



# **PENEMA Computer Simulations of Secondary Fluorescence in EPMA**

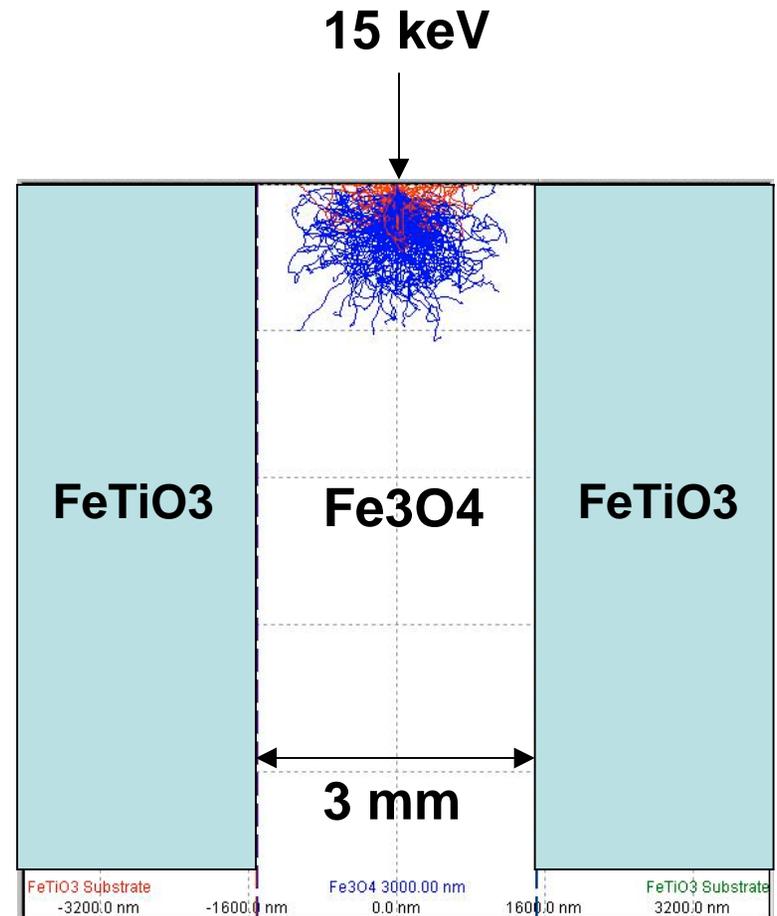
A presentation for the Advanced Instrumental Techniques  
and Software Algorithms in EPMA Workshop  
(Eugene, OR, September 13, 2007)

John Fournelle

Department of Geology and Geophysics,  
University of Wisconsin  
Madison, Wisconsin

The primary volume of x-rays generated is relatively small (~a few microns), dependent on keV and material composition.

There are several Monte Carlo programs that provide good estimates of this primary volume.

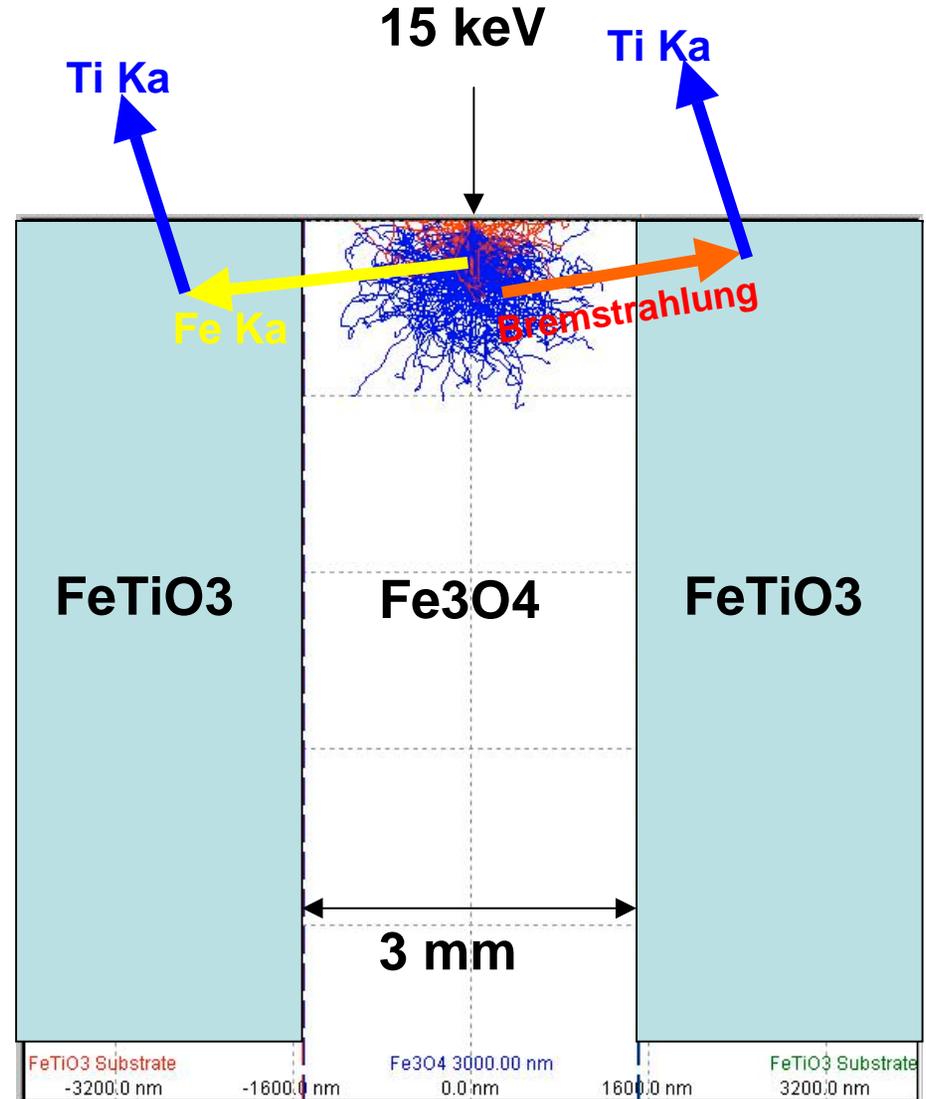


Example using *CASINO*

However ...

