass Spectrometer
  - ions are stored in stable orbits by a 3D quadrupolar RF electric field in the presence of a rarified background gas (1-10 mTorr CO_2 works fine)
  - ions are scanned out and detected by ramping the RF amplitude
  - can be used to isolate individual ions for fragment analysis (MS/MS)

* The AP-MALDI was merged with a GCMS proposed by a German and French team for the ExoMars mission; It is part of the *MOMA* suite which also includes Pyr-GC-EI-MS

MOMA Science Requirements

What are our requirements?

1. the mass analyzer will need to be compatible with both laser desorption and GCMS
2. laser desorption will be carried out in situ, on solid samples presented at Mars atmospheric pressure
3. the mass range should encompass that expected for establishing the existence of organic or potentially biological relevant molecules (e.g. small peptides), ca 2,000 Da
4. the instrument will need to accommodate two ionization sources (LD and electron ionization)

ION Trap Selection

Why use an ion trap?

1. most compatible with external (atmospheric) ionization using laser desorption

   a. TOFs (and others) require very high vacuum and a means for sample introduction

   b. orthogonal TOFs can be used with external ionization but require very high pumping speed to achieve high vacuum

2. has the possibility for doing MS/MS for structural analysis

3. low power ion traps have been used successfully in GCMS configurations

MOMA Instrument Concept Design

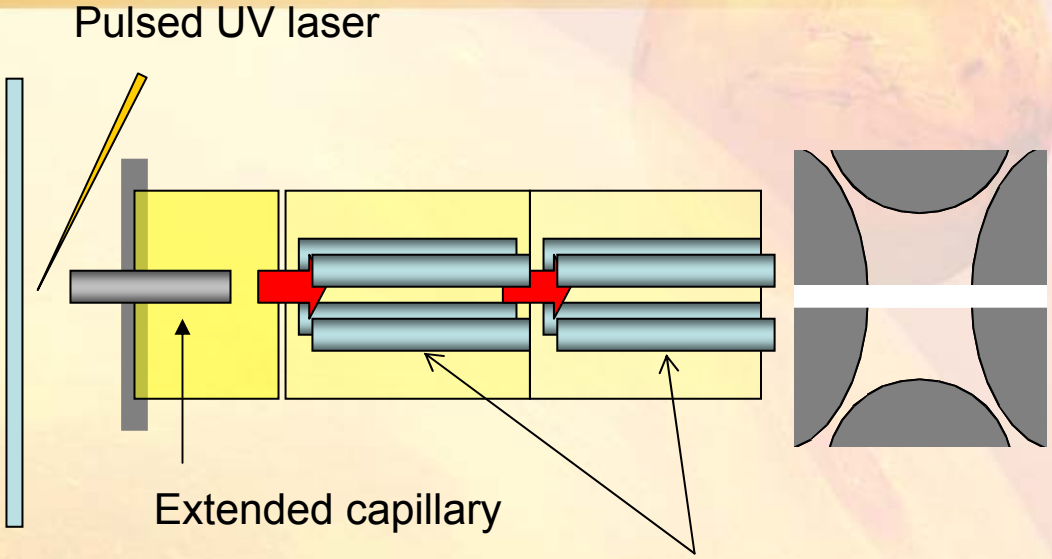
What are the specific challenges?

1. combining low voltage/low power with a sufficiently high mass range
2. transferring ions formed in the Mars environment into the vacuum chamber and the ion trap
3. accommodating two sources of ions: those generated externally by LD and those generated by the GC either internally or externally using electron ionization

MOMA LDMS Instrument Concept Design

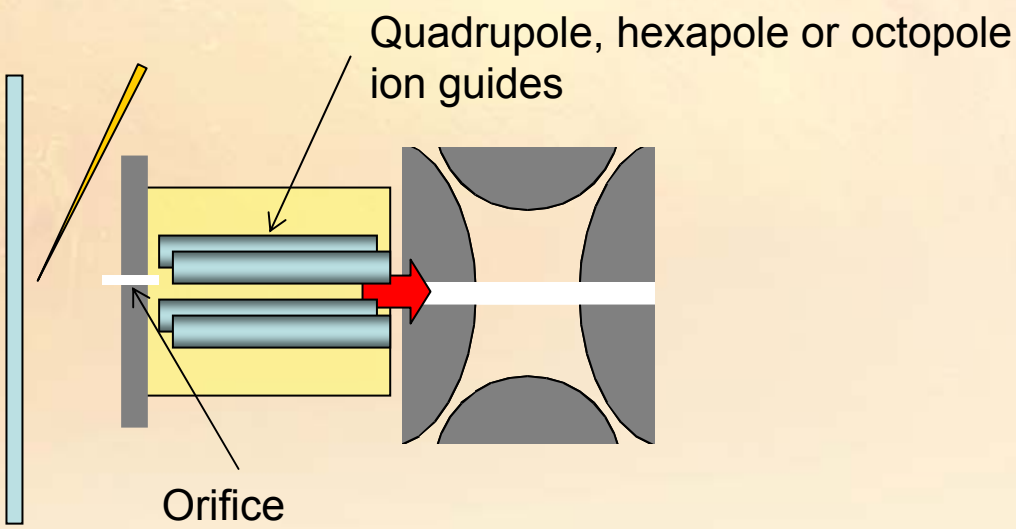
Atmospheric pressure laser desorption on **Earth**

P=760 torr



Atmospheric pressure laser desorption on **Mars**

P=5-10 torr



MOMA Instrument Concept Design

Accommodating low power/low voltage and high mass range

TABLE I. Quadrupole and Cylindrical Ion Trap Parameters						
Parameter	Finnigan	Cooks	Rosetta	Cylindrical	**Mars 1**	***Mars 2***
Fundamental _ /2[1] (MHz)	1.1	1.1	0.6	1.1	**1.0**	***0.8***
Maximum amplitude V_{max} (0-p)	7.5 kV	7.5 kV	300 V	7.5 kV	**300 V**	***300 V***
Radius r_0 (cm)	1.0	0.5	0.8	1.0	**0.5**	***0.5***
Axis $2z_0$ (cm)	1.0	0.5	1.13	1.79	**0.5**	***0.5***
Mass range (Da) in *mass-selective instability* mode q_{eject} = 0.908	650	2,600	150	600	**126**	***197***
Supplemental RF frequency (kHz)	69.9	NA	NA	425	**22.1**	***34.4***
q_{eject}	0.182	NA	NA	NA	**0.057**	***0.089***
Mass range (Da) in* resonance ejection *mode	***3,250***	***NA***	***NA***	***NA***	*2,000*	*2,000*

$$(m/z)_{max} = \frac{8V_{max}}{q_{eject}\Omega^2\left(r_0^2 + 2z_0^2\right)}$$

[a]Kaiser RE, Jr., Cooks RG, Moss J, Hemberger PH, Mass Range Extension in a Quadrupole Ion-trap Mass Spectrometer, **Rapid Commun. Mass Spectrom. 3**, (1989) 50-53

[b]March RE, Todd JF, Quadrupole Ion Trap Mass Spectrometry, John Wiley & Sons, Inc. Hoboken NJ, 2005

Uniqueness of MOMA Design

What are the specific innovations?

