



# **Secondary Fluorescence Corrections for EPMA: Using PENELOPE Monte Carlo Simulations**

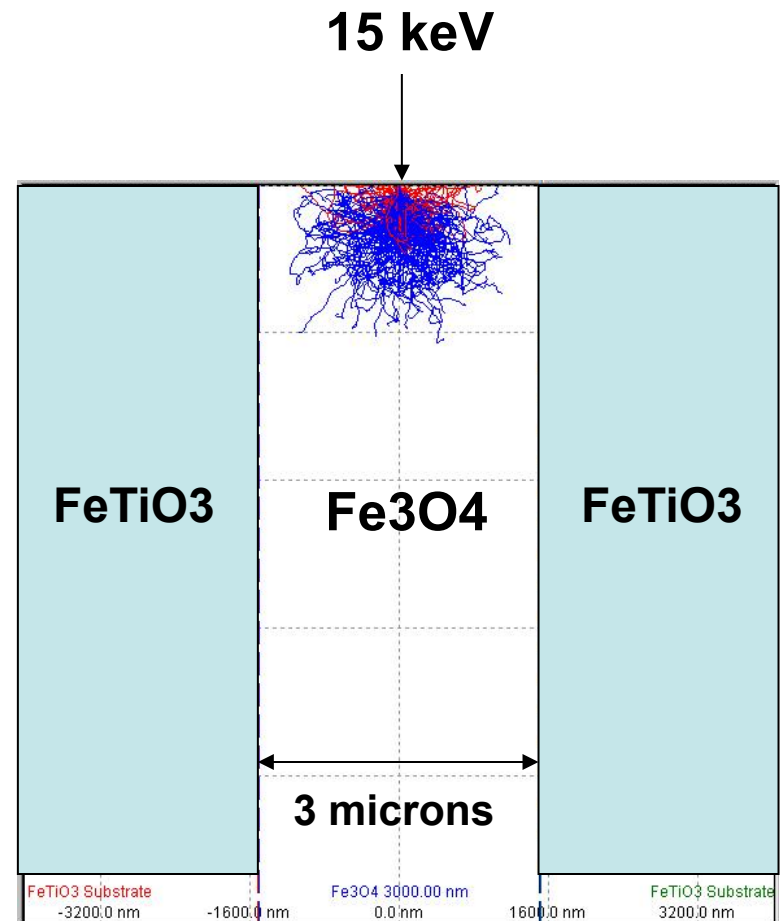
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The primary volume of x-rays generated is relatively small -- dependent on keV and material composition.

Here in geologic material, at 15 keV, it is ~a few microns,

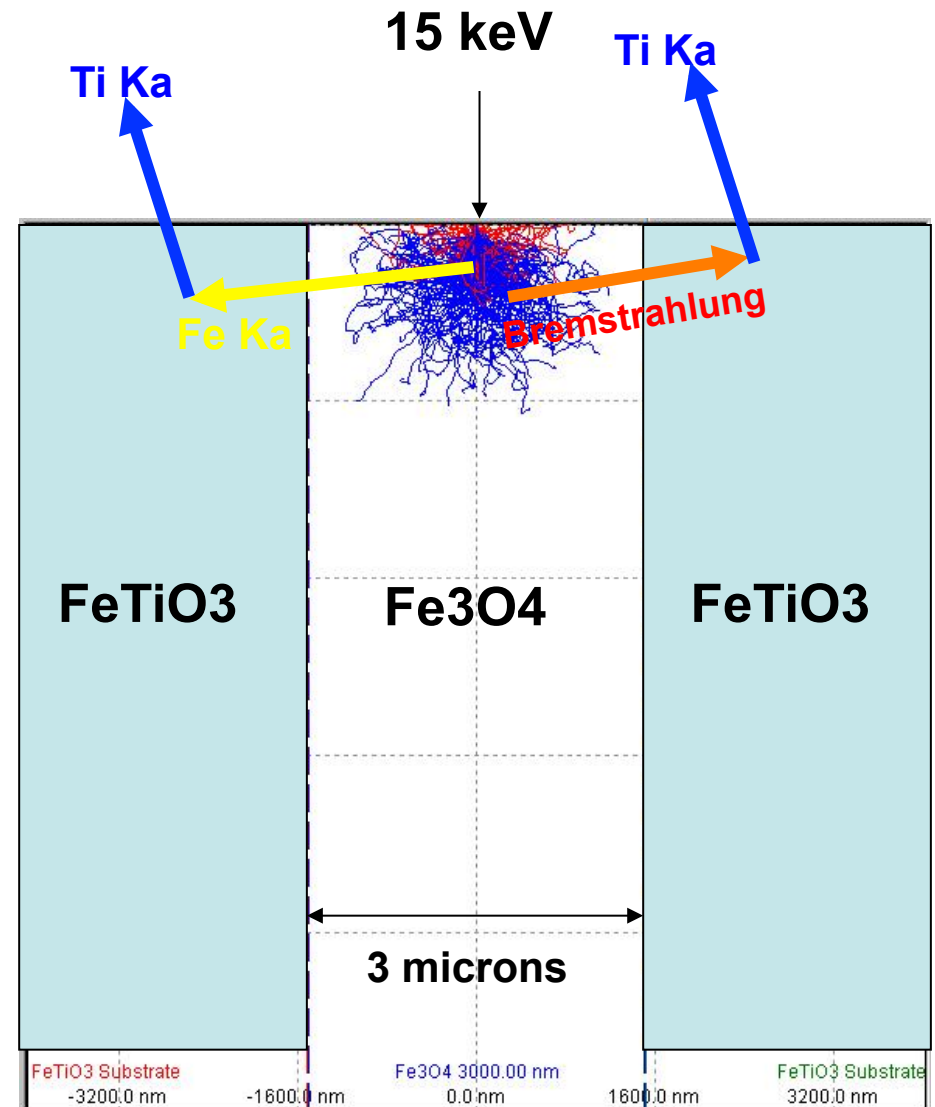


Example using *CASINO*

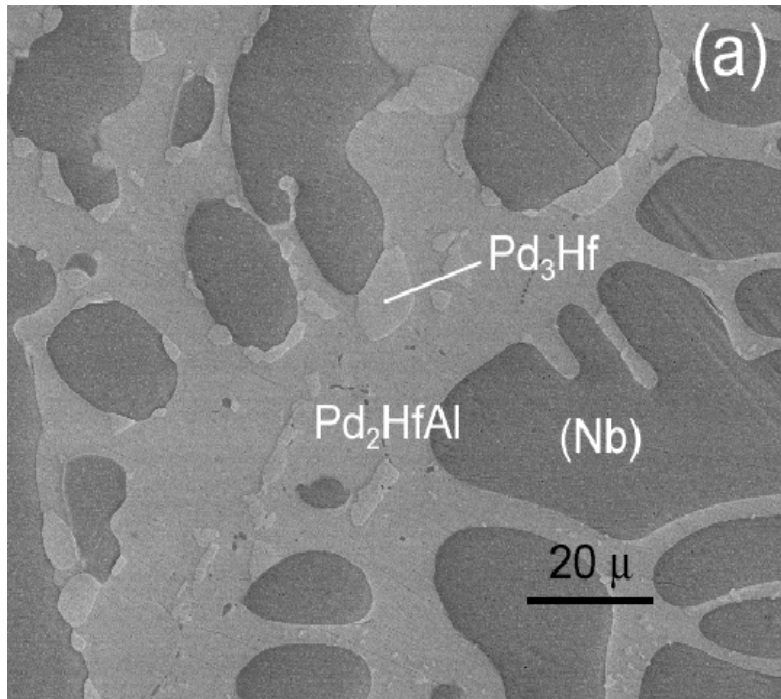
However ...

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

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



We had a problem...  
in a specimen in Nb-Pd-Hf-Al bearing phases



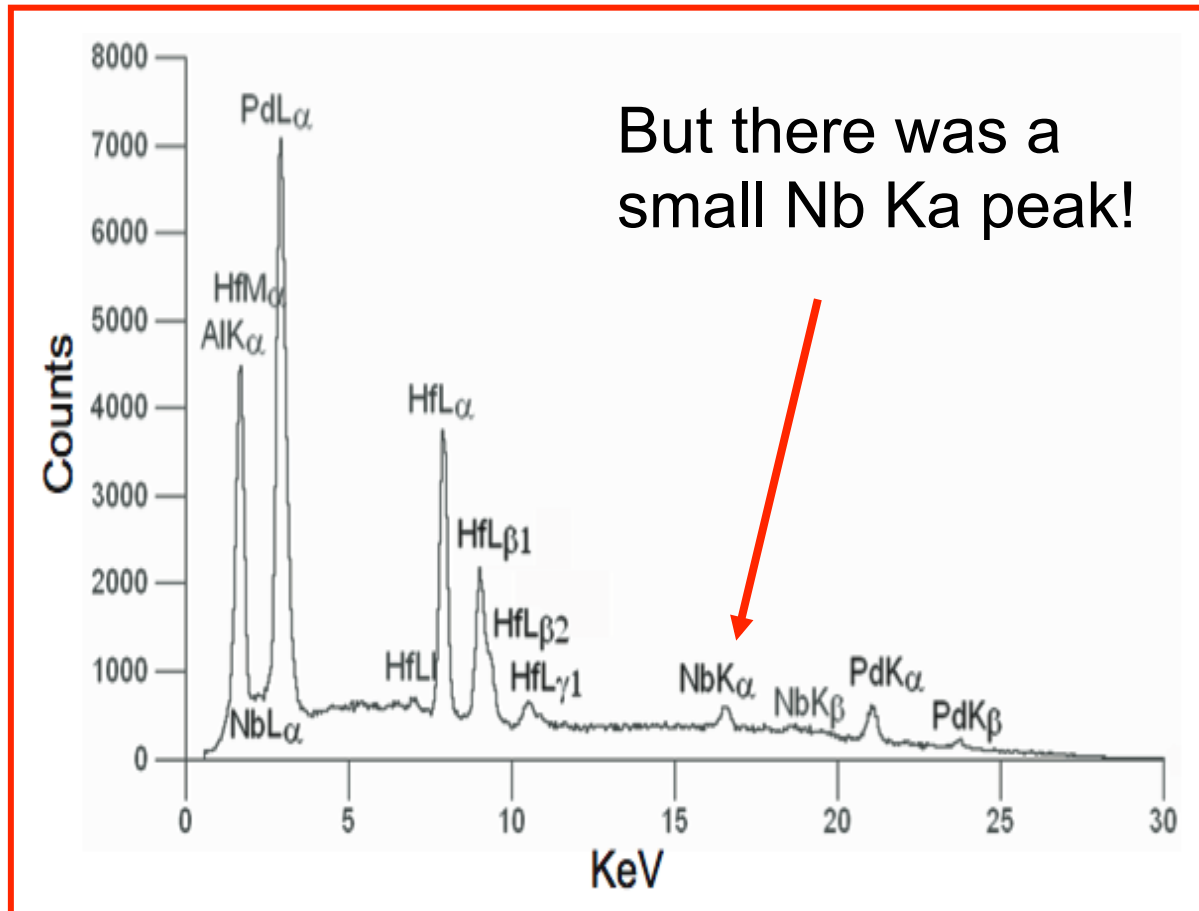
Some researchers claimed **10 wt% Nb** in 2 phases where our PI suggested Nb should be absent.