The x-rays generated in the primary volume can easily travel far outside the original volume — producing **SECONDARY FLUORESCENCE (SF)** in a different material.

The detector will register those SF x-rays as coming from the primary excitation volume.

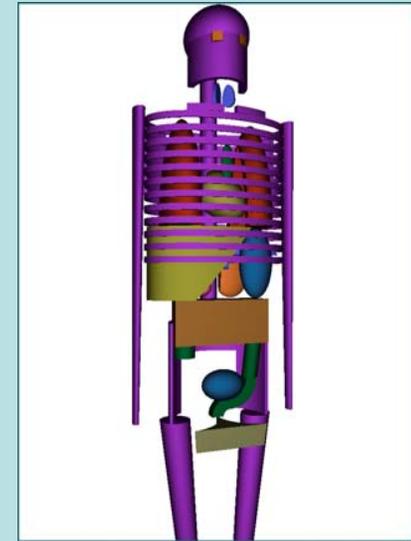


## How to Handle Secondary Fluorescence?

- Experimentally separate the grains of interest from the “contaminating” surrounding material/matrix
- Or decrease EPMA accelerating voltage if possible (but can be difficult, creates other problems)
- Or do EPMA on a experimentally produced sample with well defined geometry and composition of material of interest with adjacent “contaminating” material, so that “extraneous” counts are clearly artifacts (“non-diffused couple”)
- Or simulate with a physical model, e.g. a Monte Carlo program

# ***PENELOPE***

- created to model high energy radiation in **bodies of complex geometries**
- simulates x-ray generation and x-ray absorption/secondary fluorescence, using first principles (cross sections)
- a new version developed for EPMA, with EDS-like spectral output (=PENEPMA)
- a FORTAN program, runs with G77 compiler under OS X, Linux, Windows
- developed by Salvat, Llovet et al. of Universitat de Barcelona ... and free



**PENEPMA, a Monte Carlo code for the simulation of x-ray emission spectra using PENELOPE**

Xavier Llovet<sup>1</sup> and Francesc Salvat<sup>2</sup>

<sup>1</sup> Serveis Científico-Tècnics, Universitat de Barcelona, Lluís Solé i Sabarís, 1-3, 08028 Barcelona, Spain.

<sup>2</sup> Facultat de Física (ECM), Universitat de Barcelona, Diagonal 647, 08028 Barcelona, Spain.

## **Abstract**

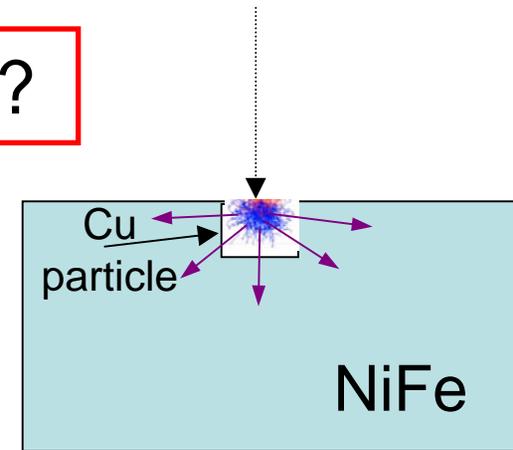
The computer program PENEPMA performs Monte Carlo simulations of x-ray emission spectra from complex material structures irradiated by monoenergetic electron beams. The program uses the general-purpose Monte Carlo code system PENELOPE (version 2006) for electron and photon transport, which implements the most elaborate interaction models available for arbitrary materials. The structure and operation of PENEPMA are similar to those of the generic main program PENMAIN, which is part of the PENELOPE distribution package. PENEPMA is designed to allow occasional users to simulate EPMA experiments and x-ray generators without having to write a PENELOPE main program. The user defines the details of his or her experiment (electron-beam characteristics, geometrical structure and composition of the target, photon detectors) and the simulation control parameters by editing the input file. The program delivers energy spectra of photons that enter the various detectors, as well as characteristic line intensities, with fluorescence contributions given separately. Optionally, PENEPMA can generate a three-dimensional distribution of x-ray generation.

**KEYWORDS:** X-ray spectra. Electron probe microanalysis. Electron-photon showers. Monte Carlo simulation. PENELOPE

Date: 27 July, 2006

## Fe Diffusion in Cu inclusions?

Cu in most stony meteorites occurs as 1-20  $\mu\text{m}$  grains associated with troilite (FeS) and NiFe.



Duke and Brett (1965) considered the concentration of Fe in 10-20  $\mu\text{m}$  Cu grains in a stony meteorite. Their EPMA measurements gave **1-4 wt% Fe**.

