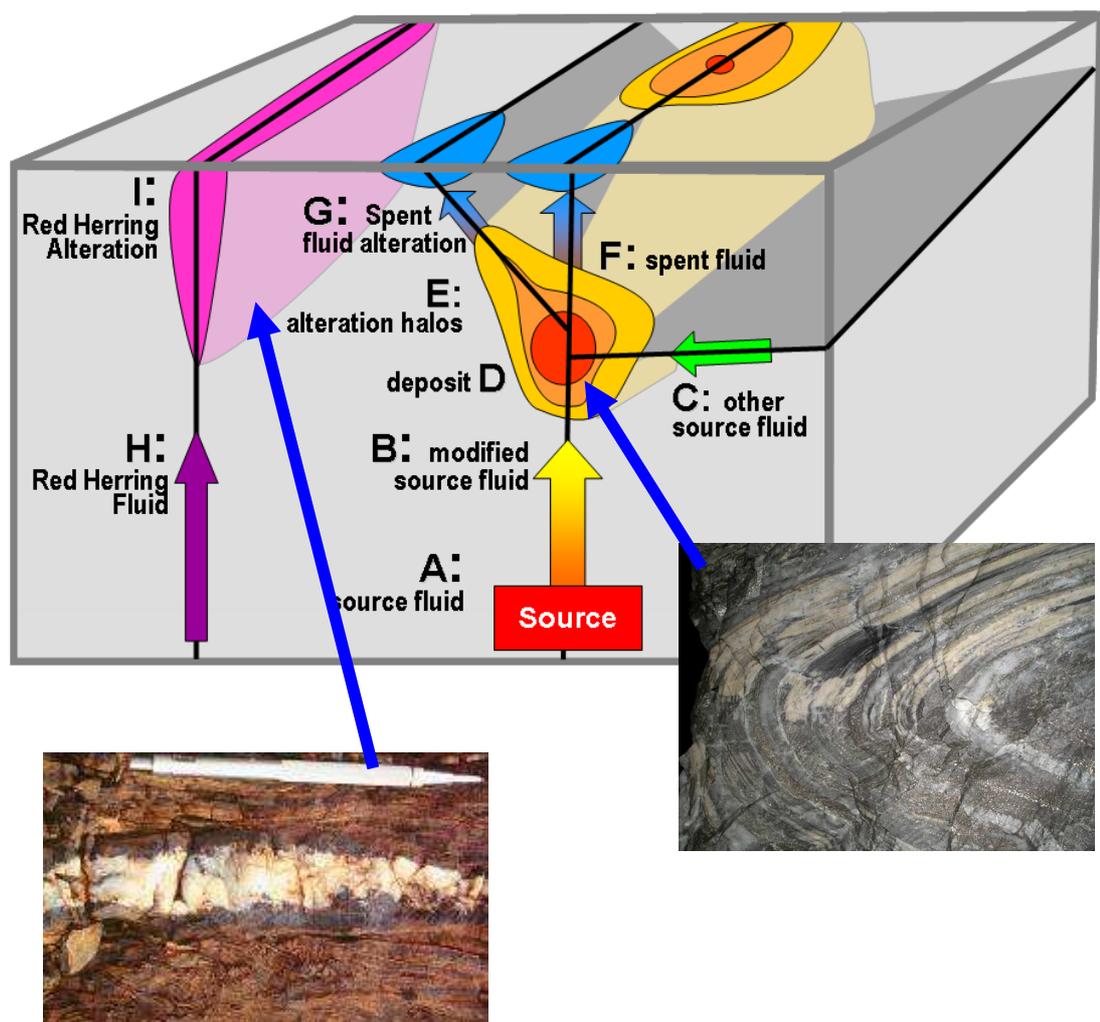


HOW TO CONNECT ROCK OBSERVATIONS AND GEOCHEMISTRY TO UNDERSTAND LARGE HYDROTHERMAL ORE SYSTEMS

Part 2: Starting with geochemistry and sampling Including some practical exercise examples

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This module forms part of a series on use of veins, alteration, geochemistry and structures to identify which features can be used to recognise 'vectors' to potential sites of mineralization. The principles were developed through field- and laboratory observations and short course development for undergraduate & postgraduate students at several Australian Universities, as well as open-audience and site-specific industry workshops (e.g. Vancouver Roundup, PDAC, Predictive Mineral Discovery CRC, SEG workshops). The principles are most suited to alteration and vein recognition in deformed, metamorphic rocks, but have application elsewhere.



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INTRODUCTION

Sampling for geochemical reasons is commonly quick, relatively cheap, and a fairly standard procedure in operating mines, usually aimed at orebody delineation or sterilization. Less common is the use of stable isotopes, because they have little relationship to ore production issues, and have not been used successfully as an independent exploration tool anywhere in the world (at least to my knowledge), unlike, for example, geochemistry or geophysics. However, the basic principles discussed below for geochemical sampling also apply to stable isotopes, and stable isotopes are a very useful tool for determining the source of fluid, and the nature of fluid/rock interaction, especially if used in combination with other techniques. More on this later.

During exploration or regional exploration-related mapping, it is relatively easy to justify a short-term stream-sediment or rapid field-rock-chip sampling program, but more difficult to justify a detailed geochemical sampling program that takes up a lot of your (and other peoples') time. This section deals with some sampling strategies that can save you time and money, as well as improve your ability to then be able to interpret the results. With the introduction and increasing use of portable XRF devices, this field is set to expand in routine drill core logging and exploration targeting.

