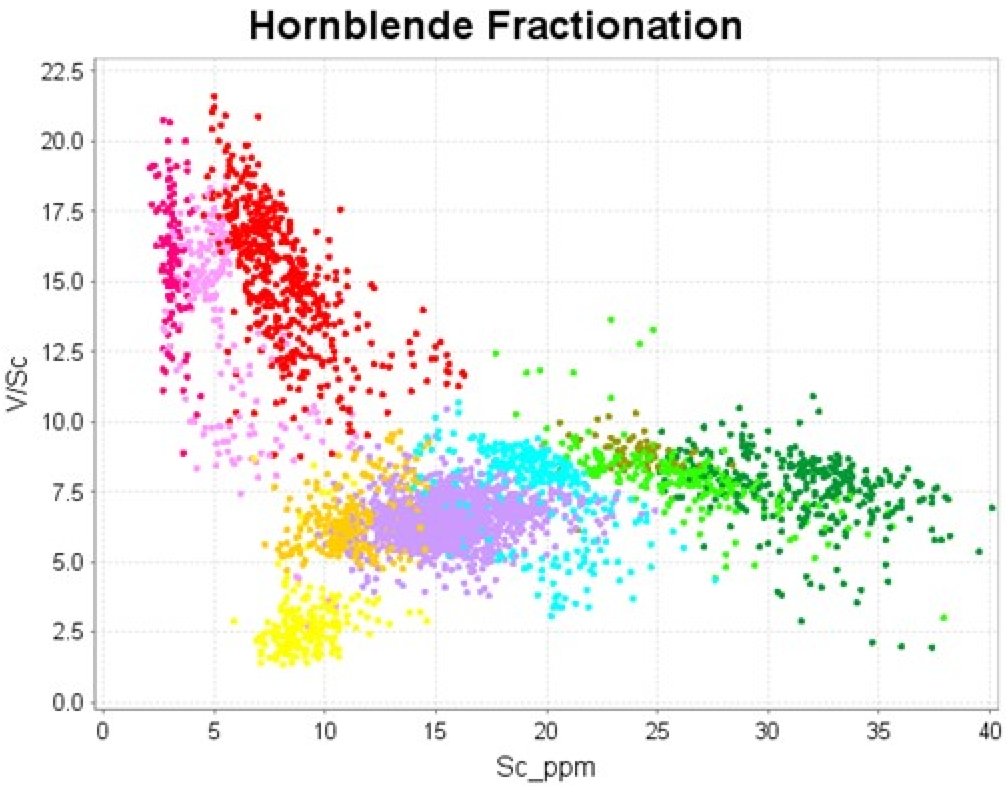
Understanding magmatic fractionation processes using multielement geochemistry



Scott Halley 28/06/2021

Mineral Mapping

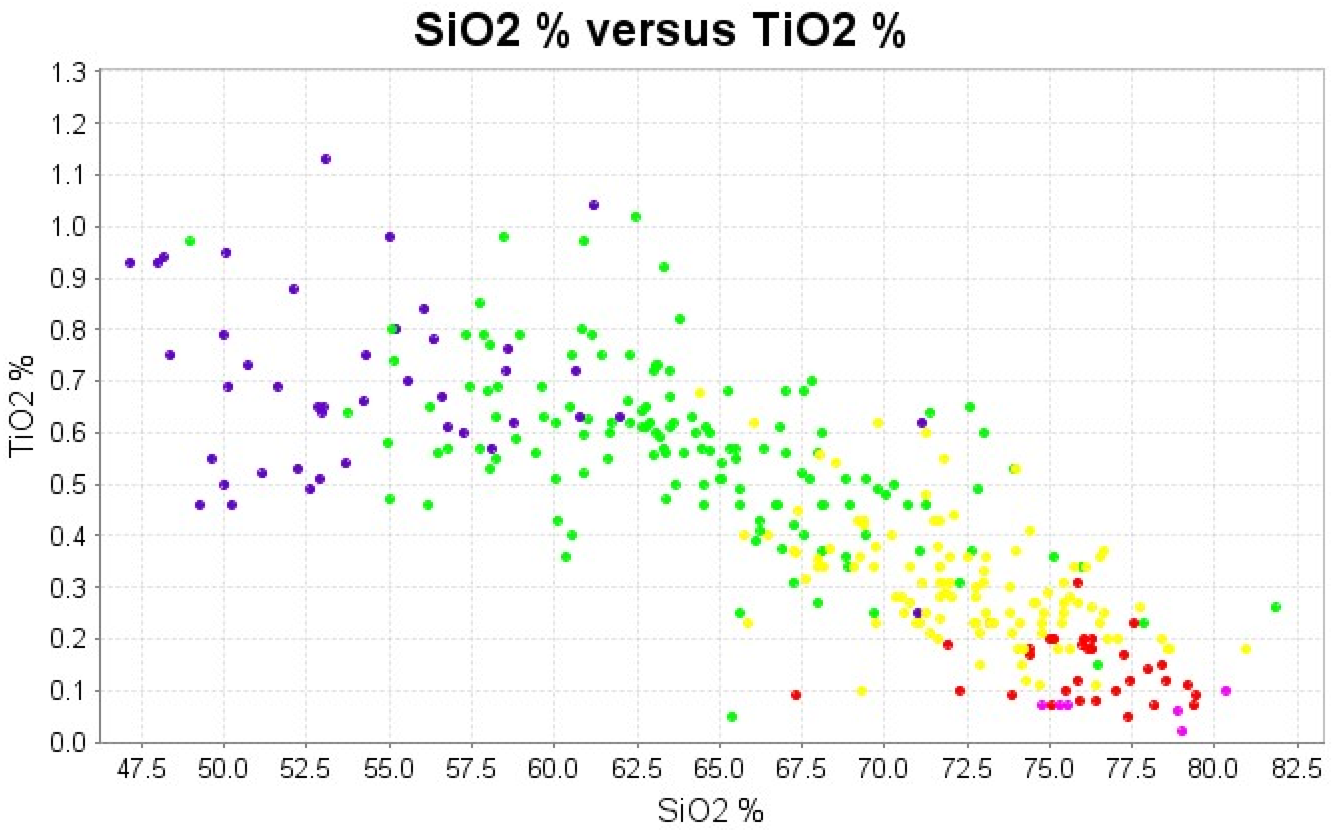
Summary

- Fractional crystallization; segregation of crystals from a melt in a cooling magma.
- Concentrates volatiles in the melt.
- Volatile saturation produces a hydrothermal system and hopefully an orebody.

- This presentation
  - ➢ low pressure, mid-crustal melts
  - ➢ compare fractionation from high-pressure hydrous melting (eg porphyry Cu)
  - ➢ Diversity of Archean granites

Compatible elements have decreasing abundance with increasing SiO2

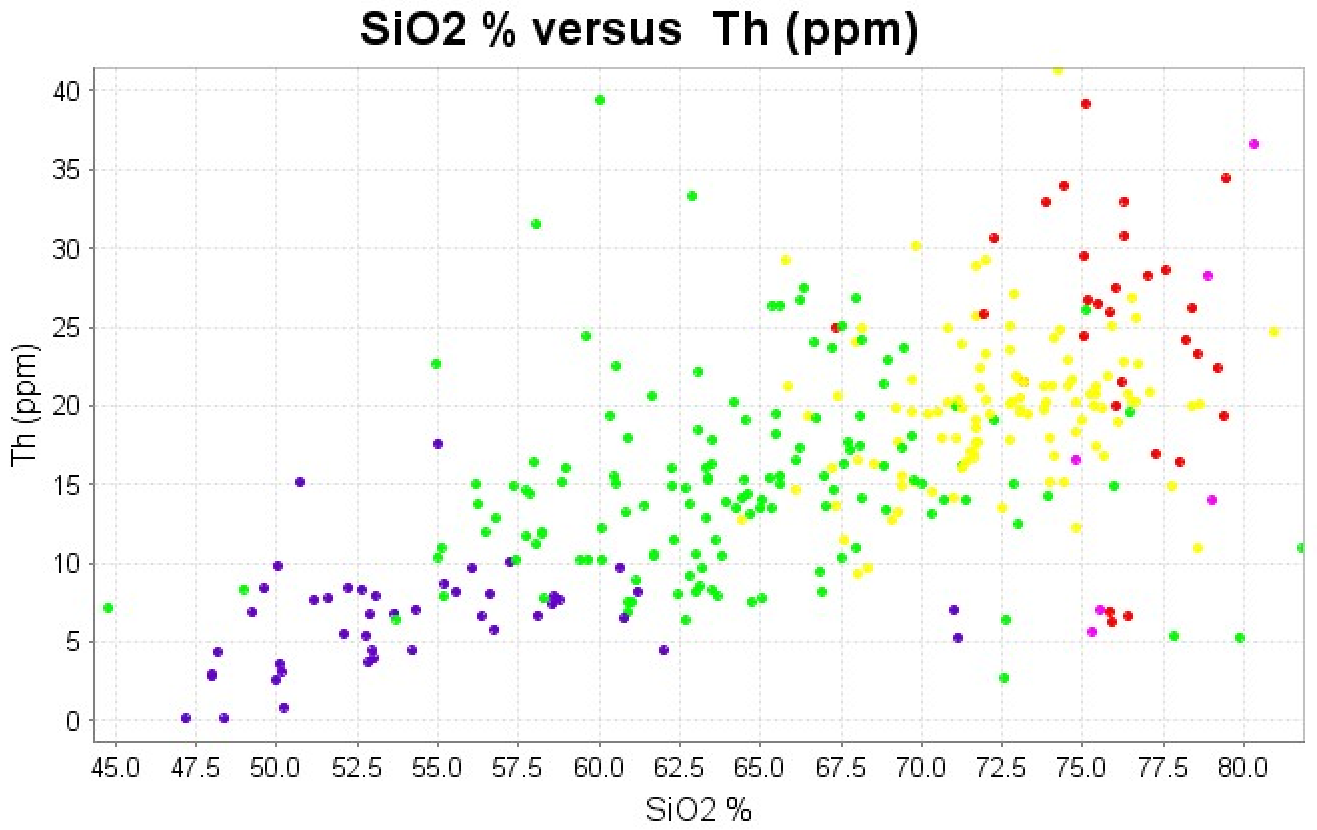
Example: Ti is a *compatible* element.



Zebedee Zivkovic, Mount Read Volcanics Lithogeochemistry M.Sc. Project, CODES

Incompatible elements have increasing abundance with increasing SiO2

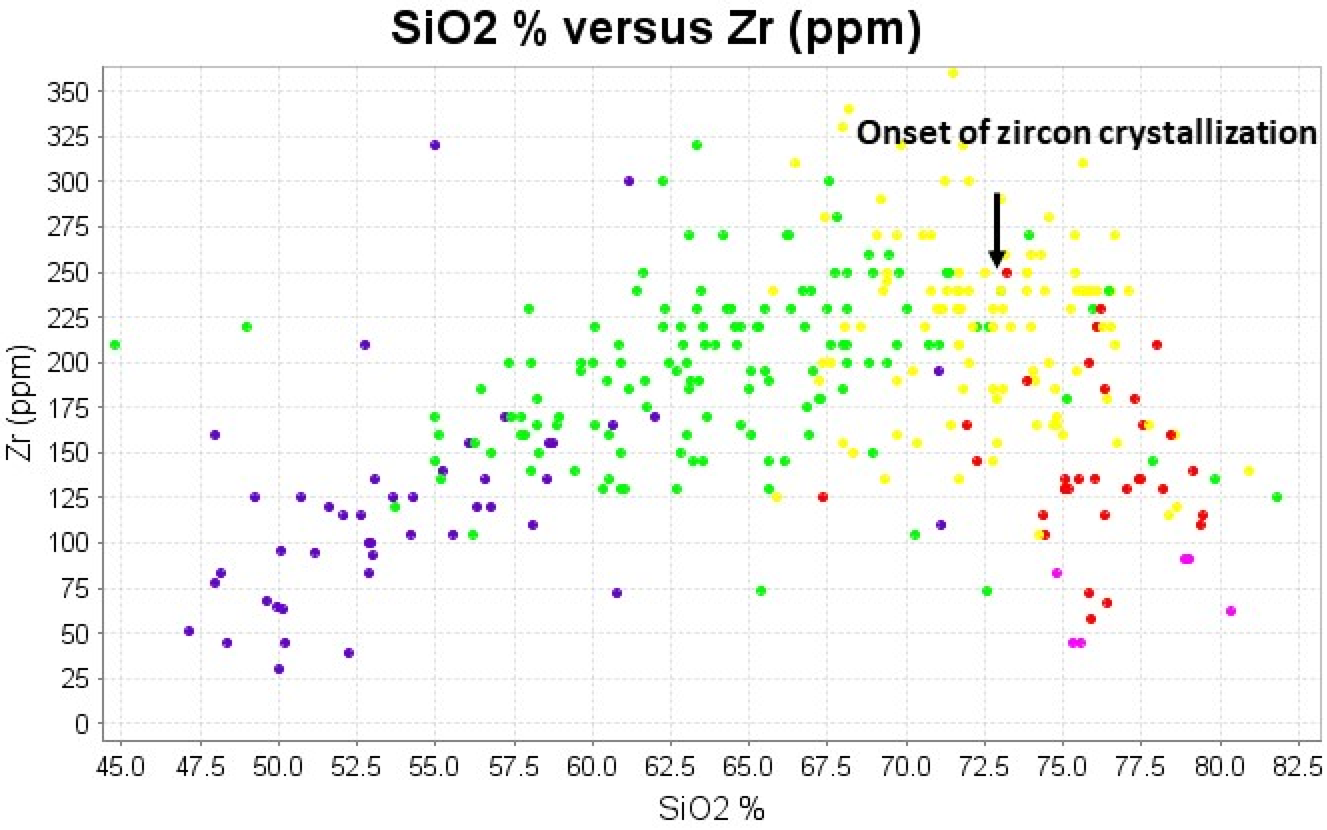
Example: Th is an in*compatible* element.



Zebedee Zivkovic, Mount Read Volcanics Lithogeochemistry M.Sc. Project, CODES

Accessory mineral phases control HFSE distribution patterns

Example; zircon crystallization begins at around 800^{o}C; Zr changes from incompatible to compatible behavior at around 70% SiO_2

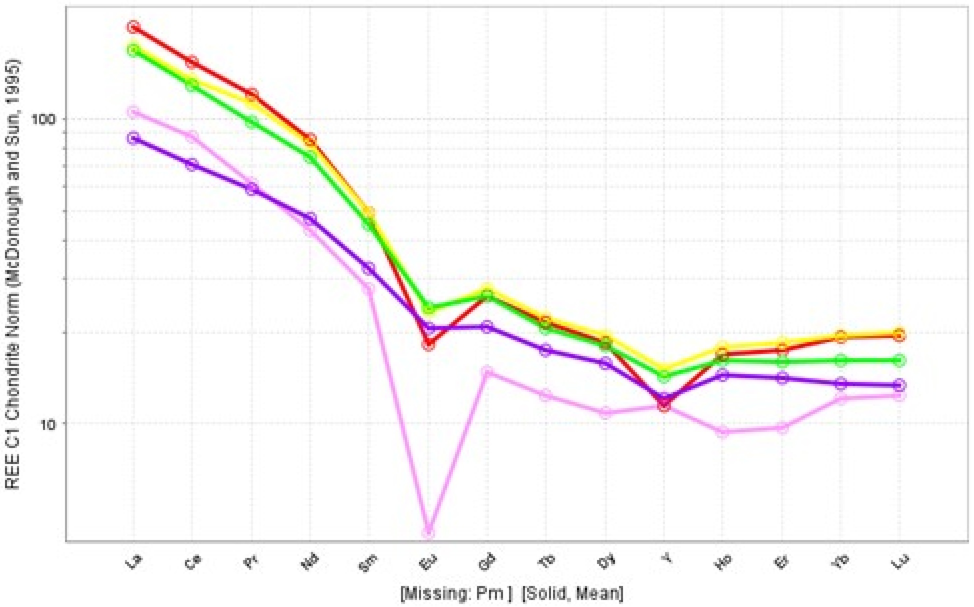


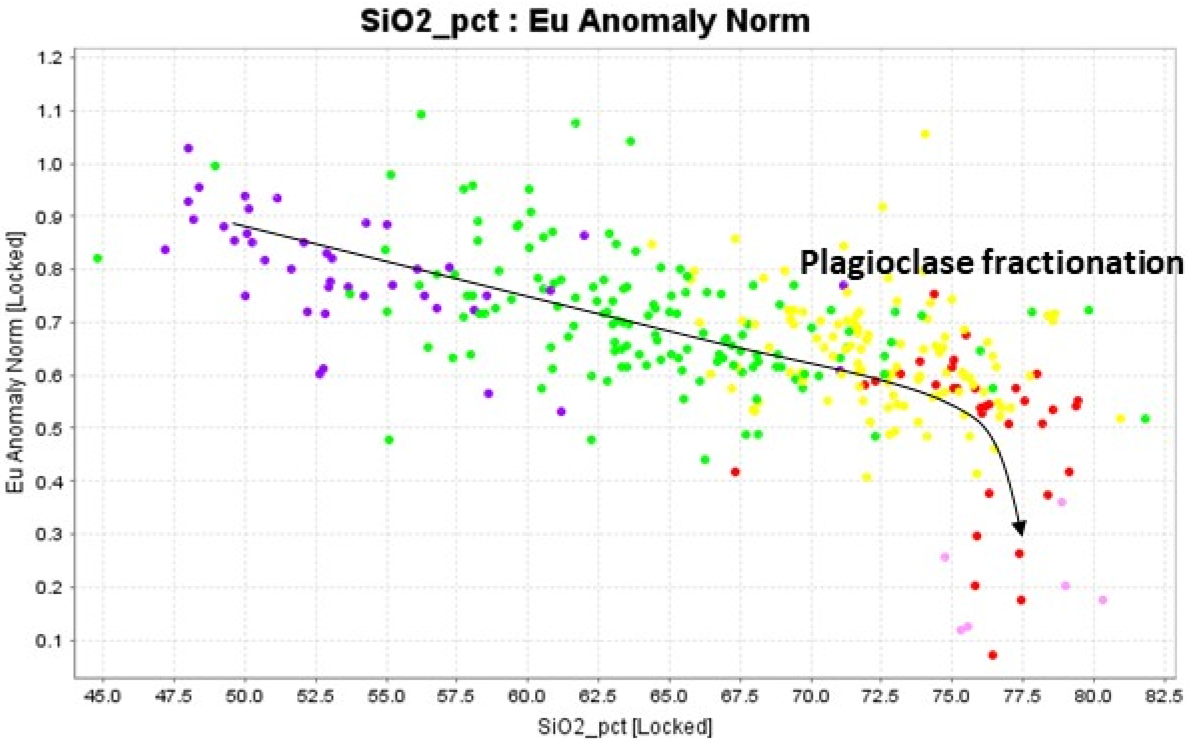
Zebedee Zivkovic, Mount Read Volcanics Lithogeochemistry M.Sc. Project, CODES

Fractionation in low pressure (crustal) hydrous melts

Plagioclase Fractionation

REE's valency 3^+. Eu can be 2^+.In reduced to moderately oxidized melts, Eu^{2+} substitutes for Ca^{2+}. Plagioclase fractionation removes Eu from a melt relative to other REE's.





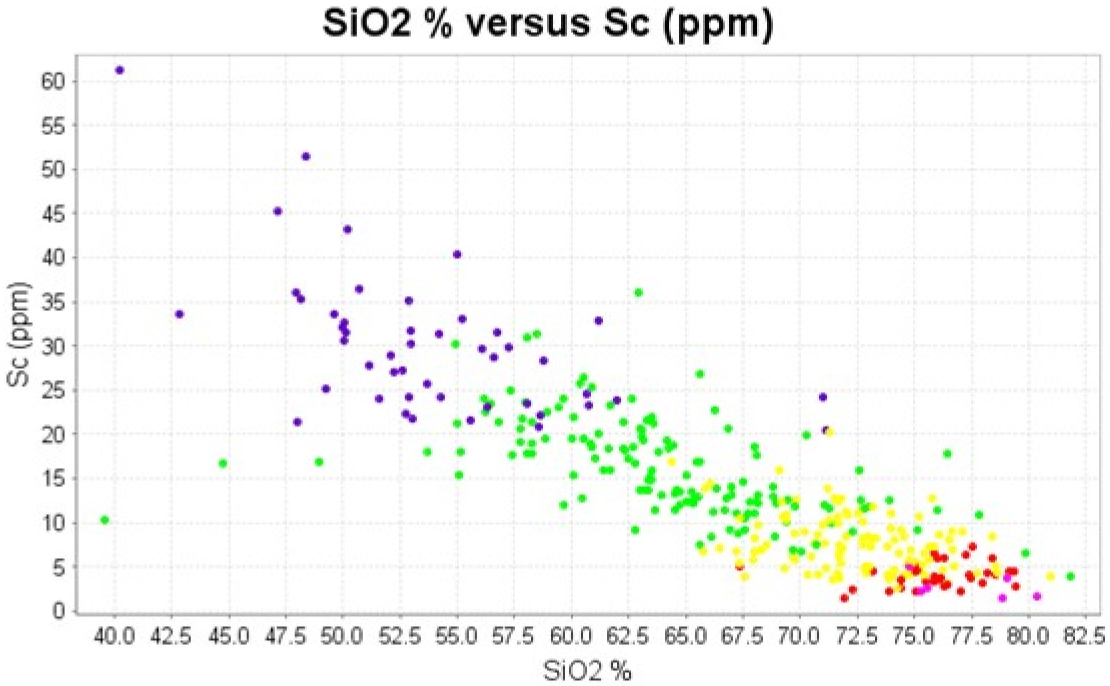
Fractionation in low pressure (crustal) hydrous melts

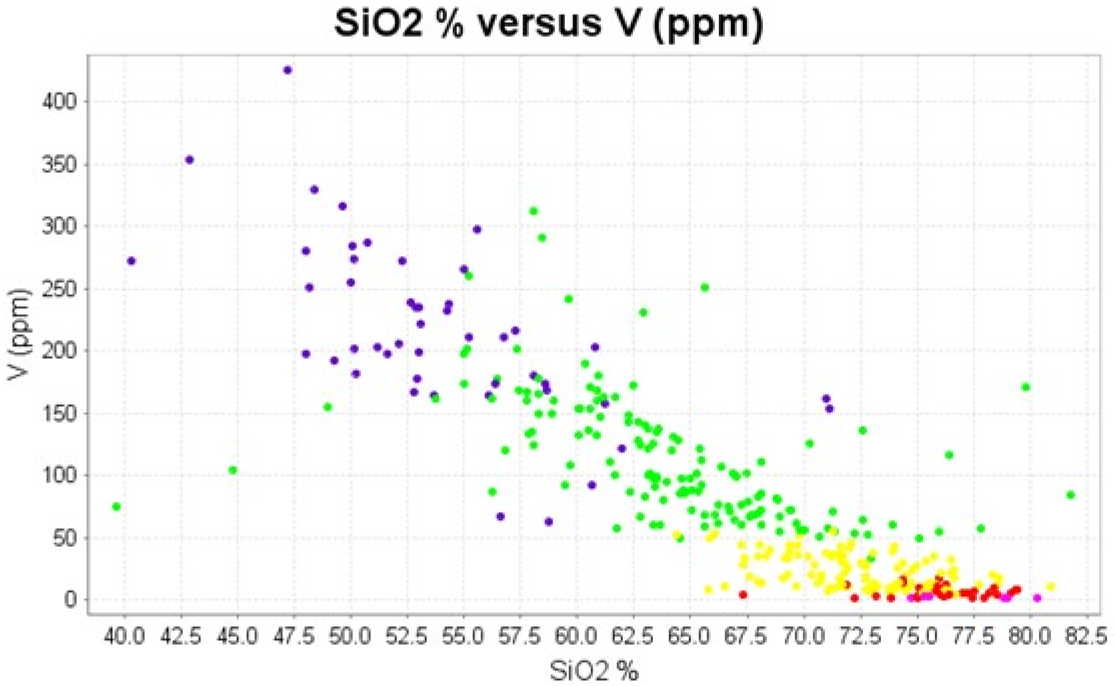
Trace Element Pairs

Sc and V^{3+} are both are compatible elements with similar partition coefficients. Sc and and V^{3+} substitute for Fe in silicate minerals (behaves like the silicate-hosted component of Fe).

