

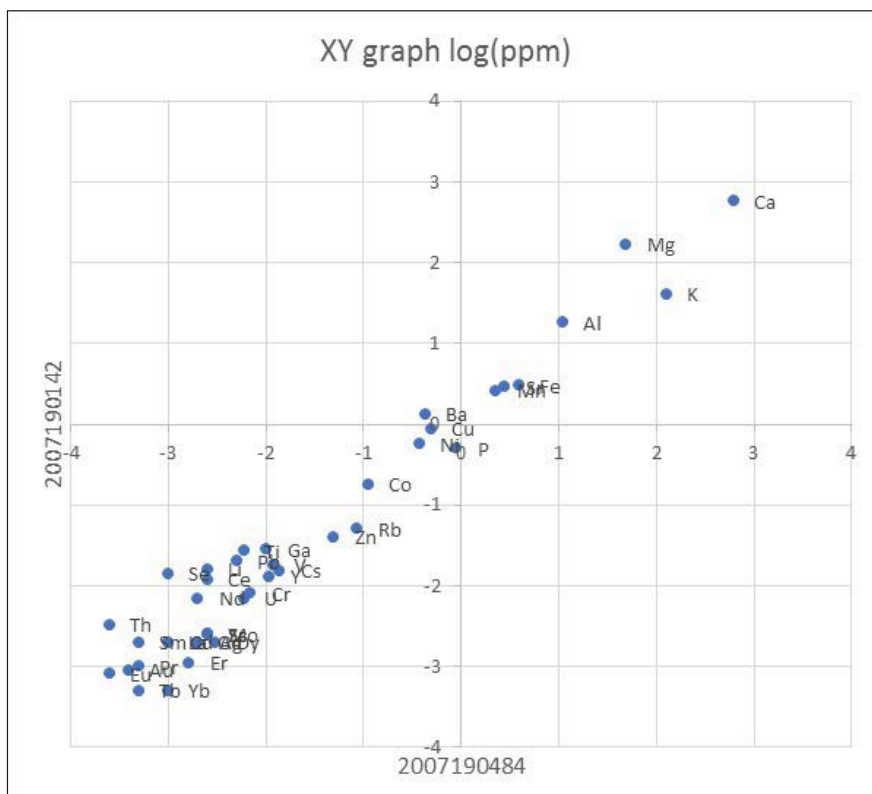
# DEGREE OF GEOCHEMICAL SIMILARITY (LITHOID) BETWEEN MMI™ SAMPLES USING SPEARMAN RANKING AND CORRELATION

## INTRODUCTION & BACKGROUND

MMI™ analysis commonly provides analytical information for over 50 elements. There is a wealth of information contained within that data, particularly in relation to the lithology from which the soil was derived, but because of its multi-element nature this information is difficult to utilise fully.

Mann, de Caritat & Sylvester (2016) first published a method for statistical comparison of two samples which allowed for objective assessment and display of this multi element information in a form which allowed areas of similar lithology to be recognised and mapped. The method was based on converting MMI™ data to log(ppm) values and then obtaining a Pearson  $r$  between pairs of samples as shown in Figure 1.

In most samples Ca or Mg is in highest concentration after MMI™ extraction, and Au or Eu lowest. If assessed in this way these elements systematically dominate the calculation of  $r$ , as indicated in Figure 1. In the correlation calculations, samples differences from the mean are used; samples far from the mean on the XY diagram have greatest weight in the calculation. Whilst the method provided mainly positive high values for  $r$  it did discriminate between for example granitoid and mafic derived soils, marine and pedogenic carbonates, and was diagnostic for areas prospective to Cu mineralisation. As a form of pattern recognition, it relies heavily on careful selection of a reference sample of known provenance for comparison with all others. An improved methodology has been developed (Caritat de & Mann (2018)) in which soil elemental values are ranked prior to applying the correlation function, thus providing a Spearman  $r_{sp}$  coefficient which avoids systematic domination by elements in high or low concentrations. This document examines the validity and some of the outcomes of using this methodology on soil samples obtained after MMI™ extraction.



**Figure 1: XY Scatter Plot for the Plot of Log (ppm) Values of Two Samples after MMI™ Extraction to Obtain a Pearson Correlation Coefficient of  $r=0.98$ .**

## LithoID METHODOLOGY

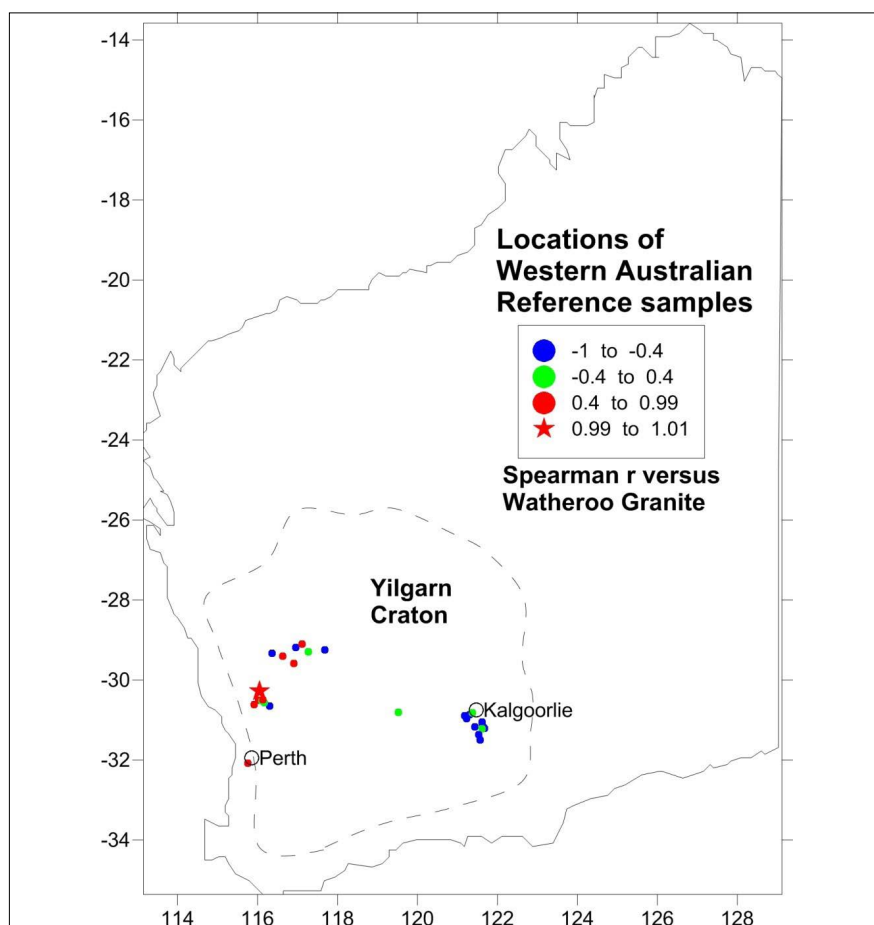
The following are the steps in the updated LithoID methodology (Caritat de & Mann, 2018).