PRECURSOR ROCK VARIABILITY

Issues of scale are important to address with regard to the primary lithological variation in your area, relative to a) the scale of the alteration systems, and b) the scale (and time, cost etc.) of your sampling program. For example, think of the ways we could geochemically sample the pattern depicted in Figure 1:

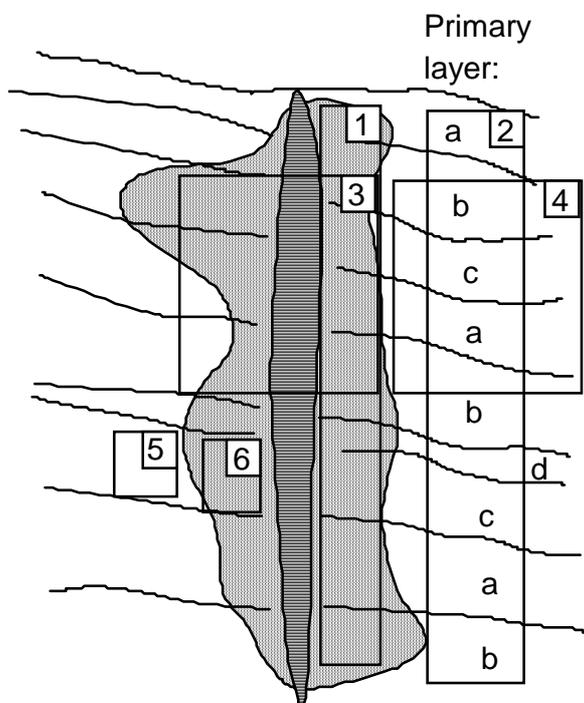


Figure 1: Possible sampling strategies around a vein and its alteration zone

Sample 1 vs Sample 2: This looks ideal, as it samples the widest possible variability of precursor rocks, and thus would best smooth out the effects of the primary variations. However, what if the primary chemical variations are actually more extreme than those (on average) for the change from the precursor average to the altered rock average? And look at the shape of the boxes - it may not be that easy to sample this way. And the vein is not accounted for - there may be mineralization etc. important in the vein, that is not displayed elsewhere in the system.

Sample 3 vs Sample 4: OK, better shaped samples so perhaps easier to deal with physically, and this time it

incorporates the vein. But not all the layer types are covered - what if layer D is particularly

unusual? And sample 3 has a decent chunk of unaltered rock in it, from layers A and B, but not C, will this affect the results?

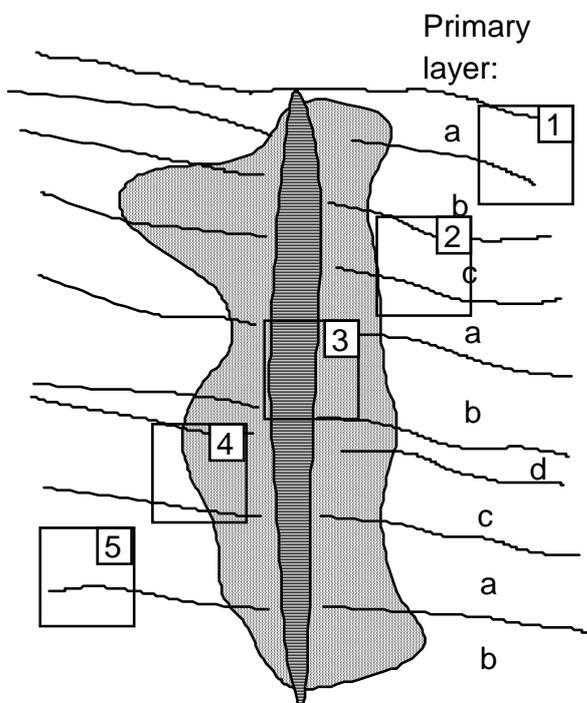
Sample 5 vs Sample 6. This is a very tightly constrained comparison, for it won't involve any averaging problems - you have sampled at the scale of the layer, and so you know exactly what is involved in the conversion of layer C to its altered equivalent. But you don't know what's happened to the other layers, and you still haven't analysed the vein.

Time, money, urgency etc.

So a properly constrained rock/geochemical sampling program requires a bit of thought at the start - and you may not have time to deal with it in this way - perhaps you're not doing the sampling yourself, and you have to give directions to someone else? The key elements are precursor (or less altered), altered equivalent, and infill. If these three components can be separately sampled, or grouped in a way that makes sense (e.g. samples 3 & 4), then you will achieve far more with the two (or three) samples than you could possibly have done with just one (especially if that one is sampled randomly).

Dealing with random samples

In many situations, you will have to deal with a geochemical data set that is essentially collected randomly. Obviously, there will be some primary aim behind the sampling, but perhaps such data is collected off mine benches that are moving down so fast that the engineers, let alone the geologists, are having trouble keeping up with the production rates. Or, because you have just joined a project, you have to deal with a previous dataset, and you don't have access, or time, to examine the previous sampling program or drill logging. In



comparison to the above situation where you can consider a sampling strategy, you have little choice here, and have to try to interpret the available data. Relative to our previous (strategic) sampling, perhaps your sampling program looks more like this (above):

Figure 2: Some random samples collected across an alteration zone around a vein - compare Fig. 1

This is a very common problem for drill core assay data. In this case, we can still use the data, but it will be a lot harder to interpret - at least at this sort of scale - than the previous data set. Consistent patterns can arise from doing such sampling, but at what expense? Samples 1, 2, & 5 will be less iron-rich than 3 and 4, but the variability of 1, 2 & 5 might mask the fact that sample 4 is actually partly within the alteration zone. What if your sample set didn't include sample 3?

