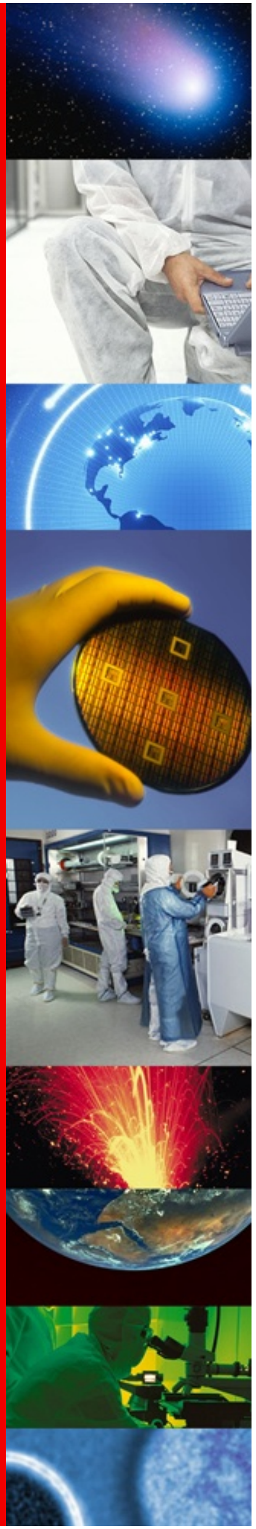

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Atom Probe Tomography: Capability and Applications

Ludovic Renaud, David J. Larson, Peter H. Clifton, and Robert Ulfig

Aux limites de la caractérisation élémentaire 2013

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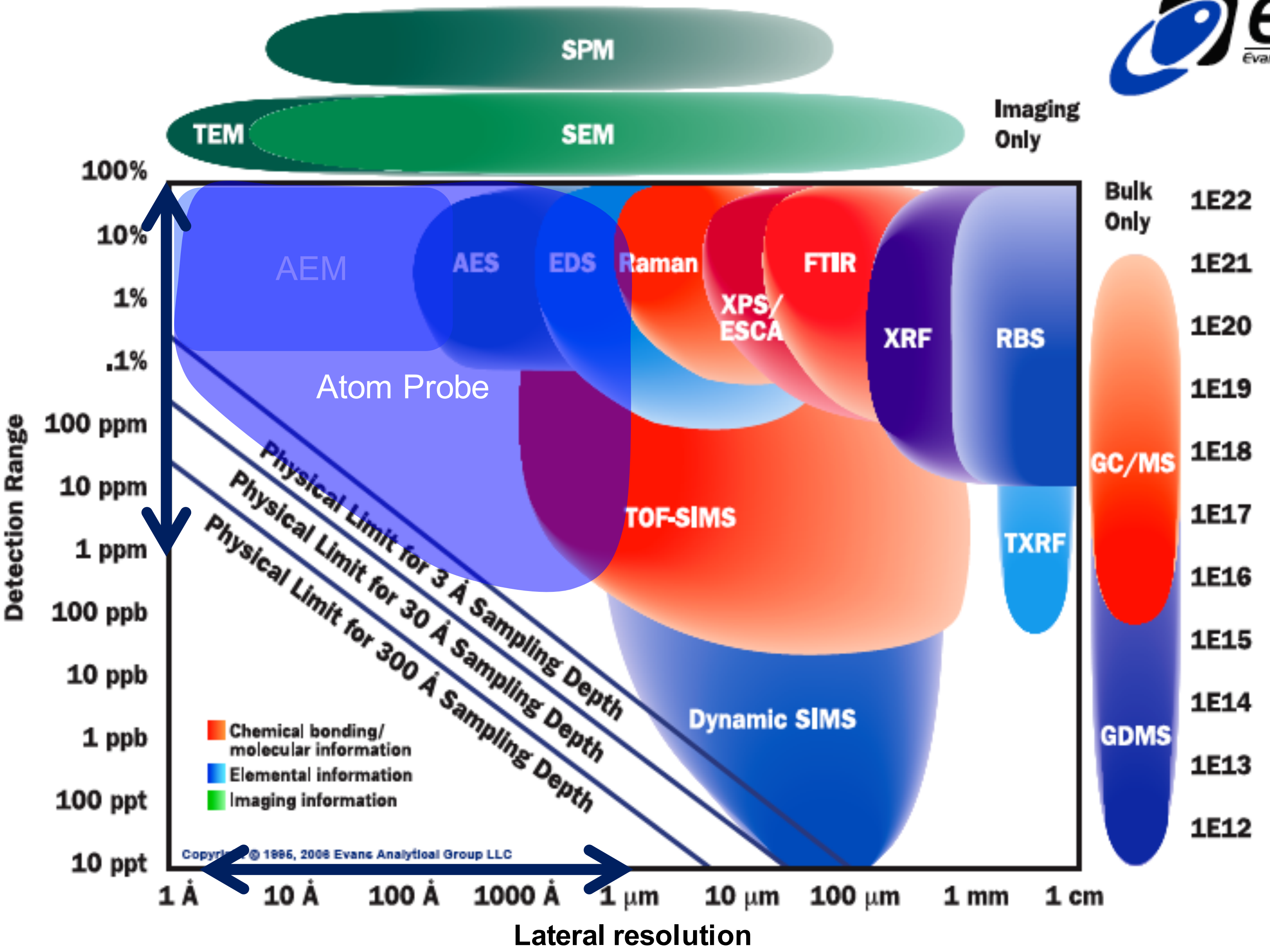
Extending Spatial and Chemical Sensitivity



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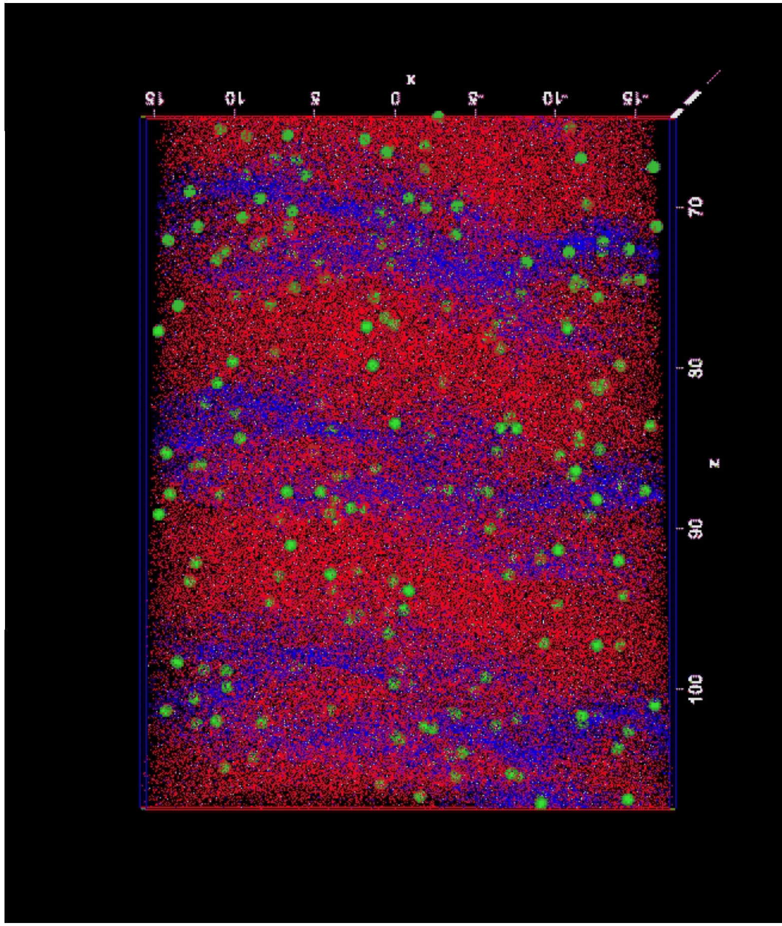
What is an Atom Probe?

- A point-projection microscope that uses time-of-flight spectroscopy to identify single atoms or small molecular fragments

- Specimen base temperature ~20 to 70K
- Projection magnification ~10^6X
  - 0.2 nm ⇨ 0.2 mm at detector
- >50% detection efficiency
  - independent of m/n
  - Limited by current technology (MCPs)



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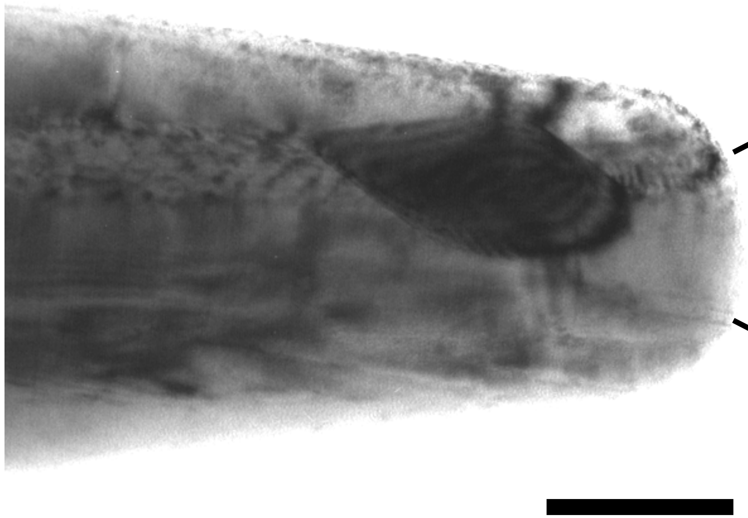
Very High Magnification of the Surface

TEM image of field ion specimen



~100nm

"Ball model" of sample surface

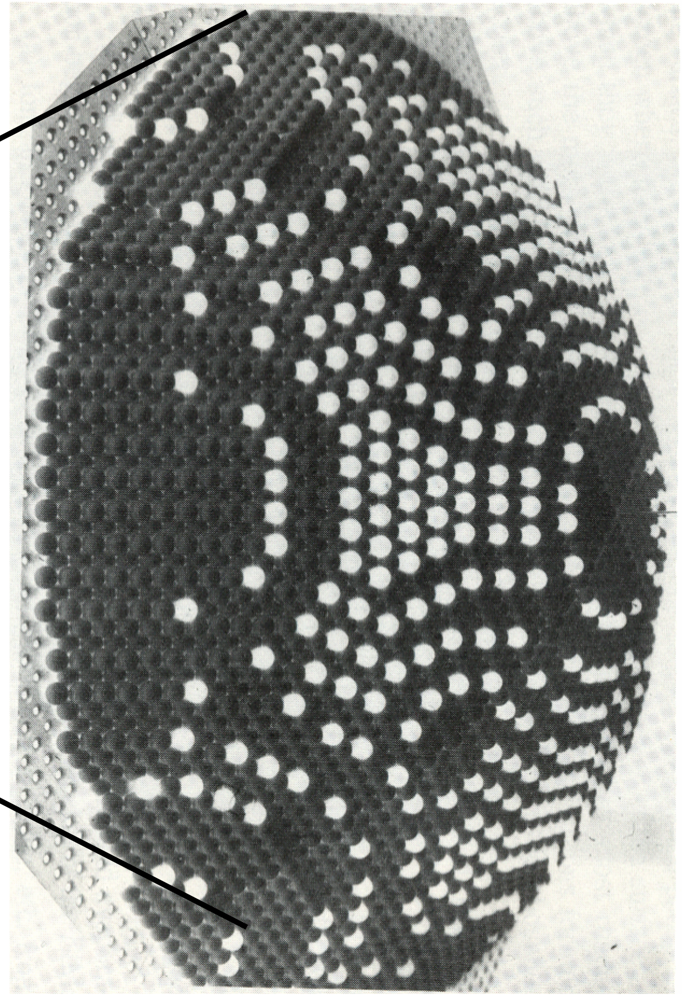
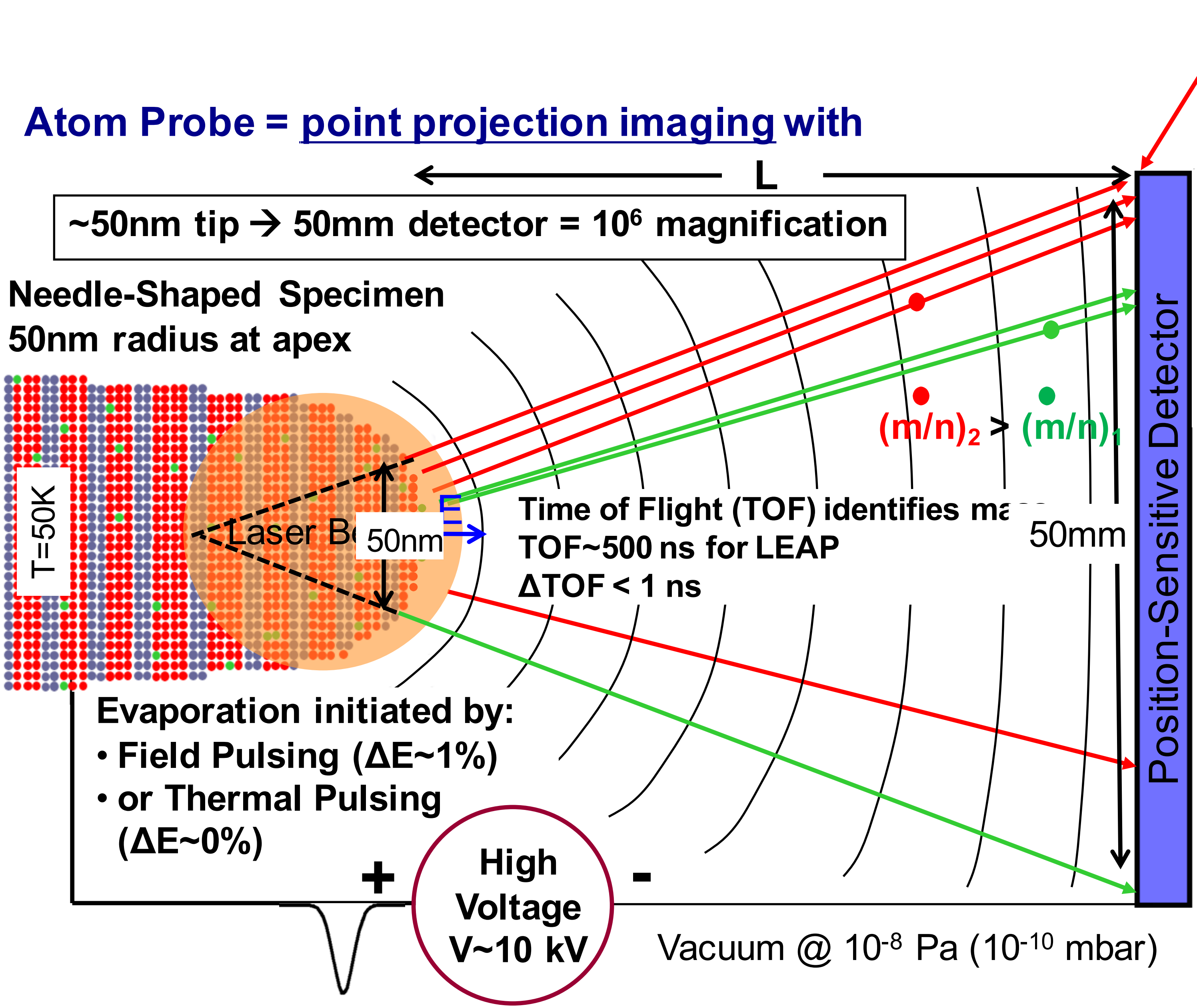


Figure from Miller, Atom Probe Tomography (2000)

- High magnification image achieved by using a highly curved surface as the specimen (R_{spec} ~ 100nm)
- Distance from the specimen to detector is ~100mm

Description of Atom-Probe Operation

Atom Probe = point projection imaging with



$neV = \frac{1}{2}mv^2$

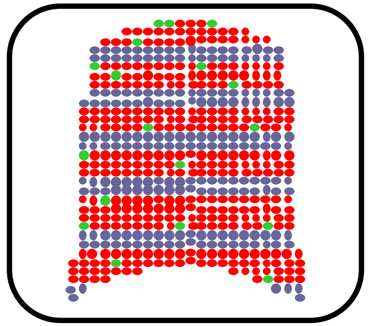
$v = L/t = $ constant

⇨ $m/n = 2eV\, t^2/L^2$

2D Detector

Determines x,y coordinates of atom

Data are collected and interpreted



3-Dimensional Reconstructed Model of Specimen

z is determined from sequence of evaporation events

Performance Evolution: 2001 to 2011

- Field of View
  - ~25 nm ➔ 250 nm
- Speed of Data Acquisition
  - ~ 30 ions/s ➔ > 30,000 ions/s
- Increased Analysis Volumes (avg)
  - ~ 10,000 nm^3 ➔ 5,000,000 nm^3
- Mass Resolving Power
  - ~ 300 FWHM ➔ > 1000 FWHM (500 FWTM & 300 FW1%M)
- Application Range (voltage-mode)
  - Bulk metals (electro-polishing)
  - Bulk and site-specific metals analyses (FIB specimen preparation)
- Application Range (laser mode)
  - Not available!
  - Metals/ coatings/ thin films, semiconductors, compound semi, device structures, oxides and ceramics

- Dramatic improvement in all aspects of performance!
  - Installed base < 5 ➔ ~ 50

CAMECA APT Installed Base

66 Systems in 11 Countries

NA: NWU (Chicago), **ORNL**, UNT (Denton), Sandia, UoA (Tuscaloosa), ISU (Ames), **IBM (East Fishkill)**, PNNL (Richland), UCSB (Santa Barbara), INL (Idaho National Lab), **NIST (Gaithersburg, Boulder)**, Michigan U, Harvard, CSM, Semi company, McMaster

Europe: **Oxford**, QUB (Belfast), Chalmers, IM2NP (Marseille), **Leoben**, CNT (Dresden), MPIE(Dusseldorf), ETH (Zurich), **GPM (Rouen)**, IMEC (Leuven), LETI (Grenoble), Univ. Saarlandes, IFOS (Kaiserslautern), CEA Saclay, Julich, KIT (Karlsruhe), RWTH/Aachen

Region	
NA	19
JAPAN	12
EUROPE	20
APAC/ ROW	15
Total	66

Japan: **CRIEPI**, NIMS, **Tohoku (Oari, IMR, WPI)**, Kobelco, Japan Steel Co., KEPCO/ INSS, **Semi Company**, Materials Company