- The other researchers did EPMA by EDS at 30 keV, measuring Nb K $\alpha$ .

- **But our lab measured Nb L $\alpha$  (WDS at 18 keV) and got ~0 wt% Nb.**



We checked out the phase ( $\text{Pd}_2\text{HfAl}$ ) we found to have zero Nb in, acquiring an EDS spectrum (at 28 keV).



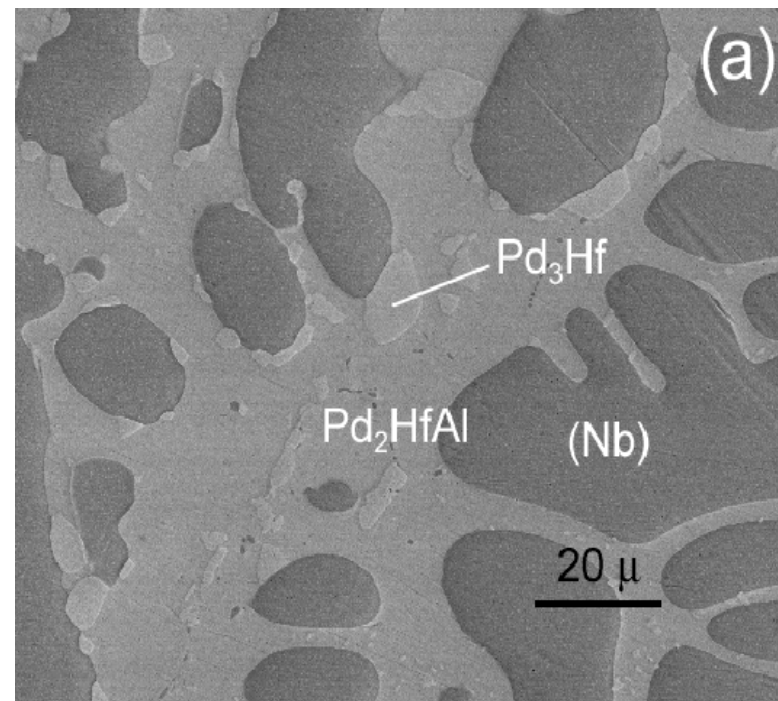
First thought:

Secondary fluorescence might explain the discrepancy, as

- problematic phases just a short distance from Nb phase
- Pd Ka x-rays strong enough to excite K edge of Nb

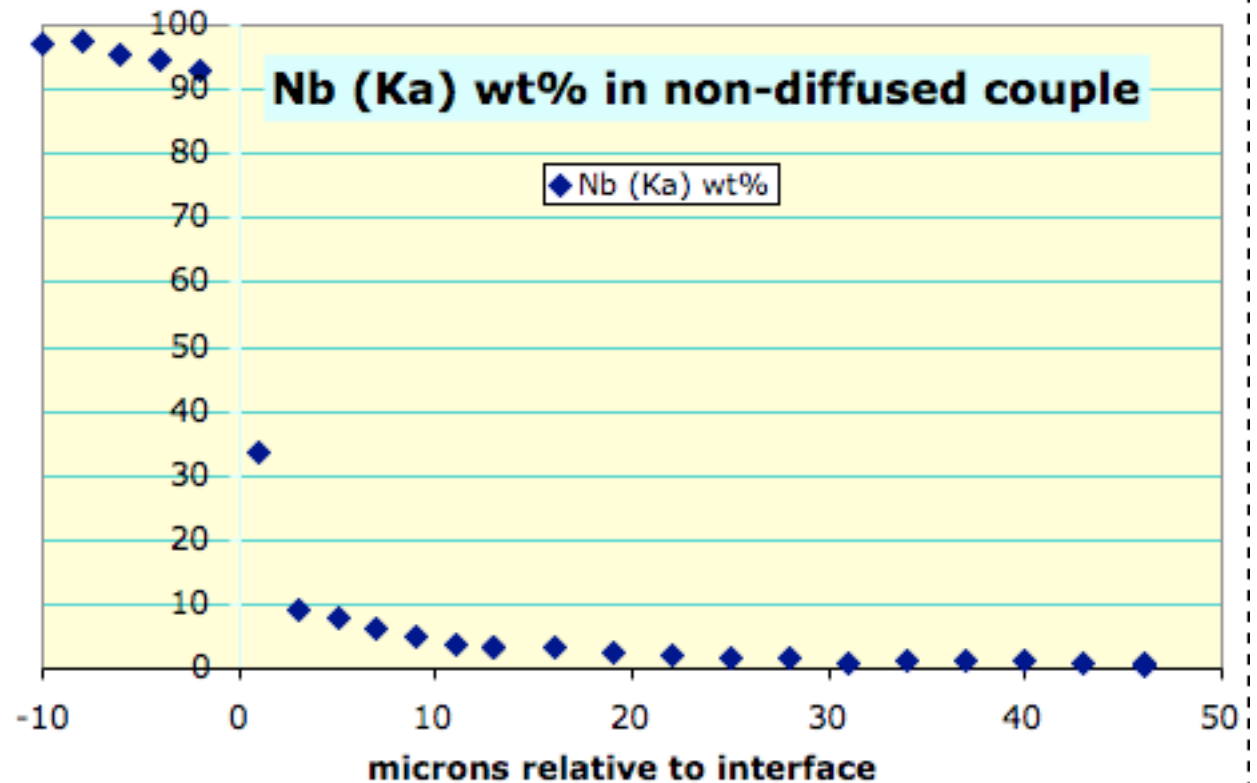
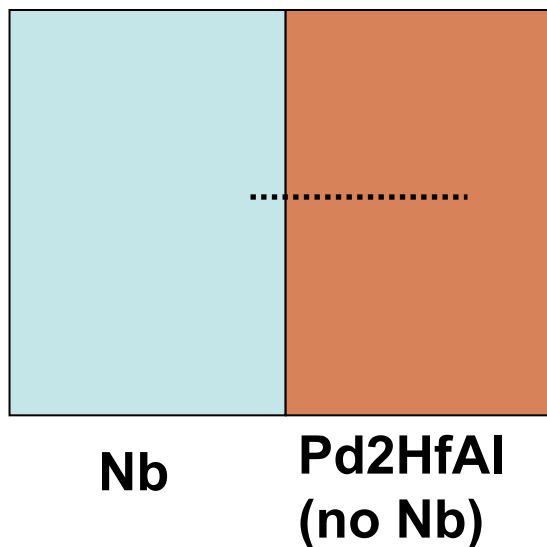
	K edge	Ka
Nb	18986 ev	16615 ev
Pd	24350 ev	21177 ev

But can we prove it?



## 2 ways to address the problem

1. Experimentally: Create a 'non-diffused couple' of Nb against Pd<sub>2</sub>HfAl, and measure the Nb K $\alpha$  with distance away from the boundary. (LIF220 crystal needed for WDS -- took some time to acquire). --The data were consistent with secondary fluorescence.



2. But while waiting to get LIF220 installed on our electron probe, we learned about the PENELOPE program - which we discovered had been shown to successfully reproduce Secondary Fluorescence.

We acquired a copy of PENELOPE, and began to learn how to run it... on both a WinPC and under MacOS X, using easily accessible G77 compilers.

```
File: MANUAL.TXT

PPPPP EEEEE N N EEEEE L OOOO P P P P EEEEE
P P E MN N E L O O P P E
P P E N N N E L O O P P E
PPPPP EEEE N N N EEEE L O O P P P P EEEE
P E N N N E L O O P P E
P EEEEE N N EEEEE LLLLL OOOO P EEEEE

                                         (version 2003).

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----- GENERAL INFORMATION -----

The FORTRAN 77 code system PENELOPE performs Monte Carlo simulation
of coupled electron-photon transport in arbitrary materials. Initially,
it was devised to simulate the PENetration and Energy Losses of Positrons
and Electrons in matter; photons were introduced later. The adopted
scattering model allows the simulation of electron/positron and photon
transport in the energy range from 100 eV to 1 GeV. PENELOPE generates
random electron-photon showers in complex material structures consisting
of any number of distinct homogeneous regions (bodies) of different
compositions.

PENELOPE allows the user to write her/his own simulation program,
with arbitrary geometry and scoring, without previous knowledge of the
intricate features of scattering and transport theories. PENELOPE has
been devised to do a great part of the simulation work. The MAIN
program, which is provided by the user, only has to control the
evolution of the simulated tracks and keep score of the relevant
quantities.

For the sake of brevity, we use the term 'particle' to refer to
either electrons, positrons or photons. Interactions with the medium
cause particles to lose energy, change their direction of movement and,
occasionally, produce secondary particles. PENELOPE incorporates a
scattering model that combines information from numerical databases with
simple analytical differential cross section models. The considered
interactions and the corresponding differential cross sections are the
following:

A) Elastic scattering of electrons and positrons: MW differential
cross section model with parameters determined from the mean free
path and first and second transport mean free paths read from the
```



It wasn't as easy as running snazzy GUI-front ended programs ...

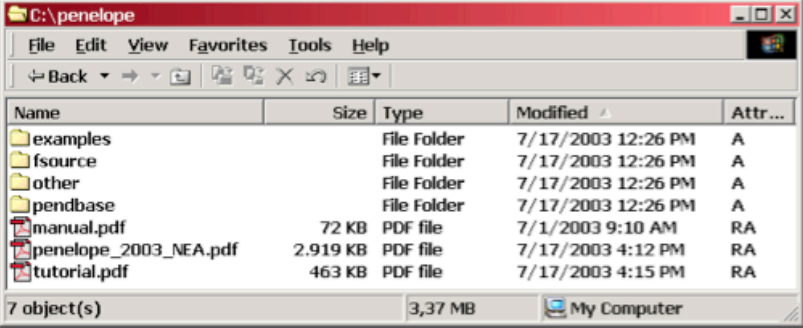
```
Terminal — penepma — 97x24
electron2go2:~/Penelope/April2005-new/run22-15um johnfournelle$ ./penepma <epma.in
Number of simulated showers = 7.7900000E+02
Number of simulated showers = 1.5260000E+03
Number of simulated showers = 2.2860000E+03
Number of simulated showers = 3.0660000E+03
Number of simulated showers = 3.8120000E+03
Number of simulated showers = 4.5720000E+03
Number of simulated showers = 5.3500000E+03
Number of simulated showers = 6.1140000E+03
Number of simulated showers = 6.8660000E+03
Number of simulated showers = 7.6240000E+03
Number of simulated showers = 8.3830000E+03
Number of simulated showers = 9.1510000E+03
Number of simulated showers = 9.9230000E+03
Number of simulated showers = 1.0789000E+04
Number of simulated showers = 1.1445000E+04
Number of simulated showers = 1.2213000E+04
Number of simulated showers = 1.2977000E+04
Number of simulated showers = 1.3741000E+04
Number of simulated showers = 1.4515000E+04
Number of simulated showers = 1.5299000E+04
Number of simulated showers = 1.6067000E+04
Number of simulated showers = 1.6833000E+04
Number of simulated showers = 1.7614000E+04
```

...but with a little perserverance it became fairly easy.