Grainsize of the sample

In the same way that precursor bedding variability can influence sampling strategies, so can grainsize. There are statistical procedures that can be used to advise you on how to do this, but assuming that you don't want to waste any more time than necessary, your sampling size must account for the inhomogeneity within the sample. As an example, consider a rare-earth-bearing pegmatite and a surrounding tourmaline-rich alteration halo:

The problem here is that most of the trace elements are contained in the "accessory" minerals, so a geochemically useful XRF/ICPMS sample would account for this by sampling a large amount of rock. This "geochemically useful" sample size may not equate to something that is physically realistic in some pegmatites, because of the very large grainsize. Basalts, microgranites, massive siltstones - no problem. Pegmatites, irregularly layered turbidites, BIFs, breccias, conglomerates - these are a problem because of the likely size and shape of your sample relative to where the compositional heterogeneity lies in your sample.

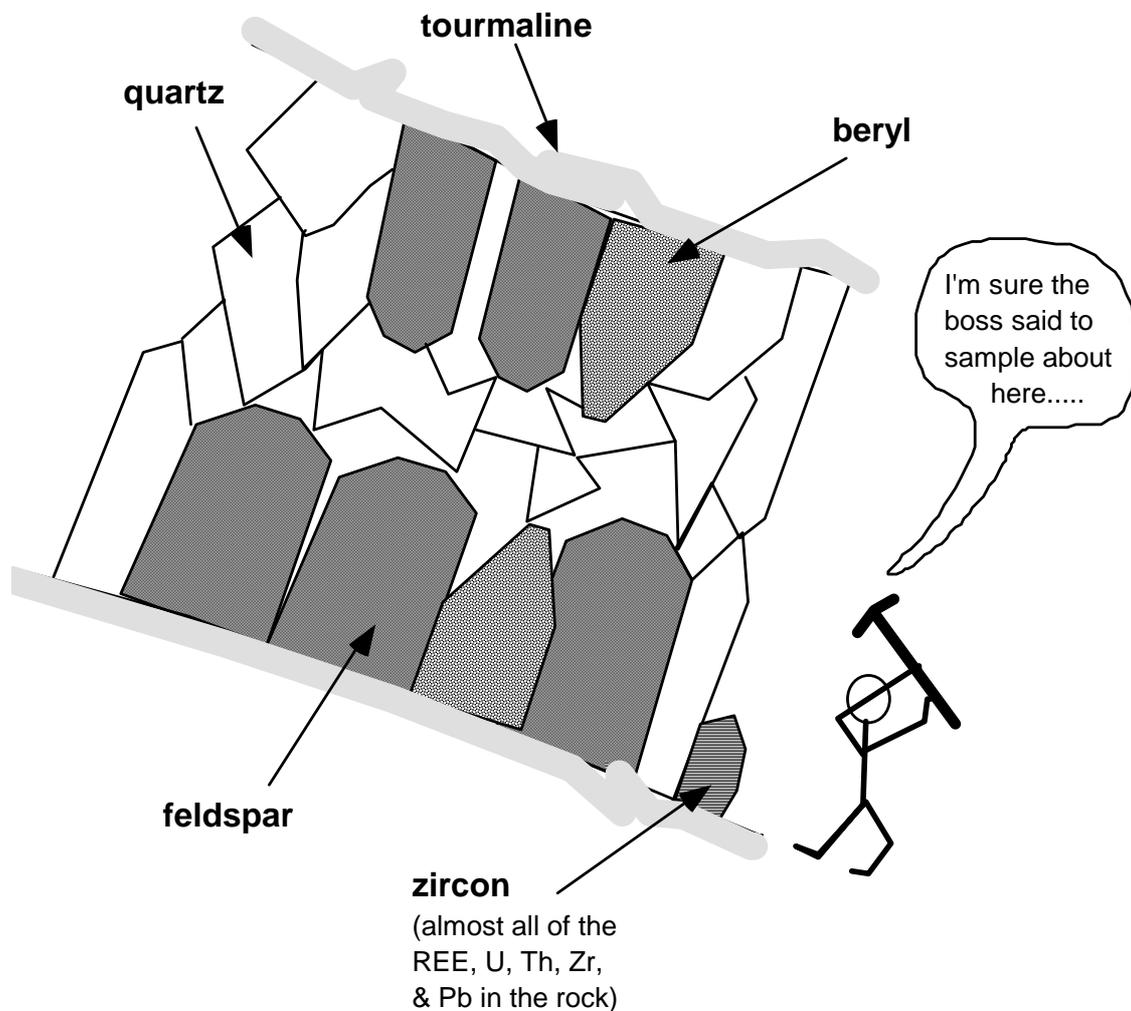


Figure 3: Problems associated with geochemical sampling are very apparent in coarse grained rocks

ELEMENT MOBILITY - THE KEY TO UNDERSTANDING GEOCHEMICAL CHANGES

The best way you can deal with a “random” data set, and the best way you can interpret a well-constrained dataset, is by appreciation of the relative mobility of elements during hydrothermal alteration. This allows you to deal with the range of sampling scenarios presented above, to a greater or lesser degree. For an almost completely random dataset, this approach allows you to sort out what geochemical changes are due to rock-type variations, and what are due to fluid-induced alteration. For a well-constrained geochemical data set, this allows you to determine exactly what elements have moved (and to what degree) in response to the passage of ore forming fluids.