1. Arrange elements in alphabetical order in MMI™ file, remove any with >50% of values <LLD.
2. Replace any remaining element values <LLD with 0.5\*LLD
3. Calculate rankings
4. Select a reference sample
5. Calculate Spearman  $r_{sp}$  values vs reference
6. Plot distribution of sample  $r_{sp}$  vs reference sample(s)
7. Prepare XY scatter diagram of rankings any two samples

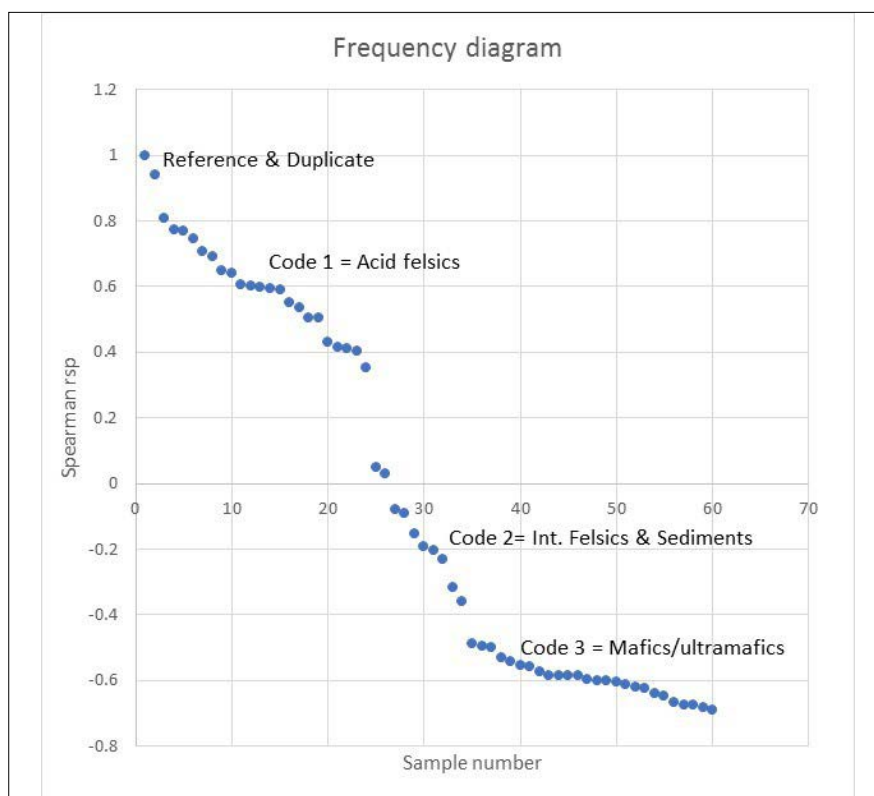
## TESTING THE VALIDITY OF LithoID METHODOLOGY ON WESTERN AUSTRALIAN REFERENCE SAMPLES

Soil samples of known geological provenance were taken at thirty locations in the Yilgarn Craton Western Australia where (a) geological maps (Geological Survey of Western Australia 1:250,000 series) suggested surface outcrop (b) they were on an upslope or the top of a hill to avoid sheet-wash contamination and (c) where hard rock sample could be taken for verification and archive material. Duplicate samples (2m apart) were taken and analysed for 52 elements by ICPMS after MMI™ extraction.; a third sample in each case was archived, along with a rock sample.

The locations for the samples are shown on Figure 2. In this figure the Watheroo granite sample (location shown with a red star) is used as the initial reference sample. The Spearman  $r_{sp}$  values for all other samples against this reference provide initial "proof of concept". Samples mapped as "granite", "gneiss" or "migmatite" have Spearman  $r_{sp}$  values above 0.4, whilst samples mapped as "mafic", "gabbro" or "ultramafic" have Spearman  $r_{sp}$  values <-0.4 against the granite reference. The Spearman  $r_{sp}$  values versus the Watheroo granite are used to colour code the Classed Post Map cohorts in Figure 2.



**Figure 2: Locations of Western Australian Samples with Spearman  $r$  Values Relative to Watheroo Granite Reference Sample. The Reference Sample Location is Shown with a Red Star**



**Figure 3: Sorted Spearman  $r_{sp}$  Values Versus Watheroo Granite as the Reference**

Most of the granitoid samples (red dots) are indicated having come from the western part of the Yilgarn Craton whilst blue dots (mafic/ultramafic rocks) are prevalent in the Eastern Goldfields (Kalgoorlie area). Green dots are from samples derived from sedimentary material. The choice of these thresholds can be verified by examining the frequency diagram shown in Figure 3. In this diagram three large natural “breaks” occur in the slope of the frequency curve which indicate large changes in geochemistry and in turn provide convenient “thresholds” to apply to the data.

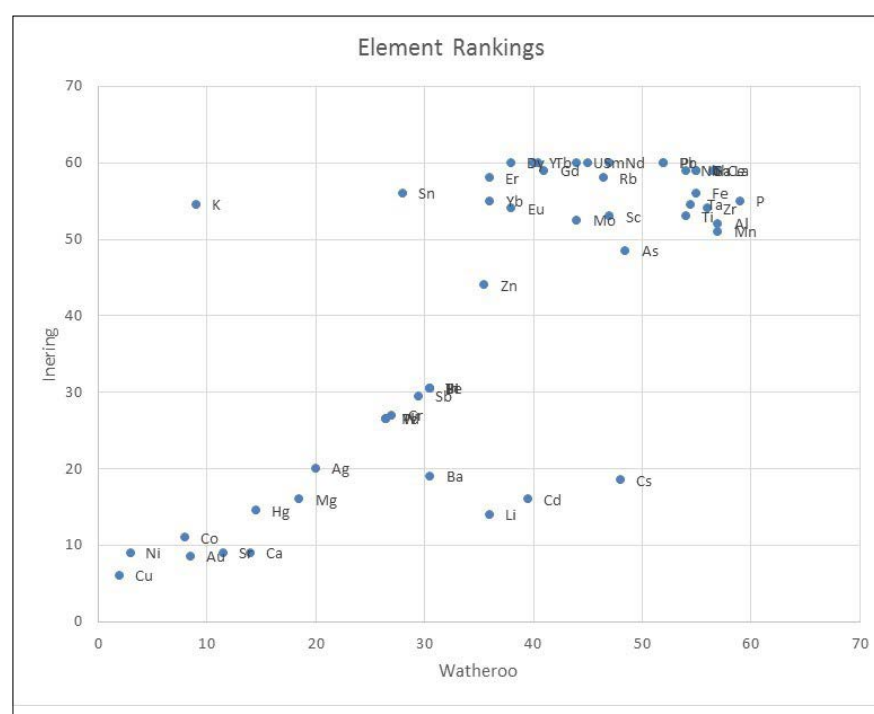
The natural breakpoints at 0.8 to 0.9, 0.1 to 0.3 and -0.4 to -0.5 can be seen on Figure 3 highlighting quite clearly three cohorts or groups of data (apart from the reference and its duplicate). The first breakpoint is between the reference sample, it's duplicate and sample with closest LithoID – a gneiss sample from Inering; a threshold of 0.9 is appropriate. This first cohort contains only granites, gneisses and migmatites – all acid felsics in composition. The second breakpoint, is between acid felsics and intermediate felsics/sediment samples and occurs at close to a threshold of  $r_{sp}=0.4$ , whilst the third occurs at  $r_{sp}=-0.4$  between this group and those samples over mafic and ultramafic lithology.

Other samples were chosen in turn as the primary reference sample, and the validity of the methodology tested against a range of reference types. A summary of the broad outcomes is shown in Table 1.

