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The Problem of Secondary Fluorescence in EPMA in the Application of the Ti-in-Zircon Geothermometer and the Utility of PENEPMA Monte Carlo Program

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Zircon (ZrSiO4) is a small mineral highly resistant to chemical changes; this robustness has led it to be used for estimating earth conditions eons ago. It has been used to date geologic events, measuring its radiogenic Pb, U and Th isotopes. The oldest dated mineral on Earth is a zircon from Australia, and its oxygen isotope value suggests Earth's crust was cool and wet as long ago as 4.3 billion years [1]. Watson and Harrison [2] experimentally determined that the amount of Ti incorporated in zircon (~1 to 1000s of ppm), coexisting with a high-Ti mineral (e.g., rutile TiO2 or ilmenite FeTiO3), was proportional to the temperature at which the zircon crystallized and could be used as a geothermometer. In cases where the level of Ti is extremely low (1-100 ppm), the preferred method of quantification is ion probe (SIMS). However, there are situations where EPMA is used to measure Ti: (1) for original validation of the abundance of Ti in zircons grown experimentally (i.e., for SIMS standards), (2) by geologists who do not have ready access to SIMS, or (3) where the large SIMS spot size (~25 microns) is prohibitive. However, as has been long recognized, the electron beam's interaction volume is tiny relative to the volume excited by both characteristic and continuum x-rays generated in the primary electron beam volume. The question that has perplexed microanalysts is, exactly what is the amount of secondary fluorescence (SF) that is measured during EPMA—particularly critical for trace element levels. The problem potentially can be addressed experimentally for some systems, but is not trivial. An alternative approach is via Monte Carlo simulations. The PENEPMA program, based upon PENELOPE [3], has been shown to accurately predict the extent of SF [4] and has been recently modified to explicitly state SF intensity [5].

Two cases have been modeled here by PENEPMA, both at 15 keV, with 40° take off angles. There is only SF from the continuum. Case 1 examines the potential for SF in experimentally grown zircons that have crystals of rutile either touching them or present in the vicinity, and all are in a glass which also has Ti present in it (6 wt%). Fig 1 shows the geometry (cross section and plan views), with a 30 μm diameter zircon (0 wt% Ti) in a matrix, with 5 rutiles (30 μm diameter) spread out 15 μm away. Table 1 presents the results of using different matrix materials, and 2 different sizes of the surrounding rutiles, following various configurations described in [2]'s experimental zircons. Row 1 shows that if the experimental glass were left present during EPMA of a zircon core, over 400 ppm of fictitious Ti could result from SF of it alone. If 5 equal size rutiles were scattered in the glass matrix 15 μm away, an additional 500 ppm of spurious Ti counts would result by SF. The researchers in [2] recognized the problem of the glass and dissolved it, replacing it with a Pb-glass to attempt to minimize the SF of Ti with the commingled rutile. Row 3 shows that the Pb-glass moderates the SF effect but does not eliminate it. If the same number and size rutiles are moved back further from the zircon (60 μm away) the SF effect drops drastically, down to 25 ppm. Simulations were also done in an epoxy matrix: the effect of replacing a glass matrix with epoxy caused an increase in the SF effect (row 4), apparently due to a lowered absorption of the continuum x-rays moving out from the zircon, and also a lowered absorption of SF-produced Ti Ka x-rays. The last simulations of much smaller rutiles (4 μm diameter) attached to the edge of the zircon yielded ~10 ppm of fictitious Ti per attached grain.

Case 2 examines the potential for SF in a rock where zircons are surrounded by ilmenite, hematite and biotite (suggested by C. Morisset, Univ. British Columbia). Here it is less easy to model a realistic geometry as the zircons are irregular in shape. A simple planar geometry (Fig 2) was modeled for a first approximation of the effect. Fig 3 shows the extent of SF in zircon from 5 to 100 μm away from the ilmenite boundary. In the actual case, the distance to the boundary is not always easy to determine, but generally is 10-40 μm, for which PENEPMA gives SF values between 100-1000 fictitious ppm Ti. The actual EPMA measurements in one sample range from 162-645 ppm Ti in zircon, increasing as the analysis point gets closer to the ilmenite—matching fairly well the PENEPMA simulation. In a second sample, there is a single measured value of 2559 ppm at ~20 μm distance, 6X that from SF, but adjacent ilmenite may be plunging below the surface of the zircon.

PENEPMA is a valuable tool for estimating the effect of secondary fluorescence, particularly in evaluating EPMA measurements of Ti in zircon. SF can cause spurious Ti counts in zircon ranging from >10 ppm at 100 um distance, or >250 ppm at 25 um distance from a large Ti-rich phase. Small Ti-rich grains on rims of zircons could give 10s of ppm of fictitious Ti in the zircon by EPMA.

References

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Table 1

	Rutile Diameter	Distance Zirc Rim-Rutile Rim	Number Rutiles	Matrix Material	Spurious Ti (ppm)
1	30	-	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	10	epoxy	120

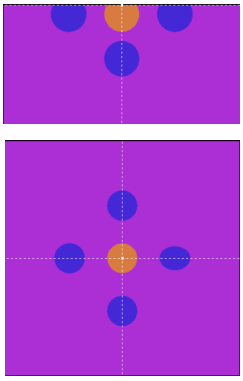

Figure 1 (above). Case 1, cross section (top) and plan (bottom) views, zircon in center, rutiles surround.

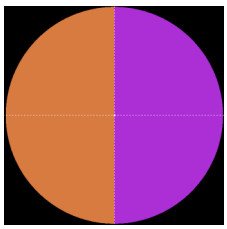

Figure 2 (right). Plan view, Case 2, ilmenite (FeTiO3) to left, zircon to right. The beam position moves to the right, away from the ilmenite interface.

Figure 3