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pXRF assessment of new magmatic fertility indicators in the Macquarie Arc

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SUMMARY

This research presents a new method for assessing magmatic fertility using pXRF in altered terranes using Zr and Y ratios. A study of global batholith related mineralised porphyries, highlights a low Zr fractionation trend. The depletion in Zr is associated with early crystallisation of titanite. Yttrium depletion is related to early crystallisation of both titanite and amphibole, an indication of hydrous melts. Previously differentiation of hydrous, potentially ore-forming (fertile) porphyries relied on Sr/Y from whole rock assay of least altered rocks. Finding samples in porphyry terranes where Sr can be demonstrated to be immobile is difficult given the ubiquity of hydrothermal alteration associated with porphyry emplacement. The requirement for unaltered samples is based on the mobility of Sr which precludes the widespread use of pXRF as quantitative assessment of LOI% (as a proxy for alteration) is beyond the current capabilities of the technology. Using comparatively immobile Zr and Y overcomes issues with alteration and provides a more reliable new indicator of magmatic fertility. In this case study, using a systematic workflow pXRF was successful in identifying the mineralising intrusions in the Northparkes intrusive complex using a Zr/Y vs. Y fertility indicator.

Key words: porphyry, fertility, pXRF, Macquarie Arc

INTRODUCTION

A common issue in the mineral exploration industry is the cost of assay and the lag time between drilling and assay results, with turnarounds in the order of three months. Geochemical data is vital in the development of drilling proposals and guiding future drill campaigns in both brown- and green fields. This research presents a cost effective, precise and accurate method for assessing magmatic fertility in a significantly reduced time frame (hours to days rather than months) utilising immobile element ratios from pXRF technology.

Magma fertility is a function of the potential for an intrusive complex to exsolve metal rich fluids and vapours (Sillitoe, 2010). Assessment of dissolved H_2O in the melt can be proxied using ratios of Sr/Y vs Y. Where Strontium substitutes for Ca in plagioclase, and Y behaves like the HREE, partitioning into hornblende, titanite, and zircon. The ratio of Sr/Y is shifted upward due high H_2O in the melt which supresses plagioclase crystallisation in favour of hydrous phases nominally amphibole (Richards et al., 2012). The ratio of Sr/Y vs. Y is often cited as a reliable indicator of porphyry fertility (Richards et al., 2012; Loucks, 2012; Loucks, 2014); however, the rocks must be relatively unaltered with plagioclase as a stable mineral (e.g. twinning still visible) as Sr is highly mobile during alteration (Loucks, 2014). The abundance of plagioclase destructive alteration in porphyry systems negates the use of Sr ratios, particularly by pXRF (Ahmed et al., 2019) where quantitative assessment of alteration based on other elements (e.g. LOI <3%) is impossible.

Assessment of magmatic fertility in altered terranes requires an element ratio that is immobile during alteration. To overcome the issues with altered rocks, Zr may be used in place of Sr. Zirconium is one of the least mobile elements, its concentration can be used to approximate the hydrous content of source melts. Zircon saturation in melts is a product bulk rock composition and crystallisation temperature (Bulk rock composition M is calculated from cation fractions of major oxides; Watson and Harrison, 1983; Boehnke et al., 2013). Provided the rocks being analysed contain hornblende, the hydrous content (H_2O) and temperature of crystallisation of the melt can be proxied using Zr content (Lu et al., 2015). Hornblende-bearing rocks of intermediate composition (M = 1.6-1.7) and Zr contents between 100 and 150 ppm should have ~10-12 wt.% H_2O (Lu et al., 2015).