In summary LithoID methodology places soils over the various rock classes into separate discrete groups or cohorts consistent with the underlying rock type to which a code number can be applied for plotting purposes. Sediments are in the same group as intermediate felsics at this level (but can be distinguished with specific references), and so the three major code groups are Cohort 1 (code 1) = acid felsic, Cohort 2 (code 2) = intermediate felsic/sediments and Cohort 3 (code 3) = mafic/ultramafic. The Spearman  $r_{sp}$  of the duplicate sample 2m away is always higher than that of any other soil; this importantly suggests that each rock type produces a soil with a diagnostic geochemical signature. With additional reference samples this may lead to eventually categorising e.g. i-type and

**Table 1: Details of Rock Types Chosen and Outcomes for Samples of Known Provenance from the Yilgarn Craton of Western Australia.**

Class of Rock type	Reference samples chosen	Broad outcomes
Acid felsic (=Code 1)	2x2 granites 2x2 migmatites 1x2 gneiss 1x2 acid felsic	All acid felsics have $r_{sp}>0.4$ versus e.g. Watheroo granite; all mafic/ultramafics $r_{sp}<-0.4$ Duplicate $r_{sp}=0.94$
Intermediate felsic/sediments (=Code 2)	3x2 Intermediate felsic 1x2 granodiorite 2x2 quartzite 1x2 chert 2x2 Banded Iron Formation 1x2 glauconite sand 1x2 marine limestone 1x2 metasediment 1x2 conglomerate	Int. felsics some mafics and granodiorite have $r_{sp}>0.4$ versus e.g. Mandilla felsic Duplicate $r_{sp}=0.92$ All acid felsics have $r_{sp}>0.4$ versus e.g. Coomberdale chert Mafics, ultramafics, BIF, limestone have $r_{sp}<-0.4$ versus chert. Duplicate $r_{sp}=0.96$
Mafic/Ultramafic (=Code 3)	2x2 mafic 1x2 basalt 4x2 high magnesium basalt 3x2 ultramafic 1x2 gabbro	Most mafic/ultramafics & BIF have $r_{sp}>0.5$ versus e.g. Warriedar mafic; most acid felsics (granites) have $r_{sp}<0$ . Duplicate $r_{sp}=0.79$



**Figure 4: Ranking Diagram for Inering Gneiss Sample Versus Watheroo granite ( $r_{sp}=0.71$ )**

s-type granites, marine from pedogenic carbonates, sediments from intermediate felsics and tholeiitic basalts from other basalt types.

Plotting the individual rankings of any two samples provides additional useful information, and in fact provides reasons for the Spearman  $r_{sp}$  differences between samples. In this particular case (60 samples in all) rankings for each element are from 1, the lowest, to 60 for the highest concentration value; where there are two or more concentrations which are equal (tied) the RANK.AVG formula provides an average ranking to each (e.g. 8.5). The rankings of the Inering gneiss and Watheroo granite samples are shown in Figure 4.

Figure 4 makes it clear that both the Watheroo and Inering samples are low in Cu, Ni and Au and higher in Pb, Zr, Rb and rare earths relative to other samples in the database. The Spearman  $r_{sp}$  value for these two samples is relatively high ( $r_{sp}=0.71$ ) as shown in Figure 4. Both samples are acid felsics but of subtly different composition; the Inering sample has higher ranking for K, the Watheroo sample has higher ranking for Cd, Li, and Cs.

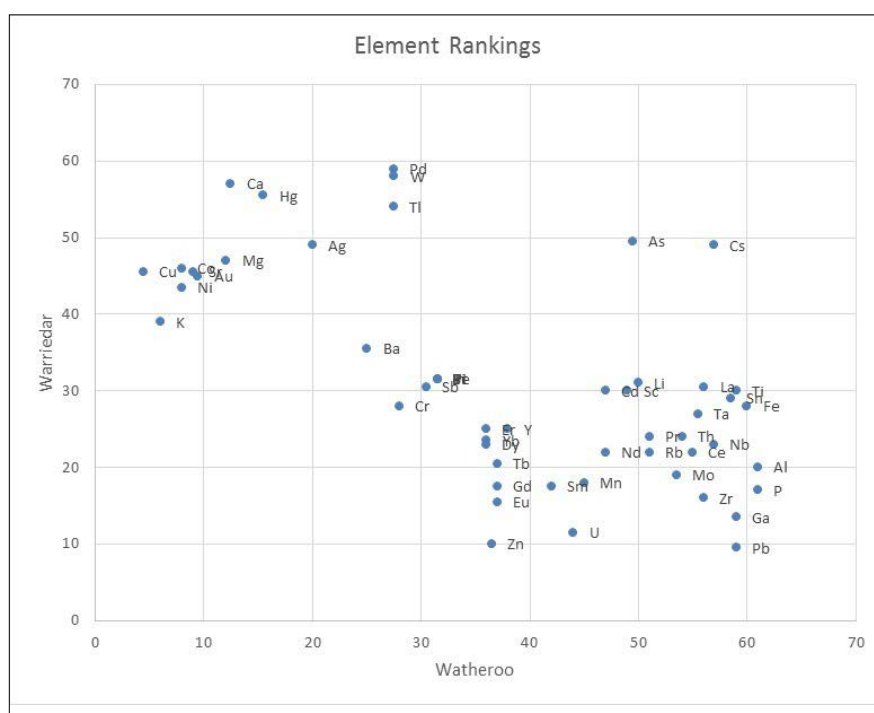
The rankings of the Watheroo reference granite compared to (say) the Warriendar mafic are shown in Figure 5.

It is evident looking at this diagram (Figure 5) that there is not a high degree of correlation between the samples – it is a negative correlation. As expected the granite sample has higher rankings for Al, Pb, Zr, Sn and the rare earth elements, and the mafic for K, Mg, Cu and Ni. The Spearman correlation coefficient is -0.63.

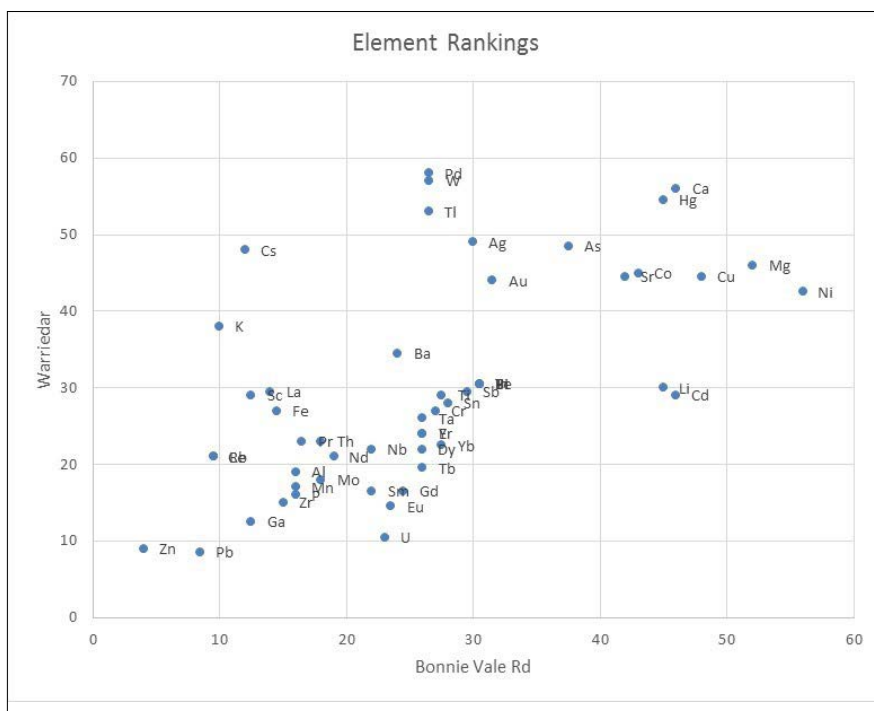
The Bonnie Vale Rd ultramafic when used as a reference sample results in soil samples over rocks of the mafic/ultramafic class having high correlation with the reference, in general  $r_{sp}>0.5$ . The ranking differences between soils over an ultramafic and mafic rock are evident in Figure 6.

