Novel Mass Spectrometric Approaches to the *in situ* Chemical Analysis of Galactic and Cometary Dust Particles

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This investigation is part of a broader research program to examine hypervelocity impacts involving objects ranging from interstellar dust to asteroids using time-of-flight mass spectrometry

Principal Research Directions

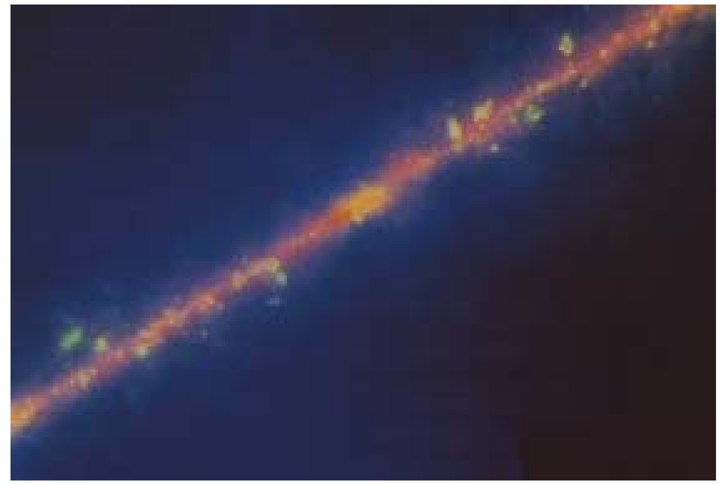
- Development of improved instrument for *in situ* analysis of cosmic dust
- Better understanding of results from previous cosmic dust mass spectrometers
- Understand impact ionization process
- Speciation in shock vaporization of minerals

Outline of Presentation

1. Cosmic dust
2. Instrumentation for cosmic dust analysis
3. The Dustbuster
4. Results of Dustbuster testing using lasers
5. Hypervelocity microparticle impact testing of Dustbuster
6. Problems with hypervelocity impact models
7. Interpretation of dust spectra
8. Analysis of organics in ice particles

What is Cosmic Dust?

- Interplanetary dust: microparticle debris from comets, asteroids, etc.
- Interstellar dust: particles originating outside the solar system
- Man-made particulate debris near Earth



Zodiacal Light

The inner Solar System is suffused with a vast cloud of 'interplanetary dust.' This dust cloud is visible with the naked eye as the zodiacal light - a triangular glow rising above the horizon shortly after sunset or before sunrise.

The Hale-Bopp comet appears against a background of zodiacal light.

What can Cosmic Dust tell us?

- Small chemical sample from a distant object
- Elemental and isotopic distribution and fractionation in astronomical processes
- Nucleosynthesis, formation and evolution of planets and stars

Methods for Studying Cosmic Dust

Remote Sensing

- radar, zodiacal light, thermal emissions
- dynamics and distributions

Collection from atmosphere and surface of Earth

- composition and structure
- particles altered by atmosphere

In situ analysis

- study properties of individual dust grains
- limited by weight, power, automation

Sample capture and return

- study properties of individual grains
- capture is difficult, return takes many years

Properties of Cosmic Dust

Size and charge

- typically 0.1 to 10 microns
- typically charged to +4 V within solar system
- 1-micron grain has charge of 0.2 fC (1500 e^-)

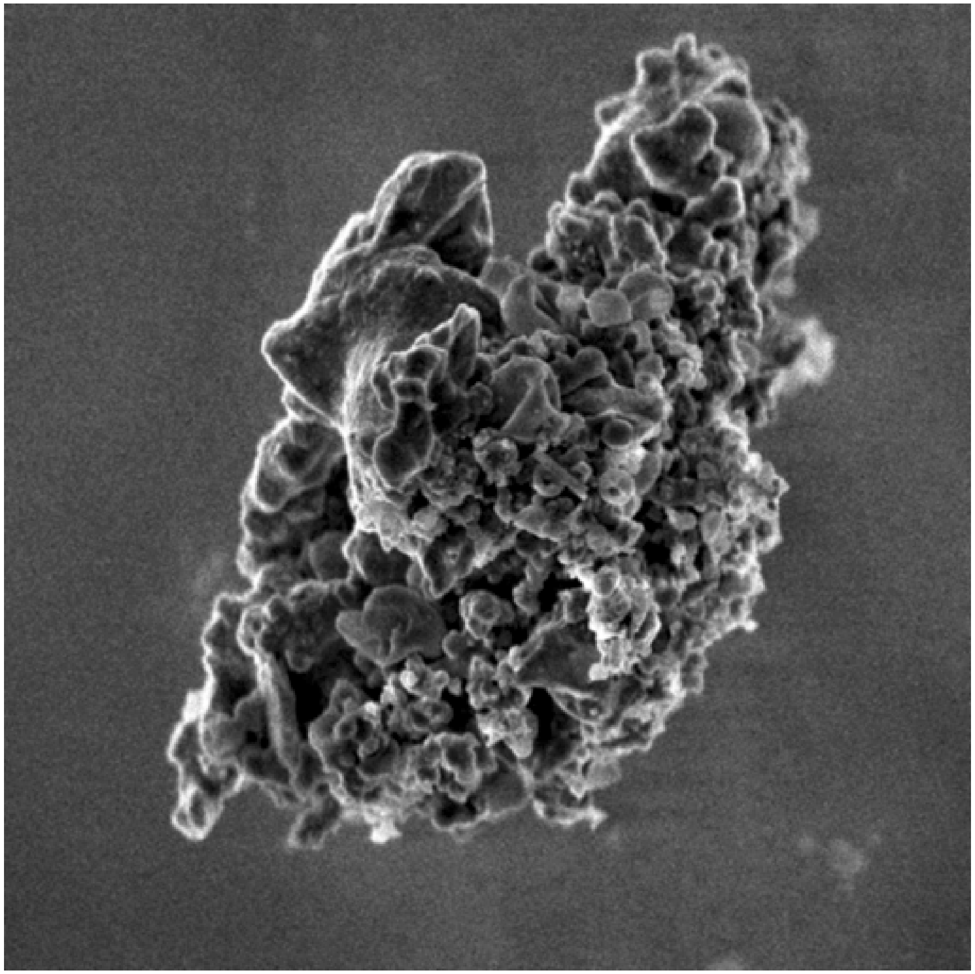
Composition

- mostly mineral grains, some metals
- frequently enriched in refractory trace elements
- organic molecules

Distribution in space

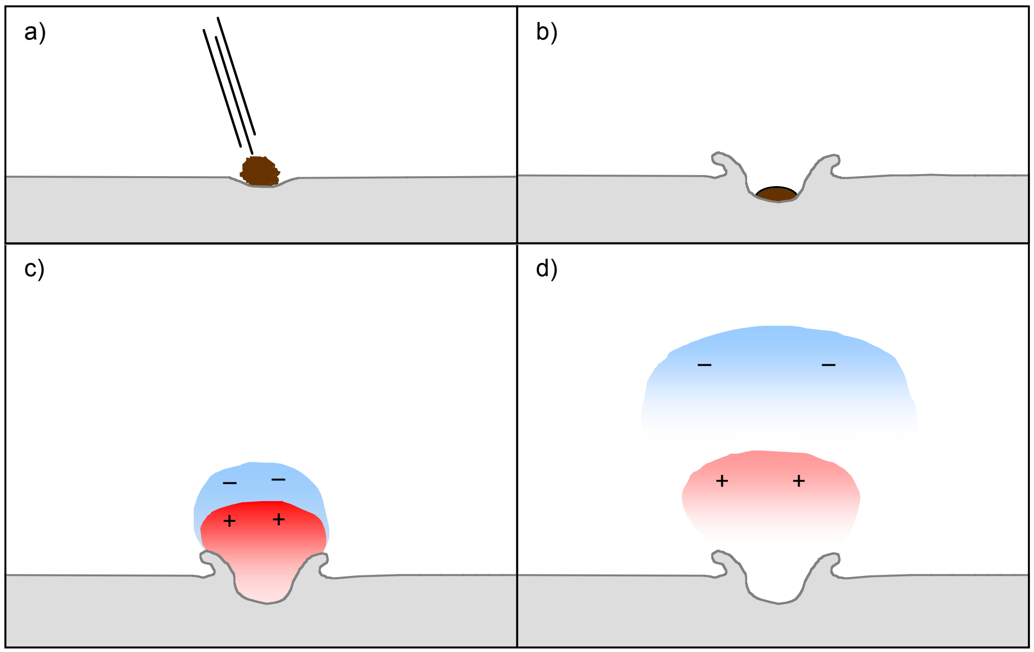
- interstellar dust: 1 grain per km^3
- much more dense in comet tails, dust rings
- complex dynamics

Cosmic Dust Particle



Instrumentation for *in situ* Dust Analysis Relies Mainly on Impact Ionization and Mass Spectrometry

Impact ionization of a fast microparticle



Impact ionization:

- typical encounter velocities: 10-80 km/s*
- particle partially vaporized and ionized
- ions and/or electrons are detected
- mass spectrometric analysis of ions

*These velocities are not easily achieved in laboratory studies of accelerated particles

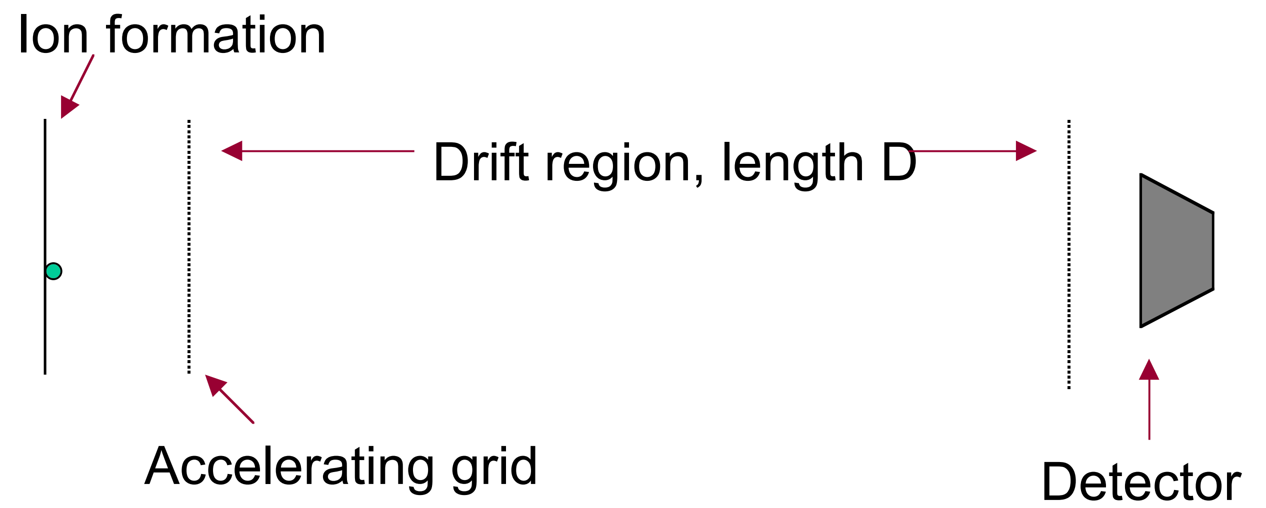
Previous *in situ* Dust Analyzers

Missions with impact-ionization dust analyzers

Mission	Launch	Object	Velocity, km/s
Vega 1, 2	1984	Halley	79
Giotto	1985	Halley	69
Galileo	1989	IP/IS dust	2-70
Ulysses	1990	IP/IS dust	2-70
Cassini	1997	IP/IS dust	1-70
		Saturn (2004)	
Stardust	1999	Wild 2 (2004)	6
		IP/IS dust	20-50
Contour	2002	Encke (2003)	28
		SW (2006)	14
		d'Arrest (2008)	12

From Hornung, K.; Malama, Yu. G.; Kestenboim, K.S. *Astrophys. Space Sci.* **2000**, *274*, 355-363.