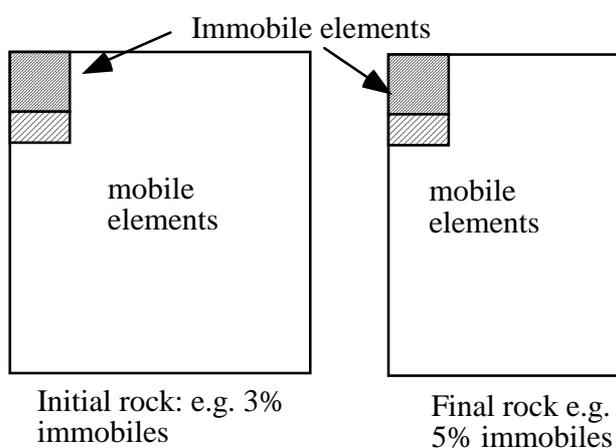


Figure 4: The right-hand rock has not gained 2% immobiles, rather it has lost 40% silica! 40% silica loss in this scenario will give an apparent enrichment in immobile elements, that can be simply checked by looking at the immobile element ratios, which should be constant if the two sampled rocks have the same precursor.

For most hydrothermal systems, the order of relative “mobility” of the elements is approximately as follows, starting with the least mobile first: {Zr, Ti} < {Y, Ga, Al} < {Ce, La, Mg} < {Mn, Cr, Fe, Sc, Cu, Zn, Pb, V, Ni} < {Si, Na, K, Ca, Rb, Sr, Ba}. As the amount or salinity of fluid

increases, then these elements all become increasingly mobile. Variations in the order occur with extremely unusual fluids, e.g. some carbonic fluids can mobilize Zr and Ti to a greater degree than Mg, for example, and Si can be near-immobile in CO₂-rich systems. In general Zr through Al are commonly treated as “immobiles”, although during intense alteration Al may become moderately mobile (e.g. advanced argillic alteration in epithermal systems), and Mg, Ti and Y can sometimes misbehave too. In seafloor hydrothermal systems, Mg may be quite mobile (e.g. Ca/Mg exchange is common). This range can also be treated as a scale of mobility: under fixed conditions of fluid salinity and amount, Zr and Ti may be mobile at very small scales (e.g. mm) whereas Na, K etc. are mobile at large scales (e.g. 100 - 1000m). For the purposes of comparing two (unaltered vs. altered) rocks, then, those elements which have a mobility at < cm scale are “immobile” whereas those that are mobile at > cm scale are effectively mobile, for a given alteration system. Again you can appreciate the scale-dependence of these comments (See Short course Module 1).

Manipulating geochemical data by inspection of immobile element ratios

The above observations about element mobility provide the best way to inspect a geochemical data set, be it one that you have generated yourself, or one that you’ve inherited. If two rocks are linked by an alteration process, then their immobile element ratios should be fairly constant, give-or-take the analytical errors (usually trivial) and sampling problems

discussed previously (potentially major). Because some components (e.g. Al, Ti) are relatively immobile during alteration, and others are mobile, rocks can change volume during alteration by removal or addition of mobile elements (such as Si). Because there is no change in the mass of immobile elements, when dissolution (volume loss) occurs in the bulk rock, it appears as though the immobiles have increased. Immobile element ratios will not change, however, and this can be used to pin down the actual volume change. Likewise, dilation or volume increase will result in the apparent decrease in immobiles.

DEALING WITH LARGE DATASETS

Dealing with large datasets requires that you can distinguish primary lithological variations from alteration-related variations. In this regard, the following are key points:

- in sedimentary and metasedimentary rocks, elements that are normally immobile during hydrothermal alteration can commonly vary considerably due to primary sedimentary variations. This is because those elements are most commonly contained within mechanically and chemically resistant accessory minerals e.g. zircon, ilmenite, titanite etc. These minerals have a tendency to be concentrated in sands, to be moderate to rare in shales, and very rare in chemical sediments. So a sequence of siliciclastic and/or carbonate rocks will commonly show a wide variation of these components.
- in igneous rocks, the elements that are "immobile" in hydrothermal systems are actually commonly quite variable, mainly because of solubilities in different composition melts, and fractionation-related effects. For example, Ti is a common component in basalts due to its high solubility in mafic melts, but is rare in strongly-fractionated granites. Zr has its greatest solubility in the range 750 - 900°C in melts, and so tonalites (which crystallize in this range) have far more Zr than true granites and pegmatites (which crystallize in the range 550 to 700°C). Thus, ratios of hydrothermally "immobile" elements in a differentiated igneous suite will show quite a range depending on the specifics of the igneous differentiation process.
- volume changes during visible alteration are normally $< \pm 50\%$, i.e. it is not common for more than 50% of a rock to dissolve during alteration; likewise it is not common for rocks to dilate more than 50% - and in the latter case the rock is likely to be riddled with veins and other features of dilation. So, combining this information with the above points, a change from one sample (e.g. 20ppm Zr) to another (e.g. 300 ppm Zr) involving a very large change in a likely immobile element, is going to reflect a basic rocktype change, not an alteration-related feature (although alteration may be superimposed on this scenario).
- scanning through a dataset for immobile element ratios will thus reveal some "clangers" - samples for which the ratios that are fairly consistent for several other samples all of a sudden go "haywire". This normally reflects a rock type change.
- filter your dataset using either your own observation on primary rocktype, or, if you can't see the rocks (e.g. percussion chips, old data, powders without samples), try to work out an

appropriate discriminant that might reflect primary variations. For example, try an Al-saturation index in igneous rocks, or Mg-content (both Mg and Al are reasonably resistant to hydrothermal changes in many alteration situations); other ratios of hydrothermally inert elements (Zr, Ti, Y, Ce, Nd etc.) can also be useful.

