UNLIMITED SCOPE

Observations Regarding Automated SEM and SIMS Analysis of Minerals

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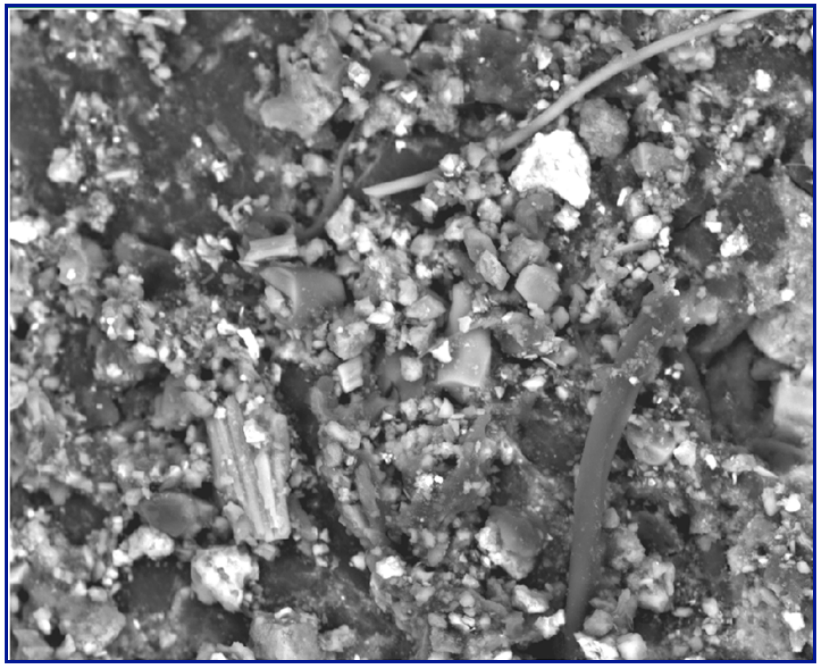
Forensic Geoscience

- A field of inquiry that utilizes techniques developed in the geosciences (geology, geomorphology, botany, biology, and statistics) for application to civil and criminal judicial proceedings.

The Two Classic Questions:

- What is it?
- Is it important??

Premise



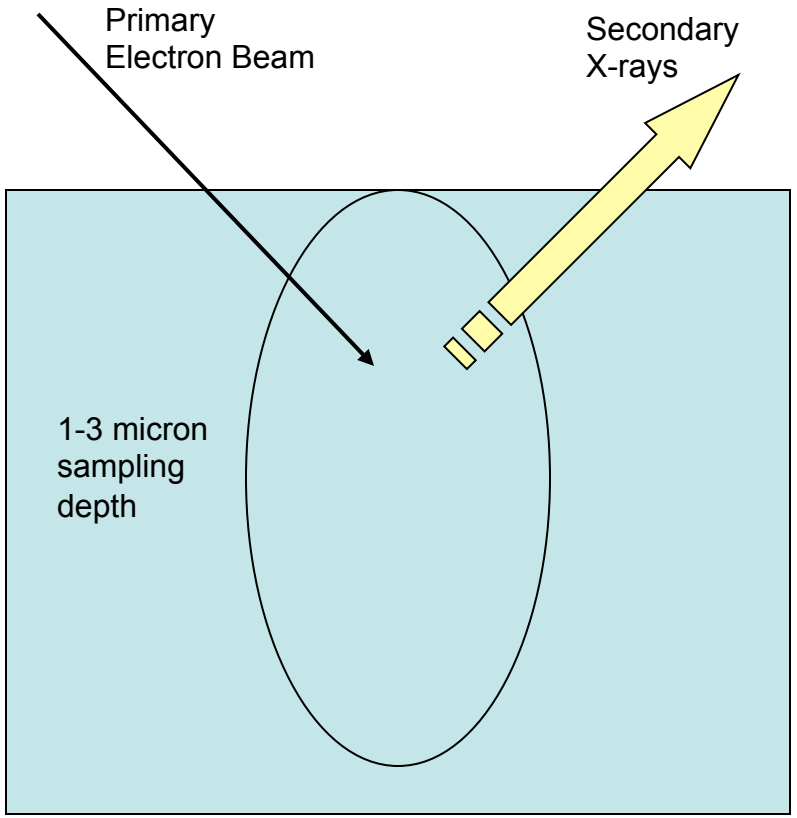
Soils/sediments are comprised not only of naturally occurring rocks and minerals, but also of biological and anthropogenic components such as

- Glass
- Paint fragments
- Metallic particles
- Building materials
- Hairs, fibers
- Floura, fauna

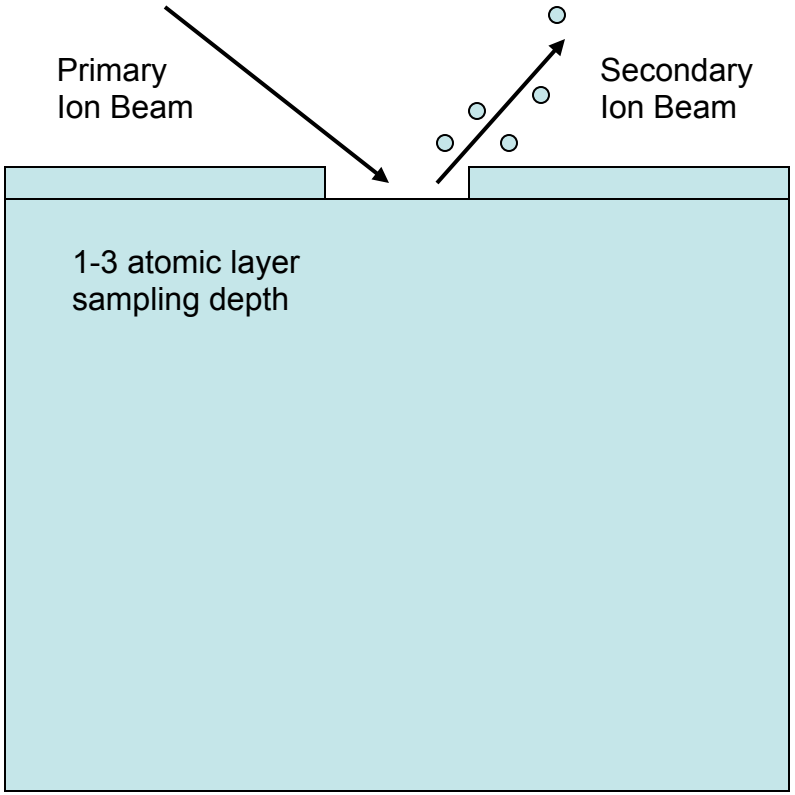
Thus a sample of soil/sediment recovered from clothing, a vehicle or a crime scene has a large, almost unlimited number of characteristics which make it unique.

Aspex and SIMS Physical Phenomena

SEM



SIMS



Case Study of Soil Found on a Shoe

Associative data collected on the soil data sheets

Specimen	Soil color	Minerals present	Minerals (%)	Ions present	Morphology
KS1	5Y 7/2	Quartz	88	Na^+, Cl^-	Rounded
		Hornblende	2		
		Garnet	5		
		Hematite	Trace[a]		
		Magnetite	1		
		Limonite	Trace		
		Tourmaline	1		
		Shell parts	2		
QS1	5Y 7/2	Quartz	88	Na^+, Cl^-	Rounded
		Hornblende	2		
		Garnet	5		
		Hematite	Trace[a]		
		Magnetite	1		
		Limonite	Trace		
		Tourmaline	1		
		Shell parts	2		

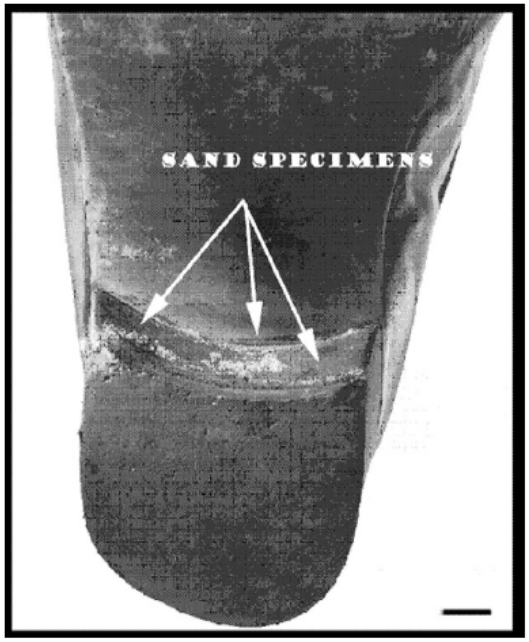


Fig. 1. Depicted is the right shoe with the questioned sand specimen QS1 adhering to heel as indicated by the arrows. The black bar is equal to 12 mm.

Guidelines for optical microscopy
Analysis suggest 250-300 particles.