A precise and accurate measure of Zr and Y (comparable to traditional assay methods) can be obtained using a systematic approach to pXRF analysis and data reduction (Fisher et al., 2014; Gazley et al., 2015; Wells et al., 2018; Ahmed et al., 2019). Using Zr/Y ratios with pXRF allows for rapid assessment of magmatic fertility in altered terranes. The calculated ratios can be used to inform drilling and exploration campaigns in a much shorter time frame than previously possible. Both Zr and Y have been highlighted as potential indicators of porphyry fertility globally (Loucks, 2012; Richards et al., 2012; Loucks, 2014). This study will focus on the Middle- to Late Ordovician and Devonian intrusive complexes in the Macquarie Arc.

METHODS

Fifty-eight samples from the Northparkes district were submitted for full characterisation whole rock analysis at ALS laboratories, Brisbane. Element abundances were measured

using; ME-XRF26 method for majors, trace elements by ME-MS81, ME-MS42 ME-4AC81 methods, C and S by LECO analysis (S-IRO8, C-IRO7). Ore grade samples were given a special treatment (Cu-OG62). These commercial standard whole rock assays form a comparative data set for the pXRF analyses. Analyses of the same 58 samples were conducted using an Olympus Delta X Premium pXRF over three analytical runs at CODES-University of Tasmania following the methods outlined in Fisher et al. (2014) and Gazley et al. (2015)

Each whole rock analysis from Northparkes was replicated using pXRF. Each sample was analysed as a rock/core sample and as a pulverised equivalent. Three spot analyses were conducted on each sample with spot sites moved to representative sections of the rock rather than repeats at the same location. This was done in order to obtain an average for the rock mass and to limit the effects of texture (i.e., not analysing a single phenocryst phase). Pulp samples were placed in mylar cups, with a 4µM mylar film, and analysed three times to obtain an average. Standards and blanks were analysed with and without mylar film to provide a reasonable comparison to the rock (no film) and pulp samples (with film). A calibration chip was analysed at the start of each analytical session and a silica blank was analysed along with matrix matched standards TASBAS, TASMONZ and TASGRAN (Yu et al., 2003; Chang et al., 2011).

Data was separated into three files; raw data, standards and blanks. Standard data were used to calculate three-point calibration curves for the correction of the raw data as well as monitoring instrumental drift. Correction factors based on linear regressions were applied to the raw data and a separate, corrected data file was generated. Data was maintained in four formats; raw, standard, correction calculation, and corrected, in order to be able to reassess the data if required.

RESULTS AND DISCUSSION

Comparison of Sr/Y vs. Y and Zr/Y vs. Y magmatic fertility indicators was conducted using a global porphyry reference data set (Figure 1, Table 1). The two fertility indicators show similar patterns and the data plot in similar fields. The Sr/Y vs. Y method correctly identifies ~70% of mineralising intrusions compared to >80% of mineralising intrusions identified by Zr/Y vs. Y (Table 2).

Whole rock assay and pXRF analyses of Zr and Y from the Northparkes intrusions are presented in Figure 2. Correlation between pXRF and wholerock analysis from Northparkes are robust (R^2 pulp sample Zr = 0.92 Y = 0.99; Figure 2). Strong correlation between pXRF and assay data indicate that magmatic fertility can be assessed using pXRF on Zr and Y with similar results to traditional assay (Figure 3).

Mineralising intrusions from the Northparkes district (K-QMP, KA-QMP; Lickfold et al., 2003) plot in the prospective field (defined from figure 1) on the Zr/Y vs Y diagram. The pre- and post- mineral intrusions at Northparkes plot in the mixed and un-prospective fields (Figure 3). Ordovician intrusive rocks of unknown mineralising potential from the Cargo and Copper Hill area have similar but less pronounced depletions in Zr and Y compared to Northparkes intrusions. Intrusive rocks from Peak Hill and Cadia-Champagne (historical mining area) unexpectedly plot in the un-prospective field. Devonian monzonitic intrusions from the Yeoval area plot across the prospective and mixed field and un-prospective fields.