- Vein-filtering: If veins are large and well-spaced in your system, then they can be sampled appropriately. But, as is often the case, if your veins are small, densely packed, or for whatever other reason get included in your dataset, then you should be looking at your dataset with a view to picking up big positive volume changes, corresponding approximately to your vein density. If you can identify the vein mineralogy, you can attempt to separate this out from the dataset to arrive at the actual alteration geochemistry. This point is a variation on the theme described above in Figures 11 & 12.

This is intended to give you an idea of the sorts of approaches to rock and alteration observations, either with or without geochemical data. It will require some hands-on training and a suite of appropriate samples (e.g. yours!) to gain maximum benefit from the methods. More details of how to use the isocon method are shown in a companion link to an Excel sheet.

Exercise 1: Hand specimen appraisal of different fluid-rock systems

Exercise 2: Determining mass and volume changes by inspection

Exercise 3: Manipulating a large geochemical dataset

Exercise 1 Hand specimen appraisal of different fluid-rock systems

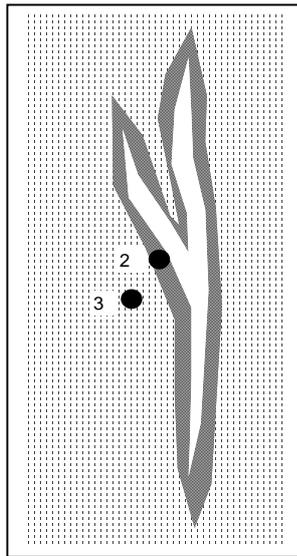
In this exercise, the main aim is to try to use field- or core-based mineralogical and geometric observations to make a first-pass determination of whether or not significant mass transfer has occurred for a given vein, breccia, or alteration system. Secondly, the samples will introduce you to aspects of scale, because a hand-specimen observation must always be coupled with a broader appreciation of the surrounds.

1. Examine several samples. Firstly attempt to distinguish primary layering (bedding), foliations, alteration zones, and veins. Make a sketch distinguishing these clearly. The sample may not contain all of these, depending on the type of fluid-rock interaction and the size of the specimen.
2. Identify, if you can, the mineralogy of the different parts of the sample. For the rocks and/or alteration zones, this can be very difficult if it is fine grained or complex. Don't worry if you have trouble identifying minerals, I am there to help. You will also have to draw on your experience of what certain rock types should have in them!
3. From your sketch and now knowledge of the mineralogy, you have to try to work out the scale of mass transfer for particular elements. This means that you have to mentally convert the observed mineralogy of the different zones into some idea of the bulk composition of that part of the sample. A Deer, Howie & Zussman can be handy here of course. Attempt to construct a profile of rock chemistry across the key vein/wallrock etc interface; examples are given in Section 2 of your notes, particularly Fig. 8 on p13. You should only construct profiles for the elements that you can see are pertinent e.g. if there is a biotite-rich zone in one part of the rock, and a biotite-poor zone in another part, and you believe they are linked by an alteration process, then you should consider K_2O (and/or another alkali or alkali-earth it has swapped for, e.g. Na, Ca), $FeO \pm MgO$, SiO_2 , and Al_2O_3 particularly as the latter is normally fairly immobile in many alteration processes (see next section).
4. Then, for each element of interest, ask the question of whether its gain or loss could be accounted for elsewhere in the specimen e.g. if you have a quartz vein, is there a nearby zone of quartz depletion from which the silica may have been derived? This will help you decide on which type of system you are dealing with. Note you should expect different types of behaviour for different elements because they have differing degrees of mobility – so some of your components might show “closed system” behaviour whereas others may be open.

Exercise 2 Determining mass and volume changes by inspection

This exercise is using the same principles as for Exercise 1, but this time using whole rock geochemical data. Careful sampling, as described in the notes, can help you make the right decision about sample pairs. This type of exercise is particularly important for field- or mine-geochemical sampling when you are concerned with understanding not only the effects of alteration on the distribution of grade (e.g. Au), but also the accompanying overall geochemical changes as these may help you make some general steps to improve orebody delineation including visual recognition of cutoff boundaries for junior geologists, samplers, and miners. The example here is a straightforward test of whether a particular alteration type (here biotite-staurolite) is crucial for enriched grades. If it is crucial, then clearly it is easy for someone to look for this alteration type in the broader area as a possible pathfinder.