V^{4+} behaves more like Ti; it is less compatible in silicates but more compatible in oxides.

Sc and V have the same trajectories in reduced magma, but different trajectories in oxidized melts.



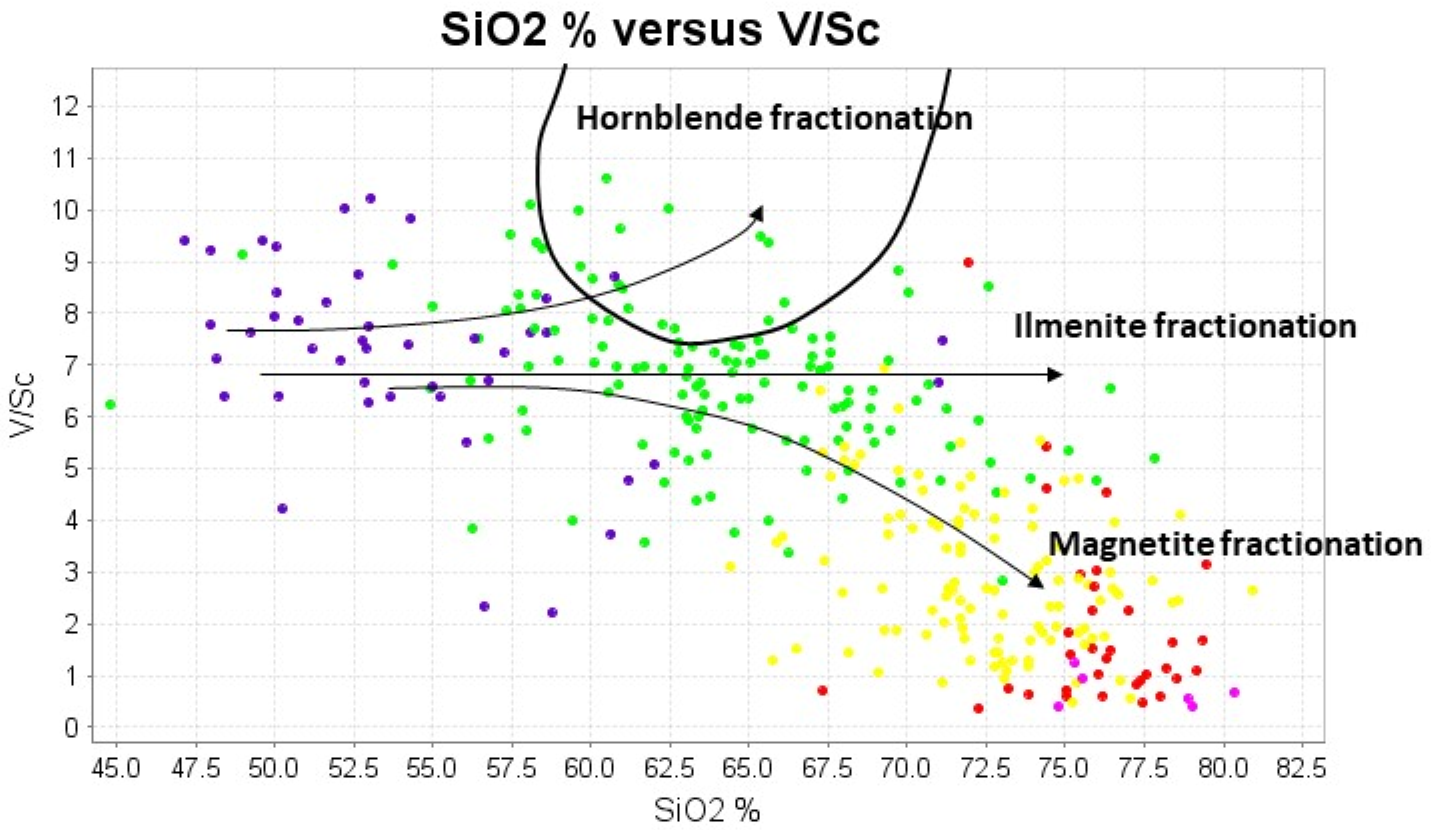


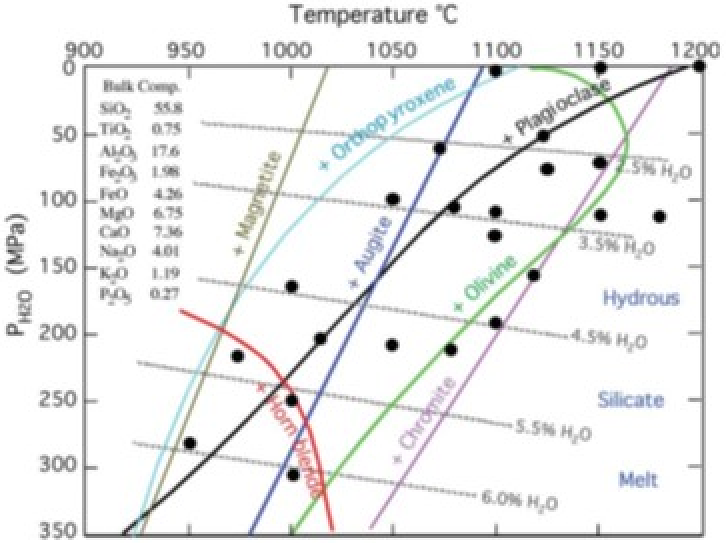
Zebedee Zivkovic, Mount Read Volcanics Lithogeochemistry M.Sc. Project, CODES

Fractionation in low pressure (crustal) hydrous melts

Magnetite versus Hornblende fractionation

In an oxidized melt (ie some V4+), if magnetite crystalizes before hornblende, then V is removed from the melt faster than Sc, and the V/Sc ratio declines. In an oxidized melt where V4+ is somewhat incompatible in silicates, crystallization of hornblende before magnetite causes the V/Sc ratio to increase. The pattern shown in this figure is typical of low pressure, magnetite-bearing crustal melts.

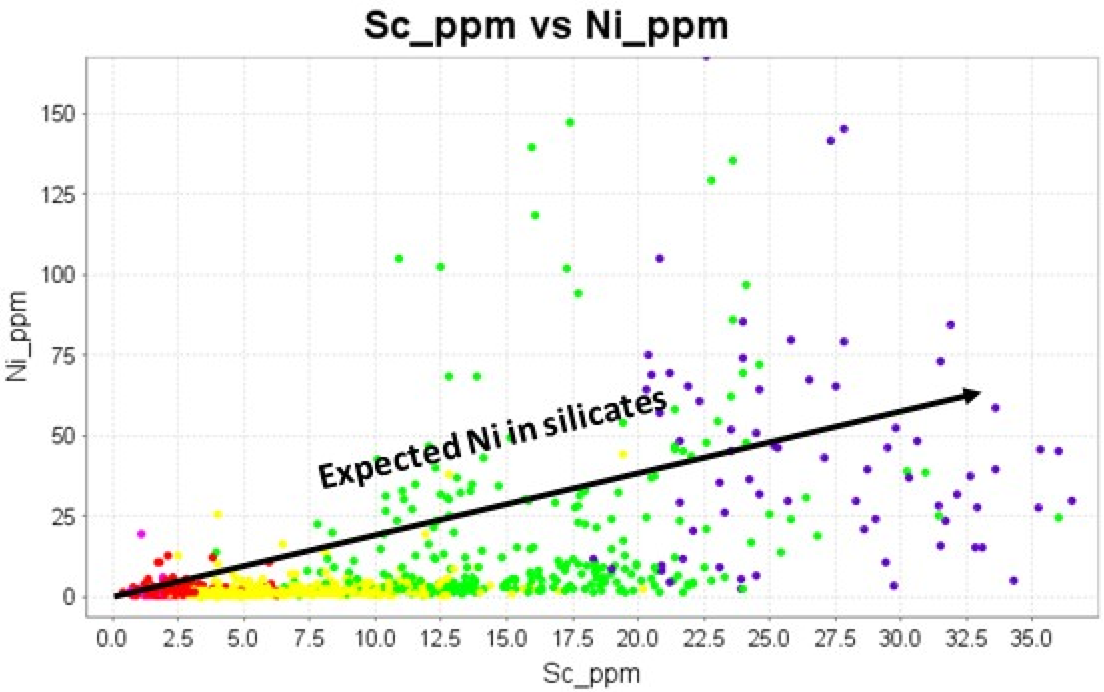


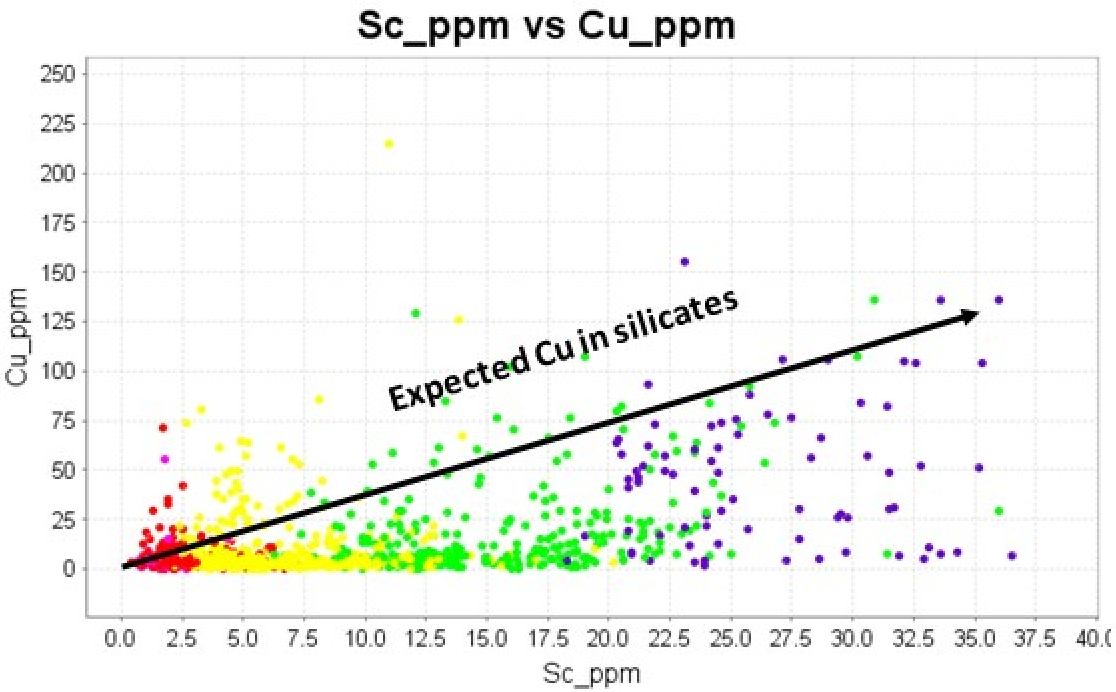


Fractionation in low pressure (crustal) hydrous melts

Sulfide Saturation

Magmas that fractionate magnetite are invariably sulfide saturated.
This is evident from depleted Ni and Cu relative to Sc.



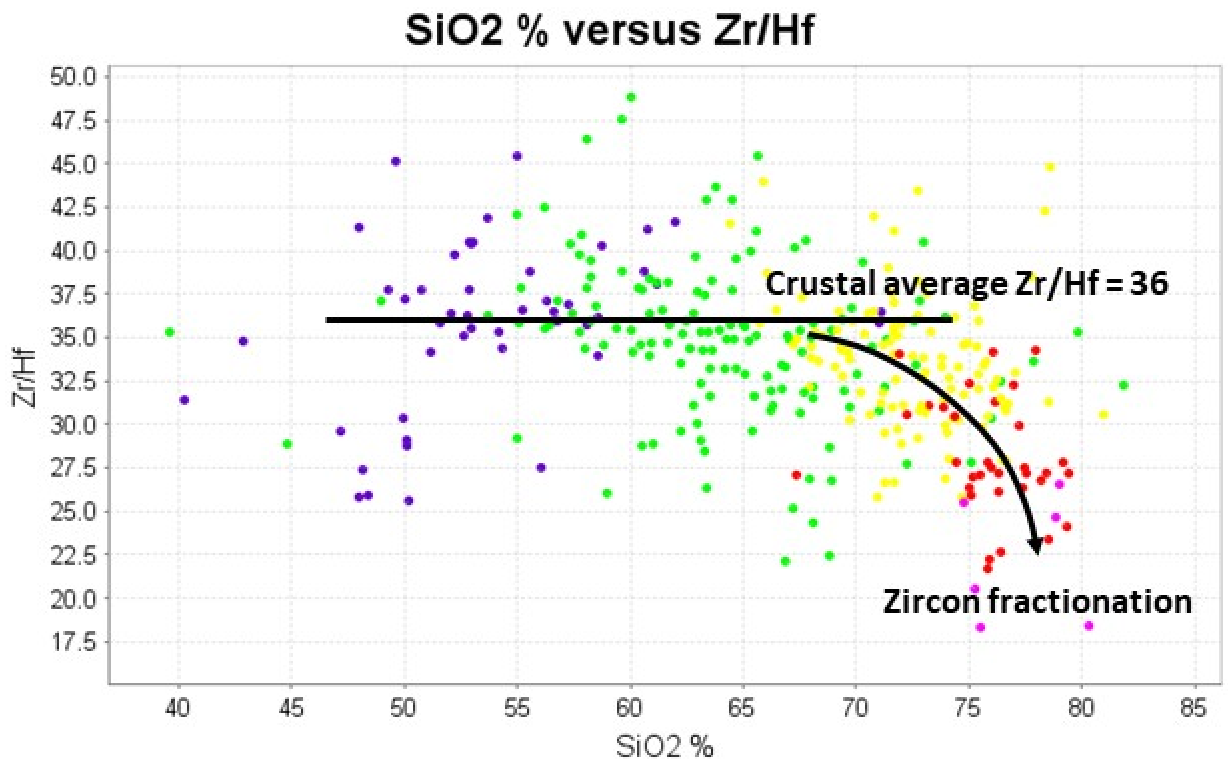


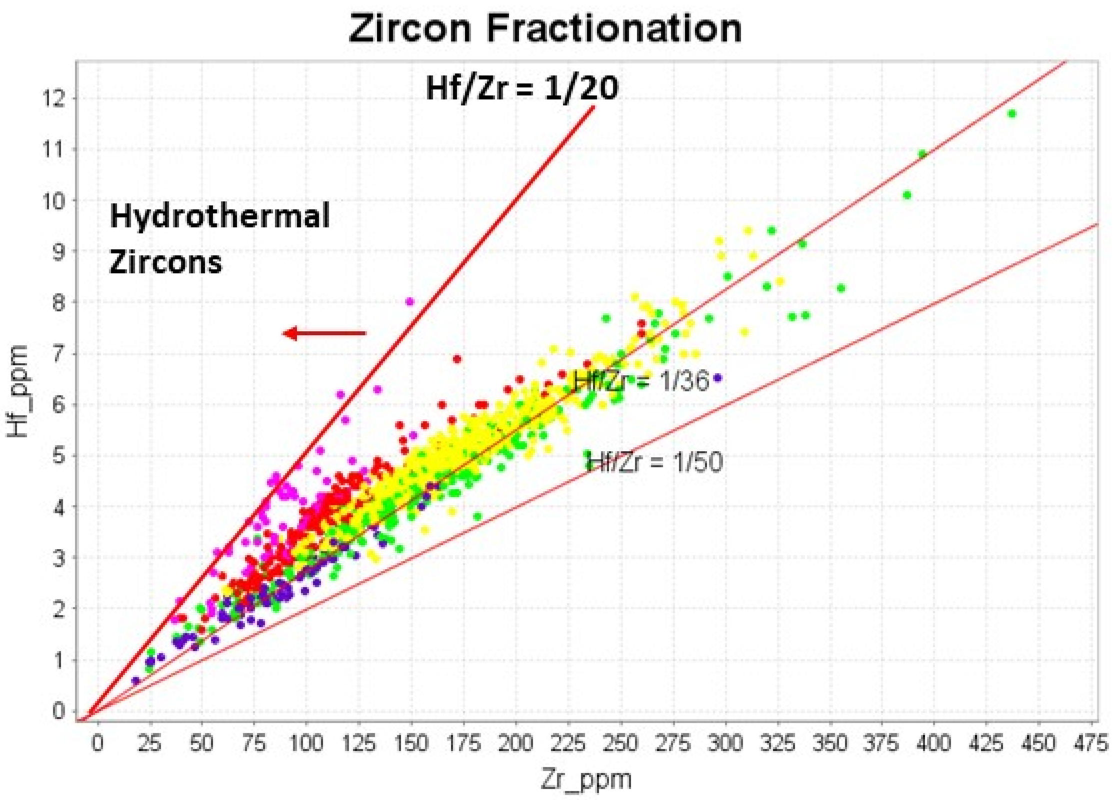
Fractionation in low pressure (crustal) hydrous melts

Accessory mineral phases control HFSE distribution patterns

Example; Hf always follows zirconium. K_D for Hf in Zircons is <1,

Therefore zircon fractionation causes Zr/Hf ratio to decrease. (at > 70% SiO_2)



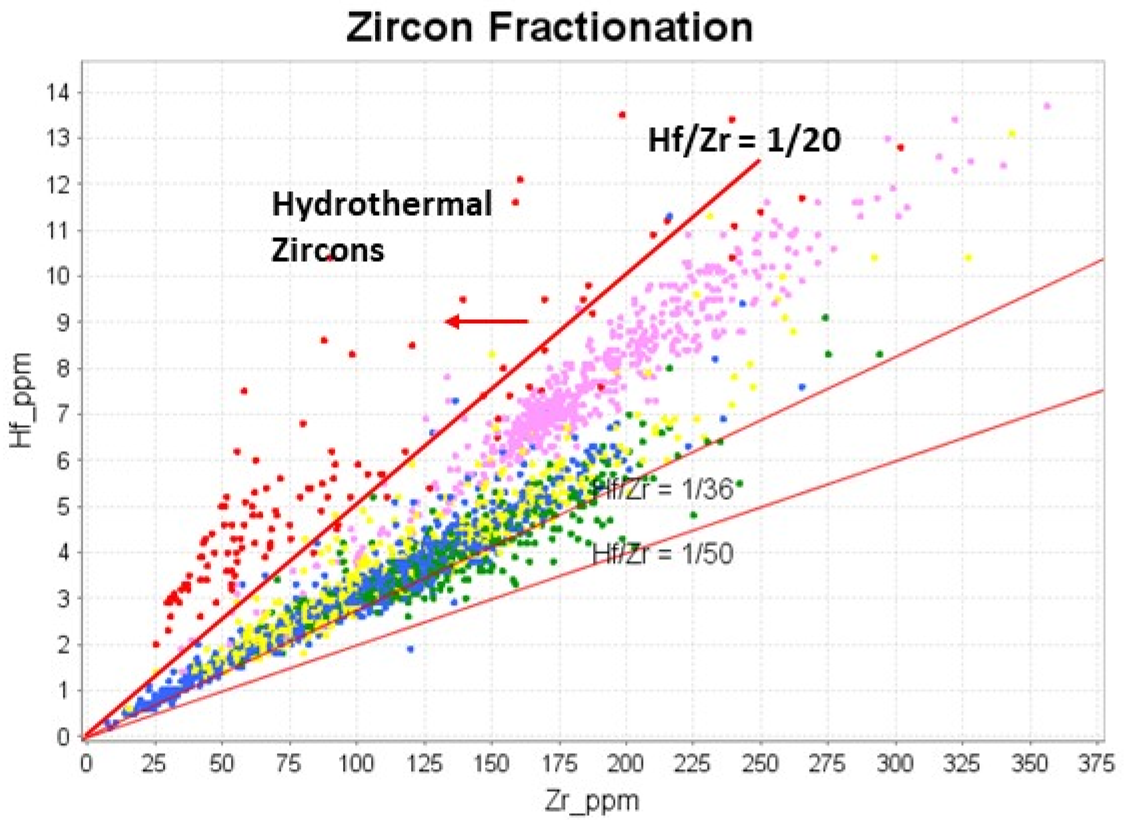


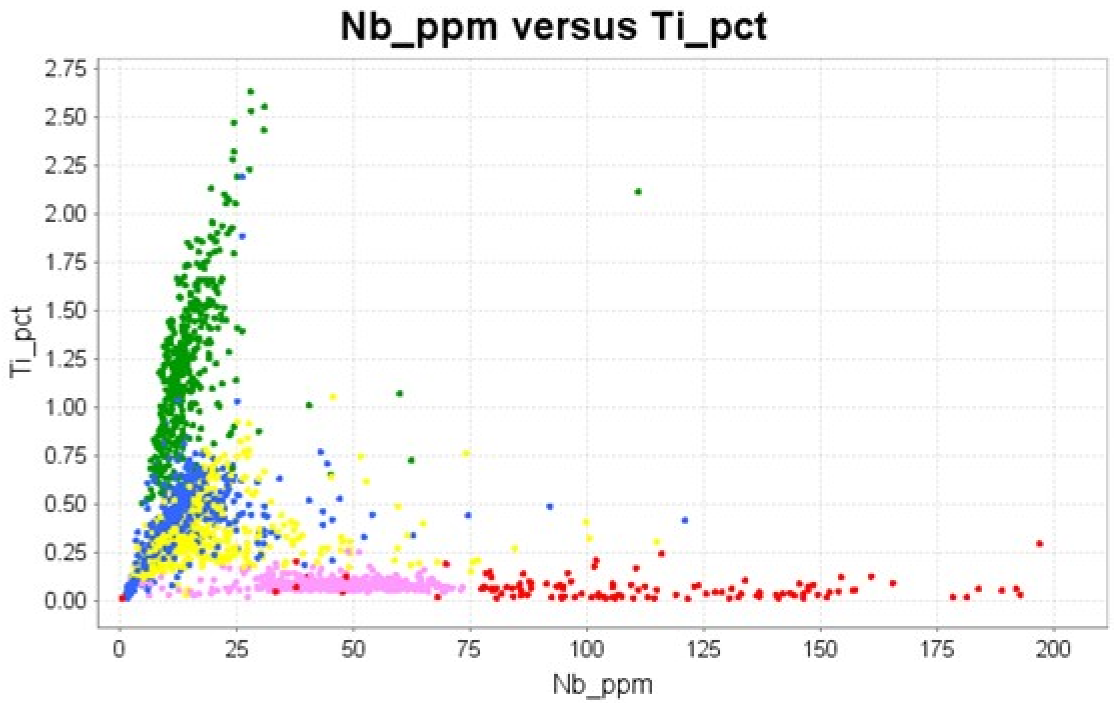
Fractionation in low pressure (crustal) hydrous melts
Zircon Zr/Hf ratio; example from a major Sn granite deposit

