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A PRACTICAL METHOD TO ENHANCE DISCOVERY IN GEOCHEMICAL DATA USING STATISTICALLY DERIVED RELATIVE VALUES (R), AND GEOLOGICALLY CONCEIVED DISCRIMINATION FACTORS (D)

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Contents

INTRODUCTION

A practical methodology that enhances discovery opportunities in the analysis of geochemical data is presented. The technique uses: (i) statistical identification of anomalous populations, (ii) simple renumbering of anomalous and background populations so that the obtained relative values (**R**-values) are additive, (iii) the addition of **R**-values to form geologically meaningful discrimination factors (**D**-factors), (iv) the direct application of **D**-factors to the interpretation of complicated, multi-element data sets, and (v) the location of mineral deposits and rock types based on geologically determined multi-element **D**-factors built from **R**-values.

Relative factors (**R**) are determined visually from log-probability plots and stem-leaf plots. A bimodal, log-normal population generally is assumed and values for each element are assigned **R**-values as follows: **1** = equal or below the median, **3** = above median to mixed population, **5** = mixed population, **7** = anomalous population immediately above mixed population, **9** = strongly anomalous population, and **11** = rare outlier with markedly anomalous concentrations. Because geochemical elements are changed to numbers with genetic population significance, those that occur in disparate amounts can be combined without the overshadowing of one element by another. For example, lead with an anomalous concentration of 100 ppm (say, **R** = 9) can be combined with zinc with an anomalous concentration of 2,500 ppm (say, **R** = 7) giving an **R**-value average of 8

that is not overshadowed by the relatively higher zinc concentration. Given chemically related elements the average of the **R**-values is probably more robust than any single element. Specifically, K and Rb correlate closely and the combination of the two using averaged **R**-values is stronger than either element by itself.

Discrimination factors (**D**-factors) are the sum of the **R**-factors divided by the number of R-factors summed. Examples are **D**-factors for precious metal deposits (**DPrec**, i.e. Au & Ag focused) and mafic rocks (**DMafc**), where: **DPrec** = (**R**Ba + **R**Cu + **R**Ag + **R**Au + **R**Hg + **R**Tl + **R**P + **R**As + **R**Sb + **R**Bi + **R**S + **R**Se + **R**Te)/13, and **DMafc** = (**R**Mg + **R**Sc + **R**Y + **R**Ti + **R**V + **R**Nb + **R**Cr + **R**Fe + **R**Co + **R**Ni)/10. In both these cases the associated **R**-values are for elements that provide a geological-association-description of precious metal deposits or mafic rocks. Because completeness of geochemical data sets vary, **D**-formulas must be modified with respect to the elements that are available. Generally, a **D**-factor of 4 or above represents values that are almost certainly statistically anomalous. The break between background and anomalous values is generally clear on distribution plots, such as a stem-leaf plots.

This methodology, a "geologists' factor analysis", allows geological interpretation of data in a way that has genetic significance related to: (i) identification of anomalous populations, (ii) determining underlying rock types, and (iii) locating mineral deposits of specific types. The approach, which defines factors using geological knowledge and experience, complements traditional approaches that commonly determine relevant statistical factors that subsequently have to be interpreted geologically.

This practical method will aid in discovery of mineral deposits from large regional geochemical data sets and detailed geochemical soil grids. It also provides zoning vectors in deposit-scale geochemical data from drill holes, etc.

Example applications of **R**- and **D**-values to lake sediment data will be presented.

Additional organizational and analytical comments are in Appendices.

RELATIVE VALUES (R) FOR NORMALIZING GEOCHEMICAL DATA

Relative factors (**R**) are determined visually from probability plots and stem-leaf plots. Two populations (anomalous and background) are assumed, although

commonly a third population might be determinable. This bimodal population (anomalous and background) generally is assumed in calculating R-values. The R-values, estimated mainly from log-probability plots and stem-leaf plots, are as follows: **1** = Lower Background Population that is equal or below the third quartile or upper hinge, **3** = Upper Background Population that is above upper hinge to mixed population, **5** = Mixed Population (generally includes the inflection point), **7** = Clearly Anomalous Population immediately above mixed population, **9** = Highly Anomalous Population, and **11** = Outlier with markedly anomalous concentrations.

Note that that arithmetic-probablility plots are almost always invalid, because geochemical data is typically log-normal. This means that most statistical procedures that are based on a single log-normal are invalid. This includes—although they are very useful—commonly used "box-plots"; just be aware that the Tukey definitions of outside values are arbitrary and are based on single population statistics.

Starting with a log-normal probability plot one must pick an inflection point that basically divides the "background population" from the "anomalous population". This anomalous population might sometimes include two anomalous populations. The pick of the upper threshold for **R** = 1 is arbitrary. The object is to assign a "1" to background "junk" to get it out of the way. Commonly, the upper quartile or 75 percentile is appropriate. Sometimes the median or lower quartile is more important. The point is to minimize the range of R = 3 between R = 1 and R = 5, and this will depend upon the proportion of the anomalous sample.