1. combining low voltage/low power and a mass range up to 2,000 Da using lower trap frequency and a supplemental excitation with very low q_{eject} value
2. accommodating LD and EI using internal electron ionization with the electron source on the ring electrode
3. supplemental voltage frequency scanning of the mass range
4. use of CO_2 as a bath gas in the LD mode

MOMA Prototype Design Concept

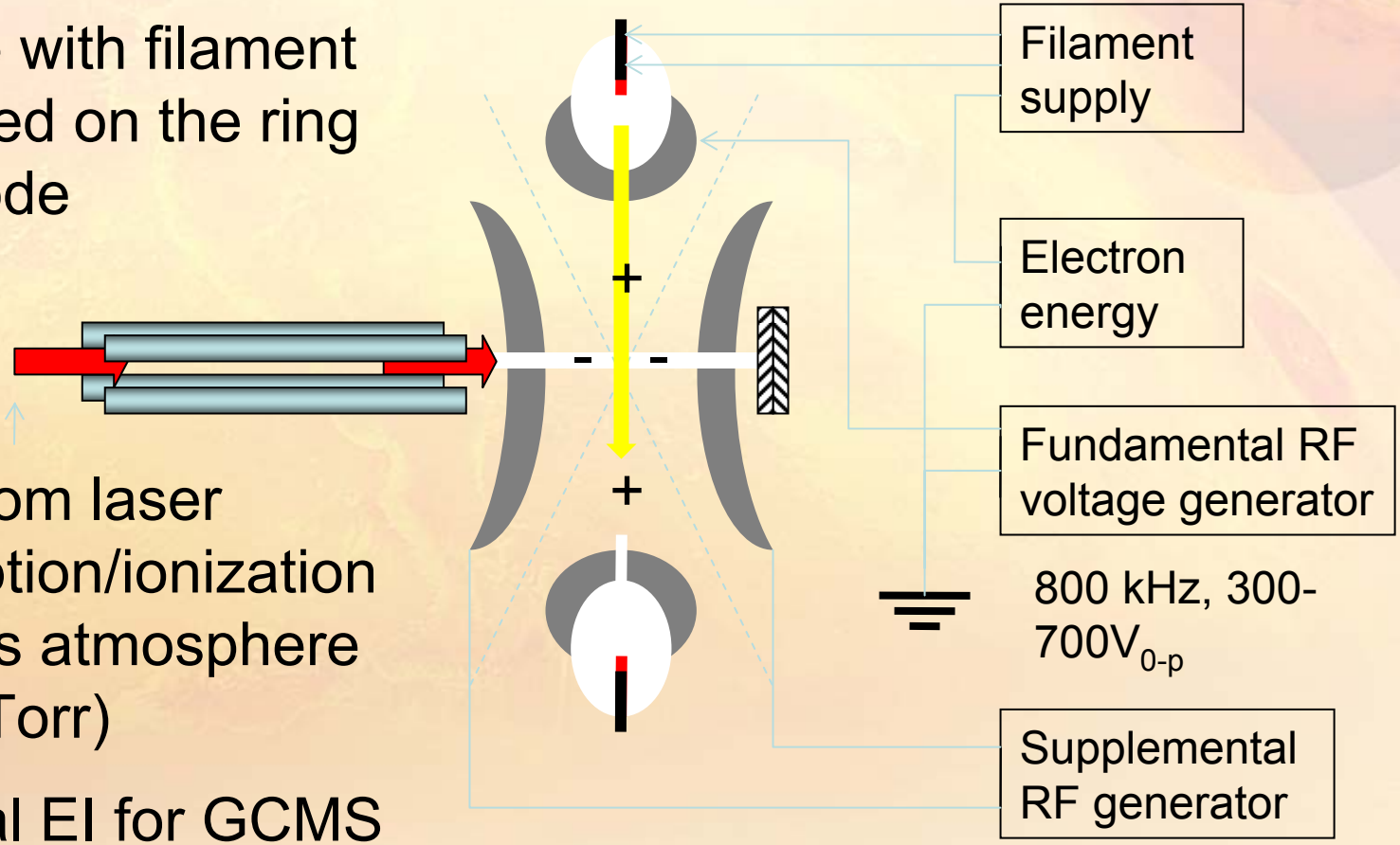
Low voltage/low power and high mass range using lower trap frequency and supplemental excitation at very low q_{eject} value

MOMA Ion Trap Parameters:	Mars 2
Fundamental _ /2¹	800 kHz
Maximum amplitude V_{max} (0-p)	300 V
Radius r_0	0.5 cm
Axis $2z_0$	0.5 cm
Mass range in *mass-selective instability* mode q_{eject} = 0.908	197 Da
Supplemental RF frequency	34.4 kHz
Supplemental RF voltage (axial modulation)	5-10 V
q_{eject}	0.089
Mass range in *resonance ejection* mode	2,000 Da
Bath gas	He or CO_2

Ionization:	laser desorption at Mars atmosphere (5 -10 Torr)
Ion introduction:	RF quadrupole ion guide

MOMA Instrument Concept

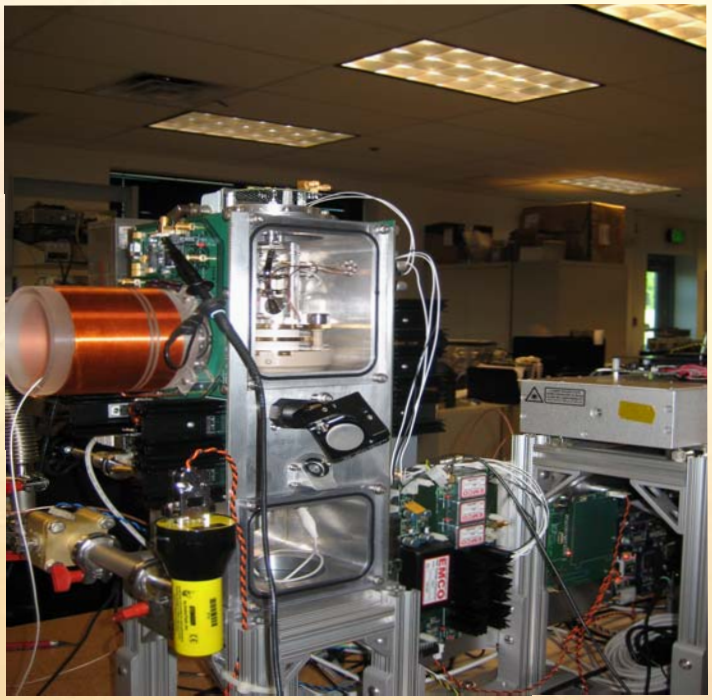
A novel internal EI source with filament mounted on the ring electrode

