Static SIMS: A Powerful Tool to Investigate Nanoparticles and Biology

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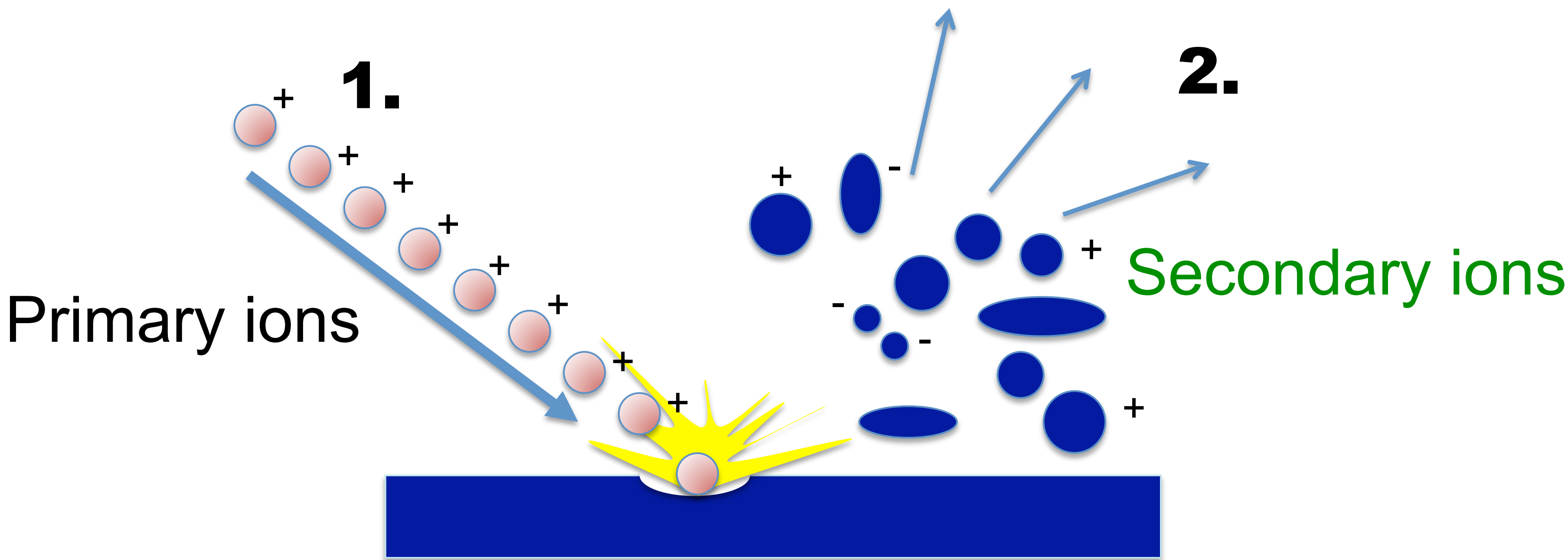
NESAC/BIO

The ideas encompassed in this talk:

- Semiconductor processing
- Nanotechnology
- Biology
- Physics
- Surface Science
- Analytical Chemistry
- Multivariate Statistics
- Environmental Sciences

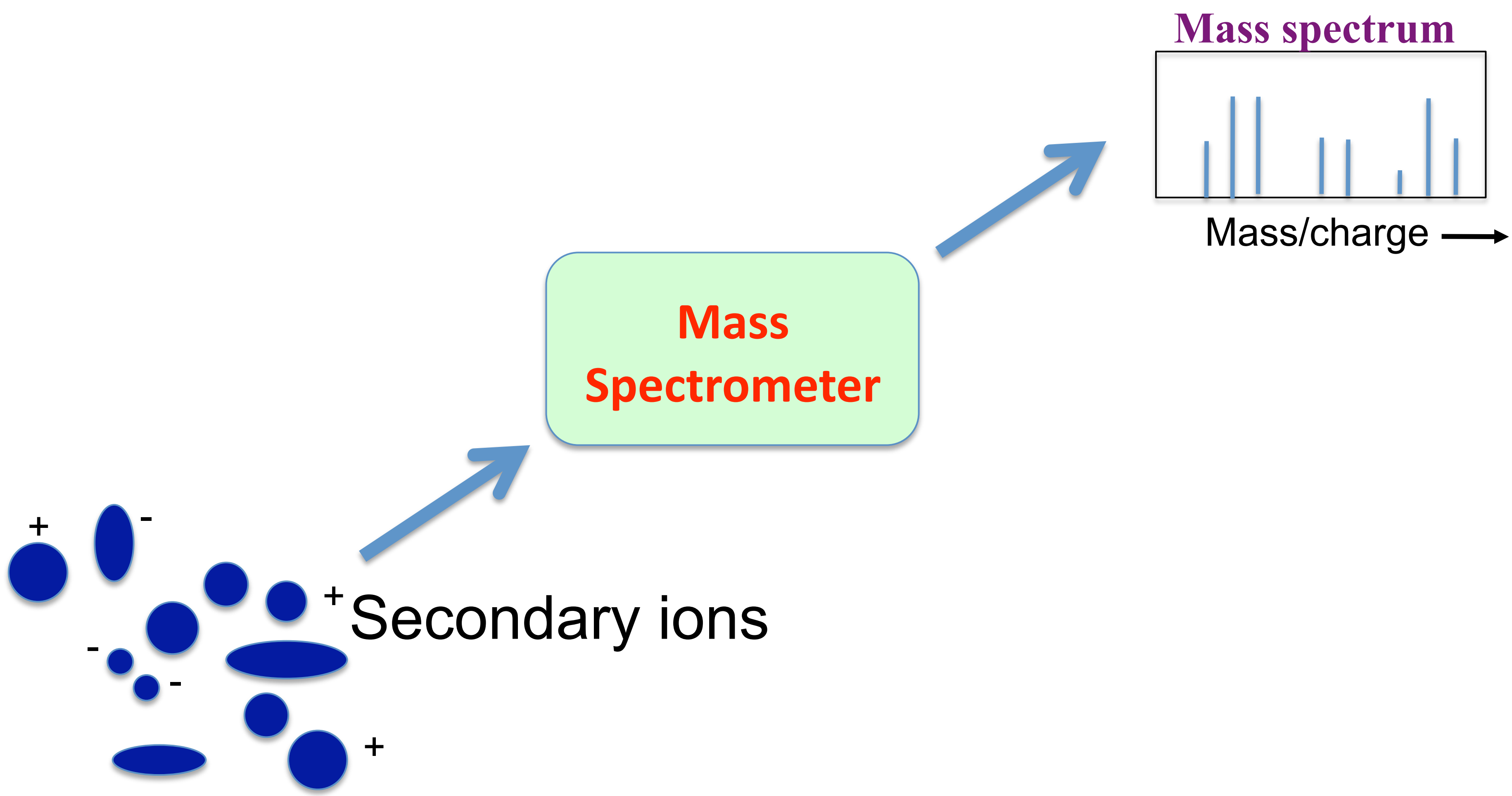
SIMS: The central focus of this talk

secondary ion mass spectrometry



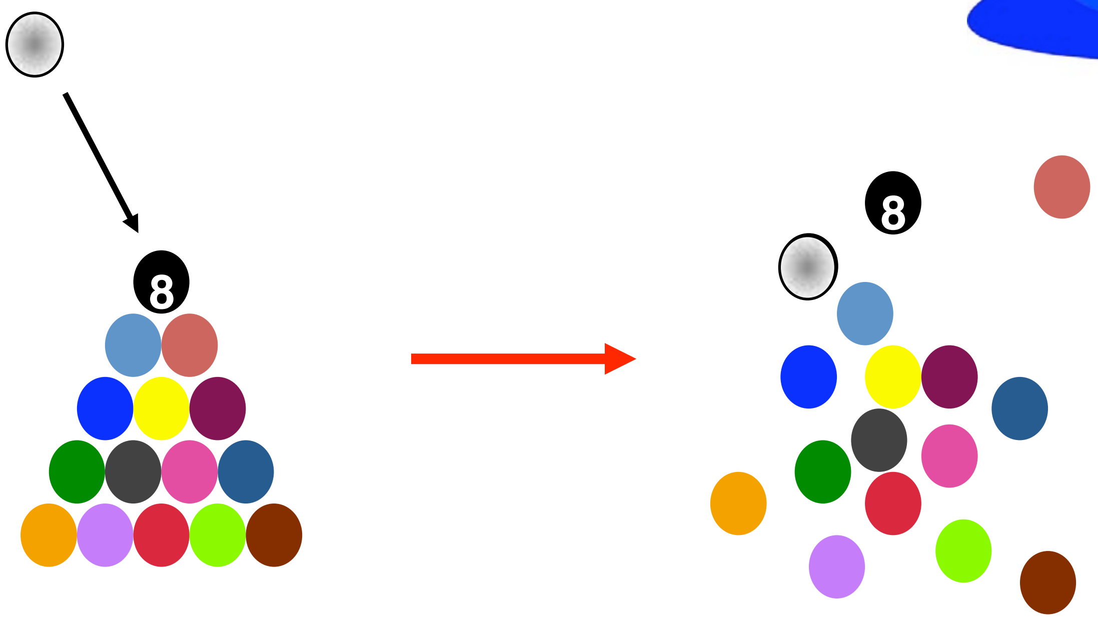
SIMS

secondary ion mass spectrometry

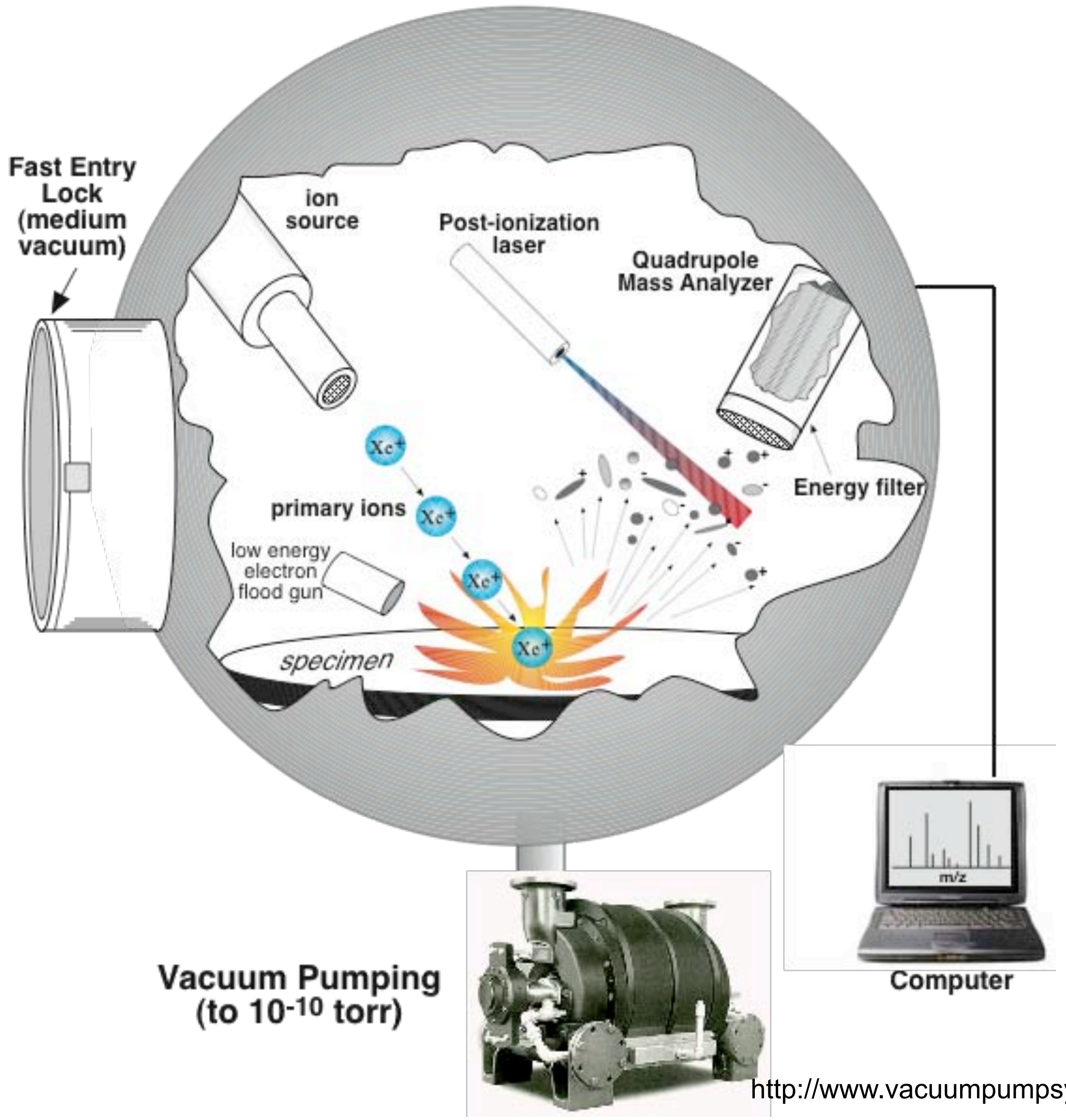


The pool table analogy for SIMS:

Can we reconstruct what was originally there by examining the events that occur and viewing what is left behind?



