Trace Element Geochemistry of Igneous Rocks: Geochemical Nomenclature and Analytical Geochemistry

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INTRODUCTION

Since the early 1970's there has been an enormous growth in the use of trace elements in igneous geochemistry/petrology. This growth reflects, amongst other things:

- the development of a variety of analytical techniques and instrumentation;
- increasingly complex petrogenetic and tectonic models; and
- the realization that alteration and metamorphism of igneous rocks (particularly volcanics) often makes the major element element chemistry suspect, *i.e.*, not representative of the original or primary chemistry, thus rendering classification based on the alkali elements and silica (*i.e.*, TAS - total alkalis versus silica) or normative compositions invalid.

At the same time the geochemical nomenclature of the elements, and the methods by which rock names are established and data are presented, has also expanded. For example, Figure 1 illustrates a common diagram in use to classify altered or metamorphosed igneous rocks. This diagram makes use of the immobile or alteration resistant elements Zr, Ti, Nb and Y, and allows a comparison with a definition making use of silica, a potentially mobile element. In this diagram and the ones that follow, I have separately plotted a reference suite of unaltered or fresh volcanics and a similar suite of altered Ordovician equivalents. Figure 2 illustrates another type of diagram often used today, *i.e.*, one relating chemistry of volcanic rocks to tectonic environments of formation, or a tectonic discriminant plot.

Since there is often a well established relationship between tectonic environment of formation and type of associated mineral deposit (Swinden *et al.*, 1989), or more locally a stratigraphic association of a particular rock type and location of a mineral deposit (Swinden and Jenner, 1992) - it is of practical, as well as academic, importance to understand what elements are reliable to define geochemical signatures (fingerprints) in altered volcanics. However, not only must an element be reliable in defining a geochemical signature, we must be able to determine its concentration in a cost-effective, accurate and precise way.

The paper is structured as follows:

- first, the geochemical nomenclature of the elements and element groups is reviewed;
- second, some multi-element normalized plots are considered. These are a useful tool, both for recognizing tectonic environments of formation and assessing data quality;
- third, some of the more popular analytical techniques are reviewed, with discussion as to evaluation of the data.

REVIEW OF BASIC GEOCHEMISTRY

The periodic table forms the basis for the names chemists usually use in describing the elements (Greenwood and Earnshaw, 1984). However, whereas geochemists are familiar with these names, they are not consistently used, a geochemical nomenclature is often adopted. The broadest subdivision of the elements is that into: siderophile (iron-loving); chalcophile (forming sulphides); lithophile (forming silicates); and atmophile (gaseous elements) (Fyfe, 1974; Gill, 1989). Within the siderophile, chalcophile and lithophile groups, a subdivision is often made based on volatility, reflecting how the elements behaved during condensation in the solar nebula. Volatile elements are gaseous at relatively low temperatures, while refractory elements are those remaining solid up to very high temperatures (Gill, 1989). Alternatively, these classifications also reflect the condensation sequence; with refractory elements condensing at > 1400°C, transitional between ~1350 and 1250°C, moderately volatile between ~1250 and 800°C, and volatile at <800°C (McDonough and Sun, 1995; see Table 1).

Table 1. *Classification of the elements*

Lithophile elements	
Refractory	Be, Al, Ca, Sc, Ti, V, Sr, Y, Zr, Nb, Ba, REE, Hf, Ta, Th, U
Transitional	Mg, Si, Cr
Moderately volatile	Li, B, Na, K, Mn, Rb, Cs
Highly volatile	F, Cl, Br, I, Zn
Siderophile elements	
Refractory	Mo, Ru, Rh, W, Re, Os, Ir, Pt
Transitional	Fe, Co, Ni, Pd
Moderately volatile	P, Cu, Ga, Ge, As, Ag, Sb, Au
Highly volatile	Tl, Bi
Chalcophile elements	
Highly volatile	S, Se, Cd, In, Sn, Te, Hg, Pb

Modified from McDonough and Sun (1995)

Classification of trace elements

In terms of their abundance elements can be classified as: major elements - those with concentrations greater than 1%; minor elements - those with concentrations between 0.1% to 1%; and trace elements - those with concentrations less than 0.1% or 1000 ppm. It is common to refer to major and minor elements as simply the major elements and report these as oxides, and the trace elements are reported elemental. Elements do not always follow these simple divisions and particularly potassium (K), phosphorus (P), and titanium (Ti) can occur as major or trace elements.

Trace elements are often referred to as incompatible or compatible. Incompatible elements are those that favour the melt phase over the solid during melting or crystallization. Compatible elements favour the solid phase over the melt/magma. Compatibility is often used in trace element classifications, *e.g.*, hygromagmatophile. To classify an element based on compatibility there must be assumptions made regarding the phases present in the magma or left behind in the source, the weight fraction of these phases, and a knowledge of the partition coefficients for all of the elements between the solid and liquid (at the appropriate conditions of pressure, temperature, volatile content and overall composition of the system), so that a bulk distribution coefficient (D) can be calculated. If D is greater than 1, the element is compatible; less than 1 - incompatible. This is not an easy task, and can be confusing when discussing a suite of rocks in which elements that are incompatible in a basalt (*e.g.*, Rb) become compatible in a felsic rock.

An alternative method to classify elements is based on a ratio of ionic radius to ionic charge. This has the advantage of being independent of distribution coefficients (Saunders *et al.*, 1980), and elements with similar ratios are expected to have very similar geochemical behaviour (Rollinson, 1993). Saunders *et al.* (1980) proposed a definition based on the ionic radius/ionic charge (ir/ic), with those having ir/ic > 0.2 called low field strength elements, and those with ir/ic <0.2 called high field strength elements; they also separated out the rare earth element group (REE). This grouping has found widespread acceptance, particularly for the high field strength elements (see Table 2). Rollinson (1993) uses a similar approach based on ionic charge/ionic radius (or ionic potential), which gives rise to a different grouping of the elements (see Table 2).

Another commonly used element group, large ion lithophile elements (LILE), includes elements with ionic radii ranging between 0.94 and 1.67 angstroms (see Table 2; Schilling, 1973; Krauskopf and Bird, 1995). Rollinson (1993) notes that the LILE group corresponds to his LFSE grouping. The original definition of the LILE group (see Saunders *et al.*, 1980) includes the LFSE + two of the rare earth elements (La and Ce). It is common to see authors refer to the element groups in the combination of LILE, REE and HFSE. I would discourage this since the LILE include some of the REE, and therefore it is unclear what the authors are referring to. It would seem more sensible to use the same element definition mechanism (ir/ic) and groups as Saunders *et al.* (1980). For the purposes of this paper, and as a matter of course, I use the definitions of LFSE and HFSE proposed by Saunders *et al.* (1980) and the REE group. From a practical point of view, these groups also make sense when discussing alteration (see below).

Some other commonly used element groups are given in Table 2. The PGE do not strictly include gold (Au); however, it is commonly included on PGE plots and is associated with the PGE subdivision (Rollinson, 1993).

Since most of the volcanic rocks that geochemists, and those interested in finding VMS deposits, study have undergone metamorphism and/or alteration, it is common to see trace elements referred to as mobile or immobile. This type of division is difficult to substantiate rigorously. The conditions under which elements remain immobile or become mobile are many and varied. Even some of those elements generally accepted as immobile can become mobile under extreme conditions. Table 3 lists a summary of mobile and immobile element behaviour based on the authors own experience and an extensive survey of the literature (see Kean *et al.*, 1995). Based on experimental seawater - basalt interaction experiments (Mottl and Seyfried, 1980), rock dominated systems are here defined as those with a fluid/rock mass ratio < 50, and seawater dominated systems are those with a fluid/rock mass ratio > 50. In general, rock dominated systems are operative during alteration of the oceanic crust, and while seawater dominated systems are crucial for formation of VMS deposits they are (unfortunately) not that common. In general, if rims of pillow lavas and margins of dykes are avoided, and the most intensely altered areas are avoided, especially those with carbonate veins, the HFSE and REE will remain immobile. However, it is

Table 2 *Trace Element classifications*

Field Strength	ionic radius / ionic charge (Saunders *et al.*, 1980)
low field strength elements (LFSE)	ir/ic >0.2 - Cs, Rb, K, Ba, Sr, Th, U, Pb
high field strength elements (HFSE)	ir/ic <0.2 - Zr, Hf, Nb, Ta, Ti, P
Rare earth elements	La - Lu (REE) + often Y is included
light rare earth elements (LREE)	La, Ce, Pr, Nd
middle rare earth elements (MREE)	Sm, Eu, Gd, Tb, Dy, Ho
heavy rare earth elements (HREE)	Er, Tm, Yb, Lu
Large ion lithophile	Cs, Rb, K, Ba, Sr, Th, U, Pb, La, Ce (Schilling, 1973)
Ionic potential	ionic charge / ionic size (Rollinson, 1993)
low field strength elements (LFSE)	Cs, Rb, K, Ba, Pb, Sr, Eu
high field strength elements (HFSE)	Sc, Y, Th, U, Pb, Zr, Hf, Nb, Ta, Ti + La-Lu
Hygromagmatophile	bulk distribution coefficient (Wood *et al.*, 1979)
less hygromagmatophile (D~0.1)	Sr, P, Ti, Y, HREE (Zr, Hf)
more hygromagmatophile (D<0.01)	Cs, Rb, K, U, Th, Th, Nb, Ba, La, Ce (Zr, Hf)
Transition elements	TE - Cr, Ni, Sc, V, Co, Cu, Zn (Ti, Fe, Mn)
Platinum Group elements	PGE - Ru, Rh, Pd, Os, Ir, Pt
Ir-group (IPGE)	Os, Ir, Ru
Pd-group (PPGE)	Rh, Pt, Pd
Base metals	Ag, Cu, Ni, Zn, Cd, Mn, Pb
Noble or precious metals	Ru, Rh, Pd, Os, Ir, Pt, Au, Ag
Refractory metals	Mo, W, Re (Gill, 1989)

best to assume the LFSE are mobile under all circumstances. As well, the transition elements are usually a reliable indicator of the original chemistry. Th, which is strictly defined as a LFSE, seems to behave as an immobile element under most circumstances. This is important, since LFSE/HFSE ratios and behaviour are important in distinguishing tectonic environments of formation, and all the other LFSE are mobile. The importance of the immobility of the HFSE and Th is illustrated in Figures 1 and 2.

Normalized trace element data

It is now common practice to present trace element data on primitive mantle-normalized diagrams. These diagrams are referred to in a number of ways including extended REE plots, spider diagrams or spidergrams and others (Rollinson, 1993; Sun and McDonough, 1989). Of these the most geochemically unsound terminology is spider diagrams or spidergrams, and this colloquial usage should be avoided (*cf.*, Rollinson, 1993). The order, or sequence, of elements (from left to right) reflects the bulk distribution coefficients (lowest on left and increasing to the right) during partial melting of a peridotitic mantle that gives rise to a normal mid-ocean ridge basalt (N-MORB; see Figure 3). Unfortunately, there are a variety of sets of normalizing values and some variation in the order of the elements. Sun and McDonough (1989) provide a complete set of normalizing values and the rationale used in establishing the order of the elements. This order and normalizing values

Table 3. Trace element classification and behaviour during alteration and metamorphism.

