Scott Halley, 28/06/2016

Using the ALS ME-MS61 method to characterize igneous rocks in porphyry Cu systems.

The following is a recommended scheme for classifying rock compositions and mapping fractionation trends in potentially fertile porphyry copper magmas.

1. Plot Sc vs Th, Ti, V, Zr, P and Nb.
2. Plot Ti vs Sc, Th, V, Zr, P and Nb.
3. Plot Nb vs Ti.
4. Plot V vs Sc.
5. Plot Hf vs Zr.

Igneous rocks are usually subdivided with a classification scheme that reflects the silica content, eg basalt, andesite, rhyolite. Changes in silica content are coupled with changes in Mg, Fe, Ca, Na, K etc. Geochemical analyses with the ME-MS61 method include all of the major elements except for Si. However the major elements are relatively soluble in hydrothermal fluids. Much more useful and discriminating classification schemes can be constructed using the trace elements, rather than majors.

From the ME-MS61 package, the most immobile elements are Ti, Zr, Hf, Nb, Ta, Cr, Th, Sc, V, Al, Ce and La. These elements are primarily hosted in resistate heavy minerals like ilmenite, rutile, zircon, apatite, spinels, etc. These are minerals that generally survive through intense weathering and alteration (which is why the elements are called immobile). One of the most useful elements for classifying broad compositional groups is scandium. Sc substitutes for Fe into common silicate minerals such as hornblende, pyroxene, chlorite, etc. Sc can be considered as a proxy for the Fe content, but it is much less mobile than Fe during alteration and weathering.

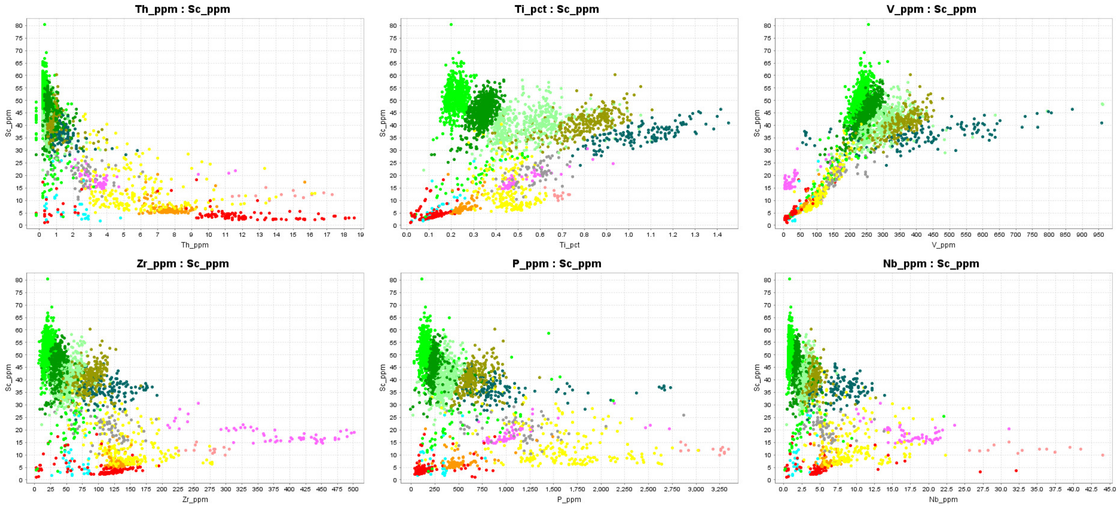
As a guide;

- basalt will have 30 to 50 ppm Sc,
- andesite 20 to 30ppm,
- dacite 10 to 20, and
- rhyolite less than 10ppm.

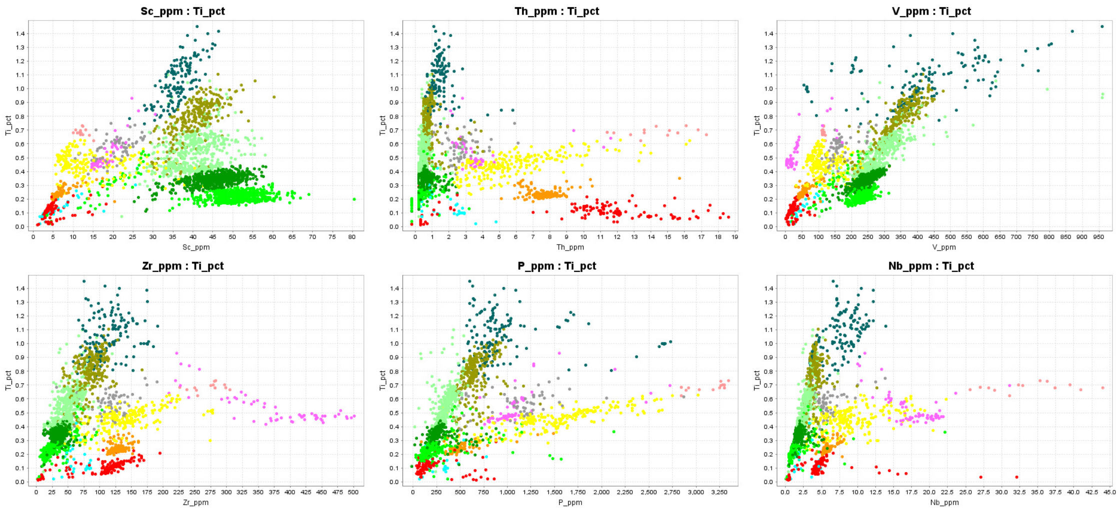
A useful methodology for distinguishing rock types is to;