APAC/ROW: **Sydney, SHU (Shanghai)**, DMRL (Hyderabad), Monash, **KAUST (Saudi Arabia)**, NCNT (Korea), Optoelectronics Company (Korea), Optoelectronics Company (Korea), Semi Company (Korea), Semi Company (Korea), Deakin (Australia), KIST (Korea)

● 1 system ● 2 systems ● 3 systems

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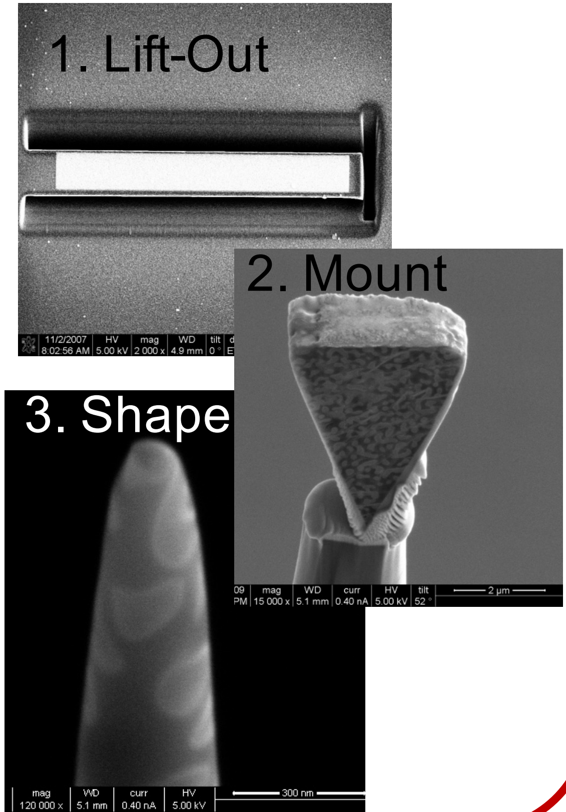
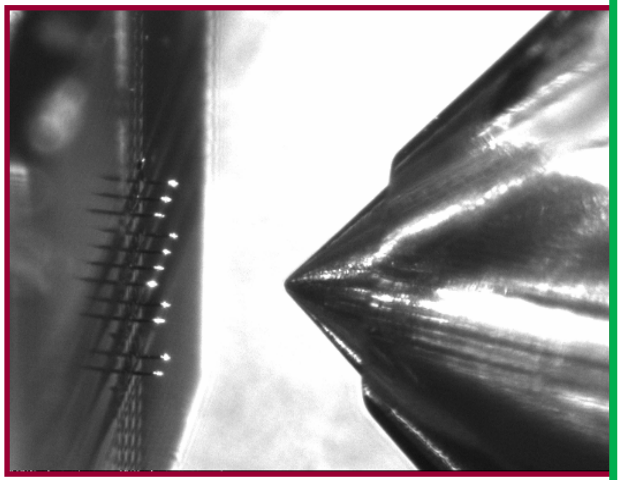
LEAP Design Philosophy

- Develop APT such that it is capable for adoption as a general material science tool.
- LEAP combines high data quality, large analysis volumes, applicability to a wide range of materials with speed, reliability and ease-of-use.

- Mature FIB-based specimen preparation

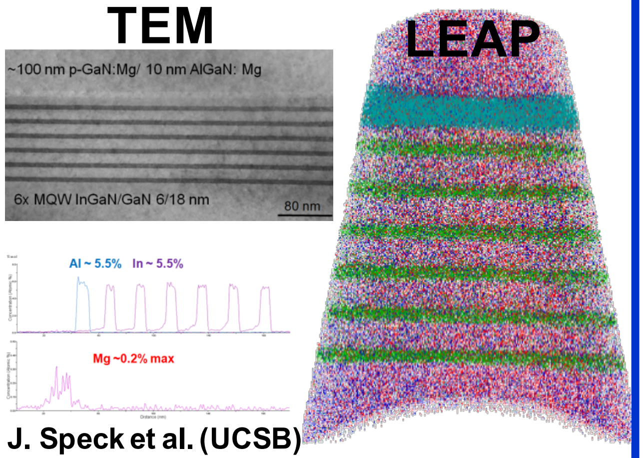


- LEAP enables microtip-based specimen handling



- Efficient specimen transport FIB to LEAP
- Reduced specimen transfer time

- Fast data acquisition
- Up to 5M atoms/s & up to 1 MHz pulsing



J. Speck et al. (UCSB)

- An example analysis of an entire device structure (100M atoms) captured in < 2 hrs

~ 3 hours

~ 2-4 hours

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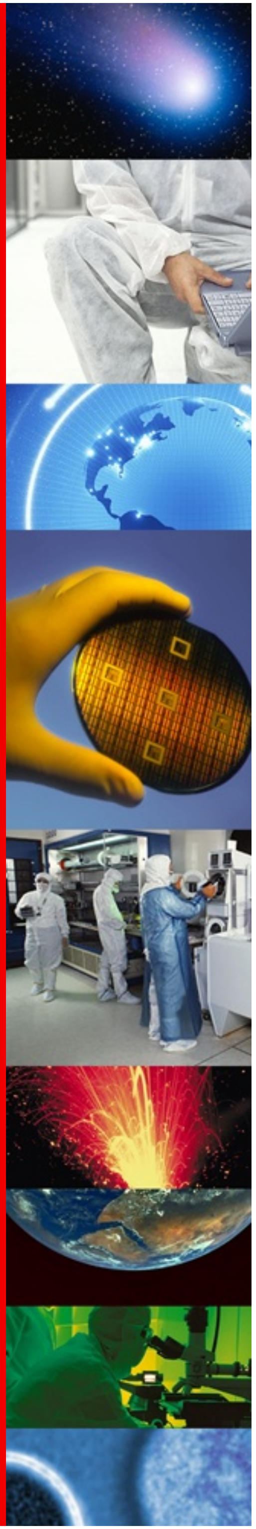

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APT Data Format

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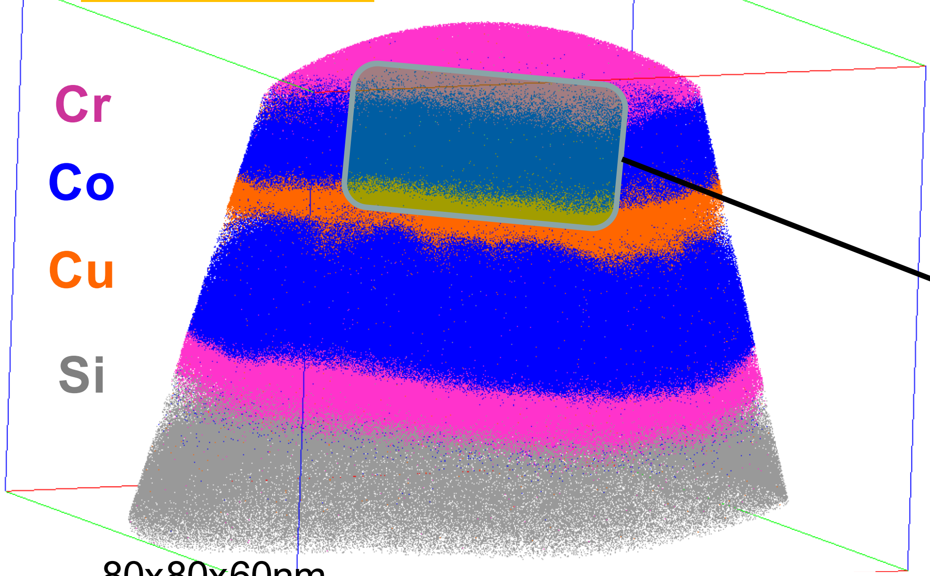
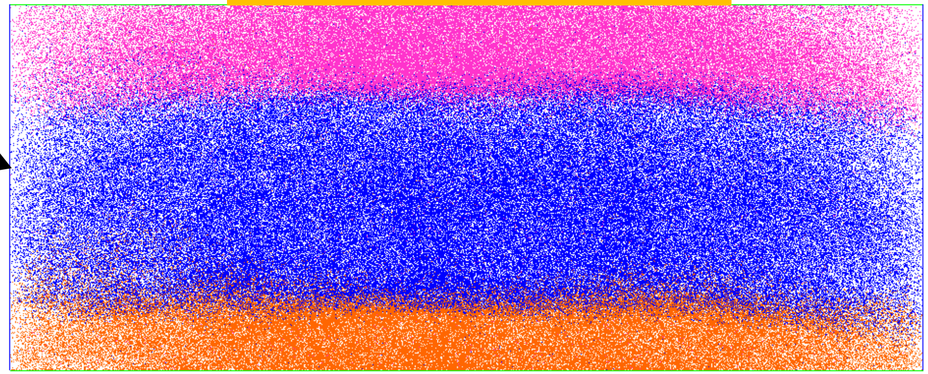
Data Format & Information of Interest

3D Atom Map



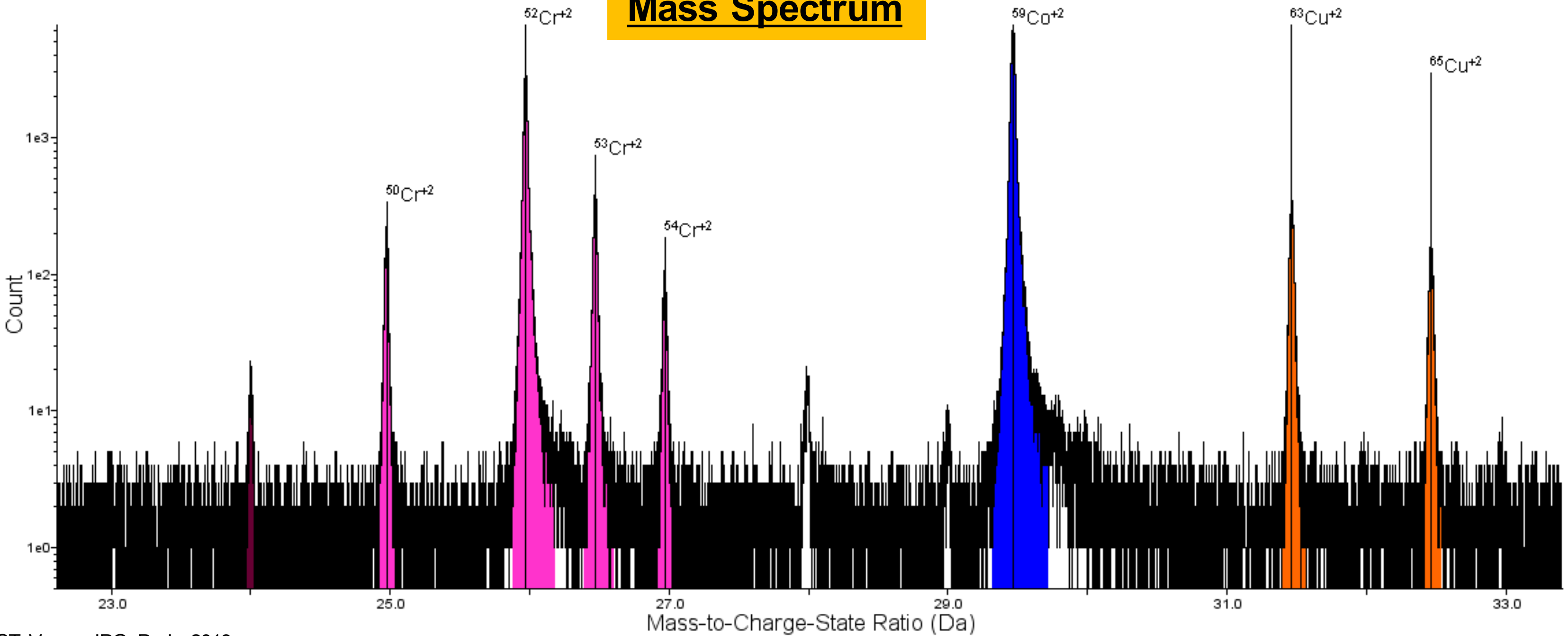
80x80x60nm

Selected Area Atom Map

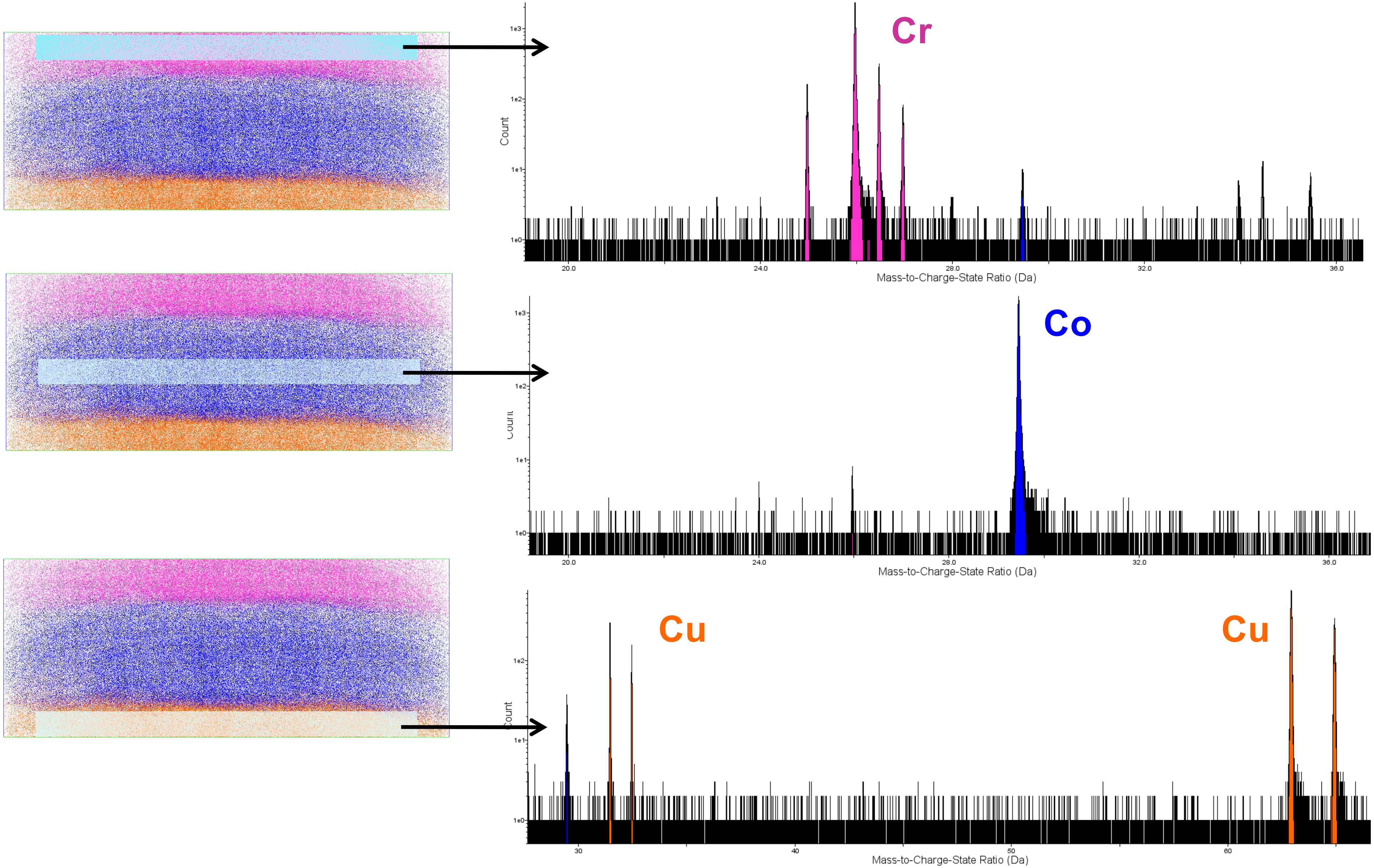


35x35x14nm

Mass Spectrum



Selected Regions: Spectra Analysis



- Selected area mass analysis provides very fast evaluation of what is present in different regions of space

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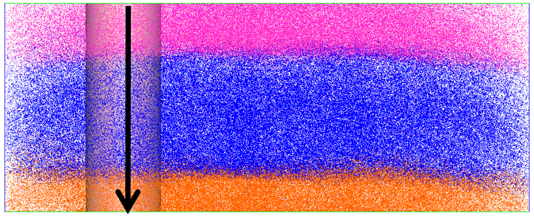
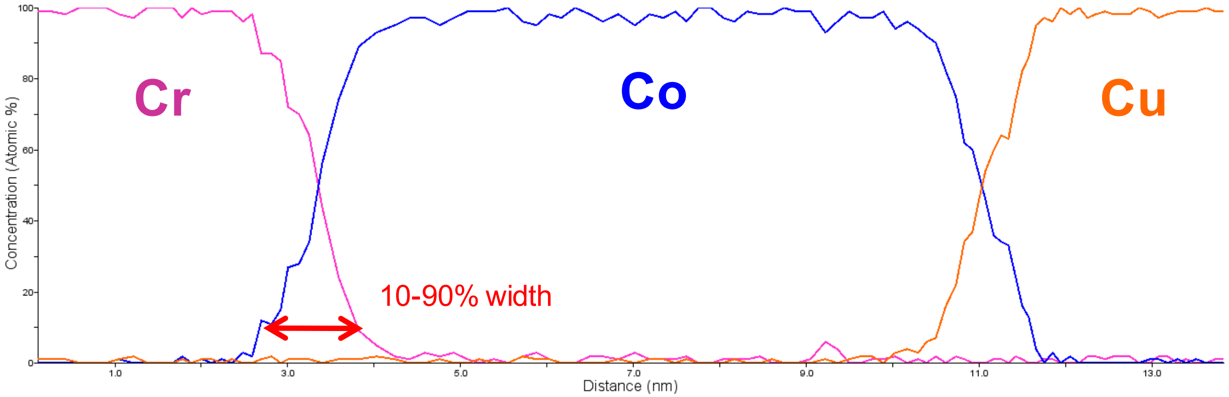
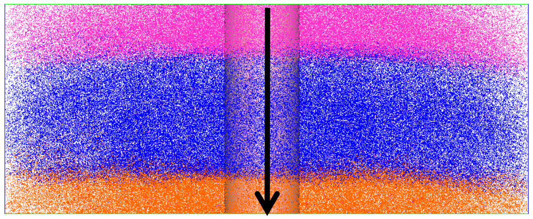
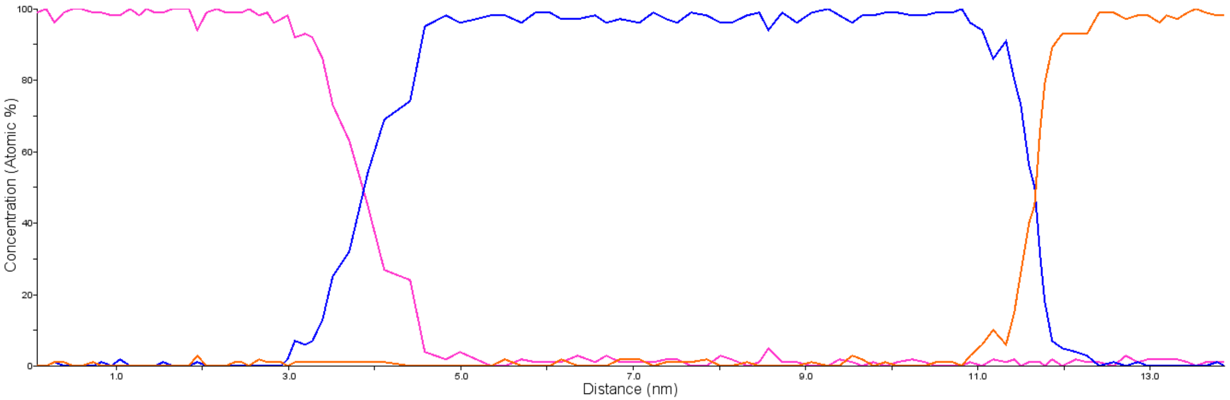
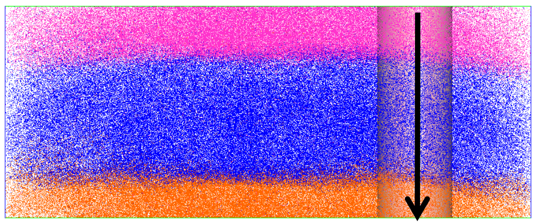
Selected Regions: Interfacial Chemistry