Time-of-flight Mass Spectrometry

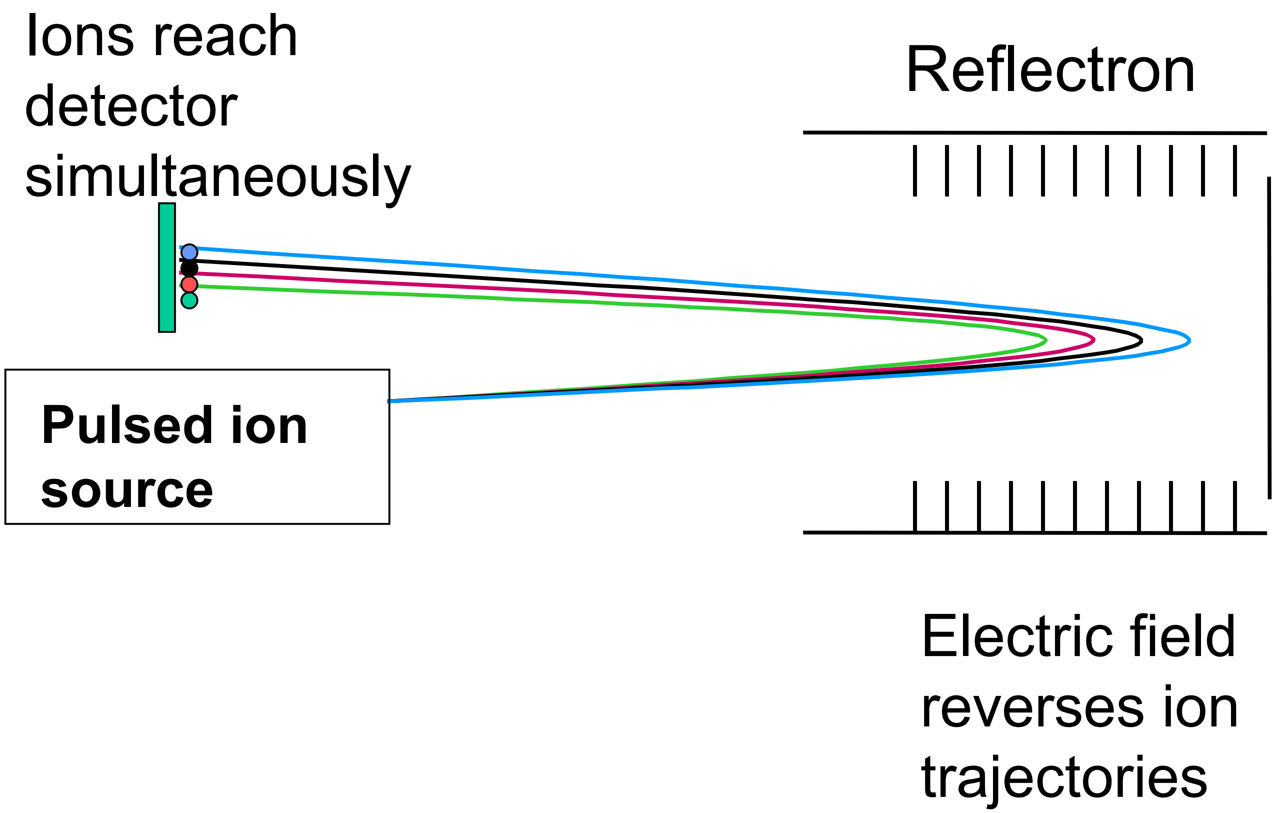


Ions are accelerated by a voltage (V) to the same kinetic energy, and the arrival time is dependent only on mass:

The mass resolution for a TOF-MS is

Resolution is often limited by spread in initial ion kinetic energies

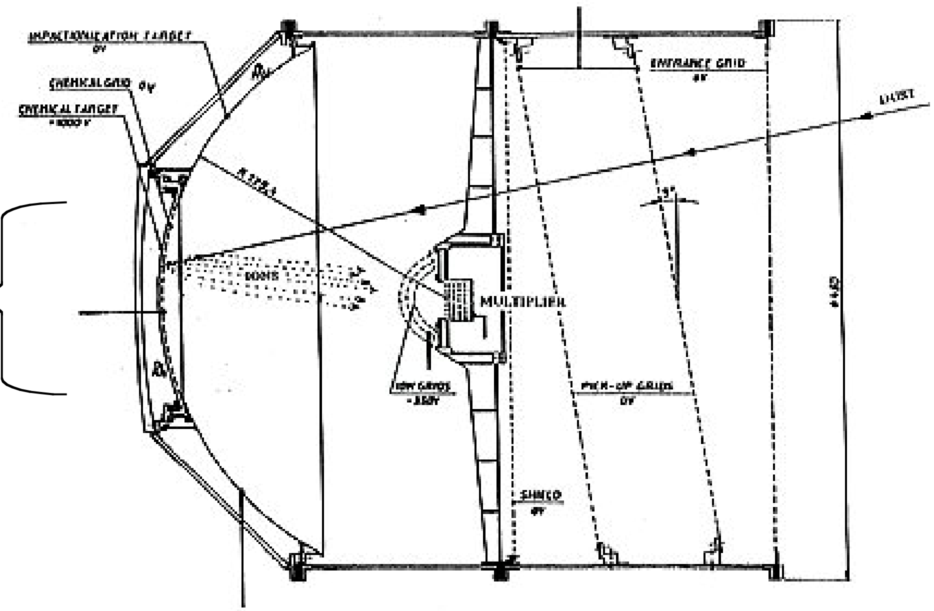
The Reflectron Provides Improved Mass Resolution for TOF-MS

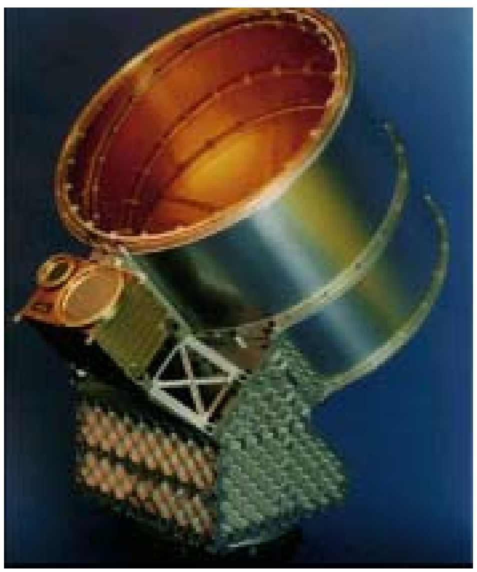


Developed in 1973 by Mamyrin and coworkers

Cassini Cosmic Dust Analyzer (CDA)

Chemical
analyzer
target



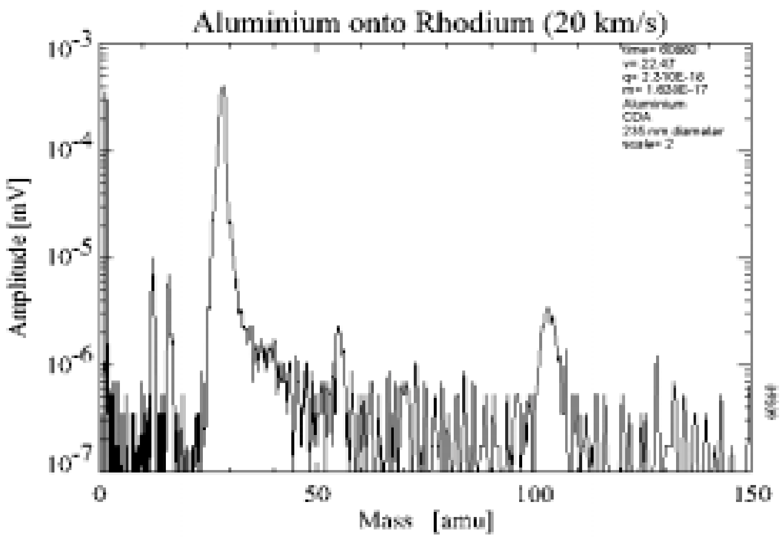


- 50 cm^2 target plate in order to acquire more impacts
- No reflectron; resulting spectra have low resolution
- Weighs 17 kg; power: 30 W

Cassini Cosmic Dust Analyzer (CDA)

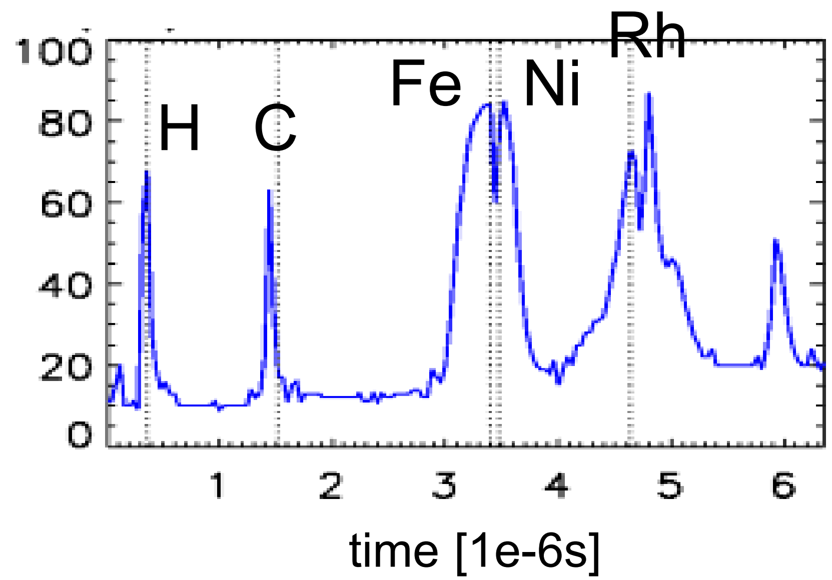
CDA lab testing

Al projectile, 20 km/s
with Rh target



CDA in-flight data

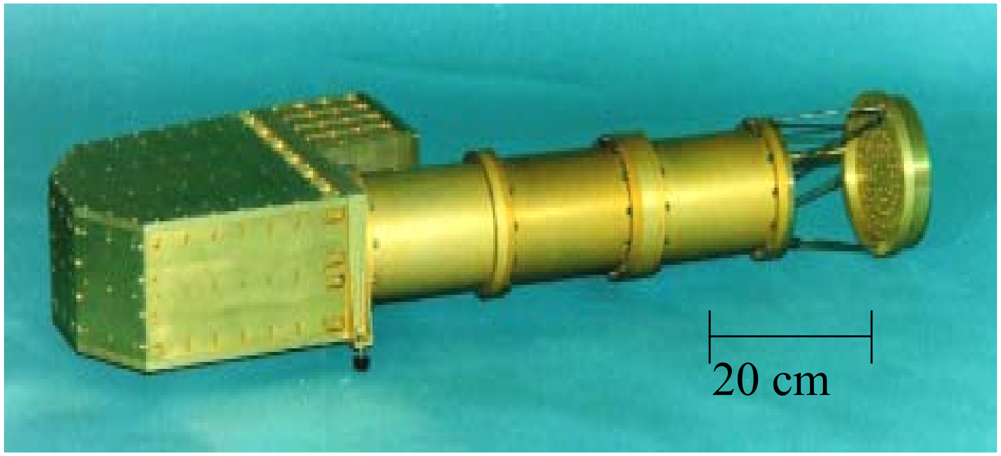
Interstellar dust grain,
20 km/sec, 2 x10^{-17} kg