As expected elements Mg, Ni and Cu have higher rankings in the ultramafic (Bonnie Vale Rd) sample.

The outcomes provide a basis for assurance that the methodology is diagnostic, and the  $r_{sp}$  values for the outcomes provide some idea of the



**Figure 5: Ranking Diagram for Warriendar Mafic Sample Versus Watheroo Granite ( $r_{sp}=-0.63$ )**



**Figure 6: Element Rankings for an Ultramafic Sample (Bonnie Vale Rd) and Mafic Soil Sample (Warriendar) for Which the Spearman  $r_{sp}=0.59$**

thresholds which need to be applied. While there is some (diagnostic) variation between soils over rocks within a class, there is even wider (and diagnostic) variation between rock classes. Any variations caused by regolith considerations have been minimised in this exercise. It is of course the intention over time to extend the range and location of reference samples. It remains to be seen how universal such reference samples will prove to be; suffice to say there is no better reference than a known sample taken close to the particular project area, perhaps as part of the soil sampling program. Individual high (or low) values of a key element e.g. Al, Au, Ca, Ce, Cu, Fe, or Ni can be a key to choice of a diagnostic reference sample; needless to say the skill of a good geochemical practitioner is required. To illustrate the usefulness of selection of reference samples from within a database, application to the samples obtained from the National Geochemical Survey of Australia (NGSA) will now be investigated.

## MAPPING OF SPEARMAN<sup>RSP</sup> VALUES FROM THE NATIONAL GEOCHEMISTRY SURVEY OF AUSTRALIA (NGSA)

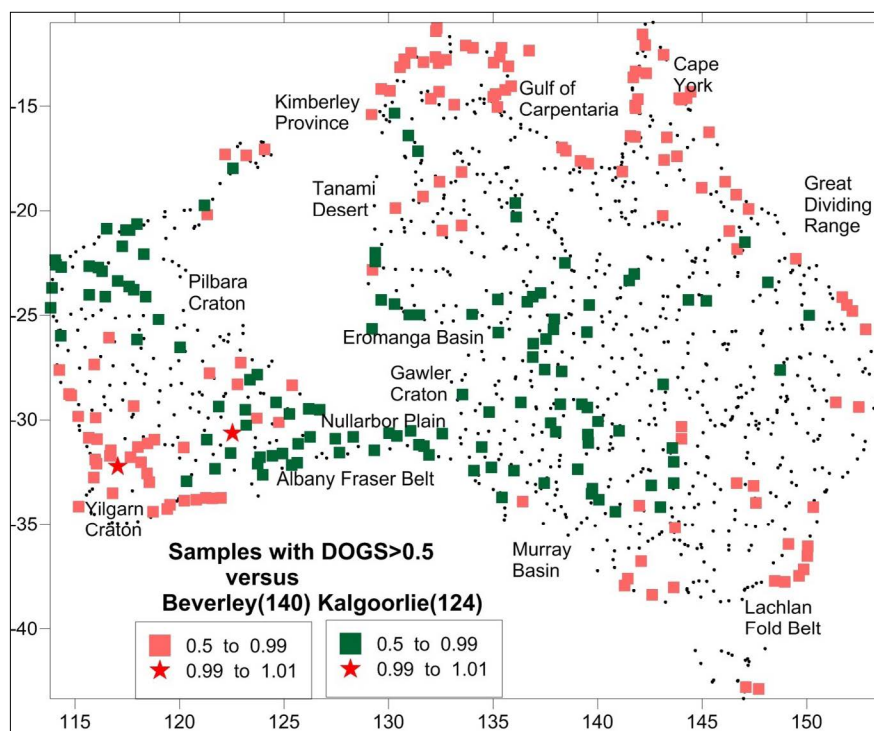
The NGSA survey organised by Geoscience Australia, sampled Top Outlet Soils (TOS) from major catchment outlets over most of Australia in 2007. From this 1202 samples were subject to MMI<sup>TM</sup> extraction and analysis at the Perth SGS laboratory. As this survey is low density, and from catchment sediment samples, it has to be emphasised that outcomes are of a regional geological nature and where applied to mineralisation are related to mineralisation areas or corridors, not individual mineral deposits. A Spearman rankings spreadsheet was prepared for this data set as described above.

Table 2 shows reference samples that were selected from the NGSA data set, on the basis of known provenance, high (or low) MMI<sup>TM</sup> values for key elements, or both.

A granite dominated catchment from the western Yilgarn Craton in Western Australia (WA) viz. #2007191559 near Beverley, was selected as a granite reference against which to test all other samples in the NGSA database; the

**Table 2: Parameters for Sample Sites Chosen as References for LithoID Comparison, NGSA MMI<sup>TM</sup> Data**

Sample number	Location	Geology/mineralisation	MMI values
#2007191559	Beverley, W.A.	Granite	9.98ppm Ce
#2007190484	Kalgoorlie, W.A.	Greenstone	0.0025ppm Ce
#2007190159	Nullarbor, S.A.	Marine Limestone	1410ppm Ca
#2007190065	Mt Isa, Qld	Cu SEDEX style	4.22ppm Cu
#2007191289	L. Frome, S.A.	Cu IOCG style	0.54ppm Cu
#2007190917	Coolgardie, W.A.	Archaean Au	0.0011ppm Au
#2007190042	Ballarat, Victoria	Ordovician Au	0.0026ppm Au



**Figure 7. Samples with LithoID > 0.5 Versus the Beverley Granitoid Reference (#2007191559) in Pink and the Kalgoorlie Greenstone Reference (#2007190484) in Green. The Red Stars Signify the Position of the Reference Samples.**

samples with a Spearman correlation > 0.5 relative to it are shown as pink squares on Figure 6. A catchment dominated by greenstone (#2007190484) east of Kalgoorlie, was chosen as a greenstone (mafic) reference and samples with  $r_{sp}$  values > 0.5 with respect to it are shown as green squares on Figure 7.

The samples with a high LithoID relative to #2007191559 (granitic) are well spread over the Australian continent as shown in Figure 6. Obviously a number of them occur in the Yilgarn Craton particularly the western side; interestingly a number occur immediately to the south of it indicating that the Albany Fraser Belt has similar composition but in younger metamorphosed (Proterozoic) rocks. A number of granitoids with LithoID > 0.5 also occur in the Great Dividing Range of

the east coast. The granites at Weipa and Gove on east and west sides of the Gulf of Carpentaria respectively are responsible for bauxite formation and commercial exploitation.

