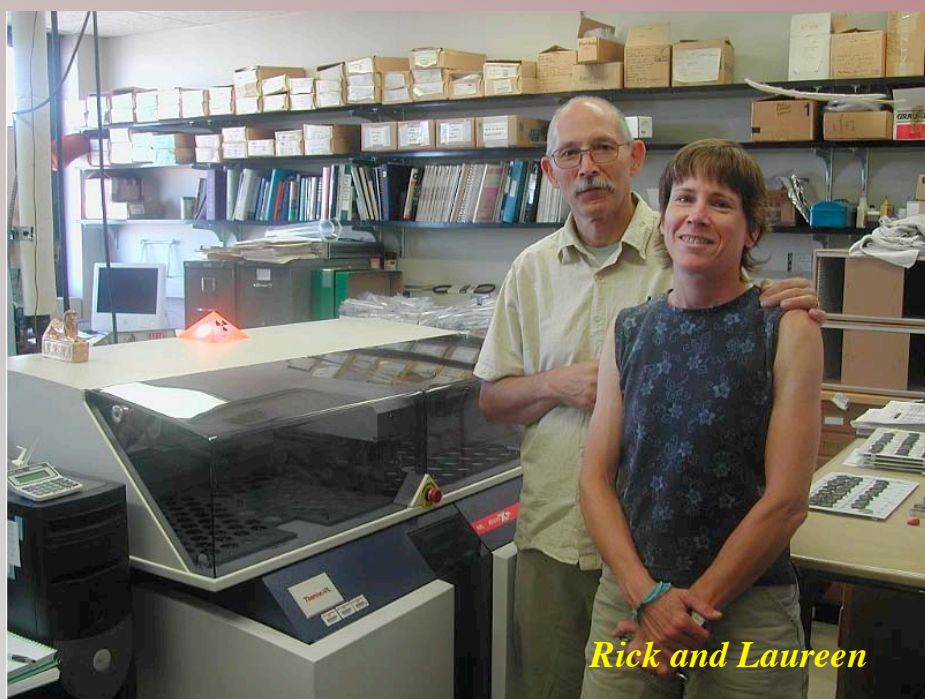


# XRF at the WSU GeoAnalytical Lab: decades of service with graphite crucibles and a smile



Richard M Conrey  
Laureen C Wagoner\*  
Diane J Cornelius\*  
John A Wolff

GeoAnalytical Lab  
<http://www.sees.wsu.edu/Geolab/index.html>  
School of Earth and  
Environmental Sciences  
P.O. Box 642812  
Pullman, WA 99164 USA

*\* graduates of Univ. of Western Ontario XRF course*



## *Mission of the XRF portion of our lab*

Since our founding circa 1973 by Peter Hooper we have served thousands of researchers with X-Ray Fluorescence data

Our client base is chiefly other universities around the USA and the world, our own students and faculty, and government agencies both local and federal

We strive to provide research quality data at an affordable price and to educate both our students and visitors in the methods of sample preparation and X-Ray Fluorescence analysis

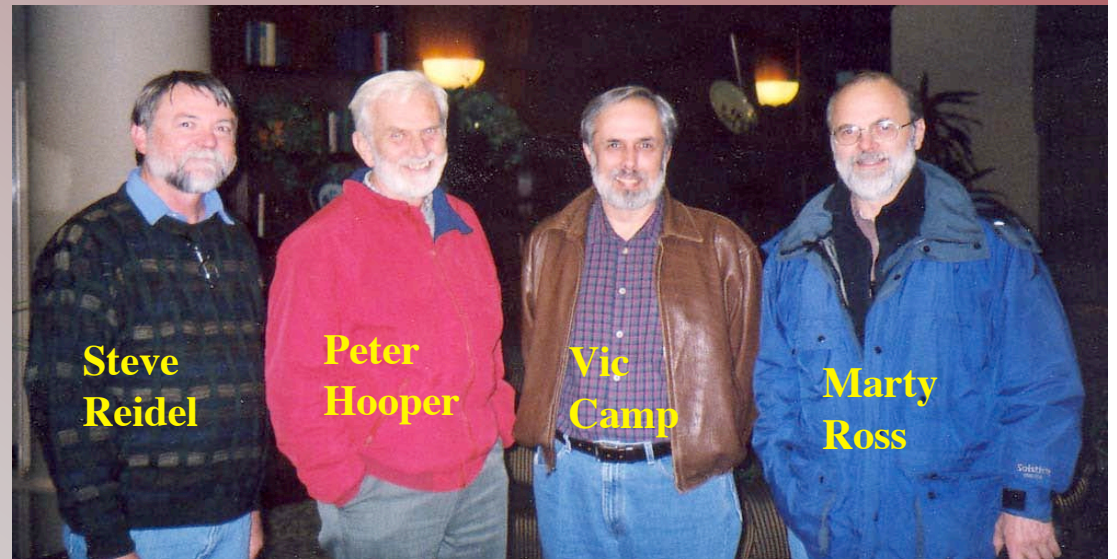
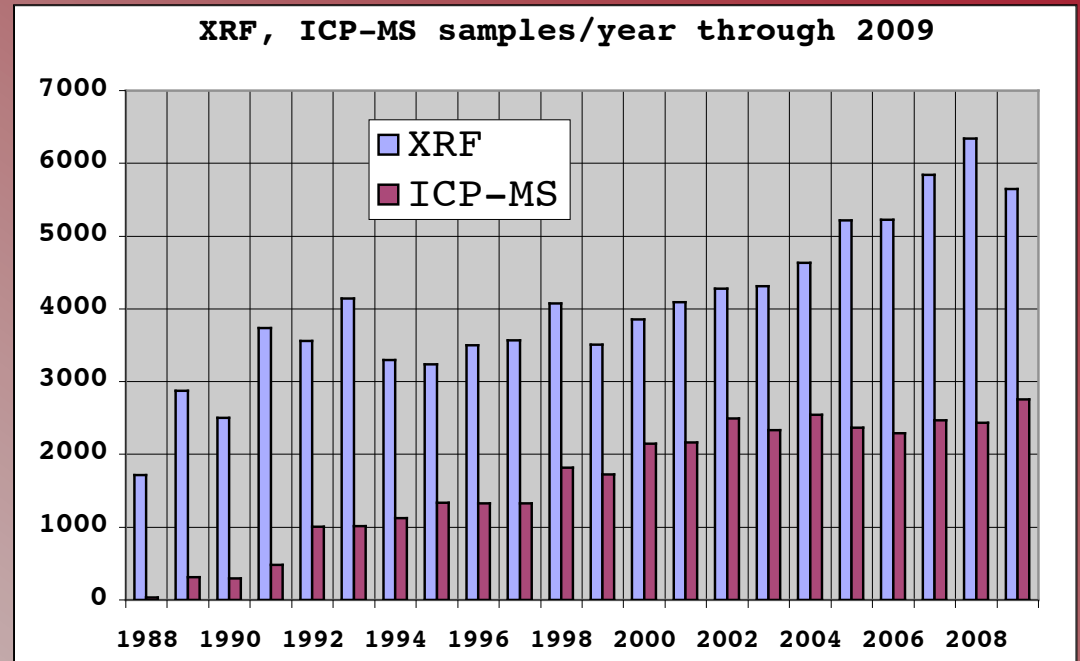
A graduate level X-Ray Analysis course has been taught at WSU by Nick Foit for three decades, with a focus on XRD, XRF and electron microprobe analysis