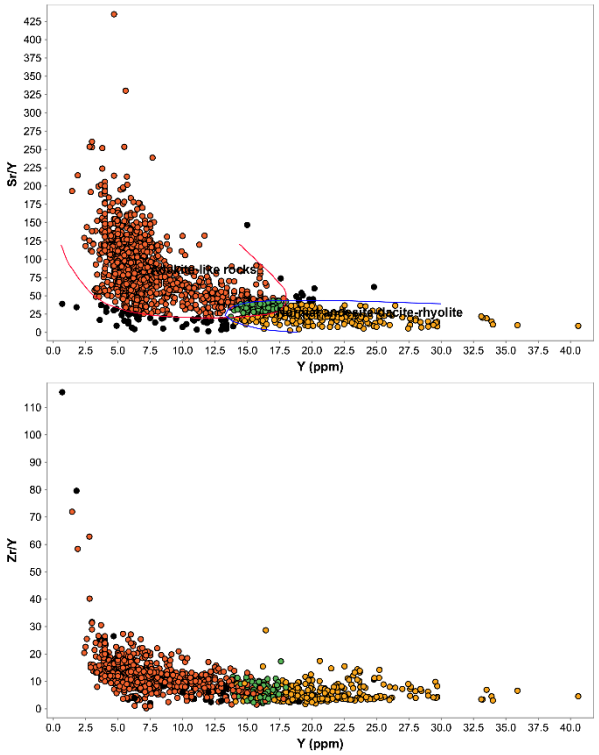

Figure 1. Sr/Y vs. Y and Zr/Y vs. Y plots of global porphyry data. Colours represent prospective (orange) mixed (green) and un-prospective (yellow) fields in Sr/Y vs Y plot.

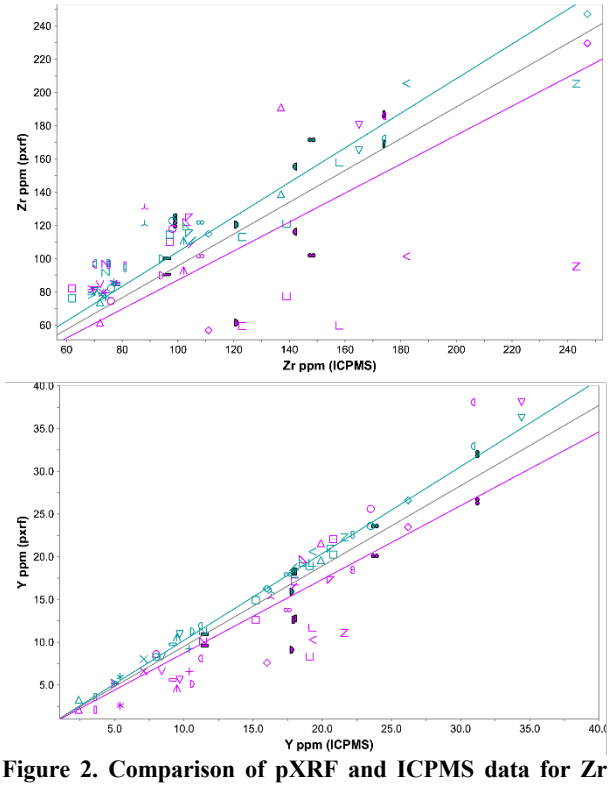

Figure 2. Comparison of pXRF and ICPMS data for Zr and Y. Blue points are pulp analyses, purple are rock analyses. Grey line is regression of all data. Point shapes represent different samples.