... eventually 5 grad students, some with no programming or command line experience, quickly learned how to run it on their laptops.

### Tutorial for PENELOPE (version 2003)

The distribution package looks like (in Windows)



Name	Size	Type	Modified	Attr...
examples		File Folder	7/17/2003 12:26 PM	A
fsource		File Folder	7/17/2003 12:26 PM	A
other		File Folder	7/17/2003 12:26 PM	A
pendbase		File Folder	7/17/2003 12:26 PM	A
manual.pdf	72 KB	PDF file	7/1/2003 9:10 AM	RA
penelope_2003_NEA.pdf	2,919 KB	PDF file	7/17/2003 4:12 PM	RA
tutorial.pdf	463 KB	PDF file	7/17/2003 4:15 PM	RA

7 object(s) 3,37 MB My Computer

where:

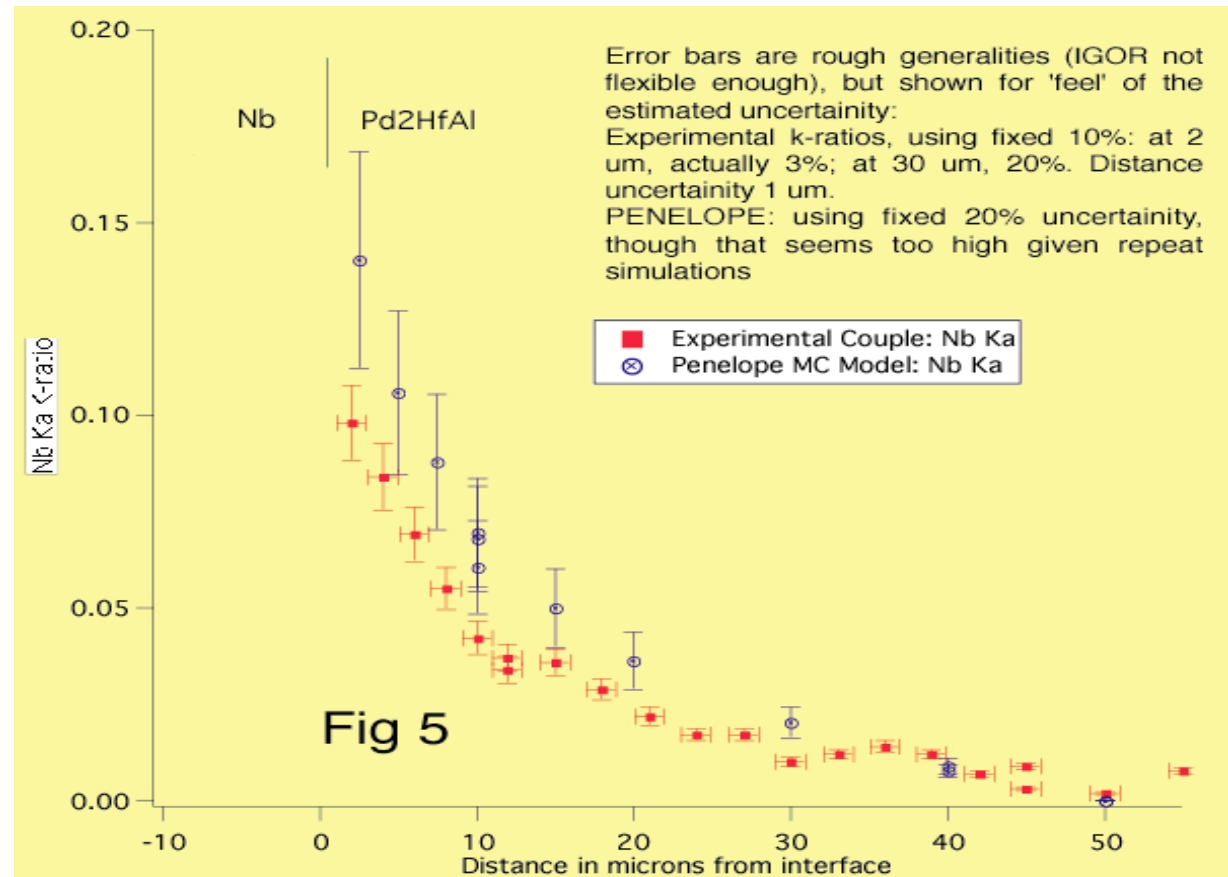
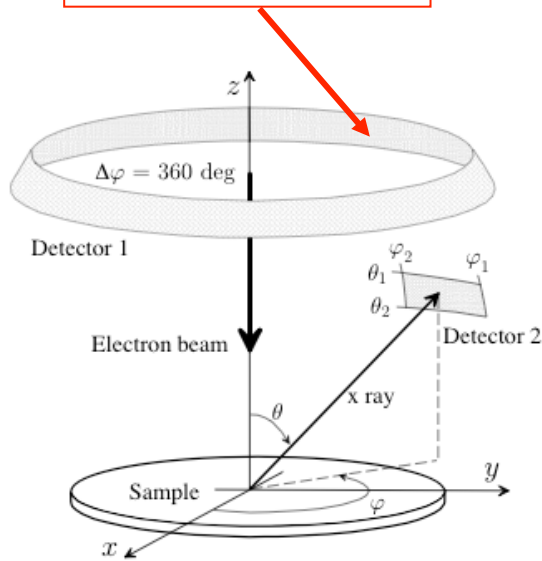
- tutorial.pdf** This file.
- manual.pdf** Provides a brief description of the PENELOPE system and its use. *It is the document to have at hand in the initial stages of the use of PENELOPE.*
- penelope\_2003\_NEA.pdf** Official release by the OECD Nuclear Energy Agency Data Bank of the PENELOPE documentation, distributed together with version 2003. This is the reference to be used in any publication. Cite it as: F. Salvat, J.M. Fernández-Varea and J. Sempau, "PENELOPE - A Code System for Monte Carlo Simulation of Electron and Photon Transport" (OECD Nuclear Energy Agency, Issy-les-Moulineaux, France, 2003).

The subdirectories shown contain:

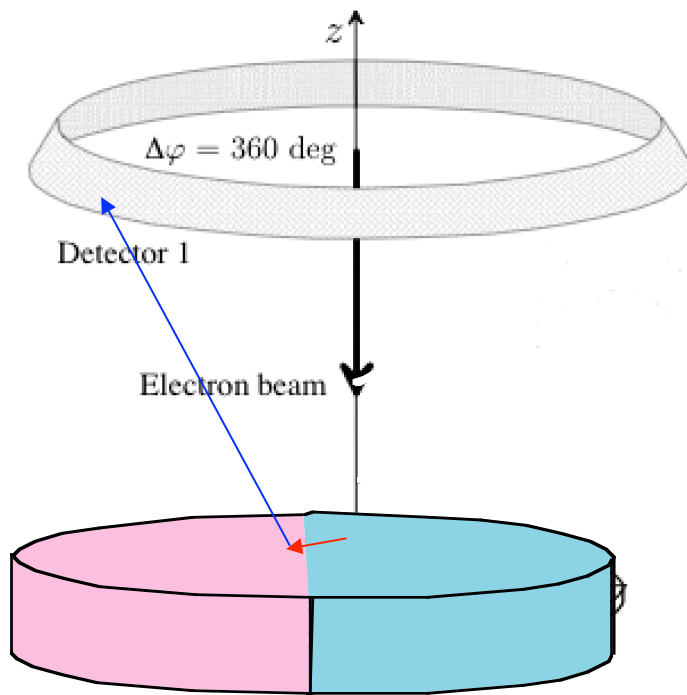
- \fsource\** FORTRAN 77 source files of the PENELOPE code system. Includes the transport/physics routines (**penelope.f**), the quadric geometry package (**pengeom.f**), variance-reduction routines (**penvared.f**), the main program to create cross-section data files (**material.f**) and a program to generate tables of material interaction properties (**tables.f**).
- \pendbase\** Files necessary for creating cross-section data (to be used together with **material.exe** and **shower.exe**).
- \other\** Additional software for geometry visualization (**\gview\**), display of particle tracks (**\shower\**), plotting (scripts for the plotting program GNU PLOT in subdirectory **\plotter\**), and a routine package for including static electromagnetic fields (**\emfields\**).

We started with a simple geometry and the default PENELOPE detector (annular) ... And reproduced the Nb-Pd<sub>2</sub>HfAl non-diffused couple data fairly well, but found some slight differences.

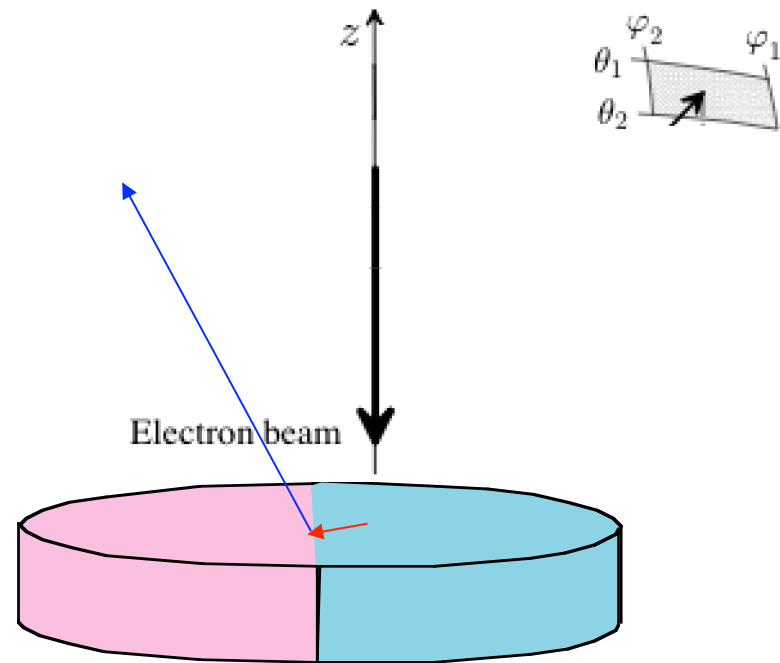
Annular detector



Could geometry -- orientation of the sample relative to the detector -- be causing the discrepancy between the “ideal” annular detector, and the real WDS spectrometer geometry?