Our lab also houses a JEOL 8500F field emission electron microprobe, Siemens D-500 powder X-ray diffractometer, Agilent 7700 ICP-MS, Thermo-Finnegan Neptune multi-collector ICP-MS, Thermo-Finnegan Element2 high precision ICP-MS, Finnegan Delta S gas source mass spectrometer, and a Perkin-Elmer Spectrum GX FTIR

## *XRF at WSU - a brief history*

- ~1973: XRF lab started by Peter Hooper and his graduate students working on the Columbia River basalts
- Peter adopted the low dilution fusion in graphite method to measure both major and trace elements based upon his prior experience in Wales
- ~1976: first XRF: a “biologically automated” Philips PW1410
- 1980s: radioactive waste project at Hanford provides steady work
- 1986: automated Rigaku 3370 XRF
- 1984 - 2009: the XRF lab blossoms under Diane Johnson Cornelius
- 1997: Peter retires, John Wolff assumes directorship of the GAL
- 2004: Thermo-ARL Advant'XP+ XRF spectrometer installed
- 2010: XRF lab now run by Rick Conrey and Laureen Wagoner, both former students of Peter Hooper



## *Graphite has many advantages*

- Ease of maintenance, fabrication, and cleaning, inert, inexpensive, efficient, rare to make unusable pellet, no releasing agent required
- Allows single recipe with Li-tetraborate for nearly all samples - we analyze nearly all rock types, minerals and soils with the exception of ores - little need\* to know beforehand what you are analyzing
- Allows low dilution strategy - traces measured on same pellet as majors; full matrix correction for all elements
- \* Mg-, Fe-, Ca-, P, or Mn-rich samples can be diluted with pure fused silica to ensure good glass formation upon cooling

### *Life of a graphite crucible*



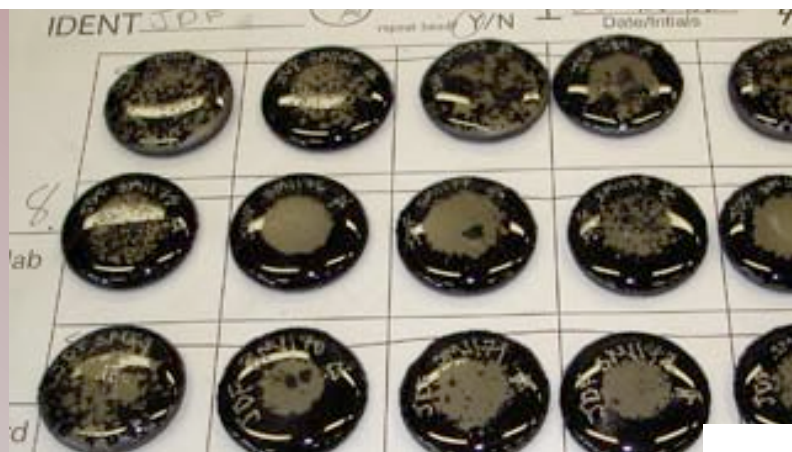
**~ 60 fusions/crucible**

- **Graphite crucible cost - \$US 8**
- **machined in-house from ultra-pure rod**
- **nearly all WSU ICP-MS analyses begin with a graphite fusion**



## Graphite doubly fused beads - glass with some carbon on top

## *Graphite fusions*



- homogeneity requires re-grind (30 sec/bead) and re-fusion of graphite static fused beads
- loss of powder is immaterial at re-grind stage
- buffing reduces carbon load before re-grind



graphite crucible loading



powders are weighed into plastic jars, mixed with a Vortex mixer, and passed over an anti-static bar prior to loading