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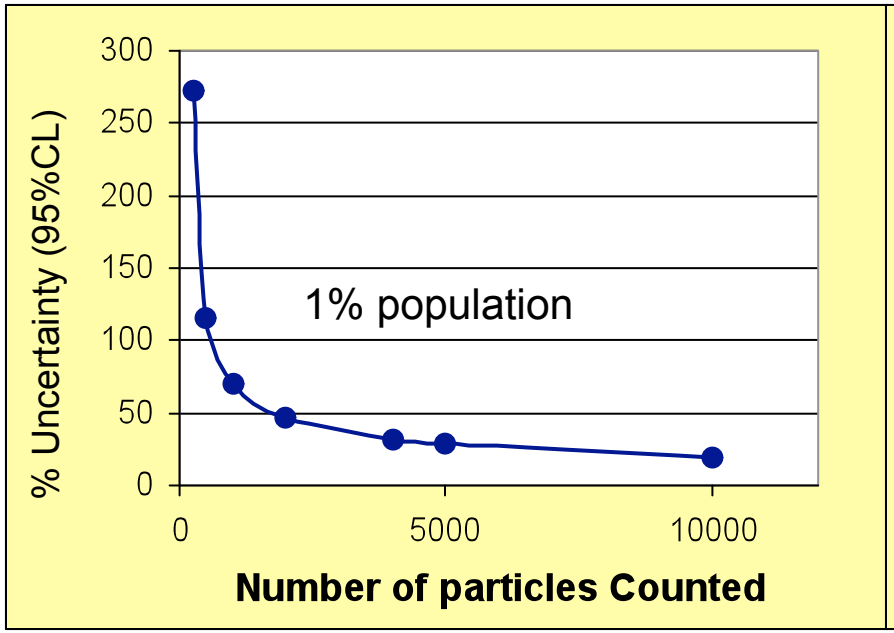
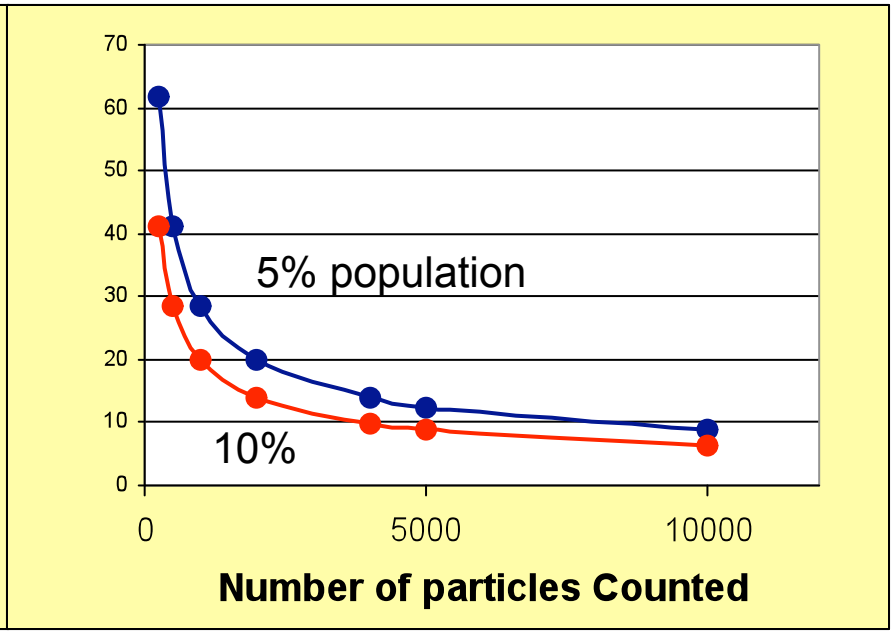
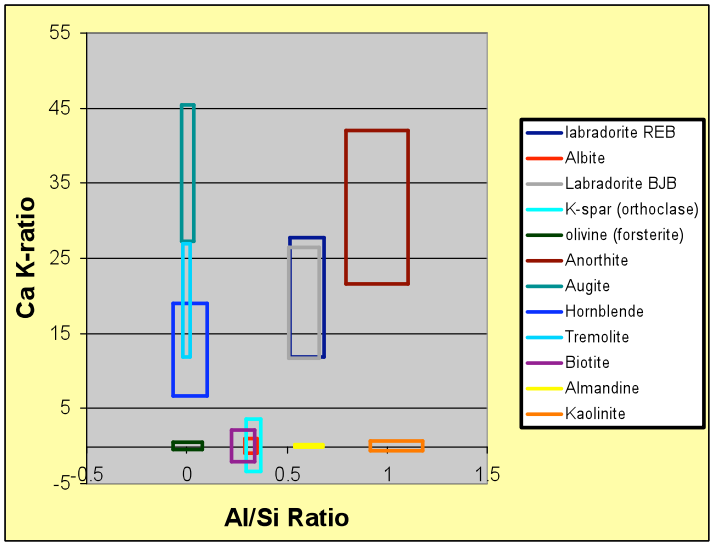
Counting Statistics

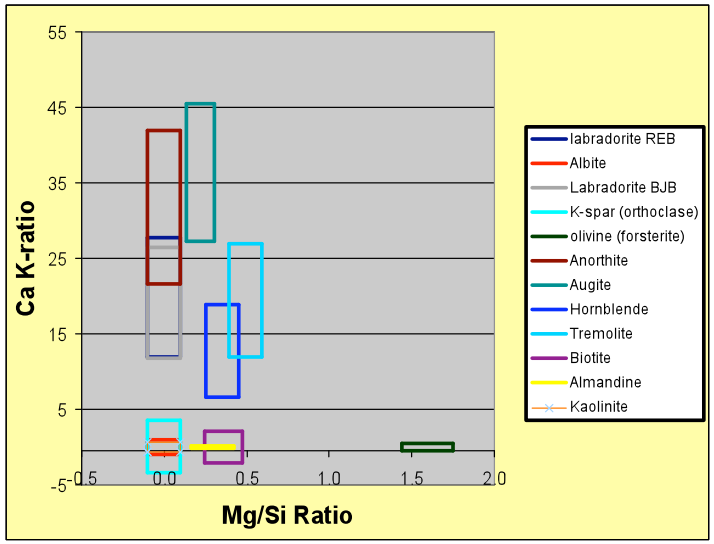
Uncertainty from Counting Statistics at 95% CL							
	250	500	1000	2000	4000	5000	10000
10% concentration	41	28	20	14	10	9	6
5% concentration	62	41	28	20	14	12	9
1% concentration	272	115	70	47	32	28	20

