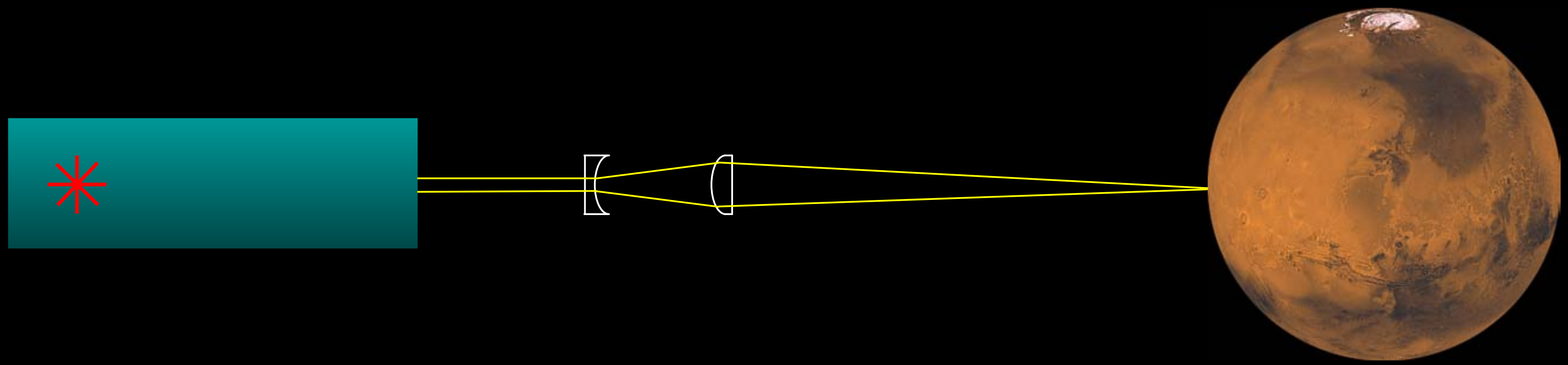


# Laser TOF-MS instrumentation for planetary missions

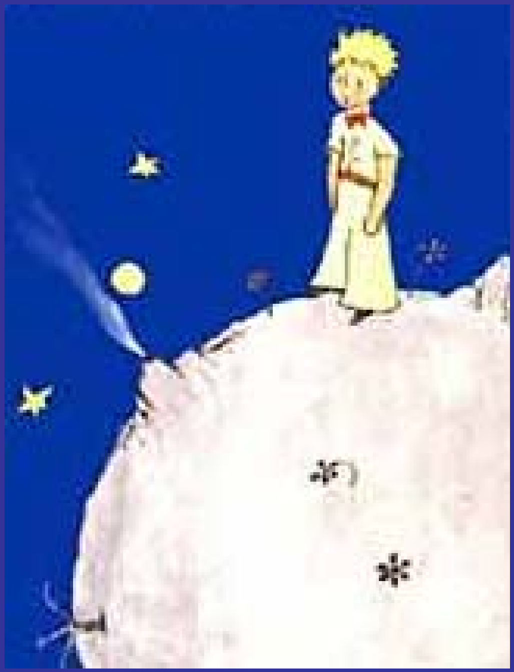
Will Brinckerhoff, Cari Corrigan, Tim Cornish, Scott Ecelberger, Anita Ganesan (JHU/APL); Tim McCoy, Ed Vicenzi (Smithsonian NMNH); Paul Mahaffy (NASA/GSFC)

# Outline

1. Some missions and their objectives
2. General features of miniature LD-TOF-MS
3. LAMS
4. DS-TOF
5. Tower TOF
6. Sample handling and vacuum stuff
7. Other LDMS projects
8. Acknowledgements

# Example Planetary Missions

- Mars rovers and sample returns
- Asteroids
- Comets
- Jovian satellites, Venus, Titan, other moons



# Mars

Goals: Understand Mars' history; figure out how similar Mars was to Earth and how it diverged; locate water, organics, other chemicals, resources; find life (or lack)

Conditions: Atmosphere ~ 7 Torr $CO_2$ and cold!

- Mars Exploration Rovers (MER) - operating
- Phoenix Mars Scout (2007)
- Mars Science Laboratory (2009)
- ExoMars
- Astrobiology Field Laboratory
- Mars Sample Return

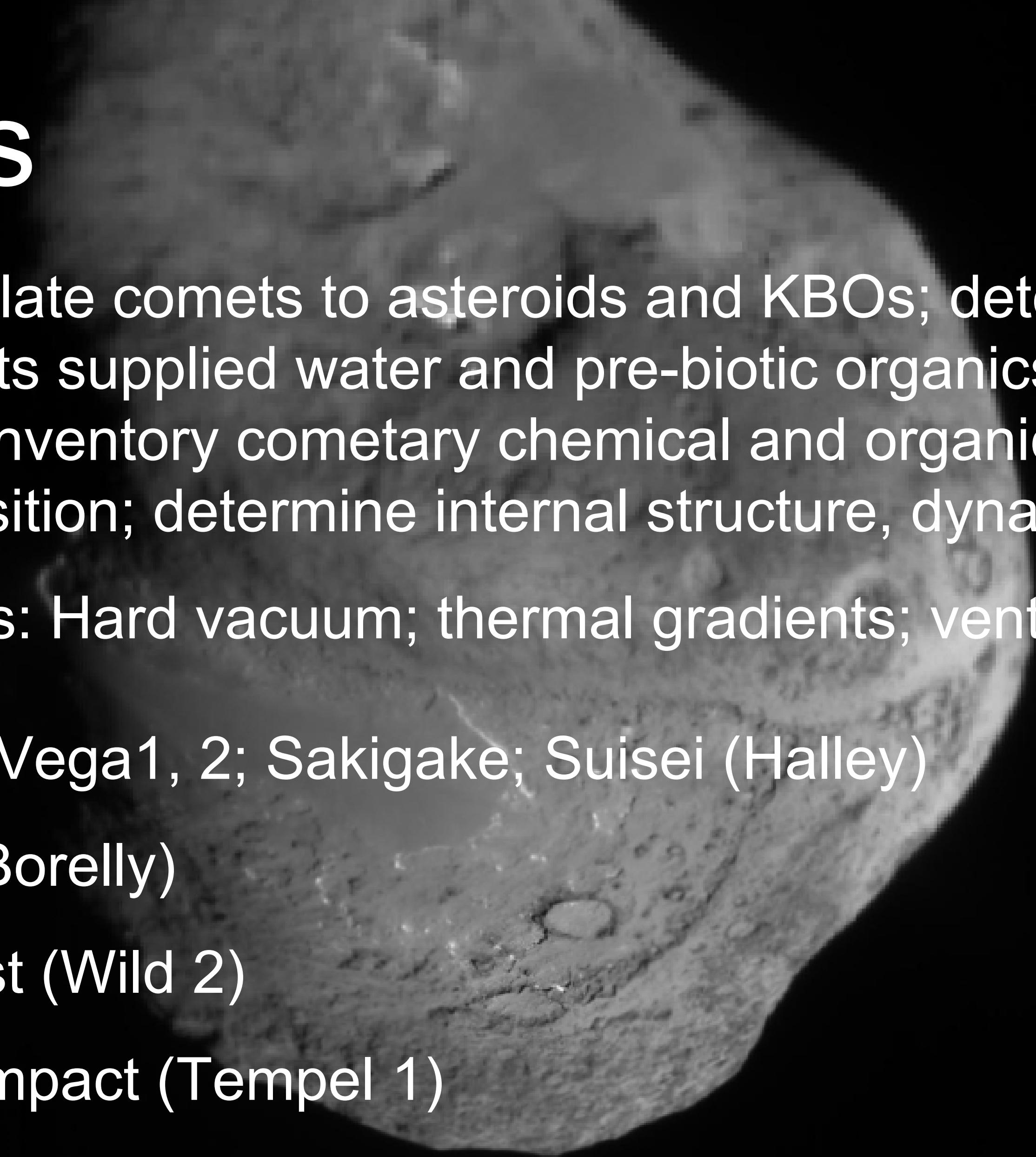
# Asteroids

Goals: Relate asteroids to solar and planetary compositions to understand solar system formation; link meteorite and asteroid classes; search for organics, water, metals; determine internal structure

Conditions: Hard space vacuum; thermal gradients

- NEAR (Eros)
- Hayabusa (Itokawa)
- Dawn (Vesta and Ceres)
- Future landers / sample returns

# Comets



Goals: Relate comets to asteroids and KBOs; determine if comets supplied water and pre-biotic organics to Earth; inventory cometary chemical and organic composition; determine internal structure, dynamics

Conditions: Hard vacuum; thermal gradients; vents (!)