Greenstone dominant catchments with high degree of similarity to the Kalgoorlie (#2007190484) reference are prevalent not only in the Eastern Goldfields of the Yilgarn Craton, but also the Proterozoic Albany Fraser Belt to the east and south of it. The number of samples with  $r_{sp}$  > 0.5 relative to the Kalgoorlie reference suggest that geochemically this terrain is closely related to the Eastern Goldfields and that soil geochemistry is likely to be a useful tool for exploration here. The recently-commissioned Tropicana Au Mine is in this belt. Catchments with soils closely related to the Kalgoorlie greenstone



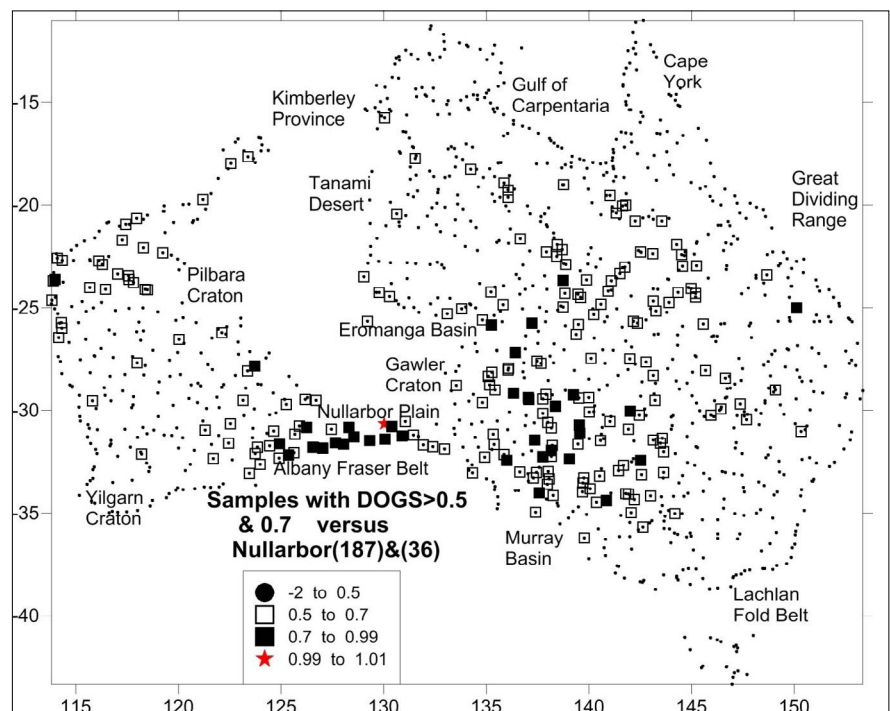
reference #2007190484 are shown in the Gawler Craton of South Australia, along the Great Dividing Range of Queensland, several areas of the Northern Territory and the Pilbara Craton of WA. Although some drainages from the eastern Yilgarn Craton and Albany Fraser Belt exit via the Nullarbor Plain the samples shown there with high LithoID versus Kalgoorlie are likely to be “false positives”, probably due to the similar high calcium and magnesium content of soils over greenstones and marine carbonate sediments; maybe the chosen threshold correlation coefficient of 0.5 is too low in this case.

The Classed Post Map showing samples with high LithoID to the Nullarbor reference (#2007190159) are shown in Figure 8. In this case we will investigate the consequence of choosing two different thresholds for plotting against a single reference.

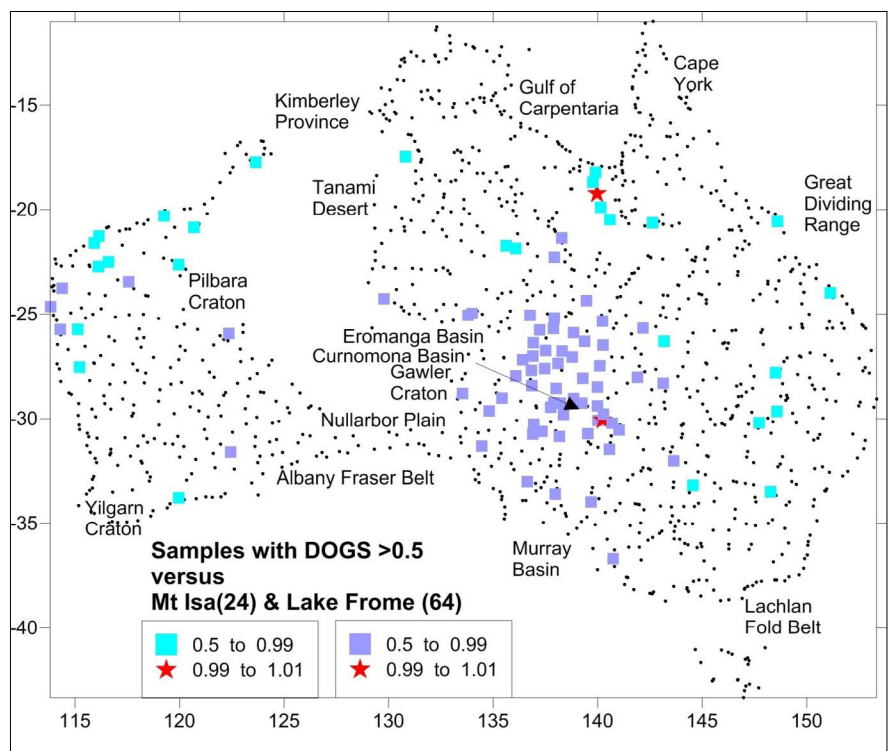
The Nullarbor Plain is one of the most extensive areas of marine limestone (Miocene). There are 223 samples with  $r_{sp} > 0.5$  relative to the Nullarbor reference sample #2007190159; not all shown are from this region. Pedogenic carbonate occurs in many arid and semi-arid areas of Australia. When the threshold for comparison with Nullarbor reference #2007190159 is raised to 0.7, shown in black on Figure 8, the true extent of marine limestone is shown. It is limited to the Nullarbor Plain (Eucla Basin) and the Miocene Murray and Eromanga Basins to the east. The remainder, samples with between  $r_{sp}$  values of 0.5 and 0.7 relative to the Nullarbor reference, shown in light grey are pedogenic carbonates, better known as calcretes.

The Mt Isa district in north-west Queensland hosts a number of economic copper deposits of the sedimentary exhalative (SEDEX) type. The Leichardt River which drains into the Gulf of Carpentaria is downstream from Mt Isa, and where it is joined by the Gunpowder Creek, reference sample #2007190065 was chosen; it contains 4.2ppm Cu after MMI™ extraction. Samples with  $r_{sp} > 0.5$  versus this reference are shown in pale blue on Figure 9.

The light blue squares signifying  $r_{sp} > 0.5$  Spearman correlated samples relative to the Mt Isa reference are well spread throughout Western Australia, the



**Figure 8: Samples with DOGS >0.5 (Open Squares) and >0.7 (Black Squares) Versus the Nullarbor Reference Shown as a Red Star Shown to the Eastern Side of the Nullarbor Plain**