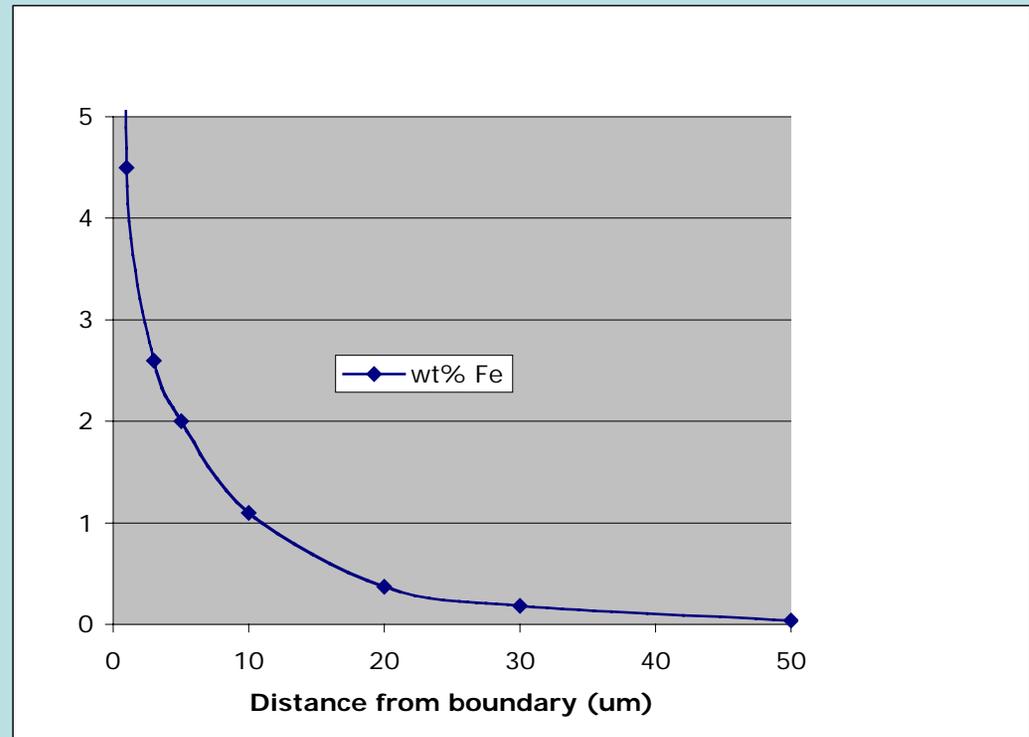
Cu formed @ 475°C in equilibrium with Fe has <0.2 wt% Fe in solid solution. **Secondary fluorescence???**

(Their EPMA conditions: 25 keV, TOA 52.5° on ARL probe. We calculate Cu Ka x-ray range as <1.5  $\mu\text{m}$ )

## Fictitious Fe Diffusion in Cu

PENELOPE simulates 1 wt.% Fe in Cu at 10  $\mu\text{m}$  away from pure Fe. A 10  $\mu\text{m}$  (dia.) sphere could show 2 wt% Cu.

If you are interested in trace levels, SF yields 34 ppm Fe at 100 microns away from the Fe material.



PENELOPE allows simulating any takeoff angle (here 52.5°) and keV (25)

This simulation matches closely recent experimental work (Llovet and Galan, 1996).

## Trace level of Ti and Al in Quartz

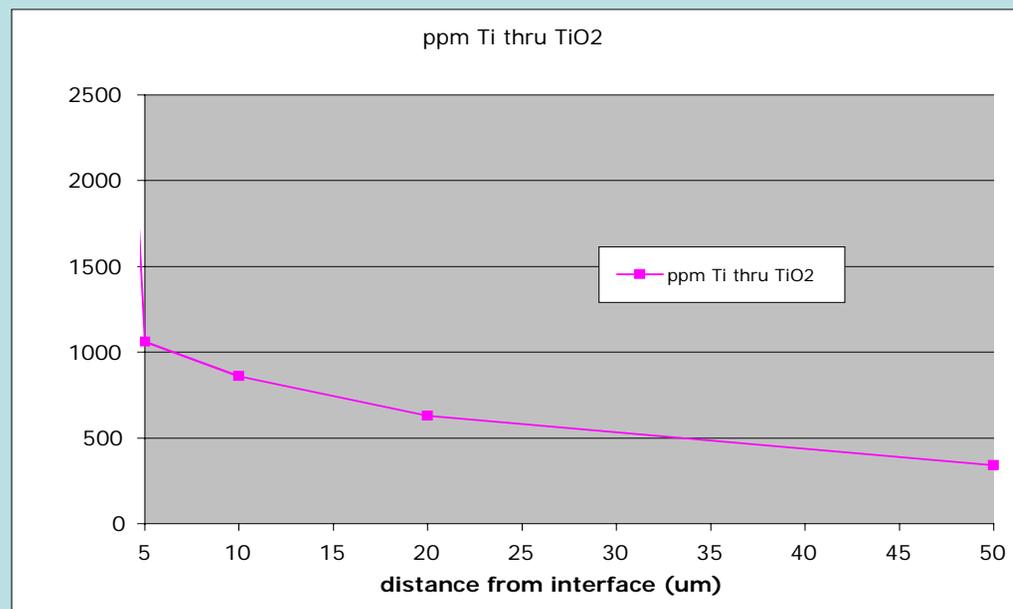
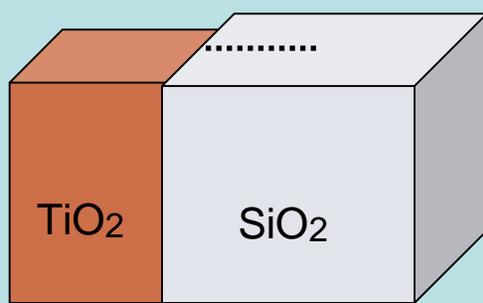
EPMA many times used to measure some trace element concentrations in minerals.

... one example is quartz

Possible problem: SF of Ti-rich phases either within or adjacent to quartz (e.g. rutile needles in quartz).