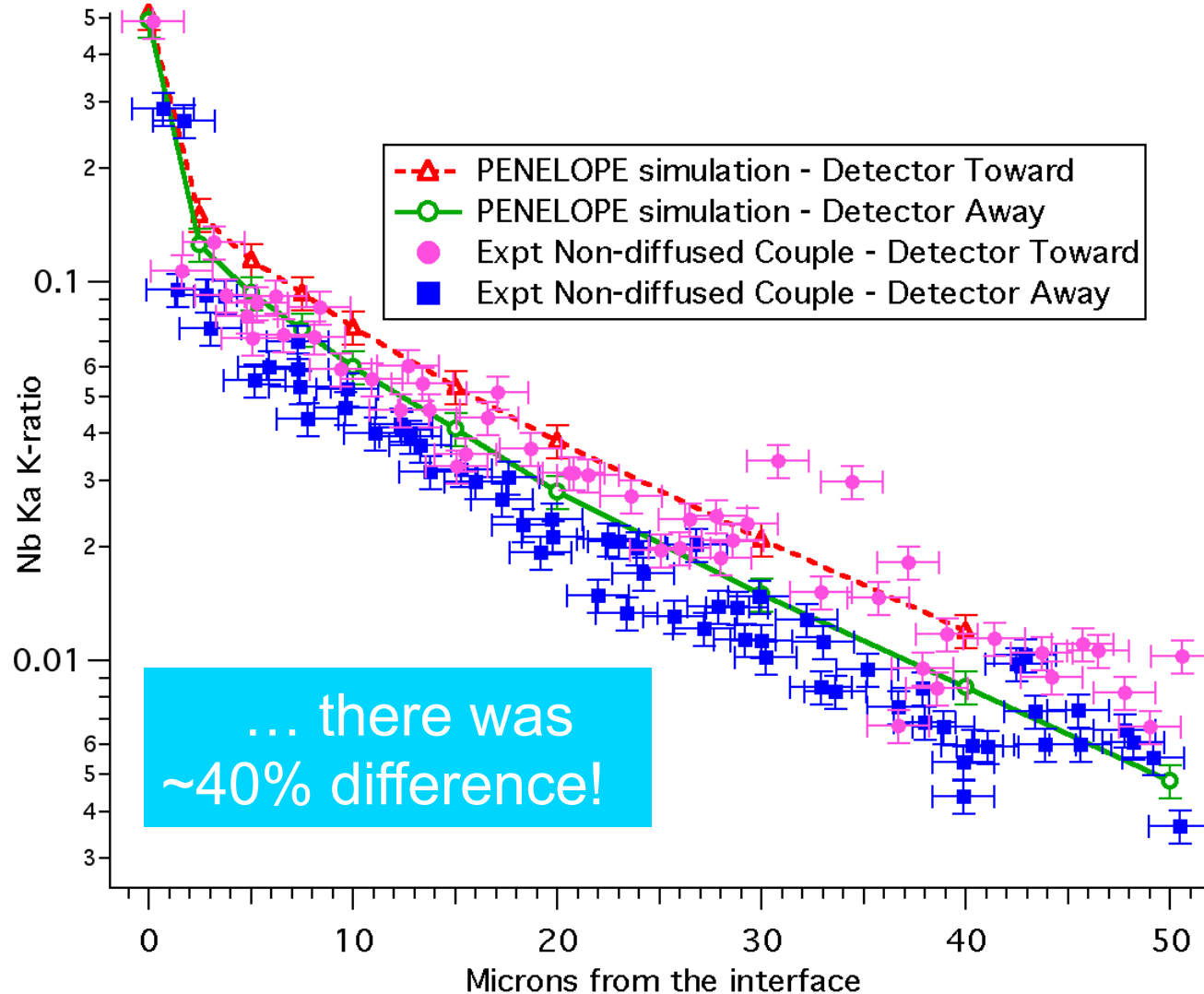


PENELOPE  
annular detector



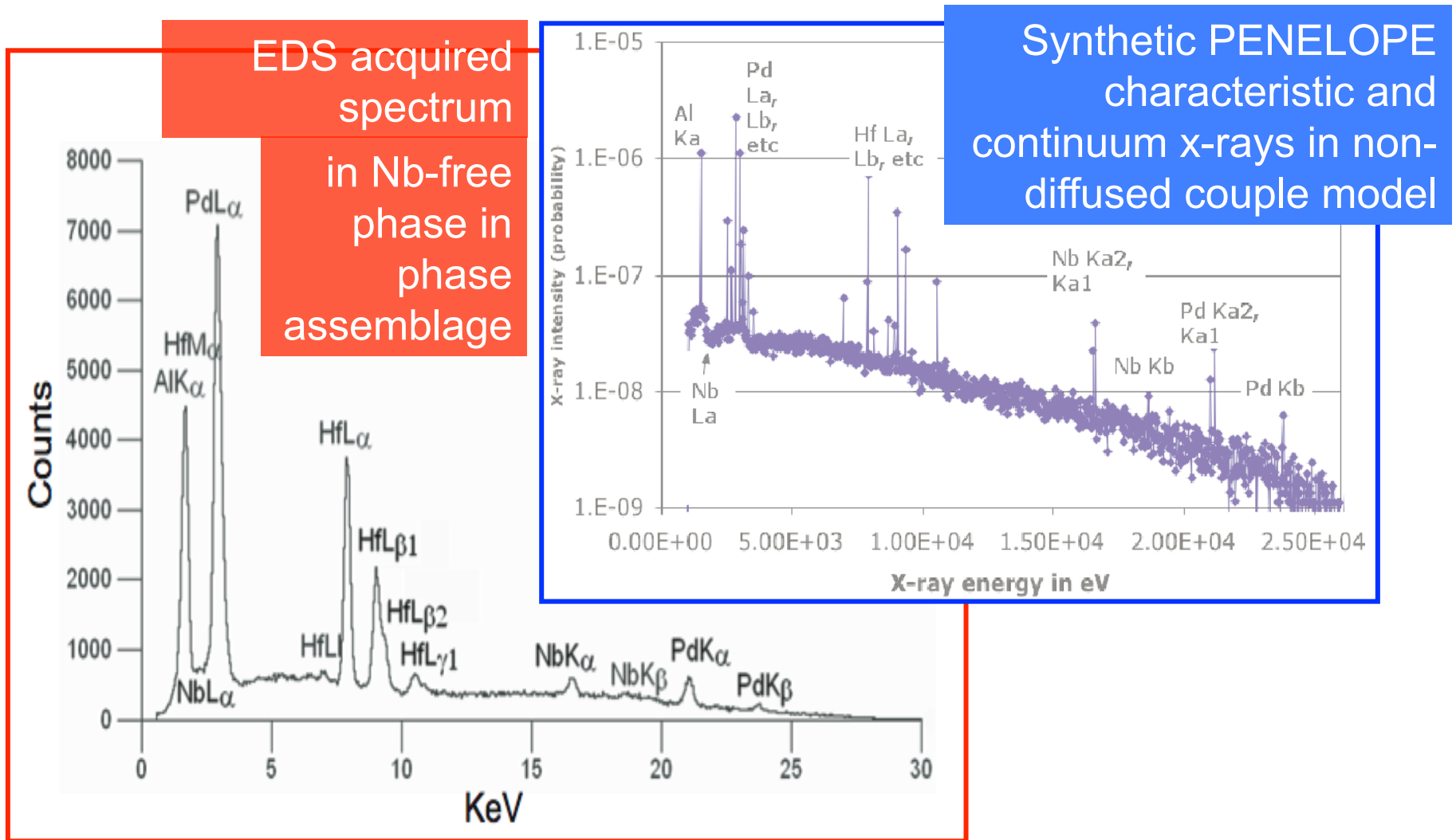
Actual WDS sample-  
detector geometry

We set up distinct experimental (non-diffused couple) and PENELOPE models: one with the Nb side facing the detector, the other 180° away ...



- Difference in amount of SF could be explained by differences in absorption: higher mac for Nb Ka thru the Pd2HfAl (57) vs thru Nb (20)
- This confirmed Secondary Fluorescence as the problem – and showed that PENELOPE is a good tool for simulating the effects of SF -- valuable when it is difficult or impossible to create experimental non-diffused couple.

Incidentally, Penelope can generate an EDS-like spectrum





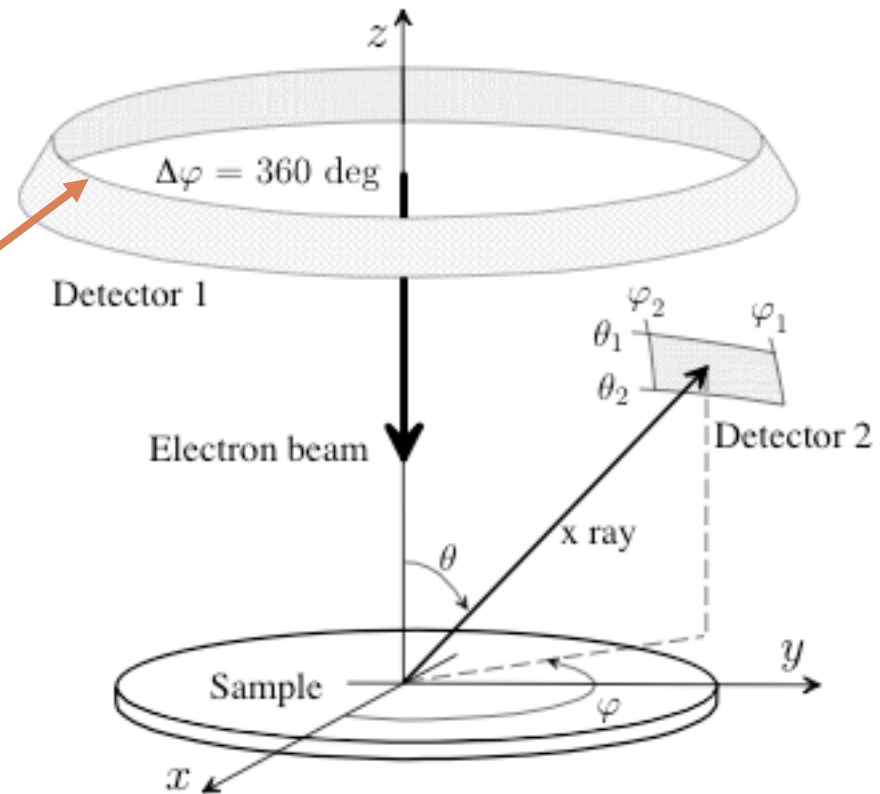
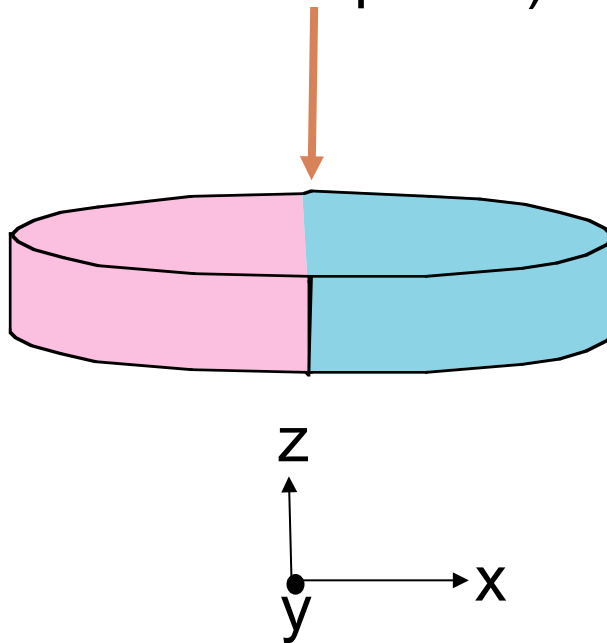
As an EPMA class project, UW-Madison students simulated various models of interest with PENELOPE on their personal computers.