	KAN58- KAN58		
	3	-2	
wt%	Unaltered	Altered	Alt/unalt Change
SiO ₂	61.89	37.62	0.61
TiO ₂	0.79	1.41	1.78
Al ₂ O ₃	16.51	29.52	1.79
Fe ₂ O ₃	10.69	17.54	1.64
MnO	0.25	0.64	2.56
MgO	3.47	5.16	1.49
CaO	0.29	0.36	1.24
Na ₂ O	0.29	0.30	1.03
K ₂ O	3.59	5.00	1.39
ppm			
SO ₃	773	35	0.05
Cr	96	197	2.05
Ce	101	188	1.86
Nd	40	78	1.95
V	102	183	1.79
Cu	218	365	1.67
Zn	155	339	2.19
Ni	47	70	1.49
Ga	23	39	1.70
Zr	227	393	1.73
Y	35	64	1.83
Sr	12	10	0.83
Rb	173	243	1.40
Density	2.91	3.46	



The geochem. dataset, from the Kanmantoo Cu mine in South Australia, shows two XRF analyses for a less- and more altered schist from the altered rocks in the open cut. The ore is chalcopyrite-magnetite, hosted in pelitic schists. The samples shown represent general ore host rock (58-3) outside the intense alteration envelope of the ore, and a reaction rim or alteration zone (58-2) developed around a quartz vein, that locally contains andalusite and chalcopyrite as minor constituents. These veins occur outside the main, intense alteration around the ore itself, but lie in a broader (km-scale) alteration halo.

- By looking at the ratios of elements in the two rocks, attempt to identify elements that may have been immobile during the alteration process - choose your own error limits, indicate these by "=" in the changes column.
- Likewise, once you have recognised the key range of ratios representing likely element mobility, use "-", "+" for those elements that have definitely undergone change, and \geq or \leq if you're uncertain (depends on the error limits you have chosen in section a).
- What does the ratio of immobile elements most likely mean for the overall alteration process - was it constant mass or was there

substantial overall mass loss or gain (going from unaltered to altered). Can you determine by inspection what was the major element(s) that moved out of the system? Then what is the significance of finding this alteration immediately around quartz veins?

- Note that if you assumed that there was no net mass transfer in the alteration, then a very wide range of elements would be calculated as having been transported. In particular, take a look at the data for the base metals, given that this is a copper mine. Compare this with the results you have determined from the "proper" mass balance exercise. Would you use this alteration as a pathfinder for Cu mineralization? Why/why not?

Exercise 3 Manipulating a large geochemical dataset + isocon analysis

Background

It is obviously important to recognise the way in which mass has been redistributed in a given alteration system. It allows you to recognise whether material has come from or been lost to a region outside your study area (i.e. an exotic component) or whether it could have been derived from within the system. It allows you to recognise and trace fluid pathways and thus determine the primary controls on fluid flow. It allows you to qualitatively or quantitatively determine the transport history of ore components in the alteration system. A knowledge of these things will allow you to formulate an ore genesis model relevant to further exploration or further development of an existing mine. It may allow you to determine the effects of fluids at large scales during metamorphism; it may give you insights as to links between fluid flow, fluid chemistry, and rock deformation.

To use this data quantitatively

Quantitative analysis of the data ranges from simple mass transfer equations through to mass transfer modelling using thermodynamic and/or experimental solubility data. Mass transfer equations can be simply derived by using the actual amounts of component loss and gain determined from your isocon analysis, coupled with solubility data for that species. e.g.