- Giotto; Vega1, 2; Sakigake; Suisei (Halley)
- DS-1 (Borelly)
- Stardust (Wild 2)
- Deep Impact (Tempel 1)
- Rosetta (Churyumov-Gerasimenko)
- Future landers / rendezvous / CSSR / CNSR

# In Situ Astrobiology at Comets


***"Extreme Close-Up" of a comet nucleus?***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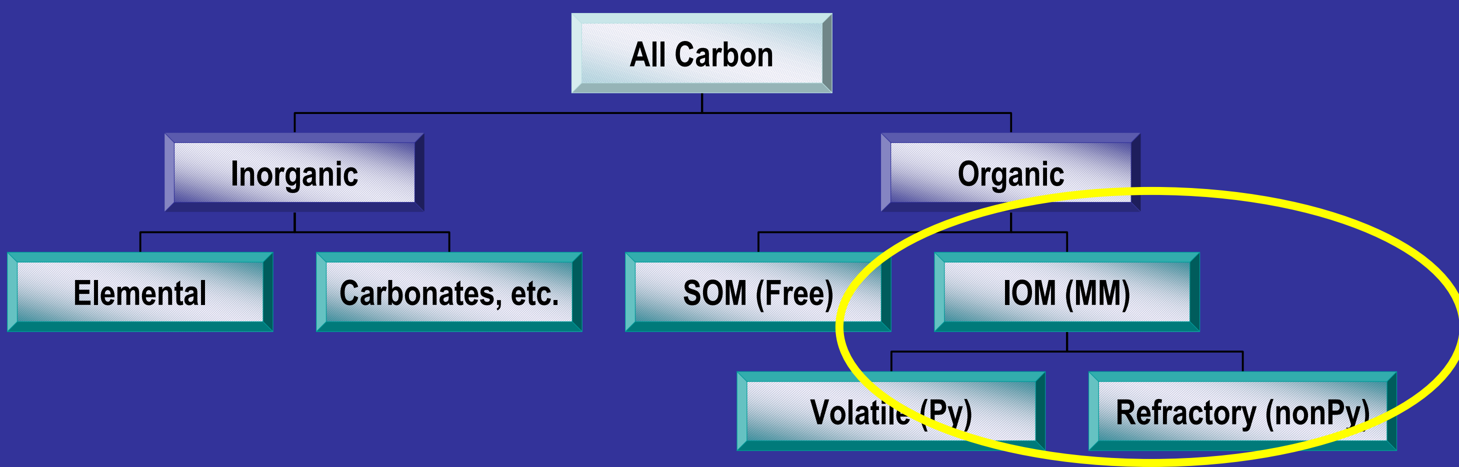
# High-Mass Organics

Refractory organics with m >> 100 Da comprising insoluble organic matter (IOM):

- encode formation processes and timescales (aromatic / aliphatic)
- associate with key ISM organics (amino acids, nucleobases, sugars)
- dominate the organic fraction of comet nuclei (as they do in c-chondrites)



# Outer Planetary Satellites

## Europa

- Ocean?
- Life?
- Ice chemistry is key goal
- Surface vs subsurface
- Radiation
- Fissure upwellings
- Lander w/drill
- Hard mission!

## Titan

- Seas!
- "Pre-biotic" chemistry
- Atmospheric density is high
- Long-term goal: A mobile lander (or aerobot/lander) equipped with a mass spec!
- Expensive but not so difficult to do.

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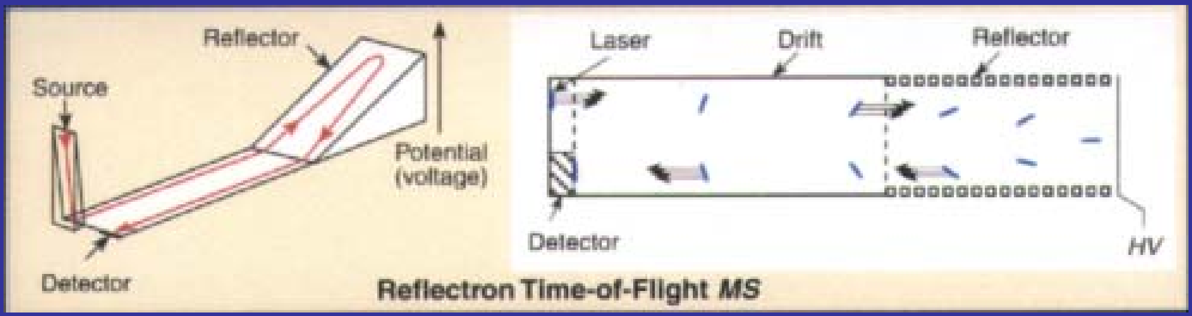
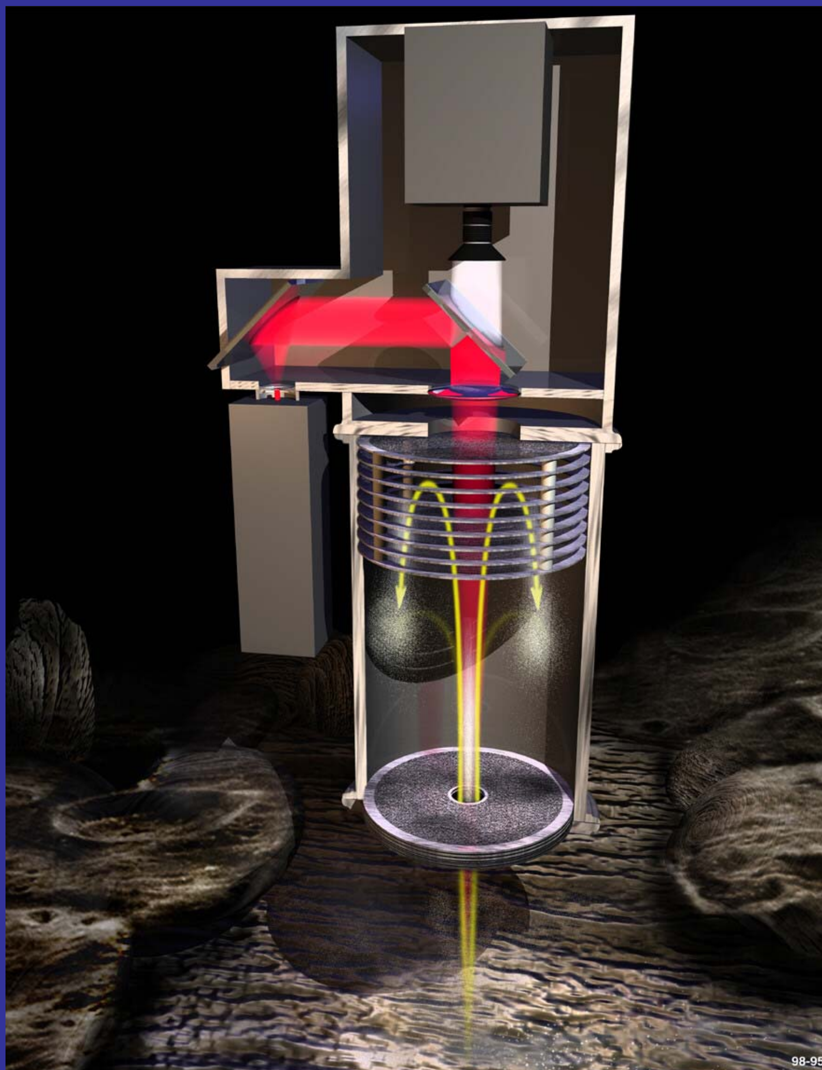
# Miniature LD-TOF-MS

- Relatively speaking, laser TOF-MS can be miniaturized without extensive performance degradation compared to laboratory instruments, and instrument complexity is quite low.
- With carefully designed gridless ion optics, a low-noise detector assembly, and a nonlinear "ideal" reflectron, one can achieve surprisingly high mass resolution and low detection limits with straightforward prompt LDI from unprepared samples.