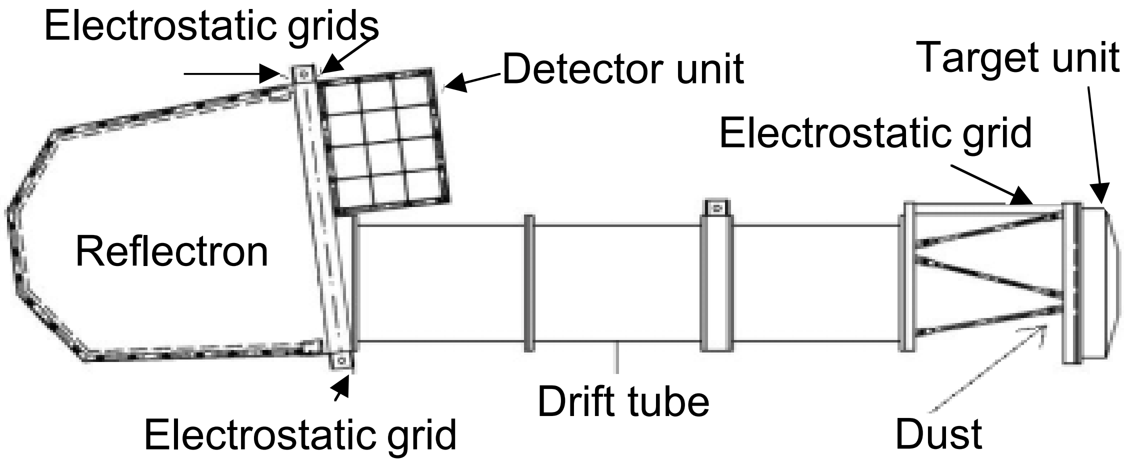


Stardust Cometary and Interstellar Dust Analyzer (CIDA)

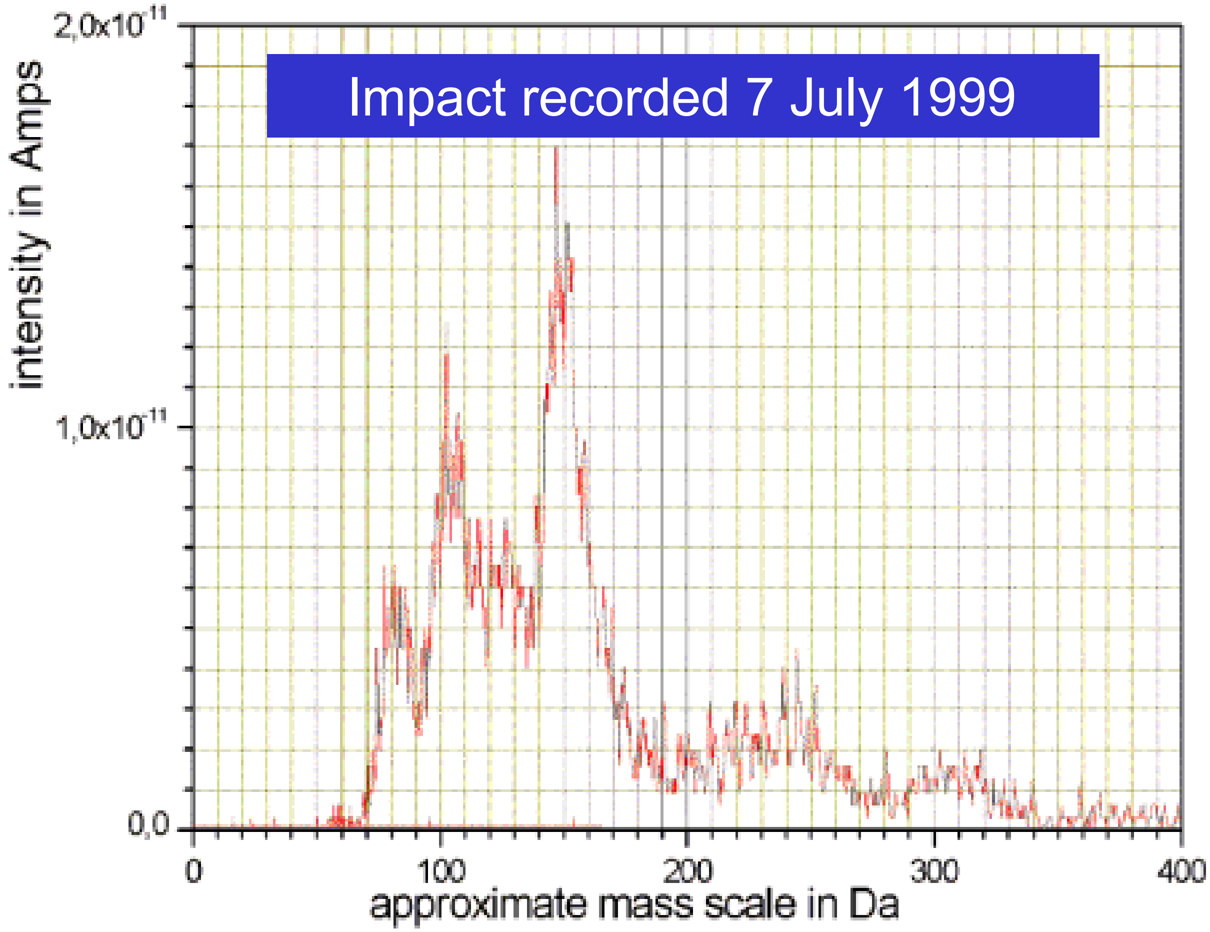
Same design as Vega I, II, and Giotto instruments

- Small target area for high dust flux (5 cm^2 on Vega, Giotto, 50 cm^2 on Stardust)
- Reflectron provided correction of ion energies, produced high mass resolution
- mass: 16 kg, power: 30 W





Stardust Cometary and Interstellar Dust Analyzer (CIDA)



A tentative analysis suggested that this spectrum may be due to a mixture of complex organic molecules, including polyaromatics.

Franz R. Krueger and Jochen Kissel. "First Direct Chemical Analysis of Interstellar Dust," *Sterne und Weltraum* p 326-329, v 39, May 2000.

Design Objectives for Improved Dust Analyzer

- Compact, lightweight instrument
- High mass resolution
- Large impact target area
- Useful in a variety of dust environments

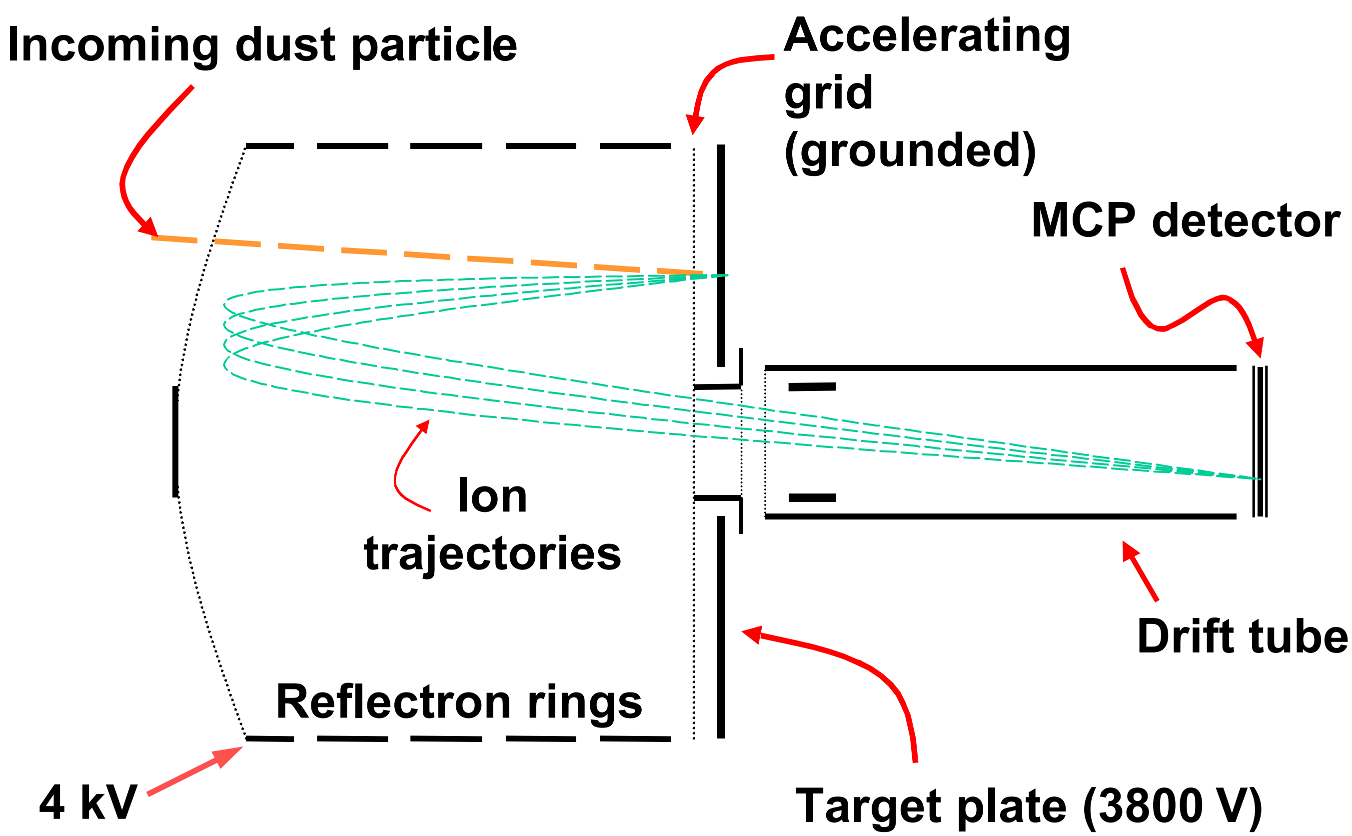
Dustbuster

Size matters…….

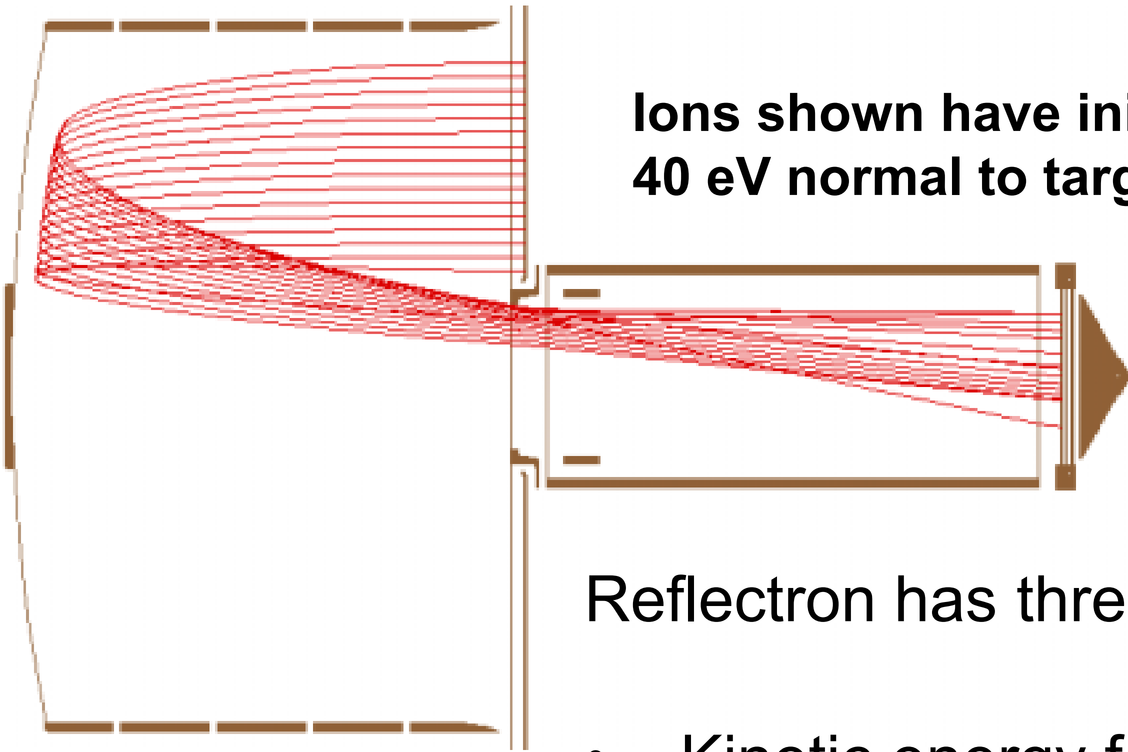
Jochin Kissel with CIDA Instrument

Sarah Austin with Dustbuster

Dustbuster Design



The Dustbuster Reflectron



Ions shown have initial K.E. of 40 eV normal to target plate

Reflectron has three functions:

- Kinetic energy focusing
- Spatial Focusing
- Elimination of neutrals, droplets, other ejecta, and secondary ions

Dustbuster Testing

Laser desorption/ionization simulating particle impacts

- Pulsed nitrogen laser delivers 10^9 W/cm^2 to metal or mineral sample embedded in target plate

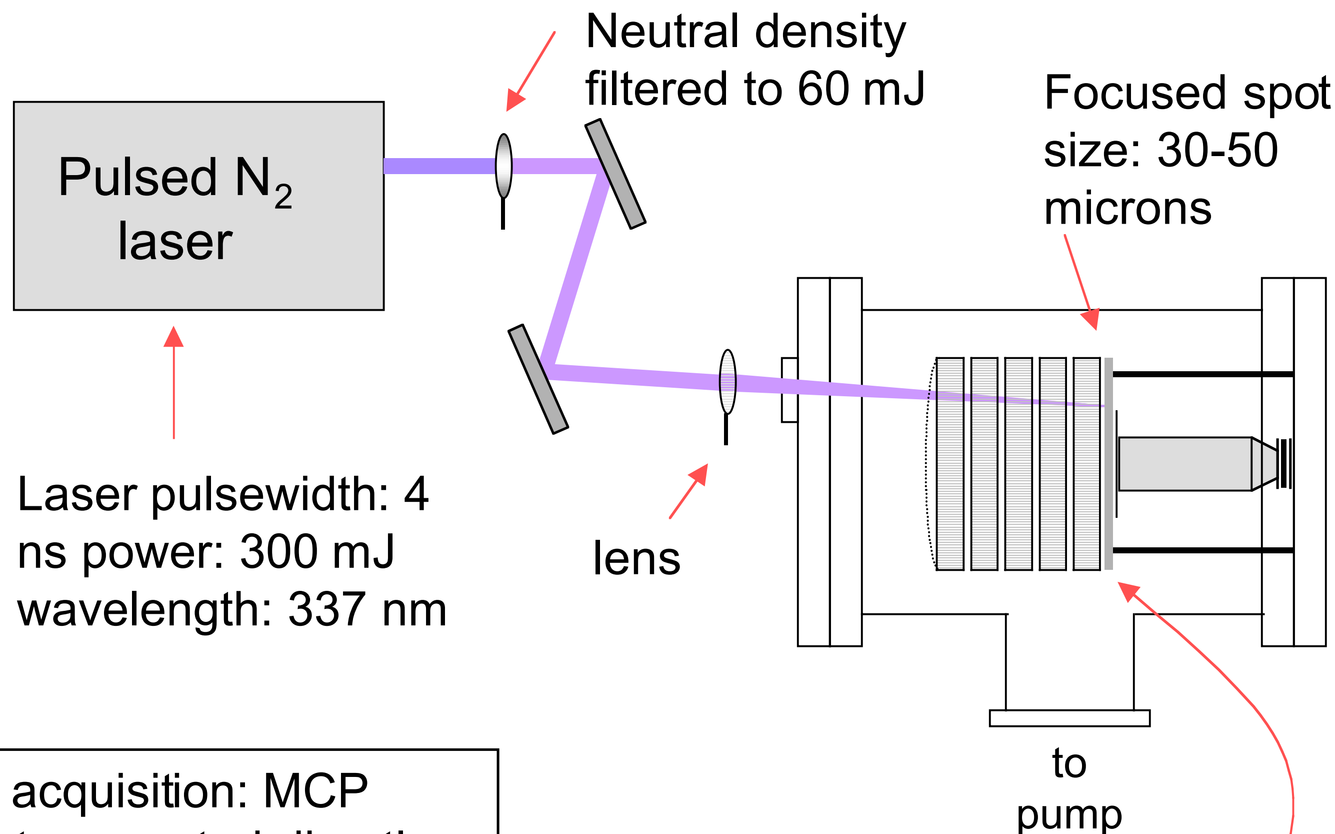
High-velocity iron and copper particle impacts

- Accelerated using 2 MV Van de Graaff accelerator

High-velocity ice particle impacts

- (currently underway)
- Electrosprayed droplets introduced to vacuum, then pulsed with 5-20 kV

Laser ionization testing of Dustbuster



Metal and mineral samples embedded in target plate

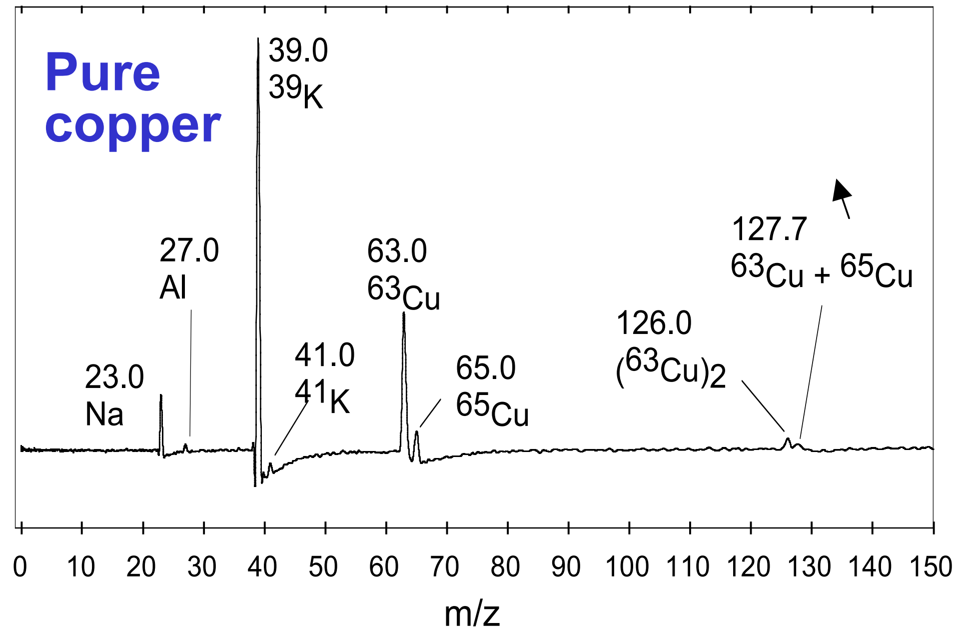
samples studied: copper, chalcopyrite, olivine, and chlorite

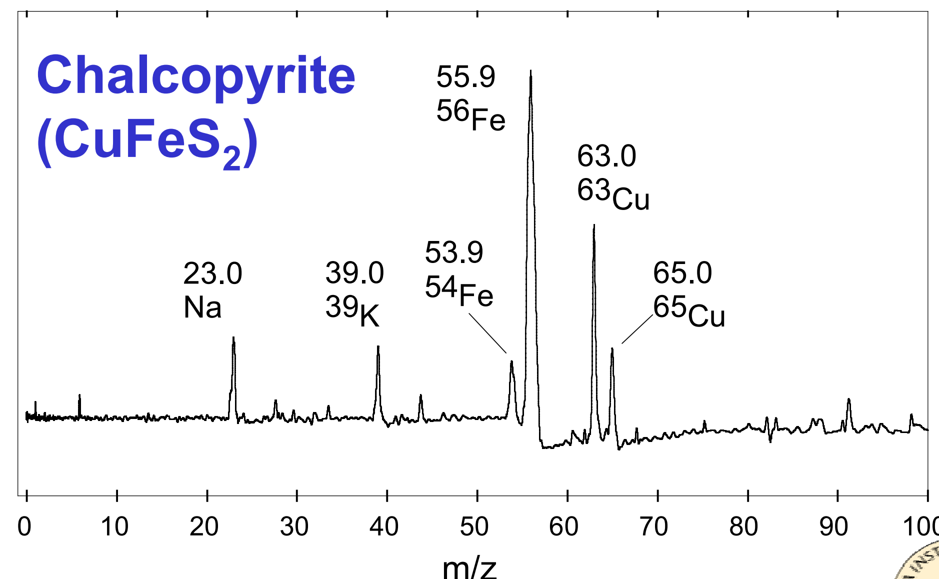
Data acquisition: MCP output connected directly to EG&G Ortec fast preamp, then to 150 MHz digital oscilloscope

Austin, Ahrens, & Beauchamp, *Rev. Sci. Instrum.* **2002**, 73(1), 185.

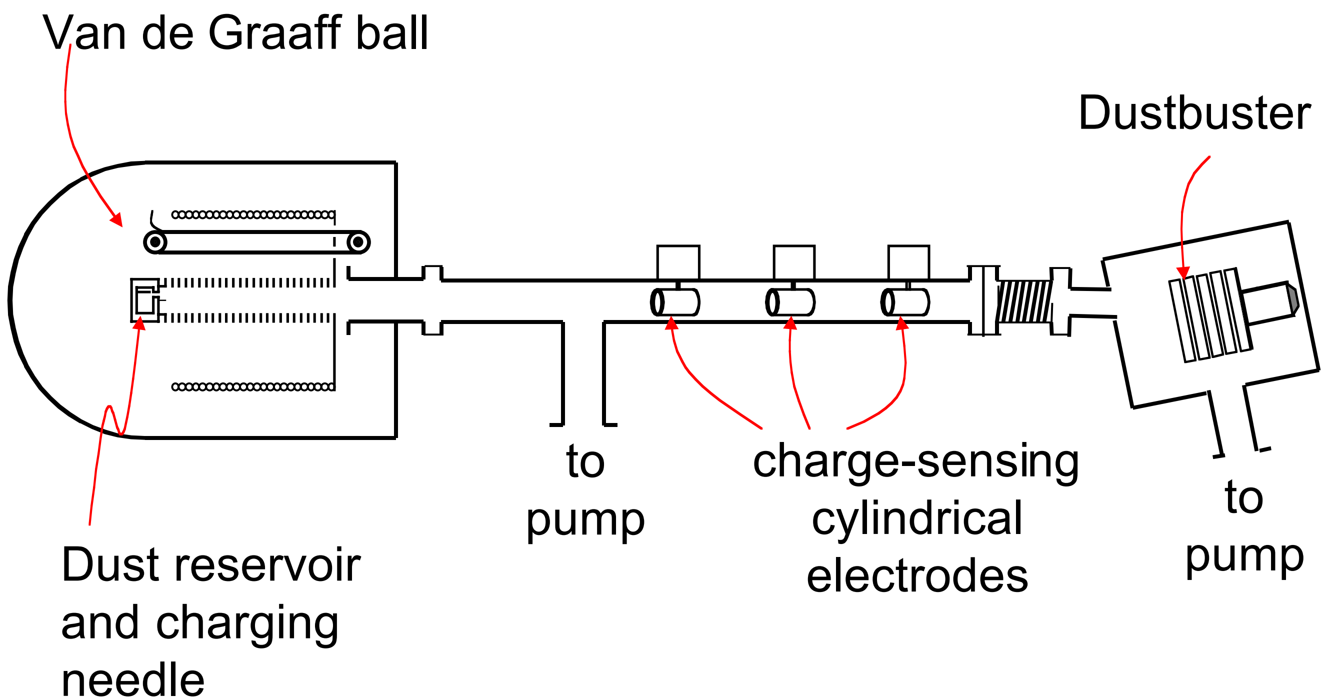
Laser Ionization Testing of Dustbuster

Note absence of low mass peaks (m/z 1, 12, 16)





