Electron Microprobe Analysis of Hf in Zircon: Suggestions for Improved Accuracy of a Difficult Measurement

John Fournelle* and John M. Hanchar**

- Cameron EPMA Lab, Department of Geoscience, University of Wisconsin-Madison

** Department of Earth Sciences, Memorial University of Newfoundland

91500 Round Robin (2004)

Weidenbach, et al.'s (2004) study of the 91500 zircon demonstrated the spread (in accuracy) of possible EPMA values for six EPMA lab vs the 0.695 wt% HfO2 (ID-TIMS Hf) :

Vol. 28 — N° 1 05 04 p. 9-39

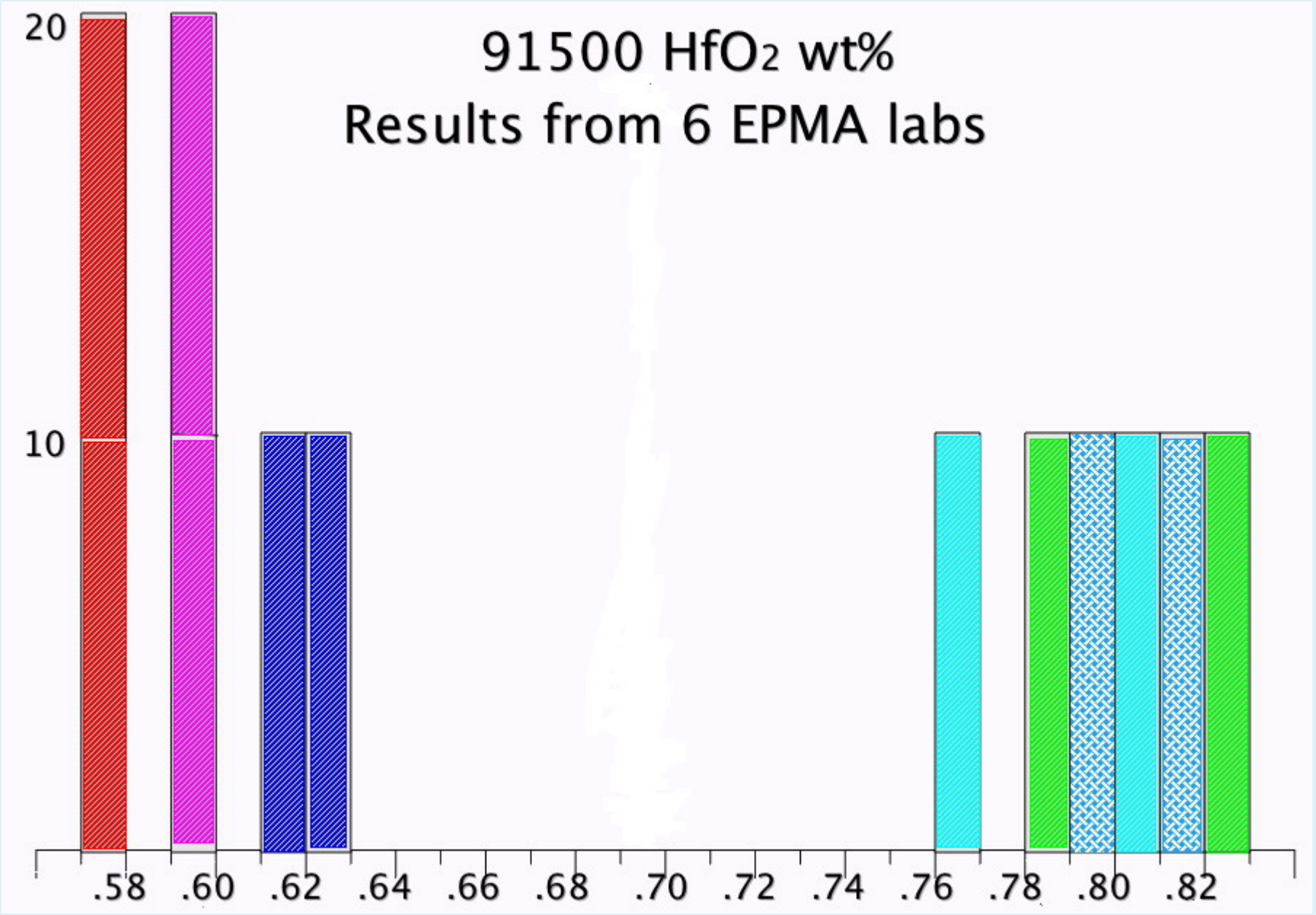
GEOSTANDARDS and GEOANALYTICAL RESEARCH

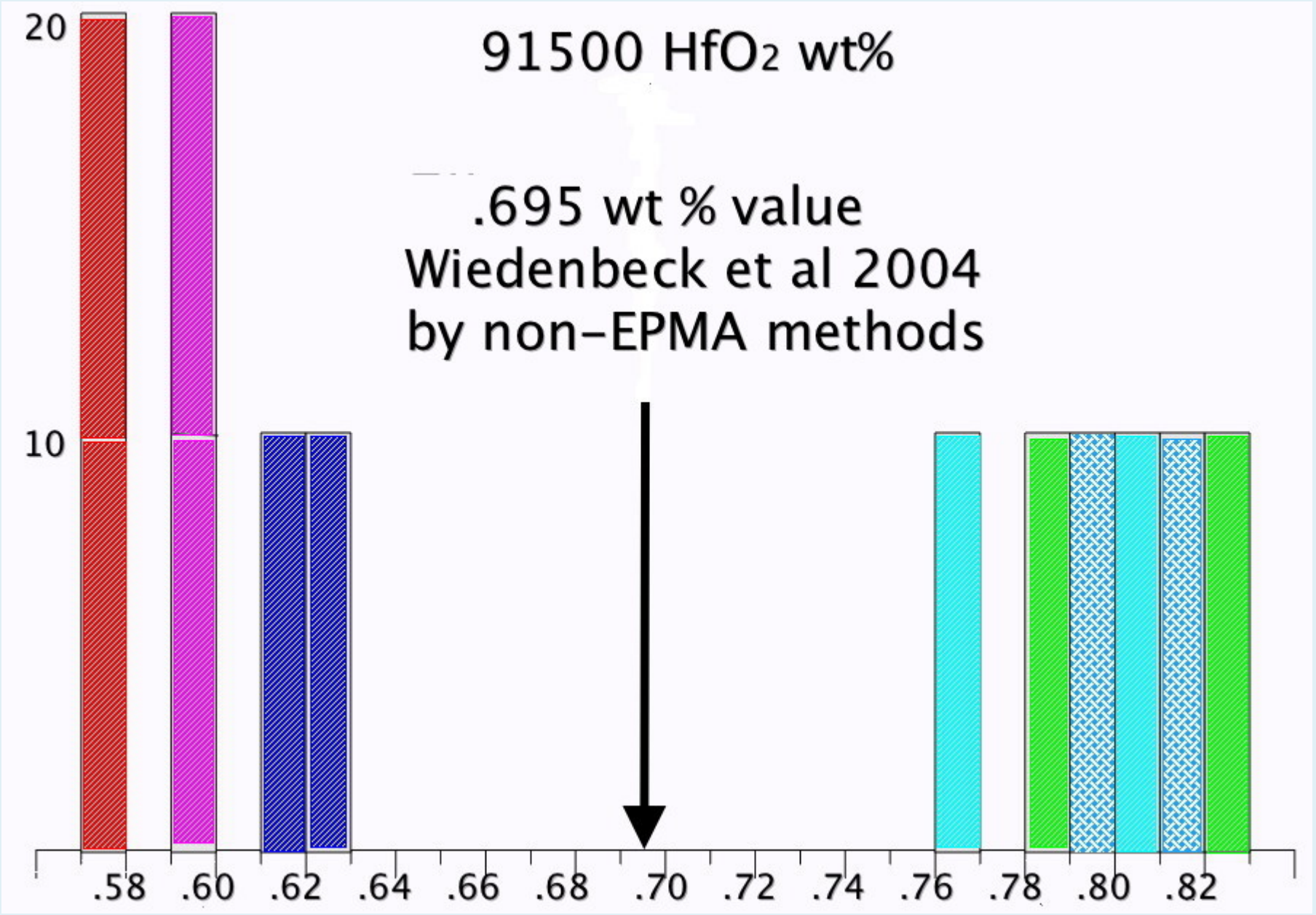
Further Characterisation of the 91500 Zircon Crystal