The Basic SIMS Experiment



The Basic SIMS Experiment:

In a UHV chamber, a beam of accelerated ions (xenon in this case) is impacted into the sample of interest. Positive ions, negative ions, neutrals and free radicals are sputtered from the surface. The masses of the positive and negative ions are measured in a mass analyzer.

Additional neutral species can be ionized by a laser to yield a higher ion count.

http://www.vacuumpumpsystems.com/

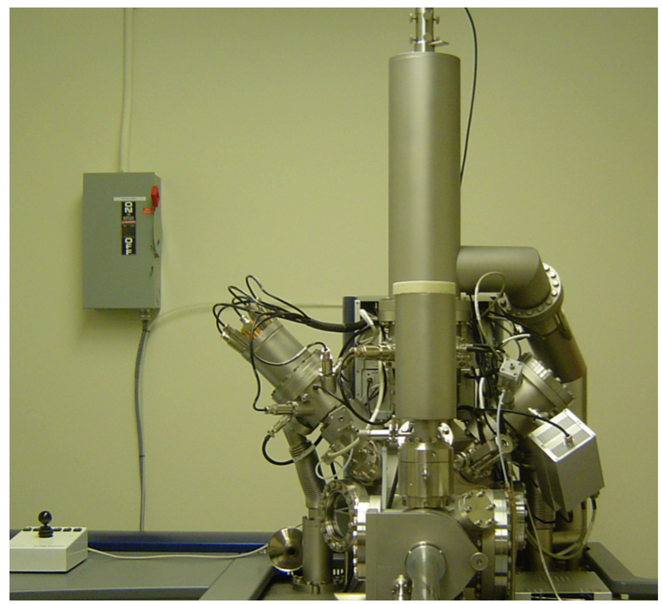
SIMS Evolves

1960's

Prof. Alfred Benninghoven
(Static SIMS, 1969)

1980-2000

Quadrupole
TOF-SIMS
Imaging
Cluster Ions

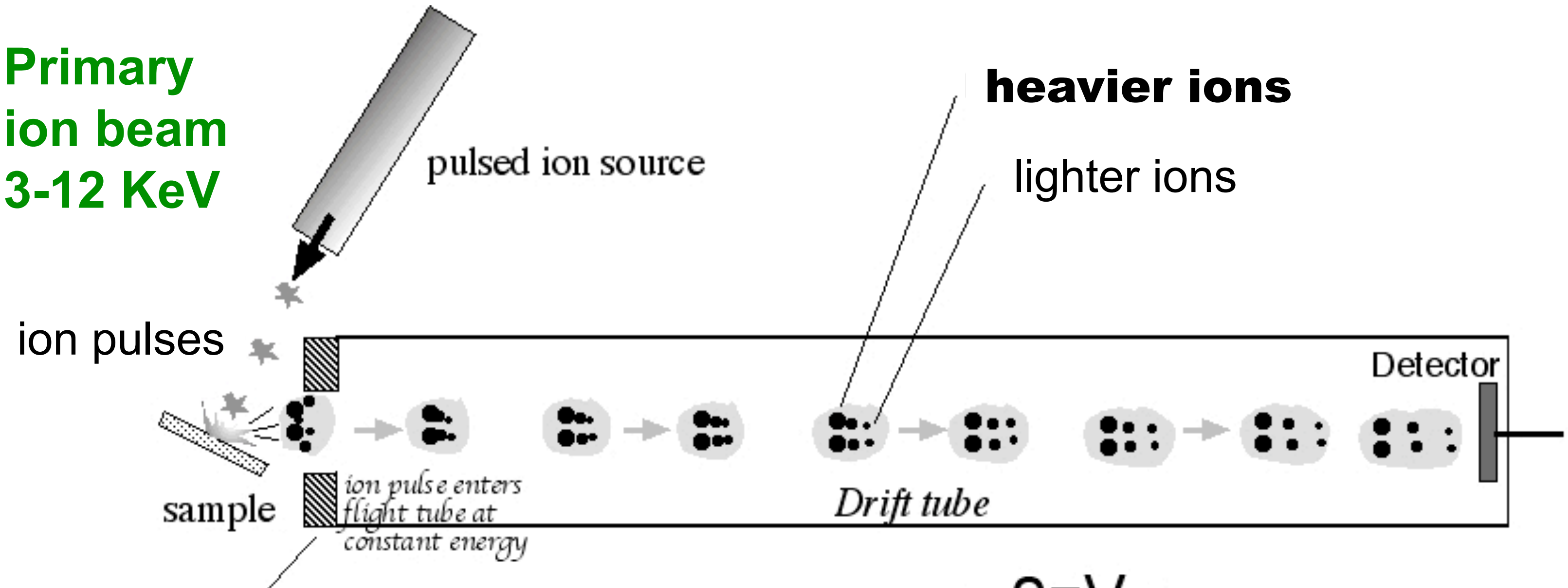


2000+

Information processing
Image processing

SIMS Instrumentation

Time-of-flight (ToF) mass analyzer



High energy ion extraction field

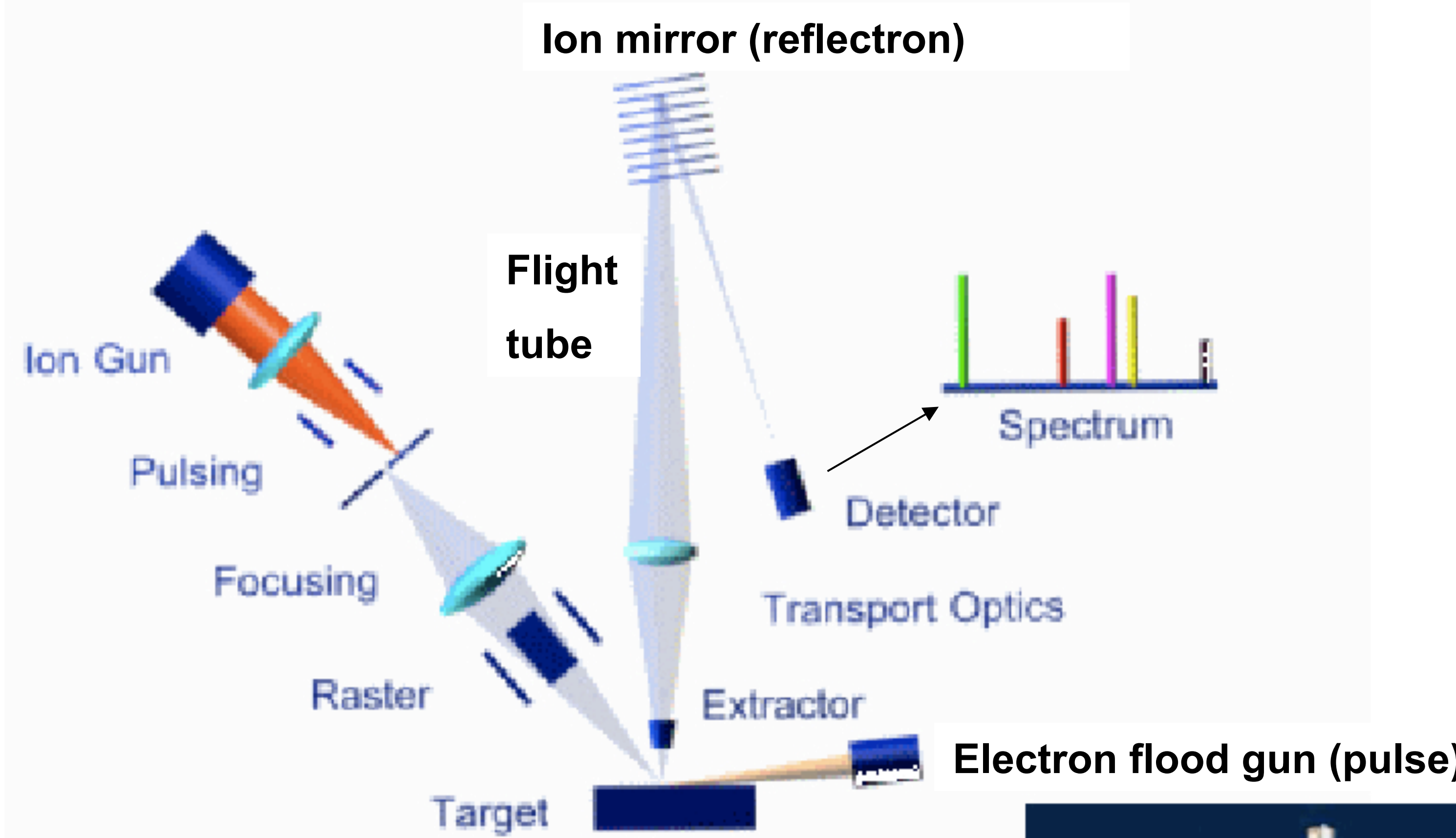
3-20 KeV

μ= velocity $\quad \mu = \left(\frac{2zV}{m} \right)^{0.5}$

$$\text{time-of-flight} = \frac{l}{\mu} = \left(\frac{l^2}{2V}\right)^{0.5} \cdot \left(\frac{m}{z}\right)^{0.5}$$

V = constant energy electric field
m = mass
z = charge
l = distance to the detector

