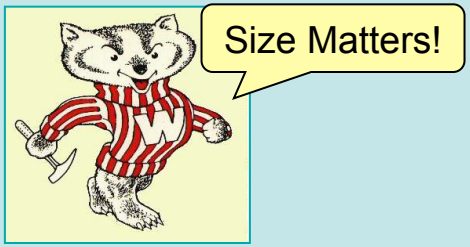

NIST-MAS Particle Workshop 2006

Complications of Primary Fluorescence in Particle Analysis in EPMA: The Standard vs Unknown "Size Discrepancy Issue"

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There are particles …. and there are particles….

"Raw" 3-dimensional objects present complications for EPMA, particularly for modeling and correcting absorption in the specimen --

But another issue, generally unrecognized, deals with particles that are polished for traditional EPMA, be they crystals in a rock, or individual separated crystals (including standards!) mounted in epoxy – *"Primary Fluorescence" or the lack thereof in either the standard or the unknown will lead to errors in quantitative EPMA!*

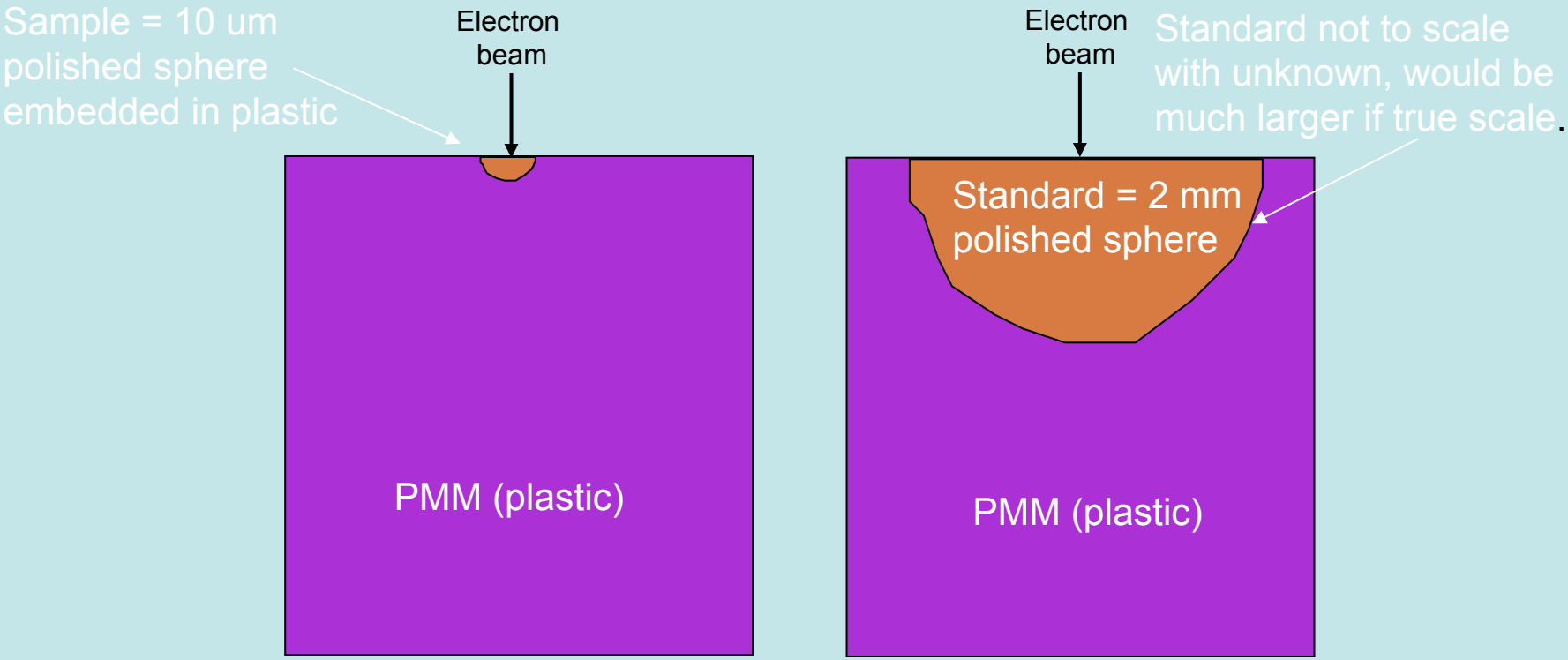
Abstract

The potential for erroneous quantitative EPMA analysis resulting from secondary fluorescence across phase boundaries in multiphase samples is recognized, though the ability to correct the effect have been difficult unless a specific geometry is experimentally created and evaluated. The development of the PENELOPE Monte Carlo program has provided one mechanism to quantify the extent of secondary fluorescence, and to simulate otherwise difficult to experimentally produce geometries.