Michael **Wiedenbeck** (1)*, John M. **Hanchar** (2), William H. **Peck** (3), Paul **Sylvester** (4), John **Valley** (5), Martin **Whitehouse** (6), Andreas **Kronz** (7), Yuichi **Morishita** (8), Lutz **Nasdala** (9),

and

J. **Fiebig** (10), I. **Franchi** (11), J.-P. **Girard** (12), R.C. **Greenwood** (11), R. **Hinton** (13), N. **Kita** (8), P.R.D. **Mason** (14), M. **Norman** (15)§, M. **Ogasawara** (8), P.M. **Piccoli** (16), D. **Rhede** (1), H. **Satoh** (8), B. **Schulz-Dobrick** (9), Ø. **Skår** (17), M.J. **Spicuzza** (5), K. **Terada** (18), A. **Tindle** (19), S. **Togashi** (8), T. **Vennemann** (20)‡, Q. **Xie** (21)† and Y.-F. **Zheng** (22)


91500 HfO2 wt%
Results from 6 EPMA labs
20
10
.58
.60
.62
.64
.66
.68
.70
.72
.74
.76
.78
.80
.82
Wt % HfO2


91500 HfO2 wt%
.695 wt % value
Wiedenbeck et al 2004
by non-EPMA methods
20
10
.58
.60
.62
.64
.66
.68
.70
.72
.74
.76
.78
.80
.82
Wt % HfO2

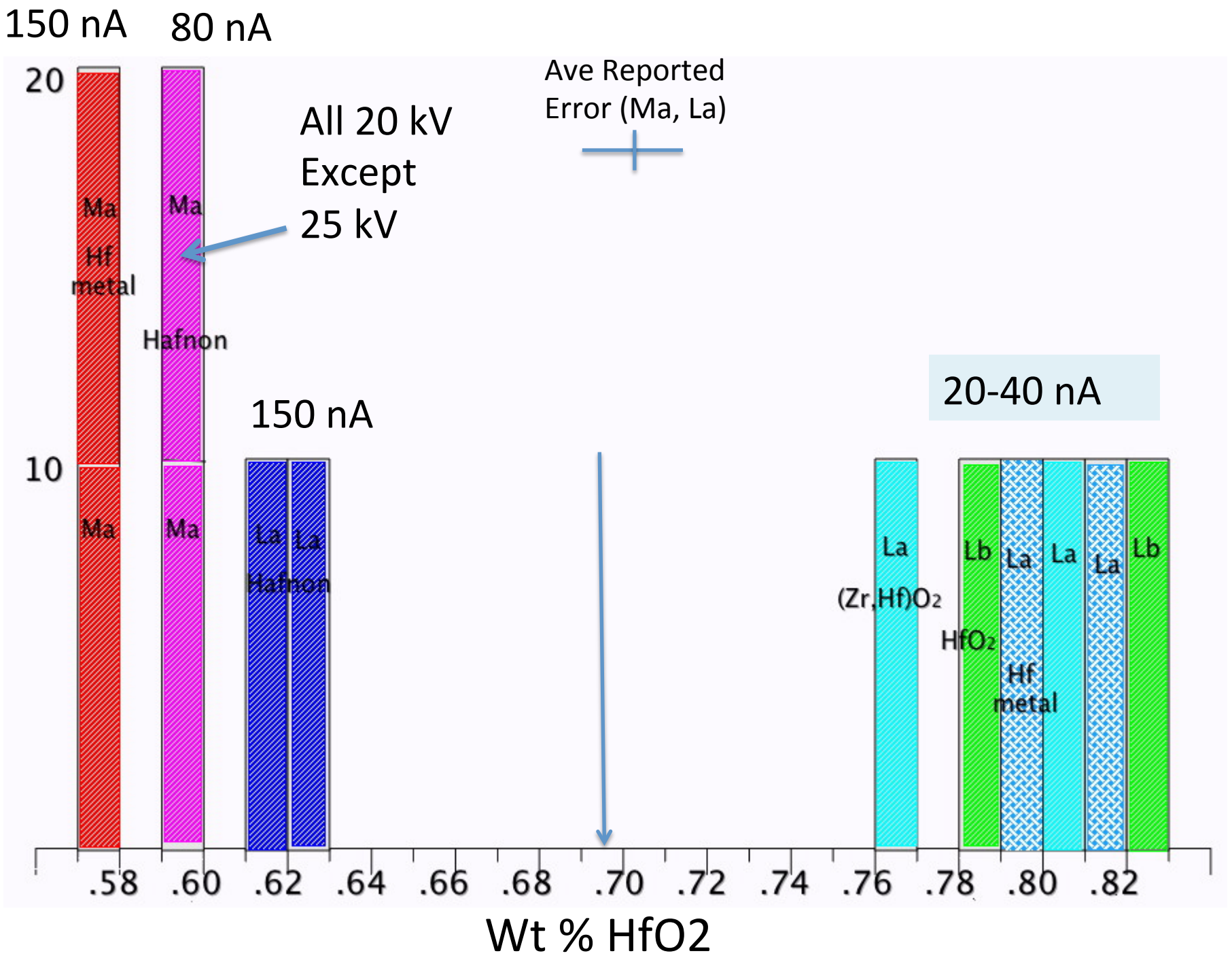
The fact that none of the six EPMA data sets, despite having analysed independent and random fragments, were consistent with the earlier isotope dilution data suggests that significant bias may still plague this approach.

Wiedenbeck et al, 2004, Further Characterization of the 91500 Zircon Crystal, page 22

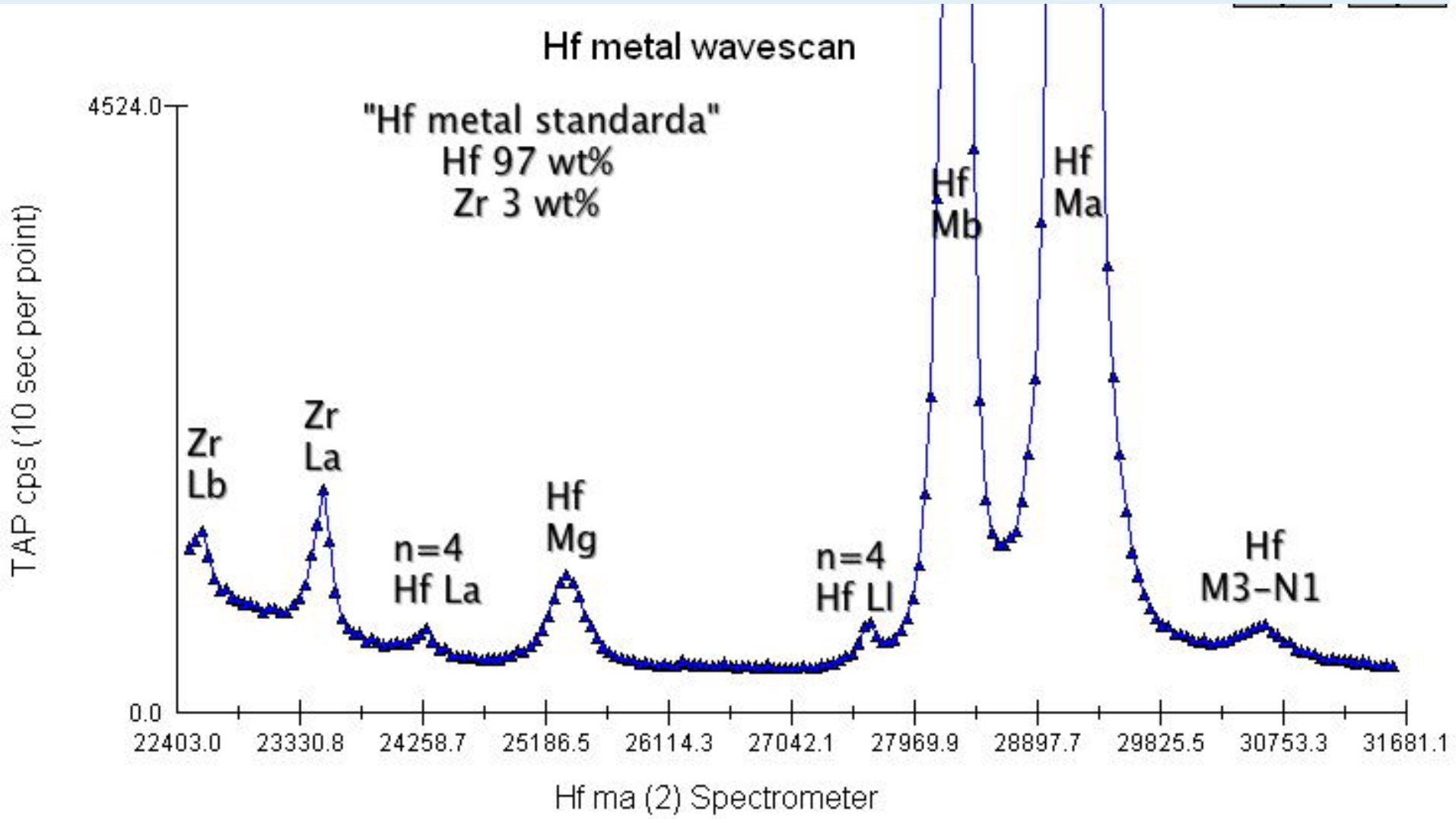
Why different EPMA results?