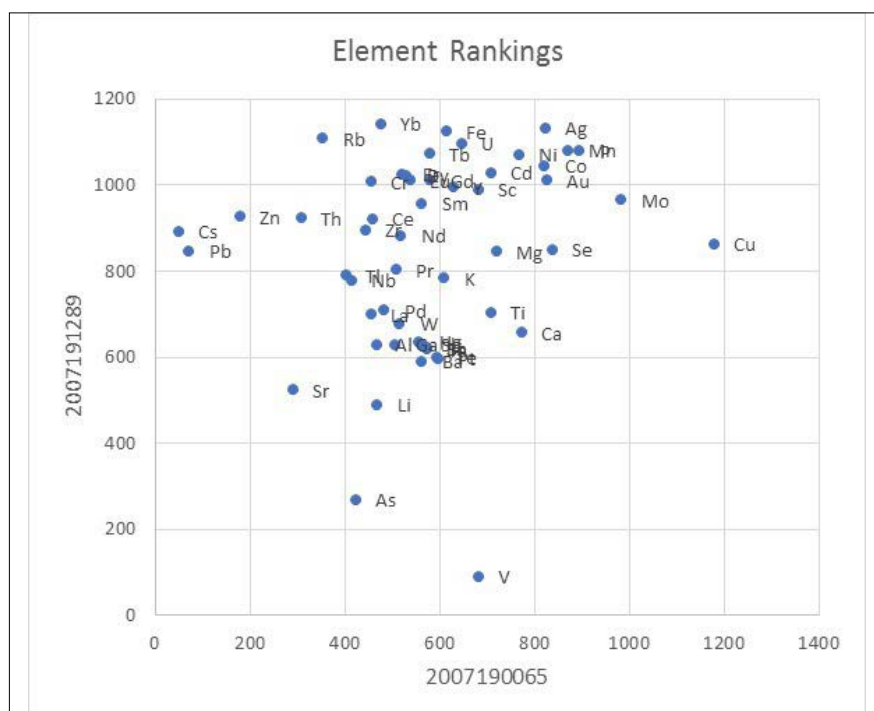
**Figure 9: Samples with  $r_{sp} > 0.5$  DOGS to Mt Isa Reference (Pale Blue Squares) and Lake Frome Reference (Dark Blue Squares)**

Lachlan Fold Belt of New South Wales and the Northern Territory – but not South Australia. The Gawler Craton and the Curnomona Basin to the east of it contain many known Iron Oxide Copper Gold (IOGC) deposits e.g. Olympic Dam, Prominent Hill and Carapateena. This issue is resolved when the sample #2007191289 is chosen as a second reference; it is a TOS sample from a drainage system into the northern end of Lake Frome which is in the centre of the Curnomona Basin close to the border with New South Wales. As shown on Figure 8, a number of samples (in dark blue) have close affinity with this reference sample; a majority of them are located in the Gawler Craton and the Curnomona Basin. Figure 10 is the ranking diagram comparing the Mt Isa and Lake Frome samples.

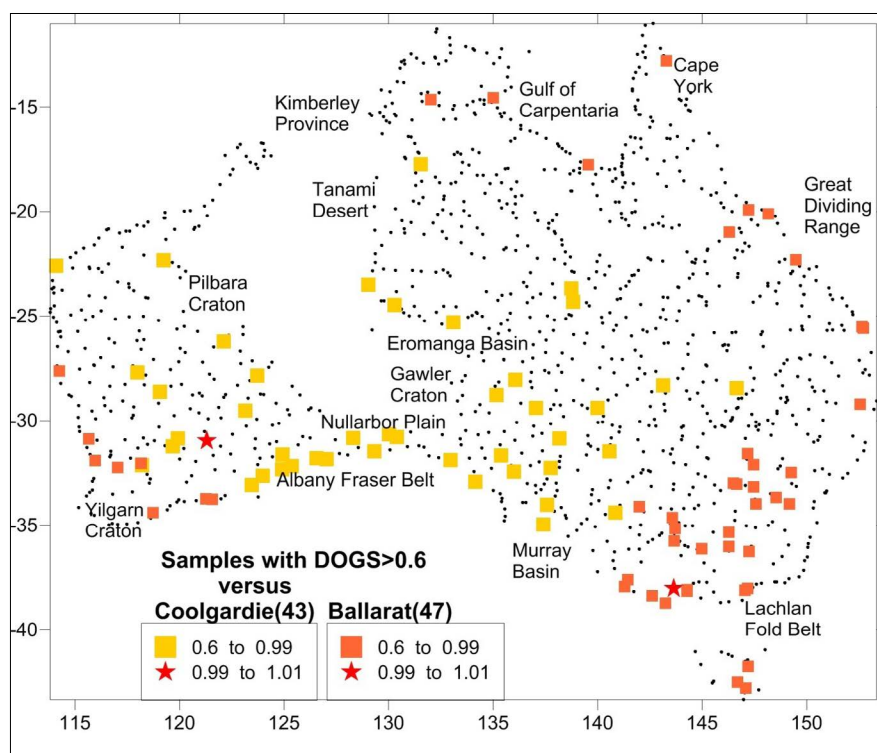
Both the Mt Isa style and Lake Frome type samples contain high rankings of Cu and Mo as shown on Figure 10. The Mt Isa reference sample #2007190065 has significantly higher rankings only for V and As, whereas the Lake Frome sample has higher rankings than Mt Isa for a large number of elements including Fe, Au, Ag and U, elements all commonly observed in IOCG deposits. It is concluded that the LithoD methodology is reflecting those (and other) differences in geochemistry in the NGSA MMI™ outlet sediment samples on a regional basis.

Coolgardie is an historic gold mining centre in the Archaean Eastern Goldfields of Western Australia. Reference sample #2007190717 is from the edge of a small salt lake 12km east of the town; it contains 1.1ppb Au after MMI™ extraction. Samples from the NGSA survey with a LitholD>0.6 relative to this reference sample are shown in gold on Figure 11.

The distribution map of samples with  $r_{sp} > 0.6$  relative to the Coolgardie reference shows samples in the Eastern Goldfields of the Yilgarn Craton, the Albany Fraser Belt, the Gawler Craton, the Pilbara Craton and the Tanami Desert area of the Northern Territory, all areas with known gold deposits. Two areas in the south-west and south-east of the Northern Territory are not known for gold mineralisation and warrant further interest. What is most surprising is that samples in the vicinity of the gold deposits of Victoria and New South Wales in the Lachlan Fold



**Figure 10: Ranking Diagram for the Mt Isa (SEDEX), #2007190065 and Lake Frome (IOCG), #2007191289 Reference Samples**



**Figure 11: Samples with LithoID>0.6 Relative to Coolgardie, #2007190717 and Ballarat, #2007190042 Reference Samples**

Belt do not appear to be geochemically similar to the Coolgardie reference.

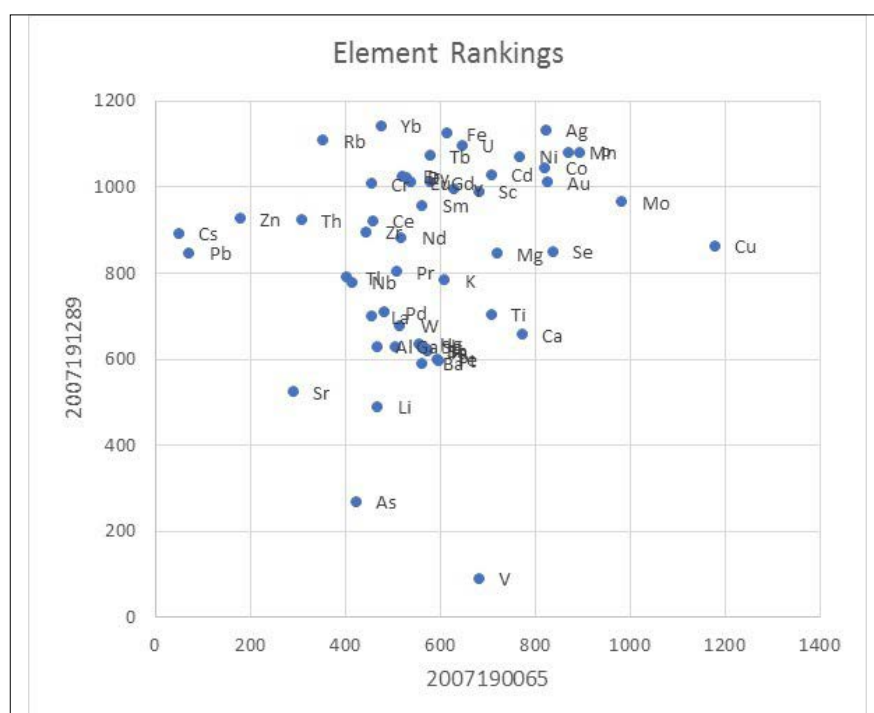
The reference sample #2007190042 lies just south of Ballarat and contains 2.6ppb Au after MMI™ extraction; Ballarat includes sediments of Ordovician age. Samples from the NGSA survey with a LithoID of >0.6 relative to it are shown in orange on Figure 10. Most lie in the Lachlan Fold Belt of Tasmania, Victoria, New South Wales and the rocks of The Great Dividing Range in Queensland (also known for gold mineralisation). These samples via the LithoID technique are responding to the soil geochemistry derived from these younger rocks. What is most interesting is why samples from the drainages in the western Yilgarn Craton which host mafic granulite and porphyry Au deposits (e.g Boddington) are more closely related to the Ballarat reference rather than the Coolgardie reference.