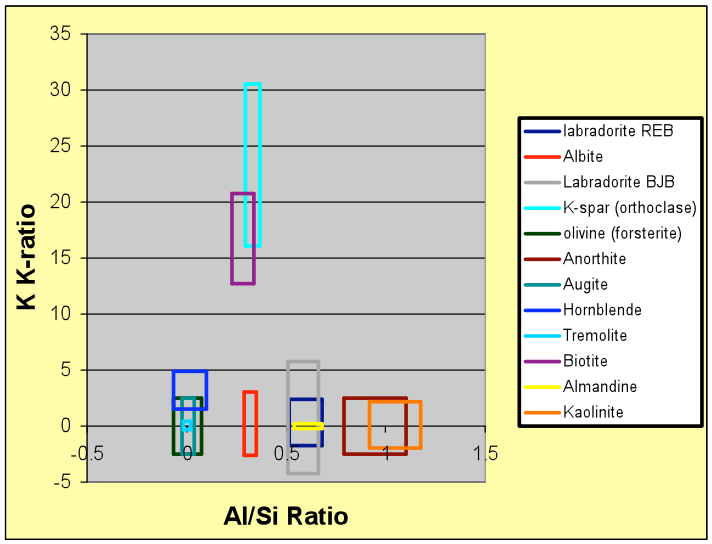


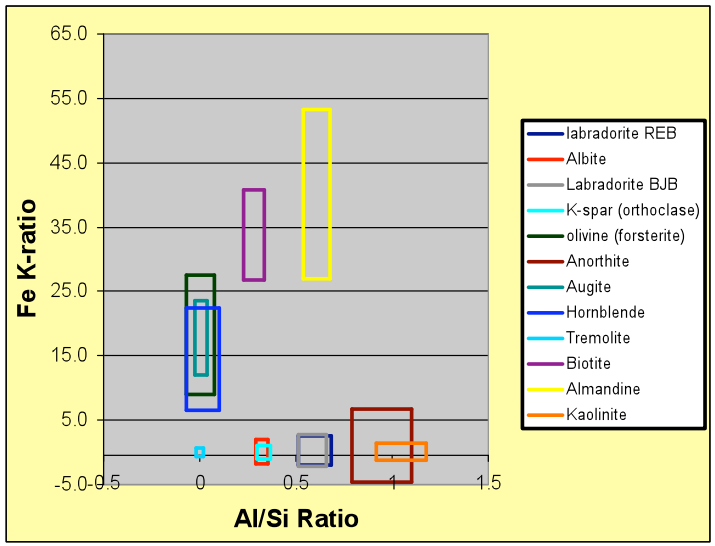


Aspex Case 1 Mineral Identification



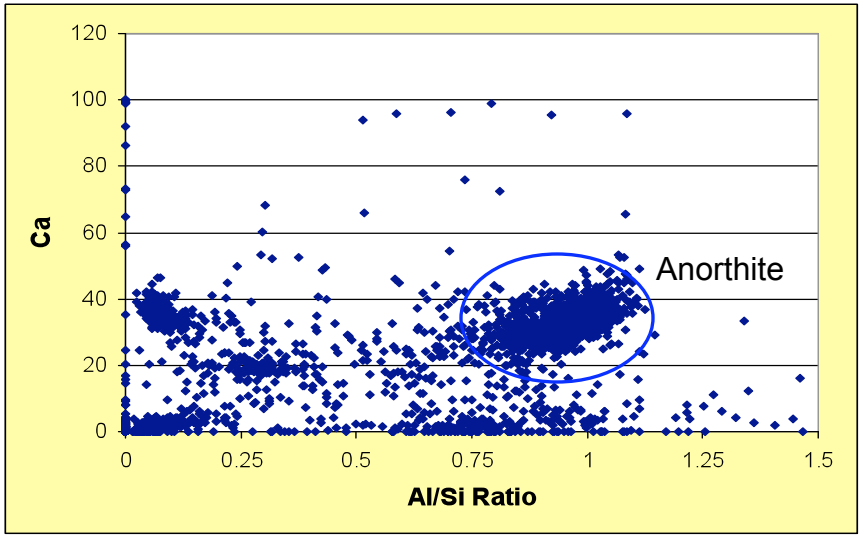


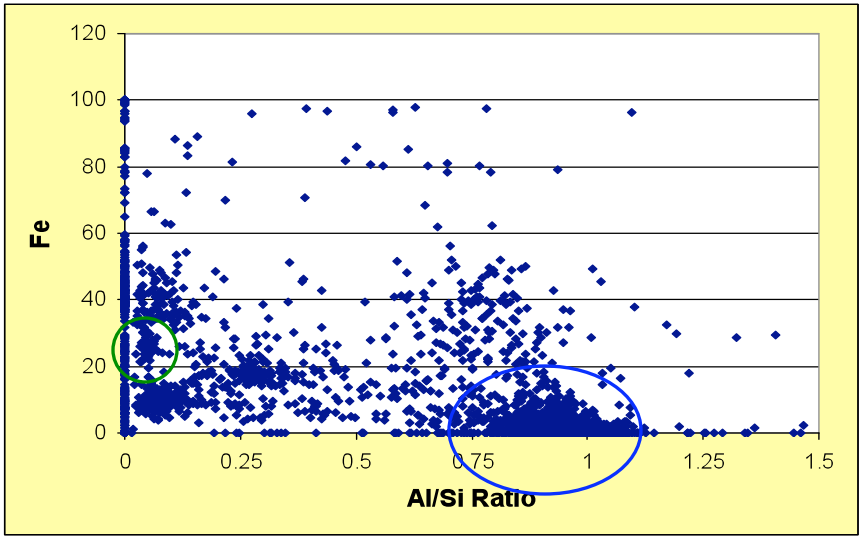


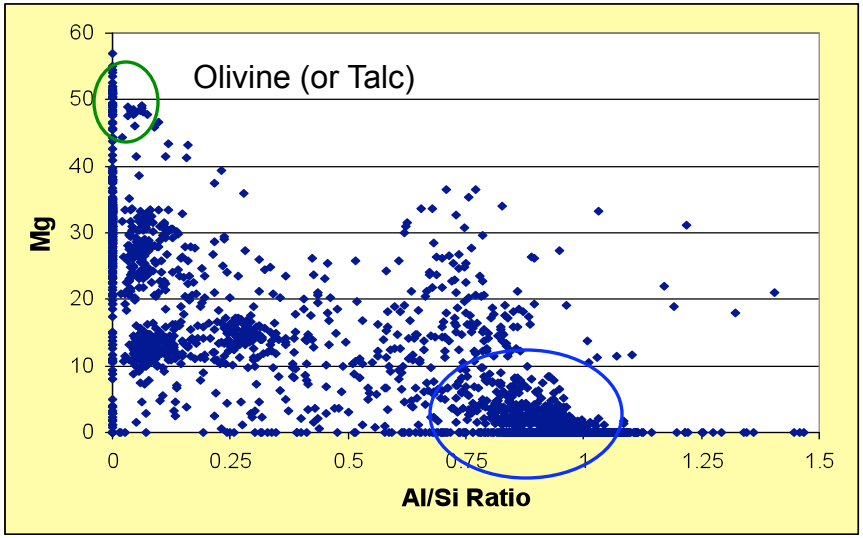


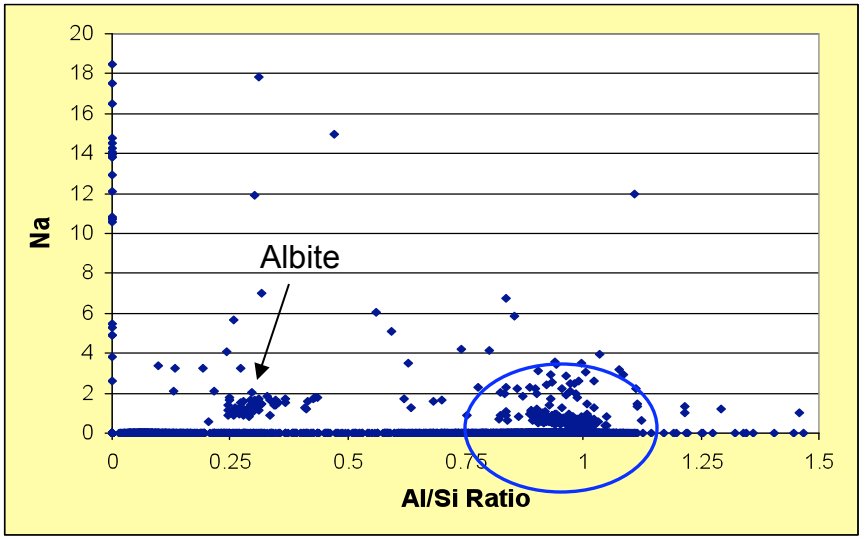
Boxes represent 95% confidence limits

Aspex Case 2: Anorthite

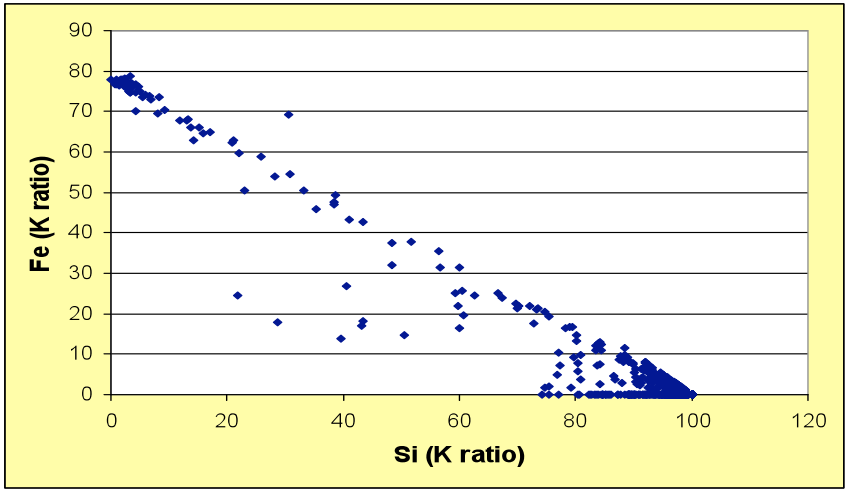


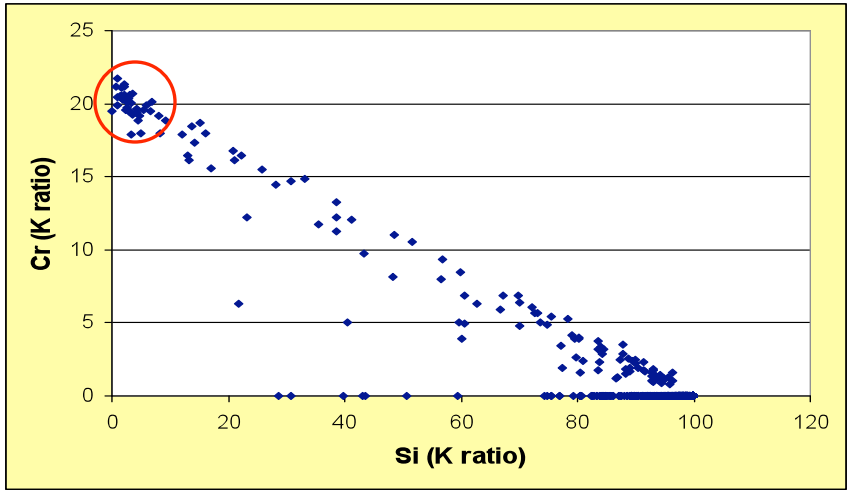


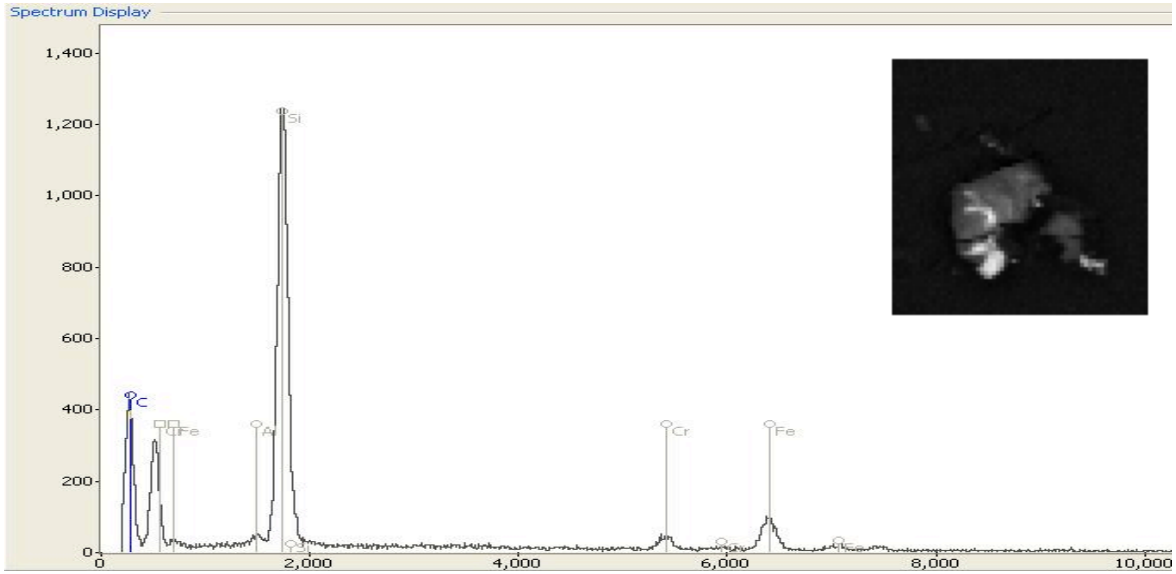




Aspex Case 3: 400 series SS in Quartz







- 400 series stainless steel contains 11-30% Cr.

Limitations to SEM analysis

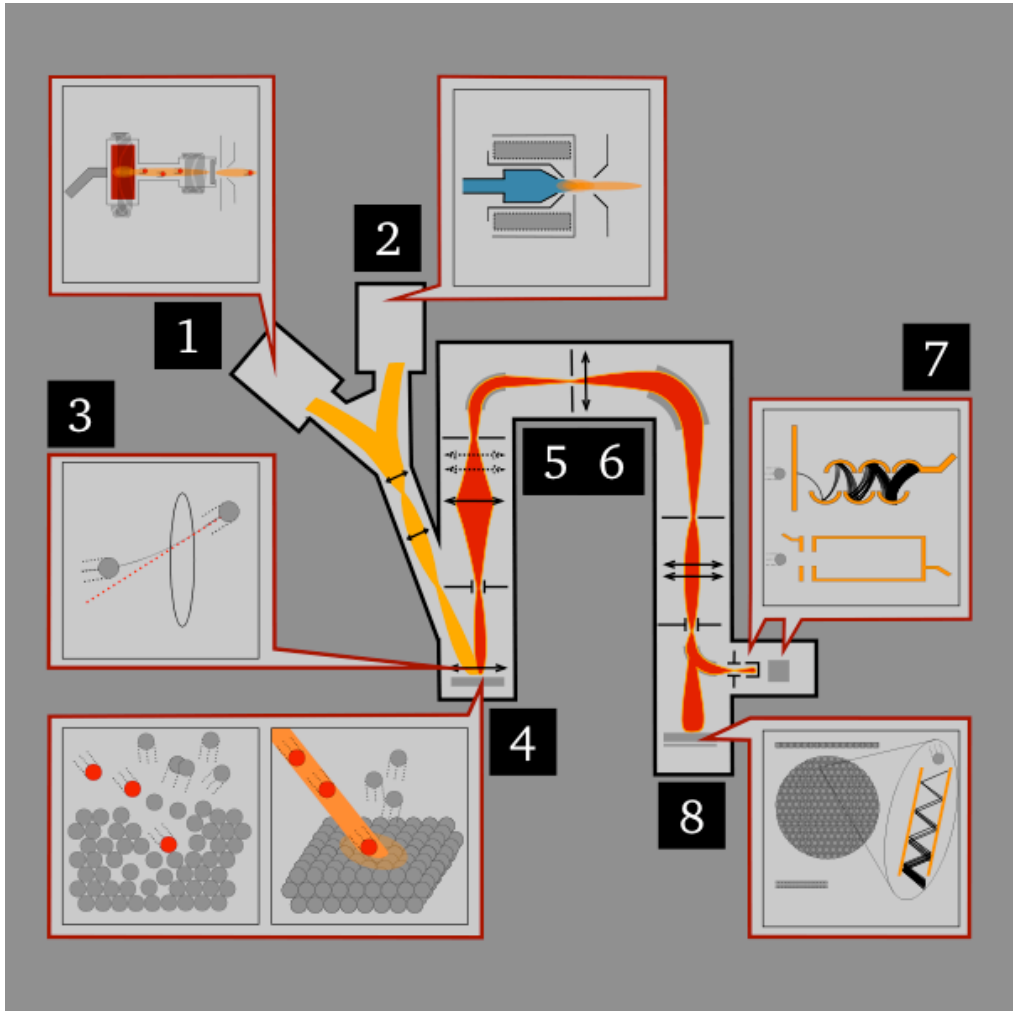
- Relatively high continuum background.
  - Analytical sensitivity limited to 10^{-15} to 10^{-16} g
- Detection limits ~1000 ppm
  - ~1% for 3-6 second measurement with Aspex
- Micrometer sampling volume
- Can't see light elements
  - H, Li, and often B.
- Common spectral overlaps