A range of different EPMA operating conditions:

- Different accelerating voltages
  - 20 keV, 25 keV (both > 17.99 keV)
- Different analytical lines
  - Ma, La, Lb
- Different standards
  - Hf metal, Hafnon, HfO_2, (Zr,Hf)O_2
- Beam currents
  - 20, 30, 40, 80, 150 nA
  - Same or different for Hf std and 91500?
- PHA settings?

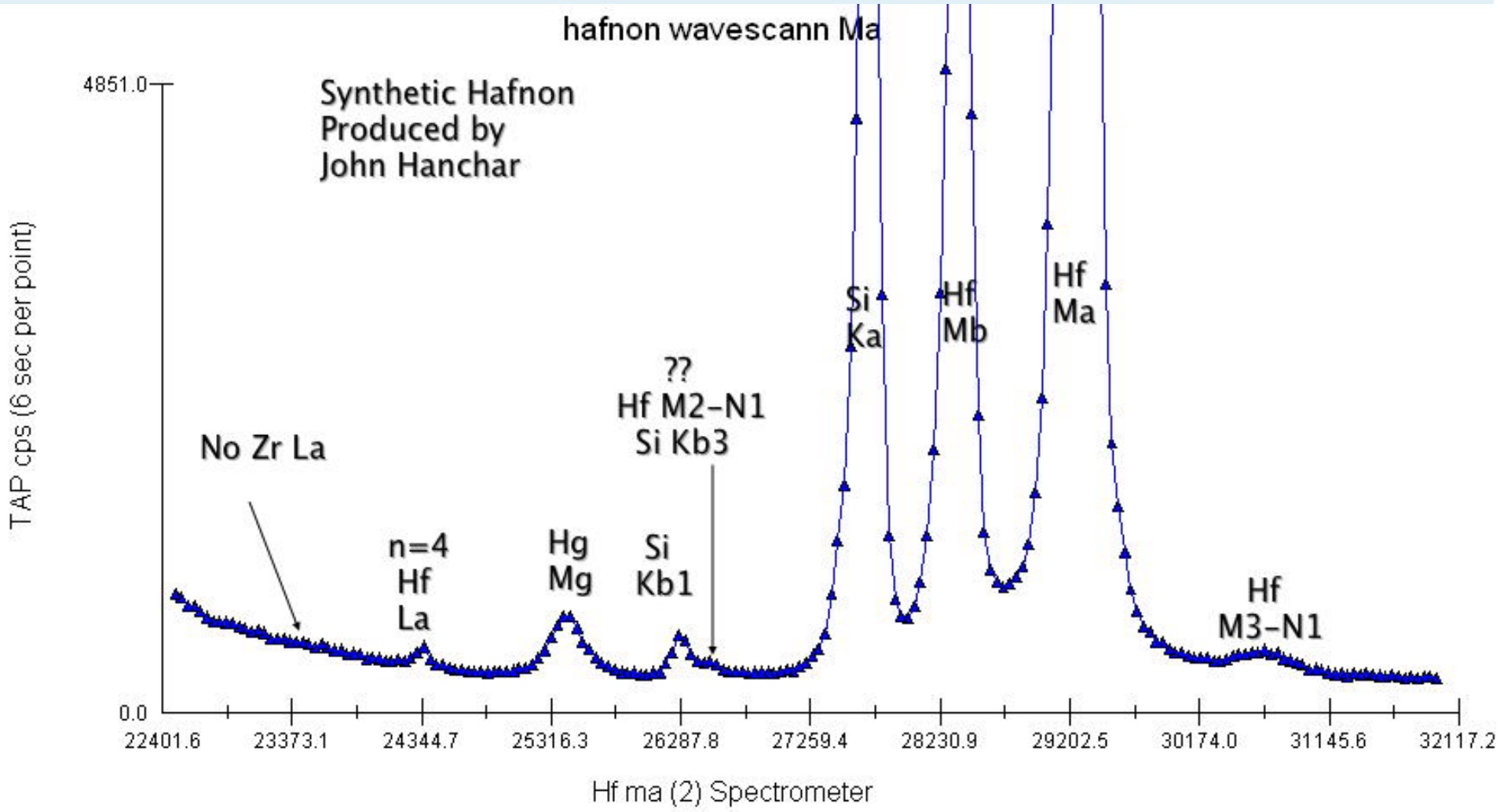

150 nA
80 nA
20
10
All 20 kV
Except
25 kV
Ave Reported
Error (Ma, La)
Ma
Hf
metal
Ma
Hafnon
Ma
Ma
150 nA
La
La
Hafnon
20-40 nA
La
(Zr,Hf)O2
Lb
HfO2
La
Hf
metal
La
La
Lb
.58
.60
.62
.64
.66
.68
.70
.72
.74
.76
.78
.80
.82
Wt % HfO2

Hf Ma in “Hf metal” … @ 17 keV



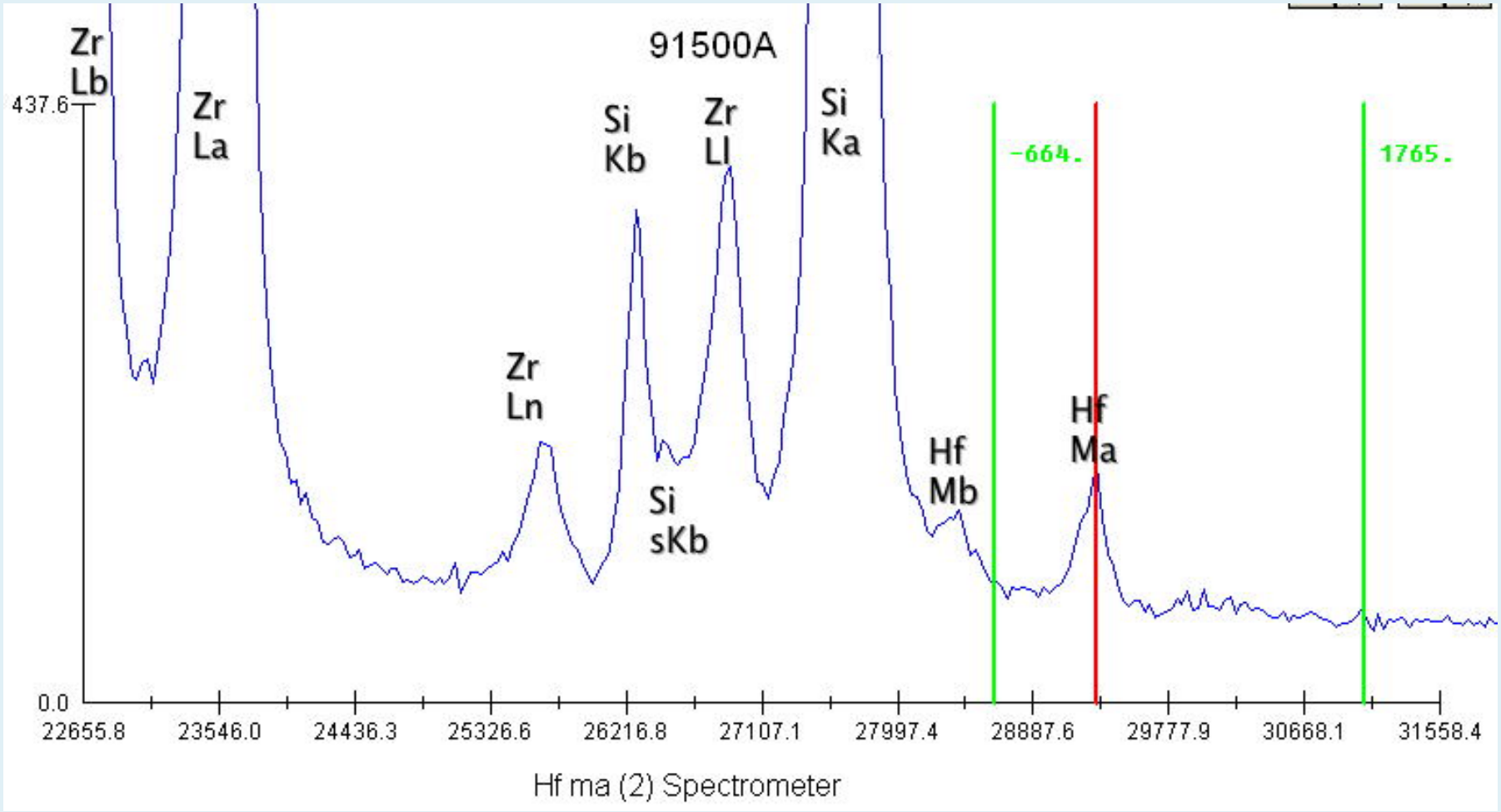
Hf Ma sits at low end of spectrometer where the background is curved….