Most rocks have Zr/Hf = 36

Zircon fractionation at WR SiO2 > 70% Zr/Hf goes from 36 to 20

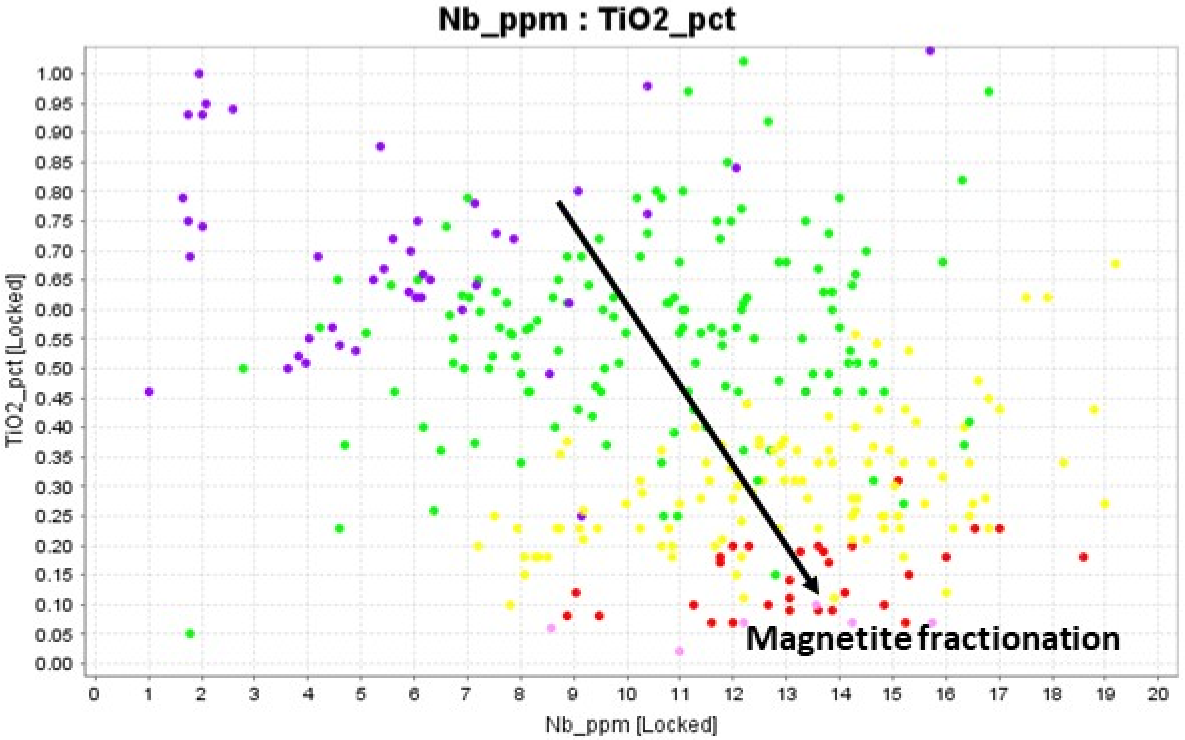
Hydrothermal zircons, eg in pegmatites and aplites Zr/Hf < 20

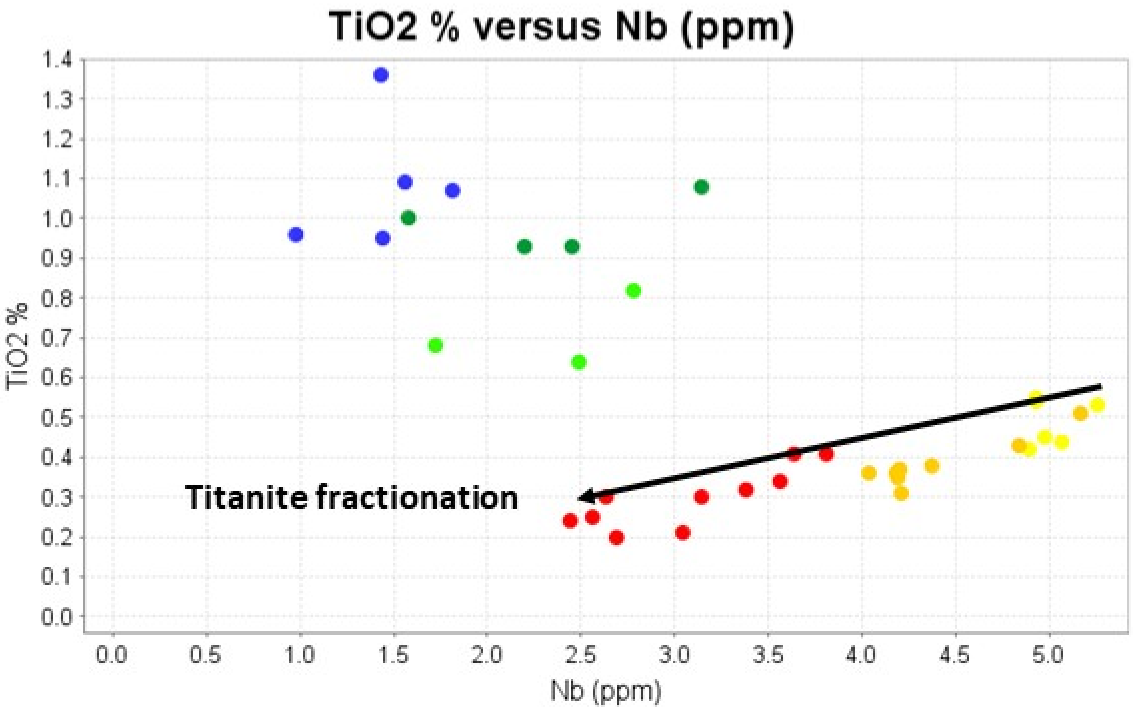




Fractionation in low pressure (crustal) hydrous melts

Ti versus Nb tells you a lot about the opaque oxide minerals. In crustal melts, Nb increases as Ti decreases.

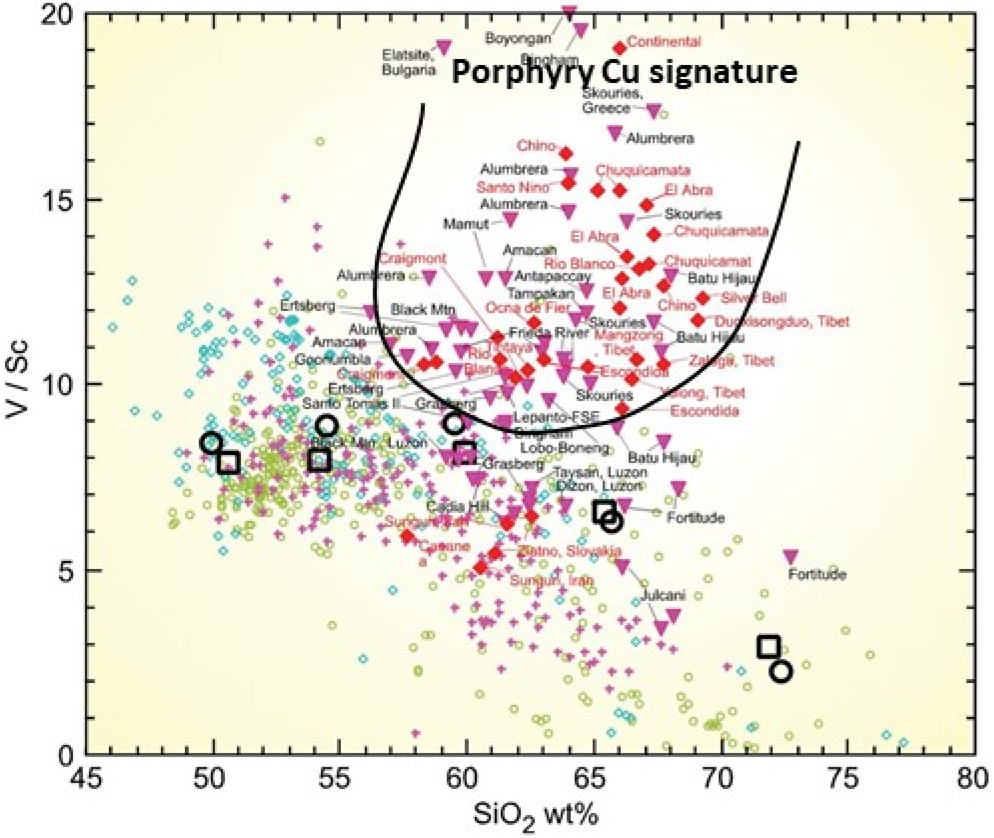


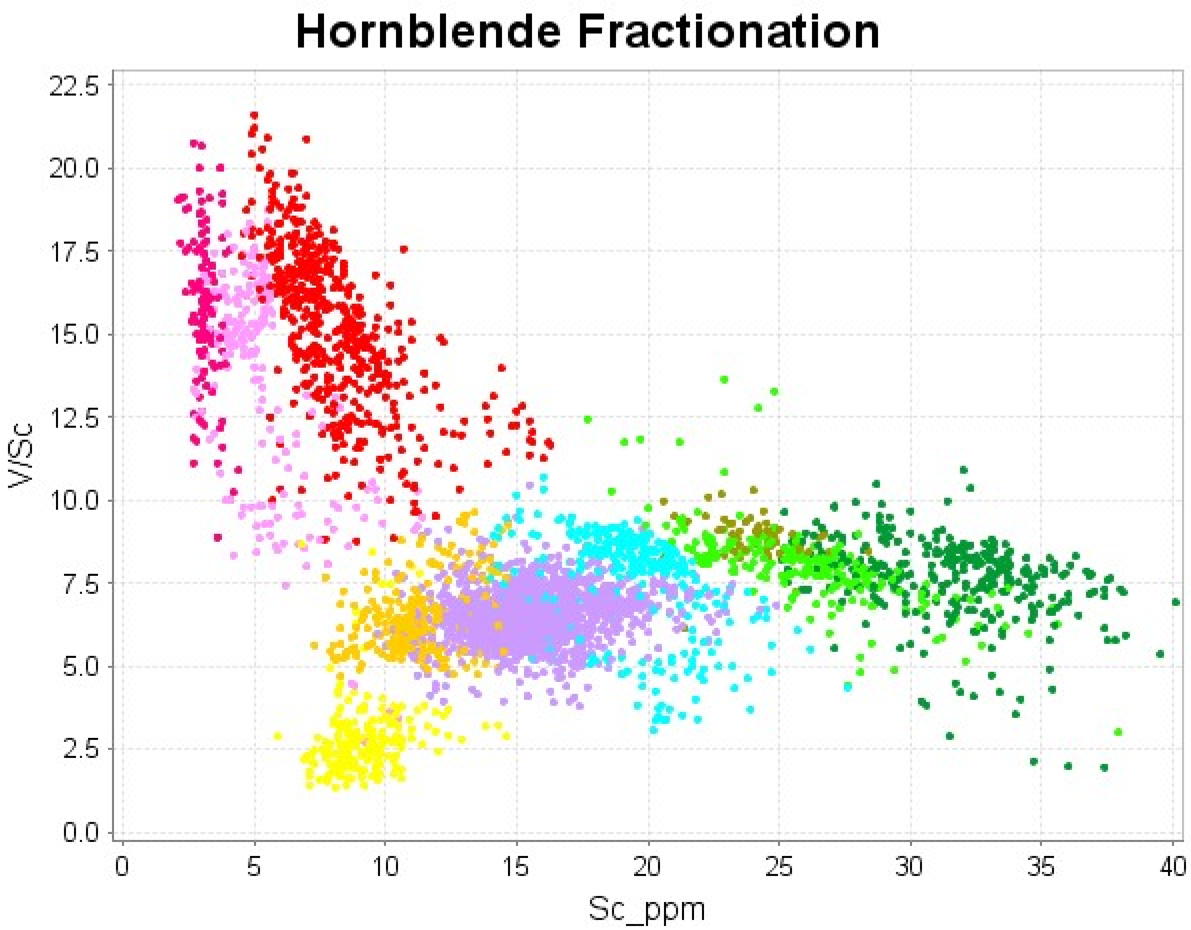


Fractionation in high pressure hydrous melts (porphyry Cu systems)

Hornblende fractionation leads to increasing V/Sc with increasing SiO2.

This is a diagnostic characteristic of magmas associated with porphyry Cu systems.





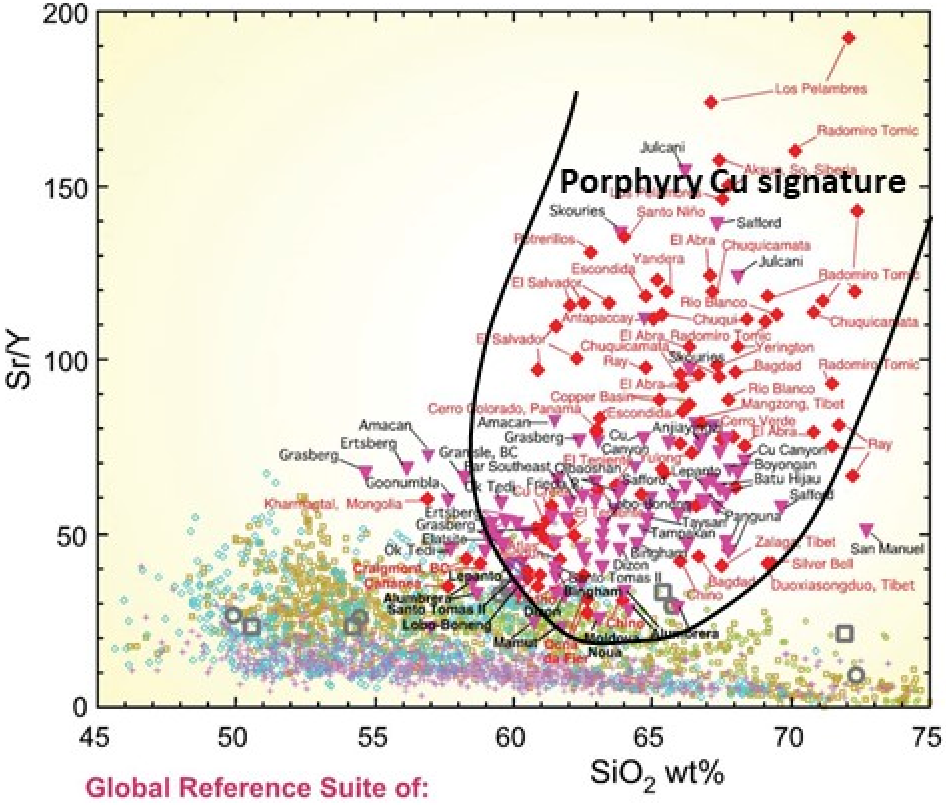
R.R. Loucks (2014) Distinctive composition of copper-ore-forming arcmagmas, Australian Journal of Earth Sciences: An International Geoscience Journal of the Geological Society of Australia, 61:1, 5-16

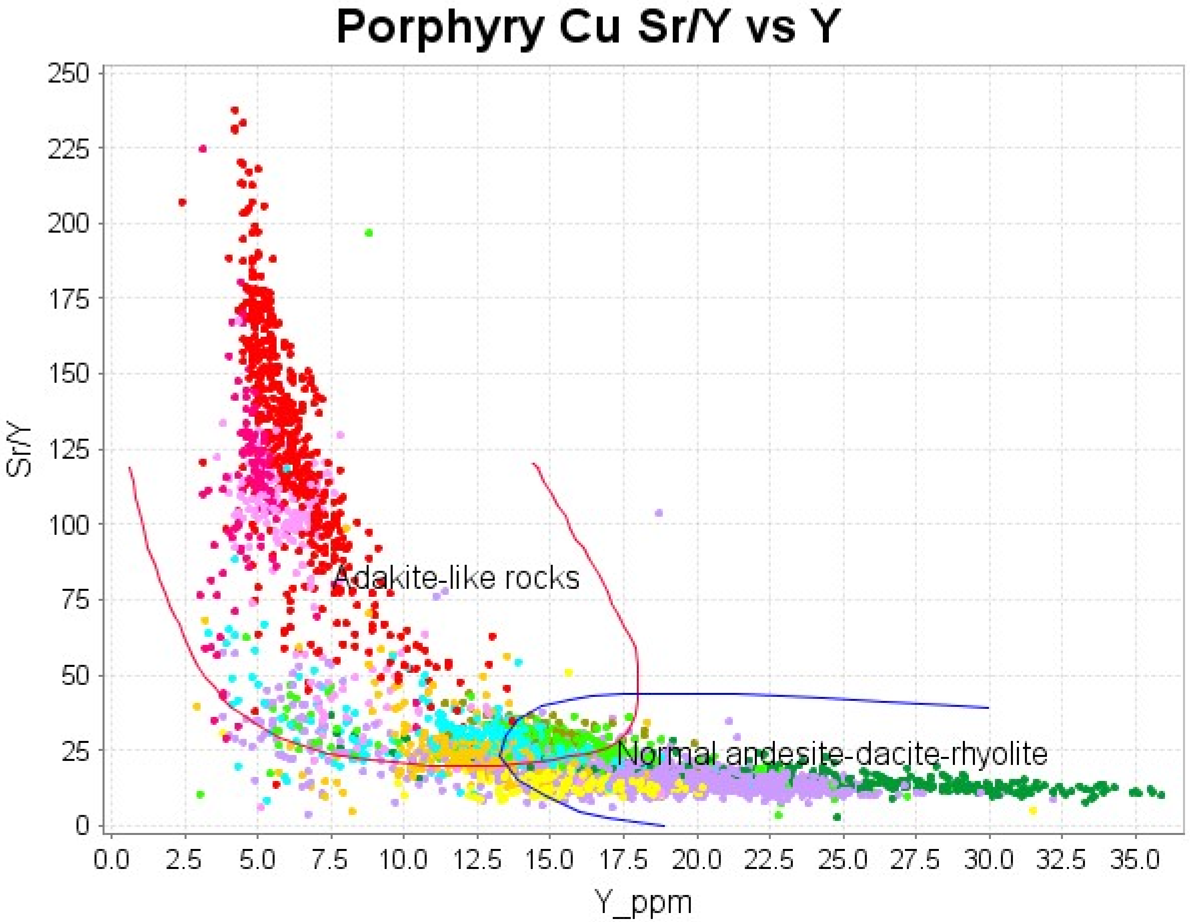
Fractionation in high pressure hydrous melts (porphyry Cu systems)

Strontium versus Yttrium

Garnet-stable source region retains Y => low Y magma

High water content lowers the plagioclase liquidus; delayed onset of plag crystallization = high Sr magma

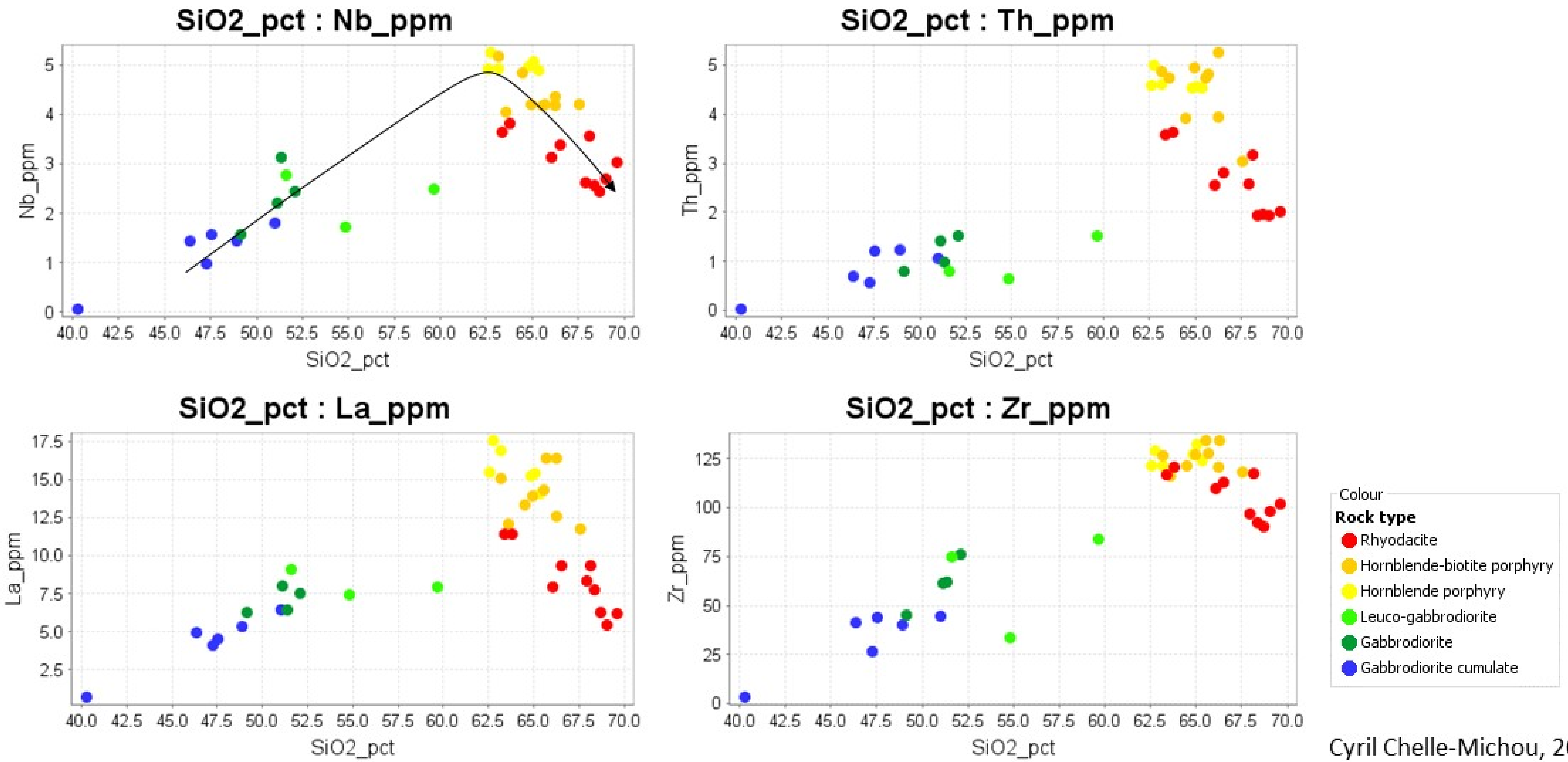




R.R. Loucks (2014) Distinctive composition of copper-ore-forming arcmagmas, Australian Journal of Earth Sciences: An International Geoscience Journal of the Geological Society of Australia, 61:1, 5-16