Advantages of SIMS

- Low backgrounds
  - 0.1 cps or less
- Detection Limits ~ ppb level
  - ~10's of ppm with reasonable analysis times
- Several atomic layer sampling volume
  - Allows thin film and depth profile analysis
- Detects all elements (H to U)
- Can use resolution or energy filtering to remove common spectral overlaps

* Trace element composition is an increasingly significant factor in determination of exact nature and origin of microparticles.

SIMS Technique

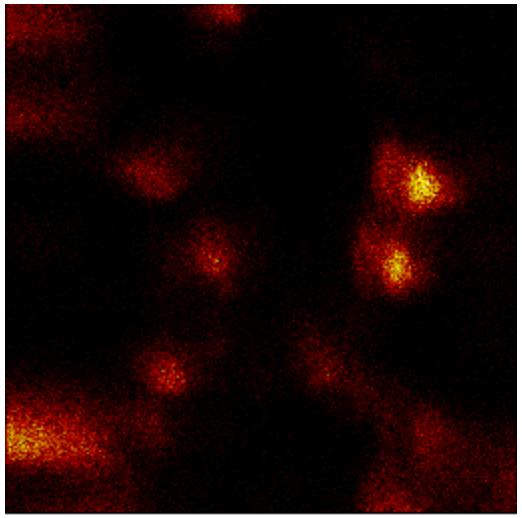


For rapid automated particle analysis two detectors can be used.

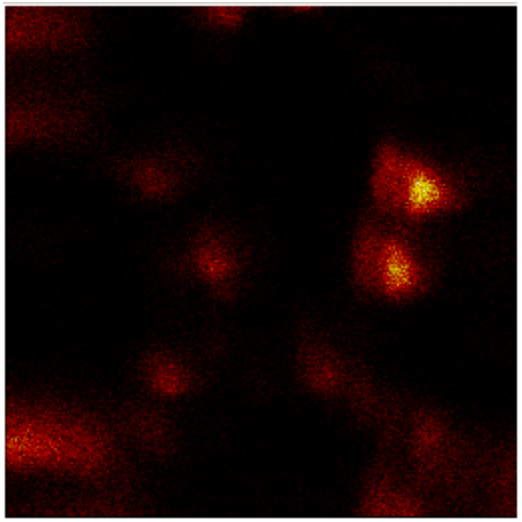
- Rastered (focused) ion beam using the electron multiplier detector
- Static (defocused) ion beam using a position sensitive RAE detector

Image obtained from http://serc.carleton.edu/research_education/geochemsheets/techniques/SIMS.html

Particle Search Software



Al



Si

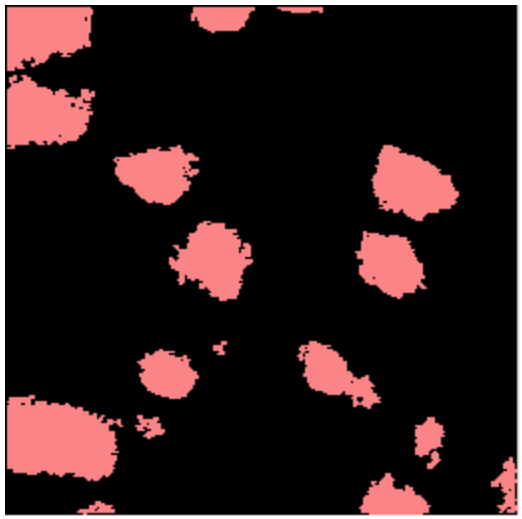
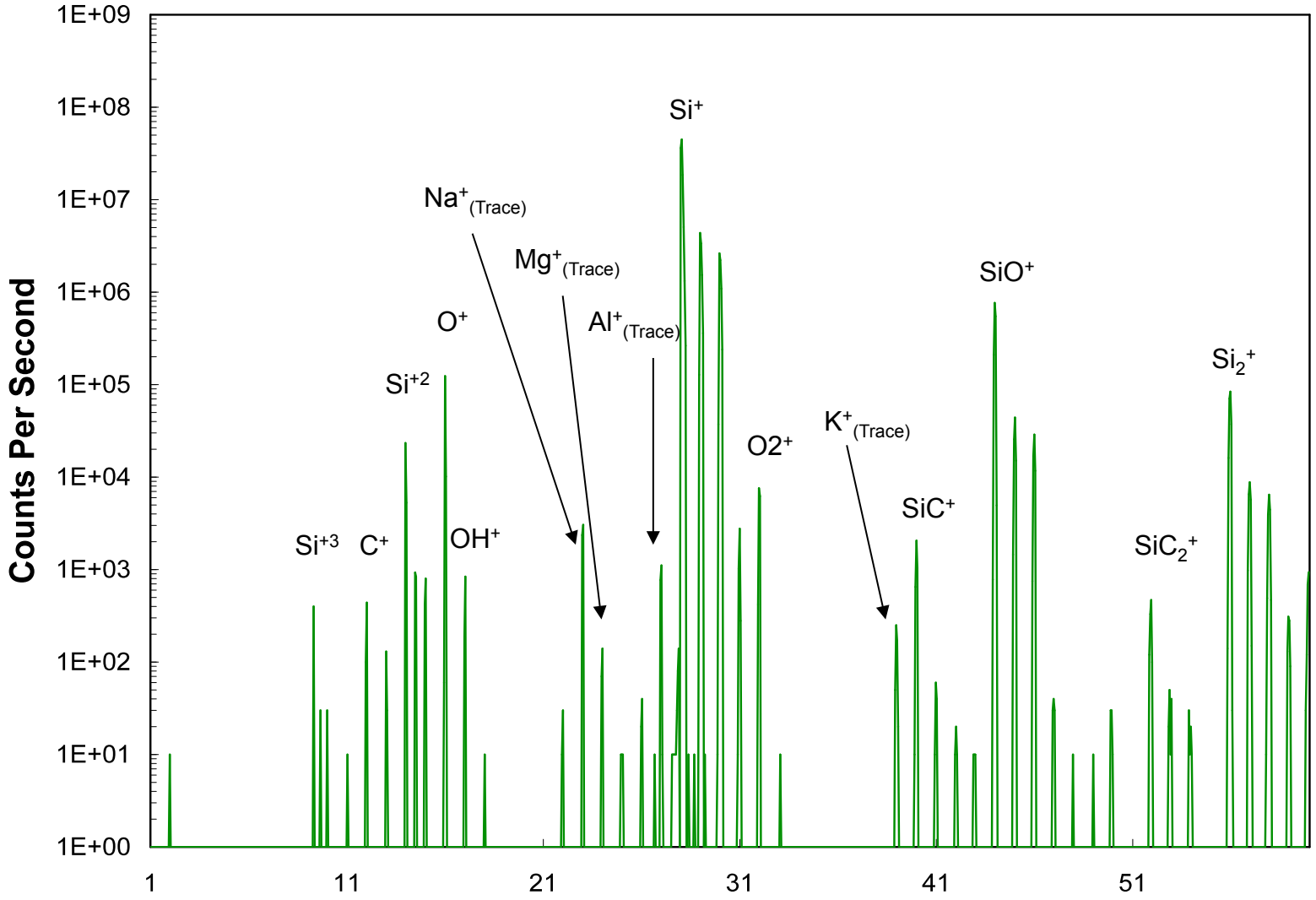


Image processing software overlaps the ion images and defines particle boundaries

“Simple” Si Spectrum



SIMS Quantification: Challenges

- It is well-known that the most serious problems of the quantification of SIMS is that the secondary ion yield of elements varies strongly with matrix and concentration
- Modification of matrix by implanted primary ions
- Adsorbed ion on the surface (hydrocarbons, O2, Cs)
- Crystal orientation
- Electronic character of the matrix
- Ionization potential of sputtered species