Figures 1 to 5 and Table 1, below, define the methodology for visually assigning **R**-values.
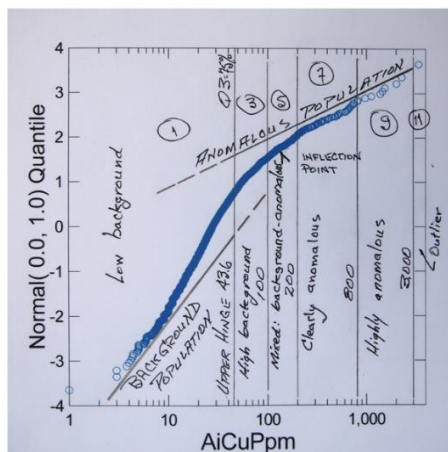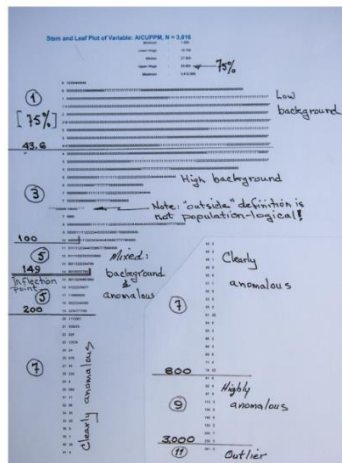
Figure 1. Visual definition of background and anomalous populations.
R <=1 is the 75 percentile. **R** = 5 surrounds the visually picked inflection point.
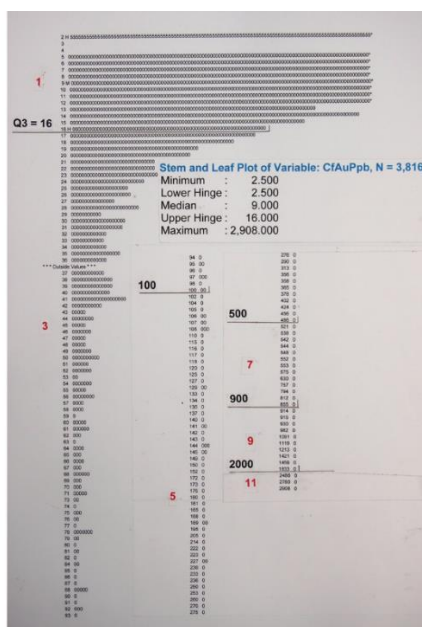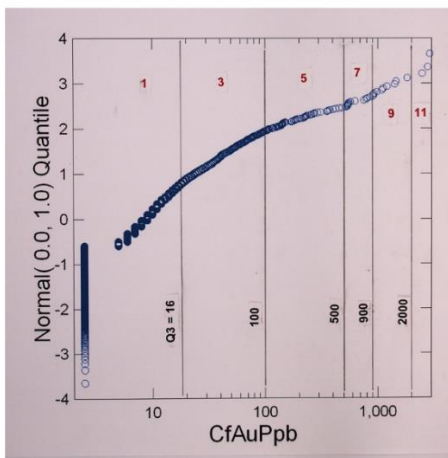
Figure 2. Assigning of R-values to gold data from 3,800 stream sediment samples.
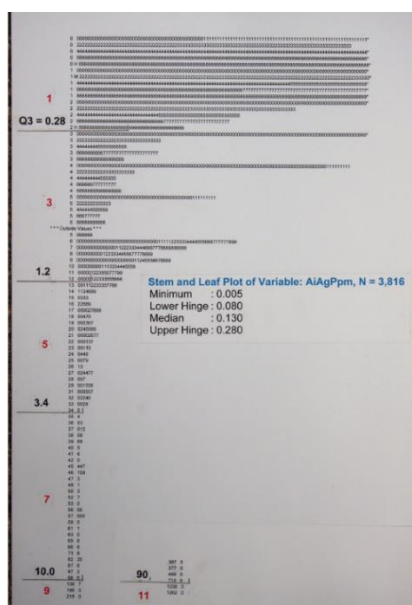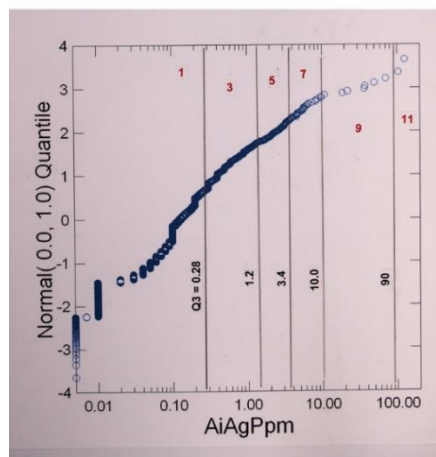
Figure 3. Assigning of R-values to silver data from 3,800 stream sediment samples.

Points at bottom left corner of the graph represent analyses below the detection limit.
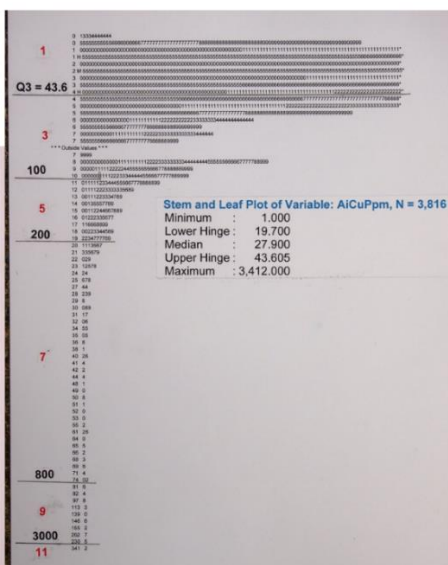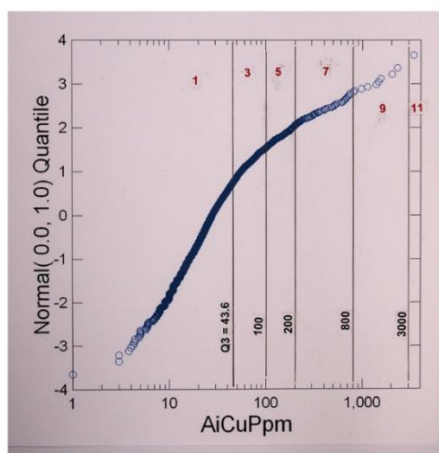
Figure 4. Assigning of R-values to copper data from 3,800 stream sediment samples.

Boundary between **R** = 3 and **R** = 5 is somewhat subjective. The kink at the boundary between **R** = 7 and **R** = 9 might indicate that **R** = 9 is a genetically