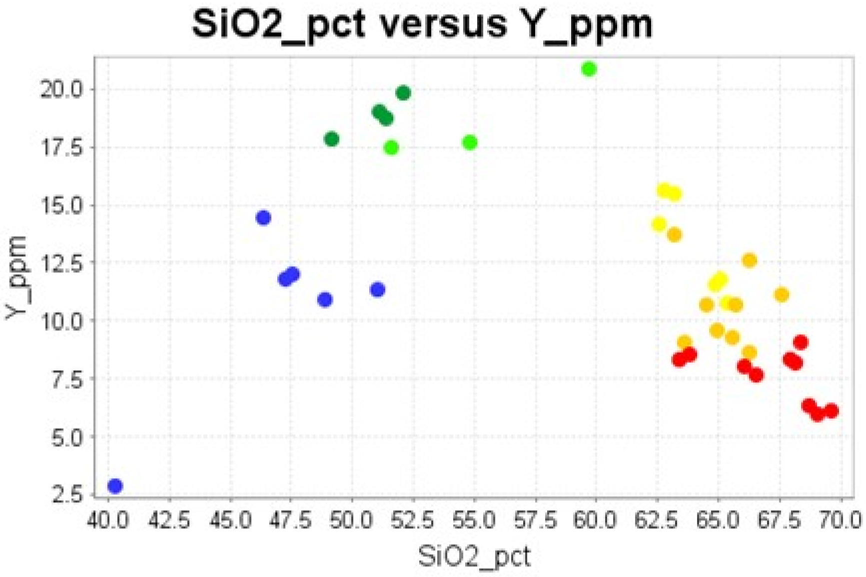
The role of titanite ($CaTiSiO_5$) in HFSE patterns in porphyry Cu systems

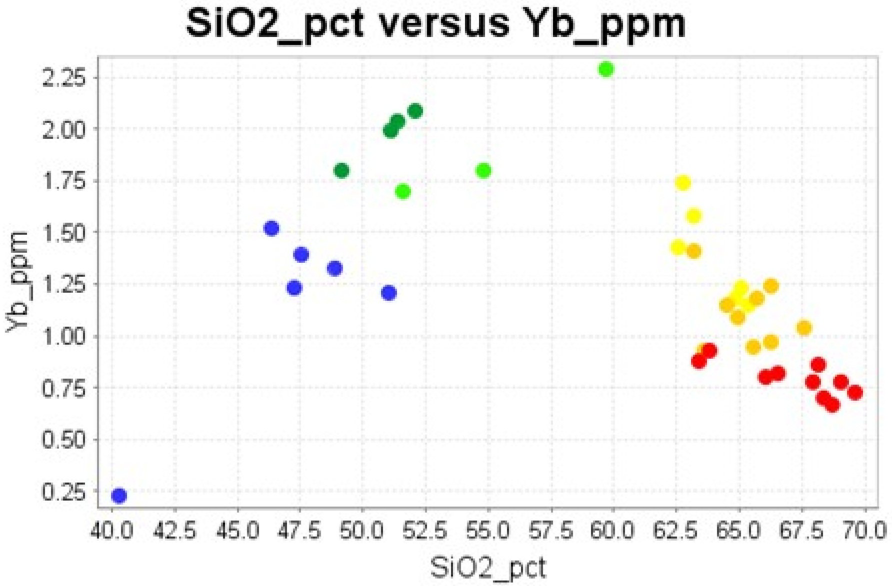
The onset of titanite crystallization in porphyry Cu magmas causes "compatible" behaviour of Nb, Th, REE's, Zr, Y and U above ~62% SiO_2

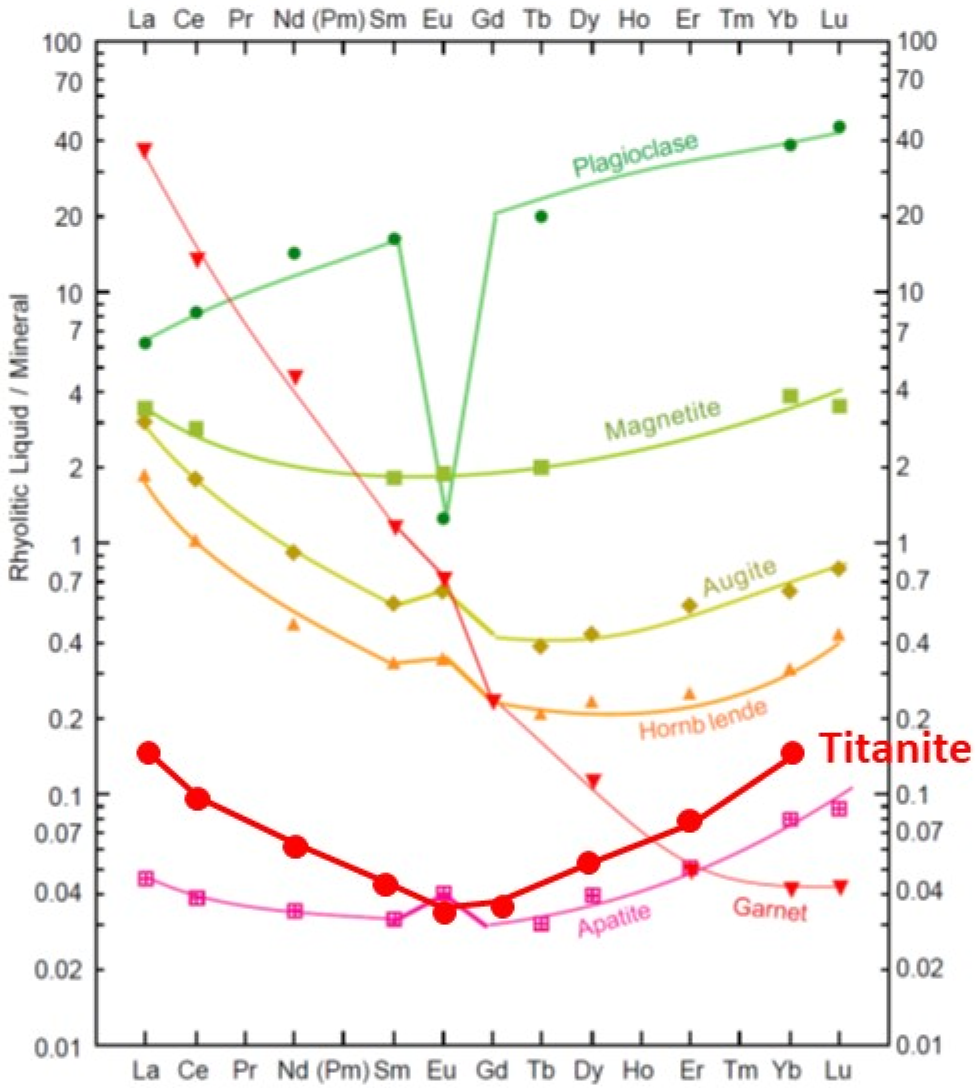


Cyril Chelle-Michou, 2013

Titanite fractionation MUST have a significant impact on whole-rock Y (equivalent to MHREE)







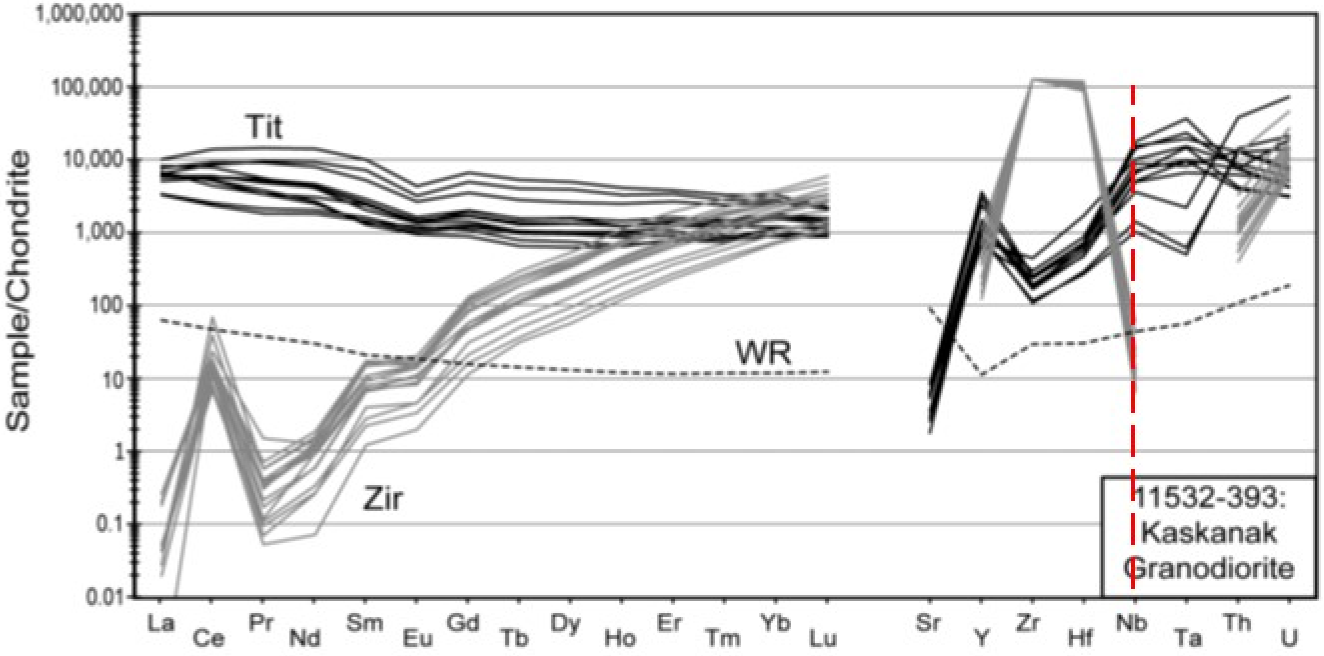
Tiepolo, M., Oberti, R. and Vannucci, R., 2002. Trace-element incorporation in titanite: constraints from experimentally determined solid/liquid partition coefficients. *Chemical Geology*, *191*(1-3), pp.105-119.

R.R. Loucks (2014) Distinctive composition of copper-ore-forming arcmagmas, Australian Journal of Earth Sciences: An International Geoscience Journal of the Geological Society of Australia, 61:1, 5-16

The role of titanite ($CaTiSiO_5$) in HFSE patterns in porphyry Cu systems

Representative REE and HFSE contents of titanite, zircon, and wholerock normalized to chondrite. Chondrite values from McDonough and Sun (1995)

Fractionation of titanite accounts for the compatibility of Nb, Ta, REE's, Th, Zr, Hf

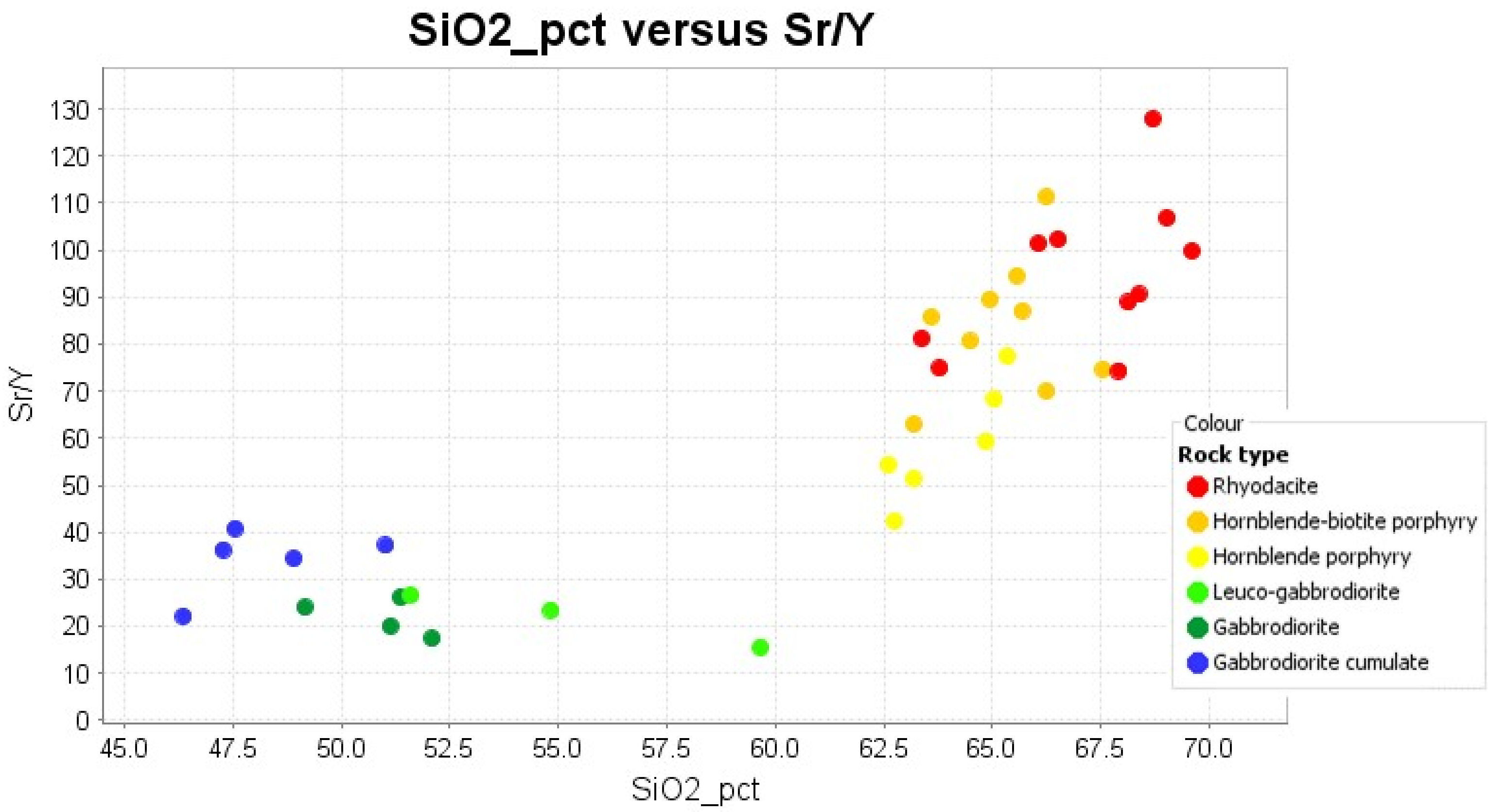


Olson, N.H., Dilles, J.H., Kent, A.J. and Lang, J.R., 2017. Geochemistry of the Cretaceous Kaskanak batholith and genesis of the Pebble porphyry Cu-Au-Mo deposit, southwest Alaska. American Mineralogist: Journal of Earth and Planetary Materials, 102(8), pp.1597-1621.

The role of titanite ($CaTiSiO_5$) in HFSE patterns in porphyry Cu systems

The increase in Sr/Y as porphyry Cu magmas evolve is a result of titanite fractionation rather than the effect of Y retention in garnet at the source region.

The trend of increasing Sr/Y in porphyry Cu magmas is commonly interpreted to result from increasing depth (pressure) at the source of melting.



Cyril Chelle-Michou, 2013

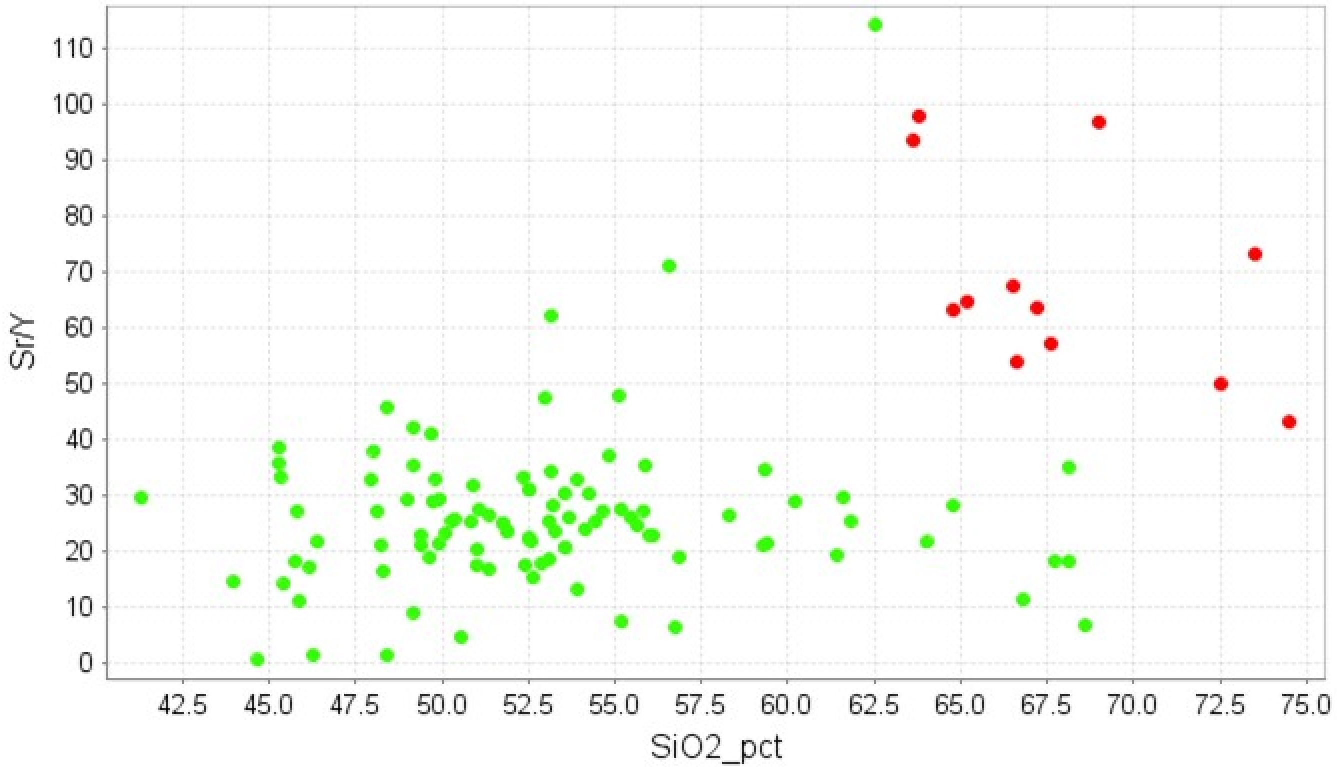
The role of titanite ($CaTiSiO_5$) in HFSE patterns in porphyry Cu systems

Sr/Y patterns in different porphyry Cu environments all look the same!!

Oceanic Island Arc porphyries, (thin crust)
Andean porphyries
SW USA, (thick crust)
Porphyry Mo (very thick crust)

This example is from the Indonesian Arc
Red = hornblende diorite (porphyry Cu)
Green = basaltic andesite country rock

Indonesian Porphyry Cu; SiO2 vs Sr/Y

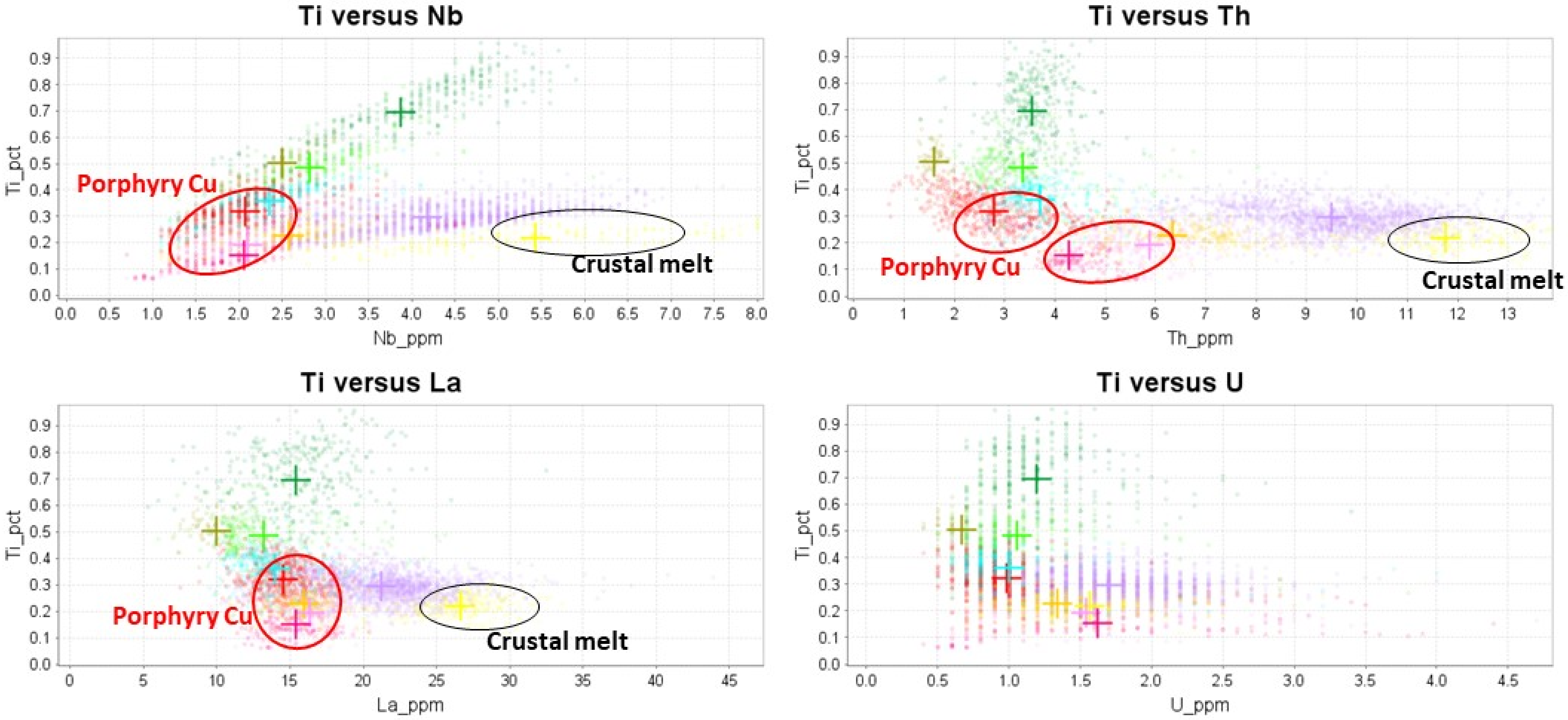


Fractionation in high pressure hydrous melts (porphyry Cu systems)

High Ca magma favours titanite fractionation.

