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**Application of indicator mineral methods to
bedrock and sediments**

M.B. McClenaghan and D. Layton-Matthews

2017



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Application of indicator mineral methods to bedrock and sediments

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2017

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Application of Indicator Mineral Methods to Bedrock Sediments

Convenors: M.B. McClenaghan and D. Layton-Matthews

October 22, 2017, Toronto, Ontario, Canada

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INTRODUCTION

This report contains the workshop notes that were provided for a one-day short course during This open file report contains the workshop notes for “Workshop 5: Application of Indicator Mineral Methods to Bedrock and Sediments” that was convened on October 22, 2017 in Toronto, Canada, as part of Exploration '17, the sixth decennial exploration and mining conference in a series that has been held in the seventh year of every decade since 1967 (<http://www.exploration17.com/>). The theme of the Exploration '17 conference was “integrating the geosciences: the challenge of discovery”. Workshop 5 reviewed the principles, methods, and developments in the application of indicator mineral methods to mineral exploration around the world. The talks and workshop notes were presented by some of the most experienced practitioners in the field. Indicator mineral methods for the exploration for a broad range of deposit types were reviewed, including gold, diamonds, volcanogenic massive sulphide, porphyry copper, rare metals, and tungsten. Topics also included heavy mineral sample processing methods and microanalytical techniques. Support for convening the workshop and production of conference workshop notes and this report was generously provided by the Geological Survey of Canada through its Targeted Geoscience Initiative (TGI-5) and Geo-mapping for Energy and Minerals (GEM) programs.

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Porphyry indicator minerals and their mineral chemistry as vectoring and fertility tools

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Intrusion-centred mineral districts host a diversity of ore deposits of variable metal associations, alteration assemblages and genesis. Porphyry systems represent particularly important exploration targets but the prioritization of conventional geochemical or geophysical anomalies that might represent a deposit, particularly when systems are buried, is extremely difficult. Three key questions arise: (1) Is the alteration (particularly when only propylitic alteration is observed) related to a porphyry system? (2) How can the fertility of a system be assessed at an early stage of exploration in order to reduce exploration risk? (3) How can the centre of the system (in 3 dimensions) be predicted ahead of extensive, potentially deep, drilling? These fertility and vectoring challenges have been the subject of recent work, primarily based on mineral chemistry, in a series of AMIRA projects based out of the University of Tasmania, now also being continued at the Natural History Museum in London.

The approach to assessing the possible presence of a porphyry system has been to establish mineral chemical criteria that discriminate between porphyry and non-porphyry environments based on (1) the composition of igneous minerals (e.g. plagioclase, zircon, apatite, magnetite); and (2) the composition of hydrothermal alteration phases, particularly those developed in the propylitic domain (epidote, chlorite, magnetite, calcite, quartz). Many of these phases may

be reworked via erosion into paleo or modern sediment transport systems and are thus available for assessment from catchment areas. Some of the characteristics of these minerals may allow the distinction between extensively mineralized and ostensibly barren environments (the system "fertility") by tracing key igneous processes (Wilkinson, 2013); clearly these features are of significant exploration utility (Fig. 1).

The vectoring challenge has been addressed by the completion of numerous orientation studies on known porphyry systems to establish any systematic spatial variations in mineral chemistry that may exist, primarily within the propylitic environment. These studies have shown that characteristic and, to variable degrees, reproducible patterns of major and trace element variation exist that enable vectoring towards the centre of a hydrothermal system, as well as discrimination between porphyry-related and non-porphyry mineral assemblages (Cooke et al., 2014a, 2015, 2017; Baker et al., 2015, 2017; Wilkinson et al., 2015a, 2017). In particular, chlorite has proven to be particularly effective for prediction of absolute distances to the system centre, even allowing estimation of the depth of a buried system. Both epidote and chlorite appear to contain signals that reflect the potential metal endowment of a system. The ability to define these characteristics of a system from a limited number of samples of distal "green rocks" marks a major step-change in the way

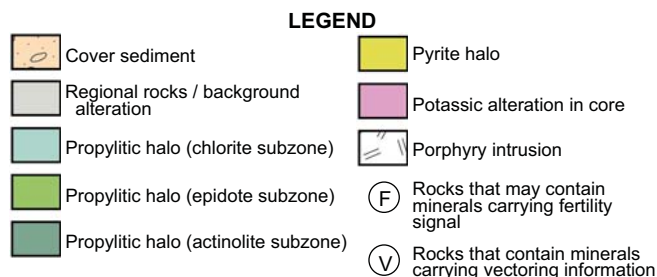
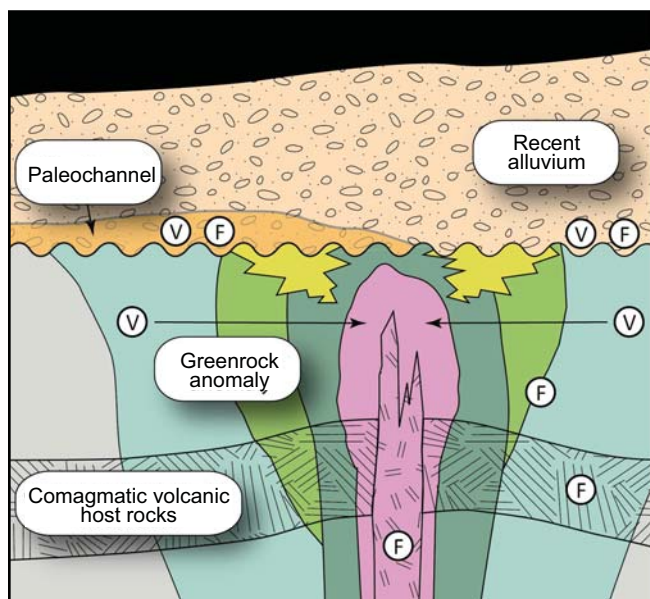


Figure 1. Schematic diagram of an eroded and reburied porphyry system illustrating potential sources of fertility and vectoring information.

that exploration for porphyry systems can be done (Fig. 1).

PORPHYRY INDICATOR MINERALS

The ability to discriminate minerals from a porphyry magmatic-hydrothermal system as opposed to other kinds of hydrothermal, geothermal, or metamorphic environments would be a valuable addition to the porphyry exploration toolbox. Clearly, the field recognition of characteristic mineral assemblages is an obvious first step, as well as delineating these assemblages and their textural variations. Extending this to transported grains is possible, where the occurrence of relatively characteristic minerals (e.g. molybdenite) and, more usefully, composite grains (containing typical mineral associations) may be indicative of an eroded bedrock porphyry source. However, many minerals that occur in porphyry-type deposits are not diagnostic, even when occurring in mineral assemblages. This is particularly true in the distal, propylitic alteration environment, where there is little chance of finding anything that could be indicative of a nearby porphyry centre.