LFSE	**Seawater (SWD) or Rock (RD) dominated**	**Comments**
K, Rb, Cs, U, Pb	mobile SWD or RD	assume mobile
Ba, Sr	mobile SWD ? RD	best considered mobile until proven otherwise. However in RD systems can still be a useful petrogenetic indicator
Th	immobile RD ? SWD	potentially mobile, but in general appears to remain immobile
HFSE		
Ti, Zr, Hf, Nb, Ta	immobile RD and SWD	immobile - until proven otherwise
P	immobile RD ? mobile in SWD	immobile to slightly mobile
Y	immobile RD and SWD	immobile - until proven otherwise
REE		
La, Ce, Nd, Sm	immobile RD ? mobile in SWD	can be mobile, but for most altered volcanics seem to be immobile. Be careful if you see -ve Ce anomaly.
Eu	slightly mobile to mobile in RD/SWD	the most unreliable of the REE for petrogenetic interpretation in altered rocks
Gd, Tb, Dy, Er, Yb, Lu	immobile in RD, slightly mobile in SWD	generally immobile in systems where water is dominant fluid. Addition of carbonate can make these mobile. Look out for S-shaped patterns in the HREE
TE		
Cr, Ni, Sc, V	immobile in RD and SWD	Ti-V very useful immobile element ratio

have been used in Figure 3. Implicit in the values and element order proposed by Sun and McDonough (1989) are some important geochemical ratios found in oceanic volcanics, namely: Nb/U = 47±100; Ce/Pb=25±5; K/U=12700±200; Ba/Rb=11.6±0.3; 1000*Cs/Rb=13.1±0.4; Nb/Ta=16-18; Zr/Hf =35-40; P/Nd=74±13; Ti/Zr=100; see also Hofmann and White, 1983; Jochum *et al.*, 1983; Hofmann *et al.*, 1986). The HFSE ratios, in particular, are also useful in verifying analytical data since there are few processes that can fractionate these ratios. It is also useful to know these ratios when trying to meld sets of normalizing values together, or evaluate whether the values proposed for either primitive mantle or N-MORB are valid.

It is also important to be aware of the fact the normalization is to primitive mantle. Primitive mantle is the hypothetical mantle which existed after core separation, but before crust/mantle differentiation. The primitive mantle is not chondritic, *i.e.*, the bulk silicate Earth is not chondritic, because fractionation/condensation events affected the refractory and moderately volatile lithophile elements differently. The primitive mantle, while it may be hypothetical, is nonetheless fairly tightly constrained and of direct relevance to our understanding the Earth and its processes. For this reason

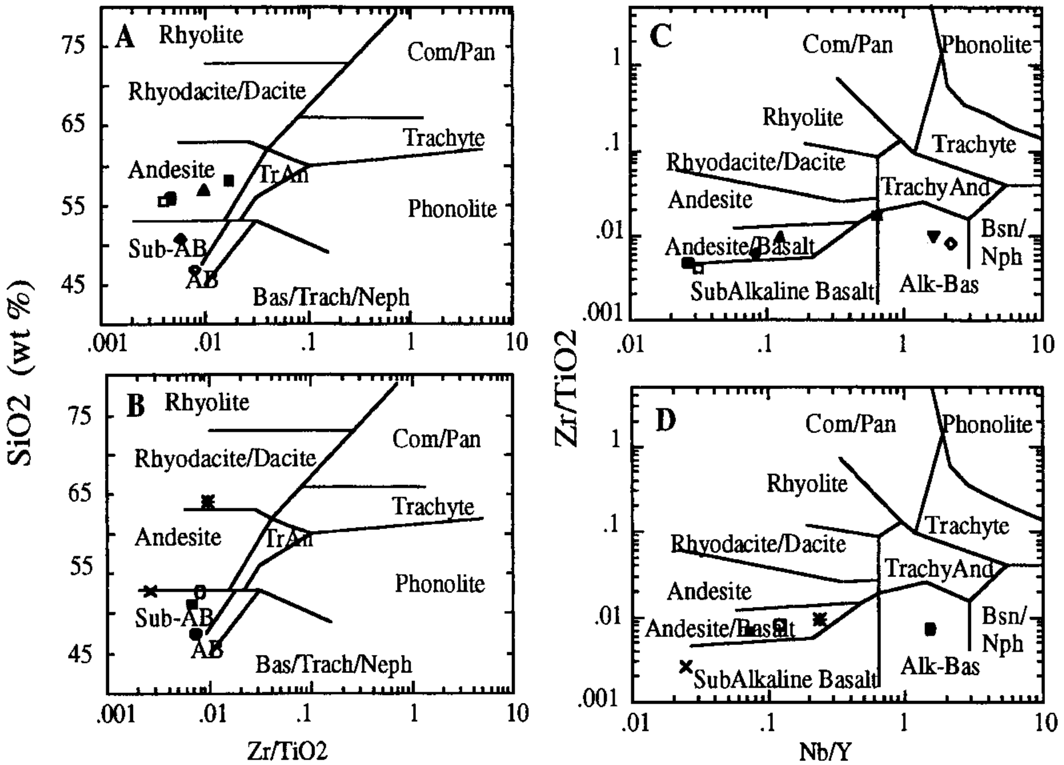


Figure 1 *Geochemical discrimination diagrams by Winchester and Floyd (1977). These diagrams were constructed to illustrate how different magma series and volcanic rock types could be distinguished in metamorphosed and altered volcanic rocks using immobile trace elements. A and C show data from fresh, young volcanic rocks. B and D show data from altered Ordovician volcanic rocks. Com= Comendite; Pan = Pantellerite; Bsn = Basanite; Teph = Tephrite; Neph = Nephalinite; Bas = Basalt ; AB = Alkaline Basalt; And = Andesite.*

the logic suggested by Rollinson (1993) that we should use chondritic values and the order suggested by Thompson (1982) simply because we can measure chondritic concentrations directly is not valid. Moreover, some flexibility is allowed in the order of the elements, providing no major geochemical rules are broken.

Examples of mantle-normalized diagrams for mafic-intermediate volcanic rocks from a variety of modern settings are illustrated in Figures 3A and 3B. The non-arc rocks are oceanic island and mid-ocean ridge basalts, taken from Sun and McDonough (1989) and Chaffey *et al.* (1989) (NMORB = normal mid-ocean ridge basalt, OIB = ocean island basalt, SH = St. Helena). The arc rocks are a boninite (Jenner, 1981 and unpublished data), an island arc tholeiite (IAT; glass data taken from Rautenschlein *et al.*, 1985), a back-arc basin tholeiite (BAB; Vallier *et al.*, 1991) and a calc-alkaline andesite (CAS; from Vanuatu, unpublished data). Examples of altered Ordovician rocks (Swinden *et al.*, 1989; Swinden and Jenner, 1992; Kean *et al.*, 1995) are shown for comparison. Modern arc rocks are characterized by the presence of irregular enrichment in the LFSE, relative to the HFSE and REE. Most diagnostic of arc rocks are the low normalized abundances of Nb and Ta relative to the LFSE and La, *i.e.*, the negative Nb (Ta) anomaly or arc geochemical signature. In Figure 3C and 3D, the LFSE are probably mobile and this leads to some confusion in identifying the tectonic environment of formation. Note in particular the enrichment in the LFSE in the altered rocks

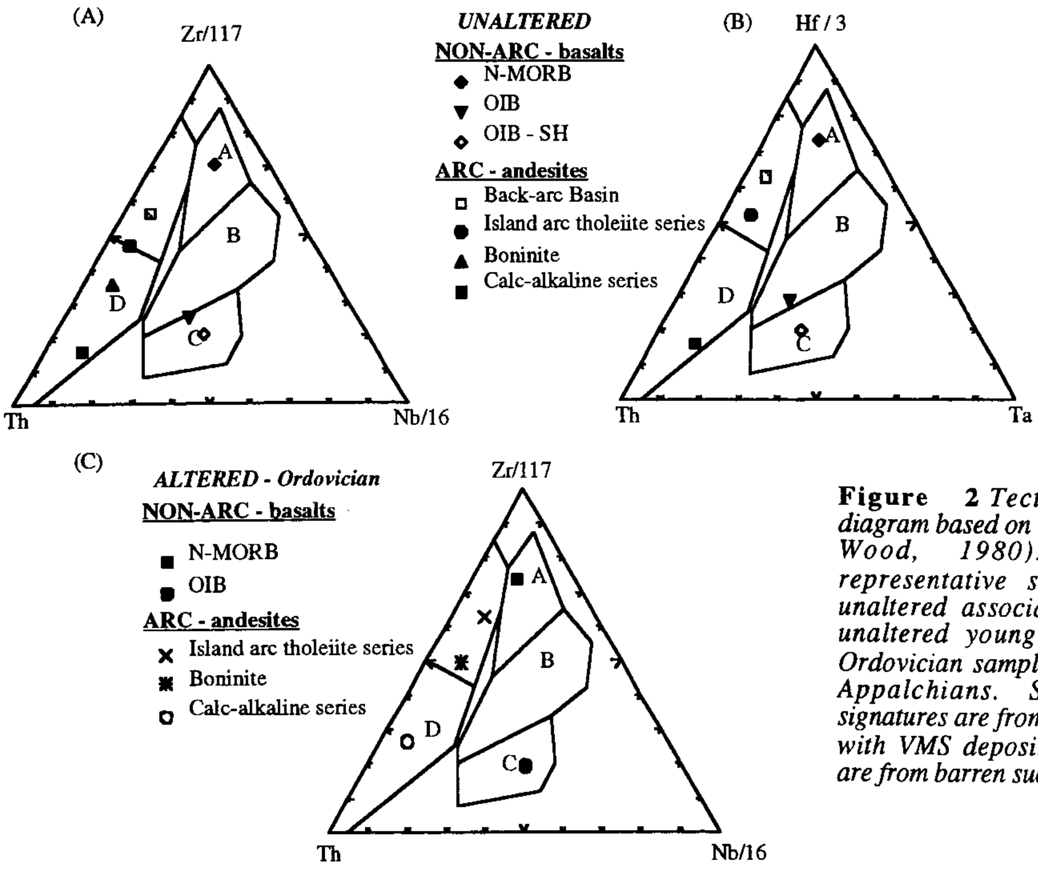


Figure 2 *Tectonic discrimination diagram based on Th, Zr, Nb and Ta (after Wood, 1980). (A) Th/Zr/Nb- representative samples from young, unaltered associations; B) Th/Hf/Ta - unaltered young volcanic rocks; (C) Ordovician samples from Newfoundland Appalchians. Samples with ARC signatures are from successions associated with VMS deposits. NON-ARC samples are from barren successions.*

interpreted to be OIB and N-MORB on the basis of no negative Nb anomaly and REE patterns. The mobility of the LFSE is less noticeable in the arc rocks, as expected, but the LFSE pattern shown by the altered CAS is very unusual. To circumvent the problems introduced by mobility of the LFSE during alteration, it is recommended that only Th be used to represent this group in altered rocks. A set of immobile element mantle-normalized plots are shown in Figure 4. Note how much easier it is to distinguish the altered rocks into arc and non-arc groups in these figures.

It is also common to see normalized multi-element plots that use N-MORB as the normalizing values. The rationale for this diagram is outlined in Pearce (1983) and Rollinson (1993). While the difference between non-arc and arc rocks is clear for the fresh rocks, the picture is much more confusing when altered rocks are considered. Note that altered OIB (Fig. 5C) looks strikingly similar to the unaltered CAS in Figure 5B. There is no objection to N-MORB normalized plots for unaltered rocks. For altered rocks, however, I suggest that the elements and order should be more like those used in the alteration resistant or immobile element mantle normalized plots shown in Figure 4. Sun and McDonough (1989) provide compilations of N-MORB, E-MORB and OIB which can be used to construct normalized plots (*cf.*, Hofmann, 1988). Those interested in constructing their own plots should be aware of the variability in N-MORB compilations, and use the crucial element ratios noted above to ensure they are not creating anomalies with their choice of normalizing values.