1. Meteorites: Fe diffusion In Cu particles
2. Trace Ti and Al in quartz
3. Trace Mg in olivine, Fe in plagioclase
4. Pyroxene geothermometry: Ca in opx lamellae in clinopyroxene

Recall: done Fall 2004

Simplified Model used:

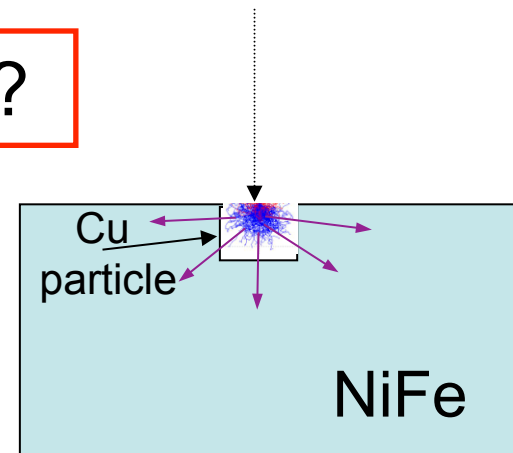
1. Annular detector only
2. Non-diffused couple (infinite half-spaces)





## 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%**.

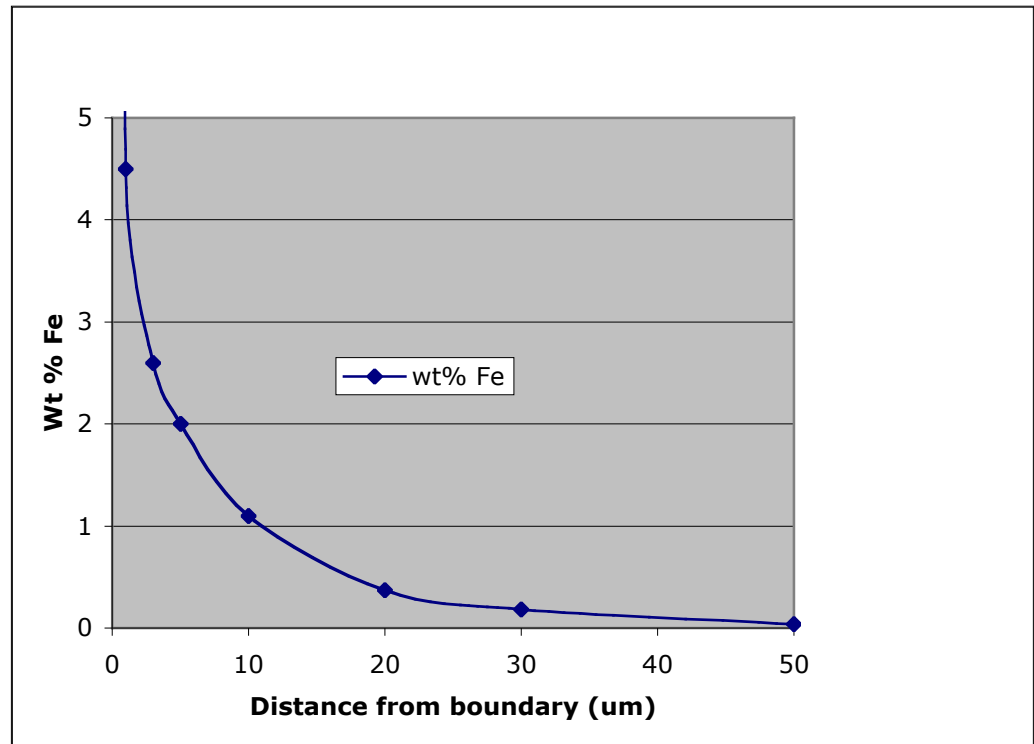
Cu formed @ 475°C in equilibrium with Fe has <0.2 wt% **Fe** in solid solution. **Secondary fluorescence???** They attempted to show with non-diffused couples.

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

## Fe Diffusion in Cu

PENELOPE simulates 2 wt.% Fe in Cu at 5  $\mu\text{m}$  away from pure Fe (e.g. a 10  $\mu\text{m}$  diameter Cu sphere could show 2 wt% Fe in its center.)

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  $52.5^\circ$ ) and keV (25)

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

## Trace level of Ti and Al in Quartz

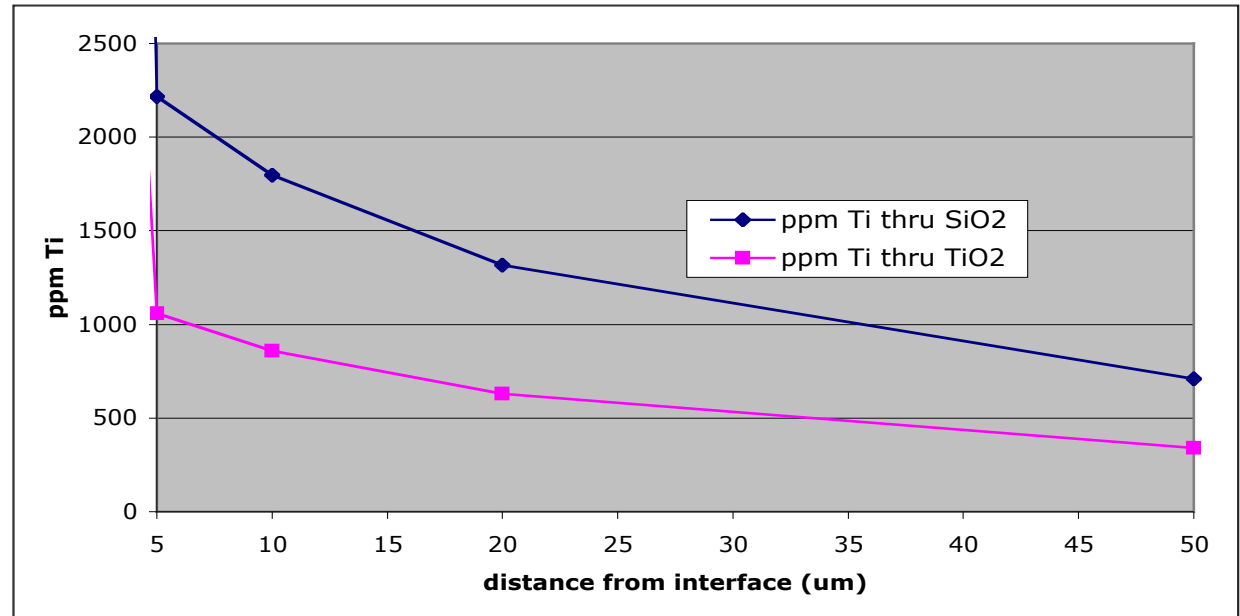
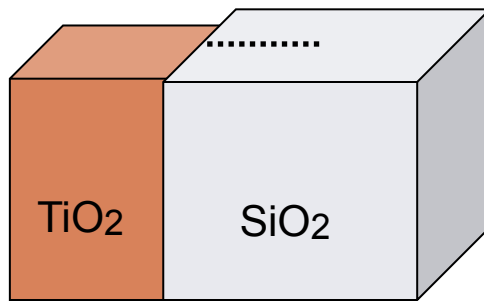
EPMA many times used to measure some trace element concentrations in minerals.

... one example is quartz

But is it really in the quartz?: low concentration of Al and Ti measured by EPMA: could this be from SF of Al or Ti-rich phases either within or adjacent to quartz (e.g. rutile needles in quartz)?

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

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

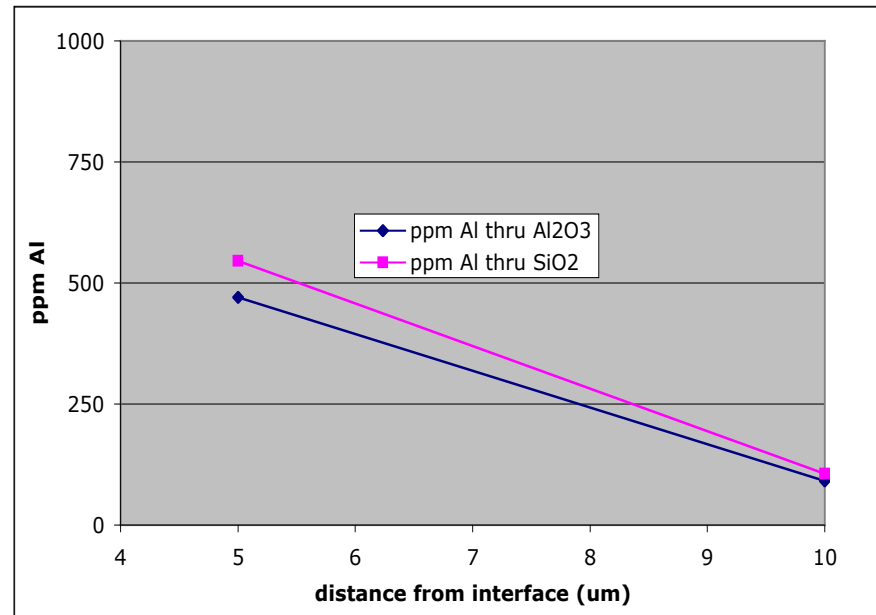
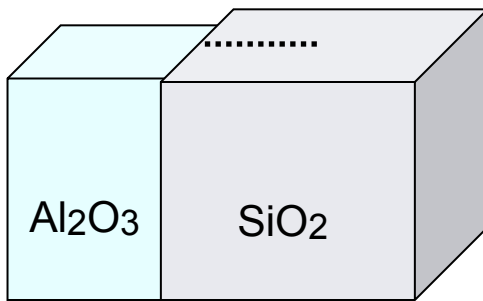


The 2 curves represent different paths out of the sample to the detector (different mass absorption values.)

It is clearly possible to get 500-1200 ppm of apparent Ti within 30 microns of the interface.

This is all from continuum x-ray excitation ( $E_0 = 20$  keV).

## “Al” in Quartz near corundum

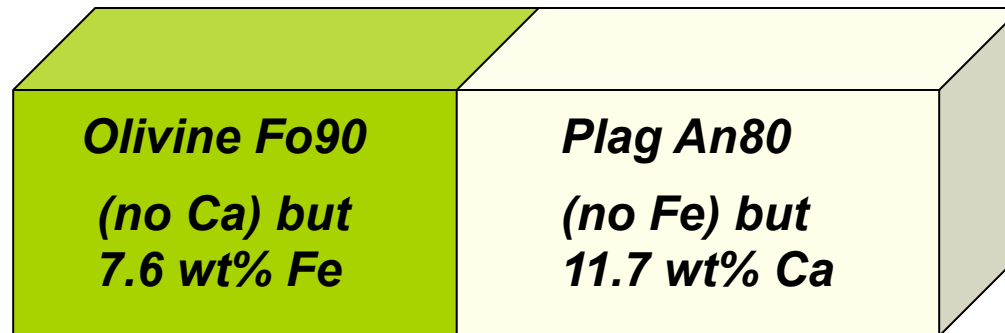


PENELOPE suggests that you need to be at least 10 microns away from a lateral Al-rich phase to be certain that SF producing less than 100 ppm of apparent Al.

A worst case scenario would be 500 ppm of Al at 5 microns distance.