As a result, recent work has increasingly focused on mineral chemistry, particularly trace element chem-

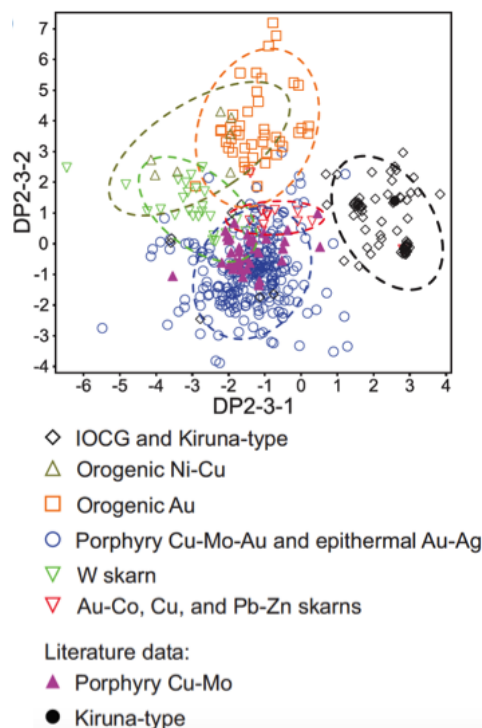


Figure 2. Discriminant projection plot separating apatite from porphyry-epithermal systems from other deposit types. There is significant overlap between porphyry and skarn-related apatite on this diagram. Elements used are Mg, Mn, Y, Ce, Eu, Dy, Yb, Pb, Th, and U. From Mao et al. (2016).

istry, in the hope that distinctive “porphyry” signatures may exist. Much of this work has been made possible by the development and decreasing cost of laser ablation inductively-coupled-plasma mass spectrometry (LA-ICP-MS). This technique, with its high spatial resolution (generally 25–50 μm) and low limits of detection (in the 10s of ppb range for many elements), now allows the simultaneous determination of approximately 40 elements in a wide range of silicate, oxide, and sulphide minerals—subject to careful checks on analytical artefacts such as mass spectrometer interferences.

Apatite

Limited work has been done on assessing the utility of apatite for porphyry discrimination. Mao et al. (2016) analysed 20 samples from a variety of porphyry system types and found that these types could be distinguished quite effectively from one another using multivariate discriminant projection. Porphyry-type deposits in general could also be distinguished to some degree from other hydrothermal ore types (Fig. 2), but the authors made no attempt to compare porphyry-related apatite with that from unmineralized rocks. Rukhlov et al. (2016) also analysed apatite from a variety of porphyry systems and showed that alkalic porphyry systems could be discriminated from calc-alkalic systems, probably due to the more oxidized state and less

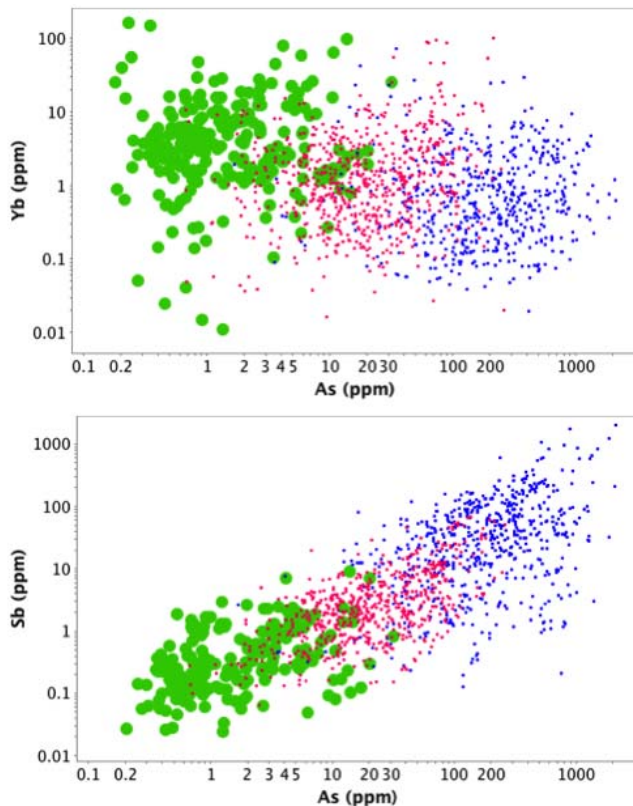


Figure 3. Epidote compositions from Cu-Au (pink dots) and Cu-Mo (blue dots) porphyry systems (Baguio district, El Teniente, Resolution) compared with metamorphic chlorite (large green dots) from the Dalradian and Moine Supergroups in Scotland ($n = 288$), and the Proterozoic Georgetown Inlier ($n = 29$) and Harts Range ($n = 46$) in Australia. Note that a large proportion of metamorphic analyses (not shown) were below the limit of detection for As and Sb (typically ~ 1 ppm for As and 0.1 ppm for Sb). Data from AMIRA P1060 project.

evolved magmas associated with the former. Bouzari et al. (2016) carried out a similar study and showed that apatite associated with different porphyry alteration styles could be discriminated by cathodoluminescence colour and certain chemical characteristics such as Mn/Fe ratio. Again, however, there was no explicit discrimination of porphyry-related apatite from other sources of the mineral.

Epidote

The potential utility of epidote as an indicator mineral for porphyry systems stems from its frequent occurrence within porphyry alteration assemblages. It can occur within the potassic zone (e.g. El Teniente, Chile: Vry et al., 2010) and within two surrounding domains (actinolite and epidote subzones; Cooke et al., 2014b; *see also* Fig. 1). However, epidote frequently also occurs in regional metamorphic rocks (e.g. Wilson and Leake, 1972) and geothermal systems (Bird and Spieler, 2004), as well as in other hydrothermal settings such as skarn deposits and granite-associated veins (e.g. Lindgren, 1933). In addition, it is generally only

abundant in intermediate to mafic volcanic country rocks and is much less common in felsic igneous rocks, such as those that host many deposits in southwest USA.

