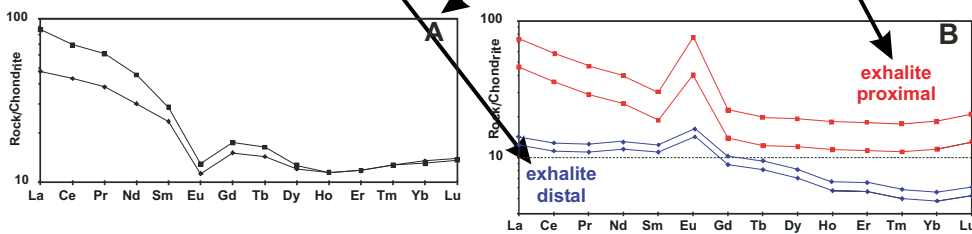
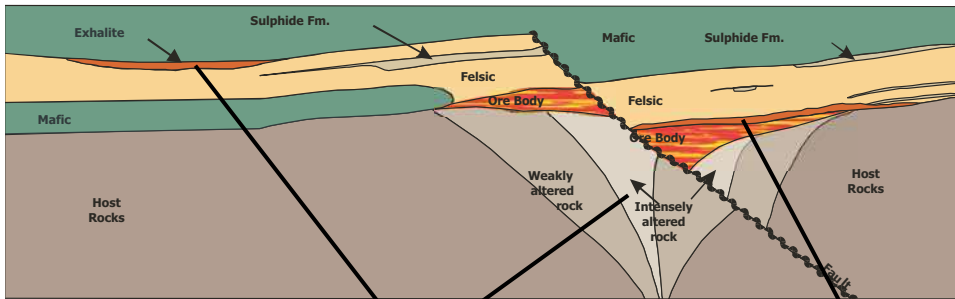


# LITHOGEOCHEMISTRY FOR RESEARCH AND MINERAL EXPLORATION



Eu may be leached out of footwall rocks in the hottest part of the hydrothermal system. A chondrite normalized plot would reflect this Eu depletion (Figure A). This Eu may be precipitated in the exhalative horizon proximal to the deposit. A chondrite normalized plot would reflect this Eu enrichment (Figure B). This positive Eu anomaly often becomes weaker as one becomes more distal to the deposit. This provides a potential vectoring device for the exploration geologist.

Figures modified from: Gale, G.H., Dabek, L.B., and Fedikow, M.A.F., 1997. The application of rare earth element analyses in the exploration for volcanogenic massive sulphide type deposits. *Explor. Mining Geol.*, Vol. 6., number 3., P.233-252.



**Activation Laboratories Ltd**  
41 Bittern Street  
Ancaster, Ontario, Canada L9G 4V5  
Tel: +1.905.648.9611  
Fax: +1. 905.648.9613  
Email: [ancaster@actlabs.com](mailto:ancaster@actlabs.com)



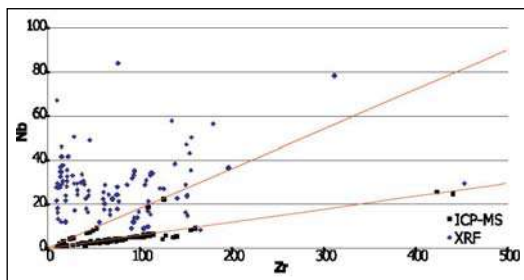
[www.actlabs.com](http://www.actlabs.com)

Major advances in analytical technology have occurred. Most notably, has been the introduction of the fourth generation inductively coupled plasma emission mass spectrometer (ICP/MS) and new sample introduction technologies. When this ICP/MS technology is combined with Actlabs' innovative lithium metaborate-tetraborate robotic fusion and inductively coupled plasma emission spectroscopy (ICP/OES), Actlabs offers a formidable new analytical technology. These advances have brought major and trace element geochemistry into the realm of being a cost-effective, rapid and highly accurate means of solving complex geological situations.

### HISTORICAL METHODOLOGIES FOR MAJOR OXIDES AND TRACE ELEMENTS

XRF whole rock analysis using lithium metaborate-tetraborate fused glass disks has been used for several decades for major oxide determination (Code 4C). Trace elements are poorly determined on the fused glass disk, due to sample dilution from the fusion matrix. To achieve lower detection limits for the trace elements, a pressed powder pellet (Code 4C1) is often employed. There are some analytical shortfalls that may exist for certain samples such as those with high Ba, which has a severe interference on TiO<sub>2</sub>. Other major elements may also be affected to a lesser extent through improper matrix modelling. Kerrich and Wyman (1996) have even shown that using XRF pressed pellets for trace Nb determination is not nearly as good as fusion ICP/MS.