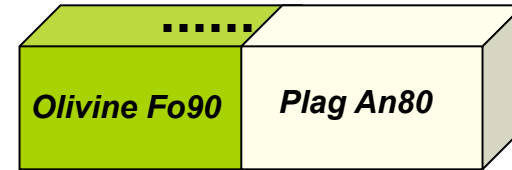
## Adjacent olivine and plagioclase

What SF can do...for trace levels of Ca in olivine  
and of Fe in plagioclase

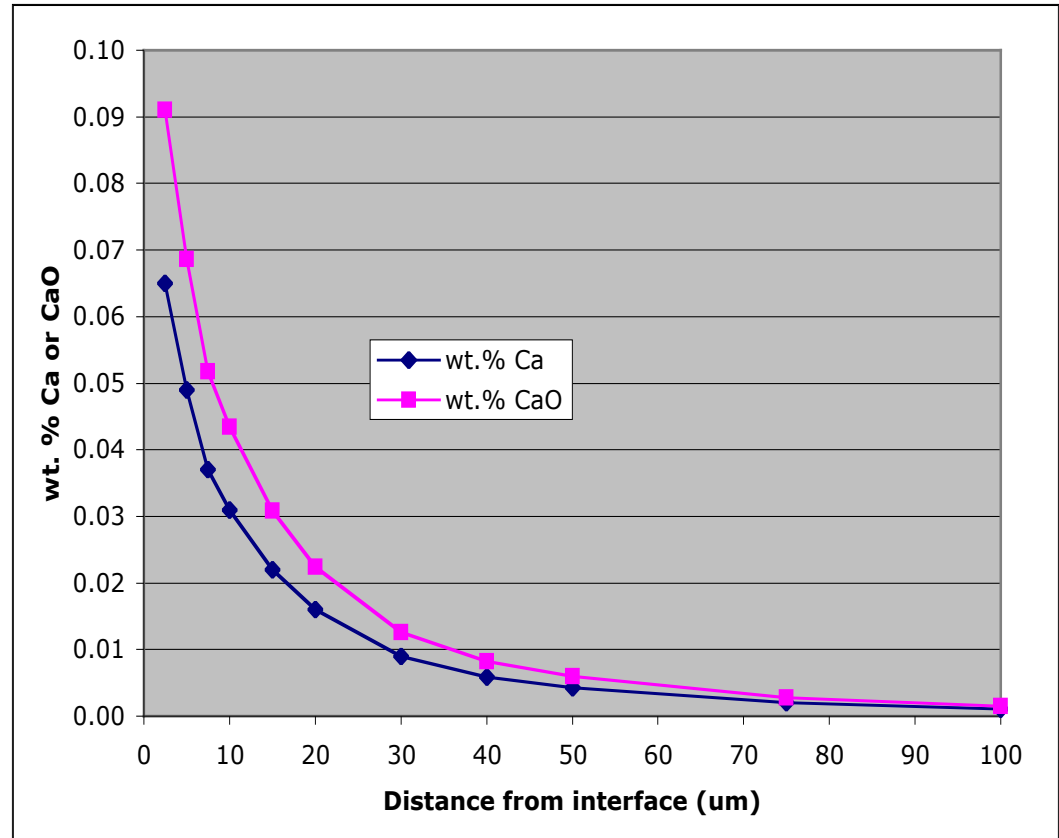


Conditions: 15 keV, 40° take off angle

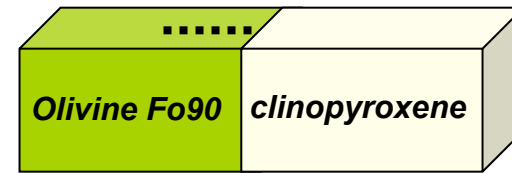
# Trace level of Ca in olivine



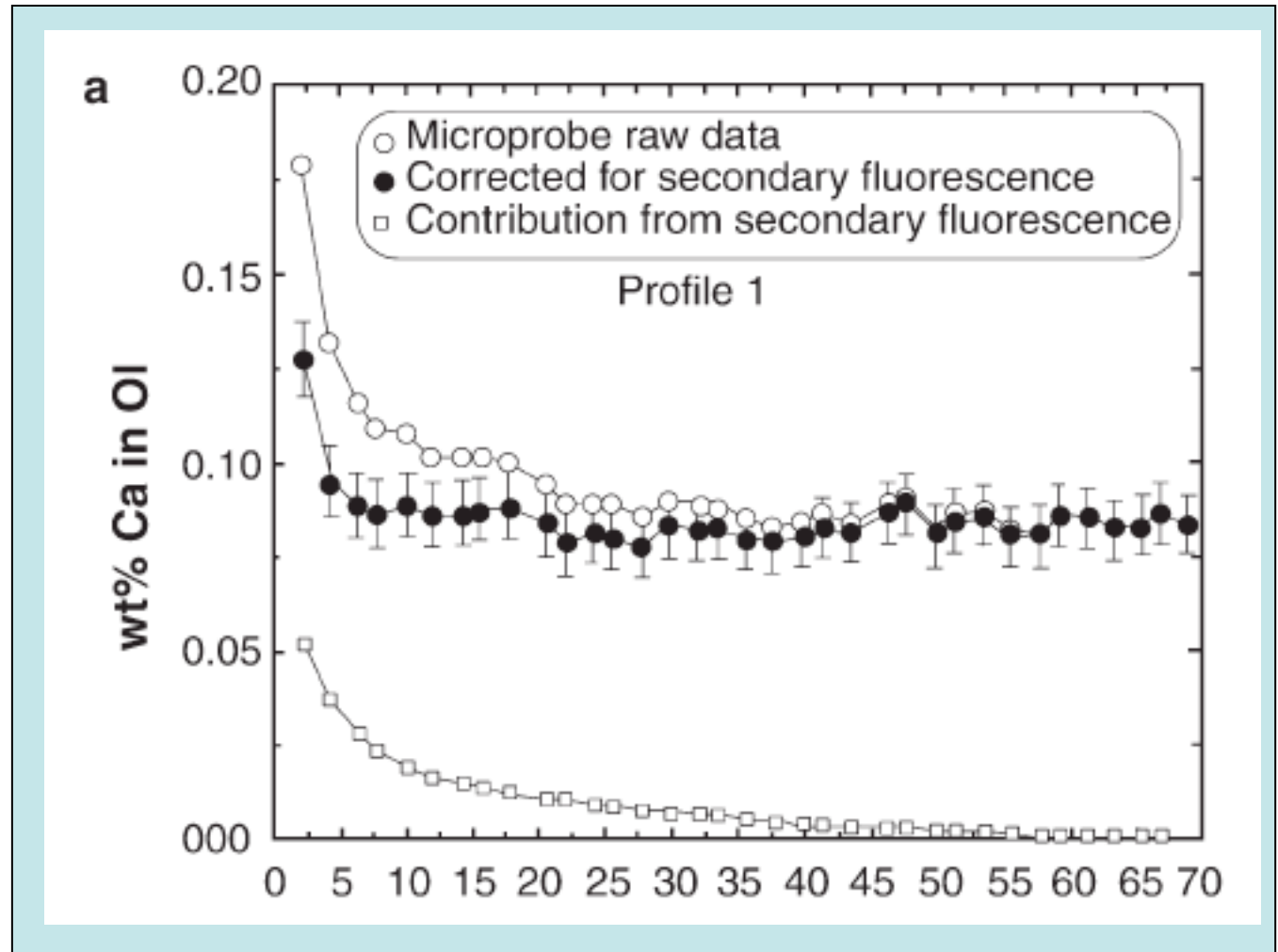
Secondary fluorescence can easily boost the Ca content particularly within 25 microns of rim adjacent to Ca-bearing phases.



# Correction for secondary fluorescence

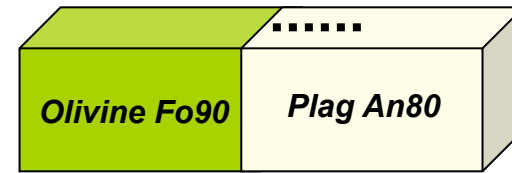


Llovet and Galan (2003) showed the correction for Ca in olivine adjacent to clinopyroxene using PENELOPE simulation:





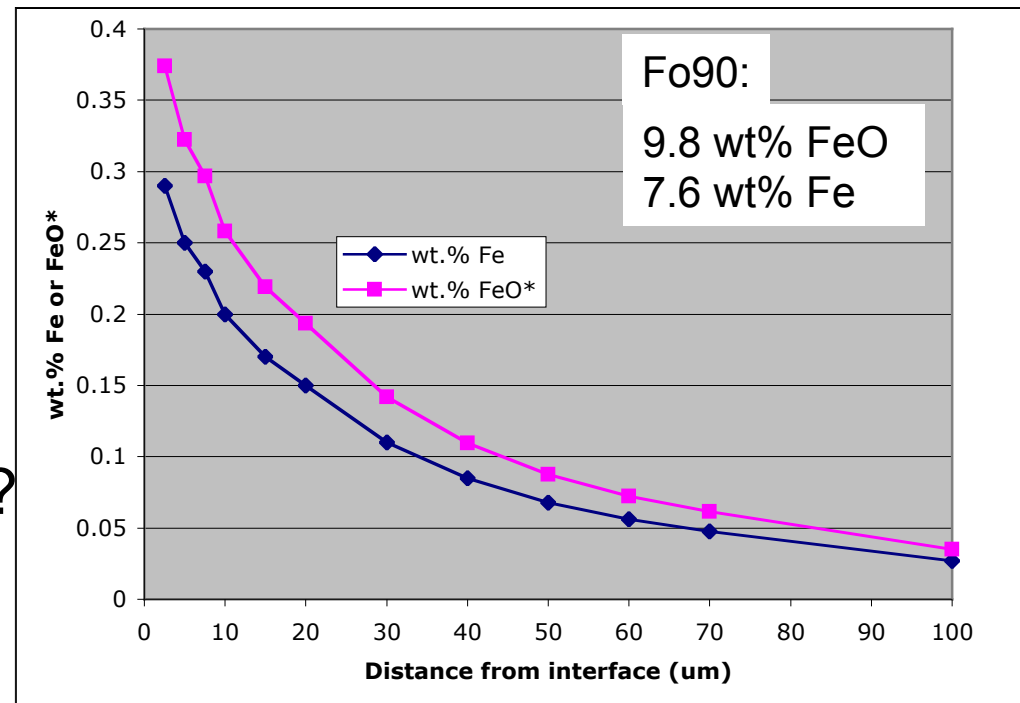
# Trace level of Fe in plagioclase



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

How much is due to secondary fluorescence?

> Quite a bit. And if olivine was fayalite ( $\text{Fe}_2\text{SiO}_4$ ), it would be much higher.



Model assumptions: 15 keV; olivine has 9.8 wt% FeO (7.6 wt% Fe)

## Ca in orthopyroxene lamellae within clinopyroxene

Coexisting compositions of ortho- and clinopyroxenes are used as a geothermometer.