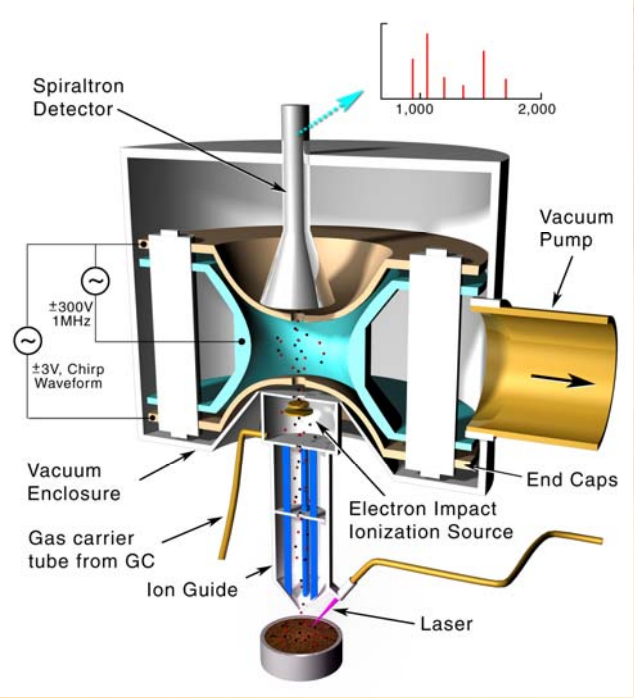


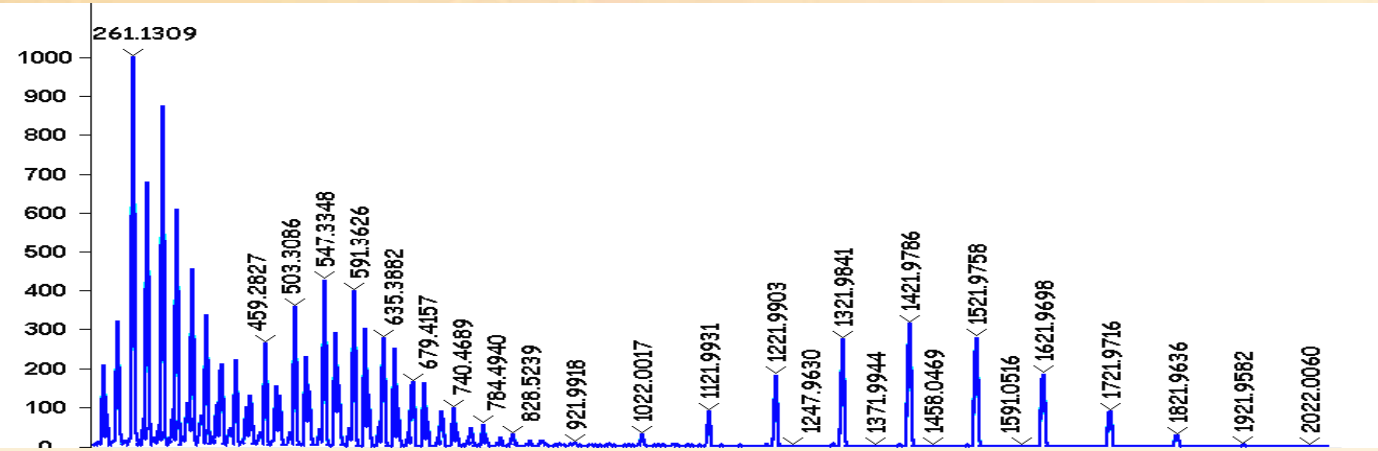
Ions from laser desorption/ionization at Mars atmosphere (5-10 Torr)

Internal EI for GCMS

MOMA Mars Organic Molecule Analyzer



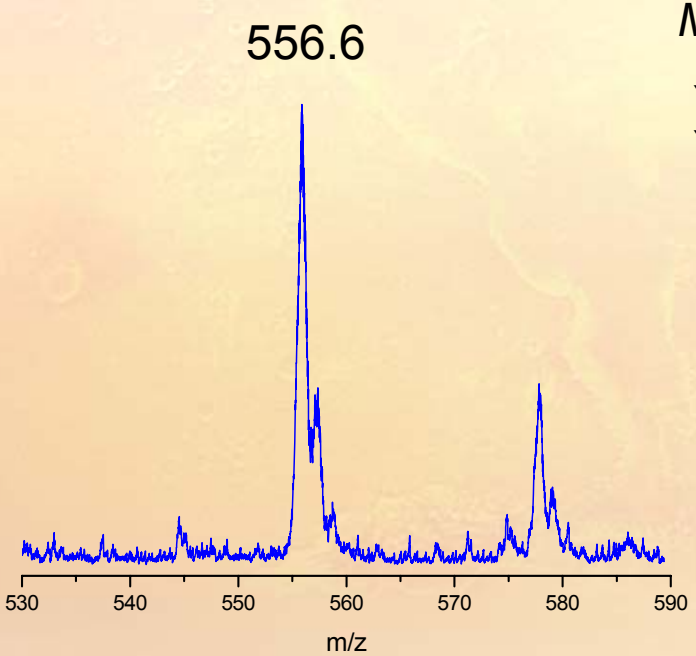




MOMA ITMS Operational Requirements

MOMA ITMS must be capable of:

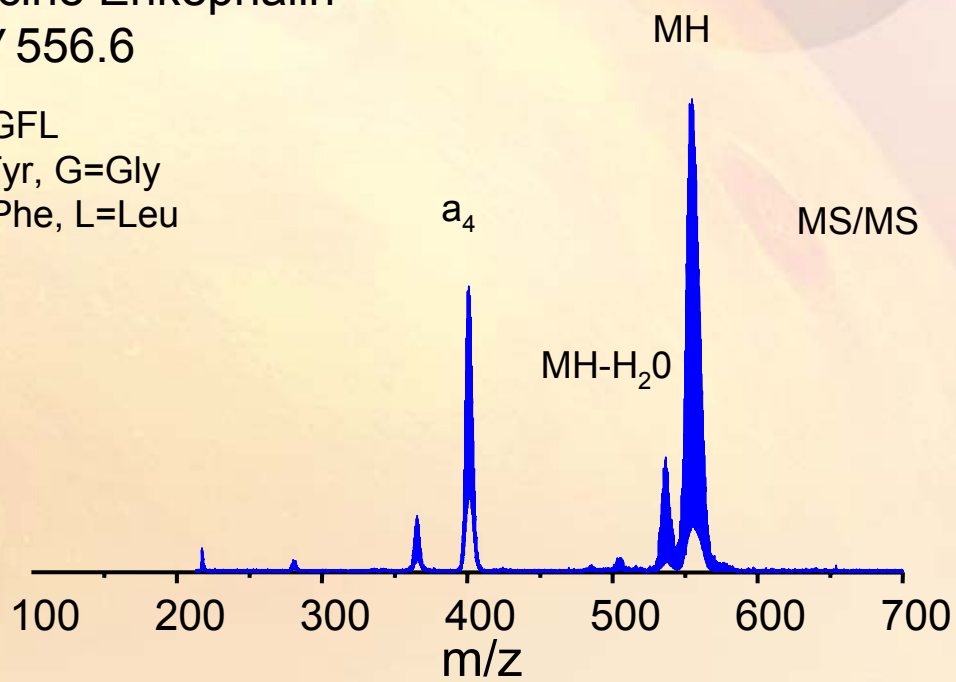
1) Operating with CO_2 as a bath gas
2) Unit Mass Resolution
3) MS/MS capability