1. Start by plotting Sc against Ti, Th, V, Zr, P and Nb. The Scandium levels will show you whether the general compositions are felsic, intermediate or mafic. Sc will have a broad

positive correlation with Ti, V and P, and usually a negative correlation with Zr, Th and Nb.

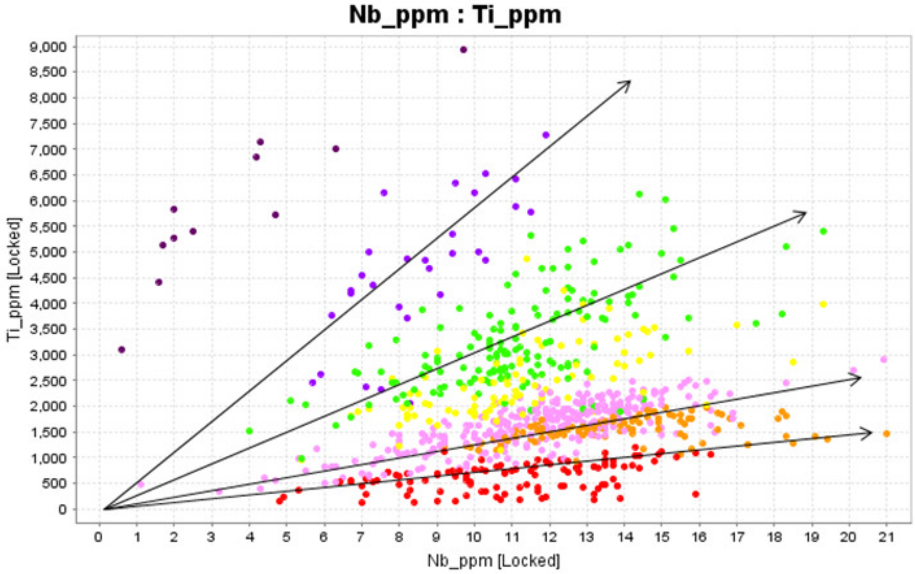


2. Secondly, move Ti to the top of the list; plot Ti against Sc, Th, V, Zr, P and Nb. By doing this, we are effectively plotting minerals that crystallize early in a fractionation trend against minerals that crystallize late. Scandium shows us about the broad compositions, but the other elements show differentiation between different types of basalts or andesites or different porphyry phases.



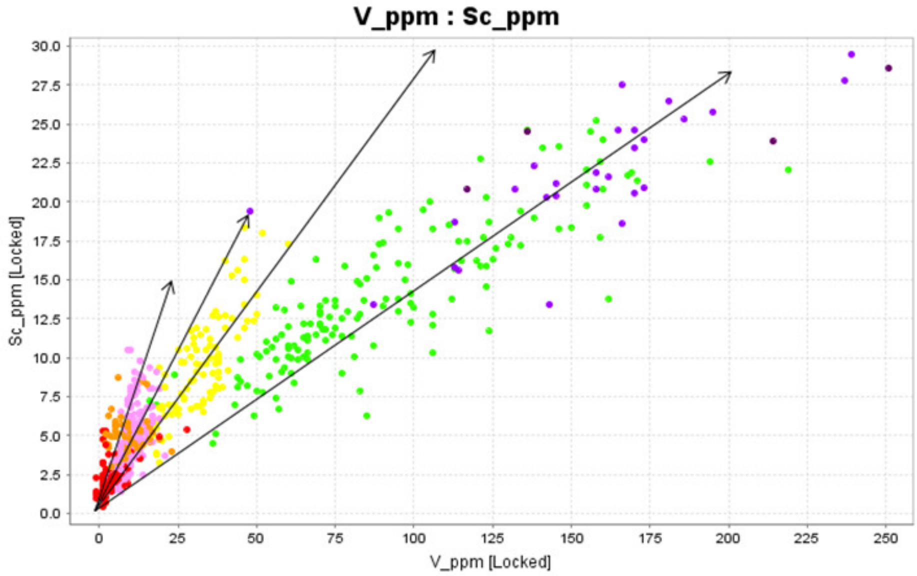
Much of this procedure is about pattern recognition and defining clusters in the data to pick the compositional families. Create scatterplots of the immobile trace elements and look for clusters in the data; the point density overlay function in ioGAS is a very useful tool to help with this. Don't use absolute values (eg strict thresholds in elemental values or fixed boundaries on discrimination plots) to classify the rocks.