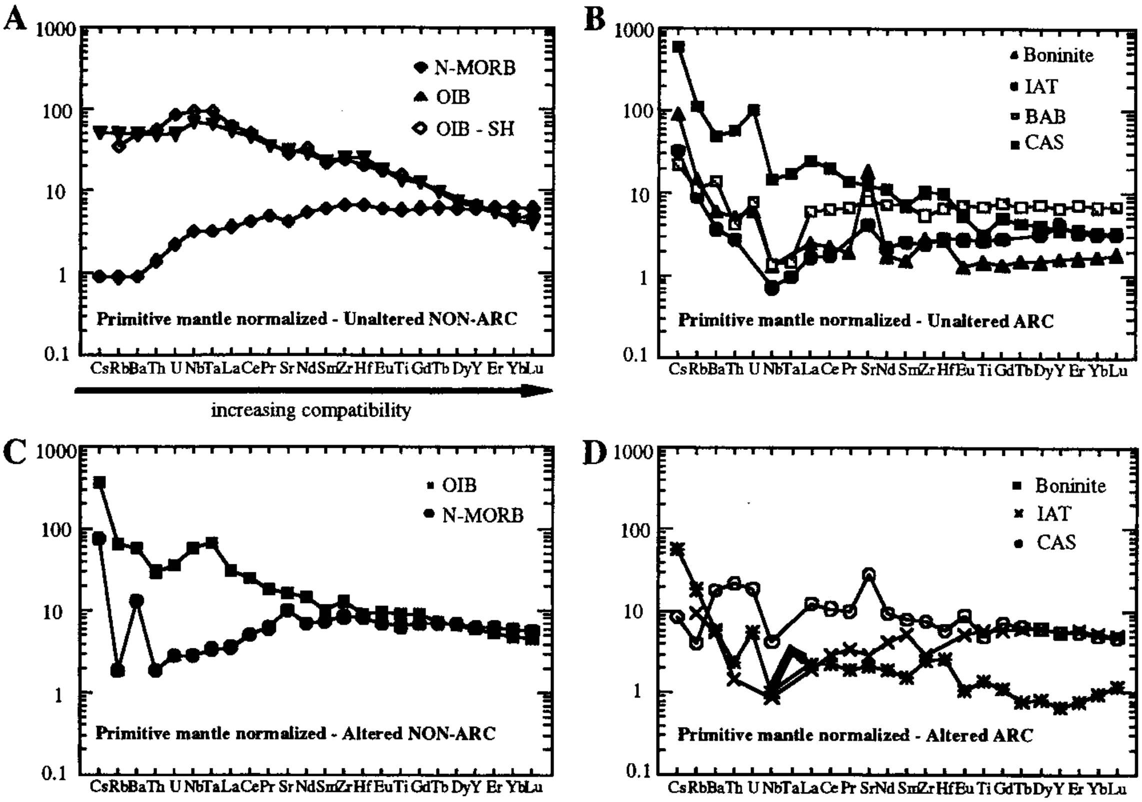


Figure 3 *Primitive mantle normalized plots of unaltered and altered volcanic rocks. Normalizing values and element order adopted from Sun and McDonough (1989). Arrow under A) shows direction of increasing compatibility for the elements. A) and B) are for young, unaltered volcanic rocks; C) and D) are for altered Ordovician volcanic rocks.*

ANALYTICAL GEOCHEMISTRY

There are a large number of elements that geochemists are interested in and most of these occur as trace elements (Fig. 3 and Fig. 6A). Since the 1970's there has been an explosion in the number of analytical instruments and methods available to acquire trace element data. Of particular note to geochemists are X-ray fluorescence spectrometry (XRF), neutron activation analysis {NAA, both radiochemical (RNAA) and instrumental (INAA)}, inductively coupled plasma - atomic emission spectrometry (ICP-AES or sometimes ICP), and inductively coupled plasma - mass spectrometry (ICP-MS). These techniques, excepting RNAA, are now widespread because of their relatively low cost, fast data acquisition times and good detection limits. Other techniques like spark source mass spectrometry (SSMS) or thermal ionization mass spectrometry (TIMS) are also valuable tools to the research geochemist, but are too expensive and slow for many routine analyses.

In this section of the paper some important concepts in analytical geochemistry will be reviewed, as well as the sample preparation procedures and techniques in common use. The detection limits and elements that can be determined for a number of techniques are also briefly reviewed.

Accuracy, precision and detection limits

All three of these parameters are critical in assessing geochemical data; however, only one (precision) is consistently and easily defined. Precision is a measure of analytical reproducibility (over days or weeks) and/or repeatability (a given analytical session; *cf.*, Keith *et al.*, 1983; Long and Winefordner, 1983; Potts, 1987; Mark and Workman, 1990; Rollinson, 1993). The precision

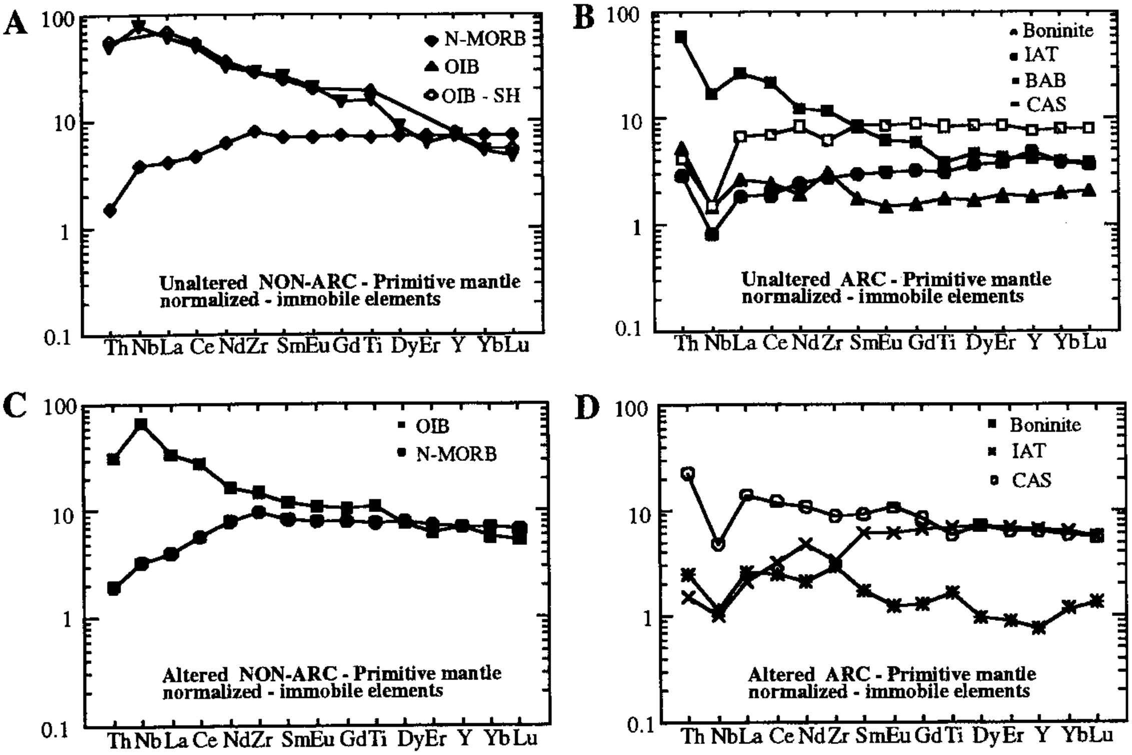


Figure 4 *Primitive mantle normalized plots for unaltered and altered volcanic rocks. Normalizing values and element order adapted from Sun and McDonough (1989). In this plot note that only immobile elements have been used. A) and B) are for young, unaltered volcanic rocks; C) and D) are for altered Ordovician volcanic rocks.*

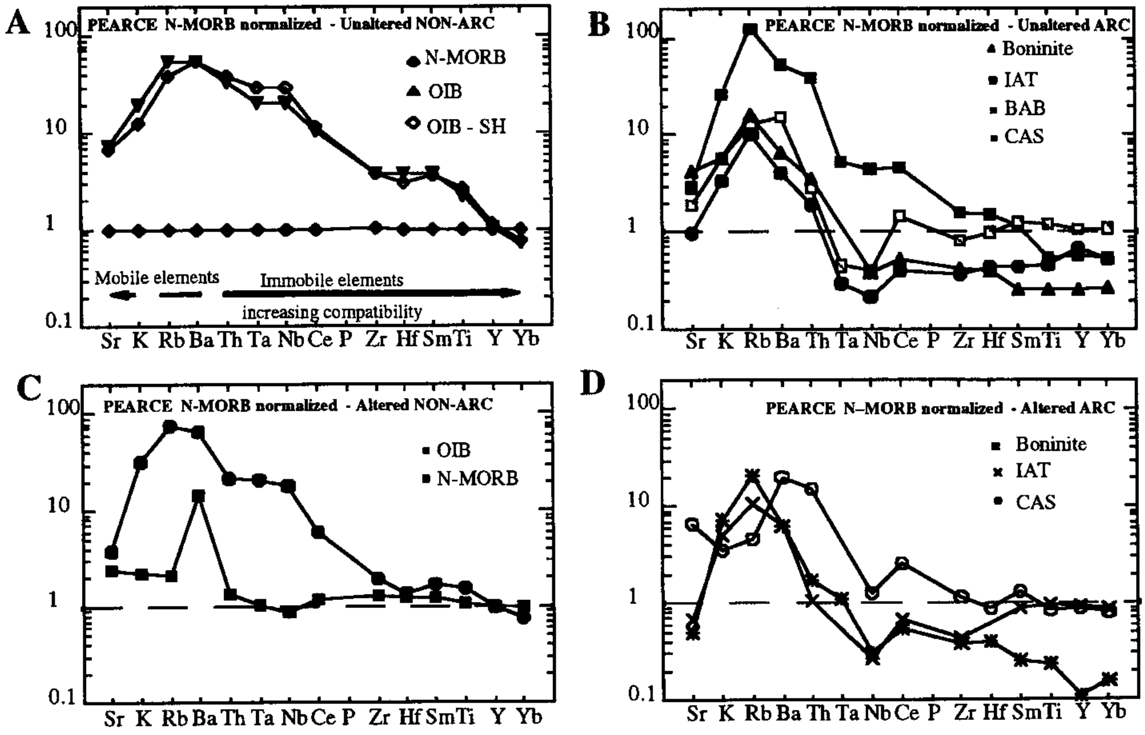


Figure 5 *N-MORB normalized plots of unaltered and altered volcanic rocks. Normalizing values for N-MORB from Sun and McDonough (1989). Element order in this plot is based on Pearce (1983). Some of the rationale for the element order is shown in A). Dashed line in B), C) and D) is reference line for an N-MORB. A) and B) are for young, unaltered volcanic rocks; C) and D) are for altered Ordovician volcanic rocks.*