CO_2 pressure	Peak width
1.2×10^{-4} Torr	0.5 Da
10^{-3} Torr	1.5 Da

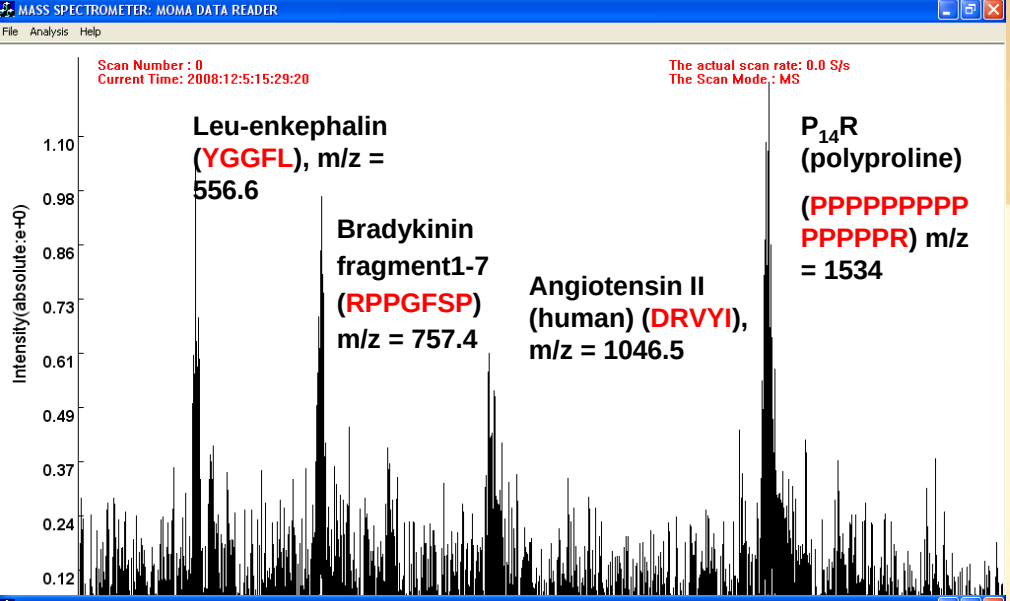
Leucine Enkephalin
MW 556.6

YGGFL
Y=Tyr, G=Gly
F= Phe, L=Leu



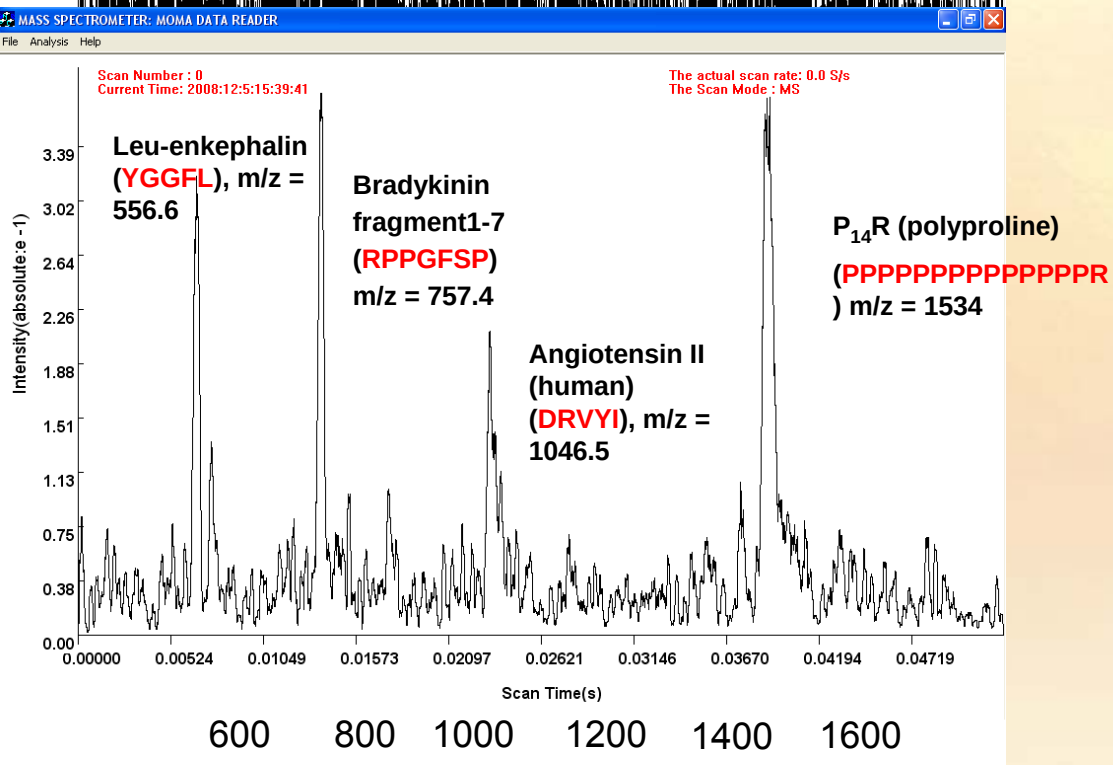
V. Doroshenko, SESI

MOMA Prototype-1



4 peptide mixture; original or 'raw' data

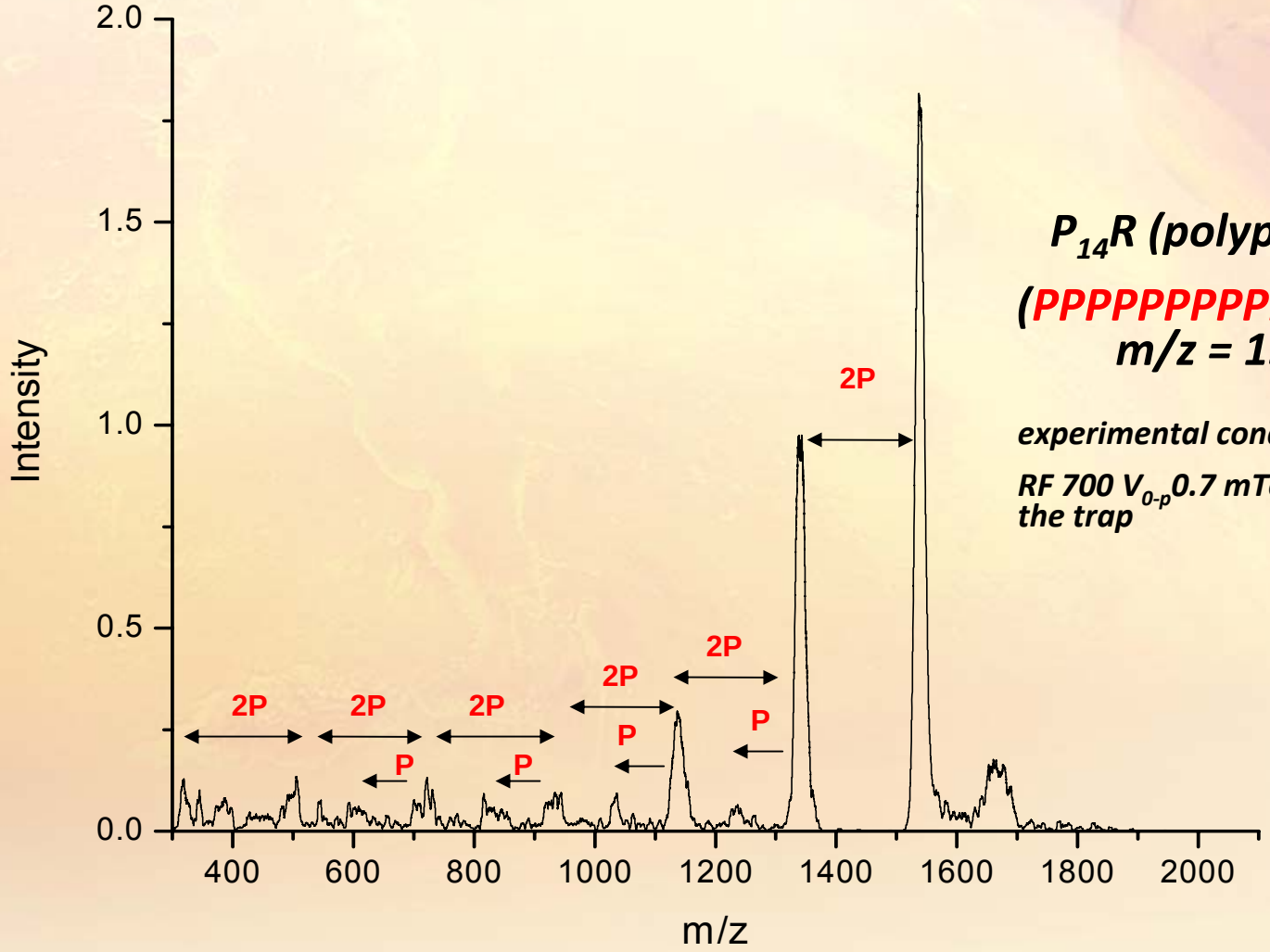
