Using PENEPMA to Model Some Problems in EPMA

Statement of the Problem

A long standing -- and difficult -- issue in electron probe microanalysis has been **secondary fluorescence across phase boundaries**.

There is general understanding that the incident electron beam hits the target material with a small spot and scatters some within the material. Primary x-rays are generated in an "interaction volume" a few cubic microns in width-depth.

What is more difficult to comprehend is the extent to which the primary x-rays (both continuum and characteristic) can travel long distances and excite different material, resulting in secondary x-rays that can "contaminate" the detected spectrum. This is most serious for two recognized cases:

(1) trace element analysis, and

(2) analysis of small bodies, i.e. inclusions, lamal-lae,

as well as one unrecognized case:

(3) "the size discrepancy problem", where there is a large difference in the sizes of the standard and the unknown.

(Above) Irradiating a zircon with 15kV electrons generates Si Ka, Zr La, O Ka (and associated lines) and continuum x-rays -- but all will be well constrained within a few microns of the impact spot.

However, adjacent phases are susceptible to wandering x-rays generated from within the primary excitation volume in the zircon: in the above case, only continuum x-rays will be > 4.96 keV needed to excite Ti Ka.

If Hf is present (it usually is), then Hf La (7.9 keV) will happily excite Ti Ka also.

How to Deal with Secondary Fluorescence?

There are 4 approaches:

(1) separate the material from the second phase, eliminating the problem (this is generally very difficult),

(2) minimize the effect by running at a lower kV (and using L lines vs K lines, etc), which can create other analytical difficulties,

(3) model it experimentally--possible for diffusion couples, creating non-diffused couples,

(4) model it with a Monte Carlo simulation that tracks x-rays as well as electrons.

Modeling Secondary Fluorescence with the Monte Carlo Program PENEPMA-PENELOPE

The PENEPMA Monte Carlo program, based upon PENELOPE, has been shown to accurately predict the extent of secondary fluorescence in EPMA.

PENELOPE is a computer program developed to model high energy radiation transport in bodies with complex geometries, using Monte Carlo procedures. (One of its main intended uses was to model radiation treatments in cancer patients. EPMA capabilities have been added in collaboration with EPMA users.)

It differs from other Monte Carlo programs used by the EPMA/SEM community in that it follows each electron and each x-ray and records the types of interactions and the location. Thus, an x-ray generated by the primary electron beam is followed throughout the modelled geometry and any secondary interactions are recorded. Evaluating secondary fluorescence then is possible.

The program is written in Fortran and can be compiled under various operating systems (though a useful geometry viewer runs only under Windows). It runs using 3 input files that are edited to contain specific information about (1) the EPMA conditions, (2) all the physics needed for each element involved, and (3) the geometry desired. There is a fairly steep learning curve, but with ~2 hours of instruction a committed user can be up and running PENEPMA for a problem they are concerned with, using one of the simple geometries.

Major and minor element x-ray spectra in a simple single body geometry can be generated quickly, but for multiple body geometries where secondary fluorescence at trace element levels is the issue, it can take many hours to get results that are above a (low) detection limit -- but in my opinion, that is an acceptable trade-off, giving its usefulness.

The authors are working to make it more accessible and user friendly. Output specifically refined to show secondary fluorescence was added in 2006 in response to requests from the EPMA community.

Fe Diffusion in Cu Inclusions in Meteorites

Cu in most stony meteorites occurs as 1-20 um grains associated with troilite (FeS) and NiFe. Duke and Brett (1965) considered the concentration of Fe in 10-20 um Cu grains in a stony meteorite. Their EPMA measurements (25 kV on ARL) gave 1-4 wt% Fe. However, Cu formed @ 475C in equilibrium with Fe has <0.2 wt% in solid solution, so the results were confusing.

A simulation was run with PENEPMA with the same operating conditions (25 kV, TOA 52.5°) for a simple diffusion couple geometry (Cu-Fe), showing 1 wt% Fe apparently present in the Cu at 10 um distance from the Fe. This matches closely recent experimental work (Llovet and Galan, 1996).