20 keV, 40° takeoff angle; electron range in quartz 3-4 microns

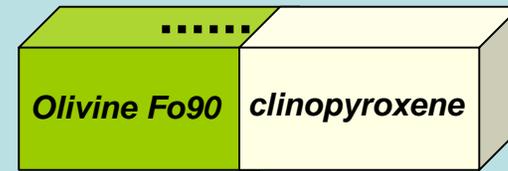
## “Ti” in Quartz if there is nearby rutile



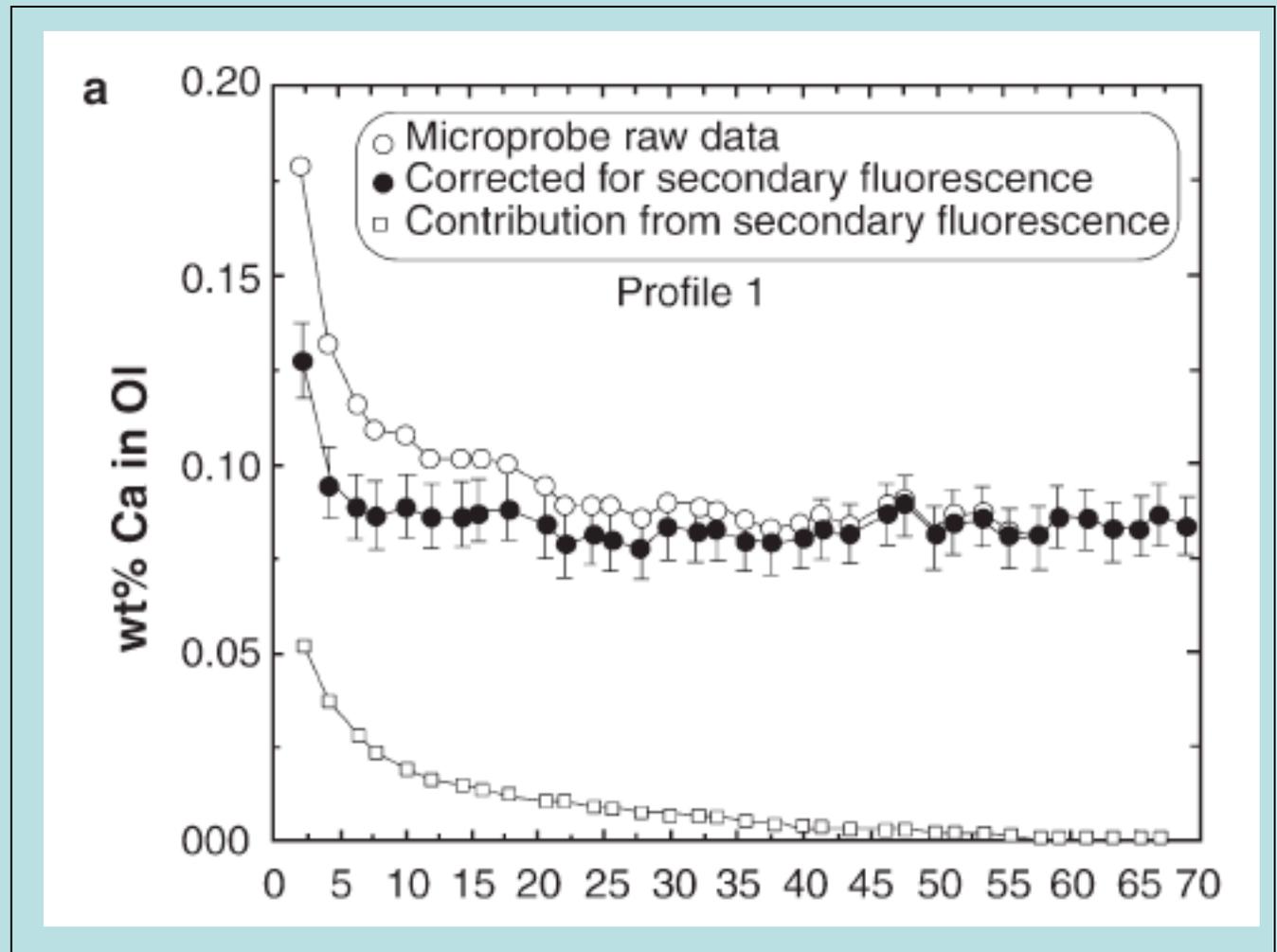
It is possible to get several hundred ppm of fictitious Ti within 50 microns of the interface.

This is all from continuum x-ray secondary fluorescence ( $E_0 = 20 \text{ keV}$ ).

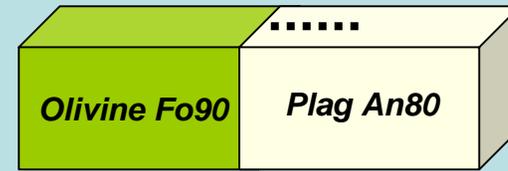
# Correction for secondary fluorescence of Ca in olivine



Llovet and Galan (2003) showed the correction for Ca in olivine adjacent to clinopyroxene using PENELOPE simulation:

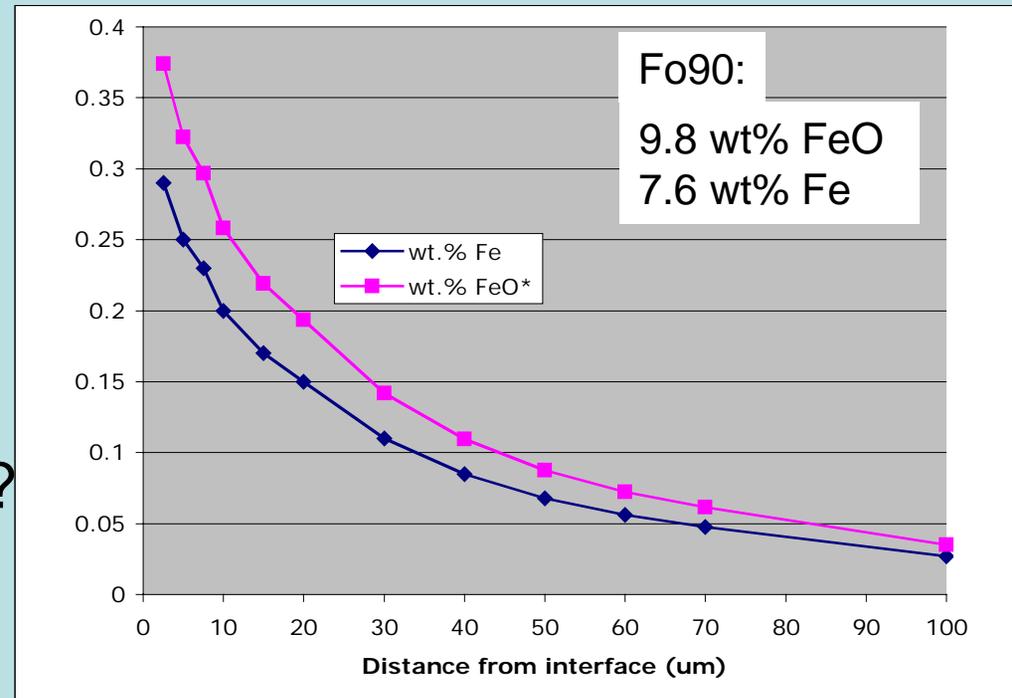


# Trace level of Fe in plagioclase



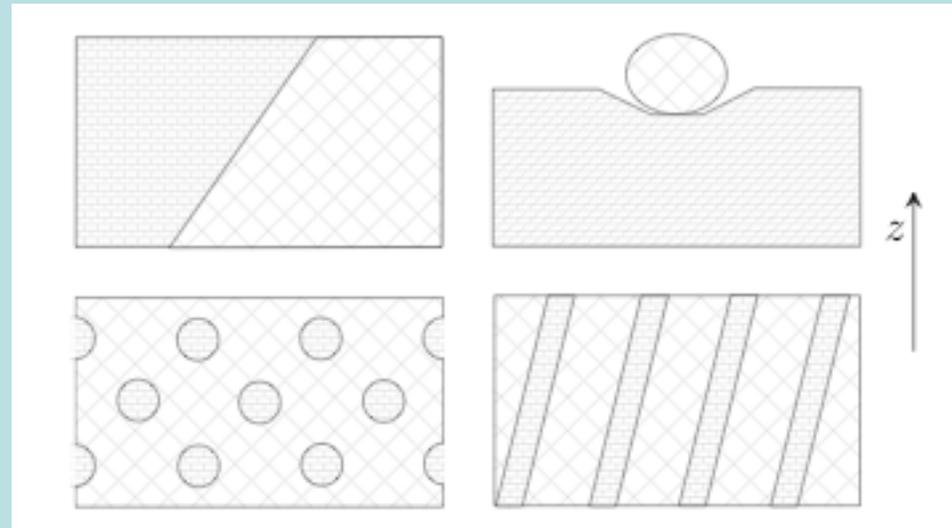
EPMA analyses of plagioclase normally have several tens of wt.% FeO.

How much is due to secondary fluorescence?



PENELOPE provides the ability to evaluate and/or correct for secondary fluorescence.

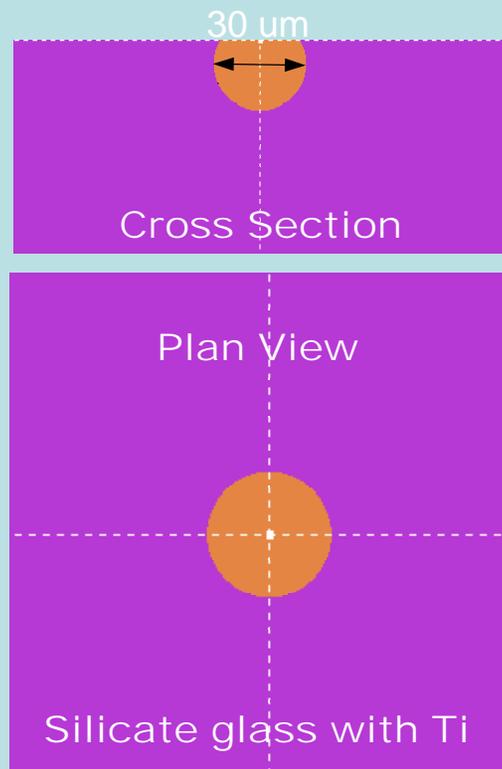
# New PENELOPE geometries



More realistic geometries are now available, and there are 2d and 3d viewers available with the program for assistance in creating more exact geometries relevant to specific problems being examined

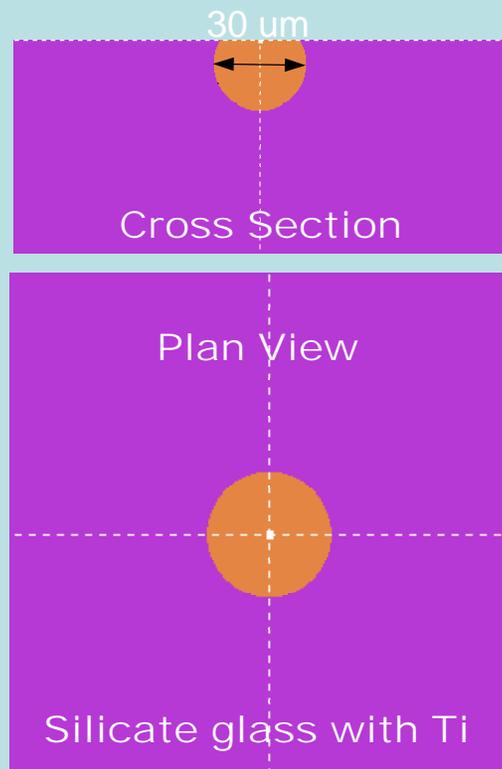
## Using more realistic geometries: Zircon with Adjacent Rutile —

An important new  
geothermometer (Ti in zircon)  
that has been suggested for  
studying the thermal history of  
old zircons



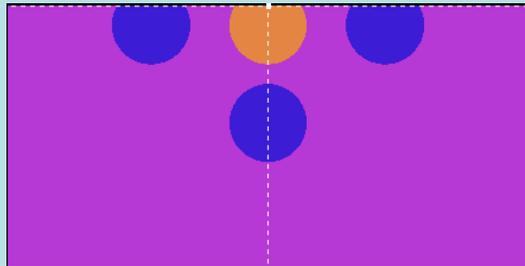
## Zircon with surrounding silicate glass containing Ti