separate or second anomalous population distinct from the highly anomalous **R** = 9 population.
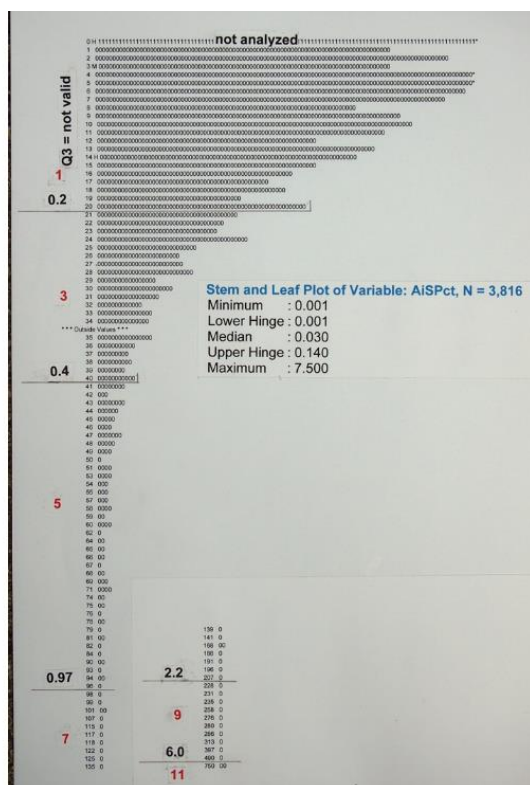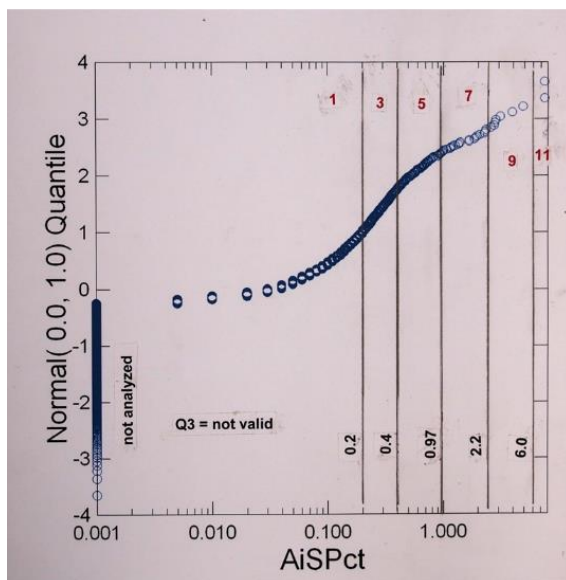
Figure 5. Assigning of R-values to sulfur data from partial stream sediment data set.

Points at bottom left corner of the log probablility graph represent samples not analyzed. Where there are significant numbers of not analyzed samples the data cannot be used in calculation of **D**-values; however, the **R**-values can be plotted to mark abundances where analyzed.

GEOLOGICALLY BASED GEOCHEMICAL DISCRIMINATION FACTORS (F) FOR GEOCHEMICAL IDENTIFICATION OF ROCK TYPES & MINERAL DEPOSITS (GEOLOGIST'S FACTOR ANALYSIS)

Discrimination factors (**D**) are like a geologist's factor analysis. Discrimination factors (**D**) are sums of Relative factors (**R**), as determined visually from log-probability plots and stem-leaf plots. A bimodal population (anomalous and background) generally is assumed in calculating these **R**-values (see above). Note the **D**-factors are the sum of the **R**-factors divided by the number of **R**-factors summed. Generally, an **F**-factor of 4 or above represents values that are almost certainly statistically anomalous; the anomalous number might be lower than 4 where there is an absence of anomalous **R**-values for some elements. The break between background and anomalous values is generally clear on a distribution plot, such as a stem-leaf plot.

The **D**- or **R**-factor numbers can be squared to give a wider range of values that might help emphasis of anomalous data in bubble plots; thus for example, a **D** = 1 remains 1, an **D** = 5 becomes 25, and an **D** = 10 becomes 100.

D-factors for common Rock Types and Major Types of Mineral Deposit are defined below. Element groups generally related by position in the Periodic Table are underlined. Italicized elements are elements that might be debateable for inclusion, which might depend upon area characteristics and district experiences. Consequently, it is anticipated that the groupings will be modified with experience and with specific deposit and area focus.

There are a number of guiding ideas to the system presented for deposit analysis below:

1. Given chemically related elements (often adjacent in Periodic Table columns) the average of these **R**-values is more robust than any single element. For example, K and Rb generally correlate closely and the combination of the two is considered to be more rigorous than either element by itself in indicating, in this case, overall "potassium characteristics".

2. In Periodic Table columns where there are long strings of elements related chemically, it is appropriate to divide them into light and heavy groups. Thus, Column One can be grouped: Li + Na, and K + Rb $\pm$ Cs, and Column Two can be grouped: Be + Mg, and Ca + Sr, and separately Ba (because of

common deposit association). The REE's are divided into light (La, Ce, Pr, Nd, Pm & Sm), mid-Europium (Eu—commonly unique +2 valence, Gd & Tb—four valence) and heavy (Dy, Ho, Er, Tm, Yb & Lu). Note that the saw-like abundance variation between adjacent REE elements is not important when **D**-values are used.

3. The idea of element associations for major classes of rocks should provide a chemical way of partitioning the data into separate geological groups. It could be, for example, that mafic units (andesite/basalts) have higher values in copper than felsic rocks. Anomalies of copper in the felsic rocks might be lost in the analysis if not looked at separately from the andesite/basalt rocks. The copper might present itself in Probabilty Plots in such instances as three populations. Three populations are difficult to interpret, whereas division into only two populations, anomalous vs. background, is rapid and convenient, but not necessarily completely accurate. Partitioning into rock types (chemically or by observation) and/or Geological Terranes should lessen the problem of working with these three (or more) population distributions.

4. The use of multiple **R**-values for different elements in defining **D**-factors, and the identification of anomalous groups based on geological experience, allows broad trends within anomalous populations to be examined. The concept is to identify these trends as anomalous statistically, and not by some arbitrary percentile that has no genetic significance. Elements of specific interest can be plotted on top of these trends to pin-point areas of particular interest. For example, the Precious Metal Factor (**DPrec**—mainly for gold and silver) can be color-contoured to define general trends and gold and/or silver alone then can be plotted as bubble plots on top of the colored background to identify the most anomalous points.

Note that the **D**-formulas must be modified wrt the elements that are in the analytical set available.

D-FACTORS FOR ROCK AND FERRICRETE DESCRIMINATION

DCarb: Carbonate rock factor

DCarb = (**R**Mg + **R**Ca + **R**Sr + **R**Ba + **R**P + **R**BpH)/6

Note that **R**BpH = relative basic pH value.

DFect: Ferricrete (hydromorphic anomaly) factor

DFect = (**R**Fe + **R**Mn + **R**Co + **R**Ni + **R**P + **R**Zn + **R**Cd)/7

DFels: Felsic rock factor

DFels = (<u>**R**Na + **R**K + **R**Rb</u> + <u>**R**Zr + **R**Hf</u> + **R**Th + **R**U + <u>RGa + RGe</u> + <u>RNb + RTa</u>)/11

DMafc: Mafic rock factor

DMafc = (**R**Mg + <u>RSc + RY</u> + **R**Ti + <u>**R**V + RNb</u> + **R**Cr + **R**Fe + **R**Co + **R**Ni)/10

Note that plotting of CrPpm or **R**Cr or **Q**Cr on top of **D**Mafc should facilitate differentiation between andesite and basalt or ultramafic rocks.