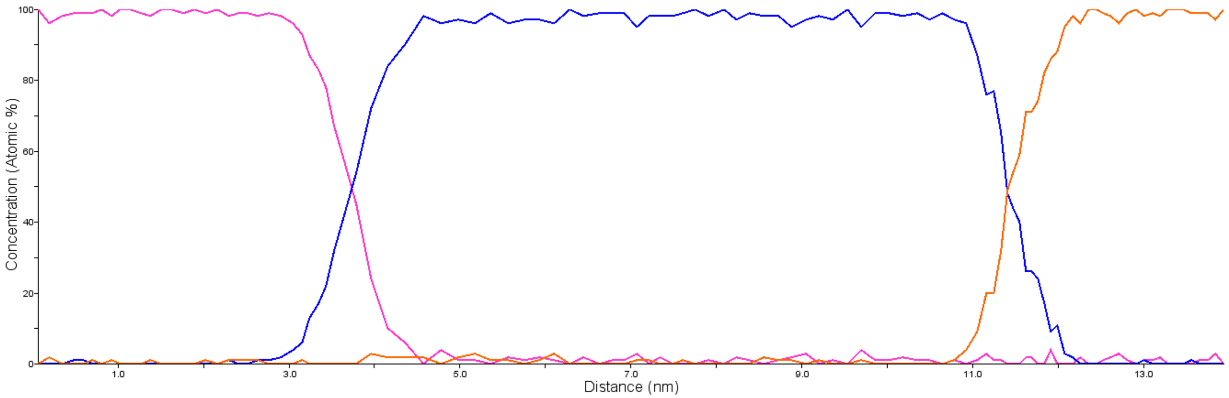












- Composition plotted vs. distance provides estimates of interfacial chemistry

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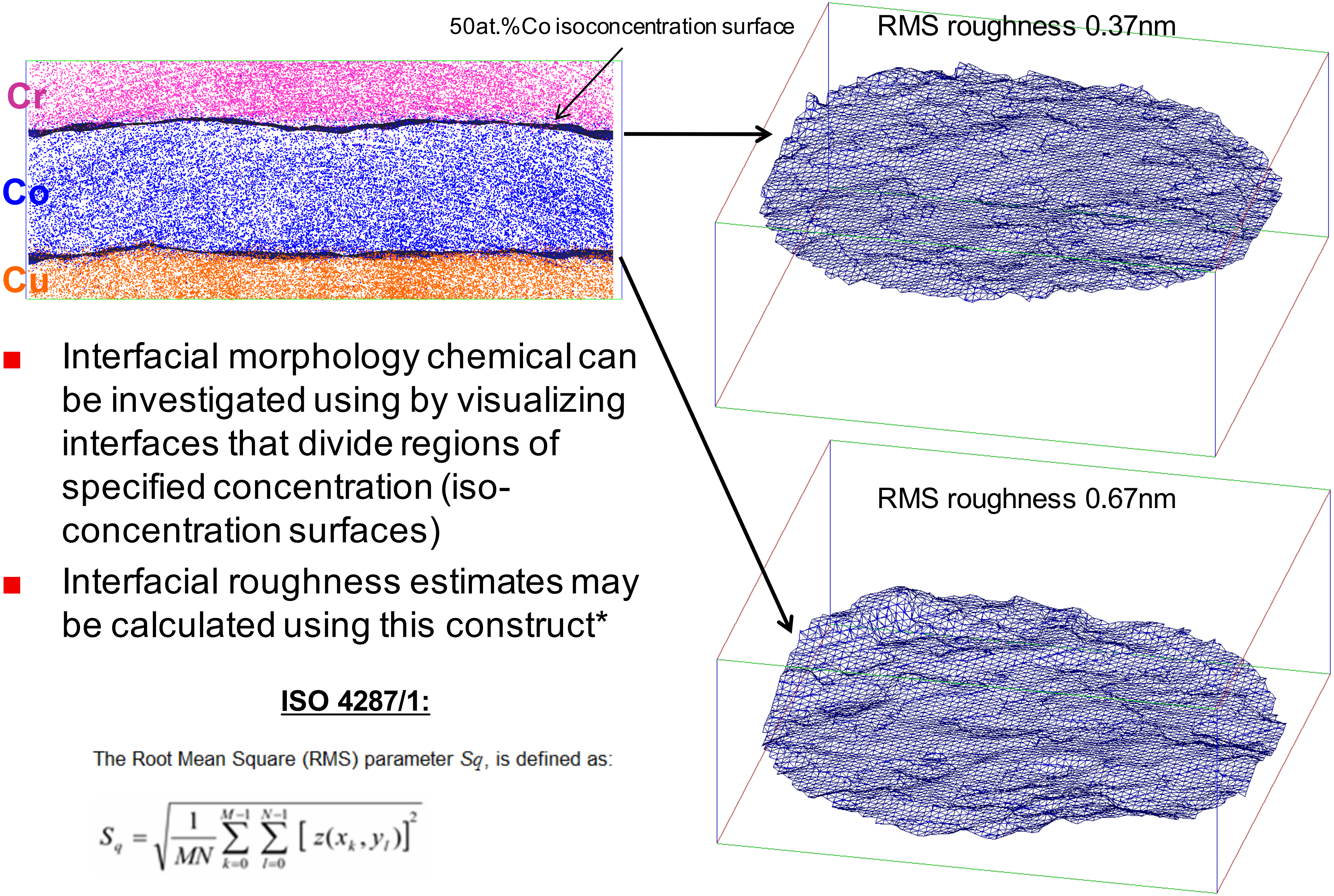
Interfacial Morphology



- Interfacial morphology chemical can be investigated using by visualizing interfaces that divide regions of specified concentration (iso-concentration surfaces)
- Interfacial roughness estimates may be calculated using this construct*

ISO 4287/1:

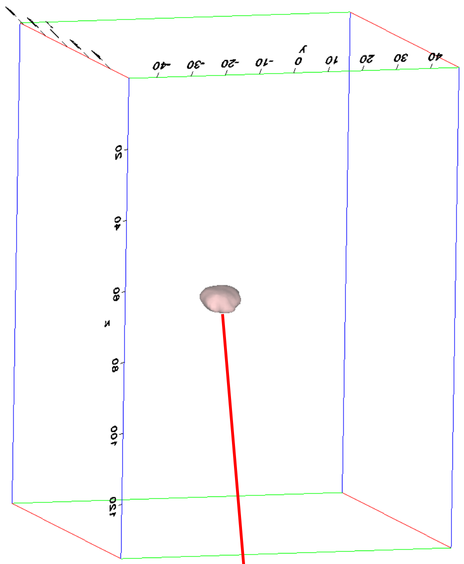
The Root Mean Square (RMS) parameter Sq, is defined as:

$$S_q = \sqrt{\frac{1}{MN}\sum_{k=0}^{M-1}\sum_{l=0}^{N-1}\left[z(x_k, y_l)\right]^2}$$

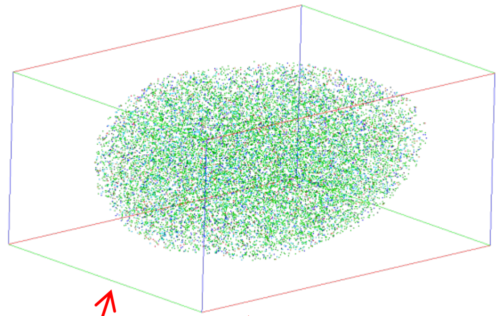
* R. W. O'Neill et al., *Microscopy and Microanalysis* **2006**, 12(S2), 1746CD

Local Compositional Analysis

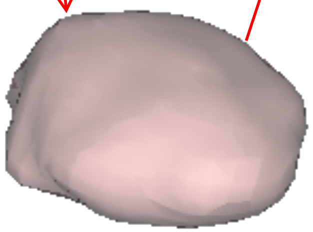
Interface Visualization



Precipitate atoms



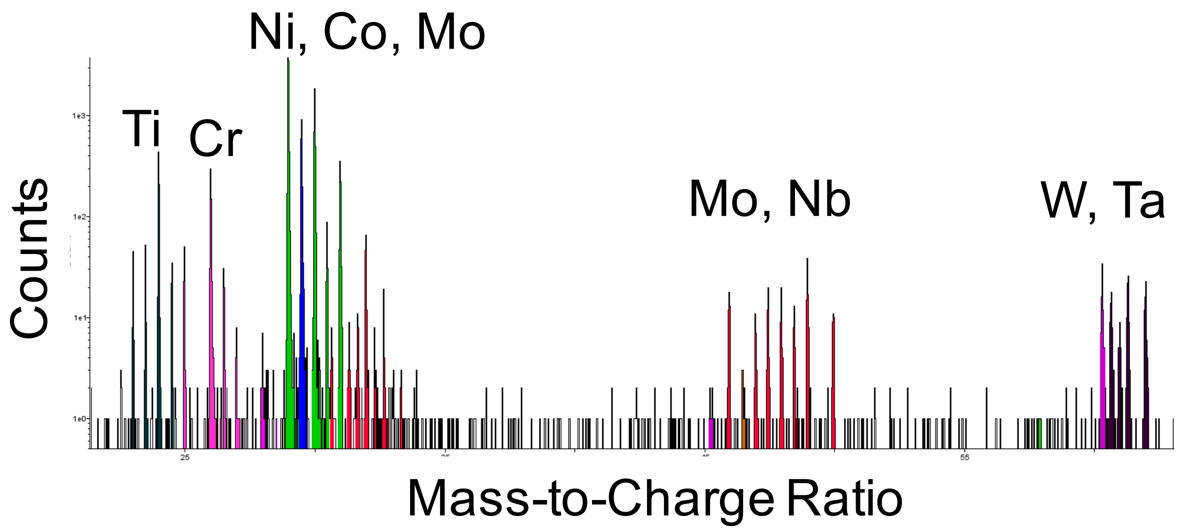
~ 4 nm



Selected area analysis

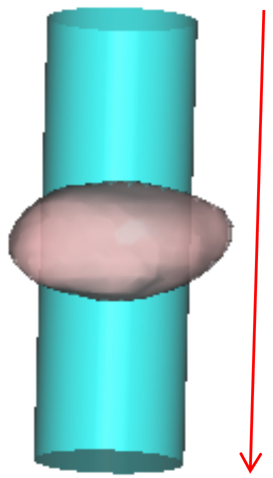
Composition of Particle		
Element	No ions	At %
Ni	11929	62.81%
Al	2777	14.62%
Co	1791	9.43%
Ti	880	4.63%
Cr	679	3.58%
Mo	541	2.85%
W	246	1.30%
Ta	86	0.45%
B	17	0.09%
Fe	16	0.08%
Nb	10	0.05%
Si	9	0.05%