Although a full evaluation of epidote discrimination between such settings using major and trace element chemistry remains to be done, some initial findings provide hope that this may be possible. For example, skarn-associated epidote may be relatively depleted in heavy rare earth elements (HREE) (if coeval with garnet) or enriched in HREE (if it has replaced garnet), and is typically enriched in As, Sb, Sn, Ga, Ge, Pb, U, and Th relative to other types of epidote (Wilkinson et al., 2015a,b). Porphyry-related epidote tends to be enriched in elements that are fluxed by porphyry-hydrothermal fluids and that are compatible in the epidote structure, such as As, Sb, Zn, and Pb (Fig. 3), and also in Au, Ag, and Bi, which could be hosted by nano-inclusions (e.g. Cooke et al., 2014a; Pacey, 2017). By contrast, metamorphic epidote is conspicuously depleted in these elements, plus Ta, U, and Th, and tends to be relatively enriched in Hf, Y, and the HREE (e.g. Fig. 3). In addition, there is a difference between epidote from Cu-Mo and Cu-Au systems, with the former being enriched in As and Sb and depleted in Yb.

The application of multivariate statistical methods is increasingly being used in attempts to discriminate indicator minerals formed in different environments (e.g. Mao et al., 2016). In a study of the Oyu Tolgoi porphyry Cu-Au system, Hart et al. (2015) used this approach to distinguish epidote that was associated with the ore-forming system from a later generation unrelated to ore (Fig. 4). The second event overprints post-ore Carboniferous volcanic rocks and granitoids, as well as the host rock sequence; clearly, recognizing two distinct events within the same sequence is critical for a realistic interpretation of vectoring or fertility information.

Chlorite

Chlorite is widely developed in porphyry systems, occurring in late chlorite-sericite assemblages in more proximal positions, and throughout the epidote and chlorite subzones of the propylitic domain. From work done in the AMIRA projects (Cooke et al., 2015, 2017; Wilkinson et al., 2017), we know that it falls into the compositional range of clinocllore but with significant minor and trace element variation. As with epidote, chlorite is very common in many other geological environments, meaning that the discrimination of porphyry-related propylitic chlorite is critical for identifying the distal parts of potentially mineralized hydrothermal systems.

Again, it is fairly early in the development of tools for the discrimination of porphyry-related chlorite.

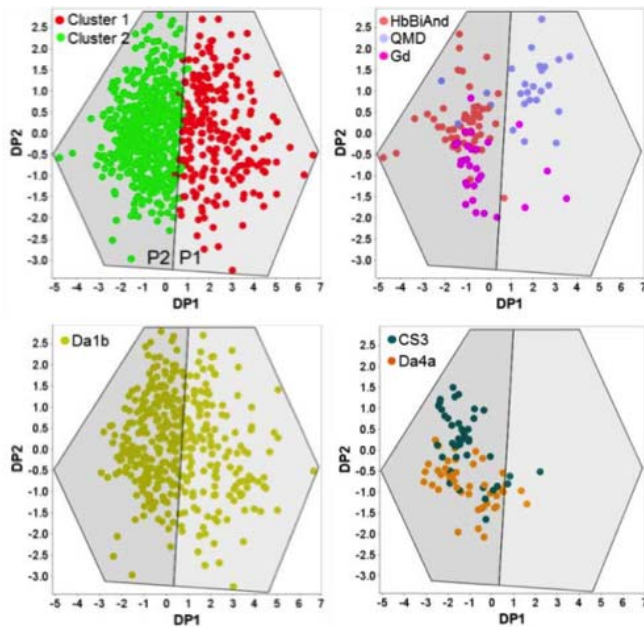


Figure 4. Discriminant projection plots of epidote data from the Oyu Tolgoi district, Mongolia (from Hart et al., 2015). All epidote data were classified into two groups (P1, P2) based on cluster analysis. Epidote data from intrusive units (top right) shows that the Devonian causative intrusions (QMD) classify in P1 whereas Carboniferous granodiorite- and hornblende-biotite andesite-hosted epidote mostly classify in P2. Data from the Devonian augite basalt host rocks (lower left) classify in both groups, which is consistent with primary propylitic and secondary overprinting (Carboniferous) epidote. Epidote data from the post-mineralization, allochthonous Heruga Sequence basaltic volcanic breccia (Da4a) and post-mineralization Carboniferous basaltic-andesitic volcanics (CS3) classify in P2.

However, comparison of spatial mineral chemistry data from the propylitic halo of the Batu Hijau Cu-Au system, Indonesia (Wilkinson et al., 2015a), showed Fe and Li contents in metamorphic chlorite were fairly distinct from those of porphyry-related chlorite (Fig. 5). Although metamorphic compositions overlap with proximal chlorite compositions for Al, Si, Ca, and Sr, there is a clear distinction between those from distal propylitic chlorite (Wilkinson et al., 2015a). This is the key capability; it is only for the porphyry-distal chlorites in very nondescript propylitic rocks without whole rock geochemical anomalies that discrimination is of paramount importance for exploration.

Other elements that are useful for discrimination purposes are Ag, Sb, and As. Probably for similar reasons as epidote, these elements appear to be taken up at low concentrations in chlorite in the propylitic halos of porphyry systems but are not present at significant levels in metamorphic fluids, and/or are not partitioned into crystallizing metamorphic chlorite.

Magnetite

Magnetite offers significant promise as a tool for discrimination of different kinds of magmatic and

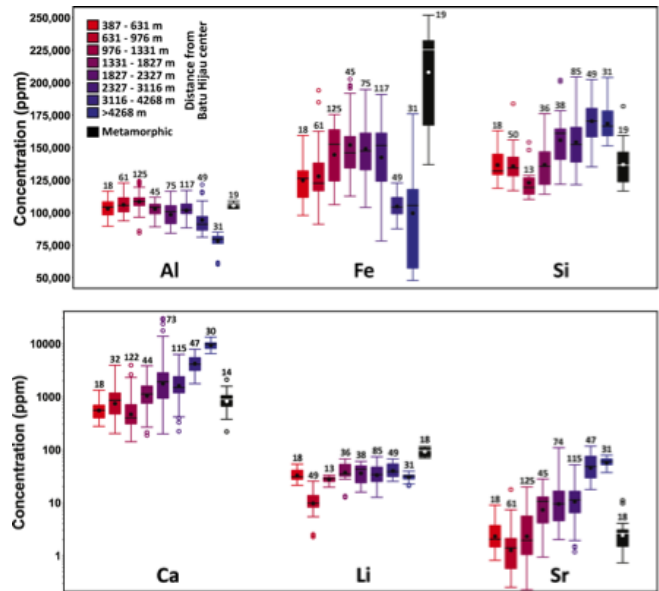


Figure 5. Comparison of metamorphic chlorite compositions (black symbols) with chlorite from Batu Hijau binned by the distance of the samples from the porphyry centre (warm colours are more proximal). Box-and-whisker symbols show: mean value (black/white dot), median (horizontal line), second and third quartiles (extent of box), whiskers (maximum and minimum values that are not outliers), circles (outliers that are greater than 1.5 times the interquartile range from the box). Numbers of analyses included in each bin are shown. From Wilkinson et al. (2015a).

hydrothermal environments because of its wide range of potential element substitutions. Furthermore, its magnetism and relatively robust character mean that it survives within, and is easily sampled from, sediments and soils.