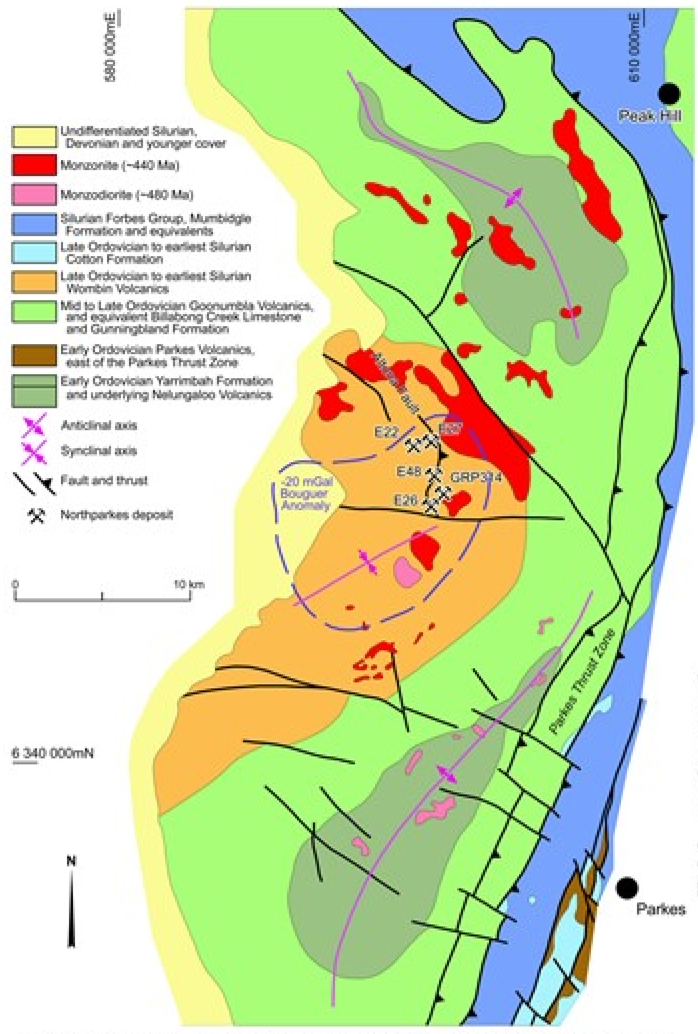
Titanite fractionation removes Nb, Th, Zr, REE's and U from the melt.

Porphyry Cu magmas typically have 0.2 to 0.4% Ti, 2 to 4ppm Th, 2 to 4ppm Nb



Application

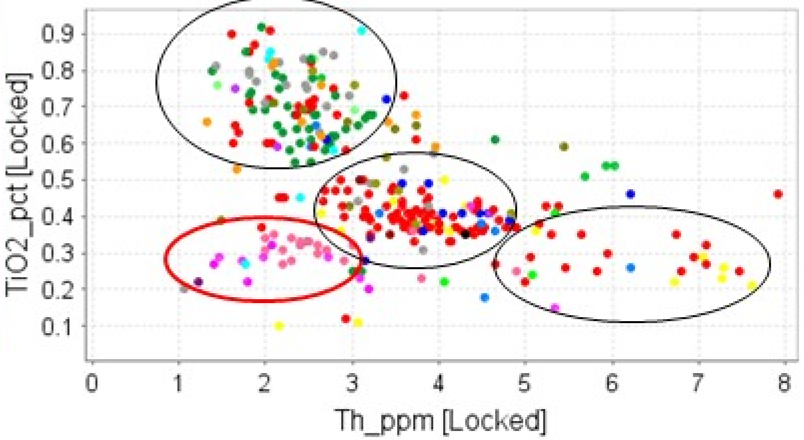
In a porphyry district, sample all of the mapped intrusions and classify them geochemically. Identify the prospective suite on your maps. Note there are 4 different magma suites in this data.



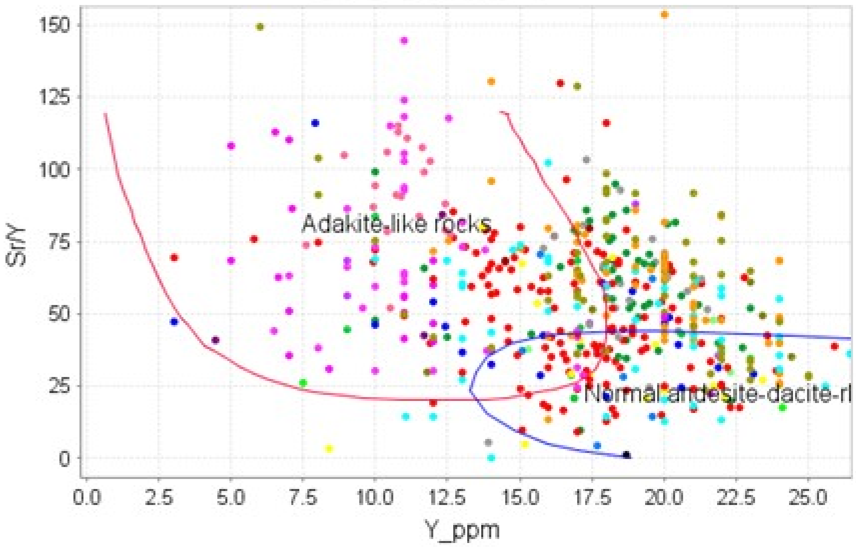
Geological setting of the Goonumbla Volcanic Complex, Macquarie Arc, Central Western New South Wales. After Pacey *et al.* (2019), Owens *et al.* (2017), Simpson *et al.* (2005), Lickfold *et al.* (2003), Raymond *et al.* (1995).

Ralph Porter; http://www.portergeo.com.au/

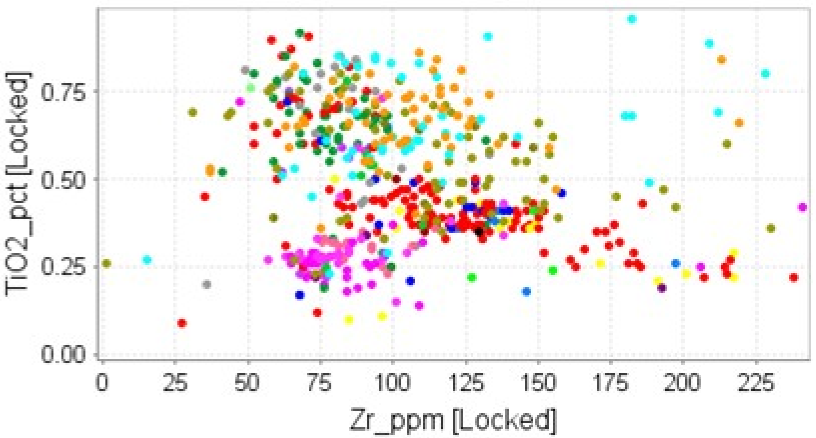
Th_ppm : TiO2_pct



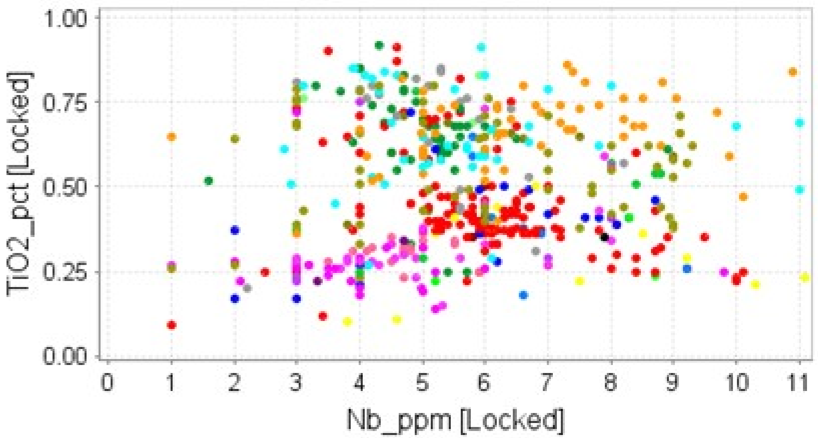
Sr/Y versus Y



Zr_ppm : TiO2_pct



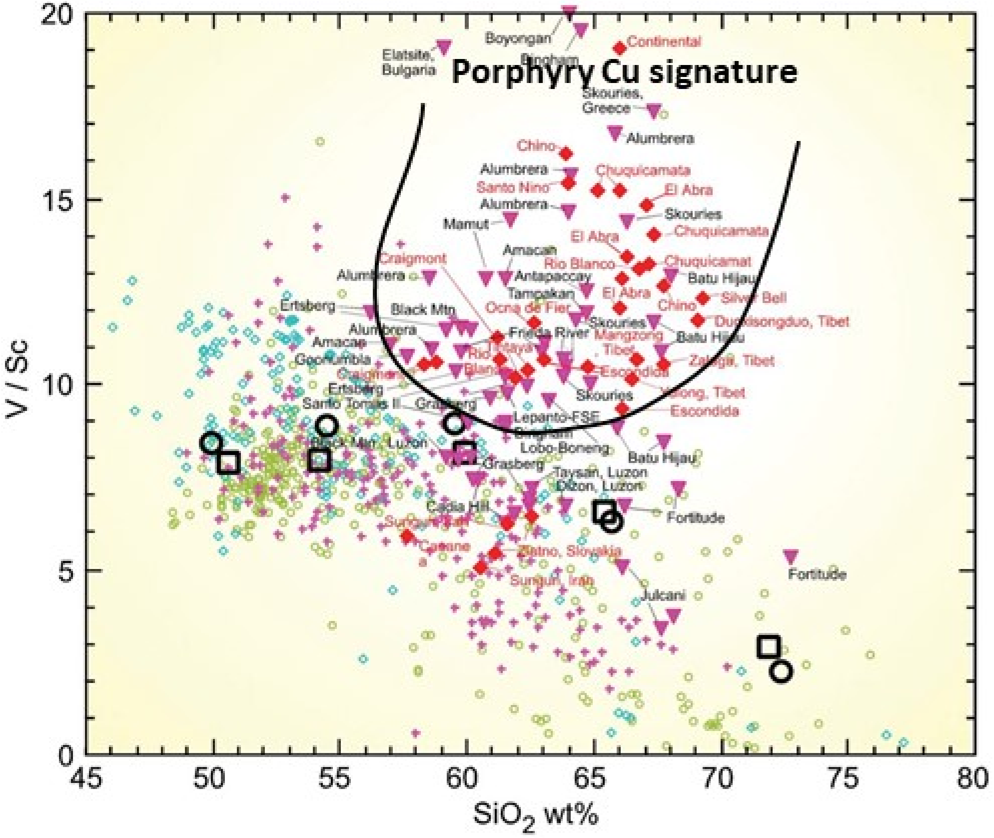
Nb_ppm : TiO2_pct

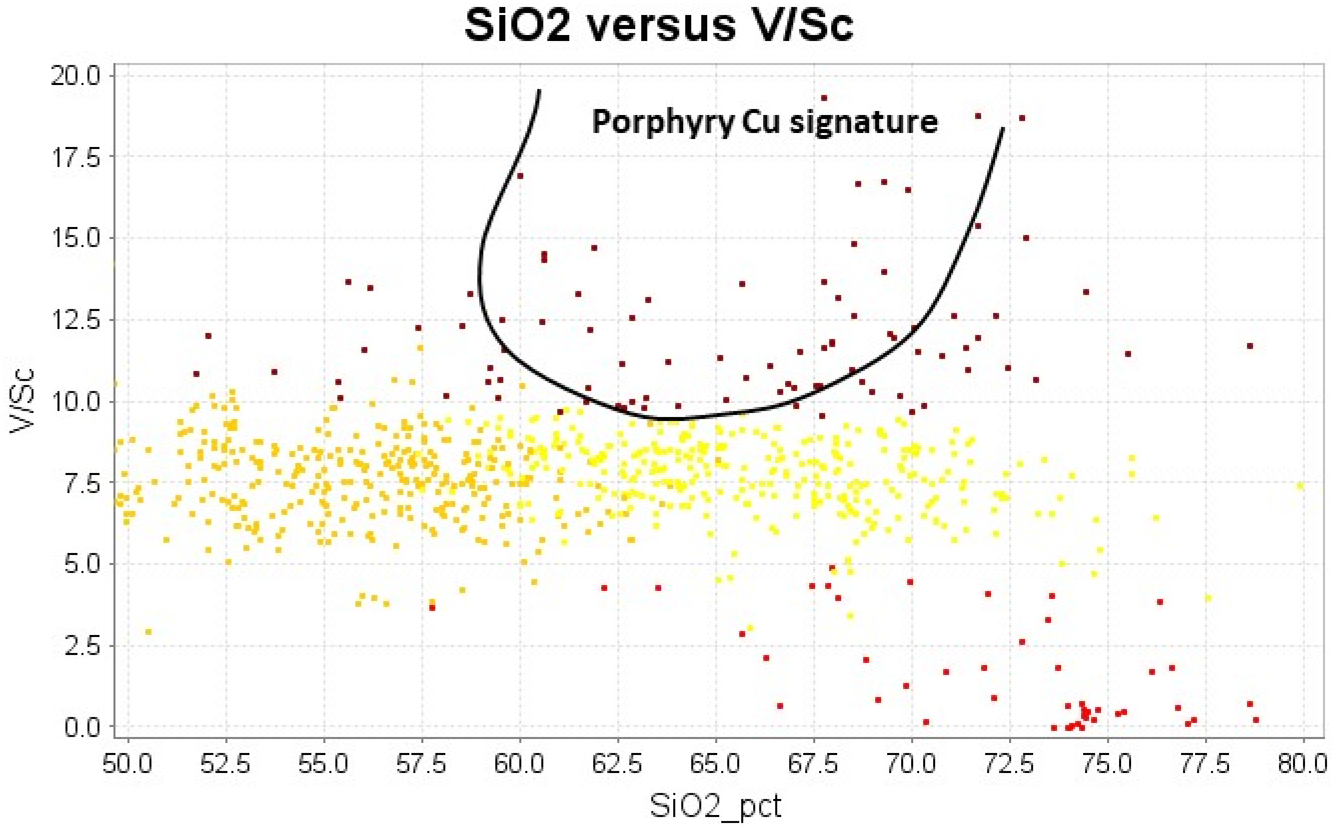


Pacey, A., Wilkinson, J.J., Owens, J., Priest, D., Cooke, D.R. and Millar, I.L., 2019. The anatomy of an alkalic porphyry Cu-Au system: geology and alteration at Northparkes Mines, New South Wales, Australia. Economic Geology, 114(3), pp.441-472.

Fractionation in Archean Granites

Among the Archean rocks there are signatures of both magnetite fractionation or hornblende fractionation.
Increasing V/Sc with increasing SiO2 in NOT unique to porphyry Cu systems.



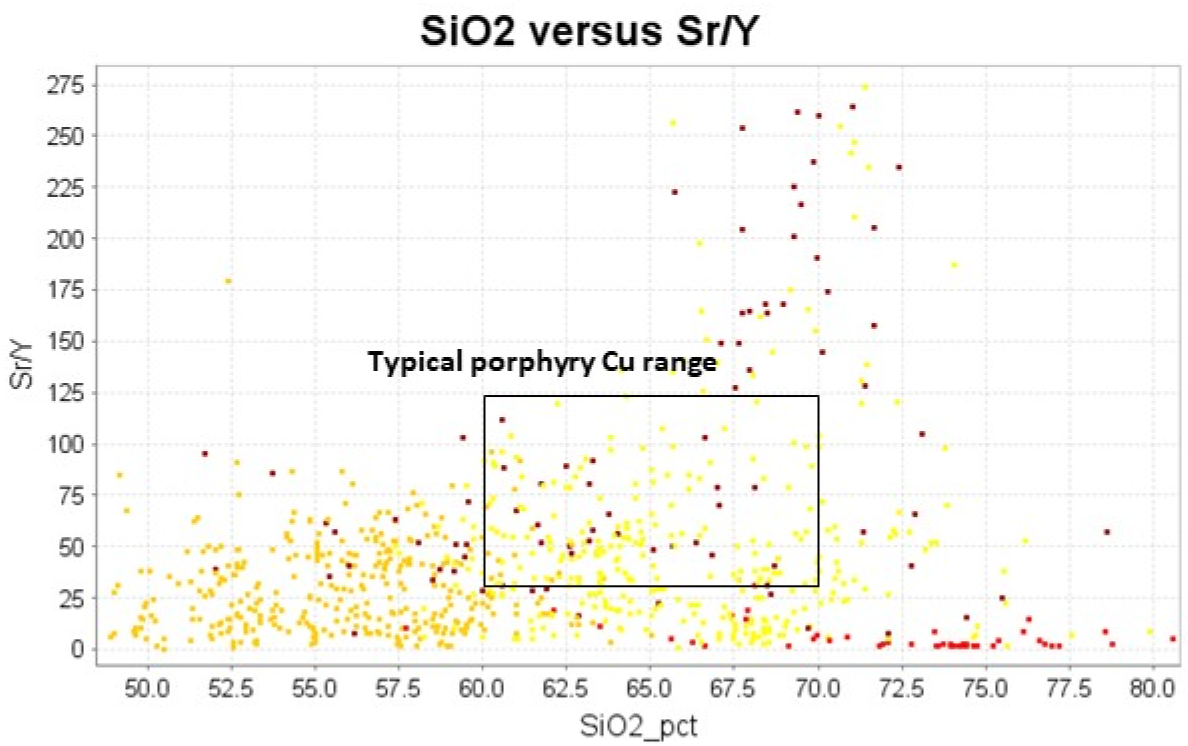


R.R. Loucks (2014) Distinctive composition of copper-ore-forming arcmagmas, Australian Journal of Earth Sciences: An International Geoscience Journal of the Geological Society of Australia, 61:1, 5-16

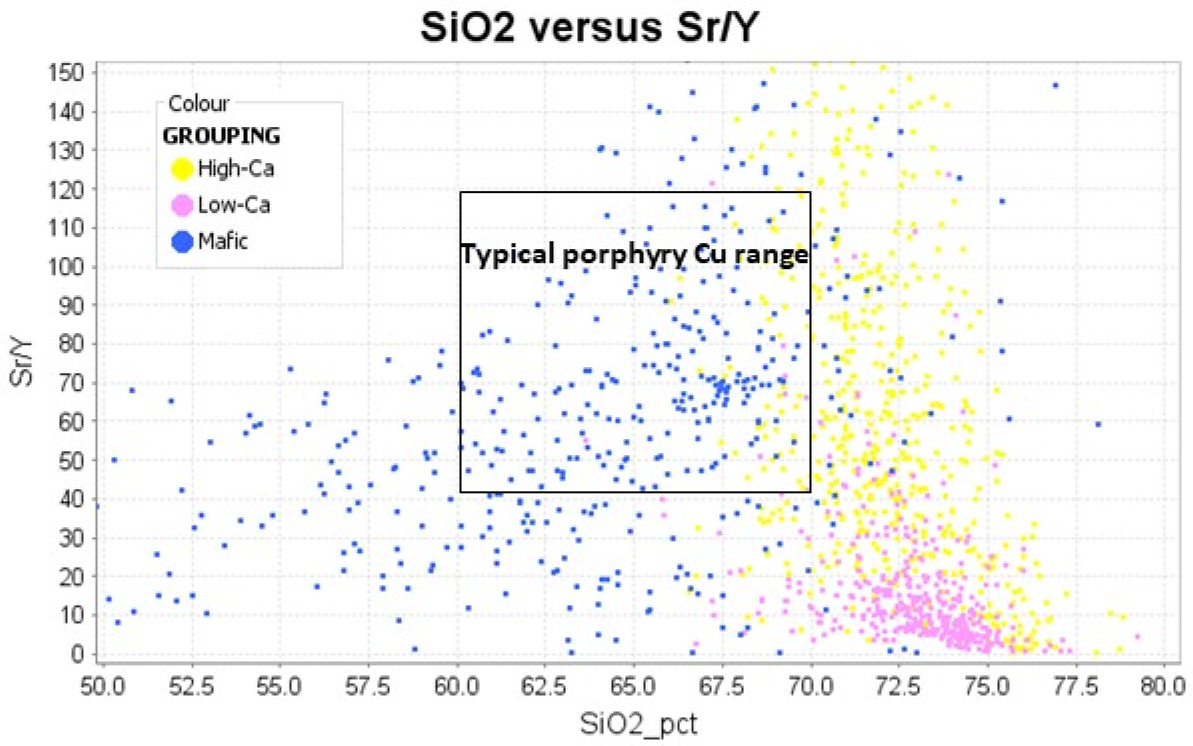
Fractionation in Archean Granites

Many Archean granites show the high Sr/Y signature found in porphyry Cu systems; indicative of high pressure melting of a hydrous source region.