Kimwipe + compressed air cleaning



re-grinding

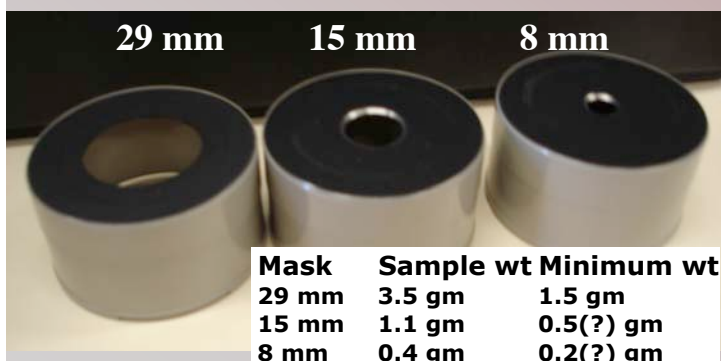


## Sizing/lapping of graphite fused beads

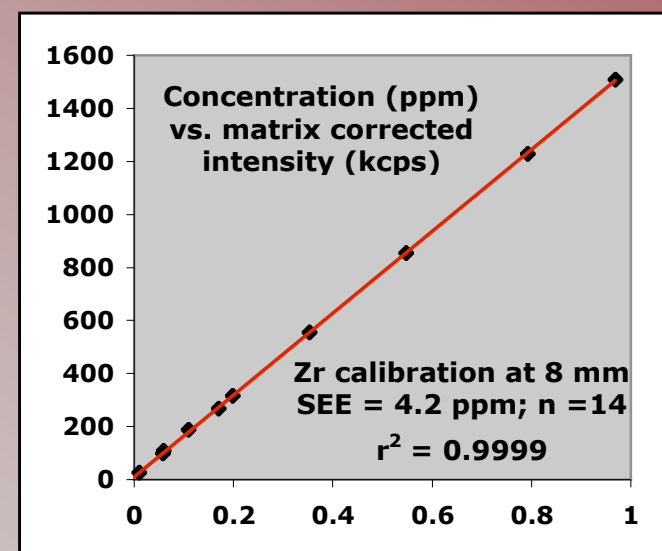
- diamond grinding in water is fast (total 2-3 min/bead)
- final cleaning in sonicator with ethanol
- lapping removes diffusion profile at contact of glass and crucible - final surface finish is 15 microns



machined template assures accurate sizing



## Small sample analyses



We calibrate with smaller masks for beads down to 8 mm diameter

Not simply a reduction in counts across the spectrum - varies with 2-theta because of crystal geometry so many parameters change

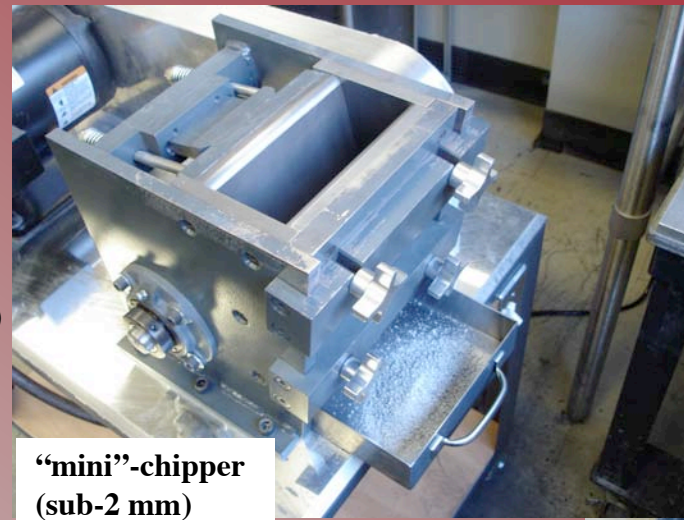
Precision varies as square root of counts so degraded by factor ~2 each step down in size - we count twice as long at 15 mm and 4x at 8 mm



50 ton anvil press

It's important not to contaminate during chipping - need a very hard surface

Our custom-made (WSU Tech Services) chipmunks use hardened tool steel plates - we're still using the original 35+ yr old plates

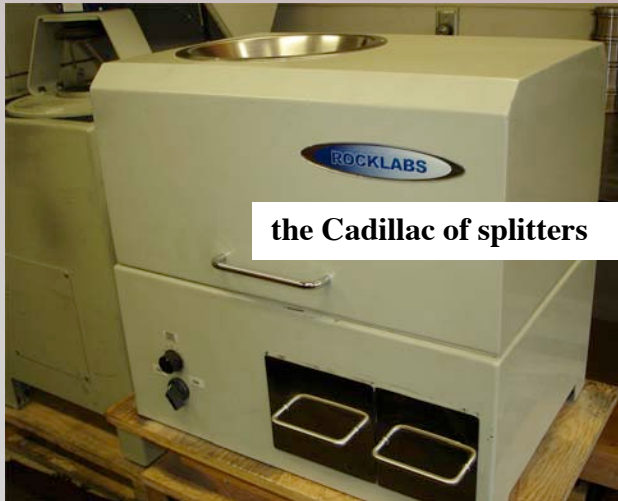


"mini"-chipper (sub-2 mm)