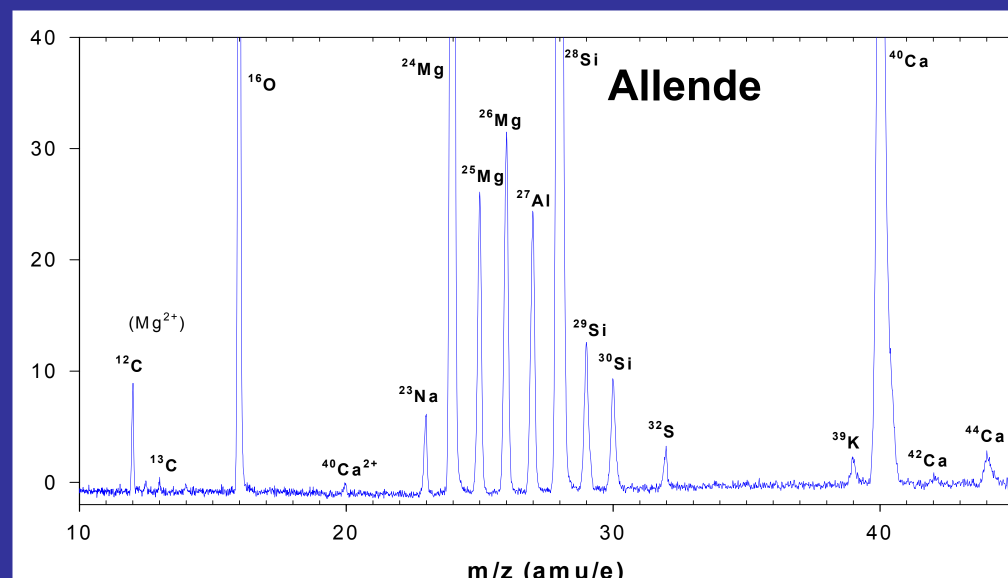



**The reflectron corrects TOF dispersion: ions with same m/z but different energies arrive at the detector simultaneously. A nonlinear reflectron focuses LA and LD ions (wide KE band) as well as organic product ions.**

# LAMS



- 1064 nm Qsw pulses < 10 mJ @ 1 Hz or less
- No sample preparation or contact needed
- Elemental and isotopic analysis
- Elemental LODs to ppmw in bulk phase
- Probe on fine scales (spot size 10-100 μm)
- Complementary to Pyr-GCMS & other methods

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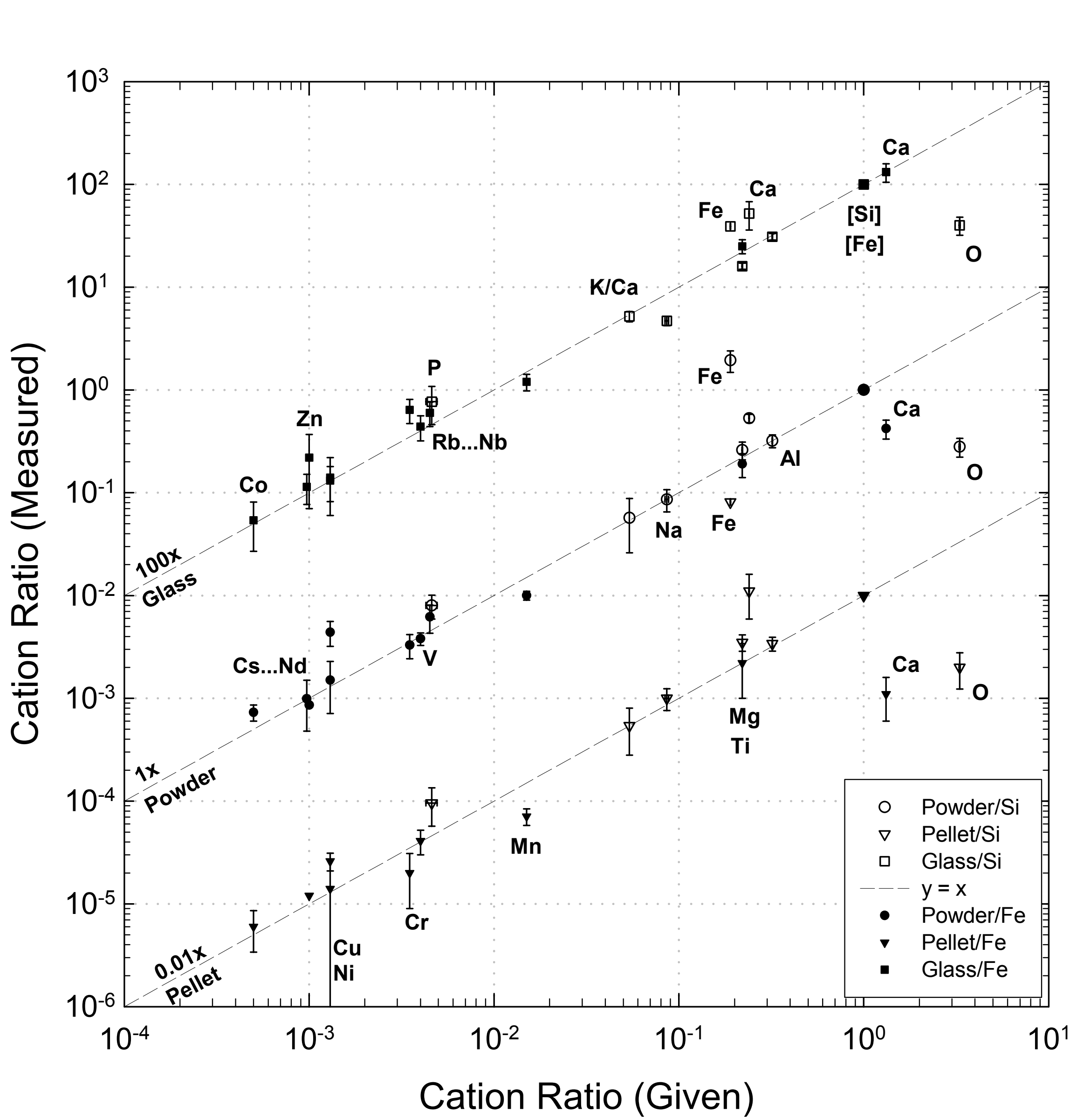
# BHVO-2 Basalt Standard

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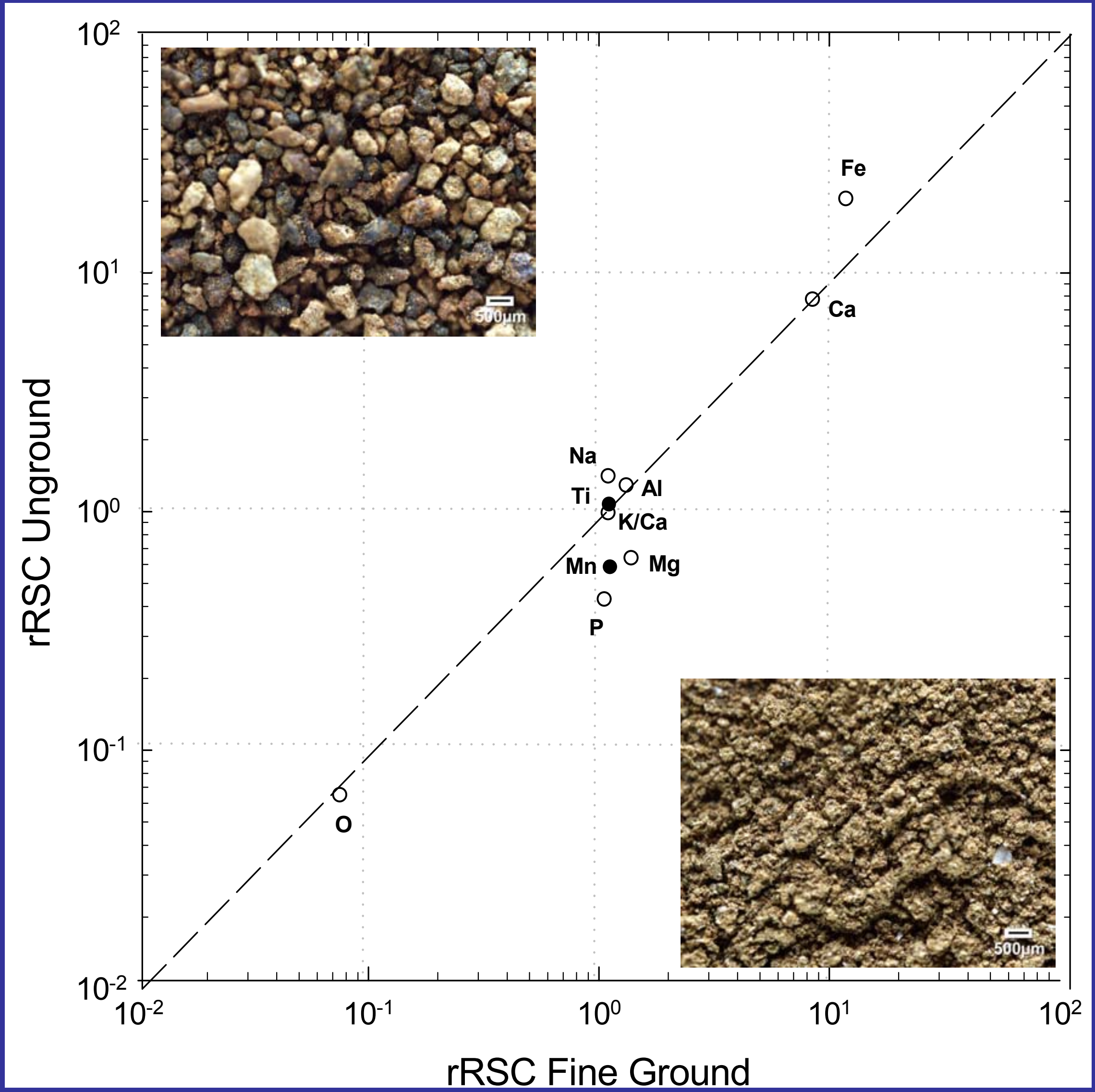
# JSC Mars-1 Simulant