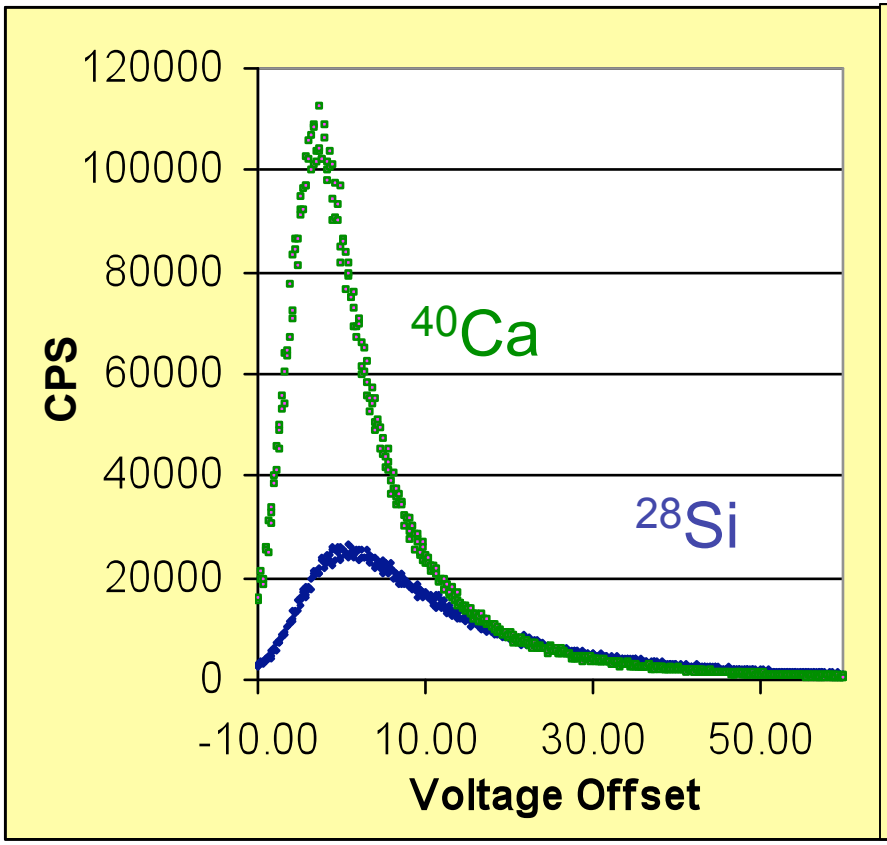
RSF's

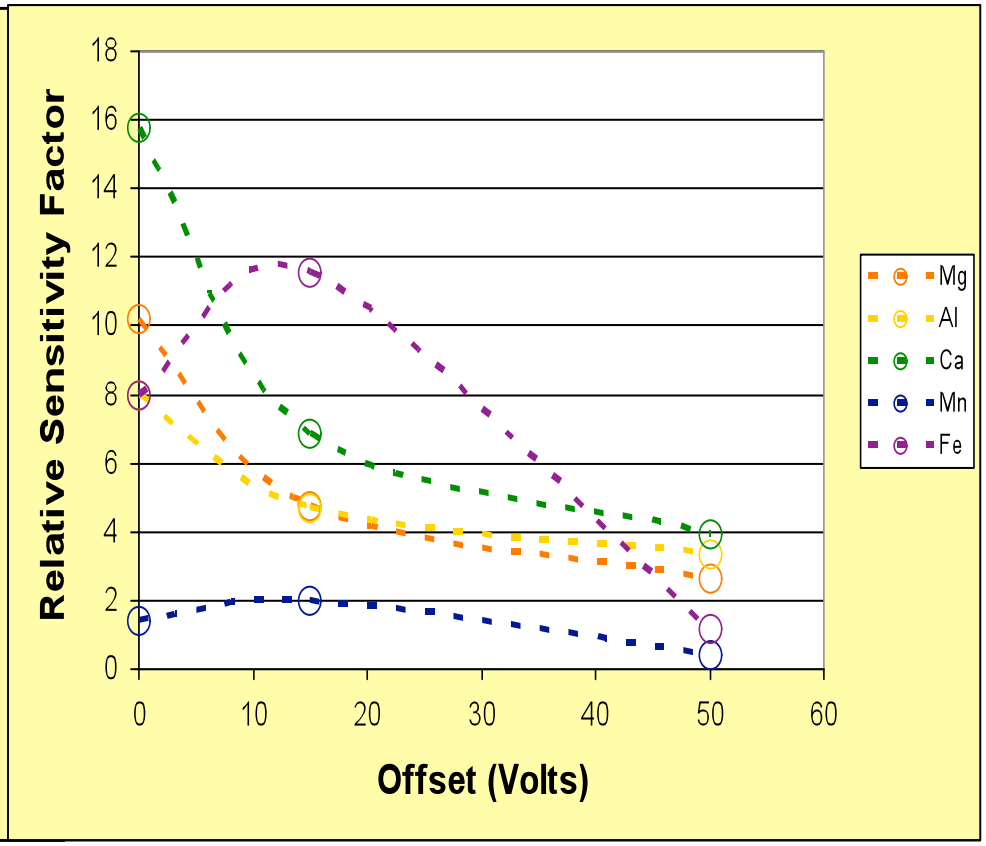
- Instrumental parameters can influence measured RSF's by a factor of 5-60.

$$RSF\ (x/R) = (I_x/C_x{*}F_x)/(I_R/C_R{*}F_R)$$

X - species of interest
R - reference species (matrix)
I - ion intensity
C - concentration
F - abundance of isotope measured

Effect of Energy Filtering on RSF





Stability of RSF For two NIST Glasses

- NIST411

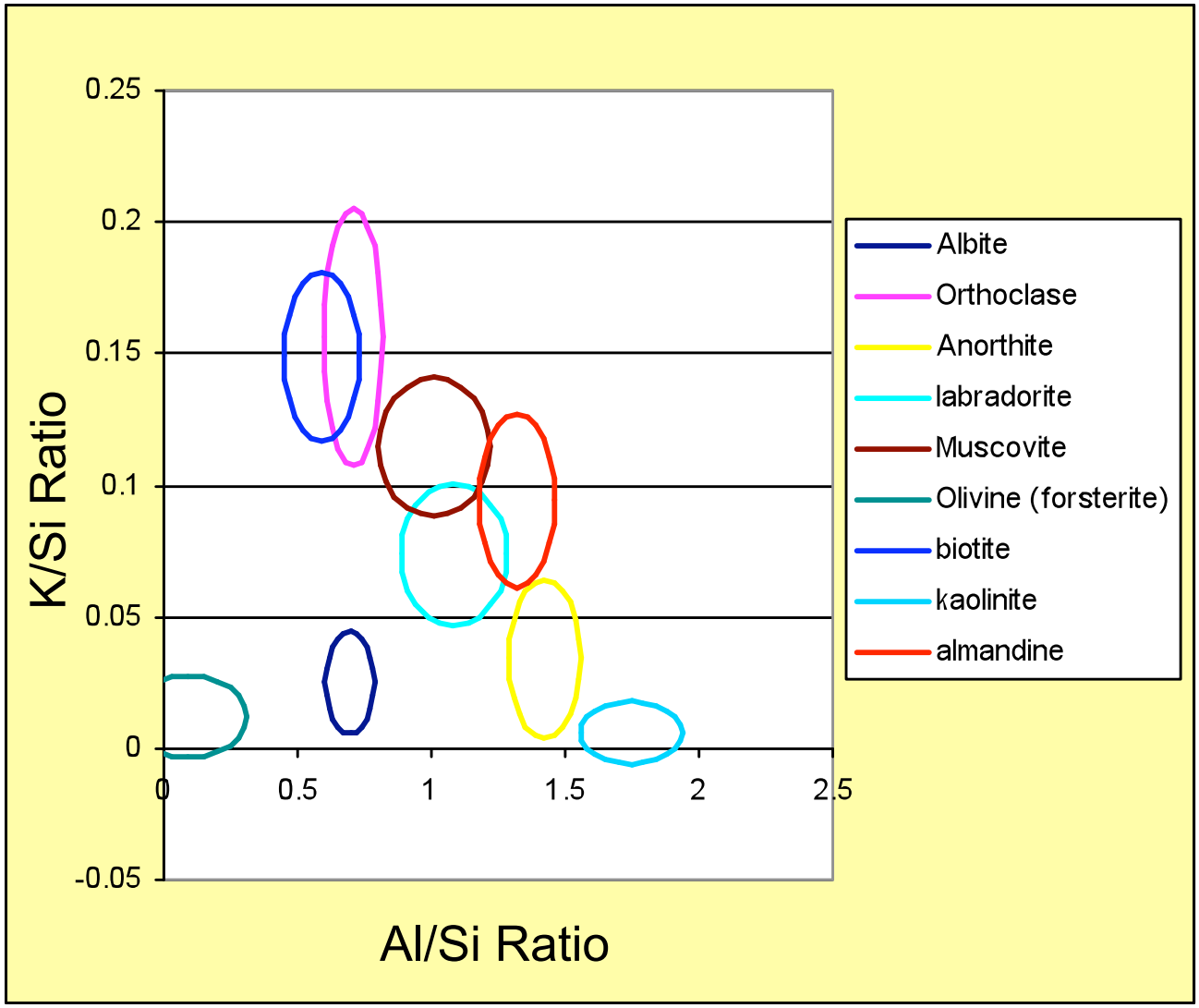
Element	Mg	Al	Si	Ca	Mn	Fe
Atom %	8.2864	-	20.575	6.281	0.1	4.5697
1	3.51			2.70	0.24	0.49
2	3.61			2.90	0.25	0.52
3	3.54			2.62	0.21	0.48
4	3.66			2.89	0.22	0.49
5	4.24			3.52	0.24	0.45
6	3.79			2.72	0.27	0.55
7	3.77			2.76	0.26	0.55
8	3.73			2.74	0.27	0.54
9	3.68			2.59	0.25	0.52
10	3.69			2.62	0.25	0.53
11	3.70			2.83	0.26	0.44
12	3.42			2.19	0.20	0.39
13	2.94			2.37	0.24	0.40
Average	3.74			2.82	0.25	0.51
Stdev	0.19			0.27	0.02	0.04
RSD%	5.10			9.59	8.39	7.93