Hf Ma in Hafnon … @ 20 keV



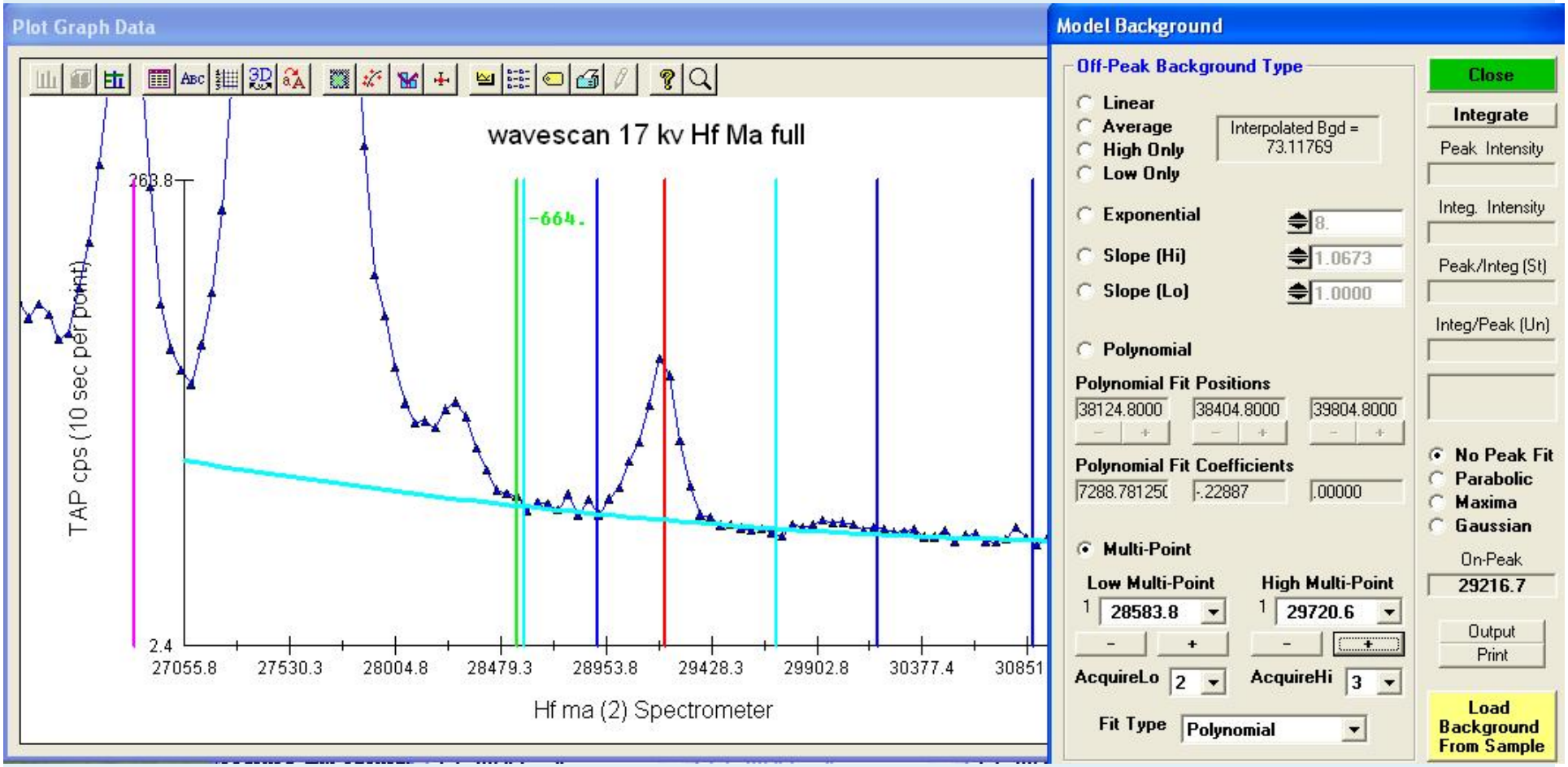
Hf Ma sits at low end of spectrometer where the background is curved….

Hf Ma in 91500 …



- Hf Ma sits in a complicated part of the zircon spectrum

Background modeling… curved at the low end of the spectrometer



It is essential to have software which is able to model curved backgrounds

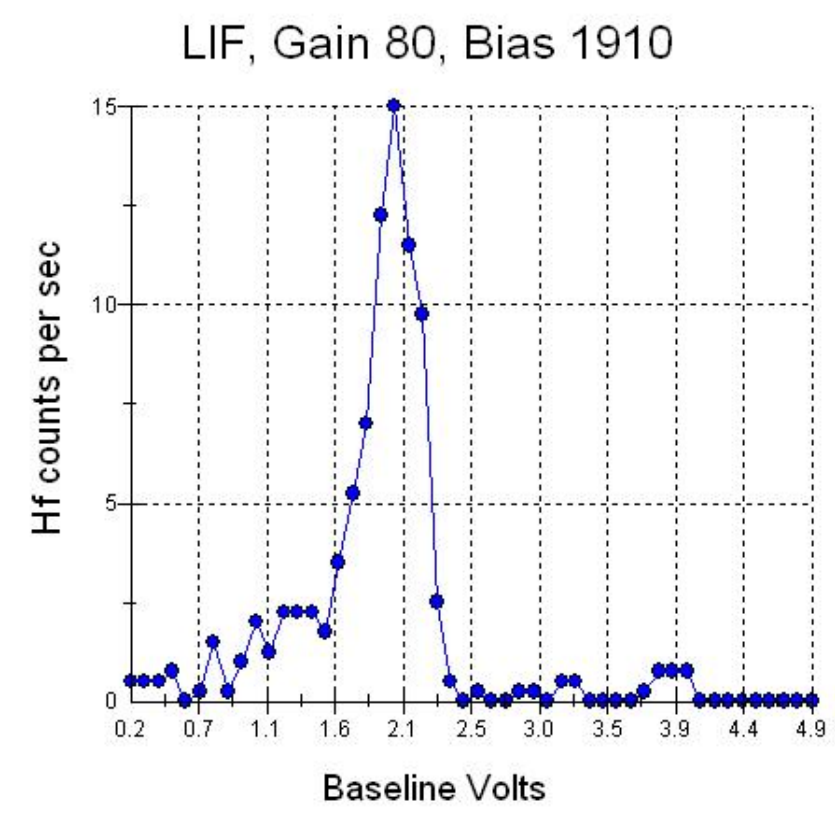
Hf La…

- Hf La sits astride a pathological 2nd order Zr Ka overlap when the E0>17.99 keV

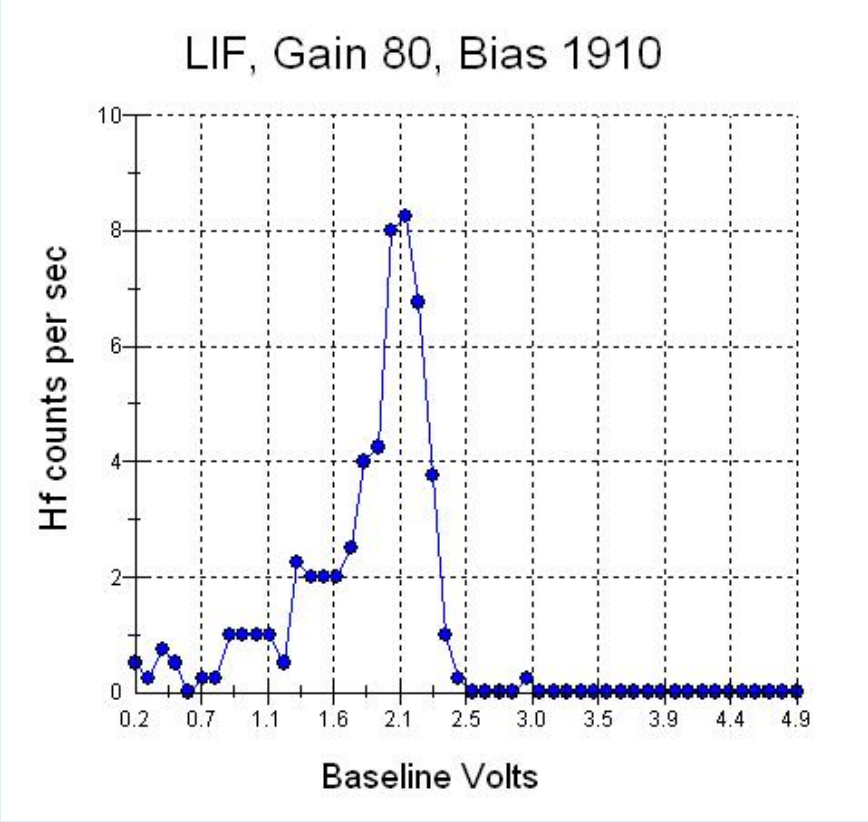
- Hf La = 1.5696 Å
- Zr Ka = 0.7873 Å so 2* 0.7873 = 1.5746 Å

Hf La?