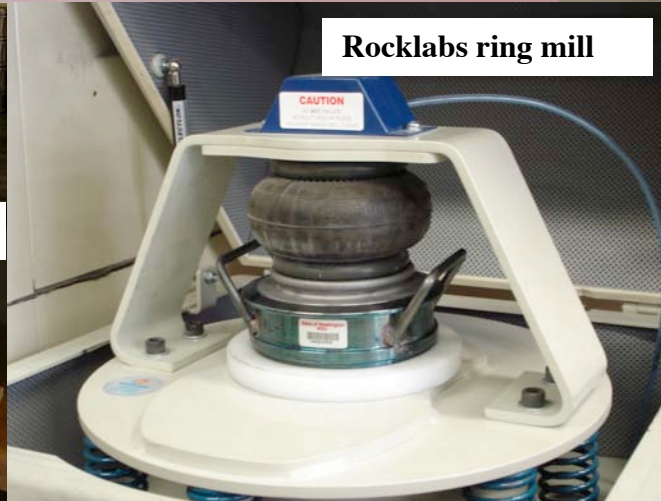
Coarse chipmunk

*Breaking and chipping, splitting and grinding*



the Cadillac of splitters

Rocklabs ring mill



Retsch planetary ball mill



Random sub-sampling of rocks is critical: we mini-chip coarse samples and reduce splitting error to the level of analytical error with a Rocklabs rotary splitter

We normally grind in Ta-free Rocklabs WC (< 120 g) for both XRF and ICP-MS or in agate (< 20 g) on request or for soils; small ball mills are used for < 3 g samples

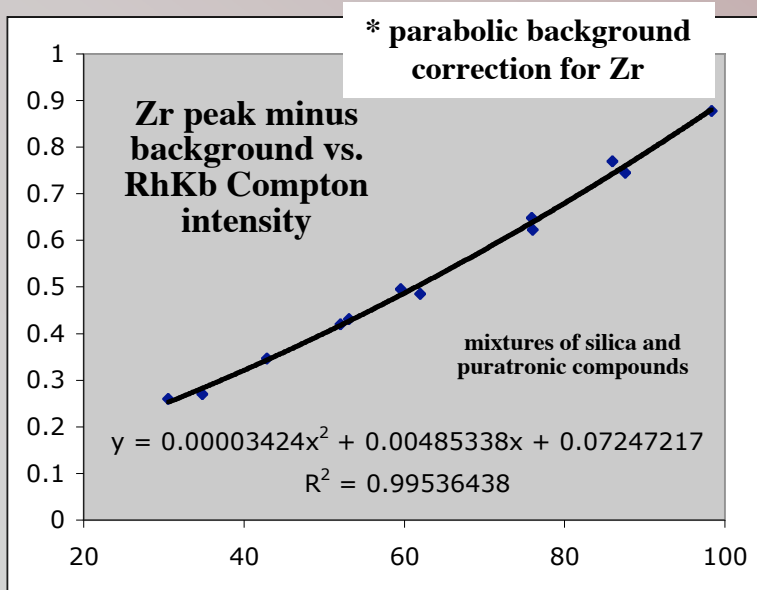


WC and agate ball mills

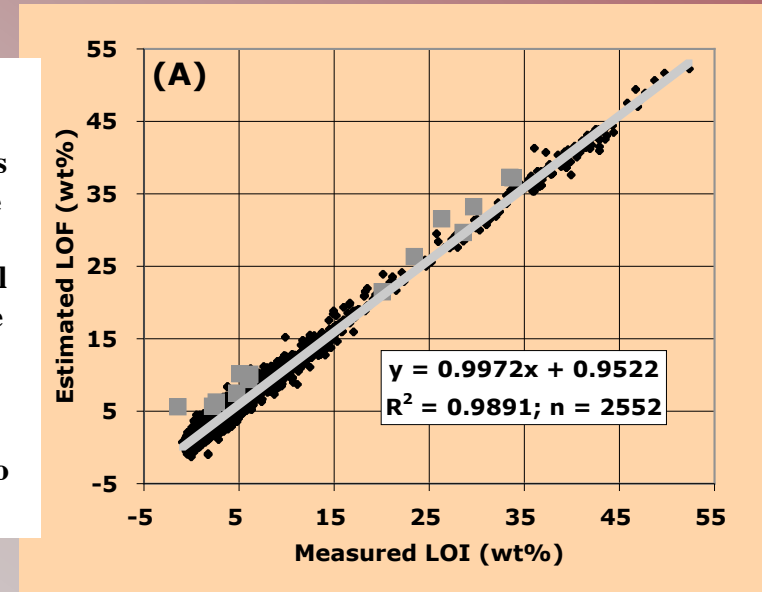
## The nitty gritty of a WSU GeoAnalytical Lab XRF analysis

- collect intensities at 36 peak and 25 background positions (~ 66 min/sample) for all samples
- calculate net peak minus background intensity for each element (often require linear and even parabolic\* matrix-dependent background slope correction)
- correct the net intensities for 135 spectral interferences (pk on pk, pk on bgd, Compton tails)
- calculate raw concentrations from corrected intensities using the calibration curves (set with 75 to 105 highly diverse CRMs)
- calculate matrix corrected concentrations from the raw concentrations by iteration using the fundamental parameters method (with the absorbance values of the NIST-GSC using Al, Ba, Ca, Cl, Cr, Fe, K, Mg, Mn, Na, P, S, Si, Sr, Ti, Zr and estimated LOF as matrix elements)
- recalculate the corrected concentrations by iteration using an estimated loss on fusion (LOF; simply 100 minus the analytical sum) to correct for raw powder\*\* analysis and volatile loss of weighed rock powder upon fusion (correction for not truly 2:1 flux:rock mixture)

\*\* raw powder is much preferred due to potential sample damage and partial analyte losses (chiefly of Pb, K, and Rb) during ignition loss measurements, especially for halide-rich samples