experimental conditions: V_{RF} = 700 V_{0-p}; P = 0.7 mTorr (CO_2) in the trap



4 peptide mixture; 300 points smoothing

experimental conditions: V_{RF} = 700 V_{0-p}; P = 0.7 mTorr (CO_2) in the trap

MS/MS MOMA Prototype-1



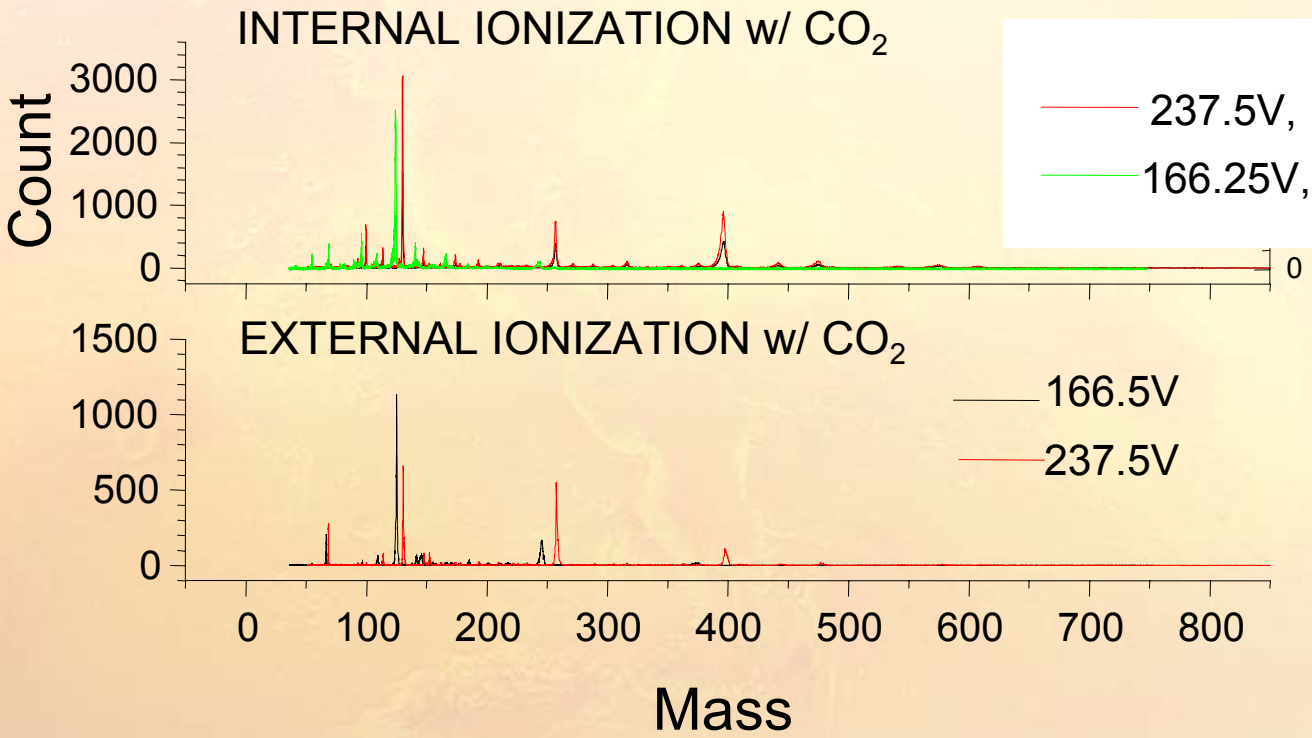
$P_{14}R$ (polyproline)

(PPPPPPPPPPPPPPR)