- NIST412

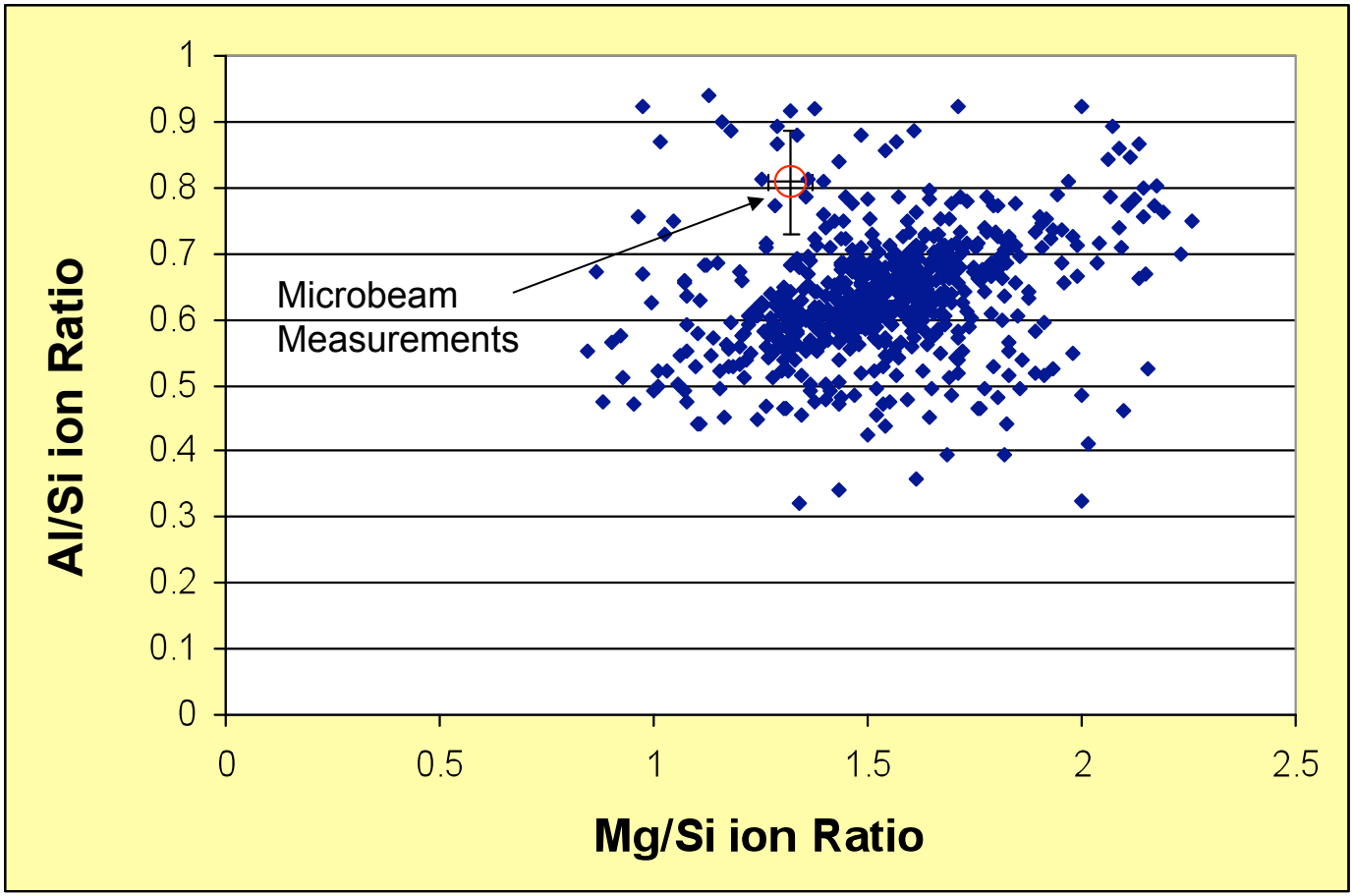
Element	Mg	Al	Si	Ca	Mn	Fe
Atom %	10.659	4.0418	16.775	6.0445	0.1	3.0813
1	3.71	3.57		3.31	0.24	0.80
2	3.43	3.50		2.97	0.22	0.65
3	3.63	3.57		3.08	0.23	0.68
4	3.61	3.54		2.72	0.21	0.59
5	3.62	3.43		2.71	0.21	0.60
6	3.50	3.71		2.68	0.20	0.55
7	3.58	3.69		2.80	0.20	0.57
8	3.30	3.22		2.93	0.24	0.73
9	3.73	3.57		2.70	0.22	0.51
10	3.47	3.94		2.58	0.19	0.54
11	3.18	3.46		2.47	0.27	0.55
12	3.62	3.32		2.76	0.16	0.50
13	3.73	3.40		2.72	0.20	0.52
Average	3.51	3.50		2.80	0.21	0.59
Stdev	0.17	0.18		0.16	0.02	0.07
RSD%	4.77	5.16		5.80	11.01	11.73

5nA $O2^+$ primary beam, 400 CA,
30 eV ES, 40V ES offset.

SIMS Mineral Analysis

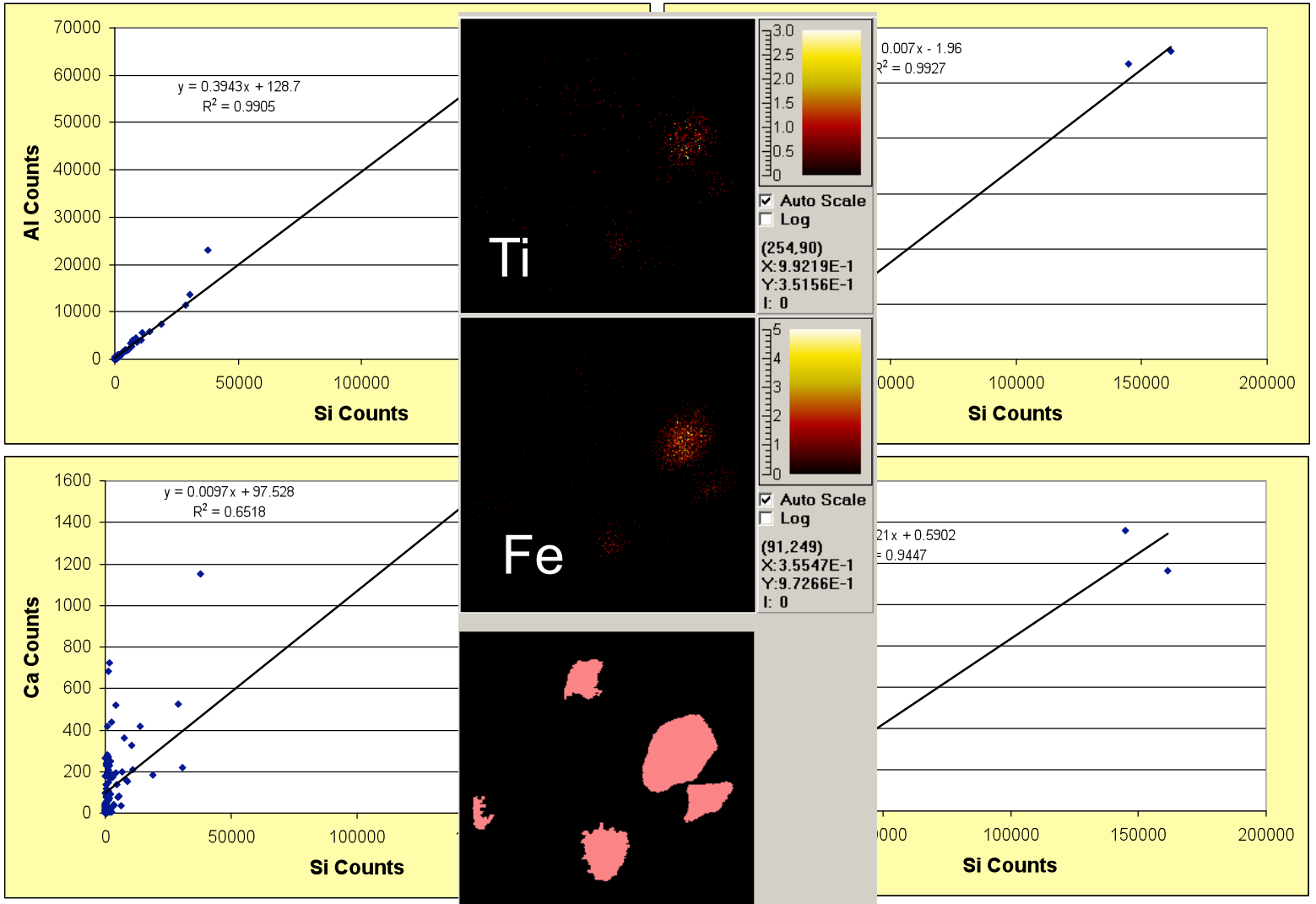


SIMS PSearch vs Microbeam



NIST K412 glass

Trace Detection - Automated Search



NIST K93 glass reference (atom %): 0.8526 Al, 0.0067 Fe, 0.0034 Ca, 0.0067 Ti

Surface contamination

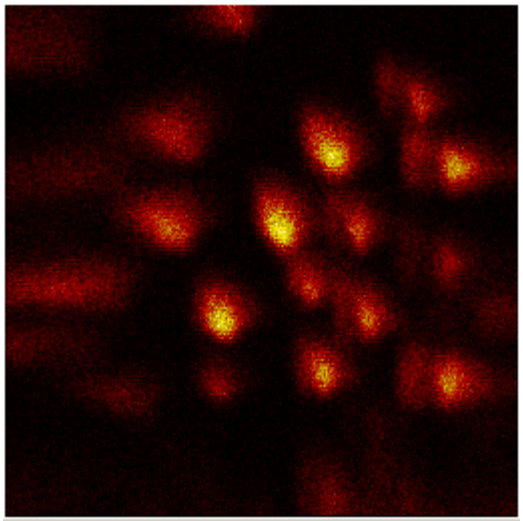
- Great care must be taken to minimize surface contamination of sample during its preparation and analysis.

- Polished cross sections can smear softer elements and embed polishing materials in sample.

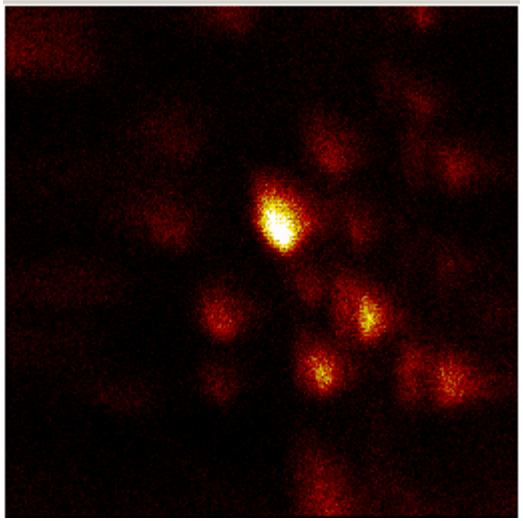
- Gold/carbon coating can contain trace impurities which are seen by SIMS.