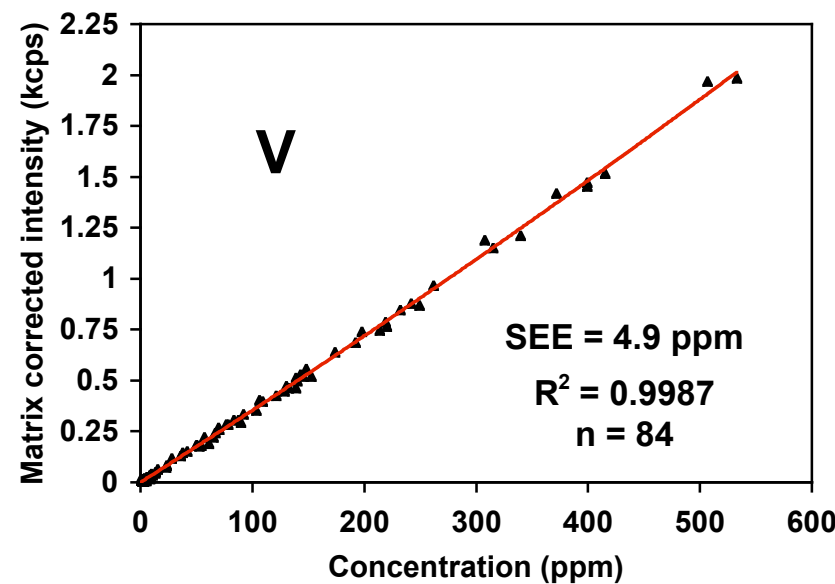
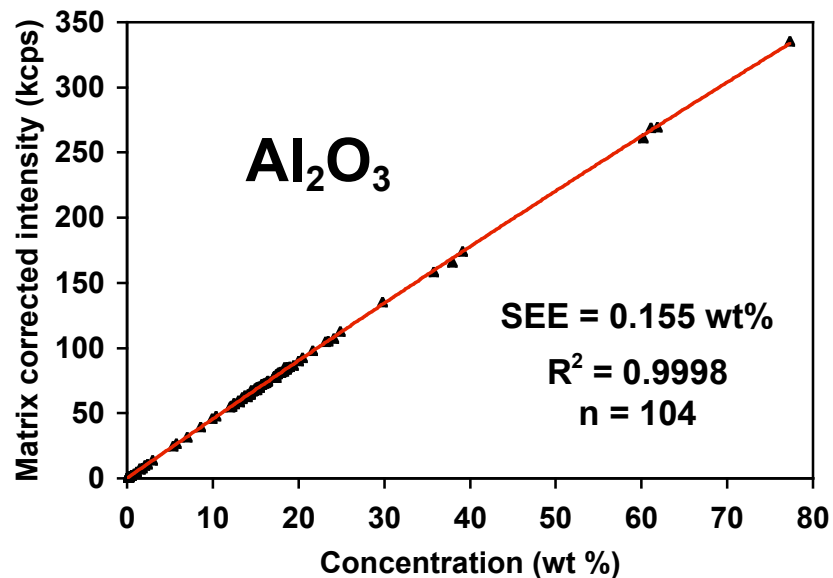
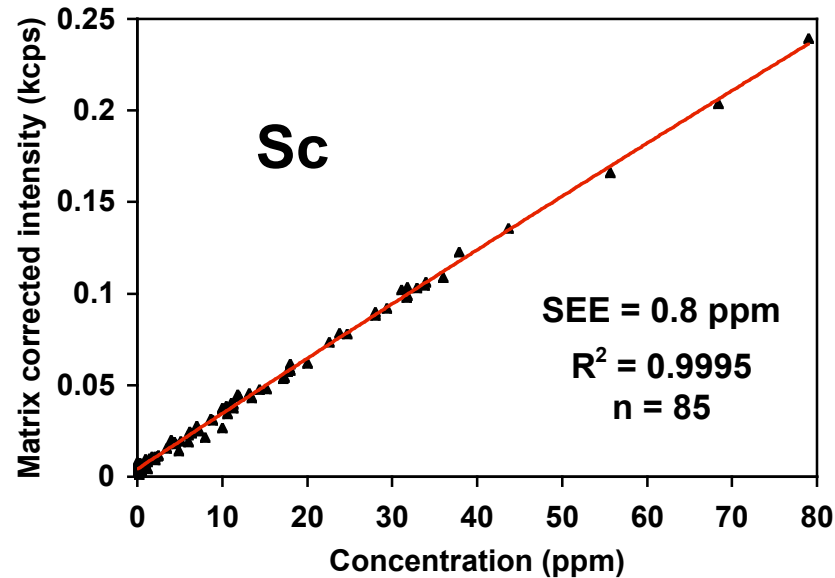
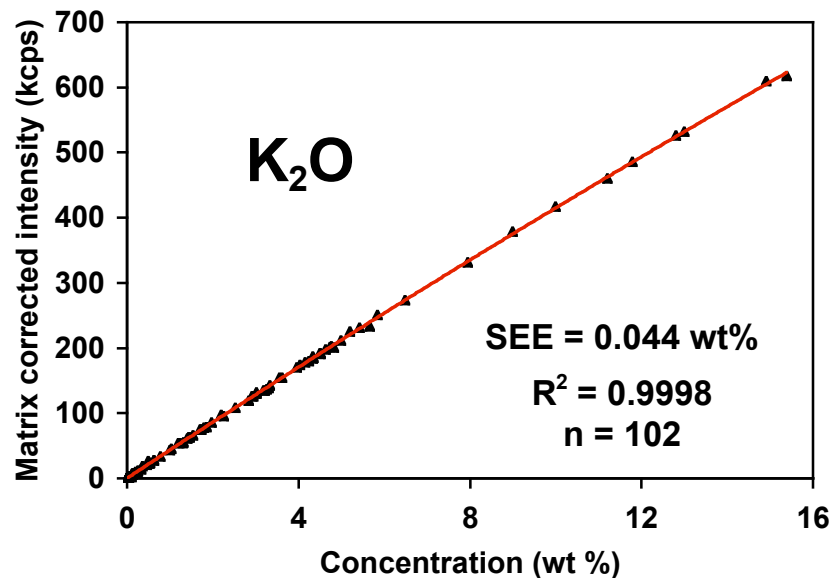


estimated loss on fusion is a robust approximation of loss on ignition - we have employed this correction for several years now on diverse lithologies. Very Fe-rich samples (gray squares) have high estimated LOF due to reduction of  $Fe^{+3}$



