Lithogeochemistry Using a Portable X-Ray Fluorescence (pXRF) Spectrometer and Preliminary Results From the Eagle Ford Shale

Dr. Mark T. Ford and John M. Dabney
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Collaborators: Federico Cernuschi (OSU), Darrick Boschmann (Washington DNR), Dr. Thomas McGehee (TAMUK) and a number of TAMUK undergraduates.
Undergraduate students get REALLY excited about the chance to do primary research!
Introduction:
pXRF – LOTS of uses!
  Archeological (pottery, glass, obsidian)
  Paint pigment chemistry (forgeries, non-destructive)
  Metals (scrap yards and assay)
  and many more....
Introduction:
pXRF – Geologic uses too!
  Soils (contamination, etc.)
  Reconnaissance soil sampling (metals)
  Whole rock geochemistry (too many to list...)
  Mineral chemistry (identification, trace elements)
  Marker horizons in shale
  and many more....
You remove an inner shell electron and an outer shell electron “cascades” down to fill the hole. This gives off “characteristic” energy.
Many people are disappointed with their pXRF results on rocks.

These are NOT tricorders, they are instruments that need consistent sample prep and analytical methods.

Many of these instruments were developed for analysis of metals in metallurgy, not complex aggregates of minerals in rocks.
Maybe a Better Title: Portable X-Ray Fluorescence (pXRF) – More Than Just “Point and Shoot”

Matrix effects, calibration and ideal energies, spectral interferences, sample homogeneity including grain size, density (grain size) and more!
Does this mean that we can not get good results?
No – We have proven that you can get GREAT results:

An others... Mn, V, Mo, Cd, Y Cr, and more!
Fair - U, Th, Al (better with a vacuum)
So, how do strive for get good results?

Many people are disappointed with their pXRF results on rocks.

“Never ever believe numbers unless you know the physics”
- Dr. Bruce Kaiser, inventor of the pXRF

The power needs to be in your hands...
   For rocks, user defined calibrations are a must!
   Most machines use proprietary calibration methods...
      You can not adjust them.
   Use of influence calibration coefficients allows for much more accurate results on rock samples.
Consistency is Key! Homogeneity is a Must.

Consistent sample preparation, especially sample surface but grain size too, if you can.

Inhomogeneous – we agree. But they are all silicate minerals?

Homogeneous – are we sure?
Mass attenuation coefficients
Examples (99% analyzed depth) (energy dependent)
- Cu = 0.05 mm
- Ni = 0.04 mm
- Co = 0.01 mm
- Si = 0.50 mm
- Al = 0.65 mm
- Mg = 0.00 mm - Air attenuates!

Your depth of analyses for many elements is not much!
Surface (and homogeneity) matters!
Example of “major element” spectra (15kV a5 35 mA)

Experimental procedures enhance lower energy lines, typically major elements

Lower energy on the tube (filament) = a focus on lower Z elements
Most of the “major elements”
Si, Al, K, Ca, Ti, Fe and a few others
Example of “minor element” spectra (40kV at 17.1 mA)

Experimental procedures enhance higher energy lines, typically minor elements

Higher Z = MUCH better sensitivity – The K-shell really does not want to be vacant!
Example – Ca peak – 13 wt% while the Rb peak is only 12 ppm!
Peak vs. Background Sensitivity (noise): Example – Ni
Peak has 1011 counts. “noise” (once Bremsstrahlung is stripped) is ~30 counts.
You need at least 3X background. If you have a Gaussian distribution, 6X background will get you to $2\sigma$ – other factors too... FWHM (peak shape), internal error, etc.
Other Issues: Safety
Always error on the side of safety.
Time.  Distance.  Shielding.

Be mindful of the beam – design workspace to minimize risk.

If using the remote trigger, there is no need to be this close.

Use shielding whenever possible.

Time... limit scans to 60 seconds, if possible – no need for 10 minute scans.
Some Examples of Lithogeochemistry
Other projects we are working on:
Lithogeochemistry of (Mostly Igneous) Rocks in BBNP
Pros:  Great for undergraduates (amazing variety of rocks)
The “local” volcanoes
LOTS of work to be done with igneous rocks/geochem
Beautiful area to work with fair access
Ties to the oil industry
  ➔ Ash chemistry
  ➔ Boquillas Fm sedimentary rocks (EF proxy?)
More specific questions: Can we use lithogeochemistry determined by the pXRF to correlate some of the discontinuous mafic and intermediate flows, tuffs, potential lahar sources, etc. in BBNP?

Answer: I think so! Why?

We’ve done it before.
Lithogeochemistry of Basalts in Oregon

Proof of concept: Could the pXRF be used to “map” discontinuous basalt flows that often look similar?

Methods – Extensive field work, thin section petrography and laboratory geochemical methods compared to results from the pXRF.

Result – The pXRF is a useful tool for this type of work. There are likely 10X the number of basaltic eruption than previous thought in the Oregon High Lava Plains.
Geologic Map of The Glass Buttes Area, Oregon

pXRF used in the field for basalt chemistry (and checked in the lab)
Lithogeochemistry of Eagle Ford Shale

A strong correlation between elemental analyses, clay species, sedimentation rates and hydrocarbon potential

Example elemental correlation – see John Dabney poster:

Using pXRF to Identify Pay Zones in Hydrocarbon-Rich Shales: Lithogeochemical Analysis of The Eagle Ford Shale

John M. Dabney, Mark T. Ford, David J. Wood, Jake D. Ewing
Lithogeochemistry of Eagle Ford Shale
More work to be done here:
  What other elements are of interest?
  Are there differences within the Eagle Ford?
  Can this method be applied to other shale plays?
  How are elemental distributions related to paleo-redox conditions and hydrocarbon potential?

Methods development:
  Are the calibrations optimum for these rocks?
  How much does grain size (density) and inhomogeneity alter results?
  How can we improve efficiencies in analyzing?
Your turn for Questions!

Thank You!

Students working at the John S. Buckley Geosciences Field Station, 2015
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References:
- Ford and Cernuschi; in prep for 2015