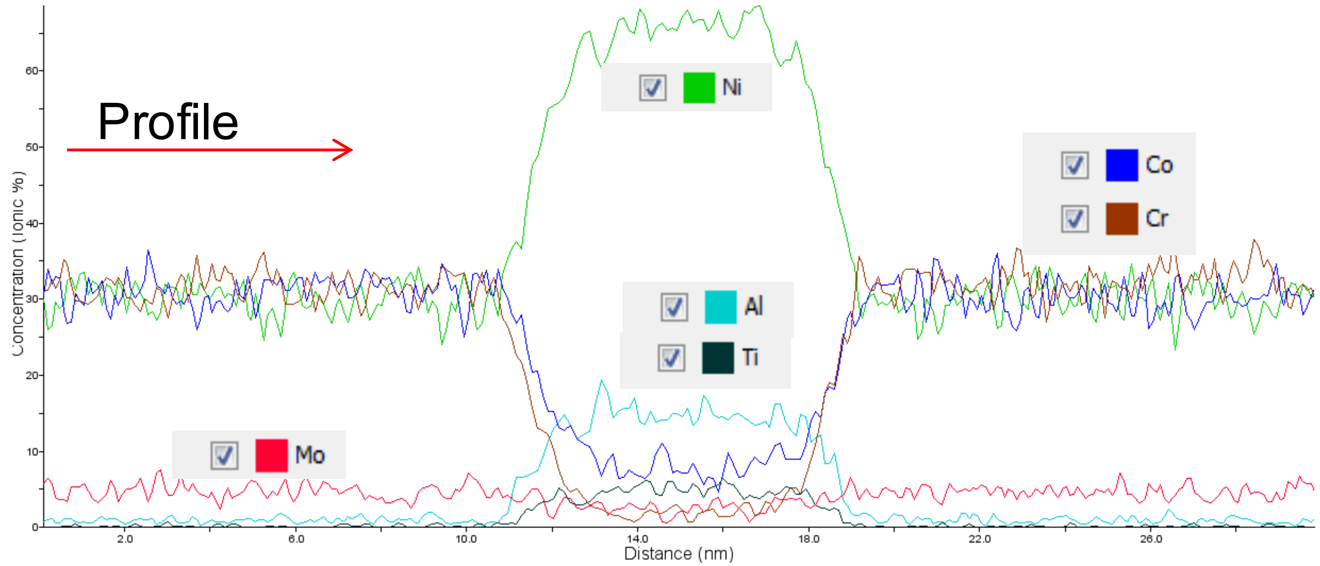
Selected Area Mass Spectrum



Compositional Profiling: 1-D and Proxigram

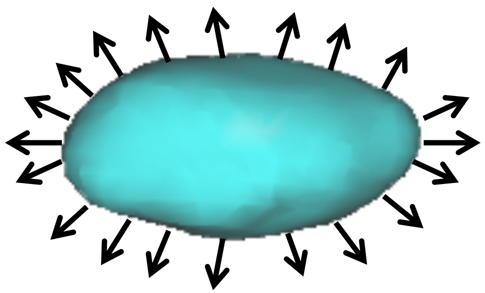
Traditional 1-D profile

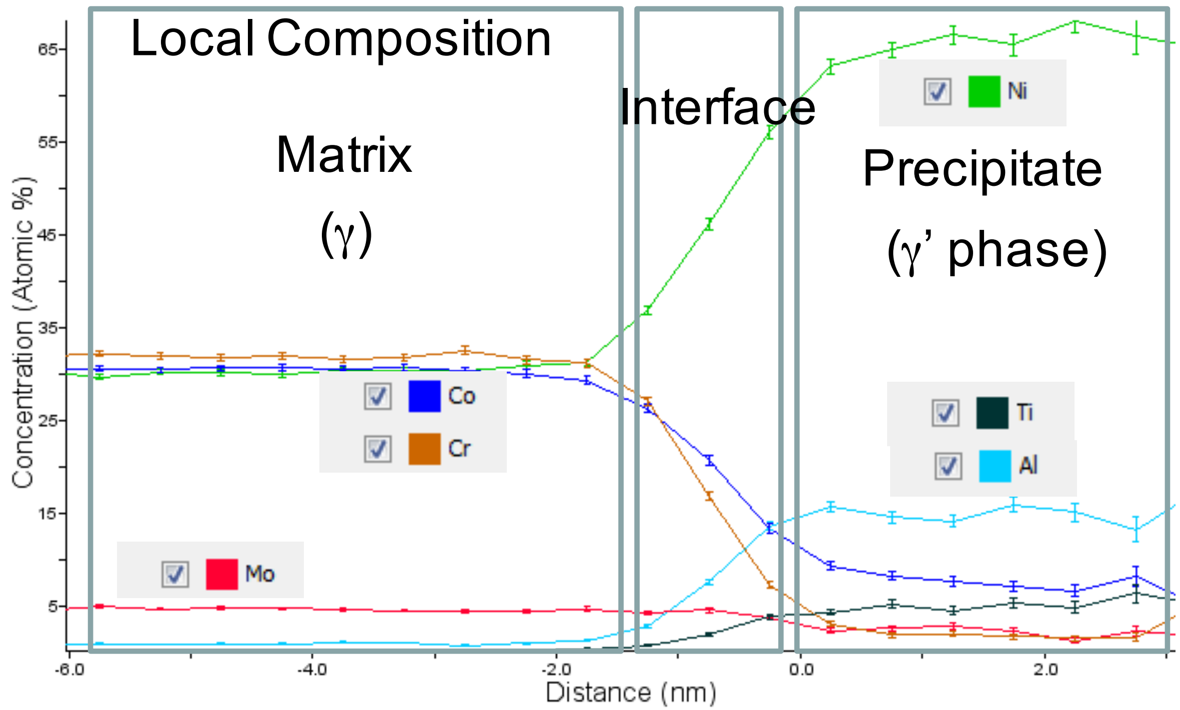




Proximetry Histogram (Proxigram*) Method

~ 4 nm

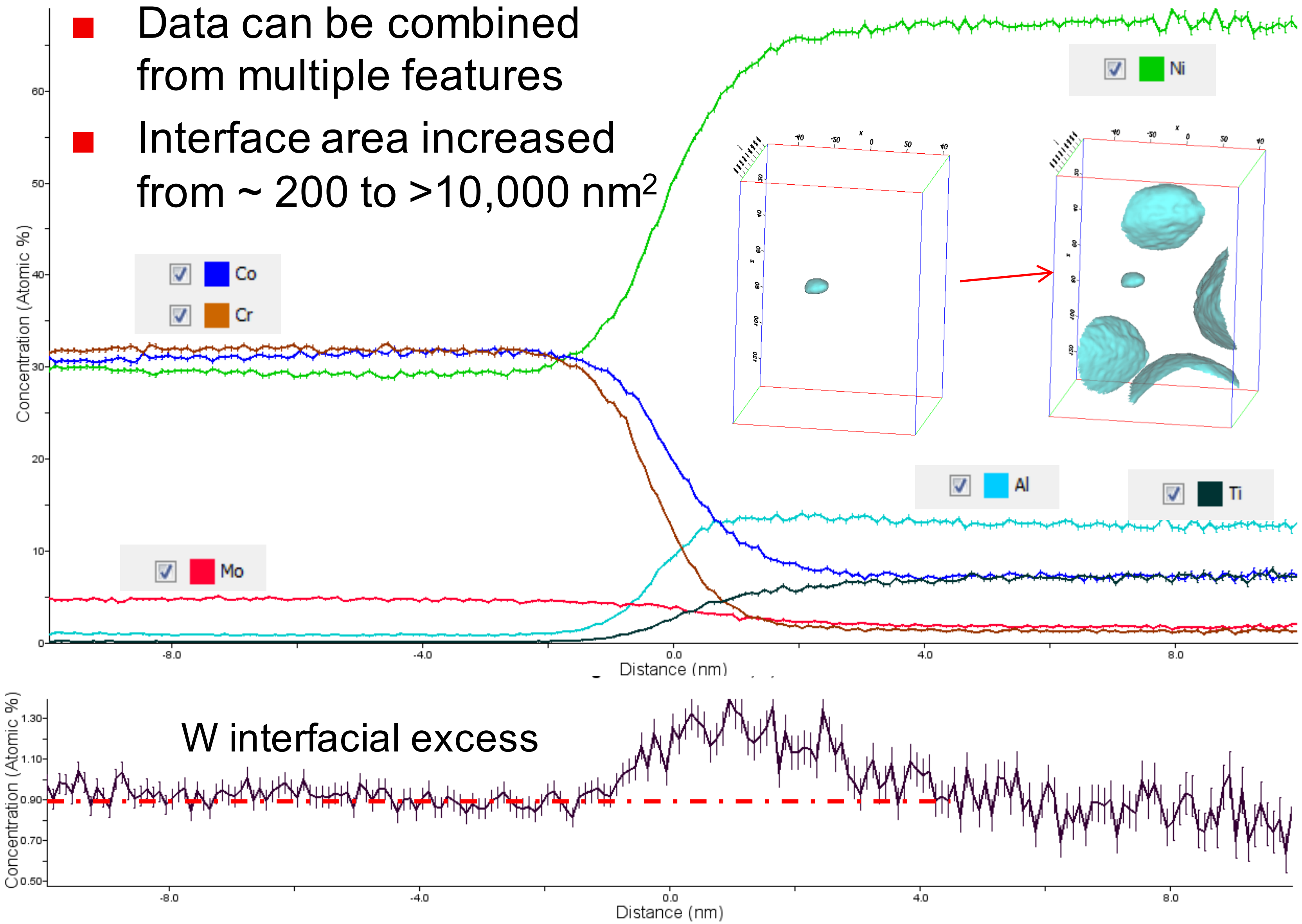




*O. C. Hellman et al., Microsc. Microanal. 6 (2000) 437

Compositional Profiling: Proxigram Advantages

- Data can be combined from multiple features
- Interface area increased from ~ 200 to >10,000 nm^2



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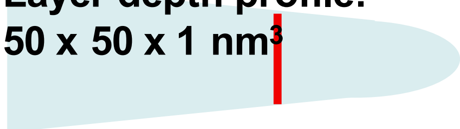
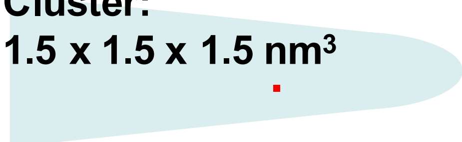
Detection Limit & Accuracy

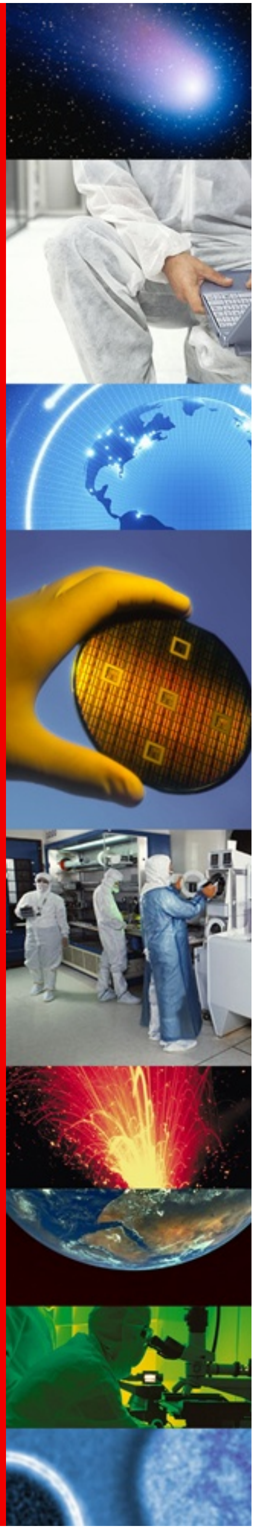
- **Analytical Sensitivity metrics based on #atoms/volume fail for small volumes**
- **Atom Fraction metrics (appm, appb) fail for small numbers of atoms**

- Example:

Boron-doped silicon (d = 50 at/nm3). Analyzer efficiency: 60%
Detection limit arbitrary defined as 10 detected ions .

Application	**Atomic conc.**	**Nb of atoms**	**Nb of ion detected (N)**	**Statistical accuracy +/- √(N)**	**DL for 10 ions**
“bulk” (!) analysis: **50 x 50 x 100 nm^3** 	100 at% 1 at% 100 ppm	1.25E7 1.25E5 1250	7.5E6 7.5E4 750	100 +/- 0.04 at% 1 +/- 0.004 at% 100ppm +/- 4 ppm	1.3 ppm (= 0.00013 at%)
Layer depth profile: **50 x 50 x 1 nm^3** 	100 at% 1 at%	1.25E5 1250	75000 750	100 +/- 0.4 at% 1 +/- 0.04 at%	130 ppm (= 0.013 at%)
Cluster: **1.5 x 1.5 x 1.5 nm^3** 	100 at% 1 at%	169 1.7 (?)	101 1 (?)	100 +/- 10 at% Not detectable	10 at%

- **Detection limit will also depend on mass resolution, noise level, number of isotopes and charge states, etc…**



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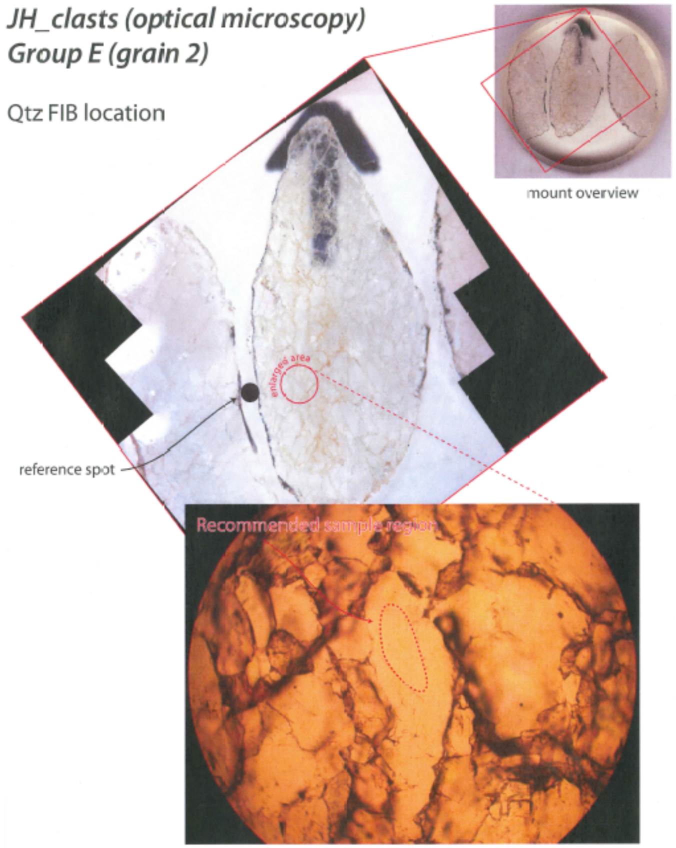

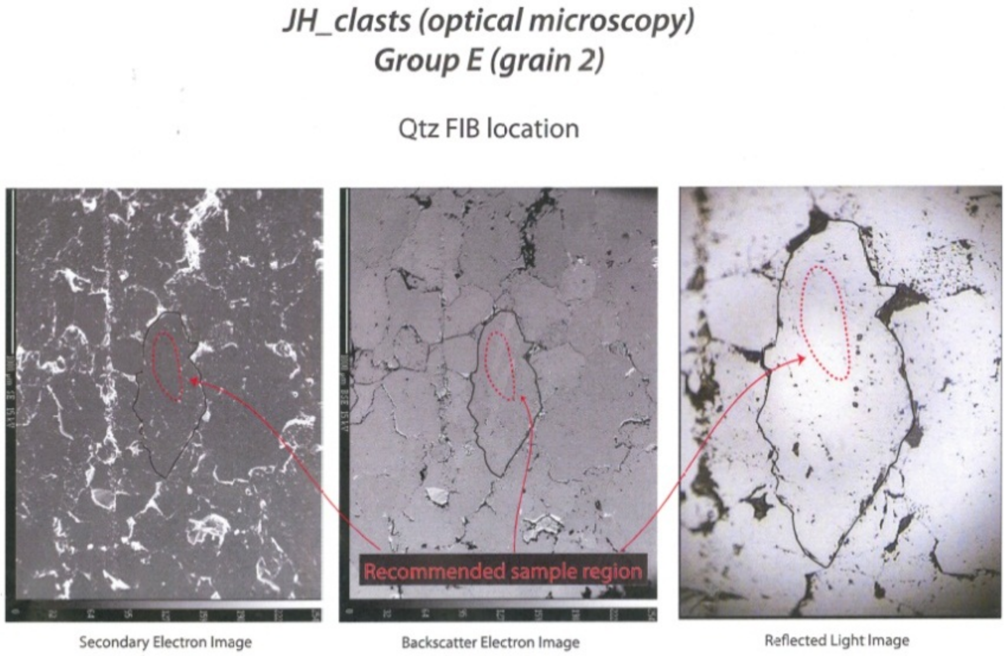

- Collaboration with Prof. Bruce Watson (Department of Earth & Environmental Sciences, Rensselaer Polytechnic Institute)
- Interested in the spatial distributions of trace elements K and Mg in the glass
- Specimen preparation using focused ion beam milling allows site specificity

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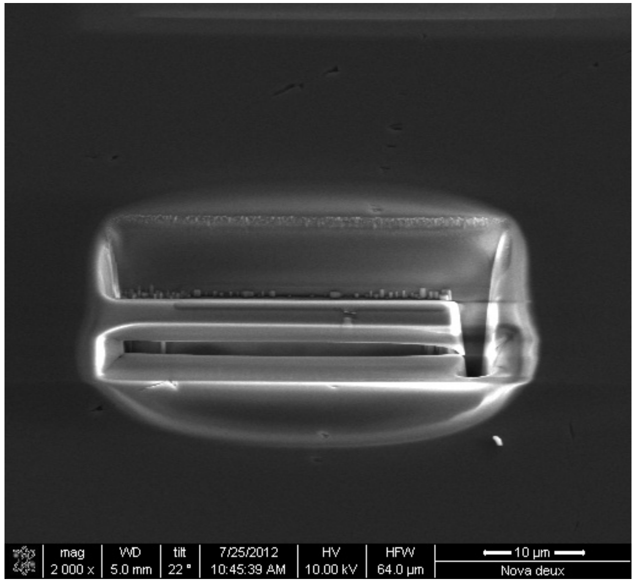
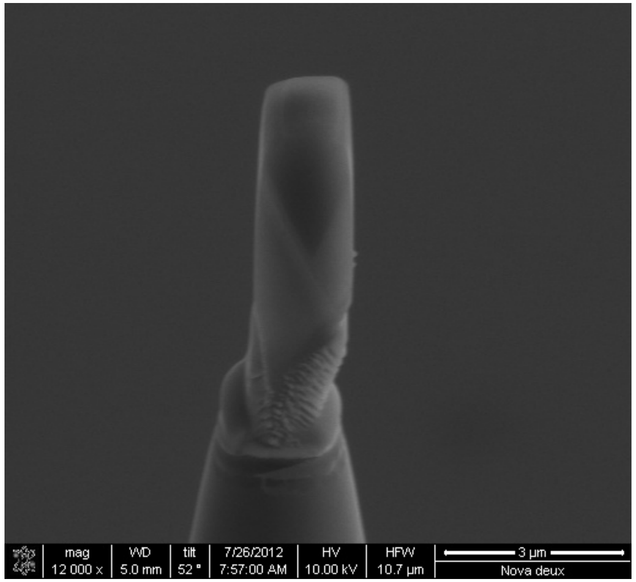
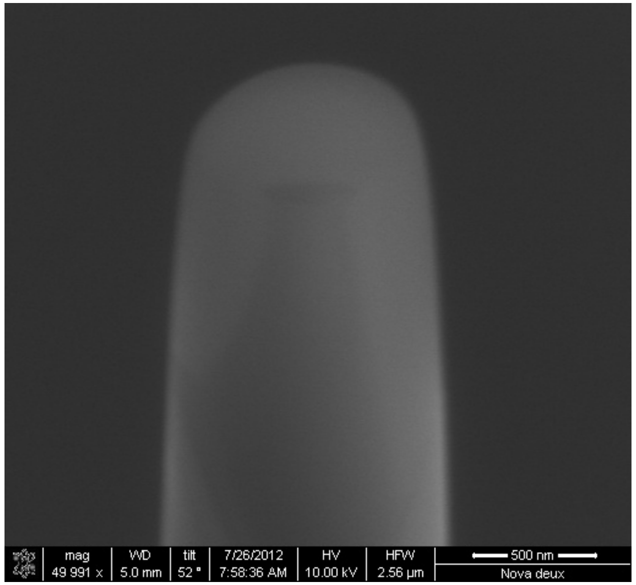
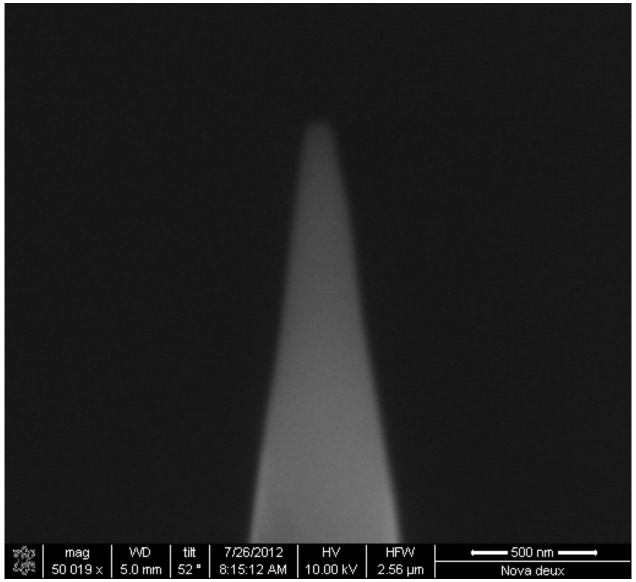
Specimen Preparation by Focused Ion Beam Milling*

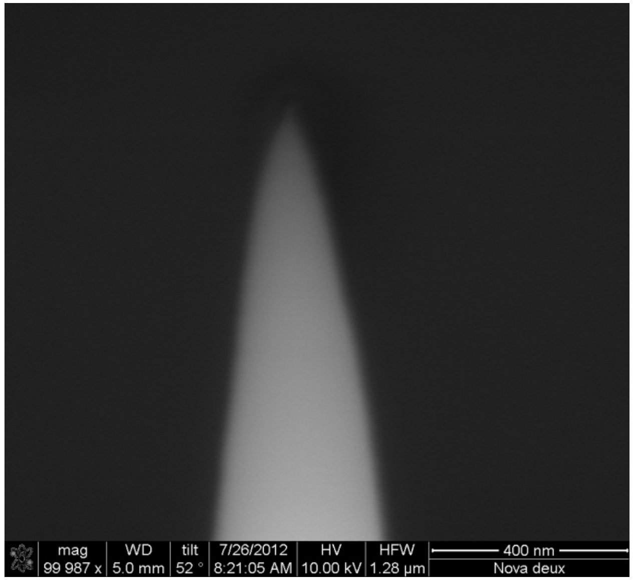




- Sections of the specimen wedge were mounted to a series of microtip posts
- Each specimen was then sharpened through a series of annular mills to form the final specimen tip (below)







* D. J. Larson et al., “Atom Probe Tomography for Microelectronics”; in *Handbook of Instrumentation and Techniques for Semiconductor Nanostructure Characterization*, World Scientific Publishing (2011) p. 407.