Reflectron Time of Flight Analyzer

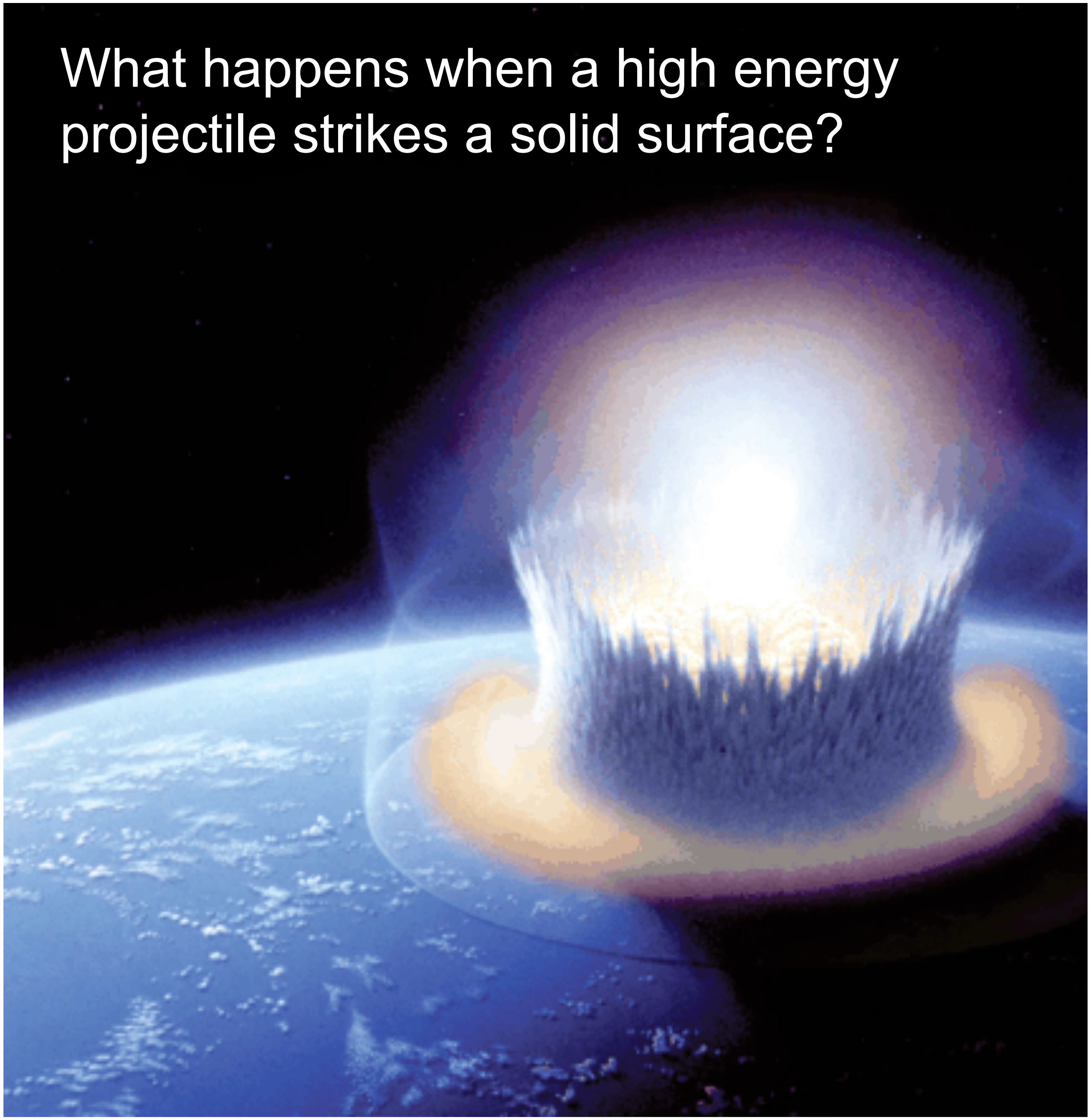


http://www.ion-tof.com/html/time_of_flight.html

Ion-ToF IV
http://www.ion-tof.com

Secondary Ion Mass Spectrometry (SIMS)
Time-of-flight (ToF) SIMS; Static SIMS

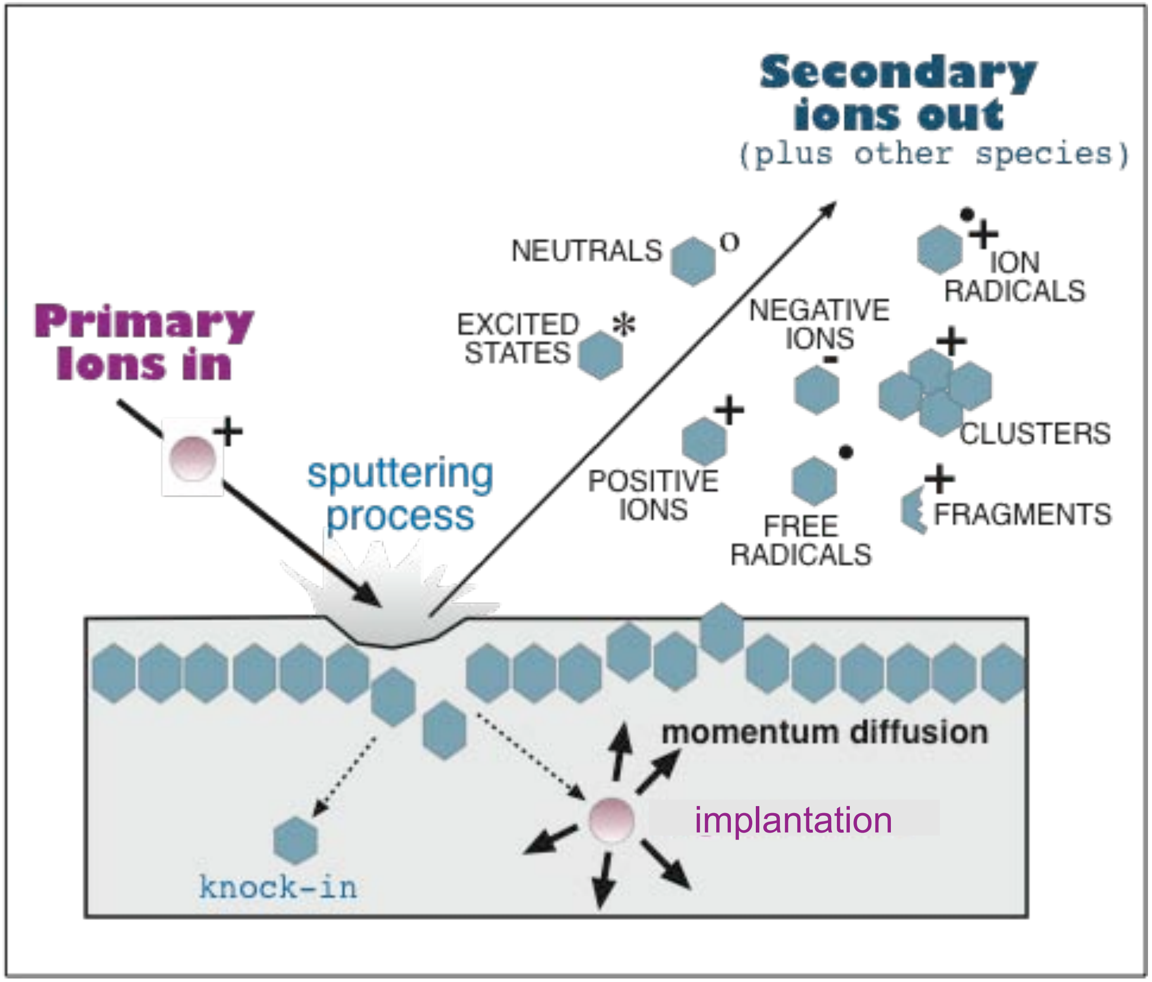
Probably the most information-rich of the modern surface analysis methods



http://www.pnas.org/content/vol101/issue11/cover.shtml

SIMS Surface Mechanisms

In the secondary ion mass spectrometry (SIMS) process, a surface is bombarded under vacuum with energetic ions (primary ions). Some of these ions transfer sufficient momentum to other atoms or molecules in the surface zone to permit their sputtering from the surface into the vacuum phase.



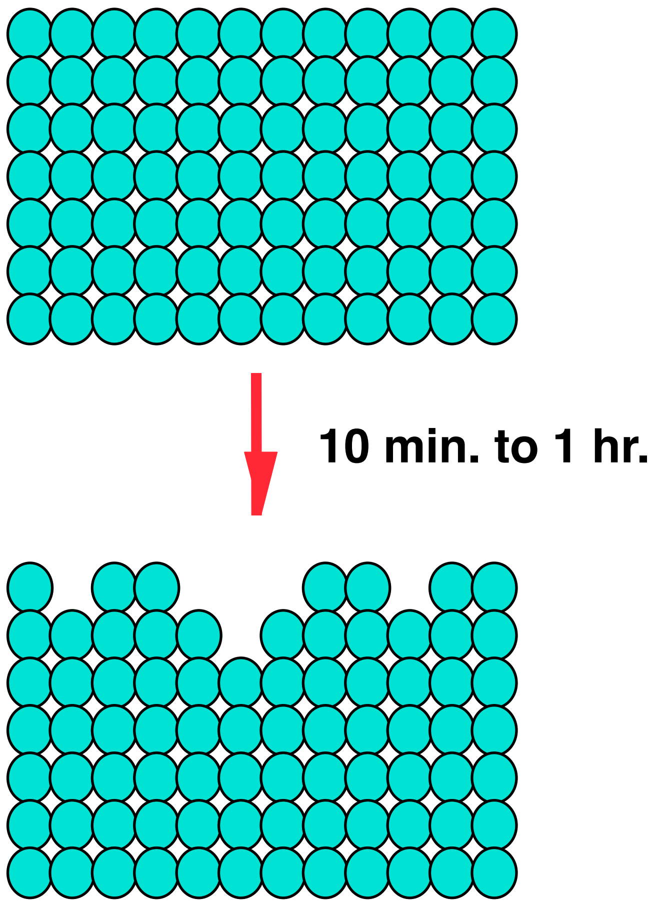
- We measure only ions
- It is surface sensitive because ions emitted from below the first layer or two are neutralized and lose their charge
- Two modes:

  Static SIMS (10^{-9} ampere beam current of 1 cm^2 for typically 10^2-10^3 sec)

  Dynamic SIMS (10^{-6} ampere beam current of 1 cm^2 for typically 20 sec or more)