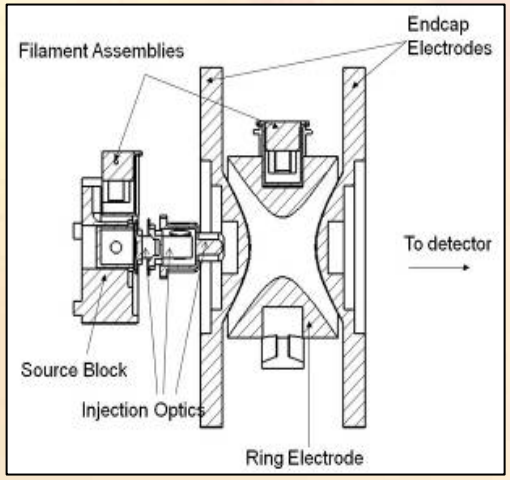
m/z = 1534

experimental conditions: trap RF 700 $V_{0\text{-}p}$ 0.7 mTorr CO_2 in the trap

MOMA GCMS Interface



JHU SOM

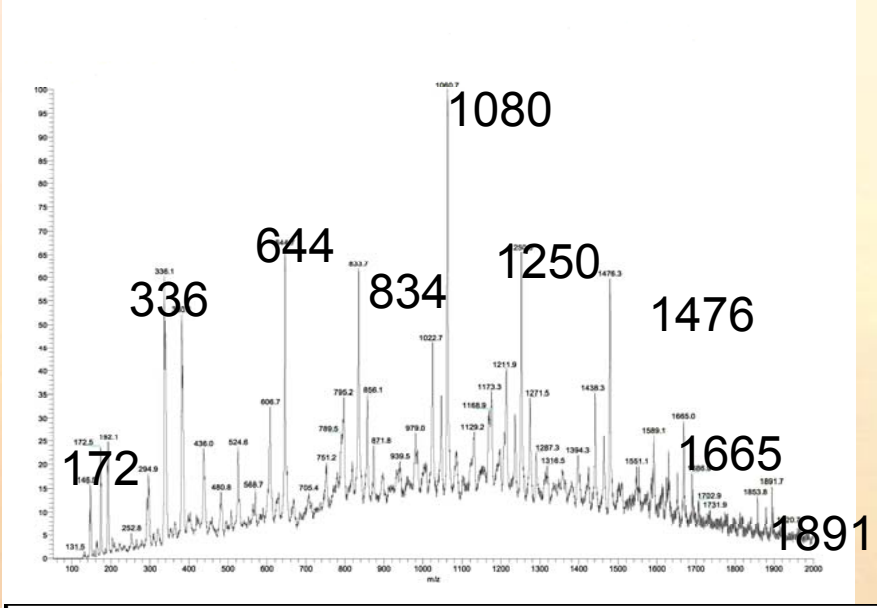


T. Evans-Nguyen

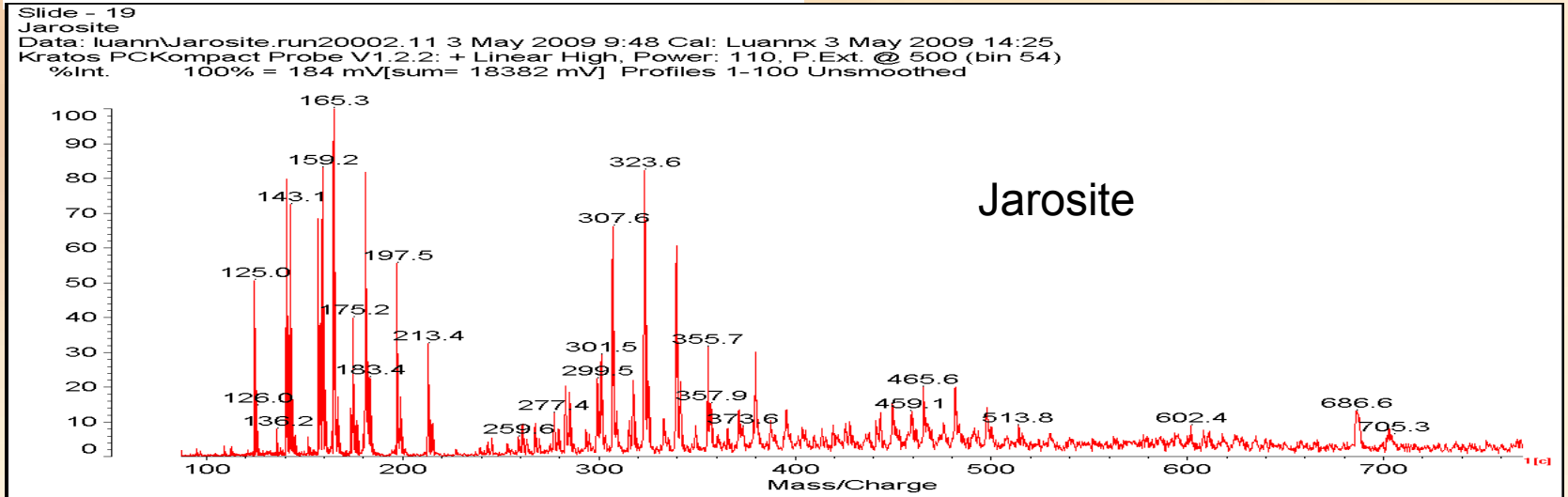
<u>CO_2 as the bath gas</u>

Gold Standard LD Ion Trap Mass Spectrometer