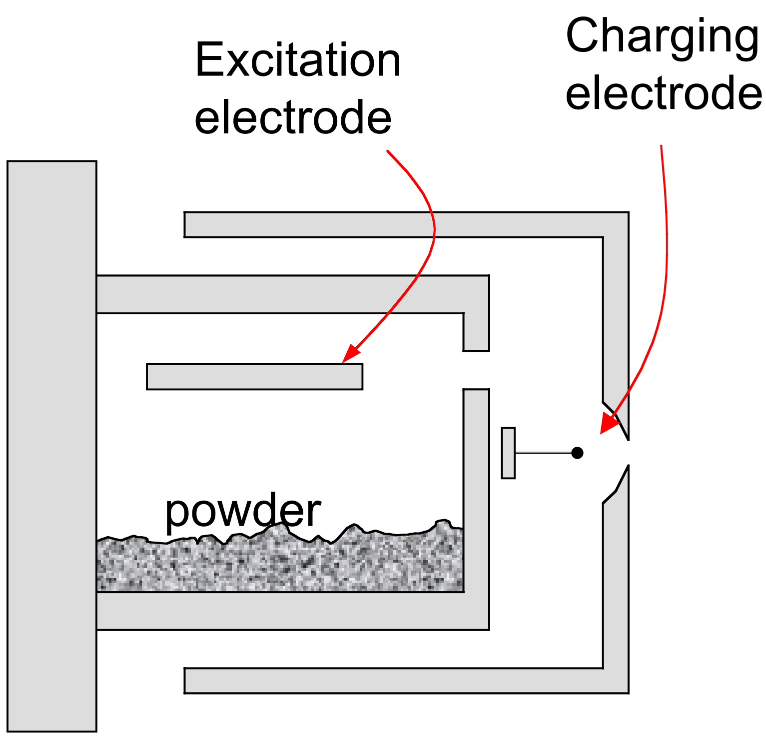
Impacts using 2 MV Van de Graaff Dust Accelerator



Concordia College Physics Dept.
(Moorhead, MN)

Dr. Heidi Manning

Impacts using 2 MV Van de Graaff Dust Accelerator

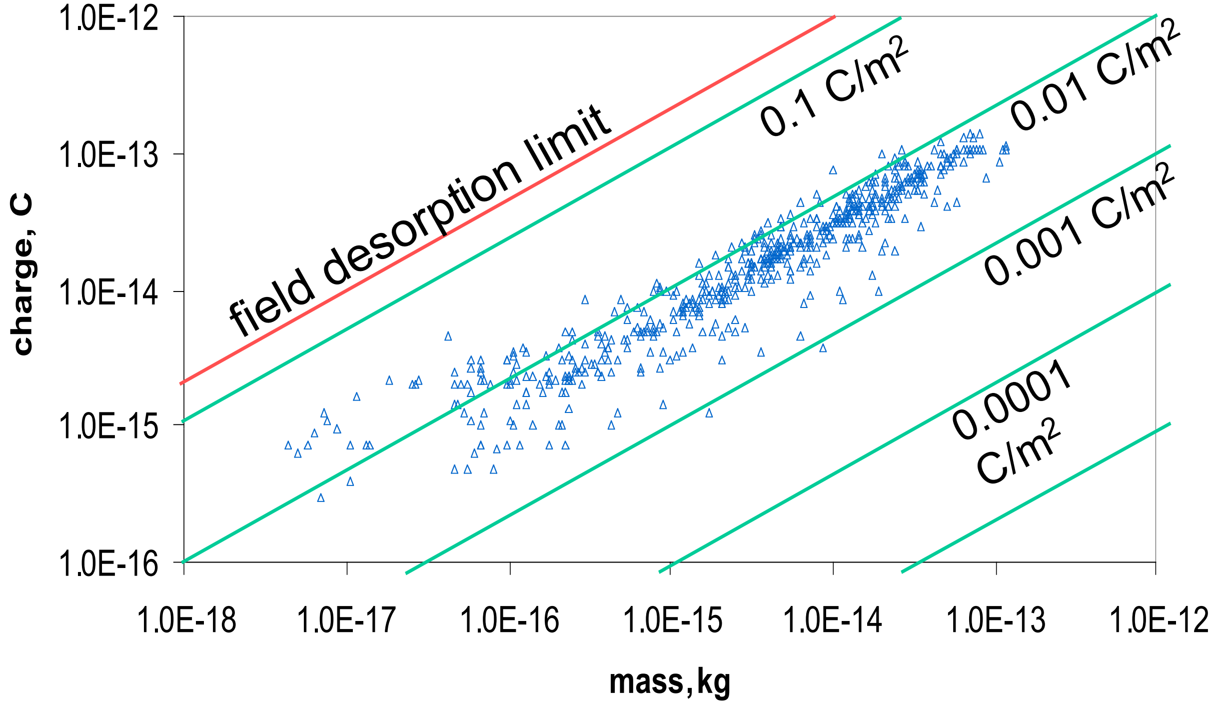


Dust consisted of iron and copper spheres, 0.1-3 micron diameter

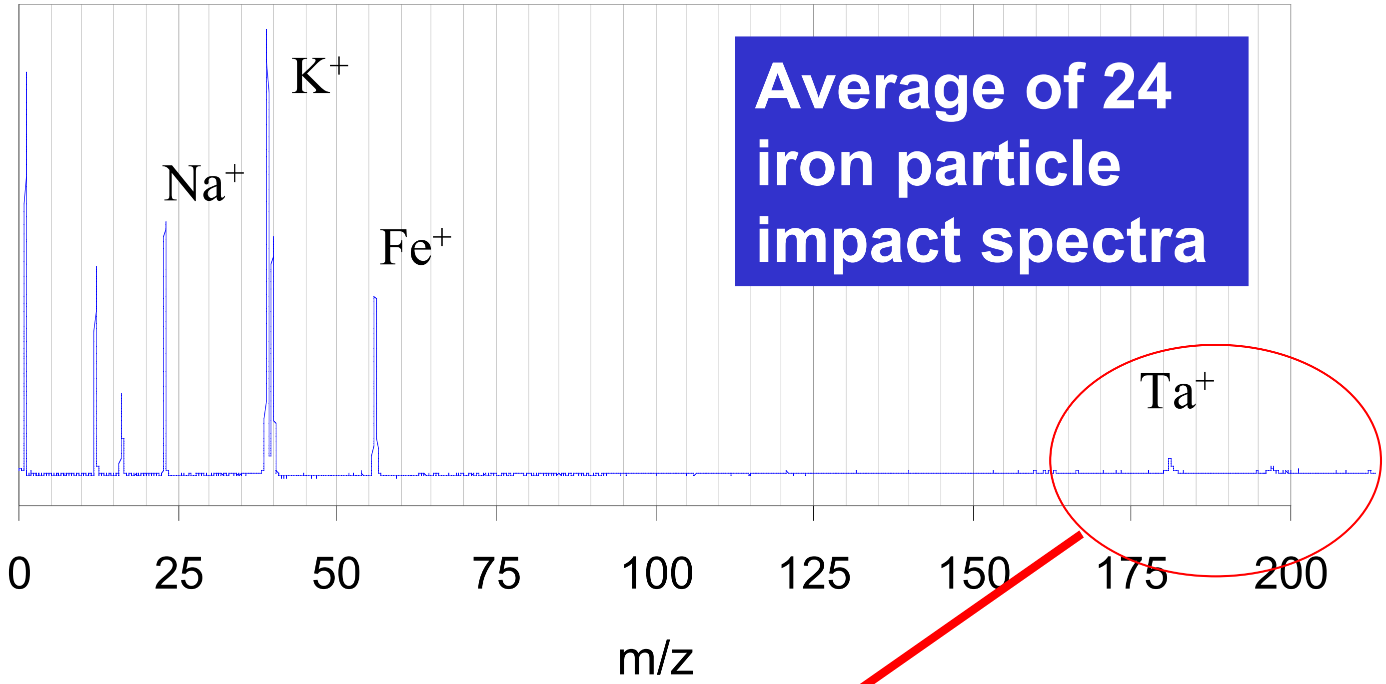
Dust Reservoir and Charging Needle

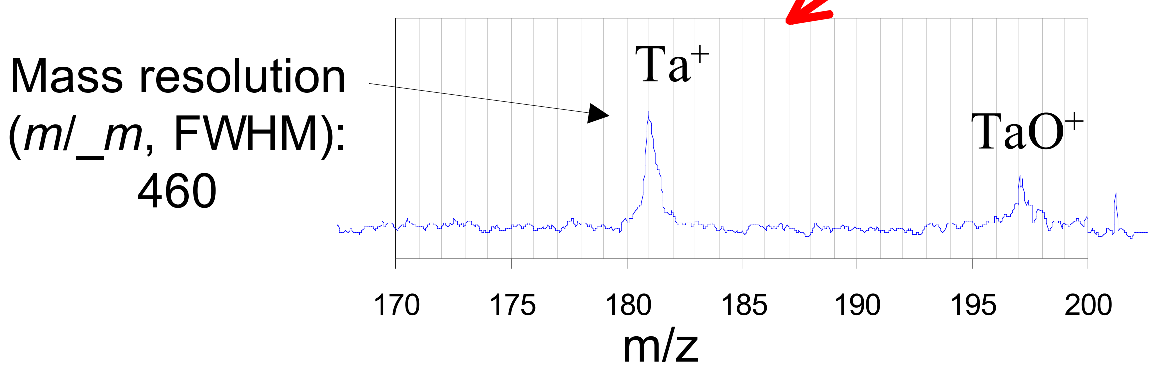
Impacts using 2 MV Van de Graaff Dust Accelerator

Mass and charge of accelerated particles, shown with lines of constant surface charge density for iron spheres



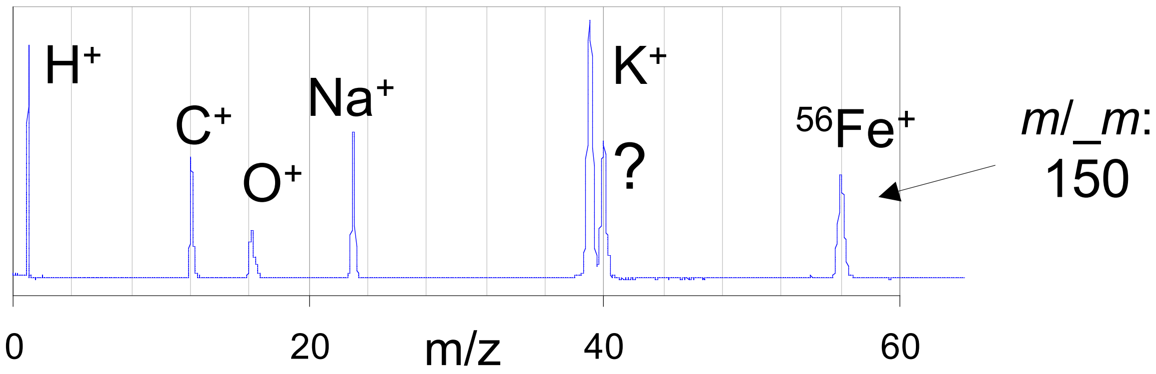
Impacts using 2 MV Van de Graaff Dust Accelerator