The Ca + Al + Mn vs. Ti + V plot developed by Dupuis and Beaudoin (2011) was one of the first attempts to distinguish magnetite derived from porphyry, iron-oxide Cu-Au, skarn, Kiruna-type, Fe-Ti and V deposits, and banded iron formations. Calcium contributes only negligible amounts to the overall cation sum (typically 1–2 orders of magnitude less than the concentrations of Al and Mn) and can effectively be dropped from the y-axis (cf. Nadoll et al., 2014). Ga and Sn have also been identified as useful in the discrimination of magnetite from various hydrothermal systems, with porphyry- and skarn-related hydrothermal magnetite having elevated Ga (>10 ppm) relative to other types (Nadoll et al., 2014), potentially due to a higher temperature of formation.

The Ti vs. Ni/Cr plot proposed by Dare et al. (2014) for the discrimination of hydrothermal and igneous magnetite from felsic magmatic-hydrothermal systems has been shown to be ineffective (Siewwright, 2017). In fact, the simplest and most robust way to separate the two types is based on Ti alone, with a cut-off at 1 wt% correctly separating them in 97.5% of cases in the database of Sievwright (2017). The correct identification of

hydrothermal and igneous populations of magnetite in either rock, heavy mineral concentrates, or soils is a key first-step in the interpretation of its mineral chemistry. Although hydrothermal magnetite is relatively easy to identify we do not yet have a robust tool for identifying porphyry-related populations from those developed in other types of system. However, it is possible to discriminate porphyries of different metal tenor (Siewwright, 2017).

PORPHYRY FERTILITY INDICATORS

“Fertility” — the mineralization potential — of a porphyry system can be assessed at several stages and on several scales of exploration. The fertility of arc segments can be evaluated using a variety of igneous minerals (e.g. zircon, magnetite, apatite) and can indicate whether magmas were suitably hydrous, oxidized, and sulphur-rich to be capable of developing extensive hydrothermal systems with mineralization potential. These tools can also be used on a district scale to identify magmatic complexes, or individual intrusions within such complexes, that may be most likely to host mineralization. Such tools are thus particularly useful as a way of prioritizing geophysical targets. Once a hydrothermal system has been identified, but potentially just its distal propylitic domain, other minerals can be used to evaluate whether it may be extensively mineralized or not (e.g. epidote, chlorite, hydrothermal magnetite).

Zircon

Zircon is extremely useful in the study of igneous and metaorphic petrogenesis because of its robustness through weathering, its utility as a geochronometer, the sensitivity of certain trace element substitutions to intensive parameters, and its resistance to high-temperature diffusive re-equilibration.

One aspect of zircon chemistry that has received significant recent interest is the effect of magmatic redox conditions on partitioning rare earth elements Ce and Eu. Experimental studies have shown that the magnitude of Ce and Eu anomalies varies as a function of melt fO_2 (e.g. Burnham and Berry, 2012), such that zircons from more oxidized systems have larger positive Ce anomalies, and smaller negative Eu anomalies. This redox sensitivity is of particular relevance in the exploration for porphyry deposits because they appear to form from especially oxidized arc magmas (Sillitoe, 2010; Richards, 2014). Zircons from magmatic rocks closely associated with mineralization have been shown to have high values of Ce^{4+}/Ce^{3+} and Eu/Eu^* , with moderately elevated Ce/Ce^* (Fig. 6; *see* Loader et al., 2017), ascribed by most authors to oxidizing conditions at the time of crystallization (e.g. Dilles et al., 2015; Shen et al., 2015; Lu et al., 2016). It was suggested by these authors that this characteristic may be

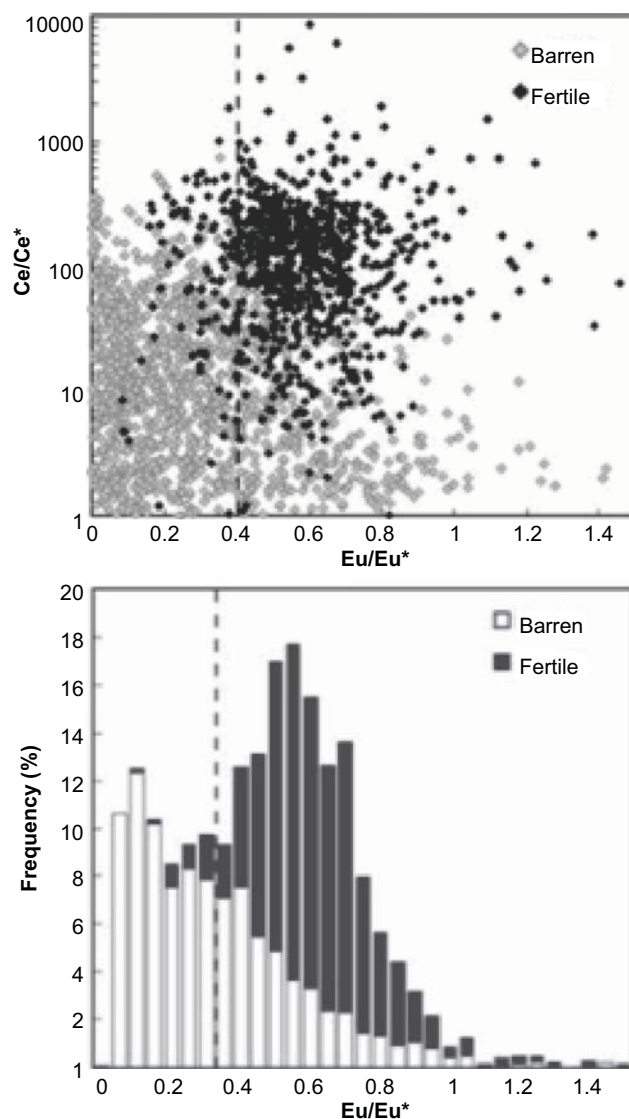


Figure 6. Comparison of Eu/Eu^* and Ce/Ce^* zircon data from barren and fertile igneous suites. From Loader et al. (2017).

used to distinguish magmatic systems with high and low ore-forming potential.