Cassidy and Champion; High Ca granite = high Sr/Y, Low Ca granite = low Sr/Y



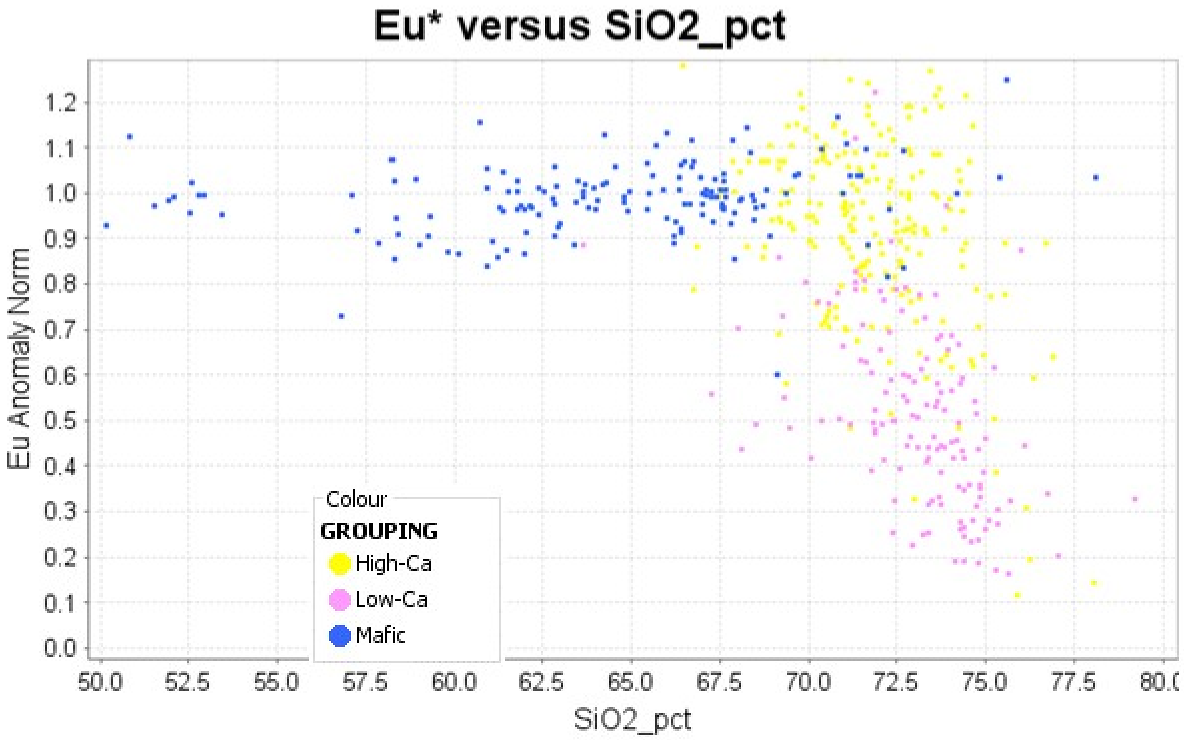
Smithies, RH and Lowrey, JR 2020, Eastern Goldfields greenstone geochemical barcoding project: notes to accompany 2020 data release: Geological Survey of Western Australia, Record 2020/6, 4p

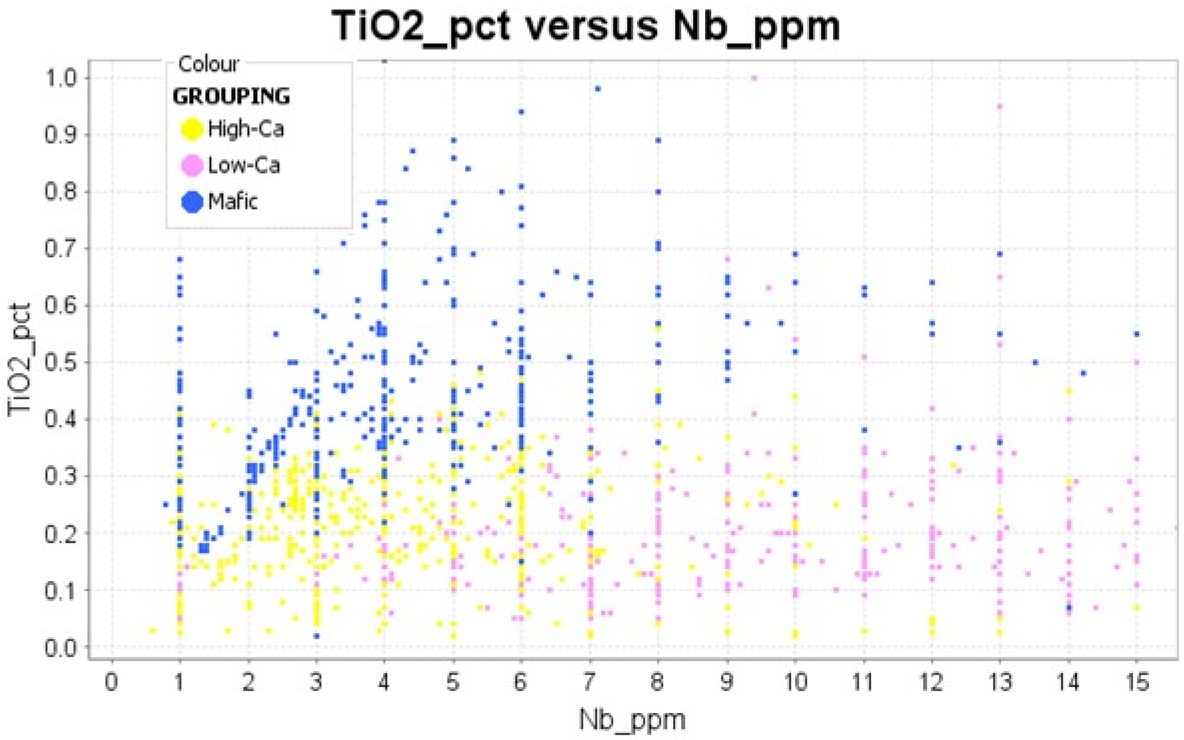


AMIRA P482. Kevin Cassidy and Dave Champion, Yilgarn Granites

Fractionation in Archean Granites

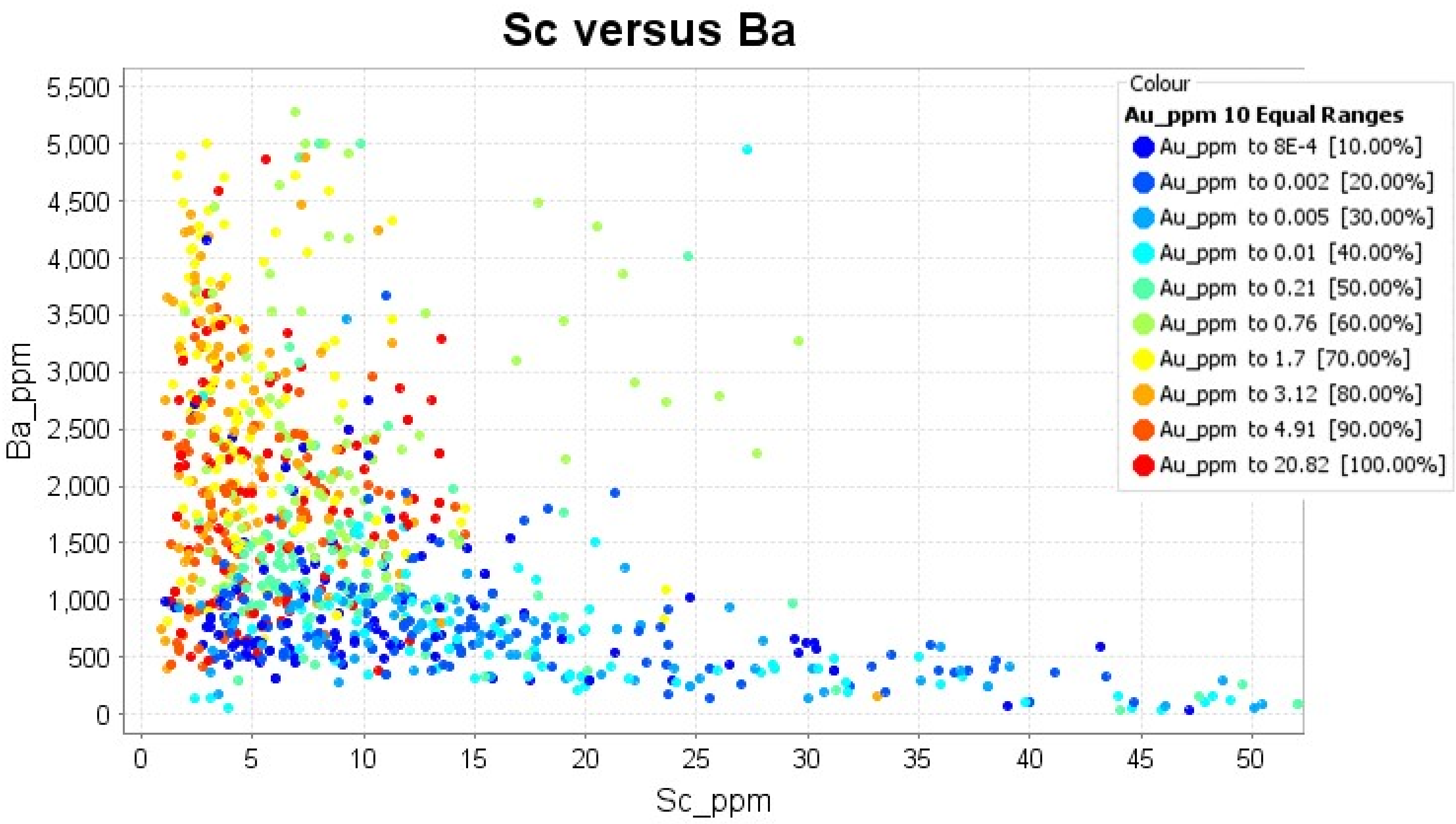
High high Sr/Y granite has NOT fractionated plagioclase and has low abundances of Nb, Th, Zr, REE's, U etc.
Low Sr/Y granite shows incompatible behaviour of HFSE's
Titanite fractionation; same pattern as in porphyry Cu magmas.





Fractionation in Archean Granites

Very distinct spatial association of hornblende diorites with gold deposits, where those diorites have fractionated hornblende, titanite, but NOT plagioclase, AND where the magmas are sourced from a metasomatized mantle. Signature of this is Ba>1000ppm.



Eastern Goldfields; >20 diorite intrusions with 1moz to 40moz Au at grades of 0.2 to 0.5ppm.

- Very sulfur-rich!!
- Intrinsically Au-rich
- Distinct trace element signatures
- Partial melts of metasomatised mantle,

Beta Porphyry, Kambalda. Pyrite +/- anhydrite.
Mean gold grade 0.37ppm Au

Santa Anna Trondhjemite, Kambalda..
Mean gold grade 0.5ppm Au

Fractionation in Yilarn Granites

Very distinct spatial association of hornblende diorites with gold deposits.

Low-Ca granites

Low pressure mid-crustal melting/fractionation

- High K melt
- Low Ca-Sr
- Decreasing Sr/Y with increasing SiO_2
- Eu* anomaly
- Decreasing V/Sc
- Incompatible behaviour of REE's, Nb, Th, Zr, U

High-Ca granites

High pressure melting/fractionation of oxidized hydrated mafic

- High Ca-Sr melt
- Increasing Sr/Y with increasing SiO_2
- No Eu* anomaly
- Increasing V/Sc
- Compatible behaviour of REE's, Nb, Th, Zr, U

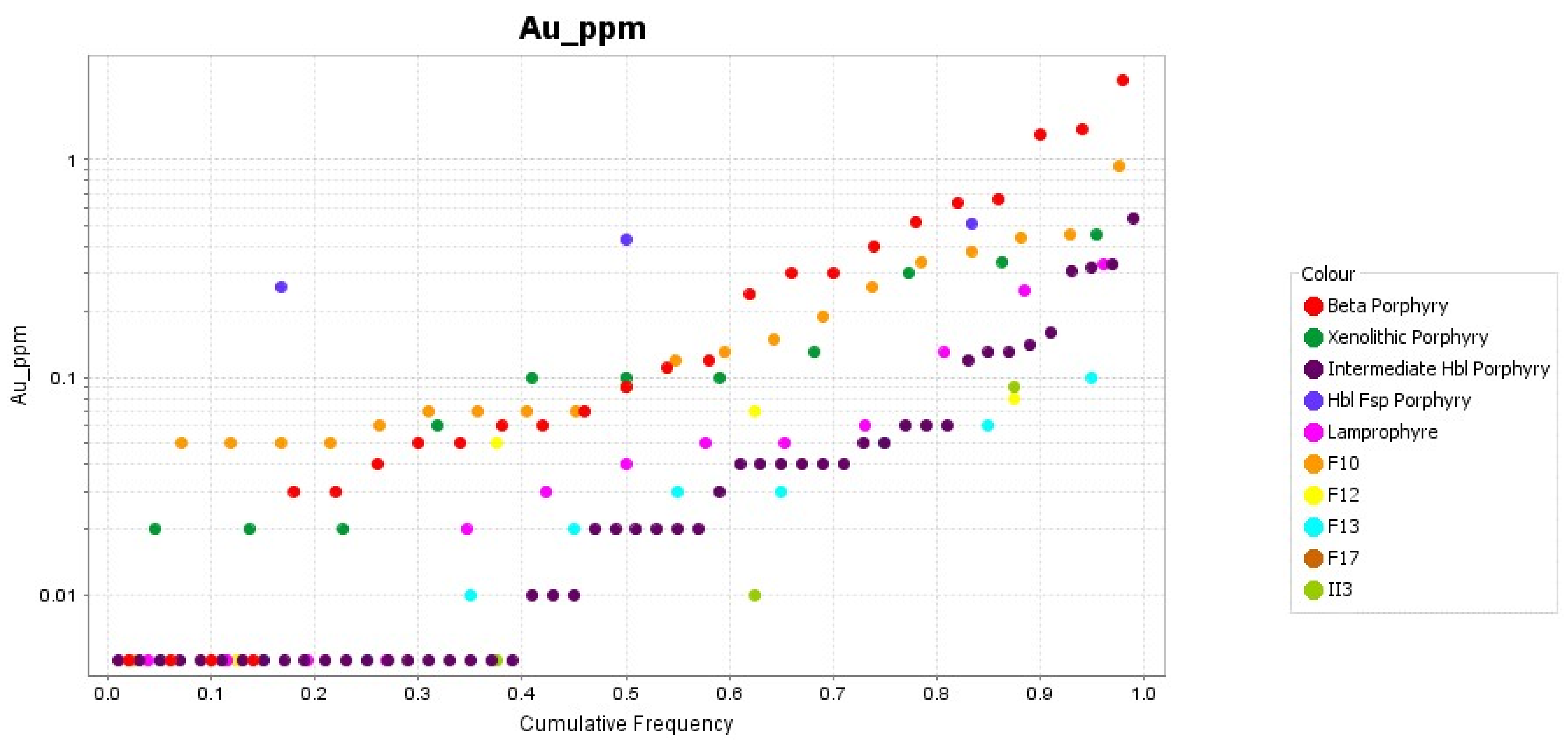
Alkalic (Syenites)

Low degree partial melting of metasomatized source

- High K-Na melt
- High Sr and Ba, but also high Y
- No Eu* anomaly
- Very high V/Sc
- Strongly enriched in REE's, Nb, Th, Zr, U
- Zr/Hf commonly up to 50

Yilgarn Granites

diorite intrusions with 1moz to 40moz Au at grades of 0.2 to 0.5ppm.

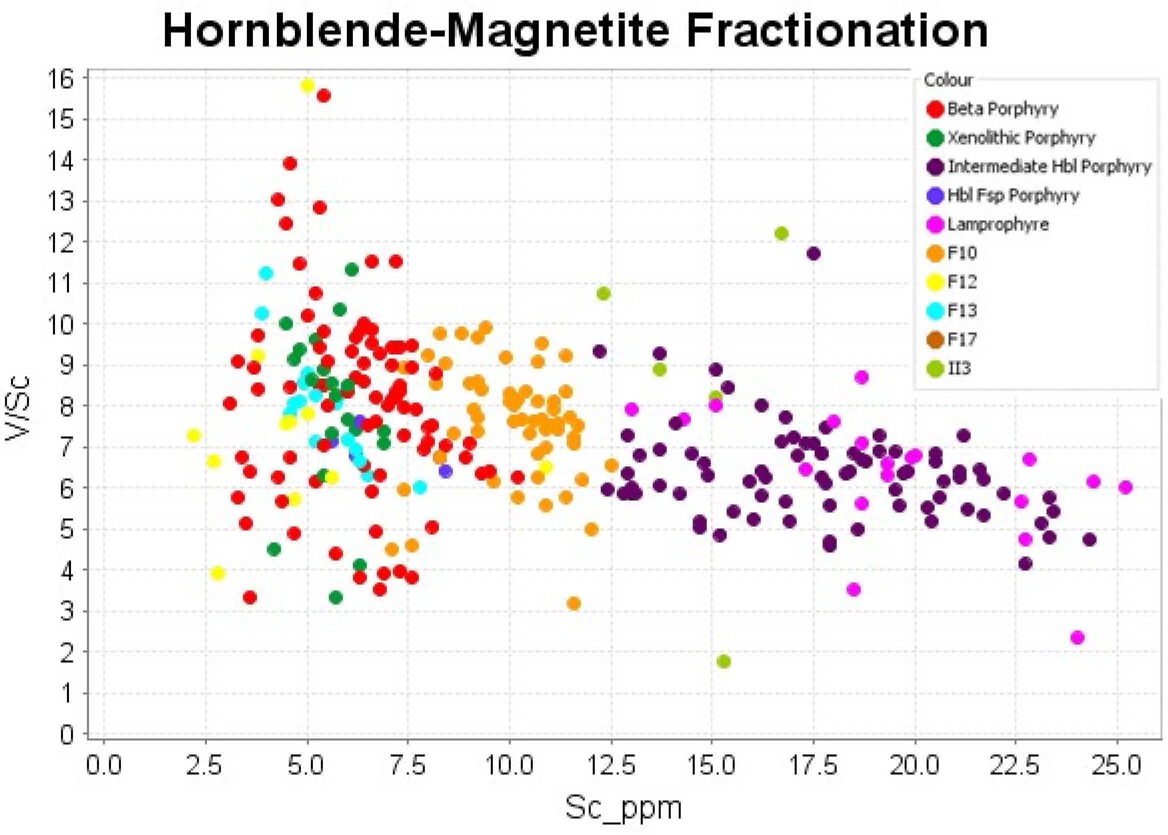


Compare Yilgarn Granites with porphyry Cu magmas

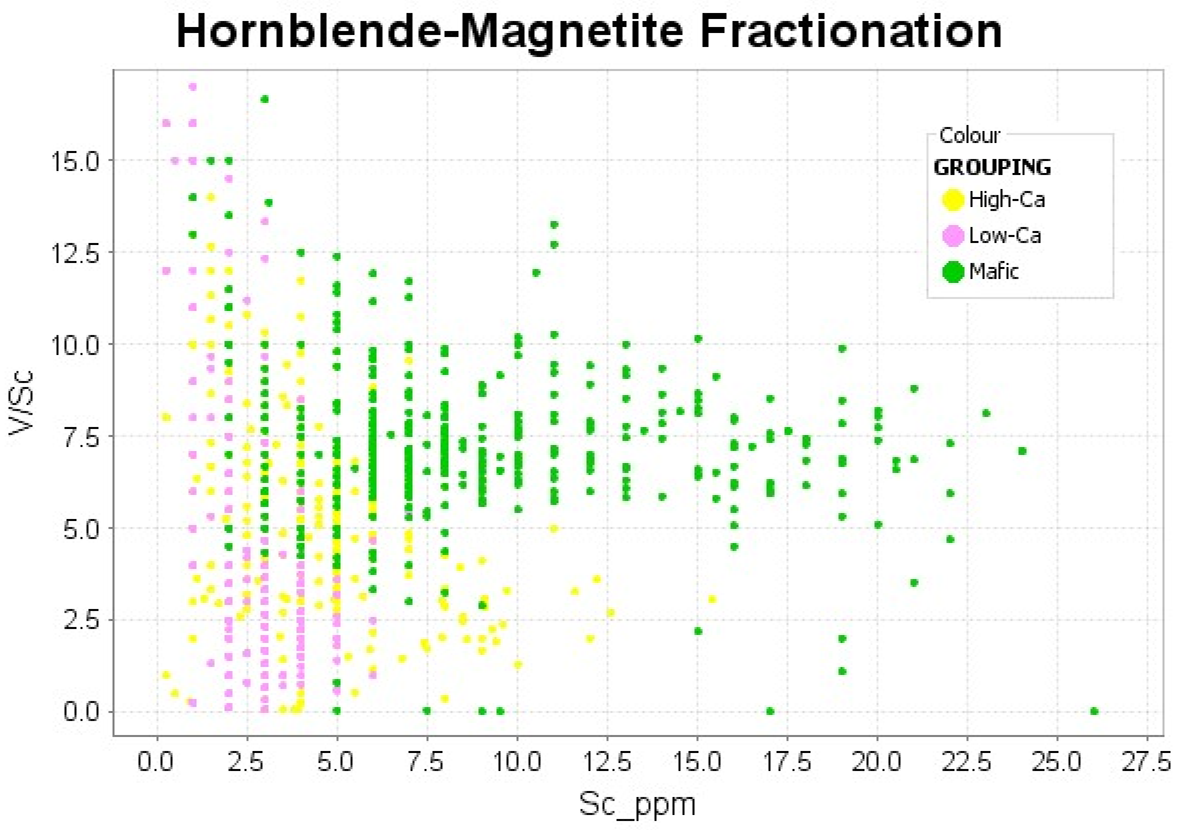
Low Ca-granites have declining V/Sc; magnetite fractionation

Some high Ca-granites have increasing V/Sc; hornblende fractionation

Beta porphyry (red) is a mineralized intrusion at St Ives.