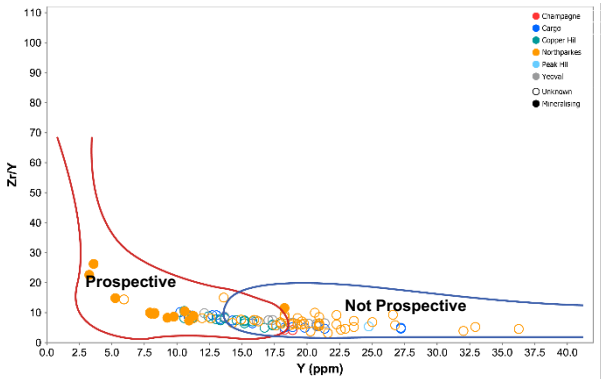

Figure 3. Magmatic fertility assessment of the Northparkes intrusive complex and other intermediate intrusive rocks from the Macquarie Arc. Polygons represent prospective (red) and un-prospective (blue) fields taken from the global porphyry reference suite (Figure 1).

CONCLUSIONS

The ratio of Zr/Y vs Y provides comparable results to the Sr/Y vs Y magmatic fertility indicator. From the 205 data points that plot outside of the defined fields on the Sr/Y vs. Y diagram of global porphyry data, 22 are recognised mineralising intrusions. The Zr/Y diagram correctly identifies twelve of these. Whether their initial misclassification by Sr/Y vs. Y is due to alteration or some other factor requires further investigation. Using immobile Zr rather than highly mobile Sr allows for analyses to be conducted on altered rocks, eliminating the requirement for more complicated analyses to evaluate Sr mobility. The ability to analyse altered rocks enables the use of pXRF as a method of rapid assessment of magmatic fertility. The use of pXRF can drastically reduce the down time between drilling and assay. Provided a systematic approach is taken to data collection and correction pXRF can provide comparable results to wet chemical assay. Pulping of samples overcomes textural issues inherent with spot analysis of highly porphyritic rocks.

The rationale for the Zr/Y vs Y indicator is based around the early crystallisation of titanite and hornblende. Titanite scavenges Zr and the MREE, Y depletion is a product of both titanite and hornblende crystallisation. Early crystallisation of hornblende is a product of the hydrous nature of the melts which can be approximated for hornblende bearing intermediate rocks using Zr content. Shallow emplaced hornblende bearing intermediate rocks (M= ~1.5-1.7) with a Zr content of between ~100-150 ppm have a hydrous content of ~10-12 %.

The Zr/Y vs Y magmatic fertility indicator picks 92% of mineralising intrusions in the Northparkes district. Further to this it suggests there is significant exploration potential for some intrusive rocks in the Cargo and Copper Hill areas where some mineralisation is known. Peak Hill and Champagne plot as un-prospective and to date no significant porphyry style mineralisation has been discovered in these areas. Peak Hill does host epithermal gold mineralisation however the causative intrusions has never been identified and potentially a fertile porphyry remains at depth. The inclusion of some Yeoval samples in the prospective field indicates there may be mineralising potential in the Devonian intrusive complexes which significantly increases the prospectivity of the broader Macquarie Arc.

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Table 1. Global porphyry data, counts of mineralised, barren and undefined samples.

	Samples Sr/Y	*Mineralised*	*Unmineralised*	*Unknown*
Total	*1764*	*1007*	*548*	*209*
Unaltered < 3% LOI	*1086*	*618*	*279*	*189*
Altered >3%LOI	*488*	*217*	*267*	*4*
Unknown LOI	*190*	*172*	*2*	*16*
	Samples Zr/Y			
Total	*1621*	*866*	*548*	*207*
Unaltered < 3% LOI	*1024*	*556*	*279*	*189*
Altered >3%LOI	*479*	*208*	*267*	*4*
Unknown LOI	*118*	*102*	*2*	*14*

Table 2. Accuracy of Classification of mineralising intrusions by classification method. Note that use of Sr/Y is not advised for LOI > 3%.

Sample subset	*Sr/Y identified*	*% accuracy*	*Zr/Y identified*	*% accuracy*
<3% LOI	*482 of 618*	*78%*	*465 of 556*	*83%*
>3% LOI	*173 of 217*	*79%*	*182 of 208*	*87.5%*
All samples	*711 of 1007*	*70%*	*707 of 866*	*81%*