Impacts using 2 MV Van de Graaff Dust Accelerator

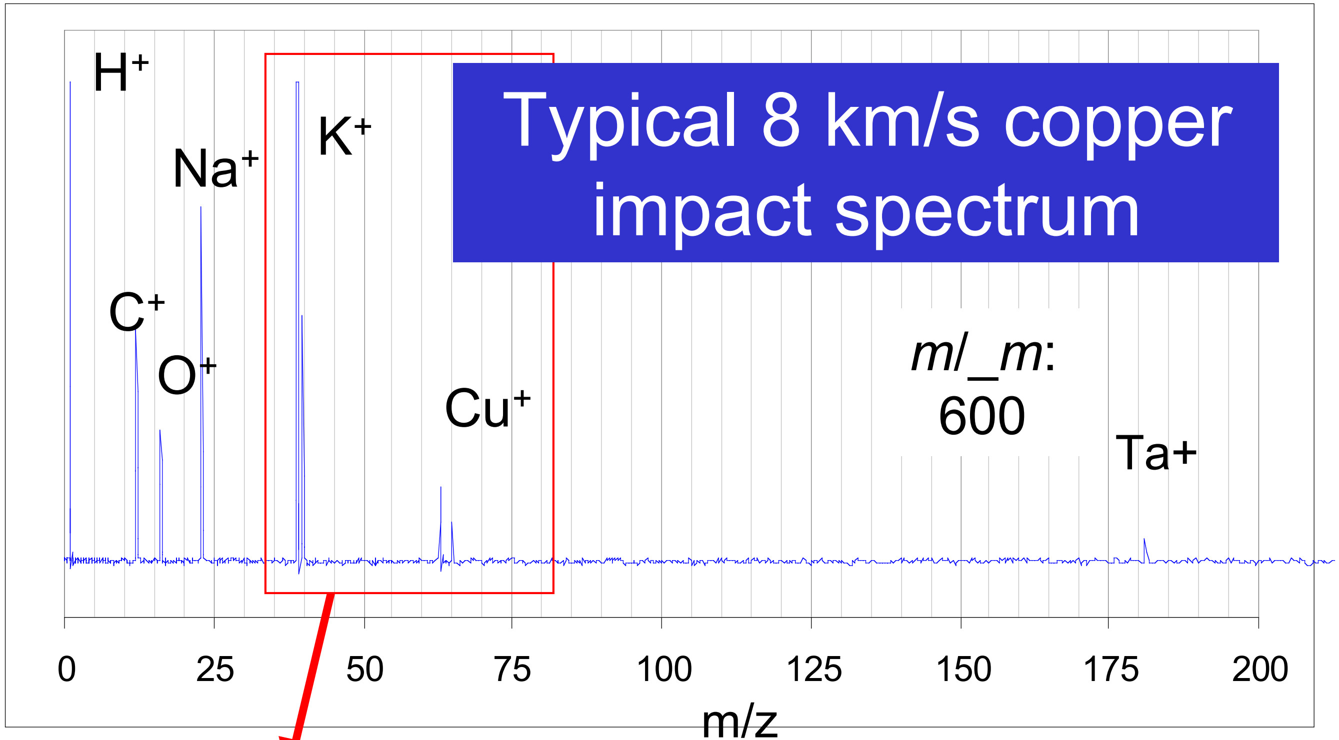
Enlargement of 0-60 mass region

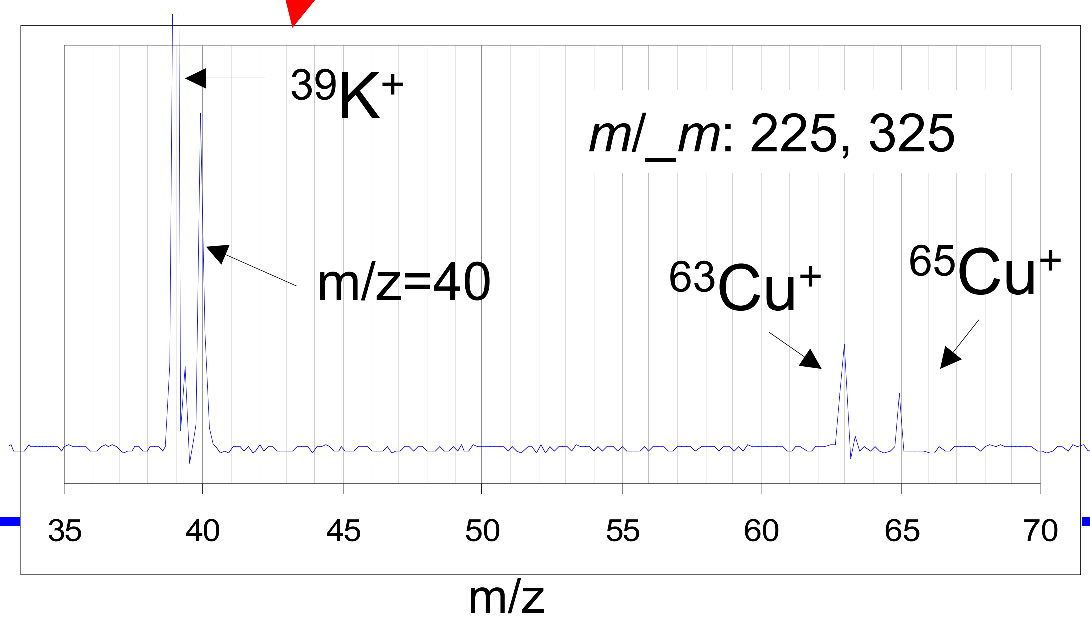


Average of 24 iron particle impact spectra

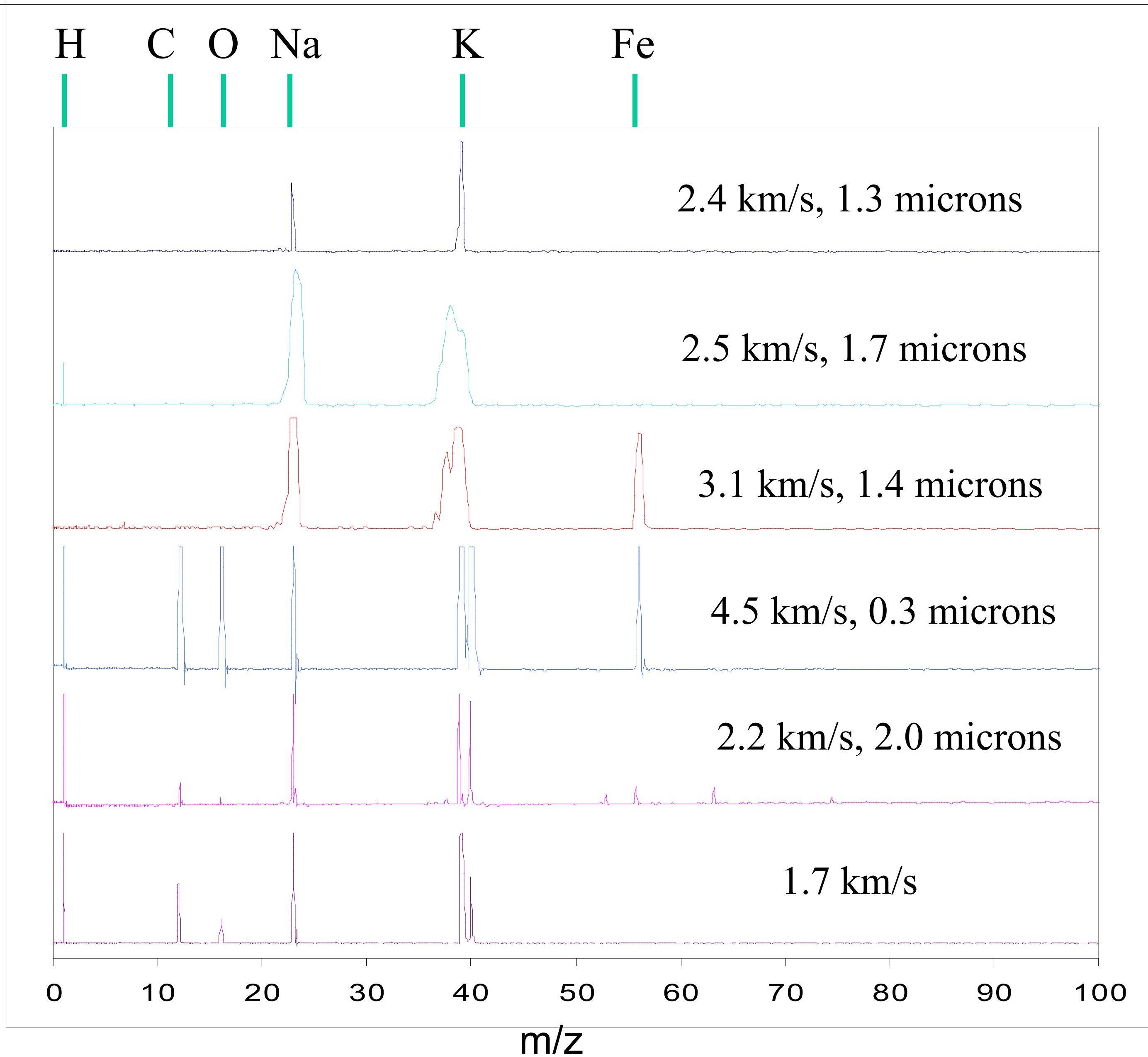
Note presence of low mass peaks (m/z 1, 12, 16)

Accelerator Testing

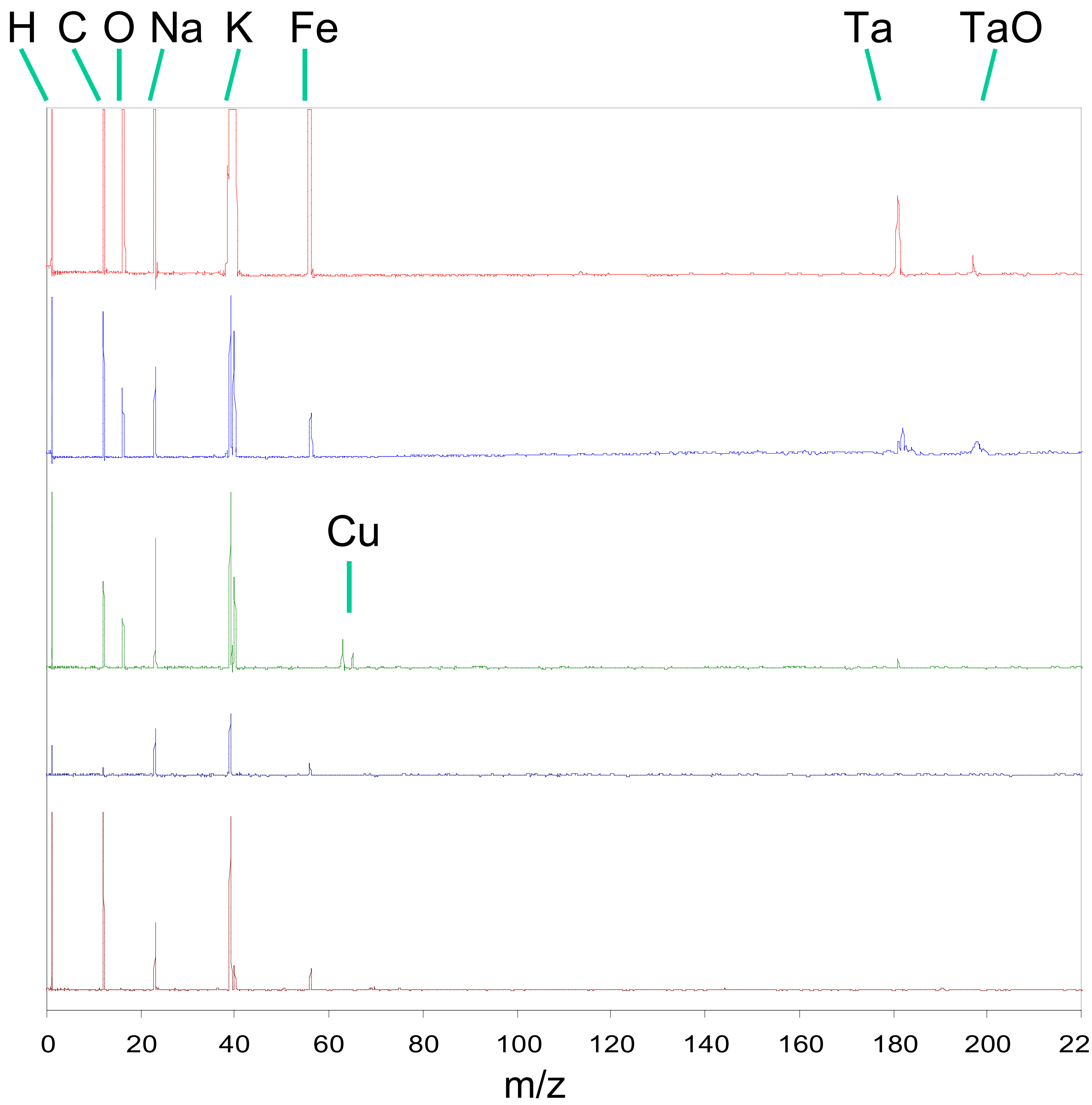




Typical Spectra from Iron Impacts

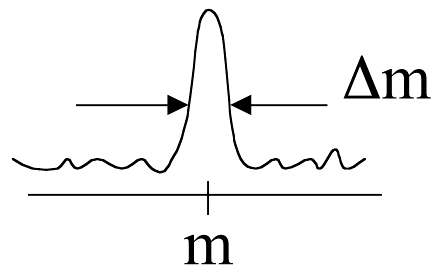


Typical spectra from particles with unknown mass and velocity



Dustbuster Performance: Mass Resolution

The mass resolution is



at FWHM

Mass range	species	typical resolution
Heavy (>100 amu)	Ta, TaO	200-600
medium (30-100)	Fe, Cu	150-300
light (1-30)	H, C, O	50-150

Dustbuster Meets Major Design Goals

- Same peaks observed as in previous impact ionization mass spectrometry experiments
- Sufficiently large target plate for statistically significant number of dust impacts in deep space
- Smaller and lighter than any previous *in situ* dust analyzer
- Higher mass resolution than any previous dust analyzer
- Impacts at various angles and at various locations on the target plate produce spectra of similar quality

Not Everything is Good News

- Why do we see iron and copper ions in 3 and 4 km/s impacts?
- Why do we see C, H, and O ions at all? Why are they present in the accelerator study and absent in the laser ablation study?
- If C, H, and O are from pump oil, where are the fragment ion peaks?
- How do we derive particle composition from the spectra?
- Why do we see H_2^+ and a peak at m/z = 40?