Dave Champion, Geoscience Australia, St Ives porphyry study, 2008



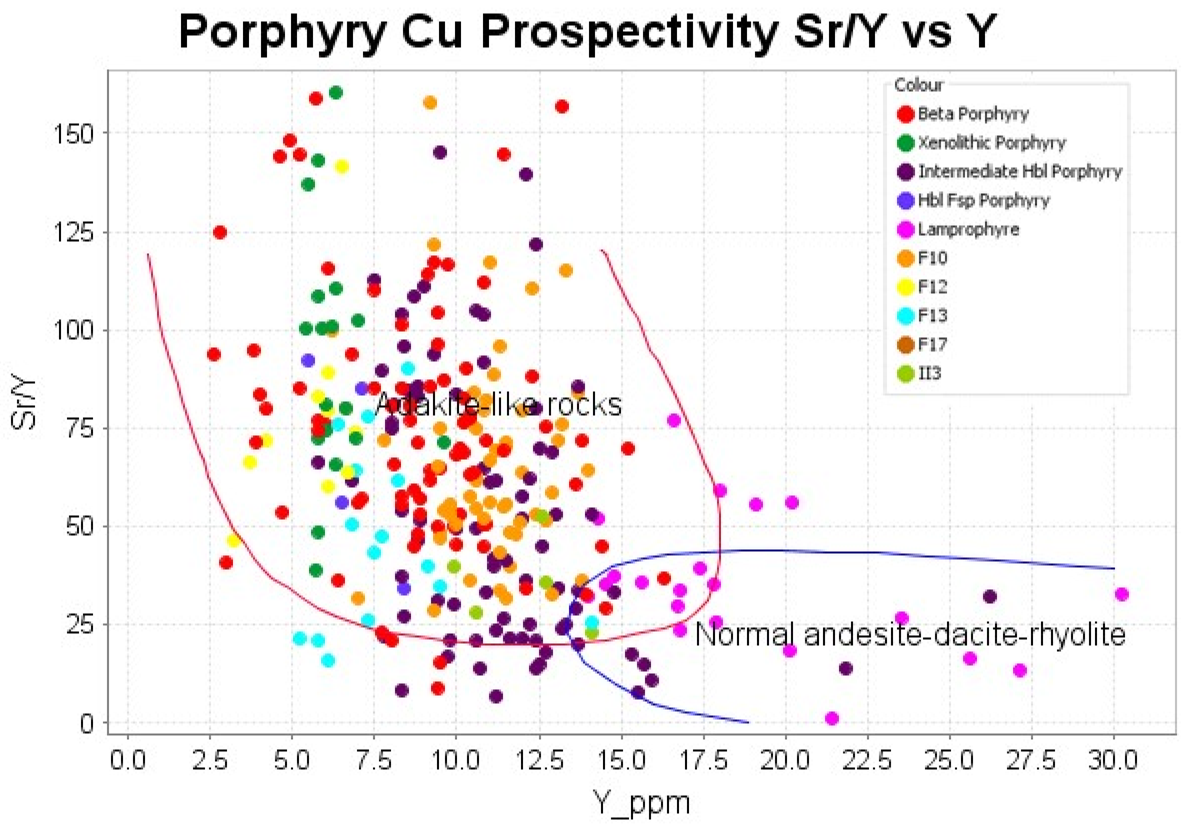
AMIRA P482. Kevin Cassidy and Dave Champion, Yilgarn Granites

Compare Yilgarn Granites with porphyry Cu magmas

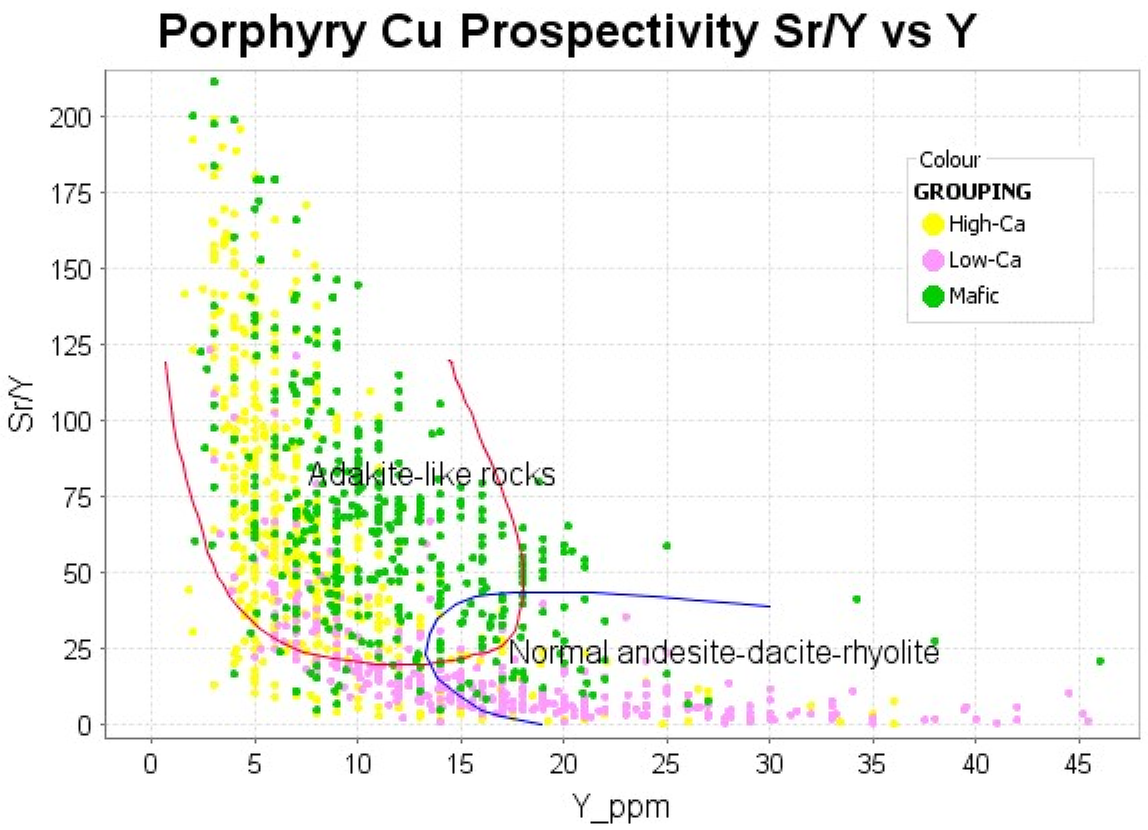
Low Ca-granites have low Sr/Y (Sr declines with plagioclase fractionation)

High Ca-granites have increasing Sr/Y (titanite fractionation before plagioclase crystallization)

Beta porphyry (red) is a mineralized intrusion at St Ives.



Dave Champion, Geoscience Australia, St Ives porphyry study, 2008

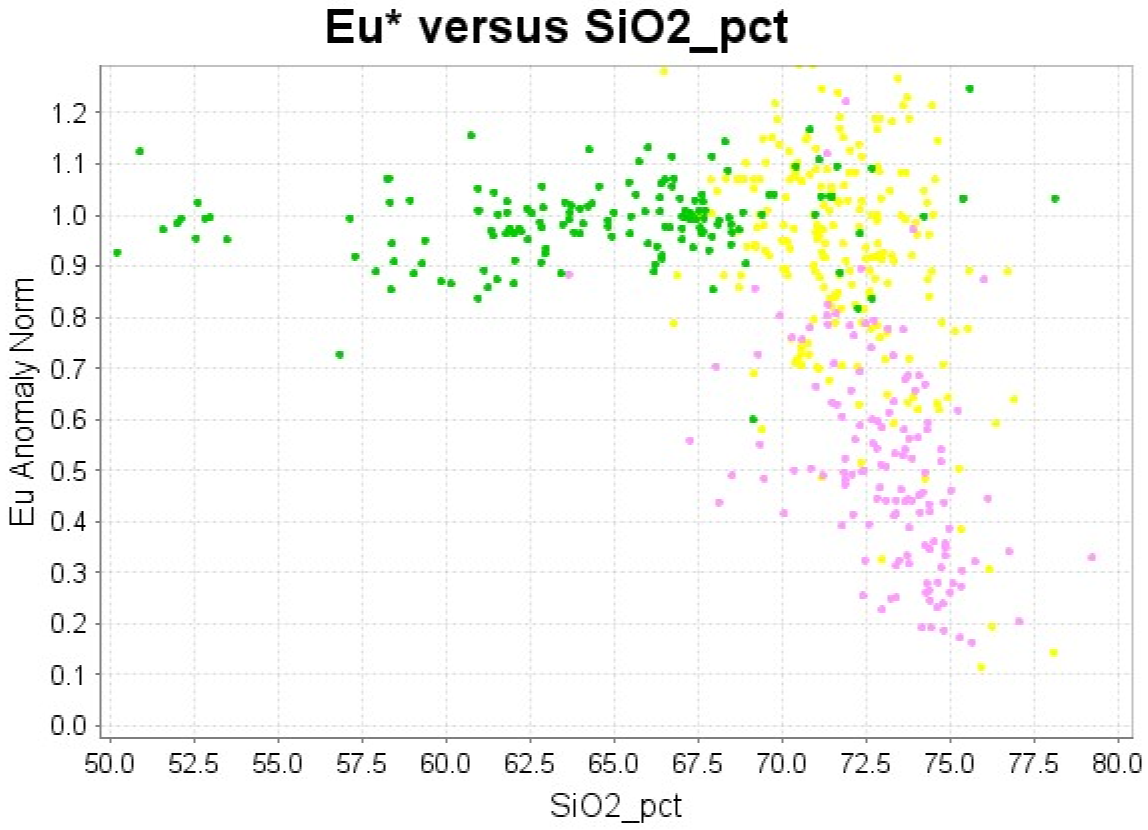


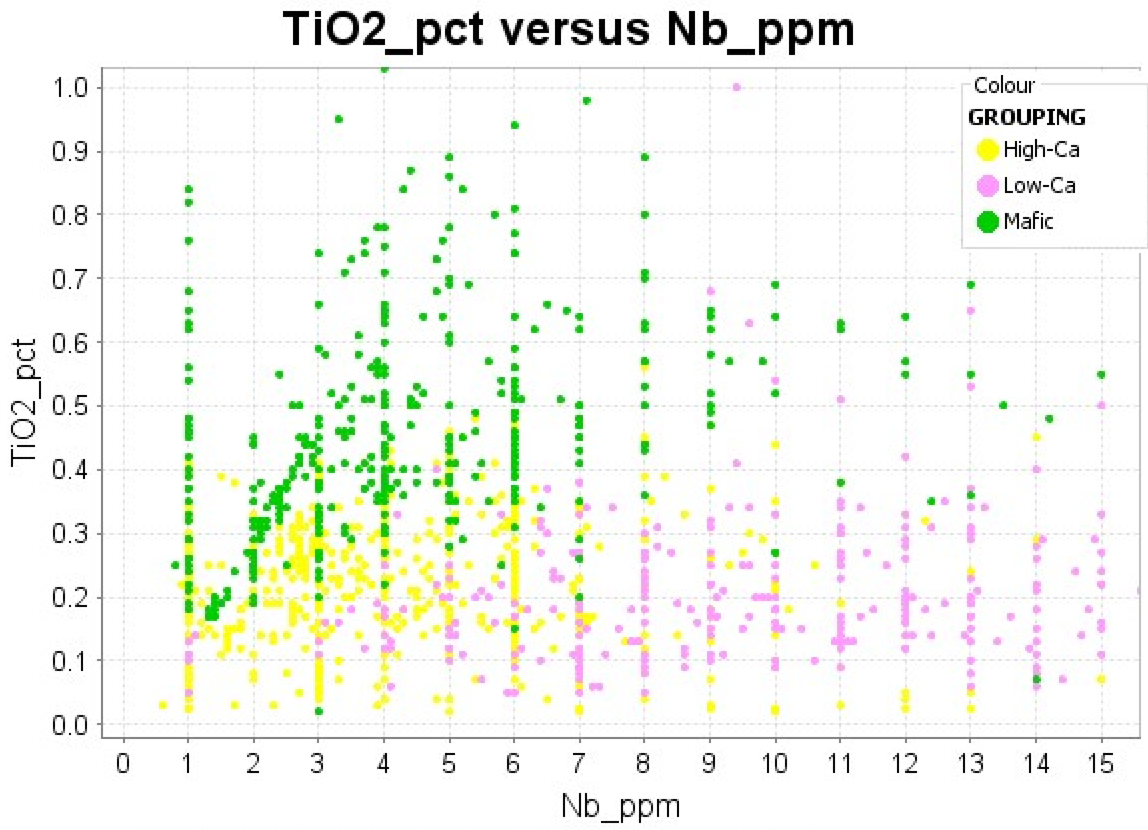
AMIRA P482. Kevin Cassidy and Dave Champion, Yilgarn Granites

Compare Yilgarn Granites with porphyry Cu magmas

Low Ca-granites have negative Eu anomaly AND incompatible HFSE's

High Ca-granites have NO Eu anomaly AND compatible HFSE's (titanite fractionation)



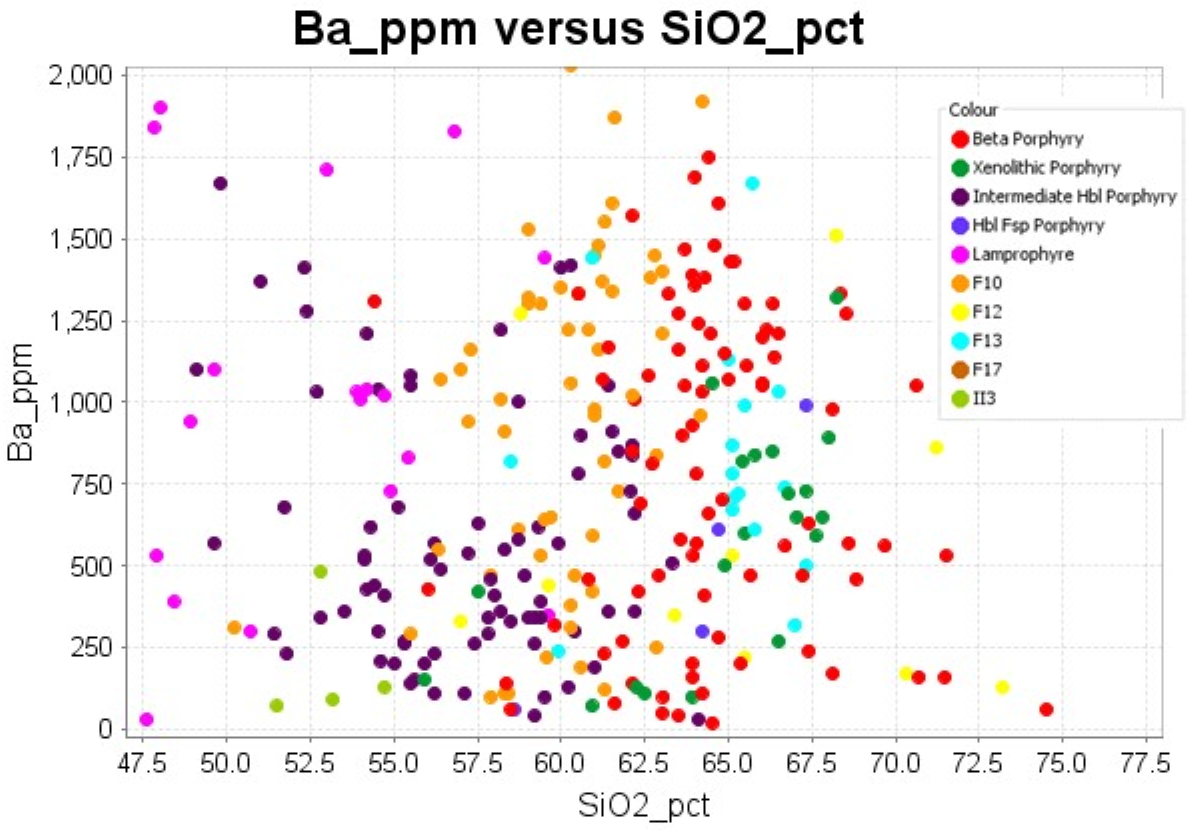


AMIRA P482. Kevin Cassidy and Dave Champion, Yilgarn Granites

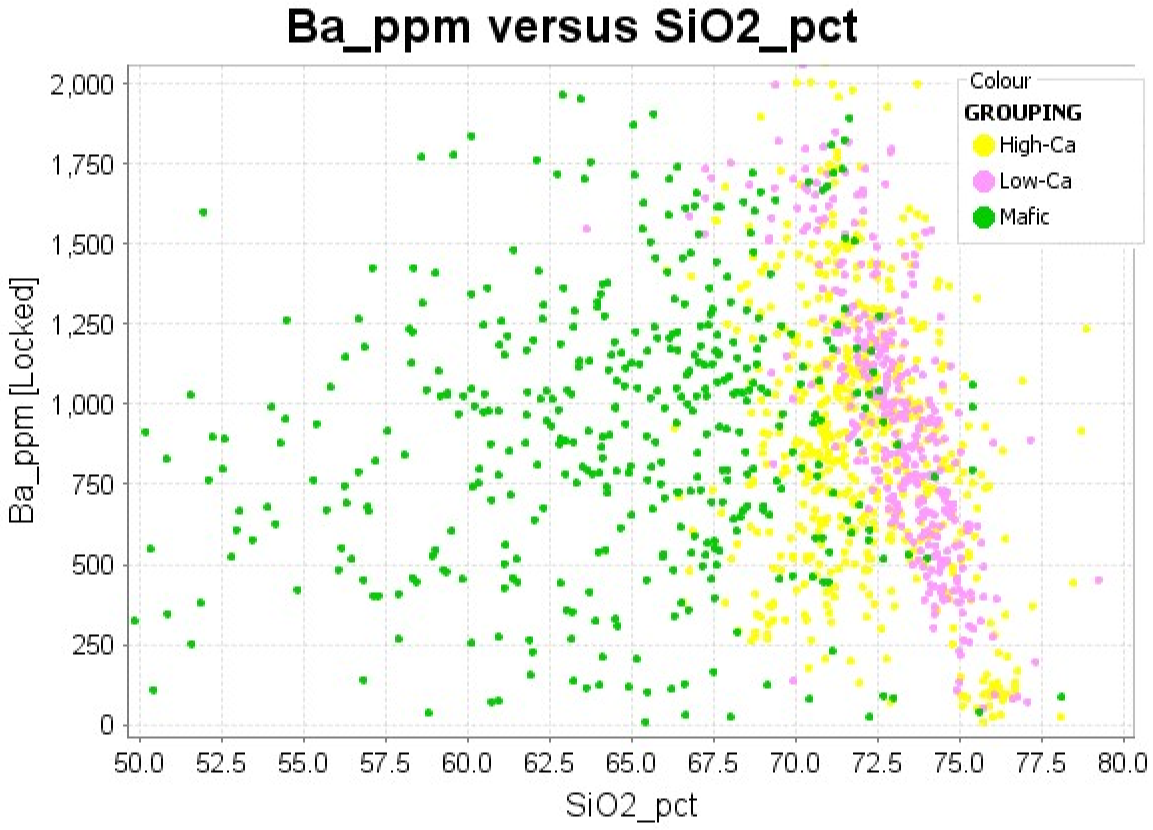
Compare Yilgarn Granites with porphyry Cu magmas

Low Ca-granites usually have high Ba (high K, high Ba)

Mineralized High Ca-granites have high Ba, indicative of a metasomatized mantle source!



Dave Champion, Geoscience Australia, St Ives porphyry study, 2008

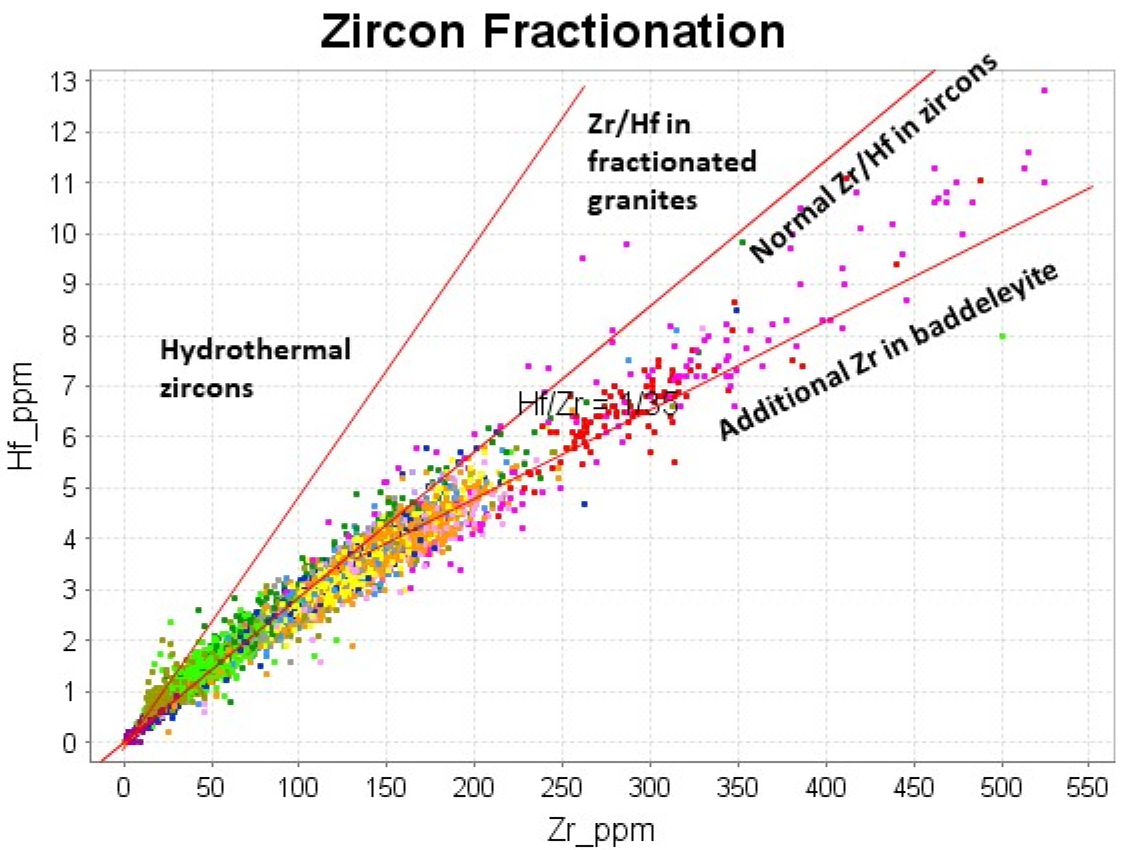


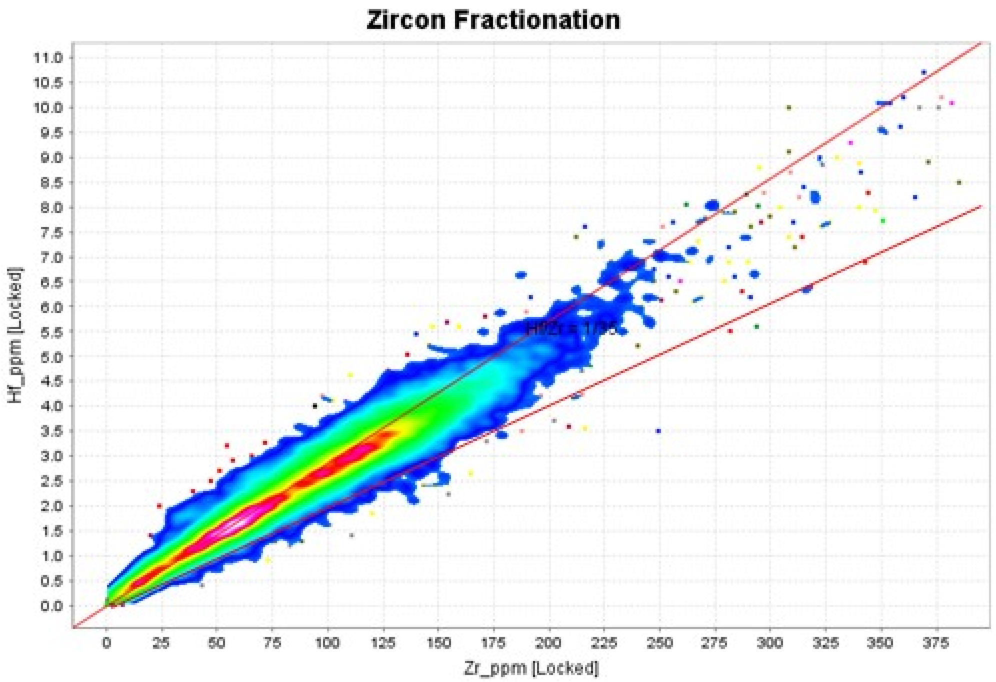
AMIRA P482. Kevin Cassidy and Dave Champion, Yilgarn Granites