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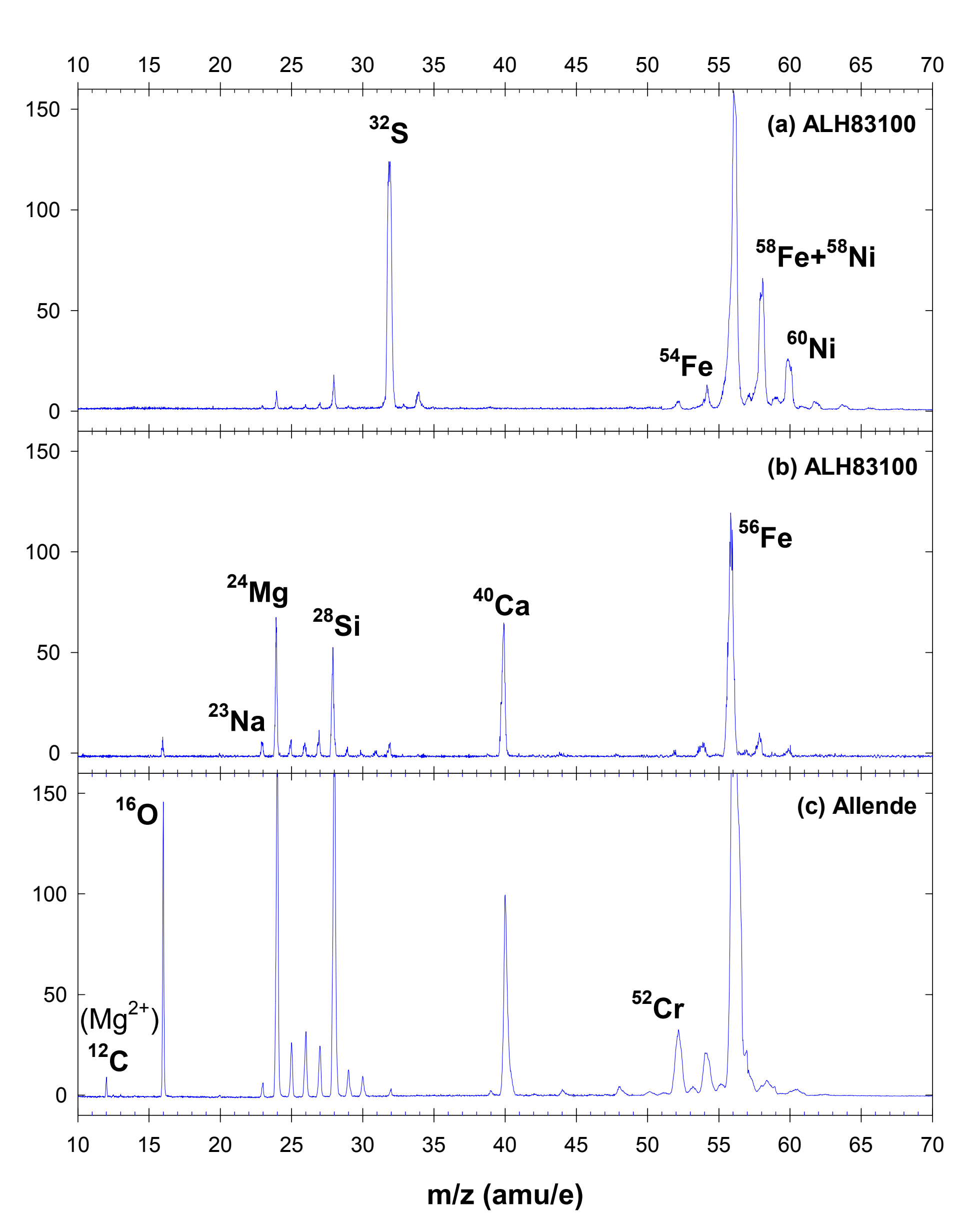
# Meteorites




Pentlandite (FeNiS) Grain

Dark Matrix

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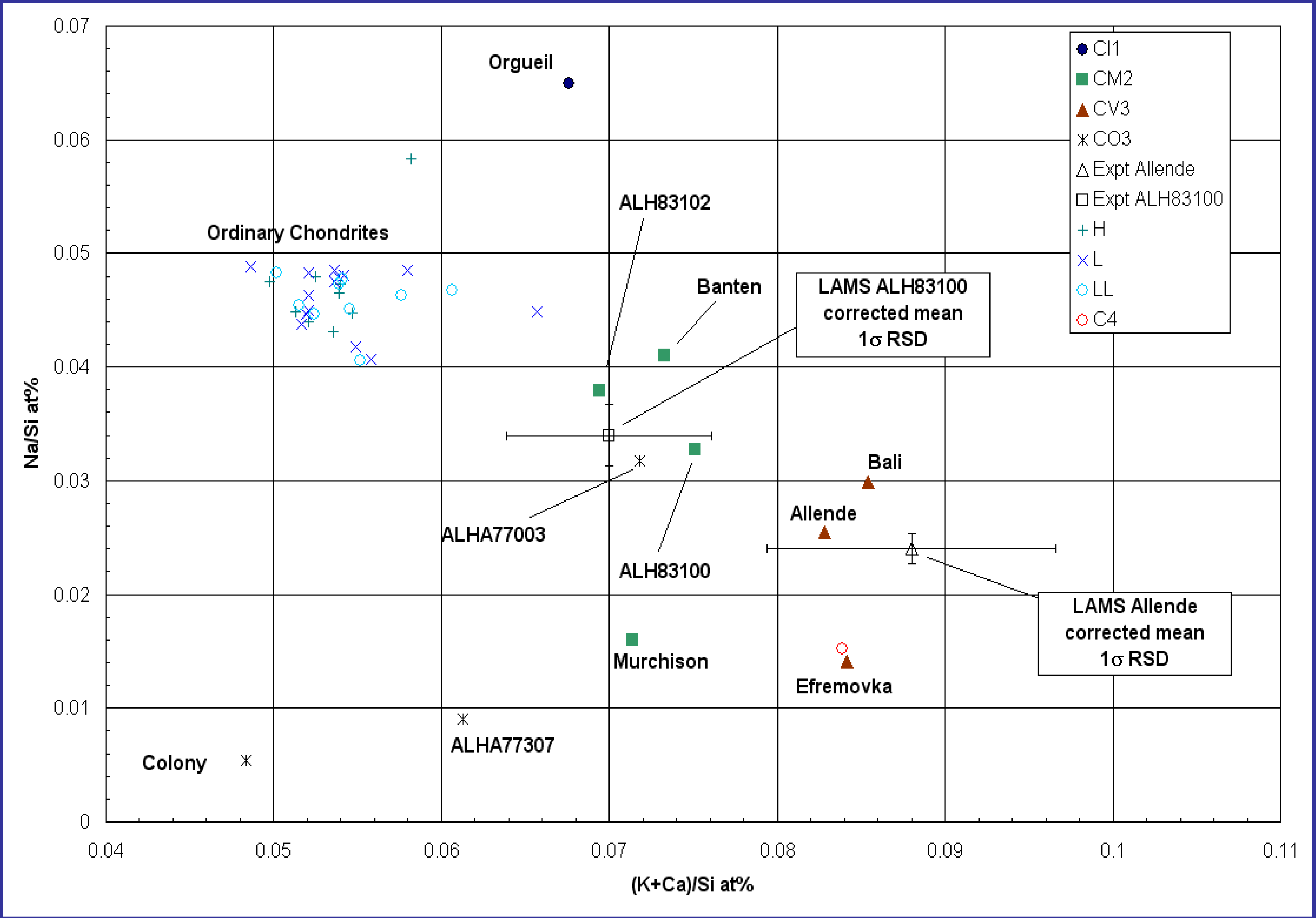