two SIMS modes

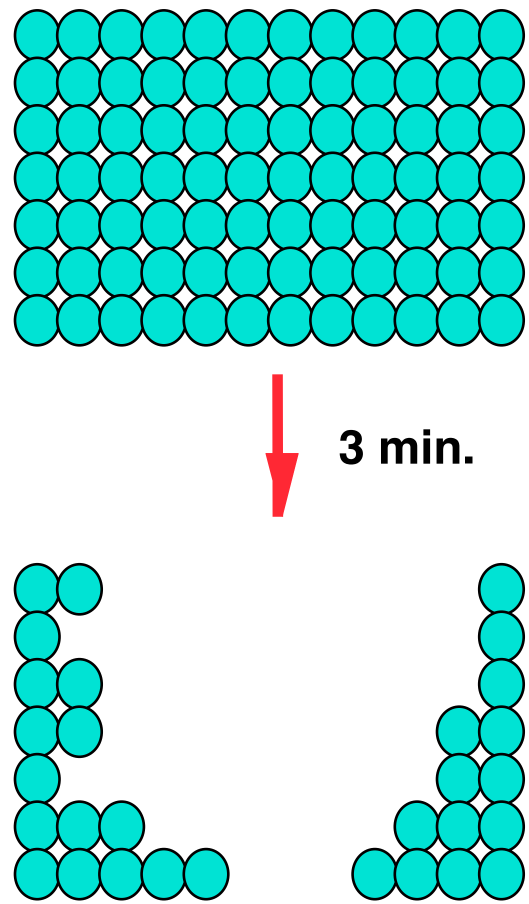
Static SIMS



In an atomic solid, if there are 10^{15} atoms/cm^2

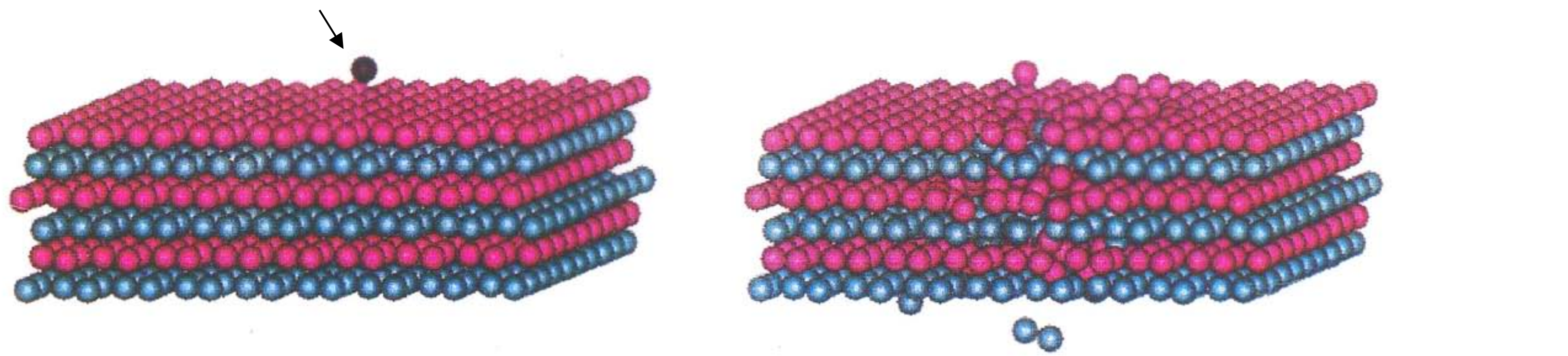
$<10^{14}$ ions/cm^2

Dynamic SIMS

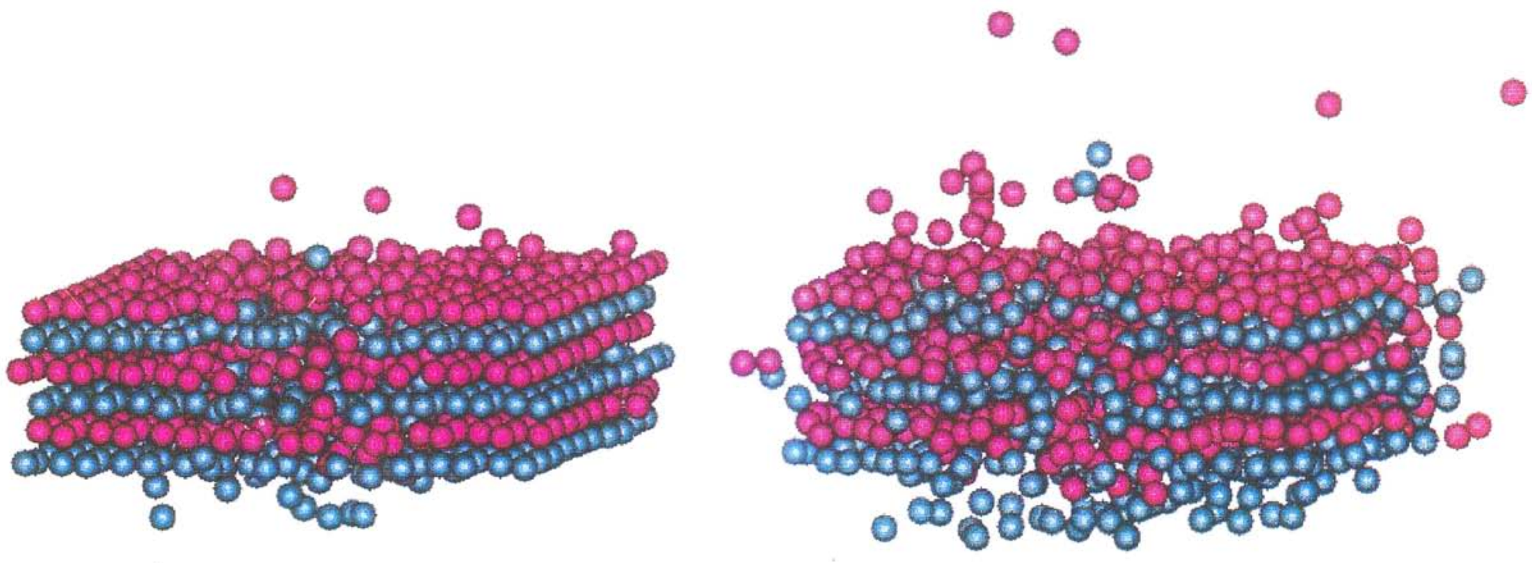


Sputtering rates of 10nm/min are not uncommon

Ion-Solid Interactions Modeled



Simulations at the femtosecond time scale



Images courtesy of Barbara Garrison and Nicholas Winograd, Penn State

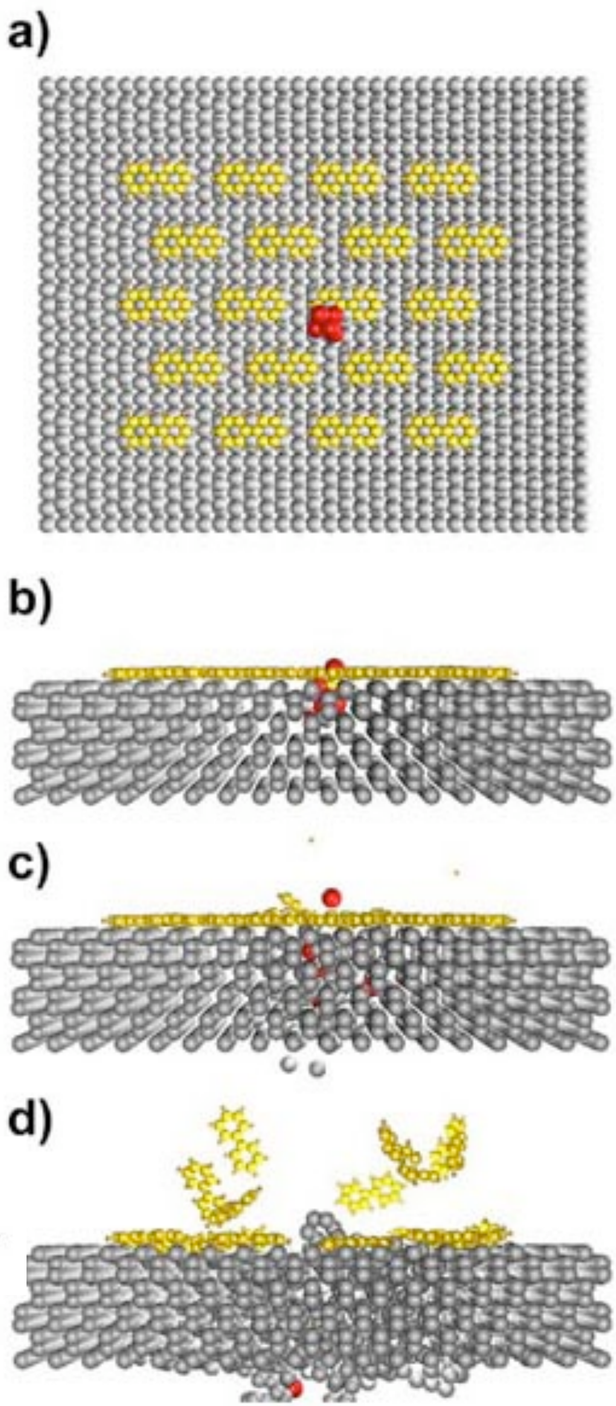


Figure 1 in:
Molecule Liftoff from Surfaces,
B. J. Garrison, A. Delcorte and K. D. Krantzman,
Accts. Chem. Res. 33, 69-77 (2000).

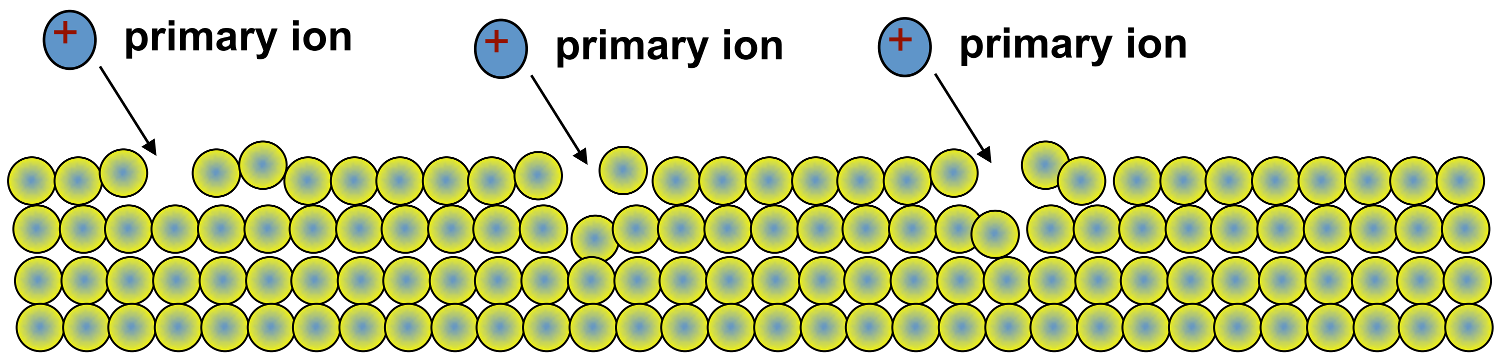
Some of the events occurring:

- **Ejection**
- **Molecular damage**
- **Scrambling**
- **implantation**

The Static SIMS Criterion

For semiconductors, there are approximately 10^{15} molecules/cm^2

You do not want to damage more than 10^{14} (10%).



The consequence of exceeding the static SIMS limit is increased atomic ions and decreased, information-rich moleculars -- interpreted as evidence of extensive long-range damage to the polymer

Factors important in fulfilling the static SIMS criterion:

- primary ion flux
- area analyzed
- time of bombardment
- rastered or diffuse beam
- sample density

Impact craters are well spaced apart

In static SIMS we try to not sample already damaged areas.

Two Primary Ion Sources:

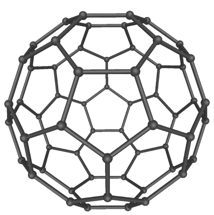
Bi_3^+:

Good mass resolution

Good spatial resolution

Sample damage

Spectroscopy



C_{60}^+:

Poor lateral resolution

Poor mass resolution

Minimal sample damage

Etching

Other primary ions: Cs^+, Au^+, Au_3^+

Special Advantages of SIMS

High mass resolution (easily >0.001AMU)

High analytical sensitivity (very sensitive)

High information content

High spatial resolution (x,y, image) (15nm)

Shallow or deep sampling depth

Information from a static SIMS experiment

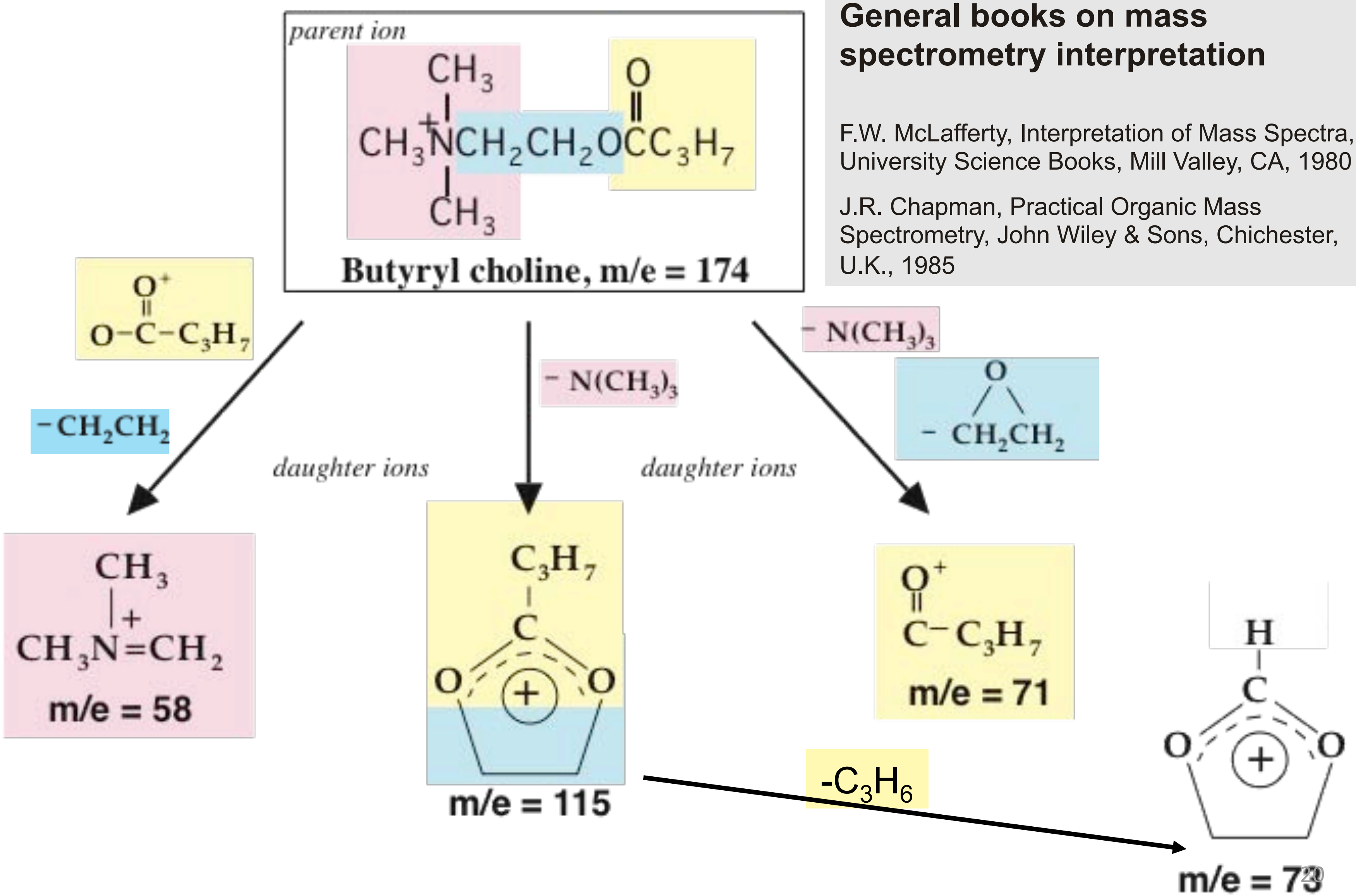
in the uppermost 10-15Å:

1. Atomics (what element is present?) (e.g., $Na^{+} = 23$)
2. Parent ions
3. Molecular fragments for structural determination
4. Molecular fragment/atomic fragment ratio
5. Molecular fragment ratios
   - mobility
   - conformation
   - molecular orientation
   - assembly orientation
   - molecular interactions
   - crystallinity
   - quantification
   - sample damage

   "coded information"
6. Information on surface localization and depth

Organics spectral interpretation in SIMS

The principles of SIMS spectral interpretation are closely related to those used for mass spectrometry



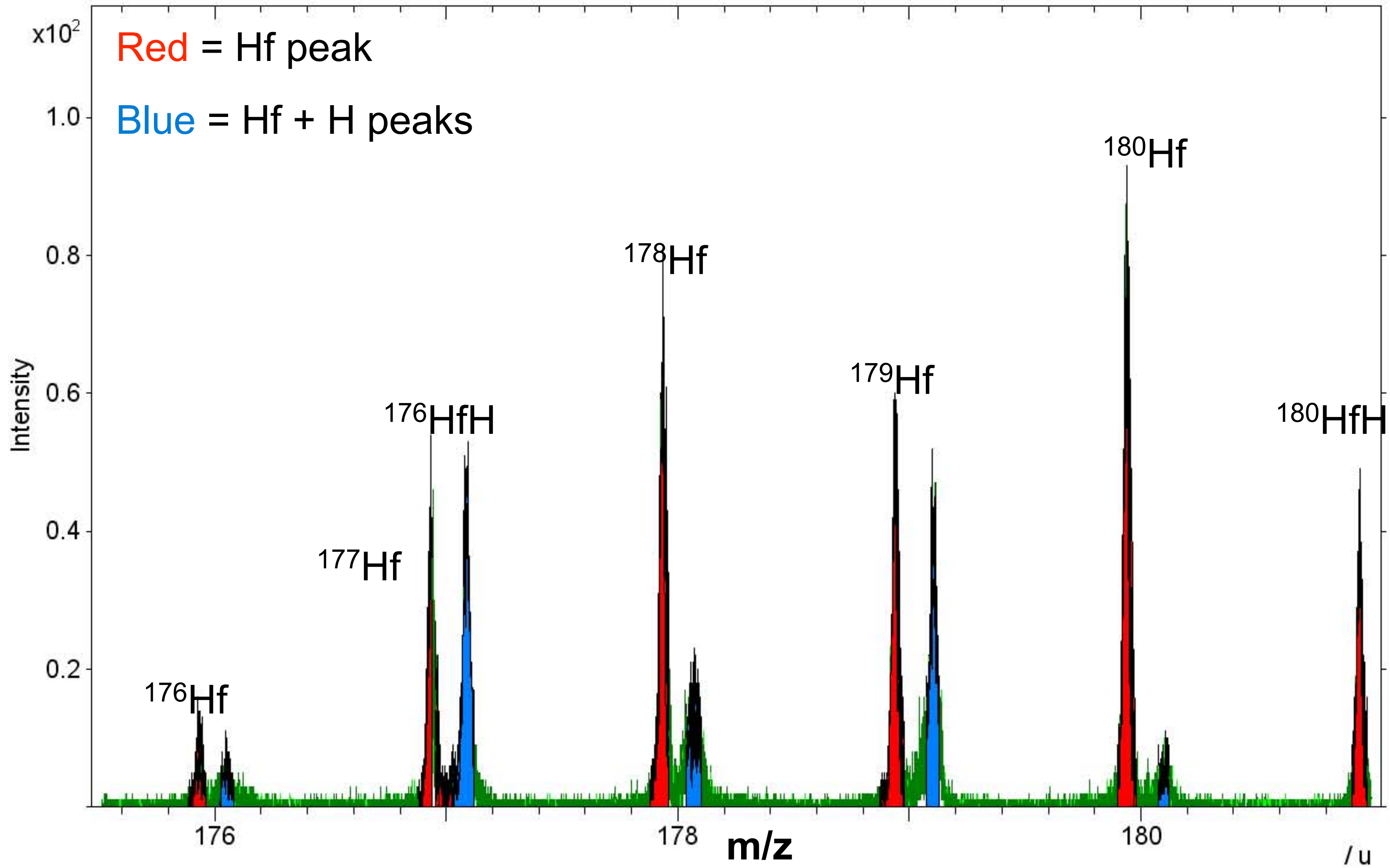
General books on mass spectrometry interpretation

F.W. McLafferty, Interpretation of Mass Spectra, University Science Books, Mill Valley, CA, 1980

J.R. Chapman, Practical Organic Mass Spectrometry, John Wiley & Sons, Chichester, U.K., 1985

Inorganics are easier for interpretation, but we need to look at isotopes

HfO_2 Mesh Particles Positive Spectra (Hf Isotopes)

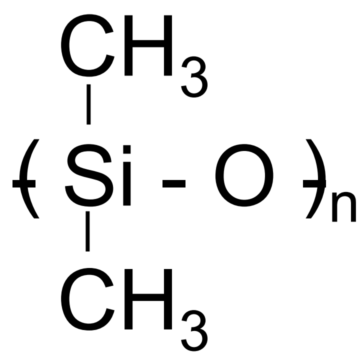


Commonly Observed SIMS Fragments

Positive Ion m/z		Negative Ion m/z	
1	H^+	12	C^-
12	C^+	13	CH^-
13	CH^+	14	CH_2^-
14	CH_2^+ or N^+	19	F^-
15	CH_3^+	24	C_2^-
18	H_2O^+ or NH_4^+	25	C_2H^-
19	H_3O^+ or F^+	31	CH_3O^-
23	Na^+	35	Cl^-
26	$C_2H_2^+$ or CN^+	55	$CH_2{=}CH{=}CO^-$
27	$C_2H_3^+$ or CHN^+	69	CF_3^-
28	$C_2H_4^+$ or CO^+ or Si^+	80	SO_3^-
29	$C_2H_5^+$ or CHO^+	85	$C_4H_5O_2^-$
31	CH_3O^+	97	HSO_4^-
41	$C_3H_5^+$		
43	$C_3H_7^+$ or $C_2H_3O^+$		
57	$C_4H_9^+$		
71	$C_5H_{11}^+$		
73	$C_2H_5OSi^+$		
91	$C_7H_7^+$ (aromatic)		

[green] = hydrocarbon series

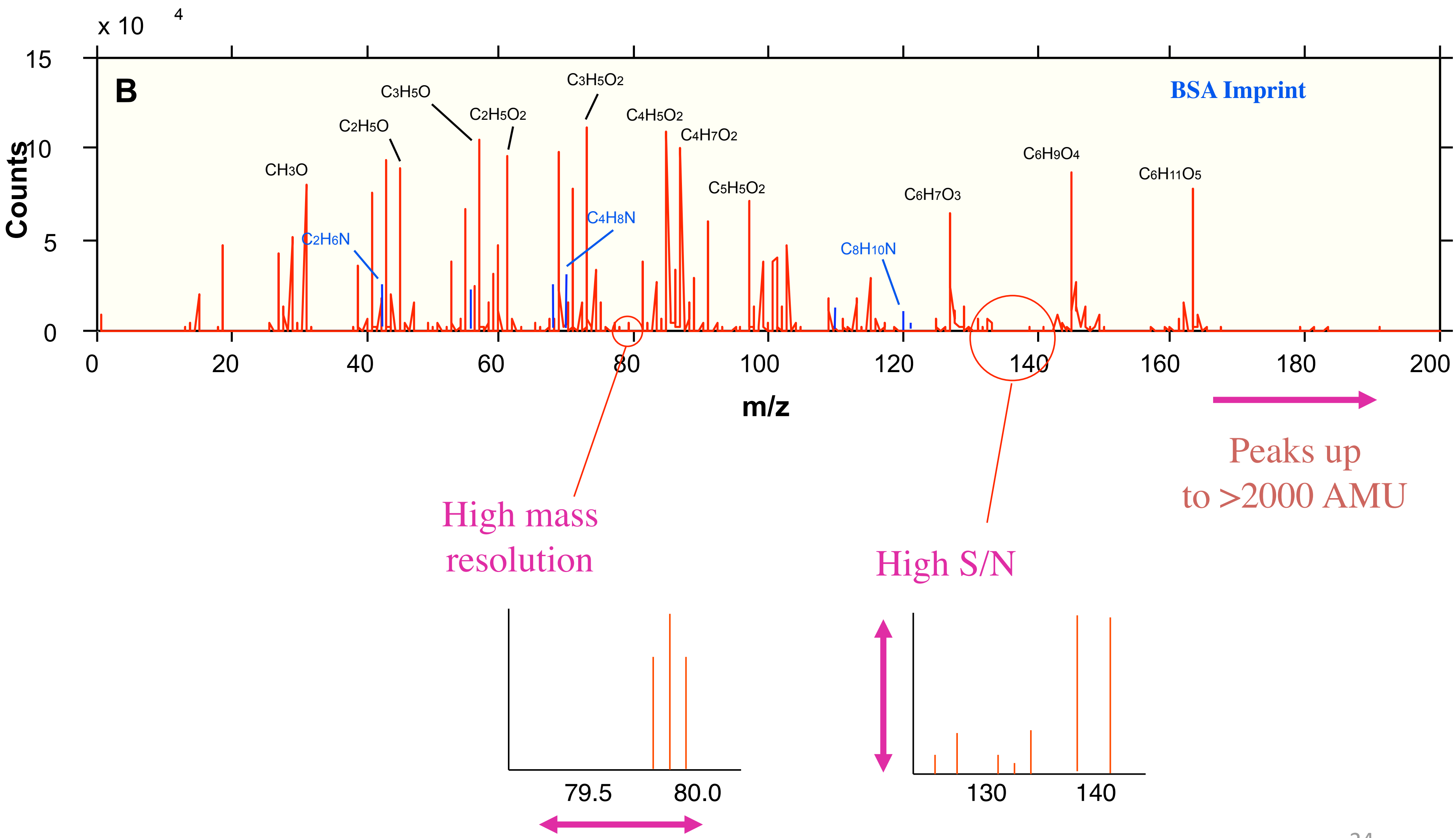
Characteristic Poly(dimethyl siloxane)(PDMS) SIMS Peaks