- Hf La sits dead on a pathological 2nd order Zr Ka overlap if the E0>17.99 keV



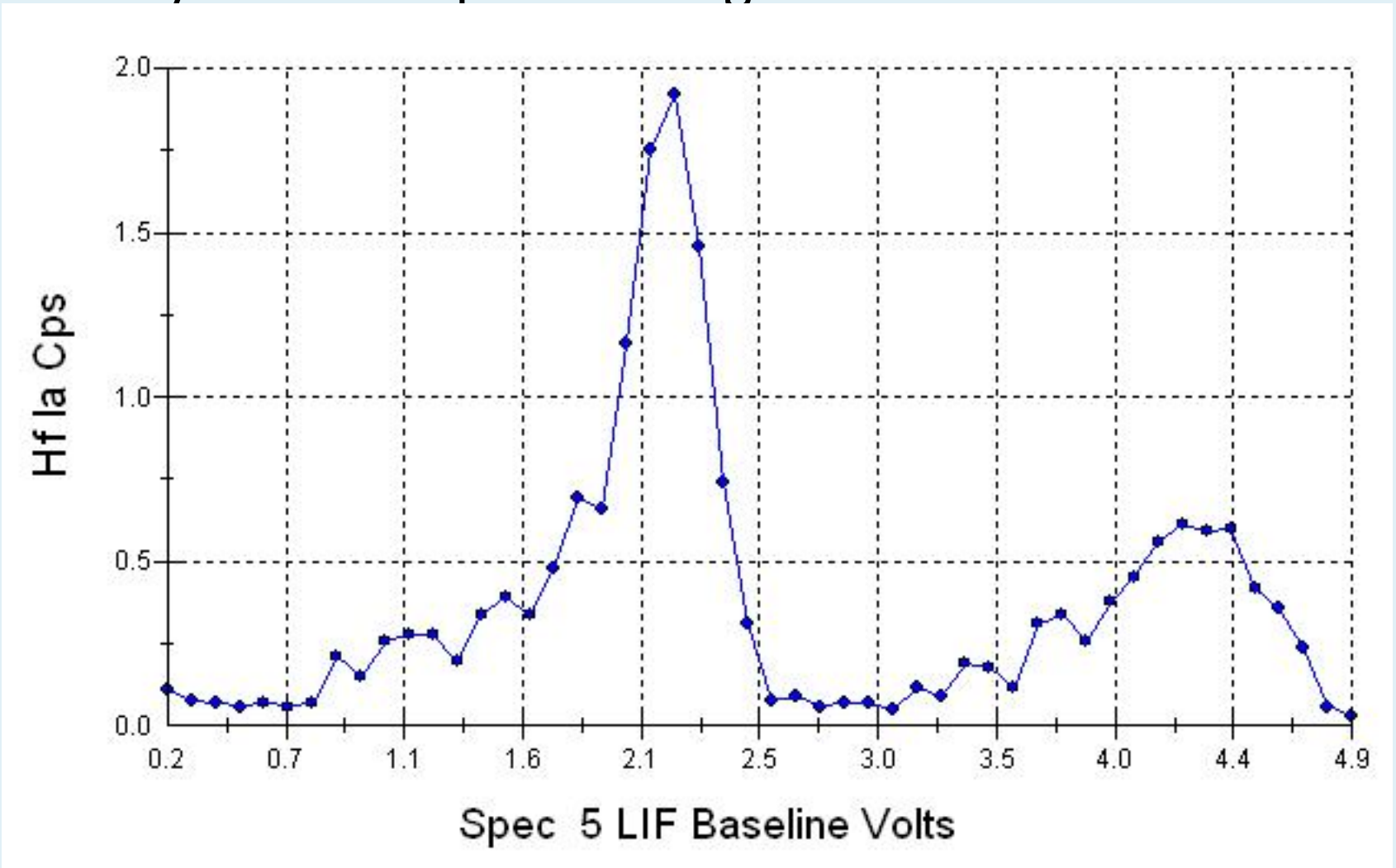
91500 **at 20 keV**. Note 2nd order Zr La pulse at 3.9 volts, relative to 1st order Hf Ma pulse at ~1.95 volts



91500 **at 17 keV**. Note no 2nd order Zr La pulse at 3.9 volts

Hf La…

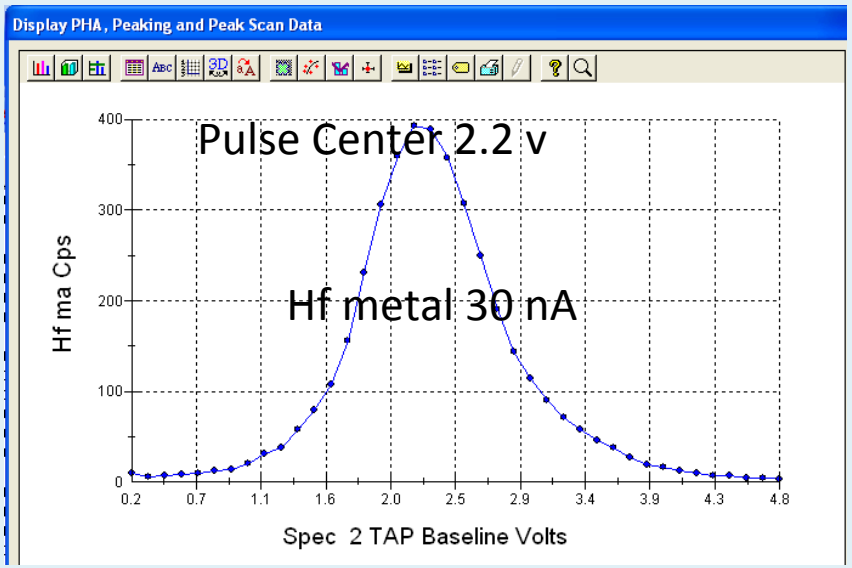
- And if you crank up the voltage to 25 keV...