In troubleshooting low analytical totals in chromite, $(Mg,Fe)Cr_2O_4$, grains (mineral separates mounted in epoxy and polished for EPMA), at the same time that I was evaluating secondary fluorescence errors in another material by running PENELOPE simulations, a light bulb went off -- and I set up simulations on a simple Cr_2O_3 particle, where the fluorescence materials were the Cr_2O_3 and the epoxy in which it was embedded.

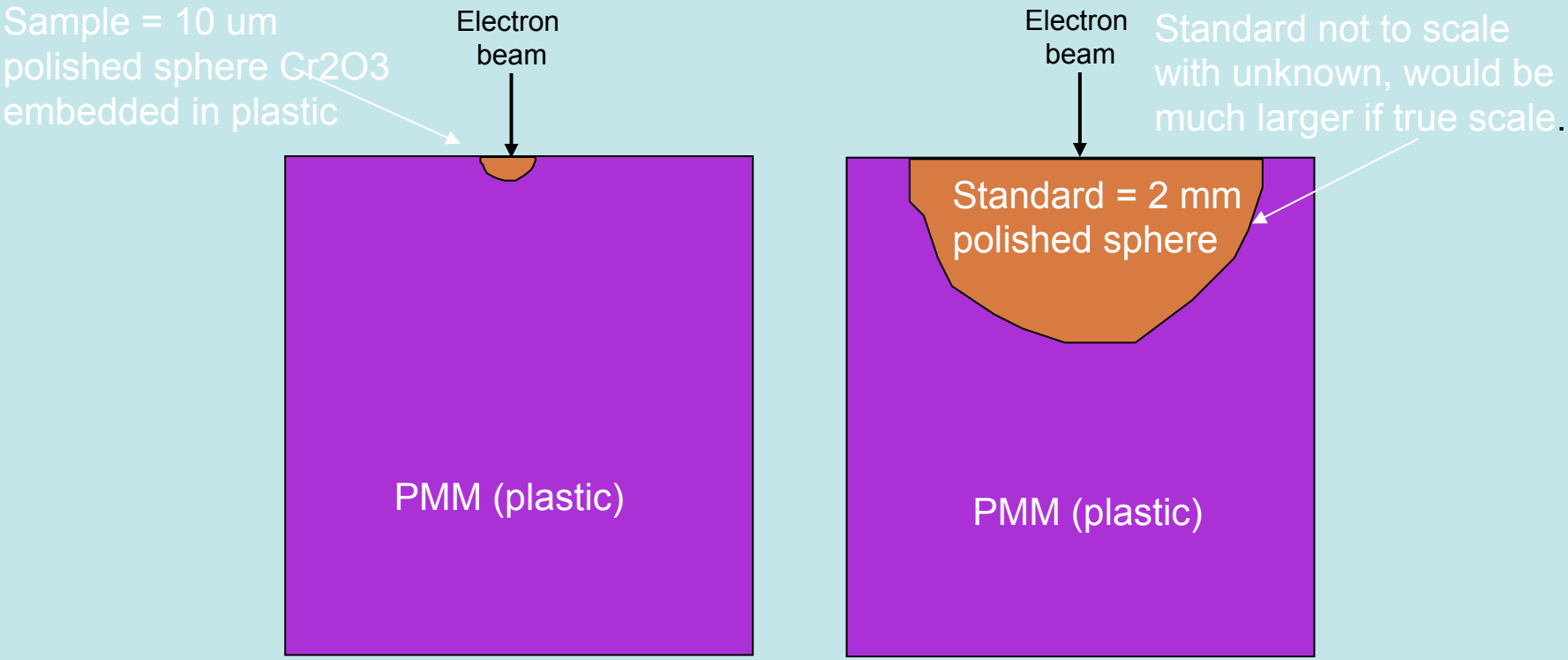
The result was surprising: a non-trivial amount of Cr Ka x-rays is produced at a significant distance from the primary electron excitation volume, due to continuum fluorescence (E_0 = 20 keV). If the Cr_2O_3 ***standard*** is a typical "large" particle, e.g. 2 mm in diameter, but the unknown (here, same Cr2O3) is ***significantly smaller***, e.g. 10 micron diameter, the Cr Ka K-ratio is 0.975 -- where one would expect it to be 1.000. Or, another way of looking at it is, we are missing 2.5% of Cr Ka x-rays because there is no Cr_2O_3 out where the epoxy is? This would cause a situation of erroneously low K-ratios. The reverse is where small grains are used as the standard (not atypical for certain compounds that are synthesized and then used as EPMA standards "because that's all we got"); in this case, large unknowns would have erroneously high K-ratios.