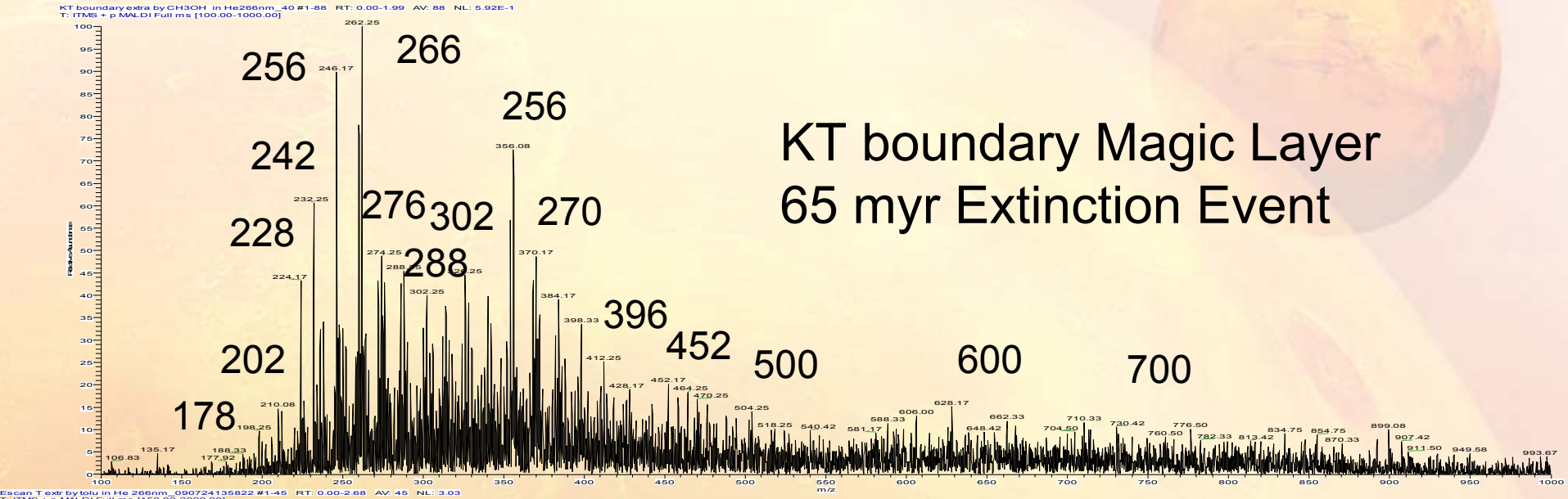
Thermo LD ITMS SESI Peru Desert



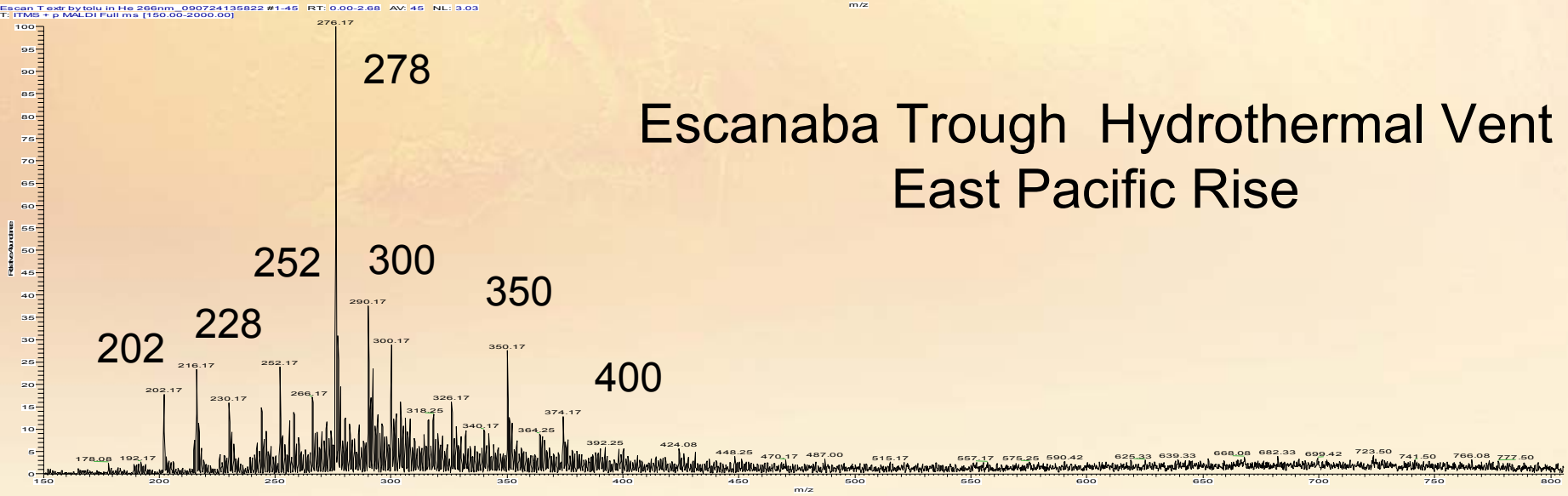
JHU PHA Gold Standard



Martian Analog Samples

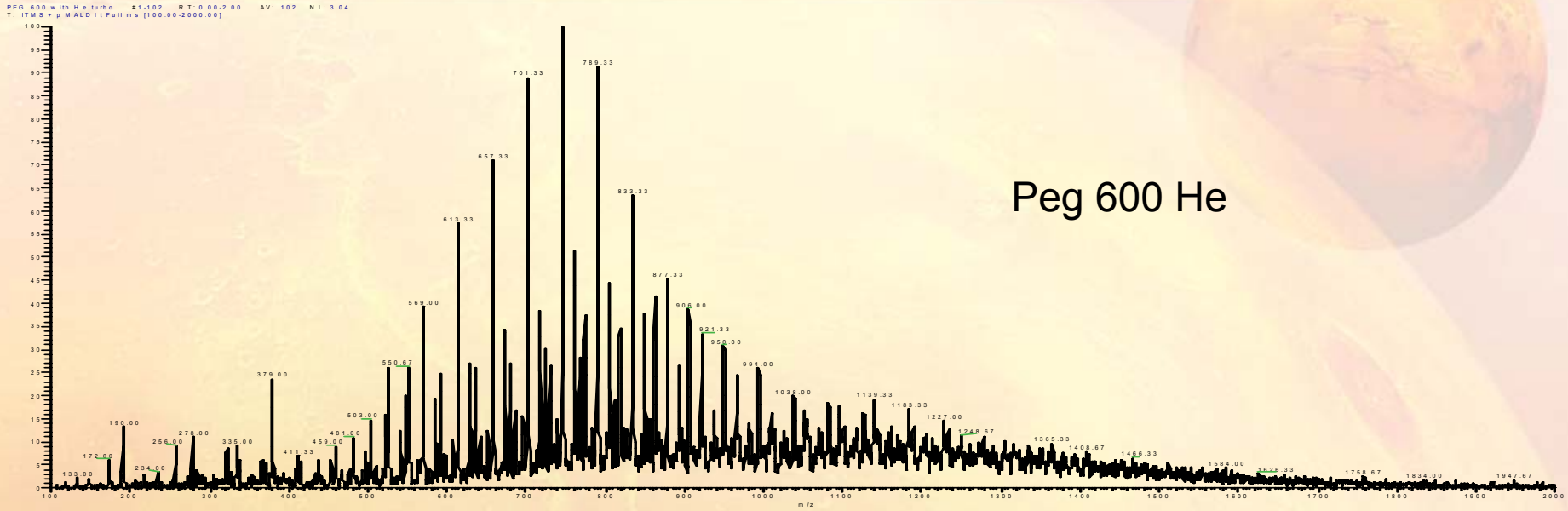


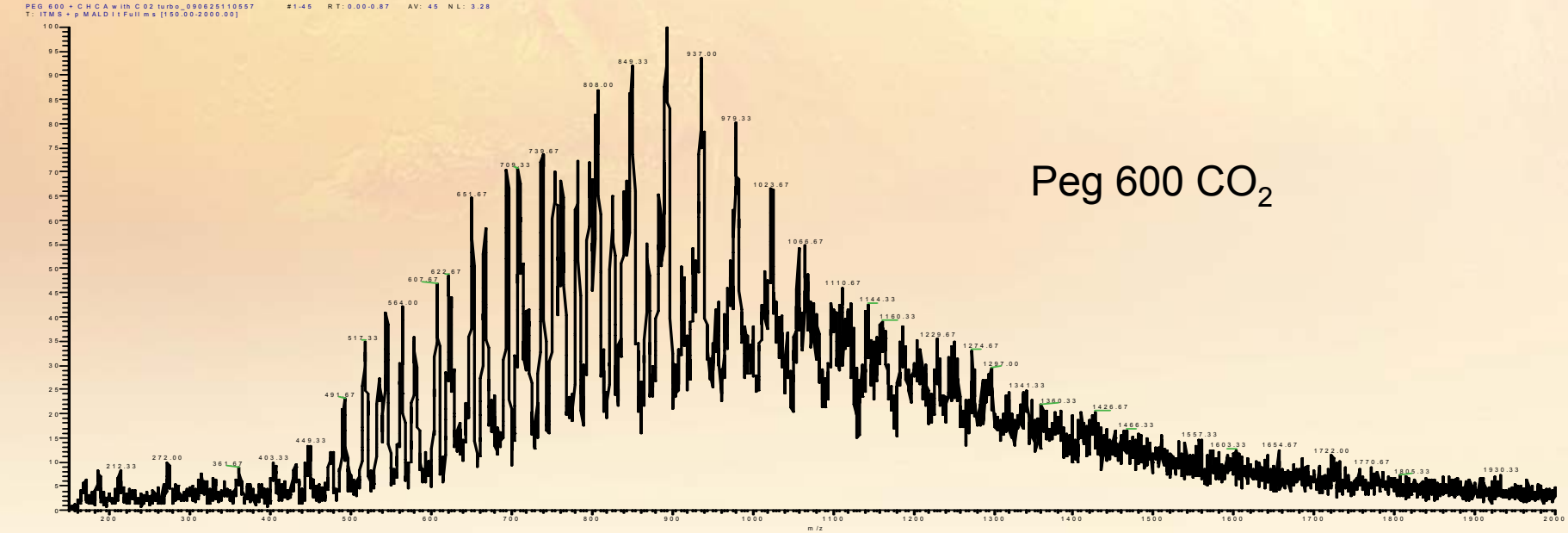
KT boundary Magic Layer
65 myr Extinction Event