Alkalic Magmas

There is a relatively rare compositional group of Archean gold-related intrusions classified as syenites. These have;

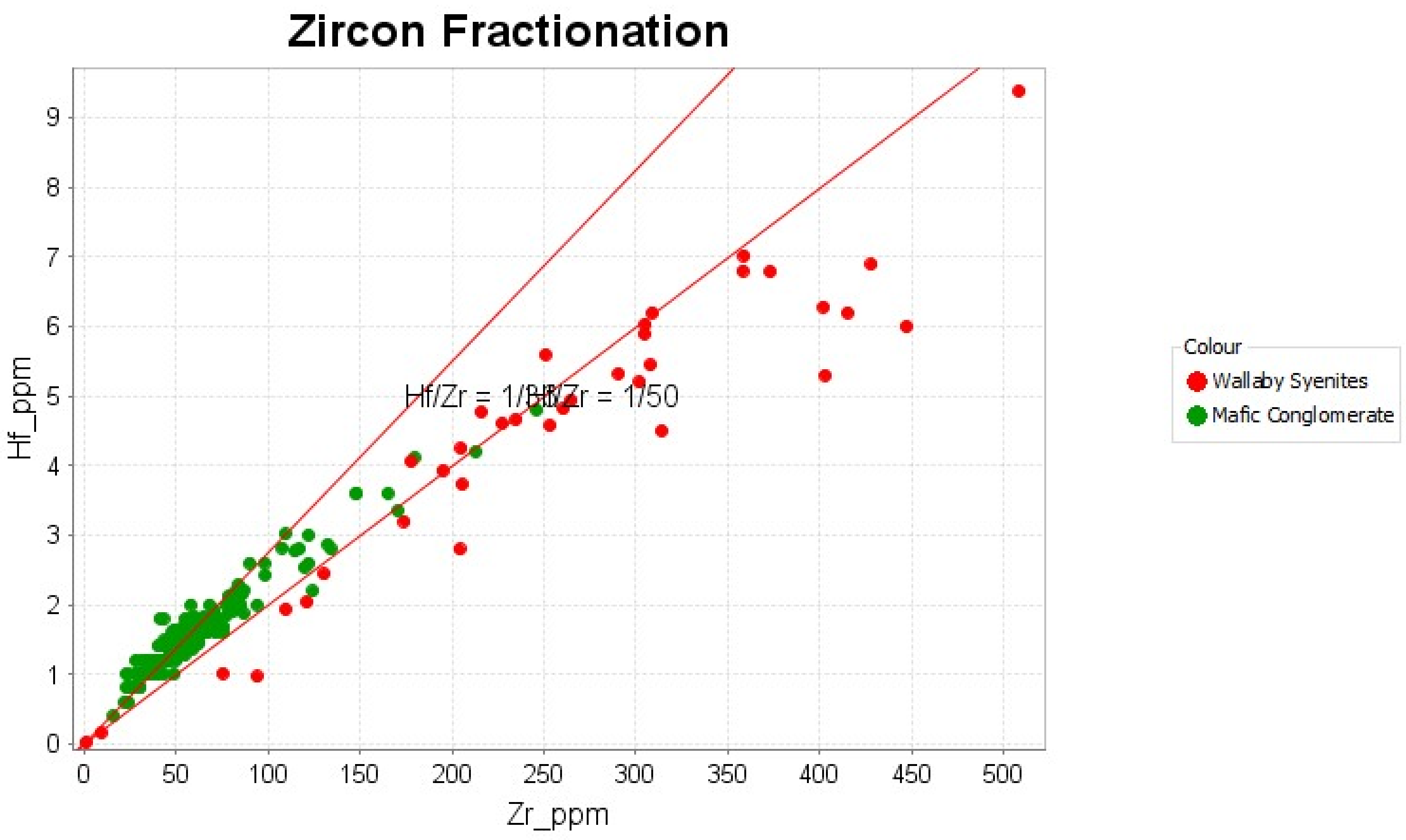
- increasing V/Sc with increasing SiO2,
- strong enrichment in P, LREE's, Th and Zr
- Ba>1000ppm, enrichment in Sr but not depletion in Y.
- Unique signature of zircon + baddeleyite, increases Zr/Hf ratio from background of 36 up to 50.





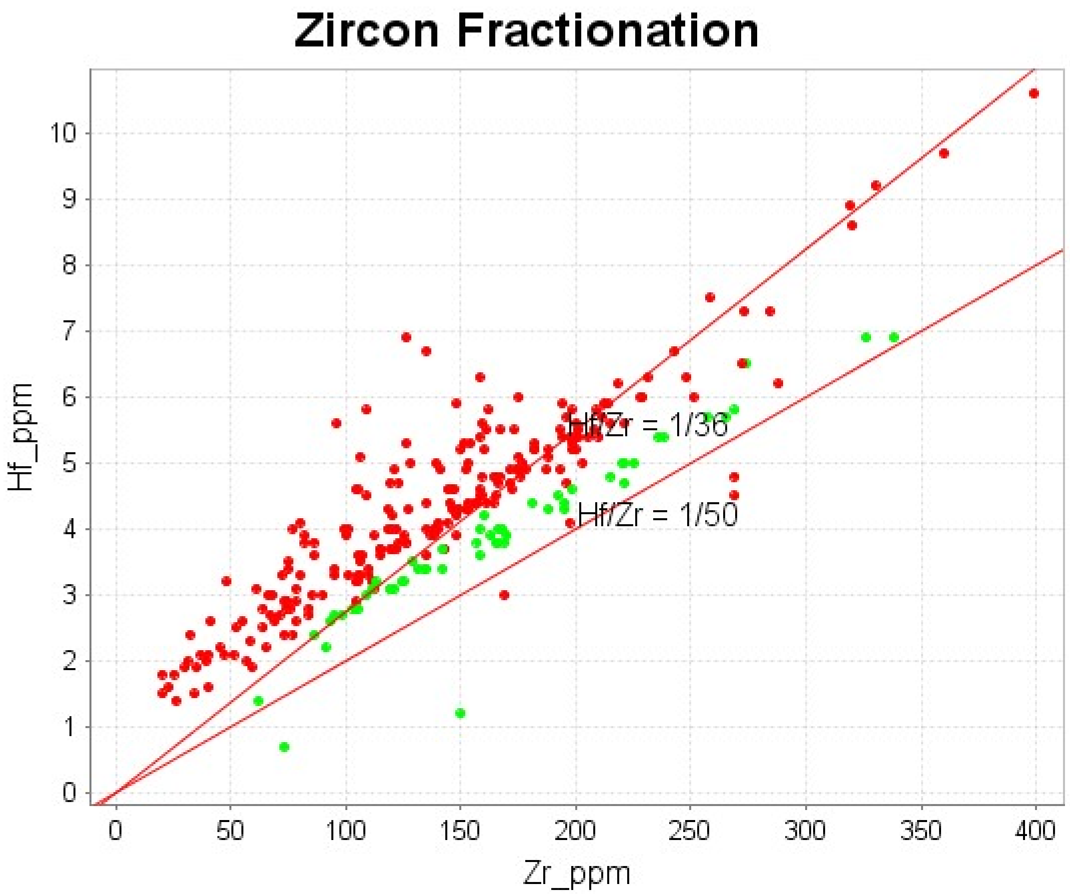
Alkalic Magmas

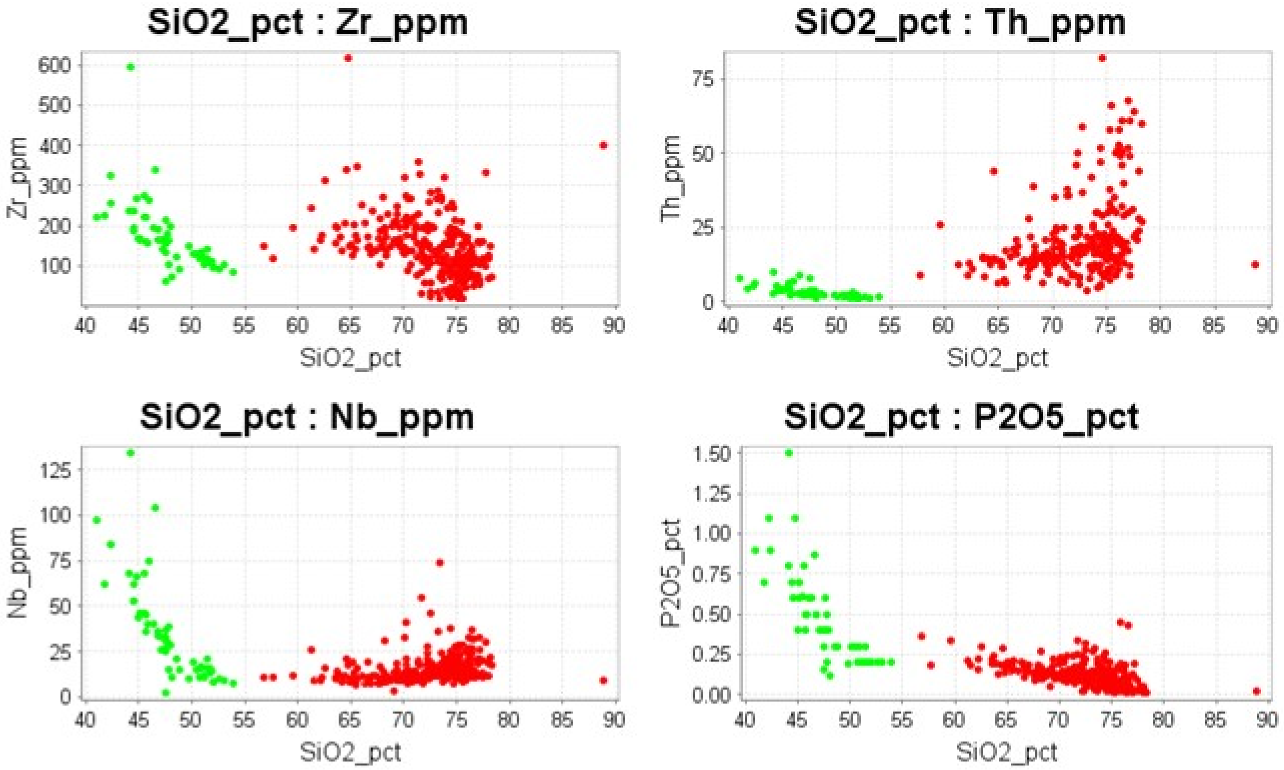
Most notable examples of Alkalic systems are Wallaby (Laverton) and Porgera



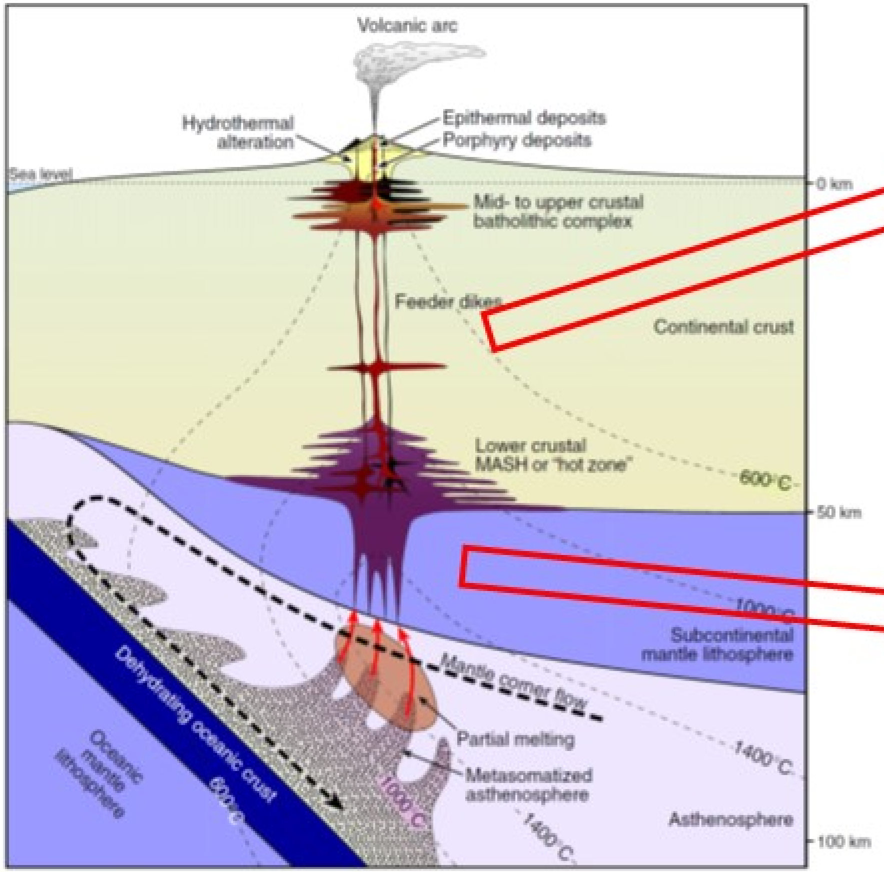
Alkalic Magmas

Tasmanian Devonian Granites (red) and Tertiary Alkali Basalts (green)





Summary



Low pressure mid-crustal melting/fractionation

- High K melt
- Low Ca-Sr
- Decreasing Sr/Y with increasing SiO2
- Eu* anomaly
- Decreasing V/Sc
- Incompatible behaviour of REE's, Nb, Th, Zr, U

High pressure melting/fractionation of oxidized hydrated mafic

- High Ca-Sr melt
- Increasing Sr/Y with increasing SiO2
- No Eu* anomaly
- Increasing V/Sc
- Compatible behaviour of REE's, Nb, Th, Zr, U

Magmatic to hydrothermal metal fluxes in convergent and collided margins
Jeremy P. Richards

Conclusions

- Exsolution of volatiles from fractionating magmas is a critical process in many hydrothermal mineral systems.
- Trace element pairs with a common mineral host are sensitive indicators of fractionation.
- The order and degree of mineral fractionation is determined by source composition, pressure, temperature, water content, oxidation state, sulfide saturation etc. All of these impact on the potential to create a mineral deposit.

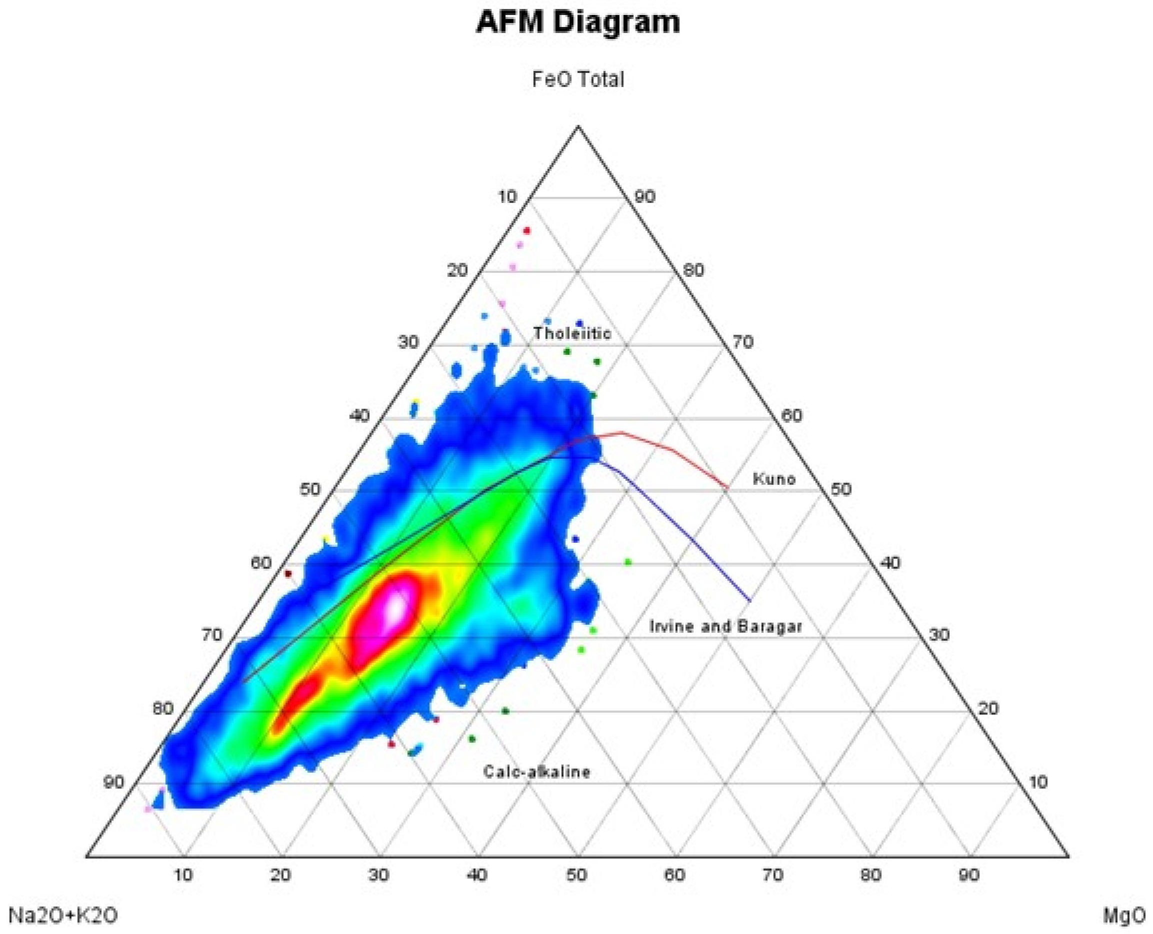
- Exploration and Mine geologists can use routine 4 acid digest ICP-MS data to create the plots presented here to understand the nature of igneous rocks in their drill holes.

References

- Loucks, R. R. (2014). Distinctive composition of copper-ore-forming arcmagmas. *Australian Journal of Earth Sciences*, *61*(1), 5-16.
- Richards, J.P., 2011. High Sr/Y arc magmas and porphyry Cu±Mo±Au deposits: just add water. Economic Geology, 106(7), pp.1075-1081.
- Smithies, RH and Lowrey, JR 2020, Eastern Goldfields greenstone geochemical barcoding project: notes to accompany 2020 data release: Geological Survey of Western Australia, Record 2020/6, 4p
- Olson, N.H., Dilles, J.H., Kent, A.J. and Lang, J.R., 2017. Geochemistry of the Cretaceous Kaskanak batholith and genesis of the Pebble porphyry Cu-Au-Mo deposit, southwest Alaska. American Mineralogist: Journal of Earth and Planetary Materials, 102(8), pp.1597-1621.
- Halley, S., 2020. Mapping magmatic and hydrothermal processes from routine exploration geochemical analyses. *Economic Geology*, *115*(3), pp.489-503.
- Chelle-Michou, C., 2013. Geochronologic and petrologic evolution of the magmatic suite associated with the Eocene Coroccohuayco deposit, and its role in the genesis of the associated Cu (-Au) porphyry-skarn mineralization, Tintaya district, Peru (Doctoral dissertation, University of Geneva).
- Smithies, R.H., Lu, Y., Kirkland, C.L. et al. Oxygen isotopes trace the origins of Earth's earliest continental crust. Nature 592, 70–75 (2021). https://doi.org/10.1038/s41586-021-03337-1

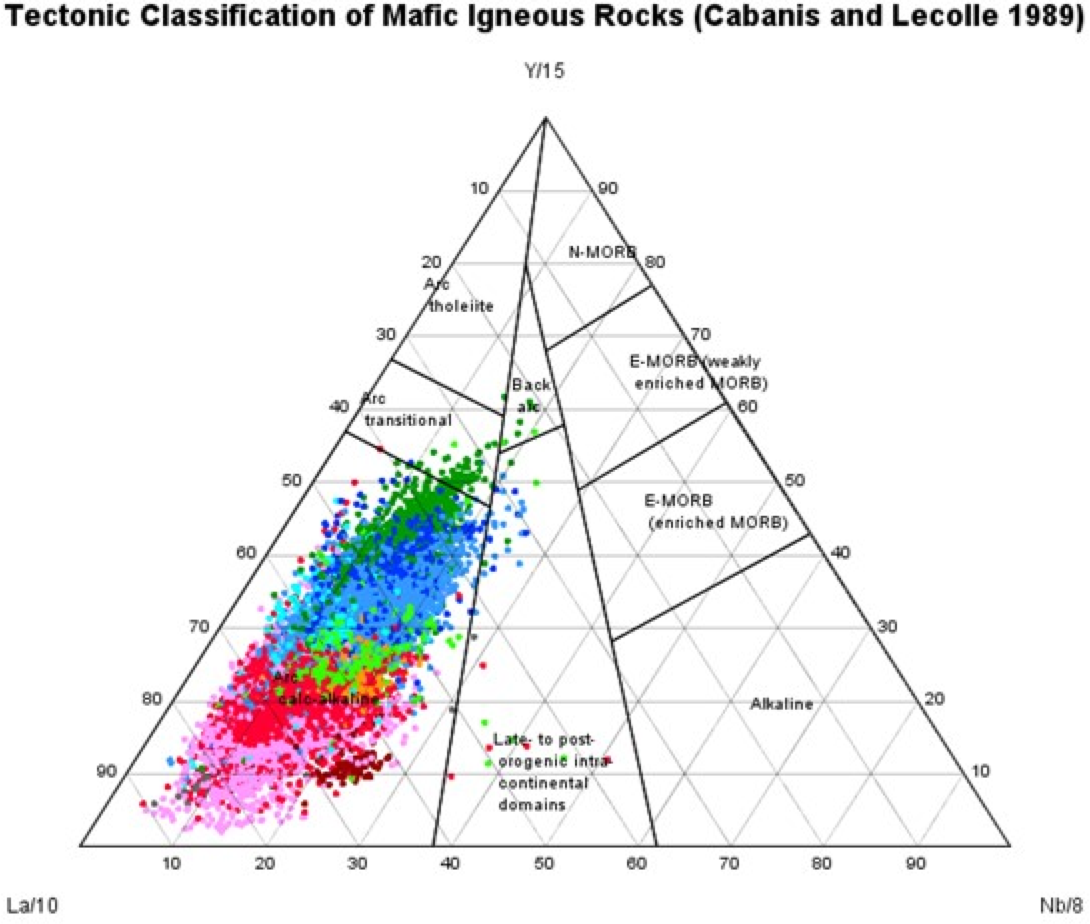
Conclusions

- Don't use major element diagrams to classify compositions of altered rocks!



Conclusions

- Use 1980's style trace element classifications with caution! Many of these are ambiguous. Many are designed to compare igneous series at comparable SiO2 contents



Conclusions

- Spider diagrams are way too confusing. Don't use statistical methods. Use the actual assay numbers and interpret these in terms of the host mineral compositions.