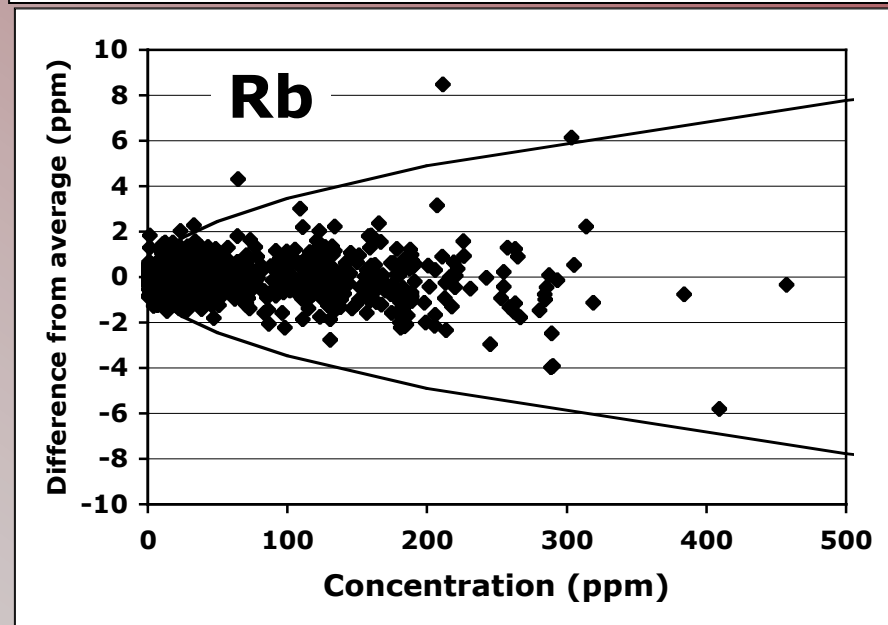
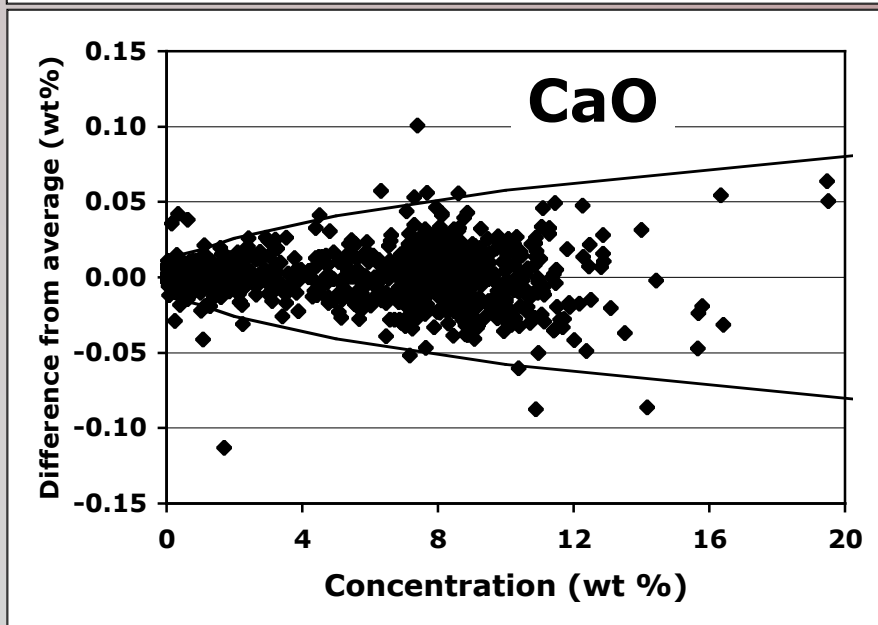
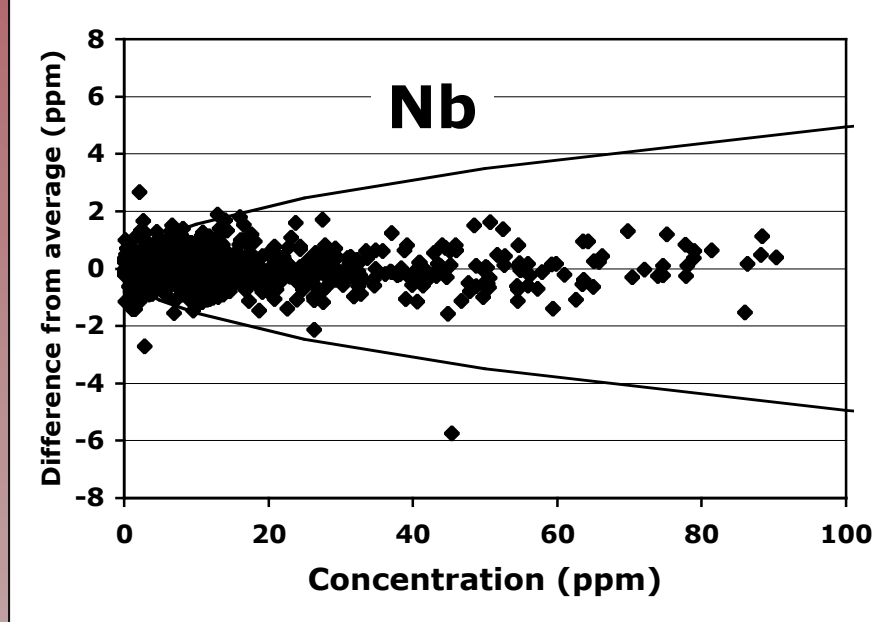
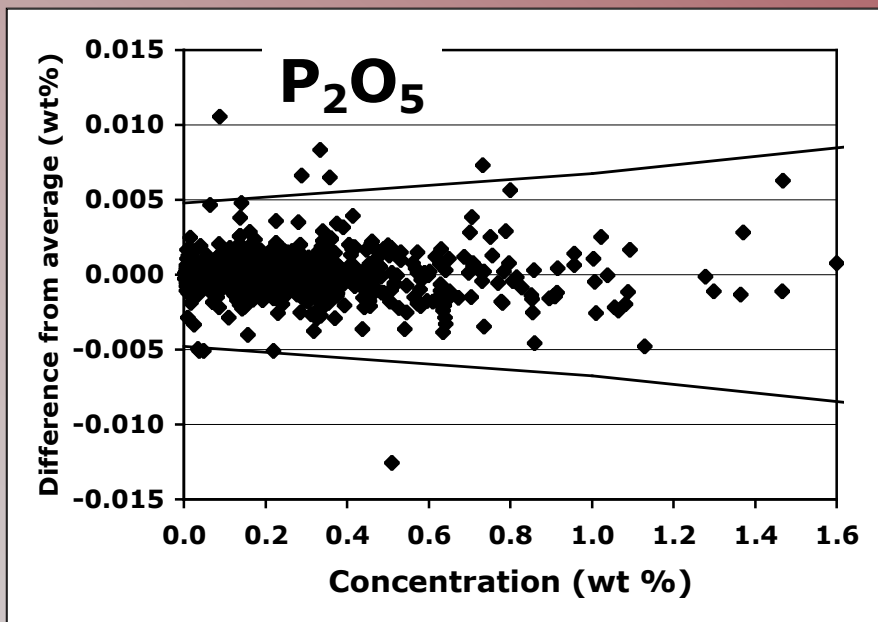