Geometry 1: 30  $\mu\text{m}$  zircon, no rutile, only Ti in surrounding silicate glass (6 wt% Ti) => 452 ppm SF Ti

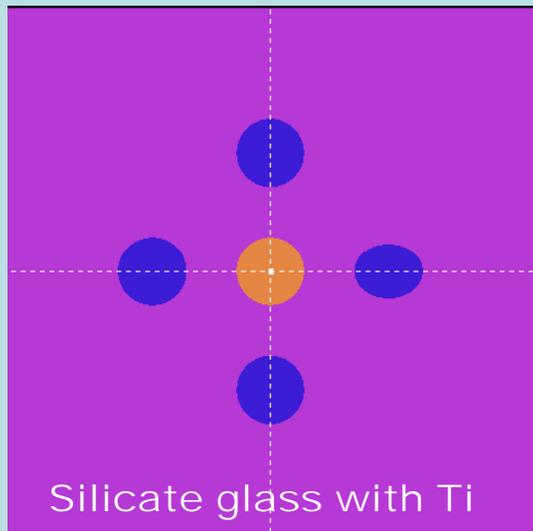


Incident beam (15 kV) impacts center of round zircon here and in all cases

Geometry 2: 30 um zircon, 5 large rutiles 15 um away, Ti in surrounding glass (6 wt% Ti)  
=> 948 ppm SF Ti

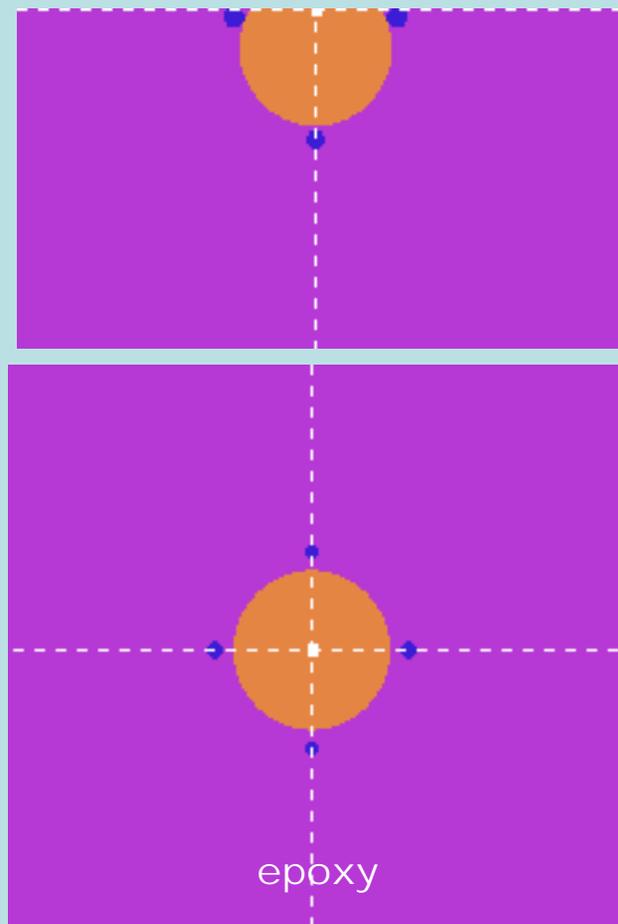


Each rutile contributes ~100 ppm Ti to the level already present from the matrix glass.



Silicate glass with Ti

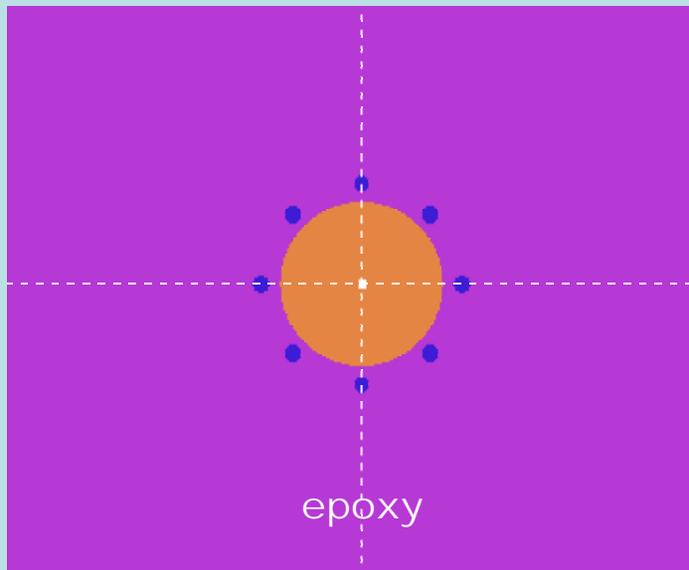
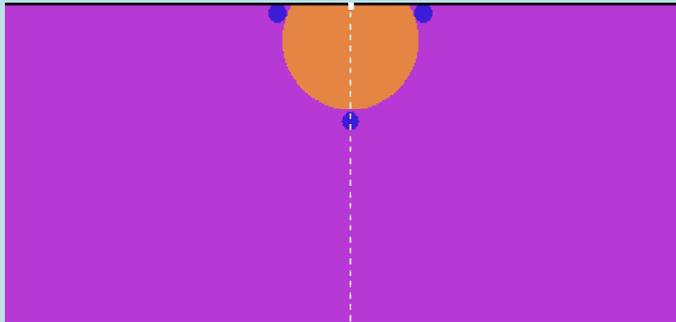
Geometry 3: 30  $\mu\text{m}$  zircon, 5 tiny 4  $\mu\text{m}$  rutiles  
0-1  $\mu\text{m}$  away, in epoxy  $\Rightarrow$  61 ppm SF Ti



What if tiny rutiles sitting on the  
outside edge of the zircon?