The element rankings for these two reference types are shown in Figure 11.

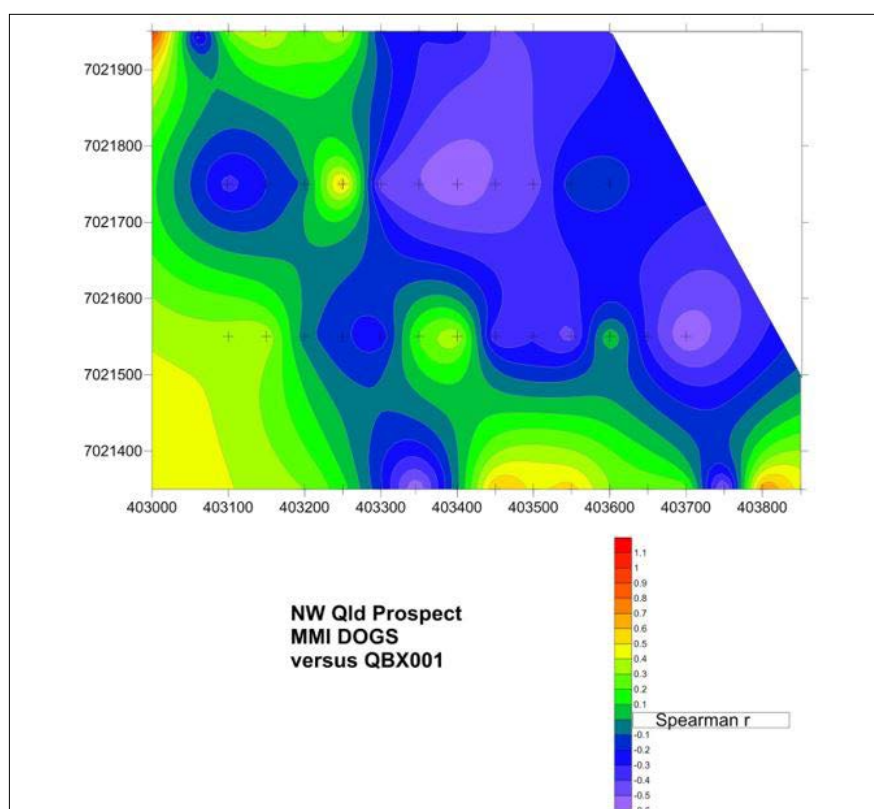
Both reference samples have a high ranking for Au despite the fact that it is in relatively low concentration in both samples – other samples have lower concentrations. The Coolgardie reference #2007190717 has significantly higher rankings for Ca, Cu, Sr, Cs, Hg, Ti and K. The Ballarat reference #2007190042 has significantly higher rankings for the rare earths, Co, Pb, Zn and Zr.

## APPLICATION OF LithoID TO A PROSPECT SCALE PROJECT IN NORTH-WEST QUEENSLAND

The MMI™ technique has been applied (successfully) to a number of prospects in north-west Queensland by Richard Lilly (Xtrata & MIM). In the 48 sample dataset investigated here the highest Au value is 3.9ppb i.e. there is extensive surficial cover, more than enough to obscure the nature of the rock types involved. The steps detailed previously in this document were used to obtain rankings for the 39 elements employed. In the first instance, sample QBX001, in the north-west corner of the survey with a Ce value of 1470ppb (=ranking 48) was used as a reference sample for “background”, against which to obtain Spearman  $r_{sp}$  values for all other samples, which were “Kriged” and plotted



**Figure 12: Element Rankings for the Coolgardie (#2007190717) and Ballarat (#2007190042) Gold Reference Samples**



**Figure 13: Kriged Contour Image of Spearman  $r_{sp}$  Values for all Samples Against the Reference Sample QBX001 in a 48 Sample North-west Queensland Prospect-scale Survey**



as the “z variable”. The resultant contour plot for Spearman  $r_{sp}$  values is shown in Figure 13.

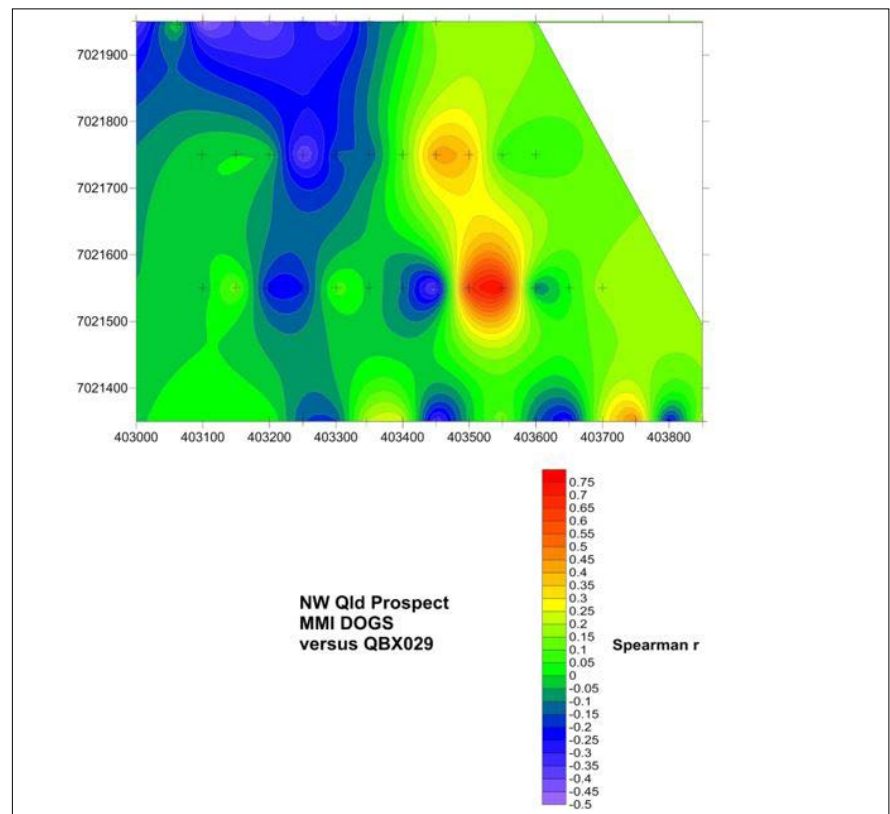
It is immediately apparent that positive values for  $r_{sp}$  occur on the western and southern side and negative values for  $r_{sp}$  occur on the eastern side of the surveyed area. When sample QBX029 is used as the reference sample ( $Au=3.9ppb$ ), the distribution pattern is almost the reverse as shown on Figure 14.