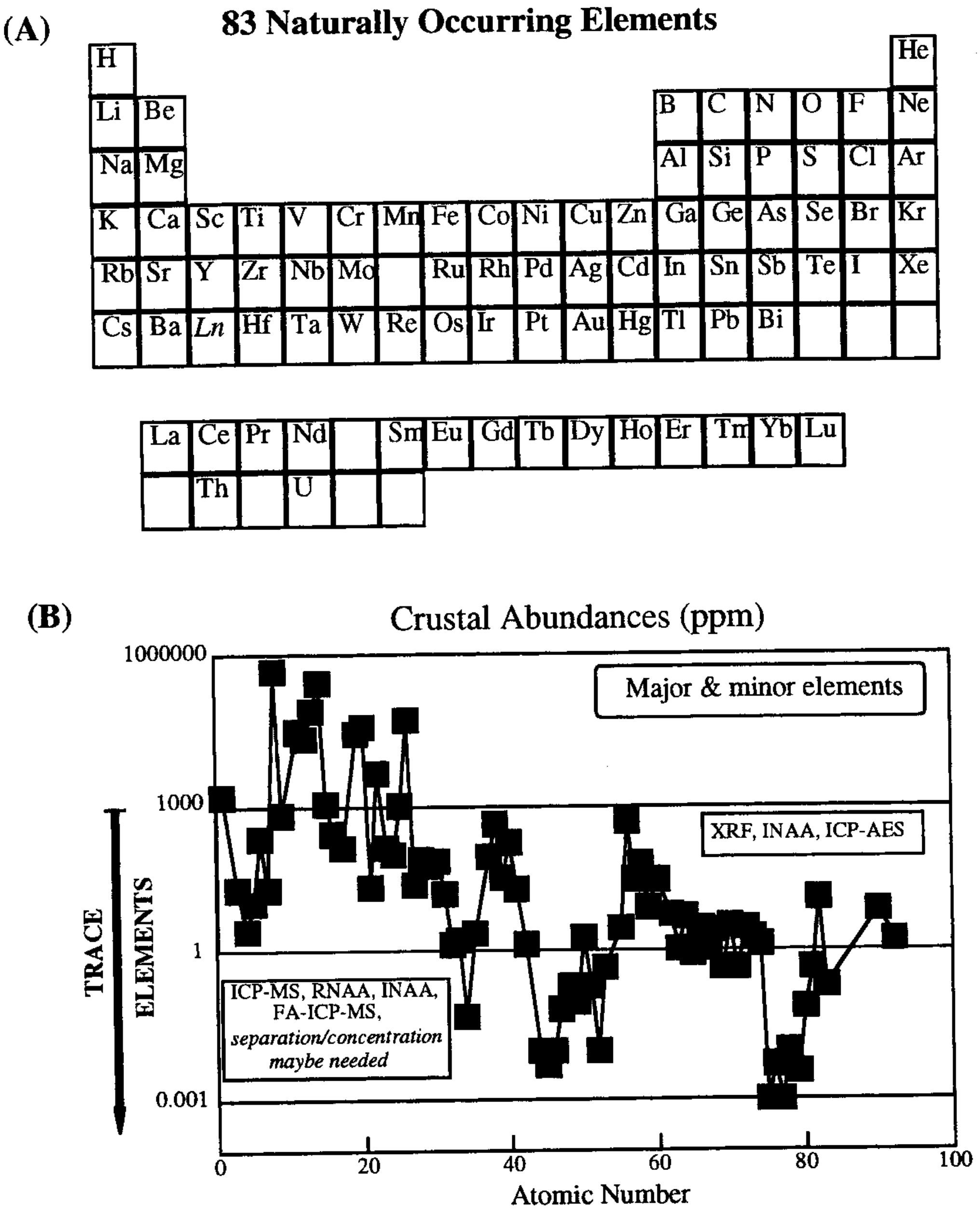


Figure 6 *(A) Periodic table illustrates the 83 naturally occurring elements for which geochemists need to have an appropriate analytical technique. (B) Illustrates the average crustal abunadnces for these elements. Most occur at trace levels (< 1000 ppm). Inset boxes show analytical technique most appropriate (generalized) for the levels between 1 - 1000 ppm and < 1 ppm. Those techniques for the latter group are not excluded from use in determining trace elements at higher levels, but the converse may not be true. Abundances from Taylor and McLennan (1985). See text for definition of analytical acronyms.*

for an element measured by any given technique is determined by comparing the results of a number of measurements, and normally involves calculating the sample standard deviation (s), a function common in many spreadsheets. Precision is usually reported as the relative standard deviation (RSD), or its equivalent the coefficient of variation (CV), which is 100* s/x (where x = sample mean). Most labs report precision for their techniques, based on replicate analyses over a long period of time; however, anyone making use of these facilities should include a number of duplicate/triplicate samples to allow their own evaluation of precision. Note that precision is concentration dependent, and that as the detection limit is approached RSD's will increase.

Accuracy is a measure of correctness, or how close the value obtained is to the 'true' value. To assess the accuracy of analyses, information must be presented for international geochemical reference materials (IGRMs). There are many IGRMs available to the analytical community; for example, sets of these spanning the 'normal' compositional spectrum of igneous rocks in particular are available from the Geological Survey of Japan (GSJ) and the United States Geological Survey (USGS). Compilations of data on IGRMs are usually used by geochemists in assessing accuracy; however, the 'true' composition of even these materials is often poorly known (Jochum and Jenner, 1994; Jochum *et al.*, 1994). Many analytical techniques use IGRMs to calibrate with (for example, XRF), and uncertainties or biases in the IGRMs used for this purpose can be (have been) propagated through the geochemical literature (*i.e.*, data for yttrium - Y and Nb; Jochum *et al.*, 1990; Jochum and Jenner, 1994). Accuracy is reported as percent difference, relative to the 'true' values. In evaluating accuracy, it is important to ensure that data on the IGRMs reported are at similar concentration levels and in a similar matrix, to the samples; *i.e.*, accurate Ni data on an ultramafic IGRM, like GSJ JP-1, is not of much use if most of the samples are granites.

The most problematic parameter to define when assessing geochemical data or an analytical technique is detection limit (Potts, 1987). Detection limit describes the lowest concentration level of the element that an analyst can determine to be statistically different from a blank (Keith *et al.*, 1983; Long and Winefordner, 1983). Detection limits can be defined in a number of ways, for example, Longerich (1995) reports three separate measures of detection limit, and Keith *et al.* (1983) note the concepts of a method limit of detection (MLD - refers to the lowest concentration of an analyte that a method can detect reliably in either a sample or a blank) or an instrument limit of detection (ILD - refers to the smallest signal above background noise that an instrument can reliably detect).

Potts (1987) gives a thorough discussion of detection limits and proposes that there should be a series of terms used to describe detection limits, *i.e.*, a lower limit of detection (LLD), a limit of determination (LoD), and a limit of quantification (LOQ). In brief his argument is as follows:

(1) detection limits are related to the confidence in distinguishing a signal from the background measurement.

(2) assume random errors and a normal distribution of a background signal x_B and a standard deviation s_B

(3) $x_B + 3s_B$ = the lower limit of detection (LLD) (3 sigma or 3σ);

(4) $x_B + 6s_B$ = the lower limit of determination (LoD) (6σ);

(5) $x_B + 10s_B$ = the limit of quantification (LOQ) (10σ).

These suggestions are not all in common usage. Most times the detection limit referred to by equipment manufacturers are defined at a 2σ level, which is not acceptable (Keith *et al.*, 1983). Increasingly, the detection limit or limit of detection (LOD) is specified at the 3σ level (or Potts' LLD) and this should be the common definition (Keith *et al.*, 1983). Between 3σ and 10σ results are in a region of less certain quantification, above 10σ results are quantitative (Keith *et al.*, 1983). Although Potts (1987) quotes LoD in his book, this usage is not common, and not particularly desirable given the arguments of Keith *et al.* (1983).

In practical terms, the limit of quantification (LOQ) is the most important parameter, and quantitative interpretation should be limited to data above this level. That is, if the LOD (3 sigma) for an element is specified to be 0.3 ppm, then above 1 ppm the reported data for this element can be considered quantitative. Assuming a precision of 10%, data points at 1.1 and 1.5 ppm can be considered different. Data between 0.3 and 1 ppm, may or may not be different.

Most detection limits reported are instrumental detection limits, Poisson counting statistics detection limits, calibration limit of detection and, occasionally, method limits of detection (*e.g.*, Jackson *et al.*, 1990; Longerich, 1993, 1995; Longerich *et al.*, 1990). Method limits of detection take into account reagent contamination (Jackson *et al.*, 1990; Longerich *et al.*, 1990) and are usually the most appropriate to use (*cf.*, Longerich, 1995). Users of any technique should be aware that regardless of the way detection limit is specified, it often represents the best case scenario. Detection limits are dependent on many factors and may vary significantly for a given technique both between labs and even with time in a given lab. For example, detection limits for ICP-MS are quite variable even when the same procedure is used in the same lab (Jenner *et al.*, 1990). To insure that data are quantitative depends on the ability to know what the detection limits were when the samples were analysed. In practical terms, the user is wise to put in sample(s) with known concentration levels at or near the stated detection limits and use this to evaluate how well the procedure has worked.

Sample preparation and contamination

In general, samples must be crushed and ground to a powder before they are used directly in an analytical technique such as INAA or XRF pressed pellet, or continue to a dissolution or fusion stage. Concerns about sample heterogeneity require that powders should be > 200 mesh or < 75 µm in size (Potts, 1987). As a general rule, for most silicate rock samples a 1 kg sample is usually sufficient to begin with, and only 200 g of this need be powdered after coning and quartering (Potts, 1987). However, the amount of material that needs to be sampled and crushed depends on the homogeneity of the rock, and can also be affected by the elements of interest (*i.e.*, major elements *versus* PGE; Potts, 1987).

During this sample preparation process there is ample opportunity for contamination. For example, samples are often slabbed before crushing and it is possible to contaminate the sample with the cooling/lubricating solution used. Oil cooled or recycling water cooled saws should be avoided, as should new saw blades (scrapped off paint can contaminate). If slabs are used, then they should be washed in acetone and distilled water before any further crushing. Steel jaw crushers are often used to reduce the sample down from chunks or slabs to 2-5 mm particles. These can contribute metal fragments to the sample, contaminating the transition elements in particular. An alternative is to crush the sample using a hydraulic press and opposing tungsten carbide plates. Provided the finest particles are avoided, this latter technique is probably the cleanest and least contaminating one to use. To go from particles to powder requires the use of a swing mill. Swing mills can be made of a variety of substances including tungsten carbide, aluminum ceramic and agate. Tungsten carbide is one of the most common, being robust and relatively inexpensive. However, tungsten carbide contaminates the sample with Co, Ti, W, Ta and Nb (Potts, 1987; Jochum *et al.*, 1990). These contaminants can compromise the determination of not only these elements but also others, due to interferences, if INAA is used. In general, Ta cannot be determined in rocks which have been crushed in tungsten carbide, while Nb is generally not contaminated too badly, except for low level (<0.1 ppm) samples. Agate is usually the preferred material to grind in; however, it too can cause contamination, *e.g.*, Pb (Jochum *et al.*, 1990) and requires more grinding time to produce the minimum required grain size. New agate mortars or swing mills should be cleaned repeatedly with silica sand before use on unknowns, to avoid contamination from the material used to polish the agate. Agate mills unfortunately are expensive and fragile, and are used less and less. Aluminum ceramic mills are used successfully in at least one major lab the author is familiar with (*cf.*, Potts, 1987), and my only experience with problems is that they do not always seem to produce a fine enough powder for some forms of sample dissolution (*e.g.*, sodium peroxide sinters for ICP-MS) or XRF pressed powder pellets.

Excluding contamination from the sample preparation material, the next major source of contamination is probably cross contamination from other samples. The easiest way to avoid this is to clean well between samples, and ideally introduce a minimum amount of the new sample, grind this and throw it away. For swing mills this may be preferable to grinding with sand in between samples, since the sand itself may have high levels of contaminants. Needless to say, it makes sense to prepare your samples in batches of similar lithologies, and not as a random mix or just in the order they were collected in the field.

Sample dissolution

A big advantage of purely instrumental techniques like INAA and XRF pressed powder pellets, is that it is not necessary to dissolve the sample. For most other techniques, it is necessary to put the sample into solution and/or fuse it before it can be introduced into the analytical instrument.

One of the most common methods of rock dissolution is acid dissolution using hydrofluoric acid (HF) ± perchloric acid ($HClO_4$) ± nitric acid (HNO_3) ± hydrochloric acid (HCl). The combination of acids used in addition to HF depends on the instrument to be used and the preferences of the analyst. Perchloric acid is potentially very dangerous unless the proper fume hoods are available, and often it can be difficult to get perchlorates into solution. Most ICP-MS labs use an HF-HNO_3 method and avoid Cl-bearing acids (Jenner *et al.*, 1990). For most trace element analysis the acids used should be distilled using either quartz sub-boiling stills or 2 bottle stills. Reagent grade acids often contain unacceptable blank levels. High purity water should also be used, and generally this is not a problem to acquire since the development of Nanopure™ and Millipore™ water systems. Dissolution is normally done in teflon open beakers or teflon screw top bombs. The latter is preferred, since it enhances the probability of getting resistant minerals (*e.g.*, zircon, spinel, titanite, garnet, corundum) into solution. In typical situations, 100 to 200 milligrams of sample are dissolved for ICP-MS and 0.5 to 1g for ICP-AES (Potts, 1987; Roelandts, 1988). Reagent blanks should be run routinely. Following dissolution, the sample is usually diluted (to 100 - 250 ml) prior to introduction into the machine and some chemicals (*e.g.*, oxalic and/or boric acid) may be added to stabilize the solution.