— Still a significant Ti contribution

Geometry 4: 30  $\mu\text{m}$  zircon, 10 tiny rutiles 0  
 $\mu\text{m}$  away, in epoxy  $\Rightarrow$  120 ppm SF Ti



What if increase from 5 to 10 tiny  
rutiles on the outside of the  
zircon?

— Additive effect:  $\sim 10$  ppm Ti per  
rutile

# Complications of Secondary Fluorescence: The “Size Discrepancy Issue”

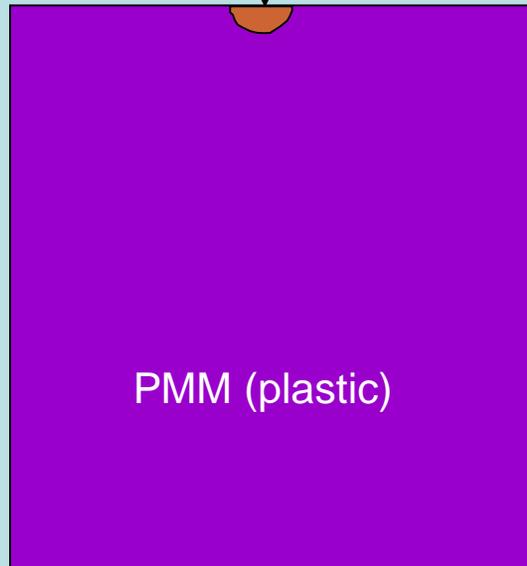
In troubleshooting low totals, the question arose: if there is a several order magnitude size difference between unknowns (small grain separates) and standard (large), what could result?

This is a problem that PENEPMMA can easily address.

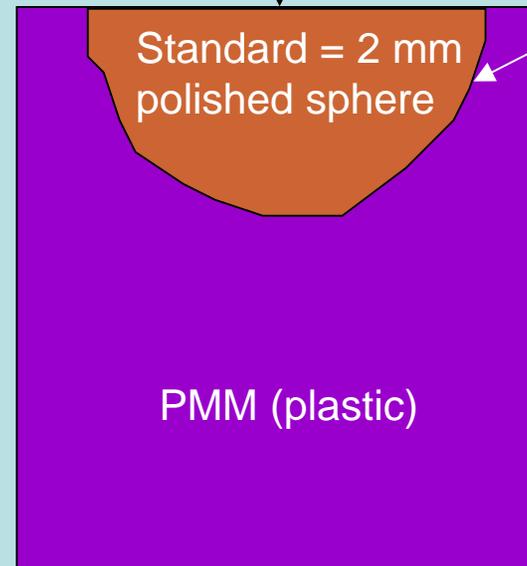
# Difference between small sample and large standard

Sample = 10  $\mu\text{m}$   
polished sphere  $\text{Cr}_2\text{O}_3$   
embedded in plastic

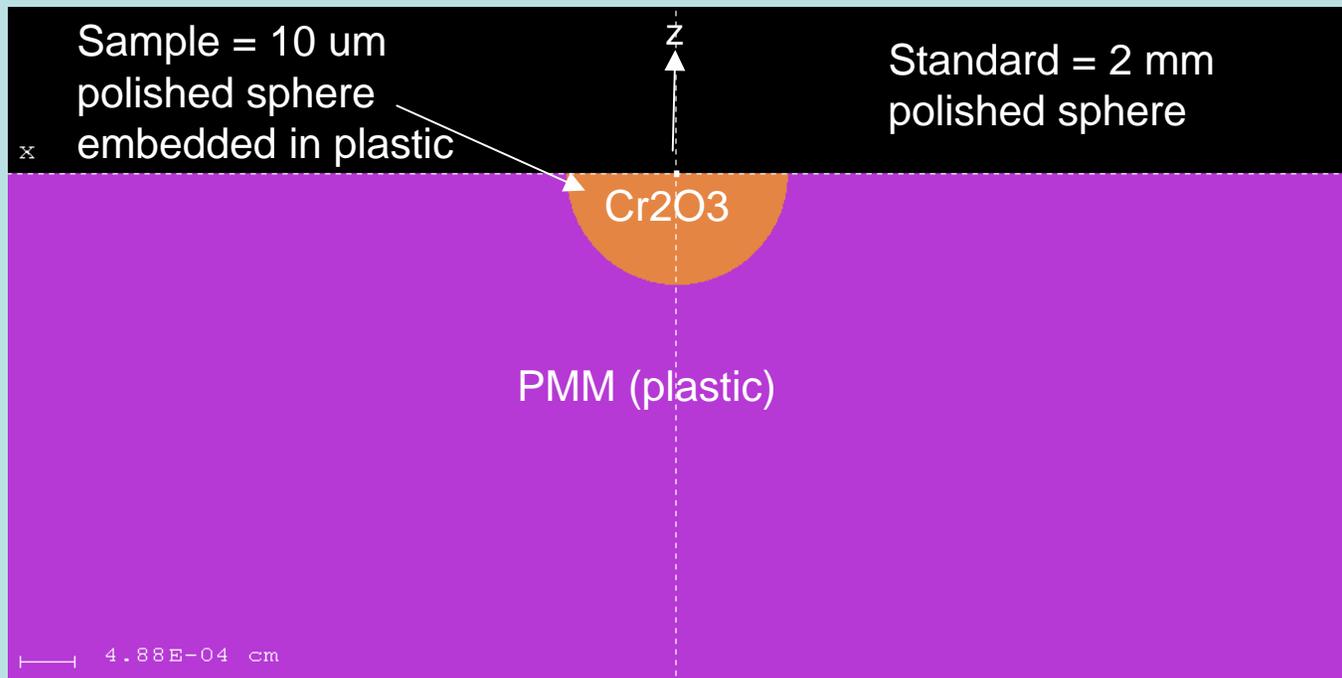
Electron  
beam



Electron  
beam



Standard not to scale  
with unknown, would be  
much larger if true scale.