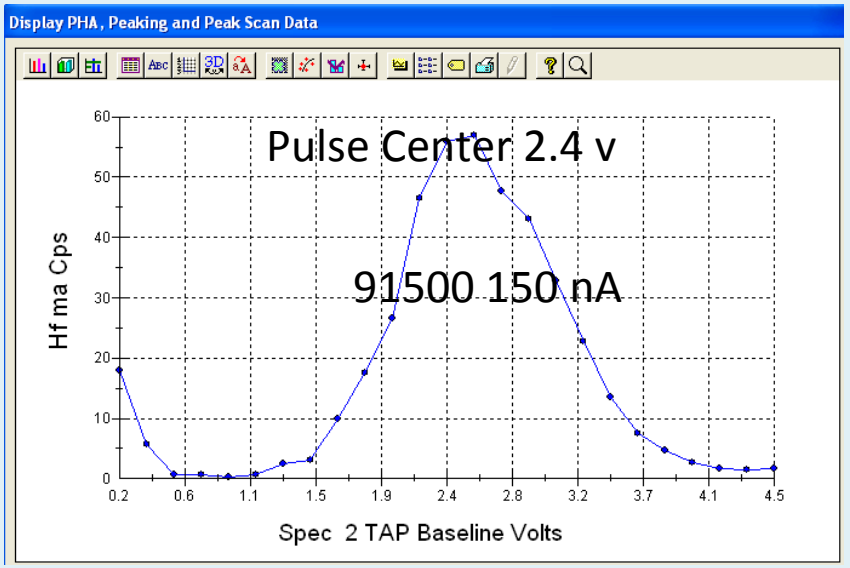


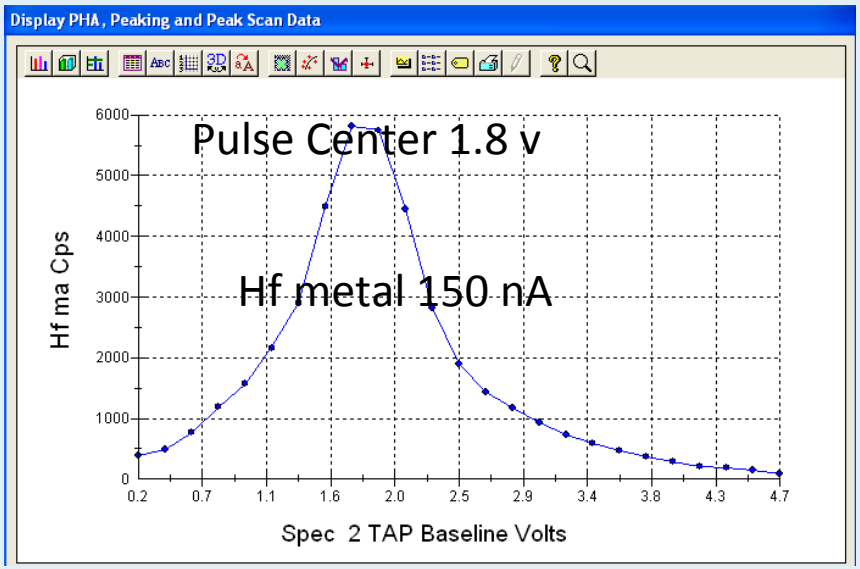
This is a synthetic zircon (ORNL) with very low Hf (=2.2 v pulse) and with the 2nd order Zr La pulse having ~30% of its intensity.

Be Careful with PHAs

All 17 keV, Hf Ma

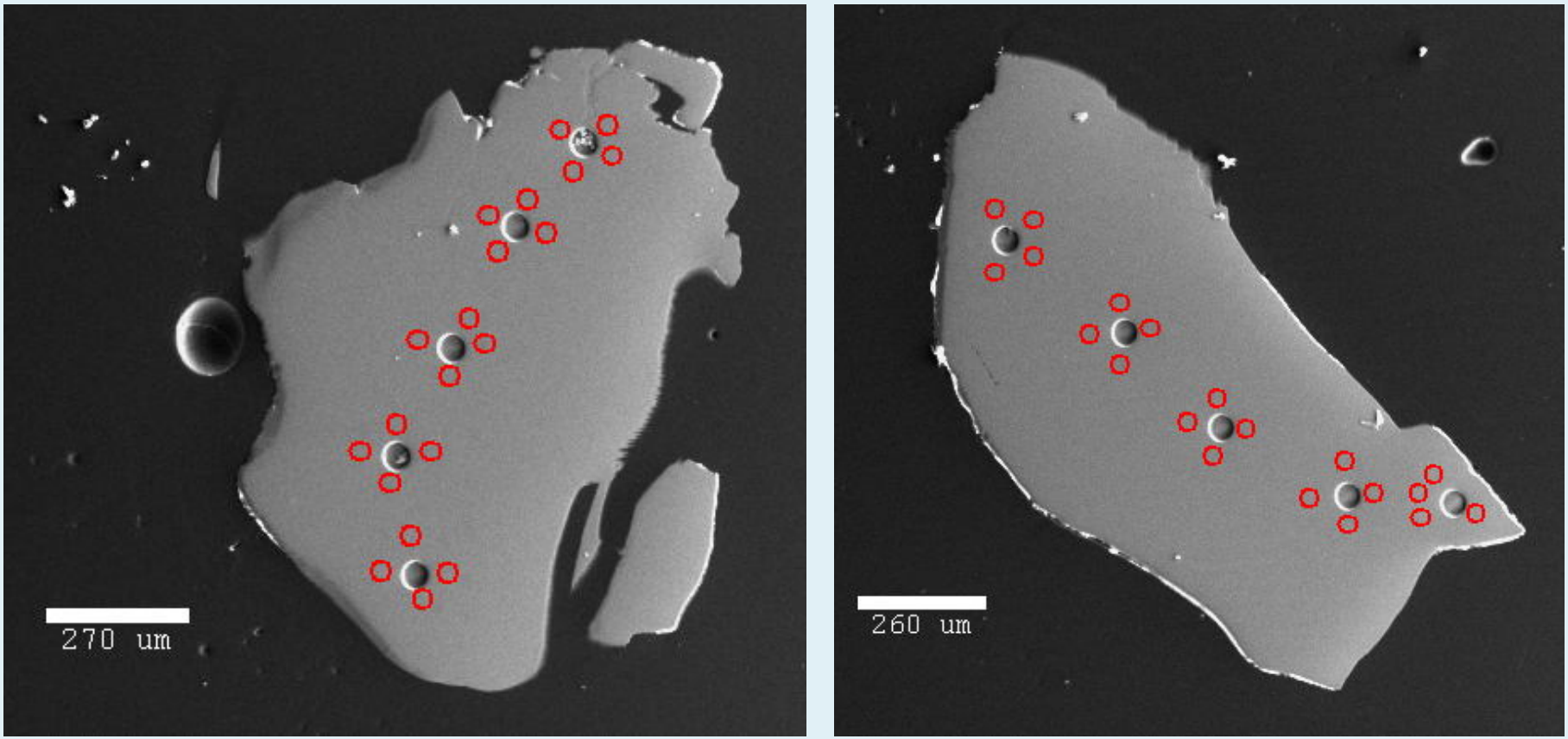






For all PHA scans, the bias and gain are the same values

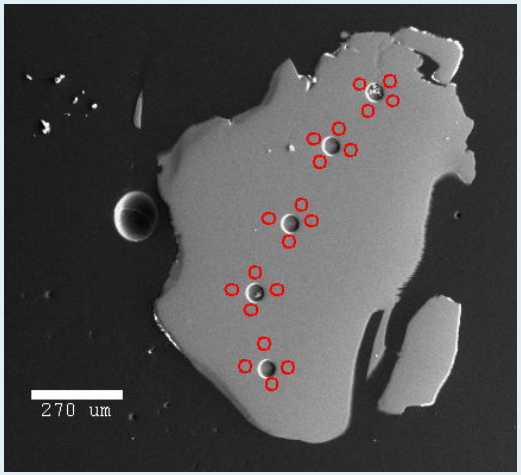
Approach: EPMA[1] and LA-ICPMS[2] on same grains of 91500



1 o EPMA: UW-Madison SX51 **2** O LA-ICPMS: Memorial University of Newfoundland

This follows complete EPMA coverage of each grain (needed for ICPMS)

91500A



Original data 40 pts
Scattered over all
Grain:
.735 wt% HfO2

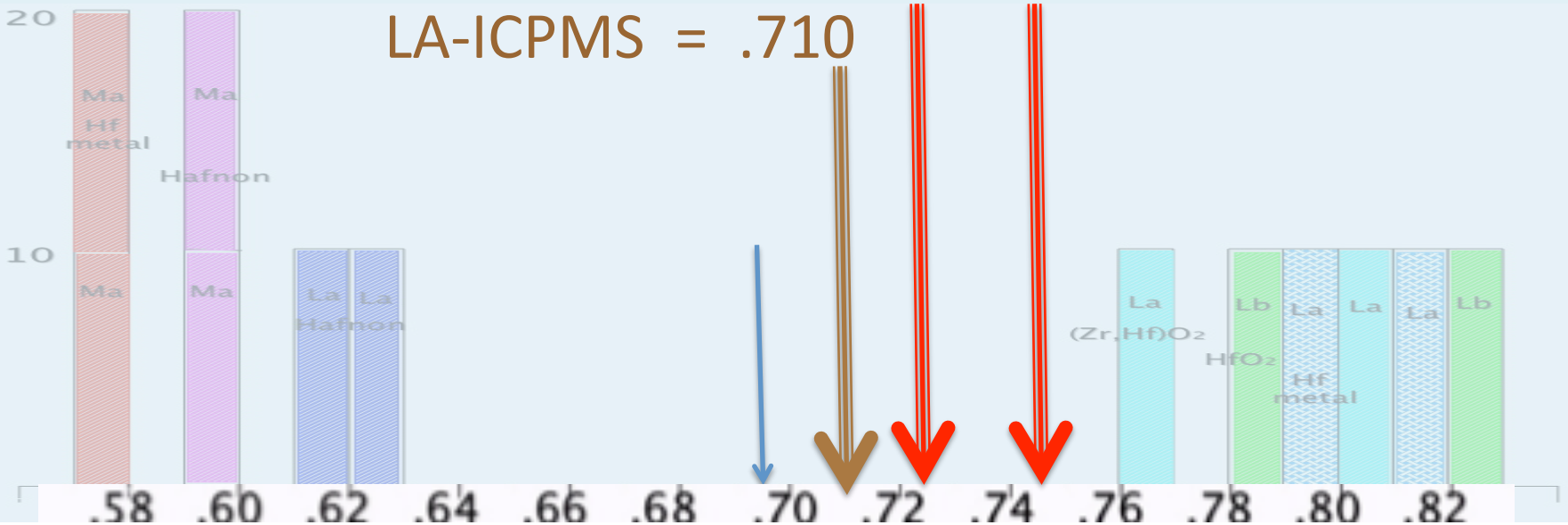
This and next 3 plots:
30 nA Faraday current and
50 seconds peak and 50
seconds background