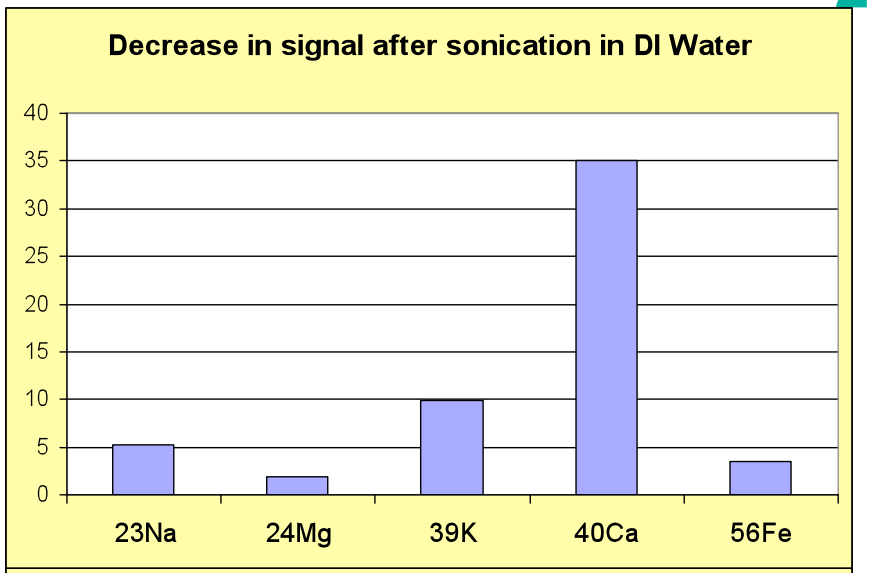
Blank Planchet/Sonication in DI H_2O

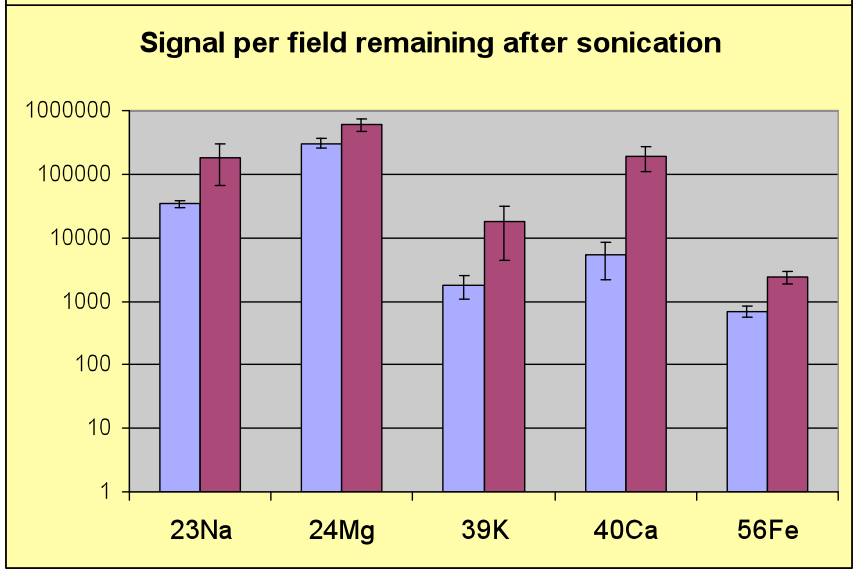
Na



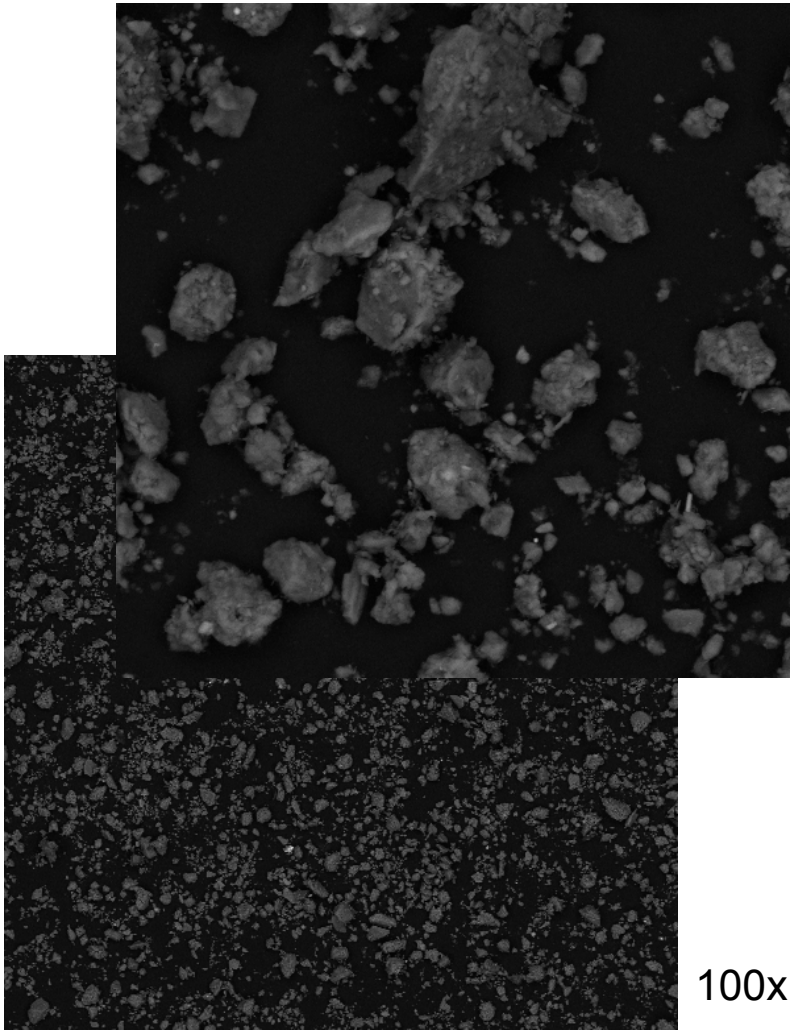
Ca



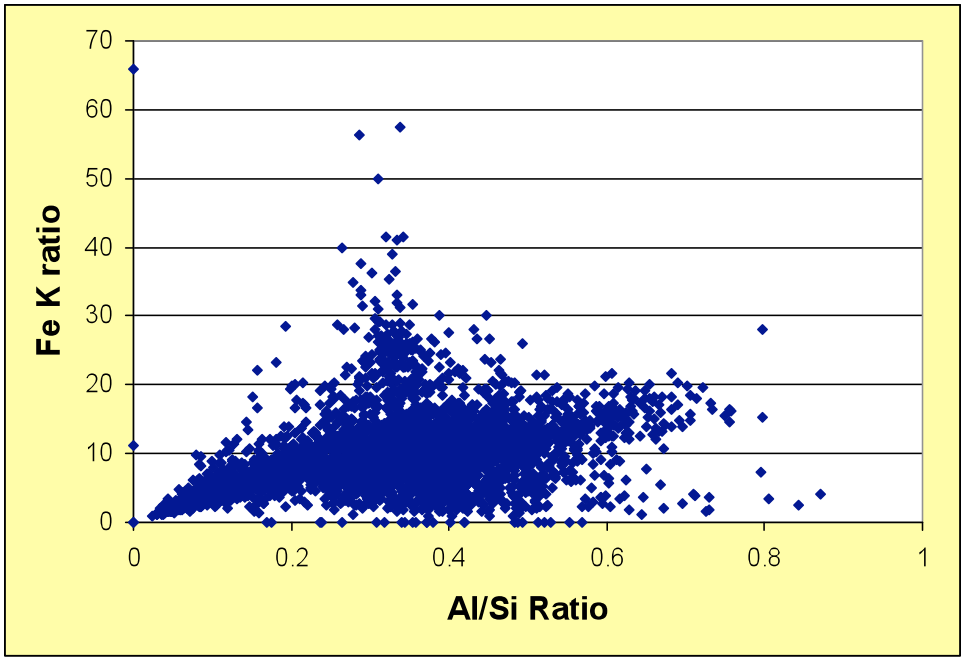




Importance of Good Sample Prep.

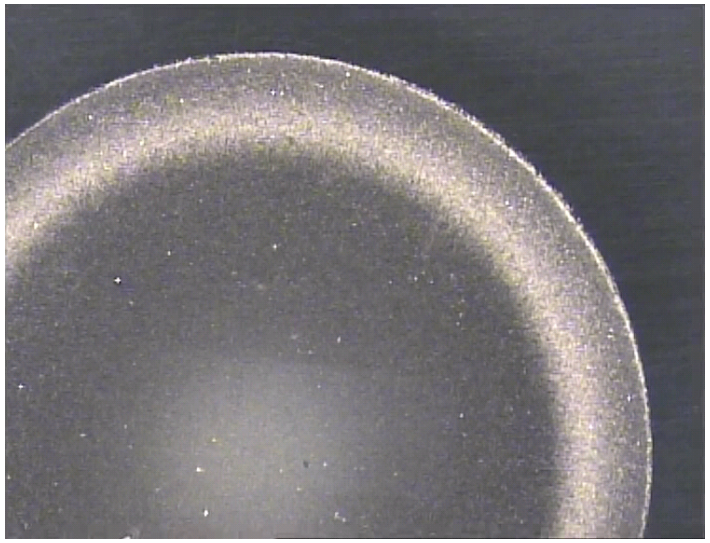


750x magnification



100x magnification

Vacuum Impactor

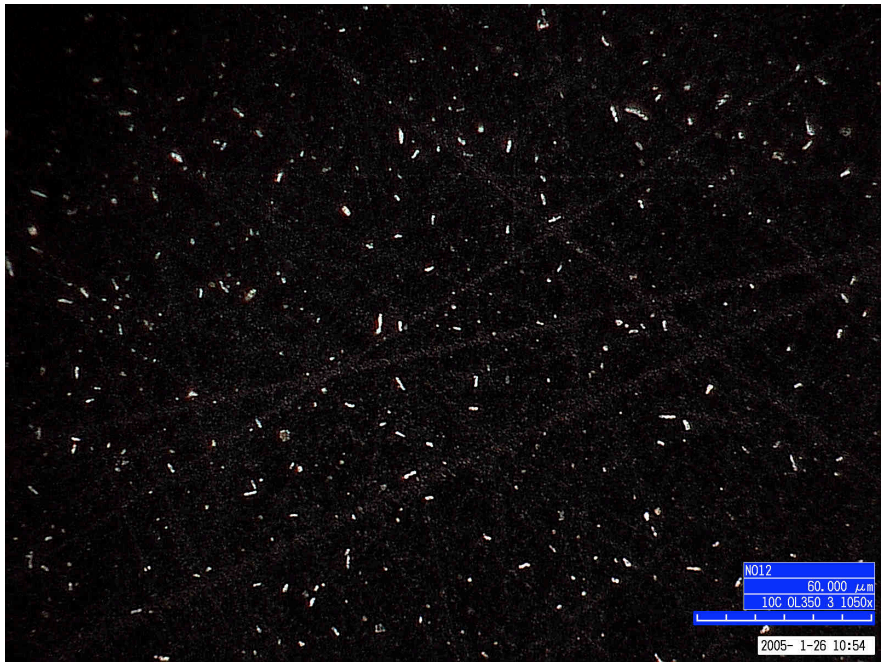


The VI sample prep takes very little material.