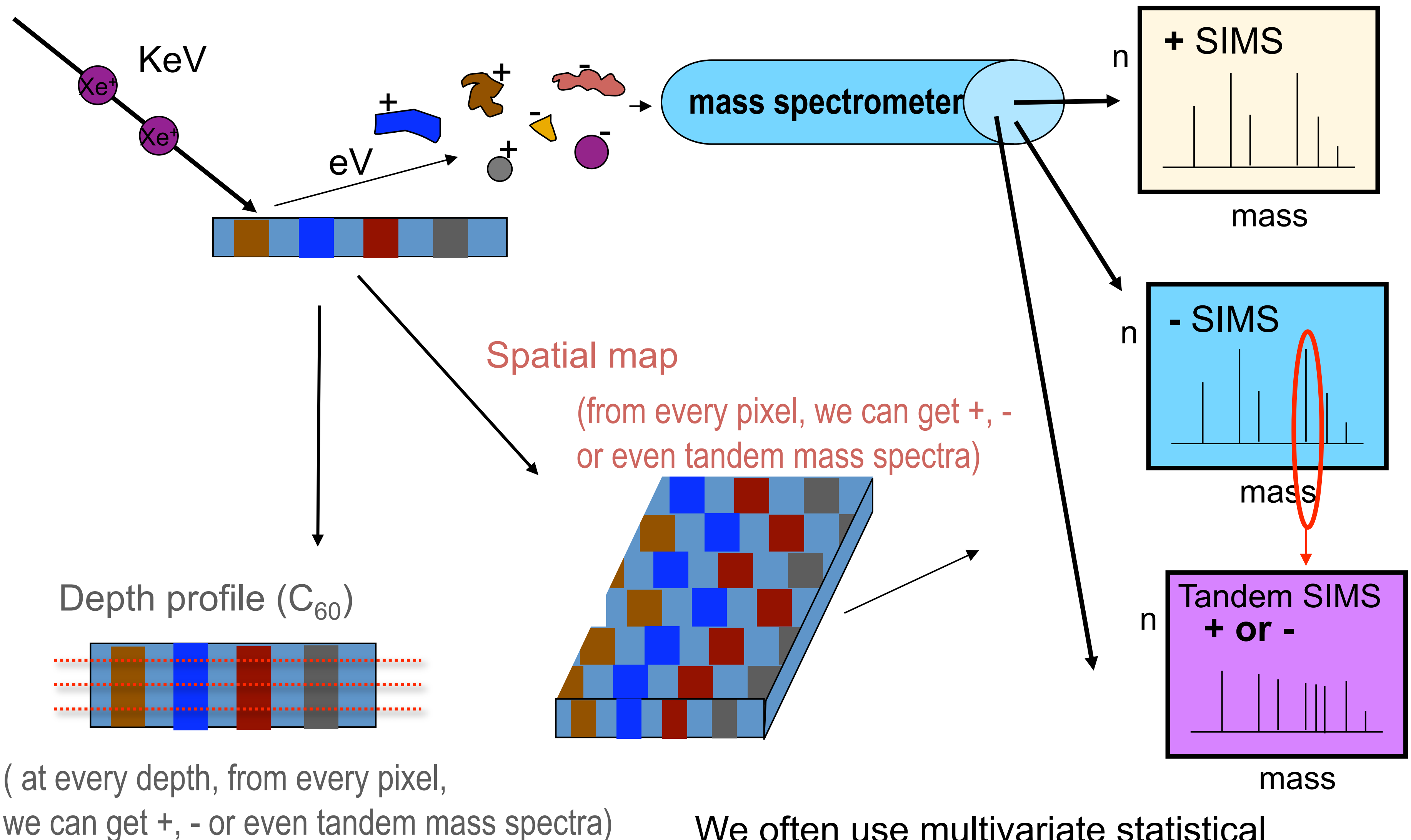
Molecular fragment	Nominal mass (Da)	Exact mass (Da)
$SiCH_3^+$	43	43.000403
$Si(CH_3)_3^+$	73	73.047353
$(CH_3)_3Si\text{-}O\text{-}Si(CH_3)_2^+$	147	147.06615
$Si_3C_5H_{15}O_3^+$	207	207.04460

Organosilicones are extremely common contaminants -- the characteristic positive ion peak signature of 43, 73, 147, 207 usually indicates silicones at the surface

SIMS spectra are information-rich



Huge amounts of information from SIMS



We often use multivariate statistical methods to deal with this "data overload"

We can generate huge amounts of data!

How can we convert data into useful information?

Multivariate analysis methods, sometimes called “chemometrics”

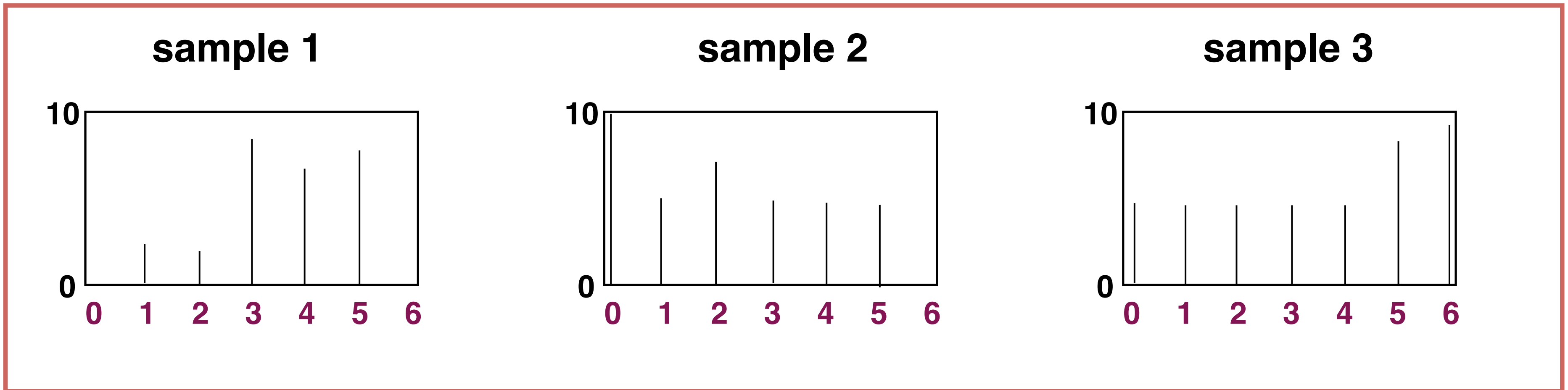
Allows us to identify trends that might be hidden in the data

Makes use of large amounts of data

Uses all the data, not just that which we think is important

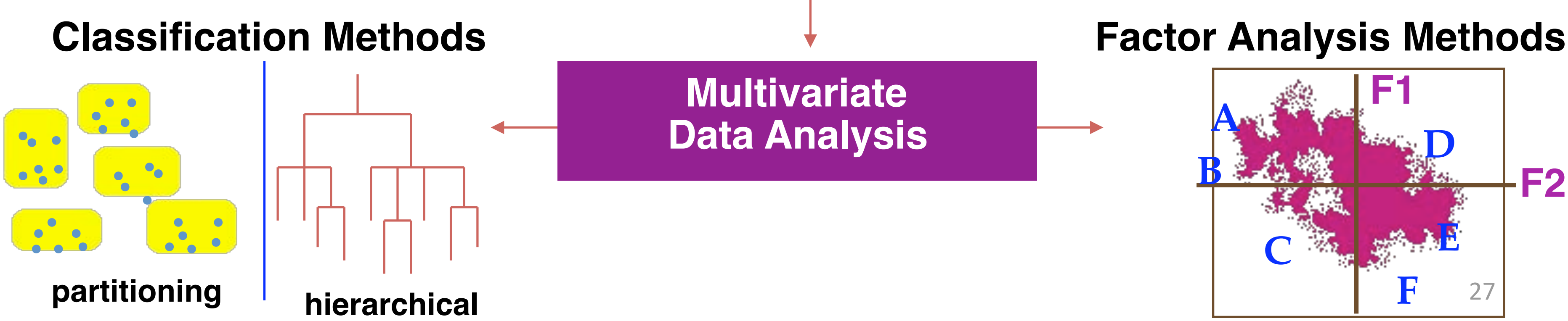
A hypothesis generator!

Addressing Large Data Sets

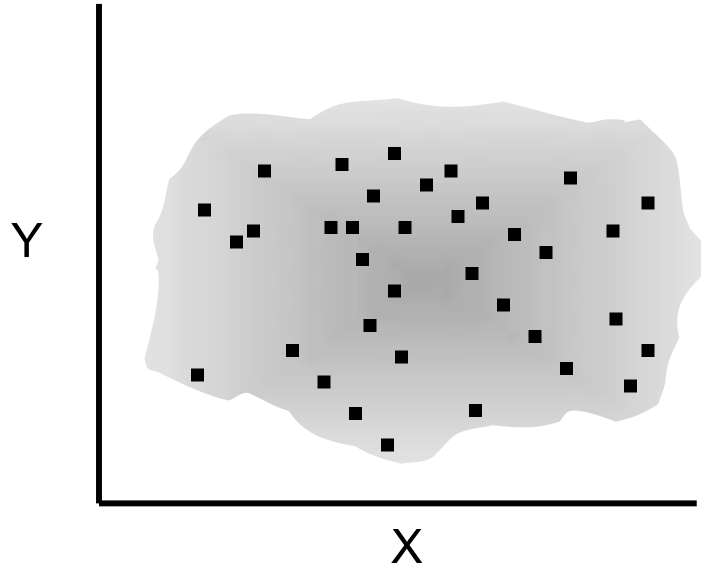


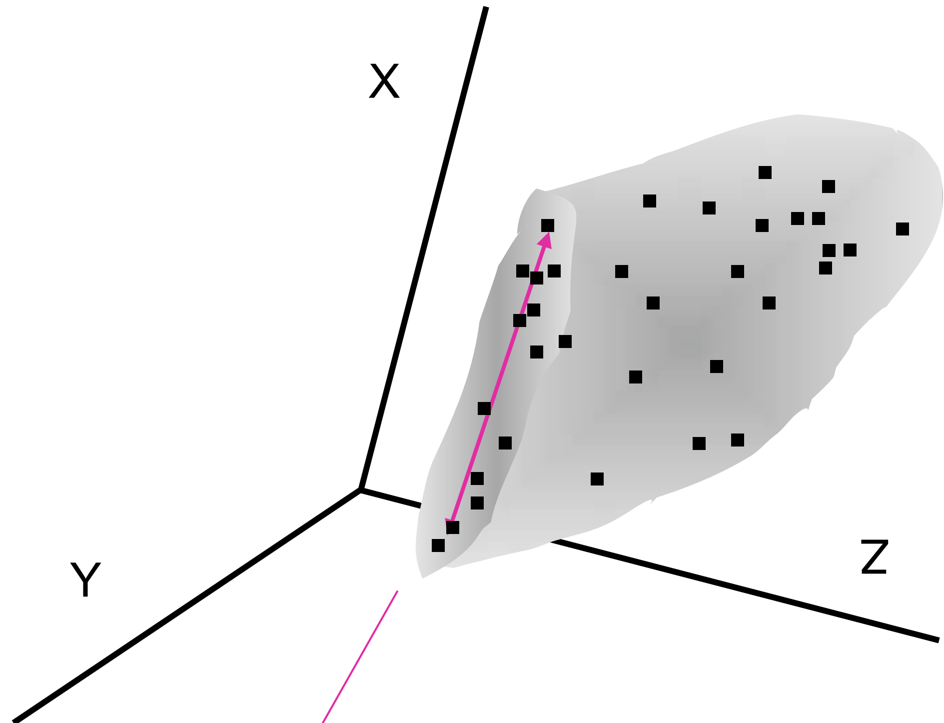
Data Table

	0	1	2	3	4	5	6
sample 1	0	3	2	8	6	7	0
sample 2	10	5	7	5	5	5	0
sample 3	4	4	4	4	4	7	9



No clear relationship between points





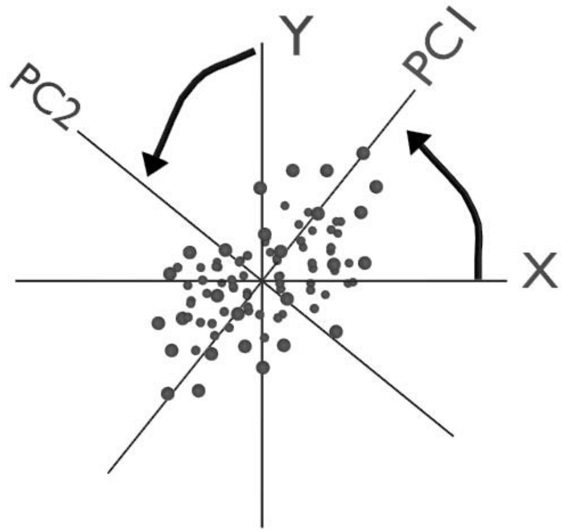
A high correlation between points

We can visualize 2D and 3D, but we "lose it" at 4D – what about 1000D?