DOrgn: Organic ooze (e.g. lake sediment ooze) or organic soil factor

DOrgn = (**R**Loi + **R**Mn + **R**ApH)/3

Note that **R**Loi = relative loss on ignition, and **R**ApH = relative acid pH value.

DShal: Shale basin rock factor

DShal = (<u>**R**V + RNb</u> + <u>**R**Al + RGa</u> + <u>RS + RSe</u>)/6

D-FACTORS FOR MINERAL DEPOSIT DISCRIMINATION

FZnPb = (PpmZn/PpmPb) to look at relative dispersion in geochem or zoning in deposits

D-Factors for Deposit Types

DBolv: Bolivia Ag-Sn-base metal deposit factor for Andes

DBolv = (<u>RV + RNb</u> + **R**Mo + **R**W + <u>**R**Cu + **R**Ag + **R**Au</u> + <u>**R**Zn + **R**Cd + RHg</u> + **R**B + <u>RGa</u> + <u>RGe</u> + **R**Sn + **R**Pb)/15

DCarl: Carlin deposit factor

DCarl = (<u>**R**Sr + **R**Ba</u> +**R**La + **R**U + <u>**R**Ag + **R**Au</u> + <u>**R**Zn + **R**Cd + RHg</u> + <u>**R**Ga + RIn + **R**Tl</u> + **R**P + <u>**R**As + **R**Sb + **R**Bi</u>+ **R**Te)/17

Note that most characteristic geochemical elements in Carlin deposits are: Au, As, Hg, Tl & Te. Those elements associated with Carlin deposits that are upwelling/black shale/SEDEX related are: U, P, La & Ga. Those elements associated with Carlin deposits that are basinal brine related are: Ba, Zn, U, Mo, V, Ni, Cu, Cd & Ag. Thalium is particularly important. It can have a +3 valence, in which case it acts like its associated group: B, Al, Ga & In. However, more common is a +1 valence where it has properties of K^{+1} and Ag^{+1}. It forms chloride

and sulfur complexes up to 200°C where TlCl^{0}, TlHS^{0}, Tl$_2$HS^{+} are probably important, because these are the complexes associated with gold/silver hydrothermal transport. Thalium is closely associated with K-based minerals, consequently, I suspect that thalium reflects magmatic fluids exsolved from late-differentiated intrusive, porphyry-type-like bodies at depth.

DCobl: Cobalt - Great Bear Lake – Chanarcillo Ag-Co-Ni deposit factor

DCobl = (**R**Ba + **R**Co + **R**Ni + **R**Cu + **R**Ag + **R**Au + *RZn* + *RCd* + **R**Hg + **R**Pb + **R**P + **R**As + **R**Sb + **R**Bi)/14

DCbhs: Carbonate hosted deposit factor

FCbhs = (**R**Ca + **R**Sr + **R**Ba + **R**Zn + **R**Cd + *RHg* + **R**Pb + **R**S + **R**Se + **R**F + **R**Fw + **R**BpHw)/12

Note that **R**Fw = relative value of fluorine in water, and **R**BpHw = relative basic pH in water.

DCrbt: Carbonatite deposit (REE & U-Th) factor

DCrbt = (**R**Mg + **R**Ca + **R**Sr + **R**Ba + **R**Y + **R**La + **R**Ce + **R**Th + **R**Pr+ **R**Nd + **R**U + **R**Sm + **R**Eu + **R**Gd + **R**Tb + **R**Dy + **R**Ho + **R**Er + **R**Tm + **R**Yb + **R**Lu+ **R**Nb+ **R**Ta + **R**Zr + **R**P + **R**F + **R**Fw)/27

Note that **R**Fw = relative value of fluorine in water.

DIocg: Iron oxide – copper – gold deposit factor

DIocg = (**R**Li + **R**Na + *RK + RRb* + *RCa + RSr* + *RSc* + **R**Y + **R**La + **R**Ce + **R**Th + **R**Nd + **R**U + **R**Zr + **R**Hf + **R**Fe + *RCo* + *RNi* + **R**Cu + *RAg* + **R**Au + **R**P + *RAs*)/23

DPegm, DPgcr: Pegmatite deposit & Pegmatite core ration factors

DPegm = (**R**Li + **R**Na + **R**K + **R**Rb + **R**Cs + **R**Be + **R**Sc + **R**Y + **R**La + **R**Zr + **R**Hf + **R**Ce + **R**Th + **R**Nd + **R**U + **R**Pm + **R**Sm + **R**Eu + **R**Gd + **R**Tb + **R**Nb + **R**Ta + **R**Mo + **R**W + **R**B + **R**Ga +**R**In + **R**Ge + **R**Sn + **R**P + **R**F + **R**Fw)/32

Note that **R**Fw = relative value of fluorine in water.

DPgcr = (**R**K + **R**Rb)/(**R**Sr + **R**Ba)

DPged: Platinum group deposit factor

DPged = (**R**Mg + *RSc* + **R**Ti + **R**V + **R**Fe + **R**Co + **R**Ni + **R**Pd + **R**Pt + **R**Cu + **R**Au + **R**As)/12

DPorp, DPcor, DPrim, DPcrm: Porphyry deposit, Porphyry core, Porphyry rim & Porphyry core-rim factors

DPorp = (**R**K + **R**Rb + **R**Cs + **R**Th + **R**U + **R**Mo + **R**W + **R**Re + **R**Cu + **R**Ag + **R**Au + **R**B + **R**S + **R**Se)/14

DPcor = [(**R**K + **R**Rb+ **R**Cs)/3]/[(**R**Sc + **R***Y* + **R**Ti + **R**Zr + **R**Hf + **R**Al)/6

Note core = potassic major elements / immobile elements, resulting high ratios are core-related .

DPrim = [(**R**Ca + **R**Sr + **R***Ba*)/3]/[(**R**Sc + **R***Y* + **R**Ti + **R**Zr + **R**Hf + **R**Al)/6]

Note rim = propylitic major elements / immobile elements, resulting high ratios are rim-related.

DPcrm = [(**R**Mo + **R**W + **R**Cu + **R**Ag + **R**Au)/5]/[(**R**Zn + **R**Cd + **R**Pb)/3

Note core/rim = core metals / peripheral metals, resulting high ratios are core-related.