EPMA @ 17 kV

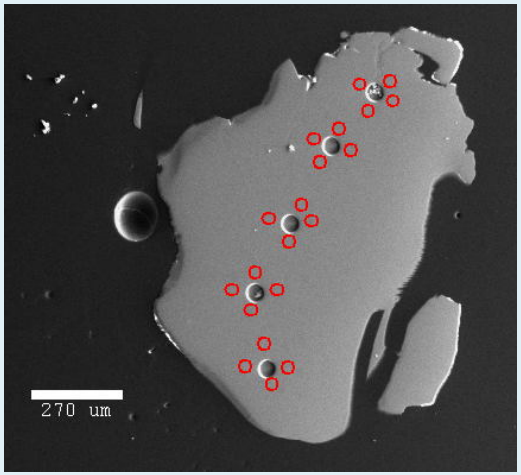
17 kV Ma **.724 (±6%)**

17 kV La **.744 (±6%)**

LA-ICPMS = .710



91500A



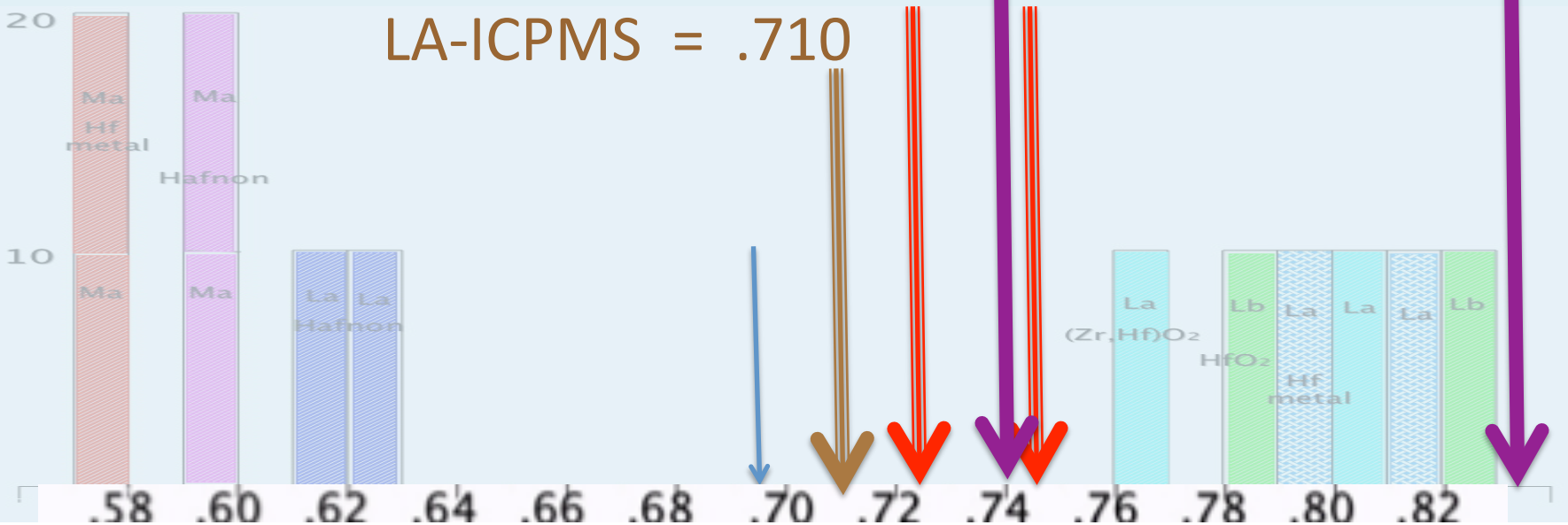
Inte

EPMA @ 20 kV

20 kV La PHA Diff **20 kV La PHA**

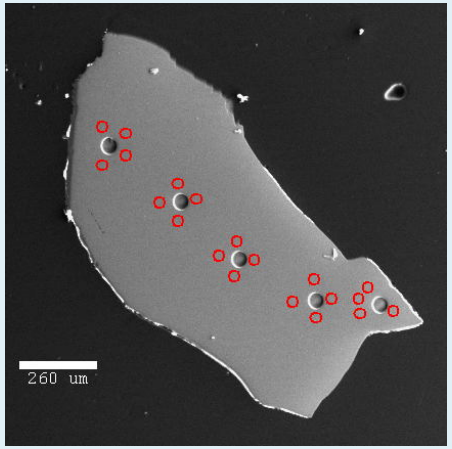
.740 (±5%) **.834 (±5%)**

LA-ICPMS = .710



91500C

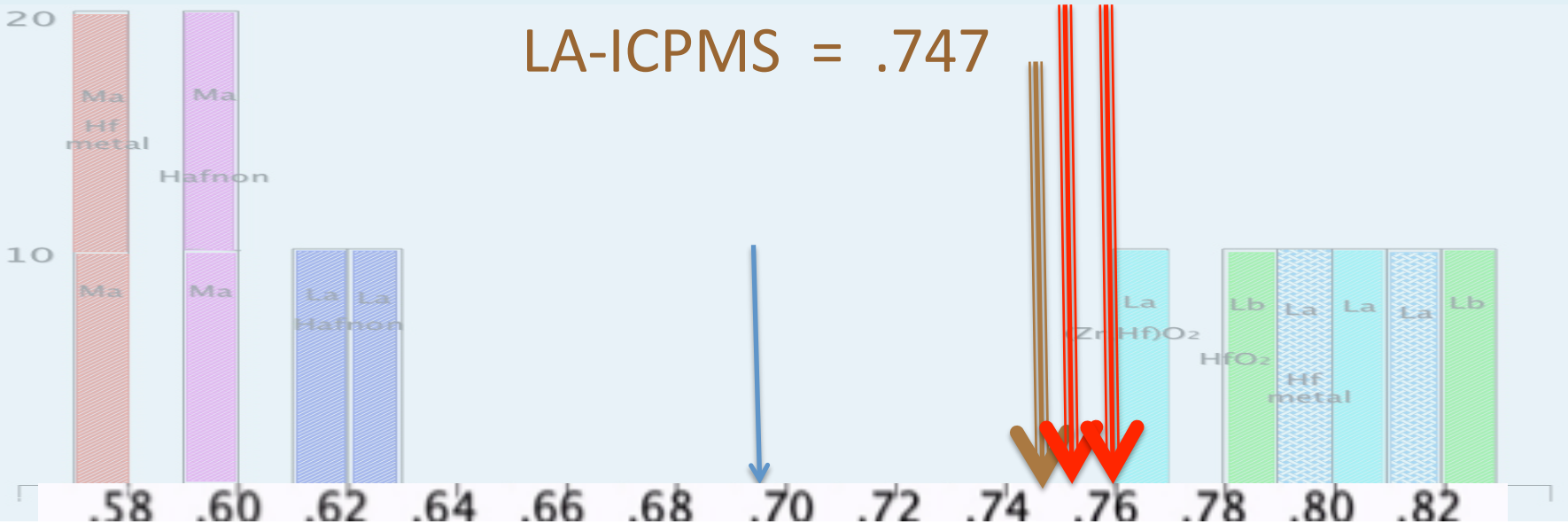
Original data 40 pts
Scattered over all Grain:
.755 wt% HfO2