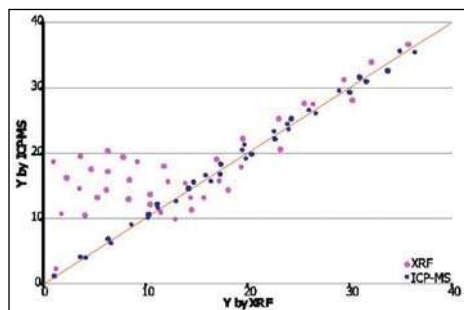
This work, shown in the figure below is a plot of Nb vs Zr by XRF compared to fusion ICP/MS. Clear trends are shown in the



ICP/MS data, while the XRF data shows no correlation on the same samples. Similarly, in the plot of Y

by XRF vs Y by Fusion ICP/MS, Kerrich and Wyman (1996) showed that the ICP/MS data is far superior to XRF at lower levels.

Jenner (1996) and others, noted that alteration and metamorphism often makes major element chemistry unreliable in

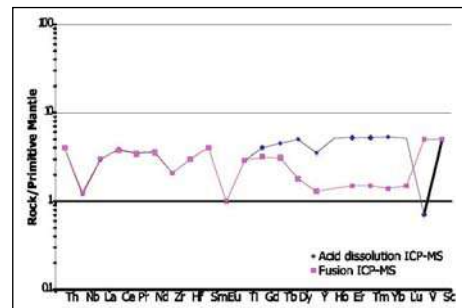


classifications which are based on SiO<sub>2</sub> and alkalis. Immobile trace elements could be used but other analytical techniques, such as INAA (instrumental neutron activation analysis) had to be used for Hf, Ta, Th, Sc, U and REE (Codes 4A or 4E research).

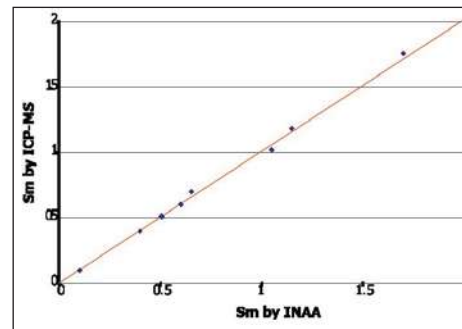
For a long period of time, INAA was the established standard for trace element analysis, particularly for high field strength elements (HFSE) and REE. During the last few years, ICP/MS has supplanted INAA as the standard for REE and other HFSE since all REE are analyzed and the detection limits are often substantially lower than by INAA.

### METHODS FOR REE ANALYSIS

There are a number of methodologies for the digestion of solid samples that have been used for REE determination. These include multiacid digestion, sodium peroxide fusion and lithium metaborate-tetraborate fusion. Hall and Plant (1992) in a comparison of multiacid digestion versus INAA, have noted that REE cannot easily be dissolved from very resistate phases, particularly for HREE. Similar results were found by Kerrich and Wyman (1996) who have shown similar severe discrepancies for heavy REE from the same sample using a multiacid dissolution



versus a fusion. The chondrite-normalized plot of their findings is attributable to incomplete dissolution of certain phases (zircon, monazite, xenotime, etc).



The figure on the left from the same study shows an excellent correlation between fusion ICP/MS and INAA (the standard for total metals).

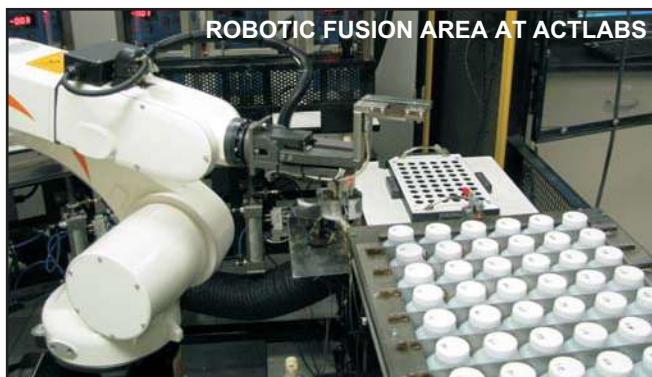
...Totally fused or dissolved samples analyzed by x-ray fluorescence, inductively coupled plasma-emission spectroscopy, and/or inductively couple plasma-mass spectrometry usually provide adequate data