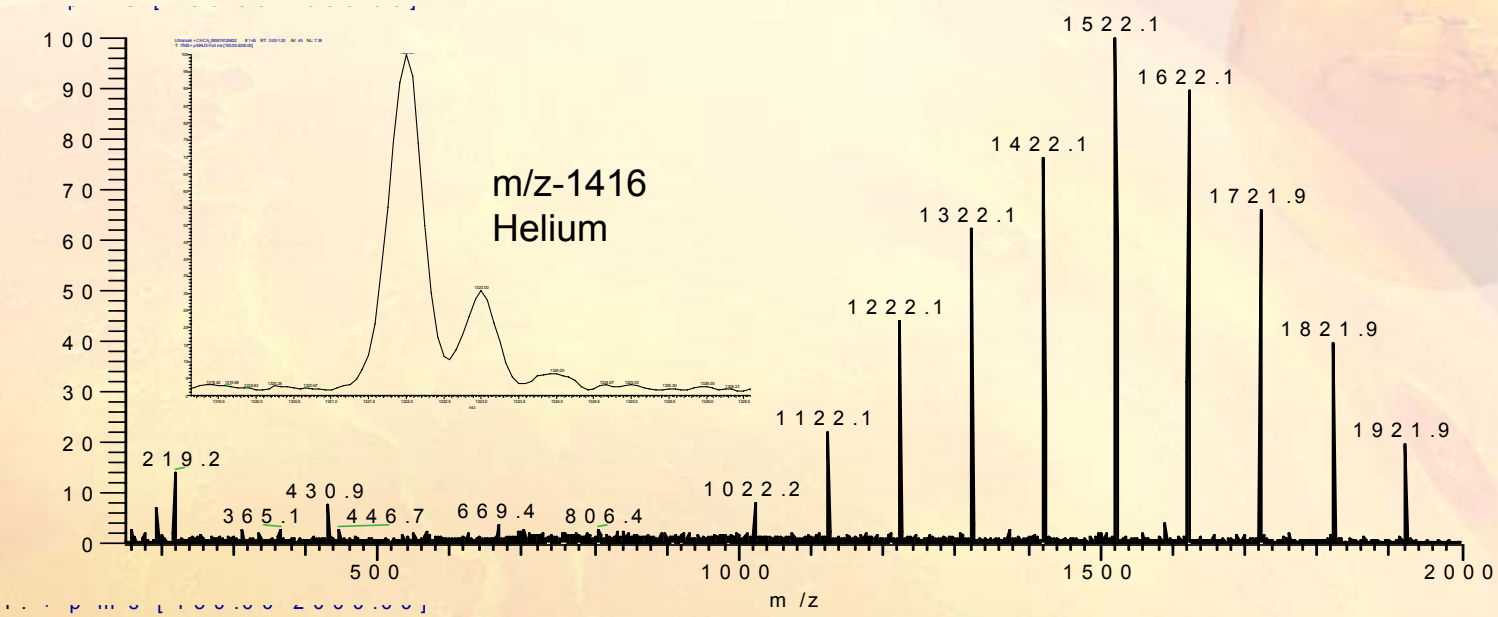
Escanaba Trough Hydrothermal Vent
East Pacific Rise

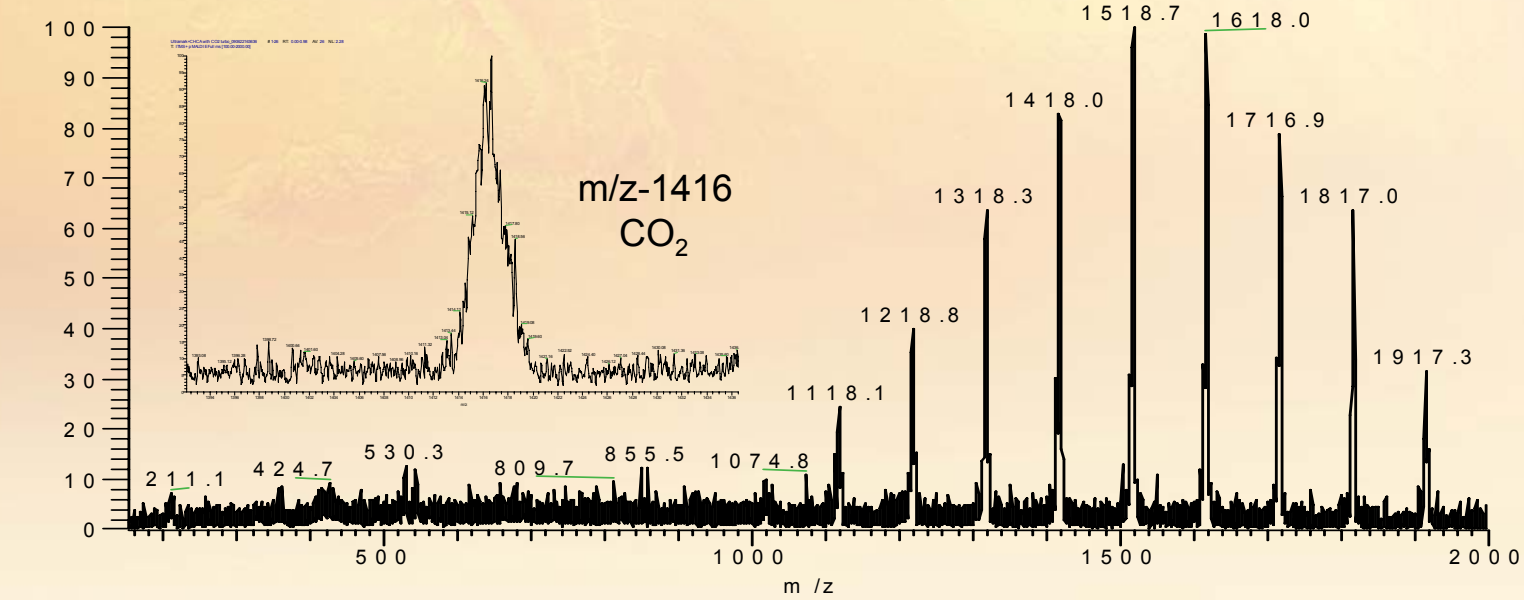
PEG 600 with He and CO_2





Helium vs CO_2





THE MARTIAN HANDLING MACHINE - Sketch by Michael Trim