DPrec: Precious metal (Au, Ag) deposit factor

DPrec = (**R**Ba + **R**Cu + **R**Ag + **R**Au + **R**Hg + **R**Tl + **R**P + **R**As + **R**Sb + **R**Bi + **R**S + **R**Se + **R**Te)/13

DSedx: SEDEX deposit factor

DSedx = (**R**Sr + **R**Ba + **R**V + **R***Nb* + **R**Zn + **R**Cd + **R**Hg + **R***Ge + R**Sn* + **R**Pb + **R**P)/11

DSulf: Sulfide proximity

DSulf = (**R**Fe + **R***B + R**Al + R**Ga* + **R**S + **R**Se + **R**ApH)/7

Note that **R**ApH = relative acid pH.

DVolc: Volcanogenic deposit factor

DVolc = (**R**Sr + **R**Ba + **R**V + **R***Nb* + **R**Cu + **R**Ag + **R**Au + **R**Zn + **R**Cd + **R**Hg + **R***Ge + R**Sn* + **R**Pb + **R**P)/14

D-FACTORS FOR COMMONLY ASSOCIATED ELEMENTS

In addition to the **D**-factors for deposit types, above, it is useful to define **D**-factors simple and common element associations. This will allow focus to **D**-factors for deposits that might have low values because so many elements have been lumped together. It can also help in distinguishing the overlap among

different types of deposits, because of common element association. Some examples of commonly associated elements are:

DAsSb-Arsenic & Antimony
DAsSb = (**R**As + **R**Sb)/2 to use these pathfinders for precious metal deposits

DAuAg-Gold & Silver
DAuAg = (**R**Au + **R**Ag)/2 to focus on precious metal deposits

DCaSr-Calcium & Strontium
DCaSr = (**R**Ca + **R**Sr)/2 to mark more mafic or carbonate related rocks and deposits

DCoNi-Cobalt & Nickel
DCoNi = (**R**Co + **R**Ni)/2 to help locate ultramafic and mafic rocks and Cobalt-type deposits

DCuMo-Copper& Molybdenum
DCuMo = (**R**Cu + **R**Mo)/2 to focus on calc-alkalic porphyry deposits

DCrNi-Cromium & Nickel
DCrNi = (**R**Cr + **R**Ni)/2 to help identify mafic and ultramafic rocks and ultramafic – related ore deposits

DHgTl-Mercury & Thallium
DHgTl = (**R**Hg + **R**Tl)/2 to help identify mobile elements related to epithermal and Carlin-type deposits

DKRb-Potassium & Rubidium
DKRb = (**R**K + **R**Rb)/2 to focus on felsic rocks or potassic (K-rich) alteration

DLaCe-Lanthanum & Cerium
DLaCe = (**R**La + **R**Ce)/2 to help focus on rare earth and carbonatite deposits

DMoW-Molbdenum & Tungsten
DMoW = (**R**Mo + **R**W)/2 to help identify lithophile related deposits

DNbTa-Niobium & Tantalum
DNbTa = (**R**Nb + **R**Ta)/2 for "coltan" search with lithophile and/or pegmatitic tendencies

DPbZn-Lead & Zinc

DPbZn = (**R**Pb + **R**Zn)/2 to help focus search for carbonate-hosted, SEDEX and VMS deposits

DSnW-Tin & Tungsten

DSnW = (**R**Sn + **R**W)/2 to help identify lithophile related deposits and S-type granite – related deposits

DSSe-Sulfur & Selenium

DSSe = (**R**S + **R**Se)/2 to help source sulfides and sulfates

DThU-Thorium & Uranium

DThU = (**R**Th + **R**U)/2 to help focus on uranium mineralization, carbonatites and rare earth deposits

OTHER MEASURES THAT SHOULD BE SYSTEMATICALLY TABULATED WITH R-FACTORS

Q & M-Factors, e.g. QCu, MHg

Other measures that are helpful and can be tabulated with **R**-values include: **Q**-value = analysis divided by the first quartile or lower hinge, **M**-value = analysis divided by the median. Like **R**-values, these factors can be coded with these letters as prefixes, e.g. **Q**Cu, **M**Hg, etc.

Dividing each element analysis by the quartile, called here a **Q**-values (e.g. **Q**Cu, **Q**Ag, **Q**W, etc.), is particularly helpful because high values are emphasized. However, **Q**-values lose the genetic sense of whether or not the number is related to an anomalous or background population. Some elements will have very high **Q**-values; therefore, they are not additive because the very high numbers from a few elements will dominate summed values. However, these **Q**-values are particularly useful in stacked histograms along lines. In these stacked histograms the **R**-values and **Q**-values also can be both plotted so that variation and genetic type are discernable in one graph.

F-Factor Fractions (ratios), e.g. FRbSr, FNiCr

Linear Correlation = [xx] vs. relatively immobile elements [**R**Sc, *R*Y (need 4-acid digestion for Sc)] or [**R**Ti, **R**Zr (Ti is a good choice, because it is generally more abundant than Zr, and 4-acid digestion values are not reliable for Zr)] or [**R**Al, **R**Ga, **R**In, **R**Tl]. Since **R** = Relative Value, ratios can be expressed as **F**-factors = *f*ractions. Ratios might be more varied and sensitive if analytical values (e.g. Ppm)

are used, although **Q**-factors of the **F**-values might be helpful, and could be called **QF**-factors.

Some possibly useful **F**-factors:

FEuSm = (PpmEu/PpmSm) to look for +2 europium anomalies

FMgTi = (PpmMg/PpmTi)

FNiCr = (PpmNi/PpmCr) to help distinguish basalt and ultramafics from andesite

FRbSr = (PpmRb/PpmSr) to help distinguish felsic, or potasic, from mafic rocks, or propylitic, rocks

APPENDIX A. ASSAY COLUMN CODE NAMES

Analytical data sets vary in quality and methods analyzed. It is critical to keep track of different sample digestions and analytical methods. Geochemical reports commonly: (i) provide different numbers of elements analyzed, (ii) use variable digestions resulting in less reliability or poor detection of some elements (e.g. digestion of W, Sn and Zr can be problematic), and (iii) yield results that vary by analytical technique (e.g. W is not an easy element in which "accuracy" in analysis can be achieved). For this reason both Method of Analysis and Type of Digestion is assigned as a prefix to the name of every element. With this approach the presentation of analyses is compact and all pertinent background information is more easily retained.