Franklin, 1999

The lithium metaborate-tetraborate fusion dissolution procedure has long been recognized as the best technique for ensuring geological samples go into solution. In the past, this lithium metaborate-tetraborate solution was not highly compatible with ICP/MS sample introduction systems. Research and development conducted by Actlabs into sample introduction into the ICP/MS has solved this shortfall. This unique procedure allows Actlabs to offer an unrivalled package for the analysis of major oxides by ICP/OES and a suite of 43 trace elements by ICP/MS. This group of packages (Codes 4Litho, 4Lithores and their subsets) provides highly accurate results in a cost-effective and rapid manner. The advantage of this procedure for major oxide analysis over XRF is that it is more matrix independent and any rock type (including sulphide-bearing samples) can be analyzed without special calibration or pre-treatment. Detection limits offered with Code 4B are also better for Na<sub>2</sub>O and K<sub>2</sub>O by ICP/OES than XRF. In addition to whole rock data, Ba, Sr, Y, Zr, Sc, Be and V are included with low ppm detection limits with major element analysis at no additional cost. The most significant advantage of our fusion method is that this same solution can now be analyzed by ICP/MS without further preparation. Although chalcophile elements (Ag, As, Bi, Co, Cu, Mo, Ni, Pb, Sb, Sn, W and Zn) are included in the ICP/MS package, they may be better determined by alternate techniques such as ICP/OES (Cu, Pb, Zn, Ni, Ag - Code 4B1) or INAA (As, Sb, Co - Code 4B-INAA). Mineralized samples should be analyzed with the Quant option, which automatically provides assays for the elements which are overrange.

### RARE EARTH ELEMENT EXPLORATION

Recently exploration for rare earth elements has become very popular. Accurate determination of rare earth elements at higher levels required the introduction of the Code 8REE package which provides assays quality data for REE as well as other associated elements. **There is no upper limit for any element with this method. Our robotic fusion process also ensures very reproducible results impossible with manual fusion processes.** Samples with greater than 0.3% P<sub>2</sub>O<sub>5</sub> should



have Nb, Ta and Zr assayed by fusion XRF processes as these will partially precipitate in the presence of large amounts of phosphate.

### SAMPLING AND PREPARATION CONSIDERATIONS

Pearce (1996) provides a good rationale for sampling. The main goal is to collect sufficient random samples so that the main geochemical variations are adequately represented. 'The temptation to collect from only the hardest and freshest outcrops should be resisted as this can lead to sampling bias.' Pearce (1987) describes the statistical bias for sampling but suggests 'as a rough guide, around 15 samples are on average required to characterize each distinct lava unit'.

**Remember: Sampling variance is almost always much greater than analytical variance**

In order to provide good quality results, it is an imperative that the samples be prepared properly. Modern crushers contribute very little contamination, however, pulverization tends to create most of the contamination. Most modern labs use ring mills also known as swing mills. These mills consist of a series of rings and pucks contained within a sealed bowl. The rings, pucks and bowls can be made of agate, ceramic, case hardened mild steel, hardened steel, tungsten carbide or zirconia. We have found that case hardened mild steel provides the best grinding medium as it only contaminates with a trace of Fe (usually negligible with respect to the amount of Fe present in most rocks). Listed below are some of the contaminants that may be encountered with other types of mills. Hardened steel, tungsten carbide and zirconia mills are not really recommended for any litho geochemistry, as they severely contaminate samples. Ceramic and agate mills do not make as fine a pulp as these mills are lighter. Another consideration against ceramic and agate milling is that the cost of preparation is almost double the cost of using mild steel.

Our suggestion for the preparation process is to crush the whole sample to -10 mesh, mechanically split and pulverize to (95%) -200 mesh. If you feel the pulp between your thumb and forefinger, there should be no grittiness. In between samples, run a blank flush or split of the next sample to be pulverized as the flush, and then discard. Improper cleaning of the mill between samples is the most likely source of contamination.

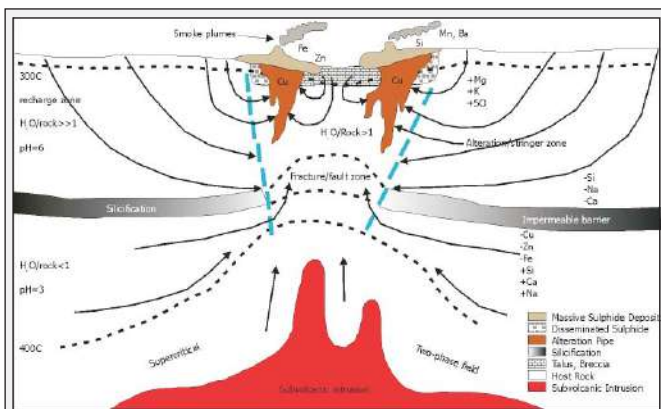
Mild steel (best choice) - Fe up to 0.2%  
Hardened Steel - Fe up to 0.2%, Cr up to 200 ppm, trace Ni, Si, Mn and C  
Ceramic - Al up to 0.2%, Ba, trace REE  
Tungsten Carbide - W up to 0.1%, Co, C, Ta, Nb, Ti and Hf  
Agate - Si up to 0.3%, Al, Na, Fe, I, Ca, Mg and Pb