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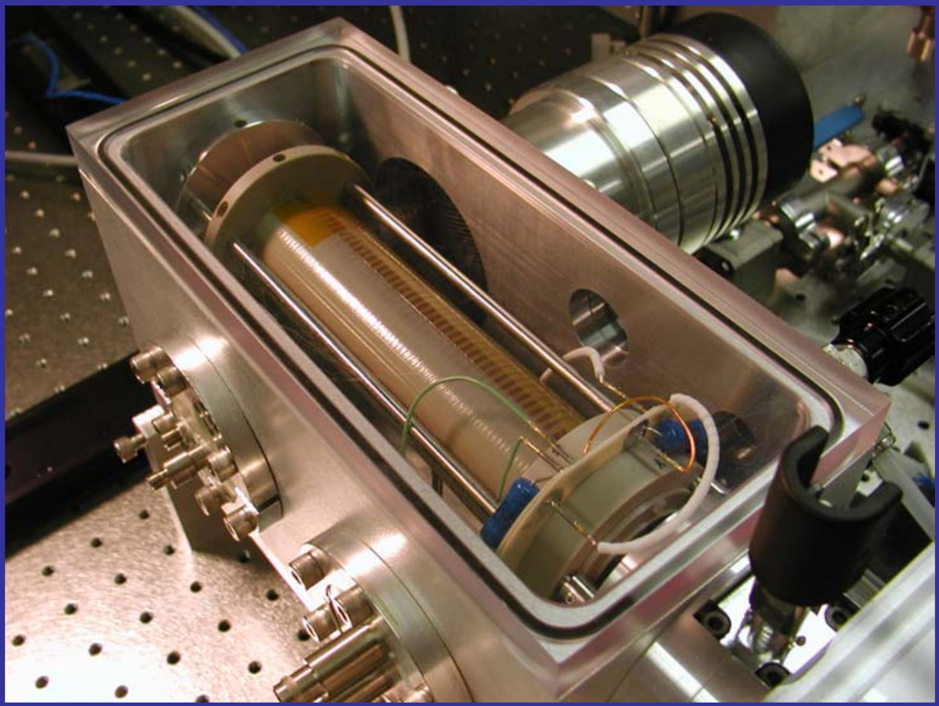
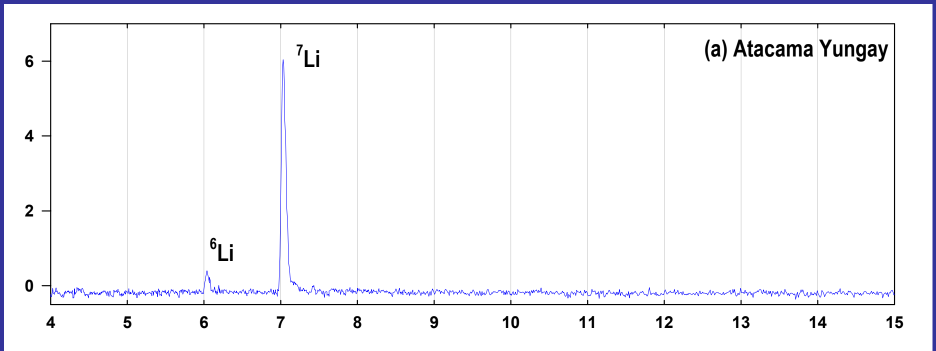
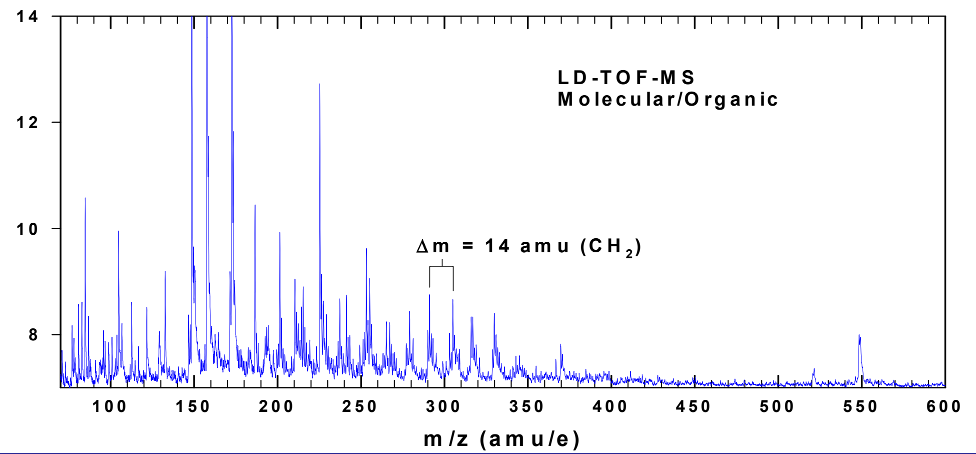
# DS-TOF



- 355 or 337 nm pulses < $10^8$ W $cm^{-2}$ (1 - 20 Hz)
- Unprepared chips or powders, mounted on insertion probe and held at +5 kV
- Monolithic nonlinear reflectron
- Double-sided detector system
- Organic and elemental analysis capabilities
- Refractory organic LODs in low ppbw range
- Probe on fine scales (spot size <100 μm)

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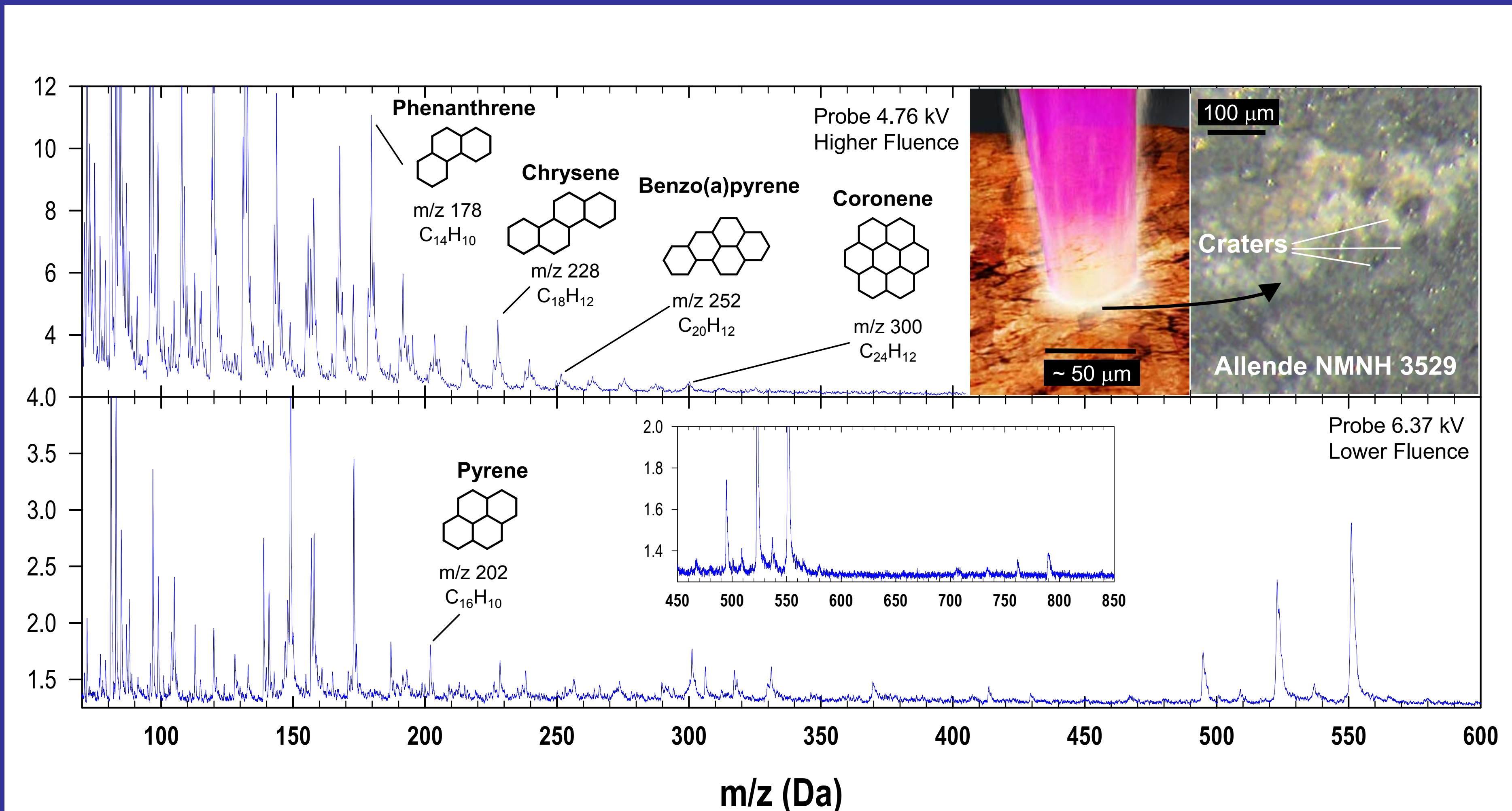
# LD-TOF-MS of Allende Matrix