However, as shown by Buret et al. (2016), the co-crystallization or prior crystallization of apatite and/or titanite can significantly impact zircon trace element chemistry. Furthermore, Loader et al. (2017) demonstrated that titanite crystallization can have a major effect on Eu anomalies. It was recommended that only high-Ta zircons (>0.2 ppm Ta) should be used to test for magmatic redox because these are not likely to have had their chemistry modified by titanite crystallization. Ce/Ce^* may be unaffected but is difficult to determine accurately; Loader et al. (2017) proposed the use of the formulation $Ce^* = Nd_N^2/Sm_N$ to estimate Ce^* in the absence of precise analytical data for La and/or Pr. A lot of overlap exists between barren and fertile magmas in terms of Ce/Ce^* but values above ~ 100 are only rarely seen in barren suites and, when combined with

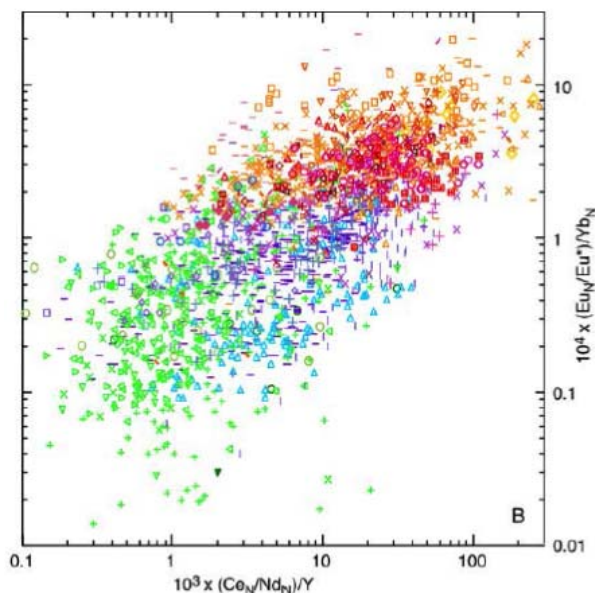


Figure 7. Comparison of $(Eu_N/Eu^*)/Yb_N$ versus $(Ce_N/Nd_N)/Y$ for zircon from barren (blue/green) and fertile (orange/red) igneous suites. From Loucks et al. (2016).

robust Eu/Eu^* values above 0.4 (Fig. 6), provides a powerful discriminator of fertile rocks.

Loucks et al. (2016) developed some additional parameters in zircon ($Eu_N/Eu^*/Yb_N$ and $Ce_N/Nd_N/Y$) that can help to discriminate barren and fertile igneous suites. Zircons are thought to inherit the negligible negative Eu anomaly that characterizes fertile magmas as recognized in whole rock data and also to acquire a large positive Ce anomaly in fertile, oxidized melts. Normalizing either of these “fertile-high” parameters to HREE that are typically low in fertile magmas (assuming that zircon inherits this feature too), such as Yb or Y (as a proxy for Ho), enhances the fertility signal (Fig. 7). Because of the difficulty in precisely measuring Ce/Ce^* , the Ce anomaly proxy Ce_N/Nd_N was proposed.

Plagioclase

Recent interest in the potential application of plagioclase as a fertility indicator has come from the recognition that it appears to be unusually enriched in Al – above normal stoichiometric levels – in fertile porphyry systems (Williamson et al., 2016; *see* Fig. 8). Although these results are promising, there remains more work to be done to confirm that this behaviour is systematically observed in mineralized systems and, indeed, what it represents. Experimental studies by Kyono and Kimata (2001) suggested that this may be due to substitution of water into vacancy sites $[]Si_4O_8$ as a result of high H_2O_{melt} .

Apatite

Limited work has investigated apatite chemistry as a potential tool for assessment of fertility, although it

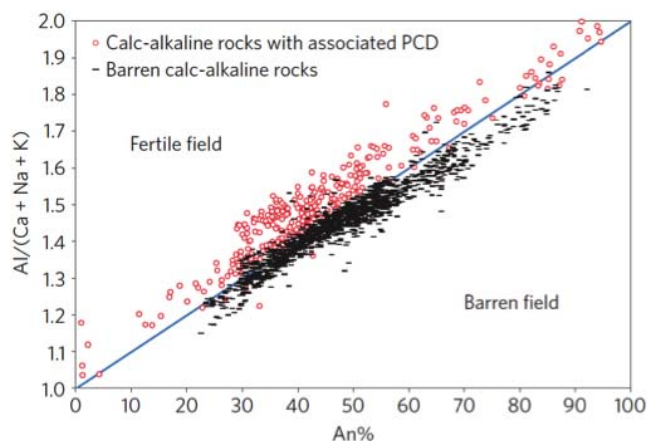


Figure 8. Plot of excess Al in plagioclase (atomic proportion of $Al/(Ca+Na+K)$) as a function of anorthite content. Plagioclase from barren systems falls on or below the stoichiometric line shown, whereas grains from mineralized systems fall above the line. From Williamson et al. (2016).

undoubtedly offers significant potential because it can track key melt parameters, such as halogen content (or Cl/H_2O ratio), sulphur content, redox sensitive elements like Mn (Miles et al., 2013), and tracers of melt evolution like the REE.

Belousova et al. (2002) showed that low Mn, low $Y/\Sigma REE$, high La/Sm and high Ce/Th characterized apatite from more oxidized igneous rocks, but these authors did not study porphyry systems specifically. Rukhlov et al. (2017) evaluated apatite composition as a proxy for the oxidation states of porphyry Cu-Mo-Au deposits and concluded that S, V, and Eu correlated with the oxidation state of the magmas. However, there was no explicit assessment of differences between mineralized and unmineralized systems. Recently, Brugge et al. (2017) illustrated the complexity of apatite chemistry that can be observed in a single porphyry system (Chuquicamata, Chile; *see* Fig. 9), emphasizing that our understanding of its chemistry in porphyry deposits is in its infancy.

Epidote

The chemistry of propylitic epidote in part reflects metasomatic mass transfer by magmatic-hydrothermal fluids, as well as crystallization conditions, precursor phase chemistry (if formed by replacement), and competition with co-crystallizing minerals. Cooke et al. (2014a) suggested that chalcophile metalloids As and Sb, which may be incorporated into epidote, are preferentially sequestered by pyrite within the pyrite halo of porphyry systems, leading to low concentrations in other phases. However, in the more distal propylitic zones where H_2S has been consumed, their concentrations in epidote increase. Assuming As and Sb are primarily derived from magmatic-hydrothermal fluids, the levels attained in epidote may be a qualitative proxy for the total metal flux in the system.