The system presented, below, allows all of the above problematic factors, above, to be tracked. The method uses alternating upper and lower case prefixes and suffixes for ease of reading. Letters are close-spaced because some computer programs balk at divided headings. With a little familiarity the headings are easy to read and will appear on graphics providing more complete information to the viewer.

A1. SUFFIXES TO ELEMENT OR OXIDE ANALYZED DEFINE DIGESTION, TYPE OF ANALYSIS, CONCENTRATION & WEIGHT ANALYZED

One or More Letters for Chemical Symbol of Element or Oxide Reported
Cu, **Mo**, **W**, **CaO**, etc.

Followed by three-letter suffix after element or oxide for concentration (upper case letter, followed by two lower case letters)
Pct = percent, **Ppm** = ppm, **Ppb** = ppb, **Ppt** = ppt

Followed by One Letter Upper Case for Digestion
? = unknown, **A** = *a*qua regia, **B** = *b*orate fused disk, **C** = *c*upellation (fire assay with fused melt), **D** = *d*ilute aqua regia, **E** = *e*ncapsulated, **F** = *f*our acid, **H** = dilute 6m *H*Cl, **L** = *l*oose powder (-80 mesh), **P** = *p*ressed powder pellet, **T** = ace*t*ic acid, **W** = water, **Z** = mixed methods (see original certificates).

Followed by One Letter Lower Case for Type of Analysis
? = unknown, **a** = atomic absorption (AA—includes Au by MIBK), **b** = bottle roll CN, **c** = colorimetric, **d** = DNA = *d*elayed neutron counting, **f** = fire assay—aa or ICP-MS

finish (**g** = fire assay—*g*ravimetric), **i** = *I*CP-MS (**e** = ICP-*E*S), **l** = *l*eco, **n** = INNA = *in*strumental *n*eutron activation a*n*alysis, **p** = *p*otentiometric, **s** = *s*pecific ion, **u** = fl*u*orometric, **x** = XRF, **z** = best estimate from combined analyses (generally best value).

Followed by Number forWeight in Grams Analyzed

Weight is written as a number for grams digested/analyzed. For varied weights used, "Var" = variable is the suffix. If weight is unknown use an upper case question mark where "?" = unknown.

A2. EXAMPLES OF ELEMENT HEADINGS

All prefixes and suffix are close spaced, but are easily read because of divisions by upper and lower case letters. Examples are:

- **CuPpmAi0.5** = copper—parts per million—aqua-regia digestion—ICP-MS analysis—o.5 grams analyzed,
- **AuPpbAa5** = gold—parts per billion—aqua-regia digestion—atomic absorption following MIBK extraction—5 gram sample,
- **ZnPpmLx20** = zinc—parts per million—loose powder sample—XRF analysis—20 grams analyzed,
- **WPpmEn2** = tungsten—parts per million—encapsulated sample—INNA analysis—2 grams analyzed,
- **AlPctFi0.5** = aluminum—percent—four-acid digestion—ICP-MS analysis—0.5 grams analyzed,
- **PbPpmZzVar** = lead—parts per million—several analyses—best estimate (generally best value)—variable weight analyzed,
- **SnPpmEn2** = tin—parts per million—encapsulated sample—INNA analysis—2 grams analyzed, and
- **AuPptHi0.5** = gold—parts per trillion—dilute HCl digestion—ICP-MS analysis—0.5 grams analyzed.

APPENDIX B. CORRECTION (Cal) FOR CALICHE DILUTION IN SOIL SAMPLES

B.1. ASSUMPTIONS

Assumptions for fudging caliche-rich geochemical values assume:

1. All sulfur is in gypsum,
2. All calcium is in gypsum or in calcite,
3. All sodium is in NaCl-salt.

This of course is not true, because there are a number of minerals that will also contain these elements, e.g. sodium nitrate. However, the object is to make sure that the volume dilution from caliche-related minerals is mitigated. The derivation follows:

CALCITE (CaCO3 =molec wt 105)

1g of Ca would equal 105/40 = 2.6g of CaCO3

SALT (NaCl = molec wt 58)

1g of Na would equal 58/23 = 2.5g of NaCl

GYPSUM (CaSO4.2H2O = molec wt 172)

1g of S would equal172/32 = 5.4g of gypsum

1g of Ca would equal 172/40 = 4.3g of gypsum

Now 1%S yields 5.4% gypsum and 5.4 g of gypsum has 5.4/4.3 = 1.3 g of Ca

B2. CALCRETE CORRECTION FACTOR (Cal)

Cal = [(SPc*5.4) + [(CaPc-(1.3*SPc))*2.5] + (NaPc*2.50]/100

B3. ADJUSTED VALUES USING CORRECTION FACTOR (Cal)

Adjusted values, e.g. for CuPpm, would equal the original value plus original value times the correction factor. E.g. for copper (CuPpm) the adjusted value, CuCalPpm would be:

CuCalPpm = [CuPpm + (Cal*CuPpm)]

APPENDIX C: PROTOCOL FOR pH MEASUREMENTS ON SOIL & SELECDTIVE LEACH BULK SAMPLES

The following is after information from Dave Heberlein.

C1. Equipment needed:

- pH meter with spare batteries (it is useful to have a backup meter on hand).

- Distilled or deionized water. Carry about 1 gallon per day. Use consistent brand or batch throughout the sampling campaign.

- Tap water, about 1 gallon per day

- Wash bottles for the two kinds of water, clearly marked to differentiate them.

- Calibration/ buffer solutions: pH 4.00 and 7.00 for acid environments; 7.00 and 10.00 for alkaline environments (use NIST standard solutions).

- Two 100-ml beakers with markings every 20 ml or better

- Stainless steel spatulas for stirring

- 10% HCl in a bottle that allows dispensing by the drop. Same thing usually carried by field geologists for identifying carbonates. Mix up a batch at the start of the program sufficient to carry you through the entire program. Use the same acid batch and same dropper bottle throughout the program.

C2. Sampling

For the pH measurement, do two samples: One at the surface (top mm) and one at 10 cm depth. Take two pH measurements at each, one with plain distilled or deionized water, and one after adding one drop of 10% HCl.

C3. Procedure

IMPORTANT! Standardize everything you can. Whatever you do, do it with regimented consistency. This is crucial!

Determination of pH is as follows:

1. At the beginning of the day, hydrate the meter by soaking the electrode in tap water for 30 minutes, then calibrate your pH meter with two buffers (pH 7.00 and either 10.00 or 4.00 depending on the environment). Between samples, keep a piece of paper towel saturated with tap water in the meter cap to keep the hydration level adequate.