Simulations closer to the boundary run much faster since the probability of Fe Ka generation is higher, but at greater distances (e.g. 100 microns), several hours may be necessary to achieve x-ray intensity that is statistically meaningful. In this case, we see secondary fluorescence producing 34 ppm of Fe at 100 micron away from the Fe metal.

Adjacent olivine and plagioclase

Secondary fluorescence can easily boost the Ca content in olivine, particularly within 25 um of the rim adjacent to Ca-rich phases, such as plagioclase, modelled here.

This will happen in plagioclase that is adjacent to an Fe-rich phase (e.g. olivine, magnetite, basaltic glass). Typically EPMA analyses of plagioclase show some tenths % FeO, some/most of which could be due to secondary fluorescence.

Ca in Opx Next to Clinopyroxene

Coexisting opx and cpx are commonly utilized as a geothermometer. The opx has a small amount of Ca; the question that PENEPMA can answer is, how much error in temperatures can be attributed to Ca caused by secondary fluorescence from nearby cpx?

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

The far left plot shows the apparent (false) Ca content in Ca-free opx, adjacent to cpx, decreasing with distance away from the couple boundary. The near left plot shows the errors due to Ca produced by secondary fluorescence: the maximum error is 20-25° too low for measurement 3 microns away from cpx, slowly reaching the correct value 30-40 microns away from the cpx. The error is slightly reduced if the subtraction of the fluorescence amount is done prior to ZAF correction (method 1), rather than after (method 2).

Ti in Zircon Thermometry

Watson and co-workers experimentally determined that the amount of Ti incorporated in zircon (~1 to 1000s ppm), coexisting with a high-Ti mineral (e.g., rutile or ilmenite), was proportional to the temperature at which the zircon crystallized, and could be used as a geothermometer. For the low levels being measured, SIMS is the preferred method. However, sometimes EPMA is used, and then secondary fluorescence must be considered. Here, PENEPMA is used to model two situations: experiments where rutile may be in close proximity to zircon (above right), and in a polished probe mount where zircon is adjacent to ilmenite (below).

Geometry model 6   Geometry model 2-4

	Rutile Diameter	Distance Zirc Rim-Rutile Rim	Number Rutiles	Matrix Material	Spurious Ti (ppm)
1	Zircon Only		0	Glass w/ Ti	452
2	30	15	5	Glass w/ Ti	948
3	30	15	5	Pb-glass	390
4	30	15	5	epoxy	1179
5	30	60	5	Pb-glass	25
6	4	0	5	epoxy	61
7	4	0	5	epoxy	120

Seven different cases have been modelled here, simulating 15 kV beam spots in the center of 30 um diameter synthetic zircons surrounded by various glasses or epoxy, and embedded with rutiles of various sizes and spacings. Two geometries are shown (cross section and plan views, above left). In the table, Geometry 1 shows that with no rutile and only silicate glass with 6 wt% Ti, there will be apparent 452 ppm Ti. Geo 2 adds 5 rutiles (30 um diameter, 15 um distance rim-rim), and now the apparent Ti is 948 ppm. If the Ti-bearing glass is dissolved and replaced by Pb-glass (Geo 3), 60% of the secondary fluorescence (SF) is suppressed (but 40% remains). If the glass is replaced by epoxy, the apparent Ti goes up to almost 1200 ppm! Two points: this is all continuum SF; and conceptually, we can view the Ti phases from point of "solid angle" that they present to the x-rays generated in the incident electrons' primary excitation volume.

Above is a BSE image of a rock where zircons are surrounded by ilmenite, hematite and biotite (from C. Morisset, Univ. British Columbia). The points indicate EPMA analyses for Ti in zircons; data and inferred temperatures not taking secondary fluorescence into account, range from 162 ppm, 1064°C (Zr1) to 645 ppm, 1314°C (Zr4). Modelling a simple diffusion couple with PENEPMA shows that these could be easily caused by secondary fluorescence from the nearby ilmenite (and biotite).

Does Size Matter in EPMA?... yes

PENEPMA simulations show that a significant difference in size between an unknown and the standard will lead to some errors.

Standard=2000 μm Cr2O3
Unknown = smaller Cr2O3