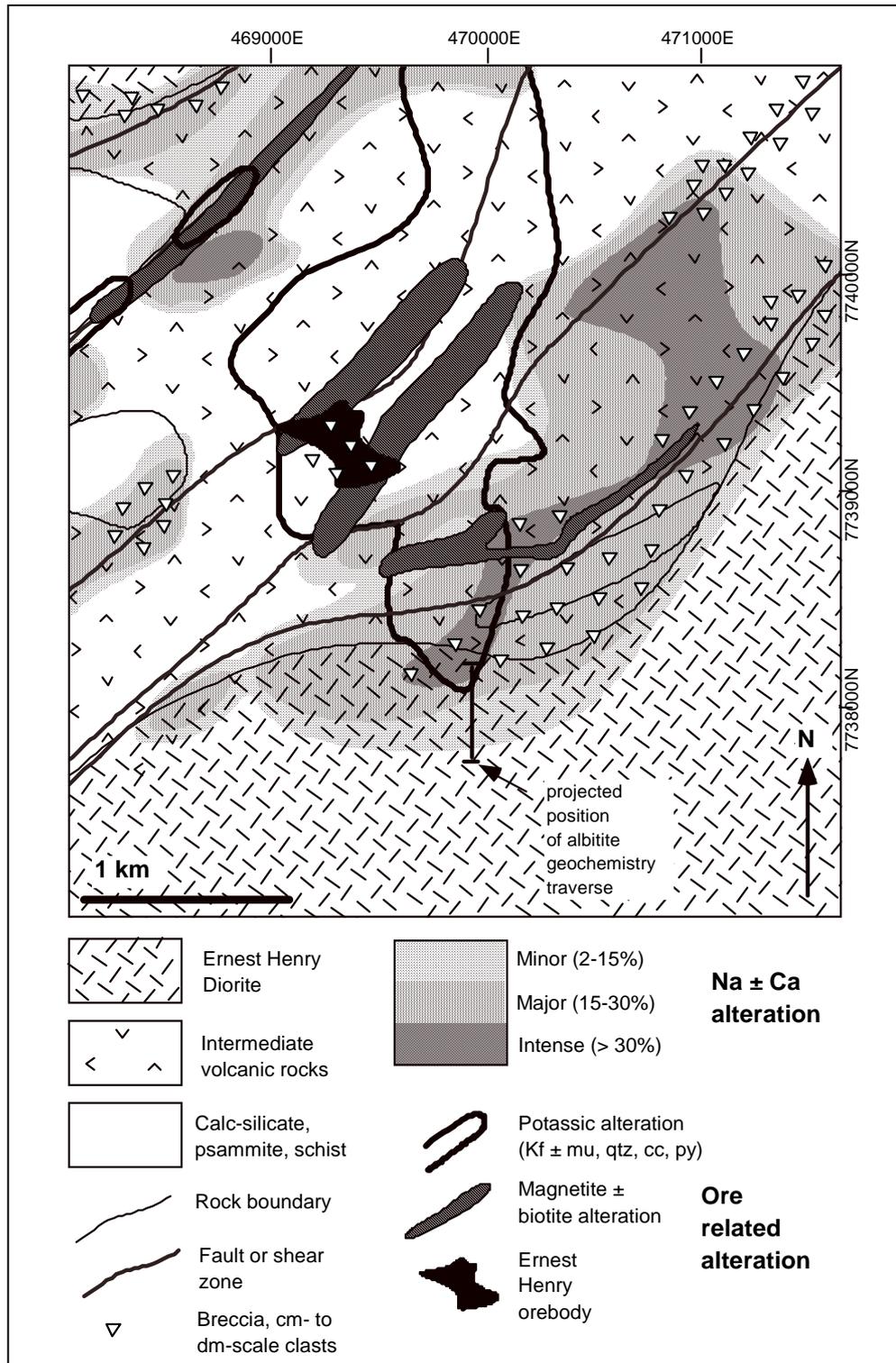


This is the type of information needed to do a hydrothermal geochemical simulation of alteration zonation – but we won't do that here!

More practically, this is the type of information that allows you to:

1. recognise and distinguish distal and proximal alteration suites that relate to ore proximity, by checking that a particular component is showing a halo effect across a number of different rock types
2. isolate and discard alteration suites that are not relevant to the exploration model of interest: e.g. if your model, and the known orebody, are marked by strong potassium metasomatism then alteration that reveals K decrease may not be directly related to ore targeting
3. applying the same principles in weathered rock profiles can assist you in determining what elements and trends are appropriate for consideration in a soil and/or weathered rock chip geochemical survey
4. the method also allows you to determine the origins of a particular (horribly) altered rock when there are no exposed rocks that are unaltered in your pit/weathered outcrop/sludge sample
5. and finally, enrichments or depletions for a particular element in the transition from unaltered to more altered rocktypes can sometimes be revealed to be a product of the addition or removal of other elements (i.e. dilution or dissolution), so that the element you are looking at is only residually enriched or depleted. This impacts on geochemical vector identification.

The Ernest Henry Fe-oxide Cu-Au deposit has a broad alteration halo of albitic alteration which is overprinted by the orebody-related biotite-magnetite alteration (Figure). Is the albitic (Na-Ca) alteration related in anyway to the orebody-proximal alteration?



Step 1: Testing for precursor variability. Do all of the rocks sampled have the same protolith? Use your worksheet or a provided one. Here at Ernest Henry, most of the samples were thought to be

diorites in the field, however the origin of some of them was obscured due to alteration and brecciation, so it is likely that the dataset for these rocks includes some other rocktypes.

With samples arranged in columns and elements in rows, use several rows at the bottom of your spreadsheet to calculate some ratios of elements that might be immobile during alteration: if these are immobile then you may be able to distinguish primary rocktype variations. Try various ratio pairs of the following elements: Ti, Zr, Nb, Al, Ga, Y. Also, you could plot these as X-Y graphs to assist recognition of different primary rock types using the principles discussed in the practical and lectures (key points: look for linearity on X-Y plots with projected intercepts of 0 and good R values). Try to identify the outliers by inspection of the spreadsheet ratios in your new rows. Once you think you've identified the "ring-ins", move those columns aside and concentrate on the isolated rocks that you think look like they were the same precursor. With each rock type, you can calculate the average of the immobile element ratios ("=average(B32:N32)" for example). Then calculate the standard deviation of these ratios ("=stdev(B32:N32)" for example), and then determine how much the standard deviation is compared to the average as a %. The "best" element pair for characterising the immobile element signature of the diorites will be the pair with the lowest standard deviation expressed as a % of the average.

Step 2: Identifying the mobile elements.

Plot ratios of the major and minor elements likely to show mobile behaviour. Now that you've already established which elements show near-immobile behaviour. You can select these elements by inspection. What you are trying to do is establish a set of indices that discriminate between "fresh", partly altered and intensely altered samples. This type of index is the type that can be applied to exploration or ore-envelope calculations (once you've established the alteration of interest is useful!). In almost all alteration systems I've come across you should start with the alkali and alkali-earth elements – these always move around somehow! (Na, K, Ca, Rb, Sr, Ba). Using this information, sort the rocks into an order from least to most altered (hint: for Ernest Henry, the figure already tells you the altered rocks are albitized). Which major elements are the most sensitive? Which minor elements? From the outcomes of Steps 1 and 2, write a list of which elements were immobile, which elements were near-immobile or too scattered to make sense, and which elements were added and which were lost (i.e. =, ≈, +, -).

Step 3: Constructing an isocon plot and determining whether the albite alteration could have contributed to the ore-related alteration.