Ionization in equilibrium plasma follows Saha eqn:

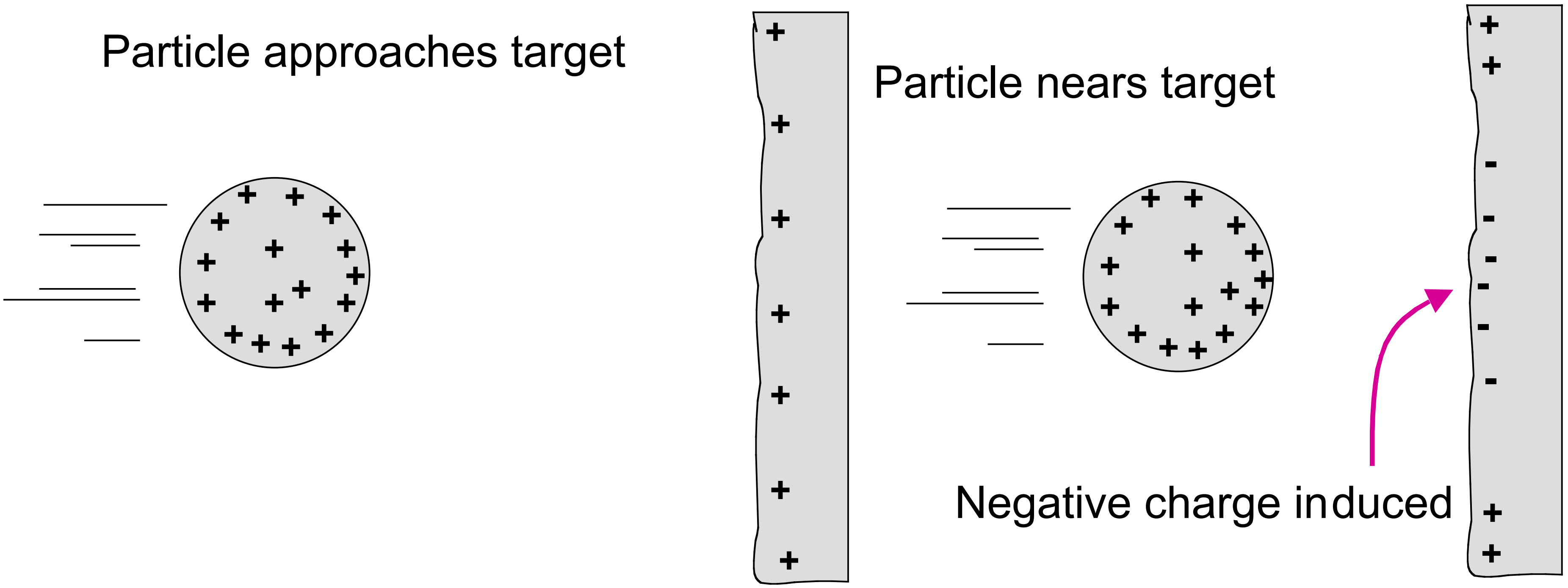
Equilibrium plasma theory predicts ion yields lower than observed with low impact velocities

Simulations of impact ionization using continuum mechanics, hydrocode, or molecular dynamics also predict low ion yield

These methods also predict higher value for threshold impact speed for ion formation

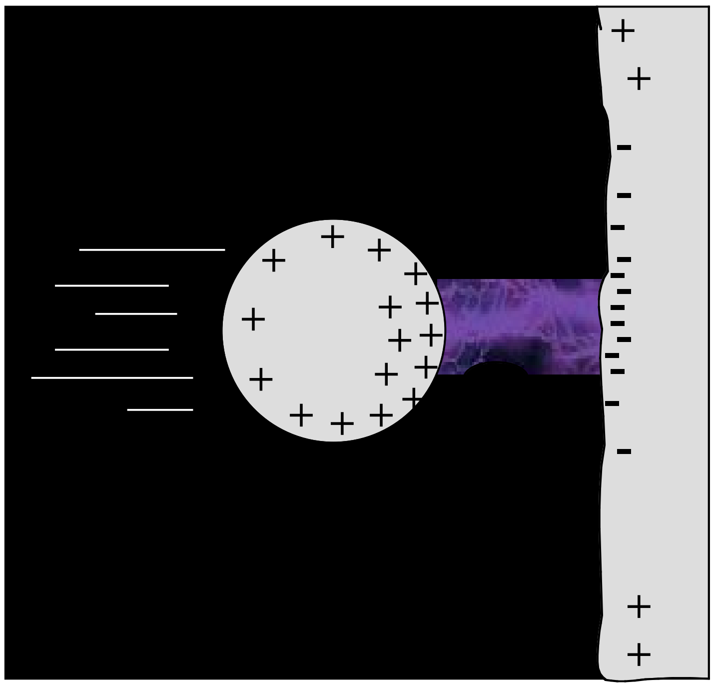
$\boxed{\text{Another ionization mechanism is at work}}$

Electron Emission Ionization Model



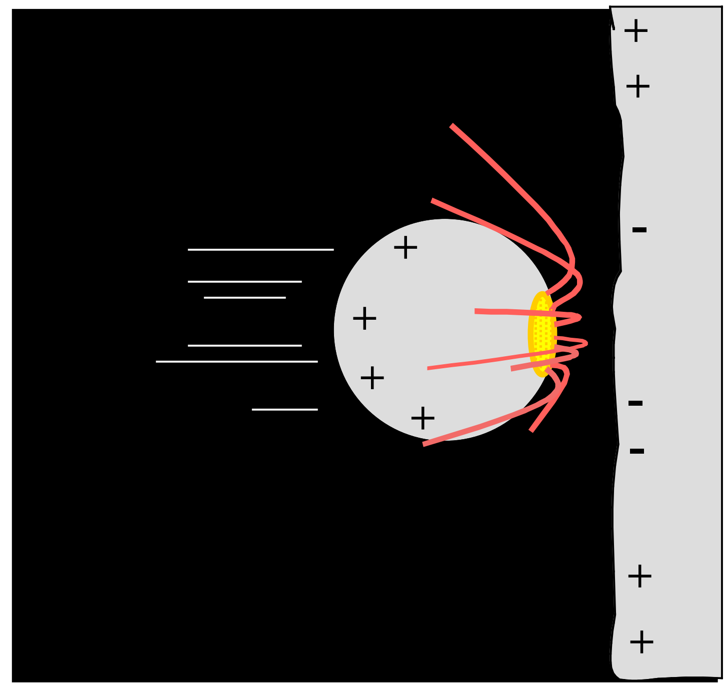
(Sysoev et al., *Nucl, Instrum. Meth. B*, **1997**, *122*, 79.)

Electron Emission Ionization Model



Electric field exceeds field emission limit for electrons

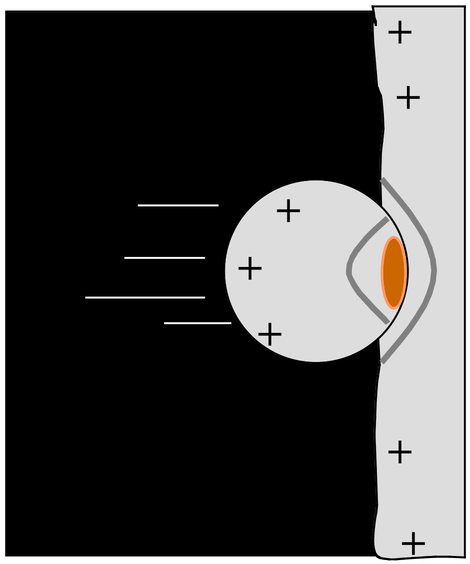
Electrons leave target surface and strike particle



Electron-induced desorption and ionization

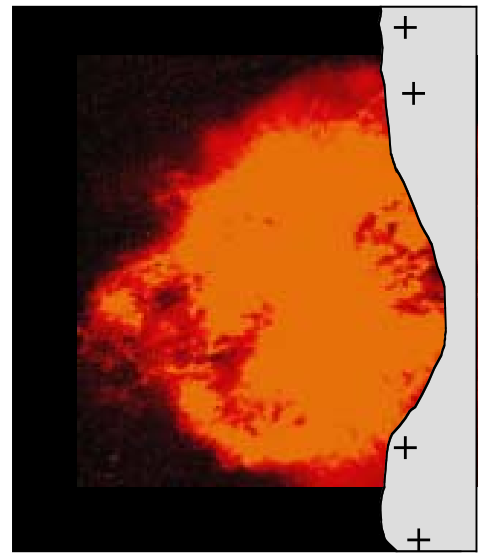
Spot heating and thermal desorption

Electron Emission Ionization Model



Impact, shock
wave heating

Normal impact
ionization



Vaporization and
ionization of particle
and target

Impact flash

Electron Emission Ionization Model

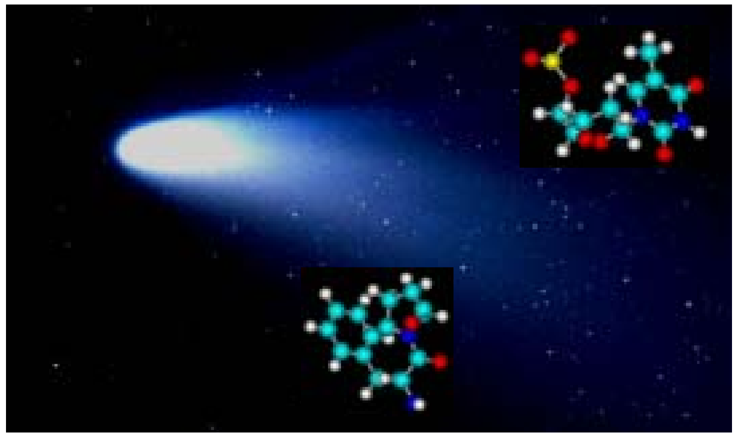
- C, H, and O probably from contaminants on particle surface (pump oil, adsorbed H_2, H_2O, CO)
- Electron emission ionization of surface contaminants results in complete atomization (no or few fragments)
- H_2^+ formed from recombination in dense plasma
- Fe^+ and Cu^+ observed in slow impacts formed by electron desorption ionization prior to impact
- m/z = 40 peak could be Ar^+ or Ca^+
- Interestingly, spark source MS also shows ionizaed H, C, O, and sometimes Ar

Implications for *in situ* Analysis of Cosmic Dust

- Charge on dust will affect the impact mass spectra
- Interpretation of spectra requires measurement of charge before impact (charge-sensitive grid)
- Spectra may be dominated by species on the surface rather than in the interior of the grain
- It may be difficult to infer particle composition from the mixture of ions due to electron emission ionization and impact vaporization/ionization