An alternative to acid dissolution is to use lithium metaborate or lithium tetraborate/metaborate fluxes and fuse the rock in a crucible (Pt) . Fusion cakes are dissolved in acid prior to use in ICP-AES analysis (Watkins and Nolan, 1990) Use of a flux is thought to ensure that acid-resistant mineral phases will go into solution, although there is some doubt about its effectiveness (Potts, 1987). Fusions are quicker, do not involve use of dangerous acids like HF and $HClO_4$, but may introduce contaminants (*e.g.*, La, alkali elements). Some ICP-AES techniques combine acid dissolution and fusions, which minimizes the amount of flux needed (Roelandts, 1988). Lithium borate fluxes are also used to prepare glass disks for analysis of major and occasionally some trace elements by XRF. For use with this technique, lanthanum oxide is added to enhance the suppression of matrix effects (the principal reason for using a flux; Potts, 1987).

Robinson *et al.* (1986) and Longerich *et al.* (1990) describe the use of a sodium peroxide sinter technique to dissolve samples. This sintering technique is successful in dissolving acid resistant mineral phases, and has low blanks for REE, Th, and the HFSE. Since the rock is not melted, cheaper crucibles (Ni) can be used and the furnace required need not go to very high temperatures (<600°C).

Direct fusion of whole rocks to glasses using a strip-heater has been described by Fedorowich *et al.* (1993), as a method of preparing samples for LAM-ICP-MS. This technique of sample preparation has a lot to offer, ensuring complete homogenization with minimal possibility of contamination.

Common analytical methods

XRF

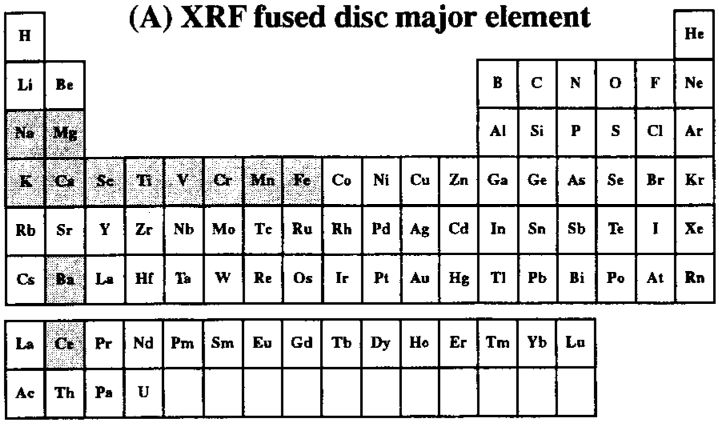
XRF is one of the most common techniques in use for the analysis of major and trace elements in geological samples. Analyses are performed on glass disks for major and some trace elements, and pressed powder (5-10 g) pellets for most trace elements. XRF uses a primary X-ray beam to excite secondary X-rays (X-ray fluorescence), which can be detected by a crystal spectrometer for wavelength dispersive or WD-XRF, or a solid state Si(Li) detector for energy dispersive or ED-XRF. ED-XRF has not found as much acceptance as WD-XRF, although it is a useful technique (Potts, 1987; Potts *et al.*, 1990). This discussion will focus on WD-XRF.

As illustrated in Figure 7, the elements which can be determined are numerous and fall into a number of geochemical element classification groups. Detection limits for selected trace elements are given in Table 4. WD-XRF analysis has played a major role in the development of many of the popular trace element discrimination diagrams, primarily because of its utility in determining Ba, Rb, Sr, Y, Zr, Nb, Ti, V, Cr, and Ni. WD-XRF analysis has continued to evolve in the last few years with improvements in crystals and become simpler to use with end window Rh-tubes as a primary X-ray source and more sophisticated computer data reduction schemes (Longerich, 1993, 1995). Calibration of XRF is often done using IGRMs and therefore is dependent on the values reported for these standards. Proper combination of analytical operating conditions and the best available non-XRF data for calibration can also lead to improvements in XRF analysis both in terms of detection limits and accuracy (Jochum *et al.*, 1990; Longerich, 1995). The precision and accuracy of WD-XRF analysis is difficult to generalize, but should be on the order of 1-10%.

Table 4 *WD-XRF: trace elements routinely analyzed and their detection limits (ppm)*

	Cu	Zn	Cr	Ni	Sc	V	Ba	Rb	Sr	Ga	Zr	Nb	Y	Th	U	Pb	Ce
A	2	1	6	3	4	4	24	0.5	0.6	1	0.7	0.4	0.3	2	2	2	31
B	6	9	10	6	8	10	24	3	3	6	6	6	3	9	6	6	30

A - 3 sigma, method limit of detection from Longerich (1995).
B - 6 sigma, limit of determination for "routine" analysis from Potts (1987).


(A) XRF fused disc major element

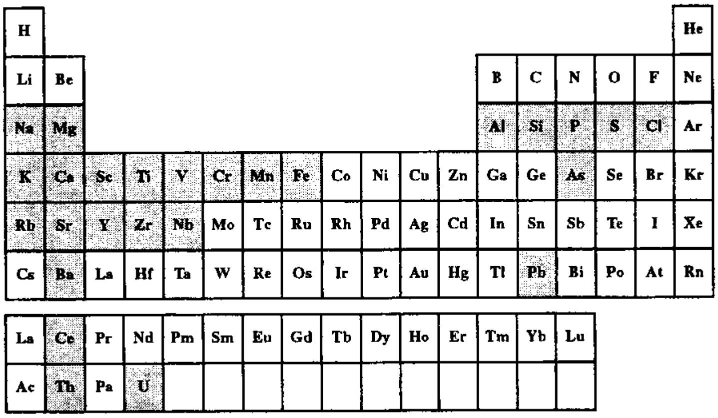

(B) XRF trace element pressed pellet

Figure 7 *(A) Major and trace elements determined by XRF on fused discs. (B) Trace elements determined by XRF on pressed pellets. Information from Longerich (1993, 1995, pers. comm., 1996). Elements that can be determined are indicated by shading.*

NAA

Neutron activation analysis requires irradiation of the sample (~100 mg) by a neutron flux, in a nuclear reactor. The sample, standards and flux monitor are irradiated for ~20 to 40 days, removed and the gamma radiation being emitted by the radioactive isotopes is counted using solid state detectors (intrinsic Ge, Ge(Li)). The gamma ray spectrometry is done at a number of intervals; the first may be within hours of removal from the reactor, followed by countings after a few days and then a few weeks. The spectra produced are complicated and require relatively sophisticated peak search and peak fitting/peak area routines. Calibration is often done using a IGRM irradiated in the same batch as the unknowns. The detector geometry (planar or coaxial), detector material (pure Ge, or lithium-drifted Ge), flux rate, counting times and sophistication of the software used all play a role in determining what elements can be measured, and what their detection limits will be (Potts, 1987). The most common NAA method is strictly instrumental and is referred to as INAA. It is also possible to do separation chemistry on the sample after irradiation, radiochemical NAA (RNAA), and this method will give much better detection limits, and expand the list of elements that can be determined. Research quality PGE determinations are usually done using RNAA. However, RNAA suffers from having to do chemistry on irradiated materials, and is not a commonly offered package. Whereas PGE can be measured by INAA, most commercial labs offer this only as a choice if combined with fire assay (FA) concentration.

Elements commonly determined by INAA and their detection limits are shown in Figure 8A and Table 5, respectively. INAA is a common choice amongst geochemists because of its relatively low cost, ease of sample preparation and wide selection of elements. For geochemists, INAA is attractive because it gives the LFSE Th, the HFSE Ta and Hf, plus some of the REE. INAA REE patterns are usually easily identified by the common absence of Dy and Er, and sometimes they also lack Gd. La is now commonly determined, but early work (1970s) lack this element. Precision and accuracy in INAA is generally on the order of 2-10% (Potts, 1987; Roelandts, 1988).

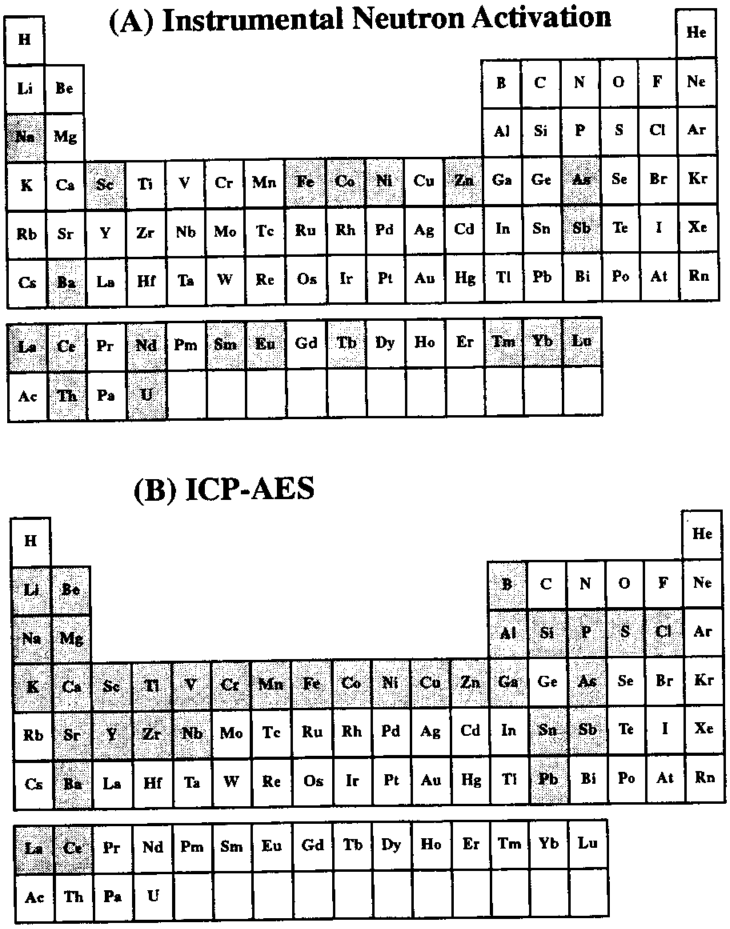


Figure 8 *(A) Elements routinely determined using INAA. (B) Elements routinely determined by ICP-AES. Based on information in Potts (1987) and references cited in the text.*

ICP-AES

ICP-AES or inductively coupled plasma - atomic emission spectrometry is becoming the technique of choice in commercial labs and in many academic institutions. The technique makes use of a high temperature inductively coupled plasma and with simultaneous detectors, can produce high quality major and trace element data in a very short period of time (20 to 60 elements in 2-3 minutes, Potts, 1987). The spectra emitted in ICP-AES are not simple, but are becoming much better understood, and are free of the degree of chemical interferences found in atomic absorption spectrometry (AAS). The range of elements, accuracy and precision of ICP-AES is similar to that found using XRF; however, unlike trace elements analysis using XRF, the samples must be dissolved before analysis. The need to dissolve the sample increases the cost, preparation time, possibilities of contamination and incomplete dissolution and solution stability/concentration problems. With the addition of a chemical separation stage, the REE elements can be determined using ICP-AES, with an accuracy and precision comparable to that of INAA or better (Potts, 1987; Roelandts, 1988; Watkins and Nolan, 1990). In general, for labs which are used to doing a lot of wet chemistry, ICP-AES has replaced AAS and is an alternative to INAA and XRF. Detection limits are given in Table 5 and the range of elements determined with no chemical separation is shown in Figure 8B.