Difference between small sample and large standard

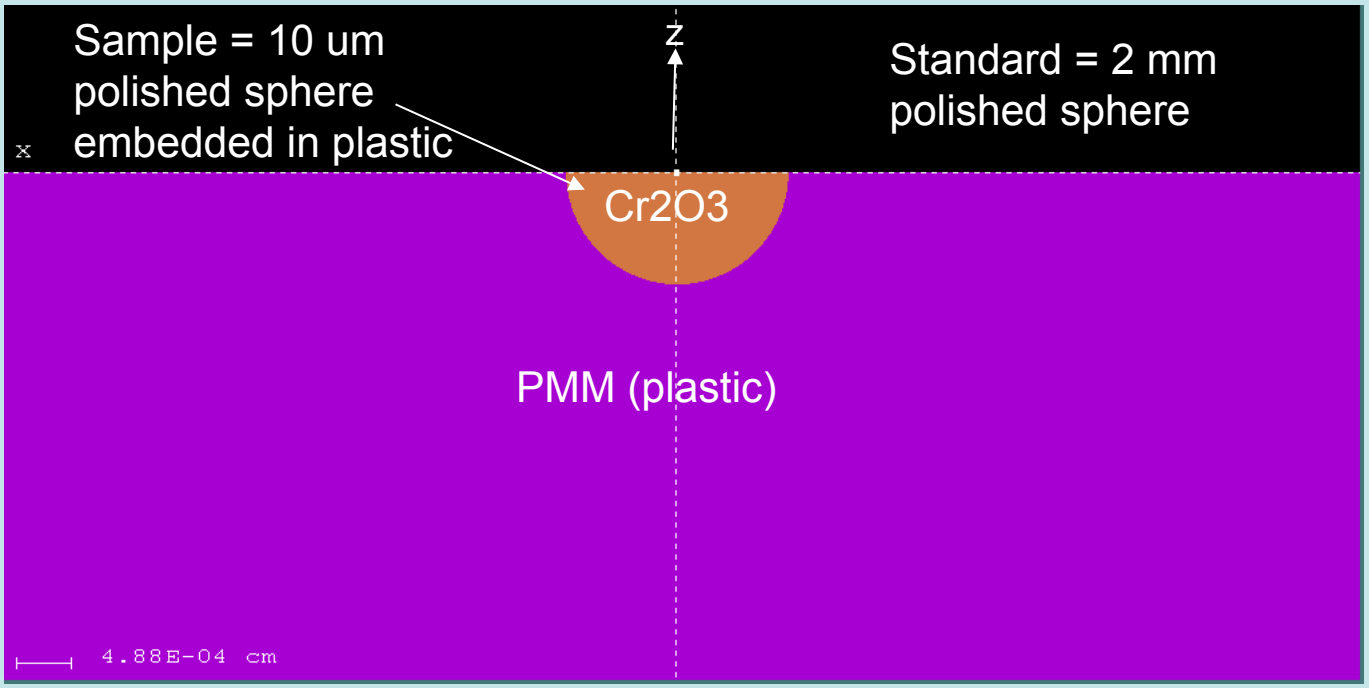


In troubleshooting low totals, the question arose: if there is a several order magnitude size difference between unknowns (small grain separates) and standard (large), what could result?