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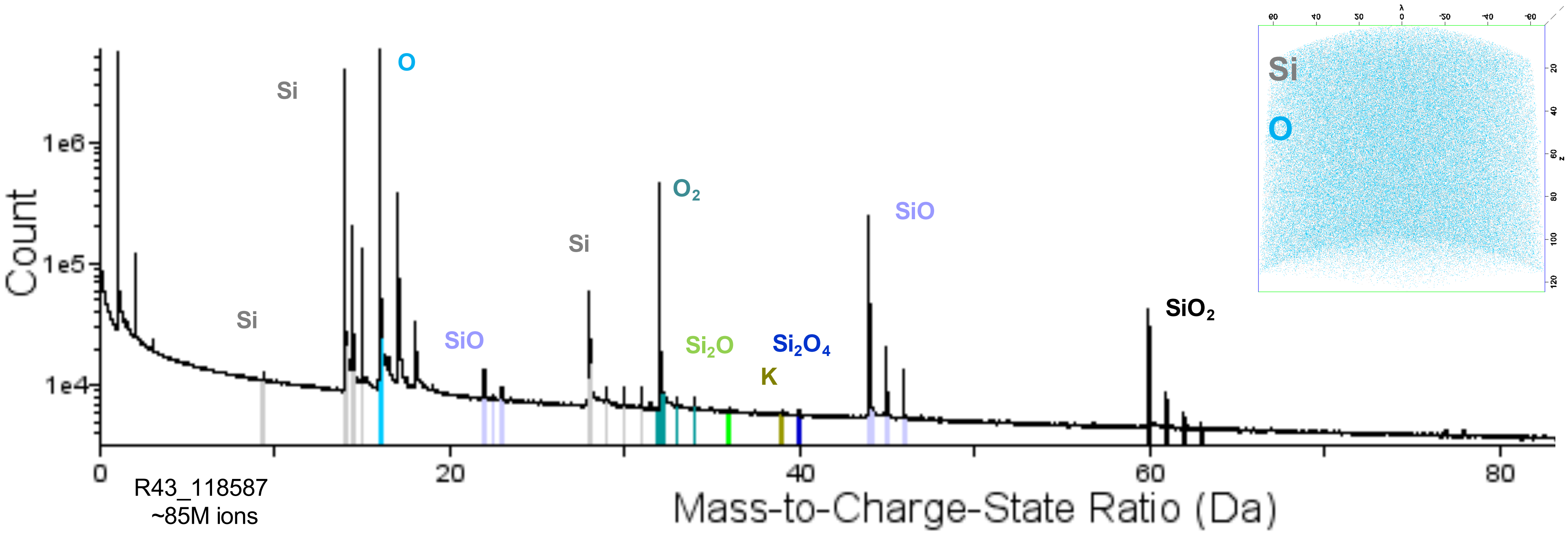
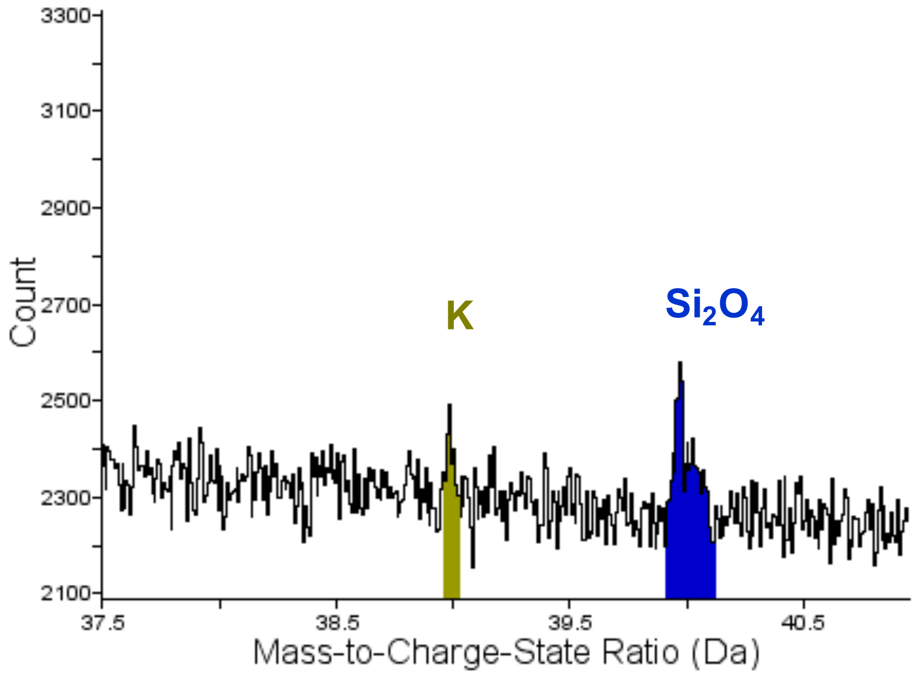
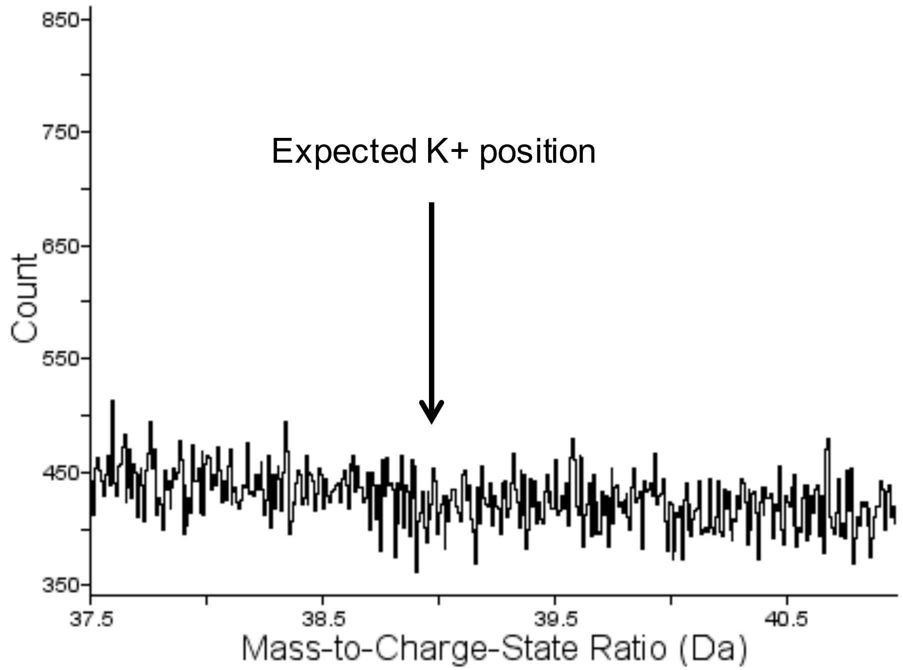
Quartz Mass Spectrum



- All data were acquired with the LEAP 4000XHR, with a detection rate from 0.2 to 0.5%, a laser energy from 150 to 700pJ, a base temperature of 50K and a frequency of 200kHz.
- Most prominent peaks can be identified as Si and O ions or as ions containing combinations of these species such as SiO, SiO_2 (referred to as complex ions)
- Small peaks can also be observed between the primary peaks and have been identified as individual or complex ions which include K and Mg (see following slides)

Trace Elements Analysis: K





- Low level (~60ppm) of K was observed in the K^+ charge state in the R43_118587 data set
- No K was observed in the other data sets (above, right, R43_118569)
  - Given the background level of this data set, as much as 30ppm K could be present in the 1+ charge state and still be obscured by the background level
- No K peaks were observed in the 2+ or 3+ charge states in any of the data sets (not shown)

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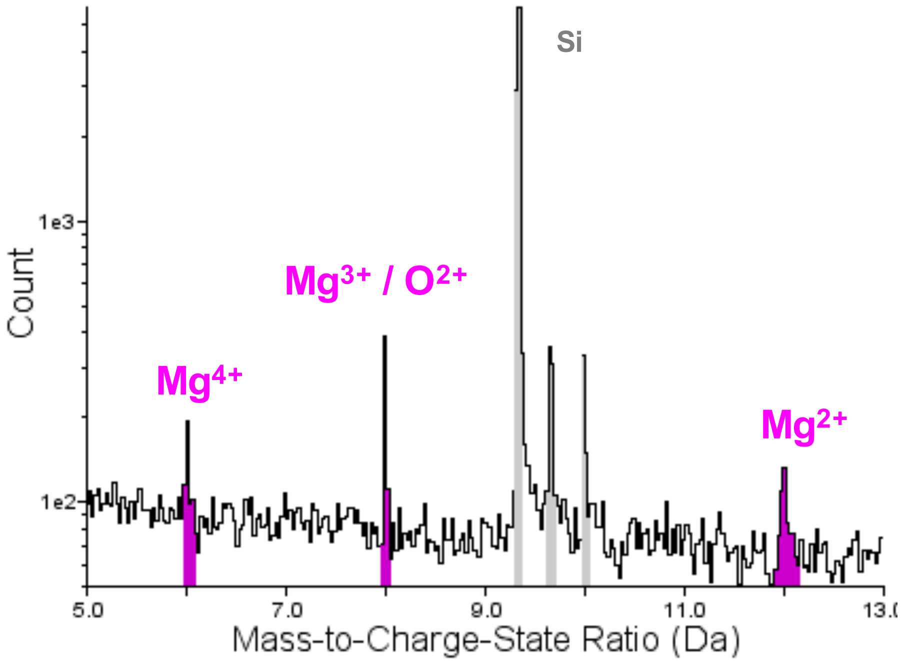
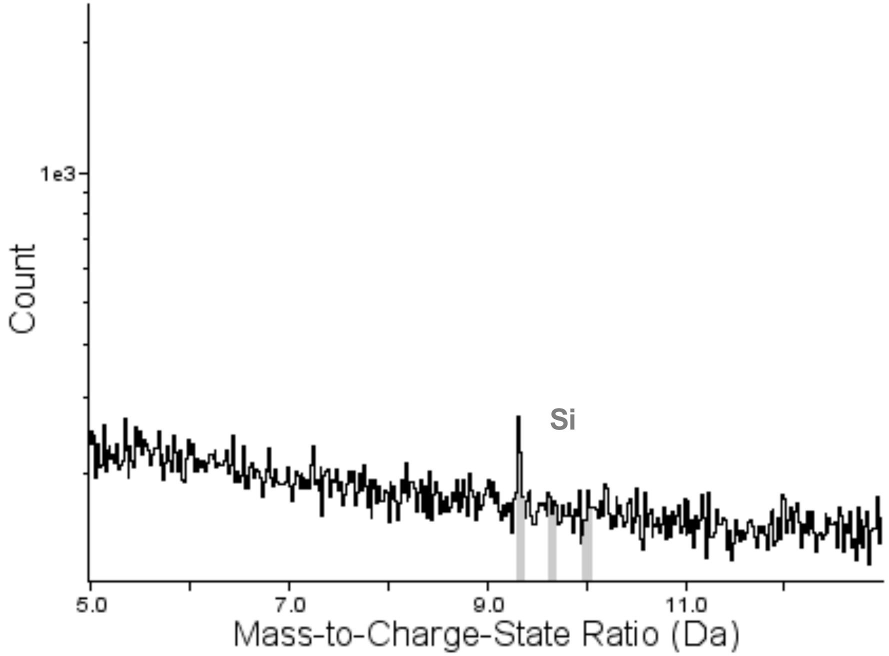
Trace Elements Analysis: Mg





- Mg peaks were observed only 1 data set (R43_118568, above, left)
- The other 3 data sets showed no indication of Mg (above, right, R43_118584)
- At 8Da, there is a possible overlap between O^{2+} and Mg^{3+}

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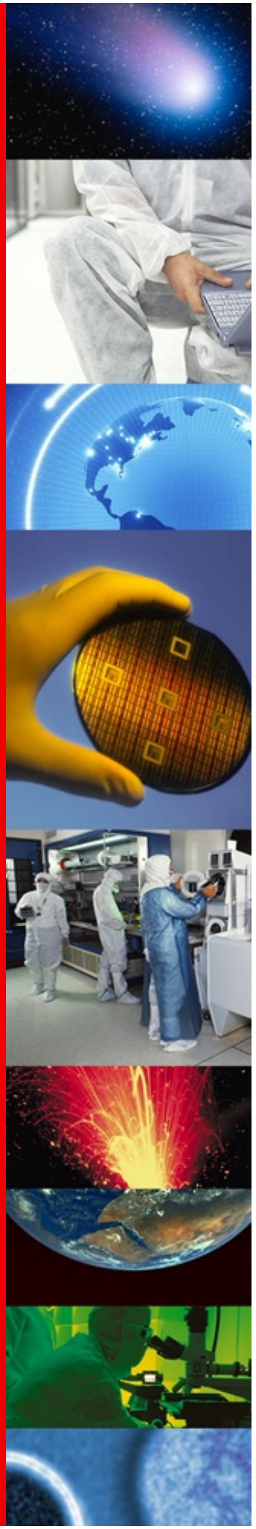

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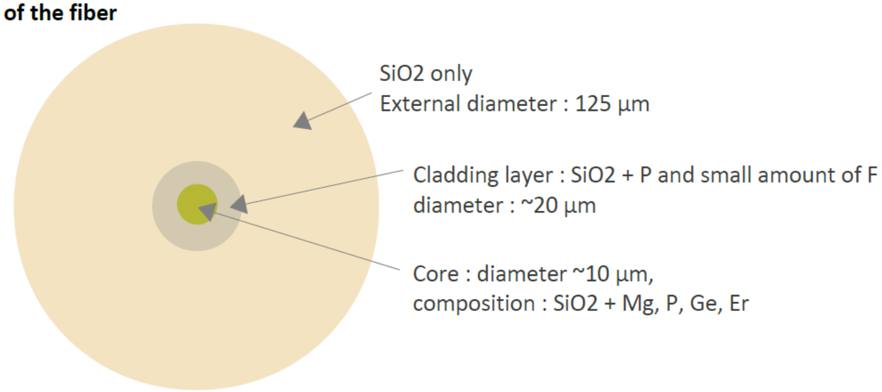
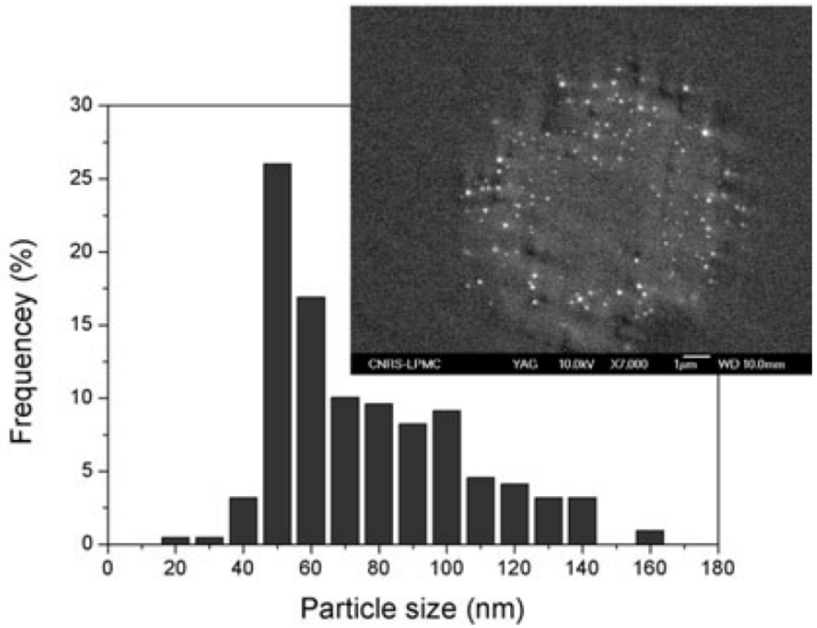
Low Level Dopants in Optical Fibers

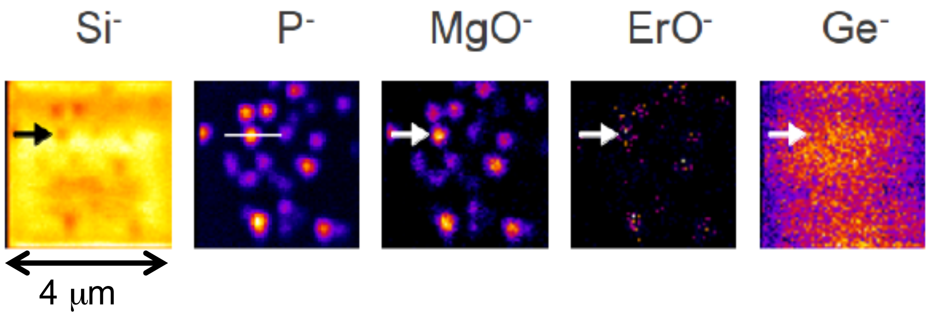
Structure of the fiber



Particle Distribution (SEM)*



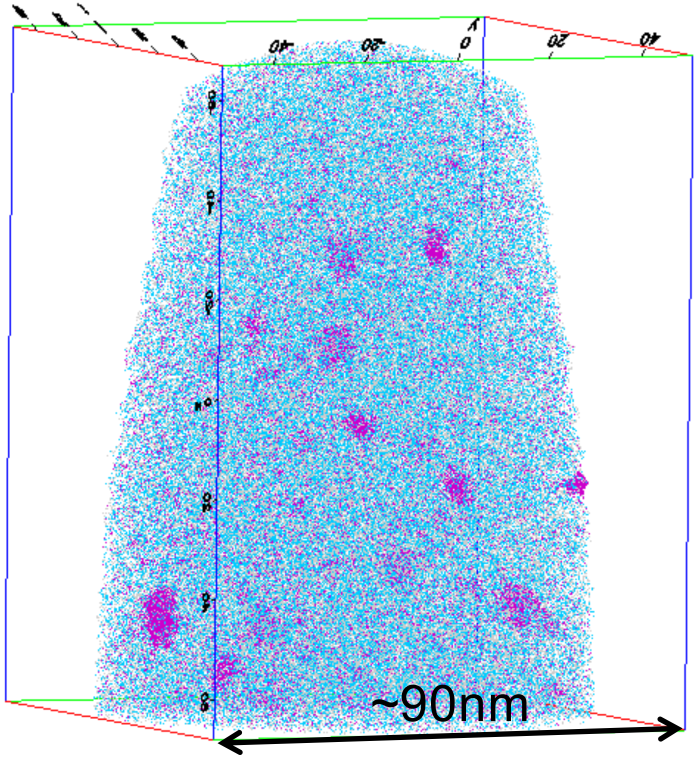
NanoSIMS of Particles**

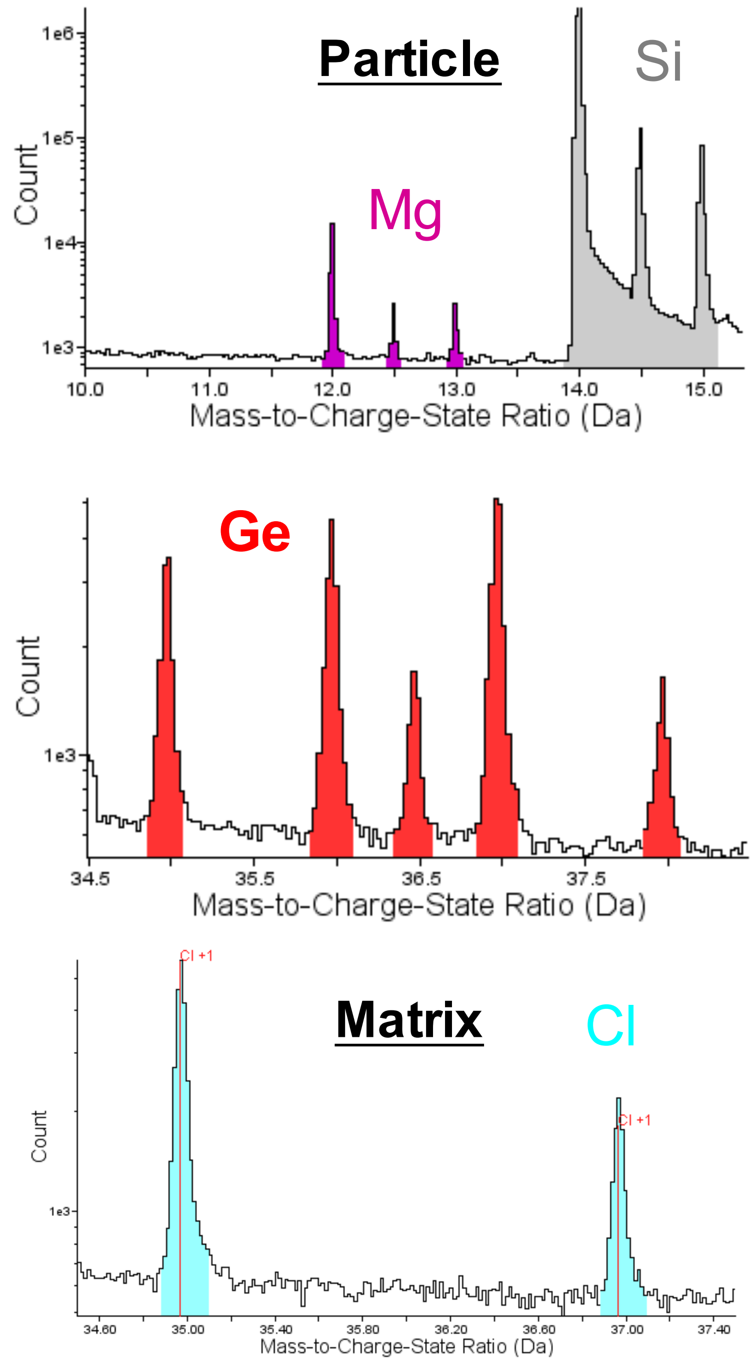


- Collaboration with Prof. Wilfried Blanc (CNRS, Nice FRANCE)
- Ge and P are added to increase refractive index
- Er (contained in Mg nanoparticles) at ~100ppm modifies the fluorescence properties
- The level of Mg determines the size distribution of the nanoparticles
- Minimal information from very small particles (<20nm)