ICP-MS (solution and laser)

Inductively coupled plasma - mass spectrometry couples the high temperature plasma of the ICP to the rapid scanning, high sensitivity and good resolution capabilities of a quadrupole mass spectrometer. The technique can produce high quality data on a wide range of elements, using a variety of sample weights (0.1 to 100 mg). Isotope ratios can be measured using ICP-MS, with sufficient precision for certain U-Pb dating (and other isotope applications) and allow for isotope dilution as a method to determine element concentration. ICP-MS is becoming the method of choice in many geochemical facilities, replacing INAA, RNAA, and XRF for trace element determinations. ICP-MS is not without difficulties, including problems with matrix, drift, interferences, memory and background; problem areas that are often interrelated (Jenner *et al.*, 1990; Longerich *et al.*, 1990). Nonetheless, this technique has proven itself capable of matching isotope dilution thermal ionization mass spectrometry and spark source mass spectrometry in terms of accuracy and precision at low trace element concentrations (Jenner *et al.*, 1990; Jochum and Jenner, 1994; Jochum *et al.*, 1994).

Sample dissolution for the ICP-MS is usually done by acid decomposition using HF and HNO_3 (Jenner *et al.*, 1990). The solution ICP-MS technique described produced data on 28 elements with 26 of these having precision and accuracy better than 3-7%. Longerich *et al.* (1990) describe sample dissolution using a sodium peroxide sinter technique, which produces data for all the REE, plus Zr, Hf, Ta, Nb, Y and Th. Combining sample separation techniques with ICP-MS allows the determination of precious metals at levels comparable to those obtainable by RNAA, and makes this a useful technique for studying ore deposits and doing petrogenetic research (Jackson *et al.*, 1990). Elements commonly analysed, and some detection levels using the sodium peroxide (Na_2O_2) sinter and HF-HNO_3 acid digestion methods, are given in Table 5 and illustrated in Figure 9. Precision and accuracy are illustrated in Figure 10. Elements determined in the precious metal technique, plus detection limits and examples are illustrated in Figure 11.

An alternative method of introducing the sample into the ICP-MS is by laser ablation of glasses or minerals (laser ablation microprobe - ICP-MS or LAM-ICP-MS; Jackson *et al.*, 1992; Fedorowich *et al.*, 1993; Jenner *et al.*, 1993). LAM-ICP-MS offers an increasingly viable new method for whole rock analysis, since melting the sample without a flux produces an uncontaminated, homogeneous glass. Detection limits in LAM-ICP-MS depend largely on the size

Table 5 - Routine elements and their detection limits for ICP and INAA (in ppm).

	La	**Ce**	**Pr**	**Nd**	**Sm**	**Eu**	**Gd**	**Tb**	**Dy**	**Ho**	**Er**	**Tm**	**Yb**	**Lu**
ICP-AES	7 (10)	15 (8.5)	40 (145)	30 (22)	15 (34)	2 (12)	5 (8.5)	80 (740)	15 (20)	15 (91)	15 (31)	2 (27)	1 (2)	0.4 (5.5)
ICP-MSs	0.01	0.01	0.01	0.04	0.03	0.01	0.03	.006	0.02	.006	0.02	0.07	0.02	.006
ICP-MSsi	0.17	0.30	0.03	0.14	0.07	0.02	0.07	0.02	0.10	0.02	0.04	0.01	0.03	.006
INAA -pl	5	2.1		4.6	0.1	0.05	4.6	0.09		1.7		0.34	0.14	0.10
INAA-cx	0.5 (0.7)	1.5 (0.9)		15 (3.5)	(0.2)	0.05 (0.3)	(7.7)	0.17 (0.8)		(10)		(4.6)	0.34 (0.3)	0.07 (1)
	Nb	**Ta**	**Zr**	**Hf**	**Th**	**U**	**Pb**	**Rb**	**Sr**	**Y**	**Sc**	**Co**	**V**	
ICP-AES	10 (14)	10 (350)	6 (0.5)	6 (19)	30 (353)	80 (3800)	20 (0.2)		2 (0.1)	2 (0.4)	2 (0.2)	2 (.02)	4 (.03)	
ICP-MSs	0.02 (.03)	.004 (0.1)	0.05	0.02 (.06)	0.01 (.12)	0.01 (0.5)	0.07	0.12 (0.2)	0.20 (.01)	0.01	2			
INAA		0.07 (1.8)	100	0.20 (0.7)	0.2 (2.4)	0.05		10			0.03	0.14		

ICP-AES - from Potts (1987). 6 sigma detection limits.

ICP-MSs - from Jenner et. al (1990) acid digestion. 3 sigma detection limits. ICP-MSsi - from Longerich et al. (1990) sinter digestion. 3 sigma detection limits.

INAA - pl (planar detector) or -cx (coaxial detector) from Potts (1987). 6 sigma detection limits.

Detection limits for INAA are the best possible ones in the data shown by Potts (1987).

Numbers in brackets are primitive mantle normalized values (using values from Sun and McDonough (1989) or Taylor and McLennan (1985)).

of the ablation pit, with a 10X increase in the pit diameter giving 2 orders of magnitude improvement in detection limits (Fig. 12A). Coupled to a high sensitivity mass spectrometer, LAM-ICP-MS produces data for samples as depleted as komatiites with acceptable precision and accuracy (Fig. 12B). For higher level samples, the precision and accuracy are comparable to the best solution ICP-MS data. A distinct advantage of LAM-ICP-MS is that not introducing the sample as a solution removes the question of solution stability, and memory effects in the ICP-MS are radically reduced. These last two factors are often the source of major problems in solution ICP-MS for elements like Th and the HFSE.

ANALYTICAL STRATEGIES AND PRACTICAL DATA EVALUATION

Integrating data from different techniques

No single analytical technique will provide a geochemist with all the elements of routine geochemical interest. Therefore it will be necessary to integrate data from a variety of different techniques. What techniques are used will depend on a variety of factors including: funding available; problem to be addressed and end use of the data; amount of sample; the timeframe within which the analyses are needed; and the required levels of detection, accuracy and precision. Integrating data from different techniques requires knowledge of which elements are determined best by each technique and some knowledge of the choices available. Integrating the data can be an exacting experience, and often highlights the problems with various analytical techniques: at the same time it is a worthwhile learning experience.

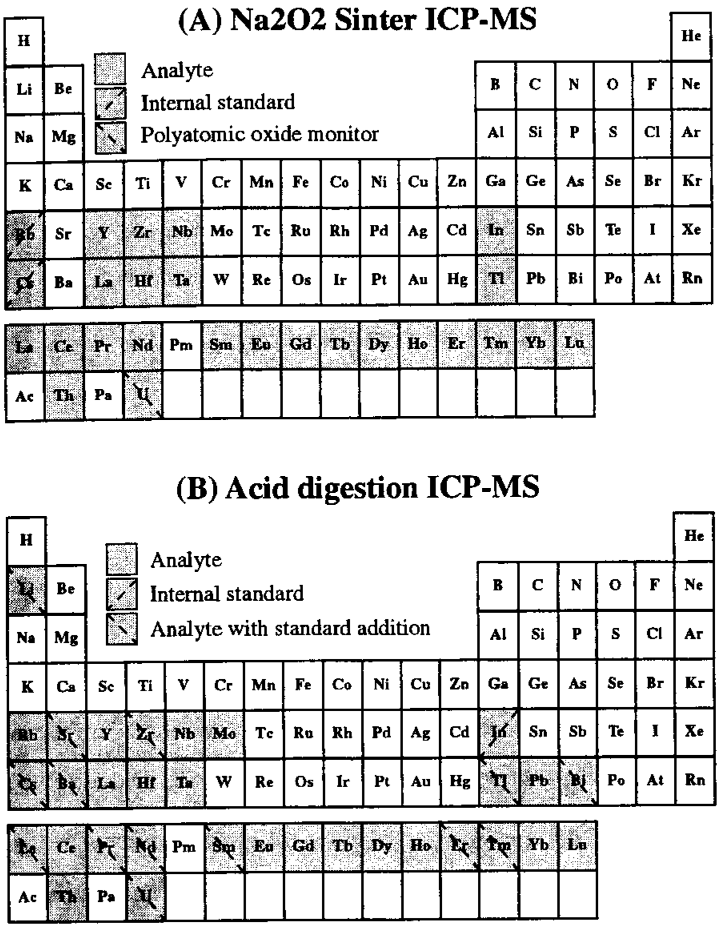


Figure 9 *(A) Elements determined using ICP-MS and a sample dissolution using a sodium peroxide sinter technique. Based on Longerich et al. (1990). (B) Elements determined using ICP-MS and an HF/HNO$_3$ acid dissolution technique. Based on Jenner et al. (1990).*

To address the question of integrating data I will use an example based on the situation at Memorial University, where a variety of XRF and ICP-MS techniques are routinely used. Given unlimited time and funds, and assuming a large amount of an unaltered, modern basalt, the methods I would choose for the different elements are listed in Table 6. Thorium, Hf, Ta and the REE could come from either acid digestion ICP-MS or sinter dissolution ICP-MS. However, there would be no advantage in using the sinter technique on this type of rock, so everything could come from the acid digestion ICP-MS analysis. PGEs would have to be obtained using the fire assay ICP-MS technique. These techniques would require a combined total of ~20 grams of sample, probably take at least 2 months to obtain, with a cost on the order of $150 to $200.

If the rock in question was an altered basalt, but everything else was the same - I would forego the acid digestion ICP-MS and do a sinter ICP-MS. The elements I would lose by doing this are probably mobile and of no primary, petrogenetic significance. I would also consider, foregoing the major elements by XRF fusion, and simply use the XRF pressed powder data, which are adequate for most elements - given that I will not calculate a norm on this rock, nor use the K and Na in classifying it. These two decisions would save about $50, and might speed up the data acquisition.If the PGEs were not required, removing these would significantly speed up the analysis time and lower the cost by another $50-$75. For pressed pellet XRF and sinter ICP-MS

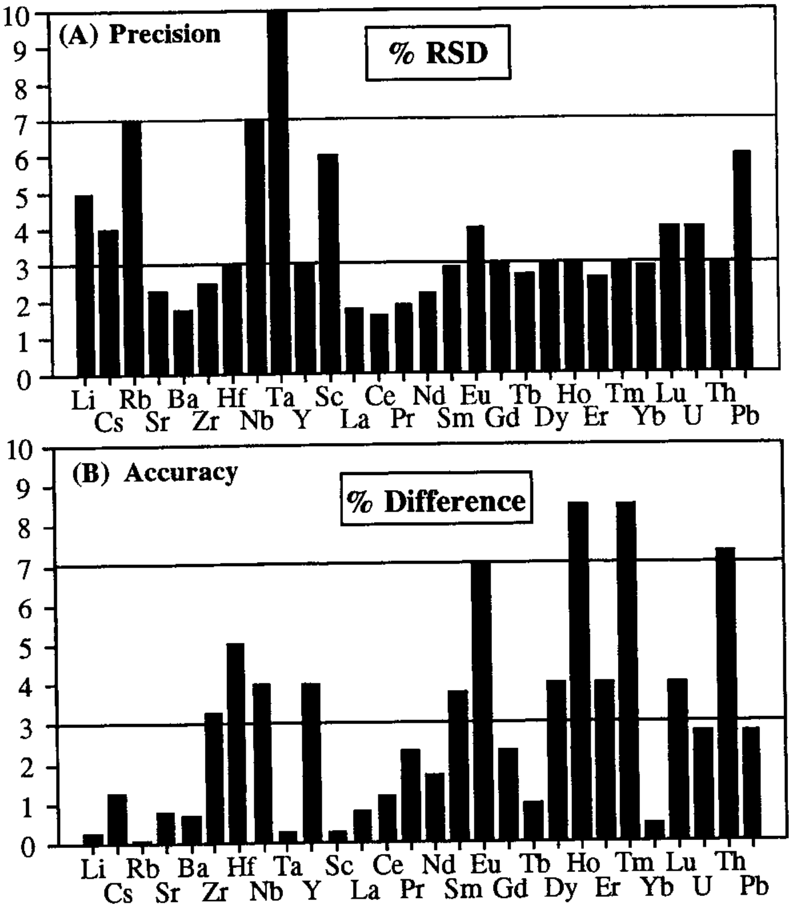


Figure 10 *Precision (RSD) and and Accuracy (% difference) for selected elements in IGRM, determined using the acid digestion ICP-MS technique decribed in Jenner et al. (1990).*

only 6 grams of sample would be necessary, and the analysis could be completed in under two weeks in a best case scenario. For small samples (<1 gram), either altered or fresh, solution ICP-MS would give the widest range of trace elements. An alternative would be to prepare a glass in a furnace or strip heater and use LAM-ICP-MS, and microprobe work to obtain the major elements (needed for internal calibration).