2. For the surface sample, take several (about 10 to 15) small scoops, a few ml each, from several locations (e.g. from a 5 m in diameter circle). For each small scoop, pick up only the topmost sediment grains, skimming the top 1 mm with the edge of your trowel. Choose sand, silt, clay size, avoid gravel to

cobble size. Avoid animal burrow spoils that may bring caliche from depth. Pick up a total of about 40 ml and place it directly into the beaker.

3.   Stir the dry sample in the beaker, letting the coarser grains float to the top and finer grains settle. Scrape out the coarser grains with the spatula till you are down to exactly 20 ml, well-settled. Add deionized water and bring up the volume to 40 ml. Stir until all grains are wet and the clay size fraction is suspended, forming an uniform slurry.

4.   Insert the pH meter. Stir it around a little in the solution. Keep the electrode suspended in the liquid fraction; that is, do not let the electrode rest on the sediment. After 20 seconds record the pH (note that the values may not have stabilized by this time. Do not wait for stabilization). Record the value. Remove the pH meter, rinse it with tap water.

5.   Add one drop of 10% HCl to the solution. It is important that the size of the drop be uniform from one sample to the next. You may want to get the dropper bottle flowing properly by letting a few drops go onto the ground first until it is clear that sequential drops are of consistent size. Alternatively you could use a calibrated auto-pipette to dispense a precise amount of acid. If you sense an inconsistent drop size because of a bubble or wind or two drops falling, start over with a fresh sample. Stir thoroughly to allow acid-sediment interaction and reinsert the pH meter. Take the pH reading after 20 seconds following the same procedure used for the non-acidified sample. Note that pH may initially drop, then pause, then start to climb again as soil carbonates start reacting. Be consistent. Remove the pH meter, rinse it with tap water.

6.   For the 10-cm sample, use the scraped-bare area from which the bulk sample was taken (in a salt lake an auger sample from 10cm can be used). There is no need to integrate from as large an area as the surface sample used. (it would be nice, but is impractical). Sediment at that depth is commonly a bit damp, so winnowing out coarser material (as in step 3) does not work too well. Instead, put a few (around 5) ml of deionized water into the second beaker and add sediment to the 20 ml level, then add deionized water to bring the volume to 40 ml. Stir to form slurry.

7.   Read pH, same as step 4.

8.   Add one drop 10% HCl and read pH, same as step 5

9.   Make notes on the grain size distribution in the two beakers, for instance "high clay silty fine sand," or "low clay poorly sorted fine to medium sand," etc. Also record any unusual aspect of the soil or sample site, particularly if you are seeing anomalous values. Parameters to record systematically include: sample colour, texture, presence of carbonates or sulphates, characteristics of the sample site, nearby disturbance etc.

10.   Empty the beakers. Rinse the beakers and stirring spatulas with tap water, and dry with a (reasonably) clean towel. Cap the pH meter. Secure everything for transport to the next site.

APPENDIX D: PORTABLE XRF RELIABILITY

D1. GeoFile 2013-06.

Determination of major and trace element concentrations in Canadian sediment reference samples using portable energy-dispersive X-ray fluorescence (ED-XRF) spectrometer and implications for geochemical surveys. By A.S. Rukhlov. BC GEOLOGICAL SURVEY

Concentrations of 24 elements (S, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, As, Se, Rb, Sr, Zr, Mo, Sn, Cs, Ba, W, Pb, Th, U) were determined in 12 Canadian sediment reference samples using a portable energy-dispersive X-ray fluorescence (ED-XRF) spectrometer and Compton scatter radiation for matrix correction. The reference samples represent till, stream sediments, and lake sediments that have been widely used as quality-control standards in geochemical surveys A total of 11 international certified reference materials were analyzed to calibrate the ED-XRF spectrometer using error-weighted least-squares regression of the measured and the recommended data. The ED-XRF results are consistent with the published data within the uncertainties for V, Cr, Ni, Cu, Zn, As, Rb, Sr, Zr, Mo, W, and Pb in the reference sediment samples. Magnitude of bias for S, Ca, K and Ba concentrations appears to correlate with high loss-on-ignition (mainly H2O) contents (up to 44 wt. %) in these samples. Concentrations of Ti, Mn and Fe in all samples show small but significant systematic error, whereas Cs, Ba, Th and U concentrations may reflect spectral interferences in some samples. Concentrations of Co, Ag, Cd, Sb, Au, and Hg in the analyzed reference samples are all below the detection levels of the portable ED-XRF. Precision of the ED-XRF analyses is better than 6% (average 1.6%) at the 2σ level for most of the trace elements, except Cs The portable ED-XRF spectrometer, with Compton scatter normalization for matrix correction, can be used for precise and accurate analysis of till, stream- or lake-sediment samples in mineral exploration, geochemical mapping and environmental monitoring. Compared to other analytical methods, the technique is fast, non-destructive, and requires less sample preparation.

Reference:
http://www.emprgov.bc.ca/Mining/Geoscience/PublicationsCatalogue/GeoFiles/Pages/2013-06.aspx

APPENDIX E: APPLICATION OF GOLDSCHMIDT'S RULES

E1. GOLDSCMIDT'S RULES

Rules for ion substitution in minerals is determined by:

1) **Similar size**: Ionic radii must differ by less than 15%.

2) **Charge** can differ by 1 unit if electrical neutrality is maintained by coupled substitution.

e.g. Ca, Al for Na, Si in plagioclase

If charges of ions differ by > 1 unit, substitution is slight.

3) **Ionic potential**:

the ratio of ionic charge (electronic charges) to radius (Å)

Measure of the density of electrical charge on the surface of ion, and determines the strength of the electrostatic bond that will form. (ionic potential of K^+ is less than As^{5+})

When two different cations can occupy a particular position in a crystal, the ion with higher ionic potential forms a stronger bond with surrounding anions and is preferentially substituted.