* W. Blanc et al., J. Am. Ceram. Soc. 94(8) 2011 2315
** W. Blanc et al., Optical Materials Express 2(11) (2012) 1504

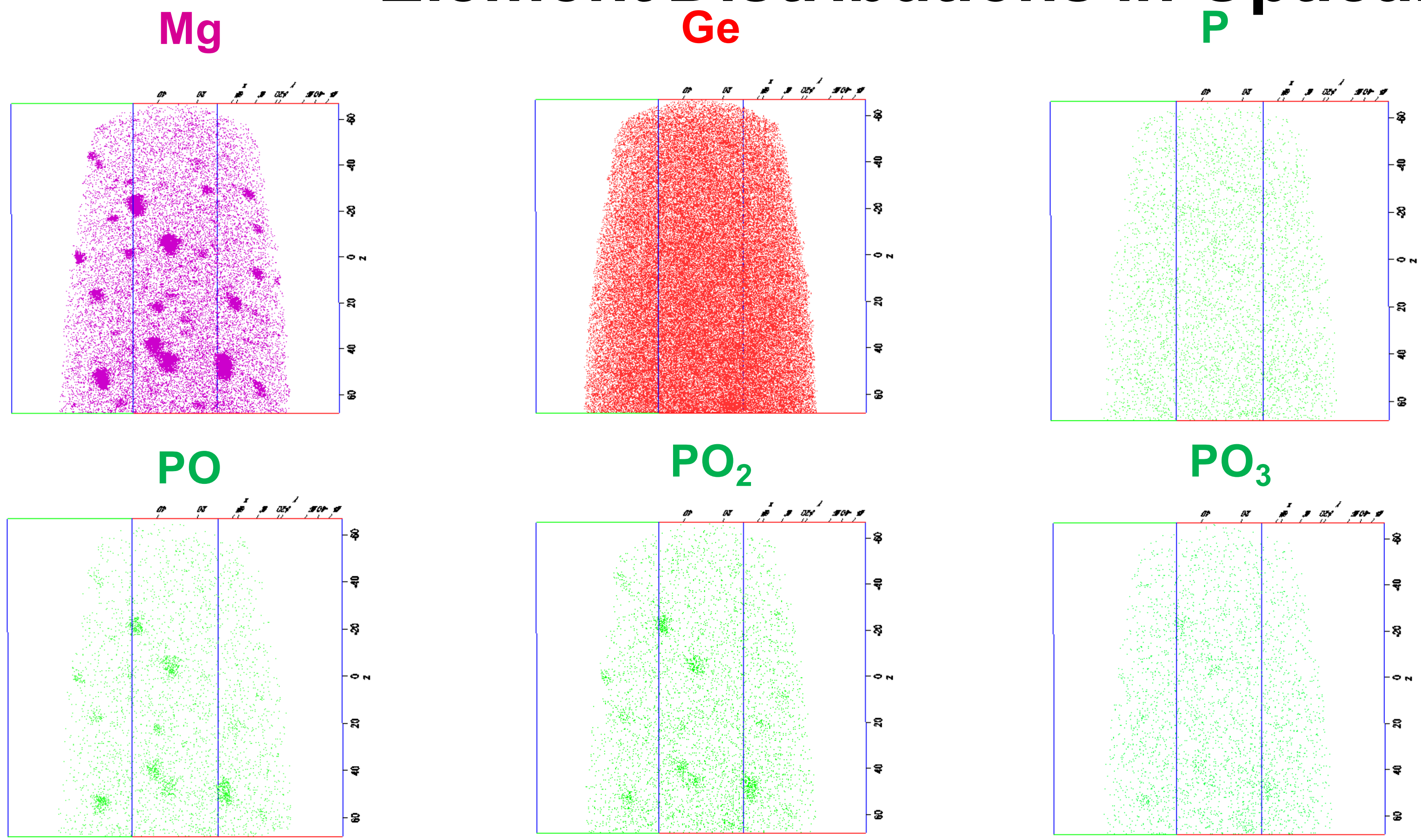
APT of Core & Matrix of Optical Fiber





- Atom probe analysis was performed both in the matrix and in the core of the fibers
- Mg, Ge, Cl, P observed

Element Distributions in Optical Fiber



- The elemental distribution for Mg, Ge, P and P(O)x are shown on top
- Six ‘large’ particles of Mg are detected as well as 29 ‘smaller’ particles
- Ge appears uniformly distributed
- P seems appears enriched in some of the largest particles

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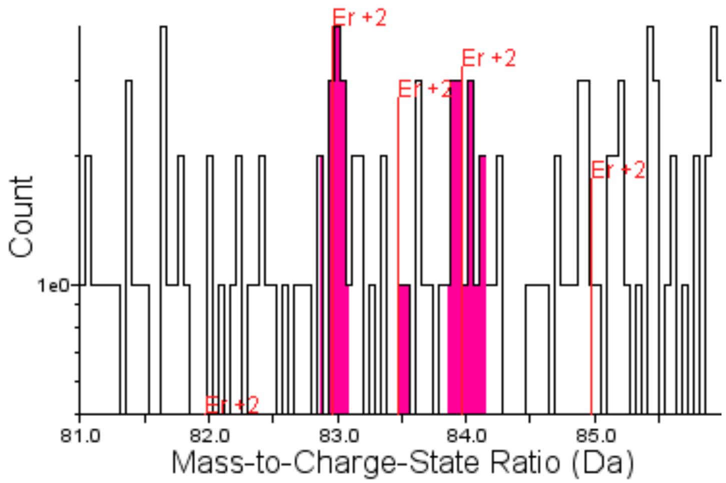
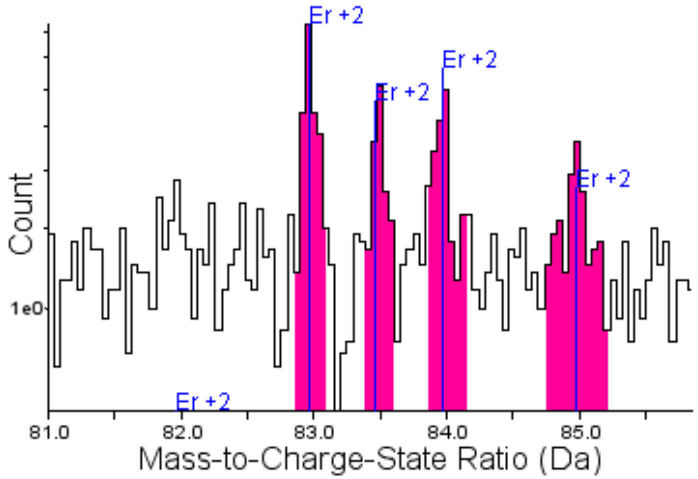
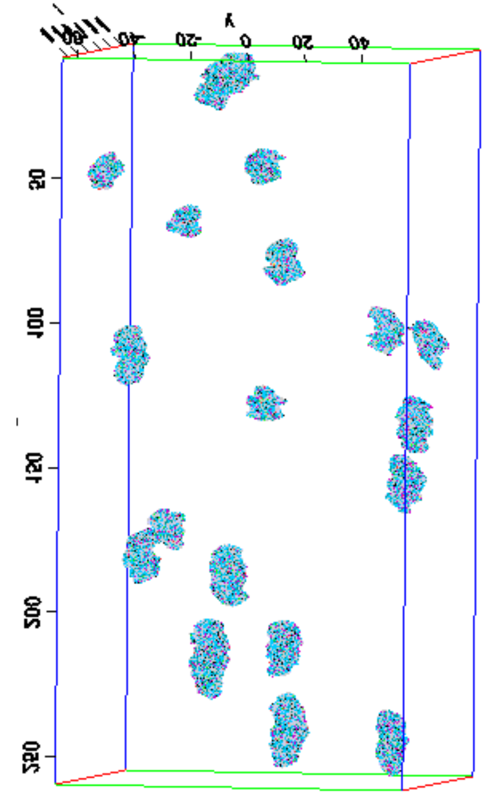
Can we Find the Er??

<u>**Selected Particles <100nm^3**</u>



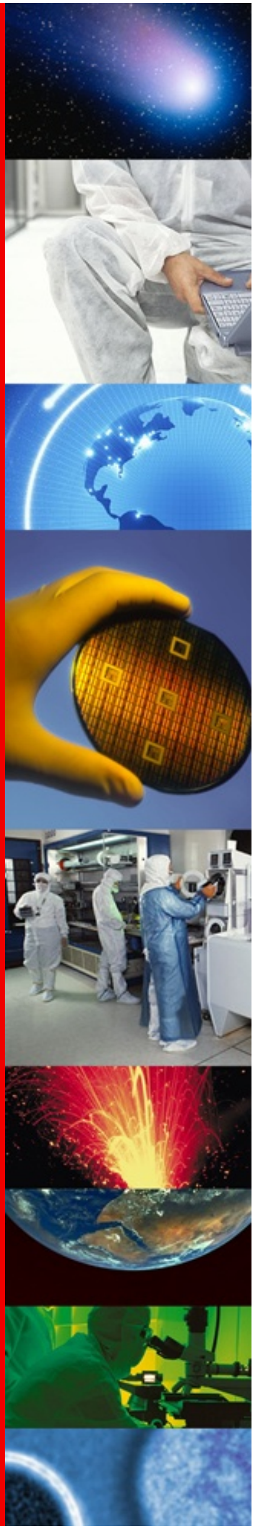
<u>**Selected Particles >400nm^3**</u>





	Si	O	Mg	Ge	P	Er	Cr
M08	35.1	58.4	5	0.4	0.8	0.1	0.07

- The Er is believed to be in the Mg particles
- Because of its low content, it did not appear in the mass spectrum of the complete analysis
- In a selection of the largest particles (>400nm^3) the Er peaks appear more clearly in the mass spectra (above, right)
- For comparison, the mass spectrum of the particles <100nm^3 is shown above left
- The average concentration of all the particles are given in the top table



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Applications

Alumina

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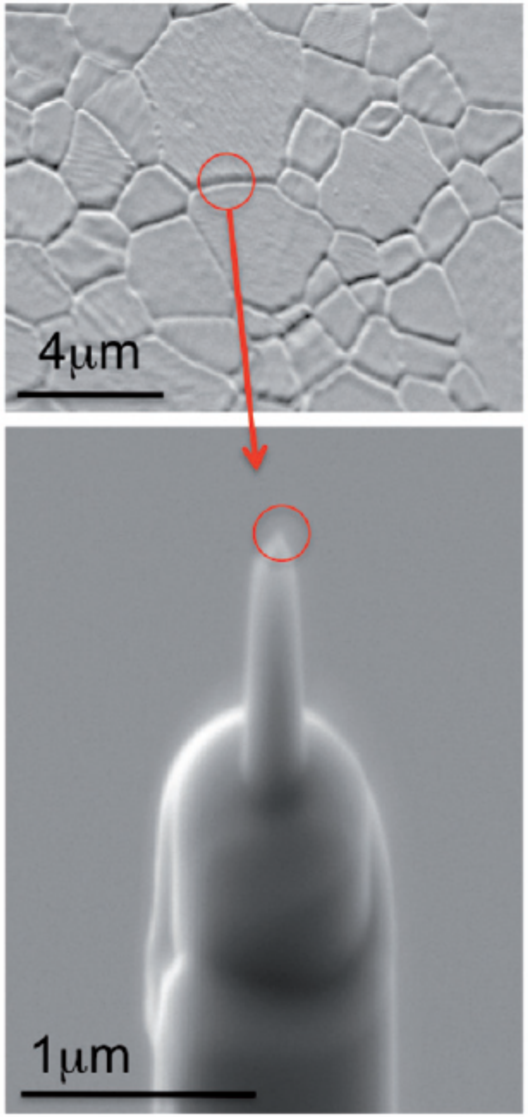
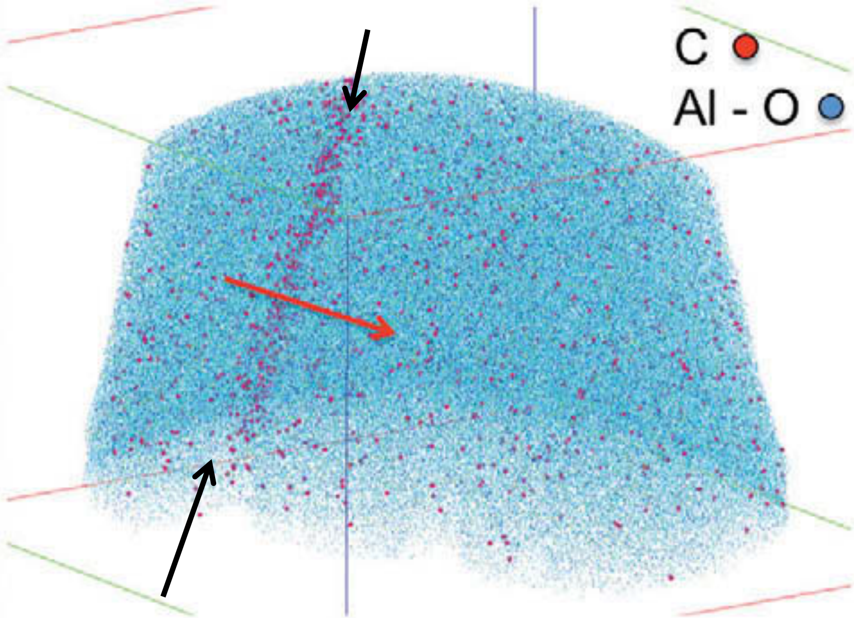
Functional Electrically Insulating Materials: Alumina

Emmanuelle A. Marquis[a]*, Noor A. Yahya[a], David J. Larson[b], Michael K. Miller[c], Richard I. Todd[a]
[a] Department of Materials, University of Oxford, Oxford, United Kingdom
[b] Cameca Instruments Inc., Madison, WI
[c] Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, TN
42 materialstoday OCTOBER 2010 | VOLUME 13 | NUMBER 10

Specimen Preparation



- SiC additions improve the mechanical properties of alumina although the particle volume fraction is not high - at room temperature alumina/SiC nanocomposites exhibit a change in fracture mode from inter- to trans-granular, and better wear resistance compared to un-reinforced alumina
- Can APT determine the location of the C in this material? This analysis is challenging for TEM.