Purchase of all analyses from outside labs increases the range of choices. ICP-AES could serve as the most cost effective way to obtain the major elements and a selection of trace elements. INAA would provide a useful selection of the REE and provide Th, Hf and Ta data. Given the low cost of acquiring XRF pressed powder trace element data, it would be advisable to obtain this data, since Rb is not obtained by either INAA or ICP-AES. Depending on the sample, XRF would also provide good Nb and Zr data to compare with the INAA Hf and Ta. ICP-AES may provide Zr data, but Nb may be questionable. There is enough overlap between ICP-AES and XRF pressed pellet to evaluate the potential for dissolution problems. A combination of ICP-AES, XRF pressed pellet and ICP-MS would also provide good coverage of the elements, with lower detection limits and more accuracy and precision for many of the trace elements determined by INAA. For example, if either boninites or samples with the abundances found in the USGS IGRM basalt BIR-1 were in the suite, INAA would not provide adequate determination for Th, Ta and some of the REE. To convince yourself of this, compare the primitive mantle normalized abundances of the 6 sigma detection limits (*1.66 to reach LOQ) for INAA in Table 5 with the primitive mantle normalized abundances illustrated on Figure 13.

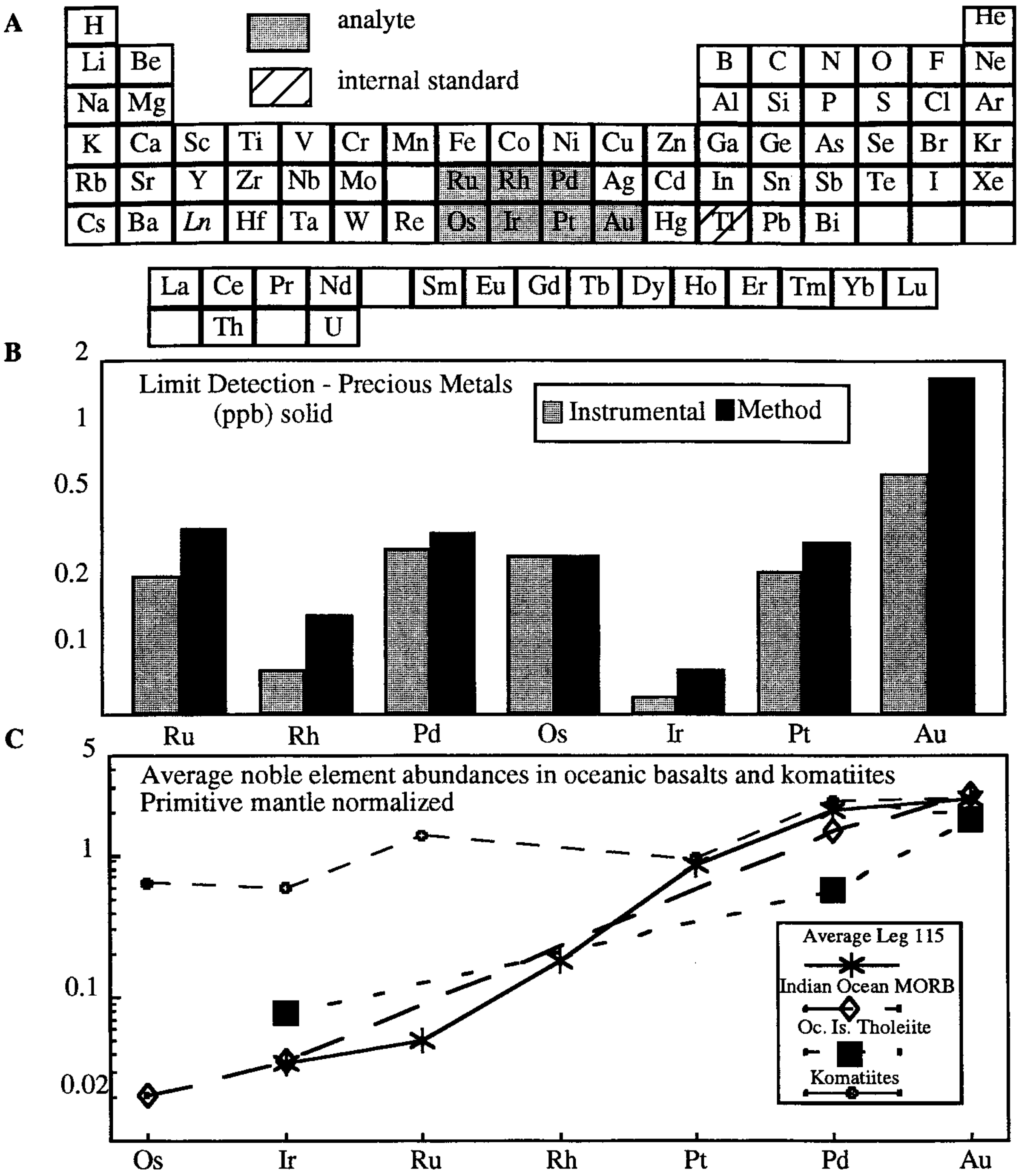


Figure 11 *ICP-MS precious metals technique (A) elements determined; (B) limits of detection; (C) examples of samples analysed and the primitive mantle normalized patterns. After Jackson et al. (1990). See text for discussion of MLD and ILD*

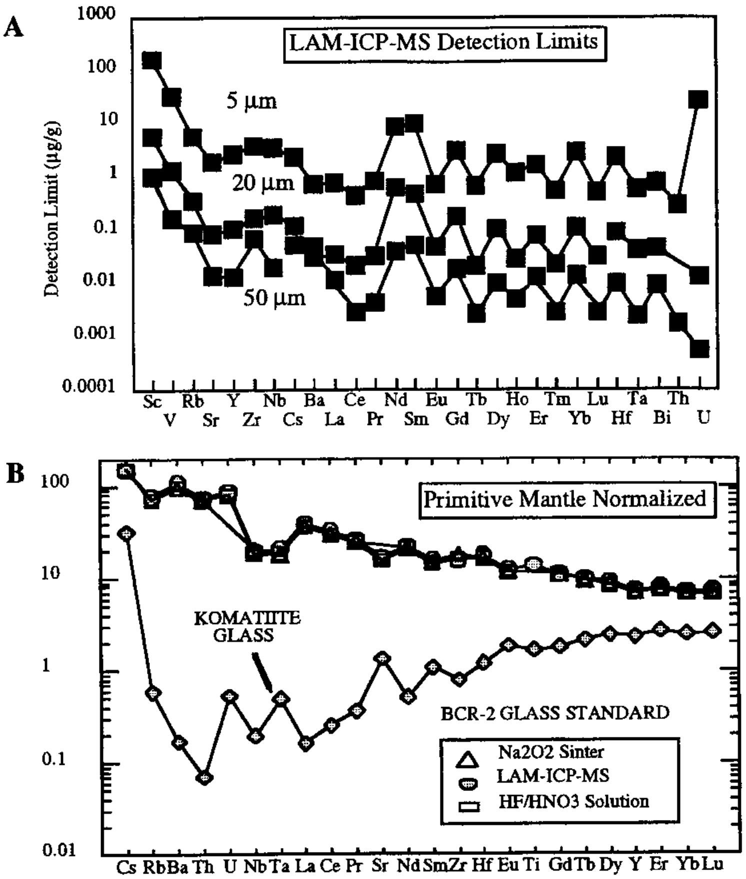


Figure 12 *(A) Detection limits of the LAM-ICP-MS procedure used at Memorial University. Note the change in detection limits as a function of ablation pit size. (B) Results obtained on the LAM-ICP-MS on the new USGS IGRM BCR-2 and a komatiite glass standard provided by K. Jochum. Comparison of results for the sinter and acid dissolution techniques (see Figs. 9 & 10) on BCR-2 also shown.*

Table 6 *Preferred method for each element in basalt which can be determined at Memorial University using XRF and ICP-MS techniques. See text for assumptions used, and how cost, time and rocktype can change the choice of preferred method. Elements common to both pressed pellet XRF and acid digestion ICP-MS allow evaluation of the need for sinter ICP-MS.*

PREFERRED METHOD	ELEMENT
Fused disc XRF	Na, Mg, Al, Si, P
Pressed pellet XRF	Fe, Mn, K, Ca, Sc, Ti, V, Cr, Ni, Cu, Zn, Ga, As, Rb, Sr, Y, Zr, Nb, S, Cl,
Acid digestion ICP-MS	Th, Pb, Ba, Cs, U, Hf, REE, (Rb, Sr, Y, Zr, Nb,)
Pressed pellet XRF - Acid Digestion ICP-MS overlap	Rb, Sr, Y, Zr, Nb (Pb, Ba, Ce, Th, U)
Fire Assay ICP-MS	Ru, Rh, Pd, Os, Ir, Pt, Au