A heavy deposit from a single spot (~50-100 M particles)

Vacuum Impactor

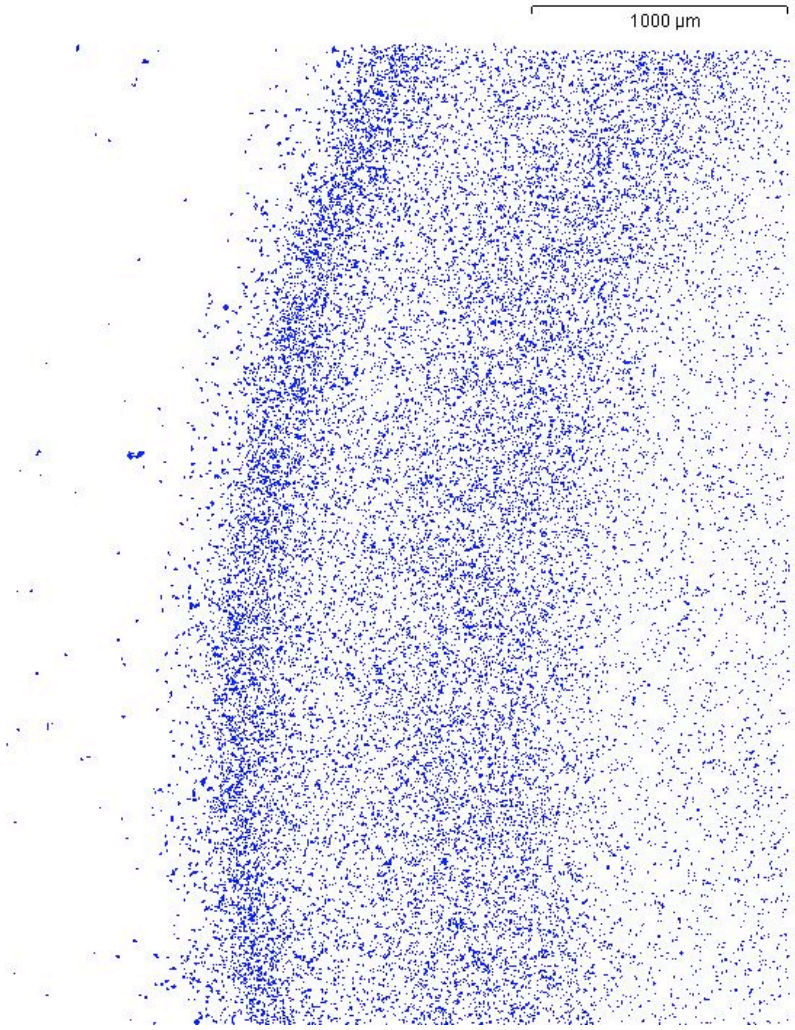
Vacuum impactor made of teflon

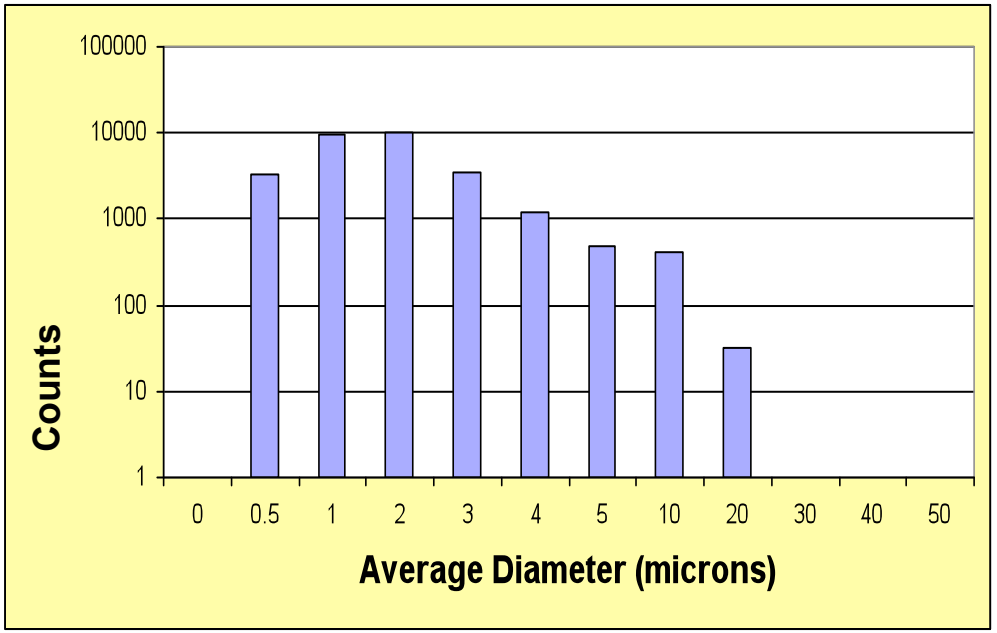


Particle distribution (Magnification 1050x).

Small particles (a few micrometers in diameter need no special treatment as they can not support a large enough potential difference from the mount to disturb the primary or secondary ion beam.

Vacuum Impactor Preparation





Sample prepared from the <88micron portion of a sandy soil.

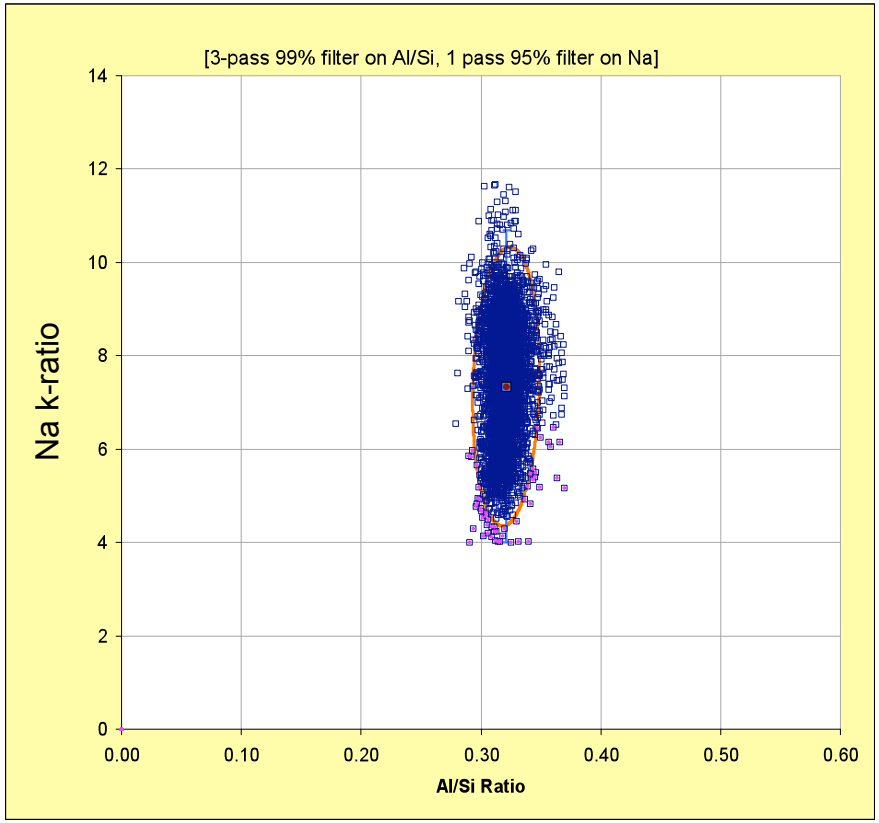
Analytical Techniques

- Aspex
- General
- 0.1% sensitivity
- Particle is defined by optical paratmeters

- SIMS
- Targeted
- ppb sensitivity
- Particle defined by analytical parameters.

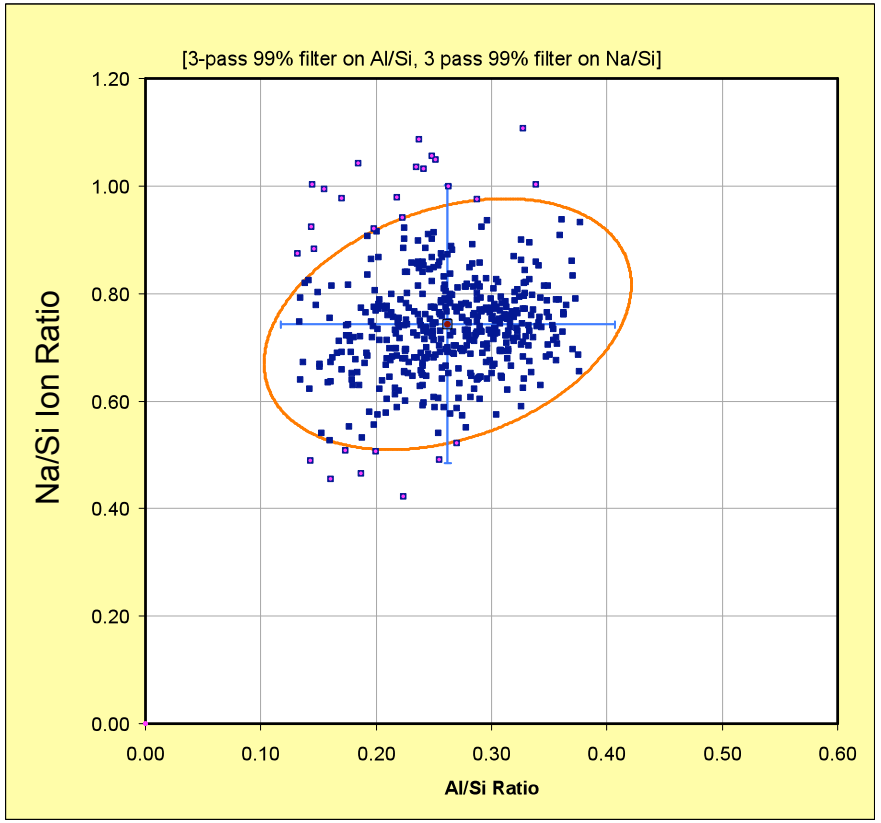
Comparison of Automated Methods

Aspex



RSD Al/Si ratio 3%
RSD Na k-ratio 17%

SIMS



RSD Al/Si ratio 21%
RSD Na k-ratio 13%

Summary

- Aspex is an excellent, flexible tool for mineral identification
- SIMS is more “powerful,” but must be applied judiciously
- Sample preparation is critical
  - Planchet cleaning
  - Vacuum Impactor method should be investigated further
- SIMS instrument settings should be finalized
- Standard protocol should be developed