The isocon technique (Grant, 1986) works as follows: The vertical axis is the less altered rock, the horizontal axis the more altered. For each component (e.g. SiO₂ %, Zr ppm), you multiply the concentration of each component by a convenient factor for both the unaltered and altered rock, with a different factor for each component, so that all components are conveniently spaced out along your arbitrary axes. Because the aim of these diagrams is to select a mass ratio slope from which the mass change can be calculated, it doesn't matter what the multiplication factors are as long as your data is sufficiently distributed so that you can select the appropriate Fv. e.g. if SiO₂ in the altered rock is 52 wt %, Zr is 230 ppm, and Ca is 8 wt %, then you might multiply SiO₂ x 0.1 (giving 5.2 for the altered rock and whatever for the unaltered), and you might multiply Zr x 0.01 (giving 2.3) and you might leave Ca as it is (8) so that these elements are nicely distributed on a X-Y plot with both axes running from 0 to 10. Do this for all the elements in the Ernest~2 worksheet, then plot all of these on an X-Y plot, labelling each element appropriately. To select an isocon try to identify a suite of elements which lie on a straight line running through the origin. These will most likely be the

immobile elements, whereas elements that plot way off this line are those that have been gained or lost during the alteration.

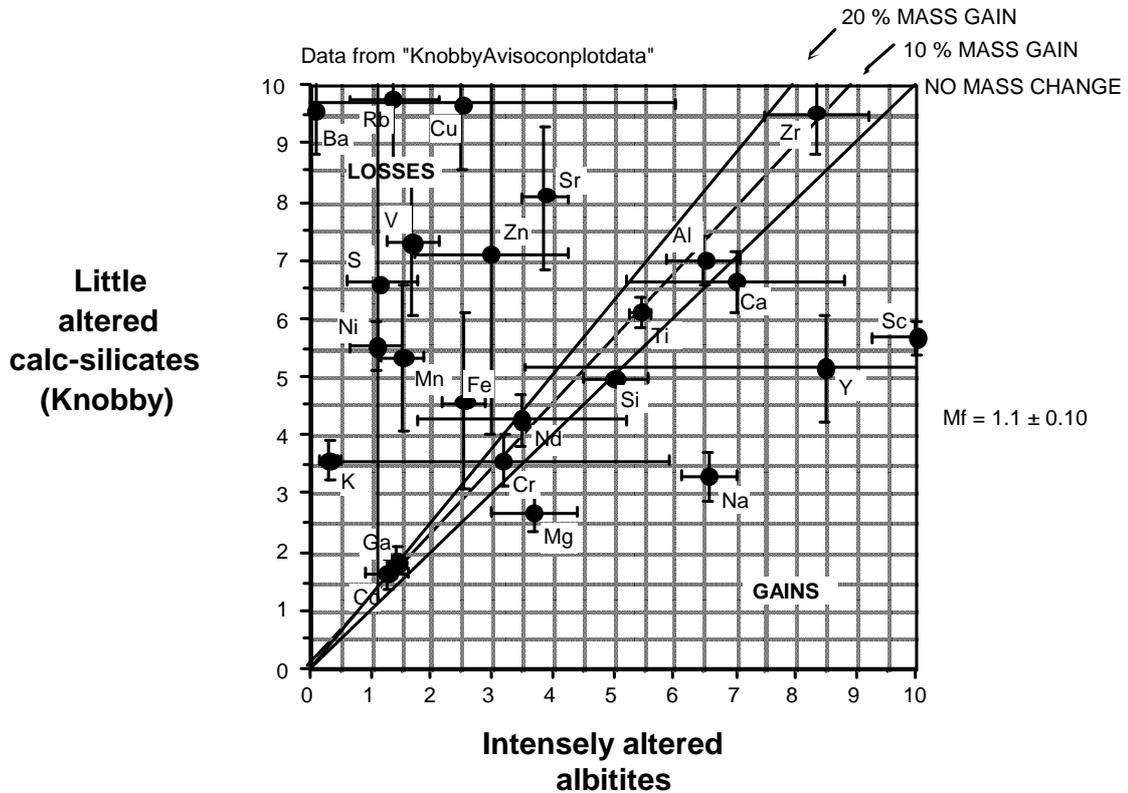


Figure Isocon plot showing mass changes involved in transition from Mary Kathleen Fold Belt calc-silicates to adjacent albitites, in the alteration zone approached up to a calcite vein. Location: Knobby Quarry. Six samples of unaltered rock, and 4 samples of altered rock, were averaged to produce the errors shown, plotted as standard deviation. Note the use of mass terms here: M_f is the equivalent of F_v in the Gresens expression, except that here the densities haven't been specifically taken into account. Mass increase (as in this case) could occur by density increase of the new minerals, or volume increase.

If you have a few of these fairly immobile elements in a linear array on an isocon plot then you are doing fine - you can draw an isocon by best-fit (visual here, computer is better). Elements lying below the isocon have been gained during alteration, elements above the isocon have been lost (Figure). The slope of the isocon defines the total mass change for the system - whether bulk mass loss (i.e. net dissolution) or bulk mass gain (i.e. net precipitation or dilation). As you did for section 2 of this exercise, write a list of elements that were immobile, near immobile, or gained or lost.

See the Excel sheet attached for more assistance here. There are difficult to do the first time, then easy, and then finally, they are understandable and can be used to guide exploration or new geochemical sampling programs.

And the answer is? Compare results from part 2 and 3. A) Were the same elements immobile in both types of alteration? Discuss why/why not. B) Which of the elements that were lost/gained during albitic alteration showed the inverse pattern for ore-related alteration? C) what is the best alteration index for albitic alteration? For ore-related alteration? D) What are the missing ingredients? What elements gained in the ore-related alteration cannot be found as lost elements in the albitic alteration? Discuss why these elements are important in the context of the scales of mass transfer in this system.