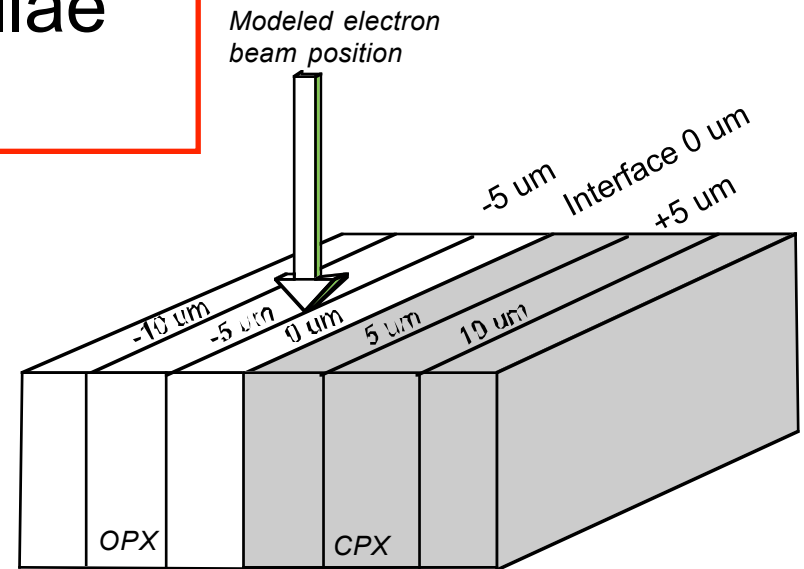
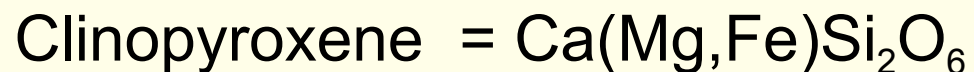


Figure 2. Cartoon illustrating model run positions. Negative values indicate a position in the orthopyroxene grain; positive values indicate a position in the clinopyroxene grain.

There is only a small amount of Ca in orthopyroxene; we decided to see if PENELOPE could tell the potential for error in Ca content of thin orthopyroxene lamellae, and the resulting error in temperatures.



# Additional Ca from secondary fluorescence of adjacent cpx

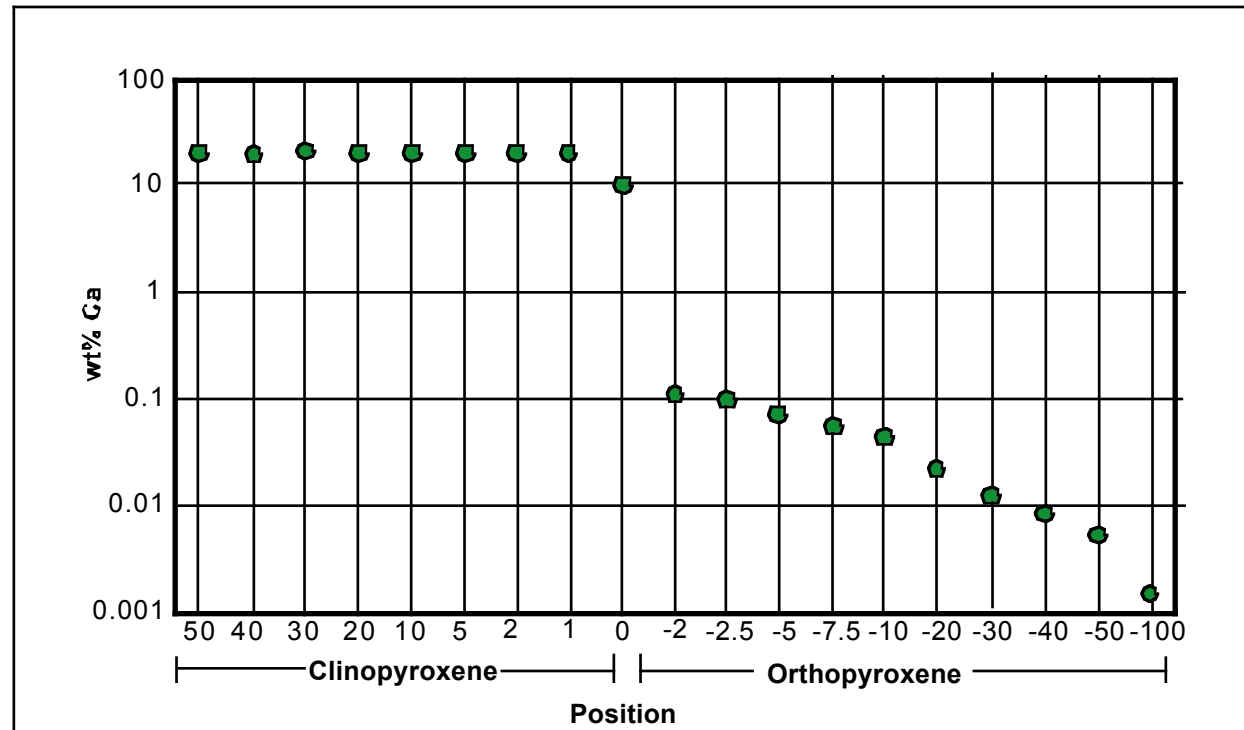


Figure 4. Log plot of wt % Ca from fluorescence in the system cpx-opx.

## PENELOPE SIMULATION

# IMPACT ON GEOTHERMOMETRY

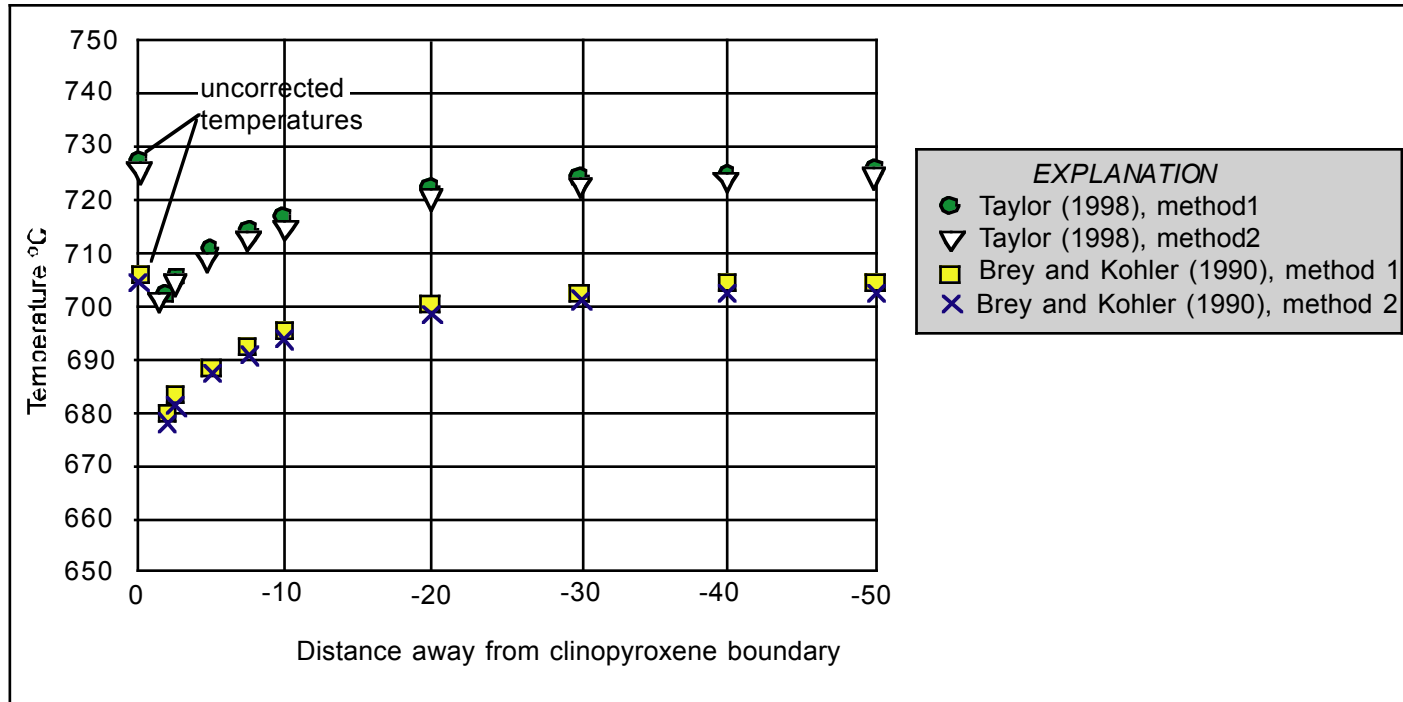


Figure 6. Plot illustrating change in calculated temperature based on subtracting the effects of fluorescence from orthopyroxene analyses. Method 1 = subtraction of fluorescence before ZAF correction. Method 2 = subtraction of fluorescence after ZAF correction.