## REE FOR ROCK IDENTIFICATION & STRATIGRAPHIC CORRELATION

REE can be used to help sort out rock type interpretations or stratigraphic correlations. Take for example a case where rock types in drill core have been very poorly visually classified due to pervasive alteration. REE are relatively immobile with some exceptions. Plotting chondrite diagrams may clearly elucidate this situation.

Recent work by Gale et al., (1997) examined the applicability of using REE determined by ICP/MS for VMS exploration. In REE chondrite plots, both stratigraphy and proximity to mineralization were clearly defined. In part, the Eu signature strength was found to be integral in defining hangingwall versus footwall and distal versus proximal in several examined deposits.



Composite section through a volcanogenic massive sulphide system. Note locally advection seawater near the deposit, which could form a Na-depleted, Mg-enriched alteration zone. (figure modified after Franklin, 1999)

## REFERENCES

- FRANKLIN, J., 1999. Systematic Analysis of Lithochemical Data, in Franklin, J.M., and Gibson, H.G., eds., Exploration Tools for Volcanogenic Massive Sulphide Deposits: Geological Association of Canada and Mineral Deposits Research Unit, U.B.C., short Course Notes, Section 4.
- GALE, G.H., DABEK, L.B., and FEDIKOW, M.A.F., 1997. The application of rare earth element analyses in the exploration for volcanogenic massive sulphide type deposits. Explor. Mining Geol., Vol. 6., number 3., p. 233-252.
- HALL, G.E.M., AND PLANT, J.A., 1992. Analytical errors in the determination of high field strength elements and their implication in tectonic interpretation studies: Chemical Geology, v. 95, p. 141-156.
- JENNER, G.A., 1996. Trace element geochemistry of igneous rocks: geochemical nomenclature and analytical geochemistry, in Wyman, D.A., ed., Trace Element Geochemistry of Volcanic Rocks: Applications for Massive Sulphide Exploration: Geological Association of Canada, Short Course Notes, v. 12, p. 51-77.
- PEARCE, J.A., 1987. An expert system for the tectonic characterization of ancient volcanic rocks: Journal of Volcanological and Geothermal Research, v. 32. p. 51-65.

## WHEN USING LITHOGEOCHEMICAL DATA FOR VMS EXPLORATION:

1. Lithochemical data should be treated systematically, and can be a useful tool in testing volcanic strata for VMS potential. Good quality whole rock data are required; partial extraction data can only be used for examining the relationships of indicator elements in sulphides (base and precious metals) or carbonates (Fe, Mn).
2. All calculations to examine for alteration effects should be done on single rock types. The first step in analyzing data should be to test for petrochemical homogeneity of each lithology.
3. 'Prepackaged' indices should be used with caution; most were established for a specific geological setting, and may not be more broadly applicable.
4. Once separate lithologies are established and the data are so identified in a spreadsheet form, the frequency distributions of suspected mobile (alteration-related) elements should be examined. Most studies have found that Na<sub>2</sub>O, CaO and Sr are highly mobile at regional scales that are useful for exploration purposes. Al<sub>2</sub>O<sub>3</sub> is usually not mobile, but as it may remain as normative corundum, calculation of the latter parameter can be another very useful indicator of VMS potential. TiO<sub>2</sub>, Zr, Nb, Y and the REE are generally not mobile, and may be convenient references against which to compare the more mobile constituents.
5. Mass balance studies can be very useful in simultaneously examining the mobility of components that may be key indicators of mineralization.

## WHAT SHOULD YOU ASK THE LAB FOR?

All major elements, including S and CO<sub>2</sub> if appropriate to the geological situation to be investigated; the typical immobile element suite (Zr, Y, Nb and Ba) are essential; so are the transition metals (Ni, Co, Cr, Zn, Cu, Pb and less importantly Ag, Th, Sr, Rb, V and Sc). The REE should be obtained on a subset of samples, if lithological assignment is a problem.

## OBJECTIVES OF USING LITHOGEOCHEMICAL DATA

1. Establishing rock types
2. Establishing subgroups of samples for further examination for alteration effects
3. Examining the data for indications of alteration
4. Examining the data to gain an indication of the process of mineralization.

(Franklin, 1999)

Actlabs provides values on certified reference materials, recommended values and replicates which are run at no extra charge.