In this case high values shown in red, orange and yellow indicative of positive values for  $r_{sp}$  and prospective mineralised lithology occur to the south and east, and blue colours indicative of negative  $r_{sp}$  values relative to the reference sample QBX029 occur in the north and west of the surveyed area. The relative elemental rankings of the QBX001 and QBX029 samples are shown on Figure 14.

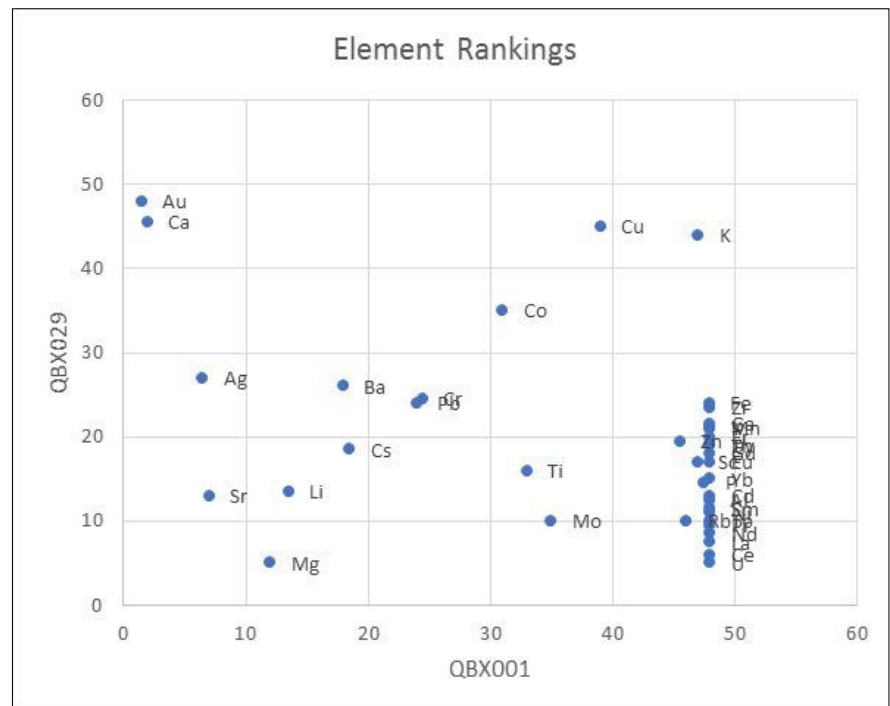
The “background reference” sample QBX001 has a large number of elements with extremely high rankings – including the rare earths, U, Rb, Ni, Cd, Zn, Zr and Fe as indicated on the right hand side of Figure 15. The mineralised reference sample QBX029 has a significantly higher ranking only for Au, Ca and Ag, in the upper left quadrant of Figure 14.

Clearly at least two very different lithologies are evident; if the samples from this NW Qld prospect are one by one compared to the 60 samples in the Western Australian reference data base, they can be identified with one of the three broad classes listed in Table 1 and the “Inferred geology” pattern emerges as shown in Figure 16.

Comparison of the soil samples from this north-west Queensland prospect with the Western Australian derived reference library data base suggests that most of the soil samples depicted in Figure 16 are “mafic”, whilst the remainder are “Intermediate felsic” derived. Every “unknown” sample had a Spearman  $r_{sp}>0.5$  with respect to the closest sample from within the WA reference list, with the highest being a correlation of sample QBX037 with an “Int. felsic” of the reference library of  $r_{sp}=0.87$ . It is further apparent that the contact between these two rock types has an influence on location of gold and copper mineralisation. Potentially useful exploration information has been derived from this multi-element



**Figure 14: Kriged Contour Image of Spearman  $r_{sp}$  Values Versus the “Mineralised” Reference QBX029 in the North-west Queensland Survey**



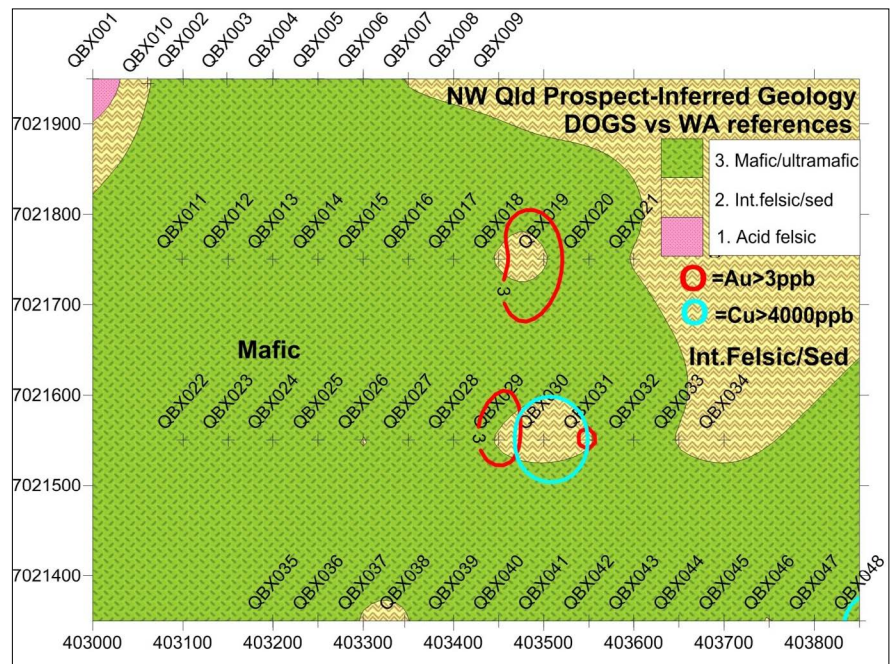
**Figure 15: Element Rankings for the “Background Reference” QBX001 Versus the “Mineralised Reference” QBX029**

data set “objectively”, despite the fact that the reference database is located remotely and the classification of rock types has been deliberately kept broad; clearly the choice of reference sample(s) and  $r_{sp}$  has to be undertaken with due diligence and care to ensure the maximum amount of reliable information is drawn from the database. In time expansion of the reference sample database to other rock types and other locations appears warranted, and will enable even better diagnosis of “unknowns”.

The Lithold technique in principle can be applied to any multi-element data set derived from any analytical technique and in fact may have applications beyond geochemistry.

## REFERENCES

- A. MANN, P. de CARITAT & G. SYLVESTER 2016. Degree of Geochemical Similarity (Lithold): a simple statistical method to quantify and map affinity between samples from multi-element geochemical data sets. Australian Journal of Earth Science 63, (1), P111-122.
- CARITAT de, P. & MANN, A. 2018. An improved method for assessing the Degree of Geochemical Similarity (Lithold) between samples from multi-element geochemical data sets. In preparation.



**Figure 16: Lithology and Contact Location Derived by Referencing MMI™ Soil Data for a North-west Queensland Gold Prospect Versus the Western Australian Lithold MMI™ Reference Library of 60 Samples**

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