Difference between small sample and large standard



If the primary electron “interaction volume” is confined within the material, and therefore the primary x-ray generation is also confined therein, is the lack of “additional” Cr x-ray counts resulting from primary fluorescence outside the primary electron interaction volume of any importance in “normal” EPMA???



Set up a PENELOPE Monte Carlo simulation:

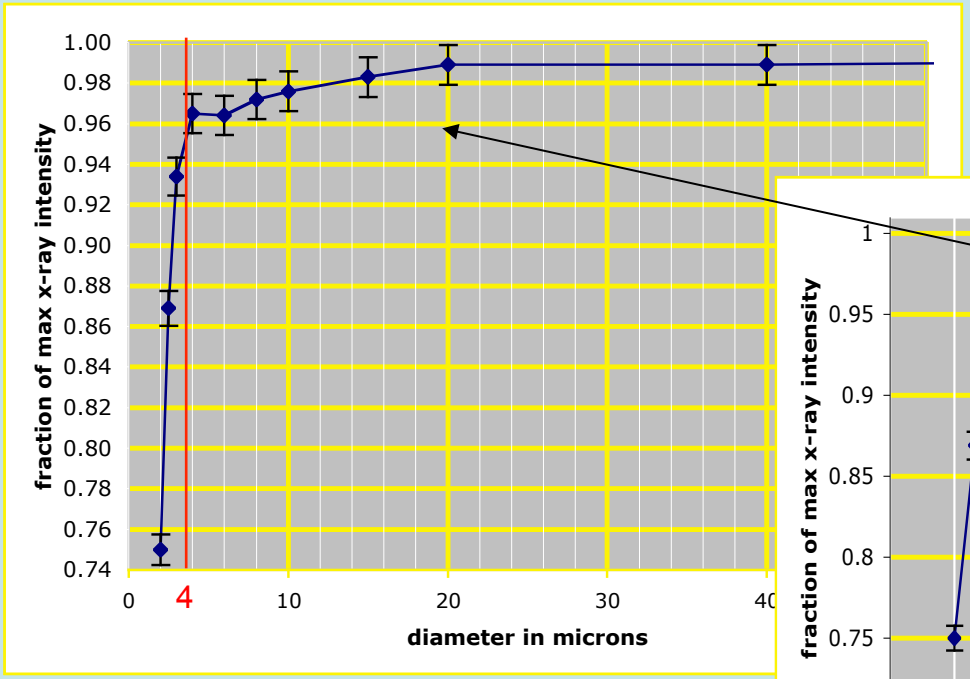
Standard of “huge size”, 2 mm

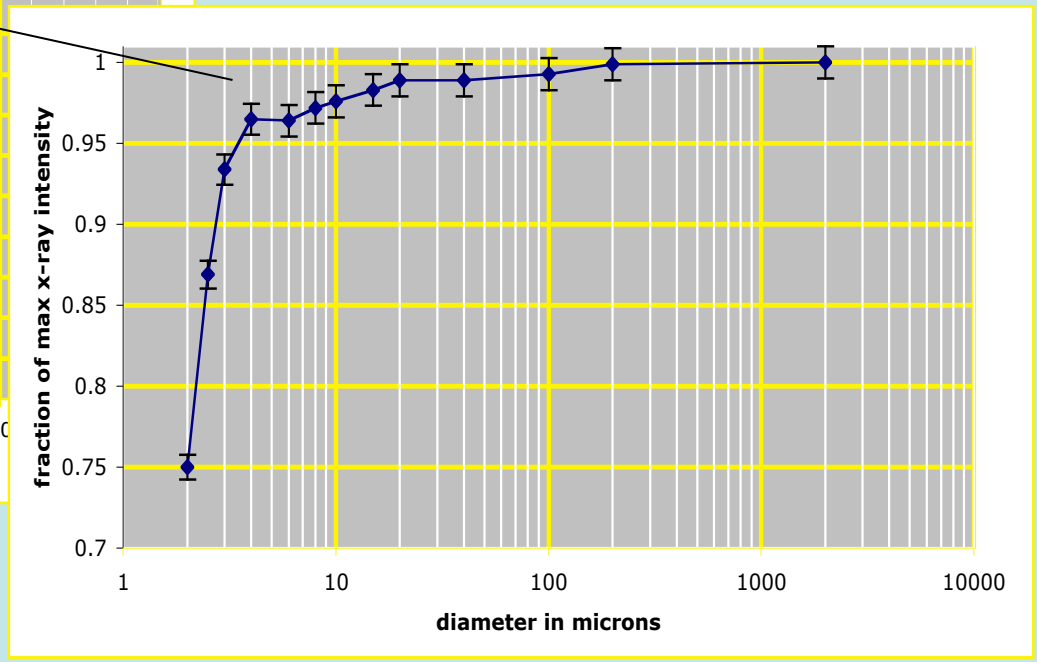
Unknowns of much smaller size

Accelerating voltage of 20 keV, takeoff angle 40°

Yes, Fluorescence can cause problems

Standard=2000 μm Cr2O3
Unknown = smaller Cr2O3





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

A 100 μm grain of pure Cr2O3 will have 1% low Cr K-ratio, and a 10 μm 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)

Conclusion

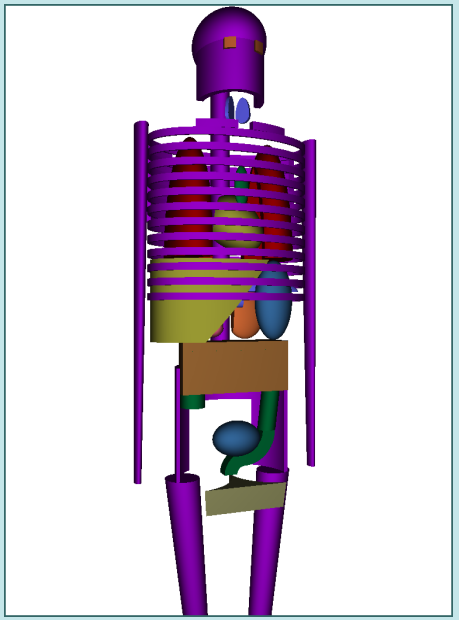