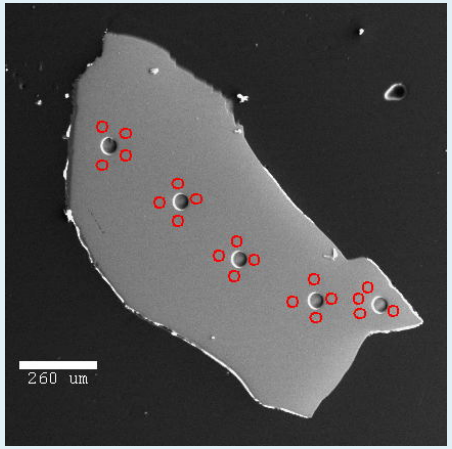
EPMA @ 17 kV

17 kV Ma **17 kV La**
.754 (±4%) **.760 (±6%)**

LA-ICPMS = .747



91500C

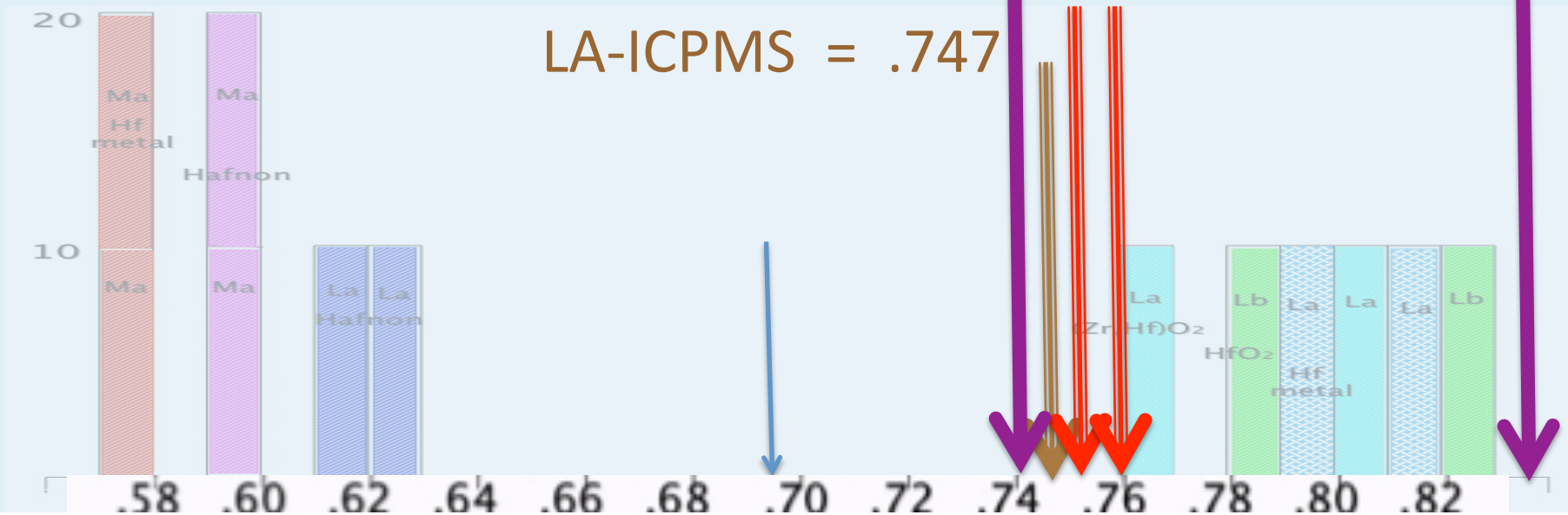


EPMA @ 20 kV

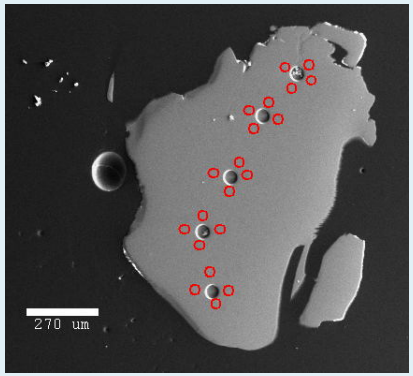
20 kV La PHA Diff
.740 (±5%)

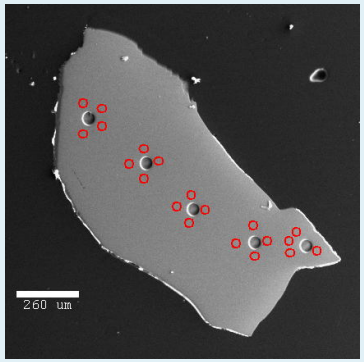
20 kV La PHA Inte
.834 (±5%)

LA-ICPMS = .747



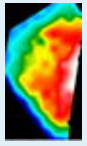
Summary from combined studies of these two 91500 grains





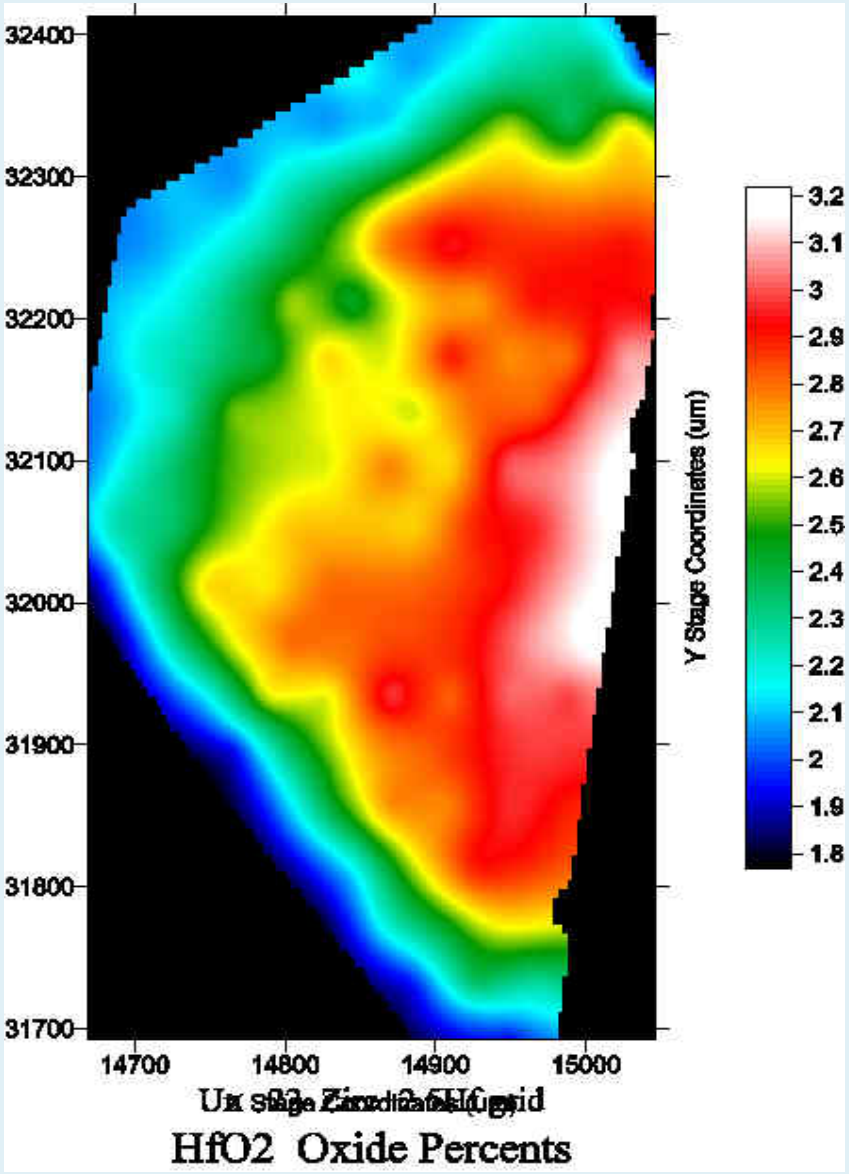
- For each sample: We can reproduce by EPMA both Ma and La values using both Hf metal and Hafnon standards. At 20 kV reproduces if differential mode used.
- EPMA values are, within analytical error, same as the LA-ICPMS values
- Between two samples, a slight variation in compositions, both a bit higher than the (bulk) isotope dilution value

Conclusions

1. Specific grains of 91500 may have discrete compositions varying some from isotope dilution value of .695 wt% HfO_2 → critical to have proper EPMA procedure
2. Hf La: Caution >18 keV
3. Hf Ma: Non-linear background modeling critical (~multipoint)
4. Check PHAs, esp. if mixing high and low currents
5. Primary standards (hafnon, zircon) available*
6. Secondary Hf-doped zircon standard* will be very helpful 

*Contact John Hanchar

Synthetic Zircon with 2.5 wt% HfO_2



Grown by John Hanchar, Memorial University of Newfoundland

127 gridded analysis points

Min 1.8 wt% HfO2
Max 3.2 wt% HfO2
Ave 2.5 wt% HfO2

Zoned, obviously (one week growth)
BUT a known quantity, so with some further refinement and check of many more xtals, could be a good secondary standard

Opportunity for Students Doing Research involving Microanalysis!

Funding to attend

IUMAS-6

August 2-7 Hartford, CT USA

For more info: <www.iumas6.org>

Thank you

Hf Ma vs La?

- Hf Ma sits in a complicated part of the zircon spectrum