## PENELOPE SIMULATION

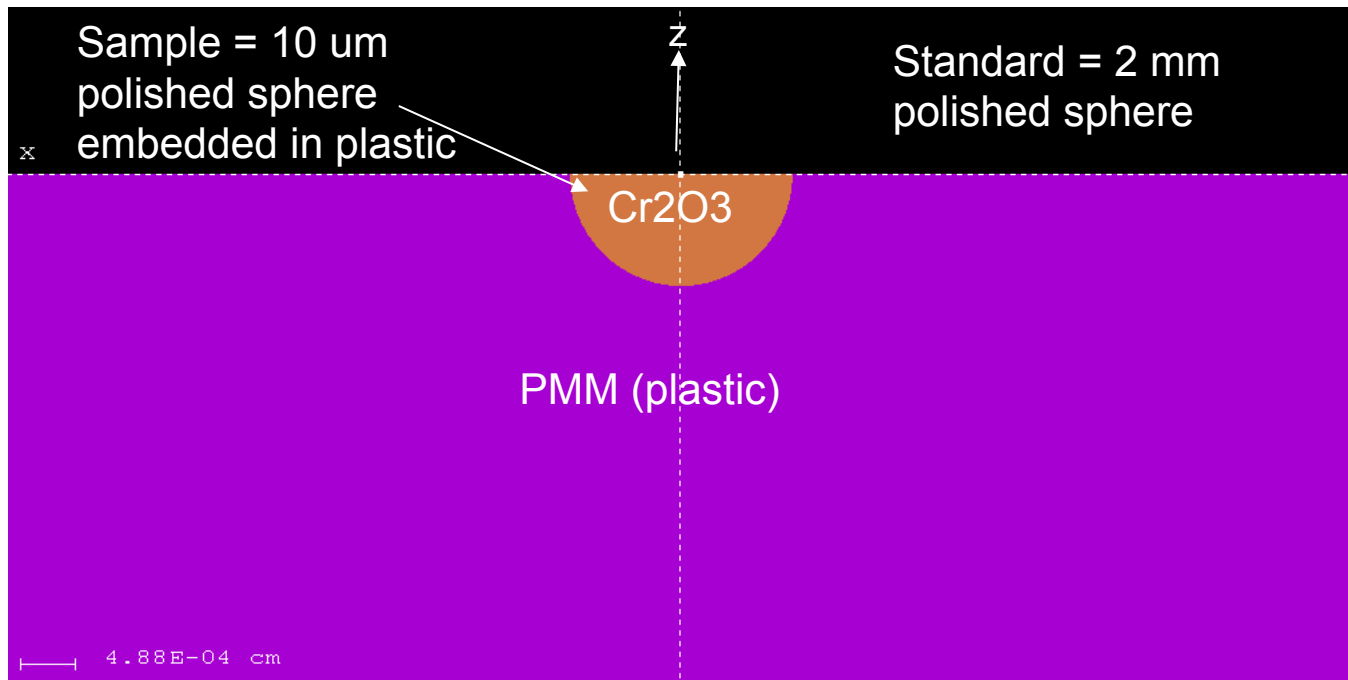
... and something else

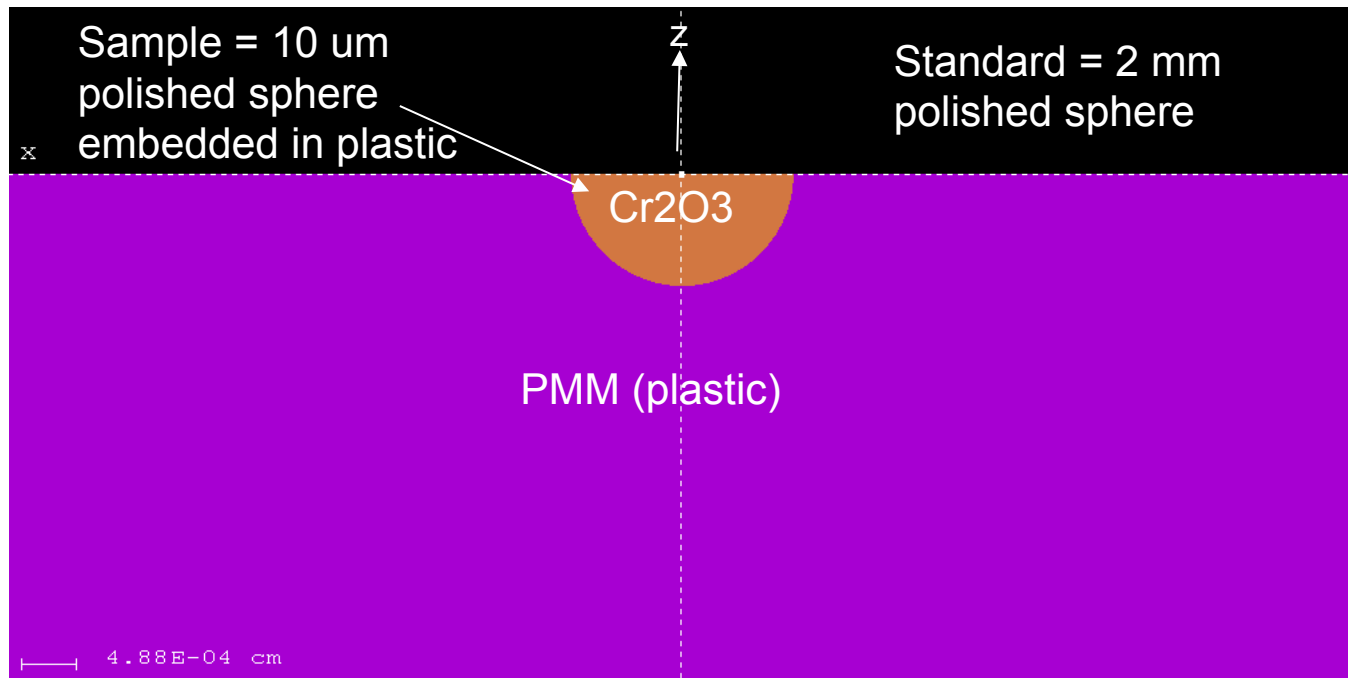
In troubleshooting low totals in chromite grain mounts, the question arose: if there is a several order magnitude size difference between unknowns (small grain separates) and the standard (large), what could result?

Can PENELOPE help?

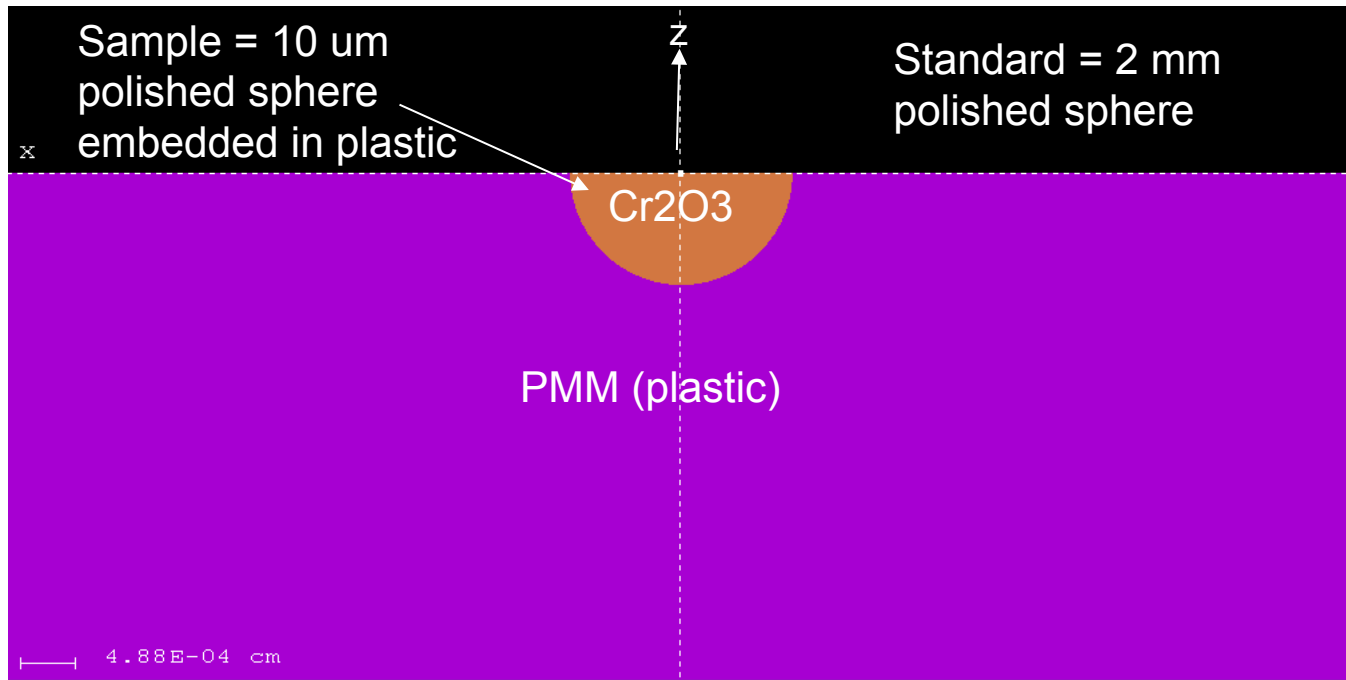
## Using the new PENELOPE geometry:

Compare a small sample (modelled here) sitting in plastic (epoxy) and a much large standard sitting in plastic





Is the lack of “additional” Cr x-ray counts resulting from “normal, within same phase” fluorescence responsible???

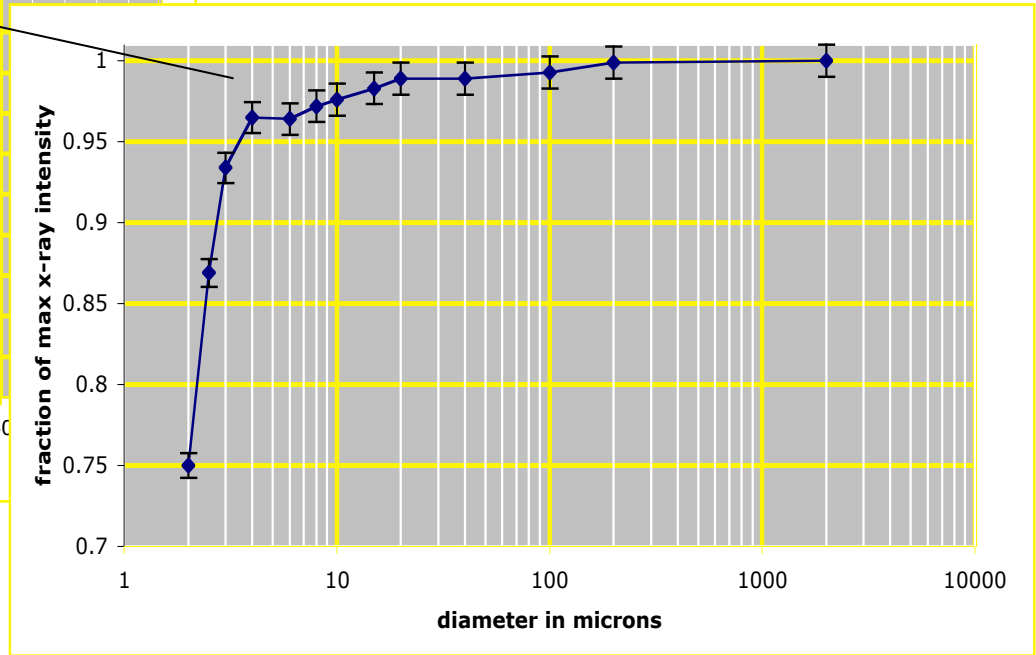
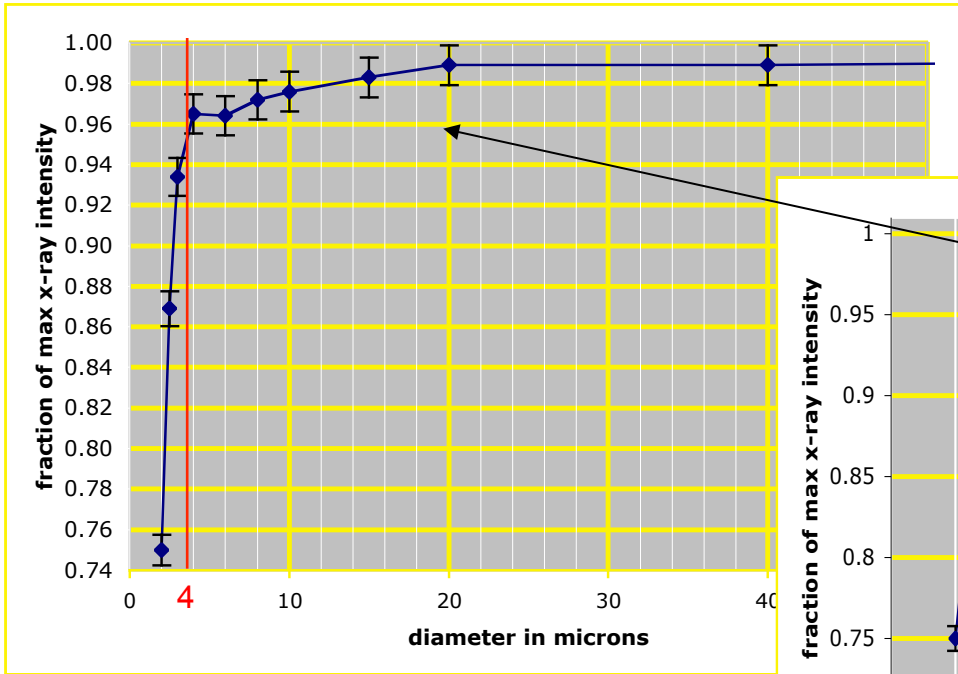


Set up a PENELOPE simulation: Standard of “huge size”, 2 mm; Unknowns of smaller sizes  
Accelerating voltage of 20 keV, TOA 40 degrees



# Yes, “missing” fluorescence may 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.

# In conclusion

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

PENELOPE provides a useful tool to evaluate -- and correct -- this secondary fluorescence.

Gross differences in sizes between standards and unknowns may introduce unsuspected errors due to “missing” fluorescence