Set up a Penepma Monte Carlo simulation:

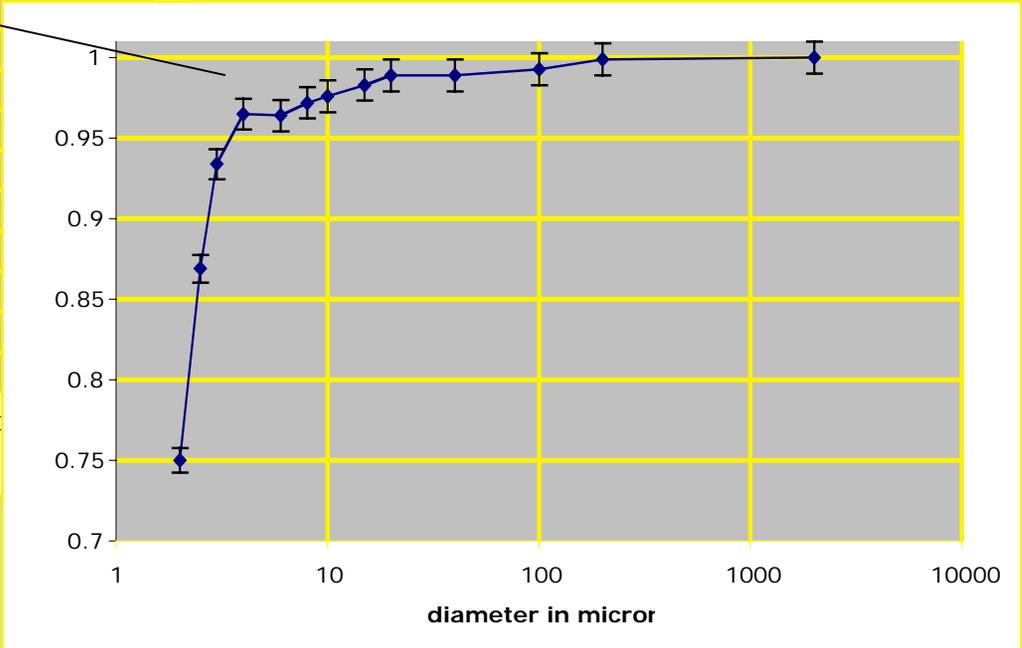
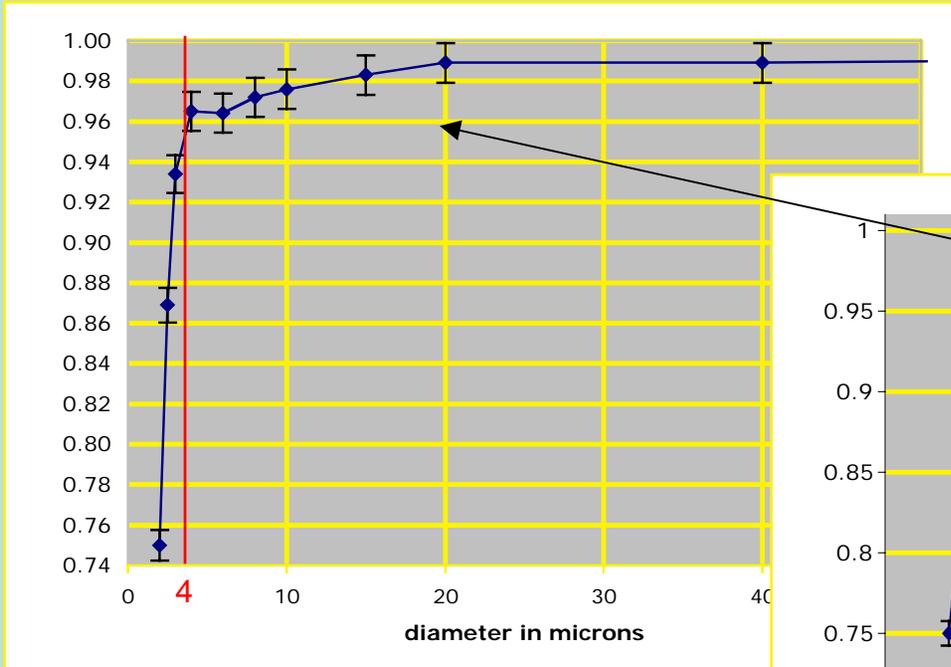
Standard of “huge size”, 2 mm

Unknowns of much smaller size

Accelerating voltage of 20 kV, takeoff angle 40°

# Yes, Secondary Fluorescence can cause problems

Standard=2000  $\mu\text{m}$   $\text{Cr}_2\text{O}_3$   
Unknown = smaller  $\text{Cr}_2\text{O}_3$



Electron range (K-O): 1.7 micron  
Cr Ka X-ray range (A-H): 1.6 micron

**A 100  $\mu\text{m}$  grain of pure  $\text{Cr}_2\text{O}_3$  will have 1% low Cr K-ratio, and a 10  $\mu\text{m}$  grain will have a K-ratio 2.5% low.**

(plots show K-ratios produced in centers of various discrete sized diameter cut-off spheres imbedded in epoxy simulations)

Discrepancies in size between unknown and standard can lead to small, but noticeable errors, because secondary fluorescence yields

- additional x-rays beyond the primary electron impact-x-ray production volume in the same phase if the phase is large,

or

- a lack of additional x-rays if the phase is small and mounted in epoxy.

# Conclusion

Secondary fluorescence across phase boundaries has been a difficult issue to address in the past.

PENELOPE/PENEPMA provides a powerful tool to evaluate, and correct for, this secondary fluorescence.

If there is interest, I will offer an informal tutorial on running PENEPMA, at the December AGU meeting.