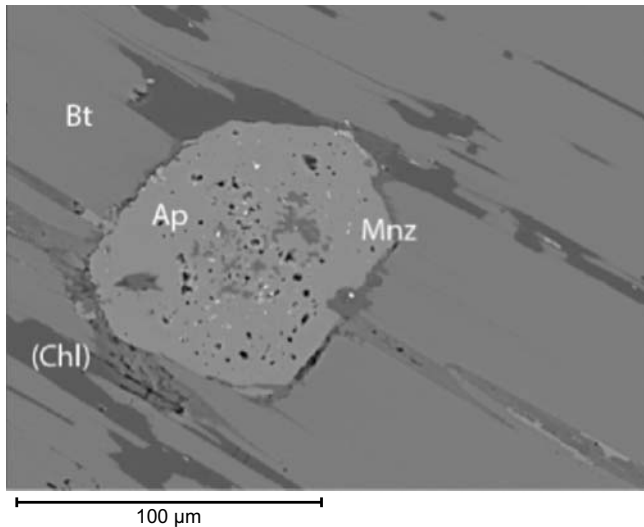


Figure 9. Primary igneous apatite in biotite from Chuquicamata, Chile, overprinted by secondary alteration resulting in crystallization of monazite and pitting (from Brugge et al., 2017). Note: Ap = apatite; Bt = biotite; Chl = chlorite; and Mnz = monazite.

Enrichments of other fluid-mobile metals that can be incorporated into epidote, such as Zn, may also prove to be useful for assessing metal endowment in porphyry systems but remain to be evaluated.

Chlorite

Chlorite chemistry offers a lot of potential as a fertility tool, but there is no information in the public domain to date. However, results from the AMIRA projects show that the Mn and Zn contents in chlorite are potential indicators of endowment in porphyry systems (Fig. 10). It is also evident that these elements reach a peak concentration in chlorite at distances of ~1-3 km from porphyry centres, coincident with the whole rock geochemical maxima that are commonly observed for these metals (e.g. Pacey, 2017).

PORPHYRY VECTORING TOOLS

Epidote

Propylitic epidote shows some fairly systematic spatial variations in relation to the ore zone of porphyry systems. In the Baguio district, Philippines, Cu, Mo, Au, and Sn were found to be high proximal to the known porphyry centres but it is not yet clear if this is related to substitution of these elements into the epidote structure or if it reflects an increased abundance of nano-inclusions (Cooke et al., 2014a). Similar to chlorite, Mn and Zn are enriched in epidote just outside the pyrite halo, as are La, Y, Zr, and Sr. Elements that are enriched most distally are As, Sb, and Pb. Broadly similar patterns are reported for the El Teniente system, Chile (Fig. 11), indicating that epidote shows comparable behaviour in both Cu-Au and Co-Mo porphyry environments (Wilkinson et al., 2017).

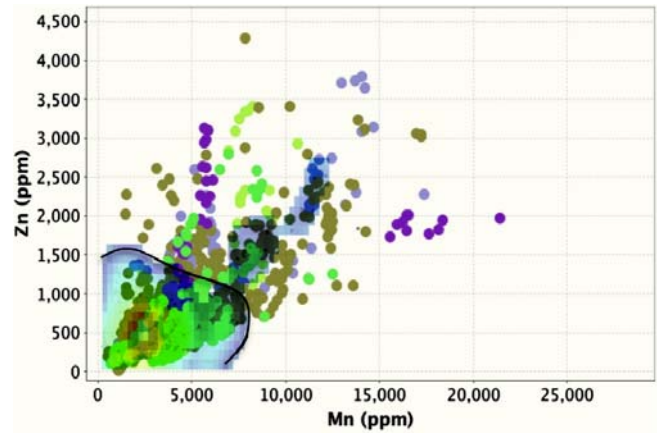


Figure 10. Zn versus Mn plot (n = 5015) for chlorite from porphyry systems. Contoured data are from metamorphic background, prospects, and small deposits (West Scotland, Georgetown Inlier, Harts Range, Shebandowan Greenstone Belt, Central Chile, Baguio district); 97.7% of the data from these systems fall below the black line indicated. A large proportion of the giant porphyry system data (coloured symbols: Batu Hijau, El Teniente, Collahuasi District) also fall below the line, but the majority of data that fall above it (95.0%) are from these fertile settings. Thus, chlorite with elevated Mn and Zn content are fairly characteristic of the propylitic halo of economic porphyry deposits. Data from AMIRA P1060 project.

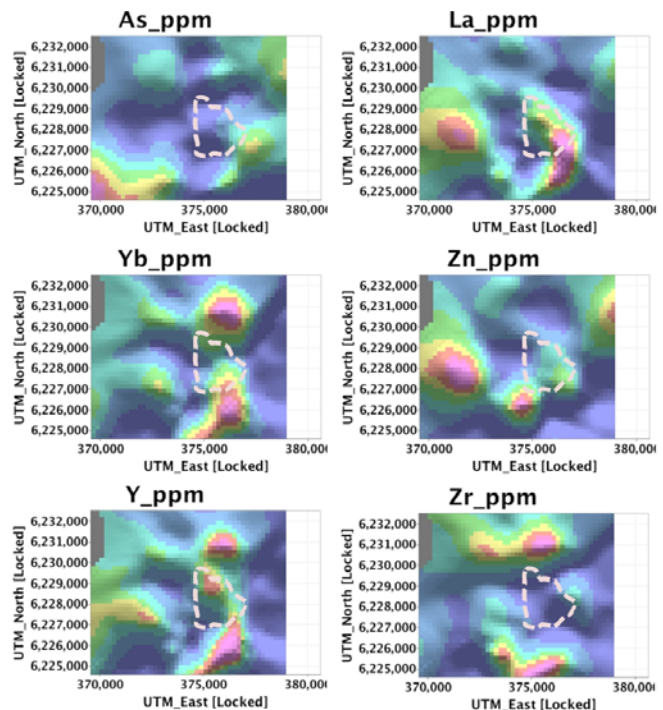


Figure 11. Gridded epidote compositional data (log of sample average, cell size 200 m, minimum smoothing distance 4 cells) for trace elements in epidote from El Teniente, Chile, showing proximal lows and highs just outboard of the ore zone. Outline of the 0.5 wt% Cu shell is shown for reference. Note the apparent westward offset between some of the epidote anomalies and the location of the orebody at depth, possibly due to post-ore westward tilt. From Wilkinson et al. (2017).