4) **Electronegativity:** Substitution may be limited, even when the size & charge criteria are satisfied, when the competing ions have different electronegativities and form bonds of different character.

e.g., little substitution between Na^+ (ionic bonds) & Cu^+ (covalent/ metallic bonds), even though IR are nearly identical

E2. IMPLICATIONS OF GOLDSCHMID'S RULES

The amount of substitution in ionic crystals depends on:

1) concentration of ions in melt or solution in which crystals are growing

2) temperature

3) compatibility of bonds and coordination numbers

E3. PERIODIC TABLE (see www.ptable.com)

E4. IONIC RADIUS

CPK Atomic-Ionic Radii
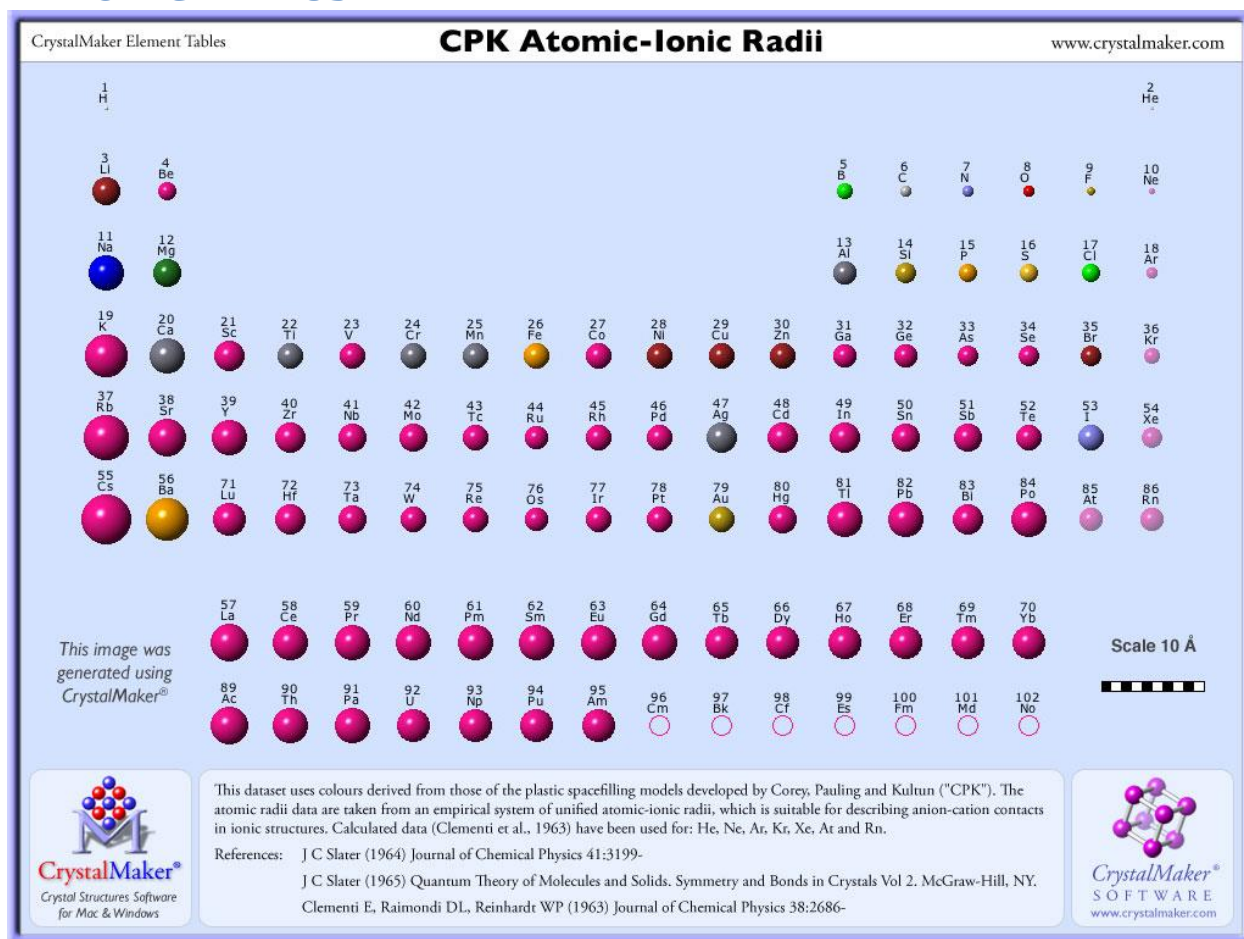
- For a given element the ionic radius decreases with increasing positive charge and increases with increasing negative charge.
  e.g. $r(Pb^{4-}) = 2.15$ Å, $r(Pb^0) = 1.74$ Å, $r(Pb^{2+}) = 1.18$ Å, $r(Pb^{4+}) = 0.78$ Å
- Radii of elements in the same vertical column of the Periodic Table with identical ionic charge increase in size with increasing atomic number.
  e.g. $r(Li^{1+}) = 0.74$ Å, $r(Na^{1+}) = 1.02$ Å, $r(K^{1+}) = 1.38$ Å, $r(Rb^{1+}) = 1.49$ Å, $r(Cs^{1+}) = 1.70$ Å
- Radii of ions with the same electronic configuration, but with increasing positive charge, decrease in size.
  e.g. $1s^2\ 2s^2\ 2p^6$, $r(O^{2-}) = 1.40$ Å, $r(F^{1-}) = 1.33$ Å, $r(Na^{1+}) = 1.02$ Å, $r(Mg^{2+}) = 0.72$ Å, $r(Al^{3+}) = 0.53$ Å, $r(Si^{4+}) = 0.40$ Å
- Anions are usually larger than cations
  e.g. $r(O^{2-}) = 1.40$ Å, $r(Cl^{1-}) = 1.81$ Å

Ionic Radius and Group

As you move down a group in the periodic table, additional layers of electrons are being added, which naturally causes the ionic radius to increase as you move down the periodic table.

Ionic Radius and Period

As you move across a row of period of the periodic table, the ionic radius decreases for metals forming cations, as the metals lose their outer electron orbitals. The ionic radius increases for nonmetals as the effective nuclear charge decreases due to the number of electrons exceeding the number of protons.

Ionic Radius and Atomic Radius

The ionic radius is different from the atomic radius of an element. Positive ions are smaller than their uncharged atoms. Negative ions are larger than their atoms.

Crystallization and Incompatible Elements

Ions become sorted by size and charge during crystallization of a magma. Ions not fitting into major rock forming minerals are incompatible and are enriched in residual magma. Incompatible elements include:

K^+, Rb^+, Cs^+, Be^{2+}?, Sr^{2+}, Ba^{2+}, Th^{4+}, REU, Zr^{4+}, Hf^{4+}, Nb^{5+}, Ta^{5+}, B^{3+}?, Al^{3+}?