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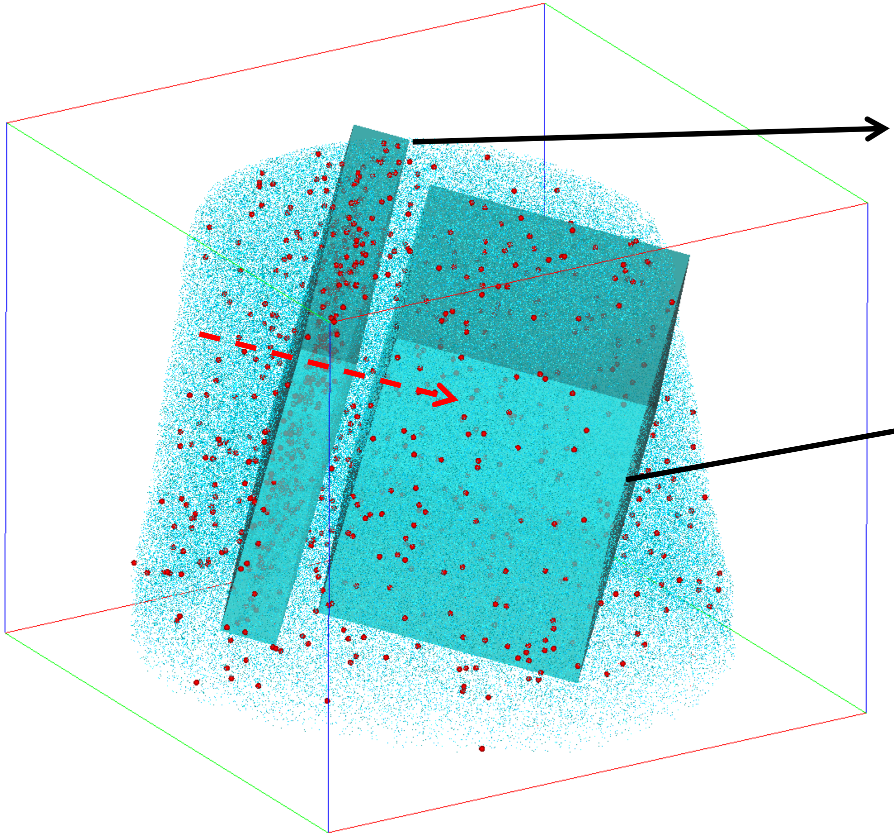
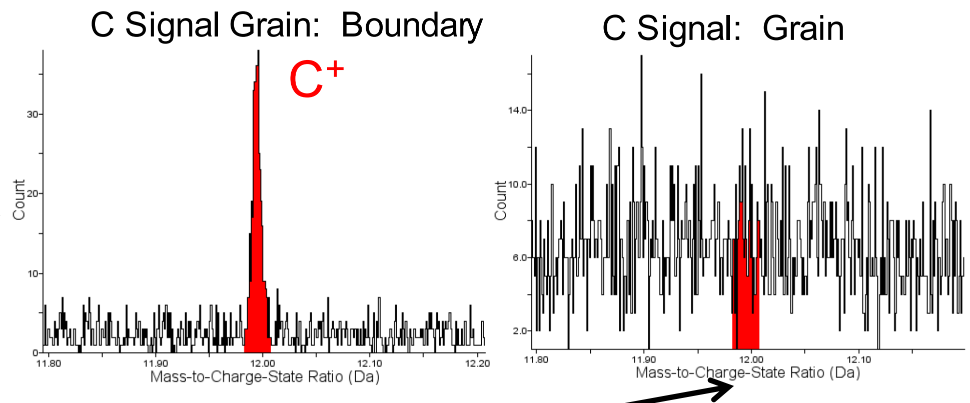
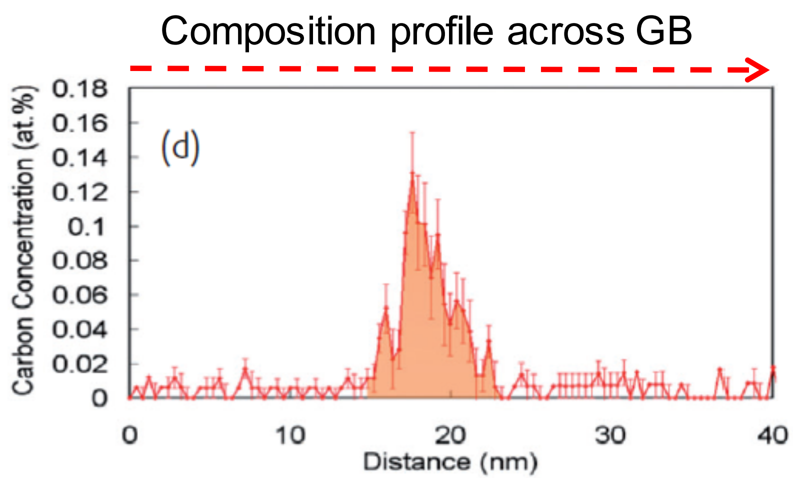
Functional Electrically Insulating Materials: Alumina







- The level of carbon segregation at grain boundary shown at right is 1.5±0.5 atom/nm2 (corresponding to the shaded area in (d))
- No measureable carbon is found within the alumina grains (detection sensitivity limits ~ 40 ppm).

42 materialstoday OCTOBER 2010 | VOLUME 13 | NUMBER 10

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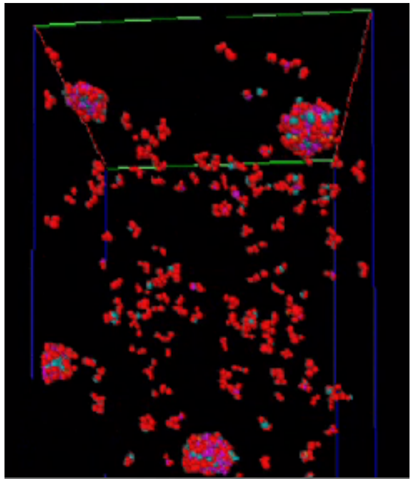
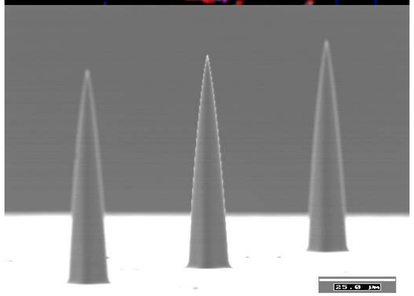
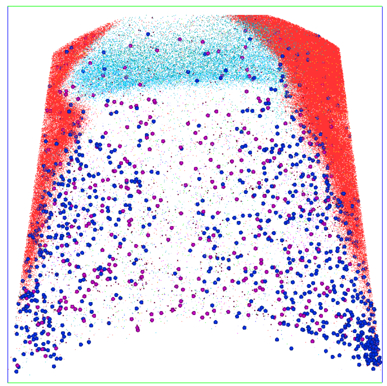
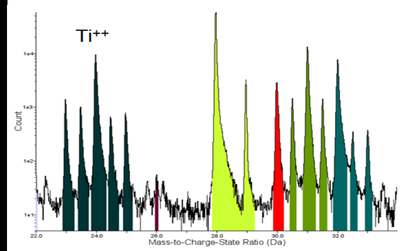
Summary

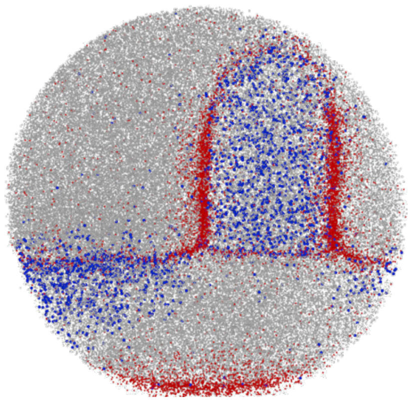
- **Atom probe tomography provides** *atomic-scale* *compositional* **characterization at** *high sensitivity* **in** *3D*
  - Key for the characterization of ***buried interfaces***
- **Site-specific lift-out and APT technology enables many new applications**
  - Materials research
  - Semiconductor device development
  - Competitive analysis, Failure analysis
  - Organic materials analysis is coming
- **Advances in APT technology are moving toward Atomic-Scale Tomography**

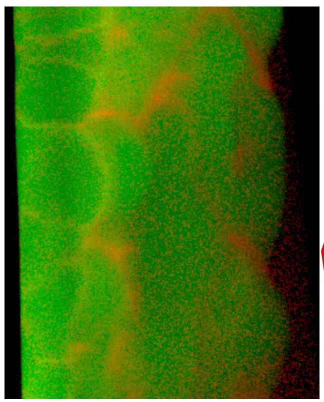


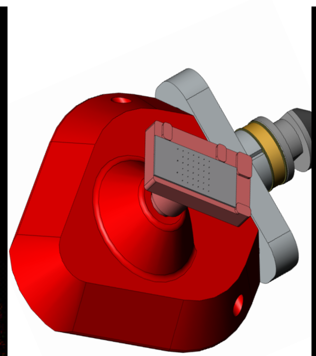


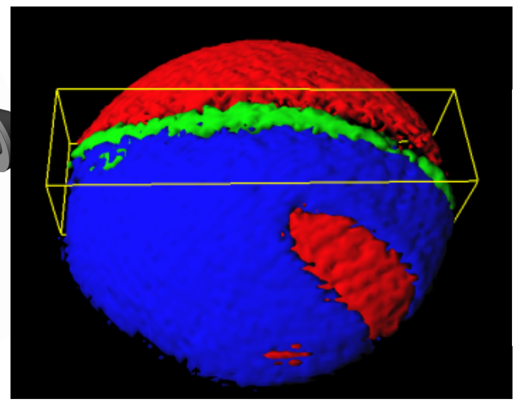












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Acknowledgements

- T. F. Kelly, D. Lawrence, D. Olson, R. M. Ulfig, and I. Martin (CAMECA)
- B. Watson (Rensselaer Polytechnic Institute, Troy, NY USA)
- W. Blanc (CNRS, Nice FRANCE)

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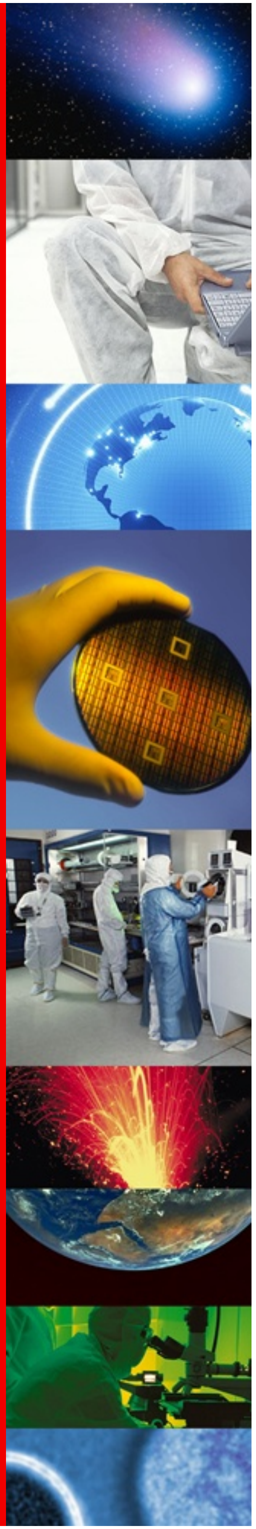

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From Earth

Collaboration with Prof. J. W. Valley and Dr. T. Ushikubo
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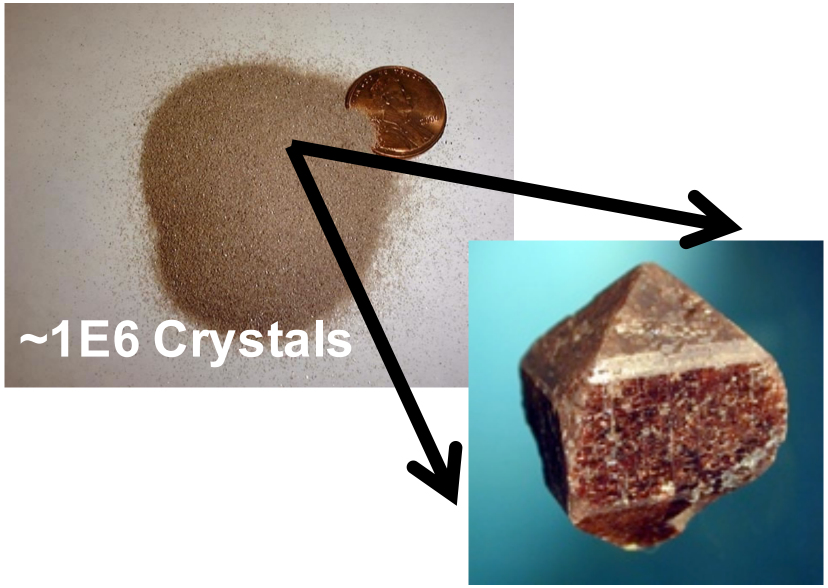
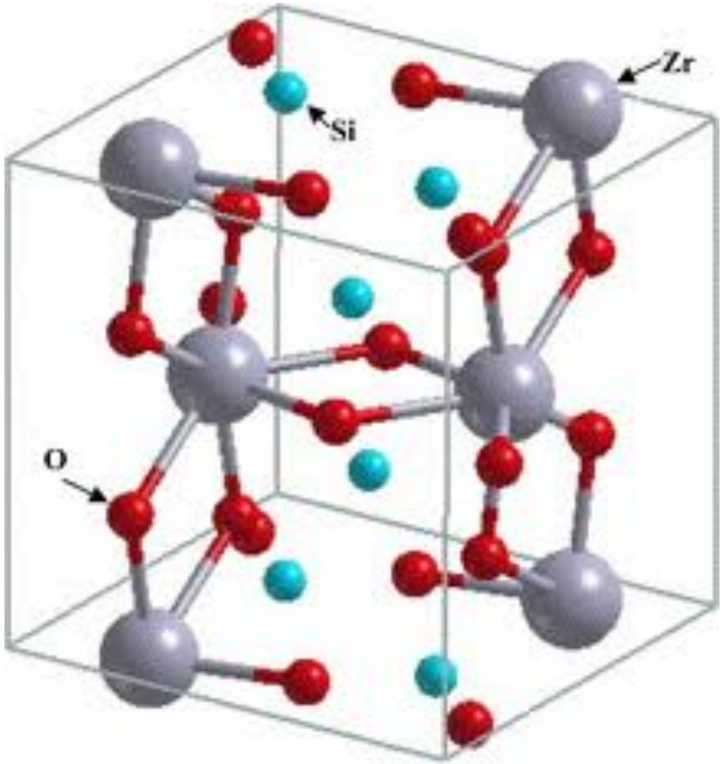
What is a Zircon?



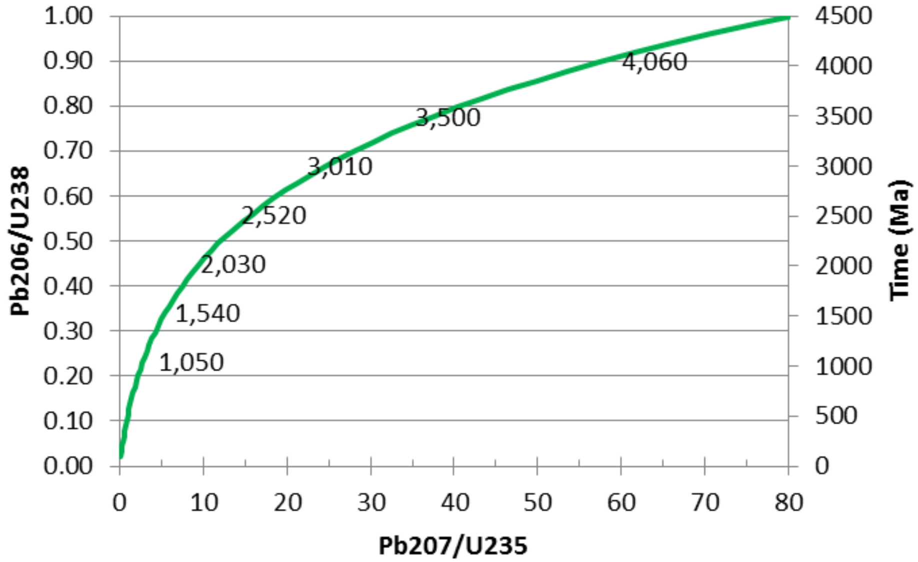


Ion	Radius Å
$^{VIII}Zr^{+4}$	0.84
$^{VIII}U^{+4}$	0.95
$^{VIII}Pb^{+2}$	1.29

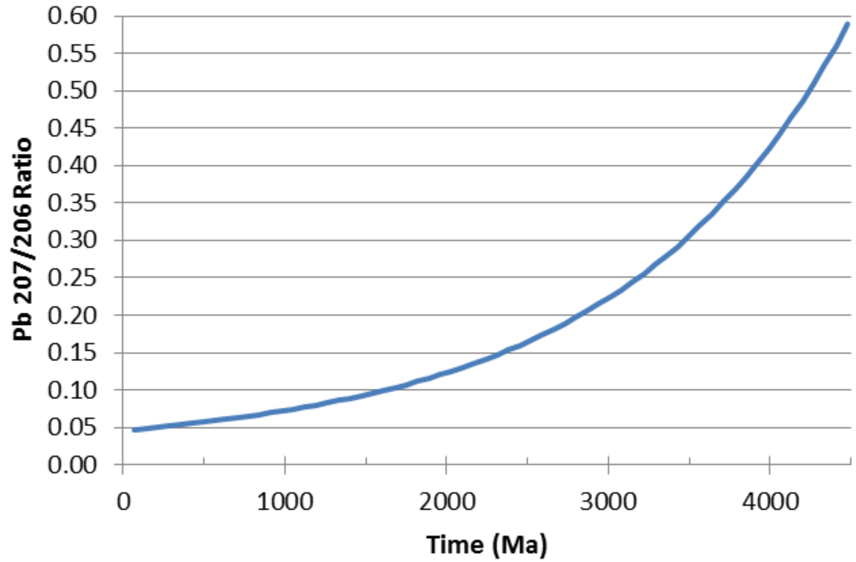
- A zircon is simply zirconium silicate ($ZrSiO_4$) – the eightfold sites in the tetragonal structure for the positions for the Zr and U
- Upon formation of the silicate, Pb will be rejected – due to its valence and size there is no low energy site for it to reside
- Zircon is a useful asset for geochronology due to its stability and ability to incorporate uranium – upon formation of the zircon a “geologic clock” is started

Geochronology

Lead-Uranium Dates



Lead-Lead Dates



- If a zircon has been well preserved for its life (free from melting or cracks), ratios of the uranium and lead isotopes form an accurate clock indicating age and also providing a self check called concordance (shown above left)
- A date estimate may also be obtained using just lead isotopes (shown above right)
- The latter is often useful in the case of atom probe data due to of molecular complexes and potential overlaps and associated with uranium

$x10^9y$	$^{207}Pb/^{206}Pb$	$e^{\lambda_1 t}-1$	$e^{\lambda_2 t}-1$
0.0	0.04604	0.0000	0.0000
0.2	0.05012	0.0315	0.2177
0.4	0.05471	0.0640	0.4828
0.6	0.05992	0.0975	0.8056
0.8	0.06581	0.1321	1.1987
1.0	0.07250	0.1678	1.6774
1.2	0.08012	0.2046	2.2603
1.4	0.08879	0.2426	2.9701
1.6	0.09872	0.2817	3.8344

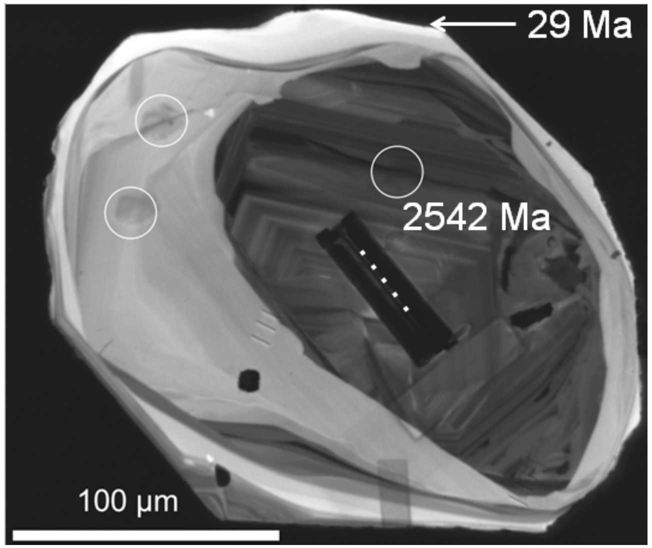
$\lambda_1\,(^{238}U) = 1.55125 \times 10^{-10}\,y^{-1}$