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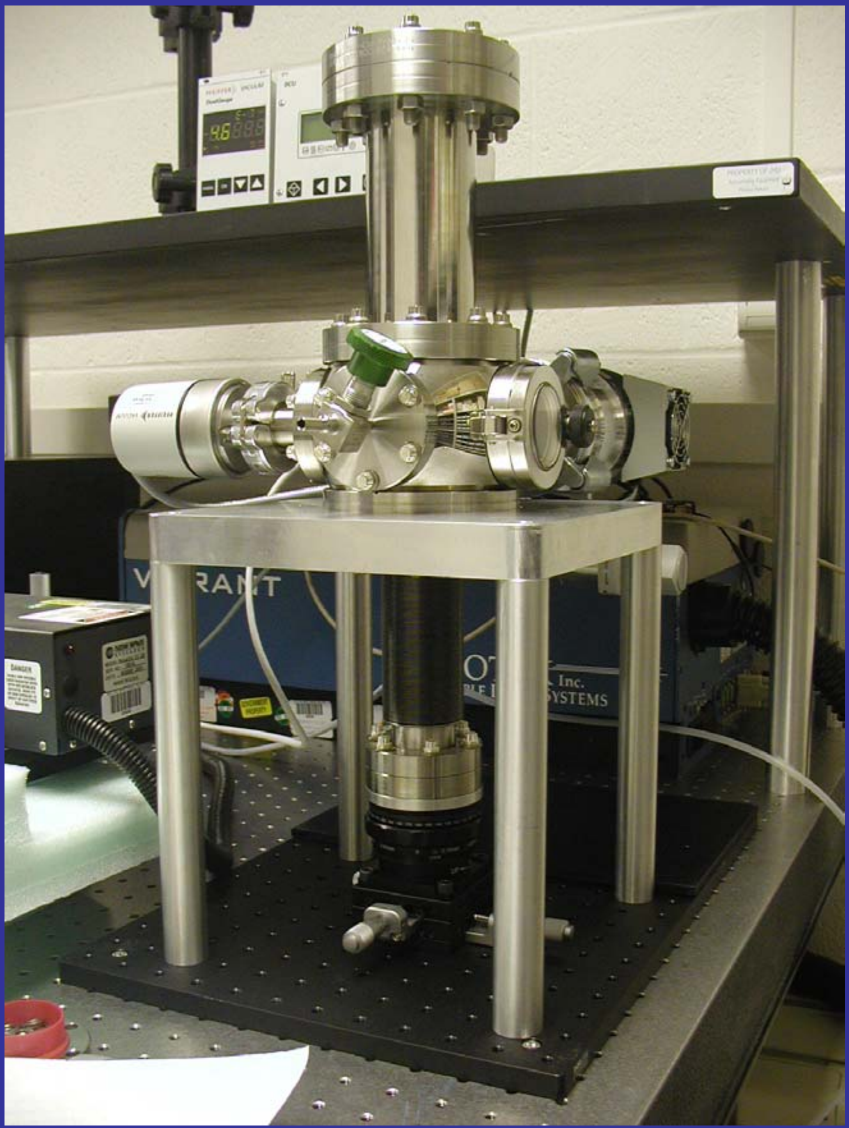
# Allende High Mass Organics

| LDMS High-Mass Sequence in Allende | | |
|---|---|---|
| | | |
| $M^+$ | $[M+^{23}Na]^+$ | $[M+^{39}K]^+$ |
| **428** | **451** | **467** |
| **456** | **479** | **495** |
| 484 | **507** | **523** |
| 512 | **535** | **551** |
| **540** | **563** | **579** |
| | | |
| 666 | 689 | **705** |
| 694 | 717 | **733** |
| 722 | 745 | **761** |
| 750 | 773 | **789** |
| 778 | 801 | 817 |

**Bold** = detected m/z;
Non-bold = inferred m/z

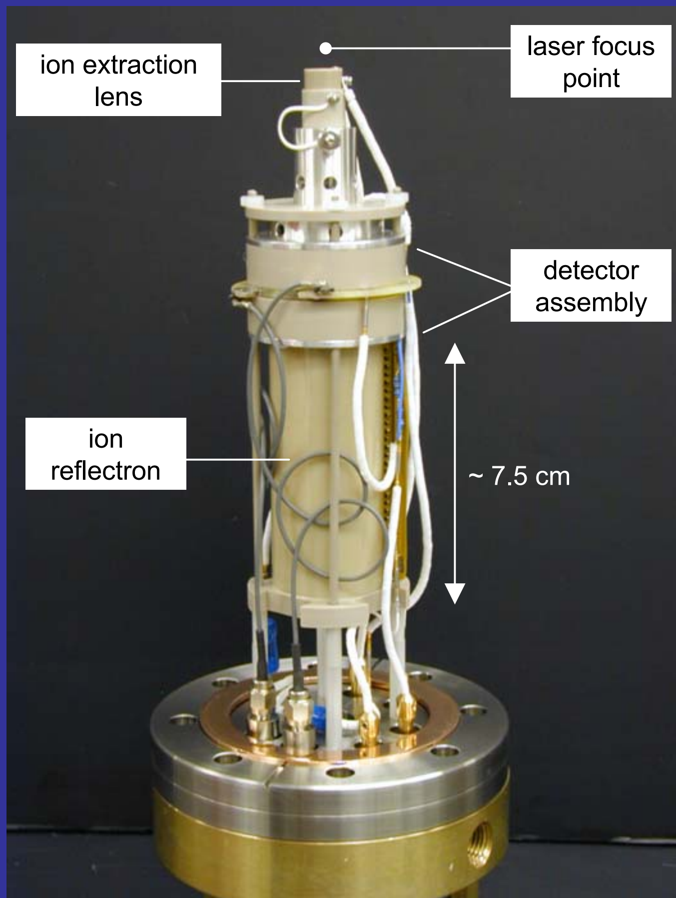
- High-mass (m/z > 300 Da) signal in Allende consistent with previous LDMS and other observations of known macromolecular IOM in C-chondrite acid residues (Becker et al. 1997, Kissin et al. 2003).
- Particular pattern may be due to sequence of sodiated and potassiated parent compounds. Major adduct steps are $\Delta m/z = 28$ Da (dimethyl, $C_2H_4$, $CH_2N$, etc.)
- Possible parent PAH @ 428 Da (octacene or equiv.)
- Prompt LDI PAH ratios do not match REMPI ratios (Plows et al. 2003, Elsila et al., 2004).