Discrepancies in size between unknown and standard can lead to small, but noticeable errors, because secondary fluorescence yields

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

or

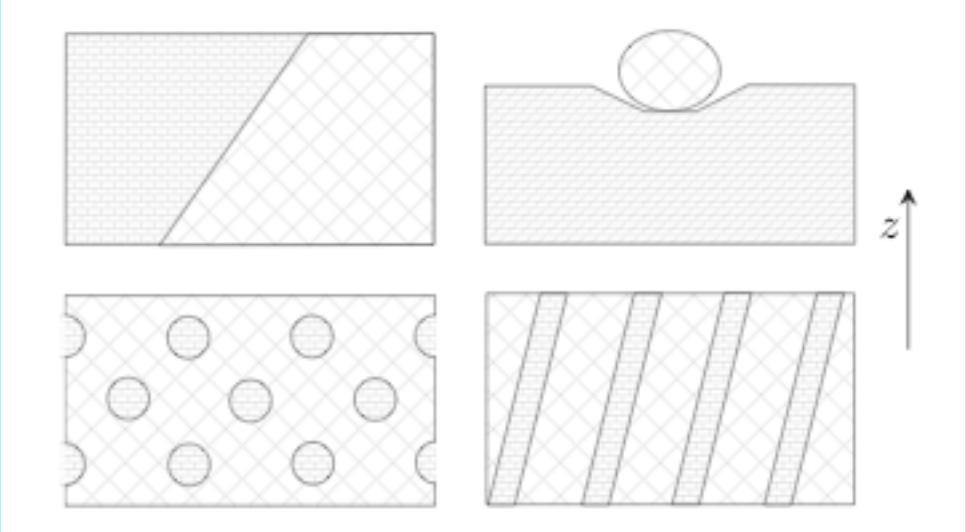
- a lack of additional x-rays if the phase is small and mounted in epoxy.

PENELOPE



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

New PENELOPE geometries



More realistic geometries are now available

Penelope Hands-on Workshop

- August 4-5, immediately following the M&M 2006 conference in Chicago
- Nearby in Madison, Wisconsin
- Instructors Francesc Salvat and Xavier Llovet
- Two days of hands on instruction, development of geometric models, optimization of parameters, particularly for compositions and geometries of interest to participants. Particular attention paid to problems of secondary fluorescence.
- Sponsored by UW-Madison and the Microbeam Analysis Society
- Details available from John Fournelle