Multivariate Analysis – the are many methods

PCA

Principal Components Analysis



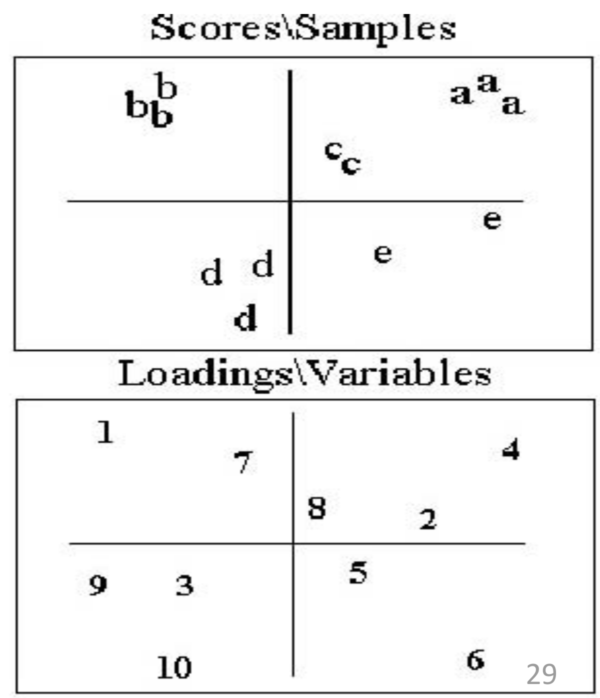
matrix rotation

- ***PC1***: **direction of the greatest variance**

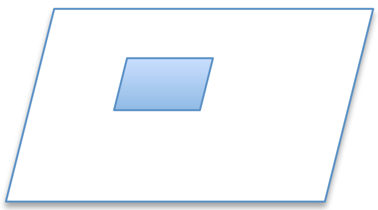
- ***PC2***: **orthogonal axis defining the next greatest of variance**

- ***Scores***: **projection of the samples onto the new PC axes**

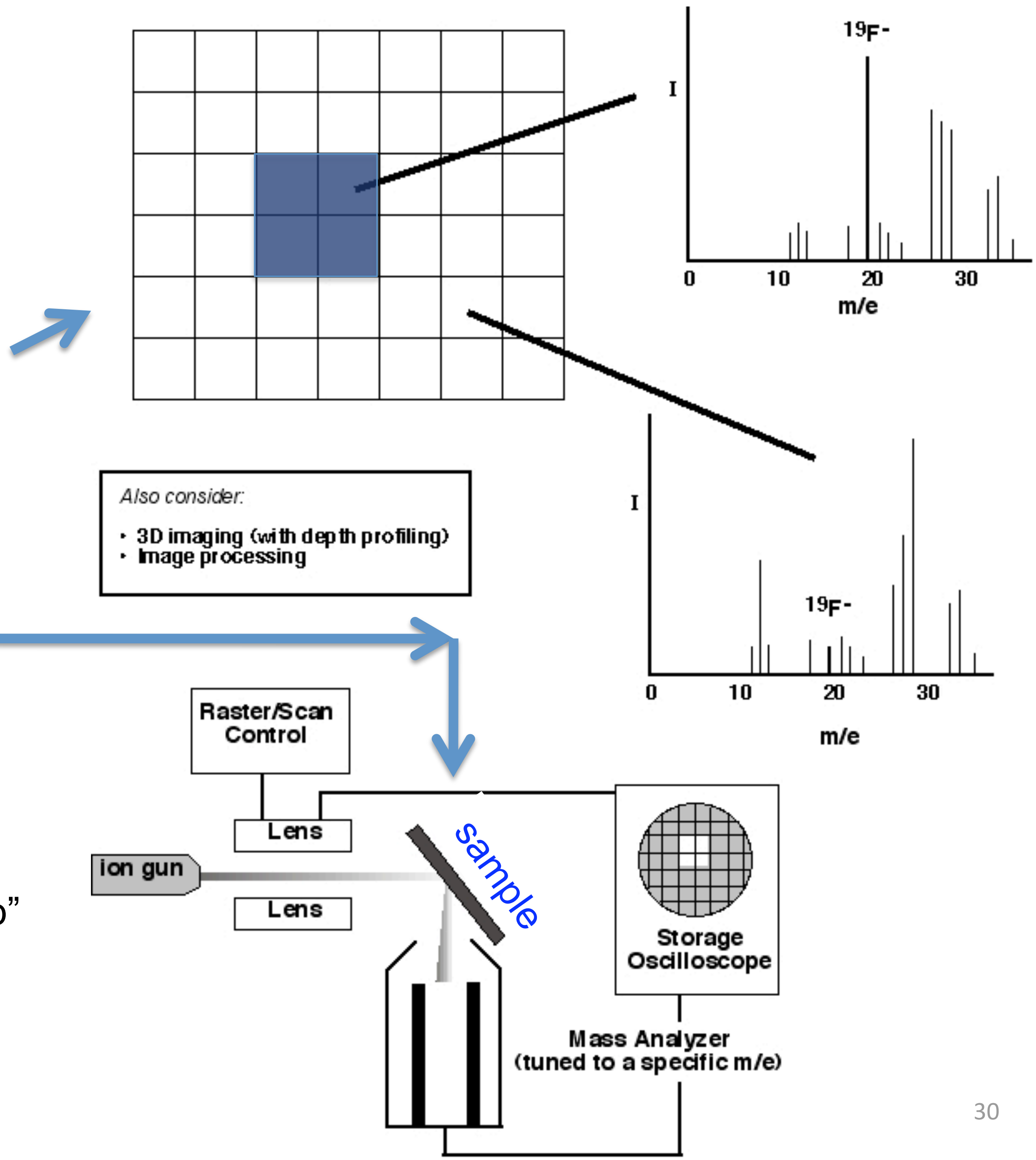
- ***Loadings***: **direction cosines of the matrix rotation**



SIMS Imaging

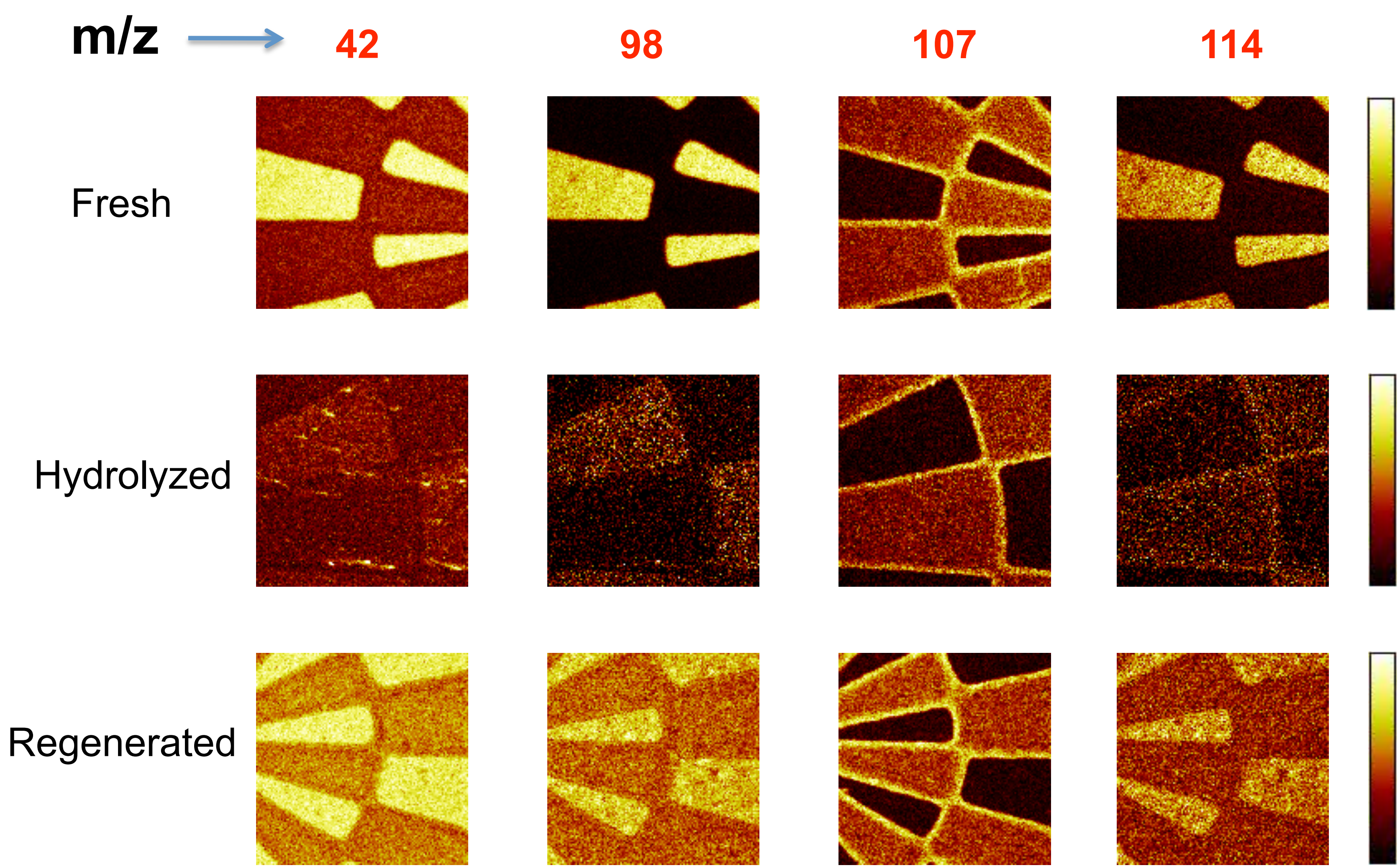


A fluorinated area on our surface (blue)



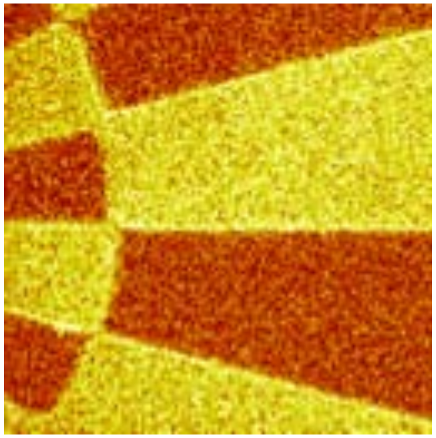
Raster the focused ion beam and “map” the signal intensity for mass=19 (negative ion)

Negative ToF-SIMS images of patterned slides



500 µm x 500 µm images

Images by Prof. David Castner, University of Washington



Characteristics of Chemical State Imaging

Chemical State Imaging <u>facilitates effective communication</u> of information about spatial distributions of chemical information in a system

but the image contains massive data content…

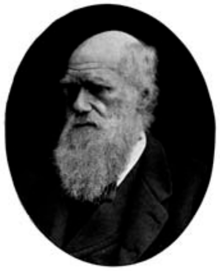
Data are not information!

Contemporary data manipulation routines are the route to extract the important information from the data

There are critical problems that might be solved with SIMS imaging

Challenges in SIMS Imaging

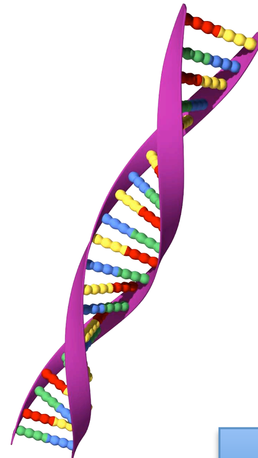
- Hard to distinguish topography and chemistry
- Compound identification requires several ions
- Low Signal-to-Noise Ratio
  - Poor image contrast
  - Poor resolution of regions
- Huge Data Sets
- 3D images using new cluster ions probes greatly magnify the amount of data.