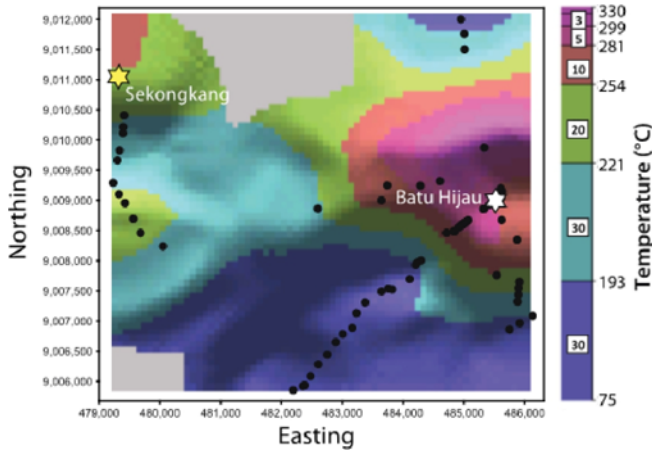


Figure 12. Gridded chlorite geothermometry results (sample mean data, 100 m pixels) for the Batu Hijau porphyry Cu-Au system, Indonesia. Chlorite clearly maps out the thermal anomaly associated with the ore deposit as well as a west-northwest-trending ridge that follows the underlying intrusive complex and a zone of elevated (inner propylitic) grade at surface. Sample locations are shown. From Wilkinson et al. (2015a).

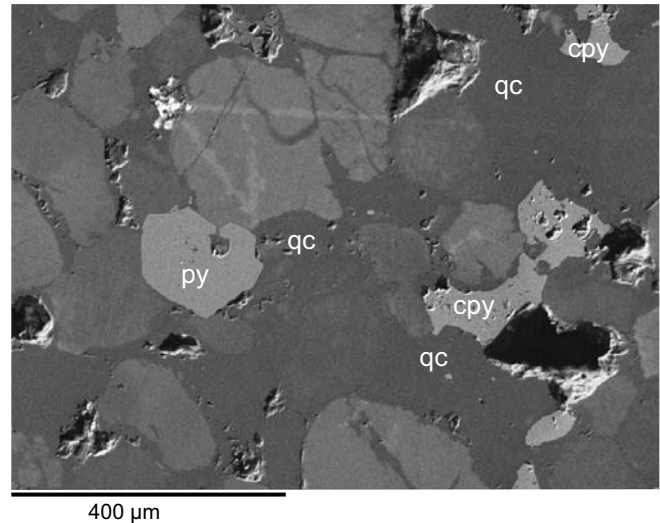


Figure 14. Scanning electron microscope-cathodoluminescence image of quartzite from the Bingham Canyon porphyry system, Utah. The sample, which was collected 1310 m from the deposit centre, shows dull grey luminescent quartz cement (qc) that has overgrown and cuts detrital grains, and is associated with pyrite (py) and chalcopyrite (cpy). Image courtesy of Jo Taylor, AMIRA P1060 project.

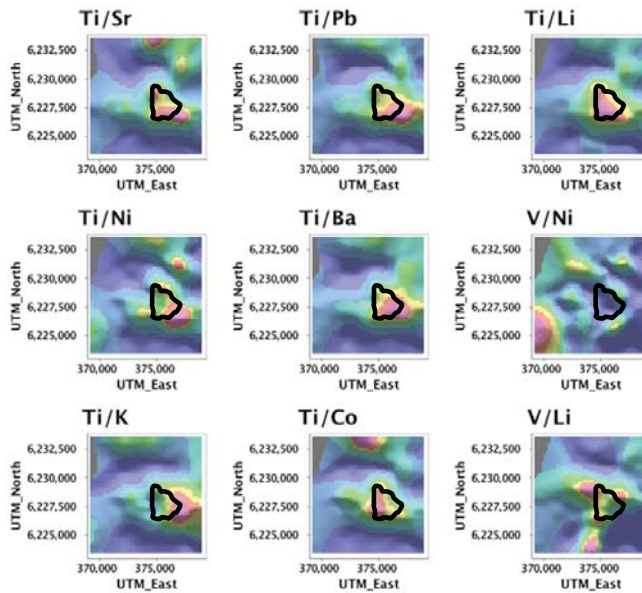


Figure 13. Gridded chlorite trace element ratios (log of sample average, cell size 200 m, minimum smoothing distance 5 cells) for samples from El Teniente, Chile. Outline of the 0.5 wt% Cu shell is shown for reference. From Wilkinson et al. (2017).

These systematic zonation patterns can be used as a broad vectoring tool within the propylitic halos of porphyry systems. Decreases in As, Sb, and Pb content in epidote would be expected as the centre is approached, with a range of other elements increasing to a maximum on the fringes of the pyrite halo. Proximal high elements should be supportive of other geological evidence (potassic alteration, whole rock anomalism of normal porphyry pathfinder elements) indicating that a hydrothermal centre is nearby. They may even be

indicative of mineralization as opposed to just a barren hydrothermal system, but this has yet to be tested.

Chlorite

Propylitic chlorite has been convincingly demonstrated to delineate the thermal anomaly associated with porphyry systems (Fig. 12) as well as display systematic major and trace element variations as a function of distance from the hydrothermal centre (Baker et al., 2015; Wilkinson et al., 2015a, 2017). Furthermore, trace element ratios can be used to predict the absolute distance to the system centre. A range of ratios have been proposed (e.g. Ti/Sr, Ti/Ni, Ti/Li, Ti/Pb, Ti/Ba, Mg/Sr, Mg/Ca, V/Ni) that vary up to four orders of magnitude and therefore provide clearly recognizable, roughly exponential gradients (e.g. Fig. 13). Thus, chlorite is extremely useful for exploring within fairly unremarkable greenrock terrains and for buried deposits.

Quartz

Quartz veins are ubiquitous in all but some alkalic porphyry systems but form over a wide range of temperature and from diverse fluids. Consequently, a significant degree of heterogeneity might be expected in quartz trace-element chemistry, as indicated by microprobe studies (Rusk et al., 2008). However, in some sediment-hosted porphyry systems, such as Bingham Canyon, quartzite host rocks are pervasively cemented by hydrothermal quartz (Fig. 14) that can show more systematic trace element behaviour.