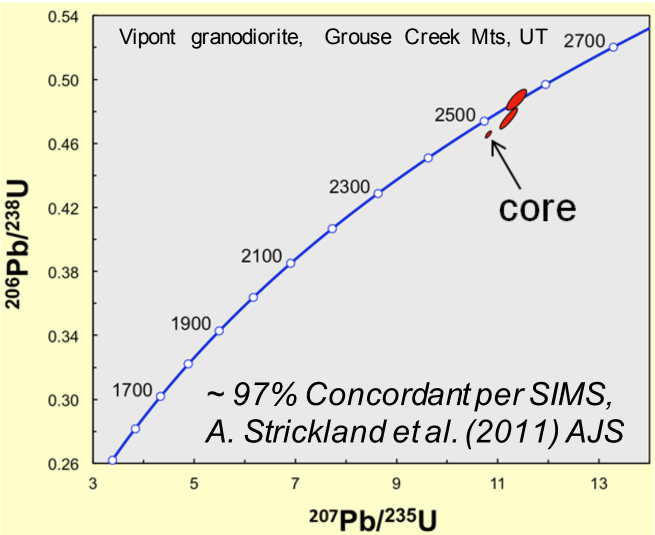
$\lambda_2\,(^{235}U) = 9.8485 \times 10^{-10}\,y^{-1}$

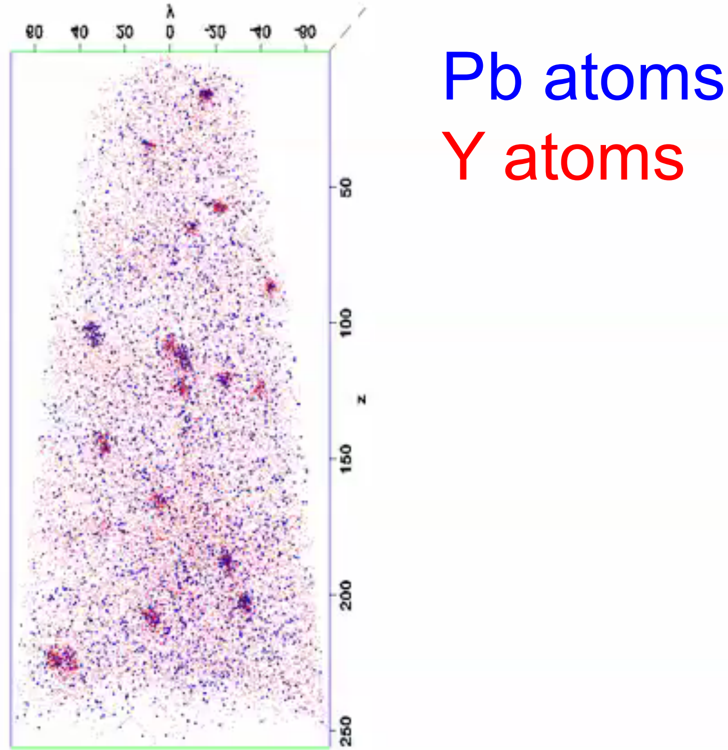
$$\left(\frac{^{206}Pb}{^{207}Pb}\right)^* = \frac{1}{137.88}\;\frac{e^{\lambda_2 t}-1}{e^{\lambda_1 t}-1}$$

$$\frac{^{206}Pb^*}{^{238}U} = e^{\lambda_1 t}-1 \qquad \frac{^{207}Pb^*}{^{235}U} = e^{\lambda_2 t}-1$$

Investigation of a 2.5Ga Zircon*





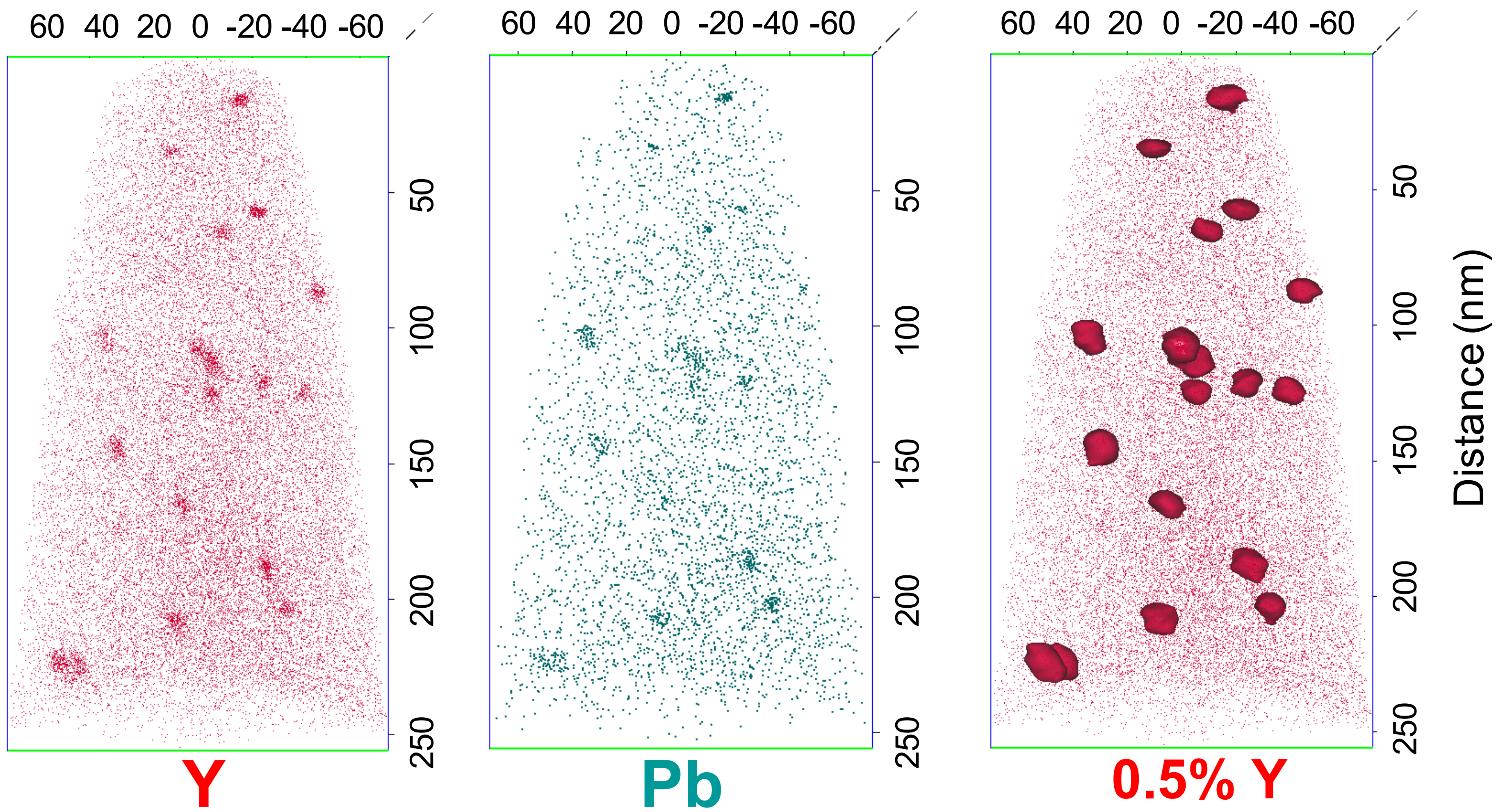


Atom probe data shows that the materials is NOT homogenous at the nano-scale. Pb is found in precipitates, but there is no supporting uranium present

- A zircon grain from the Grouse Creek Mountains in Utah was analysed by SIMS at the three points (above left) – result was nearly concordant 2.5 Ga age (note the 29 Ma overgrowth, which suggests a high temperature event at this point in time)
- However, there is more information available in this material at a level much smaller than the ~10um SIMS spot size

* J. W. Valley AGU presentation (2012)

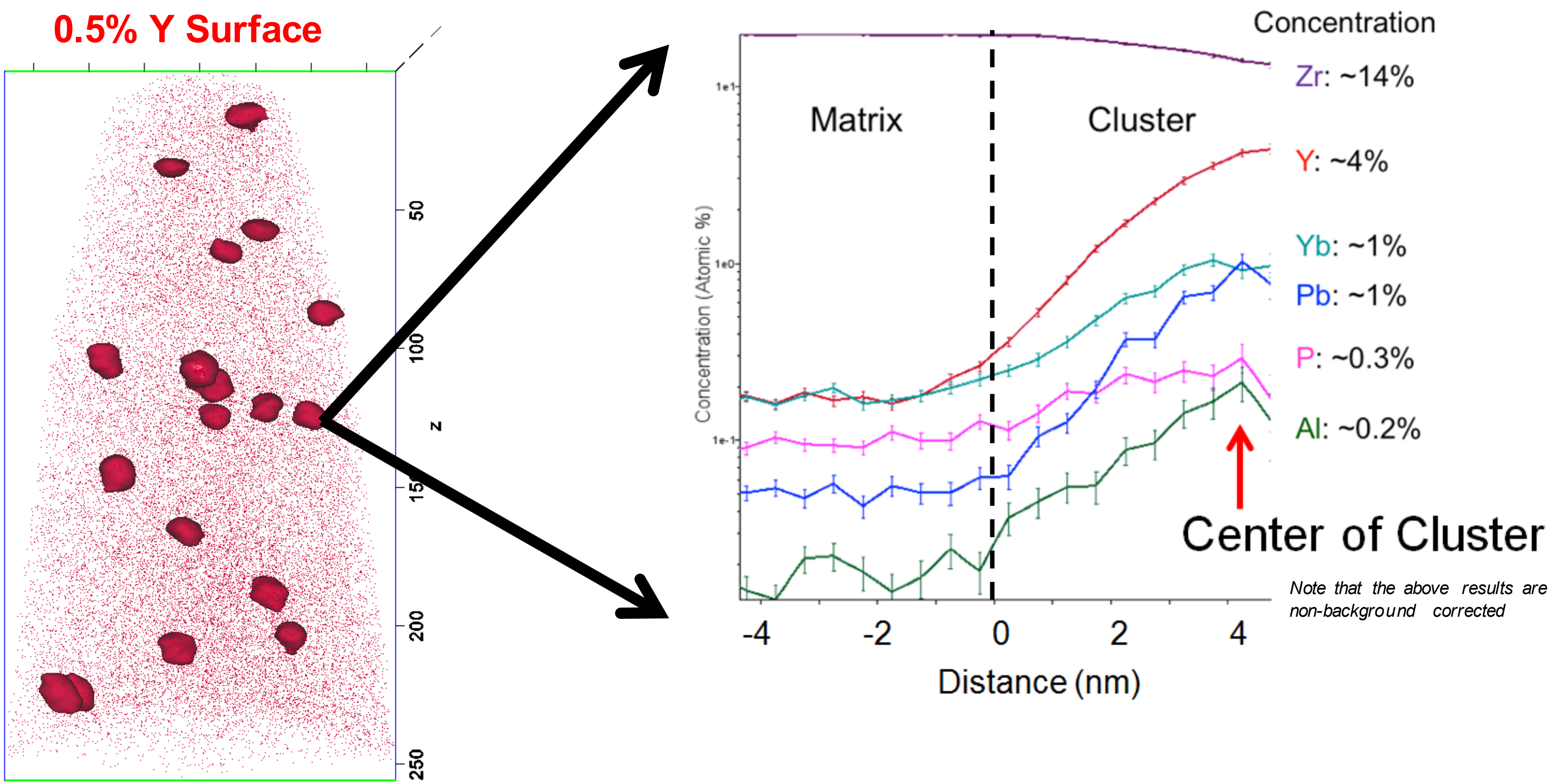
Individual Atom Maps of Y and Pb*



- 18 clusters are observed in this particular specimen (<10 nm ~50 nm apart)
- The lack of uranium together with the lead is evidence of lead diffusion
- An isoconcentration surface may be used to isolate the volume inside of these clusters and subsequently create a concentration profile from inside to outside of the clusters

* J.W. Valley APT Users Meeting, July 27,(2013) Madison, WI

Proximity Histogram of the Clusters*



- A proximity histogram provides a means to minimize our statistical variation by averaging over all of the clusters
- Pb is substantially enriched (together with Y, Yb, P, and Al) in the clusters, while less Zr is observed in the same regions

* J. W. Valley AGU presentation (2012)

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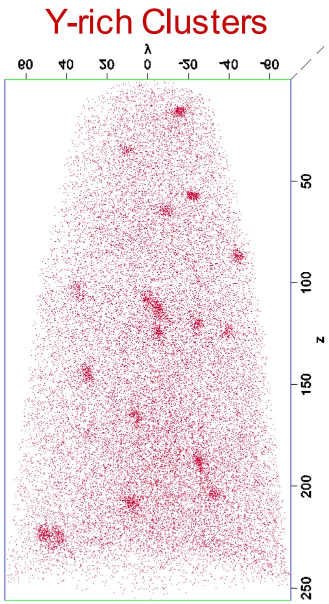
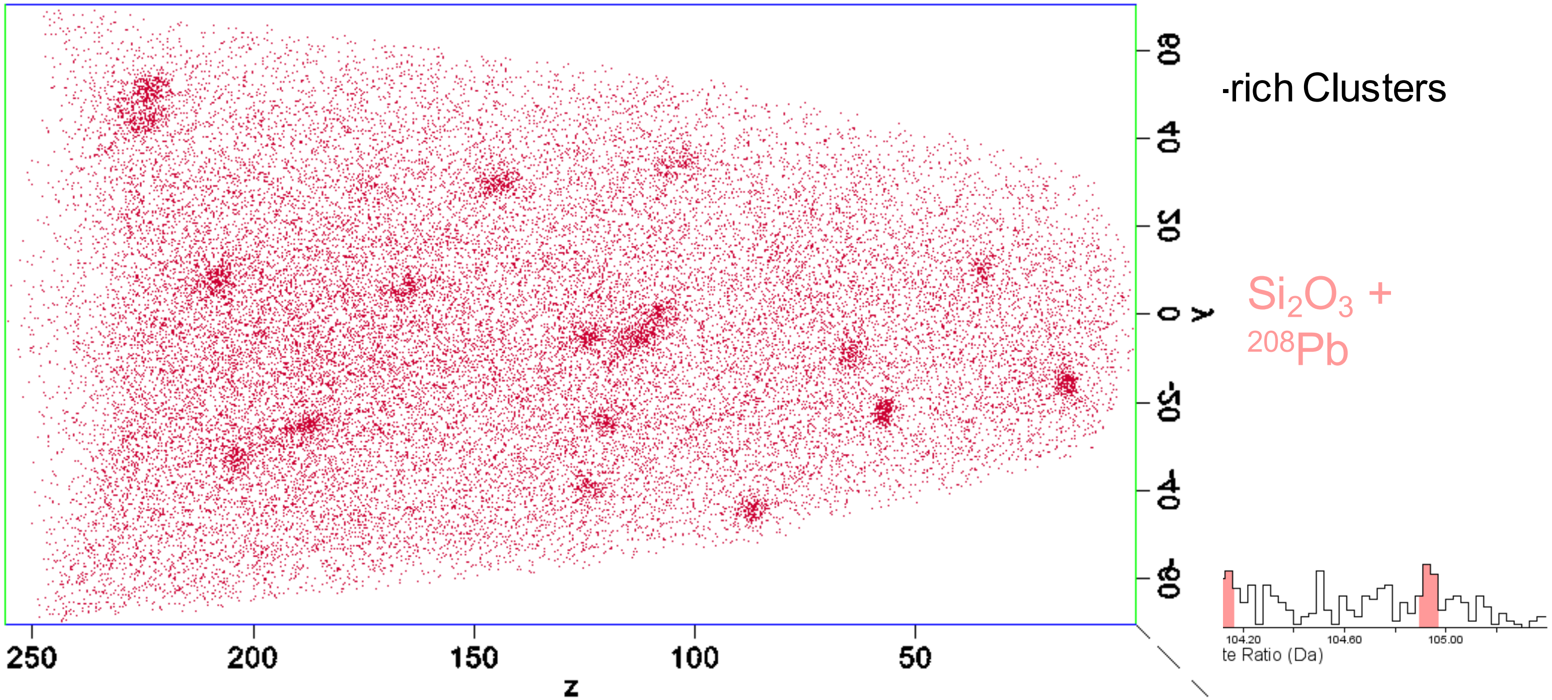
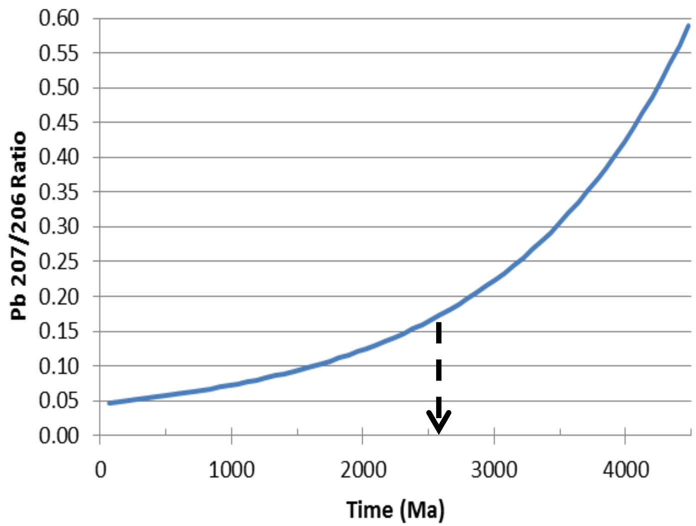
Unsupported Pb Distribution





- In the 2.5 Ga zircon Y-rich clusters were observed throughout the analyzed volume
- No lead was observed outside the clusters
- The ^{207}Pb to ^{206}Pb ratio was measured to be 0.17 ± 0.07 (2σ: ± 40%), SIMS: 0.1684
- The resultant age of ~2.6 Ga (in very good agreement with SIMS) is the time between the origination of the crystal and a heating event which drove the Pb diffusion to the recoil-based defects



* J. W. Valley AGU presentation (2012)