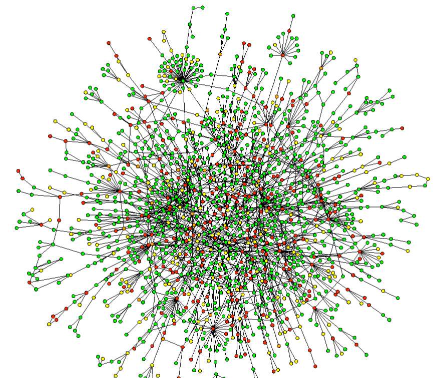


Darwin’s Birth: Feb. 12, 1809

Biology Evolves

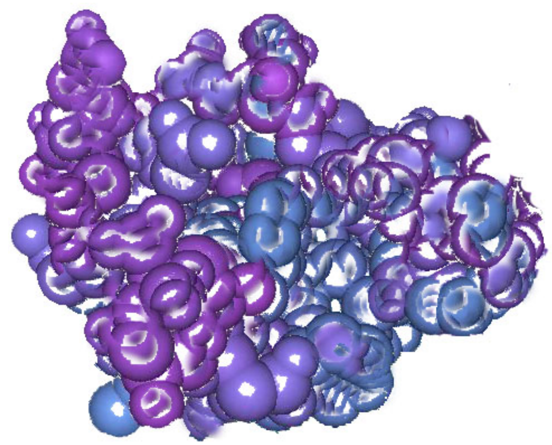
1700-1930 | **1930-1990** | **1990+**





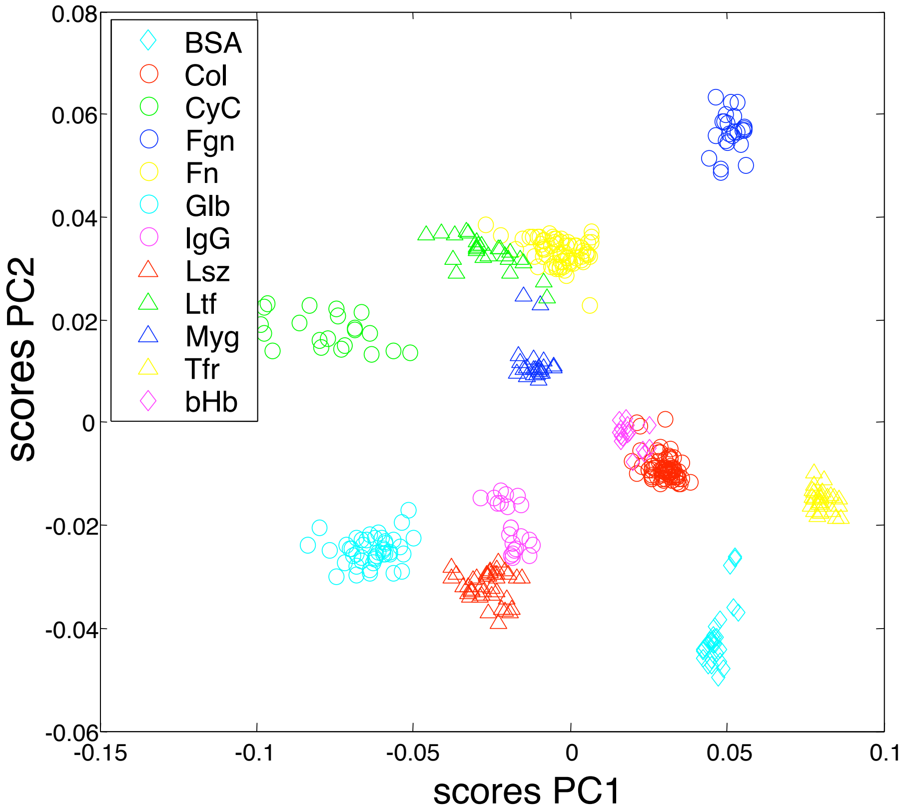
Protein map, Rick Durrett

Cataloging birds & flowers → **Molecular biology** → **Information science**

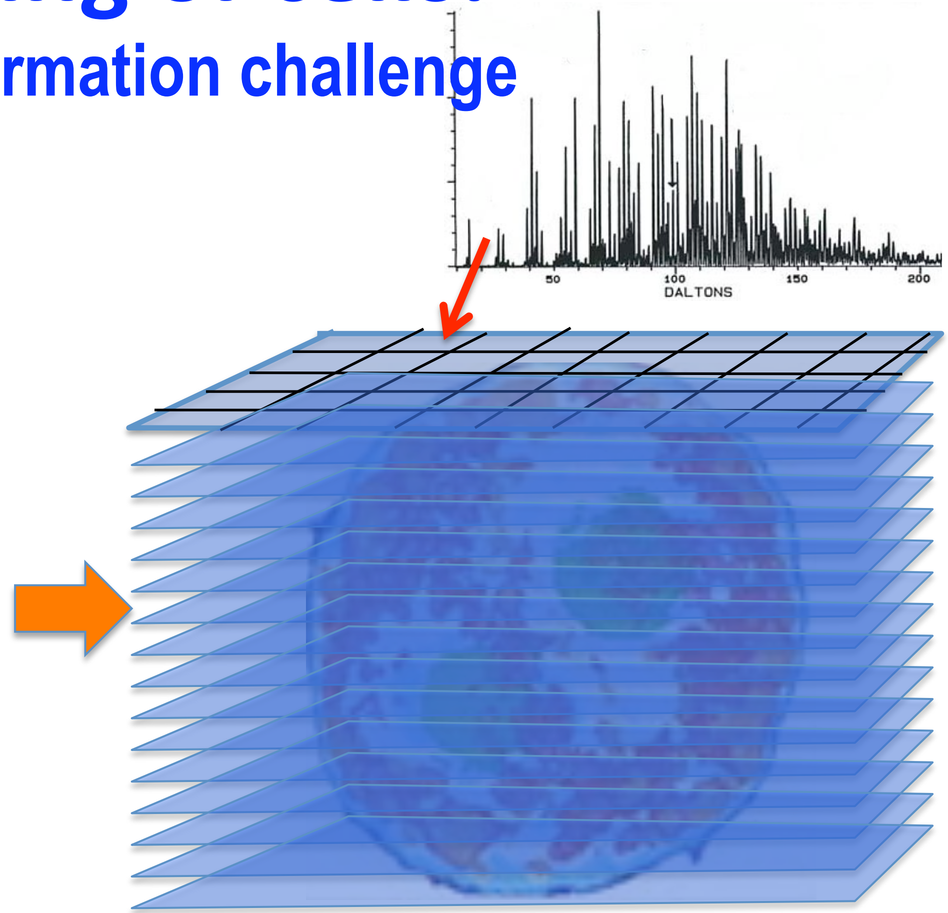


SIMS imaging of cells:

The massive information challenge



PCA Studies from Castner, et al have shown that from the protein fragmentation pattern many proteins can be identified



An MIT 3D visualization of a cell

Other issues:

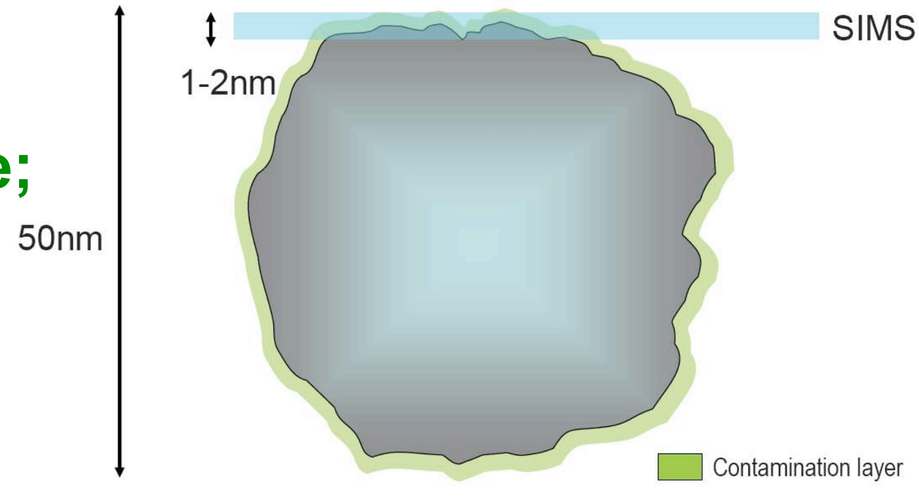
- **cell fixation and dehydration**
- **sample damage**

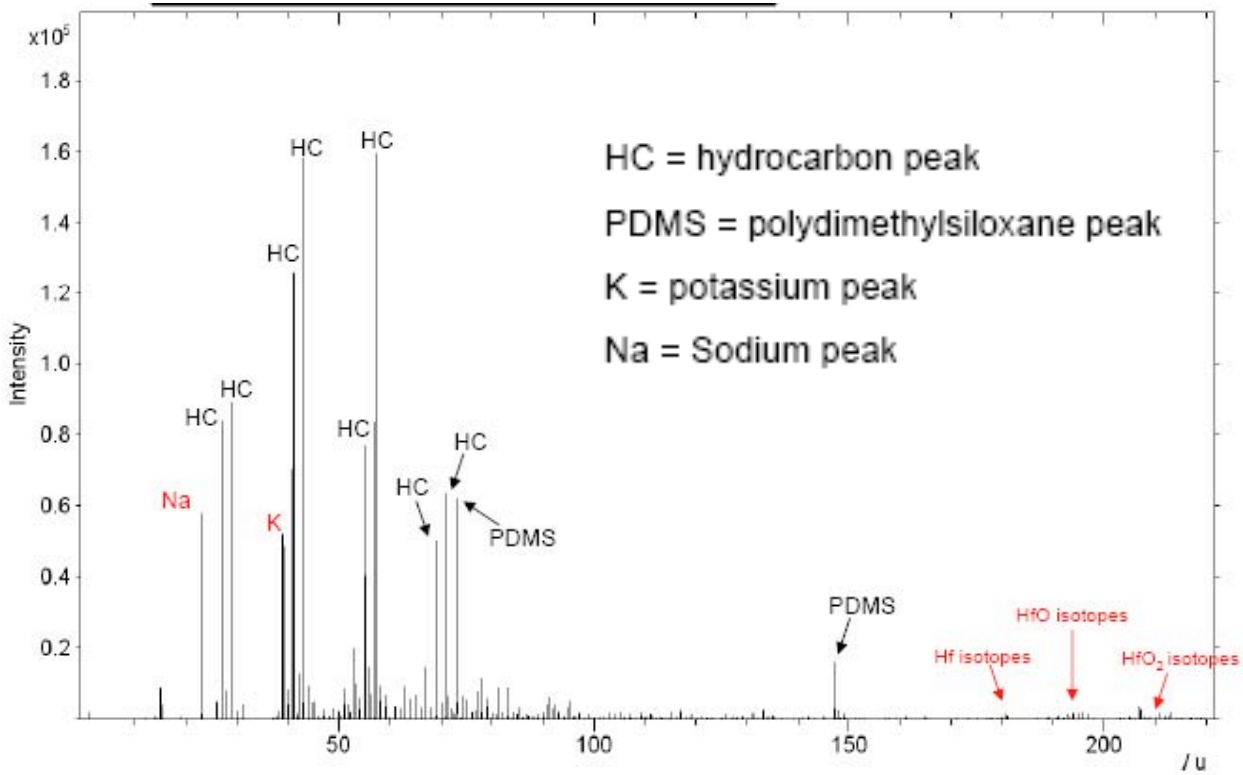
Toxicology/Safety Concerns About Nanoparticles

Hypothesis: It's not the "nano-size" that leads to toxic properties. Rather, nanoparticles have high surface areas and high surface energies and thus will adsorb chemical from their manufacturing environments and take those chemicals into cells –
i.e., it's the junk on the surface that's toxic, not the particle.

SIMS OF NANOPARTICLES

SIMS looks at a 1nm surface zone;
SIMS is hugely sensitive!





Nanoparticle Impurities

Negative Spectra Impurities

mass	ID	Ref Micron	NP1 20 nm	NP2 1-2 nm
13	CH			X
16	O	X	X	X
17	OH	X	X	X
24	C_2			X
25	C_2H			X
35	Cl	X		
37	C_3H	X		
63	COCl		X	
79	^{79}Br		X	
81	^{81}Br		X	
221	AuS		X	

- "X" represents presence of molecule
- Molecules representative of influential loadings using PCA for negative spectra vs. tape

Positive Spectra Impurities

mass	ID	Ref Micron	NP1 20 nm	NP2 1-2 nm
27	C_2H_3	X	X	X
29	C_2H_5	X	X	X
39	C_3H_3	X	X	X
41	C_3H_5	X	X	X
43	C_2H_3O	X	X	X
45	C_2H_5O	X		X
55	C_4H_7	X	X	X
57	C_4H_9	X	X	X
77	C_2H_9OSi (?)	X		X
91	C_7H_7			X
115	C_9H_7			X
118	$C_5H_{12}NO_2$			X
135	$C_7H_9N_3$			X
161	$C_{11}H_{13}O$			X

Surface Characterization Summary/ Preliminary Conclusions

SIMS Analysis

Impurity	Ref Micro	NP1 20 nm	NP2 1-2 nm
Light Organics (<100 MW)	+	+	+
Heavy Organics (>100 MW)			+
Silicon	+		+
Chlorine	+	+	
Bromine		+	
Rare Earth Metals	+	+	+

- The nature of the impurities varied depending on the source of the NPs