## Major and trace element calibration with graphite double fusions



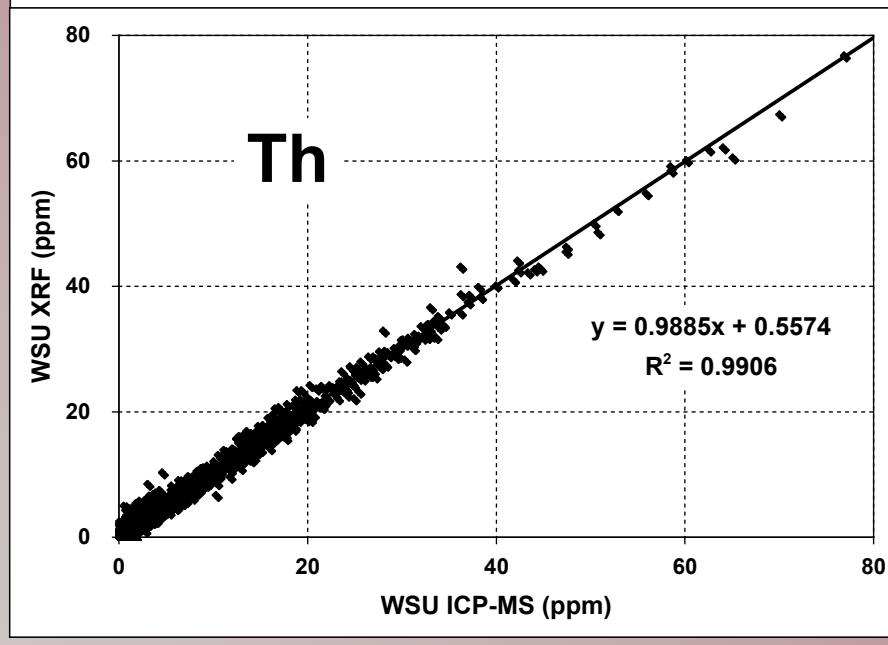
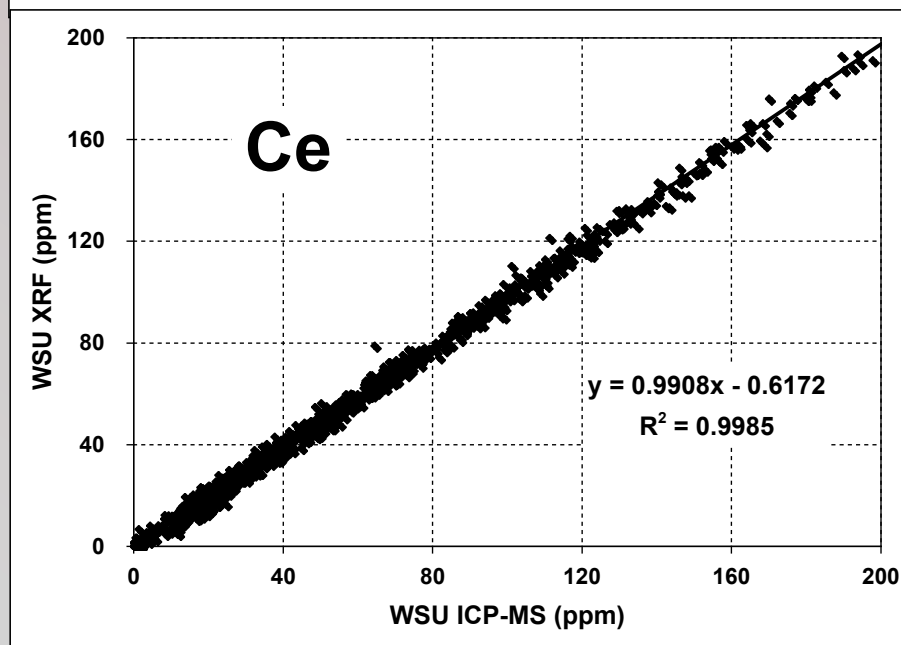
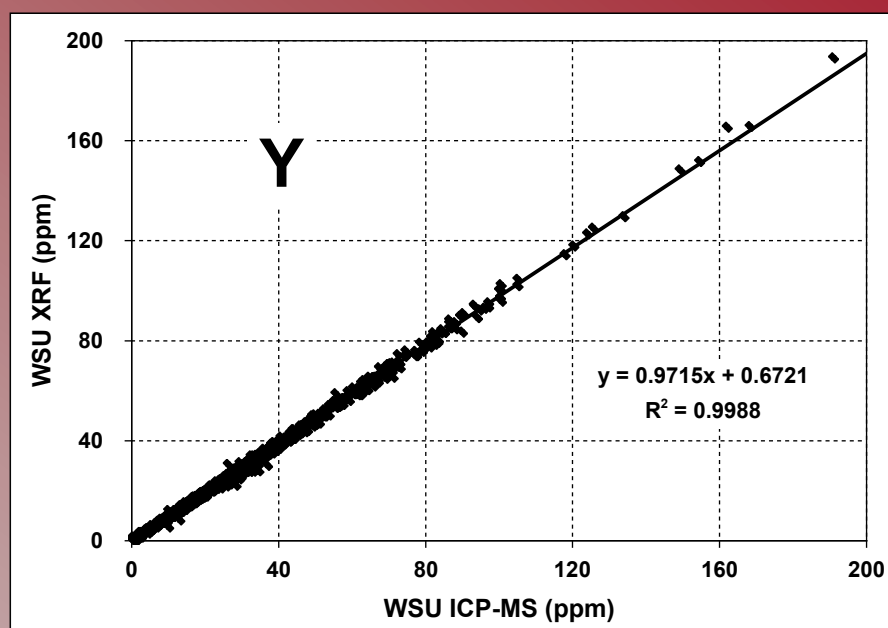
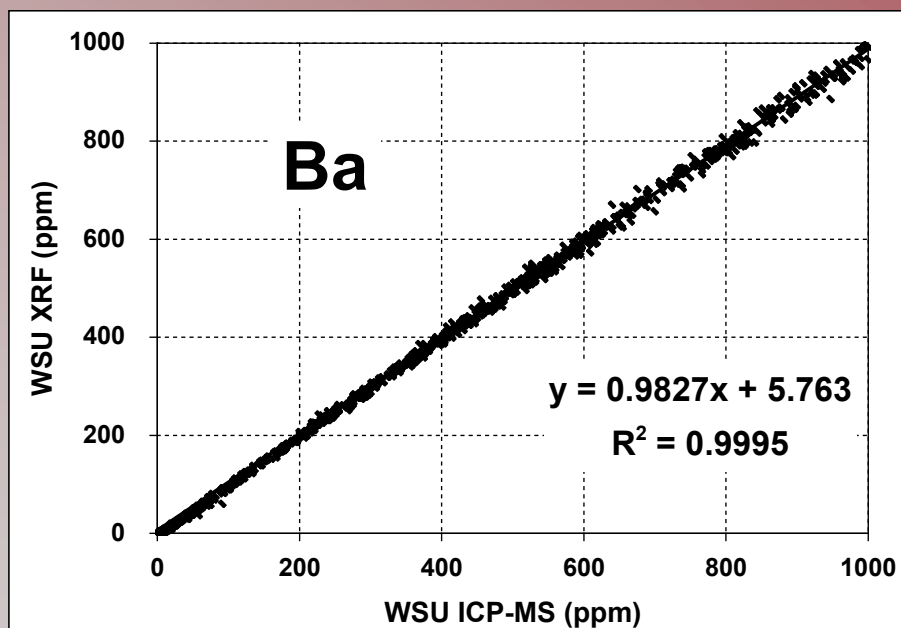
Calibration requires 5 days at ~66 min/CRM but calibrations hold for 3-10 months

*Reproducibility of major and trace elements using graphite double fusions (n = 850)*



Duplicate analyses of 850 diverse same sample powders performed over a 5 year period, 2004-2009

*Graphite fused XRF versus graphite fused- acid digested ICP-MS trace elements (n = 1224)*



All 1224 analyses performed over an eight month period in 2009 on a single XRF calibration

## *Summary*

- Our lab has served a broad Earth science research clientele over the past 35 years using low dilution graphite fusions for XRF analysis
- Graphite provides more than sufficient reproducibility for the vast majority of bulk rock analyses (our lab is often chosen for certification studies due to our consistent performance on GeoPT samples)
- Graphite allows employment of a robust low dilution fusion strategy for nearly all geologic materials save ores
- We thank Charles Wu and the instructors of the University of Western Ontario XRF course for their excellence in instruction and in preparation of course materials. The UWO courses have deepened the knowledge base of our technical staff and helped us further our goals of providing education and good data at a reasonable cost.