Nb follows Ti, and substitutes into all the Fe-Ti oxide minerals. However it is more incompatible than Ti, so the Nb:Ti ratio increases with fractionation. On a Nb versus Ti plot, co-magmatic samples typically plot in linear arrays that project back towards the origin.

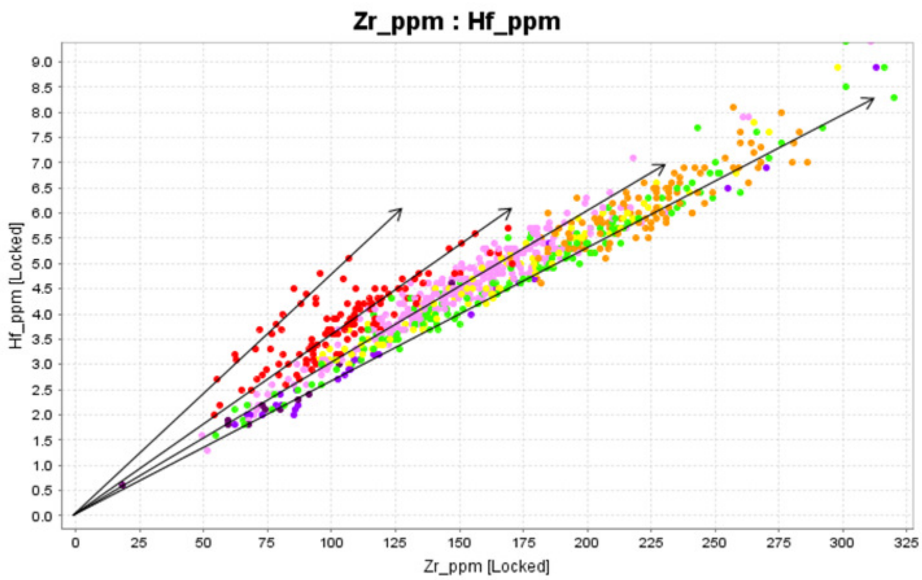


In porphyry copper systems there are some very useful fractionation indicators. In reduced (ilmenite series) magmas, V3+ behaves the same way as Sc3+; both substitute for Fe into silicate minerals. They will plot with a strongly correlated linear trend with V:Sc around 7:1. Magmas that are at least moderately oxidized crystallize magnetite rather than ilmenite. In magnetite series magmas, V is 4+ rather than 3+, and it behaves like Ti rather than Sc. V partitions strongly into magnetite, so fractional crystallization of magnetite causes a decreasing V:Sc ratio.

In hydrous and oxidized magmas, as in porphyry Cu systems, the water content, oxidation state and depth of magma accumualtion (pressure) favours fractional crystallization of hornblende, and magnetite crystallizes relatively late. Sc is removed from the magma with the hornblende, so the V:Sc ratio increases with fractionation. This is a signature of potentially fertile porphyry Cu magmas. The example shown below is from a calc-alkaline suite where magnetite has crystallized early and removed V relative to Sc.



Zircon is usually a late crystallizing accessory mineral phase. However in hydrous magmas, water de-polymerizes silicate chains, so island silicates like zircon, tend to crystallize somewhat earlier in the sequence than framework silicates. This increases the liklihood of fractional crystallization of zircons. Hf always follows Zr, but it is a little more incompatible than Zr. Hf versus Zr usually plots with a very linear trend with a ratio of 1:38. However, with fractionation, the Hf:Zr ratio increases in the residual melt. Fractional crystallization means that some of the early crystalized zircons are left behind in the source region. Therefore, a decreasing total zirconium content, but increasing Hf:Zr ratio is an indicator of fractional crystallization of zircons, and this is probably a result of having a very hydrous melt.



Therefore, in porphyry copper systems, scatterplots of V/Sc versus Nb/Ti, and Hf/Zr versus Nb/Ti are very usuful fractionation indicators that are independent of hydrothermal alteration. These

are good indicators of porphyry copper fertility and are very useful plots for correlation magma chemistry from drill hole to drill hole.

As a precautionary note, zircon is difficult to dissolve, and it is likely that the Zr and Hf results will under-report, especially in younger rocks where there is less radiation damage in the zircon lattice. Ti and Nb might not be totally dissolved either, but the diagrams here rely more on the geometry of the patterns rather than absolute values.

The two figures below contrast fractionation trends for a suite of intrusions that are prospective for porphyry Cu mineralization (top) with typical calc-alkaline fractionation that might be prospective for epithermal gold, or VMS in submarine volcanic settings.