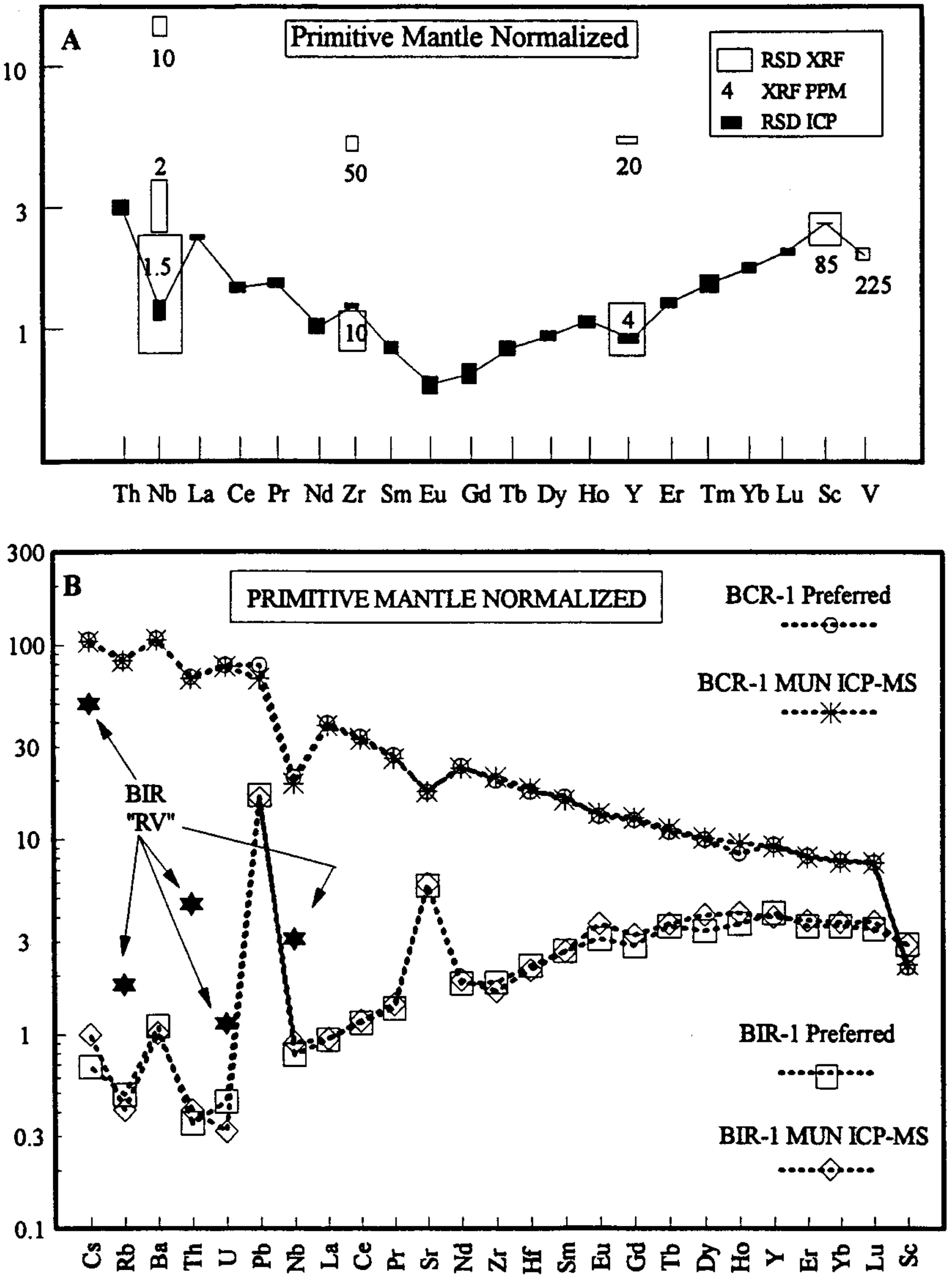


Figure 13 *Primitive mantle normalized plots of (A) boninite and (B) USGS IGRM BCR-1 and BIR-1. In (A), boninite was chosen to compare precision of XRF and ICP-MS in a sample characterized by low abundances of alteration resistent elements. Open boxes with concentration levels in ppm, illustrate precision for the XRF and its variations with concentration. In (B) preferred values for BCR-1 and BIR-1 are compared with results obtained from acid dissolution. ICP-MS technique decribed by Jenner et al. (1990). RV - values from a variety of techniques, but primarily spark source mas spectrometry, other ICP-MS and NAA (see Jenner et al., 1994). Compare normalized concentration levels with those reported in Table 5. Boninite is an unpublished analysis.*

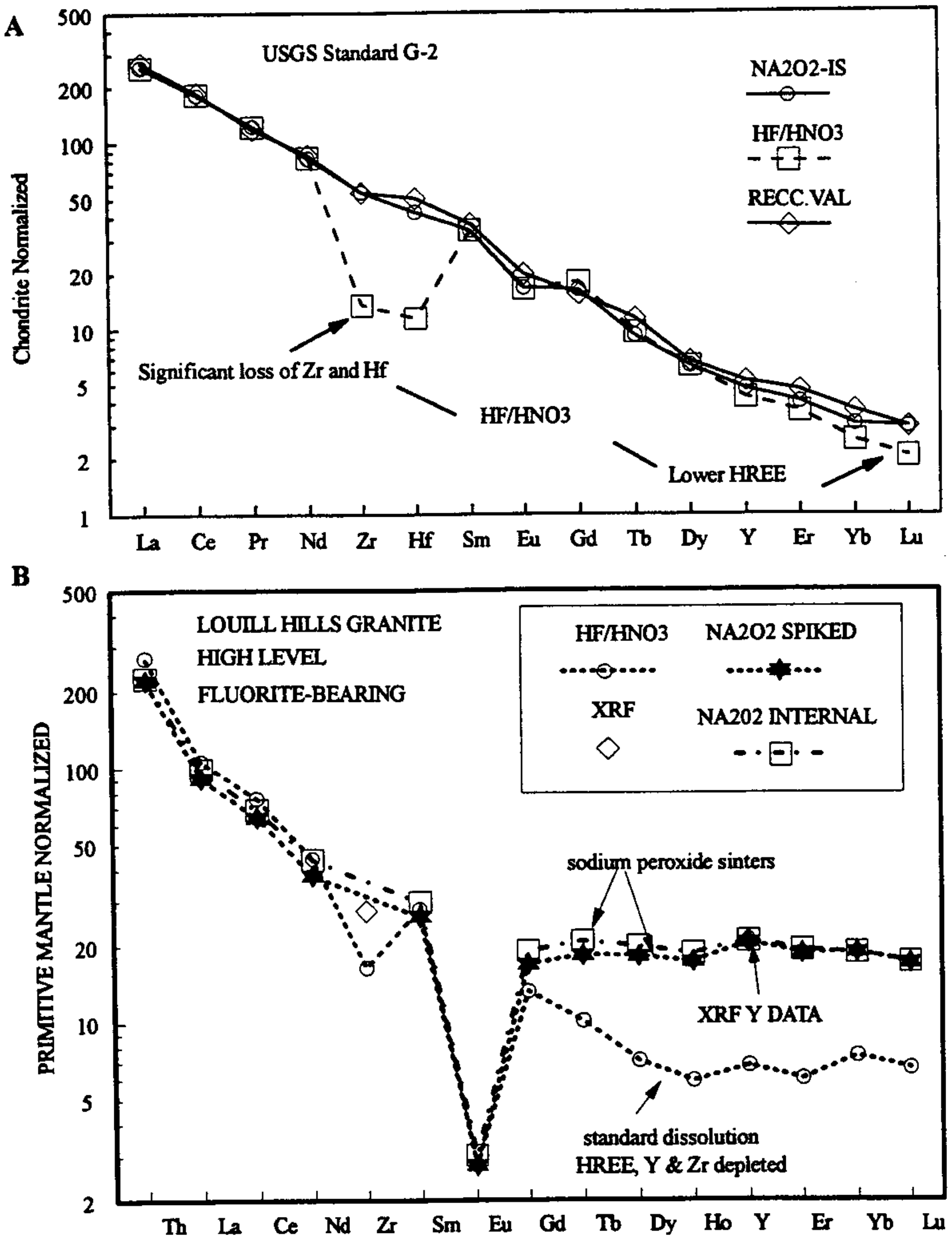


Figure 14 *Primitive mantle normalized plots of (A) USGS IGRM G2 - granite and (B) the Louill Hills granite (an unknown) illustrating incomplete dissolution using acid digestion. Comparison with data aquired using ICP-MS with another dissolution technique (sinter) and/or XRF pressed powder data is shown, to illustrate how to identify problems in analytical data.*

Trouble Shooting

One of the advantages in combining data from different techniques, especially if this involves comparing different dissolution techniques (acid digestion *versus* flux or sinter) and/or results from a purely instrumental technique, is the ability to identify analytical problems. Figure 14A shows the results obtained on the USGS IGRM granite G2 for acid digestion (HF/HNO_3) ICP-MS and sinter ICP-MS (Longerich *et al.*, 1990). Compared to the recommended values for Zr and Hf (reflecting XRF pressed pellet and INAA, respectively) the values for acid digestion are significantly lower, and Y and the HREE are somewhat lower. However, the sinter ICP-MS results are comparable to the recommended values. This suggests that the acid digestion procedure failed to completely dissolve the sample, probably by leaving behind zircon. Figure 14B shows an example obtained during analysis of an unknown fluorite-bearing granite. Comparison of the XRF pressed pellet data and the acid digestion ICP-MS data showed a serious discrepancy between the Y values obtained in the two techniques, with the ICP-MS data being 1/3 of that by XRF. Sodium peroxide sinter analyses of the same granite, using 2 different calibration techniques, showed that the XRF data were correct and that the acid dissolution procedure had failed to completely dissolve the sample, probably leaving substantial amounts of fluorite behind. In addition to illustrating the value of comparing different analytical techniques, these figures also illustrate the utility of using normalized plots, where elements of similar geochemical behaviour are plotted together, in evaluating data quality.

Examples like those illustrated in Figure 14, lead to an analytical protocol in which XRF results are required for all samples that undergo ICP-MS analysis. The results are compared and if differences exist outside the stated analytical uncertainty, the sample is reanalysed by both techniques. If a discrepancy continues to exist, an alternative sample preparation technique for the ICP-MS is adopted.

Analytical discrepancies between methods are not restricted to granites. There have been heated discussions in the literature concerning the abundance of HFSE in ultramafics and some USGS standards, *i.e.*, BIR-1 (Jochum *et al.*, 1994 and references therein). These arguments are not simply analytical ones, since significantly different petrogenetic processes have been implied based on small differences in HFSE, and the presence or absence of anomalies in these elements relative to the surrounding REE and Th. Large differences between recommended values for BIR-1, based on compiled values, versus selected data for techniques with much better detection limits, accuracy and precision have also occurred and are highlighted in Figure 13B (see also Jochum and Jenner, 1994). These arguments highlight the need for the geochemist and users of geochemical data to be aware of detection limits and calibration techniques when data are being evaluated (Jochum and Jenner, 1994). These arguments again illustrate the usefulness of normalized plots or knowledge of predictable element ratios (such as Nb/Ta ~16 and Zr/Hf ~35-40) in assessing analytical data. The Nb/Ta ratio in the BIR-1 recommended values was >30, and this combined with the odd behaviour of Nb relative to Th and La (Fig. 13B) - should have raised the possibility of analytical problems (see also Jochum *et al.*, 1990). Use of this same information indicates that a problem may exist with the Nb and Ta data for the komatiite in Figure 12B. The Nb/Ta ratio in this sample is ~6 and the normalized abundance of Ta is higher than that of Nb. At this stage it is not clear where the problem lies, since INAA Ta in this sample agrees with the ICP-MS Ta, and this looks like the anomalous element.

CONCLUSIONS

Trace element geochemistry is an important tool for research geochemists, geologists and exploration geologists. To use trace element data in geologic problem solving, it is necessary for the end-user to have at least some familiarity with the analytical techniques, their limitations and how the quality of the data can be assessed. It is also important to be aware of element behaviour, both to evaluate data quality and to make sure that primary geochemical signatures are being identified. For most geologists working on altered volcanic rocks, it is necessary to acquire quality analytical data on Th, Nb (or Ta), Y, Zr (or Hf), La, Ce, Nd, Sm, Eu, Gd, Dy, Er, Yb, Lu. To do this it is recommended that at least 2 analytical techniques be used, even if one is capable of giving all the elements of interest. XRF is good for Nb, Zr and Y, but detection limits for Nb can be limiting. INAA is useful for Ta, Hf, Th and many REE, but again detection limits need to be looked at closely. To be of use in identifying arc/non-arc signatures in depleted basalts and arc rocks, Nb should have a 3 sigma detection limit (LOD) of ~1 ppm or better. Using the Nb/Ta ratio of 16, this means that Ta needs to have a LOD of 0.06 ppm. Similarly, to identify the arc/non-arc signature Th needs to be quantifiable (LOQ) in the concentration range of 0.085 to 0.85 ppm. ICP-MS is probably the most useful all round technique for the elements of interest, and LAM-ICP-MS may be the technique used in future. At present ICP-MS usually involves putting the sample into solution, either by acid digestion or a flux/sinter. However, potential dissolution problems and other analytical problems do exist and the user is advised to have data from at least XRF to ensure good data quality. ICP-AES may also fulfill the role of XRF data, but cannot replace either INAA or ICP-MS data, unless a separation is done to concentrate the elements.

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