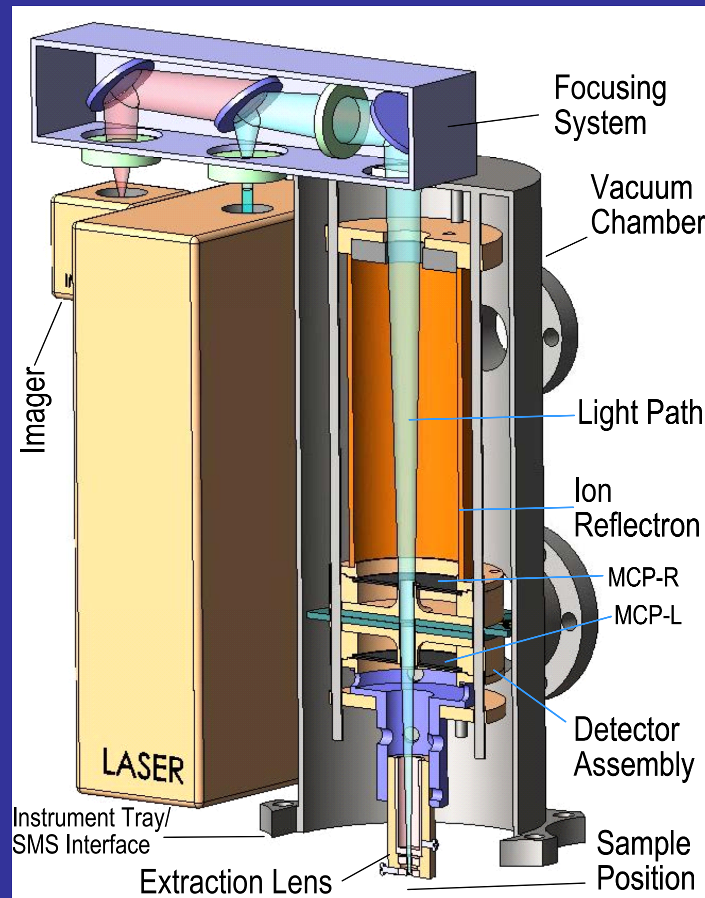
# Tower TOF




- Normal incidence desorption at 266, 355, or 1064 nm with New Wave Tempest
- Lateral postionization at 235 – 390 nm with doubled Opotek Vibrant
- Unprepared samples mounted on XYZ stage using custom bellows assembly with 13 mm lateral and 25 mm vertical travel
- Instrument and samples are vertical
- Samples are at electrical ground; flight tube biased to negative voltage
- No pre- or post-acceleration grids
- Sensor about 50% size of DS-TOF
- Goal: elemental and organic chemical imaging at resolutions ~ 50 $\mu$m
- Still under development

# “Flight-Scale” TOF-MS




*Sensor is ~ 50% size of DS-TOF prototype, and mounts on 450CF flange. Flight model bundles laser and microscopic imager in common optical system.*

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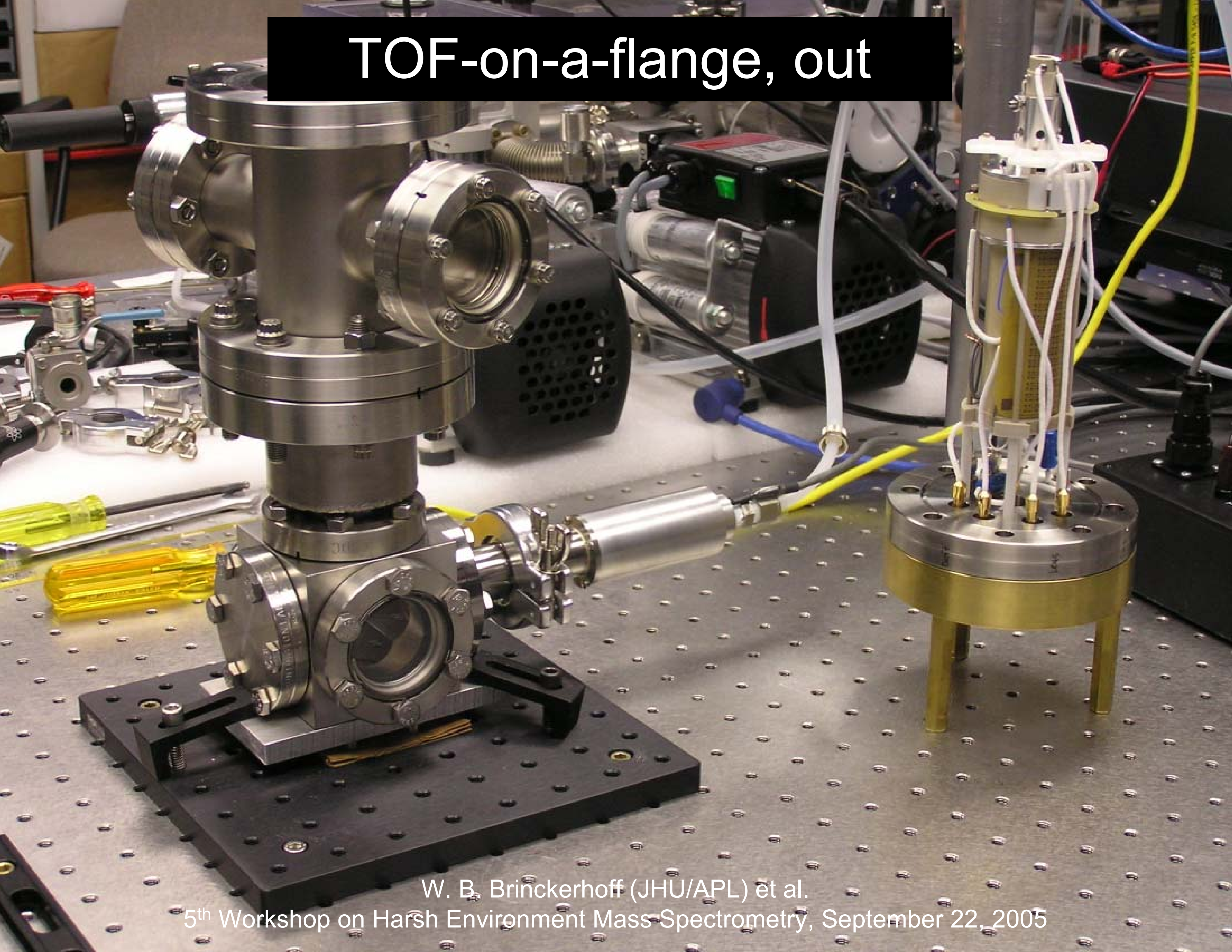
# TOF-on-a-flange, out