At Bingham, quartz cements show consistent decreases of over ~3 orders of magnitude in trace element ratios, including Ti/As, Cu/Sr, Cu/Li and Ti/Li,

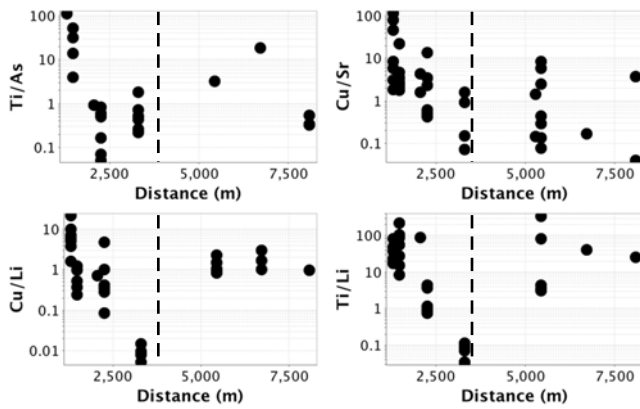


Figure 15. Chemistry of quartz cement in quartzites from the halo of the Bingham Canyon porphyry system. Systematic, approximately exponential, decreases in trace element ratios are observed out to ~3.5 km. Data from AMIRA P1060 project.

out to ~3.5 km (Fig. 15), beyond which there is either a lot of scatter or ratios stabilize to a constant value (e.g. Cu/Li). Ti substitution in quartz is known to be thermally controlled (Wark and Watson, 2006) so the high proximal concentrations observed at Bingham are not unexpected. Copper also appears to substitute into quartz in greater concentrations near the orebody, although the existence of nano-inclusions of sulphides cannot be ruled out. Trace elements that are low in proximal quartz are the same as those that are depleted in proximal chlorite, suggesting that chemical controls on partitioning are not important; we assume that fluid properties and complexation behaviour of these elements prevent their incorporation into silicates at the elevated temperature and lower pH/higher fO_2 conditions likely to exist in more proximal regions.

Hydrothermal magnetite

Hydrothermal magnetite is common in the potassic zone of porphyry systems and is particularly abundant in porphyry Cu-Au deposits. However, it also extends beyond the typical potassic zone in biotite-magnetite domains (e.g. Northparkes, New South Wales; Pacey, 2017) and further into the propylitic domain. Sievwright (2017) showed that hydrothermal overprinting of precursor igneous magnetite is common in propylitic rocks, with euhedral overgrowth of magnetite on igneous titanomagnetite and/or partial recrystallization/re-equilibration of igneous magnetite (e.g. Fig. 16).

In exploration, just the proportion of hydrothermal magnetite in a stream sediment concentrate may be a useful indicator of the likely location of a hydrothermal centre relative to stream catchments. Sievwright (2017) developed this further and showed that the alteration association of hydrothermal magnetite (i.e. whether magnetite was derived from potassic, propylitic, phyllic, or intermediate argillic domains) could be discriminated (Fig. 17). Similar vectoring potential is offered by apatite (Bouzari et al., 2016). Given the instability of magnetite in phyllic and intermediate argillic alteration, it is assumed that magnetite present in these domains is a partially overprinted relic from precursor potassic or propylitic assemblages. The magnetite discrimination plot allows hydrothermal magnetite from different domains to be identified, which would be particularly useful when using stream sediments to map catchment areas.

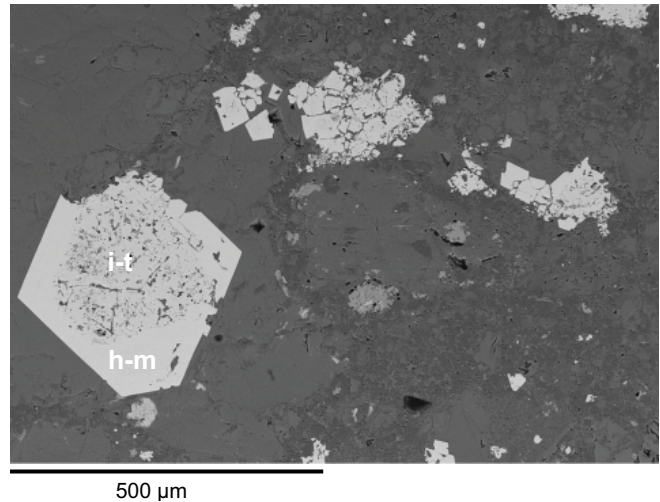


Figure 16. Backscattered scanning electron microscope image showing euhedral hydrothermal magnetite overgrowth (h-m) on an igneous titanomagnetite (i-t) core. Volcanic lithic breccia sample collected 1.1 km from the deposit centre, Batu Hijau, Indonesia. Image from AMIRA P1060 project.

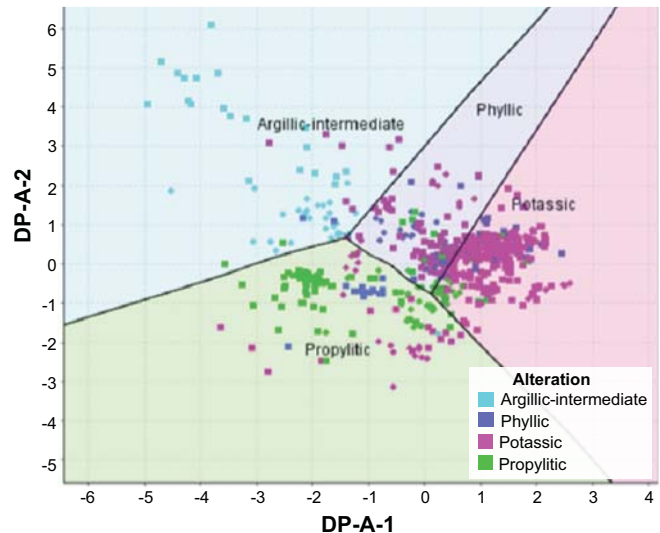


Figure 17. Discriminant projection plot showing that hydrothermal magnetite from different alteration domains can be quite effectively discriminated using multivariate trace element geochemistry (from Sievwright, 2017).

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SUMMARY

The major and trace element chemistry of a range of igneous and alteration phases associated with porphyry

systems provide a valuable record of processes that resulted in the genesis of these major ore deposits. Recognizing and deciphering these fingerprints remain, for the most part, in their infancy but there is now clear evidence that valuable information is locked up in these indicator minerals that can be utilized as valuable discrimination, fertility, and vectoring tools. In concert with conventional approaches, these methods have a good chance of improving discovery success for porphyry ore deposits, particularly under cover.

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