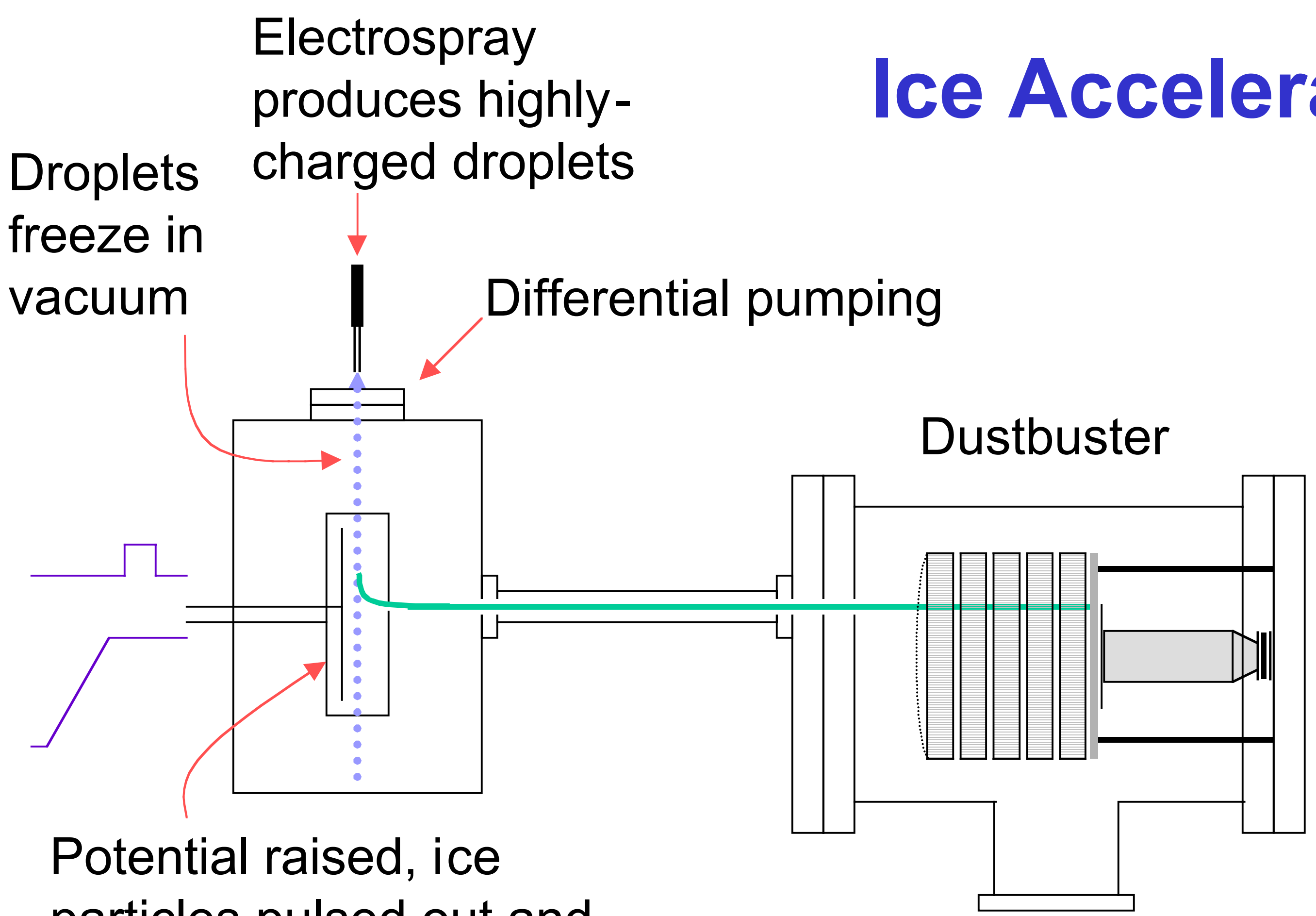
Impacts of High-velocity Ice Particles

(experiments currently underway)



- Much of the dust encountered contains ice
- Ice particles are believed to contain significant amounts of dissolved organic species
- Because they are nonconducting, no one has looked at impacts of accelerated ice particles
- Water and organic species on Earth may have originated from cometary matter

Ice Accelerator



Velocity is measured using time between push-out pulse and impact

Ice Accelerator
….some expectations

- Principal ion formed will be H_3O^+ with additional waters attached
- Chemical ionization of organic species
  $$H_3O^+ + M \rightarrow MH^+ + H_2O$$
- Soft ionization produces intact organic molecules
- Additional ions such as K^+ and Na^+ formed
- Better control of surface ionization effects
- Setup can also be used to accelerate aerosols, bacteria, etc.

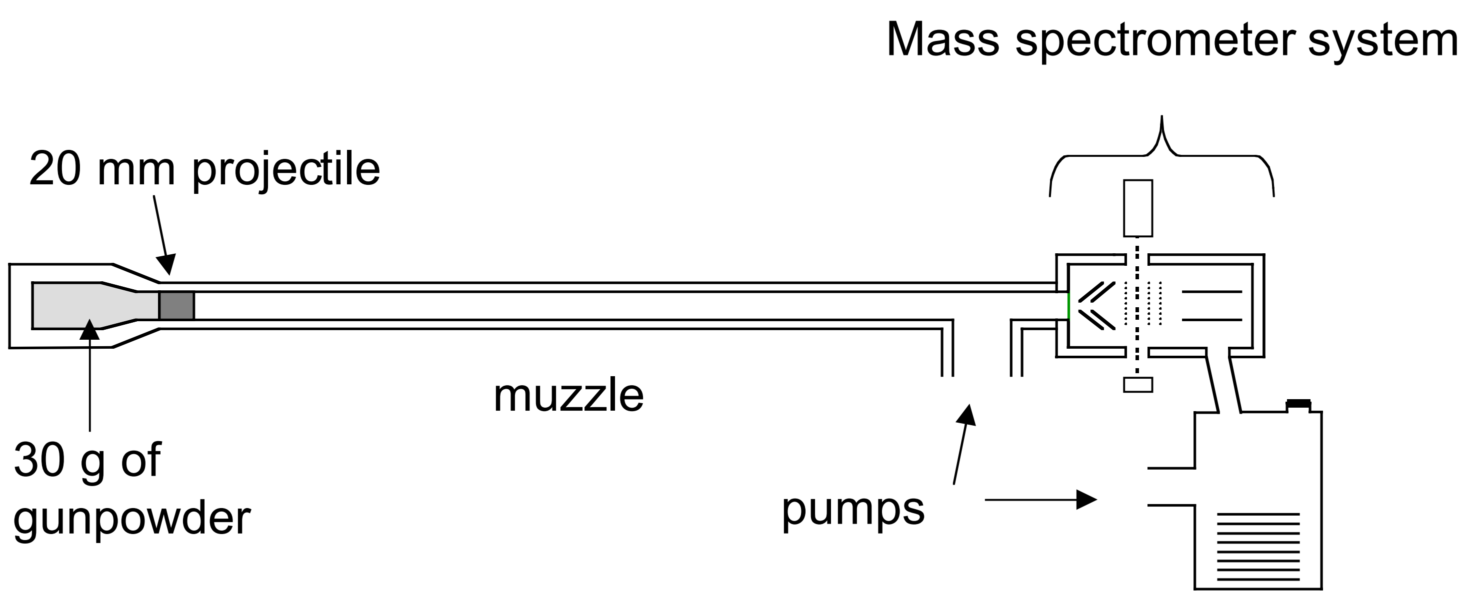
Did the Chicxulub asteroid impact kill off the dinosaurs???

Impact vaporization mass spectrometry

Chicxulub asteroid impact

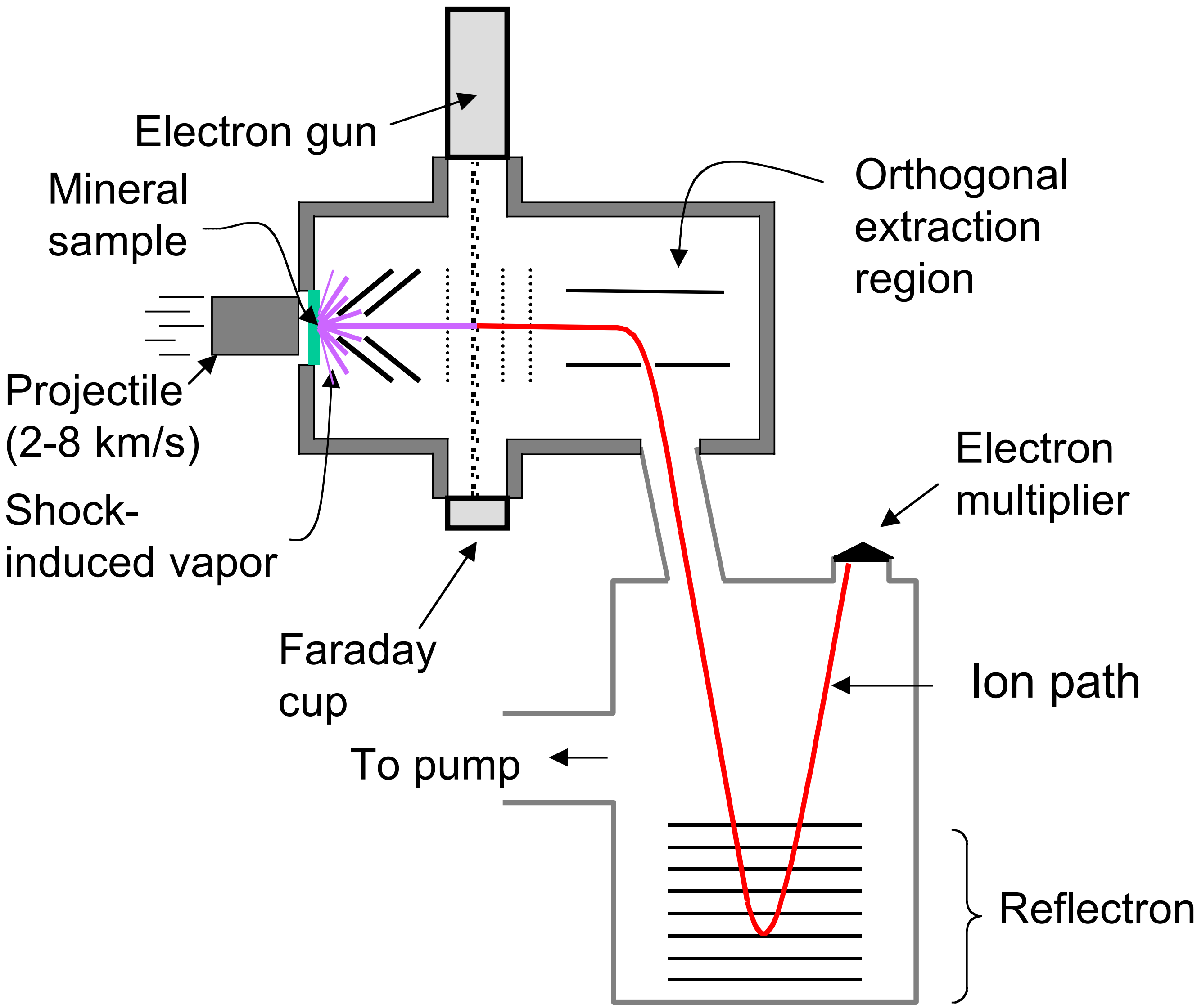
- Occurred at same time as dinosaur extinction (65 Myr ago)
- Vaporized or melted 200 km^3 of rock, mostly $CaCO_3$ and $CaSO_4$
- Uncertainties in types and amounts of gases released into atmosphere (CO_2, SO, SO_2, SO_3)

Shock Vaporization/Ionization Mass Spectrometry (in progress)



This is a thinly disguised gun, which destroys the ion source of the mass spectrometer each time it is fired (clearly a harsh environment)!

Shock Vaporization/Ionization Mass Spectrometry



Summary

- Dustbuster performs well in both laser desorption ionization and hypervelocity microparticle impact experiments
- Impact ionization in general does not follow standard theory; electron emission must be considered in spectra interpretation when particles are highly charged
- Ice impacts may also yield ions, particularly from dissolved organic species
- Experiments are underway to study chemical speciation in shocked minerals. Studies will be expanded to study neutrals produced in hypervelocity impacts.

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