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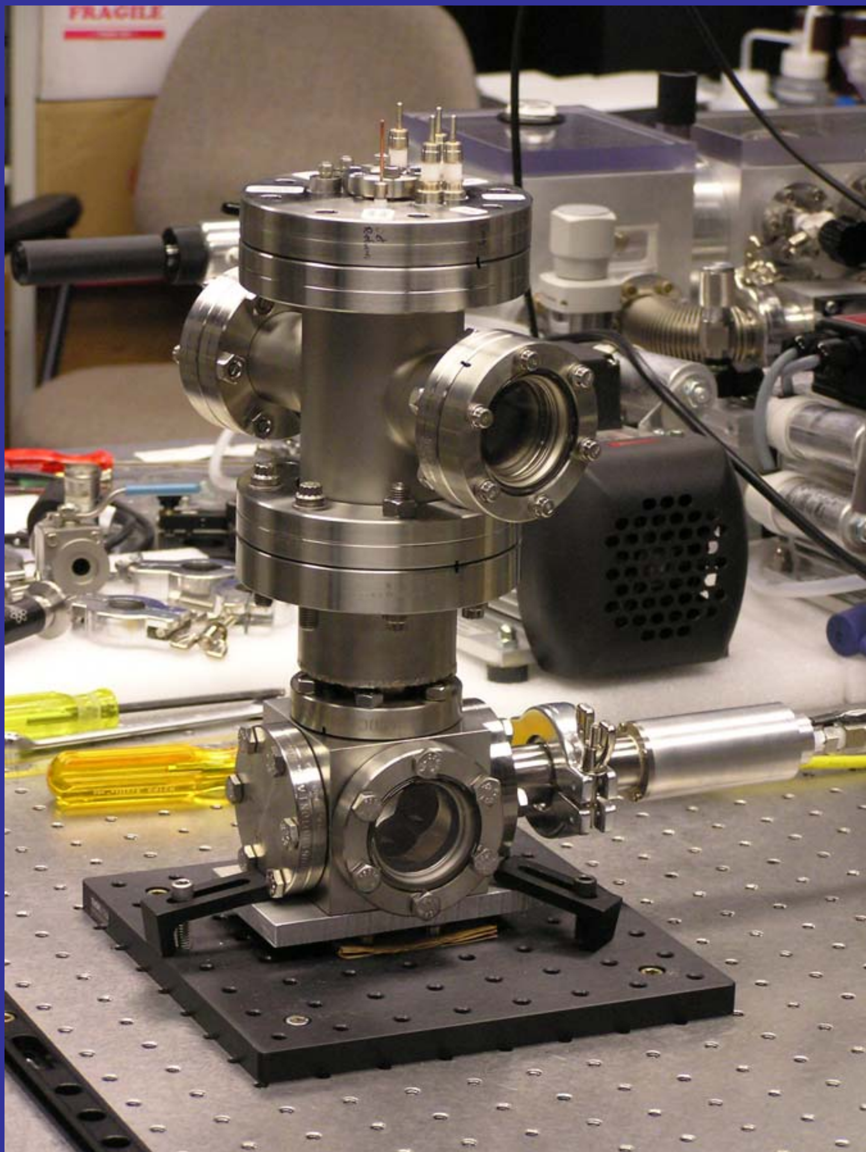
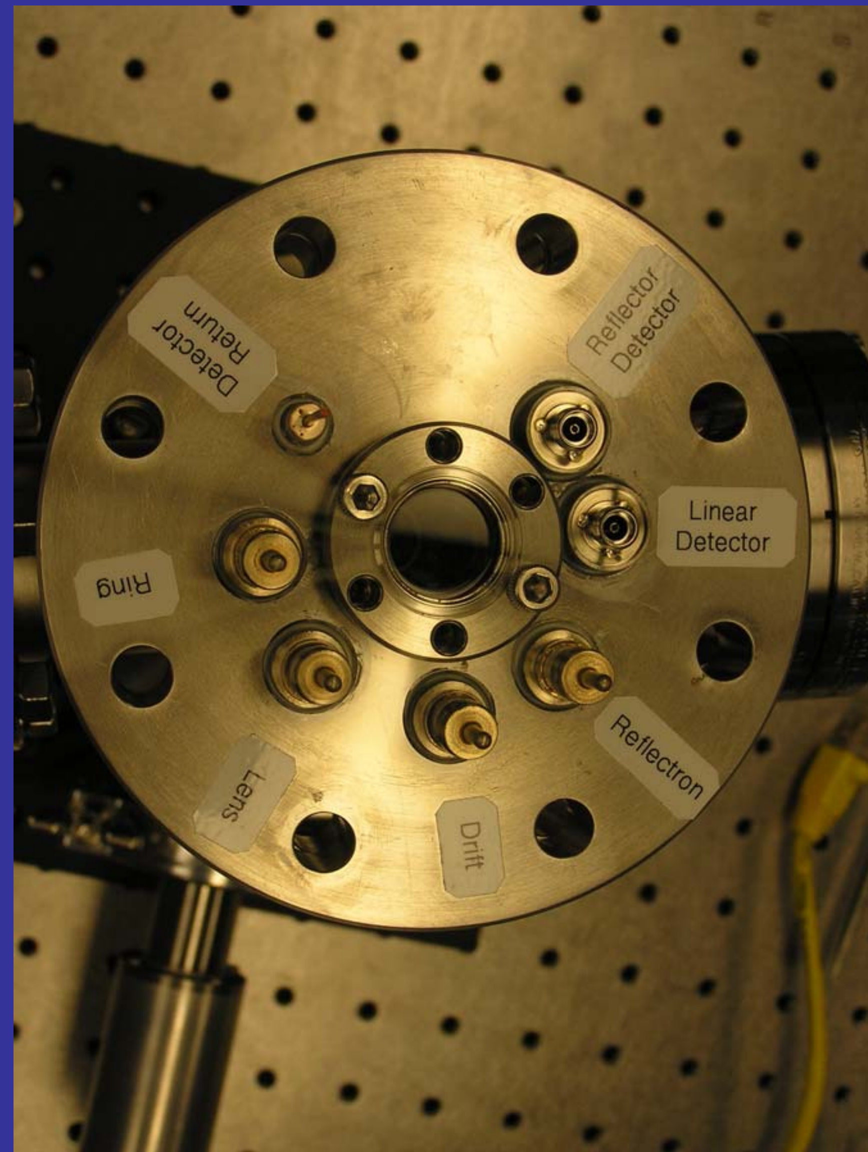
# TOF-on-a-flange, in

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# Sample Handling and Vacuum Stuff

**High-resolution in situ chemical imaging**

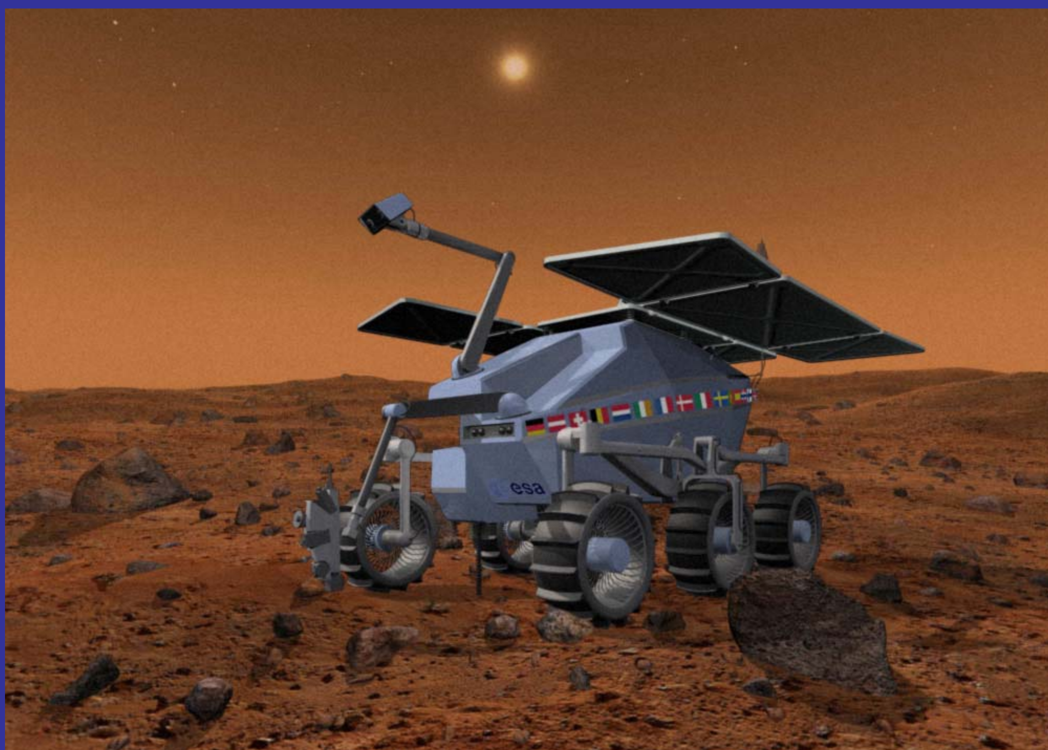
- xyz sample manipulation system developed in collaboration with Honeybee Robotics
- examine location of organics in meteorites

**Other Honeybee Robotics Collaborations**

- MSL Sample Acquisition/Sample Handling and Processing (SA/SPaH) system
- Precision subsampling systems

**Vacuum Issues (Mars)**

- **Method 1:** ("brute force") Acquire samples; use vacuum seals/valves; pump out.
- **Method 2**: ("relax requirements") Sample and/or ionize at ambient pressure; draw into dynamically-pumped MS; consider designs that tolerate higher operating pressure.
- Evaluating current generation of Creare mini TMD pumps (to be flown in SAM on MSL)

- A planned ESA Mars rover mission
- Launch: Plan 2011 (2013?)
- Strong exobiology orientation
- Distinguish ExoMars from MSL
  - Exobiology payload
  - 2 m drill
- Instrument payload nominally selected through 2-year process
- Includes combo LD-GC-EI-ITMS

# Acknowledgements

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# The End

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